High-Capacity Cool Thermal Energy Storage for Peak Shaving

— A Solution for Energy Challenges in the 21st Century

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Abstract

Due to climatic change, increasing thermal loads in buildings and rising living standards, comfort cooling in buildings is becoming increasingly important and the demand for comfort cooling is expanding very quickly around the world. The increased cooling demand results in a peak in electrical power demand during the hottest summer hours. This peak presents new challenges and uncertainties to electricity utilities and their customers.

Cool thermal storage systems have not only the potential to become one of the primary solutions to the electrical power imbalance between production and demand, but also shift cooling energy use to off-peak periods and avoid peak demand charges. It increases the possibilities of utilizing renewable energy sources and waste heat for cooling generation. In addition, a cool storage can actually increase the efficiency of combined heat and power (CHP) generation provided that heat driven cooling is coupled to CHP. Then, the cool storage may avoid peaks in the heat demand for cooling generation, and this means that the CHP can operate at design conditions in most of time.

Phase Change Materials (PCMs) used for cool storage has obtained considerable attention, since they can be designed to melt and freeze at a selected temperature and have shown a promising ability to reduce the size of storage systems compared with a sensible heat storage system because they use the latent heat of the storage medium for thermal energy storage.

The goal of this thesis is to define suitable PCM candidates for comfort cooling storage. The thesis work combines different methods to determine the thermophysical properties of tetradecane, hexadecane and their binary mixtures, and demonstrates the potential of using these materials as PCM for comfort cooling storage. The phase equilibrium of the binary system has been studied theoretically as well as experimentally, resulting in the derivation of the phase diagram. With knowledge of the liquid-solid phase equilibrium characteristics and the phase diagram, an improved understanding is provided for the interrelationships involved in the phase change of the studied materials. It has been indicated that except for the minimum-melting point mixture, all mixtures melt and freeze within a temperature range and not at a constant temperature, which is so far often assumed in PCM storage design. In addition, the enthalpy change during the phase transition (heat of fusion) corresponds to the phase change temperature range; thus, the storage density obtained depends on how large a part of the phase change temperature range is valid for a given application.

Differential Scanning Calorimetry (DSC) is one frequently used method in the development of PCMs. In this thesis, it has been found that varying results are obtained depending on the DSC settings throughout the measurements. When the DSC runs at a high heating/cooling rate it will lead to erroneous information. Also, the correct phase transition temperature range cannot be obtained simply from DSC measurement. Combining phase equilibrium considerations with DSC measurements gives a reliable design method that incorporates both the heat of fusion and the phase change temperature range.

The potential of PCM storage for peak shaving in different cooling systems has been demonstrated. A Computer model has been developed for rapid phase equilibrium calculation. The use of phase equilibrium data in the design of a cool storage system is presented as a general methodology.

Keywords: Comfort cooling, peak shaving, PCM, cool thermal storage system, DSC, phase change temperature range, the heat of fusion, phase equilibrium, phase diagram.
Sammanfattning

Komfortkylbehovet ökar mycket snabbt runt om i världen, dels till följd av ökad termisk belastning intern i byggnader, och dels till följd av ökad levnadsstandard. Detta ökade kylbehov leder bland annat till ökade eleffektbehov under topplasttimmar de varmaste dagarna på året, vilket kan leda till s.k. eleffektbrist. Ett ökat toppeffektbehov leder till nya utmaningar och osäkerheter för elbolagen och deras kunder.


Fasändringsmaterial (PCM) i kyllager har väckt stor intresse på senare tid eftersom dessa kan designas till att smälta/frysa vid en rad olika temperaturer beroende på applikation. I PCM-lager nyttras smältevärnet hos det aktuella materialet, och sådana lager kan därmed minska erforderlig storlek, givet en viss lagerkapacitet, jämfört med s.k. sensibla lager (t ex vattenlager) som endast nyttra en temperaturändring i materialet. Detta bidrar till att nyttja en utomstående kyla sönder flera timmar.


Potentialen för PCM-lager med blandningar av tetra- och hexadekan har slutligen studerats för några applikationer. En simuleringssilver har tagits fram för att snabbt kunna innehålla fasändringsinformation vid design av lagret. Användningen av fasändvikter vid design av smältvärmelager presenteras här som en generell modell.
List of Appended Papers

This thesis is based on the following papers, referred to by Roman numerals I – VI.

I. He B., Gustafsson E.M. and Setterwall F. Tetradecane and hexadecane binary mixtures as phase change materials (PCMs) for cool storage in district cooling system. *Energy 1999; 24: 1015-1028.*

II. He B., Martin V. and Setterwall F. Liquid-solid phase equilibrium study of tetradecane and hexadecane binary mixtures as phase change materials (PCMs) for comfort cooling storage. *Fluid Phase Equilibria 2003; 212: 97-109.*


These papers are appended after the summary.
Related Works

The following papers cover the related issue but have not been included in this thesis.


He B., Martin V. and Setterwall F. Phase change materials (PCMs) for cool storage - An investigation of possible candidates of lower temperature PCMs in thermal energy storage applications: in household refrigeration. In: *Proceedings of the 4th workshop of Annex 14, Istanbul, Turkey, 2001*.


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1. Introduction

The global demand of energy and electricity is increasing steadily. In the International Energy Outlook 2003, world energy consumption is projected to increase by 58% percent between 2001 to 2025 [57]. A new, major study from International Energy Agency (IEA) World Energy Investment Outlook indicates that if present trends continue, the world will need to invest trillion of dollars over the next three decades to maintain and expand energy supply. In addition, without these investments, the world economy may suffer [121].

The challenge of energy in the future is clear, we must develop and expand new technologies to reduce the demand for energy, increase energy supply by using renewable energy and to effectively use the available energy. During the last two decades many research and development activities related to energy have concentrated on efficient energy use and energy savings and conservation. Energy efficiency is the ability to use less energy to produce the same amount of useful work or services. The energy-saving result of such an efficiency improvement is often called energy conservation. Conservation is closely related and simply means using less energy. Utilizing energy wisely should involve increasing both energy efficiency and conservation [79]. Improved energy efficiency and conservation should reduce energy consumption and costs, while maintaining equivalent service in homes, offices, etc.

In this context, Thermal Energy Storage (TES) systems can play an important role as they provide great potential for an improved energy efficiency and they are a necessary component for the efficient utilization of renewable energy sources and for energy conservation. For example, solar energy seems to be the most promising renewable energy source, however, it is not continuous. In addition, utilization of waste heat may increase if a TES is integrated to match the waste heat supply to some heat demand. Thermal energy storage systems enable greater and more efficient use of these fluctuating energy sources by matching the energy supply with demand [86 and 113].

Thermal energy storage can also be used for cooling to reduce or eliminate the demand for electricity and hence avoid an electricity peak load. When thermal energy storage is used in a combined heat and power (CHP) system to keep a constant heat demand, it may increase the efficiency of the CHP plant.

1.1 Cool thermal energy storage

Cool thermal energy storage systems store lower temperature energy for later use as a heat sink. It bridges the time gap between energy requirements and energy use and is an excellent energy management strategy.
1.1.1 Background

Early refrigeration systems used blocks of ice cut from frozen lakes as stored cooling. With the introduction of mechanical refrigeration, most stored cooling systems were replaced by instantaneous cooling systems sized to meet the maximum expected load at any time. In the 1970s and 1980s, when electricity utility companies recognized the need to reduce the peak demand on their generation and distribution systems, interest in cool storage for commercial applications grew [30].

A good internal climate is important in buildings where people live and work. Comfort cooling in buildings is becoming increasingly important due to a number of factors. For example, climatic change, increasing thermal loads in buildings due to better insulation of the buildings in combination with the installation of heat-generating electrical equipment, and because of rising living standards. Hence, the demand for comfort cooling is expanding very quickly around the world. For example, demand for artificial cooling has traditionally been lower in Europe than the USA, however, clear signs of a growing “air conditioning culture” has started to appear recently [2]. The increased cooling demand results in an electrical power peak demand during the hottest hours in the summer, when the electricity may be the most expensive. In a report from the REHVA project - Apascue [87] indicates that the energy demand for cooling is 30 kWh/m² in the residential sector in Southern European countries. In offices and commercial buildings, the cooling demand is much higher. In a typical modern office building, the amount of energy used for cooling purposes is 20% of the total energy use. Further, during the day in summer periods, the cooling loads reach their maximum values between 16:00 and 17:00. A peak power demand of 54 GW for cooling will develop in the European Union, which is equivalent to the output of 180 power stations, 300 MW each [87]. This clearly indicates that electrically driven cooling will create a severe imbalance in the European Union’s power supply strategy.

In Asia and the United States, comfort cooling demands are much larger than in Europe [108]. Adnot et al. reported that the non-residential conditioned building area in the USA is eight times higher than in the EU [33]. From 1990 to 2001, the US national summer peak cooling demand has increased by about 30% [63]. Air conditioning is the main reason for the peak load. For example, in Southern California the peak summer demand for electricity has risen by about 50% between 1980 and 2000. Here, in-state electricity generation has failed to keep up the pace [93].

The electric power blackout may trigger interest in the use of cool thermal storage to avoid the peak electricity demand during the hottest hours in the summer. This blackout on August 14, 2003 affected in large portions of the Midwest and Northeast US and Ontario Canada [70].

Cool thermal energy storage technology has the potential to become one of the primary solutions to the electrical power imbalance between production and demand. In areas of the world where the electricity rate is time-based (e.g., Japan) this may be a cost-saving solution since cool storage system shift cooling energy use to off-peak periods and thus avoids peak demand charges. Also, lowering the peak demand of electricity will lower the amount of electricity generated with the most expensive fuel and will thus be beneficial for the utility company. The most expensive fuel is often also the most harmful to the environment. Cool storage thus helps both utilities and their customers to meet these challenges while minimizing their risks and maximizing their benefits.
Heat driven cooling technology, e.g. absorption cooling is another option to avoid electrical power peak demand and provide environmentally sound cooling. It has been demonstrated that absorption technology is an efficient way for a utility company to use district heating or waste heat (lower temperature heating) to produce and sell comfort cooling during summer. Integrating a cool storage with an absorption cooling system provides peak shaving and economic advantages [99].

Cool storage systems may become an economically attractive alternative if one or more of the following conditions exist [10]:

- short period of cooling demand;
- frequently varying cooling loads;
- infrequent or cyclical loads;
- cooling demand and supply do not match;
- economic incentives are provided to use off-peak energy
- energy supply is limited by the utility company, thus making it impossible to satisfy the maximum load directly;
- the capacity of an existing chiller is too low to provide peak load.
- electricity production from CHP plant.

Thus, cool storage can provide many energy-related benefits in cooling applications and in CHP production.

1.1.2 Benefits of cool thermal energy storage

Load shifting is typically the main reason to install a cool storage system. And some key benefits of such load shifting are summarized as below [4, 10, 27, 34 and 36]:

- Reduced chiller size and capital cost savings. A cool storage system utilizes smaller chillers, auxiliary equipments (e.g., cooling tower, pumps and fans), as well as piping and ductwork. Often, the electrical distribution system that supplies power for cooling can also be made smaller.
- Energy savings. Cool storage systems permit chillers to operate more at night when lower condensing temperatures improve equipment efficiency; furthermore, it increases the fraction of on-design load operation, minimising inefficient part-load performance.
- Increased flexibility. With a cool storage system, cooling can be available on any desired schedule, independently of the operation of the chillers (within limits). The cool storage unit may be able to deliver cooling at a higher rate than the chillers, or to supplement the chillers.
- Extend the capacity of an existing system.
- Energy cost savings. When electricity prices differ between peak hours and off-peak hours, cool storage provides the potential for using off-peak energy to produce cooling. Additionally, when electricity is produced from CHP, a cool storage system can increase the efficiency of a CHP system running at full load, and thus increase the cost efficiency.
1.1.3 The operating strategies of cool storage system

A cool storage system may supply cooling to a demand from either storage, a chiller, or both. The operating strategy determines what portion of the load at any given time is met by the storage and what portion is met by direct chilling. The operating strategy defines the overall method of controlling the cool storage system in order to achieve the design intent [26, 50 and 115].

Operating strategies are generally classified as either full storage or partial storage, referring to the amount of cooling load transferred from on-peak to off-peak operation. A full-storage operating strategy (Fig. 1) shifts the entire on-peak cooling load to off-peak hours. The storage takes care of the whole peak-cooling load, and the chiller does not run at all during on-peak hours. The full-storage strategy requires a relatively large storage capacity and chiller and therefore is the most suitable when on-peak demand charges are high or the on-peak period is short [32].

With a partial-storage strategy, the capacity of the chiller is significantly less than the maximum load. The chiller only meets part of the on-peak cooling load and the remaining part is met by the storage. Such operating strategies can be further subdivided into load-levelling and demand-limiting.

In a load-levelling system (Fig. 2), the chiller typically runs at or near its full capacity for 24 hours on the design day. When the load is less than the chiller output, the excess cooling is stored. When the load is higher than the chiller output, the additional demand is supplied from the storage. This approach minimizes the required chiller and storage capacities and is suitable when the peak-cooling load is much higher than the average load.

In a demand-limiting partial-storage system (Fig. 3) the chiller does not operates at constant capacity like in the load-levelling system. Instead, it operates during on-peak hours, at a reduced capacity at a predetermined level. The demand-limiting strategy falls between load shifting and load levelling.

![Fig. 1 Full storage operating strategy](image-url)
1. Introduction

Fig. 2 Partial-storage load-leveling operating strategy

Fig. 3 Partial-storage demand-limiting operating strategy

1.2 Cool storage types and storage media

The basic types of thermal energy storage techniques can be described as in [107]:

- Sensible thermal energy storage, in which the temperature of storage materials varies with the amount of energy stored.
- Latent thermal energy storage, which makes use of the energy stored when a substance changes from one phase to another by melting or freezing (e.g., ice to water).
- Thermochemical storage, in which energy is stored in the form of the heat of reaction associated with a chemical reaction in the storage medium.

There are many different types of cool storage systems representing different combinations of storage media. Cool storage systems can be classified according to the type of thermal storage medium and the way in which the storage medium is used. The most common cool storage media are water, ice and other phase change materials (PCMs). These media differ in the amounts of energy stored per unit volume, in the temperatures at which they store cooling and in the physical conditions for storing energy. The types of cool storages further discussed bellow are chilled water storage, ice storage and PCM storage.
1.2.1 Chilled water storage systems

Chilled water storage systems use the sensible heat capacity of water to store cooling. The amount of stored cooling energy depends on the temperature difference between the chilled water stored in the storage tank and the warm return water from the load. Chilled water is most often generated and stored at 4-7 °C. These temperatures are directly compatible with conventional water chillers and distribution systems. To achieve effective chilled water storage, some form of separation must be maintained between the stored cold water and the warm return water. In the past, various physical methods have been used to create the separation, such as stratification, multiple tanks, membranes or diaphragm, labyrinths and baffles [32 and 114].

Stratified chilled water storage is generally considered the simplest, most efficient, and most cost-effective method of chilled water storage [30]. Stratified chilled water storage tanks rely on the tendency of water to form horizontal layers; or temperature zones; based on its density. The density of water is directly related to its temperature and as water get colder, the water becomes denser, until it reaches 4 °C. Cold water at 4 °C will then collect and stabilize in the lowest regions of the tank while warmer water, 10 to 18 °C, will collect in the upper regions of the tank. A large temperature gradient exists in the interface separating the warm and cold water. The small thickness of the interfacial zone is called a thermocline. In a well-designed stratified storage system, the thickness of this thermocline zone should be as small as possible. A disturbance in the thermocline results in the loss in the available cooling capacity [81]. During the charging cycle, cold water from chilling equipment enters the tank through diffusers at the bottom, and warm water exits the tank at the top. As the volume of chilled water increases and warm water is displaced, the thermocline rises. The total volume of water in the tank remains the same. For a discharging process, the system draws chilled water from the low portion of the tank and sends warm return water into the top of the tank [47 and 82].

The performance of the stratified storage is influenced by several factors such as the operating temperature, temperature range, thermo-physical properties of the storage fluid and storage tank material, geometry of the storage tank, methods for fluid to enter and exit the tank, and heat transfer between the storage tank and the outside environment [81-82]. Experiments and computer modelling have been conducted to study and improve the performance of stratified chilled water storage systems [9, 11, 48, 53-54 and 94]. Stratified storage has achieved widespread use in cooling applications because water is cheap and has favourable thermal properties. However, the problem for chilled water storage is that it uses sensible heat to store cooling. Especially for cool storage this results in a low density and large storage volume requirements since the temperature difference over the storage can only be about 10-20 °C.

1.2.2 Ice storage systems

Ice thermal energy storage uses the latent heat of fusion of water (335 kJ/kg) to store cooling, i.e. the heat required to change water from a solid to a liquid state. In the system, ice is generated to charge the thermal storage. The cooling capacity of the ice storage depend on the heat of fusion and the rate at which ice can be melted to satisfy the cooling demand. The main advantages of ice storage systems over chilled water storage systems are a larger cooling capacity, lower space requirement, and lower thermal losses to the surrounding environment due to the smaller surface area [30].
An ice storage system can be classified as a static process, in which heat transfer takes place via a solid surface, or a dynamic process, in which the heat transfer medium and storage medium are in direct contact [104]. External melt ice-on-coil, internal melt ice-on coil [18-19, 51, 65 and 132] and encapsulated ice storage systems [31] belong to the static process. Ice-harvesting [22] and ice slurry storage systems [71 and 112] are dynamic processes. In the case of a static process ice storage system, as the storage is charged, a layer of ice builds on the heat transfer surface. The layer increases the resistance to heat transfer, which cause the evaporating temperature to fall and results in a reduced coefficient of performance (COP) for the chiller. This problem can be avoided in dynamic process ice storage systems because the ice is periodically or continually removed and there is no ice layer on the surface for a long time [47].

Ice thermal energy storage stores cooling in the form of ice at its freezing point 0 °C. To store this energy, refrigeration equipment must operate at a temperature well below the normal operating range for comfort cooling application. Due to operation at this lowered temperature, the chiller efficiency decreases and the cost increases. Depending on the ice storage technology, either special ice-making equipment is used, or standard production chillers are selected for low temperature service.

1.2.3 Phase Change Material (PCM) storage system

PCM, or latent heat storage is one of the most efficient ways of storing thermal energy. The latent heat storage system provides a much higher energy storage density, with a smaller charging/discharging temperature range, as compared to sensible heat storage system. The above mentioned ice storage is of course a special case of PCM storage.

Phase Change Materials (PCMs) can be produced in various chemical formulations that are designed to melt and freeze at a selected temperature [59]. They use the latent heat of the storage medium for thermal energy storage and have shown a promising ability to reduce the size of a storage system compared with water storage that uses sensible heat to store energy. The main criteria for a candidate PCM for thermal energy storage are [1 and 90]:

- the phase transition process must be completely reversible and only temperature dependent;
- the phase transition temperature must match the practical temperature range of applications;
- the material should have a large latent heat and high thermal conductivity;
- the material is chemically stable such that no chemical decomposition occurs;
- the material must be non-toxic, non-corrosive and non-explosive;
- the material is available in large quantities at a low cost.

