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TREATMENT OF NATURAL GAS

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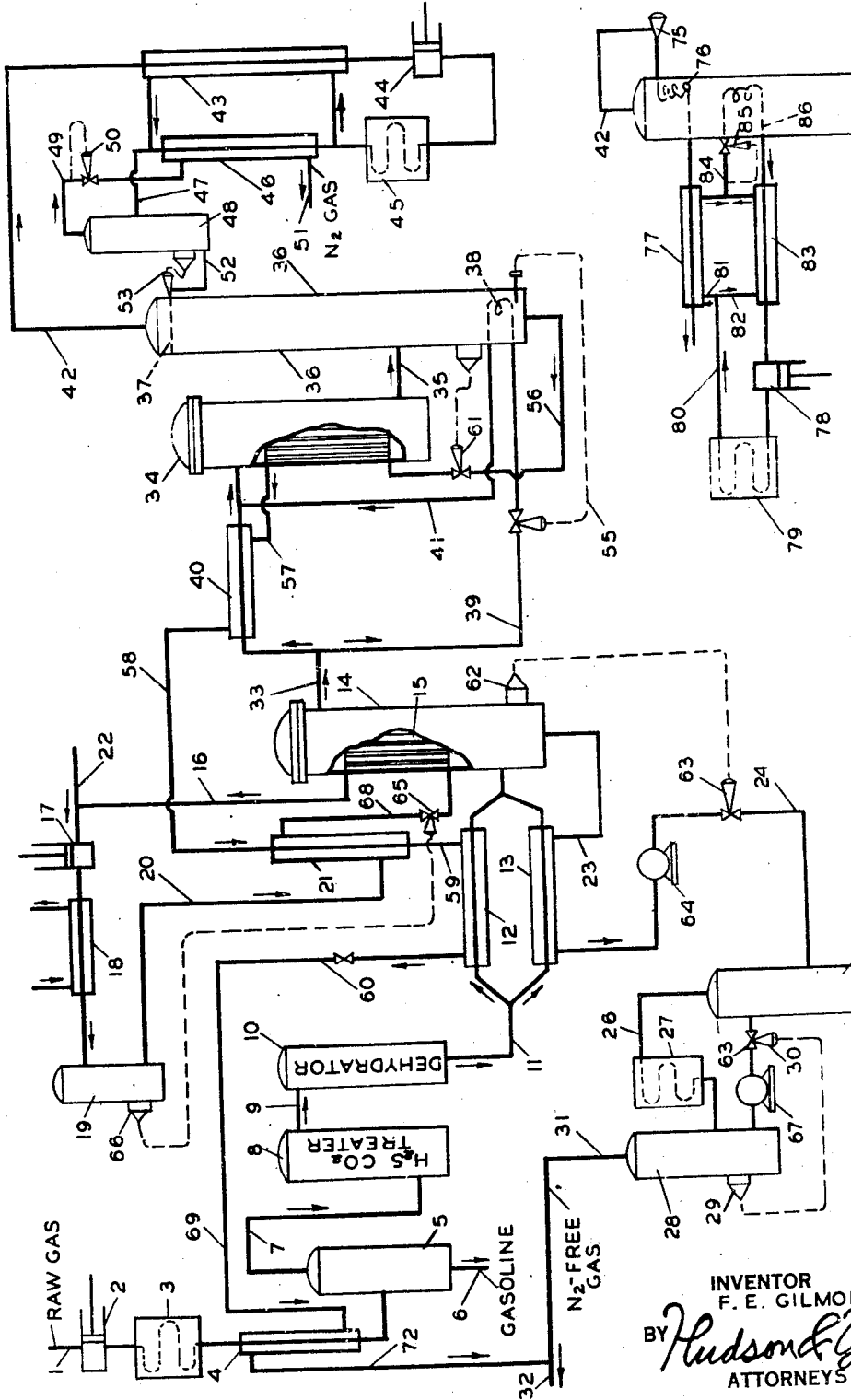


FIG.-1A

FIG.-1

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TREATMENT OF NATURAL GAS

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This invention relates to the treatment of hydrocarbon gases. In one of its more specific aspects it relates to the treatment of hydrocarbon gases for the removal of nonhydrocarbon gaseous constituents.

