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Pachaly

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[54] LNG EXPANDER CYCLE PROCESS EMPLOYING INTEGRATED CRYOGENIC PURIFICATION

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[58] **Field of Search** 62/23, 24, 27, 28, 26, 29, 62/38, 39, 40, 54, 52, 53, 30, 40

[56] **References Cited**

UNITED STATES PATENTS

3,675,435	7/1972	Jackson	62/28
3,292,381	12/1966	Bludworth	62/27
2,600,110	6/1952	Hachmuth	62/26
3,348,384	10/1967	Harmens	62/38

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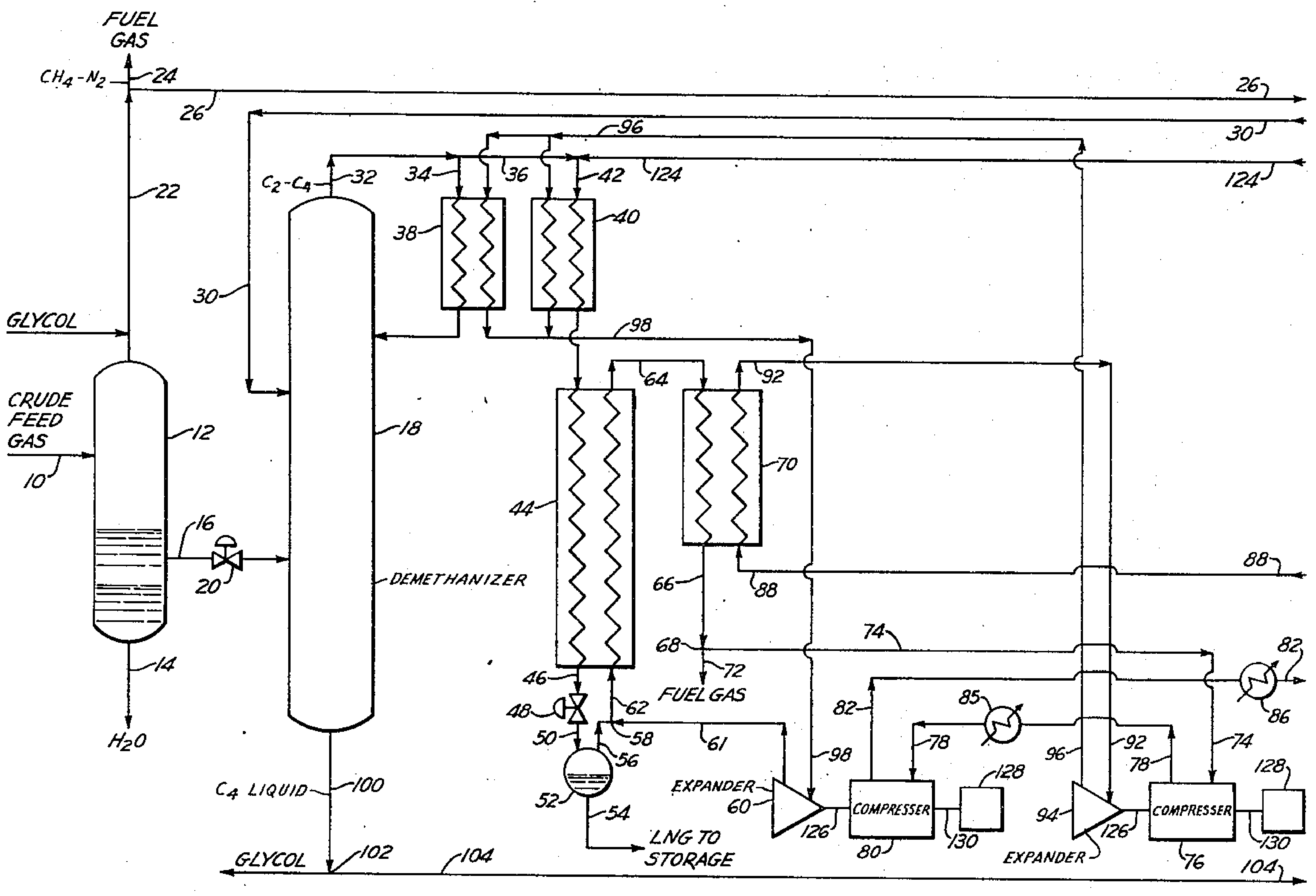
[57] ABSTRACT

A process and apparatus for the liquefaction of natural gas wherein raw feedstock is cryogenically fractionated to remove essentially all of the carbon dioxide and C_{5+}hydrocarbons therefrom, and wherein the cryogenically purified feedstock is cooled and liquefied under pressure in a cryogenic heat exchanger. The pressurized cold liquid from the heat exchanger is isenthalpically expanded to reduce the pressure and further cool the liquid while at the same time flashing a minor gas fraction. Refrigeration for the liquefaction of the natural gas is supplied by a circulating refrigerant stream which is compressed and work-expanded to obtain the necessary cooling. The minor flash gas portion of the liquefaction step is commingled with the circulating refrigerant stream so that the analysis of the refrigerant stream is always rich in the lighter portions of the liquefaction stream, thus aiding in maintaining refrigeration temperature differentials to drive the liquefaction step. The work-expanded refrigerant portion undergoes a compression cycle and is work-expanded in a series of expansion turbines. The expansion turbines furnish at least part of the power necessary to drive the compressor system in the refrigerant gas cycle.

