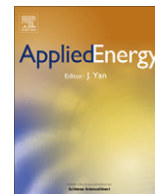


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Intercomparative tests on phase change materials characterisation with differential scanning calorimeter

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HIGHLIGHTS

- ▶ Advances in intercomparative tests of enthalpy of phase change material (PCM).
- ▶ Enthalpy of PCM determined by DSC is influenced by certain factors.
- ▶ The influence factors were identified.
- ▶ A methodology to avoid these influences for heating measurements is proposed.
- ▶ Forthcoming steps are focused on calibration and cooling measurements.

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ABSTRACT

For the correct design of thermal storage systems using phase change materials (PCMs) in any application, as well as for their simulation, it is essential to characterise the materials from thermophysical and rheological standpoints (phase change enthalpy, thermal conductivity in solid and liquid phases, viscosity and density in function of temperature). Taking advantage of the different research groups facilities available in two international networks: within the IEA (International Energy Agency), the ECES Implementing Agreement (Energy Conservation through Energy Storage IA) and SHC Programme (Solar Heating and Cooling) Task 42/Annex 24 “Compact Thermal Energy Storage – Material Development for System Integration”, and the COST Action TU0802 “Next generation cost effective phase change materials for increased energy efficiency in renewable energy systems in buildings (NeCoE-PCM)” a set of Round Robin Tests (RRTs) was proposed. The objective was to come to comparable results for PCMs using Differential Scanning Calorimetry (DSC) to determine their melting enthalpy as well as their melting and solidification behaviour. The first RRT was without defining the procedure, the second one with a predefined procedure for the measurements, but not for calibration and the third one with a predefined procedure for calibration, for the measurements and also for the data evaluation. This paper presents the conclusions after the three RRT. The main conclusion of the paper is that enthalpy in function of temperature determined using a dynamic method for DSC can be influenced by certain reasons and finally a methodology to avoid these influences have been proposed.

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1. Introduction

Phase change materials (PCMs) are widely proposed as thermal storage materials. Arce et al. [1] showed that thermal energy storage meant energy savings in the buildings and industrial sectors, the possible reduction of waste thermal energy on a national and continental scale, respectively, as well as the associated CO₂ emissions cut-down. Moreover, recent reviews [2–6] show that thermal energy storage using PCM can contribute enormously in the development of new thermal systems to decrease energy consumption, increase energy efficiency and decrease CO₂ emissions.

Using PCM means using the melting and solidification enthalpy to store or to release heat. For the correct design of thermal storage systems using these PCM as well as for their simulation, it is essential to characterise the materials from thermophysical and rheological standpoints (phase change enthalpy, thermal conductivity in solid and liquid phases, viscosity and density in function of temperature). Lately, many researchers are either developing new phase change materials [7–13] or characterising existing ones to be used as PCM [14–16]. For these materials to be commercialised as such, reproducibility of the results is essential, but still many differences are shown between literature values [2,6].

The importance of the knowledge on thermophysical properties as a function of temperature of the material increases as the reachable storage capacity and the benefit compared to sensible heat storage materials is very closely connected to it. It is known that if there is an error in the determination of temperature and the enthalpy curve in function of temperature, the error in estimation of the storage capacity is significant. As an example, Dolado et al. [17] show that improving the determination of the melting temperature range from ± 1 °C to an uncertainty of ± 0.25 °C, entails 25% enhancement in the uncertainty of the PCM to air heat exchange rate determination.

From an experimental point of view, phase change materials present phenomena that hinder the determination of properties (subcooling, hysteresis, crystallisation problems due to sample size, wide melting range, etc.). This can be due to the fact that the phase change materials employed are not usually pure substances. Furthermore, differences in results can be found between different techniques or even between different test conditions using the same technique (different cooling or heating rate, for example). These differences are reported in literature. For example, He et al. [18] concluded that the lack of phase equilibrium within the sample including thermal equilibrium and chemical equilibrium in a DSC with a high heating rate is the reason why DSC (using an inadequate heating rate) fails to provide correct information. Castellón et al. [19] studied the different methods for heat-flux DSC analysis to investigate their accuracy in the determination of enthalpy in function of PCM temperature. Günther et al. [20] concluded that a DSC, using the isothermal step mode, offers sufficient precision for typical PCM applications when a temperature uncertainty $\delta T < 1$ K in the determination of enthalpy in function of temperature is required. All these experimental issues encountered make the interpretation of the results very difficult.