It has been found that some natural gases as produced contain appreciable amounts of gaseous impurities such as carbon dioxide, nitrogen or hydrogen sulfide. A gas containing as much as 10 to 20 per cent impurity presents serious considerations when marketing is contemplated. The presence of carbon dioxide and nitrogen lowers the heating value of a gas merely by their presence while such a material as hydrogen sulfide causes the gas to be corrosive and to possess a foul odor. Combustion products of the latter possess a disagreeable odor as well as being corrosive especially when moist. In appreciable concentrations hydrogen sulfide is poisonous. In view of these and other considerations the removal of hydrogen sulfide from natural gas to be used in domestic heating, process work or metallurgical work is imperative.

Carbon dioxide and nitrogen affect a natural gas for the most part only by dilution since both these materials are substantially inert in a combustion zone. Transportation of such a natural gas by pipeline presents many difficulties and problems especially when the economics of the problem are considered. For example, when transporting, say 100,000,000 cubic feet per day of a gas containing 10% by volume of nitrogen through a long pipeline, the operation involves repeated compression of 10,000,000 cubic feet of an inert gaseous material and the construction of the pipeline with a capacity 10 per cent greater than would be necessary were the nitrogen removed. The cost of such compressions may amount to hundreds of thousands of dollars per year and the additional cost of the pipeline may be greater than the cost of a plant to remove the nitrogen. In addition, the diluting effect of such a gas materially lowers the heating value, as for example, a gas having a calorific value of say 1050 B. t. u. to approximately 945 B. t. u. Natural gas must usually be maintained as 1000 B. t. u. gas, in which case gas containing nitrogen must not be completely stripped of its condensible hydrocarbon content, or a naturally lean gas may have to be enriched.

It is suggested that a natural gas having a relatively high nitrogen content may be treated for removal of this inert nitrogen thereby "upgrading" the heating value. In case such a gas contains hydrocarbons of the gasoline boiling range or is "wet" as termed by the art, these hydrocarbons may at least in part be extracted from the gas in the form of natural gasoline, and upon substantial removal of the inert nitrogen still leave a natural gas of sufficiently high or satisfactory calorific value.

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It is one object of this invention to provide an economic process for the removal of relatively large amounts of nitrogen from natural gas.

Another object of this invention is to provide a process for the simultaneous removal of inert nitrogen and extraction of condensible hydrocarbons from a natural gas containing these materials.

Still another object of this invention is to provide a process for the simultaneous removal of inert nitrogen and extraction of condensible hydrocarbons from a natural gas containing these materials and still leave a natural gas of sufficiently high calorific value and without substantial loss of the main component of the treated gas.

Still other objects and advantages will be apparent to those skilled in the art from a careful study of the following disclosure.

Figure 1 illustrates one form of apparatus in which the process of my invention may be practiced, and I do not wish to be limited thereby since this one embodiment is merely exemplary of the broad aspects of my invention.

Figure 1A is an illustration of a second method for refluxing of the fractionation tower.

Broadly speaking, my process involves removal of condensible hydrocarbons from a natural gas, dehydration of the remaining gas, and removal of a further quantity of condensible hydrocarbons. The resultant "dry gas" is compressed and chilled to such a temperature that methane condenses to a liquid. This liquified methane contains some nitrogen and is fractionated to separate the nitrogen from the methane. Methane, as liquid, is used as a refrigerant to assist in liquefying the methane in process and is in turn evaporated and warmed. My unique application of heat exchange steps makes the necessary low temperatures economically feasible.

