

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

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

[57] **ABSTRACT**

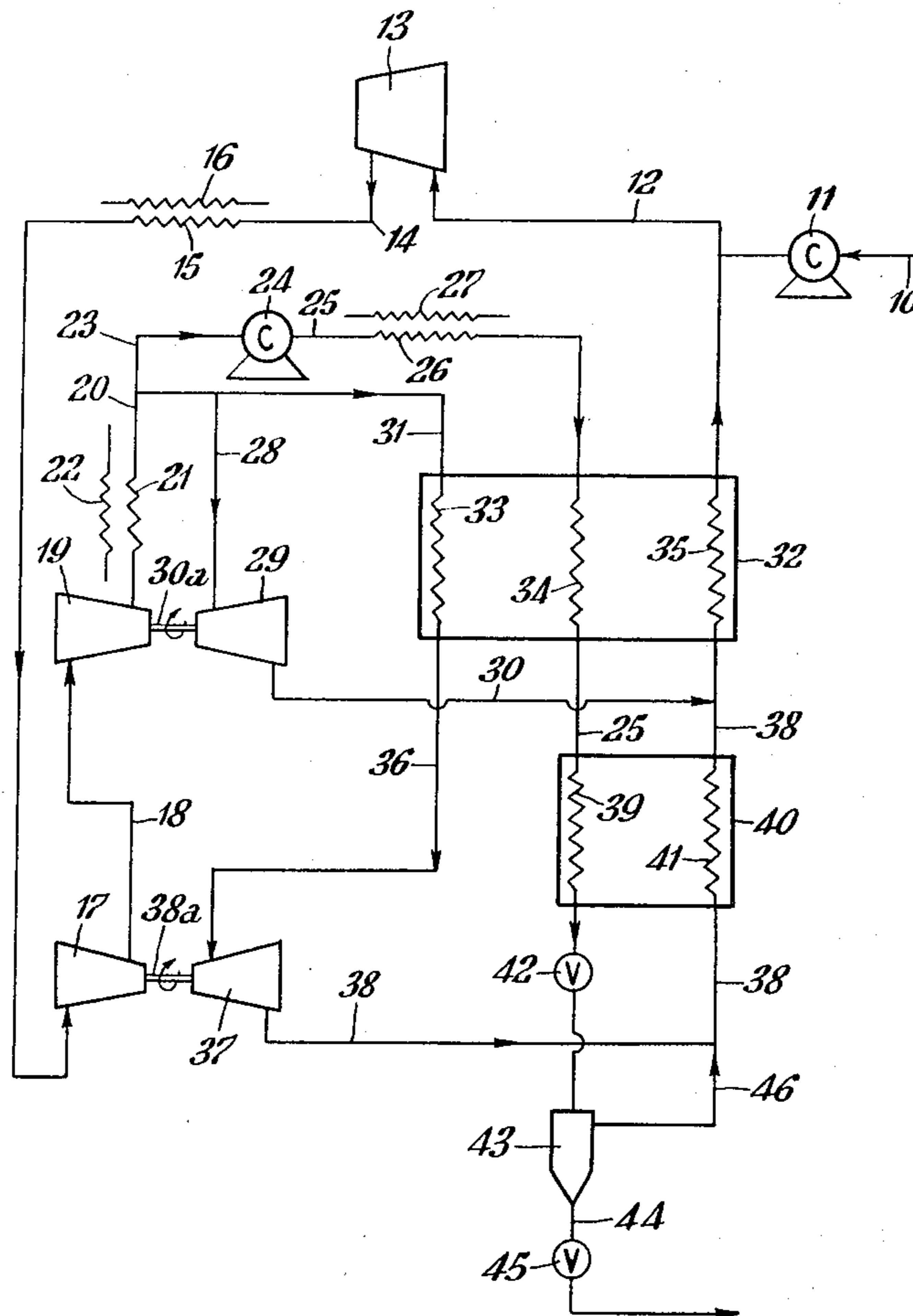
This invention relates to a method and apparatus for the liquefaction of low boiling gases for example nitrogen and natural gas. By the use of parallel refrigerant expansion engines and feed compression the product cooling curve in the liquefaction zone is altered so that the specific heat of the feed 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.

