Universitat de Lleida

Thermal energy storage (TES) using phase change materials (PCM) for cold applications

Eduard Oró Prim

Dipòsit Legal: L.288-2013
http://hdl.handle.net/10803/110542

ADVERTIMENT. L'accés als continguts d'aquesta tesi doctoral i la seva utilització ha de respectar els drets de la persona autora. Pot ser utilitzada per a consulta o estudi personal, així com en activitats o materials d'investigació i docència en els termes establerts a l'art. 32 del Text Refós de la Llei de Propietat Intel·lectual (RDL 1/1996). Per altres utilitzacions es requereix l'autorització prèvia i expressa de la persona autora. En qualsevol cas, en la utilització dels seus continguts caldrà indicar de forma clara el nom i cognoms de la persona autora i el títol de la tesi doctoral. No s'autoritza la seva reproducció o altres formes d'explotació efectuades amb finalitats de lucre ni la seva comunicació pública des d'un lloc aliè al servei TDX. Tampoc s'autoritza la presentació del seu contingut en una finestra o marc aliè a TDX (framing). Aquesta reserva de drets afecta tant als continguts de la tesi com als seus resums i índexs.

ADVERTENCIA. El acceso a los contenidos de esta tesis doctoral y su utilización debe respetar los derechos de la persona autora. Puede ser utilizada para consulta o estudio personal, así como en actividades o materiales de investigación y docencia en los términos establecidos en el art. 32 del Texto Refundido de la Ley de Propiedad Intelectual (RDL 1/1996). Para otros usos se requiere la autorización previa y expresa de la persona autora. En cualquier caso, en la utilización de sus contenidos se deberá indicar de forma clara el nombre y apellidos de la persona autora y el título de la tesis doctoral. No se autoriza su reproducción u otras formas de explotación efectuadas con fines lucrativos ni su comunicación pública desde un sitio ajeno al servicio TDR. Tampoco se autoriza la presentación de su contenido en una ventana o marco ajeno a TDR (framing). Esta reserva de derechos afecta tanto al contenido de la tesis como a sus resúmenes e índices.

WARNING. Access to the contents of this doctoral thesis and its use must respect the rights of the author. It can be used for reference or private study, as well as research and learning activities or materials in the terms established by the 32nd article of the Spanish Consolidated Copyright Act (RDL 1/1996). Express and previous authorization of the author is required for any other uses. In any case, when using its content, full name of the author and title of the thesis must be clearly indicated. Reproduction or other forms of for profit use or public communication from outside TDX service is not allowed. Presentation of its content in a window or frame external to TDX (framing) is not authorized either. These rights affect both the content of the thesis and its abstracts and indexes.

PhD Thesis

Thermal energy storage (TES) using phase change materials (PCM) for cold applications

Author

Eduard Oró Prim

Directors of the PhD thesis

Dr. Luisa F. Cabeza (University of Lleida, Spain)

Dr. Mohammed M. Farid (The University of Auckland, New Zealand)

Departament d’Informàtica i Enginyeria Industrial

Escola Politècnica Superior

Universitat de Lleida

Thermal energy storage (TES) using phase change materials (PCM) for cold applications

Memòria presentada per optar al grau de Doctor per la Universitat de Lleida redactada segons els criteris establerts en l’Acord núm. 19/2002 de la Junta de Govern del 26 de febrer de 2002 per la presentació de la tesis doctoral en format d’articles.

Programa de doctorat: Enginyeria i Tecnologies de la Informació
Directors de la Tesis: Dra. Luisa F. Cabeza i Dr. Mohammed M. Farid

La Dra. Luisa F. Cabeza, Catedràtica de l’Escola Politècnica Superior de la Universitat de Lleida i el Dr. Mohammed M. Farid, Catedràtic de la Facultat d’Enginyeria de la University of Auckland.

CERTIFIQUEN:

Que la memòria “Thermal energy storage (TES) using phase change materials (PCM) for cold applications” presentada per Eduard Oró Prim per optar al grau de Doctor s’ha realitzat sota la seva supervisió.

Lleida, 11 de desembre de 2012

Acknowledgements

I would like to thanks Dr. Luisa F. Cabeza and Dr. Mohammed M. Farid for all what they have done for me since I was enrolled in GREA research group, not only as the directors of the PhD thesis but also to trust me and push me to next steps of my life.

I would like to express my gratitude to the University of Lleida for my research fellowship.

I would like to thank the national project number ENE2008-06687-CO2-01/CON, ENE2011-22722, Effebuildings and COST Action for the fundings during these years.

And obviously I would like to thank all my colleagues from GREA, KTH (Royal Institue of Technology) and The University of Auckland to help me during this time.

M'agradaria donar les gràcies a aquelles persones, que no cal nombrar-les on arreglem el món fent cafès i sobretaules.

Last but not least, gràcies als amics i a la meva família, que sempre estan allí.

Universitat de Lleida

Resum

Degut als canvis alimentaris i al increment de la població mundial, en aquests moments estem davant una situació on el transport i l'emmagatzematge de productes refrigerats/congelats són una preocupació mundial. La carga de calor més important dels sistemes de fred ve a través de les parets i les portes. Però a més a més, els usuaris, mitjançant l'obertura de portes aporten aire calent i humit al interior, augmentant així la temperatura. Està demostrat que les fluctuacions de temperatura tenen un efecte negatiu en la qualitat dels productes congelats, provocant una incorrecta recristal·lització dels gelats i una pèrdua d'aigua dels aliments com la carn. Per tant, poden provocar una pèrdua econòmica important tant als supermercats com als distribuïdors.

L'emmagatzematge d'energia tèrmica (TES) utilitzant materials de canvi de fase (PCM) és capaç d'absorbir/cedir una gran quantitat d'energia durant la fusió/solidificació en un interval petit de temperatura. Aquesta propietat pot ser utilitzada doncs, per a reduir les fluctuacions de temperatura durant l'emmagatzematge i el transport dels productes congelats.

L'objectiu d'aquesta tesis doctoral és el desenvolupament d'un sistema TES mitjançant la utilització de PCM per aplicacions a baixa temperatura, en particular, per a congeladors comercials. Es provarà tant experimental com numèricament la millora de les condicions de l'emmagatzematge i també la millora de la qualitat dels aliments emmagatzemats/transportats. També inclou la investigació de nous PCM, estudiant la modificació de la temperatura de canvi de fase i analitzant velocitats de degradació i corrosió amb els materials recipients. Es presenten varis estudis d'investigació basats en la implementació de sistemes de TES en aplicacions de baixa temperatura tals com congeladors comercials, recipients de transport de productes a baixa/alta temperatura i recipients de gelats. Els resultats obtinguts a les diferents aplicacions estudiades demostren el clarament el benefici de la utilització de PCM, reduint les fluctuacions i les caigudes de temperatura tant al interior dels sistemes com del producte, i per tant millorant la qualitat d'aquests.

Resumen

Debido a los cambios alimentarios y al incremento de la población mundial, en estos momentos estamos en una situación donde el transporte y el almacenamiento de productos refrigerados/congelados se han convertido en una preocupación mundial. La carga de calor más importante en los sistemas viene desde el exterior a través de las paredes y las puertas. Pero además, los usuarios mediante aperturas de las puertas, llenan de aire caliente y húmedo el interior, aumentando la temperatura. Está probado que las fluctuaciones de temperatura causan un efecto negativo en la calidad de los alimentos congelados, provocando una incorrecta re-cristalización en los helados y una pérdida de agua en alimentos tales como la carne. Por lo tanto pueden provocar unas pérdidas económicas importantes tanto en supermercados como distribuidores.

El almacenamiento de energía térmica (TES) utilizando materiales de cambio de fase (PCM) es capaz de absorber/ceder una gran cantidad de energía durante la fusión/solidificación en un intervalo de temperatura pequeño. Esta propiedad puede ser utilizada para reducir las fluctuaciones de temperatura durante el almacenamiento y transporte de los productos congelados.

El objetivo de esta tesis doctoral es el desarrollo de un sistema de TES mediante la utilización de PCM para aplicaciones a baja temperatura, en particular, para los congeladores comerciales. Se probará experimental y numéricamente la mejora de las condiciones de almacenamiento, y también la mejora de la calidad de los alimentos almacenados/transportados. También incluye la investigación de nuevos PCM, estudiando la modificación de la temperatura de cambio de fase y analizando velocidades de degradación y corrosión con los materiales contenedores. Se presentan varios estudios de investigación basados en la implementación de sistemas de TES en aplicaciones de baja temperatura tales como congeladores comerciales, recipientes de transporte de productos a baja/alta temperatura y contenedores de helados. Los resultados obtenidos en las diferentes aplicaciones demuestran el beneficio de usar PCM, reduciendo las fluctuaciones y las caídas de temperatura tanto del interior de los sistemas como del producto almacenado y por tanto la mejoría de la calidad de éstos.

Summary

Food transport and storage at low temperature is a matter of concern worldwide due to changes of the dietary habits and the increasing of the population. Chilled and frozen foods require storage temperature from 14 ºC to below -18 ºC. Refrigeration systems are used to remove heat loads and control temperature. The major heat load comes from the outside environment of the storage space through insulated walls and the glass door in commercial applications. Moreover, door openings by the costumers bring warm and moist air into the cold storage space, raising the temperature. Furthermore, in many countries, such as India, there are restrictions on the daily use of the electricity due to power shortage.

It is well known that those temperature fluctuations could cause negative dramatic effect to the quality of the frozen food, inducing for example recrystallization in ice creams and drip loss of frozen meat and therefore could induce great economical losses to supermarkets and devalue the quality of frozen food. Thermal energy storage (TES) using phase change materials (PCM) are capable of absorbing a large amount of heat during melting over a small temperature range. This property can be used to minimize temperature fluctuations when the cold store is under electrical power failure or door openings and therefore enhance food quality.

The aim of this PhD thesis is to develop a TES system using PCM for cold temperature applications in particular for commercial freezers testing experimentally and numerically the improvement of its thermal performance and the food quality stored. This thesis also includes the research on PCM with attractive properties for low temperature applications such as controllable phase change temperature and low corrosion and degradation rate. Here, several research studies based on the implementation of TES systems in low temperature applications such as commercial freezers, chilly bins and ice cream containers are presented. The results obtained in the proposed applications have proved the benefit of using PCM in the proposed cold applications based on reduction of the interior/product temperature fluctuations and rise, and therefore improvement of the storage and transport conditions of frozen food.

Nomenclature

CMC	Oxyethylmethylcellulose
CFD	Computational fluid dynamics
DoE	Design of experiments
DSC	Differential scanning calorimetry
FDA	Food and Drug Administration code
HDPE	High density polythylene
MAPCM	Molecular alloys as phase change materials
PCM	Phase change materials
PET	Polyethylene terephthalate
PP	Polypropylene
PS	Polystyrene
TES	Thermal energy storage

Contents

CONTENTS

CONTENTS

List of Figures

1 Introduction

1.1 Transport and storage of frozen food

Many industries require their products to be stored and transported at low temperatures. Chilled and frozen foods require storage temperature ranging from ambient temperature to below -18 ºC. Storage and transportation facilities such as cold stores, refrigerated trucks, domestic and commercial refrigerators and freezers are some of the systems used to maintain products at the desired temperatures.

Moreover, frozen food transportation and storage at low temperature are becoming an important issue worldwide as it is related to lifestyle and growing population. The issue of improving the cold chain applies to different applications such as low temperature storage (domestic or commercial freezers and refrigerators, low temperature warehouses) and food transportation (refrigerated truck or van).

Refrigeration systems are used to remove heat gains and control the temperature of the units. There are constant heat gains from the environment through the insulated walls and the front glass in commercial options. Door openings by the users are another source of heat gain. Here, warm and moist air from the outside environment exchanges with the cool dry internal air when the doors of the cold storage space are opened. This raises the temperature inside the storage space, and also brings in moisture. Moreover, it could occur without previous notice an electrical power failure, and therefore having the refrigeration system not running. Also during defrosting, when the refrigeration system is stopped, a heater is used to melt the ice placed on the evaporator tubes and therefore direct heat gain to the store occurs.

It is well known that temperature fluctuations during the storage which are caused by the commented situations in commercial freezers could cause negative dramatic effects to the quality of the frozen food [1-3]. Moreover, temperature drops during a partial thawing from an electrical power failure is another important problem during both storage and transport of low sensitive temperature products, causing for example deterioration of the food products [4].

Storage and transport of frozen products at the final steps of the cold chain could be enhanced in order to improve the quality of food at this last stage in refrigerated (freezers, refrigerated vans and trucks) and non-refrigerated (ice cream trolleys non refrigerated vans) systems which are not designed to extract heat from the load but to maintain the temperature of the frozen products using insulation. The quality of these perishable foodstuffs can be very seriously affected by the temperature control during storage and transport from processing to consumer. This can be explained by the large impact that temperature and time can have on both microbial and chemical properties of the perishable products. Because of the importance of storage and transport temperature almost all countries in Europe, USA and many other countries have signed the ATP-Agreement on the international carriage of perishable foodstuffs and on the special equipment to be used for such carriage [1].

All these situations could devaluate the quality of frozen food and therefore induce great economic losses to supermarkets and distributors. Furthermore, refrigerated transport is necessary for maintaining the quality and prolonging the shelf-life of fresh, frozen and perishable products during transportation and this sector is increasing constantly. The production facilities of cold vapour compression involve high energy demand, and may represent a high economic environmental impact. Therefore an increased energy demand with associated increase in CO_2 emissions is expected in the near future and hence it is necessary to reduce the energy demand and CO_2 emission by improving energy efficiency and utilizing energy waste.

Consequently there is an important opportunity for efficiency improvement not only in electricity generation but also in road transport, household, industrial, and commercial sectors.

1.2 Thermal Energy Storage

TES systems for both heat and cold are necessary for good performance of many industrial processes [6-7]. High energy storage density and high power capacity for charging and discharging are desirable properties of any storage system. TES could be the most appropriate way and method to correct the gap between the demand and supply of energy and therefore it has become a very attractive technology. It is well known that there are three methods of TES: sensible, latent and chemical heat storage.

1.2.1 Sensible heat

The energy storage density in sensible heat storage is determined by the specific heat capacity of the storage media and the temperature changes of the material. This temperature change ($\Delta T=T_2-T_1$) depends on the application and is limited by the heat source and by the storage system. The sensible heat stored in any material can be calculated as follows:

$$Q_{sensible}=\int_{T_1}^{T_2} C_p \cdot dT$$

Where $Q_{sensible}$ is the sensible heat stored, C_p the specific heat of the material, and dT the temperature change.

