

# Electrification of heat demand using advanced thermal energy storage technologies across multiple temperature levels

A. Carro <sup>a,f,\*</sup>, S. Fogel <sup>b</sup>, S. Unger <sup>c</sup>, R. Chacartegui <sup>d,g</sup>, C. Ortiz <sup>e,f</sup>

<sup>a</sup> Dpto. de Ingeniería, Universidad Loyola Andalucía, Sevilla, Spain, [acarro@uloyola.es](mailto:acarro@uloyola.es), CA

<sup>b</sup> Helmholtz-Zentrum Dresden-Rossendorf, Institute of Fluid Dynamics, Dresden, Germany, [s.fogel@hzdr.de](mailto:s.fogel@hzdr.de)

<sup>c</sup> Helmholtz-Zentrum Dresden-Rossendorf, Institute of Fluid Dynamics, Dresden, Germany, [s.unger@hzdr.de](mailto:s.unger@hzdr.de)

<sup>d</sup> Dpto. Ingeniería Energética, Universidad de Sevilla, Sevilla, Spain, [ricardoch@us.es](mailto:ricardoch@us.es)

<sup>e</sup> Dpto. de Ingeniería, Universidad Loyola Andalucía, Sevilla, Spain, [cortiz@uloyola.es](mailto:cortiz@uloyola.es)

<sup>f</sup> Instituto de Investigación en Energía, Tecnología y Sostenibilidad (LETS), Universidad Loyola Andalucía, Sevilla, Spain

<sup>g</sup> Laboratory of Engineering for Energy and Environmental Sustainability, Universidad de Sevilla, Sevilla, Spain,

## Abstract:

The industrial sector is a fundamental pillar of global gross product; however, its thermal dependency accounts for 40% of global CO<sub>2</sub> emissions, positioning it as a critical axis for the energy transition. This paper evaluates a systematic framework of advanced thermal energy storage (TES) technologies designed to achieve the deep electrification of industrial thermal demand across multiple temperature ranges. The research focuses on the modelling and optimisation of three complementary technological pillars: transcritical CO<sub>2</sub>-based Carnot batteries for low-to-medium temperature trigeneration (<200 °C), methanol-syngas thermochemical routes for medium-temperature process steam (250–400 °C), and calcium-based thermochemical energy storage (TCES) for high-temperature intensive applications (up to 950 °C). The analysis employs a homogeneous thermodynamic characterisation of process streams and TES units, including phase-change materials and innovative chemical carriers. The results show that transcritical CO<sub>2</sub> cycles offer promising opportunities for meeting hot water demand and providing flexible cooling down to -40 °C, as well as the potential for integration with transport networks and geological storage of captured CO<sub>2</sub>. The methanol-based production chain highlights the versatility of synthetic fuels as storable energy carriers, which can be used in existing gas networks and diesel engines, whilst also meeting flexible thermal demand. Calcium-based cycles (CaL and CaO/Ca(OH)<sub>2</sub>) demonstrate their ability to provide a stable, high-density heat supply to sectors where it is difficult to reduce emissions, overcoming the deactivation challenges associated with multiple CaO cycles through the hybrid integration of complementary technologies, with thermal conversion efficiencies that could exceed 85%. The study concludes that this multi-technology architecture maximises power flexibility and offers a scalable, modular solutions for diverse industrial scenarios. By decoupling renewable generation from final demand, the proposed framework represents a viable and robust pathway towards achieving climate neutrality by 2050, enhancing the stability and security of the industrial energy transition.

## Keywords:

Power-to-heat, Transcritical CO<sub>2</sub> cycles, efuels, Thermal energy storage, Industrial decarbonisation.

## 1. Introduction

The decarbonisation of the energy system constitutes one of the main global challenges, driven by the need to mitigate climate change, reduce greenhouse gas emissions, and move towards greater independence from fossil fuels [1]. Progressive electrification supported by renewable sources has consolidated itself as a key strategy [2]. In this scenario, the massive implementation of variable renewable energies, such as solar and wind, plays a fundamental role in the electrification of the energy system, but simultaneously introduces new challenges associated with their intermittent and non-dispatchable nature [3]. The growing penetration of these sources demands the development of storage systems capable of temporally decoupling renewable generation from final demand, ensuring security of supply and system stability [4]. On the other hand, a significant fraction of global energy consumption is associated with thermal demand (nearly half of total final energy consumption and 38 % of energy-related CO<sub>2</sub> emissions [5,6]), both in residential applications and industrial processes. The replacement of fossil fuels in heat supply poses specific technical and operational

challenges, particularly when high temperature levels are required, highlighting the need for flexible energy solutions capable of integrating renewable generation and efficient thermal energy management [7].

Direct electrification of energy demand is not viable in all cases. The so-called hard-to-abate industries, such as iron and steel, chemical manufacturing, refining, or cement production, present demanding thermal requirements characterised by high temperatures, high heat fluxes, and continuous operation that limits supply flexibility [8]. In these sectors, the inherent variability of renewable sources poses an additional barrier [9]. They may have highly diverse thermal demands, ranging from refrigeration services and hot water production to the generation of steam and process heat at medium and high temperatures, in many cases exceeding several hundred degrees Celsius [2,10]. These demands differ not only in temperature levels but also in terms of pressure, thermal fluid phase, and operational continuity, imposing strict requirements on the quality and availability of energy supply, which hinders the transition from fossil fuels to carbon-free systems. Strategies such as carbon capture and storage have been widely studied, but their large-scale implementation faces technological, economic, and social acceptance challenges that hamper their widespread adoption [11].