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15 Claims, 6 Drawing Figures



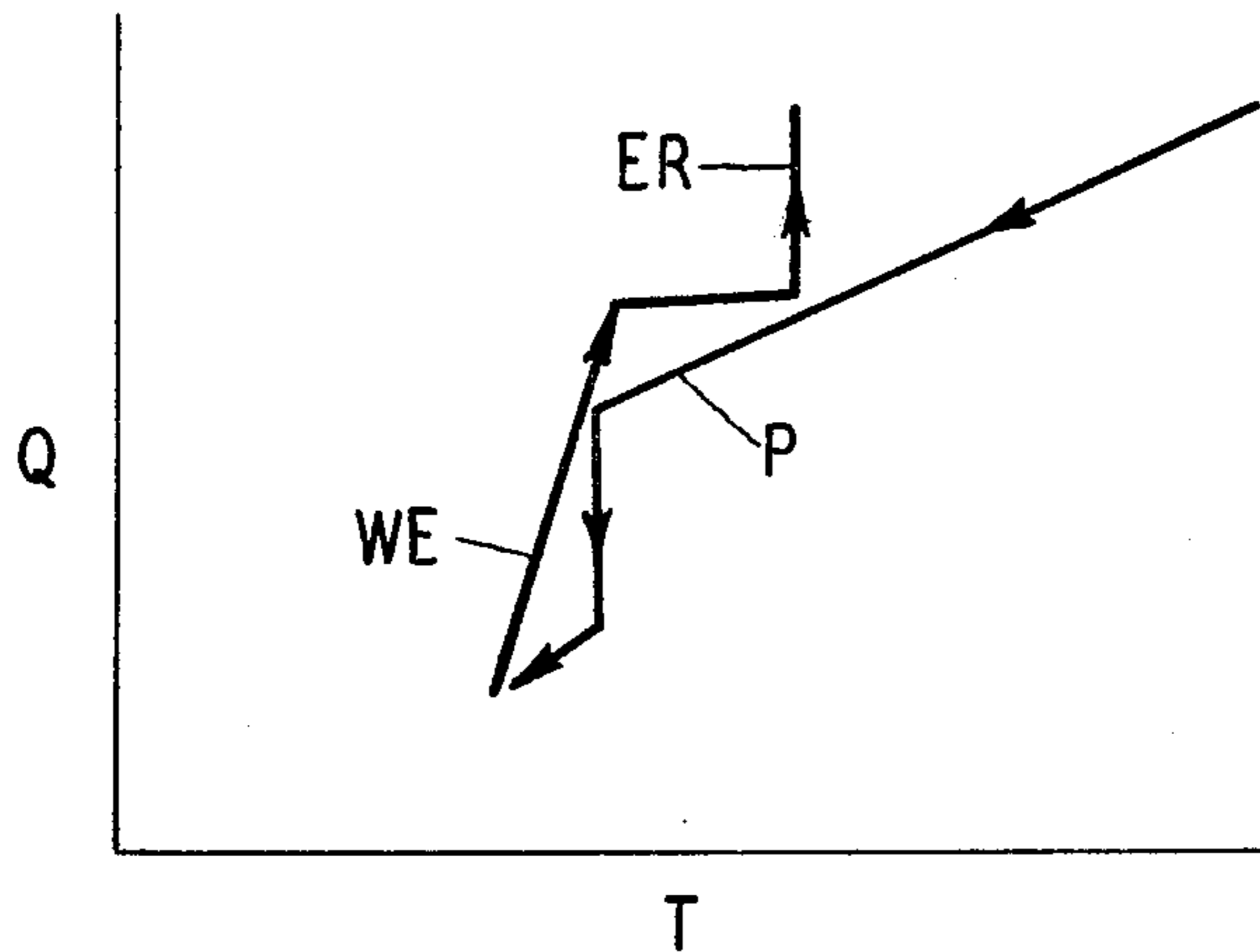


Fig. 1

