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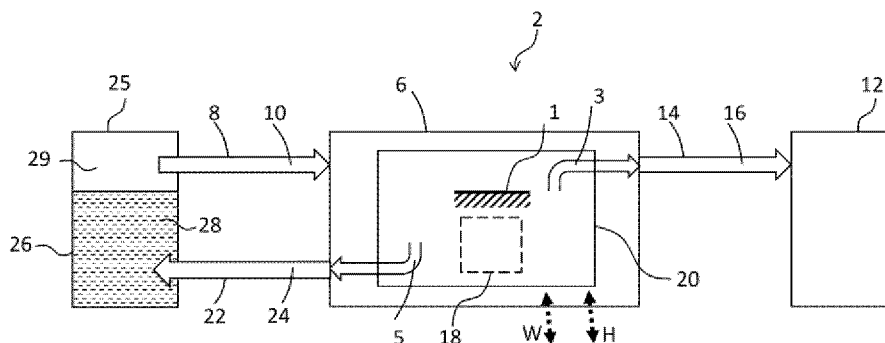
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(54) Title: METHOD OF, AND APPARATUS FOR, COOLING FLUID

Figure 2:



(57) Abstract: A method of cooling hydrogen, the method comprising the steps of: (a) flowing an inflow stream of hydrogen vapour from an upstream device into a cooling system; (b) within the cooling system, heating a cold-side solid heat transfer surface with heat transferred, directly or indirectly, from hydrogen undergoing cooling, and providing at least some or all of the cooled hydrogen as a supply of cooled hydrogen; (c) within the cooling system, heating hydrogen with heat transferred by direct contact with the cold-side solid heat transfer surface to form heated hydrogen; and (d) within the cooling system or the upstream device, exposing hydrogen, which hydrogen is in, or to be comprised in, the heated hydrogen and/or the supply of cooled hydrogen, to a catalyst which endothermically yields a net conversion of para-hydrogen to ortho-hydrogen. Also disclosed is an apparatus for cooling hydrogen for implementing the method. There is also disclosed a method and apparatus for cooling a fluid using a regenerator.

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Method of, and Apparatus for, Cooling Fluid

[01] The present invention relates to a method of cooling fluid and an apparatus for cooling fluid. Examples of fluids cooled by the method and apparatus set out in the present invention include liquids and vapours comprising hydrogen, helium, nitrogen, oxygen, natural gas, petroleum gas, carbon dioxide, argon, ammonia, or ethylene, and mixtures thereof.

[02] It is known to those skilled in the art that it is advantageous to cool and/or liquefy fluids in order to increase their density and thereby to facilitate storage and transport; or to cool fluids as part of a cyclic process in which energy is stored and recovered; or to cool fluids in preparation for their use as a process coolant or feedstock.

[03] It is known to those skilled in the art that national and international commitments to reduce carbon dioxide emissions necessitate use of liquid hydrogen in hard-to-decarbonise applications. Shipping of liquid hydrogen is needed in order to trade zero carbon energy across oceans, buffering and moving clean energy flexibly from regions of excess supply to regions of excess demand. Furthermore, liquid hydrogen is a key component of plans to achieve net-zero aviation. Liquid hydrogen technology underpins a broad set of carbon-neutral solutions that are a major focus of investment in the manufacturing (e.g. zero-carbon blast furnaces), energy and transport industries (including sea, road, rail, air and space).

[04] It is well known that liquid hydrogen suffers from the problem of boil-off. A central challenge for liquid hydrogen systems is evaporation of the liquid hydrogen due to ingress of heat from the environment. Many propulsion and industrial applications are able to make use of the hydrogen gas as it boils off, for example a hydrogen transporter may use the boil-off gas in its engines, or a liquid hydrogen supply system at an airport may be able to dispense liquid hydrogen to aircraft while compressing boil-off gas for use in ground vehicles. However if the rate of boil-off exceeds the utilisation or export rate of hydrogen vapour, the excess boil-off should be reliquefied, stored by some other means, or either oxidised to water or diluted beyond its flammability limit to avoid accumulation of flammable or explosive hydrogen gas mixtures.

[05] Liquefaction of hydrogen requires cooling to -253° Celsius (20 Kelvin), and current very large scale and complex hydrogen liquefaction plants utilise around one third of the calorific value of the liquid hydrogen fuel in order to convert hydrogen into liquid (40 MJ/kg vs 120 MJ/kg).

[06] It is known to those skilled in the art that boil-off is a problem for various liquefied gases, in addition to hydrogen, that are liquefied by cooling gas below the temperature of the environment, and that boil-off gas can present an economic cost and/or an environmental harm. Various approaches are known to those skilled in the art for utilising, reliquefying or safely

dispersing boil-off, but such approaches incur economic or environmental costs, or may compromise other aspects of system performance. As in the case of hydrogen, reliquefaction of boil-off gases requires an energy input. There is a need in the art for an improved method and apparatus for cooling fluid, and for example cooling gas sufficiently to form liquid thereby reliquefying a portion of the boil-off gas from liquified gas, which can use a small fraction of the energy typically used by current technologies to cool the fluid to a desired temperature, or to reliquefy gas.

[07] There is also a need in the art for an improved method and apparatus for cooling fluid, and for example cooling gas sufficiently to form liquid by reliquefying a portion of the boil-off gas from liquified gas, which can use simple low-cost and light-weight equipment that can operate within the size and weight limitations of the (relatively) small scale of a ship, aircraft, transport vehicle, or filling station.

[08] There is also a need in the art for an improved method and apparatus for more efficiently cooling fluid to a desired temperature as compared to known cooling processes, particularly when reliquefying a portion of the boil-off gas from liquified gas.

[09] The present invention aims to provide a method of cooling gases and an apparatus for cooling gases which meets one or more of these needs in the art.

[010] The present invention accordingly provides a method of cooling hydrogen the method comprising the steps of:

- (a) flowing an inflow stream of hydrogen vapour from an upstream device into a cooling system;
- (b) within the cooling system, heating a cold-side solid heat transfer surface with heat transferred, directly or indirectly, from hydrogen undergoing cooling, and providing at least some or all of the cooled hydrogen as a supply of cooled hydrogen;
- (c) within the cooling system, heating hydrogen with heat transferred by direct contact with the cold-side solid heat transfer surface to form heated hydrogen; and
- (d) within the cooling system or the upstream device, exposing hydrogen, which hydrogen is in, or to be comprised in, the heated hydrogen and/or the supply of cooled hydrogen, to a catalyst which endothermically yields a net conversion of para-hydrogen to ortho-hydrogen.

[011] The specific total enthalpy of the heated hydrogen after said exposure may be greater than that of the inflow stream and the supply of cooled hydrogen combined.

[012] The specific total enthalpy of the heated hydrogen may be the specific total enthalpy of the heated hydrogen after the step of transferred by direct contact with the cold-side solid heat transfer surface to form heated hydrogen, or where the heated hydrogen is additionally exposed to the catalyst, after exposure to the catalyst.

[013] The heated hydrogen may be heated solely by heat transfer by direct contact with the cold-side solid heat transfer surface and exposure to the catalyst.

[014] The present invention further provides an apparatus for cooling hydrogen, the apparatus comprising: an upstream device configured to contain hydrogen vapour, a cooling system comprising a cold-side solid heat transfer surface, an inflow conduit connecting the upstream device and the cooling system for flowing an inflow stream of hydrogen vapour from the upstream device into the cooling system, and a catalyst for converting para-hydrogen to ortho-hydrogen in hydrogen within the cooling system or within the upstream device, wherein the cooling system is configured to heat the a cold-side solid heat transfer surface with heat transferred, directly or indirectly, from hydrogen undergoing cooling, to provide at least some or all of the cooled hydrogen as a supply of cooled hydrogen, to heat hydrogen with heat transferred by direct contact with the cold-side solid heat transfer surface to form heated hydrogen; and the catalyst is configured to be exposed to hydrogen within the cooling system or the upstream device, which hydrogen is in, or to be comprised in, the heated hydrogen and/or the supply of cooled hydrogen.

[015] The present invention additionally provides a method of cooling a fluid, the method comprising the steps of:

- (A) flowing an inflow stream of vapour of the fluid from an upstream device into a cooling system;
- (B) within the cooling system, heating a cold-side solid heat transfer surface with heat transferred, directly or indirectly, from fluid undergoing cooling, and providing at least some or all of the cooled fluid as a supply of cooled fluid; and
- (C) within the cooling system, heating fluid with heat transferred by direct contact with the cold-side solid heat transfer surface to form heated fluid, wherein the cold-side solid heat transfer surface forms a surface of a solid regenerator material in a regenerator, the surface of the solid regenerator material is exposed to fluid originating from the inflow stream, and fluid within the regenerator is displaced

and pressurised periodically whereby the regenerator surface exchanges heat with the fluid periodically, in step (B) heat is transferred from the fluid undergoing cooling to the regenerator surface and in step (C) heat is transferred from the regenerator surface to the heated fluid, and a temperature or enthalpy gradient is established between relatively hot fluid in one part of the regenerator and relatively cold fluid in another part of the regenerator, and the relatively hot fluid is collected as heated fluid and the relatively cold fluid is collected as cooled fluid.

[016] The present invention further provides an apparatus for cooling a fluid, the apparatus comprising: an upstream device configured to contain vapour of the fluid, a cooling system comprising a cold-side solid heat transfer surface, an inflow conduit connecting the upstream device and the cooling system for flowing an inflow stream of vapour from the upstream device into the cooling system, wherein the cooling system is configured to heat the a cold-side solid heat transfer surface with heat transferred, directly or indirectly, from fluid undergoing cooling, to provide at least some or all of the cooled fluid as a supply of cooled fluid, to heat fluid with heat transferred by direct contact with the cold-side solid heat transfer surface to form heated fluid, wherein the cold-side solid heat transfer surface forms a surface of a solid regenerator material in a regenerator, the surface of the solid regenerator material is configured to be exposed to fluid originating from the inflow stream, and the cooling system is configured to displace and pressurise periodically fluid within the regenerator whereby the regenerator surface exchanges heat with the fluid periodically, whereby heat is transferred from the fluid undergoing cooling to the regenerator surface and heat is transferred from the regenerator surface to the heated fluid, and a temperature or enthalpy gradient is established between relatively hot fluid in one part of the regenerator and relatively cold fluid in another part of the regenerator, and the cooling system is configured to collect the relatively hot fluid as heated fluid and the relatively cold fluid as cooled fluid..

[017] Preferred or optional features of the methods and apparatus of the present invention are defined in the dependent claims and in the clauses disclosed at the end of this description.

[018] As is known to those skilled in the art, hydrogen molecules exist in a high energy ortho and a low energy para state. The equilibrium para-hydrogen volume fraction depends on temperature and is close to 99.8 vol% at the normal boiling point and 25 vol% at atmospheric temperature. Liquid nitrogen is sometimes used to precool hydrogen to around 77 K prior to liquefaction, at which temperature the equilibrium para-hydrogen fraction is about 50 vol%.

[019] The equilibration process is slow, and for example takes many days in a large tank, but can be accelerated by contact with a suitable catalytic material (e.g. iron (III) oxide).

[020] It is known in the art that catalysts suitable for acceleration of the conversion of para-hydrogen into ortho-hydrogen may take the form of a granular material that may be retained within a fluid by porous screens or affixed to a supporting structure, or the catalyst may take the form of a coating affixed to a supporting structure, or the catalyst may take the form of a self-supporting structure.

[021] If liquid hydrogen is to be kept liquid for more than a few days it is usual to catalyse the ortho-to-para transition during liquefaction, since subsequent transition in the storage vessel would release heat and cause a large proportion of the liquid to evaporate.

[022] Therefore the liquid hydrogen (also called LH2 herein) loaded onto LH2 carrier ships is likely to have more than 90 vol% para-hydrogen and potentially more than 99 vol% para-hydrogen.

[023] Liquid hydrogen with less than 90 vol% also may be provided, for example for applications where immediate use or relatively short term storage is intended.

[024] It is known in the art to use the conversion of ortho-hydrogen into para-hydrogen in the process of liquefying ortho-rich hydrogen gas into a para-rich hydrogen liquid.

[025] In contrast, a particular method and apparatus of the present invention specifically involves a net conversion of para-to-ortho hydrogen.

[026] In a particular method and apparatus of the present invention, as hydrogen boil-off gas evaporates and warms up, the endothermic para-to-ortho transition can be used to absorb heat. The catalysis of the para-to-ortho transition enhances the cooling potential of the boil-off gas but, by itself, cannot achieve liquefaction of hydrogen gas. The method and apparatus of the preferred embodiments of the present invention's application to hydrogen cooling are use of additional thermofluid processes that allow the para-to-ortho conversion to enhance cooling, and typically liquefaction.

[027] The Second Law of Thermodynamics implies theoretical limits for the minimum work input (whether electrical or mechanical) required for each unit of mass that is liquefied (work per unit of mass that is liquefied is also called specific work herein). The theoretical values of the minimum specific work input required to liquefy ambient temperature normal hydrogen are 3.3 kWh/kg without conversion of normal hydrogen into para-hydrogen and 3.9 kWh/kg with conversion of normal hydrogen into para-hydrogen.

[028] Accordingly, in the application of the method and apparatus of the present invention to cooling of hydrogen, there is potential for superior performance, i.e. a reduced specific work

input, as compared to the liquefaction of ambient temperature hydrogen. This is because the method and apparatus of the present invention can receive hydrogen that is at sub-atmospheric temperature and is already rich in para-hydrogen. The conversion of para-hydrogen into ortho-hydrogen, to provide an outflow stream having a higher fraction of ortho-hydrogen as compared to an inflow stream, can improve the potential performance, for example by reducing specific work input or increasing specific work output, compared to hydrogen cooling or liquefaction systems that do not employ para-to-ortho conversion.

[029] In the method and apparatus of the present invention, an operation with lower reliquefaction fractions offers a potential reduction in specific work input, or increased specific work output. Herein the reliquefaction fraction is the proportion of an amount of vapour that is condensed into liquid. A heat input from the environment or from an external heat source can reduce the minimum specific work input, or increase the potential specific work output. Overall, the catalysed cooling or partial reliquefaction methods and apparatuses employed in the preferred embodiments of the present invention can achieve substantial power savings compared to established technologies for cooling or liquefying hydrogen and other condensable fluids.

[030] In the method and apparatus of the present invention, the cooling of condensable fluid may be carried out adiabatically or diabatically by providing a net input of work or, if a net external heat input is provided, may be carried out with no net transfer of work and potentially with a net output of work. It is known to those skilled in the art that it is impractical to thermally isolate processes or components entirely and herein the term adiabatic is used in the sense that it describes something that is approximately adiabatic. For relatively low inflow temperature and lower reliquefaction rates, for example for hydrogen reliquefaction rates up to 40 %wt with inflow temperatures up to 40 K, adiabatic systems can give satisfactory performance, and also tend to have greater simplicity and lower cost than diabatic systems. Furthermore, an adiabatic partial reliquefaction system may be housed integrally within a liquid storage tank, avoiding need for an additional cold-box and reducing the amount of heat ingress between a boil-off gas (BOG) extraction point and an input of the reliquefaction system.

[031] For relatively high inflow temperature and higher reliquefaction rates, including reliquefaction rates of up to 100%wt, heat is additionally rejected to a coolant medium and/or to the environment.

[032] In many embodiments of the method of the present invention, the outflow stream will still be very cold and work may be recovered by supplying the cold gas to a heat engine, or the

power consumption of any further compression will be lower on account of the low temperature of the outflow gas.

[033] The preferred embodiments of the present invention can provide various advantages as compared to known technology for using, storing and transporting condensable fluids, particularly in liquid form.

[034] For example, the preferred embodiments of the present invention can provide that hydrogen can be stored/transported with reduced insulation requirements, allowing a greater mass of hydrogen to be carried, or the same mass can be kept liquid for longer. Hydrogen can be stored/transported for longer in vessels with a given pressure rating, allowing lower cost and safer systems.

[035] In addition, the preferred embodiments of the present invention can provide short start-up times for reliquefaction plant, and flexibility in the fraction of boil-off gas reliquefied, e.g. as required for propulsion applications and systems such as filling stations/airports that have variable demand.

[036] The preferred embodiments of the present invention can provide a substantial reduction in the complexity and lifecycle cost as compared to conventional liquefaction plant.

[037] The preferred embodiments of the present invention can provide an energy consumption of less than 1 kWh/kg for hydrogen reliquefaction, which is lower than achievable by current hydrogen storage and transportation technology, thereby allowing delivery of a greater fraction of the hydrogen energy to the end application or use.

[038] In the preferred embodiments of the present invention, a system of pipework, valve gear, sensors and controls selectively draws boil-off gas from close to the liquid-vapour interface in the storage tank.

[039] The preferred embodiments of the method of the present invention may incorporate use of one or more refrigerant fluids, such as helium, undergoing a thermodynamic cycle and transferring heat from the stream of cooled fluid into the heated outflow stream and/or into a separate coolant medium and/or the environment.

[040] The preferred methods may incorporate liquefaction or reliquefaction of separate cryogenic fluids, such as natural gas, in addition to the cooled condensable fluid.

[041] The preferred methods may reject heat to a separate cryogenic fluid, such as natural gas, as part of a process to gasify or heat the cryogenic fluid.

[042] The preferred methods may be thermally integrated with a process to condense or freeze pollutants, such as carbon dioxide, from an exhaust stream.

[043] The outflow stream, if present, may be used as fuel, coolant or feedstock in a fuel cell, engine, combustion system or manufacturing process.

[044] The outflow stream may be processed in order to achieve temperature and pressure conditions in the outflow stream required for its use in a fuel cell, engine, combustion system, manufacturing process, hydrogen storage process, or hydrogen distribution process.

[045] The residual cold or exergy of the outflow stream may be utilised in an external system in a heat engine that utilises the temperature difference between the outflow stream and the temperature of the environment (air, water, geothermal, solar radiation) or other heat source (combustion products, exhaust gas, process heat) to produce additional power.

[046] Embodiments of the present invention will now be described by way of example only with reference to the accompanying drawings, in which:

Figure 1 is a schematic diagram of an apparatus for cooling hydrogen according to a first embodiment of the present invention;

Figure 2 is a schematic diagram of an apparatus for cooling hydrogen according to a second embodiment of the present invention;

Figure 3 is a schematic diagram of an apparatus for cooling hydrogen according to a third embodiment of the present invention;

Figure 4 is a schematic diagram of an apparatus for cooling hydrogen according to a fourth embodiment of the present invention;

Figure 5 is a schematic diagram of an apparatus for cooling hydrogen according to a fifth embodiment of the present invention;

Figure 6 is a schematic diagram of an apparatus for cooling hydrogen according to a sixth embodiment of the present invention;

Figure 7 is a schematic diagram of an apparatus for cooling hydrogen according to a seventh embodiment of the present invention;

Figure 8 is a schematic diagram of an apparatus for cooling hydrogen according to an eighth embodiment of the present invention;

Figure 9 is a schematic diagram of an apparatus for cooling hydrogen according to a ninth embodiment of the present invention;

Figure 10 is a schematic diagram of an apparatus for cooling hydrogen according to a tenth embodiment of the present invention;

Figure 11 is a schematic diagram of an apparatus for cooling hydrogen according to an eleventh embodiment of the present invention;

Figure 12 is a schematic diagram of an apparatus for cooling hydrogen according to a twelfth embodiment of the present invention;

Figure 13 is a schematic diagram of an apparatus for cooling hydrogen according to a thirteenth embodiment of the present invention;

Figure 14 is a schematic diagram of an apparatus for cooling hydrogen according to a fourteenth embodiment of the present invention;

Figure 15 is a schematic diagram of an apparatus for cooling hydrogen according to a fifteenth embodiment of the present invention;

Figure 16 is a schematic diagram of an apparatus for cooling hydrogen according to a sixteenth embodiment of the present invention;

Figure 17 is a schematic diagram of an apparatus for cooling hydrogen according to a seventeenth embodiment of the present invention;

Figure 18 is a schematic diagram of an apparatus for cooling hydrogen according to an eighteenth embodiment of the present invention

Figure 19 is a schematic diagram of an apparatus for cooling hydrogen according to a nineteenth embodiment of the present invention; and

Figure 20 is a schematic diagram of an apparatus for cooling hydrogen according to a twentieth embodiment of the present invention.

[047] Referring to Figure 1, there is schematically shown an apparatus 2 for cooling hydrogen in accordance with an embodiment of the present invention.

[048] The apparatus 2 for cooling hydrogen comprises an upstream device 4 configured to contain hydrogen vapour. The upstream device 4 may comprise a store for hydrogen vapour, or may comprise a conduit for conveying hydrogen vapour, for example from a process or device in which hydrogen vapour is generated or used. The apparatus 2 further comprises a cooling system 6. An inflow conduit 8 connects the upstream device 4 and the cooling system 6 for flowing an inflow stream 10 of hydrogen vapour from the upstream device 4 into the cooling system 6. A pump (not shown) may be provided for pumping the inflow stream 10 of hydrogen vapour from the upstream device 4 into the cooling system 6, and the pump may be controlled by a controller (not shown) in the cooling system 6; in any of the embodiments described herein, such a pump for the inflow stream of hydrogen vapour from an upstream device to a cooling system may be provided. The apparatus 2 further comprises a downstream device 12 configured to receive hydrogen vapour from the cooling system 6. An outflow conduit 14 connects the cooling system 6 and the downstream device 12 for flowing an outflow

stream 16 of heated hydrogen vapour, derived from the inflow stream, from the cooling system 6 to the downstream device 12.

[049] The cooling system 6 comprises a catalyst 18 for converting para-hydrogen to ortho-hydrogen in hydrogen within the cooling system 6. The cooling system 6 further comprises a thermal transfer device 20 for transferring heat to a cold-side solid heat transfer surface 1 with heat transferred, directly or indirectly, from hydrogen undergoing cooling 5 to provide a supply of cooled hydrogen 24 and for transferring heat from the cold-side solid heat transfer surface 1 by direct contact with hydrogen undergoing heating 3 and collecting the heated hydrogen into the outflow stream 16 of heated hydrogen. The catalyst 18 and the thermal transfer device 20 and the cold-side solid heat transfer surface 1 are shown highly schematically in Figure 1. In the illustrated embodiment, the cooled hydrogen 5 is separated from the inflow stream 10 within the cooling system 6, then the cooled hydrogen 5 is cooled to provide the supply of cooled hydrogen 24, and subsequently the supply of cooled hydrogen 24 is returned to the upstream device 4 using a supply conduit 22.

[050] The catalyst 18 converts para-hydrogen into ortho-hydrogen in the heated hydrogen 3 within the cooling system 6; such a conversion is endothermic, and the cooling resulting from the endothermic conversion is used to transfer heat from the cold-side solid heat transfer surface 1 into heated hydrogen 3. Direct or indirect heat transfer from the cooled hydrogen 5 to the cold-side solid heat transfer surface 1 both cools the cooled hydrogen 5 which forms the supply of cooled hydrogen and heats the heated hydrogen 3 which forms the outflow stream 16. The supply of cooled hydrogen 24 returned to the upstream device 4 is at a lower temperature and/or specific enthalpy than the inflow stream 10. By returning the supply of cooled hydrogen 24 to the upstream device 4 by the supply conduit 22, the hydrogen in the upstream device 4 can be cooled. In other embodiments the cooled hydrogen 5 may instead or additionally be exposed to the catalyst 18.

[051] In any of the embodiments of the present invention, the catalyst 18 may comprise or consist of iron hydroxide (goethite) or iron (III) oxide (hematite). Other catalysts for converting para-hydrogen to ortho-hydrogen are known to those skilled in the art.

[052] Typically, the thermal transfer device 20 includes a heat exchanger (not shown) and the catalyst material 18 is fixed within the heat exchanger and the hydrogen is exposed to the catalyst 18 by flowing the hydrogen over the catalyst material 18 fixed within the heat exchanger.

[053] In any of the embodiments of the present invention, the hydrogen which is exposed to the catalyst 18 may comprise about 50 vol% para-hydrogen, may comprise greater than 50

vol% para-hydrogen or may comprise greater than 95 vol% para-hydrogen, or about 99 vol% para-hydrogen, each vol% being based on the total volume of the hydrogen exposed to the catalyst 18.

[054] In this embodiment, a portion of the hydrogen supplied to the cooling system 6 in the inflow stream 10 is separated from the inflow stream 10 to provide a stream of cooled hydrogen 5 that is then cooled and upon departure from the cooling system 6 constitutes the supply of cooled hydrogen 24 which is then returned to the upstream device 4. The remainder, or a portion, of the inflow stream 10 after separating the cooled hydrogen 5 forms the stream of heated hydrogen 3. In the apparatus and method of this embodiment, thermal energy is transferred to the heated hydrogen 3 from the cooled hydrogen 5 and the cooled hydrogen 5 forms the supply of cooled hydrogen 24, and the heated hydrogen 3 forms the outflow stream 16. The heated outflow stream 16 can then be utilised in various different downstream apparatuses or processes within, or further downstream of, the downstream device 12.

[055] As shown in Figure 1, the cooling system may be configured to utilise external work transfer W and/or external heat transfer H to produce the supply of cooled hydrogen 24. In a first set of embodiments according to Figure 1 the cooling system is configured with no external work and no external heat transfer. In another set of embodiments according to Figure 1 the cooling system 6 is configured to utilise a net work input in combination with either a net heat input, a net heat output, or adiabatically with no net external heat exchange. In a further set of embodiments according to Figure 1 the cooling system 6 is configured to produce a net work output in combination with a net heat input.

[056] Operation of the apparatus for cooling hydrogen 2 may be adjusted or controlled to vary the proportion of the inflow stream 10 that is provided as a supply of cooled hydrogen 24, for example by varying thermodynamic conditions in the upstream device or in the downstream device, or by varying the magnitude and/or direction of external work (W) and heat (H) fluxes provided to the cooling system 6. Apparatus 2 may be configured and operated to provide a range of values for the proportion of the inflow stream 10 that is provided as a supply of cooled hydrogen 24, including the limiting case where all of the inflow stream 10 is provided as a supply of cooled hydrogen 24 and no outflow stream 16 is provided. Operation with no outflow of heated hydrogen 16 provides a zero-loss mode of operation.

[057] A more particular embodiment of the apparatus of Figure 1 is illustrated in Figure 2.

[058] In this embodiment, the upstream device comprises a vessel 26 in which hydrogen is stored in the liquid phase 28. The vessel 26 also contains boil-off hydrogen gas 29, which has evaporated from the stored liquid hydrogen. As well-known to those skilled in the art, it is

typical for a store of liquid hydrogen also to contain a portion of boil-off hydrogen gas. The inflow stream 10 of hydrogen vapour comprises boil-off hydrogen gas from the vessel 26. The boil-off hydrogen gas is fed by the inflow conduit 8 to the cooling system 6 which is configured to cool, and partially liquefy, the boil-off hydrogen gas. The cooling system 6 may therefore comprise a hydrogen reliquefaction system, which returns a reliquefaction stream 24 to the vessel 26 by the supply conduit 22 and outputs, as an export stream along outflow conduit 14, the outflow stream 16 of hydrogen vapour, derived from the inflow stream 10, from the cooling system 6, which is fed to the downstream device 12. As shown in Figure 2, an external heat transfer H and/or external work transfer W may be utilised by the cooling system 6 to produce the reliquefaction stream 24. In a first set of embodiments according to Figure 2 the cooling system operates adiabatically with a net work input. In a second set of embodiments according to Figure 2 the cooling system operates diabatically with a net work input. In a third set of embodiments according to Figure 2 the cooling system operates with a net heat input and a net work transfer that may be into the cooling system 6, out of the cooling system 6, or zero.