The candidates for PCM are generally divided in two groups: organic and inorganic compounds. Inorganic compounds include salt hydrates, salts, metals and alloys. Organic compounds are categorized into paraffins and non-paraffins [1, 37 and 47].

Salt hydrates are attractive materials for use in thermal energy storage due to their high volumetric storage density (between 250-400 MJ/m³), relatively high thermal conductivity and reasonable cost. For example, Glauber salt (Na₂SO₄ ·10H₂O) has been studied as early as 1952. It has a melting temperature of around 32.4 °C, a high latent heat of 254 kJ/kg (377
MJ/m³) and the thermal conductivity of 0.544 (W/m K). Glauber salt is one of the cheapest materials and has been used as a PCM for thermal energy storage [61].

The major problem in using salt hydrates as a PCM is that most of them melt incongruently (phase segregation), i.e. they melt to form a saturated aqueous phase and a solid phase that is generally a lower hydrate or the anhydrous form of the same salt. The general chemical formula of crystalline salt hydrates can be described as X(Y)n·mH₂O. When heating up to the melting temperature, one of the following reactions will occur:

\[ X(Y)_n \cdot mH_2O \rightarrow X(Y)_n \cdot kH_2O + (m-k)H_2O \]

\[ X(Y)_n \cdot mH_2O \rightarrow X(Y)_n + mH_2O \]

Due to the density difference, the solid phase settles out and collects at the bottom of the container. This phenomenon is irreversible, i.e. the solid phase does not combine with the saturated solution to form the original salt hydrate during freezing. Another important problem with salt hydrates is their poor nucleating properties and hence liquid salt hydrate must be sub-cooled prior to freezing. A third problem is corrosion, which means that they have short service lives or high packing and maintenance cost. To prevent incongruent melting, several techniques, such as thickening agents, rotating devices and direct contact heat transfer have been studied. Similarly, sub-cooling can be prevented by adding nucleating agents or by promoting nucleation by rough container walls or using the cold finger technique [1, 20, 61, 85 and 110].

Paraffin waxes are petroleum products, consisting mostly of straight-chain hydrocarbons, i.e., alkanes with the chemical formula CₙH₂n+2. The melting point and the latent heat of alkanes increases with the number of carbon atoms. Paraffin waxes have been found to exhibit many desirable characteristics for use in thermal energy storage, for example, their reasonably high volumetric storage density (around 200 kJ/kg or 150 MJ/m³) and their availability in a large temperature range. Their need for sub-cooling is negligible since they are self-nucleating, they are chemically inert and stable, give raise to no phase segregation, and they are commercially available at reasonable cost. However, they have rather low thermal conductivity. This may reduce the power of the heat storage that is the heating/cooling extraction during the melting and solidification cycles. Another undesirable characteristic of paraffin waxes is their potential hazard because of being flammable materials. However, a fire barrier has been suggested to be sufficient in handling this problem [1, 52, 61 and 68].

Non-paraffin organics include a wide variety of organic materials such as fatty acids, esters, alcohols and glycols. Fatty acids are characterised by CH₃(CH₂)₂nCOOH with latent heat values comparable to those of paraffins. Some fatty acids such as caprilic, capric, lauric, myristic, palmitic and stearic acids have been studied as PCMs for thermal energy storage by many researchers [14, 24, 46, 59, 83, 100-101 and 130]. These fatty acids and their mixtures exhibit excellent melting/freezing characteristics without any sub-cooling. However, the major drawback is that their cost is almost three times greater than paraffin waxes.

Some special encapsulations of PCM have been developed [97]. There are many advantages of microencapsulated PCM; for example: increased heat transfer area; reduced reactivity towards the outside environment; and the ability to control the changes in the storage material volume during phase change [38 and 95]. Ye et al. [127] has investigated a compound PCM, which consists of paraffin as a dispersed PCM and a high-density polyethylene (HDPE) as a supporting material. This new generation PCM, that has a latent heat of 157 kJ/kg, is very suitable for application in direct contact heat exchangers.
A wide range of PCMs has been investigated for different applications. Depending on the applications, the PCM should firstly be selected based on their phase transition temperature. PCMs with low phase-change temperatures (between –20 to –10 °C) can be used for process and storeroom cooling and food freezing. PCMs with phase-change temperatures between 2-15 °C can be used for air-conditioning, e.g. comfort cooling applications [17, 25, 38, 78, 96 and 124]. High phase change temperature PCMs can be used for industrial applications [39 and 107]. PCMs with phase change temperatures between 20 to 60 °C can be applied in solar and space systems, greenhouses and so on [12, 69, 73, 76-77, 103, 116 and 133-134]. Khudhair [60] has listed nine PCM candidates with phase change temperature range between 16-26 °C for building applications. These applications include PCM heat storage for peak shifting in space heating, PCM wallboards and PCM concrete, as well as under-floor heating with PCM storage.

A review concerning the history of PCM thermal energy storage with liquid-solid phase change has been carried out [128]. The review focused on the materials, heat transfer analysis and the applications of PCM storage systems and gave 117 inorganic and organic materials including eutectic and non-eutectic mixtures for potential use as a PCM, as well as 45 commercial PCMs that are available in the market. In the review, 146 materials and 22 commercial PCMs were listed with the phase change temperature ranging between 20 and 800 °C, i.e. PCM to be used for heating applications. For cooling applications, 19 materials with phase change temperature between 0 to +20 °C were listed, along with three commercial PCMs with phase change temperature between 7-15 °C, and 20 commercial PCMs with phase change temperature between –3 and –33 °C. From this, it can be seen that the research of PCM storage has so far been mostly concerned with heating applications.

1.3 Objectives

PCMs have been used for various heat storage applications since the 1800s and a large amount of PCMs have been developed as heating storage media. However, PCM storage for cooling applications has not been the focus of as much research and development. In order to follow the quickly expanding demand for comfort cooling, PCMs with phase transfer temperature matching those of comfort cooling applications must be developed.

In this thesis, the objective is to develop PCM storage systems for comfort cooling applications. The goals of this thesis is to define suitable PCM candidates for comfort cooling and determine the thermophysical properties of these PCM candidates, including the phase transition melting and freezing temperature, the latent heat, the thermal stability and the volume change of liquid-solid phase transition process. The phase equilibrium of the PCM candidates has been studied theoretically, as well as experimentally, resulting in the derivation of the phase diagram. With knowledge of the liquid-solid phase equilibrium characteristics and these phase diagrams, an improved understanding is provided for the interrelationships involved in the phase change, as well as the thermophysical characteristics of the candidates. Using this knowledge as a basis, the use of phase equilibrium data in the design of a cool storage is presented as a general methodology. Finally, the potential of PCM storage for peak shaving in different cooling systems has been demonstrated.
2. Phase Change Material Candidates for Comfort Cooling Storage

As compared to sensible heat storage, using PCMs in cool storage systems provides a system with a higher energy density and a narrower temperature range for charging and discharging of the storage. Thus, PCM storages are advantageous in reducing the storage volume, heat loss and size of the chilling equipment. In this chapter the paraffin waxes tetradecane, hexadecane and their binary mixtures are considered as PCM candidates for comfort cooling storage. Different experimental methods, e.g. temperature sensor and Differential Scanning Calorimetry (DSC) are used to generate thermal data. The thermal properties of tetradecane, hexadecane and their binary mixtures are discussed and the potential of using them as PCMs for cool storage is demonstrated. This chapter is based on the paper I.

2.1 Materials

Paraffin waxes are saturated hydrocarbon mixtures and normally consist of a mixture of mostly straight-chain n-alkanes, with the chemical formula \( \text{CH}_3-(\text{CH}_2)_n-\text{CH}_3 \). The crystallization of the \( -(\text{CH}_2)_n \)- chain releases a large amount of the latent heat. Both the melting point and the heat of fusion increase with an increasing chain length. The various paraffin waxes, products of petroleum refining, are available in a selection of phase transition temperature ranges, so that a good match can be made between the phase change temperature range and system operation temperature [52 and 62].

If PCMs are utilized for comfort cooling storage, they should according to Schlayman and Fortuin [105] have a phase transition temperature of around 5-10 °C. Paraffin waxes with a phase transition temperature near this range are tetradecane \( \text{CH}_3-(\text{CH}_2)_{12}-\text{CH}_3 \), pentadecane \( \text{CH}_3-(\text{CH}_2)_{13}-\text{CH}_3 \) and hexadecane \( \text{CH}_3-(\text{CH}_2)_{14}-\text{CH}_3 \). All three substances are well-characterized chemicals. They are stable up to approximately 250 °C. The liquid state of paraffin wax is non-polar and does not mix with polar liquids such as water or alcohol. As previously mentioned, paraffin waxes melt without the segregation of components and require no subcooling, they are non-toxic, non-corrosive and chemically inert, and have no unpleasant odors [52 and 117]. Table 1 shows the thermal properties of the materials [61].

Because pentadecane costs twice as much as tetradecane and hexadecane, it is not considered further as a candidate in the present work. Instead, mixtures of tetradecane and hexadecane were chosen. The selected PCM mixtures must have a transition temperature compatible with the design temperature of a chiller for comfort cooling application. This means that various mixtures must be tested.
### Table 1
The thermal properties of three paraffin waxes [Lane, 1983]

<table>
<thead>
<tr>
<th>Alkane</th>
<th>No. of carbon atoms</th>
<th>Melting point °C</th>
<th>Heat of fusion kJ/kg</th>
<th>Specific heat C(_p)kJ/kg°C</th>
<th>State at room temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetradecane</td>
<td>14</td>
<td>5.8</td>
<td>227</td>
<td>-20 – 0 1.68</td>
<td>Solid</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>+25 2.18</td>
<td>Liquid</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>42 – 65 2.22</td>
<td>Liquid</td>
</tr>
<tr>
<td>Pentadecane</td>
<td>15</td>
<td>9.9</td>
<td>206</td>
<td>+20 – 0 1.75</td>
<td>Solid</td>
</tr>
<tr>
<td>Hexadecane</td>
<td>16</td>
<td>18.1</td>
<td>236</td>
<td>+28 2.22</td>
<td>Liquid</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>48 – 75 2.13</td>
<td>Liquid</td>
</tr>
</tbody>
</table>

### 2.2 Methods

Several methods have been used to determine the thermal properties of the PCM candidates. These thermal properties include: the melting and freezing temperature, the heat of fusion, thermal stability and the volume expansion during liquid-solid phase change. The methods used are further described below.

#### 2.2.1 Determination of the melting and freezing point

Laboratory-grade (\(\geq\) 99%) materials have been utilized for experiments and thirty-two mixtures with different ratio of tetradecane and hexadecane were prepared. Each mixture was stirred well in a beaker with a magnetic stirrer and was transferred to a tube. A beaker was filled with ice and maintained at 0 °C. The test tube was immersed in the beaker and a temperature sensor was inserted into the test tube. The temperature sensor with a 0.1 °C resolution was calibrated against the freezing point (0 °C) and boiling point (100 °C), and the temperature reading of the mixture was observed continuously. The temperature decreased continuously until it reached a constant value – the freezing point of the mixture. Only after the mixture was frozen did the temperature start to decrease further.

The test tube with the frozen contents was then immersed in a beaker of water (the water was at room temperature). The temperature of the mixture then increased slowly until it reached the melting point of the mixture. The entire mixture melted and the temperature then increased faster than before.

#### 2.2.2 Thermal stability

A mixture with a freezing point around 7 °C was subjected to fifty heating and cooling cycles. The mixture was first cooled to below its freezing point (reaching around 0 °C), and then heated to 35 °C. During these cycles, the freezing point of the mixture was measured by temperature sensor.
2.2.3 Volume expansion during a phase change

A glass volume expander with accurate graduations (± 0.02 ml) was used to measure the volume expansion during a phase change. A liquid sample was placed in the expander and the volume $V_1$ was observed; the expander was then immersed in a beaker filled with ice and maintained at 0 °C. After the sample was frozen completely, the volume $V_2$ of the solidified sample was determined. The volume expansion during the phase change was then calculated using Eq (1):

$$\Delta V\% = \frac{(V_2 - V_1)}{V_1} \times 100$$  \hspace{1cm} (1)

2.2.4 Differential Scanning Calorimetry (DSC) measurements

The thermal behavior of the mixtures was recorded using a Perkin-Elmer DSC-7. Indium was used for temperature calibrations and the analysis was carried out in a constant stream of nitrogen.

Samples were placed in aluminum pans that were hermetically sealed before being placed on the calorimeter thermocouples. The heating rate was 5 °C/min. At first, the DSC cell containing a PCM sample was cooled to a lower temperature than the freezing point of the sample. As the heating block was heated at a constant rate, the temperature of the reference sample pan also increased at a constant rate. If there was no phase change in the PCM pan, the temperature difference between the PCM sample and the reference sample pan produced an almost horizontal straight line. If there was a phase change in the PCM sample pan, the temperature difference between the two pans followed a curve that deviated from the straight line. The area between the straight line and the curve represents the energy consumed for the phase change, which is integrated numerically by a program built into the DSC. Both the phase transition temperature and the heat of fusion ($\Delta H$) are recorded during a heating scan [40].

A typical DSC output curve of indium is shown in Fig. 4. The x-axis indicates the temperature and the y-axis indicates the heat flow rate. Herein, the melting curve of indium (an endothermic process) is plotted “upwards” (positive direction).

![Fig. 4 A typical DSC output curve](image-url)
2.3 Results

The results from the thermal property measurements of the PCM candidates are described below.

2.3.1 The phase change temperature via temperature sensor

The freezing points of thirty-two samples with different proportions of tetradecane and hexadecane have been measured by temperature sensor, while the phenomena of freezing and melting were observed. The freezing point and melting range were obtained from temperature curves as exemplified in Fig. 5 and 6.

The phase change temperature of each sample obtained using this technique (listed in Table 2 of paper I) is plotted in Fig. 7 (versus concentration of tetradecane by volume). The left-hand axis of the figure (0%) corresponds to pure hexadecane and the right-hand axis (100%) to pure tetradecane. The mixture is completely melted above the curve. These mixtures melt over a temperature range rather than at a single temperature, beginning 2-3 °C lower than the freezing point.

The phase change temperature of pure hexadecane was determined to 17.9 °C and that of pure tetradecane to 5.3 °C. These values should be compared to the manufacturer’s data: 18.0 °C and 5.5 °C. Fig. 7 shows that in the range of 10% to 80% of tetradecane, the phase change temperature is significantly lowered as the amount of tetradecane increases. It further shows that from 99% to 92% of tetradecane, the phase change temperature of the mixtures decreases when hexadecane is added. The minimum point of the laboratory-grade tetradecane-hexadecane mixture occurs at 91.7% by volume of tetradecane, and the phase change temperature at this point is approximately 1.7 °C.

![Fig. 5 Temperature change of mixture containing 50% (v-%) tetradecane during freezing](image-url)
2.3.2 Thermal stability

During fifty heating and cooling cycles, the material showed good thermal stability. The freezing point of the mixture with 50% by volume tetradecane remained at the same value (Fig. 8), showing that the phase change is reversible without degradation.

2.3.3 Volume contraction during the phase change

The volume expansion of some samples during the liquid-solid phase change was measured. The results are shown in Fig. 9, plotted against the proportion of tetradecane. The results indicate that the phase change of all tested samples from the liquid to solid state is accompanied by a volume contraction and that the volume contraction is less than 10%.
2. Phase Change Material Candidates

Fig. 8 The freezing point during a sequence of heating and cooling cycles

Fig. 9 Volume contraction during the liquid-solid phase change

2.3.4 The freezing temperature via DSC

The freezing point of mixtures of tetradecane and hexadecane (Fig. 10) were determined by DSC. The data of Fig. 7 are shown for comparison. The freezing temperature of both the pure components and the minimum point mixture were determined by the extrapolated peak onset temperature. Although determining the freezing temperature of the mixture is not easy, the peak temperature is a good approximation according to Höhne [56], who reported this for determining the phase diagram of the binary system benzil/acetanilide. In the present investigation, the agreement between the data recorded by the temperature sensor and DSC (Fig. 10) appears to be good, however, some differences are noticeable.
2.3.5 The heat of fusion via DSC

DSC was used to determine the heat of fusion of eighteen samples with different composition with regards to tetradecane and hexadecane.

Fig. 11 shows the heat of fusion versus the concentration of tetradecane by volume (more detailed data given in paper I). Here, the heat of fusion varied between 227 and 146 kJ/kg depending on the concentration of tetradecane. As can be seen, the heat of fusion of the mixtures are lower than those of both pure tetradecane and hexadecane. The material with the highest heat of fusion is pure hexadecane. The addition of hexadecane to tetradecane or vice versa leads to a considerable decrease in the heat of fusion. With a tetradecane and hexadecane composition ranging between 30% and 90%, the heat of fusion remained constant at approximately 146 kJ/kg.

Fig. 10 Freezing point of the mixtures of tetradecane and hexadecane as determined by DSC and temperature sensor

Fig. 11 The heat of fusion for mixtures of tetradecane and hexadecane
A report from Choi et al. [23] also mentioned that the heat of fusion for mixtures (10 to 90% tetradecane) is smaller than for the pure materials. The results from Fig. 11 show good agreement with this report. However, in their work the highest heat of fusion was not obtained for the pure material, and the change in the heat of fusion with concentration was not regular between 0-20% and between 80-100%. Also, between 20-80% tetradecane, they obtained a value for the heat of fusion around 200 kJ/kg, i.e. much higher than the value obtained herein.

The test results of DSC also show that when large amounts of tetradecane were added, the shape of the DSC curves changed. This may be due to a molecular rearrangement in the solid phase or because of a solid-solid phase change occurring at the temperature lower than the melting temperature, resulting in a lowering of the primary freezing point and the heat of fusion of the mixture [61].

The melting temperature and the heat of fusion measured by DSC for laboratory-grade tetradecane and hexadecane were listed in Table 2 and were compared with the data given by Lane [61].

![Table 2]

<table>
<thead>
<tr>
<th>A-Alkane</th>
<th>Melting temperature °C</th>
<th>Heat of fusion kJ/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetradecane</td>
<td>Lane 5.8</td>
<td>Measured 5.4</td>
</tr>
<tr>
<td>Hexadecane</td>
<td>Lane 18.1</td>
<td>Measured 17.9</td>
</tr>
</tbody>
</table>

2.4 Concluding remarks

The phase change temperature and the heat of fusion of laboratory-grade tetradecane and hexadecane and thirty-two mixtures with different ratios were obtained respectively by temperature sensor measurements and DSC analysis. The phase change temperatures range from 1.7 to 17.9 °C and the heats of fusion lie between 227 and 146 kJ/kg.

The temperature sensor is a well-known method, and its main advantage is that there is enough time during the experiment for the phase change to occur and ensure approximate thermodynamic equilibrium at every moment. The method may provide more reliable results than e.g. DSC. It is essentially the same as the method that in recent years has been going under the name “the T-history method”.

Three aspects dominate the advantages of the DSC method: simplicity, rapidity and economy in its sample requirements. The main disadvantage of DSC is that it is relative and not absolute. It is claimed from our experimental results that DSCs give better results at very low scanning rate. The experimental error for DSC came mainly from operational parameters, for example, the effect of scanning rate, and the systematic influences from the instrument and inherent error sources. The difference between the readings from the temperature sensor and the DSC measurements are presumably due to the scanning rate (5 °C/min) not being slow enough. To investigate this further, different scanning rates were used for the mixture of 50% by volume of tetradecane. When the scanning rate were 5 °C/min and 0.5 °C/min, the freezing
point were 6.3 and 4.9 °C, respectively. However, the DSC results also indicate that the scanning rate does not affect the heat of fusion strongly. For example, the heat of fusion of at 5 °C/min and 0.5 °C/min were 153.8 kJ/kg and 154.2 kJ/kg, respectively.

