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PROCESS AND APPARATUS FOR CRYOGENIC STORAGE

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3 Sheets-Sheet 1

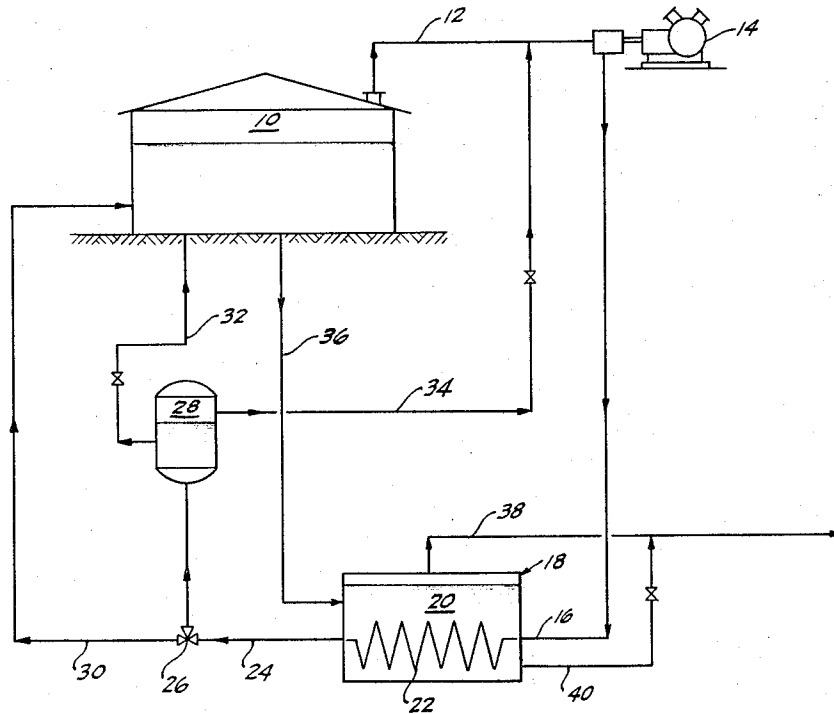


FIG-1

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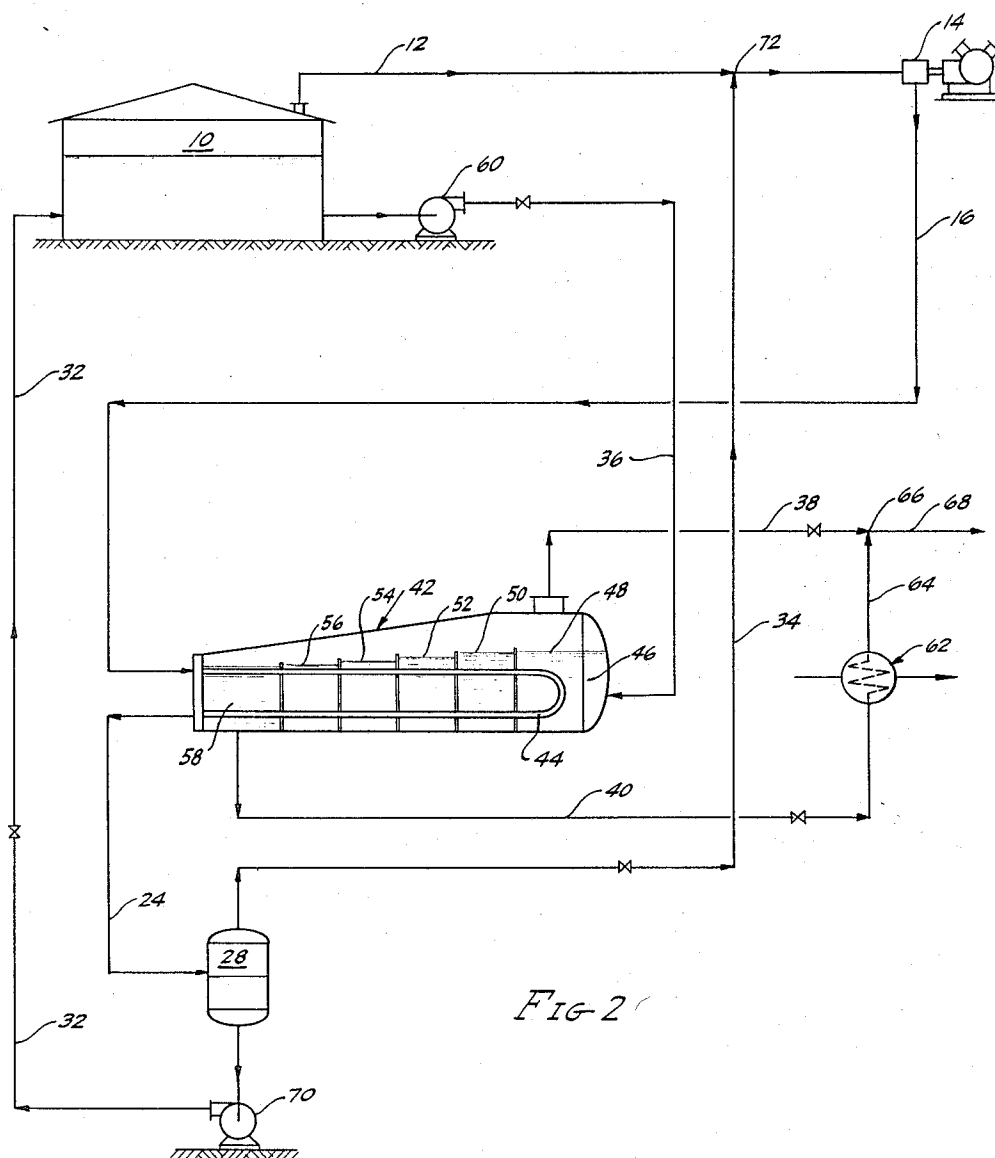
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3 Sheets-Sheet 2



