Simulation of helium–methane mixture separation on selectively permeable membranes

V S Naumkin
Kutateladze Institute of Thermophysics, Siberian Branch of the Russian Academy of Science, Ac. Lavrentiev ave., 1, Novosibirsk, Russia
E-mail: vsnaumkin@itp.nsc.ru

Abstract. In the article, the helium-methane mixture separation on the various types of membranes was considered. A flat membrane module was studied. It was made of two channels connected by a semipermeable membrane. It was shown that high membrane selectivity could not always provide a high degree of mixture separation.

1. Introduction
Currently, natural and petroleum gases are the raw material for production of helium. Helium content in the Russian oil fields in the Far East and Eastern Siberia is up to 0.6% (mole fraction). The method of low-temperature rectification is used to extract helium in the industrial scale [1]. Technical and economic evaluations show that it is promising to use the membrane technology for helium extraction [2]. The combined process is the most promising: enrichment of helium gas mixture using membranes and subsequent processing of helium concentrate on the low-temperature plants.

Wide-scale testing the plate membrane modules on natural gas containing about 5% helium was carried out by "Union Carbide Corporation" in 1970-72 years. The two-stage system with asymmetric membranes made of cellulose acetate allowed obtaining the helium concentrate with 82.5% of helium content at 62% recovery. Productivity was 18.7 m$^3$/h.

In Russia, now there is an experimental pilot plant for membrane helium extraction from natural gas [3]; it is possible to increase the helium content in helium concentrate from 0.5 to 30% by volume for two stages of separation. In [3], it is also pointed out that despite availability of highly selective membranes for gas separation to solve a particular task, it is necessary to take into account many factors determining the problem: pressure, concentration of the feed mixture components, and others.

The authors of [4] proposed to use the cenospheres to extract helium from a gas mixture. In [4], the cenospheres are placed in a container with gas mixture, helium diffuses into the cenospheres. Then, the pressure has been sharply decreased. By pressure decreasing, helium has been started to come out of cenospheres. The advantage of this method is high selectivity of helium extraction. The main disadvantage is the need to "recharge" cenospheres, i.e., impossibility of continuous operation.

In [5], it is proposed to use a xeolite membrane for separating mixtures containing methane, but it does not consider the possibility of helium-methane mixture separation. An advantage of xeolite membranes as compared to cenospheres is continuity of work. In [5], the xeolite membrane selectivity is considered in detail for pair gases: nitrogen/methane, carbon dioxide/methane. The helium flow through the xeolites was experimentally determined in [6].
Most studies of methane mixture separation consider the removal harmful impurities from natural gas: carbon dioxide, hydrogen sulfide, water vapor, etc. [7-10]. Harmful impurities can impede methane transport and contribute to corrosion of gas pipelines.

According to Australian Society membrane [11] and [12], polymer membranes can have high selectivity (about 4000) for the pair of gases helium/methane.

2. Problem formulation

In this paper, helium-methane mixture separation with the helium mass fraction of 0.1% on the membranes with different permeability coefficients is considered (Table 1).

Gas separation was simulated in a flat co-current flow membrane module, consisting of two channels, connected by a membrane with different permeability coefficients for helium and methane (Fig. 1). Module length is 1 m, the height of each channel is 2 mm. The influence of sidewalls was neglected. The approximation of narrow channel was used to simulate the flow. In this case, the gas dynamics equations are similar to the boundary layer equations. The flow of the gas mixture is stationary and laminar. The flows of gas mixture components through membrane were determined by difference of partial pressures above and below the membrane. The pressure in the lower channel was assumed to be $P=40$ atm., in the top channel, it was 1 atm. The properties of gas mixture components were determined by the polynomial dependence of [13]. It was believed that the thickness of the membrane selective layer is $\delta=10^{-6}$ m and $\delta=10^{-5}$ m. The influence of substrate membrane is neglected. The gas flow in the bottom channel is $G=10^{-2}$ kg/s, the Reynolds number is calculated by the hydraulic diameter and it is $Re_d = 1770$.

