

Physicochemical Bases of Membrane-Assisted Gas Absorption of Industrial Gases

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Relevance of the Research Topic. Ammonia is one of the most in-demand products of the chemical industry. Its global production exceeds 183 million tons/year. Russia produces about 10% of this amount and is a world leader in the export of mineral fertilizers, with a share of 22% of world exports. About 75% of exported mineral fertilizers are nitrogen fertilizers produced from ammonia. By 2050, the demand for ammonia is projected to grow to 680 million tons, of which 37% will be used for fertilizer production, 28% as transport fuel, and 20% as a hydrogen carrier in the context of the hydrogen economy.

The industrial synthesis of ammonia is implemented using the Haber-Bosch process. The product stream, after separation of the target product by cooling, contains unreacted nitrogen and hydrogen, as well as residual ammonia. Its presence in the recycle shifts the reaction equilibrium towards decomposition, reducing conversion. Therefore, the task of deep purification of the recycle gas from ammonia is key to intensifying the entire process.

Traditional low-temperature condensation does not ensure complete ammonia recovery. Alternative methods include adsorption, absorption, membrane, and hybrid methods. Among these, membrane-assisted gas absorption (MAGA) is a method implemented by combining selective absorption and membrane gas separation. This method has high potential due to moderate energy consumption, the absence of thermal regeneration of the absorbent, and the possibility of a wide selection of materials to solve a specific problem. However, as applied to the NH_3 – N_2 – H_2 system, the method has been insufficiently studied; there are no experimental data on the selection of membrane–absorbent pairs, and equipment solutions have not been developed.

The aim of the work is to develop the physical and chemical foundations and technical solutions to improve the efficiency of ammonia separation from the recycle gas of the Haber-Bosch process using the membrane-assisted gas absorption method.

Objectives of the work:

1. To experimentally determine the gas transport characteristics of commercially available membranes for separating ammonia-containing gas mixtures.
2. To experimentally determine the sorption capacity and absorption kinetics of ammonia by promising liquid absorbents: aqueous solutions of PEG-400, ionic liquids ($[\text{bmim}][\text{Tf}_2\text{N}]$, $[\text{bmim}][\text{BF}_4]$, $[\text{bmim}][\text{PF}_6]$, $[\text{bmim}][\text{MeSO}_3]$), deep eutectic solvents (DES) based on NH_4SCN with urea, ethylene glycol, and glycerol.
3. To establish the influence of the absorbent layer thickness on the efficiency of ammonia separation.

4. To develop and construct a membrane-assisted gas absorption apparatus with a hollow fiber cell configuration implementing the "fiber-in-fiber" principle.

5. To conduct an experimental evaluation of the efficiency of the developed module in separating binary and multicomponent model mixtures simulating the recycle composition.

6. To study the kinetics of reaching a steady state for radial and hollow fiber configurations.

Scientific Novelty:

1. For the first time, the process of ammonia separation by membrane-assisted gas absorption method from a nitrogen-hydrogen mixture has been systematically studied in relation to the Haber-Bosch process.

2. The permeability and selectivity coefficients of industrial membranes (PSF, PEI+PI, PVTMS, Lestosil) for NH_3 , N_2 , H_2 , Ar, CH_4 under MAGA conditions have been determined.

3. For the first time, a design of a hollow fiber MAGA module of the "membrane-in-membrane" type has been proposed and implemented, ensuring a uniform absorbent layer and process scalability.

4. The kinetics of absorbent saturation and the establishment of a steady-state permeate flow depending on the feed flow rate and the type of sweep gas have been experimentally characterized.

5. A comparative evaluation of the efficiency of various membrane-absorbent systems, including combinations of hydrophobic membranes with DES, has been carried out, and the advantages of using PSF and NH_4SCN :Urea/EG have been demonstrated.

6. A scheme for using a part of the technological stream (nitrogen-hydrogen mixture) for sweeping the low-pressure cavity has been proposed and substantiated, which increases the driving force of the process and reduces the impurity content in the permeate.

Theoretical and Practical Significance. The theoretical significance lies in establishing the relationship between the transport characteristics of polymer membranes, the sorption properties of absorbents, and the parameters of the hybrid process. The obtained data on gas diffusion and the influence of the liquid layer thickness on the separation factor expand the understanding of mass transfer in gas/liquid/polymer systems.

The practical significance consists in the creation of a laboratory sample of a hollow fiber MAGA apparatus suitable for scaling up. The developed configuration is protected by Russian Patent No. 2810484, published on December 27, 2023. The possibility of reducing the ammonia concentration in the recycle from 4.5 to 1.5 vol.% with the production of permeate containing up to 97.5 vol.% NH_3 has been experimentally confirmed. The results can be used in the

modernization of existing ammonia production facilities and the creation of new energy-efficient chemical-technological systems.

Statements to be defended:

1. The operating conditions and process configuration for ammonia separation from a binary gas mixture by membrane-assisted gas absorption method using an aqueous PEG-400 solution as the absorbent in combination with various commercially available membranes.
2. The effect of the absorbent layer thickness in a membrane-assisted gas absorption module on the separation factor for the nitrogen–ammonia binary mixture.
3. The operating conditions, process configuration, and materials enabling intensification of ammonia separation from a ternary nitrogen–hydrogen–ammonia gas mixture.
4. The design and fabrication of a membrane-assisted gas absorption module based on asymmetric hollow fiber membranes.
5. The experimental determination of the kinetics of steady-state attainment during the separation of ammonia-containing gas mixtures by membrane-assisted gas absorption in modules with radial and hollow fiber configurations.
6. The operating conditions, process configuration, membrane and absorbent materials for ammonia recovery from a five-component recycle stream of the Haber–Bosch process using a hollow fiber membrane-assisted gas absorption module.