Selection of phase change materials for thermal energy storage integrated with a solar powered vapour absorption system

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Abstract: In the present study, 13 phase change materials are first scrutinised from the commercially available PCMs for temperature operating range from 90°C to 120°C to be integrated into a solar-powered single effect LiBr-H_2O vapour absorption system. Thermo-physical properties have been taken as the criteria of the selection and relative weights have been finalised using an analytical hierarchy process. The ranking is done with the help of the TOPSIS tool. Multi-objective decision-making is also used to analyse the superiority of the PCMs by drawing variations between the two functions of thermal energy storage per unit volume and thermal diffusivity. PlusICE A118, PlusICE S117 and PlusICE H120 have been ranked 1, 2 and 3 respectively based on the obtained results from TOPSIS tool and further validated using multi-objective decision-making examination.

Keywords: phase change material; multi-attribute decision-making; solar vapour absorption system; analytical hierarchy process; multi-objective decision-making.

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1 Introduction

Energy needs are increasing day by day with the best comfort conditions and increasing population. Interest is rapidly increasing on the use of solar-based air conditioning to meet space cooling demand in the abundant solar areas (Al-Abidi et al., 2012; Fan et al., 2014). It is well understood that solar energy availability is during part of the day, whereas cooling demand is continuous. Solar cooling can be achieved through many ways such as solar PV vapour compression system; sorption-based cooling methods using solar thermal energy, etc. (Sharma et al., 2020). Out of these, solar thermal-based vapour absorption systems proved as the most suitable option for the abundant solar areas. It is noted that a vapour absorption system efficiently operates at a specific constant temperature heat supply to its generator. Therefore, thermal energy storage is usually integrated into a solar-powered vapour absorption system to control the temperature swings due to non-uniform solar intensity and also to facilitate the supply of heat during non-sunshine hours.

Thermal energy storage (TES) is primarily of two types: sensible heat thermal energy storage (SHTES) and latent heat thermal energy storage (LHTES). In the early installations of solar-powered vapour absorption cooling systems, SHTES is incorporated within the systems to manage smooth energy transactions between solar thermal collectors and vapour absorption machine (VAM). SHTES does not reflect any heat transfer issue, and integration within the system is quite convenient and economical too. However, low energy density and variation in heat supply temperature significantly affect performance and consistent operation of VAMs in the low or zero solar intensity hours.

With the new advancements in the LHTES in recent years, it has been observed that specific characteristics of LHTES such as isothermal heat supply, high energy storage, etc. may offer solutions to the issues with the SHTES as reported.

LHTES offer nearly isothermal solidification and melting at the phase change transition temperature of phase change materials (PCMs) that helps to meet the demand of constant energy input for the vapour absorption system (Dincer and Rosen, 2011; Zalba et al., 2003). In addition to this, an LHTES must have several other characteristics also. Gasia et al. (2017b) mentioned some significant requirements of an efficient LHTES through a selection of proper PCM by analysing thermo-physical, chemical, kinetic, environmental, and economic aspects. There is a wide range of PCMs available on a commercial basis. Hence the selection of PCM is a crucial part of the thermal energy storage design with objectives of constant temperature heat supply and a large amount of heat storage in low volume to perform the uninterrupted operation of the solar vapour absorption system.

Sharma et al. (2009), Zalba et al. (2003) and Abhat (1983) have given overviews of PCMs. A broad classification includes them as paraffin, salt hydrates and fatty acids. Paraffin is mostly used PCMs due to its wide range of phase change transition temperature. Paraffin is abundant and inexpensive. On the other hand, fatty acids are of bio-origin and come from the vegetables and meat byproducts. Fatty acids are renewable and abundant but costlier than the previous category of PCMs. Salt hydrates are the earliest member of this PCM family. These are also available in the most extensive range of phase transition temperature along with high thermal conductivity at a lower cost. There are several other materials which also proposed as PCMs. Del Barrio et al. (2017) studied on the sugar alcohols to check compatibility to use them as PCMs. They reported various issues such as low thermal stability along with non-favourable crystallisation kinetics. Bayón et al. (2016) reported the use of liquid crystals as PCMs. Each of the groups of PCM has its applications, characteristics, advantages and limitations. The selection of PCM is a crucial factor while designing any LHTES along with a proper heat transfer mechanism. Hence, the selection of PCMs incorporating the different criteria and needs is a complex and crucial decision-making process.

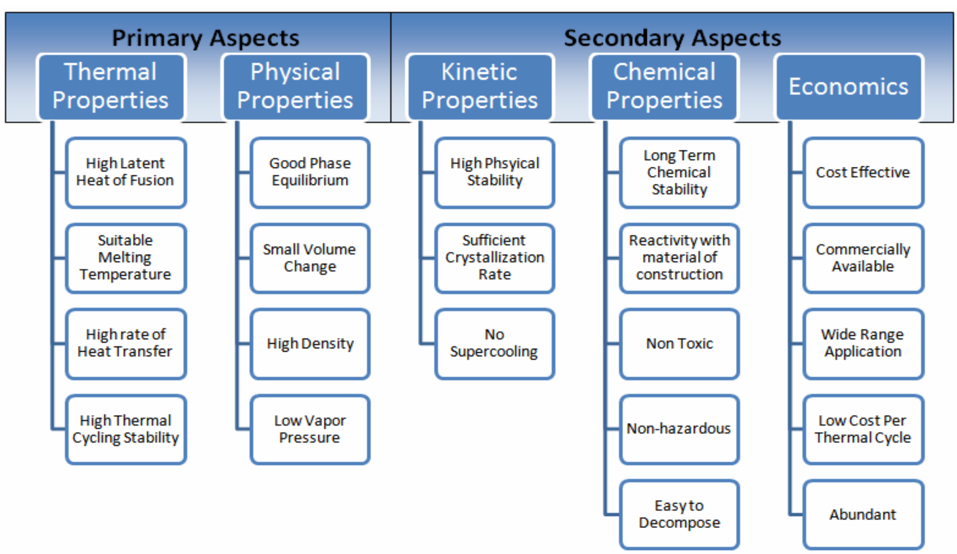
The selection of PCM is case sensitive and multi-objective at the same time as it requires fulfilling criteria such as high latent heat of fusion, high thermal conductivity, high density and high heat capacity. In addition to these, a PCM must be chemically inert; non-hazardous; inexpensive; abundant; non-flammable and non-toxic. No PCM can fulfil all these entire requirements. Therefore, a decision-making process is expected to be exploited in the final selection of the right PCM based on the requirement of LHTES. Some earlier research attempted to fulfil the requirement of an efficient LHTES with the systematic approach to identifying the appropriate PCM. Multi-attribute decision-making (MADM) and multi-objective decision-making (MODM) processes are suggested to select PCM by offering a balance between different thermo-physical properties (Xu et al., 2017; Rathod and Kanzaria, 2011). In addition to this, Gasia et al. (2017a) targeted their study towards the hazardous effects associated with the commercially available PCMs. Miró et al. (2016) also studied the selection of PCM based on health hazards along with cycling and thermal stability. Xu et al. (2017) presented a systematic approach for the selection of PCM for a solar-powered vapour absorption system based on thermophysical properties with the help of MADM as a tool. Rathod and Kanzaria (2011) included cost factor while going for MADM and compared two priority modes; first with the help of the technique of order preference similarity to the ideal solution (TOPSIS) and second with fuzzy TOPSIS. Another MADM tool VIKOR (Vise Kriterijumska Optimizacija I Kompromisno Resenje) was used for the selection of PCMs for low-temperature applications (Wang et al., 2015). Gasia et al. (2017a) reported PCM selection for an LHTES operating under partial load conditions as a result of the thermal process with whom they were coupled.

