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A Short Review on Membranes for Helium Separation and Purifications

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ABSTRACT

Preponderance of membranes have Helium (He) selectivity which causes their gas separation has a potential for helium revival and purification. This review conveys the recent investigations and patent reports for membranes embarking on separation of He. This involves direct retrieval from natural gas which is an auxiliary stage in natural gas processing, alongside niche applications where helium recycling is capable. A summary of the available literatures on polymeric and inorganic membranes for helium separation is presented. In comparable gas industries, discussion on commercial gas separation membranes is with regard to their capacity for helium separation. This paper includes the assorted patented designs of helium recovery and purification by membranes from variety of sources, considering that these exhibit the viability of current available polymeric membranes to separate helium. The review particularly emphasizes processes in which membranes are utilized together with other available separation technology such as pressure swing adsorption (PSA). The combination of technology able to generate high-purity helium gas. This paper also aims to demonstrate the viability of membrane separation process for helium recovery and purification. Current process is focusing on reusing helium instead of separation from its raw sources.

Keywords:

Helium separation; separation membranes; polymeric membranes

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1. Introduction

Helium is a well-known noble gas that has crucial role in scientific, medical and industrial sector due to its characteristics of having a very low boiling temperature and is chemically inert [1]. Example

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of helium application can be seen in magnetic resonance imaging (MRIs) used in hospitals in which it usually used helium as the coolant and the gas is a component in breathing gas mixtures for marine scuba divers. Next, helium is also applied in welding as an inert gas, a carrier gas in both analytical equipment and scientific equipment and in rocket technology, where it is located at pressurizing and purging pressure vessels. Not more than approximately 8% of the worldwide helium market is consumed for party balloons [2].

Demand for helium is rising globally, powered predominantly by request from Asian countries especially China and India which are currently developing economically [3]. From the year 2000 until 2015, international helium usage had increased to 900 million cubic feet and the price was notably seen rising from US\$50 to US\$104 per thousand cubic feet during that period of fifteen years [4]. To meet the increasing demands, brand-new helium production facilities have been set up in Qatar and Australia. Over the coming decades, global helium production is nonetheless foreseen to be deficient of the global demand [5]. In addition, the increment in helium pricing is predicted to drive more interest in existing helium recovery and recycling industries as low-quality helium reservoirs become attractive. Commonly, helium recovery technology as well as helium purification count on cryogenic liquefaction and PSA, which was noted to be energy demanding as concentration of helium is decreasing in the feed [6]. Going off that, unorthodox technologies that are able to separate and purify helium will progressively be researched since they possibly benefit the economic compared to the conventional method. Membrane gas separation is one of the unconventional technologies that possesses substantial potential in helium processing and purification. This review talks over the currently used sources of helium and the prospective recycling applications which offer new advancement for membranes. Also presented and analysed are the recent literatures on polymeric and inorganic membranes for helium separation. Discussion on helium retrieval approaches in this paper comprised the ones patented in the past literatures, provided that membrane process is essential in economics of gas separation [3]. Thus, this work intent to notify the membrane researchers about the possibility of helium separation application.

2. Helium Sources

Prime supply of helium for commercial purposes are natural gas. Helium was reported to mount up across ages resulted from uranium and thorium radioactive decay inside the Earth [7, 8]. In Western USA where the largest commercial reserves of natural gas with helium abundance located, helium is separated by cryogenic liquefaction and PSA [4]. In spite of being the largest reserves, the concentration of helium is in general less than 1%, while high quality reserves such as in New Mexico reported a concentrations of 4.05% and Alaska, USA with helium concentrations of 2.54% [9]. Qatar, Australia, Poland and Algeria are the other countries that commercial helium-rich natural gas reserves subsist and there are potential reserves situated in Russia, Iran, Italy, Tanzania and India with inadequate list of fields globally. Two of most crucial gas fields in USA are Hugoton Panhandle Field, in parts of Oklahoma, Texas and Kansas and LaBarge gas plant located in Wyoming [9]. The idea of helium separation from atmospheric air is only proposed under the intense conditions given the concentration is 5.2 ppm [10].

