

EVALUATION OF THE ABSORBING PERVAPORATION TECHNIQUE FOR AMMONIA RECOVERY AFTER THE HABER PROCESS

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A novel absorbing pervaporation hybrid technique has been evaluated experimentally for the recovery of ammonia from the gas mixture in a recycle loop of synthesis plants. This process of hybridization brings together the combination of energy-efficient membrane gas separation based on poly(dimethylsiloxane) poly(diphenylsilsesquioxane) with a high selective sorption technique where a water solution with polyethylene glycol 400 (PEG-400) was used as the liquid absorbent. Process efficiency was studied using the pure and mixed gases. The influence of PEG-400 content in aqueous solutions on process selectivity and separation efficiency was studied. The ammonia recovery efficiency evaluation of an absorbing pervaporation technique was performed and compared with the conventional membrane gas separation. It was shown that the absorbing pervaporation technique outperforms the conventional membrane method in the whole range of productivity, producing the ammonia with a purity of 99.93 vol.% using the PEG 80 wt.% solution. The proposed method may be considered as an attractive solution in the optimization of the Haber process.

Keywords: gas separation, absorbing pervaporation, ammonia, process intensification, membrane

1. INTRODUCTION

Nowadays, ammonia is the most commonly produced chemical in the world with the annual capacity of more than 196 million tons (Varotto, 2015). Therefore, the separation of ammonia from the gas mixture in the recycle loop happens to be an important task on a large scale. The ammonia synthesis technology has not undergone any significant changes since its invention by Haber and Bosch in 1909. The major drawback of that technique is that the conventional separation method does not provide sufficient recovery and the gas mixture in the recycle loop contains a significant amount of ammonia which decreases the production efficiency; cryogenic purifiers require large amount of refrigerant, so the whole process becomes very energy intensive. Moreover, that technique is advantageous only on a very large scale. On small and intermediate scales, ammonia can be recovered using a sorption technique. However, that approach also has some drawbacks such as high investment costs, complex operation, and the loss of sorbent solution due to its degradation (Helminen et al., 2000). Thus, the development of advanced physicochemical ap-

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proaches focused on improving the performance of purification technology is of great importance, especially concerning the enhancement of separation efficiency, maximization of productivity, and reduction of energy consumption. Because of that, the membrane-based separation technique may be considered as a perspective approach (Favre et al., 2012; Vorotyntsev et al., 2006; Vorotyntsev et al., 2011) instead of the conventionally applied cryogenic purifiers.

A lot of research has been dedicated towards the polymeric membrane with a particular interest in polyvinylammonium thiocyanate (Cussler et al., 1991; Laciak et al., 1988) and perfluorosulfonic acid (Cussler et al., 1992; Cussler et al., 1995; Timashev et al., 1991). These membranes provide a high selectivity in the ammonia recovery process and promising performance characteristics. However, they are unable to withstand the extreme operating conditions of the ammonia production process. Considering the high pressure/high temperature system of ammonia manufacture, polymeric membranes would be destroyed without some cooling of the gas and are therefore unsuitable in practice.

Another approach to optimize and intensify the ammonia production process is the design of a membrane-based process, such as membrane contactors, which demonstrate some advantages in the ammonia recovery applications. A mathematical model of hollow fiber microporous membrane contactor (Karami et al., 2013) was proposed for ammonia removal from purge gases. The results show that the hollow fiber membrane contactors can separate ammonia from the purge gas very efficiently and with a recovery higher than 99%. Moreover, membrane contactors have some advantages with respect to the conventional apparatus, including higher mass transfer rates, independent control of gas and liquid rates, a known and constant interfacial area and easy scale-up. However, it requires two elements (an absorber and a desorber) when it is necessary to regenerate the liquid absorbent due to its degradation.

The novel separation technique – absorbing pervaporation (Vorotyntsev et al., 2006; Vorotyntsev et al., 2017) is deprived of these drawbacks. It is a hybrid process which combines membrane gas separation with a sorption technique. For easy explanation we can conditionally distinguish two main stages of the process. In the first step, gas is introduced directly to the liquid sorbent and is dissolved in it. Then, the gas moves through the liquid sorbent to the membrane and further vaporizes through the membrane to the low pressure cavity. To perform efficient separation, it was necessary to solve two major problems: choose the most sufficient liquid absorbent and membrane material.

