Pervaporation technology for regeneration of diethylene glycol at Russian complex gas treatment plants with the use of ceramic membranes HybSi

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ABSTRACT
Conventional methods of regeneration of diethylene glycol used as an absorbent for natural gas dehydration at complex gas treatment plants in the Russian gas fields are analyzed. An alternative method of regeneration by pervaporation using tubular ceramic membranes coated on the inside with the HybSi material is proposed. Experimental study of pervaporation dehydration of diethylene glycol in concentration ranges 97–99.5 wt% and 93.5–99.5 wt% corresponding to saturation levels 2.5 wt% and 6.0 wt%, respectively, is carried out in the temperature range 70–90ºC and vacuum pressure range 5–30 mm Hg. Increase in saturation level from 2.5 wt% to 6.0 wt% leads to inessential increase in the required surface area of HybSi membranes. Results of the experimental study are compared with experimental results obtained by other researchers for SepraTek hollow-fiber polymer membranes. Losses of diethylene glycol through HybSi membranes are shown not to exceed losses at conventional stripping and to be lower by two orders of magnitude than losses through SepraTek membranes. Use of pervaporation instead of stripping for diethylene glycol regeneration leads to more than two-fold energy saving.

1. Introduction

Dehydration of natural gas in the Russian gas fields has conventionally been carried out at complex gas treatment plants (CGTP, also known as UKPG in the Russian gas industry) by absorption using diethylene glycol (DEG) as an absorbent (Fig. 1) (Gritsenko et al., 1999; Lanchakov et al., 2000). The effective Russian Gas Industry Standard "OST 51.40–93" requires water dew point of natural gas to be reduced at CGTP to –20ºC during the cold period of the year and to –10ºC during the warm period of the year for Northern gas fields (where much of the natural gas in Russia is produced) before transportation through existing pipelines (Gritsenko et al., 1999). Obeying this standard guarantees that no hydrates will form during transportation; automation equipment will work reliably; corrosion wear of pipelines, gas compressor stations and process equipment will be minimum (Vyakhirev et al., 2002). For meeting the above requirements, a highly concentrated aqueous solution of DEG is required. Level of saturation of the DEG solution with water in the absorber does not exceed 2.5 wt%, in line with the Russian Industrial Sector Norm for Process Designing "ONTP 1–86"; however, there exists evidence that the saturation level up to 6 wt% is technically achievable and economically feasible for absorbers in the Northern gas fields (Bekirov and Lanchakov, 1999).

Conventionally, Russian CGTP regeneration of rich DEG (i.e. DEG solution containing the absorbed water) has been carried out in the stripper (Fig. 1) (Zhdanova and Khalif, 1984). Stripping at atmospheric pressure gives lean DEG concentration up to 97.5 wt% (Zhdanova and Khalif, 1984). To meet the "OST 51.40–93" requirements, a higher concentration of lean DEG is often needed. Stripping under vacuum gives lean DEG concentration up to 99.3 wt%. Stripping at atmospheric pressure with stripping gas (dehydrated natural gas) fed to the evaporator gives lean DEG concentration up to 99.5 wt%, and stripping at atmospheric pressure with stripping gas fed to the stripper bottom gives lean DEG concentration up to 99.8 wt% (Zhdanova and Khalif, 1984). Use of the stripping gas requires its efficient regeneration to avoid environmental pollution and emissions of greenhouse gases into the atmosphere. Lean DEG of higher concentrations cannot be obtained due to temperature limitations of the stripping process at 164ºC, which is DEG's thermal degradation temperature (Lanchakov et al., 2000). A portion of DEG inevitably degrades into carboxylic acids, aldehydes, ketones, etc. with the formation of resins as undesired by-products, e.g. on flame tubes of the evaporator, if a fired heater is used (which is often the case due to energy expenditure concerns at CGTP), and leads to losses of DEG (Lanchakov et al., 2000; Zhdanova and Khalif, 1984). Additional losses of DEG occur at the stripper top together with water condensate from the reflux region. In line with data (Bekirov and Lanchakov, 1999), these two types of losses of DEG during stripping constitute up to 10–15% of all DEG losses occurring at various CGTP of the Yamburg gas field. DEG degradation also results in corrosion of equipment leading to contamination of DEG with corrosion products as well as resins (Zhdanova and Khalif, 1984). Since absorption is carried out at temperatures below 50°C (Zhdanova and Khalif, 1984), rich DEG must be heated by ~100ºC before it enters the stripper; similarly, lean DEG must be cooled by the same amount before it enters the absorber; hence, high efficiency heat exchangers must be used. Thus, the conventional stripping method for DEG regeneration at CGTP has many severe drawbacks.

