

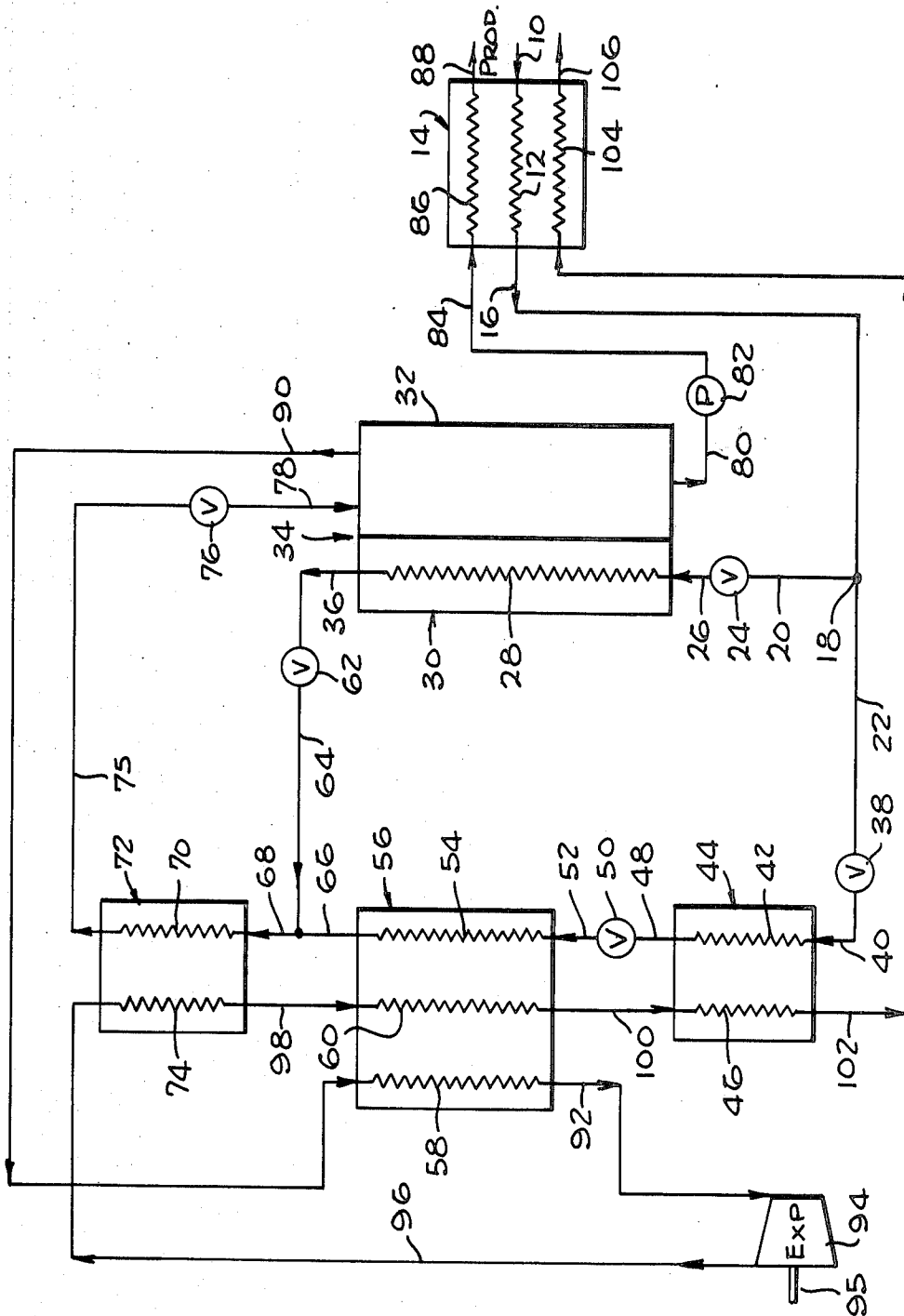
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M. L. HOFFMAN

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SEPARATION OF MIXTURES OF NITROGEN AND HYDROCARBONS

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MICHAEL L. HOFFMAN
INVENTOR.