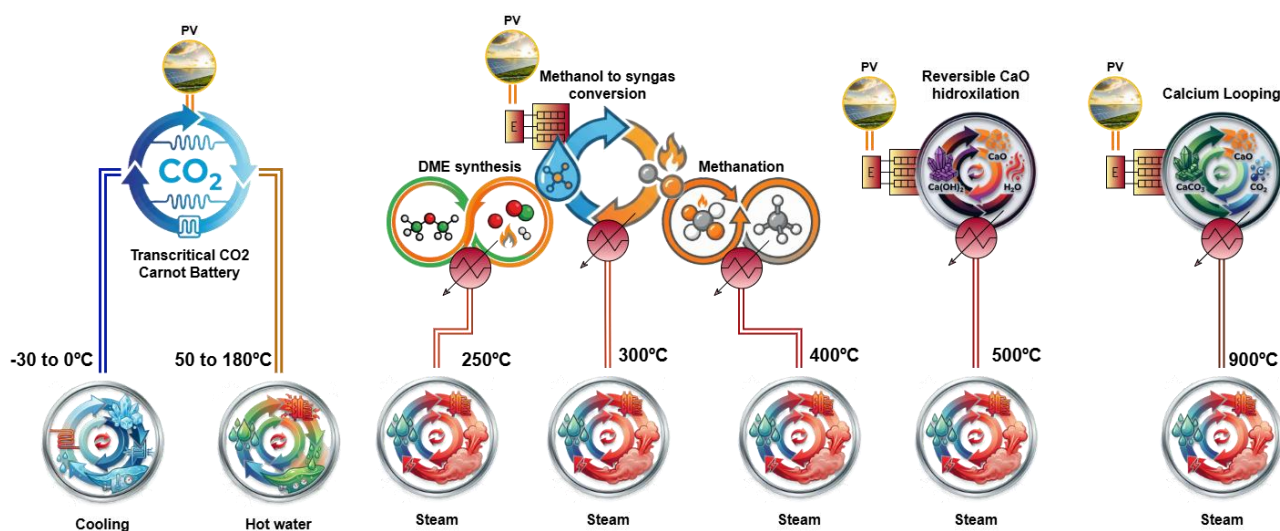
In recent years, various advanced thermal storage technologies have been developed and proposed with the aim of providing flexibility and expanding the range of applications covered by renewable energies [12]. Among them, Carnot batteries or reversible heat pumps emerge as a mature and highly efficient solution for storing electricity (PV, wind) in the form of thermal energy, and the subsequent flexible generation of electricity, cooling, and low-temperature heat [13]. Thermochemical energy storage (TCES) systems are based on combined endothermic and exothermic chemical reactions at low, medium, and high temperatures, acting as flexible storage and generation systems, offering a promising route for decoupling generation and consumption [14]. They can act as storage systems in large concentrated solar power (CSP) or electrical plants (PV, wind), and meet flexible thermal or electrical demand by coupling a power block [15,16]. A promising application of TCES systems is the production of synthetic fuels [17]. Proper process design enables the storage of renewable thermal energy in chemical form and its subsequent flexible recovery, providing added value to the synthetic fuel production chain [18]. Together, these technologies could define a set of complementary solutions capable of meeting thermal demand at various temperature levels using renewable electricity, reinforcing the role of advanced thermal storage as a key element in the industrial energy transition.

The present work presents a comparative analysis of advanced thermal energy storage technologies capable of operating across different temperature ranges, with the objective of achieving the electrification of flexible thermal demand using renewable energy. Representative solutions based on transcritical CO<sub>2</sub> cycles, calcium-based thermochemical systems, and production routes for synthetic fuels and chemical carriers are studied, evaluated from a homogeneous thermodynamic perspective. The adopted approach is based on the detailed characterisation of process streams (pressure, temperature, quality, enthalpy, entropy, and density) as well as the definition of the properties of the thermal demands potentially covered, encompassing refrigeration, hot water, and steam generation at different pressure and temperature levels. In this way, the work provides a novel systematic framework for comparing heterogeneous advanced thermal storage technologies within a context of electrification, providing useful technical criteria for the conceptual design of energy systems aimed at the decarbonisation of multi-temperature thermal demand.

## 2. Methods

### 2.1. Description of thermal energy storage technologies by temperature level

**Figure 1** presents a conceptual diagram of the advanced thermal energy storage technologies considered in this study, organised according to temperature level and the type of thermal demand they can cover within an electrification context.



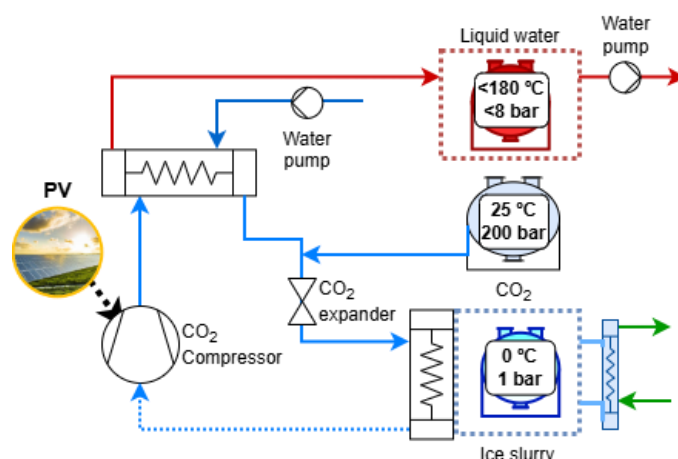
**Figure 1.** Conceptual diagram of advanced thermal energy storage technologies for the electrification of thermal demand at different temperature levels: Carnot battery using transcritical CO<sub>2</sub> cycles for the provision of refrigeration and hot water, thermochemical storage routes based on methanol-derived synthetic fuels for medium-temperature steam generation, and calcium-based thermochemical systems oriented towards medium and high-temperature steam production

The set of solutions analysed ranges from low-temperature applications, associated with refrigeration and liquid water heating, to the generation of process steam at low, medium, and high temperatures, representative of industrial applications. All technologies share a common approach based on the conversion of renewable electricity into stored thermal or thermochemical energy, which can be released in a controlled manner to meet various thermal demands flexibly. This classification allows for a coherent comparison between technologically heterogeneous alternatives, highlighting their operating range, degree of maturity, and potential contribution to the electrification of multi-temperature thermal demand.

### 2.1.1 Transcritical CO<sub>2</sub> heat pump for cooling and hot water supply

Heat pumps coupled with thermal storage systems represent one of the most mature solutions for the electrification of low-temperature thermal demand. These technologies allow electricity, preferably from renewable sources, to be converted into usable thermal energy, simultaneously offering refrigeration services and heat production. Their high efficiency and ability to operate flexibly make them a particularly suitable option for applications where different thermal levels are required within the same system. Heat pumps employing transcritical CO<sub>2</sub> cycles offer interesting applications as low-temperature trigeneration systems. Mercangoz and Morandin [19,20] laid the foundations for electro-thermal energy storage systems using transcritical CO<sub>2</sub> cycles, demonstrating electricity-to-electricity conversion efficiencies of around 50–60%. This enables flexible electricity production and direct coverage of thermal energy demands (heating and cooling) through the storage of dispatchable thermal energy at two temperature levels and a levelised cost of electricity (LCOE) of 70–140 USD/MWh [21]. The thermodynamic properties of transcritical CO<sub>2</sub> cycles are well-coupled with thermal energy storage in water and ice (low-cost, widely available, and easily accessible materials with low environmental impact and good thermodynamic properties) [22].

