New database to select Phase Change Materials: chemical nature, properties, and applications

Camila Barreneche[1,2], M. Elena Navarro[1], Luisa F. Cabeza[2], A. Inés Fernández[1]

[1]Departament de Ciència dels Materials i Enginyeria Metal·lúrgica, Universitat de Barcelona, C/Martí i Franquès, 1-11, 08028, Spain, Phone: +34-934021316, Fax: +34-934035438, ana_inesfernandez@ub.edu

[2] GREA Innovació Concurrent, Edifici CREA, University of Lleida, Lleida, Spain, Phone: +34-973003576, Fax: +34-973003575, e-mail: lcabeza@diei.udl.cat*

Abstract

Today, thermal energy storage materials are proposed as a promising solution to increase the energy efficiency in building sector and to reduce the total energy demand because building sector accounts up to 34% of total energy consumption. Under this situation, phase change materials (PCM) are well-considered as materials to store energy allowing high energy densities (between 50-600 MJ/cm^3). Available materials to be used as PCM for building application in literature were added to a database for to be used with CES Selector software. More than three hundred PCM whit phase change temperatures between -50 ºC and 150 ºC and considering commercial and non-commercial PCM were listed and classified by their properties and the values available of the materials have been introduced in this database. The main objective of this study is to generate a PCM database and draw on it in order to facilitate the selection of the most suitable PCM depending on the building application.

Keywords: Phase Change Materials (PCM), Thermal Energy Storage (TES), Material Selection, Selection Data-base

*corresponding author: lcabeza@diei.udl.cat

1. Introduction

Today, thermal energy storage materials are proposed as a promising solution to increase the energy efficiency in building sector and to reduce the total energy demand because building sector accounts up to 34% of total energy consumption in developed countries as state International Energy Agency [1,2]. In Figure 1 the energy consumption in building sector divided by world areas and differentiating between residential and commercial buildings is shown. Notice that developed countries account more energy consumption in commercial buildings than in residential ones.

Materials used to store thermal energy are divided in three types concerning the method used to store the energy. The first one consists on the heat stored produced when a temperature gradient is applied to a media (solid, liquid or gas) which is known as sensible heat (SHTES) [3]. The second is the one concerning the latent heat stored or released during a phase change state (LHTES) [3]. This method used phase change material (PCM) to store thermal energy. The last one consists on store the thermal energy produced when a reaction takes place. This method is known as thermochemical storage (TCS) and thermochemical materials (TCM) are used for storage [4]. Thermal energy storage (TES) is proposed as one way to improve the gap between energy consumption and energy supply [5]. Actually, there are different compilations to collect all the reported information about PCM properties, not only the thermophysical ones but also other relevant properties [6,7].

In addition, phase change materials (PCM) are well-considered as materials to store energy allowing high energy densities (between 50-600 MJ/cm^3). The phase change temperature range will define the final application where this material/substance can be implemented: heating, cooling, domestic hot water, cold storage, etc. Therefore, it is a material selection parameter. Moreover, PCM are divided in several groups of PCM depending on their chemical nature: paraffin, fatty acids, salt hydrates, sugar polyol, etc. [8].

CES Selector is a software database developed by Granta Design [9]. This software is a very intuitive tool to help researchers and designers to select the most appropriate material for a determined application taking into account the constrains. CES Selector was used by Navarro et al. in order to define the best material candidate to store thermal energy as sensible heat [10], as well as Khare et al. [11]. This software has been used as a tool being the aim of this paper to build a new database and to use this tool for the first time in order to obtain proper graphs that will help PCM selection.

Therefore, this paper aims to show the scope of creating a PCM database for CES Selector. The main source of data of PCM for building applications is the one considered in the review that Cabeza et al. published in 2011 [12]. Available materials to be used as PCM (commercialized and standard substances) for building applications in literature were listed in this review [12] as well as materials commercialized as PCM. More than three hundred PCM were listed and classified by their properties and introduced in this database. This database is a simple and intuitive method to obtain a general PCM list for certain application depending on the thermophysical properties required.This tool is very used in material science field but it is non-existent in the PCM field.

The main objective is to create a database that facilitates the selection of the most suitable PCM depending on the application. Moreover, the information that can be extracted from the data presented in this paper will be discerned by presenting a case study for domestic hot water application in buildings.

