

Available online at www.sciencedirect.com**ScienceDirect**

Energy Procedia 91 (2016) 218 – 225

Energy

Procedia

SHC 2015, International Conference on Solar Heating and Cooling for Buildings and Industry

Stability of D-mannitol upon melting/freezing cycles under controlled inert atmosphere

Margarita-Manuela Rodríguez-García^{a,*} Rocío Bayón^b, Esther Rojas^b^aCIEMAT-PSA, Plataforma Solar de Almería, Carretera de Senés km 4, 04200, Tabernas, Almería, Spain^bCIEMAT-PSA, Av. Complutense 40, 28040, Madrid, Spain

Abstract

D-mannitol has been selected as phase change material for direct steam generation. Since its stability in air cannot be assured, according to previous studies, this paper deals with the behavior of this material under inert atmosphere. Using a device, specifically designed for this study at the Plataforma Solar de Almería, the thermal behavior of D-mannitol when cycled between 100°C and 190 °C under inert atmosphere, up to 50 times, as well as its loss in mass when heated during a certain time in inert atmosphere is presented. After being cycled, a change in the melting temperature interval as well as in the supercooling range of temperatures is stated. In addition to this, a change in color and consistency after having a sample at 180 °C for a determined period of time prove the degradation and hence then non-feasibility of the D-mannitol as PCM.

© 2016 Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Peer-review by the scientific conference committee of SHC 2015 under responsibility of PSE AG

Keywords: phase change material, D-mannitol, cycling in inert atmosphere

1. Introduction

Thermal energy storage is a decisive part of a solar-based system. In this way, the study of phase change materials (PCMs) has been attracting much attention since they are among the best options when latent heat from steam wants to be stored. Within the framework of REELCOOP European project [1] a latent heat storage module with improved heat transfer configuration and intended for the temperature range 130 °C-170 °C is going to be

* Corresponding author. Tel.: +34 950387800; fax: +34 950365015.
E-mail address: margarita.rodriguez@psa.es

developed. Among other PCMs, the sugar alcohol D-mannitol with molecular formula $C_6H_8(OH)_6$, with the structure shown in Fig. 1, could be a good candidate to be used in such storage module since it has a reported melting point of 165 °C-168 °C and 246-338 kJ/kg of melting enthalpy [2]. Other physical properties and relevant data of D-mannitol are recorded in Table 1. However, previous studies of D-mannitol, [3], have shown that it undergoes strong and fast degradation when cycled under air, with a deterioration of its thermal properties.

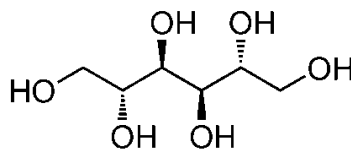


Fig. 1. D-mannitol structure.

Table 1. D-mannitol physical parameters and relevant data taken from different data sources. [4-7].

T_m [°C]	ΔH_{fus} [kJ/kg]	Specific heat at 25 °C [kJ/kgK]	Technical issues	Human/ environm. risk	Price [€/kg]
165-168	246-338	1.383	supercooling	Food additive	<50

Therefore the aim of this work is to check the D-mannitol long-term thermal stability under inert atmosphere and determine its feasibility as PCM, not only for the REELCOOP prototype but also for any other latent storage application. In this way two different kinds of tests have been performed with D-mannitol under either Ar or N_2 : on the one hand melting/freezing cycles between 100 °C and 185 °C and on the other hand long time melting at 180 °C for different time periods.

The present paper is organized as follows. The testing device is presented in the next section where the SUBMA facility at PSA-CIEMAT is described, section 3 presents the tests performed with D-mannitol, being section 3.1 depicted to the thermal behavior after cycling it in Argon and Nitrogen, and section 3.2 to the long-term melting of D-mannitol under Ar and N_2 atmosphere at 180 °C. Section 4 outlines the visible and ultraviolet spectrum analyses, and section 5 summarizes the main conclusions.