**Figure 2** shows the conceptual diagram of a heat pump based on a transcritical CO<sub>2</sub> cycle. In this system, renewable electricity is used to drive a compressor that raises the CO<sub>2</sub> pressure into the supercritical region, allowing heat transfer for the storage of pressurised hot water. Simultaneously, the cycle provides low-temperature refrigeration through evaporation at reduced pressure, allowing thermal energy storage at a constant temperature compatible with cooling applications. The use of CO<sub>2</sub> as a working fluid enables operation at high pressures, achieving high power densities and facilitating system integration in compact applications [23].



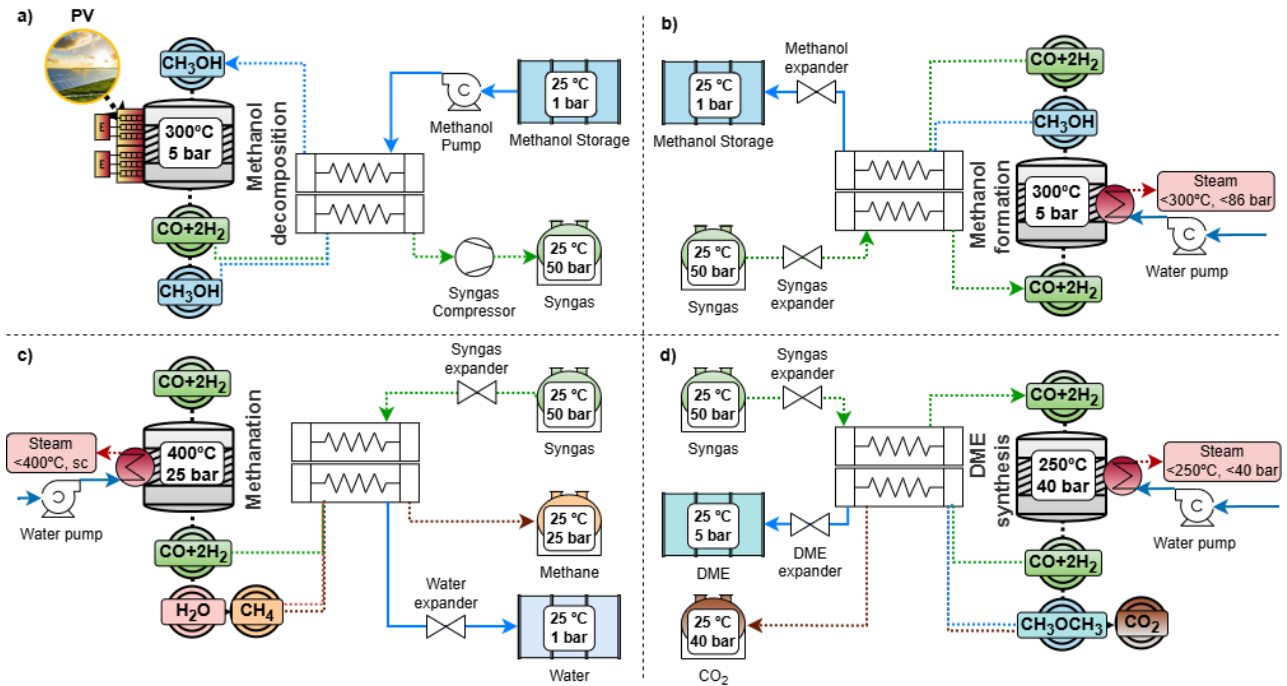
**Figure 2.** Conceptual diagram of a heat pump based on a transcritical CO<sub>2</sub> cycle for the provision of refrigeration and hot water.

The system allows for multiple design configurations whose impact extends to both energy efficiency and flexibility in meeting thermal demand. The introduction of recuperative heat exchangers improves the integration of CO<sub>2</sub> temperature profiles, increasing system efficiency [24,25]. Segmenting high-temperature thermal storage into several stages allows for better matching between supercritical and subcritical profiles, expanding the temperature levels available for direct hot water use and reinforcing the multi-temperature nature of the system. The phase-change temperature depends on the evaporator pressure and is the fundamental factor upon which the system's refrigeration applications depend. Evaporator pressures below 30 bar can extend the refrigeration range from 0°C to -40°C, in which case it operates at 8.6 bar [24]. It also influences the hot water temperature, as the lower the phase-change temperature, the higher the compressor outlet temperature, exceeding 200°C [26].

A recent evolution of the Carnot battery concept based on transcritical CO<sub>2</sub> cycles is its integration with carbon capture and geological storage systems, leading to hybrid configurations that combine thermal storage, energy conversion, and geological injection and production processes [27]. In this approach, CO<sub>2</sub> not only acts as the working fluid for the surface thermoelectric cycle but is also stored temporarily or permanently in deep geological formations, enabling the integration of Carbon Capture and Storage (CCS) functions [28,29]. This integration opens the possibility of benefiting from CO<sub>2</sub> sequestration mechanisms, providing added value as a complement to CCS systems [30]. These configurations are currently in the development phase, as demonstrated by the European Horizon programme project "CO<sub>2</sub>-based Electrothermal Energy and Geological Storage" (CEEGS) [31], completed in 2025, which proved the scientific feasibility of the concept by addressing the challenges at the interface between the surface transcritical cycle and underground CO<sub>2</sub> storage, with 20 kW laboratory-scale tests placing the technology at a maturity level of TRL 4 [32,33].

## 2.1.2 Synthetic fuel-based TES systems for medium-temperature steam generation

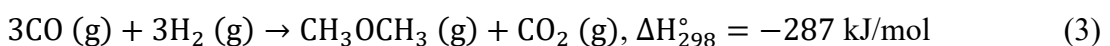
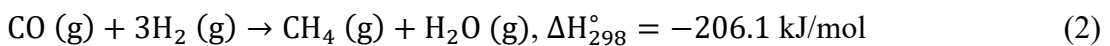
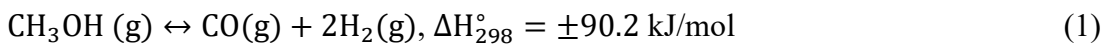
Renewable synthetic fuels are part of the "Power-to-X" suite of technologies, which convert renewable electricity into chemical vectors such as hydrogen, synthetic methane, methanol, ammonia, or advanced liquid fuels. Synthetic fuel production systems using renewable energy present high potential for integration into energy storage networks and thermal demand coverage. This energy can be stored for long periods and subsequently released in the form of process heat, providing a suitable solution for industrial applications with more demanding thermal requirements. **Figure 3** illustrates a novel synthetic fuel production chain with different routes and thermochemical storage based on methanol and its derivatives, designed for medium-temperature steam generation. These configurations employ syngas as the main axis and include methanol decomposition and synthesis processes, dimethyl ether (DME) synthesis, and methanation, which allow the energy vector and the thermal level of the released heat to be adapted to specific demand needs. By using synthetic fuels as a storage medium, these systems combine high energy density with great operational flexibility, facilitating the temporal decoupling between renewable electricity availability (PV) and industrial thermal supply.



