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Filed May 23, 1962

3 Sheets-Sheet 1

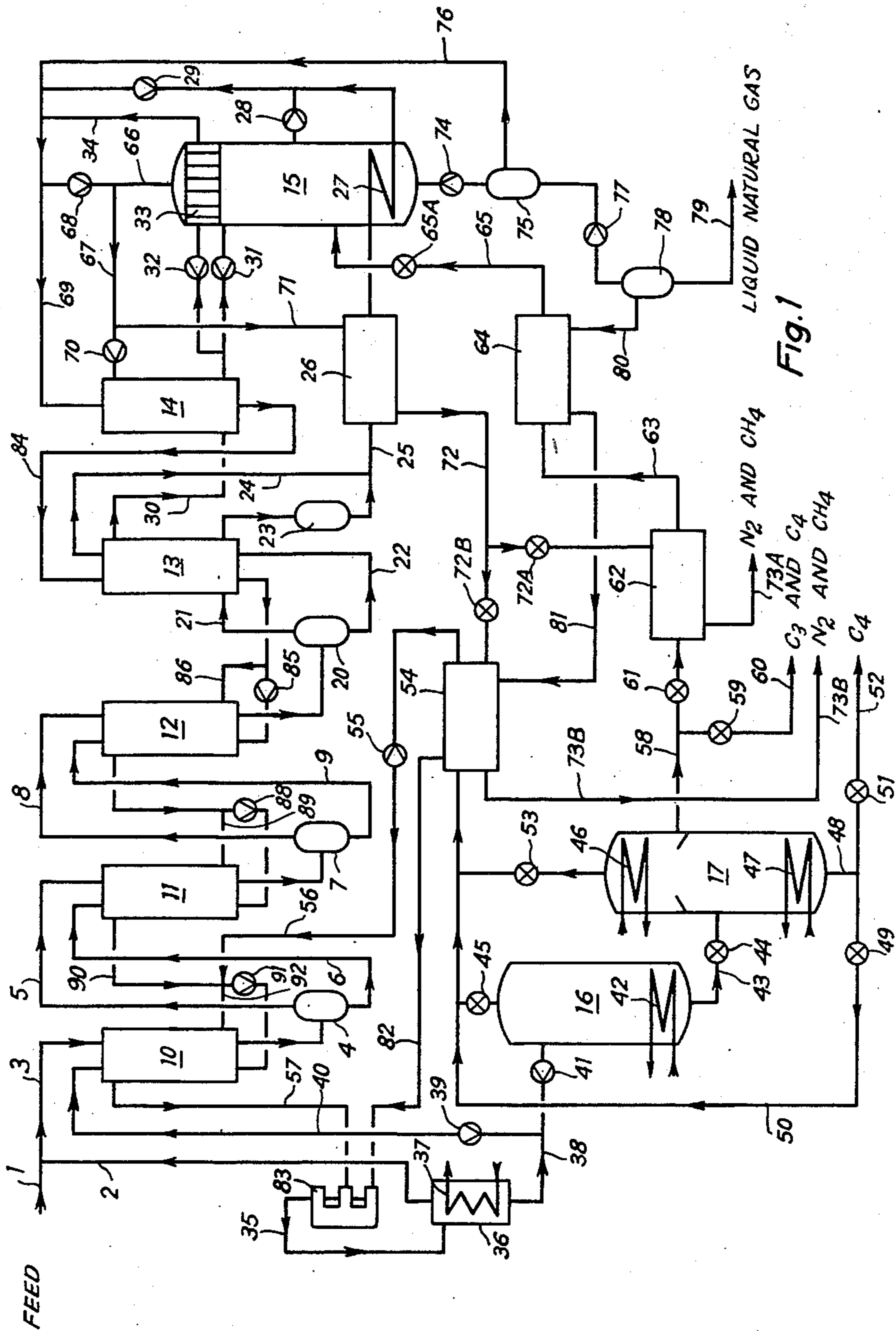


Fig. 1

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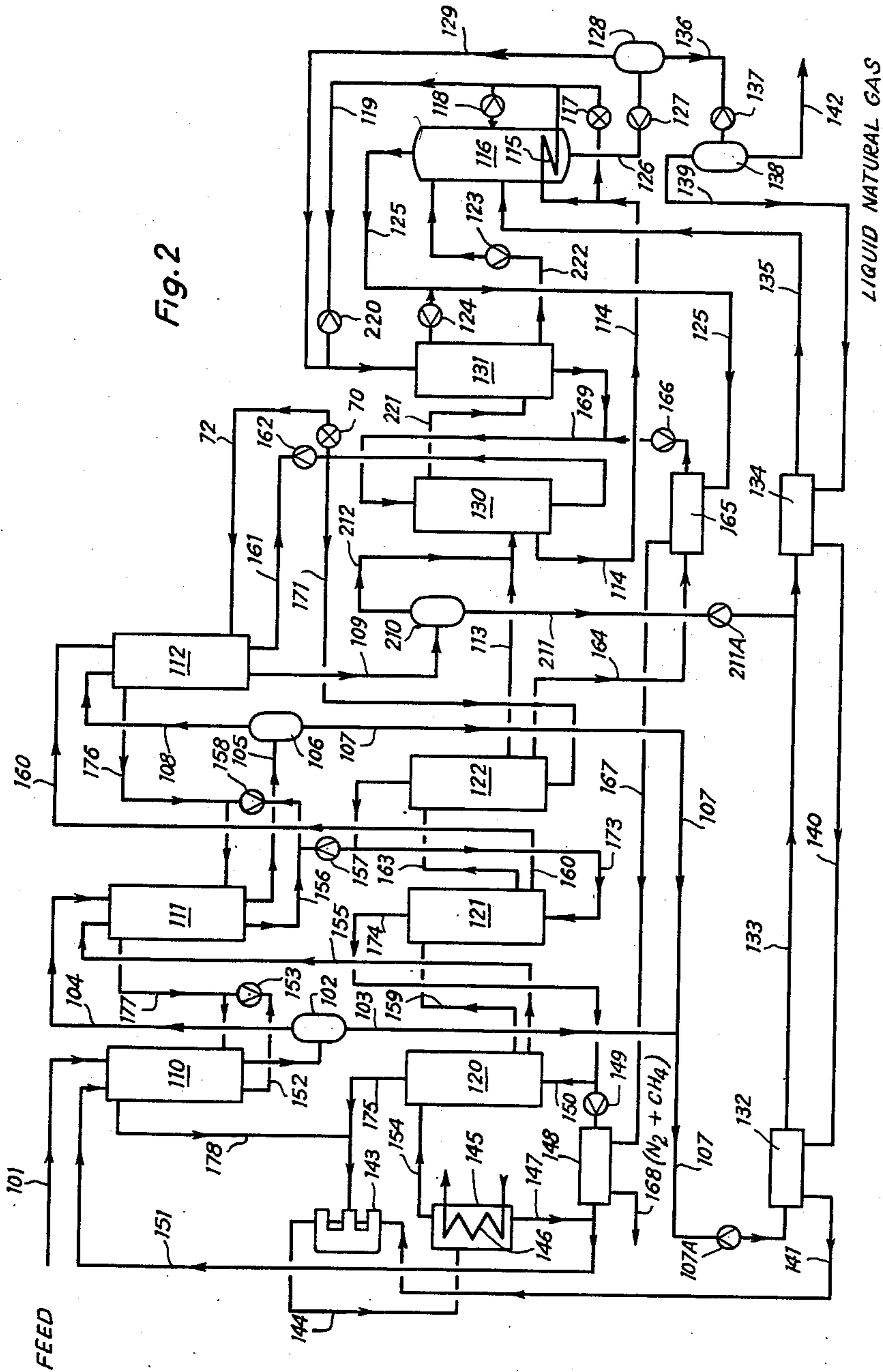
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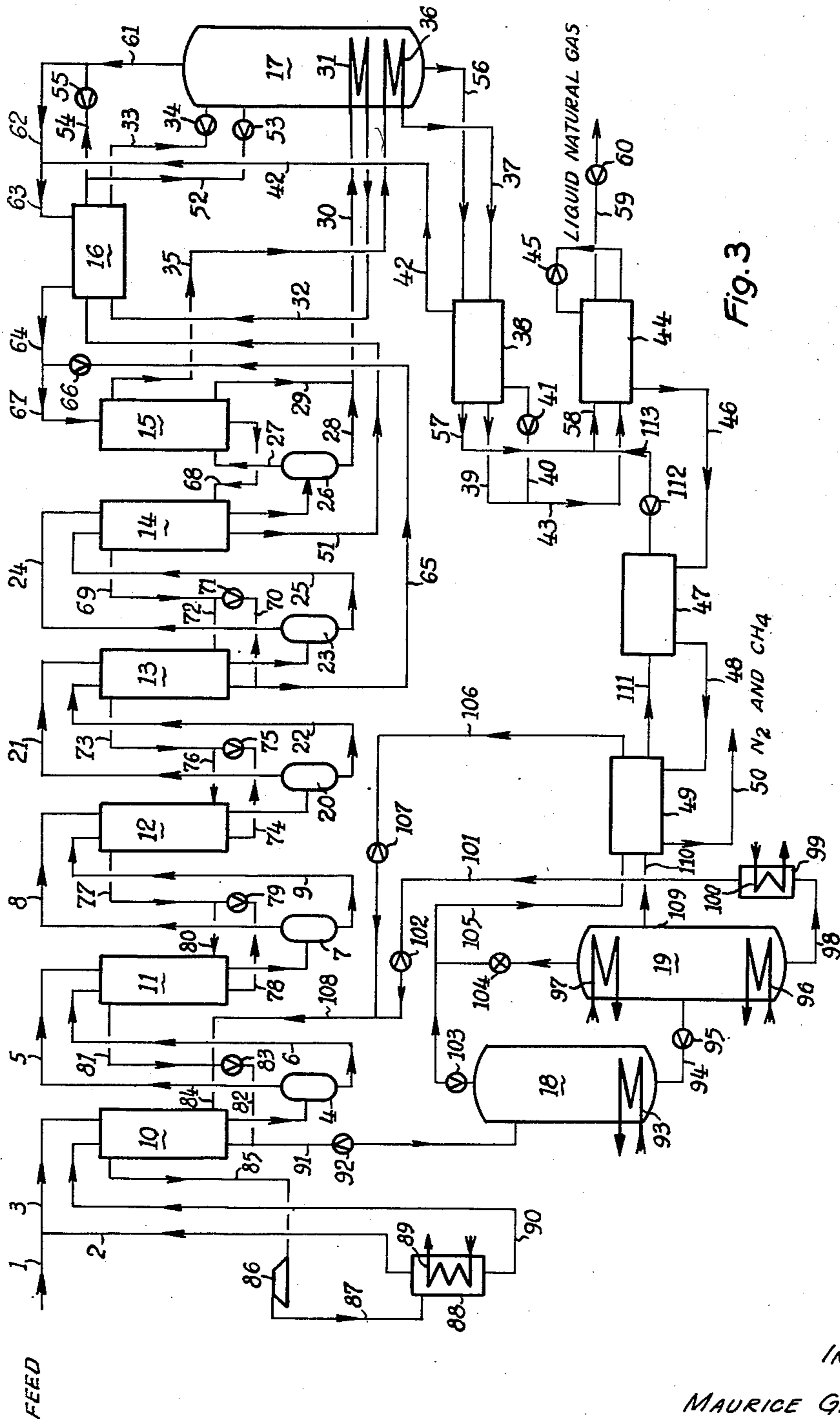


Fig. 3

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**PROCESS FOR COOLING A GAS MIXTURE
TO A LOW TEMPERATURE**

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Patent 1,302,989; Sept. 5, 1961, 872,325, Patent 80,294
7 Claims. (Cl. 62-26)

The present invention relates to a process for cooling a gaseous mixture to low temperatures and for producing at least one component of this mixture in the liquid state. The invention is applicable more particularly although not exclusively to the production of moderately low temperatures which cannot be achieved with the aid of a simple refrigerator but which are above the temperature at which air is liquefied, that is to say between -60° C. and -180° C., and to the liquefaction and/or the separation of gaseous mixtures condensing in this temperature range, for example natural gas.

The process usually recommended for the production of temperature in the above range is the process known as the "cascade" process, which consists in liquefying a first refrigerating fluid under pressure, in expanding it to a lower pressure and in vaporising it in heat-exchange with a second more volatile refrigerating fluid under pressure, in expanding the second refrigerating fluid at a lower pressure and in vaporising it in heat exchange with a third more volatile refrigerating fluid, and so on, each of the successive refrigerating fluids enabling a lower temperature to be reached. However, this process requires the use of an equipment which is very complicated and which presents great regulation difficulties, each of the refrigerating fluids travelling through its own closed cycle and requiring a compressor, a condenser, an expansion valve and a heat-exchanger.

