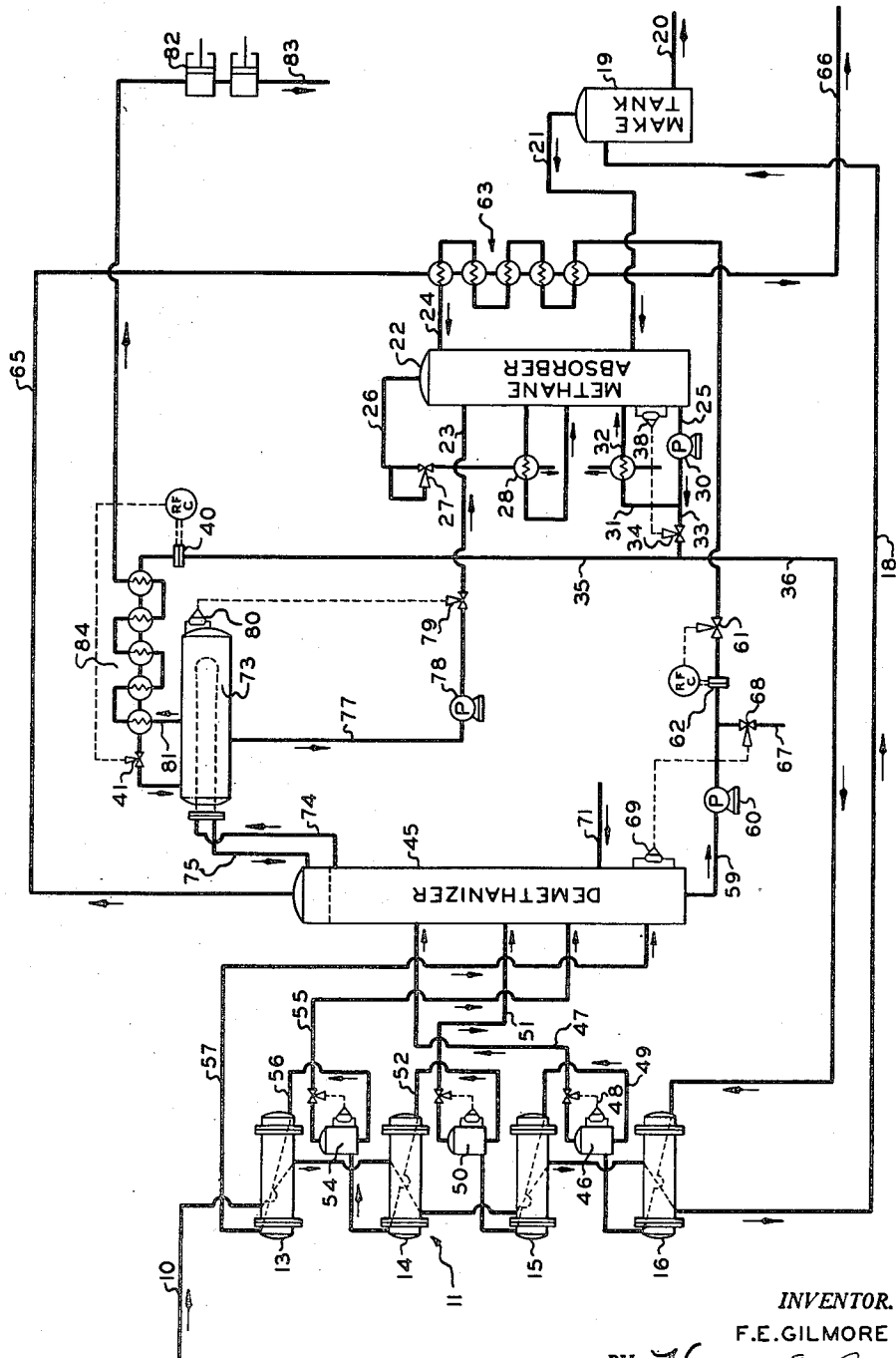


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METHOD OF AND APPARATUS FOR SEPARATING
THE CONSTITUENTS OF HYDROCARBON GASES
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METHOD OF AND APPARATUS FOR SEPARATING THE CONSTITUENTS OF HYDROCARBON GASES

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This invention relates to a method of and apparatus for separating the constituents of hydrocarbon gases, such as natural gas.

