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

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ABSTRACT

This study presents a methodology to determine the specific heat capacity (C_p) 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 C_p determination. To perform this study, the C_p of three materials commonly used in sensible TES systems, slate, water, and potassium nitrate (KNO_3), 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.

1. Introduction

The current perspective of lack of fossil energetic resources along with its price and the need to decrease CO_2 emissions [1,2], has lead researchers to focus on developing new energy systems able to take profit of renewable energy and be environmentally friendly and less expensive.

Thermal energy storage (TES) systems are presented as one of the possible solutions to accomplish this demand and have been widely studied and applied in a great variety of engineering fields. Solar energy is a good example case, as it is an abundant and clean energy source, easy accessible. The problem resides on the intermittency of its use, as the hours of maximum energy demand match with the hours of no solar irradiation (night hours). Therefore, and with the aim to fill this existing energy supply gap, TES systems are presented as the solution to store the energy and use it anytime.

One of the most used TES technologies is sensible heat storage, the process by which the heat is accumulated due to the increase of the material temperature without experimenting structural changes, thus, no phase change [3]. Other TES techniques are latent heat storage, which involves a phase change of the material to store or release the energy, and thermochemical energy, which implies the heat storage of a both sided chemical reaction of a thermochemical material (TCM) [4,5]. A key parameter for the performance of all the TES storage techniques just mentioned is the material selection. A high storage capacity of this material is needed to ensure a good an efficient performance of the system, hence it is important to perfectly know the thermo-physical properties of the material [6–8].

The energy storage capacity in the sensible heat storage depends, according to Eq. (1), of the specific heat capacity of the material (C_p), the temperature differential (dT) and the sample mass (m).

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

Therefore, to enhance the energy stored, it is important that the material used in the sensible heat storage system has a high specific heat capacity.

The importance of knowing the specific heat capacity of materials for sensible heat energy storage in TES systems along with the lack of a clear and common methodology in the literature has lead the authors to focus on this issue. Therefore, the most used

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DSC methods for C_p measurement have been reviewed [9–12] and the three main ones selected to be used in the proposed methodology for C_p measurements of materials for TES systems. The *dynamic method* has traditionally been used to measure PCM latent heat but also for C_p measurements applying high heating rates in the temperature range of study [13]. The *areas method* is specifically based on the C_p value, thus, how much heat flux is needed to heat up a material for temperature increase, and consists of consecutive isothermal stages differing 1 °C with no heating segments amid [14]. The *isostep method* is an intermediate between these two, as it is a succession of dynamic methods applied to heat up the material just 1 °C between isothermal segments. This method has been tested in glass transition pharmaceutical studies with good results obtained [15], but it has not been used for TES materials C_p determination, thereby its selection for this study.

The aim of the present study is to test the proposed methodology's performance with each DSC method by determining the C_p of three materials, water, slate and potassium nitrate (KNO_3), commonly used in sensible TES systems, compare the results and find out the measurement errors in order to select the best DSC method to determine the C_p of TES materials.

2. Materials

To ensure the performance of the methodology in a representative variety of material phase forms and chemical structures, three different materials widely used in sensible heat storage systems have been chosen to perform this study.

- *Water*. Its thermal properties are well known, and therefore, these values can be used as a reference to see the approach on the measurements each method has. Commercial Bi-distillated water from Panreac has been used to perform the experiments.
- *Slate*. It is a widely used construction material and its performance depends on its specific heat capacity, therefore authors find it an interesting material to be tested. The slate samples used in this study were taken from a quarry in the Catalan Pyrenees.
- *Potassium nitrate*. It is an inorganic salt mainly used as molten salt in concentrated solar power plants (CSP Plants). It has high melting point (320 °C) and, as all inorganic salts, a complex chemical structure, and that is why it is also found to be useful for this paper's purpose.

It is important to remark that this material selection responds to the need to test the methodology and not to tie it to a concrete material type or a specific TES application. Therefore, materials used in different TES systems and with which authors commonly work have been selected.