1.2.2 Latent heat

Another means of storing energy is by using phase change materials (PCM). The energy density could be increased by using PCM, having a phase change within the temperature range of the storage. Considering the temperature interval ($\Delta T=T_2-T_1$) the stored heat in a PCM can be calculated as follows:

$$Q_{latent} = \int_{T_1}^{T_{pc}} C_{p,s} \cdot dT + \Delta H_{pc} + \int_{T_{pc}}^{T_2} C_{p,l} \cdot dT$$

Where Q_{latent} is the sensible and latent heat stored and ΔH_{pc} is the heat of fusion at the phase change temperature T_{pc}.

The phase change could be solid/liquid or liquid/gas; however, liquid/gas transformations are not practical due to the large volume changes or high pressures required to store the materials in the gas phase.

Latent heat TES is particularly attractive due to its ability to provide high energy storage density per unit mass in quasi-isothermal process. This means that in a specific application where the temperature range is important, for instance in transport of sensitive temperature products, the use of PCM becomes very useful since it can store material at constant temperature corresponding to the phase-transition temperature of the PCM.

Furthermore, any materials to be used for PCM in TES systems must have high latent heat and high thermal conductivity. They should have a melting/freezing temperature lying in the practical range of operation, melt/freeze congruently within minimum subcooling and be chemically stable, low in cost, nontoxic and non-corrosive [6].

Figure 1 shows the families of phase change heat storage materials: divided as organic and inorganic materials. Organic materials are further classified as paraffin and non-paraffins (fatty acids, eutectics, and mixtures). Experiments (melting and freezing cycles) using these materials showed that they crystallize with little or no subcooling and are usually non-corrosive and very stable.

Inorganic materials are further classified as compounds and eutectics. An eutectic material is a composition of two or more components, which melts and freezers congruently forming a mixture of the component crystals during crystallization. Eutectic mixtures nearly always melt and freeze without segregation, leaving little opportunity for the individual components to separate and melts almost at constant temperature. Main inorganic materials are salts, salt hydrates, aqueous solutions and water.

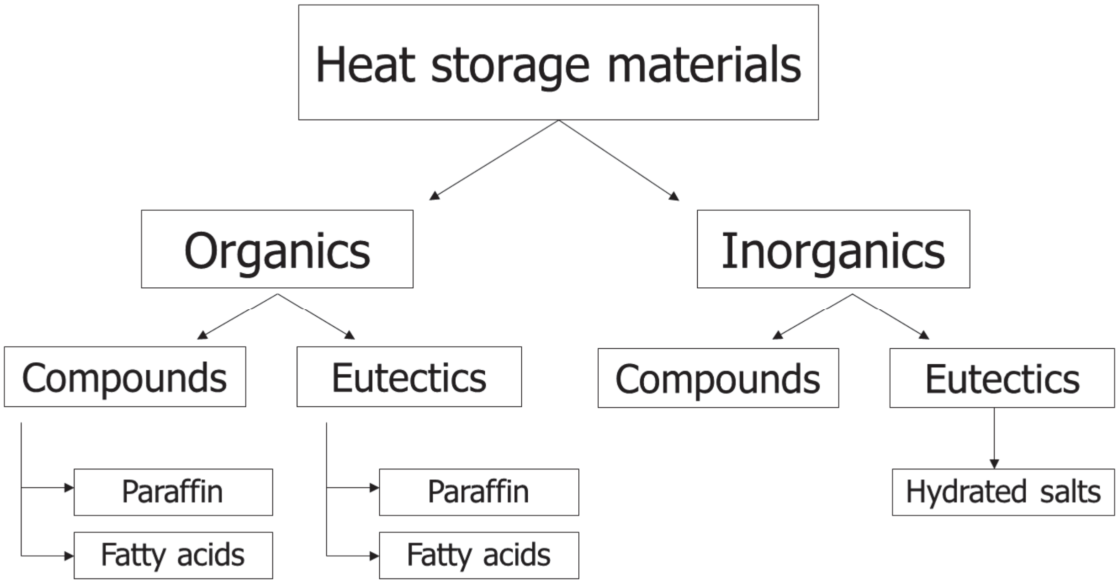


Figure 1. Families of phase change heat storage materials.

1.2.3 Chemical Heat Reactions

Heat can also be stored by means of a reversible thermo-chemical reaction. The working principle is the following one:

$$A + HEAT \leftrightarrow B + C$$

First, in the charging period, chemical A is transformed into two new chemicals, B and C, because of heat absorption (endothermic reaction). Subsequently, the two new chemicals must be stored in separate vessels at ambient temperature. Second, in the discharging period, chemical B reacts with chemical C to form the original chemical A while releasing the stored heat (exothermic reaction).

The energy of thermo-chemical reactions is the highest of all the systems introduced, and so it is the most compact way to store thermal energy. So far, there are several types of reversible thermo-chemical reactions which have been studied the most: solid-gas, liquid-gas and gas reactions.

1.3 Thermal Energy Storage using Phase Change Materials for low temperature applications

Here the use of PCM in different applications is presented, differentiating those ones that are already in the market from those ones that have been studied by researchers. PCM offer the possibility of thermal protection due to its high thermal inertia. This protection could be used against heat and cold, during transport or storage. Protection of solid food, cooked food, beverages, pharmaceutical products, blood derivatives, electronic circuits and many other is possible. Some of the different applications for cold storage presented are the following ones:

- Cooling: use of off-peak rates and reduction of installed power, ice bank.
- Thermal protection of food: transport, hotel trades, ice-cream, etc.
- Medical applications: transport of blood, operating tables, cold therapies.
- Industrial cooling systems: re-gasification terminal.

1.3.1 Commercial applications

1.3.1.1 General containers for temperature sensitive food

One of the most known applications of PCM is that of transport of temperature sensitive food in containers. These containers must be kept in the refrigerator/freezer before use in order to solidify the PCM in it. An example of such a device is the container commercialized by SOFIGRAM [8] with PCM melting points of 0 ºC, -15 ºC and -20 ºC (Figure 2). Some companies only commercialize PCM pads for use in any container, such as TCP RELIABLE, Inc. [9], PCM Thermal Solutions [10] or PCM products [11].

Figure 2. Gel packs of SOFIGRAM [8].

1.3.1.2 Beverages

One application that has been commercialized is the so-called "isothermal water bottle", specially developed for cycling. It is a double wall bottle, with a PCM as active part. This concept could be used for many other products, such as isothermal maintenance of fresh drinks like wine, champagne, soft drink, etc. (Figure 3).

Figure 3. Isothermal water bottle available in the market.

1.3.1.3 Catering products

In many catering applications, cooked meals or frozen products are produced in one point and have to be transported to another destination (Figure 4). PCM containers (Figure 5) could also be used to avoid breaking the cold chain during transportation of precooked meals, smoked salmon, milk products, ice-creams and many others. The main companies that commercialize these products are Rubitherm [12], Climator [13], and Teap PCM [14].

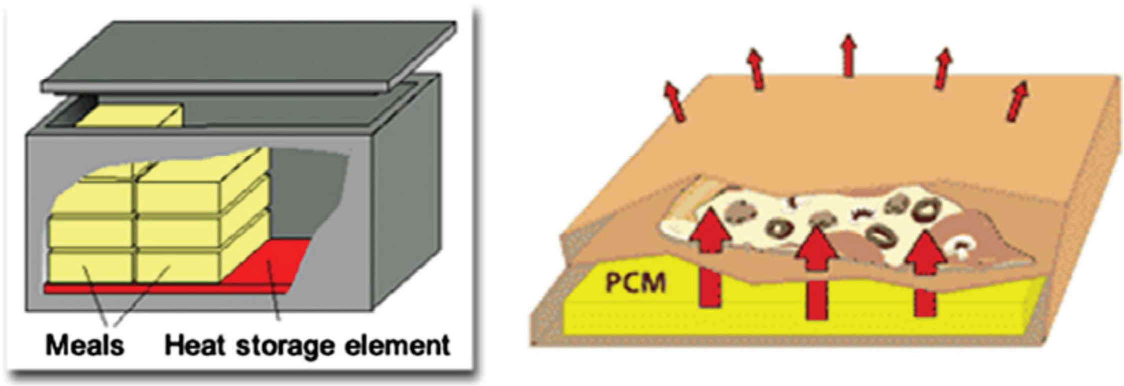


Figure 4. Concept of catering applications [12].

Figure 5. Different PCM containers [12][14].

1.3.1.4 Medical applications

In the medical sector, one of the main applications is the transport of blood (Figure 6) and organs. Containers used for these purposes work similar to those explained before. Other medical applications can be hot or cold pads to treat local pain in the body.

Figure 6. Containers to transport blood and organs containing PCM [12].

1.3.2 Peak load shifting

Cold storage technology is an effective mean of shifting peak electrical loads as part of the strategy for energy management in buildings. Such systems can help the electrical utilities reducing peak loads and increasing the load during off peak periods which could improve the utilization of base load generating equipment, and thereby reducing the reliance on peaking units which have higher operating costs. An example of cold TES system is the storage of coolness generated electrically during off peak hours to be used during subsequent peak hours. There are mainly three types of cold storage systems being considered [15]:

- Chilled water storage systems. Here water is not used as PCM.
- Ice storage systems. Water is used as PCM to take advantage of its high latent heat of fusion removed during the charging cycle which results to ice formation.
- Eutectic salt storage system. Eutectic salts are another commonly used medium to store cooling energy.

1.3.3 Transport and storage of temperature sensitive materials

In the past decade the application of PCM in transport containers became one of the first fully commercial PCM applications. Therefore many researchers put effort in order to study the incorporation of PCM in different systems as follows:

- Domestic refrigerators.
- Domestic freezers.
- Domestic refrigerator and freezer combination.
- Refrigerated trucks.
- Industrial refrigeration plants.
- Temperature sensitive products transportation and storage.

Notice that the use TES with PCM in commercial freezers was not evaluated in the literature before the publication of the papers exposed in this thesis.

1.3.3.1 Domestic refrigerators

Figure 7 shows the refrigerator modification with PCM plates done by Azzouz et al. [16] who placed the PCM slab in the back side of the evaporator inside a household refrigerator in order to improve its efficiency and to provide a storage capacity allowing several hours of cold storage without power supply. Here, two PCM were compared (water and water with an eutectic mixture with a freezing point of -3 ºC).

1.3.3.2 Domestic freezers

The effect of door opening, defrost cycle, and loss of electrical power on a domestic freezer with and without PCM was studied by Gin et al. [17]. Figure 8 shows a schematic of the domestic freezer and the placement of the PCM panels inside it used in the experimentation.

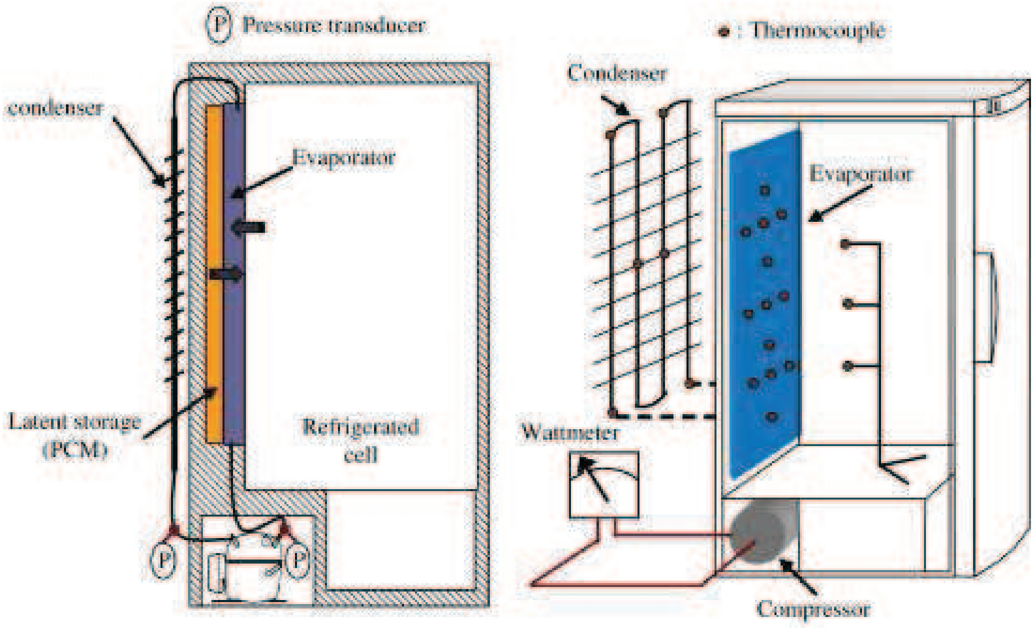


Figure 7. Refrigerator components and instrumentation used by Azzouz et al. [16].

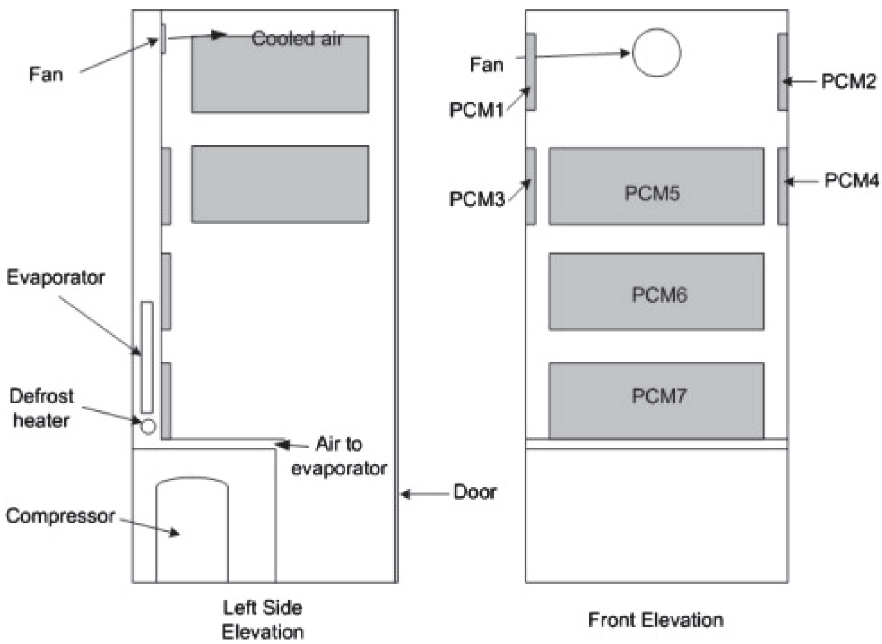


Figure 8. Schematic of the domestic freezer showing positions of the evaporator, defrost heater, and placement of the PCM panels [17].

