Helium Shortage 4.0: How to Face the Problem Through its Energy-efficient Recovery from Natural Gas

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Helium is an extraordinary commodity. Its many remarkable properties, i.e., lightness, inertness, small atomic size, low liquefaction temperature, make this element play a crucial role in advanced technological sectors. Despite it is the second-most-abundant element in the universe, the only viable helium sources are certain natural gas fields, where helium accumulates because of α-decay of Uranium-238 and Thorium-232. Helium production from natural gas has long been discouraged by the marginal economic revenue compared with the required operating costs. However, the helium shortage we are experiencing today has revived the interest in its recovery. In this panorama, the development of efficient processes for helium separation from natural gas and its upgrading is of paramount importance. The aim of this work is to analyse the cryogenic helium recovery from natural gas. Single-column and double-column process configurations are discussed, to identify their applicability range depending on the feed compositions. To benefit from the high flexibility of the single column configuration, its application to CO_2 containing mixtures is investigated, to lighten the upstream acid gas removal section, thus enabling significant energy savings in the overall gas-treatment chain.

1. Introduction

Helium (He) has many remarkable properties and applications. The helium atom is smaller than any other element and second only to H_2 in lightness. Due to its small atomic size, it has the ability to diffuse through many solid materials. Its gaseous thermal conductivity is 5-6 times higher than all other gases but H_2. Helium's low liquefaction temperatures make it desirable for purging, pressurization, and cryogenic applications.

Helium accumulation in natural gas fields is due to α-decay of Uranium-238 or Thorium-232 and can be expected when tectonic activity creates faults, enabling the gas collection in the reservoir (Grynia and Griffin, 2016). For this reason, helium is a non-renewable resource, leading to concerns about its exhaustibility and allocation.

Helium markets have undergone several periods of supply shortage since 2006. The helium shortage 4.0 experienced nowadays is mostly due to the outage of the U.S. Bureau of Land Management's (BLM) purifier, removing more than 10% of global capacity from the market. Because of the lower supply, helium prices have increased by 50-100%, this evidence reviving the interest in its recovery. In this context, the development of energy-efficient recovery and upgrading helium processes from natural gas is of paramount importance. Generally, natural gas containing more than 0.3 mol% He is considered viable for its extraction. Since helium presence is typically associated with a non-negligible nitrogen content, He recovery is integrated with N_2 rejection. The typical operations required for extracting helium from nitrogen-rich natural gas (N_2 inlet content > 5-8 mol%) is depicted in Figure 1.
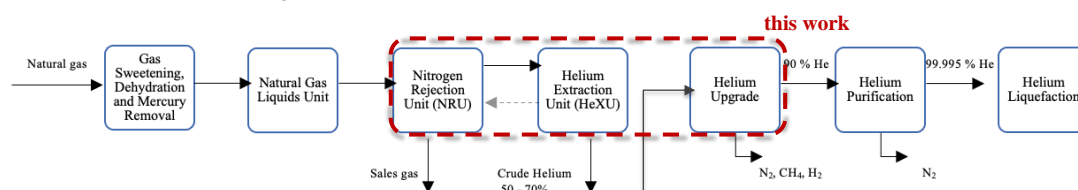

Figure 1. Nitrogen-rich natural gas processing steps (adapted from Hamedi et al., 2019).

The aim of this work is to analyze two different cryogenic helium recovery and upgrading schemes, namely the single column and the double column configurations. Process simulations for a number of representative case-studies are performed through Aspen HYSYS V11® simulation software (AspenTech, 2019). The operating conditions for each case are refined to assess the system behavior and its sensitivity to process specifications. Variable feed compositions are considered, referring to the typical helium-bearing natural gases. For the single column configuration, the process tolerance to carbon dioxide is examined, to assess the maximum admissible CO_2 content in the feed stream to avoid solidification issues (Pellegrini et al., 2020).

2. Process configuration

The configurations mainly exploited for cryogenic helium recovery from natural gas are the single column and the double column process, possibly completed with an additional pre-separation column. Both of them are described in the following sections.

