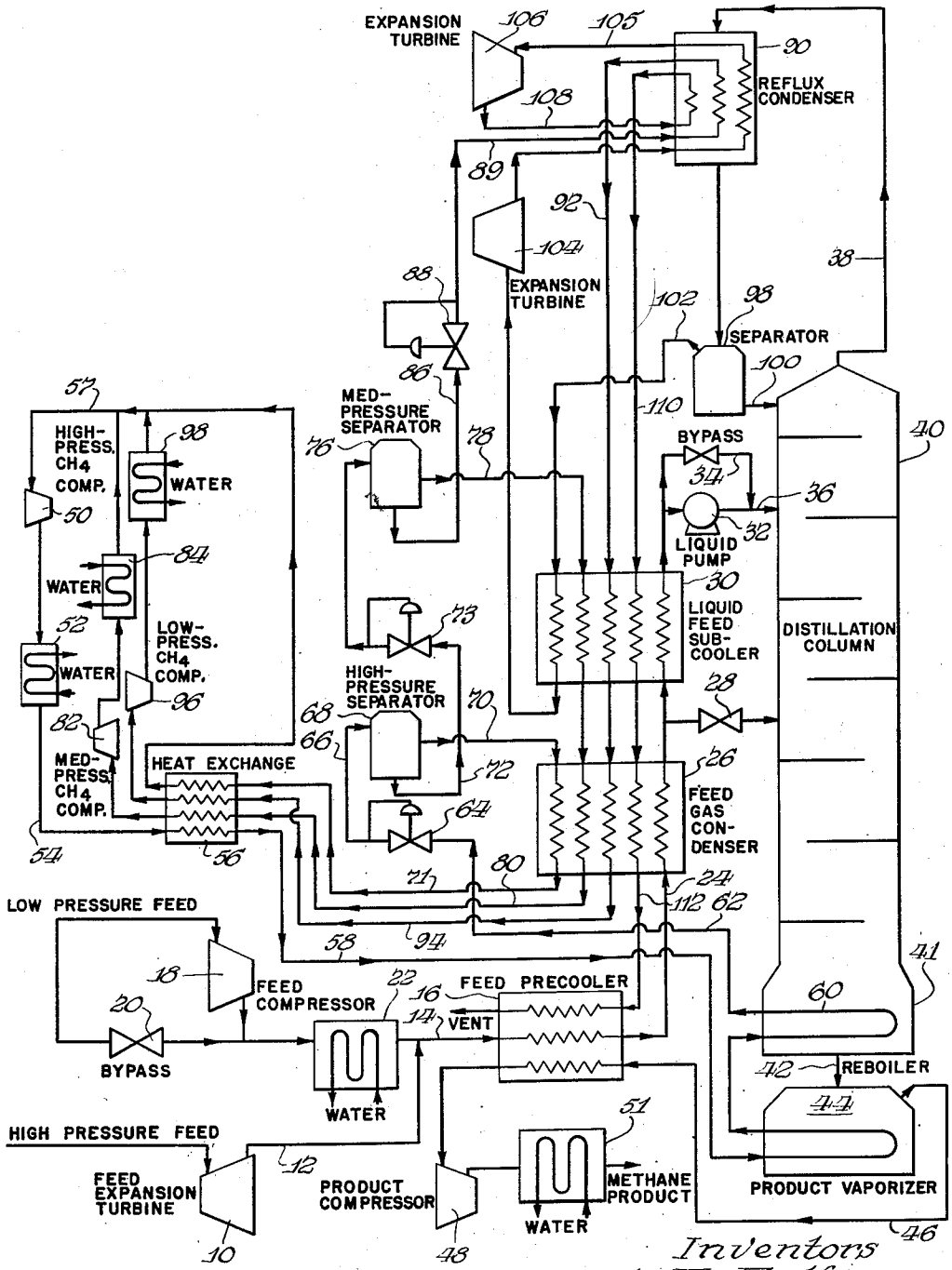
Feb. 18, 1958 B. E. EAKIN ET AL 2,823,523

SEPARATION OF NITROGEN FROM METHANE

Filed March 26, 1956



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United States Patent Office 2,823,523 Patented Feb. 18, 1958