2. Selection materials methodology

Following a materials selection strategy the main goal is to obtain a small number of materials candidates among a given database taking into account a specific application. The systematic selection of the best materials for a given application begins by knowing the most relevant properties that has to be considered. CES Selector is software from GRANTA Design at the University of Cambridge that allows combining the information on materials from its specific database and presenting the results in friendly material charts. Moreover, it has a tool, the CES constructor, that allows creating your own data base to apply the materials selection methodology comparing different materials from your database, the CES Selector database and also those found in the literature that are used in the desired application.

One of the main purposes of this work is to create a new database of PCM to select them depending on their properties and their application. Therefore, a new database was created using the CES Constructor software to introduce the main properties such as melting point and latent heat of fusion from the PCM found in the literature and also from commercial PCM.

More than 300 PCM references were introduced in this software to be used to select material candidates for TES in several applications for building sector. The data introduced is based on the review published in 2011 by Cabeza et al. [12]. Moreover, the main cited classification of PCM by groups is used in this database which considered the chemical nature of the substances used to store energy by their latent heat of phase change and the main properties that will characterize the thermal behaviour of a PCM are the working temperature range (based on the peak temperature of the phase change) and the heat of fusion (energy that one substance is able to store as latent heat). These two properties are considered for all the PCM available in the new database. It is also important to remark that there are several properties that are very relevant as density, thermal conductivity, specific heat, etc. which were also introduced in the new database even though there is not data available for all references.

3. Results and case study for domestic hot water

There are 6 main groups or families that PCM are divided depending on their chemical nature which are represented in the Figure 2. Each PCM family has its own characteristics:

- Organic / Eutectic Organic / Paraffin / Fatty acids: these substances almost do not present corrosion problems. However, it is difficult to ensure the thermal stability of cycling stability after many thermal cycles.
- Inorganic / Eutectic Inorganic / Salt hydrate / water solution: are the PCM with the highest capacity to store energy but they present corrosion problems that must be taken into account from the beginning of the system design.

However, one of the most important parameter to take into account during the PCM selection step is the energy density which is calculated following Eq. (1), where ρ_{en} is the energy density, ρ is the density of the material and ΔH is the phase change enthalpy.

$$\rho_{en} = \rho \cdot \Delta H \quad (1)$$

This software is able to discern the materials with highest ρ_{en} which are located in the upper part of Figure 3. Note that the materials with highest energy density using latent heat to store thermal energy are salt hydrates.

Otherwise, the working temperature range will define the final application of the PCM. Different bubble colour of Figure 4 means different application of PCM and commercial PCM are shown in black colour (independently of the application).

In addition, Figure 4 shows the PCM working temperature range selected for thermal comfort in buildings applications where particular applications are defined: heating, cooling, domestic hot water, and thermal comfort.

In detail, it is important to highlight that the PCM available for thermal comfort in buildings are not many substances. Therefore, new substances can be developed or enhanced to be used in this material gap (see Figure 5).

Moreover, the thermophysical properties variation for such a substance, for example butyl stearate (see Figure 5.b), is due to the dispersion in the values available in the literature: the melting temperature for butyl stearate is reported between 18-23 ºC and the latent heat of fusion is accounted between 123 – 200 kJ/kg. This circumstance is mainly due to a lack on the standardization for the thermophysical properties measurements [13].

Furthermore, using this available data it is possible to correlate which is the main component of one PCM available in the market. Taking into account Figure 6, we may correlate octadecane as the main component of RT27 which is commercial product from Rubitherm because both materials have the same melting temperature and the same chemical nature, and the difference between both substances might be the melting enthalpy due to the additives the commercial PCM has.

Moreover, this database could be completed by collecting other important properties for PCM filed as thermal conductivity, specific heat, density, wholesale cost, etc. which must be considered during the design step of the system as well. Collection of all these data is difficult and time consuming but some of the substances reported in this database have these properties available and they are presented in Figure 7 that shows thermal conductivity vs. density. Note that salt hydrates are the PCM with highest thermal conductivity while paraffin is the PCM group with the lowest density.

Case study: Domestic hot water

Domestic hot water is a field studied several times in order to implement PCM successfully. For example, Mazman et al. [14] studied how the addition of PCM modules at the top of the water tank produces higher storage density and compensates heat loss at the top layer. Moreover, several researchers have developed models to predict the behaviour of hot water tanks under several working conditions [15–17]. Furthermore, Barba and Spiga [18] studied the discharging process for encapsulated PCM in storage tanks and stated that among different geometrical configurations of the PCM, it is found that the shortest time for complete solidification is matched for small spherical capsules. All PCM used in these studies (eutectic mixture of palmitic and stearic acids, encapsulated 37.5% NH_4NO_3+62.5% $Mg(NO_3)_2 \cdot 6H_2O$, paraffin and stearic acid, TH58) have been included in the new database. The temperature range fitted to this application is between 50-65 ºC [14].