2.1 Single column recovery scheme

In the single column process configuration, the separation of CH_4 from a gaseous N_2 stream collecting the original He content is accomplished through a single distillation unit, equipped with both partial condenser and reboiler. The advantages of this configuration are recognized for N_2 inlet content in the feed stream up to 30 mol%, as higher nitrogen concentrations make the condenser duty increase (Spatolisano and Pellegrini, 2021a). The simulated process scheme is depicted in Figure 2. The natural gas feed is precooled in the main heat exchanger (LNG-100) by the bottom column products, expanded below N_2 critical conditions (P_c = 34 bar) and fed to the distillation column T-100. The bottom product is the purified natural gas, which is expanded, to allow heat recovery, and then compressed for gas grid distribution. The overhead N_2 product has less than 1 mol% of CH_4 and about 4-5 mol% of He. This vapor stream is compressed in K-100, chilled in LNG-101, expanded and fed to the helium fractionation column (T-101), equipped with a reboiler only, to operate the last separation. Crude helium, nearly an equimolar mixture of He and N_2, is withdrawn from the top and undergoes a further upgrading in a series of cooling stages (LNG-100-2 and LNG-101-2), where a purity of 90 mol% can be pursued.
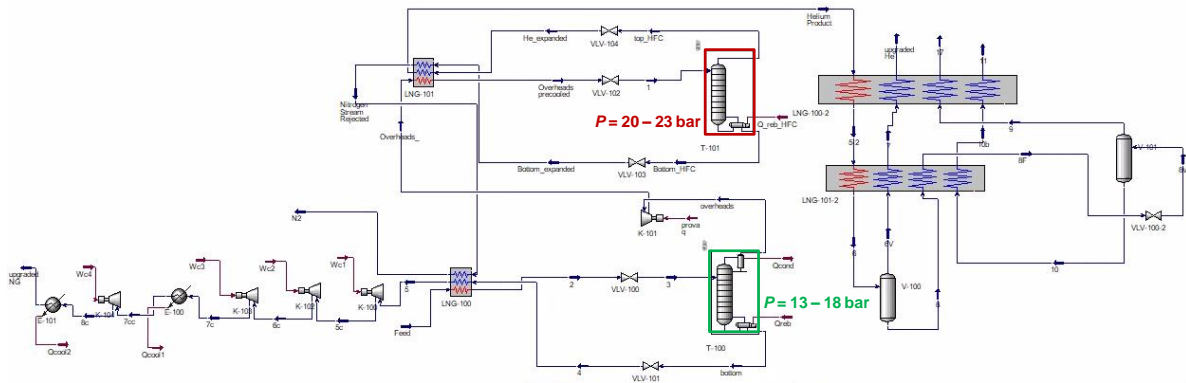

Figure 2. Single column He recovery, with downstream He upgrading. Simulation in Aspen HYSYS V11®.

2.2 Double column recovery scheme

The double column configuration consists of a high-pressure (HP) rectifying column thermally linked with a low-pressure (LP) column, to perform the simultaneous N_2 rejection and crude He production maximizing the heat integration. Because of the very cold temperature profile of the LP column, the reduction of carbon dioxide inlet content down to few ppm is crucial to avoid solidification issues (Rufford et al., 2012).

Gas with a N_2 content below 20 – 30 mol% cannot be processed successfully in the basic double column process scheme. The typical N_2 inlet content suitable for this technology is in the range 25 – 70 mol% (De Guido et al., 2019). Figure 3 shows the simulated double column process scheme. The feed stream is precooled into sequential process-process heat exchangers (E-100, LNG-100, LNG-101) and, after expansion, is fed to the HP column. The liquid N_2-rich stream exiting the condenser provides reflux for both HP and LP columns. The vapor stream exiting the condenser is the crude helium fed to the downstream upgrading section. The bottom product of the HP column is chilled in LNG-102, expanded and fed to the LP column. Two essentially pure streams, N_2 from the top and CH_4 from the bottom, are withdrawn from this column. The bottom product is pumped in P-100 and used for refrigeration recovery in LNG-101 and LNG-100, before being compressed for gas grid distribution.
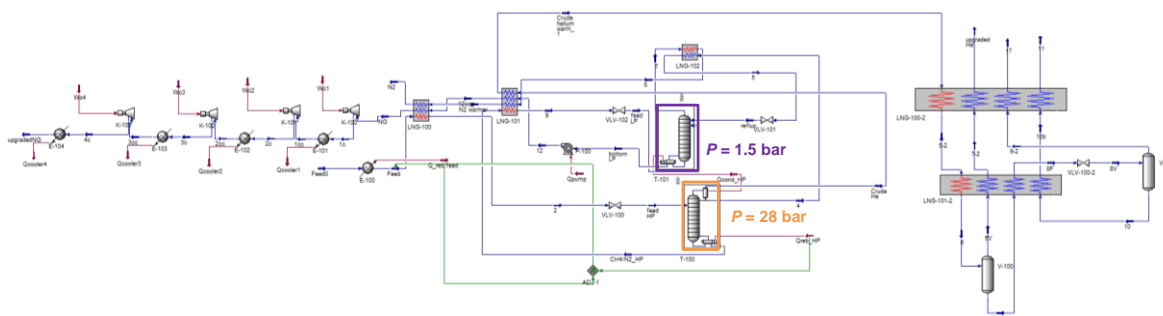
Figure 3. Double column He recovery, with downstream He upgrading. Simulation in Aspen HYSYS V11®.

