

PHASE-CHANGE MATERIAL FOR THERMAL ENERGY STORAGE

FIELD OF THE INVENTION

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The present invention relates to a phase-change material for thermal energy storage and a method of determining a type of phase-change material in encapsulated form for use in a latent thermal energy storage system for a district cooling system.

10 BACKGROUND

Presently, widely implemented thermal energy storage technologies in district cooling systems employ either ice or chilled water as the storage medium. Ice possesses a high latent heat of fusion of 334kJ/kg at a phase-change temperature of 0°C. However, the
15 main drawback for this is that many systems do not operate around this temperature due to inefficiency and the requisite higher cost equipment and working medium. Ice as a phase-change material has poor applicability in district cooling system conditions due to the low phase-change temperature, leading to increased capital and operating cost as facilities have to provide for and operate glycol chillers to achieve the desired sub-
20 zero cooling temperatures.

It is therefore desirable to provide a new phase-change material for thermal energy storage, a method and a thermal energy storage system that seek to address at least one of the problems described hereinabove, or at least to provide an alternative.

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SUMMARY OF INVENTION

In accordance with a first aspect of the invention, a phase-change material for thermal energy storage is provided. The phase-change material comprises a mixture of n-
30 Tetradecane and n-Hexadecane, wherein the amount of each of n-Tetradecane and n-Hexadecane is selected to provide a phase-change temperature in a range between 2°C and 12°C.

In one embodiment, the phase-change material is in encapsulated form.

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In accordance with a second aspect of the invention, an encapsulated article comprising a receptacle and a mixture of n-Tetradecane and n-Hexadecane is provided. The

amount of each of n-Tetradecane and n-Hexadecane is selected to provide a phase-change temperature in a range between 2°C and 12°C.

5 In accordance with a third aspect of the invention, a method for determining a type of phase-change material in encapsulated form for use in a latent thermal energy storage system for a district cooling system is provided. The method comprises assessing a set of user's requirements and user's constraints; and determining a set of variables that matches the user's requirements and/or addresses the user's constraints, wherein the set of variables include type of phase-change material and its properties, type of
10 encapsulation of the phase-change material; packing density of the encapsulated phase-change material in the latent thermal energy storage system; and operating flow of the latent thermal energy storage system, wherein the type of phase-change material is selected from a mixture of n-Tetradecane and n-Hexadecane, wherein the amount of each of n-Tetradecane and n-Hexadecane is selected to provide a phase-change
15 temperature in a range between 2°C and 12°C.

Brief Description of the Drawings

20 The above features of a phase-change material and method in accordance with this invention are described in the following detailed description and are shown in the drawings:

Figure 1 illustrates a charge and discharge loading of a thermal energy storage (TES) system for a typical district cooling system's chiller operation.

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Figure 1 illustrates a spread of phase-change material types across different temperature and latent heat ranges.

30 Figures 3(A)-(D) illustrates a novel spherical encapsulation type with a combined press-fit screw-lock cap for improved packing density and security in leak prevention in accordance with an embodiment of the present invention. Figure 3(A) shows a single ball encapsulation type while Figures 3(B) and 3(C) show a connected-ball-column encapsulation type.

35 Figure 4 is a chart showing the packing density variation with relative diameter ratio for spherical encapsulation.

Figure 5 is a chart showing the inlet and outlet temperatures for a reference commercial encapsulated ice thermal energy storage system over its charging and discharging periods. This chart shows the cooling load demand during on/off peak hours of a typical thermal energy storage system.

Figure 6 shows the framework of the Encapsulated Phase-Change Material Latent Thermal Energy Storage (ECPM LTES) sizing and design methodology in accordance with an embodiment of the present invention.

Figure 2 is a graph showing the range of phase-change material properties based on the variation of Hexadecane wt% in Tetradecane.

Figure 3 illustrates the charging and discharging flow direction variation of a district cooling system.

Figure 4 is a flowchart showing the flow optimisation methodology in accordance with an embodiment of the present invention.