1.3.3.3 Domestic combined refrigerator and freezer

Subramaniam et al. [18] designed a method of a novel dual evaporator (refrigerator and freezer combination) based on a domestic refrigerator with PCM which provided TES in order to improve food quality and extend compressor off period. Figure 9 shows the schematic diagram of the dual evaporator proposed.

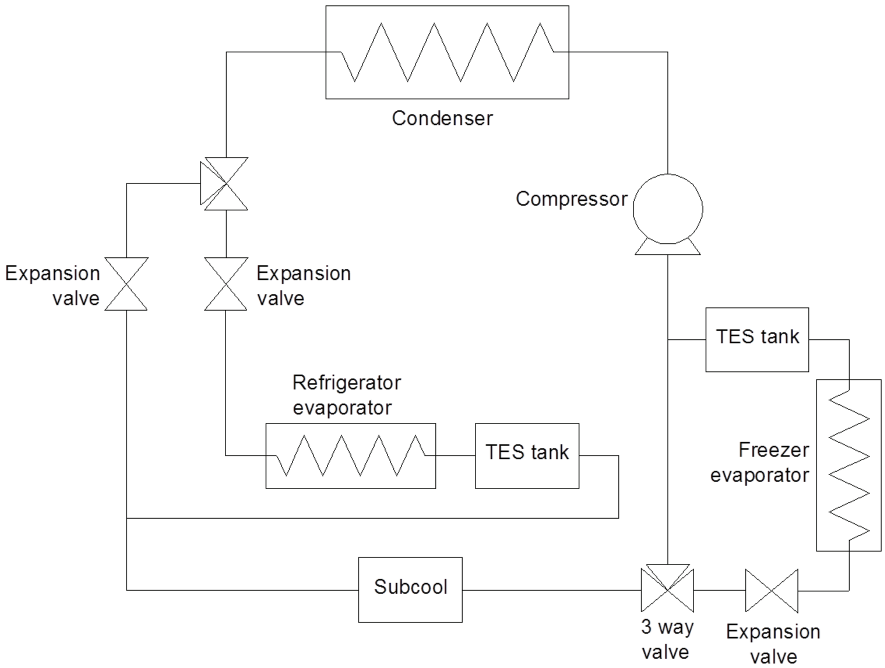


Figure 9. Schematic diagram of the dual evaporator based on a domestic refrigerator with PCM used in Subramaniam et al. [18].

1.3.3.4 Refrigerated trucks

Ahmed et al. [19] modified the conventional method of insulation of a refrigerated truck trailer by adding PCM on the walls (Figure 10). Later Liu et al. [20] developed an innovative refrigeration system incorporating PCM to maintain refrigerated trucks at the desired thermal conditions. Figure 11 shows the schematic diagram for refrigerated trucks. The PCM storage tank (the PCM was encapsulated into thin flat containers) was charged by a refrigeration unit located outside the vehicle when stationary and provides cooling when in service. The storage tank was located as well at the exterior of the refrigerated space.

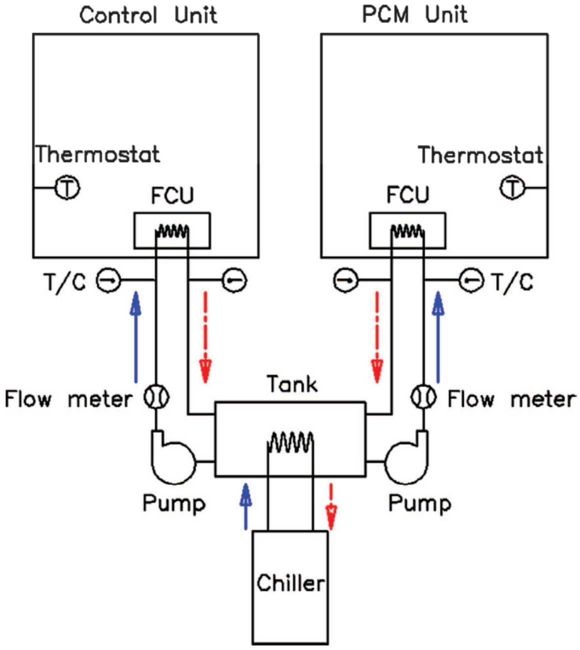


Figure 10. Schematic of the cooling diagram for the refrigerated trucks used by Ahmed et al. [19].

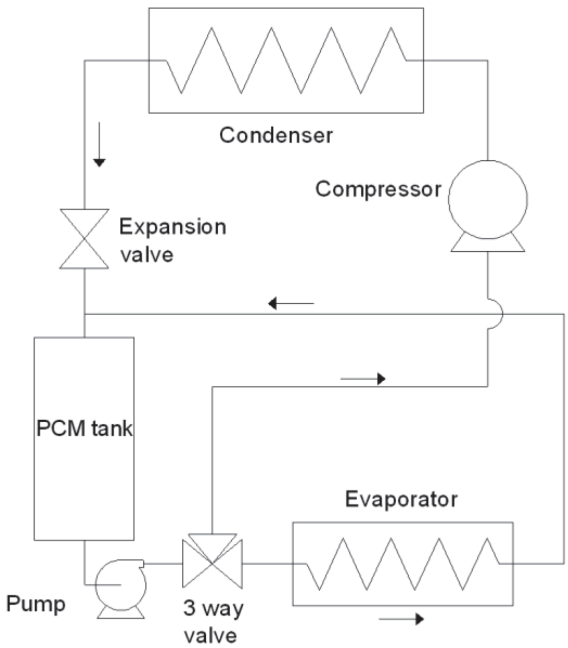


Figure 11. Scheme of the configuration of the refrigeration system for refrigerated trucks used by Liu et al. [20].

1.3.3.5 Industrial refrigeration

Cheralathan et al. [21] carried out an experimental investigation on the performance of an industrial refrigeration system integrated with encapsulated PCM based on cold TES system. The experimental apparatus consisted of two parts, a cold TES tank and a vapour compression refrigeration system. Figure 12 shows the schematic diagram of the experimental set-up introduced by Cheralathan et al. [12]. A vertical storage tank was integrated with the evaporator of the refrigeration system.

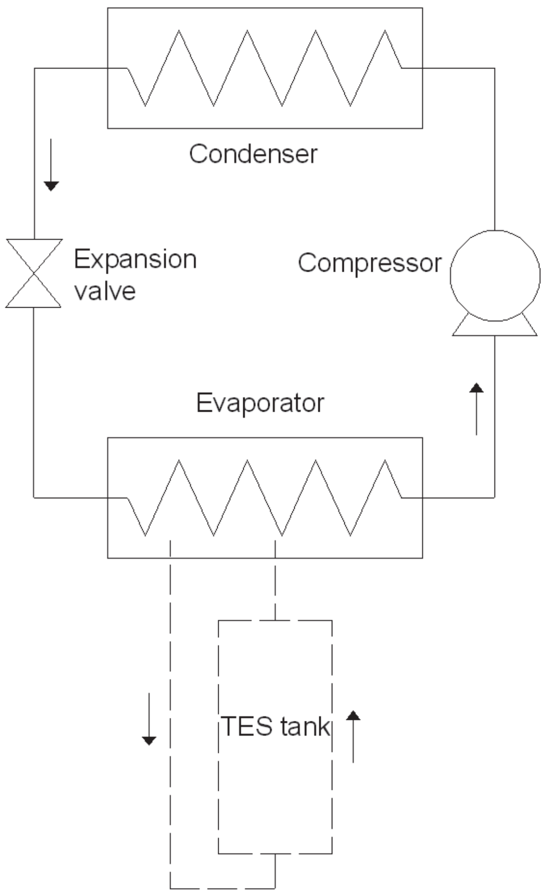


Figure 12. Schematic diagram of the experimental set-up used in Cheralathan et al. [21].

Wang et al. [22] studied the enhancement of a vapour compressor refrigeration system locating PCM in some parts of it. They located a PCM heat exchanger with a shell and tube structure in different places of the refrigerated system for refrigeration plants, such as after the compressor (PCM A), after the condenser (PCM B), and after the evaporator (PCM C), doing three different configurations and evaluating them separately (Figure 13).

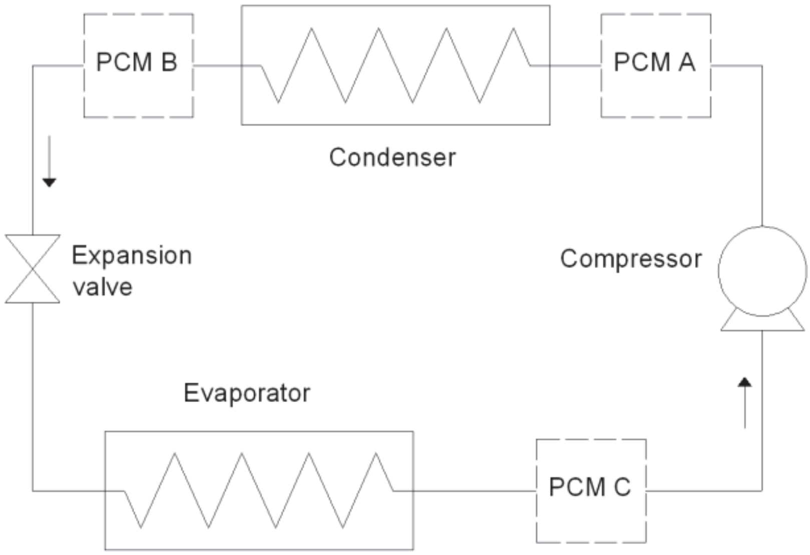


Figure 13. PCM heat exchanger at different locations in the refrigeration cycle used by Wang et al. [22].

1.3.3.6 The use of molecular alloy PCM for sensitive products transportation and storage

Molecular alloys as phase change materials (MAPCM) offer additional solutions that have been studied over the years. Here different applications of temperature sensitive products both transportation and storage using MAPCM are presented. Some investigations studied different application of MAPCM for thermal protection of biomedical products [23], sensitive temperature food [24], and drinks [25]. Figure 14 shows the packaging developed by Mondeig et al. [23] for blood thermal protection.

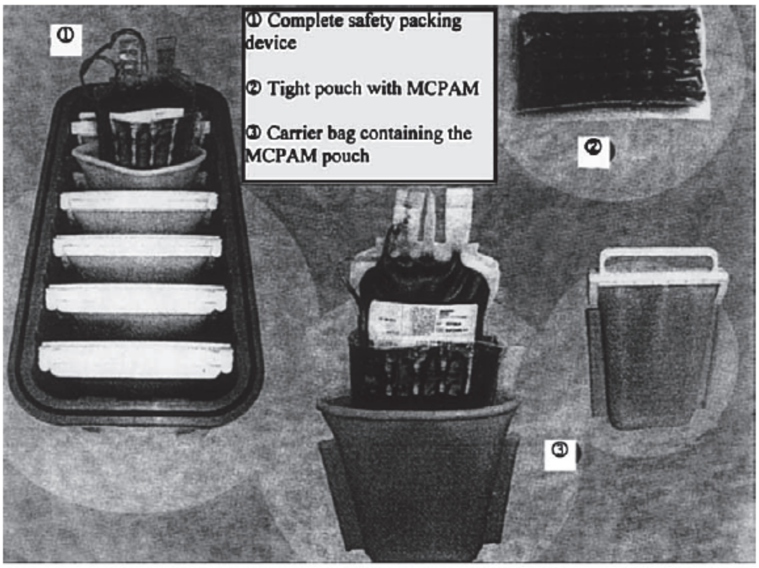


Figure 14. Packaging for blood thermal protection developed by Mondeig et al. [23].

2 Objectives

The main objective of this PhD thesis is to study and to develop a new TES system using PCM for cold applications, in particular for commercial freezers. To accomplish the aforementioned objective, several specific objectives were detected:

- To perform a state-of-the-art review of TES for cold storage applications using solid-liquid PCM. The objective of this initial work was to provide the required background and knowledge for the development of the research.

- To investigate the suitable PCM candidates for low temperature applications. This objective has divided in two different studies:

    - To study possible PCM candidates for low temperature applications in particular for commercial freezers.
    - To study the corrosion effect and the degradation rate of different metals and polymer material in contact with both, commercial PCM and our own PCM formulation used in low temperature processes.

- To investigate experimentally the use of PCM in low temperature storage in particular for commercial freezers in terms of thermal performance and enhancement of food quality under both door openings and electrical power failure.

- To mathematically model commercial freezers incorporating PCM.

- To investigate experimentally and numerically the use of PCM in low temperature applications. This objective has divided in two different studies:

    - Food applications.
    - Industrial applications.

Figure 15 shows graphically some questions that came out before starting this thesis and encourage the PhD student to study the enhancement of low temperature applications by the use of TES systems.

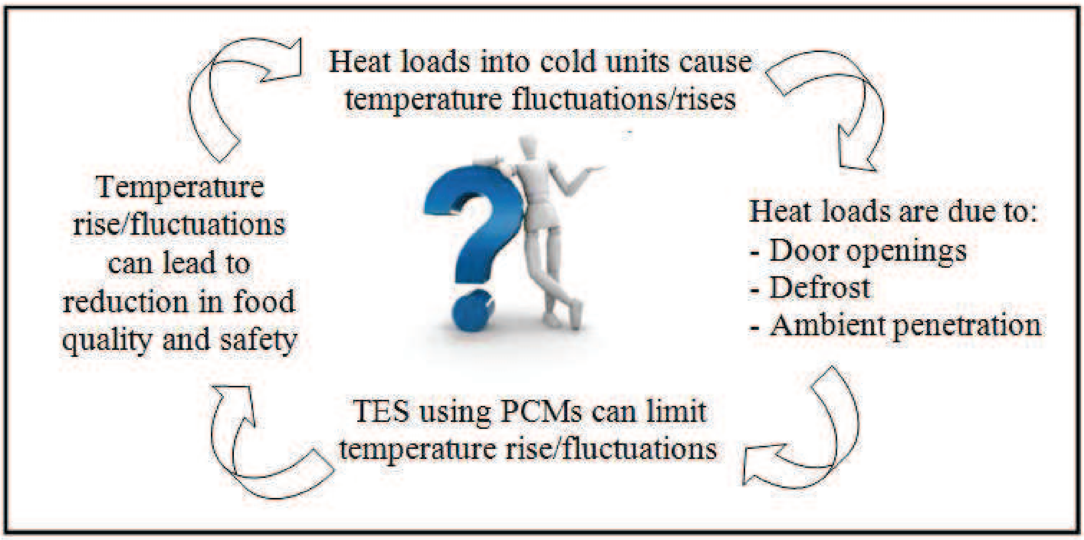


Figure 15. Initial questions and basis of the thesis.

