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USE OF PHASE CHANGE MATERIALS TO STORE ENERGY FOR REFRIGERATION IN CHEMICAL PRODUCTION PROCESSES

Abstract

Systems and methods for storing energy for refrigeration in a chemical separation process of a chemical plant. Some such systems comprise: a phase change material (PCM); and a refrigerant circuit configured to circulate a refrigerant fluid in thermal communication with the PCM such that the PCM absorbs thermal energy from the refrigerant fluid at a point in a refrigeration cycle of the process. Some such methods comprise: during a discharge cycle, circulating a refrigerant fluid in thermal communication with a phase-change material (PCM) such that the PCM absorbs thermal energy from the refrigerant fluid at a point in a refrigeration cycle of the process; where the PCM absorbs at least 10 MWh of energy from the refrigerant fluid during a 24-hour period. The PCM is typically configured to transition from an initial state to a higher enthalpy state at a transition temperature that is below a lowermost working temperature at the point in the refrigeration cycle.

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Background/Summary

FIELD OF DISCLOSURE

[0001] The present disclosure is generally related to refrigeration loops in processes for producing chemicals and, more particularly but not by way of limitation, to the use of phase change materials (PCMs) to store energy for refrigeration in processes for producing chemicals.

BACKGROUND

[0002] As chemical plants move from burning fossil fuels to meet daily power needs to using electricity from the power grid and/or from renewable sources, the availability and cost of electricity will vary over time. For example, electrical energy from the power grid is typically more expensive during peak consumption hours. Additionally, production of solar and wind energy varies with time of day and weather conditions—e.g., night hours and overcast time periods reduce or interrupt the generation of electricity by solar panels. Likewise, during periods when wind is slower or non-existent, generation of electricity by wind turbines is reduced or interrupted.

Additionally, utilities may offer discounts to customers that can be flexible in their consumption demands during peak hours when electricity production or grid capacity are stressed. Storing energy can shift some consumption of energy from external sources (e.g., grid, solar, wind or the like) away from hours during which energy is more expensive (e.g., peak grid hours) or of limited availability (e.g., dark hours for solar or still hours for wind). Reducing external energy needs during peak grid hours also has the added benefit of encouraging stability of the grid.

Commercially, however, it is typically important for a chemical plant to maintain consistent throughput, even during periods when external energy needs are reduced—i.e., even when drawing relatively less electricity from external sources.

SUMMARY

[0003] The present systems and methods utilize phase change material (PCM) to absorb thermal energy to run or supplement refrigeration cycles in chemical separation processes for chemical plants, for example in refrigeration cycles where the compressor(s) is/are driven by electric drivers (as opposed to burning fossil fuels). A PCM is “charged” by removing thermal energy from the PCM to transition the PCM from an initial state to a higher enthalpy state, such that the PCM can be then be “discharged” by absorbing thermal energy from the refrigeration cycle to reduce the external power (e.g., from electricity or combustion of fossil fuels) that is required by the refrigeration cycle. For example, the PCM can be used to reduce external power requirements during periods when electricity from renewable energy sources is less available or not available (e.g., during periods of reduced sunlight for solar power sources, or reduced wind for wind power sources), or when electricity from a power grid is more expensive or not available (e.g., during peak hours, when a utility requests reduced consumption for grid stability, or during grid outages). Such uses of PCMs are believed to have not previously been used for refrigeration in chemical separation processes in chemical plants due at least in part to the massive energy requirements of such chemical separation processes. The magnitude of such energy requirements has traditionally not only been cost prohibitive, but have also been hampered by the technical challenges inherent in

using PCM to “store” such large amounts of energy. Moreover, chemical processes utilizing refrigeration loops (e.g. steam crackers and ammonia synthesis plants) have utilized steam derived from the combustion of fossil hydrocarbons as the primary source of power for refrigeration; although they emit CO₂, they are relatively unaffected by variations in electrical prices or demands on the electrical supply. Additionally, some prior uses of PCMs to “store” energy have typically reclaimed that energy in the form of electricity, resulting in reduced efficiency relative to the present use of PCM to absorb thermal energy from a chemical separation process (which does not require further conversion of thermal energy to electricity).

[0004] When used for refrigeration in chemical separation processes, PCMs will typically have scalability advantages and other benefits over cryogenic liquefaction storage systems. For example, a PCM may be selected from nonflammable materials, so large amounts can be stored with lower safety risk. This could be done for liquefaction systems, for example using liquid nitrogen instead of liquid ethylene, but at the expense of inferior properties in terms of heat capacity and energy storage density relative to hydrocarbon liquefaction. Another advantage includes avoiding the undesirable properties of vapor phase materials, such as large required volumes and poor thermal conductivity. Liquefied gases generally have a relatively high energy storage density, but such gases when in a gaseous state typically require massive storage volumes (unless using air that can be vented to the atmosphere, but doing so requires the intake of replacement air at ambient temperatures). Additionally, liquid thermal conductivities are typically 10 times or higher than vapor thermal conductivities; for example, the thermal conductivities of liquid ethylene and liquid nitrogen are 0.18 and 0.155 W/m/K, respectively, while the thermal conductivities of both ethylene and nitrogen vapor are only 0.017 W/m/K. Higher thermal conductivity is important in being able to access the stored energy across the large energy storage volume in a reasonable amount of time. Even so, there is a tradeoff in that enthalpies of fusion are generally much smaller than that of the enthalpy of vaporization for the same material. As an example, the enthalpy of fusion of ethylene is only 119 kJ/kg, while its enthalpy of vaporization is 482 kJ/kg. Nevertheless, this tradeoff is typically outweighed by the other benefits of using a solid-liquid PCM relative to cryogenic liquefaction that instead relies on a gas-liquid transition.

[0005] Solidifying a PCM requires removing thermal energy from the PCM; however, such removal of energy from the PCM is referred to herein as “charging” the PCM because the removal of the thermal energy to “charge” the PCM requires power (from electricity or combustion of fossil fuels) to drive one or more compressors in a refrigeration cycle that cools the PCM. Once cooled and thereby solidified, the PCM can then absorb thermal energy from a chemical separation process that would have otherwise required further operation of compressor(s) to continue to drive a refrigeration cycle for the chemical separation process. As such, the initial removal of thermal energy from the PCM effectively “stores” the power that would have otherwise been required to run the refrigeration cycle for the chemical separation process during the period when the PCM is being “discharged” by absorbing thermal energy from the chemical separation process.

[0006] When, for example, a chemical plant draws power from an electrical grid, differences in the price of electricity at different times of the day can make it advantageous to draw more power from the grid to both (a) run compressor(s) in a refrigeration cycle for a chemical separation process and (b) charge a PCM during non-peak hours (when electricity is less expensive), and then to draw less power from the grid during peak hours (when electricity is more expensive) by using the PCM to absorb thermal energy from the chemical separation process instead of or in combination with the compressor(s) that may be used exclusively in the refrigeration cycle during non-peak hours. In some configurations, compressor(s) in the refrigeration cycle for the chemical separation process may be larger than required for the chemical separation process such that the compressor(s) may be used both for the chemical-separation refrigeration cycle and for a PCM refrigeration cycle to charge the PCM. In other configurations, one or more separate compressor(s) may be used for a distinct PCM refrigeration cycle that is used when charging the PCM.

[0007] In some configurations of the present systems for storing energy for refrigeration in a chemical separation process of a chemical plant, the system comprises: a phase change material (PCM) (e.g., disposed in one or more thermally insulated vessel(s)); a refrigerant circuit configured to circulate a refrigerant fluid in thermal communication with the PCM such that the PCM absorbs thermal energy from the refrigerant fluid at a point in a refrigeration cycle of the process; where the PCM is configured to transition from a first state to a second state at a transition temperature that is below a lowermost working temperature at the point in the refrigeration cycle; where the PCM requires at least 10 MWh (e.g., 20 MWh, 30 MWh, 50 MWh, 100 MWh, 150 MWh, 200 MWh, 300 MWh, 500 MWh, 1000 MWh, or more) to transition from the first state to the second state.

[0008] In some configurations of the present systems, the refrigerant circuit is part of a refrigeration system that comprises a compressor configured to compress the refrigerant fluid such that the refrigerant fluid can be circulated to receive thermal energy in the process, and the system is configured to either: receive cooled refrigerant fluid from the refrigeration system and circulate the cooled refrigerant fluid through the refrigerant circuit such that the refrigerant fluid absorbs thermal energy from the PCM; or receive warmed refrigerant fluid from the process and circulate the warmed refrigerant fluid through the refrigerant circuit such that the PCM absorbs thermal energy from the warmed refrigerant fluid. In some such systems, the refrigerant fluid is a first refrigerant fluid and the refrigerant circuit is a first refrigerant circuit, and the system further comprises: a PCM refrigeration circuit comprising a compressor, and a second refrigerant circuit configured to circulate a second refrigerant fluid in thermal communication with a the PCM such that the second refrigerant fluid absorbs thermal energy from the PCM.

[0009] In some configurations of the present systems, the one or more insulated vessels are first insulated vessel(s) and the PCM is a first PCM, and the system further comprises: one or more second insulated vessels; a second phase change material (PCM) disposed in the second thermally insulated vessel(s), the second PCM configured to transition from an initial state to a higher enthalpy state at a second transition temperature that is above the transition temperature of the first PCM; where the second PCM requires at least 10 MWh to transition from the initial state to the higher enthalpy state. In some such configurations, the PCM, the second PCM, or both the first PCM and the second PCM together, requires at least 100 MWh (e.g., 150 MWh, 200 MWh, 300 MWh, 500 MWh, 1000 MWh, or more) to transition from the first state to the second state.

[0010] In some implementations of the present methods of storing energy for refrigeration in a chemical separation process of a chemical plant, the method comprises: during a discharge cycle, circulating a refrigerant fluid in thermal communication with a phase-change material (PCM) such that the PCM absorbs thermal energy from the refrigerant fluid at a point in a refrigeration cycle of the process; where the PCM is configured to transition from an initial state to a liquid state at a transition temperature that is below a lowermost working temperature of the refrigerant at the point in the refrigeration cycle; and where the PCM absorbs at least 10 MWh of energy from the refrigerant fluid during a 24-hour period. In some such implementations, the method further comprises: during a recharge cycle, circulating a refrigerant fluid in thermal communication with the PCM such that the refrigerant fluid absorbs thermal energy from the PCM until a majority (e.g., substantially all) of the PCM is in a solid state. In some such implementations, a 24-hour period includes one or more discharge cycles lasting a total 2-22 hours, and one or more recharge cycles lasting a total of 2-22 hours. In some such implementations, the lengths of the charge and discharge cycles are adjusted or selected based on a methodology selected from the group of methodologies consisting of: in response to a request from a power grid operator to reduce consumption of electric power; to reduce the total cost of electricity to continuously run the process over the 24-hour period, taking into account variations in the price of electricity over the 24-hour period; and in response to a temporary outage of at least one source of electricity to the process.

[0011] In some implementations of the present methods, the temperatures at which thermal energy is transferred between the PCM and the refrigerant fluid are selected such that performing the

process in combination with the PCM during the discharge cycle requires a Reduced Total Energy, performing the process without the PCM over the same length of time requires a Baseline Total Energy, and charging the PCM during the charge cycle requires a Total Charge Energy in excess of the total energy required to perform the process over the same length of time; and where the equation (Baseline Total Energy—Reduced Total Energy)-Total Charge Energy equals 60% or more.

[0012] Some implementations of the present methods further comprise: during the recharge cycle, operating a compressor to simultaneously cool the refrigerant fluid that is circulated in thermal communication with the PCM and refrigerant fluid that is used in a propylene or ethylene refrigeration system for the process.

[0013] In some configurations of the present systems and implementations of the present methods, the compressor is electric and, optionally, a majority of the electricity to run the compressor(s) is obtained from renewable sources.

[0014] In some configurations of the present systems and implementations of the present methods, the PCM comprises one or more component selected from the group of components consisting of: a paraffinic hydrocarbon (e.g., isopentane; n-hexane; 2-methylpentane; 2,3-dimethylbutane; n-octane; 2,3,3-trimethylpentane); an alcohol (e.g., ethylene, glycol, 1-propanol, sec-butanol); polydimethylsiloxane; water; an aqueous salt solution; a water-salt mixture; an organic chemical; a mixture of two or more organic chemicals; a eutectic mixture of two or more organic chemicals; and a mixture of two or more inorganic chemicals. In some such systems and implementations, the PCM comprises a water-salt mixture that comprises one or more components selected from the group of components consisting of: calcium dichloride (CaCl.sub.2); calcium dichloride (CaCl.sub.2); lithium chloride (LiCl); magnesium chloride (MgCl.sub.2); zinc chloride (ZnCl.sub.2); hydrogen chloride (HCl); lithium sulfate (Li.sub.2SO.sub.4); sodium chloride (NaCl); potassium chloride (KCl); aluminum nitrate (Al(NO.sub.3).sub.3); combinations of any two or more of the foregoing components.

