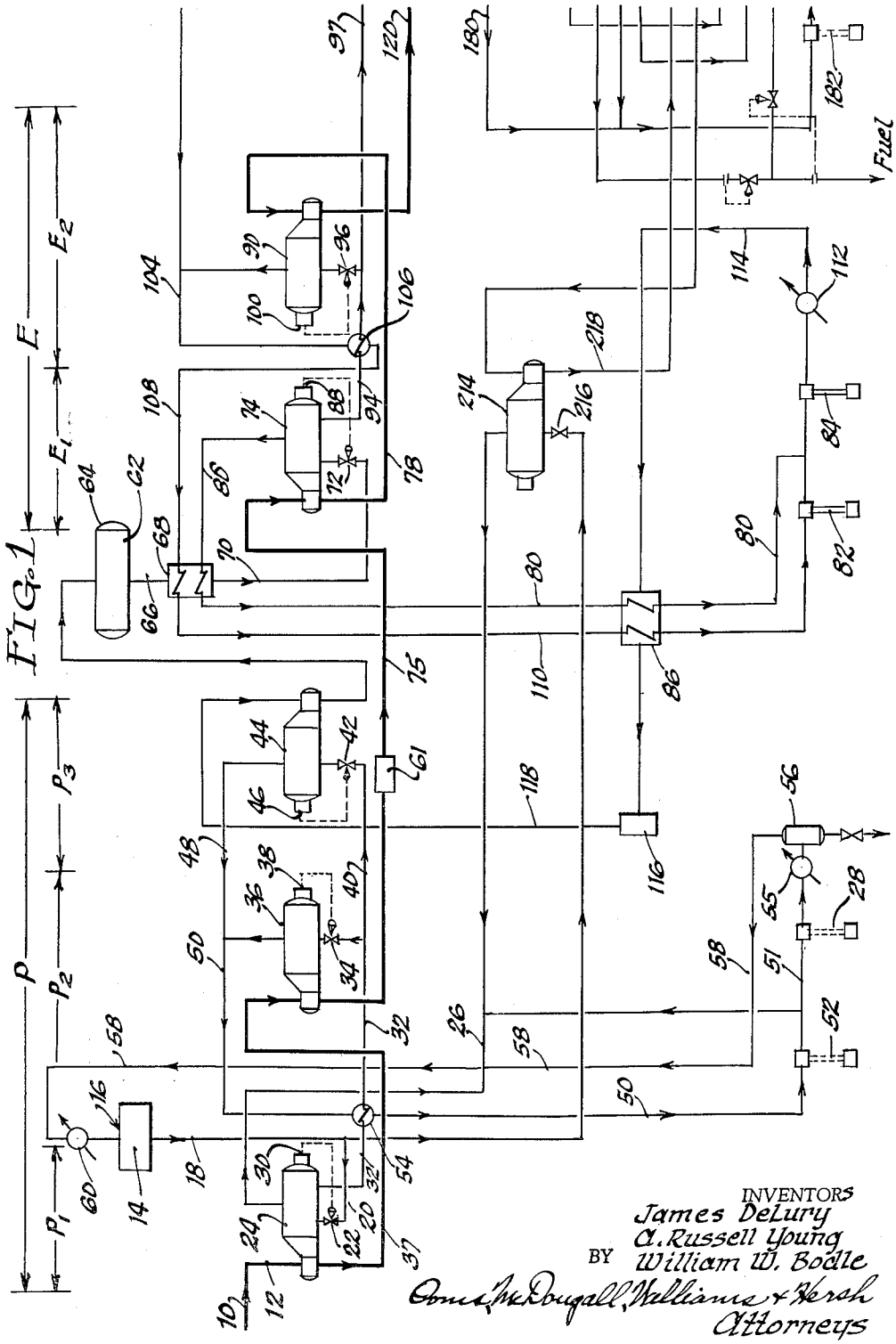
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METHOD AND APPARATUS FOR LIQUEFACTION OF NATURAL GAS

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FIG. 1



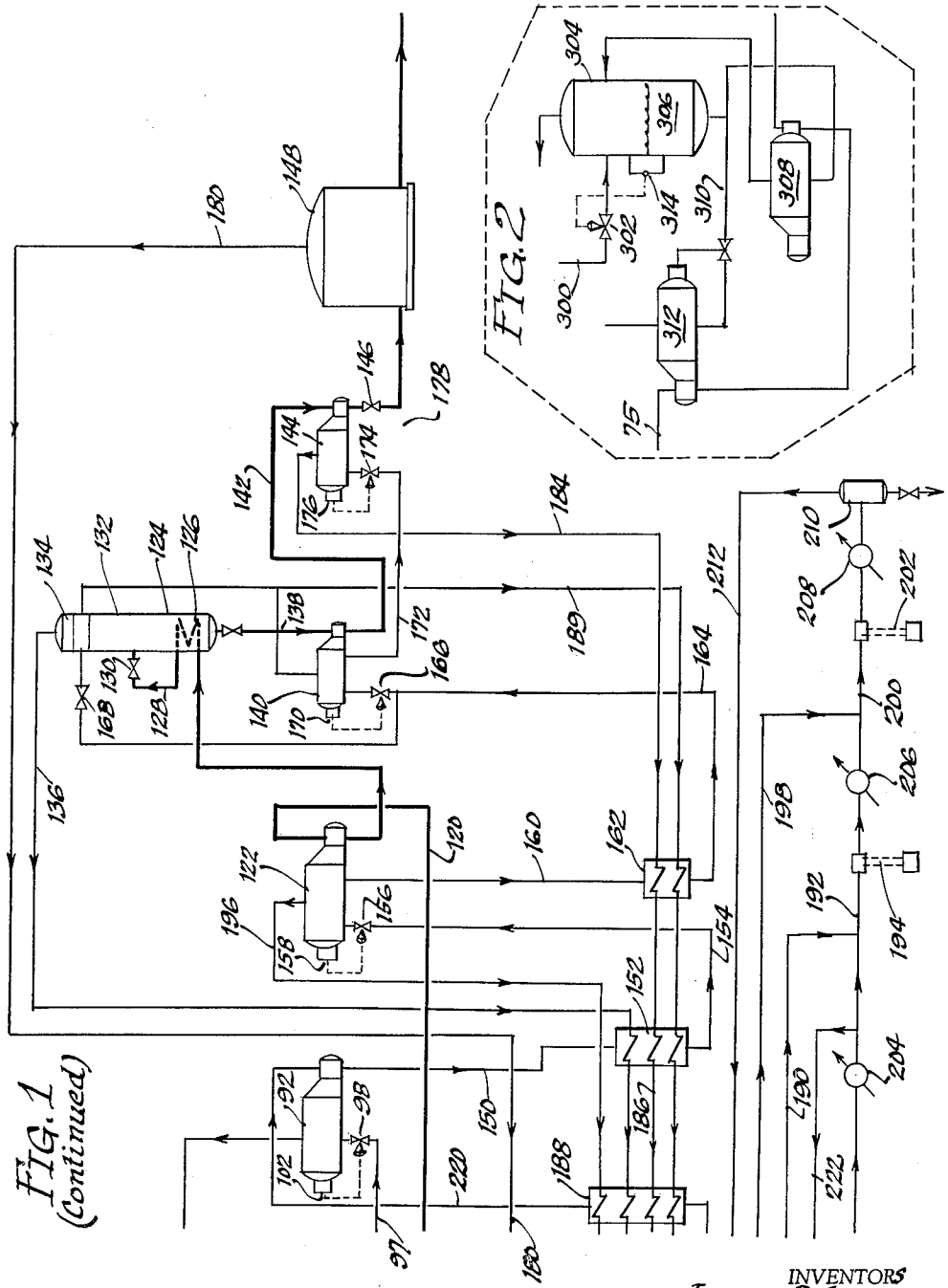
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METHOD AND APPARATUS FOR LIQUEFACTION OF NATURAL GAS

