

June 7, 1966

Y. M. B. ROCHE ET AL

3,254,496

NATURAL GAS LIQUEFACTION PROCESS

Filed April 2, 1963

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Fig. 1

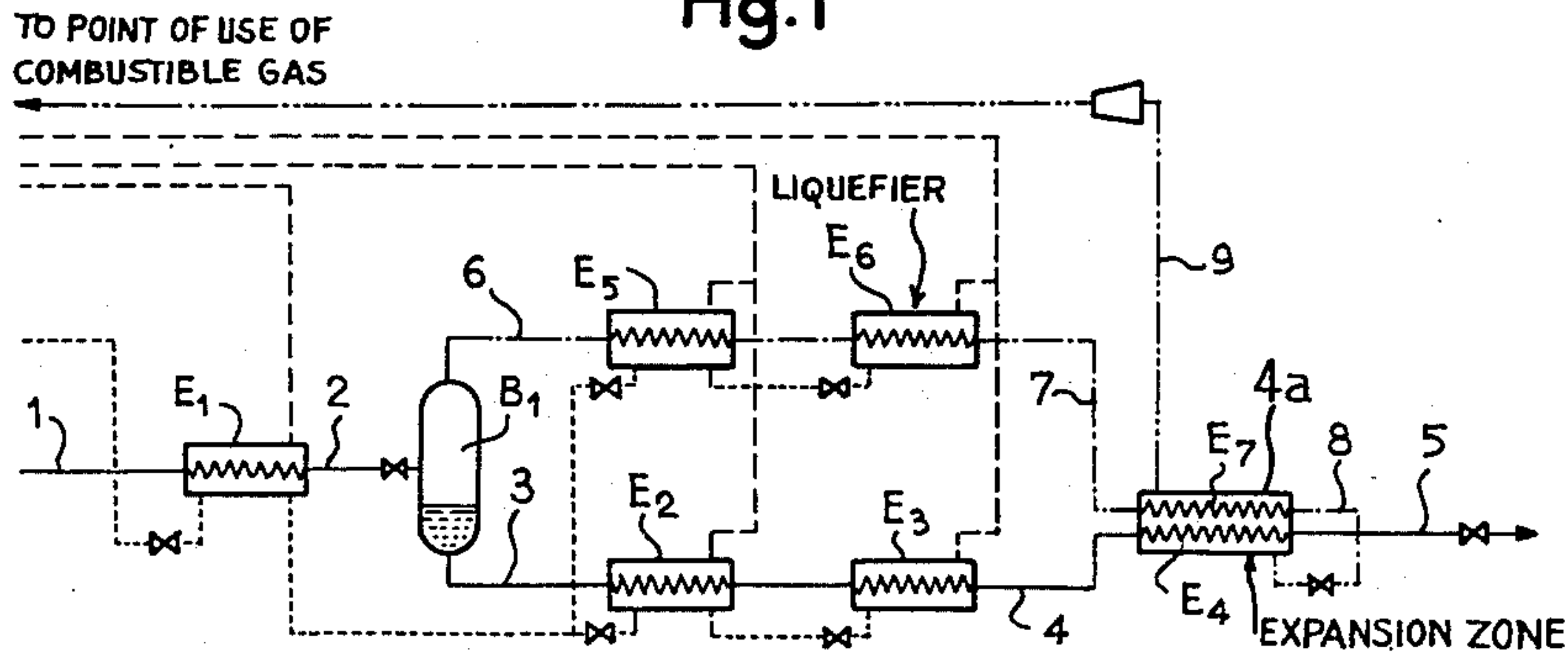


Fig. 2

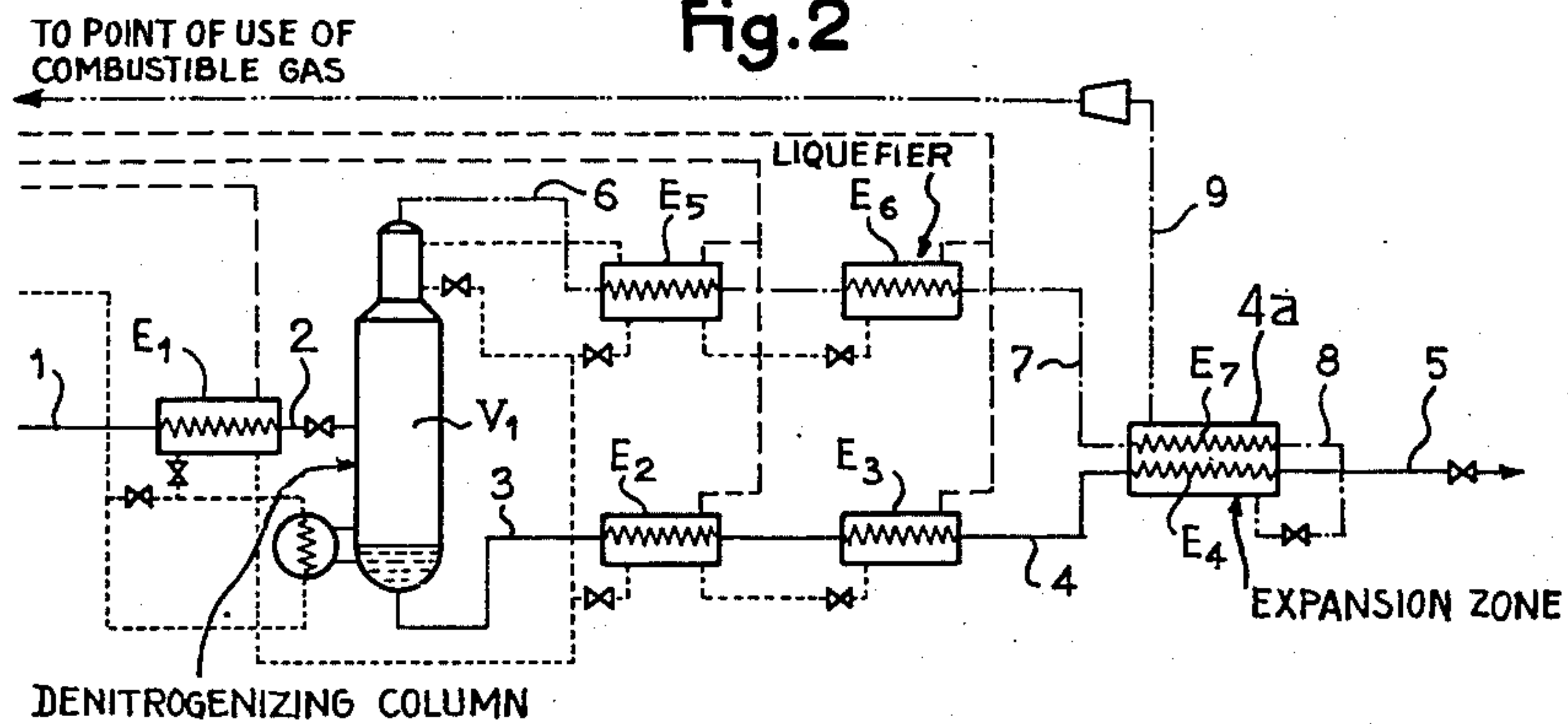
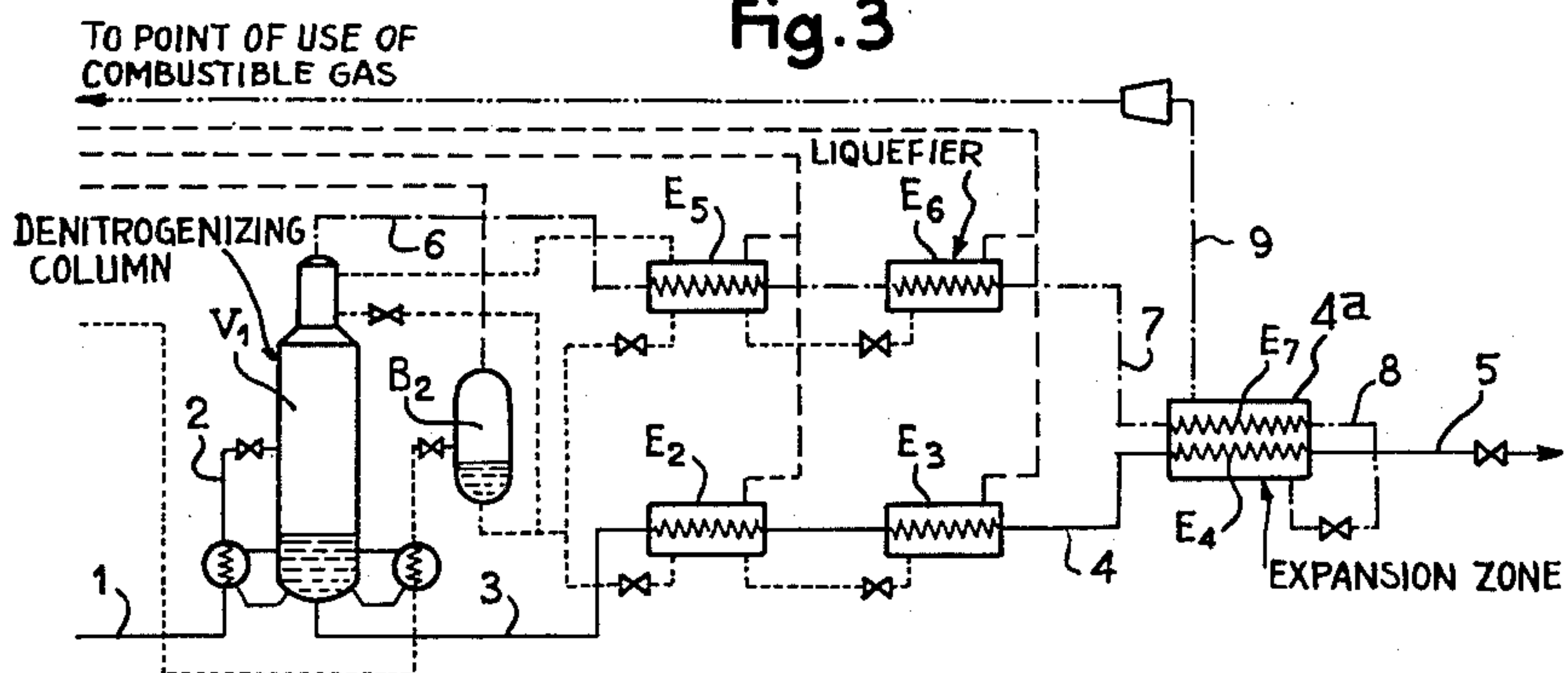


