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Review on phase change materials for sub-zero temperature application in transport refrigeration

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This paper reviews the use of phase change materials (PCMs) in road transport refrigeration. The use of thermal energy storage systems in transport refrigeration focusing particularly on PCMs that have been used in recent years is reviewed. The majority of PCMs are used in building applications for space heating and cooling, greenhouse heating applications, solar cookers, and storage of solar energy for water heating. However, there is minimal focus in the literature on their use in road transport refrigeration in low temperature (sub-zero) application for maintaining frozen foodstuff (products). The focus of this work is on latent heat storage (LHS) materials used in road transport refrigeration and their benefits in the refrigeration of perishable foodstuffs for short- and long-distance transportation. The benefits of using LHS materials over a conventional mechanical vapour compression system are explored with reference to the environmental impact and their disadvantages in the long term. This paper also focuses on the need to develop new PCMs with high thermal cycles and minimal degradation to ensure their successful use in the transport refrigeration industry. Criteria for selecting suitable PCMs for different applications were summarised, and classification of PCMs based on their melting temperature and latent heat were tabulated. Heat transfer materials for increasing PCM performance were analysed as well as the effect of container material corrosion on PCM stability. The different thermal techniques used for determining the properties of PCMs were summarised, and the accuracy of each technique was explored based on similar research work by other researchers. The PCMs that have been used in transport refrigeration as well as the thermo-physical criteria that are needed for different applications were analysed.

Keywords: eutectic, global warming potential, latent heat of fusion, phase change material, thermal energy storage

Oorsig van faseveranderingsmateriaal vir sub-zero temperatuurtoepassings in verkoelingsvervoer: Hierdie artikel bied 'n oorsig van die tradisionele gebruik van faseveranderingsmateriaal (FVM) in verkoelingsvervoer. Die meerderheid faseveranderingsmateriale in bouwerk en konstruksie word vir ruimtelike verwarming en verkoeling, kweekhuis-verhitting, kook met sonkrag, en die berging van son-energie vir waterverhitting gebruik. Daar is egter 'n merkbare afwesigheid van literatuur oor die aanwending van faseveranderingsmateriaal vir gebruik om bevrore voedselprodukte te bewaar. Hierdie oorsig fokus op latente hittebewarings (LHB) materiale se gebruik in padvervoer by 'n lae temperatuur (sub-zero), en van die voordele vir die verkoeling van bederfbare voedsel oor kort- en lang-afstande. Die voordele van die gebruik van latente hitte-bewaringsmateriaal, eerder as 'n konvensionele meganiese verdampings-kompressiesisteem, word ondersoek met die klem op die omgewingsimpak en moontlike langtermyn nadele. Die studie fokus ook op die noodsaaklikheid om nuwe faseveranderingsmateriaal met hoë termiese siklusse en minimale degradering te ondersoek, ten einde die suksesvolle gebruik in verkoelingsvervoer oor die langtermyn te verseker. Kriteria vir die seleksie van toepaslike faseveranderingsmateriaal word opgesom, en 'n klassifikasie van faseveranderingsmateriaal, gebaseer op smelttemperature en latente warmte, word getabuleer. Faseveranderingsmateriaal en die oordrageienskappe daarvan is ontleed ten einde die eienskappe van faseveranderingsmateriaal op te som, en die akkuraatheid van elke navorsingstegniek word beoordeel op grond van soortgelyke studies wat deur ander navorsers publiseer is. Die faseveranderingsmateriaal wat in verkoelingsvervoer gebruik word, is empiries ontleed, en termiese-fisiese kriteria wat noodsaaklik is vir verskillende toepassings is ook onder die vergrootglas geplaas.

Sleutelwoorde: Eutekties, globale verhittingspotensiaal, latente smeltwarmte, faseveranderingsmateriaal, termiese energiebewaring.

Introduction

Nowadays, due to population growth, there is a rising demand for frozen and chilled products by consumers (Fioretti et al., 2016). Refrigeration is therefore necessary for preserving the quality, safety and prolonging the shelf-life of temperature-sensitive foodstuffs. Transport refrigeration of perishable foodstuffs is currently dominated by the use of a mechanical vapour compression system that utilises a refrigerant as a medium to successfully maintain the quality of foodstuffs at a set temperature However, there is a need for an alternative refrigeration system that does not use high global warming potential (GWP) refrigerants. Thermal energy storage systems (TESS) with PCMs focusing on LHS could be an option to reduce the environmental impact associated with greenhouse gas emissions (Anisur et al., 2013). South Africa has committed to the phasing-out of the use of refrigerants that deplete the ozone layer, as amended in the Montreal Protocol agreement on substances that deplete the ozone layer (Programme, 2016). The rise in greenhouse gas emissions is the driving force behind the development of renewable energy sources (Sharma et al., 2009). To successfully use PCMs as alternative refrigeration systems, the system performance has to be of the same standard as the conventional mechanical vapour compression system. PCMs with latent heat energy storage work by utilising three fundamental activities: charging (freezing), storing thermal energy, and discharging (melting) (Fernandes et al., 2012, Dincer and Rosen, 2011). When consideration energy consumption, greenhouse gas emissions and cost, the development of sustainable energy sources with TESS is a promising alternative for transport refrigeration. The use of PCMs could save up to 40% of greenhouse gas emissions that are emitted by a vapour compression refrigeration system powered by a diesel engine (Tassou et al., 2009). The conventional vapour compression refrigeration system has high noise levels during operation due to moving parts, and requires extensive maintenance. The operation of a eutectic system with LHS materials is different from a conventional refrigeration system, as a cold source is provided by the storage material, and the eutectic system operates quietly, is reliable and provides rapid cooling for a certain period of time (Tassou et al., 2012). When analysing the current literature on major PCM applications, it is evident that little research has been done on their use in transport refrigeration for low temperature application.

The majority of thermal energy storage materials are used in building application, solar energy storage application, solar cooker, and greenhouse application (Anisur et al., 2013). There are different application areas where PCMs have been used. Early application of PCMs includes cold storage in railroad and trucking transportation with the use of eutectic plates filled with PCM, while water, ice, and eutectic salts were used as the storage material. PCMs have been used since the 1800s as seat warmers for British railroad cars in winter. Sodium thiosulfate pentahydrate with a melting and freezing temperature of 44.4 °C placed in rubber bags was used as a storage media (Dincer and Rosen, 2011).