[0015] In some configurations of the present systems and implementations of the present methods, the PCM has a melting point of from -170° C. to 40° C. (e.g., -150° C. to 30° C., -120° C. to 20° C., -100° C. to 10° C., and/or -75° C. to 5° C.).

[0016] In some configurations of the present systems and implementations of the present methods, the refrigerant comprises ethylene, propylene, ethane, propane, butane, ammonia, hydrofluorocarbons, hydrochlorofluorocarbons, or mixtures thereof.

[0017] In some configurations of the present systems and implementations of the present methods, the PCM is in a form selected from the group of forms consisting of: a slurry in which the PCM is directly suspended in a liquid within the insulated vessel(s); an encapsulated slurry in which the PCM is encapsulated in casings that are suspended in a liquid within the insulated vessel(s); and a plurality of containers each containing a portion of the slurry and including at least one heat-transfer surface configured to permit thermal communication with the PCM. In some such configurations and implementations, the PCM is in a slurry or encapsulated slurry form and the system is configured to agitate the PCM within the insulated vessel(s).

[0018] In some configurations of the present systems and implementations of the present methods, the process is selected from the group of processes consisting of: a steam cracking process, an ammonia synthesis process, a hydrogen production process, a para-xylene production process, propane dehydrogenation, olefin metathesis, and natural gas processing.

[0019] The term “coupled” is defined as connected, although not necessarily directly, and not necessarily mechanically; two items that are “coupled” may be unitary with each other. The terms “a” and “an” are defined as one or more unless this disclosure explicitly requires otherwise. The term “substantially” is defined as largely but not necessarily wholly what is specified (and includes what is specified; e.g., substantially 90 degrees includes 90 degrees and substantially parallel includes parallel), as understood by a person of ordinary skill in the art. In any embodiment of the

present apparatuses, kits, and methods, the term “substantially” may be substituted with “within [a percentage] of” what is specified, where the percentage includes 0.1, 1, 5, and/or 10 percent.

[0020] The terms “comprise” (and any form of comprise, such as “comprises” and “comprising”), “have” (and any form of have, such as “has” and “having”), “include” (and any form of include, such as “includes” and “including”) and “contain” (and any form of contain, such as “contains” and “containing”) are open-ended linking verbs. As a result, an apparatus or kit that “comprises,” “has,” “includes” or “contains” one or more elements possesses those one or more elements, but is not limited to possessing only those elements. Likewise, a method that “comprises,” “has,” “includes” or “contains” one or more steps possesses those one or more steps, but is not limited to possessing only those one or more steps.

[0021] Further, an apparatus, device or system that is configured in a certain way is configured in at least that way, but it can also be configured in other ways than those specifically described.

[0022] Any embodiment of any of the present apparatuses and methods can consist of or consist essentially of—rather than comprise/include/contain/have—any of the described steps, elements, and/or features. Thus, in any of the claims, the term “consisting of” or “consisting essentially of” can be substituted for any of the open-ended linking verbs recited above, in order to change the scope of a given claim from what it would otherwise be using the open-ended linking verb.

[0023] Details associated with the embodiments described above and others are presented below.

[0024] Some details associated with the aspects of the present disclosure are described above, and others are described below. Other implementations, advantages, and features of the present disclosure will become apparent after review of the entire application, including the Brief Description of the Drawings, Detailed Description, and the Claims.

Description

BRIEF DESCRIPTION OF THE DRAWINGS

[0025] The following drawings illustrate by way of example and not limitation. For the sake of brevity and clarity, every feature of a given structure is not always labeled in every figure in which that structure appears. Identical labels or reference numbers do not necessarily indicate an identical structure. Rather, the same reference number may be used to indicate a similar feature or a feature with similar functionality, as may non-identical reference numbers. Dimensioned figures are drawn to scale (unless otherwise noted), meaning the sizes of the depicted elements are accurate relative to each other for at least the embodiment depicted in the figures.

[0026] FIG. 1 depicts a flowchart of an example of the present methods.

[0027] FIGS. 2A and 2B, respectively, depict a conceptual block diagram of a first example of the present PCM energy storage Systems in combination with a chemical separation process, during charge and discharge cycles.

[0028] FIGS. 3A and 3B, respectively, depict a conceptual block diagram of a second example of the present PCM energy storage systems in combination with a chemical separation process, during charge and discharge cycles.

[0029] FIGS. 4A and 4B depict examples of encapsulated PCM configurations.

[0030] FIG. 5 depicts a schematic process diagram of an example of ethylene and propylene refrigeration systems for a Naphtha cracker.

[0031] FIG. 6 depicts a schematic process diagram for a first example of one of the present one-level PCM energy storage systems for the propylene refrigeration system of FIG. 5, during a charge cycle of the PCM energy storage system.

[0032] FIG. 7 depicts a schematic process diagram of the PCM energy storage system of FIG. 6, during a discharge cycle of the PCM energy storage system.

[0033] FIGS. 8A-8B depict a schematic process diagram for a first example of one of the present

three-level PCM energy storage systems for the ethylene and propylene refrigeration systems of FIG. 5, during a charge cycle of the PCM energy storage system.

[0034] FIGS. 9A-9B depict a schematic process diagram of the PCM energy storage system of FIGS. 8A-8B, during a discharge cycle of the PCM energy storage system.

[0035] FIGS. 10A-10B depict a schematic process diagram for a second, high-efficiency example of one of the present three-level PCM energy storage systems for the ethylene and propylene refrigeration systems of FIG. 5, during a charge cycle of the PCM energy storage system.

[0036] FIGS. 11A-11B depict a schematic process diagram of the PCM energy storage system of FIGS. 10A-10B, during a discharge cycle of the PCM energy storage system.

[0037] FIG. 12 depicts a chart showing power demand over a 24-hours day for the PCM energy storage systems of FIGS. 6-11B.

[0038] FIG. 13 depicts a schematic process diagram of an example of an ammonia refrigeration system.

[0039] FIG. 14 depicts a schematic process diagram for a further example of one of the present one-level PCM energy storage systems for the ammonia refrigeration system of FIG. 13, during a charge cycle of the PCM energy storage system.

[0040] FIG. 15 depicts a schematic process diagram of the PCM energy storage system of FIG. 14, during a discharge cycle of the PCM energy storage system.

[0041] FIG. 16 depicts a schematic process diagram for a further example of one of the present one-level PCM energy storage systems for the ammonia refrigeration system of FIG. 13 with the PCM energy storage system configured for asymmetric charge and discharge cycles, during a charge cycle of the PCM energy storage system.

DETAILED DESCRIPTION

[0042] Referring now to the drawings, and more particularly to FIGS. 1 and 2A-2B, FIG. 1 depicts a flowchart of one example 10 of the present methods of using phase change material for a refrigeration cycle in a chemical separation process of a chemical plant, and FIGS. 2A and 2B depict conceptual block diagrams of an example of such PCM energy storage system 100 with PCM 104 in combination with a chemical separation process 108 in a chemical plant during a charge cycle (FIG. 2A) and a discharge cycle (2B). In some implementations, the method or process depicted in FIG. 1 is implemented by a digital controller such as a processor that executes instructions from memory to implement the steps described below with reference to FIG. 1. In the example of FIGS. 2A and 2B, a common refrigeration cycle 112 (e.g., with one or more oversized compressor(s) that is/are larger than otherwise needed for the chemical separation process alone) both provides refrigeration to the chemical separation process 108 and charges the PCM 104.

[0043] In an initial step 14, PCM 104 is “charged” by removing thermal energy from the PCM. In at least some implementations, sufficient amounts of thermal energy are removed to solidify at least some of the PCM—i.e., to transition the PCM from a liquid state to a solid state. As indicated by the arrows in FIG. 2A, during charging of the PCM, thermal energy is removed from PCM 104 and from chemical separation process 108 using common refrigeration cycle 112.

[0044] At a step 18, the method involves determining whether a discharge trigger event has occurred. Such a discharge trigger event can be or include, for example, reaching a time at which PCM 104 is scheduled to be “discharged” by absorbing thermal energy from chemical separation process 108, receiving a request from an operator of a power grid to reduce power consumption from the grid, observing a significant increase in the instantaneous cost of electrical energy supplied from the grid, a predictive model indicating future significant increase in the cost of electrical energy, or detecting an interruption of power from the grid or from local sources (e.g., renewable sources or combustion of fossil fuels). If a discharge trigger event has not occurred, then the process may include determining whether the PCM is fully charged and, if not, reverting to step 14 to continue charging the PCM. In some implementations, the process includes adjusting the rate at which the PCM is charged (i.e., the rate at which thermal energy is removed from the PCM)

based on the level of “charge” of the PCM. For example, the rate at which thermal energy is removed from the PCM may be slowed as the PCM approaches a fully charged state. In some implementations, if the PCM is fully charged, then the solidified or “charged” state of the PCM is maintained by continuing to remove thermal energy from the PCM at a rate approximating the rate at which the PCM absorbs thermal energy from environmental sources (e.g., due to inherent limitations of thermal insulation).

[0045] If instead a discharge trigger even has occurred, the method proceeds to a step **22** at which the PCM is discharged via absorption of thermal energy from the chemical separation process (e.g., via a refrigerant that is circulated in thermal communication with the chemical separation process and with the PCM). As indicated by the solid arrow in FIG. **2B**, thermal energy from PCM in **104** is used for process refrigeration in **108**. The dashed arrow in FIG. **1B** is optional and indicates that additional process refrigeration for **108** can be provided by refrigeration cycle **112** operating at reduced load. Refrigeration cycle **112** can, in at least some instances or implementations, be shut down entirely such that all refrigeration for the chemical separation process is provided via the PCM's absorption of thermal energy from the chemical separation process. In some implementations, such transfer of thermal energy from the chemical separation process to the PCM can be direct (e.g., passing a fluid of the chemical separation process in direct thermal communication with the PCM) or indirect (e.g., passing the fluid of the chemical separation of process in thermal communication with a heat-transfer fluid that is, in turn, passed in direct thermal communication with the PCM). In this context, “direct thermal communication” means that there is not an intervening heat-transfer fluid, and does not preclude thermal communication through intervening physical structures such as, for example, conduits for directing flow of process or heat-transfer fluids or through the walls of containers in which the PCM is disposed.

[0046] At a step **26**, the method involves determining whether a charge trigger event has occurred. Such a charge trigger even can be or include, for example, reaching a time at which PCM **104** is scheduled to be “charged” by removing thermal energy from the PCM, receiving a an indication from an operator of a power grid that higher power consumption from the grid can be resumed or the expiration of a period during which the operator requested reduced power consumption, observing a significant decrease in the instantaneous cost of electrical energy supplied from the grid, a predictive model indicating future significant decrease in the cost of electrical energy, or detecting the resumed availability of power from the grid or from local sources (e.g., renewable sources or combustion of fossil fuels). If a charge trigger event has not occurred, then the process may include determining whether the PCM is fully discharged and, if not, reverting to step **22** to continue discharging the PCM. In some implementations, when sufficient power is available (even if at a higher price), the process includes operating the compressor(s) of refrigeration cycle **112** at a reduced rate (relative to full or desired rate when running the chemical separation process and charging the PCM at a full or desired rate) to remove thermal energy from chemical separation process **108**, from PCM **104**, or from both the chemical separation process and the PCM based (as indicated by the dashed arrows in FIG. **2B**), for example, on the level of “charge” of the PCM and/or on the amount or cost of power available from the grid or other sources. For example, the rate at which thermal energy is absorbed by the PCM may be slowed as the PCM approaches a fully discharged state. In some implementations, if the PCM is fully discharged and power is available from other sources (even if at a higher price), then the process refrigeration cycle is operated solely to run the chemical separation process without charging the PCM. If a charge trigger event has occurred and sufficient power is available from the grid or other sources, then the method reverts to step **14** at which the PCM is charged, either at a full or desired charging rate; or, if more power is available than is needed to run the chemical separation process but not enough power to also charge the PCM at the full or desired charging rate, then the PCM is charged at a reduced rate (relative to a full or desired charging rate).