BY *Max Gelden*

ATTORNEY

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SEPARATION OF MIXTURES OF NITROGEN AND HYDROCARBONS

Michael L. Hoffman, Beverly Hills, Calif., assignor to
McDonnell Douglas Corporation, Santa Monica, Calif.

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ABSTRACT OF THE DISCLOSURE

Method and system particularly designed for separating methane from mixtures of nitrogen and methane, and which generally contain a major proportion of nitrogen, which involves, according to one embodiment, cooling a compressed feed mixture, e.g., one containing 60% nitrogen and 40% methane, passing a major portion, e.g., 90%, of the cooled compressed feed mixture into indirect heat exchange relation with a fractionating column to supply heat to the column, further cooling the remaining minor portion, e.g., 10%, of the cooled compressed feed mixture, withdrawing the resulting cooled major portion of the compressed feed mixture from heat exchange relation with the column, combining the last-mentioned major portion of the compressed feed mixture with the further cooled minor portion of the compressed feed mixture, further cooling the resulting combined compressed mixture, reducing the pressure of such combined compressed mixture, introducing the last-mentioned mixture as feed into the fractionating column, effecting a separation of the last-mentioned mixture in the column, withdrawing hydrocarbon in substantially pure liquid form from the bottom of the fractionating column, withdrawing nitrogen containing a minor portion of hydrocarbon, as overhead vapor from the fractionating column, and passing such overhead vapor into heat exchange relation with the minor portion of the compressed feed mixture and with the combined compressed mixture for further cooling same as aforesaid. Preferably, the overhead vapor from the fractionating column is brought in several passes in series, in heat exchange relation with the minor portion of the compressed feed mixture and with the combined compressed mixture, employing work expansion following at least one of such passes for greater efficiency. There is recovered substantially pure hydrocarbon product at a pressure close to that of the feed pressure, and by allowing some of the hydrocarbon to be taken off with the overhead nitrogen from the column and which is discarded as waste, substantially no net external power is required.

This invention relates to the separation of the components of mixtures of nitrogen and hydrocarbons, particularly mixtures of nitrogen and methane, by low temperature rectification, and is particularly concerned with procedure for the separation of methane in substantially pure form from mixtures thereof with nitrogen, and particularly wherein nitrogen is present in major proportion, employing a high pressure feed mixture, and recovering substantially pure methane product at a pressure of about 75% of the pressure of the feed, preferably employing in the fractionating zone or column the principles of "differential" distillation, and with the system for carrying out such procedure.

The processing or separation of the components of natural gas containing low-boiling hydrocarbons and nitrogen, such as, for example, mixtures of methane and nitrogen, to recover substantially pure hydrocarbon, e.g., methane, for use as a low cost fuel which can be readily transported by pipeline and stored, has assumed considerable importance. By the term hydrocarbons or methane

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"in substantially pure form" as employed herein, is intended to denote such hydrocarbon or methane of at least 95% purity, and preferably of order of 97% or greater.

Further, where a high pressure feed mixture is available, it is desirable to obtain the hydrocarbon, e.g., methane, product at a pressure as close to the feed pressure as possible, while at the same time minimizing the power requirement for refrigeration, and effecting the desired fractionation or rectification so as to produce high purity product.

According to the invention, there is provided a process and system for the separation of a mixture of gases consisting essentially of a low-boiling hydrocarbon and nitrogen, e.g., one containing a major proportion of nitrogen and a minor proportion of methane, which comprises the steps of cooling a compressed feed mixture of such gases, passing a major portion of the cooled compressed feed mixture along a fractionating column in heat exchange relation therewith to supply heat to the column, further cooling the remaining minor portion of the cooled compressed feed mixture, withdrawing the resulting cooled major proportion of the compressed feed mixture from heat exchange relation with the column, combining the last-mentioned cooled major portion of the resulting compressed mixture with said further cooled minor portion of the cooled compressed feed mixture, further cooling the resulting combined compressed mixture, reducing the pressure of such further cooled combined compressed mixture, introducing the last-mentioned mixture as feed into the fractionating column, effecting a separation of the last-mentioned mixture in the column, withdrawing hydrocarbon in substantially pure liquid form from the bottom of the fractionating column, withdrawing nitrogen containing a small amount of hydrocarbon, as overhead vapor from said fractionating column, and passing the overhead vapor into heat exchange relation with said minor portion of the compressed feed mixture and with said combined compressed mixture for further cooling same as aforesaid.

