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Dehydration of Diethylene Glycol by Pervaporation Using HybSi Ceramic Membranes

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Abstract—The pervaporation dehydration of diethylene glycol using ceramic tubular membranes with a hydrophilic selective layer formed from HybSi material was experimentally studied. The experiments were carried out over the process temperature range of 70–90°C at pressures in the permeate part of membrane unit in the range of 5–30 mm Hg and at diethylene glycol concentrations in the range of 93.5–99.8 wt %. Dependences of the membrane surface area required for the dehydration of diethylene glycol over a predetermined range of concentrations on productivity, process temperature, and vacuum were determined.

Keywords: pervaporation dehydration of diethylene glycol, pervaporation, HybSi ceramic membranes, hybrid material, membrane processes, membrane technology

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INTRODUCTION

The application of membrane processes in industrial technologies, both in combination with traditional processes (distillation, absorption, etc.) and as a complete replacement for

those processes, allows for significant economic benefit to be obtained. Pervaporation process is one of the promising types of membrane processes. It is known that various types of distillation widely used in industrial technologies are rather energy-consuming. By contrast, the application of the pervaporation process, for example, to dehydrate organic solvents allows energy saving up to 60% to be achieved compared to distillation or adsorption processes [1, 2]. There are examples of successful industrial application of pervaporation units for dewatering ethanol, isopropanol, n-butanol, tetrahydrofuran, acetonitrile, etc. using hydrophilic membranes; for the isolation of phenol, ethanol, etc. from water using hydrophobic membranes; and for separating components of organic mixtures by means of organoselective membranes [1].

In the membrane technology, there is a problem related to lifetime of operated membranes when they work under high temperature conditions, aggressive working medium conditions, etc. The application of ceramic membranes is one of the alternative solutions for this problem. The resistance of these membranes to the medium and process conditions is determined by a material of the selective layer applied on the support. Membranes with a selective layer based on hybrid silica [3, 4] are the most promising in this regard. These membranes demonstrated high stability over several years of continuous work. The longest test, which lasted for 3 years, was carried out in the process of dehydration of n-butanol/water mixture at the temperature of 150°C [5]. During the entire test period, the permeate stream and membrane selectivity remained practically at unchanged level. When subjected a short-term exposure to high temperatures, these membranes revealed hydrothermal stability up to 190°C. Moreover, membranes with selective layer based on hybrid silica demonstrated chemical resistance towards various aggressive organic solvents upon changing pH value up to two units [3].

In this work, a membrane with a selective layer was used based on HybSi silica (Pervatech Company) developed at the Energy Research Center of the Netherlands in collaboration with the University of Amsterdam and the University of Twente [5]. In this organic-inorganic hybrid material, inorganic part imparts hydrophilicity and mechanical strength to the material, while the organic part imparts hydrothermal resistance and increased viscosity [4, 6].

In this work, the process of the dehydration of diethylene glycol (DEG) has been studied. Currently, there is a limited amount of known data on using membrane processes to dehydrate DEG. For example, recently, an article on the results of these investigations performed on polymer hollow-fiber membranes [7] was published. The process of

dehydration of DEG is used industrially, e.g., to regenerate rich DEG solution in gas complex processing plants at gas fields. The degree of saturation of DEG solution with water upon absorption is not more than 2.5 wt %, although the degree of saturation up to 6 wt % can technically be achieved at the northern gas fields of Russia [8]. Desorption at atmospheric pressure makes it possible to achieve a concentration of lean DEG of up to 97.5 wt %. DEG concentration up to 99.3 wt % is achieved upon vacuum desorption; it achieves value of 99.5 wt % upon the supply of stripping gas (dried natural gas) to an evaporator and 99.8 wt % upon its supply at the bottom of a desorber [9]. Achieving higher concentrations of DEG is restricted by the temperature of thermal decomposition of DEG at 164.4°C. The aim of the present work was to evaluate the performance of a plant operated with HybSi ceramic membranes, their mechanical strength, thermal stability, and chemical stability based on the experimental study of the pervaporation dehydration of DEG. Experimental studies were carried out over a concentration range of 93.5–99.8 wt %, which is of practical importance.

EXPERIMENTAL

The scheme of experimental pervaporation unit is shown in Fig. 1 [10]. The unit consists of a feed (retentate) and a permeate parts which are separated by a membrane module. In the feed part, the circulation of the feed between the feed tank 1 and the membrane module 3 takes place through lines 1 and 2 by means of a vortex-type pump 2. Membrane module 3 contains four tubular ceramic membranes connected in series and having the following dimensions: length of 500 mm, inner diameter of 7 mm, outer diameter of 10 mm, and total area of the membrane surface of 0.04 m². The selective layer of the HybSi material with thickness of ~200 nm and pore size of no more than 1 nm is applied on the inner surfaces of tubes. An intermediate layer made of amorphous silica having thickness of ~2000 nm and pore size of ~4 nm is located between the selective layer and the ceramic porous support. Selectivity and the permeate flux are determined by material of the membrane selective layer. According to manufacturer data, the membrane selectivity may be in the range of 321–1125 for the permeate flux of 1.2 kg/(m²h) upon dehydration of 95% isopropanol solution at the process temperature of 70°C and under a vacuum of 10 mm Hg. The feed moves through the membrane with the linear velocity of not less than 2.5 m/s (which makes it possible to maintain the Reynolds criterion $Re \geq 5000$ in the case of DEG) to decrease the concentration polarization [11, 12]. Permeate vapors are introduced into the intertubular space of membrane module 3, which is generated in a vacuum by a membrane-type vacuum pump 5. Permeate

vapors move from membrane module 3 through line 3 into shell and tube condenser 4 where they condense and flow into collection vessel 6. Water cooled to the temperature of +5°C by a KRIO-VT-05-02 cryostat serves as a cooling agent for the condenser.

