TREATMENT OF GASEOUS HYDROCARBON MATERIAL STREAMS

FIG. 1.

FIG. 2.

INVENTORS.

BY

ATTORNEYS
This invention relates to methods for separating nitrogen from methane and from other mixtures, particularly natural gas. In one particular aspect it relates to methods for increasing the heating value of gas streams containing nitrogen, particularly natural gas. In another particular aspect it relates to methods for decreasing the volume occupied by natural gas by removing inert materials therefrom, and thereby greatly reducing the cost of pipe line transportation. In still another aspect it relates to a new method of treating natural gas to remove nitrogen, produce a methane stream and an ethane stream.

Natural gas as it comes from producing wells often contains considerable quantities of nitrogen. Wells in the Panhandle area of Texas, for example, yield gas in which the nitrogen content is from 12 to 15 mol per cent. An example is the natural gas from the Hugoton field in Texas. Natural gas produced in certain sections of Kansas and elsewhere is objectionably high in nitrogen content. For many uses the presence of nitrogen in such proportions is not particularly disadvantageous, but transportation of such inert diluent over long distances is costly and it is often desirable to increase the heating value of the gas by eliminating inert materials.

It has become customary to employ natural gas in city gas systems. The natural gas may be employed in the form in which it is received by the city or it may be used to enrich ordinary manufactured gas to increase the heating value thereof. In either event and especially where the natural gas is used for enrichment of manufactured gas, it is desirable that the natural gas have as high a B. t. u. value as possible. At the same time it is customary to remove from the natural gas at or near the point of its production, as much of the heavier components as is economically possible. This may be done by the ordinary processes of making natural gasoline. The heavier components (especially propane and heavier), when separated and liquefied, bring a much higher price than they would if they were left in the gas and sold in the gaseous form. At the same time there are minimum specifications on the heating value of natural gas sold for fuel purposes. Usually it is required that the gas have a minimum heating value of 1000 B. t. u. per cubic foot. This prevents the natural gas manufacturer from “cutting” too deeply into the gas for extraction of Cs and heavier components, especially if the gas contains substantial quantities of nitrogen. For example, a gas having a heating value of 1000 B. t. u. per cubic foot and containing 15 per cent by volume of nitrogen will have a heating value of 1,150 B. t. u. upon removal of this nitrogen. Then also, a gas of this latter heating value can yield a considerable quantity of liquefiable components (such as gasoline hydrocarbons) and yet maintain a heating value of 1000 B. t. u.

A typical natural gas from the Texas Panhandle area may be analyzed as follows:

<table>
<thead>
<tr>
<th>Component</th>
<th>Mol Fraction</th>
<th>Heating Value of Pure Component</th>
<th>Heating Value Contributed to Gas</th>
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<tr>
<td>Nitrogen</td>
<td>0.1238</td>
<td>1215 B. t. u./cu. Ft.</td>
<td>1,150 B. t. u./cu. Ft.</td>
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<tr>
<td>Methane</td>
<td>0.7558</td>
<td>1,013 B. t. u.</td>
<td>1,013 B. t. u.</td>
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<tr>
<td>Ethane</td>
<td>0.0634</td>
<td>882 B. t. u.</td>
<td>882 B. t. u.</td>
</tr>
<tr>
<td>Propane</td>
<td>0.0441</td>
<td>520 B. t. u.</td>
<td>520 B. t. u.</td>
</tr>
<tr>
<td>Butane</td>
<td>0.0179</td>
<td>278 B. t. u.</td>
<td>278 B. t. u.</td>
</tr>
<tr>
<td>Pentane</td>
<td>0.0035</td>
<td>23 B. t. u.</td>
<td>23 B. t. u.</td>
</tr>
<tr>
<td>Hexane</td>
<td>0.0019</td>
<td>10 B. t. u.</td>
<td>10 B. t. u.</td>
</tr>
<tr>
<td>C5+</td>
<td>0.0013</td>
<td>9 B. t. u.</td>
<td>9 B. t. u.</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>1,150 B. t. u./cu. Ft.</td>
<td>1,150 B. t. u./cu. Ft.</td>
</tr>
</tbody>
</table>

From the foregoing it will be seen that the removal of nitrogen from natural gas is very important. Various means have heretofore been proposed for effecting removal of nitrogen from natural gas. Previous proposals may be divided broadly into two classes which in turn may be subdivided broadly into two classes, as follows:

1. Chemical methods, (1) fixation of nitrogen as by causing the nitrogen selectively to chemically react with a chemical element or compound to form a compound which may then be separated from the unreacted hydrocarbon residue gas, (2) selective reaction of the hydrocarbon with a suitable material, such as reaction with water to form the hydrate which may be separated and treated in known manner to regenerate the hydrocarbon; and (2) Physical methods, (1) separation of nitrogen from hydrocarbon gas by scrubbing with a solvent which selectively dissolves the nitrogen and is relatively a non-solvent for the hydrocarbons, by a diffusion method taking advantage of the difference in diffusion rates of the nitrogen and the hydrocarbon.
through a suitable membrane or diffusion mem-
ber. (2) separation of hydrocarbon from nitrogen 
as by scrubbing the gas with a solvent which 
dissolves the hydrocarbon and is relatively a 
non-solvent for nitrogen, or by so-called "deep 
refrigeration" in which the natural gas is lique-
fied and at a temperature and pressure that will 
discharge the hydrocarbon material. This pro-
cess, has been found to be advantageous when 
separating hydrocarbons at high temperatures. 
For various reasons, no plan for the remo-
val of nitrogen has been used commercially.

Each of the previously advanced proposals has 
involved various disadvantages, such as exces-
sive capital, insufficient separation factor, etc. 
Low temperature fractional distillation to re-
move nitrogen from natural gas or methane has 
not proven practical or economical because the 
reflux to the column is substantially pure nitro-
gen, which has a relatively low latent heat in 
comparison to methane, and the nitrogen reflux 
must be condensed at a very low temperature, 
with the net result that the power requirements 
for this refrigeration load are very great. Selec-
tive adsorption separation processes, such as 
the known continuous moving bed selective ad-
sorption processes, are, at present, not advantageously applied to 
the separation of nitrogen from natural gas or 
the methane contained therein because the 
highly predominant component, methane, must 
be adsorbed and this requires a high circulation 
rate of adsorbent, such as activated-carbon, 
and large equipment to handle a comparatively 
small amount of gas.

We have invented a combination process for 
treating a gaseous mixture comprising nitrogen, 
methane and C2 and higher-boiling hydrocarbon 
materials, which can advantageously be applied 
to removing nitrogen from natural gas. In carry-
going on the process of our invention in treating a 
gas containing C2 and higher-boiling hydrocarbon 
materials as well as nitrogen and methane, we 
compress and cool the gaseous mixture to con-
dense C2 and higher-boiling hydrocarbon ma-
terials. The resulting gaseous mixture of nitrogen 
and methane is then fractionally distilled at low 
temperature to yield an overhead mixture of ni-
rogen and methane and a bottoms of methane.

The overhead mixture contains sufficient 
methane so as to have permitted condensation of a 
methane-rich reflux, thereby refluxing the low-
temperature fractional distillation zone with a 
reflux stream which is rich in methane and in 
equilibrium with the overhead mixture of nitrogen 
and methane, permitting operation at a 
higher temperature than normal with far less 
refrigeration. The resulting overhead methane 
and nitrogen stream is then separated in a selective 
adsorption separation zone, preferably a continu-
ous moving bed selective adsorption separation 
zone utilizing activated-carbon, to produce a 
nitrogen stream and a methane stream. Since 
the quantity of methane has been greatly re-
duced by the low-temperature fractional distilla-
tion operation, the capacity of the selective ad-
sorption separation equipment has been in-
creased or, for example, less circulation of ad-
sorbent in moving bed systems is required. In 
addition, the low-temperature fractional distilla-
tion step provides a nitrogen and methane feed 
stream to the selective adsorption separation 
zone at a low temperature, thus aiding adsorp-
tion and increasing the capacity of the selective 
adsorbent.

In a modification of the process of our inven-
tion, the condensate of C2 and higher-boiling hy-
drocarbons resulting from compressing and cool-

ing the feed gas mixture, for instance, natural 
gas, is fractionally distilled to yield an overhead 
methane and C2 hydrocarbon stream which is fed 
to the selective adsorption separation zone of 
our invention. If a natural gas is being treat-
ed deethanization results in recovering methane 
unavoidably condensed along with ethane and 
higher-boiling hydrocarbon materials in the com-
pressing and cooling step of the process of our 
invention. The selective adsorption separation 
step of our invention is then operated to recover an 
overhead nitrogen stream, a side product 
methane stream and a bottoms C2 hydrocarbon 
stream.

Another object of our invention is to provide a 
method for the separation of nitrogen from me-
thane and from other mixtures, such as natural 
gas, in a simple and economical manner.

Another object of our invention is to provide a 
method in which refrigeration requirements are 
very much lower than in so-called "deep refrig-
eration" or low-temperature fractional distilla-
tion processes for nitrogen removal.

