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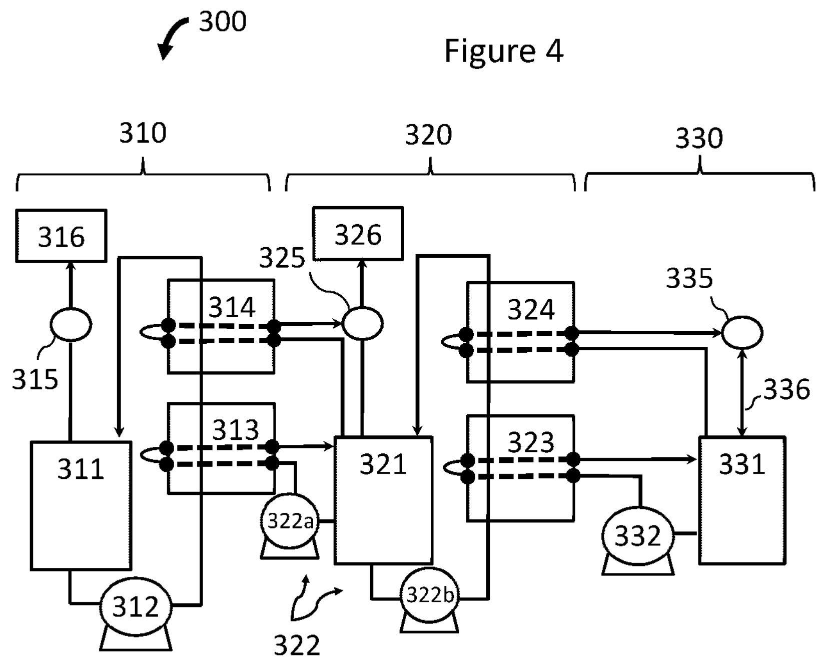

(57) Abstract: A system and method of operation is described wherein a cryogenic liquid transport fluid is used as in a thermal cascade with at least one volatile gas. The volatile gas in the liquid state enables transport thereof. In operating this system, the liquid volatile gas is maintained at a temperature below its boiling point, below its flash point, but above its freezing point.

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SUBCOOLED CRYOGENIC STORAGE AND TRANSPORT OF VOLATILE GASES

Technical Field

[0001] This disclosure relates to a system for transporting volatile gases in a cryogenic liquid carrier fluid. More specifically, the disclosure relates to a system and method for subcooling of a volatile gas in a liquid state during transport.

Background Art

[0002] Transportation of valuable, volatile chemicals as pure substances or as certain mixtures under pressure is commercial practice. Generally, this pressure containment adds weight and cost to the transportation of a chemical. Refrigeration of volatile chemicals lowers the working pressure needed to transport a chemical gas and reduces the need for pressure containment. Refrigeration equipment systems add expense to the transportation of volatile chemicals and risk of refrigeration equipment failure, particularly for compressor-based systems. If a volatile chemical escapes pressure containment, or a refrigerated chemical warms to ambient temperature, it poses a significant risk to the transportation vehicle, operators, and local environment.

[0003] The transportation of liquefied natural gas (LNG) is a commercially established industry that replaces compressors with other pump configurations. Various publications have described the storage and transport of LNG, mixtures of LNG, and optionally containing minor amounts of a gas impurity as a liquid mixture at cryogenic temperatures, below about -150°C (-258°F). Others have described the implementation of LNG as a carrier or transport fluid for intentionally introduced, high concentrations of a single selected gas impurity or dopant. A gas dopant is typically one other commercially valuable, volatile gaseous compound that is heavier than methane. The gas dopant admixed into a transport fluid such as LNG under cryogenic conditions has a reduced toxicity or explosive potential in this configuration. However, there are thermodynamic and chemical limitations to the number and types of gas dopants that may be admixed into a transport fluid for transportation.

[0004] In recent commercial practice ethane is transported as a cryogenic liquid at its boiling point. Ethane maintained at its boiling point using one or more refrigeration systems on board the transport vehicle, typically an insulated tanker of substantially the same design as an LNG tanker. Ethane transportation in this system includes a higher risk during a refrigeration system partial or complete failure. Specifically, a failure would result in the production of a vapor cloud having a slightly higher density than air and that sinks very slowly. This ethane vapor cloud remaining near the ship and its environs would also have a substantially higher energy of combustion than methane, leading to the aforementioned higher risk.

Summary

[0005] A method for storage and transporting gases is disclosed herein, comprising the steps of charging a transport fluid to a transport fluid system at cryogenic conditions, charging a first volatile gas to a first volatile gas system, maintaining the first volatile gas in a first subcooled liquid phase by heat transfer with the transport fluid or with a refrigerant, charging a second volatile gas to a second volatile gas system, pre-cooling the second volatile gas to below its normal boiling point at storage pressure, maintaining the second volatile gas in a second subcooled liquid phase by heat transfer with the first subcooled volatile gas or the transport fluid or a refrigerant, and transporting the first and second liquid phases.

[0006] The transport fluid comprises at least one component chosen from the group consisting of oxygen, nitrogen, argon, methane, ethane, ethylene, propane, propylene and combinations thereof.The first volatile gas or the second volatile gas may comprise oxygen, carbon monoxide, argon,

propane, propylene, 1-butene, silane, tetrafluoromethane, ethane, liquid natural gas, methane, acetylene, monochlorotrifluoroethane, chlorotrifluoromethane, ethylene chlorodifluoromethane, chlorodifluoromethane, isobutane, krypton, trifluoromethane, vinyl chloride, perfluoroethene, tetrafluoroethylene, dimethyl ether, isobutene, n-butane, methyl ethyl ether, carbonyl sulfide, chloro-2-difluoro-1,1-ethylene, difluoromethane, dichloromonoflurormethane, phosphine, neopentane, phosgene, acetaldehyde, difluoroethane, chloro-1-tetrafluoro-1,1,2,2-ethane, hydrogen chloride, xenon, ethylene oxide, 1,1,1- trifluoroethane, 1,2-butadiene, 1,3-butadiene, dichlorodifluoroethane, chloro-2-trifluoro-1,1,1- ethane, chlorine, 1,1,1,2-tetrafluoroethane, hexafluoroethane, methyl chloride,methyl bromide, formaldehyde, dinitrogen oxide, hydrogen sulfide, hydrogen fluoride, methyl fluoride, ammonia, pentafluoroethane and combinations thereof. In certain configurations, the transport fluid comprises oxygen, nitrogen, argon, liquid natural gas, methane, ethane, ethylene, propane, propylene and combinations thereof.

[0007] The transport fluid, first volatile gas, and second volatile gas are maintained in separate liquid phases by a cryogenic thermal cascade or conventional refrigeration systems. The volatile gases will be charged to the transport vessel and maintained below their boiling points, below their flash points, and above their freezing points. Loss of cooling will not result in immediate production of vapor from the subcooled volatile gases. These additional operational steps substantially improve the safe storage and transport of the volatile gases as subcooled liquids as well as reduce the shipboard requirements for refrigeration either by conventional methods or thermal cascade. In instances, the level of subcooling of the volatile gases will allow them to be transported and maintained below their boiling point without external cooling in properly designed transport vessels with reduced or even without external cooling. In instances the level of subcooling of the volatile gases will allow them to be transported and maintained below their flash point without external cooling in properly designed transport vessels with reduced or absent external cooling.

Brief Description of the Drawings

[0008] For a detailed description of the preferred embodiments of the invention, reference will now be made to the accompanying drawings in which:

[0009] FIGURE 1 illustrates a schematic of thermal cascades in the present disclosure

[0010] FIGURE 2 illustrates a schematic of direct thermal cascades in the present disclosure

[0011] FIGURE 3 illustrates a schematic of indirect thermal cascades in the present disclosure.

[0012] FIGURE 4 illustrates an indirect thermal cascade system for cryogenic gas storage and transport according to the present disclosure.

[0013] FIGURE 5 illustrates a table of representative chemical compounds that may be transported as a first or second volatile gas liquid with an LNG transport fluid

[0014] FIGURE 6 illustrates a table of the representative chemical compositions that may be co-transported with various first volatile gases with an LNG transport fluid.

[0015] FIGURE 7 illustrates a table of representative chemical compounds that may be transported as a first or second volatile gas liquid with an ethane transport fluid.

[0016] FIGURE 8 illustrates a table of representative chemical compounds' boiling point, flash point and the differences therein for cotransport as a subcooled volatile gas.

Description of Embodiments

[0017] The production of certain volatile substances and their consumption as a reactant for an industrial process require overland or marine transportation. Volatile substances or hereinafter volatile gases are transported under pressure containment, at refrigerated temperatures, or combinations thereof. Safety and infrastructure constraints negatively impact shipping costs and potential markets for these gases. For example, large-volume pressurized shipping containers are heavy, and some compounds cannot be transported to certain markets due to the potential for unintentional depressurization release, resulting in a public hazard. Also, large volume refrigerated shipping containers require refrigeration and compressor infrastructure both during transportation and unloading that some markets may not be able to accommodate sufficiently to receive and store certain compounds.

[0018] Additionally, normal operation of refrigeration systems servicing cryogenic volatile gases only utilize the necessary refrigeration to maintain a volatile substance in a liquid state at or near its boiling point. From an engineering design standpoint this minimizes the working heat load on the refrigeration system a transport vessel. In such systems, a refrigeration system partial or complete failure results in thermal energy and temperature increase of the refrigerated liquid volatile substance and vaporization. This vaporization, or boil off, increases pressure within the transport vessel to be mitigated for vessel integrity and safety.

[0019] It is commercial practice to transport LNG at its boiling point at storage pressure in insulated cryogenic transport vessels. Storage pressure is typically at or below 34.5kpa (5psig). As thermal energy such as environmental or ambient heat enters the stored LNG during transport, some LNG is boiled away. Although this LNG may be used as a fuel for the transport vehicle, in certain instances the LNG may be allowed to boil off or vent to the atmosphere. It is relatively safe to allow LNG boil off to escape containment to the atmosphere because the principle component of LNG is methane. Methane is substantially less dense (lighter) than air, thus ascends into the atmosphere. Additionally, methane has a relatively low energy of combustion (-890 KJ/mol).

[0020] One method of arranging a direct or an indirect thermal cascade between a transportation or transport fluid and a volatile gas offers a means to reduce costs associated with storage, containment, transportation, and infrastructure. A thermal cascade is the arrangement of heat transfer between a volatile gas and a transport fluid. The transportation fluid is utilized as a heat transfer medium to keep a volatile gas within a predetermined temperature range. A thermal cascade is configured such that the transport fluid is cooled to a liquid state. The thermal cascade is configured to keep the transportation fluid in a liquid state and the volatile gas in a liquid state. The transportation fluid is cooled to a liquid state at a cryogenic temperature.