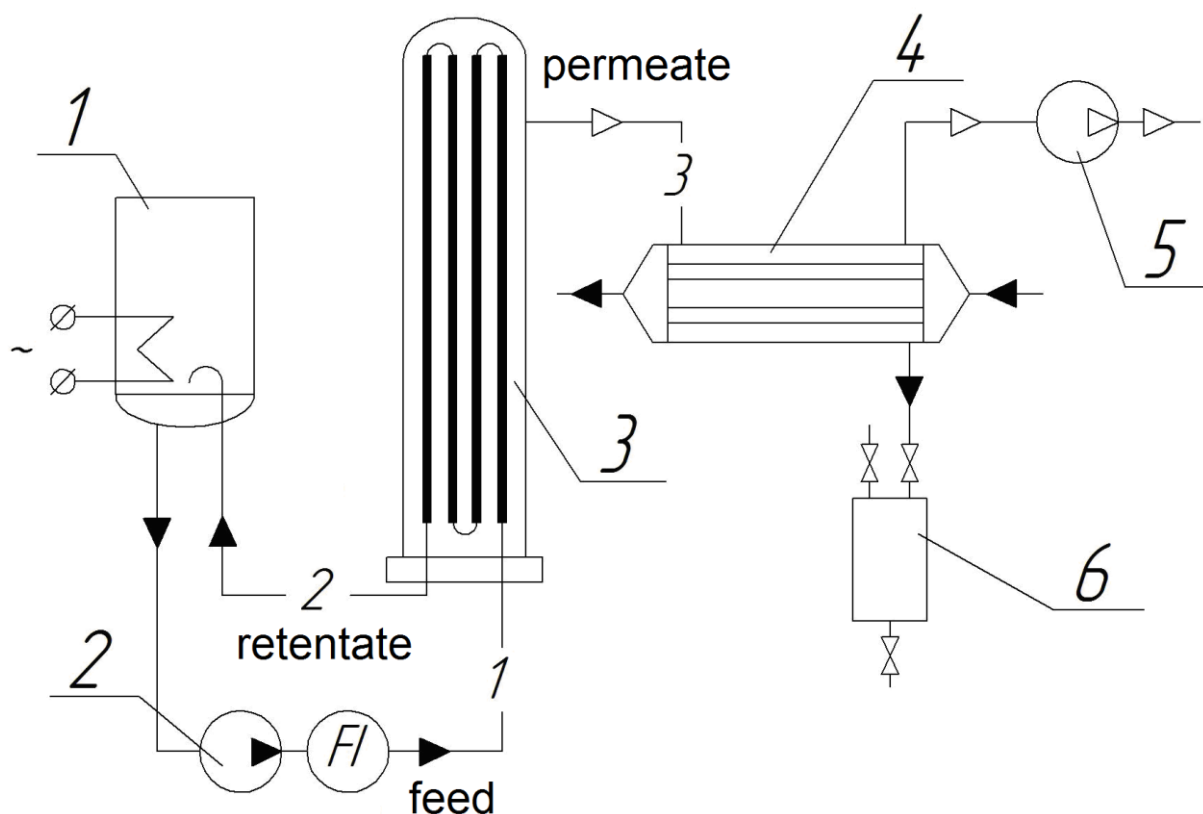


Fig. 1. Scheme of experimental pervaporation unit: (1) feed tank; (2) feed pump; (3) membrane module; (4) condenser; (5) vacuum pump; (6) permeate collection vessel.

EXPERIMENTAL PROCEDURE

A DEG/water model mixture is prepared from demineralized water obtained by means of an Osmodemi 12 unit (specific conductivity of 5 $\mu\text{S}/\text{cm}$) and DEG of A grade according to GOST 10136-77 with the following physicochemical properties: specific weight at 20°C of 1116–1117 kg/m^3 ; saponification number of less than 0.1 mg of KOH per 1 g of the product; DEG weight concentration of more than 99.5%; water weight concentration of less than 0.05%; and admixtures with weight concentrations of less than 0.4%, including ethylene glycol up to 0.15%, and an acid weight concentration of less than 0.005% in terms of acetic acid. The starting mixture is poured into feed tank 1 in the amount of 1.5 kg. The feed part of the plant is preliminarily purged with nitrogen to decrease the concentration of oxygen (Fig.

1). Then, the plant is brought to predetermined operating conditions in terms of temperature and velocity of movement of feed inside the membrane. After achieving the predetermined parameters, a vacuum is established in the intratubular space of membrane module 3. It takes less than 1 h of unit operation to achieve the adaptation of the membrane to temperature, feed composition, and vacuum (which is also confirmed by studies of work [13]). The temperature of the feed in feed tank 1 and vacuum level in the intratubular space of membrane module 3 are kept constant during the experiment.

