

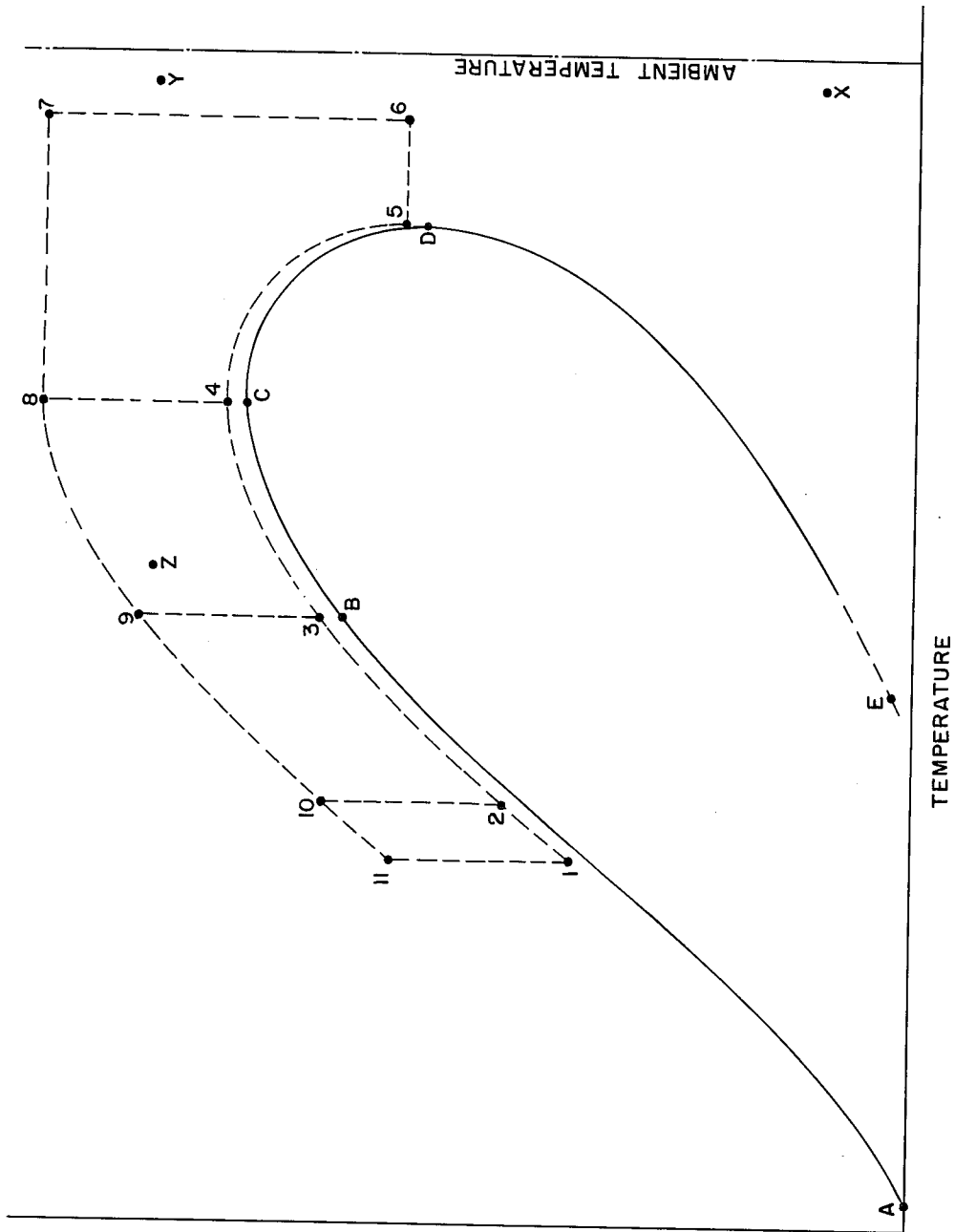
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H. C. SECORD ET AL

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METHOD OF STORING NATURAL GAS FOR TRANSPORT

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PRESSURE

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3,232,725

**METHOD OF STORING NATURAL GAS FOR TRANSPORT**

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This invention relates to the storage and transportation of natural hydrocarbon gases and, more particularly, to a method whereby a natural gas is contained in a dense single-fluid state suitable for transport, particularly by ship, at minimal compression, refrigeration and containment costs per unit weight of gas.