20 DETAILED DESCRIPTION

This invention relates to thermal energy storage (TES) technologies implemented in district cooling systems. Thermal energy storage system is the backbone of the district cooling system as it helps to reduce a plant's peak cooling load and shift the cooling load to off-peak hours when electricity tariff is much cheaper compared to peak hours; thereby reducing the plant's installed capacity and lower operation costs. In addition, the thermal energy storage system can also be treated as a stabiliser to follow dynamic fluctuating load demand while chillers are operating at their best efficiencies, and/or the thermal energy storage system can discharge required cooling during anomalous conditions, for example, during sudden power outage or chiller breakdowns. Figure 1 illustrates a charge and discharge loading of a thermal energy storage system for a typical district cooling system's chiller operation while meeting the cooling load demand.

In the present invention, a phase-change material (PCM) made from a mixture of paraffin types, in place of chilled water or ice in a storage-tank configuration, constituting a latent thermal energy storage (LTES) is provided. The paraffin mixture is tailored to be of energy storage capacity comparable with that of ice, at a phase-change temperature

suitable for the district cooling system operating temperature range and contained within sturdy high-density polyethylene encapsulation of varying configurations for structural integrity and controlled heat gain and heat release characteristics. The phase-change material TES-integrated district cooling system is controlled by an optimisation programme that optimises decisions pertaining to chilled water flow distribution and charging/discharging of latent thermal energy storage by cooling demand, leading to a better energy efficiency compared to ice storage systems and better energy carrying capacity compared to chilled water storage systems.

Paraffins occupy a range of phase-change properties that better match the operating ranges of district cooling systems. However, pure paraffin substances that perfectly match the operating temperature ranges are few and far between. To address this, a mixture of two paraffins is employed to tailor the phase-change material to its desired thermophysical properties to match the operating conditions of the district cooling system. Figure 5 is a chart showing a spread of different phase-change material types across the different temperatures and their respective latent heat of fusion. Paraffins are in a temperature range between 0°C and 100°C with latent heat of fusion in the range between 160 and 200 kJ/L.

Accordingly, in a first aspect of the present invention, a phase-change material for thermal energy storage is provided. The phase-change material comprises a mixture of n-Tetradecane and n-Hexadecane, wherein the amount of each of n-Tetradecane and n-Hexadecane is selected to provide a phase-change temperature in a range between 2°C and 12°C.

In various embodiments, the weight ratio of n-Tetradecane to n-Hexadecane in the mixture ranges between 30:70 and 95:5.

The mixture of n-Tetradecane and n-Hexadecane displays no expansion during solidification process and appears to possess a low amount of undercooling during solidification when used in a district cooling system.

In one embodiment, the phase-change material is provided in encapsulated form. The present invention incorporates known range of encapsulation shapes and forms, as well as a novel encapsulation method as design decision parameters. The material of the encapsulation is also taken into consideration.

The phase-change material of the present invention can be encapsulated within a shell or receptacle of any suitable type and form including, but not limited to, slab-type, tube-type, ball-type and corrugated ball-type. While these encapsulated forms are known, there are a myriad of other ways of improving the storage and heat transfer efficiency of the encapsulation on the whole.

In various embodiments, the phase-change material is encapsulated within a receptacle made of high-density polyethylene. In one embodiment, the phase-change material is encapsulated in the form of a connected-ball-column encapsulation type. An exemplary embodiment of this encapsulation type is shown in Figure 3. The connected-ball-column encapsulation type comprises a receptacle 301 and a combined press-fit screw-lock cap 302 extending from the receptacle 301. The combined press-fit screw-lock cap is provided for more efficient filling and sealing of the phase-change material within the receptacle. The receptacle is spherical in shape. The connected-ball-column encapsulation type can be provided in the form of a single ball (Figure 3A) or in a column consisting of two or more balls connected to form a column (Figure 3B or 3C). The connected-ball-column encapsulation type maximises the surface area of a tube-type encapsulated phase-change material while also improves on the packing density of a ball-type encapsulated phase-change material.