During the experiment, sample collection of permeate and retentate is performed every 60 min, with each sample being weighed on an AJ-1200CE scale (with accuracy of 0.01 g) to complete a material balance based on the experiment results. All condensed permeate trapped in the collection vessel 6 is poured into a vessel. Part of sample is analyzed at 20°C on a temperature-controlled IRF-454B2M Abbe refractometer. DEG content in the sample is calculated from the measured refractive index using a piecewise-polynomial dependence plotted from the experimental data [14]. Retentate for analysis is collected through a sampler in line 2 into 1.5 mL vials and is also analyzed on the refractometer to determine the composition. After completing the experiment, residues from the feed and permeate parts of the unit are poured under nitrogen pressure into collecting tanks. Residues are weighed; the obtained values are summed with the weight of collected samples and the material balance is completed based on the experiment results. In all of the experiments, divergence from the starting amount of the feed was no more than 3%, which may be considered satisfactory taking into account the volume of the whole unit.

RESULTS AND DISCUSSION

The main characteristics of a pervaporation membrane are the permeate flux through the membrane

$$J = \frac{m_p}{A_m \Delta t} \quad (1)$$

and selectivity

$$\alpha = \frac{y_a/y_b}{x_a/x_b} \quad (2)$$

wherein m_p is a permeate weight [kg] collected over period of time Δt [h]; A_m is a membrane surface area [m²]; x_a and x_b are weight concentrations of components a and b in retentate,

respectively; and y_a and y_b are weight concentrations of components a and b in permeate, respectively (component a is water, component b is DEG).

Figure 2 shows the curve of change in DEG concentration in the feed over time upon dehydration from 88 to 99.8 wt % at the temperature of 90°C and pressure in the permeate part of the unit of 20 mm Hg. As can be seen, it takes approximately 5.5 h to achieve the increase in the DEG concentration from 88 to 98 wt %, this time being only ~30% of the whole experiment time. The remaining 70% of time is accounted for by the increase in DEG concentration by the remaining 1.8 wt %, where approximately half of this time is due to the increase in the DEG concentration from 99.5 to 99.8 wt %.

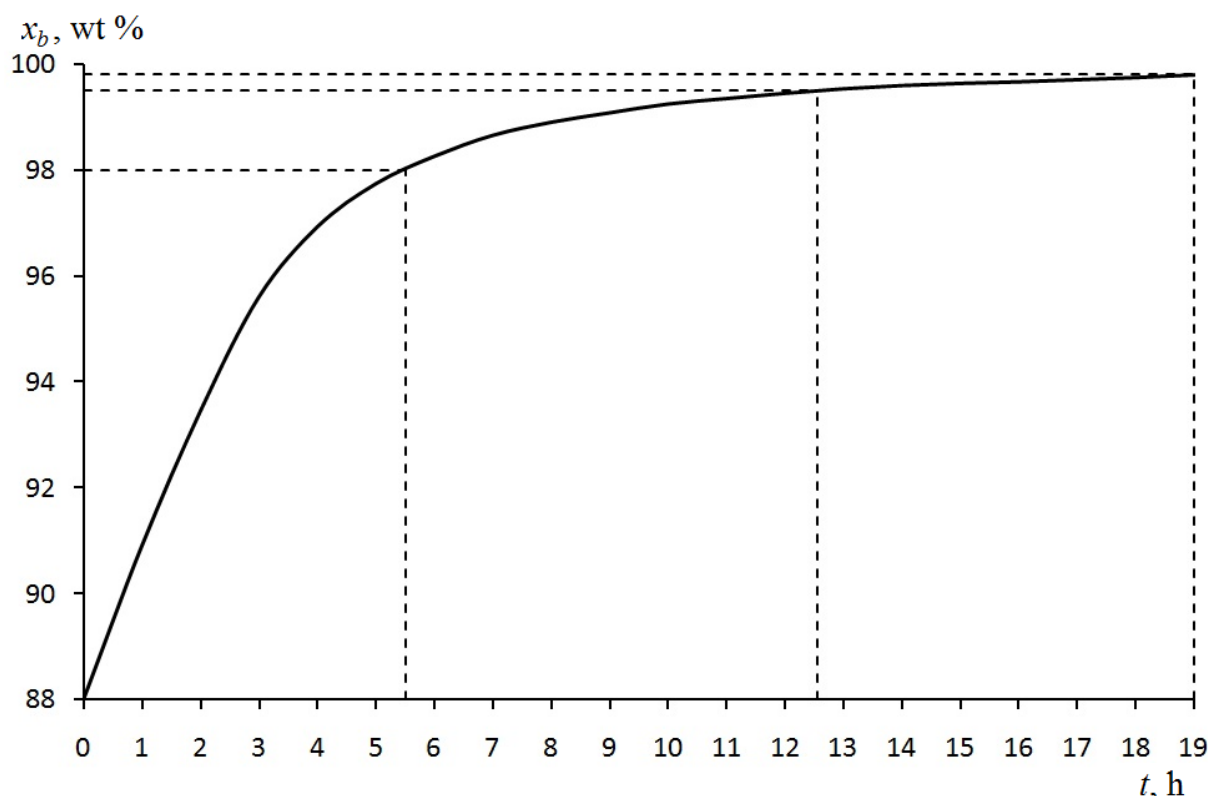


Fig. 2. Curve of DEG concentrations of 88–99.8 wt % for the process temperature of 90°C and pressure in the permeate part of the unit of 20 mm Hg.

The DEG concentration in the permeate throughout the entire experiment was not more than 1 wt % due to the high selectivity of HybSi membranes towards separation of the DEG/water mixture. Therefore, based on expression (2), the selectivity changed from 1500 (at water concentration in retentate of 6.5 wt %) to 20000 (at water concentration in retentate of 0.5 wt %). In view of the high values of membrane selectivity towards separation of the

DEG/water mixture, a study of change in membrane selectivity with change in the process conditions was not performed.

