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[54] **REMOVING NITROGEN FROM AND SUBSEQUENTLY LIQUEFYING NATURAL GAS STREAM**

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[58] **Field of Search** 62/23, 24, 27, 28, 29, 62/43, 40

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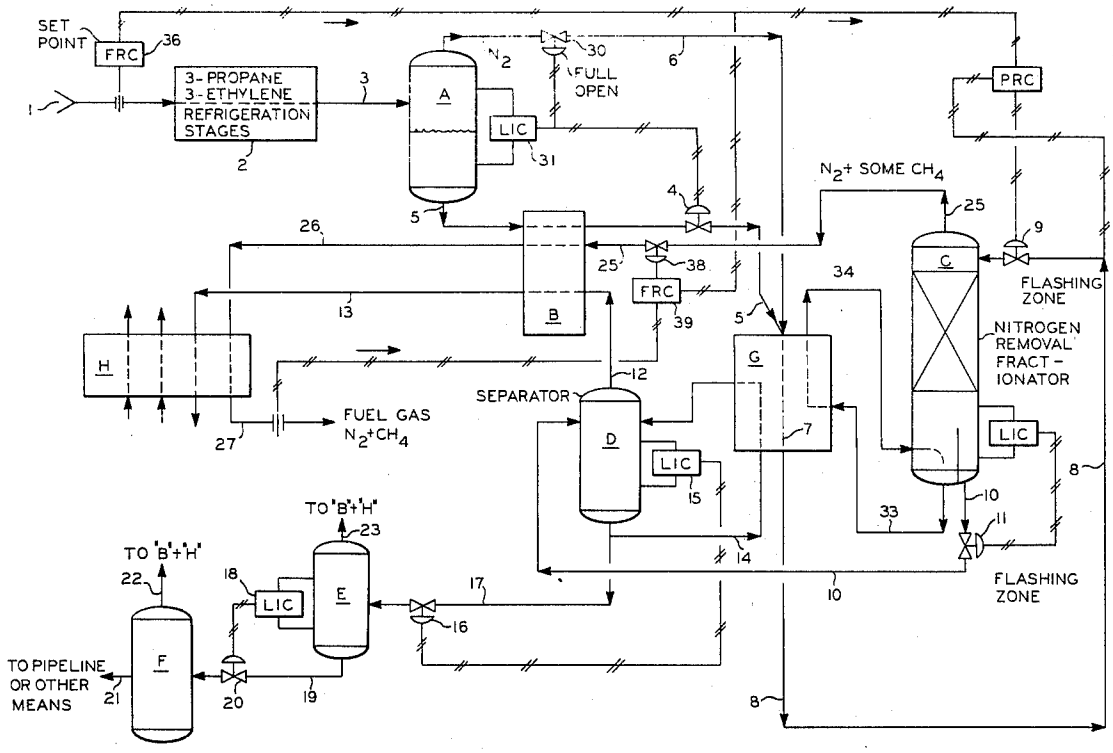
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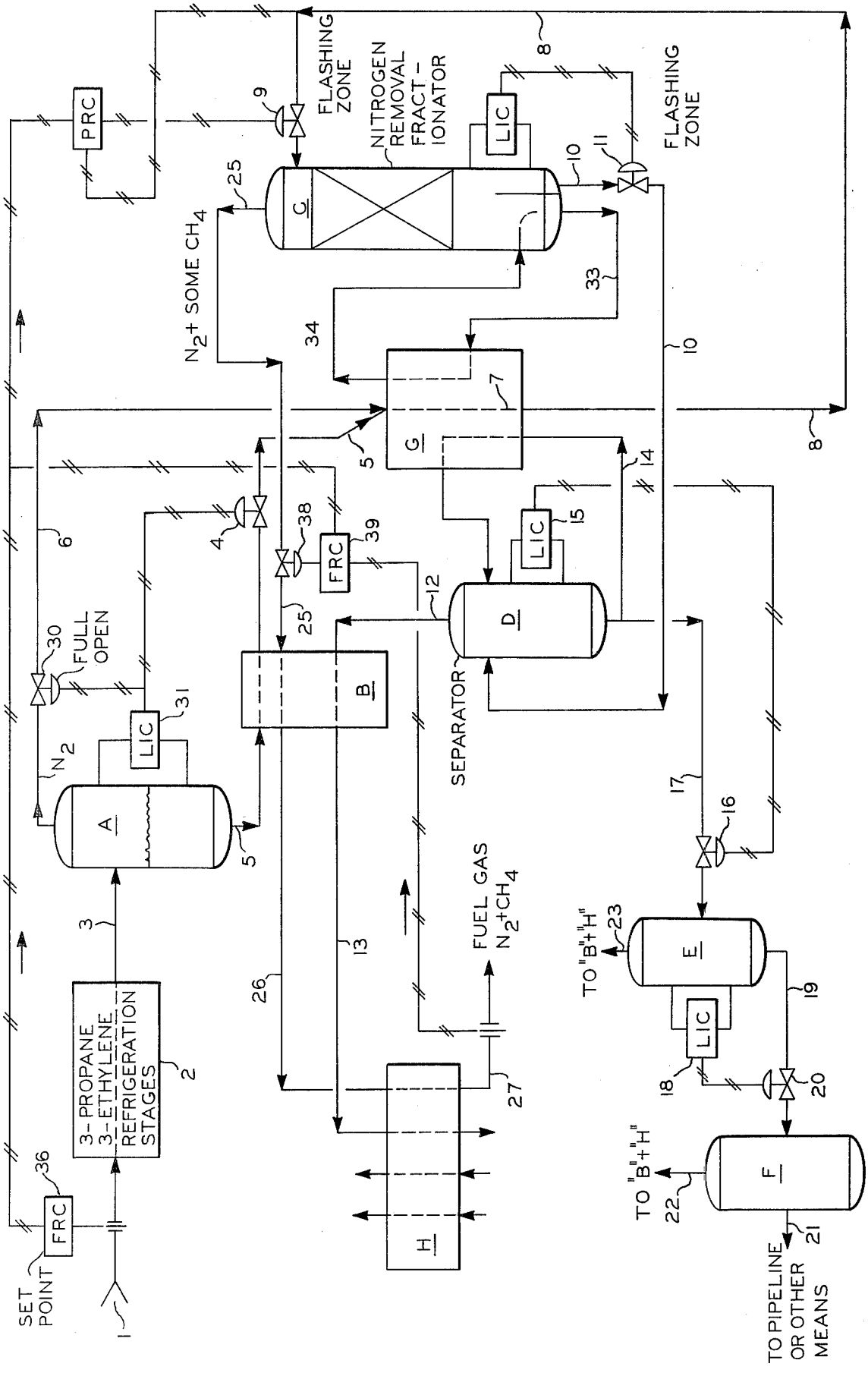
[57] **ABSTRACT**