This PhD thesis propose the implementation of TES systems using PCM to improve both the thermal performance of low temperature storage and transport units and the frozen food quality during long and short storage time. Figure 16 outlines the main objectives of the thesis and the flow of the chapters and the journal papers that came from the research. Notice that different boxes have been used in the flow; a double box indicates the chapters of the thesis, a continued box has used for those studies that have been published while non-continuous boxes were used for those studies that are under journal review.

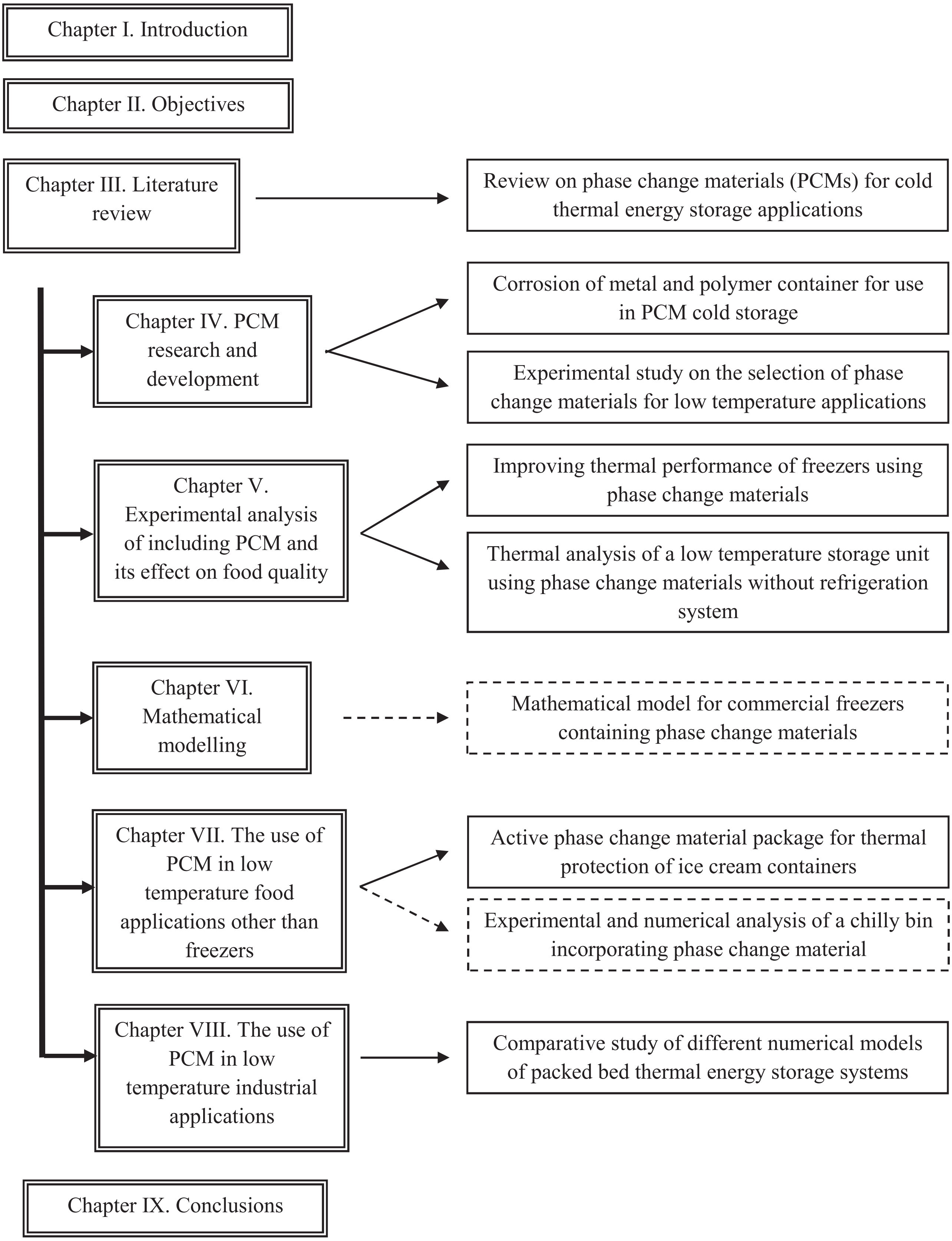


Figure 16. Flow diagram representing the structure of this thesis.

3 Review on phase change materials for cold thermal energy storage applications: A-state-of-the-art review

3.1 Introduction

Chapter III gives a state-of-the-art review on PCM for cold TES applications using solid-liquid phase. It is well known that TES could be the most appropriate way and method to correct the gap between the demand and supply of energy and therefore it has become a very attractive technology with a high potential for different thermal applications. Moreover, latent heat storage using PCM is one of the most efficient methods to store thermal energy [6-7].

The scope of the work was focussed on different aspects:

- Phase change materials available either in the market or under research. Problems in long term stability of the materials, such as corrosion, phase segregation, stability under extended cycling or subcooling are discussed.
- Different methods of PCM encapsulation.
- Heat transfer enhancement.
- Applications of PCM at low temperature.

Literature shows extensive publications for different applications of PCM such as domestic hot water tanks [27-28], space heating and cooling of buildings [29], peak load shifting [30], solar energy applications and seasonal storage [31], including many reviews [6-7], [26], [32-35]. Only the applications working with potential PCM with melting temperature lower than 20 ºC have been considered in this literature review. Over 88 materials that can be used as PCM and about 40 commercially available PCM have been listed over 150 references.

The most thoroughly studied PCM at low temperature is water for obvious reasons; water is cheap, has the best thermal properties, and also presents good long term stability. However, for applications at low working temperature, such as conservation and transport of frozen products or advanced medical transport, the melting temperature of water is not suitable. And then is when other PCM can compete against water.

3.2 Contributions to the state-of-the-art

TES systems using PCM have been studied for many years, and therefore a state-of-the-art review is fundamental to provide the required background and knowledge for the development research. So, in this Chapter III is given a state-of-the-art review on PCM for cold applications published as:

- E. Oró, A. De Gracia, A. Castell, M.M. Farid, L.F. Cabeza. Review on phase change materials (PCMs) for cold thermal energy storage applications. Applied Energy 99 (2012) 513-533.

The main contributions to the state-of-the-art can be summarized in the following points:

- The main characteristics required for a food PCM are:

  - Thermophysical properties:

    - Melting temperature in the desired operating temperature range.
    - High latent heat of fusion per unit volume.
    - High specific heat to provide additional significant sensible heat storage.
    - High thermal conductivity of both solid and liquid phases.
    - Small volume change on phase transformation and small vapour pressure at operating temperature.
    - Congruent melting of the phase change material for a constant storage capacity of the material with each freezing/milting cycle.
    - Reproducible phase change.

- Nucleation and crystal growth:

    - High nucleation rate to avoid subcooling of the liquid phase during solidification, and to assure that melting and solidification process occurs at the same temperature.
    - High rate of crystals growth, so that the system can meet the demand for heat recovery from the storage system.

- Chemical properties:

    - Complete reversible freeze/melt cycle.
    - No degradation after a large number of freeze/melt cycles.
    - No corrosiveness to the construction/encapsulation materials.
    - Non-toxic, non-flammable and non-explosive.

- Economics:

    - Abundant.
    - Available.
    - Cost effective.
    - Easy recycling and treatment.
    - Good environmental performance based on lice cycle assessment.

- Most of the PCM analysed by the researchers and commercial companies with a melting temperature below 0 ºC are eutectic water salt solution and above 0 ºC are organic PCM.

- Eutectic salts solutions are good in terms of thermophysical properties, such as enthalpy of phase change and they are cheap but they could be chemically unstable and may be corrosive.

- Most organic PCM are non-corrosive and chemically stable, however they have lower thermal conductivity, lower latent heat, larger volume change between solid and liquid phase and they are relatively expensive.

- A PCM with an easily adjustable melting temperature would be necessary as the melting point is the most important criteria for the selection of the PCM for any application.

- The use of PCM in many applications, and especially at low temperature, requires the use of nucleating and thickening agents to minimize subcooling and phase segregation. Moreover it is important to study its long term stability, phase segregation, corrosion and subcooling effects.

- Looking at the commercial applications, such as the use of PCM for catering and medical purposes, significant improvements to existing catering systems can be done. Transportation of temperature sensitive materials is another area in which PCM can play an important role and more work is needed.

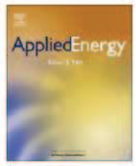
3.3 Journal paper

Applied Energy 99 (2012) 513–533

Contents lists available at SciVerse ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy



Review on phase change materials (PCMs) for cold thermal energy storage applications

E. Oró [a], A. de Gracia [a], A. Castell [a], M.M. Farid [b], L.F. Cabeza [a,*]

[a] GREA Innovació Concurrent, Universitat de Lleida, Edifici CREA, Pere de Cabrera s/n, 25001 Lleida, Spain
[b] Department of Chemical and Materials Engineering, The University of Auckland, Auckland, New Zealand

http://www.sciencedirect.com/science/article/pii/S0306261912002784

4 PCM research and development

4.1 Introduction

It is well known that PCM are one of the possible solutions to provide high energy density in TES systems. The addition of PCM in different cold storage systems and units have been investigated in order to enhance food quality and to reduce electricity consumption during storage and transportation as it has been shown before.

Nowadays, different types of chemicals such as inorganic salts, organic compounds as alkenes and water are used as low temperature PCM for cold storage. However, most aqueous salt solutions are corrosive to metals and hence a special care needs to be taken in the selection of PCM containers. Moreover, the selection of the suitable PCM for each specific application is an important matter. The development and improvement of PCM has been of great interest to many researchers over the years from the viewpoint of the application [37-40], even though it is hard to know which PCM is suitable for a specific or general application.

PCM are encapsulated in containers in order to prevent leaking when liquid phase its present, hence the interest remains in designing a lightweight, high conductive, non-corrosive and low cost container. Moreover, the selection of the potential PCM regards as well in their melting range, latent heat, stability under cycling and cost for low temperature storage is needed.

4.2 Contribution to the state-of-the-art

This Chapter presents the PCM research and development for low storage applications in particular for commercial freezers which has a normal working temperature about -18 ºC. This research was developed in two different publications:

- E. Oró, C. Barreneche, M.M. Farid, L.F. Cabeza. Experimental study on the selection of phase change materials for low temperature applications. Renewable Energy. Accepted, doi: 10.1016/j.renene-2013-01-043.
- E. Oró, L. Miró, C. Barreneche, I. Martorell, M.M. Farid, L.F. Cabeza. Corrosion of metal and polymer containers for use in PCM cold storage. Applied Energy 57 (2013) 130-136.

Here a wide range of PCM for low temperature applications has been studied using the design of experiments (DoE) methodology. Thermal cycling test was performed to determine thermal reliability of form-stable PCM in terms of phase change temperatures and latent heats after a large number of thermal cycles. In addition, thermal properties of the PCM candidates were determined by differential scanning calorimetry (DSC) analysis.

Moreover the corrosion/degradation rate of metal/PCM and polymer/PCM combinations used in low temperature processes is analysed after one, four and 12 weeks. In this Chapter, commercial PCM and in-house prepared PCM formulation used in low temperature processes are analysed. Moreover, visual phenomena (bubbles or precipitates) and pH changes in PCM formulations were analysed. Copper, aluminium, stainless steel and carbon steel were the metals considered as containers. Polypropylene (PP), high density polythylene (HDPE), polyethylene terephthalate (PET) and polystyrene (PS) were the polymers selected.

The main contributions to the state-of-the-art can be summarized in the following points:

- Sub-eutectic ammonium chloride (NH_4Cl) concentrations of 16 wt%, as well as super-eutectic concentrations up to 22 wt% and eutectic concentrations 19.7 wt% were analysed. Moreover, different additive concentrations were used for two purposes; reducing subcooling and phase segregation by increasing the viscosity of the material with oxyethylmethylcellulose (CMC) and altering the phase change temperature (NaCl or AlF_3).

- When CMC was used in the PCM formulation the stability of the PCM under long cycling was significantly improved.

- From the DoE results one equation for each additive (NaCl and AlF_3) was developed in order to predict the material phase change temperature as a function of the concentration of the components in its formulation. These formulas are of great importance since the phase change temperature is a key factor in the implementation of TES systems using PCM in cold applications.

  According to the original components a linear model to suit the experimental data can be expressed as shows in Eq. 1 and Eq. 2, depending on the percentage of the additive that is used in the PCM formulation:

  - $Tpc = -18.39 + 0.044 \cdot NH_4Cl - 1.77 \cdot NaCl - 0.35 \cdot CMC$ Eq. 1
  - $Tpc = -14.8 + 0.0512 \cdot NH_4Cl - 0.0045 \cdot AlF_3 - 0.3 \cdot CMC$ Eq. 2

- Cooper and carbon steel must be avoided as PCM containers in any case due to their high corrosion rate mainly, but also because of the presence of precipitates and pH changes.

- Aluminium is not recommended because of pitting and bubbles appearance on its surface which could cause changes in material properties such as holes in the container.

- Stainless steel 316 alloys are highly recommended for long use as PCM container material.

Figure 17 shows some of the changes in appearance during the corrosion tests between metals and the PCM.