**Figure 3.** Conceptual diagram of a thermochemical energy storage system based on a production chain of methanol-derived synthetic fuels with medium-temperature steam generation: a) Methanol decomposition into syngas, b) Syngas-methanol conversion at approximately  $300^\circ\text{C}$ , c) Methanation at  $400^\circ\text{C}$ , d) DME synthesis at  $250^\circ\text{C}$ .

The fuel production chain presents an integrated scheme of a thermal energy storage system designed for medium-temperature steam generation from renewable electricity and the production of liquid and gaseous fuels. The system is organised around a set of interconnected thermochemical routes, where electricity from renewable sources is used to drive chemical synthesis and conversion processes, allowing energy storage in the form of chemical carriers and its subsequent release as process heat. The upper part of **Figure 3a** represents methanol decomposition as the initial chemical conversion stage and the charging phase of the thermal storage system. Methanol acts as the primary energy vector and can be thermally decomposed to produce syngas ( $\text{CO} + \text{H}_2$ ) under moderate temperature and pressure conditions [18]. This syngas constitutes the central node of the system, from which different conversion routes are enabled depending on the desired chemical vector and the thermal level of the demand to be met.

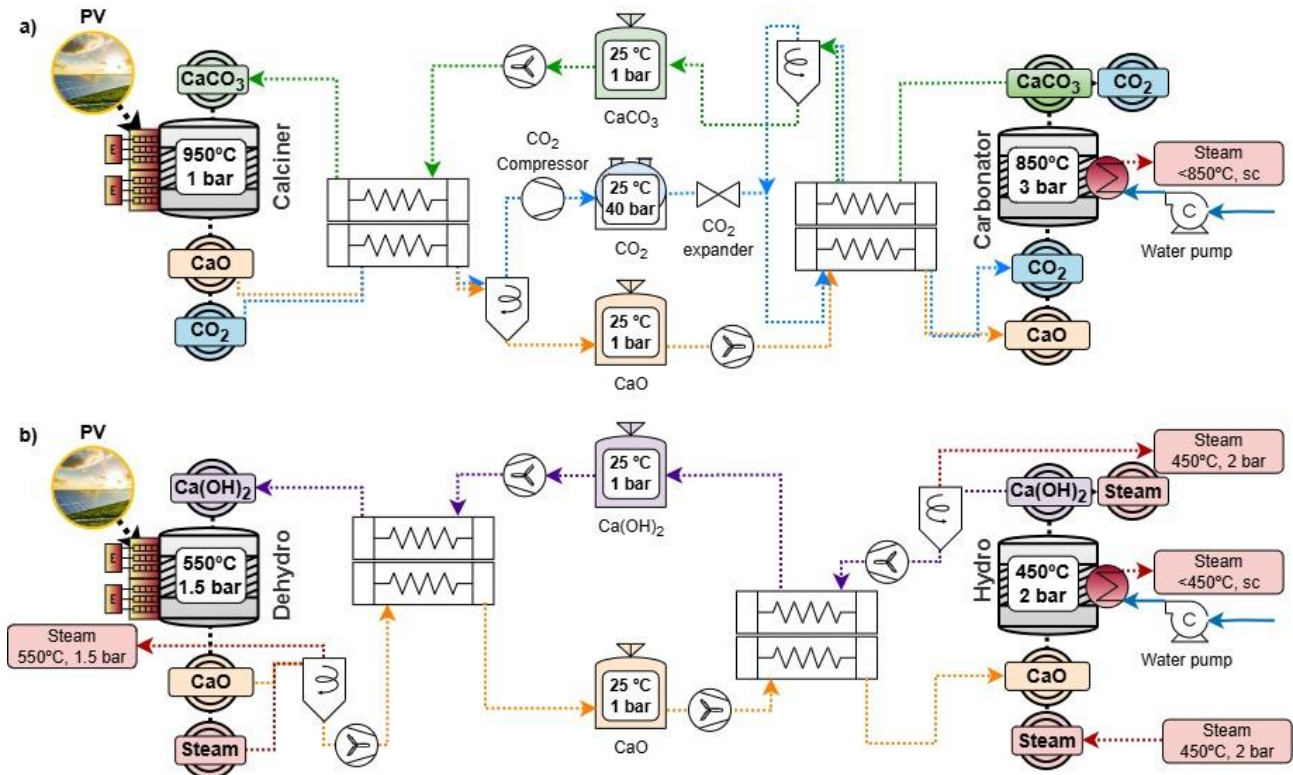
From the syngas, the scheme contemplates several chemical synthesis routes. On one hand, syngas can be reconverted into methanol (**Figure 3b**), closing a chemical cycle that allows for the flexible storage and recovery of thermal energy at around  $300^\circ\text{C}$ . On the other hand, it includes methanation (**Figure 3c**) at  $400^\circ\text{C}$  [18] and DME synthesis (**Figure 3d**) at approximately  $250^\circ\text{C}$  [34], processes that generate alternative synthetic fuels with different thermodynamic properties and operating conditions. These can be used as alternatives in existing gas networks for electricity generation, heating, and seasonal storage, or as diesel in heavy transport and machinery. See equations 1–3. The production chain highlights the modularity and flexibility of synthetic fuel-based storage systems, as well as their capacity to integrate multiple chemical conversion routes and meet heterogeneous thermal demands through high-energy-density thermochemical storage. It enables the generation of process steam at medium temperatures, below  $400^\circ\text{C}$ , with different pressure levels and a wider range depending on the selected route. The system can adapt to various industrial steam demands, maintaining a temporal decoupling between the renewable resource and final thermal consumption, significantly expanding the temperature range covered by electrification and positioning itself as a key option for medium-temperature steam production in an industrial decarbonisation scenario.



This fuel conversion route has been recently proposed in the Horizon Europe project METHCESFUEL ("Production of multiple synthetic fuels from renewable methanol", 2025–2029) [35], which proposes innovative and flexible pathways starting from the synthesis of renewable methanol, obtained from captured CO<sub>2</sub> (via amine scrubbing, direct air capture, or industrial sources) and electrolytic hydrogen. The project aims to develop a laboratory demonstrator (TRL 4), laying the foundations for industrial scalability through advanced catalysis and digital modelling, thereby accelerating the decarbonisation of hard-to-abate sectors.