[0021] Accordingly, international patent application serial number PCT/US19/12966 filed January 12, 2018, details a method to transport one or more valuable volatile gases as liquids using a cryogenic transport liquid wherein the transport liquid boils off to maintain the valuable cryogenic gases in their liquid state, below their boiling point. Cryogenic temperatures as used herein may refer to any temperature below about -40°C (-40°F), alternatively any temperature below about -120°C (-184°F), and preferably any temperature below about -150°C (-238°F).

[0022] However, in that configuration the transport fluid is the refrigerant or thermal sink responsible for maintaining volatile gases below their boiling point in the transportation vessel. The transport fluid must be in thermal communication with a volatile gas in order to maintain it in the liquid state at cryogenic temperatures. The method herein described comprises maintaining a volatile gas in a liquid state is through thermal cascade from a transport fluid or direct refrigeration to a subcooled liquid state. Herein, the subcooled liquid state refers to a condition wherein the volatile gas is maintained at a temperature of at least 10°C above the volatile gas's freezing point. In certain conditions, volatile gas is maintained at a temperature of at least 30°C above its freezing point, alternatively at least 50°C above its freezing point. As may be understood, in certain circumstances, a subcooled liquid has a temperature that is higher than a cryogenic temperature that would otherwise find the volatile gas in the solid phase.

[0023] Additionally, many volatile gases have flash points, herein defined as the lowest temperature at which vapors of the volatile gases will ignite, when given an ignition source. For reasons of safer operation, it is advisable to maintain these gases while being transported below their flash point. Thus, even though the volatile gases may be contained at a temperature that is below their boiling point, that temperature may be above the flash point. As described herein, the volatile gases are maintained at a temperature below their boiling point, below their flash point, but above their freezing point.

[0024] In further configurations described herein, subcooled may refer to the state of cycling refrigerant in a refrigeration system. Refrigeration systems herein, may include without limitation pumps, compressors, condensers, coolant conduits, evaporative coolers, air coolers, water coolers, auto-refrigeration, or gas-expansion systems, both on the transport vehicle or at loading and off-loading terminals for volatile gases. In a subcooled system the refrigerant maintains its liquid form throughout a refrigeration cycle and particularly at the thermostatic expansion valve, while providing cryogenic refrigeration to a transport fluid or volatile gas. In some refrigeration systems, a transport fluid is a refrigerant.

[0025] Further, the volatile gas is thermally regulated in a predetermined temperature range below its boiling point prior to introduction or charging into the transport or containment vessel. Subcooling a volatile gas before charging to a containment vessel wherein the ambient conditions are above the gas's boiling point provides for a delay in vaporization. It may be appreciated that during loading or offloading of a volatile gas at a terminal, the thermal cascade described herein and previously, may experience temperature fluctuations. Exemplary fluctuations herein may include charging a volatile gas vessel, wherein the vessel has not reached a temperature at or below the volatile gases boiling point. As such, introducing a subcooled liquid volatile gas, delays vaporization. During those fluctuations, it may be important to maintain one or more volatile gases in the liquid state and such a vaporization delay permits the initiation of additional refrigeration systems required to maintain the volatile gas in its liquid state.

[0026] Additionally, subcooling may be maintained during transportation by the thermal cascade or by active refrigeration systems. The degree of subcooling, as used herein to mean the temperature reduction below a volatile gas boiling point, may permit systems used by the transport vessel to be turned off for various periods where having active on-board refrigeration operations would be risky. Additionally, the degree of subcooling may allow systems that partially or completely fail, time for the repair and restoring of functional or full operation prior to development of an unsafe situation, such as a release of volatile gas.

[0027] The transportation fluid is a pure or substantially pure gaseous composition at standard temperature and pressure (STP), defined herein as 0°C (32°F) and 101.325 kPa (1 atm). The transport fluid gaseous composition is a liquid at cryogenic temperatures, below about -150°C (-238°F) without additional pressurization, for example at standard pressure of 101.325kPa (1 atm). The transport fluid may be any fluid kept under cryogenic temperatures with low pressurization, for example at a pressure of less than about 506.625 kPa(5 atm), alternatively at a pressure of less than about 303.975kPa (3 atm), and in some instances, at a pressure of less than about 202.650 kPa (2 atm).

[0028] The transport fluid may be considered a pure or substantially pure gaseous composition at STP if at least about 85% concentration by volume is a single gas component; alternatively, at least about 90% concentration by volume is a single gas component; or at least about 95% concentration by volume is a single gas component. In certain instances, the transport fluid is considered pure or substantially pure if at least about 99% concentration by volume is a single gas component at STP. A transport fluid may be any pure or substantially pure gas component that is at least 85% liquid by volume at cryogenic temperatures; alternatively at least 90% liquid by volume; or at least 95% liquid by volume at cryogenic temperatures depending on composition. A transport fluid may also be any composition that is at least 99% liquid by volume at cryogenic temperatures.

[0029] The volatile gas may be considered a pure or substantially pure gaseous composition according to the definitions presented for the transport fluid. The volatile gas may comprise one or more pure or substantially pure gases that are mixed. In mixed gas component instances, a volatile gas may have any ratio of mixed components between a first gas and a second gas and for example, a ratio of first gas to second gas can range from about 1:1000 to about 1000:1. Any gas component that is mixed into another may be considered an impurity or dopant. This includes multiple components mixed to form a volatile gas and any volatile gas that is mixed into a transport fluid. Mixing of volatile gases or transport fluid may be in the gas or liquid phase.

[0030] The volatile gas has a boiling point, or temperature of phase change from liquid to gas, that is higher than the boiling point of the transport fluid at STP. In some applications, the volatile gas has a freezing point that is lower than the boiling point of the transportation fluid. In mixed volatile gas configurations, a first gas may be used as a heat transfer medium between the transportation fluid and a second gas, such that the first gas and the second gas are kept within predetermined temperature ranges. In instances, the predetermined gas temperature range is subcooled or alternatively the temperature range is lower than the boiling point of a volatile gas. In instances the volatile gases are subcooled below their boiling point prior to or during transport and storage to a temperature at least 10°C below their boiling point, and more preferably to a temperature at least wherein the volatile gas is maintained at a temperature of at least 10°C above the volatile gas's freezing point. In certain conditions, volatile gas is maintained at a temperature of at least 30°C above its freezing point, alternatively at least 50°C above its freezing point. In instances the volatile gases are cooled and maintained at a temperature below its flash point.

[0031] While not outside the envisioned scope of the present disclosure, there are thermal cascade configurations that may be unfavorable to transport a volatile gas in a transport fluid. More specifically, it may be unfavorable when the volatile gas has a freezing point above the boiling point of a transport fluid, resulting in a volatile gas solid or the boiling point of the volatile gas that is below the boiling point of the transportation fluid and resulting in a volatile gas. Transporting volatile gases in the solid or gaseous state may require additional, duplicate, or alternative heat transfer media or process steps from those found herein.

[0032] Figure 1 schematically illustrates a thermal cascade 100 between a transport fluid 110 and a volatile gas 120. The transport fluid 110 is maintained at a cryogenic temperature. The volatile gas 120 is in thermal communication with the transport fluid 110. The volatile gas 120 is maintained at a subcooled temperature by the thermal communication with the transport fluid 110. The volatile gas 120 is maintained at a subcooled temperature by heat transfer to the transport fluid 110. The volatile gas 120 subcooled temperature is below its boiling point, below its flash point, but above its freezing point. Transport fluid 110 is a heat transfer medium for the volatile gas 120.

[0033] In some configurations, the volatile gas 120 may also be in thermal communication with a second volatile gas 130. In these configurations, the volatile gas 120 may be considered a first volatile gas 120. The transport fluid 110 is maintained at a cryogenic temperature. The first volatile gas 120 is in thermal communication with the transport fluid 110 is maintained at a subcooled temperature. The second volatile gas 130, in thermal communication with the first volatile gas 120, is thus maintained at a temperature below its boiling point, below its flash point, above its freezing point, and thus, optionally at a subcooled temperature. Transport fluid 110 is a heat transfer medium to the first volatile gas 120 and the second volatile gas 130. The first volatile gas 120 is a heat transfer medium to the transport fluid 110 from the second volatile gas 130. The thermal communication between the transport fluid 110 and any volatile gases, such as the first volatile gas 120 and the second volatile gas 130, forms a thermal cascade 100.

[0034] Referring now to Figure 2, the thermal cascade 200 may result from the direct heat transfer between the transport fluid 210, the first volatile gas 220, and the second volatile gas 230. A direct heat transfer configuration comprises admixing a volatile gas directly into the transport fluid 210 in a single container or vessel. The first volatile gas 220 is admixed into the transport fluid 210, in the gas phase, the liquid phase, or combinations thereof. The first volatile gas 220 may be considered an impurity or a dopant in the transport fluid 210. Also, the second volatile gas 230 may be admixed directly into the transport fluid 210 in the gas phase, the liquid phase, or combinations thereof. This may be simultaneous or sequential with directly admixing the first volatile gas 220 into the transport fluid 210. The second volatile gas 220 may also be considered an impurity or a dopant in the transport fluid 210. Further, the second volatile gas 220 may be considered a high boiling liquid gas. Schematically, this may be represented by thermal cascade A.

[0035] Alternatively, the second volatile gas 230 may be directly admixed into the first volatile gas 220, in the gas phase, the liquid phase, or combinations thereof. The second volatile gas 230 may be considered a high boiling liquid gas, an impurity, or a dopant in the first volatile gas 220. The admixed second volatile gas 230 and first volatile gas may then be directly admixed into the transport fluid 210 in the gas phase, the liquid phase, or combinations thereof. The first volatile gas 220 may completely surround and isolate the second volatile gas 230 from the transport fluid 210. Further, the second volatile gas 220 may be considered a high boiling liquid gas. Schematically, this may be represented by thermal cascade B.

[0036] Figure 3 illustrates an indirect thermal cascade 400. Indirect heat transfer refers to the exchange of thermal energy without admixing gas components into a single container or vessel. The thermal energy is transferred by heat transfer devices such as vessels, conduits, heat exchangers, other equipment, or infrastructure systems. As such, the transportation fluid system 410, the first volatile gas system 420, and the second volatile gas system 430 maintain gases that are isolated, sealed, or prevented from mixing. The transportation fluid system 410, the first volatile gas system 420, and the second volatile gas system 430 are configured independently with the exception of a shared heat transfer step between each system. A heat transfer step may be any heat exchanger configuration that keeps a cryogenic liquid, a subcooled volatile gas liquid, or gas thereof in separated, sealed conduits. More specifically, the transportation fluid system 410 is in thermal communication with a subcooled, first volatile gas system 420 by a thermal transfer step 413. The subcooled, second volatile gas system 430 is in thermal communication with the first volatile gas system 420 by a thermal transfer step 423. In certain configurations, the second volatile gas system 430 is in thermal communication with the transportation fluid system 410 by a thermal transfer step 433.