Vast amounts of hydrocarbon gases are taken from oil-fields in regions so far removed or separated by water from sources of demand that much of it has not heretofore been put to commercially profitable use. Certain heavier gases rich in propane and/or butane sometimes are recovered and transported as liquids (L.P.G.), but the lighter natural gases consisting principally of methane are more often flashed off and burned or vented at the well-head. It is the broad purpose of this invention to provide a new and improved method for storing and transporting these lighter hydrocarbon gases which are rich in methane and thus make their enormous energy potential available in all parts of the world. In particular, the new method is intended to make use of ships by which gas can be transported in bulk.

Several methods have been proposed heretofore for the storage and shipment of light hydrocarbon gases rich in methane but none of them has been entirely satisfactory. One common approach has been to liquefy the gas at the extremely low temperature ( $-258^{\circ}$  F.) at which pure methane liquefies at atmospheric pressure. Though this concept of liquefying methane-rich natural gas produces about a 600-fold increase in density, the cost of refrigerating commercial quantities of the gas is virtually prohibitive in most practical applications.

Broadly stated, the invention provides a method of storing for transport a natural gas containing at least 50 mol percent methane and at least 75 mol percent methane-plus-ethane, the remainder being heavier hydrocarbons and up to 20 mol percent inert constituents, and having a gross calorific value of from 800 B.t.u./s.c.f. to 1800 B.t.u./s.c.f. (The "gross" calorific value is intended in all references to B.t.u. ratings hereinafter set forth, and is that total or gross heating value obtained by burning one cubic foot of the gas mixture at 14.7 p.s.i.a., with air, cooling the products of combustion to  $60^{\circ}$  F., and condensing the moisture formed.) The steps of the method include compressing and refrigerating the gas to an operating state characterized by certain limits of pressure and temperature. The maximum operating temperature is  $20^{\circ}$  F. less than ambient temperature but not above  $32^{\circ}$  F. The minimum operating temperature is about the critical temperature of methane. The maximum operating pressure is 500 p.s.i. above the bubble point-dew point pressure of the gas at operating temperatures less than the cricondenbar of the gas and is 500 p.s.i. above the cricondenbar pressure of the gas at operating temperatures in excess of the cricondenbar of the gas. The minimum operating pressure is 50 p.s.i. above the bubble point-dew point pressure of the gas at operating temperatures less than the cricondenbar of the gas and is 50 p.s.i. above the cricondenbar pressure of the gas at operating temperatures in excess of the cricondenbar of the gas. When the gas is thus compressed and refrigerated, it is contained in the operating state to prevent expansion of the gas.

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Then the contained gas is thermally insulated against heat leakage into the gas so that it remains in the operating state throughout the duration of its containment. As a result, the gas is maintained in a dense single-fluid phase without ullage suitable for transport at minimal compression, refrigeration and containment cost per unit weight of gas.

The term "natural gas" as used herein in regard to the method of the invention is intended to include mixtures of hydrocarbon gases containing at least 50 mol percent methane and at least 75 mol percent methane-plus-ethane together with propane and butane and in most instances some heavier hydrocarbons and inert constituents. Such gases will have a gross calorific value of from 800 to 1800 B.t.u./s.c.f. This definition of the term includes well-head gases, gases separated from crude oil at a wellhead and tail gases from oil refineries and other processing plants, but it excludes propane-butane mixtures conventionally handled in the liquid state as "L.P.G." and artificially prepared solutions of pure methane dissolved in a heavier carrier such as ethane.

