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Helium separation through polymeric membranes: selectivity targets

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ABSTRACT

Gas separation membranes have the potential to recovery and purify helium from natural gas. This can be through direct separation of helium from methane or as part of a natural gas liquefaction process where helium is recovered from the nitrogen rejection unit (NRU) exit gas. Here, membrane gas separation process simulations are undertaken in Aspen HYSYS to determine the required membrane selectivity and process conditions needed to perform these separations. It was determined that two and three membranes in series processes can separate helium directly from natural gas utilizing currently available polymeric membrane selectivities, if the helium composition in the feed is greater than 1 mol% and at high pressure. However, for lower quality natural gas fields' improvement in He/CH_4 selectivity is required for membrane separation to be viable. The recovery of helium from the NRU exit gas and concentration to 70 mol% is also possible through two or three membranes in series process with a He/N_2 selectivity above 5. However, this selectivity requires a significantly high pressure driving force across the membrane stages, because the process is operated at very low stage-cuts. A He/N_2 selectivity greater than 25 enables recovery of helium and concentration to 70 mol% with significantly lower pressure driving force. The upgrading of helium from 70 mol% to 90 mol%, before final purification, is the most viable separation that can be undertaken with existing gas separation membranes and the energy duty of a two membranes in series process is comparable with existing technology. Hence, current polymeric membranes for helium separation can perform many of the process stages in helium recovery and purification. However, improvements in polymeric membranes' He selectivity enables the various separation stages to become increasingly viable when compared with existing separation technologies.

1. Introduction

Helium is a high value product desired for its chemical inertness, lighter than air property and ability to achieve cryogenic temperatures near absolute zero. As such, helium has found application in a wide range of industries, in electronics and fiber optics fabrication, weather balloons and airships, as a heat transfer agent in rocket technology and in cryogenic applications such as medical MRI scanners [1]. The vast majority of helium is sourced from natural gas fields, where it can be concentrated as high as 4 mol% (New Mexico, USA), but on average commercial fields are between 0.2 and 0.5 mol% [2–4]. Recent increases in the helium price because of increasing demand [5] have made previously uneconomic fields attractive and hence there is increasing interest in low cost separation technologies that can recovery helium.

Traditional helium separation from natural gas is achieved in a three stage process, producing purity of 99% or higher. These stages consist of the initial recovery of helium from natural gas, helium upgrading to ~70% and the final helium purification (Fig. 1). Helium recovery from natural gas is integrated with nitrogen removal through cryogenic distillation, known as the nitrogen rejection unit (NRU) [1,6]. Dependent on the particular natural gas field, the exit gas from the NRU has helium at concentrations of 1%–3%, with the remainder nitrogen, oxygen and hydrogen. Helium upgrading can be achieved through cryogenic condensation to remove the majority of components and leaving helium in the gas phase. The final stage of helium purification is achieved through catalyzed oxidation of hydrogen and molecular sieve pressure swing adsorption (PSA) [1,6,7]; removing trace amounts of nitrogen and hydrogen. The resulting product then undergoes liquefaction for transport.

For many of these helium recovery process stages, polymeric membrane gas separation is a potential alternative separation technology. This is because the majority of polymeric membranes have selectivity for helium, and the conditions within natural gas and the subsequent separation stages favor a strong helium driving force across a membrane. Only the final helium purification stage to achieve very high purity is poorly suited for membrane

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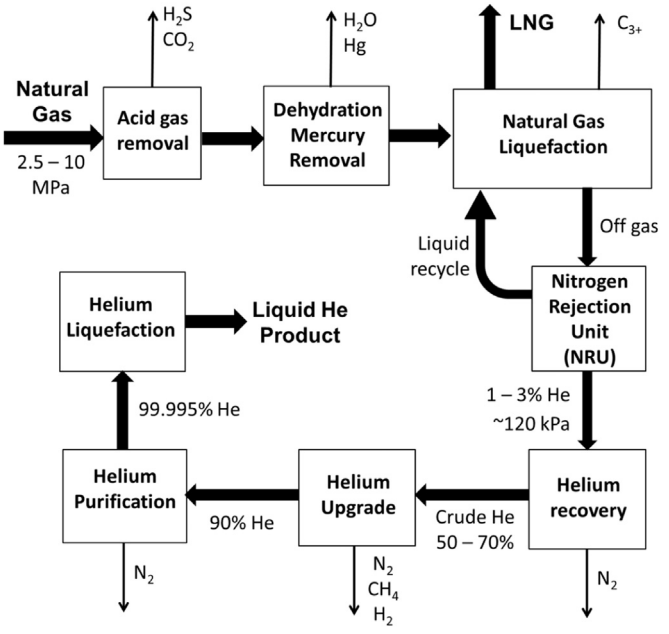

Fig. 1. Process stages and purity targets for helium separation from natural gas [6].

separation, because of the presence of hydrogen [7]. Indeed, one of the first applications trialed for gas separation membrane technology was the recovery of helium from natural gas [8], though the poor selectivity of membranes at the time meant this separation was not feasible. Currently, a number of commercial membrane processes exist that are marketed for helium recovery [9–11]. However, their market penetration is minor and associated with niche industries based on recycling helium rather than extraction from natural gas. To the best of the authors' knowledge no large scale helium recovery and purification process utilizing membranes exists, in part because PSA technology dominates this industry [12].