Both Castellón et al. [19] and Günther et al. [20] showed that measurements of PCM using DSC needed a slow heating and cooling rate, usually lower than 1 K min^{-1} , which does not compile with the typical standards used in DSC analysis of polymers or other substances [21].

Taking advantage of the different research groups facilities available in two international networks: within the IEA (International Energy Agency), the ECES Implementing Agreement (Energy Conservation through Energy Storage IA) and SHC Programme (Solar Heating and Cooling) Task 42/Annex 24 “Compact Thermal Energy Storage – Material Development for System Integration” [22],

and the COST Action TU0802 “Next generation cost effective phase change materials for increased energy efficiency in renewable energy systems in buildings (NeCoE-PCM)” [23] a set of Round Robin Tests was proposed. The objective was to come to comparable results for PCMs using DSC to determine their melting enthalpy as well as their melting and solidification behaviour and, therefore, to establish the reproducibility of this analysis. This paper presents the conclusions after the three Round Robin Tests (RRTs) carried out so far. The first RRT was without defining the procedure, the second one with a predefined procedure for the measurements, but not for calibration and the third one with a predefined procedure for calibration, for the measurements and also for the data evaluation.

2. Materials and methods

2.1. Materials

Octadecane (98.11 wt%) was chosen as reference PCM, which is a synthetic octadecane produced by Sasol Wax using the Fischer-Tropsch process. The chemical data are presented in Table 1.

The thermal properties for pure octadecane are given in different references which are collected by the National Institute of Standards (NIST) [24]. Table 2 shows the values used in this paper as reference. Fig. 1 shows the enthalpy of octadecane in function of temperature built with the reference values.

Table 1
Composition of the reference octadecane used as testing material.

Name	Parafol 18–97
C16	0.07 wt%
C18	98.11 wt%
iC18	0.4 wt%
C20	0 wt%
Bromine	0.01 mg/100 mg

Table 2
Reference values of the thermal properties of pure octadecane.

Property	Value	Value (SI)	References
Constant pressure heat capacity of solid	485.64 J mol ⁻¹ K ⁻¹	1.91 J/(g K)	[25]
Constant pressure heat capacity of liquid	568.325 J mol ⁻¹ K ⁻¹	2.23 J/(g K)	[26]
Enthalpy of fusion	61,500 J mol ⁻¹	241.65 J/g	[27]
Temperature of fusion	301.3 K	28.15 °C	[27]

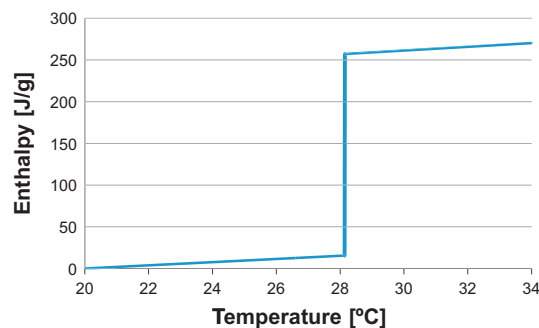


Fig. 1. Enthalpy vs. temperature curve of octadecane built from the reference values (NIST values).

2.2. Methods

A set of Round Robin Tests (RRTs) was proposed. Using DSC, different institutions measured the same reference material. The first RRT was without defining the procedure, so each participant measured the reference material as they used to do so. The second one was set out with a predefined procedure for the measurements, but not for calibration. Finally, the third one was with a predefined procedure for calibration, for the measurements and also for the data evaluation. All the data evaluation was carried out following Mehling and Cabeza [28].

A comparison of sensitivity data calculated from enthalpy calibration and from heat capacity calibration of one DSC is shown in Mehling and Cabeza, [28] for five different standard materials, here regarding water and indium for the third RRT. Furthermore, the accuracy of DSC measurements of standard materials is discussed in detail by Richardson [29] and Rudtsch [30].