Referring now to the drawing, raw, impure natural gas containing appreciable amounts of nitrogen reaches my treating system through a main inlet gas line 1. The impure gas in line 1 may come directly from a gas producing field or from an intermediate gas storage system, not shown. For purposes of illustration, I will assume that the gas from line 1 to be processed is maintained at a pressure ranging from 100 pounds to 1000 pounds per square inch, as for example, about 250 pounds per square inch and at atmospheric temperature. Natural gas, as produced, in addition to condensible and noncondensable hydrocarbons usually contains hydrogen sulfide, carbon dioxide, moisture and some mercaptan sourness, as well as inert materials such as nitrogen or in exceptional cases helium. These impurities occur in natural gases in amounts varying from substantially none or traces in many gases to appreciable proportions in other gases. In exceptional gases the nitrogen or carbon di-

oxide content may be so high that the gas will burn with difficulty or even not at all. Carbon dioxide or nitrogen wells are known. However, for purposes of illustration I will discuss my invention as applied to the purification of a natural hydrocarbon gas containing from say 10% to 25% gaseous nitrogen, and in the specific case described the gas contained 15% by volume of this inert gas.

From the field line 1 the raw, impure gas may be compressed, if necessary, by a compressor 2 to increase the pressure of the inlet gas to a favorable processing pressure. From the compressor the gas passes to a cooler 3, thence to a gas-to-gas heat exchanger 4 in which the gas is cooled to about 32° F. by indirect heat exchange with previously cooled and processed gas. From this exchanger the cooled gas passes to a liquid-gas separator 5 in which condensate formed in the exchanger may be separated from the uncondensed material. Much of the sourness, CO₂ and moisture are dissolved in this hydrocarbon condensate or condensed simultaneously and may be removed from the gas treating system upon withdrawal of condensate from separator 5 through draw line 6 and passed to disposal, not shown. The uncondensed hydrocarbons and gaseous impurities pass from the separator 5 by a line 7 to a treater apparatus 8 in which such impurities as hydrogen sulfide and carbon dioxide are removed. This treater may well be one utilizing a conventional process or processes, and the H₂S and CO₂ may be removed together or separately as desired. From this treating apparatus 8 the CO₂ and H₂S free gas passes by way of a line 9 to a dehydrator 10. This dehydrator may likewise, be apparatus of conventional design employing a conventional process and may consist of two or more vessels for alternate on-stream and regeneration as found necessary. The moisture must be efficiently removed from the gases to prevent hydrate formation in subsequent low temperature steps of the process.

The well dried hydrocarbon gases leave the dehydrator by a line 11 which line branches and permits a portion of the gas stream to pass through a gas cooled condenser 12 and the remaining portion to pass through a liquid cooled condenser 13. After emerging from these condensers the two portions of the gas stream are combined and enter the lower portion of a refrigerated condenser 14. This latter condenser may be substantially any type of condenser, provided, of course, it is of suitable design and construction for such low temperature service as herein contemplated. The gas passes upward through the tube section 15 of this condenser which is cooled to the low temperature of from -30° to -100° F. by an independent refrigeration unit. In this unit such a low boiling refrigerant as ethylene, for example, may be used. In the ethylene cycle, the ethylene previously liquefied, acquires heat indirectly from the hydrocarbon gases being cooled, boils and evaporates in the tube section 15 of exchanger 14. The ethylene vapors are then withdrawn by a line 16 and pass through a compressor 17, a condenser 18, from which latter the liquefied refrigerant passes into an accumulator or surge tank 19. From the surge tank the said liquefied refrigerant passes by a return line 20 to a cooler 21 and thence into the lower portion of the refrigerated condenser 14 to complete the ethylene cycle. Makeup ethylene may be added through a line 22 on the suction side of the compressor 17.

Condensed hydrocarbons which accumulate in the bottom of the condenser 14 are cold and may well serve as a cooling medium. Accordingly, these liquefied hydrocarbons are removed by a line 23 the flow being controlled by the liquid level apparatus 24 and the motor valve 25 into the liquid to gas exchanger 13 to chill a portion of the feed stock previous to entrance into the refrigerated condenser 14. This liquid material after giving up a portion of its "coldness" or after being somewhat warmed in the liquid cooled condenser 13, passes by way of a line 24 into a stabilizer 25 which may be of conventional design but suited for low boiling hydrocarbon stabilization. Overhead gases from this stabilizer exit by way of a line 26, pass through a condenser 27, and the condensate in which at least some propane is condensed accumulates in reflux accumulator 28. Liquid level is controlled by a level controller 29 which operates a motor valve 30 to permit return of liquid reflux to the top tray of the stabilizer 25.