Other processes for regeneration of DEG and other glycols such as "Drizo" (azeotropic distillation) have not achieved common acceptance in the Russian gas industry (Gritsenko et al., 1999). As to membrane technologies, their application to regeneration of glycols has been limited so far to reverse osmosis only based on information from the open literature (Zhdanova and Khalif, 1984); overheating of glycols is avoided with the use of this process. However, the process has not achieved a wide application due to low capacity of available membranes (Zhdanova and Khalif, 1984). As to pervaporation (PV), its application, to our knowledge, has never been considered as a method of regeneration of DEG at CGTP up to the present time. Until recently, the only glycol whose dehydration by PV studied in the laboratories was ethylene glycol (EG) (Feng and Huang, 1996; Guo et al., 2007; Du et al., 2008; Xu et al., 2010;

Hu et al., 2012; Yu et al., 2012). However, two papers recently published reported results of DEG dehydration by PV (Akberov et al., 2014; Yim and Kong, 2013). In (Yim and Kong, 2013), PV dehydration was accomplished using hollow-fiber polymer membranes PVHF-085060BW of the SepraTek company (Incheon, Republic of Korea) having a selective layer made of a material based on polyvinyl alcohol (PVA), hereinafter referred to as SepraTek membranes. The paper (Akberov et al., 2014) dealt with dehydration of DEG by PV using tubular ceramic membranes having a selective layer made of the HybSi material developed at Energy Research Center of the Netherlands (Castricum et al., 2008; van Veen et al., 2011), hereinafter referred to as HybSi membranes. In (Yim and Kong, 2013), results of experimental studies were obtained for DEG dehydration from 98 wt% to 99.5 wt%, whereas (Akberov et al., 2014) described results of experimental studies for DEG dehydration from 97 wt% to 99.5 wt% and from 93.5 wt% to 99.5 wt%. In the present work, we consider some of the most important aspects of application of PV with the use of HybSi membranes for conditions present at CGTP, compare results of studies of PV dehydration using HybSi membranes with results of studies using SepraTek membranes and present advantages of the PV technology of DEG regeneration with HybSi membranes over the conventional stripping technology.
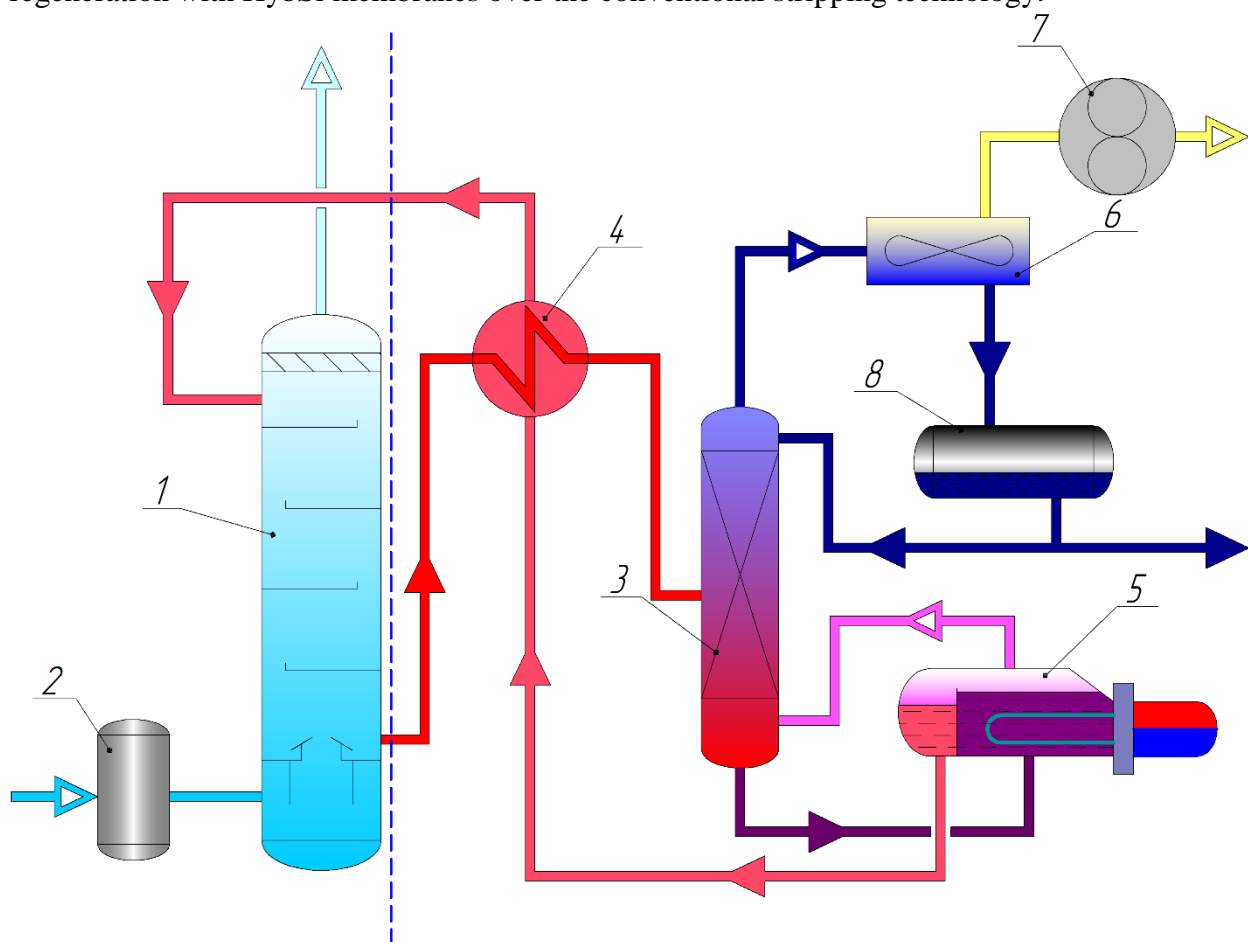