In rural areas of South Africa where there is no access to the power (electricity) grid, PCMs can be used for maintaining frozen food products after they have been transported from urban areas. South Africa still faces power cuts due to high electricity demands; the use of PCMs can assist in preserving foodstuffs during power cuts. Oró et al. (2012b) studied the use of PCMs to preserve food products in household refrigerators in order to simulate the performance of a non-refrigerated vehicle during transportation and found that the frozen product temperature was maintained when PCMs were used. Warm climatic conditions in South Africa and long distances between farms and cities require effective and innovative refrigeration systems during transportation to prevent food spoilage. In short- and long-distance transportation between cities, the use of PCMs as an innovative system, can keep food products fresh and assist in alleviating greenhouse gas emissions. Although the vast majority of developed PCMs have high latent heat of fusion, their range of melting temperatures makes them unsuitable for maintaining the quality of frozen foodstuff in transport refrigeration. This review illustrates the need for better thermo-physical PCM properties that can be utilised in transport refrigeration.

Phase change materials (PCMS)

When a material changes phase from solid to liquid, it absorbs heat energy and when it changes from liquid to solid it releases heat energy. This phase change process is used for storing thermal energy in PCMs (Dincer and Rosen, 2011). The classification of PCMs affects the area in which they will be used and the container materials used are important to ensure thermal energy storage during charging and discharging. The following are different classifications of the PCM and container geometry that are normally used.

a) Organic

Organic materials with their eutectic mixtures have been successfully implemented in many commercial applications, such as food industries, space heating in buildings, cooling of electronic devices, refrigeration and air conditioning (Xu et al., 2015). This organic material has low thermal conductivity which in turn requires a large heat transfer surface area (Alva et al., 2017, Xu et al., 2015). Organic materials are classified as paraffin and non-paraffin. These materials have high melt-freeze cycles without phase segregation and degradation of the latent heat of fusion of the material.

PCMs classification

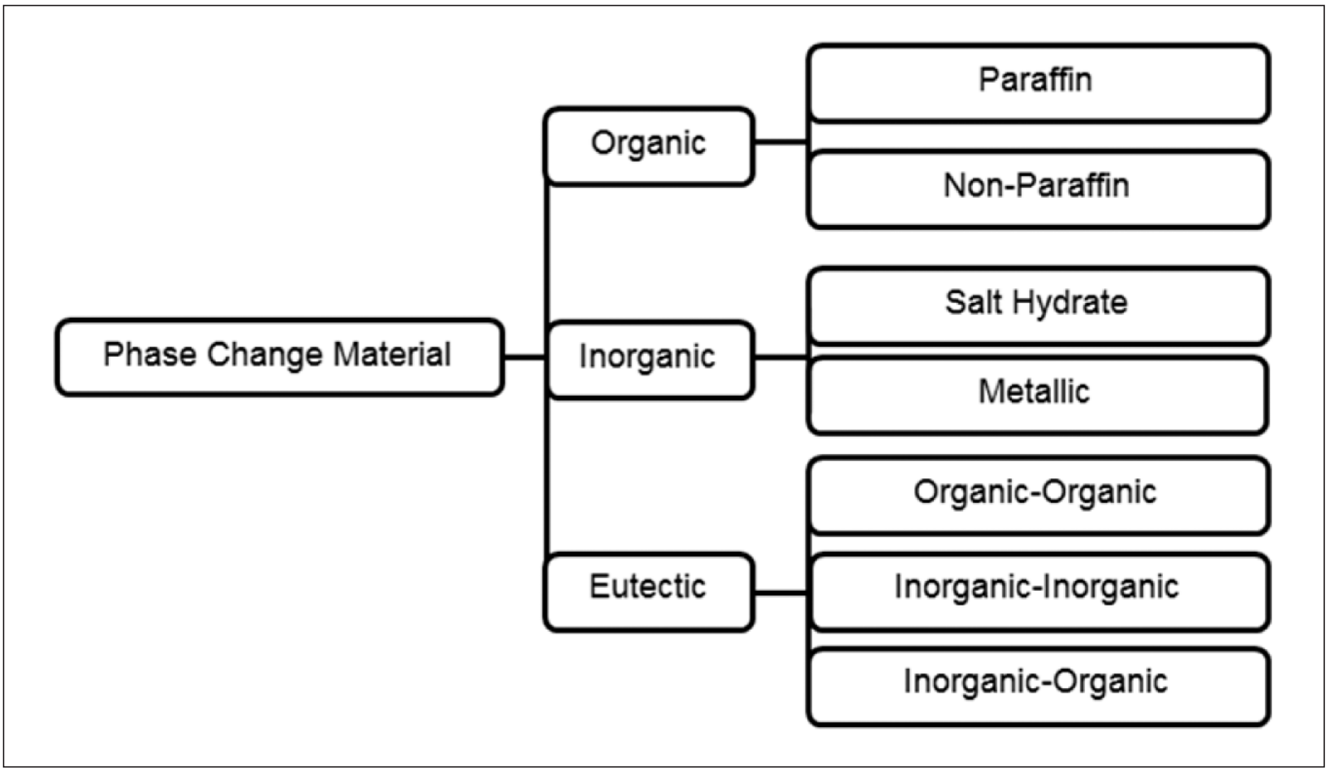

FIGURE I: Classification of PCMs (Abhat, 1983)

- Paraffin

Paraffin waxes are widely used as they are cheap with reasonable thermal storage density. Systems that use paraffin are considered to have a long freezing-melting cycle (Sharma et al., 2009). Paraffin waxes and pure paraffin still possess better properties at 1 000 to 2 000 melt/freeze cycles (Alva et al., 2017). The advantage with the use of paraffin is that its melting temperature and latent heat of fusion increase with an increase in carbon atoms within certain limits (Zalba et al., 2003). Its undesirable properties include: (i) very low thermal conductivity, (ii) non-compatible with plastic containers and (iii) they are moderately flammable. Paraffin is less expensive, safe, and non-corrosive.

