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(54) **THERMAL ENERGY STORAGE USING SUPERCRITICAL FLUIDS**

(75) Inventor: **GANI B. GANAPATHI**, La Crescenta, CA (US)

(73) Assignee: **California Institute of Technology,** Pasadena, CA (US)

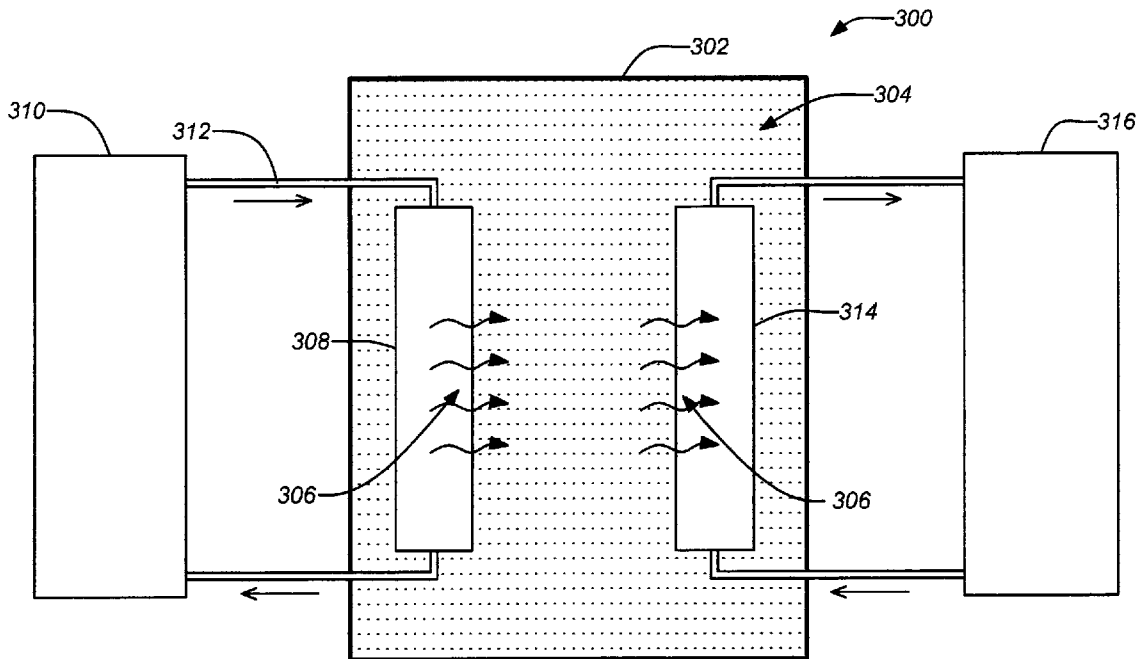**Publication Classification**

(57) **ABSTRACT**

A thermal energy storage system is described employing latent heat storage of a supercritical fluid instead of typical phase change materials. Two fundamental thermodynamic concepts are invoked. First, by using the latent heat of liquid/vapor phase change, high energy density storage is feasible. Second, by operating the thermal energy storage system at a higher pressure, the saturation temperature is increased to operate at molten salt temperatures and above. Beyond the two-phase regime, supercritical operation permits capturing and utilizing heat taking advantage of latent and sensible heat, both in the two-phase regime as well as in supercritical regime while at the same time, reducing the required volume by taking advantage of the high compressibilities.
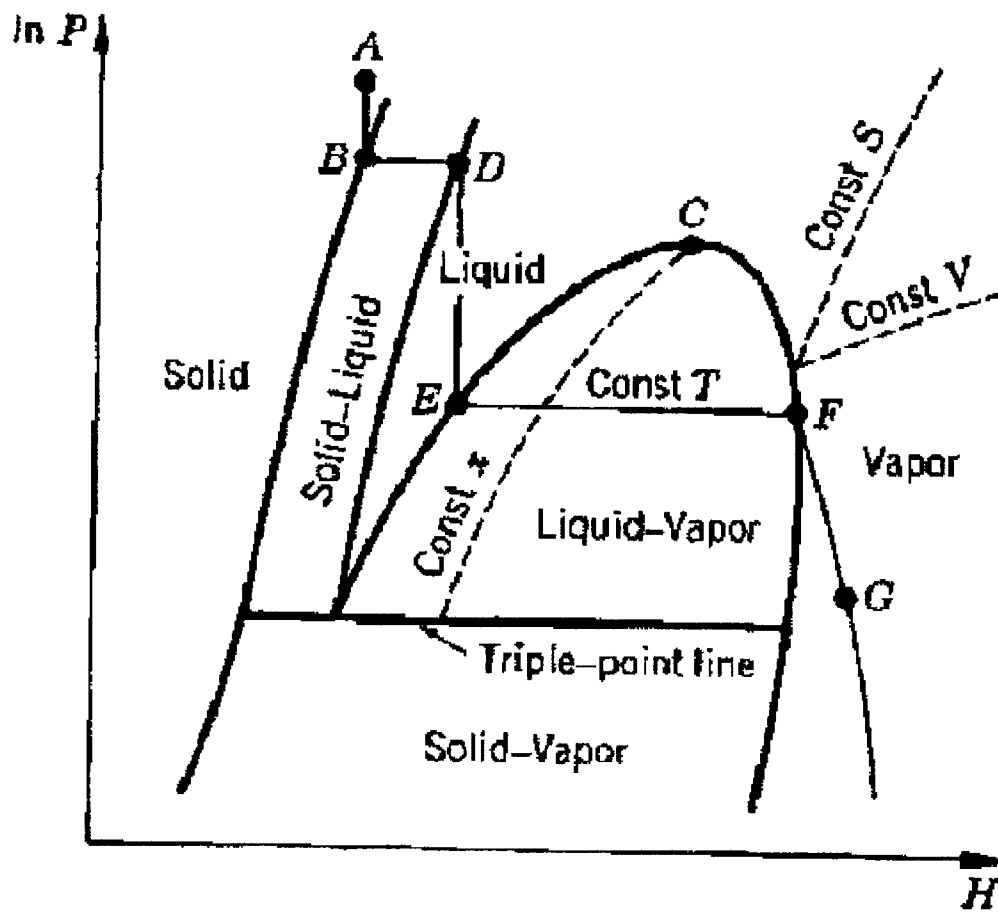
FIG. 1A

Thermodynamic Properties for Selected Supercritical TES Working Fluid Candidates.

Fluid Name	T_c (K)	T_c (°C)	T_b (K)	T_b (°C)	H_{vap} (cal/gm-mole)	MW (gm)	H (at 384 °C)
Pthalic Anhydride	810	537	560	287	11850	148.118	9563
Benzoic Acid	752	479	523	250	12100	122.124	8236
Naphthalene	748.4	475.4	491	218	10340	128.174	6732
3,4 Xylenol	729	456	500	227	11900	124.126	7241
Glycerol	726	453	563	290	14600	92.095	9680
Iodobenzene	721	448	4614	188.4	9440	204.011	5361

