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METHOD AND APPARATUS FOR SAMPLING REFRIGERATED VOLATILE LIQUIDS

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FIG. 1

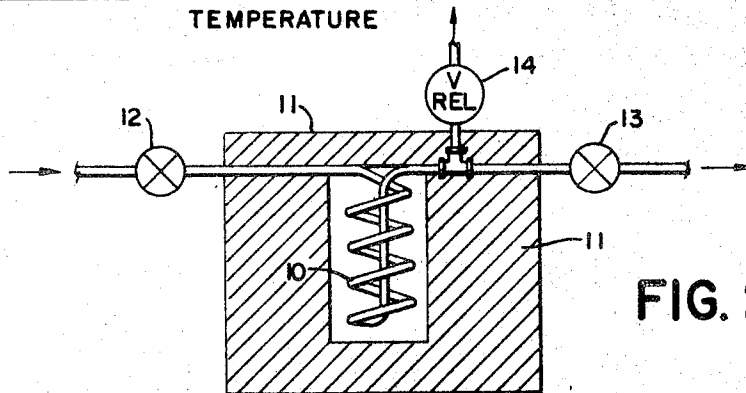
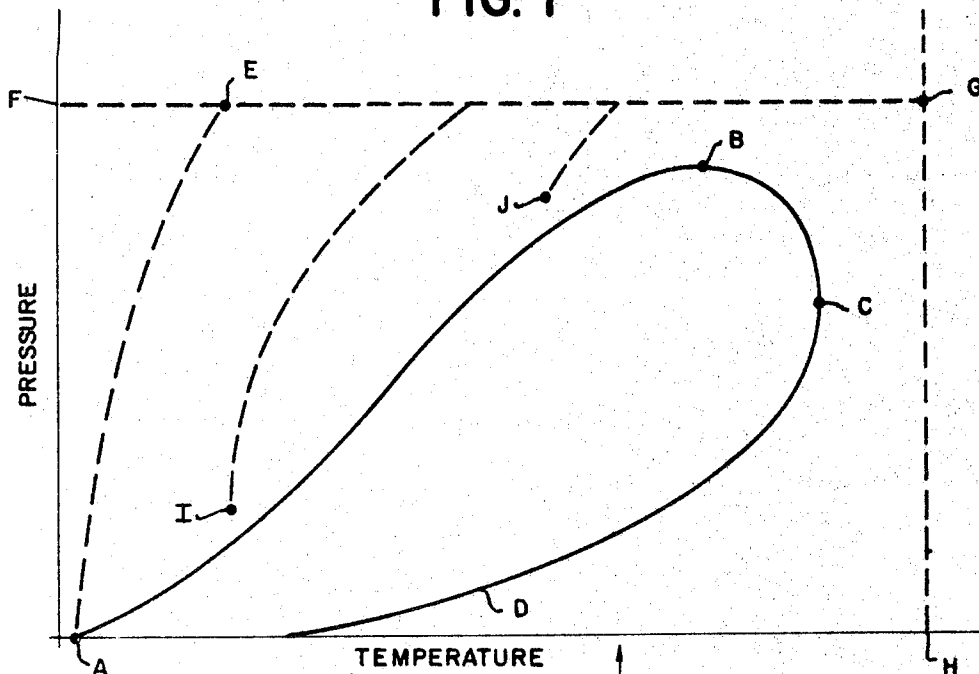


FIG. 2

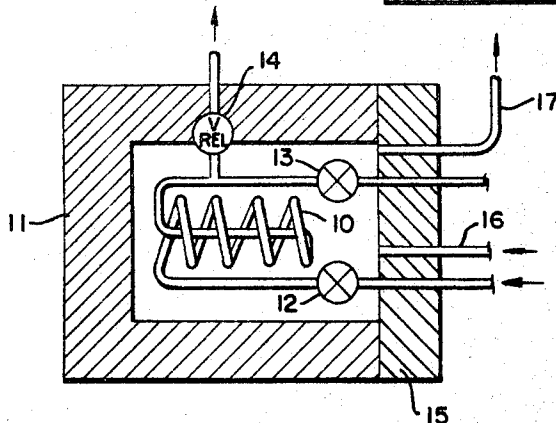


FIG. 3

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METHOD AND APPARATUS FOR SAMPLING REFRIGERATED VOLATILE LIQUIDS

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10 Claims

ABSTRACT OF THE DISCLOSURE

Method and apparatus for sampling refrigerated mixtures of volatile liquids are disclosed. A sample of the mixture is flowed into an insulated, pre-cooled sample container until the container is completely filled, whereupon it is sealed. The sample is warmed at constant volume until the pressure attains a predetermined value substantially greater than the cricondenbar of the mixture, at which point a pressure relief valve is actuated and the sample is further warmed at constant pressure until the desired sample temperature is reached. If the sample temperature is lower than the cricondenbar of the mixture, the sample can be confined in the apparatus indefinitely. If the sample temperature is higher than the cricondenbar of the mixture, the pressure of the sample can be reduced and the now gaseous sample can be analyzed or transferred to another container. By this procedure the sample is vaporized without fractionation; it is maintained in the single-phase fluid state, and never allowed to separate into a two-phase liquid-vapor condition.