[0037] Transport fluid 110, first volatile gas 120 and second volatile gas 130 may be any volatile gas component, providing a thermal cascade arrangement. Thus, transport fluid 110, first volatile gas 120 and second volatile gas 130 may comprise oxygen, carbon monoxide, argon, propane, propylene, 1-butene, silane, tetrafluoromethane, ethane, liquid natural gas, methane, monochlorotrifluoroethane, chlorotrifluoromethane, ethylene chlorodifluoromethane, chlorodifluoromethane, isobutane, krypton, trifluoromethane, vinyl chloride, perfluoroethene, tetrafluoroethylene, dimethyl ether, isobutene, n-butane, methyl ethyl ether, carbonyl sulfide , chloro-2-difluoro-1,1-ethylene, difluoromethane, dichloromonoflurormethane ,phosphine, neopentane, phosgene, acetaldehyde, difluoroethane, chloro-1-tetrafluoro-1,1,2,2-ethane, hydrogen chloride, xenon, ethylene oxide, 1,1,1-trifluoroethane, 1,2-butadiene, 1,3-butadiene, dichlorodifluoroethane, chloro-2-trifluoro-1,1,1-ethane, chlorine, 1,1,1,2-tetrafluoroethane, hexafluoroethane, methyl chloride, methyl bromide, formaldehyde, dinitrogen oxide, hydrogen sulfide, hydrogen fluoride, methyl fluoride, ammonia, pentafluoroethane and combinations thereof. In certain configurations, the transport fluid 110 comprises oxygen, nitrogen, argon, liquid natural gas, methane, ethane, ethylene, propane, propylene and combinations thereof.

[0038] Referring now to Figure 4, there is illustrated a system 300 for the indirect thermal cascade during subcooled gas storage and transport. Generally, the system 300 comprises a transportation fluid system 310, a first volatile gas system 320, and a second volatile gas system 330. The transportation fluid system 310 comprises a vessel 311, a pump fed conduit 312, a first heat exchanger 313, a second heat exchanger 314, a regulator 315, and boil-off system 316. The first volatile gas system 320 comprises a vessel 321, a pump fed conduit 322, a first heat exchanger 323, a second heat exchanger 324, a regulator 325, and a boil-off system 326. The second volatile gas system 331 comprises a vessel 331, a pump fed conduit 332, a regulator 335, and a recirculation system 336.

[0039] Generally, the vessels 311, 321, 331, are configured as volatile gas liquid storage vessels, cryogenic liquid storage vessels, or subcooled liquid storage vessels. Vessels 311, 321, 331, may comprise any refrigeration equipment, including without limitation pumps, compressors, condensers, coolant conduits, evaporative coolers, air coolers, water coolers, auto-refrigeration, or gas-expansion such that they are thermally regulated in a predetermined temperature range. The vessels 311, 321, 331 may be configured for pressure containment at any elevated pressure that is less than about 5 atm (506.625 kPa), when charged with a volatile gas liquid, whether the gas liquid is cryogenic or subcooled. The vessels 311, 321, 331 comprise any volume between about 0.0001 m^3 and to about 500,000 m^3, and in certain configurations the vessels comprise multiple individual vessels, containers, sections, chambers, baffles, honeycombs, conduits, or combinations thereof without limitation. The vessels 311, 321, 331 may have a dynamic volume that changes to accommodate the volume and pressure of a volatile gas liquid when charged, injected, or introduced therein. Likewise, the vessels 311, 321, 331 may have any size or volume to meet local storage or transportation demands. In the latter examples, sizes may range from less than liter of a volatile gas liquid for laboratory use or transportation about a research facility, to about the size of a railroad car or semi-truck for a manufacturing facility storage and supply or overland transportation thereto. The configuration of the vessels 311, 321, 331 may extended to about the size of any marine vessel, such as a marine gas tanker or a marine gas super-tanker.

[0040] Generally, pump fed conduits 312, 322, 332 withdraw a cryogenic liquid from the vessel 311, and a subcooled liquid from vessel 321, 331, respectively. The pump fed conduits 312, 322, 332 comprise any conduit configured for conveying a cryogenic liquid or subcooled volatile gas liquid, including but not limited to any material and any insulation acceptable for maintaining the volatile gas in a subcooled liquid phase or at a cryogenic temperature. The pump fed conduits 312, 322, 332 further comprise any apparatus or device configured to provide motive force to a volatile gas liquid, such as but not limited to a compressor pump, a reciprocal pump, or a centrifugal pump. The pump fed conduits 312, 322, 332 may convey a volatile gas liquid from point to point, or they may be configured to form a circuit that begins and ends in the vessels 311, 321, 331, respectively. In exemplary configurations, it may be envisioned there are multiple pump fed conduits originating from and returning to a vessel. For example, first volatile gas system 320, comprising vessel 321, has a first pump fed conduit 322a and a second pump fed conduit 322b. While only this embodiment is shown in the Figure 2, similar configurations of pump fed conduits 312, 332 for vessels 311, 331 found respectively in the transportation fluid system 310 and the second volatile gas system 330 are within the envisioned scope of this disclosure.

[0041] The pump fed conduits 312, 322, 332 convey the subcooled volatile gas liquid or cryogenic fluid to the first heat exchangers 313, 323 and the second heat exchangers 314, 324. The first heat exchangers 313, 323 may be any heat exchanger configured for liquid to liquid thermal transfer between cryogenic fluids or subcooled volatile gas liquids. The second heat exchangers 314, 324 may be any heat exchanger configured for vapor or gas to liquid heat transfer. First heat exchangers 313, 323 and second heat exchangers may be of any design such that heat exchange can occur through indirect means when acting upon cryogenic fluid or volatile gas liquid streams comprising liquids, gases, solids, or combinations thereof. Additional heat exchangers may be utilized in the pump fed conduits 312, 322, 332 as needed to configure a thermal cascade for system 300.

[0042] Regulators 315, 325, 335 are configured to regulate the vapor or pressure in the vessels 311, 321, 331 respectively below a predetermined flash point. Regulators 315, 325, 335 may be a gas or vapor flow to keep the vapor flowing at a constant volume per time or pressure to maintain vessels 311, 321, 331 at a predetermined containment pressure. Additionally, regulators 315, 325, 335 may include configurations that permit counter directional flow of vapors and liquids, such that condensate returns to the respective vessel 311, 321, 331. Regulator 335 controls vapor from second volatile gas vessel 331 in recirculation conduit 336. Recirculation conduit 336 circulates and condenses vapors for return to the second gas vessel 331. Regulators 315, 325 disposed in the transportation fluid system 310 and the first volatile gas system 320, control the vapor flow to the boil-off systems 316, 326 respectively.

[0043] Boil-off systems 316, 326 may comprise any system configured to capture or maintain containment of a vapor that has boiled off of a subcooled volatile liquid gas or cryogenic fluid below the flash point of the subcooled volatile liquid gas or cryogenic fluid, respectively. Boil-off systems 316, 326 may comprise compressors, pumps, or refrigeration systems that condense the vapors to reform a subcooled liquid gas. Boil-off systems 316, 326 may comprise a fuel supplementations system that captures the vapors for use as a fuel or fuel additive in combustion or other energy processes, such as but not limited to refrigeration, motive transport, electricity production, water desalination and waste recycling. In certain circumstances, the boil-off systems 316, 326 may be configured to permit controlled release of certain predetermined vapors to the atmosphere.

[0044] In operation, the transport fluid (TF) is charged to the transport fluid system 310 under cryogenic conditions. A first volatile gas (VG1) is charged to the first volatile gas system 320 as subcooled liquid and a second volatile gas (VG2) is charged to the second gas system 330 as a subcooled liquid. The transportation fluid is kept at cryogenic conditions to maintain a subcooled liquid state of the first volatile gas and the second volatile gas Operation of the system, circulates the first volatile gas and the second volatile gas in thermal communication with transportation fluid, thus keeping them in a subcooled liquid state.

[0045] In certain operations the transportation fluid is maintained in vessel 311, near but below its natural boiling point, for example under subcooled conditions. Also, transport fluid may be maintained at a containment pressure defined by regulator 315. Transport fluid moves through pump fed conduit 312 to first heat exchanger 313. In certain instances, the first heat exchanger 313 acts as liquid to liquid heat exchanger. First volatile gas leaves vessel 321 via pump fed conduit 322a and flows through first heat exchanger 313. This permits thermal communication or heat transfer from first volatile gas in first volatile gas system 320 to transportation fluid in transportation fluid system 310. Heat exchange between the transport fluid and first volatile gas results in some vaporization of transport fluid and cooling of the first volatile gas. Thus cooled, the first volatile gas is returned to vessel 321. The partially vaporized transport fluid may be returned to vessel 311.

[0046] In other operations, the partially vaporized transport fluid in pump fed conduit 314 flows to a second heat exchanger 314. The second heat exchanger 314 is a liquid vapor condenser. In the second heat exchanger 314, the transport fluid is further vaporized by first volatile gas vapor or boil off from vessel 321. The partially vaporized transport fluid from the second heat exchanger 314 is returned to the vessel 311.

[0047] As vapor accumulates in vessel 311, there may be an increase in gas pressure. Regulator 315 controls the release of transport fluid vapor from the vessel 311 to the boil off system 316. Transport fluid vapors are maintained below their flashpoint and can be utilized as a source of energy for multiple purposes, including, but not limited to refrigeration, motive transport, electricity production, water desalination and waste recycling.

[0048] In operations, the first volatile gas (VG1) contained as a subcooled liquid in vessel 321. More specifically, it is envisioned that the first volatile gas is maintained at a temperature between that of the transport fluid in transportation fluid system 310 or vessel 311 and the temperature which would result from the first volatile gas reaching its flash point. The boiling point of the first volatile gas is controllable by pressure defined by a pressure control valve such as regulator 325. In certain configurations, if the first volatile gas containment pressure is maintained below the first volatile gas boiling point, no vapors will pass into the boil-off system 326. Alternatively, if the liquid in the vessel 321 of the first volatile gas system 320 is allowed to heat to a temperature and thus pressure that is higher than regulator 325 is configured to contain, the first volatile gas vapors will pass into the boil off system 226. Boil off system 226 may be configured identically, similar, connected, or in communication with boil off system 315 described herein. Alternatively, the first volatile gas vapors may be vented to atmosphere in predetermined situations for predetermined compositions. Still further, the first volatile gas vapors may be directed by regulator 325 to the second heat exchanger 314 as a vapor for condensing. As described here, the first volatile gas vapor in second heat exchanger 314, configured as liquid vapor condenser, is condensed by heat exchange with the transport fluid. The condensed first volatile gas is returned to the vessel 321.

[0049] A second volatile gas (VG2) may be co-transported in a second volatile gas system 330 that is in thermal communication with transport fluid system 310 and first volatile gas system 320. The second volatile gas (VG2) may be considered a high boiling liquid (HBL). The second volatile gas is thusly in thermal communication or thermal cascade arrangement with and for co-transportation with the transport fluid and the first volatile gas. In this configuration, second volatile gas is retained in vessel 331 as a subcooled liquid under refrigerated conditions as described here.

