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[54] **APPARATUS AND PROCESS FOR LIQUEFACTION OF NATURAL GASES**

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[58] **Field of Search**.........................62/9, 11, 23, 38, 62/39, 40, 54, 18, 26, 30, 18; 55/33, 62

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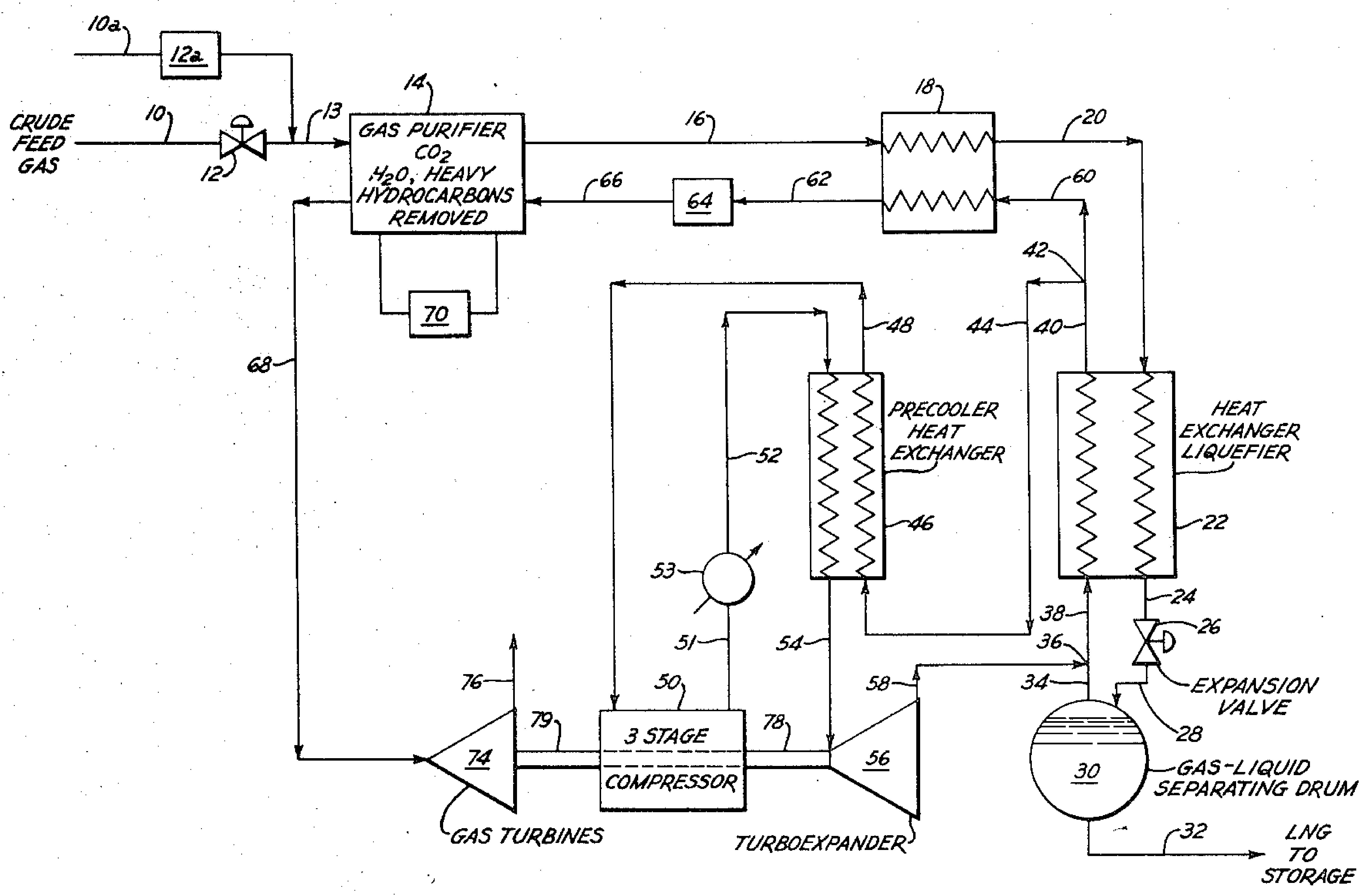
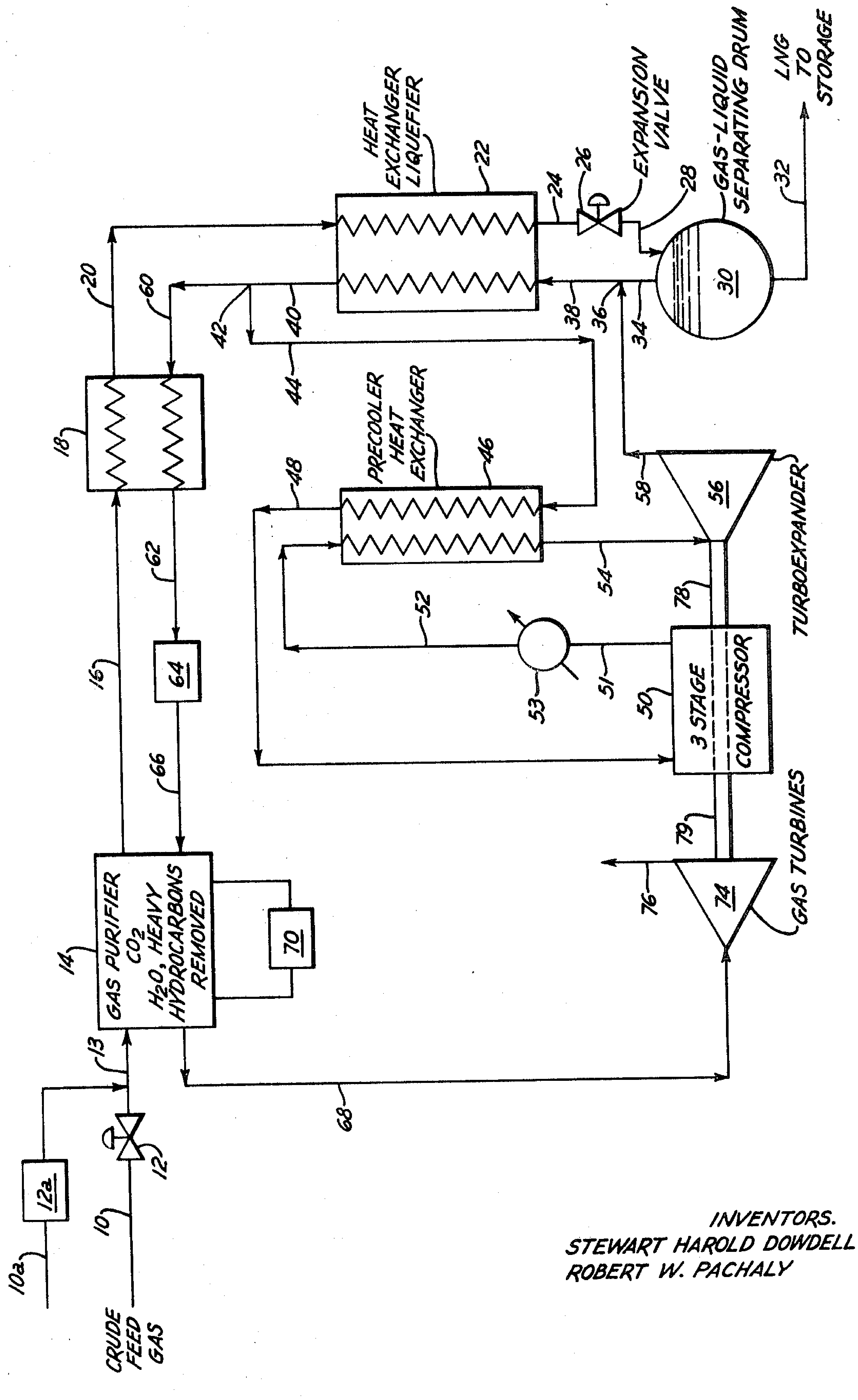
[57] **ABSTRACT**