Preferably, the process includes throttling the cooled minor portion of the feed mixture and throttling the cooled major portion of the compressed mixture withdrawn from heat exchange relation with said column, prior to the combining of such major and minor portions of the compressed feed mixtures, and includes throttling such combined mixture for reducing the pressure thereof, e.g., to the pressure in the fractionating column, prior to introducing such combined mixture as feed into the fractionating column.

In preferred practice, the above-noted overhead vapor of nitrogen and a minor portion of hydrocarbon removed from the top of the fractionating column is work expanded and further cooled during passage of the vapor into heat exchange relation with the minor portion of the compressed feed mixture and with the combined compressed mixture, for cooling such mixtures.

The separation in the fractionating column using indirect heat exchange between the major portion of the cooled compressed feed mixture along the fractionating column, results in effecting a differential distillation of the vapor-liquid mixture in the fractionating column, thereby increasing the efficiency thereof.

The process and system of the invention are particularly designed for separating high pressure nitrogen-methane mixtures, e.g., above 800 p.s.i., containing a major proportion of nitrogen, e.g., 50 to 70% nitrogen, and a minor proportion of methane, to provide a substantially pure hydrocarbon, e.g., methane, product at as high a pressure as possible, e.g., at a pressure up to about 75% or more, of the pressure of the feed mixture, with no net external power requirement, by permitting

a portion of the original hydrocarbon or methane, e.g., 10 to 15% thereof, to be discarded with the crude overhead nitrogen from the fractionating column. Thus, for example, utilizing a feed mixture at a pressure of 1200 p.s.i. and containing 40% methane and 60% nitrogen, a product containing 97% methane and 3% nitrogen at a pressure between about 600 and 900 p.s.i. can be obtained, the waste gas containing about 7% methane and about 93% nitrogen.

The process and system of the invention have the further advantage of requiring relatively few operational steps and a minimum of components, thereby substantially reducing maintenance and initial equipment costs.

Preferably, cooling of the initial compressed gas mixture prior to introduction of a major portion of such compressed mixture into heat exchange relation with the fractionating column, is effected by passing the feed in countercurrent heat exchange relation with cold product and waste gas streams.

The invention will be understood more clearly by the description below taken in connection with the accompanying drawing showing a schematic representation of a preferred form of separation system for separating substantially pure methane from a mixture of methane and nitrogen.

Referring to the drawing, a natural gas feed mixture 10 containing 40% methane and 60% nitrogen, compressed to a pressure of 1200 p.s.i. and at a temperature of 540° R. (Rankine), is passed through coil 12 of a main heat exchanger 14 in countercurrent heat exchange relation with cold product and waste gas streams, as will be described more fully hereinafter.

The resulting feed mixture 16 at a pressure of 1150 p.s.i. and a reduced temperature of 334° R., is divided at 18 into a first stream 20 and a second stream 22, the first stream 20 constituting a major portion, e.g., about 85 to about 95%, of the cooled compressed feed mixture 16, and the stream 22 constituting a minor portion, e.g., about 5 to about 15%, of the cooled compressed feed mixture 16.

The major portion of the compressed feed mixture 20 is throttled at 24 to a reduced pressure of 900 p.s.i., and the resulting mixture 26 at a temperature of 334° R. is introduced into the lower end of one or more passages 28 of a heat exchanger 30 in heat exchange relation with a fractionating column or zone 32, both forming the distillation unit 34. The major portion of compressed feed mixture passing upwardly through passages 28 in heat exchange relation along the column 32 provides reboil heat along the column and effects a fractionation and a separation of the feed mixture in the column, as described in greater detail hereinafter. The resulting cooled compressed portion of feed mixture exiting the upper ends of passages 28 at a temperature of about 200° R. is removed at 36.