- Non-paraffin

Non-paraffin consists of a large category of materials that can be used as phase change storage. Their advantage over paraffin with similar properties is that they have their own properties with variation in temperature. Fatty acids are organic compounds with heat of fusion in a similar range to paraffin. Fatty acids are also known for the reproducible melting and freezing cycles, they have little or no supercooling required and their disadvantage is their cost which is 2 to 2.5 times higher than that of paraffin (Sharma et al., 2009).

Fatty acids were investigated for use in solar cooling and heating applications (Sarı and Kaygusuz, 2001). Table I shows selected paraffin and non-paraffin PCMs. Based on their melting temperatures it can be concluded that the majority of these PCMs are suitable for use in solar heating. They are, however, not suitable in maintaining frozen food products based on their melting temperatures.

b) **Inorganic**

Inorganic materials are also categorised as salt hydrate and metallic. These materials do not supercool appreciably and no degradation of the heat of fusion due to thermal cycling takes place. There are some salt hydrates that supercool from the liquid state before crystallisation due to poor nucleation properties, but a nucleation agent can be added to help with crystallisation. Salt hydrates have high latent heat of fusion and high thermal conductivity but their disadvantage is incongruent melting which takes place when the salt is not completely soluble in water at melting point (Sharma et al., 2009). Metallic PCMs have not been used due to weight limitations, but their advantage is that they have high thermal conductivity and high heat of fusion per unit volume (Sharma et al., 2009). Table II summarises inorganic PCMs that are used.

c) **Eutectic**

A eutectic material is a combination of two or more materials and is classified as organic and inorganic compounds. The eutectic mixture freezes and melts without segregation and also discharges thermal energy at a constant temperature (Oró et al., 2012a). An aqueous solution, salt hydrates, salts, and water are also considered to be eutectic mixtures. Table III lists PCMs that can be used for the preservation of frozen products.

TABLE I: Thermal properties of selected paraffin and non-paraffin PCMs (Abhat, 1983, Sharma et al., 2009, Sharma and Sagara, 2005)

Type	Composition	Melting temperature (°C)	Heat of fusion (KJ/Kg)	Density (Kg/m³)	Thermal conductivity (W/mK)
Paraffin	6106	42 – 44	189	900	0.21 (solid)
	P116	45 – 48	210	817	–
	6035	58 – 60	189	920	0.21 (solid)
	6403	62 – 64	189	912	0.21 (solid)
	6499	66 – 68	189	930	0.21 (solid)
Non-Paraffin	Formic acid	7.8	247	1226.7	–
	Glycerin	17.9	198.7	1260	–
	D – Lattic acid	26	184	1249	–
	Caprylone	40	259	–	–
	Camphene	50	238	–	–
Fatty Acid	Capric acid	32	152.7	878 (l), 1004 (s)	0.153
	Lauriic acid	44	177.4	862 (l), 1007 (s)	0.147
	Stearic acid	69	202.5	848 (l), 965 (s)	0.172
	Palmatic acid	64	185.4	850 (l), 989 (s)	0.162
	Myristic acid	58	186.6	861 (l), 990 (s)	

TABLE II: Summarised inorganic PCMs (da Cunha and Eames, 2016, Abhat, 1983, Sharma et al., 2009)

Type	Compond	Melting temperature (°C)	Heat of fusion (KJ/Kg)	Density (Kg/m³)	Thermal conductivity (W/mK)
Salt hudrates	Water	0	333	920	1.60 (s), 0.61 (l)
	$KF.4H_2O$	18.5	231	1447 by 20 °C	–
	CaCl2.6H2O	29.7	171	1710 by 25 °C	–
	$Na_2SO_4.10H_2O$	32.4	254	1485 (s)	0.544
	$Ba(OH)_2.8H_2O$	78	267	2180 (s)	1.17 (s)
Metallic	Gallium	30	80.3	–	–
	Cerrolow eutetic	58	90.9	–	–
	Bi-Cd-In eutetic	61	25	–	–
	Cerrobend eutetic	70	32.6	–	–
	Bi-Pb-In eutetic	70	29	–	–

TABLE III: Properties of low-temperature PCMs (Abhat, 1983, Sharma et al., 2009, Liu et al., 2012, Oró et al., 2012b, Li et al., 2013)

Type	Composition	Melting temperature (°C)	Heat of fusion (KJ/Kg)	Density (Kg/m³)	Thermal conductivity (W/mK)
Eutetic Salt Water	NaBr (40.3 wt.%) + H2O	-28	175.69	–	–
Eutetic Salt Water	NaCl (22.14 wt.%) + H2O	-21.2	222	1165 (s), 1108 (l)	–
Eutetic Salt Water	$NaNO_3$+ H_2O + additives	-18	306	1300	0.5 – 0.7
Eutetic Salt Water	$NaNO_3$ (36.9 wt.%) + H_2O	-17.7	187.79	–	–
Eutetic Salt Water	NH_4NO_3 (41.2 wt.%) + H_2O	-17.35	186.29	–	–
Eutetic Salt Water	$Ca(NO_3)_2$ (35 wt.%) + H_2O	-16	199.35	–	–
Eutetic Salt Water	NH_4Cl (19.5 wt.%) + H_2O	-16	248.44	–	–
Eutetic	Diethylene glycol	-10	247	1200 (l)	–
Eutetic Organic	Tridecane (40 wt.%) + Dodecane (60 wt.%)	-9.7	159	–	–
Organic	n-Dodecane	-9.6	216	–	2.21 (l)
Eutetic Salt Water	$BaCl_2$ (22.5 wt.%) + H_2O	-7.8	246.44	–	–
Organic	Triethylene glycol	-7	247	1200 (l)	–
Eutetic Organic	Tridecane (80 wt.%) + Dodecane (20 wt.%)	-5.4	126	–	–
Organic	n-Tridecane	-5.3	154.5	756 (l)	–
Eutetic Organic	Tetradecane + octadecane	-4.02	227.52	–	–
Eutetic Salt Water	KNO_3 (9.7 wt.%) +H_2O	-2.8	296.02	–	–
Water	H_2O	0	333	920 (s)	1.6 (s), 0.61 (l)

From Table III it can be seen that the majority of the PCMs are eutectic saltwater solutions. The melting and freezing temperature of water is 0 °C. The freezing point of water can be lowered by adding salt. As salt is added to water the freezing point of water is lowered until it reaches a eutectic point of the saltwater solution (Li et al., 2013). At this eutectic point, the saltwater solution melts and freezes at the same temperature. Saltwater solutions are preferred due to their high latent heat of fusion and melting temperature. To have a variation in melting temperatures, the salt quantity in a saltwater solution can be varied and it is clearly shown from the Table that sub-zero temperature PCMs are extensively available as saltwater solutions. Degradation at high thermal cycles of these saltwater PCMs limits their applications and reliability, since loss of latent heat storage capacity during freezing after extended use of the PCM is always the case (Cantor, 1979).