Ammonia has a high solubility in water, but because of its physical properties, such as high volatility and low boiling point, it is impossible to use water as an absorbent for ammonia in modern technological schemes. However, an extensive body of published papers showed that its use in combination with organic solvents, for example, poly-ethylene glycol (PEG) aqueous solutions, allows for achieving an increase in the gas solubility rate (Zhang et al., 2011; Zhang et al., 2013). Poly-ethylene glycol 400 (PEG-400) is an important industrial solvent, which may be used in the cleaning of exhaust air and gas streams from industrial production plants because of its favorable properties, such as low vapor pressure, low toxicity, high chemical stability, and low melting point. On the other hand, PEG presents native hydrogen bonding sites, which increase the solubility of aggressive gases like NH_3 and SO_2 . Choosing the membrane, the attention was given to its permeability rather than selectivity due to the fact that main separation action takes place in the liquid absorbent.

The current study deals with the optimization of ammonia recovery using the energy-efficient proposed technique – absorbing pervaporation. The efficiency of ammonia recovery was studied on the example of separation of two binary gas mixtures containing ammonia as a target component with nitrogen and hydrogen as impurities. Moreover, the influence of the PEG-400 content on the separation efficiency in the aqueous solution was studied.

2. MATERIALS AND METHODS

2.1. Test gas mixtures

In order to study and optimize the system, it is of interest to perform the experimental study using two binary gas mixtures consisting of ammonia and attendant impurities – nitrogen and hydrogen. For that purpose, NH_3/N_2 and NH_3/H_2 gas mixtures were prepared with NH_3 content of 50 vol.% for separation on commercially available elastomeric poly(dimethylsiloxane)poly(diphenylsilsesquioxane) membrane (LESTOSIL™) covered with an uniform layer of the PEG-400 aqueous solution. The LESTOSIL™ membrane was purchased from Vladimir PolimerSintez JSC (Vladimir, Russia) and had a composite structure with a thin 5 μm skin layer on porous fluoropolymer support. High purity single gases: hydrogen (99.9999 vol.%), nitrogen (99.9999 vol.%) and ammonia (99.9999 vol.%) were purchased from Monitoring Ltd. (Moscow, Russia). Pressurized test mixtures were prepared in cylinders by a static volumetric method. The pure component permeances through different membrane-PEG-400 aqueous solution systems were measured according to the Dynes-Barrer technique (Barrer et al., 1939; Daynes, 1920) in a constant-volume variable-pressure apparatus for gas permeability measurements at the initial transmembrane pressure of 110 kPa and at ambient temperature (25 °C). The experimental procedure is well illustrated in our previous works (Davletbaeva et al., 2016; Trubyanov et al., 2017).

2.2. Experimental setup

The experimental setup designed for separation efficiency evaluation of different membrane-PEG-400 aqueous solution systems is shown schematically in Fig. 1. The test unit was equipped with a gas chromatography (GC) system based on Chromos GC-1000 (Chromos Ltd, Russia). Gas chromatograph equipped with a Valco PDHID system (D-2-I model, VICI, USA) was used for analysis of flow sample composition.

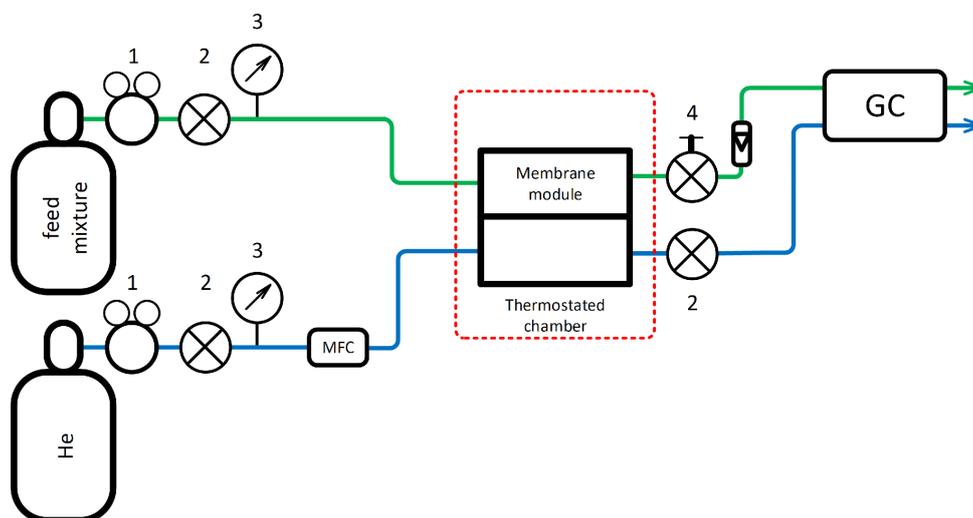


Fig. 1. The principal scheme of the experimental setup. 1 – pressure regulator; 2 – filter; 3 – valve; 4 – pressure gauges; 5 – needle valve

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 (300 ± 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 (Trubyanov et al., 2016; Vorotyntsev et al., 2003; Vorotyntsev et al., 2010).

