Health hazard, cycling and thermal stability as key parameters when selecting a suitable Phase Change Material (PCM)

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Abstract

From the literature review it was observed that there is no stablished methodology, neither a common pattern, when selecting a phase change material for a thermal energy storage application. Melting temperature and enthalpy have traditionally been the considered thermal properties for the material selection. Therefore, the authors of this paper propose a new method of investigation on the suitability of a PCM that takes into account not only thermal properties but also health hazard and both cycling and thermal stability. Health hazard is related with the handling of the material, and both cycling and thermal stabilities with durability. This methodology is applied to five different PCM in the 150–200 °C range: salicylic acid, benzanilide, d-mannitol, hydroquinone, and potassium thiocyanate. Results show that for an application in the 150–200 ºC range the suitable PCM are benzanilide and d-mannitol. Moreover, hydroquinone is also suitable but only in closed systems.

Keywords: thermal energy storage (TES); methodology; phase change materials (PCM); thermal stability; cycling stability; health hazard.

1 Introduction

Thermal energy storage (TES) technologies absorb and store energy for a period of time and release it according to the energy supply needs. These systems can bridge temporal and geographical gaps between energy supply and demand. According to the storage temperature needed, TES technologies can be grouped as low, medium or high temperature systems. Some of them have already showed significant levels of deployment [1]. In fact, there is an increasing interest in the medium temperature level in which applications like solar cooling or industrial waste heat can be found. Moreover, there is a gap in full characterised TES material in this range.

Solar cooling technologies have become more and more important for human comfort since the primary energy used, solar energy, is the cheapest and most extensively available renewable energy. Moreover, there is a need to develop and promote environmentally sustainable cooling technologies because of the high energy consumptions and the peak loads caused by the conventional systems. There are different ways through which heat can be stored in PCM in a solar cooling facility, such as: heat storage to be supplied to thegenerator, produced cool energy storage and solar collectors heat storage for later use [2].

Waste heat represents a significant opportunity to improve the efficiency of global energy systems. Its use is dependent of both energy demand and availability of TES networks in nearby areas. PCM could be used to match the heat supply with the demand where temporal or geographic gaps exist [1]. Technologies to recover and use industrial waste heat (IWH) have been previously categorized by Brueckner et al. [3]. These technologies can be used for recycling or reusing waste heat within an industry to heat or preheat other processes. In [3] authors collected exhaust gas temperature from different industrial processes with the final objective of detecting opportunities for IWH recovery. Based on this study Table 1 shows the industrial processes in which PCM having a melting point in the 150–200 °C temperature range could be applied for IWH recovery.

To design a real equipment involving PCM in this temperature range a previous and appropiate characterization of the PCM needs to be done.

Table 2 lists the available highly pure PCM for the abovementioned processes [4][5], along with their thermophysical properties, characterization technique, and stability study, if any. It is important to highlight that composites are out of the scope of this paper.

A similar approach was published by Haillot et al. [6] for the 120-150 °C temperature range. Authors based their methodology selection criterion on toxicity and ecological impact, economics, hygroscopy, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC) complemented with quadrupole mass spectrometry (QMS) gas analysis. The paper also emphasizes the importance of measurement conditions to characterize PCM (open/closed crucible, type of atmosphere) and suggest that long term stability tests are required.

DSC characterization provides both phase change temperature and enthalpy at the melting and solidification points.Moreover, melting/solidification cycles can be performed seeking for thermal cycing stability. Nonetheless, other equipment can also be used for this purpose, such as T-History [13] and thermal cyclers, [14]. In addition, besides checking the thermophysical properties before and after cycling by the already explained means and to go deeper on the study of PCM candidates, other techniques such as IR and TGA should be used. IR confirms if the chemical structure of the material remains unchanged, thus, if the PCM will behave as expected. TGA gives information about the decomposition temperature and when, if so, the mass loss of a sample starts. This is relevant to know the maximum permissible temperature the PCM can work at (see Section 3).