[059] In Figure 2, the vessel 26 and the cooling system 6 are shown as separate entities. However, in alternative embodiments the vessel 26 and the cooling system 6 may be combined into an integral unit; for example, the cooling system 6 may be located within an external housing 25 of the vessel 26.

[060] Figure 3 illustrates in greater detail one preferred embodiment of the cooling system 6 illustrated more generally in Figures 1 and 2, and in particular shows how the catalyst 18 may be used to cool the supply of cooled hydrogen 24 to partially condense input hydrogen vapour 10 and thereby provide a supply of reliquefied hydrogen, which is typically returned to a store of liquid hydrogen.

[061] In Figure 3, the cooling system 6 is configured to re-liquefy partially the boil-off hydrogen gas to provide a liquid fraction which is returned to the vessel (not shown) and a gaseous fraction, wherein at least a portion of the gaseous fraction forms the outflow stream 16.

[062] As shown in Figure 3, the inflow stream 10 of hydrogen vapour comprises boil-off hydrogen gas in the inflow stream 10 from the vessel 26. However, the cooling system 6 of Figure 3 may be used to cool hydrogen vapour from any source.

[063] The inflow stream 10 enters the cooling system 6. The cooling system 6 comprises a splitter 30 for splitting the inflow stream 10 into a cooled hydrogen stream 5 and a heated hydrogen stream 3. An adiabatic compression and/or expansion device 34 is provided for subjecting the supply of cooled hydrogen to adiabatic compression and/or expansion to

increase the temperature differential between the cooled hydrogen stream 5 entering the heat exchanger 40 and the heated hydrogen stream 3 entering the heat exchanger 40.

[064] As shown in detail in Figure 3, the cooled hydrogen stream 5 is adiabatically compressed by a compressor 36 which pressurises and raises the temperature of the cooled hydrogen stream 5. The pressurised cooled hydrogen stream 5 is supplied to a relatively hot side 38 of a heat exchanger 40. The heat exchanger 40 comprises a thermal transfer device 20 as shown generally in Figure 1. The heat exchanger 40 transfers heat from the cooled hydrogen stream 5 into the cold-side solid heat transfer surface 1 and transfers heat from the cold-side solid heat transfer surface 1 into the stream of heated hydrogen 3. Thereby the cooled hydrogen stream 5 rejects heat to the opposite relatively cold side 42 of the heat exchanger 40. After exiting the relatively hot side 38 of the heat exchanger 40, the cooled hydrogen stream 5 is expanded through an expansion device 43 comprising an adiabatic work-producing expander 44 and/or an adiabatic throttle 46. This expansion cools the supply of cooled hydrogen to form a saturated mixture of hydrogen liquid and hydrogen vapour. Therefore, the adiabatic compression and/or expansion device 34, comprising compressor 36 and expansion device 43, is configured adiabatically to compress the supply of cooled hydrogen prior to being supplied to the heat exchanger 40 and adiabatically to expand the supply of cooled hydrogen after exiting the heat exchanger 40.

[065] Although this embodiment uses adiabatic compression and expansion, in alternative non-adiabatic embodiments heat may be transferred between the compression and/or expansion device and the environment or other external heat or cold sources, for example by heat exchange between the environment or other external heat or cold source and the compression and/or expansion device 34.

[066] Figure 4 illustrates an alteration of the embodiment in Figure 3 wherein the outflow of the adiabatic compressor 36 supplies the inflow of a diabatic compression system 7 that both compresses the flow of cooled hydrogen 5 and transfers heat H from the cooled hydrogen to the exterior of the cooling system. The diabatic compression system 7 may comprise any number of intercooling heat exchangers that transfer heat from the flow of cooled hydrogen to the exterior of the cooling system and any number of adiabatic compressors. Typically the diabatic compression system rejects heat directly or indirectly to a coolant, such as liquid nitrogen or liquefied natural gas, or to the environment.

[067] With reference to the embodiments illustrated in Figures 3 and 4 the saturated mixture exiting the expansion device 34 is fed to a separator 48 for separating hydrogen liquid and hydrogen vapour from the saturated mixture of hydrogen liquid and hydrogen vapour. A

supply conduit 22 is connected to the separator 48 for returning the hydrogen liquid to the upstream device, i.e. the vessel 26. A recirculation conduit 52 is also connected to the separator 48 for recirculating the hydrogen vapour in the separator 48 to be combined with the heated hydrogen stream 3.

[068]

[069] With reference to the embodiments illustrated in Figures 3 and 4 the compression and/or expansion device 34 operates with a net work input wherein, according to Figures 3 and 4, the adiabatic compressor 36 and, if present, the diabatic compression system 7 as shown in Figure 4, receive a net work input and the adiabatic expander 44 produces a net work output. The net work transfers are typically performed by means of a power transmission apparatus. A power transmission apparatus may comprise a mechanical drive or magnetic coupling, or an electrical power transmission between electrical generators and/or electrical motors some of which are connected to components of the compression and/or expansion device 34, or other methods and apparatuses known to those skilled in the art. In other embodiments a portion or all of the work produced by the adiabatic expander 44 is provided by a power transmission apparatus to the compressors 34 and/or 7, if present.

[070] As shown in Figure 3, the outflow stream 16 from the splitter 30 is fed to a catalytic converter 54 comprising the catalyst 18, as shown generally in Figure 1. Additionally, the catalyst may be provided in the relatively cold side 42 of the heat exchanger 40. In alternative embodiments, the catalytic converter 54 is omitted and the catalyst is provided in the relatively cold side 42 of the heat exchanger 40.

[071] In each of these arrangements, the catalyst 18 contacts the outflow stream 16 to convert para-hydrogen to ortho-hydrogen in the outflow stream 16. This conversion is endothermic, and occurs at least partly within the heated hydrogen 3 upstream of and/or within the cold side 42 of the heat exchanger 40. Therefore, consequently, heat is rejected from the cooled hydrogen 5 in the relatively hot side 38 of the heat exchanger 40 and is absorbed by the heated hydrogen stream 3 in the opposite relatively cold side 42 of the heat exchanger 40.

[072] This thermal transfer cools the supply of cooled hydrogen and enhances the reliquefaction of hydrogen in the supply of cooled hydrogen. Since hydrogen vapour is input to the cooling system 6 and hydrogen liquid is output from the cooling system 6, and the output hydrogen liquid is cooler than the input hydrogen vapour, in the sense that it has a lower temperature and/or has a lower specific enthalpy, an amount of the hydrogen fed to the cooling system 6 is cooled and the cooled hydrogen 5 provides a supply of cooled hydrogen 24 and the supply of cooled hydrogen is typically fed back to the source of the input stream 10.

[073] Since hydrogen in the outflow stream 16 is exposed to the catalyst 18, the outflow stream 16 has a lower fraction of para-hydrogen, and a higher fraction of ortho-hydrogen, as compared to the inflow stream 10. Typically, the inflow stream 10 comprises at least 50 vol% para-hydrogen, and typically up to 99.2 vol% para-hydrogen. Typically, the catalyst 18 within the cooling system 6 reduces the para-hydrogen vol% from the value in the inflow stream 10, which is around 95% in some relevant applications, to a value close to the equilibrium composition at the temperature of the outflow stream 16, which is less than 50 % in some relevant applications.

[074] In the embodiment of Figures 2, 3 and 4, the reliquefied hydrogen is returned to the vessel 26. Consequently, operation of the cooling system tends to increase the total amount of liquid hydrogen in the vessel 26 and to reduce the average temperature and/or specific enthalpy of the hydrogen in the vessel 26.

[075] In an alternative embodiment, the expansion device 43 may be configured to adiabatically expand and cool the supply of cooled hydrogen to form a saturated mixture of hydrogen liquid and hydrogen vapour, and a supply conduit connected to an output of the expansion device returns the saturated mixture of hydrogen liquid and hydrogen vapour to the upstream device.

[076] Alternatively, in a modification of Figure 3 or Figure 4, instead of providing the recirculation conduit 52 connected to the separator 48 for recirculating the hydrogen vapour in the separator 48 with the heated hydrogen 3, recirculation conduit 52 is configured for recirculating the hydrogen vapour in the separator 48 to be combined with the inflow stream 10 (not shown).

[077] Alternatively, in a modification of Figure 3 or Figure 4, instead of providing the recirculation conduit 52 connected to the separator 48 for recirculating the hydrogen vapour in the separator 48 with the heated hydrogen 3, the recirculation conduit 52 is configured for recirculating hydrogen vapour in the separator 48 to be combined with the cooled hydrogen 5 (not shown).

[078] Alternatively, in a modification of Figure 3 or Figure 4 shown in Figure 5, instead of providing the recirculation conduit 52 connected to the separator 48 for recirculating the hydrogen vapour in the separator 48 to be combined with the heated hydrogen 3, the recirculation conduit 52 is configured to supply a stream of recirculated hydrogen vapour 9 from the separator 48 to the inlet of the cold side of a recuperator heat exchanger 40b in which the recirculated hydrogen vapour absorbs heat rejected from the flow of cooled hydrogen 5 downstream of the hot side 38a of heat exchanger 40a, and a second recirculation conduit

conveys the recirculated hydrogen vapour 9 from the cold-side outlet of the recuperator heat exchanger 40b to combine the recirculated hydrogen vapour 52 with the heated hydrogen 3 upstream of the cold-side inlet of heat exchanger 40a. A connection conduit is provided to connect the flow of cooled hydrogen from the outlet of the hot side 38a of heat exchanger 40a to the hot side inlet of the recuperator heat exchanger 40b, and a conduit conveys cooled hydrogen 5 from the outlet of the hot side 38b of the recuperator heat exchanger 40b to the expansion device 43, thereby to recuperatively heat the recirculation stream 52 prior to combining it with the heated hydrogen stream 3. Alternatively in a modification of Figure 5, the recuperator heat exchanger 40b is integrated with the heat exchanger 40a and the recirculation stream 52 is combined with the heated hydrogen 3 within the integrated heat exchanger (not shown).

[079] Alternatively in a modification of Figure 3 or 4 or 5, a portion or all of the work produced by the adiabatic expander 44 is converted into thermal energy within the cooling system 6, for example in an eddy current brake. The thermal energy derived from work produced by the adiabatic expander is transferred to the heated hydrogen 3 and/or transferred to the outflow stream 16 and/or transferred out of the cooling system 6 as an external heat transfer.

[080] In use, the work transfers (W) shown in Figure 3 are configured to achieve a desired quantity of cooled hydrogen supply 24 as a proportion of the quantity of the inflow stream 10, within the constraints of the Laws of Thermodynamics. The embodiments shown in Figures 4 and 5 optionally provide for external heat rejection and thereby allow for liquefaction of a range of proportions of the inflow stream 10 that optionally includes liquefaction of all of the inflow stream 10. By liquefying all of the inflow stream 10 and providing the liquefied hydrogen as a supply of cooled hydrogen 24, the embodiments illustrated in Figures 4 and 5 provide for zero-loss operation in which there is no net flow in the outflow hydrogen stream 16.

[081] Figure 6 illustrates in greater detail one preferred embodiment of the cooling system 6 illustrated more generally in Figures 1 and 2 in accordance with a further embodiment of the present invention.

[082] In Figure 6, the cooling system 6 is configured to cool or re-liquefy a portion of the boil-off hydrogen gas to provide a cooled portion which is returned to a vessel (not shown) and a heated portion, wherein at least a portion of the heated portion forms the outflow stream 16. Operation of the cooling system 6 may be controlled in order to cool or liquefy a range of different proportions of the inflow hydrogen, and that range can include cooling or liquefaction

of all of the inflow hydrogen, in which extreme case there is no net mass flow through the outflow conduit 14 and the outflow conduit 14 may be removed from the device.

[083] Operation of the cooling system 6 may also be controlled in order to vary the amount of conversion between orthohydrogen and parahydrogen within the cooling system 6. Typically the system is configured and controlled to achieve a net conversion of para-hydrogen into ortho-hydrogen, but the same configuration may be controlled so as to achieve a range of amounts of conversion that can include no net conversion or alternatively a net conversion of ortho-hydrogen into para-hydrogen.

[084] As shown in Figure 6, the inflow stream 10 of hydrogen vapour comprises boil-off hydrogen gas in the inflow stream 10 from the vessel (not shown). However, the cooling system 6 of Figure 6 may be used to cool hydrogen vapour from any source.

[085] The inflow stream 10 enters the cooling system 6 via an inflow conduit 8. The flow of the inflow stream 10 through the inflow conduit 8 is controlled by an inflow valve 78. The inflow valve 78 periodically admits hydrogen from the inflow stream 10 into a regenerator 11 in a manner that substantially prevents reversal of flow within the inflow conduit 8. The regenerator 11 comprises a regenerator matrix 13 that is permeable to flow of hydrogen. Typically the inflow valve 78 operates as a non-return valve which opens when the pressure of the hydrogen within the regenerator 11 is lower than the hydrogen pressure within the inflow conduit 8 upstream of valve 78. In operation, the regenerator 11 has a hotter region at a first end functioning as a hot end 71 and a colder region at a second end functioning as a cold end 73. The inflow hydrogen typically is introduced into a region of the regenerator 11 in between the hot end 71 and the cold end 73 with an intermediate temperature where the temperature of the regenerator matrix 13 is similar to the temperature of the inflow hydrogen. The regenerator matrix 13 has a surface which serves as the cold-side solid heat exchanger surface 1 and the regenerator 11 is configured to expose the cold-side solid heat exchanger surface 1 to hydrogen gas provided by the inflow stream 10. Typically the regenerator matrix 13 consists of a packed bed of fine screens or packed particles or a porous monolith comprising solid material. The regenerator matrix 13 provides a high heat capacity relative to the hydrogen gas within the regenerator matrix 13 and is configured to provide a relatively high thermal resistance between the hot and cold ends 71, 73 of the regenerator 11. In alternative embodiments, the regenerator 11 may have a different structure, for example a network of microtubes (not shown), to provide the thermodynamic functions described above. The regenerator 11 comprises a thermal transfer device, and is a specific embodiment of the thermal transfer device 20 illustrated in Figure 1.

[086] The outflow conduit 14 is disposed towards the hot end 71. The supply conduit 22 is disposed towards the cold end 73. An external heat exchanger 63 is provided at the hot end 71 of the regenerator 11 configured to transfer heat from heated hydrogen 3 out of the cooling system 6. The external heat exchanger 63 removes heat from cooling system 6 for the purpose of reducing the specific enthalpy of the cooled hydrogen or increasing the quantity of the supply of cooled hydrogen 24 as a proportion of the inflow hydrogen 10.

[087] Alternatively, in a modification to Figure 6, the external heat exchanger 63 is omitted and the cooling system 6 operates adiabatically.

[088] The cooling system 6 is configured to establish a net flow of hydrogen through the regenerator 11 from the inflow conduit 8 to the supply conduit 22 at the cold end 73 of the regenerator 11. The flow of hydrogen exiting from the cold end 73 of the regenerator matrix 13 is cooled hydrogen 5. Cooled hydrogen 5 flows from the cold end 73 of the regenerator matrix 13 and is collected in a supply collector 74.

[089] The supply collector 74 is shown highly schematically in Figure 6 and serves to collect cooled hydrogen forming the supply of cooled hydrogen 24 from the regenerator 11 and to provide the supply of cooled hydrogen 24 to the supply conduit 22. Typically the port of the supply conduit is located at a relatively low elevation compared to the supply collector 74 so that gravity aids the transport of liquid hydrogen within the collector 74 into the supply conduit 22, and/or the supply collector 74 comprises wicking materials or structures configured so that capillary action, fluid dynamics and gravity aid transport of condensate within the collector 74 into the supply conduit 22.

[090] The flow of the supply of cooled hydrogen 24 through the supply conduit 22 is controlled by a supply valve 80. The supply valve 80 periodically admits a flow of the supply of cooled hydrogen 24 along the supply conduit 22. Typically the supply valve 80 operates as a sprung non-return valve that opens when the pressure in the supply of cooled hydrogen upstream of the supply valve 80 exceeds the pressure in the supply of cooled hydrogen downstream of the supply valve 80 by a threshold pressure difference in order to prevent flow reversal in the supply conduit 22 and to control the average pressure level in the regenerator 11 and to control the mass flow split between the outflow stream 16 and the supply stream 24. Operation of the supply valve 80 may be controlled, for example by adjusting pre-load on the valve spring, if present, to vary the pressure differential at which the supply valve 80 opens and closes with respect to the pressure difference at which the inflow valve 78 and/or the outflow valve 76 open and close. Typically the supply valve 80 remains substantially closed during the majority or all of the period in the cycle that the inflow valve 78 is open.

[091] The cooling system 6 is configured to establish a net flow of hydrogen through the regenerator 11 from the inflow conduit 8 to the outflow conduit 14 at the hot end 71 of the regenerator. The flow of hydrogen exiting from the hot end 71 of the regenerator matrix 13 is heated hydrogen 3. Heated hydrogen 3 flows from the hot end of the regenerator 11 and exchanges heat with the external heat exchanger 63, if present. The external heat exchanger 63 receives a stream of cold coolant 66 and returns a stream of heated coolant 68. The heated hydrogen is collected into the outflow conduit 14 and forms the outflow stream 16. The flow of the outflow of hydrogen 16 through the outflow conduit 14 is controlled by the outflow valve 76. The outflow valve 76 periodically admits a flow of the outflow of heated hydrogen 3 along the outflow conduit 14. Typically the outflow valve 76 operates as a sprung non-return valve that opens when the pressure in the outflow hydrogen 16 upstream of the outflow valve 76 exceeds the pressure in the outflow hydrogen downstream of the outflow valve 76 by a threshold pressure difference in order to prevent flow reversal in the outflow conduit 14 and to control the average pressure level in the regenerator 11 and to control the mass flow split between the outflow stream 16 and the supply stream 24. Operation of the outflow valve 76 may be controlled, for example by adjusting pre-load on the valve spring, if present, to vary the pressure differential at which the outflow valve 76 opens and closes with respect to the pressure difference at which the inflow valve 78 and/or the supply valve 80 open and close. Typically the outflow valve 76 is configured to remain closed during the majority or all of the period of the operating cycle during which the inflow valve 78 is open.

[092] As described further hereinbelow, the cooling system 6 of Figure 6 is provided with an oscillatory system which generates periodic variations of the average pressure within the regenerator 11 and periodic variations of the displacement of hydrogen fluid between the hot end 71 and the cold end 73 of the regenerator 11. The oscillatory system is provided with a net input of energy during the operating cycle, typically by provision of mechanical or electrical power. Typically the phase angle of the cyclic pressure oscillation produced by the oscillatory system differs from the phase angle of the fluid displacement oscillation produced by the oscillatory system. Typically the peak cyclic pressure occurs between 45 and 135 degrees and more preferably close to 90 degrees in advance of the peak displacement of hydrogen fluid towards the cold end 73 of the regenerator 11. The cyclic variation of pressure and fluid displacement is similar to that in the reverse Stirling cycle known to those skilled in the art, with the distinction that the cooling system 6 operates with an open cycle whereas the reverse Stirling cycle is typically understood by those skilled in the art as a closed thermodynamic cycle.

[093] Oscillatory systems commonly utilised in reverse Stirling cycle coolers are known to those skilled in the art and the same types of oscillatory systems typically are employed in cooling system 6. Such systems typically consist of at least one oscillator device and at least one displacer system. Typically the oscillator device comprises either a reciprocating piston in so-called Stirling-type devices or, in so-called Gifford-McMahon devices, a valve system that alternately connects the fluid contained within the regenerator to a high pressure supply (such as the outflow of a compressor) and a low pressure supply (such as the inflow to a compressor). Typically the displacer system comprises either a solid body displacer or a fluidic displacer contained in a so-called pulse tube, wherein the dynamic behaviour or actuation of the displacer is configured to achieve the required phase difference between pressure and fluid displacement within the regenerator.

[094] Figure 6 illustrates an embodiment in which the oscillator device is a reciprocating piston 70 at the hot end of the regenerator 11. The oscillator piston 70 may be driven by various means (not shown) known to those skilled in the art, including crank mechanisms and electromagnetic linear actuation. The oscillator piston 70 may be suspended by various means known to those skilled in the art including by gas bearings and/or by planar springs with high stiffness to transverse displacement relative to their stiffness to axial displacement. In the embodiment illustrated in Figure 6 the oscillator piston 70 is driven by electromagnetic linear actuation (not shown) and suspended by planar springs (not shown). In Figure 6 a sensor (not shown) for the position of the oscillator piston provides a signal that is used to control the electromagnetic actuation of the oscillator piston. In alternative embodiments the oscillator device operates without a piston position sensor. The reciprocating piston 70 illustrated in Figure 6 comprises a Stirling-type oscillator but in alternative embodiments a Gifford-McMahon-type oscillator is used.

[095] Figure 6 illustrates an embodiment in which the displacer is another reciprocating piston 72 at the cold end of the regenerator. The periodic motion of the displacer piston 72 may be driven, may be passive, or may extract work from the fluid motion. The motion of the displacer piston 72 illustrated in Figure 6 is passive, and the displacer moves in response to the pressure and viscous forces exerted by hydrogen in contact with its surface and in response to a restoring force provided by planar springs (not shown) that suspend the displacer piston.

[096] The arrangement of oscillatory device and displacer system illustrated in Figure 6 implements an open-cycle cooling process analogous to the alpha-type Stirling cooler. Other embodiments of the invention implement the open-cycle cooling process in configurations analogous to closed-cycle configurations used for implementation of the reverse Stirling cycle,

including beta-type and gamma-type Stirling configurations in which the working fluid passes around the solid displacer: for example in one such implementation the working fluid passes around the sides of the displacer piston which is moving within a larger-diameter cylinder, or, in another such implementation the displacer motion causes the working fluid to pass through the interior of a porous displacer piston that also serves as the regenerator matrix, or, in another such implementation the motion of a displacer piston within a cylinder displaces working fluid within a conduit connecting the region of the cylinder on one side of the displacer piston to the region of the cylinder on the other side of the displacer piston with the regenerator matrix located within the connecting conduit.

[097] A para-hydrogen to ortho-hydrogen conversion catalyst 18 is provided within the cooling system 6. The catalyst 18 is in contact with hydrogen originating from the inflow stream 10. Contact between the hydrogen and the catalyst 18 is provided within the regenerator matrix 13 and within the external heat exchanger 63 and within a portion of the heated 3 or cooled 5 hydrogen outside of either the regenerator matrix 13 or the external heat exchanger 63. In alternative embodiments the catalyst within the regenerator matrix may be omitted. In alternative embodiments the catalyst within the external heat exchanger 63 may be omitted. In alternative embodiments the catalyst outside of either the regenerator 13 or the external heat exchanger 63 may be omitted. In application to the partial reliquefaction of hydrogen boil-off with a high para-hydrogen concentration, preferably the catalyst 18 is provided within regions of the regenerator 11 where the cycle-averaged temperature of the regenerator matrix is higher than the equilibrium temperature corresponding to the para-hydrogen/ortho-hydrogen ratio of the inflow stream 10 in order to effect a net increase in the proportion of ortho-hydrogen.

[098] The catalyst 18 within the regenerator may be provided by various means including as a powder packed into the regenerator matrix, as a partial or complete coating on the surface of the regenerator, as an oxidised layer on the surface of the regenerator matrix, as a mesh interspersed with regenerator matrix, the catalyst may comprise regenerator matrix, or the regenerator matrix may comprise catalyst. In the embodiment illustrated in Figure 6 a granular catalyst is packed within the regenerator matrix. In alternative embodiments of Figures 1 and 2 the catalyst may be provided by other means such as those set out in this paragraph.

[099] The catalyst 18 typically is an effective catalyst both for the conversion of para-hydrogen into ortho-hydrogen and for the conversion of ortho-hydrogen into para-hydrogen. The cooling system illustrated in Figure 6 may be operated in a manner that achieves a net conversion of ortho-hydrogen into para-hydrogen, or a net conversion of para-hydrogen into ortho-hydrogen, or no net conversion between para-hydrogen and ortho-hydrogen. Operating

parameters that affect the inter-conversion between para-hydrogen and ortho-hydrogen in the cooling system include the valve settings of valves 76, 78 and 80 and the amplitude of the oscillator piston motion and the inflow stream temperature and pressure and the temperature and flow rate of the external coolant flow 66, if present. The operating parameters of the cooling system 6 may be adjusted or controlled so as to vary the net amount of para-hydrogen converted into ortho-hydrogen or the net amount of ortho-hydrogen converted into para-hydrogen. Typically there is a net conversion of para-hydrogen into ortho-hydrogen when reliquefying boil-off gas from a store of liquid hydrogen wherein the para-ortho ratio in the inflow stream is close to the equilibrium value for the normal boiling-point (approximately 99.2% para-hydrogen by volume). Typically there is a net conversion of ortho-hydrogen into para-hydrogen when the embodiment shown in Figure 6 is configured and operated to liquefy hydrogen gas from a supply of gaseous normal hydrogen.

[0100] In Figure 6 a separator 48 is provided in order to separate liquid and gaseous hydrogen within the supply of cooled hydrogen 24. A portion or all of the gaseous hydrogen separated within the supply of cooled hydrogen forms a recirculation stream 9 and flows through a recirculation conduit 52. The recirculation conduit shown in Figure 6 flows the recirculation stream into the inflow conduit 8 where it is combined with the inflow stream 10. A throttle 46 is provided within the recirculation conduit 52 in order to maintain the supply of cooled hydrogen 24 at a relatively higher pressure compared to the inflow of hydrogen 10, providing a pressure difference that can be used to drive flow of the supply of cooled hydrogen 24 to the liquid store in an upstream tank 26, if present. Incorporation of the recirculation stream 9 into the inflow stream 10 reduces the temperature of the inflow stream 10 and reduces the specific enthalpy of the supply of cooled hydrogen 24. In other embodiments (not shown), the recirculation conduit 52 is alternatively or additionally configured to flow a portion or all of the recirculation stream 9 from the separator 48 into the cold end 73 of the cooling system 6 through a valve (not shown), such as a non-return valve, that periodically transmits flow of the recirculation stream 52 when the pressure in the separator 48 is greater than the pressure in the cold end 73 of the regenerator 11. Alternatively the separator 48 and recirculation conduit 52 may be omitted from the system and any vapour within the supply of cooled hydrogen 24 passes out of the cooling system 6 through the supply conduit 22. Figure 7 schematically illustrates an apparatus 102 for cooling hydrogen in accordance with a further embodiment of the present invention.

[0101] The apparatus 102 for cooling hydrogen comprises an upstream device 104 configured to contain hydrogen vapour. As described with respect to the embodiment of Figure 1, the

upstream device 104 may comprise a store for hydrogen vapour, or may comprise a conduit for conveying hydrogen vapour, for example from a process or device in which hydrogen vapour is generated or used. The apparatus 102 further comprises a cooling system 106. An inflow conduit 108 connects the upstream device 104 and the cooling system 106 for flowing an inflow stream 110 of hydrogen vapour from the upstream device 104 into the cooling system 106. The apparatus 102 further comprises a downstream device 112 configured to receive hydrogen vapour from the cooling system 106. An outflow conduit 114 connects the cooling system 106 and the downstream device 112 for flowing an outflow stream 116 of hydrogen vapour, derived from the inflow stream, from the cooling system 106 to the downstream device 112.

