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[54] **REFRIGERATION CYCLE FOR THE ALIQUEFACTION OF NATURAL GAS**

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[51] **Int. Cl.**..............**F25j 1/00**, F25j 5/00, F25j 1/02
[58] **Field of Search**......................62/9, 11, 23, 24, 40

[56] **References Cited**

UNITED STATES PATENTS

3,364,685	1/1968	Perret	62/40
3,274,787	9/1966	Grenier	62/28
3,548,606	12/1970	Kuerston	62/40

FOREIGN PATENTS OR APPLICATIONS

895,094	5/1962	Great Britain	62/40
1,557,019	1/1969	France	62/40

OTHER PUBLICATIONS

Kleemenko, A. P.; One Flow Cascade Cycle in Progress in Refrigeration Science & Technology, Pergamon Press 1960 pp. 34–39.

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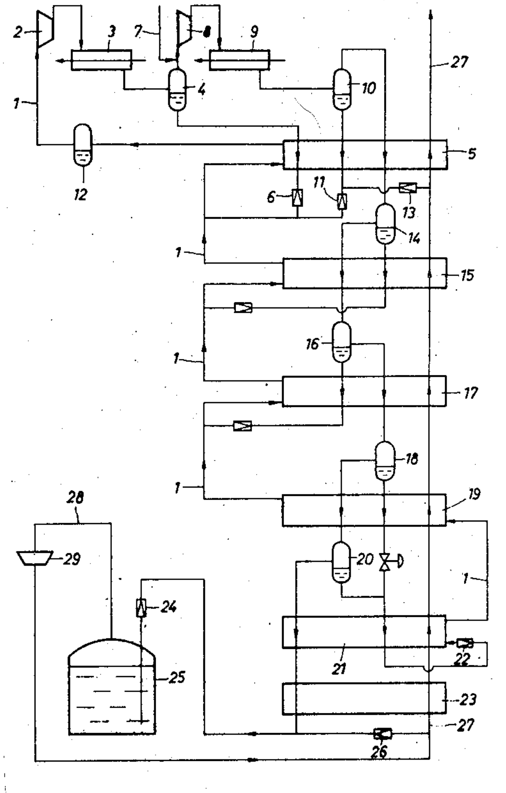
[57] **ABSTRACT**

In the liquefaction of natural gas wherein the refrigeration cycle fluid contains natural gas components, and such components are subjected to fractional condensation to obtain different temperature levels of refrigeration, the system is improved by adjusting the C_3–C_6 content of cycle fluid and the pressure of at least one intermediate pressure stage of the circulation pressure in such a manner that condensate is formed in the corresponding intercooler of said pressure stage. This condensate is then separated and subjected to heat exchange to utilize its refrigeration values and recirculated to the circulation compressor via an expansion valve. In this way, a substantial concentration of heavy hydrocarbons can be utilized to increase the refrigeration capacity of the refrigeration cycle, but said hydrocarbons do not deleteriously affect the lower temperature levels of refrigeration.