In the present study, a systematic approach for selection from commercially available PCMs for the efficient and effective design of TES for a solar-powered single effect VAM is carried out using MADM tools TOPSIS and MODM examination. As it is noted from the literature that the selection of PCM is earlier made mostly based on the temperature of phase transition and latent heat. Thermal conductivity, density and specific heat are some other critical thermo-physical properties that need to be involved in the decision-making process of selection. In addition to this, there is quite a few literatures reported the selection of PCMs for TES to be integrated within a solar-powered VAM.

2 Essential aspects of PCMs selection aligned with thermal energy storage

PCMs are the future of thermal energy storage due to their capabilities of high energy storage density, isothermal charging and discharging, etc. Selection of PCM involves primary and secondary aspects which are discussed in the upcoming sections and shown in Figure 1.

Figure 1 Essential properties of phase change material (see online version for colours)



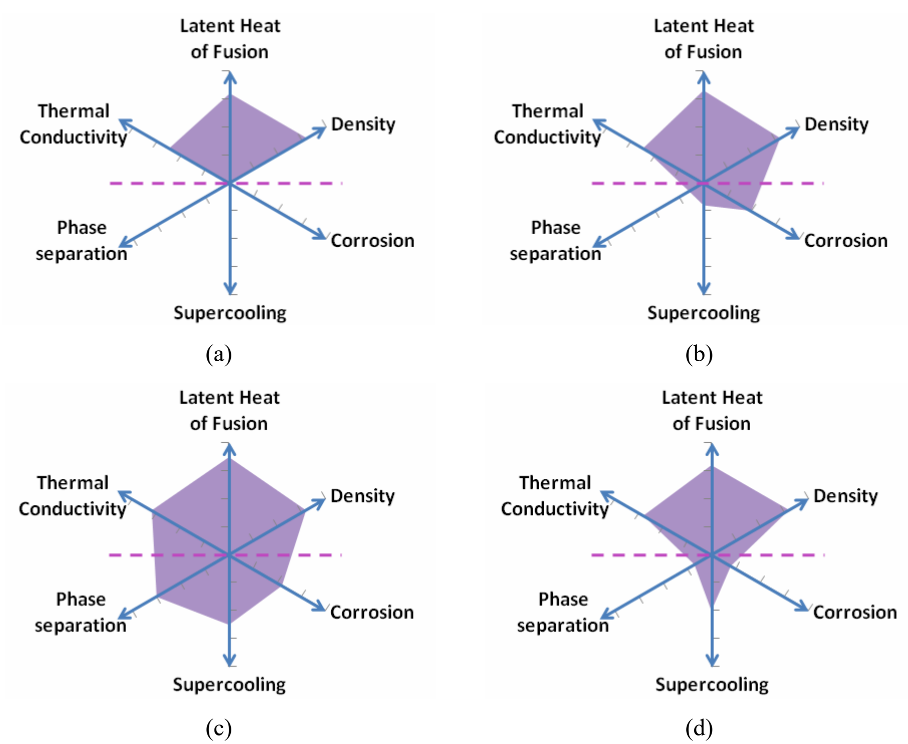
2.1 Primary aspects

Thermo-physical properties play an essential role in the performance out of thermal energy storage, and hence need critical study. It is well known that PCMs melts and freezes at a specified temperature of fusion. In addition to this, thermal cycling ensures the best performance of PCMs for a designated number of operating cycles. Thus, a discussion is presented in this section regarding thermo-physical properties and thermal cycling stability.

2.1.1 Thermo-physical properties

PCMs are an essential need of the thermal energy storage primarily due to their favourable thermo-physical properties. Melting temperature, latent heat, specific heat and density are some of the thermo-physical properties mostly considered while selecting PCM for any thermal storage application. Figure 2 is showing a balance of various properties for different categories of PCMs (Khan et al., 2017). While the criterion for selection mainly depends upon the working temperature, heat storage density and charging and discharging behaviour described. As in the case of a vapour absorption system powered by solar energy, the melting temperature of PCM should be around the operating temperature of the VAM to exhibit maximum performance. Along with this, the higher energy density is also expected to have a maximum period of operation during non-sunshine hours. A higher value of specific heat is essential for storing a large amount of heat. Thermal conductivity is often considered as the sole parameter while considering the rapid charging of thermal energy storage. In contrast, slow charging is managed by other practices such as by varying the flow rate etc. A PCM candidate having higher density is preferred as it is capable of storing a large amount of heat in a small volume and thus offers a high energy density.

