

Helium extraction and nitrogen removal from LNG boil-off gas

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Abstract: The helium bearing boil off gas (BOG) from liquid natural gas (LNG) storage tank in LNG plant, which has a helium concentration of about 1%, has attracted the attention in China as a new helium source. As the BOG is usually reused by re-condensing to recover methane, it is likely to cause continuous accumulation of nitrogen in the unit, thus a nitrogen removal process must be integrated. This paper describes a conceptional cryogenic separation system aiming at recovering methane, helium and nitrogen from BOG based on cryogenic distillation and condensation process.

1. Introduction

Helium is an invaluable rare gas as it has a lot application in industrial and research. At present, helium is produced mainly from helium bearing natural gas (NG) which contains 1~8 vol% helium [1]. Figure 1 describes a conventional processes of a base load LNG plant [2]. In the case of the helium rich NG feed gas, a helium extraction system is commonly integrated with the nitrogen rejection unit in the LNG plant to recover helium. However, most of helium reserves dissolved in natural gas is located in only few countries in the world. The low concentration of helium in Chinese NG field makes extracting helium from the NG uneconomical. Accordingly, it is important to explore possible nonconventional helium sources especially in China to mitigate the helium shortage. Therefore, the helium bearing BOG from LNG storage tank in LNG plant, which has a helium concentration of about 1vol%, has attracted the attention in China as a new helium source. However, as the BOG is usually sent back to the liquefaction unit to recover methane in most LNG plant, it is likely to cause continuous accumulation of nitrogen in the unit. Generally, the concentration of nitrogen in BOG may be as high as 10 vol%, which resulting in an additional power consumption in the liquefaction process. For this reason, this paper depicts a conceptional cryogenic system for extracting helium and removing nitrogen from BOG.



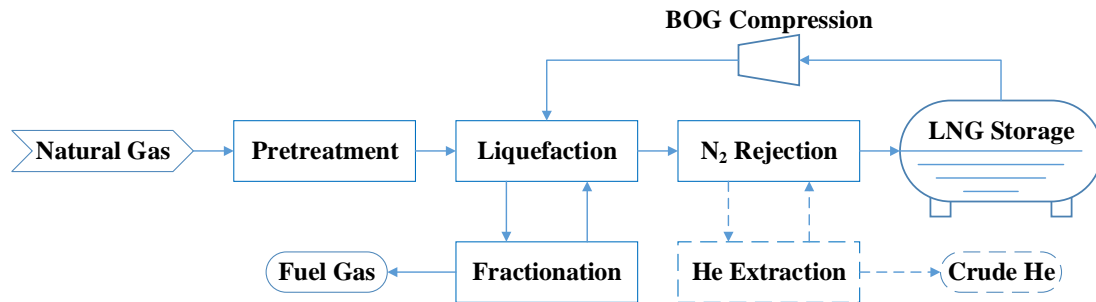


Figure 1 Conventional process of a base load LNG plant

2. BOG Conditions and Recover Requirement

Typically, the BOG from LNG storage tank consists mainly of methane, nitrogen, hydrogen, helium and small amount of heavy hydrocarbon. As an example, a 3000000m³/day LNG plant in China will produce 4900NM³/h BOG stream. The site test data about the composition of BOG are listed in Table 1. This LNG plant is operated as a base-load plant without any helium extraction unit before, now a helium extraction and nitrogen removal unit (HeX-NRU) is being considered to be integrated in this plant as shown in Figure 2.

Table 1 Composition of Helium-bearing BOG from LNG storage tank

Component	BOG (vol %)
Methane	88.799
Ethane	6.573×10^{-3}
Propane	1.056×10^{-5}
i-C ₄	7.6203×10^{-8}
n-C ₄	1.8204×10^{-8}
Nitrogen	9.8565
Hydrogen	0.2829
Helium	1.05459