17 Claims, 2 Drawing Figures



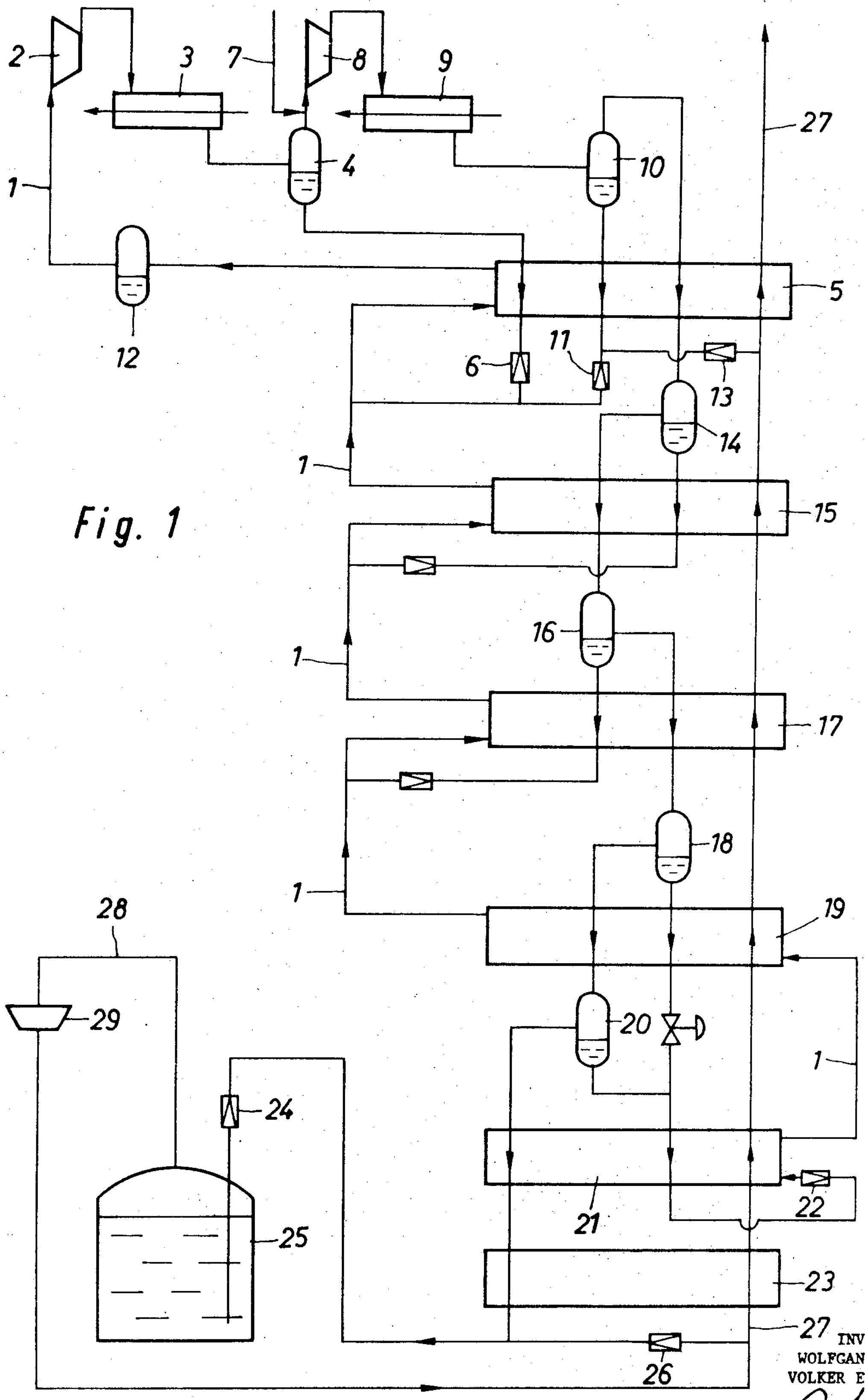


Fig. 1

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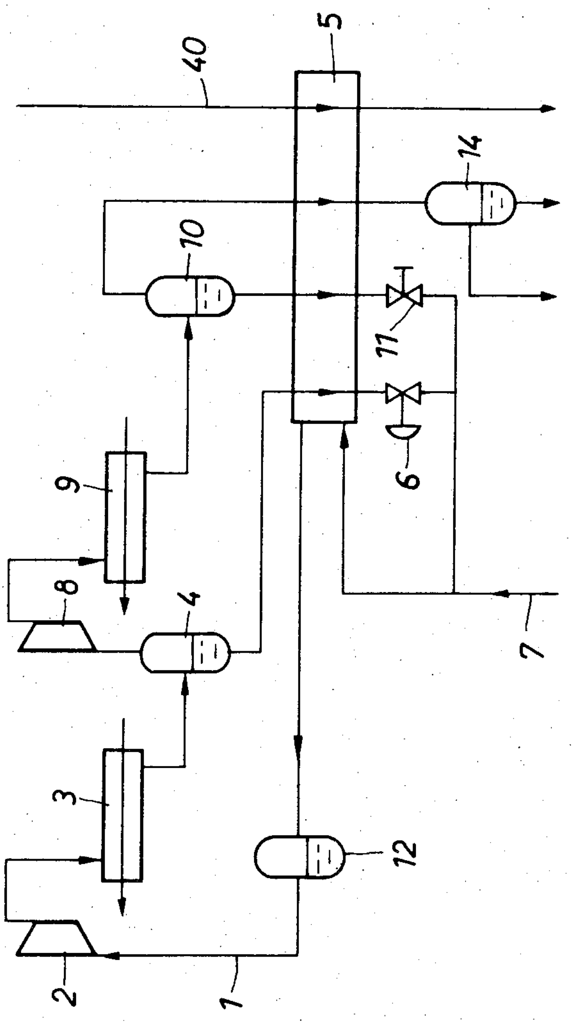
Fig. 2