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3,020,723
METHOD AND APPARATUS FOR LIQUEFACTION OF NATURAL GAS

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11 Claims. (Cl. 62—9)

This invention relates to the liquefaction of a gas and it relates more particularly to a method and apparatus for the liquefaction of natural gas which is normally composed mostly of methane but which may contain heavier hydrocarbons such as ethane, propane, butane and the like, small amounts of aromatic hydrocarbons and variable amounts of non-hydrocarbons such as nitrogen, helium, carbon dioxide, hydrogen sulfide and the like. Illustration of this invention will hereafter be made with reference to the liquefaction of natural gas but it will be understood that the concepts employed are capable also of application to other low boiling liquefiable gases such as nitrogen, helium, air, oxygen and the like.

There are many purposes for which natural gas is desired to be reduced to a liquefied state. The main reason resides in the resultant reduction at equivalent pressure by about 1/600 in volume when reduced from the gaseous state to a liquefied state thereby to enable storage and transportation in containers of more economical and practical design.

For example, when gas is transported by pipe line from the source of supply to a distant market, it is desirable to operate under substantially constant high load factor. Often times the flow capacity will exceed demand while at other times, the demand may exceed the capacity of the line. In order to shave off the peaks where demand would exceed supply, it is desirable to store gas when the supply exceeds demand whereby peaks in demand can be met by material in storage. For this purpose, it is desirable to provide for storage in a liquefied state and to vaporize liquid in amounts to meet demand.

Liquefaction of natural gas is of even greater importance in making it possible to transport the gas from a source of plentiful supply to a distant market where a deficiency exists, especially when the source of supply cannot be directly joined with the market by a pipe line or the like means for the transportation of the gaseous fuel in a gaseous state. By way of illustration, surplus natural gas is available in the Gulf states of the United States, in Venezuela, and in the Persian gulf, while deficiencies exist in the northern parts of the United States, the European countries, and Japan, yet these sources of supply cannot be joined by pipe line with some of the markets. Ship transportation in the gaseous state would be uneconomical unless the gaseous materials were highly compressed and then the system would not be commercial because it would be impractical to provide containers of suitable strength and capacity.

It has been determined that natural gas, when shipped from the United States or Venezuela in large volumes in liquefied state, can be made available in Great Britain, for example, at a price which is considerably less than locally manufactured gas. For shipment in large volume, it is desirable to house the liquefied natural gas in suitable insulated containers of large capacity at about atmospheric pressure or preferably slightly above atmospheric but not at such high pressures as would unduly limit the economical capacity of the tank. Depending upon the amount of higher boiling heavier hydrocarbons present in the natural gas, the liquefied natural gas will have a boiling point within the range of —240° F. to —258° F. at atmospheric pressure.

The objective of this invention is to provide an apparatus and method for the economical and efficient conversion of a gas, especially natural gas, from a gaseous state to a liquefied state for storage and transportation.

Another object of this invention is to provide a process for the liquefaction of natural gas which makes use of a minimum amount of horsepower of refrigeration; which makes use of a minimum amount of process equipment; which is capable of being carried out in a continuous operation with a minimum amount of labor and materials; which is relatively free of the necessity of shutdown for the repair or replacement of equipment; which makes use of materials, such as refrigerants, which are readily available or available as by-products of the process; which supplies a relatively pure liquefied gas at about atmospheric pressure; which is safe in operation, and which is flexible in operation to enable adjustments to meet existing conditions from the standpoint of gas analysis or increase in capacity due to shut-downs in adjacent lines or the like.

These and other objects and advantages of this invention will hereinafter appear and for purposes of illustration, but not of limitation, an embodiment of the invention is shown in the accompanying drawing, in which—

FIG. 1 is a flow diagram of a process for the liquefaction of natural gas in accordance with the teachings of this invention, and

FIG. 2 is a diagrammatic sketch of a modification in the refrigeration systems.

The process will hereinafter be described in detail with reference to the liquefaction of natural gas at a source of supply using an operative set of temperature and pressure conditions. We want it understood, however, that the conditions set forth are merely illustrative and may easily and properly be varied in consonance with the design and capacity of the apparatus, the character of the gas from the standpoint of composition, temperature and pressure, and the conditions under which the liquefaction is carried out as influenced by the volume of material, types of refrigerants and the like, all within the scope of the invention. In the example, the gas liquefied will be a lean gas from which the moisture, acid gases such as carbon dioxide, hydrogen sulfide and the like will previously have been removed by pretreatment in the form of desiccators, amine extractors and the like. In this typical example, a cleaned lean gas is used having about 91 mol percent methane, about 7 mol percent ethane, less than 2 mol percent propane, less than 1 mol percent higher hydrocarbons and possibly up to 2 mol percent nitrogen. It will be understood that natural gas capable of being processed in accordance with the teachings of this invention may have up to 20–25 mol percent heavier hydrocarbons, up to 20 mol percent nitrogen and up to 5 mol percent carbon dioxide or hydrogen sulfide, but usually the amount of methane will exceed 75–80 mol percent and will more often be above 90 mol percent of the natural gas.

The natural gas **10** will be fed through pipe **12** into the liquefaction system at elevated pressure and temperature, such as 700 p.s.i. pressure and 100° F. temperature. The refrigeration cycle for reducing the compressed gas to a liquefied state by a modified cascade system and a modified expansion system will be divided into a sequence of refrigeration steps including a propane refrigeration cycle P, an ethane refrigeration cycle E, and a methane refrigeration cycle M, each of which is adapted to achieve a reduction in temperature of the compressed gas in the area where each of the cycle subdivisions can be operated with greatest efficiency from the standpoint of horsepower of refrigeration required to achieve the desired refrigeration.

Propane refrigeration cycle

The propane refrigeration cycle P can be in turn subdivided into a high level propane refrigeration cycle P_1, a low level propane refrigeration cycle P_2, and an ethane condensing cycle P_3.