The gas emerging from an oil or gas well ordinarily contains a major proportion of methane, a minor proportion of heavier hydrocarbons, such as propane, butane, pentane and the like, and a minor proportion of gases, such as nitrogen and carbon dioxide. In the early period of oil production, it was common practice to ignite the gas flowing from the wells and thereby waste the entire hydrocarbon content thereof. Subsequently, methods were devised for recovering the heaviest hydrocarbons and transforming them into a stable gasoline mixture, the lighter products, such as ethane and methane, being allowed to escape as waste gases. Still later, processes were developed to recover the lighter constituents, such as butane and propane and, recently, some commercial systems have been developed for recovering ethane. In each of these systems, however, the residue gas, predominantly methane, contained the nitrogen originally present in the gas mixture, the percentage of nitrogen sometimes being as high as 10 to 20 per cent.

The nitrogen in the methane acted as a diluent which substantially increased the cost of transporting gas having a specified or predetermined heating value per thousand cubic feet. In many instances, in order to obtain a specified B. t. u. content, it was necessary to add higher boiling hydrocarbons, such as butane or propane, to the diluted gas. With the increasing demand for hydrocarbons, such as propane or butane, in the liquefied petroleum gas industry, as well as in polymerization and alkylation processes, it has become uneconomical to add such compounds to the methane-nitrogen mixture in order to increase the B. t. u. content thereof.

It has been proposed to remove the nitrogen by the liquefaction of the natural gas and the separation of nitrogen from methane by fractionation. This is a difficult separation and requires an excessive amount of refrigeration at low temperature levels.

In accordance with the present invention, the nitrogen and other inert materials are effectively removed from the natural gas without the use of excessive refrigeration and at higher temperatures than have heretofore been possible. In addition, the ethane and heavier hydrocarbons are effectively separated from the methane and substantially completely recovered. The removal of nitrogen and other inert materials increases

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the B. t. u. content of the methane residue and substantially eliminates or greatly minimizes the necessity of adding higher boiling point hydrocarbons to the methane gas. Furthermore, due to the elimination of the inert material, pipe lines with less compressor capacity and smaller gas holders and other equipment are required for the transportation of the gas.

The present invention contemplates the cooling of well gases to a temperature above the boiling point of methane but below the boiling point of ethane and heavier hydrocarbons, thereby causing the heavier hydrocarbons to condense and leave a residue gas consisting essentially of methane and nitrogen. This mixture is contacted with a suitable absorbent liquid, such as ethane, to preferentially absorb the methane and thereby separate it from the nitrogen or other waste gases. The waste gases are expanded to provide refrigeration for taking up the heat of absorption of methane by the liquid ethane. The temperature of the rich absorption liquid containing methane is raised by heat exchange with the incoming stream of natural gas, after which it is fractionated to provide a bottom product consisting of the denuded liquid absorption material, which is recycled to the absorber unit, and a top product consisting of gaseous methane which, in many instances, is transported great distances through pipe lines to market. Before entering the fractionation tower, the rich absorption liquid containing methane is separated into several streams of fluid of different temperatures and compositions, these streams being passed into the fractionating tower at regions where the tower temperatures and compositions are similar to those of the respective incoming streams. This procedure improves the heat transfer efficiency in the heat exchangers, the ease of separation in the fractionator and greatly reduces the amount of refrigeration needed in the fractionation column.

A portion of the rich absorption liquid containing methane is separated from the main stream leaving the bottom of the absorber, expanded, and fed to an evaporator wherein flashing of the rich absorbent cools and condenses reflux fluid for the fractionating tower. The flashing of the absorption liquid produces a methane rich vapor stream and cools the partially denuded absorption liquid which is recycled to an intermediate point of the absorber. The temperature of the methane rich gas leaving the system is extremely low and, accordingly, it is advantageously utilized in heat exchangers to

reduce the temperature of the rich absorbent being passed to the evaporator and the denuded absorption material recycled to the absorber. In this manner, a minimum of external refrigeration is required for the process, due to the efficient transfer of heat between hot and cold streams. The whole process is advantageously conducted at a high pressure, in order to elevate the boiling points of the constituents used, and it is a feature of the invention that the outlet gases are discharged at substantially the same pressure with which they enter the process, a minimum of compression being needed to supply losses occurring in the apparatus.

It is an object of the invention to provide an improved method of separating the constituents of a hydrocarbon gas mixture, such as natural gas.

It is a further object of the invention to provide apparatus for obtaining such results.

It is a still further object of the invention to provide a method of and apparatus for effectively removing nitrogen and other diluents from methane.

It is a still further object of the invention to provide a system in which the need for external refrigeration is reduced to a minimum by utilizing efficient heat transfer methods within the system.

It is a further object of the invention to provide a system which is reliable in operation, efficient, and which requires a minimum of power in the form of refrigeration and compression.