Fig. 3 shows the values of the permeate flux through the membrane depending on the water concentration in the feed stream and its temperature which were evaluated using expression (1).

It is easy to see from the graph shown in Fig. 3 that an increase in the temperature of the feed stream results in an increase in the permeate flux which may be associated with an increase in the saturated water vapor pressure, in the coefficient of diffusion in the membrane, and changes in adsorption effects.

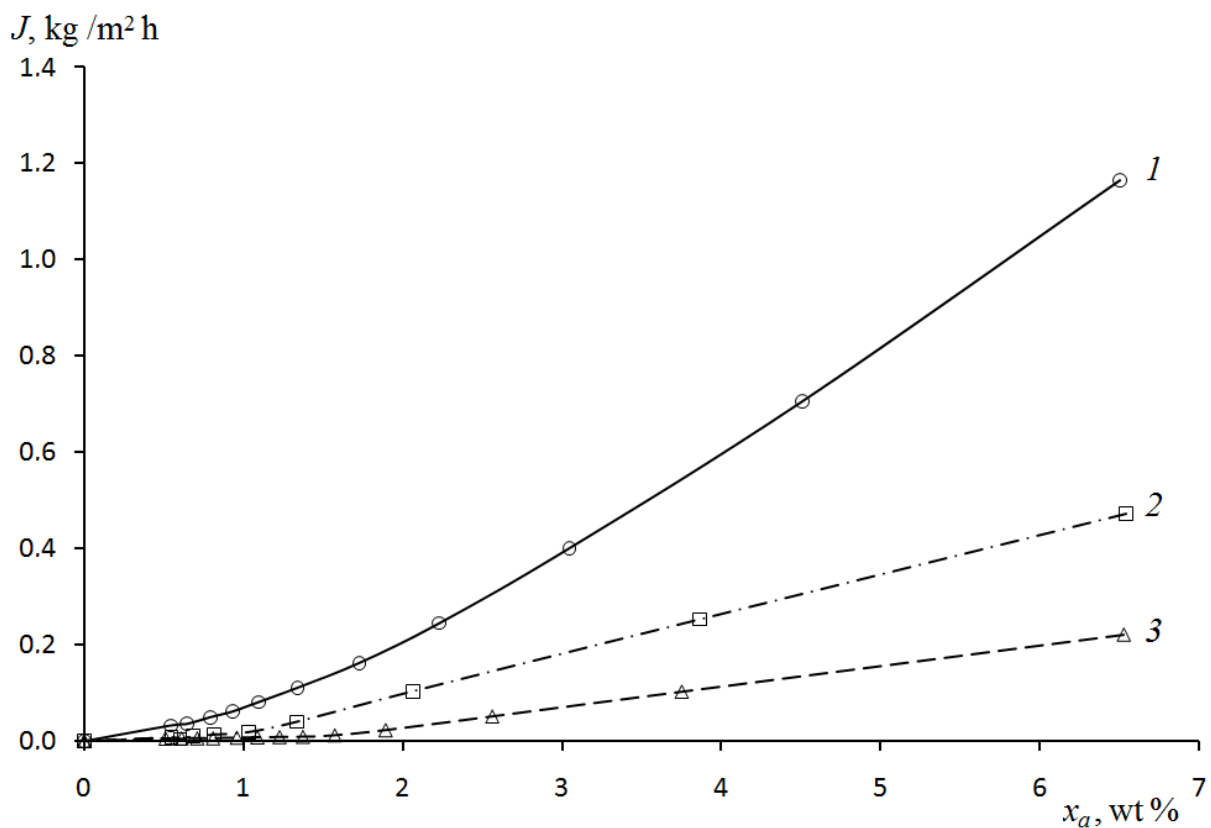


Fig. 3. Permeate flux at pressure of 20 mm Hg and the process temperature of 90 (1), 80 (2), and 70°C (3); lines represent approximation, points represent the experimental data.

The permeate flux through the membrane may be written using the Fick's law:

$$J = -D \frac{\partial C}{\partial z} \approx D \frac{C_f}{\delta} \quad (3)$$

wherein D is an effective diffusion coefficient of water [m²/s] which takes into account the water diffusion in the membrane and adsorption phenomena and is usually referred to as a

penetration coefficient [15], C_f is the volume-weight concentration of water in the feed stream [kg/m^3], and δ is the thickness of the selective layer [m]. The last equality in Eq. (3) is obtained from the assumption of linear decrease in water concentration across the selective layer of membrane as well as the fact that value of the water vapor density is two to three orders lower than value of C_f . With knowledge of the flux value, it is easy to determine the values of the penetration coefficients from expression (3). The results of these calculations are shown in Fig. 4, from which it can be seen that the penetration coefficient is four orders lower than the values of diffusion coefficient of water in DEG [16].