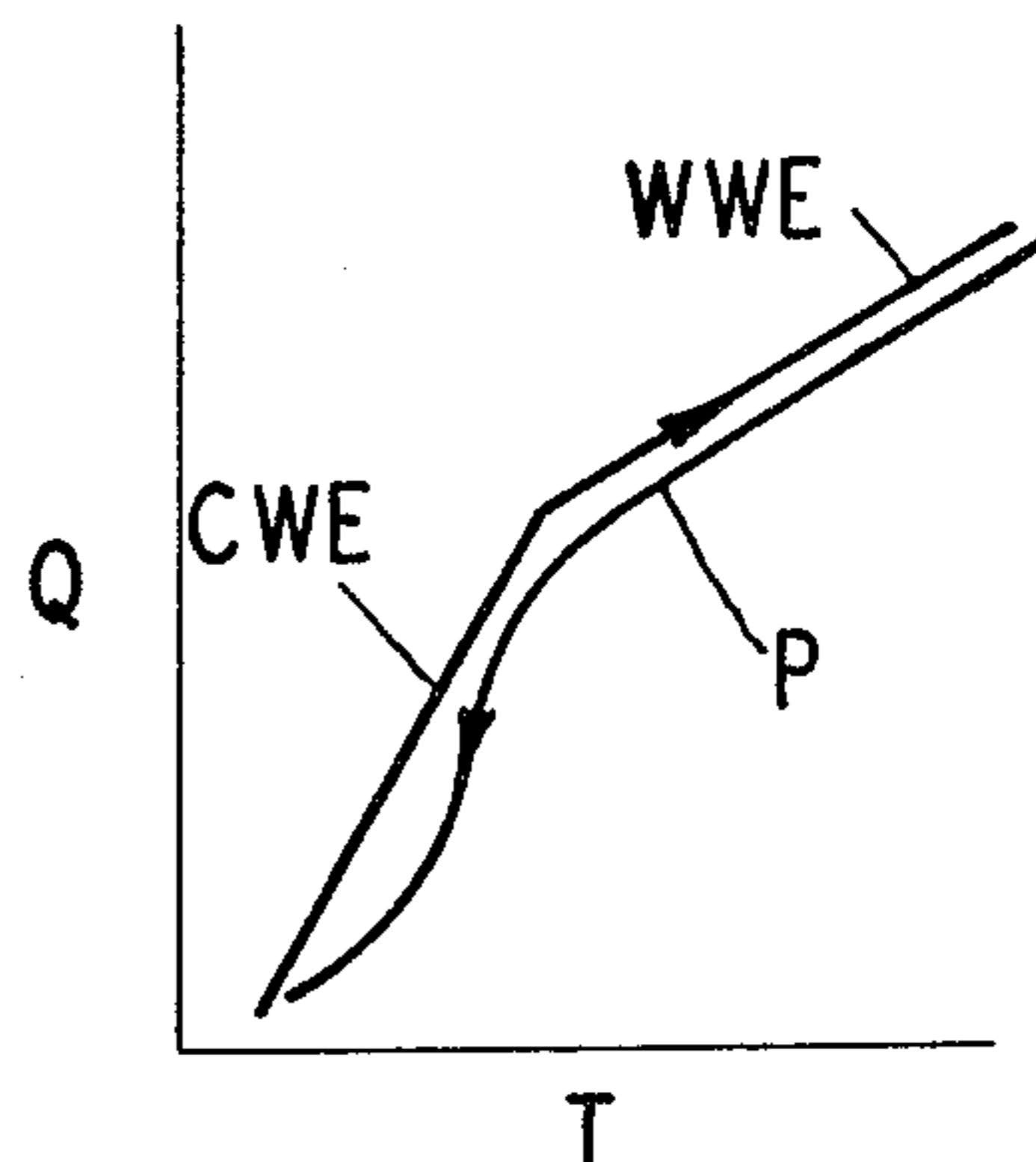


Fig. 2

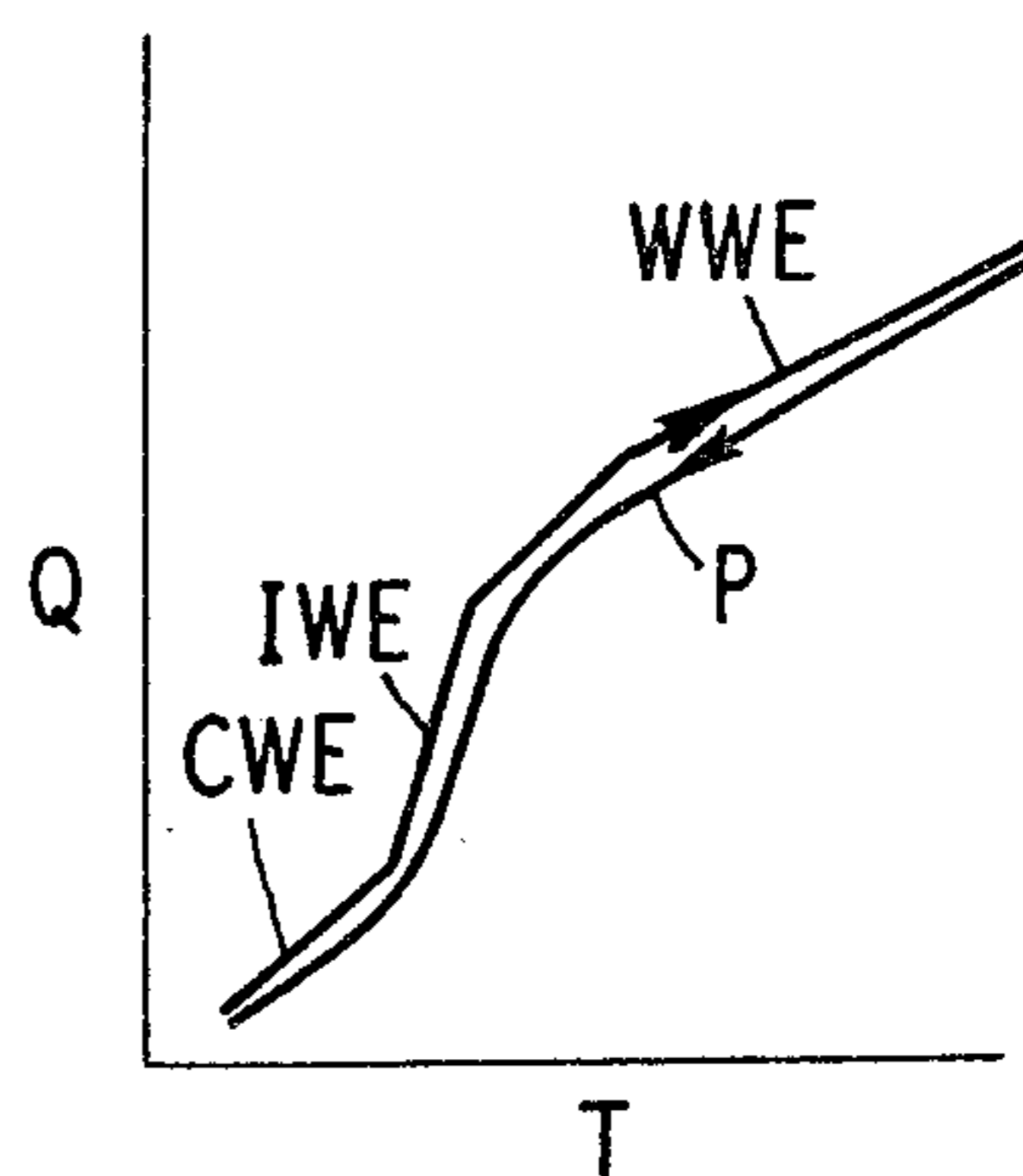


