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Thermal Analysis of D-mannitol for Use as Phase Change Material for Latent Heat Storage

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Abstract: The aim of this study was to investigate the thermal properties of D-Mannitol as a Phase Change Material (PCM) for latent heat storage system. Heat absorbed by D-Mannitol causes it to undergo a change from the solid to the liquid phase and this heat is stored as the latent heat of fusion. The stored energy can then be retrieved at a later time for various applications. The melting point and enthalpy of the fusion of D-Mannitol are important properties and these were determined by Differential Scanning Calorimetry (DSC) measurements. Melting was found to begin at 162.15°C and attained a peak at 167.8°C while the enthalpy of fusion was found to be 326.8 J g⁻¹ for 10°C min⁻¹. Furthermore the change in melting temperature and enthalpy of fusion for different heating rates were studied experimentally by DSC. D-Mannitol's thermal stability was studied using the TG-DTG (thermogravimetry-derivative thermogravimetry) and TG-DTA (thermogravimetry-differential thermal analysis) curves. The TG-DTG curves revealed that thermal decomposition began at 300.15°C. The DTA curve had a sharp endothermic peak at 169.2°C followed by a broad exothermic one at 297°C. The curves showed that D-Mannitol decomposes in one prominent mass loss stage. The measurement of latent heat (enthalpy of fusion), melting point and decomposition point showed that D-Mannitol with a latent heat 326.8 kJ kg⁻¹ and melting temperature 167.8°C is the most suitable PCM candidate for medium temperature applications because of a large temperature difference of 132°C between its melting point and decomposition temperature.

Key words: Differential scanning calorimetry, latent heat storage, phase change material, endothermic, enthalpy of fusion, thermal stability

INTRODUCTION

Energy storage is essential primarily when the rate of energy consumption is greater than the rate of production. Additionally, energy storage is bound to be beneficial in the present time when most of the non-renewable energy sources are being rapidly depleted. For example, in India, LPG is widely used as a source of energy for cooking purposes (<http://mospi.nic.in>). Utilizing solar energy instead, would certainly help conserve LPG for other applications, where the use of alternative sources of energy is highly restricted. However, sunlight is intermittent and is not available for about 15 h out of 24. Hence, an efficient energy storage system could help store part of the solar energy captured during the day. The stored energy can be used to cook, even the absence of sunlight. Furthermore, in recent times, energy storage has attracted a lot of interest in areas, such as water heating and waste heat utilization. It is thus safe to say that the storage of energy is a useful tool for increasing energy efficiency and savings (Zalba *et al.*, 2003).

In thermal energy storage, the useful energy transferred to the storage medium in the form of latent heat and sensible heat. Among the two, latent heat storage is more attractive than sensible heat storage because of its high storage density with smaller temperature swing. In latent heat storage systems, energy that is supplied to the storage material goes into changing the state of the material. Consequently, energy storage occurs at a constant temperature unlike in sensible heat storage, where the energy supplied is stored by raising the temperature of the storage material (Sharma *et al.*, 2009). In any case, irrespective of the method of energy storage and application, it is desirable to have a storage material that has high specific heat capacity and latent heat values.

A wide range of PCMs with their properties, advantages and limitations have been comprehensively reported by Farid *et al.* (2004), Sharma and Sagara (2007), Sharma *et al.* (2009), Zalba *et al.* (2003) and Agyenim *et al.* (2010). Every latent heat thermal energy storage system requires a suitable PCM for use in a particular kind of thermal energy storage application. One of the important