PCM container – eutectic plates

The PCM containers are filled with PCM solution in a liquid state and then frozen to the desired temperature point depending on the PCM being used. The application of LHS is limited by the insufficient stability between the storage material and container. This is due to corrosion between the container and the PCM material and poor stability of the PCM properties due to thermal cycling (Zalba et al., 2003). When considering the layout of eutectic plates in refrigerated vehicles, the layout of these plates is not optimised as they are usually mounted on the inside top of a roof which leads to non-uniform temperature distribution which can cause quality deterioration of the cargo. The eutectic plates filled with a PCM having poor thermo-physical properties and without optimisation of the plate layout, might be the reason why few developments for the use of LHS systems in transport refrigeration have been made. Optimal utilisation of the eutectic plate’s layout must be ensured in order to achieve uniform temperature distribution inside the load space. From the published literature it is evident that the commonly used container forms are rectangular, shell, tubular and cylindrical in shape (Agyenim et al., 2010). After the desired PCM’s thermo-physical properties are achieved, the container material to be used has a direct impact on the heat transfer of the system (Agyenim et al., 2010). Surface pitting and degradation of container material contaminates PCM solutions, thereby contributing to the loss of PCM thermal storage capacity. When the storage capacity is reduced, it will directly affect the preservation of frozen products during service as there will be low heat transfer between the products and the container surface. Ferrer et al. (2015) and Oró et al. (2013) studied the corrosion between PCMs and metal containers and found that copper and carbon steel have high corrosion rates when used as PCM containers. The long-term use of a PCM and container material requires proper selection, as failure to do so can affect the performance of the thermal storage system.

Heat transfer enhancement in eutectic plates – When a latent heat storage material undergoes melting, there is a solid-liquid interface present that continues to move away from the container surface (heat transfer surface). This decreases the heat flux due to an increase in thermal resistance caused by the growing layer of the solid-liquid interface (Cabeza et al., 2002). Other techniques for heat transfer enhancement involve the insertion of the metal matrix in the PCM. Cabeza et al. (2002) tested the use of stainless steel, copper, and graphite matrix as heat transfer enhancement materials with water as the PCM. The highest heat transfer was observed with the use of copper and graphite matrix with graphite matrix showing the highest heat transfer rate. Oró et al. (2012b) successfully used a stainless steel container for encapsulating the PCM. Two different PCMs with the latent heat of fusion of 306 and 233 KJ/Kg were used with melting temperatures of -18 and -21.3 °C respectively. The PCMs were used to maintain frozen food at low temperature. The PCM containers were inside a vertical freezer when the electrical power of the freezer was switched off for 12 to 24 hrs and it was concluded that the PCMs used provided great benefits by maintaining low temperature without the use of a refrigeration system (Oró et al., 2012b). This study of the use of PCMs with no refrigeration system shows that transportation of frozen products can be successfully achieved with no deterioration of the quality of the transported products. Gin and Farid (2010) used aluminium as a PCM container. The aluminium plates were placed on three sides of the inside walls of a vertical freezer. A eutectic composition of ammonium chloride and water was used as PCM and they concluded that the use of PCM to maintain frozen food at low temperature preserves the quality of frozen food.

Criteria for PCM selection

There are criteria to be met to ensure the successful application of LHS materials. Table IV shows the important characteristics of PCMs that need to be considered for different areas of application. Even though some PCMs have poor properties, they can be improved to suit the need of the application, for example nanoparticles can be added to improve thermal conductivity of a particular PCM (Pielichowska and Pielichowski, 2014).

TABLE IV: Summary of the characteristics required for a PCM (Anisur et al., 2013, Oró et al., 2012a)

Properties	Criteria
Thermo-physical properties	High latent heat of fusion
	High thermal conductivity in solid and liquid phase increases thermal charge and discharge rate
	High density allows for high energy storage density and it requires a small volume container for the system
	An appropriate freezing-melting temperature is desired
	High thermal cycles
Nucleation and crystal growth	High crystal growth to facilitate with energy demand during heat recovery is required
	High nucleation rate is required to ensure that melting and freezing process occurs at the same temperature
Chemical properties	No corrosion to the encapsulating material
	Non-toxic and non-explosive
	No degradation of material is desired after freezing-melting cycle
Economics	Cost effective – cheap
	Available

Thermal properties required

- Latent heat

When a material changes phase from solid to liquid, it absorbs heat energy, and when it changes from liquid to solid it releases heat energy. A PCM that undergoes phase transition is a LHS material. This phase change process is used for storing thermal energy in PCMs (Dincer and Rosen, 2011). The use of PCMs in low-temperature application requires the use of LHS materials. The benefits of LHS materials are their high energy storage density per unit volume and per unit mass, and they store heat energy at a constant temperature, corresponding to the melting temperature of the PCM (Sharma and Sagara, 2005). The latent heat energy released by a PCM during melting from a solid to liquid phase is the property which is useful for maintaining food products at their required temperature. The higher the latent heat energy that a PCM can store, the less volume of the PCM will be required. High latent heat energy is preferred.

- Melting temperature

The melting temperature of a PCM determines the area of its application. There are different PCMs each with its own unique melting temperature: a PCM with a sub-zero melting temperature can be used for maintaining frozen foodstuffs, 0 °C to 18 °C melting temperature PCMs can find their application in food chilling, and a PCM with a melting temperature of 18 °C to 25 °C can be used in air conditioning. Other areas of application based on the melting temperature where PCMs can be used, are electronic device cooling, engine cooling in the automotive industry, space heating and cooling, and in the food industry for reducing the rise in food temperature (Pielichowska and Pielichowski, 2014).