Nomenclature

Vis-UV	Visible-Ultraviolet
Symbols	
A	absorbance
c	molar concentration
d	path length
m_{total}	total sample mass
T_m	melting temperature
V	total solution volume
ΔH_{fus}	enthalpy of fusion
ϵ	extinction coefficient

2. SUBMA test device

In order to perform melting/freezing cycles and long term melting under inert atmosphere of PCMs, a testing device, named SUBMA, has been designed and manufactured at Plataforma Solar de Almeria (see Fig. 2). SUBMA is formed by a vessel closed by two flanges where a melting crucible can be introduced. In the upper covering flange, a J-type thermocouple has been installed in order to record sample temperature with the corresponding bulkhead fitting to avoid any gas leakage. The lower flange is provided with two connections: one for gas inlet and the other for gas outlet, in which thermocouples are inserted to measure the corresponding gas temperatures. Each gas pipe is connected to a valve that allows gas entrance and exit and keeps the pressure in the device at a user-defined pressure range. The gas facility is prepared for using Ar or N₂, but any other gas might be used. The whole device is enclosed in a furnace with a controller that allows performing heating/cooling ramps and whose inner temperature is additionally monitored.

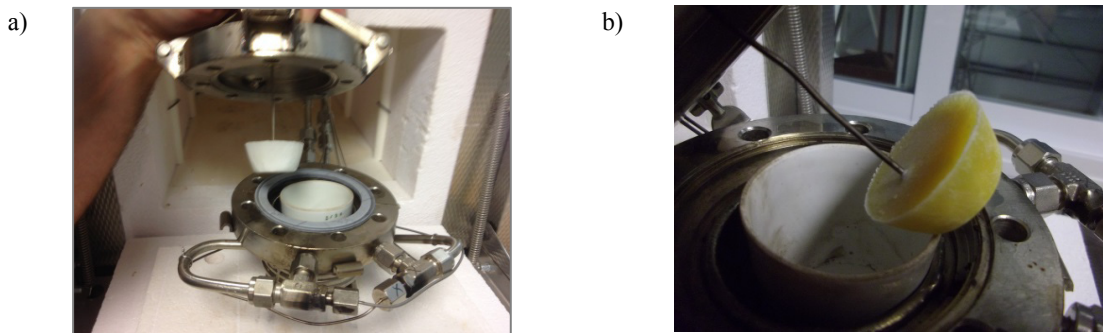


Fig. 2. SUBMA device picture with the melting crucible and the sample after (a) first melting test and (b) after 50 cycles in argon atmosphere.

3. Test performance

In this work, two kinds of tests have been performed. On the one hand melting/freezing cycles between 100 °C and 190 °C and on the other hand long time melting at 180 °C for different time periods. For both of them either Ar or N₂ were used as inert atmosphere at a pressure inside the SUBMA device up to 0.1 MPa.

As stated by Bayón [3], the D-mannitol presents strong supercooling which leads to a freezing temperature of about 107 °C. This is why melting/freezing cycles had to be performed in a temperature range down to 100°C.

The D-mannitol used for these experiments was 99% purity technical grade and the initial sample mass was around 20 g. During the melting/freezing tests sample temperature evolution was monitored and for the samples used in long term melting mass variation was checked. After each test, D-mannitol samples were dissolved in water and analyzed by recording their corresponding Vis-UV spectra in the interval 190 nm-600 nm with a Zenyth 200rt spectrophotometer.

3.1. D-mannitol cycling under Ar and N₂ atmosphere.

Consecutive melting/freezing cycles were performed for D-mannitol between 190 °C and 100 °C under 0.1 MPa gas pressure (Ar or N₂). Samples could be heated at a constant rate (2 °C/min), however since the furnace did not have any cooling device, they were allowed to cool down naturally with the door closed.