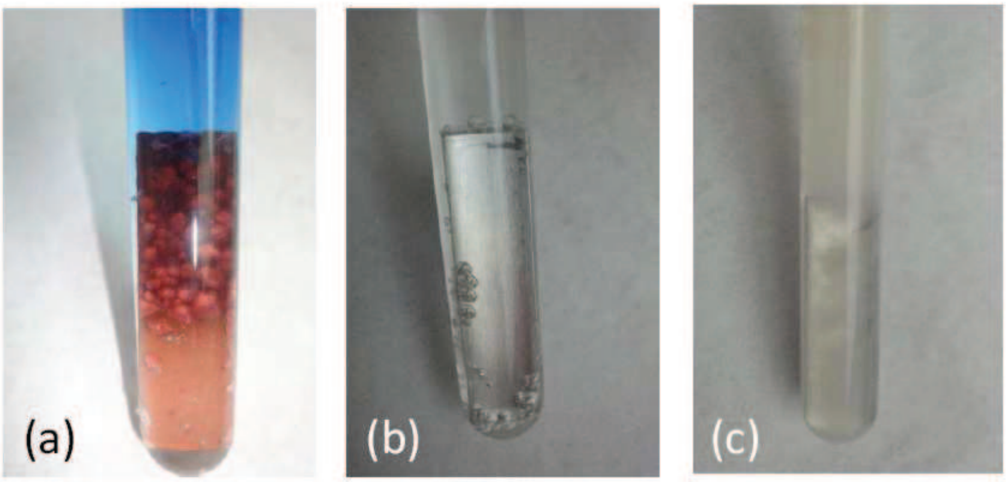


Figure 17. Changes in appearance during the corrosion tests. (a) Cooper, Cu oxidation and salts precipitation. (b) Aluminium, production of bubbles. (c) Stainless steel, no physical effects.

- In all cases analysed, the candidates that were thickened provides a great improvement in preventing corrosion.

Figure 18 shows the corrosion rate between all the metals analysed and different PCM formulations. The difference between both PCM formulations is that PCM-H did not have CMC agent in its formulation while PCM-I had. The reason is probably that the addition of CMC changes considerable the viscosity of the solution, therefore ions diffusion decreases and the concentration of ions in the layer in contact with the metal may decrease.

- Any of the plastics analysed (PP, PS, PET, and HDPE) did not show important changes in weight or physical appearance of the samples therefore they are compatible with the PCM studied.

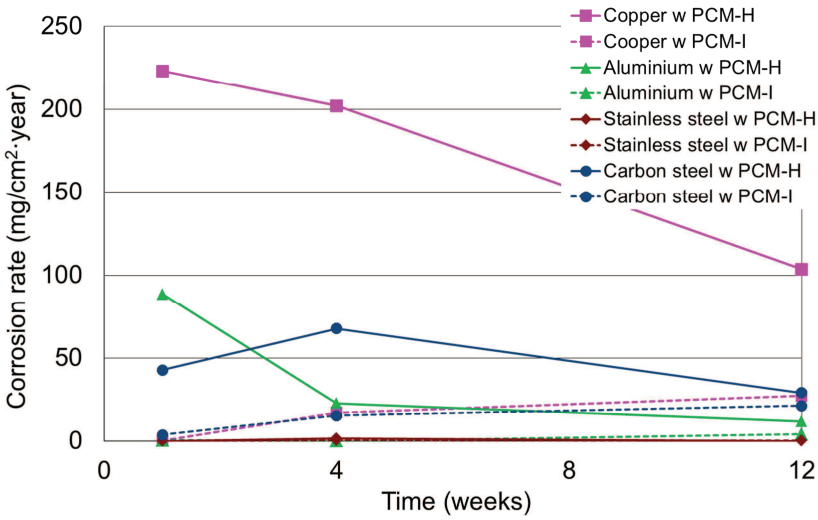


Figure 18. Corrosion rate between metals and PCM with and without thickening agent.

4.3 Journal paper

4.3.1 Paper 1

Renewable Energy 57 (2013) 130–136

Contents lists available at SciVerse ScienceDirect

Renewable Energy

journal homepage: www.elsevier.com/locate/renene

ELSEVIER

Experimental study on the selection of phase change materials for low temperature applications

Eduard Oró [a], Camila Barreneche [a,b], Mohammed M. Farid [c], Luisa F. Cabeza [a,*]

[a] GREA Innovació concurrent, Edifici CREA, Universitat de Lleida, Pere de Cabrera s/n, 25001 Lleida, Spain
[b] Department of Materials Science & Metallurgical Engineering, Universitat de Barcelona, Martí i Franquès 1 11, 08028 Barcelona, Spain
[c] Department of Chemical and Materials Engineering, The University of Auckland, 20 Symonds Street, Auckland, New Zealand

http://www.sciencedirect.com/science/article/pii/S0960148113000815#

Paper 2

ARTICLE IN PRESS

Applied Energy xxx (2012) xxx–xxx

Contents lists available at SciVerse ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy

ELSEVIER

Corrosion of metal and polymer containers for use in PCM cold storage

Eduard Oró [a], Laia Miró [a], Camila Barreneche [a,b,1], Ingrid Martorell [a], Mohammed M. Farid [c], Luisa F. Cabeza [a,*]

[a] GREA Innovació Concurrent, Universitat de Lleida, Edifici Crea: Pere de Cabrera s/n, 25001 Lleida, Spain
[b] Department of Materials Science & Metallurgical Engineering, Universitat de Barcelona, Martí i Franquès 1-11, 08028 Barcelona, Spain
[c] Department of Chemical and Materials Engineering, University of Auckland, 20 Symonds Street, Auckland, New Zealand

http://www.sciencedirect.com/science/article/pii/S0306261912007684

5 Experimental analysis of including PCM and its effect on food quality

5.1 Introduction

Food transport and storage at low temperatures is a matter worldwide due to changes of the dietary habits and the increasing of the population. The issue of improving food storage and transportation applies at different low temperature applications such as commercial freezers, refrigerated trucks and vans, etc.

It is well known that temperature fluctuations during long storage which are caused by the commented situations in freezers when could cause negative dramatic effects to the quality of the frozen food such as physical and chemical changes such as oxidation of lipids, enzymatic browning, formation of eutectics, freezing injury and recrystallization [1-3], [41-43]. Temperature drop during a partial thawing is another important problem during both storage and transport of low sensitive temperature products, causing deterioration of the stored food products [4]. Product and air temperature drops and fluctuations in low temperature stores are caused by:

- Electrical power failure.
- Door openings.
- Heat generated during defrosting system.

For ice cream to have smooth texture one of the major requirements is to have small ice crystals [44]. Since temperature fluctuations cause recrystallization, the quality of the ice cream is badly affected, and thus ice cream has been the subject of investigations into the effects of storage conditions. Moreover, if the product is melted and then refrozen, recrystallization of the ice occurs as well since ice crystals can shrink and grow when they melt and refreeze during temperature fluctuations [1].

Recrystallization is the process of changes in number, size and shape of ice crystals during frozen storage. Although the amount of ice stays constant with constant temperature throughout this process (dictated by the equilibrium freezing curve) recrystallization can alter and damage the structure and texture of the ice cream. Recrystallization basically involves small crystals disappearing (isomass recrystallization), large crystals growing at the expense of smaller crystals (migratory recrystallization) and crystals fusing together (accretion) [45-46].

At normal storage conditions ice crystal size is approximately 40-50 μm [48]. Figure 19 shows the typical microstructure of frozen ice cream samples stored at -30 ºC showing ice crystals and air bubbles [45-46]. Then when the same ice cream sample is stored at higher temperatures (-16 ºC) the ice crystal sizes increased and span of the distributions showing evidence of recrystallization after the hardening period (Figure 20).

Moreover, the results from a PhD dissertation from Bin [47] showed that fluctuating temperature have caused the ice crystal size to increase from 40-50 μm to 70-80 μm at the end of a week power loss period in a domestic freezer [47]. Figure 21 shows the ice crystal size in ice cream sample stored at steady temperature of -16 ºC while Figure 22 shows the ice crystal size increment during periodic power loss in the storage unit.

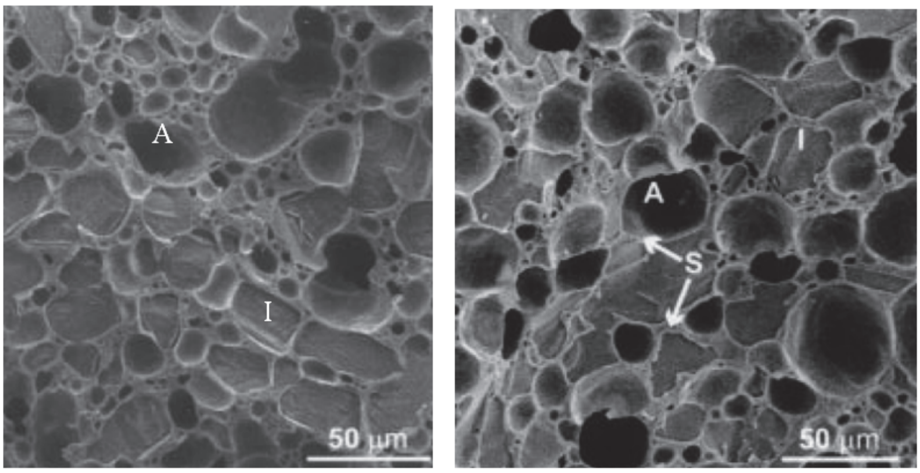


Figure 19. Typical microstructure of frozen ice cream sample. Key: air bubbles (A), serum phase (S), and ice crystals (I) [45-46].

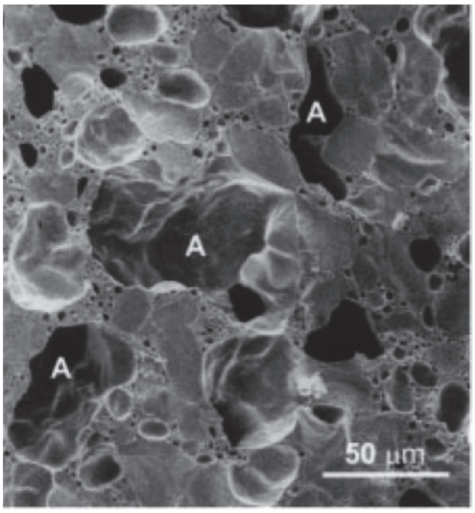


Figure 20. Microstructure of ice cream sample after 4 week of storage at -16 ºC. Key: air bubbles (A).

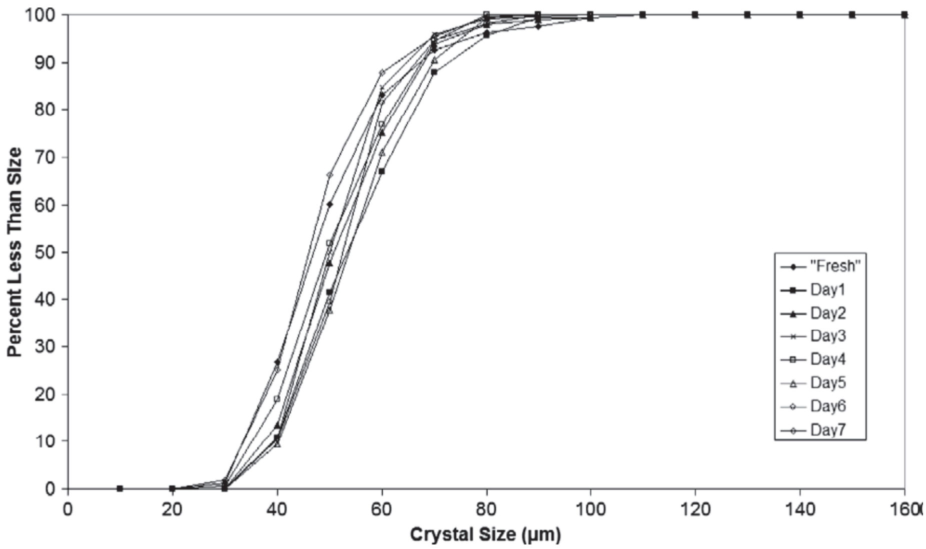


Figure 21. Ice crystal size distributions in 1 l block ice cream during storage at constant temperature [47].

Some researchers have been studied the effect of PCM in different low temperature applications such as domestic refrigerators and freezers [16-18], refrigerated trucks [19-20] and even refrigerated plants [21-22]. However there are no studies in the literature with regards to the effects of PCM systems on the behaviour of commercial freezers, or non-refrigerated vans which are not designed to extract heat from the load but to maintain the temperature of the frozen products using insulation.

Restrictions on daily use of the electricity in some countries and regular electrical power failure could induce significant economical losses to supermarkets due to devaluation of frozen food quality. Moreover, the customers in every supermarket unconsciously cause significant heat gains to the system due to frequent door openings of commercial freezers. The aim of this Chapter is to prove experimentally the improvement of the thermal performance of commercial freezers using PCM under door openings and electrical power failure.

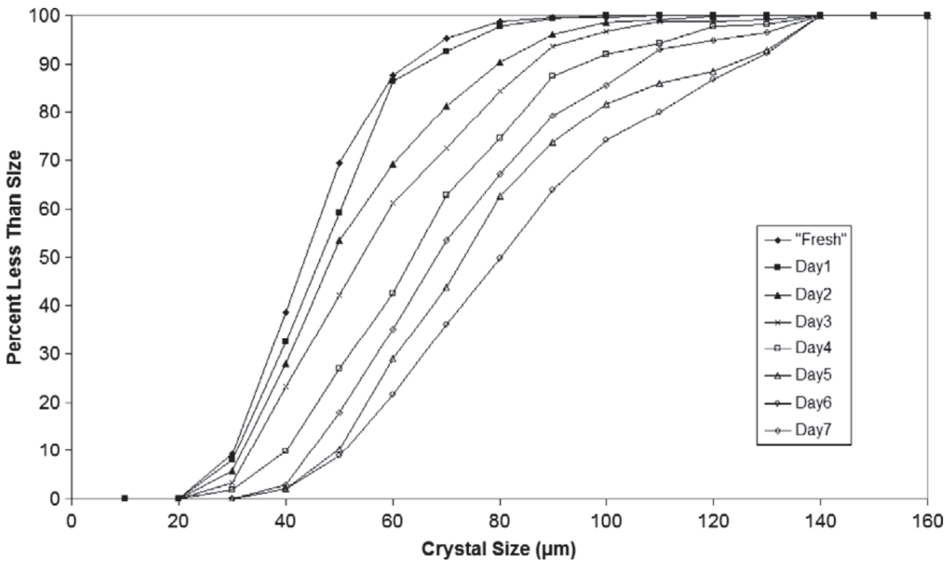


Figure 22. Ice crystal size distributions in 1 l block ice cream during storage with regular power loss [47].