Fig. 3





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Fig. 5

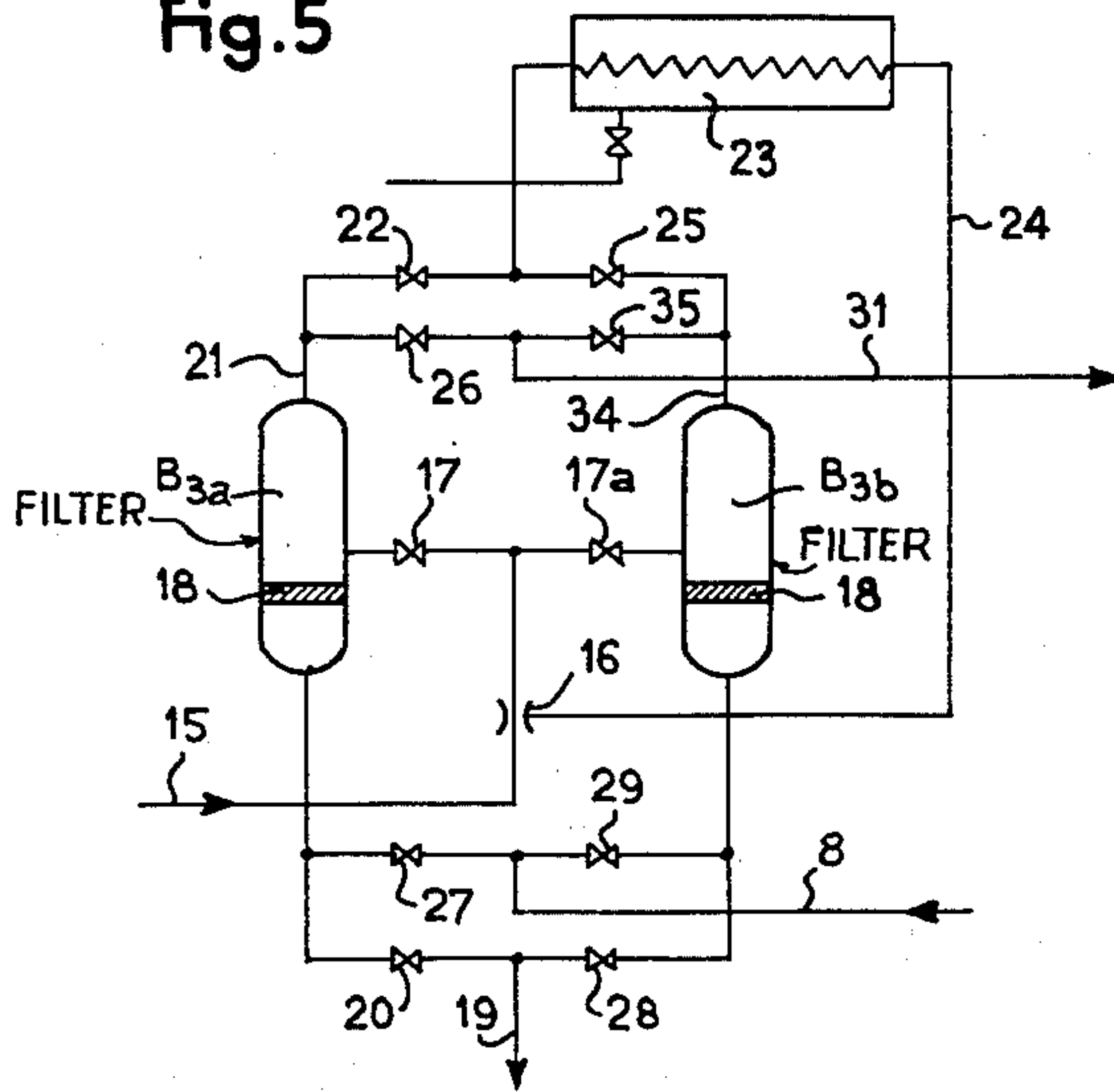
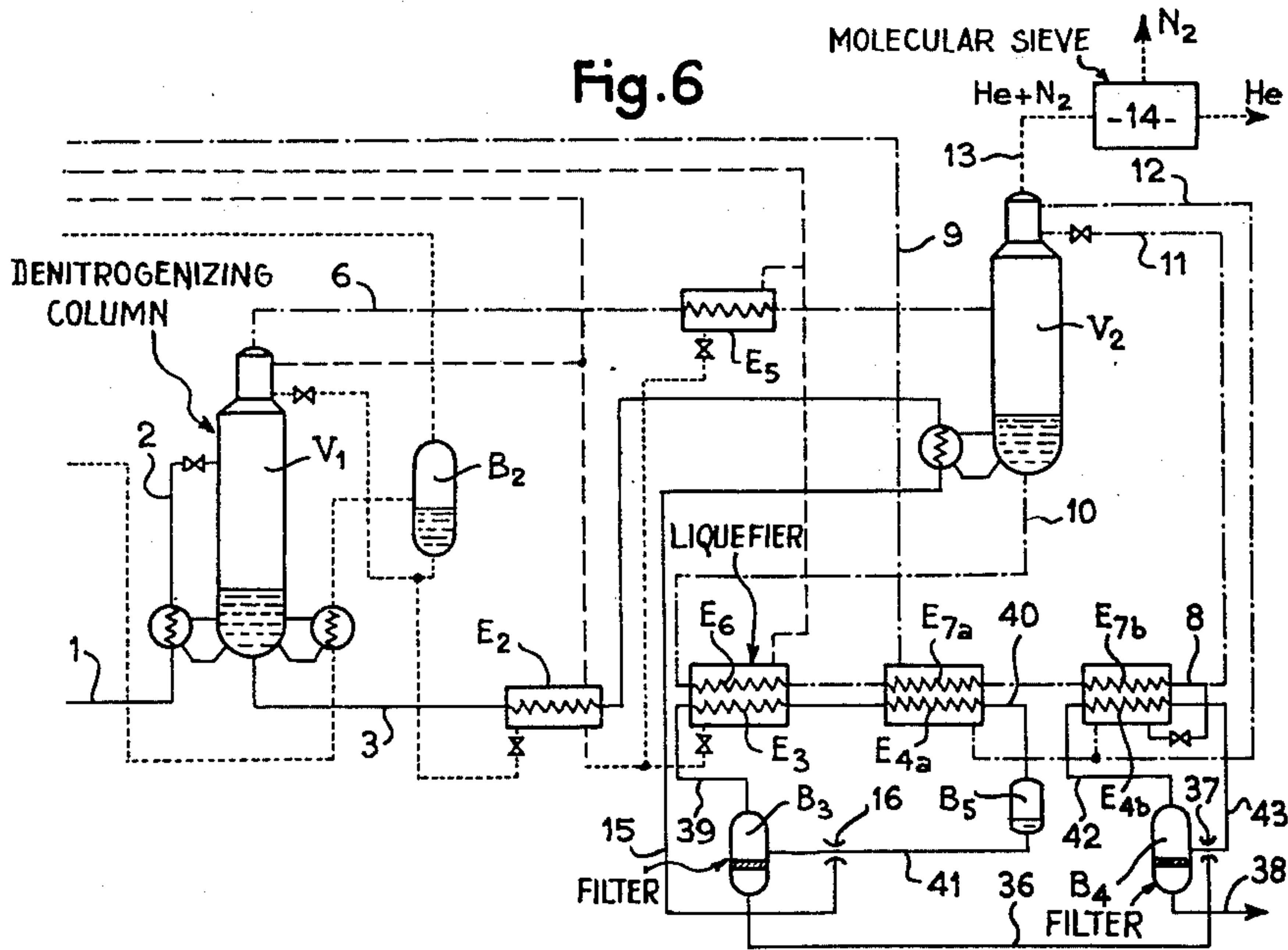