Fig. 3 displays temperature/time curves of a D-mannitol sample for the 1st, 25th, 40th and 50th melting/freezing cycle under Ar atmosphere. As can be seen the melting temperature interval for the first cycle has a well-defined plateau at 165°C-168 °C corresponding to D-mannitol melting which lasts around 40 minutes. After 25 cycles the shape of this interval is very similar to the first cycle, but it lasts only about 20 minutes. After 40 cycles the melting interval has changed to a different slope curve that starts at a lower temperature, and after 50 cycles, some extra

peaks appear during the melting interval. These extra peaks could be due to the formation of degradation products as will be discussed in the section 4. Regarding the supercooling, in the first cycle the sample starts freezing at 130 °C after which its temperature suddenly increases due to the latent heat delivery reaching 165 °C. However during the 50th cycle, freezing starts at 128 °C and the temperature reached only 145 °C. Again, this variation must be related to the formation of new components.

As can be seen in Fig. 2 a) and b), the appearance of D-mannitol sample after 50 cycles in Ar atmosphere has changed from white to dark yellow color, which confirms that it has undergone certain degradation.

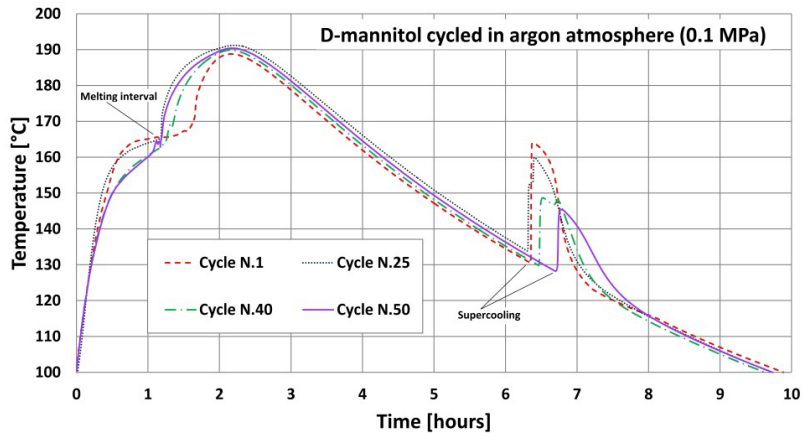


Fig. 3. Melting/freezing cycles of D-mannitol in Ar atmosphere.

The same melting/freezing cycles were performed for D-mannitol in N₂ atmosphere but in this case the sample was cycled only 17 times. As can be seen in Fig. 4, the melting interval after 17 cycles presents some extra peaks that are probably due to the formation of new components that makes the melting interval time longer, i.e. for the first cycle the melting interval lasted around 40 minutes, while for the 17th cycle the melting interval lasts 70 minutes approximately. As for the freezing peak, it starts at 130 °C for the first cycle, and changes to 126 °C after 17 cycles.

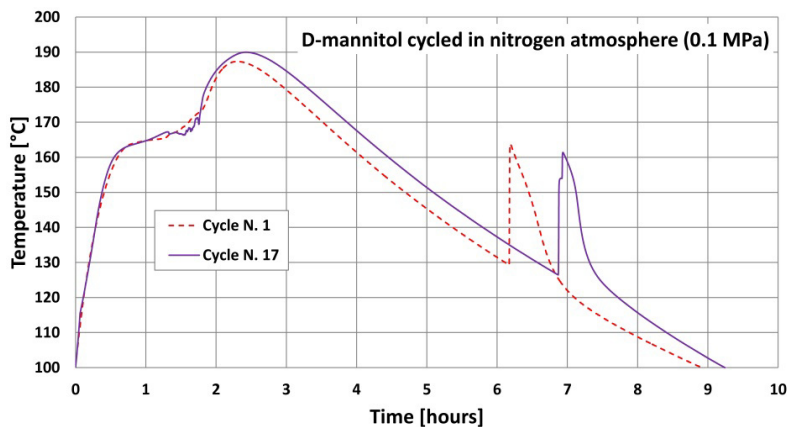


Fig. 4. Melting/freezing cycles of D-mannitol in N₂ atmosphere.