2,823,523

SEPARATION OF NITROGEN FROM METHANE

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Application March 26, 1956, Serial No. 573,865

2 Claims. (Cl. 62—175.5)

This invention relates to an improved process for separating nitrogen from methane, or natural gas, which consists essentially of methane. The use of natural gas in the United States has expanded enormously in recent years and the demand continues to increase. As the reserves of relatively pure natural gas are depleted, natural gas of higher nitrogen content becomes a more valuable resource. It is desirable, however, to remove as much nitrogen as possible from this lower grade natural gas before introducing it into the pipelines. First of all, removal of the nitrogen reduces the volume of gas being conveyed so that only that portion which actually has heating value is sent through the line. Secondly, a gas containing any substantial quantity of nitrogen cannot be employed by consumers without adjustment of the appliance burners. In other words, the low grade gas could be made interchangeable with the high grade natural gas containing essentially methane.

The present process involves low temperature liquefaction of the feed gas followed by fractional distillation. In prior processes of this type the gaseous mixture of methane and nitrogen is rectified and the separated nitrogen is compressed, cooled and used as the agent for supplying refrigeration for liquefaction. In the present invention the major portion of the refrigeration requirements are supplied originally by the latent heat of vaporization of a recirculating stream of liquid methane. The refrigeration available in the low temperature nitrogen, separated from the cooled feed gas, is used to supply a portion of the refrigeration requirements. By utilizing a condensing methane cycle to provide refrigeration, a substantial savings in power requirements can be effected, amounting to one-third less than the power required where refrigeration is supplied primarily from the separated nitrogen and a recirculated nitrogen stream. This savings is effected by the reduced quantity of material recirculated and the lower operating pressures required when methane is used as the refrigerant instead of nitrogen. The condensing methane cycle operates so that each pound of methane provides refrigeration equal to its heat of vaporization plus sensible heat effect, a considerable advantage over the nitrogen cycle where only the sensible heat effect is used for refrigeration.

Briefly, the invention consists first in compressing a portion of the methane product gas (or methane from any suitable source, herein referred to as "refrigerant" methane) to superatmospheric pressure and cooling the compressed refrigerant methane to below its condensation temperature by passing it in heat exchange relationship with the product methane being discharged from the fractionating or distillation column. As the recirculated refrigerant methane is condensed it supplies the heat for vaporization of the product methane and the heat requirements for the distillation column reboiler. The distillation column, of course, is the portion of the apparatus in which the feed gas is rectified, the nitrogen being taken off at the top in gaseous form and the more easily liquefiable methane being removed in liquid form at the bottom of the column. Then the compressed condensed refrigerant methane is expanded stepwise to a lower pressure. At each step the entire liquid stream is expanded to the desired lower pressure, and a minor proportion of the liquid at such pressure is separated from the stream for further expansion at the next step. The major proportion of the expanded refrigerant methane stream, which consists of both a gaseous and liquid phase, is sent through coils in a heat exchanger to absorb heat from and condense the feed gas (methane and nitrogen mixture). The separated liquid is again expanded to form a mixture of gas and liquid. A portion of the liquid phase is advanced to the third and final expansion step, while the remaining gas and liquid mixture is used to subcool the condensed feed gas, or for other cooling purpose. The third expansion step results in gasification of all the liquid to substantially atmospheric pressure. The heat absorbed by the vaporization of liquid after the third expansion step is preferably employed in condensing the reflux nitrogen required for the distillation column.