### 2.1.3 Calcium-based TCES systems to produce medium- and high-temperature steam

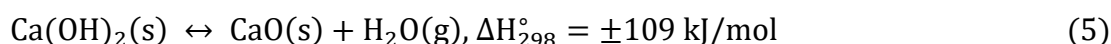
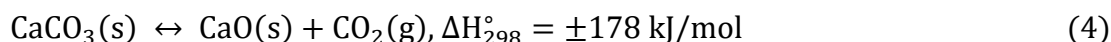
Thermochemical energy storage systems based on reactive solid materials, and particularly those relying on reversible calcium reactions, emerge as a robust and highly suitable alternative for meeting demanding thermal requirements. These systems allow energy to be stored in the form of chemical energy associated with endothermic reactions and subsequently release large amounts of heat at high temperatures through well-controlled exothermic reactions. Cycles based on calcium oxide, both through carbonation–calcination processes (calcium looping) and hydroxylation–dehydroxylation cycles (CaO/Ca(OH)<sub>2</sub>), present high energy densities, material stability, and an operating temperature range compatible with numerous industrial applications. **Figure 4** shows two representative configurations of these systems, oriented respectively towards high-temperature steam generation and medium-temperature steam production. In both cases, renewable electricity is used to supply the necessary heat for the endothermic stages, enabling long-duration renewable energy storage and its subsequent conversion into process heat on demand. Thus, calcium-based TCES systems expand the scope of thermal demand electrification into temperature ranges traditionally dominated by fossil fuels, consolidating themselves as a key component in deep industrial decarbonisation strategies.



**Figure 4.** Conceptual diagram of calcium-based thermochemical storage systems for medium and high-temperature steam generation: a) calcium looping system based on the reversible processes of carbonation and calcination (CaO/CaCO<sub>3</sub>), oriented towards the production of superheated steam at elevated temperatures; and b) system based on the hydration and dehydration cycles of calcium oxide (CaO/Ca(OH)<sub>2</sub>), designed for medium-temperature steam generation.

**Figure 4a** represents a system based on the calcium looping cycle, which exploits the reversible calcination and carbonation reactions of calcium carbonate (CaCO<sub>3</sub>/CaO). During the charging stage, CaCO<sub>3</sub> decomposes endothermically at high temperature, producing CaO and CO<sub>2</sub>, thereby storing energy in chemical form [36]. Renewable electricity is used to supply the heat required in this stage. In the discharge

phase, the carbonation reaction releases heat at elevated temperatures, which is used for steam generation at temperatures up to 850°C [37]. **Figure 4b** presents an alternative system based on the reversible hydroxylation and dehydroxylation cycles of calcium oxide (CaO/Ca(OH)<sub>2</sub>). In this case, the charging stage consists of the endothermic dehydroxylation of calcium hydroxide, driven by electrical input, allowing energy to be stored in chemical form at moderate temperatures [38]. During discharge, the exothermic hydroxylation reaction releases heat at intermediate temperatures, typically in the range of 400–500°C, suitable for medium-temperature steam production [39]. See equations 4–5. Both schemes show the main heat exchangers, solids handling devices, and steam streams associated with thermal charging and discharging. Together, they demonstrate the versatility of calcium-based thermochemical systems for renewable energy storage and the coverage of industrial thermal demand at medium and high temperatures, highlighting their potential as deep electrification solutions in sectors traditionally dependent on fossil fuels.



Calcium looping (CaL) has established itself over the last decade as one of the most promising technologies for CO<sub>2</sub> capture and high-temperature thermochemical energy storage, thanks to the use of abundant, low-cost materials and its high energy density [40,41]. Following its pilot-scale demonstration in post-combustion capture applications (TRL 7) [42], CaL has evolved towards its integration into energy storage and renewable energy production systems, reaching validation in relevant environments (TRL 5) with entrained-flow reactors and modular configurations [43]. The European H2020 SOCRATCES project [44], focused on integrating calcium looping for thermochemical energy storage in CSP plants, concluded in 2021 after the experimental campaign on the world's first kW-scale TCES-CaL prototype using entrained-flow reactors [45]. The state of the art identifies multi-cycle deactivation of CaO due to sintering and loss of porosity, as well as the complexity of solids transport and handling at high temperatures, as the main challenges. In response, recent research explores advanced strategies to improve sorbent stability [46], such as CaCO<sub>3</sub>/Ca(OH)<sub>2</sub> integration through interleaved reversible hydroxylation (HydroCaL) [47], and the design of compact reactors where the complete calcination/carbonation process takes place, avoiding solids transport. These lines of work have demonstrated fast carbonation kinetics (on the order of seconds), operation at the kW scale [45], and have paved the way for more flexible and modular CaL systems, oriented towards both thermochemical storage and negative emissions applications in combination with biomass and renewable sources [48].

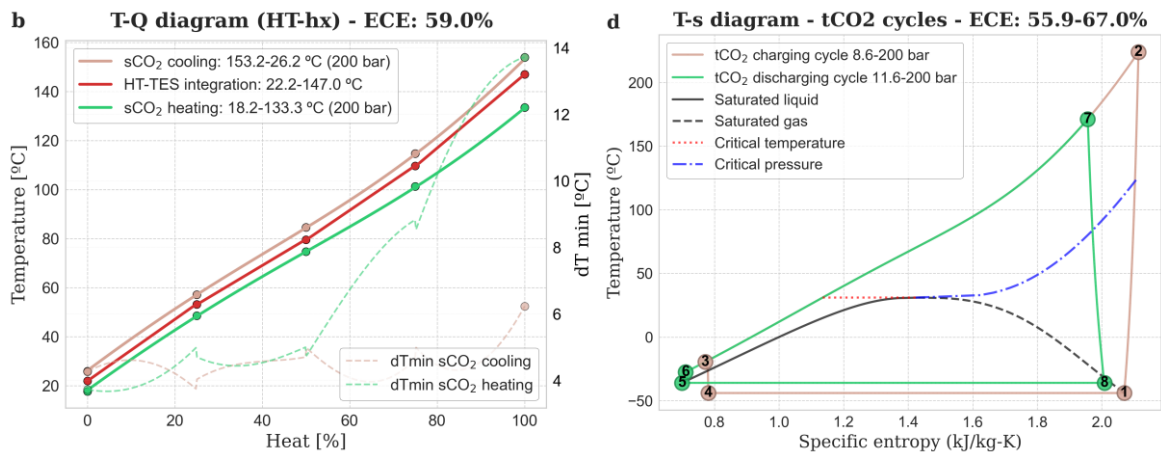
The joint integration of CaCO<sub>3</sub>/CaO and Ca(OH)<sub>2</sub>/CaO cycles constitutes a promising route to combine medium and high-temperature storage and, simultaneously, mitigate the multi-cycle deactivation of CaO in calcium looping systems [46,49]. On the other hand, the thermochemical storage system based on the reversible hydroxylation and dehydroxylation reaction of calcium oxide (CaO/Ca(OH)<sub>2</sub>) in isolation, unlike calcium looping, exhibits high multi-cycle stability of the reactive material, with conversions near 90–100% maintained over dozens or even hundreds of cycles, significantly reducing CaO degradation issues [50]. From a system perspective, recent studies have demonstrated the technical feasibility of integrating the CaO/Ca(OH)<sub>2</sub> cycle into concentrated solar power plants through ambient-temperature storage configurations of the reaction products, high thermal efficiency (>80%) [38], and the possibility of completely decoupling the charging and discharging phases [51]. One of the critical aspects identified is the management of latent heat associated with the water phase change during dehydration and hydration, which can represent up to 40% of the energy involved in the process [38]; advanced solutions such as latent heat recovery systems, auxiliary ammonia Rankine cycles, or pressurised steam storage have been proposed for this purpose. Furthermore, recent work has expanded the scope of this technology through its integration with indirect power cycles [39] (Rankine, ORC, and Brayton with subcritical and supercritical CO<sub>2</sub>), reaching electrical efficiencies on the order of 35–40%, clearly superior to those of conventional CSP systems using molten salts [52].