Various natural gases are therefore suitable for the practice of this invention. For example, a Sahara gas having a critical temperature of  $-53^{\circ}$  F. and a critical pressure of 1144 p.s.i.a., with a calorific value of 1200 B.t.u./s.c.f., has the following composition on a mol percent basis:

Methane -----	83.92
Ethane -----	7.83
Propane -----	3.17
Isobutane -----	0.87
Normal butane -----	1.08
Isopentane -----	0.55
Normal pentane -----	0.41
Hexane -----	0.52
Inerts -----	1.65

On the other hand, a typical Venezuelan gas having a critical temperature of  $+10^{\circ}$  F. and a critical pressure of 1200 p.s.i.a., with a calorific value of 1534 B.t.u./s.c.f., is of the following mol percent composition:

Methane -----	61.37
Ethane -----	16.84
Propane -----	11.68
Isobutane -----	1.53
Normal butane -----	4.29
Isopentane -----	0.84
Normal pentane -----	1.39
Hexane -----	0.61
Inerts -----	1.45

By containing natural gas in the operating state described previously, its density can be increased to a very great extent with surprisingly minimal compression and refrigeration costs. As a result, the gas is capable of being transported, particularly by ship, at far less expense than by conventional atmospheric pressure liquefaction processes.

The contemplated compression and refrigeration is particularly favorable for shipment of rich hydrocarbon gases having relatively high critical temperatures (for example,  $-50^{\circ}$  F. at 1200 B.t.u./s.c.f. to  $0^{\circ}$  F. at 1500 B.t.u./s.c.f.), whereas with known liquefaction processes it is not economical to carry much propane, butane or pentane along with methane due to wasteful over-refrigeration of these components. Since all associated gas and much "dry field" gas are rich in these heavier hydrocarbons, the present method is of great commercial importance inasmuch as it economizes with higher operating temperatures and lower operating pressures while transporting the valuable heavier components to the market for separation after shipment. Even leaner

gases (from 800 to 1200 B.t.u./s.c.f.), can be shipped more cheaply by the method of the invention where the voyage is relatively short (less than 2000 miles) because the low fixed cost for refrigeration, which is independent of distance, much more than offsets the higher containment costs on board ship due to higher pressures required and lower absolute densities.

The method of the invention may be better understood by referring to the accompanying drawings, which is a pressure-temperature diagram of a representative natural gas showing the contemplated operating state.

Absolute values are not given in this diagram but the shape of the various curves is illustrative of a typical natural gas composition of the type described previously. The curve ABCDE defines the envelope wherein the gas exists in a two-phase state, part liquid and part vapor. Point A indicates the liquefaction temperature of the gas at atmospheric pressure and in absolute terms it might be approximately  $-258^{\circ}$  F. Point B is the true critical point of the gas at which the various lines of uniform liquid and vapor concentrations within the two-phase region of the envelope converge. Point C is the cricondenbar of the gas, marking the point of highest pressure, regardless of temperature, at which the two-phase condition can exist. Point D is the cricondentherm of the gas and it indicates the point of highest temperature, regardless of pressure, at which the two-phase condition can exist.

From A to B the envelope curve is generally referred to as the bubble point line since it marks those definite equilibrium states where vapor will begin to appear, for example during isothermal expansion of the gas. From the critical point B to the point E on the envelope, the curve is commonly referred to as the dew point line at which liquid begins to condense, for example during isobaric cooling of the gas. Critical points of representative natural gases contemplated for use in this method are at pressures of about 675 p.s.i.a to 2000 p.s.i.a. and temperatures of about  $-125^{\circ}$  F. to  $+145^{\circ}$  F.

Within the two-phase envelope ABCDE, it can properly be said that the gas exists as a "liquid" and a "vapor" but outside the envelope it 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 is compressed from the point X to Y and then cooled to Z, its density would gradually change without a distinct change in phase. Only when changes in gas temperature and pressure are carried out through the two-phase envelope, for example directly between X and Z, 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 compressible single-phase fluid.

