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Thermal Energy Storage Capacity of some Phase changing Materials and Ionic Liquids

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Abstract : More than sixty phase changing materials including organic, inorganic, eutectic and ionic liquids are reviewed here with respect to their thermal energy storage capacity. This review is based on some of their crucial properties like melting temperature, heat of fusion, thermal conductivity and density. After a rigorous study of their properties, a concluding list of nine promising phase changing materials appropriate for thermal energy storage is prepared. Due to lack of information of properties of some of the ionic liquids, we were unable to place them in the final list.
Keywords: Thermal Energy Storage (TES), Phase Changing Materials (PCM), Ionic Liquids.

Introduction

Thermal Energy and its Storage

The demand and supply gap for energy sources is widening day by day. Moreover, the fact that the energy can neither be created and nor destroyed has resulted in focussing of scientific research in the direction of storing the different forms of energy using diverse devices [1, 2, 5]. Thermal energy is one such energy which is of interest to researchers worldwide [2, 3, 4]. Thermal energy could have several geneses but storage of solar thermal energy is one of the principal areas of investigation [1]. In recent years, various conventional and unconventional materials are investigated for their capability to store thermal energy. These thermal energy storage devices (TESD) are selected on the basis of some crucial physical, chemical and economic properties. Melting Point, Heat of fusion, density, heat capacity, thermal conductivity, compatibility with container and cost of production are the chief parameters for selection of TESD [2,4]. It is a genuine challenge to find out an ultimate TESD as the overall suitability of materials to be used as TESD is governed by a multifaceted interplay between several properties of those materials.

Properties Affecting TES

Melting Point

Melting point is the temperature at which the first crystal of the material collapses. DSC thermograms can accurately measure the melting and freezing point of the materials. It is imperative to have the melting point of TESD within the temperature range of application. As such, the melting point as such does not affect the energy storage capacity of a material. However, as a phase change is involved in melting, the inclusion of melting point in temperature range of application can permit the use of phase change as an on-off switch. Phase change starts and stops the flow of materials which in turn can connect and disconnect the thermal circuit and offer a smooth path for heat transfer. Under cooling is a phenomenon which is clearly visible with inorganic TESDs [4]. Melting of a solid is usually very quick but the solidification of molten materials requires relatively longer time and reduced temperature. Due to this, a difficulty arises in disconnecting the thermal circuits rapidly. Hence, materials with low under cooling properties are preferred TESDs. If the melting point of a potential TESD lies in the temperature range of application, heat of fusion, density and thermal conductivity are the next three properties to be considered for selection of a material as TESD. Melting points lower as well as higher than the temperature range of application prohibits the use of materials as TESD.

Heat of Fusion (ΔH)

Heat of fusion (ΔH) also known as enthalpy of fusion or latent heat of fusion is a very important property useful in selecting a TESD. It refers to the amount of thermal energy that a material must absorb or evolve in order to change its phase from solid to liquid or vice versa. These values can be straight away calculated from the area included in the DSC melting endotherm. Large values of heat of fusion leads to more efficient TESDs. Certain ionic liquids possessing liquid crystalline behaviour can have multiple values of heat of fusion. These values correspond to the morphological change in the material occurring in the same phase. The changes usually occur in a narrow temperature range. Thus it is possible to use ILs as TES devices. While using ILs as TESD, the summation of small heat changes occurring in the neighbourhood of the phase change temperature can be considered as effective heat of fusion.

Heat Capacity

Heat capacity refers to the amount of energy per molecule that a compound can store before the increase in its temperature. This energy is generally stored in translational, vibrational and rotational modes. Thus materials with greater number of atoms in its composition are expected to have higher heat capacity. Modulated differential scanning caloriemetry (MDSC) imposes time varying heat rate on the linear ramp used in DSC. By analysing the heat flow at temperatures other than those of transitions one can directly obtain the values of heat capacity.