Fig. 3

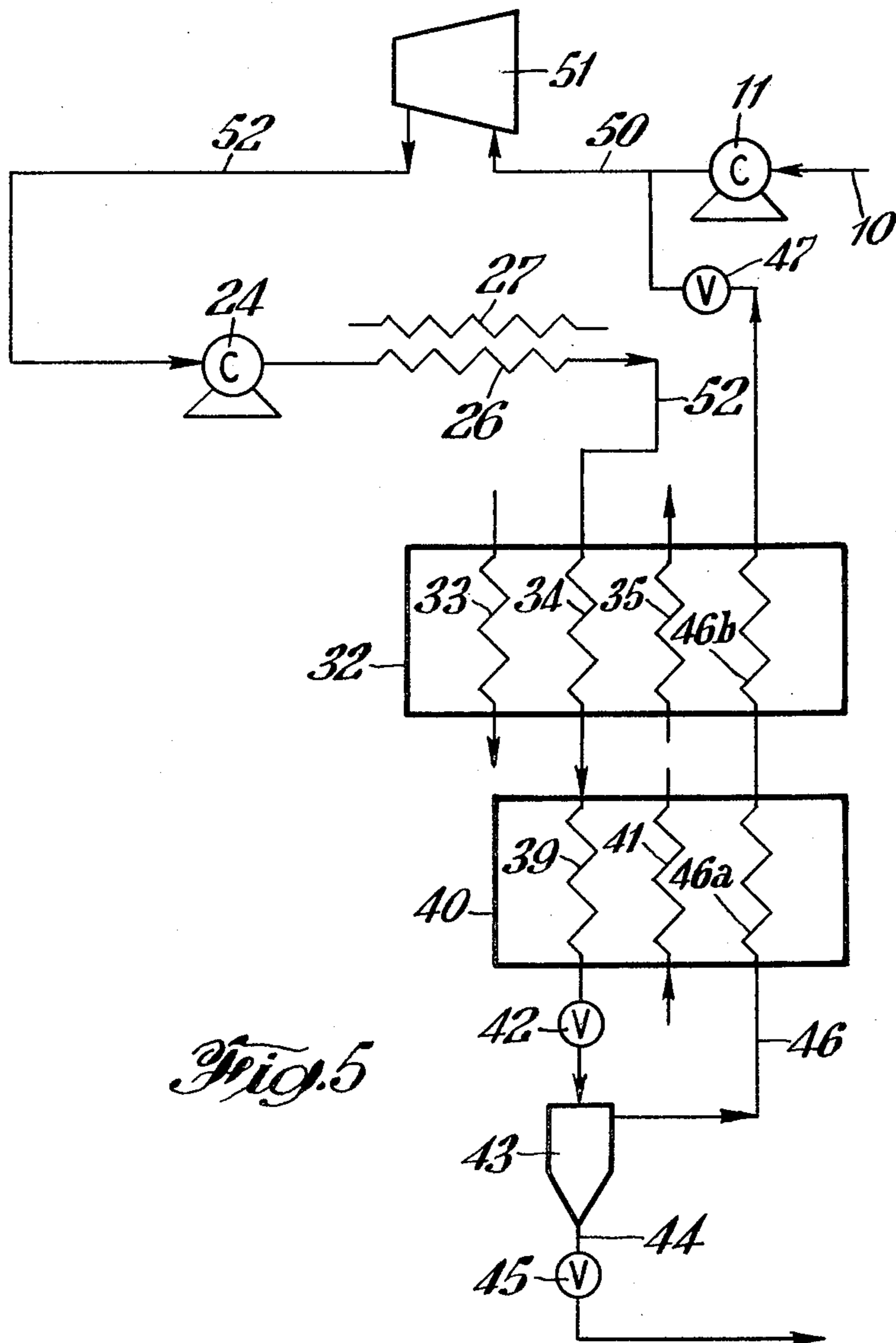


Fig. 5