Fig. 6



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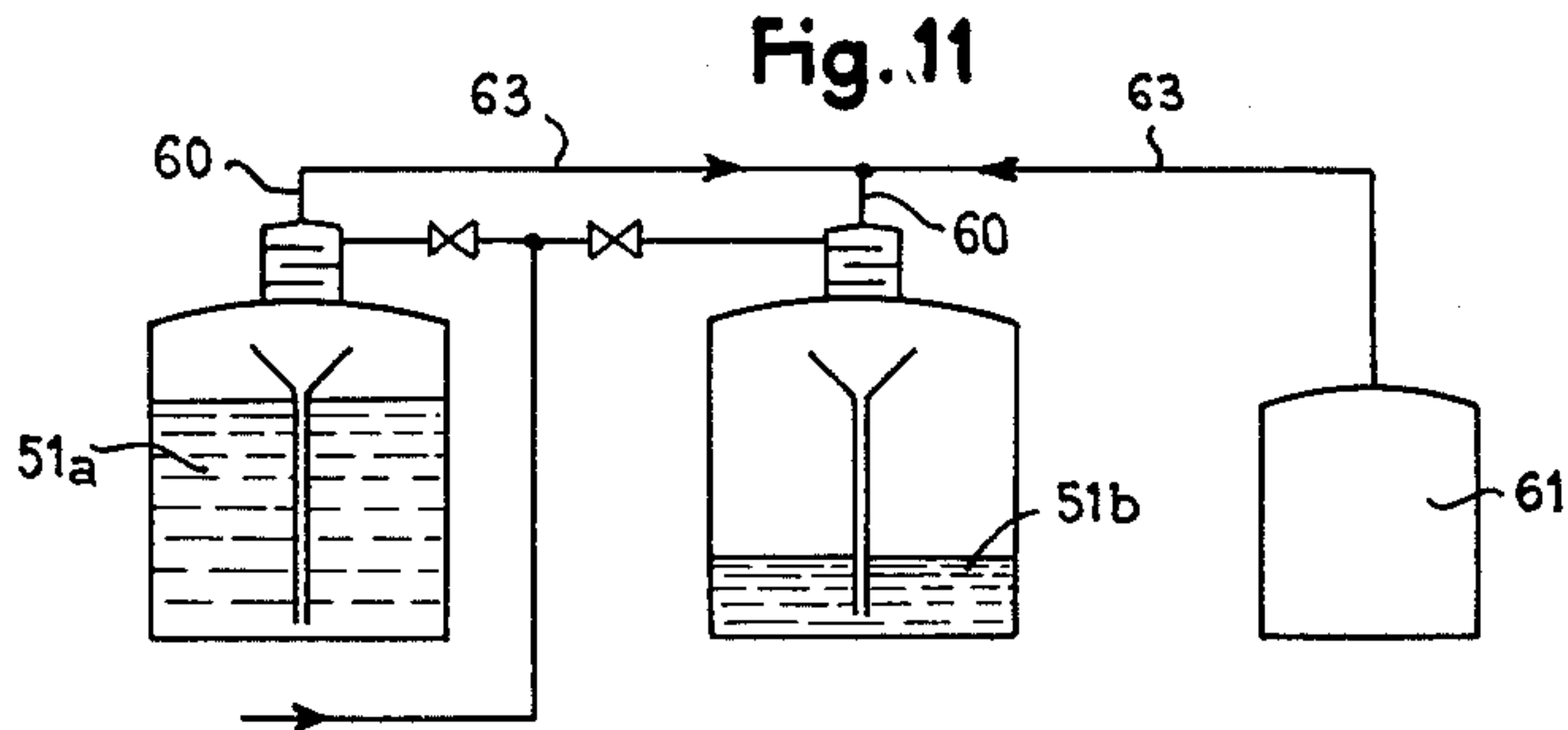
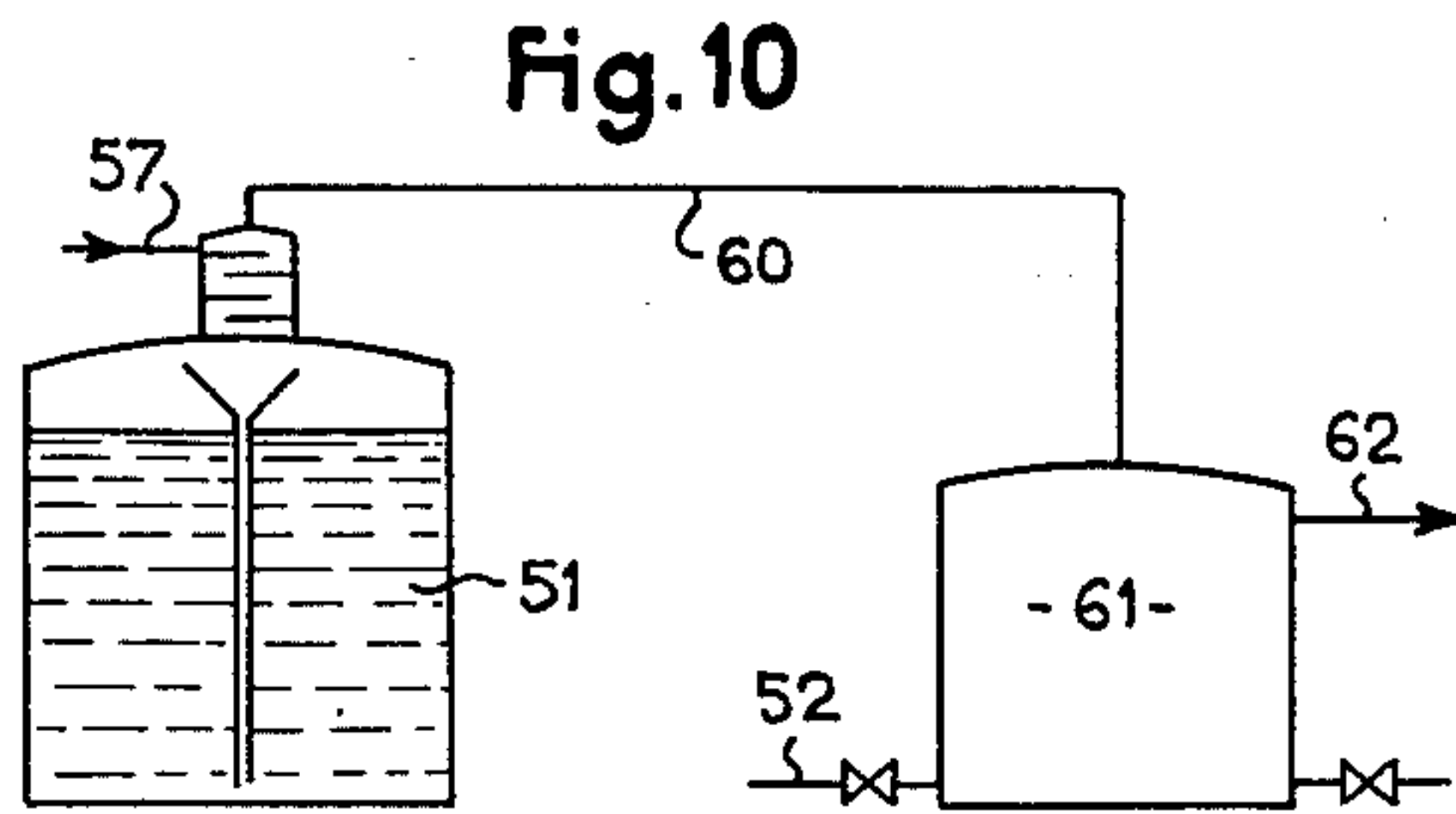