3.2. Long-term melting of D-mannitol under Ar and N₂ atmosphere at 185 °C.

In order to study D-mannitol long-term stability, samples were kept melted at 180 °C for a certain period of time either in Ar or in N₂ atmosphere. Gas pressure during these tests was kept at 0.1 MPa. For these experiments no sample temperature was recorded in order to avoid any mass loss due to thermocouple removal. Since the sample was in a pressurized vessel, it had to be cooled down in order to open the SUBMA device and remove the crucible with the sample. To be sure that the sample did not suffer any cooling/freezing cycling process that could affect the sample composition; a new sample was used for each experiment and weighed before and afterwards.

After 72 hours (3 days) D-mannitol presented a brown color, after 122 hours (5 days) the sample was dark brown as can be in Fig. 5a. However, after 171 hours (7 days) and 268 hours (11 days) a deep brown dense syrup that did not crystallized as a hard solid was obtained (see Fig. 5 b).

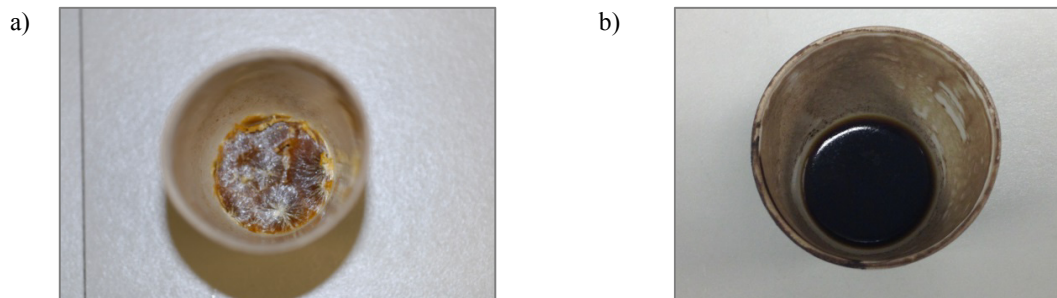


Fig. 5. External appearance of D-mannitol after (a) 122 hours and (b) 268 hours in Ar atmosphere at 185 °C.

In addition to the sample browning, a decrease in volume was clearly observed. Actually in all cases a decrease of D-mannitol mass was obtained not only for the samples kept in Ar but also for the sample kept in N₂. In Fig. 6 the remaining mass percentage of D-mannitol has been represented as a function of time and we can see that it decreases almost linearly. The percentage of D-mannitol mass loss during 11 days at 180 °C is 12%. This mass loss of D-mannitol taking place when kept melted for long time clearly indicates that together with sample degradation a great amount of volatile species are produced during the heating.

For the case of the sample kept in N₂ only one test was performed (7 days) being the mass loss under this atmosphere a little bit smaller than the mass loss in Ar.

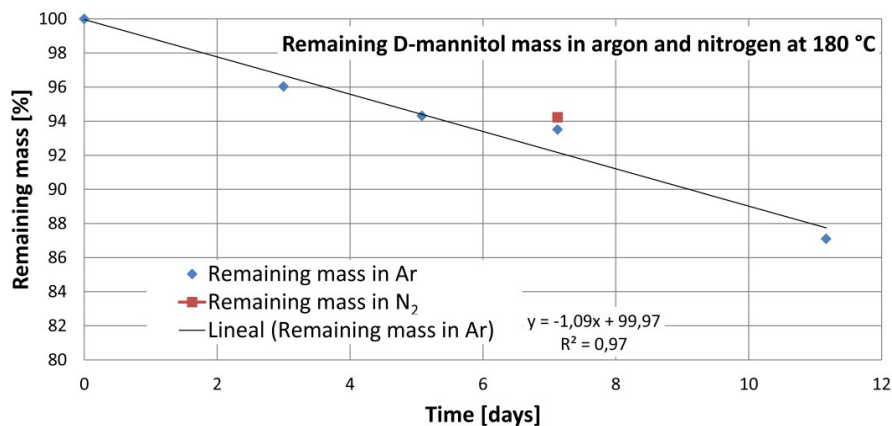


Fig. 6. Loss of D-mannitol mass in argon and nitrogen at 185 °C.