A natural gas containing substantial nitrogen is refrigerated to below minus 120°F in usual propane-ethylene refrigeration system using a cascade arrangement. Vapor and liquid thus obtained are separated and the liquid passed into the tubes of a refrigeration heat exchanger. The vapor and liquid, which has been further refrigerated, as a liquid, are recombined to effect uniform distribution of the vapors into the further refrigerated liquid for a flow through the heat exchanger tubes. Thus, admixed liquid and vapor streams are further refrigerated by heat interchange with bottoms from a fractionation zone into which the feed has been flashed, thus reboiling the fractionation zone bottoms. The nitrogen to be separated and some hydrocarbon, e.g., methane, are taken as overhead from the fractionation zone. Also, the overhead is used to refrigerate the liquid first obtained when refrigerating the feed after separation of vapors therefrom. Further, refrigeration of the recombined vapor and liquid is effected by flashing the natural gas containing fractionation zone bottoms in several stages, using liquid obtained upon a first flashing of said bottoms to refrigerate the recombined vapor and liquid streams described and using vapors from each flashing step practiced upon the fractionation zone bottoms to further refrigerate in order to the liquid first separated from the feed after separation of vapors therefrom and the incoming feed gas resulting in a fuel gas containing some nitrogen. The remainder of the several times flashed fractionation bottoms is now substantially at atmospheric pressure and constitutes liquefied natural gas substantially free from nitrogen which is the product of the process.