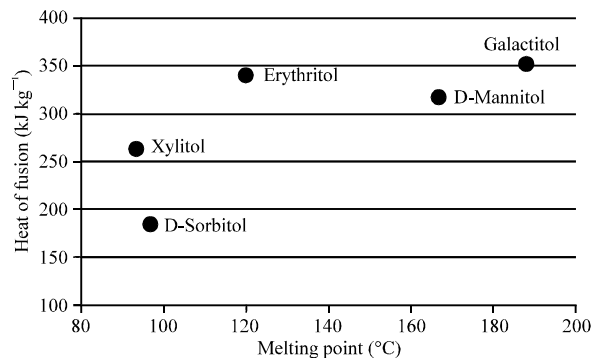


Fig. 1: Scatter diagram showing the melting points and heat of fusion for various sugar alcohols

factors to be considered when choosing an appropriate PCM is the life of the PCM, i.e., its ability to resist change in the melting temperature and latent heat of fusion with time due to thermal cycling. Shukla *et al.* (2008) performed a thermal cycling test of selected inorganic and organic PCMs. They concluded that paraffin waxes show reasonably good thermal reliability and Erythritol, a sugar alcohol, is a promising PCM for high temperature thermal energy storage, as its latent heat began to show only gradual degradation after 500 thermal cycles. There are a number of sugar alcohols available commercially. Choosing one that is appropriate for effective heat storage is imperative. Though the sugar alcohols have good thermal reliability (Kaizawa *et al.*, 2008), other thermophysical properties need to be considered for effective heat storage systems. Two such parameters are the melting temperature and latent heat of fusion. Figure 1 below shows a scatter diagram depicting the melting temperatures and heat of fusion of five sugar alcohols (Kakiuchi *et al.*, 1998).

From Fig. 1, it can be seen that the sugar alcohols have high latent heat storage capacity and melting temperature and therefore, they are promising PCMs for practical Latent Heat Thermal Energy Storage (LHTES) applications performed at 90-190°C. It can be clearly noted from the Figure that, D-Mannitol has a slightly lower value of latent heat of fusion than Erythritol; however, it has a higher melting point than Erythritol. Several works have been attempted by using Erythritol as a PCM for LHTES applications, due to its high latent heat of fusion, its non-toxic nature and its easy availability (Kakiuchi *et al.*, 1998; Kaizawa *et al.*, 2008). According to Kaizawa *et al.* (2008), Erythritol, Xylitol and D-Mannitol appears to be a reliable PCM for high temperature applications, due to large latent heat and good operational safety.

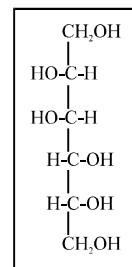


Fig. 2: Axis symmetric chemical structure of D-Mannitol

D-Mannitol is a natural polyol having a low molecular weight of 182.17. It is most commonly used in pharmaceutical and food industries due to its characteristic sweet taste and comparatively low energy content. Consequently it makes a suitable substitute for sugar in the food industry and provides sweetness to drugs (Bama *et al.*, 2010). The potential use of D-Mannitol as a phase change material is supported by its thermal properties. Its ability to retain heat effectively in its liquid state affirms its capability for use as a PCM. Furthermore, D-Mannitol's relatively high density of 1.52 g cm⁻³ allows a large quantity of D-Mannitol to be packed into a small volume. This, coupled with its high specific heat of fusion allows for large amounts of energy to be absorbed for storage (Kaizawa *et al.*, 2008). As regards the cost, D-Mannitol is quite cheap, selling at 1000 Indian Rupees (US \$ 25) per kg (www.srlchem.com). The axis symmetric chemical structure of D-Mannitol is shown in Fig. 2.

The objective of this paper is to study the feasibility of D-Mannitol as a PCM candidate from three thermophysical property view points, namely, enthalpy of fusion, melting temperature and decomposition temperature.

MATERIALS AND EXPERIMENTATION

D-Mannitol Extrapure AR [CAS No. 69-65-8] having a labelled purity of 99% mass fraction, was purchased from Sisco Research Laboratories Pvt. Ltd. Mumbai, India and used without further purification. The D-Mannitol was handled in a dry N₂ atmosphere, to prevent contamination by moisture. All the experiments were carried out at the Sophisticated Analytical Instrumentation Facility, Indian Institute of Technology Madras, Chennai, India.