FIG. 1B
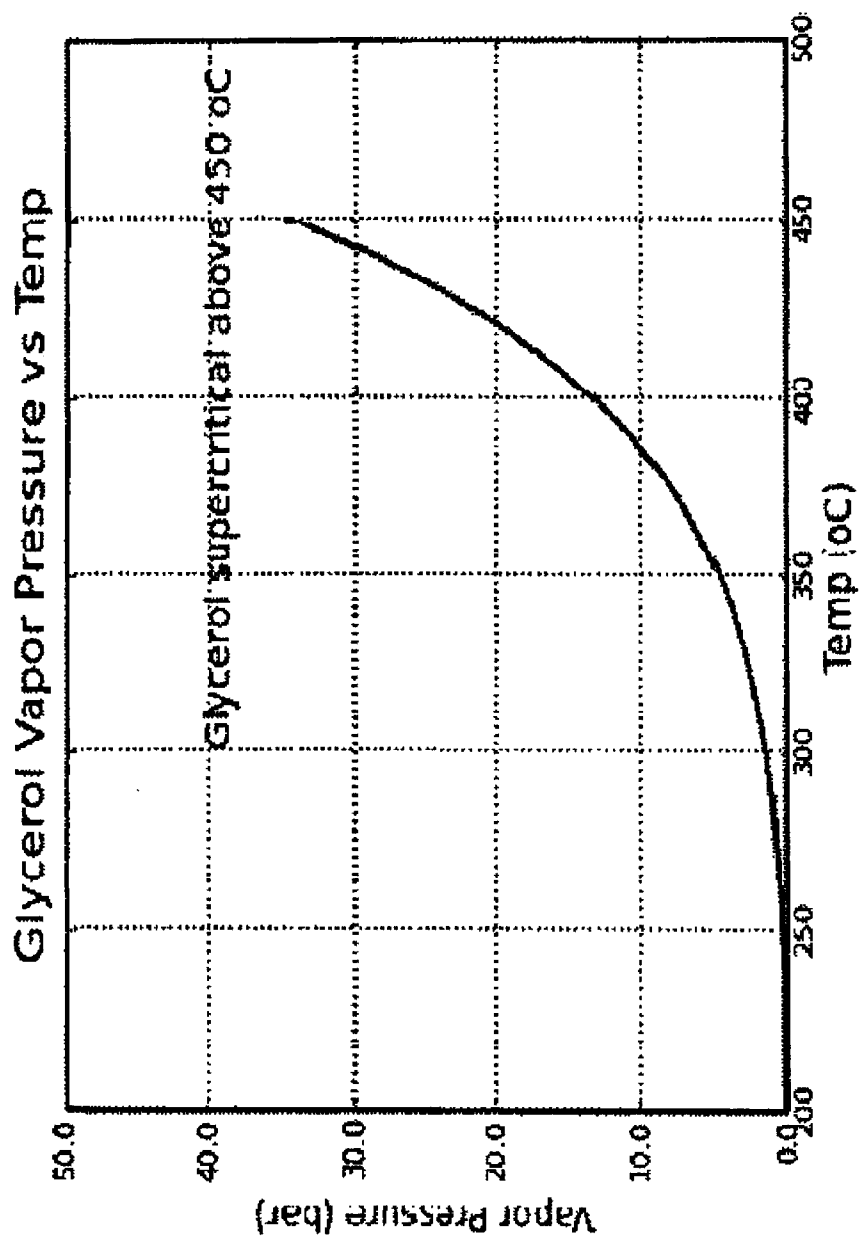
FIG. 1C

	MoltenSalt	Glycerol
Cost/kg ($)	1.00 – 2.00	0.25
Material amt (1010 MWh storage)	28500	10000
Material cost ($M)	28.5 – 47.0	2.5
Material cost/kWh	28 – 47	2.5
Total plant cost estimate ($/kWh)	40 – 60	?

FIG. 1D

Moderate Temperature Application (T_{cold} = 373K, T = 100K)		
	Specific Storage (kJ/kg)	Volumetric Storage Capacity (kJ/m³) (vapor press at 200 °C)	$/kWh ($/kg)
Compressed water	418	362,000 (15 atm)	Negligible
Therminol (VP-1)	229	228,700 (<1 atm)	78 ($5/kg)
Glycerol	241	303,850 (<1 atm)	8 ($0.55/kg)
Naphthalene	200	216,609 (<1 atm)	16 ($1/kg)
High Temperature Application (T_{cold} = 563K, T = 100K)		
Supercritical Glycerol	720	324,741 (66 atm, z = 0.25)	2.75 ($0.55/kg)
Supercritical naphthalene	541	387,122 (66 atm, z = 0.219)	6.50 ($1.00/kg)
Molten Salt (NaNO₃, KNO₃)	145	129,860 (2 tanks)	25 – 50 ($1-$2/kg)

FIG. 2

FIG. 3A

FIG. 3B

Start

400

Store a storage fluid within a pressurized storage vessel.