Höhne [56] has reported that there is not yet an international agreement on procedures for the temperature calibration and caloric calibration of DSCs, which has been verified both theoretically and experimentally. There is no complete theory of DSCs that takes full account of the systematic influences from the instrument and inherent error sources. They investigated some relevant calibration regulations and results indicate that some basic limits should be set for the reliability of measurements. However, the situation is still quite unsatisfactory.

In the report of Choi and coworkers, the authors only used the DSC method to obtain the melting points and the heat of fusion of mixtures. They focused on these mixtures mainly in two extreme ranges (i.e., 0% to 10% and 90% to 100%) as potential phase change material slurries to enhance the convective heat transfer performance of district cooling systems rather than as a media for cool storage. The report stresses the use of DSC results in calculating the melting temperature depression of the mixture’s main component in the two ranges. However, they did not discuss DSC extensively and they did not give the heating rate used in the DSC measurement, a very important parameter for interpreting the results of DSC.

The experimental results presented herein indicate that tetradecane, hexadecane and their binary mixtures are excellent candidates as PCM for cool storage due to their availability in a low temperature range and their reasonably high heat of fusion. Furthermore, they are able to melt congruently and, due to their self-nucleating properties, they freeze without sub-cooling. They also show a good stability over a large number of heating and cooling cycles. The volume contraction of these mixtures during freezing is less than 10%. Such a volume contraction of these mixtures cannot be neglected in a cool storage system. All these experimental results provide large amounts of information for PCM manufacturers to produce paraffin waxes PCMs with different phase transfer temperature for cooling applications.
3. A Study of the Liquid – Solid Phase Equilibrium of Binary Mixtures of Tetradecane and Hexadecane

Phase diagrams (equilibrium diagrams) for depicting the concentration-temperature-pressure relationships of a chemical system at equilibrium are invaluable to PCM thermal storage design since it enables the prediction of system behaviour during phase changes. This chapter presents the study of the liquid-solid phase equilibrium and the phase diagram of the binary system formed by tetradecane and hexadecane. The physicochemical properties of these binary mixtures are determined by theoretical models and experimental measurements. The phase equilibrium study and phase diagram provides a better understanding for the interrelationship involved in the phase change. Furthermore, a large amount of information concerning the type of binary system and its use in PCM application has been obtained. This chapter is based on the paper II.

3.1 The binary system of tetradecane and hexadecane

The properties and characteristics of normal alkanes and the isobaric temperature-concentration phase diagrams of various alkane mixtures have been discussed by Mazee [72], Mnyukh [74], and Turne [117]. They described different system possibilities. The simplest binary system exhibits a single liquid phase and two completely immiscible components in the solid state. These three phases (i.e. the liquid, pure solid $I$ and pure solid $II$) will be in equilibrium at the eutectic point (as shown in Fig. 12 (a)). The next simplest binary mixture is the isomorphous (solid solution) type in which the two components are completely miscible in both the liquid and the solid phases (Fig. 12 (b)). Other binary systems are those which exhibit a minimum and/or a maximum melting point, i.e. an azeotrope (Fig. 12 (c)), a fact that points to a less ideal behaviour of the components. It is however possible to confuse this type of phase equilibrium with that of a eutectic, which is also a minimum melting mixture. However, in binary eutectics, each of the three phases has a different composition. At the minimum melting point of a binary isomorphous system, the liquid and the solid phases have the same composition [61 and 75].

From previous experimental results (see Fig. 7, chapter 2), a minimum temperature in the binary system of tetradecane and hexadecane has been found. In order to prove that the binary system is a solid solution system and not a eutectic system, some further experiments have been conducted. Two binary mixtures (53 and 33% mole fraction of tetradecane) have been tested. The samples were cooled down to form crystals. Then after separating the liquid and solid, the cooling was continued, and crystallisation and separation was repeated in several steps. The crystals first allowed to melt and froze again. The freezing temperatures of the separated crystals were measured by a temperature sensor. For a eutectic system, the crystals formed should be the pure material [75]. However, these separated crystals did not exhibit the same freezing temperature as pure hexadecane. The freezing temperatures of these separated crystals were instead close to the freezing temperature of the previous mixture.
3.2 Theoretical phase equilibrium modelling

The basic equations for calculating the liquid-solid phase equilibrium of an \( m \)-component mixture are given by:

\[
T_{\text{liq}} = T_{\text{sol}}, \quad P_{\text{liq}} = P_{\text{sol}}, \quad \mu_{\text{liq}} = \mu_{\text{sol}}
\]  

(2)

It means that the phases are all in thermal equilibrium and in mechanical equilibrium, hence having a common temperature \((T)\) and a common pressure \((P)\). Finally, phase equilibrium requires that the chemical potential \((\mu_i)\) of a given component must be the same in every phase [119].

The function \(f\), the fugacity, of any component in any system, whether solid, liquid or gas, pure or mixed, ideal or not, is defined for an isothermal change as [119]:

\[
\mu_i - \mu_i^o = RT \ln \frac{f_{i}}{f_{i}^0}
\]  

(3)

Here, \(\mu_i^o\) or \(f_{i}^0\) are the chemical potential and fugacity at a reference state, respectively. One of these is arbitrary, so that both may not be chosen independently; i.e., when one is chosen, the other is fixed.

Using the fugacity, the equation to calculating the liquid-solid phase equilibrium of an \( m \)-component mixture can be represented by Eq. (4) and (5), below [91].

\[
f_i^{\text{liq}} = f_i^{\text{sol}}
\]  

(4)

The thermodynamic equilibrium equation between a solid and liquid phase can be written:

\[
x_i^{\text{sol}} = \frac{\chi_i^{\text{liq}} x_i^{\text{liq}}}{\chi_i^{\text{sol}}} \left( \exp \left( - \frac{\Delta H}{R} \left[ \frac{1}{T_m} - \frac{1}{T} \right] \right) \right)
\]  

(5)
Here, $\gamma^{\text{liquid}}$ and $\gamma^{\text{solid}}$ are the activity coefficient in the liquid and solid phase, respectively, and they denote the deviation from an ideal mixture. Furthermore, $x^{\text{liquid}}$ is the mole fraction in the liquid state, $\Delta h$ the enthalpy of fusion, $T_m$ the melting temperature of the pure substance, and $T$ is the temperature of the system. Eq. (5) neglects correction terms proportional to $\Delta C_p$ (specific heat difference between liquid and solid) because these corrections tend to be small in comparison with uncertainties in the activity coefficient. From Eq. (5), a theoretical evaluation of the thermodynamic equilibrium between the liquid phase and solid phase of the tetradecane, hexadecane, and their mixtures is possible. In the present investigation, several previously published approaches were compared.

One approach is the group-contribution method called UNIFAC [43]. This method has been developed for estimating activity coefficients in non-electrolyte liquid mixtures. The method is useful for calculating the activity coefficient $\gamma^{\text{liquid}}$. Here, the activity coefficient consists of two parts: the combinatorial contribution, due mostly to differences in molecular size and shape; and the residual contribution, arising mostly from differences in intermolecular forces of attraction. For a component $i$ in a multi-component solution:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R$$

$$\ln \gamma_i^C = \ln \frac{\phi_i}{x_i} + \frac{z_i}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \phi_i \sum_j x_i l_j$$

The residual contribution to the activity coefficient is related to the composition and temperature through:

$$\ln \gamma_i^R = \sum_k \nu^{(i)}_k \left[ \ln \Gamma_k^{(i)} - \ln \Gamma_k^{(i)} \right]$$

all group in the solution

Another approach used is the model of Won [120], which uses regular solution theory, such that the activity coefficients are determined from the solubility parameters $\delta_i$ of the individual components. This results in an improved representation of liquid-solid phase equilibrium (Eq. (9)).

$$\frac{x_i^{\text{solid}}}{x_i^{\text{liquid}}} = \exp \left\{ \frac{\Delta H}{RT} \left( 1 - \frac{T}{T_m} \right) + \frac{V_i}{RT} \left( \delta_i^{\text{liquid}} - \delta_i^{\text{solid}} \right)^2 - \left( \delta_i^{\text{solid}} - \delta_i^{\text{solid}} \right)^2 \right\}$$

A modification of Won’s model is one where Pedersen and Skovborg [89] have given a general correction for the liquid-solid phase solubility parameters $\delta$ (in (cal/cm$^3$)$^{0.5}$). Then,

$$\delta_i^{\text{liquid}} = 7.41 + 0.5914 \ln(n/7), \quad \delta_i^{\text{solid}} = 8.50 + 5.763 \ln(n/7)$$

This is an empirical expression and $n$ denotes the carbon number. Using this modification of Won’s model, solubility parameters of paraffin waxes from C$_7$ to C$_{40}$ were presented by Pedersen and Skovborg [89].
3.3 Experimental method

Experimental work has also been conducted by testing the 32 samples that were used for thermal properties measuring (mentioned in chapter 2). A TA DSC 2920 was used to obtain quantitative and qualitative data. For the DSC measurements, about 7-10 mg of each sample was weighed to ±0.001mg on a microbalance directly into hermetic sample pans. The DSC was calibrated for temperature and heat flow values using the melting point and enthalpy of fusion of high purity indium according to the standard procedures described in the user’s manual of the instrument.

Different thermal treatment steps were employed for each sample in the study. At first, each sample was brought to equilibrium at 30 °C, and modulated ±0.5 °C every 60 s, keeping it isothermal for 2 min. Then the sample was cooled at a constant rate 5 °C/min, to –20 °C. After this, it was kept isothermal for 2 min, and then heated again to 30 °C at the same rate. The same procedures were repeated at different rates: 2 °C/min and 0.5 °C/min with the temperature range at the rate of 0.5 °C/min being 20 to –15 °C.

3.4 Phase diagram

The phase diagram of the binary system of tetradecane and hexadecane has been obtained by theoretical modelling and experimental measurements.

3.4.1 Theoretical modelling results

As mentioned before, there is a minimum temperature in the binary system of tetradecane and hexadecane. Consequently, in the theoretical modelling the binary system has been treated as two ascendant diagrams, to the left and right of the minimum point. The previous experimental equilibrium freezing temperature and transitional enthalpy were used in the theoretical modelling to obtain the melting curves. Eq. (5) combined with the previously mentioned methods (Eq. (6)-(10)) was used to determine the activity coefficient of different components in the liquid and solid phase. Fig. 13 shows the resulting temperature-composition phase diagram for the binary system of tetradecane – hexadecane, which forms a continuous series of solid solutions. The upper curve \((T-x_i)\) is the liquidus or freezing point curve as obtained by previous experimental measurements. The lower curve is the solidus or melting point curve, obtained by the applying the UNIFAC method \((T-x_i (UN))\), the Won model \((T-x_i (W))\) and the Pedersen model \((T-x_i (P))\) (all calculation results have been listed in paper II). From Fig. 13, it can be seen that the UNIFAC method results in values very close with the model of Won. The result from the Pedersen model is a slightly lower compared to the UNIFAC method and Won model. However, the differences are nevertheless small.

Any system represented by a point above the liquidus is completely molten, and any point below the solidus presents a completely solidified mass. A point within the area enclosed by the liquidus and solidus curve indicates an equilibrium mixture of liquid and solid solution. These two curves approach and touch at point \(M\).

From Fig. 13, the phase reactions occurring when cooling a given mixture can be traced as follows. If a homogeneous liquid represented by point \(A\) is cooled slowly, it starts to crystallize when point \(L_1\) is reached. The composition of the first crystals is given by point \(S_1\).
As the temperature is lowered further, more crystals are deposited but their composition changes successively along curve $S_1S_6$ and the liquid composition changes along curve $L_1L_6$. When the temperature is reduced to $L_6S_6 (T_6)$, the system solidifies completely. The overall composition of the solid system at some temperature represented by point $A'$ is the same as that of the original homogeneous melt, assuming that no crystals have been removed during the cooling process.

![Liquid–Solid Phase Equilibrium Study](image)

Fig. 13 The liquid-solid phase diagram of binary mixture of $C_{14}H_{30}$ and $C_{16}H_{34}$ from theoretical modelling

Although the solid solution deposited at the point $M$ has a definite composition, it is not a chemical compound. The components of such a minimum point mixture are rarely, if ever, present in stoichiometric proportions. Point $M$, therefore, is not a eutectic point: the liquidus curve is completely continuous, it only approaches and touches the solidus at $M$. The changes occurring when a solid mixture $A'$ is heated can be traced in a manner similar to the cooling operation [75].

### 3.4.2 Experimental results from DSC measurements

As previously described, several scanning rates were tested in the DSC measurements. Depending on the particular scanning rate, a different thermal trace was obtained for the same sample. The phase diagram of the binary system of tetradecane and hexadecane constructed with DSC results was also compared with the theoretical modelling results.
3.4.2.1 Thermal analysis

DSC was used to measure thermal properties as a function of temperature and a DSC curve offers quick information on the total measuring process. When the steady state is disturbed by thermally activated heat production or consumption in the sample, a peak in the measured heat flow curve appears. A large number of DSC measurements were made on the binary \( n \)-alkane systems, \( \text{C}_{14}\text{H}_{30} + \text{C}_{16}\text{H}_{34} \). Fig. 14 shows the thermal traces for a binary mixture of \( \text{C}_{14}\text{H}_{30} + \text{C}_{16}\text{H}_{34} \) at the cooling rate (freezing process) of 2 °C/min. Herein, the peaks in the heat flow rate curves, which are assigned to exothermal processes, are plotted “upwards” (positive direction). All presented measured DSC curves are arranged in the order of increasing concentration (\( n \), or mole-%) of tetradecane.

Fig. 14 Freezing curves at 2 °C/min scan rate of \( \text{C}_{14}\text{H}_{30} + \text{C}_{16}\text{H}_{34} \) binary mixtures, the mole-% of \( \text{C}_{14}\text{H}_{30} \) is given as \( n \).

The following features have been observed. All components have exhibited one major peak corresponding to the liquid-solid phase transition. The peak of the pure components and some mixtures, with composition very close to a pure material, are more sharp and narrow as compared to other mixtures. Most mixtures exhibit a lower peak height accompanied with an enlarged temperature range. In the concentration range of \( \text{C}_{14}\text{H}_{30} \) between 22 and 91 mole-%, an increase in the mole fraction brings about an increase in the peak height and the movement of the peak towards a lower temperature. For the mixtures with a concentration between 92 and 100%, an increase in the tetradecane concentration results in an increase in the peak height and the movement of the peak towards a higher temperature.

In the concentration range between 22-36 mol-% tetradecane, the DSC curves show the existence of two peaks. The lower temperature peak is very weak and could possibly be an
3. Liquid – Solid Phase Equilibrium Study

indication of a solid–solid phase transition. Also, this secondary peak is dependent on the mixture composition and appears to weaken as the concentration of tetradecane increase. When the tetradecane mole fraction reaches approximately 39 %, the second peak disappears in the temperature range between 30 and -20 °C.

Fig. 15 presents the thermal traces for binary mixtures of C\textsubscript{14}H\textsubscript{30} + C\textsubscript{16}H\textsubscript{34} at a heating/cooling rate of 0.5 °C/min. In Fig. 15, two peaks appear clearly in the C\textsubscript{14}H\textsubscript{30} range of 22-36 mol-%. Also, the freezing curves indicate that the position of the low temperature peak is dependent on the concentration of C\textsubscript{14}H\textsubscript{30}. From the melting curves it can be seen that the two peaks become more resolved or separated as the concentration of C\textsubscript{14}H\textsubscript{30} is increased. When the mole fraction of C\textsubscript{14}H\textsubscript{30} reaches 40 %, the lower temperature peak cannot be seen in the freezing curve and melting curve for the temperature range of 20 to –15 °C.

Hammami et al. [45] and Paunovic et al. [88] reported that in a binary eutectic mixture system of alkanes, the eutectic peak is independent of the mixture composition and appears at a constant temperature. From the DSC measurement presented here, an indication is obtained that the binary system is a solid-solution system since a eutectic peak, independent of mixture composition, is not present. The low temperature solid-solid peak, appearing in a short mixture concentration interval, can be due to the fact that perfect miscibility does not occur.

3.4.2.2 DSC data interpretation —finding the liquid-solid phase diagram

The characteristic temperatures from DSC measurements are: the initial peak temperature (T\textsubscript{i}), the extrapolated peak onset temperature (T\textsubscript{e}), the extrapolated end temperature (T\textsubscript{c}), the peak temperature (T\textsubscript{p}) and the end peak temperature (T\textsubscript{f}). All of these are shown in Fig. 16 a typical freezing curve. Not all characteristic temperatures can be reproduced with equal accuracy. The use of T\textsubscript{e}, T\textsubscript{c} and T\textsubscript{p} is recommended by Hetakeyama and Quinn [49] for both
the melting and freezing peak characteristics. The extrapolated peak onset temperature is defined as the intersection between the tangent to the maximum rising slope of the peak and extrapolated sample baseline.

![Graph](image)

Fig. 16 Definition of DSC characteristic temperatures for a freezing curve

The data of the DSC measurement using a scanning rate of 2 °C/min has been used to construct the binary phase diagram of $C_{14}H_{30}$ + $C_{16}H_{34}$. Here, $T_c$ is systematically too large. Instead, $T_e$ for cooling (freezing) curves has been used to construct the liquidus.

It is not easy to determine the solidus by using the extrapolated peak onset temperature of melting curves at a 2 °C/min scanning rate. The onset temperature of obtained melting (heating) curves does not indicate the solid-liquid phase transition temperature of the binary mixtures of $C_{14}H_{30}$ + $C_{16}H_{34}$. In Fig. 15 two peaks are present in the melting curves obtained with a scanning rate of 0.5 °C/min. The lower temperature peaks may indicate solid-solid phase transition. However, these small solid-solid phase transition peaks are not shown separately in the melting curves when using a 2 °C/min scanning rate.

The data obtained from Fig. 15 shows that before reaching concentrations at which two peaks are expected, $T_e$ of the melting curves is in good agreement with the peak freezing temperature at both a 2 and 0.5 °C/min scanning rate. Over the range of 22-36 mole-% of tetradecane, two peaks appear. Then $T_e$ of melting curves at a 2 °C/min scanning rate are much lower than the peak freezing temperatures. But the $T_e$ of the higher temperature peak at a 0.5 °C/min scanning rate are in good agreement with the peak freezing temperature at a 2 °C/min scanning rate. In the ranges of 63-100 mole-% of tetradecane, the peak temperatures of the cooling curves are very close to $T_e$ of the melting curves. It seems that when the freezing curve reaches the peak, most of the sample in the pan was frozen. For these reasons, the peak freezing temperatures of cooling curves have been used to construct the solidus.