Table 2 shows that almost all published studies about experimental characterization of PCM in the 150-200 °C temperature range use differential scanning calorimetry (DSC) as the characterization technique. Only two studies, published by Rathgeber et al. [7][8], use another calorimetric technique (T-History) with a different operational basis. Furthermore, only two studies [9][10] perform stability tests coupled with infrared spectroscopy (IR), other two use

TGA [11][12], and another one performs cycling stability tests with a DSC-TGA coupled to a QMS [6].

Therefore, from the literature review it has been observed that there is no established methodology, neither a common pattern, when selecting a PCM in the 150-200 °C temperature range.

The common methodology to select the suitable PCM for an application is mainly based on a basic research on the supplier product specifications and a later DSC characterization. Only few researchers perform thermal cycles to ensure PCM long life, neither IR to check chemical degradation, if any, nor TGA to know the maximum operating temperature so that the material does not decompose. These features are highly important to design a real application involving PCM in this temperature range. Therefore, the main objective of this paper is to provide a complete step-by-step methodology to follow when selecting a PCM, with a case study in the 150-200 °C application range. Few PCM selection procedures are presented in the literature for this working temperature range but there are many for higher temperatures [19][20][21].

The authors of this paper consider the methodology proposed in this article as basic, considering minimum requirements. Extra analysis could be helpful and recommendable.

2 Materials

Five PCM with melting temperatures between 150 to 200 °C are selected. As this case study aims to be representative, they have been selected from different PCM groups: organic, sugar alcohols, aromatic compounds, and inorganic. Their melting peak temperature, heat of fusion, and purity provided by the manufacturer, are listed in Table 3.

3 Proposed methodology

It can be previously seen in the literature that a PCM can be characterised by using different technologies [23]. Among all of them, authors propose to take into account a minimum of three: health hazard, cycling stability and thermal stability. Extra analysis are recommendable if possible. Figure 1 shows the diagram of the methodology here proposed. All the involved stages are complementary to each other and they converge to a common goal which is the proper material selection.

Moreover, thermal stability analysis have been performed both in sealed and in open/pierced crucibles. The reasons why sealed and open/pierced experiments have been conducted are first, because of equipment requirements of piercing crucible lids at temperatures around 200 °C and, second, because it is possible to detect the influence of the oxidation (contact with air) of the materials proposed in this analysis.

3.1 Health hazard

One important parameter to take into account when performing a material screening for a certain application is health hazard [6][19]. The degree of health hazard of a chemical or material is based on the form or condition of the material, as well as its inherent properties.

Usually the manufacturer provides it in specific datasheets, called material safety data sheets (msds), that reveal how hazardous the substance is. The degree of health hazard of a material should indicate the degree of personal protective equipment required to work safely with the material. This parameter needs to be accounted due to the specific standards to be accomplished for each one of the different applications where the material is thought to be implemented.

The National Fire Protection Association (NFPA) has developed a system to indicate the health, flammability, reactivity and special hazards for many common chemicals through the use of the NFPA 704 Diamond [24]. The standard "NFPA 704: Standard System for the Identification of the Hazards of Materials for Emergency Response" is followed here, specifically the blue indicator that corresponds to health hazard, which is graded from 0 to 4, being 0 non-hazardous substances and 4 the ones that could cause death or major residual injury by very short exposure.

3.2 Thermal stability

Thermal stability is another key factor when selecting a PCM for a specific application. Thermogravimetric analyses (TGA) have been performed in order to understand the thermal decomposition of the sample within the temperature range considered to be applied for solar cooling applications.

The tests are run with open pans in a TGA, simulating an open system to ensure that the material can be used in the application temperature range with no mass losses. The thermogravimetric device used was a TA Instrument Simultaneous SDTQ600 under N_2 atmosphere. The heating rate used to perform the PCM decomposition tests was 10 K/min from 30 °C to 250 °C and the opened 100 µL alumina crucibles were filled with around 20 mg of material.

3.3 Cycling stability

When designing a heat storage unit, it is of great importance to ensure its long term performance, that is, the long term stability of the material used. Its thermal properties (melting temperature and enthalpy) need to remain almost constant during a specific number of cycles to guarantee the efficiency of the unit. Therefore, the cycling stability is the other essencial parameter to be considered.