The third Round Robin Test (RRT) took place during a workshop on DSC organised by Fraunhofer ISE, Freiburg (Germany) from 23th to 27th May 2011. The objective was to come to comparable results for PCM using DSC to determine their melting enthalpy as well as their melting and solidification behaviour. Four different

commercial DSC were used to measure octadecane as phase change material, all of them belonging to the heat flux type and measurements were performed following a dynamic operation mode [31], detailed in the results section. Table 3 shows the models and trademarks of the equipment used.

3. Results and discussion

Different techniques applied in different institutes were used to measure the enthalpy in function of temperature in the first Round Robin Test (RRT). These first measurements were obtained without using a defined measurement procedure, so each participant used its own procedure. Fig. 2 shows the first results of the RRT.

These first results on comparative specific heat as a function of temperature determination in the Round Robin Test showed that reproducibility is not achieved. These results give a good impression how comparable are values which are published by different labs today and it underlines the importance of having a common standard for the characterisation of PCM.

Behind the disagreements in the results, a list of factors of influence can be deduced, such as, measurement procedure, DSC itself, DSC calibration, sample preparation and sample crucibles, and data evaluation.

In order to evaluate the influence of the procedure, a second Round Robin Test was conducted according to a common procedure. This procedure was according the one proposed by a Quality Association PCM founded in 2004 by several internationally active enterprises. The objective was to develop proper quality assurance procedures [32]. This procedure, called RAL procedure, ensures that the measurement is not dependent on heating and cooling rate and on the sample mass because the procedure guarantees the thermal equilibrium in the sample and the sample holder.

Results of the second RRT are presented in Fig. 3. Enthalpy curves when heating and cooling are shown for each instrument. For the heating process, Fig. 3a, enthalpy values are reproducible with the exception of Mettler-Toledo and TA instruments which present a deviation of ± 25 kJ/kg from the theoretical value. Moreover, the melting temperature of octadecane differ in 2 °C within the performed experiments and is stressed for the offset (phase change totally completed), which reflects higher deviation from the theoretical value, being the lower value 26.8 °C and the higher, 29.4 °C. The onset temperatures of all curves are reproducible. In Fig. 3b, cooling curves present the same enthalpy uncertainty as the heating process, when compared to theoretical value. Also, the onset temperatures are in agreement, notwithstanding that subcooling is clearly reflected so all curves present a lower solidification temperature than the expected, being the major difference

Table 3
DSC devices used.

Trademark	Model
TA Instruments	DSC Q200
Perkin Elmer	Jade DSC
Mettler Toledo	DSC 1 Starte System
Netzsch	DSC 204 F1 Phoenix

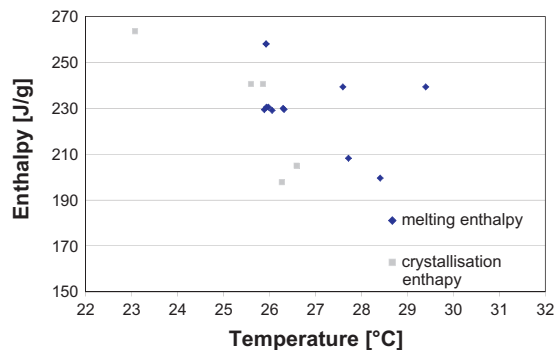


Fig. 2. State of the art in DSC-measurement. Comparison of results from different laboratories.

