Experimental Evaluation of the Membrane-Assisted Gas Absorption Technique Efficiency Using an Aqueous Solution Of PEG-400 for the Ammonia Capture

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Abstract. This work is carried out in order to identify the most effective mode of operation of the membrane-assisted gas absorption setup in the problems of ammonia recovery. The study was conducted to determine the effect of the adsorbent layer thickness on the efficiency of ammonia separation from a binary mixture of NH₃/N₂, with an ammonia content of 15 vol.%, by the method of membrane-assisted gas absorption. The study used a commercially available elastomeric poly(dimethylsiloxane)poly(diphenylsesquioxane) membrane (LESTOSIL™) as the membrane, and an aqueous solution of PEG-400 was used as the absorbent. The experiment was carried out at seven different thicknesses of the absorbent layer, from 0 (without absorbent) to 6.5 mm, for each of them the separation efficiency value was obtained at a gas flow of 30 ml/min. There is an inversely proportional dependence of the ammonia concentration in the retentate stream on the thickness of the liquid absorbent layer. The highest separation efficiency (4375.48) was achieved with an absorbent layer thickness of 6.5 mm.

1. Introduction
At present, ammonia is one of the main and most important products of the chemical industry [1]. Ammonia is widely used in the agricultural industry, in the microelectronic industry, it is used to produce nitrogen fertilizers and nitrogen compounds. Ever-increasing requirements for the purity of ammonia, reducing the environmental impact, and improving the energy efficiency of the process require new and new engineering solutions. However, the technique for synthesizing ammonia has not undergone significant changes since its invention by Haber and Bosch in 1909 [2]. Large volumes of refrigerant for cryogenic purifiers and high concentrations of ammonia in the recirculating stream characterize the method as very energy-intensive, insufficiently efficient and makes the ammonia production process cost-effective only at very large production volumes. For this reason, at small and medium production volumes, sorption technologies are used to separate ammonia. Sorption methods are characterized by high efficiency of gas separation, however, this method is characterized by high energy consumption, losses of the sorbent due to its degradation, high capital and operating costs, as well as high environmental load.
Another approach to solving the problem is the use of membrane technologies. They do not require special energy consumption, constant monitoring of the system units, and are characterized by free scalability and environmental friendliness. In the field of membrane gas separation, there are two main directions: research of membrane materials [3–6] and design and optimization of processes and devices [7,8]. The vast majority of scientific papers are devoted to the study and synthesis of new materials, when much less attention is paid to the intensification of processes, although in this direction there is a prospect for the development of membrane technology in general.

The most promising alternative is the combined technology of membrane contactors, which uses the advantages of sorption and membrane methods. However, just as in the sorption method, the gas separation process occurs in the volume of two devices – the absorber and the desorber, and the process of regeneration of the sorbent is accompanied by its heating and subsequent cooling.

To solve these problems, a new technology was developed – membrane-assisted gas absorption (MAGA) [9,10]. The design of the unique module, designed specifically for the problems of ammonia recovery, allows you to obtain the product in one stage, in the volume of one mass transfer device, without additional energy costs for heating and cooling the sorbing liquid. The principle of the method is to supply the feed stream under pressure to the volume of liquid absorbent located on the surface of the membrane. Under the influence of pressure, the components dissolved in the sorbent penetrate into the submembrane space and are removed from there. The study of the effectiveness of the method in the problem of ammonia recovery using an aqueous solution of PEG-400 as an absorbent was conducted earlier in the paper [11]. This study shows the effect of the thickness of the absorbent layer above the membrane on the efficiency of ammonia release in the Haber-Bosch process using PEG-400 aqueous solution as an absorbent.

2. Materials and methods
To evaluate the efficiency of the membrane-assisted gas absorption method, a binary NH₃/N₂ gas mixture with an ammonia content of 15 vol.% was prepared. Gas separation occurs in the volume of the membrane-assisted gas absorption module, where a commercially available elastomeric poly(dimethylsiloxane)poly(diphenylsesquioxane) membrane (LESTOSIL™) was selected as the membrane, and an aqueous solution of PEG-400 was used as the absorbent.

2.1. Experimental setup
An experimental setup for evaluating the efficiency of membrane-assisted gas absorption shown in figure 1. The setup has a gas chromatography system (GC) based on the Chromos GC-1000 gas chromatograph (Chromos Ltd, Russia) equipped with the Valco PDHID system (D-2-I model, VICI, USA) used for gas flow analysis.

![Figure 1](image.png)

**Figure 1.** The principal scheme of the experimental setup. 1 – pressure regulator; 2 – filter; 3 – valve; 4 – pressure gauges; 5 – needle valve.
A gas mixture was continuously supplied from the cylinder to the feed side of the membrane module through a pressure regulator (1) and a filter (2) with a constant pressure maintained at (400 ± 5) kPa. Permeated components removed from the cell by a sweep gas (He), also used as a gas carrier in GC system. The pressures of both the feed and permeate sides were monitored by pressure gauges (4) with an accuracy of 0.4% of full scale. The retentate withdrawal flow was regulated by the needle valve (5) and introduced into the flow-through sampling valve of the gas chromatographer and then neutralized. During the analysis, the components of the sample were separated in the chromatographic column under isothermal conditions and detected by the pulsed discharge helium ionization detector. Carrier gas flow controller served to supply the required flows of the carrier gas (Helium 99.9999 %). The detailed GC-analysis conditions are presented in Table 1. GC determination of nitrogen and ammonia using Porapak Q column is also presented in detail in [12,13].