In the broadest form of the new method, the gas is compressed and refrigerated to an operating state circumscribed by the dotted lines connecting points 1 to 11 on the diagram. Thus, the gas is to be brought to a temperature below the dotted line connecting the points 6 and 7 in the drawing, which should not be more than  $+32^{\circ}$  F. and in no event in excess of  $20^{\circ}$  F. below ambient temperature. By "ambient temperature" is meant the environmental temperature at the point where the gas is compressed and refrigerated into the operating state. Some refrigeration is therefore necessary in all forms of the contemplated method, if only by expansion cooling with work as the gas is loaded into containers. The diagram also indicates the minimum operating temperature by the dotted line 11-1, which is the critical temperature of methane ( $-116^{\circ}$  F.). In no case should the gas be cooled below about  $-116^{\circ}$  F. in this new method of storage for shipment because refrigeration costs begin to rise steeply, the gain in density falls off, and the cost of metal containers with the required high

degree of notch toughness markedly increases at temperatures below that region.

The minimum operating pressure contemplated by the invention is shown in the diagram by the dotted line connecting the points 1 to 6. It is never less than 50 p.s.i. above the bubble point-dew point pressure of the gas at temperatures less than the cricondentherm D; and, at operating temperatures in excess of the cricondentherm D, the minimum operating pressure is 50 p.s.i. above the cricondentherm pressure. The latter will be an effective lower pressure limit only when the two-phase envelope ABCDE does not project its cricondentherm D beyond the maximum temperature line 6 to 7, which may or may not be the case depending upon the composition of the gas. It should be noted that the point 5 in the diagram is not actually on the envelope curve, but rather it marks a point which is equal in temperature to the cricondentherm D but 50 p.s.i. above it, and therefore point 5 is outside the envelope.

This parameter of minimum pressure insures that the gas will always be stored and transported in the single-phase compressible fluid state by avoiding entry into the two-phase envelope ABCDE where an interface of liquid and vapor will begin to appear. Ullage, a vapor pocket over the liquid, cannot therefore be present with its attendant disadvantage of liquid slop, and indeed there is no need for it in the present method (as there is in L.N.G. and L.P.G. methods) because a rise of temperature is accompanied by a tolerable rise in pressure in the single-phase highly compressible fluid operating state. In addition to the problem of slop, operation with ullage in the two-phase region encounters greatly reduced densities which prevent full use of costly containers.

The maximum operating pressure in the broad form of the method is shown in the diagram by the dotted line connecting the points 7 to 11. At operating temperatures less than the cricondenbar C, the upper pressure limit is 500 p.s.i. above the bubble point-dew point line. The limit continues at operating temperatures above the cricondenbar C as 500 p.s.i. above the cricondenbar of the gas. This upper limit on operating pressure should not be exceeded because above it the cost of compressing, refrigerating and containing the gas becomes quite uneconomical.

This broad form of the method may be utilized to transport a natural gas by ship. Once the gas is brought into the operating state it may be loaded into a multiplicity of metal pressure bottle containers closely stacked in the holds of large fast ships or barges. These containers are resistant internally to the chosen operating temperature and pressure. The holds should be internally insulated throughout to keep the gas and its containers essentially at the loading temperature throughout the delivery voyage and also to keep the substantially empty containers near that temperature during the return voyage. At all times during loading and unloading of the containers, the gas is maintained in the single-phase compressible fluid condition which characterizes the operating state, in order to insure uniformity of composition and minimal undesirable temperature effects. Since the gas is best prepared at a relatively constant rate for such shipment and delivered with similar uniform flow rates to consumers, one ship is preferably available for loading at all times while another is unloading and the remainder of the fleet plies between the two terminal ports. Thus, at least four ships are required. This avoids the costs and double loading and unloading operations from static storage tanks which otherwise would be required at both ports. Such storage is of course not precluded where site conditions and special circumstances, such as delivery to several terminals, favor it. In some instances, it may be profitable to add propane to a leaner natural gas prior to shipment in order to obtain a higher critical temperature for the mixture and thus to reduce the operating pressure at the chosen operating temperature, the

propane being separated on delivery and returned on the ship to the loading port for re-use.