The melting temperature and enthalpy of fusion were determined by the DSC. The differential scanning calorimeter used, was the Netzsch DSC 204 manufactured by Netzsch, Germany.

The quantity of 11.97 mg of D-Mannitol was tested in an open aluminium crucible. The temperature range employed during the experiment was from 25.15 to 250.15°C. The heating rate was kept constant at 10°C min⁻¹. The experiment was repeated for different heat input rate.

The thermal stability-decomposition temperature and percentage of mass change of D-Mannitol were studied using the TG-DTA. The instrument used was the Netzsch STA 409 C/CD manufactured by Netzsch, Germany. 12.39 mg of D-Mannitol was tested in an alumina crucible in N₂ atmosphere. The temperature range used during the experiment was from 25.15 to 1200.15°C. The heating rate was maintained at 10°C min⁻¹ for the DSC and TG/DTG/DTA studies. The DSC experiment was repeated five times for each heating rate and the data obtained was averaged.

RESULTS AND DISCUSSION

The DSC curve of D-Mannitol obtained after conducting the experiment is shown in Fig. 3.

From Fig. 3a, it can be seen that a sharply endothermic peak, corresponding to the melting process has an onset point of 162.15°C. The curve then peaks at a temperature of 167.8°C (Gombas *et al.*, 2003; Ye and Byron, 2008; Telang *et al.*, 2003). The area under the peak denotes the enthalpy of fusion of D-Mannitol. The value obtained for the enthalpy of fusion is

326.8 J g⁻¹ (Kaizawa *et al.*, 2008). The change in melting temperature and enthalpy of fusion was observed for different low heating rates of 0.5, 1.0 and 2.0°C min⁻¹. The marginal change in melting point temperature and enthalpy of fusion in DSC curves was observed in Fig. 3b-d due to heating rate variation.

The TG-DTG curve is shown in Fig. 4 and it can be seen that the mass loss of the sample is completed in one stage. The D-Mannitol remains stable below 300.15°C (Kaizawa *et al.*, 2008). The result showed that D-Mannitol can store thermal energy without any mass loss when 300.15°C is the maximum operating temperature. Beyond this temperature, the D-Mannitol begins to lose mass. The rate of mass loss reaches a maximum at about 365°C and almost all its mass is lost at about 397°C.

The simultaneously recorded TG and DTA curve is shown in Fig. 5. On the TG curve a single weight loss step is marked at 300.15°C. The DTA curve in Fig. 6 shows the three endothermic and two exothermic heat effects during decomposition in an inert atmosphere (nitrogen). The first endothermic effect of the main degradation of the sample was observed, as expected, at 169.2°C and followed by an exothermic effect at 332.4°C. Consequently the peak which corresponds to a temperature of 169.2 and 332.4°C, indicates the melting temperature and highest available temperature of D-Mannitol in the given experimental conditions (Bruni *et al.*, 2009). This is seen to be consistent with the interpretation of the TG-DTG curve done earlier. The subsequent exothermic peak at 378.7°C