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3 Sheets-Sheet 3

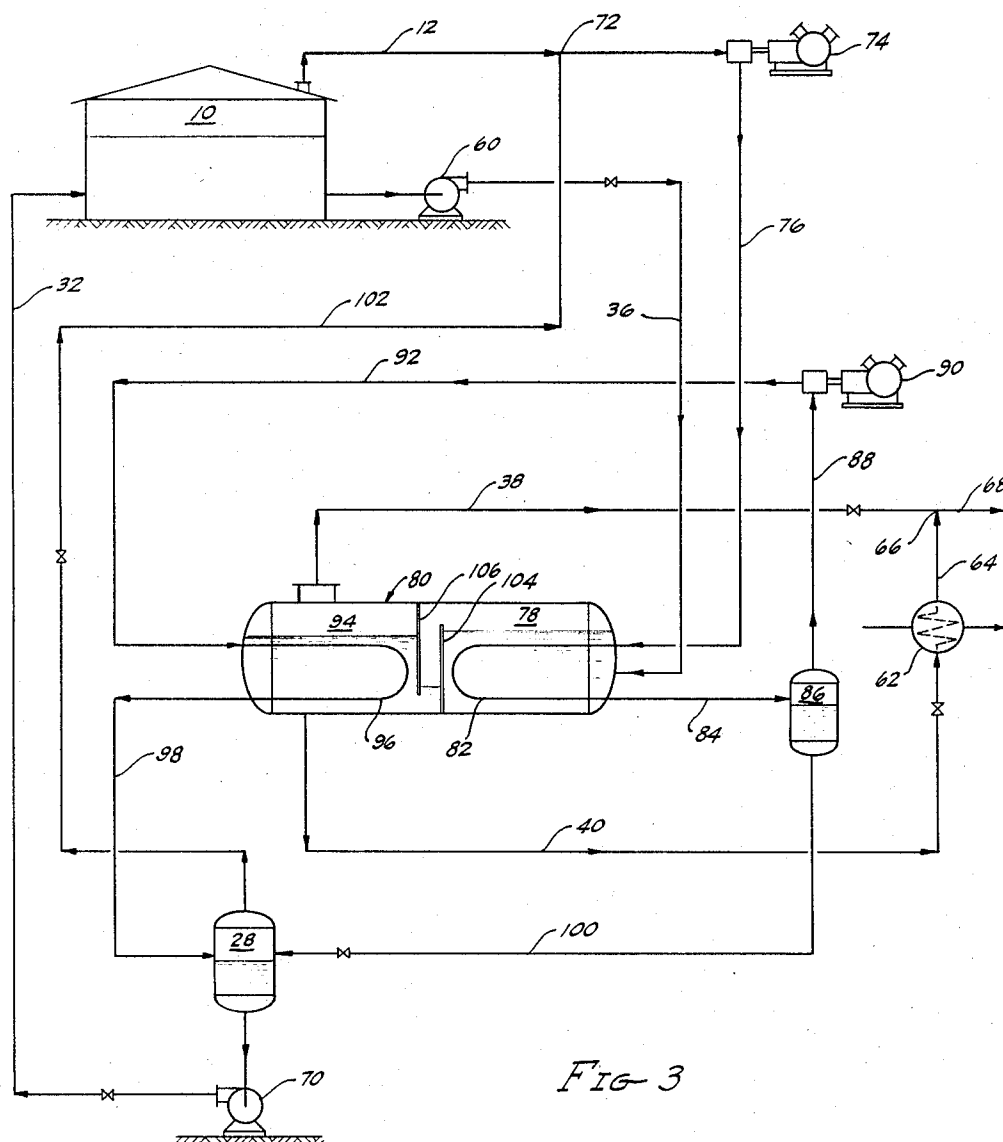


FIG 3

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1

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PROCESS AND APPARATUS FOR CRYOGENIC STORAGE

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8 Claims. (Cl. 62—51)

This invention relates to the storage of cryogenic liquids, more particularly, this invention relates to the storage of multi-component cryogenic liquids.

The storage of multi-component cryogenic liquids presents several difficulties due to the fact that the most volatile or lightest component of the mixture tends to boil off leaving a residue of heavier, less volatile materials. Both the evolved volatile vapor and the residual heavier liquid are generally unsuitable for the use intended for the multi-component cryogenic liquid because they differ substantially in composition from that cryogenic liquid.

It is therefore an object of this invention to provide for the storage of multi-component cryogenic liquids whereby the composition of the stored body of cryogenic liquid remains substantially constant.

It is a further object of this invention to provide for the storage of multi-component cryogenic liquids whereby the proportions of the components in that body of cryogenic liquid remain at substantially constant values and the composition of the product removed for use has a substantially constant predetermined composition.

Additional objects and advantages will become apparent upon reading of the following specification taken in conjunction with the accompanying drawings, and in practicing this invention.

The phenomenon by which the lower boiling components of a multi-component cryogenic liquid preferentially boil off in storage is known as "weathering." The result of weathering is an increase in the fraction of the heavier components remaining in storage.

Weathering is particularly undesirable in stored bodies of liquified natural gas. The methane and nitrogen, if present, will preferentially boil off in time leaving a liquid body containing principally ethane, propane and higher hydrocarbons. The vapor emitted from a stored body of liquified natural gas during weathering is principally, say 96 to 99 mole percent, methane and 1 to 4 mole percent