Another object of our invention is to provide a 
process whereby nitrogen removal is accom-
plished while at the same time a methane stream 
and a C2 hydrocarbon stream are produced.

Other objects and advantages of the process of 
this invention will become apparent, to one 
skilled in the art, upon reading this disclosure.

The drawings which accompany and are a part 
of this disclosure are diagrammatic flow charts 
setting forth preferred specific embodiments of 
the process of our invention. The drawings are 
an embodiment of the process of our invention 
used to remove nitrogen from a gaseous mixture 
comprising nitrogen, methane and C2 and higher-
boiling hydrocarbon materials, such as a natural 
gas, and to produce a methane stream and a C2 
and higher-boiling hydrocarbon stream. Figure 2 
depicts an embodiment of the process of our 
invention used to produce a C2 hydrocarbon 
stream, an ethane stream if natural gas is treat-
ed, as well as to remove nitrogen and produce a 
methane stream.

Referring now to Figure 1, the following is a 
discussion of a preferred specific embodiment of 
the process of our invention wherein a feed gas 
stream comprising nitrogen, methane and C2 
and higher-boiling hydrocarbon materials, such 
as a natural gas, is treated to remove nitrogen, 
produce a methane stream and a C2 and higher-
boiling hydrocarbons stream. The feed gas stream 
is passed via line 4 into compression and cooling 
zone 6 wherein it is compressed and cooled to 
condense C2 and higher-boiling hydrocarbon ma-
terials. Resulting condensed materials are with-
drawn via line 8 for further treatment, as dis-
cussed hereinafter with regard to the modifica-
tion of our invention shown in Figure 2, or to be 
used as desired.

A gaseous mixture, resulting from such com-
pressing and cooling and containing nitrogen 
and the methane uncondensed, is withdrawn via 
line 10 and passed into fractionation zone 12 
wherein a fractional separation of nitrogen and 
methane is made. Fractionation zone 12 is op-
erated to produce a nitrogen and methane stream 
which is withdrawn via line 14 and a methane 
bottoms stream which is withdrawn via line 16. 
This methane stream which is preferably 
substantially free of nitrogen is combined
with another methane stream, produced as hereinafter set forth, and withdrawn from the system or it can be used as desired. Fractionation zone 12 is operated so that considerable methane is carried overhead with the nitrogen, and through this overhead gas stream is in equilibrium with liquid reflux to fractionation zone 12, the liquid reflux is relatively rich in methane, thus requiring less refrigeration and allowing for higher operating temperatures than would be possible in making a relatively finite separation between nitrogen and methane.

The nitrogen and methane mixture withdrawn overhead from fractionation zone 12 via line 14 is passed into selective adsorption separation zone 18 which is preferably a continuous moving bed selective adsorption separation zone. There in nitrogen and methane are separated. The nitrogen is removed from selective adsorption separation zone 18 via line 20 and the methane is removed via line 22. We prefer to use a portion of the methane stream, stripped from the selective adsorbent, preferably activated-charcoal, in the stripping section of selective adsorption zone 18 as the stripping medium. However, other stripping means can be used. A portion of the methane stream in line 22 is withdrawn via line 24, heated in indirect heat exchange means 25 and passed into the lower portion of the stripping section, thus furnishing heat to strip methane from the selective adsorbent. On Figure 1 a gas-lift system, using nitrogen withdrawn from line 20 via line 26 and pressured by blowers 30, is used to elevate selective adsorbent back into the upper portion of selective adsorption separation zone 18 via line 22. However, other elevating means, such as mechanical elevating means, can be used. Methane remaining on the selective adsorbent passed back into the upper portion of selective adsorption separation zone 18 is removed by passing a portion of the nitrogen overhead gas up through the select adsorbent prior to its introduction into the adsorption section. This nitrogen gas containing removed methane is withdrawn via line 34 and can be used as a low B.t.u. fuel gas or as desired. The methane stream withdrawn via line 22 can be withdrawn from the system or combined via line 36 with the methane bottoms stream from fractionation zone 12.