The invention will be better understood by reference to the accompanying drawing, which illustrates diagrammatically the flow of materials in accordance with the present invention. Referring now to the drawing, the feed gas which consists of a mixture of methane and nitrogen, the proportion of nitrogen ranging up to, say, 30%, is either compressed or expanded depending upon its initial pressure. The distillation column will be operated at elevated pressure, say, from 200 to 300 pounds per square inch. If the pressure of the feed gas is higher than the operating pressure of the distillation column, then it is permitted to expand in the feed expansion turbine **10** from which it is discharged at the desired pressure. The expanded feed gas exits from turbine **10** through line **12** and enters the feed precooler **16** through line **14**. In the event the feed gas pressure is below that maintained in the distillation column, its pressure must be increased and this is done by passing the low pressure feed through the compressor **18**. By-pass **20** is provided around the compressor in the event the feed gas is of substantially the same pressure as the distillation column and requires no treatment. In compressing the feed gas, a certain amount of heat is generated and to remove this heat the gas is passed through after-cooler **22** which is supplied with cooling water. Feed gas at a temperature slightly higher than the cooling water temperature and at a pressure just in excess of the column operating pressure then enters the feed precooler **16** which is essentially a heat exchanger. The refrigeration for the precooler is supplied by nitrogen discharged from the system and methane product gas, as will be explained hereafter.

The pressurized feed gas, in passing through the feed precooler, is reduced to a temperature slightly higher than the boiling point of the methane product at the operating pressure of the column. From the precooler **16** the compressed gas flows through the line **24** into the feed gas condenser **26** where sufficient heat is removed to condense the feed gas. The temperature to which the gas must be cooled in order to condense it depends, of course, upon the pressure and the composition of the feed gas. However, where the distillation column is operating at around 200 pounds per square inch, a 30% nitrogen-70% methane mixture would be cooled to approximately —230° F. The liquefied gas at this temperature and just in excess of 200 pounds per square inch pressure may be introduced directly into the distillation column through valved line **28**, or it may be still further cooled by passing through the liquid feed subcooler **30**. The liquid feed subcooler cools the compressed condensed gas to approximately —250° F.

This subcooled liquid is then introduced into the distillation column, either through the liquid pump **32** or the by-pass **34**, depending upon the feed pressure. It is essential, of course, that the pressure in the line **34** or **36** be in excess of the pressure prevailing within the distillation column **40**. In the distillation column the feed is rectified, the nitrogen being taken off as gaseous overhead in line **38**, and the methane as liquid product through line **42** into product vaporizer **44**. The heat of vaporization of the product methane is utilized to cool the recirculated methane gas which is cycled through the heat exchangers utilized for cooling and condensing the feed stock. As the product methane gains heat, it is converted back to the gaseous phase and passes from the product vaporizer **44** through the line **46** into the precooler **16** where it absorbs heat from the warm feed gas flowing through the line **14**. The product methane gas, now heated to about atmospheric temperature, is compressed to the desired transmission pressure in the product compressor **48**, after-cooled in the heat exchanger **51** and sent to storage or into the pipeline, as desired. The heat exchanger **51** is cooled by means of water flowing through the coil disposed therein.

To provide the refrigeration required for cooling the feed gas we employ a circulating condensing methane system. Methane comprising part of the product gas, or supplied from any convenient source, is compressed in the compressor **50**, shown to the far left of the drawing, and is circulated constantly from the compressor through the system in a closed circuit. This methane may be called "refrigerant methane," as distinguished from the product methane. The gas is compressed to a pressure about 10 pounds per square inch greater than the column operating pressure. The compressed gas is after-cooled in the heat exchanger **52** and flows through the line **54** into heat exchanger **56** where it is precooled by gaseous methane which is returning to the compressors from the feed gas condenser **26**. The precooled compressed refrigerant methane gas then flows through the line **58** into the product vaporizer where it is cooled and partially condensed by the product methane which is being converted back to the gaseous phase in the vaporizer **44**. Further cooling is effected by passing the compressed refrigerant methane through the coil **60** disposed in the distillation column reboiler **41**. The temperature of the liquid methane in the column reboiler is sufficiently low to condense the compressed and precooled methane which is flowing through coil **60**. The liquid methane which has a temperature about 5° F. higher than the column product stream at a pressure about 10 pounds per square inch higher than the column operating pressure then flows through the line **62** and is expanded through the valve **64** to approximately one-half of the column pressure. During expansion the liquid methane is partially converted to the gaseous phase and the two phases flow through line **66** into the high pressure separator **68**. In the separator a small portion of the liquid phase is withdrawn from the bottom through line **72** and the major portion of the liquid phase and all the gaseous phase is discharged from the side through line **70**. The two phase methane stream from line **70** is directed through coils in the feed gas condenser **26** where it absorbs large quantities of heat from the feed gas flowing countercurrent thereto as the liquid is vaporized and the gas warmed. The warmed gas is discharged through the line **71**, passes through heat exchanger **56** where it gives up most of the remaining refrigeration therein to compressed methane flowing from the compressor system countercurrent through the exchanger **56** via line **54**. At this point the methane gas is at substantially atmospheric temperature. From the heat exchanger **56** the gaseous stream is directed through the main line **57** of the compression system into the main compressor **50**, from which it is recycled.