BACKGROUND OF THE INVENTION

This invention relates to the sampling of liquefied gas mixtures for analytic purposes, and more particularly to a method and apparatus for obtaining a representative sample of a refrigerated volatile liquid mixture with no fractionation of the sample.

With the increasing processing, custody transfer and uses of liquefied gases and liquefied natural gas (LNG) in particular, there is an important need to obtain representative samples of such liquefied gases for analysis. Because these liquefied gases are frequently composed of compounds having varying degrees of volatility or are likely to contain impurities having different degrees of volatility, there is the difficult problem of maintaining the integrity of the composition of a sample as it is brought from its refrigerated liquid state to conditions of higher temperature where it can be conveniently analyzed or transported for analysis.

As one example, LNG is a mixture of hydrocarbon compounds of varying volatilities. When a sample of LNG is heated in an ordinary sample receptacle, methane tends to vaporize first, then ethane; thus, fractionation of the sample takes place, altering the composition of the sample mixture. In the case of some liquefied gases (helium, hydrogen and oxygen are examples) small concentrations of impurities can be very important; it is very difficult, sometimes impossible, to make precise determinations of the impurity levels or to repeat the results of these determinations by the use of conventional sampling methods.

Previous attempts at solving this problem have been through two procedures: (1) to flow the sample through a warming coil for a period of time considered to be long enough to establish vapor of steady composition at the outlet of the coil or (2) to vaporize a small sample of the liquid in a sufficiently large previously evacuated volume to contain all (or nearly all) the resulting vapor. These procedures are not completely satisfactory because

of the time consumed and the uncertainty as to time required in (1) and because of the unknown composition of the quantity of necessarily vented gas in (2).

SUMMARY OF THE INVENTION

The present invention provides a novel and precise method and apparatus for obtaining a representative homogeneous and compositionally unaltered sample of a refrigerated volatile liquid mixture. The invention relies upon the fact that such fluid mixtures exist in one of two distinct conditions: either as a single-phase fluid wherein the mixture is either a liquid or a gas, or in a two-phase condition wherein the mixture exists as both liquid and vapor. In this two-phase condition of the fluid mixture, the composition of the vapor is different from the composition of the liquid, and neither is the same as the composition of the refrigerated volatile liquid mixture sampled. In bringing a sample of such volatile mixture from its refrigerated liquefied condition to a warmed gaseous condition the present invention ensures that the sample is maintained in the single-phase fluid state and does not enter the two-phase condition where fractionation occurs.

In the practice of the invention a sample of refrigerated volatile liquid mixture is flowed from a source into a sample container. The fluid in the container is heated at constant volume until the pressure has attained a predetermined value greater than the cricondenbar of the mixture. Thereafter the fluid in the sample container is heated while the pressure of the fluid is maintained above the cricondenbar of the mixture until it attains a desired temperature. When the desired temperature is greater than the cricondenbar of the mixture, the fluid can be brought to a lower pressure for convenient analysis or transferred to another container for shipping or holding.

The apparatus of the invention comprises a sample container for holding a quantity of the refrigerated fluid, the container having volume means for maintaining the fluid within it at essentially constant volume; pressure means for maintaining the pressure of the fluid within the container at or below a predetermined maximum pressure greater than the cricondenbar of the sampled mixture; and temperature means for raising the temperature of the fluid in the sample container.

Further objects and advantages of the present invention will become apparent when the following description is read in connection with the accompanying drawing.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a pressure-temperature diagram showing the phase boundary of a volatile liquid mixture and illustrating the limits generally contemplated in the practice of the present invention.

FIG. 2 is a schematic diagram of a first specific embodiment of the sampling apparatus of the present invention.

FIG. 3 is a schematic diagram of a second specific embodiment of the sampling apparatus of the present invention.

DESCRIPTION OF THE SPECIFIC EMBODIMENTS

The method and apparatus of the present invention are adapted for use with various refrigerated volatile liquids, and particularly liquefied natural gases (LNG) comprised of hydrocarbon gas mixtures. The phase boundary diagram of FIG. 1 is representative of the characteristics of a typical LNG composition. Absolute values are not given in this diagram. The curve ABCD defines an envelope wherein the gas mixture exists in a two-phase condition, part liquid and part vapor. Point B is the cricondenbar of the gas mixture, marking the highest pressure, regardless of temperature, at which the two-phase condition can

exist. Point C is the cricondentherm of the mixture, indicating the point of highest temperature, regardless of pressure, at which the two-phase condition can exist.