A controls system designed to render the system essentially automatic and to keep it in balanced operation is described.

4 Claims, 1 Drawing Figure




FLASHING ZONE
NITROGEN REMOVAL FRACT-IONATOR
FLASHING ZONE
PRC
LIC
FRC
N_2+ SOME CH_4
N_2
FULL OPEN
SEPARATOR
FUEL GAS N_2+CH_4
TO "B"+"H"
TO "B"+"H"
TO PIPELINE OR OTHER MEANS
SET POINT
3- PROPANE 3-ETHYLENE REFRIGERATION STAGES
A
B
C
D
E
F
G
H

REMOVING NITROGEN FROM AND SUBSEQUENTLY LIQUEFYING NATURAL GAS STREAM

REMOVING NITROGEN FROM AND LIQUEFYING NATURAL GAS

This invention relates to the production of liquefied natural gas substantially freed of nitrogen which is orginally contained. It also relates to a combination of steps wherewith to remove nitrogen from a natural gas containing same in substantial quantities.

In one of its concepts, the invention provides a process wherein a natural gas containing methane and nitrogen is fractionated in steps including refrigerating the natural gas to liquefy at least a substantial portion or all of the gas, separating the refrigerated gas into a liquid stream and a gas stream, refrigerating the separated liquid stream combining the refrigerated liquid stream and the separated gas stream, further refrigerating the combined streams, the natural gas being fed to the system at a suitable elevated pressure of the order of several hundred pounds per square inch, flashing the thus refrigerated stream into a fractionation zone, in said zone separating nitrogen as a vapor stream and a natural gas from which substantial nitrogen has been removed as a liquid stream and recovering from last-mentioned liquid stream a natural gas product substantially freed from nitrogen.

In a further, concept of the invention, it provides a process as described wherein the overhead from the fractionation zone is used to cool the first separated liquid stream.

In a further concept of the invention, there is provided a process as described wherein a portion of the liquid from the fractionation zone is heat interchanged with the feed to the fractionation zone before said feed is flashed thereinto and the thus warmed fractionation zone liquid returned to said fractionation zone to warm the bottom thereof.

In a still further concept of the invention, it provides steps in combination as described herein wherein bottoms from the fractionation zone are flashed to a lower pressure and separated into a vapor which can also be used to cool said first separated liquid and into a liquid which is used to refrigerate the combined liquid and vapor streams, the thus warmed and thus used liquid thereby being partially vaporized and passed as a cold vapor into heat interchange with said first obtained separated liquid stream.

In still another concept of the invention, the fractionation bottoms after flashing and separation into vapor and liquid which are used as described and some of which constitute a liquid still are now passed as said liquid through at least one pressure reduction step generating vapor and liquid at a reduced temperature which is useful as a refrigerant in the process and a remaining product which is liquefied natural gas substantially freed from nitrogen.

At a time of impending natural gas shortages some of which have been experienced already and which have resulted in layoffs and other undesirable situations, we have conceived a combination of steps as described herein which permit processing certain kinds of natural gases, particularly gases containing substantial quantities of nitrogen which must be removed from the said gases to accomplish an acceptable product.