The energy density vs. melting point of the PCM available included in the new database is presented in Figure 8 as well as the thermal conductivity vs. melting point.

In order to select the most suitable PCM to be used for domestic hot water application the temperature range of work must be fitted between 50-65 ºC melting temperature and they must present the highest energy density as well as the highest thermal conductivity (materials located in the upper-right corner of the graphs). Within this area there are several PCM such as mixtures of $Mg(NO_3)_2$ and $MgCl_2$, $Na_2S_2O_3$, mixtures of $Mg(NO_3)$ and NH_4NO_3, being all of them salt hydrates. These are almost all selected in the studies described above [14–17]. Moreover, not only salt hydrates present high thermal conductivity but also several paraffin commercial wax which must be doped with conductive particles because the thermal conductivity of paraffin is low, around 0.2 W/m·K. Therefore, salt hydrates are the most suitable substances to be used as PCM for DHW but several paraffin accounts high thermal conductivity enough becoming suitable candidates by losing a little bit of energy density. Finally, the wholesale cost is one of the most important issues when selecting materials for an application. In general, the salt hydrates wholesale cost is around 0.5 US$/kg and paraffin wax is around 1-1.5 US$/kg. This fact also agrees with the previous material selection when salt hydrates are identified as one of the most proper materials to be used in this application.

4. Conclusions

A new developed PCM database is presented in this paper. This database includes properties from available PCM within the temperature range between -50 ºC and 150 ºC considering commercial and non-commercial PCM. The properties collected in this database are mainly the melting temperature and the latent heat of fusion which are two of the most important properties to take into account during the PCM selection step. However, there are many other properties which are important, not only thermophysical properties as thermal conductivity, specific heat (which are available for some PCM in the literature), but also density, wholesale cost as well as embodied energy, water usage, etc.

Completing and complementing the information available in this database, facilitates the selection of the best candidate for a given application, considering at the same time several properties of the materials.

Acknowledgements

The research leading to these results has received funding from the European Commission Seventh Framework Programme (FP/2007-2013) under grant agreement No ENER/FP7/1295983 (MERITS) and under grant agreement n° PIRSES-GA-2013-610692 (INNOSTORAGE). Furthermore, the work is partially funded by the Spanish government (ENE2011-28269-C03-02 and ENE2011-22722). The authors would like to thank the Catalan Government for the quality accreditation given to their research groups GREA (2014 SGR 123) and DIOPMA (2014 SGR 1543).

References

[1] IEA, Energy Technology Perspectives (ETP) 2012., 2012.

[2] IEA, Technology Roadmap. Solar Heating and Cooling., 2010.

[3] H. Mehling, L. Cabeza, Heat and cold storage with PCM, Springer-Verlag, 2008. ISBN-13: 9783540685562.

[4] A. Solé, X. Fontanet, C. Barreneche, A.I. Fernández, I. Martorell, L.F. Cabeza, Requirements to consider when choosing a thermochemical material for solar energy storage, Sol. Energy. 97 (2013) 398–404.

[5] A.M. Khudhair, M.M. Farid, A review on energy conservation in building applications with thermal storage by latent heat using phase change materials, Energy Convers. Manag. 45 (2004) 263–275. http://www.scopus.com/inward/record.url?eid=2-s2.0-0141510020&partnerID=40&md5=afb9a447d9699dcde0d44119197faa4a.

[6] IEA, Task 42/Annex 24 International Energy agency. Available from: http://archive.iea-shc.org/task42/, 2010.

[7] B. Zalba, J.M. Marín, L.F. Cabeza, H. Mehling, Review on thermal energy storage with phase change: Materials, heat transfer analysis and applications, Appl. Therm. Eng. 23 (2003) 251–283. http://www.scopus.com/inward/record.url?eid=2-s2.0-0037289573&partnerID=40&md5=7a2e981c4d5bec884b0a0e58a47ba49f.

[8] A. Abhat, Low temperature latent heat thermal energy storage: heat storage materials, Sol. Energy. 30 (1983) 313–332.

[9] Granta, C. University, CES Selector 2012 Software, (2012).