ethane. This vapor is unsuitable for consumption by most natural gas users. The proportion of ethane, propane and heavier hydrocarbons in the liquid increases with time until the liquid is composed essentially of these components. When the methane content of the liquid drops below about 50 to 60 mole percent, this liquid becomes unsuitable for use as natural gas when volatilized.

A stored body of liquified natural gas may be used to supplement a continuous supply of natural gas during periods of peak requirement. This process of supplying additional natural gas during a peak period of use is called "peak shaving."

Broadly, the process of this invention comprises the steps of compressing that vapor which is emitted from the body of stored multi-component cryogenic liquid, condensing the resultant pressurized vapor, and then flashing the condensate to produce a liquid fraction and a vapor fraction. The liquid fraction is returned to the stored body of cryogenic liquid and the vapor fraction is returned to the compression step where it is cycled through the process again.

Advantageously, in the condensing step, the pressurized vapor is contacted in an indirect heat exchange relationship, such as by, for example, the passage of this pres-

2

surized vapor through the tube side of a shell and tube heat exchanger, with a portion of the body of cryogenic liquid. Conveniently, the cryogenic liquid is passed through the shell side of a shell and tube heat exchanger. During contacting the more volatile components are volatilized from that portion of the body of cryogenic liquid which is used as the heat exchange medium. The residual liquid remaining from this volatilization is rich in the higher boiling components of the multi-component cryogenic liquid. In the case of natural gas the more volatile component is methane and the residual liquid is composed primarily of ethane and propane.

A portion of the residual liquid is withdrawn from the shell side of the heat exchanger, vaporized and combined with the more volatile components which were evolved from it during the heat exchanging step. The volatile component and residual liquid streams are so proportioned that the resultant combined stream has a predetermined composition, preferably that required for the intended use of the stored cryogenic liquid.