There is a further advantage in using this broad form of the method to transport natural gas by ship, as compared to conventional transportation by L.P.G. and L.N.G. techniques. Because of the relatively high temperatures in the present method, heat leakage into the contained gas during the voyage is greatly reduced and far less insulation, which is costly both in itself and because of its bulk and weight, is required. The minor amount of heat leakage which does occur can be fully off-set by the use of some of the gas cargo as fuel for the ship or, if oil fuel is cheaper, by a few degrees extra initial refrigeration. In any case, there is never any need for positively induced refrigeration of the gas cargo on board the ship or of venting boil-off gas.

Within the broad range of maximum and minimum temperatures and pressures described previously, economic considerations in the practice of the method may favor operation at the lowest temperature feasible with low-alloy steel bottles. Therefore, it can be said that there is a preferred operating temperature range of from  $-50^{\circ}$  F. to  $-80^{\circ}$  F., the latter being safely above (about  $35^{\circ}$  F.) the Nil Ductility Test temperature for materials such as 1 to 2 percent nickel steel which has been quenched and tempered to secure an ultimate tensile strength approaching 120,000 p.s.i. Such material has a thickness limitation of about 0.75 inch, and with a safety factor UTS/3.2 this limits the operating pressure accordingly to about 1340 p.s.i.a. in gas containers having an outside diameter of 42 inches which is typical of present design limitations for containers made with "line pipe." For very lean gases, it limits the operating pressure to about 1875 p.s.i. with gas containers having a diameter of 30 inches.

The optimum operating conditions within these practical limits will depend on the composition of the mixture to be shipped, the preferred working pressure ranging from a minimum of about 600 p.s.i.a. for a 1750 B.t.u./s.c.f. gas to about 1100 p.s.i.a. for a 1200 B.t.u./s.c.f. gas or to about 1800 p.s.i.a. for a 900 B.t.u./s.c.f. gas containing a relatively large amount of inerts. The minimum temperature of  $-80^{\circ}$  F. in this preferred range is so far below the critical temperature of very rich gases that the single-phase fluid is relatively less compressible and operation far above the bubble point pressure is less economical. With leaner gases having critical temperatures near or even below the minimum temperature of  $-80^{\circ}$  F., operation considerably above the bubble point pressure may be more economical.

Having described the broad operating states contemplated in the present method and also a relatively narrow region of operating temperature therewithin, some attention should be given to the basic subdivisions of the operating state distinguished by operation above and below the critical temperature of the gas. In one form of the new method, the gas is refrigerated and compressed to an operating state wherein the maximum operating temperature is the critical temperature of the gas and the minimum operating temperature is about  $-90^{\circ}$  F. Within these temperature limits, the operating pressure may vary depending upon the composition of the gas mixture, but in all instances it will be at least 50 p.s.i. above the bubble point pressure of the gas at the operating temperature and not in excess of 500 p.s.i. above the bubble point pressure of the gas at the operating temperature.

The accompanying pressure-temperature diagram indicates these limits. The maximum operating temperature is shown by the dotted line connecting the points 3 and 9, the minimum operating temperature is shown by the dotted line connecting the points 2 and 10, the maximum operating pressure is indicated by the dotted line connecting the points 9 and 10, and the minimum operating pressure is indicated by the dotted line connecting the points 2 and 3.

