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L. KNIEL
LIQUEFACTION PROCESS EMPLOYING
CASCADE REFRIGERATION

3,362,173

3 Sheets-Sheet 1

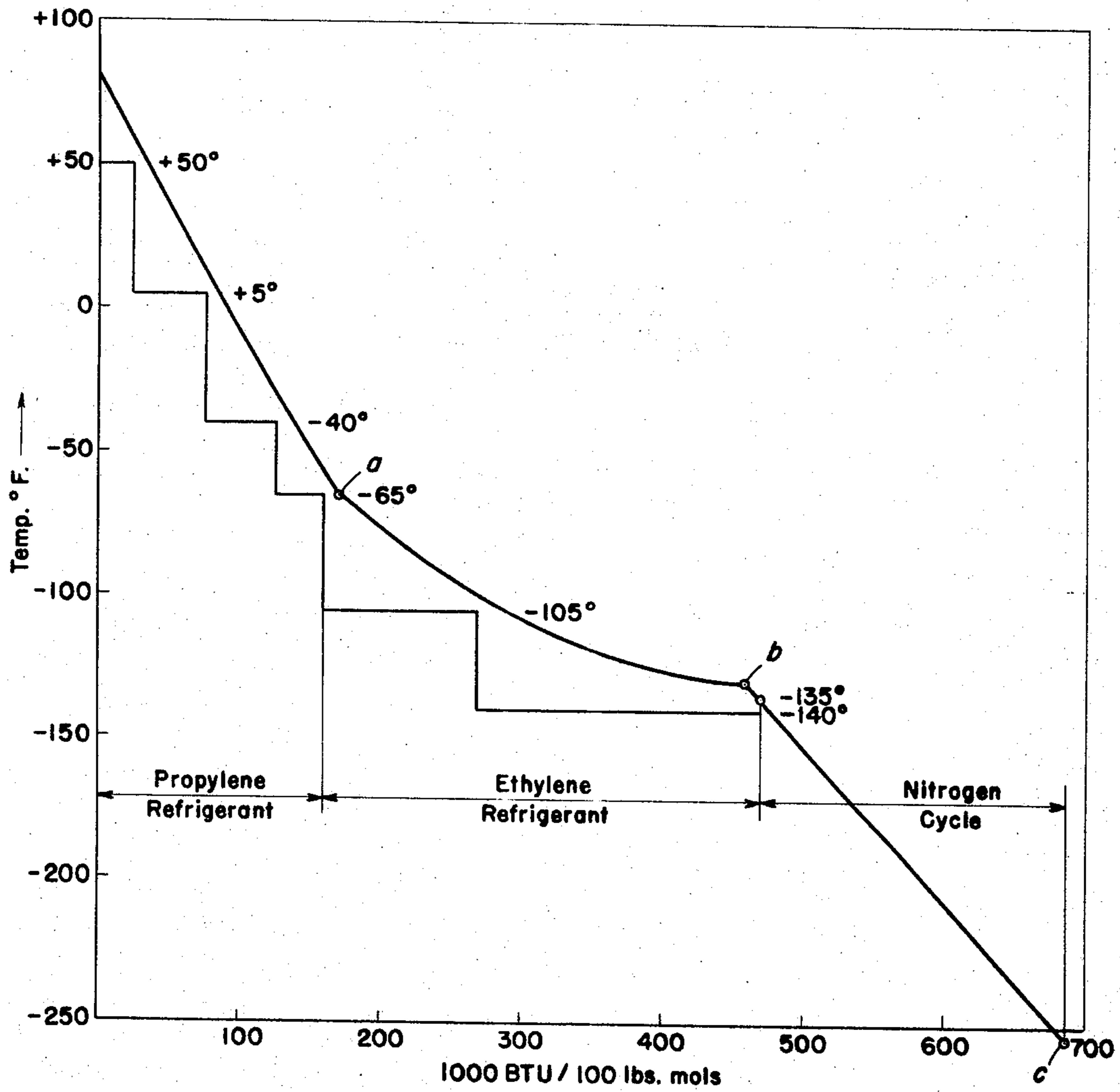


Fig. 1.