[0050] In operation, the second volatile gas is conveyed via pump fed conduit 332 to heat exchange 323. At or about the same time, the first volatile gas is conveyed via pump fed conduit 322b from the vessel 321 in the first volatile gas system 320 to the first heat exchanger 323. Generally, first heat exchanger 323 may be analogous to the first heat exchanger 313 in the transportation fluid system 310. The first heat exchanger 323 is configured as liquid-to-liquid heat exchanger. The first heat exchanger 323 permits thermal transfer between subcooled liquids at refrigerated temperatures. Configured thusly, the second volatile gas as a liquid transmits heat to the first volatile gas and may partially vaporize the first volatile gas below its flash point. The second volatile gas is condensed and returned to the second volatile gas system 330 and specifically vessel 331. The first volatile gas, in liquid or partially vaporized phase, is returned to vessel 321.

[0051] In further operations, second volatile gas may be increase in temperature and thus pressure in vessel 331. As such the boiling point of second volatile gas may be controlled by regulator 335, as previously described. In instances where the second volatile gas is maintained at a pressure and temperature, such that vapor is produced in vessel 331 and maintained below its flash point. The second volatile gas vapor passes through regulator 335 and may be conveyed to a second heat exchanger 324. Second heat exchanger 324 may be analogous to the previously described second heat exchanger in the transportation fluid system 314. The second volatile gas thermally exchanges heat with the partially vaporized first volatile gas. The heat exchange that occurs in the second heat exchanger 324 results in condensation of second volatile gas vapor. The condensed second volatile gas is returned to vessel 331, below its flash point. The partially vaporized first volatile gas is returned to vessel 321 of the first volatile gas system 320.

[0052] In the operational processes described herein, transport fluid, first volatile gas, and second volatile gas may contain no vapor, no liquid, or a mixture of liquid and vapor, depending upon the properties of each and operation of the system 300. Still further, regulators 315, 325, 335 may operate at the same pressure, a lower pressure, or a higher pressure than any other regulator in the system, though each is configured to keep the liquid gas vapor temperature and pressure below their predetermined flash point. For example, regulators 315, 325, 335 are operated at independent and different pressures or at the same operating pressure. Pump fed conduits 312, 322, 332 will preferentially be designed to move liquids, including cryogenic or subcooled liquids, but may be capable of partial or complete compression of gases.

[0053] Although not shown and described specifically, additional equipment can be utilized to provide cooling of specific streams utilizing refrigeration, evaporative cooling, air cooling and other sources of heat or cold which are not specifically cross-exchange of heat between the active fluids. All pressure control valves and operating valves may be manually operated, automatically operated or self-actuating. Although a controllable and safe control of the gases' flash point during operation is desired, no emergency equipment for maintaining pressure or temperature is specifically included or excluded at this time, but may be useful to prevent unsafe or undesirable conditions from developing within the equipment. It is also presumed that all liquids can be transferred into or out of any or all containment vessels shown herein, although such transfer equipment is not depicted in Figure 4.

[0054] Referring now to Figure 4 and Figure 2, the controllable and safe operation of the system 300 may allow for intermingling of the first volatile gas with the second volatile gas, or the first volatile gas with the transportation fluid, the second volatile gas with the transportation fluid, or any combination thereof. It is envisioned that there will be circumstances that it is desirable that a low temperature transport fluid (TF) be utilized as the heat transfer medium in the liquid state. It is further sometimes desirable that the more volatile gas, the first volatile gas (VG1) be maintained in its subcooled liquid state, such that it does not form solid fractions at storage conditions. It is further desirable that the first volatile gas vapor pressure does not exceed the pressure of containment at the controlled storage temperature. It is also understood that this invention is not limited to pure compounds or formulations. The transport liquid (TF) may be a pure compound or a mixture of compounds that has a desired boiling point or range at the desired operating pressure range of the system. The first volatile gas may be a mixture of compounds that as a mixture has a freezing point below that of the boiling point of the transport fluid, while having a boiling point at containment conditions above the boiling point of the transport fluid. In addition, a second volatile gas (VG2) may be a mixture of compounds or a pure substance that has a freezing point below that of the boiling point of the first volatile gas, while having a boiling point at containment conditions above or below the controlled temperature of the first volatile gas. In some cases, the boiling point of the second volatile gas will exceed the boiling point of the first volatile gas. In some cases, the boiling point of the second volatile gas will equal to or be lower than the boiling point of the first volatile gas. Although examples are contained within for a system of three distinct fluids, the number of fluids so contained could be greater. There is no limitation inferred as to the relative amounts of each fluid. The amount of one or more transport fluids needs to be great enough and no greater than adequate to move one or more first volatile gas and one or more second volatile gas as liquids from export location to import location taking into account expected losses due to vaporization to the environment and in some cases, its use as a source of transport fuel or power source for refrigeration. The amount of the first volatile gas needs to be only large enough to provide adequate cooling of and heat transfer away from the second volatile gas and may or may not consist of a saleable or valuable chemical for export. There may in some cases be versions of the first volatile gas and second volatile gas wherein the purpose of second volatile gas is to be a saleable product and that of the first volatile gas serves as a non-reactive heat transfer fluid. There may in some cases be multiple transport fluids, first volatile gas, and second volatile gas transported on the same overland transport or marine vessel. There may be cases wherein all substances are saleable but import locations are different for each material or portions of each substance or mixture made possible by the combined contents.

[0055] Referring to Figure 5 there is shown a table of representative chemical compounds that may be shipped as a first or second volatile gas liquid (eg. VG1, VG2). In these exemplary configurations, the transport fluid consisting or comprising liquid natural gas (LNG). The list of liquid volatile gases may be co-transported with the LNG in a thermally or cascade manner and system as discussed previously. The co-transported liquid volatile gases may be in direct or indirect thermal communication with the LNG, when implemented as a transportation fluid. Furthermore, the list of compounds is not exhaustive nor is the invention intended to be limited to this list of compounds, substances or their mixtures. Figure 5 is used for illustrative purposes only.

[0056] The LNG substantially comprises methane. It is also understood that impurities in the LNG which are not methane may be present. These other impurities can alter the boiling point and freezing point of the LNG. It is also understood that the pressure of containment of the co-transported compound will affect its boiling point. The pressure of transport can also change the boiling point of the LNG.

[0057] In general, Figure 5 demonstrates the fluid properties of freezing point and boiling point at normal or standard atmospheric pressure of many liquid volatile gas compounds. For example, if the boiling point of a volatile compound, substance or mixture is above that of the boiling point of the transport fluid (TF), and the freezing point of a more volatile gas, compound, substance or mixture (e.g. VG1, VG2) is lower than the boiling point of the transport fluid, then transport of the volatile gas liquid is enabled by use of the TF as an active or passive source of refrigeration such that the temperature of the volatile gas liquid may be maintained at or somewhat above the boiling point of the TF by boil-off or external refrigeration of the TF during transport or storage. In the rightmost column of Figure 5 this condition is identified by those liquid volatile gases as “Liquid”. Pure compounds with a freezing point above that of the boiling point of methane would form solids and would not with certainty be transported in the liquid state. Pure compounds with a boiling point below that of the boiling point of methane would form gases and would not with certainty be transported in the liquid state.

[0058] The exemplary concept described for LNG in Figure 4 may be extended to other compounds, such as nitrogen, which can be transported as a cryogenic liquid, as shown further illustrated in Figure 6. Employing nitrogen as the transport liquid (TF), the volatile gases (VG1, VG2) that can be co-transported as a liquid include oxygen and carbon monoxide. Further, compounds such as methane and ethane would solidify were nitrogen used solely as the transport liquid (TF). Therefore, in more general terms, if the boiling point of a volatile substance, compound or mixture in a volatile gas (e.g. VG1, VG2) is above that of a working constant temperature fluid compound or mixture that serves as the transport fluid (TF), and the freezing point of the volatile gas (VG1, VG2) is lower than that of a working constant temperature fluid compound or mixture that serves as the transport fluid, then transport of the volatile compound or mixture (VG1, VG2) as a liquid is enabled by use of the working constant temperature fluid acting as an active or passive source of refrigeration such that the temperature of the volatile gas, substance or mixture is maintained at or somewhat above the boiling point of the working constant temperature transport fluid compound or mixture during transport or storage. Use of liquid nitrogen as the transport fluid is advantageous when used as a boil off fluid as its release to the atmosphere does not result in increased carbon emissions nor release of combustible gases.

[0059] An example of fluid transport offers advantages for transporting select volatile gas liquids, but as shown in Figures 5 and 6, many compounds may be excluded if only LNG or methane and nitrogen are considered as adequate low value, low temperature boiling materials for co-transport of volatile compounds as liquids at or near the boiling temperature of the working constant temperature fluid.

In instances, using ethane as the transport liquid, for example, many more compounds become eligible for co-transport as liquids as is shown in Figure 7. Because ethane boils at a higher temperature than methane at atmospheric pressure, higher temperature boiling compounds can be transported as a liquid using ethane as a working constant temperature fluid. Normally, ethane has much greater economic value than LNG or methane and would not be considered a material that one would desire to lose to boil-off or combustion as fuel, but many compounds, including several of those shown here, are normally much more valuable than ethane on a mass basis, and the financial loss of ethane could be offset by the ability to transport and not lose to boil off a much more valuable compound.

[0060] Some compounds are much less safe to transport in pressurized vessels due to the potential for unintentional depressurization release resulting in a hazard. In instances should pressure control fail to provide operating pressures within the normal operating pressure of the containment, especially for the situation where low pressures result from reduction of temperature in a closed vessel, an inert gas can be charged to the closed containment vessel to avoid vacuum conditions. The inert gas may be LNG vapors, volatile gas (VG1, VG2) vapors, nitrogen, an unreactive gas or a noble gas such as argon or helium. Example inert gases for maintaining pressure in a vessel include nitrogen, argon, methane, ethane, propane, helium, hydrogen, and oxygen without limitation.

[0061] Recent advances in gas exploration, including fracking, have resulted in greater availability of ethane at substantially lower cost, making ethane a reasonable choice as a heat transfer liquid or mixture component for more volatile compounds in some markets. In light of the advances in fracking, both ethane and methane are much more available in certain regions of the world where fracking is widely employed. In those regions, LNG and ethane transport are desirable and suitable for cryogenic transport as described above. Ethane and mixtures of ethane can be transported as a stable liquid near atmospheric pressure using methane or LNG as the lower economic value, lower boiling transport or sacrificial fluid, such as to boil off or combustion. Ethane, and several other compounds as shown in Figure 7 can be maintained as a liquid at the normal boiling temperature of LNG or it can be maintained nearer to or at its boiling point at low pressure utilizing ordinary temperature control technology without the need for high pressure containment using active or passive flow control with heat exchangers in concert with a refrigeration apparatus the liquid ethane can be controlled to any temperature between the boiling point of the transport liquid and its own boiling point, which will be a result of the pressure maintained. Alternatively, employing ethane as an example only, the ethane can be allowed to heat to its boiling point and allowed to vaporize or even boil off as does LNG in typical LNG transport vessels. In another instance, the ethane boil-off gases can be recondensed by a heat exchanger wherein the cooling fluid is liquid LNG and the condensed ethane is returned to the ethane storage vessel.

