

[54] METHOD AND APPARATUS FOR LIQUEFYING GASES

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[56] References Cited

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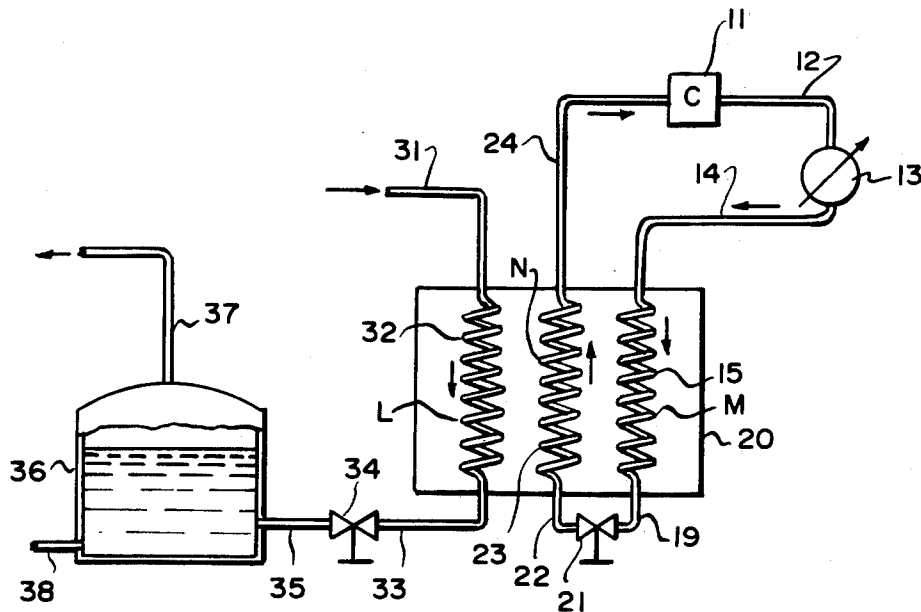
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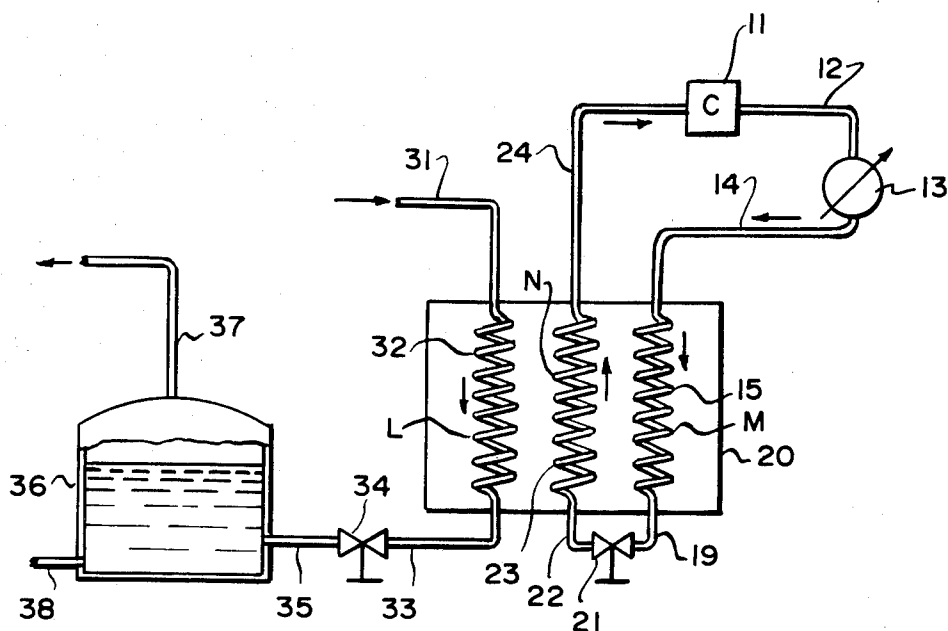
ABSTRACT

A process for liquefying natural gas employing a closed loop refrigeration process which uses a refrigerant consisting essentially of methane and propane. The refrigerant is compressed to a high pressure, the high pressure refrigerant is cooled to ambient air or water temperature and passed through a heat exchanger to cool the refrigerant substantially below ambient temperature. The refrigerant is isenthalpically expanded through an expansion valve to give a cold low pressure refrigerant and then passed back through the same said heat exchanger and then to the compressor to thereby reduce the temperature of the high pressure refrigerant passed therethrough and give extra refrigeration for removing heat from a product.