[10] M.E. Navarro, M. Martínez, A. Gil, A.I. Fernández, L.F. Cabeza, R. Olives, et al., Selection and characterization of recycled materials for sensible thermal energy storage, Sol. Energy Mater. Sol. Cells. 107 (2012) 131–135. http://www.scopus.com/inward/record.url?eid=2-s2.0-84865968590&partnerID=40&md5=10820b0819ed12de88c134db4d858ccb.

[11] S. Khare, M. Dell'Amico, C. Knigh, S. McGarry, Selection of materials for high temperature sensible heat energy storage., Sol. Energy Mater. Sol. Cells. 115 (2013) 114–122.

[12] L.F. Cabeza, A. Castell, C. Barreneche, A. De Gracia, A.I. Fernández, Materials used as PCM in thermal energy storage in buildings: A review, Renew. Sustain. Energy Rev. 15 (2011) 1675–1695.

[13] A. Lazaro, C. Peñalosa, A. Solé, G. Diarce, T. Haussmann, M. Fois, et al., Intercomparative tests on phase change materials characterisation with differential scanning calorimeter, Appl. Energy. 109 (2013) 415–420. http://www.scopus.com/inward/record.url?eid=2-s2.0-84879315600&partnerID=40&md5=9b26c7a6a01365f5e85c5fbfbb77d878.

[14] M. Mazman, L.F. Cabeza, H. Mehling, M. Nogues, H. Evliya, H.O. Paksoy, Utilization of phase change materials in solar domestic hot water systems, Renew. Energy. 34 (2009) 1639–1643. http://www.scopus.com/inward/record.url?eid=2-s2.0-59049088108&partnerID=40&md5=7b8fbf70c2e1f370d5d4c8187e7f0741.

[15] A. De Gracia, E. Oró, M.M. Farid, L.F. Cabeza, Thermal analysis of including phase change material in a domestic hot water cylinder, Appl. Therm. Eng. 31 (2011) 3938–3945. http://www.scopus.com/inward/record.url?eid=2-s2.0-84860390549&partnerID=40&md5=2915793a977d00bb269bdf40fdeb2722.

[16] M. Ibáñez, L.F. Cabeza, C. Solé, J. Roca, M. Nogués, Modelization of a water tank including a PCM module, Appl. Therm. Eng. 26 (2006) 1328–1333. http://www.scopus.com/inward/record.url?eid=2-s2.0-33645026166&partnerID=40&md5=bc788c3dd8dbc1de676e4f41efffcd4e.

[17] N.K. Bansal, D. Buddhi, An analytical study of a latent heat storage system in a cylinder, Energy Convers. Manag. 33 (n.d.) 235–242.

[18] A. Barba, M. Spiga, Discharge mode for encapsulated PCMs in storage tanks, Sol. Energy. 74 (2003) 141–148.

Figures

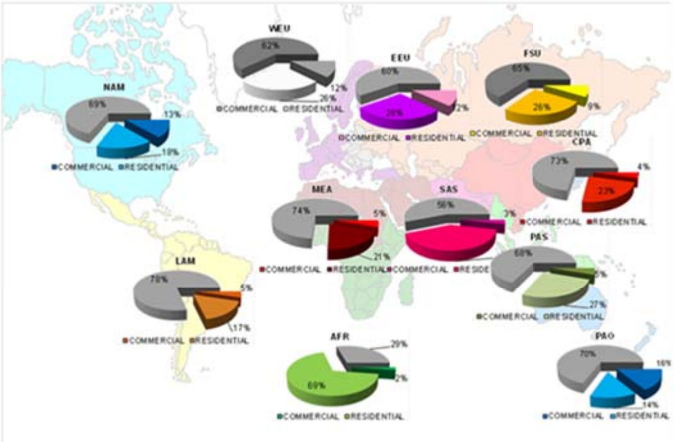

Figure 1. World zones energy consumption distribution divided by commercial and residential subsectors and others for 2010 [2]