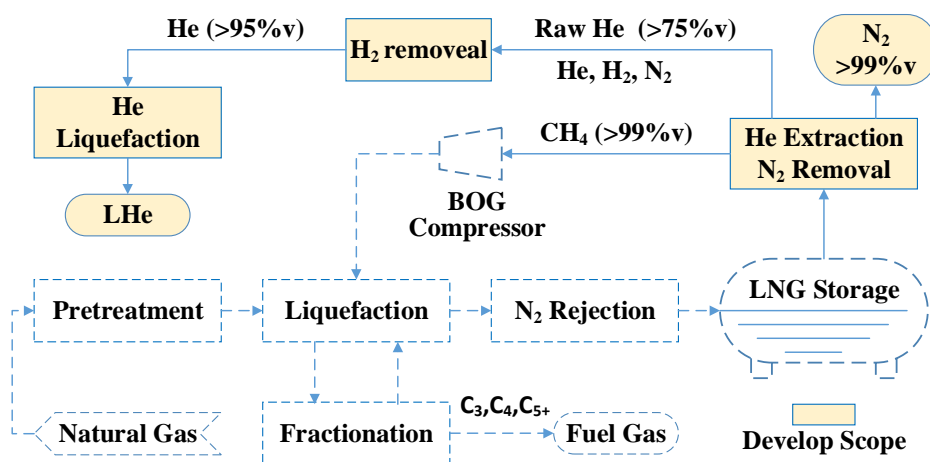


Figure 2 Helium extraction and nitrogen removal from BOG

According to the helium recovery requirements, the designed HeX-NRU has the full function of recovering methane, nitrogen and extracting helium from BOG. The required purities for recovered methane and nitrogen should be no less than 99 vol %, and the extracted helium should have the purity of larger than 95 vol % after dehydrogenation.

3. Technologies for Helium Extraction

At present, there are variety of techniques for the separating and recovering of helium from helium bearing multicomponent gas mixtures. Such techniques include membrane technique, pressure swing adsorption (PSA) technique and cryogenic technique. Among these techniques, cryogenic processes are the most economical method and have been commonly used to produce helium at high recovery and/or purity from NG or other streams containing low purity helium [3].

The standard boiling temperatures of methane, nitrogen, hydrogen and helium are 111.7K, 77.36K, 20.28 and 4.22K respectively. Due to the boiling temperature difference between helium, nitrogen, hydrogen, methane and other components, we can use either condensation-based, distillation based or the integration of condensation and distillation based cryogenic process to extract helium from NG.

To meet the high requirements of the product purities, the separation between methane and nitrogen is suggested to use distillation process as they have close volatilities. Through the distillation process, most methane and other hydrocarbons are recovered as bottom product, and the left overhead gas, which is the mixture of nitrogen, helium and hydrogen, can be further separated by cryogenic condensation process.

Figure 3 is a schematic layout of the HeX-NRU based on the integration of distillation and condensation process. In this process, methane and other few hydrocarbons are firstly separated with N_2 , He and H_2 through cryogenic distillation. Then the N_2 is separated with He and H_2 through cryogenic condensation at a lower temperature.