Various other objects, advantages and features of the invention will become apparent from the following detailed description taken in conjunction with the accompanying drawing, in which the figure is a schematic flow diagram of the system of the present invention.

Referring now to the drawing in detail, the gas to be separated is fed through a line 10 to a multi-stage heat exchanger 11. This gas is composed of a major portion of methane, a minor portion of higher boiling hydrocarbons, such as ethane, propane, butane, and the like, together with a minor portion of gases, such as nitrogen, which have a lower boiling point than methane. Preferably, the feed gas enters the system at room temperature, and at a high pressure. Thus, after a suitable dehydration treatment, feed gas may be conveyed to the system directly from the high pressure well where it originates.

In the heat exchanger 11, heat is removed from the gas to cool it to a sufficiently low temperature as to liquefy the higher boiling hydrocarbons, while permitting the methane and low-boiling point constituents to remain in the gaseous phase. To this end, the feed gases are passed by line 10 into high temperature stage 13, intermediate temperature stages 14, 15 and low temperature stage 16 of the heat exchanger. At the same time, a relatively cold rich absorption liquid is passed through the heat exchanger so that it flows countercurrently with respect to the flow of gas from line 10, as will hereinafter be described in detail.

The cooled natural gas from the heat exchanger, consisting of a mixture of higher boiling hydrocarbons in the liquid phase together with methane and low boiling point constituents in the gaseous phase, is passed through a conduit 18 to make tank 19, wherein separation of the liquid and vapor phases occurs. The liquid higher boiling hydrocarbons, sometimes called raw natural gasoline, are withdrawn by a line

20, from which they may flow to a de-ethanizer unit, or other processing as desired. The uncondensed gaseous methane together with low-boiling constituents is fed through a line 21 to a bottom portion of an absorption tower 22.

The gas admitted to the tower through line 21 flows in an upward direction and is intimately contacted by an absorption liquid flowing downwardly through the tower, the absorption liquid entering the tower through lines 23, 24 from sources to be hereinafter described. Preferably, the absorption material is liquid ethane, although I contemplate that other suitable materials, such as propane, propylene, and ethylene, which will preferentially absorb methane from the ascending gas, may be used. The tower 22 is preferably of the bubble tray type, although a packed tower may be used with some loss in efficiency.

The scrubbing action occurring between the absorption liquid and gas causes substantially all the methane to be preferentially absorbed by the liquids. Accordingly, rich liquid containing absorbed methane passes from the bottom of the tower through line 25 while gaseous low-boiling constituents, principally nitrogen, pass through line 26 at the top of the tower.

The heat balance within the tower 22 is important. The rich liquid leaving the tower through line 25 should be at approximately the same temperature as the cooled fluid leaving heat exchanger 11 through conduit 18 while the temperature of the absorption liquid entering through lines 23, 24 should be substantially lower. Clearly, the absorption liquid must also enter the tower at a temperature substantially below its own boiling point so that it will remain in the liquid phase as it passes through the tower. Finally, in order to preserve these temperature conditions, the heat of absorption of the methane must be removed from the tower.

In accordance with the invention, part of the necessary refrigeration is supplied by expansion of the low-boiling constituents leaving the tower through line 26. To this end, an expansion valve 27 or expansion motor such as a turbine is inserted in line 26 and the cooled expanded gases are fed through a heat exchanger 28 to the atmosphere in countercurrent flow to liquid passing from an intermediate portion or tray of the tower 22 to a lower region or tray of the tower. If desired, the gases from valve 27 may be passed in heat exchange relation to the liquid in line 24 before entering heat exchanger 28. A relatively small amount of supplementary refrigeration may be required to completely remove the heat of absorption of methane from the tower. To this end, a portion of the rich liquid leaving the tower through line 25 is circulated by a pump 30, and a conduit 31, through a heat exchanger 32 to an intermediate region of the absorption tower. Refrigerant material is passed countercurrently through the heat exchanger 32 from any suitable refrigerant system, such as an ethane compression system. However, I prefer to use a multi-stage ammonia absorption system as disclosed in my copending application, Serial No. 770,055, filed August 22, 1947.

The remainder of the rich absorbent from conduit 25 passes through pump 30 and a line 33, under the control of a valve 34, to branch conduits 35 and 36. Automatic valve 34 is controlled by a liquid level unit 38 to regulate the proportion of fluid flowing through lines 31 and 33 in accordance with the liquid level within the

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tower. The proportion of fluid flowing through lines 35 and 36 is regulated, in turn, by a rate of flow controller 40 which actuates an automatic valve 41.