By carrying out the process of this invention, the proportion of the more volatile components in a stored body of multi-component cryogenic liquid may be made to remain constant or even increase if desired. The overall operation of this process results in continuously condensing and recycling the boil-off fraction from a stored body of multi-component cryogenic liquid in a closed cycle to maintain the composition of that stored body of liquid at a substantially constant value. The product resulting from the operation of the process has a composition approximating that of the original stored body of liquid.

For a more complete understanding of the invention, reference is made to the accompanying drawings in which:

FIGURE 1 is a schematic representation of one embodiment of this invention;

FIGURE 2 is a schematic representation of a further embodiment of this invention; and

FIGURE 3 is a schematic representation of this invention in which a two-stage operation is depicted.

Referring particularly to FIGURE 1, 10 is an insulated storage vessel, 12 is a vapor vent line, 14 is a compressor, 16 is a conduit for carrying compressed vapor to heat exchanger 18 having a shell side 20 and a tube side 22. Conduit 24 is provided for conducting condensed pressurized liquid to valve 26. Depending upon the positioning of valve 26, the pressurized liquid will flow into flasher unit 28 or into conduit 30. In flasher unit 28, the pressurized liquid is flashed down to substantially the ambient pressure prevailing in vessel 10. The liquid fraction is conveyed by a conduit 32 from flasher unit 28 into vessel 10. The vapor fraction from flasher unit 28 is conveyed back to compressor 14 by way of conduit 34. When flasher unit 28 is bypassed and the pressurized liquid is conveyed directly to vessel 10 through conduit 30, flashing takes place within vessel 10 and the vaporous fraction is returned to compressor 14 through line 12.

To accomplish heat exchanging, a portion of the body of cryogenic liquid in vessel 10 is withdrawn through conduit 36 and introduced into the shell side 20 of heat exchanger 18. In the process of absorbing heat from the pressurized vapor in the tube side 22 of heat exchanger 18, the more volatile components of the heat exchange medium on the shell side 20 are evolved from the liquid and removed through conduit 38. The liquid remaining in shell side 20 of heat exchanger 18 is constantly enriched in the less volatile components of the cryogenic liquid. A portion of this enriched residue is withdrawn through conduit 40 and intermingled with the vapor in conduit 38 to produce a combined stream having a predetermined composition.

Referring specifically to FIGURE 2, 10 is an insulated storage vessel, vent line 12 conducts the boil-off vapors from storage vessel 10 to compressor 14. Compressed vapors are conducted by conduit 16 to a heat exchanger indicated generally at 42. Heat exchanger 42 comprises a tube side 44 and a shell side 46. The shell side is composed of a series of cascade compartments 48, 50, 52, 54, 56 and 58, respectively.

The heat exchange medium to be used in the shell side 46 is withdrawn from the body of multi-component cryogenic liquid stored in vessel 10 by means of pump 60 and conveyed through conduit 36 to the shell side of heat exchanger 42. The heat exchange medium is introduced first into cascade section 48 and thereafter cascades from cascade section 48 through section 58, decreasing in volume and being enriched in higher boiling fractions in each cascade section due to the boil-off therefrom of the lighter components in the heat exchange medium.

The enriched residue in cascade section 58 is conducted via conduit 40 to a vaporizer indicated generally at 62, and then by way of conduit 64 it is conducted to a commingling point 66 whereat it is intermingled with the vapor carried in conduit 38 to produce a composite gas stream having a predetermined composition. The composite gas stream is then conveyed away for use through conduit 68.

The tube side 44 of heat exchanger 42 receives pressurized vapor from conduit 16 and brings it into indirect heat exchange relationship with the heat exchange medium in shell side 46, whereby a condensate is formed in the tube side 44. This condensate is conveyed away from tube side 44 through conduit 24 into flasher unit 28. In flasher unit 28 the pressure over the condensate in conduit 24 is reduced to about that prevailing in storage vessel 10.

The liquid fraction produced by flashing is pumped by pump 70 through conduit 32 back to storage vessel 10. The vaporous fraction from flasher unit 28 is conducted through conduit 34 to commingling point 72 whereat it is intermingled with the vapor evolving from the stored body of multi-component cryogenic liquid in vessel 10, and the commingled vapor stream is supplied to compressor 14 from whence the cycle is repeated.