17 Claims, 2 Drawing Figures



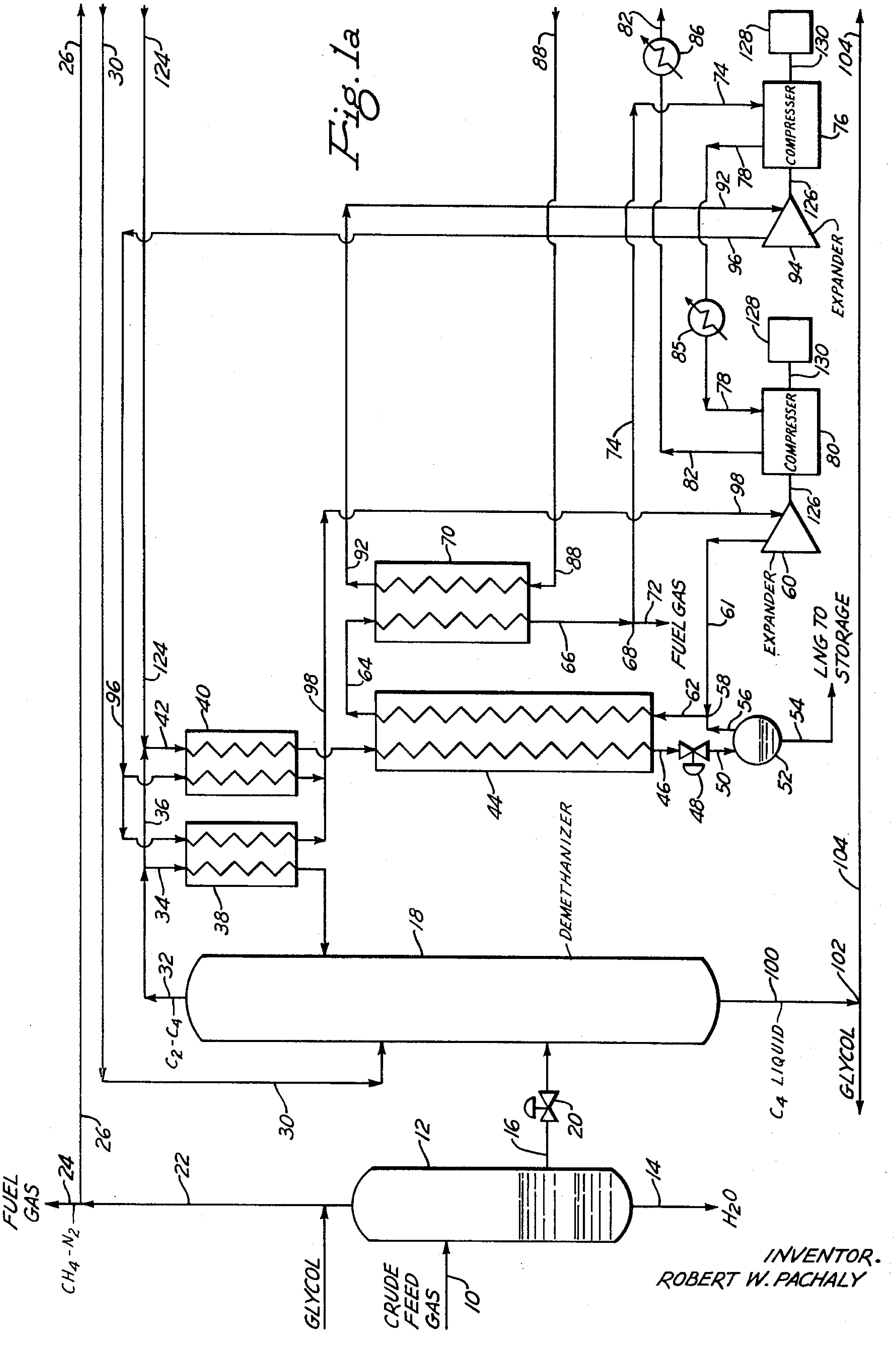


Fig. 1a

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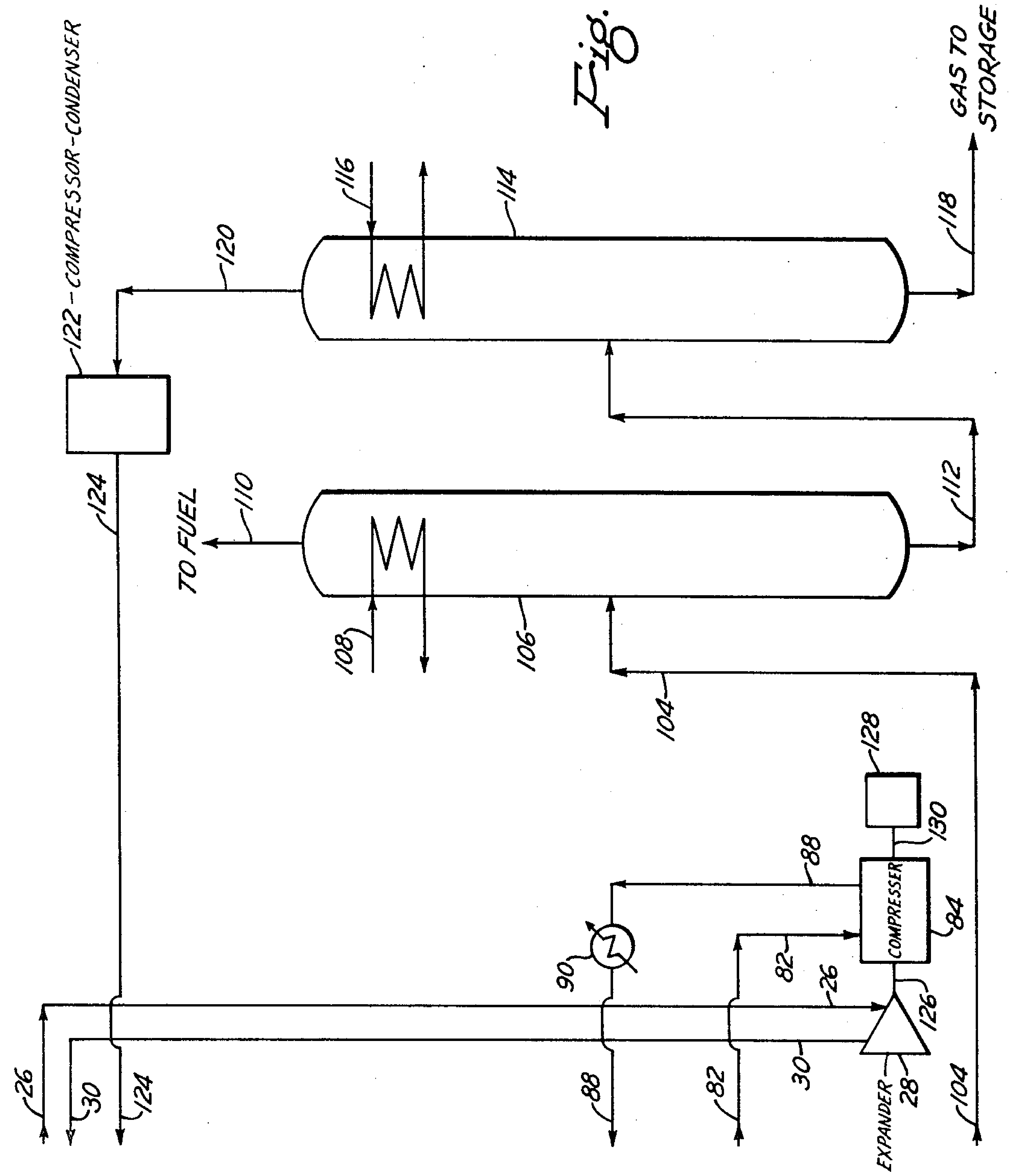
Fig. 1b



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LNG EXPANDER CYCLE PROCESS EMPLOYING INTEGRATED CRYOGENIC PURIFICATION

RELATED APPLICATIONS

This application is related to Ser. No. 36,277, filed May 11, 1970 and entitled Apparatus and Process for Liquefaction of Natural Gases.

BACKGROUND OF THE INVENTION

This invention relates to the liquefaction of a gas; and, more particularly, to a method and apparatus for the liquefaction of natural gas. Even more particularly, this invention relates to a LNG expander cycle process employing an integrated cryogenic purification, and to apparatus therefor.

Natural gas is mostly composed of methane, but usually contains small amounts of heavier hydrocarbons such as ethane, propane, butane and the like as well as small amounts of aromatic hydrocarbons. Natural gas also contains minor amounts of non-hydrocarbons, such as water, nitrogen, carbon dioxide and the like. Thus, the present invention is directed to a cryogenic purification of raw natural gas to remove substantially all of the water, carbon dioxide and heavy hydrocarbons therefrom, and to the subsequent liquefaction of the purified natural gas to form a liquid product stream comprised mainly of methane and substantially free from carbon dioxide and heavy hydrocarbons.

Recently, there has been an increasing demand for a simple yet economic process for reducing natural gas to a liquified state. One of the reasons is that natural gas wells are being discovered in remote parts of the world where transporting the gas to the point of consumption by pipeline is difficult or impossible. Transportation of natural gas in the gaseous state by marine vessels would be uneconomical, unless the gaseous materials were compressed, and this in turn would be impractical since the containers would have to be exceptionally strong and extremely large to hold the gas to be transported. The cost of such containers and the industrial hazards that attend their use are so great that the transportation of compressed gas is impractical.

Accordingly, an efficient process for the liquefaction of natural gas is of great importance, particularly, where the supply thereof is in a remote area and there is a demand at a distant market place. Such a process is particularly important where the gas must be transported by marine vessels since, by liquefaction of natural gas, the volume thereof can be reduced to nearly one six-hundredth its volume and the containers need not be of the thickness, strength, and capacity necessary for the shipment of compressed gas.

DESCRIPTION OF THE PRIOR ART

Many attempts have been made to find an economical process for liquifying natural gas, but numerous of the prior art processes have major disadvantages or limitations. For example, the power consumption of certain prior art liquifier systems is prohibitively high, while in others the need for the use of an inordinately large number of expensive heat exchangers and compressors exists. In addition, some liquifying systems which are acceptable in more industralized areas are often less suited for use in some of the more underdeveloped and remote areas of the world. For example, a system that requires molecular sieves and/or specific adsorbents for the initial purification of raw natural gas feedstock is less economically operated in areas where such sieves and adsorbents are not readily available and/or where spent sieves and adsorbants have essentially no salvage value. Still other prior art system require complicated high pressure equipment which is difficult to maintain and to control automatically. And yet others require the use of expensive refrigerants which must be shipped to the liquifying plant.

At present, there are three known basic cycles for liquefaction of natural gases. These are generally referred to as the "Cascade Cycle", "Multicomponent Refrigerant Cycle" and "Expander Cycle". Many minor variations can be effected in the design of each type of cycle to adapt it to the specific process requirements.

Briefly, the "Cascade Cycle" consists of a series of heat exchanges with the feed gas, each exchange being at successively lower temperature until the desired liquefaction is accomplished. The levels of refrigeration are obtained with different refrigerants or with the same refrigerant at different evaporating pressures. Frequently, a combination of both approaches is used. The high efficiency of the "Cascade Cycle" is offset by rather high investment cost in the extensive heat exchange and compression systems. Piping costs are high and considerable area is necessary for the large amount of equipment. This type of plant is more easily justified when fuel costs are high such as at the delivery end of a pipeline system. This system would be impractical, however, where there is limited space or poor soil conditions as exists in many of the remotely located gas wells discovered in the world.

A "Multicomponent Refrigerant Cycle" has been operated on a pilot scale but no large commercial operation has been achieved to date, although the basic design is known to those skilled in the art. This process was designed in an effort to eliminate some of the complexity of the "Cascade Cycle" and still retain the low power requirement. The process uses a carefully controlled analysis of the hydrocarbon refrigerant stream so that at successive temperature levels of cooling specific liquid fractions are obtained. Each of these liquid fractions, condensed at high pressure, is then evaporated to obtain the required refrigeration. The composition changes of the successively condensed fractions when evaporated at a constant pressure furnish distinct temperature levels of heat exchange. In this respect, the system operates as an autocascade cycle.

The compression system of the foregoing plant is simple since only one refrigerant is used. However, the heat exchange system and its controls are extensive and costly. The nature of the equipment requires series flow of all refrigerant gas over the cascade type of exchangers. This can be accomplished by vertically stacking the exchangers to a height of over 200 feet. Unless good soil bearing is available, the support of such a unit is difficult and the erection of such unit on the deck of a floating vessel presents serious problems of stability. To segmentize the heat exchangers would require very large vapor lines in the range of 5 to 6 feet in diameter.

Therefore, this type of cycle would be impractical in a liquefaction plant near off-shore wells, where the soil bearing is poor or where the wells are in a nonindustralized part of the world. A large Multicomponent Refrigerant cycle also requires a complete hydrocarbon fractionating unit to prepare the pure components required to maintain the carefully controlled refrigerant analysis.

The "Expander Cycle" is similar to that used on most of the large air separation plants today and it does have the advantage of simplicity over a "Cascade Cycle". In this cycle, gas is compressed to a selected pressure, cooled, then allowed to expand through an expansion turbine, thereby performing work and reducing the temperature of the gas. It is quite possible to liquify a portion of the gas in such an expansion. The low temperature gas is then heat exchanged to effect liquefaction of the feed. The power obtained from the expansion is usually used to supply part of the main compression power utilized in the refrigeration cycle. If the expander cycle is a closed cycle, any suitable refrigerant gas can be used. If it is an open cycle liquid natural gas plant, the refrigerant would have to be methane or a methane-nitrogen mixture as this would be flashed from the gas-liquid separator in the process.