[0102] The cooling system 106 comprises a splitter 130 for splitting the inflow stream 110 into a cooled hydrogen stream 105, constituting a supply of cooled hydrogen 124, and a heated hydrogen stream 103 constituting the outflow stream 116. The cooled hydrogen stream 105 is subjected to a first process 170 and the heated hydrogen stream 103 is subjected to a second process 172, and the first and second processes 170, 172 are integrated so that heat H is transferred from the cooled hydrogen stream 105 to cold-side solid heat transfer surface 101 and from the cold-side solid heat transfer surface 101 to the heated hydrogen stream 103. The supply of cooled hydrogen 124 derived from the cooled hydrogen stream 105 is thereby cooled by the first process 170, and returned to the upstream device 104 through conduit 122. The heated outflow stream 116 derived from the heated hydrogen stream 103 exits the second process 172 and is fed to the downstream device 112.

[0103] Either or both of the first and second processes 170, 172 in the cooling system 106 may comprise a catalyst for converting para-hydrogen to ortho-hydrogen in hydrogen within the cooling system 106 to enhance the transfer of heat, directly or indirectly, into the heated hydrogen stream 103 from the cooled hydrogen stream 105, thereby to cool hydrogen in the upstream device 104. In Figure 7, no external heat is transferred to or from the first and second processes 170, 172 in the cooling system 106 so that the integrated process within the cooling system 106 is carried out adiabatically. However, in alternative embodiments external heat may be exchanged with the first and/or second processes 170, 172.

[0104] In Figure 7, a net work input is provided to process 170 and there is no external work transfer provided for process 172. However in alternative embodiments there may be work input, work output or no work provided to process 170 and work input, work output or no work provided to process 172. Alternative embodiments may also provide for a work transfer from process 170 to 172 or from process 172 to process 170.

[0105] Figure 8 schematically illustrates an apparatus 202 for cooling hydrogen in accordance with a further embodiment of the present invention.

[0106] The apparatus 202 for cooling hydrogen comprises an upstream device 204 configured to contain hydrogen vapour. As described with respect to the embodiment of Figure 1, the upstream device 204 may comprise a store for hydrogen vapour, or may comprise a conduit for conveying hydrogen vapour, for example from a process or device in which hydrogen vapour is generated or used. The apparatus 202 further comprises a cooling system 206. An inflow conduit 208 connects the upstream device 204 and the cooling system 206 for flowing an inflow stream 210 of hydrogen vapour from the upstream device 204 into the cooling system 206. The apparatus 202 further comprises a downstream device 212 configured to receive hydrogen vapour from the cooling system 206. An outflow conduit 214 connects the cooling system 206 and the downstream device 212 for flowing an outflow stream 216 of hydrogen vapour, derived from the inflow stream, from the cooling system 206 to the downstream device 212.

[0107] The cooling system 206 comprises a splitter 230 for splitting the inflow stream 210 into a cooled hydrogen stream 205, constituting a supply of cooled hydrogen 224, and a heated hydrogen stream 203 comprising the outflow stream 216. As described above for the embodiment of Figure 7, the cooled hydrogen stream 205 is subjected to a first process 270 and the heated hydrogen stream 203 is subjected to a second process 272, and the first and second processes 270, 272 are integrated so that heat is transferred from the cooled hydrogen stream 205 to the cold-side solid heat transfer surface 201 and from the cold-side solid heat transfer surface 201 into the heated hydrogen stream 203. The supply of cooled hydrogen 224 derived from the cooled hydrogen stream 205 is thereby cooled by the first process 270, and a portion thereof is returned to the upstream device 204. The heated outflow stream 216 comprises the heated hydrogen stream 203 and exits the second process 272 and is fed to the downstream device 212. Either or both of the first and second processes 270, 272 in the cooling system 206 may utilise a catalyst for converting para-hydrogen to ortho-hydrogen in hydrogen within the cooling system 206 to enhance the transfer of heat, directly or indirectly, into the heated hydrogen stream 203 from the cooled hydrogen stream 205, thereby to cool hydrogen in the upstream device 204.

[0108] In this embodiment, downstream of the splitter 230 the cooled hydrogen stream 205 is compressed by a compressor 236 which heats the cooled hydrogen stream 205. External work W is input to the compressor 236. The cooled hydrogen stream 205 is supplied to a first heat exchanger 280 which rejects heat H externally of the cooling system 206, for example to reject heat to the environment and/or to a coolant fluid, and/or to provide heat to an external system

(not shown) or fluid therein. The coolant may include any suitable coolant medium, such as atmospheric air, river or sea water, liquefied natural gas, liquid nitrogen, helium, hydrogen, etc. The coolant may be used to cool additional mechanical or electrical components, which may be internal or external of the system, such as generators, motors, electrical circuits, controllers, computers, power converters, etc.

[0109] Subsequently, the cooled hydrogen stream 205 is passed through a relatively hot side 238 of a second heat exchanger 240. The cooled hydrogen stream 205 rejects heat to the opposite relatively cold side 242 of the heat exchanger 240 via the cold-side solid heat transfer surface 201. The heat exchanger 240 thereby directly transfers heat from the cooled hydrogen stream 205 into the heated hydrogen stream 203.

[0110] After exiting the relatively hot side 238 of the heat exchanger 240, the cooled hydrogen stream 205 is passed through a relatively hot side 288 of a third heat exchanger 290. After exiting the relatively hot side 288 of the third heat exchanger 290, the cooled hydrogen stream 205 is expanded through an expansion device 243 which outputs work externally of the cooling system 206. This expansion cools the cooled hydrogen stream 205 to form either a cooled hydrogen vapour or a saturated mixture of hydrogen liquid and hydrogen vapour.

[0111] A portion of the cooled hydrogen vapour, or of the saturated mixture of hydrogen liquid and hydrogen vapour, or liquid hydrogen separated from the saturated mixture by a separator (not shown) as described in Figure 3, is returned, by supply conduit 222, to the upstream device 204, the returned hydrogen being cooler than the inflow stream 210.

[0112] At a divider 298, which may comprise a separator as described above, a portion of the cooled hydrogen vapour is divided from the supply of cooled hydrogen 224 into a recirculation conduit 252 and fed as a recirculated stream to a relatively cold side 292 of the third heat exchanger 290. The recirculated stream of hydrogen vapour is pre-heated by the third heat exchanger 290 and then combined with the inflow stream 210.

[0113] Downstream of the splitter 230, the heated hydrogen stream 203 passes through the relatively cold side 242 of the second heat exchanger 240 and downstream of the second heat exchanger forms the outflow stream 216 and exits the cooling system 206 and is fed to the downstream device 212. The second heat exchanger 240 directly transfers heat from the cooled hydrogen stream 205 to the heated hydrogen stream 203 via the cold-side solid heat transfer surface 201.

[0114] Any of the thermal transfer processes in the cooling system 206 may comprise a catalyst for converting para-hydrogen to ortho-hydrogen in hydrogen within the cooling system 206 to

enhance the transfer of heat, directly or indirectly, into the heated hydrogen stream 203 from the cooled hydrogen stream 205, thereby to cool hydrogen in the upstream device 204.

[0115] Figure 9 schematically illustrates an apparatus 302 for cooling hydrogen in accordance with a further embodiment of the present invention.

[0116] The apparatus 302 for cooling hydrogen comprises an upstream device (not shown) configured to contain hydrogen vapour, as described with respect to the embodiment of Figure 1. An inflow conduit 308 flows an inflow stream 310 of hydrogen vapour from the upstream device into a cooling system 306. Typically, the inflow stream 310 comprises boil-off hydrogen vapour from a liquid hydrogen storage facility comprising the upstream device, and the boil-off hydrogen vapour typically comprises about 99 vol% para-hydrogen. The apparatus 302 further comprises a downstream device (not shown) configured to receive hydrogen vapour from the cooling system 306. An outflow conduit 314 flows an outflow stream 316 of hydrogen vapour, derived from the inflow stream 310, from the cooling system 306 to the downstream device.

[0117] The cooling system 306 comprises a splitter 330 for splitting the inflow stream 310 into a cooled hydrogen stream 305, constituting a supply of cooled hydrogen 324, and a heated hydrogen stream 303 constituting the outflow stream 316. As described above for the embodiment of Figure 7, the cooled hydrogen stream 305 is subjected to a first process 370 and the cooled hydrogen stream 305 is subjected to a second process 372, and the first and second processes 370, 372 are integrated so that heat is transferred from the cooled hydrogen stream 305 to the heated hydrogen stream 303. The supply of cooled hydrogen 324 derived from the cooled hydrogen stream 305 is thereby cooled by the first process 370, and a portion thereof is returned to the upstream device. The heated hydrogen stream 303 forms the heated outflow stream 316 and exits the second process 372 and is fed to the downstream device.

[0118] In this embodiment, the second process 372 in the cooling system 306 comprises a catalyst 318 for converting para-hydrogen to ortho-hydrogen in hydrogen within the cooling system 306 to enhance the transfer of heat into the outflow stream 316 from the supply of cooled hydrogen, thereby to cool hydrogen in the upstream device.

[0119] In this embodiment, downstream of the splitter 330 the cooled hydrogen stream 305 is, in turn, compressed by a first compressor 336a which heats the cooled hydrogen stream 305, passed through a relatively hot side 378a of a first heat exchanger 380a to reject heat to a relatively cold side 382a of the first heat exchanger 380a via its cold-side solid heat transfer surface 301a, compressed by a second compressor 336b which further heats the cooled hydrogen stream 305, passed through a relatively hot side 378b of a second heat exchanger

380b to reject heat to a relatively cold side 382b of the second heat exchanger 380b via its cold-side solid heat transfer surface 301b, and then expanded through an expansion device 343 which cools the cooled hydrogen stream 305 to form a saturated mixture of hydrogen liquid and hydrogen vapour.

[0120] At a separator 348, as described above with respect to Figure 3, liquid hydrogen in the saturated mixture is returned to the upstream device along a supply conduit 322 as a supply of cooled hydrogen 324, the supply of cooled hydrogen being cooler than the inflow stream 310. At the separator 348, a portion or all of the cooled hydrogen vapour is divided from the saturated mixture into a recirculation conduit 352 and fed as a recirculated stream to be combined with the cooled hydrogen stream 305.

[0121] Downstream of the splitter 330, the heated hydrogen stream 303 is fed to a first catalytic converter 354b comprising the catalyst 318. The catalyst 318 contacts the heated hydrogen stream 303 to convert para-hydrogen to ortho-hydrogen in the heated hydrogen stream 303. The heated hydrogen stream 303 then passes, in turn, through the relatively cold side 382b of the second heat exchanger 380b, a second catalytic converter 354a comprising the catalyst 318, and the relatively cold side 382a of the first heat exchanger 380a.

[0122] The combination of the first and second catalytic converters 354b, 354a and the first and second heat exchangers 380a, 380b ensure that a significant amount of heat is transferred from the cooled hydrogen stream 305 into the heated hydrogen stream 303, which correspondingly significantly cools the portion of the cooled hydrogen stream 305 which is reliquefied and returned to the upstream device as a supply of cooled hydrogen 324.

[0123] Figure 10 schematically illustrates an apparatus 402 for cooling hydrogen in accordance with a further embodiment of the present invention.

[0124] The apparatus 402 for cooling hydrogen comprises an upstream device (not shown) configured to contain hydrogen vapour, as described with respect to the embodiment of Figure 1. An inflow conduit 408 flows an inflow stream 410 of hydrogen vapour from the upstream device into a cooling system 406. Typically, the inflow stream 410 comprises boil-off hydrogen vapour from a liquid hydrogen storage facility comprising the upstream device, and the boil-off hydrogen vapour typically comprises about 99 vol% of para-hydrogen. The apparatus 402 further comprises a downstream device (not shown) configured to receive hydrogen vapour from the cooling system 406. An outflow conduit 414 flows an outflow stream 416 of hydrogen vapour, derived from the inflow stream 410, from the cooling system 406 to the downstream device.

[0125] The cooling system 406 comprises a splitter 430 for splitting the inflow stream 410 into a cooled hydrogen stream 405, from which a supply of cooled hydrogen 424 is derived, and a heated hydrogen stream 403 from which the outflow stream 416 is derived. As described above for the embodiment of Figure 7, the cooled hydrogen stream 405 is subjected to a first process 470 and the heated hydrogen stream 403 is subjected to a second process 472, and the first and second processes 470, 472 are integrated so that heat H is transferred from the cooled hydrogen stream 405 to the heated hydrogen stream 403. The cooled hydrogen stream 405 is thereby cooled by the first process 470, and a portion thereof is returned to the upstream device as a supply of cooled hydrogen 424 by a supply conduit 422. The heated hydrogen stream 403 exits the second process 472, forms the outflow stream 416, and is fed to the downstream device.

[0126] In this embodiment, the second process 472 in the cooling system 406 comprises a catalyst 418 for converting para-hydrogen to ortho-hydrogen in hydrogen within the cooling system 406 to enhance the transfer of heat into the heated hydrogen stream 403 from the cooled hydrogen stream 405, thereby to cool hydrogen in the upstream device.

[0127] In this embodiment, downstream of the splitter 430 the cooled hydrogen stream 405 is, in turn, compressed by a first compressor 436 which heats the cooled hydrogen stream 405, flowed through the hot side 480 of heat exchanger 478 wherein the cooled hydrogen rejects heat H that is transferred to the cold-side solid heat transfer surface 401 and then expanded through a first expansion device 443 which cools the cooled hydrogen stream 405 to form a saturated mixture of hydrogen liquid and hydrogen vapour. As illustrated, the compressor 436 and expansion device 443 form an adiabatic system, for example as described in earlier embodiments. Any suitable type of compressors and expansion devices may be used, for example turbine or throttle expanders. However, alternatively a diabatic system could be provided.

[0128] At a separator 448, as described above with respect to Figure 3, liquid hydrogen in the saturated mixture forms the supply of cooled hydrogen 424 and is returned to the upstream device, along supply conduit 422, the supply of cooled hydrogen being cooler than the inflow stream 410. At the separator 448, a portion or none of the cooled hydrogen vapour is divided from the saturated mixture into a recirculation conduit 452, forming a recirculated stream. The recirculated stream is combined with the cooled hydrogen stream 405.

[0129] Downstream of the splitter 430, the heated hydrogen stream 403 is fed to a catalytic converter 454 comprising the catalyst 418. The catalyst 418 contacts the heated hydrogen stream 403 to convert para-hydrogen to ortho-hydrogen in the heated hydrogen stream 403. The heated hydrogen stream 403 then passes, in turn, through a second adiabatic expansion

device 496, through the cold-side 482 of heat exchanger 478 in which heat is transferred from the cold-side solid heat transfer surface 401 to the heated hydrogen stream 403 and which additionally comprises the catalyst 418 to contact the heated hydrogen stream 403 to convert para-hydrogen to ortho-hydrogen, and then a second adiabatic compressor 498.

[0130] In the embodiment of Figure 10, the expansion of the heated hydrogen stream 403 upstream of the heat exchanger 478 reduced the cold-side 482 temperature. Consequently, the cooled hydrogen stream 405 entering the separator 448 is highly cooled and partially liquefied, and the portion of the cooled hydrogen stream 405 which is liquefied is returned to the upstream device as a supply of cooled hydrogen 424.

[0131] Referring to Figure 11, there is schematically shown an apparatus 502 for cooling hydrogen in accordance with a further embodiment of the present invention.

[0132] The apparatus 502 for cooling hydrogen comprises an upstream device 504 configured to contain hydrogen vapour. As described above with respect to Figure 1, the upstream device 504 may comprise a store for hydrogen vapour, or may comprise a conduit for conveying hydrogen vapour, for example from a process or device in which hydrogen vapour is generated or used. The apparatus 502 further comprises a cooling system 506. An inflow conduit 508 connects the upstream device 504 and the cooling system 506 for flowing an inflow stream 510 of hydrogen vapour from the upstream device 504 into the cooling system 506. The apparatus 502 further comprises a downstream device 512 configured to receive hydrogen vapour from the cooling system 506. An outflow conduit 514 connects the cooling system 516 and the downstream device 512 for flowing an outflow stream 516 of hydrogen vapour, derived from the inflow stream, from the cooling system 506 to the downstream device 512.

[0133] The cooling system 506 further comprises a thermal transfer device 520 for transferring heat, directly or indirectly, via the cold-side solid heat transfer surface 501, into heated hydrogen 503 that comprises the outflow stream 516 from cooled hydrogen 505 comprising a supply of cooled hydrogen 525, thereby to cool hydrogen in the upstream device 504. The supply of cooled hydrogen 525 is integral with or thermally coupled to remaining hydrogen 521 in the upstream device 504. The thermal transfer device 520 is shown highly schematically in Figure 11. In the illustrated embodiment, the supply of cooled hydrogen 525 is retained within the upstream device 504; for example, the supply of cooled hydrogen 525 may be retained in a hydrogen store 527 which is separate from, or integral with, the upstream device 504. The supply of cooled hydrogen 525 is therefore retained hydrogen.

[0134] In the illustrated embodiment there is a net supply of work W to the heat transfer device 520. In other embodiments there is no net supply of work to the heat transfer device 520. In other embodiments there is a net work output from the heat transfer device.

[0135] The inflow stream 510 is heated within the cooling system 506, and external heat is applied to the cooling system 506. The inflow stream 510 is heated so that the outflow stream 516 exiting the cooling system 506 is heated relative to the inflow stream 510.

[0136] At least some of the external heat employed to heat the inflow stream 510 is heat H that is rejected from the supply of cooled hydrogen 525 and absorbed by hydrogen in the cooling system 506. Consequently, the supply of cooled hydrogen 525 which is retained in the upstream device 504 is cooled by the cooling system 506. As a result, heat from the supply of cooled hydrogen 525 retained in the upstream device 504 is rejected into hydrogen in the cooling system 506.

[0137] In the embodiment of Figure 11, a catalyst 518 for converting para-hydrogen to ortho-hydrogen in hydrogen is provided.

[0138] In one example of this embodiment, the catalyst 518 may be provided, as illustrated highly schematically, within the supply of cooled hydrogen 525, which is retained hydrogen. Since the catalyst 518 converts para-hydrogen to ortho-hydrogen, and such a conversion is endothermic, by converting para-hydrogen to ortho-hydrogen in the supply of cooled hydrogen 525, the supply of cooled hydrogen is cooled both by the endothermic conversion of para-hydrogen into ortho-hydrogen within the supply of cooled hydrogen and by the transfer of heat H from the hydrogen store 527 to the cooling system 506.

[0139] In another example of this embodiment, which is not illustrated, the catalyst 518 may be provided within the cooling system 506. The endothermic conversion of para-hydrogen to ortho-hydrogen absorbs heat from the supply of cooled hydrogen 525 into hydrogen in the cooling system 506, and that heat is absorbed by the heated outflow stream 516.

[0140] A more particular embodiment of the apparatus of Figure 11 is illustrated in Figure 12.

[0141] In this embodiment, in the apparatus 602 the upstream device 604 comprises the supply of cooled hydrogen 625, which is retained in the upstream device 604. The upstream device 604 may optionally comprise a vessel (not shown) in which hydrogen is stored in the liquid phase and the vessel also contains boil-off hydrogen gas, which has evaporated from the stored liquid hydrogen. The supply of cooled hydrogen 625 is integral with or thermally coupled to remaining hydrogen 621 in the upstream device 604.

[0142] The inflow stream 610 of hydrogen vapour, which may optionally comprise boil-off hydrogen gas from the vessel, is fed by the inflow conduit 608 to the cooling system 606. The

cooling system 606 incorporates a thermal transfer device 620 and a refrigeration system 660. The refrigeration system 660 receives an input of work W , and functions to absorb heat H_3 from the cooled hydrogen 605 comprising the supply of cooled hydrogen 625, which is therefore cooled, and thereby functions to cool the hydrogen in the upstream device 604.

[0143] The refrigeration system 660 rejects heat, shown by arrow H_1 , into the cold-side solid heat transfer surface 601. The cold-side solid heat transfer surface 601 rejects heat to heated hydrogen 603 comprising the outflow stream 616, formed from the inflow stream 610 of hydrogen vapour, which is thereby heated and fed through conduit 614 to the downstream device 612. The refrigeration system 660 may also reject heat externally of the cooling system 606, shown by arrow H_2 , for example to reject heat to the environment and/or to a cooling fluid and/or to an external device or fluid. Fundamentally, the refrigeration system 660 in the cooling system 606 is used indirectly to transfer heat, shown by arrow H_3 , from the supply of cooled hydrogen 625 retained in the upstream device 604 into an outflow stream 616 of hydrogen vapour from the cooling system 606.

[0144] The endothermic catalysis of para-hydrogen to ortho-hydrogen may be carried out in the supply of cooled hydrogen 625, as shown by catalyst 618 in Figure 12, and/or in the heated hydrogen 603 comprising the outflow stream 616 to enhance the cooling of the supply of cooled hydrogen 625, and thereby cooling of hydrogen in the upstream device 604. Therefore the upstream device 604 may be provided with a retainer within which the supply of cooled hydrogen 625 is retained within the upstream device 604, and the refrigeration system 660 is configured so that the supply of cooled hydrogen 625 rejects heat into the refrigeration system 660 and the heated hydrogen 603 comprising outflow stream 616 absorbs heat from the refrigeration system 660. The supply of cooled hydrogen 625 may be retained in a hydrogen store 627 which is separate from, or integral with, the upstream device 604. The supply of cooled hydrogen 625 is therefore retained hydrogen.

[0145] Therefore, the cooling system 606 comprises the refrigeration apparatus 660 for transferring heat from the supply of cooled hydrogen 625 into the outflow stream 616 indirectly, the refrigeration apparatus 660 being configured to absorb heat from the supply of cooled hydrogen 625 and to reject heat into the outflow stream 616.

[0146] Figure 13 shows a further embodiment of the apparatus of the present invention.

[0147] In this embodiment, the apparatus 702 for cooling hydrogen comprises an upstream device 704 configured to contain hydrogen vapour. As described above with respect to Figure 1, the upstream device 704 may comprise a store for hydrogen vapour, or may comprise a conduit for conveying hydrogen vapour, for example from a process or device in which

hydrogen vapour is generated or used. The apparatus 702 further comprises a cooling system 706. An inflow conduit 708 connects the upstream device 704 and the cooling system 706 for flowing an inflow stream 710 of hydrogen vapour from the upstream device 704 into the cooling system 706. The inflow stream 710 of hydrogen vapour may optionally comprise boil-off hydrogen gas from a vessel storing hydrogen. The apparatus 702 further comprises a downstream device 712 configured to receive hydrogen vapour from the cooling system 706. An outflow conduit 714 connects the cooling system 706 and the downstream device 712 for flowing an outflow stream 716 of hydrogen vapour, derived from the inflow stream 710, from the cooling system 706 to the downstream device 712.

[0148] The inflow stream 710 enters the cooling system 706. The cooling system 706 comprises a splitter 730 for splitting the inflow stream 710 into a stream of cooled hydrogen 705, constituting a supply of cooled hydrogen, and a stream of heated hydrogen 703 constituting the outflow stream 716. The cooled hydrogen stream 705 is subjected to a first process 770 and the heated hydrogen stream 703 is subjected to a second process 772, and the first and second processes 770, 772 are integrated so that heat is transferred from the cooled hydrogen stream 705 to the heated hydrogen stream 703.

[0149] The cooling system 706 comprises a refrigeration system 760 which is disposed between the first and second processes 770, 772. The refrigeration system 760 is configured so that the supply of cooled hydrogen, in the cooled hydrogen stream 705, rejects heat into the refrigeration system 760 and the heated hydrogen stream 703 absorbs heat from the refrigeration system 760, shown by arrow H1. The refrigeration system 760 receives an input of work W, and functions to absorb heat, shown by arrow H2, from the cooled hydrogen stream 705, comprising a supply of cooled hydrogen, which is therefore cooled. The cooled hydrogen stream 705 is returned to the upstream device 704 as a supply of cooled hydrogen 724 by a supply conduit 722, and functions to cool the hydrogen in the upstream device 704.

[0150] The refrigeration system 760 rejects heat, via the cold-side solid heat exchanger surface 701, into the heated hydrogen 703 comprising outflow stream 716, shown by arrow H1, which is thereby heated and fed to the downstream device 712. The refrigeration system 760 rejects heat externally of the cooling system 706, shown by arrow H3, for example to reject heat to the environment and/or to a cooling fluid and/or to an external device or fluid.

[0151] Fundamentally, the refrigeration system 760 in the cooling system 706 is used indirectly to transfer heat from the cooled hydrogen stream 705, comprising a supply of cooled hydrogen 724 which is returned to the upstream device 704, into a heated hydrogen stream 703 comprising the outflow stream 716 of hydrogen vapour from the cooling system 706. A catalyst

for the endothermic conversion of para-hydrogen into ortho-hydrogen may be provided (not shown) in contact with the heated hydrogen stream 703 to enhance the cooling of the supply of cooled hydrogen, and thereby cooling of hydrogen in the upstream device 704.

[0152] Figure 14 shows a further embodiment of the apparatus of the present invention.

[0153] In this embodiment, the apparatus 802 for cooling hydrogen comprises an upstream device comprising a vessel 826 storing liquid hydrogen. The inflow stream 810 of hydrogen vapour comprises boil-off hydrogen gas from the vessel 826.

[0154] The inflow stream 810 enters the cooling system 806 and is compressed by a compressor 836 which pressurises the inflow stream 810. The cooling system 806 comprises a splitter 830 for splitting the inflow stream 810 into a cooled hydrogen stream 805, constituting a supply of cooled hydrogen, and a heated hydrogen stream 803 constituting an outflow stream 816 in an outflow conduit 814.

[0155] The cooled hydrogen stream 805 is supplied to a relatively hot side 838a of a first heat exchanger 840a which rejects heat to a refrigeration system 860, described in detail hereinbelow. After exiting the relatively hot side 838a of the first heat exchanger 840a, the cooled hydrogen stream 805 is optionally expanded through an expansion device 843 comprising an expander and/or a throttle, as described above with respect to Figure 3. This expansion cools the cooled hydrogen stream 805 to form a saturated mixture of hydrogen liquid and hydrogen vapour.

[0156] The saturated mixture is optionally fed to a separator 848 for separating hydrogen liquid and hydrogen vapour from the saturated mixture of hydrogen liquid and hydrogen vapour. A supply conduit 822 is connected to the separator 848 for returning the hydrogen liquid to the upstream device, i.e. the vessel 826. If the separator 848 is provided, a recirculation conduit 852 is also connected to the separator 848 for recirculating the hydrogen vapour in the separator 848 to be combined with the inflow stream 810.

[0157] The heated hydrogen stream 803 from the splitter 830 is fed to a first catalytic converter 854a comprising the catalyst 818. The catalyst 818 contacts the heated hydrogen stream 803 to convert para-hydrogen to ortho-hydrogen in the heated hydrogen stream 803. The heated hydrogen stream 803 then passes, in turn, through the relatively cold side 842b of a second heat exchanger 840b wherein the heated hydrogen stream absorbs heat from the cold-side solid heat transfer surface 801b, a second catalytic converter 854b comprising the catalyst 818, and the relatively cold side 842c of a third heat exchanger 840c wherein the heated hydrogen stream 803 absorbs heat from the cold-side solid heat transfer surface 801c. The second and third heat

exchangers 840b, 840c transfer heat from a refrigeration system 860, described in detail hereinbelow.