Figure 2 Thermal properties of various PCMs, (a) paraffin waxes (b) fatty acids (c) salt hydrates and eutectics (d) refrigerant hydrates (see online version for colours)



PCMs usually expand while melting and causes volume expansion which needs to be accounted for selecting the PCM and designing the LHTES. It is reported in the literature that 15% volume expansion (Gasia et al., 2017a) for paraffin is an acceptable range. Above this, PCMs are generally avoided but can be used in with the melting temperature and latent heat. Commercially available PCMs are provided with the thermo-physical properties.

2.1.2 Thermal cycling stability

A PCM used in the thermal energy storage applications has to go under several charging/discharging cycles (usually, it can be considered one charging and one discharging per day of operation) (Rathod and Banerjee, 2013). Thermal cycling stability is a significant factor while selecting any PCM to identify the period of operation with a maximum performance of the system. Literature report that repeated thermal cycling deteriorates the thermo-physical properties. Hence, it is essential to test the thermal cycling stability keeping acceptable limits of the thermo-physical properties according to the nature of the application. However, thermal cycle stability is generally tested for accelerated charging and discharging under laboratory test conditions to save time (Sharma et al., 1999). However, the effect of real-time thermal cycling stability on thermophysical properties is not reported in the literature. Kenisarin and Mahkamov (2007) reported that thermo-physical properties of a PCM must be stable for at least 1,000 thermal cycles while proposing it for a commercial grade. It is also reported in the literature that thermo-physical properties quoted for a commercial PCM may vary while in the application. Hence, thermo-physical properties must be verified in a laboratory-scale before finalising a PCM for any application (Rathod and Banerjee, 2013).

2.2 Secondary aspects

Performance of the PCM-based TES is entirely necessary but it must be understood that a PCM must be abundant and cost-effective at the same time. In the other relevant factors, disposal of PCMs, hazardous effects and reactivity with the TES and encapsulation materials have been discussed.

2.2.1 Cost

Cost is one of the critical factors while selecting the PCM for the LHTES. In this regard, commercial-grade materials are preferred candidates as PCM due to their ease of availability and low cost. There is a wide range of PCMs available commercially. As in this specified temperature range, there are decidedly fewer options, and those are costlier as compared to those of in the lower temperature. Most of these are non-paraffin and non-fatty acids. Furthermore, it is to be noted that it would be fruitful to estimate the cost factor of latent thermal energy storage in conjunction with thermal cycling. This helps to overcome the difficulty of deciding about the actual life cycle and maintenance schedule of the replacement of the thermal energy storage system. It is evident from the literature that LHTES-based vapour absorption systems are around 2–4% costlier than those of SHTES. However, the use of the LHTES system results in the improved performance and life of solar-based applications such as solar water heater and solar vapour absorption system.

2.2.2 Disposal

One of the essential concerns while using PCM-based thermal energy storage system is the disposal of the PCM used. Paraffin candidates are not eco-friendly as well as hard to decompose. Other candidates in the organic category such as alcohols, esters, fatty acids, etc. are more natural to decompose. It is favourable to use a PCM which is biodegradable or more natural to decompose.

Paraffin is having a perfect life but hard to decompose due to their long-chain alkanes, and these present environmental problems when these are disposed of in a landfill. It will take decades to decompose. Vegetable base PCMs are comparatively safe and eco-friendly. Fatty acids are more manageable to decompose. Many vegetables-based PCMs were found stable up to 30 years during accelerated ageing tests, but same will degrade within six months when disposed of in a landfill. Salt hydrates come from the oldest family of PCMs. Disposal of salt hydrates is still less studied. These are mostly water-based and stability is a significant concern.

On the other hand, vegetable-based PCMs are compatible with wallboards or similar materials that would absorb water from hydrates and make the salt hydrates less effective as PCM. However, due to physical stability issues, salt hydrates are not used in microencapsulation. Whereas the vegetable-based PCMs are the first choice for microencapsulation.

2.2.3 Hazardous effects

Several PCMs show serious consequences when they come in human contact while several others are marked as dangerous in fire hazards. The study of hazardous effects is necessary to identify potential personal and environmental risks for the PCMs. Therefore, results from the health hazard indicate the standards and procedures which need to be followed during the handling and operation of the PCM. A safety data sheet is primarily provided with the commercial PCMs by the manufacturer. The health hazard is designated according to the National Fire Protection Association (NFPA) standard 704 which is further complemented with the help of the Globally Harmonised System (GHS) classification (NFPA 704, 2018). NFPA 704 provides the risk level of many common chemicals through coloured diamonds (red – flammability; blue – health hazard; yellow – chemical reactivity and white for special hazards) each on a scale of 0 to 3 from non-hazardous to severe consequences (Gasia et al., 2017a). Minor health hazards include skin irritation, serious eye irritation and respiratory irritation whereas severe hazards involve damage to organs while prolonged exposure and may cause cancer and genetic effects too. However, NFPA standards identify health hazards rating but still safety measures should be strictly followed (Miró et al., 2016).

2.2.4 Reactivity of PCMs with containment materials

Life of LHTES is mainly a function of the reactivity between PCM and the storage tank also, and to be aligned with the total life cycle as per application for which it is designed. Hence, PCMs those are chemically non-reactive are primarily preferred. Reactivity is required to be studied in conjunction with the storage tank material. Specific categories of PCMs are corrosive, whereas some of them are highly reactive to the material of the storage tank.

Some studies have been made to investigate the reactivity of the PCMs with metal and non-metals. Browne et al. (2017) conducted a study to investigate the corrosive properties of PCMs with the metals and plastic to ensure a trouble-free design of LHTES over a long operational life. Copper, aluminium, brass, mild steel, stainless steel and Perspex were tested for reactivity with five different PCMs (three fatty acids, a salt hydrate and Micronal®) for 722 days. Out of these, stainless steel was entirely non-reactive, and aluminium can be comfortably used with fatty acids with a corrosion rate of 12.4 mg/cm^2-year. Brass and copper are also having fewer corrosion rates of 1.67 g/cm^2-year and 22.15 g/cm^2-year respectively. Moreno et al. (2014) reported material selection for thermal energy storage tanks using salt hydrates as PCM. They tested two metals and two metal alloys with a total of eleven PCMs. Another study by Ferrer et al. (2015) showed corrosion effects when putting in contact carbon steel, copper, aluminium, stainless steel 316, and stainless steel 304 and with one ester, one inorganic mixture, and two fatty acid eutectics. Based upon the results, stainless steel 304 and 316 found compatible and less reactive with any of the studied PCMs.