The minor portion 22 of compressed feed mixture is throttled at 38 and the resulting throttled mixture 40, at a pressure of 900 p.s.i. and a temperature of 334° R. is passed through coil 42 of a heat exchanger 44 in countercurrent heat exchange relation with a waste gas stream passing through coil 46 of the heat exchanger. The exiting cooled stream 48 is then further throttled at 50, and the throttled mixture 52, at a reduced pressure of 400 p.s.i. and reduced temperature of 220° R. is further cooled by passage through coil 54 of a heat exchanger 56 in countercurrent heat exchange relation with cold waste gas streams passing through coils 58 and 60 of heat exchanger 56.

The major portion of compressed feed mixture exiting the distillation unit 34, at 36, is throttled at 62 to a reduced pressure of 400 p.s.i. and reduced temperature of 195° R., with the resulting throttled mixture at 64 is combined with the minor portion 66 of cooled compressed feed mixture exiting the heat exchanger 56. The combined feed mixture at 68 is then further cooled by passage

through coil 70 of a heat exchanger 72 in countercurrent heat exchange relation with a cold waste gas stream passing through coil 74, and the resulting combined cooled feed mixture 75, at a pressure of 400 p.s.i. and reduced temperature of 188° R. is then throttled at 76 to reduce pressure of 100 p.s.i. and a temperature of 188° R., and the resulting throttled combined feed mixture at 78 is introduced as liquid feed into the top of the fractionating column 32.

In the fractionating column 32, methane in substantially pure form, containing a minor amount of nitrogen, is withdrawn as product from the bottom of the column at 80, at a temperature of 244° R. and a pressure of about 102 p.s.i., and such liquid is pumped at 82 up to a pressure of 640 p.s.i., and the discharge fluid 84 at a temperature of 253° R. is introduced into coil 86 of the main heat exchanger 14 to cool compressed feed mixture in coil 12, and the exiting stream at a pressure of about 600 p.s.i. and a temperature of about 495° R., and containing 97% methane and 3% nitrogen, is taken off as product at 88.

From the top of the fractionating column 32, an overhead vapor 90 is withdrawn at a pressure of about 100 p.s.i. and a temperature of 188° R., such overhead stream containing about 92.6% nitrogen and about 7.4% methane. The overhead vapor 90 is passed through coil 58 of heat exchanger 56 for cooling the minor portion of the compressed feed stream at 54, and the exiting heated vapor stream at 92, at a pressure of 98 p.s.i. and a temperature of 212° R. is introduced into an expander or turbine 94 where it is work expanded to a reduced temperature of 20 p.s.i. and reduced temperature of 159° R. The expander 94 can be suitably coupled at 95 to the pump 82 to supply the energy for pumping the liquid hydrocarbon product at 80 to delivery pressure, as above described.

The work expanded cooled discharge vapor stream 96 is then passed through the coil 74 of the heat exchanger 72 in countercurrent heat exchange relation with the combined compressed feed stream at 70, for cooling same, and the resulting heated vapor at 98, at a pressure of 19 p.s.i. and a temperature of 188° R., is then passed through coil 60 of the heat exchanger 56 to aid in cooling the minor portion of compressed feed stream at 54, and the exiting vapor at 100, at a pressure of 18 p.s.i. and temperature of 212° R., is passed through coil 46 of the center of curvature of said arcuate surface is displaced heat exchanger 44 to cool the minor portion of compressed feed mixture at 42. The heated exiting vapor 102, at a pressure of 18 p.s.i. and a temperature of 300° R., is passed through coil 104 of the main heat exchanger 14 for cooling incoming compressed feed at 12, and the heated exiting vapor, at ambient pressure and a temperature of 495° R., containing 7.4% methane and 92.6% nitrogen, as noted above, is discharged as waste at 106.

Hence, it is seen that the process and system described above and shown in the drawing, provide a relatively simple system employing a minimum of components, for separation of substantially pure methane from a mixture thereof with nitrogen. The system is particularly designed for use with an initial feed mixture at a pressure above 800 p.s.i., and for obtaining substantially pure hydrocarbon or methane product at a pressure up to 75% or greater of the feed mixture pressure. In the system described and shown in the drawing, it is seen that the work expansion of the overhead nitrogen vapor by the expander 94 provides adequate refrigeration for cooling compressed feed mixture prior to introduction thereof as feed into the fractionating column 32, and by operating the column under conditions permitting a minor portion of the original methane present in the feed mixture, e.g., about 12%, to be discarded with the crude overhead nitrogen vapor at 90 from the column, and preferably employing the energy derived from such work expansion to pump methane product to delivery pressure, no net external power requirement is necessary.