4. Vis-UV spectrum analyses

Although D-mannitol does not present any absorbance in the Vis-UV range, the products leading to the sample browning were expected to be active in this wavelength interval. Therefore, samples from D-mannitol kept at 180°C under Ar for different times were dissolved in water and their Vis-UV recorded in the interval 190 nm-600 nm. A good advantage of Vis-UV absorption spectra is that they are related to species concentration through the Bourger-Lambert-Beer equation in which the absorbance, A , is proportional to molar concentration of the absorbing species, c (in mol/l), the path length, d (in cm), and the extinction coefficient, ϵ :

$$A(\lambda) = \epsilon(\lambda)cd$$

Unfortunately, in our case we don't know the concentration of the absorbing species and we only know the total mass concentration (m_{total}/V in g/l) of the solution we are measuring. Therefore all spectra were normalized by dividing absorbance curves by sample concentration in g/l in order to compare the evolution of absorbing species from one sample to another. Vis-UV spectra of brown D-mannitol samples could be deconvoluted in three Gaussian peaks at 208 nm, 260 nm and 314 nm after pure D-mannitol curve was subtracted as baseline and abscise axis was changed to wavenumber in cm^{-1} . In Fig.7 Vis-UV spectra of D-mannitol samples kept at 180°C under Ar for 3 days (a) and 7 days (b) and the spectra of samples kept for 7 days in N_2 (c) and air (d) are displayed together with their corresponding deconvolution in the above mentioned peaks.

