Characterization, equation formulation and enhancement of phase change materials (PCM) for thermal energy storage (TES)

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Characterization, equation formulation and enhancement of phase change materials (PCM) for thermal energy storage (TES)

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CERTIFIQUEN:

Que la memòria “Characterization, equation formulation and enhancement of phase change materials (PCM) for thermal energy storage” presentada per Gerard Ferrer Muñoz per optar al grau de Doctor s’ha realitzat sota la seva supervisió.

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Resum

L'edificació, la indústria i el transport són els tres principals sectors consumidors d'energia, representant el 96 % de l'energia final consumida a la Unió Europea, i essent responsable de gairebé la totalitat de les emissions de CO_2. El programa Horizon 2020 de la Comissió Europea expressa la necessitat de reduir el consum d'energia i les emissions d'efecte hivernacle en un 20 % per l'any 2020. Per tant, es necessiten millores en els tres sectors que exigeixen la integració i un ús complet d'energies renovables. L'emmagatzematge d'energia és un dels principals camps considerats i desenvolupats per reduir les emissions, doncs permet emparellar la demanda i el subministrament d'energia amb sistemes simples i eficients.

Els sistemes d'emmagatzematge d'energia tèrmica (TES) permeten emmagatzemar densitats d'energia elevades per poder variar la demanda d'energia i facilitat l'ús d'energia renovables. Aquesta tesi està principalment enfocada en l'emmagatzematge de calor latent, una tecnologia què, tot i que ha estat àmpliament estudiada, encara necessita millores i presenta buits importants. Un dels principals objectius és el de millorar la caracterització de materials de canvi de fase (PCM), centrant-se en millorar les metodologies existents i proposant-ne de noves, tal i com s'ha fet per a la determinació de la capacitat calorífica específica (C_p).

Aquest document també presenta contribucions per a la millora del disseny dels sistemes de TES. Les equacions empíriques permeten conèixer les propietats d'un material amb anterioritat, sense la necessitat d'experiments, proporcionant dades de confiança i d'errors petits per millorar les simulacions del sistema i, conseqüentment, el seu disseny. Aquesta tesi presenta equacions empíriques per determinar la viscositat i la C_p de parafines i àcids grassos utilitzats com a PCM.

Finalment, la nano-tecnologia és una de les tecnologies utilitzades per millorar les propietats dels PCM i augmentar el rendiment dels sistemes de TES. En aquesta tesi es revisa l'estat de desenvolupament que aquesta tecnologia té en el camp del TES i el potencial per la seva expansió i ús futur.

Resumen

La edificación, la industria i el transporte son los tres principales sectores consumidores de energía, representando el 96 % de la energía total consumida en la Unión Europea, y siendo responsables de casi la totalidad de las emisiones de CO_2. El programa Horizon 2020 de la Comisión Europea expresa la necesidad de reducir el consuma de energía i las emisiones de efecto invernadero en un 20 % para el año 2020. Por consiguiente, se necesitan mejoras en los tres sectores que exijan la integración y un uso completo de energías renovables. El almacenaje de energía es uno de los principales campos considerados y desarrollados para reducir las emisiones, pues permite emparejar la demanda y el subministro de energía con sistemas simples y eficientes.

Los sistemas de almacenaje de energía térmica (TES) permiten almacenar densidades de energía elevadas para poder variar la demanda de energía y facilitar el uso de energías renovables. Esta tesis está principalmente enfocada en el almacenaje de calor latente, una tecnología que, aunque ha sido ampliamente estudiada, aún necesita mejoras y presenta vacíos importantes. Uno de los principales objetivos es el de mejorar la caracterización de materiales de cambio de fase (PCM), centrándose en mejorar las metodologías existentes y proponiendo de nuevas, tal y como se ha hecho para la determinación de la capacidad calorífica específica (C_p).

Este documento también presenta contribuciones para la mejora del diseño de los sistemas de TES. Las ecuaciones empíricas permiten conocer las propiedades de un material con anterioridad, sin la necesidad de experimentos, proporcionando datos de confianza y de errores pequeños para mejorar las simulaciones del sistema y, consecuentemente, su diseño. Esta tesis presenta ecuaciones empíricas para determinar la viscosidad y la C_p de parafinas y ácidos grasos usados como PCM.

Finalmente, la nano-tecnología es una de las tecnologías utilizadas para mejorar las propiedades de los PCM y aumentar el rendimiento de los sistemas de TES. En esta tesis se revisa el estado de desarrollo que esta tecnología tiene en el campo del TES y el potencial para su expansión y uso futuro.

Summary

Buildings, industry and transport are the three main energy consuming sectors, representing the 96 % of the final energy consumption in the European Union, and being responsible of almost the totality of the CO_2 emissions. The horizon 2020 program of the European Commission expresses the need to reduce by 20 % the energy consumption and greenhouse emissions by the year 2020. Improvements in the three sectors are therefore needed and require the integration and full use of renewable energies. Energy storage is one of the main fields considered and developed to reduce emissions, allowing to match energy demand and supply with simple and efficient systems.

Thermal energy storage (TES) systems allow the storage of high energy densities in order to shift the energy demand and ease the use of renewable energies. This thesis is mainly focused in latent energy storage, a technology that despite having been widely studied, still requires improvements and presents important gaps. One of the main objectives is to improve phase change materials (PCM) characterization, focusing in upgrading the current methodologies and proposing new ones, such it has been done for specific heat capacity (C_p) determination.

Contributions to improve TES system design are also presented in this document. Empirical equations allow determining material properties in advance and without the need of experimental runs, providing low error reliable data to improve systems simulations, and therefore, its design. Empirical equations for viscosity and C_p determination of paraffin and fatty acid PCM are presented in this thesis.

Finally, nanotechnology is one of the technologies used to enhance PCM properties and improve the performance of TES systems. This thesis reviews the development this technology currently has in the TES field and the potential of its spreading and future use.

Nomenclature

IEA	International energy agency
DSC	Differential scanning calorimeter
DTA	Differential thermal analysis
HTF	Heat transfer fluid
PCM	Phase change materials
NEPCM	Nano-enhanced phase change materials
TCM	Thermochemical materials
TES	Thermal energy storage
TGA	Thermogravimetric analysis

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1 Introduction

One of the main focuses of the European Commission Horizon 2020 program in order to face the climate change challenge is the reduction of energy consumption and carbon footprint by 2020 and 2030 [1]. Other important specific objectives in which the program is structured are low cost electricity supply, alternative fuels and mobile energy sources, the development of one single European electricity grid, and the market uptake of energy and ICT innovation. Research activities involved to accomplish these priorities include photovoltaics, concentrated solar power, wind energy, ocean energy, hydro power, geothermal energy, renewable heating and cooling, energy storage, biofuels and alternative fuels, carbon capture and storage. The use of low carbon technologies as primary energy sources is presented as one of the most affordable, cost-effective and efficient solutions to reduce the consumption of fossil fuel energies in buildings, industry and heating and cooling services.

The European Commission stated in the 2011 Energy Efficiency Plan that the greatest energy saving potential lies in buildings. Reduction of the energy consumption of about 60-80 MToe/year can be obtained with the minimum energy savings in buildings, just with small rigorous and sustainable changes [2].

1.1 Energy consumption in Europe

The final energy consumption by sector in the European Union (EU) shows (Figure 1) that the building sector represents more than one third of the total energy market and that just 30 % of this energy comes from renewable sources. Natural gas, oil and coal still represent 37 % of energy sources, while electricity provides 28 % of buildings. Moreover, 70 % of this consumption is for heating and appliances in cold climates and for water heating and cooking in moderate and warm climates [3].

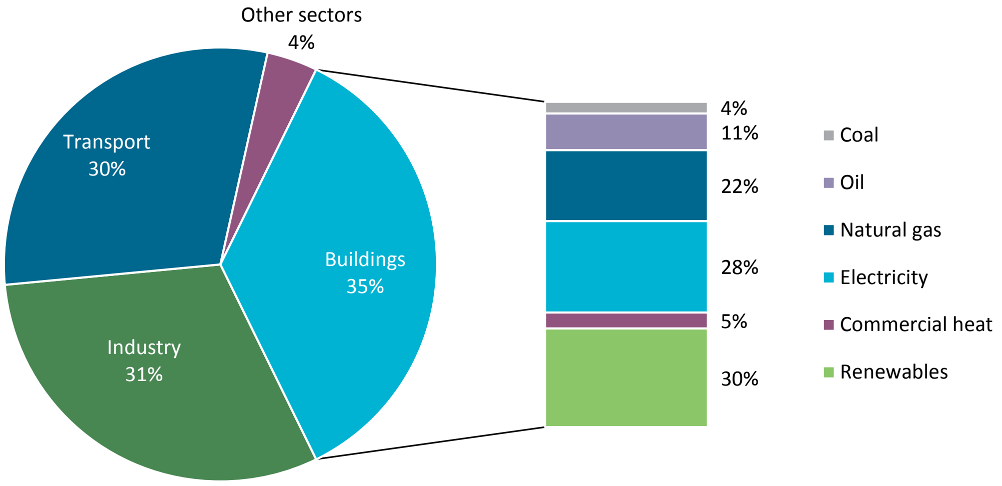


Figure 1. Final energy consumption by sector and buildings energy mix, 2010 [3]

In addition, the building stock outstands among the other energy consuming infrastructures as the one with most life span, being building energy consumption also responsible of almost 40 % of total carbon dioxide (CO_2) related emissions in EU [4].

Industry and transport are the other two main energy consuming sectors in which emissions need to be reduced. Transport is the sector that consumes most petroleum products with 76 % of the total, while industry consumes around 75 % of the total solid fuel energy sources [5]. Consequently, important CO_2 emissions are originated in these two sectors.