The liquid methane withdrawn from the bottom of the separator **68** into the line **72** is then expanded again through valve **73**, this time to a medium pressure of approximately one-fourth the column operating pressure and the resulting two phase stream enters the medium pressure separator **76**. Again the gas phase and most of the liquid phase are utilized in cooling, being conveyed through the line **78** into the liquid feed subcooler **30**, where the liquid is vaporized and the gas warmed, and also through separator coils in the feed gas condenser **26** from which it is directed back to the compressor system through the line **80**. This gas also passes through heat exchanger **56** to absorb heat from the freshly compressed methane flowing back to the distillation system through the line **54**. Medium pressure methane goes through a first stage compressor **82**, an after-cooler **84** and then flows into the main stream **57**. It is further compressed in the compressor **50** along with the returned methane from line **72**.

Again, the liquid methane withdrawn from the medium pressure separator **76**, flows through the line **86** and is expanded through the valve **88** to the final low pressure. The resulting two phase stream is directed to the reflux condenser **90** through line **89**. As the liquid is vaporized in passing through the reflux condenser it absorbs heat from the gaseous nitrogen which flows countercurrent thereto, condensing the liquid reflux required by the column. The nitrogen stream is introduced at the top of the condenser through the line **38**. To utilize all of the remaining refrigeration in the methane gas, which is at the temperature of liquid nitrogen upon being discharged from the reflux condenser, it is directed through the line **92** into the liquid feed subcooler **30** and the feed gas condenser **26** from which it is conveyed through the line **94** back to the compressor system. The treatment is similar to that of the gaseous methane returning through lines **72** and **80**. It passes first through heat exchanger **56** and then into the low pressure compressor **96**, through the after-cooler **98**, and back into the main stream **57**. Thus, it will be seen that all three returning methane gas streams are joined in the line **57** and subsequently compressed to the desired pressure before being recondensed and recycled through the stepwise expansion system used for supplying the refrigeration for the process.

All of the refrigeration required is not provided directly by the methane condensing cycle just recited. A certain amount of refrigeration is available from the gaseous nitrogen (originally cooled by methane as part of feed gas) being discharged from the top of the distillation column and it is, of course, most economical to utilize the ability of this gas to absorb heat. It is, therefore, passed through the reflux condenser **90** into the separator **98**. The temperature of the nitrogen after passing through the reflux condenser is sufficiently low so that at least a portion of the nitrogen has been condensed to a liquid. The liquid phase flows from the bottom of the separator through the line **100** back into the distillation column where it is utilized as reflux for the distillation column. The gaseous portion of the nitrogen is discharged from the top of the separator **98** through the line **102** and through liquid feed subcooler **30** to assist the circulating methane in cooling the condensed feed gas. From the subcooler **30** the gaseous nitrogen flows through the expansion turbine **104** where mechanical energy is recovered and the temperature and pressure of the nitrogen reduced, and then through the reflux condenser **90** to help cool nitrogen flowing therethrough from line **38**. The partially expanded nitrogen gas then flows through a second turbine **106** via line **105** and after this expansion is circulated once again through the reflux condenser via line **108** at substantially atmospheric pressure. After the second pass through the reflux condenser, the nitrogen flows through line **110** to the subcooler **30** and condenser **26**. The remaining

refrigeration in the gas is utilized in the feed precooler 16. The nitrogen flows from the line 112 through the feed precooler 16 and is then vented to the atmosphere or used as a feed stream for chemical manufacture.