Thermal Conductivity (k)

Thermal Conductivity (k) measures the ability of a material to conduct heat. Greater values of k imply an efficient heat transfer. A thermal conductivity cell must be constructed for measuring thermal conductivity using a potentiostat/galvanostat. This cell can be made by welding pure tantalum wire to silver leads out of which one is bent at 90^o at one end and both the leads are inserted in sealed glass tubes. The cell then put in a tube containing the sample and the complete assembly immersed in a uniform temperature bath can be used to measure the voltage for constant current applied for one or two seconds. However, it also increases the dissipation of heat. Thus, thermal conductivity is a property which needs to be optimised. Since thermal conductivity is phase dependant property, it is important to know values of k in both the solid as well as molten phases. It has been observed that most of molten materials exhibit much higher values of thermal conductivity as compared to that in their solid state. Higher values of thermal conductivity in molten state can facilitate an efficient heat transfer and smooth operation of the thermal circuits in TESD.

Density (ρ)

Density (ρ) of a material refers to its mass per unit volume. Density values can readily be measured using densitometers. Materials with higher density thus occupy less space which in turn increases the energy storage capacity. However, the linearity of this relation holds only up to some extent. Materials with high density obviously possess higher energy storage capacity but many of them show a significant decrease in density in their molten state. This is due to the expansion of their volume. Thus, if the TESD is placed in a sealed container in its solid phase, empty space equivalent to its volume expansion must be kept in the container. Considering the above, it can be generalised that materials with high density but very small change in density at the phase change temperature are attractive TESDs [6].

Other Properties

In addition to the above mentioned properties, material compatibility with container, thermal stability, phase separation, inflammability and economic factors play a vital role in determining the right contender for thermal energy storage [7, 8, 9]. While inorganic materials are corrosive and exhibit phase separation, the organic ones are generally inflammable and remain stable only in a limited temperature range [10].

Materials for TES

Classical PCMs

Considering the above properties, more than sixty organic, inorganic and hybrid materials are being used for thermal energy storage. Paraffins and fatty acids are the most preferred organics whereas water and hydrated salts of alkali metals, alkaline earth metals as well as some transition metals are popular inorganic TESDs [2, 3, 4, 5]. It has not been possible to achieve all of the above mentioned properties at their best in pure organic or inorganic compounds. This is attributed to the fact that a pure compound having best of all the properties has not yet been identified. As we select a material with one or two of the properties with best values, the remaining properties get compromised. The overall efficiency of a TESD is a result of a complex interplay between all the properties. In order to overcome this difficulty, eutectics and other mixtures of fatty acids and paraffins are also investigated for their ability to store thermal energy.

Ionic Liquids

Ionic liquids are salts of organic cations with low melting temperatures. They are characterised by wide usable temperature range, high thermal stability, high ion density and designability. Several organic cations like imidazolium, ammonium, pyridinium and anions including halides, nitrates, hexafluorophosphate, tetrafluoroborate, thiocyanate and sulfanilimide are being used for making these materials. These resultant ionic liquids mostly possess intermediate physical and chemical properties to organic and inorganic compounds. However, they also known to exhibit unique thermal properties. Thus, we have also included a few selected ionic liquids as potential thermal energy storage device.

Comparison of different materials for TES according to their properties

Melting Point

Sixty TESDs are reviewed here on the basis of their melting temperature. It is seen that these materials melt over a wide range of temperature from -89 °C to 897°C. Due to a large number of moieties being reviewed, it became necessary to plot two different graphs with ranges -89 °C to 29 °C and 32.4 °C to 897 °C. It is apparent from the graphs that the imidazolium based ionic liquids are concentrated in the temperature range of -89 °C to 25 °C whereas the paraffins occupy the range of -29 °C to 66 °C. Also, alkali metal salts and hydroxides melt at a very high temperature as shown in the graphs. Tunability of melting points has enabled variable positions for the eutectic mixtures. Materials with extremely high or low melting points can find only niche potential applications. Temperature between -10 °C to 100 °C is considered to be the most popular application range for thermal energy storage. More than thirty materials reviewed here fall in this melting range.