To give response to the current energy situation, 20 % of reduction in greenhouse gas emissions and energy consumption was expressed in the Horizon 2020 program of the European Commission. In 2012 the International Energy Agency (IEA) already gave some clues about the pathways that need to be followed to reduce the fossil fuel energy consumption and summarized the impact that existing and the new energy technologies can have in the global energy consumption and CO_2 emissions reduction [6]. Action on appliances, equipment and systems are the key to achieve early low-cost CO_2 emission reduction and accomplish the stablished goals.

Industrial waste heat (IWH) is a potential energy source and is considered an important tool for CO_2 mitigation in industry. The waste heat of an industrial process can be recovered and reused in other processes onsite or be transformed into electricity, cold or other reused heat inputs. If this waste heat is not captured and used, it is released to the atmosphere, being considered extra CO_2 emissions contributing to the global warming process [7].

Improvements in the building sector are needed in order to transform the existing building stock to nearly zero energy consuming buildings. These improvements require the integration and full use of renewable energies, and energy storage technologies are one of the main solutions considered and developed. Storage is an important asset as it allows matching energy demand and supply with compact and competitive systems.

1.2 Thermal energy storage

Thermal energy storage (TES) systems are presented as a potential solution in energy conservation [8-9]. The energy demand in building and industry sectors is not constant and can experience daily, weekly and seasonal fluctuations. The use of TES allows overcoming this gap existing between energy demand and supply by using different peak load shifting strategies, allowing the use of waste heat.

High energy storage densities are desired in any storage system in order to shift the energy demand and favour the use of renewable energies. It is well known that thermal energy can be stored by three different technologies: sensible, latent and thermochemical energy storage.

1.2.1 Sensible energy storage

Sensible energy storage uses materials that undergo no phase change in the temperature range in which the system operates. Moreover, and to increase the competitiveness of these TES systems, materials must be cheap and have proper thermal conductivity. Typical materials used in sensible energy storage are water, bricks and soils [10]. The energy stored per mass unit $(\dot{Q})$ in a sensible heat storage system depends on the specific heat capacity of the material (C_p), the temperature differential (dT) and the sample mass (m), and can be determined with equation 1.

$$\dot{Q} = \int_{T_i}^{T_f} m \cdot C_p(T)\,dT \tag{1}$$

Sensible heat storage is the most used way of thermal energy storage. It is applied in hot water heat storages for domestic hot water in every household [11]. Other applications using this technology go from cold storage to solar power plants [12-13]. The main drawback of sensible storage systems is the low storage capacity when compared to latent heat and thermochemical systems [14].

1.2.2 Latent energy storage

Latent energy is the energy involved in the phase change of a material, presenting higher storage density than sensible energy. As Figure 2 shows, the temperature remains constant during the phase change, while the amount of energy stored is substantially increased.

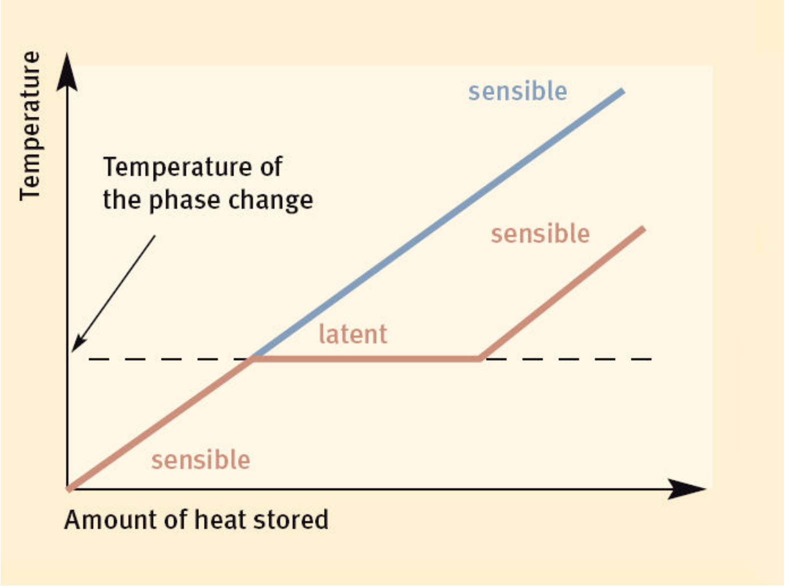


Figure 2. Energy stored by latent and sensible technologies vs temperature

The energy involved in the phase change can be calculated with equation 2.

$$Q_{latent} = \int_{T_1}^{T_{pc}} C_{p,s} \cdot dT + \Delta H_{pc} + \int_{T_{pc}}^{T_2} C_{p,l} \cdot dT \qquad (2)$$

There are three different phase changes of a material: solid-solid, solid-liquid and liquid-gas. Solid-solid phase change has lowest energy density while liquid-gas phase change has the highest energy density of the three possible phase changes, but important problems to control the volume expansion of the process are found. Solid-liquid phase change presents high latent energy and no pressure control problems and is, therefore, the most used option in latent energy storage [14].

The materials used in this type of storage technology are called phase change materials (PCM). The main requirements that a material has to fulfil to be used in a latent energy system are to have high latent heat and high thermal conductivity. Other important considerations are that the material should have a melting/solidification temperature in the proper range of operation, congruent melting/solidification points with low or no subcooling, and a proper cycling stability [15]. This includes the thermal, chemical and physical properties of the material, which should remain constant or almost constant after a number of repeated cycles. In addition, it is desirable for the PCM to not be toxic, have corrosion resistance and be inexpensive. PCM can be classified as Figure 3 shows. Commercial and technical grade of all material types are nowadays available in the market.

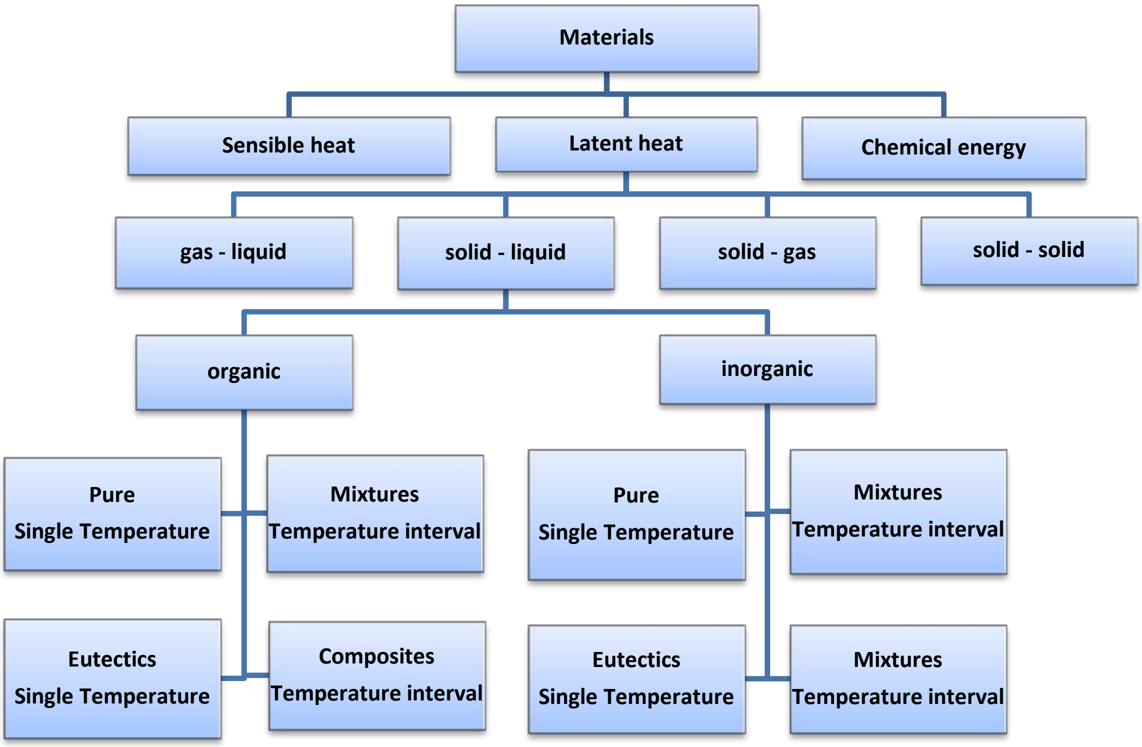


Figure 3. Classification of PCM used in TES

PCM are classified in two main groups: organic and inorganic materials. Inorganic PCM (salt hydrates and metal alloys) stand out due to their high phase change enthalpy and proper thermal conductivity, being subcooling, phase separation, and low cycling stability their main drawbacks. In addition, most inorganic PCM are corrosive. On the other hand, organic PCM (paraffin, fatty acid and sugar alcohols) are usually non-corrosive materials with low or null subcooling and good cycling stability [15]. However, these materials are flammable and have lower energy storage capacity compared to inorganic materials. Some of the just mentioned drawbacks can be minimized or even overcome with the formulation of composites, which improve the thermal conductivity, and the use of nucleating agents, that lower the subcooling [16-17]. Furthermore, the use of nanomaterials has lately spread in the TES field as a remarkable tool to improve material properties [18-19]. By the dispersion of nanomaterials in a base material (PCM, sensible storage material, or heat transfer fluids (HTF)) their thermo-physical can be enhanced, overcoming some of the material drawbacks former mentioned, and enhancing the performance of the TES systems as well [20].

Due to their more recent development, latent TES systems are less widely applied than sensible storage technologies [21]. Nevertheless, research in these systems has spread over the past years and promising results have been obtained in order to apply latent storage technologies in real applications, already reaching this last stage for some applications such as solar power plants [22], which use molten salts as storage mediums. Important development can also be noticed in applications such as building comfort [23], domestic hot water [24], and cold storage [25]. In addition, the International Energy Agency (IEA) has some expert groups working on the development of more efficient heating and cooling TES systems (IEA Task 42) and improvement of the existing ones.

1.2.3 Chemical energy storage

Chemical energy storage technologies are the most recent studied solutions, and due to its still early development no clear classification about the different chemical energy storage means can be found in the literature. Nevertheless, most researchers tend to differ between sorption and thermochemical processes [26].