[0047] FIGS. **3A** and **3B**, respectively, depict a conceptual block diagram of an alternate

configuration **100a** of the present PCM energy storage systems in combination with a chemical separation process, during charge and discharge cycles. The operation of configuration **100a** is substantially similar to that of configuration **100** (FIGS. 2A-2B), with the primary exception being that configuration **100a** includes an additional PCM refrigeration cycle **116** with its own compressor(s). As such, at step **14** of the method depicted in FIG. 1, process refrigeration cycle **112** removes thermal energy from chemical separation process **108**, and PCM refrigeration cycle **116** removes thermal energy from PCM **104** to charge the PCM. Likewise, at step **22** of the method depicted in FIG. 1, the PCM is discharged via absorption of thermal energy from the chemical separation process **108**, as indicated by the solid arrow in FIG. 3B. Additional process refrigeration may optionally be provided by the process refrigeration cycle **112** as indicated by the dashed line in FIG. 3B. Process refrigeration cycle **112** and PCM refrigeration cycle **116** can, in at least some instances or implementations, be shut down entirely such that all refrigeration for the chemical separation process is provided via the PCM's absorption of thermal energy from the chemical separation process and such that thermal energy is not simultaneously being removed from the PCM. As described above for configuration **100** of FIGS. 2A-2B, in some implementations, such transfer of thermal energy from the chemical separation process to the PCM can be direct (e.g., passing a fluid of the chemical separation process in direct thermal communication with the PCM) or indirect (e.g., passing the fluid of the chemical separation of process in thermal communication with a heat-transfer fluid that is, in turn, passed in direct thermal communication with the PCM). [0048] As described above for configuration **100** of FIGS. 2A-2B, for configuration of **100a**, in some implementations, when sufficient power is available (even if at a higher price), the method includes operating the compressor(s) of process refrigeration cycle **112** at a reduced rate (relative to full or desired rate when running the chemical separation process solely with the process refrigeration cycle) to remove thermal energy from chemical separation process **108**, operating the compressor(s) of PCM refrigeration cycle **116** at a reduced rate (relative to full or desired rate when charging the PCM at a full or desired rate) to remove thermal energy from PCM **104**, and/or both running the compressor(s) of the process refrigeration cycle at a reduced rate and running the compressor(s) of the PCM refrigeration cycle at a reduced rate (as indicated by the dashed arrows in FIG. 3B). In some implementations, if the PCM is fully discharged and power is available from other sources (even if at a higher price), then only the compressor(s) of process refrigeration cycle **112** is operated to run the chemical separation process without running the compressor(s) of PCM refrigeration cycle **116** to charge the PCM.

[0049] While the process example of FIG. 1, and the system examples of FIGS. 2A-2B and 3A-3B utilize a single PCM, the present methods and system can include multiple PCMs (e.g., at different temperatures) and multiple refrigeration cycles, for example, two PCMs with different freezing temperatures, or three PCMs with three different freezing temperatures, for example to provide staged cooling for a process refrigeration cycle.

Phase Change Material (PCM)

[0050] Phase change materials generally have the ability to absorb or release (preferably large) quantities of heat at specifically targeted temperatures of interest and, for at least some implementations the present systems and methods, preferably with minimal volumetric change. Generally, physical phase transitions of condensed phase materials exhibit this type of behavior. A transition from the solid phase to the liquid phase is one type of transition that typically meets this criteria. However, other transitions can also be utilized in certain implementations of the present systems and methods. For example, some PCMs may change from a solid state to a liquid state in the operating conditions (e.g., temperature) of certain implementations. By way of further example, some PCMs may exhibit other types of phase changes in which the enthalpy changes non-linearly at a particular temperature (or over a particular temperature range), such as from one solid state to another solid state (e.g. change in crystal structure due to molecular rearrangements), from an amorphous state to a solid state, from a gel state to a solid state, from a liquid state to a gel state, or

from an amorphous state to a different amorphous state. In a multicomponent mixture, there may or may not also be some compositional shift between one state and another, for example a liquid solution of a solvent and a solute forming a 2:1 solvent and solute compound in the solid phase. To generally describe this without enumerating all the specific phases of the many possible systems, the PCM can be described as transitioning between a first state and a second state when heat is added to the PCM and transitioning from the second state to the lower-enthalpy first state when heat is removed from the PCM.

[0051] Various materials and mixtures can be used for the PCM, such as, for example, a paraffinic hydrocarbon (e.g., pentane; n-hexane; 2-methylpentane; 2,3 dimethylbutane; n-octane; 2,3,3 trimethylpentane), an alcohol (e.g., ethylene glycol; 1-propanol; sec-butanol; ethanol, isopropyl alcohol), polydimethylsiloxane, water, an aqueous salt solution, a eutectic salt solution, a eutectic mixture of two or more organic or inorganic chemicals and/or combinations thereof (e.g., a combination of two paraffinic hydrocarbons, a combination of two alcohols, a combination of an alcohol and an aqueous salt). Various salts can be used in a salt solution, such as, for example, calcium dichloride (CaCl_2); lithium chloride (LiCl), magnesium chloride (MgCl_2), zinc chloride (ZnCl_2), hydrogen chloride (HCl), lithium sulfate (Li_2SO_4), sodium chloride (NaCl), potassium chloride (KCl), aluminum nitrate ($\text{Al}(\text{NO}_3)_3$), various commercially available eutectic salt solutions (e.g., E-65 available from PCM Products Ltd., Cambridgeshire, UK), and combinations thereof. Moreover, different PCM components can be mixed in proportions to achieve a desired freezing point for a given refrigeration cycle. For example, the refrigeration system for a C2 splitter and de-ethanizer in a naphtha cracker typically operates over a temperature range from about -42°C . to about 0°C ., for which a PCM could be a eutectic salt mixture with a transition temperature of -65°C . By way of further example, the de-methanizer in a naphtha cracker typically operates over a lower temperature range with a lower end of about -100°C ., so a PCM with a lower phase transition would be needed, for example pure ethanol (-114°C .) or a eutectic mixture of ethanol and water (-118°C .) or ethanol and another alcohol such as methanol.

[0052] There are several options for containment of a PCM in the present systems and methods. First, PCM can be disposed in one or more insulated vessels through which heat-exchange conduits define flowpaths for refrigerant. The conduits (e.g., tubes, shells, fins, or the like) disposed within the vessel(s) permit heat transfer between the refrigerant within the conduits or heat exchangers and the PCM within a given vessel (outside the conduits). In at least some configurations, the PCM is stirred or agitated within the vessel(s) to prevent temperature gradients and improve the heat transfer. In this first option, the volume of PCM typically will include more than the minimum needed for a desired thermal capacity, because a consistent liquid phase will typically be required to facilitate stirring or agitation during “charging” of the PCM to facilitate the consistent transfer of thermal energy out of the PCM. For example, the PCM can be suspended in a liquid (i.e., a slurry when the PCM is in a solid form). The relative proportions of liquid and solid can be designed according to the system needs. For example a relatively large, passive storage system may have continuous and somewhat separated solid and liquid phases. The stirring or agitation system can be configured to control the PCM in a slurry of smaller particles that is easily pumped and transferred to heat transfer equipment, or simply suspended by fluid circulation to homogenize the system with heat storage capacity. In some implementations, the PCM may be present in the form of small, encapsulated beads that contain the PCM in both its liquid and solid states, such that the beads can be suspended in a liquid with a lower freezing point than the PCM. When the PCM is suspended as a slurry in a solution or as an emulsion (e.g., n-decane in water/ethylene glycol ($\text{CH}_2(\text{OH})-\text{CH}_2(\text{OH})$) solution), without the PCM being encapsulated, nucleating agents may be included in the liquid to encourage nucleation during freezing to occur in the solution rather than on heat-transfer surfaces where nucleation can interfere with or inhibit the transfer of thermal energy through those surfaces. Some such systems and methods may include supercooling or subcooling

before nucleation/crystallization occurs. For example, liquid solutions can sometimes be cooled below their freezing point without solidifying in the absence of a nucleating reaction to form crystals, in which case nucleating agents can be introduced and/or the liquid can be agitated to begin the nucleation process and thereby solidify the liquid.

[0053] A second option includes containing the PCM in a larger number of relatively smaller, insulated containers (e.g., formed of HDPE). These containers can be shaped, either individually or in combination with other such containers, to contour to and contact refrigerant conduits to improve heat transfer between the refrigerant and the PCM. For example, with conduits having a circular cross-section like a typical pipe, the containers can include circular passages or semi-circular indentations to contact the conduit. By way of further example, conduits can be shaped to have a relatively flat, rectangular cross-section sized to fit against a planar wall of a container.

[0054] In a third option, the PCM can be contained in multiple plastic or metal enclosures the geometry of which is selected such that these may be stacked or hung (e.g., in parallel) inside the insulated vessel such that the refrigerant or heat transfer fluid (when a secondary circuit system is employed) can pass between (and/or through) and in contact with the individual containers to transfer thermal energy between the PCM and the refrigerant or heat-transfer fluid through the walls of the containers. This approach provides a large surface area for the transfer of thermal energy. FIG. 4A depicts an example of such a container that is formed of polymer and is substantially rigid to allow multiple containers to be stacked. As shown, the container of FIG. 4A defines a number of grooves to maximize the surface area available for the transfer of thermal energy between the PCM inside the container and the refrigerant or heat-transfer fluid outside the container. FIG. 4B depicts another example of such a container that is formed from a polymer and is flexible (like a plastic kitchen bag). As shown, the container of FIG. 4B also defines a number of grooves along which the two sides of the bag structure are joined to define an elongated zig-zag passage to maximize surface area for heat-transfer, provide for ease of bag filling, and to promote even distribution of PCM within the bag structure when the bag structure is hanging in a vessel through which the refrigerant or heat-transfer fluid circulates.

[0055] The first of these three PCM-containment options has the advantage of smaller overall vessel size, simpler construction, and higher heat transfer rates. The second of these three PCM-containment options offers lower corrosion rates by fully containing the refrigerant in conduits and fully containing the PCM in individual containers. And the third of these three PCM-containment options offers advantages of a large heat exchange area in a conveniently-handled form factor. In some implementations with a single PCM, the PCM can be configured to require at least 10 MWh (e.g., 20 MWh, 30 MWh, 50 MWh, 100 MWh, 150 MWh, 200 MWh, 300 MWh, 500 MWh, 1000 MWh, or more) to transition from the initial state to the higher enthalpy state. In other implementations with multiple PCMs, the PCMs can be configured to together require at least 100 MWh (e.g., 150 MWh, 200 MWh, 300 MWh, 500 MWh, 1000 MWh, or more) to transition from the initial state to the higher enthalpy state.

Refrigerants

[0056] Various refrigerants can be used for chemical separation process refrigeration and/or PCM charging. Examples of refrigerants that are suitable for certain implementations of the present methods and systems include ethylene, propylene, ethane, propane, butane, ammonia, hydrofluorocarbons, hydrochlorofluorocarbons, and mixtures thereof. As will be appreciated by those of ordinary skill in the art, a refrigerant for a given refrigeration cycle can include one or more components selected such that the refrigerant will be in a gaseous state at an upper temperature of the refrigeration cycle and will be in a liquid state at a lower temperature of the refrigeration cycle.

Heat Transfer Fluid

[0057] For configurations in which a heat transfer fluid indirectly transfers thermal energy between the PCM and the refrigerant of a given chemical-separation refrigeration cycle, the heat transfer

fluid can include one or more of any components known for such heat-transfer fluids. Suitable heat transfer fluids remain in the liquid phase under the conditions of both the relevant part of the refrigeration cycle and the conditions under which heat transfer occurs between the heat-transfer fluid and the PCM. For example, diethyl ether (which freezes at 154 ± 7 K and, at atmospheric pressure, boils at 307.7 ± 0.2 K) is a suitable heat transfer fluid for use with a typical demethanizer refrigeration system.

EXAMPLES

Examples 1-3: Naphtha Cracker Refrigeration Systems

[0058] Several examples were modeled for the use of the present PCM energy storage systems and methods to run refrigeration cycles for ethylene production via Naphtha crackers, particularly Naphtha crackers utilizing a front-end demethanizer configuration. FIG. 5 depicts an example **200** of a refrigeration system for a Naphtha cracker and, more specifically, depicts a schematic process diagram of that example that includes an ethylene refrigeration system **204** and a propylene refrigeration system **208** for the Naphtha Cracker. The refrigeration systems in the examples provide several different temperature levels for process chilling duties in various portions of the Naphtha Cracker.

[0059] The typical or “existing” ethylene refrigeration system **204** includes a first compressing stage with a first evaporator **212** and a first compressor **216**, a second compressing stage with a second evaporator **220** and a second compressor **224**, and a single condensing stage with a first condenser **228** and a second condenser **232**. The pressure of the condensed ethylene is let down across valves **240** and **236**, which reduces the boiling point of the ethylene such that cooling may be obtained. Valve **240** lets the pressure down to about 4.5 bara which results in a mixture of vapor and liquid boiling at about -73° C. Valve **236** lets the pressure down to about 1.1 bara which results in a mixture of vapor and liquid boiling at about -102° C. In operation, a portion of the ethylene from valve **240** is sent to second evaporator **220** and the ethylene from valve **236** is sent to first evaporator **212**. In first evaporator **212**, the liquid phase ethylene absorbs thermal energy and boils to a gaseous state at a temperature of -102° C. and a pressure of 1.1 bara. The gaseous ethylene from first evaporator **212** is then routed to first compressor **216** where the gaseous ethylene is compressed to a first pressure of 4.5 bara (Bar absolute). In second evaporator **220**, the liquid phase ethylene absorbs thermal energy and boils to a gaseous state at a temperature of -73° C. and a pressure of 4.5 bara. The gaseous ethylene from second evaporator **220** is then mixed with the compressed ethylene from first compressor **216**, and the combined gaseous ethylene is then routed to second compressor **224**, where the combined gaseous ethylene is further compressed to a second pressure of 15.6 bara. The compressed gaseous ethylene from second compressor **224** is then routed to the condensers, where it is partially condensed in first condenser **228** and then further condensed in second condenser **232**. In the depicted configuration, a heat transfer fluid is circulated through the first condenser **228** to absorb thermal energy from the condensing ethylene for use in the propylene refrigeration system, and a heat-transfer fluid is also circulated through the second condenser **232** to absorb additional thermal energy from the condensing ethylene also for use in the propylene refrigeration system.