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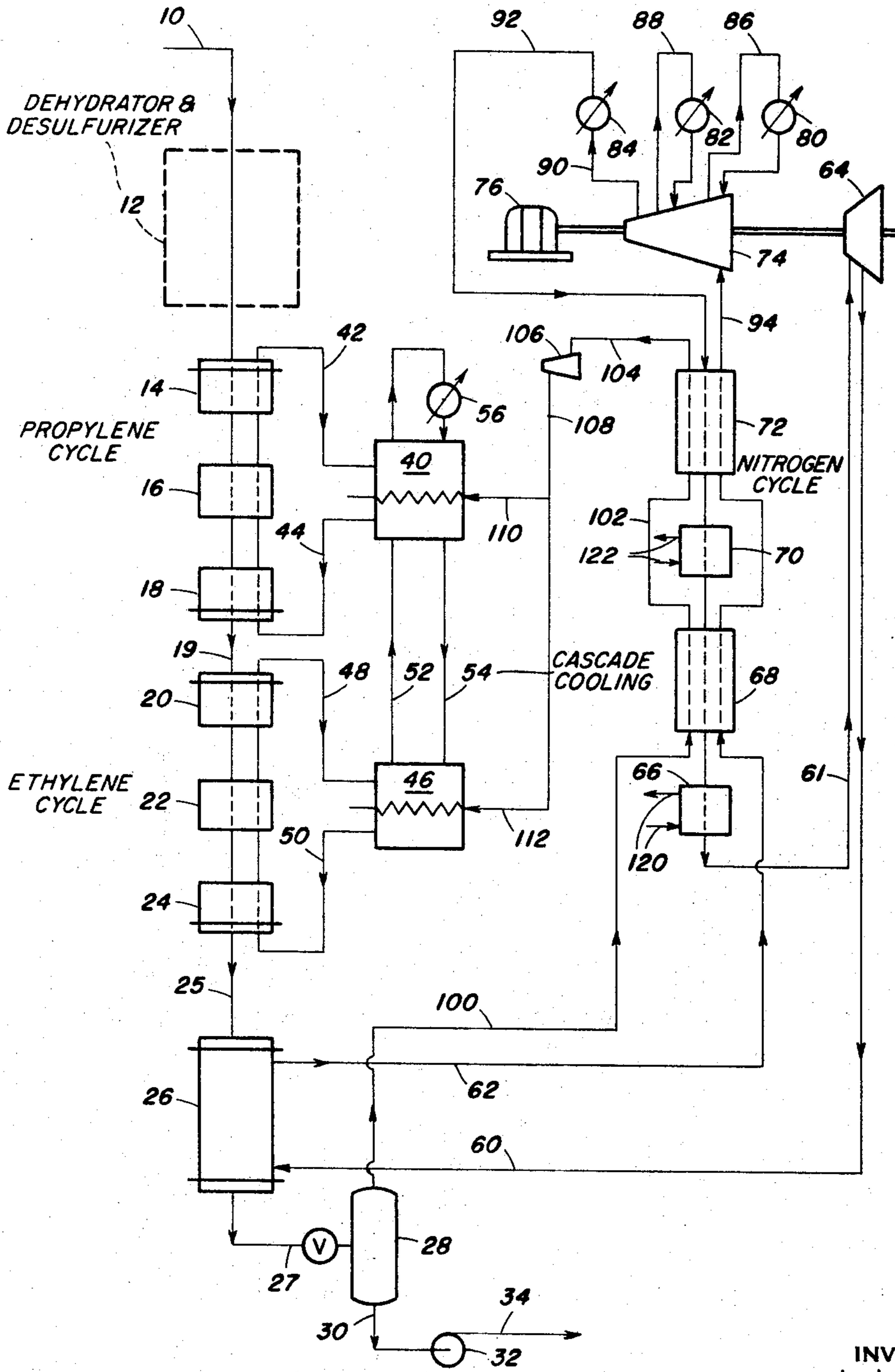


Fig. 2.