From pressure tank testing application, it is observed that recycling helium sources is linked with leakages and gas wastage problems [11]. In general, the recycled sources contain mixture of helium and air with far greater concentration than discovered in natural gas. For these applications, concentration of helium is able to reach up to 99% except that it is frequently diluted by the air because of direct exposure towards outside environment [12]. The amount of gas for treatment is yet normally insignificant and exist only in some industries. For instance, reports on gas leakage

problem in modern MRIs is rare while in pressure tank testing is sporadic. Hence, the goal is to reduce helium waste industrially [13]. Since membranes were initially established as a technology, the notion of splitting helium from natural gas via membranes was widely demonstrated and discussed by other researchers [14]. Nonetheless, as far as the author knows, so far, there is none of large-scale membrane plant that specifically working on helium separation and purification. Partly due to ascendancy of PSA in the industry [14]. Likewise, recycled or purified helium from industrial practices, for example, coolant leakage and waste gas from pressure tanks are theoretically feasible by membrane separation. An array of commercial membrane procedures presently obtainable for helium revival from localized supplies is the pro of using membranes in helium recycling [15, 16].

2.1 Inorganic Membranes

Besides, the application of inorganic membranes for helium separation has also been studied [2, 12]. Membranes are able to endure more inhospitable conditions like high temperatures and corrosive gases which are their few advantages over polymeric membranes [17, 18]. On the other hand, the literature focuses on separation of hydrogen with helium infusion as one of the gases that is exploited for characterization in lieu of specific application. It is complicated to attain the selectivity seen in polymeric membranes for the reason that all of the described inorganic membranes are porous [19]. As helium is inert in nature, porous membrane would not experiencing surface diffusion and capillary condensation [20, 21]. Quite a number of stated inorganic membranes are having selectivity above the Knudsen diffusion selectivity of 1.9 for He/N₂ and 2 for He/CH₄ [22] which implies that helium molecular sieving can occur given that helium diameter is 2.6 Å, N₂ is 3.64 Å and CH₄ is 3.8 Å [23].

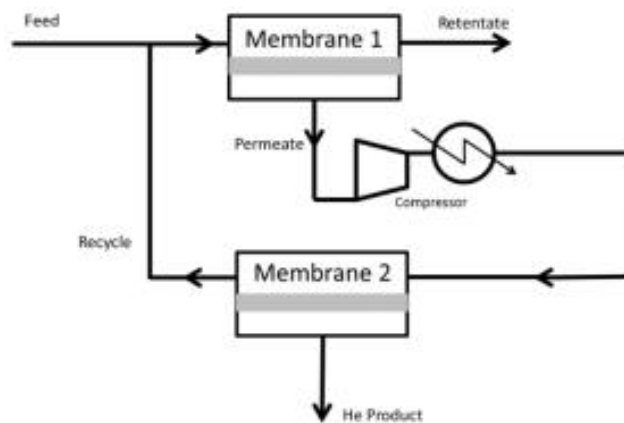
For inorganic-based membranes, metal organic framework (MOF) membranes offer high selectivity because to a certain extent, the morphology of framework is able to be specifically constructed to allow diffusion of helium but prevent penetration of other gases. Deposition of silica sol on alumina support layer membranes created microporous silica which comparably able to reach very high helium permeation and selectivity [24-26]. This is owing to the fact that the diameter of the silica pores is of the helium's which resulted in outstanding molecular sieving, whilst the technique for deposition can produce a steady layer without any shortcomings. Therefore, microporous silica membranes have the potential to yield helium with high purity from those abovementioned helium sources although large scale manufacture is still a concern. Based on the author's knowledge, there is none inorganic membrane module available in the market specialized for helium separation. Inorganic membranes will continue to be researched actively going into the future but expectation is, helium separation is going to be deemed as a minor application.

2.2 Membrane Processes

For both inorganic and polymeric-based membranes, the process design must be economically attractive and competitive contrary to the existing process design in order to have helium recovery viability. For that reason, membrane research in helium recovery has the foremost attention on developing process designs that will drop energy burden and diminish size of the equipment plus the membrane area. It is demonstrated in other gas separation applications that advancements in the process design possess greater effect on economic competitiveness of the membranes in lieu of only augmentation of permeable membrane selectivity, and this claim is accountable for recovery of helium too [27]. Based on both research and patent literatures, there are numerous designs for helium recovery processes using membrane technology from variety of sources. As for direct helium