It is an object of this invention to produce a purified liquefied natural gas. It is another object of this invention to provide a process with which to purify a natural gas. It is another object of the invention to provide a process for the removal of nitrogen from a natural gas containing the same in substantial quantity. It is a further object of the invention to remove nitrogen from a natural gas. It is a further object still to provide a combination of steps wherewith to process a natural gas to remove an undesired impurity therefrom in an economical and convenient manner.

Other aspects, concepts, objects and the several advantages of this invention are apparent from a study of this disclosure, the drawing and the appended claims.

According to the present invention, a combination of steps are provided for removing nitrogen from a natural gas containing the same wherein the natural gas is compressed to an elevated temperature of the order of several hundred pounds per square inch, is refrigerated, a vapor and a liquid stream are obtained following said refrigeration, a liquid stream is further refrigerated and then combined with the vapors for further refrigeration whereupon the thus refrigerated combined streams are flashed into a fractionation zone so operated as to obtain therefrom as overhead substantially all of the nitrogen and as bottoms therefrom a liquid stream substantially reduced in nitrogen which upon further flashing will yield a liquid residue which is a natural gas liquid substantially free from nitrogen and a fuel gas containing nitrogen and some methane.

Also according to the present invention, the liquid from the bottoms from the fractionation zone is heat interchanged with the feed coming into said fractionation zone and before it is flashed thereinto and thus to refrigerate the feed while warming a fractionation zone bottoms liquid.

Also according to the invention, vapors obtained upon flashing the fractionation zone bottoms are used to refrigerate a first separated liquid obtained upon refrigerating the incoming feed natural gas while liquid obtained upon flashing said fractionation zone bottoms is used to refrigerate the feed to the fractionation zone before it is flashed thereinto, yielding vapors which are also used to refrigerate said first separated liquid.

Other features and advantages of the combination of steps according to the invention are evident from the following description of the drawing which illustrates the now contemplated best mode for combining the steps of the invention and the operating conditions involved.

Referring now to the drawing, there is shown in diagrammatic form a flow plan according to the invention which provides the economy of equipment and operational costs which characterize the novel combination of steps or arrangement of the invention.

A nitrogen containing natural gas feed, as can be obtained in the gas fields in Algeria, enters by 1 at about 589 psia and atmospheric temperature and is cooled to about −127°F at 547 psia passing through heat exchangers at 2 in which the entering fluid is heat exchanged with several stages of ethylene and propane refrigerants in the case of the design here described three of each in the order stated. Cascade arrangement, not shown, is employed. Such arrangements are well known and are omitted for sake of clarity of the drawing. The substantially condensed gas is passed by 3 into vapor separator A which is at about −127°F and 547

psia. The overhead from A is largely nitrogen but does contain some hydrocarbon. A is maintained partly full of liquefied gas and on a level control **31** which is connected to operate valve **4** in pipe **5** which passes into and through heat exchanger zone B in which it is heat exchanged with streams later identified. According to the invention, a liquid from A is further cooled in B and then is combined with overhead stream **6** from A, the combined steams passing through **7** in heat exchanger zone G. The thus cooled vapors and liquid combined stream is passed by **8** through flash valve **9** into fractionator C from which overhead **25** is nitrogen and some methane at about −173°F. The bottoms from the fractionator at 355 psia are passed by **10** through flash zone **11** and to vapor separator D at about −184°F and at about 179 psia. Overhead from D is passed by **12** into B and therein is heat inter-changed with liquid feed passing through B in **5** and later with the feed stream in H.

Liquid in D is passed by **14** into heat interchange in G with the combined vapors and liquid from A in **7** and then back into the vapor space in D. D is maintained on the liquid level control **15** connected to liquid draw-off flash valve **16** in **17**, the flashed liquid and vapors generated being passed to E, also a vapor-liquid separator at about −224°F and at about 59 psia. The liquid from E which is maintained on liquid level control **18** is passed by **19** through release valve **20** into F from which the final liquefied natural gas product is passed at about atmospheric pressure to a pipeline or storage as desired by **21.**

The vapors taken off from F at **22** and from E at **23** are heat interchanged in B with the liquid in **5** and in H with the feed stream.