Fig. 1. Conventional natural gas dehydration system at CGTP by DEG absorption with regeneration of DEG in the vacuum stripper: *1* – absorber; *2* – inlet scrubber; *3* – stripper; *4* – lean-rich DEG heat exchanger; *5* – fired heater; *6* – condenser; *7* – vacuum pump; *8* – reflux tank

2. Pervaporation process

A possibility of separation of liquid mixtures by PV was discovered back at the turn of the 20th century, but the first recorded industrial application of the technology took place only in 1982 when the GFT Company implemented its first ethanol dehydration pilot plants in Brazil demonstrating the competitiveness of PV versus azeotropic distillation. The essence of the

process involves evaporation of the permeating component of the initial liquid mixture being under atmospheric pressure on the surface of the selective (active) layer and permeation of the evaporated component through the membrane due to vacuum applied on the opposite side of the membrane. The permeating component of the liquid mixture must have greater affinity with the material of the membrane's selective layer in comparison with the remaining components of the mixture for efficient removal (Mulder, 1996).

Main separation characteristics of a PV membrane are permeate flux, J, and selectivity, α (α is often called as separation factor):

$$J = \frac{m_p}{A_m \Delta t},$$

$$\alpha = \frac{y_a / y_b}{x_a / x_b},$$

where m_p is weight of permeate (kg) collected within sampling time Δt (h); A_m is membrane surface area (m^2); x_a and x_b are mass concentrations of components a and b in retentate (i.e. in the feed), respectively (wt%); y_a and y_b are mass concentrations of the components a and b in permeate, respectively (wt%); component a is water; component b is DEG.

3. Ceramic membranes HybSi

For regenerating DEG at CGTP, hydrophilic membranes must be used. Stability of a membrane to the feed liquid and process conditions is determined by a material of the selective layer placed onto the support. One of the most perspective materials for the selective layer of hydrophilic ceramic membranes is HybSi, which stands for hybrid silica (Castricum et al., 2008; van Veen et al., 2011); the material was developed at Energy Research Centre of the Netherlands in collaboration with the University of Amsterdam and the University of Twente (Fig. 2).