[0158] The combination of the first and second catalytic converters 854a, 854b and the first, second and third heat exchangers 840a, 840b, 840c which operate in conjunction with the refrigeration system 860, ensure that a significant amount of heat is transferred from the cooled hydrogen 805 comprising the supply of cooled hydrogen 824 into the heated hydrogen 803 comprising the outflow stream 816, which correspondingly significantly cools the cooled hydrogen stream 805, or a portion thereof, which is reliquefied and returned to the upstream device, i.e. vessel 826, as retained hydrogen.

[0159] In alternative embodiments, one or both of the catalytic converters 854a, 854b may be omitted and the catalyst is provided in the relatively cold sides 842b, 842c of either or both of the second and third heat exchangers 840b, 840c.

[0160] The refrigeration system 860 comprises a closed loop 851 containing a working fluid as refrigerant, for example helium. The refrigeration system 860 comprises, in turn in the direction of flow of the working fluid around the closed loop 851, a (or at least one) adiabatic compressor 861, optionally one or more diabatic compression systems 863, optionally one or more heat rejectors 865, the hot side 838c of the third heat exchanger 840c, the hot side 838b of the second heat exchanger 840b, an (or at least one) expander 857, for example a turbine or throttle expander, the cold side 842a of the first heat exchanger 840a, optionally a flow path 859a through the second heat exchanger 840b and optionally a flow path 859b through the third heat exchanger 840c. The fluid passing through flow paths 859a and 859b, if provided, absorbs heat from the fluid passing through the hot sides 838b and 838c of heat exchangers 840b and 840c respectively.

[0161] The first heat exchanger 840a is configured to transfer heat from the cooled hydrogen 805 and the second and third heat exchangers 840b, 840c are configured to transfer heat into the heated hydrogen 803.

[0162] In operation, heat is rejected from the cooled hydrogen stream 805 into the refrigeration system 860 by heat passing from the hot side 838a of the first heat exchanger 840a into the cold side 842a of the first heat exchanger 840a. This cools the cooled hydrogen stream 805.

[0163] Heat is absorbed into the heated hydrogen stream 803 from the refrigeration system 860 by heat passing from the hot side 838b of the second heat exchanger 840b into the cold side 842b of the second heat exchanger 840b, and by heat passing from the hot side 838c of the third heat exchanger 840c into the cold side 842c of the third heat exchanger 840c.

[0164] Further heat exchangers may optionally be provided in the outflow conduit 814 and in the refrigeration system 860 to reject heat into the outflow stream 816, which enhance heat being rejected from the cooled hydrogen stream 805 into the refrigeration system 860.

[0165] The optional diabatic compression system 863 and/or the optional heat rejection system 865 reject heat to a fluid in the environment, for example air or sea water, or to another coolant medium. The diabatic compression system may comprise a combination of adiabatic compression devices and heat rejection devices, typically arranged in a series configuration. The diabatic compression system 863 and the heat rejection system 865 therefore additionally transfer heat from the cooled hydrogen 805 into the environment and/or to a coolant fluid.

[0166] The outflow stream 816 flows to a downstream device (not shown) where the chemical energy or thermodynamic exergy in the outflow stream 816 may be used in various downstream applications, for example in an engine, fuel cell, etc. as described above.

[0167] The apparatus 802 is operated to provide reliquefaction of a range of proportions of the inflow stream 810. If the optional diabatic compression system 863 and/or the optional heat rejector 865 are provided then the range of proportions of the inflow stream 810 that can be reliquefied includes reliquefaction of all of the inflow stream 810 into a liquid supply of cooled hydrogen 824 with no discharge of an outflow stream 816.

[0168] Figure 15 shows a further embodiment of the apparatus of the present invention. In particular, Figure 15 illustrates how the apparatus for cooling hydrogen may be integrated into a power generation or propulsion system.

[0169] In this embodiment, a vessel 926 for storing liquid hydrogen is provided. A conduit 938 is provided for filling the vessel 926 with liquid hydrogen. The inflow stream 910 of hydrogen vapour comprising boil-off hydrogen gas from the vessel 926 and optionally hydrogen gas from an external supply provided through conduit 939 is fed to a cooling system 906, as described in various embodiments above, which liquefies a portion of the hydrogen gas in the inflow stream 910 and supplies the hydrogen liquid to the vessel 926 by a supply conduit 922.

[0170] The cooling system 906 incorporates a catalyst (not shown) for endothermically converting para-hydrogen to ortho-hydrogen, as described above in various arrangements, for further cooling the retained hydrogen which is returned to the vessel 926.

[0171] An outflow stream 916 of hydrogen gas is fed to a fuel preparation system 907. The fuel preparation system 907 heats the input hydrogen gas to a desired temperature, and optionally controls the gas flow to be at a desired pressure, so that the hydrogen gas can be fed to, and used as a fuel in, a fuel cell stack 909. A fuel line 911 connects the fuel preparation system 907 to the fuel cell stack 909, and excess hydrogen gas may be exported, along an

export line 913 connected to the fuel line 911, to other downstream apparatus/processes. The fuel cell stack 909 generates electrical or mechanical power which is supplied to a power-consuming system 915. In one embodiment according to Figure 15 the power-consuming system 915 is a propulsion system or auxiliary power system for a vehicle on which the liquid hydrogen storing vessel 926 is borne. In another embodiment according to Figure 15 the power-consuming system is an electricity distribution network with one or more electrical loads connected to that network.

[0172] In this illustrated embodiment, optionally the hydrogen storage and utilisation apparatus described above is thermally and/or electro-mechanically integrated with a liquid air energy storage system as described hereinbelow.

[0173] A vessel 927 for liquid air, which has a higher boiling point than liquid hydrogen, is provided. The vessel 927 has an output line 929 connected to an air regasification system 931 to supply liquid air to the air regasification system 931, which emits gaseous air to the atmosphere 937. An input line 933 of vessel 927 is connected to an air liquefaction system 935 which liquefies gaseous air from the atmosphere 937, and supplies liquid air to the vessel 927.

[0174] In use, the heat flows in the entire power generation system of Figure 15 are as follows.

[0175] As shown by the arrows marked H in Figure 15, the fuel preparation system 907 receives heat, to prepare the hydrogen gas for use as a fuel, from the air liquefaction system 935 (H1) and the fuel cell stack 909 (H2). The fuel cell stack 909 also provides heat (H3) to the air regasification system 931. Some additional heat to the fuel preparation system 907 (H4) and to the air regasification system 931 (H5) may also come from the environment. Furthermore, some heat from the environment (H6) may also inevitably, and unavoidably, pass into the liquid hydrogen in the vessel 926 even though the vessel 926 is highly thermally insulated.

[0176] In use, electrical or mechanical work (i.e. power) is provided to the cooling system 906 and the air liquefaction system from the electrochemical power system 909, the fuel preparation system 907 and the air regasification system 931, as shown by the arrows marked W in Figure 15. Also, electrical or mechanical work (i.e. power) is provided to the one or more power-consuming systems 915 from the fuel cell stack 909.

[0177] The air liquefaction system 935 typically is operated intermittently as a means to recover and store cold and power from the hydrogen system. The regasification system 931 typically is operated intermittently as a means to provide cold to the hydrogen system and power to the hydrogen system and/or the power-consuming system 915.

[0178] In a modification of the embodiment illustrated in Figure 16, the regasification system 931 and the air liquefaction system are integrated into a single system.

[0179] Figure 16 shows a further embodiment of the apparatus of the present invention. In particular, Figure 16 illustrates how the apparatus for cooling hydrogen may alternatively be integrated into a power generation or propulsion system.

[0180] In this embodiment, a vessel 1026 for storing liquid hydrogen is provided. The inflow stream 1010 of hydrogen vapour comprising boil-off hydrogen gas from the vessel 1026 is fed to a cooling system 1006, as described in various embodiments above, which reliquefies a portion of the boil-off hydrogen gas in the inflow stream 1010 and returns the hydrogen liquid to the vessel 1026 by a supply conduit 1022, which may incorporate a spray mechanism 1051 within the vessel 1026.

[0181] The cooling system 1006 incorporates a catalyst (not shown) for endothermically converting para-hydrogen to ortho-hydrogen, as described above in various arrangements, for further cooling the retained hydrogen which is returned to the vessel 1026.

[0182] The cooling system 1006 may optionally be provided with a heat rejection flow conduit 1053, incorporating a heat exchanger 1055, for rejecting heat from the hydrogen gas in the inflow stream 1010 to a coolant (not shown) or to the environment.

[0183] Therefore, the cooling system 1006 may be configured to provide a flow of cooled hydrogen from the cooling system 1006, and the flow of cooled hydrogen may be used to cool the upstream device i.e. the vessel 1026, or used to cool another device e.g. a power generator as described below, or any other component connected to the upstream device or connected to the other device. Any such upstream device, other device or component connected to the upstream device or the other device may therefore be provided with a cooling device comprising a flow of coolant, and the flow of cooled hydrogen is configured to cool the flow of coolant in the cooling device. The flow of cooled hydrogen from the cooling system may be exposed to a second catalyst which endothermically yields a net conversion of para-hydrogen to ortho-hydrogen, whereby hydrogen in the flow of cooled hydrogen may be transitioned towards an equilibrium ratio of para-hydrogen to ortho-hydrogen.

[0184] The vessel 1026 storing liquid hydrogen may be provided with a pump 1041 and an exit conduit 1043 connected thereto for flowing liquid hydrogen, as desired, from the vessel 1026 to an external apparatus or process. The vessel 1026 storing liquid hydrogen may also be provided with a gas exit line 1045 incorporating a flow control valve 1047 and a pressure relief valve 1049.

[0185] An outflow stream 1016 of hydrogen gas is fed to a power generation system 1009. The outflow stream 1016 of hydrogen gas may be fed through a first heating module 1011 and a second heating module 1013 prior to entering the power generation system 1009.

[0186] The first heating module 1011 comprises a heat exchanger 1015 which absorbs heat into the outflow stream 1016 from thermal insulation 1017 surrounding the vessel 1026 and optionally is provided with a catalyst 1018, in the heat exchanger 1015 or in an adjacent catalytic converter (not shown), for endothermically converting para-hydrogen to ortho-hydrogen. The first heating module 1011 therefore cools the insulation layer 1017 and reduces the rate of heat ingress into vessel 1026.

[0187] Then, the hydrogen gas passes through the second heating module 1013 which comprises a heat exchanger 1019 which absorbs heat into the outflow stream 1016 from the power generation system 1009 and optionally is provided with a catalyst 1018, in the heat exchanger 1019 or in an adjacent catalytic converter (not shown), for endothermically converting para-hydrogen to ortho-hydrogen. The second heating module 1013 therefore cools the power generation system 1009 and heats hydrogen in the outflow stream 1016 provided to the power generation system as fuel.

[0188] In the power generation system 1009, the hydrogen gas is oxidised by a flow 1021 that contains oxygen, or a source of oxygen, to generate an output power W which is supplied to provide a net power output and/or may be supplied to the cooling system 1006 to provide work into the cooling system 1006, as shown by the dashed lines in Figure 16. The power generation system 1009 oxidises the input hydrogen gas and provides an exhaust 1023 which may be used to provide propulsion, for example as a jet.

[0189] In this embodiment, the downstream device comprises the power generation system 1009 in which power is generated by oxidation of hydrogen in the outflow stream 1016. The power generation system 1009 may comprise (i) an electrical power generator; (ii) a mechanical power generator having an output mechanical shaft; (iii) a propulsion power generator providing output power in the form of, for example, jet propulsion, driving of a propeller, driving of a tractive drive or electromagnetic propulsion. As shown in Figure 16, the power generation system 1009 may be configured to provide power to the cooling system 1006.

[0190] Figure 17 shows a further embodiment of the apparatus of the present invention. In particular, Figure 17 illustrates how the apparatus for cooling hydrogen may alternatively be integrated into a system for storing in, and transferring liquid hydrogen between, two storage vessels for liquid hydrogen. For example, a first storage vessel may be a mobile tank (e.g. a marine tanker or a tanker truck) and a second storage vessel may be located in a fixed on-land

storage facility. Typically valve gear is provided to control the operation of the apparatus (not shown in Figure 17 but exemplified in Figures 18 to 20). Typically pipe couplings are provided that allow the first and second vessels to be disconnected (not shown in Figure 17 but exemplified in Figures 18 to 20).

[0191] In this embodiment, the upstream device comprises a first vessel 1226a for storing hydrogen in the liquid phase and/or a second vessel 1226b for storing hydrogen in the liquid phase. The first and second vessels 1226a, 1226b are each surrounded by thermal insulation 1277a, 1277b, as is well known in the art of storing cryogenic liquids such as liquid hydrogen.

[0192] A transfer system 1227 is provided between the first and second vessels 1226a, 1226b for transferring hydrogen between the first and second vessels 1226a, 1226b. The transfer system 1227 includes a cooling system 1206, as generally hereinbefore described in various arrangements. The cooling system 1206 is configured to cool hydrogen transferred by the transfer system 1227 between the first and second vessels 1226a, 1226b and/or hydrogen displaced from the first or second vessels by the transfer of hydrogen. In the illustrated embodiment, the cooling system 1206 is shown as being separate from the first and second vessels 1226a, 1226b, but alternatively the cooling system 1206 may be combined with one of the first and second vessels into an integral unit 1226a or 1226b.

[0193] The transfer system 1227 also includes a transfer device 1201. The transfer device 1201 is thermally insulated from the environment by insulation 1277c. The transfer system 1227 is additionally configured to transmit liquid hydrogen through the transfer device 1201 as it passes in either direction between the first and second vessels 1226a and 1226b. In specific embodiments the transfer system 1227 may be configured to transmit liquid hydrogen in only one direction between the first and second vessels 1226a and 1226b. In the illustrated embodiment, the transfer device 1201 is shown as being separate from the first and second vessels 1226a, 1226b and from the cooling system 1206, but alternatively the transfer device 1201 may be combined with one of the first and second vessels and/or the cooling system into an integral unit 1226a, 1226b, or 1206.

[0194] A conduit 1207a is provided to pass a stream of hydrogen 1203a between the first vessel 1226a and the transfer device 1201. A conduit 1207b is provided to pass a stream of hydrogen 1203b between the second vessel 1226b and the transfer device 1201. Conduits 1207a and 1207b and the transfer device 1201 are configured such that streams 1203a and 1203b convey a net transfer of liquid hydrogen either from the first vessel 1226a to the second vessel 1226b or from the second vessel 1226b to the first vessel 1226a.

[0195] Optionally, an additional conduit 1209a is provided to pass a stream of hydrogen 1205a between a vapour space in the first vessel 1226a and the transfer device 1201, and/or an additional conduit 1209b is provided to pass a stream of hydrogen 1205b between a vapour space in the second vessel 1226b and the transfer device 1201. Typically hydrogen streams 1205a and 1205b are predominantly in the vapour phase. Conduits 1209a, 1209b and the transfer device 1201 are configured such that streams 1205a and 1205b convey a net transfer of vapour hydrogen either from the first vessel 1226a to the second vessel 1226b or from the second vessel 1226b to the first vessel 1226a.

[0196] Typically the flow direction in streams 1205a and 1205b are in the opposite sense to streams 1203a and 1203b respectively so that, when streams 1203a and 1203b provide a net transfer of liquid from the first vessel 1226a to the second vessel 1226b, the streams 1205a and 1205b provide a net transfer of vapour from the second vessel 1226b to the first vessel 1226a, and vice-versa.

[0197] Optionally one or more pumps (not shown) may be connected to or within conduits 1207a and/or 1207b and/or 1209a and/or 1209b to provide a net transfer of liquid hydrogen in either direction between the first vessel 1226a and the second vessel 1226b through conduits 1207a, 1207b.

[0198] Optionally one or more valves (not shown) may be connected to or within conduits 1207a and/or 1207b and/or 1209a and/or 1209b to control the transfer of hydrogen between the first vessel 1226a and the second vessel 1226b through conduits 1207a, 1207b.

[0199] The transfer system 1227 is additionally configured to feed streams of hydrogen vapour to the cooling system 1206 from the first vessel 1226a (stream 1210a) and/or from the second vessel 1226b (stream 1210b) and/or from the transfer device 1201 (stream 1210c), and the combined hydrogen vapour stream comprises the inflow stream 1210 of hydrogen vapour flowed into the cooling system 1206 along an inflow conduit 1208. The inflow conduit 1208 is connected to the first vessel 1226a by a conduit 1208a which conveys inflow stream 1210a and/or connected to the second vessel 1226b by a conduit 1208b which conveys inflow stream 1210b and/or connected to the transfer device 1201 by a conduit 1208c which conveys inflow stream 1210c. Hydrogen cooled, typically re-liquefied, by the cooling system 1206 is provided to the first vessel 1226a and/or the second vessel 1226b and/or the transfer device 1201 along a supply conduit 1224. Supply conduit 1222 is connected to the first vessel 1226a by a conduit 1222a which conveys supply stream 1224a, and/or connected to the second vessel 1226b by a conduit 1222b which conveys supply stream 1224b, and/or connected to the transfer device 1201 by a conduit 1222c which conveys supply stream 1224c. Typically, the inflow stream

1210 of hydrogen vapour comprises boil-off hydrogen gas from the first vessel 1226a and/or second vessel 1226b and/or transfer device 1201, and the cooling system 1206 is configured to partially re-liquefy the boil-off hydrogen gas to provide a liquid fraction which is returned to the first vessel 1226a and/or the second vessel 1226b and/or the transfer device 1201 and a gaseous fraction, wherein at least a portion of the gaseous fraction forms the outflow stream 1216.

[0200] The outflow stream 1216 is fed away from the cooling system 1206 by one or more outflow conduits, including at least one out of conduits 1214a, 1214b, 1214c, 1214d, 1214e and/or 1214f. If more than one of conduits 1214a, 1214b, 1214c, 1214d, 1214e and/or 1214f are provided, valve gear is provided (not shown) to control the proportion of the outflow passing along each of conduits 1214a, 1214b, 1214c, 1214d, 1214e and/or 1214f that is provided.

[0201]

- a. If present, conduit 1214a transmits stream 1216a comprising all or a portion of the outflow stream 1216 from conduit 1214 to the first vessel 1226a. Typically, in use, the flow of stream 1216a into the first vessel 1226a serves to pressurise the fluid within the first vessel 1226a.
- b. If present, conduit 1214b transmits stream 1216b comprising all or a portion of the outflow stream 1216 from conduit 1214 to the first vessel 1226b. Typically, in use, the flow of stream 1216b into the first vessel 1226b serves to pressurise the fluid within the first vessel 1226b.
- c. If present, conduit 1214c transmits stream 1216c comprising all or a portion of the outflow stream 1216 from conduit 1214, optionally through heat transfer device 1219c, and onwards to a downstream apparatus or process 1231, as described hereinabove in various embodiments. Heat transfer device 1219c transfers heat from some part of transfer device 1201 into the hydrogen stream 1216c, thereby cooling some part of transfer device 1201.
- d. If present, conduit 1214d transmits stream 1216d comprising all or a portion of the outflow stream 1216 from conduit 1214 to a downstream apparatus or process 1231.
- e. If present, conduit 1214e transmits stream 1216e comprising all or a portion of the outflow stream 1216 from conduit 1214, optionally through heat transfer device 1219a, and onwards to a downstream apparatus or process 1231. Heat

transfer device 1219e transfers heat from some part of the first vessel 1226a into the hydrogen stream 1216e, thereby cooling some part of the first vessel 1226a.

- f. If present, conduit 1214f transmits stream 1216f comprising all or a portion of the outflow stream 1216 from conduit 1214, optionally through heat transfer device 1219b, and onwards to a downstream apparatus or process 1231. Heat transfer device 1219f transfers heat from some part of the second vessel 1226b into the hydrogen stream 1216f, thereby cooling some part of the second vessel 1226b.

[0202] Optionally, any portion of the outflow streams 1216c, 1216d, 1216e, 1216f provided to the downstream device 1231 may be routed through a heat transfer device 1219e in order to cool some part of the downstream device. Optionally the streams provided to heat transfer device 1219e may be put into contact with a catalyst 1218 that accelerates the endothermic conversion of para-hydrogen into ortho-hydrogen either upstream of or within heat transfer device 1219e in order to increase the cooling provided.

[0203] Optionally, any of outflow streams 1216c, 1216e, 1216f that are provided to heat transfer devices 1219a, 1219b, 1219c, may be put into contact with a catalyst 1218 that accelerates the endothermic conversion of para-hydrogen into ortho-hydrogen either upstream of or within said heat transfer devices in order to increase the cooling provided.

[0204] Figure 17 illustrates an embodiment in which the cooling system 1206 and the transfer device 1201 are each provided with an external work input, W. In other embodiments such work inputs may be generated by the downstream device.

[0205] Figure 17 illustrates an embodiment in which the cooling system 1206 is configured to cool the first vessel 1226a by absorbing heat flux H1, to cool the second vessel 1226b by absorbing heat flux H2 and to cool the transfer device 1201 by absorbing heat flux H3. The cooling system 1206 is configured to reject heat H4 to the environment or other coolant medium. In other embodiments any or all of these heat fluxes (H1 to H4) may be omitted. In other embodiments, the heat flux H4 may be reversed so that the cooling system absorbs heat from the environment or other heat source.

[0206] In use, hydrogen gas from the first vessel 1226a, second vessel 1226b or transfer device 1201 can be cooled by the cooling system 1206 and, if desired, transferred to the first vessel 1226a or the second vessel 1226b. The transfer system 1227 can transfer at least a portion of the hydrogen gas outflow stream 1216 to the first vessel 1226a or the second vessel 1226b. Optionally the transfer system 1227 is provided with conduits 1209a and 1209b configured to

connect a vapour space of the first vessel 1226a with the second vessel 1226b, and/or to a vapour space of the second vessel 1226b with the first vessel 1226a, to enable the transfer of hydrogen gas directly between the first vessel 1226a and the second vessel 1226b.

[0207] In use, the transfer system 1227 may be operated so as to vary the proportions of the inflow stream that comprises the cooled supply and the proportion that comprises the outflow 1216 as desired. The range of possible proportions includes operation where the cooled supply comprises all of the inflow stream, providing a zero-loss mode of operation.

[0208] In use, the transfer system 1227 may be operated so as to vary the proportion of the outflow stream 1216 that comprises streams 1216a, 1216b, 1216c, 1216d, 1216e and 1216f.

[0209] In the embodiment of Figure 17, the method and apparatus for cooling hydrogen in accordance with this preferred embodiment of the present invention can partially or wholly reliquefy hydrogen vapour generated during tank-to-tank transfer of the cryogenic liquid. Typically, a tank-to-tank transfer system is provided, and liquid in the supply tank is either discharged by pressurising the ullage gas or using a cargo transfer pump. The fluid in the transfer pipeline is controlled to be at sub-cooled conditions, on account of its elevated pressure. Due to heat ingress and pressure loss in the pipework evaporation may occur within the pipework or within the receiving tank. In the supply tank, or in the transfer device, or in the receiving tank the evaporated vapour is separated from the liquid which is delivered to the receiving tank, forming a boil-off gas stream which is passed to the cooling system. Vapour that is displaced from the receiving tank may also be passed, entirely or in part, to the cooling system. By using the method and apparatus for cooling hydrogen in accordance with this preferred embodiment of the present invention, by partially or wholly reliquefying hydrogen vapour generated during tank-to-tank transfer of the cryogenic liquid, as compared to currently known apparatus and processes in which a few percent of the liquid product typically evaporates during each a tank-to-tank transfer, the present invention can typically halve, or potentially eliminate, the amount of liquid hydrogen product that gets vaporised during the transfer process.

[0210] In any of the embodiments of the present invention, the apparatus for cooling hydrogen may be combined with any liquid hydrogen storage or supply system known in the art. For example, the apparatus for cooling hydrogen may be used in combination with a fixed land-based hydrogen storage or usage facility, or may be incorporated into a vehicle or part of cargo to be carried by a vehicle. Such a vehicle may be, for example, an aircraft or other airborne vehicle, a truck or any other land vehicle, a ship or other water-borne vehicle, etc. The airborne vehicle may be selected from, for example, rockets, missiles, aeroplanes, sea-planes, airships,

hot-air balloons etc. The water-borne vehicle may be selected from, for example, boats, ships, floating production platforms, and submarines. The land vehicle may be selected from, for example, a road or off-road vehicle, a truck, a train, etc. Typically, the vehicle may be provided with a detachable hydrogen storage/transport unit, for example a tank, e.g. in the form of an intermodal container, which can be hoisted onto/off a vehicle, typically such as a ship, truck or train.

[0211] In the preferred embodiments of the present invention, the upstream device may be, or comprise, a storage tank, a transport tank, a fuel tank, a pump, or pipework, each of these containing hydrogen in liquid form, and/or cold hydrogen gas. Alternatively, the upstream device may be an electrical component selected, for example, from an electric motor, generator, power converter or transmission cable which has been cooled by hydrogen in liquid form and/or cold hydrogen gas, so that the electrical component can exhibit superconducting properties.

[0212] In the preferred embodiments of the present invention, any generation of hydrogen vapour in the upstream device may typically result from boiling due to ingress of heat from the environment, boiling due to viscous dissipation within the fluid, boiling due to heating from electrical components, application of liquid hydrogen in order to reduce the temperatures within the device, or application of liquid hydrogen in order to maintain the temperature of the device.

[0213] The apparatus and method of the preferred embodiments of the present invention system may have particular application in the following systems/processes: during transfer of liquid hydrogen from one tank to another, including during deliveries and dispensing of liquid hydrogen fuel; land or marine storage of liquid hydrogen; transport of liquid hydrogen by road tanker, rail tanker, carrier ship, spacecraft, small liquid hydrogen transfer vessels, etc; fuel systems for space, air, marine, rail, road transport, including for fuel cells and combustion engines; cooling of superconducting electrical components on hydrogen-fuelled vehicles with electrical power transmission (e.g. turboelectric aircraft).

[0214] Figure 18 illustrates one preferred embodiment of the tank-to-tank transfer system illustrated more generally in Figure 17 and, in particular, shows a configuration of the transfer system with a disconnectable supply tank 1326a. The disconnectable supply tank 1326a may be moveable, for example as cargo tank on board a liquid hydrogen carrier ship, and the receiving tank 1326b may be stationary, for example as part of a liquid hydrogen receiving terminal.

[0215] In Figure 18 the cooling system 1306 is configured to partially or wholly reliquefy hydrogen boil-off gas received from the transfer device 1301 and hydrogen evaporated and/or displaced from the second vessel 1326b. While the supply tank 1326a is disconnected, the cooling system 1306 can continue to provide cooling to boil-off gas generated by ongoing evaporation in the second vessel 1326b.

[0216] A disconnectable supply tank 1326a is connected to a liquid hydrogen receiving terminal 1383 by disconnectable conduits 1316a and 1307a. The disconnectable conduit 1316a can be disconnected by closing valves 1367 and 1369 and detaching the piping at point 1381. The disconnectable conduit 1307a can be disconnected by closing valves 1371 and 1373 and detaching the piping at point 1379.

