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Efficient Extraction of Helium from Natural Gas by Using Hydrogen Extraction Technology

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Helium (He), the lightest inert gas, is used in various medical, scientific and industrial sectors where its global demand increases since years. The gas can be generated by nuclear fusion of hydrogen, but it is mainly found in natural gas fields at low concentrations (0.2 - 4 % (v/v)). As He is mostly required in high quality (≥ 99 % (v/v)) upgrading is necessary. For the extraction of He from natural gas, a mixture of several substances like methane, nitrogen, oxygen, carbon dioxide, other hydrocarbons, helium, hydrogen and others, several upgrading process chains are established. Commonly cryogenic distillation is used for He production due to its good economics of scale. However, as it is cost- and energy intensive the potential of several emerging technologies based on adsorption and/or membrane separation have been investigated.
As helium and hydrogen are quite comparable in terms of their separation characteristics, this work presents a process, which has been developed for hydrogen separation from natural gas, to extract helium. The hybrid process based on membrane technology and pressure swing adsorption (PSA) is investigated via process simulation. The presented results of the hybrid process (containing two membrane separation steps and a pressure swing adsorption) indicate a specific energy consumption of 0.4 to 0.7 kWh m^{-3} to gain Helium with 99.9 % (v/v) at 25.81 bar. Furthermore, the influence of several parameters like feed composition, chosen membrane selectivity and PSA recovery on the required amount of specific energy is shown.

1. Introduction

Helium (He) is the smallest and lightest inert gas used in several medical, scientific and industrial sectors (e.g. electronics, rocket technology, cryogenic applications). It is non-flammable and has an extremely low boiling point. The gas is mainly found in natural gas fields at low concentrations of 0.2 % to 4 % (Sunarso et al., 2017), where it has to be extracted from natural gas mixtures. Commonly this is done via cryogenic distillation, which is cost- and energy intensive technology, but has good economics of scale. For a higher energy efficiency the potential of several emerging technologies based on adsorption and/or membrane separation have been investigated (Rufford et al., 2014). A known state-of-the-art technology to produce high quality gases is pressure-swing-adsorption (PSA) which is capital intensive due to its complexity (optimised PSA systems have 12 and more adsorber columns resulting in many pipes, valves, etc.). For mediate product quality, or a first enrichment, membrane technology can be used which is simple in operation, compact and cost-efficient for small units (Shao et al., 2009).
Natural gas fields are commonly under enhanced pressure, which makes the exploitation and distribution more energy efficient. While cryogenic distillation prefers low pressures (for most gases the temperature can be reduced by pressure reduction due to Joule-Thomson effect), PSA and membrane separation prefer enhanced pressures.
In membrane technology a substream is separated from the feed mixture, leaving the remaining gas (almost) at feed pressure. Based on the membrane material this substream, called permeate, is selectively taken. Via helium selective membranes the permeate stream is helium enriched. As it is only enriched and not pure helium, a PSA (smaller as it should only handle a small substream) is used to ensure the required product quality.
This hybrid process concept based on membrane technology and PSA has been intensively studied for the separation of hydrogen from natural gas using a stepwise approach. In a first step, high pressure membrane permeation experiments and PSA breakthrough analysis have been conducted (Liemberger et al., 2016a) and

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an extended experimental analysis of membrane and PSA step regarding the influence of PSA feed composition and PSA purge time has been executed (Liemberger et al., 2017a). Subsequently, single adsorber experiments with feed pressure variation have been performed (Liemberger et al., 2016b). Finally, process optimisation via process simulation for the system $H_2/CH_4/CO_2$ has been performed and was then used to create a reduced model based on trained artificial neural network approach (Liemberger et al., 2018). This has led to a simplified model that is able to describe a highly efficient and competitive process for the extraction of hydrogen co-transported in the natural gas grid. As hydrogen and helium are similar in terms of their physical properties, the current work uses the same approach.