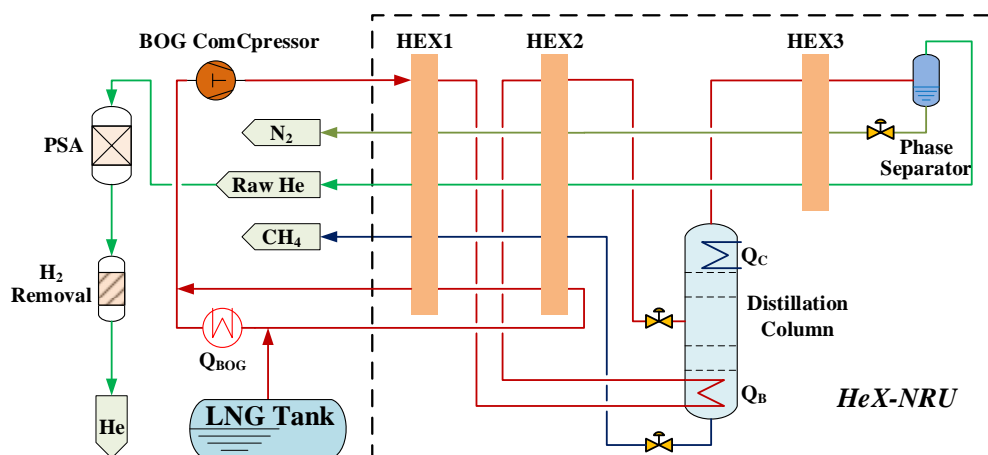


Figure 3 Flow Diagram of HeX-NRU integrated in LNG plant

The distillation column in Figure 3 is designed for the deep stripping off helium, hydrogen and nitrogen. The bottom product of the column is high-purity LNG with low nitrogen content. It is depressurized in a J-T valve and flows back through the first two heat exchangers to provide the main cold duty for the condensation of BOG.

The overhead product of the distillation column, which is helium and nitrogen rich gas collected as gas phase at the top of the distillation column, is further cooled in the third heat exchanger and flashed in a phase separator. The liquid phase accumulated in the bottom of the phase separator is liquid nitrogen. It's throttled to an intermediate pressure, passes back through the three heat exchangers and finally becomes high-purity warm nitrogen gas.

The gas phase stream at the top of the phase separator is raw helium gas composed of helium, nitrogen and hydrogen. It is delivered to a pressure swing adsorption (PSA) unit after cold recovery. In the PSA unit most nitrogen is adsorbed. The outlet stream of PSA unit has a hydrogen content of 10~20%, which will be removed in the followed dehydrogenation unit. Thus most impurities in the raw Helium stream are selectively removed and pure helium product of larger than 95% purity is obtained. It can be further purified and liquefied in a helium liquefier.

In addition, as the temperature of BOG evaporated in a LNG tank is 116.7K at 1.5 bar, part of the cold BOG can be sent to HeX-NRU for the precooling of the high pressure BOG stream, and the left cold BOG should be heated to warm temperature before it is compressed in a BOG compressor.

4. Cryogenic Distillation

The cryogenic distillation column is an effective device to fulfil the high methane purity requirement for recovering NG. However, because of the difficulty to find proper cooling media for the condenser of the cryogenic distillation column, a Claude cycle nitrogen refrigerator with the cold BOG precooling has been designed to supply the necessary condensing power for the distillation process (see Figure 4).

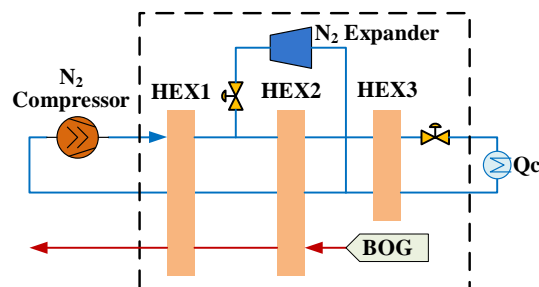


Figure 4 Nitrogen refrigerator integrated in HeX-NRU

In order to operate the HeX-NRU and the nitrogen refrigerator economically to recover methane with specified purity, we need to pay attention to the condenser duty of a cryogenic distillation, which is dependent on the feed temperature and the pressure level of the distillation column. Figure 5 indicates that the higher operating pressure, the higher condenser duty Q_c is expected. For a given pressure there exists an optimized feeding temperature at which the required Q_c has the lowest value.

If the feeding temperature is low, the vapor fraction of the feed is small, so there are less volatized gas contents at the upper part of the column, thus needs less condenser duty. However, if the feeding temperature becomes too lower, the condenser duty will become larger again. The possible reason may be that at very lower temperature, the enthalpy decreases dramatically (see figure 6). Thus to keep the thermal balance and the required temperature levels at both the top and bottom ends of the column, much more re-boiler duty Q_B is required (see Figure 7). Consequently, more evaporated gas may be accumulated at the top column, resulting in an increased condenser duty (see Figure 8).