The major portion of absorption liquid containing methane flows through lines 25, 33, 36 and heat exchanger 11 to a fractionating tower or demethanizer 45 wherein it is separated into gaseous methane and liquid absorbent. In order to provide proper fractionation, the temperature in the fractionating zone must vary from approximately the boiling point of the ethane or other absorption liquid to approximately the boiling point of methane. Thus, the temperature of at least a portion of the absorption liquid passing through line 36 must be raised to a temperature near the boiling point of the absorption liquid to provide feed for the lower end of the tower 45. At the pressure used within the tower, the boiling point of the absorption liquid is approximately 60° F., that is, the temperature of the feed gases entering the system through line 10, while the temperature of the liquid in line 36 is approximately equal to the temperature of the cooled feed gases leaving heat exchanger 11 through line 18, that is, temperature above the boiling point of methane but below the boiling point of the higher boiling hydrocarbons in the feed mixture. Accordingly, optimum conditions are established in the heat exchanger for obtaining the most efficient and rapid transfer of heat.

In accordance with the invention, the rich liquid from line 36 passes through the low temperature stage 16 of the heat exchanger to a vent chamber 46. The fluid in the chamber 46 is, of course, at a higher temperature than the liquid in line 36 and, as a result, a methane-rich vapor is vented from chamber 46. This fraction passes through a conduit 47 to a region of the fractionating zones whose temperature and composition are similar to those of the incoming vapor fraction, an automatic valve assembly 48 being provided to regulate the amount of gas passing through conduit 47 so as to maintain a liquid level in vent chamber 46. The liquid from chamber 46 passes through a line 49 and intermediate stage 15 of the heat exchanger 11 to a second vent chamber 50. The vapor fraction passing from chamber 50 through line 51 is at a higher temperature and is less rich in methane than the vapor fraction taken from chamber 46 and, accordingly, said fraction is fed to a lower region of the fractionating zone wherein the temperature and composition are similar to those of the incoming vapor fraction.

Liquid from vent chamber 50 passes through a conduit 52 and intermediate stage 14 of the heat exchanger to a vent 54 from which a third vapor fraction is removed through a line 55, this fraction being at a higher temperature than the vapor passing through line 51 and being less rich in methane so that it is fed to a still lower region of the fractionating zone. The liquid from chamber 54 passes through a conduit 56 and the highest temperature stage 13 of the heat exchanger 11 to a conduit 57 which communicates with the bottom region of the fractionating tower. The absorption liquid passing through conduit 57 is at the boiling point of the absorption liquid (room temperature, in the present example) and it is practically free from methane.

Accordingly, it will be apparent that the absorption liquid containing methane which passes through line 36 is raised to successively higher

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temperatures at each stage of the heat exchanger and a vapor fraction is removed from the main stream at each temperature, these fractions becoming successively leaner in methane as the temperature is increased. Thereupon, the fractions are fed to the fractionating tower at regions where the temperature and composition are similar to those of the respective entering fractions, the absorption liquid passing through line 57 being considered as a residue fraction which has been freed or denuded of the major portion of the absorbed methane. Since the vapors are removed at each stage of the heat exchanger, a minimum of vapors are present in the heat exchange tubes with the result that the efficiency of heat transfer is substantially increased. Finally, the introduction of feed into the tower as a plurality of fractions of different composition and temperature with each fraction being admitted at the optimum point in the tower with respect to the temperature and composition at that point obviates the necessity for providing supplementary refrigeration in the tower, and increases the ease of separation. If the rich absorbent were all heated to its boiling point and admitted to the fractionator at one point, in accordance with the prior practice, the separation would be much more difficult and would require a much higher reflux ratio which, in turn, would require an external refrigeration system. The entire heat requirement for the fractionator is obtained by the indirect heat exchange with the incoming raw natural gas which is thereby separated into a raw natural gasoline liquid and vapor residue gas. In this way, the more conventional oil extraction step has been eliminated, the extraction of natural gasoline increased beyond the limits of a conventional absorption unit, and a much higher heating value residue gas produced. The denuded liquid absorption material from the bottom of the fractionating tower passes through a line 59, a pump 60, a valve 61 controlled by a rate of flow controller 62, and a heat exchanger 63 to the conduit 24 from which it flows into the top of absorption tower 22. In heat exchanger 63, the lean absorbent is cooled by indirect heat exchange with the cold gaseous methane which passes from the top of the demethanizer 45 to a line 65, the heat exchanger 63, and an outlet conduit 66, from which it passes to a utility pipe line or other market.

