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(54) Title: HANDLING LIQUID HYDROCARBON

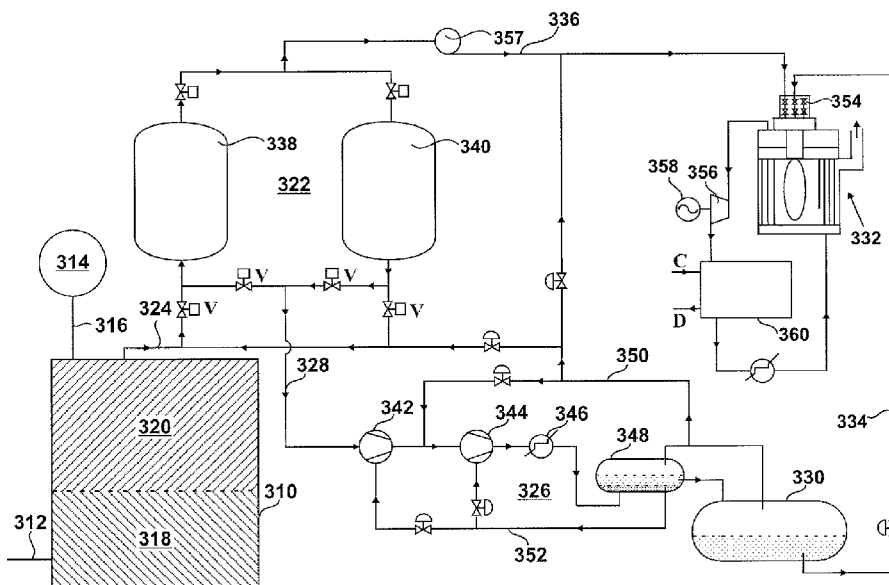


Fig 3

(57) Abstract: Crude oil is loaded into a tank and subsequently offloaded. During offloading, the tank is backfilled with inert blanket gas from a blanketing system. During loading, vent gas comprising a mixture of blanket gas with VOC vapor is vented from the tank. The vent gas is delivered to an activated carbon absorptive vapor recovery unit to capture VOC vapor from the vent gas. VOC vapor captured is then stripped, liquified and delivered to a liquid VOC store. Liquid VOC from the liquid VOC store is delivered as fuel to a combustion plant that produces steam to generate electricity and desalinate water.

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## HANDLING LIQUID HYDROCARBON

### FIELD OF THE INVENTION

**[0001]** This invention relates to the handling of liquid hydrocarbon particularly but not necessarily crude oil, in land-based facilities, or in marine facilities on oil tankers or floating storage and offloading (FSO) vessels or floating production storage and offloading (FPSO) vessels, or in refineries or in other plant producing or using liquid hydrocarbon.

### BACKGROUND OF THE INVENTION

**[0002]** Oil and other volatile liquid hydrocarbon, especially when it is agitated e.g., during loading into a tank or subject to the movement of a tanker at sea, gives off a variety of volatile organic compounds, commonly called VOC.

**[0003]** The amount of VOC released from storage and loading operations worldwide is estimated at more than  $3 \times 10^9 \text{ m}^3$  per annum, and its release gives rise to five notable problems. First, it represents a resource which should not be wasted: equivalent to more than  $5 \times 10^6 \text{ m}^3$  per annum of liquid crude oil or, otherwise expressed, at as much as 0.15% of any consignment. Second, VOC escaping into the atmosphere is environmentally damaging because they result in an atmospheric photochemical reaction that produces harmful ozone: methane is especially damaging as a greenhouse gas, possibly 20 or more times as damaging as carbon dioxide. Third, the volatility of these compounds means there is a risk of fire or explosion in the presence of air: to counter this, oil in storage tanks is routinely blanketed with an inert gas which excludes air. Fourth, the VOC commonly carries toxic contaminants such as hydrogen sulfide and poisonous compounds. And finally, inasmuch as VOC is heavier than air, any discharge to atmosphere from cargo tank vents tends to settle downwards and can trigger gas-sensing alarms at the facility (resulting in the expense of shut-down and evacuation) and/or carry problematic particulate matter into air intakes of machinery.

**[0004]** The containment of VOC is a particular problem when an oil storage tank is being loaded. As the oil is loaded into the tank, the inert blanket gas is displaced, mixed with VOC given off by the oil. The mixture is known as vent gas, and those skilled in the art will appreciate that evaporation of the oil during loading means that (a) the proportion of VOC in the vent gas increases as loading proceeds and (b) that the volume of vent gas is actually greater than that of the loaded oil (typically by a growth factor of 10-25%).

[0005] For the avoidance of uncertainty it should be noted at this point that the term “gas” as used herein is intended to include vapor, and the term “gaseous” is to be interpreted accordingly.

[0006] Attempts to recover VOC go back at least 90 years, to 1922, when US 1,490,782 described an arrangement in which refrigerant was circulated around a container in the upper part of an oil storage tank to condense and collect the vapor accumulating there. Various other arrangements were proposed over the years, and in 2001, US 7,032,390 described a VOC recovery system for use during loading of a tanker in which the displaced vent gas is compressed and collected in a condensate tank, VOC condensate drawn from the tank is used to fuel a boiler, and steam from the boiler is used to drive the compressors of the recovery system.

[0007] There is a significant drawback in the arrangement proposed in US 7,032,390. It requires compression of all the vent gas whereas the VOC may be less than 20% of that. Therefore the compressor is over-dimensioned in both capacity and power and inefficient in relation to compressing the VOC. In short, recovering VOC present in vent gas by compressing all the vent gas is needlessly expensive.

[0008] It is an object of the present invention to recover VOC from vent gas more cheaply and efficiently.

#### SUMMARY OF THE INVENTION

[0009] Thus according to a first aspect of the invention there is provided a method of handling liquid hydrocarbon in which the liquid hydrocarbon is loaded into a tank and subsequently offloaded from the tank, the tank being backfilled with inert blanket gas during offloading and vent gas comprising a mixture of blanket gas with VOC vapor being vented from the tank during loading, wherein:

[0010] (a) the vent gas is delivered to a vapor recovery unit operative by means of adsorption to capture VOC vapor from said mixture;

[0011] (b) VOC vapor captured by the vapor recovery unit is liquefied and delivered to a liquid VOC store; and

[0012] (c) liquid VOC from the liquid VOC store is delivered as fuel to a combustion plant.

[0013] For the avoidance of doubt it should be noted that the term “combustion plant” as used above and elsewhere herein should be deemed to include any exothermic apparatus in which fuel is burned to produce useful heat.

[0014] The use of adsorption in the vapor recovery unit means that the VOC vapor is captured without the need for compressing the vent gas: more particularly, gas other than VOC does not have to be compressed. Thus preferably the vent gas is delivered uncompressed to the vapor recovery unit and captured VOC vapor is liquefied downstream of the vapor recovery unit, and the VOC vapor captured in the vapor recovery unit may be compressed before delivery to the liquid VOC store. By this means only the captured VOC vapor is compressed, in contrast with the arrangement proposed in US 7,032,390, and so the invention provides a substantial saving in both compressor size and cost.

[0015] Weak gas consisting of the residue of the vent gas after capture of VOC vapor therefrom in the vapor recovery unit may be delivered as fuel to the combustion plant.

[0016] The combustion plant may conveniently produce steam that can be used for a variety of purposes including powering an electrical generator (electricity from which may be sold, at least from land-based facilities, as an added value by-product) and to operate a desalination plant (clean/potable water from which may also be sold as an added value by-product).

[0017] It is preferred that, after the tank is loaded, the vapor recovery unit is inoperative and only liquid VOC from the liquid VOC store fuels the combustion plant.

[0018] Exhaust gas from the combustion plant may be used as said inert blanket gas backfilling the tank during offloading.

[0019] Liquid hydrocarbon being loaded or off loaded or in the tank may be supplemented with liquid VOC from the liquid VOC store, so as to maximize the value of the load.