- Thermal conductivity

A PCM's ability to conduct thermal heat is of high importance when latent heat materials are used. Low thermal conductivity in PCMs limits efficient utilisation of the stored thermal energy. To increase the utilisation of the latent heat energy, the thermal conductivity of PCMs should be improved (Li, 2013). A PCM with high thermal conductivity easily absorbs and releases latent heat energy.

Thermal property testing of PCMs

A PCM becomes reliable when it is chemically, thermally and physically stable after repeated thermal cycles. However, due to long use, the properties of the PCM may degrade and significant degradation is not desirable. Zalba et al. (2003) reviewed PCMs from different sources and pointed out that there is considerable inconsistency in the available data for the latent heat and melting temperatures of PCMs. The thermo-physical properties of the available PCMs are recommended to be evaluated before use by performing repeated thermal cycles in the laboratory (Rathod and Banerjee, 2013). By determining the melting and freezing characteristics of phase change LHS materials, their application can be assured (Abhat, 1983). There are measuring techniques for determining the thermal cycles and melting and freezing characteristics of PCMs. It is critically important to analyse the latent heat of sub-zero temperature PCMs using an accurate technique that can give the correct phase transition. The different techniques used are summarised as follows:

Differential scanning calorimeter (DSC)

The differential scanning calorimeter is a widely used laboratory technique for determining the heat of fusion and melting temperature of a PCM. The DSC measures the amount of heat energy required to increase the temperature of a sample and a reference material as a function of temperature (Rathod and Banerjee, 2013). The sample and reference material are heated and cooled in separate furnaces as shown in Figure II. The results from the DSC are presented in an energy-time-diagram (thermograph)-format and only a small quantity of the sample needs to be tested. From the available literature it is evident that many authors make use of the differential scanning calorimeter to determine the melting and freezing properties of PCMs. The DSC fails to offer meaningful results on the freezing point and degree of supercooling for salt hydrates PCMs (not suitable for testing PCMs that supercool) (Abhat, 1983). An experimental setup that uses thermostatic water bath as shown in Figure III is used by many researchers to determine the supercooling effect of salt hydrates and eutectic saltwater solutions (Yinping and Yi, 1999, Marín et al., 2003, Yilmaz S, 2010, Liu et al., 2015, He et al., 2012).

Differential thermal analysis (DTA)

The DTA technique works the same way as the DSC. The DTA differs from the DSC by using the same heating and cooling furnace as shown in Figure II. The DTA technique is older than the DSC technique, and a DTA is less sensitive to small heat change than a DSC (Klančnik et al., 2010).

Temperature-history method

Yinping and Yi (1999) developed a temperature-history method for determining the thermal conductivity, specific heat, melting temperature and heat of fusion of PCMs. Unlike DSC and DTA that use small samples for analysis, the properties of the samples tested by the DSC and the DTA technique usually differ from the bulk material used in practice. When a salt hydrate PCM is placed in a small container, an increase in supercooling is observed with a decrease in phase segregation (Abhat, 1983). The cost of DSC and DTA is high and this equipment cannot measure the thermo-physical properties of some PCMs simultaneously (Yinping and Yi, 1999). Marín et al. (2003) improved the temperature-history method by comparing results with those obtained from DSC, using pure paraffin C_{16} as PCM. The advantage of this method over DSC and DTA is that it is not complicated and is cost-effective. This technique makes use of hot and cold water baths and is able to clearly show supercooling of PCMs, unlike a DSC which cannot give a meaningful melting curve for saltwater solutions.

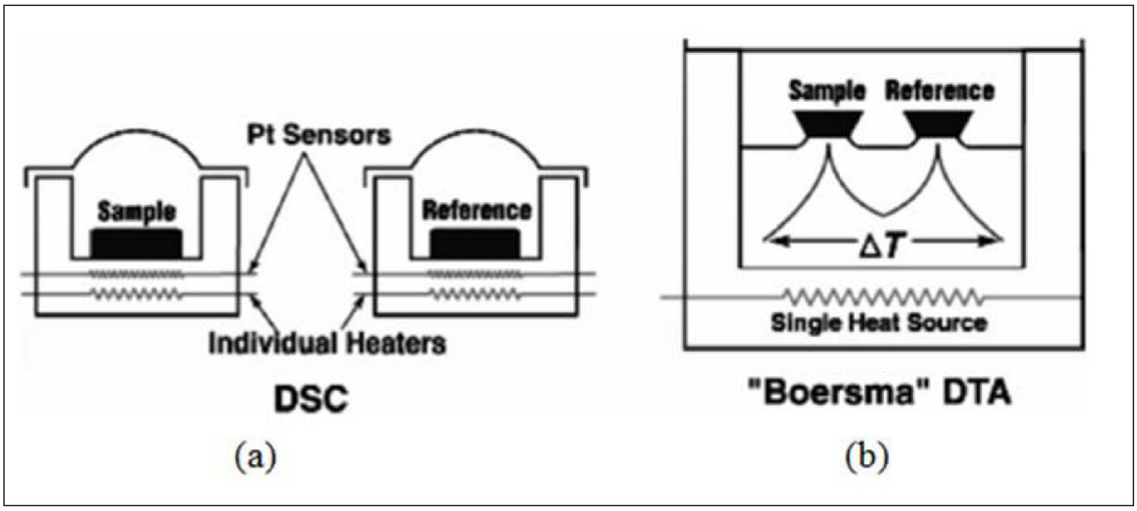

FIGURE II: Sample and reference material layout in a (a) DSC, and (b) DTA machine (Klančnik et al., 2010)