Table 1. The operating conditions of the GC system

Component of the GC	Characteristics
Detector	PDHID D-2-I, 100 °C
Chromatographic column	Porapak Q, 80/100 mesh, 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 radial absorbing pervaporation membrane module made of AISI 316 stainless steel with PTFE sealing. The mathematical model and experimental investigation of gas purification process in membrane module of this type were presented by Vorotyntsev et al. in (Vorotyntsev et al., 2002; Vorotyntsev et al., 2011). Figure 2 shows the schematic design and the principle flow scheme of the membrane module used.

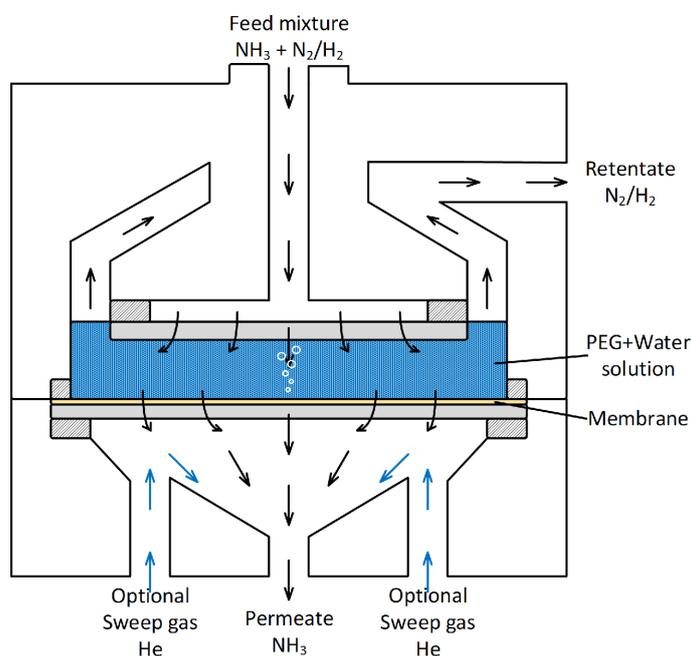


Fig. 2. Principle flow scheme of the radial absorbing pervaporation membrane module

A flat-sheet membrane covered with a uniform liquid absorbent layer with the same size as the inner diameter of the module is placed on a porous stainless steel support inside the module and dividing the system into upstream and downstream compartments. A PTFE sealing is used to prevent gas leakage at the film edge from the upstream to the downstream side of the module and to avoid gas exchange between the compartments of the module and the exterior atmosphere.

The feed gas enters the center of the module and flows radially from the center to the periphery of a stainless steel supporting disc and then introduced to the liquid absorbent placed on the high-permeable membrane. The solute gas is moved through the absorbent to the low-pressure compartment and removed with the sweep-gas flow. This principle eliminates any trapped gas or dead zones in the module. The main separation action takes place in the liquid absorbent, while the membrane serves as a support and provides a withholding of a liquid under the pressure gradient between two compartments.

The diameter of the membrane area available for separation is 4.2 cm, corresponding to a membrane area of approximately 13.85 cm². The practical active volume of the feed side available for gas separation is situated in a 2 mm gap between the distribution disc and the membrane and equals approximately 2.8 cm³.

2.3. Stability test of the LESTOSIL™ membrane

The stability of the LESTOSIL™ membranes in the absorbent was first investigated. The film was immersed in a PEG-water solution at room temperature for two weeks. After cleaning with ethanol and pure water, the film was then dried in an oven for attenuated total reflectance-Fourier transform infrared spectrometry (ATR-FTIR) and contact angle (CA) analysis. ATR-FTIR was used to check the chemical composition, while CA test was used to examine the variation of membrane hydrophobicity. Details on the CA measurement are well described in our previous work (Akhmetshina et al., 2017). The fingerprints of phenyl and methyl groups could be clearly identified, as well as those related to the siloxane backbone. Actually, the absorptions associated to the siloxane bonds were broad and did not present differences in position or intensity.