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In the fractionating column 32 of the system described above and shown in the drawing, pressure is maintained at about 100 p.s.i., but can range from about 100 to about 300 p.s.i. At pressures above 100 p.s.i. the amount of methane in the waste stream at 90 and at 106 is increased. However, increased pressure in the column has the advantage of permitting the attainment of product pressures above 75% of the feed pressure, if desired.

The major portion of the compressed feed mixture which is passed in heat exchange relation with the mixture being separated in the fractionating column 32, functions as a heat pumping fluid to provide continuous incremental addition of reboil heat to the fractionating column 32, resulting in a continuous heat transfer along the column 32 between the fluid or compressed feed in passages 28 and the vapor-liquid mixture in the column, and a non-adiabatic differential distillation in the column. In this manner, equilibrium is much more closely approached throughout column 32 and a more efficient distillation therein occurs. In the system of the invention described above and illustrated in the drawing, since heat is added to the column 32 along its entire length by passage of the compressed feed mixture through passages 28, column 32 in effect functions entirely as a stripping column.

If desired, instead of employing a single expansion of the overhead vapor 90 for cooling of the incoming compressed feed mixture at 74, 60 and 46, there can be employed, for example, two work expansions of such overhead nitrogen vapor containing a small amount of the hydrocarbon, to provide additional cooling for the compressed feed mixture.

The heat exchange passages or constructions 28 for passage of the major compressed portion of the feed mixture, can be in the form of a plate-fin exchanger (not shown) arranged in heat exchange relation with channels bearing the liquid-vapor mixture being separated in the fractionating column 32. Such channels may be constructed in the manner of a series of vertically spaced horizontal perforated partitions extending across the column and forming a series of enclosed spaces, as described in the copending application Ser. No. 685,013, filed Nov. 22, 1967, of Michael L. Hoffman et al., or can be formed of two or more series of corrugated vertically spaced sheets, each of the two series of sheets extending horizontally, with one series of such sheets being offset from the other series, and forming a plurality of vertical channels or paths for a vapor-liquid mixture, as described in the copending application Ser. No. 685,012, filed Nov. 22, 1967, of Michael L. Hoffman. Also, a heat exchanger arrangement or construction of the type disclosed in the copending application, Ser. No. 572,135, filed Aug. 12, 1966, of James D. Yearout, now Pat. No. 3,508,412 can be employed. Since such heat exchanger arrangements or constructions per se form no part of the present invention, they are not shown herein, but the description thereof set forth in the above-identified applications are incorporated herein by reference. However, any other suitable form of heat exchanger apparatus can be employed in providing the unit 34 containing the fractionating column 32 positioned in indirect heat exchange relation with the passages 28, as described above and shown in the drawing, so as to effect the above-described differential distillation in the fractionating zone 32.

Feed mixtures which can be advantageously separated to provide substantially pure hydrocarbon product at high pressure according to the invention, include mixtures containing nitrogen and any low-boiling hydrocarbon such as methane, ethane, ethylene, propane, and the like. As previously noted, although compositions containing from about 50 to about 70% nitrogen and about 30 to about 50% methane are particularly advantageously separated according to the invention, natural gas compositions containing smaller amounts of nitrogen and larger amounts

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of methane can also be employed in the invention process, e.g., mixtures containing a minor proportion of nitrogen, e.g., about 40% nitrogen, and a major proportion of methane, e.g., about 60% methane.

While I have described particular embodiments of my invention for the purpose of illustration, it should be understood that various additional modifications and adaptations thereof may be made within the spirit of the invention, and within the scope of the appended claims.