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REFRIGERATION CYCLE FOR THE ALIQUEFACTION OF NATURAL GAS

BACKGROUND OF THE INVENTION

This invention relates to a process and an apparatus for the liquefaction of natural gas with the use of at least one refrigeration cycle, and in particular to such a process wherein the heat exchange fluid in the refrigeration cycle is a mixture of natural gas components. This cycle fluid is compressed, cooled, liquefied, expanded, evaporated and warmed in heat exchange with itself and with the natural gas to be liquefied. It is then recycled to the inlet of the circulation compressor.

The function of the refrigeration cycle is to produce the refrigeration required for liquefying natural gas [depending on climatic conditions having an ambient temperature (generally about −20° – +40°C.)]. Because the natural gas contains components having different liquefaction temperatures, a refrigeration cycle fluid is advantageously employed which is composed of components also having differing boiling points, as disclosed, for example, by A. P. Kleemenko (Comptes rendus du Congres du Froid de Copenhague 1959, pp. 34–39).

The cycle fluid is then partially condensed in multiple stages, each liquid fraction being separated from the gaseous phase, expanded, vaporized, heated and recycled to the compressor. The components having low boiling points, such as methane and nitrogen, yield the refrigeration required at the lowest temperature level whereas the fraction containing ethane and propane yields refrigeration values at an intermediate temperature level. The refrigeration required for the precooling step, i.e. for cooling to a temperature corresponding approximately to the boiling point of ammonia at atmospheric pressure (−33°C.), is produced by the vaporization of a mixture of higher hydrocarbons, such as propane, butane, and higher-boiling compounds.

From the standpoint of refrigeration it is desirable that the higher hydrocarbons are present in the cycle fluid in large quantities. This is the case because they exhibit a higher latent heat of vaporization than the lower-boiling cycle fluid components, so that, with an increase in their concentration, the refrigerating capacity of the cycle, based on 1 Nm^3 of circulated cycle gas, likewise increases. However, serious problems ordinarily result from the use of a high concentration of higher hydrocarbons. Specifically, during the subsequent partial condensation steps, an unacceptable amount of higher hydrocarbon remains in the gaseous phase, passes with the low-boiling cycle gas components into the final expansion stages, and in such final stages elevates the vaporization temperature above the desired refrigeration level and, in certain cases, gives rise to solid deposits in the refrigeration cycle, causing eventual damage or shut-down of the process.

SUMMARY OF THE INVENTION

Bearing the above problems in mind, a principal object of this invention is to provide an improved process for the liquefaction of natural gas so that the refrigerating capacity of the cycle fluid is increased without deleteriously affecting the temperature level of the lower temperature refrigerating stages.

Another object is to provide apparatus for conducting such a process.

Upon further study of the specification and appended claims, other objects and advantages of the invention will become apparent.

These objects are attained, according to this invention, by adjusting both the concentration of the C_3–C_6 hydrocarbons in the cycle fluid and the pressure of the intermediate stages of the circulation (cycle) compressor in relation to each other so that a condensate is formed after the cooling step following the intermediate compression stage. This condensate is then separated, expanded, vaporized, and then heated in heat exchange with both the natural gas to be liquefied and the cycle fluid. After the latter heat exchange step, the resultant warmed gas is recycled to the inlet side of the circulation compressor. It is important to note that the condensate is expanded (pressure-reduced) exclusively of any condensate of the vapor phase separated therefrom in the preceding step; the resultant separated vapor is then recompressed downstream of the intermediate compression stage, and then subjected to multiple stages of condensation, phase separation, and expansion of resultant condensates to produce the required multiple stages of decreasing temperature necessary for liquefying the natural gas.