In restricting the operating temperature to below the critical temperature of the gas in this manner, it is preferable to achieve a 350 to 400-fold increase in density of the gas relative to its density at atmospheric pressure and temperature. For example, a rich gas of 1535 B.t.u./s.c.f. and 0.9 specific gravity (relative to air) at  $-75^{\circ}$  F. has a bubble point pressure of about 650 p.s.i.a. and it would preferably be loaded to a pressure of 750 p.s.i.a. to give a density of 27 lb./ft.<sup>3</sup>, which is 388 times its normal density and about the same density as that of normally lean natural gas liquefied by refrigeration alone at substantially atmospheric pressure. On the other hand, a lean gas of 1080 B.t.u./s.c.f. and 0.67 specific gravity would call for a working pressure of about 1350 p.s.i.a. at  $-75^{\circ}$  F., giving approximately 18 lb./ft.<sup>3</sup> and a 350-fold increase.

In another form of the new method, the minimum operating temperature is the critical temperature of the gas and the maximum operating temperature is  $20^{\circ}$  F. less than ambient temperature but not above  $32^{\circ}$  F. These upper and lower limits on temperatures are shown respectively by the dotted lines in the diagram connecting points 6 and 7 and points 3 and 9. The operating pressure may again vary within these temperature limits depending upon the composition of the gas mixture, but in no event will it exceed 500 p.s.i. above the dew point pressure of the gas at operating temperatures less than the cricondenbar temperature of the gas or 500 p.s.i. above the cricondenbar of the gas at operating temperature in excess of the cricondenbar temperature of the gas. Relating this to the diagram, the dotted line connecting the points 8 and 9 indicates the maximum pressure at operating temperatures in this form of the method below the temperature of the cricondenbar C and the dotted line connecting the points 7 and 8 indicates the maximum pressure for operation at temperatures in excess of the cricondenbar C. The minimum operating pressure in this embodiment is 50 p.s.i. above the upper dew point pressure of the gas at operating temperatures less than the cricondenbar temperature of the gas and is 50 p.s.i. above the cricondenbar pressure of the gas at operating temperatures in excess of the cricondenbar of the gas. Again relating this to the diagram, the dotted line connecting the points 3 to 5 indicates the minimum pressure at operating temperatures less than the cricondenbar D, and the dotted line connecting the points 5 and 6 indicates the minimum pressure at operating temperatures in excess of the cricondenbar D. As noted previously, the minimum pressure indicated by the dotted line connecting the points 5 and 6 may be of no consequence in the event the cricondenbar D of the gas extends beyond the upper temperature limit indicated by the dotted line connecting the points 6 and 7.

For a better understanding of the invention, there follows a description of the method as it applies to the transport by ship of the 1534 B.t.u./s.c.f. Venezuelan gas mentioned previously. This gas is piped from the wellhead along with its associated crude oil and is delivered to separator facilities. Here the gas is flashed from the crude oil in three stages of descending pressure and is dehydrated by a process employing a molecular sieve. The dehydration treatment temperature is approximately  $120^{\circ}$  F. After dehydration, the gas is compressed to 1765 p.s.i.a. in centrifugal compressors. Subsequent to this compression the gas is cooled to  $105^{\circ}$  F., which at that pressure maintains the gas completely in the single-fluid phase.

Since the method of the invention particularly contemplates the transportation of natural gas by ship, it may be necessary to carry the gas from the compression and dehydration facilities by means of a pipeline to a ship-loading platform. Depending upon the topographical conditions where the method is practiced, this pipeline may traverse land or water or both. When the gas reaches the loading platform, it is reduced in pressure and tem-

perature to about 1500 p.s.i.a. and 80° F. and it is still in the single fluid phase. Thereafter, the gas is refrigerated and expanded to its operating state of 950 p.s.i.a. and -50° F. and a density of 24.7 pounds per cubic foot. A suitable refrigerant is propylene which is vaporized at atmospheric pressure and -54° F. From that vaporized state the propylene is compressed to 258 p.s.i.a. and is condensed to liquid at 105° F.