Sorption is the term by which researchers refer to adsorption and absorption processes. Adsorption is the process by which a substance (sorbate) is adhered to the surface of another substance (sorbent) due to hydrogen bonds or van de Waals forces and that does not imply a molecular change of the compound. Oppositely, absorption implies the incorporation of one substance (sorbate) to the bulk volume of another substance (sorbent) in a different state. In a sorption process the heat is stored by breaking the binding force between the sorbent and the sorbate [27].

Thermochemical energy storage is based in a three step reversible chemical reaction by which a chemical A, is transformed in two other chemicals, B + C. These are normally gas-solid or liquid-solid systems and the materials used are called thermochemical materials (TCM) [28].

$$A + Q \leftrightarrow B + C$$

At first, heat is absorbed to start the reaction and transform chemical A into products B and C. These two products are then easily separated and stored in different containment vessels at ambient temperature. Finally, whenever the heat is needed and at the proper ambient conditions (pressure, temperature, relative humidity), products B and C react to form chemical A again, releasing all the heat absorbed and stored in the previous stages. Figure 4 shows the explained.

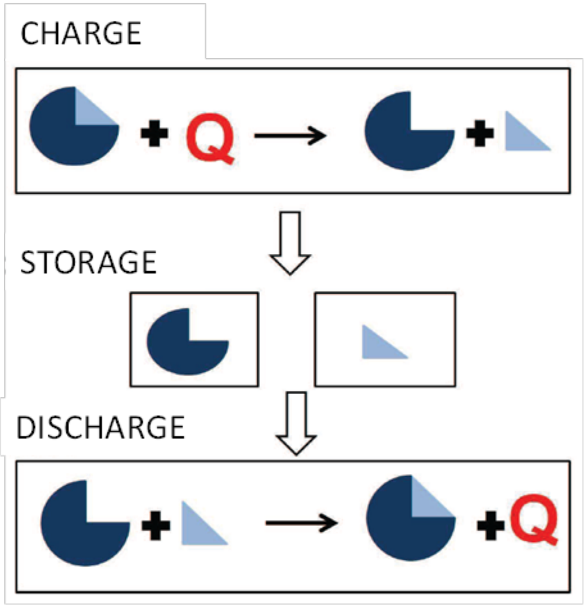


Figure 4. Steps of a thermochemical energy storage process

Despite the benefits that these systems offer, drawbacks such as the configuration complexity of closed systems, the poor mass and heat transfer in chemical reactions, the low heat storage densities obtained with the actual systems along with the expensive investments need to be assessed.

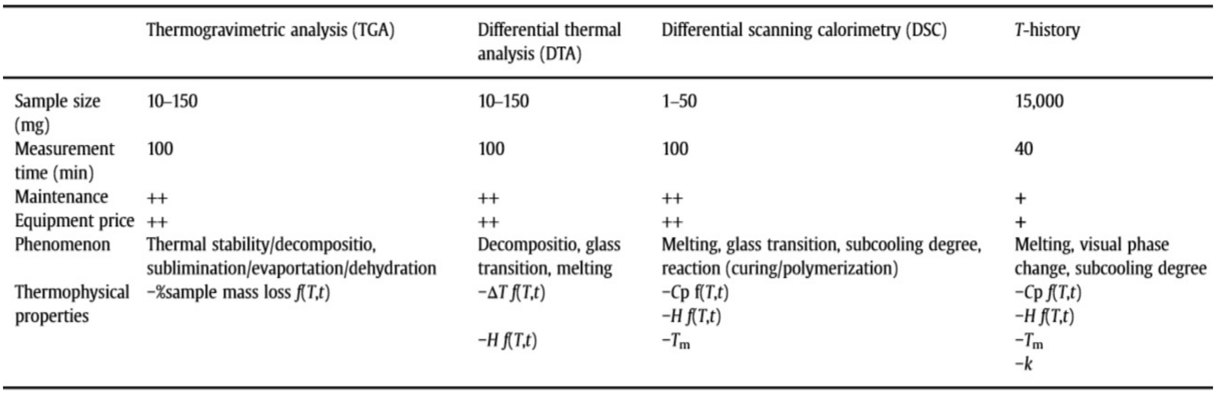
According to the Energy Technology Systems Analysis Program (IEA-ETSAP) and the International Renewable Energy Agency IRENA, from all the presented thermal energy storage technologies, thermochemical storage shows the highest potential for energy saving and CO_2 emission reduction. Storage capacities higher than 250 kWh/m^3 are expected to be reached with these systems, being able to operate at temperatures higher than 300 ºC with efficiencies over 75 %, overcoming by far the 100 kWh/m^3 storage capacity of PCM and sensible storage systems, with low storage capacities of 10-50 kWh/m^3 [29].

1.3 PCM characterization

The determination of the thermo-physical properties is a key step not just for the application itself but also for the material selection to define the suitability of a material for use in TES. There are different thermal analysis techniques to characterize materials and the convenience to use them relies on the properties that want to be determined.

The main thermal analysis methods are listed in Table 1. From the four thermal analysis methods presented, thermogravimetric analysis (TGA), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) are commercially available, while T-history is not commercially available and there just exist few devices in different research centres.

Table 1. Comparison of the most common thermal analysis techniques to characterize PCM [30]



	Thermogravimetric analysis (TGA)	Differential thermal analysis (DTA)	Differential scanning calorimetry (DSC)	*T*-history
Sample size (mg)	10–150	10–150	1–50	15,000
Measurement time (min)	100	100	100	40
Maintenance	++	++	++	+
Equipment price	++	++	++	+
Phenomenon	Thermal stability/decompositio, sublimination/evaportation/dehydration	Decompositio, glass transition, melting	Melting, glass transition, subcooling degree, reaction (curing/polymerization)	Melting, visual phase change, subcooling degree
Thermophysical properties	−%sample mass loss $f(T,t)$	$-\Delta T\ f(T,t)$ $-H\ f(T,t)$	$-Cp$ f(T,t) $-H\ f(T,t)$ $-T_m$	$-Cp\ f(T,t)$ $-H\ f(T,t)$ $-T_m$ $-k$

In past years, differential thermal analysis (DTA) was the most used technique to determine the phase change temperatures and enthalpy of a substance. DTA plots the behaviour of a material as a function of temperature or time. However, the development of differential scanning calorimetry (DSC) allowed to have the material heat flow as a function of both temperature and time, widening up the properties that could be determined and consequently, leading researchers to use it as the main characterization technique, replacing DTA [31]. DSC is nowadays the most used technique to determine the melting/solidification points and the latent heat of phase change and specific heat capacity of PCM. It is also useful to observe other phenomena such as subcooling, hysteresis and glass transition [30]. The DSC characterization can be complemented by a thermogravimetric analysis (TGA), technique by which the thermal stability of the material can be studied. In fact, over recent years, manufacturers have started commercializing DSC-TGA integrated devices in order to match these two main characterization techniques in one single device [32].

T-history was developed by Yinping et al. [33] in 1999 as an answer to some DSC limitations such as the small sample masses used in the experiments, parameter from which the material response obtained depends, or the expensive costs of the device. Ten times bigger samples are used in T-history, obtaining temperature-time curves from which the phase change temperature, enthalpy, specific heat, subcooling and even thermal conductivity can be determined. In addition, it is a much less expensive device, cheaper to maintain as well. However, it is not commercially available and just some research labs have built their own device, improving the original Yingping et al. [33] invention.

As said, thermal conductivity can be determined with the T-history method. However, there are more appropriate techniques available for this purpose, being the hot-wire method, laser flash, and hot plate/box measurements the main ones [34].

Another important property in material selection is thermal cycling stability. It is important that a PCM has a good cycling stability and that their thermal, chemical and physical properties stay stable when the material undergoes a repeated number of thermal cycles [35]. As it will be further explained in chapter III of the present thesis, there is no standard technique or device by which PCM cycling stability is tested, and researchers use from their own designed devices, to thermal cyclers, yet being DSC the most used technique to thermal cycle the materials.

Other chemical, physical and mechanical properties that are also of relevance in the characterization of PCM can be determined with the devices and techniques described in Fernández et al. [36] and Miró et al. [37].

All in all, and despite the existence of such number of characterization techniques, the development of latent heat applied technologies is hindered due to the lack of international standards for some of the exposed techniques. This gap has lead researchers to use their own methodologies of characterization, obtaining diverse results, difficult to compare between institutions. Latent heat, specific heat capacity, thermal conductivity, and thermal stability are the main measurements for which no standards can be found. As a consequence, researchers tend to repeat the experiments, a material and time consuming effort that would not be necessary with the existence of common standards used for the whole scientific community involved in TES.

In regard to DSC measurements, a group of experts on materials gathered together forming a working group as part of International Energy Agency (IEA) ECES IA Task 42/Annex 29 in order to develop a standard for DSC latent heat measurements. The resulting document is available in [38].

1.4 DSC measurements

There are two types of DSC devices, power compensated DSC and heat flux DSC [39]. The former has two different furnaces, one for the sample and one for the reference, keeping them at the same temperature by independent heating. When a heat-consuming process takes place in the sample its furnace heats the sample up to keep the temperature equal to the reference one, measuring the energy needed for it. Oppositely, a heat flux DSC has just one furnace (Figure 5) in which both reference and sample crucibles are placed. When a heat-consuming process takes place in the sample, the DSC measures the temperature difference between the sample and the reference and calculates the heat flow involved in the process.