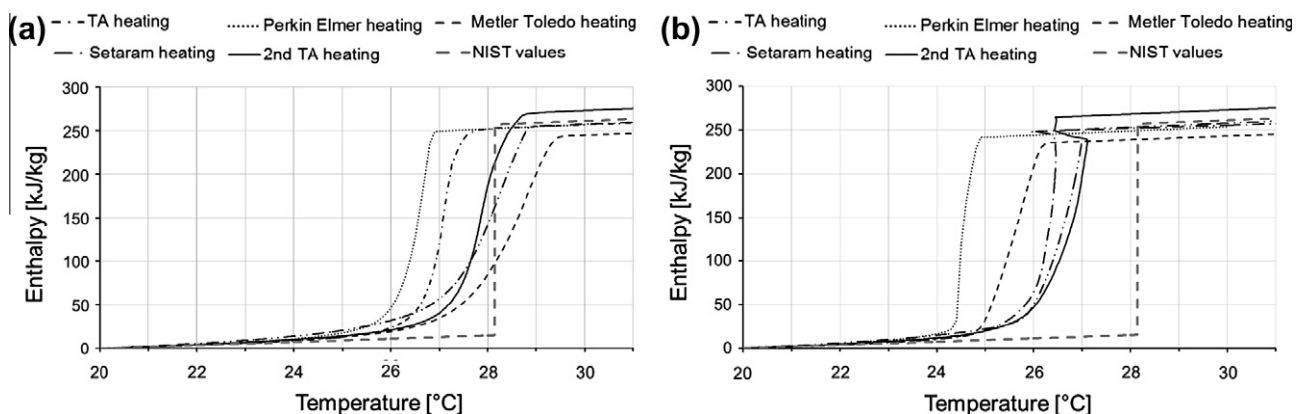


Fig. 3. Comparison of the 2nd RRT results obtained for (a) heating, and (b) cooling.

3.6 °C. Enthalpy values obtained in the second RRT are reproducible, but phase change temperatures reflect still high uncertainty, above all in cooling curves.

As the resulting temperatures are much related to the DSC and the whole procedure from the calibration of the device to the preparation of samples and its measurement, it was decided to organise a workshop on DSC measurement to have the chance to learn more about the differences of DSC and to establish a common basis for the measurement procedure within the institutes participating in the Round Robin Tests.

The final procedure measurements in the DSC workshop (third RRT) consist of:

- Measurement according to RAL procedure using the reference PCM. Here it was observed that all DSC, using a sample mass close to 5 mg of octadecane, have to go below 0.5 K min^{-1} to avoid the heating rate influence in the results. Mehling and Cabeza [28] showed that when measuring PCMs with any DSC, the heating and cooling ramps should be very small to ensure thermal equilibrium within the sample, recommending a maximum of 0.5 K min^{-1} . Furthermore, Günther et al. [20] proved that results differ considerably with different heating rates and sample mass, recommending a slow heating rate in.

- Temperature and enthalpy calibration measurements using water and indium.
- Baseline (a measurement using two empty crucibles) from 10 °C to 40 °C at 0.2 K min^{-1} with calibration files with water and indium. Two 5 min isothermal at 10 °C and at 40 °C were carried out before and after the dynamic measurement. In this case the reference crucible was closed and the empty sample crucible was open (with lid but not sealed).
- Measurement of octadecane from 10 °C to 40 °C at 0.2 K min^{-1} with calibration files with water and indium, using closed crucibles. Two 5 min isothermal at 10 °C and at 40 °C were carried out before and after the dynamic measurement. Sample mass: 5 mg. The same crucible used in baseline-measurement was used.

As it can be seen in Fig. 4, the Netzsch and Mettler Toledo devices show unstable baselines. For the Netzsch DSC the measurement was repeated at the University of Zaragoza (where a similar device is available), where much more stable baseline was obtained (Fig. 5). For the Mettler Toledo DSC, the measurement was repeated at the University of Basque Country (Fig. 5). In this case, the baseline was measured using two closed crucibles. Fig. 6 compares the heating curves of these measurements.