HybSi is an organic-inorganic hybrid material (with an inorganic base), in which every silicon atom is connected not only to oxygen atoms as in siloxane bridges (Si–O–Si) but also to carbon atoms of the organic group $(-CH_2-)_n$, where n equals 1 or 2 depending on the precursor. Thus, in addition to the siloxane group (Si–O–Si), the group $(Si-(CH_2)_n-Si)$ is also used, which implies that the organic fragments are sewed in the spatial structure of amorphous silica. The inorganic part imparts hydrophilicity (wetting angle is ~70º) as well as mechanical strength, whereas the organic part imparts hydrothermal stability and enhanced viscosity so that propagation of nanocracks through the material decreases resulting in essential increase in the membrane's life in service.

The longest test of the HybSi membranes, which lasted three years, was accomplished at Energy Research Centre of the Netherlands on dehydration of the n-butanol/water mixture at temperature 150ºC (van Veen et al., 2011). For the duration of the test, selectivity of the membranes was virtually constant. At short-term exposures to high temperatures, the membranes showed hydrothermal stability up to temperature 190ºC. Besides, the HybSi membranes showed excellent chemical stability to various aggressive organic solvents when varying pH between eight and two (Castricum et al., 2008).
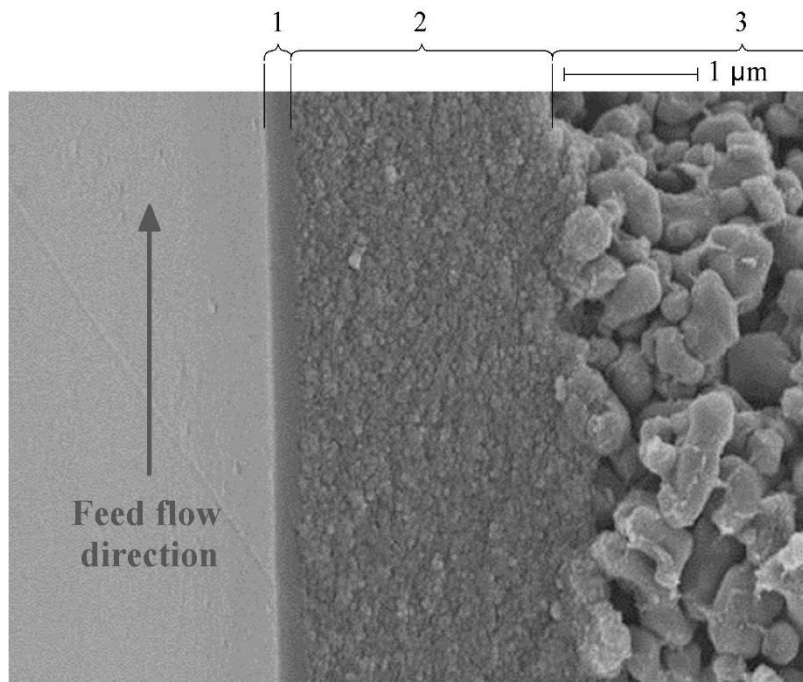
Fig. 2. Microphotograph of a cross-section of the HybSi membrane: *1* – selective layer made of HybSi of thickness ~200 nm (the pore size is less than 1 nm); *2* – intermediate layer made of amorphous silica of thickness ~2000 nm (the pore size is ~4 nm); *3* – ceramic support. Membrane tubes of the Pervatech BV Company are coated with HybSi on the inside.

In this study, four tubular ceramic membranes (Pervatech BV, the Netherlands) were used with dimensions: length – 500 mm, inner diameter – 7 mm and outer diameter – 10 mm; total membrane surface area is 0.04 m^2. The tubes are coated on the inside with the HybSi material of thickness ~200 nm using the sol-gel technology with the pore size being no more than 1 nm. Between the selective layer and the ceramic support, there is an intermediate layer made of amorphous silica of thickness ~2000 nm with the pore size being approximately 4 nm. Arrangement of the tubes is in-series. A liquid feed flows inside the tubes and the permeating component vapor moves outwards to the space of the membrane module's shell under vacuum. Based on data from the manufacturer, separation characteristics of the membranes for dehydration of the isopropanol/water mixture (95/5 wt%) at temperature 70ºC and vacuum pressure 10 mm Hg are as follows: total permeate flux J is 1.2, 1.2, 1.2 and 1.1 kg/(m^2 h); selectivity α is 466, 321, 1125 and 643.