During normal operation of the system, a certain amount of higher hydrocarbons, such as ethane and propane, accumulate in the system. This accumulation is removed through a pipe 67 which communicates with line 59 through an automatic valve 68, the valve being operated by a liquid level regulator 69 on the demethanizer unit. Gaseous absorption material, such as demethanizer overhead gases, may be added to the demethanizer through a pipe 71 to supply additional heat for methane removal and, as an optional feature, the flow through pipe 71 may be controlled by a temperature regulator responsive to the temperature in the base of the demethanizer. The liquid absorption material may be conveniently furnished from the de-ethanizer unit of the raw gasoline stabilization unit.

A reflux condenser 73 is associated with the demethanizer unit, overhead vapors being passed from the tower through a conduit 74 to the condenser coils, and the liquid condensate returning to the demethanizer tower as reflux through a conduit 75. The refrigeration necessary for condensing the reflux is supplied by expanding

a portion of the rich absorption liquid containing methane which passes through conduit 35 into the condenser 73, it being understood that the pressure in the reflux condenser is substantially less than the pressure of the liquid in line 35 and absorption tower 22. As a result of this expansion, a low temperature is maintained in the evaporator 73 which is sufficient to condense a portion of the methane vapor passing overhead from the fractionator.

The expansion of the rich absorption liquid containing methane results in the vaporization of a substantial portion of the absorbed methane. The heat of vaporization is utilized to condense the reflux for the demethanizer and to cool the partially denuded absorption liquid which is returned to the upper portion of the absorber through a conduit 77, a pump 78 and the line 23. The rate of flow of this liquid is controlled by an automatic valve 79 operated by a liquid level control unit 80 in the condenser 73. The gaseous methane resulting from the vaporization in the unit 73 passes through a conduit 81 to a compressor unit 82 which increases the pressure from the relatively low value in condenser 73 to the original pressure of the system. The compressed gas is then fed through an outlet line 83 to market. A heat exchanger 84 utilizes the cold methane vapors from the condenser to remove heat from the liquid absorption material containing methane which passes through the line 35 to the condenser 73.

The operation of the complete system will now be apparent to those skilled in the art. The feed gas passing through line 10 is cooled to a sufficiently low temperature in heat exchanger 11 as to condense components of higher boiling point than methane, and these components are fed from separating tank 19 to a conventional recovery system for the separation of ethane, liquefied petroleum gas, and gasoline hydrocarbons. The uncondensed vapors, consisting principally of methane and nitrogen, pass to absorption tower 22 where they are scrubbed by a suitable absorption liquid, such as liquid ethane, which removes the methane from the nitrogen residue. Thereupon, a major part of the absorption liquid containing methane is fractionated in tower 45 to separate its components, the gaseous methane being marketed and the liquid absorption material being recycled to the tower 22. The rest of the absorption liquid containing methane is expanded and the resultant temperature drop is utilized to condense reflux vapors in the unit 73. The expansion in condenser 73 also vaporizes methane from the rich absorption liquid, the gas being compressed and passed to market, while the cold, partially denuded liquid absorbent is recycled to the absorption tower.

It is a feature of the present system that the heat balance is preserved so as to require a minimum of supplementary refrigeration. In heat exchanger 11, heat is removed from the incoming natural gas and utilized to raise the temperature of the feed to the demethanizer tower, the temperature of the fluids in the heat exchanger being such as to provide heat transfer at maximum efficiency. A vapor fraction of the fluid to be heated is removed at each stage of the heat exchanger to prevent vapors from building up in the heat exchange tubes and creating excessive pressure drop in the heat exchange unit. I also minimize refrigeration requirements for fractionating tower 45 and eliminate the need for an external refrigeration system by passing

the feed stream through a plurality of heat exchange steps and passing the vapors overhead in each step to the optimum point in the fractionator. This procedure minimizes the amount of heat added to the fractionator and consequently minimizes the amount of heat removal necessary at the low temperature required at the top of the tower. The high pressure waste gases, principally nitrogen, from the absorption tower 22 are expanded and the resultant cold vapors are utilized to withdraw the heat of absorption of methane from said tower. As a result, only a minimum amount of supplementary refrigeration is required for the absorber unit. Finally, the methane gases which leave the apparatus for market are at a very low temperature and these gases are utilized in heat exchangers 63, 84 to cool the recycled absorption liquid to a proper temperature for introduction into the absorption tower 22 and condenser 73.

