ABSTRACT: Natural gas containing nitrogen is cooled and liquefied by a cascade system having two closed refrigeration circuits operating on multicomponent refrigerant mixtures. The liquefied gas is distilled into three fractions: nitrogen, a mixture of nitrogen and methane, and liquid natural gas substantially free of nitrogen. The mixture of nitrogen and methane provides the refrigerant in a third and coldest open circuit of the cascade system to subcool the liquid natural gas to storage temperature.
This invention relates to a process for the liquefaction of natural gas containing nitrogen, in countercurrent heat exchangers by means of closed circuits of multicomponent refrigerant mixtures, arranged in cascade manner. Dutch Patent 108,678 discloses that natural gas can be cooled this way down to its storage temperature, approximately −160°C. By using multicomponent refrigerant mixtures which, preferably, are made up of components of the natural gas, it is possible to operate with a very small number of cascade circuits. It is possible to accomplish the total liquefaction and subcooling of the natural gas by means of only two circuits having multicomponent refrigerant mixtures, each of which mixtures goes through only one pressure stage. However, thermodynamically, it is not favorable to extend the temperature ranges of the individual refrigeration circuits too much. It is therefore advisable to use a third circuit. However, an additional circuit ordinarily requires its own compressor as well as the necessary control and regulating devices.

It is a principal object of this invention to simplify the third refrigeration circuit and thereby lower investment and operating costs for the liquefaction and subcooling of nitrogen-containing natural gas.

SUMMARY OF THE INVENTION

In accordance with this invention, natural gas having an appreciable content of nitrogen is cooled, liquefied and subcooled in countercurrent heat exchangers which include closed circuits of multicomponent refrigerant mixtures, arranged in cascade manner, each circuit going through only one pressure stage. After completion of liquefaction and prior to subcooling the liquefied natural gas to storage temperature, the lower-boiling inert components, particularly nitrogen, are removed therewith by distillation in a column. In order to subcool the liquefied natural gas to storage temperature, at least partially gaseous mixture of methane and nitrogen is withdrawn from the column, liquefied by heat exchange with the multicomponent refrigerant mixture of the colder closed circuit in the cascade system, subcooled against itself in expanded condition, and finally expanded; this expanded stream then subcools the liquefied natural gas and is desirably also used to cool the vapor in the top portion of the column. After its expansion and the transfer of its refrigeration, the gaseous mixture of the added and coldest refrigeration circuit in the cascade system can be used for the generation of heat and energy. Inasmuch as this added circuit is an open circuit, no compressor is needed and thereby investment and operating costs are reduced.

In a preferred embodiment of this invention, the multicomponent refrigerant mixture of the colder closed circuit is first cooled in the vessel of the refrigerination distillation column. Then, it is expanded and used to subcool the liquefied natural gas to a temperature of about −140°C. If desired, before expanding the refrigerant mixture of the colder closed circuit, it may be further cooled by passage through a coil in the middle portion of the distillation column. Furthermore, the nitrogen withdrawn from the top of the column and the vent gas from the liquid natural gas storage tank can be utilized as sources of refrigeration in the heat exchangers used to liquefy and subcool the liquefied natural gas. It is advantageous to expand each of the multicomponent refrigerant mixtures in the closed circuits to a pressure between about 3 and 5 atmospheres absolute instead of atmospheric pressure since, in this way, the pressure drop in the circuit is smaller, i.e., energy is saved and less heat exchanger surface is needed.

DESCRIPTION OF A PREFERRED EMBODIMENT

The accompanying drawing is a flowsheet illustrating a preferred embodiment of this invention.

Natural gas with an appreciable content of nitrogen is supplied through line 1 at high pressure and approximately ambient temperature to heat exchangers 2 and 3 whereby it is cooled and liquefied. Hence, the liquefied natural gas flows through first sump coil 5 to heat the liquid in the sump of nitrogen distillation column 6, and thereby to be further cooled. It is then expanded through expansion valve 7 and discharged into column 6. Column 6 operates at a pressure of about 14 atmospheres absolute. Therein, the natural gas is separated into three fractions. Substantially nitrogen-free, liquid natural gas is withdrawn from the sump of column 6. Substantially pure nitrogen is withdrawn from the top of column 6. From the middle portion of column 6, a mixed methane and nitrogen fraction is withdrawn, its volume and composition being controlled so as to cool the liquid methane to a storage temperature of −160°C. The nitrogen-free liquid natural gas is withdrawn from the sump of column 6 through line 8 and flows through the two heat exchangers 4 and 9 where it is subcooled to −160°C. Thereafter, the liquid natural gas is expanded and discharged into a storage tank.

Nitrogen withdrawn from column 6 through line 10 flows successively through heat exchangers 9, 4, 3 and 2, and thus is heated to ambient temperature.

Refrigeration is supplied by a cascade arrangement of two closed circuits with multicomponent refrigerant mixtures as well as the open and coldest circuit with the mixture of methane and nitrogen featured by this invention.