Dheep and Sreekumar (2018) investigated the corrosion characteristics of glutaric acid for solar thermal energy storage applications. It was reported that glutaric acid tends to be a potential PCM being of less corrosive nature on containment materials. Oró et al. (2013) presented an analysis of corrosion of metal and polymer containers for PCM cold storage. Studied PCMs were encapsulated in containers and then used in the available system. Therefore safety constraints as the compatibility of the PCM with other materials have to take into account. Hence the primary goal of this research work is to study the corrosion effect of different metals and polymer materials in contact with some PCM used in low-temperature applications. Results show that copper and carbon steel must be avoided as PCM containers, and aluminium is not recommended; stainless steel 316 is recommended when in contact with the tested PCM. In the non-metals, high-density polyethene, polypropylene and polyethene terephthalate are mostly preferred as encapsulation materials due to their non-reactivity with the most of the PCMs.

3 Bulk latent heat storage versus encapsulated PCMs

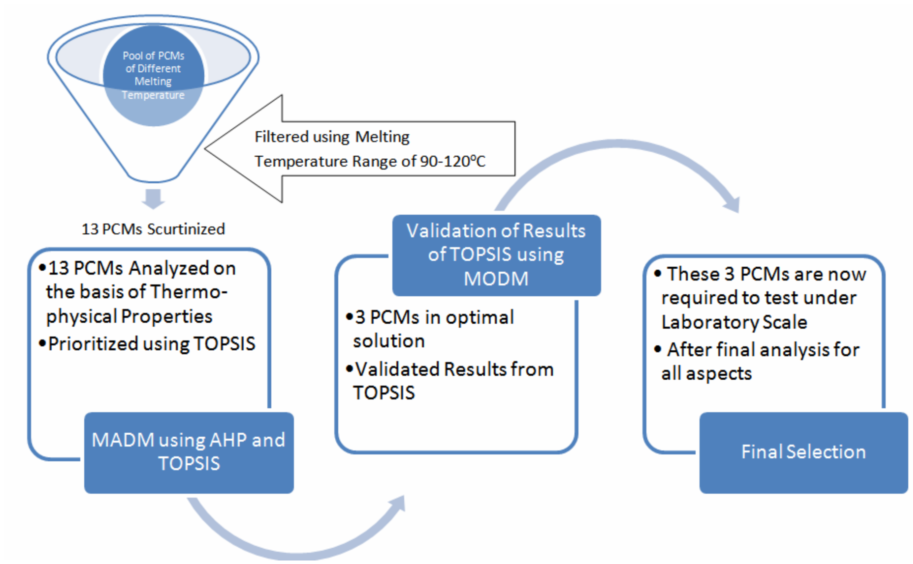
The demand for an improved design of TES is nowadays fulfilled in the form of LHTES. LHTES may be further classified as bulk latent heat storage and encapsulated PCMs arranged inside the SHTES tank. Literature details that a bulk latent heat storage is capable of storing a large amount of heat in a compact size and also able to charge and discharge at a constant temperature. Hence, it is precisely meeting with the requirement of heat supply to a single-effect VAM. However, bulk latent heat storage is cost-intensive and there are several handling issues. It is worthy of mentioning here that solar heating circuits mostly have tiny diameter tubes which do not allow the flow of most of the PCMs inside and hence, charging and discharging of TES is typically done by placing heat exchangers inside the LHTES, which further increases the cost and complexity of the TES. However, still, bulk latent heat storage faces poor heat transfer due to the overall less heat transfer area of the heat exchanger. In addition to this, the quenching of heat into PCMs further affects the release/store latent heat due to phase transition. Heat transfer in bulk LHTES is mostly considered as conduction dominated, and the thermal conductivity of PCMs is usually low, which results in reduced heat transfer rate.

Literature shows the use of encapsulated PCMs arranged inside a SHTES called a packed bed latent thermal energy storage system to design efficient, effective and economical thermal energy storage for prescribed applications. It is mainly because of high thermal energy storage density and nearly isothermal charging and discharging without using conventional heat exchangers. Regin et al. (2008) summarised the essential requirements of PCM containment. They identified that PCM containment must act as a barrier to PCM and environment interaction to avoid harmful effects as well as able to provide a large surface area for enhanced heat transfer. Therefore, it is a very excellent choice to offer PCMs in an encapsulated form which will reduce the risks of hazardous effects along with the cost without much affecting the performance of TES. In the earlier sections, a significant discussion is shown for the reactivity of the materials of storage with the PCMs. Therefore, this will be quite helpful while designing the whole TES keeping all aspects of the selection of PCMs in mind. However, the thermal stratification issue will be less as proper melting and solidification is a feature of the encapsulated PCMs. Thermal cycling stability plays a crucial role due to the timely replacement of PCMs to ensure proper performance from the TES. However, the replacement of encapsulated PCMs is more convenient and economical compared to bulk LHTES. It may be concluded from the above discussion that encapsulated PCMs thermal energy storage is advantageous over a bulk LHTES.

4 Methodology

The present investigation is expected for the selection of PCM for a single effect LiBr-H_2O vapour absorption system powered by solar thermal energy. The system requirement is to supply heat at a constant temperature of 90°C along with high thermal energy storage density. The objective of the study is to select a suitable PCM out of various commercially available PCMs taking various factors into considerations such as melting point temperature, density, specific heat, thermal conductivity, latent heat, thermal cycle stability, toxicity, cost, etc. However, thermo-physical properties are only taken into this study as criteria of selection of PCMs. Water is used as heat transfer fluid for a thermal energy storage tank, generator (vapour absorption system) and solar collector circuit. As stated earlier, a balanced and systematic selection approach is used to incorporate the properties mentioned above and the requirements of PCM for the optimised performance of thermal energy storage. This is done with the help of the MADM tools; refer to Figure 3 for the methodology adopted. The detailed methodology is expressed in the different sections followed in this article.