In the high level propane refrigeration cycle P_1, liquid propane **14**, maintained in a receiver **16** at about 187 p.s.i. pressure and 100° F., is fed through pipe **18** for subsequent subdivision into an increment which is fed through pipe **20** to an expansion valve **22** wherein the pressure is let down to about 60 p.s.i. for introduction into the high level propane heat exchanger **24**. At 60 p.s.i. pressure, the propane will be maintained at a temperature of 25° F. The vapor which is flashed off upon expansion and the vapor which is formed by boiling in the heat exchanger upon extraction of heat from the process stream will be collected for passage through line **26** at 60 p.s.i. pressure for return to a pipe **51** between the low and high stages of compressors **52** and **28** respectively. The liquid propane is maintained at a desired level within the heat exchanger **24** by means of a level control device **30** to which the valve **22** is responsive.

When the process stream **10** is continuously advanced through the heat exchanger **24**, heat will be extracted from the natural gas in amounts to reduce the temperature of the process stream from 100° F. to about 32° F. with only slight reduction in pressure. If the process stream were to be supplied at a temperature considerably below 100° F., the described high level propane refrigeration step can be omitted in favor of a single heat exchange step through the low level propane refrigeration cycle.

In the low level refrigeration cycle P_2, liquid propane is supplied from the heat exchanger **24** through line **32** for subdivision wherein a portion is fed to an expansion valve **34** wherein the pressure is let down to slightly above atmospheric pressure, such as 18.4 p.s.i., for introduction into the low level heat exchanger **36**. At this pressure the propane will be maintained at a temperature of about —34° F.

The process stream in the line **37** will enter the low level propane heat exchanger **36** at 32° F. and will leave at about —29° F. while still at about 700 p.s.i. pressure. The liquid propane within the heat exchanger **36** will be maintained to a desired level by means of a level control device **38** to which the valve **34** is responsive.

The other increment of propane in line **32** continues in line **40** to an expansion valve **42** wherein the pressure is let down to about the same pressure level as through valve **34** before introduction into the heat exchanger **44**, or ethane condenser, wherein recompressed vapors of ethane in the ethane refrigeration cycle are cooled down to effect a liquefaction. Again propane is maintained at a desired level within the heat exchanger **44** by means of a liquid level control device **46** to which the valve **42** is responsive.

The flash vapors from the pressure reduction through the valves **34** and **42** and the vapors boiled off in the heat exchangers **36** and **44** are collected for passage together through lines **48** and **50** to the ingoing side of a low stage compressor **52**. The vapors removed through lines **48** and **50**, at approximately 16–18 p.s.i. pressure and at —34° F. will have a considerable amount of refrigeration which can be recovered by passing the cold vapors through the heat exchanger **54** in heat exchange relationship with the propane liquid in line **32** to cool the liquid from 25° F. to a temperature of about —8° F. Reduction in temperature of the liquid propane will reduce the amount of flash upon subsequent expansion through valves **34** and **42**. At the same time, the temperature of the recycled vapors will be raised from —34° F. to about 10° F. This is a much safer temperature for subsequent processing through the compressors since otherwise the cold vapors might raise lubrication problems.

The propane vapor in line **50** is compressed in the low stage compressor **52** to raise the pressure to a level which corresponds to the pressure of the vapor released from the heat exchanger **24** (about 60 p.s.i.) so that the two streams of propane vapor can be joined for subsequent processing through the high stage compressor **28**. The high stage compressor raises the pressure of the propane vapors to a pressure level at which they can be readily condensed, as by a water cooler. In the example it is raised to about 187–189 p.s.i. for subsequent liquefaction and storage in the receiver **16**. Heat of compression in the first low stage compression raises the temperature of the increment of the propane vapor in line **50** from 10° F. to about 91° F. Upon admixture with the effluent from the heat exchanger **24**, the combined stream will have a temperature of about 62° F. After recompression in the second high level stage compressor **28**, the temperature will be in the order of about 160° F.

It will be apparent that by the combination of high level and low level stages of heat exchange only a fraction of the vapor will be dropped to the lower pressure so that only this same fraction need be recompressed to the higher pressure stage thereby to conserve on power required to carry out the refrigeration cycle. Further, by division of the propane refrigerant between a low level refrigeration cycle and a high level refrigeration cycle, we are able to remove heat from the process stream at more efficient levels for each refrigerant material thereby further to reduce the horsepower of refrigeration required to achieve a desired reduction in the temperature of the process stream. If we were to extract all of the heat with the refrigerant at —34° F., for example, we would have less efficient heat transfer and we would have to recompress all of the propane from 16 pounds to the higher level.

Heat of compression need not be removed from the propane delivered by the low stage compressor because the temperature is not high enough to present problems in subsequent processing nor is it high enough for water cooling. After compression of all of the propane to 189 p.s.i. pressure the propane is passed through a heat exchanger **55** in which use can be made of water as the heat exchange liquid to extract heat of compression from the propane. It is preferred to reduce the temperature of the vapors to a level low enough to condense lubricant oil vapors which might remain in the propane but high enough to prevent condensation of propane. In the example, the temperature is reduced to about 10–15 degrees above the dew point of the propane but below the condensation temperature for lubrication vapors that might otherwise remain in the vapor stream so that trace amounts of lubricating oils can be condensed out of the stream for separation without confusion with the condensed propane. For example, the propane will be cooled in the heat exchanger **55** to about 110° F.

The recompressed propane issuing from the heat exchanger **55** is then processed through a fluid separator **56**, such as a packed vessel, to agglommerate and separate oils and other impurities from the propane cycle. Instead of a packed vessel, removal of the oils and other foreign material from the propane can be effected by an absorbent or other conventional removal means.

The recompressed and clean propane is recycled through the passage **58** to a propane condenser **60** for passage in heat exchange relation with an available refrigerant, such as cooling water, to reduce the temperature of the propane to its condensation temperature at the pressure conditions existing (100° F. at 187 p.s.i. pressure) whereby the liquid propane **14** is returned to the receiver **16** to complete the propane cycle.

Ethane refrigeration cycle

The ethane refrigeration cycle E is, in a similar man-

ner to the propane cycle, subdivided into a high level ethane refrigeration cycle E_1, a low level ethane refrigeration cycle E_2, and a methane cooling cycle E_3.

In a stepwise cooling system of the type described, it is desirable to prevent condensate from plating out onto the surfaces or the walls of the heat exchangers so as to maintain highest efficiency in the transfer of heat. For this purpose, the moisture content of the process stream is reduced to as low a level as possible prior to advancement of the natural gas to the described liquefaction system. In the example, the lean gas was treated by a desiccant to reduce the moisture content down to a dew point of about −40° F. prior to processing through the propane cycle. This resulted in a very low relative humidity. Now when the process stream is at a temperature of −20° F. as distinguished from 100° F., the same amount of moisture will provide high relative humidity where a desiccant can be used again effectively to remove moisture prior to processing the natural gas through the ethane cycle. Thus it is a concept of this invention to subject the process stream to a drying operation during processing through the refrigeration cycle to remove moisture and other undesirable impurities when at a stage or in a condition where removal can be efficiently and economically effected, as by a drier or by a molecular sieve. In this way the content of moisture and other materials such as aromatics can be kept low enough in the cycle to prevent freezing or plating out on the surfaces of the heat exchangers. This concept is illustrated by the use of the drier **61** in the process stream between the propane and ethane cycle. It can be located elsewhere and more than one drier or desiccant or molecular sieve can be employed at various stages in the system.