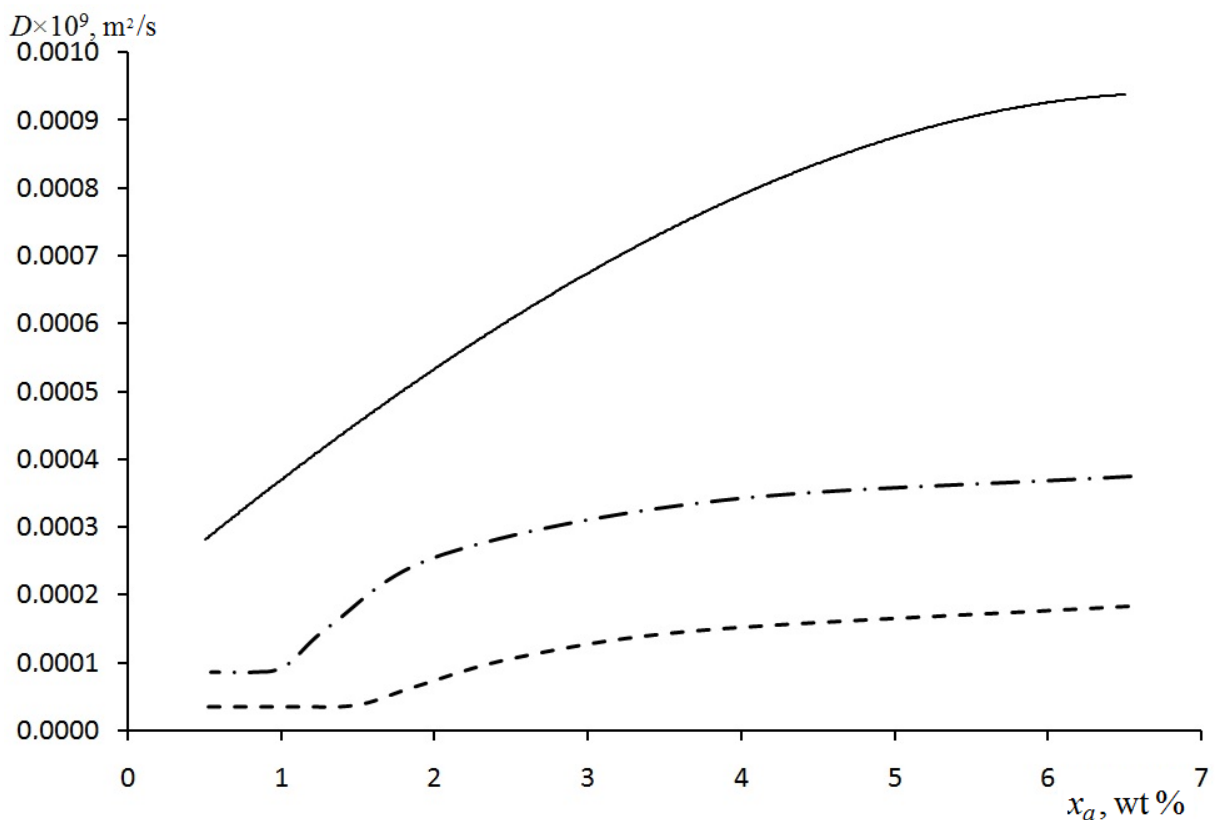


Fig. 4. Water penetration coefficient at the pressure of 20 mm Hg and the process temperature of 90 (solid line), 80 (dash and dot line), and 70°C (dash line).

An important characteristic for calculation of membrane plants is the value of membrane surface area depending on the required degree of separation and productivity. Assuming that the feed stream moves inside a membrane tube according to the ideal displacement mode and only water component of the mixtures penetrates through the membrane (a membrane with infinite selectivity), the following expression for small volume inside the tube may written:

$$GdX = -J(X)dA \quad (4)$$

where G is the weight flux of the feed stream [kg/h] and X is a mass fraction of water in retentate. By integrating expression (4), the following relation is obtained:

$$\int_{X_{\text{final}}}^{X_{\text{start}}} \frac{dX}{J(X)} = \frac{A_m}{G} \quad (5)$$

Figure 5 illustrates the values of the reduced membrane surface area depending on the final mass fraction of water in retentate at initial mass fraction $X_{\text{start}} = 0.065$ for three temperatures calculated using expression (5).