| №  | Membrane                | He          | CH$_4$        | Selectivity He/CH$_4$ |
|----|-------------------------|-------------|---------------|------------------------|
| 1. | Silicone rubber         | 2.3×10^-8   | 5.9×10^-8     | 0.39                   |
| 2. | Phenylene silicone rubber | 1.5×10^-8   | 2.0×10^-8     | 0.75                   |
| 3. | Nitrile silicone rubber | 0.79×10^-8  | 1.0×10^-8     | 0.79                   |
| 4. | Polycarbonate           | 6.7×10^-9   | 0.36×10^-9    | 19                     |
| 5. | Teflon FEP              | 6.2×10^-9   | 0.14×10^-9    | 44                     |
| 6. | Polystyrene             | 3.5×10^-9   | 0.23×10^-9    | 15                     |
| 7. | Trithene B              | 3.4×10^-9   | 0.0084×10^-9  | 400                    |
| 8. | Ethyl cellulose         | 3.1×10^-9   | 0.64×10^-9    | 4.9                    |
| 9. | Ethylene-vinyl acetate  | 2.1×10^-9   | 1.1×10^-9     | 1.9                    |
| 10. | Viton A                | 1.7×10^-9   | 0.016×10^-9   | 110                    |
| 11. | Polyvinyl chloride (plasticized) | 1.4×10^-9  | 0.2×10^-9     | 7                      |
| 12. | Polyvinyl fluoride      | 1.8×10^-10  | 0.0065×10^-10 | 280                    |
| 13. | Mylar                  | 1.0×10^-10  | 0.006×10^-10  | 170                    |
| 14. | Saran                  | 6.6×10^-12  | 0.025×10^-12  | 260                    |
3. Results

Distributions of helium and methane flows along the channel length for selective layer membrane thickness $\delta=10^{-6}$ m are shown in Fig. 2. It can be seen for all investigated membranes that the helium mass flow is much less than the methane flow. This is because the methane is the main component of the mixture. For this reason, the methane flow is constant all along the membrane length. The helium mass flow is reduced by the length of the membrane module.

\[
\begin{align*}
\text{Impermeable wall} & & \text{Membrane} \\
P_{20}, G_{20} & & h_2=2 \text{ mm} \\
K_{He}, K_{CH4} & & \\
\Delta P & & \\
P_{10}, G_{10} & & h_1=2 \text{ mm} \\
K_{He}, K_{CH4} & & \\
\end{align*}
\]

**Figure 1.** Gas flows in the membrane module.

\[j_{He} \times 10^5 \ \text{kg / m}^2\text{s}\]
\[j_{CH4} \times 10^5 \ \text{kg / m}^2\text{s}\]

**Figure 2.** Longitudinal (a) helium and (b) methane flow distributions for various types of membrane: 1) Silicone rubber, 2) Phenylene silicone rubber, 3) Nitrile silicone rubber, 4) Polycarbonate, 5) Teflon FEP, 6) Polystyrene, 7) Trithene, 8) Ethyl cellulose, 9) Ethylene-vinyl acetate, 10) Viton A, 11) Polyvinyl chloride, 12) Polyvinyl fluoride, 13) Mylar, 14) Saran.

In both channels, there is a change in composition because the membrane is passed by the mixture components at different speeds. Fig. 3 shows a change in helium concentration along the channel, where the gas is blown. It is seen that most helium permeable membrane (No. 1, 2 and 3) as well as the least permeable (No. 12, 13, 14) have the worst separate properties. The first group combines the membranes, highly permeable to methane, the second group combines the membranes with a low permeability coefficient. Membrane No. 7 has the greatest separation factor among all examined
membranes. This membrane allows obtaining the most enriched helium concentrate. Only membrane No. 10 Viton A matches with membrane No. 7. The separation factor of membrane No. 10 is three times less than this factor of membrane No. 7. Two above-mentioned membranes keep 70% of helium in the separated mixture.