[0062] A further advantage of allowing a first volatile gas (VG1) such as ethane to be transported at its boiling temperature, or substantially above the boiling temperature of the transport fluid is to allow a second and even more volatile gas compound or mixture (eg VG2) to be transported as a liquid at or near the maintained operating temperature of the ethane which, conversely, would not be a liquid at the temperature of boiling LNG transport (i.e. phosgene, ethylene oxide). Advantages of this method include avoiding storage of the volatile gas liquids (VG1, VG2) at elevated pressures and avoidance of the requirement of active refrigeration by standard refrigeration equipment including compressors.

[0063] The transport of materials that have economic value or are useful as conveyance heat transfer fluids, can be transported as liquids at pressure at temperatures at or below, and preferable significantly below local ambient temperature conditions are envisioned in this disclosure. Although ethane has been used as an example of a first volatile gas (VG1) which enables transport of a second volatile gas (VG2), other compounds, such as ethylene, which have a slightly lower boiling point than ethane, would serve to enable transport of some compounds that ethane does not. For example propane has a much higher boiling point, yet a lower freezing point than ethane, and would have a wider range of applicability than ethane. In some cases, ethylene (VG1), would be co-transported relative to ethane (VG2) or other non-reactive refrigerant such that the ethylene transfers heat away from the ethane and the ethane transfers heat away from the second volatile gas, protecting the second volatile gas from direct contact with a potentially reactive first volatile gas. In some cases it would be possible to have separate storage for the transport liquid, first volatile gas, and second volatile gas to enable transport of second volatile gas. In certain instances, during offloading one or more of these substances are allowed to be mixed such that the mixture is a valuable and salable commodity of a liquid volatile gas mixture. In some cases it would be possible to transport the first and second volatile gases as a mixture that is easier and safer to transport, more valuable as a finished product, or more useful in a final processing step. Nonexclusive examples of such a situation may include transporting chemicals such as phosgene, phosphine, ethylene oxide or carbonyl sulfide solvated in ethane where the more volatile transported chemical will be reacted later to form new compounds while the ethane serves as its solvent. In some cases it is possible that systems will include multiple transport fluids, and volatiles gases in order to convey multiple valuable gases from one or more export locations to one or more import locations using various disclosed heat transfer methods.

[0064] In certain configurations, the any transport vessel may have its internal pressure controlled by the introduction of other compressed, cryogenic, inert, or other gases, without limitation. In certain instances, these pressure controlling gases may include nitrogen, argon, methane, ethane, propane, helium, hydrogen, oxygen, or combinations thereof.

Examples

[0065] The Examples herein are meant to demonstrate various embodiments of the present invention. As examples, they are not exhaustive and there are variations not shown here that fall within the scope of the present disclosure.

Example 1

[0066] LNG is loaded onto a vessel capable of transporting LNG and other cargo and serves as the transport fluid. Liquid ethane is loaded into a separate containment and cooled to a temperature wherein the ethane does not boil at storage pressure, which in this case is chosen to be 101.325kPa to 136.789kPa (1 atm to 1.35 atm) for all fluids on the transport vessel. Therefore, LNG will be stored at approximately -161°C (-258°F) and the ethane will be stored below -89°C (-128°F) with a flash point of -135 °C. The high boiling liquid (VG2) is vinyl chloride, a recognized high-volume commodity chemical used in diverse locations of the world to make polyvinyl chloride. The vinyl chloride freezes at -154°C (-245°F) and boils at -14°C (7°F) at atmospheric pressure and has a flash point of -78°C. The vinyl chloride can be maintained as a liquid between those temperatures without pressure containment. A working temperature difference of at least 20°C for each fluid to more easily accommodate standard heat transfer equipment will be used. The LNG maintains itself through boiling at -161°C (-258°F), the ethane is cooled by the LNG and maintained at -141°C (-222°F) which is below its flash point and the vinyl chloride is maintained at -121°C (-186°F), which is significantly above its freezing point and well below its boiling point and flash point. Should the temperature difference drop between the ethane and the vinyl chloride, the minimum temperature that will be reached is -141°C (-222°F) which is above the freezing point of vinyl chloride. This is an example of one primary cryogenic liquid being used to maintain one secondary liquid in the liquid state which in turn is used to maintain a third substance in the liquid state while both are maintained below the flash point of each that could not be reliably maintained in the liquid state, with freezing prevented, by heat transfer with the primary cryogenic liquid.

Example 2

[0067] LNG is loaded onto a vessel capable of transporting LNG and other cargo. Liquid propane is loaded into a separate containment and cooled to a temperature wherein the propane does not boil at storage pressure, which in this case is chosen to be 101.325kPa to 136.789kPa (1 atm to 1.35 atm) for all fluids on the transport vessel. Therefore, LNG will be stored at approximately -161°C (-258°F) and the propane will be stored below -42°C (-44°F), its normal boiling point while considering the flash point of propane is -104 ˚C. The high boiling liquids (VG2s) will be ethylene oxide with a liquid state range between -111°C (-168°F) and 11°C (12°F) and a flash point of -29˚C, a recognized high volume commodity chemical used in diverse locations of the world to make polymers and various chemicals and phosgene, another high volume commodity chemical with a liquid state range of -128°C (-198°F) and 8°C (46°F) at atmospheric pressure without a recognized flash point. A useful working temperature for the propane could be 5°C higher than the higher freezing temperature of the high boiling compounds, or -106°C (-159°F) so the ethylene oxide cannot freeze. Assuming a working temperature difference of at least 20°C for each fluid, the ethylene oxide is maintained at -81°C (-114°F) and the phosgene is maintained at -81°C (-114°F). The LNG maintains itself through boiling at -161°C (-258°F), the propane is cooled by the LNG and maintained at -106°C (-159°F) and the high boiling compounds are maintained at -81°C (-114°F), which is significantly above their freezing points of -128°C (-198°F) and -111°C (-168°F), respectively and well below their boiling points of 11°C (12°F) and 8°C (46°F), respectively, as well as below the flash point of -29˚C for ethylene oxide. As these chemicals are explosive and highly reactive, ethylene oxide, and highly toxic, phosgene, containment and isolation may be enhanced with double wall shells and/or pressure rated containment. This is an example of one primary cryogenic liquid being used to maintain one secondary liquid in the liquid state which in turn is used to maintain two separate substances in the liquid state that could not be reliably maintained in the liquid state, with freezing prevented, by heat transfer with the primary cryogenic liquid wherein all substances with flash points are maintained below their flash points

Example 3

[0068] Ethylene dichloride (EDC) can be made by reaction of ethylene and chlorine at modest temperatures as low as 20°C (68°F). To prevent the mixing of these reactants during transport, a separate substance can be used as a heat transfer medium, for example, **isobutane**. In this scenario, LNG or methane is the transport fluid that is allowed to boil off and provide ultimate cooling for all the system liquid components. Isobutane's liquid state at atmospheric pressure ranges from 113K up to 261K. Ethylene's liquid state at atmospheric pressure ranges from 104K up to 169K. Chlorine's liquid state at atmospheric pressure ranges from 171K up to 239K. LNG is maintained at its boiling point of 111K. Ethylene will serve as the first volatile gas and will operate at 131K (-142˚C), below its flash point of -136˚C, exchanging heat with LNG. Isobutane will serve as second volatile gas and will operate at 188K (-85˚C), below its flash point of -83˚C, and exchange heat with ethylene. Although ethylene has a freezing point that is above that of ethane, neither liquid can fall below the boiling point of methane which sets the minimum temperature for the system, therefore assuring that neither chemical will freeze. Finally, the chlorine is the second volatile gas of the system, exchanges heat with isobutane, and is maintained above 184K (-89˚C). Chlorine temperature is allowed to operate between 184K and its boiling point of 239K. Chlorine does not have a known flash point.

Example 4

[0069] Ethylene freezes at 104K and boils at 169K at atmospheric pressure and has a flash point of 137K. Its freezing point is below methane's boiling point of 111K. LNG is loaded onto a vessel capable of transporting LNG and other cargo and serves as the transport fluid (TF). Liquid ethylene is subsequently cooled and loaded as a volatile gas liquid into a separate containment compartment that is thermally in contact with LNG wherein the ethylene does not boil at storage pressure, which in this case is chosen to be 1 atm to 1.35 atm (101.325kPa to 136.789kPa) for all fluids on the transport vessel. Therefore, LNG will be stored at approximately 111K, its boiling point, and the ethylene will be stored below 169K at 132K which is below its flash point. Using heat exchange or thermal cascade, liquid ethylene is maintained at a temperature below its boiling point by cross exchange of heat with LNG. In this example there is no third liquid.

Example 5

[0070] Propylene freezes at 88K and boils at 225K at atmospheric pressure. Its freezing point is below methane's boiling point of 111K. LNG is loaded onto a vessel capable of transporting LNG and other cargo and serves as the Primary Cryogenic Liquid. Liquid propylene is loaded into a separate containment and cooled to a temperature wherein the propylene does not boil at storage pressure, which in this case is chosen to be 1 atm to 1.35 atm (101.325kPa to 136.789kPa) for all fluids on the transport vessel. Therefore, LNG will be stored at approximately 111K, its boiling point, and the propylene will be stored below 225K and preferentially below its flash point of 165K. Using heat exchange or thermal cascade, liquid propylene is maintained at a temperature below its boiling point and flash point by cross exchange of heat with LNG. In this case, there is no third liquid.

Example 6

[0071] Ethylene is loaded onto an insulated cryogenic liquid transport ship that is designed to transport ethylene as a cryogenic fluid between its boiling point (169K) and freezing point (104K). Ethylene is loaded onto the ship at -140 C (133K), below its flash point of 137K. The insulated cargo ship is designed to permit heat ingress equivalent to LNG boiloff during transport of 5% during its voyage of 14 days. The ship design utilizes a mass ratio of methane to ethylene of 1:9. At -258˚C the heat of vaporization of methane is 3521 BTU/lbmol or 220 btu/lbm. At -140˚C the heat capacity of liquid ethylene is 0.578 Btu/lbm R. For every lbm of methane vaporization at storage conditions, equivalent and compensating heating of 19 lbm of ethylene will be 20 R or 11˚C. Over the two week voyage, when not cooled by LNG vaporization, the ethylene will heat from -140˚C to -129˚C. In this case, no refrigeration will be required for the ethylene to remain in the liquid state prior to unloading which could be used to reduce or eliminate the need for the LNG cooling or any other method of refrigeration. The final temperature of the ethylene would exceed its flash point temperature.