402

Occasionally transfer heat energy between the storage fluid and at least one working fluid with at least one heat exchanger coupled to the pressurized storage vessel and in contact with the storage fluid such that the storage fluid changes from a two-phase state to a supercritical state as the heat energy is transferred from the at least one working fluid to the storage fluid and the storage fluid changes back to the two-phase from the supercritical state as the heat energy is transferred from the storage fluid to the at least one working fluid.
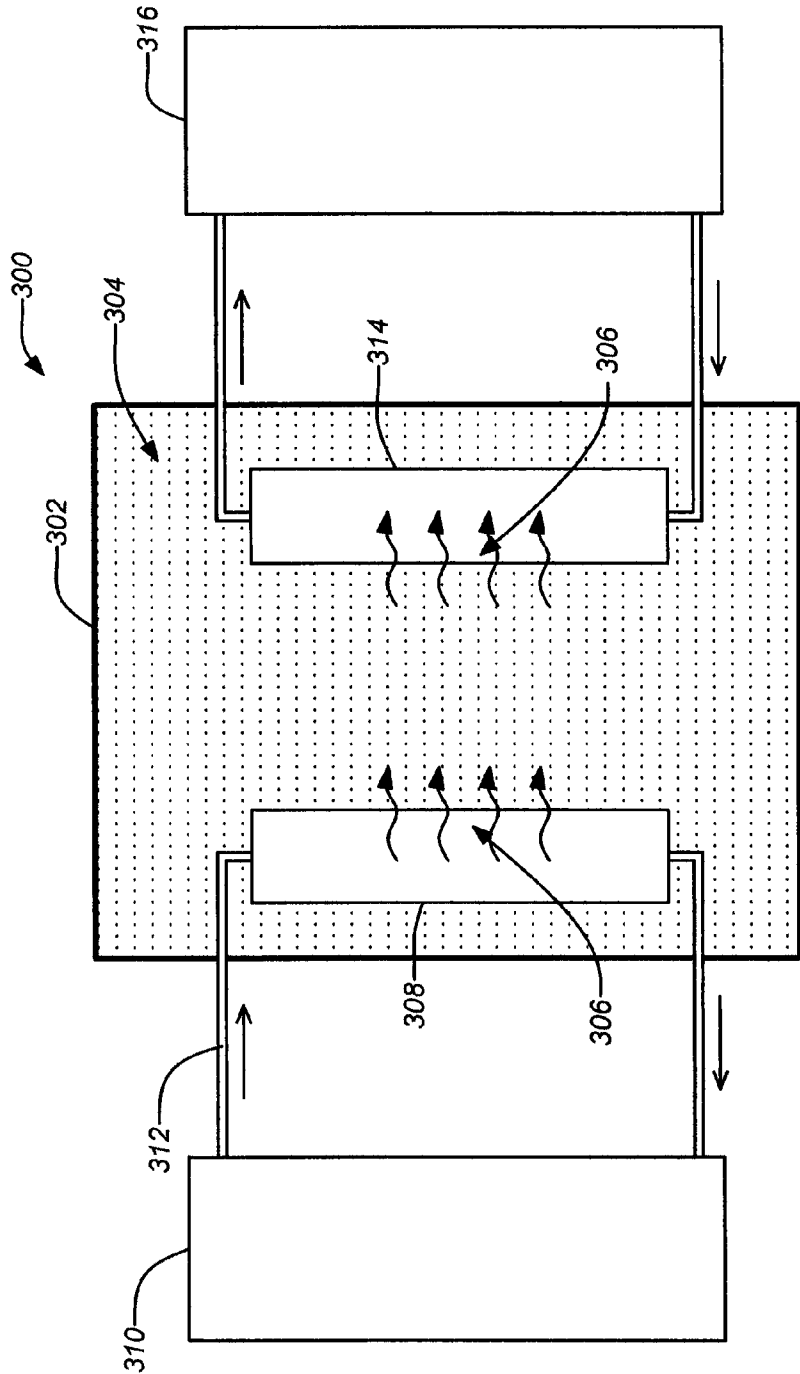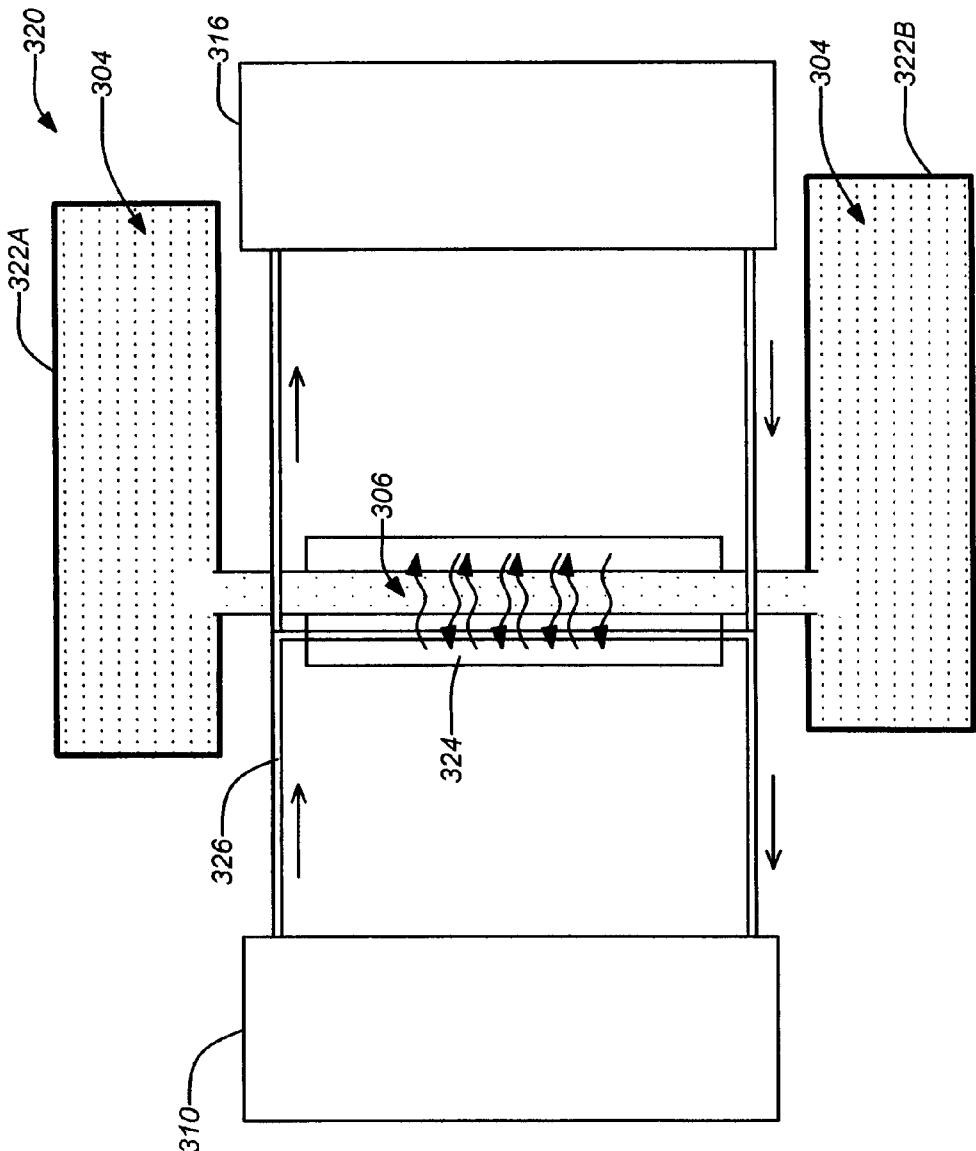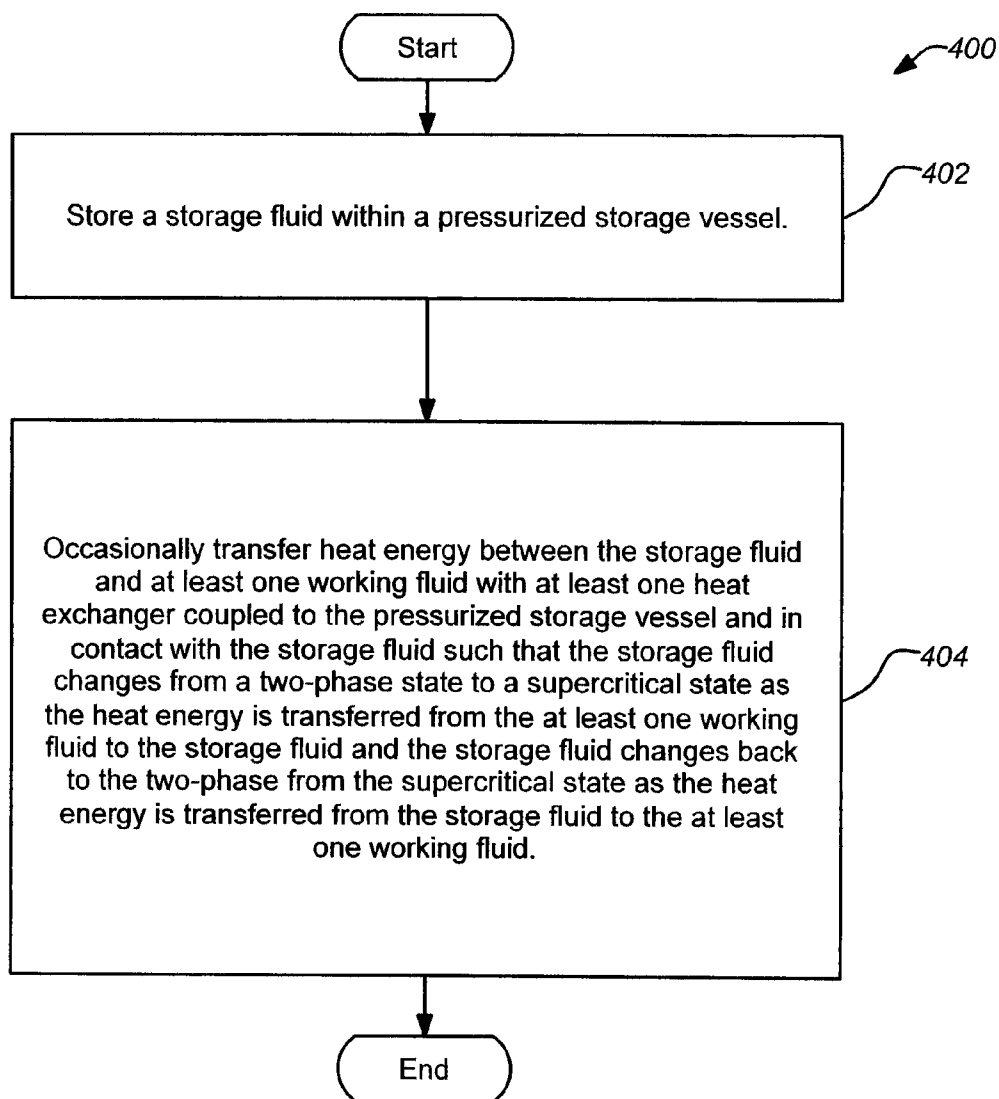
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End

FIG. 4

THERMAL ENERGY STORAGE USING SUPERCRITICAL FLUIDS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit under 35 U.S.C. §119(e) of the following U.S. provisional patent application, which is incorporated by reference herein:

[0002] U.S. Provisional Patent Application No. 61/384,635, filed Sept. 20, 2010, and entitled "Thermal Energy Storage with Supercritical Fluids", by Ganapathi (Attorney Docket CIT-5441-P2).

