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Dynamic Modeling and Analysis of a Disruptive Thermochemical Energy Storage Suitable for Linear Focus Solar Technologies

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Abstract. The industrial sector is a significant energy consumer, primarily reliant on fossil fuels. Nevertheless, the potential of Concentrated Solar Power (CSP) technologies for decarbonizing the industry is promising and the challenges posed by variability in weather and seasons can be effectively addressed through the use of seasonal storage methods, such as Thermochemical Energy Storage (TCES). This study presents a dynamic lumped-capacitance model, implemented in Dymola, designed to simulate a continuous suspension reactor employing salt hydrates like calcium oxalate monohydrate/anhydrous. The model mainly comprised (i) heat balances, (ii) reaction kinetics for the dehydration process and (iii) a heat transfer model. Furthermore, the study delves into a comprehensive case study involving the integration of CSP and TCES into a dairy processing facility located in Spain, addressing both daily operational requirements and seasonal energy storage demands. The solar field, heating demand, and storage tanks are described in detail. The transient simulation results for July showcase the efficacy of the solar installation and sensible energy storage for day-to-day operations, resulting in a total solar contribution of 47.3%. Notably, the thermochemical energy stored during this period can cover 22.1% of the low-temperature energy demand in January. The study underscores the importance of TCES in sustainable energy systems and paves the way for further optimization, economic assessment, and expanded applications. Future work will focus on enhancing the model and incorporating additional thermochemical materials, supported by additional experimental data.

Keywords: Thermochemical Energy Storage, Solar Heat Industrial Process, Seasonal Storage

1. Introduction

The industrial sector accounted for 37% of global energy use in 2022, corresponding to around 166 EJ per year. A large fraction is covered by fossil fuels burned in conventional boilers, mainly relying on natural coal (28%), oil (19%) and gas (18%) with a very limited contribution from renewable energy sources due to their unpredictability and lack of dispatchability on seasonal base. In this context, Concentrated Solar Power (CSP) is one of the promising technologies for achieving the industrial decarbonization. However, the variability of this resource is an important challenge. This variability is present in short-term periods, due to clouds and the day-night cycle, but also in long-term periods (seasons), since the amount of solar energy available during summer can be much higher than in winter, especially in high latitudes. It limits the competitiveness and application of this technology. Therefore, energy storage technologies can play a key role because they allow to supply the demand independently of the variability of the resource. In particular, seasonal energy technologies (SST) are also able to store the excess energy during summer and provide it during high-demand periods, such as winter. Thermochemical Energy Storage (TCES) can offer viable solutions since has the potential to store energy with higher energy storage densities, for theoretically unlimited periods with non-heat losses (solids are stored at ambient temperatures) and distances (solids can be transported). Among the different alternatives, those based on reversible reactions including water (e.g., H_3BO_3, CaC_2O_4, $MgSO_4$) are of particular interest due to their high reversibility, proper kinetics, reaction heat, stability, material recyclability, low environmental impact, and reduced cost. Due to its reaction temperatures (100-200 °C), this system can be conveniently integrated with medium-temperature CSP, particularly linear focus collectors for solar heat applications (industrial process and district heating) or electricity generation trough Organic Rankine cycles.

This study focuses on a continuous suspension reactor utilizing the well-known calcium oxalate (CaC_2O_4). As depicted in Figure 1, the concept offers the capability to provide both daily sensible heat storage and seasonal thermochemical energy storage, seamlessly integrated with parabolic trough technology. The concept also includes a conventional gas boiler as a backup system. Initially, a transient thermochemical energy storage model was developed, and subsequently, it was integrated with a model representing a solar field operating in conjunction with a variable heating demand.