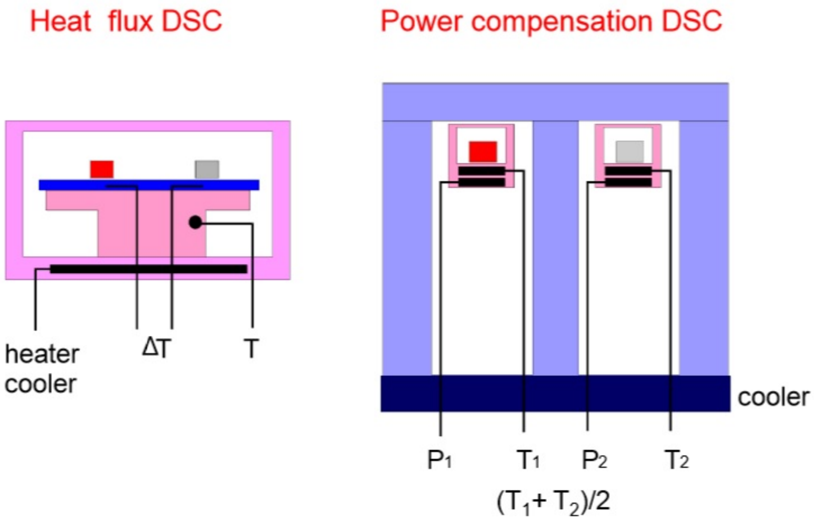


Figure 5. Heat flux and power compensated DSC schemes

However, the results obtained with each DSC type have some differences. A power compensation DSC can heat faster, having more resolution for sharp events but with a less stable signal. Contrary and although it cannot reach such fast rates, a heat flux DSC provides more stability in the base line signal, providing better sensitivity for subtle thermal changes. For this reason, the heat flux DSC is the most used device in TES research.

DSCs are normally calibrated with at least two reference materials of known properties. Common materials used for this purpose are water, sapphire, gallium, indium and zinc. The total heat flow measured in a heat flux DSC can be calculated with equation 3:

$$\phi = m \cdot C_p \cdot \beta + \Delta H_p \cdot \frac{d\alpha}{dt} \tag{3}$$

where ϕ is the heat flux in [mW], *m* the mass of the sample [g], C_p the specific heat capacity [J/g·ºC], β the heating rate [ºC/s], ΔH_p the enthalpy of the process [J/g] and $\frac{d\alpha}{dt}$ the conversion per unit of time [g/s].

The capacity of the DSC to measure very small and weak effects is called sensitivity, while the resolution is defined as the ability to separate two close-lying effects. Therefore, for C_p measurements high sensitivities are desired and thus, high heating/cooling rates are used. Oppositely, as high resolution is needed for latent heat determination, low rates are programed in the measurements.

One of the main uses of DSC in TES is the determination of the enthalpy-temperature relation of PCM. To do so, different scanning modes can be used, being the dynamic method and the step method the most used ones [34].

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2 Objectives

The present thesis aims to contribute in widening the knowledge of the thermal energy storage (TES) field. The main technology in which this thesis is focused is latent energy storage. This technology has been widely researched and used for industrial and domestic purposes. However, there are still gaps in both material and design levels that require improvement. Therefore, one of the main objectives of this thesis is to improve phase change materials (PCM) characterization with new methodologies, particularly regarding specific heat capacity determination. Furthermore, it is desired to contribute to the improvement of TES system design with time saving tools that ease and improve simulation. In addition, this thesis research is also focused in the development of PCM with enhanced properties for their use in TES. To accomplish these general goals, the following specific objectives were completed:

- To review the state-of-the-art of TES systems and phase change materials (PCM) along with the characterization technologies used in the field.
- To determine the compatibility between some of the most used container materials and PCM.
- To characterize materials for TES systems applications with DSC, focusing in latent heat and specific heat capacity determination and providing solutions if gaps or inconsistencies are noticed in the characterization methodologies.
- To formulate empirical equations to determine beforehand PCM family properties for their use in TES system design with the aim of improving simulations.
- To review the state-of-the-art of nanotechnology for TES purposes and characterize by DSC materials enhanced with nanoparticles.

3 PhD Structure

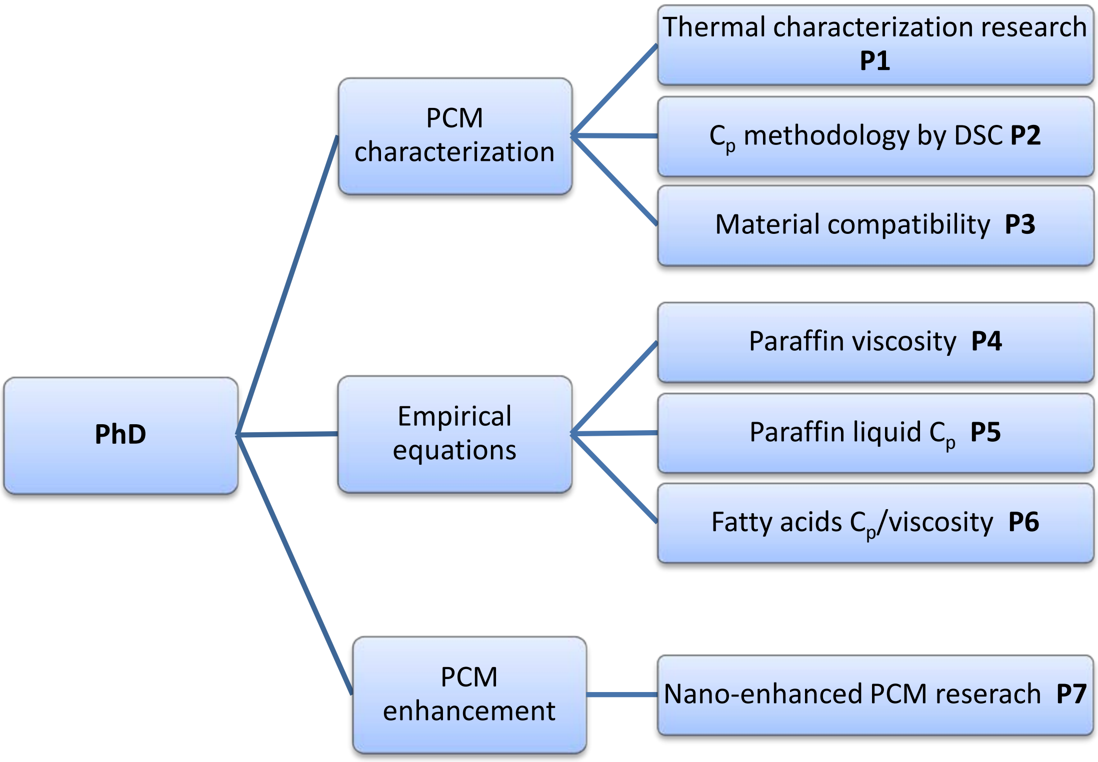
The PhD thesis is based on seven papers divided in three general blocks: PCM characterization, empirical equations and PCM enhancement. Two of the papers have already been published in international high impact scientific journals while the other six have been submitted.

The chronological order followed in this thesis matches with the numeration given to the papers. Hence, the PCM characterization part was first studied, followed by the development of empirical equations, and the final PCM enhancement block.

The first step was to review the literature on the thermal energy storage field as an introduction to the topic and in order to localize gaps in the characterization of materials. A lack of standards for thermal cycling characterization was noticed and is discussed and presented in **Paper 1**. Furthermore, the lack of a standard for DSC C_p measurements was noticed when reviewing the existing characterization studies and therefore one new methodology is proposed in **Paper 2.** Another aspect that was found relevant from this literature review was the importance that corrosion studies have in the design of a TES system. Therefore, and in parallel to the first article, the compatibility of some commonly used PCM for building comfort with some of the most used container materials was studied in **Paper 3**, completing with this paper the first general block of the thesis regarding PCM characterization.

The need of predictive tools for TES system design was another of the main issues withdrawn. The formulation of empirical equations is of importance in simulations as those are time saving tools by which the material properties can be determined beforehand, avoiding high error approximations and obtaining this way better and more reliable results. To fill this existing gap, the second block of the present thesis is focused on developing empirical equations for some of the most used PCM families in building applications. **Paper 4** presents an empirical equation to calculate the viscosity of paraffin PCM while in **Paper 5** an equation to calculate the liquid C_p of paraffin PCM is developed. **Paper 6** research was focused in the fatty acid family and presents three different equations to respectively determine viscosity, solid C_p and liquid C_p of any of the fatty acid PCM.

The third main block of the thesis is focused on the thermal properties enhancement of PCM. Nanotechnology is one of the newest technologies implemented in TES to improve the thermal properties of PCM. The development this technology currently has in the TES field is evaluated in **Paper 7** of the thesis, where the patented inventions regarding the use of nanomaterials in TES systems are reviewed.



4 Review on the methodology used in thermal stability characterization of phase change materials

4.1 Introduction

TES technologies are one of the main fields that have lately been studied and developed as a solution to reduce the environmental impact of fossil fuel energies [1]. These systems use PCM to store and release heat depending on the needs and its performance relies on the material thermal properties. PCM are classified as organic, which enclose paraffin, fatty acids and sugar alcohols; and inorganic, being water solutions, salt hydrates and metal alloys the most used ones [2]. The requirements for their implementation in TES are, among others, high latent heat, proper thermal conductivity, and suitable phase change temperature range. Besides, a PCM is suitable to be used if it has a proper cycling stability, that is, if their thermal, chemical and physical properties remain constant after a repeated number of thermal cycles (thermal stress) [3].

The scope of this study was to review the importance given to thermal cycling stability in order to monitor the existence or not of a standard methodology to determine this property. Therefore, this review is specially focused in the data provided by authors in their papers, the equipment and the analysis methods used in the different studies regarding the cyclability of both organic and inorganic PCM.

4.2 Contribution to the state-of-the-art

The main contributions to the state-of-the-art are, first the review itself of all the studies published in which the thermal cycling stability of PCM is assessed. In recent years several papers regarding the thermal cycling properties of different organic and inorganic PCM have been published contributing in the development of TES technologies. In this review all these contributions are classified by PCM type, equipment used, cycling methodology, and number of cycles that the PCM have undergone.