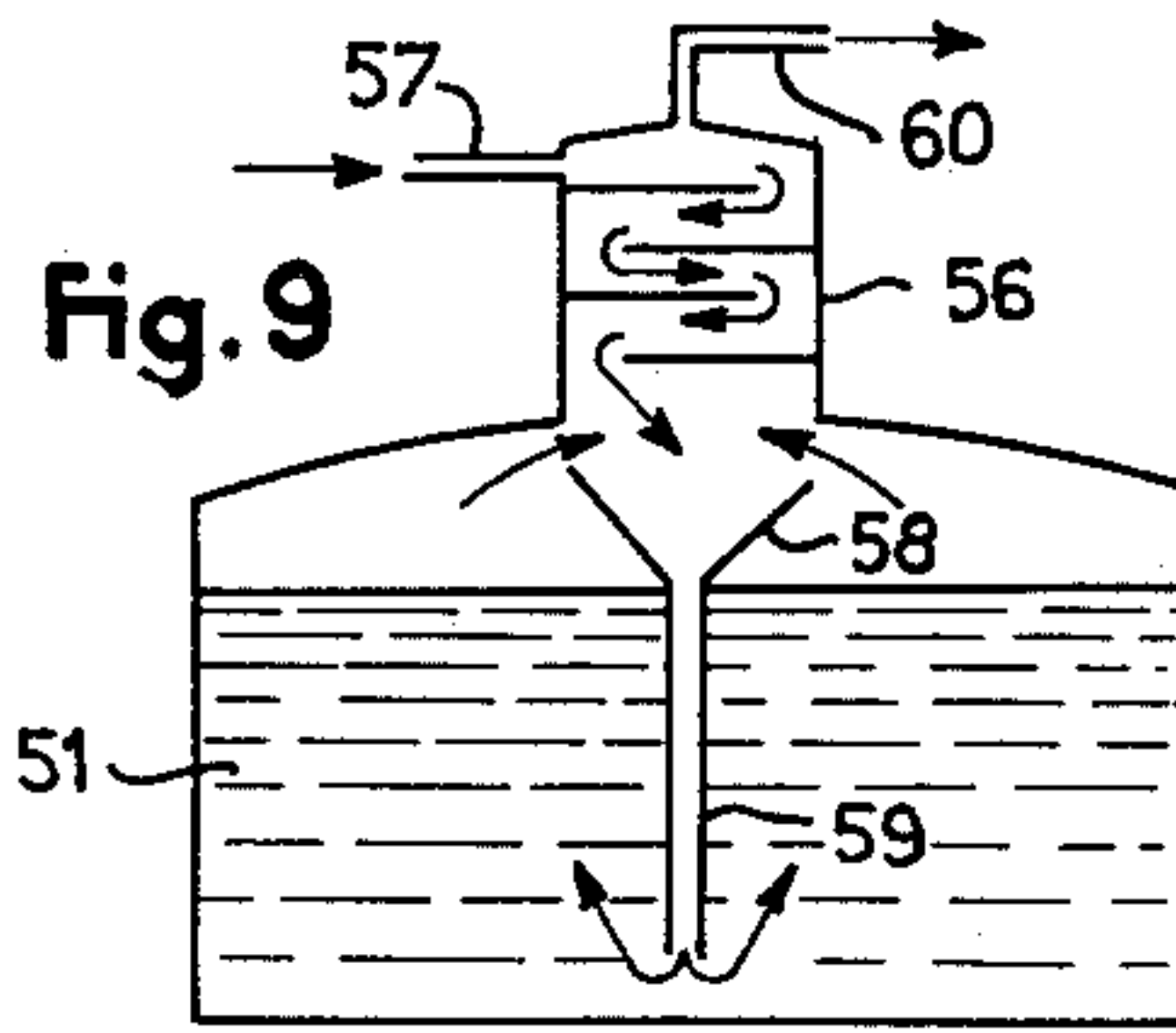
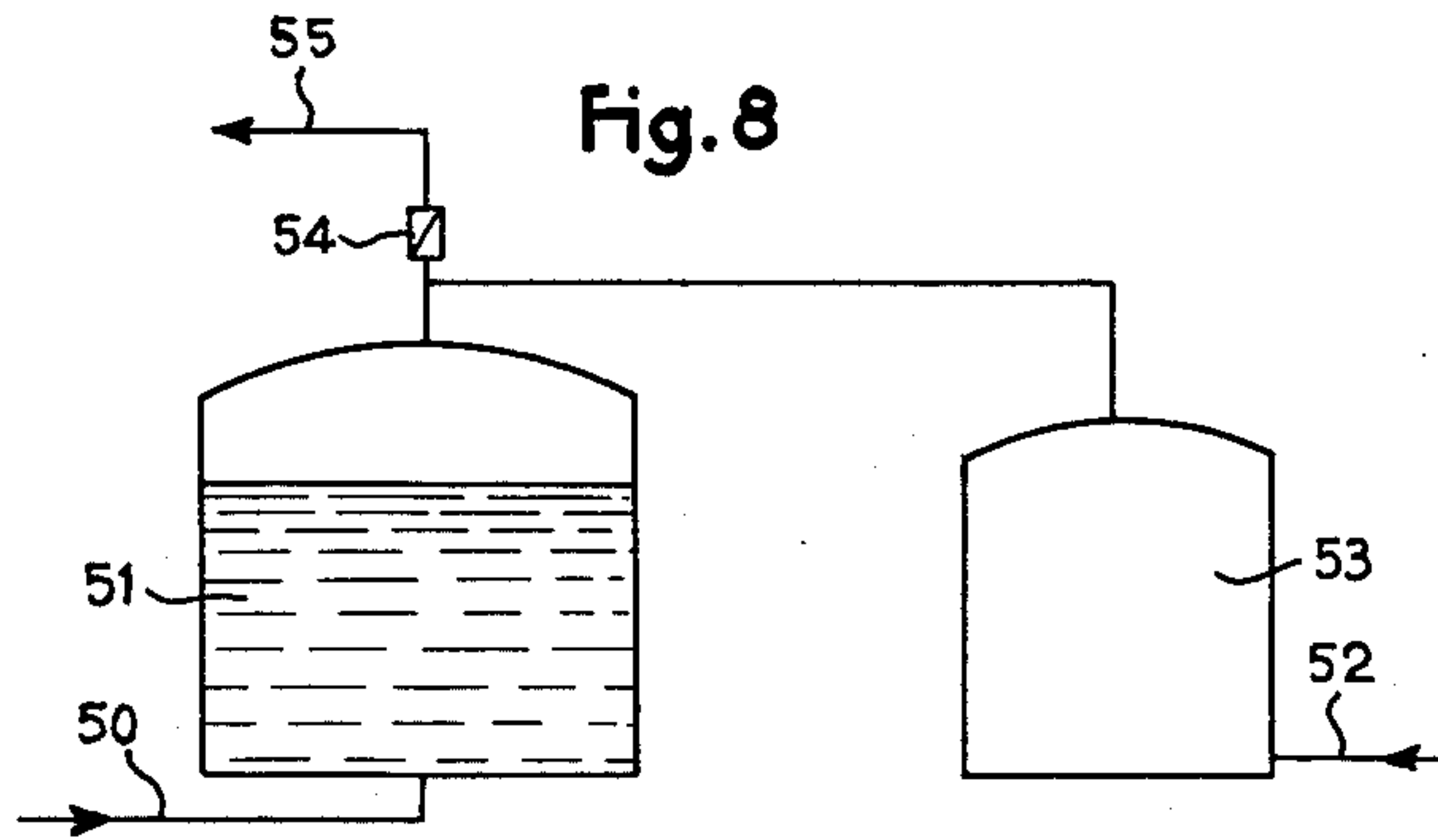
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## NATURAL GAS LIQUEFACTION PROCESS