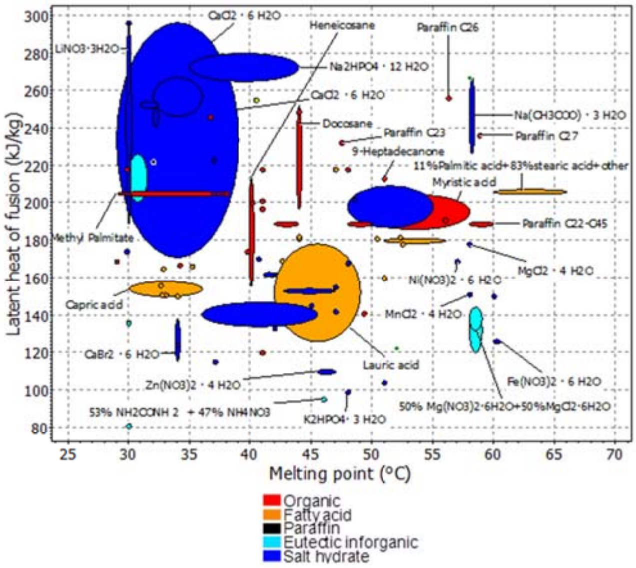

Figure 2. PCM representation of latent heat of fusion vs. melting point between 25-70 ºC

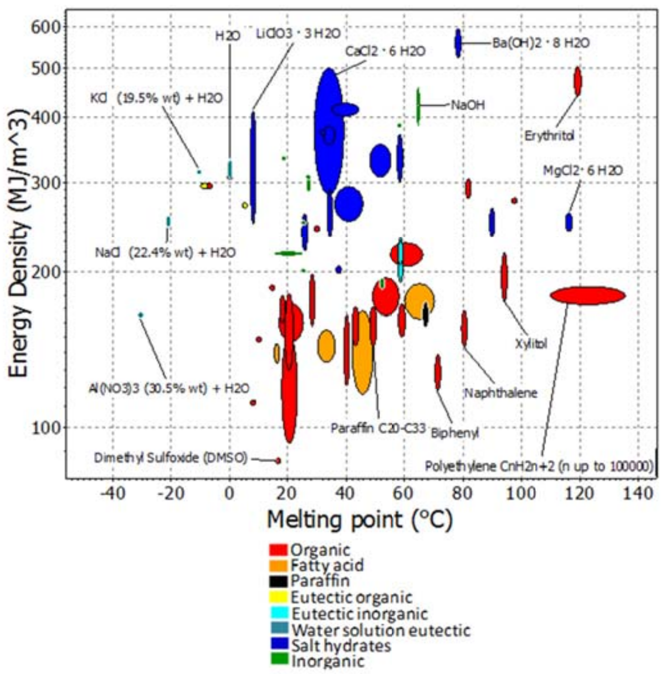

Figure 3. Theoretical energy density vs. melting temperature from the PCM database

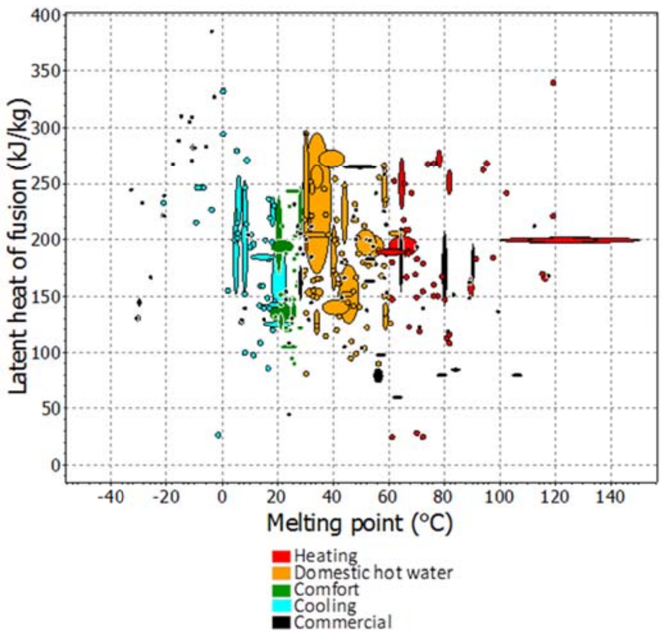

Figure 4. Latent heat of fusion vs. melting temperature of materials introduced into the PCM database