The binary system phase diagram of $C_{14}H_{30}$ and $C_{16}H_{34}$ based on the DSC measurements is presented in Fig. 17. Here, the theoretical model’s results from Fig. 13 are shown for comparison. In Fig. 17, the two lines of $t-x_l$ and $t-x_s$ (P) are from Fig. 13 and $t-x_s$ (P) is calculated using the Pedersen model. The data of $t$ (DFO) (DSC Freezing curve Onset temperature) and $t$ (DFP) (DSC Freezing curve Peak temperature) come from DSC
measurements. Deviation between the DSC measurements and the theoretical modelling are clearly present. Over the range of 0 to 50 mole-% of tetradecane, the measured and calculated results are in very good agreement with each other. However, over the range of 60 to 90 mole-% of tetradecane, the deviations is significant, around 3 °C.

![Phase diagram of binary mixture system](image)

Fig. 17 The liquid-solid phase diagram of binary mixture system of C\textsubscript{14}H\textsubscript{30} and C\textsubscript{16}H\textsubscript{34} by DSC

### 3.5 Concluding remarks

Any solid to liquid PCM is in intimate contact during melting or freezing with at least one solid phase. These phases’ interrelationship can be understood best by studying the system under conditions of heterogeneous equilibrium. The temperature-composition phase diagram of the binary system of C\textsubscript{14}H\textsubscript{30} + C\textsubscript{16}H\textsubscript{34} has been obtained by theoretical calculations and DSC measurements. The diagram illustrates a binary, isomorphous system with a temperature minimum.

The deviation between the theoretical model, the temperature sensor measurements, and the DSC measurement is partly a result of the systematic influences from the instruments, and the inherent error sources, also from experimental conditions. In every case, a slow heating/cooling rate during the DSC measurements should be used to ensure approximate thermodynamic equilibrium at every moment during the experiment. This will avoid a “coring” of the DSC curve, and thus will avoid incorrect temperatures. The phenomenon of “coring” means non-equilibrium freezing in which each solidified unit has a higher-melting centre surrounded by layers of material of increasingly lower melting point. The melting process will tend to retrace the path of the freezing process, if the system is at a uniform temperature [61]. The phenomenon of “coring” will result in large deviations if the DSC scanning rate is not slow enough.
The thermodynamic basis of solubility of organic substances in the solid state has frequently been discussed in the literature. Briefly summarised, these discussions state that the formation of solid solutions of organic compounds can occur if the mixed molecules are similar in form and dimensions. However, a mutual solubility of such compounds over the entire concentration range is only possible if the crystal symmetry of the pure components is the same [72, 74 and 117]. Whether such solid solutions approach ideal behaviour or exhibit varying degrees of non-ideality depends how well the compounds match with regards to the lattice dimensions and the chemical similarity of the compounds. An ideal solution results if the “guest” component does not disrupt the attractive-repulsive forces within the crystal lattice of the “host” component. Such disruption may cause positive deviations from ideality due to repulsive tendencies, or negative deviations caused by attractive force [61]. Positive deviations are the most common.

Paraffin wax consists of a mixture of mostly straight-chain (normal) \(n\)-alkanes, \(\text{CH}_3-(\text{CH}_2)_n-\text{CH}_3\). In the solid state, pure \(n\)-alkanes form single crystals of four crystal systems. The type of system depends on the temperature and the number of carbon atoms in the molecule. There are the hexagonal (\(\alpha\)-phase), rhombic (\(\beta\)-phase), monoclinic (\(\gamma\)-phase) and triclinic (\(\delta\)-phase) system [15]. \(n\)-Alkanes with \(n = 12, 14, 16, 18\) and 20 form triclinic crystals below their melting point, and \(n\)-alkanes with \(n = 11-43\) form hexagonal crystals. Furthermore, Agafonov et al. [3] have also reported a consideration of component structural characteristics which reveals that the interaction of components having similar structures (\(\alpha\)-\(\alpha\), \(\beta\)-\(\beta\), \(\gamma\)-\(\gamma\) and \(\delta\)-\(\delta\)) results in the formation of continuous solid solutions.

As the pure tetradecane and hexadecane solids have a similar structure (triclinic crystals), the binary system contains all conditions for the formation a solid solution. In the \(\text{C}_{14}\text{H}_{30} + \text{C}_{16}\text{H}_{34}\) system investigated herein, the minimum temperature is not a eutectic point. This has been proved through the DSC measurements since a eutectic peak, independent of mixture composition, is not present in all DSC thermograms. In addition, some further experiments were done that showed that the crystals formed during a freezing process did not have the freezing point of pure hexadecane.

Agafonov et al. [3] also reported their research about the patterns of phase diagram change in a series of \(n\)-alkane binary systems. Forty-five systems were classified into five series of \(n\)-alkane systems each containing one constant component. These were studied by low-temperature differential thermal analysis (DTA). The diagram from the present results (Fig. 13 and 17) showed good agreement with the trend of phase diagram changes of the binary system of tetradecane and hexadecane, which has been presented qualitatively by Agafonov et al..

Here, some mixtures’ DSC curves have exhibited a low temperature solid-solid transition peak. It means that these mixtures possibly exhibit polymorphism. In general, polymorphic forms of a substance are differentiated either by the arrangement of molecules in a lattice or by the molecular orientation. Continuous cooling of \(n\)-alkanes with \(n = 11-33\) (odd \(n\)) and 35-43 below melting point have been reported to cause the \(\alpha\Rightarrow\beta\) phase transition, and cooling \(n\)-alkanes with \(n = 22, 24\) and \(n = 26, 28, 30\) and 32 results in \(\alpha\Rightarrow\delta\) and \(\alpha\Rightarrow\gamma\) transition, respectively (\(n\) is the number of carbon atoms in \(n\)-alkane) [15]. However, so far no article has been found to report the \(\text{C}_{14}\) and \(\text{C}_{16}\) solid-solid transfer. Hence, the low temperature solid-solid peak, appearing in a short mixture concentration interval, may instead be explained from the fact that miscibility does not occur.
From the phase diagram and DSC results presented, it has been found that these binary mixtures of tetradecane and hexadecane melt and freeze over a temperature range and not at a constant temperature. The behaviours of the binary mixtures is far more complicated than considered in earlier studies. The obtained phase diagram and all information from the DSC measurements will be of importance for the proper design of PCM storage system.
Paraffin waxes have been studied widely as PCMs for thermal energy storage because of their advantageous thermal properties. In these studies, most of the PCMs are binary or ternary mixtures of paraffin waxes, and they have been considered to have a constant phase transition temperature during freezing and melting. However, the present study of the phase equilibrium for the binary system of tetradecane and hexadecane indicates that these binary mixtures melt and freeze in a temperature range and not at a constant temperature, except for the minimum-freezing point mixture. Further, the heat of fusion varies throughout this temperature range. In this chapter, the phase transition temperature interval and storage density corresponding to the phase transition temperature is discussed. It has been pointed out that a correct phase transition temperature range cannot be obtained simply from DSC measurements. Also, when a DSC runs at different heating/cooling rates, the measurements give different results. Combining phase equilibrium consideration with DSC measurement will give a reliable design method to incorporate both the heat of fusion and the phase change temperature range. This chapter is based on the paper III.

4.1 Property data of PCMs from the literature for use in storage design

As previously described, using PCMs in thermal energy storages results in desirable storage properties such as, high energy density (kWh/kg or kWh/m³) and a narrow temperature range for charging and discharging the storage. This temperature range corresponds to the phase transition temperature of the PCM.

A variety of PCMs have so far been investigated in the literature, including salt hydrates, paraffin waxes and non-paraffin organic compounds for different applications. Matching the transition temperature range of the PCM to the temperature for a given application is an important aspect of PCM thermal energy storage design. Experiments have been conducted to study the thermal performance of PCM storage systems and numerous publications have been found [12, 44, 67, 80 and 92]. According to these publications, binary and ternary mixtures of paraffin waxes have been used as PCM for many applications. When designing the storage system, these mixtures have been considered to have a constant phase change temperature during freezing and melting. For example, Cho et al. [21] have reported the thermal characteristics of paraffin in a spherical capsule during the freezing and melting processes. Experiments were performed with a mixture of tetradecane (40%) and hexadecane (60%), and the melting temperature was considered to be constant at 6.8 °C, with a corresponding heat of fusion of 121 kJ/kg.

DSC is one frequently used testing method in the development of PCMs. It has been used for selecting a PCM from candidates, and for the evaluation of PCM prototypes, and for investigating the reproducibility of PCM thermal characteristics [66, 102, 122 and 126-127]. Various scanning rates have been employed in these DSC measurement processes. For example, Banu et al. [13] reported that the DSC was running at a heating/cooling rate of 2
4. Phase Change Temperature Range and Storage Density

°C/min and 0.2 °C/min to determine the thermal characteristics of PCM wallboard. Marinkovic et al. [69] used DSC with a 5 °C/min scanning rate to determine the melting temperature, the enthalpy of fusion and the heat capacity of the two binary mixtures of Ca(NO₃)₂ ⋅ 4H₂O + CaCl₂ ⋅ 6H₂O and CH₃CONH₂ + Ca(NO₃)₂ ⋅ 4H₂O for an agricultural greenhouse application. Sari [101-102] used DSC at a 10 °C/min scanning rate to test the thermo physical properties of palmitic and stearic acid as PCMs for thermal energy storage. In the present chapter, it will be shown that when DSC runs at a higher scanning rate, it will not give design information that is sufficiently accurate.

For designing a PCM thermal energy storage system, the storage density and phase change temperature are very important parameters since they decide the storage system’s capacity, size and application range. When incorrect phase transition parameters are used in the PCM storage design, it will result in a lower than expected storage capacity.

4.2 The determination of PCM storage design parameters by using phase equilibrium diagram

The study of phase equilibrium indicates that the binary system of tetradecane and hexadecane forms a continuous series of solid solutions. The phase equilibrium diagram of the binary system has been described before (see Chapters 2 and 3). In this chapter, the phase transition occurring when cooling a given mixture is traced in more detail in order to obtain the physicochemical characteristics of the binary mixture.

Referring to Fig. 13 in Chapter 3, during the phase transition, when a homogeneous liquid with composition L₁ is cooled to point B₂, equilibrium mixtures of liquid and solid solution of compositions L₂ and S₂, respectively, are formed. The quantitative information about the liquid and solid phases is available by the “lever principle”, allowing the relative amounts of two phases present at equilibrium to be calculated. The relative amounts of the two phases at point B₂ can be calculated from the “lever arms” along the line (Eq. (11) and (12)).

\[
\text{mass of solid solution} \quad \text{length} \quad \frac{B₂L₂}{B₂S₂} \quad (11)
\]

\[
\text{mass of liquid} \quad \text{length} \quad \frac{B₂L₂}{S₁L₂} \quad (12)
\]

Here, Eq. (12) gives the fraction of solidification in the equilibrium mixture. In this example composition, the storage density for any temperature range between T₁ and T₆ can be calculated. For example, the storage density for any temperature range between T₁ and T₂ is:

\[
\text{Storage density} = \frac{\text{length}}{\text{length}} \frac{B₂L₂}{S₂L₂} \times \Delta H_{pc} \quad (13)
\]

Here, \( \Delta H_{pc} \) is the total enthalpy of phase change (heat of fusion) of the homogenous liquid with composition L₁ when the temperature changes from T₁ to T₆. As an example, a homogenous liquid containing 22% tetradecane is cooled to solidify completely and the total enthalpy of phase change for this mixture was obtained by DSC measurement, i.e. \( \Delta H_{pc} \) is 158 kJ/kg. At point B₂, the calculated fraction of the mixture solidified by Eq. (12) becomes 30%,
and with a corresponding storage density for the T1-T2 temperature range (12.8-12.0 °C) of 48 kJ/kg. This storage density should be compared to the total enthalpy of phase change for this mixture (158 kJ/kg). This example illustrate how assuming a phase change temperature of 12.8 °C, with 0 °C phase transition range, will lead to erroneous design of a PCM thermal energy storage. Yet such assumptions are frequently reported in the literature regarding the design of PCM storage.

Similar calculations can be done for from point B2 to B5 in Fig. 13. In Table 3, the change in the liquid-solid phase equilibrium composition, the percent of solidification and storage density of a homogenous liquid with composition L1 (L1=22% tetradecane) in a phase transition temperature range between T1 (T1=12.8 °C) and T6 (T6=9.7 °C) are given.

Table 3
Characteristic parameters during solidification of a homogenous liquid with composition 22 mole-% tetradecane

<table>
<thead>
<tr>
<th>Point B&lt;sub&gt;i&lt;/sub&gt;</th>
<th>Equilibrium liquid composition L&lt;sub&gt;i&lt;/sub&gt; (%)</th>
<th>Equilibrium solid solution composition S&lt;sub&gt;i&lt;/sub&gt; (%)</th>
<th>Equilibrium phase change temperature Ti (°C)</th>
<th>The percent of solidification (B&lt;sub&gt;i&lt;/sub&gt;L&lt;sub&gt;i&lt;/sub&gt; / S&lt;sub&gt;i&lt;/sub&gt;L&lt;sub&gt;i&lt;/sub&gt; (%)</th>
<th>Storage density (Enthalpy change) (kJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>22</td>
<td>10</td>
<td>12.8</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>B2</td>
<td>26</td>
<td>13</td>
<td>12.0</td>
<td>30</td>
<td>48</td>
</tr>
<tr>
<td>B3</td>
<td>29</td>
<td>15</td>
<td>11.3</td>
<td>50</td>
<td>79</td>
</tr>
<tr>
<td>B4</td>
<td>33</td>
<td>18</td>
<td>10.7</td>
<td>68</td>
<td>107</td>
</tr>
<tr>
<td>B5</td>
<td>36</td>
<td>20</td>
<td>10.1</td>
<td>86</td>
<td>136</td>
</tr>
<tr>
<td>B6</td>
<td>38</td>
<td>22</td>
<td>9.7</td>
<td>100</td>
<td>158</td>
</tr>
</tbody>
</table>

In Fig. 18, the upper curve shows the storage density corresponding to a temperature in the phase transition temperature range of this particular mixture, and the lower curve indicates the percent of solidification as it changes with temperature within this range. From Fig. 18 it can be seen that when the temperature reaches 12.8 °C (point A), the homogenous liquid starts to freeze and the first crystals form. When the temperature has decreased to 10.7 °C (point B), nearly 68% of the equilibrium mixture (point D) has been solidified and the storage density is 107 kJ/kg (point E). The system is cooled continuously until 9.7 °C (point C) is reached and the homogenous liquid solidifies completely (point F). The phase transition temperature range of the homogenous liquid with a composition of 22% is 3.1 °C (from A to C) and the total enthalpy change of phase transition is 158 kJ/kg (point G). A similar analysis can be done for any mixture composition by way of the equilibrium diagram.

In Fig. 19, the phase transition temperature range versus the tetradecane composition is plotted (the data of phase transition temperature ranges of all compositions indicated with a dot in Fig. 13 are given in paper III). When the mole fraction of tetradecane is between 0 to 15%, the phase transition temperature range increases linearly with concentration. Between 15 to 40% tetradecane, the temperature range is the highest and almost constant at 3 °C. Then, as the mole fraction increase from 40% to 92%, the phase transition temperature range decreases until 0 °C at 92% (point M). Finally, as the mole fraction increases further to 98%, the phase transition temperature range rises again to 1 °C. With pure tetradecane, the phase transition occurs at one fixed temperature so there is no temperature range involved. It can be seen from the diagram (Fig. 19) that the mixtures with composition between 72 to 100% have a very narrow phase transition range, lower than 1 °C, and thus such mixtures should be very
4. Phase Change Temperature Range and Storage Density

attractive for PCM storage application. The phase change temperature of all the mixtures varies from 5.8 to 1.7 °C.

![Graph showing phase equilibrium temperature and storage density](image)

**Fig. 18** Phase equilibrium temperature of the homogenous liquid with composition 22% tetradecane versus the storage density (enthalpy change) and the percent of solidification

![Graph showing phase transition temperature range](image)

**Fig. 19** Phase transition temperature range versus mole-% of tetradecane

4.3 Characteristic temperature of phase transition processes as determined from DSC measurements

A large number of DSC measurements data on the binary n-alkane system hexa- and tetradecane have been presented in chapter 3. A further analysis of these data is made in this chapter. As an example, characteristic DSC temperatures of the mixture with a 22% mole fraction of tetradecane at three DSC heating/cooling rates (5 °C/min, 2 °C/min and 0.5 °C/min) are shown in Fig. 20 (freezing) and Fig. 21 (melting). It can be seen from the two
figures that the DSC curves of the binary mixture vary in shape depending on the DSC scanning rate. The values of $T_p$ (peak temperature) and $T_c$ (extrapolated end temperature) obtained at a rate of 5 °C/min are quite different from the values obtained at 2 and 0.5 °C/min. From Fig. 20 and 21, all the characteristic temperatures previously described in chapter 3 are summarized in Table 4. Where two peaks appear (for 0.5 °C/min), “high” and “low” in the table indicate the high temperature peak and low temperature peak, respectively. In this table, the temperature range for the phase change is the temperature difference between $T_c$ and $T_e$.

Table 4
Characteristic temperature of mixture with a 22% mole fraction of $C_{14}H_{30}$

<table>
<thead>
<tr>
<th>DSC heating/cooling rate</th>
<th>Freezing process characteristic temperature °C</th>
<th>Melting process characteristic temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Onset $T_e^f$ (°C)</td>
<td>End $T_e^f$ (°C)</td>
</tr>
<tr>
<td>5 °C/min</td>
<td>+12</td>
<td>-4.6</td>
</tr>
<tr>
<td>2 °C/min</td>
<td>+11.6</td>
<td>+0.8</td>
</tr>
<tr>
<td>0.5 °C/min</td>
<td>+11.5</td>
<td>High:+7.6</td>
</tr>
<tr>
<td></td>
<td>Low:+5.8</td>
<td>Low:+6.8</td>
</tr>
</tbody>
</table>

Table 4 indicates that a higher scanning rate gives the result of a wider temperature range. The temperature range reached 16.5 °C for the freezing process, and 18 °C for the melting process at a 5 °C/min scanning rate. When the scanning rate is slower, 2 °C/min, the temperature range is 11 °C for the freezing and 14 °C for the melting. However with a scanning rate of 0.5 °C/min, two peaks appear and the temperature range of the high temperature peak is only 3.9 °C in the freezing process and 5 °C in the melting process, respectively. As discussed in chapter 3, the low temperature peak is presumably due to a solid-solid phase transition.

Fig. 20 DSC freezing curves of the mixture with 22 mole-% fraction tetradecane at different scanning rates
4. Phase Change Temperature Range and Storage Density

4.4 Enthalpy change (storage density) of phase transition processes as determined from DSC

The enthalpy change of the phase transition process (storage density) can also be determined by DSC measurements. The area of a DSC peak can be used to estimate the enthalpy change of phase transition. From theoretical modelling, it can be calculated by the below equation:

\[ Q_{pc} = \int_{t_1}^{t_2} \left( \frac{\delta Q}{\delta t} \right)_{pc} dt \]  

Here, \( \left( \frac{\delta Q}{\delta t} \right)_{pc} \) is the heat flow in unit w/g and \( t \) is time. The software automatically calculates the total peak area, i.e. the total enthalpy change (\( Q_{pc} \)) of the phase transition. However, the enthalpy change (storage density) in any temperature range within the phase transition cannot be obtained directly. There are two ways to get the enthalpy change in any temperature range according to Eq. (14). The first way is to utilize the DSC curves (Fig. 22) that give the heat flow versus temperature (a) to obtain the value of heat flow \( \left[ \left( \frac{\delta Q}{\delta t} \right)_{1} \right. \) and \( \left. \left( \frac{\delta Q}{\delta t} \right)_{2} \right] \) at any temperature range (T1 and T2). Then, according to the heat flow \( \left[ \left( \frac{\delta Q}{\delta t} \right)_{1} \right. \) and \( \left. \left( \frac{\delta Q}{\delta t} \right)_{2} \right] \), the time range (t1 and t2) is obtained from the curve of the heat flow versus time (b). Finally, Eq. (14) is used to calculate the enthalpy change at any temperature range.