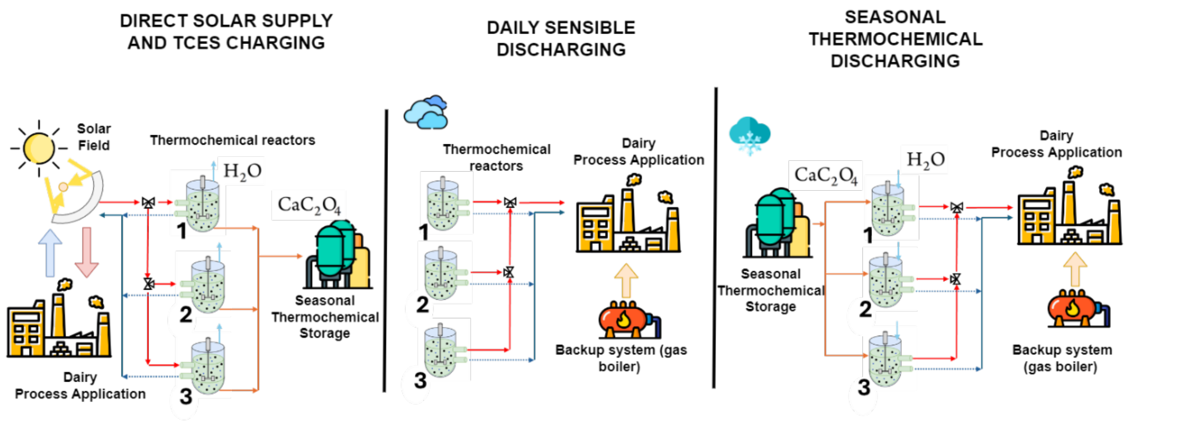

Figure 1. *Scheme of the proposed concept that couples sensible and thermochemical energy storage for both daily and seasonal storage.*

2. Thermochemical Energy Storage Model

The thermochemical model has been implemented in the Modelica language and subsequently translated into numerical simulation code using Dymola, which employs the differential-algebraic system solver DASSL. In this section, we provide a comprehensive description of the modeling work and present the underlying hypotheses that have been considered. The model is composed by (i) heat balances, (ii) reaction kinetics, (iii) heat transfer model and (iv) other phenomena such as external film mass transfer and bubble rising. Finally, the model has been validated against the similar method described by Garofalo et al. [1], which also implies experimental work at lab-scale.

Although transient charging process is evaluated considering the reaction kinetics of dehydration, it is necessary to note that the kinetics governing rehydration remain unknown. As a result, the released heat generated by the thermochemical reaction is solely accounted for in the context of seasonal storage, with its dynamic behaviour left unmodeled. Nevertheless, as part of the Horizon 2020 RESTORE project, there is a plan to conduct an experimental kinetic study to gather additional insights into these aspects.

2.1 Heat Balances

The simulation of the thermochemical energy storage unit relies on a lumped-capacitance model. This model simplifies the thermal system by dividing it into discrete "lumps", assuming that the temperature difference within each lump is negligible. Consequently, the system components, such as thermal oil or particles, are treated as having a uniform temperature and integral heat transfer interaction between them is modelled (see Figure 2). This approach results in a straightforward and computationally efficient transient heat transfer model for simulating the entire system. General heat balances are now presented for charging process, involving the integration of various components.

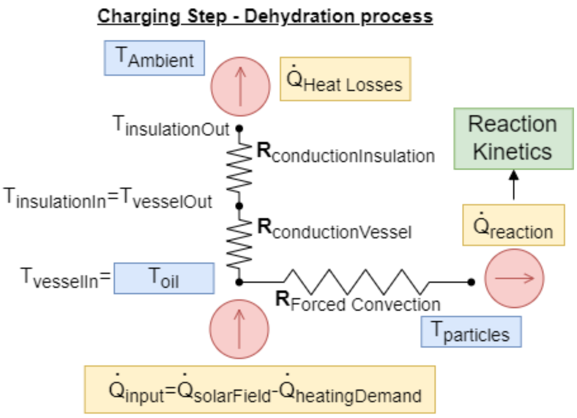

Figure 2. *Simplified scheme of the lumped-capacitance model.*

The heat balance in the oil is considered as follows

$$m_{TOT} \cdot f_{oil,0} \cdot c_{p,oil} \cdot \frac{dT_{oil}(t)}{dt} = \dot{Q}_{\ input} - \dot{Q}_{\ convection,oil-particles} - \dot{Q}_{\ heat\ losses} \quad (1)$$

where m_{TOT} represents the total mass of the suspension, $f_{oil,0}$ is the initial feed mass fraction of thermal oil in the suspension and $c_{p,oil}$ refers to the specific heat. The parameter $\dot{Q}_{\ input}$ corresponds to the power introduced into the energy storage units, generated in the solar field.