Figure 3 Layout of the methodology for PCM selection (see online version for colours)



4.1 *Pre-screening of PCMs*

A wide range of PCMs is available in the market to choose among them. There is a variety regarding temperature, latent heat of fusion, density and many ways. Therefore, firstly, a prescreening is done based on the operating temperature of the single effect vapour absorption systems. Temperature range of 90–120°C is considered in this scenario. Only commercially available PCMs are shortlisted during the study. Scrutinised PCMs are of organic, inorganic, and salt hydrates category. It is essential to mention that there are limited options in this temperature range compared to a temperature range below 90°C. The maximum operating temperature is considered to be 130°C. Hence, PCMs not falling under this criterion have been eliminated. Table 1 is showing pre-screened candidates with thermo-physical properties based on the criteria mentioned above, arranged in the descending order of melting temperature (120–90°C).

Table 1 Prescreened PCM candidates in the specified melting temperature range of 90–120°C

PCM candidates	*Notations*	*P Density (kg/m³)*	*L Latent heat (kJ/kg)*	*K Thermal conductivity (W/m-K)*	*Cp Specific heat (kJ/kg-K)*
PlusICE X120 (PlusICE, 2013)	A1	1,245	180	0.360	1.500
PlusICE H120 (PlusICE, 2013)	A2	2,220	120	0.506	1.510
PlusICE A118 (PlusICE, 2013)	A3	1,450	340	0.500	2.700
PlusICE S117 (PlusICE, 2013)	A4	1,450	160	0.700	2.610

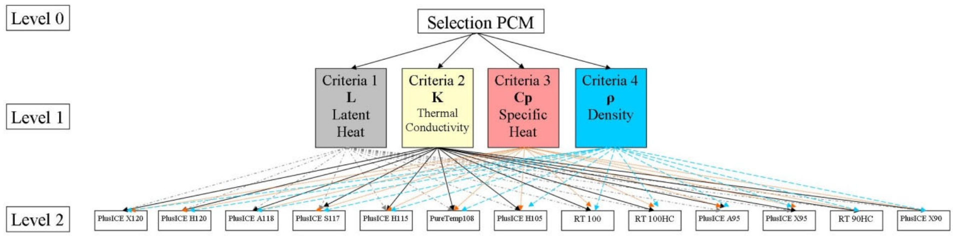
Table 1 Prescreened PCM candidates in the specified melting temperature range of 90–120°C (continued)

PCM candidates	*Notations*	*P* *Density* *(kg/m³)*	*L* *Latent heat* *(kJ/kg)*	*K* *Thermal conductivity* *(W/m-K)*	*Cp* *Specific heat* *(kJ/kg-K)*
PlusICE H115 (PlusICE, 2013)	A5	2,200	100	0.503	1.505
PureTemp 108 (PureTemp108, 2018)	A6	870	180	0.250	2.170
PlusICE H105 (PlusICE, 2013)	A7	1,700	125	0.500	1.500
RT100 (Datasheet-Rubitherm GmbH)	A8	880	124	0.200	2.000
RT100HC (Datasheet-Rubitherm GmbH)	A9	1,000	180	0.200	2.000
PlusICE A95 (PlusICE, 2013)	A10	900	205	0.220	2.200
PlusICE X95 (PlusICE, 2013)	A11	1,215	140	0.360	1.510
RT90HC (RT90HC)	A12	950	170	0.200	2.000
PlusICE X90 (PlusICE, 2013)	A13	1,200	135	0.360	1.510

4.2 Evaluation of criteria weights

Four thermo-physical properties are considered for the prioritisation of the PCMs; density, latent heat, specific heat and thermal conductivity. These are independent and seem to have no interrelation among them. For this nature of complex problems involving multiple criteria, Saaty and Wind (1980) proposed the analytical hierarchy process (AHP) to suggest a solution. AHP method is helpful to establish the relative importance among the different criteria in MADM. For the understanding of the goal or objective followed with criteria of selection and alternatives, a model is developed as shown in Figure 4. Level 0 shows the goal or objective of the MADM problem. Level 1 involves the identification of the criteria. The relative weights of a set of criteria are finalised with expert opinions. This process further involves the use of the eigenvector method to yield criteria weights. Level 2 lists the available alternatives for the present problem. One more advantage is that AHP can incorporate tangible and non-tangible both types of factors (Rao, 2004).

Figure 4 Different levels of MADM (see online version for colours)



Proceeding stepwise, firstly comparison matrix between criteria was prepared as shown below:

$$A = \begin{bmatrix} 1 & a_{12} & \cdots & a_{1n} \\ a_{21} & 1 & \cdots & a_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ a_{n1} & a_{n2} & \cdots & 1 \end{bmatrix} = \begin{bmatrix} 1 & 1 & \frac{1}{3} & \frac{1}{2} \\ 1 & 1 & \frac{1}{3} & \frac{1}{2} \\ 3 & 3 & 1 & 2 \\ 2 & 2 & \frac{1}{2} & 1 \end{bmatrix} \left\{ a_{ji} = \frac{1}{a_{ij}} \text{ and } a_{ij} \neq 0 \right\} \quad (1)$$

This matrix is drawn using the criteria weights assumed using AHP. This is adapted from the Xu et al. (2017) as the application was similar to the present study.

Further, the arithmetic mean is taken row-wise to find the relative normalised weights (W_i) for each criterion using the following formula:

$$AM_i = \left(a_{i1} + a_{i2} + a_{i3} + \cdots + a_{ij}\right)/n \quad (2)$$

and

$$W_i = \frac{AM_i}{\sum_{j=1}^{j=n} AM_i} \quad (3)$$

In some cases, the geometric mean is considered in place of Arithmetic mean (Rathod and Kanzaria, 2011). The effect of taking geometric mean in place of arithmetic mean is not reported in the literature.