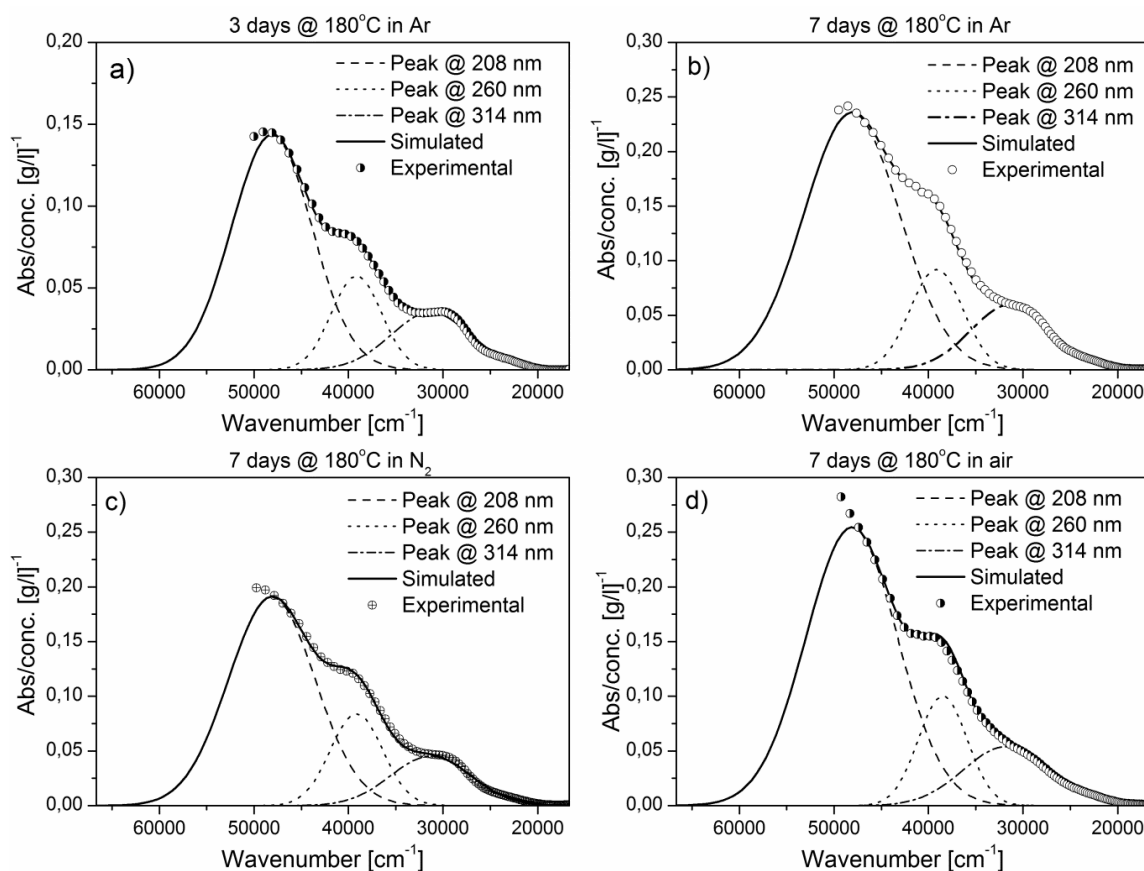


Fig. 7. Vis-UV normalized absorption spectra for D-mannitol samples kept at 180°C under Ar for 3 days (a) and 7 days (b) and for 7 days in N_2 (c) and air (d).

As reported in another work [8], the intensity of the Vis-UV spectra increased as D-mannitol was kept for longer times at 180°C under air, which means that the amount of absorbing species also increased. In this way the formation of absorbing species were clear indicators of D-mannitol thermal degradation. As we can see in the spectra recorded in Fig. 6 (a) and (b), the same behavior is observed for D-mannitol samples kept in Ar. Actually if we compare the spectra of Fig. 6 (b), (c) and (d) similar degradation is observed after 7 days for samples kept melted under Ar, N₂ and air atmospheres respectively.

In order to better see the time evolution of the absorbing species, the areas of the three deconvolution peaks of the normalized spectra were calculated for the samples kept at 180°C in Ar and N₂ and plotted together in Fig. 7 with the values obtained for D-mannitol samples kept in air and reported elsewhere [8].

For the samples kept in air we observed that the areas of the three peaks increase exponentially with time and so should do the concentration/s of the species giving place to these absorptions. For the case of samples kept melted under Ar atmosphere an increase of peak areas is also obtained but with a clearly different time evolution. These differences seem to indicate that degradation reactions might proceed in a different way (or with different kinetics) although the species responsible for the sample browning are apparently the same (since they display similar spectra) independently on the atmosphere used during the sample melting.

It is important to mention here that the samples cycled in Ar also underwent browning and hence degradation. For these samples, the calculated peak areas could be correlated to time melted at 180°C as if one cycle was about one hour. This means that the sample cycled 50 times in Ar displayed a spectrum and peak areas as if it had been kept melted at 180°C for 50 hours (i. e. less than 3 days). This proves that sample cycling is not really representative of what might happens to the D-mannitol under long-term operation [8].

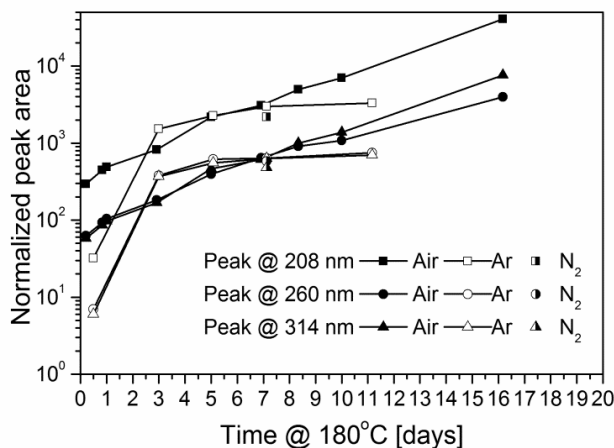


Fig. 8. Time evolution of normalized peak area for D-mannitol kept melted at 180°C in air, Ar and N₂ atmosphere.