Example 7

[0072] Ethylene is loaded onto an insulated cryogenic liquid transport ship that is designed to transport ethylene as a cryogenic fluid between its boiling point (169K) and freezing point (104K). Ethylene is loaded onto the ship at -140 C (133K), below its flash point of 137K. The insulated cargo ship is designed to permit heat ingress equivalent to LNG boiloff during transport of 5% during its voyage of 14 days. The ship does not carry LNG. At -258˚C the heat of vaporization of methane is 3521 BTU/lbmol or 220 btu/lbm. At -140˚C the heat capacity of liquid ethylene is 0.578 Btu/lbm R. For every lbm of methane vaporization at storage conditions, equivalent and compensating heating of 19 lbm of ethylene will be 20 R or 11˚C. Over the two week voyage the ethylene will heat from -140˚C to -129˚C without refrigeration. In this case, no refrigeration will be required for the ethylene to remain in the liquid state prior to unloading which could be used to reduce or eliminate the need for the LNG cooling or any other method of refrigeration but the final temperature of the ethylene would exceed the flash point temperature. Therefore, refrigeration equivalent to LNG boiloff of 7/11 of 5% or 3.2% will be applied to maintain the ethylene below its flash point.

Example 8

[0073] Ethylene is loaded onto an insulated cryogenic liquid transport ship that is designed to transport ethylene as a cryogenic fluid between its boiling point (169K) and freezing point (104K). Ethylene is loaded onto the ship at -150 C (123K), below its flash point of 137K. The insulated cargo ship is designed to permit heat ingress equivalent to LNG boiloff during transport of 5% during its voyage of 14 days. The ship design utilizes a mass ratio of methane to ethylene of 1:9. At -258˚C the heat of vaporization of methane is 3521 BTU/lbmol or 220 btu/lbm. At -150˚C the heat capacity of liquid ethylene is 0.578 Btu/lbm R. For every lbm of methane vaporization at storage conditions, equivalent and compensating heating of 19 lbm of ethylene will be 20 R or 11˚C. Over the two week voyage, when not cooled by LNG vaporization, the ethylene will heat from -150˚C to -139˚C (134 K). In this case, no refrigeration will be required for the ethylene to remain in the liquid state prior to unloading which could be used to reduce or eliminate the need for the LNG cooling or any other method of refrigeration. The final temperature of the ethylene would not exceed its flash point temperature.

Example 9

[0074] Ethane is loaded onto an insulated cryogenic liquid transport ship that is designed to transport ethane as a cryogenic fluid between its boiling point (184K) and freezing point (90K). Ethane is loaded onto the ship at -140 C (133K), below its flash point of 138K. The insulated cargo ship is designed to create LNG boiloff during transport of the liquid ethane of 2% during its voyage of 21 days which can also be used as fuel and a source of energy for other ship operations to maintain the loading temperature. The ship design utilizes a mass ratio of methane to ethylene of 1:9. At -258˚C the heat of vaporization of methane is 3521 BTU/lbmol or 220 btu/lbm. At -140˚C the heat capacity of liquid ethylene is 0.557 Btu/lbm R. For every lbm of methane vaporization at storage conditions, the equivalent and compensating heating of 49 lbm of ethane will be 8.1 R or 4.5˚C. Over the three week voyage the ethane will heat from -140˚C to -135.5˚C (137.6K). In this case, no refrigeration will be required for the ethylene to remain in the liquid state prior to unloading, which could justify reducing or eliminating the need for the LNG cooling or any other method of refrigeration during transit. The final temperature of the ethylene would not exceed the flash point temperature under these conditions.

Example 10

[0075] Propylene is loaded onto an insulated cryogenic liquid transport ship that is designed to transport propylene as a cryogenic fluid between its boiling point (225K) and freezing point (88K). Propylene is loaded onto the ship at -140 C (133K), below its flash point of 165K. The insulated cargo ship is designed to permit heat ingress equivalent to 10% LNG boiloff during transport of the liquid propylene during its voyage of 21 days. The ship design utilizes a mass ratio of methane to propylene of 1:9. At -258˚C the heat of vaporization of methane is 3521 BTU/lbmol or 220 btu/lbm. At -140˚C the heat capacity of liquid propylene is 0.521 Btu/lbm R. For every lbm of methane vaporization at storage conditions, the same energy ingress results in heating of 9 lbm of propylene by 47 R or 26˚C. Over the three week voyage the propylene will heat from -140˚C to -114˚C (159 K). In this case, no refrigeration will be required for the propylene to remain in the liquid state prior to unloading which could be used to reduce or eliminate the need for the LNG cooling or any other method of refrigeration. The final temperature of the propylene would not exceed the flash point temperature.

Claims:

1. A method for storage and transporting gases, comprising:

charging a transport fluid to transport fluid system at cryogenic conditions;

charging a first volatile gas to a first volatile gas system;

maintaining the first volatile gas in a first subcooled liquid phase by heat transfer with the transport fluid below its boiling point at storage pressure,

charging a second volatile gas to a second volatile gas system;

maintaining the second volatile gas in a second subcooled liquid phase below its boiling point by heat transfer with the first subcooled volatile gas;

and transporting the first and second liquid phases.

2. The method of claim1, wherein transport fluid comprises at least one component chosen from the group consisting of: oxygen, nitrogen, argon, liquid natural gas, methane, ethane, ethylene, propane, propylene and combinations thereof.

3. The method of claim 1, wherein the transport fluid is maintained at a temperature at a predetermined pressure by boiling or external refrigeration.

4. The method of of claim 1, wherein the first volatile gas comprises at least one gas component chosen from the group consisting of: oxygen, carbon monoxide, argon, propane, propylene, 1-butene, silane, tetrafluoromethane, ethane, methane, monochlorotrifluoroethane, chlorotrifluoromethane, ethylene chlorodifluoromethane, chlorodifluoromethane, isobutane, krypton, trifluoromethane, vinyl chloride, perfluoroethene, tetrafluoroethylene, dimethyl ether, isobutene, n-butane, methyl ethyl ether, carbonyl sulfide, chloro-2-difluoro-1,1-ethylene, difluoromethane, dichloromonoflurormethane, phosphine, neopentane, phosgene, acetaldehyde, difluoroethane, chloro-1-tetrafluoro-1,1,2,2-ethane, hydrogen chloride, xenon, ethylene oxide, 1,1,1-trifluoroethane, 1,2-butadiene, 1,3-butadiene, dichlorodifluoroethane, chloro-2-trifluoro-1,1,1-ethane, chlorine, 1,1,1,2-tetrafluoroethane, hexafluoroethane, methyl chloride, methyl bromide, formaldehyde, dinitrogen oxide, hydrogen sulfide, hydrogen fluoride, methyl fluoride, ammonia, pentafluoroethane and combinations thereof.

5. The method of claim 1, wherein the first volatile gas is precooled to a subcooled liquid phase prior to charging the first volatile gas system.

6. The method of claim 5, wherein the subcooled first volatile gas comprises a freezing point below the boiling point of the transport fluid and a boiling point above that of transport fluid at operating pressure.

7. The method of claim 6, comprising maintaining the subcooled first volatile gas temperature below its flash point at operating pressure.

8. The method of claim 7, comprising maintaining the first volatile gas temperature above its freezing point at operating pressure.

9. The method of claim 1, comprising cooling the first volatile gas to a temperature that will enable transport from a loading location to an off-loading location such that the first volatile gas will not reach its boiling point at operating pressure during transit without applied cooling or with reduced applied cooling.

10. The method of claim 1, comprising cooling the first volatile gas to a temperature that will enable transport from a loading location to an off-loading location such that the first volatile gas will not rise above its flash point temperature at operating pressure during transit without applied cooling or with reduced applied cooling.

11. The method of claim 1, wherein the second volatile gas comprises at least one gas component chosen from the group consisting of: oxygen, argon, propane, propylene, 1-butene, silane, tetrafluoromethane, ethane, methane, monochlorotrifluoroethane, chlorotrifluoromethane, ethylene, chlorodifluoromethane, chlorodifluoromethane, isobutane, krypton, trifluoromethane, vinyl chloride, perfluoroethene, tetrafluoroethylene, dimethyl ether, isobutene, n-butane, methyl ethyl ether, carbonyl sulfide, chloro-2-difluoro-1,1-ethylene, difluoromethane, dichloromonoflurormethane, phosphine, neopentane, phosgene, acetaldehyde, difluoroethane, chloro-1-tetrafluoro-1,1,2,2-ethane, hydrogen chloride, xenon, ethylene oxide, 1,1,1-trifluoroethane, 1,2-butadiene, 1,3-butadiene, dichlorodifluoroethane, chloro-2-trifluoro-1,1,1-ethane, chlorine, 1,1,1,2-tetrafluoroethane, hexafluoroethane, methyl chloride, methyl bromide, formaldehyde, dinitrogen oxide, hydrogen sulfide, hydrogen fluoride, methyl fluoride, ammonia, pentafluoroethane, and combinations thereof.

12. The method of claim 1, comprising maintaining the second volatile gas temperature below its boiling temperature and above its freezing temperature at operating pressure.

13. The method of claim 12, wherein the second volatile gas comprises a freezing point above the boiling point of at least one first cryogenic liquid and a boiling point at or lower than the boiling point of at least one second cryogenic liquid.

14. The method of claim 13, wherein second volatile gas has a freezing point above the boiling point of the transport fluid and a boiling point above the boiling point of the second volatile gas.

15. The method of claim 1, comprising controlling the temperature in any system by using refrigeration, one or more evaporative coolers, one or more air coolers, one or more water coolers, auto-refrigeration, or gas-expansion.

16. The method of claim 1, further comprising maintaining pressure in a storage vessel by the introduction of a gas comprising at least one from the group consisting of: nitrogen, argon, methane, ethane, propane, helium, hydrogen and oxygen.

17. A system configured for subcooled volatile liquid gas transport, comprising

a transport fluid vessel, configured to contain a cryogenic liquid gas;

a first volatile liquid gas vessel, in thermal communication with the transport fluid vessel and configured to contain a first subcooled liquid gas; and

a second volatile liquid gas vessel, in thermal communication with the transport fluid vessel and configured to contain a second subcooled liquid gas.

18. The system of claim 17, where in the second volatile liquid gas vessel is in thermal communication with the first volatile liquid gas vessel.

19. The system of claim 17, comprising a refrigeration system in thermal communication with the transport fluid vessel, the first volatile liquid gas vessel, and the second volatile liquid gas vessel.

20. The system of claim 17, wherein the cryogenic liquid gas, the first subcooled liquid gas, or the second subcooled liquid gas comprise a gas chosen from the list consisting of: oxygen, nitrogen, argon, liquid natural gas, methane, ethane, ethylene, propane, propylene, carbon monoxide, 1-butene, silane, tetrafluoromethane, ethane, methane, monochlorotrifluoroethane, chlorotrifluoromethane, ethylene chlorodifluoromethane, chlorodifluoromethane, isobutane, krypton, trifluoromethane, vinyl chloride,

perfluoroethene, tetrafluoroethylene, dimethyl ether, isobutene, n-butane, methyl ethyl ether, carbonyl sulfide, chloro-2-difluoro-1,1-ethylene, difluoromethane, dichloromonoflurormethane, phosphine, neopentane, phosgene, acetaldehyde, difluoroethane, chloro-1-tetrafluoro-1,1,2,2-ethane, hydrogen chloride, xenon, ethylene oxide, 1,1,1-trifluoroethane, 1,2-butadiene, 1,3-butadiene, dichlorodifluoroethane, chloro-2-trifluoro-1,1,1-ethane, chlorine, 1,1,1,2-tetrafluoroethane, hexafluoroethane, methyl chloride, methyl bromide, formaldehyde, dinitrogen oxide, hydrogen sulfide, hydrogen fluoride, methyl fluoride, ammonia, pentafluoroethane and combinations thereof.