[0020] According to a second aspect the invention provides apparatus for handling liquid hydrocarbon comprising:

[0021] (a) a tank into which the liquid hydrocarbon is loaded by way of a delivery line and from which it is subsequently offloaded by way of an offloading line;

[0022] (b) a blanketing system connected to the tank by way of a blanket line and operative during offloading to backfill the tank with inert blanket gas;

[0023] (c) a vapor recovery unit connected to the tank by way of a vent line to receive therefrom vent gas displaced from the tank during loading, the vent gas comprising a mixture of blanket gas and VOC vapor and the vapor recovery unit being operative by means of adsorption to capture VOC vapor from the vent gas;

[0024] (d) a liquefaction system connected to the vapor recovery unit by way of a recovery line to receive and liquefy VOC vapor captured by the vapor recovery unit;

[0025] (e) a liquid VOC store connected to the liquefaction system to receive liquefied VOC therefrom; and

[0026] (f) a combustion plant connected to the liquid VOC store by way of a primary fuel line and thereby fuelled by liquid VOC from the liquid VOC store.

[0027] As in the method set forth above, capturing the VOC content of the vent gas by adsorption is more efficient than heretofore inasmuch as it is not necessary to compress all the vent gas.

[0028] To maximize this advantage it is preferred that the vapor recovery unit captures the VOC vapor without compressing said mixture.

[0029] The vapor recovery unit may comprise an adsorption system operative to capture the VOC vapor and comprising at least two adsorption vessels each packed with activated carbon to capture the VOC vapor and control means operative to open the vessels to the vent line alternately to receive the vent gas from the tank during loading. The vapor recovery unit may further comprise a regeneration system operative under the control means to strip off the captured VOC vapor from the adsorption vessels alternately, which regeneration system comprises a vacuum pump.

[0030] The recovery line may include:

[0031] (a) a compressor downstream of the vacuum pump, which compressor is operative to compress the VOC vapor stripped off thereby;

[0032] (b) a condenser downstream of the compressor, which condenser is operative to condense the compressed VOC vapor;

[0033] (c) a separator configured and arranged to separate the condensed VOC from any uncondensed VOC; and

[0034] (d) a gas return line configured and arranged to return uncondensed VOC in the separator to a point in the recovery line upstream of the compressor.

[0035] The vacuum pump and the compressor may each be liquid ring machines sealed with seal fluid, the separator may be configured and arranged to separate any seal fluid from the condensed hydrocarbon vapor and the apparatus may comprise a seal fluid return line configured and arranged to return seal fluid from the separator to the vacuum pump and the compressor.

[0036] Preferably the vapor recovery unit is connected to the combustion plant by way of a secondary fuel line, possibly including a gas blower, whereby weak gas comprising the residue of said mixture after capture of VOC vapor in the vapor recovery unit is delivered as fuel to the combustion plant.

[0037] Preferably the combustion plant comprises a burner system including a primary fuel inlet open to the primary fuel line to receive thereby liquid VOC from the liquid VOC store, a secondary fuel inlet open to the secondary fuel line to receive thereby weak gas from the vapor recovery unit, a combustion air supply and burner control means operative automatically to adjust the delivery of liquid VOC and weak gas according to the Wobbe Index and flow rate thereof. The burner system is preferably operative to burn both the liquid VOC and the weak gas during loading and otherwise to burn only the liquid VOC.

[0038] The combustion plant may be connected to the tank by way of a blanket line, whereby exhaust from the combustion plant is delivered to the tank as blanket gas backfilling the tank during offloading.

[0039] The apparatus may include a cargo supplement line extending from the liquid VOC store to supplement liquid hydrocarbon stored in the tank or being loaded into or offloaded from the tank.

[0040] The combustion plant may comprise a steam boiler, and in addition a variety of units may be powered or operated by the steam including an electrical generator, a desalination plant, a cargo pump for offloading liquid hydrocarbon from the tank, which cargo pump is powered by steam from the boiler, and a cargo heater in the tank.

[0041] The invention will now be described by way of example only with reference to the accompany drawings, which are purely schematic and not to scale.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0042] FIG. 1 illustrates emission of vent gas from a tank being loaded with crude oil;

[0043] FIG. 2 illustrates graphically variation of vent gas composition as loading of the tank continues;

[0044] FIG. 3 illustrates a system embodying the present invention for capturing and utilizing VOC in the vent gas;

[0045] FIG. 4 illustrates an adaptation of the system of FIG. 3 for marine use, shown during loading;

[0046] FIG. 5 illustrates an adaptation of the system of FIG. 4 in which captured VOC supplements oil being offloaded;

[0047] FIG. 6 illustrates an adaptation of the system of FIG. 4 in which captured VOC supplements oil being loaded;

[0048] FIG. 7 illustrates in more detail the means whereby liquid VOC is added to oil being offloaded;

[0049] FIG. 8 illustrates means whereby liquid VOC is added to oil being loaded; and

[0050] FIG. 9 illustrates means whereby liquid VOC is added to stored oil.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[0051] Referring first to FIG. 1, this shows an oil tank 110. For purposes of illustration the tank 110 will be regarded as being a cargo tank of a seagoing oil tanker being loaded with heavy crude oil from an FSO. However the tank 110 may be an oil storage tank on an FSO or FPSO or in a land-based facility or in a refinery or other plant producing or using liquid hydrocarbon. It is also to be understood that, rather than heavy crude oil, a tank such as the tank 110 may be loaded with lighter crude or refined oil or other liquid hydrocarbon.

[0052] The tank 110 is being loaded with crude oil from the FSO (not shown) by way of a delivery line 112, and within the tank 110 the crude oil 114 is covered with an inert gas blanket 116 in conventional fashion. (The blanket gas typically contains some VOC left over from previous cargoes, but it will still be deemed “inert” within the meaning of the 1974 International Convention on the Safety of Life at Sea (*SOLAS*) which requires in Regulation 62 an inert gas system ‘capable of providing on demand a gas or mixture of gases to the cargo tanks so deficient in oxygen that the atmosphere within a tank may be rendered inert, i.e., incapable of propagating flame.’ Similarly, whilst the blanket gas picks up VOC from the present cargo as described below, it remains “inert” in relation to *SOLAS*.)

[0053] In FIG. 1 the transfer of VOC from the oil 114 to the blanket 116 is illustrated by arrows A. The VOC (including methane and usually in association with hydrogen sulfide) evaporates and diffuses from the surface of the oil 114. In addition, low pressure in the delivery line causes VOC to flash off from the oil as it is loaded.

**[0054]** As loading continues, the level of the oil 114 in the tank 110 rises and thus displaces vent gas comprising a mixture of blanket gas and VOC into a vent riser 118, as indicated by arrow B. The volume of vent gas is greater than that of the incoming oil because evaporation of the oil adds vapor to the vent gas. (For the avoidance of uncertainty it should be remarked here, as noted earlier, that the term “gas” is used in the present application to include vapor). Typically the so-called “growth factor” is 10-25%, but it may be substantially higher: for instance, if oil 114 is loaded at a rate of 8000 m<sup>3</sup>/hr, the vent gas may comprise 8000 m<sup>3</sup>/hr displaced volume plus 8000 m<sup>3</sup>/hr VOC evaporation, i.e., a total of 16000 m<sup>3</sup>/hr.

**[0055]** Both flow rate and composition of the vent gas change as loading proceeds. This is graphically illustrated by FIG. 2, in which volumetric flow F through the vent riser is plotted against time T. When the oil 114 first begins to enter the tank 110 (FIG. 1) the total volumetric flow F of vent gas through the vent riser is high, but it decreases over time T as indicated by the line 210. When the oil 114 first begins to enter the tank 110, at time 202, most of the vent gas is inert gas 212, and the proportion of VOC 214 in the vent gas is low; but the proportion of VOC in the vent gas increases over time T until, towards the end of loading at time 204, the vent gas is saturated with VOC.

**[0056]** Generally, for environmental, regulatory and economic reasons, the vent gas cannot be discharged to atmosphere, and FIG. 3 shows how the present invention manages vent gas.

**[0057]** Referring then to FIG. 3, this shows a tank 310 in a land-based facility, into which tank 310 oil or other liquid hydrocarbon is loaded by way of a delivery line 312. A blanketing system 314 connected to the tank 310 by way of a blanket line 316 is operative during offloading to backfill the tank 310 with inert blanket gas, and thus the oil 318 in the tank is overlaid by a mixture 320 of blanket gas and VOC. A vapor recovery unit indicated at 322 is connected to the tank 310 by way of a vent line 324 so as to receive vent gas mixture displaced from the tank 310 during loading. As will be described in more detail later, the vapor recovery unit 322 is operative by means of adsorption to capture VOC vapor from the vent gas mixture.