Moreover, the lack of a standard methodology to characterize the thermal cycling stability of PCM is proven. The different researchers perform the cycling tests with the equipment they dispose of, applying different methods to cycle the samples and cycling them a random number of times, depending on their study needs, not following any specific pattern.

This paper is a step forward in thermal cycling characterization of PCM as it clearly states the lack of a standard to study this property and its need in the scientific community to have more reliable and comparable results.

4.3 Contribution of the candidate

The candidate reviewed all the literature regarding PCM thermal stability and proposed a first structure of the paper that was later complemented by the co-authors. In addition, all the graphical support of the paper was developed by the candidate. The final writing was leaded by the candidate, who received assistance of the co-authors in the discussion of the paper and the introduction preparation.

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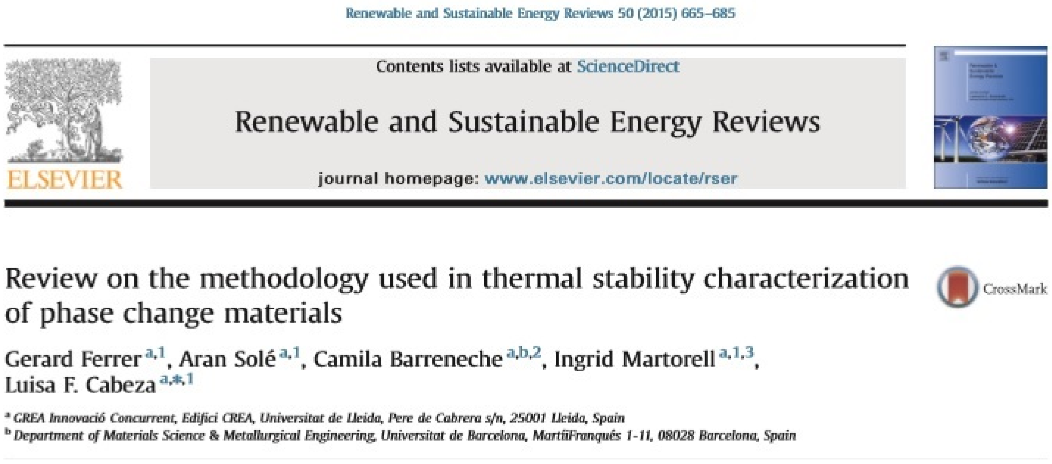
4.5 Journal Paper



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Review on the methodology used in thermal stability characterization of phase change materials

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doi:10.1016/j.rser.2015.04.187

5 New proposed methodology for specific heat capacity determination of materials for thermal energy storage (TES) by DSC

5.1 Introduction

Sensible energy storage is one of the most used TES technologies and consists in increasing the temperature of a material causing no phase change on it. The energy is stored due to this temperature increase and depends directly on the C_p of the material used, obtaining better system performances as higher the C_p is [1].

DSC is nowadays the most used technique to measure enthalpy changes (ΔH) and specific heat capacity (C_p) of materials [2]. Complementing the review done in Chapter IV on the methodologies used to study thermal cycling stability, literature regarding the methodologies used to determine de C_p of a material by DSC was also reviewed, withdrawing the lack of a common standard to perform this type of measurements. Consequently, and as observed in the consulted literature, diverse C_p values of the same material are obtained by researchers due to the different methodologies and DSC methods used, making them incomparable [3-4].

The scope of this paper was to fulfil the existing gap on C_p determination with DSC by proposing a new methodology. In addition, the three most used DSC measurement methods were applied with the methodology proposed and the results obtained with each of them were compared in order to see which method has the best performance and, therefore, must be further used.

5.2 Contribution to the state-of-the-art

The paper is a step forward in TES as it fills an important gap regarding PCM characterization with DSC. A methodology to determine the specific heat of PCM by DSC is described and proposed in this paper. It requires three measurements (blank, reference material and sample) to obtain reliable results. In addition, the three most used DSC methods have been used and their results compared in order to monitor their performance and determine which one is the most suitable DSC method to be used with the proposed methodology.

This study is focused in the material characterization, an important issue in the design of a TES system, and provides researchers of a new methodology of C_p determination with DSC by which results with less than 3 % of error are obtained. In addition, it proves that the performance of the two most common used DSC methods in C_p measurements, dynamic and isostep, is lower than the one obtained with the areas method, suggested as the best and most proper method for this type of characterization.

5.3 Contribution of the candidate

The methodology was discussed and agreed by all the authors. The candidate was responsible to lead the experimental part of this study, first proposing the material selection and discussing it with the co-authors, and later preparing samples and programming the different experiments in the DSC. All the graphical support and data treatment were done by the candidate as well. The final writing of the article was also leaded by the candidate, receiving the co-authors support in the results discussion and the introduction section along with a general revision of the whole document.

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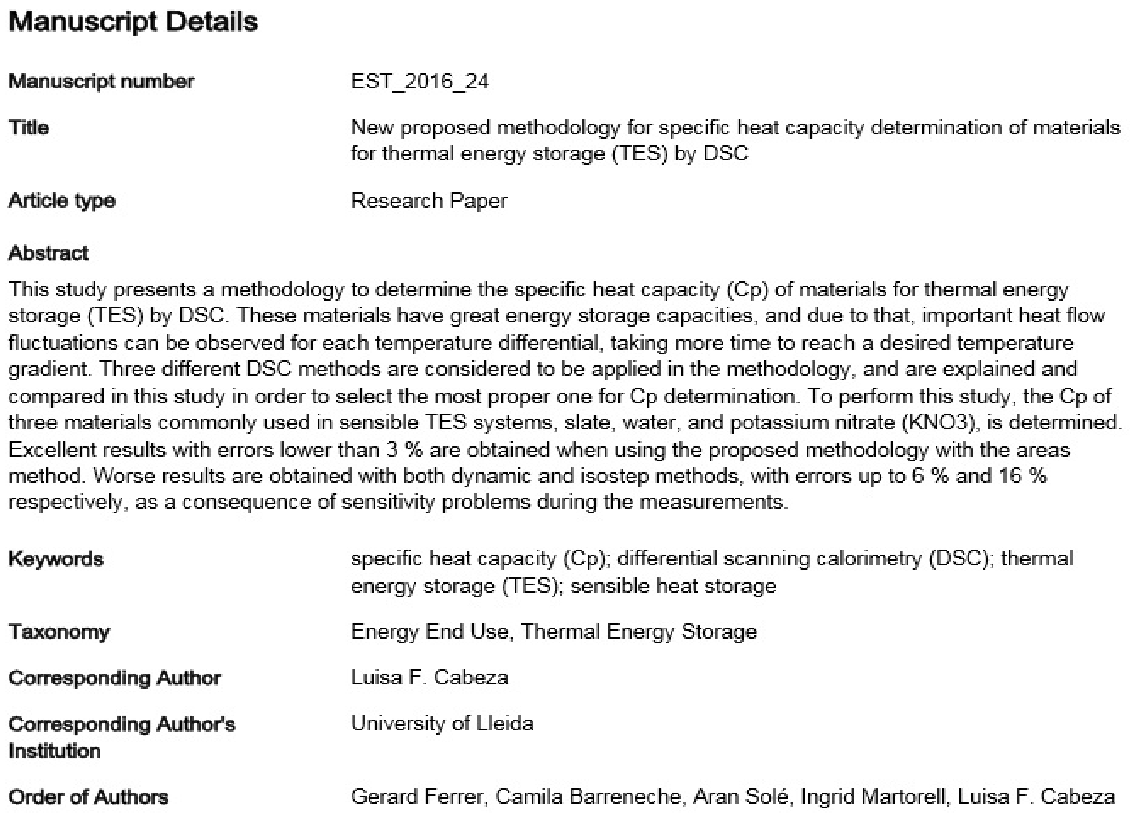

Manuscript Details

Manuscript number EST_2016_24

Title New proposed methodology for specific heat capacity determination of materials for thermal energy storage (TES) by DSC

Article type Research Paper

Abstract

This study presents a methodology to determine the specific heat capacity (Cp) of materials for thermal energy storage (TES) by DSC. These materials have great energy storage capacities, and due to that, important heat flow fluctuations can be observed for each temperature differential, taking more time to reach a desired temperature gradient. Three different DSC methods are considered to be applied in the methodology, and are explained and compared in this study in order to select the most proper one for Cp determination. To perform this study, the Cp of three materials commonly used in sensible TES systems, slate, water, and potassium nitrate (KNO3), is determined. Excellent results with errors lower than 3 % are obtained when using the proposed methodology with the areas method. Worse results are obtained with both dynamic and isostep methods, with errors up to 6 % and 16 % respectively, as a consequence of sensitivity problems during the measurements.

Keywords specific heat capacity (Cp); differential scanning calorimetry (DSC); thermal energy storage (TES); sensible heat storage

Taxonomy Energy End Use, Thermal Energy Storage

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Ferrer G, Barreneche C, Solé A, Martorell I, Cabeza LF. New proposed methodology for specific heat capacity determination of materials for thermal energy storage (TES) by DSC. Submitted to Journal of Energy Storage, 2016.

6 Corrosion of metal containers for use in PCM energy storage

6.1 Introduction

In any TES application PCM are normally encapsulated in containers. Latent heat, thermal conductivity and specific heat are some of the important parameters of a PCM that need to be considered when selecting the proper material for a specific application. Nevertheless, another key aspect in the material selection is the compatibility between the PCM and the container material [1]. Most inorganic PCM are corrosive to metallic containers, while not that much information is found regarding corrosion with organic PCM [2]. Steels, aluminium and copper are examples of metals employed, among other things, for containment uses in TES systems [3].

The aim of this study was to determine the compatibility of some of the most common metals in PCM containment with organic and inorganic PCM used in building comfort applications. To accomplish this goal, the corrosion rate of each metal/PCM combination was monitored during twelve weeks, following ASTM G1-03 standard for corrosion tests.