Referring now to Figure 2, the following is a discussion of a preferred specific modification of the process of our invention wherein a feed gas stream like that treated according to Figure 1, as hereinbefore discussed, is treated to remove nitrogen, produce a methane stream and, in addition, recover more methane and produce a C3 hydrocarbon stream, an ethane stream if natural gas is being treated. The same reference numerals are used on Figure 2 as used on Figure 1 where the equipment performs the same operation or the same operation is carried out. In this embodiment of the process of our invention, the C3 and higher-bolling hydrocarbon materials withdrawn from compression and cooling zone 6 via line 9 are selectively distilled in fractionation zone 38 where, if a natural gas is being treated, would be a deethanizer, to produce a methane and C3 hydrocarbon stream overhead, which is withdrawn via line 40, and a higher-boliling hydrocarbon material stream as bottoms, which is withdrawn via line 42 to be treated or used as desired.

The methane and C3 hydrocarbon stream, which contains methane condensed in compression and cooling zone 6, is passed via line 48 into selective adsorption separation zone 42, which is designed to make a methane side-product stream and is preferably a continuous moving bed selective adsorption separation zone, using activated-charcoal as the selective adsorbent. This stream is introduced at a point below the point of withdrawal of the methane-side product stream which in turn is below the point of introduction of the nitrogen and methane feed stream introduced via line 14. The methane introduced in the feed streams is separated, removed via line 44 as a side-product stream and withdrawn from the system, or it can be combined with the methane stream from fractionation zone 12 via line 46 and withdrawn from the system. In this method of operation the methane in the gas stream treated is substantially completely recovered free of nitrogen to be available for sale or use as fuel-gas. C3 hydrocarbon is separated and withdrawn from selective adsorption zone 42 via line 48. Any suitable striping medium can be used to strip the C3 hydrocarbons from the selective adsorbent in the lower stripping section of selective adsorption separation zone 42 but we prefer to use a portion of the C3 hydrocarbon stream in line 48. A portion of this stream is withdrawn via line 50, heated in indirect heat exchange means 52 and passed into the lower portion of the stripping section. C3 hydrocarbon remaining on the selective adsorbent elevated back into the upper section of zone 42 is removed by passing a portion of the nitrogen overhead gas up through the selective adsorbent prior to its introduction into the adsorption zone. This nitrogen gas and removed C3 hydrocarbon is withdrawn via line 34 to be used as desired, such as a low B.t.u. fuel-gas.

In carrying on the process of our invention and its modification, as set forth heretofore, we find it particularly advantageous to apply to treating a natural gas containing from .10 to 30 mol per cent or more nitrogen, from 55 to 75 mol per cent methane and the remainder C3 and higher-boiling hydrocarbon materials. We prefer to compress and cool to a pressure of from 200 to 1000 pounds per square inch absolute and a temperature of from 50° F. to 200° F., more preferably to a temperature of from 80° F. to 165° F. Compression and cooling is preferably carried out to an extent that the nitrogen and methane stream passed to the denitrification zone, fractionation zone 12, contains no more than 1.5 mol per cent C3 and higher-boiling hydrocarbon materials.

We prefer to operate fractionation zone 12 at a pressure of from 200 to 500 pounds per square inch absolute and a top temperature of from 80° F. to 280° F. to produce an overhead feed gas stream for selective adsorption separation zones 18 and 42 containing from 55 to 75 mol per cent nitrogen and 25 to 45 mol per cent methane. Such an overhead gas stream provides a methane rich reflux stream, with which it is in equilibrium, to reflux fractionation zone 12. Selective adsorption separation zones 18 and 42 are preferably operated at a pressure of from 200 to 500 pounds per square inch absolute.

In the modification of our invention as depicted by Figure 2, fractionation zone 38 is normally and preferably operated to produce an overhead gas to feed selective adsorption separation zone 42 containing from 30 to 70 mol per cent methane and from 30 to 65 mol per cent...
C₃ hydrocarbon or ethane, if natural gas is being treated. The discussions set forth hereinbefore of the preferred embodiment of the process of our invention and the drawings will serve as examples of the process of our invention. However, such discussions, drawings, operating conditions, compositions, materials, etc., are not to unduly limit the scope of our invention.

As will be evident to those skilled in the art, various modifications of this invention can be made or followed, in the light of this disclosure and discussion, without departing from the spirit or scope of this disclosure or from the scope of the claims.

We claim:

1. A process for treating a gaseous mixture comprising nitrogen, methane, and C₂ and higher-boiling hydrocarbon materials which comprises: compressing and cooling said mixture, thereby condensing said C₂ and higher-boiling hydrocarbon materials; passing resulting uncondensed nitrogen and methane into a low-temperature fractional distillation zone, thereinafter effecting a fractional separation of nitrogen and methane; withdrawing an overhead stream containing nitrogen and methane from said low-temperature fractional distillation zone, passing same into a selective adsorption separation zone and therein separating nitrogen and methane; and withdrawing a resulting overhead nitrogen stream and a bottoms methane stream from said selective adsorption separation zone.