The increase in the temperature of the particles is used to drive the endothermic chemical reaction. Consequently, the heat balance in the particles is represented in Eq. 2.

$$m_{TOT} \cdot f_{particles,0} \cdot c_{p,particles} \cdot \frac{dT_{particles}(t)}{dt} = \dot{Q}_{\ convection,oil-particles} - \dot{Q}_{\ reaction} \quad (2)$$

where $f_{particles,0}$ is the initial feed mass fraction of particles in the suspension and $c_{p,particles}$ refers to the specific heat of the particles. It is necessary to mention that dehydrated particles and rehydrated particles present different values of thermal properties (e.g., specific heat or density), thus, the specific heat of the particles has been defined as in Eq. 3, taking into account the reaction advancement, where x signify the degree of conversion of the reaction.

$$c_{p,particles} = (1-x)c_{p,COM} + xc_{p,COA} \quad (3)$$

Finally, the heat losses to the ambient have been modelled considering natural convection with the surrounding air.

2.2 Reaction Kinetics

The kinetics of the calcium oxalate monohydrate dehydration suppose the core of the charging process and it is governed by the Eq. 4.

$$R = \frac{dx}{dt} = k_0 exp(-\frac{E}{R_g T_{particles}})\mathcal{F}(x) \quad (4)$$

R means the rate of reaction, k_0 is the pre-exponential factor, E the apparent activation energy, and R_g the gas constant. Additionally, $\mathcal{F}(x)$ is the conversion function, depending on the reaction mechanism. According to Vlaev et al. [2], the mechanism of phase boundary reaction R_3 (spherical symmetry) is the most probable, thus, the corresponding expressions that have been used are reported in Table 1.

Table 1. *Parameter of the reaction kinetics [1], [2].*

Parameter	Values
k_0	6.7 x 10^{13} min^{-1}
E	118.6 kJ/mol
$\mathcal{F}(x)$	$3(1 - x)^{2/3}$
$\Delta H_{Dehydration}$	56.09 kJ/mol (at 200 °C)
$\Delta H_{Rehydration}$	-21.29 kJ/mol (<100 °C)

The difference between the enthalpy of Dehydration and Rehydration are mainly associated to the vaporization of water (in case of Dehydration produced water is in gas state while in the rehydration, it is in liquid state). The rate of stored energy of the thermochemical reaction is calculated as follows

$$\dot{Q}_{reaction} = \Delta H_{Dehydration} \cdot moles_{particles} \cdot R \quad (5)$$

where $\Delta \boldsymbol{H_{Dehydration}}$ is the reaction enthalpy at 200 °C, which has been considered ideally constant during the complete charging step, and $\boldsymbol{moles_{particles}}$ are calculated based on the molecular weight. Finally, with regards to the rehydration, which exhibits lower enthalpy [1], the released energy during the complete process is calculated from Eq. 6.

$$E_{released\ Energy} = \Delta H_{Rehydration} \cdot moles_{particles} \cdot x \quad (6)$$

2.3 Heat Transfer Model

In Eq. 7, $\dot{Q}_{convection,oil-particles}$ models the oil-to-particle heat transfer inside the suspension. The primary assumptions for this heat transfer are as follows: (i) the particles are considered spherical, characterized by a particle diameter d_p; (ii) the particles are isolated, i.e., there are no particle-particle interactions; (iii) heat transfer resistance is present solely within the liquid film surrounding the particle and (iv) the effect of agitation is negligible.

$$\dot{Q}_{convection,oil-particles} = h \cdot A_{particles} \cdot (T_{oil}(t) - T_{particles}(t)) \quad (7)$$

where h is the convective heat transfer coefficient and $A_{particles}$ is the heat transfer surface, which is determined by summing the total surface areas of the spherical particles. In order to estimate the Nusselt correlation, it is essential to find an appropriate expression for the slip velocity between the oil and the particles. In an agitated solid suspension, the turbulent hydrodynamic field is complex and includes interactions between solid particles, making it challenging to precisely define a relative fluid-particle velocity. Consequently, this relative velocity has been assumed to be equal to zero, i.e., a conservative scenario where heat transfer is affected only by conduction. Therefore, it can be demonstrated that the Nusselt number equals 2 and the corresponding expression for the heat transfer coefficient is provided in Eq. 8.