As an illustrative example of a system embodying the present invention, a natural gas consisting, for example, of 72 per cent methane, 18 per cent nitrogen, and 10 per cent ethane together with heavier hydrocarbons, is fed to inlet conduit 10 at a pressure of approximately 525 pounds per square inch, it being understood that the pressures utilized in this example are absolute pressures. Before entering the system, the gas is dehydrated to a dew point below -50°F. for 514 pounds per square inch absorption pressure. This gas enters the heat exchanger 11 at room temperature and is discharged at a temperature of about -40°F. In the tank 19, substantially all the ethane and higher-boiling hydrocarbons are liquefied and passed to the demethanizer, or other portions of the separation system. The uncondensed gases, consisting essentially of methane and nitrogen, are fed to the absorption tower 22 which is operated at a pressure of 514 pounds per square inch and these gases are scrubbed by a descending current of liquid ethane within the tower, thereby absorbing substantially all the methane. The residue gases passing through line 26 consist essentially of nitrogen with a very small proportion of methane and higher hydrocarbons, and expansion valve or engine 27 reduces the gas to a suitable refrigeration temperature. In the heat exchanger 28, the temperature of the expanded gases is raised with a corresponding drop in the temperature of the absorption fluid fed through the other line of the heat exchanger. The supplementary refrigeration unit 32 may be conveniently fed by a refrigerating cooler operating at about -70°F.

The ethane containing absorbed methane which passes through conduits 25, 35, 36 is at a temperature of about -50°F. , approximately the same as that of the cooled feed gases entering the tank 19 from line 18. Thus, the fluids at the outlet of heat exchanger stage 16 are at substantially the same temperature, thereby promoting efficient heat transfer. The vapor fractions taken from the chambers 46, 50, 54 are all of different compositions, but all are methane-rich, the temperature of these fractions being within the range of approximately -25°F. to 25°F. The ethane-rich fraction flowing through conduit 57 has a temperature of about 59°F. , which is approximately the boiling point of ethane at the demethanizer pressure of 514 pounds per square inch. The compositions and temperatures within the fractionating zone are substantially the same as those of the respective

entering fractions. Ethane liquid leaving the tower 45 at 60° F. is cooled to about -100° F. in the heat exchanger 63 by heat exchange with the methane vapors leaving the tower 45 at their boiling point of -130° F.

In the heat exchanger 84, liquid ethane containing absorbed methane at -50° F. is cooled by heat exchange and expanded in the evaporator 73 from the absorber pressure of 514 pounds per square inch to approximately 50 pounds per square inch. As a result of this expansion, the temperature of the liquid in the evaporator is lowered to about -140° F., thereby condensing a reflux for the demethanizer at a temperature of about -130° F. The partially denuded, cold absorbent leaving the condenser through conduit 71 is thus recycled to the absorber unit 22 and the methane gas leaving the condenser is heated by the exchanger 84. The compressor 82 raises the pressure of this gas from the condenser pressure of about 50 pounds per square inch to the pressure desired for market of about 500 pounds per square inch.

From the foregoing specific example, it will be apparent that the temperatures required are not nearly as low as required for condensation of methane by refrigeration only. No outside heat is added to the process, except in the de-ethanizer, and some of this heat is carried to the demethanizer in the ethane gas introduced near its base. The water supply requirements of this plant are small, approximately 100 barrels per million cubic feet of raw gas. The fuel requirements are also less than those of a high propane recovery conventional gasoline absorption plant. The recovery of propane and heavier constituents from the gas is practically 100%.

While the invention has been described in connection with a present, preferred embodiment thereof, it is to be understood that this description is illustrative only and is not intended to limit the invention, the scope of which is defined by the appended claims.

Having described my invention, I claim:

1. The method of separating the constituents of natural gas which comprises removing heat from natural gas to cool it to a sufficient extent as to condense components of higher boiling point than methane, contacting a cold absorbent liquid with the resulting mixture and containing nitrogen and methane to preferentially absorb methane therefrom, and fractionating the absorption liquid containing methane to separate methane from the absorption liquid.

2. The method of separating the constituents of natural gas which comprises removing heat from natural gas to cool it to a sufficiently low temperature as to condense components of higher boiling point than methane, contacting a cold absorption liquid with the uncondensed gases to preferentially absorb methane therefrom, establishing a fractionating zone for separating methane from said absorption liquid, establishing a circulation of reflux fluid in said fractionating zone, introducing a portion of the cold absorption liquid containing methane into said fractionating zone, passing another portion of said liquid in heat transfer relation to said reflux fluid and simultaneously expanding said liquid, thereby to condense the reflux fluid and separate methane from the absorption liquid in the expanded fluid, and recycling the absorption liquid.