[0217] During tank-to-tank transfer, a stream of hydrogen 1303a flows from tank 1326a through conduit 1307a to transfer device 1301 wherein vapour within the stream is separated from liquid within a separator 1363. A stream of hydrogen 1303b flows from the separator 1363 through conduit 1307b, then passes through a control valve 1372, and discharges into receiving tank 1326b. Some or all of the vapour separated within the separator 1363 flows as an inflow stream of hydrogen 1310c through conduit 1308c, passing through control valve 1374 and into the inflow conduit 1308 of the cooling system 1306.

[0218] Hydrogen vapour within the second vessel 1326b flows into conduit 1308b forming an inflow stream 1310b. Inflow stream 1310b flows through a control valve 1376 within conduit 1308b and then flows into inflow conduit 1308 wherein it is combined with inflow stream 1310. The inflow stream 1310 flows into the cooling system 1306 through inflow conduit 1308. The control valve 1376 is controlled to transmit a rate of flow so as to maintain the second vessel 1326b at a desired pressure level.

[0219] The cooling system 1306, according to embodiments as described hereinabove, is provided with an inflow stream 1310 and issues a supply of cooled hydrogen 1324 derived from the inflow hydrogen stream through supply conduit 1322. Outflow conduits 1314a, 1314d and 1314f are provided to receive outflow streams 1316a, 1316d and 1316f respectively from the cooling system 1306, and control valves 1367, 1378, and 1365 are provided within the respective conduits to control the proportions and total amount of the outflow stream passing through the respective conduits. Outflow conduit 1314f flows outflow stream 1316f through heat transfer device 1319b wherein the outflow stream 1316f absorbs heat from the structure or insulation 1377b of the receiving tank 1326b, so as to cool the structure or insulation and thereby reduce heat ingress into the hydrogen stored within the receiving tank 1326b. Outflow streams 1316d and 1316f are flowed through conduits 1314d and 1314f into a downstream

system 1331. The proportion of the total flow rate of streams 1316d and 1316f that flows through conduit 1314f as stream 1316f is controlled by setting control valves 1365 and 1378 to provide a desired rate of cooling of the insulation or structure 1377b. Optionally, contact with a catalyst 1318 for the endothermic transition of para-hydrogen into ortho-hydrogen is provided within or upstream of heat transfer device 1319b to cool stream 1316f and increase the cooling of 1377b provided by heat transfer device 1319b. When the cooling system 1306 operates in its zero-loss mode the control valves 1367, 1365 and 1378 are closed so that the total flow rate of the outflow streams 1316a, 1316d and 1316f is equal to zero. When the cooling system is in use but not operating in its zero-loss mode, and the transfer system 1327 operates in its zero-loss mode, valves 1365 and 1378 are closed and all heated hydrogen outflow from the cooling system 1306 passes through conduit 1314a into the supply tank 1326a. The flow of outflow stream 1316a into the supply tank 1326a pressurises the hydrogen within the supply tank 1326a thereby contributing to the driving force for the discharge of hydrogen from the supply tank 1326a through conduit 1307a.

[0220] The cooling system 1306 may optionally be provided with a heat rejection line 1353, incorporating a heat exchanger 1355, for rejecting heat from the hydrogen gas in the inflow stream 1310 to a coolant (not shown) or to the environment.

[0221] The downstream system 1331 receives the outflow hydrogen streams 1316d and 1316f. Figure 18 illustrates a particular embodiment in which system 1331 comprises a power producing device 1361 and a hydrogen compression device 1359. The power producing device 1361 is a fuel cell stack supplied with a portion or all of the outflow hydrogen streams 1316d and 1316f and with air 1321, producing outputs of electrical power (W) and an exhaust containing unreacted parts of the air and water 1323. The power producing device 1361 is configured to provide power (W) to the cooling system 1306, to the compression device 1357 and/or externally to another downstream system (not shown). The compression device 1359 is configured to receive an electrical power input (W) from the power producing device and/or an external power supply and compresses gaseous hydrogen from the outflow hydrogen streams 1316d and 1316f to provide an export stream 1357 to a subsequent downstream device (not shown) which may be a gas supply pipe network. Controls and valve gear are provided (not shown) to vary the proportion of the outflow hydrogen that is consumed by the power producing device 1361 and compressed by the hydrogen compression device 1359 to provide a desired output of electrical power and/or compressed hydrogen.

[0222] The supply conduit 1322 is provided to flow the supply of cooled hydrogen 1324 out of the cooling system 1306 and into the transfer device 1301 wherein the supply of cooled

hydrogen is combined with stream 1303a. Thereby the flow of hydrogen into the receiving tank 1326b is cooled and the rate of export of hydrogen to the downstream system 1331 can be reduced.

[0223] Figure 19 illustrates one preferred embodiment of the tank-to-tank transfer system illustrated more generally in Figure 17 and, in particular, shows a configuration of the transfer system with a disconnectable receiving tank 1426b. The disconnectable receiving tank 1426b may be moveable, for example as a cargo tank on board a liquid hydrogen carrier ship, and the supply tank 1426a may be stationary, for example as part of a liquid hydrogen loading terminal.

[0224] In Figure 19 the cooling system 1406 is configured to partially or wholly reliquefy hydrogen boil-off gas received from the transfer device 1401 and/or from the supply tank 1426a and/of from the receiving tank 1426b. While the receiving tank 1426b is disconnected, the cooling system 1406 can continue to provide cooling to boil-off gas generated by ongoing evaporation in the supply tank 1426a.

[0225] A disconnectable receiving tank 1426b is connected to a liquid hydrogen supply terminal 1496 by disconnectable conduits 1408b and 1407b. The disconnectable conduit 1408b can be disconnected by closing valves 1476 and 1469 and detaching the piping at point 1481. The disconnectable conduit 1407a can be disconnected by closing valves 1471 and 1487 and detaching the piping at point 1479.

[0226] During tank-to-tank transfer, a supply pump 1485 provides a stream of hydrogen 1403a flows from tank 1426a into conduit 1407a. Supply pump 1485 is provided with a work input (W). Conduit 1407a is provided to flow the stream of hydrogen 1403a to transfer device 1401 wherein vapour within the stream is separated from liquid within a separator 1463. A stream of hydrogen 1403b flows from the separator 1463 through conduit 1407b, then passes through a control valve 1487, and discharges into receiving tank 1426b. Some or all of the vapour separated within the separator 1463 flows as an inflow stream of hydrogen 1410c through conduit 1408c, passing through control valve 1474 and into the inflow conduit 1408 of the cooling system 1406. The flow within conduit 1408 comprises inflow stream 1410. Inflow stream 1410 flows into the cooling system 1406 through inflow conduit 1408.

[0227] Hydrogen vapour within the supply tank 1426a flows into conduit 1408a forming an inflow stream 1410a. Inflow stream 1410a flows through control valve 1484 within conduit 1408a and then flows into inflow conduit 1408 wherein it is combined with inflow stream 1410. The control valve 1484 is controlled to transmit a rate of flow so as to maintain the supply tank 1426a at a desired pressure level.

[0228] Hydrogen vapour within the receiving tank 1426b flows into conduit 1408b forming an inflow stream 1410b. Inflow stream 1410b flows through a control valve 1476 within conduit 1408b and then flows into inflow conduit 1408 wherein it is combined with inflow stream 1410. The inflow stream 1410 flows into the cooling system 1406 through inflow conduit 1408. The control valve 1476 is controlled to transmit a rate of flow so as to maintain the receiving tank 1426b at a desired pressure level.

[0229] The cooling system 1406, according to embodiments as described hereinabove, receives an inflow stream 1410 and issues a supply of cooled hydrogen 1424 derived from the inflow hydrogen stream through supply conduit 1422. The cooling system 1406 is provided with a power input (W). The cooling system 1406 may optionally be provided with a heat rejection line 1453, incorporating a heat exchanger 1455, for rejecting heat from the hydrogen gas in the inflow stream 1410 to a coolant (not shown) or to the environment. Outflow conduit 1414 is provided to receive outflow stream 1416 from the cooling system 1406.

[0230] Outflow stream 1416 flows through the outflow conduit 1414 into a downstream system 1431. The downstream system 1431 is shown highly schematically in Figure 19. System 1431 comprises a hydrogen storage system and a hydrogen liquefaction system. System 1431 receives the outflow stream of hydrogen 1416 and an external supply of cooled hydrogen 1425 and an external supply of power (W) and rejects heat (H) to the outside of system 1431. The liquefaction system in 1431 liquefies a portion or all of hydrogen streams 1425 and 1416 and provides a stream of liquefied and/or cooled hydrogen 1489 that flows through conduit 1486 into the supply tank 1426a. The storage system within 1431 permits the downstream device to operate with an imbalance between the total rate of inflow of hydrogen (streams 1425 and 1416) and the total rate of outflow of hydrogen stream 1489, causing the hydrogen store to accumulate or deplete. The combination of hydrogen store and liquefaction apparatus provides a load-balancing capability, so that the liquefaction plant can operate closer to a preferred rate of throughput despite fluctuations in the rates of supply of cooled hydrogen contributed by streams 1425 and 1416. The load-balancing capability is increased furthermore by use of the cooling system 1406 to cool or reliquefy a portion or all of the inflow stream 1410c and to provide the cooled or reliquefied hydrogen as a supply stream 1424 to the transfer device 1401, thereby reducing the flow rate of outflow stream 1416 received by the downstream device 1431.

[0231] The supply conduit 1422 is provided to flow the supply of cooled hydrogen 1424 out of the cooling system 1406 and into the transfer device 1401 wherein the supply of cooled hydrogen is combined with stream 1403a. Thereby the flow of hydrogen into the receiving tank

1426b is cooled and the rate of export of hydrogen to the downstream system 1431 can be reduced. For operation with the receiving tank 1426b disconnected, conduit 1422a is provided to convey the supply of cooled hydrogen 1424 from the supply conduit 1422 into the supply tank 1426a. Valve 1490 is provided to control or prevent flow of cooled hydrogen through conduit 1422a while the receiving tank 1426b is connected.

[0232] Figure 20 illustrates one preferred embodiment of the tank-to-tank transfer system illustrated more generally in Figure 17, and in particular shows a configuration of the transfer system with a disconnectable supply system 1596 comprising a supply tank 1526a. The disconnectable supply system 1596 may be moveable, for example as part of a liquid hydrogen road tanker, and the receiving tank 1526b may be stationary.

[0233] In Figure 20 the cooling system 1506 is configured to partially reliquefy hydrogen boil-off gas received from the transfer device 1501 and/or from the supply tank 1526a and/or from the receiving tank 1526b. While the receiving tank 1526b is disconnected, the cooling system 1506 can continue to provide cooling of boil-off gas generated by ongoing evaporation in the supply tank 1526a.

[0234] A receiving tank 1526b is connected to a liquid hydrogen supply system 1596 by disconnectable conduits 1508b and 1507b. The disconnectable conduit 1508b can be disconnected by closing valves 1576 and 1569 and detaching the piping at point 1581. The disconnectable conduit 1507a can be disconnected by closing valves 1571 and 1587 and detaching the piping at point 1579.

[0235] During tank-to-tank transfer, the supply tank 1526a is pressurised by communication of pressure through supply stream 1524a in conduit 1522a. Pressurisation of supply tank 1526a drives a flow of liquid hydrogen stream 1503a into conduit 1507a. Stream 1503a flows through conduit 1507a into a transfer device 1501 wherein conduit 1507a is connected to conduit 1507b and stream 1503a flows into stream 1503b. Stream 1503b flows through conduit 1507b into the receiving tank 1526b.

[0236] A conduit 1508a is provided to flow vapour comprising stream 1510a from supply tank 1526a into inflow conduit 1508. Control valve 1584 is provided within conduit 1508a to control the rate of flow through conduit 1508a so as to maintain the pressure in supply tank 1526a within a desired pressure range.

[0237] A conduit 1508b is provided to flow vapour comprising stream 1510b from receiving tank 1526b into inflow conduit 1508. Control valve 1576 is provided within conduit 1508b to control the rate of flow through conduit 1508b so as to maintain the pressure in receiving tank 1526b within a desired pressure range.

[0238] Conduit 1508 flows inflow stream 1510 comprising streams 1510a and 1510b into the cooling system 1506.

[0239] The cooling system 1506 according to embodiments hereinabove is shown highly schematically in Figure 20 and comprises a separator 1554 that separates the supply of cooled hydrogen into a vapour supply stream 1524a and a predominantly liquid supply stream 1524c. Conduit 1522c flows the liquid supply stream from separator 1554 through control valve 1586c and then into conduit 1507a wherein it combines with stream 1503a. Conduit 1522a connects the vapour space of separator 1554 to the supply tank 1526a. Control valve 1586a is provided within conduit 1522a to control or prevent the flow of stream 1524a through conduit 1522a. Control valve 1586c is provided within conduit 1522c to control or prevent the flow of stream 1524c through conduit 1522c. Control valves 1586a and 1586c are configured to provide a supply 1522c that is predominantly liquid.

[0240] A conduit 1514 is provided to flow the outflow stream 1516 from the cooling system 1506 to a downstream system 1531. The downstream system illustrated in Figure 20 comprises a power producing device 1591, an electrical energy storage device 1592, and a hydrogen storage device 1593, and apparatus 1594 for packing hydrogen into the hydrogen store, and apparatus 1595 for recovering hydrogen from the hydrogen store. Typically the power producing device 1591 is a fuel cell stack that is supplied with a flow of oxidiser 1521 (typically air) and generates an exhaust flow 1523 (typically humid oxygen-depleted air). Typically the electrical energy storage device 1592 is a battery. Typically the hydrogen storage device 1593 is a compressed gas cylinder. Typically the apparatus 1594 for packing hydrogen into the hydrogen store is a diabatic compressor (work and heat flows not shown). Typically the apparatus 1595 for recovering hydrogen from the hydrogen store is an expander (work and heat flows now shown). The power producing device 1591 typically generates electrical power (W) which is transmitted to the cooling system 1506 and/or the storage apparatus 1594 and/or exported outside of the downstream system, and/or the energy storage device 1592. Work recovered by the energy storage device typically is transmitted to the cooling system 1506 and/or exported outside of the downstream system.

[0241] Typically a portion of the work exported from the downstream device is used for propulsion and ancillary power consumption of a vehicle bearing the disconnectable supply system 1596. The downstream system 1531 thereby provides the functions of energy conversion and energy storage within a hybrid power train for vehicle propulsion.

[0242] The preferred embodiments illustrated in Figures 1 to 20 and described hereinabove with respect to the cooling and/or liquefaction of hydrogen can be applied in general to

compressible and condensable fluids other than hydrogen. These embodiments may be engineered to enable a single device to cool one fluid composition, or a set of more than one different fluid compositions, including or excluding hydrogen, either without any modification of the apparatus or by modifying the construction and/or operation of the apparatus (for example by changing the working fluid and pressure levels in a closed circuit refrigeration sub-system 860). Provision of catalysts and catalytic converters for conversion of para-hydrogen to ortho-hydrogen typically is beneficial only to the cooling of hydrogen, and therefore such catalysts and catalytic converters described hereinabove optionally may be omitted or removed from systems intended for or converted for cooling of fluids other than hydrogen.

[0243] In any example set out, including the following examples, the specific total enthalpy of the heated hydrogen after said exposure may be greater than that of the inflow stream and the supply of cooled hydrogen combined. An enthalpy gradient may exist between the heated hydrogen after said exposure may be greater than that of the inflow stream and the supply of cooled hydrogen combined.

[0244] In any example set out, including the following examples, within the cooling system, hydrogen is heated with heat transferred by direct contact with the cold-side solid heat transfer surface to form heated hydrogen with specific total enthalpy greater than that of the inflow stream and the supply of cooled hydrogen.

[0245] In any example set out, including the following examples, the specific total enthalpy of the heated hydrogen may be the specific total enthalpy of the heated hydrogen after the step of transferred by direct contact with the cold-side solid heat transfer surface to form heated hydrogen, or where the heated hydrogen is additionally exposed to the catalyst, after exposure to the catalyst.

[0246] In any example set out, including the following examples, the temperature is the final temperature, and not an intermediate temperature.

[0247] In any example set out, including the following examples, the temperatures referred to are the temperatures when the fluid exits the cooling system or where the method has been completed, not the local temperatures arising part way through the method.

[0248] In any example set out, including the following examples, heated hydrogen may or may not be exposed to the catalyst, so the heated hydrogen may be output or finalised at two different points, either before or after the catalyst. The final temperature may be either before or after the catalyst.

[0249] In any example set out, including the following examples, the heated hydrogen may be heated solely by heat transfer by direct contact with the cold-side solid heat transfer surface and exposure to the catalyst.

[0250] In any example set out, including the following examples, reference to conversion is to net conversion, and reference to endothermically yielding a conversion is to endothermically yielding an overall net conversion.

[0251] In any example set out, including the following examples, the temperature difference may be achieved by heat transfer from the cooled hydrogen, excluding any heat received from environment.

[0252] In any example set out, including the following examples, the temperatures referred to are the temperatures when the fluid exits the cooling system or where the method has been completed, not the local temperatures arising part way through the method.

[0253] Various features and aspects of the present invention are disclosed in the following clauses:

- 1) A method of cooling hydrogen, the method comprising the steps of:
 - (a) flowing an inflow stream of hydrogen vapour from an upstream device into a cooling system;
 - (b) within the cooling system, heating a cold-side solid heat transfer surface with heat transferred, directly or indirectly, from hydrogen undergoing cooling, and providing at least some or all of the cooled hydrogen as a supply of cooled hydrogen;
 - (c) within the cooling system, heating hydrogen with heat transferred by direct contact with the cold-side solid heat transfer surface to form heated hydrogen; and
 - (d) within the cooling system or the upstream device, exposing hydrogen, which hydrogen is in, or to be comprised in, the heated hydrogen and/or the supply of cooled hydrogen, to a catalyst which endothermically yields a net conversion of para-hydrogen to ortho-hydrogen.
- 2) A method according to clause 1 wherein the method further comprises the following steps after step (c), and before, during or after step (d), of:
 - (e) collecting at least some or all of the heated hydrogen into a heated outflow stream that is separate from the supply of cooled hydrogen; and

- (f) flowing the heated outflow stream from the cooling system to the upstream device and/or to a downstream device.
- 3) A method of cooling hydrogen according to clause 1 or clause 2 wherein the supply of cooled hydrogen is produced within the cooling system and is flowed into (i) the upstream device; or, if dependent on clause 2, (ii) the downstream device that also receives the heated outflow stream; or, if dependent on clause 2, (iii) a second downstream device;.
 - 4) A method of cooling hydrogen according to clause 1 or clause 2 wherein the hydrogen constituting the supply of cooled hydrogen remains within the upstream device, whereby the hydrogen in the upstream device is cooled.
 - 5) A method according to clause 2, or clause 3 or clause 4 when dependant on clause 2, wherein, in step (d), hydrogen that subsequently flows from the cooling system as the heated outflow stream is exposed to the catalyst within the cooling system, whereby the heated outflow stream has a lower fraction of para-hydrogen, and a higher fraction of ortho-hydrogen, than the inflow stream.
 - 6) A method according to any foregoing clause wherein, in step (d), within the cooling system or the upstream device, hydrogen constituting the supply of cooled hydrogen is exposed to the catalyst to convert para-hydrogen to ortho-hydrogen in hydrogen constituting the supply of cooled hydrogen.
 - 7) A method according to any foregoing clause wherein the cold-side solid heat transfer surface forms a surface of a solid regenerator material in a regenerator, the surface of the solid regenerator material is exposed to hydrogen originating from the inflow stream, and hydrogen within the regenerator is displaced and pressurised periodically whereby the regenerator surface exchanges heat with the hydrogen periodically, in step (b) heat is transferred from the hydrogen undergoing cooling to the regenerator surface and in step (c) heat is transferred from the regenerator surface to the hydrogen undergoing heating, and a temperature or enthalpy gradient is established between relatively hot hydrogen in one part of the regenerator and relatively cold hydrogen in another part of the regenerator, and the relatively hot hydrogen is collected as heated hydrogen and the relatively cold hydrogen is collected as cooled hydrogen.
 - 8) A method according to clause 7 wherein the periodically pressurised and displaced hydrogen is exposed to the catalyst that catalyses the conversion of parahydrogen to orthohydrogen, whereby a net conversion of parahydrogen to orthohydrogen occurs within the periodically pressurised and displaced hydrogen.

- 9) A method according to clause 8 wherein the periodically pressurised and displaced hydrogen is exposed to the catalyst that both catalyses the conversion of parahydrogen to orthohydrogen and provides the cold-side solid heat transfer surface that periodically exchanges heat with the hydrogen.
- 10) A method according to any foregoing clause wherein the cold-side solid heat transfer surface is part of a heat exchange apparatus that transmits heat from a relatively higher temperature to a relatively lower temperature, and, in step (b) heat is transferred from the cooled hydrogen into the heat exchange apparatus and, in step (c) heat is transferred from the cold-side solid heat transfer surface of the heat exchange apparatus into the heated hydrogen.
- 11) A method according to any one of clauses 1 to 10 wherein the cold-side solid heat transfer surface is part of a heat pump apparatus that transmits heat from a relatively lower temperature to a relatively higher temperature, and, in step (b) heat is transferred from the cooled hydrogen into the heat pump apparatus and, in step (c) heat is transferred from the cold-side solid heat transfer surface of the heat pump apparatus into the heated hydrogen.
- 12) A method according to clause 10 or clause 11 when dependent on clause 2 wherein, within the cooling system and upstream of the heat exchange apparatus or heat pump apparatus, the inflow stream is split into the supply of cooled hydrogen and the outflow stream, the supply of cooled hydrogen rejects heat into the heat exchange apparatus or heat pump apparatus and the outflow stream absorbs heat from the heat exchange apparatus or heat pump apparatus.
- 13) A method according to any one of clauses 10 to 12, when dependent on clause 2, wherein, within the cooling system and upstream of the heat exchange apparatus or heat pump apparatus, the inflow stream is split into the supply of cooled hydrogen and the outflow stream, and at least one or both of the supply of cooled hydrogen and the outflow stream are subjected to compression and/or expansion to maintain a temperature differential between the cooled stream of hydrogen and the cold-side solid heat transfer surface throughout the heat exchange apparatus or heat pump apparatus.
- 14) A method according to clause 13 wherein hydrogen within or to be comprised within the supply of cooled hydrogen is compressed prior to being supplied to the heat exchange apparatus or heat pump apparatus, and when supplied to the heat exchange apparatus or heat pump apparatus the supply of cooled hydrogen is at a pressure which is higher than a pressure of the outflow stream supplied to the heat exchange apparatus

or heat pump apparatus, and after exiting the heat exchange apparatus or heat pump apparatus, the supply of cooled hydrogen is expanded thereby to cool the supply of cooled hydrogen.

- 15) A method according to any one of clauses 11 to 14, when dependent on clause 11, wherein the heat pump apparatus comprises a closed loop containing a working fluid, and the closed loop comprises at least one compressor, at least one expander and one or more heat exchangers configured to absorb heat originating from the supply of cooled hydrogen and configured to reject heat so that some part of the rejected heat is transferred to the heated outflow of hydrogen.
- 16) A method according to any one of clauses 11 to 14, when dependent on clause 11, wherein the heat pump apparatus employs a regenerative refrigeration cycle and comprises a working fluid that undergoes cyclic variation of pressure and displacement, and at least one pressure oscillator and at least one regenerator that absorbs heat from the working fluid during part of the cycle and rejects heat from the working fluid during another part of the cycle and one or more heat exchangers configured to absorb heat originating from the supply of cooled hydrogen and configured to reject heat so that some part of the rejected heat is transferred to the outflow of hydrogen.
- 17) A method according to any one of clauses 11 to 14, when dependent on clause 11, wherein the heat pump apparatus is a refrigeration apparatus which employs a magnetic refrigeration cycle in which a magnetocaloric material is exposed to a magnetic field in a manner such that the magnetic field within the magnetocaloric material varies with time and the magnetocaloric material periodically absorbs heat originating from the supply of cooled hydrogen and periodically rejects heat that is transferred to the outflow of hydrogen.
- 18) A method according to any one of clauses 1 to 17 wherein the supply of cooled hydrogen comprises a saturated mixture of hydrogen liquid and hydrogen vapour, which mixture is (i) returned to or remains within the upstream device; (ii) separated into hydrogen liquid, which is returned to or remains within the upstream device, and hydrogen vapour, which is combined with the inflow stream; (iii) when dependent on clause 10 or clause 11, separated into hydrogen liquid, which is returned to or remains within the upstream device, and hydrogen vapour, which is combined with the stream comprising, or to be comprised in, the supply of cooled hydrogen upstream of the heat exchange apparatus or heat pump apparatus; (iv) when dependent on clause 2 and clauses 10 or 11, separated into hydrogen liquid, which is returned to or remains within

the upstream device, and hydrogen vapour, which is combined with the outflow stream upstream of the heat exchange apparatus or heat pump apparatus; (v) separated into hydrogen liquid, which is flowed to a downstream device, and hydrogen vapour, which is combined with the inflow stream; or (v) when dependent on clause 2 and clauses 10 or 11, separated into hydrogen liquid, which is flowed to a downstream device, and hydrogen vapour, which is combined with a stream of hydrogen comprising, or to be comprised in, the supply of cooled hydrogen upstream of the heat exchange apparatus or heat pump apparatus; or (vi) when dependent on clause 2 and clauses 10 or 11, separated into hydrogen liquid, which is flowed to a downstream device, and hydrogen vapour, which is combined with the outflow stream upstream of the heat exchange apparatus or heat pump apparatus.

- 19) A method according to any foregoing clause wherein the cooling system comprises a further heat exchanger which additionally transfers heat from hydrogen in, or to be comprised in, the supply of cooled hydrogen into the environment and/or to a coolant fluid.
- 20) A method according to any foregoing clause wherein the upstream device comprises a vessel in which hydrogen is stored in the liquid phase and the cooling system cools the inflow stream from the vessel.
- 21) A method according to clause 20 wherein the vessel and the cooling system are combined into an integral unit.
- 22) A method according to clause 20 or clause 21, when dependent on clause 2, wherein the inflow stream of hydrogen vapour comprises boil-off hydrogen gas from the vessel, and the cooling system partially re-liquefies the boil-off hydrogen gas to provide a liquid fraction which is returned to or remains within the vessel and a gaseous fraction, wherein at least a portion of the gaseous fraction forms the outflow stream.
- 23) A method according to clause 2 or any clause dependent on clause 2 wherein the downstream device comprises a power generator in which power is generated by oxidation of hydrogen in the outflow stream.
- 24) A method according to clause 23 wherein the power generator comprises (i) an electrical power generator; (ii) a mechanical power generator having an output mechanical power transmission device; (iii) a propulsion power generator providing output power in the form of jet propulsion, driving of a propellor, driving of a tractive drive or electromagnetic propulsion.