A process and apparatus for liquefaction of natural gas wherein the gas is cooled and liquified under pressure in a heat exchanger-liquifier. The pressurized cold liquid from the heat exchanger-liquifier 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 comingled with the circulating refrigerant stream so that the analysis of the refrigerant stream is always rich in the lighter portions of the liquefaction stream. This analysis difference aids in maintaining refrigeration temperature differentials to drive the liquefaction step. The work-expanded refrigerant portion undergoes a compression cycle and is work-expanded in an expansion turbine. The expansion turbine furnishes at least part of the power necessary to drive the compressor system in the refrigerant gas cycle.

13 Claims, 1 Drawing Figure





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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.

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 nitrogen, helium, carbon dioxide, hydrogen sulfide and the like. The present invention is directed to the liquefaction of purified natural gas which is primarily composed of methane. Even following purification of the crude gas, however, there may still be present with the major portion of methane a small quantity of low boiling gases such as low molecular weight hydrocarbons, i.e., up to about six carbon atoms, nitrogen and helium.

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 1/600 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, and in others the need for the use of an inordinately large number of expensive heat exchangers and compressors exists. In some of the prior art systems, complicated high pressure equipment which is difficult to maintain and control, automatically, is necessary. Still other processes require the use of expensive refrigerants which must be shipped to the liquifying plant.

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 and 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 nonindustrialized 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 exchange cycle of this process is operated under 400 to 1,000 psia head 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 adsorb 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 adsorb 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 light of these inherent problems associated with the production of liquified natural gas, the foregoing prior art processes do not aid in finding a practicable system for liquifying natural gas in remote non-industrial parts of the world where the soil bearing is poor.

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 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, instead of recycling this combined mixture to the feed stream as described in the heretofore mentioned prior art.

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.

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 installation of the standard type of cryogenic equipment is not feasible due to poor soil stability and/or the cost of installation is prohibitive in remote non-industrialized areas of the world.

An object of the present invention is to provide a process which will product liquified natural gas employing moderate head pressures (200–1,000 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 the floating platform construction as described above.

Another object of the present invention is to accomplish liquefaction by employing a countercurrent heat exchanger-liquifier 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 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. Therefore, the refrigerant system is allowed to operate effectively at lower temperatures and pressures than processes heretofore employed. Thus, 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 gas from the heat exchanger-liquifier equivalent to the flow rate of the flash gas coming from the gas-liquid separator. This bleed stream can be employed to purge or regenerate an adsorbent purification system, if such is employed in connection with the liquefaction plant. Additionally, the bleed stream can be directly employed or after removal from the purification system as fuel for a gas turbine system which in turn furnishes part of the power required to drive the compressors in the refrigeration cycle. By forming this bleed stream from the warmed effluent gas from the heat exchanger-liquifier, it has been unexpectedly found that the operating energy balance of the entire system can be effected.

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 liquefaction plant.

In accordance with this invention there is provided a process for liquifying a substantially water-free, hydrogen sulfide-free and carbon dioxide-free natural gas mixture comprising nitrogen and hydrocarbons containing up to about six carbon atoms under elevated pressure. This natural gas mixture under elevated pressure is cooled by heat exchange with a combined, methane-nitrogen gas mixture obtained elsewhere in the process so as to effect liquefaction of a predominant portion of the natural gas mixture while heating the combined 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 hydrocarbons having at least two carbon atoms. 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 gas mixture mentioned previously and, as also mentioned previously, this combined gas mixture is employed to cool the natural gas mixture in the liquefaction heat exchange step. A major portion of the heated combined gas mixture leaving the liquefaction heat exchange step is compressed to provide a compressed, methane-nitrogen gas mixture. This gas mixture, after suitable precooling, is substantially isentropically expanded in a work recovery engine 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 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 gas mixture after leaving the liquefaction heat exchange step is removed from the circulating refrigerant system. The quantity of such minor portion removed from the refrigerant system is substantially equal in isenthalpic to the minor methane-nitrogen gas fraction formed by the isenthalpic pressure reduction previously described.

The mechanical energy obtained from the work recovery engine is employed at least to compress partly the major portion of the combined gas mixture.