The advantages of using the ball-type or the connected-ball-column encapsulation type of the phase-change material are that the phase-change material balls can be easily filled inside a thermal energy storage tank. The balls can be packed in bags or plastic containers and can be easily transported to a temporary storage area. The bags or containers can be delivered into the top of the thermal energy storage tank with overhead crane or the like. This allows easy and efficient way of filling up the thermal energy storage tank with the phase-change material balls.

In a second aspect of the invention, an encapsulated article comprising a receptacle and a mixture of n-Tetradecane and n-Hexadecane contained within the receptacle is provided. The amount of each of n-Tetradecane and n-Hexadecane present in the mixture is selected to provide a phase-change temperature in a range between 2°C and 12°C. In one embodiment, the receptacle is made of high-density polyethylene. The receptacle can be of any suitable shape and size. In one embodiment, the receptacle is spherical in shape. In one embodiment, the encapsulated article is in the form of a single spherical ball. In another embodiment, the encapsulated article is in the form of a connected-ball-column comprising two or more spherical balls connected to form a

column. The encapsulated article is adapted for use in a cooling system including, but not limited to, district cooling system.

Encapsulating the phase-change material allows for an impermeable interface between the phase-change material and heat transfer fluid, and prevents cross contamination between the phase-change material and the heat transfer fluid. Additionally, encapsulation serves as a boundary that ensures a constant heat transfer from the contained phase-change material and the heat transfer fluid. In existing systems where ice is contained on the outside of the heat transfer fluid path, the phase-change boundary expands outwards, leading to a non-uniform phase-change and heat transfer process. In the present invention, the mixture of n-Tetradecane and n-Hexadecane displays no expansion during solidification process and containing the phase-change material of the present invention into smaller-scale, granular units within a comparably large 'bed' ensures uniformity in heat transfer across the 'bed' with respect to the heat transfer fluid flow. Encapsulating the phase-change material also allows for easy installation and removal of the encapsulated phase-change material during downtime and maintenance.

Different encapsulated types of the phase-change material are applicable for use in different types of thermal energy storage tanks. Some encapsulated types are suitable for use in horizontal thermal energy storage tank while others are suitable for use in short vertical thermal energy storage tank. Thus, application-specific encapsulation type, material and sizing tailored to capacity requirements of the thermal energy storage tank and real estate constraints can be designed.

The relative dimensions between the thermal energy storage tank size and the encapsulation size greatly affect the packing density as well as the rate of heat transfer in a district cooling system. As illustrated in Figure 4, depending on the ratio of the thermal energy storage tank's inner diameter ("D") to the outer diameter of the encapsulated phase-change material ("d"), the occupied volume ratio of spherical-type encapsulated phase-change material can vary greatly from ratios between 1 and 10 and taper off at 0.62 once the ratio exceeds 10. In other words, a large thermal energy storage tank diameter to ball encapsulation diameter ratio for example, would result in a maximum packing density of around 0.62 while for a smaller system, if that ratio decreases to below 10 then the packing density and hence the total energy storage quantum would decrease sharply. Based on user's requirements for heat transfer rate and cold storage capacity, the relative sizes of the encapsulation and the tank's diameter

can be designed. This method is applicable not only to ball-type or connected-ball-column type of encapsulated phase-change material, it also applies to phase-change material of other encapsulated types.

- 5 The operating heat transfer fluid flow conditions of a district cooling system determine the delivery and storage rates of an Encapsulated Phase-Change Material Latent Thermal Energy Storage ("EPCM LTES") system. Consequently, the flow conditions also determine the efficiency and cost of the system. The present invention aims to optimise the flow patterns of an EPCM LTES system to match the cooling load and on/off
- 10 peak hours of the demand as shown in Figure 5.

The present invention provides a method for determining the type of encapsulated phase-change material to be used in a latent thermal energy storage system based on the district cooling system's cooling requirements while taking into account its

15 constraints and operating conditions. The method comprises three key components as the decision parameters and the components include: (i) the phase-change material composition and its corresponding thermophysical properties; (ii) encapsulation form, size and material of the phase-change material; and (iii) the operating flow conditions of the heat transfer fluid in the district cooling system. These parameters form the basis for

20 matching the EPCM LTES system with a set of user's requirements and constraints. Design requirements include total cooling storage capacity, operating temperature bounds, peak cooling delivery rate and loading fraction. Constraints include the real estate availability and footprint of district cooling system distribution network.