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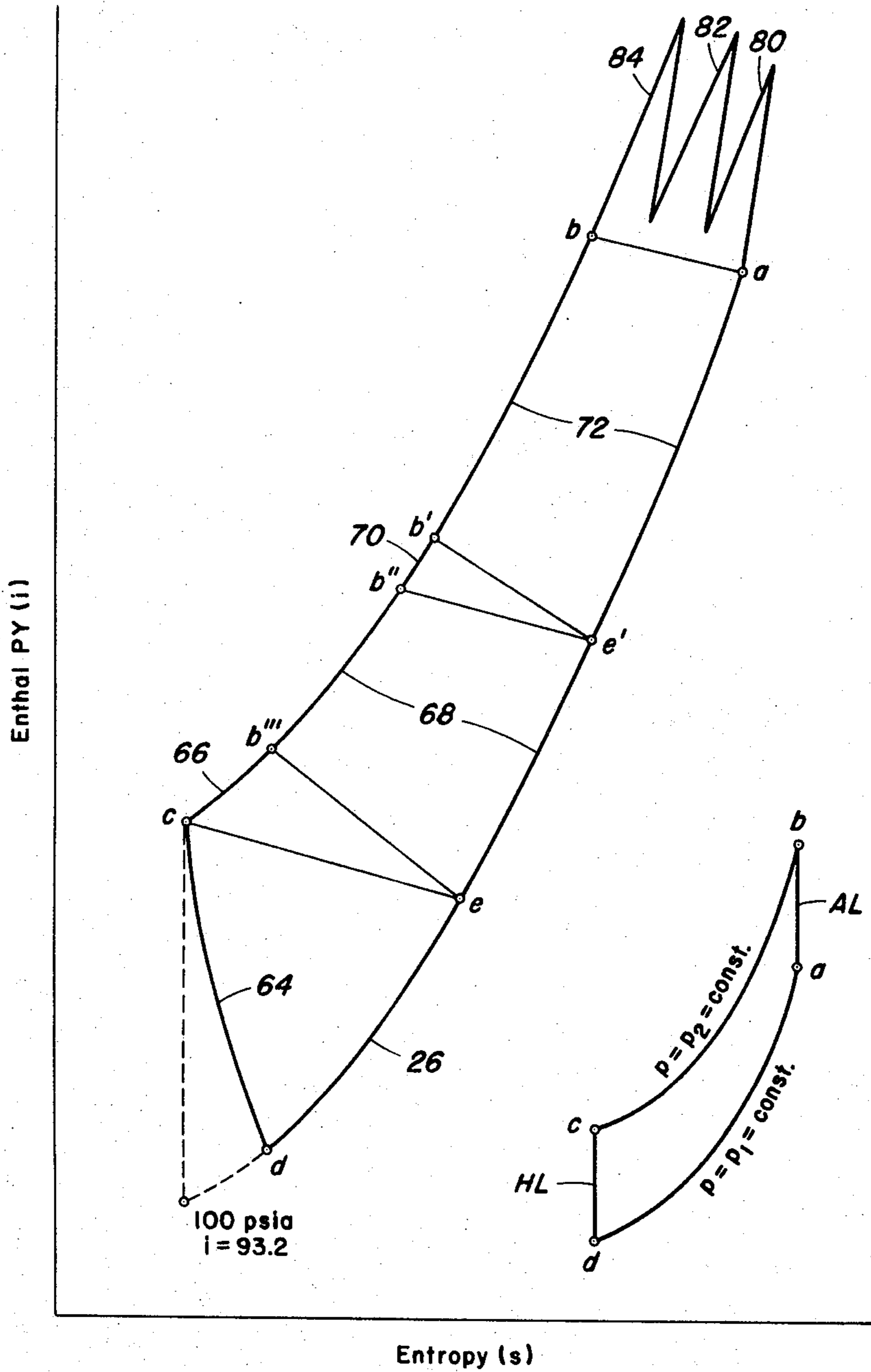
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Entropy (s)

Fig. 3.