2. The process of claim 1 wherein said low-temperature fractional distillation zone is refluxed with a methane rich reflux in equilibrium with said overhead stream containing nitrogen and methane withdrawn from said low-temperature fractional distillation zone.

3. A process for treating a gaseous mixture containing from 10 to 30 per cent nitrogen, from 55 to 75 per cent methane and C₂ and higher-boiling hydrocarbon materials which comprises: compressing said mixture to a pressure of from 200 to 1000 pounds per square inch absolute and cooling same to a temperature of from —50 to —200 °F., thereby condensing said C₂ and higher-boiling hydrocarbon materials; passing resulting uncondensed nitrogen and methane into a low-temperature fractional distillation zone operating at a pressure of from 200 to 500 pounds per square inch absolute and a top temperature of from —250 °F. to —80 °F. and therein effecting a fractional separation of nitrogen and methane; withdrawing an overhead stream containing methane and from 55 to 75 per cent nitrogen from said low-temperature fractional distillation zone, passing same into a continuous moving bed selective adsorption separation zone, operating at a pressure of from 200 to 500 pounds per square inch absolute and therein separating nitrogen and methane; withdrawing a resulting overhead nitrogen stream and a bottoms methane stream from said selective adsorption separation zone.

4. A process for treating a gaseous mixture comprising nitrogen, methane and C₂ and higher-boiling hydrocarbon materials which comprises: compressing and cooling said mixture, thereby condensing said C₂ and higher-boiling hydrocarbon materials; passing resulting uncondensed nitrogen and methane into a first fractional distillation zone operating at low-temperatures, therein effecting a fractional separation of nitrogen and methane and withdrawing an overhead stream comprising nitrogen and methane; passing said C₂ and higher-boiling hydrocarbon materials stream resulting from said compressing and cooling into a second fractional distillation zone, therein effecting a fractional separation and withdrawing an overhead stream comprising methane and C₂ hydrocarbons, passing said nitrogen and methane stream from said first fractional distillation zone and said methane and C₂ hydrocarbons stream withdrawn from said second fractional distillation zone into a selective adsorption separation zone and thereinafter effecting a fractional separation of nitrogen, methane, and C₂ hydrocarbons; and withdrawing an overhead nitrogen stream, a side product methane stream and a bottoms C₂ hydrocarbon stream from said selective adsorption separation zone.

5. A process for treating a gaseous mixture comprising nitrogen, methane and saturated C₂ and higher-boiling hydrocarbon materials which comprises: compressing and cooling said mixture to a pressure of from 200 to 1000 pounds per square inch absolute and a temperature of from —50 °F. to —200 °F., thereby condensing said C₂ and higher-boiling hydrocarbon materials; passing resulting uncondensed nitrogen and methane into a first fractional distillation zone operating at a pressure of from 200 to 500 pounds per square inch absolute and a top temperature of from —250 °F. to —80 °F., therein effecting a fractional separation of nitrogen and methane; withdrawing an overhead stream containing methane and from 55 to 75 per cent nitrogen; passing a C₂ and higher-boiling hydrocarbon materials stream resulting from said compressing and cooling into a de-ethanization zone, therein effecting a fractional separation and withdrawing an overhead stream containing from 35 to 70 per cent methane and from 30 to 65 per cent ethane; passing said nitrogen and methane stream withdrawn from said first fractional distillation zone and said methane stream withdrawn from said de-ethanization zone to a continuous moving bed activated-charcoal selective adsorption separation zone operating at a pressure of from 200 to 500 pounds per square inch absolute and therein effecting separation of nitrogen, methane, ethane and separating a nitrogen stream, a side product methane stream, and a bottoms ethane stream from said selective adsorption separation zone.

6. A process for separating a gaseous mixture comprising nitrogen and methane which comprises, passing said mixture into a low-temperature fractional distillation zone and therein effecting a fractional separation of nitrogen and methane, thereby producing an overhead stream of nitrogen and methane in equilibrium with a methane rich stream, using said methane rich stream to reflux said low-temperature fractional distillation zone, separating said overhead nitrogen and methane stream in a selective adsorption separation zone to produce an overhead nitrogen stream and a methane stream.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

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<thead>
<tr>
<th>Number</th>
<th>Name</th>
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<td>2,329,219</td>
<td>Carey</td>
<td>Feb. 4, 1941</td>
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<tr>
<td>2,475,957</td>
<td>Gilmore</td>
<td>July 12, 1949</td>
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<td>2,519,343</td>
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