In general, the molecular weight of the condensate after the cooling step following the intermediate compression stage is about 40 to 70, preferably 50 to 60, and that of the resultant vapor about 20 to 40, preferably 20 to 30.

The advantage of the above described system resides in that the refrigeration capacity of the cycle is increased, due to the presence of larger amounts of C_3–C_6 hydrocarbons, and that simultaneously, by the partial condensation after the intermediate cooling in the intercooler, the partial pressure of these hydrocarbons in the refrigeration medium passing into the lowest temperature stages is maintained at such a low level that there is no undesired increase of the vaporization temperature in such stages.

BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 is a schematic diagram of a preferred embodiment of this invention wherein the natural gas is intermixed with cycle fluid.

FIG. 2 is a schematic diagram of another preferred embodiment wherein the natural gas is liquefied independent of any intermixing with cycle fluid.

DETAILED DISCUSSION

In order to obtain the desired molecular weight of condensate and vapor after the cooling step following the intermediate compression stage, the pressure of the intermediate compression stage and the content of C_3–C_6 hydrocarbons in the cycle fluid are adjusted. When the natural gas to be liquefied is intermixed with cycle fluid, it is advantageous for the pressure of the intermediate compression stage to be the same or substantially the same as the natural gas pressure, generally about 45 to 35, preferably 10 to 25 atmospheres absolute. Under such conditions the cycle gas must have about the following composition:

Component	General % by Volume	Preferred % by Volume

N_2	0–5		0.05–2
CH_4	30–50	35–40	
C_2H_6	20–50	20–40	
C_3H_8	10–40	10–30	
C_4H_{10}	0–15	4–12	
C_5H_{12}	0–3	1–2	
C_6H_{14}	0–2	1–2	

When the natural gas to be liquefied is not intermixed with the cycle gas, the pressure of the intermediate compression can be altered with even greater flexibility, for example, in the range of 2 to 20, preferably 10 to 15 atmospheres absolute. Under such conditions, the cycle fluid can have the following analysis:

Component	General % by Volume	Preferred % by Volume
N_2	0–10	2–6
CH_4	10–40	30–40
C_2H_6 or C_2H_4	20–40	35–45
C_3H_8	0–20	0–3
C_4H_{10}	10–20	10–15
C_5H_{12}	0–20	5–10
C_6H_{14}	0–20	5–10

For optimum economics, a chemical engineer can select the precise conditions of the process, depending on energy costs at the plant site, etc. It is also to be noted that these minor components may exist in the cycle gas, such as helium, CO_2 and H_2S and, if so, appropriate adjustments will again be made to optimize the process.

In any case, there is no question that a chemical engineer will be able to make the necessary adjustments of the pressure in the intermediate circulation compressor and the content of C_3- C_6- hydrocarbons in the cycle fluid to obtain a condensate after the cooling step following the intermediate compression step. For this purpose, such cooling steps will generally be conducted so that the cycle fluid is cooled to about 10° to 35°, preferably 20° to 30°C., dependent on the cooling water temperature.

The invention is applied in a particularly suitable manner to a process wherein the required refrigeration is produced by a single cycle, and the cycle fluid is subjected to a multi-stage partial condensation, where, in each instance, the condensate is separated, expanded to the inlet pressure of the circulation compressor, vaporized and warmed in heat exchange with cycle fluid and natural gas, and recycled to the circulation compressor. By this process, a high liquefaction efficiency is obtained with a low expenditure in apparatus, and, furthermore, the process can be easily adapted to various natural gas compositions and operating conditions.

The apparatus for conducting the process according to the invention comprises as the essential novelty, a separator connected after at least one intercooler of the circulation compressor, which separator is in communication in the gas phase via a conduit, with the subsequent compression stage and, in the liquid phase, via an expansion valve, and the refrigerating cycle path of a heat exchanger, with the inlet side of the circulation compressor, and associated conduit.