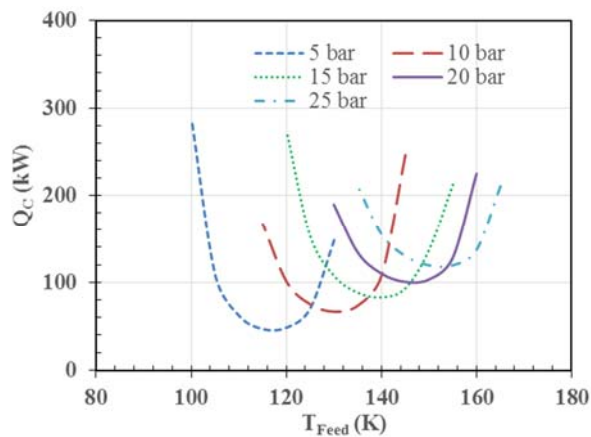
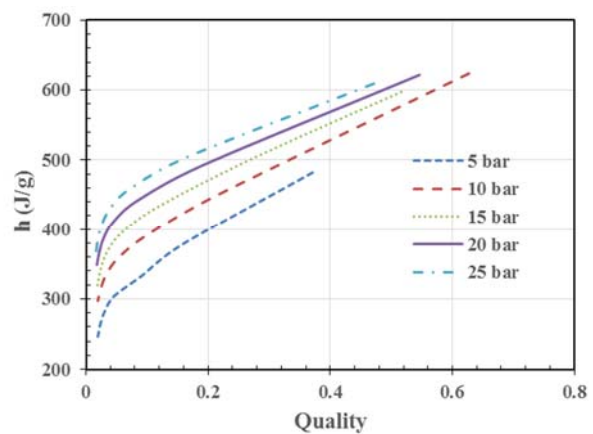
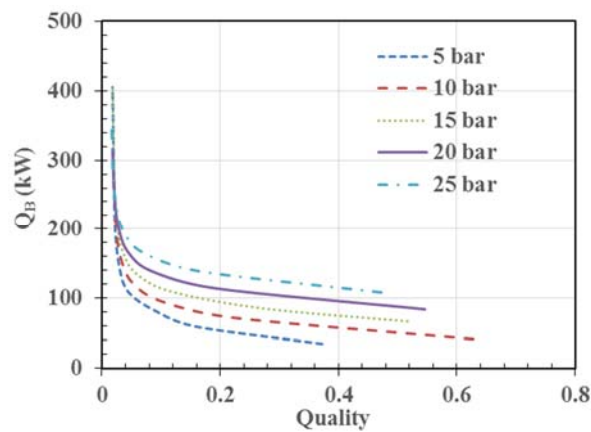
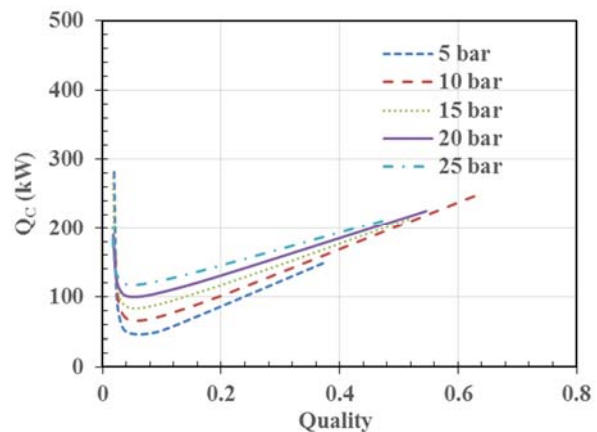
Figure 5 Effect of feed temperature on the Q_c 

Figure 6 Enthalpy change with the vapor quality

Figure 7 Effect of feed vapor quality on the Q_B Figure 8 Effect of feed vapor quality on the Q_c

5. Result and Discussion

Based on the BOG conditions and the requirements for the helium extraction from a 3000000m³/day LNG plant, the recovery performance of HeX-NRU defined by Figure 3 is showed in Table 2.

From the point of view of producing pure gas helium product by condensation process, high condensation pressure level is usually required to improve the gas helium purity. However, for the distillation process higher pressure leads to a higher condenser duty and therefore increases the power consumption of the nitrogen refrigerator.