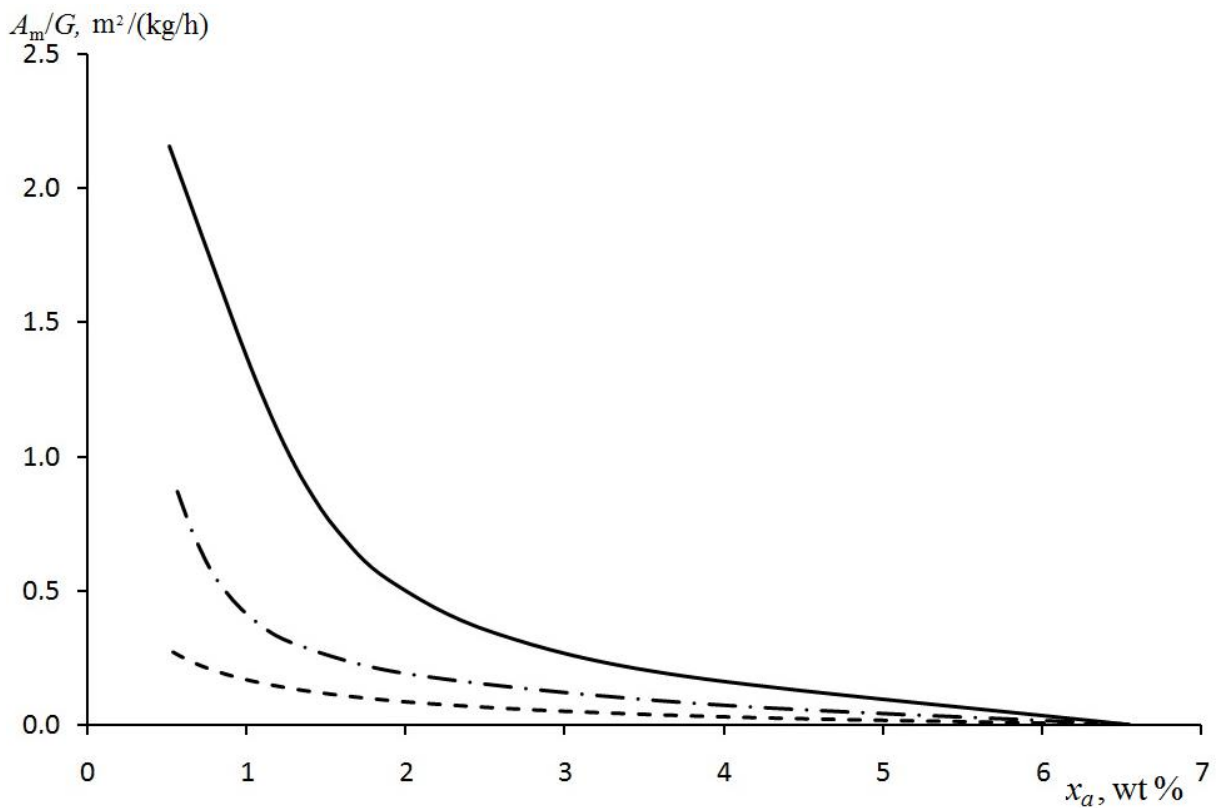


Fig. 5. Reduced membrane surface area at the pressure of 20 mm Hg and the process temperature of 90 (dash line), 80 (dash and dot line), and 70°C (solid line).

The results shown in Figs. 3–5 indicate a significant dependence of the efficiency of the DEG/water mixture pervaporation process using HybSi ceramic membranes on temperature. Thus, to achieve the same concentration in retentate, a change in the process temperature from 90 to 70°C may result in an increase in the required membrane surface by one order of magnitude and, therefore, to a significant increase in the cost of the pervaporation plant. According to our evaluations, the energy conservation achieved upon decreasing the process

temperature below 90°C is not able to compensate for the expenditures for acquiring an additional membrane surface area. In quantitative terms, to achieve a DEG concentration of 99.5 wt % in retentate, the rate of increase of the required membrane surface area with the decrease in the process temperature from 90 to 80°C should be equal to 0.062 m²/°C for a plant productivity of 1 kg/h. Upon decreasing the process temperature from 80 to 70°C, the rate increases approximately twofold. It should be noted that pervaporation does not occur (inappreciable on the membrane surface area of 0.04 m²) at temperatures below 70°C. Note also that, in our experiments, the process temperature is limited from above by the value of 90°C due to risk of the thermal decomposition of DEG in the feed tank in points of feed heating where the feed local temperature achieves ~163°C upon increasing the process temperature from 90 to 100°C and higher. This restriction relates only to the study described here and may be lifted upon designing a full-scale pervaporation unit in the future (HybSi membranes are temperature resistant up to 150°C and up to 190°C in short term period).

Figures 6–8 show the results that demonstrate the influence of the value of pressure in the permeate part of the unit on the permeate flux, the penetration coefficient, and the membrane surface area (according to expression (5)).

As can be seen from these figures, a decrease in pressure in the permeate part of the unit results in an increase in the permeate flux. However, the change in the value of the flux, as well as of the penetration coefficient (Fig. 7), turns out to be not as strong as upon varying the process temperature. Moreover, it is obvious that, upon changing the pressure, the change in the value of the flux and in the penetration coefficient decreases with a decrease in pressure. For example, the flux hardly changes upon going from 20 to 5 mm Hg, which indicates the existence of a certain limit, below which decrease in pressure will be inadvisable.