The study is done by DSC and as some of the materials can experience oxidation with air, the first step was to decide whether the DSC pans needed to be pierced or closed. For this purpose, two samples of each PCM were prepared, piercing the pan lid in all cases to check, if so, the quantity of material lost due to the lid hole during cycling. The DSC measurements were done using a dynamic mode method between 100 ºC and 200 ºC at a constant heating rate of 0.5 K/min under a 200 ml/min N_2 flow rate. Ten minute isothermal stages were programmed to stabilize the material temperature before and after each heating/cooling segment. The materials underwent four complete heating/cooling cycles in this conditions.

In order to quantify the mass loss, the pans were weighed before and after each cycle. The following Table 4 shows the results obtained after 1, 2, 3 and 4 cycles. Hydroquinone and salicylic acid were the materials that experienced important mass losses due to the piercing of the lid. These mass losses could also be consequence of possible oxidation with air. Mostly all salicylic acid was lost within just two cycles. Oppositely and as it can be seen, none of the other materials experienced important mass losses.

Therefore, these results made the authors decide to proceed the study with closed pans and none pierced lids. At the same time and as a preventive measure against oxidation, it was decided to fill the pans mostly to the top, leaving a thin layer of air inside the crucible; therefore the oxygen presence in the crucibles would be very low and oxidation may be neglected.

3.3.1 Cycling characteristics

The methodology is designed to study the cycling stability of all the PCM during 50 cycles. In order to see the evolution of the thermal parameters along these 50 cycles, three measurement points were stablished:

- 1st measurement (used as a reference) : 0 cycle
- 2nd measurement: 10th cycle
- 3rd measurement: 50th cycle

In order to achieve repeatability in the results, two samples of each one of the five PCM candidates were prepared for each measurement point. That is, ten samples for the initial measurements (cycle 0), ten samples to be cycled 10 times (10th cycle measurement point) and ten samples to undergo 50 cycles (50th cycle measurement point). The thermophysical properties were only measured at cycles 0, 10 and 50. 100 μL aluminium pans 2/3 filled (to avoid oxidation) and hermetically closed were used in the DSC. All materials were cycled in a Mettler Toledo DSC 822e under 200 ml/min constant N_2 flow rate. Two heating/cooling rates (Figure 2) were stablished in this procedure:

- 10 K/min rate was used to cycle the PCM
- 0.5 K/min rate was used in the last cycle to measure the thermal parameters of the PCM

The authors run a previous cycle at 10 K/min rate to all samples in order to melt and crystallize the PCM under the same conditions. Therefore, this cycle is considered as a pretreatment in order that the initial study point is the same for every sample.

To cycle the PCM, a dynamic mode method between 100 °C and 200 °C was used to characterize the materials. As Figure 2 shows, this method consists on a 10 min isothermal stage at 100 °C, followed by a heating stage at constant rate were temperature is increased from 100 °C to 200 °C and another 10 min isothermal stage at 200 °C to ensure the complete melting of the PCM. Then the material is cooled at constant rate down to 100 °C and another 10 min isothermal stage is applied at this temperature to ensure the total solidification of the material.

Based on the experience of the authors and study cases [13,26] low heating/cooling rates are applied when measuring thermohysical properties of the PCM in order to obtain reliable results.

3.3.2 Chemical stability

FT-IR spectroscopy has been performed in order to study the chemical stability of the selected PCM after the cycling process. A Perkin Elmer MID Spectrum Two™ spectrometer that works in the 400–4000 cm^{-1} wave number range was used, with a 4 cm^{-1} resolution accounting 4 IR scans each analysis. Its functionality is based on the characteristic wave numbers at which the molecules vibrate in infrared frequencies. This can be seen as characteristic peaks for each substance. By using the FT-IR technique, the PCM degradation through the cycling stability test described in former paragraphs can be followed. The disappearance of the characteristic peaks, the appearance of new peaks or the characteristic peaks decrement can indicate that the material is being oxidized or degraded.