STATEMENT OF GOVERNMENT RIGHTS

[0003] The invention described herein was made in the performance of work under a NASA contract, and is subject to the provisions of Public Law 96-517 (35 USC 202) in which the Contractor has elected to retain title.

BACKGROUND OF THE INVENTION

[0004] 1. Field of the Invention

[0005] This invention relates to thermal energy storage systems. Particularly, this invention relates to thermal energy storage systems using supercritical fluids as the storage medium.

[0006] 2. Description of the Related Art

[0007] Solar thermal power (also referred to as Concentrated Solar Power [CSP]) is currently viewed as one of the most cost effective options to convert solar radiation into electricity. Example systems employing solar thermal power have been operationally proven in California since the mid-1980s. In 1984, the first solar electric generating systems (SEGS) plant was installed in southern California by Luz International, Inc. The most recently commissioned plant was in 2008, a 64 MW plant, called the Nevada Solar One. Purchase agreements for nearly 1 GW of solar thermal from the Nevada Solar One have been completed, or are in the final stages, in the southwest U.S.

[0008] One advantage of parabolic trough solar power plants is their potential for storing solar thermal energy for use during non-solar periods and to dispatch the energy when it is most needed. As a result, thermal energy storage (TES) allows parabolic trough solar power plants to achieve higher annual capacity factors—from approximately 25% without thermal storage up to 70% or more with it. Other related advantages include the capability of buffering during transient weather conditions, improved dispatchability or time-shifting, more even distribution of electricity production and capability to achieve full load operation of the steam cycle at high efficiency.

[0009] Thermal energy storage systems are broadly rated on the following technical requirements. High energy density of the storage material (per-unit mass or per-unit volume) and good heat transfer between heat transfer fluid (HTF) and the storage medium are primary rating factors. In addition, mechanical and chemical stability of storage material and chemical compatibility between HTF, heat exchanger and/or storage medium are important considerations. Complete reversibility for a large number of charging/discharging cycles, low thermal losses, and ease of control are also considerations. See e.g., Herrmann et al., "Overview on Thermal Storage Systems," FLABEG Solar Int. GmbH, Dave Kearney (Kearney & Assoc), which is incorporated by reference

herein. In terms of cost, cost of the storage material itself, heat exchanger for charging and discharging the system and the cost for the space and the enclosure for the thermal energy storage are the important factors.

[0010] In general, there are three mechanism types for thermal energy storage. These mechanisms can be broadly classified as under sensible heat storage, latent heat storage and chemical energy storage. Storage and removal of energy using sensible heat storage involves merely a temperature change of the storage medium in either solid, liquid or gasous form. Storage and removal of energy using latent heat storage involves a state change of the storage medium, e.g. liquid to gas. Storage and removal of energy using chemical energy storage involves a chemical change in the storage medium, e.g. burning hydrogen. Some different specific energy storage systems that have been studied include two-tank direct, two-tank indirect, single-tank thermocline, and thermal energy storage media. See http://www.nrel.qov/csp/trouqhnet/thermal_energy_storage.html.

[0011] One example two-tank direct system used mineral oil (Caloria) heat transfer fluid which was also used to store energy for later use (hence the term "direct"). It was first demonstrated in the Luz trough plant, SEGS and operated between 1985 and 1999 to dispatch solar power to meet Southern California Edison (SCE) winter evening peak demand period needs. The fluid was later replaced with Therminol VP-1, which is a higher temperature fluid (but unfortunately, a higher vapor pressure fluid as well). The operating temperature of these systems is limited to less than approximately 370° C.

[0012] Another demonstrated energy storage system is the two-tank indirect system. The term "indirect," refers to the fact that the storage fluid is different from the HTF. The heat from the HTF is transferred to one of the tanks which is then transferred to the power generation system when needed by discharging the fluid into another tank through the use of heat exchangers. Molten salt eutectic mixtures of $NaNO_3$ and KNO_3 are used for the storage medium. Due to its development maturity, this system is currently favored over the other options even though the costs of the storage fluid are very high. The most advanced implementation of its type is the Andasol 1 plant in Spain, with a storage capacity of 1 GWh (under 7.5 hr full load operation).

[0013] In a single-tank thermocline system, a single tank stores both the hot fluid as well as the cold fluid, operating on the principle that a hot fluid is lighter than cold and will remain at the top of the tank. Sandia National Laboratories has demonstrated a 2.5 MWh packed-bed thermocline system with molten salt fluid and quartzite rock and sand for filler material. The cost of such a system depends on the storage fluid cost. The system has to be well designed to maintain the thermocline zone (the zone between the hot and cold fluids) so that it does not expand to fill the entire tank, at which point the system is no longer operational.

[0014] One other tested form of thermal energy storage employs a thermal energy storage (TES) medium. Solid TES media such as concrete, castable ceramic materials are being considered as potential TES candidates. This option is primarily driven by the low cost of the solid media itself as well as other advantages, such as long life. In this case, an HTF passes through an array of pipes embedded in the solid medium to transfer the thermal energy to and from the medium during plant operations. The German Aerospace

Center (DLR) and Ciemat have performed initial testing of castable ceramic and high-temperature concrete in a thermal energy storage system.

[0015] All the technologies described above rely on sensible heat energy. In contrast, phase change materials (PCMs) rely on the latent heat energy and can therefore store very large amounts of heat. The DOE had studied the possibility of using PCM for heat storage in the 1980's, but did not pursue it further primarily due to the complexities of the required system and the operational uncertainty over lifetime of the PCMs. Work performed by Luz International Ltd. on the use of low temperature salts such as $NaNO_3$, KNO_3, and KOH indicated that the performance of the materials degrade after a moderate number of freeze-melt cycles. Additionally, the heat transfer characteristics for PCMs have two major problems. They have relatively poor thermal conductance across regions of solid PCM compared to convective heat transfer in the heat transfer fluid (HTF). In addition, there is a "pinch-point" problem which refers to the relatively small temperature differences between the PCM and the charging or discharging HTF which occurs in the heat exchanger where the PCM is just dropping below or rising above the phase change temperature. At these points, large heat transfer areas are needed for the transfer of heat due to the small temperature differences.

[0016] More recently, the DOE has reinitiated funding for TES and HTF and has funded several proposals, representing approximately $68M in 2008, to look at alternate technologies as well as address many of the problems with prior approaches. However, the proposed technologies were either sensible heat-based approaches or very advanced technologies, where it is not clear whether such technologies will deliver adequate low-cost energy storage.

[0017] The U.S. Department of Energy (DOE) has identified improved thermal energy storage (TES) as the most critical technology development needed to allow solar thermal power to replace non-renewable power generation sources (e.g. coal and gas). The DOE estimates that the cost of TES must be around $20/kWh or better to make a significant impact on power production with CSP by bringing the cost down from current 11-13¢/kWh to approximately 7¢/kWh by 2015 with 6 hours of storage for intermediate power markets and to approximately 5¢/kWh by 2020 with 16 hours of storage for baseload power markets. The currently favored thermal storage option is two-stage indirect storage with molten salts (eutectic mixtures of $NaNO_3$ and KNO_3) for which the fluid costs alone range from $27-$54/kWh.