2. Aim of the work

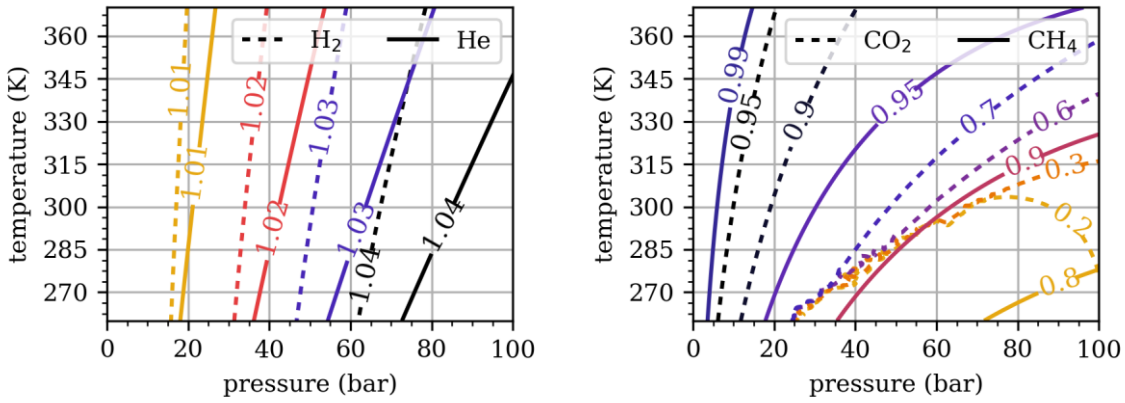
The work uses a hybrid process of membrane separation and PSA to extract helium from natural gas with an optimised process originally developed for the hydrogen extraction from mixtures with natural gas. The helium, only a few percent (e.g. 1 - 4 % (v/v); see Sunarso et al., 2017) of the supplied feed gas, is extracted and enriched to ≥ 99.9 % (v/v). The other components (mainly methane and carbon dioxide) are recompressed and reinjected to the grid.

3. Theory and background

The work focuses on gas separation of helium (He), methane (CH_4) and carbon dioxide (CO_2) and, as existing technology is used, hydrogen (H_2). Table 1 shows some for the separation relevant physical properties.

Table 1: Selected properties of investigated gases. Physical properties taken from (Lemmon et al. 2017). Permeances and selectivities of H_2, CH_4 and CO_2 taken from (Liemberger et al. 2017a). Permeance of He measured for this publication.

Property	Unit	H_2	He	CH_4	CO_2
Molecular weight	g mol^{-1}	2.0159	4.0026	16.0425	44.0095
c_v (at 1.0123 bar)	J mol^{-1} K^{-1}	20.521	12.473	27.410	28.936
c_p (at 25 °C)	J mol^{-1} K^{-1}	28.840	20.786	35.802	37.446
κ (c_p/c_v)	-	1.4053	1.666	1.306	1.294
Permeance	m^3 m^{-2} s^{-1} bar^{-1}	1.05 x 10^{-9}	1.37 x 10^{-9}	1.39 x 10^{-11}	3.12 x 10^{-10}
Ideal selectivity (H_2 / X)	-	1	0.76	75.68	3.37
Ideal selectivity (He / X)	-	1.31	1	99.06	4.41



a) Compressibility factor of H_2 and He

b) Compressibility factor of CH_4 and CO_2

Figure 1: Compressibility factor of H_2, He, CH_4 and CO_2 as function of pressure and temperature. Presented data taken from Lemmon et al. (2017).

Membrane simulation is commonly modelled via a solution-diffusion approach, which assumes ideal gases and uses the ideal gas law, a simplified equation of state. The deviation of real gas to the ideal gas equation can be expressed as compressibility factor. As it can be seen in Figure 1a, the ideal gas equation is able to predict hydrogen and helium properly for a wide pressure and temperature range. In contrast, Figure 1b shows that the ideal gas equation is only suitable in some regions to predicting CH_4 and CO_2 with a certain accuracy. While the

deviation of 10 - 15 % for CH_4 has been chosen to be in an acceptable range, the one of CO_2 is not (especially close to its critical point). Anyhow, CO_2 plays only a minor role in this work and is only present in small concentrations. Therefore, the model uncertainty was tolerated.
Adsorption is commonly described by adsorption isotherms. While activated carbon, the used material, can adsorb high amounts of CH_4 and especially CO_2 the amount of H_2 is little (e.g. see Figure 4 in Liemberger et al. (2017a)). For helium the amount is even less and therefore negligible (Bae and Do, 2003).

4. Method

The current work uses process simulation to investigate an optimised process for hydrogen extraction for the production of helium. The flowsheet, presented in Figure 2, has a first membrane separation step, to extract a substream. This substream is then compressed and applied as PSA feed where the pure product gas is gained at PSA pressure and compressed to the required product pressure. The PSA offgas, at reduced pressure, is recompressed and returned to the grid. To increase the overall process efficiency a recovery membrane is added which recycles unused product gas. Additionally, a part of the PSA offgas can be used as sweep stream for both membrane separation steps to increase their efficiency.