In the high level ethane cycle, liquid ethane **62**, maintained in a receiver **64**, for example, at 142 p.s.i. sure and −27° F., is fed through pipe **66** through a heat exchanger where the temperature is further reduced to −53° F. The cooled liquid ethane at 142 p.s.i. pressure continues through pipe **70** to an expansion valve **72** which lets the pressure down to 53 p.s.i. for introduction into the high level heat exchanger **74**. At this pressure, the temperature of the ethane in the exchanger will be maintained at about −78° F. The main process stream in line **75** enters the heat exchanger **74** at −29° F. and slightly less than 700 p.s.i. pressure and leaves the heat exchanger through pipe **78** at −74° F. A slight pressure drop will take place upon passage through the exchanger. The ethane which is flashed off upon expansion through valve **72** and which is vaporized in the heat exchanger **74** is returned through line **80** to interstage between the low stage compressor **82** and the high stage compressor **84**. The refrigeration available in the vapor is recovered in the heat exchanger **68** to cool the liquid ethane fed from the reservoir **64** to the heat exchanger **74** and it is subsequently passed through a second heat exchanger **86** for extracting heat of compression from the ethane recycled through the compressors **82** and **84** to cool the compressed ethane to a temperature as in the propane cycle to slightly above liquefaction temperature but below the temperature for condensation of lubricating oil vapors which are present in the ethane stream.

The ethane liquid within the heat exchanger **74** is maintained at a desired level by the level control device **88** to which the valve **72** is responsive. Sufficient amount of ethane liquid is removed from the heat exchanger **74** for flow through line **94** to supply the needs of the low level heat exchanger **90** and the methane cooler **92**. The portion of the stream flowing to the low level heat exchanger **90** is passed through a pressure reduction valve **96** which lets down the pressure to about 18 p.s.i. for introduction into the heat exchanger. At this pressure, the ethane in the heat exchanger **90** will be maintained at a temperature of about −120° F. In the example, the process stream enters the low level heat exchanger at about −74° F. and leaves at about −116° F.

The other increment of liquid ethane is advanced through pipe **97** to the pressure valve **98** wherein it is let down to the same pressure level as in the heat exchanger **90** for introduction into the cooler **92** wherein the recompressed methane vapors are processed for reduction in temperature. Both of the heat exchangers **90** and **92** are provided with level controllers **100** and **102** respectively to which the valves **96** and **98** are responsive for maintaining the desired level of liquid methane in the exchangers.

The vapors from the heat exchangers **90** and **92** are joined in line **104** for return to the low pressure side of the compressor **82** but the refrigeration is first recovered from these vapors by passing the cold vapors through a heat exchanger **106** in heat exchanger relation with the increment of ethane flowing from the high level exchanger **74** to the low level exchangers **90** and **92** to reduce the temperature of the ethane from −78° F. to −95° F. From the exchanger **106**, the cold vapors at about −92° F. are advanced through lines **108** and **110** through the heat exchangers **68** and **86** previously described. The ethane from the exchangers **90** and **92** will be at about atmospheric pressure and will have been heated up to a temperature of about 19° F. prior to entrance into the low level side of the compressor **82**. The first stage of compression will raise the ethane vapors to 49 p.s.i. pressure and to a temperature of about 120°. The ethane delivered from the first compression stage is combined with the vapor from the heat exchanger **74** to provide a combined feed to the second stage of compression at a temperature of about 99° F. and a pressure of about 49–50 p.s.i.

The ethane issuing from the high stage compressor **84** at 200° F. and 147 p.s.i. pressure is passed through a water cooler **112** and comes out at about 144 p.s.i. pressure and 100° F. From the heat exchanger, the recompressed ethane vapors are advanced through line **114** to the heat exchanger **86** wherein it is cooled to about 46° F. while warming the recycled gas from −44° F. to 19° F. in the case of the vapors from the exchangers **90** and **92** and from −41° to 24° F. in the case of the vapors from the exchanger **74**. The ethane vapors at 144 p.s.i. and 46° F. are treated in the separator **116** to remove lubricating oils which might there become entrained with the ethane during recompression thereby to protect the heat exchangers from the plating out of oily constituents on the walls thereof. From the separator, the compressed ethane is advanced through line **118** to the ethane condenser **44** in the propane cycle. It enters at 46° F. and leaves as a condensate at −27° F. and about 142 p.s.i. pressure for return to the receiver **64**.

The process stream continues from the heat exchanger **90** through the line **120** to a high level methane heat exchanger **122** which it enters at −116° F. and leaves at −156° F. The process stream at −116° F. and about 650–700 p.s.i. pressure will be substantially in a liquefied state prior to passage through the heat exchanger **122**. However, upon passage through the heat exchanger the process stream at −156° F. may for all practical purposes be considered to be in a liquefied state and any nitrogen within the amounts described will usually remain dissolved in the liquefied material.

While the liquefied process stream can be expanded directly to the desired pressure (slightly above atmospheric pressure) for storage and transportation at a temperature within the range of −240° F. to −258° F. (depending upon the pressure and amount of higher boiling hydrocarbons), it is desirable to embody means within the process for the removal of nitrogen, when substantial amounts of nitrogen are present, prior to advancement of the liquefied material to storage. This not only

provides a liquid of higher fuel content but it makes it possible to carry out a further concept of this invention in the use of the vapors from storage as a refrigerant and to make use of the refrigerant cycle for reliquefaction of the flash into storage and vapors coming off in storage.

For this purpose, the process stream, now in the form of a liquid at —156° F. and a pressure which may have fallen down by this time to between 650–675 p.s.i., is processed through a tower **124** having coils **126** in a reboiler section at the bottom thereof through which the cold and compressed stream of liquefied natural gas is advanced to a line **128** outside the reboiler having a pressure reduction valve **130** wherein the pressure of the liquefied stream is let down to about 125 p.s.i. This will result in a reduction in the temperature of the process stream to about —190° F. for re-introduction into an intermediate portion of a stripper portion **132**. Upon reduction in pressure, a portion of the liquefied natural gas stream will be flashed to provide a mixture of vapor and liquid. A reflux condenser **134** in the form of a heat exchanger cooled with boiling methane from the methane refrigeration cycle is provided at the outlet near the top of the tower to reflux vapors coming off.