[0060] The typical or “existing” propylene refrigeration system **208** includes three compressor stages and a condenser stage. The first compressing stage includes a first evaporator **244**, parallel second evaporator **248**, and a first compressor **252**. The second compressing stage includes a third evaporator **256**, a parallel fourth evaporator **260**, and a second compressor **264**. The third compressing stage includes a fifth evaporator **268** and a third compressor **272**. The condenser stage includes a single condenser **276**. In operation, the pressure of the condensed propylene from condenser **276** is let down to three different pressure levels via valves **288**, **284**, and **280**, which reduces the boiling point of the propylene and is thus able to provide cooling to the process. Upon pressure letdown, a mixture of vapor and liquid is obtained at a temperature determined by the boiling point at the letdown pressure. These mixtures are routed to the evaporators **244**, **248**, **256**,

260, **268** of the first, second, and third compressing stages. In first and second evaporators **244**, **248**, the liquid phase propylene absorbs thermal energy and boils to a gaseous state at a temperature of -46°C . and a pressure of 1.1 bara. As indicated by the dashed line from first condenser **228** of ethylene refrigeration system **204**, thermal energy from that first condenser **228** is used as a source of thermal energy in evaporator **256** to boil the propylene. The gaseous propylene is then routed to first compressor **252** where the gaseous propylene is compressed to a first pressure of 4.5 bara and a temperature of -46°C . In third and fourth evaporators **256**, **260**, the liquid phase propylene absorbs thermal energy and boils to a gaseous state at a temperature of -23°C . and a pressure of 2.8 bara. As indicated by the dashed line from second condenser **232** of ethylene refrigeration system **204**, thermal energy from that second condenser **232** is used as a source of thermal energy in evaporator **244** to boil the propylene. This gaseous propylene from evaporators **256**, **260** is then mixed with the compressed propylene from first compressor **252**, and the combined gaseous propylene is then routed to second compressor **264**, where the combined gaseous propylene is further compressed to a second pressure of 7.8 bara and temperature of 41°C . In fifth evaporator **268**, the liquid phase propylene absorbs thermal energy and boils to a gaseous state at a temperature of 10°C . and a pressure of 7.8 bara. This gaseous propylene from evaporator **268** is then mixed with the compressed propylene from second compressor **264**, and the combined gaseous propylene is then routed to third compressor **272**, where the combined gaseous propylene is further compressed to a third pressure of 18.3 bara. The compressed gaseous propylene from third compressor **272** is then routed to condenser **276**, where it is condensed. In normal operation valves **280**, **284**, and **288** are used to let down the pressure of the flowing propylene. During operation utilizing PCM for discharging, these valves may also be used to shut off flow or propylene. A first valve **280** can be closed to prevent the flow of propylene to first and second evaporators **244**, **248**; a second valve **284** can be closed to prevent the flow of propylene to any of third and fourth evaporators **256**, **260** or first and second evaporators **244**, **248**; and a third valve **288** can be closed to prevent the flow of propylene to any of fifth evaporator **268**, third and fourth evaporators **256**, **260**, or first and second evaporators **244**, **248**.

[0061] As described above, the three modeled systems are “charged” by freezing the PCM by transferring thermal energy from the PCM to a refrigerant to freeze the PCM and boil the refrigerant, and the systems are “discharged” by transferring thermal energy from the refrigerant in a gaseous state to condense the refrigerant and melt the PCM to a liquid state. For example, the PCM for these modeled examples assume an aqueous eutectic salt mixture that undergoes a liquid-solid phase change at a single temperature.

[0062] In each of these three examples, the process is modeled with a “symmetric” cycle in which the cycle for “charging” is equal in length of time to the cycle for “discharging” the PCM. For example, the PCM can be “charged” for 12 hours, and “discharged” for 12 hours during each 24 hour period, as shown in FIG. 12. Absorption of thermal energy from external (e.g., ambient) sources was not accounted for (assumed to be zero). In design of a real-world system, such external thermal energy can be accommodated by oversizing thermal capacity of PCM volume and compressor(s), taking into account particular insulation values. These models assumed the PCM to be directly dispersed in a slurry or encapsulated in small spheres within a slurry. Process simulations were performed in CHEMCAD, using the SRK method.

[0063] In each of Examples 1 and 2, the respective system is modeled with compressors in the propylene refrigeration system providing additional compression within that refrigeration system to charge the PCM. Such compressors can, for example, be enlarged when converting an existing system to operate using the present PCM energy storage systems, or can simply be sized large enough to provide such additional compression when developing a new system. In Example 3, the system is modeled with (relative to the system without the added PCM system) an additional refrigeration train or circuit with independent compressors for “charging” each PCM reservoir. The PCM refrigeration circuit or train is used only for “charging” the system when surplus power is

available. In all of these three examples, the existing refrigeration trains that interact with the PCM system are modified with new exchangers to transfer thermal energy to the PCM for condensing propylene vapor. These three systems were also modeled assuming the existing refrigeration train would be, or would be modified to be, driven by electric drivers (as opposed to burning fossil fuels), and assuming that the added PCM refrigeration train would also be driven by electric drivers.

[0064] The single-level or single-stage system of Example 1 uses a single PCM reservoir to store “cold” during periods of surplus or lower-cost power, and then that stored “cold” is utilized when power supply is short or available at a higher cost. This single-level system is the simplest and therefore the lowest cost to construct (relative to the multi-stage systems of Examples 2-3).

[0065] As will be appreciated by those of ordinary skill in the art, the selection of charging temperatures (pressures) can impact efficiency of the energy storage; however, for simplicity, Examples 1 and 2 assumed the charging train would operate at same temperature and pressure levels as the existing train without the PCM. In Example 3, efficiency was significantly improved by selecting charging train operating pressures to reduce temperature differences, as discussed in more detail below.

[0066] Modeling revealed that a three-level PCM system with three PCM reservoirs would be needed for maximum power cycling, and to enable shutting down the propylene compressors during discharging, as discussed in more detail below with reference to Examples 2 and 3.

Example 1: One-Level PCM System for Naphtha Cracker Ethylene & Propylene Refrigeration Systems

[0067] FIG. 6 depicts a schematic process diagram for the modeled example of a one-level PCM energy storage system **300** for propylene refrigeration system **208** of FIG. 5, during a charge cycle of the PCM energy storage system, and FIG. 7 shows PCM energy storage system **300** during a discharge cycle. As shown, the addition of the PCM system includes adding a PCM system evaporator **304** to the first compression stage of propylene refrigeration system **208**, with first PCM system evaporator **304** in parallel with first and second evaporators **244**, **248**; and adding a PCM system condenser **308** to the second compression stage of propylene refrigeration system **208**, with PCM system condenser **308** in parallel with third and fourth evaporators **256**, **260**. The addition of the PCM system also includes a pump **312** and a PCM reservoir **316** and conduits and valves to route a heat-transfer fluid from the PCM to the PCM system evaporator and condenser.

[0068] As shown in FIG. 6, during charging of PCM reservoir **316**, a PCM slurry or a heat transfer fluid is circulated by pump **312** from PCM reservoir **316** to evaporator **304**, where thermal energy is transferred from the PCM slurry or heat-transfer fluid to the propylene at a temperature of -46°C . to boil the propylene. In the case where a heat transfer fluid is utilized, heat-transfer fluid then returns to PCM **316** where the heat-transfer fluid absorbs additional thermal energy from the PCM reservoir at the PCM's freezing point of -34°C ., and so on, until the PCM is fully “charged” or solidified or charging is otherwise suspended. In the case where the PCM is contained in a slurry, the PCM “charges” or solidifies as it is chilled and returns to the PCM reservoir, eventually resulting in a fully charged slurry of PCM in the reservoir. At the modeled charging rate, evaporator **304** removes thermal energy from the PCM slurry or heat-transfer fluid at a rate of 109.1 MW, such that during a 12-hour charging period, 1309 MWh of energy is removed from PCM **316** reservoir. Stated another way, 1309 MWh of cold or thermal capacity is “stored” such that the PCM reservoir can later absorb up to 1309 MWh (less any inefficiencies, e.g., introduced by absorption of thermal energy from external sources) of thermal energy from the propylene refrigeration system when the PCM reservoir is “discharged.” As indicated by the differences between FIG. 5 and FIG. 6, the compressors are required to input additional energy to provide the required compression to “charge” the PCM reservoir. Specifically, first compressor **252** increases from 7.6 MW (FIG. 5) to 22.6 MW (FIG. 6), second compressor **264** increases from 20.7 MW to 44.4 MW, and third compressor **272** increases from 28.0 MW to 55.9 MW. Overall, the power demand for the

compressors increases from 66.8 MW for the ethylene and propylene refrigeration systems **204** and **208** alone (FIG. 5) to 133.4 MW for the propylene refrigeration system **208** in combination with the PCM energy storage system **300** (FIG. 6).

[0069] As shown in FIG. 7, during discharging of PCM reservoir **316**, a PCM slurry or a heat transfer fluid is circulated by pump **312** from PCM reservoir **316** to condenser **308**, where thermal energy is transferred from the propylene vapor to the PCM slurry or heat-transfer fluid at a temperature of -23°C . to condense the propylene at a pressure of 2.8 bar. The condensation of propylene vapors in condenser **308** occurs simultaneously with the evaporation of propylene liquid in evaporator **256**. These flows can be achieved at essentially the same pressure due to a thermosiphon effect, where the boiling liquid in evaporator **256** reduces the density of the fluid providing a driving force for the liquid condensed in condenser **308** to take its place. Alternatively, the propylene can be pumped through a conduit that is in thermal communication with the PCM slurry (e.g., a conduit passing through a container in which the PCM slurry is disposed. The PCM slurry or heat-transfer fluid then returns to PCM **316** where the PCM reservoir absorbs thermal energy from PCM slurry or heat-transfer fluid at the PCM's freezing point of -34°C ., and so on, until the PCM is fully “discharged” or liquefied, or discharging is otherwise suspended. As indicated by the differences between FIG. 5 and FIG. 7, the compressors are required to input less energy to provide the required compression to operate propylene refrigeration system **208**. Specifically, first compressor **252** stays the same at 7.6 MW (FIGS. 5, 7), second compressor **264** decreases from 20.7 MW to 0 MW, and third compressor **272** decreases from 28.0 MW to 3.3 MW. In the embodiment of FIG. 7, two “X”s are shown to indicate that the propylene refrigeration cycles can essentially be operated as two independent cycles; a low pressure cycle where 2.8 bar propylene is condensed using stored PCM in **308**, and a high pressure cycle where 18.3 bar propylene is condensed with ambient cooling in **276**. Overall, the power demand for these compressors decreases from 66.8 MW for the propylene refrigeration system **208** alone (FIG. 5) to 21.4 MW for the propylene refrigeration system **208** in combination with the PCM energy storage system **300** (FIG. 7). In other implementations, it may be beneficial to maintain at least a nominal load on the second compressor (**264**).

[0070] Table 1 summarizes the condenser power inputs during operation of the ethylene and propylene refrigeration systems, both alone and in combination with the PCM energy storage system in its charging cycle and discharging cycle:

TABLE-US-00001

TABLE 1 Power Inputs & Outputs for One-Level PCM System											
Single-level PCM No Charging			Discharging			Cycling			Cycle		
Base			Refrig			Train			Shaft Power, MW		
Ethylene stage 1			3.7	3.7	3.7	Ethylene stage 2			6.8	6.8	6.8
Propylene stage 1			7.6	7.6	7.6	Propylene stage 2			20.7	20.7	0
Propylene stage 3			28.0	28.0	3.3	Base train shaft power, MW			66.8	66.8	21.4
Charging Train - Shaft Power, MW			Ethylene stage 2			N/A	N/A	N/A	Propylene stage 1		
Propylene stage 2			0.0	23.7	0.0	Propylene stage 3			0.0	27.9	0.0
Charging train shaft power, MW			0.0	66.6	0.0	Total refrig train shaft power, MW			66.8	133.4	21.4
Added energy during charging, MW			66.6	0.0	0.0	Energy reduction during discharging, MW			45.4	Efficiency of power storage	68.2%
Power stored over 24 hour cycle, MWh			545								

[0071] In battery terms, the additional 66.6 MW of power used over the 12-hour charge period (799 MWh) to charge a thermal “battery,” then during discharge reduces the amount of power required to run the refrigeration system **200** by 45.4 MW over the 12-hour discharge period (545 MWh), resulting in an efficiency of 68.2%. The efficiency is reduced at least in part by the modeled temperature spread of 23°C . between the charging temperature of -46°C . at evaporator **304** and the discharging temperature of -23°C . at condenser **308**. In other implementations, that efficiency can be improved by reducing the magnitude of that temperature spread.