A refrigeration cycle known as the "single flow cascade cycle" has recently been proposed (AP Kleemenko, Reports on the Refrigeration Congress at Copenhagen, 1959, page 34), in which at least a part of the condensed fractions is expanded, vaporised in heat-exchange with the mixture under pressure during cooling, then recompressed to the initial pressure and combined with the mixture under pressure. Thus, for example, natural gas under pressure is subjected to a fractional liquefaction of those fractions which have (a) a high butane and propane content and (b) a high ethane content, each of them being expanded to atmospheric pressure and revaporised in heat exchange with the natural gas under pressure; the remaining gaseous methane under pressure is then expanded to atmospheric pressure and partly liquefied, the methane vapours being reheated by heat exchange with the natural gas under pressure, combined with the previously separated fractions, recompressed to the pressure of the natural gas and mixed with the latter.

Such a cycle requires the use of only a single compressor instead of a compressor for each refrigerating fluid. The energy consumption for compression is however higher than that of a cascade cycle with separate flows of the type previously known. Furthermore, the separation of the less volatile fractions by fractionated condensation is not very good, and this presents disadvantages, especially when it is desired to separate certain of their constituents in the pure state.

It is an object of the invention to provide a process which obviates the disadvantages mentioned above in connection with the single flow cascade cycle, and, in particular, it is an object of the invention to provide a process for the production of low-temperatures for the liquefaction of a gaseous mixture and for the separation

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in a substantially pure state of at least some of the components of the gas mixture, without employing a higher energy consumption than with the normal "cascade" process having separate flows of the various refrigerating fluids.

It is a further object of the invention to provide a process for the liquefaction of natural gas available under a relatively low pressure, for example, of the order of a few tens of kg./cm.², and for the separation in a substantially pure state of methane, ethane, propane and the butanes contained in natural gas.

Furthermore, it is an object of the invention to provide a process which is adapted for simple operation and regulation of the installation used for liquefaction and/or separation of natural gas.

According to the invention there is provided a process for cooling a gaseous mixture to a low temperature and for the production of at least one component of the gas mixture in the liquid state. The gaseous mixture is subjected to a fractionated condensation and at least one of the condensed fractions is expanded, vaporised in heat exchange with the mixture being condensed and then recompressed and mixed with the gaseous mixture to be cooled. The component to be obtained in the liquid state is condensed and expanded to the pressure at which it is to be collected. It is particularly pointed out that the vaporization of at least the major part of the fraction intended to be recompressed and mixed with the gaseous mixture to be cooled is effected at a pressure higher than that under which occurs the production of the component to be recovered in the liquid state where the production pressure is, for instance, the tank storage pressure.

According to one embodiment of the invention, the component to be produced in the liquid state is subjected, prior to its expansion to the pressure under which its production takes place, to a supercooling sufficient for this expansion not to result in appreciable partial vaporization. All of the fraction or fractions intended to be recompressed and mixed with the gaseous mixture to be cooled are vaporised at a pressure higher than that at which there takes place the production of the component to be recovered in the liquid state. The aforesaid supercooling can be obtained with the assistance of any appropriate source of cold. Nevertheless, it is particularly advantageous, when the gaseous mixture to be cooled comprises at least one component which is more volatile than the component to be produced in the liquid state, to carry out this supercooling by vaporisation of the fraction which is more volatile than this latter component. The more volatile fraction has remained in the gaseous state during the fractionated condensation of the gaseous mixture and has been liquefied by heat exchange with a less volatile liquid, for example with the actual component to be produced in a liquid state previously expanded to a pressure lower than that of the fractionated condensation, and then itself expanded. All or part of this vaporisation can be effected at a pressure substantially equal to the vaporisation pressure of the fractions intended to be recompressed and mixed with the gaseous mixture to be cooled, and the vaporised more volatile fraction is mixed with these latter fractions. All or part of this vaporisation can also be effected at a pressure lower than the vaporisation pressure of the said latter fractions, but the vaporised more volatile fraction, which can then not be mixed with these latter fractions, must then be evacuated.

The liquefied more volatile fraction is itself preferably super-cooled, before its expansion, concurrently with the component to be produced in the liquid state.

In the case of the liquefaction of natural gas which frequently contains a certain quantity of nitrogen which

is more volatile than the methane to be liquefied, a mixture of methane and nitrogen, existing as gaseous residue after the liquefaction of the methane, is preferably employed as the more volatile fraction thereby permitting the super-cooling of the liquefied methane to be effected. After the vaporisation of the mixture of methane and nitrogen and after it has been reheated to the region of ambient temperature, at least a part of this mixture is evacuated to be utilised for example as a fuel for the feeding of boilers.

According to a second embodiment of the invention, at least one fraction condensed during the cooling of the gaseous mixture is separated from the gaseous mixture and super-cooled before being expanded and vaporised in heat exchange with the mixture being condensed. There is thus obtained a cooling to a lower temperature by the vaporisation of this fraction than when it is not super-cooled.

According to a third embodiment of the invention, the fraction vaporised in heat exchange with the mixture being vaporised, then recompressed, is at least in part cooled between the ambient temperature and a temperature which is intermediate between the ambient temperature and the minimum temperature reached by the gaseous mixture to be cooled, independently of this latter, before being mixed therewith. There is thus assured a more convenient separation by condensation of the components contained in this fraction, at temperatures not so low as for the initial gaseous mixture to be separated. When the gaseous mixture to be separated contains at least one component more volatile than the component to be separated in the liquid state (this being more especially the case with the nitrogen contained in the natural gas, which is more volatile than methane), it may be subjected after liquefaction of this latter to a degasification from these components at an intermediate pressure between the initial pressure of the gaseous mixture and the pressure at which occurs the vaporisation of the fraction intended to be recompressed and mixed with this mixture, and the separated and reheated volatile component is not mixed with the gaseous mixture to be cooled. This facilitates the condensation of the component to be separated in the liquid state, which would be impeded, if it was carried out with the initial mixture, by the presence of these volatile components.

When the gaseous mixture contains a component which is difficult to separate by simple fractionated condensation because of its low concentration and/or because of a volatility close to that of another component (for example, ethane in certain natural gases), at least the fraction with the closest volatility (that is to say, immediately below or immediately above) is subjected after its condensation to a rectification with the object of separating this component therefrom. The separated component is then expanded and mixed with the fraction being vaporised and intended to be recompressed and mixed with the initial gaseous mixture.

Finally, when the gaseous mixture contains a component which is difficult to separate by liquefaction and possible rectification at low temperature, one of the fractions which are vaporised, recompressed and subjected afresh to the cooling is a fraction with a relatively high content of this component. The fraction is recycled in a proportion sufficient to facilitate the subsequent separation of this component by liquefaction and possibly rectification during the fresh cooling operation.