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**LIQUEFACTION PROCESS EMPLOYING
CASCADE REFRIGERATION**

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4 Claims. (Cl. 62-9)

ABSTRACT OF THE DISCLOSURE

A process for liquefying a gas such as natural gas, wherein the gas is cooled and liquefied in a plurality of refrigeration stages and the liquefied gas is sub-cooled by indirect heat transfer with a closed compression-expansion nitrogen cycle. The nitrogen after subcooling the liquefied gas is passed in an indirect heat transfer relationship with compressed nitrogen gas, compressed and the compressed nitrogen gas cooled by the aforementioned indirect heat transfer. The compressed nitrogen gas is expanded and employed for subcooling the liquefied gas.

This invention relates, in general, to a method of removing heat at low temperatures and, more particularly, at temperatures between the boiling point of methane at elevated pressures (about -120° F.) and the boiling point, at about atmospheric pressure, of air or nitrogen (about -320° F.). The invention finds application in processes for liquefying cryogenic gases such as air, nitrogen, methane, natural gas and the like, under circumstances wherein it is necessary to reduce the temperature of the already-liquefied material in order to reduce its vapor pressure to atmospheric or near atmospheric pressure for the purpose of storing or transporting it.

Illustration of the invention will hereinafter be made with reference to natural gas, but it will be understood that the concepts employed are also capable of application to other low-boiling, liquefiable gases such as air, nitrogen, helium, oxygen and the like.

There are many purposes for which natural gas is desired to be reduced to a liquefied state. The main reason resides in the resultant reduction, at equivalent pressure, by about $\frac{1}{600}$ in volume when reduced from the gaseous state to a liquefied state, thereby to enable storage and transportation in containers of more economical and practical design.

For example, when gas is transported by pipeline from the source of supply to a distant market, it is desirable to operate under substantially constant high load factor. Often times the flow capacity will exceed demand, while at other times the demand may exceed the capacity of the line. In order to shave off the peaks where demand would exceed supply, it is desirable to store gas when the supply exceeds demand, whereby peaks in demand can be met by material in storage. For this purpose, it is desirable to provide for storage in a liquefied state and to vaporize liquid in amounts to meet demand.

Liquefaction of natural gas is of even greater importance in making it possible to transport the gas from a source of plentiful supply to a distant market where a deficiency exists, especially when the source of supply cannot be directly joined with the market by a pipeline or like means for the transportation of the gaseous fuel in a gaseous state. By way of illustration, surplus natural gas is available in the Gulf States of the United States, in Venezuela, and in the Persian Gulf, while deficiencies exist in the northern parts of the United States, the European countries, and Japan, yet these sources of supply cannot be joined by pipeline with some of the markets. Ship transportation in the gaseous state would be uneconomical, unless the gaseous materials were com-

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pressed, and then the system would not be commercial because it would be impractical to provide containers of suitable strength and capacity.

It has been determined that natural gas, when shipped from the United States or Venezuela in large volumes in liquefied state, can be made available in Great Britain, for example, at a price which is considerably less than locally manufactured gas. For shipment in large volume, it is desirable to house the liquefied natural gas in suitable insulated containers of large capacity at about atmospheric pressure, or preferably slightly above atmospheric, but not at such high pressures as would unduly limit the economical capacity of the tank. Depending upon the amount of higher boiling heavier hydrocarbons present in the natural gas, the liquefied natural gas will have a boiling point within the range of -240° F. to -258° F. at atmospheric pressure.

The present invention contemplates the initial liquefaction of natural gas in incremental steps by use of a plurality of refrigerants in such a manner that each refrigerant is used to remove the maximum amount of heat, followed by sub-cooling the liquefied gas in a closed compressor-expander nitrogen system. The liquefied natural gas is then reduced in pressure for storage purposes, an off-gas produced on reduction of pressure being used to cool the compressed nitrogen gas prior to expansion.

Heretofore, a variety of processes have been employed for liquefying natural gas in a cascade type of system and further sub-cooling of the liquid. Generally, such processes employ a component of the liquid stream obtained by expansion of the liquid to near atmospheric pressure for sub-cooling of the liquid.