6.2 Contribution to the state-of-the-art

This paper contributes to the state-of-the-art providing the scientific community that works in TES with useful data regarding the selection of materials for both energy storage and containment. One inorganic salt and three organic PCM used to improve thermal comfort in buildings are considered in this study and combined with five common metals (stainless steel 304, stainless steel 316, carbon steel, aluminium, and copper), recommending and discarding the use of each combination based on the results obtained.

This study provides useful information to TES design researchers as it shows some metal/PCM combinations that cannot be implemented in any system, recommending suitable solutions as well.

6.3 Contribution of the candidate

Complementary to the literature review done in chapter IV and in order to get familiar with the use of PCM in TES, a general literature review on the TES field was done by the candidate. The relevance of corrosion in the material selection was noticed from the literature reviewed and was the reason why the present study was conducted. The metal and PCM selection were proposed by the co-authors to the candidate, who performed the experiments. Data treatment and results analyses were also done by the candidate, who was responsible for the scientific article writing as well. The co-authors assessed the candidate and contributed in the writing of the introduction and conclusions sections.

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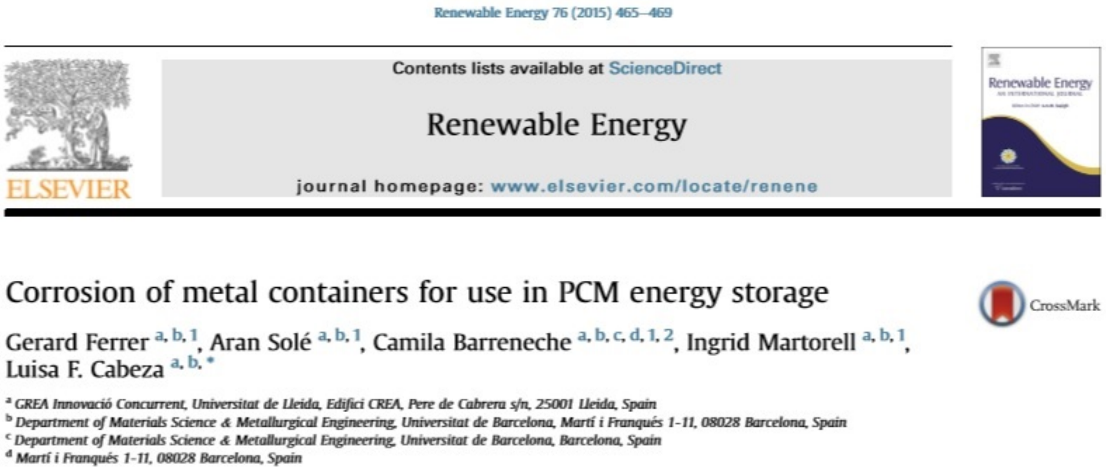

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Corrosion of metal containers for use in PCM energy storage

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doi:10.1016/j.renene.2014.11.036

7 Empirical equation to estimate viscosity of paraffin

7.1 Introduction

Simulations are of big relevance in the design process of a TES system. In them, the properties of the PCM considered for use in the system need to be known. In most of the cases, constant values or approximations of each property are used to run the simulation, obtaining not despicable errors in the results that can lead to more important errors in the whole system design [1].

Viscosity is one of the important properties that are taken into account when selecting a material for a TES application because it is not constant with temperature. Therefore, and to optimize simulations, the beforehand knowledge of the material viscosity as a function of temperature is of big relevance [2]. Empirical equations are used in different engineering fields to predict materials behaviour, and provide researchers with reliable data without the need of running experiments to obtain it [3].

Paraffin are one of the most used PCM families in TES due to their proper latent heat and stable phase change temperatures [4]. However, no specific equation to calculate paraffin PCM viscosity was found in the literature review done prior to the start of this study. Therefore, the scope of this article was to provide the scientific community with an empirical equation to determine the viscosity of any paraffin PCM as a function of temperature. To fulfil this goal, the viscosities of three paraffin PCM (RT21, RT27, and RT55) were measured and adjusted, using another paraffin (n-octadecane Parafol 18/97) to validate the equation found.

7.2 Contribution to the state-of-the-art

An empirical equation to determine the viscosity of paraffin PCM for use in TES system simulations and design is presented in this study. It contributes to ease and improve the simulation and design of TES systems using paraffin PCM providing reliable data in the whole temperature range. Three different commercial paraffin (RT21, RT27, and RT55) were used to formulate the equation presented, which was validated with the measurements of commercial paraffin (n-octadecane Parafol 18/97).

The empirical equation presented is a powerful and time saving tool that allows to formerly know the viscosities of the whole paraffin family without the need of experimentation. Moreover, data is obtained with less than 5 % of error.

7.3 Contribution of the candidate

Experimental data measured by the co-authors was given to the candidate, who was responsible of the data treatment to formulate the empirical equation presented in this paper. All the graphical support was also generated by the candidate, who also leaded the writing of the article. The candidate discussed the results with all the co-authors, who also reviewed the whole document.

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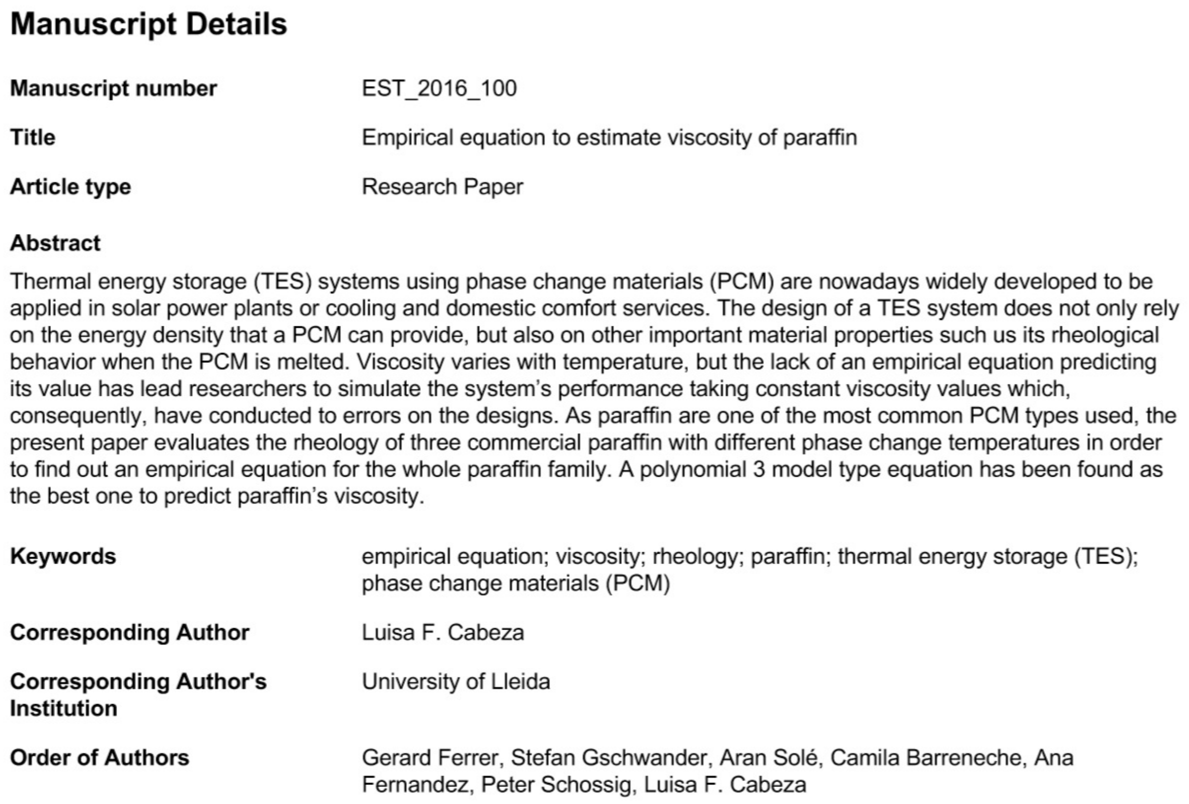
7.5 Journal paper



Manuscript Details

Manuscript number	EST_2016_100
Title	Empirical equation to estimate viscosity of paraffin
Article type	Research Paper

Abstract

Thermal energy storage (TES) systems using phase change materials (PCM) are nowadays widely developed to be applied in solar power plants or cooling and domestic comfort services. The design of a TES system does not only rely on the energy density that a PCM can provide, but also on other important material properties such us its rheological behavior when the PCM is melted. Viscosity varies with temperature, but the lack of an empirical equation predicting its value has lead researchers to simulate the system's performance taking constant viscosity values which, consequently, have conducted to errors on the designs. As paraffin are one of the most common PCM types used, the present paper evaluates the rheology of three commercial paraffin with different phase change temperatures in order to find out an empirical equation for the whole paraffin family. A polynomial 3 model type equation has been found as the best one to predict paraffin's viscosity.

Keywords	empirical equation; viscosity; rheology; paraffin; thermal energy storage (TES); phase change materials (PCM)
Corresponding Author	Luisa F. Cabeza
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Ferrer G, Gschwander S, Solé A, Barreneche C, Fernández AI, Schossig P, Cabeza LF. Empirical equation to estimate viscosity of paraffin. Submitted to Journal of Energy Storage, 2016.

8 Empirical equation for specific heat capacity determination of paraffin in liquid phase

8.1 Introduction

C_p is the property that determines, along with the latent heat of phase change, the energy storage capacity of a material. It is therefore a key property of the material and needs to be considered in the design process of any TES system [1]. The existence of an equation to accurately determine the C_p of a material in advance, with no need of experimental runs, is of big relevance in system simulations and can improve the results, leading to less design errors and better predictions of the system behaviour [2]. The present chapter continues the research line presented in former Chapter VII regarding the use of empirical equations in TES system design, and is focused in paraffin PCM.