Fig. 21 DSC melting curves of the mixture with a 22 mole-% tetradecane at different scanning rates
As an example, the DSC curves of heat flow versus time of the homogenous liquid with a composition of 22% at different scanning rates are shown in Fig. 23. From this composition, the enthalpy change (storage density) in a number of temperature ranges within the phase transition temperature range can be obtained by integrating the DSC curve of heat flow versus time and are listed in Table 5.

Fig. 22 DSC curves of heat flow versus temperature (a) and time (b)

Fig. 23 DSC freezing curves (heat flow versus time) of a mixture with 22 mole-% of tetradecane at various scanning rates
### Table 5

<table>
<thead>
<tr>
<th>DSC heat/cooling rate</th>
<th>Freezing process total enthalpy change $\Delta H_{pc}^f$ (kJ/kg)</th>
<th>Melting process total enthalpy change $\Delta H_{pc}^m$ (kJ/kg)</th>
<th>Thermophysical properties of freezing process</th>
<th>Thermophysical properties of melting process</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_f$ ($^\circ$C)</td>
<td>$\Delta T_i = T_e - T_f$ ($^\circ$C)</td>
<td>Storage density (enthalpy change) at $T_f$ $\Delta H_i$ (kJ/kg)</td>
<td>Percentage of solidification $\Delta H_i / \Delta H_{f\text{total}}$ (%)</td>
</tr>
<tr>
<td>5 °C/min</td>
<td>150</td>
<td>159</td>
<td>7</td>
<td>5</td>
</tr>
<tr>
<td>2 °C</td>
<td>149</td>
<td>159</td>
<td>6.6</td>
<td>5</td>
</tr>
<tr>
<td>0.5 °C</td>
<td>157</td>
<td>170</td>
<td>7.5</td>
<td>4</td>
</tr>
</tbody>
</table>

The second way to get the enthalpy change (storage density) in a certain temperature range is to utilize the associated software that make up the thermal analysis system to obtain DSC integral curves. The DSC integral curves of the homogenous liquid with composition 22% during the freezing and melting process are shown in Fig. 24 and 25, respectively and pure tetradecane integral curves are shown for comparison. It can be seen that the integral curves of pure tetradecane are much sharper than the mixtures’ curves, and the mixtures’ curves at lower scanning rate are sharper than at higher scanning rate. The storage densities obtained from integral curves in any temperature range are given in Table 6.

### Table 6

Storage densities at any temperature from integral curves

<table>
<thead>
<tr>
<th>DSC heat/cooling rate</th>
<th>$T_f$ ($^\circ$C)</th>
<th>$\Delta T_i = T_e - T_f$ ($^\circ$C)</th>
<th>Storage density (enthalpy change) at $T_f$ $\Delta H_i$ (kJ/kg)</th>
<th>Percentage of solidification $\Delta H_i / \Delta H_{f\text{total}}$ (%)</th>
<th>$T_m$ ($^\circ$C)</th>
<th>$\Delta T_i = T_m - T_e$ ($^\circ$C)</th>
<th>Storage density (enthalpy change) at $T_m$ $\Delta H_i$ (kJ/kg)</th>
<th>Percentage of solidification $\Delta H_i / \Delta H_{m\text{total}}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 °C/min</td>
<td>7</td>
<td>5</td>
<td>47</td>
<td>31%</td>
<td>9.3</td>
<td>5</td>
<td>-33</td>
<td>21%</td>
</tr>
<tr>
<td>2 °C/min</td>
<td>6.6</td>
<td>5</td>
<td>85</td>
<td>57%</td>
<td>8.8</td>
<td>5</td>
<td>-38</td>
<td>24%</td>
</tr>
<tr>
<td>0.5 °C/min</td>
<td>7.5</td>
<td>4</td>
<td>102</td>
<td>65%</td>
<td>9.3</td>
<td>4</td>
<td>-55</td>
<td>32%</td>
</tr>
</tbody>
</table>
4.5 Concluding remarks

A phase diagram of the binary system of hexa- and tetradecane depicts the concentration-temperature relationships at equilibrium and visualizes how these relations change with temperature and chemical composition. For a given application, where the storage system charges/discharges in a certain temperature range, the storage density may or may not reach the value of heat of fusion $\Delta H_{pc}$, depending on whether the allowed temperature range is as large as the phase change temperature range $\Delta T_{pc}$. From an analysis of the phase diagram, the phase transition temperature range of the binary mixture system of tetradecane and hexadecane is shown to be a function of the composition of the mixture.
The DSC measurements results (shown in Table 4) indicate that the characteristic temperatures strongly depend on the DSC heating/cooling rate. However, $T_e$ is almost the same whereas the $T_c$ is quite different, depending on the heating / cooling rate. In the melting process, there is a large temperature range compared to the freezing process at the same rate, and a higher scanning rate gives a wider temperature range. One reported problem with DSC measurements is that the extrapolated end temperature ($T_c$) is systematically too large. Gimzewski et al. [42] reported that ideally the onset of crystallization will occur at exactly the same temperature as the termination of the melting processes, if the cooling / heating rates are sufficiently slow. However, even at the scanning rate of 0.01 °C/min, they found the disparity to be significant. So the extrapolated end temperature ($T_c$) should not be considered as the equilibrium temperature of mixtures during the freezing and melting processes.

The large extrapolated end temperature is likely a result of a thermal relaxation process in the DSC and also in the sample. Relaxation is the time-dependent return to equilibrium (or to a new equilibrium) after a disturbance. The thermal relaxation time in the melting process is larger than in the freezing process and it results in an enlarged extrapolated end temperature in the melting process as compared to the freezing process. The reason for this is because of the lower heat conductivity and poor heat convection properties of the solid state compared to the liquid phase. The DSC results also indicate that the higher the DSC scanning rates, the larger the extrapolated end temperature.

Dong and Hunt [29] reported that when large heat fluxes are present, the DSC thermocouples do not measure the temperature of the sample. The temperature measured is the temperature of the surrounding furnace. So that incorrect information will be given by DSC measurement during a higher scanning rate.

Non-equilibrium freezing at a higher scanning rate also needs to be considered. As illustrated in Fig. 13, when the homogenous liquid with composition $L_1$ is cooled, the first solid, of composition $S_1$, begins to form at temperature $T_1$. As the temperature drops to $T_{6_1}$, the solid composition follows the solidus curve so that solid of different compositions to $S_1$ deposit on the already present crystals. Chemical diffusion then occurs in the solid until the solid composition is homogenous. If the characteristic diffusion time of the PCM is too long, chemical equilibrium in the solid will not be reached before the subsequent melting process starts, and this could artificially enlarge the temperature range of melting in a DSC measurement. The phenomenon of called “coreing” may happen [62].

The results from Table 5 indicate that the total enthalpy change via a complete phase change process, $\Delta H_{pc}$, is almost independent of the DSC heating / cooling rate, whereas the predicted enthalpy change (storage density) in any temperature range within $\Delta T_{pc}$ depends very much on the DSC rate. One explanation is that when the phase change process has not been completed, any temperature change will lead to a latent heat change, and the relation of latent heat change with temperature varies with the DSC rate.

For designing a PCM thermal energy storage system, storage density and phase change temperatures are very important parameters since they decide the storage system’s capacity, size and application range. When incorrect phase transition parameters are used in the PCM storage design, it will result in a lower than expected storage capacity. For example, Yamaha [123] has reported results from theoretical modelling of a PCM storage unit in an air distribution system for peak shifting. The binary mixtures of tetradecane and hexadecane with
melting point around 13, 15, 17, 19, 21 and 23 °C were utilised separately as PCMs to simulate the storage. The air ran through a closed circuit of the PCM storage tank and the air conditioners. After the charge cycle, the air conditioning would start operating. The conditioned air was projected into the room and returned to the air conditioner, mixing with outdoor air. In this operation, the air was assumed to bypass the PCM storage tank. For discharging operation, the air went through the PCM storage tank to the room. The air temperature during charging was 12 °C. However, experimental results indicated that the PCM with a melting temperature around 13 °C did not work at all. With the PCM phase transition temperature of 15 °C, the charging process could not be completed. The present investigation presents one explanation that these materials actually freeze and melt in a temperature range. In the example above, the phase transition temperature range could not be covered completely when charging the storage with air at 12 °C. To correctly design a thermal energy storage system, it is hence very important to know the phase transition temperature range.

In PCM cooling storage applications, the storage density and phase transition temperature will determine the storage system capacity, size and application. The study of phase equilibrium and phase diagram becomes very important and useful. A phase diagram can give the correct phase transition temperature range and present the energy storage density. If incorrect values are utilised for a cool storage system design, it will result in a lower cooling capacity and economic losses. Therefore, the phase equilibrium study is invaluable to PCM thermal energy storage researches and developers. Combining phase equilibrium considerations with DSC measurements makes it possible to properly interpret the DSC data. This gives a reliable method that incorporates both the heat of phase change and the temperature range.
5. Designing PCM Cool Storage Systems for Peak-Load Management in Various Cooling Applications

In a variety of cooling applications, integrating a PCM cool storage for peak shaving can provide economic advantages. In this chapter, a computer model has been developed to study phase equilibrium and design paraffin wax-based cool storage systems. Based on the presented phase equilibrium diagram and the heat of fusion of the binary mixtures of tetracane and hexadecane, several polynomial equations have been derived through curve fitting. The polynomial equations provide a convenient way to obtain the phase change temperature range and storage density. Based on this model, applications with integrated cool storage in an absorption district cooling system and a borehole cooling system have been analysed. The results indicate that the PCM storage is a promising concept for peak shaving and improving the energy efficiency of cooling systems for cooling applications. Finally, this chapter provides insights into the commercial feasibility of PCM storage in cooling applications. A commercial product, i.e. a technical grade paraffin wax, RT5 has been examined as a PCM for comfort cooling storage along with an estimate of the capital cost of a dynamic process storage using the examined PCM material. This chapter is based on papers IV, V and VI.

5.1 Computer model for phase equilibrium study

Computer simulation programs have been widely developed for various energy systems. The report of Annex 14, subtask 3, has mentioned around thirty computer softwares, which can be used for the cool storage system [7]. The majority of these simulation programs are used to study the feasibility of the cost and energy performance of the system. A few models have also been developed to study the PCM itself. For example, Yamaha [125] has developed a simulation model for the thermal response of a PCM installed in an air distribution system. This model was used to evaluate the performance of PCM storage systems. In the present study, a computer model has been developed to study the phase equilibrium of paraffin waxes for the design of cool storage with such materials. In here, section 5.1 is based on paper IV.

5.1.1 The principle of the model

For a system forming a continuous series of solid solutions, the thermodynamic equilibrium relationship between a solid and liquid phase has been described in Eq. (5). Based on Eq. (5), a computer model has been developed. The purpose of the model is to make the phase equilibrium calculation quick and easy, and to get numerical data from the temperature-concentration phase equilibrium diagram in a direct way. Based on the phase diagram, a series of polynomial equations \( T = f(x_{\text{liquid}}, \text{ or } x_{\text{solid}}, \text{ or } x_{\text{solid}} = f(T)) \) have been fitted to the data obtained from the model. These polynomial equations provide an easy way to choose a material with a suitable phase change temperature for a practical application.

The principle of the model can be described as below (Fig. 26):
In the model, $\Delta H_{pc}$, $R$, and $T_m$ are considered as constant. The input data file contains the liquid composition ($x_i^l$) and the activity coefficient ($\gamma_l$). Calculated results can be obtained from the output data file, which contains liquid phase composition ($x_i^l$), solid phase composition ($x_i^s$) and temperature ($T$) at equilibrium condition. After this step, there are different options. For example, the phase diagram of the system can be obtained, or just the melting curve (solidus), or the freezing curve (liquidus). From curve-fits, polynomial equations are provided for the phase equilibrium interrelationships. The model can also be used as a calculator to do simple phase equilibrium calculations.

### 5.1.2 Polynomial equations

The phase equilibrium calculation of the binary system of tetradecane and hexadecane can be quickly obtained by the computer model presented above, and the phase diagram of the binary system is obtained directly. Based on the phase diagram, polynomial equations have been derived and they are presented below.

#### 5.1.2.1 The relationships between the freezing point and liquid composition

Based on the freezing curve (liquidus), the polynomial equations describing relationships between the temperature and liquid mole fraction of tetradecane ($T$ and $x_{\text{liquid}}$) are shown below (Eq. (15) and (16)):
5. Designing PCM Storage System for Peak Shaving

\[
T(x'_i)(K) = \begin{cases} 
  a'_0 + a'_1(x'_i - \bar{x}'_a) + a'_2(x'_i - \bar{x}'_a)^2 + a'_3(x'_i - \bar{x}'_a)^3 & 0.00 \leq x'_i \leq 92.53 \\
  b'_0 + b'_1(x'_i - \bar{x}'_b) + b'_2(x'_i - \bar{x}'_b)^2 + b'_3(x'_i - \bar{x}'_b)^3 & 92.53 \leq x'_i \leq 100
\end{cases} 
\]

Here,
\[
\begin{align*}
  a'_0 &= 279.9502K \\
  a'_1 &= -0.17456K \\
  a'_2 &= 0.00029K \\
  a'_3 &= -0.000007K
\end{align*}
\]
\[
\begin{align*}
  b'_0 &= 275.7144K \\
  b'_1 &= 0.47588K \\
  b'_2 &= 0.051795K \\
  b'_3 &= 0.000000K
\end{align*}
\]
\[\bar{x}'_a = 54.43 \quad \bar{x}'_b = 95.98\]

Here, \(T(x'_i)\) is the freezing point of the mixture with a mole fraction \(x'_i\).

Also,
\[
x'_i(T) = \begin{cases} 
  a''_0 + a''_1(T_i - \bar{T}'_a) + a''_2(T_i - \bar{T}'_a)^2 + a''_3(T_i - \bar{T}'_a)^3 & 0.00 \leq x'_i \leq 92.53 \\
  b''_0 + b''_1(T_i - \bar{T}'_b) + b''_2(T_i - \bar{T}'_b)^2 + b''_3(T_i - \bar{T}'_b)^3 & 92.53 \leq x'_i \leq 100
\end{cases} 
\]

Where,
\[
\begin{align*}
  a''_0 &= 52.2789K^0 \\
  a''_1 &= -5.8749K^{-1} \\
  a''_2 &= -0.1431K^{-2} \\
  a''_3 &= 0.0319K^{-3}
\end{align*}
\]
\[
\begin{align*}
  b''_0 &= 96.5323K^0 \\
  b''_1 &= 2.1742K^{-1} \\
  b''_2 &= -0.3131K^{-2} \\
  b''_3 &= 0.0000K^{-3}
\end{align*}
\]
\[\bar{T}'_a = 280.36K \quad \bar{T}'_b = 276.01K\]

5.1.2.2 The relationship between the melting temperature and solid composition

Based on the melting curve (solidus), the polynomial equations describing relationships between temperature and solid fraction of tetradecane \(T\) and \(x^{\text{sol}}\) are shown in Eq. (17) and (18).

\[
T(x''_i)(K) = \begin{cases} 
  a''_0 + a''_1(x''_i - \bar{x}''_a) + a''_2(x''_i - \bar{x}''_a)^2 + a''_3(x''_i - \bar{x}''_a)^3 & 0.00 \leq x''_i \leq 92.34 \\
  b''_0 + b''_1(x''_i - \bar{x}''_b) + b''_2(x''_i - \bar{x}''_b)^2 + b''_3(x''_i - \bar{x}''_b)^3 & 92.34 \leq x''_i \leq 100
\end{cases} 
\]

Here,
\[
\begin{align*}
  a''_0 &= 279.0488K \\
  a''_1 &= -0.1344K \\
  a''_2 &= 0.0009K \\
  a''_3 &= -0.0000004K
\end{align*}
\]
\[
\begin{align*}
  b''_0 &= 275.6018K \\
  b''_1 &= 0.6231K \\
  b''_2 &= 0.1259K \\
  b''_3 &= 0.0000K
\end{align*}
\]
\[\bar{x}''_a = 44.56 \quad \bar{x}''_b = 97.1\]

In Eq. (17), \(T(x''_i)\) is the melting point of the mixture with a mole fraction of tetradecane \(x''_i\).

In addition,
\[
x''_i(T) = \begin{cases} 
  a''_0 + a''_1(T_s - \bar{T}''_{a}) + a''_2(T_s - \bar{T}''_{a})^2 + a''_3(T_s - \bar{T}''_{a})^3 & 0.00 \leq x''_i \leq 92.34 \\
  b''_0 + b''_1(T_s - \bar{T}''_{b}) + b''_2(T_s - \bar{T}''_{b})^2 + b''_3(T_s - \bar{T}''_{b})^3 & 92.34 \leq x''_i \leq 100
\end{cases} 
\]

Where,
5.2.1.3 The relationship between the heat of fusion and liquid composition

Based on Fig. 11, the polynomial equation for the heat of fusion versus the liquid mole fraction of tetradecane ($\Delta H_{pc}$ vs $x_i^l$) has also been obtained and is shown below:

$$
\Delta H_{pc} (kJ / kg) = c_0 + c_1 (x' - \bar{x}') + c_2 (x' - \bar{x}')^2 + c_3 (x' - \bar{x}')^3
$$

where $c_{0-3}$ are constants with the unit kJ/kg as follows:

$c_0 = 146.1705 \quad c_1 = 0.1561 \quad c_2 = 0.0085 \quad c_3 = -0.0013 \quad \bar{x}' = 58.06$

The error between the theoretical model and the results from polynomial equations can be indicated by the curve-fit standard deviation (S.D.):

$$
S.D. = \sqrt{\frac{\sum_{i=1}^{n} (y_{calculated} - y_{fit})^2}{n - 1}}
$$

The obtained curve-fit standard deviation is around 0.05 for the phase diagram and 3 for the heat of fusion.

5.2 Applications with integrated cool storage

Improvements in the efficiency of energy usage and energy conservation can be achieved in many ways. For comfort cooling, district cooling contributes to an overall improvement in the efficiency of energy use, as well as to minimize the use and corresponding leakage of ozone-depleting refrigerants. These efficiency improvements are largely caused by the increased potential in a district system for using natural cooling (e.g., cold surface water or ambient air), and waste cooling (from e.g. heat pumps), and solar energy and waste heat driven cooling technology. To increase the usage of natural cooling, waste cooling and heat or solar energy, thermal energy storage and heat driven cooling technology can play an important role in cooling applications.