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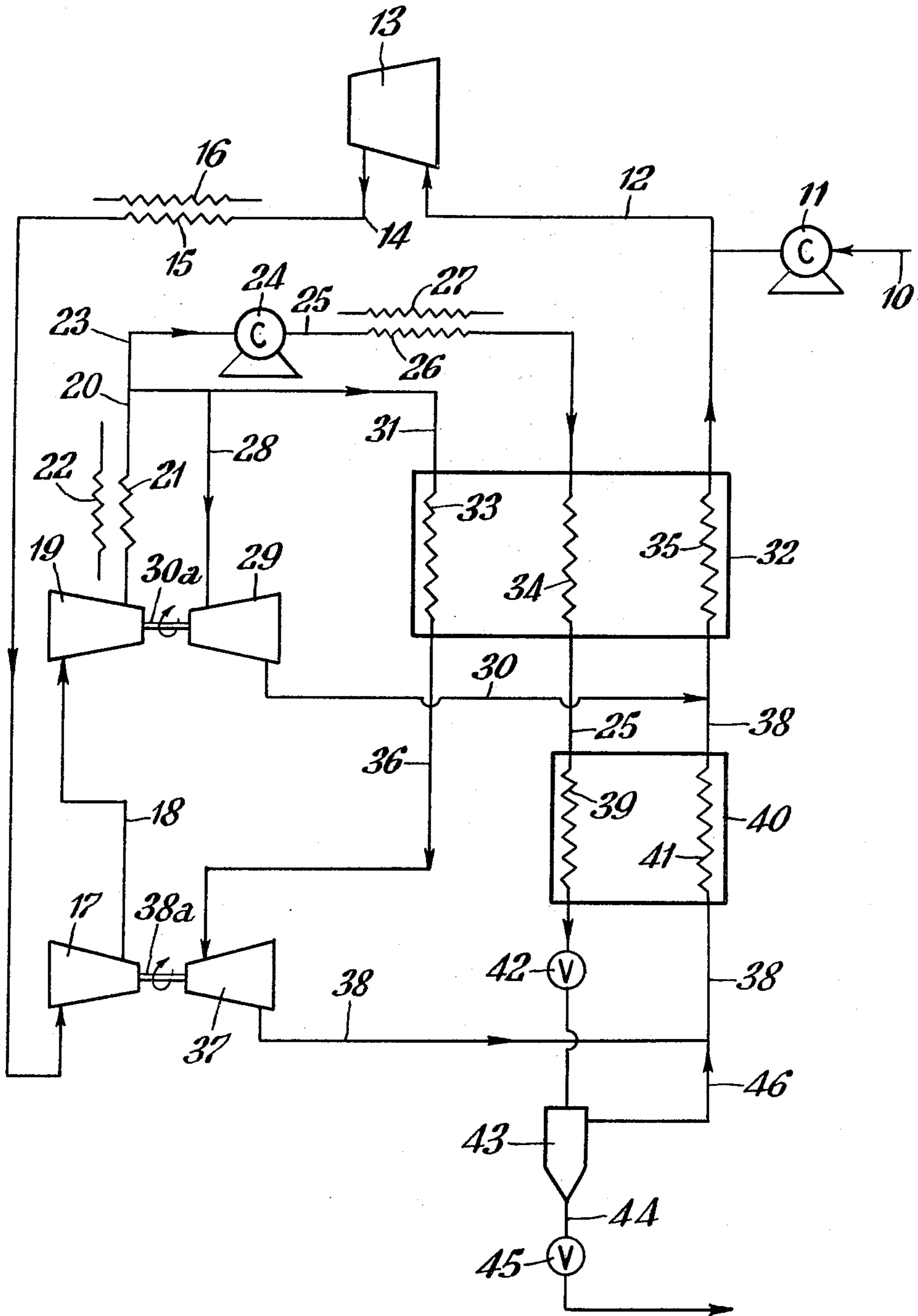