The overhead **25** from fractionator C is passed through flow control valve **38** into B into heat interchange with the liquid portion of the feed in **5** and thence by **26** into heat interchange with the feed in H and is then taken from the system at **27** as fuel gas.

Residual gas flow from the top of separator A is controlled by valve **30** in pipe **6** also manipulated by level controller **31.** In normal operation, valve **30** is wide open and valve **4** is opened and closed by controller **31** to maintain the liquid in tank A at a desired level. However, when valve **4** is wide open and the liquid level in tank A continues to rise, valve **30** is partially closed by controller **31** thereby increasing the pressure in tank A and forcing liquid out the bottom through pipe **5.** Valve positions according to the output signal pressure from controller **31** are as follows:

Controller Output Pressure, psig	Valve Position	
	4	30
3	Closed ↓opening	Wide open ↕
9	Wide open ↕	Wide open ↓closing
15	Wide open	Closed

The liquid in pipe **5** is combined with the gas in pipe **6** in heat exchanger G and passed through heat exchanger G via passageways **7.** The purpose in separating the liquid from the gas in separator A and then recombining the same separated streams is to permit equal distribution of liquid and vapor through the numerous passageways of heat exchanger G. Devices for combining liquid and gas streams and then dividing the mixture among several passageways in a heat exchanger so as to insure equal amounts of liquid and vapor in each passageway are known.

The combination of such a system of control of vapor and liquid flows, according to the invention, permits an efficient utilization of the separated components of the stream in **3.**

The natural gas in passageways **7** is additionally liquefied and subcooled in passing through exchanger G by indirect heat exchange with bottoms from fractionator C in two steps. In the first step cold bottoms from the fractionator are passed through exchanger G via pipe **33** countercurrently to the feedstream in passageways **7** thereby cooling said feedstream while warming and vaporizing part of the liquid in pipe **33.** The now partially vaporized bottoms from fractionator C is returned to the fractionator via pipe **34.** Thus fractionator G is reboiled by heat exchanging bottoms with feedstream in passageways **7.**

Additional cooling of the stream in passageways **7** is obtained in a second step wherein bottoms from fractionator C are flashed by passage through valve **11** from 355 psia to 179 psia and −184°F and then conducted via pipe **10** to flash drum D. Liquid circulates from drum D via pipe **14** through exchanger G by the the thermosiphon principle and flows back into drum D. The natural gas feedstream in passageways **7** is thereby cooled by countercurrent heat exchange with the cold liquid in pipe **14.**

The cold feedstream exits exchanger G at 540 psia via pipe **8** and is flashed into the top of nitrogen removal fractionator C by passage through flash valve **9.** By flashing from 540 psia to 355 psia, some of the liquid evaporates with a reduction in temperature to −173°F in the top of fractionator C. Flash valve **9** is manipulated by pressure controller **35** in response to the pressure in pipe **8.** The set point of controller **35** is manipulated by flow controller **36** in response to its primary set point and to a measurement of the rate of flow of gas entering the plant.

Fractionator C effects a separation between nitrogen and other low boiling impurities such as hydrogen, helium, etc. and methane and heavier hydrocarbons. The nitrogen product together with some methane exits the fractionator in the gaseous state at the top and passes via pipe **25** to exchanger B wherein it cools the feedstream in pipe **5.** The nitrogen product then passes through exchanger H via pipe **26** wherein it cools a refrigerant stream and exits via pipe **27** as fuel gas. Flow rate of nitrogen product in pipe **25** is controlled by valve **38** which is manipulated by flow controller **39** in response to the measured flow in pipe **26.** The set point of controller **39** is in turn manipulated by flow controller **36** in response to its applied set point and measurement of the flow rate of gas entering the plant.