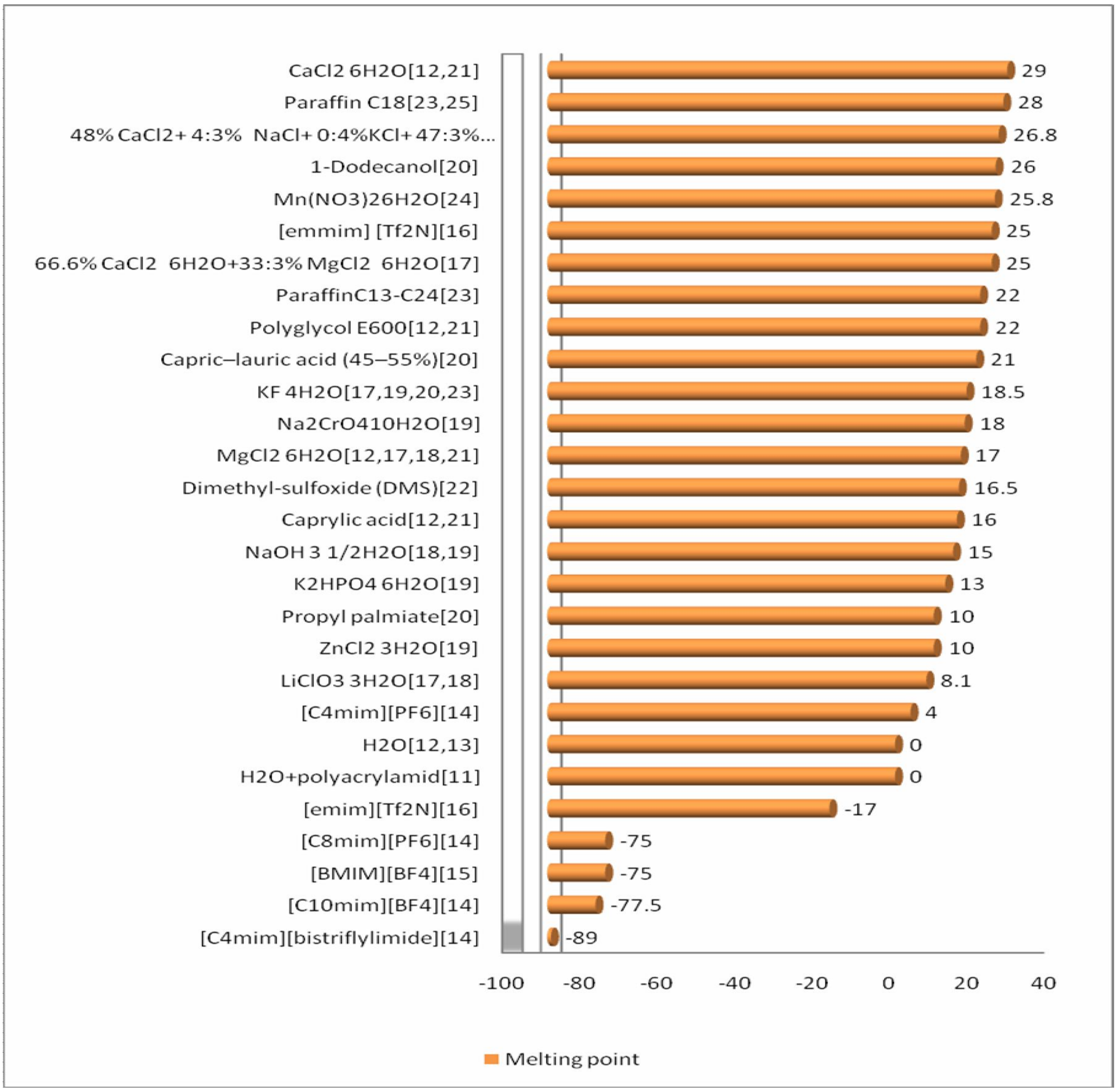

Figure 1A : Melting points (°C) of PCMs in the range of -100°C to 40°C

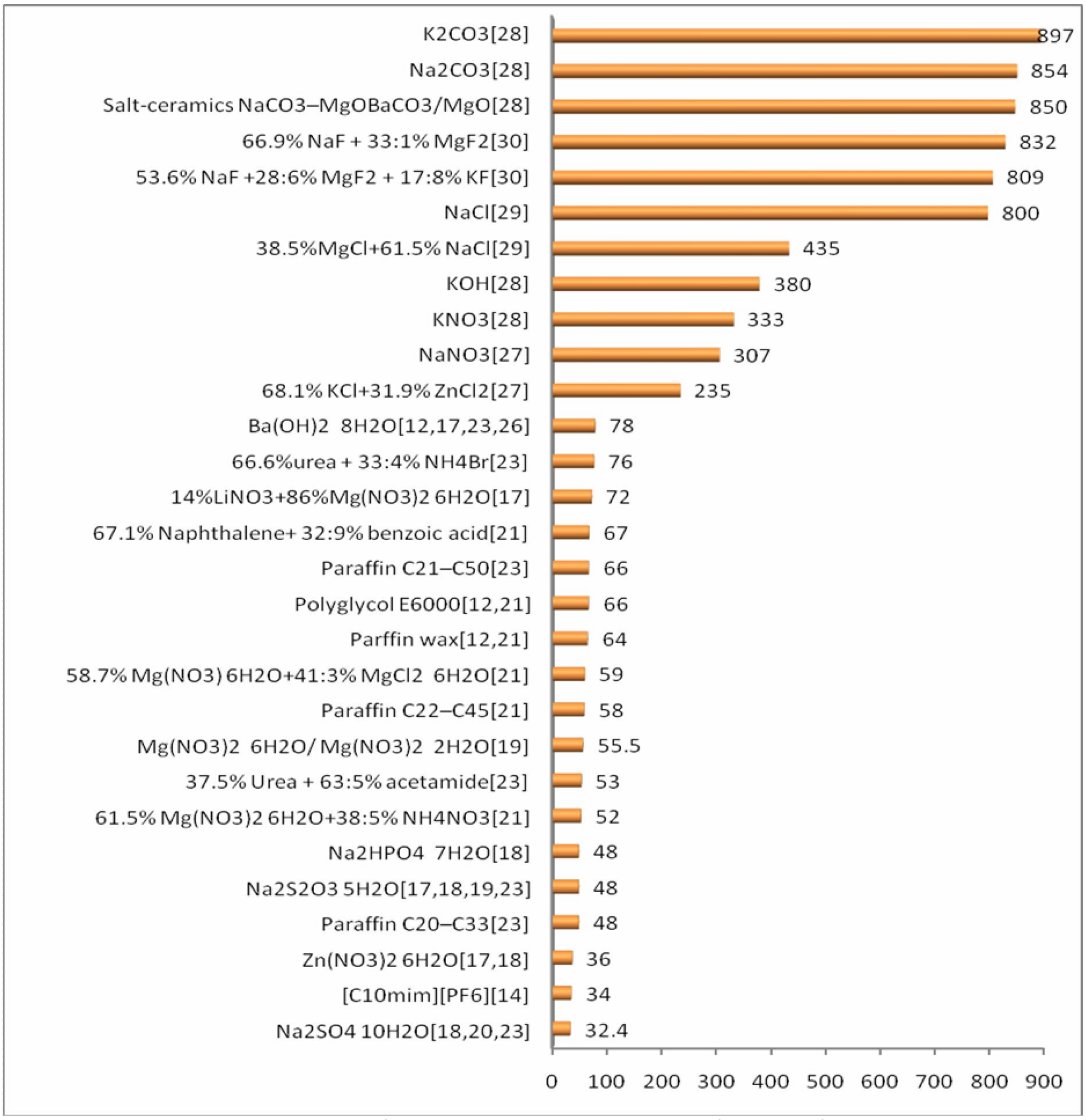

Figure1B Melting Points (^{o}C) of PCMs in the range of $0^{o}C$ to $900^{o}C$

Density

Forty TESDs are reviewed here on the basis of their density at 20 ^{o}C. Density values of ionic liquids are available only near their melting temperatures. Hence the temperature values are indicated in parenthesis. Relatively small variation is observed in the density of the studied materials. Here, the all the paraffins reviewed show the density values in the range of 760 to 830 Kg/m^3 which are below the density value of water (998 Kg/m^3). 1200 to 1400 Kg/m^3 is the density range for most of the ionic liquids shown here while the density values of common organic liquids used for thermal energy storage are in the vicinity of 1100 Kg/m^3. The inorganic materials and their eutectic mixtures used for the purpose have very high density ranging from 1440 to 2260 Kg/m^3. Interestingly, ionic liquids being composed of organic and inorganic portions exhibit density values that are lower than inorganic salts but higher than the corresponding organic compounds.