Uncondensed hydrocarbons from the accumulator 28 pass by way of a line 31 to a main nitrogen free gas line 32 which conducts the finally treated and purified gas from my treating system to be further fully explained to a pipeline for transportation to a market or to a gas holder for storage, not shown, or to other disposal as desired.

Stabilized natural gasoline passes from the base of the stabilizer through a line 34 to storage or other disposal, as desired.

The uncondensed gases consisting of nitrogen and methane with substantially no ethane or heavier hydrocarbons issue from the refrigerated condenser 14 through a pipe 33 into an auxiliary chiller 40 and finally are passed through still another exchanger or condenser 34 wherein a major portion of the methane is condensed to liquid methane and most of the nitrogen, of course, remains as a gas. This mixture of gaseous nitrogen and liquid and gaseous methane passes from the said condenser 34 by way of a pipe 35 into a fractionator tower 36 herein termed the "denitrogenizer." This vessel may usually be a conventional bubble cap fractionator, but so designed and constructed as to operate at low temperature and high pressure as required by such service as herein discussed.

The fractionator or denitrogenizer 36 is equipped with conventional type bubble cap trays, a reflux apparatus 37 and a reboiler coil 38. As mentioned above, charge stock to this column contains largely liquid methane, some gaseous or uncondensed methane, nitrogen and any other difficulty condensible material having a boiling point near that of methane or below which has not been previously removed. Liquid methane containing some dissolved nitrogen descends through the fractionator the nitrogen being fractionated out in the descent until the liquid accumulating in the reboiler section is almost pure methane. Reboiling coil 38 furnishes heat to boil this methane to produce the desired rectification in the fractionator. Heat for said reboiling is furnished by passing a small portion of the partially chilled methane and nitrogen from the line 33 through a bypass line 39 into the reboiler coil. The exhaust from the reboiler coil is passed through a pipe 41 and is discharged into condenser 34 with the gases from the chiller 40.

The upper portion of the denitrogenizer is for the most part constructed in a manner similar to that of conventional fractionators. A pipe 42

removes overhead vapors and gases from the fractionator, which material in my case consists mainly of gaseous nitrogen and uncondensed methane. This material passes through the line 42 to a heat exchanger 43 and after being warmed it is compressed by a compressor 44 and cooled in a cooler 45. The stream issuing from cooler 45 is split, one portion passing through exchanger 43 and the other portion passing through an exchanger 46. These two stream portions issuing from said exchangers combine in a line 47 and are passed to a reflux accumulator vessel 48. In this vessel methane which has been condensed in exchangers 43 and 46 separates from the gaseous nitrogen and some uncondensed methane. The nitrogen and uncondensed methane are removed from the top of this accumulator by a pipe 49, expansion being permitted by an expansion valve 50 set to operate according to a desired pressure in accumulator 48. The refrigeration available from this expansion absorbs heat in the exchanger 46 to chill and condense some methane from the methane-nitrogen mixture which passes in indirect heat exchange therewith. The expanded nitrogen-methane mixture then issues from a line 51 for such disposal as desired. I prefer to operate the plant in such a manner that this off gas contains from 25 to 50% nitrogen, the remainder being methane, and in this manner sufficient methane is available for plant power purposes.

The liquid methane which has accumulated in the accumulator 48 is returned to the top of the denitrogenizer by a line 52 to serve as a wet refluxing material. The level of the liquid in accumulator 48 may be controlled by a motor operated valve 53 actuated by a liquid level mechanism on the accumulator tank. Upon opening of the motor controlled valve 53 the liquid methane passes therethrough from the pressure originating in the compressor 44.

A thermoregulator assembly 55 which controls the amount of flow of cold gas in line 39 to the reboiler 38 is actuated in response to the temperature of the liquid in the base of the column 36. This substantially nitrogen-free liquid methane is passed from the base of this column through a line 56 in which is placed a motor operated valve 61 actuated by a liquid level mechanism on the "denitrogenator" 36, to the space around the tubes of the heat exchanger in exchanger vessel 34. In the space around these tubes much or all of the liquid vaporizes under a lower pressure than the gas inside the tubes imparting its low temperature to the higher pressure methane inside the tubes by which operation the latter at least in part condenses. The vaporized methane issues from the refrigerated condenser by a line 57 and is led to the exchanger 40. From this exchanger the methane passes by way of a line 58 to still another exchanger 21, thence by a line 59 to yet another exchanger 12, previously termed the gas cooled condenser. From this condenser the methane gas passes by a line 69 into the first mentioned gas to gas exchanger 4, thence by line 72 into the main product line 32.