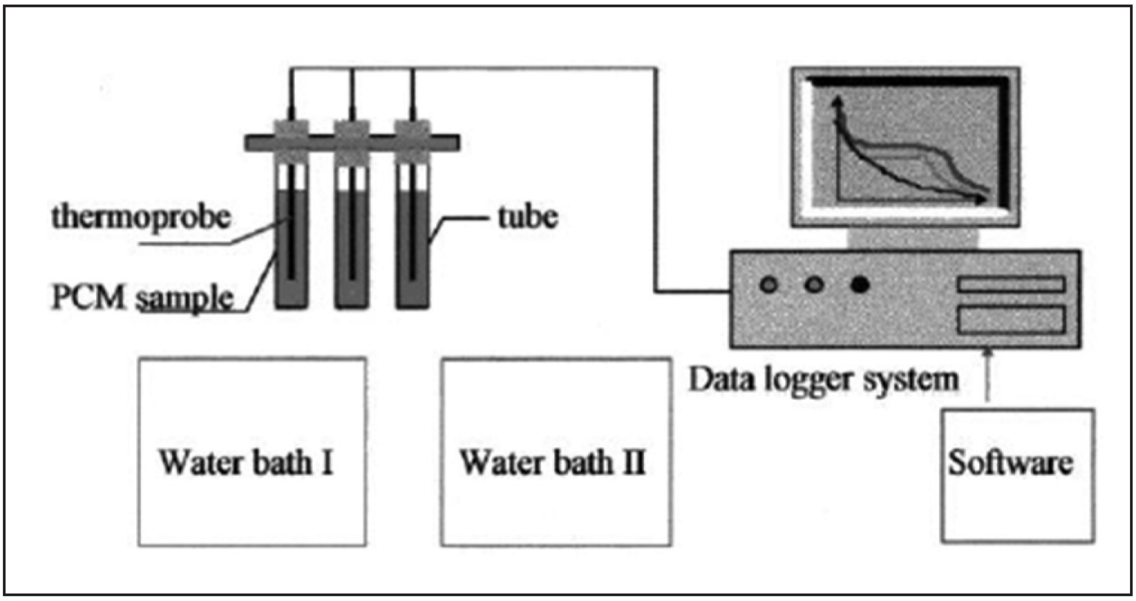

FIGURE III: Temperature-history experimental setup (Yinping and Yi, 1999)

The experimental results of pure paraffin C_{16} done by (Marín et al., 2003), showed that the accuracy of a testing method is important. A misleading rating of the PCM latent heat can negatively impact its application in food preservation for sub-zero temperature application, as the storage capacity determines the period of use. Table V shows different latent heat results using different testing methods on the same material.

TABLE V: Difference in latent heat value between a DSC and a temperature-history method (Marín et al., 2003)

Test method	Latent heat (kJ/kg)
Temperature-history method	252.01
DSC	235

The results in Table V show that it is critically important to choose the correct testing method to study sub-zero temperature PCMs as the latent heat values differ by 7%. The supercooling effects of sub-zero temperature PCMs, particularly saltwater PCMs, should be established using a temperature-history method. Marín et al. (2003) suggested an improvement in the temperature-history method be made, as there were errors encountered due to the experimental setup. Saltwater PCMs, as listed in Table III, tend to supercool which makes the freezing process longer. To minimise supercooling effect, nucleating agents such as nanoparticles can be added to reduce the freezing time as nanoparticles tend to increase crystallization of the PCM. Liu et al. (2015) used the temperature-history method to study the supercooling of water-graphene oxide nanofluid; the study showed the possibility of a 69.1% reduction in supercooling on a 0 °C melting temperature PCM.

Application of PCMS in the transportation of temperature-sensitive products

There are different PCMs that have been described in the literature that focus on the reduction of heat transfer rate by incorporating a PCM in the insulation panel of the container. Minimal (low) heat transfer between the outdoor environment and the inside of a refrigerated vehicle is required to reduce energy consumption. High heat transfer across the walls means more energy is required to maintain the products at a certain temperature. Ahmed et al. (2010) incorporated the use of a paraffin-based PCM in the insulation of a refrigerated truck trailer wall. The results of the test show a reduction in heat transfer rates, which in turn reduces pollution from diesel-powered refrigeration system as less energy is required to power the system thus reducing energy consumption. A reduction of 16.3% heat transfer from the outside of the trailer to the refrigerated load space of the trailer was achieved by the addition of a PCM to the insulation foam used in the trailer walls. An experiment that used a PCM system for maintaining a refrigerated truck at certain thermal conditions was conducted by Liu et al. (2012). The PCTSU (phase change thermal storage unit) is charged by a refrigeration unit when the vehicle is in the warehouse. The PCTSU is located outside the load space due to the PCM used being considered hazardous under the European Directive 1999/45/EC. The refrigeration unit is only connected when the system is being charged. The system is as shown in Figure IV.

This system has a heat transfer fluid that circulates through the piping connection from the PCTSU to the cooling unit

