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Thermal stability test of sugar alcohols as phase change materials for medium temperature energy storage application

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Abstract

Sugar alcohols are potential phase change materials candidates as they present high phase change enthalpy values, are non-toxic and low cost products. Three promising sugar-alcohols were selected: D-mannitol, myo-inositol and dulcitol under high melting enthalpy and temperature criterion. Thermal cycling tests were performed to study its cycling stability which can be determining when selecting the suitable phase change material. D-mannitol and dulcitol present poor thermal stability. Myo-inositol shows almost no decrease in thermal properties after 50 cycles for the heating process, however in the solidification part a decrease of 20 % of enthalpy and 11 % of temperature values is observed.

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1. Introduction

Thermal energy storage (TES) with phase change materials (PCM) is a very good option to increase energy efficiency of several systems. Sugar alcohols (SA) melting temperatures make them suitable for medium

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temperature applications for solar process heat or waste heat recovery [1]. High melting enthalpy (see Table 1) compared to other PCMs is another important reason for studying sugar alcohols as PCM.

SA have been studied in a lesser extent to be used as PCM when compared to paraffin and salt hydrates. D-mannitol as PCM has been characterized by Barreneche et al. [2]. The authors conclude that the material is suitable to be used as PCM regarding its thermophysical properties. Nevertheless, a recent review about thermal stability of phase change materials [3] shows no published results concerning SA, only Shukla et al. [1] show results concerning erythritol. These materials are very interesting since they are available in bulk scale, are non-toxic, present high enthalpy values and are low cost [4].

Thermal stability tests are essential when developing new PCM as they will be melted and frozen at least once a day in their final application. [5]. The main goal of this paper is to perform thermal cycling tests of D-mannitol, myo-inositol and dulcitol to study their cycling stability.

2. Materials and methodology

Three sugar alcohols were selected as phase change material candidates for medium temperature applications. The bases of the selection criterion were mainly two points: (1) high phase change enthalpy and (2) melting temperatures between 150 and 250 °C, as shown in Table 1.

Table 1. Chemical and thermophysical properties of the selected sugar-alcohols.

	D-mannitol	Galactitol/Dulcitol	Myo-inositol
Chemical formula	C ₆ H ₁₄ O ₆	C ₆ H ₁₄ O ₆	C ₆ H ₁₂ O ₆
T _m (°C)	166/176.9	188.5/187	224-227/223.9/225
ΔH _m (kJ kg ⁻¹)	279/308/294/290	358/330	266/260
References	Pitkänen et al. 1993 [6] Arias et al. 1998 [7] Barone et al. 1990 [8] Barreneche et al. 2012 [2]	Barone et al. 1990 [8]	Barone et al. 1990 [8] Raemy and Schweizer 1983 [9]

Thermal reliability tests were carried out by differential scanning calorimetry (DSC) at 10 K min⁻¹. Before and after thermally cycling the PCMs their thermophysical properties were measured by DSC at 1 K min⁻¹. Sample masses used were between 5.18 and 7.64 mg, placed in 40 μl closed aluminum crucibles, under 50 ml min⁻¹ of N₂ atmosphere. To ensure repeatability, two samples of each SA were analyzed, following the described methodology.

3. Results and discussion

3.1. Thermal cycling tests

DSC results when heating at 1 K min⁻¹ concerning D-mannitol, myo-inositol and dulcitol are shown in Table 2.

Table 2. Melting temperature and enthalpy of three sugar-alcohols, before cycling and after 20 and 50 cycles.

No. of cycles	D-mannitol		Myo-inositol		Dulcitol	
	T_m (°C)	H_m (kJ kg ⁻¹)	T_m (°C)	H_m (kJ kg ⁻¹)	T_m (°C)	H_m (kJ kg ⁻¹)
0	150.96	234.35	216.29	185.25	180.07	257.15
20	138.25	152.60	220.34	211.10	-	-
50	131.92	99.48	214.94	167.50	-	-

Melting temperature (T_m) and enthalpy (H_m) are presented before the cycling test and after 20 and 50 cycles. DSC response of dulcitol sample after cycling was not as expected, since the baseline was unstable and no solidification peak was observed.