In contrast to the foregoing, it has now been discovered that substantial economies may be effected by carrying out the sub-cooling with a closed, compressor-expander nitrogen system, economy being measured in this instance in terms of the energy necessary to extract heat from the liquid.

It is accordingly an object of the present invention to provide an improved method of removing heat from liquid, cryogenic gases in general and natural gas in particular, the same being accomplished with a lower expenditure of energy than has heretofore been possible.

Various other objects and advantages of the invention will become clear in the following description of an embodiment thereof, and the novel features will be particularly pointed out in connection with the appended claims. A better understanding of the invention will be gained by referring to the accompanying drawings in conjunction with the description, and in which:

FIGURE 1 is a condensation curve for natural gas at 500 p.s.i.a., showing the amount of heat which must be removed per 100 mols of gas between 50° and -250° F.;

FIGURE 2 is a simplified flow sheet or flow diagram illustrating an embodiment of the invention as applied to the liquefaction and sub-cooling of natural gas; and

FIGURE 3 is a Mollier diagram of the nitrogen cycle as employed in the invention.

In the following description, the natural gas or liquefied natural gas ("LNG") has the following composition, it being understood that water and acidic components are removed therefrom by conventional means prior to liquefaction:

	Vol. percent
65 Methane -----	87.0
Ethane -----	11.0
Propane and higher -----	2.0

In FIGURE 1, temperature is plotted as the ordinate and the amount of heat removed (below 80° F.) for 100 mols of gas is plotted as the abscissa. The curve shown is for natural gas of the above-noted composition at 500

p.s.i.a, this being a convenient pressure in that it corresponds approximately to well-head pressures generally found.

As can be seen from FIGURE 1, condensation of the gas begins at point *a*, the first discontinuity, at a temperature of -65° F. Liquefaction is completed at point *b*, the second discontinuity, at a temperature of -127° F. To accomplish liquefaction (i.e. to reach point *b*) it is necessary to remove 458,000 b.t.u. per 100 mols of gas. As shown in FIGURE 1, this may be done by, firstly, a propylene refrigeration cycle and, secondly, an ethylene refrigeration cycle.

In order to store the LNG of the above composition at or near atmospheric pressure, it must be cooled from the temperature of liquefaction, -127° F., to -252° F., where its vapor pressure will be 17.7 p.s.i.a. Of course, vapor pressure will vary with composition, and one skilled in the art will select a temperature appropriate to the storage or transport facilities to be employed. To lower the temperature to -252° F., it is necessary to extract an additional 218,000 b.t.u. per 100 mols of LNG, that is, to go from point *b* to point *c* in FIGURE 1. As pointed out in detail hereinbelow, this is accomplished with the closed nitrogen cycle which is a principal feature of the present invention.

In FIGURE 2 there is illustrated a simplified schematic flow sheet of a preferred embodiment of the invention as it is applied to the liquefaction and sub-cooling of natural gas. It is to be understood that various additional pieces of apparatus will be employed in any given plant, which pieces are not shown in FIGURE 2; for example, pumps, valves, control means and circuitry, and the like. Their placement and usage, however, will be obvious to those skilled in the art.

With reference to FIGURE 2, natural gas entering through line 10 is first desulphurized and dehydrated so as to remove all acid components and water vapor; means for accomplishing the foregoing are indicated generally at 12. The gas is first cooled to about -30° F. over chillers 14, 16, and 18, it being understood that the number of chillers employed in this and other steps of the process may be varied to suit the conditions of a particular installation. For this first-stage cooling, a propylene refrigerant in lines 42, 44 is employed, refrigeration system 40 completing the propylene cycle. Following the first-stage cooling, the gas is further cooled to -127° F. in chillers 20, 22 and 24, wherein an ethylene refrigerant is supplied in lines 48, 50, and refrigeration system 46 completes the system. The two refrigerant systems 40, 46 are coupled in the manner of a cascade, propylene traveling through line 52, propylene condenser 56, and line 54. One skilled in the art will recognize that the foregoing is a conventional method of coupling separate refrigeration cycles.