Referring specifically to FIGURE 3, there is illustrated a two-stage operation. Vapor evolved, during the process of weathering, from the body of multi-component cryogenic liquid stored in storage vessel 10 is conducted by vent line 12 to a first stage compressor 74. The resultant pressurized vapor is conducted through conduit 76 to the first stage 78 of a heat exchanger, indicated generally at 80. The compressed vapor is condensed in the tube side 82 of first stage 78. The resultant pressurized condensate is conducted through conduit 84 to separator 86 wherein non-condensed vapors are separated for removal by conduit 88 to second stage compressor 90.

Preferably, second stage compressor 90 is operated at a higher pressure than first stage compressor 74. The pressurized vapor from second stage compressor 90 is conducted through conduit 92 to second stage side 94 to heat exchanger 80. The pressurized vapor is at least partially condensed in the tube side 96 of second stage 94. The pressurized condensate from tube side 96 is conducted by conduit 98 to flasher unit 28.

Flasher unit 28 receives pressurized condensate through conduit 100 from separator 86, as well as through conduit 98 from the second stage 94 of heat exchanger 80. Flashing reduces the pressure over the combined condensates to about that prevailing in storage vessel 10. The liquid fraction resulting from this flashing is pumped by pump 70 through conduit 32 back into storage vessel 10. The vapor fraction produced in flasher unit 28 is conducted by way of conduit 102 to commingling point 72 and then to first stage compressor 74 from where it proceeds through the cycle again.

Heat exchanger 80 comprises a first stage 78 and a second stage 94. First stage 78 receives a heat exchange

medium through conduit 36 from the body of multi-component cryogenic liquid stored in vessel 10. The heat exchange medium is utilized in the shell side of heat exchanger 80. As the heat exchange medium leaves first stage 78 it overflows baffle 104 and flows under baffle 106. The vapor evolved from the heat exchange medium in first stage 78 also passes under baffle 106 and bubbles up through the heat exchange medium in second stage 94. The vapor collected in second stage 94 is withdrawn through conduit 38. The enriched liquid residue of the heat exchange medium is withdrawn from second stage 94 through conduit 40. Conduit 40 conveys this enriched liquid to vaporizer 62 and conduit 64 removes the resultant vapor to commingling point 66 where it is mixed with vapor carried in line 38. A composite stream having a predetermined composition leaves the operation through conduit 68.

For a specific example of the operation of this invention reference is made to FIGURE 3. The operation is described with respect to the storage of liquified natural gas. However, the description herein is applicable to any multi-component cryogenic liquid which suffers from weathering when stored for a period of time. The body of multi-component cryogenic liquid stored in vessel 10 has a composition of about 73 mole percent methane, 26 mole percent ethane, and 1 mole percent propane and other higher hydrocarbons, and a temperature of about -258° F. The vapor emitting during the process of weathering from this body of stored cryogenic liquid has a composition of about 9.6 mole percent methane and about 0.4 mole percent ethane.

In the first stage compressor 74 methane rich vapor produced by weathering is compressed to about 100 pounds per square inch gage. The resultant compressed vapor has a temperature of about -140° F. The temperature of the heat transfer medium in first stage 78 of heat exchanger 80 is about -210° F.

A substantial portion of the methane rich vapor from first stage compressor 74 is condensed in the tube side 82 of first stage 78. The pressurized mixture of condensate and vapor leaving the tube side 82 is still under a pressure of about 100 pounds per square inch gage and has a temperature of about -200° F.

Separator 86 is maintained under a pressure of about 100 pounds per square inch gage. The vapor and condensate leaving tube side 82 are separated in separator 86. The vapor leaving separator 86 through conduit 88 is substantially pure methane. This methane stream, still under a pressure of about 100 pounds per square inch gage, is conducted to second stage compressor 90 wherein it is compressed to a pressure of about 600 pounds per square inch gage. The temperature of this compressed methane is about -33° F.

The pressurized condensates from separator 86 and tube compressor 90 is conducted into the tube side 96 of second stage 94 of heat exchanger 80, wherein partial condensation of this pressurized methane takes place. The temperature of the heat exchange medium in second stage 94 is about -120° F. and the temperature of the vapor-ous-condensate mixture leaving tube side 96 is about -110° F.

The pressurized condensate from separator 86 and tube side 96 are conducted to flasher unit 28 wherein they are flashed to about a pressure of 1 atmosphere and a temperature of -258° F. The liquid fraction produced in flasher unit 28 is pumped back to the body of liquified natural gas stored in vessel 10. The composition of this returned stream is about 99.6 mole percent methane and 0.4 mole percent ethane.