Table 2 Criteria weights based on AHP

	Latent heat	*Thermal conductivity*	*Specific heat*	*Density*	*Criteria vector (W_i)*
Latent Heat	1	1	0.333	0.50	0.141
Thermal Conductivity	1	1	0.333	0.50	0.141
Specific Heat	3	3	1	2	0.455
Density	2	2	0.50	1	0.263

Source: Xu et al. (2017)

Now, matrix *X*, which denotes the n-dimensional column vector (priority vector) describing the sum of the weighted values for the degree of importance of the alternatives is shown in Table 2.

$$W = [W_1, W_2, W_3, \ldots, W_n]^T \tag{4}$$

$$X = A \times W = \begin{bmatrix} 1 & a_{12} & \cdots & a_{1n} \\ a_{21} & 1 & \cdots & a_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ a_{n1} & a_{n2} & \cdots & 1 \end{bmatrix} \begin{bmatrix} W_1 \\ W_2 \\ \vdots \\ W_n \end{bmatrix} = \begin{bmatrix} C_1 \\ C_2 \\ \vdots \\ C_n \end{bmatrix} \tag{5}$$

The consistency values (CV) for the group of alternatives is calculated as represented by the vector

$$CV_i = \frac{C_i}{W_i} \tag{6}$$

The maximum eigenvalue $\lambda_{\max}$ is evaluated as the average of the consistency values which is 4.0103.

AHP is an exercise to determine the criteria weights using the pair-wise comparison between different criteria. It is mostly done with expertise and previous experience. Thus, the consistency index (CI) of the outcome is calculated to validate this exercise. It should be noted that the quality of the output of the AHP is strictly related to the consistency of the pair-wise comparison judgments. So, the CI for the present scenario is calculated using the equation here.

$$CI = \frac{(\lambda_{\max} - n)}{(n-1)} \tag{7}$$

Here, *n* is the no. of criteria which is 4 in this particular case and thus CI is 0.0034 upon solving equation (7).

Table 3 Relative index values

N	1	2	3	4	5	8	9	10	11
RI	0	0	0.58	0.9	1.12	1.41	1.45	1.48	1.49

After that, a consistency ratio (CR) is evaluated to compare whether the process for identifying criteria weight is accurate and related to the standard value presented in Table 3. A revision is expected in the pair-wise comparison of AHP weights if this CR results above 0.1 till a lower value is achieved (Wang and Yang, 2007). CR is calculated as a ratio of CI and RI, refer to equation (8) below:

$$CR = \frac{CI}{RI} \tag{8}$$

From Table 3, *n* is equal to 4; hence RI for 4 criteria is 0.9, and CR is calculated above as 0.0038. This value of CR is comfortably less than 0.1, so it is proved that the AHP exercise presented here is highly consistent.

4.3 Prioritisation using TOPSIS method

The column normalisation matrix is prepared using

$$N_{ij} = \frac{X_{ij}}{\sqrt{\sum_{i=1}^{m} X_{ij}^2}}, \qquad i = 1, 2, 3, \ldots, m \text{ and } j = 1, 2, 3, \ldots, n \tag{9}$$

The next step is to multiply the columns of new matrix N[mn] with the criteria weights obtained by AHP to obtain a new matrix.

$$R_{ij} = N_{ij} \times W_j \tag{10}$$

Further, the positive ideal solution (R^+) and the negative ideal solution (R^-) are calculated as per the given formula with the equations below:

$$\begin{aligned} R^+ &= \left\{ \left(\sum_i^{\max} R_{ij} / j \in J \right), \left(\sum_i^{\min} R_{ij} / j \in J \right) \middle/ i = 1, 2, 3, \ldots, m \right\} \\ &= \left\{ R_1^+, R_2^+, R_3^+, \ldots, R_n^+ \right\} \end{aligned} \tag{11}$$

Similarly,

$$\begin{aligned} R^+ &= \left\{ \left(\sum_i^{\min} R_{ij} / j \in J \right), \left(\sum_i^{\max} R_{ij} / j \in J \right) \middle/ i = 1, 2, 3, \ldots, m \right\} \\ &= \left\{ R_1^-, R_2^-, R_3^-, \ldots, R_n^- \right\} \end{aligned} \tag{12}$$

where $J = (j = 1, 2, \ldots, n)/j$ is set of beneficial criteria (larger the-better type) and $J' = (j = 1, 2, \ldots, n)/j$ is set of non-beneficial criteria (small-the-better type), refer Table 4.

Now, the separation (distance) between alternatives is measured by the n-dimensional Euclidean distance. The separation of each alternative from the positive-ideal solution is given as follows:

$$S_i^+ = \sqrt{\sum_{j=1}^{n} \left(R_{ij} - R_j^+ \right)^2} \qquad i = 1, 2, 3, \ldots, m \tag{13}$$

and

$$S_i^- = \sqrt{\sum_{j=1}^{n} \left(R_{ij} - R_j^- \right)^2} \qquad i = 1, 2, 3, \ldots, m \tag{14}$$

The relative closeness of all alternatives from the ideal solution was observed using the given equation, and then alternatives are ranked in descending order of the relative closeness.

$$C_i = \frac{S_i^-}{S_i^+ + S_i^-} \tag{15}$$

The final rankings are done as mentioned above and shown in Table 5.