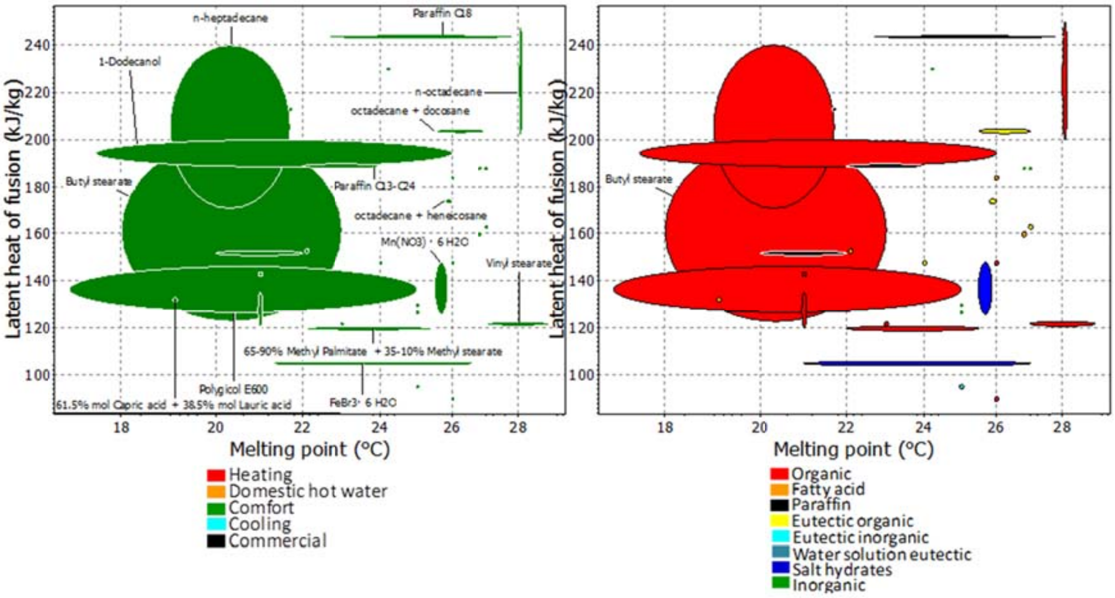

Figure 5. Substances to be used as PCM for thermal comfort in building applications divided by application (a) and by PCM groups (b).

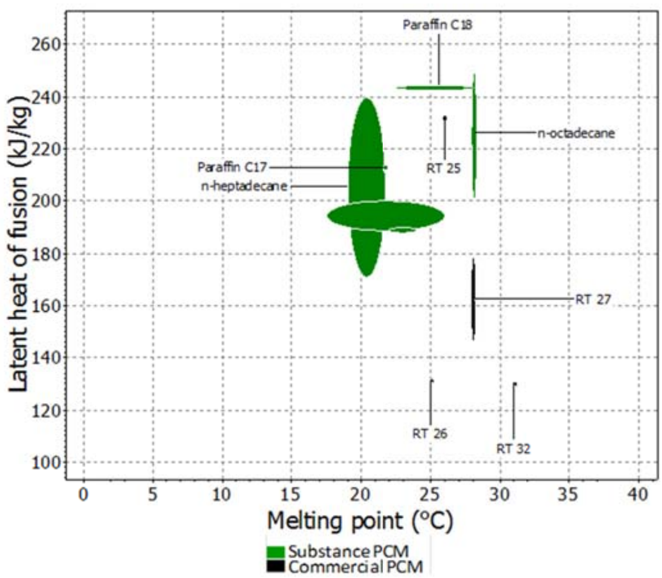

Figure 6. Correlation between substances used as PCM and commercial products

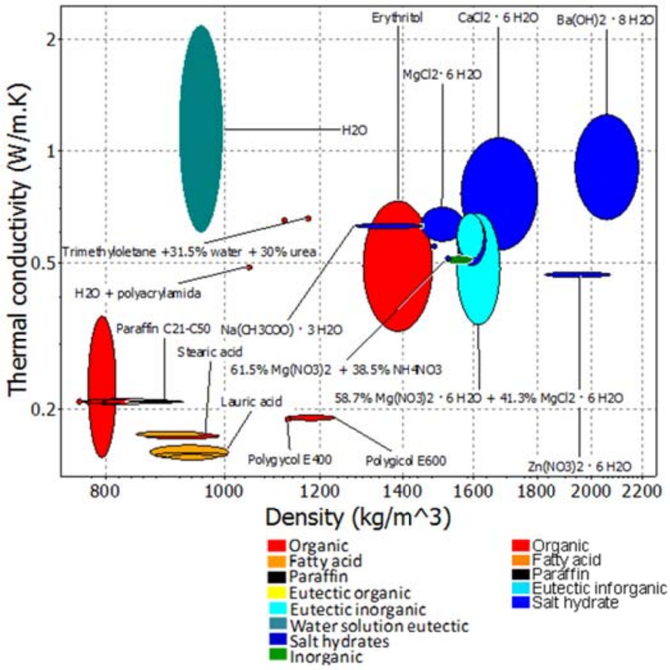

Figure 7.Thermal conductivity vs. density of PCM introduced in the database