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LIQUEFACTION OF NATURAL GAS AT SUPERCRITICAL PRESSURE
EMPLOYING A SINGLE REFRIGERATION CYCLE

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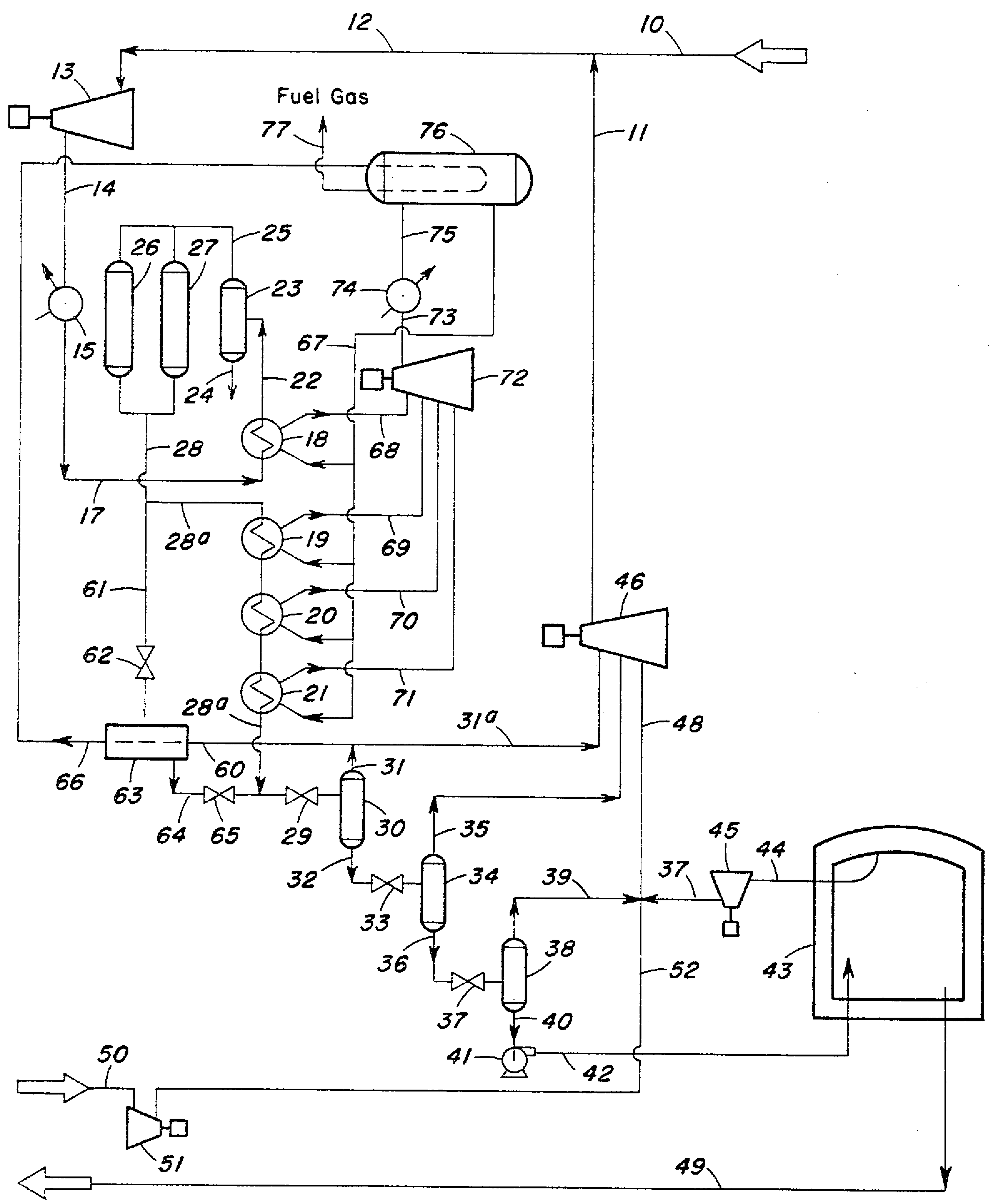

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LIQUEFACTION OF NATURAL GAS AT SUPER-CRITICAL PRESSURE EMPLOYING A SINGLE REFRIGERATION CYCLE

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Continuation-in-part of application Ser. No. 437,621, Feb. 18, 1965, which is a continuation-in-part of application Ser. No. 358,789, Apr. 10, 1964. This application July 6, 1967, Ser. No. 651,587

9 Claims. (Cl. 62—23)

ABSTRACT OF THE DISCLOSURE

A process for liquefying natural gas by compressing the gas to a pressure above the critical pressure thereof, cooling the gas by indirect heat transfer with a single refrigerant to a temperature slightly above the normal boiling point of the refrigerant and expanding the cooled gas to effect liquefaction thereof.