The natural gas feed stock suitable for charging to the initial liquefaction heat exchange step of this invention must be free of carbon dioxide, water, hydrogen sulfide and heavier hydrocarbons, below the solubility levels of these materials in the condensates formed throughout the length of the liquefaction exchanger. Usually, however, natural gas streams as obtained from the well contain significant quantities of carbon dioxide, water and hydrogen sulfide as well as some heavier hydrocarbons. This is true for both natural gas obtained from a crude oil well (associated gas) or from a gas well (non-associated gas) with the associated gas typically containing more higher boiling constituents than the non-associated gas. Generally, a natural gas will be comprised of from about 80 to about 99 mole percent of methane with the balance being carbon dioxide, nitrogen, hydrogen sulfide and other hydrocarbons. The carbon dioxide and nitrogen contents can each be as high as about 10 to 15 mole percent, although more typically the concentrations are about 1 to 2 mole percent or less.

Additionally, 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, non-associated gas obtained from the well head may be at an undesirably high pressure for direct employment in the present invention, e.g., greater than about 1,000 psia. On the other hand, however, 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 heat exchange liquefaction step of the present invention, it would appear that there is little practical advantage to be gained by employing pressures in excess of 1,000 psia in this step unless the gas 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 600 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 500 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 prior to introduction into the initial liquefaction step. Conversely, an extremely high pressure natural gas stream, such as a non-associated gas, can be reduced in pressure prior to processing. 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 heat exchange liquefaction step to a maximum of about 150°F., preferably, however, the maximum temperature will not exceed about 75°F. and it is particularly advantageous to employ temperatures below about 50°F. Selection of the exact processing temperature can depend on the processing sequence selected for gas purification as discussed below.

The carbon dioxide, water, hydrogen sulfide and heavier hydrocarbons can be removed from the natural gas containing the same by means of various techniques including, for example, a cryogenic separation or fractionation or by adsorption with materials such as molecular sieves, charcoal and activated carbon. It is essential that these materials be eliminated prior to the introduction of the natural gas into the process of the invention in order to avoid the formation of solid materials in the processing equipment under the conditions employed.

It will be understood, of course, that the selection of the particular operating pressure as well as the temperature employed in the liquefaction heat exchange 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, in the liquefaction heat exchange the temperature of the natural gas mixture is reduced to a level sufficient to liquify a predominant portion of such natural gas mixture at the particular pressure employed. At least about 85 percent of the natural gas mixture is liquified in this initial step of the process and preferably at least 90 percent, more preferably 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 the liquefaction heat exchange, the pressure of the natural gas is isenthalpically reduced to a pressure just slightly above atmospheric pressure, generally falling in the range of from about 16 to about 30 psia, and preferably in the range of from about 20 to about 25 psia. This isenthalpic 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 from about 10 to about 30 mole percent of the total liquified natural gas mixture and preferably comprises at least 15 mole 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 to effect liquefaction of a major portion of the particular composition 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., −245° to −260°F.

The minor gas fraction which has been flashed consists essentially of methane and nitrogen with a greater proportion of the nitrogen initially contained in the natural gas mixture being present in the minor gas fraction, while the remaining liquid fraction will contain substantially all of the C_2 and heavier hydrocarbons present in the liquified natural gas plus only a small part of the nitrogen in the original natural gas.

After combining this 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 natural gas from the liquefaction heat exchange but will be completely in the gaseous state due to the difference in pressures of the combined gas mixture and the predominantly liquified natural gas mixture.

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 incoming 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 two to about four times the flow rate of the incoming natural gas mixture, expressed in moles per hour. Preferably, the flow rate of the combined gas mixture is in the range from about 2.5 to about 3 times the flow rate of the incoming 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 incoming 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 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 exchange. 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 at 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 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 multi-stage compression. Advantageously, multi-stage 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 engine so as to assist in control of the final combined gas temperature to the natural gas liquefaction. Thus, in the heat exchanger the temperature of the heat exchanged, compressed methane-nitrogen refrigerant gas mixture will be substantially the same as the temperature of the combined gas mixture leaving the liquefaction heat exchange. Usually a temperature approach of about 5° to 10°F. is used in design. Furthermore, from an equipment 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 and thus the temperature of such gas must be raised prior to compression. Additionally, the increase in the temperature of the gas due to compression must 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 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 above the liquefaction point of such a mixture at the outlet pressure of the work recovery engine, which pressure is maintained slightly above atmospheric pressure. The expansion temperature is controlled by the inlet temperature as previously mentioned. Generally, this pressure is in the range from about 16 to about 30 psia and preferably in the range from about 20 to about 25 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.

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 work recovery engine is employed to supply a portion of the horse-power required by the compression operation. It will be understood, of course, that since the efficiency level of a work recovery engine, such as a turbo expander, does not exceed about 75 to 85 percent and the efficiency of a compressor is about 75 percent and that same quantity of material is being expanded as is being compressed, the mechanical energy available from the expander will provide only about 50 percent of the horse-power required for compression. Accordingly, therefore, the remaining percentage of the mechanical energy required for compression is supplied by an external source.

In one specific embodiment of this invention the purification of the natural gas mixture to be processed can be effected by subjecting a crude natural gas stream to adsorption by contact with molecular sieves and activated carbon. In this operation a molecular sieve can be employed to remove water, another molecular sieve can be employed to remove carbon dioxide and hydrogen sulfide and the activated carbon can be employed to remove undesired high freezing point hydrocarbons. These adsorbents may be employed in single multilayer beds or in separate beds.

When employing this adsorption technique for purification, the minor portion of the combined gas mixture removed from the refrigerant system can be employed to purge or regenerate the adsorption beds. Additionally, this minor portion of the combined gas mixture can also be heat exchanged against the purified natural gas mixture so as to cool the natural gas mixture prior to its introduction into the liquefaction heat exchange. Also this minor portion of the combined gas mixture removed from the refrigerant system can be employed to power a gas turbine in order to supply the remaining requirement for mechanical energy of the compression system. If used as turbine fuel after purging the activated carbon bed of heavy hydrocarbons, these heavy hydrocarbons also become available for power in the process.

In a particularly preferred embodiment the minor portion of the combined gas mixture removed from the main refrigerant system can be employed sequentially first in heat exchange against the incoming natural gas mixture, then to purge the adsorption beds and finally after purging to power the gas turbine.