- 25 The method of the present invention involves taking into account the user's requirements versus the constraints to define a set of key decision variables that will solely define the EPCM LTES design and sizing, computing the result and then proceed to iterate within a stipulated range of values on the most optimal design and size point. An exemplary method is illustrated in Figure 6.

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Accordingly, in a third aspect of the invention, a method for determining a type of phase-change material in encapsulated form for use in a latent thermal energy storage system for a district cooling system is provided. The method comprises assessing a set of user's requirements and user's constraints; and determining a set of variables that matches

35 the user's requirements and/or addresses the user's constraints, wherein the set of variables include type of phase-change material and its properties, type of encapsulation of the phase-change material; packing density of the encapsulated phase-change

material in the latent thermal energy storage system; and operating flow of the latent thermal energy storage system, wherein the type of phase-change material is selected from a mixture of n-Tetradecane and n-Hexadecane, wherein the amount of each of n-Tetradecane and n-Hexadecane is selected to provide a phase-change temperature in a range between 2°C and 12°C.

“User’s requirements” as used herein include, but are not limited to:

- a. Temperature bounds – the supply and return temperatures of the chilled water or heat transfer fluid.
- b. Total Energy Storage – the total cooling energy quanta that will be stored by the EPCM LTES defined as the sensible cooling of the heat transfer fluid, phase-change material and encapsulation within the temperature bounds (1a) and the latent heat of fusion carried by the encapsulated phase-change material.
- c. Cooling Delivery rate – the peak cooling load demanded by the user (in kW) that may have to be fully or partially carried by the EPCM LTES during discharging periods, computed by the instantaneous sensible heat loss by the heat transfer fluid across the EPCM LTES during discharging.
- d. Charge/Discharge timeframe - the allowed hours for charging and discharging the EPCM LTES. In the context of a commercial district cooling system this would be highly dependent on the operating hours of the users being served.
- e. System loading - a full or partial loading can be specified by the user, wherein a full loading would necessitate that the EPCM LTES provides for the district cooling system’s entire cooling load during discharging and partial loading would mean that the EPCM LTES only meets a fraction of that cooling load.
- f. User’s preference - the priority of the district cooling system operator is also a key consideration parameter in the decision methodology and the relative importance of each of the objectives (system efficiency, cost, energy density) should be determined quantitatively prior to the sizing and design exercise.

“User’s constraints” as used herein relates to the installation and sizing of the EPCM LTES system which include, but are not limited to, maximum allowable footprint which

is the available area for installation of the EPCM LTES system, which directly affects the energy density, cooling delivery rate and system efficiency; and distribution footprint which is the area of cooling distribution of the district cooling system, directly affecting the possible piping and transfer losses incurred by the network, which affects system efficiency.

The variables or design variables that the method of the present invention has to decide on as a basis for the design and sizing of the EPCM LTES system include phase-change material properties; encapsulation form; packing density and operating flow configuration.

“Phase-change material properties” as used herein refers to the thermophysical properties of the phase-change material including, but are not limited to, density, latent heat of fusion, phase-change temperature, specific heat capacity in solid and liquid phases, etc.

The “encapsulation form” as used herein includes, but not limited to, the shape, design, size and material of the encapsulation used, which affect the energy density and cooling delivery rate of the EPCM LTES system.

“Packing density” as used herein refers to the occupied volume fraction of the encapsulated phase-change material in the EPCM LTES system, which affects the energy density and the system efficiency.

The operating flow configuration determines the delivery and storage rates of the EPCM LTES system.

The design outputs as illustrated in the flowchart of Figure 6 show the outputs from the computation of the objective functions from the decision variables that have to be minimised or maximised to obtain the optimal solution. The outputs include, but are not limited to, system efficiency, energy density and total annualised cost.

System efficiency is computed based on the ratio of the day-averaged cooling delivery rate to the power consumption for driving the district cooling system.