**[0058]** A liquefaction system indicated at 326 is connected to the vapor recovery unit 322 by way of a regeneration line 328 to receive and liquefy VOC vapor captured by the vapor recovery unit 322. A liquid VOC store 330 is connected to the liquefaction system 326 to receive the liquefied VOC vapor.

[0059] A combustion plant indicated at 332 is connected to the liquid VOC store 330 by way of a primary fuel line 334, which delivers liquid VOC to the combustion plant 332 as fuel. The combustion plant 332 is also connected to the vapor recovery unit 322 by a secondary fuel line 336.

[0060] The construction and operation of the vapor recovery unit 322 will now be described.

[0061] The vapor recovery unit 322 comprises two adsorption vessels 338 and 340 each of which is packed with activated carbon. The two adsorbers 338 and 340 are identical and are controlled by control means comprising a set of automatic valves V to operate alternately, so that one is on-stream in adsorption mode while the other is in regeneration mode, and vice versa. When the adsorber 338 is on-stream it receives from the vent line 324 an upward flow of vent gas comprising a mixture of inert gas and VOC vapor. Substantially all the NMVOC vapor in this mixture is adsorbed by the activated carbon, leaving residual weak gas (inert gas with methane and some ethane, plus hydrogen sulfide) to be discharged into the secondary fuel line 336. (In relation to the foregoing statement that substantially all the NMVOC vapor is captured, it may be noted here for the avoidance of doubt that the adsorbers 338 and 340 capture little methane. However the adsorbers 338 and 340 capture VOC in a general sense, and this term is used elsewhere herein). At the same time, the adsorber 340 is in the regeneration mode in which VOC vapor previously adsorbed by the adsorber 340 is stripped off by means of a regeneration system operating in association with the valves V and comprising a vacuum pump 342.

[0062] It will be noted that the vapor recovery unit 322 captures the VOC vapor in the vent gas without compressing the mixture.

[0063] The stripped-off VOC vapor is liquefied by the liquefaction system 326, as will now be described.

[0064] The liquefaction system 326 comprises a liquid ring compressor 344 downstream of the vacuum pump 342 and operative to compress the VOC vapor stripped off by the vacuum pump 342. A condenser 346 such as a mechanical refrigeration condenser is arranged downstream of the compressor 344 to condense the compressed VOC vapor. Downstream of the condenser 346 is a three-phase separator 348 configured and arranged to separate the condensed VOC from any uncondensed VOC, and a gas return line 350 is configured and arranged to return uncondensed VOC vapor in the separator 348 (a) to a point upstream of the

compressor 344 and optionally also to (b) the vapor recovery unit 322 for re-adsorption and (c) the secondary fuel line 336 to supplement the weak gas as fuel for the combustion plant 332.

**[0065]** The vacuum pump 342 and the compressor 344 are each liquid ring machines (although those skilled in the art will appreciate that other forms of machine may be used, such as screws or sliding vane machines). The liquid ring vacuum pump 342 and the compressor 344 are each sealed with seal fluid comprising a specially blended ethylene glycol-based sealing fluid. The three-phase separator 348 receives this fluid mixed with the VOC condensate and non-condensed VOC vapor and separates out the sealing fluid as well as separating the VOC condensate from any non-condensed VOC. From the separator 348, the VOC condensate is passed to the store 330 for storage, non-condensed VOC is sent back to the on-stream absorber 338/340 and the sealing fluid is cooled and returned to the vacuum pump 342 and the compressor 344 by way of line 352.

**[0066]** The combustion plant 332 comprises a steam boiler equipped with a dual-fuel burner 354 enabling it to be fuelled with both liquid VOC (delivered from the store 330 by way of the primary fuel line 334) and weak gas (delivered from the vapor recovery unit 332 by way of the secondary fuel line 336, through which the weak gas is blown by a gas blower 357). The burner 354 is of the kind described in WO 2011/092450 and comprises: a primary fuel inlet open to the primary fuel line 334 to receive thereby liquid VOC from the liquid VOC store 330; a secondary fuel inlet open to the secondary fuel line 336 to receive thereby weak gas from the vapor recovery unit 322 (the weak gas comprising inert gas, some methane and ethane and, depending upon the source of the oil, probably some hydrogen sulfide) a combustion air supply (not detailed in FIG. 3); and burner control means operative automatically to adjust the delivery of liquid VOC and weak gas according to Wobbe Index and flow rate. (The Wobbe Index is a measure of the calorific value or "heating content" of a fuel and various known meters are known for determining this. Thus the amounts of liquid VOC and weak gas can be relatively adjusted, to maintain effective combustion and to ensure incineration of hydrogen sulfide in the weak gas).

**[0067]** Steam produced by the combustion plant is expanded through a steam turbine 356 to drive an electrical generator 358, electricity from which can be used to run the system and/or sold to third parties as an added value by-product.

[0068] Downstream of the turbine 356 the steam is fed to an evaporator 360 of a desalination system receiving sea water at C and outputting fresh water at D, which fresh water can like the electricity be sold as an added value by-product. And steam/water leaving the evaporator 360 is returned to the boiler of the combustion plant 332.

[0069] After loading of the oil tank 310 is complete, the vapor recovery unit 322 is inoperative and the boiler of the combustion plant 332 is then fired using only liquid VOC from the store 330 to produce steam to generate electricity and fresh water for export locally.

[0070] Those skilled in the art will appreciate that land-based facilities of the kind described above in relation to FIG. 3 have more potential than marine facilities to sell electricity and fresh water because (a) they are generally larger and therefore give rise to more usable VOC and (b) on land it is much easier to construct a distribution infrastructure. Nevertheless the invention has significant additional benefits in marine applications, as will now be described.

[0071] FIGS. 4 and 5 (which have reference numbers in common) show a marine adaptation of the invention in which a system like that of FIG. 3 is adapted for mounting in or on a marine vessel indicated at 410. In this adaptation the system captures VOC, stores it in liquid form in a VOC store as described above in relation to FIG. 3 and uses it for a variety of purposes including electrical power generation. And as in FIG. 3 combustion of the weak gas stream prevents emissions to atmosphere and also reduces the cost of fuelling the boiler. Differences from the system of FIG. 3 will be apparent from the following description.

[0072] The vessel 410 is equipped with tanks 412, comprising a number of tanks such as tank 413, into which oil 414 is loaded by way of a delivery line 416 and covered with blanket gas 418. As the oil 414 is loaded into the tanks 412 as depicted in FIG. 4, vent gas comprising a mixture of blanket gas and VOC is displaced into a vent header 420, from where it is delivered to a vapor recovery unit 422 generally of the same form as the unit 322 of FIG. 3 and operative by means of adsorption to capture VOC vapor from the vent gas mixture. A liquefaction system indicated at 424 is connected to the vapor recovery unit 422 to receive and liquefy VOC vapor captured by the vapor recovery unit 422. A liquid VOC store 426 is connected to the liquefaction system 424 to receive the liquefied VOC vapor. A combustion plant indicated at 428 is connected to the liquid VOC store 426 and thereby receives liquid VOC as fuel, indicated by arrow F. The combustion plant 428 is also connected to the vapor recovery unit 422 to receive weak gas as secondary fuel at G. The combustion plant 428 is

furnished with a multifuel burner which can also receive fuel oil at H and fuel gas (if available) at I.

[0073] As in the system of FIG. 3, the combustion plant 428 produces steam driving an electrical generator 430. Electricity from the generator 430 is used to run the system and for other onboard purposes. It is not generally feasible to export electricity from a marine facility, and similarly it may not be feasible to export fresh water, in contrast with the land-based system of FIG. 3. However, in the system of FIGS. 4 and 5, steam from the combustion plant 428 is fed to a heater 432 in the tanks 412, which heater heats the oil 414 to combat waxiness. (Crude oil is commonly waxy, in that at regular temperatures paraffin hydrocarbons and/or naphthenic hydrocarbons contained in the oil tend to solidify and make it difficult to pump the oil. This problem can be overcome by heating the oil).

[0074] As noted, FIG. 4 illustrates the system during the loading of oil into the tanks 412. Turning now to FIG. 5, this illustrates the system while the oil is being off loaded.