I claim:

1. A process for the separation of a mixture of gases consisting essentially of a low-boiling hydrocarbon and a substantial proportion of nitrogen, which comprises the steps of cooling a compressed feed mixture of said gases, passing a major portion of said cooled compressed feed mixture along the entire length of a fractionating column in indirect heat exchange relation therewith to supply heat to said column, along the entire length of said column and further cooling said major portion of said cooled compressed feed mixture along the entire length of said column, and effecting a non-adiabatic differential distillation in said column, further cooling the remaining minor portion of said cooled compressed feed mixture, withdrawing the resulting further cooled major portion of said compressed feed mixture from heat exchange relation with said column, combining said last mentioned further cooled major portion of the resulting compressed mixture with said further cooled minor portion of said cooled compressed feed mixture, further cooling the resulting combined compressed mixture, reducing the pressure of said further cooled combined compressed mixture, introducing said last-mentioned mixture as feed into the top of said fractionating column, effecting a separation of said last-mentioned mixture in said column, withdrawing hydrocarbon in substantially pure liquid form from the bottom of said fractionating column, withdrawing nitrogen containing a small amount of hydrocarbon as overhead vapor from said fractionating column, and passing said overhead vapor into heat exchange relation with said minor portion of said compressed feed mixture and with said combined compressed mixture, for further cooling same as aforesaid.

2. A process as defined in claim 1, wherein said overhead vapor of nitrogen containing a small amount of hydrocarbon is work expanded and further cooled during passage of said vapor into heat exchange relation with said minor portion of said compressed feed mixture and with said combined compressed mixture, for cooling same, and wherein said liquid hydrocarbon is pumped up to a predetermined delivery pressure.

3. A process as defined in claim 1, which includes throttling said further cooled minor portion of said feed mixture and throttling said further cooled major portion of said compressed feed mixture withdrawn from indirect heat exchange relation with said column, prior to said combining said major and minor portions of said compressed feed mixtures, and including throttling said combined mixture for reducing the pressure thereof prior to introducing same as feed into said fractionating column.

4. A process as defined in claim 3, wherein said major portion of said compressed feed mixture is introduced into indirect heat exchange relation with said column adjacent to the bottom thereof, and removed from indirect heat exchange relation with said column adjacent to the top thereof, and wherein said throttled combined major and minor portions of said feed mixture is introduced as liquid feed into the top of said fractionating column.

5. A process as defined in claim 4, wherein said overhead vapor of nitrogen containing a small amount of hydrocarbon is work expanded and further cooled during passage of said vapor into heat exchange relation with said minor portion of said compressed feed mixture and with said combined compressed mixture, for cooling same, and wherein said liquid hydrocarbon is pumped up to a

predetermined delivery pressure, and employing the energy derived from said work expansion for said pumping.

6. A process as defined in claim 1, wherein said overhead vapor of nitrogen containing a small amount of hydrocarbon is passed first in heat exchange relation with said minor portion of said cooled compressed feed mixture, the resulting heated nitrogen-hydrocarbon vapor is work expanded and cooled, and said cooled work expanded vapor then passed in heat exchange relation with said combined compressed mixture, and including passing the resulting exiting heated nitrogen-hydrocarbon vapor again into heat exchange relation with said minor portion of said cooled compressed feed mixture.

7. A process as defined in claim 1, wherein said mixture of low-boiling hydrocarbon and nitrogen gases is a nitrogen-methane gas mixture consisting of about 50 to 70% nitrogen and a minor proportion of methane, said nitrogen-methane feed mixture being initially compressed above about 800 p.s.i.

8. A process as defined in claim 1, including throttling said major portion of said cooled compressed feed mixture prior to passing same indirect in heat exchange relation along said fractionating column, initially throttling the remaining minor portion of said cooled compressed feed mixture, initially further cooling said throttled minor portion of compressed feed mixture, further throttling said last-mentioned further cooled minor portion of compressed feed mixture, again cooling said further throttled minor portion of compressed feed mixture, and throttling said major portion of compressed feed mixture withdrawn from heat exchange relation with said column, and wherein said last-mentioned throttled major portion of the compressed feed mixture is combined with said further throttled cooled minor portion of compressed feed mixture, and wherein the resulting combined mixture is reduced in pressure by throttling prior to introduction as feed into said fractionating column.