DETAILED DESCRIPTION OF DRAWINGS

Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention to its fullest extent. The following preferred specific embodiments are, therefore, to be construed as merely illustrative, and not limitative of the remainder of the disclosure in any way whatsoever.

FIG. 1 shows a process with an open cycle, i.e. wherein the natural gas to be liquefied is compressed and brought to a low temperature together with the cycle gas. The cycle fluid has approximately the following composition:

1–5% N_2
35–55% CH_4
27–38% C_2H_6
12–25% C_3H_8
1–6% C_4H_{10}
0.5–2.5% C_5H_{12}
0–2% C_6H_{14}

20,000 Nm³/h of the cycle gas is fed at about 6 atmospheres absolute through conduit **1** to the inlet side of the first compressor stage **2**, compressed at that point to about 20 atmospheres absolute, and brought to the cooling water temperature in the intercooler **3**. 1,000 Nm³/h of the cycle fluid are liquefied during this step, separated from the gaseous phase in the separator **4**, cooled to about 280°K. in the heat exchanger **5**, and expanded through valve **6** into the conduit **1** whereupon it is then reintroduced to the first stage of the compressor. The gas leaving the separator **4**, together with 6,000 Nm³/h of natural gas (freed of CO_2, H_2S, and H_2O), is compressed in the second compressor stage **8** to about 35 atmospheres absolute. In the final cooler **9**, there is again obtained about 1,000 Nm³/h of liquid, the latter being collected in the separator **10** and subcooled in heat exchanger **5**. The major portion of the subcooled liquid expanded by valve **11**, into the conduit **1**, is then vaporized and heated in heat exchanger **5**. Before the resultant cycle gas is again returned to the first compressor stage, it passes through the liquid trap **12**, the latter protecting the compressor from liquid impacts, for example when the plant is placed on stream, or in case of operating errors.

A small portion of the subcooled liquid from separator **10** is expanded, at the cold end of the heat exchanger **5**, via valve **13** into the conduit **27** leading to the gasometer. In this connection, the amount and composition of this stream are chosen so that the C_3- and higher hydrocarbons entering the plant together with the natural gas again are discharged from the plant by this path.

The gas from the separator **10** is cooled, in heat exchanger **5**, to about 280°K. and is partially condensed during this step. In the separator **14**, the liquid, about 4,200 Nm³/h, is separated from the vapor. Both fractions are cooled in heat exchanger **15** to about 245°K. The subcooled liquid is expanded, admixed to the returning cycle gas, and vaporized in heat exchanger **15**. The gas is once again partially condensed and separated, in separator **16**, into a liquid and a gaseous phase. The amount of the thus-formed liquid is about 6,000 Nm³/h.

Both phases are now cooled in heat exchanger **17** to about 195°K. The subcooled liquid is expanded, in the manner described above, into the recycling cycle gas, and vaporized in head exchanger **17**. The partially condensed vapor is again separated, in separator **18**, into the two phases which are cooled, in heat exchanger **19**, to about 185°K. The liquids from the separators **18** (7,300 Nm^3/h) and **20** (500 Nm^3/h) are combined, subcooled together in heat exchanger **21**, and thereafter expanded in the valve **22**. During this process, a temperature of about 140°K. is reached. The liquid is now vaporized and warmed in heat exchangers **21** and **19**, then mixed with the liquid from separator **16**, which liquid was subcooled in heat exchanger **17**, and recycled in the manner described above to the circulation compressor.

The vapor separated in separator **20** is cooled, liquefied, and subcooled in heat exchangers **21** and **23**. The liquid passes at a temperature of about 115°K. into the storage tank **25** by way of expansion valve **24**. The temperature at the cold end of the heat exchanger **23** is obtained by expansion and vaporization of a portion of the liquid leaving the heat exchanger **23**; this liquid is expanded via valve **26** into the conduit **27** leading to the gasometer, and is discharged from the plant via the heat exchangers **23**, **21**, **19**, **17**, **15**, and **5**. The gas vaporized in the storage tank **25** by the effect of heat is withdrawn via conduit **28** and conveyed, through the cold gas blower **29**, and via conduit **27** to the gasometer.