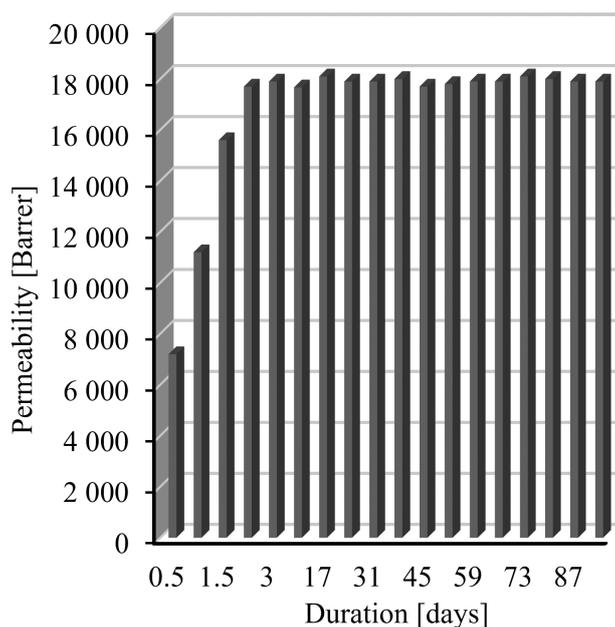


Fig. 3. The LESTOSIL™ Membrane permeability for NH₃

Moreover, a study of the LESTOSIL™ membrane stability was performed at the room temperature of 25 °C under the pressure of (300 ± 5) kPa for 90 days to determine the ability of the polymer to maintain mass transfer properties under the influence of ammonia for a long time. As can be seen from Fig. 3, the membrane permeability varies within the instrument error, which indicates the stability of the material. Measurement of membrane permeability (presented in the article) in a combination with CA and ATR-FTIR data allow us to conclude, that the membrane able to maintain its properties under the influence of ammonia for a long time.

2.4. 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 AUV220D 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 DISCUSSIONS

During the experimental comparison of the two approaches to ammonia removal from gas mixtures containing hydrogen and nitrogen as impurities, the permeability of the single gases was determined through the LESTOSIL™ membrane and the combined system of membrane covered with liquid absorbent PEG-400 and its aqueous solutions. An experimental efficiency comparison of the methods described above was performed using the laboratory setup, which is described in the experimental section. Moreover, the membrane material stability was evaluated and the degradation degree under the influence of ammonia as the time function was found. This approach can comprehensively assess the proposed technique – absorbing pervaporation for the ammonia recovery from the syngas in the Haber process.

3.1. Single gases permeability test

To obtain and compare the values of mass transfer properties the permeability of NH_3 , N_2 and H_2 single gases were measured through the LESTOSIL™ membrane and the combined system consisting of the membrane and liquid absorbent PEG-400 and its aqueous solutions. The results are shown in Table 2. The choice of these gases is justified by the gas mixture composition entering cryogenic purifier in the Haber process technological scheme. In that case, ammonia is the target component to be recovered and nitrogen and hydrogen are attendant impurities to be removed.

Table 2. Pure gas permeability coefficients

Gas	Permeability, Barrer			
	Membrane gas separation	Absorbing pervaporation		
		PEG 400 content in solution, wt.%.		
		100	90	80
NH_3	17 900	11 950	22 710	25 400
N_2	960	60	150	33
H_2	2210	78	120	63

Measured at 25°C, 110 kPa. 1 Barrer = 3.346×10^{-16} mol m s⁻¹ m⁻² Pa⁻¹

The measurement of the membrane permeability for the chosen gases was carried out in the steady-state system operational mode. The results of the experiment confirmed the conclusion made in the previous section that the membrane material is able to maintain its mass-transfer properties for a long time. In addition, it was shown that the ammonia permeability exceeds the permeability of hydrogen and nitrogen by more than an order of magnitude. In the case of the membrane-liquid absorbent system, the ammonia permeability increases with the increase of water content of the solution. The nitrogen and hydrogen

permeability decreases, which in turn increases the combined system selectivity (Table 3). However, it is important to note that to determine the nature of this dependence, additional experimental studies on a wider range of solutions are required, for example, with a step of 5 wt.% of water in solutions.