Installations for the liquefaction and separation of natural gas in accordance with the invention will be hereinafter described by way of non-limitative examples and by reference to the accompanying drawings in which:

FIGURE 1 represents an installation which may be used for liquefying natural gas and which permits a possible separation of the heavier constituents of this gas mixture, i.e., the butanes and propane;

FIGURE 2 represents an installation similar to that of FIGURE 1, but which is adapted to be employed with-

out separation of the constituents of natural gas other than methane, and in which the recompressed and recycled fractions are cooled independently of the natural gas in a certain temperature range before being reunited therewith; and

FIGURE 3 represents an installation similar to that of FIGURE 1, but in which the methane to be produced in the liquid state is supercooled before its expansion, and there is no recycling of gas at low pressure.

The natural gas to be liquefied, available at a pressure of 30 kg./cm.² absolute and at a temperature of 30° C., with a flow rate of 1000 cubic metres per hour (brought to normal conditions), has the following composition:

	Percent by volume
Methane -----	83.7
Ethane -----	7.9
Propane -----	2.1
Butane -----	1.0
Nitrogen and other light gases -----	5.3

In the installation shown in FIGURE 1, which it will be presumed first of all not to effect the separation of the propane and butanes, the natural gas to be liquefied is cooled in a series of heat exchangers 10 to 14, then introduced into the degasification column 15. Fractions with high contents of propane and butanes are separated in the rectification columns 16 and 17. The vaporised and reheated fractions are recompressed by the compressor 83 to the pressure of the natural gas, before being reunited therewith.

The natural gas arriving by way of the conduit 1, to which is added through the conduit 2 a recycled fraction, the origin of which will be referred to hereinafter, passes through the conduit 3 into the heat exchanger 10, where it is cooled to about -15° C. in counter-current with a recycled fraction partially in the liquid state. There is condensed a liquid with a high content of butanes, and this liquid is separated from the remaining in the separator 4. This liquid is conveyed by way of the conduit 6 into the exchanger 11, where it is supercooled to about -18° C. concurrently with the treated natural gas, then it is expanded in the valve 88 to about 7 kg./cm.² and introduced into the recycled fraction which is being reheated and which arrives by way of the conduit 89 at the cold end of the exchanger 11.

The remaining natural gas leaving the separator 4 passes through the conduit 5 into the exchanger 11 where it is cooled to -48° C., while a fraction with a high propane content is condensed, and this fraction is separated in the separator 7. This liquid passes through the conduit 9 into the exchanger 12, where it is supercooled to -72° C., then it is expanded in the valve 85 and reunited with the fraction being reheated and arriving by way of the conduit 86 at the cold end of the exchanger 12. The natural gas, remaining at -48° C., is then introduced through the conduit 8 into the exchanger 12, where it is cooled to about -72° C., while a fresh fraction composed mainly of ethane is condensed, and this fraction is separated from the gas in the separator 20. This liquid is conveyed through the conduit 22 to the exchanger 13, which lowers its temperature to -85° C. Meanwhile the gas is returned through the conduit 21 into the same exchanger, where the methane is partially liquefied. The liquid methane which is formed is collected in the receiver vessel 23 and supercooled liquid originating from the separator 20 is added thereto, this liquid arriving by way of the conduit 24. The two combined liquids are introduced through the conduit 25 into the exchanger 26, by which they are supercooled to about -105° C., by heat exchange with a gas with a high nitrogen content, the origin of which will be hereinafter referred to. The liquid methane is then supercooled to -110° C. in a coil 27 disposed in the boiler of the degasification column 15, then the major part thereof is expanded in the valve 28 to 15 kg./cm.² approximately and introduced into the central portion of this column. A

regulatable fraction of the liquid is still not introduced into the column, but is expanded in the valve 29 to about 7 kg./cm.² and combined with different gaseous fractions intended to be recycled in heat exchange with the natural gas.

The remaining gas at the outlet of the exchanger 13, passes through the conduit 30 into the final exchanger 14, where it is cooled to about -112° C. in heat exchange with different gaseous or liquid fractions originating from the degasification column 15. Practically all the remaining methane is condensed. It is divided into two portions; the first is expanded in the valve 31 to 15 kg./cm.² and introduced into the upper end of the degasification column 15; the other portion is expanded in the valve 32 to 7 kg./cm.² and introduced into the condenser at the head of the column 15; it is vaporised therein, thereby assuring the reflux in this column, and then it is evacuated through the conduit 34.

The methane fraction not condensed in the exchanger 14 and containing a large proportion of nitrogen and other volatile gases is expanded in the valve 70 to 15 kg./cm.² and reunited with a portion of gas released at the head of the column 15 and arriving by way of the conduit 67. The combined stream is then returned through the conduit 71 into the heat exchanger 26, where it is heated to -85° C. while supercooling the liquefied gases originating from the exchanger 13. It then passes through the conduit 72 and the valve 72A (the valve 72B being closed) to the exchanger 62, where it is reheated substantially to the ambient temperature in heat exchange with a mixture of liquid butanes and propane originating from the rectification column 17, which will hereinafter be described. It is then conveyed through the conduit 73A to the point of use, for example as a fuel.

The degasification column 15 is thus fed on the one hand in its central portion with liquid methane containing a certain quantity of less volatile impurities (more particularly ethane) and on the other hand at the upper end with liquid methane containing particularly more volatile impurities (nitrogen); in addition, there is introduced by way of the conduit 65 a mixture of liquid butanes and propane originating from the rectification column 17.

At the head of the column 15, there is discharged a gas containing a high proportion of volatile compounds (nitrogen), this taking place through the conduit 66. A portion thereof is reunited by way of the conduit 67 with the non-liquefied gas in the exchanger 14 and expanded in the valve 70, as already indicated; the other portion is expanded in the valve 68 to approximately 7 kg./cm.² and conducted through the conduit 69 to the cold end of the exchanger 14, after having added thereto gaseous fractions originating from the previously mentioned condenser 33 and expansion valve 29, as well as another gaseous fraction originating from the separator 75, to which reference is still to be made.

On the other hand, a liquid containing methane and heavier hydrocarbons, with a small amount of residual nitrogen, in the liquid state is withdrawn from the bottom of the column 15. This liquid is expanded in the valve 74 to approximately 7 kg./cm.² and introduced into the separator 75. The vapours formed by the expansion are conducted through the conduit 76 to the cold end of the exchanger 14, with the gaseous fractions referred to above. The remaining liquefied natural gas is expanded once again in the valve 77 to 1.3 kg./cm.² and introduced into the separator 78. The liquefied natural gas substantially free from gases more volatile than methane is then conducted through the conduit 79 to a storage reservoir (not shown). The low-pressure vapours formed in this last expansion are recycled; they are first of all returned through the conduit 80 to the exchanger 64, where they are reheated to approximately -80° C. in heat exchange with the mixture of liquid butanes and propane to be fed into the degasification column 15. They then pass through the conduit 81 into the exchanger 54, where they are reheated to approximately

the ambient temperature in heat-exchange with the released vapours at the top of the rectification columns 16 and 17, and finally pass through the conduit 82 to the first compressor stage 83, provided for compressing the recycled vapours to the pressure of the treated natural gas.