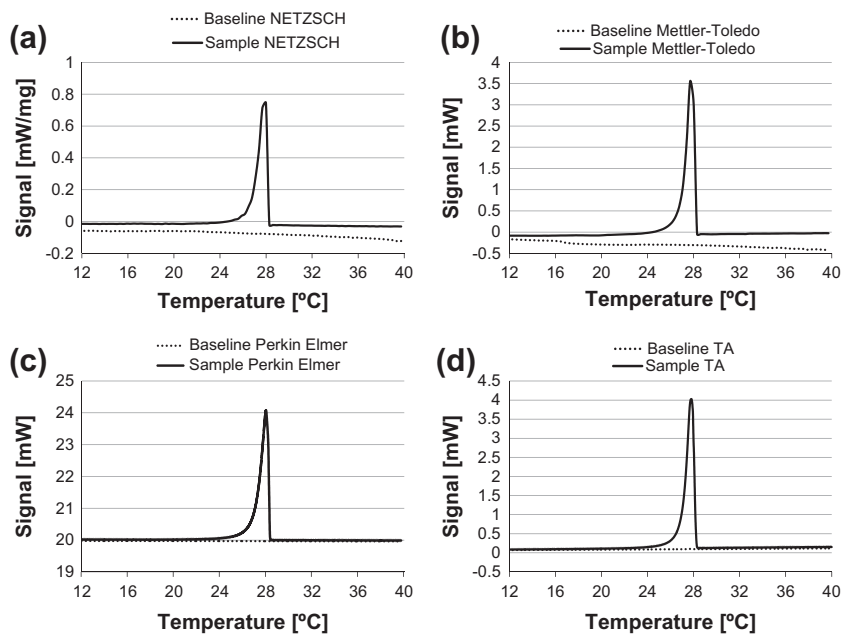


Fig. 4. Results of the PCM measurements after calibration with ice. (a) Netzsch (b) Mettler Toledo, (c) Perkin & Elmer, and (d) TA-Instruments.

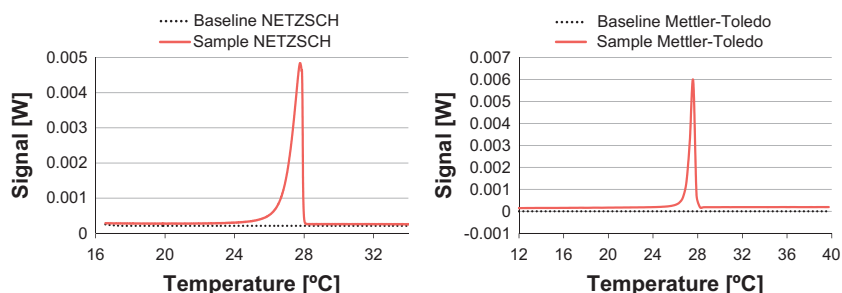


Fig. 5. Measurement for the Netzsch device which was repeated at the University of Zaragoza (left) and for the Mettler Toledo which was repeated at the University of Basque Country (right).

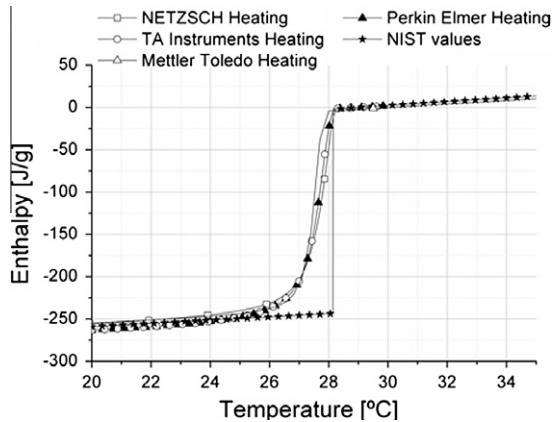


Fig. 6. Comparison of the DSC enthalpy as a function of temperature results for heating.

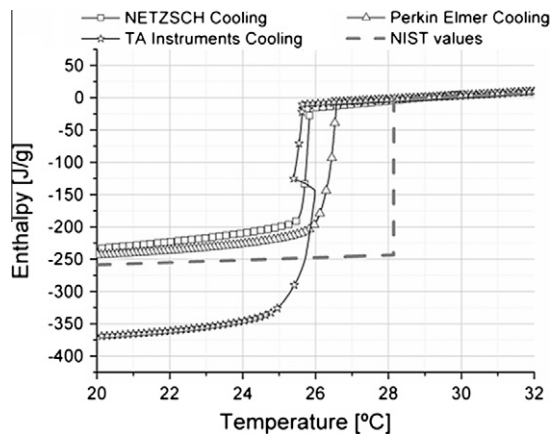


Fig. 7. Comparison of the result enthalpy as a function of temperature obtained for cooling.

The results of the measurements for heating accomplished according to the described procedure show good agreement in enthalpy and in temperature. Reproducibility is ensured regarding the third RRT procedure.

The same temperature program was set out for the cooling measurements. The results obtained from the cooling measurements (Fig. 7) show more problems related to the agreement, the specific heat values and the total enthalpy change than the results from heating measurements. As it can be seen, results obtained for the cooling measurements are not comparable with those obtained for heating.

Several additional conclusions were obtained during the workshop:

- Only calibration with Indium. No calibration in the temperature range 0–100 °C (the solution adopted in the workshop was calibration using ice).
- Unstable baselines make it difficult to determine enthalpy versus temperature.
- The crucible used for the baseline should be the same as the one used afterwards for the sample. Crucibles that lose material in their sealing process cause wrong results.