- 25) A method according to clause 24 wherein the power generator provides power to the cooling system.
- 26) A method according to any foregoing clause wherein the upstream device comprises a first vessel provided for storage of liquid hydrogen and a second vessel provided for storage of liquid hydrogen and a transfer system provided to transfer hydrogen between the storage vessels and the cooling system is provided with an inflow of hydrogen from the first storage vessel and/or the second storage vessel and/or the transfer system.
- 27) A method according to clause 26 wherein the cooling system provides an outflow of heated hydrogen vapour to the first storage vessel and/or the second storage vessel and/or the transfer system and/or another downstream device.
- 28) A method according to clause 26 or clause 27 wherein the cooling system provides a supply of cooled hydrogen to the first storage vessel and/or the second storage vessel and/or the transfer system and/or another downstream device.
- 29) A method according to any one of clauses 26 to 28 wherein the cooling system provides cooling to the first storage vessel and/or to the second storage vessel and/or to the transfer system and/or to a downstream device.
- 30) A method according to any one of clauses 26 to 29 wherein the cooling system is combined with the first storage vessel and/or the second storage vessel into an integral unit.
- 31) A method according to one of clauses 26 to 30 wherein the cooling system is combined with the transfer system into an integral unit.
- 32) A method according to any one of clauses 26 to 31 wherein the transfer system provides a pump that drives liquid hydrogen from one of the first and second storage vessels to the other of the first and second storage vessels.
- 33) A method according to any one of clauses 26 to 32 wherein the transfer system provides a valve that controls flow of liquid hydrogen from one of the first and second storage vessels to the other of the first and second storage vessels.
- 34) A method according to any one of clauses 26 to 33 wherein one or both of the first and second storage vessels are attached, or detachably attachable, to a vehicle to transport one or both of the first and second storage vessels.
- 35) A method according to any foregoing clause wherein the cooling system provides the supply of cooled hydrogen as an outflow of cooled hydrogen from the cooling system and/or the cooling system provides the heated hydrogen as an outflow of heated hydrogen from the cooling system, and the outflow of cooled hydrogen or outflow of

heated hydrogen is used to cool the upstream device, a downstream device or any component connected to the upstream device or the downstream device.

- 36) A method according to clause 35 wherein the upstream device, the downstream device or any component connected to the upstream device or the downstream device is provided with a cooling system comprising a flow of coolant, and the outflow of cooled hydrogen or the outflow of heated hydrogen is used to cool the flow of coolant in the cooling system.
- 37) A method according to clause 35 or clause 36 wherein the outflow of cooled hydrogen from the cooling system or the outflow of heated hydrogen from the cooling system is exposed to a second catalyst which endothermically yields a net conversion of para-hydrogen to ortho-hydrogen, whereby the cooling potential of hydrogen in the outflow of cooled hydrogen or outflow of heated hydrogen is increased.
- 38) A method according to any foregoing clause, when dependent on clause 2, wherein in the downstream device the heated outflow stream (i) is used to condense or freeze pollutant species from the exhaust gas of a fuel cell, engine, combustion system, or industrial process; (ii) is used to absorb heat in a process of liquefying or solidifying cryogenic fluids or maintaining cryogenic substances in a condensed state; (iii) is processed in order to achieve temperature and pressure conditions in the outflow hydrogen required for its use as an input to a fuel cell, engine, combustion system or manufacturing process; (iv) is processed in order to provide cooling to a fuel cell, engine, combustion system or industrial process; (v) is used in a process that receives heat from the environment or from a waste heat source; or (vi) is supplied into a heat engine that utilises temperature difference between the outflow stream and either the environment or another heat source in order to produce power.
- 39) An apparatus for cooling hydrogen, the apparatus comprising: an upstream device configured to contain hydrogen vapour, a cooling system comprising a cold-side solid heat transfer surface, an inflow conduit connecting the upstream device and the cooling system for flowing an inflow stream of hydrogen vapour from the upstream device into the cooling system, and a catalyst for converting para-hydrogen to ortho-hydrogen in hydrogen within the cooling system or within the upstream device, wherein the cooling system is configured to heat the a cold-side solid heat transfer surface with heat transferred, directly or indirectly, from hydrogen undergoing cooling, to provide at least some or all of the cooled hydrogen as a supply of cooled hydrogen, to heat hydrogen with heat transferred by direct contact with the cold-side solid heat transfer surface to

form heated hydrogen; and the catalyst is configured to be exposed to hydrogen within the cooling system or the upstream device, which hydrogen is in, or to be comprised in, the heated hydrogen and/or the supply of cooled hydrogen.

- 40) An apparatus according to clause 39 further comprising a conduit connecting the cooling system and the upstream device for flowing a heated outflow stream of the heated hydrogen from the cooling system to the upstream device which is configured to receive hydrogen vapour from the cooling system and/or further comprising a downstream device which is configured to receive hydrogen vapour from the cooling system and an outflow conduit connecting the cooling system and the downstream device for flowing a heated outflow stream of the heated hydrogen from the cooling system to the downstream device.
- 41) An apparatus according to clause 39 or clause 40 comprising (i) a conduit connecting the cooling system and the upstream device for flowing a stream of cooled hydrogen from the cooling system to the upstream device which is configured to receive cooled hydrogen from the cooling system; (ii) a conduit connecting the cooling system and a downstream device for flowing a stream of cooled hydrogen from the cooling system to the same downstream device which is configured to receive cooled hydrogen from the cooling system; or, if dependent on clause 40 wherein a downstream device is configured to receive hydrogen vapour from the cooling system, (iii) a conduit connecting the cooling system and the downstream device configured to receive hydrogen vapour from the cooling system for flowing a stream of cooled hydrogen from the cooling system to the downstream device configured to receive hydrogen vapour from the cooling system, which is also configured to receive cooled hydrogen from the cooling system.
- 42) An apparatus according to clause 39 or clause 40 wherein the cooling system comprises a thermal transfer device, including the cold-side solid heat transfer surface, for transferring heat, directly or indirectly, into the heated hydrogen from the supply of cooled hydrogen, wherein the supply of cooled hydrogen is separated from the inflow stream or is retained within the upstream device, and thereby to cool hydrogen in the upstream device.
- 43) An apparatus according to clause 40, or clause 41 or clause 42 when dependent on clause 40, wherein within the cooling system the catalyst is arranged to contact the

heated outflow stream to convert para-hydrogen to ortho-hydrogen in the heated outflow stream.

- 44) An apparatus according to any one of clauses 39 to 43 wherein within the cooling system or the upstream device the catalyst is arranged to contact the supply of cooled hydrogen to convert para-hydrogen to ortho-hydrogen in the supply of cooled hydrogen.
- 45) An apparatus according to any one of clauses 39 to 44 wherein the cold-side solid heat transfer surface forms a surface of a solid regenerator material in a regenerator, the surface of the solid regenerator material is configured to be exposed to hydrogen originating from the inflow stream, and the cooling system is configured to displace and pressurise periodically hydrogen within the regenerator whereby the regenerator surface exchanges heat with the hydrogen periodically, whereby heat is transferred from the hydrogen undergoing cooling to the regenerator surface and heat is transferred from the regenerator surface to the heated hydrogen, and a temperature or enthalpy gradient is established between relatively hot hydrogen in one part of the regenerator and relatively cold hydrogen in another part of the regenerator, and the cooling system is configured to collect the relatively hot hydrogen as heated hydrogen and the relatively cold hydrogen as cooled hydrogen.
- 46) An apparatus according to clause 45 wherein the cooling system is configured to expose the periodically pressurised and displaced hydrogen to the catalyst whereby a net conversion of parahydrogen to orthohydrogen occurs within the periodically pressurised and displaced hydrogen.
- 47) An apparatus according to any one of clauses 39 to 46 wherein the cooling system comprises a heat exchanger, including the cold-side solid heat transfer surface, for directly transferring heat from the supply of cooled hydrogen into the heated outflow stream.
- 48) An apparatus according to any one of clauses 39 to 47 wherein the cold-side solid heat transfer surface is part of a heat pump apparatus that transmits heat from a relatively lower temperature to a relatively higher temperature, and the heat pump apparatus is configured whereby heat is transferred from the cooled hydrogen into the heat pump apparatus and heat is transferred from the cold-side solid heat transfer surface of the heat pump apparatus into the heated hydrogen.

- 49) An apparatus according to clause 47 or clause 48 when dependent on clause 40 wherein, within the cooling system and upstream of the heat exchanger apparatus or heat pump apparatus, the cooling system further comprises a splitter for splitting the inflow stream into the supply of cooled hydrogen and the outflow stream, the heat exchange apparatus or heat pump apparatus being configured for the supply of cooled hydrogen to reject heat into the heat exchanger apparatus or heat pump apparatus and the outflow stream to absorb heat from the heat exchanger or heat pump apparatus.
- 50) An apparatus according to any one of clauses 47 to 49, when dependent on clause 40 or any clause dependent thereon, wherein, within the cooling system and upstream of the heat exchanger or heat pump, the apparatus further comprises a splitter for splitting the inflow stream into the supply of cooled hydrogen and the heated outflow stream, and a compression and/or expansion device for subjecting at least one or both of the supply of cooled hydrogen and the heated outflow stream to compression and/or expansion to provide a temperature differential between the supply of cooled hydrogen and the heated outflow stream upstream of the heat exchanger or heat pump, wherein the heat exchanger or heat pump has a heat output side and a heat input side, and in the heat exchanger or heat pump the supply of cooled hydrogen is configured to be supplied to the heat input side of the heat exchanger or heat pump and the heated outflow stream is configured to be supplied to the heat output side of the heat exchanger or heat pump.
- 51) An apparatus according to clause 50 wherein the compression and/or expansion device is configured to compress the supply of cooled hydrogen prior to being supplied to the heat exchanger or heat pump and to expand the supply of cooled hydrogen after exiting the heat exchanger or heat pump.
- 52) An apparatus according to any one of clauses 48 to 51 when dependent on clause 48 wherein the heat pump apparatus comprises a closed loop containing a working fluid, and the closed loop comprises at least one compressor, at least one expander and one or more heat exchangers configured to absorb heat originating from the supply of cooled hydrogen and configured to reject heat so that some part of the rejected heat is transferred to the heated outflow of hydrogen.
- 53) An apparatus according to any one of clauses 48 to 51 when dependent on clause 48 wherein the heat pump apparatus employs a regenerative refrigeration cycle and comprises a working fluid that is arranged to undergo cyclic variation of pressure and displacement, and at least one pressure oscillator and at least one regenerator that is

configured to absorb heat from the working fluid during part of the cycle and to reject heat from the working fluid during another part of the cycle and one or more heat exchangers configured to absorb heat originating from the supply of cooled hydrogen and configured to reject heat so that some part of the rejected heat is transferred to the heated outflow of hydrogen.

- 54) An apparatus according to any one of clauses 48 to 51 when dependent on clause 48 wherein the heat pump apparatus is a refrigeration apparatus which is configured to employ a magnetic refrigeration cycle in which a magnetocaloric material is exposed to a magnetic field in a manner such that the magnetic field within the magnetocaloric material varies with time and the magnetocaloric material periodically absorbs heat originating from the supply of cooled hydrogen and periodically rejects heat that is transferred to the outflow of hydrogen.
- 55) An apparatus according to any one of clauses 39 to 54 wherein the expansion device is configured to expand and cool the supply of cooled hydrogen to form a saturated mixture of hydrogen liquid and hydrogen vapour, and the apparatus further comprises (i) a return conduit connected to an output of the expansion device for returning the saturated mixture of hydrogen liquid and hydrogen vapour to the upstream device; (ii) a separator for separating hydrogen liquid and hydrogen vapour from the saturated mixture of hydrogen liquid and hydrogen vapour, a return conduit connected to the separator for returning the hydrogen liquid to the upstream device, a recirculation conduit for combining the hydrogen vapour with the inflow stream; or (iii) a separator for separating hydrogen liquid and hydrogen vapour from the saturated mixture of hydrogen liquid and hydrogen vapour, a return conduit connected to the separator for returning the hydrogen liquid to the upstream device, a supply conduit for supplying the hydrogen vapour to the relatively cold side of the heat exchanger for heating the hydrogen vapour, and a recirculation conduit for combining the hydrogen vapour from the relatively cold side of the heat exchanger with the inflow stream.
- 56) An apparatus according to any one of clauses 39 to 55 wherein the cooling system comprises a further heat exchanger which is configured additionally to transfer heat from hydrogen in, or to be comprised in, the supply of cooled hydrogen into the environment and/or to a coolant fluid.

- 57) An apparatus according to any one of clauses 39 to 56 wherein the upstream device comprises a vessel in which hydrogen is stored in the liquid phase and the cooling system is configured to cool the inflow stream from the vessel.
- 58) An apparatus according to clause 57 wherein the vessel and the cooling system are combined into an integral unit.
- 59) An apparatus according to clause 57 or clause 58, when dependant on clause 40, wherein the inflow stream of hydrogen vapour comprises boil-off hydrogen gas from the vessel, and the cooling system is configured partially to re-liquefy the boil-off hydrogen gas to provide a liquid fraction which is returned to or remains within the vessel and a gaseous fraction, wherein at least a portion of the gaseous fraction forms the outflow stream.
- 60) An apparatus according to clause 40 or any clause dependant on clause 40 wherein the downstream device comprises a power generator in which power is generated by oxidation of hydrogen in the outflow stream.
- 61) An apparatus according to clause 60 wherein the power generator comprises (i) an electrical power generator; (ii) a mechanical power generator having an output mechanical power transmission device; (iii) a propulsion power generator providing output power in the form of jet propulsion, driving of a propellor, driving of a tractive drive or electromagnetic propulsion.
- 62) An apparatus according to clause 61 wherein the power generator is configured to provide power to the cooling system.
- 63) An apparatus according to any one of clauses 39 to 62 wherein the upstream device comprises a first vessel for storing hydrogen in the liquid phase and a second vessel for storing hydrogen in the liquid phase, and further comprising a transfer system provided between the first and second vessels for transferring hydrogen between the first and second vessels, and the cooling system being configured to be provided with an inflow of hydrogen from the first storage vessel and/or the second storage vessel and/or the transfer system.
- 64) An apparatus according to clause 63 comprising a conduit connecting the cooling system to the first storage vessel and/or the second storage vessel and/or the transfer system and/or another downstream device for flowing a stream of heated hydrogen vapour from the cooling system to the first storage vessel and/or the second storage vessel and/or the transfer system and/or another downstream device respectively.

- 65) An apparatus according to clause 63 or clause 64 comprising a conduit connecting the cooling system to the first storage vessel and/or the second storage vessel and/or the transfer system and/or another downstream device for flowing a supply of cooled hydrogen from the cooling system to the first storage vessel and/or the second storage vessel and/or the transfer system and/or another downstream device respectively.
- 66) An apparatus according to any one of clauses 63 to 65 comprising a heat transfer device in thermal communication with the cooling system and in thermal communication with the first storage vessel and/or the second storage vessel and/or the transfer system and/or a downstream device for transferring heat into the cooling system from the first storage vessel and/or the second storage vessel and/or the transfer system and/or a downstream device respectively.
- 67) An apparatus according to any one of clauses 63 to 66 wherein the cooling system is combined with the first storage vessel and/or the second storage vessel into an integral unit.
- 68) An apparatus according to any one of clauses 63 to clause 67 wherein the cooling system is combined with the transfer system into an integral unit.
- 69) An apparatus according to any one of clauses 63 to 68 wherein the transfer system comprises a pump configured to drive liquid hydrogen from one of the first and second storage vessels to the other of the first and second storage vessels.
- 70) An apparatus according to any one of clauses 63 to 69 wherein the transfer system comprises a valve that is configured to control flow of liquid hydrogen from one of the first and second storage vessels to the other of the first and second storage vessels.
- 71) An apparatus according to any one of clauses 63 to 70 wherein one or both of the first and second storage vessels are attached, or detachably attachable, to a vehicle to transport the first and second storage vessels.
- 72) An apparatus according to any one of clauses 39 to 71 wherein the cooling system is configured to provide a flow of cooled hydrogen from the cooling system and/or the cooling system is configured to provide a flow of heated hydrogen from the cooling system, and the flow of cooled hydrogen and/or the flow of heated hydrogen is used to cool the upstream device, or any component connected to the upstream device, or, when dependent on clause 40 or any clause dependent thereon, the downstream device or any component connected to the downstream device.

- 73) An apparatus according to clause 72 wherein the upstream device, the downstream device or any component connected to the upstream device or the downstream device is provided with a cooling device comprising a flow of coolant, and the flow of cooled hydrogen and/or the flow of heated hydrogen is configured to cool the flow of coolant in the cooling device.
- 74) An apparatus according to clause 72 or clause 73 wherein a conduit containing a second catalyst for conversion of para-hydrogen to ortho-hydrogen is configured to transmit the outflow stream of cooled hydrogen from the cooling system and/or to transmit the outflow stream of heated hydrogen from the cooling system.
- 75) An apparatus according to clause 40, or any clause dependent on clause 40, wherein the downstream device that receives the heated outflow stream comprises (i) a heat transfer device in thermal communication with the heated outflow stream and in thermal communication with exhaust gas from a fuel cell, engine, combustion system or industrial process for transmitting heat from the exhaust gas into the heated outflow stream; (ii) a heat transfer device in thermal communication with the heated outflow stream and in thermal communication with other cryogenic fluid for transmitting heat from the cryogenic fluid into the heated outflow stream; (iii) a heat transfer and/or expansion and/or compression device configured to receive the heated outflow stream, to modify the temperature and/or pressure of the heated outflow stream, and to supply the heated outflow stream to a fuel cell, engine, combustion system or industrial process; (iv) a heat transfer device in thermal communication with the heated outflow stream and in thermal communication with a fuel cell, engine, combustion system or industrial process to transfer heat from the fuel cell, engine, combustion system or industrial process into the heated outflow stream; (v) a heat transfer device in thermal communication with the heated outflow stream and in thermal communication with the environment or with a waste heat source to transfer heat from the environment or waste heat source into the heated outflow stream; or (vi) a heat engine in thermal communication with the heated outflow stream and with the environment or another heat source to receive heat from the environment or heat source, to reject heat to the heated outflow stream, and to produce power.
- 76) A method of cooling a fluid, the method comprising the steps of:
- (A) flowing an inflow stream of vapour of the fluid from an upstream device into a cooling system;

- (B) within the cooling system, heating a cold-side solid heat transfer surface with heat transferred, directly or indirectly, from fluid undergoing cooling, and providing at least some or all of the cooled fluid as a supply of cooled fluid; and
 - (C) within the cooling system, heating fluid with heat transferred by direct contact with the cold-side solid heat transfer surface to form heated fluid, wherein the cold-side solid heat transfer surface forms a surface of a solid regenerator material in a regenerator, the surface of the solid regenerator material is exposed to fluid originating from the inflow stream, and fluid within the regenerator is displaced and pressurised periodically whereby the regenerator surface exchanges heat with the fluid periodically, in step (B) heat is transferred from the fluid undergoing cooling to the regenerator surface and in step (C) heat is transferred from the regenerator surface to the heated fluid, and a temperature or enthalpy gradient is established between relatively hot fluid in one part of the regenerator and relatively cold fluid in another part of the regenerator, and the relatively hot fluid is collected as heated fluid and the relatively cold fluid is collected as cooled fluid.
- 77) A method according to clause 76 wherein the method further comprises the following steps, after step (C), of:
- (D) collecting at least some or all of the heated fluid into a heated outflow stream that is separate from the supply of cooled fluid; and
 - (E) flowing the heated outflow stream from the cooling system to the upstream device and/or to a downstream device.
- 78) A method of cooling fluid according to clause 77 wherein the supply of cooled fluid is produced within the cooling device and is flowed into (i) the upstream device; (ii) a first downstream device that also receives the heated outflow stream; or (iii) a second downstream device.
- 79) A method of cooling fluid according to clause 76 or clause 77 wherein the fluid constituting the supply of cooled fluid remains within the upstream device, whereby the fluid in the upstream device is cooled.
- 80) A method according to any one of clauses 76 to 79, in which molecular hydrogen forms part of the fluid, further comprising the step (F), at any stage after step (A), of: within the cooling system or the upstream device, exposing hydrogen, which hydrogen is in, or to be comprised in, the heated fluid and/or the supply of cooled fluid, to a catalyst which endothermically yields a net conversion of para-hydrogen to ortho-hydrogen.

- 81) A method according to clause 80 when dependant on clause 77 or any clause dependant thereon, wherein, in step (F), fluid that subsequently flows from the cooling system as the heated outflow stream is exposed to the catalyst within the cooling system, whereby the heated outflow stream has a lower fraction of para-hydrogen, and a higher fraction of ortho-hydrogen, than the inflow stream.
- 82) A method according to clause 80 or clause 81 wherein, in step (F), within the cooling system or the upstream device, hydrogen constituting the supply of cooled fluid is exposed to the catalyst to convert para-hydrogen to ortho-hydrogen in the supply of cooled fluid.
- 83) A method according to clause 80 or any clause dependent thereon wherein the periodically pressurised and displaced fluid is exposed to the catalyst that catalyses the conversion of parahydrogen to orthohydrogen, whereby a net conversion of parahydrogen to orthohydrogen occurs within the periodically pressurised and displaced fluid.
- 84) A method according to clause 83 wherein the periodically pressurised and displaced fluid is exposed to the catalyst that both catalyses the conversion of parahydrogen to orthohydrogen and provides the cold-side solid heat transfer surface that periodically exchanges heat with the fluid.
- 85) An apparatus for cooling a fluid, the apparatus comprising: an upstream device configured to contain vapour of the fluid, a cooling system comprising a cold-side solid heat transfer surface, an inflow conduit connecting the upstream device and the cooling system for flowing an inflow stream of vapour from the upstream device into the cooling system, wherein the cooling system is configured to heat the a cold-side solid heat transfer surface with heat transferred, directly or indirectly, from fluid undergoing cooling, to provide at least some or all of the cooled fluid as a supply of cooled fluid, to heat fluid with heat transferred by direct contact with the cold-side solid heat transfer surface to form heated fluid, wherein the cold-side solid heat transfer surface forms a surface of a solid regenerator material in a regenerator, the surface of the solid regenerator material is configured to be exposed to fluid originating from the inflow stream, and the cooling system is configured to displace and pressurise periodically fluid within the regenerator whereby the regenerator surface exchanges heat with the fluid periodically, whereby heat is transferred from the fluid undergoing cooling to the regenerator surface and heat is transferred from the regenerator surface to the heated fluid, and a temperature or enthalpy gradient is established between relatively hot fluid

in one part of the regenerator and relatively cold fluid in another part of the regenerator, and the cooling system is configured to collect the relatively hot fluid as heated fluid and the relatively cold fluid as cooled fluid.

- 86) An apparatus according to clause 85 further comprising an outflow conduit connecting the cooling system and the upstream device for flowing a heated outflow stream of the heated fluid from the cooling system to the upstream device which is configured to receive the heated fluid and/or a downstream device which is configured to receive fluid vapour from the cooling system and an outflow conduit connecting the cooling system and the downstream device for flowing a heated outflow stream of the heated fluid from the cooling system to the downstream device.
- 87) An apparatus according to clause 86 wherein the cooling system comprises a thermal transfer device, including the cold-side solid heat transfer surface, for transferring heat, directly or indirectly, into the heated outflow stream from the supply of cooled fluid, wherein the supply of cooled fluid is separated from the inflow stream or is retained within the upstream device, and thereby to cool fluid in the upstream device.
- 88) An apparatus according to any one of clauses 85 to 87, wherein the fluid undergoing cooling contains molecular hydrogen, further comprising a catalyst for converting para-hydrogen to ortho-hydrogen in hydrogen within the cooling system or within the upstream device, and the catalyst is configured to be exposed to hydrogen within the cooling system or the upstream device, which hydrogen is in, or to be comprised in, the heated fluid and/or the supply of cooled fluid.
- 89) An apparatus according to clause 88 when dependent on clause 86 wherein within the cooling system the catalyst is arranged to contact the heated outflow stream to convert para-hydrogen to ortho-hydrogen in the heated outflow stream.
- 90) An apparatus according to clause 88 wherein within the cooling system or the upstream device the catalyst is arranged to contact the supply of cooled fluid to convert para-hydrogen to ortho-hydrogen in the supply of cooled fluid.
- 91) An apparatus according to clause 90 wherein the cooling system is configured to expose the periodically pressurised and displaced fluid to the catalyst whereby a net conversion of parahydrogen to orthohydrogen occurs within the periodically pressurised and displaced fluid.

Claims

1. A method of cooling hydrogen, the method comprising the steps of:
 - (a) flowing an inflow stream of hydrogen vapour from an upstream device into a cooling system;
 - (b) within the cooling system, heating a cold-side solid heat transfer surface with heat transferred, directly or indirectly, from hydrogen undergoing cooling, and providing at least some or all of the cooled hydrogen as a supply of cooled hydrogen;
 - (c) within the cooling system, heating hydrogen with heat transferred by direct contact with the cold-side solid heat transfer surface to form heated hydrogen; and
 - (d) within the cooling system or the upstream device, exposing hydrogen, which hydrogen is in, or to be comprised in, the heated hydrogen and/or the supply of cooled hydrogen, to a catalyst which endothermically yields a net conversion of para-hydrogen to ortho-hydrogen.
2. A method according to claim 1, wherein the specific total enthalpy of the heated hydrogen after said exposure is greater than that of the inflow stream and the supply of cooled hydrogen combined.
3. A method according to claim 1 or claim 2, wherein the specific total enthalpy of the heated hydrogen is the specific total enthalpy of the heated hydrogen after the step of transferred by direct contact with the cold-side solid heat transfer surface to form heated hydrogen, or where the heated hydrogen is additionally exposed to the catalyst, after exposure to the catalyst.
4. A method according to claim 1 or claim 2, wherein the heated hydrogen is heated solely by heat transfer by direct contact with the cold-side solid heat transfer surface and exposure to the catalyst.
5. A method according to any one of claims 1 to 4 wherein the method further comprises the following steps after step (c), and before, during or after step (d), of:
 - (e) collecting at least some or all of the heated hydrogen into a heated outflow stream that is separate from the supply of cooled hydrogen; and
 - (f) flowing the heated outflow stream from the cooling system to the upstream device and/or to a downstream device.

6. A method of cooling hydrogen according to any one of claims 1 to 5 wherein the supply of cooled hydrogen is produced within the cooling system and is flowed into (i) the upstream device; or, if dependent on claim 2, (ii) the downstream device that also receives the heated outflow stream; or, if dependent on claim 2, (iii) a second downstream device;.
7. A method of cooling hydrogen according to any one of claim 1 to 5 wherein the hydrogen constituting the supply of cooled hydrogen remains within the upstream device, whereby the hydrogen in the upstream device is cooled.
8. A method according to claim 5, or claim 6 or claim 7 when dependant on claim 5, wherein, in step (d), hydrogen that subsequently flows from the cooling system as the heated outflow stream is exposed to the catalyst within the cooling system, whereby the heated outflow stream has a lower fraction of para-hydrogen, and a higher fraction of ortho-hydrogen, than the inflow stream.
9. A method according to any foregoing claim wherein, in step (d), within the cooling system or the upstream device, hydrogen constituting the supply of cooled hydrogen is exposed to the catalyst to convert para-hydrogen to ortho-hydrogen in hydrogen constituting the supply of cooled hydrogen.
10. A method according to any foregoing claim wherein the cold-side solid heat transfer surface forms a surface of a solid regenerator material in a regenerator, the surface of the solid regenerator material is exposed to hydrogen originating from the inflow stream, and hydrogen within the regenerator is displaced and pressurised periodically whereby the regenerator surface exchanges heat with the hydrogen periodically, in step (b) heat is transferred from the hydrogen undergoing cooling to the regenerator surface and in step (c) heat is transferred from the regenerator surface to the hydrogen undergoing heating, and a temperature or enthalpy gradient is established between relatively hot hydrogen in one part of the regenerator and relatively cold hydrogen in another part of the regenerator, and the relatively hot hydrogen is collected as heated hydrogen and the relatively cold hydrogen is collected as cooled hydrogen.
11. A method according to any foregoing claim wherein the cold-side solid heat transfer surface is part of a heat exchange apparatus that transmits heat from a relatively higher temperature to a relatively lower temperature, and, in step (b) heat is transferred from the cooled hydrogen into the heat exchange apparatus and, in step (c) heat is transferred from the cold-side solid heat transfer surface of the heat exchange apparatus into the heated hydrogen.
12. A method according to any one of claims 1 to 11 wherein the cold-side solid heat transfer surface is part of a heat pump apparatus that transmits heat from a relatively lower temperature to a relatively higher temperature, and, in step (b) heat is transferred from the

cooled hydrogen into the heat pump apparatus and, in step (c) heat is transferred from the cold-side solid heat transfer surface of the heat pump apparatus into the heated hydrogen.