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Claims priority, application France, Apr. 5, 1962, 893,475  
6 Claims. (Cl. 62-15)

The present invention relates to a process for liquefying natural gases and more particularly to an improved process of the cascade type for this liquefaction.

In general, known cascade processes of liquefaction of natural gases employ refrigeration cycles which are usually:

- (a) Propane,  $\text{NH}_3$  or  $\text{F}_{12}$  cycle.
- (b) Ethylene, ethane or  $\text{F}_{13}$  cycle.
- (c) Methane cycle.

These cycles are mentioned by way of example.

These known processes permit obtaining the natural gas which is in major part liquid at atmospheric pressure, a more or less large part remaining in the gaseous state. In general, this gas, which contains the major part of the more volatile neutral gases present in the natural gas, is employed as combustible gas after the sensible heat of the latter has been recovered if desired.

The object of the present invention is to provide a process for liquefying natural gases containing more or less large amounts of more volatile neutral gases of the cascade type comprising a plurality of successive refrigeration cycles, said process comprising adding to said cascade an additional refrigeration cycle of the natural gas in which there is utilized as refrigerating fluid, in an open circuit, the combustible gas containing the major part of the more volatile neutral gases separated from the natural gas current in the course of the preceding liquefaction operations of this cascade.

"More volatile neutral gases" is intended to mean gases such as nitrogen, helium, argon etc. contained in the natural gas. In order to simplify the disclosure, they will be designated hereinafter by the simplified expression of "neutral gases" it being understood that carbon dioxide is not included therein since it is less volatile than the natural gas obtained at the end of the process.

By means of the process according to the invention it is possible:

- (a) To produce a subcooled liquefied natural gas, namely a gas cooled below the boiling temperature at atmospheric pressure obtained at the end of liquefaction by the known processes.
- (b) To separate the neutral gases contained in the natural gas, and, if desired, increase the amount of helium contained in these neutral gases so as to facilitate the subsequent separation.
- (c) To eliminate the carbon dioxide by filtration in the course of liquefaction.
- (d) To regulate the amount of nitrogen contained in the liquefied natural gas so as to reduce the losses when storing.
- (e) To store at atmospheric pressure a subcooled liquid natural gas so as to result in the minimum of losses by evaporation.

Further features and advantages of the invention will be apparent from the ensuing description, with reference to the accompanying drawings to which the invention is in no way limited.

In the drawings:

FIG. 1 is a diagram of a plant for carrying out the process of the invention when the amount of neutral gas

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which remains in the liquefied natural gas at the outlet is not limited;

FIGS. 2 and 3 are plant diagrams of utility when the amount of neutral gas in the liquefied natural gas is limited to a given value;

FIG. 4 is a diagram of a plant identical to that shown in FIG. 3 but including the separation of the neutral gas;

FIGS. 5 and 6 are plant diagrams for carrying out the invention comprising a stage for eliminating  $\text{CO}_2$  in the course of liquefaction;

FIG. 7 is a diagram of a plant for carrying out the process of the invention comprising a stage regulating the amount of nitrogen contained in the liquefied natural gas, and

FIGS. 8, 9, 10 and 11 represent diagrammatically a plant for storing the liquefied natural gas.

In the various figures, identical elements carry the same reference characters, and for the sake of clarity only the essential elements of each plant have been shown, these plants being well known in the art.

The current of natural gas under pressure is previously cooled, then condensed at a temperature in the neighbourhood of  $-100^\circ \text{C}$ . by conventional cascade or other processes, the pressure of the current of natural gas being determined so as to obtain the latter in the liquid state in the neighbourhood of this temperature. It enters the plant shown in FIGS. 1-4 and 6 at 1.

Depending on the amount of more volatile neutral gas contained in the current of natural gas and that it is desired to maintain in the liquefied natural gas obtained by the process, one or the other of the plants shown in FIGS. 1, 2 and 3 is used.

It will be understood that the process is applicable only to a current of natural gas having an amount of more volatile neutral gas (nitrogen, helium etc. . . .) which is not nil.

First Case.—The amount of neutral gas contained in the liquid natural gas is not limited (FIG. 1).

The current of natural gas under pressure in the liquid state arriving at 1 is cooled in an exchanger  $E_1$ , which is the high pressure stage of the methane cycle for example of the aforementioned conventional cascade cycle, and passes through a point 2 before being expanded in a flash flask  $B_1$ . The expansion occurs between the pressure of point 2 and a pressure between 15 and 20 kg./sq.cm. This pressure is determined by the amount of neutral gas contained in the current of natural gas and by the amount of neutral gas maintained in the liquid natural gas.

The liquid part (issuing at 3) of the flask  $B_1$ , is cooled in exchangers  $E_2$  and  $E_3$ , which are the medium and low pressure stages of the same refrigerating cycle as the preceding one. At point 4, at the outlet of exchange  $E_3$ , the natural gas is at a pressure of the same order of magnitude as that prevailing in the flash flask  $B_1$  and at a temperature in the neighbourhood of, but higher than, that of the methane boiling at the pressure of the exchanger  $E_3$ . The natural gas then passes through an exchanger  $E_4$  in shell 4a constituting an expansion zone and is obtained, at the outlet of this exchanger at 5, at a pressure in the neighbourhood of that prevailing in the flask flash  $B_1$  (15-20 kg.) and at a temperature equal to, or lower than, the boiling temperature of this same natural gas at atmospheric pressure.

The gaseous part of the flash leaving the flask  $B_1$  at 6 and which will be subsequently used as combustible gas, passes through the exchanger  $E_5$  and the exchanger or liquefier  $E_6$ , which are the medium and low pressure stages of the selected refrigeration cycle, and is partially or completely condensed at a point 7. The gas-liquid mixture obtained at point 7 in a more or less large proportion passes through an exchanger  $E_7$  in shell or ex-



pansion zone 4a at the outlet of which at 8 the gas is already completely condensed and subcooled at the pressure substantially corresponding to that of the flash flask B<sub>1</sub>. The liquid obtained is then expanded in the exchangers E<sub>4</sub> and E<sub>7</sub> to atmospheric pressure or a pressure slightly higher, depending on the amount of neutral gas contained in the combustible gas and the temperature conditions that are desired of the liquid natural gas issuing from the plant at 5.