A refrigeration system having a compressor, a high pressure refrigerant conduit from the compressor to a heat rejector, a high pressure refrigerant conduit from the heat rejector to a heat exchanger for passage of the refrigerant therethrough, a high pressure refrigerant conduit from the heat exchanger to an expansion valve for delivery of cooled high pressure refrigerant from the heat exchanger to the valve, a low pressure refrigerant conduit from the valve to the same said heat exchanger for delivery of cold low pressure refrigerant to the heat exchanger to supply refrigeration thereto, a low pressure refrigerant conduit from the heat exchanger to the compressor for delivery of the low pressure refrigerant from the heat exchanger to the compressor and a refrigerant consisting essentially of methane and propane in said system.

8 Claims, 1 Drawing Figure





METHOD AND APPARATUS FOR LIQUEFYING GASES

This application is a continuation-in-part of our co-pending application Ser. No. 116,894 filed Feb. 19, 1971 now abandoned.

This invention relates to refrigeration apparatus and processes. More particularly, this invention is concerned with a novel refrigeration process, and apparatus useful therein, for producing low temperature refrigeration adequate among other things for liquefying low boiling gases and particularly for producing cryogenic liquids.

In all mechanical refrigeration cycles, thermal energy is transferred from a region of lower temperature to a region of higher temperature by using a fluid which will evaporate and condense at suitable pressures and temperatures for practical equipment designs. The cycle is usually illustrated by a conventional pressure-enthalpy (heat content) diagram. In the simplest refrigeration cycle, a compressor is used to raise the pressure of a given refrigerant vapor sufficiently high for its saturation temperature to be slightly above the temperature of a heat rejection medium which is usually air or water. Heat is transferred from the vapor to the heat rejection medium and causes the refrigerant vapor to condense. The refrigerant liquid is then expanded to a pressure sufficiently low for its saturation temperature to be below the temperature of the product to be cooled. The difference in temperature transfers heat from the product to the refrigerant and causes the refrigerant to evaporate. The compressor removes the refrigerant vapor, recompresses it and the cycle is repeated. A simple cycle, such as described, can be used to obtain temperatures down to about -55°F . depending on the refrigerant used and the compressor limitations.

Compound refrigeration cycles employing two or three compressors in series, with a cooler between compressors, is often used to obtain temperatures down to -150°F . To obtain lower temperatures it is common to employ a cascade cycle which employs at least two and generally three separate refrigeration cycles. In a three stage cascade cycle the refrigerants methane-ethylene-propane can be used in the separate refrigeration cycles to produce temperatures to -260°F . Propane provides the first level of refrigeration to condense a second level ethylene refrigerant. The ethylene in turn provides second level refrigeration and condenses the third level methane refrigerant. Methane provides third level refrigeration, and it can be used to condense lower levels which can use nitrogen, hydrogen or helium.

The cascade cycle is quite widely used in the liquefaction of low boiling gases such as natural gas (methane), nitrogen, helium, oxygen and mixtures of these and other low boiling gases. It is used because, when operating properly, it is highly efficient and provides refrigeration with low power consumption. A cascade cycle however involves a large capital investment because of the compressors, coolers, and evaporators needed in the cycle. In addition, cascade cycles lack flexibility, and variations in the feed stream flow require adjustments in the refrigeration stages which are not easily made or controlled. Also, a small change in the flow rate of a low temperature refrigerant requires a large change in the flow rate of the warm refrigerant.

Even if the refrigeration load is maintained relatively uniform, cascade cycles quite often go out of synchronization or balance with a loss in efficiency.

Another method used to produce low temperature refrigeration is by means of an expander-type cycle. Such a system requires that the gas to be used as the refrigerant be initially available as a high pressure feed stream or be brought to a high pressure. In an expander-type cycle the high pressure gas is first precooled and then expanded through a turbo-expander to produce a low temperature gaseous stream which is utilized to cool a product by countercurrent heat exchange. Cycles of this type generally require ratios of expander flow to product flow of about 10 to 1 for an expander pressure ratio of 6 to 1. Horsepower requirements for expander-type cycles are generally about twice the power needed for a cascade cycle and the cycles require large heat exchangers to accommodate the high mass flow rates.