The cooling demand has increased in Sweden during the last decades, and the market for district cooling has expanded strongly since its introduction. This is due to factors like new building regulations, a greater use of computers and more awareness of the importance of good working conditions. District cooling was introduced in Sweden in 1992, when about 1.2 GWh cooling was supplied in a 1 km network. At the beginning of 2000, there were 21 districts cooling system in operation and 337 GWh of district cooling were supplied in 85 km of network [35]. However, the problem in the Swedish cooling systems is the short cooling period and high peak power demand. Introducing a cool storage will then provide potential for capital cost savings since a chiller can be sized for base load only. Also, the annual system efficiency will be higher in such an arrangement since it allows the chiller to operate at design conditions in a larger part of the time [58].
5.2.1 Absorption chiller and PCM storage in district cooling system

District cooling based on absorption technology has been demonstrated as an energy efficient way for utility companies to use district heating and waste heat (lower temperature heating) to produce and sell district cooling during summer [106]. This is an interesting and increasingly growing field with many opportunities for energy efficient system design, and is a quickly growing research/application area [28, 64 and 111].

Absorption chillers that use heat as their driving energy avoid the electricity consumption of conventional vapour compression cooling. In addition, the working media in absorption chillers are normally lithium bromide and water, hence ozone-depleting and global warming refrigerants may be phased-out from comfort cooling applications. It should be favourable to have a cool storage connected with an absorption chiller cooling system to decrease the size and cost of absorption chiller. A cost assessment of such a system has been presented recently [98]. In this study, it was concluded that integrating a cool storage with an absorption chiller will increase the seasonal COP due to the chiller working a large amount of hours at the design load. Further, the storage appeared to be economically feasible.

5.2.1.1 The design of a PCM storage system for peak shaving

The cooling demand fluctuates within an hour, a day and a month and the fluctuation are affected mainly by the weather condition. As an example, fluctuation in the district cooling demand of Stockholm is depicted in Fig. 27. It can be seen that there is a peak cooling load for the hottest days during July.

![Fig. 27 Fluctuation of district cooling demand in Stockholm in 2001 based on [98]](image)

A simple system layout is depicted in Fig. 28. Herein, the absorption chiller is used for the base load and the PCM storage for peak load. In this combined system, the design loads of the absorption chiller and the PCM storage system were considered to be 0.68 MW and 2.4 MWh, respectively, for the hourly cooling demand shown in Fig. 27 [98]. In the particular comfort cooling application, the cooling supplying temperature is 6 °C and maximum return temperature is 14 °C. The charging and discharging processes are controlled automatically and depend only on the cooling demand. The flow rate from the chiller is constant and the
temperature leaving the chiller is also constant. In the present investigation, the design of the PCM storage, using a mixture of tetradecane and hexadecane, has been analysed in more detail.

![Diagram of absorption chiller and PCM cooling storage](image)

Fig. 28 The combined system: absorption chiller and PCM cooling storage (Based on ([98]))

Matching the transition temperature range of the PCM to the temperature for a given application is an important aspect of PCM thermal energy storage design. According to the combined cool storage system operating parameters (as shown Fig. 28), the PCM should be completely frozen at 9 °C. The design of the PCM storage system includes choosing the PCM candidate for this application and to calculate the volume of the storage. The procedure, using the model presented in section 5.1 can be described as follows:

1) Use the $x^3$ vs $T$ polynomial (Eq. (18)) to get the composition of a binary mixture at $T$ equalling 9 °C. It means that the mixture will completely freeze at 9 °C, and that it also starts to melt at this temperature.

2) Use the $T$ vs $x_l$ polynomial (Eq. (15)) to get the freezing point of the binary mixture. In a charging process, when the freezing temperature is reached the binary mixture starts to freeze, or in a discharging process, the mixture will completely melt at this temperature.

3) Use $\Delta H$ vs $x_l$ polynomial (Eq. (19)) to get the energy density (the heat of fusion) of the binary mixture.

4) Use the energy density and the capacity of storage to get the volume of PCM storage.

Table 7 gives the results for this particular example. It can be seen from Table 7 that the binary mixture with a mole fraction 25% of tetradecane starts freezing at 12 °C and completely freezes at 9 °C. Conversely, the binary mixture starts to melt at 9 °C and is completely melted at 12 °C. The phase change temperature range of the mixture is 3 °C and the energy density is 39 kWh/m³. Assuming a 50% packing factor results in a 123 m³ required storage volume for the desired 2.4 MWh of cool storage.
Table 7
The parameters of PCM storage system

<table>
<thead>
<tr>
<th>Composition x% (mole fraction of tetradecane)</th>
<th>Freezing temperature (°C)</th>
<th>Melting temperature (°C)</th>
<th>Energy density (ΔH) kJ/kg</th>
<th>Capacity of storage (MWh)</th>
<th>Volume (m³)</th>
<th>PCM Storage</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>12</td>
<td>9</td>
<td>184</td>
<td>39</td>
<td>2.4</td>
<td>61.5*</td>
</tr>
<tr>
<td>(47000 kg)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(47000 kg)</td>
</tr>
</tbody>
</table>

* Here, only the latent heat of phase change process has been considered

5.2.1.2 On the economic feasibility

The economic feasibility of an absorption chiller system depends on many different parameters. The system capital cost and the cost of the driving heat and electricity are the most important parameters for the cooling supply cost. The cooling supply cost evaluation has been presented by Rydstrand et al. and is shown in Fig. 29. The two parameters, the cost of capital and the cost of the driving heat, are the only parameters considered. Herein, an interest rate of 6% and a depreciation time of 20 years gave an annuity of 8.7% in the study of the capital cost in [98].

![Fig. 29 Cooling supply cost at varied heat prices [98]](image)

It is clearly shown in Fig. 29 that the two storage systems have a lower capital cost as compared to the non-storage system. This is due to the fact that the peak shaving thermal storage has a lower cost compared to what the replaced absorption chiller capacity has. While the stratified chilled water storage system has the lowest cost in Fig. 29, the cost of storage volume has not been taken into account. The difference in cost at higher heat prices is larger as compared to the difference at lower heat prices due to the fact that the absorption chiller in a storage system can be operated more at design load, giving a more efficient use of the driving heat.

If the PCM storage would be allowed to cost for the “cooling supply cost” to be the same as the stratified chilled water storage, the capital cost of the two systems should be the same. A further calculation based on [98] has been done here and the result indicates that in this case, the cost for PCM should decrease by 70% to 12 Euro/kWh. However, it must be pointed out that the cost for the volume space requirement has not been included herein. If the volume cost is significant, the requirement for price reduction of the PCM is much less than 70%. In
addition, for smaller size storage, the tank cost would be relatively larger such that PCM storage could become cost-effective. Nevertheless, R&D on PCMs should focus on finding cheaper materials.

5.2.2 Borehole thermal energy storage coupled to peak load PCM storage

Cool storage with Underground Thermal Energy Storage (UTES) has been considered for commercial buildings. Several different systems for UTES have been developed and tested over the last 15 years in Sweden, see Fig. 30 [6].

![Fig. 30 Underground thermal energy storage (UTES) – different options](image)

Two of the concepts, the Aquifer and Borehole Thermal Energy Storage system (ATES and BTES), are now commercial technologies in Sweden. For example, in 1999 there were over thirty ATES in use, with recently constructed ATES being applied for large-scale cool storage (500-5000 kW). BTES on the other hand are normally used in small-scale cooling applications (50-500 kW).

In Sweden, mechanical chillers are usually connected to a BTES system for peak load. Hence, free cooling (cooling from natural air, surface water and waste cold) only covers the base-cooling load. In order to avoid using mechanical chillers and hence avoid the accompanying peak load electricity consumption, one idea examined herein is to use PCM energy storage to cover the peak cooling load. The PCM/BTES combined system gives the possibility for charging and discharging the free cooling storage at a larger power than just BTES and thus eliminates the need for auxiliary electrically driven cooling. Such a system is examined below, and this section 5.2.2. is based on paper V.

5.2.2.1 A combined PCM storage-BTES system

In a borehole cool storage (BTES), cold is charged and stored in a rock volume perforated by many vertical boreholes. These holes act as a heat exchanger between the storage and the circulating fluid. During charging, cold fluid is circulated in the boreholes and heat is transported from the rock volume into the fluid, thereby cooling the rock. During discharging,
heat is transported into the rock from the relatively warm circulating fluid. Hence, the fluid is cooled while circulating. The main advantages of a BTES system are that it can be used for both heating and cooling, and that it saves around 70-80% of prime energy as compared to conventional mechanical chillers. The system is reliable with low operation and maintenance (O&M) cost. The lifetime is approximately 40 years and thus the capital investment can be written off over many years. Furthermore, the boreholes can be placed, hidden underground, which is practical in many cases. A further detailed description of the borehole thermal energy storage technology is found in, for example, [84].

A BTES is usually used as seasonal thermal energy storage such that cooling is charged during winter and discharged during the summer. However, a PCM storage is suitable as a short-term storage, e.g. charged during the night and discharged during the day. The cooling applications of BTES in Sweden are so far related to small-scale systems (50-500 kW cooling power) and the users are often single commercial buildings. The general view in designing the BTES system is to cover around 90% of the cooling demand (50% of maximum load). The rest of the cooling is covered by heat pumps. A typical cooling demand for a large office building may be:

- total cooling demand for a building: 200 kW
- load covered by the BTES boreholes: 100 kW
- peak cooling demand: 100 kW

Only on the hottest days is the cooling demand 200 kW. A PCM storage system can be combined with the BTES system for peak shaving and thus avoid the need for mechanical chillers to cover the peak cooling demand. Such a combined system is depicted in Fig. 31. In this system, the BTES is a seasonal storage system and is charged by waste cooling from heat pumps during the winter. During the summer, the cooling is extracted to cover the cooling demand. The objective of the PCM cool storage is for peak shaving, and it is charged during night (e.g. 6 hours) from boreholes at a 50 kW rate. The cooling is released during the peak demand at 100 kW rate (e.g. during 3 hours in the afternoon). The system could, in principle, also integrate free cooling sources from the air or surface water.

Andersson et al. [5] has reported that it is of great interest for thermal energy storage that the boundary conditions related to supply and return temperature changes slowly. From the traditional 6 (supply)/12 (return) °C system, the tendency is now to design air-conditioning at a higher temperature level, e.g. 11/17 °C. In the combined storage system the charging temperature of PCM storage is thus proposed to be around 10 °C, and the discharging temperature around 15 °C. All the operating parameters of the PCM storage system are listed in Table 8.

Table 8
Desired operating parameters of peak load PCM cool storage system

<table>
<thead>
<tr>
<th>Processes</th>
<th>Rate (kW)</th>
<th>Time (hour)</th>
<th>Temperature (°C)</th>
<th>Total cooling load (Q kWh/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charging</td>
<td>50</td>
<td>6</td>
<td>10</td>
<td>300</td>
</tr>
<tr>
<td>Discharging</td>
<td>100</td>
<td>3</td>
<td>15</td>
<td>300</td>
</tr>
</tbody>
</table>
5.2.2.2 The choice of PCM

According to the desired operating parameters of the BTES-PCM combined cool storage system, the PCM should be completely frozen at 10 °C and totally melted at 15 °C. Utilizing the previously obtained computer model of the binary mixtures system of tetradecane and hexadecane, one mixture with a 20% mole fraction of tetradecane was chosen as a candidate for this application. This mixture starts to form the first crystal at around 13 °C and solidifies completely at 10 °C. The heat of fusion for this particular mixture is 181 kJ/kg. All characteristic thermal properties are shown in Table 9.

Table 9

<table>
<thead>
<tr>
<th>Freezing temperature (°C)</th>
<th>Melting temperature (°C)</th>
<th>Temperature range (°C)</th>
<th>Heat of phase change ∆H (kJ/kg)</th>
<th>Density (kg/liter)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>10</td>
<td>3</td>
<td>181</td>
<td>0.77</td>
</tr>
</tbody>
</table>

5.2.2.3 PCM storage system design

There are two kinds of storage processes for PCM storage: the static and the dynamic storage processes. In a static storage process, the heat exchange between the heat transfer medium and the storage material take places via a solid surface. The heat capacity of the static PCM storage system can be calculated according to:

\[ Q = \sum m_i C_p \Delta T + \sum m_i \Delta H_{pc} \]  

(21)

The heat transfer conditions and the size of the available heat transfer surface area are the decisive parameters, which determine the power of the static storage system. One example of a static storage system is that the heat exchanger coil is submerged in the PCM while a heat transfer fluid is circulated inside the coil. To charge the storage system, cold fluid is circulated in the tubes, causing PCM to freeze and cover the outside of the tubes. This configuration is widely used in ice-on-coil thermal energy storage [30]. Another possible
5. Designing PCM Storage System for Peak Shaving

configuration of a static storage is to use a plate heat exchanger layout where PCM is encapsulated in plates and the fluid flows in between these plates [129].

In a dynamic storage process, direct contact between storage and heat transfer medium may result in excellent heat transfer [39]. The heat capacity of a dynamic PCM storage system can be calculated according to:

\[
Q = \sum m_u C_{pu} \Delta T + \sum m_l C_{pl} \Delta T + \sum m_l \Delta H_{pc}
\]

(22)

The storage system behaves as a hybrid storage system, i.e. utilizing all the thermal storage advantages of both the sensible heat of the heat transfer medium and the latent heat of the PCM [41].

One requirement for the dynamic system is naturally that the PCM is not soluble in the heat transfer fluid. Another requirement is that there is a significant difference in density between the PCM and the heat transfer fluid. These requirements are met by the system paraffin PCM-water. Fig. 32 shows a schematic diagram of a dynamic storage system. During the charging process, cold water is sprayed into the tank from the top and drained off from the bottom. When the average temperature of the liquid PCM reaches the freezing point, a PCM shell covers the water droplets and this results in the buildup of a layer of water droplets enveloped by PCM at the interface between the PCM and water. In the discharging process, water at a temperature above the phase change temperature range of the PCM is sprayed into the system, and the frozen PCM will melt [41]. The solid structure of the porous wax provides optimum conditions for the freezing and melting processes since it provides a large surface area for heat transfer.

![Fig. 32 Dynamic cool storage process during charging](image)

5.2.2.4 Potential for PCM storage for peak cooling load

When the cold source of a BTES system is the waste cooling from a heat pump, the charging temperature of the BTES cannot be changed, i.e. the temperature decides the heat transfer rate and limits the cooling capacity (kW/m³) of the BTES system. Usually to design a BTES system the normal amount of supplied cooling is only 50% of the peak cooling effect (kW), corresponding to 90% of the yearly cooling demand (kWh). This is because the cost per kWh
will be very high to cover the other 10% with boreholes. During the summer in Sweden, a
cooling demand will increase to reach a peak level only during short periods, and hence a
conventional chiller (usually a heat pump) is normally used for this purpose. If a PCM storage
system is installed in combination with the BTES system, it can be charged during the night
from BTES and then discharged during daytime to cover peak load. This can improve the
efficiency of energy use in the BTES system and eliminate the need for a mechanical chiller.
Below, the potential for this configuration is assessed with regards to design parameters and
cost.

**Peak load storage size – a comparison with stratified chilled water storage (SCWS)**

For the typical BTES cooling application described herein, the peak cooling demand is about
200 kW and with BTES providing 50% of this demand. Hence, there is a need for an
additional 100 kW to be provided by the proposed PCM cool storage. The expected maximum
duration of this peak cooling is assumed to be three hours and hence the capacity of the
storage must be 300 kWh. For the paraffin mixture presented as a candidate PCM in Table 9,
300 kWh can be calculated as corresponding to approximately 6000 kg PCM or around 8 m³.
Usually, the total storage volume can be represented with a so-called packing factor, which
typically is around 0.5 resulting in a total required volume for the PCM storage of 16 m³.

Instead of a PCM storage, a stratified chilled water storage (SCWS) can also be considered in
combination with the BTES storage for peak shaving. Then, if the temperature difference of
the water tank storage system is 5 °C, the required storage volume is 52 m³. A comparison of
design parameters for PCM storage and SCWS is given in Table 10.

<table>
<thead>
<tr>
<th>Table 10</th>
<th>Comparison design parameters – SCWS and PCM storage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Storage system</td>
<td>Charging temperature (°C)</td>
</tr>
<tr>
<td>SCWS</td>
<td>10</td>
</tr>
<tr>
<td>Paraffin PCM</td>
<td>10</td>
</tr>
</tbody>
</table>

**Heat transfer aspects in a PCM storage**

Since one of the reasons for the inability of the BTES to provide the peak cooling demand is
its relatively poor heat transfer characteristics, it is necessary to consider whether the PCM
storage will be able to reach the desired 100 kW duty. For the static PCM storage system the
heat transfer rate is mainly determined by the heat transfer surface area. For example, Buddhi
and Sharma [16] have suggested that fins can be used to increase the heat transfer rate in a
PCM-based energy storage system. Fieback and Gutberlet [41] have reported that in a 600-
liter, paraffin-based PCM dynamic heat storage unit, a K•A values of 2000 to 4000 W/K are
technically feasible. According to this value, in the estimated 8 m³ paraffin PCM storage, the
heat transfer rate can reach at least 107 kW with a 4 °C the temperature difference. However,
more experimental investigations are desired in order to ensure that the heat transfer rate of
PCM storage are high enough to meet the desired duty of various applications.
5. Designing PCM Storage System for Peak Shaving

5.2.2.5 Economical considerations

Apart from energy efficiency, size, and heat transfer aspects, the choice of the peak cooling option must be assessed economically. Table 11 depicts an indicative economical comparison between a number of options covering an assumed 100 kW peak cooling demand of 20 MWh/year. The capital costs are based on the annuity method, using a 6% interest rate and a varying depreciation time according to the expected lifetime of each investment. It is realized that industry reaches for depreciation times as low as 2-3 years. Herein, the expected lifetime is judged more appropriate in order for the robustness of e.g., the BTES technology, to give appropriate credit. Assumptions, with regards to investment cost, lifetime etc, are summarized in footnotes at the end of this table. It needs to be pointed out that the values assumed may need to be altered depending on the local conditions for any given application. The transparency of the economics presented herein gives the opportunity to do such alterations as needed.

As shown, additional boreholes to cover the peak load appear to be the most expensive alternative despite the fact that the depreciation time is 40 years. The cheapest alternative is the stratified chilled water storage unit. Furthermore, the results indicate that PCMs need to come down in cost in order for these systems to be competitive with SWCS. However, the volume requirement for the SCWS alternative is 50 m³, which either may not be possible from a space point of view or could add extra yearly cost due to this large space requirement. The PCM storage option proposed herein is more expensive than today’s solution of adding a condenser cooling option to run heat pumps in chiller mode during summers. One explanation is the relative large cost for the PCM material, a cost that has a large potential of being reduced in the future, if the demand for such products increases significantly and development finds cheaper alternatives. Already, salt-based PCM for heating applications are much cheaper than the 3 Euro/liter assumed herein.