3. The method of separating the constituents of natural gas containing nitrogen, methane, and higher hydrocarbons which comprises removing

heat from said gas to cool it to a sufficient extent as to condense components of higher boiling point than methane, said components including the higher hydrocarbons in the natural gas, contacting liquid ethane with the uncondensed gases to absorb methane therefrom, thereby leaving a residue consisting essentially of nitrogen, fractionating the ethane containing absorbed methane, and recycling the ethane resulting from the fractionation step to the absorption step.

4. The method of separating the constituents of natural gas containing nitrogen, methane, and higher hydrocarbons which comprises removing heat from natural gas to cool it to a sufficient extent as to condense components of higher boiling point than methane, said components including the higher hydrocarbons in the natural gas, contacting liquid ethane with the uncondensed gases to absorb methane therefrom, thereby leaving a residue consisting essentially of nitrogen, passing the nitrogen residue in heat exchange relation to fluids passing through the absorption zone and simultaneously expanding the nitrogen residue, thereby to effect refrigeration of the absorption fluid, fractionating the ethane containing absorbed methane to separate these components, and recycling the liquid ethane resulting from the fractionation step to the absorption step.

5. The method of separating the constituents of natural gas containing nitrogen, methane, and higher hydrocarbons which comprises removing heat from natural gas to cool it to a temperature higher than the boiling point of methane but lower than the boiling point of the higher hydrocarbons, contacting a cold absorption liquid with the uncondensed gases containing methane and nitrogen to absorb methane therefrom, thereby producing a residue consisting essentially of nitrogen, introducing a portion of the absorption liquid containing methane into a fractionating zone whose temperature varies from approximately the boiling point of methane to approximately the boiling point of said absorption liquid, recycling absorption liquid from the fractionating zone to the absorption step, passing the rest of the absorption liquid containing methane in heat exchange relation with the reflux fluid from the fractionating zone and simultaneously expanding said liquid thereby to condense the reflux fluid, the expansion of said liquid separating it into gaseous methane and liquid absorbent, and recycling the liquid to the absorption step.

6. The method of separating the constituents of natural gas containing nitrogen, methane, and higher hydrocarbons which comprises removing heat from the natural gas to cool it to a temperature higher than the boiling point of methane but lower than the boiling point of the higher hydrocarbons, contacting liquid ethane with the uncondensed gases containing methane and nitrogen to absorb methane therefrom, thereby producing a residue consisting essentially of nitrogen, utilizing the heat removed from the natural gas to heat a portion of the ethane absorption fluid containing methane to successively higher temperature levels, withdrawing a vapor fraction at each temperature level, introducing the withdrawn fractions together with the residue fraction from the heating step into a fractionating zone whose temperature varies from approximately the boiling point of methane to approximately the boiling point of ethane, said fractions entering the fractionating zone at re-

gions where the temperatures are equal to the respective temperatures of the entering fractions, recycling liquid ethane from the fractionating zone to the absorption step, passing another portion of the ethane absorption liquid containing ethane in heat exchange relation with reflux fluid from the fractionating zone and simultaneously expanding said liquid thereby to condense the reflux fluid, the expansion of said liquid separating it into gaseous methane and liquid ethane, and recycling the liquid ethane to the absorption step.

7. The method of separating the constituents of natural gas containing nitrogen, methane, and higher hydrocarbons which comprises removing heat from the natural gas to cool it to a temperature higher than the boiling point of methane but lower than the boiling point of the higher hydrocarbons, contacting liquid ethane with the uncondensed gases containing methane and nitrogen to absorb methane therefrom, thereby producing a residue consisting essentially of nitrogen, passing the nitrogen residue in heat exchange relation with fluids from the absorption step and simultaneously expanding said nitrogen residue to refrigerate the absorption vapors and withdraw the heat of absorption of methane in the ethane absorption liquid, utilizing the heat removed from the natural gas to heat a portion of the ethane absorption liquid containing methane to successively higher temperature levels, withdrawing a vapor fraction at each temperature level, introducing the withdrawn fractions together with the residue fraction from the heating step into a fractionating zone whose temperature varies from approximately the boiling point of methane to approximately the boiling point of ethane, said fractions entering the fractionating zone at regions where the temperatures are equal to the respective temperatures of the entering fractions, recycling the liquid ethane from the fractionating zone to the absorption step, passing another portion of the ethane absorption liquid containing methane in heat exchange relation with reflux fluid from the fractionating zone and simultaneously expanding said liquid thereby to condense the reflux fluid, the expansion of said liquid separating it into gaseous methane and liquid ethane, recycling the liquid ethane, and effecting heat exchange between the relatively cold methane vapors from the fractionating zone and the expansion zone and the relatively warm ethane recycled to the absorption step.