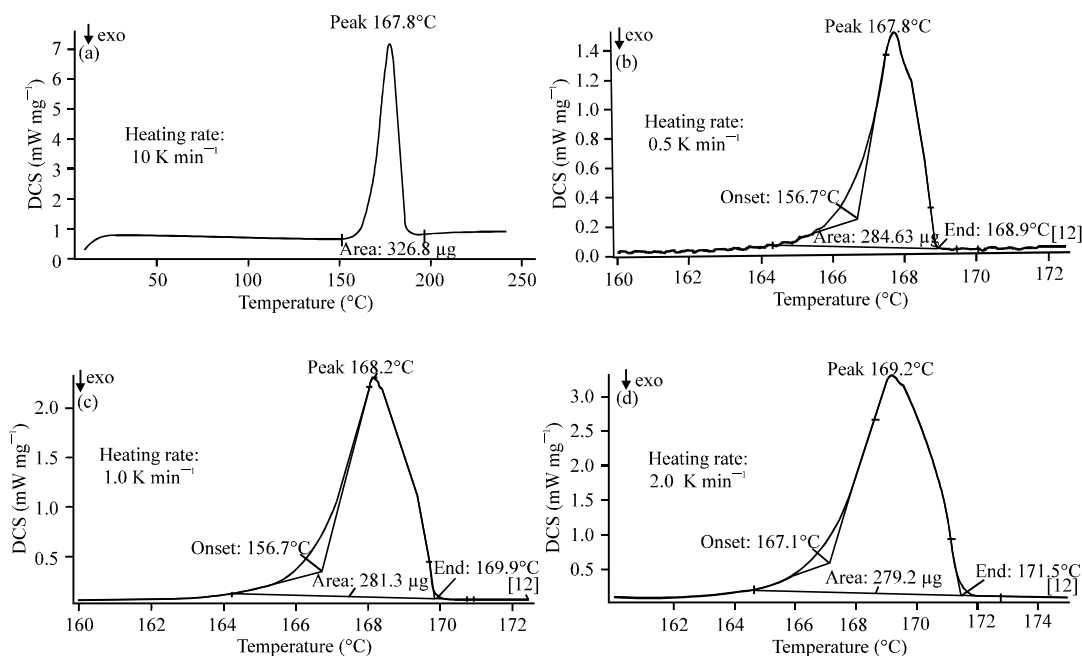


Fig. 3: DSC curves of D-Mannitol

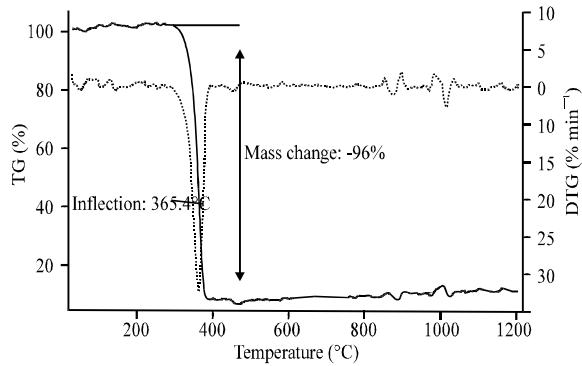


Fig. 4: TG-DTG curve of D-Mannitol

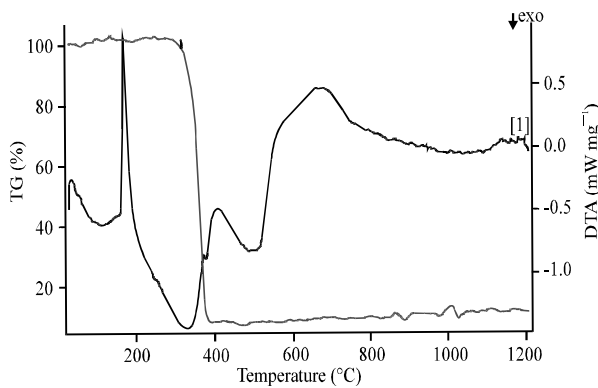


Fig. 5: TG-DTA curve of D-Mannitol

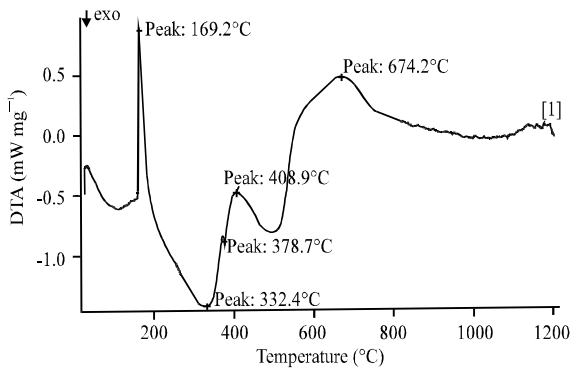


Fig. 6: DTA curve of D-Mannitol with peak points indicated

and explicit endothermic peaks at 408.9 and 674.2°C observed in DTA curve may correspond to loss of the different volatile products created during thermal degradation of the D-Mannitol (Dufaure *et al.*, 1999).