On the other hand, the vapours originating from the degasification column 15 and the separator 75 pass by way of the conduit 69 into the exchanger 14, after addition of the liquid expanded by the valve 29, are reheated therein to -90° C. approximately, in heat exchange with the natural gas undergoing condensation. They then pass through the conduit 84 into the exchanger 13, where their temperature rises again to approximately -75° C. and then, after addition through the expansion valve 85 of a supercooled liquid with a high ethane and propane content originating from the separator 7, they pass through the conduit 86 into the exchanger 12, where they are reheated to -57° C. After addition through the valve 88 of a supercooled liquid with a high butane content originating from the separator 4, they are reheated in the exchanger 11 to -31° C. Finally, after addition thereto by means of expansion valve 91 of a liquid with a high content of butanes originating from the water condenser 36 placed at the outlet of the recycling compressor 83 and supercooled in the exchanger 10 after a first expansion in the valve 39, they reach the exchanger 10 by way of the conduit 92, which exchanger restores them to the region of the ambient temperature. They are finally returned through the conduit 57 to an intermediate stage of the compressor 83.

The gaseous mixture recompressed by the compressor 83 to approximately 30 kg./cm.² is returned by way of the conduit 35 to the condenser 36, cooled by a water circulation coil 37. There is condensed therein a liquid formed mainly of butanes, which is evacuated through the conduit 38. A first portion of this liquid is expanded in the valve 39 to 15 kg./cm.² and sent by way of the conduit 40 to the exchanger 10, where it is supercooled to -15° C. before being expanded in the valve 91 and reunited with the gaseous fraction recycled during its reheating at the cold end of the exchanger 10. The second portion is expanded in the valve 41, likewise to about 15 kg./cm.², and introduced into the upper portion of the rectification column 16, heated at its lower end by a steam coil 42. The most volatile constituents (nitrogen, methane, ethane) are released at the top and are introduced through the valve 45 into the conduit 50, in which liquid butane is circulating, the origin of this butane being hereinafter referred to. After another fraction of relatively volatile gases, separated at the head of the rectification column 17, to which reference will later be made, has been added by means of the valve 53, the mixture of these gases is cooled to approximately -15° C. in the exchanger 54, in counter-current with methane originating from the low pressure separator 78 and already partially reheated in the exchanger 64. They are then expanded in the valve 55 to approximately 7 kg./cm.² and reunited by means of the conduit 56 with the gaseous fraction recycled during its reheating at the cold end of the exchanger 10.

The liquid mixture comprising propane and butanes collected at the base of the column 16 is conducted through the conduit 43 and the regulating valve 44 into the second rectification column 17, cooled at its upper end by a water circulation coil 46 and heated at its bottom end by a steam coil 47. The most volatile gases liberated at the upper end are conveyed through the regulating valve 53 into the conduit 50 already referred to. On the other hand, the substantially pure liquid butane present at the bottom of the column 17 is drawn off at a rate which can be regulated by the valve 49 (the valve 51 being closed) and evacuated through the conduit 50. Finally a liquid mixture of propane and butanes collected at the head of the column 17 is evacuated through the

conduit 58; the valve 59 being closed and the valve 61 open, it is supercooled in the exchanger 62 to approximately -75°C . in heat exchange with the mixture of methane and nitrogen separated at the head of the degasification column 15 and already partially reheated in the exchanger 26. It is then supercooled once again to approximately -110°C . in the exchanger 64 in counter-current with the methane vapours originating from the separator 78, then introduced through the conduit 65 and the regulating valve 65A into the degasification column 15.

On the other hand, if it is desired to separate fractions of liquid butanes and propane, the valves 49, 61, 65A and 72A are closed and the valves 51, 59 and 72B are opened. The liquid butane collected at the base of the column 17 is conducted to the storage container through the conduit 52 and the operation of this same column is regulated so as to discharge substantially pure liquid propane through the conduit 58; this propane is sent for storage through the conduit 60. The heat exchangers 62 and 64 are then rendered inoperative, and the mixture of methane and nitrogen arriving by way of the conduit 72 is then reheated to the proximity of ambient temperature in the exchanger 54, then conveyed to the point of use by way of the conduit 73B.

If it should be desired, it is also possible to separate a liquid ethane fraction by the liquid with a high ethane content obtained in the separator 20 being conveyed to a supplementary rectification column analogous to the columns 16 and 17.

In the installation according to FIGURE 2, the natural gas to be liquefied is first of all cooled in a series of exchangers 110, 111 and 112, while the recycled non-liquefied gas is separately cooled in a series of exchangers 145, 120, 121 and 122. The natural gas to be liquefied and the recycled gas are then reunited and cooled together in the exchangers 130 and 131, then liquefied and rectified in a column 116. The liquefied gas is sent to a storage reservoir, while the non-liquefied gas, separated from a fraction containing principally nitrogen, is reheated at two different pressures, a mean pressure in the region of 6.5 kg./cm.^2 and a low pressure in the region of atmospheric pressure; the two reheated fractions are reunited, recompressed to the pressure of the natural gas, and then subjected to cooling in the exchangers 145, 120, 121 and 122 already referred to.

The natural gas arriving by way of the conduit 101 enters the heat exchanger 110, where it circulates in parallel with a liquefied fraction of the recycled gas and in counter-current with the non-liquefied gas under a mean pressure (6.5 kg./cm.^2) to be reheated. It is cooled therein to approximately -15°C . and its heavier fractions (butane, isobutane) are condensed; at the outlet of the exchanger, they are separated from the gas remaining in the liquid separator 102, then conveyed by way of the conduits 103 and 107 and the expansion valve 107A at approximately 15 kg./cm.^2 absolute, and after addition of the condensed liquid originating from the separator 106 at lower temperature, to the heat-exchanger 132, the purpose of which will be hereinafter described.

The natural gas at -15°C . leaving the separator 102 passes through the conduit 104 into the exchanger 111, in which it is cooled by the same recycled gas under medium pressure to -45°C . approximately, while the major part of the propane which it contains is condensed.

It is then fed through the conduit 105 into the separator 106, where it is separated from the liquefied fraction with a high propane content. This latter fraction is reunited by way of the conduit 107 with the fraction having a high butane content and originating from the conduit 103, and sent with it to the exchanger 132, after expansion in the valve 107A.