5.2 Contributions to the state-of-the-art

This Chapter presents the experimental study of the inclusion of PCM in low storage applications in particular in commercial freezers regarding the thermal performance of the system and the food quality. This research was developed in two different publications:

- E. Oró, L. Miró, M.M. Farid, L.F. Cabeza. Improving thermal performance of freezers using phase change materials. International Journal of Refrigeration 35 (2012) 984-991.
- E. Oró, L. Miró, M.M. Farid, L.F. Cabeza. Thermal analysis of a low temperature storage unit using phase change materials without refrigeration system. International Journal of Refrigeration 35 (2012) 1709-1714.

The main contributions to the state-of-the-art can be summarized in the following points:

- Test packages (M-packs) were used to simulate the thermal mass of frozen food in the freezer under real conditions. In all the experimentation 42 kg were added in the freezer.

- Two commercial PCM with different melting temperature were tested:

    - ClimSel-18 from Climator (Patent: PCT/SE95/01309, 9404056-5).
    - E-21 from CRISTOPIA.

- The PCM was encapsulated in stainless steel thin containers (10 mm thick) and were placed on the evaporator plates occupying a total of only 3% of the internal volume of the storage unit. Seven PCM plates were placed in the freezer (Figure 23). The mass added by the PCM represents about 19% of the mass added by the M-packs when they were used.

- The use of PCM in a commercial freezer showed significant benefits in minimizing temperature rise of the freezer and the product in it, which occurs due to frequent door opening and electrical power failure.

Figure 23. Commercial freezer used in the experimentation and location of the PCM plates.

- Two different storage temperature condition inside the freezer was analysed (-19 ºC and -22 ºC). Regards the door opening tests, operating with a storage temperature of -19 ºC the benefit of the utilization of PCM was evident, while when the storage temperature was moved to -22 ºC, PCM did not show significant improvement due to the difference between the storage temperature and the phase change temperature of the PCM (-18 ºC) and the low heat transfer coefficient between the PCM plates and the air.

  Therefore it is important to select a PCM that has a phase change temperature near the storage temperature of the freezer to alleviate the problems associated with door openings.

Figure 24 shows the average air temperature during a five door opening of 10 seconds when M-packs were placed inside the freezer. Here the working temperature of the freezer was -19 ºC which is closed to the phase change temperature of the PCM analysed here (C-18).

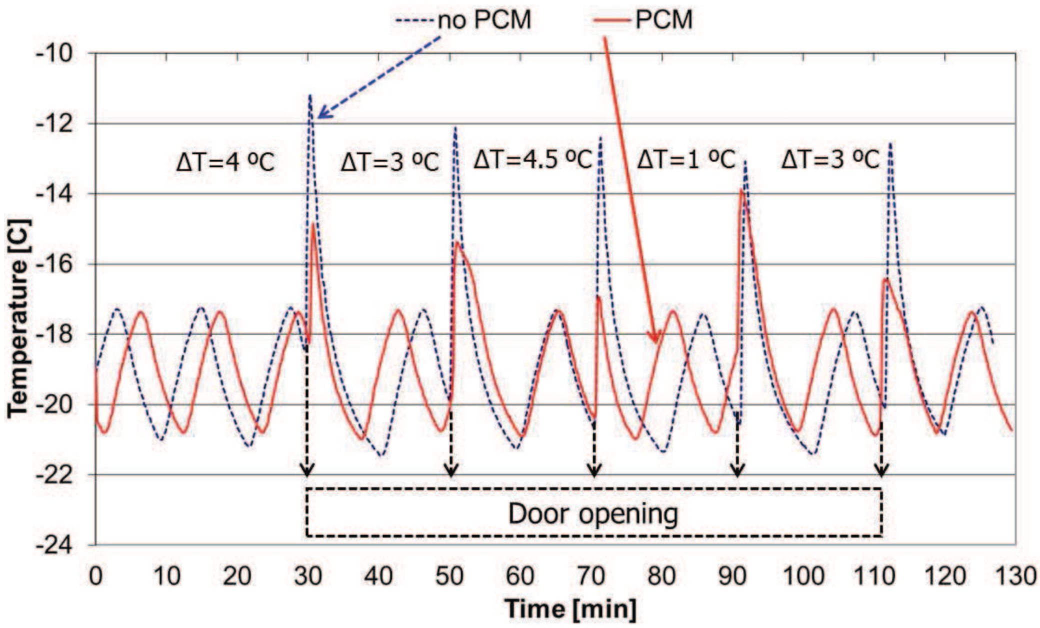


Figure 24. Average air temperature during a 5 door opening of 10 seconds with test packages (storage temperature of -19 ºC).

- In all the tests related to electrical power failure, the temperature of the M-pack, used to simulate food was always lower when PCM was used, when the storage temperature was set to -22 ºC the benefit of using PCM was greater than setting to -19 ºC due to the higher energy absorption of the PCM. Therefore, the use of PCM gave benefits to food quality under the condition of daily power cut.

Figure 25 shows the average air temperature of the freezer during an electrical power failure of 3 hours and Figure 26 shows the product temperature at same conditions. The benefit of using PCM is evident in both air and temperature drop/fluctuation response.

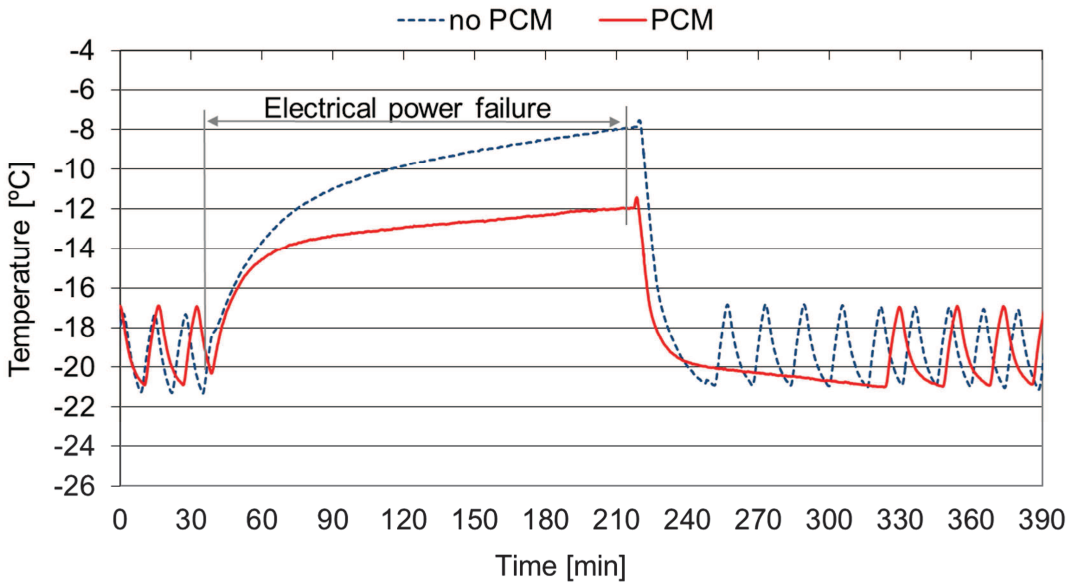


Figure 25. Average air temperature during an electrical power failure of 3 hours with test packages (storage temperature of -22 ºC).

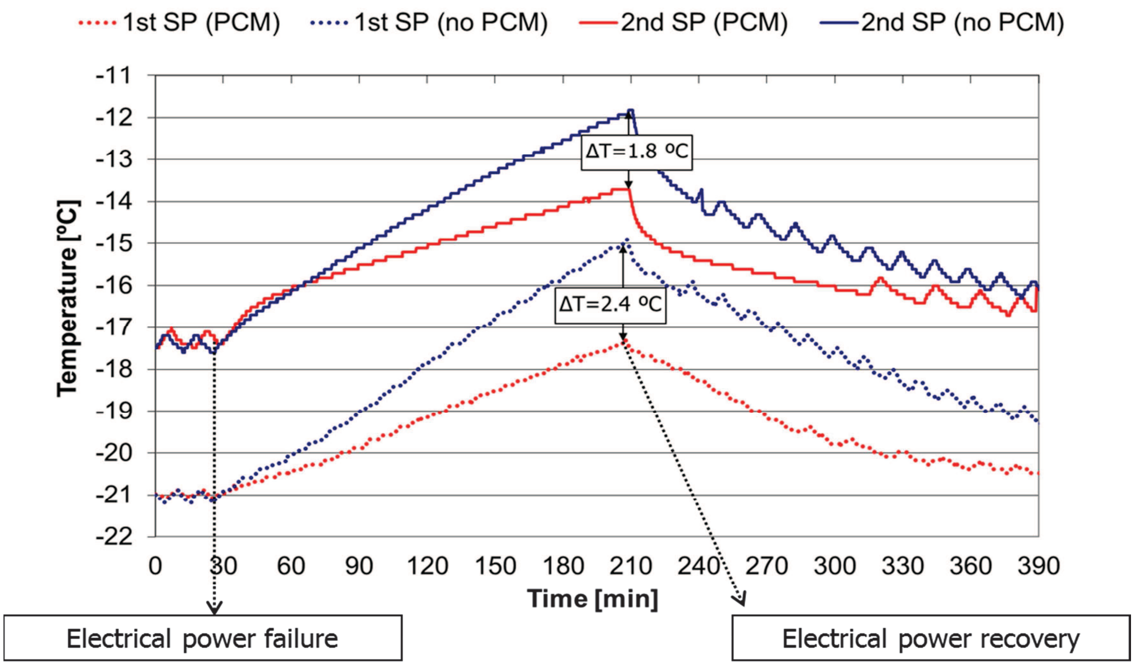


Figure 26. Product temperature during an electrical power failure of 3 (both storage temperature).

➢ In order to quantify the benefit of adding PCM in low temperature storage, a period factor was defined as the ratio of the time needed for the interior air or product to reach a fixed temperature with PCM to that without:

$$period \quad factor = \frac{period \quad PCM}{period \quad ref}$$

Therefore, when the period factor is one there is no enhancement in terms of air/product temperature. In terms of both air and frozen product temperature, the period factor is always higher than one; therefore the addition of PCM enhances the storage efficiency. Figure 27 shows the period factor versus the temperature of the product stored when two PCM were placed in the freezer. Notice that using E-21 the thermal benefit is higher. Hence the use of E-21 is more interesting than C-18 for commercial freezers working at the storage conditions analysed here.

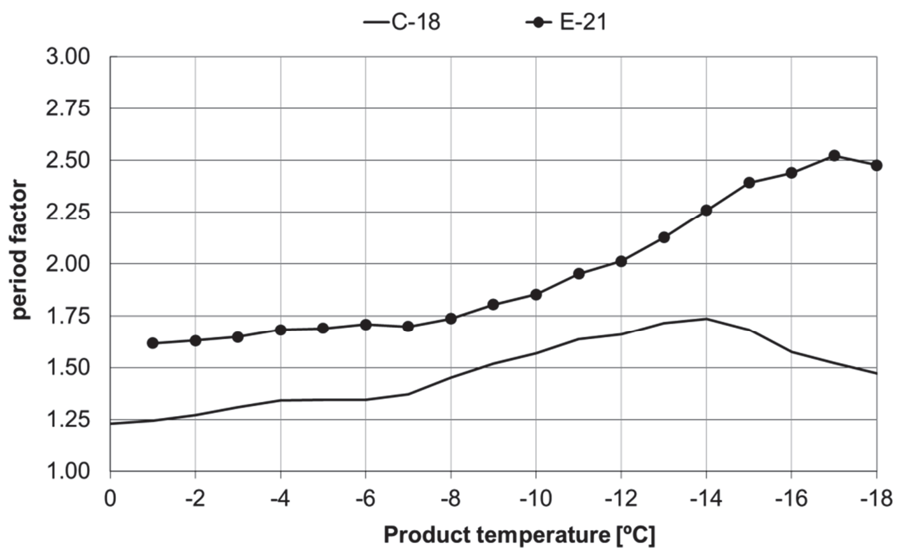


Figure 27. Period factor vs. product temperature during 24 hours without refrigeration system.

5.3 Journal paper

5.3.1 Paper 1

INTERNATIONAL JOURNAL OF REFRIGERATION 35 (2012) 984–991

Available online at www.sciencedirect.com
SciVerse ScienceDirect
journal homepage: www.elsevier.com/locate/ijrefrig

Improving thermal performance of freezers using phase change materials

E. Oró [a], L. Miró [a], M.M. Farid [b], L.F. Cabeza [a,]*

[a] *GREA Innovació concurrent, Edifici CREA, Universitat de Lleida, Pere de Cabrera s/n, 25001 Lleida, Spain*
[b] *Department of Chemical and Materials Engineering, The University of Auckland, 20 Symonds Street, Auckland, New Zealand*

http://www.sciencedirect.com/science/article/pii/S0140700712000059

5.3.2 Paper 2

INTERNATIONAL JOURNAL OF REFRIGERATION 35 (2012) 1709–1714

ELSEVIER

www.iifiir.org

Available online at www.sciencedirect.com

SciVerse ScienceDirect

journal homepage: www.elsevier.com/locate/ijrefrig

refrigeration

Thermal analysis of a low temperature storage unit using phase change materials without refrigeration system

Eduard Oró[a], Laia Miró[a], Mohammed M. Farid[b], Luisa F. Cabeza[a,*]

[a] GREA Innovació Concurrent, Edifici CREA, Universitat de Lleida, Pere de Cabrera s/n, 25001-Lleida, Spain

[b] Department of Chemical and Materials Engineering, The University of Auckland, 20 Symonds Street, Auckland, New Zealand

http://www.sciencedirect.com/science/article/pii/S0140700712001181

6 Mathematical modelling

6.1 Introduction

In previous chapters it has been said that loss or even interruption of electric supply leads to an increase in the storage temperature, which can reduce the quality and value of the stored products. TES systems using PCM can reduce the temperature rise of the storage compartment and therefore enhance the quality of the stored product. Moreover, several experimental studies have been performed on the use of PCM to enhance the thermal performance of low temperature storage systems.

Although experimental work can be conducted on domestic appliances it is difficult, time consuming and expensive exercise when work need to be done on industrial scale systems such as cold stores and refrigerated trucks. Moreover, mathematical modelling of those systems is advised whenever optimal design and PCM selection are required to optimize the thermal response of the system.