Fig. 4

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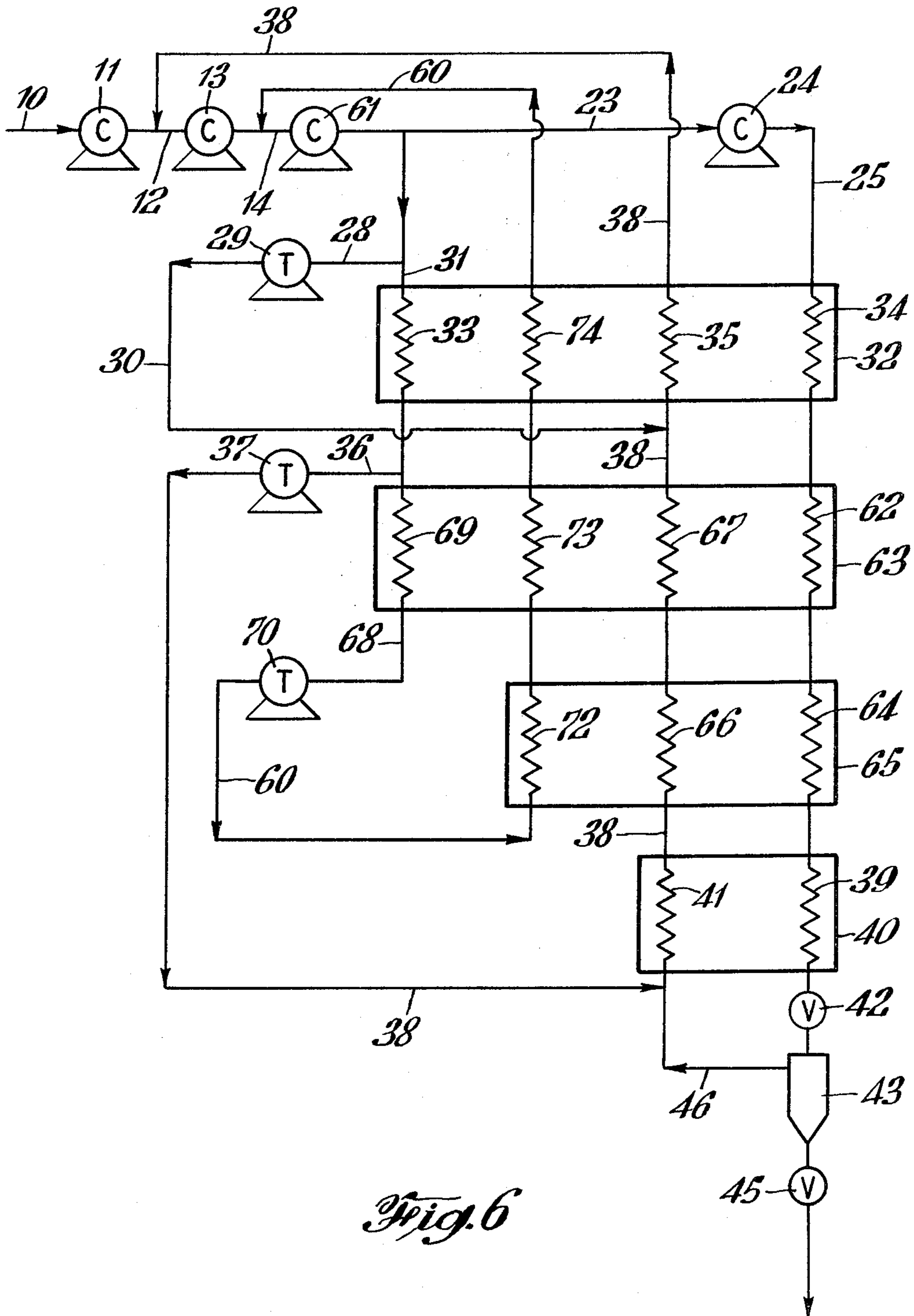


Fig. 6

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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 inter-

mediate 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 aforescribed 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 aforescribed 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 in-

tended 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 % CH₄, 6% C₂H₆, 3% N₂, 1% C₃H₈

**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 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 N₂ in cases A and B and natural gas in cases C and D having the composition of Table I. The refrigerant gas is also N₂ in cases A and B so that the feed and refrigerant are mixed. The refrigerant gas in case C is 80 mol % N₂ - 20% CH₄, 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 Refrigerant		N ₂	N ₂	Nat. Gas	Nat. Gas
		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 done 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 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;
 - 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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