An expander cycle plant is compact, has minimum items of equipment, simple control and utilizes all standard machinery and heat exchangers. This type of plant has an important added advantage of mechanical simplicity that is particularly significant when considering operations in remote areas of the world.

An efficient "Expander Cycle" method for liquefaction of low boiling gases such as oxygen and nitrogen is presently known. The heat exchanger cycle of this process is operated under 400 to 1000 psia pressure and cooling is made more efficient by causing components of the warming stream to undergo a plurality of work expansion steps with intervening reheating. In this process, two or more heat exchangers are employed in series with an intermittent refrigeration of the incoming gas. A portion of the feed stream which had been previously cooled by a warm-leg heat exchanger and a refrigeration unit is work expanded and thereafter used to absorb heat from the remaining portion of the feed stream in a countercurrent heat exchanger. The warmed effluent gas from the heat exchanger is work-expanded a second time and this cooled and expanded gas is combined with the flash gas to be used to absorb heat from the incoming feed stream in the second heat exchanger. The cold effluent from the second heat exchanger is isenthalpically expanded and passed to a gas-liquid separator to remove the liquid for storage and the flash gas is combined with the work-expanded gas as discussed above. The combined warmed effluent gas from the heat exchangers is recycled to the feed stream to be recompressed and undergoes the foregoing liquefaction.

This type of process suffers the drawback of expensive refrigerants and separate compression and expansion systems driven by an outside source of power to maintain its operation. Furthermore, such a process is not practicable in the liquefaction of natural gas since there is no provision for handling the heavy gases which freeze at the temperatures encountered in the heat exchangers. In addition, if the flash gas was recycled back to the feed stream, the lower boiling ends, i.e., nitrogen, etc. of the feed mixture would increase in the heat exchanger liquifier causing an imbalance in the system requiring additional energy to liquify and cause thermodynamic inefficiency. This latter problem is not apparent when there is only one pure material to be liquified such as nitrogen and oxygen, but when dealing with the liquefaction of natural gases which contain a plurality of gases having boiling points lower than methane, the problem is paramount.

In the above-mentioned related application, Ser. No. 36,277, filed May 11, 1970, it is pointed out that the "Expander Cycle" process can be successfully utilized in liquifying natural gas by separating a combined residual flash gas and refrigerant gas effluent from the heat exchanger-liquifier into a bleed portion and a refrigerant gas portion, in stead of recycling this combined mixture to the feed stream as described in the heretofore mentioned prior art. While this latter process offers significant advantages over the previously described prior art processes, it requires the use of molecular sieves and adsorbents to purify the raw feed gas before subjecting it to liquefaction. Accordingly, the use of this process in a remote part of the world would require periodic shipments of fresh sieves and adsorbents to the plant site, as well as shipments of the spent sieves and adsorbents to an industralized area for salvage.

In light of the inherent problems associated with the production of liquified natural gas, the foregoing prior art processes do not offer a sufficiently economic and practicable system for liquifying natural gas in remote non-industrial parts of the world where the soil bearing is poor and where expended materials have little or no salvage value.

SUMMARY OF THE INVENTION

It has now been discovered that in an "Expansion Cycle" process, a greater proportion of the natural gas feed is liquified efficiently and a substantially self-balancing process is obtained when a raw natural gas feedstock is purified by an integrated cryogenic fractionation prior to liquefaction and when the liquefaction comprises separating the combined residual flash gas and refrigerant gas used to liquify and subcool the natural gas into a bleed gas portion and a recycle refrigerant gas portion instead of recycling the entire of the flash and refrigerant gases.

Since the liquefaction apparatus and process of the present invention is compact, efficient and self-sustaining, it is capable of being prefabricated on a mobile platform which may be of a marine type that can be shipped to distant and remote parts of the world. The mobile marine means contemplated by the present invention can be of the type disclosed in the U.S. Pat. No. 3,161,492 to Keith et al., which disclosure is incorporated herein by reference. Additionally, the mobile marine platform can be of the floating type wherein the platform is not supported by mechanical means, such as caissons, engaging the marine floor but rather is supported by the buoyancy of the platform itself. Such a floating platform can take the form of a barge or conventional, self-powered ocean-going vessel such as a tanker. Such an apparatus and process prefabricated on a marine means is so designed as to permit direct loading of the liquid into a transport means such as a ship or tanker. Furthermore, by employing the apparatus of the present invention it is possible to bring the prefabricated plant to off-shore gas wells while it would be impossible using the cumbersome processes of the prior art.

More specifically, the invention contemplates the preassembly of a simplified expansion type of liquefaction plant on a marine platform which is only a portion of the size of the conventional cascade liquefaction plant disclosed in the above-cited patent, and which avoids the need for purification systems which employ molecular sieves and adsorbents that must be transported to a plant site and periodically regenerated, replaced and salvaged.

Accordingly, the present invention provides, in its preferred aspects, a process for producing a large supply of liquified natural gas in areas remotely located in the world where the source of power is limited or non-existent and where the use of molecular sieves and adsorbents is uneconomic.

An object of the present invention is to provide a process which will produce liquified natural gas employing moderate pressures (**200-1000** psia) and still maintain thermodynamic efficiency. Accordingly, this efficiency is accomplished by controlling the condensing gas pressure with relation to its analysis so that the temperature-enthalpy curve is essentially a straight line. This enhances the possibility of refrigeration by a cold gaseous stream eliminating many of the cryogenic liquid handling problems of other processes and which would be extremely difficult and hazardous in floating platform construction as described above.

Another object of the present invention is to accomplish liquefaction by employing a countercurrent heat exchanger-liquifier or subcooler whereby the cooling or refrigerant stream is maintained in the form of a gas instead of a boiling liquid refrigerant stream. This object can be accomplished since it has been unexpectedly found that the nitrogen content of the feed gas stabilizes in the refrigerant system and the actual refrigerant becomes an equilibrium mixture of methane and nitrogen gases. This analysis change assists greatly in providing the required temperature driving force to promote the liquefaction of the main stream of natural gas which because of its heavier constituents condenses at a higher temperature.

Still another object is to employ as the refrigerant material a combination of the flash gas obtained in the pressure letdown from the heat exchanger-liquifier and the cold expansion turbine effluent gas thereby causing the lower boiling point gases in the feed gas stream to reach an equilibrium in the expander refrigerant cycle. The refrigerant system is thus allowed to operate effectively at lower temperatures and pressures than processes heretofore employed. By being able to operate at lower temperatures and pressures, the equipment attending to the process of the present invention is far less expensive than processes heretofore employed.

It is another object of the present invention to form a bleed stream of the warmed effluent refrigerant gas from the heat exchanger-liquifier equivalent to the flow rate of the flash gas coming from the LNG gas-liquid separator. This bleed stream can be employed as fuel for a gas turbine system which in turn furnishes part of the power required to drive the compressors in the refrigeration cycle.

An additional object of the present invention is to control the temperature and pressure of the refrigerant gas so as continually to maintain a gaseous state in the heat exchangers and expansion turbines. It has been unexpectedly found that if the temperature-enthalpy curve of the feed gas is sufficiently straight as controlled by its pressure it is not necessary to cool the refrigerant gas in the expansion engine to such an extent that some of the gas liquifies in order to liquify the incoming gas. Therefore, the present invention has a decided advantage over the prior art processes which partially liquify the gas in the expansion turbines, thus eliminating the problem of erosion in the vanes of the turbine, which, in turn, becomes costly in the overall operating expense of the liquifaction plant.

In accordance with the present invention there is provided an integrated process for separating substantially all of the carbon dioxide and water and most of the heavy hydrocarbons from raw natural gas feedstock, and then liquifying the resulting purified natural gas mixture to form a product comprising nitrogen and hydrocarbons containing up to about **6** carbon atoms. The raw natural gas mixture is purified by first producing the crude mixture, under pressure, into an inlet separator vessel wherein condensed water and a hydrocarbon condensate are separated from the gas mixture as two substantially immiscible liquid layers. The water layer is drained from the bottom of the separator and discarded. The condensed hydrocarbon layer and the gaseous portion of the raw feed are transferred from the separator to a cryogenic LNG fractionator distilling all of the nitrogen, substantially all of the methane and essentially none of the carbon dioxide contained in the raw feed as overhead. The bottoms from the LNG fractionator, which contain a small amount of methane, as well as all of the C_{2+} hydrocarbons and essentially all of the carbon dioxide contained in the raw feed, is further fractionated to separate (a) the carbon dioxide, methane and part of the ethane at one end of the spectrum and (b) the C_{5+} hydrocarbons at the other end of the spectrum from (c) the remainder of the hydrocarbons (predominantly ethane with but minor amounts of C_3 and C_4 hydrocarbons); the latter being combined with the portion of the LNG fractionator overhead not used for reflux. This combined stream is then liquified to form the LNG product. In a preferred embodiment, after removal of the carbon dioxide fraction, the remaining C_{2+} hydrocarbons are fractionated in an LPG fractionator to separate a C_2–C_4 fraction from a C_{4+} gas liquid fraction, whereupon only the C_2–C_4 fraction is combined with the overhead from the LNG fractionator, thereby forming a substantially purified natural gas mixture that is essentially free from carbon dioxide and completely devoid of C_{5+} hydrocarbons. In any event, the carbon dioxide fraction split from the LNG fractionator bottoms may be used as fuel gas to supply part of the power requirements of the process equipment.