[0072] For heat to flow from the PCM to the refrigeration system during charging or from the refrigeration system to the PCM during discharging, there has to be a temperature difference. The temperature difference can be characterized in different ways, such as the difference in temperature

between two points of different physical location or an average temperature difference among sets of points that lie within the domain of the PCM volume from sets of points that lie within the domain of the refrigeration system. Similarly, there must be a temperature difference between the manufactured product process and the refrigeration system. In heat transfer applications, the log-mean temperature difference is commonly known and used in many analyses. Sufficient temperature difference or gradient is required even within the PCM volume to transfer the required amount of heat out (and subsequently in) during an operating cycle. Additional temperature gradient may be needed to account for the size of the PCM volume, the heat transfer area in contact with the PCM, or in the case of encapsulated PCM heat transfer through the container wall. For example, while a conventional refrigeration system requires only few degrees between the refrigerant and the process, a log mean temperature difference of 3° C., 5° C., 9° C., or more would account for heat flux into the inner region of domain of the PCM. Other considerations for the temperature driving force include providing for sufficient crystallization kinetic rates in solidifying the PCM or crystal nucleation rate for operating a charging cycle near saturation when few crystals are present. The temperature difference can be managed by designing the amount of heat transfer area that accesses the PCM surface.

Example 2: Three-Level PCM System for Naphtha Cracker Ethylene & Propylene Refrigeration Systems

[0073] FIGS. **8A-8B** depict a schematic process diagram of a modeled example **400** of a three-level PCM energy storage systems for the ethylene and propylene refrigeration systems **204**, **208** of FIG. **5**, during a charge cycle of the PCM energy storage system; and FIGS. **9A-9B** depict a schematic process diagram of the PCM energy storage system **400** during its discharge cycle. As shown, the addition of the PCM system includes adding three separate PCM levels, each with its own PCM reservoir, pump, evaporator, and compressor. Specifically, the first PCM level includes a first PCM system evaporator **404** added to the second compression stage of the ethylene refrigeration system **204** in parallel with evaporator **220**, a first PCM system condenser **408** added to the first compression stage of the propylene refrigeration system **208**, a pump **412**, and a first PCM reservoir **416**. As modeled, the PCM used in the first level (PCM reservoir **416**) has a freezing point of -50° C. and sufficient volume to store 672 MWh of energy. The second PCM level includes a second PCM system evaporator **420** added to the first compression stage of propylene refrigeration system **208** in parallel with evaporators **244**, **248**; a second PCM system condenser **424** added to the propylene refrigeration system to receive at least part of the compressed gaseous propylene output from compressor **252**; a pump **428**; and a second PCM reservoir **432**. As modeled, the PCM used in the second level (PCM reservoir **432**) has a freezing point of -34° C. and sufficient volume to store 547 MWh of energy. The third PCM level includes a third PCM system evaporator **436** added to the second compression stage of propylene refrigeration system **208** in parallel with evaporators **256**, **260**; a third PCM system condenser **440** added to the propylene refrigeration system to receive at least part of the compressed gaseous propylene output from compressor **264**; a pump **444**; and a second PCM reservoir **448**. As modeled, the PCM used in the second level (PCM reservoir **448**) has a freezing point of -6° C. and sufficient volume to store 209 MWh of energy.

[0074] As shown in FIGS. **8A-8B**, during charging of PCM system **400**, a PCM slurry or a heat transfer fluid is circulated between the ethylene or propylene refrigeration systems **204**, **208** and the respective PCM reservoir. In the first PCM level (FIG. **8A**), PCM slurry or a heat transfer fluid is circulated by pump **412** from first PCM reservoir **416** to evaporator **404**, where thermal energy is transferred from the PCM slurry or heat-transfer fluid to the ethylene at a temperature of -73° C. to boil the ethylene. The PCM slurry or heat-transfer fluid then returns to PCM reservoir **416** where the PCM slurry or heat-transfer fluid absorbs additional thermal energy from the PCM reservoir at the PCM's freezing point of -50° C., and so on, until the PCM in PCM reservoir **416** is fully “charged” or solidified or charging is otherwise suspended. At the modeled charging rate,

evaporator **404** removes thermal energy from the heat-transfer fluid at a rate of 56.0 MW, such that during a 12-hour charging period, 672 MWh of energy is removed from PCM **416** reservoir. Stated another way, 672 MWh of cold or thermal capacity is “stored” such that PCM reservoir **416** can later absorb up to 672 MWh (less any inefficiencies, e.g., introduced by absorption of thermal energy from external sources) of thermal energy from the propylene refrigeration system when the PCM reservoir is “discharged.”

[0075] In the second PCM level, PCM slurry or a heat transfer fluid is circulated by pump **428** from second PCM reservoir **432** to evaporator **420**, where thermal energy is transferred from the PCM slurry or heat-transfer fluid to the propylene at a temperature of -46°C . to boil the propylene. The PCM slurry or heat-transfer fluid then returns to PCM reservoir **432** where the PCM slurry or heat-transfer fluid absorbs additional thermal energy from the PCM reservoir at the PCM's freezing point of -34°C ., and so on, until the PCM in PCM reservoir **432** is fully “charged” or solidified or charging is otherwise suspended. At the modeled charging rate, evaporator **420** removes thermal energy from the heat-transfer fluid at a rate of 45.6 MW, such that during a 12-hour charging period, 547 MWh of energy is removed from PCM reservoir **432**. Stated another way, 547 MWh of cold or thermal capacity is “stored” such that PCM reservoir **432** can later absorb up to 547 MWh (less any inefficiencies, e.g., introduced by absorption of thermal energy from external sources) of thermal energy from the propylene refrigeration system when the PCM reservoir is “discharged.”

[0076] In the third PCM level (FIG. **8B**), PCM slurry or a heat transfer fluid is circulated by pump **444** from third PCM reservoir **448** to evaporator **436**, where thermal energy is transferred from the PCM slurry or heat-transfer fluid to the propylene at a temperature of -23°C . to boil the propylene. The PCM slurry or heat-transfer fluid then returns to PCM reservoir **448** where the PCM slurry or heat-transfer fluid absorbs additional thermal energy from the PCM reservoir at the PCM's freezing point of -6°C ., and so on, until the PCM in PCM reservoir **448** is fully “charged” or solidified or charging is otherwise suspended. At the modeled charging rate, evaporator **436** removes thermal energy from the heat-transfer fluid at a rate of 17.4 MW, such that during a 12-hour charging period, 209 MWh of energy is removed from PCM reservoir **448**. Stated another way, 209 MWh of cold or thermal capacity is “stored” such that PCM reservoir **448** can later absorb up to 209 MWh (less any inefficiencies, e.g., introduced by absorption of thermal energy from external sources) of thermal energy from the propylene refrigeration system when the PCM reservoir is “discharged.”

[0077] As indicated by the differences between FIG. **5** and FIGS. **8A-8B**, the compressors are required to input additional energy to provide the required compression to “charge” the PCM reservoir. Specifically, ethylene second compressor **224** increases from 6.8 MW (FIG. **5**) to 22.5 MW (FIG. **8A**), propylene first compressor **252** increases from 7.6 MW to 22.4 MW, propylene second compressor **264** increases from 20.7 MW to 49.4 MW (FIG. **8B**), and propylene third compressor **272** increases from 28.0 MW to 55.9 MW. Overall, the power demand for the compressors increases from 66.8 MW for the ethylene and propylene refrigeration systems **204**, **208** alone (FIG. **5**) to 159.8 MW for the ethylene and propylene refrigeration systems **204** and **208** in combination with the three-level PCM energy storage system **400** (FIGS. **8A-8B**).

[0078] As shown in FIGS. **9A-9B**, during discharging of PCM system **400**, a PCM slurry or a heat transfer fluid is circulated between the propylene refrigeration system **208** and the respective PCM reservoir. In the first PCM level (FIG. **9A**), PCM slurry or a heat transfer fluid is circulated by pump **412** from first PCM reservoir **416** to condenser **408**, where thermal energy is transferred from the propylene to the PCM slurry or heat-transfer fluid at a temperature of -46°C . to condense the propylene. The PCM slurry or heat-transfer fluid then returns to PCM reservoir **416** where the PCM reservoir absorbs thermal energy from the PCM slurry or heat-transfer fluid at the PCM's freezing point of -50°C ., and so on, until the PCM in PCM reservoir **416** is fully “discharged” or liquefied or charging is otherwise suspended.

[0079] In the second PCM level, PCM slurry or a heat transfer fluid is circulated by pump **428** from second PCM reservoir **432** to condenser **424**, where thermal energy is transferred from the

propylene to the PCM slurry or heat-transfer fluid at a temperature of -23°C . to condense the propylene. The PCM slurry or heat-transfer fluid then returns to PCM reservoir **432** where the PCM reservoir absorbs thermal energy from the PCM slurry or heat-transfer fluid at the PCM's freezing point of -34°C ., and so on, until the PCM in PCM reservoir **432** is fully “discharged” or liquefied or charging is otherwise suspended.

[0080] In the third PCM level (FIG. **9B**), PCM slurry or a heat transfer fluid is circulated by pump **444** from third PCM reservoir **448** to condenser **440**, where thermal energy is transferred from the propylene to the PCM slurry or heat-transfer fluid at a temperature of 10°C . to condense the propylene. The PCM slurry or heat-transfer fluid then returns to PCM reservoir **448** where the PCM reservoir absorbs thermal energy from the PCM slurry or heat-transfer fluid at the PCM's freezing point of -6°C ., and so on, until the PCM in PCM reservoir **448** is fully “discharged” or liquefied or charging is otherwise suspended.

[0081] As indicated by the differences between FIG. **5** and FIGS. **8A-8B**, the compressors input less energy to provide the required compression to operate the refrigeration systems **204** and **208**. Specifically, propylene first compressor **252** decreases from 7.6 MW to 0 MW (FIG. **9A**), propylene second compressor **264** decreases from 20.7 MW to 0 MW (FIG. **9B**), and propylene third compressor **272** decreases from 28.0 MW to 0 MW. Overall, the power demand for the compressors decreases from 66.8 MW for the ethylene and propylene refrigeration systems **204**, **208** alone (FIG. **5**) to 10.5 MW for the ethylene and propylene refrigeration systems **204**, **208** in combination with the three-level PCM energy storage system **400** (FIGS. **9A-9B**).

[0082] Table 2 summarizes the condenser power inputs during operation of the ethylene and propylene refrigeration systems, both alone and in combination with the three-level PCM energy storage system in its charging cycle and discharging cycle:

TABLE-US-00002 TABLE 2 Power Inputs & Outputs for Three-Level PCM System													
Three-level PCM No Charging			Discharging			Cycling			Cycle				
Base Refrig			Train - Shaft Power, MW										
Ethylene stage 1	3.7	3.7	3.7	Ethylene stage 2	6.8	6.8	6.8	Propylene stage 1	7.6	7.6	0.0		
Propylene stage 2	20.7	20.7	0.0	Propylene Stage 3	28.0	28.0	0.0	Base train shaft power, MW	66.8	66.8	10.5		
Charging Train - Shaft Power, MW			Ethylene stage 2	0.0	15.7	0.0	Propylene stage 1	0.0	14.8	0.0			
Propylene stage 2	0.0	28.7	0.0	Propylene Stage 3	0.0	33.8	0.0	Charging train shaft power, MW	0.0	93.0	0.0		
Total refrig train shaft power, MW			66.8	159.8	10.5	Added energy during charging, MW			93.0	Energy reduction during discharging, MW			
			56.3	Efficiency of power storage			60.5%	Power stored over 24 hour cycle, MWh					
			676										

[0083] In battery terms, the additional 93 MW of power used over the 12-hour charge period (1116 MWh) to charge a thermal “battery,” then during discharge reduces the amount of power needed to run refrigeration system **200** by 56.3 MW over the 12-hour discharge period (676 MWh), resulting in an efficiency of 60.5%. The efficiency is reduced at least in part by the modeled temperature spreads of (1) for the first PCM level, 27°C . between the charging temperature of -73°C . at evaporator **404** and the discharging temperature of -46°C . at condenser **408**; (2) for the second PCM level, 23°C . between the charging temperature of -46°C . at evaporator **420** and -23°C . at condenser **424**; and (3) for the third PCM level, 33°C . between the charging temperature of -23°C . at evaporator **436** and the discharging temperature of 10°C . at condenser **440**. In other implementations, that efficiency can be improved by reducing the magnitude of that temperature spread. Overall, the three-level system increases the thermal capacity of the PCM system by 24%, but the increased capacity comes with increased complexity and the corresponding cost of constructing the more-complex system.