Table 11
Economical comparison for 100 kW peak cooling options in BTES cooling application

<table>
<thead>
<tr>
<th>Peak Cooling Option</th>
<th>Investment Cost (kEuro)</th>
<th>Yearly Capital Cost (kEuro)</th>
<th>Yearly O&amp;M Cost (kEuro)</th>
<th>Total Yearly Cost (kEuro)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Additional Boreholes</td>
<td>68.5І</td>
<td>4.5ІІ</td>
<td>0.1ІІІ</td>
<td>4.6</td>
</tr>
<tr>
<td>Existing Heat Pump with added Condenser Cooler</td>
<td>11ІV</td>
<td>1.1V</td>
<td>1ІVI</td>
<td>2.1</td>
</tr>
<tr>
<td>SCWS</td>
<td>11ІІ VII</td>
<td>0.8ІІІ</td>
<td>0.1ІІІ</td>
<td>0.9</td>
</tr>
<tr>
<td>PCM Storage</td>
<td>3.5 (tank)ІІІ</td>
<td>0.26 (tank)ІІІ</td>
<td>0.1ІІІ</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td>24 (PCM)ІX</td>
<td>2.47 (PCM)І</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Economical footnotes

І. Assuming achievable effect of 40 W/m, and a capital cost of 27.5 Euro/m.
II. Assuming 40 years depreciation time, with 6% interest gives an annuity factor of 0.066.
III. Cost of electricity. Assuming “electrical power” coefficient of performance $\text{COP}_{\text{el}} = 20$, and electricity price of 0.1 Euro/kWh

IV. The additional investment cost of the condenser cooler needed for operating heat pump in cooling mode.

V. Assuming 15 years depreciation time, with 6% interest gives an annuity factor of 0.103.

VI. (a) Cost of electricity assuming $\text{COP}_{\text{el}} = 2.5$, and electricity price of 0.1 Euro/kWh; (b) general maintenance of 0.2 kEuro/year.

VII. Assuming a cost of 220 Euro/m³ tank – approximately 50 m³ needed for SCWS and 16 m³ for the PCM storage option.

VIII. Assuming 30 years depreciation time, with 6% interest gives an annuity factor of 0.073.

IX. Assuming a cost of PCM to be 3 Euro/liter. This is somewhat lower than today’s price for paraffin PCM (4 Euro/liter) but much higher than the price for salt-based PCM materials.

5.3 Commercial feasibility of cool PCM storage

So far, applications employing mixtures of technical grade tetradecane and hexadecane have been considered. However, commercially available paraffin waxes for cool storage applications are likely to be of more practical interest because of lower cost. These are considered in this section.

Commercial PCM products with phase change temperature around 7 °C can be used for comfort cooling storage. Different storage configurations may be suitable depending on the particular commercial products, as shown in Table 12.

Table 12
Commercial production with different storage configurations

<table>
<thead>
<tr>
<th>Commercial PCM</th>
<th>Storage processes</th>
<th>Types of heat exchanger</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waxes (Rubitherm, RT5)</td>
<td>Static and dynamic</td>
<td>Tube and bubble</td>
</tr>
<tr>
<td>Salt 1 (Climsel 7)</td>
<td>Static</td>
<td>Plate</td>
</tr>
<tr>
<td>Salt 2 (TEAP 7)</td>
<td>Static</td>
<td>Tube</td>
</tr>
<tr>
<td>Salt 3 (Cristopia)</td>
<td>Static</td>
<td>Balls</td>
</tr>
</tbody>
</table>

As the present investigation deals with primarily paraffin waxes as PCMs, Rubitherm RT5 was chosen for an investigation as PCM for a dynamic storage. This section 5.3 is based on paper VI.

RT5 is a commercial product by Schümann Sasol Gmbh in Hamburg, Germany, and is based on a cut resulting from refinery production. It consists entirely of normal paraffin waxes, and its carbon distribution is shown in Table 13.

Table 13
Carbon distribution of Rubitherm RT5

<table>
<thead>
<tr>
<th>No. of carbon atoms</th>
<th>Concentration (w%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C14 (C₁₄H₃₀)</td>
<td>33.4</td>
</tr>
<tr>
<td>C15 (C₁₅H₃₂)</td>
<td>47.3</td>
</tr>
<tr>
<td>C16 (C₁₆H₃₄)</td>
<td>16.3</td>
</tr>
<tr>
<td>C17 (C₁₇H₃₆)</td>
<td>2.6</td>
</tr>
<tr>
<td>C18 (C₁₈H₃₈)</td>
<td>0.4</td>
</tr>
</tbody>
</table>
All these substances are well-characterized chemicals and their thermal properties have been considered in chapter 2.

5.3.1. The phase change temperature and the heat of fusion

The temperature sensor method has been used for measuring the freezing and melting temperature of the RT5. The experimental procedures were the same as the thermal properties measurement of tetradecane, hexadecane and their mixtures (which has been described in chapter 2). The temperature curves of the freezing and melting processes are shown in Fig. 33.

From these curves, the freezing point of RT5 can be determined to 7 °C. However, the material melts over a temperature range between 4 and 7 °C.

![Temperature curves of freezing and melting processes for RT5](image)

Fig. 33 Phase change temperature of RT5

The thermal behavior of the RT5 was also recorded by DSC using the methodology described in chapter 2. Here, the DSC scanning rate was 0.5 °C/min. Both the phase transition temperature and the heat of fusion (ΔH) were recorded. The phase change temperature of RT5 obtained by DSC is 5.2 °C (melting curve peak temperature). The heat of fusion of RT5 as determined by DSC is 158.3 kJ/kg. Just like for the mixtures of tetradecane and hexadecane, this is lower than the heat of fusion of any of the pure materials making up RT5. This is presumably due to a molecular rearrangement in the solid phase.

5.3.2 Thermal stability

15 ml of RT5 was subjected to more than 20 heating and cooling cycles. During these cycles, the freezing point of the material was measured by a temperature sensor. The material showed good thermal stability and the freezing point remained at the same value, indicating that the phase change is reversible without degradation.

5.3.3 Volume contraction during the liquid-solid phase change

A glass expander with accurate graduation (±0.02) was used to measure the volume expansion of the phase change processes. The same procedures as for the measurement on tetradecane, hexadecane and their mixtures were used herein.
The results indicate that the phase change of the sample from the liquid to solid state is accompanied by a volume contraction, and that the volume contraction is 6.32%. Such a volume contraction cannot be neglected in a cool storage system.

5.3.4 Static storage process

One possible configuration of a PCM storage using the commercial RT5 paraffin wax is some kind of static storage. For this reason, the effect of the heat transfer area on the obtained storage power has been qualitatively assessed by simple test tube studies, which are described below.

Several RT5 samples with varying volume (15, 20, 25 and 30 ml) were put in test tubes with a 20 mm diameter, and the 20 and 30 ml samples were put in test tubes with a 25 mm diameter. These samples were then frozen at the same heat transfer conditions. The temperatures of the phase change processes are plotted in Fig. 34 versus time. As can be seen, the time required for freezing these samples in the test tubes with 20 mm diameter were the same because the heat transfer surface area per unit mass are the same. The freezing times of the samples in the test tubes with 25 mm diameter were longer than those of the samples in the smaller diameter because the heat transfers area per unit mass of the sample in the bigger diameter tubes are smaller than that in a sample with smaller diameter. The diameter difference of the test tubes is 5 mm, and the freezing times differences are about 15 min. The results prove that the heat transfer surface area is a very important parameter and that it directly influences the efficiency of the static storage system.

![Fig. 34 Phase change rates in 20 and 25 mm tubes](image)

5.3.5 Dynamic storage process

The other storage configuration to be considered is a dynamic storage. Some small-scale dynamic storage experiments have therefore been conducted in order to observe the build-up of the porous PCM layer during charging along with other important factors when considering in the design of a real dynamic PCM storage using RT5.
Water was chosen as the heat transfer medium because water and paraffin waxes are immiscible and there is a significant density difference. The solid-state structure of the porous wax may provide optimum conditions for freezing and melting processes because a large surface area is available for the heat transfer \[41\].

100 ml of water and 100 ml of the RT5 material at room temperature were transferred into a 250 ml separator, and a temperature sensor was inserted in the separator. The interface of the two liquids was distinctly shown. Chilled water of about 4 °C temperature was continually sprayed into the separator from the top and drained off from the bottom. The rate of spraying was kept the same as the rate of draining water at the bottom. The phase change processes were observed and the temperature changes of the processes were recorded. When the average temperature of the liquid wax reached the freezing point, the wax shell that covers the water droplets resulted in the build-up of a layer of water droplets, enveloped by wax, at the interface between the wax and the water. This is shown in Fig. 35 (a). When all the paraffin wax was frozen, the interface layer between the wax and the water was lower than before.

In a cooling discharging process, water at a temperature above the melting point of the PCM was sprayed into the system, and the frozen wax at the top of the system melted first. When all paraffin wax was melted the interface level between the wax and the water was the same as in the initial stage, as in Fig. 35 (b). For the charging and discharging processes, the rate for draining should be kept the same as the rate of water sprayed into the system.

![Diagram of PCM storage system](image)

Fig. 35 Dynamic storage processes:
(a) the freezing process, (b) the melting process

5.3.6 Capital cost estimation of paraffin wax dynamic cool storage systems

During the life of a project, from the early stages of process development through to construction, capital and operating cost estimations are prepared in order to establish and ensure its commercial feasibility. The level of accuracy of these estimates increase with each subsequent stage. Capital costs are mainly derived from the cost of each equipment, using suitable factors that allow for civil and electrical work, piping, instrumentation etc. Considerable research has been done in arriving at these factors. The operating cost are made up of variable and fixed costs, which are estimated individually \[55\].
Capital cost estimates for chemical process plants are often based on an estimate of the purchase costs of the major equipment required for the process, the other costs being estimated as factors of the equipment costs [109].

Herein, the cool storage system of RT5 as a PCM is a dynamic storage system, and the cooling is considered to come from an absorption chiller, whose driving energy is hot water at about 90 °C. In practical applications, cone bottom vessels will be suggested as the dynamic cool storage tanks. Water is injected from the top of the tanks via spraying nozzles. The type, numbers and configuration of the nozzles will be based on the size and the shape of the storage tanks. The drain control depends on the interface level. The advantage of the dynamic storage system is that it is more efficient than a static storage system because a large heat transfer area is available. The primary features of the paraffin wax dynamic storage system are given in Table 14, which includes the thermal properties of the RT5, system operating parameters and the cost of the storage tank, PCM and chillers.

Table 14
Primary features of paraffin waxes dynamic storage system

<table>
<thead>
<tr>
<th>Paraffin wax cool storage system</th>
<th>Chiller cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific heat of PCM (kJ/kg)</td>
<td>2.0</td>
</tr>
<tr>
<td>Latent heat of fusion kJ/kg</td>
<td>158.3</td>
</tr>
<tr>
<td>Tank volume</td>
<td>0.039 m³/kW</td>
</tr>
<tr>
<td>PCM cost</td>
<td>$2.4/kg</td>
</tr>
<tr>
<td>Storage tank cost*</td>
<td>$38.3-$40.5/kWh</td>
</tr>
<tr>
<td>Charging temperature</td>
<td>4-6 °C</td>
</tr>
<tr>
<td>Discharge temperature</td>
<td>9-12 °C</td>
</tr>
<tr>
<td>Discharging fluid</td>
<td>Water</td>
</tr>
</tbody>
</table>

Absorption chiller:

<table>
<thead>
<tr>
<th>Power range</th>
<th>Cost range</th>
</tr>
</thead>
<tbody>
<tr>
<td>(5-2)x10³ kW</td>
<td>$87.2-$124.5 /kW</td>
</tr>
<tr>
<td>(2-1)x10³ kW</td>
<td>$124.5-$149.4/kW</td>
</tr>
<tr>
<td>(1-0.5)x10³ kW</td>
<td>$149.4-$186.8/kW</td>
</tr>
</tbody>
</table>

Standard water chiller: $57-$85 /kW

* The cost included the spraying nozzles.

5.3.6.1 Capital costs

There are two types of capital: fixed capital and working capital. Fixed capital is a one-time cost for all equipments of a project. Working capital is usually equal to 10-15% of the fixed capital [8]. Sinnott [109] has reported using the physical plant cost (PPC) to estimate fixed capital, which is the sum of all equipment, materials and labour cost.

Adding the fixed capital and working capital results in the total capital cost. The capital investment of the PCM dynamic cool storage system and the other types of cool storage systems are given in Table 15, and the capital costs of conventional non-storage systems are given in Table 16. The capital cost of chillers must be considered along with the cost of storage capacity. For example, if a paraffin wax dynamic cool storage ($140/kWh) is to be used for handling a peak cooling demand of 100 kW for 3 hours, the total capital cost of the paraffin storage is $42 000. However, if extra chiller capacity is to handle the peak load, the capital cost for e.g. 100 kW absorption chiller ($800/kW in 1000-2000 kW range) would be $80 000.

If ice harvester storage ($30/kWh) is to be used to cover the same peak cooling demand, the capital cost of the ice storage is $9 000. Here, a prepackaged or build-up ice making equipment ($2000/kW) will be needed to cover the base-load and to charge the storage during off-peak hours. Say that the required chiller capacity for this purpose is 100 kW, the chiller cost amounts to $200 000 in this case. Hence, the total system cost will be $209 000. If a low-temperature secondary coolant chiller ($800/kW) is used to charge an ice storage unit
($70/kWh) for the same peak demand of 100 kW and 3 hours, the total system cost will be $101 000. If on the other hand a paraffin storage will be used as above, a standard chiller covering the base-load and storage charging could be used at a significantly smaller cost of $400/kW; hence the total cost for a paraffin storage unit plus chiller will be $82 000. Furthermore, the standard chiller operating at a higher evaporator temperature will most likely have a better Coefficient of Performance (COP). Hence, in addition to the capital cost, the operating cost, including the cost for electricity, needs to be accounted for as well.

The results indicate that the capital costs of cool storage systems are much less than those of conventional chillers. When an existing facility undergoes an expansion, which requires additional capacity for the central cool system, instead of adding new chillers, the extra night time capacity of existing chillers can be used to charge a storage tank to serve the new floor space and save money [30].

### Table 15
Capital costs of cool storage systems

<table>
<thead>
<tr>
<th>Type of cool storage</th>
<th>Fixed capital ($/kW h)</th>
<th>Working capital ($/kW h)</th>
<th>Total capital ($/kW h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraffin waxes</td>
<td>121 to 128</td>
<td>12 to 12.8</td>
<td>133 to 141</td>
</tr>
<tr>
<td>Chilled water</td>
<td>29 to 94</td>
<td>2.9 to 9.4</td>
<td>32 to 103</td>
</tr>
<tr>
<td>Ice harvester</td>
<td>19 to 29</td>
<td>1.9 to 2.9</td>
<td>21 to 32</td>
</tr>
<tr>
<td>Ice Storage</td>
<td>47 to 67</td>
<td>4.7 to 6.7</td>
<td>52 to 74</td>
</tr>
<tr>
<td>Eutectic salt</td>
<td>94 to 144</td>
<td>9.4 to 14</td>
<td>103 to 158</td>
</tr>
</tbody>
</table>

### Table 16
The capital costs of conventional chillers non-storage systems

<table>
<thead>
<tr>
<th>Type of chiller</th>
<th>Fixed capital ($/kW)</th>
<th>Working capital ($/kW)</th>
<th>Total capital ($/kW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard water</td>
<td>299 to 444</td>
<td>29.9 to 44.4</td>
<td>329 to 490</td>
</tr>
<tr>
<td>Prepackaged or built-up ice making equipment</td>
<td>1643 to 2241</td>
<td>164 to 224</td>
<td>1807 to 2465</td>
</tr>
<tr>
<td>Low-temperature secondary coolant</td>
<td>299 to 745</td>
<td>29.9 to 74.5</td>
<td>329 to 819</td>
</tr>
<tr>
<td>Absorption chiller</td>
<td>(5-2)x10^3 kW</td>
<td>430 to 614</td>
<td>43 to 61.4</td>
</tr>
<tr>
<td></td>
<td>(2-1)x10^3 kW</td>
<td>614 to 737</td>
<td>675 to 810</td>
</tr>
<tr>
<td></td>
<td>(1-0.5)x10^3 kW</td>
<td>737 to 921</td>
<td>810 to 1013</td>
</tr>
</tbody>
</table>

### 5.4 Concluding remarks

The computer model presented herein makes the calculation of phase equilibrium quick and easy, and directly produces the temperature-concentration phase diagram of the binary system of tetradecane and hexadecane. Based on the phase diagram and the heat of fusion of the binary mixtures, polynomial equations have been obtained to be used in the design of PCM storage. These polynomial equations can be utilized to easily choose a mixture with a suitable phase change temperature range for a practical application and to obtain the energy density of the mixture.
When these mixtures are used as PCM for cool storage, the phase transition temperature range must be known to properly design the charging and discharging processes as discussed in chapter 4. If an incorrect phase transition temperature is assumed when designing a PCM storage, it will result in a storage capacity loss in the practical application. For example, if the storage system shown in Fig. 28 is considered to have a constant temperature 9 °C, it means that when a heat transfer medium flows into the storage with a temperature lower than 9 °C, the PCM will completely freeze and the process is a charging process. When a heat transfer medium flows into the storage with a temperature higher than 9 °C (for example, at 11 °C), the PCM will completely melt and this is a discharging process. The storage density of the PCM is considered constant as 184 kJ/kg and a total 2.4 MWh cooling is absorbed or released during the charging and discharging processes. However, in a practical process, if the heat transfer medium flows into the storage at 11 °C, the PCM will only partly melt. This is because the phase change of the PCM occurs at a temperature range from 9-12 °C. According to the phase diagram of the binary mixtures tetradecane and hexadecane, the fraction of the PCM melted and the corresponding storage energy density at 11 °C can be obtained by using the “lever principle”. This gives that 60% of the PCM is melted at 11 °C, and the corresponding energy density will be 110.4 kJ/kg (23.6 kWh/m³). As such, the capacity of the storage in this case is only 1.44 MWh cooling during the discharge process and thus 0.96 MWh of the storage capacity has not been used. This cooling loss causes an economic penalty to the system.

From Fig. 29, the size of this economic penalty can be estimated. It can be seen that the cost of supplying cooling is 30-40 Euro/MWh at a low heat price, and 60-70 Euro/MWh at high heat price. In the example with a 11 °C heat transfer medium, the storage is never fully discharged and 40% (0.95 MWh) of the cooling storage capacity is unused. At low heat prices, 0.96 MWh cooling costs 29-30 Euro. If we consider 30 discharging process during one month, the unused storage capacity will cost total 870-1140 Euro/month.

Preliminary calculations on integrating a PCM cool storage with a BTES system for small-scale comfort cooling points towards the feasibility of PCM storage to cover the system’s peak cooling load. It is possible to find a paraffin mixture with an appropriate charging/discharging temperature, and the volume of the storage will be about one third of the volume of a stratified chilled water storage. One set of experimental data for a dynamic water-paraffin direct-contact storage unit indicates that the desired effect of 100 kW would be possible. However, the sparse amount of published experimental results from pilot plants signals the need for increased activities in the demonstration stage of PCM cool storage technology. Finally, with regards to the cost-effectiveness of the proposed PCM peak load cool storage it is clearly a cheaper alternative than adding boreholes to cover 100% of the load. However, the present option using an electrically driven chiller would presumably be somewhat cheaper than a PCM storage. In the future, an increasing power demand may force a pricing of peak hour electricity that could alter this situation in favour of the PCM storage option. Further, research and development on phase change materials will hopefully lead to cheaper and more effective materials.