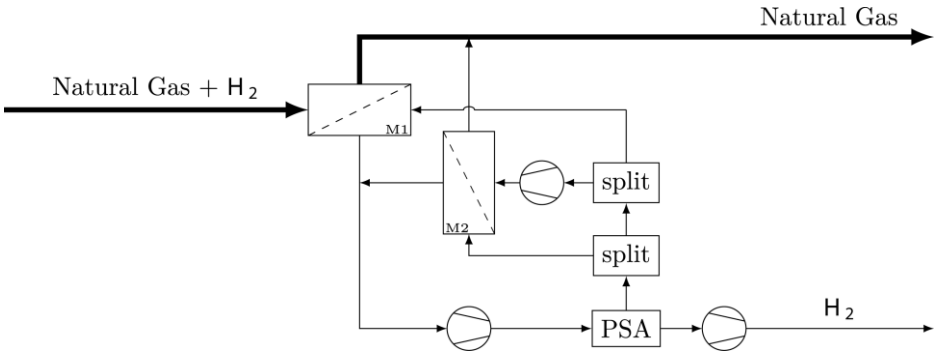


Figure 2: Efficient process concept for hydrogen extraction (Liemberger et al., 2018)

As presented in Liemberger et al. (2018), several recycling streams are possible based on the chosen split rations and recovery membrane properties. While these recycle streams can increase the overall recovery, more energy is required for recompression. This leads to a trade-off between total recovery and energy consumption which challenges process simulation to find the optimal configuration.
To identify the best process several combinations were calculated. As various parameters need to be set by the models, a sensitivity analysis was done showing the influence of these defined parameters. Beside a variation of input conditions (feed pressure and composition), separation parameters (membrane properties, PSA recovery) and compression efficiencies were analysed.
In total, this led to more than 8×10^5 different simulated cases. To speed up the calculation time and handle the large amount of data efficiently, a server node with 48 CPUs in combination with a relational database management system (MariaDB) was used.
The process simulation was carried out in MATLAB 2016b where required unit operations were developed and implemented in an object-oriented approach. The membrane was simulated via a multicomponent solution-diffusion based model with an in-house developed solver (details are shown in Halmschlager (2017)). For the PSA an adjusted splitter model (set He product content and recovery parameter) was used operating at 6 bar. The compression was calculated isentropic and adjusted via efficiency coefficient.
In order to identify the best combination, several combinations were calculated, all with a product stream of 99.9 % (v/v) He and 0.1 % (v/v) CH_4 at 25.81 bar. Figure 3 shows a simulated case (used parameters: feed: 51 bar, 4 % (v/v) He, 1 % (v/v) CO_2, 95 % (v/v) CH_4; membrane selectivity: He/CH_4: 75.68, He/CO_2: 3.37; PSA He recovery: 80 %; compression efficiency: 72 %) where only membrane areas and split ratios have been varied in order to influence the recycle streams. As it can be seen, several combinations of total He recovery and specific energy demand (two benchmark parameters) are possible. In order to get the most efficient process, the lowest energy demand at a certain total helium recovery is selected (selected points are visualised with squares and marked as optimal). The selection was done with an adopted boundary detection algorithm, based on the calculation of the convex hull and alpha shape, to identify the contour curves.
As it can be seen in the zoomed section, it is challenging to find the best curve for the optimal parameter combination. Moreover, it is pointed out that the energy demand increases with increasing total helium recovery.

The plot further shows that non-preferred process configurations increase the total energy consumption due to recycles streams without extracting a larger share of the gas. This increases the energy consumption significantly. Therefore, a proper design is necessary for an efficient process.