As the liquid combustible gas at point 8 is essentially constituted of a mixture of neutral gas (nitrogen) and methane, the boiling temperature of this expanded liquid will vary continually in accordance with the liquid-vapour states of equilibrium obtained in the exchangers E<sub>4</sub> and E<sub>7</sub>. These exchangers are consequently of the vapour recycling and counter-current type. They are divided into successive compartments, the number of compartments being selected in accordance with the minimum approach speeds to be maintained between the current of liquid natural gas and the boiling liquid. At the outlet of each compartment the vapours are mixed with the liquid overflowing from the compartment so that the gas-liquid mixture feeding the following compartment is in a liquid-vapour equilibrium state.

At the outlet of the exchangers E<sub>7</sub> and E<sub>4</sub>, the combustible gas in gaseous phase is conducted by a pipe 9 to the point of its use as fuel.

Second Case.—The amount of neutral gas contained in the liquefied natural gas is limited to a given value.

The plants shown in FIGS. 2 and 3 are practically identical, to within a few details, to the high pressure stage of the refrigeration cycle, for example the methane cycle, of the conventional cascade.

With reference to FIG. 2, the current of natural gas under pressure in the liquid state arriving at 1 is cooled in the exchanger E<sub>1</sub>, for example the high pressure stage of the methane cycle, then expanded in a de-nitrogenizing column V<sub>1</sub>. The expansion occurs between the pressure of point 2 and a pressure between 15 and 20 kg./sq.cm. This pressure is determined by the amount of neutral gas maintained in the liquid natural gas.

The liquid part of the bottom of the column V<sub>1</sub> issuing at 3 is cooled in the exchangers E<sub>2</sub> and E<sub>3</sub>, which are the medium pressure and low pressure stages of the same refrigeration cycle, for example methane cycle. At 4, the natural gas is at a pressure of the same order of magnitude as that prevailing in the de-nitrogenizing column V<sub>1</sub> and at a temperature in the neighbourhood of, but higher than, that of the methane boiling at the pressure of the exchanger E<sub>3</sub>.

The natural gas then passes through the exchanger E<sub>4</sub> and is obtained at the outlet of this exchanger at 5 at a pressure in the neighbourhood of that prevailing in the de-nitrogenizing column V<sub>1</sub>, and at a temperature equal to or lower than the boiling temperature of this natural gas at atmospheric pressure.

The reflux from the column V<sub>1</sub> issuing at 6, and which will subsequently be used as combustible gas, passes through the exchanger E<sub>5</sub> and the exchanger or liquefier E<sub>6</sub>, which are the medium and low pressure stages of the selected refrigeration cycle. The combustible gas is partially or entirely condensed at point 7, it is liquid and subcooled in the exchanger E<sub>7</sub>. At the outlet of the exchanger E<sub>7</sub> (point 8) the entirely liquid combustible gas is expanded in the exchangers E<sub>4</sub> and E<sub>7</sub> which are constituted in a manner similar to that previously described. The plant shown in FIG. 3 differs from that shown in FIG. 2 by the operation of the de-nitrogenizing column V<sub>1</sub>, the latter being so calculated that the amount of neutral gas remaining in the bottom of the column and issuing at 3 is substantially nil, the totality of neutral gas being contained in the gaseous phase issuing at 6. In this arrangement, the high-pressure stage of the methane cycle is replaced for the natural gas by the redistillers of the de-nitrogenizing column V<sub>1</sub>; a flash flask B<sub>2</sub> is used to obtain

the cooling of the methane of the refrigeration cycle for its utilization at the medium pressure stage.

The three plants (FIGS. 1, 2 and 3) just described permit obtaining by means of the process of the invention the natural gas liquefied under pressure and at a temperature which is equal to, or lower than, the boiling temperature of this natural gas at atmospheric pressure. The advantage of the process is to increase the operational pressures of the low pressure and medium pressure stages of the refrigeration cycle preceding the cycle of the process.

In the previously-described embodiment it is possible to obtain a liquid natural gas at a pressure in the neighbourhood of 10–20 kg./sq. cm. and at temperature conditions corresponding to the boiling temperature of this natural gas at atmospheric pressure. The process of the invention also permits—depending on the amount of neutral gas contained in the natural gas current and the amount of neutral gas contained at point 6 at the outlet of the flash or of the de-nitrogenizing column—obtaining in the exchangers E<sub>4</sub>, E<sub>7</sub> such boiling conditions that the liquid natural gas current at 5 is not only at a pressure in the neighbourhood of 10–20 kg. but also at a temperature very distinctly lower (of the order of 5° C.), at the boiling temperature of this gas at atmospheric pressure.

The pressure of the liquefied natural gas permits transferring the liquid current from the works to the storage plant. The subcooling of this liquid permits, by variation of its sensible heat, compensating the exterior supplies of heat, on one hand, in the transfer line and, on the other, in the storage plants, as will be explained hereinafter.

With reference to FIG. 4, the latter shows a plant for carrying out the process of the invention which permits separating the neutral gases contained in the natural gas current and, if desired, increasing the helium content in the neutral gas so as to facilitate the subsequent separation thereof. This plant is partly identical to that shown in FIG. 3, but the new elements could just as well be combined with the plants shown in FIG. 1 or FIG. 2.

The combustible gas extracted from the de-nitrogenizing column, at point 6 is partially recondensed in the exchanger E<sub>5</sub> fed by the low pressure stage of the refrigeration circuit, for example a methane circuit. The liquid-vapour current is treated in a column V<sub>2</sub> where the combustible gas is separated from the major part of the neutral gases it contains.

The bottom of the column V<sub>2</sub> issuing at 10 passes through the exchanger or liquefier E<sub>6</sub>, which is the low pressure stage of the methane refrigeration circuit, and, in passing through the point 7, passes through the exchanger E<sub>7</sub> of FIGS. 1–3 which is in this case constituted by two elements E<sub>7a</sub> and E<sub>7b</sub>. The liquid obtained at the outlet of the element E<sub>7b</sub> at 8 is separated into two currents, one of which supplies the head condenser of the column V<sub>2</sub> through the point 11, whereas the other directly supplies the exchangers E<sub>7a</sub> and E<sub>7b</sub> as well as E<sub>4</sub>. The returns from the condenser of the column V<sub>2</sub>, point 12, are reintroduced with the liquid-vapour mixture issuing from the exchanger E<sub>7b</sub> in the exchanger E<sub>7a</sub>; at the outlet of the latter, the combustible gas is wholly vapour and conducted to its point of utilization through the pipe 9. At the head of the column V<sub>2</sub> at the point 13 the vapours are constituted by a mixture of nitrogen and more volatile vapour (helium) whose concentration depends on the molar percentages of these constituents in the current of natural gases. The temperature of these vapours and the concentrations are sufficient to obtain the separation of the constituents, for example by passage on a molecular sieve 14 which thus permits the fractionation of the nitrogen and the more volatile vapour. The vapours of the neutral gases available at the outlet of this process are at the pressure chosen for the fractionation of the natural gas current of the combustible gas (pressure of column V<sub>1</sub>).



The process of the invention also permits eliminating by filtration in the course of liquefaction the CO<sub>2</sub> present in the natural gas entering the plant.

The current of natural gas under pressure contains, in addition to the more volatile neutral gases, more or less large amounts of CO<sub>2</sub>. In general, this CO<sub>2</sub> is eliminated from the natural gas current before liquefaction by washing with sodium hydroxide or ethanolamine. The utilization of such processes for eliminating CO<sub>2</sub>, apart from their cost price, increases the working costs of the liquefaction of the natural gas. Further, at the outlet of these plants the natural gas current is saturated with water at a temperature exceeding the surrounding temperature; therefore the plants for dehydrating the gas are considerably increased.

The curves of the equilibrium states of the CO<sub>2</sub> in hydrocarbons are well known and permit ascertaining the point of precipitation of the CO<sub>2</sub> in the solid state for the contemplated concentration and temperature. Thus, it is clear from these curves that the CO<sub>2</sub> precipitates in solid form at temperatures in the neighbourhood of -140° C. for concentrations of the order of 0.20% in mole.