13. A method according to claim 11 or claim 12 when dependent on claim 5 wherein, within the cooling system and upstream of the heat exchange apparatus or heat pump apparatus, the inflow stream is split into the supply of cooled hydrogen and the outflow stream, the supply of cooled hydrogen rejects heat into the heat exchange apparatus or heat pump apparatus and the outflow stream absorbs heat from the heat exchange apparatus or heat pump apparatus.

14. A method according to any one of claims 11 to 13, when dependent on claim 2, wherein, within the cooling system and upstream of the heat exchange apparatus or heat pump apparatus, the inflow stream is split into the supply of cooled hydrogen and the outflow stream, and at least one or both of the supply of cooled hydrogen and the outflow stream are subjected to compression and/or expansion to maintain a temperature differential between the cooled stream of hydrogen and the cold-side solid heat transfer surface throughout the heat exchange apparatus or heat pump apparatus.

15. A method according to claim 14 wherein hydrogen within or to be comprised within the supply of cooled hydrogen is compressed prior to being supplied to the heat exchange apparatus or heat pump apparatus, and when supplied to the heat exchange apparatus or heat pump apparatus the supply of cooled hydrogen is at a pressure which is higher than a pressure of the outflow stream supplied to the heat exchange apparatus or heat pump apparatus, and after exiting the heat exchange apparatus or heat pump apparatus, the supply of cooled hydrogen is expanded thereby to cool the supply of cooled hydrogen.

16. A method according to any one of claims 12 to 15, when dependent on claim 12, wherein the heat pump apparatus comprises a closed loop containing a working fluid, and the closed loop comprises at least one compressor, at least one expander and one or more heat exchangers configured to absorb heat originating from the supply of cooled hydrogen and configured to reject heat so that some part of the rejected heat is transferred to the heated outflow of hydrogen.

17. A method according to any one of claims 12 to 15, when dependent on claim 12, wherein the heat pump apparatus employs a regenerative refrigeration cycle and comprises a working fluid that undergoes cyclic variation of pressure and displacement, and at least one pressure oscillator and at least one regenerator that absorbs heat from the working fluid during part of the cycle and rejects heat from the working fluid during another part of the cycle and one or more heat exchangers configured to absorb heat originating from the supply of cooled

hydrogen and configured to reject heat so that some part of the rejected heat is transferred to the outflow of hydrogen.

18. A method according to any one of claims 12 to 15, when dependent on claim 12, wherein the heat pump apparatus is a refrigeration apparatus which employs a magnetic refrigeration cycle in which a magnetocaloric material is exposed to a magnetic field in a manner such that the magnetic field within the magnetocaloric material varies with time and the magnetocaloric material periodically absorbs heat originating from the supply of cooled hydrogen and periodically rejects heat that is transferred to the outflow of hydrogen.

19. A method according to any foregoing claim wherein the upstream device comprises a vessel in which hydrogen is stored in the liquid phase and the cooling system cools the inflow stream from the vessel.

20. A method according to claim 19, when dependent on claim 2, wherein the inflow stream of hydrogen vapour comprises boil-off hydrogen gas from the vessel, and the cooling system partially re-liquefies the boil-off hydrogen gas to provide a liquid fraction which is returned to or remains within the vessel and a gaseous fraction, wherein at least a portion of the gaseous fraction forms the outflow stream.

21. A method according to claim 5 or any claim dependent on claim 5 wherein the downstream device comprises a power generator in which power is generated by oxidation of hydrogen in the outflow stream.

22. A method according to any foregoing claim wherein the upstream device comprises a first vessel provided for storage of liquid hydrogen and a second vessel provided for storage of liquid hydrogen and a transfer system provided to transfer hydrogen between the storage vessels and the cooling system is provided with an inflow of hydrogen from the first storage vessel and/or the second storage vessel and/or the transfer system.

23. A method according to any foregoing claim wherein the cooling system provides the supply of cooled hydrogen as an outflow of cooled hydrogen from the cooling system and/or the cooling system provides the heated hydrogen as an outflow of heated hydrogen from the cooling system, and the outflow of cooled hydrogen or outflow of heated hydrogen is used to cool the upstream device, a downstream device or any component connected to the upstream device or the downstream device.

24. A method of cooling a fluid, the method comprising the steps of:

(A) flowing an inflow stream of vapour of the fluid from an upstream device into a cooling system;

(B) within the cooling system, heating a cold-side solid heat transfer surface with heat transferred, directly or indirectly, from fluid undergoing cooling, and providing at least some or all of the cooled fluid as a supply of cooled fluid; and

(C) within the cooling system, heating fluid with heat transferred by direct contact with the cold-side solid heat transfer surface to form heated fluid, wherein the cold-side solid heat transfer surface forms a surface of a solid regenerator material in a regenerator, the surface of the solid regenerator material is exposed to fluid originating from the inflow stream, and fluid within the regenerator is displaced and pressurised periodically whereby the regenerator surface exchanges heat with the fluid periodically, in step (B) heat is transferred from the fluid undergoing cooling to the regenerator surface and in step (C) heat is transferred from the regenerator surface to the heated fluid, and a temperature or enthalpy gradient is established between relatively hot fluid in one part of the regenerator and relatively cold fluid in another part of the regenerator, and the relatively hot fluid is collected as heated fluid and the relatively cold fluid is collected as cooled fluid.

25. A method according to claim 24 wherein the method further comprises the following steps, after step (C), of:

(D) collecting at least some or all of the heated fluid into a heated outflow stream that is separate from the supply of cooled fluid; and

(E) flowing the heated outflow stream from the cooling system to the upstream device and/or to a downstream device.

26. A method of cooling fluid according to claim 25 wherein the supply of cooled fluid is produced within the cooling device and is flowed into (i) the upstream device; (ii) a first downstream device that also receives the heated outflow stream; or (iii) a second downstream device.

27. A method of cooling fluid according to claim 24 or claim 25 wherein the fluid constituting the supply of cooled fluid remains within the upstream device, whereby the fluid in the upstream device is cooled.

28. A method according to any one of claims 24 to 27, in which molecular hydrogen forms part of the fluid, further comprising the step (F), at any stage after step (A), of: within the cooling system or the upstream device, exposing hydrogen, which hydrogen is in, or to be comprised in, the heated fluid and/or the supply of cooled fluid, to a catalyst which endothermically yields a net conversion of para-hydrogen to ortho-hydrogen.

Figure 1:

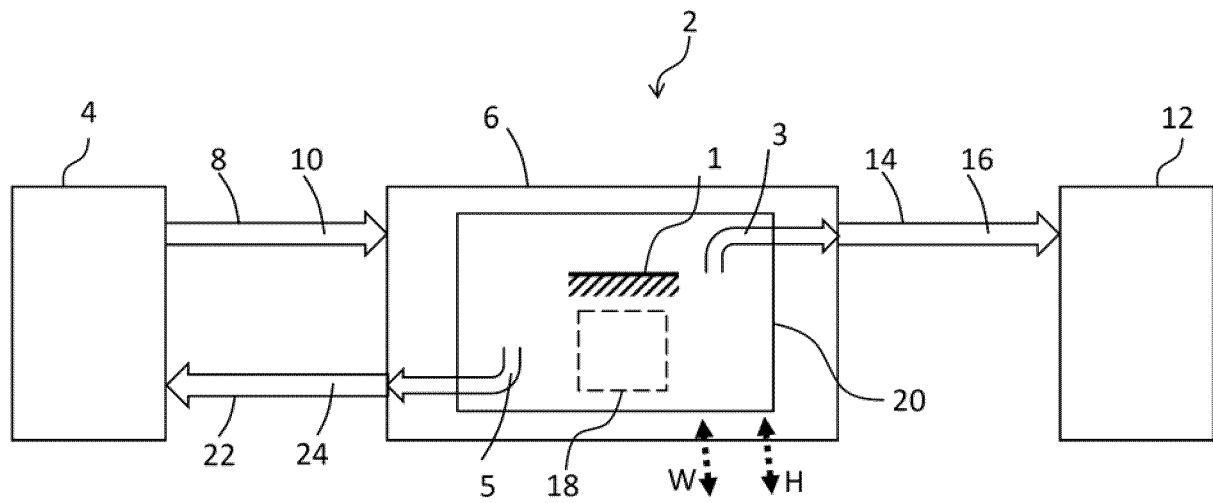


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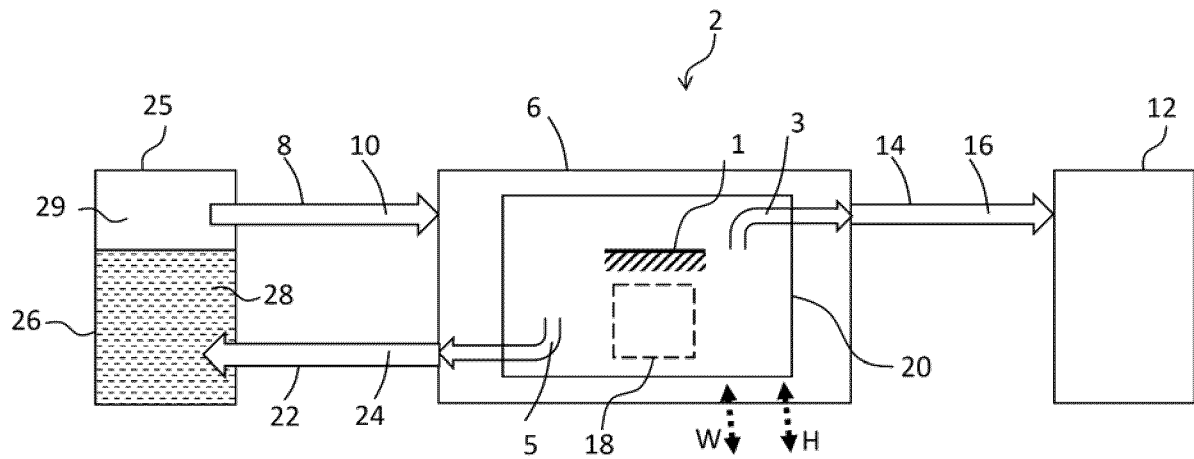


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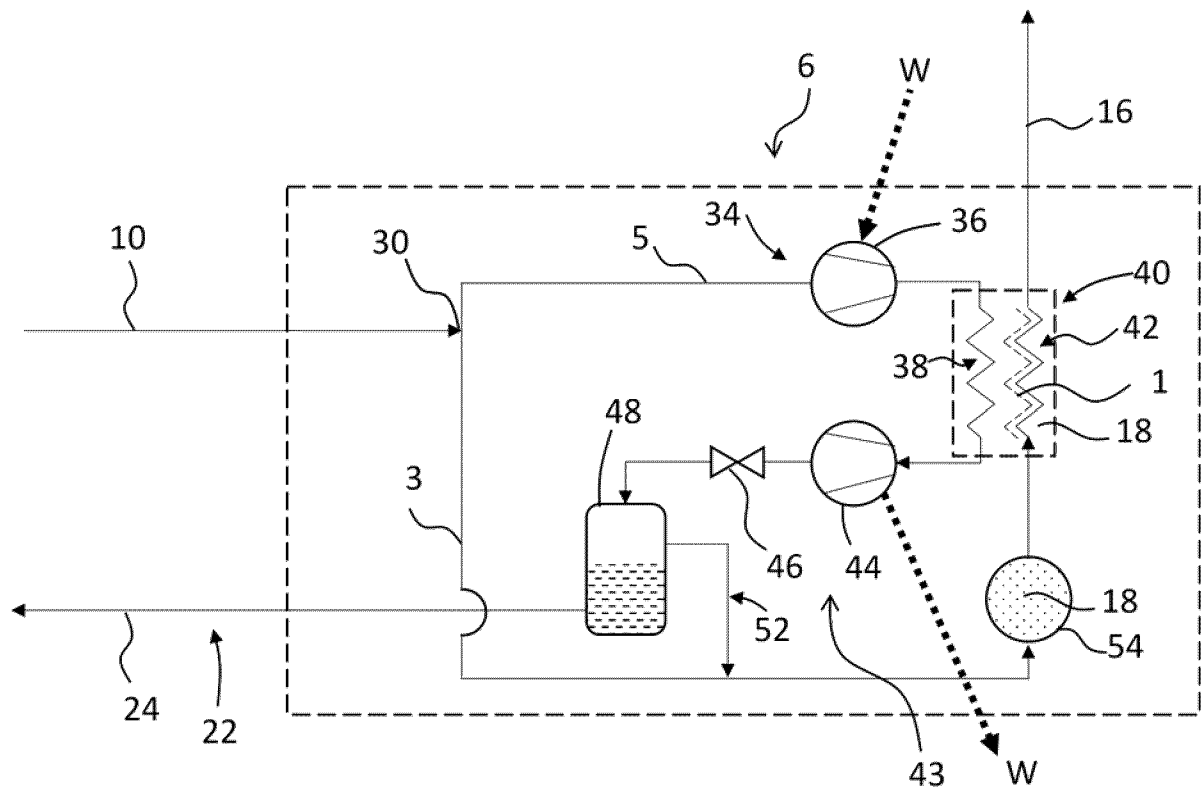


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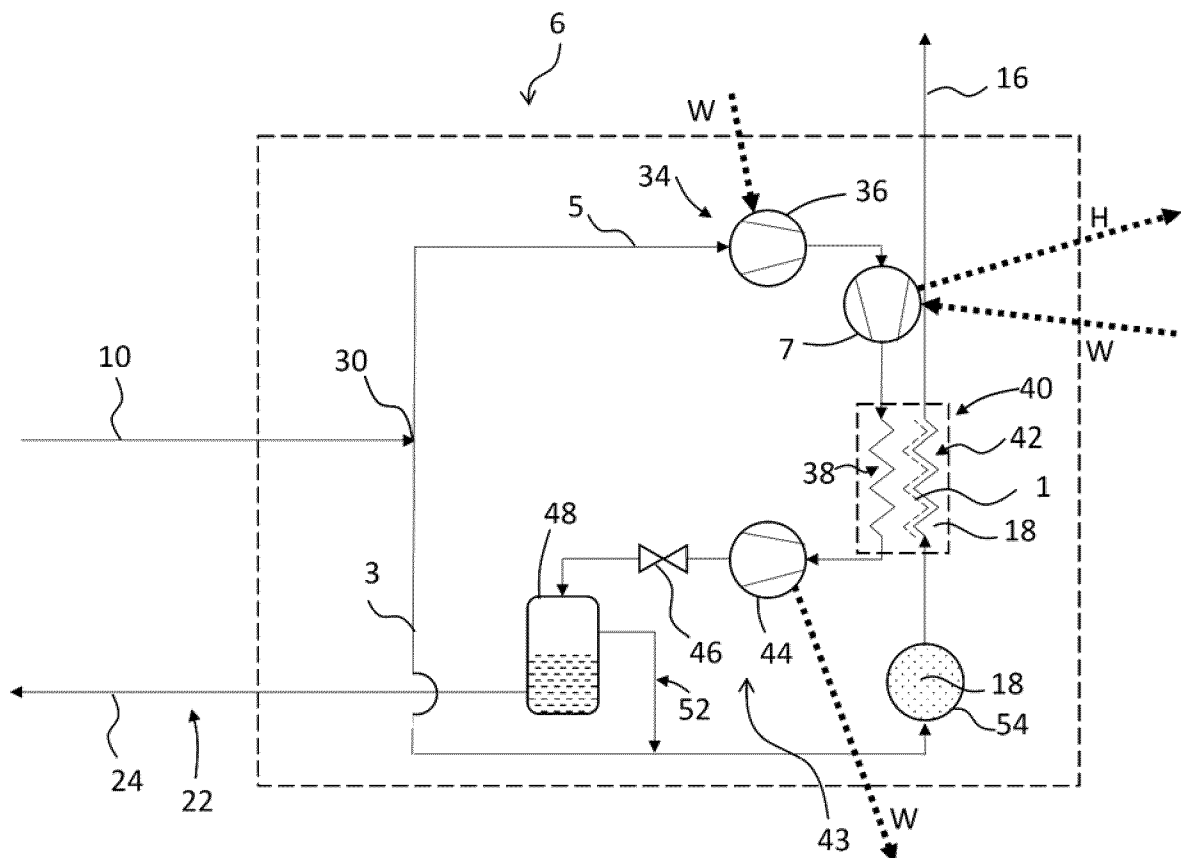


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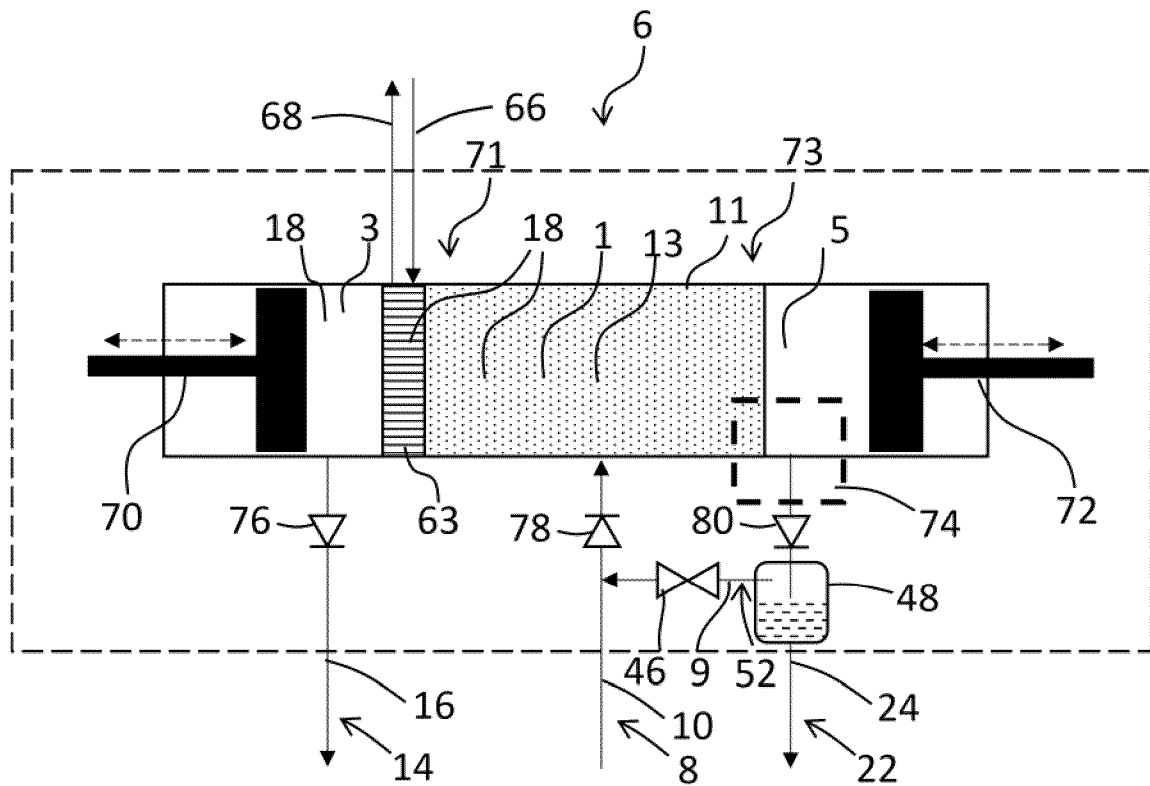


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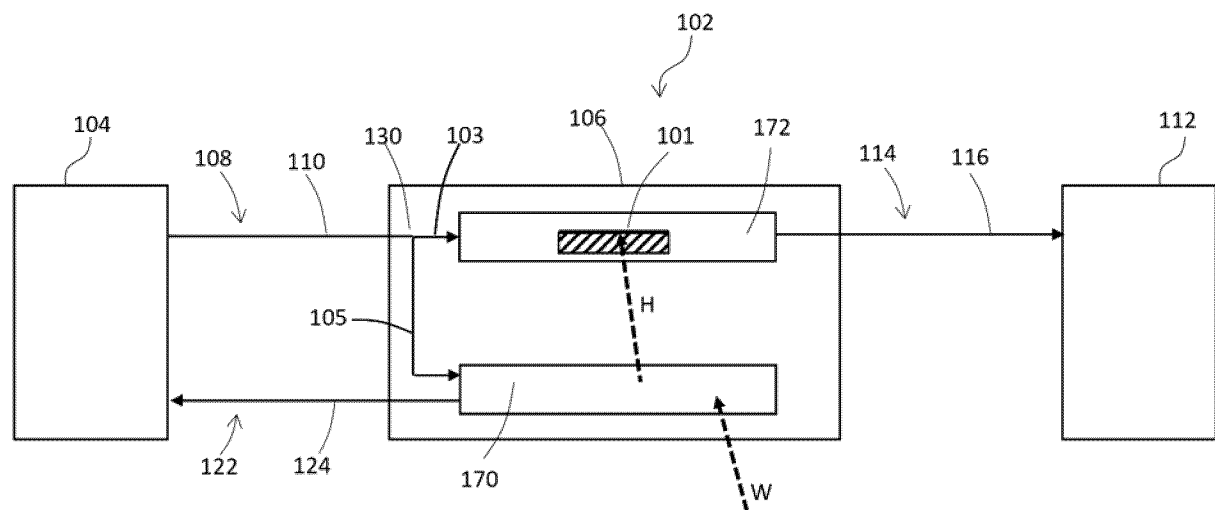


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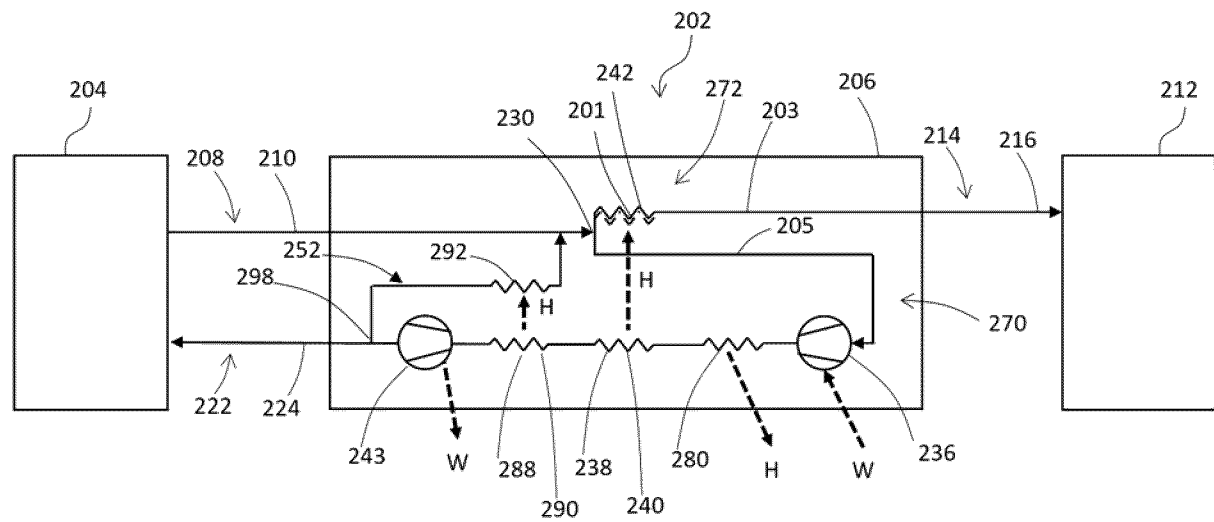


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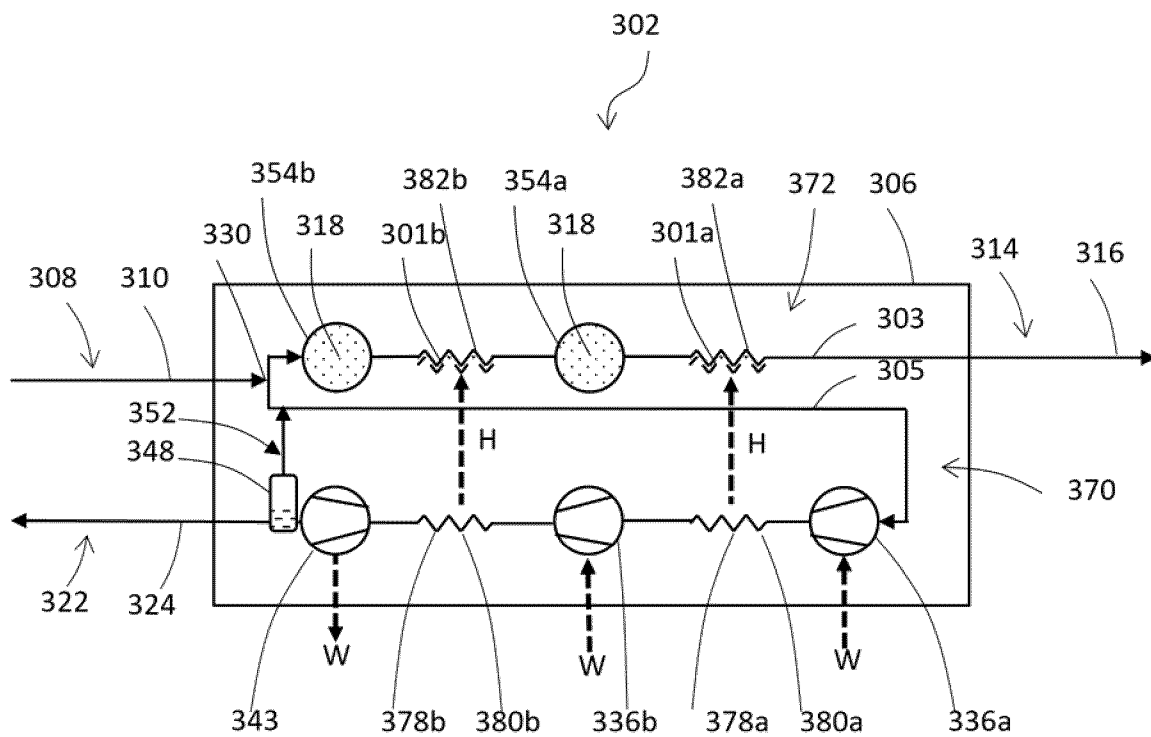