4 Results and discussion

4.1 Health hazard

The health hazard rating following NFPA 704 of the materials under study is shown in Table 5. Potassium thiocyanate presents the highest value, 3 out of 4, which stands for toxic or corrosive material and skin contact or inhalation should be avoided. This PCM, and others which may present hazardous values above 3, are suggested to be discarded at this step for the selection. Nonetheless, if a specific application requires it, they can be used, but always under the established safety measures. The other four PCM present low values of health hazard which make them suitable for application.

4.2 Thermal stability

Thermal decompositions of the PCM under study are plotted in Figure 3. These curves show that d-mannitol, benzanilide, and potassium thiocyanate are almost stable within the temperature range, up to 250 °C with open crucibles (see the horizontal line around 100 % weight loss), while hydroquinone and salicylic acid are degraded until the total decomposition of the PCM mass (see curves from 100 % weight loss to 0 %).

The decomposition/degradation of hydroquinone starts at 150-160 °C, and for salicylic acid at 120-130 °C. Based on these results, the maximum working temperature in open systems for hydroquinone and salicylic acid should be lower than 150 °C and 120 °C, respectively.

4.3 Cycling stability

4.3.1 Phase change temperatures and enthalpies

Two samples of a same PCM were cycled in each measurement point in order to representatively measure the variability of the thermophysical properties with time. Errors of 10% for melting enthalpy and a 5% for melting temperature are stated as acceptable for the DSC measurements [9][27] and are represented in the graphics with error bars.

Figure 4 shows melting and solidification enthalpies of the four PCM. D-mannitol is the PCM with higher enthalpy values, over 200 **kJ·kg**$^{-1}$even after 50 cycles, though its storage capacity seems to decrease a bit with the cycles. Hydroquinone is the other material that has enthalpies larger than 200 **kJ·kg**$^{-1}$along the 50 cycles and its storage capacity remains quite constant during this time. Benzanilide has lower heat of fusion but its values also remain constant during the 50 cycles. Potassium thiocyanate has the lowest enthalpy values and presents an unexpected pattern as its enthalpies increase with cycles. However, these differences are within the process error, so values can be taken as reliable. Salicyclic acid pans continued to experience leaks despite being closed and non-pierced, therefore data could not be collected along the 50 cycles and neither presented. Consequently, this material is not included neither in Figure 4 nor in Figure 6.

Figure 5 shows the evolution of both melting and solidification temperatures of each PCM along the 50 cycles. As displayed, hydroquinone is the PCM that does not show any kind of temperature hysteresis on its values. The graph shows that both melting and solidification temperatures remain constant along the test. On the other hand, d-mannitol presents important hysteresis between the two temperatures and this difference becomes more remarkable as the test comes to its end. Benzanilide also shows hysteresis between both temperatures but not as large as d-mannitol one. Moreover and despite the hysteresis, both phase change temperatures remained mostly constant during all the experimentation. Finally, potassium thiocyanate shows a great increase of the melting temperature from the 10th cycle on, while the solidification temperature does not suffer important changes along the cycles. This value is off the error and some experimental error like traces of other material on the DSC pan surface may explain it.

4.3.2 Chemical stability

Results obtained by FT-IR in order to follow the chemical degradation of the PCM under study are presented in Figure 6. These results show that d-mannitol, benzanilide and hydroquinone present almost no chemical degradation over cycles because the FT-IR spectrum show equal characteristic peaks with similar profiles. However, K-thiocyanate undergoes a degradation process which is reflected by the differences on the initial FT-IR spectrum and the signal obtained after 10 cycles and 50 cycles, as shown in Figure 6. This agrees with the results obtained with DSC where the thermophysical properties of K-thiocyanate also change.

Finally, Table 6 summarizes the thermal characterization performed in this study in order to select the proper PCM for thermal systems in the 150–200 °C temperature range. In addition, this table takes into account the configuration of the system (open or closed system) as well as the maximum service temperature for each configuration and the importance of the health hazard.