Another system used to obtain low temperature refrigeration employs a multicomponent refrigerant. Systems of this type are described in Grenier U.S. Pat. Nos. 3,218,816; Grenier et al U.S. Pat. 3,274,787; and Perret U.S. Pat. 3,364,685. In such systems, a multicomponent refrigerant at high pressure is partly condensed by air, water or evaporative-type heat rejection means and then directed to a vapor-liquid separation vessel from which a gaseous high pressure refrigerant stream rich in light components is removed for further processing. The liquid refrigerant stream rich in heavy components is subsequently expanded and utilized as warm refrigeration to further condense the light component high pressure refrigerant gaseous stream in countercurrent flow. Successive steps of vaporliquid separations of the refrigerant after liquid expansions ultimately produce the low temperature refrigeration. In this system, the refrigerant composition is adjusted by adding components of natural gas. This may require fractionating equipment to produce the refrigerant. In such multicomponent refrigerant systems, centrifugal compressors may be used. The large compression ratios required, however, usually exceed the capability of a single case unit. Depending on the number of vapor-liquid separations required, the complexity of the process approaches that of a cascade cycle. Operation of a plant using such a system is very sensitive to the composition of the liquid and vapor refrigerant streams. This requires chromatographic monitoring of the refrigerant streams because they operate with different refrigerant compositions. Also, because of the vapor-liquid separations, the flow rate of these separate phases must be regulated to control the process.

While the described system of the prior art can be used to produce low temperature refrigeration there is a clear need for a simpler system which can be operated and controlled easier and which involves lower investment in apparatus.

According to the present invention there is provided a novel refrigeration system or cycle, and apparatus therefor, which utilizes a multicomponent refrigerant comprising a mixture of 30 to 60, and advisably 40 to 60, mole percent methane, 30 to 60, and advisably 40 to 60, mole percent propane, 0 to 10 mole percent of other gas components such as ethane, butane and higher hydrocarbons and nitrogen, and the sum of the mole percents of methane and propane is at least 90 mole percent. The refrigerant is compressed to a suit-

able high pressure and thereafter heat is rejected from the refrigerant to a suitable ambient heat sink such as atmospheric air, water from a lake, well or river or evaporative cooling, at from 40°F. to 120°F. Partial condensation of at least 10 to 40 mole percent, and usually at least 20 to 30 mole percent, of the refrigerant occurs at this point. After the high pressure refrigerant is cooled to close to the surrounding prevailing atmospheric temperature or the temperature of water, it is passed through a heat exchanger to further cool the refrigerant to a suitable predetermined temperature substantially below ambient temperature to partially or completely condense the refrigerant or produce the refrigerant as a subcooled liquid. The cold high pressure refrigerant is then expanded isenthalpically to a predetermined lower temperature and then it is passed through the same heat exchanger countercurrent to the flow of the high pressure refrigerant. The refrigeration produced by expansion of the refrigerant not only is adequate to cool the high pressure refrigerant to the desired temperature but provides additional low temperature refrigeration which can be used for the liquefaction of natural gas, or any similar stream consisting essentially of methane, without requiring additional cooling or refrigeration means. Partial or total liquefaction of a low boiling gas product can be obtained by use of the provided refrigeration. After the low pressure refrigerant passes through the heat exchanger it is returned to the suction side of the compressor for recompression.

To employ the described refrigeration system to cool a low boiling product gas feed stream, the feed stream at an appropriate pressure can be passed through the same heat exchanger countercurrent to the flow of the low pressure expanded refrigerant and concurrent to flow of the high pressure refrigerant to be cooled in the same heat exchanger. After the feed stream has been cooled in this way to a low temperature it can be expanded to any suitable low pressure.

A refrigeration plant can be built utilizing the described system which will have fewer pieces of equipment and lower capital costs. Because there is less equipment, less interconnecting piping is needed. The heat exchanger can be of relatively simple construction. The system is also easy to control and operate since it employs only one multicomponent refrigerant and does not separate the refrigerant into phases in the cycle. The system employs a single closed loop cycle. A loss of refrigerant by leakage would not drastically affect refrigeration because the overall composition of the refrigerant is the same throughout the cycle. In prior art cycles which successively separate a multicomponent refrigerant by phase separation, a refrigerant leak can change the composition and this will substantially affect performance. The prior art processes also require control of the refrigerant with each separation of the refrigerant into phases. Such multiple control is avoided by the system of this invention. Adjustment in the system of this invention can be effected by changing the refrigerant composition or by changing the compressor suction and/or discharge pressure.