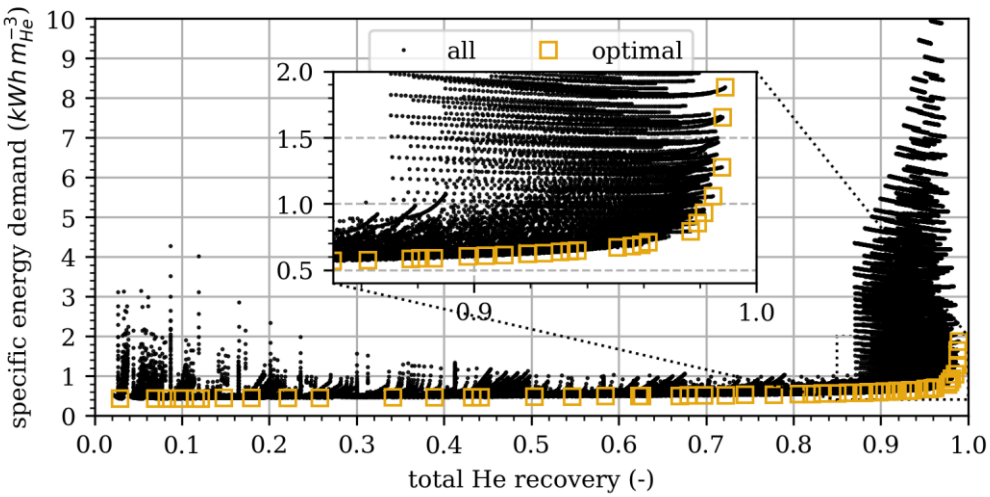


Figure 3: Overview of calculated points and those selected by the selection algorithm.

5. Results and discussion

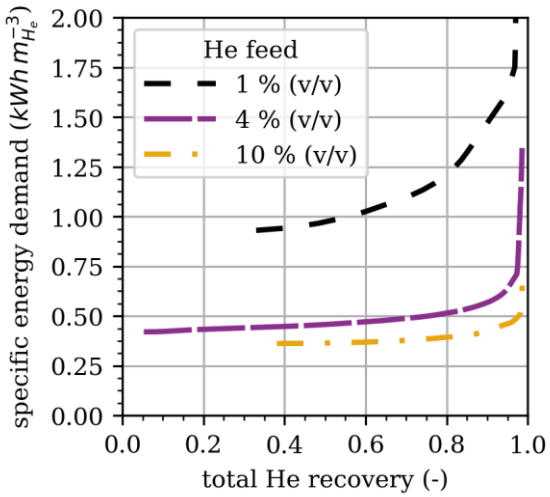
The simulations show the energy demand for different total helium recovery rates. As shown in Figure 3, Figure 4 and Figure 5 the process is able to extract a broad range of the total helium. Due to the recycle streams even total recoveries beyond the PSA recovery are possible. However, the internally cycling gas requires more compression energy, which leads to an increased energy demand (especially for total He recovery values beyond the PSA recovery rate).

5.1 Influence of feed concentration and feed pressure

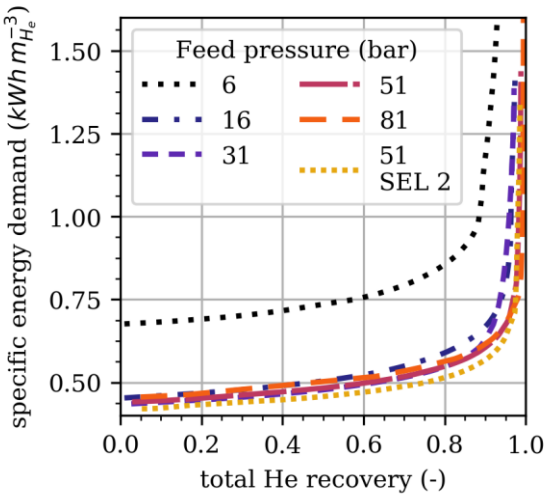
In Figure 4 (used parameters: Feed: 51 bar, 4 % (v/v) He, 1 % (v/v) CO_2, 95 % (v/v) CH4; membrane selectivity: He/CH_4: 100, He/CO_2: 3.37; PSA He recovery: 80 %; compression efficiency: 72 %) the influence of the helium feed share and feed pressure is presented. As it can be seen an increasing helium share reduces the required amount of energy, as the membrane separation is favoured. The graph (Figure 4a) shows, that an increase of helium feed content significantly decreases the energy demand. Therefore, an alternative process might be the more energy efficient option for very low helium feed shares (e.g. 0.2 % (v/v)).
Higher feed pressure levels increase the pressure difference, which favours the membrane separation. In contrast, less energy is required for the offgas recompression if the pipeline pressure level is reduced. As it can be seen in Figure 4b, a certain pressure level is necessary for an energy efficient process. Then a further pressure increase has a minor influence.
In conclusion, this means that the process is more flexible in terms of feed pressure than helium feed concentration.