Thus, according to the invention there has been provided a more efficient process for the liquefaction of natural gas, with an integrated nitrogen removal fractionator, wherein the natural gas is heat exchanged with the fractionator bottoms in two steps thereby reboiling the fractionator while cooling the natural gas feedstream. Refrigeration costs are substantially reduced as are equipment costs with our integrated liquefaction-nitrogen removal process. The following is an example given to illustrate the invention. It is based partly on knowledge of the art, including feed streams available and their composition, engineering and re-

lated knowledge which have been incorporated together.

EXAMPLE

Flow rate and composition of a typical nitrogen-containing natural gas entering the plant via pipe **1** is as follows:

Component	Flow Rate Mols/Day	Composition, Mol %
Helium	1742	0.2
Nitrogen	52951	6.3
Methane	745766	87.1
Ethane	46719	5.6
Propane	6214	0.7
Isobutane	462	0.05
n-Butane	429	0.04
C_{5+}	101	0.01
Total	854384	100.00
Temp. = 100° F. Press. = 589 psia		

Flow rate and composition of the gas as it exits exchanger **2** is, of course, the same as the feed gas to the plant but the gas has now been cooled to −127°F at a pressure of 547 psia. The gas has now been partially liquefied and consists of 382,065 mols/day of vapor and 472,319 mols/day of liquid. This mixture of vapor and liquid is passed to phase separator A from which the vapor passes overhead via pipe **6** and the liquid passes from the bottom through pipe **5.** The liquid is subcooled in exchanger B from −127°F to about −135°F and it is then remixed with the gas in pipes **7** before passage of the mixture through exchanger G. The mixture still has the same composition and flow rate as in pipe **1** and now has a temperature of about −129°F and a pressure of 544 psia. The gas-liquid mixture is equally distributed about among the several passageways in exchanger G using a device known in the art.

The gas-liquid mixture is completely liquefied in exchanger G and issues therefrom at a temperature of −176°F and a pressure of 541 psia. This liquid is then passed via pipe **8** to nitrogen-removal fractionator C wherein a portion of the liquid feed flashes into vapor passing through valve **9** which reduces the pressure from 540 psia to 355 psia. Valve **9** is manipulated by PRC–**35** in response to the pressure of the liquid passing to valve **9,** i.e., the pressure in pipe **8.** the set-point of PRC–**35** is in turn manipulated by FRC–**36** in response to the flow of feed gas entering the plant. The primary set point is applied to FRC–36. A flow rate of 855,000 moles per day, for example, is applied as set point to controller FRC–36. If the flow entering the plant as measured by flow element F–**1** decreases below 855,000 moles per day, FRC–36 manipulates the set point of PRC–35 in such a way that valve **9** must open, i.e., the set point of PRC–35 is decreased. PRC–35 thus opens valve **9** until the measured pressure in pipe **8** equals that applied as set point.

Fractionator C separates most of the nitrogen from the liquefied gas and rejects it as the overhead product. Compositions of overhead and bottoms are as follows:

Component	Overhead, Mols/day	Bottoms, Mols/day
Helium	1,742	0
Nitrogen	52,831	120
Methane	91,325	654,441
Ethane	335	46,384
Propane	3	6,211
Isobutane	0	462
n-Butane	0	429
C_{5+}	0	101
Temp., °F	−173	−151
Press., psia	343	343

Bottoms product from the fractionator is passed via pipe **10** through pressure reduction valve **11** which reduces the pressure from about 360 psia to about 179 psia. This causes a portion of the liquid to flash and a reduction in temperature of from about −151°F to about −185°F. The resultant mixture of liquid and vapor is discharged into separator D from which vapor is discharged overhead. Liquid in separator D circulates by thermo-siphon action through pipe **14** and into exchanger G wherein it refrigerates the incoming feedstream. Stream **14** is thereby partially vaporized while stream **7** is totaly condensed and subcooled. Stream **14** amounts to 775,448 mols per day of liquid entering exchanger G and has the following composition:

Component	Mole Percent
Helium	0
Nitrogen	0.66
Methane	92.10
Ethane	5.07
Propane	1.56
Isobutane	0.24
n-Butane	0.37
Heavier	Trace

Stream **14** is partially vaporized in passing through exchanger G and discharges back into tank D in the amount of 579,949 moles/day of liquid and 195,498 moles/day of vapor. Temperature is about −182.5°F and pressure is about 179 psia.