Figure 1

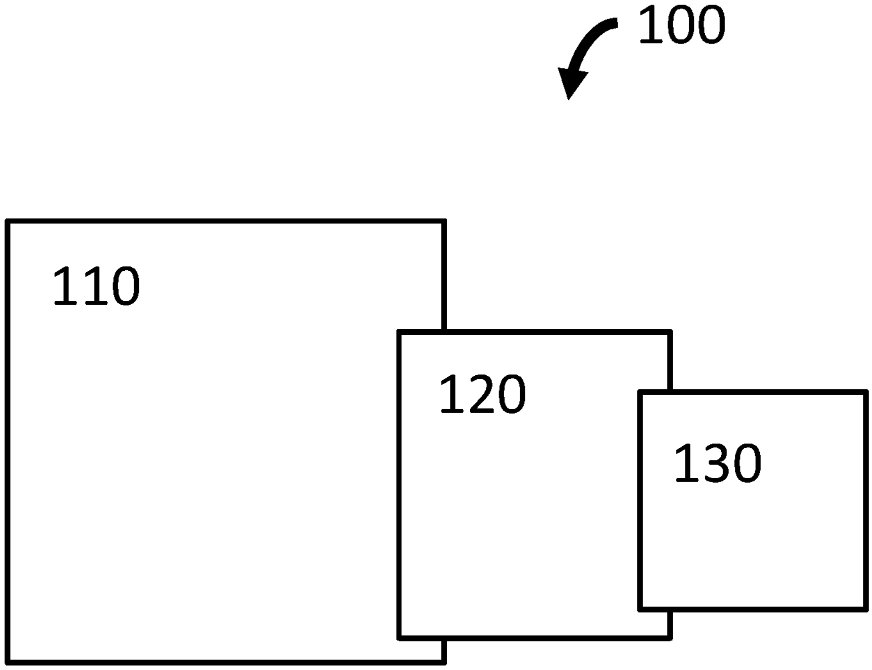


Figure 2

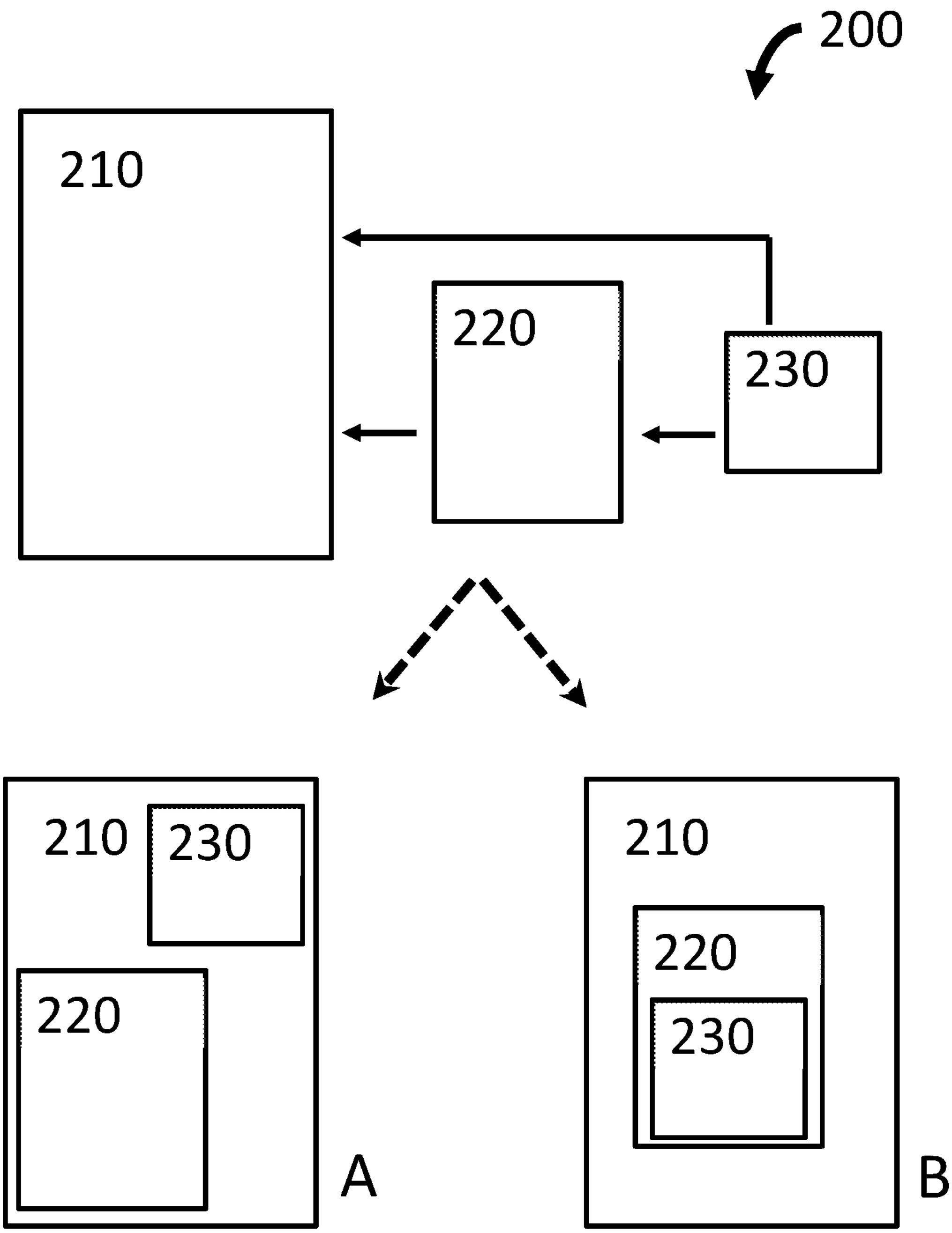
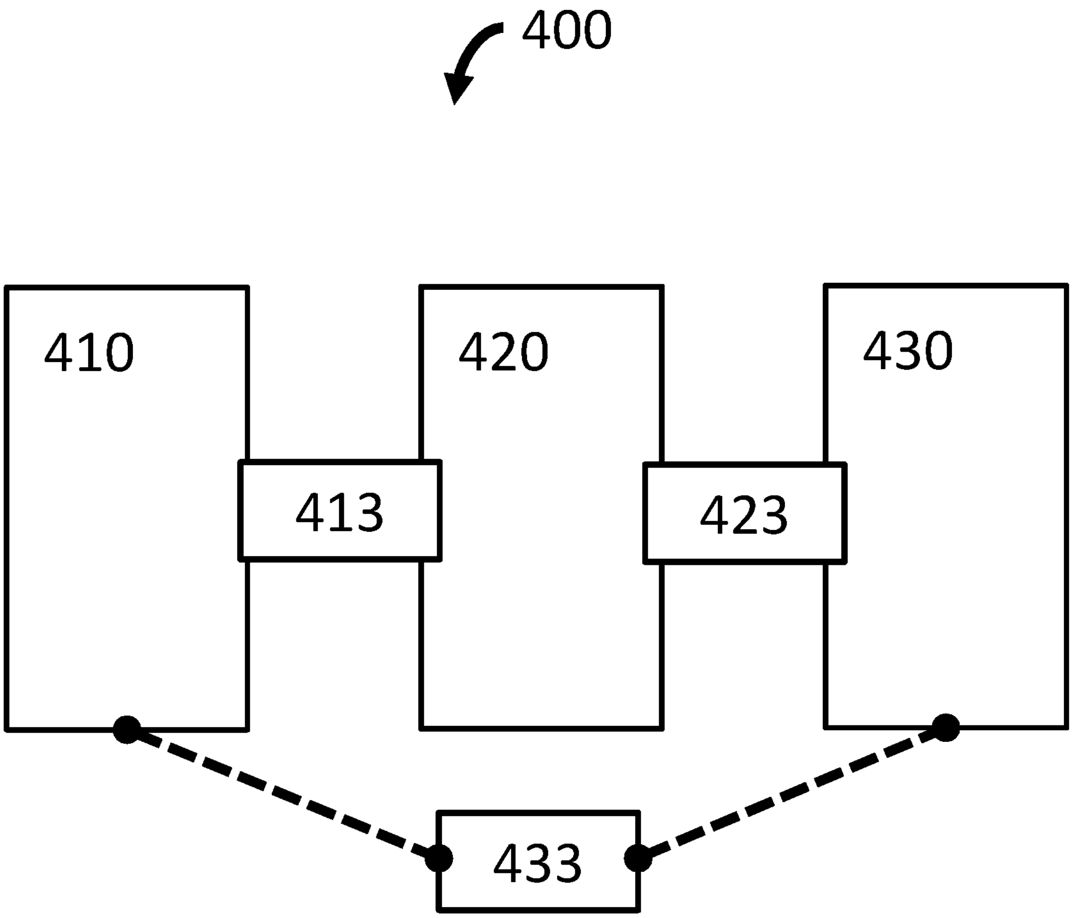