Table 3. The ideal selectivity

Gas	Membrane gas separation	Absorbing pervaporation		
		PEG 400 content in solution, wt.%.		
		100	90	80
NH ₃ /N ₂	18.7	199.0	151.4	769.7
NH ₃ /H ₂	8.0	153.0	189.3	403.2

3.2. Absorbing pervaporation efficiency evaluation

The efficiency of the absorbing pervaporation cell was evaluated in a comparison with the conventional single-stage membrane module. The separation efficiency, determined as a natural logarithm of ammonia concentration ratio in the permeate C_{perm} and retentate C_{ret} flows (1) of both methods was evaluated depending on the process stage cut value (2)

$$F = \frac{C_{perm}}{C_{ret}} \quad (1)$$

$$\theta = \frac{l_{perm}}{l_{feed}} \quad (2)$$

where l_{perm} and l_{feed} are the flow rates of the feed and permeate flows. Results are shown in Figs. 4 and 5 for NH₃/N₂ and NH₃/H₂ gas mixture separation, respectively. The graphs clearly demonstrate the dependence of the separation efficiency of the setup on the stage cut. It is experimentally shown that an increase in the stage cut increases the product purification degree. Moreover, the gas mixture separation efficiency dependence on the absorbent content was determined and compared with conventional membrane separation technique.

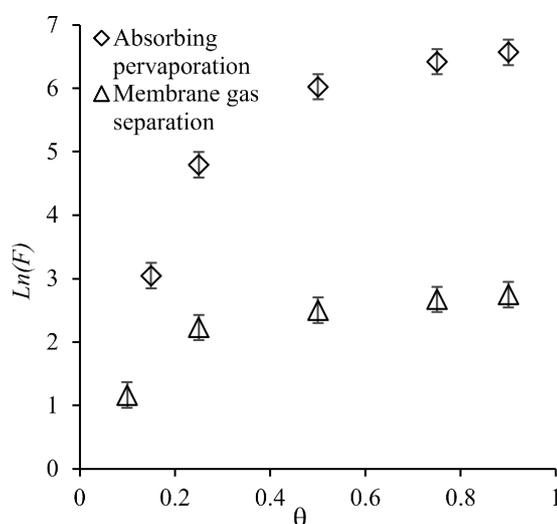


Fig. 4. Evaluation of absorbing pervaporation and membrane separation efficiency during separation of NH₃/N₂ gas mixture

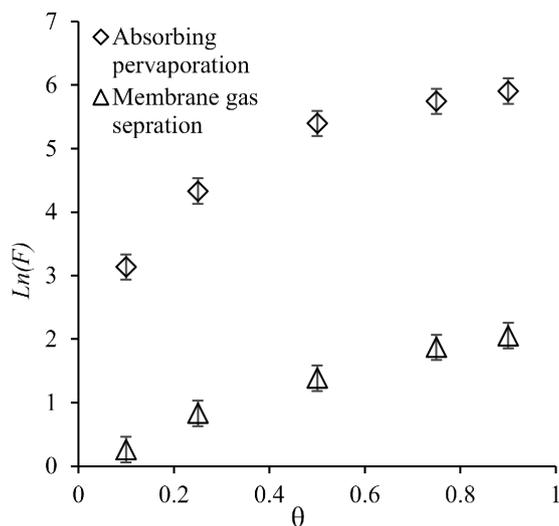


Fig. 5. Evaluation of absorbing pervaporation and membrane separation efficiency during separation of NH_3/H_2 gas mixture

It is important to note that trends illustrated by graphs are similar for all studied systems and increase in stage cut increases the separation efficiency. That system behavior is easily explained by two factors: limitation of absorbent ability to sorb the ammonia, and the membrane permeability. As the permeate is continuously refreshed with sweep gas, the concentration gradient through the membrane is maximum and constant. And the membrane-liquid absorbent system provides the maximum permeate flow rate as it is possible for chosen conditions (pressure, temperature, active membrane area etc.). Therefore, to achieve the balance in product purity vs productivity, system optimization is required.

The gas mixture separation efficiency using PEG-400 aqueous solutions with various compositions depending on stage cut was performed. The results are shown in Figs. 6 and 7. The absorbing pervaporation technique always outperforms the traditional membrane gas separation method, and the increase in water content leads to an increase in separation efficiency. This is due to the high solubility of the target component compared to the rest of the gases, with the corresponding absorbent, and the realization of the multiplicative separation effect. It is important to note that obtained results well correlate with results achieved in single gas permeability test and form similar trends.