The composition of the liquid stream returned to vessel 10 is substantially the same as the composition of that vapor which is evolved from the body of liquified natural gas during the process of weathering.

That portion of liquified natural gas which is withdrawn from vessel 10 for use as a heat exchange medium

5

in heat exchanger 80 has the same composition as does the body of liquified natural gas, namely, about 73 mole percent methane, 26 mole percent ethane, and 1 mole percent propane. A substantial amount of methane is evolved from this portion of liquified natural gas in first stage 78 of heat exchanger 80 so that the composition of the heat exchange medium in the shell side of first stage 78 is about 17 mole percent methane, 80 mole percent ethane and 3 mole percent propane. The lower boiling constituents continue to evolve from this heat transfer medium as it passes over baffle 104 and under baffle 106 into second stage 94. The composition of the heat exchange medium in second stage 94 is about 80 mole percent ethane and 20 mole percent propane.

The vapor evolved from this heat exchange medium, principally methane, bubbles out through second stage 94 of heat exchanger 80, thereby reducing the vapor pressure of the ethane in the boiling second stage and permitting a lower temperature in this stage.

A predetermined part of the liquid heat exchange medium is withdrawn from second stage 94 and taken to vaporizer 62 wherein it is vaporized. From the vaporizer the resulting vapor is conducted to commingling point 66 whereat it is mixed with the methane rich vapor withdrawn from the heat exchanger. The resulting composite gas stream has the composition 73 mole percent methane, 26 mole percent ethane and 1 mole percent propane. This composition is substantially the same as that of the body of liquified natural gas contained in storage vessel 10.

The vapor which is evolved from the body of liquified natural gas in storage vessel 10 is conducted through a closed cycle and returned to storage vessel 10 as a liquid. The net effect of this on the composition of the liquified natural gas stored in vessel 10, is to retain that composition at a fixed and unchanged value. This conveniently and efficiently nullifies the effect of weathering on the composition of the liquified natural gas in vessel 10.

The gas stream which is withdrawn from the system is that composite stream passing through conduit 68, which has substantially the same composition as does the body of liquified natural gas in vessel 10. Thus, this withdrawn gas stream is suitable for use as conventional natural gas.

Under normal conditions the amount of the composite gas stream passing through conduit 68 is quite small in relation to the total volume of stored liquified natural gas. When greater quantities of liquified gas are required, such as in "peak shaving" operations, additional quantities of liquified natural gas may be withdrawn directly from vessel 10 and vaporized to meet these requirements. The nature of this operation is such that it is readily automated thus reducing operating expenses.

Advantageously, the net effect of this process is to adjust that vapor which is inevitably evolved from a stored body of multi-component cryogenic liquid to a composition approximating that of the stored body of cryogenic liquid, while maintaining the composition of that stored body at a substantially constant value.

As will be understood by those skilled in the art what has been described are preferred embodiments of this invention, however, modifications and changes may be made therein without departing from the spirit and scope of the following claims.

What is claimed is:

1. A process comprising the steps of:

compressing the methane rich vapor emitted from a stored body of liquified natural gas;

condensing the resultant pressurized methane rich vapor by contacting said pressurized vapor in an indirect heat exchange relationship in a plurality of stages with a portion of said body of liquified natural gas to vaporize at least a part of the methane from said portion of liquified natural gas, and leave a higher boiling hydrocarbon liquid residue;

6

passing both said vaporized methane and said liquid residue through said plurality of stages together; withdrawing said vaporized methane and said liquid residue separately from the last of said stages; combining a stream of said liquid residue and said vaporized methane to produce a combined stream; flashing the pressurized condensate produced in said condensing step to produce a liquid fraction and a vapor fraction; combining said liquid fraction with the stored body of liquified natural gas; and returning said vapor fraction to said compressing step.

2. A process comprising:

conducting the vapor emitted from the body of a multi-component cryogenic liquid to a compression zone; compressing said vapor;

conducting said compressed vapor to a heat transfer zone;

separating a portion of said cryogenic liquid from the body thereof;

conducting said portion of cryogenic liquid to said heat transfer zone;

effecting heat transfer in a plurality of stages between said portion of cryogenic liquid and said compressed vapor to condense said compressed vapor, and to vaporize at least a portion of a volatile component from said portion of cryogenic liquid, leaving an enriched cryogenic liquid;

passing both the vaporized portion of said volatile component and said enriched cryogenic liquid through said plurality of stages together;

withdrawing the vaporized volatile component and said enriched cryogenic liquid separately from the last of said stages;

reducing the pressure on said compressed, condensed vapor to produce a liquid fraction and a vapor fraction;

conducting said liquid fraction to said body of multi-component cryogenic liquid;

conducting said vapor fraction to said compression zone; and

combining said volatile component and said enriched cryogenic liquid.