3. Results and discussion

The performances of both single and double column process schemes have been assessed considering the following basis of design:

- feed mixture entering the battery limits at T = 20°C, P = 50 bar, F = 5000 kmol/h, with variable molar composition reported in Table 1;
- natural gas product Wobbe Index WI ≥ 48 MJ/Sm^3 suitable for gas grid distribution;
- CH_4 content in the N_2 stream exiting the process fixed at 0.5 mol%, to minimize the hydrocarbon slip.

Table 1: List of helium bearing natural gases considered in the process simulations

CH_4 [mol%]	N_2 [mol%]	He [mol%]	Configuration	Reference
71.6	26.3	2.1	Single column Double column	Haussinger et al. (2005)
89.3	10.2	0.5	Single column	Haussinger et al. (2005)
84	15.3	0.7	Single column	Rufford et al. (2012)
85.9	12.7	1.4	Single column	De Guido et al. (2019)
93.47	6	0.53	Single column	Haussinger et al. (2005)
72.06	24.54	2.4	Single column Double column	Haussinger et al. (2005)
87.19	9.9	2.91	Single column	Haussinger et al. (2005)
60.8	36.6	2.6	Double column	Rufford et al. (2012)
67.63	31.1	1.17	Double column	Haussinger et al. (2005)
50.95	45	4.05	Double column	Haussinger et al. (2005)

3.1 Single column recovery scheme

In the case of the single column recovery scheme, the number of trays is fixed at 20, to minimize the energy demand, despite the desired separation can be also accomplished with half of the trays. As expected, the He molar content and He recovery in the overheads increase with increasing helium-to-inerts ratio in the column feed stream. For each of the feed streams considered, the maximum admissible CO_2 content has been assessed, according with two constraints: to avoid the CO_2 solidification within the plant and to respect the Wobbe Index of the natural gas product. As CO_2 is the heaviest component in the mixture, it tends to accumulate in the bottom section of the distillation unit. Being its density high, CO_2 presence influences negatively the WI (in the Wobbe Index definition the species density appears at the denominator). On the other hand, N_2 density is significantly lower: its influence on WI is not as negative as the CO_2 one. It follows that, at a high admissible CO_2 fraction in the feed stream, corresponds a lower N_2 inlet content, to meet commercial specifications (De Guido et al., 2019). To assess the maximum allowable CO_2 content in the feed stream, the "CO_2 Freeze Out" tool of Aspen HYSYS® has been used (De Guido and Pellegrini, 2022). Once the process specifications are determined, the freeze check for each stream involved in the simulation is performed, including the vapor and liquid streams within the distillation column. A safety margin of 2°C is kept between the stream temperature and the correspondent freezing temperature to ensure conservative conditions (De Guido and Spatolisano, 2021). The result of this analysis is the blue line in Figure 4. This line establishes the range of applicability of the single column process in the presence of CO_2, ensuring safe operations whenever the feed composition falls below the limiting curve. The increase of the total amount of N_2 and He in the feed stream causes a reduction of the CO_2 tolerance. Although the trend is monotonously decreasing, at least three regions can be distinguished. For

light gases content below 10 mol%, a milder reduction of admissible CO_2 fraction is observed. The slope of the limiting curve gets steeper in correspondence of 10 mol%, but returns milder at about 15 mol%. Considering the gap of composition between 16 mol% and 26 mol% of helium - bearing natural gases reported in Table 1, the blue line has been extrapolated in this region (dashed blue segment in Figure 4). The observed trend is very similar to the corresponding one for N_2 rejection only (orange curve in Figure 4). Helium effect on CO_2 solidification is the same of nitrogen: it favors solid carbon dioxide formation, as detailed elsewhere (Spatolisano and Pellegrini, 2021b).
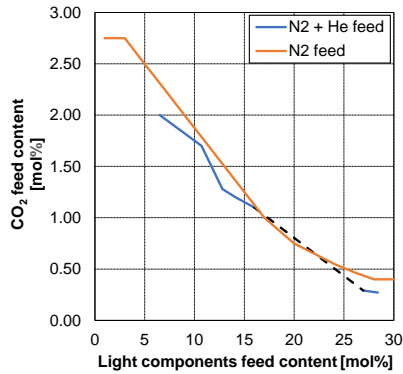

Figure 4. Maximum admissible CO_2 content in the single column process: comparison between N_2 feed (orange curve) and N_2 + He feed (blue curve).