Outside the envelope ABCD the gas is best thought of as a compressible fluid regardless of pressure and temperature, since its physical state varies primarily with respect to density. Thus, if the gas mixture is compressed from the point H to point G and then cooled to point E, its density would gradually change without an observable change in phase. Only when changes in temperature and pressure are carried out through the two-phase envelope ABCD, for example directly between G and D, can the creation of a part liquid and part vapor condition be distinctly noted. Therefore, the behavior of natural gas is referred to herein as that of a "fluid" whenever it is outside the two-phase region of the envelope, and by this is meant a single-phase fluid.

According to the method of the present invention a sample of refrigerated LNG can be obtained and brought to conditions of higher temperature and any pressure suitable for analysis with the assurance that the sample never passes through the two-phase envelope; the danger of fractionation and alteration of sample composition is eliminated. Thus, a sample of LNG at point A on FIG. 1, having typically a temperature of approximately -257° F. and essentially atmospheric pressure, is flowed into a sample container to be hereinafter described in detail. The sample of volatile fluid is initially maintained in the sample container under conditions of essentially constant volume and is permitted to warm. Upon warming at constant volume the pressure of the sample rises rapidly along the path AE shown in FIG. 1. It has been estimated that if such a fluid were warmed under such conditions the pressure would become on the order of 45,000 p.s.i. at a temperature of 150° F. However, when the pressure of the sample attains a predetermined value F at point E, a portion of the sample is vented and the sample is further heated along path EG under conditions of essentially constant pressure. The value of the predetermined pressure F is chosen so as to be substantially greater than the cricondenbar B of the fluid mixture. In typical LNG the cricondenbar occurs between 1,100 and 2,000 p.s.i.; a suitable, though arbitrary, relief pressure F which has been used in sampling such a fluid is 3,500 p.s.i.

The sample is then warmed at essentially constant pressure along the path EG until it reaches a temperature value H greater than the cricondentherm C of the mixture. At this point the sample can be further heated, analyzed in situ, transferred to another container, or brought to ambient pressure for analysis, all with the assurance that the sample has been continuously compositionally homogeneous. If the ambient temperature is less than the cricondentherm of the mixture, the sample can be maintained in the single-phase state in the sample container indefinitely.

Sampling with this method is equally practicable for samples initially in the compressed (or sub-cooled) liquid area of the phase diagram or up to or even above cricondenbar pressure. Thus, the method could easily apply to MLG and CNG liquids whose typical initial sampling points are illustrated in FIG. 1 by I and J, respectively. Other applications would be with refrigerated process streams in ethylene plants, helium purification streams, etc.

A first embodiment of apparatus for carrying out the sampling method of this invention is illustrated schematically in FIG. 2. A sample container 10 is formed of a metal coiled tube surrounded on all sides by removable thermal insulation 11. An inlet valve 12 is connected to one end of the container 10 and an outlet valve 13 is mounted in the other end. A pressure relief valve 14 is attached to the container 10 at a point between the valves 12 and 13. The pressure relief valve is adapted to vent the container when the pressure within the container reaches a predetermined value substantially greater than the cricondenbar of the fluid mixture to be sampled. In a

specific embodiment suitable for sampling LNG the pressure relief valve 14 is set to vent the sample container 10 at 3,500 p.s.i.

In the operation of the illustrated apparatus the inlet end of the sample container 10, i.e., the end controlled by valve 12, is connected to a source (not shown) of the LNG to be sampled. The LNG is flowed through the tubing until the coil is cooled to the temperature of the LNG (approximately -250° F.) and is completely filled with liquid. This condition can be determined visually by the appearance of a full liquid stream exiting from the downstream outlet control valve 13. At this point the outlet control valve 13 is closed, the inlet control valve 12 is closed, and the apparatus is disconnected from the LNG source. It will be recognized that after the initial cooling of the sample container the insulation 11 prevents ambient heat from vaporizing any of the liquid sample in the container before the valves 12 and 13 are closed. The insulation 11 is then removed from around the sample container 10, permitting the outer surface of the coil to be exposed to air at ambient temperature. The coil is warmed to the desired temperature—ambient or higher. If a temperature higher than the ambient is wanted, the coil can be placed in a hot water bath or otherwise heated. The warmed and now gaseous sample may be held in the sampling apparatus for any length of time desired, and is available for transfer to an I.C.C.-approved container for forwarding to a laboratory for analysis, or available for direct introduction into a chromatograph or other analytical instrument.

During the warming period the sample in the container 10 follows the path AEG shown in FIG. 1 and described above. The pressure of the sample rises rapidly until it attains 3,500 p.s.i. (F) at which point the pressure relief valve 14 is actuated, a portion of the sample is vented as necessary to maintain constant pressure, and the warming of the sample continues along the path EG until the desired temperature is reached.