The specific conditions to be employed in any refrigeration plant which utilizes this invention will depend initially on the product composition and pressure. The refrigeration system must then be engineered to produce temperatures cold enough to permit the feed gas, at an initial temperature and pressure, to be cooled.

The product gas fed to the system may have to be pressurized before it is cooled. While there is thus a careful balance of conditions needed to produce low temperature product feed, this is well understood and known by those skilled in the art. The main problem has been to supply the quantity of refrigeration at a proper temperature level required by the product gas undergoing refrigeration.

In designing a refrigeration plant employing this invention, the enthalpy vs. temperature curves for a mixed refrigerant, with pressure as a parameter, are observed for the high pressure and low pressure portions under consideration for use in the process. The quantity of refrigeration available at any temperature level between the two pressure curves can be read from the graph. By observing such plots, a set of pressures and a refrigerant mixture is picked which will yield the required quantity of refrigeration.

The invention will now be described further in conjunction with the attached drawing which is a schematic illustration of a novel combination of apparatus provided by the invention which can be used in practicing the refrigeration process of the invention.

With reference to the drawing, a refrigerant comprising a mixture of at least two gas component is compressed by compressor 11 to a high pressure in the range of about 300 psig to 650 psig. (All pressures herein are gauge pressures.) A centrifugal compressor can be used for this purpose. The warm high pressure refrigerant is fed from compressor 11 by conduit 12 to heat rejector 13 which removes heat from the high pressure refrigerant and lowers it to about ambient temperature. Air and/or water or evaporative cooling is advisably used as the heat sink to absorb heat from the refrigerant as it passes through heat rejector 13. The composition of the refrigerant is selected so that advisably at least about 10 to 40 mole percent of the refrigerant is condensed by passage through the heat rejector. The refrigerant exiting from heat rejector 13 to conduit 14 can be at a temperature of about 40°F. to 110°F., advisably 40°F. to 80°F., and a pressure of about 300 psig to 650 psig.

The refrigerant can be fed directly by conduit 14 through conduit 15 in heat exchanger 20 to cool the refrigerant. Further partial, or complete, condensation of the refrigerant is effected or the refrigerant may be condensed and subcooled. The refrigerant exits from conduit 15 to conduit 19 at a temperature of about -160°F. to -220°F. and a pressure of about 300 psig to 650 psig.

The cooled refrigerant is fed by conduit 19 to expansion valve 21 through which it is isenthalpically expanded and fed to conduit 22 which delivers the cold low pressure refrigerant to conduit 23 for passage through heat exchanger 20 to conduit 24 for delivery to the suction side of compressor 11. The cold low pressure refrigerant passing through conduit 23 in heat exchanger 20 cools the refrigerant fed countercurrent thereto through conduit 15. The refrigerant can be fed by conduit 22 to conduit 23 at any appropriate temperature or pressure. The temperature however will usually be about -230°F. to -160°F. and the pressure about 40 psig to 150 psig with specific conditions being selected according to the refrigeration obtainable in light of the composition of the refrigerant and the refrigerant temperature needed to obtain a predetermined refrigeration ability and capacity.

The system so far described with reference to the drawing comprises a closed loop refrigeration cycle which employs a multiple component refrigerant. It is particularly useful in obtaining low temperature refrigeration, such as is needed to liquefy cryogenic fluids and particularly natural gas, without any other refrigeration. The ability of the cycle to provide refrigeration depends to a large extent on cooling the high pressure refrigerant by passing it through a heat exchanger countercurrent to the expanded low pressure, low temperature refrigerant.

With further reference to the drawing, the described refrigeration system can be used to cool a product gas feed stream to a suitable temperature which will result in partial or total condensation of the product gas feed. A gas feed stream can be fed by conduit 31 to heat exchanger 20 for passage therethrough by conduit 32. The gas feed stream is advisably passed through the heat exchanger countercurrent to flow of the low pressure-low temperature refrigerant. The cooled feed stream, which may be partially or all condensed, is fed from the heat exchanger 20 by conduit 32 to conduit 33 which communicates with expansion valve 34. The feed stream is expanded through valve 34 to a low pressure and by conduit 35 it is fed to storage tank 36. If the cooled feed stream is warmer than the storage temperature, then a portion of the feed stream will flash to vapor upon expansion. Flash and boil-off vapors are removed from storage tank 36 by conduit 37 from which it can be returned to conduit 31 or a distribution line. Liquefied gas can be removed from tank 36 by conduit 38.