Ships used to transport gas in accordance with this invention may carry in their holds a large number of pipe-like bottles capped at both ends. One such bottle may have an outside diameter of 42 inches, a wall of 0.53 inch and a length of 50 feet. Upon completing the expansion and refrigeration stage at the ship-loading platform, the gas is passed into these bottles in the thermally insulated hold of a ship. The gas cargo in the loaded bottles is at a pressure of 950 p.s.i.a. and -50° F. and during a voyage of several days this temperature will rise only about 2° F. with no positive refrigeration. The slight thermal expansion which does occur may be compensated by using the gas cargo as fuel for the ship's diesel engines. Thus, the gas within the bottles may be at a temperature of about -48° F. and a pressure of about 875 p.s.i.a. when the ship arrives at its port of destination. One ship, for example, may transport 37.5 million pounds of this 1534 B.t.u./s.c.f. gas in this manner and when it is unloaded one million pounds may remain in the containers at 143 p.s.i.a. and -58° F. Allowing for some minor heat leakage during the return voyage and for fuel used in transit, the ship may arrive back at the point of loading with 0.35 million pounds of the gas in its containers at 51 p.s.i.a. and -45° F.

Natural gas transported in accordance with this invention may be separated at the point of destination essentially to methane for continuous supply into a transmission system and heavier ends such as ethane, L.P.G., and natural gasoline which may be piped separately to areas of use. The heavy ends may alternatively be converted mainly to methane by exothermic reaction with steam over a nickel-containing catalyst to augment further the pipe-line gas supply. In virtually all instances, the net cost to the consumer of natural gas and its components stored and transported over long distances pursuant to this method is substantially less than with any other process of water transport of gas known heretofore.

While the invention is described herein as a method of storing natural gas for transport, it applies also to the static storage of natural gas.

We claim:

1. A method of storing for transport a natural gas containing at least 50 mol percent methane and at least 75 mol percent methane-plus-ethane, the remainder being heavier hydrocarbons and up to 20 mol percent inert constituents, and having a gross calorific value of from 800 B.t.u./s.c.f. to 1800 B.t.u./s.c.f., which comprises:

(a) compressing and refrigerating said gas to an operating state wherein

(i) the maximum operating temperature is 20° F. less than ambient temperature but not above 32° F.,

(ii) the minimum operating temperature is about the critical temperature of methane,

(iii) the maximum operating pressure is 500 p.s.i. above the bubble point-dew point pressure of the gas at operating temperatures less than the cricondenbar of the gas and is 500 p.s.i. above the cricondenbar of the gas at operating temperatures in excess of the cricondenbar of the gas, and

(iv) the minimum operating pressure is 50 p.s.i. above the bubble point-dew point pressure of the gas at operating temperatures less than the cricondentherm of the gas and is 50 p.s.i. above the cricondentherm of the gas at operating

temperatures in excess of the cricondentherm of the gas;

(b) containing said gas in the operating state to prevent expansion of said gas; and

(c) thermally insulating the contained gas against substantial heat leakage into said gas so that it remains in said operating state throughout the duration of its containment;

(d) whereby the gas is maintained in a dense single-fluid phase without ullage suitable for storage and transport at minimal compression, refrigeration and containment costs per unit weight of gas.

2. A method of storing a natural gas according to claim 1 wherein the maximum and minimum operating temperatures are -50° F. and -80° F. respectively.

3. A method of storing a natural gas according to claim 2 wherein the density of the gas in the operating state is 300 to 400 times greater than its density at atmospheric pressure and temperature.

4. A method of storing natural gas according to claim 1 wherein said gas is contained in said operating state in a multiplicity of metal containers resistant to the chosen operating temperature and pressure, and said containers are surrounded by thermal insulation and transported by ship.

5. A method of storing natural gas according to claim 4 wherein said gas is loaded in and unloaded from at least four of said ships sequentially at a substantially uniform rate without static storage at the points of loading and unloading.