The natural gas cooled to -45°C . then passes through the conduit 108 into the exchanger 112, in which it is cooled, always in counter-current with the recycled gas at

average pressure, to -67°C ., while a part of the ethane which it contains is condensed. Through the conduit 109, it is fed to the separator 210, where the liquid is separated and is then conveyed through the conduit 211 and the expansion valve 211A at 15 kg./cm.^2 to the conduit 133, where it is reunited with the fractions previously condensed and supercooled in the exchanger 132, at the inlet end of the exchanger 134, the purpose of which will be set out in detail hereinafter.

The remaining natural gas, at -67°C ., is reunited through the conduit 212 with the gas recycled at the same pressure and at approximately -72°C ., arriving by way of the conduit 113 at a rate of about 4000 cubic metres per hour. The combined gas stream then enters the exchanger 130, where it is cooled to approximately -80°C . in counter-current with gas recycled at mean pressure. A fresh fraction of condensed ethane is evacuated through the conduit 114, supercooled in the coil 115 in heat exchange with the base of the rectification column 116, then expanded to about 15 kg./cm.^2 and introduced at a regulatable rate through the expansion valve 118 into this column. Another fraction passes by way of the conduit 119 to the expansion valve 220 at intermediate pressure, where it is recombined with the cold gas recycled at mean pressure, the origin of which will be hereinafter indicated.

The remaining natural gas, now composed almost exclusively of methane and more volatile gases, particularly nitrogen, is sent through the conduit 221 to the final exchanger 131, in which it is cooled to about -100°C . in heat exchange with the recycled gas at average pressure. Practically all the methane is liquefied and conducted through the conduit 222 and the expansion valve 123 at 15 kg./cm.^2 to the head of the rectification column 116. The non-liquefied fraction, constituted by a mixture of methane and nitrogen, is reunited by the expansion valve 124 with the gaseous fraction separated at the head of the rectification column 116 and discharged through the conduit 125.

The rectification column 116 is moreover supplied with liquid fractions with high contents of butanes, propane and ethane, originating from separators 102, 106 and 210, expanded to 15 kg./cm.^2 , then supercooled respectively in the exchangers 132 and 134 in counter-current with the gas discharged from the separator 138. These fractions are introduced through the conduit 135 into the middle zone of the column. The separation effected in the column 116 may be regulated by varying the rate of flow of liquid entering the coil 115, and as a consequence the rate of vaporisation in the vessel of the column, due to a bypass, adjustable by a valve 117.

The mixture of methane and nitrogen discharged at the top of the rectification column 116 is reheated in the exchangers 165 and 148 in heat-exchange with condensed liquid fractions, then evacuated through the conduit 168 in order for example to be employed as a fuel.

The liquid withdrawn at the base of the column 116 and substantially free from nitrogen and other volatile gases passes through the conduit 126 to the expansion valve 127, which expands it to a pressure of approximately 6.5 kg./cm.^2 and then to the separator 128. The fraction vaporised by the expansion is conducted through the conduit 129 to the exchanger 131, after a liquid fraction originating from the heating coil 115 has been added thereto through the expansion valve 220. The non-vaporised fraction is conducted through the conduit 136 and the expansion valve 137 at a low pressure in the region of atmospheric pressure to the separator 138. The natural gas which has remained in the liquid state is conducted through the conduit 142 to the storage reservoir, not shown. The vapours formed during this final expansion, which contain a large proportion of methane, are reheated in heat exchange with the fractions condensed in the exchangers for cooling the natural gas, in the exchangers 134 and 132, and are then returned through the conduit 141 to the recycling compressor 143.

On the other hand, the vapours released during the expansion to the intermediate pressure are reheated in the exchanger 131 to approximately -88°C ., by the combined stream of natural gas and recycled gas.

After a fraction of the recycled gas liquefied under pressure in the exchanger 122 has been added thereto through the expansion valve 166, the combined gases pass through the conduit 169 into the exchanger 130, where they are again reheated to approximately -76°C .. After a fraction of the recycled gas liquefied under pressure in the exchanger 121 and supercooled in the exchanger 112 to approximately -67°C ., has been added thereto through the expansion valve 162, the combined gases are divided into two portions.

The major portion of the cold gas recycled at mean pressure is conveyed in heat exchange with the recycling gas previously recompressed to the pressure of the natural gas into the multi-stage compressor 143. It thus enters the exchanger 122 by way of the conduit 171 and is reheated in the exchanger to -58°C .. After a fraction of recycling gas at 30 kg./cm.^2 and liquefied in the exchanger 120 and supercooled in the exchanger 111 to approximately -45°C ., has been added thereto by way of the expansion valve 157, it passes through the conduit 173 into the exchanger 121, where it continues its reheating to approximately -25°C .. Finally, it enters the exchanger 120 by way of the conduit 150, after addition through the expansion valve 149 of a fraction with a high butane content liquefied in the water condenser 145 and supercooled in the exchanger 148 in counter-current with the gas having a high nitrogen content separated at the head of the rectification column 116. It is reheated therein to approximately $+22^{\circ}\text{C}$., and, after the addition thereto, through the conduit 178, of the other gaseous fraction at mean pressure, reheated in counter-current with the natural gas, it enters an intermediate stage of the compressor 143 of the recycling gas.

The other portion of the cold gas at mean pressure, conducted in heat exchange with the natural gas to be cooled, is first of all reheated to approximately -58°C ., in the exchanger 112, then to -28°C ., in the exchanger 111, and finally to approximately $+20^{\circ}\text{C}$., in the exchanger 110; it is then reunited with the other portion at the inlet to the recycling gas compressor 143.

It will be noted that practically all the recycling gas recompressed by the compressor 143 to the pressure of the treated natural gas, namely 30 kg./cm.^2 , is supplied by the gas expanded to a mean pressure, 6.5 kg./cm.^2 , at a rate in the region of 5000 cubic metres per hour, to the inlet of the intermediate stage of the compressor, and for a very small part (about $200\text{ m.}^3/\text{h.}$) by gas previously expanded to the region of atmospheric pressure. The necessary compression energy is thus substantially that necessary for bringing the recycled gas from 6.5 kg./cm.^2 to 30 kg./cm.^2 .

The recycling gas, brought by the compressor 143 to the pressure of 30 kg./cm.^2 and to a temperature of about 32°C ., is cooled in the exchanger 145 by a water circulation coil 146. Its temperature is lowered to about 30°C ., and a fraction formed mainly of butane is liquefied. This latter fraction, discharged through the conduit 147, is divided into two portions. The first portion, after supercooling to -15°C ., in the exchanger 148 in counter-current flow with the mixture of methane and nitrogen delivered from the head of the rectification column 116, is expanded by the valve 149 and vaporised in the gas recycled at mean pressure, at the cold end of the exchanger 120. The second portion is conveyed through the conduit 151 to the exchanger 110, where it is cooled to -15°C ., in parallel with the natural gas, then it is reunited by means of the conduit 152 and the expansion valve 153 with the gas recycled at mean pressure at the cold end of the exchanger 110, and is vaporised therein.