In order to describe this invention in greater detail reference is made to the following specific examples which will be described in connection with the attached drawing.

EXAMPLE 1

Referring to the FIGURE of the accompanying drawing, raw natural non-associated gas enters the installation from a suitable source (not shown) through conduit **10** at a temperature of about 100°F. Since the pressure of non-associated gas well heads are usually over 1,000 psia, the pressure of the gas is throttled to about 610 psia by valve **12.** (Alternatively, a turbo expander can be employed in lieu of the valve **12,** thereby permitting recovery of mechanical work while effecting the pressure reduction.) The crude effluent from valve **12** enters a gas purification system **14** at a typical flow rate of about 100 moles per hour via conduit **13.** The composition in mole per cent of the gas entering the gas purification system **14** is essentially as follows: 0.70 percent nitrogen, 0.75 percent carbon dioxide, 92.2 percent methane, 3.84 percent ethane, 1.14 percent propane, 0.56 percent butanes, 0.81% C_5 and heavier hydrocarbons saturated with water. In this particular case no hydrogen sulfide is present. If it had been present, it would be removed with the carbon dioxide.

The gas purification system includes a plurality of molecular sieve beds and activated carbon adsorption beds. The first molecular sieve removes the water from the gas down to a dew point of about −150°F., followed by a second molecular sieve which removes the carbon dioxide down to less than 2 parts per million. This is followed by a heavy hydrocarbon removal bed, utilizing an activated carbon bed which eliminates benzene, cyclohexane, C_7 and other high freezing point materials found in the gas stream. The molecular sieve beds and the activated carbon beds can be in the same vessel. Although the gas purification system **14** is shown schematically as a single block in the drawing, multiple sets of adsorption beds are employed cyclically with one set actively adsorbing impurities while other sets are being purged or regenerated. The gas leaving the gas purification system has the following analysis in mole percent: 0.71 percent nitrogen, 0.00 percent carbon dioxide, 93.18 percent methane, 3.90 percent ethane, 1.15 percent propane, 0.57 percent butanes, and 0.49% C_5 and C_6. The gas contains essentially no water.

The purified dry gas from the gas purification system **14** flowing at the rate of about 98.72 moles per hour enters into a small heat exchanger **18** via conduit **16** whereby the temperature is reduced to about 40°F. The incoming feed gas gives up heat to the returning flash gas, as will be described in more detail hereinafter. From the small heat exchanger **18** the gas passes through conduit **20** to the heat exchanger-liquifier **22** which cools the gas to a temperature of about −200°F. while maintaining the pressure at about 605 psia thereby liquifying the gas. The cold effluent from the heat exchanger-liquifier **22** has a flow rate of about 98.72 moles per hour.

The heat exchanger **22** is the standard plate-fin type used in a cyogenic processes. Typically it includes a desuperheating section which reduces the gas to its dew point at about 10°F., followed by a liquefaction section which reduces the temperature of the gas to about −120°F. to produce liquefaction. Thereafter, the cold liquid enters a subcooling section which cools the liquid to about −200°F. Such a heat exchanger-liquifier typically is a single unit as shown in the accompanying drawing.

The effluent liquid from the heat exchanger-liquifier is let down through conduit **24** to an expansion valve **26** whereby the pressure is reduced to 20 psia and the temperature is accordingly reduced to about −250°F. thereby flashing a minor vapor fraction and cooling the entire vapor and liquid fractions to this temperature. The pressure of about 20 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 liquid from the expansion valve **26** is conducted through conduit **28** to gas-liquid separating drum **30** which is normally operated about half full of liquid.

The cold liquid is passed from the separating drum **30** to a storage vessel (not shown) through conduit **32** at a flow rate of about 90.72 moles per hour and at a pressure of about 50 psia. An analysis of the recovered liquid reveals the following composition in mole per cent: 0.17 percent nitrogen, 0.00 percent carbon dioxide, 92.24 percent methane, 4.90 percent ethane, 1.45 percent propane, 0.72 percent butanes, 0.60% C_5 and C_6 hydrocarbons.

The residual cold flash gas leaves the separating drum **30** through conduit **34** at a flow rate of about 8.0 moles per hour and at a temperature of about −250°F. and a pressure of 20 psia. The residual flash gas contains only about 2.80 percent nitrogen and 97.20 percent methane, recorded as mole percent. It has been found that if the residual flash gas is flashed from a main storage tank rather than the separating drum, handling problems would be encountered precluding the best recovery of refrigeration for the incoming feed gas at a low temperature level useful in the liquefaction.

The residual flash gas is slightly warmed at point **36** where it is combined with 265.0 mole per hour of a work-expanded (isentropically expanded) and cooled gas from the expansion turbine **56**, which will be described in more detail below. The combined gases pass through conduit **38** at an increased flow rate of about 273.0 moles per hour due to the flow of the gas from the expansion turbine system. The temperature and pressure of the gas in conduit **38** are about −205°F. and 20 psia, respectively.

The combined residual flash gas and isentropically expanded gas from the expansion turbine system enter the heat exchanger-liquifier **22** through conduit **38** to cool and liquify the incoming feed gas. At the designated temperature and pressure, the combined residual flash gas and expanded refrigerant gas remain in essentially a gaseous state, so as to eliminate erosion of the turbo-expander blades and simplify distribution to the liquifier heat exchanger. 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 warmed effluent gas of conduit **38** emerges from heat exchanger-liquifier **22** through conduit **40** at 10°F. and 18 psia and is thereafter separated into two streams at point **42**. A major fraction, hereinafter referred to as the refrigerant gas fraction, passes through conduit **44** to expander precooler heat exchanger **46** at a flow rate of about 265.0 moles per hour and at the same temperature and pressure as indicated hereinabove. A minor bleed or regeneration-fuel fraction emerges through conduit **60** at a flow rate approximately equal to the flow rate of the residual flash gas from the separating drum, i.e., 8.0 moles per hour. The latter fraction will be discussed following a description of the refrigeration fraction.

The low pressure refrigerant gas fraction in conduit **44** enters the expander precooler heat exchanger **46** to cool the countercurrent flow of warm, high pressure, refrigerant gas from the compressor system. The warmed low pressure, refrigerant gas leaves heat exchanger **46** through conduit **48** at a temperature of about 90°F. and a pressure of about 16 psia to be compressed in compressor system **50**. The compressor is shown in the accompanying drawing as a single unit. It will be understood that in the practice of this invention a plurality of stages, e.g., three with two intercoolers can be used. Also an after cooler positioned downstream from the last compression stage is employed.

The gas from compression passes through conduit **51** at about 475 psia to after cooler **53** wherein it is cooled to about 95°F. From thence the gas is passed via conduit **52** to the expander precooler heat exchanger **46** to be precooled by the incoming low pressure refrigerant gas from conduit **44**. The precooled, compressed refrigerant gas from the heat exchanger **46** passes through conduit **54** to expansion turbine system **56**, hereinafter referred to as the turboexpander. The flow rate of the gas entering the turboexpander is about 265.0 moles per hour at a temperature of 15°F. and a pressure of 466 psia.

The compressed and precooled refrigerant gas is isentropically or work expanded by the turboexpander to obtain a pressure of about 20 psia and a temperature of about −201°F. The cooled and work expanded refrigerant gas emerges from turbo-expander **56** through conduit **58** at 265.0 moles per hour to point **36** where the gas joins the residual flash gas from the gas-liquid separating drum **30**. The combined gases are used to cool and liquify the incoming feed gas in heat exchanger-liquifier **22** after being introduced into the same by conduit **38** as described above.

As a result of the expansion in the turboexpander, work is produced which furnishes a portion of the power necessary to drive the compressor system **50**. The power from the turboexpander is transferred to the compressor system by connecting the compressors and the turboexpanders with a common shaft **78**. Other suitable mechanical means can also be used, such as gears, torque converters, etc. The additional power required to drive the compressor system **50** is provided by a gas turbine system **74** which is also connected to the compressors by another common shaft **79**. The gas required to drive the gas turbine originates from the bleed gas or regeneration-fuel fraction obtained at point **42**. A steam turbine can also be used as an alternate drive. While gas turbine **74** is shown as being operatively connected with compressor system **50** by means of common shaft **79**, it will be understood that any other suitable mechanical linkage, such as, a gear chain, belt and pulley system, etc., can also be employed.

The bleed gas or regeneration-fuel fraction having a flow rate of 8.0 moles per hour at point **42** passes through conduit **60** to heat exchanger **18** countercurrently to the incoming feed gas to absorb some of the heat in the feed gas. The bleed gas emerges from the heat exchanger **18** through conduit **62** at about 40°F. and 16 psia. The warmed gas is recompressed in compressor system **64** thereby increasing the pressure of the gas to about 200 psia to enable the gas to be used as fuel for the gas turbine after it has been used as purge gas for the purification system.

The pressurized gas also passes into the gas purification system **14** cyclically regenerating the adsorbent beds of molecular sieves and activated carbon used to purify the incoming feed gas. The passage is via conduit **66** and results in the regeneration of the purification system.

The effluent waste gas containing all of the desorbed water, carbon dioxide, hydrogen sulfide and heavy hydrocarbons emerges from the purification system through conduit **68** and is passed to the gas turbine system **74** which furnishes the remaining power necessary to drive the compressor system **50** via common shaft **79**. The exhaust gases from the gas turbine system emerge through exhaust pipe **76.** The exhaust gases can be used to generate steam to drive turbines (not shown) employed to supply power elsewhere in the plant or can furnish heat for other processing if required. Preheater **70** is provided as part of the gas purification system to allow heating of the adsorption beds to proper regeneration temperatures (usually about 500°F.). Following the heating purge cycle the beds are cooled to operating temperature before being returned to purification service.

EXAMPLE II

Referring to the FIGURE of the accompanying drawing, this example describes the liquefaction of associated gas, i.e., gas from a crude-oil well. Since the same type of apparatus is used in this example as described in detail in Example I, only a brief description will be given herein to the accompanying drawing.

The crude natural gas enters the installation from a suitable source (not shown) through conduit **10*a*** at a temperature of about 100°F. Since the pressure of the gas from the crude-oil well head can be as low as 120 psia, the gas is compressed by compressor system **12*a*** to obtain a pressure of about 560 psia. The crude natural gas effluent from compressor system **12*a*** enters the gas purification system **14** via conduit **13** at a flow rate of about 100 moles per hour. The composition of the gas in mole per cent entering the gas purification system **14** is essentially as follows: 0.70 percent nitrogen, 0.75 percent carbon dioxide, 83.67 percent methane, 7.91 percent ethane, 4.05 percent propane, 1.89 percent butanes, and 1.03% C_5 and heavier hydrocarbons saturated with water. No hydrogen sulfide is present in this example, although in practice some is usually observed.

The dry gas emerges from the gas purification system **14** through conduit **16** having the following composition: 0.71 percent nitrogen, 0.00 percent carbon dioxide, 84.54 percent methane, 7.99 percent ethane, 4.09 percent propane, 1.91 percent butanes and 0.73% C_5 and C_6 hydrocarbons. From conduit **16,** the gas passes through heat exchanger **18** and conduit **20** at a flow rate of 98.94 moles per hour and at a temperature and pressure of 40°F. and 560 psia, respectively. From conduit **20,** the gas enters heat exchanger-liquifier **22** wherein substantially complete liquefaction in the natural gas takes place. The lower pressure employed in liquifying the gas reflects the difference in composition which allows a sufficiently straight temperature vs. enthalpy plot at the lower pressure.

The cold effluent emerges from heat exchanger-liquifier **22** through conduit **24** at a flow rate of 98.94 moles per hour and at a temperature and pressure of about −200°F. and 555 psia, respectively. This effluent is expanded and cooled further by throttle valve **26** and thereafter conducted to the gas-liquid separating drum **30** via conduit **28.** The cold liquid at a temperature of −245°F. is removed from the separating drum through conduit **32** to a storage vessel (not shown) at a flow rate of 90.94 moles per hour and at a pressure of about 20 psia. The composition of the liquid effluent has the following analysis in mole percent: 0.20 percent nitrogen, 0.00 percent carbon dioxide, 81.12 percent methane, 10.15 percent ethane, 5.19% C_3 hydrocarbons, 2.42% C_4 hydrocarbons and 0.92% C_5 and C_6 hydrocarbons.

The residual flash gas leaves the separating drum through conduit **34** at a flow rate of about 8.0 moles per hour and at a temperature and pressure of −245°F. and 20 psia, respectively. The residual flash gas contains about 2.90 percent nitrogen and 97.10 percent methane, expressed as mole per cent. The residual flash gas is combined with the work expanded and cooled gas from the expansion turbine **56** at point **36** and the mixed gases assume an equilibrium temperature. The combined refrigerant gases pass through conduit **38** at an increased flow rate of about 273.0 moles per hour and at a temperature and pressure of −205°F. and 20 psia, respectively. The gases in conduit **38** enter the heat exchanger-liquifier **22** to cool and liquify the incoming feed gas stream and emerge through conduit **40.** The warmed emerging gases have a temperature and pressure of 10°F. and 19 psia, respectively. From conduit **40** the gases are separated into a bleed fraction equal to the flow rate of the residual flash gas, i.e., 8.0 moles per hour, and a refrigeration fraction having a flow rate of 265 moles per hour at point **42.**

The refrigeration fraction is passed to precooler heat exchanger **46** via conduit **44** cooling the warm refrigerant gas from the compressor system **50.** The effluent from the heat exchanger **46** passes through conduit **48** to compressor system **50** at a temperature and pressure of 90°F. and 16 psia, respectively. The gas is compressed in the compressor system **50** and the effluent from the last stage of the compressor system **50** emerges from after cooler **53** through conduit **52** at 95°F. and 475 psia. The compressed gases are precooled in the precooler heat exchanger **46** to a temperature and pressure of 15°F. and 466 psia, respectively.

The precooled gases from the heat exchanger **46** pass through conduit **54** to expansion turbine **56** to be isentropically expanded to a pressure of 20 psia and a temperature of about −201°F. The effluent cold gas from the expansion turbine emerges through conduit **58** to join the residual flash gas at point **36** at a flow rate of 265 moles per hour, thereby completing the refrigeration cycle.

The bleed gas or regeneration-fuel fraction having a flow rate of about 8.0 moles per hour at point **42** passes through conduit **60** to heat exchanger **18** emerging via conduit **62** at a temperature and pressure of 40°F. and 16 psia, respectively. The warmed gas is recompressed in compressor system **64** thereby increasing the pressure of the gas to about 200 psia to enable the gas after purging the purification system **14** to be used as fuel for the gas turbine.

The effluent waste gas from the purification system containing all of the desorbed water, carbon dioxide, and heavy hydrocarbon emerge from the purification system through conduit **68** to the gas turbine system **74,** thereby completing the regeneration-fuel fraction cycle as described in the foregoing example. The same regeneration preheat and cooling system previously described for the purification section is used.

While description will be made to the liquefaction of natural gas from a gas well and a crude-oil well, it will be understood that the concepts hereinafter described can be employed in the liquefaction of natural gases from other known sources. One example is the reliquefaction of natural gas vapors given off during storage of the liquified gas. It is also possible, following the practice of the present invention to liquify gas from distribution pipe lines to put into practice the process of "peak shaving" whereby an amount of natural gas can be liquified for storage when the supply exceeds the demand so as to allow revaporization of this stored liquified gas for use when demand is at its peak and would otherwise exceed the supply. This technique enables the peak to be shaved down so as to provide for operation of the pipe line at maximum capacities for the most economical transportation of the natural gas.

Referring again to the drawing, as illustrated in the examples, the compressor system **50** recompresses the gas to about 475 psia, but this pressure may be varied widely to suit the overall thermodynamic balance of the system. In the case of very efficient expansion turbine systems, lower pressures may be employed to obtain the desired temperature and pressure in conduit **58.** Lower temperature precooling to the turboexpander will require lower compression pressures etc. Preferably, pressures in the range of about 400 to 600 psia are employed to match existing equipment designs and in order to maintain the desired temperature and pressure of the gas effluent from the turboexpander to maintain the gas in substantially a gaseous state in the turboexpander.

Although the gas purification system and its regeneration process have been described in general terms, it will be understood by those of skill in the art that various known engineering procedures may be employed to obtain optimum results.

In reference to Example II above, one procedure which may be used is as follows: The condensers and the separators of the compression system **12*a*** usually will remove a large part of the water and any other condensate that might have formed. It is possible to include prior to the purification system an inlet separator as an added separator vessel to catch any possible liquid that might be condensed from the feed. A York demister pad may be installed in the upper section of this separator to aid in removal of fine suspended mists.

The water removal molecular sieve may include two or three bed systems for adsorption, for regeneration and for cooling. It is desirable that each operation be on a time cycle set by economics of the particular system and that all of the flows be in a downward direction.

As it is recognized by those of skill in the art, carbon dioxide, hydrogen sulfide and heavy hydrocarbon removal by adsorption are influenced by temperature and to obtain reasonable and effective adsorption beds, the gas should first be cooled to an appropriate low temperature, such as for example about 45°F. This temperature, however, must be above the water hydrocarbon hydrate formation temperature for the gas being processed.

To achieve the necessary precooling, a refrigeration machine following the water removal molecular sieve can be employed. Such a unit would be of a conventional installation including an exchanger in which a refrigerant such as Freon or propane is evaporated against the feed gas, thereby cooling the feed stream to about 45°F. The feed gas pressure in the exchanger is about 600 psia, while the Freon or propane evaporates at appropriate pressures defined by thermodynamic conditions of these refrigerants. The evaporated refrigerant then exchanges heat by subcooling the condensed liquid refrigerant which leaves an exchanger at about 50°F. The warmed low pressure refrigerant then passes by way of a dry drum to a single stage centrifugal compressor where it is compressed to a suitable pressure for condensing by air or water cooling, e.g., about 140 psia. The compressed gas enters a water cooled or air cooled condenser where it is liquified and its temperature reduced to about 90°F. The condensed liquid is stored in a receiving drum from which it flows under its own pressure to the subcooler. The subcooled liquid is then expanded into the feed gas exchanger to cool the feed gas as described above.

After the feed gas is cooled employing the foregoing procedure or any other known engineering procedure, the feed gas is flowed to the carbon dioxide, hydrogen sulfide and heavy hydrocarbon removal beds. Preferably because of the large quantities of carbon dioxide, hydrogen sulfide and heavy hydrocarbons that have to be removed from the crude gas, the operation should be set on a short adsorption cycle in order to reduce bed quantities to economical levels. Since at times it is possible that regeneration and cooling will not be adequately handled in the period of a short adsorption cycle, it is sometimes convenient to employ a three bed operation, as will be more fully developed hereinbelow regarding the regeneration of the gas purification system. These adsorbing beds are dual layers of molecular sieves for adsorbing carbon dioxide and hydrogen sulfide and activated carbon for adsorbing heavier hydrocarbons.

It is also advantageous and economical to balance, approximately, the gas flashed in the liquefaction section plus heat leak in storage and handling operations against purification system purge gas requirements, gas turbine fuel and by-product steam production. This balancing is accomplished by purging the dry, clean flash gas from the liquefaction process and using the effluent for fuel for the gas turbine.

The engineering procedure found most preferable for the regeneration of the adsorption beds is on a heat-balance basis. By employing this procedure heat should be applied to raise the bed temperature to about 450° or 500°F., to furnish the heat of desorption of the adsorbed materials and then raise the temperature of the containing vessel to an appropriate temperature for complete desorption of the impurities. This temperature must be above the normal boiling point of the material being desorbed at the pressure of operation. As the high pressure sieve vessels would be heavy, inside insulation can be used to preclude the heating of the entire vessel mass. The allowable enthalpy change of the regenerating gas defines its quantity. On the cooling cycle, the same sensible heat factors are required, but the latent heat factor is not present. Therefore, the quantity of gas necessary for cooling is somewhat less than for heating.

In regenerating the beds using the flash gas from heat exchanger-liquifier **22,** the flash gas is compressed from 16 psia to 200 psia in the compressor system **64.** Although the drawing illustrates the compressor system as a single unit, it is possible to employ a multistage compressor with intercooling and after cooling by water and final cooling by heat exchange with the incoming cold flash gas to about 45°F. This flash gas typically contains about 3 percent nitrogen and 97 percent methane and is clean and dry.

Inasmuch as there is less cooling gas required than heating gas in the bed regeneration, the cool gas stream is split to the separate water adsorbing beds and the carbon dioxide hydrogen sulfide hydrocarbon adsorbing beds. The cooling requirement of the carbon dioxide-hydrocarbons is first satisfied and the remaining gas is sent to the water-bed regeneration. As this leaves a constant gas flow to the water-bed regeneration, the difference in the balance between heating and cooling is satisfied by using a 5-hour heating cycle and a three-hour cooling cycle on the water bed. Any of the known heating means may be employed. After the 5-hour heating period, the heater is shut down and the cool gas continues to flow through the heater and adsorption bed. In about 3 hours, the bed will be returned to its operating temperature level. At this point, the bed cycle changes and the fired heater is again brought into operation heating the previously operating bed while the cooled bed is returned to adsorption service in the process stream. The effluent gas during most of the heating cycle will leave at close to 90°F. as the temperature progresses through the beds in approximately a plane front on heating and cooling. On cooling the effluent will be closer to about 500°F.

Parallel to the operation of the water adsorbing beds part of the purging gas from the compressor system is flowing to the carbon dioxide-hydrocarbon bed being cooled for return to adsorption service. The gas leaving this bed will be at about 500°F. This gas is mixed with the effluent from regeneration or cooling of the water bed and sent to a heating unit where the temperature is brought to 500°F. for regeneration of the second bed of the carbon dioxide-hydrocarbon adsorbers. The small quantity of water that would be thus injected will have no effect at the 500°F. level. The effluent from the regeneration will leave at about 45°F. containing all of the adsorbed water, carbon dioxide and heavy hydrocarbons. This will be at 200 psia minus the small pressure drop through the various beds. By recombining the purge gas stream before regenerating the carbon dioxide and hydrocarbon purification beds, a sufficient weight of gas is obtained to satisfy the difference in heating requirements between heating and cooling of the carbon dioxide-hydrocarbon beds and still maintain a reasonable process cycle.

As the regeneration level is at 200 psia and the operating level of the beds is 600 psia, small repressuring lines and controls are provided so that the beds may be returned to operating pressure after regeneration and before being placed on the line. This will eliminate periodic surges through the system. A limiting orifice will allow gradual repressuring.

These three beds can operate on a 1-hour process cycle, a 1-hour heating cycle and a 1-hour cooling cycle. Each hour the beds must be moved forward in the operating cycle by one step. This operation can be controlled by automatically timed control valves.

All of the equipment employed in the above-described process and as components of the liquefaction plant shown as an example for practicing this invention are conventional and readily available to those skilled in the art.

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.

We claim:

1. A process for liquifying a substantially water-hydrogen sulfide- and carbon dioxide-free natural gas mixture comprising nitrogen and hydrocarbons containing up to about six carbon atoms under elevated pressure which process comprises:

1. cooling the natural gas mixture under elevated pressure by heat exchange with a combined, methane-nitrogen gas mixture produced subsequently in step (4) whereby the combined gas mixture is heated and a predominant portion of the natural gas mixture is liquified,
2. substantially isenthalpically reducing the pressure of the cooled natural gas 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 natural gas mixture to form a major liquid fraction containing methane and substantially all the hydrocarbons having at least two carbon atoms,
3. separating the minor, methane-nitrogen gas fraction from the major liquid fraction and recovering the major liquid fraction as product,

performing in sequence the following steps (4) through (10) thereby providing series flow through the operations of steps (4) through (10),

4. combining the minor, methane-nitrogen gas fraction with an isentropically expanded, methane-nitrogen refrigerant gas mixture produced subsequently in step (10) to form the combined gas mixture,
5. employing the entire combined gas mixture formed in step (4) to cool the natural gas mixture in step (1),
6. heat exchanging the heated, combined gas mixture from step (1) with a compressed and cooled methane-nitrogen refrigerant gas mixture obtained subsequently in step (8) whereby the heated, combined gas mixture is further heated to a temperature in the range from about −50° to about 300°F.,
7. compressing the further heated, combined, methane-nitrogen gas mixture from step (6) to provide a compressed, methane-nitrogen refrigerant gas mixture,
8. cooling the compressed refrigerant gas mixture from step (7),
9. employing the compressed and cooled methane-nitrogen refrigerant gas mixture from step (8) in the heat exchange of step (6) whereby the compressed and cooled refrigerant gas mixture is further cooled,
10. substantially isentropically expanding in a work recovery engine the further cooled methane-nitrogen refrigerant gas mixture from step (9) whereby mechanical energy is obtained, the refrigerant gas mixture is still further cooled and the isentropically expanded, methane-nitrogen refrigerant gas mixture is formed,
11. removing from the process prior to the compression of step (7) a minor portion of heated the combined gas mixture produced in step (1) which minor portion is substantially equal in magnitude to the minor methane-nitrogen gas fraction formed in step (2), and
12. employing the mechanical energy obtained from the work recovery engine at least to compress partly the combined refrigerant gas mixture in step (7).

2. The process of claim 1 wherein the natural gas mixture in step (1) is at a pressure in the range from about 350 to about 750 psia.

3. The process of claim 1 wherein the natural gas mixture in step (1) is maintained at a pressure so that the plot of the temperature vs. enthalpy of the mixture approaches a straight line.

4. The process of claim 1 wherein the flow rate of the combined methane-nitrogen gas mixture in step (1) is from about 2 to about 4 times the flow rate of the natural gas mixture in step (1), expressed as moles per hour.

5. The process of claim 1 wherein the compressed, methane-nitrogen refrigerant gas mixture from step (7) is at a pressure from about 400 to about 600 psia.

6. A process of claim 3 wherein the combined nitrogen-methane refrigerant gas stream charged to step (1) is maintained at a pressure in relationship to the temperature of the cooled compressed refrigerant gas stream to be expanded in step (10) so that the work expanded refrigerant gas leaving the expansion engine will thermodynamically balance the process.

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

8. The process of claim 1 wherein the natural gas mixture is subjected to purification for the removal of water, carbon dioxide, hydrogen sulfide and high freezing point hydrocarbons.

9. The process of claim 8 wherein the purification is effected by treatment with adsorbents and the minor portion of the combined gas mixture removed in step (10) is employed to purge and regenerate the adsorbents.

10. The process of claim 1 wherein the minor portion of the combined gas mixture removed in step (11) is charged to a separate work recovery engine whereby mechanical energy is obtained and employed at least to compress partly the major portion of the combined gas mixture.

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

adjusting the pressure of the incoming gas to a range from about 350 to about 750 pounds psia;

passing said pressurized gas through a plurality of molecular sieves and subsequently through a bed of activated carbon to remove water, carbon dioxide, hydrogen sulfide and heavy hydrocarbons from said pressurized gas;

cooling and liquifying a predominant portion of said pressurized gas in a countercurrent heat exchanger-liquifier;

substantially isenthalpically reducing the pressure of the cooled effluent from the heat exchanger-liquifier further to cool it and thereby flashing a minor vapor fraction while liquifying completely the balance of the natural gas to form a major liquid fraction;

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

passing all of said combined gas countercurrently to the incoming gas in said heat exchanger-liquifier at a flow rate of 2 to 4 times that of the feed gas stream whereby the combined gas effluent from the heat exchanger-liquifier is warmed;

separating the warmed effluent from said heat exchanger-liquifier into a major refrigeration gas fraction and a minor regeneration-fuel gas fraction;

sequentially passing all of the refrigeration gas fraction in series flow:

through a countercurrent heat exchanger precooler wherein it is heated;

to a compressor system wherein it is compressed to a pressure in the range from about 400–600 psia;

through said heat exchanger precooler, wherein it is cooled;

through an expansion engine, wherein it is isentropically expanded at a temperature and pressure sufficient to maintain the gas in the gaseous state in said expansion engine to form the isentropically expanded refrigeration gas, and 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 at a point prior to entry into said heat exchanger-liquifier;

purging said molecular sieves and activated carbon with the regeneration-fuel gas fraction;

utilizing the regeneration-fuel gas fraction subsequent to the purging to furnish fuel for a gas driven turbine which provides a minor portion of the mechanical energy necessary to drive said compressor system, employing the mechanical energy obtained from the isentropic expansion to provide a major portion of the mechanical energy necessary to drive the compressor system.

12. The process of claim 11 wherein the regeneration-fuel gas fraction subsequent to purging is utilized to furnish fuel for steam generation which steam in turn is used to provide a portion of the mechanical energy necessary to drive the compressor system.

13. An apparatus for liquifying natural gas (and producing power sufficient to sustain continuous production thereof without the aid of outside power to drive the refrigeration compressor system other than that derived from the incoming feed gas,) comprising in sequence:

a heat exchanger-liquifier for cooling and liquifying the incoming gas by countercurrent heat exchanger with a combined flash gas and work expanded refrigerant gas from an expansion engine;

means for isenthalpically expanding the 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; and

means for recovering the major liquid fraction as product;

a refrigeration cycle comprising in sequence so as to provide series flow therethrough:

means for passing the flash gas to said heat exchanger-liquifier as part of said combined refrigerant gas;

means for passing said refrigerant gas from said heat exchanger liquifier to a heat exchanger precooler, wherein said refrigerant gas is reheated;

compression means for compressing said heated refregerant gas from said heat exchanger precooler;

means for passing said compressed refrigerant gas to said heat exchanger precooler, wherein said compressed refrigerant gas is precooled;

an expansion engine for work expanding said precooled refrigerant gas to reduce further the temperature of said precooled gas to reduce the pressure of the precooled gas and to obtain mechanical energy; and

means for feeding said work expanded and cooled gas from said expansion engine to said heat exchanger-liquifier to join said flash gas;

and also comprising means for bleeding from the apparatus a minor portion of the combined flash gas and work expanded gas from the heat exchanger-liquefier prior to compression thereof;

said expansion turbine and said compression means being operatively cooperative whereby the mechanical energy obtained from said turbine supplies at least a portion of the work required to operate said compression means.

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