Many researchers have worked on modelling the air flow and temperature distributions inside low temperature storage and transport units based on computational fluid dynamics (CFD) [49-51], while others followed simpler heat transfer analysis [52-53].

Continuous analysis of both velocity and temperature fields are not always fully justified in engineering design situations, where cost and time must be taken into account. In the specific case analysed here it is difficult to understand the mechanism of heat transfer due to the complexity of freezer operation (compressor “on” and “off” cycles, defrosting operation, fan operation, different evaporator temperatures along the cabinet, different degrees of insulation in walls, heat loss through gaps, etc.). Moreover the main bulk of the freezer was found out experimentally to have uniform temperature distribution. Therefore the use of the more general procedure of the simultaneous solution of the mass, momentum and energy conservation equation for the fluid and the solid regions is not really justified. Then a mathematical model for cold storage units having PCM, which will allow extended storage time and transport without affecting the quality of the food was proposed.

Hereafter the mathematical model can be used to study the thermal performance of commercial freezers under different scenarios regarding to PCM and frozen product quantity, working storage temperature and melting temperature of the PCM used.

6.2 Contributions to the state-of-the-art

This Chapter presents the mathematical study of the inclusion of PCM in low storage applications in particular in commercial freezers. This research is described in the following publication:

- E. Oró, A. de Gracia, M.M. Farid, L.F. Cabeza. Mathematical model for commercial freezers containing phase change materials. International Journal of Refrigeration. Submitted (JIJR-D-12-00456).

The main contributions to the state-of-the-art can be summarized in the following points:

- A mathematical model to analyse the thermal performance enhancement of commercial freezers when PCM is used was developed. This numerical model is based in a continuous phase model which takes into account the heat transfer by natural convection by using effective thermal conductivity of the air and was validated against already published experimentally data of the system [54-55].

- The use of PCM increases the time at which the product is maintained in secure quality level when the refrigeration system is not available. Different amount of PCM inside the freezer was modelled: 3%, 6% and 9% of the internal freezer volume which meant an increasing in time of 24%, 75% and 112%, respectively when comparing with the system with no PCM.

- When PCM is added to the system, longer period with acceptable temperature values. But obviously a compromise between each application and the quantity of PCM used it has to be reached.

- The relationship between the melting temperature of the PCM and the storage temperature of the system was analysed numerically. The results showed that the phase change temperature of the used PCM has to be slightly lower than the working temperature of the unit.

6.3 Journal paper

Elsevier Editorial System(tm) for International Journal of Refrigeration
Manuscript Draft

Manuscript Number:

Title: Mathematical model for commercial freezers containing phase change materials

Article Type: Research Paper

Keywords: cold storage; low temperature unit; frozen food; phase change material; mathematical model

Corresponding Author: Prof. Luisa F. CABEZA, PhD

Corresponding Author's Institution: University of Lleida

First Author: Eduard Oró, Engineer

Order of Authors: Eduard Oró, Engineer; Alvaro de Gracia, Engineer; Mohammed M Farid, PhD; Luisa F. CABEZA, PhD

The paper is submitted but still not accepted; therefore there is no publication available yet.

7 The use of PCM in low temperature food applications other than freezers

7.1 Introduction

In commercial applications such as restaurants, the period that the ice cream container remains out of the freezer could be much longer than for example in households, and hence the heat absorbed by the ice cream may increase affecting its quality and increasing both, the near (absolute temperature) and the distant future (temperature fluctuations) quality. Moreover, the domestic and commercial transport of temperature sensitive products is commonly conducted with the use of insulated boxes.

It is well known that one of the most important factors affecting the quality of temperature sensitive products is the temperature variation during the storage and distribution stages [1-3], which could result in a reduction of quality and may shorten the shelf life of the products. The same may be said for hot products, a temperature drop due to heat losses through the packaging may affect the final consumption.

Moreover, for many researchers the mathematical modelling and the experimental analysis of heat and mass transfer in frozen food during both freezing and thawing is of great interest. The packing mode of frozen food during its distribution and storage is a key aspect since they are expected to maintain its temperature within close limits and hence ensure its optimum safety and high quality shelf life [56]. There are different ways to enhance the thermal requirements of the system which must be kept within a specific temperature range through the manipulation and the distribution chain:

- The utilization of high thermal protection by insulating containers [5], [56], [58].
- Using TES by the addition of PCM [3], [15-22], [59].
- Using TES by the addition of MAPCM [24-25].

Perishable products should be treated carefully during both storage and transport. In order to maintain food safety, the Food and Drug Administration code (FDA) [60] specifies serving temperature standards of 5 ºC or less for cold foods and 60 ºC or higher for hot foods as security temperatures. Moreover, related of the frozen desserts and ice cream, the ideal serving temperature of them is between -14.4 and -12.2 ºC [61].

The addition of PCM at the external part of the ice cream containers (Figure 28 (a)) may enhance the quality of it when the container is placed outside the freezer. On the same way, temperature sensitive product conditions when the product is placed in chilly bins (Figure 28 (b)) can be enhanced using TES systems.

(a) (b)

Figure 28. Commercially ice cream 5 l container (a) and chilly bin (b).

7.2 Contributions to the state-of-the-art

This Chapter presents the experimental and numerical study of the inclusion of PCM in low temperature food applications in particular in ice cream containers and chilly bins regarding the food quality improvement. This research was developed in two different publications:

- E. Oró, A. de Gracia, L.F. Cabeza. Active phase change material package for thermal protection of ice cream containers. International Journal of Refrigeration 36 (2013) 102-109.
- E. Oró, L. F. Cabeza, M.M. Farid. Experimental and numerical analysis of a chilly bin incorporating phase change material. Applied Thermal Engineering. Submitted (ATE-2012-3027R1).

The main contributions to the state-of-the-art can be summarized in the following points:

- A new PCM packaging prototype for commercially 5 l ice cream containers was designed. This prototype was experimentally and numerically studied.

- The addition of PCM in the external part of the ice cream container improves its thermal response when it is placed outside the freezer and exposed to high ambient temperatures showing significant benefits in minimizing temperature rise of the ice cream.

- The design with 10 mm of PCM at the bottom and 20 mm at the sides is selected as the desirable PCM package design because the additional volume occupied in the freezer is only 7% and has a high ice cream thermal protection.

- The increase in thermal energy storage capacity of the chilly bin system allows sustaining better products serving temperature for longer periods. PCM configuration was compared with that without PCM but with insulation, showing the difference between thermal insulation and TES.

- The mathematical model developed for chilly bin system was used to simulate storage and transportation of ice cream and hot products such as tea or coffee. Using PCM increased transportation time of ice cream and hot water by 400% and 320%, respectively.

7.3 Journal paper

7.3.1 Paper 1

INTERNATIONAL JOURNAL OF REFRIGERATION 36 (2013) 102–109

Available online at www.sciencedirect.com
SciVerse ScienceDirect
journal homepage: www.elsevier.com/locate/ijrefrig

Active phase change material package for thermal protection of ice cream containers

*Eduard Oró, Alvaro de Gracia, Luisa F. Cabeza**
GREA Innovació concurrent, Edifici CREA, Universitat de Lleida, Pere de Cabrera s/n, 25001 Lleida, Spain

http://www.sciencedirect.com/science/article/pii/S0140700712002368

7.3.2 Paper 2

Elsevier Editorial System(tm) for Applied Thermal Engineering
Manuscript Draft

Manuscript Number: ATE-2012-3027

Title: Experimental and numercial analisys of a chilly bin incorporating phase change material

Article Type: Research Paper

Keywords: chilly bins, frozen food, thermal protection, phase change material, numerical modelling.

Corresponding Author: Prof. MOHAMMED MEHDI FARID,

Corresponding Author's Institution:

First Author: Eduard Oro, ME in Mechanical Engineering

Order of Authors: Eduard Oro, ME in Mechanical Engineering; MOHAMMED MEHDI FARID; Cabeza Luisa F., PhD

The paper is submitted but still not accepted; therefore there is no publication available yet.

8 The use of PCM in low temperature industrial applications

8.1 Introduction

It is well known that TES plays an important role in both industrial and domestic applications. Northern European countries, such as Sweden, have a cold demand during summer time which is normally covered with a district cooling system which is based on cold water being distributed by a pipe network [62]. They use big water cavers to cool down and store the warm water from the consumption (homes, offices, hospitals, industries). Therefore, it is of great interest to study this type of storage system, enhancing the thermal performance of them; some options are:

- To enhance the stratification.
- To enhance the energy density.

One of the most attractive latent cold TES systems is the encapsulated PCM, which normally uses a cylindrical tank with spherical capsule filling in packed bed. For a packed bed, a large amount of heat transfer area can be contained in a small volume, and the irregular flow that exists in the voids of the bed enhances transport through turbulent mixing.

This chapter presents, compares and validates two different mathematical models of packed bed storage with PCM, more specifically the heat transfer during charge of the PCM [63].

Some researchers studied a storage system composed of spherical capsules filling a cylindrical tank [64-67]. The numerical solution was done using a marching technique in which the phase change problem inside the spherical capsule was coupled with the energy balance equation between the spherical boundary and the HTF, dividing the storage tank in N layers each of height equal to the spherical capsules diameter. On the other hand, other researchers [68-69] have been investigating the performance of the PCM packed bed considering that the PCM capsules behave as a continuous medium and not as a medium comprised of individual particles, where the mathematical model was also based on the energy balance between HTF and PCM.

In this Chapter two different mathematical models to describe the heat transfer and the thermal performance of a cylindrical water storage tank filled of spherically encapsulated PCM during charging process are presented. The first model is a continuous model based on the Brinkman equation which model the HTF flow inside the porous media and the second mathematical model treats the PCM capsules as individual particles and therefore the temperature gradient inside the PCM capsules can be analysed.

The experimental set up consisted mainly of a cylindrical storage tank with an internal diameter of 101 mm and a total height of 500 mm, where only 3.73 l are used for storage. Figure 29 shows the storage tank filled with PCM used in the experimentation. The PCM used was an organic material with a storage capacity of 175 kJ/kg.

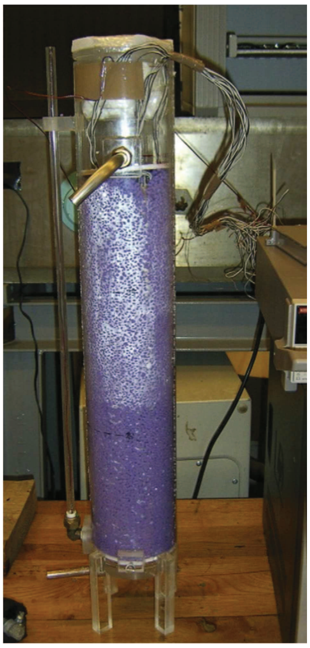


Figure 29. Storage tank used to perform the experimentation.

8.2 Contributions to the state-of-the-art

This Chapter presents two different mathematical models to predict the thermal response of a water tank filled with spherically encapsulated PCM. This research is described in the following publication:

- E. Oró, J. Chiu, V. Martin, L.F. Cabeza. Comparative study of different numerical models of packed bed thermal energy storage systems. Applied Thermal Engineering 50 (2013) 384-392.

The main contributions to the state-of-the-art can be summarized in the following points:

- Two different mathematical models for PCM packed bed TES systems are developed and validated with experimental data. These mathematical models could help in the design of new TES systems looking to enhance the actual systems.

- The results from the energy equation model show a basic understanding of cold charging. Moreover, three different Nu correlations were analysed and compared with the energy equation model. All of them showed the same temperature profile of the PCM capsules, hence any of them could be used in future models.

- The comparison between both mathematical models indicated that free convection is not as important as forced convection in the studied case.

8.3 Journal paper

Applied Thermal Engineering 50 (2013) 384–392

Contents lists available at SciVerse ScienceDirect

Applied Thermal Engineering

journal homepage: www.elsevier.com/locate/apthermeng

Comparative study of different numerical models of packed bed thermal energy storage systems

Eduard Oró [a], Justin Chiu [b], Viktoria Martin [b], Luisa F. Cabeza [a,*]

[a] GREA Innovació Concurrent, Universitat de Lleida, Edifici CREA, Pere de Cabrera s/n, 25001 Lleida, Spain

[b] KTH – Department of Energy Technology, Brinellvägen 68, SE-100 44 Stockholm, Sweden

http://www.sciencedirect.com/science/article/pii/S1359431112004929

9 Conclusions and recommendations for future work

9.1 Conclusions of the thesis

This thesis presents the study of the implementation of TES systems by using PCM in cold applications. After an extend literature review about the use of PCM in low temperature applications, it was found out that there was a gap in the implementation of TES using PCM in commercial freezers. Material research and development were carried out regarding on the specific working temperature of the cold system. The application of PCM to a commercial freezer and its effects on temperature fluctuations/rise and food quality were studied experimentally and through mathematical modelling developed in this thesis. Moreover, the implementation of PCM TES systems in food and industrial cold applications such as ice cream containers, chilly bins and water storage tanks were experimental and numerical analysed. The main conclusions that came out from this thesis are the following:

- A state-of-the-art review of the available literature was developed to provide required background and knowledge for the development research.

- The ammonium chloride (NH_4Cl) system was analysed as a possible low temperature PCM. Different additive concentrations were used for two purposes; reducing subcooling and phase segregation by increasing the viscosity of the material (CMC) and altering the phase change temperature (NaCl or AlF_3).

- When CMC was used in the PCM formulation the stability of the PCM under long cycling was significantly improved.

- From the DoE results the phase change temperature of the PCM candidate is predictable as a function of the concentration of the components in its formulation.

- Cooper and carbon steel must be avoided as PCM containers in any case mainly due to their high corrosion rate, but also because of the presence of precipitates and pH changes.

- Aluminium is not recommended because of pitting and bubbles appearance on its surface.

- Stainless steel 316 alloys are highly recommended for long use as PCM container material.

- Any of the plastics tested (PP, PS, PET, and HDPE) did not show important changes in weight or physical appearance of the samples therefore they are compatible with the PCM studied.

- The use of PCM in a commercial freezer showed significant benefits in minimizing temperature rise of the freezer and the product in it. Its use increases the time at which the product is maintained in secure quality level when the refrigeration system is not available or door openings are presented.