DSC curves when thermally cycling can be observed in Fig. 1 for both, D-mannitol and myo-inositol. From D-mannitol results it can be deduced that the change in melting temperature and latent heat with increasing number of cycles is noteworthy. After 50 cycles, melting temperature decreases by 12 %, while melting enthalpy is 58 % lower than the initial value.

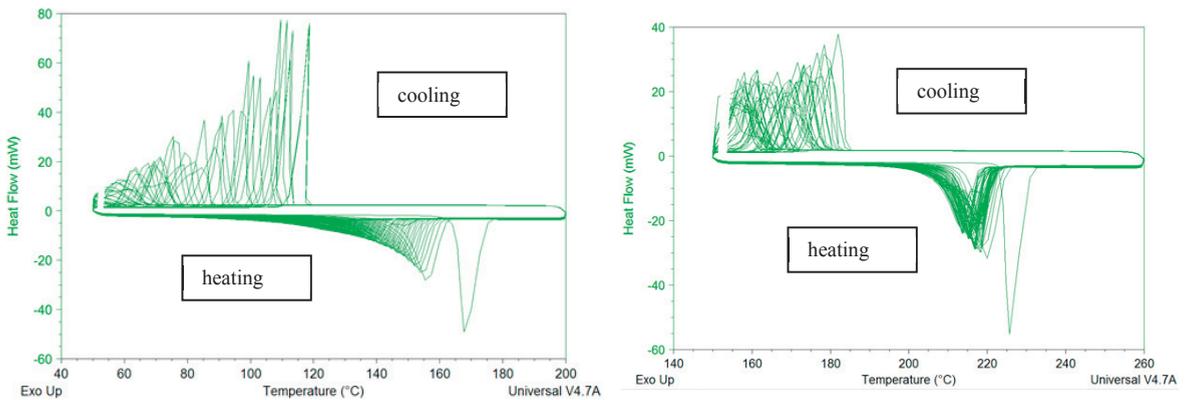


Fig.1 DSC curves from 50 thermal stability cycles, left: D-mannitol and right: myo-inositol.

Myo-inositol thermal properties during the heating process remain almost constant after having thermally cycled it 50 times. The diminution is around 10 % for the enthalpy and 1 % for the melting temperature which are within the acceptable values.

For the cooling process, solidification enthalpy and temperatures are presented in Table 3. Results concern thermophysical property values of each SA, before and after cycling them 20 and 50 times. After 50 melting/freezing cycles D-mannitol enthalpy value is half of the initial and solidification temperature has shifted from 114 to 63 °C (see Fig. 1), meaning a decrease of 45%.

Table 3. Solidification temperature and enthalpy of three sugar-alcohols, before cycling and after 20 and 50 cycles.

No. of cycles	D-mannitol		Myo-inositol		Dulcitol	
	T_s (°C)	H_s (kJ kg ⁻¹)	T_s (°C)	H_s (kJ kg ⁻¹)	T_s (°C)	H_s (kJ kg ⁻¹)
0	114.08	224.55	182.27	206.55	245.65	102.12
20	89.04	156.2	175.25	190.90	-	-
50	62.53	109.5	160.92	165.5	-	-

Moreover, myo-inositol exhibits less cycling stability when cooling as opposed to melting process. Here, a decrease of 20 % concerning solidification enthalpy and 11 % regarding solidification temperature is observed, after 50 cycles.

One important feature to highlight is the significant differences between melting and solidification temperatures for all SA presented in this paper. These differences vary from 34 to 78 °C, which is not within the acceptable values for a successful design [10]. Further research is needed in preventing this hysteresis in SA to be used as PCM.

4. Conclusions

Sugar alcohols are cost-effective PCM for solar thermal process heat. For these applications, thermal stability has to be ensured. Thermal cycling results presented here show that both D-mannitol and dulcitol present low thermal stability, under tested conditions. Myo-inositol presents better thermal stability in the heating process, however the solidification process does not show the same behavior. Further research will be based on finding reasons for low thermal stability under the tested conditions and studying the possible parameters enhancing cycling stability.

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