Experimental results indicate that the commercial product, Rubitherm RT5, a technical grade paraffin wax qualifies as a PCM for comfort cooling storage because it can be used at a low temperature, a narrow phase change range and has a reasonably high heat of fusion. Furthermore, it is able to melt congruently and freezes without sub-cooling. It also shows good stability during a number of cooling and heating cycles. The volume contraction of the liquid–solid phase change process is around 6%, which should be considered when design a
cool storage system. The experimental results also indicate that the material RT5 qualifies using in a dynamic storage system.

The capital costs estimate gives economic information for installing a new chiller and cool storage. From the results shown in Table 15 and 16, some advantages are found for the ice storage system over the other three storage systems (chilled water, paraffin waxes and eutectic salt storage systems). However, the chiller cost of the ice storage system is much more expensive than the standard water chiller and absorption chiller. A similar conclusion has been made in another study that compared ice storage with chilled water and eutectic salt storage [47].

In many cases, cool storage systems can be installed for a low initial cost than conventional non-storage systems because cool storage systems utilize smaller chillers and auxiliary equipments. The size reductions for chillers, cooling towers, pumps and fans, as well as piping and ductwork, can completely offset the cost of the needed storage tank [32].

The cooling capacity of existing systems can often be increased by installing cooling storage at a lower cost than adding conventional non-storage equipment. A cool storage tank adds cooling capacity to an existing system and avoids the high expense of installing new chillers.
A cool storage system removes heat from a thermal storage medium during a period of low cooling demand, and the stored cooling is later used to meet the same total cooling load as a non-storage system over a given period but with a smaller chiller. This may avoid a peak in the electricity power demand during the hottest summer hours, and increase the possibilities of utilizing renewable energy sources and waste heat for cooling generation by bridging gaps between cooling demand and availability of such driving energy sources. In addition, cool storage systems enable the cooling equipment to be sized for base-load operation and thus increase the number of hours the chiller can run at design conditions at high efficiency.

PCM storage is one of the most efficient ways of storing thermal energy. It uses the latent heat of the storage medium for thermal energy storage and provides; as compared to sensible heat storage systems, a much higher energy storage density with a smaller charging/discharging temperature range. The higher storage density of PCM storage system results in a promising ability to reduce the size of a storage system and decrease the cost. The problem with PCM cooling storage applications is that there are not many available materials for comfort cooling and the cost of PCMs is quite high. The heat transfer of PCM storage is another problem that need to be improved.

In order to meet the requirements of comfort cooling storage applications, the PCMs with suitable phase change temperature must be developed. The paraffin waxes tetradecane and hexadecane and their binary mixture have in the present investigation been chosen as PCM candidates for comfort cooling applications. Several experimental methods have been used to determine the thermophysical properties of tetradecane, hexadecane and their binary mixtures. These properties include the freezing temperature, melting temperature, thermal stability, volume expansion during a phase change and the latent heat. Thus, the potential of using these materials as PCM for comfort cooling storage has been demonstrated.

To study the phase change properties of these mixtures, the so-called temperature sensor method and DSC were used. The temperature sensor method is essential the same as what is also called the T-history method by Zhang et al. [131], although in the concept of the T-history method, the calculations of properties like heat conductivity, specific heat and heat of fusion is included in that methodology. At any rate, it is a well-know method, and its main advantages are that it allows enough time during the experiment for the phase change to occur and ensure approximate thermodynamic equilibrium at every moment. For studying the freezing, this method may provide more reliable results compared to DSC measurements. However, e.g. the cooling curves presented by Zhang et al. [131] do not give the melting temperature as they claim, but rather the freezing point. The melting temperature range may only be estimated from a heating curve like the one presented herein in Fig. 6, and as seen in this figure it can rather difficult to judge the melting range of a material from such a curve. This is due to the fact that there is no constant temperature in a melting curve. If PCMs melt and freeze over a temperature range, it is difficult to obtain this range by using the T-history method.
DSC has been widely used to investigate the thermal performance of PCMs. The main advantages of DSC are simplicity, rapidity and economy in its sample requirement. The main disadvantage of DSC is that it gives relative results and not absolute. The experimental error for DSC comes mainly from operational parameters, for example, the effect of scanning rate, and the systematic influences from the instrument and inherent error sources. There is not yet an international agreement for temperature calibration and caloric calibration of DSC and no complete theory of DSC exists, as reported by Höhne [56]. However, from the results of the present investigation it is claimed that DSC gives better results at very low scanning rate.

The results from temperature sensor and DSC measurements indicate that tetradecane, hexadecane and their binary mixtures qualify as PCM candidates for comfort cooling storage. The phase change temperatures of these materials are between 1.7 and 17.9 °C and a minimum temperature exists in the binary system.

The phase diagram of this binary system has been derived theoretically as well as experimentally. This phase diagram can be used to investigate the interrelationship involved in the phase change process. For the theoretical evaluation of the thermodynamic equilibrium between the liquid phase and solid phase of tetradecane and hexadecane, several methods were compared: the UNIFAC group-contribution method, the model of Won, and Pedersen’s model. The UNIFAC method has been developed for estimating activity coefficients in non-electrolyte liquid mixtures. The model of Won uses regular solution theory, such that the activity coefficients are determined from the solubility parameters of the individual components. The model of Pedersen is a modification of Won’s model, which gives a general correction for the liquid-solid phase solubility parameters. The results from calculations showed that the model by Pedersen et al. exhibits lower solid phase equilibrium composition than the UNIFAC and Won model. However, overall the results from these three methods agree well with each other. The obtained phase diagram exhibits a minimum melting point, i.e. an azeotrope, which means that the binary system is of the isomorphous (solid solution) type with a less ideal behavior of the components.

For the experimental phase equilibrium study, a large number of DSC measurements with different scanning rate (5, 2 and 0.5 °C/min) were made on the binary system. The following features have been observed. All components have exhibited one major peak corresponding to liquid-solid phase transition. The pure materials, and those mixtures with a composition very close to pure materials, exhibit a peak that is more sharp and narrow compared to the other mixtures. Most mixtures exhibit a lower peak height accompanied by an enlarged temperature range. This phenomenon may be due to a molecular rearrangement occurring in the solid phase. Some mixtures’ DSC curves show the existence of two peaks and at a slower scanning rate (0.5 °C/min), two peaks appear very clearly. The lower temperature peak is very weak and could possibly be an indication of a solid-solid transition. Also, this secondary peak is dependent on the mixture composition and appears to weaken as the concentration of tetradecane increases.

Hammami and Mehrotra [45] and Paunovic and Mehrotra [88] reported that in a binary eutectic mixture system of alkanes, the eutectic peak is independent of the mixture composition and appears at a constant temperature. From the DSC measurement presented here, an indication is obtained that the binary system is a solid-solution system since a eutectic peak, independent of mixture composition, is not present. The low temperature solid-solid peak, appearing in a short mixture concentration interval, may be due to the fact that perfect miscibility does not occur.
The thermodynamic basis for the solubility of organic substances in the solid state has frequently been discussed in the literature. Briefly summarised, these discussions state that the formation of solid solutions of organic compounds can occur if the mixed molecules are similar in form and dimensions. Agafonov et al. [3] have also reported a consideration of component structural characteristics, which reveals that the interaction of components that have a similar structure (α-α, β-β, γ-γ) results in the formation of continuous solid solutions. Also, the pure tetradecane and hexadecane solid have a similar structure (triclinic crystals, i.e. γ-γ). The binary system contains all conditions for the formation a solid solution.

In order to prove that the binary system is a solid solution system and not a eutectic system, some further experiments have been done. Results from these experiments did not exhibit the characteristics of a eutectic system.

All results illustrate that the binary mixtures of tetradecane and hexadecane form a continuous series of solid solution with a minimum-melting temperature. The minimum-melting point mixture is an invariant composition. It melts and freezes “congruently”, i.e. the solid and liquid phase have the same composition. It is also possible to confuse this type of phase equilibrium with that of a eutectic, which is a minimum-melting mixture. A eutectic, however, has two solid phases in equilibrium with the liquid phase at the melting point. Each of the three phases has a different composition. Binary eutectics are invariant from the three phases present whereas a binary minimum-melting point isomorphous system is invariant due to two phases and the equality restriction [75].

The phase diagram obtained can be used to investigate the interrelationship involved in the phase change process. From careful examination of the phase equilibrium properties of the binary system, it is evident that, except for the minimum-melting point mixture, all mixtures melt and freeze at a temperature range and not at a constant temperature. A constant temperature phase change is often assumed when designing a PCM storage. In addition, the enthalpy change during the phase transition (heat of fusion) corresponds to this phase transition temperature. The phase change temperature range and corresponding enthalpy change can be determined from the phase diagram by using the “lever principle”. However, the phase change temperature range cannot be simply determined from a DSC curve. The DSC measurement results indicate that the characteristic temperature depends heavily on the DSC heating/cooling rate. To obtain reliable results that incorporate both the heat of phase change and the phase change temperature range, combining phase equilibrium considerations with DSC measurements will be necessary and important.

DSC is one frequently used testing method in the development of PCMs. It has been used for selecting a PCM from candidates, and for evaluating PCM prototypes and investigating the reproducibility of PCM thermal characteristics. Here, it has been found from a literature review that different scanning rates have been employed in DSC measurement processes. However, the present investigation has shown that these thermal characteristics of PCMs depend heavily on the DSC setting throughout the measurements, and varying results will be obtained. When designing a PCM thermal energy storage system, the storage density and phase change temperatures range are very important parameters since they decide the storage system’s capacity, size and application range. When incorrect phase transition parameters are used in the PCM storage design, it will result in a lower than expected storage capacity.
The potential of using PCM storage for peak shaving has also been demonstrated herein. For example, when PCM storage is combined with an absorption chiller in a district cooling system for peak shaving, to store 2.4 MWh cool with only 61.5 m³ PCM is needed a charging and discharging temperature between 9-12 °C. If a stratified chilled water tank is used to store the same cooling duty, the volume of the chilled water tank is around 690 m³ i.e., the volume of chilled water tank is 11 times larger than the volume of PCM. The smaller PCM storage tank may also decrease cooling losses to the surroundings. However, the packing factor of PCM storage is not clear and should be studied further, since only a few examples have been found in the literature regarding this.

In thermal storage applications, if a sufficient heat transfer area is available, the static storage system can be used. In the dynamic process storage system, direct contact between the storage material and the heat transfer medium results in an excellent heat transfer. The main problem for paraffin waxes is that they have rather lower thermal conductivity that may reduce the rate of heat transfer during a phase change process. Paraffin waxes qualify as a storage medium to be used in dynamic process storage. However, so far paraffin waxes have only been studied for dynamic heat storage. Hence, the development of dynamic comfort cooling storage systems that use paraffin waxes as the storage medium is a very significant task for cooling applications.
7. Conclusions and Recommendations for Future Work

In this chapter, the important conclusions from this work are presented and suggestions for future studies are given.

7.1 Conclusions

The quickly growing demand for comfort cooling has resulted in a severe imbalance between electricity power supply and demand during the summer. Cool thermal energy storage technology has the potential to become one of the primary solutions to this power imbalance. Cool storage systems shift cooling energy use to off-peak periods and avoid peak demand charges. Cool storage thus helps both utilities and their customers to meet these challenges while minimizing their risks and maximizing their benefits. However, the research and development of PCM storage has not been focused much on cooling applications compared to heating applications. In the present study, PCMs with phase change temperatures matching the comfort cooling applications have been investigated.

The phase change temperature and the heat of fusion of laboratory-grade tetradecane and hexadecane and thirty-two mixtures with different ratios were obtained, respectively, by temperature sensor measurements and DSC analysis. The phase change temperatures range from 1.7 to 17.9 °C and the heat of fusions lay between 227 and 146 kJ/kg.

The experimental results indicate that tetradecane, hexadecane and their binary mixtures are excellent candidates for PCMs cool storage due to their availability in a low temperature range and their reasonably high heat of fusion. Furthermore, they are able to melt congruently and, due to their self-nucleating properties, they freeze without sub-cooling. They also show a good stability over a large number of heating and cooling cycles. The volume contraction of these mixtures during freezing is less than 10%. Such a volume contraction of these mixtures cannot be neglected in a cool storage system.

Any solid to liquid PCM, during melting or freezing, is in intimate contact with at least one solid phase. These phases’ interrelationship can be best understood by studying the system under conditions of heterogeneous equilibrium. Phase diagrams (equilibrium diagrams) depict the concentration-temperature-pressure relationships of a chemical system at equilibrium and are used to visualize how these relations change with temperature and chemical composition. Thus they are invaluable to PCMs thermal storage researchers and developers. The phase equilibrium of the binary system of tetradecane-hexadecane has been studied. The results from the theoretical evaluation of the thermodynamic equilibrium between the liquid phase and solid phase of tetradecane and hexadecane showed that the three models used agree well with each other. The phase diagram illustrates that the binary system formed by tetradecane and hexadecane is an isomorphous system with a minimum temperature.

The phase diagram of the binary mixture tetradecane-hexadecane shows that they freeze and melt in a temperature range and not at a constant temperature, except for the minimum-
melting point mixture. When these mixtures are used as a PCM for cool storage system, the phase transition temperature range must be known to properly design the charging and discharging processes. The phase transition temperature range for each homogenous liquid can be obtained directly from the phase diagram.

The results from DSC measurements demonstrate that the binary system forms a continuous series of solid solution, since in a short mixture concentration interval, a low temperature solid-solid peak appears, depending on the mixture composition. The results also indicate that these mixtures melt and freeze over a temperature range. From the DSC results presented, it is concluded that the behaviour of binary mixtures of n-alkanes is far more complicated than considered in earlier studies.

It has also been found that when making DSC measurements at different scanning rates, a material will show quite a different thermal trace and thus the resulting information on the phase transition processes varies with scanning rate. For example, when the DSC runs at a high heating/cooling rate it will give an enlarged phase change temperature range and lead to erroneous information. Due to the lack of phase equilibrium within the sample, including thermal equilibrium and chemical equilibrium, DSC measurements at a higher scanning rate will fail to provide accurate results. The DSC method, however, gives better results at very low scanning rate.

In PCM cooling storage applications, the enthalpy change and phase transition temperature range will determine the storage system’s capacity, size and application. If incorrect values are utilised for a cool storage system design, it will result in a lower cooling capacity and hence economic loss. Only when combining phase equilibrium considerations with DSC measurements will give a reliable design method to incorporate both the heat of fusion and the phase change temperature range.

The estimation of capital cost indicates that a cool storage tank adds cooling capacity to an existing system and can avoid the high expense of installing new chillers. The results also show that the cooling storage system not only saves energy and operation and maintenance costs, but also saves a significant fraction of the initial capital costs. PCM storage can be combined with different cool technologies, for example, an absorption chiller or a borehole free cooling system, and has shown a promising potential to reduce the size of storage system compared with a stratified chilled water tank.

An investigation of the feasibility of a commercial material indicates that the commercial product, Rubitherm RT5, a technical grade paraffin wax with 7 °C freezing point, qualifies as a PCM and for use in a dynamic process for comfort cooling storage. However, the boundary conditions related to the supply and return temperature changes slowly in the resulting comfort cooling system, from the traditional 6 (supply)/12 °C (return) to 11/17 °C. Consequently, more commercial products with different phase transfer temperatures should be developed in the future to meet the varying boundary conditions.

All results presented herein provide a large amount of information for PCM manufacturers to produce paraffin PCMs with different phase transfer temperatures for cooling applications and also for PCM researcher and developer to get more reliable data for designing a successful cool storage system.
7.2 Future studies

The market barriers for PCM cool storage systems may be the higher cost of the PCM and their low heat transfer rates within the storages themselves. As such, commercial PCMs with lower cost should be developed.

One suggestion for future research is to study the dynamic process PCM cooling storage to avoid the large heat transfer surface required in a static cool storage and achieve a high output. Furthermore, the heat transfer of the dynamic process needs to be characterized by studying the heat transfer principles during the freezing and melting process of PCMs, as well as the heat transfer efficiency. To achieve these general goals, the following sub-goals must be addressed:

1. Performance assessments of heat transfer characteristics in a dynamic PCM storage.
2. Optimisation of storage configuration.
8. References


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9. Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>a</td>
<td>constant</td>
</tr>
<tr>
<td>b</td>
<td>constant</td>
</tr>
<tr>
<td>Bi</td>
<td>liquid-solid mixture composition</td>
</tr>
<tr>
<td>c</td>
<td>constant</td>
</tr>
<tr>
<td>$C_p$</td>
<td>the heat capacity (kJ/kg °C)</td>
</tr>
<tr>
<td>$C_{pw}$</td>
<td>specific heat capacity of heat transfer medium (kJ/kg.K)</td>
</tr>
<tr>
<td>$C_{pi}$</td>
<td>specific heat capacity of phase change materials (kJ/kg K)</td>
</tr>
<tr>
<td>DSC</td>
<td>differential scanning calorimetry</td>
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<tr>
<td>f</td>
<td>fugacity</td>
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<tr>
<td>$H_i$</td>
<td>enthalpy (kJ/kg)</td>
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<tr>
<td>$\Delta H$</td>
<td>the heat of fusion (latent heat) (kJ/kg)</td>
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<tr>
<td>$L_i$</td>
<td>equilibrium liquid composition</td>
</tr>
<tr>
<td>$l_i$</td>
<td>pure-component constant</td>
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<td>$m_w$</td>
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<tr>
<td>$m_i$</td>
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</tr>
<tr>
<td>n</td>
<td>number of point in each series</td>
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<tr>
<td>PCM</td>
<td>phase change material</td>
</tr>
<tr>
<td>P</td>
<td>pressure (Pa)</td>
</tr>
<tr>
<td>$Q$</td>
<td>the heat of transition of phase change processes, (kJ/kg)</td>
</tr>
<tr>
<td>$\frac{\delta Q}{dt}$</td>
<td>heat flow in unit (W/g)</td>
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<tr>
<td>qi</td>
<td>gas constant</td>
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<tr>
<td>R</td>
<td>gas constant</td>
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<tr>
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<td>equilibrium solid composition</td>
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<tr>
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<td>temperature (°C)</td>
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<td>$\bar{x}$</td>
<td>average molar fraction</td>
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<td>z</td>
<td>coordination number</td>
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Greek Letters

<table>
<thead>
<tr>
<th>Symbol</th>
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<tbody>
<tr>
<td>$\gamma$</td>
<td>activity coefficient</td>
</tr>
<tr>
<td>$\phi$</td>
<td>segment fraction</td>
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0 \quad \text{area fraction}
\mu \quad \text{chemical potential}
\nu \quad \text{number of groups}
\Gamma \quad \text{group residual activity coefficient}

\text{Subscripts}

i \quad \text{component}

j \quad \text{component}

k \quad \text{molecular group}

l \quad \text{liquid phase in } x_{i(l)}

m \quad \text{melting in } T_m

pc \quad \text{phase change in}

s \quad \text{solid phase in } x_{i(s)}

\text{Superscripts}

c \quad \text{combinatorial}

f \quad \text{freezing in } T^f

l \quad \text{liquid phase in } x^l

L \quad \text{liquid phase in } x_{iL}

m \quad \text{melting in } T^m

o \quad \text{reference state in } f^o

R \quad \text{residual}

s \quad \text{solid phase in } x^s
10. Acknowledgements

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