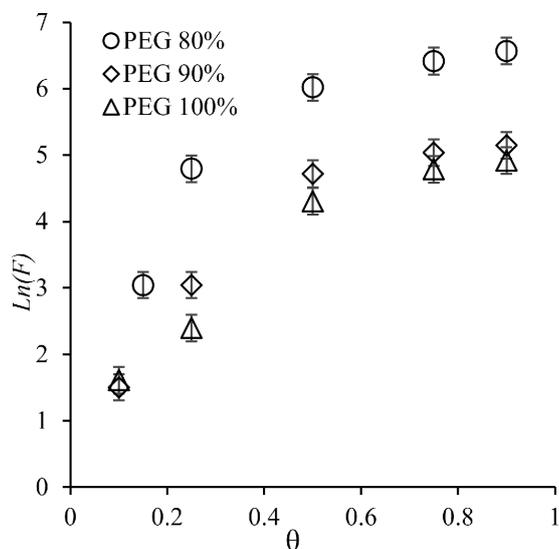


Fig. 6. Evaluation of absorbing pervaporation separation efficiency using PEG-400 aqueous solutions with various compositions during the separation of NH_3/N_2 gas mixture

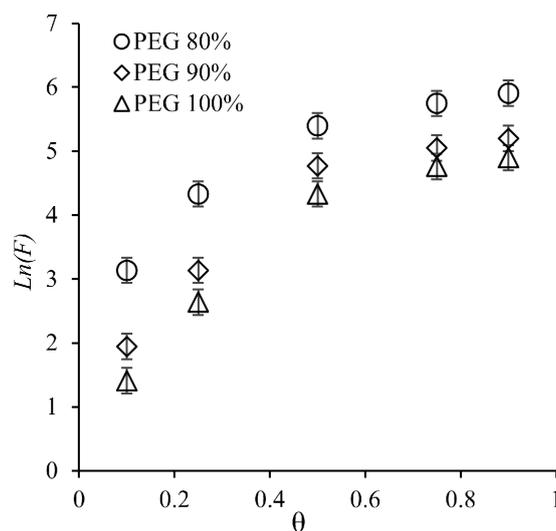


Fig. 7. Evaluation of absorbing pervaporation separation efficiency using PEG-400 aqueous solutions with various compositions during the separation of NH_3/H_2 gas mixture

The selectivity of the absorbing pervaporation process is mainly determined by the absorbent ability to solve one component and not to interact with others, in addition, the selectivity of the membrane also contributes to the separation process. Thus, gases with low solubility in water are well separated from ammonia, which provides high selectivity of the ammonia/nitrogen and ammonia/hydrogen systems. It should be noted that this process will not demonstrate high separation efficiency for gas pairs with similar solubility in water, since in this case the selectivity of the process will be determined only by the membrane selectivity.

4. CONCLUSIONS

In the current work, the application of the absorbing pervaporation technique in the process of ammonia recovery was studied experimentally, taking into account the engineering aspects (separation cell configuration, technological scheme, analytical support etc.).

A detailed experimental evaluation and comparison with the conventional membrane gas separation method during the ammonia recovery from binary gas mixtures was performed.

It was shown that absorbing pervaporation always outperforms conventional membrane gas separation, achieving ammonia purity in the permeate of 99.93% versus 96.7% for NH_3/N_2 gas system and 99.86% versus 93.6% for NH_3/H_2 system.

Moreover, the influence of liquid absorbent composition, i.e. PEG-400 content in aqueous solutions, on separation efficiency was studied experimentally. It was shown that increase in water content increased the separation efficiency. Nevertheless, a large amount of water led to an increase of solution volatility and to an undesirable loss of solution. So, it is important to study the trade-off between these two parameters in a wide range of PEG-400 concentration.

It was clearly demonstrated that the absorbing pervaporation technique may offer promising perspectives for the ammonia recovery process, where an improved separation performance is of great importance. Nevertheless, more rigorous parametric optimization strategy has to be developed for this technique in order to quickly and efficiently identify the best set of operating parameters for a given system, and target performance.

SYMBOLS

C_{ret}	feed ammonia concentration, %
C_{perm}	permeate ammonia concentration, %
F	separation degree
l_{feed}	feed flow rate, cm ³ /min
l_{perm}	permeate flow rate, cm ³ /min
θ	stage cut, %

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