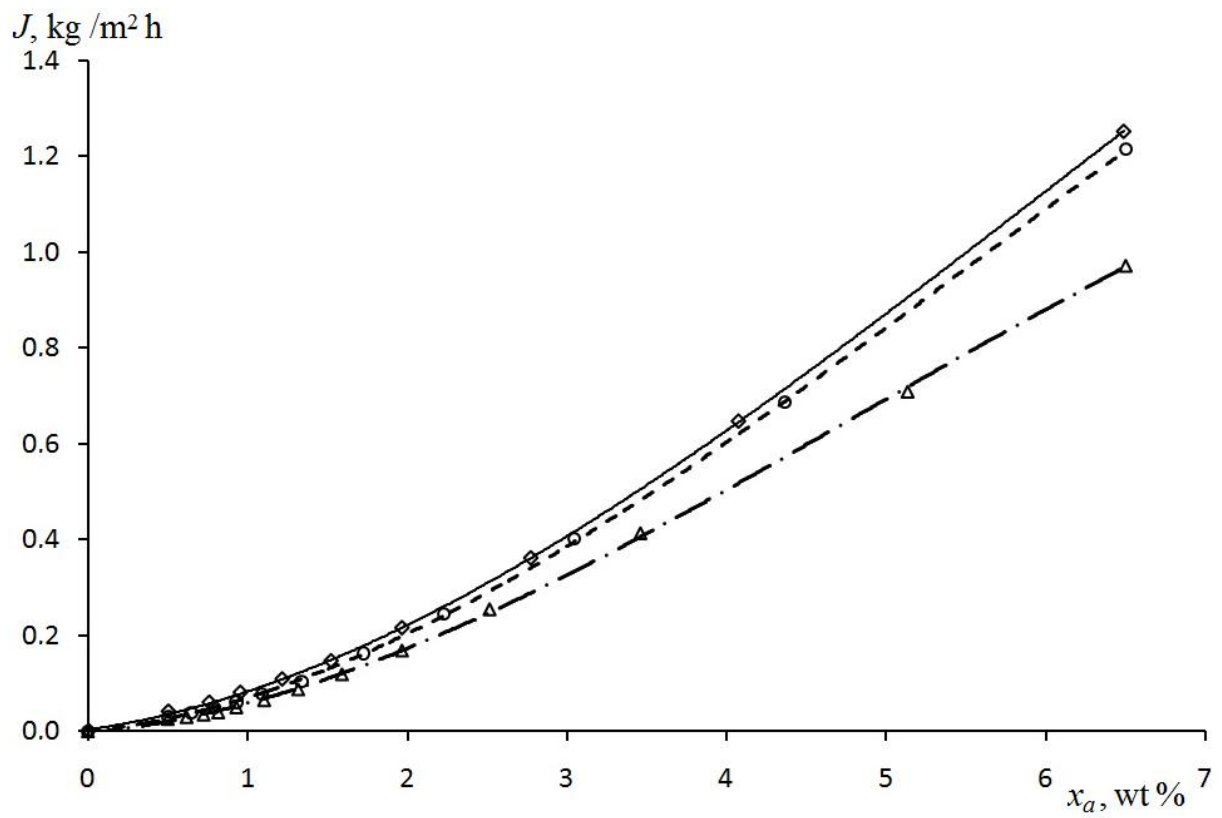


Fig. 6. Permeate flux at the process temperature of 90°C and pressure in the permeate part of 5 (solid line), 20 (dash line), and 30 mm Hg (dash and dot line). Points represent the experimental data, lines represent approximation.

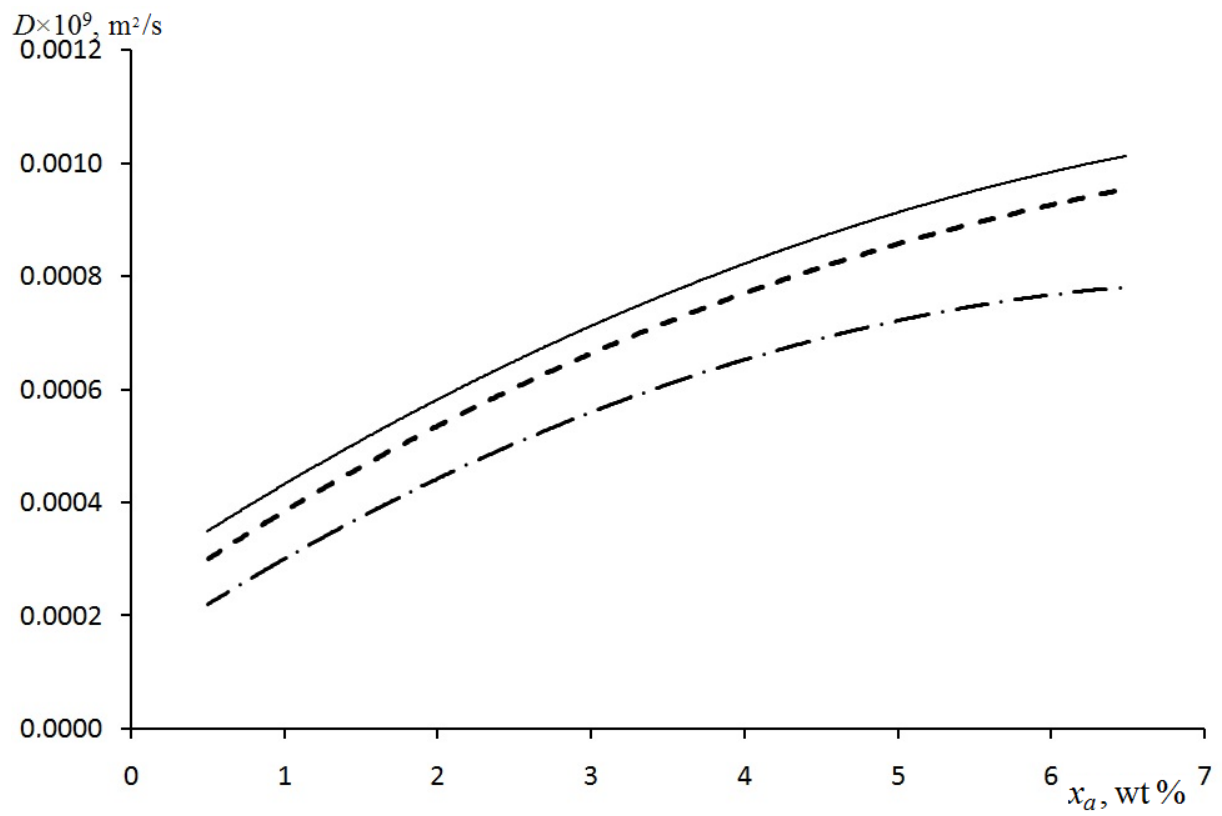


Fig. 7. Water penetration coefficient at the process temperature of 90°C and pressure in the permeate part of 5 (solid line), 20 (dash line), and 30mm Hg (dash and dot line).