Example 3: High-Efficiency Three-Level PCM System for Naphtha Cracker Ethylene & Propylene Refrigeration Systems

[0084] FIGS. **10A-10B** depict a schematic process diagram a modeled example **400a** of high-efficiency three-level PCM energy storage system for the ethylene and propylene refrigeration systems of FIG. **5** during a charge cycle of the PCM energy storage system; and FIGS. **11A-11B**

depict a schematic process diagram of PCM energy storage system **400a** during its discharge cycle. System **400a** is substantially similar to system **400**, with the primary exception being that system **400a** includes a separate refrigeration train **500** for charging the PCM reservoirs of system **400a**, and the PCM system condensers **408**, **424**, and **440** are therefore positioned in the second refrigeration train **500** with an ethylene refrigeration system **204a** and a propylene refrigeration system **208a**, as described in more detail below.

[0085] Ethylene refrigeration system **204a** is similar to ethylene refrigeration system **204**, with the primary exceptions that system **204a** omits the first compression stage (condenser **212**, compressor **216**, and valve **236**) and uses condenser **220a** to remove thermal energy from the PCM slurry or heat-transfer fluid of the first PCM level. Specifically, system **204a** includes one compressing stage with a evaporator **220a** and a compressor **224a**, and a single condensing stage with a first condenser **228a** and a second condenser **232a**. In operation, condensed ethylene from condensers **228a**, **232a** is routed to evaporator **220a**. In evaporator **220a**, the condensed ethylene absorbs thermal energy and boils to a gaseous state at a temperature of -60° C. and a pressure of 7.5 bara. The gaseous ethylene from evaporator **220a** is then routed to compressor **224a** where the gaseous ethylene is compressed to a pressure of 19.0 bara (Bar absolute) and temperature of 4° C. The compressed gaseous ethylene from compressor **224a** is then routed to the condensers, where it is partially condensed in first condenser **228a** and then further condensed in second condenser **232a**. In the depicted configuration, a heat transfer fluid is circulated through the first condenser **228a** to absorb thermal energy from the condensing ethylene for use in the propylene refrigeration system, and a heat-transfer fluid is also circulated through the second condenser **232a** to absorb additional thermal energy from the condensing ethylene also for use in the propylene refrigeration system. The ethylene refrigeration system also includes a valve **240a** that can be closed to prevent the flow of ethylene to evaporator **220a**.

[0086] Propylene refrigeration system **208a** includes three compressor stages and a condenser stage. The first compressing stage includes a first evaporator **244a**, parallel second evaporator **248a**, and a first compressor **252a**. The second compressing stage includes a third evaporator **256a**, a parallel fourth evaporator **260a**, and a second compressor **264a**. The third compressing stage includes a third compressor **272a**. The condenser stage includes a single condenser **276a**. In operation, condensed propylene from condenser **276a** is routed to the evaporators **244a**, **248a**, **256a**, **260a** of the first and second compressing stages, and directly to compressor **272a** of the third compressing stage. In first and second evaporators **244a**, **248a**, the condensed propylene absorbs thermal energy and boils to a gaseous state at a temperature of -37° C. and a pressure of 1.6 bara. As indicated by the dashed line from first condenser **228a** of ethylene refrigeration system **204a**, thermal energy from that first condenser **228a** is used as a source of thermal energy in evaporator **244a** to boil the propylene. The gaseous propylene is then routed to first compressor **252a** where the gaseous propylene is compressed to a first pressure of 4.3 bara and a temperature of 8.9° C. In third and fourth evaporators **256a**, **260a**, the condensed propylene absorbs thermal energy and boils to a gaseous state at a temperature of -10° C. and a pressure of 4.3 bara. As indicated by the dashed line from second condenser **232a** of ethylene refrigeration system **204a**, thermal energy from that second condenser **232a** is used as a source of thermal energy in evaporator **256a** to boil the propylene. This gaseous propylene from evaporators **256a**, **260a** is then mixed with the compressed propylene from first compressor **252a**, and the combined gaseous propylene is then routed to second compressor **264a**, where the combined gaseous propylene is further compressed to a second pressure of 8.6 bara and temperature of 38° C. In the third compression stage, the condensed propylene from condenser **276a** is mixed with the compressed propylene from second compressor **264a**, and the combined gaseous propylene is then routed to third compressor **272a**, where the combined gaseous propylene is further compressed to a third pressure of 18.3 bara and temperature of 78° C. The compressed gaseous propylene from third compressor **272a** is then routed to condenser **276a**, where it is condensed. The propylene refrigeration system also includes a first

valve **280a** that can be closed to prevent the flow of propylene to first and second evaporators **244a**, **248a**; a second valve **284a** that can be closed to prevent the flow of propylene to any of third and fourth evaporators **256a**, **260a** or first and second evaporators **244a**, **248a**; and a third valve **288a** that can be closed to prevent the flow of propylene to any of compressor **272a**, third and fourth evaporators **256a**, **260a**, or first and second evaporators **244a**, **248a**.

[0087] As noted above, PCM system **400a** is substantially similar to system **400**, with two primary exceptions. First, for charging the PCMs: in the first PCM level, evaporator **220a** of system **204a** is used instead of evaporator **404** (FIG. **8A**); in the second PCM level, evaporator **248a** is used instead of evaporator **420** (FIG. **8A**); and in the third PCM level, evaporator **260a** is used instead of evaporator **436**. Second, first PCM level includes a first pump **412a** for circulating PCM slurry or heat transfer fluid for “charging” and a second pump **412b** for circulating PCM slurry or heat-transfer fluid for “discharging;” the second PCM level includes a first pump **428a** for circulating PCM slurry or heat transfer fluid for “charging” and a second pump **428b** for circulating PCM slurry or heat-transfer fluid for “discharging;” and the third PCM level includes a first pump **444a** for circulating PCM slurry or heat transfer fluid for “charging” and a second pump **444b** for circulating PCM slurry or heat-transfer fluid for “discharging.” As modeled, the PCM used in the first level (PCM reservoir **416a**) has a freezing point of -50°C . and sufficient volume to store 672 MWh of energy, the PCM used in the second level (PCM reservoir **432**) has a freezing point of -29°C . and sufficient volume to store 547 MWh of energy, and the PCM used in the second level (PCM reservoir **448**) has a freezing point of 0°C . and sufficient volume to store 209 MWh of energy.

[0088] As shown in FIGS. **10A-10B**, during charging of PCM system **400a**, a PCM slurry or a heat transfer fluid is circulated between the ethylene or propylene refrigeration systems **204a**, **208**, **208a** and the respective PCM reservoir. In the first PCM level (FIG. **10A**), PCM slurry or a heat transfer fluid is circulated by pump **412a** from first PCM reservoir **416** to evaporator **220a**, where thermal energy is transferred from the PCM slurry or heat-transfer fluid to the ethylene at a temperature of -60°C . to boil the ethylene. The PCM slurry or heat-transfer fluid then returns to PCM reservoir **416** where the PCM slurry or heat-transfer fluid absorbs additional thermal energy from the PCM reservoir at the PCM's freezing point of -50°C ., and so on, until the PCM in PCM reservoir **416** is fully “charged” or solidified or charging is otherwise suspended. At the modeled charging rate, evaporator **220a** removes thermal energy from the heat-transfer fluid at a rate of 56.0 MW, such that during a 12-hour charging period, 672 MWh of energy is removed from PCM **416** reservoir. Stated another way, 672 MWh of cold or thermal capacity is “stored” such that PCM reservoir **416** can later absorb up to 672 MWh (less any inefficiencies, e.g., introduced by absorption of thermal energy from external sources) of thermal energy from the propylene refrigeration system when the PCM reservoir is “discharged.”

[0089] In the second PCM level, PCM slurry or a heat transfer fluid is circulated by pump **428a** from second PCM reservoir **432** to evaporator **248a**, where thermal energy is transferred from the PCM slurry or heat-transfer fluid to the propylene at a temperature of -37°C . to boil the propylene. The PCM slurry or heat-transfer fluid then returns to PCM reservoir **432** where the PCM slurry or heat-transfer fluid absorbs additional thermal energy from the PCM reservoir at the PCM's freezing point of -29°C ., and so on, until the PCM in PCM reservoir **432** is fully “charged” or solidified or charging is otherwise suspended. At the modeled charging rate, evaporator **248a** removes thermal energy from the heat-transfer fluid at a rate of 45.6 MW, such that during a 12-hour charging period, 547 MWh of energy is removed from PCM reservoir **432**. Stated another way, 547 MWh of cold or thermal capacity is “stored” such that PCM reservoir **432** can later absorb up to 547 MWh (less any inefficiencies, e.g., introduced by absorption of thermal energy from external sources) of thermal energy from the propylene refrigeration system when the PCM reservoir is “discharged.”

[0090] In the third PCM level (FIG. **10B**), PCM slurry or a heat transfer fluid is circulated by pump **444a** from third PCM reservoir **448** to evaporator **260a**, where thermal energy is transferred from

the PCM slurry or heat-transfer fluid to the propylene at a temperature of -10°C . to boil the propylene. The PCM slurry or heat-transfer fluid then returns to PCM reservoir **448** where the PCM slurry or heat-transfer fluid absorbs additional thermal energy from the PCM reservoir at the PCM's freezing point of 0°C ., and so on, until the PCM in PCM reservoir **448** is fully “charged” or solidified or charging is otherwise suspended. At the modeled charging rate, evaporator **436** removes thermal energy from the heat-transfer fluid at a rate of 17.4 MW, such that during a 12-hour charging period, 209 MWh of energy is removed from PCM reservoir **448**. Stated another way, 209 MWh of cold or thermal capacity is “stored” such that PCM reservoir **448** can later absorb up to 209 MWh (less any inefficiencies, e.g., introduced by absorption of thermal energy from external sources) of thermal energy from the propylene refrigeration system when the PCM reservoir is “discharged.”

[0091] As indicated by the differences between FIG. 5 and FIGS. 10A-10B, the compressors are required to input additional energy to provide the required compression to “charge” the PCM reservoir. Specifically, ethylene compressor **224a** of system **500** requires 11.1 MW (FIG. 10A), propylene first compressor **252s** requires 16.0 MW, propylene second compressor **264a** requires 17.8 MW (FIG. 10B), and propylene third compressor **272a** requires 26.5 MW. Overall, the power demand for the compressors increases from 66.8 MW for the ethylene and propylene refrigeration systems **204**, **208** alone (FIG. 5) to 138.2 MW for the ethylene and propylene refrigeration systems **204**, **208** in combination with refrigeration train **500** and three-level PCM energy storage system **400a** (FIGS. 10A-10B).

[0092] As shown in FIGS. 11A-11B, during discharging of PCM system **400a**, a PCM slurry or a heat transfer fluid is circulated between the propylene refrigeration system **208** and the respective PCM reservoir. In the first PCM level (FIG. 11A), PCM slurry or a heat transfer fluid is circulated by pump **412b** from first PCM reservoir **416** to condenser **408a**, where thermal energy is transferred from the propylene to the PCM slurry or heat-transfer fluid at a temperature of -46°C . to condense the propylene. The PCM slurry or heat-transfer fluid then returns to PCM reservoir **416** where the PCM reservoir absorbs thermal energy from the PCM slurry or heat-transfer fluid at the PCM's freezing point of -50°C ., and so on, until the PCM in PCM reservoir **416** is fully “discharged” or liquefied or charging is otherwise suspended.

[0093] In the second PCM level, PCM slurry or a heat transfer fluid is circulated by pump **428b** from second PCM reservoir **432** to condenser **424a**, where thermal energy is transferred from the propylene to the PCM slurry or heat-transfer fluid at a temperature of -23°C . to condense the propylene. The PCM slurry or heat-transfer fluid then returns to PCM reservoir **432** where the PCM reservoir absorbs thermal energy from the PCM slurry or heat-transfer fluid at the PCM's freezing point of -29°C ., and so on, until the PCM in PCM reservoir **432** is fully “discharged” or liquefied or charging is otherwise suspended.

[0094] In the third PCM level (FIG. 11B), PCM slurry or a heat transfer fluid is circulated by pump **444b** from third PCM reservoir **448** to condenser **440a**, where thermal energy is transferred from the propylene to the PCM slurry or heat-transfer fluid at a temperature of 10°C . to condense the propylene. The PCM slurry or heat-transfer fluid then returns to PCM reservoir **448** where the PCM reservoir absorbs thermal energy from the PCM slurry or heat-transfer fluid at the PCM's freezing point of 0°C ., and so on, until the PCM in PCM reservoir **448** is fully “discharged” or liquefied or charging is otherwise suspended.

[0095] As indicated by the differences between FIG. 5 and FIGS. 11A-11B, during PCM discharge, the compressors of propylene refrigeration system **208** are required to input less energy to provide the required compression to operate the refrigeration systems **204**, **208**. Specifically, propylene first compressor **252** decreases from 7.6 MW to 0 MW (FIG. 11A), propylene second compressor **264** decreases from 20.7 MW to 0 MW (FIG. 11B), and propylene third compressor **272** decreases from 28.0 MW to 0 MW. Overall, the power demand for the compressors decreases from 66.8 MW for the ethylene and propylene refrigeration systems **204**, **208** alone (FIG. 5) to 10.5 MW during PCM

discharge for the ethylene and propylene refrigeration systems **204**, **208** in combination with the three-level PCM energy storage system **400a** (FIGS. **11A-11B**).