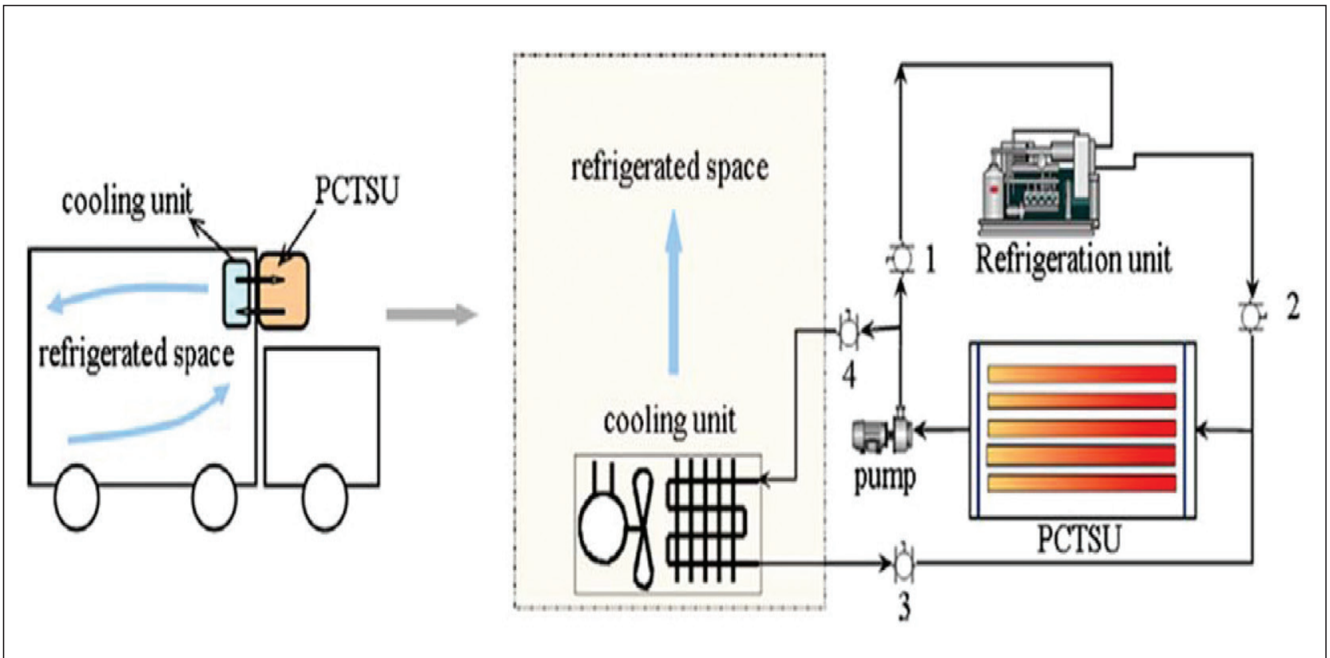

FIGURE IV: The configuration of a PCM refrigeration system (Liu et al., 2012) inside the refrigerated space. The operation time of this system is dependent on the ambient conditions and the cooling capacity of the PCM container (PCTSU), which is a disadvantage when compared to a conventional refrigerating system during high ambient temperatures. The system was found to have reduced noise level, lower greenhouse gas emissions and improved temperature control. According to (Liu et al., 2012) more work still needs to be done on the development of PCM systems. (Fioretti et al., 2016) conducted an outdoor experiment for the use of PCMs on a reefer container with the aim of reducing the cooling load; tests were conducted during the summer season. Reduction in fuel consumption by the refrigerating unit can be achieved as the PCM reduces the heat transfer through the container walls (Fioretti et al., 2016). Table VI shows different PCMs from the literature that are used in transport refrigeration.

The thermo-physical properties of PCMs that have been described in the literature show the need to improve PCM thermal cycles (freezing and melting cycles) and stability. The more a PCM is used, the more it deteriorates. Phase separation can occur at high thermal cycles in the salt PCMs listed in Table III due to incongruent melting. This happens when there is little water to melt the salt during the melting process. Loss in LHS capacity can be caused by phase separation. The addition of thickening agents and nanoparticles can reduce phase separation (Xie et al., 2017). As can be seen in Table VI, the PCMs have mostly been incorporated into the insulation walls. This reduces the heat transfer rate across the refrigerated vehicle walls which can assist in reducing energy consumption. Few developments in the use of PCMs in the eutectic system, and specifically their application in transport refrigeration, have been described in the literature, but their development and application for stationary units is extensive. It was found that the majority of the developed PCMs have poor thermal cycles and could not be used in eutectic systems for refrigerated vehicles. The poor properties of PCMs in transport refrigeration could lead to spoilage of transported food produce. A high PCM density is important as it means high thermal energy storage per unit volume (Farid et al., 2004). The PCMs listed in Table VI have low density and low thermal conductivity. Having a high-density PCM inside the eutectic plates of a refrigerated vehicle will reduce the need for a larger heat transfer area. The disadvantage of incorporating a eutectic refrigeration system in a refrigerated vehicle is that it cannot operate for long distances without recharging (freezing of storage material) when compared to a mechanical vapour compression system that operates 24 hours a day.

Conclusion

The application of phase change materials in transport refrigeration still needs the development of new PCMs and optimisation of eutectic plate layout to ensure uniform temperature distribution in the load space. There is a lot of literature that focuses on the application of PCMs in areas other than transport refrigeration. With improvements in the thermo-physical properties of storage materials, refrigerated vehicles could operate for long distances without deterioration of foodstuffs. There are some PCMs that could potentially be used for transport refrigeration, but the challenge is that these storage materials are used in stationary refrigeration units, but refrigerated vehicles always experience variation in climatic conditions and frequent door opening throughout the day. This can have an impact on the quality of the transported foodstuff. In recent developments in the application of PCMs in transport refrigeration, PCMs were incorporated in the walls of the container to reduce the heat transfer rate. Therefore, there is a need to make use of eutectic plates filled with PCMs with better thermal properties. Then latent heat storage materials can be used as alternative refrigeration systems in the transportation of perishable foodstuffs.

References

ABHAT, A. 1983. Low temperature latent heat thermal energy storage: heat storage materials. *Solar energy,* 30, 313-332.

AGYENIM, F., HEWITT, N., EAMES, P. & SMYTH, M. 2010. A review of materials, heat transfer and phase change problem formulation for latent heat thermal energy storage systems (LHTESS). *Renewable and sustainable energy reviews,* 14, 615-628.

AHMED, M., MEADE, O. & MEDINA, M. A. 2010. Reducing heat transfer across the insulated walls of refrigerated truck trailers by the application of phase change materials. *Energy Conversion and Management,* 51, 383-392.

ALVA, G., LIU, L., HUANG, X. & FANG, G. 2017. Thermal energy storage materials and systems for solar energy applications. *Renewable and Sustainable Energy Reviews,* 68, Part 1, 693-706.

ANISUR, M., MAHFUZ, M., KIBRIA, M., SAIDUR, R., METSELAAR, I. & MAHLIA, T. 2013. Curbing global warming with phase change materials for energy storage. *Renewable and Sustainable Energy Reviews,* 18, 23-30.

CABEZA, L. F., MEHLING, H., HIEBLER, S. & ZIEGLER, F. 2002. Heat transfer enhancement in water when used as PCM in thermal energy storage. *Applied Thermal Engineering,* 22, 1141-1151.

CANTOR, S. 1979. DSC study of melting and solidification of salt hydrates. *Thermochimica Acta,* 33, 69-86.

TABLE VI: Summary of different PCMs used in transport refrigeration (Liu et al., 2012, Ahmed et al., 2010, Fioretti et al., 2016)

Type	Melting Temperature (°C)	Heat of fusion (KJ/Kg)	Thermal conductivity (W/mK)	Density (Kg/m³)	Application
Inorganic saltwater solution	-26.8	154.4	–	–	Refrigerated truck – 86.4% cost reduction compared to conventional system
Paraffin wax	7	156	0.2	770	Refrigerated truck trailer – 16.3% reduction in total heat transfer was achieved
Paraffin wax	35	220	0.2	770	Reefer container – achieved 5.55% and 8.57% heat transfer rate reduction

DA CUNHA, J. P. & EAMES, P. 2016. Thermal energy storage for low and medium temperature applications using phase change materials–a review. *Applied Energy,* 177**,** 227-238.