[0075] During offloading, steam from the combustion plant 428 is expanded through a turbine 434 to power pump(s) 436 offloading oil from the tanks 412 by way of an offloading line 430. For economic reasons, oil is offloaded from FSO/FPSOs as quickly as possible, and this creates a high demand for steam to drive the offloading pump(s) 436. In the system of FIGS. 4 and 5 this demand is met by using as boiler fuel VOC captured from vent gas released from the tanks 412 as they are loaded (over a comparatively long period). This saves on the conventional and expensive use of fuel oil in the combustion plant 428.

[0076] It is convenient here to note another saving afforded by the invention in relation to FSO/FPSOs. Oil is loaded onto an FSO/FPSO comparatively slowly (in comparison with the offloading rate or with rates for tankers) so the displacement of vent gas is also relatively slow. Accordingly a vapor recovery unit on an FSO/FPSO can be relatively small.

[0077] As the oil is offloaded, the tanks 412 need to be backfilled with inert gas as a blanket, and as shown in FIG. 5 this is provided by exhaust gas from the combustion plant 428 delivered at J into the vent header 420 after treatment (e.g., to dry it and cool it in an inert gas treatment plant 440).

[0078] Fuelling the combustion plant 428 with liquid VOC from the store 426 is particularly advantageous in two ways. First, it is cheaper (being virtually free) than the fuel oil conventionally used. And second, there is little or no sulfur dioxide in the exhaust gas, and accordingly tank corrosion is greatly reduced because sulfuric acid is not produced.

[0079] As shown in FIG. 5, liquid VOC from the store 426 may also be used to supplement oil being offloaded from the tanks 412. Thus there is a supplemental connection 442 between the liquid VOC store 426 (conveniently linked to the fuel line to the combustion plant 428) and the crude oil offloading line 430. Under the control of an isolating valve 444 in the supplemental connection 442, liquid VOC at high pressure is injected at K into the stream of crude oil at low pressure.

[0080] During offloading, the liquid VOC store needs to be emptied to be ready to receive more liquid VOC when the tanks 412 are filled again, and the use of the liquid VOC as fuel F for the combustion plant 428 is a profitable way of doing this. In practice, however, in marine applications the amount of liquid VOC accumulated by capturing VOC from the vent gas is generally greater than that required as fuel during offloading or otherwise for onboard purposes. Accordingly the invention offers other profitable uses for accumulated liquid VOC, and one such is illustrated by FIGS. 6 and 7.

[0081] FIG. 6 illustrates a system that is in most respects the same as that shown in FIG. 5, but with a supplemental connection 446 between the liquid VOC store 426 (conveniently linked to the fuel line to the combustion plant 428) and the crude oil delivery line 416. Under the control of an isolating valve 448 in the supplemental connection 446, liquid VOC at high pressure is injected at L into the stream of crude oil at low pressure.

[0082] It may be noted here that, although the arrangement of FIG. 6 supplements the incoming crude oil, the supplemental connection 446 is configured and arranged to operate only during offloading from the tanks 412 (inasmuch as on FSO/FPSOs loading continues during offloading). If VOC were blended into the incoming oil stream on an FSO/FPSO then it would flash off further downstream in the vertical drop line into the cargo tanks. If the vessel is only loading then the VOC vapour will add to the flowrate and hydrocarbon concentration in the vent gas from the oil storage tanks that the VOC recovery unit has to handle: that is, there would be a continuous cycle of VOC recovery and evaporation on return to the tanks. However, if VOC is blended only into the incoming oil stream on an FSO/FPSO during offloading then flashing-off of the VOC is not problematic because the VOC recovery unit is switched off, and there is no vent gas because the oil level is falling. It follows that it is most efficient to empty any liquid VOC from the liquid VOC store 426 during offloading. And overall the system provides an economic benefit in avoiding VOC loss to atmosphere, i.e., cargo shrinkage.

[0083] As shown in FIG. 7, liquid VOC from the store 426 is injected into the crude oil being offloaded from the tanks 412 by way of the supplemental line 442 terminating in a nozzle 450 extending into the offloading line 430. It will be understood that the mass and temperature of the crude oil stream counteracts heat loss from the pressure drop in the liquid VOC as it exits the nozzle 450 and thereby prevents the formation of hydrates that could otherwise block the nozzle 450.

[0084] As shown in FIG. 8, liquid VOC from the store 426 is injected into the crude oil being loaded into the tanks 412 by way of the supplemental line 446 terminating in a nozzle 452 extending into the delivery line 416. It will be understood that the mass and temperature of the crude oil stream counteracts heat loss from the pressure drop in the liquid VOC as it exits the nozzle 452 and thereby prevents the formation of hydrates that could otherwise block the nozzle 452. Those skilled in the art will appreciate that the injection of liquid VOC into the incoming oil stream serves not only to add to the load in the tanks 412 but subsequent evaporation downstream will also supplement the blanket gas.

[0085] As shown in FIG. 9, accumulated liquid VOC may also be injected directly into the oil 414 in the tanks 412, tank 413 being shown, by way of supplemental connection 454 extending from the store 426 (not shown) to a nozzle 456 submerged in the oil 414.

[0086] On crude oil carriers, any liquid VOC remaining in store at the end of a voyage may be pumped into a truck at an offloading terminal, although it should be noted that that this may entail costs for its removal.

[0087] Various modifications of the arrangements described above may be made without departing from the scope of the present invention.

## WHAT IS CLAIMED IS

1. A method of handling liquid hydrocarbon in which the liquid hydrocarbon is loaded into a tank and subsequently offloaded from the tank, the tank being backfilled with inert blanket gas during offloading and vent gas comprising a mixture of blanket gas with VOC vapor being vented from the tank during loading, wherein:

(a) the vent gas is delivered to a vapor recovery unit operative by means of adsorption to capture VOC vapor from the vent gas;

(b) VOC vapor captured by the vapor recovery unit is liquefied and delivered to a liquid VOC store; and

(c) liquid VOC from the liquid VOC store is delivered as fuel to a combustion plant.

2. A method of handling liquid hydrocarbon as claimed in claim 1 wherein the vent gas is delivered uncompressed to the vapor recovery unit and captured VOC vapor is liquefied downstream of the vapor recovery unit.

3. A method of handling liquid hydrocarbon as claimed in claim 2 wherein VOC vapor captured in the vapor recovery unit is compressed before delivery to the liquid VOC store.

4. A method of handling liquid hydrocarbon as claimed in claim 2 wherein weak gas consisting of the residue of the vent gas after capture of VOC vapor therefrom in the vapor recovery unit is delivered as fuel to the combustion plant.

5. A method of handling liquid hydrocarbon as claimed in claim 2 wherein steam is produced by the combustion plant.

6. A method of handling liquid hydrocarbon as claimed in claim 5 wherein steam produced by the combustion plant is used to power an electrical generator.

7. A method of handling liquid hydrocarbon as claimed in claim 5 wherein steam produced by the combustion plant is used to operate a desalination plant.

8. A method of handling liquid hydrocarbon as claimed in claim 2 wherein after the tank is loaded the vapor recovery unit is inoperative and only liquid VOC from the liquid VOC store fuels the combustion plant.

9. A method of handling liquid hydrocarbon as claimed in claim 2 wherein exhaust gas from the combustion plant is used as said inert blanket gas backfilling the tank during offloading.

10. A method of handling liquid hydrocarbon as claimed in claim 2 wherein liquid hydrocarbon being loaded or offloaded is supplemented with liquid VOC from the liquid VOC store.

11. Apparatus for handling liquid hydrocarbon comprising:

(a) a tank into which the liquid hydrocarbon is loaded by way of a delivery line and from which it is subsequently offloaded by way of an offloading line;

(b) a blanketing system connected to the tank by way of a blanket line and operative during offloading to backfill the tank with inert blanket gas;

(c) a vapor recovery unit connected to the tank by way of a vent line to receive therefrom vent gas displaced from the tank during loading, the vent gas comprising a mixture of blanket gas and liquid VOC vapor and the vapor recovery unit being operative by means of adsorption to capture VOC vapor from said mixture;

(d) a liquefaction system connected to the vapor recovery unit by way of a regeneration line to receive and liquefy VOC vapor captured by the vapor recovery unit;

(e) a liquid VOC store connected to the liquefaction system to receive liquefied VOC vapor therefrom; and

(f) a combustion plant connected to the liquid VOC store by way of a primary fuel line and thereby fuelled by liquid VOC from the liquid VOC store.

12. Apparatus for handling liquid hydrocarbon as claimed in claim 11 wherein the vapor recovery unit captures the VOC vapor without compressing the vent gas.