In the event of the temperature and pressure conditions of the raw gas mixture leaving the inlet separator are such that hydrates may form during subsequent processing, a quantity of an inert dessicant, such as a solution of triethylene glycol, may be injected into the gas mixture to reduce its dew point. This may be conveniently carried out, for example, by injecting the triethylene glycol solution into the gas mixture as it leaves the inlet separator, whereafter the water-enriched glycol solution is removed from the LNG fractionator bottoms by passing the bottoms to a heavy hydrocarbon surge drum wherein the glycol solution and hydrocarbons separate, the latter then being decanted and transferred to the carbon dioxide fractionator.

The substantially purified natural gas comprising the LNG fractionator overhead and either the carbon dioxide free fraction from the carbon dioxide fractionator or the C_2–C_4 fraction from the LPG fractionator is then cooled under elevated pressure by heat exchange with a combined, methanenitrogen refrigerant gas mixture obtained elsewhere in the process so as to effect liquefaction of a predominant portion of the purified natural gas mixture while heating the combined refrigerant gas mixture. The pressure of the cooled natural gas is then substantially isenthalpically reduced, thereby further cooling it, forming (by flash evaporation) a minor gas fraction consisting essentially of methane and nitrogen and liquifying completely the balance of the natural gas mixture to form a major liquid fraction containing methane and substantially all of the C_{2+} hydrocarbons present in the purified natural gas feed. The minor, methane-nitrogen gas fraction is then separated from the major liquid fraction and the major liquid fraction is recovered as product.

The separated minor, methane-nitrogen gas fraction is combined with an isentropically expanded methane-nitrogen refrigerant gas mixture circulated in the process. This gas mixture can be produced elsewhere in the process. This combination of methane-nitrogen gas constitutes the combined refrigerant gas mixture mentioned previously and, as also mentioned previously, this combined refrigerant gas mixture is employed to cool the purified natural gas mixture in the liquefaction heat exchange step. A major portion of the heated combined refrigerant gas mixture leaving the liquefaction heat exchange step is compressed to provide a compressed, methane-nitrogen refrigerant gas mixture. This gas mixture, after suitable precooling, is substantially isentropically expanded in one or more work recovery engines whereby mechanical energy is obtained, the gas mixture is further cooled, and the isentropically expanded, methane-nitrogen refrigerant gas mixture mentioned previously is obtained. The compressed methane-nitrogen gas mixture, isentropically expanded methane-nitrogen gas mixture and the corresponding portion of the combined gas mixture constitute a circulating refrigerant system.

At least a major portion of the heated, combined refrigerant gas mixture leaving the liquefaction heat-exchange step and prior to compression is heat exchanged with the compressed, precooled methane-nitrogen refrigerant gas mixture whereby such combined gas mixture is further heated to a temperature suitable for entering the compressors. Concurrently, the compressed, methane-nitrogen refrigerant gas mixture is cooled to a temperature level such that upon work expansion as previously described appropriate temperature levels and refrigeration capacity are developed for liquefaction of the natural gas mixture.

A minor portion of the combined refrigerant gas mixture after leaving the liquefaction heat exchange step is removed from the circulating refrigerant system and is employed as fuel gas to supply a portion of the power needed to drive the above-mentioned compressors. Although this minor portion can be removed at any point in the circulating refrigerant system, it is preferred to remove it prior to compression of the combined refrigerant gas mixture. Advantageously, this minor portion is removed subsequent to the heat exchange of the combined refrigerant gas mixture with the compressed, precooled methane-nitrogen refrigerant gas mixture and prior to compression of the combined refrigerant gas mixture. The mechanical energy obtained from the work recovery engines is also employed to provide at least part of the power needed to compress the major portion of the combined gas mixture. The quantity of the minor portion removed from the refrigerant system is substantially equal in magnitude to the minor methane-nitrogen gas fraction formed by the isenthalpic pressure reduction (flash evaporation) previously described.

The raw natural gas feedstock suitable for charging to the initial separating vessel of this invention may comprise natural gas obtained from a crude oil well (associated gas) or from a gas well (non-associated gas). However, various natural gas streams may not be suitable for immediate employment in the present invention due to the source, both ultimate and immediate, from which they are obtained. Thus, for example, both associated and non-associated gas obtained directly from the well head may be at an undesirably high temperature, e.g. substantially in excess of 100°F. Further, associated gas or gas obtained from certain storage facilities may be of inadequate pressure for employment in the present process, e.g. only about 100 or 200 psia. Thus, certain natural gas streams, depending upon their source, may require certain pretreatment or preparation prior to employment in the present invention.

While there is no theoretical maximum to the pressure which can be employed in the various fractionators and heat exchangers of the present invention, it would appear that there is little practical advantage to be gained by employing pressures in excess of 1000 psia. This is particularly true in connection with the heat exchanger or subcooler employed in the liquefaction step unless the purified natural gas entering the subcooler contains a very high methane content (95%+). Preferably a maximum pressure no greater than about 750 psia is employed, thereby avoiding the necessity of very high pressure vessels. Advantageously, a maximum pressure of about 650 psia is maintained. On the other hand, it is found that a minimum pressure of about **350** psia is required for this heat exchange liquefaction and preferably a pressure of about 600 psia is maintained. The pressure selected is such that a plot of the temperature vs. enthalpy of the gas to be liquified approaches a straight line, i.e. not have a large enthalpy increase over a narrow temperature range. Thus the pressure selected will depend on the gas composition. Accordingly, therefore, a low pressure natural gas stream, such as an associated gas, can be compressed to achieve the desired pressure range either prior to introduction into the initial separator vessel or prior to introduction into the LNG fractionator, whereas an extremely high pressure natural gas stream, such as a nonassociated gas, can be reduced in pressure either prior to introduction to the initial separator vessel or, preferably, after leaving the separator vessel but prior to introduction into the LNG fractionator. This reduction of pressure can be accomplished by throttling, employment of a turbo-expander or any other expansion or pressure reducing means whether capable of recovering mechanical energy or not.

In the event that the initial temperature of the natural gas is too high it must be cooled, such as, for example, by heat exchange or other techniques well-known in the art. If the natural gas is at an undesirably high temperature and an undesirably high pressure it is possible to reduce both the temperature and pressure of the gas simultaneously by the simple technique of adiabatic expansion. By use of these well-known techniques it is possible to limit the temperature of the natural gas charged to the LNG fractionator, for example, to a maximum of about 150°F., preferably, however, the maximum temperature will not exceed about 125°F. It is particularly advantageous to employ temperatures below about 100°F. Selection of the exact processing temperature can depend on the processing sequence selected for gas purification as discussed below.

It will be understood, of course, that the selection of the particular operating pressure as well as the temperature employed in the various fractionators and in the liquefaction heat exchanger will be determined to a great extent by the particular composition of the natural gas being treated as well as by the temperature of the natural gas being charged. In any event, however, it is necessary that the temperature and pressure conditions in the liquefaction heat exchanger be maintained such that at least a predominant portion of the natural gas effluent therefrom is in the liquid state. In this latter connection, the temperature and pressure conditions in the liquefaction heat exchanger are generally such that about 85 percent or more of such natural gas is in the liquid state. Preferably at least about 90 percent, more preferably at least about 95 percent, is liquified. Usually the temperature of the cooled natural gas from the liquefaction heat exchange will be about −175° to about −225°F. when employing pressures within the ranges indicated above.

After liquefaction heat exchange, the pressure of the natural gas isenthalpically reduced to a pressure just slightly above atmospheric pressure, generally falling in the range of from about 16 to about 35 psia, and preferably in the range of from about 20 to about 30 psia. This isenthalphic reduction in pressure results in the flash evaporation of the minor gas fraction, liquefaction of the balance of the natural gas and the overall reduction in temperature of both the minor gas fraction and the remaining major liquid fraction. The minor gas fraction generally comprises up to about 15 mol percent of the total liquified natural gas mixture and preferably comprises from about 5 to about 10 mol percent of the liquified natural gas mixture. Again the exact extent of the reduction in temperature effected by the isenthalpic pressure reduction is dependent primarily upon the magnitude of reduction in pressure effected and upon the composition of the natural gas mixture. Accordingly, the magnitude of the reduction in pressure must be sufficient to reduce the temperature to a level sufficient to ensure liquefaction of a major portion of the particular composition of natural gas at the lower pressure. Thus, by way of illustration, the isenthalpic reduction in pressure of some substantially completely liquified natural gas mixtures from the range of about 600 psia down to about 20 psia will result in a further reduction in temperature of the natural gas in the range of about 40° to about 70°F. and the achievement of a temperature sufficient to liquify completely the main portion of the stream at the lower pressure, e.g., −240° to −260°F.

The minor gas fraction which has been flashed comprises about 95 mole percent (dry) methane and about 5 mole percent (dry) nitrogen, and contains a substantial portion of the nitrogen initially contained in the raw feedstock. The liquid fraction remaining after pressure let down comprises about 90 to 95 percent of the methane and essentially all of the C_{2+} hydrocarbons fed to the liquifier heat exchanger. The mole percent (dry) of nitrogen contained in the remaining liquid fraction is substantially lower than the mole percent of nitrogen in the liquified natural gas prior to pressure let down.

After combining the above minor gas fraction with the isentropically expanded methane-nitrogen refrigerant gas mixture, such combined gas mixture will be at a temperature lower than the temperature of the liquified natural gas from the liquefaction heat exchange, but will be completely in the gaseous state.