Table 1. The operating conditions of the GC system.

| Component of the GC    | Characteristics                                      |
|------------------------|------------------------------------------------------|
| Detector               | PDHID D-2-I, 100 °C                                   |
|                        | Porapak Q, 80/100 mesh,                               |
| Chromatographic column | 60 °C 3 m × 2 mm i.d. stainless steel tube            |
| Sample loop            | 1.6 ml, 70 °C                                        |
| Carrier gas            | He 99.9999%, 25 ml/min                                |

The key component of the setup is a membrane-assisted gas absorption module made of AISI 316 stainless steel. The membrane is placed on the supporting disk and clamped on both sides by two flanges of the module, thus dividing it into two cavities. A layer of liquid absorbent is applied to the surface of the membrane.

The feed gas mixture is fed into the module at a pressure of 4 bar and moves radially along the periphery of the module. Then the mixture enters the tubes, which are lowered into the absorbent, which allows maximum contact of the gas with the liquid. Components of the mixture that do not interact with the sorbent exit the absorbent and are removed from the module in the retentate stream. The components that interact with the absorbent are desorbed under pressure and transferred through the membrane, from where they are further removed in the purge gas flow. The greatest selectivity of the membrane-assisted gas absorption process is provided by the liquid absorbent, and the membrane is necessary for the allocation of the liquid and gaseous phases and provides additional selectivity of the process. The diameter of the membrane area available for separation is 7 cm, corresponding to a membrane area of approximately 38.5 cm². The schematic diagram of the membrane absorption module and its 3D image are shown in figures 2 and 3.
2.2. *Peg-water solution preparation*

PEG-400, purchased from LLC “Zavod sintanolov” (Dzerzhinsk, Russia) was dehydrated using molecular sieves before preparing the co-solvent mixtures. All PEG-400 aqueous solutions were prepared by mass, using an Shimadzu AUW220D analytical balance with sensitivity of 0.01 mg, in quantities of 10 g. In order to cover all composition ranges, the mass fractions of PEG-400, of the three binary mixtures prepared varied by 0.1 from 0.80 to 1 wt.%.

3. Results and discussion

The experimental evaluation of the membrane-assisted gas absorption module in the problems of ammonia recovery in the Haber-Bosch process at different thicknesses of the absorbent layer on the
The surface of the selective membrane layer was carried out by comparing the results of gas chromatographic analysis.

The values of the separation factor were calculated using the formula:

$$ S = \frac{C_{NH_3}^{perm}/C_{N_2}^{perm}}{C_{NH_3}^{feed}/C_{N_2}^{feed}}, $$

where $C_{NH_3}^{perm}$ and $C_{N_2}^{perm}$ - concentrations of NH$_3$ and N$_2$ in the permeate stream, $C_{NH_3}^{feed}$ and $C_{N_2}^{feed}$ - concentrations of NH$_3$ and N$_2$, respectively, in the feed gas stream.

The concentrations of components in the feed stream are constant and equal to 15 vol.% for ammonia and 85 vol.% for nitrogen.

### Table 2. Concentrations of components in the permeate stream, separation factor, and product concentration in the retentate stream at different thicknesses of the absorbent layer.

| Layer thickness (mm) | Permeate flow analysis | Retentate flow analysis |
|---------------------|------------------------|-------------------------|
|                     | C$_{NH_3}$ (vol. %)    | C$_{N_2}$ (vol. %)     | S         | C$_{NH_3}$ (vol. %) |
| 0                   | 20.709                 | 79.291                  | 1.48      | 15.628               |
| 2.6                 | 96.232                 | 3.768                   | 144.71    | 11.33                |
| 3.9                 | 98.829                 | 1.171                   | 478.36    | 9.176                |
| 5.9                 | 99.512                 | 0.488                   | 1155.98   | 6.53                 |
| 6.5                 | 99.793                 | 0.207                   | 2736.84   | 4.61                 |
| 6.7                 | 99.858                 | 0.142                   | 3987.55   | 2.947                |
| 7.8                 | 99.871                 | 0.129                   | 4375.48   | 2.23                 |

As the thickness of the adsorbent layer increases, the separation factor increases. Despite the fact that the concentration of ammonia in the permeate stream is at the same level and changes by a fraction of a percent, its concentration in the retentate stream decreases markedly with an increase in the sorbent layer. Figure 4 shows graphs of the dependence of the separation efficiency and the concentration of ammonia in the retentate stream on the thickness of the sorbent layer.

**Figure 4.** Dependence of the separation factor and the concentration of ammonia in the retentate stream on the thickness of the liquid absorbent layer.
4. Conclusions
In this paper an experimental evaluation of the effectiveness of the method of membrane-absorption gas separation with the use of PEG-400 aqueous solutions for ammonia capture was carried out. The dependence of the separation factor on the thickness of the liquid absorbent layer is experimentally established. Increasing the layer, there is an increase in the separation factor, as well as a decrease in the concentration of ammonia in the retentate.

5. References
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