$$h = \frac{2\lambda_{oil}}{d_p} \quad (8)$$

2.4 Other phenomena: External film mass transfer and bubble rising

Additionally, other phenomena such as the external film mass transfer and the bubble rising upon the dehydration process have been included in the model according to Garofalo et al. [1]. The results, based on the hypotheses of the bibliography previously mentioned, indicate that, under the specified operating conditions, the primary controlling factor influencing the process is the kinetics. Nevertheless, the effects of these phenomena will be included in forthcoming publications, encompassing a parametric study and taking into consideration additional experimental data.

3. Case Study - Description

Once, the basic model has been validated against the results showed by Garofalo et al. [1], it has been incorporated into a case study to illustrate the concept of a solar heat industrial process utilizing TCES. This concept has been implemented within a dairy process located in Pamplona, Navarre, in the northern region of Spain, with operating temperatures lower than 200 °C. In this section, descriptions of the (i) solar field, (ii) heating demand, and (iii) storage configuration of the case study are provided.

3.1 Solar Field

A simplified model of a solar field comprising parabolic trough collectors has been included. This model calculates the instantaneous power generated by the solar field based on several factors, as expressed in Eq. 9.

$$\dot{Q}_{Solar\ Field} = A_{aperture\ Area} \cdot \eta_{Optical} \cdot IAM_{Factor} \cdot \eta_{Thermal} \tag{9}$$

In this equation, $A_{aperture\ Area}$ represents the total aperture area of the solar field, $\eta_{Optical}$ is the optical efficiency (calculated using typical values for parameters such as cleanness factor, mirror reflectivity, self-shadowing factor, etc.), IAM_{Factor} is the Incidence Angle Modifier, calculated depending on sun position and evaluated through ray tracing software (Tonatiuh), and $\eta_{Thermal}$ is the thermal efficiency calculated according to Forristall's method and applied to the entire solar field.

The location experiences an annual DNI of 1550 kWh/m² and the designed solar field presents an aperture area of 1590 m², north-south orientation, temperature operation of 180°C, and the selected collector is the Eurotrough with a $\eta_{Optical}$ of 0.793.

3.2 Heating Demand

Solar energy has a great potential to be applied to the food industry since it is one of the top five energy demanding industrial sectors. Specifically, dairy companies require significant thermal energy for their heating and cooling processes like fermentation, pasteurization, drying, and cleaning. Moreover, these processes require operation temperatures lower than 200 °C, most of them in the range of 40-150 °C. Therefore, they can be effectively integrated with linear focus solar technologies and the storage concept put forth in the RESTORE project.

The heating demand of the case study is based on the publication from Quijera et al. [3]. It encompasses four distinct primary processes (see Figure 3), including: (i) high-temperature pasteurization at 150 °C, as well as low-temperature operations such as (ii) curdling at 40 °C, (iii) fermentation at 45 °C, and (iv) cleaning procedures at 60 °C. Finally, it is considered that due to the climate conditions, the heating demand during winter is 8% higher than during the summer season.

3.3 Storage tanks

The plant is equipped with three storage tanks, each measuring 2 meters in diameter and 2.5 meters in height. These tanks have a maximum thermal power capacity of 300 kW and can be operated in parallel when sufficient energy is available. The heat transfer fluid utilized is FragolTherm X-400-A, a silicon oil. The tanks contain a calcium oxalate fraction of 0.44 and employ nominal particle diameters of 1 mm. Based on the dairy process, the maximum charging temperature is set at 170 °C, while the minimum discharging temperature is maintained at 60 °C.

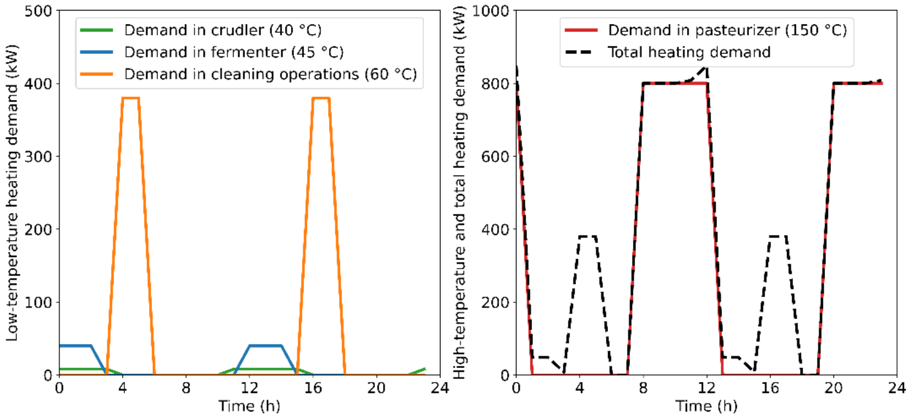

Figure 3. *Daily demand of the dairy company for each process.*

4. Case Study - Results

Initially, the analysis of particle diameter influence is presented. Figure 4 depicts the charging process at maximum thermal power (300 kW) with particle diameters of 1 mm, 10 mm, and 15 mm. High particle diameters are associated with slower thermochemical reactions, and it is worth noting that a negligible temperature difference between oil and particles is observed for d_p<1.

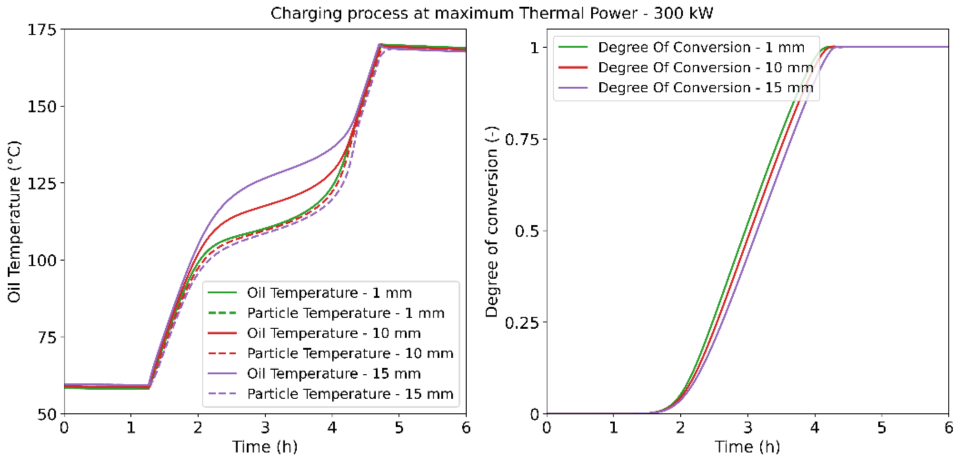

Figure 4. *Simulation of a sunny day in July: Thermal power, oil temperature and degree of conversion of each storage tank.*

Figure 5 displays the results obtained for simulating a sunny day in July. The upper chart delineates the thermal power generated by the solar field, the heating demand and the thermal power of each storage tank. Whenever solar power exceeds heating demand, the surplus energy is consecutively directed into the storage tanks, progressively elevating their oil temperatures until they reach full capacity. The first storage tank is initially charged, and when the excess thermal power exceeds 300 kW, the next storage tank is utilized, and so forth. Subsequently, when heating demand surpasses solar power, the sensible heat is discharged into the dairy process ($\dot{Q}_{tank} < 0$) concurrently with the extraction of converted solids of oxalate calcium anhydrous for seasonal storage. Therefore, the degree of conversion is reset to zero. Notably, the theoretical thermochemical reaction occurs within a temperature range below 150 °C, pending further experimental validation across a diverse array of boundary conditions. Finally, the temperature reduction observed during standby mode is attributed to heat losses falling within the range of 0.5-1 °C/hour.

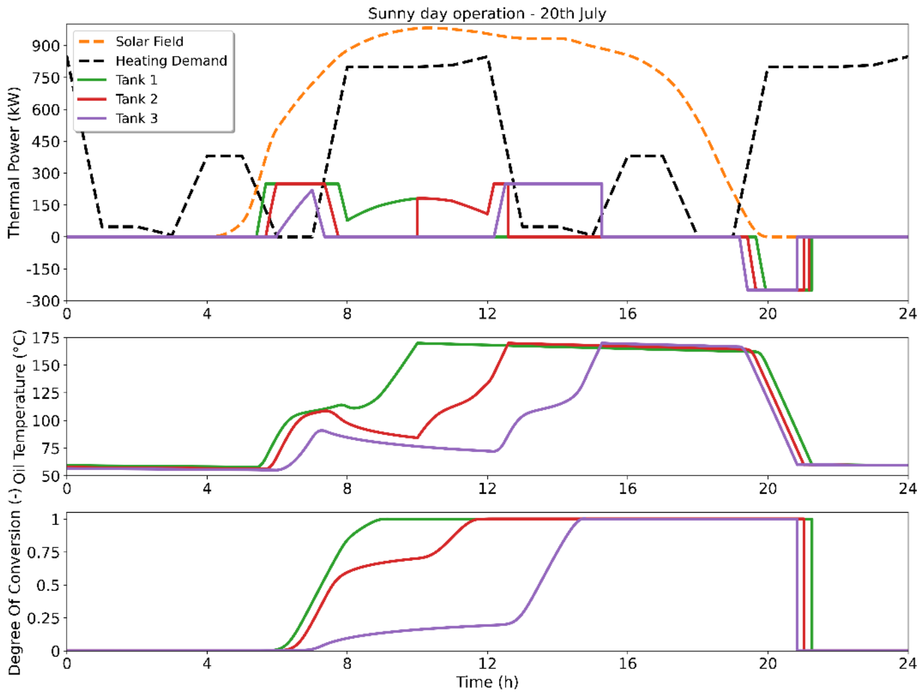

***Figure 5**. Simulation of a sunny day in July: Thermal power, oil temperature and degree of conversion of each storage tank.*

Finally, the simulation results for the month of July are reported in Table 2. With the selected configuration, the solar thermal energy could cover the 47.3 % of the demand, of which 9 % is attributed to the sensible thermal energy storage. Finally, Table 3 presents the contribution of the thermochemical energy storage for the month of January. The findings indicate that the seasonal storage accumulated during July, in the form of thermochemical storage, can meet 22.1% of the low-temperature (<100 °C) thermal demand.

***Table 2.** Energy results for July. Transient simulation.*

Parameter	Values
Thermal Energy Demand	1092.4 GJ
Direct Solar Energy provided	417.9 GJ
Sensible Heat Discharged from Storage	98.7 GJ
Total Solar Contribution	**47.3 %**
Sensible Heat Storage Contribution	**9.0 %**
Thermochemical Energy Stored	48.8 GJ

Table 3. *Energy results for January.*

Parameter	Values
Total Thermal Energy Demand	1179.8 GJ
Low-Temperature Energy Demand	221.7 GJ
Thermochemical Total Contribution	4.2 %
Thermochemical Low-Temperature Contribution	**22.1 %**

5. Conclusions and Next Steps

A dynamic model of thermochemical energy storage (TCES) has been developed, encompassing both daily and seasonal storage functionalities. The model has been examined in a case study involving the deployment of parabolic trough collectors in the dairy industry. In July, the solar thermal energy covers the 47.3 % of the demand, of which 9 % is attributed to the sensible thermal energy storage using only three small-scale tanks. Additionally, the results indicate that the energy stored in the seasonal storage during July could cover 22.1% of the demand for low-temperature processes in January. Regarding the next steps, an extensive parametric study is being carry out to optimize the installation, assess the economic implications and conduct a more in-depth analysis of potential applications. Finally, within the RESTORE project, it is planned to enhance the model by implementing dynamic discharge (rehydration) modeling and additional thermochemical materials, corroborating with experimental data.

Data availability statement

Public information about the RESTORE project with further details can be found on its website.

Competing interests

The authors declare no competing interests.

Author contributions

Francisco Cabello: Conceptualization, Investigation, Methodology, Project administration, Writing – review & editing; **Javier Baigorri**: Conceptualization, Investigation, Methodology, Writing – original draft; **Fritz Zaversky, Markus Haider, Franz Winter, Andreas Werner**: Supervision, Writing – review & editing.

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