As will be understood, the composition of the minor methane-nitrogen gas fraction determines the composition of the combined gas mixture, and while the quantity of the minor gas fraction is grossly smaller than the quantity of the purified natural gas mixture to be liquified, such minor gas fraction is allowed to build up and is recirculated within the refrigerant system such that during normal operation the flow rate of the combined gas mixture is from about 1.5 to about 4 times the flow rate of the purified natural gas mixture, expressed in moles per hour (dry). Preferably, the flow rate of the combined gas mixture is in the range from about 2 to about 3 times the flow rate of the purified natural gas mixture. The amount of refrigerant and combined gas employed is determined by the relative plots of temperature vs. enthalpy for the combined gas and the natural gas being liquified so that these curves do not cross, thereby ensuring proper heat exchange in the gas liquifier.

After having achieved the desired flow rate of the combined gas mixture, it is essential to normal operation of the process for a quantity of such combined gas mixture to be bled from the system after heat exchange with the purified natural gas mixture. The quantity of the combined gas stream removed from the system is substantially equal in magnitude to the minor methane-nitrogen gas fraction obtained by flashing. This removal is necessary to maintain the system in balance and to prevent unwanted build-up within the system once normal operations have been achieved. This removal of a minor portion of the heated combined gas mixture can be effected immediately subsequent to removal of the combined gas mixture from the liquefaction heat exchanger. Alternatively, such bleed can be effected subsequent to heat exchanging the combined gas mixture with the compressed methane-nitrogen refrigerant gas mixture but prior to such compression. Removal of this later point permits heat exchanging a somewhat greater quantity of uncompressed gas against a somewhat smaller quantity of compressed gas and can favor heat balances in certain design conditions. Again this minor gas fraction can be removed after any portion of the compression step if for any reason higher pressure gas is desired. Although this bleeding can be effected at substantially any place subsequent to removing the combined gas mixture from the liquefaction heat exchange and prior to combining the isentropically expanded methane-nitrogen refrigerant gas mixture with the minor gas fraction obtained by flash vaporization, it is considered to be advantageous to effect such bleed after heat exchange, but prior to the compression so as to avoid needlessly compressing a quantity of gas which is to be removed from the refrigerant system in any event.

The compression of the combined methane-nitrogen refrigerant gas mixture can be effected in either single or multistage compression. Advantageously, multistage compression is employed utilizing, for example, at least two stages and preferably at least three stages. The multi-stage compression can be used together with interstage cooling. Such cooling can be effected via heat exchange so as to recover heat values for use elsewhere or such cooling can be effected employing air or water as a cooling means simply for dissipating the heat from the system. Additionally, the compressed methane-nitrogen refrigerant gas mixture can be subjected to an after cooling prior to heat exchange with the combined gas mixture. Generally, the heat exchange between the combined gas mixture and the compressed methane-nitrogen refrigerant gas mixture as well as the interstage cooling is conducted so as to provide a gas temperature at compressor inlet, either single or multi-stage, above the cryogenic range, i.e. above about −50°F. Preferably, this compressor inlet temperature is maintained above about −20°F. and advantageously above about 60°F. On the other hand, however, the inlet temperature of the gas to be compressed must not be excessively high or it will place a needless burden upon the compression equipment. Accordingly, therefore, the maximum temperature employed is no greater than about 300°F. and preferably is no greater than the temperature produced in a gas line in tropical climates, i.e. about 120°F. Advantageously, however, the maximum temperature is no greater than about 90° to 100°F. Again, when employing multi-stage compression, the maximum temperature to each compression stage can be controlled by interstage cooling in the manner mentioned above.

The combined gas mixture is heat exchanged against the compressed methane-nitrogen refrigerant gas mixture so as to reduce the temperature of the compressed methane-nitrogen refrigerant gas mixture. This heat exchange is designed to control the temperature of the compressed refrigerant gas to the work recovery engines so as to assist in control of the final combined gas temperature to the natural gas liquefaction. This latter heat exchange is also designed to increase the temperature of the combined gas mixture prior to compression since, from an equivalent viewpoint, the temperature of the combined gas from the liquefaction heat exchange is at a temperature which is undesirably low, e.g. −100° F. or lower, to be handled by typical commercial compressors. Additionally, the increase in the temperature of the gas due to compression must be be offset, and if the temperature of the gas exiting from a compressor is too low, e.g. less than 32°F., fresh water coolers are inoperable and air coolers are ineffective in many, if not most, climates to accomplish the desired temperature reduction.

The isentropic expansion of the compressed methane-nitrogen refrigerant gas mixture is conducted so as to cool the methane-nitrogen gas mixture to as low a temperature as can be achieved but to a temperature about the liquefaction point of such a mixture at the outlet pressure of the respective work recovery engines, the outlet pressure of the final work recovery engine being maintained slightly above atmospheric pressure. Generally, this pressure is in the range from about 16 to about 35 psia and preferably in the range from about 20 to about 30 psia. In any event, the outlet pressure of the work recovery engine is maintained at the same level as the flash evaporated minor gas fraction. The expansion temperature is controlled by the inlet temperature as previously mentioned.

In the process of this invention the operating conditions of temperature and pressure are maintained such that at all times the combined gas mixture, the compressed methane-nitrogen refrigerant gas mixture and the isentropically expanded methane-nitrogen refrigerant gas mixture are substantially completely in the gaseous state. To phrase it in another manner, there is little, if any, liquid in the refrigeration gas cycle, of this process. However, liquid can be generated if desired but when designed for liquid type of operation special expansion engine designs are necessary to prevent erosion and special liquid distributors are required in the heat exchange system.

The mechanical energy obtained from the respective work recovery engines is employed to supply a portion of the horse-power required by the compression operation. It will be understood, that since the same quantity of material is being compressed as is being expanded, and since neither the compressors nor work recovery engines, e.g., the turboexpanders, are 100 percent efficient, the mechanical energy available from the work recovery engines will provide only a portion of the horsepower required for compression. Accordingly, therefore, the remaining portion of the mechanical energy required for compression is supplied by utilizing the fuel gas streams bled at various stages from the system and by employing one or more external sources of energy.

In order to describe this invention in greater detail, reference is made to the following specific example which will be described in connection with the accompanying two sheets of drawings designated FIGS. **1***a* and **1***b* and together illustrating an integral flow scheme. All compositions and percentage in the example are given on a dry basis, unless specified otherwise.

Referring to FIG. **1***a*, 30,408 Mols per hour of raw natural non-associated gas is delivered from a suitable source (not shown) through conduit **10** to an inlet separator **12** at a pressure of about 2350 psia and a temperature of about 85°F. The composition in mol percent of the feed entering the inlet separator **12** is essentially as follows: 1.00% nitrogen, 2.00% carbon dioxide, 83.22% methane, 6.18% ethane, 2.76% propane, 1.50% butanes, and 3.34% C_5 and heavier hydrocarbons. The raw feed also includes a total of about 3430 pounds per hour of water. In the separator **12** about 3260 pounds per hour of condensed water and about 2598 Mols per hour of a hydrocarbon condensate are separated from the remainder of the water saturated feed gas. The condensed water is removed as bottoms via conduit **14**.

The hydrocarbon condensate is transferred through conduit **16** to a demethanizer or LNG fractionator **18** at a rate of about 2598 Mols per hour. The composition in mol percent of the hydrocarbon condensate is essentially as follows: 0.35% nitrogen, 1.50% carbon dioxide, 49.37% methane, 7.75% ethane, 5.17% propane, 4.12% butanes, and 31.66% C_5 and heavier hydrocarbons. The condensate also comprises about 49 pounds of dissolved water.

A restriction orifice **20** is placed in the conduit **16** to control the flow rate of the condensate and to prevent rapid build up of pressure in the fractionator **18**. The normal operating pressure of the fractionator **18** is about 600 psia. The gas stream leaving the separator **12** through conduit **22** contains about 121 pounds per hour or about 230 ppm of water. The hydrate formation temperature of this gas is about 73°F. Therefore, to prevent hydrate formation in either conduit **22** or in subsequent processing, about 3772 pounds per hour of a 62 percent triethylene glycol solution is injected into conduit **22** near the outlet of the separator **12** by conventional means (not shown). The glycol is diluted to about 60 percent in picking up water from the gas in conduit **22**, whereby the dew point of the gas is reduced to below −50°F. The freezing point of the glycol solution is well below the processing temperatures.

A minor portion of the high pressure gas in conduit **22**, i.e., about 465 Mols per hour (dry) is bled off through conduit **24** and is employed as fuel gas in a later stage of the process. The remaining major portion of the high pressure gas from conduit **22**, i.e., about 27345 Mols per hour, is passed by means of conduit **26** (as shown in FIG. **1***a*) to a first stage expansion turbine or turboexpander **28** (shown in FIG. **1***b*), wherein the pressure of the gas is reduced from about 2350 psia to about 610 psia with a corresponding reduction in temperature from about 85°F. to about −42°F. The turboexpander **28** is designed to operate at about 80 per cent adiabatic efficiency such that a considerable amount of power is developed as the high pressure gas expands. As discussed below, this power is utilized as a partial drive for the third stage refrigeration compressor **84**.

In passing through the turboexpander **28**, about 8 mole percent of the gas in conduit **26** condenses. Accordingly, a mixed liquid and gas stream is removed from turboexpander **28** (shown in FIG. **1***b*) by means of conduit **30** and is passed via conduit **30** to LNG fractionator **18** (shown in FIG. **1***a*) at a temperature of about −42°F. and a pressure of about 610 psia. A small quantity of triethylene glycol solution enters the fractionator **18** with this mixed stream.

The LNG fractionator **18** is designed to separate between methane and carbon dioxide with an overhead temperature of about −120°F. and a bottoms temperature of about 120°F. Typically, the fractionator **18** requires about **19** actual trays at 80 percent efficiency with a 0.55/1 L/D ratio. The hydrocarbon condensate in conduit **16** is generally fed into the fractionator **18** at about the eighth tray, while the mixed liquid and gas stream in conduit **30** is fed into the fractionator at about the fourteenth tray.