At 125 p.s.i. pressure, the liquid coming off of the bottom of the tower will have a temperature of about —185° F. which is about 19° F. cooler than the feed. In the tower, the expanded liquid at about —190° F. will have the nitrogen in solution. As it descends through the tower, it will be brought into contacting relationship with warmer vapors rising through the tower. Thus the heavier vapors will condense to heat the liquid and drive out such lower boiling materials as nitrogen and/or helium. In the upper portion of the tower, the vapors from the flash and the vapors from below will be brought into contact with the cold liquid passing down through the tower to condense the heavier components while permitting the less condensable vapors composed mostly of nitrogen and some methane to continue upwardly through the reflux for passage into line **136** at about —210° F.

The process stream continues through line **138** to an intermediate level heat exchanger **140** in the methane refrigeration cycle. It enters the heat exchanger at —185° F. and about 125 p.s.i. pressure and leaves at about —212° F. From the heat exchanger **140**, the liquefied process stream continues to flow through line **142** to a lower level heat exchanger **144** wherein the liquefied natural gas which enters at —212° F. will leave at a temperature of about —246° F. From here the cold and compressed liquid is flashed through a throttling valve **146** into the chamber **148** preferably at slightly above atmospheric pressure which will bring the temperature down to about —246° to —258° F., depending upon the pressure and the amount of higher boiling hydrocarbons which are present in the natural gas stream. The chamber **148** may be a storage chamber but it is preferred to drain the product from the chamber **148** to insulated storage tanks or to transportation means (not shown).

One of the concepts of this invention resides in the ability to make use of the methane boiled off in storage and/or flashed into chamber **148** as a part of the refrigerant in the methane cycle thereby to supply methane refrigerant from the material being processed. It is for this purpose that it is desirable to effect substantially complete removal of nitrogen from the product delivered to the chamber **148**, otherwise the nitrogen will be carried into the liquefied natural gas in storage and will be the first material coming off as vapor thereby to prevent the use of such vapors in the methane refrigeration cycle. While nitrogen could be flashed from the product for separation, some nitrogen will invariably remain in solution and will be carried with the product into storage where it could enter the refrigerating system and continue to build up in the recycle. Further, too much methane would be carried out with the nitrogen.

The stripper **132** could be operated at pressures which deviate quite widely from the 125 p.s.i. described. It is desirable to operate at a presure sufficient to force circulation of the vapors through the various heat exchangers to be described for recovery of its refrigeration and for subsequent use as a fuel. In general, it is desirable to operate at a pressure in excess of 75 p.s.i. When the stripper is operated at pressures much higher than 125 p.s.i., removal of inert gases becomes more difficult and such higher pressures call for increasing amounts of refrigeration. Therefore, it is desirable to operate the stripping process at a pressure preferably above 75 p.s.i. but less than 700 p.s.i., depending somewhat and directly upon the nitrogen content. The effluent from the stripper in line **136**, after being passed through heat exchangers for the recovery of refrigeration, is generally used as a fuel.

Methane refrigeration cycle

Referring now to the methane refrigeration cycle, methane comes out of the low level ethane heat exchanger **92** in the ethane cycle at about —116° F. and at about 1210 p.s.i. pressure. At this pressure and temperature, the methane will be in the form of a dense fluid as distinguished from a liquid or a vapor because it is above its critical pressure. It is desirable to make use of such high pressures at this phase of the refrigeration cycle because such high pressures can be achieved with relatively small incremental effort while a number of advantages and economies can be derived therefrom. For example, the equivalent of latent heat of condensation can be removed from the dense fluid at relatively high temperature with considerable net savings in refrigeration horsepower. Further, when operating at the higher pressure level, the material can be expanded to lower pressures with a lesser proportion of vapor as compared to fluid thereby to minimize on the amount of vapor recycled and power required for refrigeration. Still further, at high pressures, the cooling curve for methane is made more uniform and straight so as to enable more efficient heat transfer with corresponding savings in horsepower of refrigeration. There is a point, however, of diminishing returns where the pressure lines come so close as to make it uneconomical to strive for still higher pressures. This area is in the region of 1200–1300 p.s.i. with methane.

Methane fluid from the heat exchanger **92** flows through line **150** to heat exchanger **152** where it is passed in heat exchange relationship with the methane vapors recycled from the stripper **134** (—175° F.), the heat exchanger **144** (—175° F.), and the effluent in line **136** (—210° F.). The methane entering the heat exchanger at —116° F. will leave the exchanger at about —130° F. and will continue through line **154** to the high level heat exchanger **122**. Before entering the heat exchanger **122**, the pressure is reduced through valve **156** to about 300 p.s.i. with the result that the methane refrigerant in the heat exchanger will be maintained at a temperature of about —160° F. The liquid methane is maintained at the desired level in the heat exchanger by the level control device **158** to which the valve **156** is responsive.

Methane refrigerant is removed from the heat exchanger **122** for flow through line **160** to a heat exchanger **162** where it is sub-cooled from a temperature of —160° F. to a temperature of —187° F. by passing it in heat exchange relationship with vapor from the heat exchanger **144** at —249° F. and from the reflux condenser **134** and heat exchanger **140** at —215° F. The sub-cooled methane at —187° F. is passed through line **164** for separation into two increments one of which leads to an expansion valve **166** which lets down the pressure to 75 p.s.i. with consequent drop in temperature to —215° F. prior to introduction into the heat exchanger **140**. The other increment is also let down in a separate valve **168** to the same pressure

before introduction into the reflux condenser **134** at the top of the stripper **132**. A level control device **170** is employed in the heat exchanger to control the valve **166** to maintain flow of methane in amounts sufficient to maintain a desired level in the heat exchanger **140**.

Liquid methane at —215° F. and 75 p.s.i. pressure in excess of the amount required is drained from the exchanger **140** for flow through line **172** to a valve **174** through which the liquid methane is flashed at about 25 p.s.i. pressure and —249° F. into the low level heat exchanger **144**. The heat exchanger is provided with the usual level controller **176** to control the flow through valve **174** to maintain a quantity of methane in the heat exchanger.

A receiver can be employed for the storage of the compressed methane for supply to the methane refrigeration cycle. It is preferred, however, to integrate the methane refrigerant cycle with the storage and the flash into storage. In this system the vapors flashed into storage and the vapors boiled off in storage can be added to the refrigerant methane recycled from the various units in the methane refrigeration cycle since the flash and boil-off from storage will be of a composition similar to the methane used as a refrigerant. Thus an amount of methane introduced into the inlet to the recompression stages will be in excess of that available merely from the boil-off of refrigerant. However, any excesses of liquefied methane over and above that used as refrigerant in the refrigeration cycle can be by-passed from the last heat exchanger **144** through line **178** into storage chamber **148** as product. Usually, the amount by-passed will be equivalent to the amount of vapor added to the cycle from storage.