[0018] In view of the foregoing, there is a need in the art for improved apparatuses and methods for energy storage. There is particularly a need for such apparatuses and methods using supercritical fluids. In addition, such suitable systems and methods are needed that are capable of achieving the DOE cost goal of $20/kWh. In addition, such systems and methods are needed to address many of the issues faced by the current baseline approach of a two-tank molten salt storage. These and other needs are met by embodiments of the present invention as detailed hereafter.

SUMMARY OF THE INVENTION

[0019] A thermal energy storage system is described employing latent heat storage of a supercritical fluid instead of typical phase change materials. Two fundamental thermodynamic concepts are invoked. First, by using the latent heat of liquid/vapor phase change, high energy density storage is feasible. Second, by operating the thermal energy storage system at a higher pressure, the saturation temperature is increased to operate at molten salt temperatures and above. Beyond the two-phase regime, supercritical operation permits capturing and utilizing heat taking advantage of latent and sensible heat, both in the two-phase regime as well as in supercritical regime while at the same time, reducing the required volume by taking advantage of the high compressibilities.

[0020] A typical embodiment of the invention comprises a thermal energy storage apparatus, including a pressurized storage vessel, a storage fluid within the pressurized storage vessel, and at least one heat exchanger coupled to the pressurized storage vessel and in contact with the storage fluid to occasionally transfer heat energy between the storage fluid and at least one working fluid. The storage fluid changes from a two-phase state to a supercritical state as the heat energy is transferred from the at least one working fluid to the storage fluid and changes back to the two-phase from the supercritical state as the heat energy is transferred from the storage fluid to the at least one working fluid. The storage fluid in a discharged state (when substantially all heat energy has been extracted to perform work) is in a two-phase state comprising liquid and vapor. In its charged state (heat storage mode), the storage fluid has been converted to a supercritical state where the energy is stored as heat at a pressures and temperatures above the fluid critical point.

[0021] In some embodiments, at least one of the heat exchangers is disposed within the pressurized storage vessel. The working fluid may comprise a heat source working fluid such that the heat exchanger within the pressurized storage vessel receives the heat source working fluid to transfer the heat energy from the heat source working fluid to the storage fluid. In one example, the heat source working fluid may be coupled to a solar thermal plant. Similarly, the working fluid may comprise a heat sink working fluid such the heat exchanger within the pressurized storage vessel receives the heat sink working fluid to transfer the heat energy from the storage fluid to the heat sink working fluid. For example, the heat sink working fluid may be coupled to a steam generator generating electrical power.

[0022] A number of suitable storage fluids have been identified. For example, the storage fluid may comprise glycerol, pthalic anhydride, benzoic acid, 3,4 xylenol, or iodobenzene. In addition, the storage fluid may comprise a polyaromatic hydrocarbon (PAH) such as naphthalene, methylnaphlene, dimethylnapthalene, or biphenyl. In addition, ionic fluids present another class of suitable working fluids. Glycerol and naphthalene are currently identified as strong options.

[0023] A typical method embodiment of the invention comprises storing a storage fluid within a pressurized storage vessel, and occasionally transferring heat energy between the storage fluid and at least one working fluid with at least one heat exchanger coupled to the pressurized storage vessel and in contact with the storage fluid such that the storage fluid changes from a two-phase state to a supercritical state as the heat energy is transferred from the at least one working fluid to the storage fluid and the storage fluid changes back to the two-phase from the supercritical state as the heat energy is transferred from the storage fluid to the at least one working fluid. This method embodiment of the invention may be further modified consistent with the apparatus embodiments described herein.

[0024] Another typical embodiment of the invention may comprise a thermal energy storage apparatus, including a pressurized storage vessel means for storing a storage fluid means for storing heat energy, and at least one heat exchanger means for occasionally transferring the heat energy between the storage fluid means and at least one working fluid means for transferring the heat energy, the at least one heat exchanger means coupled to the pressurized storage vessel means and in contact with the storage fluid means. The storage fluid means changes from a two-phase state to a supercritical state as the heat energy is transferred from the at least one working fluid to the storage fluid and changes back to the two-phase from the supercritical state as the heat energy is transferred from the storage fluid to the at least one working fluid. This embodiment of the invention may be further modified consistent with the apparatus or method embodiments described herein.

BRIEF DESCRIPTION OF THE DRAWINGS

[0025] Referring now to the drawings in which like reference numbers represent corresponding parts throughout:

[0026] FIG. 1A is an exemplary phase diagram of a pure component;

[0027] FIG. 1B is table showing thermodynamic properties for selected supercritical thermal energy storage fluid;

[0028] FIG. 1C shows the vapor pressure of glycerol as a function of temperature;

[0029] FIG. 1D shows a table summarizing a comparison of using pressurized and glycerol in a supercritical state compared to the reference case of the molten salt thermal energy storage system;

[0030] FIG. 2 shows a table of sample calculation results for glycerol and naphthalene as representative storage fluids in a supercritical fluid thermal energy storage system;

[0031] FIG. 3A is schematic drawing an exemplary thermal energy storage apparatus using a single tank according to an embodiment of the invention;

[0032] FIG. 3B is schematic drawing an exemplary thermal energy storage apparatus using two tanks according to an embodiment of the invention; and

[0033] FIG. 4 is a flowchart of an exemplary method of storing thermal energy storage according to an embodiment of the invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[0034] 1. Overview

[0035] A new thermal energy storage system has been proposed using pressurized supercritical fluids, which provides numerous advantages including a simpler system design, much lower fluid storage costs, improved system performance overall. Working with high temperature HTF and thermal storage yields higher system performance.

[0036] The thermal energy storage system may be described as employing latent heat storage of a supercritical fluid instead of typical phase change materials. Two fundamental thermodynamic concepts are invoked. First, by using the latent heat of liquid/vapor phase change, an efficient system is developed which will provide a constant sink/source of heat. Second, by operating the thermal energy storage system at a higher pressure, the saturation temperature is increased to operate at molten salt temperatures and above.

[0037] As previously mentioned, a thermal energy storage system may be described where a storage fluid remains in a supercritical state within a closed system comprising a pressurized storage vessel. The thermal energy storage system operates at a higher pressure to increase the saturation temperature. Heat exchangers may be disposed within the closed pressurized storage vessel such that a heat source working fluid (e.g. from a solar thermal plant) delivers heat energy and a heat sink working fluid (e.g. from a steam generator) removes heat energy. The principle of the invention may be illustrated with a discussion of the phase change of supercritical fluids hereafter.

[0038] 2. Phase Change of Supercritical Fluids

[0039] FIG. 1 is an exemplary phase diagram of a pure component. The "tie-line" EF represents the two-phase regime. By adding heat into the liquid at E, the enthalpy of the liquid/vapor system increases until it is all vapor at F. During this phase change in an enclosed system as more heat is introduced, the pressure (and temperature) of the system increases till a new equilibrium point is reached. Thus, it is possible to design a system where the entire fluid is in a supercritical state (either above or to the right of point C). In such a supercritical state, by allowing a higher system pressure, the volume of the overall system may be optimized to be more compact. However, the system pressure need not be excessive with a judicious choice of storage fluid. In a sense, this concept operates by borrowing a principle similar to steam accumulators which are employed in chemical process plants to provide short duration thermal energy storage primarily for buffering variations in heat production. However, there are some key differences. For example, in this case storage is performed with a fixed amount of fluid that does not change and heat transfer within the storage medium is performed entirely within the fluid media through internal heat exchangers.