The overhead of the fractionator **18** passes through conduit **32** where it is separated into two streams **34** and **36** for separate condensation. The stream **34** is condensed in a conventional flat plate cryogenic heat exchanger **38** designed to condense a sufficient portion of the overhead vapors for gravity run back to the fractionator **18**. The reflux is returned at its bubble point.

The reflux exchanger **38** is cooled by part of the cold refrigerant gas as from a second stage expansion turbine **94** of the refrigeration cycle described hereinbelow. Flow of the cooling refrigerant to the exchanger **38** is controlled by the top temperature of the fractionator **18**.

The main portion of the fractionator overhead not needed for reflux flows through conduit **36** to the LNG condenser **40**, also a flat plate cryogenic exchanger. Prior to entering the exchanger **40**, the overhead portion in conduit **36** is combined with an ethane, propane and butane fraction in line **124** and recovered from an LPG fractionator **114** (FIG. **1***b*) in a later section of the process. The combined stream, which becomes the LNG product stream, then enters the heat exchanger **40** through conduit **42** at a temperature of about −111° F. At this point, the combined stream is a two phase system: about **25** percent being liquid. After passing through the exchanger **40**, the temperature of the combined LNG stream is reduced to about −116°F. The pressure of the LNG stream at this point is about 600 psia. The combined LNG stream then passes through the heat exchanger-subcooler **44** wherein it is reduced in temperature to about −212°F. by a combined refrigerant gas formed in a later stage of the process and described below. Typically, the subcooler **44** comprises a standard plate type cryogenic heat exchanger. The effluent from the subcooler **44** is let down through conduit **46** to an expansion valve **48** whereby the pressure is isenthalpically reduced from about 595 psia to about 25 psia. In passing through valve **48** about 7 mole percent of the subcooled LNG stream flashes and the temperature of the mixture drops to about −246°F. The pressure of about **25** psia is selected since it is just sufficient to drive the flash gas through the heat exchangers and to the regeneration gas compression system as will be described in more detail hereinafter.

The cold and expanded mixture from the expansion valve **48** is conducted through conduit **50** to the LNG gas-liquid separating drum **52** which is normally operated about half full of liquid.

The cold LNG liquid stream is passed from the separating drum **52** to a storage vessel (not shown) through conduit **54** at a flow rate of about 25014 Mols per hour and at a pressure of about 25 psia. An analysis of the recovered liquid reveals the following composition in mol percent: 0.70% nitrogen, 0.00% carbon dioxide, 90.61% methane, 4.80% ethane, 3.20% propane, 0.69% butanes and 0.00% C_{5+} hydrocarbons.

The residual cold flash gas leaves the LNG separating drum **52** through conduit **56** at a flow rate of about 2196 Mols per hour and at a temperature of about

−246°F. The pressure of the LNG flash gas is about 25 psia. The residual flash gas contains about 5.10% nitrogen and 94.90% methane, recorded as mol percent.

The residual flash gas is then combined at point **58** with 63215 Mols per hour of a work-expanded (isentropically expanded) and cooled refrigerant gas of line **61** from a third stage expansion turbine **60** so as to form the combined refrigerant gas employed in subcooler **44**. The combined refrigerant gas thus passes through conduit **62** and enters the subcooler **44** at a flow rate of about 65411 Mols per hour and at a temperature and pressure of about −246°F. and 25 psia, respectively. At a designated temperature and pressure, the combined refrigerant gas remains in essentially a gaseous state, so as to eliminate erosion of the turbo-expander blades and simplify distribution. Although it is preferred that no liquid be present, a small quantity, i.e., 1 to 3 percent, liquid in the form of a mist can be tolerated.

The combined refrigerant gas of conduit **62** emerges from subcooler **44** through conduit **64** at −126°F. and 21 psia, hereinafter referred to as the refrigerant gas, is passed to the first stage expander precooler **70** at a flow rate of about 63215 Mols per hour and at the same temperature and pressure as indicated hereinabove.

The low pressure refrigerant gas fraction in conduit **64** enters the expander precooler **70** to cool the countercurrent flow of warm, high pressure, refrigerant gas from the compressor system. The warmed low pressure, refrigerant gas then leaves precooler **70** through conduit **66** at a temperature of about 90°F. and a pressure of about 16 psia. At point **68** a minor bleed or regeneration-fuel fraction emerges through conduit **72** at a flow rate approximately equal to the flow rate of the residual flash gas from the LNG gas-liquid separating drum **52**, i.e., about 2196 Mols per hour. As described more fully below, this latter fraction is employed as fuel gas to supply part of the power required to operate the compressor system utilized in the process. The remaining fraction is passed by means of line **74** into a first stage compressor **76** wherein the pressure of the refrigerant gas is increased to about 61 psia. The partially compressed refrigerant gas is then forced through conduit **78** to a second stage compressor **80**, and then through conduit **82** to a third stage compressor **84** (shown in FIG. *1b*). As illustrated in the drawing, intercoolers **85** and **86** are utilized to cool the refrigerant gas in conduits **78** and **82**, respectively. After leaving the third stage compressor **84** through conduit **88**, the compressed refrigerant gas is at a pressure of about 572 psia. The compressed refrigerant gas is then passed through after cooler **90** wherein the temperature is reduced to about 95°F., the pressure dropping slightly to about 562 psia. The compressed and cooled refrigerant gas is then passed to the expanded precooler **70** (shown in FIG. *1a*) to be precooled by the incoming low pressure refrigerant gas from conduit **64**. The precooled, compressed refrigerant gas from the precooler **70** then passes through conduit **92** to a second stage enpansion turbine **94**. The flow rate of the gas entering the second stage expansion turbine is about 63215 Mols per hour at a temperature of −81°F. and a pressure of 560 psia. The second stage refrigerant expander gas leaves the second stage expansion turbine **94** at about 190 psia and −170°F. and is passed through conduit **96** to the cryogenic heat exchangers **38** and **40** where it is utilized as the refrigerant. After emerging from the heat exchangers **38** and **40**, the warmed refrigerant gas is at a temperature of −126°F. and a pressure of 185 psia. The refrigerant gas is then passed through conduit **98** to a third stage expansion turbine **60** wherein the pressure is further reduced to about **25** psia with a corresponding decrease in temperature to about −246°F. As pointed out above, this low pressure, low temperature refrigerant gas is passed via conduit **61** and combined at point **58** with the LNG flash gas in conduit **56** to form the combined refrigerant gas which is passed via conduit **62** through the subcooler **44** to reduce the temperature and thereby completely liquify the LNG product stream carried in conduit **42**.

The liquid bottoms from the fractionator **18** contains substantially all of the carbon dioxide and higher boiling materials. This bottoms leaves the fractionator **18** at the reboiler temperature of 140°F. and flows under the fractionator pressure through conduit **100** to point **102** where the glycol solution is removed therefrom by conventional means (not shown).

The composition in mol percent of the glycol-free bottoms stream is as follows: 11.89% carbon dioxide, 5.34% methane, 37.14% ethane, 16.57% propane, 9.01% butanes, and 20.05% C_{5+} hydrocarbons. This stream then passes at a rate of about **5003** Mols per hour through conduit **104** to the CO_2 fractionator **106** (shown in FIG. *1b*). The fractionator **106** operates at 550 psia distilling overhead at 20°F. an azeotrope of approximately equal molar quantities of ethane and carbon dioxide. In addition, the overhead contains the methane left in the bottoms from the LNG fractionator **18**. The bottoms of the CO_2 fractionator **106** is substantially free from carbon dioxide. The fractionator **106** is reboiled at about 195°F., while overhead reflux is supplied by a refrigerant such as propane at about 15°F. in an internal cooler **108**. The use of the internal cooler **108** is desirable since it saves equipment and space. The fractionator **106** typically comprises about **35** trays and operates at an L/D ratio of about 2/1. The overhead from fractionator **106** is passed through conduit **110** and may be employed as fuel gas. In a preferred embodiment, the pressure of the overhead is reduced, e.g., to about 250 psia with a corresponding reduction in temperature to about −14°F. In this manner, the cooled overhead can be employed to supply part of the cooling capacity required in throughout the process being used as fuel gas.

The composition in mol percent of the liquid bottoms from the CO_2 fractionator **106** is approximately as follows: 35.48% ethane, 23.45% propane, 12.73% butanes, and 28.34% C_{5+} hydrocarbons. This bottoms stream is transferred at a rate of about 3545 Mols per hour and a pressure of about **555** through conduit **112** to the LPG fractionator **114**.

The LPG fractionator **114** operates at about 375 psia and fractionates an overhead containing ethane, propane and as much butane as can be tolerated to the solubility limit in LNG. To increase the quantity of butane in the overhead, a rough cut may be made between iso- and normal-butane as the iso- is more soluble in LNG. As in the case of the CO_2 fractionator **106**, the overhead of the LPG fractionator **114** is condensed by an internal cooler **116** to save equipment and space at the plant site. Typically, water is employed as the refrigerant in cooler **116**. The fractionator **114** is designed to operate with about **25** trays and a L/D ratio of about 1/1.

The gas liquids bottoms from the fractionator **116** is withdrawn at a temperature of about 470°F. and is transferred to storage through conduit **118** at a rate of about 1276 Mols per hour. The composition in mol percent of this gas liquids product stream is approximately as follows: 0.10% propane, 20.47% butanes, 16.42% pentanes, 14.52% C_6, and 48.49% C_{7+} hydrocarbons.