As discussed in previous works [3, 8] it is not clear how many different absorbing species are the responsible for the sample browning, but it is highly possible that they can be associated with caramelization products [9]. In any case the results reported in this work clearly demonstrate that D-mannitol undergoes not only mass loss but also strong browning and hence degradation even under inert atmospheres of both Ar and N₂. This means that its thermal degradation is more likely to be related with caramelization process, which do not require the presence of oxygen, and no with oxidation process as it has been claimed in some published studies [10].

5. Conclusions

In this paper melting/freezing cycles and long-term melting stability tests of D-mannitol under inert atmospheres of Ar and N₂ atmospheres have been presented. Upon cycling between 100°C and 190°C a change in the melting

interval as well as in the supercooling range of temperatures has been observed together with a color change from white to dark yellow after 50 cycles. For the long-term melting stability tests at 180°C a strong sample browning was observed in addition to a change in consistency from hard solid to soft paste and a decrease of D-mannitol mass. This means that along with sample degradation a great amount of volatile species are produced during the heating. Vis-UV spectrum analyses have been also performed to the tested samples. These analyses have shown that the absorbing species responsible for the sample browning, and probably associated with caramelization products, can be used for monitoring D-mannitol thermal degradation.

Therefore the results obtained in this work for both cycling and long-term melting tests clearly demonstrate quite fast sample degradation and hence the non-feasibility of D-mannitol as PCM even under inert atmosphere.

Acknowledgements

The authors would like to acknowledge the E. U. through the 7th Framework Program for the financial support of this work under the REELCOOP (Renewable Electricity cooperation) project with contract number: 608466, and the operation department at the PSA for their collaboration during the development of this work.

References

- [1] "Research Cooperation in Renewable Energy Technologies for Electricity (REELCOOP)" FP7 Grant agreement: 608466.
- [2] Washull J, Müller R and Römer S. Investigation of phase change materials for elevated temperatures. Effstock09, Stockholm, 2009.
- [3] Bayón R, Rojas E. Characterization of organic PCMs for medium temperature storage. EMR2015, Madrid, February 2015.
- [4] Ye P, Byron T. Characterization of D-mannitol by thermal analysis, FTIR and Raman spectroscopy. American Laboratory 40, 2008.
- [5] Burger A, Henck J, Hetz S, Rollinger J, Weissnicht AA and Stöttner H. Energy/temperature diagram and compression behavior of the polymorphs of D-mannitol. Journal of Pharmaceutical Sciences 2000;89:457-468.
- [6] Gombas A, Szabo-Revesz P, Regdon G, Eros I. Study of thermal behaviour of sugar alcohols. Journal of Thermal Analysis and Calorimetry 2003; 73:615-621.
- [7] Gallegos Lazcano MA, Yu W. Thermal performance and flammability of phase change material for medium and elevated temperatures for textile applications. Journal for Thermal Analysis and Calorimetry 2014;117:9-17.
- [8] Bayón R, Rojas E. Proving the non-viability D-mannitol as phase change material for thermal storage. Submitted to Applied Energy
- [9] Coultate T P. Sugars. Food, the chemistry of its components. 4th Ed. Royal Society of Chemistry: Cambridge UK 2002. p. 30-32
- [10] Solé A, Neumann H, Niedermaier S, Martorell I, Schossig P, Cabeza LF. Stability of sugar alcohols as PCM for thermal energy storage. Solar Energy Materials and Solar Cells, 2014;126:125-134.