3.2 Double column recovery scheme

The greatest advantage of the double column process configuration is the extensive heat integration, that enables to achieve auto-thermicity (Rufford et al., 2014). For this reason, a careful assessment of the operating pressure is necessary to allow the thermal coupling between the HP condenser and the LP reboiler, before analyzing the process performances. The mixture exiting the LP reboiler is the $CH_4 – N_2$ mixture, whose N_2 content has to be limited to 3 mol% to respect the Wobbe index specifications, while the vapor stream exiting the HP condenser is crude helium. Vapor – liquid equilibrium pressures of these two mixtures are reported in Figure 5a, at variable compositions. A suitable temperature difference between these two streams must be ensured to make the thermal coupling effective.
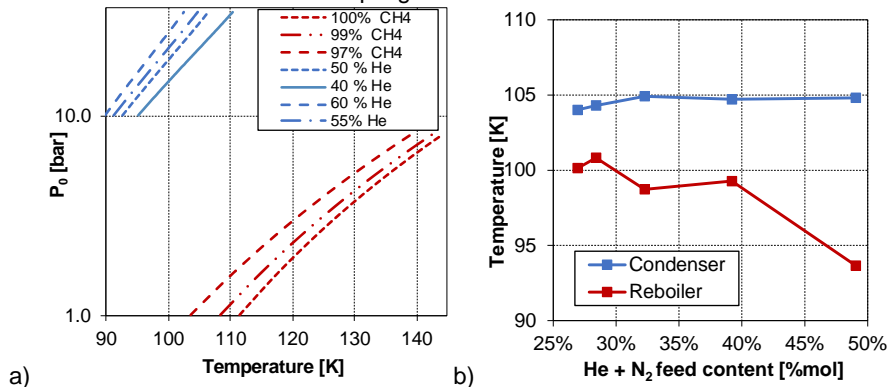

Figure 5. a) Vapor – liquid equilibrium pressures for CH_4-rich stream of the LP reboiler (red) and He-rich stream of the HP condenser (blue) and b) HP condenser and LP reboiler temperature against light gases feed content.

The thermal integration range is reduced and shifted towards lower temperatures with respect to N_2 rejection, due to the presence of helium. For pursuing the auto-thermicity, the HP column must operate at nearly 25 bar, while the operating pressure of the LP column is fixed at about 1.5 bar.
A further validation of the heat integration is provided in Figure 5b, considering the reboiler and condenser temperatures as a function of the light gases feed content. A higher He+N_2 fraction causes a reduction of reboiler temperature, increasing the temperature approach.
Made the heat integration effective, the performances of the double column process scheme can be assessed. The number of trays is fixed at 15 – 16 for the HP column and at 13 – 14 for the LP one. A higher number of trays does not improve the operability nor significantly affects the purity of the LP products.

Figure 6a displays the dependence of the HP products purity on the inlet N_2 content.
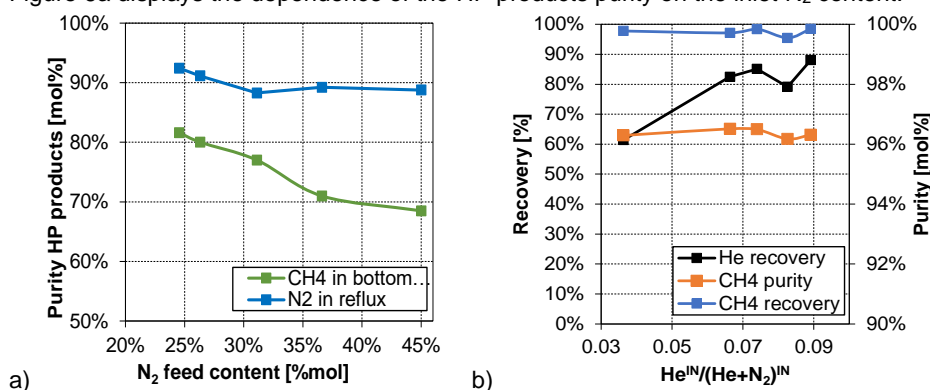

Figure 6. a) Purity of HP column products as a function of N_2 feed content and b) He recovery, CH_4 recovery and purity as a function of light gases feed content.