The main fraction of the recycling gas, which has remained in the gaseous state, passes through the conduit

154 into the exchanger 120, where it is cooled to about -15°C .. The last fractions of butane and propane are then condensed. This liquid fraction is conveyed through the conduit 155 to the exchanger 111 of the cooling circuit for natural gas, where it is supercooled to -45°C ., approximately. It then passes through the conduit 156 to the expansion valves 157 and 158, which introduce it respectively into the two fractions of recycled gas at mean pressure, where it is vaporised during the passage thereof in the exchangers 111 and 121.

The main gaseous fraction then passes through the conduit 159 into the exchanger 121, where it is cooled to about -49°C ., while a liquid formed mainly of propane is condensed. In analogous manner to the preceding liquid fraction, this liquid is conveyed through the conduit 160 to the exchanger 112 for cooling the natural gas, where it is supercooled to -67°C .; it is then expanded by the valve 162 to 6.5 kg./cm.^2 and introduced into the gas recycled at mean pressure and leaving the warmer end of the exchanger 130.

The non-liquefied recycling gas is then reunited by means of the conduit 113 with the natural gas arriving by way of the conduit 212 at a similar temperature (-67°C .).

In the installation shown in FIGURE 3, the natural gas to be liquefied, with an identical flow rate and composition, as well as the pressure and temperature according to the previously indicated values, has added thereto, by means of the conduit 2, a recycled gaseous fraction which has a high content of hydrocarbons heavier than methane, the origin of which will be hereinafter indicated. The cooling thereof is effected in a series of heat exchangers 10 to 16, while the rectification columns 18 and 19 permit the separation of a liquid fraction with a high content of propane and butanes. The liquefied gas is subjected to a degasification of its most volatile fractions in the rectification column 17 before being expanded and sent for storage.

The cooling of the natural gas takes place as follows. The mixture of natural gas and recycled vapours is introduced through the conduit 3 into the heat exchanger 10, where it is cooled to about -15°C ., in heat exchange with a mixture of gas and liquid at lower pressure (about 7 kg./cm.^2) introduced through the conduit 84, and concurrently with a liquid fraction having a high butane content introduced through the conduit 90 for the purpose of its supercooling. During this cooling of the natural gas, a liquid with a high content of butanes is condensed and this liquid is separated from the remaining gas in the separator 4. This liquid is conveyed through the conduit 6 into the following exchanger 11, where it is supercooled to about -50°C ., and then it is reunited by means of the conduit 78 and the expansion valve 79 with the recycled vapours arriving at the cold end of the exchanger 11, in which vapours it is vaporised during the reheating thereof.

The remaining natural gas leaving the separator 4 is conveyed through the conduit 5 to the exchanger 11, where it is also cooled to -50°C ., while a liquid with a high content of butanes and propane is condensed before being separated in 7 from the remaining gas. This liquid passes by way of the conduit 9 into the exchanger 12, by which it is supercooled to approximately -70°C ., and then it is introduced through the conduit 74 and the expansion valve 75 into the recycled vapours reaching this same exchanger.

The residual gas discharged from the separator 7 through the conduit 8 then enters the exchanger 12, where it is also cooled to -70°C .. The liquid with a high propane content, which is condensed, is collected at 20, sent by way of the conduit 22 to the exchanger 13, and supercooled in this latter to -85°C .. The first portion is reunited by means of the conduit 70 and the expansion valve 71 with the cold vapours reaching the exchanger 13. A second portion is introduced through

the conduit 65 and the expansion valve 66 into the gas separated from the liquefied methane leaving the exchanger 16.

The gaseous mixture under pressure, leaving the separator 20, passes through the conduit 21 into the exchanger 13, where its temperature is lowered to -85°C . The condensed liquid, rich in ethane, and collected at 23, passes through the conduit 25 to the exchanger 14, where it undergoes a supercooling to about -100°C . It then passes through the conduit 51 into the exchanger 16, where it is again cooled to about -125°C . At the cold end of this exchanger, it is divided into two portions; the major portion is reunited by means of the conduit 54 and the expansion valve 55 with the gas separated from the liquid methane in the degasification column 17 and recycled; another portion is sent through the conduit 52 and the expansion valve 53 at about 7 kg./cm.^2 into the upper portion of the column 17.

The gas remaining at the outlet of the separator 23, free from the major part of the hydrocarbons other than methane, passes through the conduit 24 into the exchanger 14, where its temperature falls to -100°C . A part of the methane is condensed and is collected in the separator 26. The remainder passes through the conduit 27 into the exchanger 15, where its temperature is progressively lowered to approximately -105°C , while the major part of the remaining methane is liquified and collected in the base of the exchanger before rejoining, through the conduit 29, the already liquefied portion leaving the separator 26 by way of the conduit 28. The liquid methane thus collected is conveyed through the conduit 30 into a coil 31, in heat exchange with the base of the degasification column 17, in which it is supercooled; it then passes through the conduit 32 into the exchanger 16 already referred to, where it undergoes a final cooling to -125°C . before being introduced through the conduit 33 and the expansion valve 34 into the head of the degasification column 17.

The residual gas, not condensed in the exchanger 15 and constituted for example of a mixture of 70% of methane and 30% of nitrogen at approximately -105°C ., is sent through the conduit 35 to a coil 36 in the base of the column 17. It leaves the latter, cooled to approximately -125°C ., and then passes through the conduit 37 into the exchanger 38, concurrently with the liquid methane withdrawn at the base of the column 17, its temperature falling to -145°C . Leaving this exchanger by way of the conduit 39, it is divided into two parts.

The first part, passing through the conduit 40, is expanded in the valve 41 to about 7 kg./cm.^2 , then returns to the cold end of the exchanger 38 so as to assure therein a first supercooling of the liquid methane originating from the degasification column 17. It is then reunited by way of the conduit 42 with the vapours discharged at the head of the column 17, and introduced with them through the conduit 63 into the exchanger 16. The second part of the mixture of approximately 70% methane and 30% nitrogen at low temperature is introduced through the conduit 43 into the exchanger 44, subjected to a last cooling to approximately -165°C . in this latter, then expanded by the valve 45 to about 2 kg./cm.^2 and returned to this exchanger with the object of ensuring the final supercooling of the liquid methane, where the methane enters this exchanger through the conduit 58 before being sent to the reservoir. The second part then passes successively through the conduits 46 and 48 into the exchangers 47 and 49, in heat exchange with a liquid having a high content of propane and butanes, then it is evacuated substantially at ambient temperatures through the conduit 50 and sent to the place for use, for example as a fuel, in view of its high content of methane.