5.2 Influence of membrane selectivity and PSA recovery

A more selective separation (higher membrane selectivity and higher PSA He recovery) decreases the overall energy demand. However, Figure 5a shows that even a selectivity increase of factor two has a minor influence on the overall energy demand (used parameters for Figure 5a and Figure 5b: Feed: 51 bar, 4 % (v/v) He, 1 % (v/v) CO_2, 95 % (v/v) CH4; membrane selectivity: He/CH_4: 75.68, He/CO_2: 3.37; PSA He recovery: 80 %; compression efficiency: 72 %).
The PSA recovery has a larger impact on the energy demand. Figure 5b shows that the process is able to gain high total helium shares when the total PSA recovery is low (e.g. 40 %). While the lines with PSA recoveries of 70 %, 80 % and 90 % have a similar trend, the one of 40 % has an angular shape. This shape can be explained in case the most energy efficient configuration has not been computed jet (imagine missing points in Figure 3 not leading to the best curve). Therefore, a slightly lower energy demand is expected.

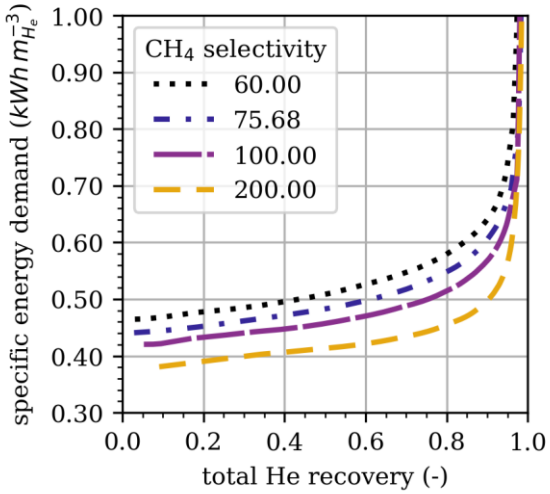


a) Influence of He feed content on energy demand and total recovery

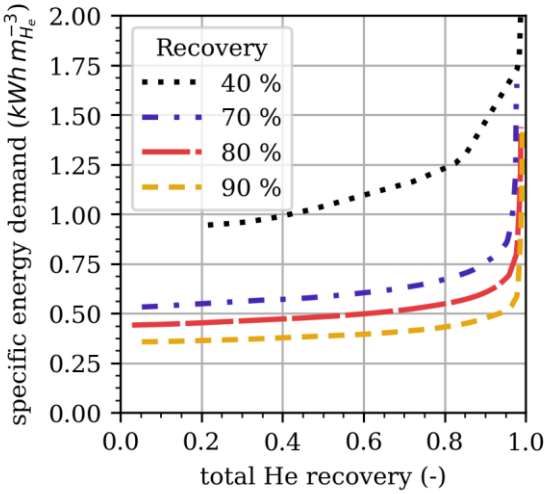


b) Influence of feed pressure on energy demand and total recovery (He/CH_4 selectivity: 75.68 except for SEL 2 where is He/CH_4 = 100)

Figure 4: Influence of feed condition on specific energy demand as function of total He recovery



a) Influence of CH_4 selectivity



b) Influence of PSA recovery

Figure 5: Influence of chosen a) membrane CH_4 selectivity and b) PSA recovery on the specific energy demand as function of total He recovery.

5.3 Compression efficiency

The compression is computed isentropic and scaled via efficiency parameter. As in Liemberger et al. (2018), an efficiency of 72 % was chosen. However, the results can be scaled easily for other compression efficiency values, as all compression steps were calculated with the same efficiency parameter. Obviously, the process requires less energy if the compression is more efficiently.

6. Conclusions and cutlook

Helium and hydrogen have similar physical separation properties. This makes it possible to use an efficient optimised process developed for the extraction of hydrogen from natural gas for the helium production. In the current work the process, a hybrid of two membrane separation step and a pressure swing adsorption, is presented and investigated via process simulation. A sensitivity analysis reveals that the required amount of specific energy depends on several parameters like total helium recovery, feed concentration, feed pressure,

membrane selectivity, PSA recovery and compression efficiency. The required specific amount of energy is in the range of 0.4 to 0.7 kWh m^{-3}. If the feed concentration, feed pressure and/or PSA recovery is low more energy is required. Anyhow, these dependencies are similar to the ones identified for the hydrogen extraction. It can be concluded that the herein depicted innovative process offers an effective alternative for the recovery of helium from natural gas. In a next step, experiments both on lab and pilot scale are envisaged in order to assess the influence of other natural gas components.

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