Condensed LNG leaves chiller 24 in line 25 slightly below the point of complete liquefaction and is passed from there into subcooler 26 wherein it is cooled to -252° F. by nitrogen, in the manner described hereinbelow. After being cooled in subcooler 26, the LNG is passed via line 27, at -252° F. and still at 500 p.s.i.a., into flashdrum 28 where the pressure is reduced to near atmospheric pressure, the LNG is passed through line 30, pump 32, and line 34 into storage or the transport means (not shown). Off-gas from flashdrum 28 passes through line 100 and is treated as described in detail hereinbelow.

For proper understanding of the nitrogen cycle which supplies refrigerant to subcooler 26, it is convenient to start with the nitrogen in line 94 just prior to compression in compressor 74. The nitrogen is compressed in three stages with intermediate heat removal in intercoolers 80 and 82 and aftercooler 84, intercooler 80 being supplied by line 86, intercooler 82 being supplied by line 88, and aftercooler 84 being supplied by line 90. Suitable drive means 76 are employed to run both compressor 74 and

expander 64, expander 64 actually helping with the work of compression.

Compressed nitrogen in line 92 is further cooled in heat exchanger 72, chiller 70, heat exchanger 68, and chiller 66. Chillers 66 and 70 are provided with ethylene refrigerant at -65° F. in line 120 and ethylene at -140° F. in line 122, respectively. Nitrogen leaves chiller 66 in line 61 at a pressure of about 620 p.s.i.a. and a temperature of -137° F., and is passed into expander 64 where the pressure is reduced to 100 p.s.i.a. and the resulting temperature is -258° F. From expander 64 the nitrogen passes in line 60 into subcooler 26 to subcool the liquefied natural gas to -252° F. Subsequently, the nitrogen passes out of subcooler 26 in line 62 and is reheated against returning, warm, high-pressure nitrogen in heat exchangers 68 and 72. This brings the nitrogen back to line 94 at a temperature of about 80° F. and a pressure of about 96 p.s.i.a., thus completing the nitrogen cycle.

As noted hereinabove, it has been the practice in the prior art to employ a component of the gas itself to accomplish the subcooling of the liquefied gas. While the present invention employs a closed nitrogen cycle for this purpose, the gas component flashed off in drum 28 is useful to the process. This gas, composed primarily of methane, leaves flashdrum 28 in line 100, is then employed as a heat exchange medium in heat exchangers 68 and 72 to cool the compressed nitrogen passing counter-current thereto, is passed in line 104 to booster compressor 106, and in lines 108, 110 and 112 to the initial chilling refrigeration systems 40 and 46.

The advantages of the closed compressor-expander nitrogen system of the invention are illustrated in FIGURE 3, which is a Mollier diagram of the nitrogen cycle. The diagram in the lower right corner of FIGURE 3 represents the idealized cycle, composed of an adiabatic compressor and expander, and a heat exchanger.

Point *a* in FIGURE 3 corresponds to nitrogen in line 94 of FIGURE 2. The nitrogen is compressed in three stages from 96 to 620 p.s.i.a., point *b*, intercoolers 80 and 82 and aftercooler 84 removing heat as indicated. The compressed nitrogen is cooled from 90° F. to -137° F., point *c*, as it passes over chillers 70, 66 and heat exchangers 72, 68. As the cooled and compressed nitrogen is passed through expander 64, it is expanded to 100 p.s.i.a. with resulting temperature of -258° F., point *d*. Between points *d* and *e* in FIGURE 3 the nitrogen passes through subcooler 26; from point *e* back to point *a*, the nitrogen is passed through line 62, heat exchangers 68 and 72, and back to line 94, the starting point indicated hereinabove, from where the cycle is repeated.

For ease of understanding of the conditions at each stage of the nitrogen cycle, the pressure, temperature and heat content (*i*) at each of the points in FIGURE 3 are set forth in Table I hereinbelow.