The first and warmer closed circuit supplies practically all the refrigeration needed between ambient temperature and approximately −75°C. In this circuit, the refrigerant mixture of methane, ethane, propane and butane is completely liquefied at ambient temperature when compressed to 42 atmospheres absolute. This mixture is compressed to 42 atmospheres absolute by compressor 10, is completely liquefied in cooler 11 by means of cooling of water, and flows through line 12 into heat exchanger 2 wherein it is subcooled against itself after having been expanded. After expansion to 3 atmospheres absolute in expansion valve 13, this refrigerant mixture transfers its refrigeration to the natural gas and the refrigerant mixture of the second and colder closed circuit passing through heat exchanger 2. Line 14 returns the refrigerant of the first circuit from heat exchanger 2 to compressor 10 and thus closes the circuit.

The multicomponent refrigerant mixture of the second and colder closed circuit flows through line 15 and heat exchangers 2 and 3 whereby it is cooled and liquefied. This liquid then flows through second sump coil 16 in column 6 and through heat exchanger 4. The thus subcooled liquid is expanded in expansion valve 17 and passed through line 18 which extends successively through heat exchangers 4, 3 and 2, whereby the mixture is warmed to ambient temperature. Line 18 returns the warmed mixture to compressor 19 where it is again compressed and, after flowing through water cooler 20, passes through line 15.

At selected operating conditions of composition and pressure after expansion, the refrigerant mixture of the second circuit can transfer practically no refrigeration below −145°C to the natural gas. It is possible, but thermodynamically not favorable, to extend the operation of this second circuit over an even greater temperature range. Rather, in accordance with this invention, the second circuit is followed by a third circuit in the cascade arrangement. This third circuit which is open operates with a mixture of nitrogen and methane to supply the natural gas with refrigeration between −145°C and −160°C, needed for subcooling. As already mentioned, the methane and nitrogen mixture for this added circuit is withdrawn from the middle portion of column 6, liquefied against the expanded, evaporating refrigerant mixture of the second circuit and, after expansion, vaporized by heat exchange with the natural gas. Thus, refrigeration is essentially supplied by a three-circuit cascade system with the following characteristics:
For the third and open circuit, a gaseous mixture of methane and nitrogen is withdrawn from column 6 through line 21 and liquefied in heat exchanger 4 with refrigeration from the second circuit. The liquid then flows through heat exchanger 9 where it is subcooled, and through expansion valve 22 where it is expanded to 3.8 atmospheres absolute. This expanded stream gives up a part of its refrigeration in cooling coil 23 of column 6 in order to produce reflux. This stream passes through line 24 back to heat exchanger 9 where it gives up the greater part of its refrigeration to subcool the liquid natural gas to \(-160^\circ\) C. It then continues to flow through heat exchangers 4, 3 and 2, whereby it is heated to ambient temperature and subsequently utilized for the generation of heat and energy.

The process of this invention permits an advantageous combination of nitrogen removal from the natural gas, which is highly desirable, and a third circuit in a cascade system. It would be thermodynamically unfavorable to extend the temperature ranges of the first two closed circuits too much. This is avoided by the present invention without necessitating an extra compressor and its control and regulating devices for an additional refrigeration circuit.

What I claim is:

1. A process for liquefying natural gas containing nitrogen and supplied at high pressure, which comprises cooling and liquefying said natural gas by countercurrent heat exchange with two closed refrigeration circuits in cascade arrangement, each of said closed circuits having a multicomponent refrigerant mixture which undergoes a single expansion, expanding the liquefied natural gas and discharging it into a rectifying zone maintained at an intermediate pressure, withdrawing at least partially gaseous mixture of nitrogen and methane from the middle portion of said rectifying zone to provide the refrigerant mixture for a third and coldest open circuit in said cascade arrangement, withdrawing liquefied natural gas substantially free of nitrogen from the bottom of said rectifying zone and subcooling it to storage temperature by countercurrent heat exchange with said open circuit.

2. The process of claim 1 wherein the refrigerant mixture of the third circuit, upon being expanded, flows through a heat exchange passage in the top portion of the rectifying zone to condense vapor in said top portion and thus provide reflux for said rectifying zone.

3. The process of claim 1 wherein the multicomponent refrigerant mixture of the colder of the two closed refrigeration circuits flows through a heat exchange passage in the bottom portion of the rectifying zone and, after being expanded, subcools liquefied natural gas substantially free of nitrogen which is withdrawn from the bottom of said rectifying zone.

4. The process of claim 1 wherein substantially pure nitrogen is withdrawn from the top of the rectifying zone and is passed in countercurrent heat exchange with the liquefied natural gas substantially free of nitrogen withdrawn from the bottom of said rectifying zone and with the natural gas containing nitrogen prior to its discharge into said rectifying zone.

5. The process of claim 1 wherein each of the two multicomponent refrigerant mixtures is expanded to a pressure higher than 2 atmospheres absolute but not exceeding about 5 atmospheres absolute.

6. The process of claim 1 wherein each of the two multicomponent refrigerant mixtures is made up of components of the natural gas containing nitrogen.