[0040] As mentioned above, the selection of fluid is crucial to the operation of the TES in an embodiment of the present invention. Embodiments of the invention may employ certain organic fluids. The selection criteria for the fluid are based on a high heat of vaporization, ΔH_{vap} and a high critical temperature, T_c, and boiling point, T_b. Some suitable fluids that can provide significant heat storage temperatures close to molten salt at 384° C. have been identified. Four hundred organic fluids were rapidly reviewed for a suitable combination of thermodynamic properties as described above. The list was reduced to approximately ten liquids based on a preference for liquids with a good combination of thermodynamic properties, material compatibilities and low cost. Thermodynamic properties were estimated using techniques outlined in Reid et al., "The properties of gases and liquids," which is incorporated by reference herein. Candidate fluids for embodiments of the invention were identified by cross-checking the estimations with data in the literature at discrete temperature values.

[0041] FIG. 1B is table showing thermodynamic properties for selected supercritical thermal energy storage fluid. Thermodynamic properties for preferred fluids for embodiments of the invention are shown in the table based on the estimation approaches recommended by Reid, et al., as described.

[0042] The ΔH_{vap}, at different temperatures were estimated by the following equation.

4

$$\Delta H_v = \Delta H_{vb} \frac{T_r}{T_{br}} \frac{\chi + \chi^q}{\chi + \chi^p} \qquad (1)$$

where,

$$\chi = \frac{T_{br}}{T_r} \frac{1 - T_r}{1 - T_{br}} \qquad (2)$$

T_r is reduced temperature given by where

$$T_r = \frac{T}{T_c},$$

where T_c is the critical temperature. Similarly T_{br} is the reduced normal boiling point of the liquid. The parameters q, and p are given by the following table.

	q	p
Liquid metals	0.20957	−0.17467
Quantum liquids (He, H2 . . .)	0.14543	0.5274
Inorganic and organic liquids	0.35298	0.13856

Based on the table of FIG. 1B, an initial selection focused on glycerol because of a good combination of all the desirable properties; glycerol meets thermodynamic requirements, material compatibility and cost.

[0043] For a single-stage TES (e.g. a single tank system), the energy stored is given by the following equation.

$$Q_{stored}^{1\Phi} = mC_p(T_{max} - T_{min}) \qquad (3)$$

where T_{max}, T_{min} are the maximum and minimum operating temperatures, and mC_p, is the thermal mass. For a two-stage TES (e.g. a two tank system), the energy stored is

$$Q_{stored}^{2\Phi} = mC_p(T_{sat} - T_{min}) + mH_v \qquad (4)$$

where T_{sat}, the saturation temperature, is a function of pressure, and H_v, the heat of vaporization, is a function of temperature.

[0044] 3. Selection of Supercritical Fluids for Thermal Energy Storage

[0045] In order to compare the storage capacities between a supercritical fluid and molten salt used in the prior art, some thermodynamic calculations may be made. The estimated minimum and maximum temperatures for both fluids may chosen to be T_{min}=291° C. and , T_{max}=384° C. These values represent the approximate limits for an exemplary two-tank molten salt approach as used in the Andasol plant described earlier.

[0046] In an exemplary system using saturated glycerol as the storage fluid, C_p for glycerol is approximately 2067 J/kg/K and ΔH_{vap} at 384° C. is 440,046 J/kg. The total energy stored while raising the temperature from 291° C. to 384° C. using equation (4) is approximately 632,406 J/kg with approximately 70% of the heat stored in latent form. On the other hand, the C_p for molten salt is approximately 1560 J/kg/L. Thus, the sensible heat stored while raising the temperature from 291° C. to 384° C. using equation (1) is approximately 145,080 J/kg. Accordingly, on a per mass basis, glycerol stores roughly 4.4 times more heat energy than molten salt. This represents a significant reduction in the amount of storage medium needed. Repeating these calculations for supersaturated glycerol at 450° C., the amount of heat stored is almost 750,000 J/kg, making the storage even more efficient. However, this increased storage is incurred at the volume cost, as discussed hereafter.

[0047] The known Andasol 1 molten salt thermal energy storage system has a capacity of approximately 1010 MWh (7.7 h) using a nitrate salt inventory of approximately 28,500 tons comprising 60% NaNO₃ and 40% KNO₃. The system employs two tanks, each providing a storage capacity of approximately 14,000 m³ with an overall diameter of approximately 38.5 m and a height of approximately 14 m. One tank is maintained at approximately 292° C. and the other at approximately 386° C. The system employs six heat transfer fluid/salt heat exchangers between the tanks.

[0048] FIG. 1C shows the vapor pressure of glycerol as a function of temperature. In order to estimate the storage volume needed, it is essential to estimate the vapor pressure at the temperature of interest. If one attempted operate the thermal energy storage system at 384° C. using glycerol instead, the corresponding vapor pressure would be approximately 10 bar. At this pressure, the vapor volume is almost 14 times the total volume of the two-tank system. Clearly, this is not a practical solution.

[0049] However, if the fluid temperature is raised above the critical temperature, the fluid becomes highly compressible (e.g. glycerol compressibility becomes approximately 0.2-0. 3). Even if an ideal gas relation is assumed in order to establish a conservative upper bound, the volume can be significantly reduced. This can be highlighted with two examples.

[0050] First, the known two-tank molten salt system, which employs two 14,000 m³ tanks to provide 1 GWh of storage, may be considered a baseline for comparison. A single tank of glycerol may be determined. Each tank of the known system has a diameter of approximately 38.5 m and a height of approximately 14 m. For simplicity, the diameter to height ratio will be held constant at approximately 2.75 in the proposed glycerol cases. In addition, 50% excess glycerol in the liquid state will be assumed under charged conditions to ensure that the heat exchangers have enough liquid for good thermal contact. (Note that the liquid state is only relevant until the critical point; beyond this threshold, the entire tank is filled with supercritical fluid.) In a first example, the glycerol is charged to 40 bar resulting in a calculated tank size of D=69.5 m, H=25 m (approximately 1.8 times the dimensions of 1 molten salt tank). The resulting volume is 96,058 m³ (approximately 3.4 times the total molten salt tank volumes). In a second example, the glycerol is charged to 66 bar resulting in a calculated tank size of D=58.9 m, H=21.4 m (approximately 1.5 times the dimensions of 1 molten salt tank). In this case the resulting volume is 58,217 m³ (approximately 2 times the total molten salt tank volumes). Thus, by operating at supercritical conditions and at higher pressures and temperatures, the footprint of the overall system can be reduced to acceptable dimensions.

[0051] FIG. 1D shows a table summarizing a comparison of using pressurized and glycerol in a supercritical state compared to the reference case of the Andasol 1 storage system, which delivers 1010 MWh storage capacity (approximately 1 GWh; 7.5 hr full load @135 MW). (Note that total plant cost estimates for a glycerol thermal energy storage system depend on a wide range of factors beyond functional considerations for practicing the invention.) As can be seen, there is a significant cost advantage (greater than ten times) to using

glycerol as the thermal energy storage fluid. In addition to these cost advantages there are some global market developments which may enhance the attractiveness of using glycerol. For example, China has been reporting shortages in the nitrates markets due to excessive use of fertilizers all over the world. This trend is likely to only increase when one considers increasing food demand rates. On the flip side, the cost of glycerol has continued to show a decreasing trend. This is due to the fact that glycerol is a byproduct of biofuel production. Biodiesel production throughout the world is increasing rapidly. The U.S. biodiesel industry is expected to produce an estimated 1.4 billion pounds of glycerin between 2006 and 2015. Crude glycerin, previously valued between 20 and 25 cents per pound, is now edging closer to 5 cents and lower. (Note that the cost estimates for the storage medium comparison is based on the higher value of $0.25/lb; at lower rates the cost differential becomes even more attractive).