The present application constitutes a continuation-in-part of application Ser. No. 437,621, filed Feb. 18, 1965, now Patent No. 3,342,037 which is a continuation-in-part of U.S. patent application Ser. No. 358,789, filed Apr. 10, 1964, now abandoned.

This invention relates to a process for the liquefaction of a gas, and more particularly relates to a process and apparatus for the liquefaction of natural gas primarily comprised of methane, and including heavier hydrocarbons such as ethane, propane, butane and the like.

There are many reasons for reducing natural gas to a liquefied state. One of the main reasons for liquefying natural gas is the resultant reduction of the volume of the gas to about 1/600 of the volume of natural gas in the gaseous state. Such a reduction in volume permits the storage and transportation of liquefied natural gas in containers of more economical and practical design. Additionally, it is desirable to maintain a supply of gas through peak demand periods whereby such periods can be met by liquefied gas held in storage. Another important reason is the transportation of liquefied natural gas from a source of plentiful supply to a distant market where the source and supply may not be efficaciously joined by pipe lines and transportation in the gaseous state would be uneconomical.

The object of this invention is to provide an apparatus and method for the economical and efficient liquefaction of a gas, particularly natural gas, for storage and transportation.

Another object of this invention is to provide a process for the liquefaction of natural gas wherein the natural gas is compressed to a pressure above the supercritical pressure, and passed in heat exchange relationship through a refrigeration system, to remove, at relatively high temperatures, the heat as sensible heat, which would be, at lower pressures, latent heat at lower temperatures.

A further object of my invention is to provide a process for liquefying natural gas wherein the gas is compressed to a pressure above the supercritical pressures, cooled in a refrigeration system having a single refrigerant to conveniently remove at relatively high temperatures the sensible heat of the natural gas, which would at lower pressures result as latent heat at lower temperature, and thereafter expanding the thus cooled natural gas in a series of stages to produce liquefied natural gas at atmospheric pressure and at a temperature of about −258° F.

A still further object of my invention is to immediately compress the vapors removed from such expansion stages and combine such vapors with the feed introduced into the initial compressor wherein the pressure of the gas is raised to a pressure of about 1.3 times the critical pressure thereof.

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Still another object of my invention is to provide a method and apparatus for the liquefaction of natural gas wherein the quantity of nitrogen in the process is maintained at a low level, and the liquefied product is substantially free of nitrogen.

Other objects and fuller understanding of my invention may be had by referring to the following description taken in conjunction with the accompanying drawing, in which,

The drawing is a simplified, schematic flow diagram of an embodiment of the invention.

The natural gas to be treated in accordance with my invention will be a gas from which a part of the moisture and acid gases, such as carbon dioxide, hydrogen sulfide and the like have been removed in a manner familiar to those skilled in the art. In one embodiment of the invention, the natural gas after such treatment, and a recycle gas stream as hereinafter described, is introduced into a feed gas compressor wherein the pressure of the combined stream is increased from a pressure of about 600 p.s.i.g. to a pressure above the critical pressure of the gas, generally a pressure of about 1.3 times the critical pressure depending on the composition of the gas. The compressed gas is thereafter passed through a cooler and a first heat exchanger of a refrigeration system to remove any condensible heavier hydrocarbons. The cooled gas is then passed through the remaining heat exchangers of such refrigeration system to refrigerate the gas to a temperature slightly above the normal boiling point of the refrigerant. In the case of ethane, as the refrigerant, the normal boiling temperature would be about −125° F. and a natural gas primarily comprised of methane would be cooled to about or slightly above the critical temperature. The refrigerant preferred is ethane since it may be supplied by the natural gas. Of course, other refrigerants can be used provided they may be condensed with a cooling medium at a temperature of about 60° F. or less. Only one refrigerant is utilized in the refrigeration system. While a portion of the water has been removed in the gas prior to compression, additional moisture will be contained in the natural gas after cooling, and accordingly, is conveniently removed between the first and second heat exchangers of such refrigeration system.