As already mentioned, the degasification column 17, heated at its base by the coils 31 and 36 and cooled at

its upper end by the arrival of supercooled liquid through the conduit 33, makes it possible to eliminate the last fractions of more volatile gases dissolved in the liquid methane. This latter is withdrawn from the base of the column through the conduit 56, supercooled in the exchangers 38 and 44 to about -162°C ., then expanded in the valve 59 to its storage pressure, which is in the region of atmospheric pressure. This liquid does not contain more than traces of nitrogen and other gases more volatile than methane.

The volatile vapours discharged at the head of the column 17 through the conduit 61, have added thereto, through the conduit 54 and the valve 55, the liquid with a high ethane content originating from the separator 23 and supercooled in the exchangers 14 and 16, and then is added through the conduit 42 with the gas having a high nitrogen content expanded in the valve 41 and reheated in the exchanger 38 in counter-current with the liquid methane. After vaporisation and reheating in the exchanger 16 to -125°C ., they are mixed with the liquid having a high propane content originating from the separator 20, supercooled in the exchanger 13 and expanded in the valve 66. The combined stream is vaporised and reheated to approximately -90°C . in the exchangers 15 and 14, then it is reheated to ambient temperature, after successive additions of liquid fractions condensed under pressure, in the exchangers 13, 12, 11 and 10. The recycled fraction leaving the exchanger 10 through the conduit 85 is then brought by the compressor 86 to the initial pressure of the natural gas, which is about 30 kg./cm.^2 .

The recycled and recompressed fraction is then sent by way of the conduit 87 to the water condenser 88, equipped with a cooling coil 89. The uncondensed gas is reunited through the conduit 2 with the natural gas to be liquefied. A fraction condensed in this condenser, formed mainly of butane and propane, is sent through the conduit 90 to the exchanger 10, where it is supercooled. A first part of this condensed fraction is reunited through the conduit 82 and the expansion valve 83 with the fraction recycled under low pressure during reheating at the cold end of the exchanger 10. The second part is sent through the conduit 91 and the expansion valve 92 at 15 kg./cm.^2 to the rectification columns 18 and 19, provided for eliminating the propane and the butane continuously introduced into the apparatus. To this end, the column 18 is heated at its base by a steam coil 93. The most volatile fractions (nitrogen, methane, ethane) are released at the head of column 18. The most volatile fractions are expanded in the valve 103 to 11 kg./cm.^2 and the residual volatile fraction released in the column 19 is added thereto by way of the valve 104 the mixture from the two columns is then sent through the conduit 105 to the exchanger 49 in counter-current with the mixture of methane and nitrogen being reheated and already mentioned. Thus cooled to about -30°C ., the volatile vapours are reunited through the conduit 106, the expansion valve 107 and the conduit 108 with the fraction recycled during the reheating, at the cold end of the exchanger 10.

The liquid mixture of propane and butanes collected at the base of the column 18 is introduced through the conduit 94 and the expansion valve 95 into the central portion of the second rectification column 19, at a pressure of about 11 kg./cm.^2 . This column is heated at its base by a steam coil 96 and cooled at its upper end by a water circulation coil 97. The volatile vapours released at the head of this column are reunited by means of the valve 104 with the vapours leaving the top of the column 18. On the other hand, a liquid fraction with a high butane content is withdrawn at the base of the column 19, and this fraction is cooled in the water condenser 99, equipped with a coil 100, and then conveyed by way of the conduit 101, the expansion valve 102 and the conduit 108 into the recycled fraction at the cold end of the exchanger 10.

Finally, in the upper part of the column 19, at 109, a liquid with a high content of propane and butanes is drawn off, and this liquid is conveyed through the conduit 110 to the exchangers 49 and 47, where it is cooled from +40° C. to approximately -145° C. in heat exchange with the mixture of methane and nitrogen to be reheated, as slowly mentioned. It is finally expanded to approximately 7 kg./cm² in the valve 112 and reunited with the liquid methane at the inlet end of the supercooling exchanger 44.

It will be noted that the saving in energy of the installation which has just been described, relatively to those FIGURES 1 and 2 of the drawing, is in fact greater than single energy of recompression of the fraction recycled at low pressure. In effect, it can be estimated approximately that the vapours which were reheated under low pressure in the installation according to FIGURES 1 and 2 are this time reheated under the same intermediate pressure as the others, so that the vaporisation of the condensed fractions takes place according to the present improvement in the presence of more volatile vapours and consequently at lower temperature. Thus, for the fractionated condensation, there is obtained a greater transmission of cold for an unchanged heat-exchange surface, this corresponding to an appreciable energy gain.

What I claim is:

1. A process for liquefying a gaseous feed mixture at a relatively low temperature, comprising the steps of:

(a) passing the gaseous mixture through a condensing zone at relatively high temperature forming a high boiling point liquid and a low boiling point gas;

(b) withdrawing the low boiling point gas from the condensing step and passing it through a cooling zone to form a second liquid fraction and a second gaseous fraction;

(c) withdrawing the high boiling liquid from step (a), passing at least part of said liquid through a cooling zone, expanding said passed liquid to a lower pressure, and passing said expanded liquid back in counterflow through at least one of said cooling and condensing zones while vaporizing the expanded liquid to form a return fluid;

(d) recompressing said return fluid of step (c); and

(e) mixing the recompressed return fluid of step (d) with the gaseous feed mixture to be condensed.

2. A process as claimed in claim 1, and condensing from said second gaseous fraction a low boiling point liquid, and withdrawing from the process as product at least most of said low boiling point liquid.

3. A process as claimed in claim 2, in which said low boiling point liquid is expanded to a pressure substantially lower than said lower pressure of step (c), before being withdrawn from the process.

4. A process as claimed in claim 3, and liquefying a gaseous state fraction more volatile than said low boiling point liquid, expanding and vaporizing said liquefied gaseous state fraction by heat exchange with said low boiling point liquid prior to the expansion of the latter, thereby subcooling said low boiling point liquid to a temperature low enough to prevent appreciable partial vaporization on its expansion.

5. A process as claimed in claim 4, wherein said gaseous state fraction is liquefied by heat exchange with a rectification zone under substantially the same pressure as said lower pressure of said expanded high boiling liquid.

6. A process as claimed in claim 4, wherein said liquefied more volatile fraction is expanded to substantially the same pressure as said lower pressure of said expanded high boiling liquid, and after being vaporized is at least partly mixed with said expanded high boiling liquid.

7. A process as claimed in claim 4, wherein said liquefied more volatile fraction is supercooled concurrently with said low boiling point liquid, before being expanded and vaporized by heat exchange with said low boiling point liquid.

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