[0096] The addition of the separate refrigeration train **500** for charging allows the temperatures differences to be reduced to improve efficiency of the PCM system. Table 4 shows the charging/discharging temperature differences between that three-level PCM system of FIGS. **8A-8B**, **9A-9B** and the high-efficiency three-level PCM system of FIGS. **10A-10B**, **11A-11B**. With the temperatures of the high-efficiency three-level system, the weighted average temperature difference is reduced from 26 to 15° C.

TABLE-US-00003 TABLE 4 Heat-Transfer Temperatures Temperatures of 3-level system, common pressures to existing train Total Charging PCM Discharging Delta Temp, ° C. Temp, ° C. Temp, ° C. Temp, ° C. Duty, MW Coldest PCM Level -73 -50 -46 27 56.0 Mid-PCM Level -46 -34 -23 23 45.6 Warmest PCM Level -23 -6 10 33 17.4 Weighted Average Delta Temp, ° C. 26.3 Temperatures of 3-level system, unique charging train pressures Total Charging PCM Discharging Delta Temp, ° C. Temp, ° C. Temp, ° C. Temp, ° C. Duty, MW Coldest PCM Level -60 -50 -46 14 56.0 Mid-PCM Level -37 -29 -23 14 45.6 Warmest PCM Level -10 0 10 20 17.4 Weighted Average Delta Temp, ° C. 14.9

[0097] Table 5 summarizes the condenser power inputs during operation of the ethylene and propylene refrigeration systems of Example 3, both alone and in combination with the three-level PCM energy storage system in its charging cycle and discharging cycle:

TABLE-US-00004 TABLE 5 Power Inputs & Outputs for HE Three-Level PCM System Three-level PCM High Efficiency No Charging Discharging Cycling Cycle Cycle Base Refrig Train - Shaft Power, MW Ethylene stage 1 3.7 3.7 3.7 Ethylene stage 2 6.8 6.8 6.8 Propylene stage 1 7.6 7.6 0.0 Propylene stage 2 20.7 20.7 0.0 Propylene Stage 3 28.0 28.0 0.0 Base train shaft power, MW 66.8 66.8 10.5 Charging Train - Shaft Power, MW Ethylene stage 2 0.0 11.1 0.0 Propylene stage 1 0.0 16.0 0.0 Propylene stage 2 0.0 17.8 0.0 Propylene Stage 3 0.0 26.5 0.0 Charging train shaft power, MW 0.0 71.4 0.0 Total refig train shaft power, MW 66.8 138.2 10.5 Added energy during charging, MW 71.4 Energy reduction during discharging, MW 56.3 Efficiency of power storage 78.9% Power stored over 24 hour cycle, MWh 676

[0098] In battery terms, the additional 71.4 MW of power used over the 12-hour charge period (857 MWh) to charge a thermal “battery,” then during discharge reduces the amount of power needed to run refrigeration system **200** by 56.3 MW of power over the 12-hour discharge period (676 MWh), resulting in an efficiency of 78.9%. The efficiency is therefore improved by the reductions in the modeled temperature spreads of (1) for the first PCM level, 14° C. between the charging temperature of -60° C. at evaporator **220a** and the discharging temperature of -46° C. at condenser **408a**; (2) for the second PCM level, 14° C. between the charging temperature of -37° C. at evaporator **248a** and -23° C. at condenser **424a**; and (3) for the third PCM level, 20° C. between the charging temperature of -10° C. at evaporator **260a** and the discharging temperature of 10° C. at condenser **440a**. Thus, the efficiency HE three-level system **400a** relative to three-level system **400** improves from 60.5% to 78.9%, although at the expense of added complexity and expense.

Examples 4-5: Ammonia Refrigeration Systems

[0099] Several examples were modeled for the use of the present PCM energy storage systems and methods to run refrigeration cycles for an ammonia refrigeration system that is representative of refrigeration systems used in a variety of chemical separation processes, such as, for example, ammonia synthesis. FIG. **13** depicts a schematic process diagram of an example **600** of such an ammonia refrigeration system. For these purposes, ammonia refrigeration system **600** was modeled with a cooling duty of 50 MW at -32° C. (1.05 bar evaporator pressure).

[0100] The typical or “existing” ammonia refrigeration system **600** includes three compressor stages. The first compressing stage includes a first evaporator **604**, a first compressor **608**, a first condenser **612**. The second compressing stage includes a first flash drum **616**, a second compressor **620**, and a second condenser **624**. The third compressing stage includes a second flash drum **628**, a

third compressor **632**, and a third condenser **636**. The ammonia refrigeration system also includes a first valve **640** that is used to let down the pressure from the first flash drum **616** to first condenser **604**, a second valve **644** that is used to let down the pressure from the second flash drum **628** to first evaporator **616**, and a third valve **648** that is used to let down the pressure from the third condenser **636** to flash drum **628**.

[0101] In operation, condensed ammonia from first flash drum **616** is routed to first evaporator **604** of the first compressing stage. In first evaporator **604**, the condensed ammonia absorbs thermal energy and boils to a gaseous state at a temperature of -32°C . and a pressure of 1.05 bara. The gaseous ammonia is then routed to first compressor **608** where the gaseous ammonia is compressed to a first pressure of 2.7 bara and a temperature of 44.2°C . In first condenser **612**, the compressed ammonia is cooled to a temperature of 35°C . at a pressure of 2.5 bara. In the second compressing stage, condensed ammonia from second flash drum **628** is routed to first evaporator **616**, and gaseous ammonia from first evaporator **616** is routed to mix with the ammonia exiting first condenser **612** to form a combined gaseous ammonia at a temperature of 31.2°C . at a pressure of 2.5 bara. The combined gaseous ammonia is then routed to second compressor **620** where the gaseous ammonia is compressed to a second pressure of 6.4 bara and a temperature of 121°C . In second condenser **624**, the compressed ammonia is cooled to a temperature of 35°C . at a pressure of 6.2 bara. In the third compressing stage, cooled ammonia from third condenser **636** is routed to second evaporator **628** of the compressing stage, and gaseous ammonia from second flash drum **628** is routed to mix with the ammonia exiting second condenser **624** to form a combined gaseous ammonia at a temperature of 35°C . at a pressure of 6.2 bara. The combined gaseous ammonia is then routed to third compressor **632** where the gaseous ammonia is compressed to a third pressure of 6.2 bara and a temperature of 121°C . In third condenser **636**, the compressed ammonia is condensed at a temperature of 35°C . at a pressure of 6.2 bara, and then routed to second flash drum **628** as described above.

[0102] In Example 4, the process is modeled with a “symmetric” cycle in which the PCM is “charged” for 12 hours, and “discharged” for 12 hours, during each 24 hour period, as shown in FIG. 12. In Example 5, the process is modeled with an “asymmetric” cycle in which the PCM is “charged” for 18 hours, and “discharged” for 6 hours, during each 24 hour period. Absorption of thermal energy from external sources (e.g., ambient) sources was not accounted for (assumed to be zero). In design of a real-world system, such external thermal energy can be accommodated by oversizing thermal capacity of PCM volume and compressor(s), taking into account particular insulation values. These models assumed the PCM to be directly dispersed in a slurry or encapsulated in small spheres within a slurry. Process simulations were performed in CHEMCAD, using the SRK method.

[0103] In each of Examples 4 and 5, the respective system is modeled with a separate refrigeration train for charging the PCM. These two systems were also modeled assuming the existing refrigeration train would be, or would be modified to be, driven by electric drivers (as opposed to burning fossil fuels), and assuming that the added PCM refrigeration train would also be driven by electric drivers.

Example 5: One-Level PCM System for 50 MW Ammonia Refrigeration System (Symmetric Charge & Discharge)

[0104] FIG. 14 depicts a schematic process diagram for the modeled example of a one-level PCM energy storage system **300a** for ammonia refrigeration system **600** of FIG. 13 during a charge cycle of the PCM energy storage system, and FIG. 15 shows PCM energy storage system **300a** during a discharge cycle. System **300a** is similar to system **300**, with the primary exception being that system **300a** includes a separate refrigeration train **600a** for charging the PCM reservoir of system **300a**, and the PCM system condenser **604a** is therefore disposed in the second refrigeration train **600a**, as described in more detail below. As shown, the addition of the PCM system includes adding a PCM system condenser **308a** to the first compression stage of ammonia refrigeration

system **600a**, with first PCM system condenser **308a** in parallel with first evaporator **604a**, a pump **312a** and a PCM reservoir **316a** and conduits and valves to route a heat-transfer fluid from the PCM to the PCM system evaporator and condenser.

[0105] PCM refrigeration system **600a** is similar to system **600** in that system **600a** includes three compressor stages, but uses propane as refrigerant instead of ammonia. The first compressing stage includes a first evaporator **604a** and a first compressor **608a**. The second compressing stage includes a first flash drum **616a** and a second compressor **620a**. The third compressing stage includes a second flash drum **628a**, a third compressor **632a**, and a condenser **636a**. The refrigeration system also includes a first valve **640a** that can be closed to prevent the flow of ammonia from first flash drum **616a** to first condenser **604a**, a second valve **644a** that can be closed to prevent the flow of ammonia from second flash drum **628a** to first flash drum **616a**, and a third valve **648a** that can be closed to prevent the flow of ammonia from condenser **636a** to flash drum **628a**.

[0106] In operation, condensed propane from first flash drum **616a** is routed to first evaporator **604a** of the first compressing stage. In first evaporator **604a**, the condensed propane absorbs thermal energy and boils to a gaseous state at a temperature of -41°C . and a pressure of 1.05 bara. The gaseous propane is then routed to first compressor **608a** where the gaseous propane is compressed to a first pressure of 2.7 bara and a temperature of -2°C . In the second compressing stage, condensed propane from second flash drum **628a** is routed to first flash drum **616a**, and gaseous propane from first flash drum **616a** is routed to mix with the propane exiting first compressor **608a** to form a combined gaseous propane at a temperature of -5°C . at a pressure of 2.7 bara. The combined gaseous propane is then routed to second compressor **620a** where the gaseous propane is compressed to a second pressure of 6.2 bara and a temperature of 33°C . In the third compressing stage, cooled propane from condenser **636a** is routed to second flash drum **628a** of the compressing stage, and gaseous propane from second flash drum **628a** is routed to mix with the propane exiting second compressor **620a** to form a combined gaseous propane at a temperature of 27°C . at a pressure of 6.2 bara. The combined gaseous propane is then routed to third compressor **632a** where the gaseous propane is compressed to a third pressure of 14.1 bara and a temperature of 66°C . In condenser **636a**, the compressed propane is condensed at a temperature of 39°C . at a pressure of 13.9 bara, and then routed to second flash drum **628a** as described above.

[0107] As shown in FIG. 14 during charging of PCM reservoir **316a**, a PCM slurry or a heat transfer fluid is circulated by pump **312a** from PCM reservoir **316a** to evaporator **604a**, where thermal energy is transferred from the PCM slurry or heat-transfer fluid to the propane at a temperature of -41°C . to boil the propane. The PCM slurry or heat-transfer fluid then returns to PCM **316a** where the PCM slurry or heat-transfer fluid absorbs additional thermal energy from the PCM reservoir at the PCM's freezing point of -37°C ., and so on, until the PCM is fully "charged" or solidified or charging is otherwise suspended. At the modeled charging rate, evaporator **604a** removes thermal energy from the PCM slurry or heat-transfer fluid at a rate of 50 MW, such that during a 12-hour charging period, 600 MWh of energy is removed from PCM **316a** reservoir. Stated another way, 600 MWh of cold or thermal capacity is "stored" such that the PCM reservoir can later absorb up to 600 MWh (less any inefficiencies, e.g., introduced by absorption of thermal energy from external sources) of thermal energy from ammonia refrigeration system **600** when the PCM reservoir is "discharged."

[0108] As indicated by the differences between FIG. 13 and FIG. 14, the compressors are required to input additional energy to provide the required compression to "charge" the PCM reservoir. Specifically, first compressor **608a** of system **600a** requires 7.0 MW (FIG. 14), second compressor **620a** requires 8.5 MW, and third compressor **632a** requires 11.1 MW. Overall, the power demand for the compressors increases from 22.5 MW for ammonia refrigeration system **600** alone (FIG. 13) to 49.1 MW for the ammonia refrigeration system **600** in combination with refrigeration train **600a** and PCM energy storage system **300a**.