Feedstream **7** was thus refrigerated by exchange with stream **14.** Feedstream **7** is additionally cooled by heat exchange with recycle stream **33** taken from the bottom of fractionator C. The fractionator is reboiled by thermo-siphon circulation of liquid stream **33** through exchanger G and back into the fractionator via pipe **34.** Stream **33** circulates at the rate of 1,014,470 moles per day and enters exchanger G at about −153°F. Stream **34** exits the exchanger at a temperature of −151.5°F and consists of 723,860 moles per day of liquid and 290,610 moles per day of vapor.

Stream **17** is removed from the bottom of separator D at about −185°F and about 179 psia, and comprises the bulk of the liquefied natural gas, now essentially free of nitrogen. It is reduced to atmospheric pressure. This is accomplished by letting the pressure down to atmospheric in two (or more) steps as shown by passage through valves **16** and **20.** Flashed gases **22** and **23** are used to help cool the incoming feed gas and then recycled. The final LNG product in pipe **21** has the following flow rate:

Component	Flow, Moles per Day
Helium	0
Nitrogen	317
Methane	669,700
Ethane	64,767
Propane	20,628
Isobutane	3,666
n-Butane	5,484
C_5+	129
Temp., °F	−257
Press., psia	15

Whie preferred operating conditions of temperature, pressure, compositions, etc. have been given for the practice of our invention, it should be understood that we may operate ouside the previously specified conditions at some decrease in operating efficiency depending on the extend of departure from the optimum conditions. The nitrogen content of the feed gas passed to the plant via pipe **1** may, for example, vary from about **1** mol percent to about 50 mol percent although it will usually be in the range of from about 2 mol percent to about 25 mol percent. The other components in the natural gas feedstock may also vary somewhat in concentration as no two natural gaes from different gas fields have percisely the same composition. Our invention lies in the separation of nitrogen from a natural gas and is relatively immune to, say the concentration of propane or butane in the feed gas.

Operating conditions for the nitrogen removal fractionator C will vary somewhat depending on the nitrogen content of the feed gas. Fractionator C will generally be operated at higher pressures and lower temperatures as the nitrogen content of the feed gas increases. For example, fractionator C may be operated in the range of from 100 to 1,000 psig, preferably in the range of from 200 to 500 psig. Fractionator C may be operated with a temperature in the top ranging from about −100°F to about −300°F, preferably in the range of from about −150°F to about −225°F. Temperature at the bottom of fractionator C may range from about −50°F to about −250°F, preferably from about −100°F to about −200°F.

Temperature of stream **8** passing to fractionator C will vary depending on its nitrogen content, said stream being lower in temperature as its nitrogen content increases. Temperature of stream **8** may range from about −50°F to about −225°F, preferably from about −100°F to about −200°F. To reduce the temperature of stream **8** to a lower level, it is necessary to flash stream **10** to a lower pressure in separator D in order to obtain a colder refrigerating stream **14** for use in cooling said stream **8** in exchanger G. Pressure in separator D may range from about 50 psia to about 300 psia, preferably from about 100 psia to about 200 psia. Temperature of stream **10** may vary from about −75°F to about −300°F, preferably from about −125°F to about −250°F.

With the pressure in flash separator D ranging from 50 psia to about 300 psia, the pressure in flash separator E will range from atmospheric (separator F not needed) to about 200 psia, preferably from about atmospheric to about 250 psia. Pressure in separator F, if needed, will be atmospheric preferably but can be maintained at slightly elevated pressure of up to about 50 psig.