13. Apparatus for handling liquid hydrocarbon as claimed in claim 11 wherein the vapor recovery unit comprises an adsorption system operative to capture the VOC vapor and comprising at least two adsorption vessels each packed with activated carbon to capture the VOC vapor and control means operative to open the vessels to the vent line alternately to receive the vent gas from the tank during loading.

14. Apparatus for handling liquid hydrocarbon as claimed in claim 13 wherein the vapor recovery unit comprises a regeneration system operative under the control means to strip off the captured VOC vapor from the adsorption vessels alternately, which regeneration system comprises a vacuum pump.

15. Apparatus for handling liquid hydrocarbon as claimed in claim 14 wherein the liquefaction system comprises:

- (a) a compressor downstream of the vacuum pump, which compressor is operative to compress the VOC vapor stripped off by the vacuum pump;
- (b) a condenser downstream of the compressor, which condenser is operative to condense the compressed VOC vapor;
- (c) a separator configured and arranged to separate the condensed VOC vapor from any uncondensed VOC vapor; and
- (d) a gas return line configured and arranged to return uncondensed VOC vapor in the separator to a point upstream of the compressor.

16. Apparatus for handling liquid hydrocarbon as claimed in claim 15 wherein:

- (a) the vacuum pump and the compressor are each liquid ring machines sealed with seal fluid;
- (b) the separator is configured and arranged to separate any seal fluid from the condensed VOC vapor; and
- (c) said apparatus comprises a seal fluid return line configured and arranged to return seal fluid from the separator to the vacuum pump and the compressor.

17. Apparatus for handling liquid hydrocarbon as claimed in claim 11 wherein the vapor recovery unit is connected to the combustion plant by way of a secondary fuel line whereby weak gas comprising the residue of the vent gas after capture of VOC vapor in the vapor recovery unit is delivered as fuel to the combustion plant.

18. Apparatus for handling liquid hydrocarbon as claimed in claim 17 wherein the secondary fuel line includes a gas blower operative to deliver the weak gas to the combustion plant.

19. Apparatus for handling liquid hydrocarbon as claimed in claim 18 wherein the combustion plant comprises a burner system including:

- (a) a primary fuel inlet open to the primary fuel line to receive thereby liquid VOC from the liquid VOC store;
- (b) a secondary fuel inlet open to the secondary fuel line to receive thereby weak gas from the vapor recovery unit;
- (c) a combustion air supply; and
- (d) burner control means operative automatically to adjust the delivery of liquid VOC and weak gas according to the Wobbe Index and flow rate thereof.

20. Apparatus for handling liquid hydrocarbon as claimed in claim 19 wherein the burner system is operative to burn both the liquid VOC and the weak gas during loading and otherwise to burn only the liquid VOC.

21. Apparatus for handling liquid hydrocarbon as claimed in claim 11 wherein the combustion plant is connected to the tank by way of a blanket line, whereby exhaust from the combustion plant is delivered to the tank as blanket gas backfilling the tank during offloading.

22. Apparatus for handling liquid hydrocarbon as claimed in claim 11 wherein a cargo supplement line extends from the liquid VOC store to supplement the liquid hydrocarbon with liquid VOC.

23. Apparatus for handling liquid hydrocarbon as claimed in claim 22 wherein the cargo supplement line extends from the liquid VOC store to the delivery line or the offloading line to supplement liquid hydrocarbon passing therethrough with liquid VOC from the liquid VOC store.

24. Apparatus for handling liquid hydrocarbon as claimed in claim 23 wherein the cargo supplement line is connected to the delivery line or the offloading line by way of a nozzle extending into the line.

25. Apparatus for handling liquid hydrocarbon as claimed in claim 22 wherein the cargo supplement line extends from the liquid VOC store to a nozzle submerged in the liquid hydrocarbon in the tank.

26. Apparatus for handling liquid hydrocarbon as claimed in claim 11 wherein the combustion plant comprises a steam boiler.

27. Apparatus for handling liquid hydrocarbon as claimed in claim 26 comprising an electrical generator powered by steam from the boiler.

28. Apparatus for handling liquid hydrocarbon as claimed in claim 26 comprising a desalination plant operated by steam from the boiler.

29. Apparatus for handling liquid hydrocarbon as claimed in claim 26 comprising a cargo pump for offloading liquid hydrocarbon from the tank, which cargo pump is powered by steam from the boiler.

30. Apparatus for handling liquid hydrocarbon as claimed in claim 26 comprising a cargo heater in the tank, which cargo heater is heated by steam from the boiler.

31. Methods of and apparatus for handling liquid hydrocarbon substantially as hereinbefore described with reference to and as shown in the accompanying drawings.