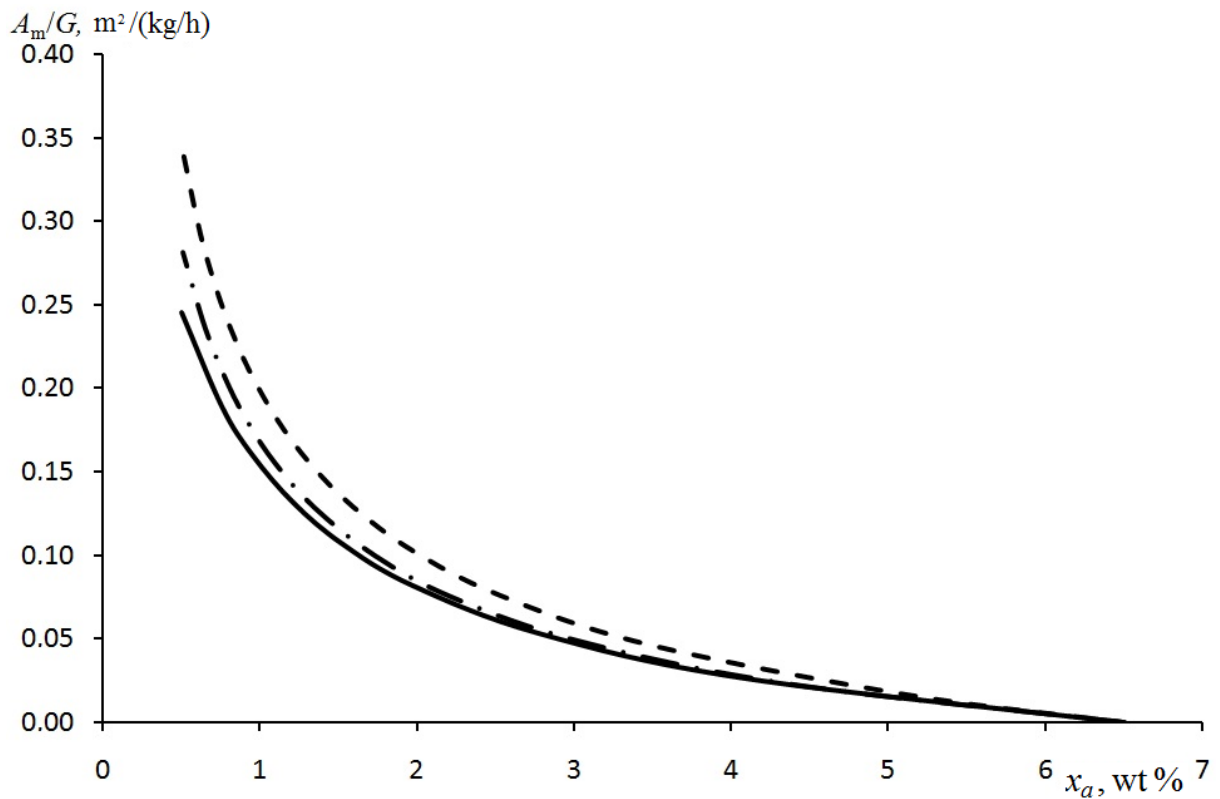


Fig. 8. Reduced membrane surface area at the process temperature of 90°C and pressure in the permeate part of 5 (solid line), 20 (dash and dot line), and 30 mm Hg (dash line).

CONCLUSIONS

The study showed that HybSi ceramic membranes produce a positive effect upon dehydration of a DEG/water mixture. The advantages of HybSi ceramic membranes over polymer membranes are as follows: mechanical strength required under conditions of possible contact with solid particles which may be present in rich DEG, thermal and chemical resistance required in the case of temperature fluctuations and the presence of chemical admixtures in a saturated solution of DEG.

Based on the conducted experimental study of pervaporation dehydration of DEG up to 99.5 wt %, one may conclude that the following operation conditions for a pervaporation unit with a HybSi membrane are close to optimal: vacuum in the permeate part of unit of 20 mm Hg and temperature of 90°C.

The pervaporation technology with application of ceramic membranes with a hydrophilic selective layer made of HybSi material may serve as an alternative for conventional technologies, such as vacuum desorption and stripping gas desorption currently

applied for the deep regeneration of DEG. Results of the study may be used to design industrial pervaporation unit for the dehydration of DEG, as well as for the construction of theoretical models of separation.

DESIGNATIONS

A_m – membrane surface area, m^2 ;

C – volume-weight concentration of water, kg/m^3 ;

D – penetration coefficient, m^2/s ;

G – mass flow rate of feed, kg/h ;

J – permeate flux through the membranes, $kg/(m^2h)$;

m_p – weight of sampled permeate, kg ;

T – process temperature, $^{\circ}C$;

t – time, h ;

t_{deh} – time required for dehydration, h ;

Δt – time between collections of samples, h ;

X – water concentration in retentate (in feed), mass fraction;

x – weight concentration of component in retentate (in feed), $wt\%$;

y – weight concentration of component in permeate, $wt\%$;

z – coordinate in normal direction to the membrane, m ;

α – selectivity;

δ – thickness of the selective layer, m .

SUBSCRIPTS

a, b – components of a binary mixture (a stands for water; b stands for DEG);

deh – dehydration;

f – feed;

m – membrane;

p – permeate;

start, final – starting and final values.

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