In actual practice, apparatus for this purpose requires from 7 to 10 minutes of initial cooling of the insulated sample container 10 for full liquid filling. No provision for heating or vaporizing low-pressure samples is normally required other than exposure of the sample container to ambient air.

A second specific embodiment of apparatus in accordance with this invention is shown in FIG. 3. Here, just as in the first embodiment, a coiled metal sample container 10 is surrounded by removable thermal insulation 11 and a removable insulated closure 15. The container is provided with inlet and outlet valves 12 and 13, respectively, and also with a pressure relief valve 14 adapted to vent the container when the pressure within the container reaches a predetermined value substantially greater than the cricondenbar of the mixture to be sampled. In addition, however, the insulation 11 is equipped with an inlet conduit 16 and an outlet conduit 17, both communicating with the space surrounding the sample container 10.

In the operation of the second embodiment of the invention, the sample container 10 is first evacuated and valves 12 and 13 are closed. The container 10 is connected at its inlet end to a source of the refrigerated mixture to be sampled and either this fluid or another cryogenic fluid (such as liquid nitrogen) is introduced through the inlet conduit 16 into the space surrounding the container circulated in contact with the surface of the container 10, and removed through the outlet conduit 17. This process pre-cools the sample container to a temperature approximating that of the mixture to be sampled, whereupon the inlet valve 12 is opened and a sample is introduced into the evacuated container 10. The valve 12 is again closed and the sampling operation is continued exactly in the manner already described in connection with the first embodiment. It should be noted that the outlet valve 13 remains closed during the sampling and none of the sampled fluid is vented during this time. This

is particularly advantageous when a flammable substance is sampled in a hazardous area, when toxic liquids are sampled, or when other conditions prevent the venting of the sampled fluid to pre-cool the apparatus.

I claim:

1. A method for sampling refrigerated volatile fluid mixture from a source comprising the steps of:
 - (a) flowing refrigerated volatile fluid at a first temperature and a first pressure from the source into a sample container;
 - (b) increasing the temperature of the fluid in the sample container while maintaining the fluid at an essentially constant volume until the fluid attains a predetermined second pressure greater than the cricondenbar of the fluid mixture; and thereafter
 - (c) continuing to raise the temperature of the fluid in the sample container while maintaining the pressure of the fluid at a value greater than the cricondenbar of the fluid mixture until the temperature of the fluid reaches a desired second temperature.
2. The method according to claim 1 wherein the second temperature is higher than the cricondenthem of the fluid mixture, and further comprising the step of reducing the pressure of the fluid in the sample container after the fluid has attained said second temperature.
3. The method according to claim 1 wherein the second temperature is ambient temperature.
4. The method according to claim 1 wherein after the fluid in the sample container attains the second pressure the fluid is maintained at said second pressure until said fluid attains the second temperature.
5. The method according to claim 1 wherein after the fluid in the sample container attains the second pressure the fluid is maintained at an essentially constant pressure until the fluid attains the second temperature.
6. The method according to claim 1 wherein the sample container is initially evacuated and cooled to a temperature at or near the first temperature.
7. Apparatus for sampling refrigerated volatile fluid mixture at a first temperature and a first pressure from a source, the apparatus comprising:

- (a) a sample container for holding a quantity of said fluid;
- (b) volume means for maintaining the fluid in the container at an essentially constant volume;
- (c) pressure means for maintaining the pressure of the fluid in the sample container at or below a second pressure greater than the cricondenbar of the fluid mixture; and
- (d) temperature means for raising the temperature of the fluid in the sample container from the first temperature to a temperature greater than the cricondenthem of the fluid mixture.

8. Apparatus according to claim 7 wherein said volume means comprises one or more valves communicating with the interior of the sample container and adapted to seal off a space within said sample container.

9. Apparatus according to claim 7 wherein said pressure means comprises a pressure relief valve communicating with the interior of the sample container and adapted to vent a portion of the fluid sample within the container when the pressure of said fluid increases to a predetermined value greater than the cricondenbar of the fluid mixture.

10. Apparatus according to claim 7 wherein said sample container is formed of a material having good thermal transfer properties having an outer surface, and said temperature means comprises means for exposing the outer surface of the sample container to a thermal transfer substance having a temperature greater than the first temperature.

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S. CLEMENT SWISHER, Primary Examiner

U.S. Cl. X.R.

62—114; 73—421.5

Dedication

3,487,692.—*Harold L. Cook, Jr.*, Houston, Tex. METHOD AND APPARATUS FOR SAMPLING REFRIGERATED VOLATILE LIQUIDS. Patent dated Jan. 6, 1970. Dedication filed Sept. 16, 1971, by the assignee, *Vehoc Corporation*.

Hereby dedicates to the Public the entire remaining term of said patent.
[*Official Gazette December 28, 1971.*]