The load stream from conduits 31 to 33 is shown on the drawing as L and the refrigerant stream being cooled from conduit 14 to conduit 19 is labeled M. N represents the refrigerant stream from conduit 22 to conduit 24 which supplies the gross refrigeration. The enthalpy difference of stream N must be equal to the sum of the enthalpy difference of L plus the enthalpy difference of M. So long as there are reasonable temperature differences between these streams the system operates satisfactorily. This requires, however, that the conditions and refrigerant be selected to meet such requirements. Such selections and determinations of conditions are well within the capability of the art when the invention is to be put into practice.

The following Table I gives representative conditions which can be used in the refrigeration system of this invention, such as shown by the drawing, employing particular mixed refrigerant compositions to liquefy specific gases.

Table I

Conduit	Refrigerant Composition	
	A 40 Mole % methane, 60 Mole % propane °F/psig	B 50 Mole % methane, 50 Mole % propane °F/psig
31	70/300	70/200
33	-190/300	-200/200
35	-260/15	-260/15
14	90/450	90/500
19	-190/450	-200/500
22	-200/50	-210/50
24	80/50	80/50
	C 57 Mole % methane 43 Mole % propane °F/psig	D 42 Mole % methane 5 Mole % ethane 43 Mole % propane

Table I-Continued

Conduit	Refrigerant Composition	
	A 40 Mole % methane, 60 Mole % propane °F/psig	B 50 Mole % methane, 50 Mole % propane °F/psig
Conduit		4.5 Mole % butane 0.5 Mole % nitrogen
31	70/390	80/320
33	-165/390	-205/320
35	-260/0.5	-260/0.5
14	87/590	80/350
19	-165/590	-205/350
22	-175/150	-215/50
24	80/150	70/50

Other mixed gases can also be used as the refrigerant including mixtures of methane, ethane and propane, mixtures of methane, propane and nitrogen, and mixtures of methane, ethane, propane and butane. It is to be understood, however, that each refrigerant composition will contain 30 to 60 mole percent methane, 30 to 60 mole percent propane, 0 to 10% of other gases and the sum of the methane and propane is at least 90%. There is no need to have any gases present in the refrigerant except methane and propane to obtain the desired refrigeration. Preferred refrigerants contain 40 to 60% mole percent methane and 40 to 60 mole percent propane and about 0 to 5% other gases. For purposes of economy, it is advisable to formulate the refrigerant from commercially available methane and commercially available propane since these are less expensive than the highly purified gases. Commercially available methane in the form of natural gas is usually at least 90% and generally at least 95%, methane with the balance being other gases such as ethane, nitrogen and higher hydrocarbons. Commercially available propane is generally at least 98% propane with the balance being other gases such as butane and higher hydrocarbons. When the commercially available grades of methane and propane are thus used as the refrigerant, there will usually be about 5 to 10% and sometimes more of other gases present. These other gases do not significantly affect the refrigeration process.

EXAMPLE

A refrigerant mixture consisting of 50% natural gas (98% methane) and 50% commercial propane is used in the closed loop refrigeration cycle shown in the drawing to liquefy a feed stream of natural gas.

The refrigerant is fed by line 24 at 70 psig and 40°F. to compressor 11. The refrigerant is fed by conduit 12 at 350 psig to heat rejector 13. Heat is there rejected to air at a temperature of 40°F. and the refrigerant temperature is lowered to about 50°F. The refrigerant at 50°F. and 350 psig is then fed by conduit 14 to conduit 15 for passage through heat exchanger 20.

The refrigerant emerges from heat exchanger 20 at -200°F. and 350 psig. It is fed by conduit 19 to expansion valve 21 from which it emerges at -210°F. and 70 psig. The refrigerant is then fed to conduit 22 and then passed through heat exchanger 20 by conduit 23. The refrigerant emerges from the heat exchanger at 40°F. and 70 psig and by means of conduit 24 is returned to the suction side of compressor 11.

A feed stream of natural gas at 90°F. and 400 psig is delivered by conduit 31 to conduit 32 in heat exchanger 20. The feed stream emerges from the heat ex-

changer at -200°F . and 400 psig and by means of conduit 33 it is fed to expansion valve 34. The feed stream emerges from the expansion valve and is fed by conduit 35 to insulated storage tank 36. The liquefied natural gas is stored at about -260°F . and 0.5 psig in tank 36 and the vapor phase from the flash expansion is removed by conduit 37 and fed to a service line and/or alternatively compressed such that it can join conduit 31. Conduit 38 is used to remove liquefied natural gas from tank 36 as needed.