The liquid hydrocarbons, that is, those more easily condensed, are removed by line 23 and the flow in which is controlled by a motor valve 63 in the line 24 which is actuated by a liquid level apparatus 62. This motor valve serves as a back pressure regulator on the liquid cooled condenser 13 to prevent undue evaporation of the cooling medium within the condenser. It also restricts

or controls the flow of condensed hydrocarbons into the stabilizer tower 25. A pump 64 serves to assist in transfer of these condensed hydrocarbons from the condenser 13 into the stabilizer in case the operating pressure on the latter is higher than that in the condenser. A pump 67 pumps liquid reflux from the accumulator into the stabilizer.

Liquid level controller apparatus 66 operates according to the level of the refrigerant in accumulator 19 to control the rate of flow of said refrigerant by actuation of a motor valve 65 in a line 68. This refrigerant upon passage through valve 65 evaporates as heat is absorbed from gas passing through the condensing tubes 15. Refrigerant gas exits through the line 16 and is recompressed by compressor 17, as mentioned hereinbefore. Makeup refrigerant may be added through the line 22.

In the operation of the process according to my invention I contemplate treating 50-100,000,000 cubic feet of a natural gas containing approximately 15% nitrogen by volume, a normal amount of sulfur sourness, carbon dioxide and some moisture.

The denitrogenizer or fractionator tower may be operated under dry reflux in place of the wet trim as mentioned above. In this case the overhead nitrogen-methane gas is expanded through a needle valve to almost atmospheric pressure the cold expanded gas passing through a closed reflux coil in the top of the tower. This very cold coil is sufficiently cold to condense considerable of the methane which latter then flows down the tower as a liquid reflux. To assist further in the dry refluxing of this denitrogenizer tower, the apparatus and flow illustrated in Figure 1A may be used. The above mentioned fractionator overhead nitrogen-methane gas line 42 connects to an expansion valve 75 which permits passage of expanded gas through the closed reflux coil 76. This cold expanded gas passes from the coil through an exchanger 77 as a refrigerant for cooling another refrigerating medium. This effluent nitrogen-methane gas may be used as the refrigerant in a supplementary unit to assist in the very low temperature closed coil refluxing of this fractionator. However, if desired, another refrigerant may be used, as illustrated in the Figure 1A. Referring to the figure this refrigerant is compressed in a compressor 78 and cooled in a cooler 79. The cooled stream passes through a line 80 and is divided into two portions as represented by lines 81 and 82. Line 81 conducts a portion of this gaseous refrigerant to the above mentioned exchanger 77 while the remaining portion in line 82 passes through another exchanger 83. Both streams of the refrigerant are cooled and may be partially or wholly condensed on passing through these exchangers, and again join in a line 84, pass through an expansion valve 85 and thence into an auxiliary closed reflux coil 86. This coil is preferably disposed below the coil 76. The expanded effluent from the coil 86 passes through the exchanger 83 in which it cools and may condense the refrigerant enroute to the reflux coil 86. If the top fractionator pressure is about 700 pounds per square inch or higher, the Joule-Thompson effect of the very cold expanding gases will refrigerate coil 76 to a low enough temperature to condense a large portion of the methane and the methane-nitrogen mixture leaving coil 76 may be utilized for fuel for power and heat needed for the operation.

The refrigerant, either the methane-nitrogen

off gas or another refrigerant, is compressed by compressor 78 to a pressure of from 1000 to 5000 pounds per square inch. Upon being cooled in cooler 79 and further cooled in exchangers 77 and 83, and when expanded in valve 84 produces sufficiently low temperature in coil 86 to condense methanes and even nitrogen if desired.