Both streams exhibit a reduction in purity for increasing N_2 contents, with the bottom being more sensitive to the variation of the feed composition. The purity of the reflux largely affects the performances of the LP column: a CH_4 molar fraction higher than 10 mol% prevents the N_2 stream exiting the LP column from reaching the specification. As the reflux is enriched in nitrogen, a lower molar flowrate is required to achieve the desired purity in the LP products. Figure 6b shows the He and CH_4 recovery of the whole scheme, together with the CH_4 purity as function of the feed light gases content. The methane recovery is always near 100%. The relative share between helium and nitrogen impacts the recovery performances: helium recovery almost uniformly increases with helium-to-light gases ratio and reaches its maximum in correspondence of the highest value (8.91%). When nitrogen is in increasing proportion, a worse recovery is achieved, since more helium remains dissolved in the liquid exiting the HP condenser.

The residual helium fraction in the nitrogen stream is lost unless a recovery by stripping, rectification or expansion of the reflux is performed (Haussinger et al., 2005).

4. Conclusions

The present work analyses two different cryogenic helium recovery processes, i.e., the single column and the double column process schemes, with the aim of making the configuration as energy effective as possible, thus lightening helium recovery and upgrading section.

In the helium recovery section, pipeline quality natural gas with a Wobbe index higher than 48 MJ/Sm^3 is separated from the crude helium vapor stream, concentrated at 50 mol%, which is further purified in the helium upgrading section. Different process simulations have been performed through the Aspen HYSYS V11® simulation software, to identify the feasibility ranges of each configuration depending on the inlet gas composition. When a non-negligible CO_2 content is available in the feed stream, together with a light gases (N_2+He) concentration below 30%, the single column configuration must be applied. In the single column configuration, CO_2 inlet content has to be limited to avoid solidification issues. A detailed analysis on the operating conditions which favour solid carbon dioxide formation, based on the proper modelling of the system's thermodynamics (De Guido and Pellegrini, 2021), has allowed to assess the maximum CO_2 content in the feed stream case by case. On the other hand, the double column configuration can tolerate only few ppm of carbon dioxide.

Figure 7 displays the feasibility range of each configuration as a function of He and N_2 molar content. Since all the simulations were performed on real helium bearing natural gases, a brief glance at this figure reveals that, typically, helium is less than 10% of the total amount of light gases.

Most of the considered helium – bearing natural gases are within the typical application range of the single-column configuration, as helium contents higher than 2 mol% are quite rare. Above 25 mol% of nitrogen, double column process proves the most advantageous solution, since the nitrogen amount is sufficient to provide the required reflux flowrate for both columns while making the overall configuration auto-thermal.

In the vicinity of the boundary between the single and the double column configurations, both schemes are applicable, in principle. The choice of the most appropriate one has to be assessed case by case: the single column configuration appears as the most flexible regarding its inlet feed composition, since it can also tolerate the CO_2 presence in the feed stream. On the other hand, the double - column process scheme does not require any external energy for the column top product condensation, being the configuration auto-thermal, at the

expenses of a deep CO_2 removal upstream. In these cases, a more detailed energy balance is needed to identify the most cost-effective helium recovery configuration.
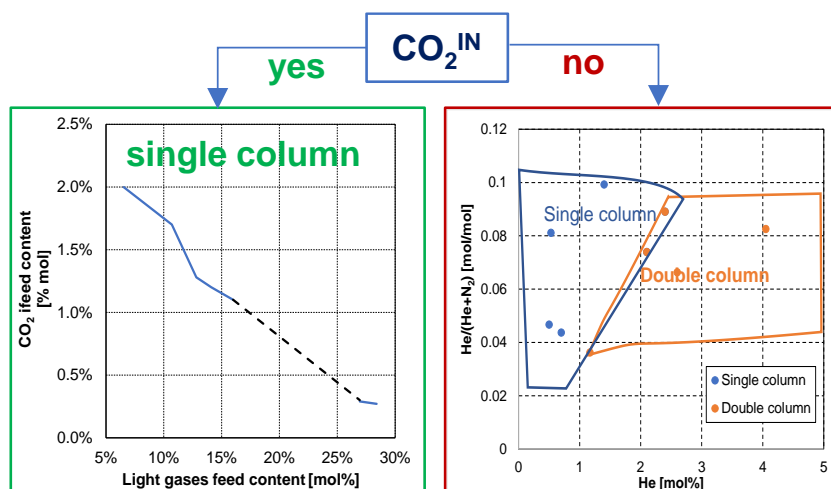

Figure 7. Feasibility ranges of process configurations analysed.

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