One of the main drawbacks of using a DSC for testing enthalpy in function of temperature of phase change materials is that accuracy is needed for low signal (only sensible heat, when the sample is

completely melted or solidified) and for high signals (sensible and latent heat, during the phase change). Therefore, the Institutes are involved in the fourth RRT according to the same procedure as in the workshop on DSC, but using calibration substances similar to PCM in temperature and in enthalpy. The results will be useful to evaluate the influence of the calibration substances in the agreement of the results.

4. Conclusions

The first comparison of results obtained for the Round Robin test show high deviation in enthalpy and in temperature. The causes encountered were the measurement procedure, the DSC itself, the DSC calibration, the sample preparation and sample crucibles used, and the data evaluation.

The first one was evaluated using the same procedure (the RAL procedure) by all institutes. The results show lower deviation in enthalpy, but high deviation in temperature.

The influence of the DSC itself, the sample preparation, the sample crucibles and data evaluation was studied within the framework of a DSC workshop. Results show then good agreement for enthalpy and temperature in heating, but high deviation for the cooling measurements.

As a conclusion of the results presented in this paper, the final procedure with good agreement in the results was:

- Determining what is the necessary heating rate to reach changes in peak temperatures of less than 0.5 K measuring the reference PCM. Therefore, the assumption of thermal equilibrium in the sample and the crucible during the measurement can be tolerable.
- Perform a calibration with the determined heating rate using ice (333.5 kJ kg^{-1} , 0 °C) and indium.
- Do a baseline measurement with the determined heating rate.
- Measure the reference PCM again (same heating rate than before).
- Subtract the baseline.
- Compare all results.

It must be ensured that the baseline is stable (no drift). An unstable baseline makes it impossible to determine the enthalpy versus temperature.

For future advances the work is focused on the improvement of the cooling results. In these measurements two points are to be considered:

- Comparison of the measurements with different cooling modes: intracooler, N_2 liq., etc.
- Specific calibration for cooling.