Reasonable variation and modification are possible within the scope of the foregoing disclosure, the drawing and the appended claims to the invention the essence of which is that there has been provided a process for the removal of an impurity, e.g., nitrogen, from a natural gas containing the same in substantial proportion which comprises compressing the gas, refrigerating the gas, separating the gas into a liquid and vapor component, refrigerating the liquid component, combining the gas and liquid component, further refrigerating the combined gas and liquid component and flashing the same into a fractionation zone wherefrom an overhead containing nitrogen is obtained and used as a heat exchange medium for further refrigerating said liquid component, bottoms from the fractionation zone are used at least in part to refrigerate the feed thereto thus to heat said portion of bottoms wherewith to reboil the fractionation zone and another portion of said bottoms are flashed in several stages to obtain vapor which can be used to further refrigerate said liquid component and a liquid which can be used and is used to further refrigerate the feed coming to the fractionation zone generating vapors which vapors can be used to further refrigerate said liquid component and a remaining portion of said fractionation zone bottoms which have been flashed or further processed to recover the natural gas substantially free from nitrogen.

We claim:

1. In a process for removing nitrogen as an impurity from natural gas comprising refrigerating said gas, generating a liquid portion and a vapor portion, separating the vapor and liquid portions from each other and further refrigerating the separated liquid portion in a first refrigeration zone, the improvement comprising the steps of

1. combining the thus refrigerated liquid portion with said vapor portion and cooling the combined portion in a second refrigeration zone under conditions to substantially liquefy the combined portion,
2. reducting the pressure of said substantially liquefied mixture obtained in step (1) to flash the liquefied combined portion into a vapor portion and a liquid portion and introducing the flashed mixture into a fractionation zone,
3. subjecting said flashed mixture to temperature and pressure conditions in said fractionation zone sufficient to separate substantially all of the nitrogen as a vapor overhead stream and a bottoms liquid stream substantially free of nitrogen,
4. passing said vapor overhead stream obtained in step (3) in heat exchange relationship with said separated liquid portion in said first refrigeration zone to cool and refrigerate said liquid portion,
5. passing a portion of said bottoms liquid stream obtained in step (3) in heat exchange relationship with said combined portion in said second refrigeration zone and returning same to a lower portion of said fractionation zone as a source of reboiling heat,
6. reducing the pressure of the remainder of said bottoms liquid stream obtained in step (3) to flash same into a vapor portion and a liquid portion and introducing the flashed stream into a separation zone,

7. removing a liquid stream from said separation zone and passing a portion of said stream in heat exchange relationship with said combined portions in said second refrigeration zone and returning same to an upper portion of said separation zone as reflux, and

8. removing a vapor stream from said separation zone and passing same in heat exchange relationship with said liquid portion in said first refrigeration zone.

2. A process according to claim **1** wherein the remaining portion of said liquid stream removed from said separation zone is further flashed to obtain nitrogen-containing gas therefrom and a final liquefied natural gas substantially free from nitrogen, and further wherein said vapor stream obtained from said separation zone upon use as a refrigerant in said first refrigeration zone is removed as a fuel gas containing nitrogen.

3. A process according to claim **1** wherein said fractionation zone is operated under conditions in which the upper portion of the fractionation zone is at a temperature in the range of −100° to−300°F and the bottom portion of the fractionation zone is at a temperature in the range of −50° to −250°F, and the temperature of the combined vapor and liquid stream after refrigeration in said second refrigeration zone is at a temperature in the range of −50° to −225°F.

4. A process according to claim **1** wherein the temperature of the liquid bottoms stream separated from said fractionation zone in step (3) is in the range of −75° to −300°F and the stream is flashed by reducing the pressure sufficiently to a pressure in the range of 50 to 300 psia to form a vapor portion and liquid portion.

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