Summarizing the obtained results, salicylic acid is discarded as a useful PCM to be implemented in both closed and open systems operating between 150 -200 °C. D-mannitol, benzanilide, potassium thiocyanate, and hydroquinone are useful materials to be implemented in closed systems operating in the 150–200 °C temperature range. D-mannitol, benzanilide and potassium thiocyanate also fit properly for open systems operating in the same temperature range, discarding hydoquinone and salicylic acid due to its impossibility to reach the operational temperature service of these installations. Finally, it is of importance to notice potassium thiocyanate toxicity, thus caution must be taken when selecting it as PCM and avoid it if possible as better matches have been found.

5 Conclusions

From the literature review it was observed that there is neither a stablished methodology nor a common pattern, when selecting a PCM for an application between 150-200 °C. Researchers traditionally select a PCM looking only at literature melting temperature and enthalpy values or often measuring these two properties in the laboratory. Facts show that the behaviour of a PCM can change when located in the specific application.

This is why the authors of this paper propose a new method of investigation on the suitability of a PCM. In this sense, a list of properties that can be studied when selecting a PCM is presented. This methodology goes one step further incorporating health hazard and both cycling and thermal stability in the minimum list of properties to be considered when selecting a suitable PCM for a given application. Health hazard is important to be considered not only for the health and safety measures to be implemented for the employees in contact with the PCM but also for facilities design and maintainance. On the other hand, cycling and thermal stability provide information regarding the durability of the PCM which is a key aspect when selecting a material for an industrial application.

In order to validate the experimental methodology presented in this study, five PCM from different PCM groups in the 150-200 °C temperature range were selected: salicylic acid, benzanilide, d-mannitol, hydroquinone, and potassium thiocyanate. In this temperature range, current research trends focus on solar refrigeration and industrial waste heat recovery as suitable applications. Evaluations of melting temperatures, enthapies, health hazards as well as cycling and thermal stability for open and closed systems are performed in order to collect the required information for an accurated PCM selection. According to this methodology, the suitable PCM for an application in the range 150-200 °C are benzanilide and d-mannitol. Hydroquine could also be considered in closed systems.

As a final conclusion, it can be said that the experimental methodology presented in this study goes one step further in the complex process of collecting essential information for a suitable PCM selection.

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7 References

[1] International Energy Agency (IEA). Technology Roadmap: Energy storage. 2014. https://www.iea.org/roadmaps/

[2] A. Gil, E. Oró, G. Peiró, S. Álvarez, L.F. Cabeza. Material selection and testing for termal energy storage in solar cooling, Renew. Energ. 57 (2013) 366-371.

[3] S. Brueckner, S. Liu, L. Miró, M. Radspieler, L.F. Cabeza, E. Laevemann. Industrial waste heat recovery technologies: an economic analysis of heat transformation technologies, Accepted in Appl. Technol.

[4] B. Zalba, J.M. Marín, L. F. Cabeza, H. Mehling. Review on termal energy storage with phase change: materials, heat transfer analysis and applications, Appl. Therm. Eng. 23 (2003) 251-283.

[5] S. D. Sharma. Latent heat storage materials and systems: a review, Int. J. Gr. Energ. 2 (2005) 1-56.

[6] D. Haillot, T. Bauer, U. Kröner, R. Tamme. Thermal analysis of phase change materials in the temperature range 120-150 °C, Thermochim. Acta 513 (2011) 49-59.

[7] C. Rathgeber, H. Schmit, P. Hennemann, S. Hiebler. Calibration of a T-History calorimenter to measure enthalpy curves of phase change materials in the temperature range from 40 to 200 °C, Meas. Sci. Technol. 25 (2014) 035011.

[8] C. Rathgeber, L. Miró, L.F. Cabeza, S. Hiebler. Measurement of enthalpy curves of phase change materials via DSC and T-History: When are both methods needed to estimate the behaviour of the bulk material in applications?, Thermochim. Acta 596 (2014) 79-88.

[9] A. Solé, H. Neumann, S. Niedermaier, I. Martorell, P. Schossig, L. F. Cabeza. Stability of sugar alcohols as PCM for thermal energy storage. Sol. Energ. Mat. Sol. C. 126 (2014) 125-134.