The natural gas at a temperature slightly above the normal boiling point of the refrigerant is thereafter expanded into a first flash drum wherein a substantial portion of the gas is liquefied during the expansion. The gaseous overhead from the first flash drum, including nitrogen, is withdrawn and a portion thereof withdrawn from the process as fuel gas, after passing such portion through a heat exchanger to recuperate the cold therefrom. The liquefied natural gas from the first flash drum is thereafter successively expanded over a series of flash drums wherein the pressure of the liquefied natural gas is eventually reduced to atmospheric pressure. The liquefied natural gas is withdrawn from the last flash drum and passed to storage and transportation.

The flashed gases from each of the flash drums, except the last flash drum, are introduced into intermediate stages of a methane recycle compressor and thereafter combined with the natural gas feed. Such combined gas stream is passed to the feed gas compressor wherein the pressure of the gas is raised to a pressure within the aforementioned pressure range. There is a slight reduction in pressure of the liquefied natural gas from the last flash drum into the storage tank, and consequently a portion of the liquefied natural gas will vaporize in the storage tank. Such vaporized portion of the natural gas is also passed to a methane recycle compressor after passing through a centrifugal booster compressor.

Referring to the figure, which is a schematic flow diagram of an embodiment of the invention, the following describes this embodiment applied to the liquefaction of natural gas. It is understood, however, that the invention is also applicable to the liquefaction of other gases containing hydrocarbons, such as refinery gases and the like.

Lean natural gas, primarily comprised of methane, in line **10**, is combined with a recycled gaseous stream, as more fully hereinafter described, in line **11**, and passed through line **12** to a feed gas compressor **13**. The natural gas is compressed from a pressure of about 600 p.s.i.g. to a pressure of about 1.3 times the critical pressure of the gas stream. The compressed gas is passed through line **14** to cooler **15** and thence through line **17** to a heat exchanger **18** of a refrigeration system including heat exchangers **18**, **19**, **20** and **21**. The cooled gas is then passed through line **22** into a separator **23**. In separator **23**, any heavier hydrocarbons which may condense during passage through cooler **15** and heat exchanger **18** are withdrawn from separator **23** through line **24** and the compressed natural gas withdrawn through line **25** and passed to dryers **26** and **27** to remove residual amounts of moisture in the gas. The dryers **26** and **27** are operated in an alternate manner which is well known to those skilled in the art.

The dried gas in line **28** is split and a portion in line **28***a* passed through the remaining heat exchangers **19**, **20** and **21** of the refrigeration system wherein the gas is cooled by a refrigerant which is expanded into the heat exchangers of the refrigeration system.

The refrigeration system utilizes a single refrigerant as will be more fully hereinafter described. An important aspect of my invention is that the natural gas passing through the refrigeration system is cooled, without liquefaction, to a temperature slightly above the normal boiling point of the refrigerant providing the cooling requirements for the refrigeration system. The gas is readily cooled at such high pressures by using a single refrigerant whereby the heat is conveniently removed at relatively higher temperatures as sensible heat, which would, at lower pressures, show up as latent heat at a lower temperature.

The natural gas in line **28***a* together with another gaseous stream as more fully hereinafter described, is expanded across valve **29** to a lower pressure, such that a substantial portion of the natural gas is liquefied during such expansion and is thereupon introduced into flash drum **30**. The liquefied gas in flash drum **30** is withdrawn through line **32**, expanded across valve **33** and introduced into a second flash drum **34** whereby the temperature of the liquefied gas is further reduced. A geaseous phase in flash drum **34** is withdrawn through line **35** while the further cooled liquefied gas is withdrawn through line **36**. The liquefied gas in line **36** is thereafter further expanded across valve **37** and introduced into flash drum **38** wherein the liquefied gas is still further cooled. The expansion of the gas in line **28***a* and the liquefied gas in lines **32** and **36** are to lower pressures, such that the pressure of the liquefied gas in the last flash drum **38** is substantially at atmospheric pressure.

A gaseous phase is withdrawn from flash drum **38** through line **39** while the liquefied natural gas at about atmospheric pressure is withdrawn through line **40**. The liquefied natural gas in line **40** is passed by pump **41** through line **42** and introduced into a storage tank, generally indicated as **43**, maintained at atmoshperic pressure. Since the storage tank **43** is maintained at about atmospheric pressure, the temperature of the liquefied gas is about −257° F. If there is a small reduction in the pressure of the liquefied gas during passage to the storage tank **43** from flash drum **38**, additional cooling of the liquefied natural gas occurs thereby vaporizing a portion of the liquefied gas. The vapors formed during such additional expansion are withdrawn from the storage tank **43** through line **44**, and compressed in a centrifugal compressor **45**.