The process of the invention does not concern the formation of this precipitate but its elimination from the liquid current. It comprises eliminating by filtration the precipitate obtained by expansion of preferably the liquid in a flash flask. The formation of the precipitate is continuous from the point of formation of the first crystal when the temperature of the liquid continues to drop. As the precipitate formed has a tendency to agglomerate into a mass which is compact but, however, fragile owing to the presence in the precipitate of heavier hydrocarbons, there can be no question of cooling the liquid in a normal exchanger, owing to stopping up and clogging.

The liquid obtained upon expansion in the flash flask, owing to the fact of the cooling, contains a large amount of CO<sub>2</sub> in the liquid state. This precipitate only decants when the speeds are substantially nil and it is filtered by passing it through a pad of glass wool, a plate of sintered metal or any other filtering material which resists the contemplated temperature conditions and stresses.

With reference to FIG. 5 which shows a detail of the plant, it can be seen that two flash flasks or filters B<sub>3a</sub> and B<sub>3b</sub> are fed in parallel with liquefied natural gases under pressure through the pipe 15 and expanded in a nozzle 16. Operation of the valves 17, 17a, 20, 28, 22, 25, 27, 29, 26, 35 permits the alternative operation of the flash flask B<sub>3a</sub> or B<sub>3b</sub>.

Assuming that the flash flask B<sub>3a</sub> is operating, the flask B<sub>3b</sub> regenerating: the valve 17 is open, 17a closed, the liquid expanded in B<sub>3a</sub> is cooled and separates into a liquid fraction and a gaseous fraction. In the liquid fraction, all the CO<sub>2</sub> precipitates, the CO<sub>2</sub> being retained inside a filter 18 placed at the lower part of the flash flask. The liquid natural gas is recovered toward the second expansion stage through the collector 19 through the medium of a valve 20 which is open.

The gaseous phase issuing from flask B<sub>3a</sub> at 21 is conducted through an open valve 22 to a condenser 23.

The recondensed vapours issuing at 24 from the condenser 23 are re-injected into the expanding means 16 feeding the flash flask B<sub>3a</sub> through the valve 17.

In this operation, the valves 17, 20 and 22 are open, the valves 25, 26, 27 and 28 being closed.

The flask B<sub>3b</sub> being in the regenerating condition, the regeneration is effected by a supply of combustible gas heated to around -50° C. coming from the pipe 8 and passing, through an open valve 29, the filter of the flash flask B<sub>3b</sub> at counter-current.

The hot gas sublimates the CO<sub>2</sub> deposited on the filter; the mixture gas-combustible+CO<sub>2</sub> being sent toward the point of utilization through the pipe 31, a valve 35 being open, the end of the regeneration of the filter is

effected when the temperature at 34 tends to reach -50° C.

With reference to FIG. 6, there is shown a complete plant comprising the filtration of the carbon dioxide in two successive expansions. Each expansion flask or filter B<sub>3</sub> and B<sub>4</sub> provided with filters is diagrammatically represented by a single flask, whereas the device shown in FIG. 5 is adapted to one and the other.

The current of liquid natural gas issuing from the column V<sub>1</sub> at the point 3 is cooled in the exchanger E<sub>2</sub>; at the outlet of the exchanger E<sub>2</sub> the liquid is cooled in the bottom of the column V<sub>2</sub> and conducted to the flask B<sub>3</sub> through the expansion orifice 16.

The filtered liquid part is evacuated through the pipe 36 to the flash flask B<sub>4</sub> and through the expansion orifice 37, the latter is expanded. The filtered liquid issuing at 38 is the liquefied natural gas.

The vapour part of the flash flask B<sub>3</sub> issuing at 39 passes through the exchanger E<sub>3</sub>, then E<sub>4a</sub>, issues at 40 and a flask B<sub>5</sub> permits the separation of non-condensed gas if desired, the liquid of the flask being sent into the flash flask B<sub>3</sub> through a pipe 41 directly into the expanding means 16. The flash vapour produced in the flask B<sub>4</sub> is recondensed through a pipe 42 in the exchanger E<sub>4b</sub>, reintroduced through a pipe 43 directly into the expanding means 37. The whole of the diagram, apart from this additional element, is in conformity with that of the plant shown in FIG. 4.

There is thus effected:

1°—The cooling for eliminating the CO<sub>2</sub> in the solid state by the expansion of the liquid natural gas containing this CO<sub>2</sub>.

2°—The recondensation of the vapours of the flash by refrigeration circuit or by the additional combustible gas refrigeration circuit.

3°—The reinjection of the condensed vapours in the liquid to be expanded at the moment of expansion.

The expansion can be effected in one or a plurality of stages depending on the amount of CO<sub>2</sub> contained in the entering gas, the available heat in the refrigerating cycles and the temperatures at which these calories are available, thus fixing the vapour condensation pressures and the value of the expansion in the flash flask.

The condensation of the vapours of the flash is for its part a direct function of the percentage of nitrogen contained in the current of the entering natural gas. The more these vapours are charged with neutral gas the more the recondensation of the vapours will require a refrigerating liquid having a low boiling point; now, the low boiling points are a direct function of the amount of neutral gases remaining in the combustible gas. There is therefore, as a function of the amount of neutral gas of the entering neutral gas, an optimum point of equilibrium between the amount of neutral gas contained in the combustible gas and that remaining in the liquid natural gas. In respect of percentages of neutral gases in the entering natural gas of the order of 7% in mole, the amount in the liquid gas cannot exceed 0.5%. However, in accordance with the process of the invention, it is possible to increase this amount of remaining neutral gas.

The reinjection of the condensed vapours through an injection nozzle placed at the expansion of the liquid to be cooled and filtered has for purpose to avoid the formation of solid deposits at the expansion orifice and consequently stopping up and to instantaneously reestablish the liquid-vapour equilibrium in the flask and thereby decrease to the maximum extent the neutral gas content of the formed vapour, which thus facilitates the recondensation of the latter.

In the process of the invention described hereinbefore in respect of normal concentrations of neutral gas in the current of natural gas, it has been found that the amount of neutral gas left in the liquefied natural gas cannot exceed 0.5%; now, it is of interest, in order to limit the



evaporations when storing and during transportation to increase this amount of neutral gas since this amount will constitute the most important element of these evaporations. Indeed, if the neutral gas content (for example nitrogen) is higher, the latter will constitute an important part of the evaporations and this will materially limit the liquefied natural gas losses when storing. In order to increase the amount of nitrogen contained in the liquefied natural gas the following is effected (see FIG. 7):

The combustible gas which is entirely liquid at Point 8 is no longer expanded in the exchanger  $E_{7b}$  but in a flash flask  $B_6$ , the vapour part of the flash being conducted through a pipe 44 into the exchanger  $E_{7b}$ . The liquid part is divided into three currents, one feeding through the pipe 11 the head condenser of the column  $V_2$ , the second feeding the exchanger  $E_{7b}$ , the third mixed with the liquid coming from the flash flask  $B_4$  in a pipe 45 through a valve 46 being evacuated from the process through the pipe line 38.

A part of the liquid of the flash flask is thus mixed with the liquid issuing from the last filtration stage so that, by the mixture of these two liquids, the neutral gas content in the liquefied natural gas is increased. A precise regulation of the amount of neutral gas mixed with the liquefied natural gas can thus be obtained, and this permits reducing by more than 50% the natural gas losses when storing.

FIGS. 8-11 show diagrammatically liquefied natural gas storage plants.

(A) *Storage without reliquefaction of the evaporations (FIG. 8).*—The liquefied natural gas feeds a storage reservoir from below at 51. There is formed above the liquid level a buffer or layer of neutral gas such as that produced by the fractionating column  $V_2$  of the preceding plants. This neutral gas, arriving at 52, is stored in a buffer reservoir constituted by a normal gasometer 53 connected to the liquid reservoir 51 at the upper end of the reservoir where an overpressure valve 54 permits moreover sending to the torch through 55 the overpressure of neutral gas due to the filling or the overpressure of natural gas when the storage reservoir 51 is full; at this moment, the heat losses are no longer compensated by the sensible heat provided by the subcooled liquefied natural gas.