Figure 3



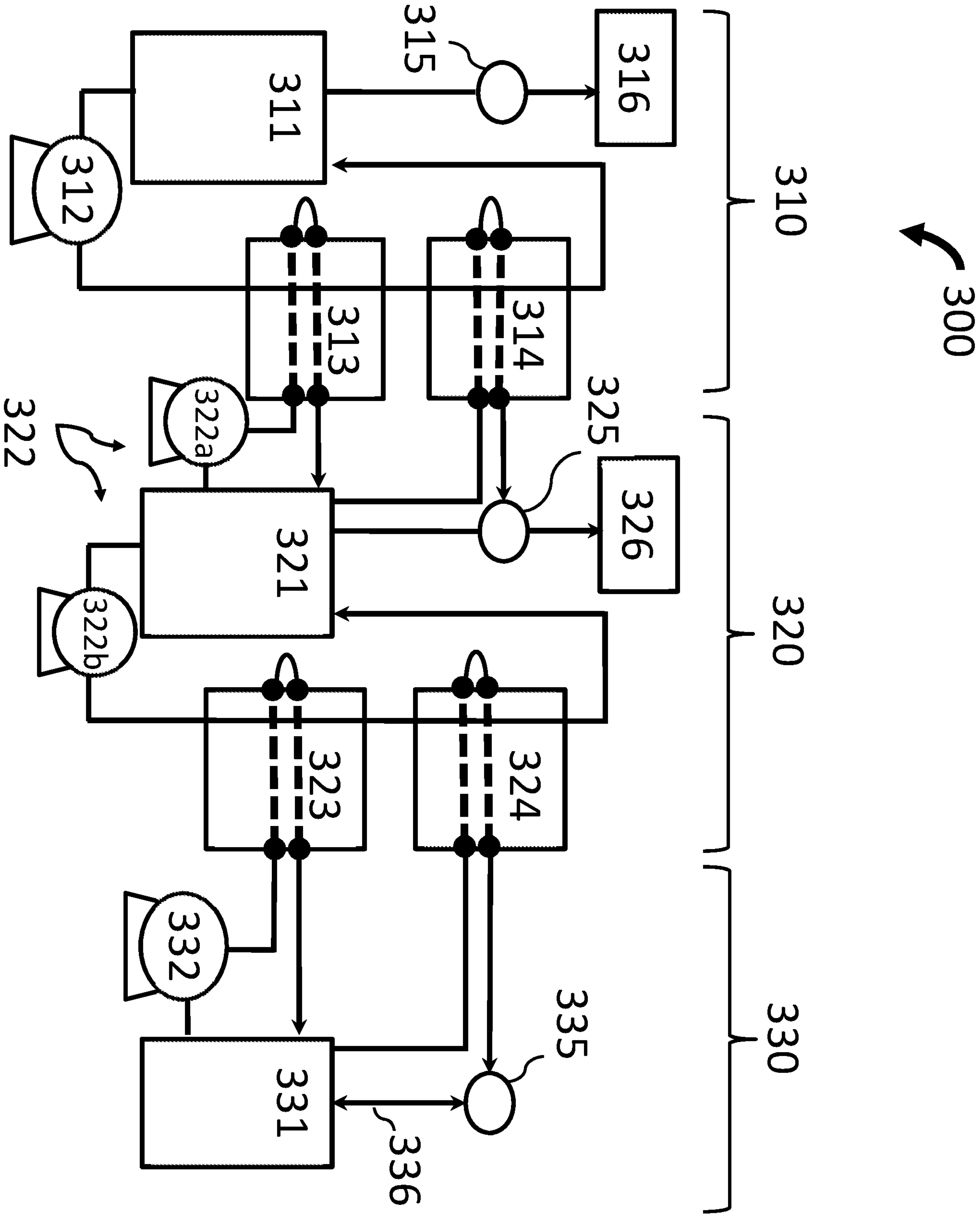

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Figure 4

Figure 5

Gas	BOILING POINT (K)	FREEZING POINT (K)	Refrigerant Identity	Phase
Helium	4	**1**		Vapor
Hydrogen	20.3	**13.8**		Vapor
Oxygen	90.1	**54.1**		Vapor
Nitrogen	77.3	**63.2**		Vapor
Carbon monoxide	81.9	**68.2**		Vapor
Argon	87.2	**84.2**		Vapor
Propane	**231.1**	**85.5**		**Liquid**
Propylene	**225.4**	**87.8**		**Liquid**
Silane	**161.7**	**88.1**		**Liquid**
Tetrafluoromethane	**145.2**	**89.1**	R14	**Liquid**
Ethane	**184**	**90**		**Liquid**
Methane	**111.7**	**90.7**		
Monochlorotrifluoroethane	**191.7**	**92**	R13	**Liquid**
Chlorotrifluoromethane	**191.7**	**92**		**Liquid**
Ethylene	**169.3**	**104**		**Liquid**
Chlorodifluoro-methane	**232.3**	113	R22	Solid
Chlorodifluoro-methane	**232.4**	113		Solid
Krypton	**119.8**	115.8		Solid
Trifluoromethane	**191**	117.9	R23	Solid
Vinyl chloride	**259.3**	119	R1140	Solid
Perfluoroethene	**197.5**	130.7		Solid
Tetrafluoroethylene	**197**	131	R1114	Solid
Methyl ethyl ether	**280.5**	134		Solid
Carbonyl sulfide	**222.9**	134.3		Solid
Chloro-2-Difluoro-1,1-ethylene	**254.5**	135.1	R1122	Solid
Difluoromethane	**221.5**	136.1	R32	Solid
Dichloromono-fluoromethane	**282**	138		Solid
Phosphine	**185.3**	139.1		Solid
Phosgene	**280.8**	145		Solid
Difluoroethane	**248.5**	156	R152A	Solid

Gas	BOILING POINT (K)	FREEZING POINT (K)	Refrigerant Identity	Phase
Chloro-1-Tetrafluoro 1,1,2,2-ethane	**262.3**	156.1	R124A	Solid
Xenon	**165**	161		Solid
Ethylene oxide	**283.6**	161.2		Solid
1,1,1-trifluoroethane	**225.5**	162.1	R-143A	Solid
Dichlorodifluoro-ethane	**301**	166.2	R123	Solid
Chloro-2-trifluoro-1,1,1-ethane	**280**	168.1	R133A	Solid
1,1,1,2-tetrafluoroethane	**246.6**	172.1	R134A	Solid
Hexafluoroethane	**194.9**	172.5	R116	Solid
Methyl chloride	**249.3**	175.4	R40	Solid
Nitrous oxide	**184.7**	182.2		Solid
Hydrogen sulfide	**212.8**	186.7		Solid
Methyl fluoride	**274.3**	194.8	R41	Solid
Ammonia	**239.7**	195.4		Solid
Pentafluoroethane	**322**	224.8	R125	Solid

Figure 6

Gas	**BOILING POINT (K)**	**FREEZING POINT (K)**	**Phase**
Helium	4	1	Vapor
Hydrogen	20.3	13.8	Vapor
Oxygen	90.1	54.1	**Liquid**
Nitrogen	77.3	63.2	
Carbon monoxide	81.9	68.2	**Liquid**
Argon	87.2	84.2	Solid
Propane	231.1	85.5	Solid
Propylene	225.4	87.8	Solid
Silane	161.7	88.1	Solid
Tetrafluoromethane	145.2	89.1	Solid
Ethane	184	90	Solid
Methane	111.7	90.7	Solid

Figure 7

Gas	BOIL POINT (K)	FREEZE POINT (K)	VG2 Viability
Helium	4	1	
Hydrogen	20.3	13.8	
Fluorine	85	54	
Oxygen	90.1	54.1	
Nitrogen	77.3	63.2	
Carbon monoxide	81.9	68.2	
Argon	87.2	84.2	
Propane	231.1	85.5	
Propylene	225.4	87.8	
1-butene	266	88	
Silane	161.7	88.1	
Tetrafluoromethane	145.2	89.1	
Ethane	184	90	
Methane	111.7	90.7	
Monochloro-trifluoroethane	191.7	92	Yes
Chlorotrifluoro-methane	191.7	92	Yes
Ethylene	169.3	104	Yes
Chlorodifluoro-methane	232.3	113	Yes
Chlorodifluoro-methane	232.4	113	Yes
Isobutane	261	113	Yes
Krypton	119.8	115.8	Yes
Trifluoromethane	191	117.9	Yes
Vinyl chloride	259.3	119	Yes
Perfluoroethene	197.5	130.7	Yes
Tetrafluoro-ethylene	197	131	Yes
Dimethyl ether	249	132	Yes
Isobutene	266	133	Yes
n-Butane	272	133	Yes
Methyl ethyl ether	280.5	134	Yes
Carbonyl sulfide	222.9	134.3	Yes
Chloro-2-Difluoro-1,1-ethylene	254.5	135.1	Yes
Difluoromethane	221.5	136.1	Yes
Dichloromono-fluoromethane	282	138	Yes
Phosphine	185.3	139.1	Yes
Neopentane	309	143	Yes
Phosgene	280.8	145	Yes
Acetaldehyde	293	150	Yes
Difluoroethane	248.5	156	Yes

Gas	BOIL POINT (K)	FREEZE POINT (K)	VG2 Viability
Chloro-1-tetrafluoro-1,1,2,2-ethane	262.3	156.1	Yes
Hydrogen chloride	188	159	Yes
Xenon	165	161	Yes
Ethylene oxide	283.6	161.2	Yes
1,1,1-trifluoroethane	225.5	162.1	Yes
1,2-butadiene	269	164	Yes
Dichlorodi-fluoroethane	301	166.2	Yes
Chloro-2-trifluoro-1,1,1-ethane	280	168.1	Yes
Chlorine	239	171	Yes
1,1,1,2-tetrafluoroethane	246.6	172.1	Yes
Hexafluoroethane	194.9	172.5	Yes
Methyl chloride	249.3	175.4	Yes
Methyl bromide	276	179	Yes
Formaldehyde	254	181	Yes
Dinitrogen oxide	184.7	182.2	Yes
Hydrogen sulfide	212.8	186.7	
Hydrogen fluoride	294	189	
Methyl fluoride	274.3	194.8	
Ammonia	239.7	195.4	
Pentafluoroethane	322	224.8	

Figure 8

Compound	Boiling Point(K)	Freezing Point(K)	Flash Point (K)	Bp-Fp (K)	Flash Point (C)
propane	231.1	85.5	169	62	-104
Propylene	225.4	87.8	165	60	-108
1-butene	266	88	193	73	-80
ethane	184	90	138	46	-135
methane	111.7	90.7	167	-55	-106
ethylene	169.3	104	137	32	-136
isobutane	261	113	190	71	-83
vinyl chloride	259.3	119	195	64	-78
dimethyl ether	249	132	232	17	-41
isobutene	266	133	197	69	-76
n-butane	272	133	190	82	-83
ethylene oxide	283.6	161.2	244	40	-29

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 20/27917

A. CLASSIFICATION OF SUBJECT MATTER

IPC - F17C 3/02; F17C 7/02; F17C 9/02 (2020.01)

CPC - F17C 13/001; F17C 13/006; F17C 3/02; F17C 7/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
See Search History document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
See Search History document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ---- A	WO 2017/067984 A1 (Linde Aktiengesellschaft) 27 April 2017 (27.04.2017) pg 1, ln 3-4, pg 3, ln 11, pg 3, ln 19-22, pg 3, ln 30-31, pg 4, ln 30-35, pg 6, ln 6-9, pg 7, ln 22-25, pg 8, ln 20-23	17, 19-20 ------------ 1-16, 18
A	WO 2011/055163 A1 (Quesada Saborio) 12 May 2011 (12.05.2011) pg 1, ln 7-9	18
A	US 2015/0204604 A1 (Cryolor) 23 July 2015 (23.07.2015) para [0003], para [0017], para [0026], para [0033], para [0034], fig. 1	1-16
A	US 2013/0174583 A1 (Lee) 11 July 2013 (11.07.2013) para [0006], para [0019], figure	1-16
X, P	WO 2019/140033 A1 (Peterson) 18 July 2019 (18.07.2019) entire document	1-20
A	US 4,292,062 A (Dinulescu et al.) 29 September 1981 (29.09.1981) entire document	1-20
A	US 2013/0327404 A1 (Papp et al.) 12 December 2013 (12.12.2013) entire document	1-20
A	US 2015/0013379 A1 (Oelfke) 15 January 2015 (15.01.2015) entire document	1-20

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- "O" document referring to an oral disclosure, use, exhibition or other means
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- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
29 July 2020	27 AUG 2020
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer Lee Young Telephone No. PCT Helpdesk: 571-272-4300