However, increasing the selective layer thickness causes membrane No. 5 being more efficient as compared to No. 7 and 10, although it has the separation factor less than other membranes. This is because membrane No. 5 has the higher coefficient of helium permeability than membranes No. 7 and No. 10.

In the lower duct, there is a decrease in helium concentration (Fig. 4). Membranes with the highest permeability coefficient (No. 1, 2 and 3) keep the least amount of helium in the separated mixture but at a small thickness of the selective layer, almost all fed mixture permeates through the membrane. Membranes No. 12, 13, 14 due to low permeability coefficients keep up to 90% of helium in the mixture. Other membranes (No. 4 -11) keep, in average, 60% of helium in retante.

![Figure 3](image1.png)
Figure 3. Mass concentration of helium in channel 2. Membrane thickness is $\delta = 10^{-6}$ m (a) and $\delta = 10^{-5}$ m (b).

![Figure 4](image2.png)
Figure 4. Mass concentration of helium in channel 1. Membrane thickness is $\delta = 10^{-6}$ m (a) and $\delta = 10^{-5}$ m (b).
4. Conclusion
The high selectivity of membrane is not always able to provide a high degree of mixture separation. Membrane No. 7 Trithene B with selectivity of helium/methane gas pair of 400, has the best gas separation properties as compared to other membranes only at a small thickness of the selective layer ($\delta=10^{-6}$ m). By increasing the selective layer thickness, membrane No. 7 demonstrates the worse separation degree than membrane No. 5 Teflon FEP with selectivity of 44 because permeability of membrane No. 5 for helium is higher than membrane permeability coefficient of membrane No. 7. These data are in good agreement with the data of [12].

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References
[1] Molchanov S A 2011 Zaschita okrushayuschey sredy v neftegasovom komplekse 11 36-42
[2] Laguntsov N I, Kurchatov I M, Karaseva M D, Solomahin V I 2014 Membrany i Membrannye Tekhnologii (International Academic Publishing Company Nauka/Interperiodica) 4 272-279.
[3] Gas industry of Russia 2013 11 698
[4] Dolgushev S V, Fomin V M 2008 Computational continuum mechanics (Permian: Institute of Continuous Media Mechanics of the Ural Branch of RAS) 1 66-75
[5] Ting Wu, Merritt C Diaz, Yihong Zheng, Rongfei Zhou, Hans H Funke, John L Falconer, Richard D Noble. 2015 Journal of Membrane Science (Elsevier Science Publishing Company, Inc.) 201–209
[6] Jonas Hedlund, Mattias Grahn, Danil Korelskiy, Mark Rayson, Sven Oberg, Patrick R. Briddon 2012 Journal of Membrane Science (Elsevier Science Publishing Company, Inc.) 271–77
[7] Mahdi Hedayat, Mohammad Soltanieh, Seyyed Abbas Mousavi. 2011 Journal of Membrane Science (Elsevier Science Publishing Company, Inc.) 191–7
[8] Raja Swaidan, Xiaohua Ma, Eric Litwiller, Ingo Pinnau 2013 Journal of Membrane Science (Elsevier Science Publishing Company, Inc.) 387–94
[9] Raja Swaidan, Bader S Ghanem, Eric Litwiller, Ingo Pinnau Journal of Membrane Science (Elsevier Science Publishing Company, Inc.) 95–102
[10] Hafez Maghsoudi, Mohammad Soltanieh 2014 Journal of Membrane Science 159–65
[11] https://www.membrane-australasia.org/polymer-gas-separation-membranes
[12] Stern S A, Sinclair T F, Gareis P J, Vandieck N P, Mohr P H 1965 Industrial and engineering chemistry 87
[13] Gordon S, McBride B J 1994 NASA RP1311 (Washington) 1