Energy density is the ratio of the total energy storage to the EPCM LTES system’s footprint, in kWh per square metre.

The total annualised cost is the total capital investment and operating cost annualised over the life cycle of the EPCM LTES system.

- 5 The mixture of the phase-change material of the present invention is customisable. The properties of the selected phase-change material are core to the operation and performance of the system as a whole. The present invention includes a variable binary tetradecane-hexadecane mixture that can be adjusted to the user's requirements. While conventionally a phase-change temperature point closer to the midpoint of the user's
- 10 temperature bounds is often desired, the method can allow for adjustment of the mixture composition such that other considerations such as the heat transfer rate and the allowed charge/discharge time come into play. A user with a longer charging time allowance for example, would be better served by a phase-change material with a phase-change temperature closer to that of the charging temperature so that charging
- 15 rate is slower but allows for a more consistent delivery of low-temperature heat transfer fluid to the user during discharging. Figure 6 shows a range of phase-change material properties based on the variation of Hexadecane wt% in Tetradecane.

- Figure 7 shows the charging and discharging flow direction variation in a district cooling system. Determination of the optimal operating flow conditions for the EPCM LTES system is also key to the overall sizing and design of the system as it directly impacts the incurred energy consumption from pumping and the charge and discharge rates, which can be determined from the peak and off-peak periods of the district cooling system based on customer's cooling load. The hourly customer's cooling demand can
- 25 be described as such:

$$Q_{cust,i} = Q_{chiller,i} \pm Q_{TES,i}, i = 1, 2, 3, \dots, 24$$

- where i refers to the hour of the day (from 1 to 24) and the subscripts cust, chiller and
- 30 TES refer to the instantaneous cooling demand from the customer, chiller cooling rate and TES cooling rate respectively. As the customer's demand is always likely to vary over the course of 24 hours, the delivery of Q_{TES} is also expected to vary over the 24 hours while ensuring that chiller efficiency is maintained, as chiller efficiency varies with the cooling load. The optimal operating flow must then be obtained via the objective
- 35 function as such:

$$\text{Objective function: } f_{obj}(L) = \sum_{j=1}^n \eta_j(l_j),$$

where the subscript n refers to the number of chillers installed in the DCS, $\sum_{j=1}^n \eta_j(l_j)$ stands for the efficiency of the j_{th} chiller at its load condition l_j , and $L=(l_1, l_2, \dots \dots l_j)$ shall be within predefined operating domain D , wherein D refers specifically to the set operating range (subject to application constraints) of design parameter L for which the objective function (as a function of L) is to be minimised to obtain the most optimal condition. As chillers have varying efficiencies at different operating load conditions, it is imperative to find out the combination of different chillers with different operating load conditions to achieve the best efficiency and the customer's demand. Therefore, the method further comprises identifying a most efficient operating flow for charging and discharging of the latent thermal energy storage by minimising the objective function using the following equation:

$$L^* = \left(\min_{L \in D} f_{obj}(L) \right)$$

Figure 8 is a flowchart illustrating the flow optimisation methodology of the present invention.

Because of the unique value proposition offered by the encapsulated phase-change material of the present invention and its use in the thermal energy storage system, the EPCM LTES system can be optimised and integrated with district cooling system applications.

The EPCM LTES-integrated district cooling system has the potential for contributions in the several economic, social and environmental aspects including cost and space savings; improvement on building and city aesthetics; efficient and reliable cooling service; flexibility and scalability; reduction of noise, fuel consumption and carbon dioxide emission; enhanced national electricity network reliability; potential integration with new and green technologies; and provides a specific district-level or building-level cooling system.

To facilitate a better understanding of the present invention, the following examples of specific embodiments are given. In no way should the following examples be read to limit or define the entire scope of the invention. One skilled in the art will recognise that

the examples set out below are not an exhaustive list of the embodiments of this invention.