6. A method of storing for transport a natural gas containing at least 50 mol percent methane and at least 75 mol percent methane-plus-ethane, the remainder being heavier hydrocarbons and up to 20 mol percent inert constituents, and having a gross calorific value of from 800 B.t.u./s.c.f. to 1800 B.t.u./s.c.f., which comprises:

(a) compressing and refrigerating said gas to an operating state wherein

(i) the maximum operating temperature is the critical temperature of the gas,

(ii) the minimum operating temperature is about -90° F.,

(iii) the maximum operating pressure is 500 p.s.i. above the bubble point pressure of the gas at the operating temperature, and

(iv) the minimum operating pressure is 50 p.s.i. above the bubble point pressure of the gas at the operating temperature;

(b) containing said gas in the operating state to prevent expansion of said gas; and

(c) thermally insulating the contained gas against substantial heat leakage into said gas so that it remains in said operating state throughout the duration of its containment;

(d) whereby the gas is maintained in a dense single-fluid phase without ullage suitable for storage and transport at minimal compression, refrigeration and containment costs per unit weight of gas.

7. A method of storing a natural gas according to claim 6 wherein the density of the gas in the operating state is 350 to 400 times greater than its density at atmospheric pressure and temperature.

8. A method of storing natural gas according to claim 6 wherein said gas is contained in said operating state in a multiplicity of metal containers resistant to the chosen operating temperature and pressure, and said containers are surrounded by thermal insulation and transported by ship.

9. A method of storing natural gas according to claim 8 wherein said gas is loaded in and unloaded from at least four of said ships sequentially at a substantially uniform rate without static storage at the points of loading and unloading.

10. A method of storing for transport a natural gas

containing at least 50 mol percent methane and at least 75 mol percent methane-plus-ethane, the remainder being heavier hydrocarbons and up to 20 mol percent inert constituents, and having a gross calorific value of from 800 B.t.u./s.c.f. to 1800 B.t.u./s.c.f., which comprises:

- (a) compressing and refrigerating said gas to an operating state wherein
- (i) the maximum operating temperature is 20° F. less than ambient temperature but not above 32° F.,
  - (ii) the minimum operating temperature is the critical temperature of the gas,
  - (iii) the maximum operating pressure is 500 p.s.i. above the dew point pressure of the gas at operating temperatures less than the cricondenbar of the gas and is 500 p.s.i. above the cricondenbar of the gas at operating temperatures in excess of the cricondenbar of the gas, and
  - (iv) the minimum operating pressure is 50 p.s.i. above the dew point pressure of the gas at operating temperatures less than the cricondenbar of the gas and is 50 p.s.i. above the cricondenbar of the gas at operating temperatures in excess of the cricondenbar of the gas;
- (b) containing said gas in the operating state to prevent expansion of said gas; and
- (c) thermally insulating the contained gas against substantial heat leakage into said gas so that it remains in said operating state throughout the duration of its containment;
- (d) whereby the gas is maintained in a dense single-fluid phase without ullage suitable for storage and

transport at minimal compression, refrigeration and containment costs per unit weight of gas.

11. A method of storing natural gas according to claim 1 wherein said gas includes among its heavier hydrocarbons an additive of propane to increase the critical temperature of the gas and to lower the minimum operating pressure of the method.

12. A method of storing a natural gas according to claim 10 wherein the maximum operating temperature is -50° F. and the density of the gas in the operating state excluding any inerts is 300 to 350 times greater than its density at atmospheric pressure and temperature.

13. A method of storing natural gas according to claim 10 wherein said gas is contained in said operating state in a multiplicity of metal containers resistant to the chosen operating temperature and pressure, and said containers are surrounded by thermal insulation and transported by ship.

14. A method of storing natural gas according to claim 13 wherein said gas is loaded in and unloaded from at least four of said ships sequentially at a substantially uniform rate without static storage at the points of loading and unloading.

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MORRIS O. WOLK, *Primary Examiner*.

**Dedication**

3,232,725.—*Herbert Campbell Secord*, Markyate Herts, England and *Bernard J. Clarke*, White Plains, N.Y. METHOD OF STORING NATURAL GAS FOR TRANSPORT. Patent dated Feb. 1, 1966. 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.*]