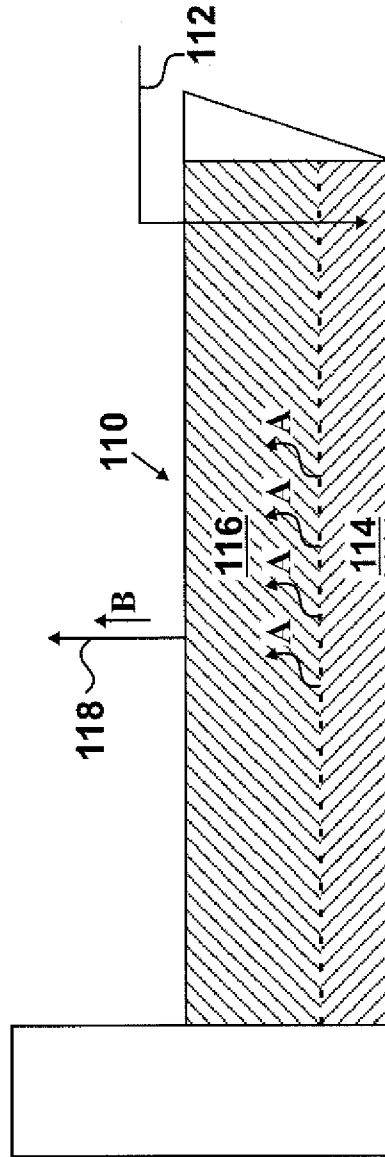


Fig 1

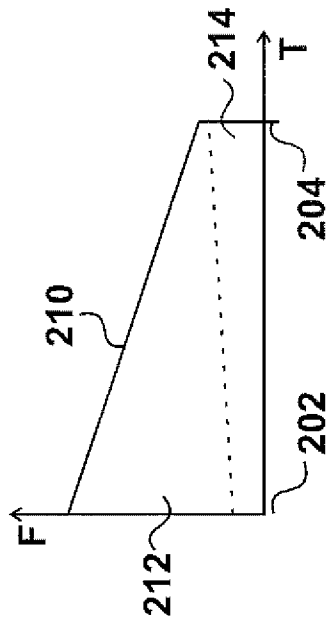


Fig 2

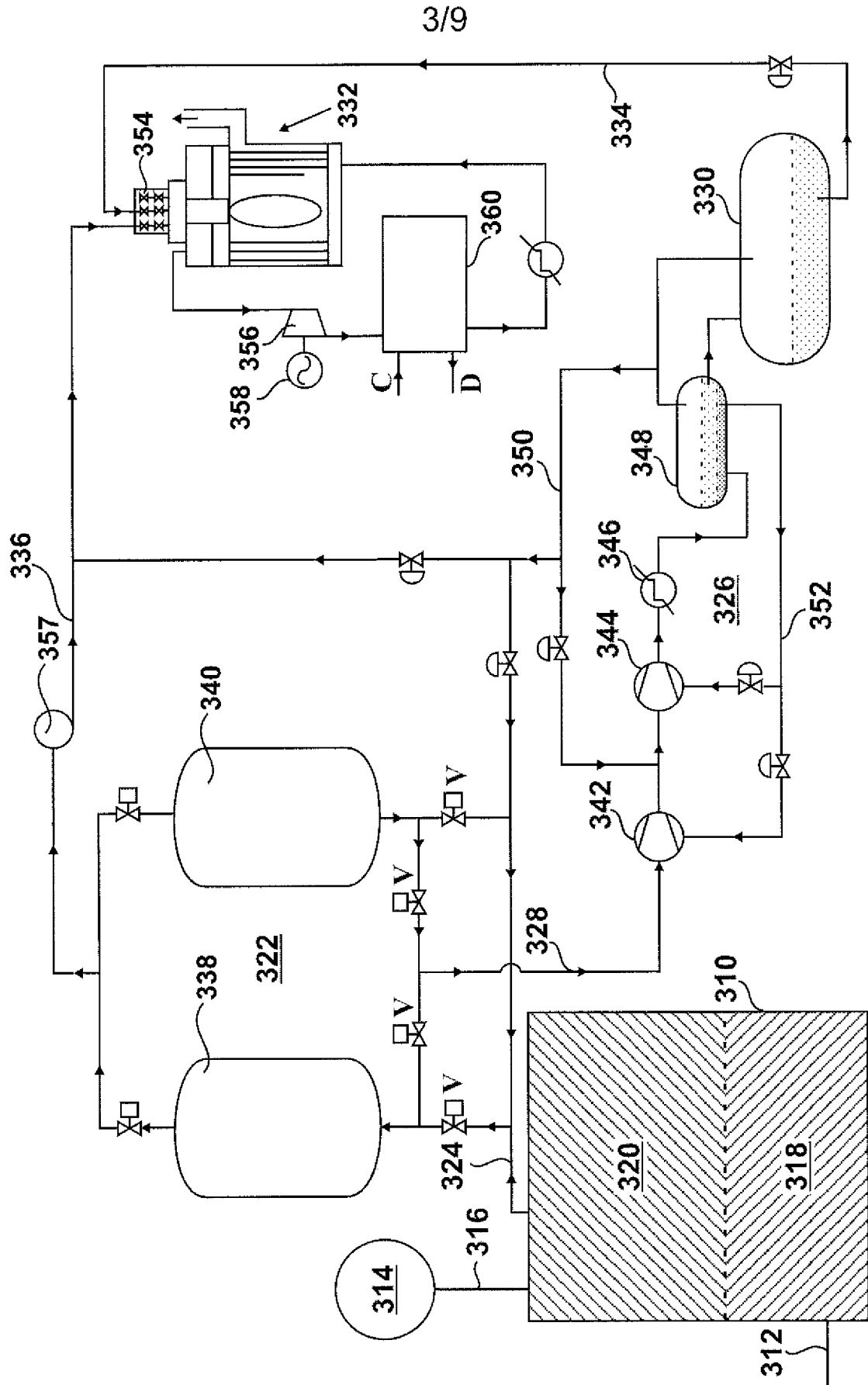


Fig 3

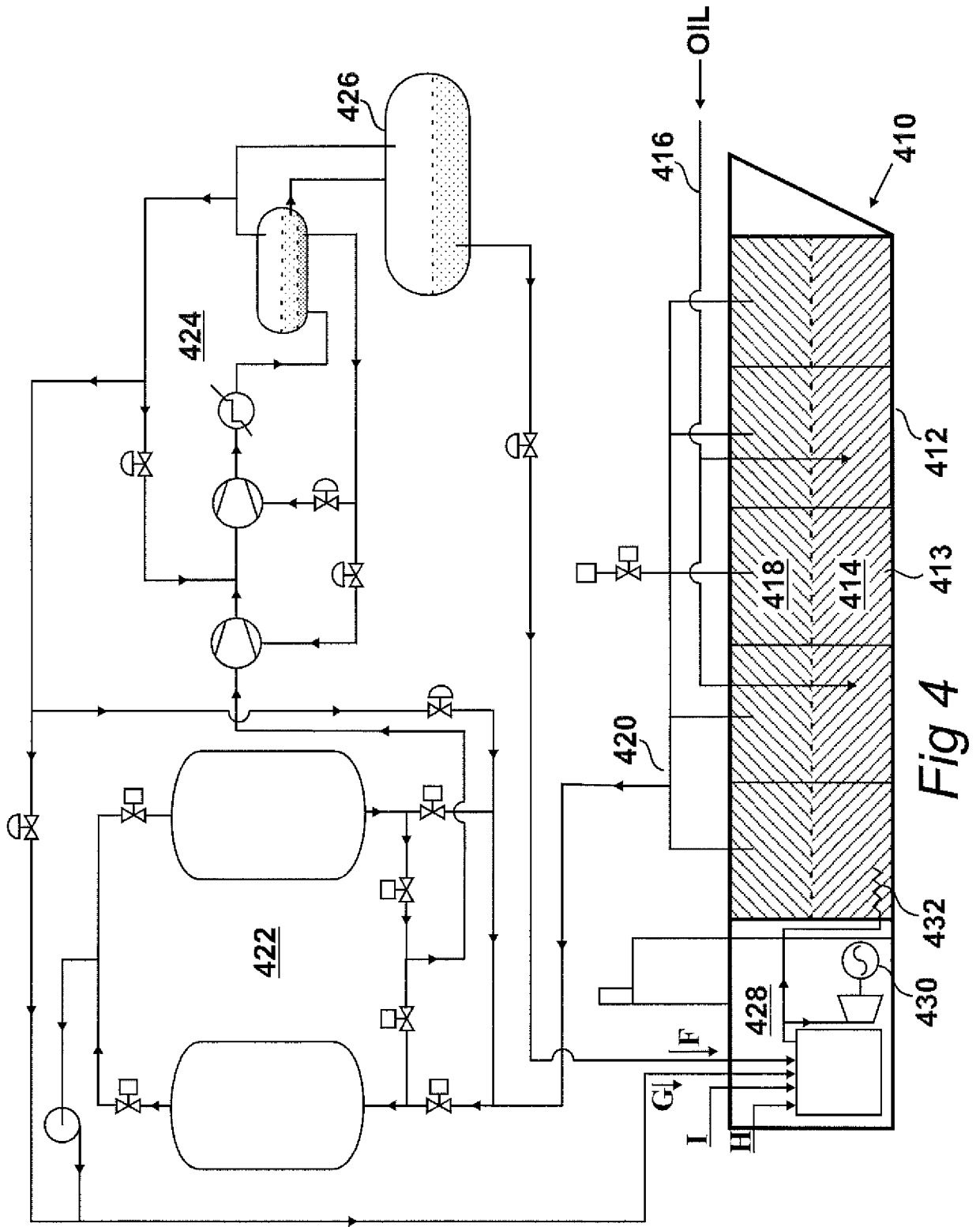


Fig 4

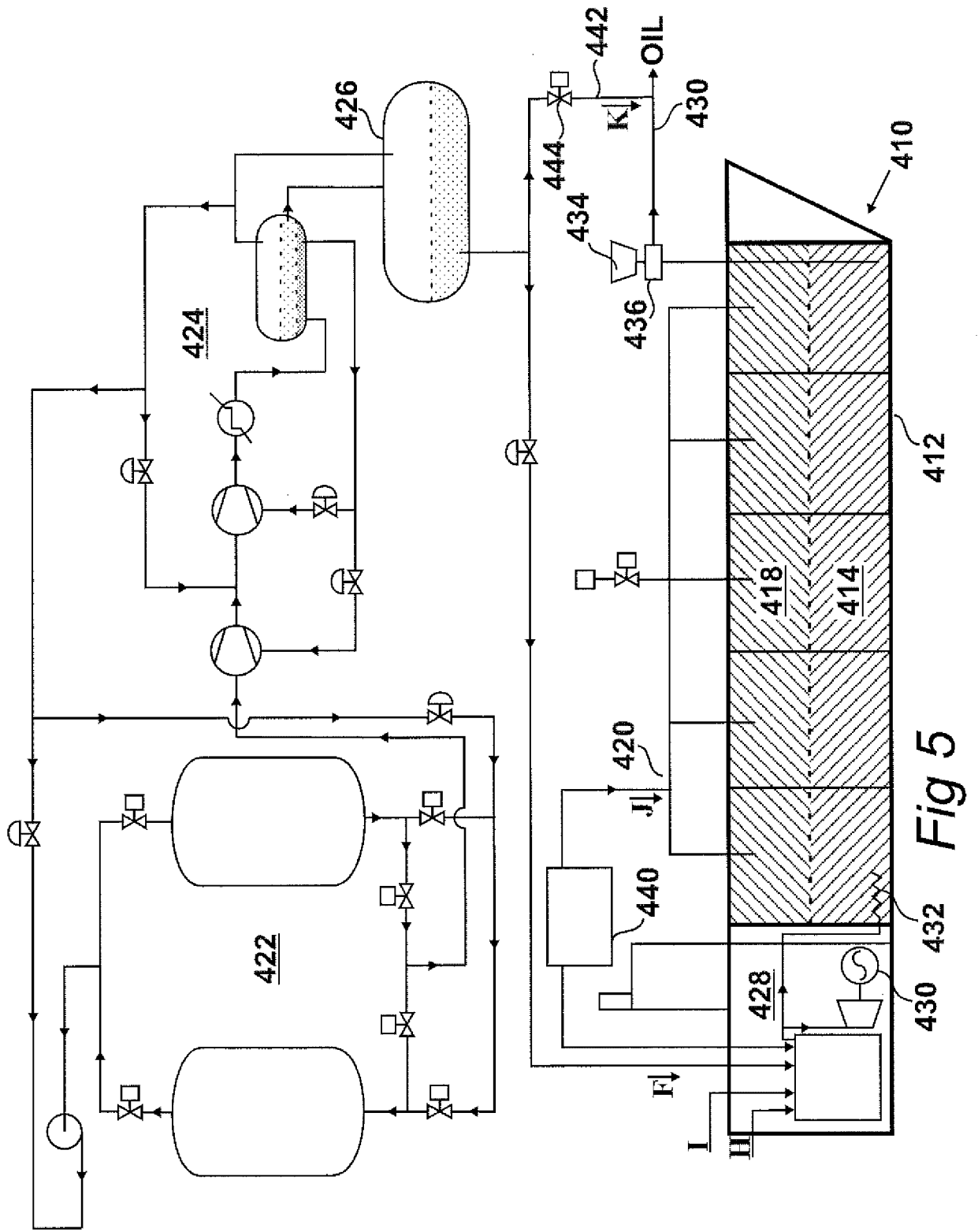


Fig 5

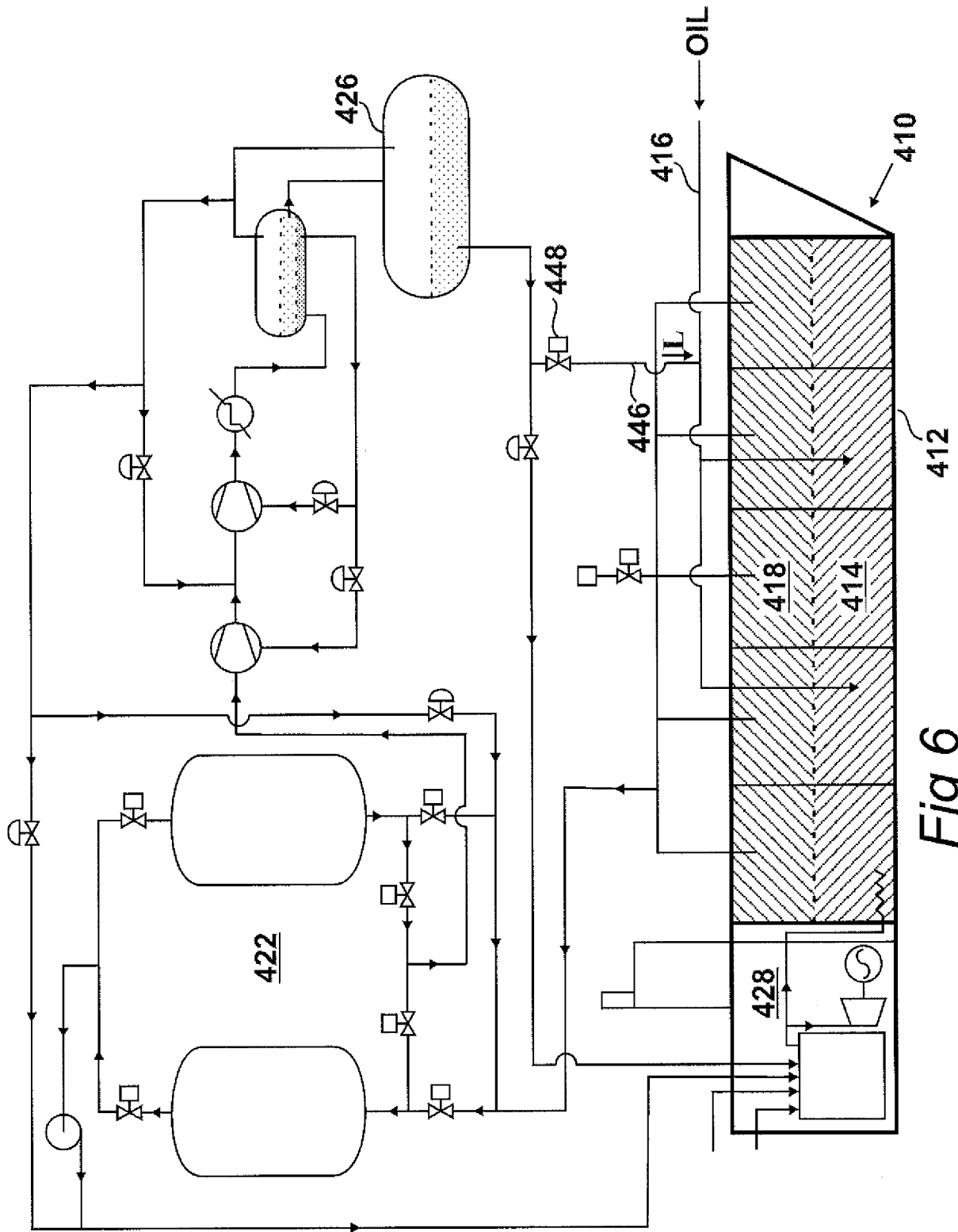


Fig 6

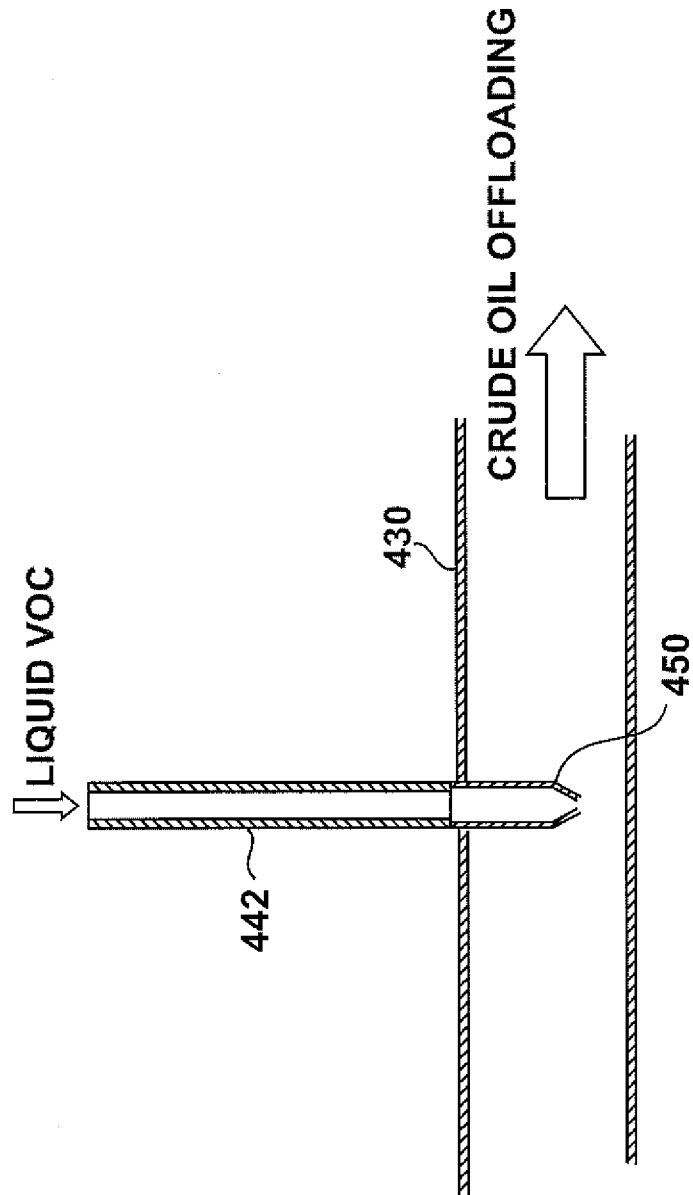


Fig 7

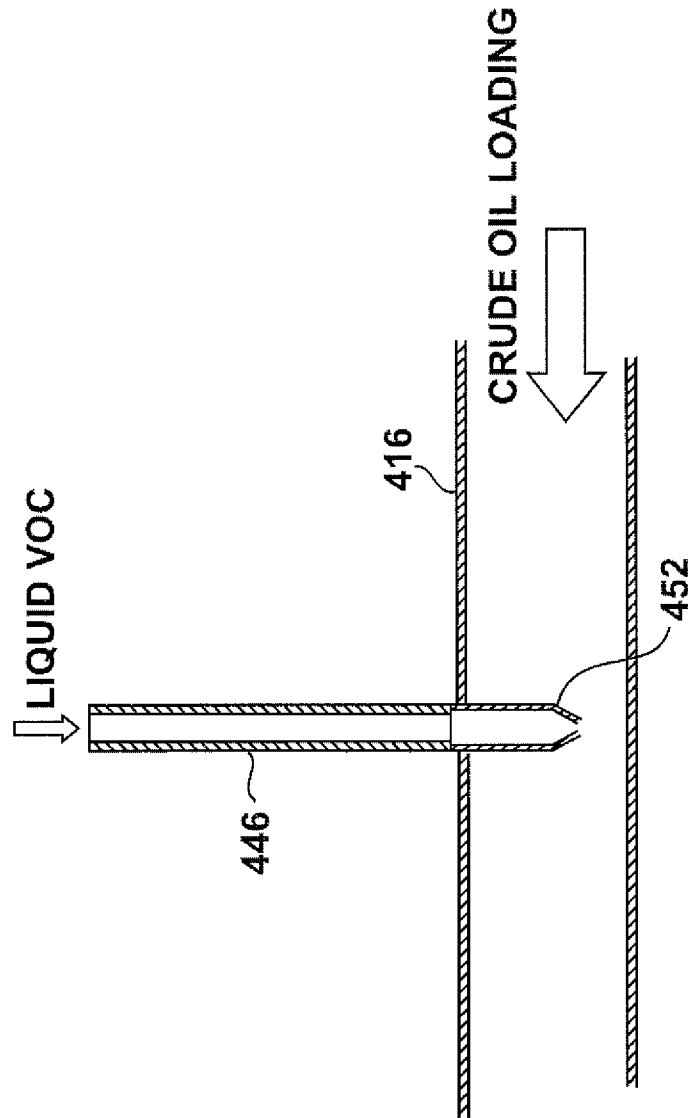


Fig 8

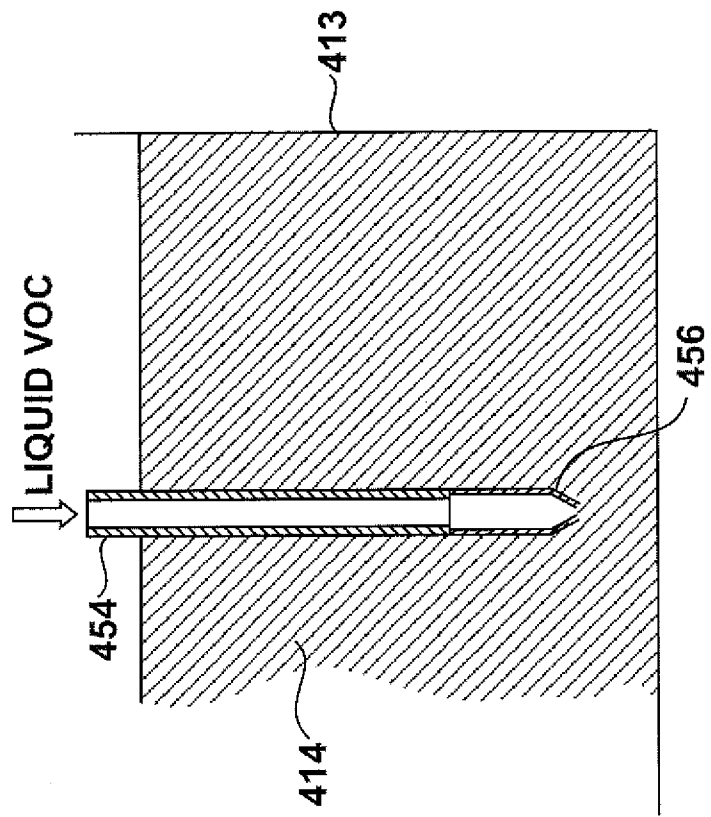


Fig 9

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US13/36930

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - B01D 53/04; F25J 3/00 (2013.01)

USPC - 55/23, 61, 180; 62/18

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

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC(8): B01D 53/04; B64D 37/32; F02B 43/00; F17C 3/10, 11/00; F25J 3/00 (2013.01)

USPC: 55/23,61, 180; 62/18, 613; 123/527

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

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

Micropatent; Google Scholar; DialogPro; IP.com -- crude, blanket, combust, electrical, heat, inert, loading, marine, offloading, power, solvent, steam, tanker, wobbe,

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2003/0056535 A1 (BEAM, CA) 27 March 2003; figure 2; paragraphs [0002], [0004], [0005], [0007], [0008], [0010], [0016], [0018], [0019], [0026], [0033]	1-30
Y	US 2007/0079816 A1 (WHITE, J et al.) 12 April 2007; figure 2; paragraphs [0011], [0012], [0023], [0024], [0026]	1-30