The flow rates of the feed stream and refrigerant are regulated so that one mole of the natural gas feed stream is cooled by three moles of refrigerant.

Various changes and modifications of the invention can be made and, to the extent that such variations incorporate the spirit of this invention, they are intended to be included within the scope of the appended claims.

What is claimed is:

1. A process for the liquefaction of a gas consisting essentially of methane, which process comprises cooling said gas under pressure by means of a refrigeration process employing a refrigerant moving through a single closed loop cycle without sidestreams, the overall composition of the refrigerant being the same at all points in the loop without separating respective components of the refrigerant, said refrigeration process consisting essentially of:

compressing a refrigerant to a high pressure, said refrigerant consisting essentially of the components

30 to 60 mole percent methane, 30 to 60 mole percent propane, 0 to 10 mole percent of other gas components, the sum of the mole percents of methane and propane being at least 90 mole percent,

cooling the high pressure refrigerant to about or below ambient temperature, so that at least 10 mole percent of the refrigerant is condensed to a liquid, by heat rejection to a member of the group consisting of ambient air, water and evaporative cooling, at a temperature below about 120°F ,

passing the cooled high pressure refrigerant through a heat exchanger to reduce the refrigerant temperature substantially below ambient temperature, resulting in subcooled liquid refrigerant,

expanding the cold high pressure refrigerant through an expansion valve to give a cold low pressure refrigerant, and

passing the cold low pressure refrigerant from the expansion valve back through the same said heat exchanger and then to the compressor to thereby provide all of the refrigeration necessary to both reduce the temperature of the high pressure refrigerant passed therethrough to a subcooled state and have extra refrigeration for cooling said pressurized gas to a temperature at which it can be liquefied without further refrigeration.

2. A process according to claim 1 in which the high pressure cooled refrigerant passed to the heat exchanger is at a pressure of about 300 psig to 650 psig and at a temperature allow about 110°F ., and the cold low pressure refrigerant passed to the heat exchanger from the expansion valve is at a pressure of about 40

psig to 150 psig and at a temperature of about -160°F . to -230°F .

3. A process according to claim 1 in which the refrigerant is essentially methane and propane in the range of 40 to 60 mole percent methane and 40 to 60 mole percent propane.

4. A process according to claim 1 in which a natural gas feed stream under pressure is passed through the heat exchanger to cool the natural gas by heat exchange with the cold low pressure refrigerant passed therethrough, and the natural gas after such cooling is directly expanded through an expansion valve to a lower pressure without additional cooling prior to the said expansion.

5. A process according to claim 2 in which the high pressure refrigerant passed to the heat exchanger is at a temperature of about 40°F . to 80°F .

6. A process according to claim 2 in which a natural gas feed stream under pressure is passed through the heat exchanger to cool the natural gas by heat exchange with the cold low pressure refrigerant passed therethrough, and the natural gas after such cooling is isenthalpically directly expanded through an expansion valve to a lower pressure without additional cooling prior to the said expansion.

7. A process for the liquefaction of a gas consisting essentially of methane, which process comprises cooling said gas under pressure by means of a refrigeration process employing a refrigerant moving through a single closed loop cycle without sidestreams, the overall composition of the refrigerant being the same at all points in the loop without separating respective components of the refrigerant, said refrigeration process consisting essentially of:

compressing a refrigerant consisting essentially of about 40 to 60 mole percent of methane and the remainder propane to a pressure of about 300 to 650 psig,

cooling the refrigerant by heat rejection to a member of the group consisting of air, water and evaporative cooling at from 40°F to 120°F , to cool the refrigerant to about 50° to 110°F at about 300 to 650 psig,

passing the refrigerant through a heat exchanger to cool the refrigerant to about -160° to -220°F at about 300 to 650 psig,

expanding the refrigerant through an expansion valve to bring the refrigerant to about 40 to 150 psig and about -160° to -230°F , and

passing the refrigerant from the expansion valve, back through the same heat exchanger and then to the compressor to thereby provide all refrigeration necessary to cool and condense the refrigerant in its initial pass through the heat exchanger at a pressure of about 300 to 650 psig and provide extra refrigeration for cooling said gas to a temperature at which it can be liquefied without further refrigeration.

8. The process of claim 7 in which said gas is natural gas.

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