As a distinct feature of my invention, I contemplate taking the flashed gases from the flash drums and the storage tank and compressing such vapors in a recycle compressor **46** and combining such compressed stream with the natural gas feed to the plant. The gaseous phases in lines **31***a* and **35** are passed to an intermediate stage of the methane compressor **46**. The gaseous phase in line **39** is combined with the compressed gas stream in line **47** and passed via line **48** to an initial stage of the methane compressor **46**.

Loading the warm tanks of a vessel with the liquefied natural gas from storage tank **43** through line **49** will effect vaporization of a small portion of the liquefied natural gas which is then returned to the plant through line **50**, compressed in dockside centrifugal compressor **51** and is combined with the gas in line **48** through line **52** for compression in compressor **46**. The now compressed gas is withdrawn from compressor **49** through line **11** to be combined with the natural gas feed to the plant in line **10**.

Most natural gases contain nitrogen as a contaminant. It is desirable in the course of liquefaction to remove as much as possible of the nitrogen from the gas since nitrogen in the liquefied natural gas reduces the value thereof, particularly when carrying the gas in bulk transportation. In accordance with equilibrium conditions in flash drum **30**, the gaseous phase in line **31** contains a higher percentage of the nitrogen than the liquid phase in line **32**, introduced into the process. A portion of such gaseous phase in line **31** is withdrawn through line **60** and is utilized as a fuel gas in compressor drives and other equipment of the plant.

Since the gas in line **60** is at a relatively low temperature, it is desirable to recover the cold potential thereof prior to using such gas as a fuel gas. To recover such potential, a portion of the compressed gas in line **28** is passed through line **61** under the control of valve **62** to heat exchangers **63** and passed in heat exchange relation with the gas in line **60**. Once equilibrium has been reached, the amount of nitrogen introduced into the process with the natural gas feed will equal the amount of nitrogen in the fuel gas in line **60**, and the liquefied natural gas in storage tank **43**. That portion of the compressed gas in line **61** is withdrawn from heat exchanger **63** through line **64** under control valve **65** and combined with the gas leaving heat exchanger **21** prior to expansion through valve **29**. The gas in line **60** after passage through heat exchangers **63** is withdrawn through line **66**.

As a distinct advantage of my system as compared to prior processes, I am able to utilize one refrigerant, such as ethane, to provide the cooling requirements for refrigeration systems. Liquefied ethane in line **67** is expanded stagewise into heat exchangers **18**, **19**, **20** and **21** to remove the sensible heat of the compressed gas in line **28**. The thus expanded ethane is withdrawn from heat exchangers **18**, **19**, **20** and **21** through lines **68**, **69**, **70** and **71**, respectively, and is passed to an ethane compressor **72**. The gaseous ethane in lines **68**, **69** and **70** are introduced into intermediate stages of the compressor **72**, whereas the gaseous ethane in line **71** is introduced into a first stage thereof. The compresesd ethane is passed through line **73** to heat exchangers **74** wherein the ethane is cooled with a cooling medium having a temperature less than about 60° F., whereby the compressed ethane is condensed into the liquid phase. The liquefied ethane is passed through line **75** to ethane receiver **76**. The fuel gas in line **66** may be passed through ethane receiver **76** to further recover the cold potential of the fuel gas stream and is subsequently passed through line **77** to the points of use (not shown).

The following is an example of my invention pertaining to a specific natural gas wherein the quantity flow in pounds actually represents the ratio of flow in pounds per pound of LNG withdrawn from the process. Such natural gas has the following analysis:

Methane	99.5
Ethane	.1
Nitrogen	.4

With reference to the figure, 1.119 pounds of natural gas at a temperature of 60° F. in line **10** after being treated to remove acid gases and moisture is combined with 1.2693 pounds of recycled gas at a temperature of —15° F. in line **11**. The combined gas stream at a temperature of 16° F. and at a pressure of 600 p.s.i.a. is compressed to 1400 p.s.i.a. in compressor **15** and cooled to a temperature of 55° F. in heat exchanger **15** during passage against a cooling medium at a temperature of 50° F. The compressed gas is further cooled in heat exchanger **18** to a tempertaure of 5° F. and passed through dryers **26** and **27** wherein residual moisture is removed.