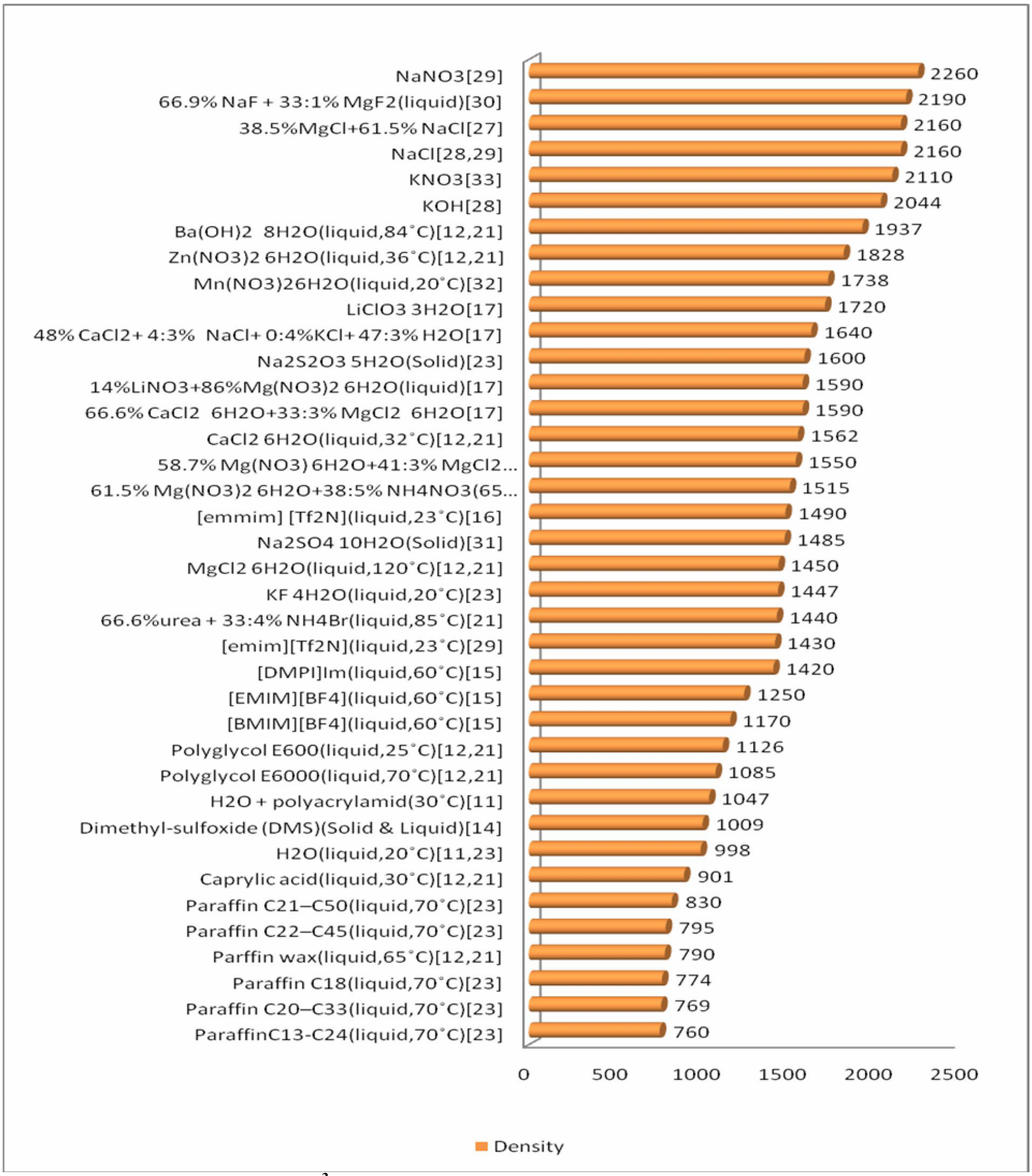

Figure 2 Density (Kg/m^3)of PCMs

Heat of Fusion

Forty two TESDs are reviewed here on the basis of their heat of fusion. The materials show the heat of fusion values in the range of 50 to 500 KJ/Kg. The ionic liquids show relatively small values of heat of fusion which are around 50 KJ/Kg. On the other hand, the inorganic materials have a very high heat of fusion of around 200 to 500 KJ/Kg and the organic materials including paraffins show these values around 100 to 200 KJ/Kg. The eutectic materials being thermoadjustable can have heat of fusion values over the entire range.