[0052] While the cost benefits shown in above focus exclusively on the choice of glycerol as the storage medium, there are other benefits which are independent of the final choice of storage medium. For example, using glycerol affords a relatively simple single tank design. In addition, no high temperature salt transfer pump is needed with glycerol as with the two-tank molten salt system. Further, no freeze protection is needed with glycerol (i.e., no heaters during night or cloudy days). Glycerol also offers potentially continuous constant temperature operation because approximately 70-80% of heat is stored in latent form. A simple bypass design may be used to provide lower temperatures when desired. In addition, no external heat exchangers, which can be a significant source of parasitic heat loss, are needed for a glycerol system.

[0053] While there are a lot of major advantages with the pressurized supercritical fluid thermal energy storage system proposed, there are some also issues must be resolved depending upon the particular design. Such solutions can be developed without undue experimentation or research. For example, supercritical fluid operation requires heat transfer fluids (HTFs) that can operate at high temperatures. The current parabolic trough systems operate with HTFs at temperatures below 450° C., so for higher temperature operations, the HTF needs to be changed, e.g. as was the case with molten salts. This is an engineering challenge and there are solutions that already exist, such as have been used with molten salts. Power tower systems operate at much higher temperatures than parabolic troughs, so this storage approach can be used directly in such systems. In addition, supercritical fluid operation requires high pressure vessels. While this will certainly add to the overall cost of the system, the lower long-term costs are expected to compensate for the initial higher capital costs. In contrast, the molten salt for a 1 GWh system for can represent as high as 50% of the total system cost. Accordingly, the much lower glycerol cost previously discussed will easily compensate for increases due to pressurized vessel cost. Furthermore, is expected that glycerol will be very benign in regard to corrosion for most construction materials.

[0054] The question of thermal stability for any selected storage fluid, particularly for organic fluids such as glycerol, as is known in the art. According to the Material Safety Data Sheet and Merck Index, glycerol is identified as thermally unstable and indicated to decompose at temperatures above 290° C. However, this is misleading for embodiments of the invention because the sources refer to the oxidative degradation of glycerine which occurs in one of two ways. Upon

prolonged storage, two hydrogen atoms of glycerine tend to lose two electrons via a catalytic reaction with air or oxygen. This, in turn, causes the glycerine to become discolored. Exposure of glycerine to elevated temperatures, such as those employed in many finished good processing applications, also results in oxidative degradation. Elevated temperatures cause electrons to become displaced within the molecule, resulting in the formation of unwanted color bodies in the glycerin.

[0055] However, in the thermal energy storage application of the present invention, the degassed and purified glycerine will be first loaded into the storage tank, and a vacuum suction will be applied to remove all traces of air, moisture. Purge gas such as nitrogen will be employed first before the vacuum, to ensure only glycerine vapor remains above the liquid. Under such conditions, heating the glycerine in the absence of air is expected to have no impact on the thermal stability. Furthermore, the thermal stability of glycerine can be enhanced by either functionally modifying it or modifying the pH if needed. Finally, it may be that the glycerine degradation occurs at a tolerable rate (e.g. 1% per year), the problem may be addressed by a combination of venting off the degradation gaseous products and adding excess capacity so that this slow degradation can be tolerated. (For example, venting is used currently in parabolic trough plants to vent and bum the benzene produced due to the decomposition of the HTF Dowtherm.) Over time, the entire storage fluid could be replaced or only a portion depending on the remaining capacity. In other embodiments, glycerol may be modified with compounds to be more thermally stable. Any one combination of the foregoing solutions can suitably address the thermal stability depending upon the particular application. However, other organic and inorganic compounds are also possible in accordance with the present invention to operate under supercritical conditions as discussed hereafter.

[0056] A simple fluid, glycerol has been selected as a candidate fluid due primarily to its low cost. In addition, since glycerol is a polar fluid, it properties such as critical temperature, etc. can be enhanced by judicious selection of modifying compounds.

[0057] 4. Thermal Energy Storage Using a Pressurized Supercritical Fluid

[0058] While glycerol has been identified as a superior candidate storage fluid, embodiments of the invention are applicable to range of other fluids. In particular the entire class of polyaromatic hydrocarbons (PAH) are attractive as supercritical storage fluids because of their inherent stability and ease of extraction from raw materials such as coal tar, which is a byproduct when coal is carbonized to make coke or gasified to make coal gas. Coal tars are complex and variable mixtures of phenols, PAHs, and heterocyclic compounds. There are about two hundred substances in all. Naphthalene, methylnaphlene, dimethylnapthalene, biphenyl are some example of the class of PAH which can be used as candidate storage fluids. Similarly, the other classes of fluids that can be used are ionic fluids whose properties can be modified and have the attractive feature of having very low vapor pressure.

[0059] FIG. 2 shows a table of sample calculation results for glycerol and naphthalene as representative fluids in a supercritical fluid thermal energy storage system. The table shows specific storage in kJ/kg, volumetric storage capacity in kJ/m3 (vapor pressure at 200 C), and estimated cost in $/kWh. Values for glycerol and naphthalene are shown at a moderate temperature (373 K) and high temperature (563 K).

Assumed pressure for both glycerol and naphthalene is set at 66 atm. For comparison, values are also shown for compressed water and Therminol VP-1 at the moderate temperature and molten salt (NaNO₃ & KNO₃ using two tanks) at the high temperature.

[0060] A typical implementation of a thermal energy storage system in accordance with an embodiment of the invention can employ heat exchangers integrated within the storage vessel such as in a shell and tube exchanger. Using this approach, the tubes contain the storage fluid and are sealed. The heat exchanging fluid will flow over the tubes and will transfer heat to or from the fluid in the tubes. While this may be a preferred approach depending upon the application, a two-tank configuration can also be employed as described in the molten salt two-tank indirect storage scheme previously referenced.

[0061] FIG. 3A is schematic drawing an exemplary thermal energy storage apparatus 300 using a single tank according to an embodiment of the invention. The apparatus 300 includes a closed system comprising a pressurized storage vessel 302 (or tank). The pressurized storage vessel 302 contains the storage fluid 304 (of the thermal energy storage apparatus 300) above the critical point (temperature/pressure) of the storage fluid, i.e. the storage fluid 304 is maintained in a supercritical state. At certain times heat energy 306 is transferred to the storage fluid 304 from a heat source 310 through a first heat exchanger 308 coupled to the pressurized storage vessel 302 and in contact with the storage fluid 304. The heat source may be a solar power plants, such as a parabolic trough solar power plant comprising a field of collectors which heat a heat source working fluid 312 (distinct from the storage fluid 304) which is directed through the heat exchanger 308 to return to the heat source 310. The heat exchanger may be a shell and tube heat exchanger or any other suitable heat exchanger type known to those skilled in the art. In a similar manner, a second heat exchanger 314 is coupled to the pressurized storage vessel 302 and in contact with the storage fluid 304 to occasionally transfer the heat energy 306 from the storage fluid 304 to a heat sink 316. In this case, the heat sink 316 is typically a power generation system of some type. For example, the heat sink 316 may comprise a steam generator for generating electrical power. The apparatus 300 may be further modified consistent with the apparatuses, methods and material parameters previously described as will be understood by those skilled in the art. It should be noted that although the system 300 is primarily described in relation to a parabolic trough solar power plant and steam power generator, embodiments of the invention are applicable to any suitable heat source and sink combination. For example, the heat source 310 may waste heat, geothermal or a radioisotope, whereas the heat sink 316 may be a turbine generator driven by any suitable working fluid or any system requiring managed heat energy delivery. The heat sink can also be used for other purposes such as for building heating and cooling (through absorption coolers).