Table 4 Normalised matrix

Notation	*Criteria*	*Density, ρ, (kg/m^3)*			*Latent heat, L, (kJ/kg)*			*Thermal conductivity, K, (W/m-K)*			*Specific heat, Cp, (kJ/kg-K)*		
	Criteria weights	*0.263*			*0.141*			*0.141*			*0.455*		
	PCM candidates	*ρ*	N_{ij}	R_{ij}	*L*	N_{ij}	R_{ij}	*K*	N_{ij}	R_{ij}	*Cp*	N_{ij}	R_{ij}
A1	PlusICE X120	1,245	0.246	0.065	180	0.284	0.040	0.360	0.247	0.035	1.5	0.214	0.097
A2	PlusICE H120	2,220	0.439	0.115	120	0.189	0.027	0.506	0.348	0.049	1.51	0.215	0.098
A3	PlusICE A118	1,450	0.287	0.075	340	0.536	0.076	0.500	0.344	0.048	2.7	0.385	0.175
A4	PlusICE S117	1,450	0.287	0.075	160	0.252	0.036	0.700	0.481	0.068	2.61	0.372	0.169
A5	PlusICE H115	2,200	0.435	0.114	100	0.158	0.022	0.503	0.346	0.049	1.505	0.214	0.097
A6	PureTemp 108	870	0.172	0.045	180	0.284	0.040	0.250	0.172	0.024	2.17	0.309	0.141
A7	PlusICE H105	1,700	0.336	0.088	125	0.197	0.028	0.500	0.344	0.048	1.5	0.214	0.097
A8	RT100	880	0.174	0.046	124	0.195	0.028	0.200	0.137	0.019	2	0.285	0.130
A9	RT100HC	1,000	0.198	0.052	180	0.284	0.040	0.200	0.137	0.019	2	0.285	0.130
A10	PlusICE A95	900	0.178	0.047	205	0.323	0.046	0.220	0.151	0.021	2.2	0.313	0.143
A11	PlusICE X95	1,215	0.240	0.063	140	0.221	0.031	0.360	0.247	0.035	1.51	0.215	0.098
A12	RT90HC	950	0.188	0.049	170	0.268	0.038	0.200	0.137	0.019	2	0.285	0.130
A13	PlusICE X90	1,200	0.237	0.062	135	0.213	0.030	0.360	0.247	0.035	1.51	0.215	0.098
	Max			0.115			0.076			0.068			0.175
	Min			0.045			0.022			0.019			0.097

Table 5 Ranking of PCMs based upon relative closeness value (C_i)

Notation	*Density (kg/m^3)*	*Latent heat (kJ/kg)*	*Thermal conductivity (W/m-K)*	*Cp (kJ/kg-K)*	*Distance from positive solution S_i^+*	*Density (kg/m^3)*	*Latent heat (kJ/kg)*	*Thermal conductivity (W/m-K)*	*Cp (kJ/kg-K)*	*Distance from positive solution S_i^-*	*Relative closeness Ci*	*Ranking*
CW	*0.263*	*0.141*	*0.141*	*0.455*		*0.263*	*0.141*	*0.141*	*0.455*			
A1	0.003	0.001	0.001	0.006	0.105	0.000*	0.000*	0.000*	0	0.031	0.226	11
A2	0	0.002	0.000*	0.006	0.093	0.005	0.000*	0.001	0.000*	0.076	0.450	3
A3	0.002	0	0.000*	0	0.045	0.001	0.003	0.001	0.006	0.103	0.699	1
A4	0.002	0.002	0	0.000*	0.057	0.001	0.000*	0.002	0.005	0.093	0.620	2
A5	0.000*	0.003	0.000*	0.006	0.096	0.005	0	0.001	0.000*	0.075	0.439	4
A6	0.005	0.001	0.002	0.001	0.096	0	0.000*	0.000*	0.002	0.047	0.329	7
A7	0.001	0.002	0.000*	0.006	0.097	0.002	0.000*	0.001	0	0.052	0.350	6
A8	0.005	0.002	0.002	0.002	0.106	0.000*	0.000*	0	0.001	0.033	0.234	10
A9	0.004	0.001	0.002	0.002	0.098	0.000*	0.000*	0	0.001	0.038	0.276	8
A10	0.005	0.001	0.002	0.001	0.094	0.000*	0.000*	0.000*	0.002	0.051	0.352	5
A11	0.003	0.002	0.001	0.006	0.108	0.000*	0.000*	0.000*	0.000*	0.025	0.190	12
A12	0.004	0.001	0.002	0.002	0.101	0.000*	0.000*	0	0.001	0.037	0.264	9
A13	0.003	0.002	0.001	0.006	0.109	0.000*	0.000*	0.000*	0.000*	0.024	0.183	13

Note: *Values are not precisely ‘0’ but nearly equal to zero, shown after rounded off.

5 MODM examination

Results from MADM are primarily influenced by the criteria weights obtained through the AHP exercise of pair-wise comparisons. Thus results obtained by the MADM tools are not directly applied to the final selection of the PCM for thermal energy storage applications. It is mainly because of high-cost intervention in such type of system. Henceforth, the objective functions of Ashby's approach are considered an accessible and useful tool of MODM. In this, system objectives are examined for consistency with the ranking goal. This is done by plotting the results of two objective functions on a single plot for different alternatives.

As previously discussed, thermal energy storage must possess high thermal energy storage density and capable of charging and discharging at a high heat transfer rate. LHTES serves both requirements, and thus selection of good PCM is essential. In the light of the above discussion, thermal energy storage per unit volume and thermal diffusivity are taken for MODM examination and both functions are intended to be maximised. Thus materials lying within the outer zone of the chart are preferred.

The first function is identified for the thermal energy storage per unit volume.

$$f_1 = \left(L + C_p \cdot \Delta T\right) \cdot \rho \quad (16)$$

where

- L (kJ/kg) is the latent heat of fusion
- C_p (kJ/kg-K) its specific heat capacity,
- ΔT the temperature interval of charge/discharge, and
- ρ (kg/m^3) is the density of PCMs.

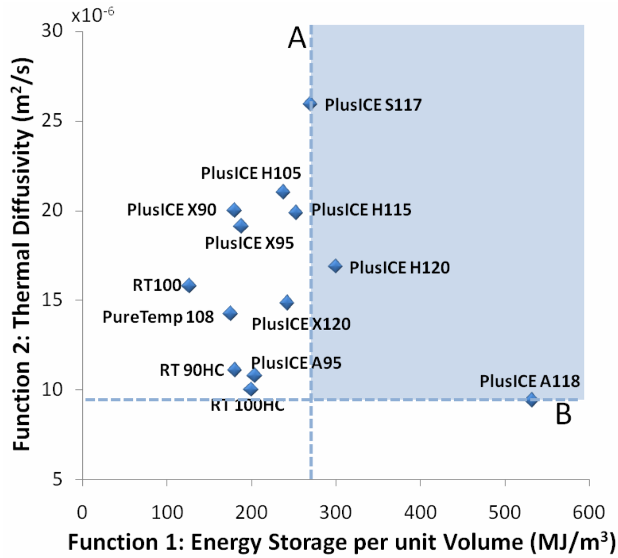
The second function, denoting the equivalent PCM thermal diffusivity, can be expressed as:

$$f_2 = \frac{k \cdot \Delta T}{\left(L + C_p \cdot \Delta T\right) \cdot \rho} \quad (17)$$

where k (W/(m-K)) is the thermal conductivity.