## 3. Results

### 3.1 Transcritical CO<sub>2</sub> heat pump for cooling and hot water supply

The heat pump system using transcritical CO<sub>2</sub> cycles demonstrates its ability to simultaneously meet refrigeration demands and produce hot water at low and medium temperatures, constituting an effective solution for the electrification of these thermal services. The analysis of the cycle's thermodynamic states shows that the system can operate stably across a wide range of pressure and temperature conditions, allowing the delivery of electricity, heat, and cooling to be adapted to specific demand needs. **Figure 5** shows

the operating diagrams of a reversible heat pump using transcritical CO<sub>2</sub> cycles for the storage of renewable electrical energy in the form of thermal energy (high and low temperature) and the subsequent recovery of thermal energy in the form of flexible power production.



**Figure 5.** Diagrams: left) temperature–heat ( $T$ – $Q$ ) of the high-temperature heat exchanger ( $HT$ - $hx$ ), and right) temperature–entropy ( $T$ - $s$ ) of the transcritical CO<sub>2</sub> cycles, of a Carnot battery or reversible heat pump operating as a tri-generation system (flexible production of electricity, hot water, or refrigeration).

**Figure 5-left** shows a staged heat transfer in the high-temperature heat exchanger, which allows for a much more efficient thermal coupling between the transcritical CO<sub>2</sub> cycle and the subcritical storage system (in this case, liquid hot water), by ensuring that the CO<sub>2</sub> heating and cooling profiles progressively follow the thermal profile of the receiving medium. This behaviour significantly reduces temperature mismatches throughout the exchange, keeping the minimum temperature approach ( $\Delta T_{min}$ ) low and relatively uniform, which results in lower irreversibilities and a direct improvement in system efficiency. Distributing the thermal exchange across a wide range of temperatures avoids concentrating heat transfer at a single thermal level and facilitates the extraction of useful heat at different temperature levels, thus reinforcing the system's ability to flexibly meet thermal energy or hot water demands. **Figure 5-right** shows an operating mode in which the evaporation temperature is reduced to values near  $-45^{\circ}\text{C}$ , significantly expanding the system's capacity to meet deep refrigeration demands while reinforcing its character as a multi-temperature Carnot battery. Shifting the evaporation point towards lower temperatures increases the available thermal gradient between the cold source and the hot source, which translates into greater operational flexibility of the cycle during charging and discharging modes. This reduction in evaporation temperature enables the provision of refrigeration services at very low temperatures without resorting to additional cycles, integrating intense cooling production and useful heat generation at medium temperatures into a single system. However, operating at such low evaporation temperatures implies an increase in the compression ratio and thermodynamic gradients within the cycle. The results show that the trade-off between electric-to-electric conversion efficiency (ECE) and thermal level is favourable, consolidating this configuration as a robust solution for scenarios in which the electrification of thermal demand requires simultaneous very low-temperature refrigeration and efficient heat recovery.

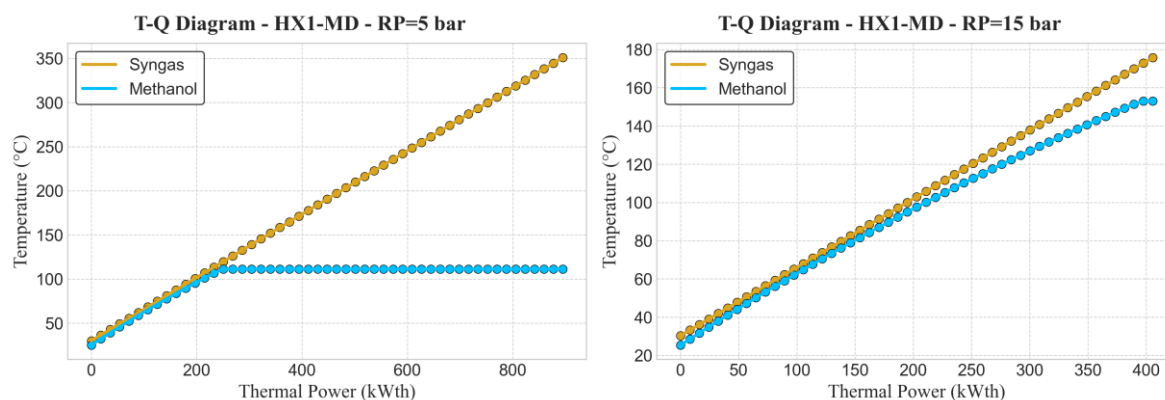
From the perspective of demand coverage, the results confirm that this configuration is particularly suitable for scenarios where continuous needs for refrigeration and low-to-medium temperature heat coexist. Furthermore, the possibility of partially decoupling renewable electricity generation from thermal demand through associated thermal storage expands the system's operational flexibility. Overall, the transcritical CO<sub>2</sub>-based Carnot battery presents itself as a mature and robust solution for the electrification of low-temperature thermal services, acting as the first tier within a multi-temperature coverage strategy based on advanced thermal energy storage technologies.