[0062] FIG. 3B is schematic drawing an exemplary thermal energy storage apparatus 320 using two tanks 322A, 322B according to an embodiment of the invention. In this case, the closed system comprises a pressurized storage vessel including two tanks 322A, 322B, a hot tank 322A and a cold tank 322B, which are coupled together. The storage fluid 304 passes between the tanks 322A, 322B to a heat exchanger 324. In this case, the heat exchanger 324 operates as a different heat exchanger at different times. During daylight for example, the heat exchanger 324 operates between the heat source 310 and the storage fluid 304 as the storage fluid 304 absorbs heat energy 306 as it passes from the cold tank 322B to the hot tank 322A. At night, the heat exchanger 324 operates between the heat sink 316 and the storage fluid 304 as the storage fluid 304 rejects heat energy 306 as it passes from the hot tank 322A to the cold tank 322B. In this case, the heat source 310 (e.g. solar power generation plant) and heat sink 316 (e.g. turbine generator) employ a common working fluid 326 (functioning as both the heat source and heat sink working fluids at different times). The apparatus 320 may be further modified consistent with the apparatuses, methods and material parameters previously described as will be understood by those skilled in the art. For example, this embodiment is similarly applicable to a range of power generation applications.

[0063] It should be apparent to those skilled in the art that one or more heat exchanger may be employed in an embodiment of the invention depending upon the particular system design. Separate heat exchangers may be used coupled to separate working fluids for the heat source and heat sink. Alternately, a single heat exchanger design is also feasible as in a shell and tube heat exchanger; after charging the system, cold heat transfer fluid can be circulated to extract the heat through the same set of heat exchangers. A common working fluid may be employed for delivering and rejecting heat (e.g. alternating heat source and heat sink flows with valves). (As used herein, a "single" heat exchanger refers to one or more exchangers carrying a single working fluid.)

[0064] FIG. 4 is a flowchart of an exemplary method 400 of storing thermal energy storage according to an embodiment of the invention. The method 400 begins with an operation 402 of storing a storage fluid within a pressurized storage vessel. In operation 404, heat energy is occasionally transferred between the storage fluid and at least one working fluid with at least one heat exchanger coupled to the pressurized storage vessel and in contact with the storage fluid. The heat energy is transferred such that the storage fluid changes from a two-phase state to a supercritical state as the heat energy is transferred from the at least one working fluid to the storage fluid, and the storage fluid changes back to the two-phase from the supercritical state as the heat energy is transferred from the storage fluid to the at least one working fluid. The method 400 may be further modified consistent with the apparatuses and material parameters previously described as will be understood by those skilled in the art. For example, a single heat exchanger and single working fluid may be used within a single storage tank such that the same working fluid transfers heat energy to and from the storage fluid (which is coming from a heat source and heat sink, respectively). Alternately, separate heat exchangers and working fluids may be employed within a single storage tank, a first heat exchanger and working fluid receiving heat energy from a heat source and second heat exchanger and working fluid rejecting heat energy to a heat sink. See FIG. 3A. In other embodiments the storage fluid may be transferred between two storage tanks passing through at least one heat exchanger coupled to one or more working fluids. A single working fluid and single heat exchanger may also be used in this case as well, delivering heat energy from heat source at some times and to a heat sink at other times. See FIG. 3B.

[0065] This concludes the description including the preferred embodiments of the present invention. The foregoing description including the preferred embodiment of the inven-

tion has been presented for the purposes of illustration and description. It is not intended to be exhaustive or to limit the invention to the precise forms disclosed. Many modifications and variations are possible within the scope of the foregoing teachings. Additional variations of the present invention may be devised without departing from the inventive concept as set forth in the following claims.

What is claimed is:

1. A thermal energy storage apparatus, comprising:

a pressurized storage vessel;

a storage fluid within the pressurized storage vessel; and

at least one heat exchanger coupled to the pressurized storage vessel and in contact with the storage fluid to occasionally transfer heat energy between the storage fluid and at least one working fluid;

wherein the storage fluid changes from a two-phase state to a supercritical state as the heat energy is transferred from the at least one working fluid to the storage fluid and changes back to the two-phase from the supercritical state as the heat energy is transferred from the storage fluid to the at least one working fluid.

2. The apparatus of claim 1, wherein the at least one heat exchanger is disposed within the pressurized storage vessel.

3. The apparatus of claim 2, wherein the at least one working fluid comprises a heat source working fluid and the at least one heat exchanger within the pressurized storage vessel receives the heat source working fluid to transfer the heat energy from the heat source working fluid to the storage fluid.

4. The apparatus of claim 3, wherein the heat source working fluid is coupled to a solar thermal plant.

5. The apparatus of claim 2, wherein the at least one working fluid comprises a heat sink working fluid and the at least one heat exchanger within the pressurized storage vessel receives the heat sink working fluid to transfer the heat energy from the storage fluid to the heat sink working fluid.

6. The apparatus of claim 5, wherein the heat sink working fluid is coupled to a steam generator generating electrical power.

7. The apparatus of claim 1, the storage fluid comprises a polyaromatic hydrocarbon (PAH).

8. The apparatus of claim 7, wherein the PAH is selected from the group consisting of naphthalene, methylnaphlene, dimethylnapthalene, and biphenyl.

9. The apparatus of claim 1, wherein the storage fluid is selected from the group consisting of glycerol, pthalic anhydride, benzoic acid, 3,4 xylenol, iodobenzene, and an ionic fluid.

10. A method of storing thermal energy, comprising:

storing a storage fluid within a pressurized storage vessel; and

occasionally transferring heat energy between the storage fluid and at least one working fluid with at least one heat exchanger coupled to the pressurized storage vessel and in contact with the storage fluid such that,

the storage fluid changes from a two-phase state to a supercritical state as the heat energy is transferred from the at least one working fluid to the storage fluid, and

the storage fluid changes back to the two-phase from the supercritical state as the heat energy is transferred from the storage fluid to the at least one working fluid.

11. The method of claim 10, wherein the at least one heat exchanger is disposed within the pressurized storage vessel.

12. The method of claim 11, wherein the at least one working fluid comprises a heat source working fluid and the first heat exchanger within the pressurized storage vessel receives the heat source working fluid to transfer the heat energy from the heat source working fluid to the at least one working fluid.

13. The method of claim 12, wherein the heat source working fluid is coupled to a solar thermal plant.

14. The method of claim 11, wherein the at least one working fluid comprises a heat sink working fluid and the second heat exchanger within the pressurized storage vessel receives the heat sink working fluid to transfer the heat energy from the at least one working fluid to the heat sink working fluid.

15. The method of claim 14, wherein the heat sink working fluid is coupled to a steam generator generating electrical power.

16. The method of claim 10, wherein the storage fluid comprises a polyaromatic hydrocarbon (PAH).

17. The method of claim 16, wherein the PAH is selected from the group consisting of naphthalene, methylnaphlene, dimethylnapthalene, and biphenyl.

18. The method of claim 10, wherein the storage fluid is selected from the group consisting of glycerol, pthalic anhydride, benzoic acid, 3,4 xylenol, iodobenzene, and an ionic fluid.

19. A thermal energy storage apparatus, comprising:

a pressurized storage vessel means for storing a storage fluid means for storing heat energy; and

at least one heat exchanger means for occasionally transferring the heat energy between the storage fluid means and at least one working fluid means for transferring the heat energy, the at least one heat exchanger means coupled to the pressurized storage vessel means and in contact with the storage fluid means;

wherein the storage fluid means changes from a two-phase state to a supercritical state as the heat energy is transferred from the at least one working fluid to the storage fluid and changes back to the two-phase from the supercritical state as the heat energy is transferred from the storage fluid to the at least one working fluid.

20. The apparatus of claim 19, wherein the storage fluid means is selected from the group consisting of glycerol, pthalic anhydride, benzoic acid, naphthalene, 3,4 xylenol, iodobenzene, methylnaphlene, dimethylnapthalene, biphenyl, and an ionic fluid.

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