As for viscosity, few general equations are found in the literature to determine the C_p of a material, finding no specific equation for paraffin PCM, one of the most used PCM materials in TES [3]. Therefore, and to continue with the research former presented, the aim of this article was to find an empirical equation to determine the C_p of any paraffin PCM. The C_ps of the same paraffin used in Chapter VII (RT21, RT27, and RT55) were measured and used to formulate the equation, validating it again with n-octadecane Parafol 18/97. In addition, and linked to previous research already presented in this thesis, all the C_p measurements for this study were done using the methodology presented in the former Chapter V.

8.2 Contribution to the state-of-the-art

This study contributes to widen up the research in the TES field providing a tool to improve the design of systems working with paraffin PCM. The empirical equation presented determines the C_p of all paraffin PCM in their whole liquid temperature range, giving low error (< 4%) values and decreasing the final errors that may be obtained in the design simulations. It is ultimately, a step forward in system design and empirical characterization of PCM and fills the lack of a specific equation for TES.

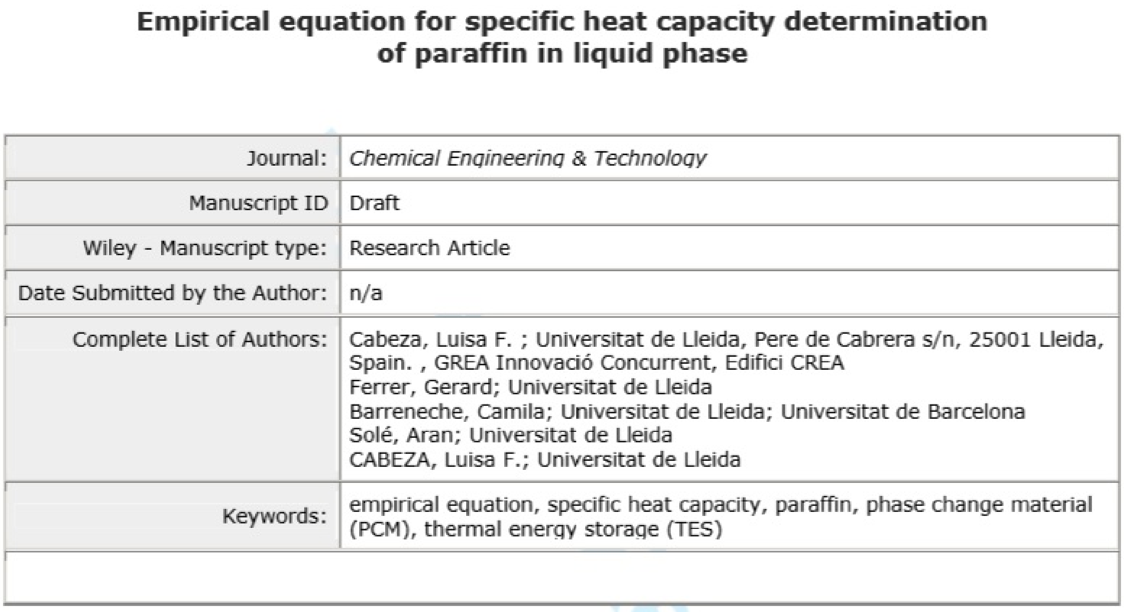
8.3 Contribution of the candidate

The candidate leaded both experimental part of the article, doing the C_p measurements of the different paraffin by DSC and the results analyses, for which he received support from the co-authors. Moreover, the data treatment to formulate the empirical equation presented was also done by the candidate, responsible of the all the graphical support as well. The co-authors assisted the candidate in the writing and reviewed the whole research and explanations given before its submission.

8.4 References

1. Pielichowska K, Pielichowski K. Phase change materials for thermal energy storage. Prog Mater Sci 2014, 67: 67–123
2. Nithyanandam K, Pitchumani R. Design of a latent thermal energy storage system with embedded heat pipes. App Energ 2014, 126:266-280
3. Cabeza LF, Castell A, Barreneche C, de Gracia A, Fernández AI. Materials used as PCM in thermal energy storage in buildings: A review. Renew Sustain Energy Rev 2011;15:1675–95

8.5 Journal paper



Empirical equation for specific heat capacity determination of paraffin in liquid phase

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Ferrer G, Barreneche C, Solé A, Cabeza LF. Empirical equation for specific heat capacity determination of paraffin in liquid phase. Submitted to Chemical Engineering & Technology, 2016.

9 Empirical equations for viscosity and specific heat capacity determination of fatty acids

9.1 Introduction

This chapter continues with the research regarding the formulation of empirical equations for use in TES systems design. As it has already been explained in former chapters, empirical equations allow determining in advance a property of a material, with no need of experimental runs. They are widely used in chemical engineering and industry, but its application in TES is barely noticeable.

Chapters VII and VIII were focused in paraffin PCM and presented two equations to determine, respectively, viscosity and C_p in liquid state. Chapter IV is focused in fatty acids, widely used PCM in TES due to their energy density storage capacity and their well-defined phase change temperature range [1]. As well as with paraffin, and besides the generic equations presented in the paper, no specific empirical equations to determine the viscosity neither the C_p of fatty acid PCM can be found in the literature. The research done in this study leaded to the formulation of three empirical equations to calculate viscosity, solid C_p and liquid C_p of fatty acid PCM. The relevance of these equations is that they are not specific for just one fatty acid, but can be used with the whole fatty acid PCM family.

Viscosity, liquid C_p and solid C_p of capric, myristic and stearic acids were measured in order to formulate the empirical equations found, which, in addition, were validated with palmitic acid measurements.

The scope of this paper was to formulate three equations to determine viscosity, liquid C_p and solid C_p of fatty acid PCM for use in the TES field and improve system design.

9.2 Contribution to the state-of-the-art

This study contributes in the development of the TES field providing three equations for system design. With these tools, viscosity, liquid C_p and solid C_p of fatty acid PCM can be determined at any temperature and with less than 5 % of error, filling the existing lack of these tools for fatty acid PCM for TES. In addition, its use can improve the system simulations and lead to better designs, with lower errors and system performances closer to real conditions.

9.3 Contribution of the candidate

The candidate was responsible of the C_p measurements and part of the viscosity measurements, for which he received assistance of the co-authors. Moreover, the candidate leaded the results analyses and data treatment in order to formulate the three equations presented in the paper. In addition, the candidate also leaded the writing of the article and the generation of all the graphics enclosed in it. The co-authors also assisted the candidate in the writing process and revision of the whole article.

9.4 References

1. Cabeza LF, Castell A, Barreneche C, de Gracia A, Fernández AI. Materials used as PCM in thermal energy storage in buildings: A review. Renew Sustain Energ Rev 2011, 15:1675–1695

9.5 Journal paper

Ferrer G, Barreneche C, Palacios A, Solé A, Fernández AI, Cabeza LF. Empirical equations for viscosity and specific heat capacity determination of fatty acids. In process. Accepted in Journal of Energy Storage, 2016.

Manuscript ID: EST_2016_65_R1

10 Recent patents on nano-enhanced materials for use in thermal energy storage (TES)

10.1 Introduction

Over past years the use of PCM in TES systems has widely spread. Many studies can be found in the literature regarding PCM implementation in a large variety of TES systems, going from cold storage [1] to concentrated solar power plants (CSP) [2]. However, PCM do not present an ideal performance and show some drawbacks that lower down the system efficiency. Subcooling, phase separation and low or null cycling stability are the common disadvantages of inorganic PCM, while flammability and lower energy storage capacity are the main weak points of organic PCM.

Composites and microencapsulated PCM have been formulated to overcome some of the just mentioned problems and improve, mainly, thermal conductivity and cycling stability. Nucleating agents are another of the solutions taken by researchers, specifically applied to decrease the subcooling of inorganic salts [3-4].

In recent years the use of nanomaterials in TES has increased and been presented as another option to overcome PCM drawbacks and improve their properties. Studies regarding the enhancement of thermal conductivity, specific heat capacity, viscosity and subcooling can already be found in the literature [5]. These improvements have also lead researchers to design new TES systems and implement them in new applications.

The scope of this paper was to review the state in which the use of nanotechnology in TES currently is. Patents are good indicators of the development a technology has in any field. Therefore, this paper was focused on reviewing all the patents related to the use of nanotechnology in TES.

10.2 Contribution to the state-of-the-art

This study shows the development that nanotechnology currently has in the TES field. It provides all the inventions using nanomaterials in TES systems patented so far and shows the potential this technology has in the field. Different PCM and HTF are enhanced in these patents, using them in such different applications as insulation and fuel cells systems are.

10.3 Contribution of the candidate

The candidate was responsible of the literature review and patent research regarding the use of nanomaterials in TES. In addition, the candidate leaded the writing of the article, assisted by the co-authors in the graphical support and conclusions section.

10.4 References

1. Veerakumar C, Sreekumar A. Phase change material based cold thermal energy storage: Materials, techniques and applications – A review. Int J Refrig 2016, 67:271-289
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10.5 Journal paper

Ferrer G, Barreneche C, Solé A, Juliá JE, Cabeza LF. Recent patents on nano-enhanced materials for use in thermal energy storage (TES). Accepted in Recent Patents on Nanotechnology on July 4th 2016.

Manuscript ID: BSP-NANOTEC-2016-HT4-3

11 Conclusions and recommendations for future work

11.1 Conclusions of the thesis

This thesis contributes to broaden the knowledge of the TES field. The thesis has mainly been focused in latent energy storage, giving a special attention to PCM. An overview of the current state on thermal stability characterization is presented, completing it with a proposal of a new methodology for C_p determination by DSC. Another relevant PCM characterization aspect is the compatibility with metals for its containment, also addressed in this work. An important part of this thesis is focused in the formulation of empirical equations for viscosity and C_p determinations of two PCM groups, paraffin and fatty acids, for its use in system design. Finally, this thesis also focuses in PCM enhancement with nanomaterials, presenting an overview of the current state of nanotechnology in TES.