The overhead vapors from the LPG fractionator **116** pass through conduit **120** to a compressor-condenser unit **122** where they are compressed to about 635 psia and then condensed to a liquid by cooling to about −10°F. The condensed and cooled $C_{2\text{-}4}$ fraction is then passed through conduit **124** for admixture with the major portion of the overhead from the LNG fractionator **18** (shown in FIG. **1***a*).

As discussed above, it is this mixed stream which passes through conduit **42** and ultimately forms the LNG product stream.

As a result of the expansion in the turboexpanders **28, 60** and **94**, work is produced which furnishes a portion of the power necessary to drive the compressors **84, 80** and **76**. The power from the turboexpanders is transferred to the compressors by connecting the respective compressors and expanders with common shafts **126**. Other suitable mechanical means can also be used, such as gears, torque converters, etc. The additional power required to drive the various compressors is provided by separate conventional gas turbines **128** connected to each of the compressors **76, 80** and **84** by common shafts **130**. Typically, the bleed gas or fuel gas removed from the process in conduits **24, 72** or **110** is employed to drive the gas turbines **138**. Steam turbines can also be used as an alternate drive. While each of the gas turbines **128** is shown as being operatively connected with a compressor by means of a common shaft **130**, it will be understood that any other suitable mechanical linkage, such as, a gear chain, belt and pulley system, etc, can also be employed.

Various modifications and alterations of this invention will become apparent to those skilled in the art from the foregoing discussion and accompanying drawing without departing from the scope and spirit of this invention and this invention is not to be limited unduly to that set forth herein for illustrative purposes.

What is claimed is:

1. A process for liquifying a natural gas mixture comprising nitrogen, carbon dioxide, water and lower boiling hydrocarbons so as to produce a substantially carbon dioxide- and water-free liquified natural gas, which process comprises:

1. Condensing the natural gas mixture under elevated pressure to form (a) a liquid water phase, (b) a heavy hydrocarbon liquid phase containing nitrogen and carbon dioxide and (c) a light hydrocarbon vapor phase containing nitrogen and carbon dioxide;
2. Removing the liquid water phase from the process;
3. Substantially isentropically expanding the light hydrocarbon vapor phase in a work recovery engine to obtain mechanical energy and to cool the light hydrocarbon vapor phase;
4. Fractionating the heavy hydrocarbon liquid phase from Step (1) and the cooled light hydrocarbon vapor phase from Step (3) to form (a) a methane-nitrogen fraction substantially free of carbon dioxide and hydrocarbons heavier than methane and (b) a carbon dioxide-hydrocarbon fraction substantially free of nitrogen and containing C_2 and heavier hydrocarbons;
5. Fractionating the carbon dioxide-hydrocarbon fraction from Step (4) into (a) a substantially carbon dioxide fraction, (b) a C_5 and heavier hydrocarbon fraction and, (c) C_2 to C_5 hydrocarbon fraction and removing the carbon dioxide and C_5 and heavier hydrocarbon fractions from the process;
6. Compressing and cooling the C_2 to C_5 hydrocarbon fraction from Step (5) to form a low temperature liquid stream;
7. Combining the low temperature liquid stream of Step (6) with at least a portion of the methane-nitrogen fraction from Step (4) so as to form a nitrogen-methane and C_2 to C_5 hydrocarbon mixture;
8. Cooling the nitrogen-methane and C_2 to C_5 hydrocarbon mixture under elevated pressure by heat exchange with a combined gas mixture consisting essentially of methane and nitrogen produced subsequently whereby the combined gas mixture is heated and a predominant portion of the nitrogen-methane and C_2 to C_5 hydrocarbon mixture is liquified so as to form a predominantly liquid, liquid-vapor mixture;
9. Substantially isenthalpically reducing the pressure of the cooled predominantly liquid, liquid-vapor nitrogenmethane and C_2 to C_5 hydrocarbon mixture so as further to cool it and to form a minor gas fraction consisting essentially of a mixture of methane and nitrogen while liquifying completely the balance of the cooled stream to form a major liquid fraction containing methane and substantially all the hydrocarbons heavier than methane through C_5;
10. Separating the minor, methane-nitrogen gas fraction from the major liquid fraction and recovering the major liquid fraction as liquified natural gas product;
11. Combining the minor, methane-nitrogen gas fraction with an isentropically expanded, refrigerant gas mixture produced subsequently and consisting essentially of methane and nitrogen to form the combined gas mixture;
12. Employing the combined gas mixture formed in Step (11) at least partially to cool the nitrogen-methane and C_2 to C_5 hydrocarbon mixture in Step (8);
13. Compressing a major portion of the heated, combined gas mixture from Step (8) to provide a compressed refrigerant gas mixture;
14. Heat exchanging at least the major portion of the combined gas mixture prior to the compression of Step (13) with the compressed refrigerant gas mixture whereby the at least major portion of the heated, combined gas mixture is further heated to

a temperature from about −50° to about 300°F. and the compressed refrigerant gas mixture is cooled;

15. Additionally cooling the compressed refrigerant gas to a temperature such that in expansion in a work recovery engine the temperature and enthalpy are sufficiently low to provide the refrigeration required for Step (8);
16. Substantially isentropically expanding the additionally cooled, compressed refrigerant gas mixture in a work recovery engine to obtain mechanical energy and to further cool the refrigerant gas, whereby the isentropically expanded, refrigerant gas mixture is formed;
17. Removing from the process system subsequent to Step (8) a minor portion of the combined gas mixture substantially equal in magnitude to the minor methane-nitrogen gas fraction formed in Step (9); and
18. Employing the mechanical energy obtained from the work recovery engines of Steps (3) and (16) to compress, at least partly, the major portion of the combined refrigerant gas mixture in Step (13).

2. The process of claim **1** wherein the nitrogen-methane and C_2 to C_5 hydrocarbon mixture in Step (8) is at a pressure in the range of from about 350 to about 750 psia.

3. The process of claim **1** wherein the nitrogen-methane and C_2 to C_5 hydrocarbon mixture in Step (8) is maintained at a pressure relative to its analysis such that the plot of the temperature vs. enthalpy of the mixture approaches as straight a line as is reasonably possible.

4. The process of claim **1** wherein the flow rate of the combined methane-nitrogen gas mixture in Step (8) is from about 1.5 to about 4 times the flow rate of the nitrogen-methane and C_2 to C_5 hydrocarbon mixture in Step (8), expressed as Mols per hour.

5. The process of claim **3** wherein the flow rate of the combined methane-nitrogen gas in Step (8) is maintained at such a rate that the temperature vs. enthalpy curve for the combined gas as closely as possible parallels the temperature vs. enthalpy curve of the nitrogen-methane and C_2 to C_5 hydrocarbon mixture; whereby more effective heat exchange between the combined gas and the nitrogen-methane and C_2 to C_5 hydrocarbon mixture is effected.

6. The process of claim **1** wherein the compressed, methane nitrogen refrigerant gas mixture from Step (13) is at a pressure from about 400 to about 600 psia.

7. The process of claim **1** wherein the compression of Step (13) is effected in a plurality of stages and the gas is cooled interstage.

8. The process of claim **1** wherein the minor portion of the combined gas mixture removed in Step (17) is charged to a separate work recovery engine whereby mechanical energy is obtained, and wherein the mechanical energy as obtained is employed at least to compress partly the major portion of the combined gas mixture.

9. A process for liquifying a natural gas mixture comprising nitrogen, carbon dioxide, water and lower boiling hydrocarbons so as to produce a substantially carbon dioxide- and water-free liquid natural gas, which process comprises:

1. Condensing the natural gas mixture under elevated pressure to form (a) a liquid water phase, (b) a heavy hydrocarbon liquid phase containing nitrogen and carbon dioxide and (c) a light hydrocarbon vapor phase containing nitrogen and carbon dioxide;
2. Removing the liquid water phase from the process;
3. Substantially isentropically expanding the light hydrocarbon vapor phase in a work recovery engine to obtain mechanical energy and to cool the light hydrocarbon vapor phase;
4. Fractionating the heavy hydrocarbon liquid phase from Step (1) and the cooled light hydrocarbon vapor phase from Step (3) to form (a) a methane-nitrogen fraction substantially free of carbon dioxide and hydrocarbons heavier than methane and (b) a carbon dioxide-hydrocarbon fraction substantially free of nitrogen and containing C_2 and heavier hydrocarbons;
5. Separating the methane-nitrogen fraction into a first portion and a second portion;
6. Heat exchanging the first portion with a first isentropically expanded methane-nitrogen refrigerant gas obtained subsequently so as to remove heat from the first portion and to heat the first isentropically expanded methane-nitrogen refrigerant gas;
7. Returning the heat exchanged first portion to the fractionation of Step (4) as reflux;
8. Fractionating the carbon dioxide-hydrocarbon fraction from Step (4) to separate carbon dioxide from the C_2 and heavier hydrocarbons and removing the carbon dioxide from the process;
9. Fractionating the C_2 and heavier hydrocarbons from Step (8) to form a C_2–C_4 hydrocarbon fraction and a C_4 and heavier hydrocarbon fraction and removing the C_4 and heavier hydrocarbon fraction from the process;
10. Compressing and cooling the C_2–C_4 hydrocarbon fraction from Step (9) to form a low temperature liquid stream;
11. Combining the low temperature liquid stream of Step (10) with the second portion of the methane-nitrogen fraction from Step (4) so as to form a nitrogen-methane and C_2–C_4 hydrocarbon mixture;
12. Cooling the nitrogen-methane and C_2–C_4 hydrocarbon mixture under elevated pressure by heat exchange with a first isentropically expanded methane-nitrogen refrigerant gas obtained subsequently, thereby heating the first isentropically expanded refrigerant gas;
13. Cooling further the nitrogen-methane and C_2–C_4 hydrocarbon mixture under elevated pressure by heat exchange with a combined gas mixture consisting essentially of methane and nitrogen produced subsequently whereby the combined gas mixture is heated and a predominant portion of the nitrogenmethane and C_2–C_4 hydrocarbon mixture is liquified so as to form a predominantly liquid, liquid-vapor mixture;
14. Substantially isenthalpically reducing the pressure of the cooled predominantly liquid, liquid-vapor nitrogen-methane and C_2–C_4 hydrocarbon mixture so as further to cool it and to form a minor gas fraction consisting essentially of a mixture of

methane and nitrogen while liquifying completely the balance of the cooled stream to form a major liquid fraction containing methane and the C_2–C_4 hydrocarbons;