This will eliminate the necessity for refrigerant re-run for purification of the refrigerant since fresh increments of methane are constantly being introduced as refrigerant in the methane refrigeration cycle. Still further, it becomes unnecessary to recycle the boil-off of product for addition to the feed of gas to be processed through the entire system described for liquefaction. This not only reduces the amount of material to be reprocessed but it will beneficially affect the capacity of the equipment without increase in the dimension thereof or power required for operation. It will be understood, however, that the flash or boil-off vapors from the product can be added to the feed for reprocessing to a liquefied state.

When the flash and vapor from storage is bled off into the refrigerant cycle, the vapor is carried through line **180** directly to the low side of the low stage recompressor **182** without recovering refrigeration by passage through heat exchangers, because the suction pressure will ordinarily be below atmospheric. The compressor **182** will bring the pressure up from 16 p.s.i. to about 70 p.s.i. while raising the temperature to about 158° F.

As previously described, the refrigerant vapor from the heat exchanger **144** is drained through line **184** through the heat exchanger **162** which raises the temperature from —249° F. to —175° F. and then through the heat exchanger **162** which raises the temperature from —249° F. to —175° F. and then through the heat exchanger **152** which further raises the temperature to —130° F. From the heat exchanger **152**, the vapor flows through line **186** to a heat exchanger **188** in the form of a pre-cooler for the recompressed methane wherein the temperature of the recycled methane is still further raised to —5° F. and then the methane vapor joins the flash and vapor from storage in line **180** for recompression by the low stage compressor **182**. The vapor from the reflux condenser **134** and from the heat exchanger **140** flows through line **189** through the heat exchangers **162** and **152**. It leaves the last heat exchanger at about —10° F. and flows through line **190** to **192** interstage between compressors **182** and **194**.

Vapors from the high level exchanger **122** flow through line **196** through the heat exchanger **188** which it leaves at 10° F. and continues through line **198** to line **200** interstage between compressors **194** and **202**.

The first stage compressor **182** raises the vapor from storage and from the exchanger **144** to a pressure of about 75 p.s.i. and about 158° F. This increment of the refrigerant can be water cooled in the heat exchanger **204** to reduce the temperature of the methane to about 115° F. The recompressed increment is then joined with the vapor recycled from the reflux condenser **134** and the exchanger **140** for further compression by the second stage compressor **194** to about 290 p.s.i. and 240° F. This corresponds with the pressure of the vapor from the heat exchanger **122** to enable joinder therewith in line **200**. Before joinder, the recompressed gases should be passed through a water cooler **206** to bring the temperature back down to about 110° F. After joinder with the vapor recycled from the exchanger **122**, the methane is compressed in the final stage compressor **202** to about 1210 p.s.i. pressure and will come out at a temperature of 248° F.

The compressed methane is water cooled in the heat exchanger **208** to bring the temperature down to about 100° F. at which temperature the lubricant vapors which might become entrained with the methane can be condensed for removal in the separator **210**. The recompressed vapors at 1210 p.s.i. pressure and 100° F. are then passed through line **212** to a heat exchanger **214** in the propane refrigeration cycle which receives propane refrigerant subdivided from line **18** and is flashed through valve **216** into the exchanger at 60 p.s.i. pressure to provide a temperature of 25° F., the same as in the high level heat exchanger **24** in the propane cycle. The recompressed methane enters the heat exchanger at 100° F. and leaves at 32° F. From the heat exchanger **214**, the methane flows through line **218** through the heat exchanger **188** for passage in heat exchange relationship with vapors recycled from the heat exchangers **144**, **140** and **122** and from the reflux condenser **134**. It leaves the exchanger at —58° F. and continues in line **220** to the ethane exchanger **92** described at the start of the methane cycle.

The gas stripped from the process stream through line **136** is also passed in heat exchange relationship through the exchangers **152** and **188** for recovering its refrigeration prior to use as a fuel. In the event that the fuel requirement is not met by this supply, additional amounts of methane at elevated pressure can be bled from line **10** or from line **192** through line **222** after recycled methane has been recompressed to an intermediate pressure sufficient to carry the vapor for use.

One of the problems in the use of product vapors as a part of the recycle to make up refrigerant is in the maintenance of a refrigerant which is free of contaminants. The ability to make use of the bleed-off and flash from the product as a part of the methane refrigeration cycle makes available an unlimited supply of refrigerant without the necessity to purchase from other sources or to require shipment from distant stations. It is imperative in any event to recover the vapors given off in storage and given off when the product is flashed down to storage pressure. Thus it is economical to process this material through the refrigerant cycle and reduce equipment and power costs.

The methane vapors are carried through three stages of compression in the described concept to correspond with the take-off of vapors at three different pressure levels from the product and from the heat exchangers thereby to necessitate recompression only of portions of the vapors which are expanded to lower pressure levels. Recompression with methane results in higher temperature build-up by heat of compression when compared with the corresponding pressure changes with ethane or propane. Thus, in the methane cycle, it is expedient to make use of a water cooling step behind each compression stage, otherwise the discharge temperatures might become excessive. For example, a temperature of about 158° F. would be reached after the first stage compres-

sion leading to a temperature build-up in excess of 380° F. at the discharge from the second stage of compression unless the heat of compression is taken out in substantial amounts. Such build-up in temperatures would lead to lubrication problems and the brake horsepower per stage would rise excessively. These same conditions would not necessarily arise in the propane and ethane recompression cycles where the amount of recompression is not so great so that water cooling would not be necessary after each recompression step.

Having described a typical cycle, reference will now be made to various concepts of the invention and modifications which may be employed in the process.

Before processing the natural gas through the liquefaction cycle, it is desirable to effect removal of carbon dioxide, hydrogen sulfide, other acid gases, water and the like. If not removed, one or the other of these materials will tend to interfere with the operation of the process because carbon dioxide or hydrogen sulfide or water, for example, would tend to solidify at some stage of the process.

The carbon dioxide need not be quantitatively removed because carbon dioxide is soluble to a limited extent in the hydrocarbons. Its presence therefore would not be harmful unless the concentration of carbon dioxide was sufficiently high to cause solidification at the temperature conditions existing, that is, when the amount of carbon dioxide exceeded its solubility in the process stream at the temperature and pressure conditions prevailing at various stages of the process. Carbon dioxide solidifies at about −109° F. at atmospheric pressure and solidification would therefore be expected to take place when the process stream is cooled below this point. Hydrogen sulfide would solidify sooner.

Water, as such, is very undesirable in the process stream since it is insoluble in the hydrocarbon and will be solidified when cooled to below water freezing temperature. In addition, water should be removed from the process stream as soon as possible since water can be combined with methane, ethane and propane to form bulky hydrates which are as effective as ice in plugging the equipment. Thus the process stream of natural gas is preferably treated in advance of entrance into the described liquefaction cycle to clean up the gas by the use of conventional amine extractors to remove carbon dioxide, hydrogen sulfide and the like and by the use of fluid or solid desiccators to reduce the moisture content to as low a level as possible and also to further reduce the acid gases. Instead of amine extractors for the removal of acid gases, use can be made of other conventional cleaning systems such as the hot potassium carbonate process. It would also be possible to scrub out the carbon dioxide with water or with caustic solutions.