Y	US 4,689,054 A (VARA, TE et al.) 25 August 1987; figures 1, 2; column 1, lines 10-12; column 6, lines 4-8; column 7, lines 24-30; column 8, lines 17-24; column 8, lines 43-46; column 10, lines 17-22; column 10, lines 50-55	3-7, 15-20, 26-30
Y	US 5,269,833 A (NITSCHKE, M) 14 December 1993; figure 1; column 2, line 65 to column 3, line 8; column 5, lines 39-42	14-16
Y	US 4,213,935 A (GOODNIGHT, HE et al.) 22 July 1980; figure 1; abstract	21
Y	US 2011/0147195 A (SHAPIRO, AP et al.) 23 June 2011; figures 1, 2; paragraphs [0007], [0018], [0028]	7, 27, 28
Y	WO 2011/059305 A1 (NADARAJAH, NC et al.) 19 May 2011; page 3, lines 1-10	10, 22-25
Y	US 2002/0066391 A1 (GOLDMAN, GK) 06 June 2002; paragraphs [0017]-[0021], [0032]-[0034]	10, 22-25
Y	US 2010/0162678 A1 (ANNIGERI, R et al.) 01 July 2010; figure 1; paragraphs [0001]-[0003], [0021], [0022]; claim 32	19, 20



Further documents are listed in the continuation of Box C.



* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier application or patent but published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

26 August 2013 (26.08.2013)

Date of mailing of the international search report

30 AUG 2013

Name and mailing address of the ISA/US

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P.O. Box 1450, Alexandria, Virginia 22313-1450

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PCT Helpdesk: 571-272-4300

PCT OSP: 571-272-7774

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US13/36930

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2011/092450 A1 (O'CONNOR, SM) 04 August 2011; abstract; figure 2; page 7, lines 23-26	29, 30