8. The method of separating the constituents of natural gas containing nitrogen, methane, and higher hydrocarbons which comprises removing heat from the natural gas to cool it to a temperature higher than the boiling point of methane but lower than the boiling point of the higher hydrocarbons, contacting liquid ethane with the uncondensed gases containing methane and nitrogen to absorb methane therefrom, thereby producing a residue consisting essentially of nitrogen, passing the nitrogen residue in heat exchange relation with fluids in the absorption step and simultaneously expanding said nitrogen residue, thereby to refrigerate the absorption fluids, applying supplementary refrigeration to the absorption fluids to withdraw the heat of absorption of methane in ethane, utilizing the heat removed from the natural gas to heat a portion of the ethane absorption liquid containing methane to successively higher temperature levels, withdrawing a vapor fraction at each temperature

level, introducing the withdrawn fractions together with the residue fraction from the heating step into a fractionating zone whose temperature varies from approximately the boiling point of methane to approximately the boiling point of ethane, said fractions entering the fractionating zone at regions where the temperatures are equal to the respective temperatures of the entering fractions, effecting heat exchange between the gaseous methane and liquid ethane removed from the fractionating zone to heat the methane and cool the ethane, recycling the cooled ethane to the absorption step, cooling the rest of the ethane absorption liquid containing methane, passing the cooled liquid in heat exchange relation to reflux fluid from the fractionating zone and simultaneously expanding said liquid thereby to condense the reflux fluid, the expansion of said liquid separating it into gaseous methane and liquid ethane, recycling the liquid ethane to the absorption step, heating the gaseous methane to provide the aforementioned cooling of the absorption liquid passing to the expansion zone, and compressing the resultant heated methane gases.

9. Apparatus for separating the constituents of natural gas comprising, in combination, a vessel for separating gaseous and liquid phases, an absorption tower, a fractionating tower, an inlet conduit communicating with said vessel, means for passing absorption material from said absorption tower to said fractionating tower, means for effecting heat exchange between said absorption material and the feed flowing through said inlet conduit, means for transferring gaseous phase from said vessel to said absorption tower, an evaporator for liquefying reflux vapors from said fractionating tower, an expansion valve communicating with said evaporator, a branch conduit for passing absorption material from said absorption tower to said expansion valve, outlet lines for removing gases from said evaporator and said fractionating tower, and connections for recycling liquid from said evaporator and said fractionating tower to said absorption tower.

10. Apparatus for separating the constituents of natural gas comprising, in combination, a multi-stage countercurrent heat exchanger, means for removing a vapor fraction at each stage of the heat exchanger, a vessel for separating gaseous and liquid phases, an absorption tower, a fractionating tower, means for passing feed gas through said heat exchanger and said vessel to an intermediate region of said absorption tower, means for passing the bottom product of said absorption tower through the heat exchanger in countercurrent flow with respect to the feed gas, means for conveying withdrawn fractions of said bottom product together with the residue fraction to successively higher temperature regions of said fractionating tower, an outlet conduit for removing the top product of said fractionating tower, a conduit for recycling the bottom product of said fractionating tower to said absorption tower, means for effecting heat exchange between the fluid in said outlet conduit and the fluid in said recycle conduit, an evaporator for said fractionating tower, means for feeding a portion of the bottom product from said absorption tower to said evaporator, said feed conduit including an expansion valve, an outlet conduit for removing gases from said evaporator, means for effecting heat exchange between the fluids in the evaporator outlet conduit and the fluid in said feed conduit, a compressor connected in said evaporator outlet conduit, and a line including a pump

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for recycling liquid from said evaporator to said absorption tower.

FORREST E. GILMORE.

REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
1,934,029	Asbury -----	Nov. 7, 1933

Number
1,951,840
1,972,061
2,175,590
2,241,716
2,265,558
2,352,295
2,376,051
2,468,514
2,469,724

14

Name	Date
Roberts et al. -----	Mar. 20, 1934
Cox -----	Aug. 28, 1934
Barton -----	Oct. 10, 1939
Roberts, Jr., et al. --	May 13, 1941
Ward et al. -----	Dec. 9, 1941
Swerdloff -----	June 27, 1944
Hachmuth -----	May 15, 1945
Rider et al. -----	Apr. 26, 1949
Gross -----	May 10, 1949