It will be apparent to those skilled in the art that variations of the process shown are possible. For example, it is not essential that the liquid methane be expanded in three different steps. It may be expanded only twice to produce one high pressure and one low pressure stream. Furthermore, there are obvious modifications which can be made in the particular form of equipment employed and it is not our intention to limit the invention otherwise than as necessitated by the scope of the appended claims.

The following table summarizes data on the methane refrigeration system in accordance with the invention, setting forth the properties of the methane cooling liquid at various points in the system. The figures are given for column pressures of 200 and 300 pounds per square inch absolute, and for feed to the column through line 28. The medium pressure separator and the liquid feed subcooler are by-passed for the system operating under these conditions.

Summary of data on methane refrigeration system for 100 MMCF. per day of 70% methane-30% nitrogen feed gas

Column pressure, p. s. i. a.	200	300
Basis, feed gas per	MCF.	MCF.
Reflux Condenser:		
Pressure, p. s. i. a.	13	22.5
Inlet temperature, ° F.	−261.5	−248.5
Inlet condition, percent liquid	75.9	81.8
Outlet temperature, ° F.	−253	−242
Flow rate, lb, stream 89	6.10	8.66
Heat load, B. t. u.	1,159	1,465
Feed Condenser:		
Low pressure methane stream 92, pressure, p. s. i. a.	13	22.5
Inlet temperature, ° F.	−253	−242
Outlet temperature, ° F.	−179	−161
Flow rate, lb	6.10	8.66
Heat load, B. t. u.	152	364
High pressure methane stream 70, pressure, p. s. i. a.	70	135
Inlet temperature, ° F.	−217.5	−199
Inlet condition (corrected for excess vapor) percent liquid	67.5	74.6
Outlet temperature, ° F.	−179	−161
Flow rate, lb	28.90	28.05
Heat load, B. t. u.	5,044	4,195
Total heat load supplied by Methane, B. t. u.	5,196	4,559
Column Reboiler and Product Vaporizer:		
Reboiler heat load, B. t. u.	2,006	2,177
Vaporizer heat load, B. t. u.	5,072	4,439
Recirculating methane pressure, p. s. i. a.	210	310
Inlet temperature, gas, ° F.	−120	−100
Outlet temperature, liquid, ° F.	−176	−158
Flow rate, lb., stream 58	34.99	36.00

What we claim as new and desire to secure by Letters Patent of the United States is:

1. In a process for separating nitrogen from a gaseous mixture of methane and nitrogen by liquefaction and fractional distillation in a distillation column maintained at elevated pressure, the steps of compressing methane refrigerant gas to above said elevated pressure, passing the compressed methane sequentially through a vaporizer containing cold product methane from the distillation column to vaporize the product methane and through cold product methane in the lower reboiler portion of the distillation column to supply heat for operating the column, thereby simultaneously reducing the temperature of the compressed methane to condense said compressed methane, firstly partially expanding said condensed methane to a gas and a liquid phase at about one-half said elevated pressure, passing the gas phase and a portion of the liquid phase through a heat exchanger to supply part of the refrigeration required to condense the feed gas, secondly further expanding the remainder of the liquid phase to a mixture of gas and liquid at about one-fourth said elevated pressure, passing the gas and most of the liquid at said reduced pressure through a second heat exchanger to supply refrigeration for subcooling said condensed feed gas before introduction into the distillation column, and finally expanding the remaining liquid from said reduced pressure to substantially atmospheric pressure to provide refrigeration for a reflux condenser connected to said distillation column.

2. A process for separating nitrogen from a gaseous mixture of methane and nitrogen feed gas which comprises compressing the feed gas to an elevated pressure and cooling it to below its condensation temperature, rectifying the condensed gas to separate its contained nitrogen and methane, passing the nitrogen resulting from said rectification through a first and second heat exchanger to supply part of the refrigeration for condensing and cooling said feed gas, compressing refrigerant methane from any source to superatmospheric pressure, cooling the compressed methane to below condensation temperature, partially expanding the cooled compressed methane to a gas and a liquid phase, and passing the gas phase through said second heat exchanger to supply a major proportion of the refrigeration required to condense the feed gas, further expanding at least a portion of said liquid phase and passing said further expanded phase through said first exchanger to supply the remainder of the refrigeration required to cool the condensed feed gas.

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