Table 2 Recovery performance of a HeX-NRU

Product	Product Pressure	Product Flow	Purity	Recovery efficiency
Raw He	20 Bar	2.31 g/s or 68 L/hr LHe	62.0%	95.3%
CH ₄	5 Bar	4387 NM ³ /h	99.0%	100%
N ₂	5 Bar	425 NM ³ /h	98.7%	86.9%

Therefore, a modified HeX-NRU is suggested as shown in Figure 9, into which a reversed Brayton Cycle helium refrigerator is integrated for the purpose of cooling BOG down to a lower temperature of 65K. At this low temperature, most of the nitrogen content can be condensed and separated more thoroughly even at a lower pressure. As a result, the pressure level of HeX-NRU can be reduced, hence less condenser duty is required by the distillation process, and the lower power consumption for the nitrogen refrigerator as well.

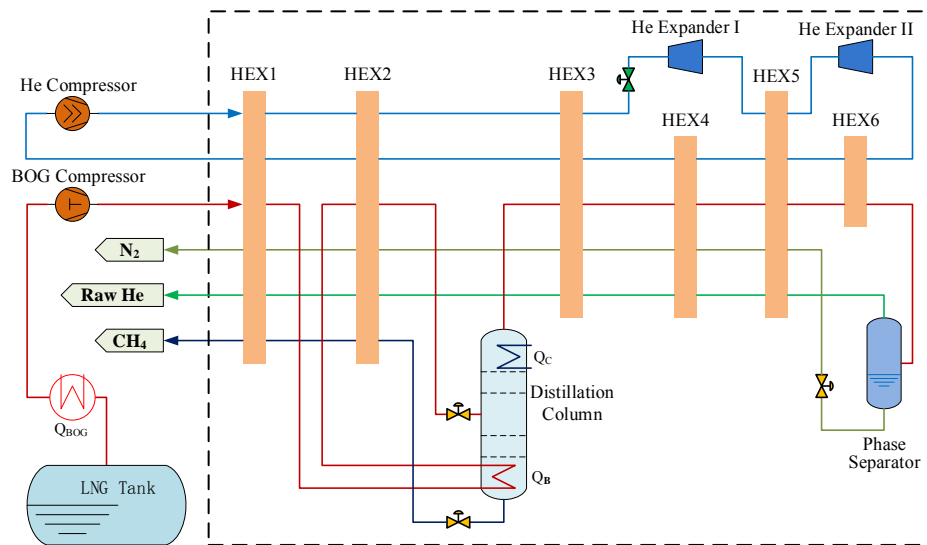


Figure 9 Flow Diagram of modified HeX-NRU

Table 3 Recovery performance of a modified HeX-NRU

Product	Product Pressure	Product Flow	Purity	Recovery efficiency
Raw He	10 Bar	2.41 g/s or 71 L/hr LHe	79.45%	99.4%
CH ₄	3.5 Bar	4387 NM ³ /h	99.0%	100%
N ₂	6 Bar	439 NM ³ /h	99.5%	90.68%

Table 4 Comparison on the power consumption between two HeX-NRUs

	Power consumption (kW)	
	HeX-NRU	Modified HeX-NRU
BOG compressor	682.7	479
N ₂ refrigerator	851	492
He refrigerator	0	110
Total	1533.7	1081

Table 3 presents the recovery performance of a modified HeX-NRU. A comparison on the power consumption between two HeX-NRUs is carried out as listed in Table 4. It is clear that the operation of

the modified HeX-NRU is more economically with higher recovery efficiencies for either helium extraction, nitrogen removal or NG recovery.

6. Conclusion

The helium bearing BOG from LNG storage tank in LNG plant is a potential unconventional helium sources. The extraction of helium from BOG is usually combined with a nitrogen removal process. The integration of condensation and distillation based cryogenic processes is an effective and feasible way for the recovery of methane, helium and nitrogen from BOG. The optimization on the temperature and pressure of the feed stream into the cryogenic distillation column should be taken into account carefully. A 65K helium refrigerator can be dedicatedly integrated into the HeX-NRU to condense the BOG to a lower temperature, which makes the stripping off nitrogen from crude helium more deeply through condensation separation process even at a relative lower pressure. The low operating pressure will in return be in favor of decreasing the condenser duty required by the distillation process as well as the power consumption of the system.

Reference

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