CONCLUSION

The selection phase change material for any latent heat thermal storage system requires good

thermophysical properties. The possibility of D-Mannitol as phase change material was examined by using DSC and TG-DTG/DTA analysis. The analysis proves that high melting temperature, decomposition temperature and latent heat of fusion of D-Mannitol make it an excellent phase change material for latent heat storage in medium temperature applications where temperature requirement is about 160-170°C and can be applied in solar thermal, industrial process heat and waste heat recovery systems. Further work, the changes in thermophysical properties of D-Mannitol before and after the number of thermal cycles is needed to study the nature of change in their thermal reliability and how to prevent it from occurring.

REFERENCES

- Agyenim, F., N. Hewitt, P. Eames and M. Smyth, 2010. A review of materials, heat transfer and phase change problem formulation for latent heat thermal energy storage systems (LHTESS). *Renewable Sustainable Energy Rev.*, 14: 615-628.
- Bama, G.K., R. Anitha and K. Ramachandran, 2010. On the thermal properties of aqueous solution of D-mannitol. *Nondestr. Test. Eval.*, 25: 67-75.
- Bruni, G., V. Berbenni, C. Milanese, A. Girella, P. Cofrancesco, G. Bellazzi and A. Marini, 2009. Physico-chemical characterization of anhydrous D-mannitol. *J. Thermal Anal. Calorimetry*, 95: 871-876.
- Dufaure, C., U. Thamrin and Z. Mouloungui, 1999. Comparison of the thermal behaviour of some fatty esters and related ethers by TGA-DTA analysis. *Thermochim. Acta*, 338: 77-83.
- Farid, M.M., A.M. Khudhair, S.A.K. Razack and S. Al-Hallaj, 2004. A review on phase change energy storage: Materials and applications. *Energy Conservation Manage.*, 23: 1597-1615.
- Gombas, A., P. Szabo-Revesz, G. Regdon and I. Eros, 2003. Study of thermal behaviour of sugar alcohols. *J. Thermal Anal. Calorimetry*, 73: 615-621.
- Kaizawa, A., N. Maruoka, A. Kawai, H. Kamano, T. Jozuka, T. Senda and T. Akiyama, 2008. Thermophysical and heat transfer properties of phase change material candidate for waste heat transportation system. *Heat Mass Transfer*, 44: 763-769.
- Kakiuchi, H., M. Yamazaki, M. Yabe, S. Chihara, Y. Terunuma, Y. Sakata and T. Usami, 1998. A study of erythritol as phase change material. IEA Annex 10-PCMs and Chemical Reactions for Thermal Energy Storage, 2nd Workshop, November 11-13, Sofia, Bulgaria.

- Sharma, A., C.R. Chen, V.V.S. Murty and A. Shukla, 2009. Solar cooker with latent heat storage systems: A review. *Renewable Sustainable Energy Rev.*, 13: 1599-1605.
- Sharma, S.D. and K. Sagara, 2007. Latent heat storage materials and systems: A review. *Int. J. Green Energy*, 2: 1-56.
- Shukla, A., D. Buddhi and R.L. Sawhney, 2008. Thermal cycling test of few selected inorganic and organic phase change materials. *Renewable Energy*, 33: 2606-2614.
- Telang, C., R. Suryanarayanan and L. Yu, 2003. Crystallization of D-mannitol in binary mixtures with NaCl: Phase diagram and polymorphism. *Pharma. Res.*, 20: 1939-1945.
- Ye, P. and T. Byron, 2008. Characterization of D-mannitol by thermal analysis, FTIR and Raman spectroscopy. *Am. Lab.*, 40: 24-27.
- Zalba, B., J.M. Marin, L.F. Cabeza and H. Mehling, 2003. Review on thermal energy storage with phase change: Materials, heat transfer analysis and applications. *Applied Thermal Eng.*, 23: 251-283.