For the removal of moisture, use can be made of solid or liquid desiccants such as activated alumina, silica gel and the like. Such desiccants will also operate in part to remove some of the acid gases such as carbon dioxide and hydrogen sulfide.

In addition to the clean-up in advance, it is desirable, as described in the process, to effect further reduction in moisture when the relative humidity rises in the process cycle as a consequence of the reduction in temperature. Removal is desirable to keep the moisture content to a level which will reduce the dew point below the lowest temperature to which the process stream will be exposed. The drier 61 is employed in the process stream for this purpose. In the example, it operates to remove moisture from the stream after it has been cooled from 100° F. to about −29° F. between the exchangers 36 and 74. With suitable desiccation at this stage of the process, it will usually be unnecessary to employ further means for moisture removal in subsequent stages of the process. Such driers in the system will serve also to remove lubricating oils and waxes which might be present in the process stream and, as such, can be referred to as a filter drier.

Differences will exist in the conditions of operation depending upon the compositions of the gas that is being processed. These differences will exist with reference to the use of a rich gas which comes directly from the field and may contain as much as 8–20 percent by weight of higher hydrocarbons including ethane, propane, butane and the like and a lean gas from which the heavier hydrocarbons including propane, butane and some of the ethane has been removed in the gasoline plant. With a rich gas, a dew point will be reached much sooner than with a lean gas because some of the heavier hydrocarbons may begin to condense out at 100° F. when under 700 p.s.i. pressure. Under such circumstances, even in the first high level heat exchanger in the propane cycle, some condensation will take place to remove latent heat as well as sensible heat at fairly high temperature levels. A rich gas will be almost totally condensed at about −90° F. at 700 p.s.i. prsssure whereas a lean gas will condense under the same pressure conditions at about −116° F. At atmospheric pressure, the rich gas will boil at about −250° F. whereas a lean gas will boil nearer −258° F.

In processing a lean gas, the major portion of heat removal will be effected at lower temperatures. With a rich gas, major temperature or heat removal will be effected at higher temperatures. Thus it is desirable to embody sufficient safety factors in design of heat exchangers for use with any kind of gas in the process stream. With a rich gas, the first exchangers operate to take out latent heat plus sensible heat as distinguished from the removal of sensible heat only in the subsequent exchangers. Thus the first heat exchangers might be made larger than the latter to provide a larger heat exchange surface. The opposite effect will be secured in the processing of a lean gas so that the first exchangers in the propane cycle could be made smaller while the latter heat exchangers could be designed to provide more heat exchange surface to take out both latent and sensible heat.

By way of still further modification, it will be apparent, especially in processing a rich gas, that some condensation of higher hydrocarbons will take place at stages in the process long before the liquefaction of the methane component. Means, such as separators, can be employed in intermediate stages of the refrigeration cycle and at various stages of the refrigeration cycle to tap off condensates. By such means a rich gas can be made to become a lean gas in processing and by such means, butanes, propanes and ethanes may be collected for use as L.P.G. gas or as raw materials in the petro-chemical industry and the like.

An important concept of this invention resides in the break-down of the refrigeration cycle into separate stages whereby use can be made of separate refrigerants in areas wherein such refrigerants are most effective as a heat exchange medium. Thus refrigeration can be made available to the system at a reduced rate of brake horsepower per ton of refrigeration. Propane has been selected for use as the refrigerant through the temperature range of 100° F. to −35° F. since it is effective in heat transfer through this range. Ethane has been selected as the refrigerant through the range of −20° to −140° F. and methane has been selected for the range below −110° F. In addition to the efficiency of refrigeration available from each within its range, the combination of propane, ethane and methane provides a unique system particularly adapted to the liquefaction of natural gas since each of the refrigerants can be made available as a by-product of the liquefaction process thereby to be supplied in unlimited amounts at little cost and effort.

From the standpoint of each of the refrigerants, it is undesirable to extend the range of use of the refrigerants to a level at which the refrigerants would operate under subatmospheric conditions in advance of the compressors. For example, it is undesirable to extend the propane refrigeration cycle to beyond −40° F. because we run into the problem of pulling a vacuum at the low pressure side of the compressor. This would tend to draw air into the refrigeration system and lead to possible dangers in operation.

It is preferred to limit the expansion of the refrigerants to a minimum of about 16 p.s.i. so that the refrigerants will remain under sufficient positive pressure to prevent such infiltration and to carry the refrigerant back to the compressors.

While not equivalent, use can be made of other refrigerant materials instead of the described propane, ethane or methane. For example, use can be made of ammonia instead of propane although the former is more expensive and requires importation from an outside source. Similarly, ethylene can be used instead of ethane and Freons can be substituted for ethane or for the refrigerant in a part of the methane cycle since Freons can be used within the range of −150° F. to −200° F. However, the latter are expensive refrigerants and difficult to replace in some locations.

By way of still further modification, the process stream can be operated under pressure conditions varying quite widely from 700 p.s.i. Such differences in pressure would have little, if any, effect on the sequence of steps or on the techniques of operation with the exception that the condensation point will shift toward the inlet at higher pressures and toward the outlet at lower pressures.

In the foregoing example used as an illustration of the process forming the subject matter of this invention, use is made of heat exchangers into which the refrigerant liquids are flashed through an expansion valve. Other means may be employed in supplying the heat exchangers with cold refrigerant liquid. One such other means is diagrammatically illustrated in FIG. 2 wherein the stream of liquid refrigerant under pressure is caused to flow through a line **300** through an expansion valve **302** into a flash tank **304**. Cold refrigerant liquid **306** at the tank can be supplied to the heat exchanger **308** in amount to provide the desired refrigeration and the remainder can be diverted through trunk line **310** to the next heat exchange unit represented by the numeral **312**. The amount of refrigerant flashed into the tank **304** can be regulated by the controller **314**. While more equipment will be required, use can be made of smaller heat exchangers in the process stream. The latter are less desirable in canned or self-contained heat exchange units.

It will be apparent from the foregoing that we have provided a new and efficient system for the liquefaction of natural gas or other gases embodying a combination of a cascade cycle for reducing the gases under pressure to a liquefied state and an expansion cycle whereby the liquid under compression is flashed to lower pressures for storage and transportation with a minimum amount of flash given off for reliquefaction. The liquefaction process described embodies a novel combination of refrigerants which gives ease of operation and results to achieve liquefaction of the natural gas with lower power requirements and therefore at lesser cost. It is believed that invention also resides in the means for removal of moisture through intermediate stages of the liquefaction cycle to minimize interferences with the operation of the cycle and in the removal of nitrogen from the liquefied gas so as to permit reliquefaction of vapors given off from the product and from the flash into the product as a part of the refrigeration cycle as distinguished from the liquefaction cycle thereby to provide a new and novel combination which effects material economies in process and results.