TABLE I

Point of Cycle	Pressure, p.s.i.a.	Temperature, $^{\circ}$ F.	Heat Content
a-----	96	80	186.0
b-----	615	90	185.96
b'-----		-47.3	149.52
b''-----	610	-60	144.71
b'''-----	605	-125	125.45
c-----	600	-137	125.45
d-----	100	-258	98
e-----	98	-140	130.3
e'-----	97	-65	149.56

It is to be emphasized that while the foregoing description has employed terminal pressures in the nitrogen cycle of 96 and 615 p.s.i.a., respectively, this is merely a preferred pressure range based solely upon the availability of heat exchangers having this range; to be effective the process does not require the maintenance of these particular pressures, and in fact, it has been determined that the cycle efficiency is somewhat improved if higher pressures, for

example 150 to 1000 p.s.i.a., are employed. Naturally, one skilled in the art will utilize the most efficient equipment available in a given location at a given time.

On the basis of the data set forth in the foregoing description of the nitrogen cycle of the invention, it has been calculated that with a compressor having an adiabatic efficiency of 0.92, together with an expander having an adiabatic efficiency of 0.83 minimum, the energy requirement for removing the aforementioned subcooling load of 218,000 B.t.u. per 100 mols, from a system at 100° F., is 225 BHP, including losses. By comparison, to effect this removal by a completely reversible process and without heat losses, 103 BHP will be required, so it can be seen that the cycle efficiency relative to that of a Carnot cycle is 46%. One skilled in the art will recognize that this is a substantial improvement over the subcooling processes heretofore employed.

It is to be understood that various changes in the details, steps, materials and arrangements of parts, which have been hereinabove described in order to illustrate the invention, may be made by those skilled in the art without departing from the scope of the invention as defined in the appended claims. Also, it will be obvious that the invention has application to the liquefaction and sub-cooling of a variety of cryogenic gases other than natural gas, the latter material being described in an embodiment of the invention hereinabove for illustrative purposes only.

What is claimed is:

1. Process for the liquefaction and sub-cooling of a cryogenic gas supplied at an elevated temperature and a high pressure that comprises:

- (a) liquefying said gas while maintaining said pressure by reducing the temperature thereof in a plurality of refrigeration stages, said refrigeration stages being interconnected in a cascade arrangement;
- (b) conveying the liquefied gas to a sub-cooling zone while still maintained at said high pressure;
- (c) passing nitrogen at a temperature below the desired final temperature of said liquefied gas in indirect heat exchange with said liquefied gas, whereby said gas is cooled to the desired temperature;
- (d) passing effluent nitrogen from step (c) in indirect heat exchange with highly compressed nitrogen, whereby said effluent nitrogen is heated and said compressed nitrogen is cooled;
- (e) compressing and cooling the effluent nitrogen in a plurality of stages;
- (f) further cooling the compressed nitrogen from step (e) by passing it in indirect heat exchange with said effluent nitrogen in step (d);
- (g) expanding the cooled, compressed nitrogen from step (f), whereby the temperature is lowered to below the desired final temperature of said liquefied gas and the pressure of said nitrogen is reduced;
- (h) passing the cold, expanded nitrogen to step (c);
- (i) reducing the pressure of the liquefied gas from step (c) to about atmospheric pressure, whereby a gaseous fraction of said gas is produced; and
- (j) passing said gaseous fraction in indirect heat transfer with refrigerant in the refrigeration stages of step (a).

2. Process for the liquefaction and sub-cooling of a cryogenic gas supplied at an elevated temperature and a high pressure that comprises:

- (a) liquefying said gas while maintaining said pressure by reducing the temperature thereof in a plurality of refrigeration stages, said refrigeration stages being interconnected in a cascade arrangement;
- (b) conveying the liquefied gas to a sub-cooling zone while still maintained at said high pressure;
- (c) passing nitrogen at a temperature below the desired final temperature of said liquefied gas in indirect heat exchange with said liquefied gas, whereby said gas is cooled to the desired temperature;

(d), whereby said compressed nitrogen is further heat exchange with highly compressed nitrogen, whereby said effluent nitrogen is heated and said compressed nitrogen is cooled;