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References

- [1] Arce P, Medrano M, Gil A, Oró E, Cabeza LF. Overview of thermal energy storage (TES) potential energy savings and climate change mitigation in Spain and Europe. *Appl Energy* 2011;88(8):2764–74.
- [2] Zalba B, Marín JM, Cabeza LF, Mehling H. Review on thermal energy storage with phase change: materials, heat transfer analysis and applications. *Appl Therm Eng* 2003;23(3):251–83.
- [3] Cabeza LF, Castell A, Barreneche C, de Gracia A, Fernández AI. Materials used as PCM for thermal energy storage in buildings. *Renew Sust Energ Rev* 2011;15(3):1675–95.
- [4] Gil A, Medrano M, Martorell I, Lázaro A, Dolado P, Zalba B, et al. State of the art on high temperature thermal energy storage for power generation. Part 1-Concepts, materials and modelling. *Renew Sust Energ Rev* 2010;14(1):31–55.
- [5] Medrano M, Gil A, Martorell I, Potau X, Cabeza LF. State of the art on high-temperature thermal energy storage for power generation. Part 2-Case studies. *Renew Sust Energ Rev* 2010;14(1):56–72.
- [6] Oró E, de Gracia A, Castell A, Farid MM, Cabeza LF. Review on phase change materials (PCMs) for cold thermal energy storage applications. *Appl Energy* 2012;99:513–33.
- [7] Chen Z-H, Yu F, Zeng X-R, Zhang Z-G. Preparation, characterization and thermal properties of nanocapsules containing phase change material *n*-dodecanol by miniemulsion polymerization with polymerizable emulsifier. *Appl Energy* 2012;91(1):7–12.
- [8] Cai Y, Ke H, Dong J, Wei Q, Lin J, Zhao Y, et al. Effects of nano-SiO₂ on morphology, thermal energy storage, thermal stability, and combustion properties of electrospun lauric acid/PET ultrafine composite fibers as form-stable phase change materials. *Appl Energy* 2011;88(6):2106–12.
- [9] Wang L, Meng D. Fatty acid eutectic/polymethyl methacrylate composite as form-stable phase change material for thermal energy storage. *Appl Energy* 2010;87(8):2660–5.
- [10] Darkwa J, Su O, Zhou T. Development of non-deform micro-encapsulated phase change energy storage tablets. *Appl Energy* 2012;98:441–7.
- [11] Sari A, Alkan C, Karaipekli A. Preparation, characterization and thermal properties of PMMA/*n*-heptadecane microcapsules as novel solid–liquid microPCM for thermal energy storage. *Appl Energy* 2010;87(5):1529–34.
- [12] Cai Y, Wei Q, Huang F, Gao W. Preparation and properties studies of halogen-free flame retardant form-stable phase change materials based on paraffin/high density polyethylene composites. *Appl Energy* 2008;85(8):765–75.
- [13] Li M, Wu Z, Tan J. Properties of form-stable paraffin/silicon dioxide/expanded graphite phase change composites prepared by sol–gel method. *Appl Energy* 2012;92:456–61.
- [14] Li M, Wu Z, Kao H. Study on preparation, structure and thermal energy storage property of capric–palmitic acid/attapulgit composite phase change materials. *Appl Energy* 2011;88(9):3125–32.
- [15] Zhang Z, Zhang N, Peng J, Fang X, Gao X, Fang Y. Preparation and thermal energy storage properties of paraffin/expanded graphite composite phase change material. *Appl Energy* 2012;9(1):426–31.
- [16] Diaconu BM, Varga S, Oliveira AC. Experimental assessment of heat storage properties and heat transfer characteristics of a phase change material slurry for air conditioning applications. *Appl Energy* 2010;87(2):620–8.
- [17] Dolado P, Mazo J, Lázaro A, Marín JM, Zalba B. Experimental validation of theoretical model: uncertainty propagation analysis to a PCM–air thermal energy storage unit. *Energy Build* 2012;45:124–31.
- [18] He B, Martin V, Setterwall F. Phase transition temperature ranges and storage density of paraffin wax phase change materials. *Energy* 2004;29:1785–804.
- [19] Castellón C, Günther E, Mehling H, Hiebler S, Cabeza LF. Determination of the enthalpy of PCM as a function of temperature using a heat-flux DSC-A study of different measurement procedures and their accuracy. *Int J Energy Res* 2008;32(13):1258–65.
- [20] Günther E, Hiebler S, Mehling H, Redlich R. Enthalpy of phase change materials as a function of temperature: required accuracy and suitable measurement methods. *Int J Thermophys* 2009;30:1257–69.
- [21] ASTM Standard E793, 2006: Standard test method for enthalpies of fusion and crystallization by Differential Scanning Calorimetry. doi: 10.1520/E0793-06, PA; 2006.
- [22] <http://www.iea-shc.org/task42/> (5.08.12).
- [23] <http://www.tu0802.eu/>, (29.10.12).
- [24] <http://webbook.nist.gov/cgi/cbook.cgi?Name=n-octadecane&Units=SI>, (25.10.12).
- [25] Messerly JF, Guthrie GB, Todd SS, Finke HL. Low-temperature thermal data for *n*-pentane, *n*-heptadecane, and *n*-octadecane. Revised thermodynamic functions for their *n*-Alkanes, C₅–C₁₈. *J Chem Eng Data* 1967;12:338–46.
- [26] Höhne GWH. Transitions of *n*-alkanes above the melting point. *Polym Bull* 1981;6:41–6.
- [27] Domalski ES, Hearing ED. Heat Capacities and Entropies of organic compounds in the condensed phase. *J Phys Chem Ref Data* 1996;III(1):1–525.
- [28] Mehling H, Cabeza LF. Heat and cold storage with PCM. Berlin: Springer; 2008.
- [29] Richardson M. Quantitative aspects of Differential Scanning Calorimetry. *Thermochim Acta* 1997;300:15–28.
- [30] Rudtsch S. Uncertainty of heat capacity measurements with differential scanning calorimeters. *Thermochim Acta* 2002;382:17–25.
- [31] Höhne GWH, Hemminger WF, Flammersheim H-J. Differential Scanning Calorimetry. 2nd ed. Berlin: Springer; 2003.
- [32] <http://www.pcm-ral.de/> (19.10.12).