### 3.2. Synthetic fuel production chain incorporating medium-temperature TES

The synthetic fuel production chain presents high potential for integration with thermochemical storage and as a solution for the electrification of medium-temperature industrial thermal demands. The system is structured around a common charging phase, based on the endothermic decomposition of methanol, and various discharge routes that allow the thermal level of the generated steam to be adapted to specific demand

needs. The recovery of heat from the streams exiting the reactor is a key factor in maintaining high efficiency in the storage of renewable energy and its subsequent recovery during the discharge phases.

During the charging phase, renewable electrical energy is used to drive the endothermic decomposition of methanol into syngas ( $\text{CO} + \text{H}_2$ ) at moderate operating conditions, around  $300^\circ\text{C}$  and 5–20 bar. This reaction allows energy to be stored in chemical form with high energy density and enables the temporal decoupling of electricity generation from thermal consumption, constituting the core of the storage system. Depending on the reactor pressure, the saturation temperature of methanol can change significantly, shifting the evaporation process to higher temperature levels. See **Figure 6**. The syngas produced acts as a flexible intermediate vector, from which different exothermic conversion routes are enabled for the discharge phase.



**Figure 6.** Temperature–heat ( $T$ – $Q$ ) diagrams of the methanol-syngas heat exchanger for different reactor pressures ( $RP = 5$  &  $15$  bar).

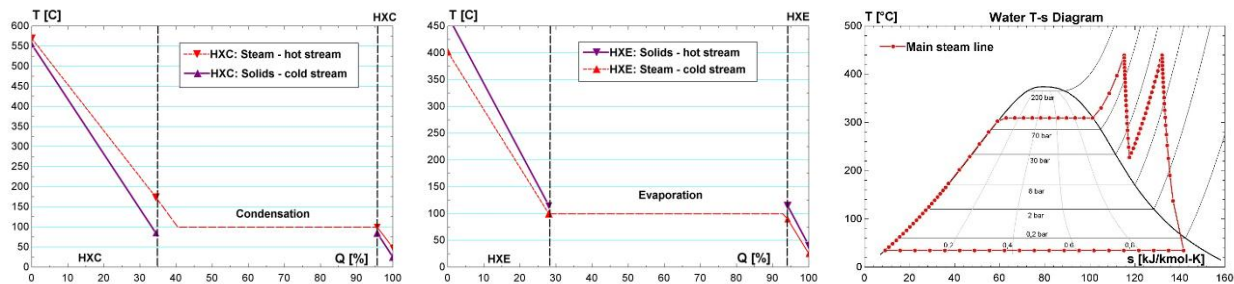
The first discharge route is based on methanol synthesis from syngas, which takes place at conditions similar to those of the charging stage (approximately  $300^\circ\text{C}$  and 5 bar). The exothermic nature of this reaction allows heat to be released in a controlled manner, generating medium-temperature process steam suitable for industrial applications requiring moderate and continuous thermal levels. This route offers the additional advantage of closing the methanol chemical cycle, facilitating the cyclic operation of the system with high operational flexibility. The challenges of this route are related to the thermal integration of the methanol phase change in the heat recovery between inlet/outlet streams. This route allows the use of syngas not only as an intermediate thermal energy carrier but also as a gaseous fuel and flexible feedstock, avoiding the limitations associated with the transport and storage of methanol—which presents greater logistical challenges—while maintaining the possibility of using both the syngas and the final methanol as energy fuels. The second discharge route corresponds to the methanation of syngas in an exothermic reaction at temperatures of around  $400^\circ\text{C}$  and high pressures, approximately 25 bar. This route allows methane to be used as a gaseous fuel directly compatible with existing natural gas infrastructure, facilitating its storage, transport, and final use for both thermal and electrical generation, in addition to allowing simple integration with conventional energy networks. The challenges are related to the utilisation of the condensation heat from the water vapour formed in the reaction. The third analysed discharge route is the synthesis of dimethyl ether (DME), which occurs exothermically at temperatures near  $250^\circ\text{C}$  and high pressures, around 40 bar. DME synthesis provides a high-energy-density liquid fuel that is easily storable and transportable, which can be used directly as a diesel substitute or as a clean industrial fuel, significantly expanding final use options beyond steam generation. The challenges are related to the utilisation of the condensation heat of the DME itself.

The joint analysis of the three discharge routes highlights the capability of the synthetic fuel-based system to meet a wide range of medium-temperature thermal demands through a single charging-phase storage scheme. The selection of the exothermic reaction in the discharge phase allows for the adjustment of both the desired fuel production and the thermal level of the generated steam without modifying the system's main architecture, providing high design flexibility. Overall, these results position synthetic fuel chains as an effective solution for the electrification of medium-temperature industrial thermal demand.

### 3.3. Ca-based TCES systems and medium- and high-temperature steam generation

Calcium-based thermochemical energy storage systems show high potential for the generation of process steam at medium and high temperatures, covering thermal ranges that cannot be reached by conventional heat pumps or other sensible thermal energy storage systems.

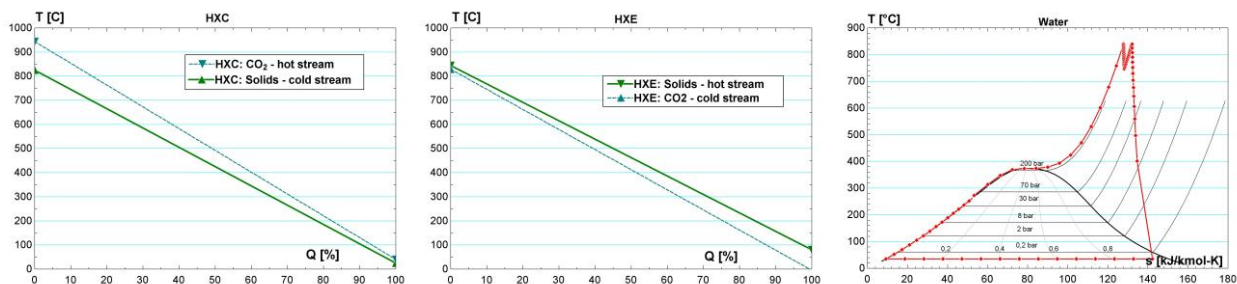
The TCES system based on the reversible  $\text{CaO}/\text{Ca}(\text{OH})_2$  reaction presents an operating profile suitable for medium-temperature steam generation. During the discharge stage, the exothermic hydration reaction releases heat at temperatures typically between 400 and 550°C, enabling the production of saturated or slightly superheated steam at moderate pressures. **Figure 7** shows the temperature profiles in the heat exchangers for efficient recovery between inlet/outlet streams and the potential indirect integration of a steam plant. The homogeneity of the outlet thermal conditions makes the system particularly attractive for continuous industrial applications requiring medium-temperature process steam with high reliability.