DINCER, I. & ROSEN, M. 2011. *Thermal energy storage: systems and applications,* West Sussex, United Kingdom, John Wiley & Sons.

FARID, M. M., KHUDHAIR, A. M., RAZACK, S. A. K. & AL-HALLAJ, S. 2004. A review on phase change energy storage: materials and applications. *Energy conversion and management,* 45**,** 1597-1615.

FERNANDES, D., PITIÉ, F., CÁCERES, G. & BAEYENS, J. 2012. Thermal energy storage:"How previous findings determine current research priorities". *Energy,* 39**,** 246-257.

FERRER, G., SOLÉ, A., BARRENECHE, C., MARTORELL, I. & CABEZA, L. F. 2015. Corrosion of metal containers for use in PCM energy storage. *Renewable Energy,* 76**,** 465-469.

FIORETTI, R., PRINCIPI, P. & COPERTARO, B. 2016. A refrigerated container envelope with a PCM (Phase Change Material) layer: Experimental and theoretical investigation in a representative town in Central Italy. *Energy Conversion and Management,* 122**,** 131-141.

GIN, B. & FARID, M. M. 2010. The use of PCM panels to improve storage condition of frozen food. *Journal of Food Engineering,* 100**,** 372-376.

HE, Q., WANG, S., TONG, M. & LIU, Y. 2012. Experimental study on thermophysical properties of nanofluids as phase-change material (PCM) in low temperature cool storage. *Energy Conversion and Management,* 64**,** 199-205.

KLANČNIK, G., MEDVED, J. & MRVAR, P. 2010. Differential thermal analysis (DTA) and differential scanning calorimetry (DSC) as a method of material investigation. *RMZ–Materials and Geoenvironment,* 57**,** 127-142.

LI, G., HWANG, Y., RADERMACHER, R. & CHUN, H.-H. 2013. Review of cold storage materials for subzero applications. *Energy,* 51**,** 1-17.

LI, M. 2013. A nano-graphite/paraffin phase change material with high thermal conductivity. *Applied Energy,* 106**,** 25-30.

LIU, M., SAMAN, W. & BRUNO, F. 2012. Development of a novel refrigeration system for refrigerated trucks incorporating phase change material. *Applied Energy,* 92**,** 336-342.

LIU, Y., LI, X., HU, P. & HU, G. 2015. Study on the supercooling degree and nucleation behavior of water-based graphene oxide nanofluids PCM. *International Journal of Refrigeration,* 50**,** 80-86.

MARÍN, J. M., ZALBA, B., CABEZA, L. F. & MEHLING, H. 2003. Determination of enthalpy–temperature curves of phase change materials with the temperature-history method: improvement to temperature dependent properties. *Measurement science and technology,* 14**,** 184.

ORÓ, E., DE GRACIA, A., CASTELL, A., FARID, M. M. & CABEZA, L. F. 2012a. Review on phase change materials (PCMs) for cold thermal energy storage applications. *Applied Energy,* 99**,** 513-533.

ORÓ, E., MIRÓ, L., BARRENECHE, C., MARTORELL, I., FARID, M. M. & CABEZA, L. F. 2013. Corrosion of metal and polymer containers for use in PCM cold storage. *Applied energy,* 109**,** 449-453.

ORÓ, E., MIRÓ, L., FARID, M. M. & CABEZA, L. F. 2012b. Thermal analysis of a low temperature storage unit using phase change materials without refrigeration system. *International Journal of Refrigeration,* 35**,** 1709-1714.

PIELICHOWSKA, K. & PIELICHOWSKI, K. 2014. Phase change materials for thermal energy storage. *Progress in Materials Science,* 65**,** 67-123.

PROGRAMME, G.-C. S. 2016. *Mitigating emissions in the transport refrigeration sector in South Africa* [Online]. S.l.: Deutsche Gesellschaft für Internationale Zusammenarbeit (GIZ) GmbH. Available: https://www.giz.de/en/worldwide/29177.html [Accessed Mar 2017].

RATHOD, M. K. & BANERJEE, J. 2013. Thermal stability of phase change materials used in latent heat energy storage systems: A review. *Renewable and Sustainable Energy Reviews,* 18**,** 246-258.

SARı, A. & KAYGUSUZ, K. 2001. Thermal performance of myristic acid as a phase change material for energy storage application. *Renewable Energy,* 24**,** 303-317.

SHARMA, A., TYAGI, V. V., CHEN, C. & BUDDHI, D. 2009. Review on thermal energy storage with phase change materials and applications. *Renewable and Sustainable energy reviews,* 13**,** 318-345.

SHARMA, S. D. & SAGARA, K. 2005. Latent heat storage materials and systems: a review. *International Journal of Green Energy,* 2**,** 1-56.

TASSOU, S., DE-LILLE, G. & GE, Y. 2009. Food transport refrigeration–Approaches to reduce energy consumption and environmental impacts of road transport. *Applied Thermal Engineering,* 29**,** 1467-1477.

TASSOU, S., DE-LILLE, G. & LEWIS, J. 2012. Food Trasport Refrigeration. *Centre for Energy and Built Environment Research, Brunel University, UK*.

XIE, N., HUANG, Z., LUO, Z., GAO, X., FANG, Y. & ZHANG, Z. 2017. Inorganic Salt Hydrate for Thermal Energy Storage. *Applied Sciences,* 7**,** 1317.

XU, B., LI, P. & CHAN, C. 2015. Application of phase change materials for thermal energy storage in concentrated solar thermal power plants: a review to recent developments. *Applied Energy,* 160**,** 286-307.

YILMAZ S, S. F., MARTORELL I, PAKSOY HO, CABEZA LF. Salt-water solutions as PCM for cooling applications. Proceedings of EuroSun 2010, international conference on solar heating, cooling and, buildings, 28 September - 1 October 2010 2010.

YINPING, Z. & YI, J. 1999. A simple method, the-history method, of determining the heat of fusion, specific heat and thermal conductivity of phase-change materials. *Measurement Science and Technology,* 10**,** 201.

ZALBA, B., MARÍN, J. M., CABEZA, L. F. & MEHLING, H. 2003. Review on thermal energy storage with phase change: materials, heat transfer analysis and applications. *Applied Thermal Engineering,* 23**,** 251-283.