9. A process as defined in claim 8, wherein said overhead vapor of nitrogen containing a small amount of hydrocarbon is passed first in heat exchange relation with said further throttled minor portion of compressed feed mixture for cooling said last-mentioned minor portion of compressed feed mixture, the resulting heated nitrogen-hydrocarbon vapor is work expanded and cooled, and said cooled work expanded vapor then passed in heat exchange relation with said combined compressed mixture for cooling same, and including passing the resulting exiting heated nitrogen-hydrocarbon vapor again into heat exchange relation with said further throttled minor portion of compressed feed mixture, and then into heat exchange relation with said initially throttled minor portion of said cooled compressed feed mixture.

10. A process as defined in claim 9, including passing substantially pure liquid hydrocarbon from the bottom of said fractionating column, and passing overhead nitrogen-hydrocarbon vapor following passage thereof in heat exchange relation with said minor portion of said initially throttled minor portion of compressed feed mixture, into heat exchange relation with said compressed feed gas mixture for cooling same.

11. A process as defined in claim 1, wherein said hydrocarbon is methane.

12. A process as defined in claim 1, wherein said mixture of low-boiling hydrocarbon and nitrogen gases is a nitrogen-methane gas mixture consisting of about 60% nitrogen and about 40% methane, said nitrogen-methane feed mixture being initially compressed above about 800 p.s.i., and wherein said minor portion of the compressed feed mixture is about 5 to about 15% of the total compressed feed mixture, said overhead nitrogen vapor contains about 10 to about 15% of the methane in said compressed feed mixture, and the substantially pure liquid

methane withdrawn from the bottom of said fractionating column is pumped to a product delivery pressure of the order of about 75% of the pressure of said compressed feed mixture.

13. A system for the separation of a mixture of gases consisting essentially of a low-boiling hydrocarbon and a substantial proportion of nitrogen, which comprises a fractionating column, heat exchange means disposed in heat exchange relation along the entire length of said fractionating column for passage of a heat exchange fluid in indirect heat exchange relation along the entire length of said column, means for introducing a major portion of said cooled compressed feed mixture into said heat exchange means, means for withdrawing the resulting major portion of said compressed feed mixture from said heat exchange means, means for further cooling the remaining minor portion of said cooled compressed feed mixture, means for combining the major portion of the compressed mixture withdrawn from said heat exchange means, with said further cooled minor portion of said cooled compressed feed mixture, means for throttling said further cooled combined compressed mixture, means for introducing said last-mentioned throttled mixture as feed into the top of said fractionating column, means for withdrawing hydrocarbon in liquid form from the bottom of said fractionating column, means for withdrawing overhead nitrogen containing a small amount of hydrocarbon, as overhead vapor from said fractionating column, and means for passing said overhead vapor into heat exchange relation with said minor portion of said compressed feed mixture and with said combined compressed mixture, for further cooling same as aforesaid.

14. A system as defined in claim 13, including means for throttling said further cooled minor portion of said feed mixture, means for throttling said major portion of the said compressed feed mixture withdrawn from said heat exchange means, prior to said combining said major and minor portions of said compressed feed mixtures, an expander, means for introducing said overhead vapor withdrawn from heat exchange relation with said minor portion of said compressed feed mixture into said expander, means for introducing the work expanded minor portion of said feed mixture into heat exchange relation with said combined compressed mixture, and means for again passing the resulting expanded vapor into heat exchange relation with said minor portion of compressed feed mixture for further cooling same.

15. A system as defined in claim 14, including a pump, means for introducing said hydrocarbon liquid from the bottom of said fractionating column into said pump, means for passing the resulting pumped hydrocarbon into heat exchange relation with said compressed feed mixture for initially cooling same, and means for passing said expanded vapor discharged from heat exchange relation with the last-mentioned minor portion of compressed feed mixture, into heat exchange relation with the compressed feed mixture for initially cooling same.

References Cited

UNITED STATES PATENTS

1,460,545	7/1923	Haynes et al.	62—40
2,503,265	4/1950	Haynes	62—28
2,658,360	11/1953	Miller	62—31
2,677,945	5/1954	Miller	62—39
2,713,780	7/1955	Williams	62—34
2,713,781	7/1955	Williams	62—39
2,823,523	2/1958	Eakin et al.	62—39

WILBUR L. BASCOMB, Jr., Primary Examiner

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62—39, 41