In the following table, the pressure and temperature conditions ambient in the individual separators are set forth (P in atmospheres absolute, T in °K.), as well as the total amount fed to each separator (F in Nm^3/h), the amount of liquid separated therein (L in Nm^3/h), and also the approximate molecular weight of the respective gaseous or liquid phase, M_G and M_L:

Separator	P	T	F	L	M_G	M_L
4	20	303	20,000	1,000	30	51
10	35	303	25,000	1,000	27	43
14	35	281	24,000	4,200	24	38
16	35	245	19,800	6,000	21	32
18	35	195	13,800	7,300	18	23
20	35	187	6,500	500	18	20

It can be seen from the above table that in the separator **4**, propane (molecular weight **44**) and the higher hydrocarbons are obtained in the liquid phase. The liquid in separator **10** consists essentially of propane; in separators **14** and **16**, the proportion of ethane (molecular weight 30) increases in the liquid. In separators **18** and **20**, a mixture of ethane and methane (molecular weight 16) is separated. The gas leaving the separator **20** is mostly methane. In a similar manner, the molecular weight of the gaseous phase decreases from separator to separator.

Referring now to FIG. 2, there is disclosed another important embodiment of this invention wherein a closed cycle is employed, i.e. when natural gas and cycle medium are always conducted separately from each other. Identical structural components bear identical reference numerals. The cycle fluid has the following compositions:

1–5% N_2
20–35% CH_4
35–50% C_2H_6
8–20% C_4H_{10}
2–7% C_5H_{12}
1–4% C_6H_{14}

The essential difference as compared to FIG. **1** resides in that the natural gas is not fed via conduit **7** to the second compressor stage **8**, but rather via conduit **40** to the heat exchanger **5** and then to the low-temperature plant disposed thereafter as in FIG. **1**. This embodiment obviates the need for a device for the removal of the high boiling hydrocarbons introduced into the cycle by the natural gas, as would correspond to the valve **13** of FIG. **1**.

From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention, and without departing from the spirit and scope thereof, can make various changes and modifications of the invention, to adapt it to various usages and conditions.

What is claimed is:

1. In a process for the liquefaction of natural gas, said process employing at least one refrigeration cycle, wherein the refrigeration cycle fluid contains natural gas components and is compressed, cooled, liquefied, expanded, vaporized and heated in heat exchange with cycle fluid and natural gas to be liquefied, and recycled to the circulation compressor, said process having multiple stages of decreasing temperature,

the improvement comprising employing as said circulation compressor, a multi-stage compressor, adjusting the concentration of C_3- to C_6- hydrocarbons in the cycle fluid, and the pressure of at least one intermediate stage of the circulation compressor, with respect to each other so that a portion of the effluent from said intermediate stage is condensible by heat exchange with cooling water; cooling said effluent from said intermediate stage in an intercooler between two successive pressure stages to form a liquid phase condensate containing a substantial concentration of heavy hydrocarbons and a vapor phase; separating said condensate from said vapor phase; pressure-reducing said condensate exclusively of any condensate of said vapor phase separated therefrom; vaporizing and heating resultant pressure-reduced condensate in heat exchange with the natural gas to be liquefied and the cycle fluid; recycling resultant heated vaporized condensate to the inlet side of the circulation compressor, recompressing said vapor separated from said condensate containing a substantial concentration of heavy hydrocarbons, and subjecting resultant recompressed vapor to multiple stages of partial condensation, phase separation, and expansion of resultant condensates to produce said multiple stages of decreasing temperature.

2. A process as defined by claim **1**, wherein the pressure of fluid leaving said intercooler is substantially the same as the pressure of the natural gas to be liquefied, said natural gas being intermixed into cycle fluid.

3. A process as defined by claim **1**, wherein the required refrigeration is produced by a single cycle, and the cycle fluid is subjected to a multi-stage partial condensation, wherein, in each partial condensation, the condensate is separated, expanded to the inlet pressure of the circulation compressor, vaporized and warmed in heat exchange with cycle fluid and natural gas, and recycled to the circulation compressor.

4. A process as defined by claim **3**, wherein the pressure of fluid leaving said intercooler is substantially the same as the pressure of the natural gas to be liquefied, said natural gas being intermixed with cycle fluid.