3. A process comprising:

the first stage steps of compressing the vapor emitted from the body of a multi-component cryogenic liquid, condensing the resultant pressurized condensate to produce a vapor fraction and a liquid fraction;

the second stage steps of compressing the resultant vapor from said first stage flashing, condensing the resultant pressurized vapor, flashing the resultant pressurized condensate to produce a vapor fraction and a liquid fraction;

combining the liquid fractions resulting from said first and second stage flashing steps and returning said combined liquid to said body of cryogenic liquid; and conducting the vapor fraction resulting from said second stage flashing step to said first stage compressing step.

4. The process of claim 3 wherein said first stage condensing step comprises:

contacting said first stage pressurized vapor in an indirect heat exchange relationship with a portion of said body of cryogenic liquid to volatilize at least a part of the more volatile components from said body of cryogenic liquid and leave a residual liquid; and said second stage condensing step comprises:

contacting said second stage pressurized vapor in an indirect heat exchange relationship with at least a portion of said residual liquid to produce an enriched residual liquid.

7

5. The process comprising the steps in a closed system of:
- withdrawing the vaporous boil-off fraction from a stored body of cryogenic liquid;
 - pressurizing said boil-off fraction;
 - withdrawing a liquid portion of said stored body of cryogenic liquid;
 - condensing said pressurized boil-off fraction by contacting it heat-exchangeably in a plurality of stages with said withdrawn liquid portion of cryogenic liquid whereby a part of said liquid portion is volatilized to produce a vapor stream and a liquid residue;
 - passing both said vapor stream and said liquid residue through said plurality of stages together; and
 - withdrawing said vapor stream and said liquid residue from said closed system at the last of said stages.
6. The process of claim 5 including the step of combining said withdrawn vapor stream and liquid residue to produce a combined stream.
7. The storage system comprising in a closed system:
- means for withdrawing the boil-off fraction from a stored body of cryogenic liquid;
 - means for pressurizing said boil-off fraction;
 - means for withdrawing a portion of said stored body of cryogenic liquid;
 - means for condensing said pressurized boil-off fraction comprising means for contacting said withdrawn portion of cryogenic liquid heat-exchangeably in a plurality of stages with said boil-off fraction to volatilize a part of said portion of cryogenic liquid to produce a vapor stream and a liquid residue;
 - means for passing both said vapor stream and said liquid residue through said plurality of stages together; and
 - means for withdrawing said vapor stream and liquid residue from said closed system at the last of said stages.
8. A cryogenic liquid storage system adapted to maintain the proportions of the components of a body of multi-

8

component cryogenic liquid at a constant value which comprises:

- an insulated storage vessel;
- compressor means adapted for compressing a vaporous material evolved from said body of liquid;
- indirect heat exchange means for cooling said compressed vaporous material to produce a pressurized liquid, said heat exchange means comprising means for contacting said vaporous material in heat-exchangeable relationship with a plurality of stages with a portion of said body of multi-component cryogenic liquid to vaporize a part of said portion and leave a liquid residue;
- means for passing both said vaporized part and said liquid residue through said plurality of stages together;
- means for withdrawing said vaporized part and said liquid residue separately from the last of said stages;
- flasher means for reducing the pressure on said pressurized liquid to produce a liquid fraction and a gaseous fraction;
- means for returning said liquid fraction to said body of liquid, and said gaseous fraction to said compressor means; and
- means for combining said vaporized part of said portion of said multi-component cryogenic liquid and a stream of said liquid residue.

References Cited by the Examiner

UNITED STATES PATENTS

2,944,405	7/1960	Basore et al.	62—54
2,959,928	11/1960	Maker	62—54
3,093,974	6/1963	Templer et al.	62—51
3,096,625	7/1963	Legatski	62—54
3,106,827	10/1963	Schlumberger	62—55 X
3,112,617	12/1963	Tafreshi	62—54
3,132,489	5/1964	Maher et al.	62—54
3,195,316	7/1965	Maher et al.	62—54

LLOYD L. KING, *Primary Examiner*.