Figure 10

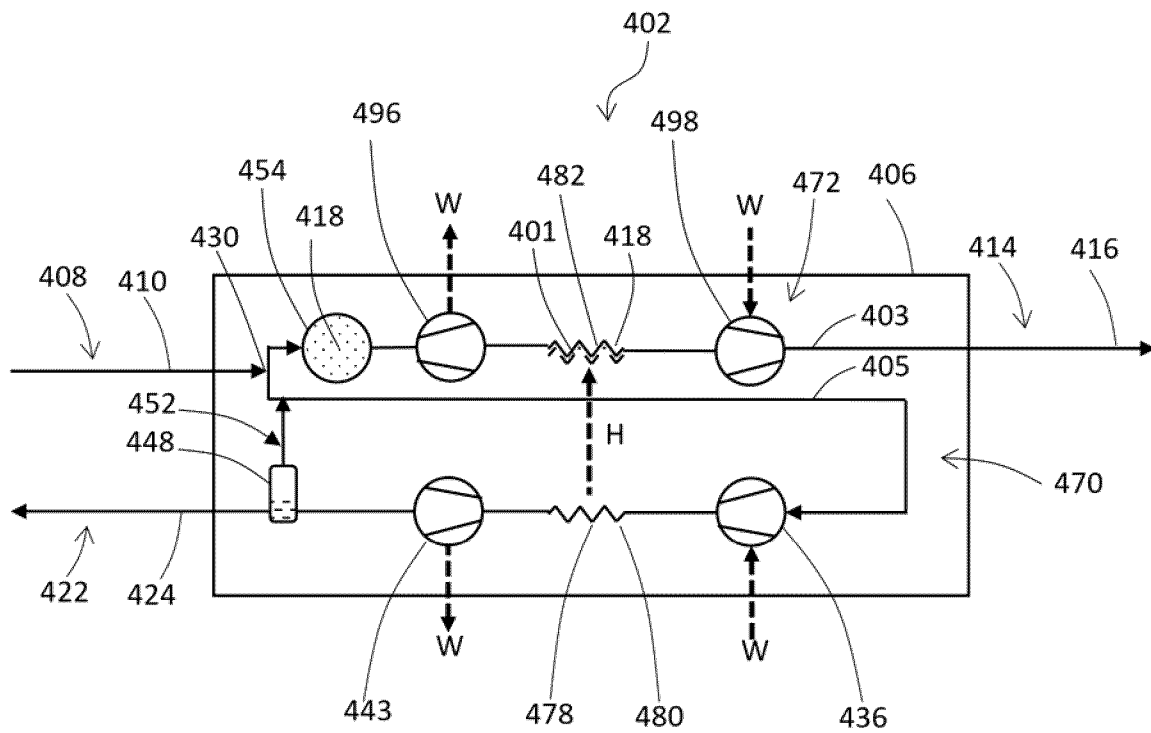


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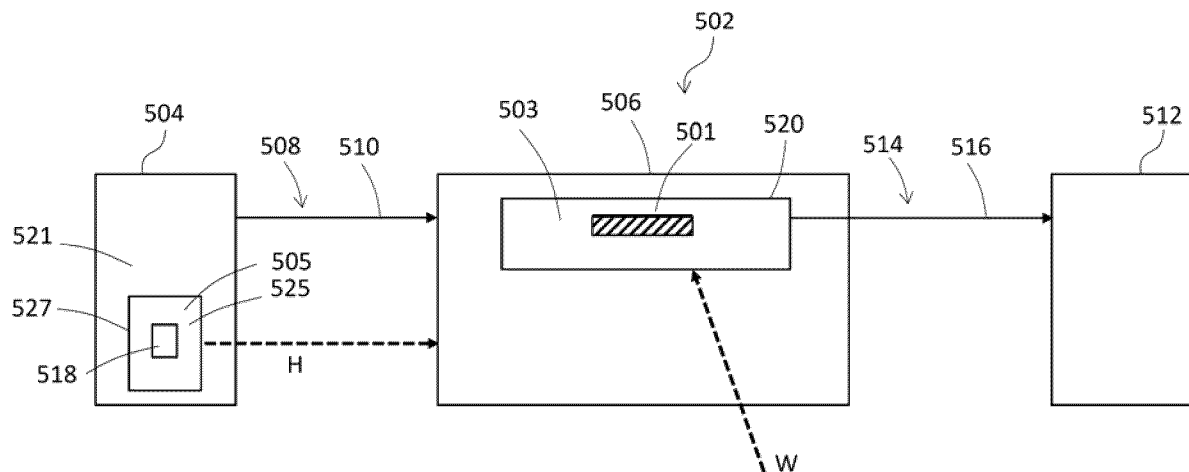


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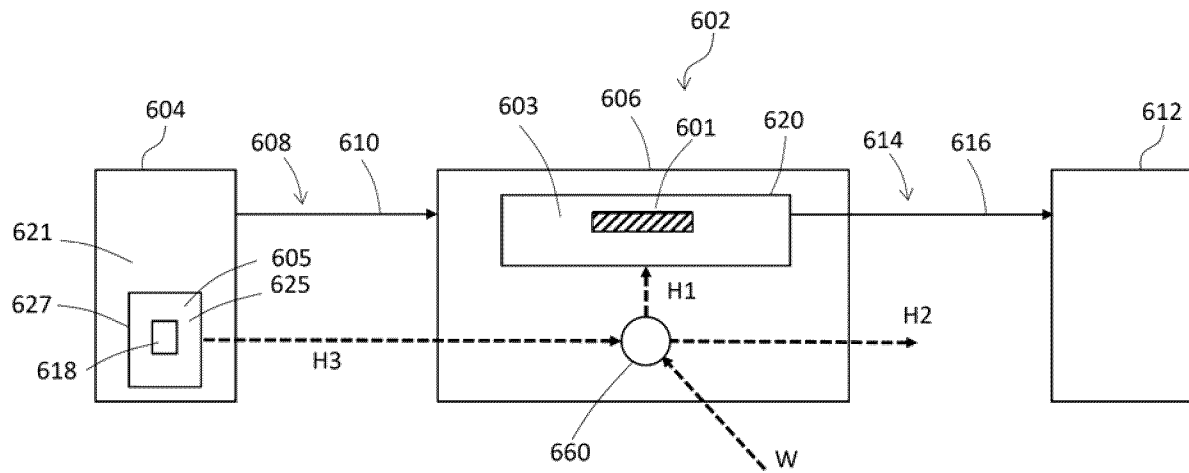


Figure 13:

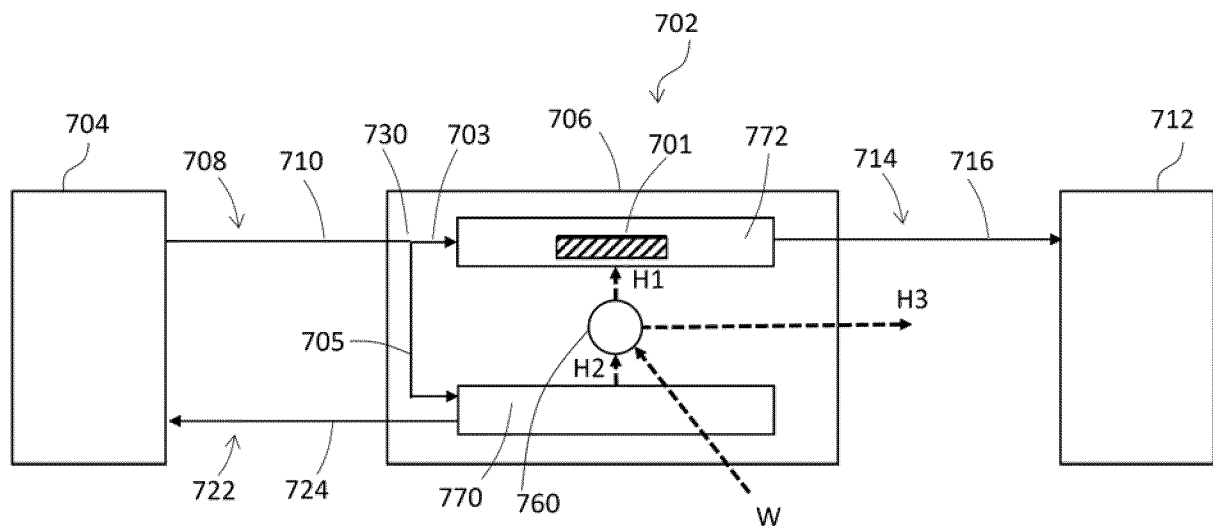


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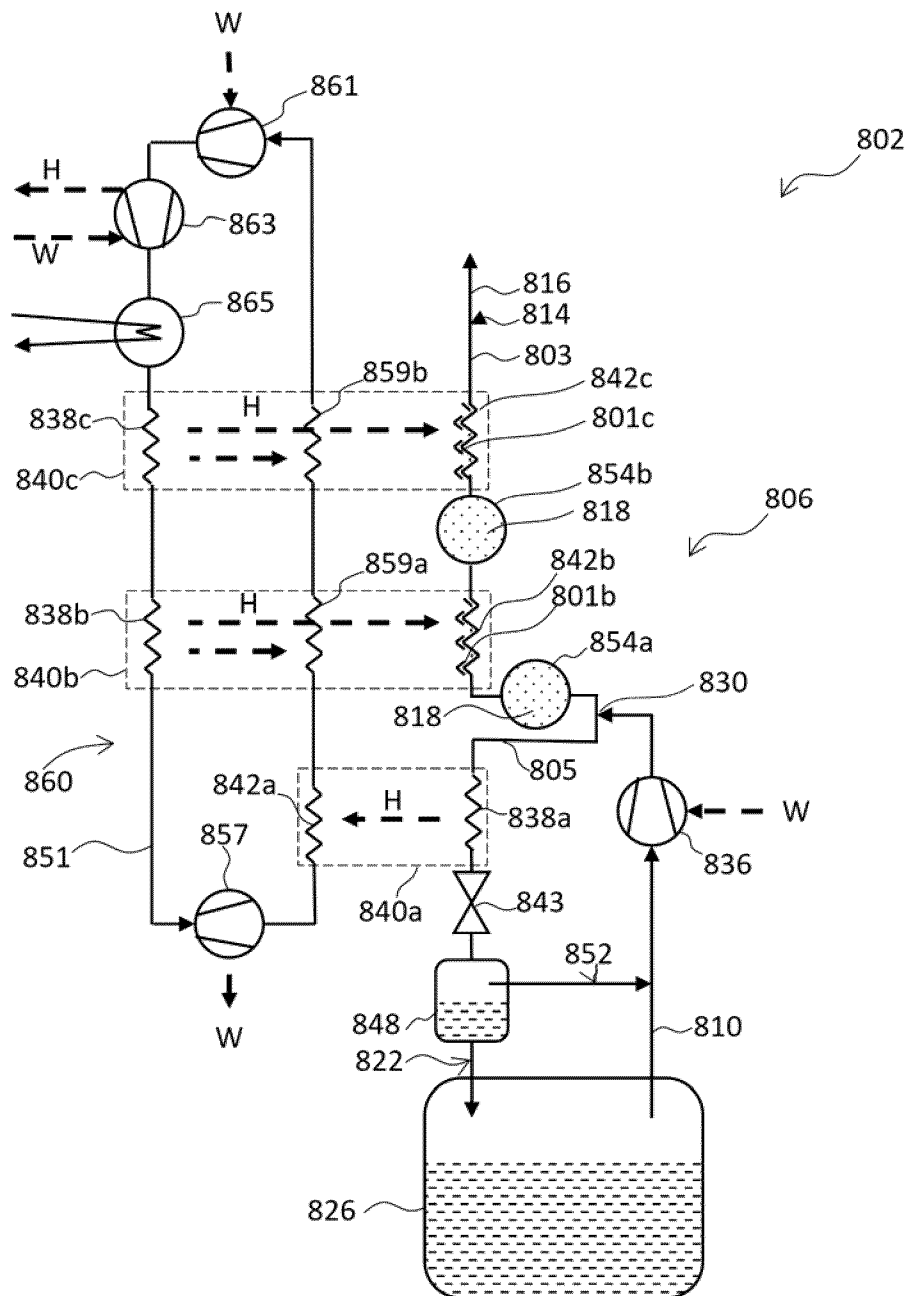


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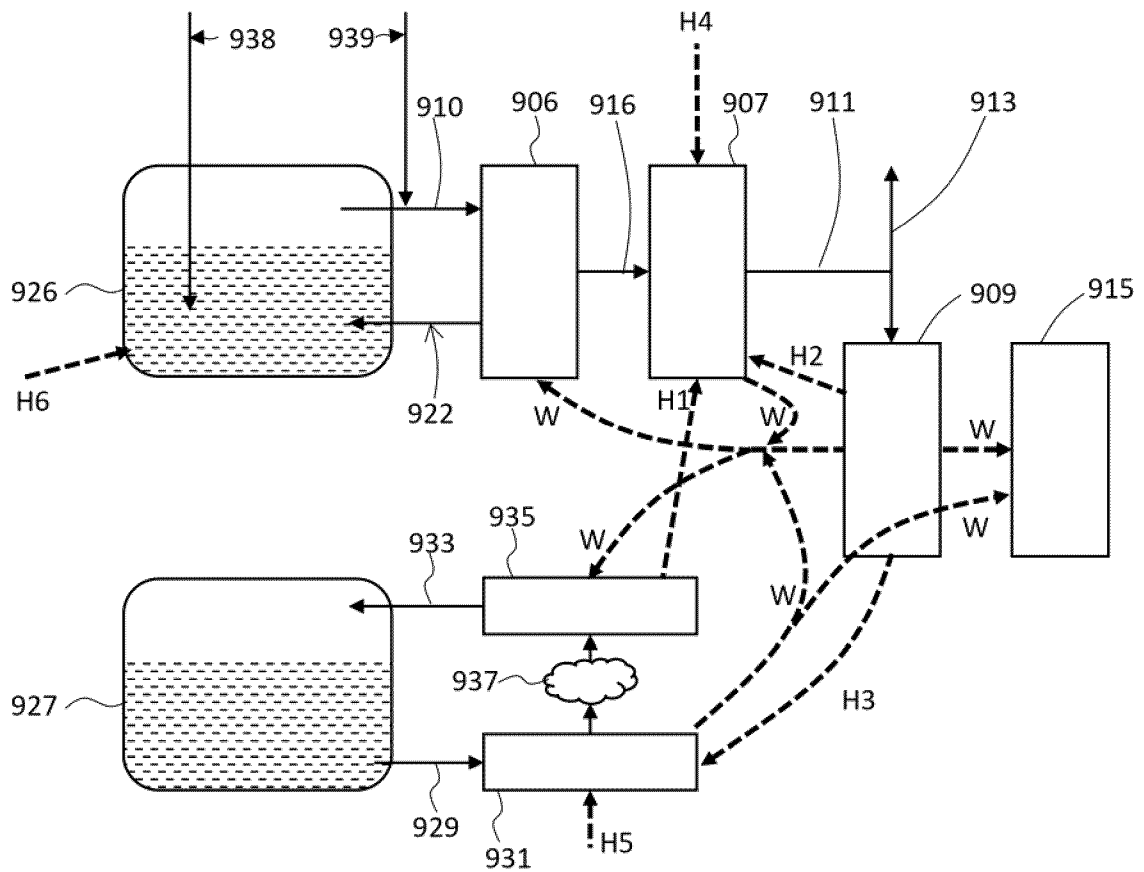


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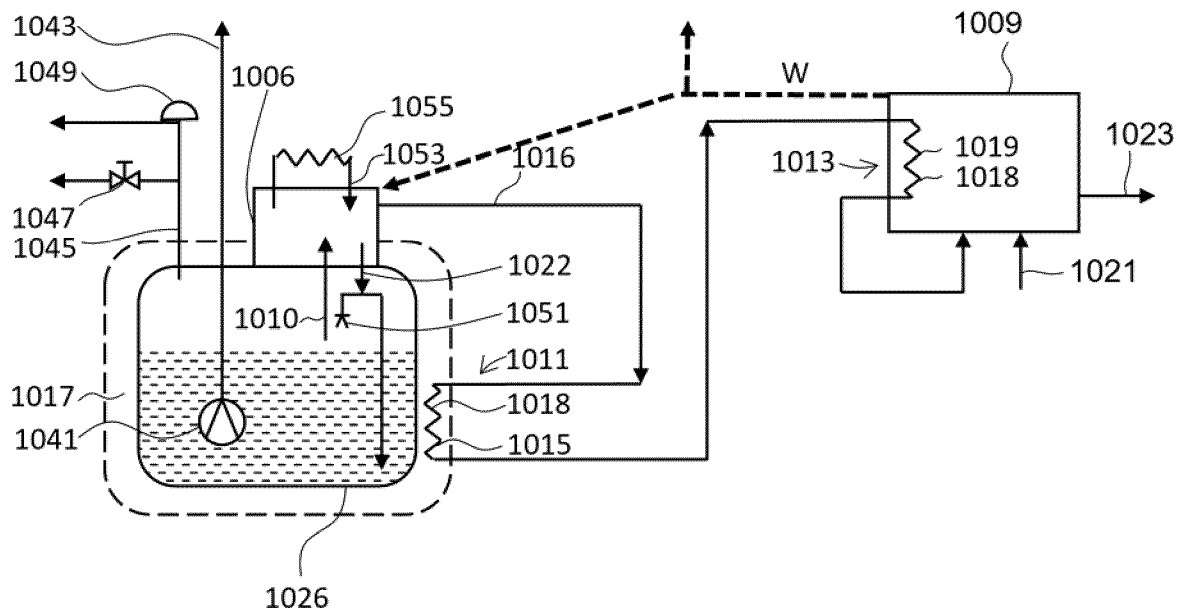


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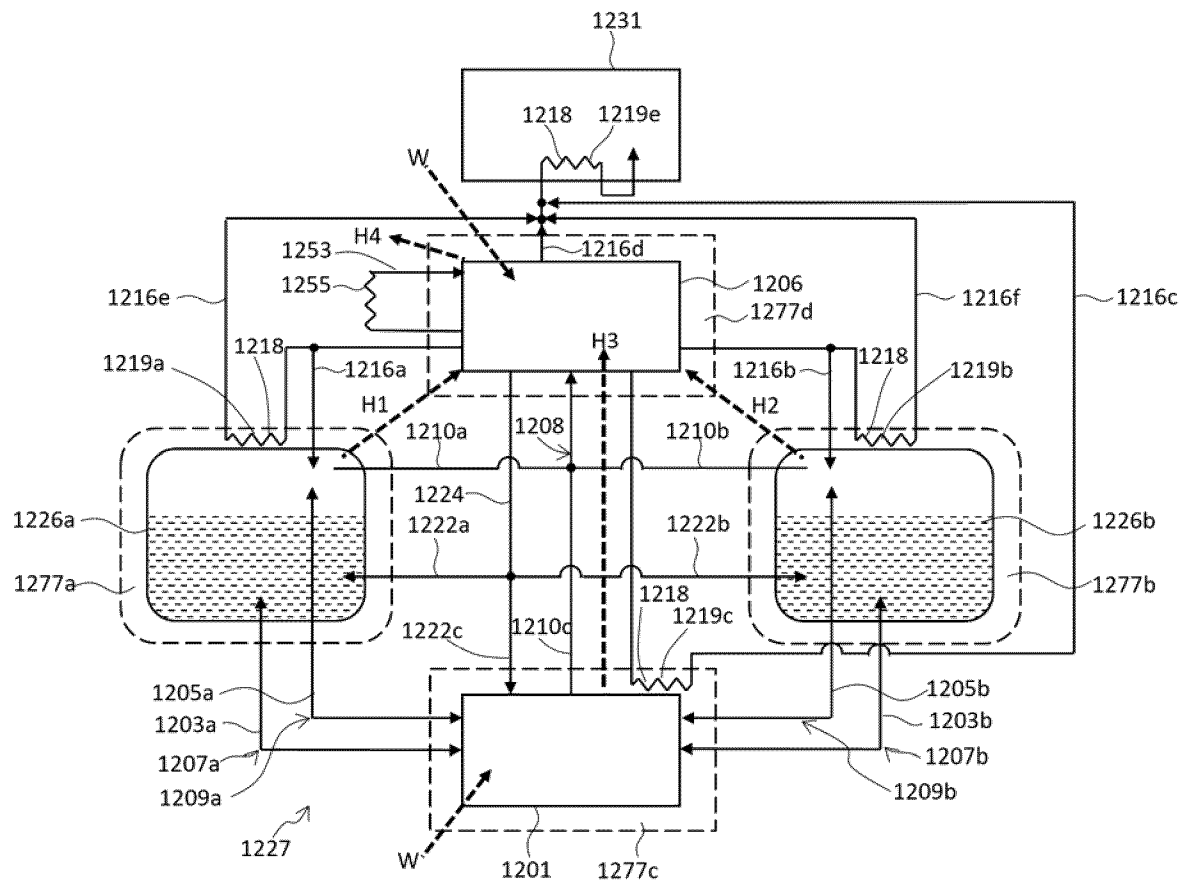


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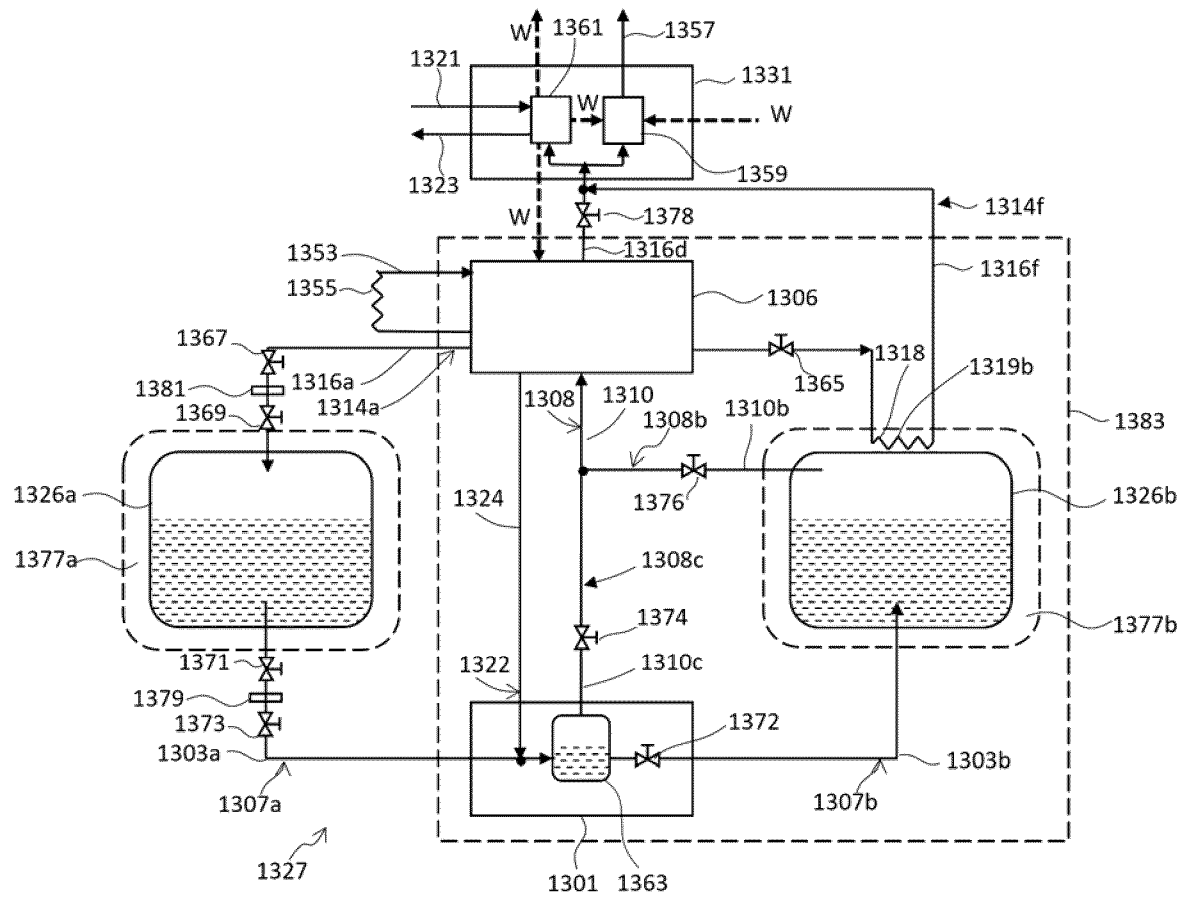


Figure 19:

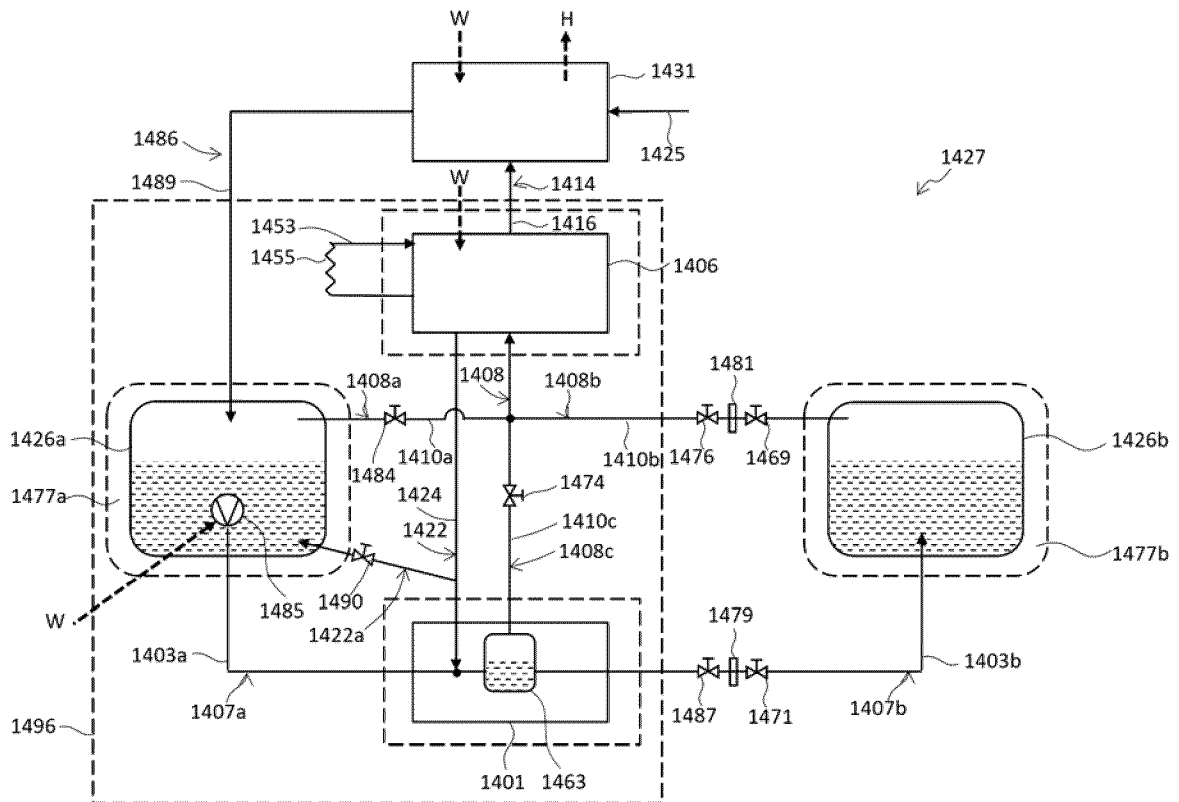


Figure 20:

