United States Patent

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[54] **GAS LIQUEFACTION PROCESS AND APPARATUS**

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[51] **Int. Cl.** **F25j 1/00,** F25j 1/02

[58] **Field of Search** 62/9, 11, 27, 28, 38, 40, 126, 62/39

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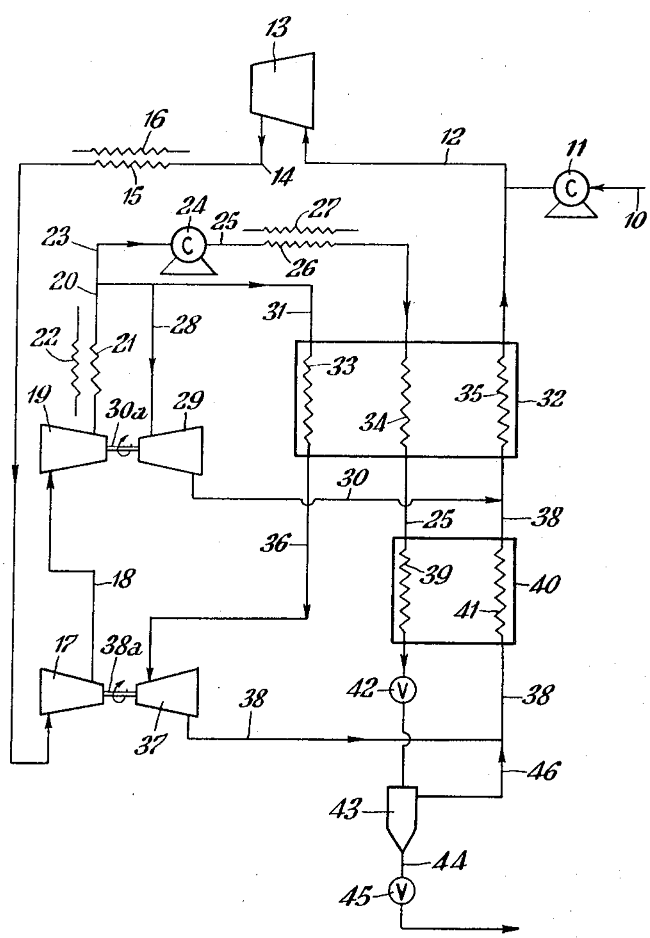
[57] **ABSTRACT**

This invention relates to a method and apparatus for the liquefaction of low boiling gases for example nitrogen and natural gas. By the use of parallel refrigerant expansion engines and feed compression the product cooling curve in the liquefaction zone is altered so that the specific heat of the feed gas in the liquefaction zone is reduced to about 1.5-15 times the specific heat of the low pressure refrigerant gas in the zone. This has the effect of distributing the refrigerant required by the feed over a substantially wider temperature range so that the average ΔT may be substantially reduced and the process efficiency improved.

15 Claims, 6 Drawing Figures



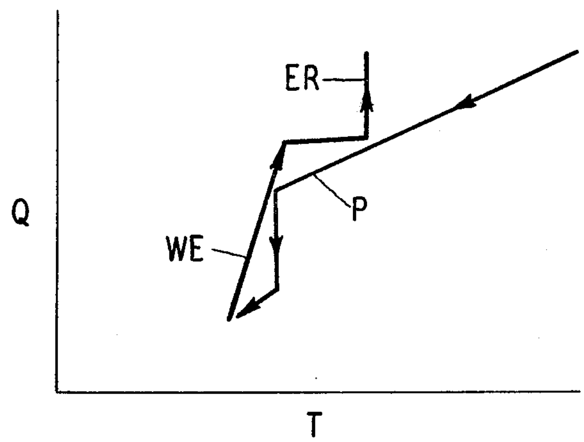


Fig.1

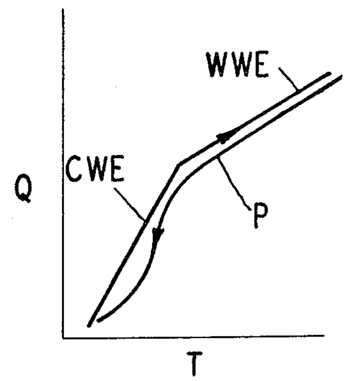


Fig.2

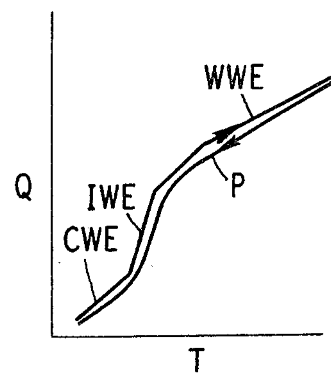


Fig.3

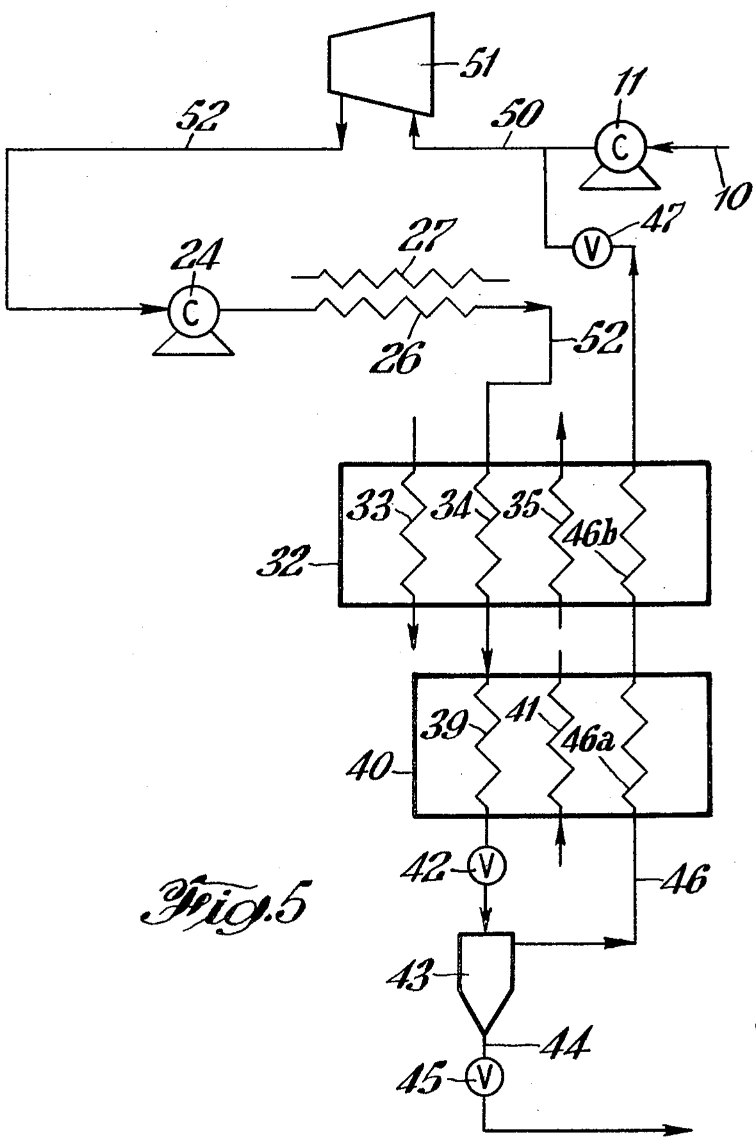


Fig.5

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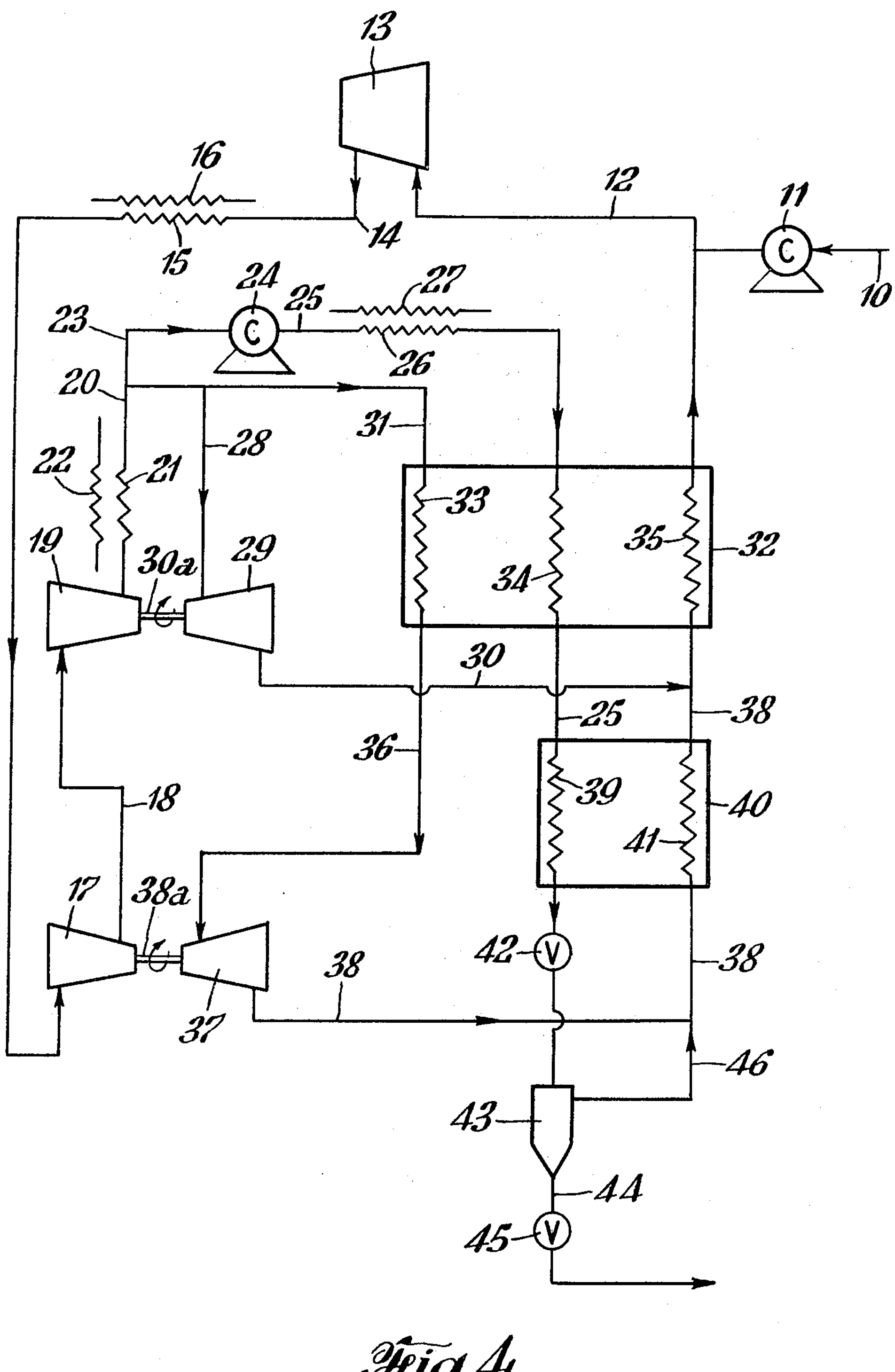

Fig. 4

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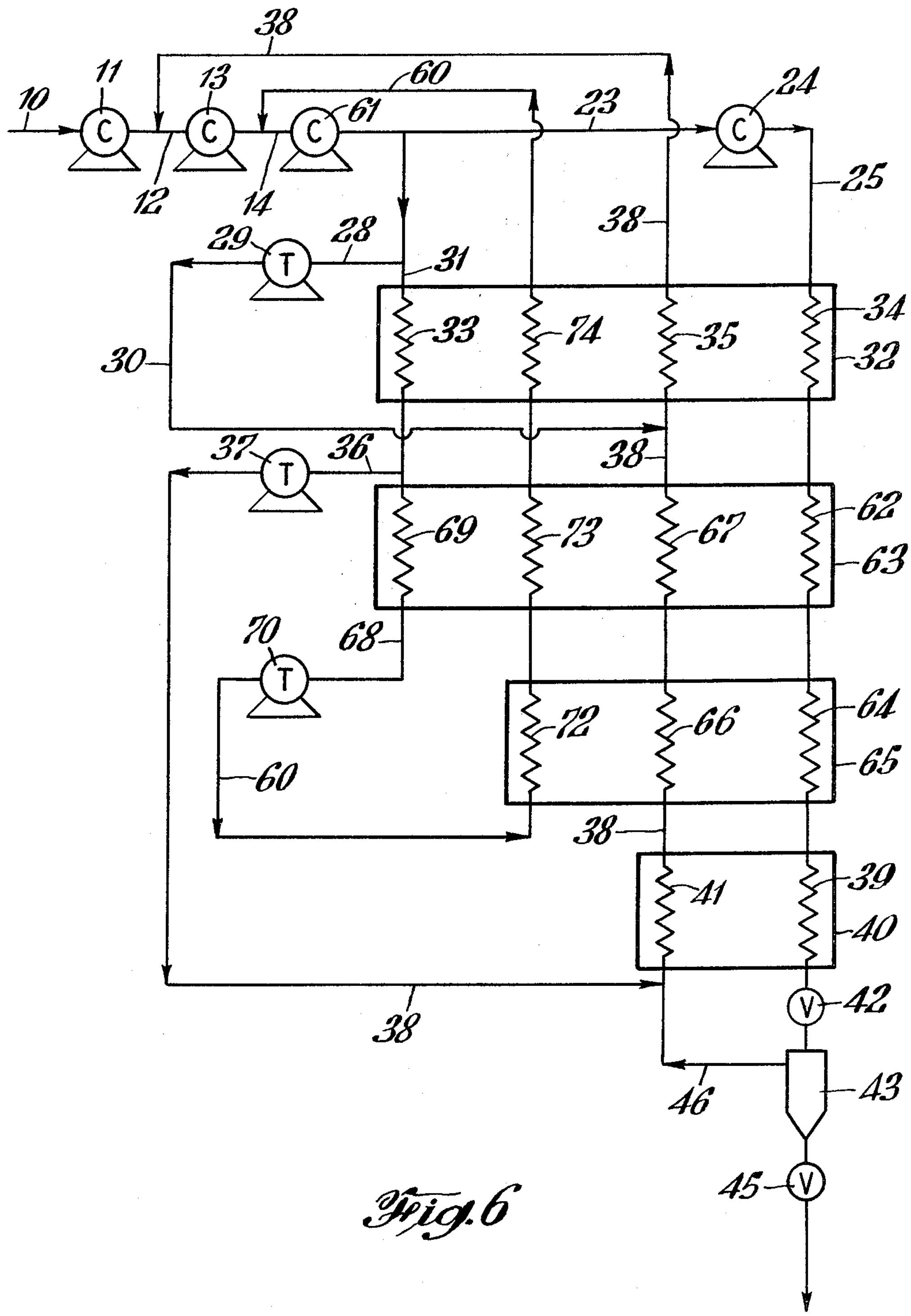

Fig. 6

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GAS LIQUEFACTION PROCESS AND APPARATUS

BACKGROUND OF THE INVENTION

This invention relates to a process of and apparatus for liquefaction of low boiling gases as for example nitrogen and natural gas.

A well-known method for liquefaction of low boiling gas as described in U.S. Pat. No. 3,144,316 to H. Koehn et al involves compression of the feed gas, e.g., nitrogen, to medium pressure such as 300 psia. The pressurized feed gas is partially cooled to intermediate temperature, e.g., 207°K. for nitrogen feed, by an external supplied refrigerant such as dichlorodifluoromethane. Refrigeration below this level is provided by cold gas which has been work expanded from a higher pressure such as 170 psia. to a relatively low pressure such as 25 psia. in either a single work expander or two work expanders connected in series.

The most significant inefficiency of this and other similar prior art liquefaction methods results from the discontinuous shape of the feed gas, i.e., product, cooling curve as illustrated in FIG. 1 and identified as P. Whereas the heat duty (Q) vs. temperature (T) curve is straight and relatively flat in the range above the liquefaction point where the external refrigerant (ER) supplies the necessary cold, a very large refrigerant load requirement occurs at the liquefaction point, e.g., about 116°K. for nitrogen. This refrigeration is required to supply the latent heat of condensation and the effective specific heat of the product ($\Delta Q/\Delta T$) is infinite. This large latent heat refrigeration load creates a temperature "pinch" (undesirably small ΔT) in the heat exchanger between the work expanded gas and product fluid at this point. A similar temperature "pinch" occurs in the warmer heat exchanger processing the external refrigerant. The combination of these two temperature pinches results in a very irregular shaped and rather inefficient cooling curve for the feed-product fluid. This in turn causes heat exchange irreversibilities or inefficiencies which increase the process power requirements.

It is an object of this invention to provide an improved process of and apparatus for liquefaction of low-boiling gases.

Another object is to provide process and apparatus requiring appreciably lower power than prior art liquefaction systems.

Still another object is to provide process and apparatus which does not require an external refrigeration-producing circuit.

Other objects and advantages of this invention will be apparent from the ensuing disclosure and appended claims.

SUMMARY

In a process embodiment of the invention, low-boiling feed gas is provided at sub-critical pressure and compressed to high pressure. As used herein, "low-boiling" feed gas refers to single and multi-component gases having a boiling point below about 193°K. at 1 atmosphere pressure. Examples of such gases are nitrogen and natural gas, the latter comprising primarily methane. The high pressure to which the feed gas is compressed is such that the feed gas Q/T cooling curve comprises a multiplicity of regions having substantially constant specific heat $\Delta Q/\Delta T$, where Q is enthalpy and T is temperature. For single component feed gas, the high pressure is supercritical pressure, i.e., above critical pressure. As used herein the term "critical" pressure refers to the pressure at which any temperature under the critical temperature will cause liquefaction. Critical temperature is the temperature at which the molecular kinetic energy of translation equals the maximum potential energy of attraction. Above the critical temperature the liquid state is impossible for a single component and compression results only in a highly compressed gas, retaining all the properties of the gaseous state. Below the critical temperature a gas may be liquefied if sufficiently compressed.

Compressed refrigerant gas is provided at sub-critical pressure and a portion thereof is "warm" work expanded to intermediate temperature and low pressure. "Work expansion" refers to passage of pressurized gas through a suitable machine such as a turbine wherein the gas is expanded to sufficiently low pressure to extract energy and appreciably cool the gas. In this process, the warm work expansion is sufficient to cool the gas so that it may in turn partially cool the high pressure feed gas and remaining compressed refrigerant gas in a warm heat exchanger.

At least part of the partially cooled remaining compressed refrigerant gas from the warm heat exchanger is "cold" work expanded to lower-than-intermediate temperature and substantially the same low pressure as the warm work expansion. All of the process refrigeration is supplied by work expansion of gas, that is, the external refrigeration source characteristic of many prior art liquefaction schemes is obviated. It should be understood that the aforedescribed two work expansion steps are designated "warm" and "cold" for comparison purposes and not relative to ambient temperature. That is, both the feed and exhaust gas temperatures of the warm work expansion step are warmer than the corresponding temperatures of the cold work expansion step.

The partially cooled high pressure feed gas from the warm heat exchanger (having been cooled in part by the warm work expanded refrigerant gas) is further cooled by the cold work expanded refrigerant gas in a cold heat exchanger. The latter gas is simultaneously partially warmed in the cold heat exchanger. The resulting further cooled feed from this exchanger is then throttled and forms the product liquid. The partially cooled high pressure feed gas and the cold work expanded refrigerant gas are at relative pressures such that the specific heat ratio of the former to the latter in the cold heat exchanger is 1.5–15.

The cold work expanded and partially warmed refrigerant gas from the cold heat exchanger is further warmed by heat exchange with the high pressure feed gas and the remaining compressed refrigerant gas in the warm heat exchanger. The so further warmed work expanded gas is recompressed and recycled as the aforementioned compressed refrigerant gas.

The warm and cold work expansion steps are each controlled to deliver the process refrigeration of the expanded gases to the feed gas temperature regions where such gas has substantially constant specific heat.

Although this process only required two work expansion steps in parallel flow relation, it may be advantageously practiced with an additional work expansion step also in parallel flow relation to the warm and cold work expansion steps. Another part of the same compressed feed gas is work expanded from the same inlet pressure to a higher discharge pressure than the gases discharged from the warm and cold work expansions. More specifically, in this embodiment the partially cooled high pressure feed gas from the warm heat exchanger is cooled in a first intermediate heat exchanger and thereafter additionally cooled in a second intermediate heat exchanger in part by cold work expanded refrigerant gas having been partially warmed in the cold heat exchanger. That is, the cold work expanded refrigerant gas flows consecutively through the cold heat exchanger, the second intermediate heat exchanger, the first intermediate heat exchanger, and the warm heat exchanger for recovery of its refrigeration prior to recompression and recycling.

Another part of the partially cooled remaining compressed refrigerant gas from the warm heat exchanger cold end is further cooled in the first intermediate heat exchanger to lower temperature. This stream is then work expanded to pressure above said low pressure and colder temperature between the intermediate temperature of the warm work expanding and the lower-than-intermediate temperature of the cold work expanding. The refrigeration of this third work expanded stream is recovered and the stream itself is progressively warmed by the high pressure feed gas in the second intermediate heat exchanger, the aforementioned another part of the partially cooled remaining compressed refrigerant gas and the high pressure feed gas in the first intermediate heat exchanger, and the remaining compressed refrigerant gas and high pressure feed gas in the warm heat exchanger. The so-warmed third work expanded stream is finally recompressed and recycled as part of the compressed refrigerant gas. In this embodiment all of the process refrigerant is provided by the three work expansions.

In the aforedescribed embodiments the feed gas and recycle refrigerant gas have been identified as two separate and distinct fluids. However, they may be of the same composition and combined for processing so that a portion of the same gas constitutes the feed gas and another portion comprises the recycle refrigerant gas. In particular, one embodiment contemplates combining the feed gas with the further warmed work expanded refrigerant. The combined gas is recompressed and a first portion thereof further compressed to high pressure as the feed gas.

In the broad apparatus embodiment of the invention, means are provided for compressing feed gas from sub-critical to high pressure and a first work expander is employed for expanding a portion of the so-compressed refrigerant gas to low pressure and intermediate cold temperature. A relatively warm heat exchanger has separate passageways for partial cooling the high pressure feed gas and remaining compressed refrigerant gas by the cold low pressure gas from the first work expander. A second work expander is provided for expanding at least part of the partially cooled remaining compressed refrigerant gas from the warm heat exchanger to about the same low pressure as the first work expander but lower-than-intermediate temperature of the first expander. The work expanders provide all of the refrigeration needed for the gas liquefaction, i.e., external refrigeration is not required other than for removal of heat of compression. A relatively cold heat exchanger has separate passageways for further cooling the high pressure feed gas from the warm heat exchanger by this cold refrigerant gas from the second work expander. Valve means are included for throttling the further cooled feed from this cold heat exchanger and thereby forming the product liquid.

Passageway means in the aforementioned warm heat exchanger are provided for further warming the low pressure refrigerant gas having been partially warmed in the cold heat exchanger and compression means serve to recompress this further warmed refrigerant gas to higher sub-critical pressure. Conduit means serve to recycle this recompressed refrigerant gas to the first work expander.

This invention also contemplates liquefaction apparatus as previously described but additionally including first and second intermediate heat exchanger arranged and positioned between the relatively warm and cold heat exchangers, and a third work expander. These heat exchangers are provided with separate passageways for respectively cooling and additionally cooling the partially cooled high pressure feed gas from the warm heat exchanger. Conduit means facilitate flow of this additionally cooled feed gas to the cold heat exchanger. Also, conduit means are included for consecutively flowing the partially warmed low pressure refrigerant gas from the cold exchanger to passageways in the second and first intermediate heat exchangers for additional and still additional warming at least in part by the high pressure feed gas, and thence to the passageway means in the warm heat exchanger for the further warming.

Passageway means are included in the first intermediate heat exchanger for further cooling another part of the partially cooled remaining compressed refrigerant gas from the warm heat exchanger. The third work expander is arranged to receive this further cooled gas and expand same to pressure above the low discharge pressure of the first and second work expanders, and to colder temperature between their intermediate and lower-than-intermediate discharge temperatures. Passageways in the second intermediate heat exchanger, the first intermediate heat exchanger and interconnecting conduits are included for progressively warming the refrigerant gas discharged from the third work expander. A compressor is provided for repressurizing this warmed refrigerant gas to sub-critical pressure and conduit means join the compressor discharge to facilitate recycling of this gas to the first work expander.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph showing the relationship between heat duty (Q) and temperature for the prior art external refrigeration - single work expansion process for low-boiling gas liquefaction.

FIG. 2 is a graph showing the same relationships as FIG. 1 for an embodiment of this invention employing two work expansions and no external refrigeration.

FIG. 3 is a graph showing the same relationship as FIGS. 1 and 2 for an embodiment employing three work expansions and no external refrigeration.

FIG. 4 is a schematic flowsheet of a two work expander embodiment employing as the recycle refrigerant, the same fluid which constitutes the feed to be liquefied.

FIG. 5 is a schematic flowsheet of a closed refrigerant circuit which may be used in the FIG. 4 embodiment instead of the illustrated open refrigerant circuit, and

FIG. 6 is a schematic flowsheet of a three work expander embodiment.

DESCRIPTION OF PREFERRED EMBODIMENTS

One of the essential features of this invention is that of cooling the feed gas at high pressure to the throttling-liquefaction temperature. The pressure is sufficiently high so that the feed-product gas Q/T cooling curve comprises a multiplicity of regions each having substantially constant average specific heat $\Delta Q/\Delta T$. The curve is relatively smooth but inflected (see P in FIGS. 2 and 3) and avoids the discontinuous shaped curve resulting from the feed stream condition passing through the fluid mixture (liquid-vapor) region at low pressures. It will also be apparent from a comparison of the curve of FIG. 1 with FIGS. 2 and 3 that this feature eliminates the very large refrigeration load at a specific temperature or range, i.e. the latter has no region of vertical heat duty (Q) approaching infinite specific heat ($\Delta Q/\Delta T$). Instead, the high pressure feed gas or product stream distributes the liquefaction heat load over a much wider temperature range. Other advantages of the high pressure cooling include more efficient recovery of product flash-off gas on throttling and lower energy consumption due to pressure drop losses.

Ideally the feed-product cooling curve is divided into four regions each represented by a relatively linear section of substantially constant average specific heat. Each region may then be approximated as a straight line. These regions are qualitatively described as follows: Region I is the gas cool-down which is the warmest level wherein the specific heat may be about 7–12 depending on the feed gas composition and pressure, and is about 8 for pure nitrogen gas at 615 psia. Region II is that of intermediate temperature or transition in which the feed gas would complete cooling and begin to liquefy at saturated conditions if it were at low pressure. For pure component feed gas such as nitrogen, this refers to the temperature region immediately above, and at which gas at sub-critical pressure begins to liquefy. Again depending on the feed gas composition and pressure, the specific heat for Region II is about **10–21** and about **14** for pure nitrogen at 615 psia. Region III is that of primary "liquefaction," wherein liquefaction would be completed at saturated conditions if the gas were at low pressure. It includes the highest specific heat of the cooling curve, i.e. highest refrigeration requirement and steepest slope in the Q vs. T plot. The specific heat may be about 28–105 and about 42 for nitrogen again at 615 psia. Region IV is that of "subcooled liquid" and the coldest level wherein "liquefied" product from III would be further cooled. The specific heat in IV may be in the range of about 10–21 and about **14** for pure nitrogen. It is emphasized that the foregoing qualitative descriptions of Regions II–IV are intended to relate the high pressure product cooling curve of this invention with a prior art low pressure product cooling curve, as illustrated by curves P in FIGS. 1–3. At the high pressures as contemplated herein, liquefaction does not occur at a single temperature (FIG. 1) but rather over the lower temperature range prior to throttling. With single-component feed gas, this liquid is not saturated until throttled; with multi-component feed, the liquid may be saturated at a particular temperature. "Subcooling" refers to cooling a particular liquid below its saturation temperature, and does not occur in the high pressure product cooling curve, although liquid may be further cooled after its formation.

It should also be understood that the specific heat in each of Regions I–IV will vary considerably on a point-to-point basis but if all possible points in the various portions of each region are plotted on a Q vs. T graph and an average line drawn therebetween, a straight line will be approximated and represents "substantially constant specific heat" as used herein.

The required refrigeration for linear Regions I–IV is supplied at small temperature differences by matching low pressure refrigerant streams each having substantially constant specific heat and each obtained by a separate work expansion of gas from a common source. Since the refrigeration requirement of the product gas is more evenly distributed over the ambient to low temperature range because of its substantially constant average specific heat characteristic, the refrigerant recycle flow rate for such work expansion may be minimized, thereby minimizing the required power and the work expander interconnecting conduit size. That is, only sufficient gas is recycled through each work expander-refrigerant gas circuit to provide the cold required by that particular linear region of the high pressure product cooling curve P. The temperature levels for each work expansion are selected so that the warming line for the work expanded gas closely parallels a selected portion of the product cooling curve P. Preferred average temperature differences between the cooling and warming curves at the heat exchanger warm and cold ends are 2°–4° C. Such low ΔT are more readily obtained with three instead of two work expansions as demonstrated by a comparison of FIGS. 2 and 3. In this invention these close ΔT's are preferably maintained by varying the refrigerant gas recycle rate for such work expansion. In general, the most efficient work expansion conditions are those at the highest temperature level, the lowest pressure level, and the lowest pressure ratio of gas inlet to discharge. Accordingly, the work expander inlet pressure is sub-critical and below the high pressure of the product gas.

Summarizing the foregoing, this invention alters the shape of the product cooling curve P in the "liquefaction zone" so that rather than the infinite specific heat as obtained for a pure component at sub-critical pressure, the specific heat is reduced to about 4–15 times the specific heat of the low pressure refrigerant gas. This has the effect of distributing the refrigerant required by the product over a substantially wider temperature range so that the average ΔT may be substantially reduced and the process efficiency significantly improved. Table I summarizes characteristics of the product cooling curve linear regions at **615** psia.

TABLE I

Typical Temp. (°K) Cooling and (Sp. Ht.) Curve Region N_2 Nat.	Gas*	Specific Heat Ratio** Broad	N_2
I 300–170°300–	225°	1–1.8	1.2
(8) (1	1)		
II 170–135°225–	205°	1.5–3.0	2
(14) (2	0)		
III 135–120°205–	180°	4–15	6
(42) (5	9)		
IV 120–90°180–	120°	1.5–3.0	2
(14) (1	1)		

*Natural Gas = 90 mole % CH_4, 6% C_2H_6, 3% N_2, 1% C_3H_8

**Based on refrigerant gas specific heat of 7.0 Ratio = product gas/refrigerant gas

FIG. 2 shows the heat duty (Q) vs. temperature relationship (T) for nitrogen liquefaction using 615 psia. nitrogen feed gas, nitrogen recycle refrigerant gas and two turbine-type work expanders. Although four turbines would be ideally employed to match the four substantially constant average specific heat linear regions of the product cooling curve, the use of two turbines operating in parallel flow relation permits a reasonably close approximation and a substantial reduction in power cost without the additional equipment investment and complexity of four turbines. The slopes of the relatively warm work expanded nitrogen refrigerant gas (identified as WWE) and the relatively cold work expanded nitrogen refrigerant gas (identified as CWE) represent the recycle flow rates required for each portion of the warming curve to maintain the desired small temperature differences in the arm and cold heat exchangers.

FIG. 3 is also based on 615 psia. nitrogen feed gas and nitrogen recycle refrigerant gas, but with three turbine-type work expanders operating in parallel flow relation (WWE, IWE, and CWE). This embodiment permits smaller temperature differences in the heat exchangers throughout the system (as compared with two expanders) due to the similar heat capacities of the high pressure product stream above and below the liquefaction zone. The latter refers to the temperature that would correspond to the condensation point if the product fluid was at sub-critical pressure. In this embodiment the temperature levels for the relatively warm and cold work expansions (WWE and CWE) were selected so that the exhaust gases could be joined at the cold end of the warm heat exchanger, thereby simplifying the piping and controls. The intermediate work expansion (IWE) is characterized by an expander inlet temperature below CWE and a discharge temperature between WWE and CWE.

Product cooling and refrigerant warming curves for other fluids such as natural gas have a similar relationship to that illustrated in FIGS. 2–3 when processed according to this invention. It should be noted that the average temperature differences in the heat exchangers are appreciably smaller than those obtained in the external refrigerant-single work expansion liquefaction process of FIG. 1.

Referring now more specifically to the FIG. 4 embodiment, feed gas is introduced through conduit **10** and pressurized in compressor **11** prior to mixing with the recycle refrigerant gas in conduit **12**. The combined feed-recycle refrigerant gas is further pressurized in compressor **13** for example at ambient temperature, and the heat of compression in the discharge gas flowing in conduit **14** is preferably removed in the aftercooler comprising compressed gas heat exchange passageway **15** and water coolant passageway **16**. The compressed and aftercooled feed-recycle refrigerant gas in conduit **14** is further pressurized to first intermediate pressure in first booster compressor **17** and the discharged gas in conduit **18** is still further pressurized in second booster compressor **19** to second higher intermediate pressure and discharged into conduit **20**. The heat of compression is preferably removed from this gas by an aftercooler comprising gas heat exchange passageway **21** and water coolant passageway **22**.

In this particular embodiment the aftercooled compressed feed-recycle refrigerant gas at second intermediate pressure in conduit **20** is divided into three portions. A first portion in branch conduit **23** is compressed to high pressure in product compressor **24** and is hereinafter identified as the product fluid. If the feed-recycle refrigerant gas has only one component, this high pressure is supercritical. If the gas is multi-component the pressure is not necessarily supercritical but high enough to provide a cooling curve having the same general shape as the same gas at supercritical pressure, i.e., a multiplicity of regions each having substantially constant specific heat, as for example represented by curves P of FIGS. **2** and **3**. The still higher pressure gas in conduit **25** is preferably aftercooled in heat exchange passageway **26** by water in coolant passageway **27**. A second portion of the compressed feed-recycle refrigerant gas in branch conduit **28** is expanded in warm level turbine **29** to low pressure and intermediate temperature of the feed gas. This gas is discharged from turbine **29** into conduit **30**. As previously indicated, no external refrigeration is provided for this process so that all required refrigeration is supplied by work expansion of process gas. This "warm" work expansion step of the FIG. 4 embodiment provides all of the refrigeration supplied by external means in the prior art process of the previously referenced U.S. Pat. No. 3,144,316 plus a portion of the refrigeration generated in the single turbine of that process. The power developed in warm expansion turbine **29** is preferably transferred directly to drive second intermediate pressure compressor **19** as by shaft **30a**. Alternatively, at least part of the work expander power may be adsorbed by other means such as an electric generator (not illustrated), and used for reducing the net power requirements of the process.

The remaining or third portion of compressed feed-recycle refrigerant gas from conduit **20** is directed through branch conduit **31** to the warm end of warm heat exchanger **32** for partial cooling in passageway **33**. The aforementioned product gas in conduit **25** at still higher pressure also enters warm heat exchanger **32** at the warm end thereof and is partially cooled in passageway **34**. These two gas streams are cooled in part by the warm work expanded second portion from conduit **30** which enters the cold end of warm heat exchanger **32** in passageway **35** and flows therethrough for discharge at the warm end.

The partially cooled third portion portion discharged from passageway **33** of heat exchanger **32** into conduit **36** is expanded in cold level turbine **37** to low pressure and lower-than-intermediate temperature. This gas is exhausted from turbine **37** into conduit **38**. The power developed in cold expansion turbine **37** is preferably transferred directly to first intermediate pressure compressor **17** as by shaft **38a**. Since warm level turbine **29** provides part of the refrigeration supplied in the prior art single turbine process, cold level turbine **37** has a somewhat lower refrigeration requirement than the latter. Turbines **29** and **37** operate at about the same inlet pressure and the same exhaust pressure, their pressures being selected so that the pressure ratio is about equal across each turbine. Slight variations in pressure may exist between the two turbines because of pressure drop in piping and heat exchangers.

The high pressure product gas emerging from the cold end of warm heat exchanger **32** in conduit **25** is directed to the warm end of passageway **39** in cold heat exchanger **40** for further cooling therein. This cooling is effected primarily by the cold work expanded third portion of feed-recycle refrigerant gas entering the cold end of passageway **41** through conduit **38**. The resulting partially warmed work expanded third portion emerging from the warm end of cold heat exchanger **40** is joined by the warm work expanded section portion of feed-recycle refrigerant gas in conduit **30**. The combined second and third portions in conduit **38** enters the cold end of passageway **35** in warm heat exchanger **32** where it is further warmed by partially cooling the compressed third portion of feed-recycle refrigerant gas in passageway **33** and the high pressure product gas in passageway **34** as previously described. The further warmed work expanded feed-recycle refrigerant gas emerging from the warm end of passageway **35** is mixed with feed gas from conduit **10** and recompressed in compressor **13**.

Returning now to the cold heat exchanger **40**, the cold product fluid discharged from the cold end of passageway **39** is throttled in valve **42** from high pressure to relatively low pressure to form saturated liquid. The resulting liquid-gas mixture in conduit **25** is flowed into phase separator **43**; the product liquid is withdrawn therefrom through conduit **44** and control valve **45** therein, and discharged from the system. The gas is vented from phase separator **43** through conduit **46** and may join the cold work expanded third portion in conduit **38** for refrigeration recovery in cold and warm heat exchangers **40** and **32**, respectively, and for recycling.

FIG. **5** illustrates an alternative feed gas flow circuit which could be used in the two-turbine embodiment of FIG. **4**. Whereas the latter mixes the refrigerant gas and feed gas at several points so that the same fluid could comprise each, the FIG. **5** embodiment completely separates the two circuits and the refrigerants gas circuit is closed to the feed gas.

Referring now more specifically to FIG. **5**, only the feed gas flow circuit has been completely illustrated in the interest of simplicity. This circuit could be substituted for the FIG. **4** feed gas circuit with minor revisions to the refrigerant gas circuit as described hereinafter. In FIGS. **5** and **6**, elements and fluid streams which correspond to elements and fluid streams in the FIG. **4** embodiment have been identified by the same number. In FIG. **5** the feed gas is discharged from compressor **11** into conduit **50** instead of being mixed with the recycle refrigerant gas in conduit **12**. The feed gas is then pressurized in compressor **51** instead of being pressurized with the recycle refrigerant gas in compressor **13**. The pressurized feed gas is discharged from compressor **51** into conduit **52** and may be aftercooled by water in a heat exchanger similar to **15-16**, then directed to compressor **24** where it is further compressed to high pressure.

Whereas in FIG. **4** compressor **24** processes a first portion of compressed feed-recycle refrigerant gas, in FIG. **5** none of the refrigerant gas is compressed to high pressure and only the feed gas is so treated. The compressed recycle refrigerant gas in conduit **20** is divided into two instead of three portions one portion being directed through conduit **28** to warm work expander **29** and the other portion being directed through conduit **31** to passageway **33** of warm heat exchanger **32**. The high pressure feed gas is aftercooled in passageway **26** and then sequentially cooled in passageway **34** of warm heat exchanger **32** and passageway **39** of cold heat exchanger **40**. The product liquid is withdrawn from phase separator **43** through conduit **44** and the evaporation gas returned through conduit **46** having valve **47** therein to feed gas conduit **10** for reprocessing. The refrigeration value of this evaporation gas is recovered in passageway **46a** of cold heat exchanger **40** and passageway ***46b*** of warm heat exchanger **32**.

The three work expansion step embodiment of FIG. **6** permits smaller temperature differences in the high pressure feed gas-work expanded refrigerant gas heat exchangers than attainable in the two work expansion step embodiments of FIGS. **4** and **5**. This is because the FIG. **6** embodiment utilizes the similar heat capacities of the product stream both above and below the liquefaction zone. The temperature levels for the work expansions are selected to allow combination of the inlet and exhaust pressure streams for the warm and intermediate feed temperature expansion turbines. The coldest inlet temperature turbine has the same inlet pressure as the other two turbines but exhausts to a higher pressure. In terms of power requirement, the FIG. **6** embodiment is more efficient than either FIG. **4** or **5**.

More specifically, the feed gas discharged from compressor **11** is joined by recycle refrigerant gas from conduit **38** and the combined stream is further pressurized in compressor **13** and thereafter joined by a second recycle refrigerant gas stream from conduit **60** at higher pressure than first recycle refrigerant gas stream in conduit **38**. This combined stream in conduit **14** is further compressed to intermediate pressure in booster compressor **61** which is functionally similar to first and second booster compressors **17** and **19** of FIG. **4**.

A first portion of the compressed feed-recycle refrigerant flows through branch conduit **23** to product compressor **24** for pressurization to high pressure and becomes the product fluid. After partial cooling in passageway **34** of warm heat exchanger **32** the first portion is cooled in passageway **62** of first intermediate heat exchanger **63** and thereafter additionally cooled in passageway **64** of second intermediate heat exchanger **65**. The first portion is then directed through cold heat exchanger **40** and throttling valve **42** for further cooling and liquefaction in a manner analogous to the FIG. **4** and **5** embodiments.

Returning now to the compressed feed-recycle refrigerant in conduit **14**, a second portion thereof is directed through conduit **28** for warm work expansion in turbine **29** and recycling through passageway **35** of warm heat exchanger **32** and recovery of its refrigeration value. A third portion in conduit **31** is partially cooled in passageway **33** of exchanger **32** and thereafter divided into two parts. One part in conduit **36** is cold work expanded in turbine **37** to lower-than-intermediate temperature and thereafter flows through conduit **38** from the cold end to the warm end of the entire heat exchanger train for recovery of its refrigeration value. That is, the cold work expanded feed-recycle refrigeration gas flows first through passageway **41** of cold heat exchanger **40** and then to the cold end of passageway **66** of second intermediate heat exchanger **65** where it additionally cools the product fluid in passageway **64**. Then the partially rewarmed cold work expanded gas enters the passageway **67** cold end in first intermediate heat exchanger **63** for further warming and simultaneous cooling of the high pressure product gas in passageway **62**.

At the warm end of passageway **67** in first intermediate heat exchanger **63** the further rewarmed cold work expanded gas in conduit **38** is joined by the warm work expanded second portion in conduit **30**. The combined gas stream in conduit **38** enters warm heat exchanger **32** at the cold end of passageway **35** where the balance of its sensible refrigeration is recovered by partial cooling of the compressed feed-recycle refrigerant third portion in passageway **33** and product gas in passageway **34**. This warmed combined gas stream in conduit **38** joins the feed gas discharged from compressor **11** and is fed through conduit **12** to compressors **13** and **61** for recycling.

Returning now to the partially cooled third portion of compressed feed-recycle refrigerant in conduit **31** at the cold end of warm heat exchanger **32**, another part thereof is directed through conduit **68** to the warm end of passageway **69** in first intermediate heat exchanger **63**. This gas stream is further cooled in exchanger **63** in part by the cold work expanded feed-recycle refrigerant gas in passageway **67**, and thereafter work expanded in turbine **70**. Gas is discharged from turbine **70** into conduit **60** at colder temperature which is between the intermediate temperature of the warm work expanded gas in conduit **30** and the lower-than-intermediate temperature of the cold work expanded gas in conduit **38**. Also, the intermediate temperature work expanded gas in conduit **60** is at higher pressure than either the relatively warm or cold work expanded gases permitting use of a relatively small and less expensive turbine as compared to turbines **29** and **37**. This intermediate temperature work expanded gas discharged from turbine **70** is thereafter partially warmed in passageway **72** of second intermediate heat exchanger **65** by the high pressure product gas in passageway **64**. The partially warmed work expanded gas in conduit **60** is then further warmed in passageway **73** of first intermediate heat exchanger **63** by the same higher pressure gas in passageway **69** (prior to work expansion) and the high pressure product or first portion in passageway **62**. The further warmed work expanded gas in conduit **60** is then directed to the cold end of passageway **74** in warm heat exchanger **32** where its remaining sensible refrigeration is recovered by the third portion of compressed feed-recycle refrigerant gas in passageway **33** and the high pressure feed gas in passageway **34**. The still further warmed work expanded gas in conduit **60** joins the feed gas in conduit **12** as the aforementioned second recycle refrigerant gas, and the combined stream is further compressed in booster compressor **61** for reprocessing.

Whereas the FIG. **6** embodiment employs the same fluid as the feed gas and the refrigerant gas and is analogous to the two work expansion FIG. **4** embodiment in this respect, two completely separate circuits for feed gas and refrigerant gas may also be used with three work expansions in a manner very similar to FIG. **5**. This could be accomplished by directing the feed gas compressor **11** discharge directly to compressor **24** (analogous to compressor **51** of FIG. **5**) and eliminating conduit **23**. At the cold end of the system, flash off gas in conduit **46** from phase separator **43** is recycled to feed gas conduit **10** instead of through passageway **41** of cold heat exchanger **40**. The refrigeration value of this flash off gas may be recovered by consecutive flow through separate passageways in cold exchanger **40**, second intermediate heat exchanger **65**, first intermediate heat exchanger **63** and warm heat exchanger **32** prior to such recycling.

Table II is a summary of typical temperatures and pressures for points in the two work expander embodiments of FIGS. **4** and **5** and the three work expander embodiment of FIG. **6**. The numbers in the left hand column refer to the identification numerals in the various figures. Two feed-product streams are included: pure N_2 in cases A and B and natural gas in cases C and D having the composition of Table I. The refrigerant gas is also N_2 in cases A and B so that the feed and refrigerant are mixed. The refrigerant gas in case C is 80 mol % N_2 - 20% CH_4 so that the refrigerant is recycled in the closed circuit of FIG. **5**.

TABLE II

Typical Process Conditions	A	B	C	D
Figure No.	2,4	3,6	5	5
Feed-Product	N_2	N_2	Nat. Gas	Nat. Gas
Refrigerant	N_2	N_2	80% N_2, 20% CH_4	N_2
Feed P in **23**	372	372	215	115
Feed Critical P	490	490	660	660
Prod. P in **25**	615	615	615	615
Prod. T to **32**	300	300	305	300
Prod. T from **32**	170	170	200	211
Prod. T from **63**	—	135	—	—
Prod. T from **65**	—	120	—	—
Prod. T from **40**	86	86	112	105
Prod. T in **43**	77	77	112	105
Refrig. P in **30**	24	23	18	22
Refrig. T in **30**	154	153	173	200
Refrig. T in **36**	170	170	201	211
Refrig. T in **38**	86	85	114	103
Refrig. P in **38**	26	26	20	25
Refrig. T in **68**	—	140	—	—
Refrig. T in **60**	—	119	—	—
Refrig. P in **60**	—	215	—	—

T = temperature, °K.
P = pressure, psia.

Table II indicates that for cases A and B the feed gas pressure of 615 psia. is supercritical, i.e., above the nitrogen critical pressure of 490 psia. For cases C and D, the feed gas pressure of 615 psia. was about 93 percent of the 660 psia. natural gas critical pressure. As previously indicated, the feed gas pressure should be sufficiently high so that the feed gas Q/T cooling curve comprises a multiplicity of regions each having substantially constant specific heat $\Delta Q/\Delta T$. For multi-component feed gases such as natural gas the feed gas cooling curve assumes this shape at pressures within about 85 percent of the critical pressure. It is not essential to compress multi-component feed gases to supercritical pressure for practicing of the invention although this may be cone if desirable for other reasons. With single component feed gas, supercritical pressure is essential to obtain the desired cooling curve.

TABLE III

Thermodynamic Analysis for Nitrogen

Liquefaction-Refrigeration	A	B	C
Figure No.	1	2,4	3 ,6
External Refrig. Y	es	No	No
No. of Work Expanders	1	2	3
Average Temp. 10– Differences	25°C.	6–12°C.	3–7°C.
Product Pressure (cooling) sub-c	sub-critical	super-critical	super-critical
Net Work, kwh/100 ft^3 Prod. 1.	93	1.64	1.52
Thermodynamic Efficiency, % 3	6	43	46

Table III summarizes thermodynamic analyses of two work expander (Case B) and three work expander (Case C) embodiments for nitrogen liquefaction using the process conditions of Cases A and B in Table II and the processes of FIGS. 4 and 6 respectively. For comparison, Case A is the external refrigerant-single work expander process of U.S. Pat. No. 3,144,316 as previously described. This invention reduces the required net work by at least 15 percent and as much as 21 percent. The thermodynamic efficiency is improved by at least 19 percent and as much as 28 percent. The average temperature differences in the heat exchangers are reduced from about 10°–25° C. to about 3°–12° C. In a preferred embodiment of the invention for nitrogen liquefaction, the average temperature difference is below about 10° C.

Although preferred embodiments of the invention have been described in detail, it is contemplated that modifications of the process and apparatus may be made and that some features may be employed without others, all within the spirit and scope of the invention.

I claim:

1. A gas liquefaction process comprising the steps of:

a. providing feed gas at sub-critical pressure and compressing same to high pressure such that the feed gas Q/T cooling curve comprises a multiplicity of regions each having substantially constant specific heat $\Delta Q/\Delta T$;

b. providing compressed refrigerant gas at sub-critical pressure below the high pressure of said feed gas in step (a) and warm work expanding a portion thereof to intermediate temperature and low pressure;

c. partially cooling the high pressure feed gas and remaining compressed refrigerant gas in a warm heat exchanger in part by the warm work expanded refrigerant gas portion;

d. cold work expanding at least part of the partially cooled remaining compressed refrigerant gas from said warm heat exchanger to lowe-than-intermediate temperature and said low pressure, all of the process refrigeration being supplied by work expansion of gas other than heat of compression;

e. further cooling the partially cooled high pressure feed gas from said warm heat exchanger by the cold work expanded refrigerant gas at relative pressures such that the specific heat ratio of said high pressure feed gas to said cold work expanded refrigerant gas is 1.5–15 and thereby partially warming said refrigerant gas in a cold heat exchanger;

f. throttling the further cooled feed from said cold heat exchanger to form product liquid;

g. further warming the cold work expanded partially warmed refrigerant gas from said cold heat exchanger by heat exchange with said high pressure feed gas and said remaining compressed refrigerant gas in said warm heat exchanger;

h. recompressing the further warmed work expanded refrigerant gas and recycling same as said compressed refrigerant gas; and

i. controlling the warm and cold work expansion steps to deliver said process refrigeration of the expanded gases to said regions of the cooling high pressure feed gas where such gas has substantially constant specific heat.

2. A gas liquefaction process according to claim 1 wherein a single component comprises said feed gas, and said feed gas compressed to supercritical pressure in step (a).

3. A gas liquefaction process according to claim 1 in which natural gas comprises said feed gas.

4. A gas liquefaction process according to claim 1 in which natural gas comprises said feed gas and nitrogen comprises said refrigerant gas.

5. A gas liquefaction process according to claim 1 in which nitrogen comprises said feed gas.

6. A gas liquefaction process according to claim 1 in which said refrigerant and feed gases are of the same composition.

7. A gas liquefaction process according to claim 1 in which the partially cooled high pressure feed gas is cooled in a first intermediate heat exchanger and thereafter additionally cooled in a second intermediate heat exchanger in part by said cold work expanded refrigerant gas having been partially warmed in said cold heat exchanger; another part of said partially cooled remaining compressed refrigerant gas from said warm heat exchanger is further cooled in said first intermediate heat exchanger to lower temperature, work expanded to pressure above said low pressure and colder temperature between said intermediate temperature of said warm work expanding and said lower-than-intermediate temperature of said cold work expanding; and progressively warmed by said high pressure feed gas in said second intermediate heat exchanger, said another part of said partially cooled remaining compressed refrigerant gas and said high pressure feed gas in said first intermediate heat exchanger, and said remaining compressed refrigerant gas and high pressure feed gas in said warm heat exchanger; and recompressed and recycled as part of said compressed refrigerant gas, all of the process refrigeration being provided by the three work expansions.

8. A nitrogen liquefaction process comprising the steps of:

a. providing nitrogen feed gas and nitrogen recycle gas at sub-critical pressure and mixing same;

b. compressing a first portion of the mixed nitrogen to supercritical pressure;

c. warm work expanding a second portion of said mixed nitrogen to intermediate temperature and low pressure;

d. partially cooling the supercritical pressure first portion and remaining mixed nitrogen portion in a warm heat exchanger in part by the warm work expanded second portion;

e. cold work expanding at least part of the partially cooled remaining mixed nitrogen from said warm heat exchanger to lower-than-intermediate temperature and said low pressure, all of the process refrigeration being supplied by work expansion of gas other than heat of compression;

f. further cooling the partially cooled super-critical pressure first portion from said warm heat exchanger by the cold work expanded mixed nitrogen at relative pressures such that the specific heat ratio of said first portion to said cold work expanded mixed nitrogen is 1.5–15 and thereby partially warming said mixed nitrogen in a cold heat exchanger;

g. throttling the further cooled first portion from said cold heat exchanger to form product liquid nitrogen;

h. further warming the cold work expanded mixed nitrogen from said cold heat exchanger by heat exchange with said supercritical pressure first portion and remaining mixed nitrogen portion in said warm heat exchanger;

i. recompressing the further warmed work expanded second and work expanded mixed nitrogen from said warm heat exchanger as said nitrogen recycle gas; and

j. controlling the warm and cold work expansion steps to deliver said process refrigeration of the expanded gases to regions of the cooling supercritical pressure first portion where such gas has substantially constant specific heat.

9. A process according to claim 8 in which the partially cooled supercritical pressure first portion is cooled in a first intermediate heat exchanger and thereafter additionally cooled in a second intermediate heat exchanger in part by said cold work expanded mixed nitrogen having been partially warmed in said cold heat exchanger; another part of said partially cooled remaining mixed nitrogen from said warm heat exchanger is further cooled in said first intermediate heat exchanger to lower temperature, work expanded to colder temperature between said intermediate temperature of said warm work expanding and said lower-than-intermediate temperature of said cold work expanding but higher pressure than said warm and cold work expanding; and progressively warmed by said supercritical pressure first portion in said second intermediate heat exchanger, said another part of said partially cooled remaining mixed nitrogen and said supercritical pressure first portion in said first intermediate heat exchanger, and said remaining mixed nitrogen portion and

said supercritical pressure first portion in said warm heat exchanger; and recompressed as part of said nitrogen recycle gas, all of the process refrigeration being provided by the three work expansions.

10. A process according to claim 1 in which the power generated by said cold work expanding is recovered to compress said feed gas to first intermediate pressure above said subcritical pressure and the power generated by said warm work expanding is recovered to further compress said feed gas from said first to second higher intermediate pressure.

11. A process according to claim 1 in which said feed gas is combined with said further warmed work expanded refrigerant gas, the combined gas is recompressed in step (h) and a first portion of the compressed combined gas is further compressed in step (a) to high pressure as said feed gas.

12. A process according to claim 1 in which said warm work expanded gas portion and the partially warmed cold work expanded refrigerant gas are combined at the cold end of said warm heat exchanger for the step (c) partial cooling and step (g) partial warming.

13. A process according to claim 8 wherein the work expansions are controlled so as to maintain the average temperature difference between the warming and cooling gases in the heat exchangers at below about 10° C.

14. Gas liquefaction apparatus comprising:

a. means for compressing feed gas from subcritical to high pressure;

b. a first work expander for expanding a compressed refrigerant gas portion from subcritical pressure below the feed gas high pressure to low pressure and intermediate cold temperature;

c. a relatively warm heat exchanger having separate passageways for partially cooling the high pressure feed gas and remaining compressed refrigerant gas by the low pressure intermediate cold temperature refrigerant gas from said first work expander;

d. a second work expander for expanding at least part of the partially cooled remaining compressed refrigerant gas from said warm heat exchanger from said subcritical pressure to said low pressure and lower-than-intermediate temperature, said work expanders providing all of the refrigeration needed for said gas liquefaction other than heat of compression;

e. a relatively cold heat exchanger having separate passageways for further cooling said high pressure feed gas from said warm heat exchanger by the low pressure lower-than-intermediate temperature refrigerant gas from said second work expander;

f. valve means for throttling the further cooled feed fluid from said cold heat exchanger and thereby forming product liquid;

g. passageway means in said warm heat exchanger for further warming the low pressure refrigerant gas partially warmed in said cold heat exchanger, by heat exchange with said high pressure feed gas and remaining compressed refrigerant gas;

h. means for recompressing the further warmed low pressure refrigerant gas from said warm heat exchanger to subcritical pressure below said feed gas high pressure;

i. conduit means for recycling the recompressed refrigerant gas to said first work expander;

j. feed gas supply conduit means joining refrigerant gas recompression means (h) to form recompressed feed-refrigerant gas; and

k. first branch conduit means joining the discharge side of recompression means (h) to feed gas compression means (a) to form said high pressure feed gas, second branch conduit means joining the discharge side of recompression means (h) to said first work expander for expansion of recompressed feed-refrigerant gas as said low pressure intermediate cold temperature refrigerant gas, and third branch conduit means joining the discharge side of recompression means (h) to passageway means in warm heat exchanger (c) for partial cooling said feed-refrigerant gas as said remaining compressed refrigerant gas.

15. A process according to claim 1 wherein said feed gas is multi-component and said high pressure of (a) is at least 85 percent of the feed gas critical pressure.

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