[10] C. Barreneche, A. Gil, F. Sheth, A. I. Fernández, L. F. Cabeza. Effect of D-mannitol polymorphism in its thermal energy storage capacity when it is used as PCM, Sol. Energ. 94 (2013) 344-351.

[11] M.A. Gallegos Lazcano, W. Yu. Thermal performance and flammability of phase change material for medium and elevated temperatures for textile application, J. Therm. Anal. Calorim. 117 (2014) 9-17.

[12] G. Kumaresan,R. Velraj, S. Iniyan. Thermal analysis of D-mannitol for use as phase change material for latent heat storage, J. Appl. Sci. 11 (2011) 3044-3048.

[13] A. Solé, L. Miró, C. Barreneche, I. Martorell, L.F. Cabeza. Review of the T-history method to determine thermophysical properties of phase change materials (PCM), Renew. Sust. Energ. Rev. 26 (2013) 425-436.

[14] G. Ferrer, A. Solé, C. Barreneche, I. Martorell, L.F. Cabeza. Review on the methodology used in thermal stability characterization of phase change materials, Renew. Sust. Energ. Rev.50 (2015) 665-685.

[15]T. Nomura, C. Zhu, A. Sagara, N. Okinaka, T. Akiyama. Estimation of thermal endurance of multicomponent sugar alcohols as phase change materials, Appl. Therm. Eng. 75 (2015) 481-486.

[16]A. Gil, E. Oró, G. Peiró, S. Álvarez, L. F. Cabeza. Material selection and testing for termal energy storage in solar cooling, Renew. Energ. 57 (2013) 366-371.

[17]A. Gil, E. Oró, L. Miró, G. Peiró, A. Ruiz, J. M. Salmerón, L. F. Cabeza. Experimental analysis of hydroquinone used as phase change materials (PCM) to be applied in solar cooling refrigeration, Int. J. Refrig. 39 (2014) 95-103.

[18]M. M. Kenisarin. Thermophysical properties of some organic phase change materials for latent heat storage. A review. Solar Energy 107 (2014) 553-575.

[19]N.L. Bruno Cárdenas. High temperature latent heat thermal energy storage: Phase change materials, design considerations and performance enhancement techniques. Renew. Sust. Energ. Rev. 27 (2013) 724–737.

[20] M. Liu, W. Saman, F. Bruno. Review on storage materials and thermal performance enhancement techniques for high temperature phase change thermal storage systems. Renew. Sust. Energ. Rev. 16 (2012) 2118– 2132.

[21] S. Khare, M. Dell'Amico, C. Knight, S. McGarry. Selection of materials for high temperature latent heat energy storage. Sol. Energ. Mat. Sol. C. 107 (2012) 20–27.

[22] M. M. Farid, A. M. Khudhair, S. A. K. Razack, S. Al-Hallaj. A review on phase change energy storage: materials and applications, Energ. Conver. Manage. 45 (2004) 1597-1615.

[23]L.F. Cabeza, C. Barreneche, I. Martorell, L. Miró, S. Sari-Bey, M. Fois, H.O. Paksoy, N. Sahan, R. Weber, M. Constantinescu, E.M. Anghel, M. Malikova, I. Krupa, M. Delgado, P. Dolado, P. Furmanski, M. Jaworski, T. Haussmann, S. Gschwander, A.I. Fernández. Unconventional experimental technologies available for phase change materials (PCM) characterization. Part 1. Thermophysical properties, Renew. Sust. Energ. Rev. 43 (2015) 1399-1414.

[24]http://www.nfpa.org/704 (last accessed 10/07/2015).

[25]Web http://pubchem.ncbi.nlm.nih.gov/compound/ (last accessed 05/02/2015)

[26]C. Barreneche, A. Solé, L. Miró, I. Martorell, A.I. Fernández, L.F. Cabeza. Study on differential scanning calorimetry analysis with two operation modes and organic and inorganic phase change material (PCM), Thermochim. Acta 553 (2013) 23-26.

[27]H. Mehling, H.P. Ebert, P. Schossig. Development of standard for materials testing and quality control of PCM, in:Seventh IIR Conference on Phase Change Materials and Slurries for Refrigeration and Air Conditioning, Lyon, France, 2006.