Here, simulated studies of membrane gas separation for helium recovery and purification are investigated and analyzed for their potential to replace other separation technologies for a number of process stages in helium separation. These stages are the direct separation and concentration of helium from natural gas; initial upgrading of the exit stream from the NRU to 70% helium and further purifying to 90% for final PSA purification (Fig. 1). These are achieved through membrane stages in series with recycle streams, with the number of membrane stages dependent on the process as well as feed and exit stream conditions (Fig. 2). The focus of the investigation is to determine the necessary helium selectivity required to achieve the degree of separation and purification in each process; and how this is dependent on the concentration of helium in the feed, the pressure driving force across the membrane stages as well as the number of membrane stages. These determined helium selectivities represent targets needed for membrane gas separation to be considered as a potential alterative technology in helium recovery. Other membrane process parameters, such as stage-cut, are important but the membranes' selectivity must be above a certain value for a process to achieve the desired product purity and recovery, irrespective of other process parameters. As such, these selectivity targets are compared for existing polymeric membranes that have been reported for helium separation to evaluate their potential. Helium permeability is another important parameter, as in the processes studied it strongly correlates with required membrane area. In addition, the energy duty of the membrane separation, and other ancillary parameters, are reported to enable comparison with existing helium separation technologies.

2. Methodology

All membrane simulations were undertaken in Aspen HYSYS (7.5), using the Peng-Robinson fluid package. The membrane simulations used an in-house module specifically designed for gas separation processes, based on mass transfer equations for cross-flow and counter-flow configurations [13–15]. The membrane separation process is broken down into 100 discrete stages and the mass balance is determined iteratively for each stage.

All membranes were operated in a cross-flow configuration without the use of a sweep gas, and assumed to operate at 35 °C. A pressure loss of 0.01 MPa was assumed for the retentate stream across the membrane. Compressor units were operated using default Aspen parameters and settings. Therefore compressors are centrifugal with an adiabatic efficiency of 75%. Heat exchangers have an assumed pressure drop of 0.04 MPa with the outlet temperatures set by the operator; gas flow through piping is assumed to have negligible temperature and pressure losses. Membrane processes consisted of one membrane stage, two membrane stages with recycle and three membrane stages with two recycles (Fig. 2). For the two membrane stages process, the permeate from the first membrane stage is the feed for the second membrane stage, and the retentate from the second membrane stage is recycled back to the feed of the first membrane stage to ensure high recovery, with the second membrane stage permeate the product stream. For the three membrane stages process, the second membrane stage permeate stream becomes the feed for the third membrane stage, with the third membrane stage retentate being recycled back to the second membrane stage feed. Additional compressors and coolers were included when necessary to generate the pressure driving force across each membrane stage and ensure the membranes operated at temperature. All membrane process configurations are designed to meet the respective purity targets in the product streams, for two and three membrane units in series the overall process is also designed to achieve 99% recovery of the helium in the feed. The membranes' stage-cuts, the fraction of the feed stream that permeates the membrane, are a process variable used to optimize the process in terms of membrane selectivity and process energy duty, the required energy per mass of He separated.

The helium composition in potential natural gas fields can vary between 0.05 and 4 mol%, a range of helium rich natural gas fields are provided in Table 1, and well head pressure can range from 2.5 to 10 MPa [1].

For direct separation and purification of helium from natural gas, the feed helium composition is varied between 0.05–4 mol%, and the pressure is 2.5–10 MPa, corresponding to potential wellhead pressures. For separation of helium from the NRU exit gas (Fig. 1), the feed helium composition is varied between 1 and 3 mol% with a pressure of 0.12 MPa that is compressed to generate the pressure driving force across the membrane. Similarly, for helium upgrading to 90 mol% in the NRU process (Fig. 1) the membrane feed is varied between 50–70 mol% and 0.12 MPa, corresponding to exit gas conditions from the helium recovery stage. Again this feed is compressed to generate the pressure driving force. For multiple membrane stages processes, each membrane has the same permselectivity and pressure driving force, unless otherwise stated.

3. Results and discussion

3.1. Helium separation from natural gas

A range of polymeric membranes have been reported for the helium–methane gas pair [8,16–19], and the Robeson's plot is