(B) *Storage with reliquefaction of the evaporations (FIGS. 9-11).*—At the top of each reservoir 51 there is placed a column 56 provided with plates which permit the intimate mixture of the vapours of the reservoir and the liquid introduced. The subcooled liquefied natural gas is introduced at the top of the column at point 57. It flows from one plate to the next and is received in the funnel 58 disposed at the base of the column and permitting, through a plunger tube 59, the bottom supply of the reservoir 51. The vapours produced by the boiling of the stored liquid escape through a pipe 60 after having passed through the mass of liquid coming from 57 through the plates of the column 56. In passing through these plates, the major part of these vapours is recondensed by the subcooled liquid.

The collector 60 is connected to a gasometer 61 (FIG. 10) which receives neutral gases, such as those obtained by the process of the invention, the pressure excess in this gasometer 61 being sent to the torch through a pipe 62. Such a device is applicable to plants provided with a single storage reservoir or with a plurality of storage reservoirs fed in parallel. When the plant comprises a plurality of storage reservoirs fed separately, there is preferably employed a device of the type shown in FIG. 11 comprising a common collector 63 which connects the points 60 of the reservoir 51<sup>a</sup>, 51<sup>b</sup>, the gasometer 61. When the first reservoir is completely full, it is no longer possible to compensate the evaporations by the supply of sensible heat of the subcooled liquid natural gas. The vapours produced in the course of the heating of the storage are therefore sent to the common collector whence

they are drawn off in major part by the reservoir which is in course of being filled and reliquefied by the subcooled liquid natural gas inside this same reservoir.

This process of liquefaction of the vapours produced is applicable in the course of lodging a methane transporting ship. The vaporations are in this case directed to the common collector of the storage reservoirs, the liquid natural gas produced by the works being then cooled at such temperature that these vapours can be in large part reliquefied in the storage reservoirs during the loading of a ship. Apart from the emanation at the start of loading, almost all the vapours can thus be reliquefied.

Owing to the utilization of the subcooled liquefied natural gas obtained by the process of the invention and of a neutral gas which is perfectly dehydrated, such as that obtained by the same process, the storage losses are considerably reduced.

The liquefaction process of the invention thus permits materially improving the liquefaction, the refining, and the storage of natural gases.

Although specific embodiments of the invention have been described, many modifications and changes may be made therein without departing from the scope of the invention as defined in the appended claims.

Having now described my invention what I claim as new and desire to secure by Letters Patent is:

1. In a process including a refrigeration cycle for liquefying natural gases containing a proportion of more volatile neutral gases which do not have an exothermic reaction with oxygen and producing a combustible gas in addition to the liquefied natural gas, the addition to said process of an additional refrigeration cycle of the natural gas in which there is utilized as refrigerating fluid in an open circuit the combustible gas containing the major part of the more volatile neutral gases separated from the natural gas in the course of the liquefaction operations of said refrigeration cycle preceding said additional refrigeration cycle, the cooled natural gas entering the refrigerating cycle preceding said additional cycle being expanded in a flash flask so as to separate it into a liquid phase mainly constituted by the liquefied natural gas and a combustible gaseous phase comprising a part of said more volatile neutral gases, and liquid phase and the gaseous phase being caused to pass through the stages of said preceding refrigeration cycle, the partially liquefied combustible gas leaving the preceding cycle being totally condensed and subcooled at a pressure in the neighbourhood of that of said flash flask and expanded to at least atmospheric pressure in an exchange in which it cools, said liquid phase leaving said preceding cycle at a temperature not exceeding the boiling temperature of the liquefied natural gas at atmospheric pressure, the combustible gas coming from said flash flask being partially condensed and fractionated in a column so as to separate the major part of the more volatile neutral gases it contains and collect the liquefied combustible gas said liquefied combustible gas being made to pass through said additional refrigeration cycle, a part of the subcooled liquid being sent back to the head of the fractionating column, the other part being sent into said exchanger of said additional cycle as cooling liquid for the liquefied natural gas, the nitrogen and helium contained in the gaseous effluent of the fractionating column being thereafter separated.

2. Process as claimed in claim 1, wherein the separation of the nitrogen and helium is effected on a molecular sieve.

3. In a process including a refrigeration cycle for liquefying natural gases containing a proportion of more volatile neutral gases which do not have an exothermic reaction with oxygen and producing a combustible gas in addition to the liquefied natural gas, the addition to said process of an additional refrigeration cycle of the natural gas in which is utilized as refrigerating fluid in an open circuit the combustible gas containing the major part of the more volatile neutral gases separated from



the natural gas in the course of the liquefaction operations of said refrigeration cycle preceding said additional refrigeration cycle, the cooled natural gas entering said preceding cycle being expanded in a denitrogenizing column so as to limit the amount of more volatile neutral gases contained in the liquefied natural gas, said denitrogenizing column being regulated as a function of said limited amount of neutral gas to be obtained, the combustible gas coming from said denitrogenizing column being partially condensed and fractionated in a column so as to separate the major part of the more volatile neutral gases it contains and collect the liquefied combustible gas, said liquefied combustible gas being made to pass through said additional refrigeration cycle, a part of the sub-cooled liquid being sent back to the head of the fractionating column, the other part being sent to said exchanger of said additional cycle as cooling liquid for the liquefied natural gas, the nitrogen and helium contained in the gaseous effluent of the fractionating column being thereafter separated.

4. In a process including a refrigeration cycle for liquefying natural gases containing a proportion of more volatile neutral gases which do not have an exothermic reaction with oxygen and producing a combustible gas in addition to the liquefied natural gas, the addition to said process of an additional refrigeration cycle of the natural gas in which there is utilized as refrigerating fluid in an open circuit the combustible gas containing the major part of the more volatile neutral gases separated from the natural gas in the course of the liquefaction operations of said refrigeration cycle preceding said additional refrigeration cycle, the carbon dioxide contained in the natural gas being eliminated by expanding the liquid natural gas in a flash flask so as to precipitate the CO<sub>2</sub> and by separating the latter by filtration in said flask, the gaseous effluent of the flash flask being made to pass through an exchanger for eliminating the CO<sub>2</sub> where it is cooled by the liquid natural gas of said preceding cycle, and the condensed vapours of the effluent being re-injected in the liquid natural gas to be expanded at the moment of expanding.

5. In a process including a refrigeration cycle for liquefying natural gases containing a proportion of more volatile neutral gases which do not have an exothermic reaction with oxygen and producing a combustible gas in addition to the liquefied natural gas, the addition to said process of an additional refrigeration cycle of the

natural gas in which there is utilized as refrigerating fluid in an open circuit the combustible gas containing the major part of the more volatile neutral gases separated from the natural gas in the course of the liquefaction operations of said refrigeration cycle preceding said additional refrigeration cycle, the liquefied natural gas being stored in a reservoir in maintaining above the surface of the liquid a layer of more volatile neutral gases, and the vapours coming from the natural gas in the course of storage being reliquefied by putting these vapours in countercurrent contact with the subcooled liquefied natural gas feeding said reservoir.

6. In a process including a refrigeration cycle for liquefying natural gases containing a proportion of more volatile neutral gases which do not have an exothermic reaction with oxygen and producing a combustible gas in addition to the liquefied natural gas, the addition to said process of an additional refrigeration cycle of the natural gas in which there is utilized as refrigerating fluid in an open circuit the combustible gas containing the major part of the more volatile neutral gases separated from the natural gas in the course of the liquefaction operations of said refrigeration cycle preceding said additional refrigeration cycle, the carbon dioxide contained in the natural gas being eliminated by expanding the liquid natural gas in a flash flask so as to precipitate the CO<sub>2</sub> and by separating the latter by filtration in said flask, the gaseous effluent of the flash flask being made to pass through an exchanger for eliminating the CO<sub>2</sub> where it is cooled by the liquefied combustible gas of said additional refrigeration cycle, and the condensed vapours of the effluent being re-injected in the liquid natural gas to be expanded at the moment of expanding.

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