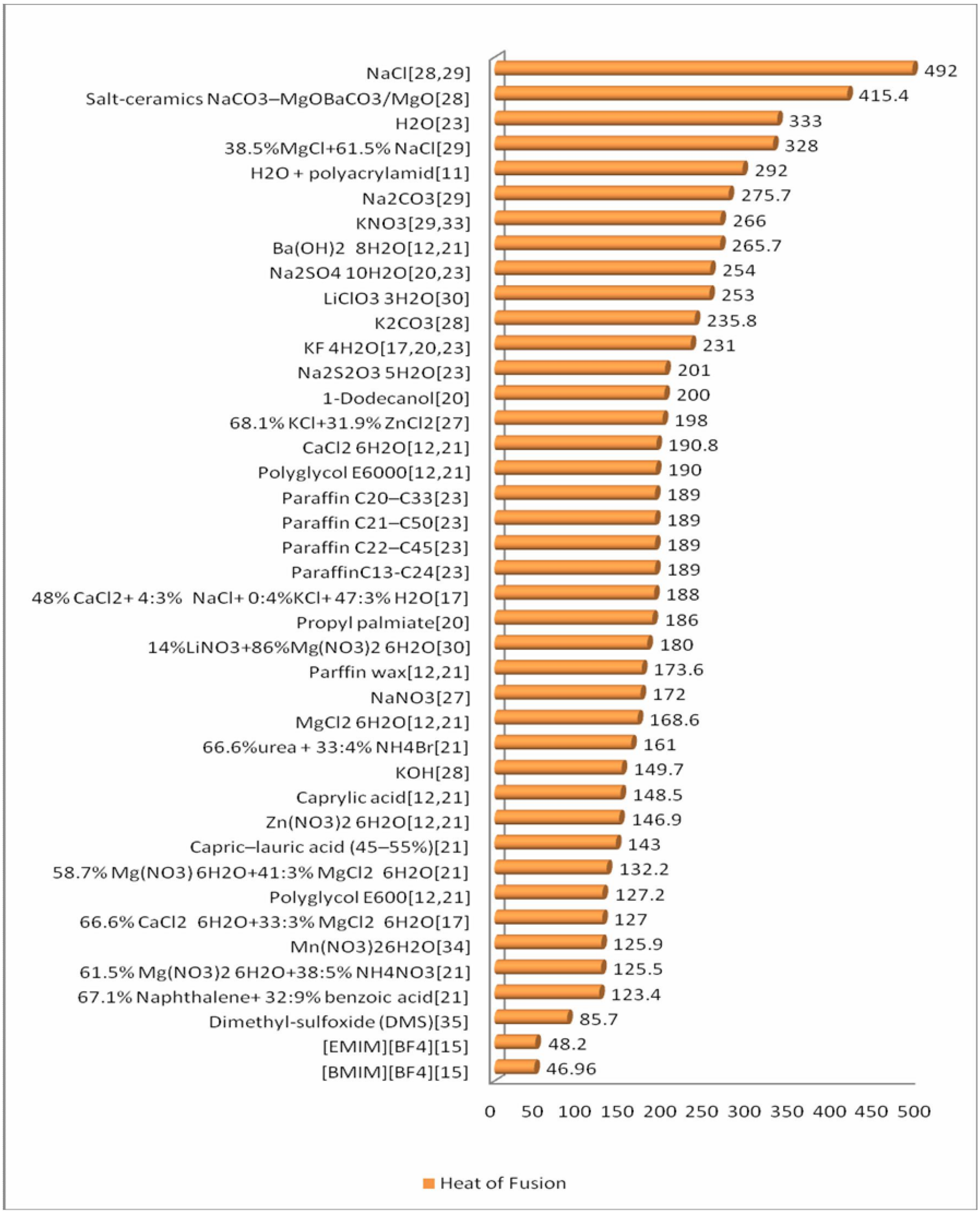

Figure 3 Heat of Fusion (KJ/Kg) of PCMs

Thermal Conductivity

Thirty two TESDs are reviewed here on the basis of their heat of fusion. These values are measured at a temperature of liquid state for most of the materials. Saturated solutions are sometimes made to measure the thermal conductivity of high melting inorganic solids. From the graph, it is apparent that majority of the TESDs have thermal conductivity between 0.1 and 1 W/m K. However, inorganic salts like sodium chloride register the values to the maximum of 5 W/m K. The graph also reveals that the organic materials as well as ionic liquids exhibit thermal conductivity values around 0.2 W/m K followed by the eutectic materials showing these values in the vicinity of 0.5 W/m K. Hydrated inorganic salts show slightly higher values of thermal conductivity (~ 0.6).