Since such an extraction plant as that discussed herein consumes considerable power, I believe it preferable and advisable to permit a relatively large concentration of methane to pass off the top of the fractionator with the nitrogen as mentioned hereinbefore. In this manner, the nitrogen can be more efficiently removed from the field gas and at the same time at less cost. Since it is a difficult and expansive operation to remove all or substantially all the methane from the nitrogen in the fractionator my proposed operation is relatively economical. In fact, I contemplate to control the nitrogen containing off-product relative to its methane content in such a manner as to furnish all or substantially all the methane needed for heat and power purposes in the process.

For carrying out such a process as herein disclosed, it is needless to say that all pipes, exchangers, valves, etc. which carry low temperature liquids or gases should be well insulated by the best thermal insulation obtainable. It might be advisable to install all the cooling equipment within a well insulated building so that the individual pieces of equipment need not be so heavily insulated. All operating controls, indicators, and instruments should be outside this building, the temperature of which should preferably be maintained as low as 0° F. or below.

The expansion valves, pipes, all vessels and all parts and members of this low temperature plant should be made of such materials and so designed as to withstand the very low temperatures of operation. Similarly, the equipment should be capable of withstanding all pressures necessary, some of which are relatively high.

It will be obvious to one skilled in the art that many variations and alterations may be made in the flow of materials, or temperatures and pressures of operation for the treatment of natural gases containing various amounts of nitrogen or other inert gas for the removal of such inert gas and yet remain within the intended spirit and scope of my invention.

I claim:

1. A process for purifying natural gas containing gaseous nitrogen as an impurity comprising compressing and cooling the gas, dividing said compressed and cooled gas into two portions, chilling one portion by a first indirect heat exchange with a refrigerated vaporized methane, chilling the other portion by a second indirect heat exchange with refrigerated liquid methane, combining these two portions and further chilling the combined stream by a third indirect heat exchange with vaporizing liquid methane to produce some liquid methane containing dissolved nitrogen and leaving uncondensed most of the nitrogen and some gaseous methane, fractionating the chilled combined stream of liquid methane containing dissolved nitrogen and gaseous nitrogen and methane to produce a liquid methane bottoms product and an overhead gaseous product of nitrogen and methane, partially condensing this gaseous product and adding the condensate to the

fractionating step as liquid reflux, and removing the nitrogen and some uncondensed methane as a product of the process; adding reboiling heat to the fractionator liquid bottoms by the second indirect heat exchange thereby producing liquid methane free from dissolved nitrogen and termed refrigerated liquid methane, vaporizing this refrigerated liquid methane in the third heat exchange thereby producing a refrigerated vaporized methane, warming this refrigerated vaporized methane in the first heat exchange thereby producing warmed vaporized methane, and removing this warmed vaporized methane as the major product of the process.

2. A process for purifying natural gas containing gaseous nitrogen as an impurity, comprising, compressing and cooling the compressed gas, dividing the compressed and cooled gas into two portions, chilling one portion by a first indirect heat exchange with a chilled gaseous methane, subsequently produced, chilling the other portion by a second indirect heat exchange with a previously refrigerated liquid methane fractionator bottoms, subsequently produced, combining these two chilled portions of compressed gas into one stream and further chilling this stream by a third indirect heat exchange with evaporating liquid methane, whereby some of the methane of the gas stream is condensed and dissolves some gaseous nitrogen, and passing as feed stock this stream of liquid methane containing dissolved nitrogen and gaseous nitrogen and methane into a fractionation zone at a point intermediate the ends thereof and therein fractionating said feed stock to produce a liquid methane bottoms free from dissolved nitrogen and an overhead gaseous product containing nitrogen and some methane, compressing and chilling said overhead product to produce a liquid condensate and uncondensed nitrogen containing some methane, adding said condensate to the top of said fractionating zone as liquid reflux, and removing said uncondensed nitrogen containing some methane as a product of the process; adding reboiling heat to the bottom of the fractionation zone by said second indirect heat exchange, vaporizing said liquid methane in said third heat exchange, and warming said vaporized methane in said first heat exchange, and removing the warmed vaporized methane from said first heat exchange, as the purified natural gas.

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