- (e) compressing and cooling the effluent nitrogen in a plurality of stages;
- (f) further cooling the compressed nitrogen from step (e) by passing it in indirect heat exchange with said effluent nitrogen in step (d);
- (g) expanding the cooled, compressed nitrogen from step (f), whereby the temperature is lowered to below the desired final temperature of said liquefied gas and the pressure of said nitrogen is reduced;
- (h) passing the cold, expanded nitrogen to step (c);
- (i) reducing the pressure of the liquefied gas from step (c) to about atmospheric pressure, whereby a gaseous fraction of said gas is produced;
- (j) passing said gaseous fraction in indirect heat exchange with said highly compressed nitrogen in step (d), whereby said compressed nitrogen is further cooled; and
- (k) passing the gaseous fraction from step (j) in indirect heat transfer with refrigerant in the refrigeration stages of step (a).

3. Process for the production of a liquid cryogenic gas storable at atmospheric pressure from a gas supplied at an elevated temperature and pressure that comprises:

- (a) liquefying said gas while maintaining said pressure by reducing the temperature thereof in a plurality of refrigeration stages, said refrigeration stages being interconnected in a cascade arrangement;
- (b) conveying the liquefied gas to a sub-cooling zone while still maintained at said high pressure;
- (c) passing nitrogen, at a temperature below the desired temperature at which said liquefied gas has a suitably low vapor pressure at atmospheric pressure, in indirect heat exchange with said liquefied gas, whereby said liquefied gas is cooled to said desired temperature;
- (d) passing effluent nitrogen from step (c) in indirect heat exchange with highly compressed nitrogen, whereby said effluent nitrogen is heated and said compressed nitrogen is cooled;
- (e) compressing and cooling the effluent nitrogen in a plurality of stages;
- (f) further cooling the compressed nitrogen from step (e) by passing it in indirect heat exchange with said effluent nitrogen in step (d);
- (g) expanding the cooled compressed nitrogen from step (f), whereby the temperature is lowered to below the desired final temperature of said liquefied gas and the pressure of said nitrogen is reduced;
- (h) passing the cold, expanded nitrogen to step (c);
- (i) removing the liquefied gas from said sub-cooling zone and reducing the pressure thereof to approximately atmospheric pressure, whereby a gaseous fraction of said gas is produced;
- (j) passing said gaseous fraction in indirect heat exchange with said compressed nitrogen in step (d), thereby further cooling said compressed nitrogen; and
- (k) passing the gaseous fraction from step (j) in indirect heat transfer with refrigerant in the refrigeration stages of step (a).

4. Process for the liquefaction and subcooling of natural gas supplied at an elevated temperature and a high pressure that comprises:

- (a) passing said gas in indirect heat exchange with a cold propylene refrigerant to reduce the temperature of said gas to about -30° F.;
- (b) liquefying said gas by indirect heat exchange with an ethylene refrigerant, said propylene and ethylene refrigerants being connected in cascade;
- (c) conveying said liquefied gas to a subcooling zone;
- (d) subcooling said liquefied gas to about -240° to

- 258° F. by indirect heat exchange with nitrogen at about —258° F.;
- (e) passing effluent nitrogen from step (d) in indirect heat exchange with highly compressed nitrogen whereby said effluent nitrogen is heated and said compressed nitrogen is cooled; 5
- (f) compressing and cooling the effluent nitrogen in a plurality of stages;
- (g) further cooling the compressed nitrogen from step (f) to about —137° F. by heat exchange with the effluent nitrogen in step (e) and by heat exchange with an ethylene refrigerant; 10
- (h) expanding the cooled, compressed nitrogen from step (g) and thereby lowering the temperature thereof to about —258° F.; 15
- (i) passing the nitrogen from step (h) to step (d);
- (j) reducing the pressure of said liquefied gas to near atmospheric pressure and removing a gaseous fraction; and

- (k) passing said gaseous fraction in indirect heat exchange with said compressed nitrogen to assist in the cooling thereof.

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