[0109] As shown in FIG. 14, during discharging of PCM reservoir 316a, a PCM slurry or a heat transfer fluid is circulated by pump 312a from PCM reservoir 316a to condenser 308a in ammonia refrigeration system 600, where thermal energy is transferred from the ammonia to the PCM slurry or heat-transfer fluid at a temperature of -32°C . to condense the ammonia. The PCM slurry or heat-transfer fluid then returns to PCM 316a where the PCM reservoir absorbs thermal energy from PCM slurry or heat-transfer fluid at the PCM's freezing point of -37°C ., and so on, until the PCM is fully “discharged” or liquefied, or discharging is otherwise suspended. As indicated by the differences between FIG. 13 and FIG. 14, during PCM discharge, the compressors of ammonia refrigeration system 600 are required to input less energy to provide the required compression to operate ammonia refrigeration system 600. Specifically, first compressor 608 decreases from 5.8 MW to 0 MW, second compressor 620 decreases from 7.9 MW to 0 MW, and third compressor 632 decreases from 8.8 MW to 0 MW. Overall, the power demand for the compressors decreases from 66.8 MW for ammonia refrigeration system 600 alone (FIG. 13) to 0 MW during PCM discharge for refrigeration system 600 in combination with PCM energy storage system 300a (FIG. 14).

[0110] Table 6 summarizes the condenser power inputs during operation of the ammonia refrigeration system, both alone and in combination with the PCM energy storage system and additional PCM refrigeration system, in each of the PCM energy storage system's charging cycle and discharging cycle:

TABLE-US-00005

TABLE 6	Power Inputs & Outputs for One-Level PCM System w/Dedicated Refrigeration Train for Charging PCM	No Charging	Discharging	Cycling	Cycle	Shaft Power, MW
Ammonia stage 1	5.8	5.8	0.0	Ammonia stage 2	7.9	7.9
Ammonia stage 2	7.9	7.9	0.0	Ammonia stage 3	8.7	8.7
Ammonia stage 3	8.7	8.7	0.0	Propane stage 1	0.0	7.0
Propane stage 1	0.0	7.0	0.0	Propane stage 2	0.0	8.5
Propane stage 2	0.0	8.5	0.0	Propane stage 3	0.0	11.1
Propane stage 3	0.0	11.1	0.0	Total shaft power, MW	22.5	49.1
Total shaft power, MW	22.5	49.1	0.0	Total average shaft power, MW	24.5	Added energy during charging, MW
Added energy during charging, MW	26.6	Energy reduction during discharging, MW	22.5	Efficiency of power storage	84.6%	Power stored over 24 hour cycle, MWh
Efficiency of power storage	84.6%	Power stored over 24 hour cycle, MWh	270			

[0111] In battery terms, the additional 26.6 MW of power used over the 12-hour charge period (319 MWh) to charge a thermal “battery,” then during discharge reduces the amount of power required to run ammonia refrigeration system 600 by 22.5 MW over the 12-hour discharge period (270 MWh), resulting in an efficiency of 84.6%. This efficiency is higher than the foregoing examples, at least in part because of the smaller temperature difference between the PCM charging and PCM discharging temperatures, specifically the difference of 9°C . between the charging temperature of -41°C . at evaporator 604a and the discharging temperature of -32°C . at condenser 308a.

Example 6: One-Level PCM System for 50 MW Ammonia Refrigeration System (Asymmetric Charge & Discharge)

[0112] FIG. 16 depicts a schematic process diagram for a further modeled example 300b of one of the present one-level PCM energy storage systems for the ammonia refrigeration system of FIG. 13, during a charge cycle of the PCM energy storage system. PCM system 300b and PCM refrigeration train 600b are substantially similar to PCM system 300a and refrigeration train 600a, respectively, of FIGS. 14-15, with three primary exceptions. First, PCM energy storage system 300b is configured for asymmetric charge and discharge cycles, specifically, to be charged for an 18 hour period and discharged for a 6 hour period, in each 24 hour period. Second, because PCM system 300b need only run ammonia refrigeration system 600 for half the time (6 hours), PCM reservoir 316b has a thermal capacity of 300 MWh (one half that of PCM reservoir 316a). Third, because PCM refrigeration train 600a only needs to “charge” 300 MWh over 18 hours instead of 12 hours, the propane compressors 608a, 620a, and 632a need not compress propane at as high a rate as the corresponding compressors when used with PCM refrigeration system 300a.

Specifically, compressor 608a need only run at a rate of 2.3 MW (versus 7.0 MW when used with system 300a for a symmetric charge/discharge cycle), compressor 620a need only run at a rate of 2.8 MW (versus 8.1 MW when used with system 300a for a symmetric charge/discharge cycle), and compressor 632a need only run at a rate of 3.7 MW (versus 8.8 MW when used with system

300a for a symmetric charge/discharge cycle). As such, either smaller-capacity compressors can be used for compressors **608a**, **620a**, **632a**, potentially reducing costs, or the same-sized compressors can be used and simply operated at lower rates of compression. Where budget permits, the relatively larger size of the system in Example 5 allows for greater flexibility because that larger system can also be operated on an asymmetric schedule, such as 18 hours charge and 6 hours discharge, or 14 hours charge and 10 hours discharge, in which case the discharge cycle will deplete only part of the thermal capacity of the PCM reservoir.

[0113] Table 7 summarizes the condenser power inputs during operation of the ammonia refrigeration system of Example 6, both alone and in combination with the PCM energy storage system and additional PCM refrigeration system, in each of the PCM energy storage system's charging cycle and discharging cycle:

TABLE-US-00006 TABLE 7 Power Inputs & Outputs for Asymmetrically Cycled One-Level PCM System w/Dedicated Refrigeration Train for Charging Single-level PCM No Charging Discharging Cycling Cycle Cycle Number of hours per day on cycle N/A 18 6 Shaft Power, MW Ammonia stage 1 5.8 5.8 0.0 Ammonia stage 2 7.9 7.9 0.0 Ammonia stage 3 8.7 8.7 0.0 Propane stage 1 0.0 2.3 0.0 Propane stage 2 0.0 2.8 0.0 Propane stage 3 0.0 3.7 0.0 Total shaft power, MW 22.5 31.3 0.0 Total average shaft power, MW 23.5 Added energy during charging, MWh 159 Energy reduction during discharging, MWh 135 Efficiency of power storage 85.2% Power stored over 24 hour cycle, MWh 135

[0114] In battery terms, the additional 8.8 MW of power used over the 18-hour charge period (159 MWh) to charge a thermal “battery,” then during discharge reduces the amount of power required to run ammonia refrigeration system **600** by 22.5 MW over the 6-hour discharge period (135 MWh), resulting in an efficiency of 85.2%. This efficiency is roughly the same as the system of Example 6, but the longer charging period and reduced PCM capacity reduce the size of the PCM refrigeration system **600a** by roughly two-thirds.

[0115] The above specification and examples provide a complete description of the structure and use of exemplary embodiments. Although certain embodiments have been described above with a certain degree of particularity, or with reference to one or more individual embodiments, those skilled in the art could make numerous alterations to the disclosed embodiments without departing from the scope of this invention. As such, the various illustrative embodiments of the present devices are not intended to be limited to the particular forms disclosed. Rather, they include all modifications and alternatives falling within the scope of the claims, and embodiments other than the one shown may include some or all of the features of the depicted embodiment. For example, components may be combined as a unitary structure, and/or connections may be substituted. Further, where appropriate, aspects of any of the examples described above may be combined with aspects of any of the other examples described to form further examples having comparable or different properties and addressing the same or different problems. Similarly, it will be understood that the benefits and advantages described above may relate to one embodiment or may relate to several embodiments.

[0116] The claims are not intended to include, and should not be interpreted to include, means-plus- or step-plus-function limitations, unless such a limitation is explicitly recited in a given claim using the phrase(s) “means for” or “step for,” respectively.

Claims

1. A system for storing energy for refrigeration in a chemical separation process of a chemical plant, the system comprising: one or more thermally insulated vessels; a phase change material (PCM) disposed in the thermally insulated vessel(s); a refrigerant circuit configured to circulate a refrigerant fluid in thermal communication with the PCM such that the PCM absorbs thermal energy from the refrigerant fluid at a point in a refrigeration cycle of the process; where the PCM is

configured to transition from an initial state to a higher enthalpy state at a transition temperature that is below a lowermost working temperature at the point in the refrigeration cycle; and where the PCM requires at least 10 MWh to transition from the initial state to the higher enthalpy state.

2. The system of claim 1, where the refrigerant circuit is part of a refrigeration system that comprises a compressor configured to compress the refrigerant fluid such that the refrigerant fluid can be circulated to receive thermal energy in the process.

3. The system of claim 2, where the refrigerant fluid is a first refrigerant fluid and the refrigerant circuit is a first refrigerant circuit, and the system further comprises: a PCM refrigeration circuit comprising a compressor, and a second refrigerant circuit configured to circulate a second refrigerant fluid in thermal communication with a the PCM such that the second refrigerant fluid absorbs thermal energy from the PCM.

4. The system of claim 3, where the compressor is electric.

5. The system of claim 1, where the PCM has a phase transition below a temperature range from -170°C. to 40°C.

6. The system of claim 1, where the one or more thermally insulated vessels comprises a first thermally insulated vessel(s) and the PCM is a first PCM, and the system further comprises: one or more second thermally insulated vessels; a second phase change material (PCM) disposed in the second thermally insulated vessel(s), the second PCM configured to transition from an initial state to a higher enthalpy state at a second transition temperature that is above the transition temperature of the first PCM; where the second PCM requires at least 10 MWh to transition from the initial state to the higher enthalpy state.

7. The system of claim 1, where the PCM comprises one or more component selected from the group of components consisting of: a paraffinic hydrocarbon; an alcohol; polydimethylsiloxane; water; an aqueous salt solution; a water-salt mixture; an organic chemical; a mixture of two or more organic chemicals; a eutectic mixture of two or more organic chemicals; and a mixture of two or more inorganic chemicals.

8. The system of claim 7, where the PCM comprises a water-salt mixture that comprises one or more components selected from the group of components consisting of: calcium dichloride (CaCl.sub.2); calcium dichloride (CaCl.sub.2); lithium chloride (LiCl); magnesium chloride (MgCl.sub.2); zinc chloride (ZnCl.sub.2); hydrogen chloride (HCl); lithium sulfate (Li.sub.2SO.sub.4); sodium chloride (NaCl); potassium chloride (KCl); aluminum nitrate ($\text{Al(NO.sub.3).sub.3}$); combinations of any two or more of the foregoing components.

9. The system of claim 1, where the PCM is in a form selected from the group of forms consisting of: a slurry in which the PCM is directly suspended in a liquid within the insulated vessel(s); an encapsulated slurry in which the PCM is encapsulated in casings that are suspended in a liquid within the insulated vessel(s); and a plurality of containers each containing a portion of the slurry and including at least one heat-transfer surface configured to permit thermal communication with the PCM.

10. The system of claim 9, where the PCM is in a slurry or encapsulated slurry form and the system is configured to agitate the PCM within the insulated vessel(s).

11. The system of claim 10, where the process is selected from the group of processes consisting of: a steam cracking process, an ammonia synthesis process, a hydrogen production process, a para-xylene production process, propane dehydrogenation, olefin metathesis, and natural gas processing.

12. A method of storing energy for refrigeration in a chemical separation process of a chemical plant, the method comprising: during a discharge cycle, circulating a refrigerant fluid in thermal communication with a phase-change material (PCM) such that the PCM absorbs thermal energy from the refrigerant fluid at a point in a refrigeration cycle of the process; where the PCM is configured to transition from an initial state to a higher enthalpy state at a transition temperature that is below a lowermost working temperature of the refrigerant at the point in the refrigeration

cycle; and where the PCM absorbs at least 10 MWh of energy from the refrigerant fluid during a 24-hour period.

13. The method of claim 12, where a 24-hour period includes one or more discharge cycles lasting a total 2-22 hours, and one or more recharge cycles lasting a total of 2-22 hours.

14. The method of claim 13, where the lengths of the recharge and discharge cycles are adjusted or selected based on a methodology selected from the group of methodologies consisting of: in response to a request from a power grid operator to reduce consumption of electric power; to reduce the total cost of electricity to continuously run the process over the 24-hour period, taking into account variations in the price of electricity over the 24-hour period; and in response to a temporary outage of at least one source of electricity to the process.

15. The method of claim 14, further comprising: during the recharge cycle, operating a compressor to simultaneously cool the refrigerant fluid that is circulated in thermal communication with the PCM and refrigerant fluid that is used in a propylene or ethylene refrigeration system for the process.

16. The method of claim 12, further comprising adjusting the rate at which the PCM is absorbing thermal energy from the refrigerant fluid.

17. The system of claim 2, wherein the refrigeration system is configured to: receive cooled refrigerant fluid from the refrigeration system; and circulate the cooled refrigerant fluid through the refrigerant circuit such that the refrigerant fluid absorbs thermal energy from the PCM.

18. The system of claim 2, wherein the refrigeration system is configured to: receive warmed refrigerant fluid from the process; and circulate the warmed refrigerant fluid through the refrigerant circuit such that the PCM absorbs thermal energy from the warmed refrigerant fluid.

19. The system of claim 9, where the PCM is in a slurry form and directly suspended in a liquid within the insulated vessel(s), a nucleating agent is added to the liquid.

20. The system of claim 6, where the first PCM and the second PCM are configured to together require at least 100 MWh to transition from the initial state to the higher enthalpy state.