revival and purification from natural gas, separation by membranes are confirmed to be probable if it is combined as two to three stages put in chain together with recycle flows as shown in Figure 1. The said design utilized current polymeric membranes with high He/CH₄ selectivity where natural gas with 1 mol% helium and greater are able to be purified in very high concentration. As an instance, the field in Alaska can have purification that reaches up to 99% in the course of three stage processes by Teflon FEP-based membrane with He/CH₄ selectivity of 44 while running at 10 MPa of pressure, otherwise with PVC-based membrane that has He/CH₄ selectivity of 71.4 at 5MPa of pressure. On the contrary, membrane made up of Hyflon AD with He/CH₄ selectivity of 157 has the ability to proceed the Alaskan field three stages process at 625 kPa of pressure [28].

2 Membrane stages in series



3 Membrane stages in series

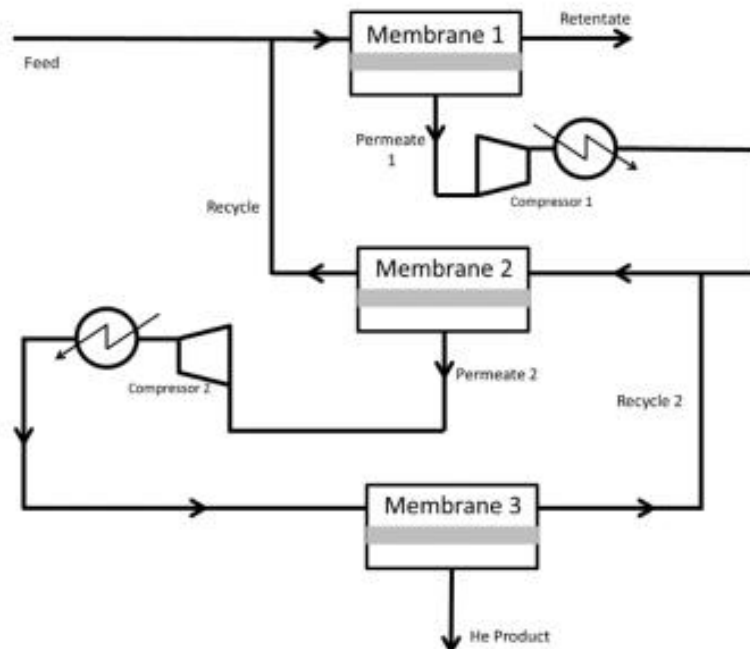


Fig. 1. Process diagram example of two and three membrane stages processes, with recycle streams, recovering helium [5]

However, to be able to accomplish such superior separation and purification, the stage-cut of membranes at number two to three stages must be minimal while the driving force in this case which

is pressure along the membranes need to be extensive. Henceforth, this entails for hefty energy compression and also the justification on direct commercialized for natural gas sweetening. Conversely, PSA is needed in this process to embark on the final purification stage and generate extremely pure helium. Going off that, membrane process designs for helium that have membranes jointed with one more separation like PSA is widely held as mention in Figure 2. This in some ways include membrane stage that responsible for first recovery stage and direct the stream full of helium into another technology for final purification [29]. In some other ways, it can comprise of different technology, say, PSA that is in charge of the helium recovery preceding membrane stage for final purification [30]. In favour of PSA, it is crucial to regenerate the adsorbent beds and in the patented paper, the innovation is to utilize retentate gas flow of membrane as regeneration gas [31]. Another originality in these processes design is the switching of gas stream between membrane unit and the PSA beds as well as the ways they are integrated together to lower compression constraints, recycle helium and rejuvenate absorbent beds.