3. Methodology

The specific heat capacity has been determined by differential scanning calorimetry (DSC) using a Mettler Toledo 822e DSC. The equipment can operate between −20 °C and 500 °C and it is calibrated with zinc and indium, with calibration checks run monthly. The DSC is always turned on 20 min prior to the beginning of an experiment in order to homogenize furnace and intracooler temperatures and operates under a constant 200 mL/min N_2 flow.

Standard 40 μL aluminium crucibles have been used in this study. To ensure repeatability three samples of 10 mg were prepared for each one of the materials, weighing them with a Mettler Toledo AG135 analytical balance with a precision of 0.01 mg.

The procedure to determine the specific heat capacity of a material consists of three different measurements, all done under the same conditions, thus, using the same DSC method:

- **Blank measurement**. It is necessary to run an experiment with an empty crucible to measure the heat flux that corresponds to

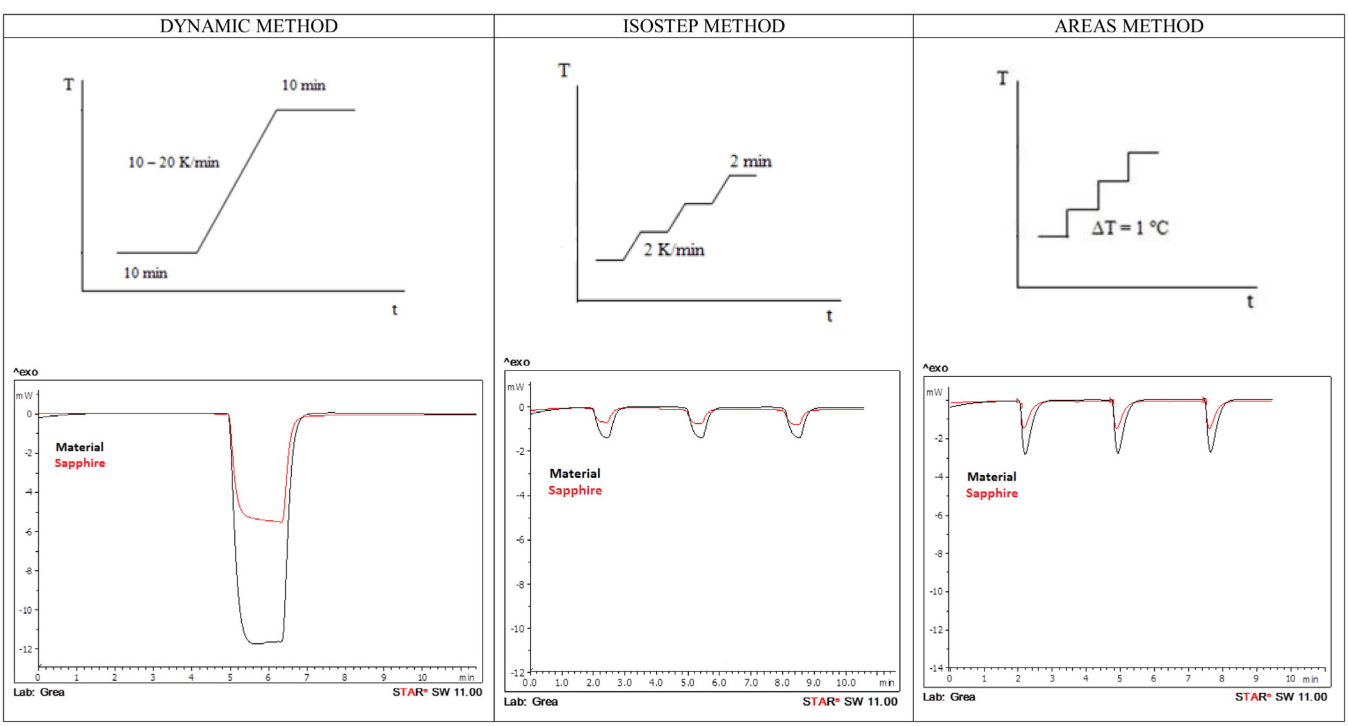

Fig. 1. Dynamic method, isostep method and areas method along with their DSC signal.