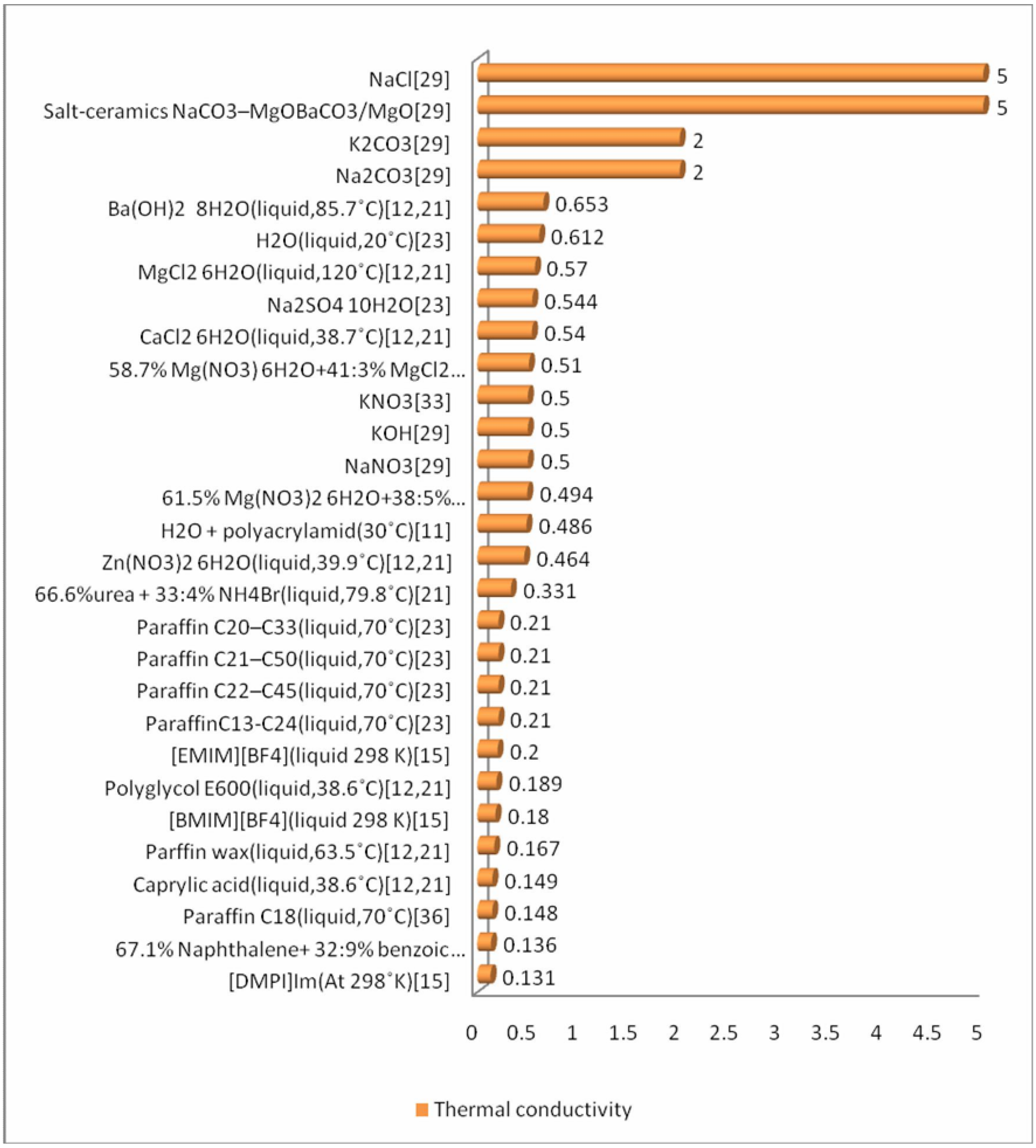

Figure 4 Thermal Conductivities (W/m K) of PCMs

Summary

From the study on above sixty PCMs evaluated for TES applications, we have conservatively selected the value ranges of different properties and again compared them. The melting temperature range of -10 °C to 100 °C is selected assuming the most popular applications. Out of the materials melting in this temperature range, those with highest heat of fusion and density are shortlisted. Due to very small difference in thermal conductivity values, it was not possible to narrow the list on the basis of thermal conductivity. Finally, nine PCMs showing fair values of each of the properties are again plotted on a common scale. Interestingly, four of them are hydrated salts of alkali