15. Separating the minor, methane-nitrogen gas fraction from the major liquid fraction and recovering the major liquid fraction as liquified natural gas product;
16. Combining the minor, methane-nitrogen gas fraction with a second isentropically expanded, refrigerant gas mixture produced subsequently and consisting essentially of methane and nitrogen to form the combined gas mixture;
17. Employing the combined gas mixture formed in Step (16) to cool the nitrogen-methane and C_2–C_4 hydrocarbon mixture in Step (13);
18. Compressing at least a major portion of the heated, combined gas mixture from Step (13) to provide a compressed refrigerant gas mixture;
19. Heat exchanging at least a major portion of the combined gas mixture prior to the compression of Step (18) with the compressed refrigerant gas mixture whereby the at least major portion of the heated, combined gas mixture is further heated to a temperature from about −50° to about 300°F. and the compressed refrigerant gas mixture is cooled;
20. Additionally cooling the compressed refrigerant gas to a temperature such that in expansion in a work recovery engine the temperature and enthalpy are sufficiently low to provide the refrigeration required for Steps (12) and (13);
21. Substantially isentropically expanding the additionally cooled, compressed refrigerant gas mixture in a work recovery engine to obtain mechanical energy and to further cool the refrigerant gas, whereby the first isentropically expanded, methane-nitrogen refrigerant gas is formed;
22. Substantially isentropically expanding the heated first isentropically expanded refrigerant gas from Step (12) in a work recovery engine whereby (a) mechanical energy is obtained, (b) the heated refrigerant gas is cooled, and (c) the second isentropically expanded methane-nitrogen refrigerant gas is formed;
23. Removing from the process system subsequent to Step (13) a minor portion of the combined gas mixture substantially equal in magnitude to the minor methane-nitrogen gas fraction formed in Step (14); and
24. Employing the mechanical energy obtained from the work recovery engine of Steps (3), (21) and (22) at least to compress partly the major portion of the combined refrigerant gas mixture in Step (18).

10. The process of claim **9** wherein the nitrogen-methane and C_2–C_4 hydrocarbon mixture in Step (13) is at a pressure in the range from about 350 to about 750 psia.

11. The process of claim **9** wherein the nitrogen-methane and C_2–C_4 hydrocarbon mixture in Step (13) is maintained at a pressure relative to its analysis such that the plot of the temperature vs. enthalpy of the mixture approaches as straight a line as is reasonably possible.

12. The process of claim **9** wherein the flow rate of the combined methane-nitrogen gas mixture in Step (13) is from about 1.5 to about four times the flow rate of the nitrogen-methane and C_2–C_4 hydrocarbon mixture in Step (13), expressed as moles per hour.

13. The process of claim **12** wherein the flow rate of the combined methane-nitrogen gas is maintained at such a rate that the temperature vs. enthalpy curve for the combined gas as closely as possible parallels the temperature vs. enthalpy curve of the nitrogen-methane and C_2–C_4 hydrocarbon gas mixture, whereby more effective heat exchange between the combined gas and the nitrogen-methane and C_2–C_4 hydrocarbon gas mixture is effected.

14. The process of claim **9** wherein the compressed, methane-nitrogen refrigerant gas mixture from Step (18) is at a pressure from about 400 to about 600 psia.

15. The process of claim **9** wherein the compression of Step (18) is effected in a plurality of stages and the gas is cooled interstage.

16. A continuous process for the liquefaction of natural gas which comprises the steps of:

Condensing the natural gas mixture under elevated pressure to form (a) a liquid water phase, (b) a heavy hydrocarbon liquid phase containing nitrogen and carbon dioxide and (c) a light hydrocarbon vapor phase containing nitrogen and carbon dioxide;

removing the liquid water phase from the process;

adjusting the pressure of the heavy hydrocarbon liquid phase and the light hydrocarbon vapor phase to a range of from about 350 to about 750 psia;

fractionating the pressure adjusted heavy and light hydrocarbon phases to form (a) a methane-nitrogen fraction substantially free of carbon dioxide and hydrocarbons heavier than methane and (b) a carbon dioxide-hydrocarbon fraction substantially free of nitrogen and containing C_2 and heavier hydrocarbons;

fractionating further the carbon dioxide-hydrocarbon fraction to form a C_2–C_4 hydrocarbon fraction and a C_4 and heavier hydrocarbon fraction and removing the C_4 and heavier hydrocarbon fraction from the process;

combining the C_2–C_4 hydrocarbon fraction with the carbon dioxide free methane-nitrogen fraction to form a substantially purified natural gas mixture;

cooling and substantially completely liquifying the purified natural gas mixture in a countercurrent heat exchanger-liquifier;

flash evaporating a minor gas fraction from the cooled effluent from the heat exchanger-liquifier by substantially isenthalpically reducing the pressure thereof, said flash evaporation causing the temperature of both the minor gas fraction and the remaining major liquid fraction to decrease;

collecting the major liquid fraction as product and returning the flashed fraction to a point where it is combined with an isentropically expanded refrigeration gas fraction produced subsequently in the process;

passing said combined gases countercurrently to the purified natural gas mixture in said heat exchanger-liquifier at a flow rate of two to four times that of the purified natural gas stream;

- separating the warmed effluent from said heat exchanger-liquifier into a major refrigeration gas fraction and a minor fuel gas fraction;
- passing the refrigeration gas fraction through a counter-current heat exchanger precooler to a compressor system to be compressed to a pressure in the range of about 400 to 600 psia;
- passing the pressurized gas from said compressor system through said heat exchanger precooler to cool the refrigeration gas;
- isentropically expanding the cooled effluent from said heat exchanger precooler with an expansion engine at a temperature and pressure sufficient to maintain the gas in the gaseous state in said expansion turbine to form the isentropically expanded refrigeration gas, whereby mechanical energy is obtained and the pressure of the refrigeration gas fraction is reduced, thereby further cooling such fraction;
- combining the further cooled, reduced pressure, isentropically expanded refrigeration gas effluent from said expansion engine with said flash gas to a point prior to entry into said heat exchanger-liquifier; and
- utilizing (a) the fuel gas fraction to furnish fuel for a gas driven turbine which provides a portion of the mechanical energy necessary to drive said compressor system and (b) the mechanical energy obtained from the isentropic expansion to provide an additional portion of the mechanical energy necessary to drive the said compressor system.

17. In an integrated apparatus for purifying and liquifying natural gas, the combination comprising:

- gas-liquid separating means for separating condensed water and a heavy hydrocarbon condensate from a pressurized natural gas mixture comprising nitrogen, carbon dioxide, water and lower boiling hydrocarbons;
- means for adjusting the pressure of the heavy hydrocarbon condensate and the water and heavy hydrocarbon condensate-free remainder of the natural gas mixture to about 350 to about 750 psia;
- means for fractionating the combined, pressure adjusted hydrocarbon condensate and water-free natural gas mixture to form a methane-nitrogen fraction substantially free of carbon dioxide and a carbon dioxide-hydrocarbon fraction substantially free of nitrogen and containing predominantly C_{2+} hydrocarbons;
- means for fractionating the carbon dioxide-hydrocarbon fraction to form a carbon dioxide fraction and a C_{2+} hydrocarbon fraction, said carbon dioxide fraction including all of the methane present in the carbon dioxide-hydrocarbon and a portion of the C_2 hydrocarbons contained therein;
- means for combining the C_{2+} hydrocarbon fraction with the methane-nitrogen fraction, thus forming a substantially water-free and carbon dioxide-free natural gas mixture;
- a heat exchanger-liquifier for cooling and liquifying the water-free and carbon dioxide-free natural gas by countercurrent heat exchange with a combined flash gas and work expanded refrigerant gas from an expansion engine;
- means for isenthalpically expanding and partially flashing the natural gas effluent from said heat exchanger-liquifier;
- gas-liquid separating means for separating said expanded effluent into a major liquid fraction and a minor flash gas fraction;
- means for recovering the major liquid fraction as product;
- means for passing the flash gas to the heat exchanger-liquifier;
- compression means for compressing the combined flash gas and work expanded refrigerant gas from the heat exchanger-liquifier;
- a heat exchanger precooler for precooling the gas coming from the compression means by countercurrent heat exchange with the combined flash gas and work expanded gas from said heat exchanger-liquifier;
- an expansion engine for work expanding said precooled gas, said engine further cooling the precooled gas and reducing the pressure thereof while generating mechanical energy;
- means for feeding the work expanded and cooled gas from said expansion engine to said heat exchanger-liquifier to join said flash gas; and
- means for bleeding from the apparatus a minor portion of the combined flash gas and work expanded gas prior to compression thereof, said expansion engine and said compression means being operatively cooperative whereby the mechanical energy obtained from said engine supplies at least a portion of the work required to operate said compression means.

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