The behaviour is drawn between these two-function taking temperature intervals of 10°C for pre-screened PCM candidates as shown in Figure 5. A vertical line passes through the PlusICE S117 is for the maximum value of thermal diffusivity. In contrast, the horizontal line is passing through the PlusICE A118 which has a maximum value of thermal energy storage per unit volume. The preferred choice of PCMs lies in the shaded zone captured by these two lines, as discussed earlier since both functions are to be maximised. Hence, three PCMs namely PlusICE S117, PlusICE A118 and PlusICE H120 lie in the preferred selection zone, and these are also in the top 3 ranks resulted from the TOPSIS is done. If results from the MODM examination do not support the MADM examination, then the process is repeated from the very initial stage of the pre-screening of PCMs keeping system goals in mind. The process will continue till a good agreement is achieved between objective function examination and MADM ranking. The decision of relative weights of different properties is highly sensitive to rankings of the MADM examination. Thus it must be done very carefully. After these selection processes, the top selected PCMs will be subject to laboratory tests and final selection will be done by judgments from the previous considerations.

Figure 5 MODM examination of prescreened PCMs (see online version for colours)



6 Results and discussion

A systematic approach is quite essential to standardise the selection process for the PCM from the commercially available PCMs to design efficient and effective thermal energy storage to be integrated within a solar-powered single-effect vapour absorption system. Hence, exercise is performed for the selection of PCM using MADM tools. First prescreening was made to select the commercially available PCMs those are having the phase transition temperature between 90 and 120°C. Thirteen PCMs cleared this process of prescreening. Then, selection out of these has to be made and to perform this systematically MADM tools AHP, TOPSIS, and MODM performed.

The latent heat of fusion, thermal conductivity, density, and specific heat were chosen as criteria. It is to note that mostly latent heat of fusion, density along with the temperature of the phase transition to design the TES. However, there are several other issues associated with the design of TES such as reduced heat transfer rate, low energy storage density within a narrow operational range, etc. Therefore, it was quite essential to focus on these issues with the proper PCM selection incorporating stated thermo-physical properties in the selection process. As stated above, four criteria have been finalised to have a more scientific and systematic approach. Hence, these criteria processed for pairwise comparison to identify the criteria weights using AHP. The identified criteria weights are evaluated through the AHP, and results show the right consistency between the different thermo-physical properties. The values assigned are taken from the (Xu et al., 2017) because of the similar nature of the application. The obtained value of CR is

0.0034 which is comfortably in the limit of the standard limit of 0.1. Thus, pair-wise judgments made are highly consistent.

Further, TOPSIS is used to prioritise the candidates based upon the thermo-physical properties using the criteria weights obtained through the AHP. Finally, the ranking is done and showed in Table 5. Based upon the results obtained through TOPSIS, a ranking is obtained for prescreened PCM candidates as A3-A4-A2-A5-A10-A7-A6-A9-A12-A8-A1-A11-A13. Since the objective is to select PCM for latent thermal energy storage of a solar-powered vapour absorption system; it is to be adequately examined as cost intervention is high. Further, to validate the results noted from the TOPSIS, MODM is usually prescribed. MODM examination here is done using two functions; thermal energy storage per unit volume and thermal diffusivity for all prescreened PCMs. The behaviour is examined through the plot between these two functions and PCMs are identified, which comes in the zone of maximum thermal energy storage per unit volume and maximum thermal diffusivity. Refer Figure 5, the zone of selection has been shown, capture using lines A and B. Results validate the TOPSIS ranking as top 3 of the ranking are in the zone of preferred selection. However, if MODM results and TOPSIS results are not complementary, then revision is expected in the relevant criteria weights of different properties established through the AHP. In the present scenario, TOPSIS results have been validated with the MODM examination.

7 Conclusions

A systematic approach is essential to streamline and standardise the selection process of PCM to design efficient and useful thermal energy storage system for a solar-powered single-effect vapour absorption system. Therefore, the first 13 commercially available PCMs were prescreened using the operational temperature range between 90 and 120°C. Thermo-physical properties have been identified as criteria and a pair-wise judgment exercise is done to finalise the criteria weights through AHP. A consistency check is also performed using a consistency ratio value of 0.0038, which is comfortably within the prescribed limit if 0.1. Further, PCMs prescreened in this exercise have been assigned ranking using TOPSIS which is further validated using the MODM examination. As a result of his algorithm PlusICE A118 is found to be the best PCM among the prescreened PCM candidates followed by the PlusICE S117 and PlusICE H120.

Further research is expected to accommodate the life cycle cost analysis and issues related to the reactivity of PCMs with the containment materials, degradation of thermal properties of PCMs concerning operated thermal cycles, decomposition of PCMs, etc. in the algorithm itself. This might be very helpful to save energy, environment and cost. Thermo-physical properties of PCMs are needed to be customised so that design of the thermal energy storage system could be carried out for a desired operational range of temperature.

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Nomenclature

AHP	Analytical hierarchy process.
AM	Arithmetic mean.
CI	Consistency index.
CR	Consistency ratio.
CV	Consistency value.
GHS	Globally harmonised system.
LHTES	Latent heat thermal energy storage.
MADM	Multi-attribute decision making.
MODM	Multi-objective decision making.
NFPA	National Fire Protection Association.
PCM	Phase change material.
RI	Relative index.
SHTES	Sensible heat thermal energy storage.
TES	Thermal energy storage.
TOPSIS	The technique of order preference similarity to the ideal solution.
VAM	Vapour absorption machine.