The compressed gas is thereafter serially passed through heat exchangers **19**, **20** and **21** and cooled to a temperature of —115° F. The gas withdrawn from heat exchanger **21** is at a pressure of 1360 p.s.i.a. as a result of a pressure drop of 40 p.s.i.a. through the aforementioned units. The gas is then expanded across expansion valve **29** into flash drum **30** to a pressure of 180 p.s.i.a. with a resulting decrease in temperature to —184° F. 1.4115 pounds of liquefied gas is withdrawn from flash drum **30** and expanded across valve **33** to a pressure of 55 p.s.i.a. and introduced into flash drum **34**. 1.1458 pounds of liquefied gas now at a temperature of —226° F. is then withdrawn from flash drum **34** and expanded across valve **37** to a pressure of 20 p.s.i.a. and introduced into flash drum **38** wherein the liquefied gas is further cooled to a temperature of —252° F. The liquefied gas in flash drum **38** is withdrawn through line **40** by pump **41** and passed to storage tank **43** maintained at 14.7 p.s.i.a. The additional slight expansion from flash drum **38** and storage tank **43** effects further cooling of the liquefied gas to a temperature of —257° F.

0.8578, 0.2657 and 0.1176 pound of a gaseous phase in lines **31*a***, **35** and **39** are passed together with 0.0282 pound of gas withdrawn from storage tank **43**, to methane recycle compressor **46** and compressed to a pressure of 600 p.s.i.a. and subsequently combined with the feed natural gas. 0.119 pound of flashed gas from flash drum **30** at a temperature of —184° F. is passed through heat exchanger **63** and ethane receiver **76** and withdrawn from the process as fuel gas in line **77**. It is understood to those skilled in the art that the above example is with respect to the natural gas of the aforementioned composition and that the temperatures and quantities will vary with the composition of the natural gas.

Gaseous ethane at a temperature of 0° F., —40° F., —80° F. and —120° F. is withdrawn from heat exchangers **18**, **19**, **20** and **21** through lines **68**, **69**, **70** and **71**, respectively, and compressed to 560 p.s.i.a. in compressor **72** and cooled in heat exchanger **74** to a temperature of 70° F. in heat exchange relation with a cooling medium having a temperature of 50° F.

The process of this invention is particularly effective for liquefying a natural gas primarily comprised of methane, i.e., greater than 98% methane, preferably greater than 99% methane. By maintaining pressures above the supercritical pressure of the gaseous stream throughout the cooling cycle, it is possible to use a single refrigerant to remove sensible heat at elevated temperatures which would, at lower pressures, result as latent heat at lower temperatures.

While I have shown and described a preferred embodiment of my invention, I am aware that variations may be made thereto, and, therefore, desire a broad interpretation of my invention within the scope of the disclosure herein and the following claims.

What is claimed:

1. A method of liquefying a hydrocarbon gas comprising:

(a) compressing said gas to a pressure above the critical pressure thereof;

(b) passing said compressed gas through a heat exchange zone, said gas being cooled by indirect heat transfer in said zone by a single expansion-compression refrigerant cycle to a temperature slightly above the normal boiling point of the refrigerant employed in the cycle, said gas being above the critical pressure during the passage through said heat exchange zone; and

(c) expanding said gas which is at the temperature attained in step (b) to effect cooling and liquefaction thereof.

2. The process of claim **1** wherein said hydrocarbon gas is natural gas.

3. The process of claim **2** wherein said refrigerant is ethane.

4. The process of claim **3** wherein said expansion is effected in a plurality of stages to reduce the pressure of the gas to about atmospheric pressure, said liquefaction occuring in the first stage.

5. The process of claim **4** wherein vapor is separated from the liquefied gas in each expansion stage and said vapor is recycled to step (a).

6. The process of claim **5** wherein a portion of the vapor separated in said first expansion stage is recovered as a fuel gas.

7. The process of claim **6** wherein the cooling in said heat exchange zone is effected in a plurality of stages, with the refrigerant for each stage flowing through a common condensing zone.

8. The process of claim **7** wherein the liquefied gas at atmospheric pressure is passed to a storage tank and the vapor from said storage tank is recycled to step (a).

9. The process of claim **8** wherein said natural gas is primarily comprised of methane.

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