**Figure 7.** T-Q diagrams of the heat exchange in the charging and discharging phases for a 100% conversion rate in both reactors, and T-s diagram of a steam plant coupled to the exothermic reactor, in the  $\text{CaO}/\text{Ca}(\text{OH})_2$  system

The solids stream entering the reactor can be adjusted with a purely sensible heat exchange temperature profile. Due to the phase change, the heating/cooling of the steam is carried out in three stages. This latent heat of condensation from the steam exiting the reactor (**Figure 7**-left) can account for 38% of the heat reaching the reactor. When the TCES system operates in isolation, the recovery of this heat is vital to achieve high thermal efficiency within the system, posing several options such as ammonia Rankine cycles or pressurised steam storage systems. However, coupling to thermal networks with energy demands for process steam allows the coupling of generation (charging phase) and consumption (discharging phase) of the quantity required by the reactions, avoiding phase change and storage in the form of liquid water. With a relatively high reaction enthalpy, results confirm that the  $\text{CaO}/\text{Ca}(\text{OH})_2$  cycle allows for a high thermal efficiency (87%), using surplus photovoltaic energy to supply stable thermal power on the order of 0.31  $\text{MW}_{\text{th}}$  in hydration and 0.27  $\text{MW}_{\text{th}}$  intended for continuous steam generation over 24 h for every  $\text{MW}_{\text{th}}$  during 8 h in the dehydration stage, highlighting its potential as a thermochemical storage system for the reliable electrification of medium-temperature industrial demands.

In the case of TCES-CaL, the exothermic carbonation reaction allows the release of large amounts of heat at high temperatures, resulting in the generation of superheated steam at temperatures that can exceed 800°C, suitable for meeting high-temperature and high-pressure steam demands typical of energy-intensive industrial processes. **Figure 8** shows the temperature profiles in the heat exchangers for efficient recovery between inlet/outlet streams and the potential indirect integration of a steam plant.



**Figure 8.** T-Q diagrams of the heat exchange in the charging and discharging phases for a 50% conversion rate in both reactors, and T-s diagram of a steam plant coupled to the exothermic reactor, in the  $\text{CaO}/\text{CaCO}_3$  system.

In this case, the heat exchanges are purely sensible, facilitating good integration within the heat recovery temperature profiles between streams. Here, the multi-cycle deactivation of CaO requires an increase in the quantity of reactants entering the reactor when conversion is reduced. Furthermore, the possibility of operating the system with recirculated CO<sub>2</sub> streams reinforces its integration with carbon management strategies without compromising the available thermal potential.

The joint analysis of both configurations highlights their complementary nature within a multi-temperature electrification strategy. While calcium looping allows for the coverage of high-temperature steam demands traditionally associated with the direct combustion of fossil fuels, the CaO/Ca(OH)<sub>2</sub> cycle positions itself as a robust solution for the electrification of medium-temperature steam demands. Additionally, recent studies show a mitigation of the progressive deactivation of CaO in the CaL process through hydroxylation–dehydroxylation cycles, resulting in higher effective conversions and an improvement in the overall performance of the thermochemical storage system.

## 4. Conclusions

This work has evaluated the potential of various advanced thermal energy storage technologies for the electrification of thermal demand at multiple temperature levels, ranging from refrigeration and low-temperature heat applications to the generation of process steam at medium and high temperatures. The results confirm that a strategy based on complementary technologies allows for a significant expansion of the scope of thermal electrification, overcoming the limitations of individual solutions.

The heat pump system with transcritical CO<sub>2</sub> cycles presents itself as a mature and flexible solution for the simultaneous coverage of refrigeration demands and hot water production at low and medium temperatures (up to approximately 200°C). These Carnot batteries integrated with CCS represent a point of convergence between thermal engineering, renewable energies, and geosciences, with notable potential for flexible, large-scale energy storage. Staged thermal integration reduces irreversibilities in heat exchange and improves overall system efficiency, while operating at very low evaporation temperatures extends the refrigeration temperature range (down to -40°C) without the need for additional cycles. These characteristics consolidate the CO<sub>2</sub>-based Carnot battery as the first tier of a multi-temperature electrification strategy.

New gaseous and liquid fuels of renewable origin are identified as particularly relevant options for transport and heavy industry, supported by technological and economic feasibility studies analysing their role in 2050 climate neutrality scenarios. Among these energy vectors, renewable methanol stands out for its versatility, high energy density, and compatibility with existing infrastructure, positioning itself as a key intermediary on the paths towards a carbon-neutral energy system. The methanol–syngas–methane–DME synthetic fuel production chain has shown high potential as a thermochemical storage system for the electrification of medium-temperature industrial thermal demands (250–400°C). The use of a common charging phase and different discharge routes allows for the adjustment of both the thermal level of the generated steam and the fuel produced, providing operational flexibility and added value to the system by enabling the use of methanol, syngas, methane, or DME as storable and transportable energy vectors.

Calcium-based thermochemical storage systems have demonstrated a remarkable capacity to meet medium and high-temperature steam demands. The CaO/Ca(OH)<sub>2</sub> cycle stands out for its high multi-cycle stability and its ability to supply steam continuously with high thermal efficiency (approximately 450–550°C), while calcium looping enables very high temperatures to be reached (850–950°C), suitable for highly energy-intensive industrial processes. Furthermore, the integration of both configurations offers a promising route to mitigate CaO deactivation, improving effective conversions and overall storage performance.

Taken together, the results highlight that the electrification of thermal demand across a wide temperature range requires a systemic approach supported by advanced and complementary storage technologies. The homogeneous characterisation framework developed in this work provides a solid foundation for the conceptual design of energy systems aimed at the deep decarbonisation of industrial sectors that are difficult to electrify.

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## Nomenclature

CaL	Calcium Looping
CCS	Carbon Capture and Storage
CEEGS	CO <sub>2</sub> -based Electrothermal Energy and Geological Storage
CSP	Concentrated Solar Power
DME	Dimethyl ether
ECE	Electric-to-electric conversion efficiency
Hydro	Reversible hydroxylation
HydroCaL	CaCO <sub>3</sub> /Ca(OH) <sub>2</sub> integration
LCOE	Levelised Cost of Electricity
ORC	Organic Rankine Cycle
PV	Photovoltaic
TCES	Thermochemical Energy Storage
TRL	Technology Readiness Level

### Subscripts and superscripts

<i>e</i>	electric
<i>th</i>	thermal

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