Y	US 4,066,423 A (MCGILL, JC et al.) 03 January 1978; figures 1, 2; column 2, lines 55-59; column 4, lines 33-47	16
A	US 4,995,890 A (CROUDACE, GR) 26 February 1991; abstract	1-30
A	US 4,414,003 A (BLAUDZUN, B) 08 November 1983; abstract; figure 1	1-30
A	US 5,345,771 A (DINSMORE, HL) 13 September 1994; abstract	1-30
A	US 4,148,599 A (REED, RD et al.) 10 April 1979; abstract; figures 1-5	17-30
A	US 6,168,708 B1 (BURBRIDGE, CS et al.) 02 January 2001; abstract; column 3, line 50-57; column 5, line 64 to column 6, line 11	10, 22-25
A	US 2010/0304316 A1 (CODRON, FT et al.) 02 December 2010; abstract; paragraphs [0025], [0026]	10, 22-25
A	US 2012/0079831 A1 (KIRZHNER, J et al.) 05 April 2012; paragraphs [0009], [0010], [0021], [0031], [0070]	10, 22-25

**Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1.  Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2.  Claims Nos.: 31  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:  
Claim 31 is an improper omnibus-type claim, and as such, constitutes an unsearchable claim.
  
3.  Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

**Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

1.  As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2.  As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3.  As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
  
4.  No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

**Remark on Protest**

- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- No protest accompanied the payment of additional search fees.