The major achievements of this thesis are the following:

- The literature reviewed showed the lack of a specific methodology for thermal cycling characterization and the necessity of developing a standard procedure to be used for the whole TES scientific community.

- The development of new standard procedures for C_p and H determination by DSC was also found necessary and urgent, given the lack of both and the incomparable results found in the different studies.

- Compatibility studies between PCM and material containers are important in the design of a TES system in order to select the proper storage/container combination to ensure long term performance and efficiency of the application.

- The development of empirical equations to determine material properties is of importance in TES given the lack of these tools in the field and the potential these show to improve system design.

- The literature reviewed and the few number of patents found show that nanotechnology still has low development in the TES field. However, the promising results obtained in the different studies already show the potential this technology has in TES to enhance material properties and system performances, denoting an increasing use of this technology in TES in the upcoming years.

The main conclusions withdrawn from the review on the methodology used in thermal stability characterization of phase change materials are:

- There is no standard specifying the most proper equipment to perform thermal stability studies.
- DSC is the technique used in all cases to characterize materials. However, there is a lack of standard specifying the best and most proper analysis conditions for latent heat determination.
- Thermal cycling tests are randomly performed by researchers. Different heating/cooling methods at various rates are used, and a large variety of cycle ranges applied, proving the lack of a standard to study the cycling stability of materials.
- In general, authors do not provide all the data regarding the equipment, experimental conditions, and thermal properties before and after the cycling tests.
- A standard for thermal cycling stability tests is needed in the scientific community to get better and more reliable data.

In respect to the lack of standards in the TES field noticed in the review, a new methodology to determine C_p by DSC was proposed and the main DSC methods used by researchers compared. The main conclusions of this study are:

- The methodology has been proved to work and results with errors lower than 3 % are obtained when doing the DSC measurements with the areas method.

- The DSC instrument requires of certain stabilization time after switching the scanning rates, which leads to wrong measurements during the first moments of the experiment when both the dynamic and isostep DSC methods are used.
- The traditionally used dynamic and isostep DSC methods have been proven as less proper methods to measure C_p than the areas method.

Regarding the compatibility study between PCM and some of the most used container materials, the main outputs of the study are:

- Stainless steel 316 and stainless steel 304 are the most proper materials to be used for PCM encapsulation. Both metals showed great corrosion resistance to all the PCM used in the study.
- PureTemp 23 is the only PCM to which all metals are resistant to and ensure long term service in the installations in which it is used.
- SP21E has a corrosive effect on aluminium, therefore, this PCM/metal combination should be avoided in any installation use.
- Corrosion is observed when copper is used with fatty acid PCM and its use should therefore be avoided.

Moving to the empirical equation block of the thesis, equations for empirical calculation of viscosity and C_p of paraffin and fatty acid PCM were presented. The main conclusions that can be withdrawn are:

- A polynomial 3 equation is found to be the best option to empirically determine viscosity. Two different polynomial 3 equations are given to respectively determine the viscosity of paraffin and fatty acids. Each equation includes a melting temperature dependant factor that allows determining the viscosity of any paraffin and fatty acid PCM in their whole temperature range, and with less than 5 % of error.

- C_p of both paraffin and fatty acid PCM are most properly determined with a polynomial 2 equation.
- In addition, it is proven that a polynomial 2 equation proposed for solid C_p calculation in the literature can also be of use in liquid C_p determination.

Regarding the use of nanotechnology for PCM property enhancement presented in the third block of this thesis, the main outcomes are:

- Thermal conductivity and specific heat capacity are the main thermal properties reported to be enhanced by the addition of nanoparticles in PCM and HTF.
- The range of application of nanotechnology in TES is wide, and goes from insulation applications to the solar energy field.
- The use of metal, metal oxide and carbon nanoparticles enhances the thermal conductivity of the majority of base materials, being them PCM or HTF. Metal oxide nanoparticles are reported to enhance the specific heat capacity of the inorganic salts used in the solar energy field as well.
- Nanotechnology provides the possibility to formulate coated nanoparticles to increase the corrosion resistance of some materials without lowering their thermal properties.
- A small number of patents regarding the use of nanotechnology in the TES field are found, which already indicates the low development this technology has in the TES field. Nonetheless, the number of patents and published papers in which nanomaterials are used in TES has grown. This fact, along with the promising results presented so far, denote the potential nanotechnology has in the TES field and expansion this technology will have in the upcoming years.

As a summary, this thesis evidences that despite the current high development of TES technologies, there is still work to do in order to improve material characterization and system design. In addition, the use of nanotechnology opens a wide new range of research options in order to enhance materials and develop better and more efficient TES systems.

11.2 Recommendations for future work

The review presented on the thermal stability characterization of materials for TES clearly denotes the lack of a standard procedure to perform this characterization. Therefore, a clear standard methodology should be developed by the research community, specifying the best equipment and measurement conditions to characterize the thermal stability of materials used in TES systems. Regarding the latent heat measurements that are necessary for thermal stability characterization, it would be of interest to use the standard procedure for latent heat measurements with DSC that has recently been developed by the group of experts of IEA Task 42/Annex 29.

The enhancement of PCM and HTF properties with nanomaterials has been proven to be a potential option to enhance the material thermal properties and increase the performances of TES systems. The good results found in the literature so far and the low development that this technology currently has should encourage researchers to go deeper in the use of NE materials in TES systems. The influence that the size, shape, and weigh percentage of the nanoparticles dispersed in PCM should be deeper addressed in order to obtain better property enhancements. In addition, the use of other nanoparticle materials such as graphene would be of interest to enhance properties such as thermal conductivity and specific heat capacity.

Another important issue that could be addressed are the nanoparticle dispersion methods used. Researchers mainly use the dispersion in water solution by ultrasound, a simple and easy method to disperse the nanoparticles in the base material. However, some problems have already been notices, such as the agglomeration of the nanoparticles in the resulting materials. Therefore, parameters such as the sonication time, the frequency of the ultra sound probe or the drying method used should be deeper addressed.

12 Other research activities

12.1 Other publications

- Miró L, Barreneche C, **Ferrer G**, Solé A, Martorell I, Cabeza LF. Health hazard, cycling and thermal stability as key parameters when selecting a suitable phase change material (PCM). Thermochim Acta 2016, 627-629:39-47
- Martorell I, Solé A, Barreneche C, **Ferrer G**, Cabeza LF. Una forma eficiente de utilizar las energías renovables incluyendo almacenaje de energía térmica estacional. 202080 - Solar News 2014, 52:20 - 22. (Spain)

12.2 Contributions to conferences

- **Ferrer G**, Solé A, Barreneche C, Martorell I, Cabeza LF. Corrosion of aluminium for use in PCM energy storage. Eurotherm Seminar #99 - Advances in Thermal Energy Storage, 2014, Lleida (Spain)
- **Ferrer G**, Solé A, Barreneche C, Martorell I, Cabeza LF. Corrosion of metal containers for use in PCM energy storage. EuroSun 2014 - International Conference of Solar Energy and Buldings, 2014, Aix-les-Bains (France)
- Barreneche C, Solé A, **Ferrer G**, Martorell I, Cabeza LF. Thermal cycling test of PCM to ensure long-term performance of domestic hot water systems. EuroSun 2014 - International Conference of Solar Energy and Buldings, 2014, Aix-les-Bains (France)
- Barreneche C; Solé A; **Ferrer G**; Martorell I; Fernández AI; Cabeza LF. PCM screening: cycling stability and durability. IX Experts Meeting of the Task 42/Annex 29 of the International Energy Agency, 2014, Lyon (France)
- Solé A, **Ferrer G**, Barreneche C, Martorell I, Fernández AI, Cabeza LF. A new setup and methodology for vacuum corrosión test for thermochemical and vessel material compatibility. Experts Meeting of the Task 42/Annex 29 of the International Energy Agency, 2015, Wien (Austria)

- Miró L, **Ferrer G**, Cabeza LF. Annex 25 Round Robin Test (KNO_3) – progress. Experts Meeting of the Task 42/Annex 29 of the International Energy Agency, 2015, Zaragoza (Spain)
- Ristic A, Furbo S, Moser C, Schranzhofer H, Lazaro A, Delgado M, Peñalosa C, Zalewski L, Diarce G, Alkan C, Gunasekara SN, Haussmann T, Gschwander S, Rathgeber C, Schmit H, Barreneche C, Cabeza LF, **Ferrer G**, Konuklu Y, Paksoy H, Rammelberg H, Munz G, Herzog T, Jänchen J, Palomo e. IEA SHC Task 42 / ECES Annex 29 WG A1: Engineering and Processing of PCMs, TCMs and Sorption Materials. International Conference on Solar Heating and Cooling for Buildings and Industry, 2015, Istanbul (Turkey)
- **Ferrer G**, Solé A, Barreneche C, Martorell I, Cabeza LF. Methodology for specific heat capacity determination by DSC. INNOSTORAGE Conference, 2016, Beer-Sheva (Israel)

12.3 Scientific foreign-exchange

During the realization of this thesis, the PhD candidate did a 3 month research stay in the Thermal Energy Storage group led by Associate Professor Frank Bruno, within the Barbara Hardy Institute, School of Engineering, University of South Australia. The candidate worked on specific heat capacity (Cp) enhancement of sodium nitrate by the use of nanomaterials. The worked included the synthesis of graphene and silica nanoparticles, its dispersion in the molten salt and differential scanning calorimetry (DSC) measurements to quantify the Cp improvements. Experimentation is still going on and additional properties such as thermal conductivity may be measured. It is expected that at least one scientific paper will be published as a result of this research.

12.4 Other

12.4.1 Scientific and technical documents or reports

- **Ferrer G**, de Gracia A, Barreneche C, Martorell I, Cabeza LF. Corrosion and cyclability test for PCM candidates for thermal energy storage using PCM in HVAC systems. (Spain) 2014