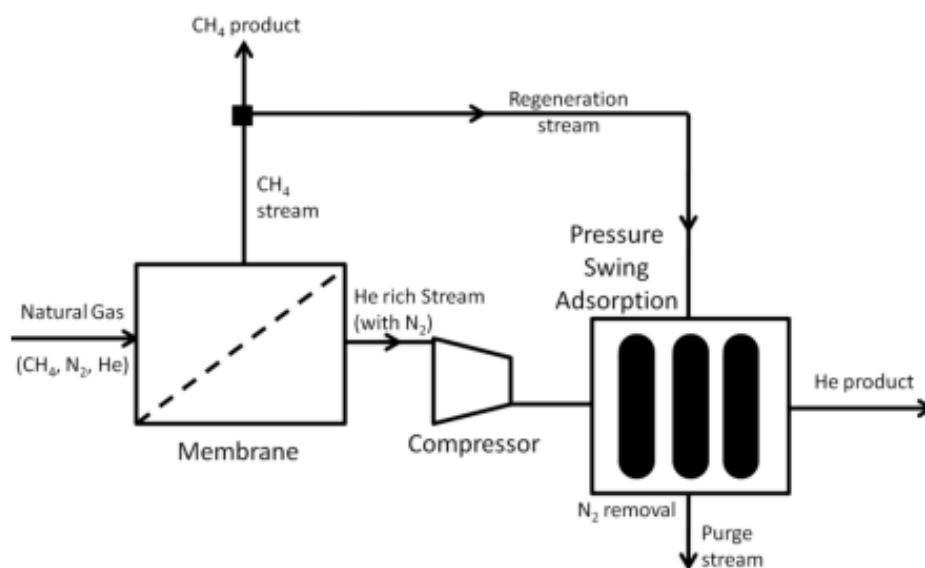


Fig. 2. Process combining membrane separation with pressure swing adsorption (PSA) for the recovery and purification of helium [28]

In United States Patent 5224350, there is a description of an invention [32] where removal of acidic gas from natural gas occurs with the help from a process called physical solvent absorption. The outcome gas from this process is saturated with helium and nitrogen and hence will go through separation passing through membrane for helium recovery. Then the helium product is submitted to PSA process for final helium purification. And so, it is evident that even the typical gas separation technology can be fused with many other separation technologies for helium recovery and purification from natural gas. Designs of the processes are realistic as existing commercialized polymeric membranes for natural gas sweetening have sufficient selectivity for, He/N₂ and He/CH₄. Nevertheless, as far as the author's knowledge goes, although there is a persistent appeal in low-graded helium reserves, there is no known large-scale operation for these membrane process designs for helium revival from natural gas; yet there will be forthcoming interest of these design growth in the lower grade helium reserves area. Moreover, expected continuous progress on membrane process designs developments in other gas processing purposes will concern helium recovery as well. Specifically, an intense incorporation with PSA is the anticipated goal.

Membranes are employed to revive and recycle the helium in other helium-rich purposes and some of the commercialized units are available in market for purchase [33,34]. As an example, GENERON membrane that is used for helium recovery from cryogenic, regulated atmospheric air and electronic applications in Innovative Gas Systems (IGS) [35]. For this membrane, they claim to achieve more than 90% purity and more than 98% recovered helium in the product. In addition, Sepuran membranes for helium recovery and recycling with the same sort of applications are sold by Evonik Industries [36]. Furthermore, Helipure system is marketed by Divex Global for atmosphere-helium mixtures that is vital for deep sea diving. This system uses a membrane to retrieve helium from the mixtures and recycle helium by recompression [37]. With this, they declare that the amount of nitrogen will lessen by a third and the amount of oxygen will drop to three quarters of their initial concentration upon a single membrane pass. To conclude, membranes are undoubtedly having market potentiality in these niche industries and with hikes in the helium pricing, industry practices with recycle prospects are predicted to be commercially studied.

3. Conclusions

This literature scrutinizes the current circumstances reported in past papers for helium retrieval and purification through membrane separation technology. The main advancements in membrane processing is the technology developments since in many of helium recovery methods, the current available polymeric and inorganic membranes require permeable selectivity for separation. Helium can be attained directly from natural gas or related gas processing and also from the recycling and recovering from industrial applications. Various example of polymeric membranes has been reced for helium separation by Robeson plot behaviour standard against nitrogen and methane gas [38]. Also widely studied in helium separation is inorganic membranes; even though their selectivity is lower than the polymer-based membranes due to its porosity. Few designs for membrane process were reported for helium retrieval and purification. Membrane processes with two and three stages are able to retrieve helium straight from natural gas as well as nitrogen rejection unit exhaust gas despite extensive compression duties are necessary [39]. The patent literature strongly emphasizes combined processing approach, in which membranes are in sequences with other technology to produce final product with high helium recovery and purity. Most often, the other separation technology is PSA where the switching of gas stream and connectivity between the PSA units and membrane are relevance for reducing total duty of helium recovery and escalating the practicality of the process design.

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