EXAMPLES

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Example 1

- 10 A mixture of n-Tetradecane and n-Hexadecane was used to approximate the required phase-change temperature point with a comparable latent heat of fusion to ice. Seven different mixture samples of varying compositions of n-Tetradecane and n-Hexadecane were obtained and analysed via a differential-scanning calorimeter (DSC). The results are as shown in Figure 7. The reported latent heat of fusion values and respective differential-scanning calorimeter curves generated from the differential-scanning calorimeter system reflect the phase-change properties of each mixture of n-
- 15 Tetradecane and n-Hexadecane. An observed range of phase-change temperatures within 0 – 20°C was found for the varying mixtures of n-Tetradecane and n-Hexadecane tested. The weight ratio of n-Tetradecane to n-Hexadecane in the various mixtures tested ranges between 30:70 and 95:5. In one embodiment, based on the properties, a weight ratio of 50:50 of n-Tetradecane to n-Hexadecane with a phase-change
- 20 temperature of 7.86°C represents the most suitable composition for use within the operating bounds of the district cooling system, carrying a latent heat of fusion of 160kJ/kg. However, it must be emphasised that a separate district cooling system operating within other operating ranges may have other ratios as the most optimal.
- 25 Although an embodiment of the present invention have been shown and described, the present invention is not limited to the described embodiments. Instead, it would be appreciated by those skilled in the art that changes may be made to the embodiments without departing from the scope of the invention, the scope of which is set forth in the following claims.

CLAIMS

1. A phase-change material for thermal energy storage comprising:
a mixture of n-Tetradecane and n-Hexadecane, wherein the amount of each of
5 n-Tetradecane and n-Hexadecane is selected to provide a phase-change temperature
in a range between 2°C and 12°C.
2. The phase-change material according to claim 1, wherein the phase-change
material is in encapsulated form.
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3. The phase-change material according to claim 2, wherein the phase-change
material is encapsulated in a receptacle made of high-density polyethylene.
4. The phase-change material according to claim 3, wherein the phase-change
15 material is encapsulated in the form of a connected-ball-column encapsulation type.
5. The phase-change material according to claim 4, wherein the connected-ball-
column encapsulation type comprises the receptacle and a combined press-fit screw-
lock cap extending from the receptacle for filling and sealing of the phase-change
20 material within the receptacle.
6. An encapsulated article comprising a receptacle and a mixture of n-
Tetradecane and n-Hexadecane, wherein the amount of each of n-Tetradecane and n-
Hexadecane is selected to provide a phase-change temperature in a range between
25 2°C and 12°C.
7. The encapsulated article according to claim 6, wherein the encapsulated article
is adapted for use in a cooling system.
- 30 8. Use of a phase-change material for thermal energy storage as defined in any
one of claims 1-5 in a district cooling system.
9. A method of determining a type of phase-change material in encapsulated form
for use in a latent thermal energy storage system for a district cooling system, the
35 method comprising:
assessing a set of user's requirements and user's constraints; and

determining a set of variables that matches the user's requirements and/or addresses the user's constraints, wherein the set of variables include type of phase-change material and its properties, type of encapsulation of the phase-change material; packing density of the encapsulated phase-change material in the latent thermal energy storage system; and operating flow of the latent thermal energy storage system,

wherein the type of phase-change material is selected from a mixture of n-Tetradecane and n-Hexadecane, wherein the amount of each of n-Tetradecane and n-Hexadecane is selected to provide a phase-change temperature in a range between 2°C and 12°C.

10. The method according to claim 9, wherein the operating flow is determined by obtaining an objective function using the following equation:

$$\text{Objective function: } f_{obj}(L) = \sum_{j=1}^n \eta_j(l_j),$$

wherein the subscript n refers to number of chillers installed in the district cooling system;

$\sum_{j=1}^n \eta_j(l_j)$ stands for efficiency of the j^{th} chiller at its load condition l_j ; and

$L = (l_1, l_2, \dots, l_j)$ is to be within a predefined operating domain D, wherein D refers to a set of operating range of the parameter L for which the objective function is to be minimised to obtain the most optimal condition.

11. The method according to claim 10, further comprising identifying a most efficient operating flow for charging and discharging of the latent thermal energy storage by minimising the objective function using the following equation:

$$L^* = \left(\min_{L \in D} f_{obj}(L) \right)$$