- A mathematical model to predict the temperature changes occurring in the commercial freezers with and without PCM panels was developed and validated with experimental data.

- The phase change temperature of the PCM should be slightly lower than the storage temperature to maximize benefits in minimizing temperature rise of the freezer and the product in it. This assessment is concluded in both numerical and experimental studies.

- A new PCM packaging prototype for commercially 5 l ice cream containers was designed using a mathematical model which was validated with experimental data. The addition of PCM in the lateral and bottom walls of the ice cream container improves its thermal response when it is placed outside the freezer and exposed to high ambient temperatures showing significant benefits in minimizing temperature rise of the ice cream.

- A mathematical model was developed for chilly bin modified with the addition of PCM to simulate storage and transport of ice cream and hot products such as tea or coffee. Using PCM increased transportation time under secure levels of ice cream and hot water by 4 and 3 times, respectively.

- Two different mathematical models for PCM packed bed TES systems were developed and validated with experimental data. These mathematical models could help in the future design of new TES systems looking to enhance the actual systems regarding the enhancement of thermal stratification and energy storage density by using PCM packed bed.

9.2 Recommendations for future work

Though a suitable PCM has been successfully developed, further work is needed to develop less corrosive PCM in contact with some metals and to search more additives to alter the phase change temperature at desirable. These will allow for adjustment of the PCM needed for different applications.

PCM panels have been successfully applied in domestic freezers for minimising temperature fluctuations during door opening and electrical power failure. The next step is to apply PCM panels to larger or different facilities, such as ice cream trolleys, delivery vans or medium cold stores.

The mathematical model could also be extended to a CFD modelling to simulate other cold applications and to simulate air flow and therefore heat transfer with different product amount/location configuration. Moreover, CFD modelling could be used to predict the optimum position and performance of PCM panels.

The quality of the frozen food has been analysed in the past mainly under temperature fluctuations. However, from the ice cream temperature behaviour during transport and storage without refrigeration system, temperature rise (melting-refreezing) is the most common behaviour. Therefore the quality of the frozen food in particular of ice cream could also be extended in terms of ice crystal size growth under temperature rise when a partial melting process occurs followed by a re-freezing.

References

[1] D.P. Donhowe, R.W. Hartel. Recrystallization of ice during bulk storage of ice cream International Dairy Journal 6 (1996) 1209-1221.

[2] T.M. Ngapo, I.H. Barbare, J. Reynolds, R.F. Mawson. Freezing rate and frozen storage effects on the ultrastructure of samples of pork. Meat science 53 (1999) 159-168.

[3] B. Gin, M.M. Farid. The use of PCM panels to improve storage conditions of frozen food. Journal of Food Engineering 100 (2010) 372-376.

[4] T.M. Ngapo, I.H. Barbare, J. Reynolds, R.F. Mawson. Frezing and thawing rate effect on drip loss from samples of pork. Meat Science 53 (1999) 149-158.

[5] B. Margeirsson, R. Gospavic, H. Pálsson, S. Arason, V. Papov. Experimental and numerical modelling comparison of thermal performance of expanded polystyrene and corrugated plastic packaging for fresh fish. International Journal of Refrigeration 34 (2011) 573-585.

[6] B. Zalba, J.M. Marín, L.F. Cabeza, H. Mehling. Review on termal energy storage with phase change: materials, heat transfer analysis and applications. Applied Thermal Engineering 23 (2003) 251-283.

[7] M.M. Farid, A. Khudhair, S.A.K. Razack, S. Al-Hallaj. A review on phase change energy storage: materials and applications. Energy Conversion and Management 45 (2004) 1597-1615.

[8] http://www.sofigram.com

[9] http://www.tcpreliable.com

[10] http://www.pcm-solutions.com

[11] http://www.pcmproducts.net

[12] http://www.rubitherm.com

[13] http://www.climator.com

[14] http://www.teappcm.com

[15] S.M. Hasnain. Review on sustainable thermal energy storage technologies. Part II: cool thermal storage. Energy Conversion and Management 39 (1998) 339-346.

[16] K. Azzouz, D. Leducq, D. Gobin. Enhancing the performance of household refrigerators with latent heat storage: An experimental investigation. International Journal of Refrigeration 32 (2009) 1634-1644.

[17] B. Gin, M.M. Farid, P.K. Bansal. Effect of door opening and defrost cycle on a freezer with phase change panels. Energy Conversion and Management 100 (2010) 372-376.

[18] P. Subramaniam, C. Tulapurkar, R. Thiyagarajan, G. Thangamani. Phase change materials for domestic refrigerators to improve food quality and prolong compressor off time. International Refrigeration and Air Conditioning Conference, Richmond (USA), 2010.

[19] M. Ahmed, O. Meade, M.A. Medina. Reducing heat transfer across the insulated walls of refrigerated truck trailers by the application of phase change materials. Energy Conversion and Management 51 (2010) 383-392.

[20] M. Liu, W. Saman, F. Bruno. Development of a novel refrigeration system for refrigerated trucks incorporating phase change material. Applied Energy 92 (2012) 336-342.

[21] M. Cheralathan, R. Velraj, S. Renganarayanan. Performance analysis on industrial refrigeration system integrated with encapsulated PCM-base cool thermal energy storage system. International Journal of Energy Research 31 (2007) 1398-1413.

[22] F. Wang, G. Maidment, J. Missenden, R. Tozer. The novel use of phase change materials in refrigeration plant. Part 3: PCM for control and energy savings. Applied Thermal Engineering 27 (2007) 2893-2901.

[23] D. Mondeig, F. Rajabalee, A. Laprie, H.A.J. Oonk, T. Calvet, M.A. Cuevas-Diarte. Protection of temperature sensitive biomedical products using molecular alloys as phase change materials. Transfusion and Apheresis Science 28 (2003) 143-148.

[24] L. Ventolà, T. Calvet, M.A. Cuevas-Diarte, D. Mondieig, H.A.J. Oonk. From concept to application. A new phase change material for thermal protection at -11 ºC. Journal of Material Research Innovation 6 (2002) 284-290.

[25] P. Espeau, D. Mondieig, Y. Haget, M.A. Cuevas-Diarte. 'Active' package for thermal protection of food products. Packing Technology Science 10 (1997) 253-260.

[26] H. Mehling, L.F. Cabeza. Heat and cold storage with PCM. An up to date introduction into basics and applications. Springers-Verlag Berlin Heidelberg; 2008.

[27] L.F. Cabeza, M. Ibáñez, C. Solé, J. Roca, M. Nogués. Experimentation with a water tank including a PCM module. Solar Energy Materials and Solar cells 90 (2006) 1273-1782.

[28] A. de Gracia, E. Oró, M.M. Farid, L.F. Cabeza. Thermal analysis of including phase change material in a domestic hot eater cylinder. Applied thermal Engineering 31 (2011) 3938-3945.

[29] A. Castell, I. Martorell, M. Medrano, G. Pérez, L.F. Cabeza. Experimental study of using PCM in brick constructive solutions for passive cooling. Energy Building 42 (2011) 534-540.

[30] W.A. Qureshi, N.K.C. Nair, M.M. Farid. Impact of energy storage in buildings on electricity demand side management. Energy Conversion and Management 52 (2011) 2110-2120.

[31] M.M. Farid, A.N. Khalaf. Performance of direct contact latent heat storage units with two hydrated salts. Solar Energy 52 81994) 179-189.

[32] A. Abhat. Low temperature latent heat thermal energy storage: heat storage materials. Solar Energy 30 (1983) 313-332.

[33] L.F. Cabeza, A. Castell, C. Barreneche, A. de Gracia, A.I. Fernandez. Materials used as PCM in termal energy storge in buildings: a review. Renewable and Suistainable Energy Reviews 12 (2011) 1675-1695.

[34] A. Sharma, V.V. Tayagi, C.R. Chen, D. Buddhi. Review on thermal energy storage with phase change materials and applications. Renewable and Suistainable Energy Reviews 13 (2009) 318-345.

[35] A.F. Regin, S.C. Solanki, J.S. Saini. Heat transfer characteristics of thermal energy storage systems using PCM capsules: a review. Renewable and Suistainable Energy Reviews 12 (2008) 2438-2458.

[36] S. Yilmaz, F. Sheth, I. Martorell, H.O. Paksoy, L.F. Cabeza. SALT-Water solutions as PCM for cooling applications. Proceedings of EuroSun 2010, International Conference on Solar Heating, Coolind and Buildings; 2010.

[37] S. Karaman, A. Karaipekli, A. Sari, A. Biçer. Polythylene glycol (PED)/diatomite composite as a novel form-stable phase change material for energy storage. Solar Energy Materials and Sollar Cells 95 (2011) 69-76.

[38] A. Hasan, A.A. Sayigh. Some fatty acids as phase-change thermal energy storage materials. Renewable Energy 4 (1994) 69-76.

[39] A. Sari. Eutectic mixtures of some fatty acids for latent heat storage: Thermal properties and thermal reliability with respect to thermal cycling. Energy Conversion and Management 47 (2006) 1207-1221.

[40] J.J. Zhang, J.L. Zhang, S.M. He, K.Z. Wu, X.D. Liu. Thermal studies on the solid-liquid phase transition in binary systems of fatty acids. Thermochimica Acta 369 (2001)157-160.

[41] E. Ben-Yoseph, R.W. Hartel. Computer simulation of ice recrystallization in ice cream during storage. Journal of Food Engineering 38 (1998) 309-329.

[42] R.D. Heap. Cold chain performance issues now and in the future. In IIR-IRHACE Conference, pages 75-87, The University of Auckland, New Zealand, 2006.

[43] H.B. Nahor, M.L. Hoang, P. Verboven, M. Baelmans, B.M. Nicolai. CFD model of the airflow, heat and mass trnasfer in cool stores. International Journal of Refrigeration 28 (2005) 368-380.

[44] A.B. Rusell, P.E. Cheney, S.D. Wantling. Influence of freezing conditions on ice crystallization in ice cream. Journal of Food Engineering 39 (1999) 179-191.

[45] A.A. Flores, H.D. Goff. Ice crystal size distribution in dynamically frozen model solutions and ice cream as affected by stabilitzers. Journal of Dairy Science 82 (1999) 1399-1407.

[46] A.A. Flores, H.D. Goff. Recrystallisation in ice cream after constant and cycling temperature storage conditions as affected by stabilizers. Journal of Dairy Science 82 (1999) 1408-1415.

[47] B. Gin. Improving Thermal Performance of Freezers through the Application of Phase Change Materials. PhD thesis, University of Auckland, New Zealand, 2010.

[48] C. Clarke. The science of ice cream. RSC paperbacks. The Royal Society of Chemestry, Cambridge, 2004.

[49] G. Cortella, M. Mazan, G. Comini. CFD simulation of refrigerated display cabinets. International Journal of Refrigeration 24 (2001) 250-260.

[50] B. Gin, M.M. Farid, P.K. Bansal. Modelling of phase change material implemented into cold storage application. HVAC and R Research 17 (2011) 257-267.

[51] O. Laguerre, S.B. Amara, J. Moureh, D. Flick. Numerical simulation of air flow and heat transfer in domestic refrigerators. Journal of Food Engineering 81 (2007) 144-156.

[52] J. Moureh, D. Flick. Airflow pattern and temperature distribution in a typical refrigerated truck configuration loaded with pallets. International Journal of Refrigeration 27 (2004) 464-474.

[53] G. Comini, G. Cortella, O. Saro. Finite element analysis of coupled conduction and convection in refrigerated transport. International Journal of Refrigeration 18 (1995) 123-131.

[54] E. Oró, L. Miró, M.M. Farid, L.F. Cabeza. Improving thermal performance of freezers using phase change materials. International Journal of Refrigeration 35 (2012) 984-991.

[55] E. Oró, L. Miró, M.M. Farid, L.F. Cabeza. Thermal analysis of a low temperature storage unit using phase change materials without refrigeration system. International Journal of Refrigeration 35 (2012) 1709-1714.

[56] S.J. James, C. James, J.A. Evans. Modelling of food transportation systems – a review. International Journal of Refrigeration 2 (2006) 947-957.

[57] M. Net, E. Trias, A. Navarro, A. Ruiz, P. Diaz, J.R. Fontenla, M. Manyalich. Cold chain monitoring during cold transportation of human corneas for transplantation, Transplantation Porceedings 35 (2003) 2036-2038.

[58] A. Yannick. 2006. European Patent No. FR 2930739.

[59] O. Laguerre, M.F. Ben Aisa, D. Flick. Methodology of temperature prediction in an insulated container equipped with PCM. International Journal of Refrigeration 31 (2008) 1063-1072.

[60] U.S. Food and Drug Administration. U.S. Department of Health & Human Services [Internet, september 2012]. Availave from http://www.fda.gov/food/foodsafety/retailfoodprotection/foodcode/default.htm

[61] International Dairy Foods Association. Available online (September 2012) in http://www.idfa.org/

[62] N.W. Chiu. Heat transfer aspects of using phase change meterial in thermal energy storage applications. Licentiate thesis in Energy Technology, stockholm (Sweden), 2011.

[63] F.P. Incropera, D.P. DeWitt, T.L. Bergam, A.S. Lavine. Fundamentals of Heat and Mass Transfer, sicth ed., (USA), 2007.

[64] A.F. Regin, S.C. Solanki, J.S. Saini. An analysis of a packed bed latent heat thermal energy storage system using PCM capsules: numerical investigation. Renewable Energy 34 (2009) 1765-1773.

[65] K.A.R. Ismail, J.R. Henríquez. Numerical and experimental study of spherical capsules packed bed latent heat storage system. Applied Thermal Engineering 22 (2002) 1705-1716.

[66] M. Rady. Granluar phase change materials for thermal energy storage: experiments and numerical solutions. Applied Thermal Engineering 29 (2009) 3149-3159.

[67] T. Kouskou, A. Jamil, P. Bruel. Asymptotic behaviour of a storage unit undergoing cyclic melting and solidification processes. Journal of Thermophysics and Heat Transfer 24 (2010) 355-363.

[68] S. Wu, G. Fang, X. Liu. Thermal performance simulations of a packed bed cool thermal energy storage using n-tetradecane as phase change material International Journal of Thermal Sciences 49 (2010) 1752-1762.

[69] S. Wu, G. Fang. Dynamic performances of solar heat storage system with packed bed using myristic acid as phase change material. Energy and Buildings 43 (2011) 1091-1096.