It will be understood that changes may be made in the details of construction, arrangement and operation without departing from the spirit of the invention, especially as defined in the following claims.

We claim:

1. The method of liquefying a gas comprising the steps of supplying the gas in a process stream at an elevated temperature and pressure, removing heat from the gas to refrigerate the gas to a temperature at which it is condensed to a liquefied state at the pressure conditions existing, expanding the liquefied gas to lower pressures for storage and transportation whereby a portion of the cold liquefied gas is flashed off upon expansion with further reduction in temperature, separating the flashed vapors from the liquid, removing moisture from the process stream to reduce the moisture content to a level below the dew point at temperature conditions existing during the process to prevent the formation of frozen solids, and in which the refrigeration system for heat exchange to remove heat from the process stream comprises a substantially closed system embodying a compression and expansion cycle wherein the expansion is subdivided into a high pressure segment and a low pressure segment with the refrigerant from the high pressure segment flowing to the lower pressure segment for further expansion and cooling and wherein the process stream passes in heat exchange relation with the refrigerant first with the high pressure segment and then with the low pressure segment.

2. The method as claimed in claim 1 in which the expanded refrigerant vapors are recompressed in multiple stages having intermediate stages corresponding to the high level expansion pressures to enable the vapors therefrom to be by-passed beyond the lower stages of recompression in the recompression cycle.

3. The method for liquefaction of a natural gas composed mostly of methane comprising the steps of supplying the natural gas in a process stream at an elevated temperature and pressure, removing heat from the process stream by heat exchange to reduce the gas to a temperature at which the natural gas condenses to a liquefied state at the pressure conditions existing wherein the heat exchange is carried out by passing the process stream in heat exchange relationship with refrigerants subdivided into separate segments in accordance with the temperature for use of separate refrigerating systems employing separate refrigerants having best performance from the standpoint of heat transfer characteristics within the temperature range of the corresponding segments comprising three segments with propane, ethane and methane as the separate refrigerants for the higher-to-lower segments of temperatures respectively, and in which the process stream is passed in heat exchange relation with refrigerants in the order of propane, ethane and methane and first with a high pressure segment and then a low pressure segment of the refrigerant system, expanding the liquefied natural gas to a lower pressure for storage and transportation whereby a portion of the cold liquefied gas is flashed off upon expansion with further reduction in temperature and then separating the flashed vapors from the liquid to form the product.

4. The method of liquefying a gas comprising the steps of supplying the gas in a process stream at an elevated temperature and pressure, removing heat from the gas to refrigerate the gas to a temperature at which it is condensed to a liquefied state at the pressure conditions existing, expanding the liquefied gas to lower pressures for storage and transportation whereby a portion of the cold liquefied gas is flashed off upon expansion with further reduction in temperature, separating the flashed vapors from the liquid, and removing moisture from the process stream to reduce the moisture content to a level below the dew point at temperature condtiions existing during the process to prevent the formation of frozen solids when a temperature drop in increments of 100° F. has been achieved in the cooling steps.

5. The method of liquefying a gas comprising the steps of supplying the gas in a process stream at an elevated temperature and pressure, removing heat from the gas to refrigerate the gas to a temperature at which it is condensed to a liquefied state at the pressure conditions existing, expanding the liquefied gas to lower pressures for storage and transportation whereby a portion of the cold liquefied gas is flashed off upon expansion with further reduction in temperature, separating the flashed vapors from the liquid, removing moisture from the process stream to reduce the moisture content to a level below

the dew point at temperature conditions existing during the process to prevent the formation of frozen solids, and in which nitrogen is removed from the process stream by expanding the process stream after it has been liquefied but while it is still under positive pressure to an intermediate pressure into a chamber provided with heat exchange means at the fluid outlet maintained at a temperature slightly above the temperature of the expanded fluid and which is provided with a reflux condenser means at the vapor outlet maintained at a temperature slightly below the temperature of the expanded fluid to extract nitrogen and other lower boiling gases which distill off with some of the methane through the vapor outlet while relatively pure methane and other heavier hydrocarbons drain off as a liquid through the fluid outlet.

6. The method for the liquefaction of a natural gas composed mostly of methane comprising the steps of supplying the natural gas in a process stream at an elevated temperature and pressure, removing heat from the process stream to reduce the natural gas to a temperature at which the gas condenses to a liquefiied state at the pressure conditions existing, expanding the liquefied natural gas to a lower pressure for storage and transportation whereby a portion of the cold liquefied gas is flashed off upon expansion with further reduction in temperature, separating the flashed vapors from the liquid product, the heat removal step being achieved by passing the gas process stream into heat exchange relationship with a refrigerant which includes a methane cycle, and which includes the step of recirculating vapors given off from the product in storage and when flashed into storage into the methane refrigeration cycle, and bleeding off into product excesses of liquefied methane from the methane refrigeration cycle.

7. The method for the liquefaction of a natural gas composed mostly of methane comprising the steps of supplying the natural gas in a process stream at an elevated temperature and pressure, removing heat from the process stream by passing the process stream in heat exchange relation with separate refrigerants for incremental reduction in temperature and in which one of the refrigerants in the refrigeration system makes use of methane, expanding the liquefied natual gas to a lower pressure for storage and transportation whereby a portion of the cold liquefied gas is flashed off upon expansion with further reduction in temperature, and separating the flashed vapors from the liquid product, said methane for the refrigeration being derived from the phase given off by the product and wherein the liquefied methane refrigerant in excess of that cycled through the methane refrigeration cycle is incorporated to form a part of the product of liquefied natural gas thereby to join the methane refrigeration cycle with the product cycle.

8. The method as claimed in claim 7 in which the methane in the methane refrigeration cycle is compressed in multiple stages to a pressure in excess of 700 p.s.i. but below 1300 p.s.i.

9. The method as claimed in claim 8 in which the heat of compression is extracted from the methane vapors following each stage of recompression.

10. The method as claimed in claim 3 which includes the step of dehydrating the process stream intermediate one of the segments of refrigeration but before the process stream has been reduced to a liquefied state at the elevated pressure to reduce the relative humidity of the compressed and refrigerated stream.

11. The method as claimed in claim 3 which includes the additional step of dehydrating the process stream between the propane refrigeration and the ethane refrigeration to reduce the relative humidity of the refrigerated process stream.

References Cited in the file of this patent

UNITED STATES PATENTS

2,541,569	Born et al.	Feb. 13, 1951
2,556,850	Ogorzaly	June 12, 1951
2,596,785	Nelly et al.	May 13, 1952
2,650,481	Cooper	Sept. 1, 1953
2,696,088	Twomey	Dec. 7, 1954
2,731,810	Hachmuth	Jan. 24, 1956
2,814,936	Morrison	Dec. 3, 1957
2,823,523	Eakin et al.	Feb. 18, 1958
2,881,595	Fetterman	Apr. 14, 1959
2,900,796	Morrison	Aug. 25, 1959