5. Apparatus for the liquefaction of natural gas, said apparatus comprising:

a condensate separator (4) having inlet means and gas outlet means and liquid outlet means;

at least one intercooler (3) having inlet and outlet means; said inlet means of said condensate separator being in communication with said outlet means of said intercooler;

a circulation compressor having at least two serially connected compression stages, said inlet means of said intercooler being in communication with the outlet of an intermediate compression stage, said gas outlet means of said condensate separator being disposed before, and in communication with the inlet side of the last serially connected compression stage (8);

an expansion valve (6) being in communication with the liquid outlet means of said condensate separator and separate unbranched conduit means for conducting liquid from said liquid outlet means exclusively to said expansion valve;

heat exchange means including separate flow paths for expanded condensate, natural gas to be liquefied, and cycle liquid; and conduit means for effecting said communications and also for recirculating resultant heated expanded condensate from said heat exchange means and said expansion valve to the inlet of said circulation compressor, and

means for effecting multiple stages of partial condensation, phase separation, and expansion of resultant condensates, said mean being in communication with the outlet side of the last serially connected compression stage (8).

6. A process as defined by claim 1 wherein fluid entering said intercooler is cooled to about 10°–30°C. in said intercooler.

7. A process as defined by claim 6 wherein fluid entering said intercooler is cooled to about 20°–30°C. in said intercooler.

8. A process as defined by claim 2, said pressure being about 15–45 atmospheres absolute.

9. A process as defined by claim 8, the cycle gas entering the intercooler having the following composition in per cent by volume:

0–5 N_2; 30–50 CH_4; 20–50 C_2H_6; 10–40 C_3H_8; 0–15 C_4H_{10}; 0–3 C_5H_{12}; and 0–2 C_6H_{14}.

10. A process as defined by claim 2, said pressure being about 10–25 atmospheres absolute.

11. A process as defined by claim 10, the cycle gas entering the intercooler having the following composition in per cent by volume:

0.05–2 N_2; 35–40 C_4; 20–40 C_2H_6; 10–30 C_3H_8; 4–12 C_4H_{10}; 1–2 C_5H_{12}; and 1–2 C_6H_{14}.

12. A process as defined by claim 1, said refrigeration cycle being a closed cycle, the pressure entering the intercooler being 2–20 atmospheres absolute and the gas entering the intercooler having the following composition in per cent by volume:

0–10 N_2; 10–40 CH_4; 20–40 C_2H_6 or C_2H_4; 0–20 C_3H_8 10–20 C_4H_{10}; 0–20 C_5H_{12}; and 0–20 C_6H_{14}.

13. A process as defined by claim 1, said refrigeration cycle being a closed cycle, the pressure entering the intercooler being 10–25 atmospheres absolute and the gas entering the intercooler having the following composition in per cent by volume:

2–6 N_2; 30–40 CH_4; 35–45 C_2H_6 or C_2H_4; 0–3 C_3H_8; 10–15 C_4H_{10}; 5–10 C_5H_{12}; and 5–10 C_6H_{14}.

14. A process as defined by claim 1, said liquid phase condensate having a substantial concentration of heavy hydrocarbons having a molecular weight of about 40–70 and said vapor phase separated therefrom having a molecular weight of about 20–40.

15. A process as defined by claim 1, said liquid phase condensate having a substantial concentration of heavy hydrocarbons having a molecular weight of about 50–60 and said vapor phase separated therefrom having a molecular weight of about 20–30.

16. A process as defined b claim 2 comprising the steps of passing said vapor separated from said condensate having a substantial concentration of heavy hydrocarbons to a final compression stage of said multi-stage compressor; cooling resultant compressed vapor to form a liquid phase and a vapor phase; passing the just-mentioned liquid phase through a heat exchanger, and expanding a portion of resultant heat exchanged fluid and discharging the latter from said liquefaction cycle, said portion being of sufficient amount and of a composition to remove C_3 and higher hydrocarbons from the natural gas intermixed with said cycle fluid.

17. A process as defined by claim 1, said condensate from said intercooler being employed as a cooling medium only in the higher temperature stages of said multiple stages of decreasing temperature.

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