and alkaline earth metals. Three paraffins have also found a place in most suitable TESDs in the selected temperature range. Water and mixture of water and polyacrylamide have also carved a niche in this list. The eutectic mixtures could not find a place in our final list. Ionic liquids could not find a place in the final list due to a lack of the knowledge of the heat of fusion values for some of them. However, it is very likely that in future, with an increase in property database of ionic liquids, they will also find a befitting place in the list of most suitable phase changing materials to be used as thermal energy storage devices.

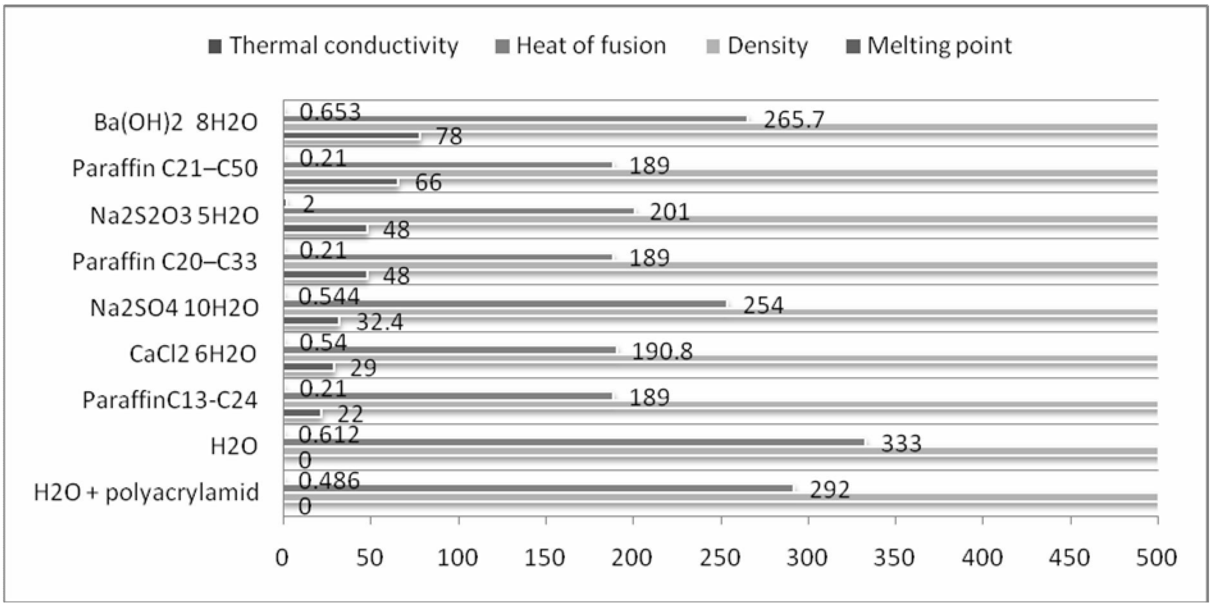

Figure 5 Properties of most suitable PCMs

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