4. Experimental pervaporation unit

The schematic of the experimental PV unit used for studying DEG dehydration through HybSi membranes is given in Fig. 3 (Akberov et al., 2014). The unit consists of a feed (retentate) part and a vacuum (permeate) part. In the feed part, circulation of the feed between feed tank *1* and membrane module *3* takes place through lines *1* and *2* by means of vortex pump *2*. Pressure inside the closed loop is near atmospheric. The feed tank wall is equipped with a thermocable for maintaining a constant process temperature. PV takes place inside membrane module 3 containing four tubular ceramic membranes connected in series.
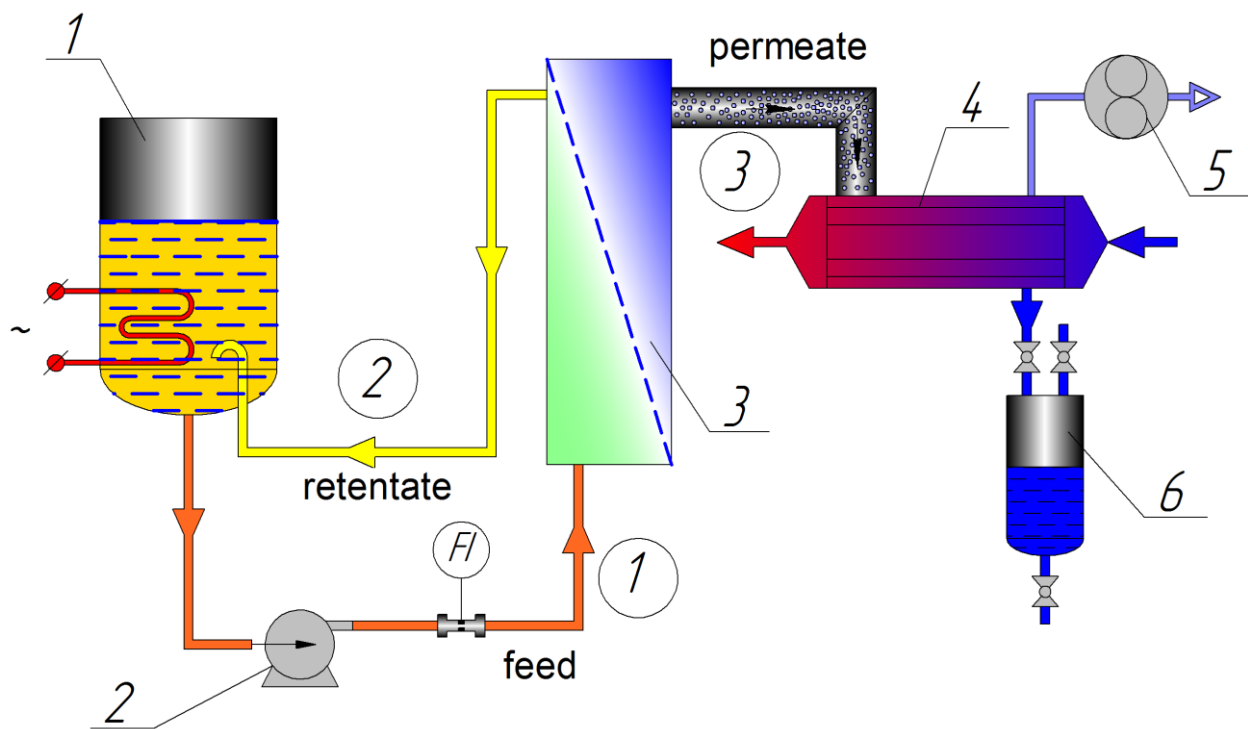
Fig. 3. Schematic of the experimental PV unit: *1* – feed tank; *2* – feed pump; *3* – membrane module; *4* – condenser; *5* – vacuum pump; *6* – permeate collection vessel.

The feed moves inside a membrane tube with linear velocity of not less than 2.5 m/s (the Reynolds number≥5000), which is high enough for preserving concentration polarization at a low level (Nagy, 2010; Vane et al., 1999). The permeate vapor leaves outwards to the intertubular space of the membrane module staying under vacuum created by vacuum pump of the membrane type *5*. The permeate vapor moves from membrane module *3* through line *3* and into shell-and-tube condenser *4* where it condenses and leaks down into collection vessel *6*. The cooling agent for the condenser is water cooled to temperature +5ºC by the KRIO-VT-05-02 cryostat (LLC Termex, Russia).

5. Experimental procedures

A DEG/water model mixture is prepared from demineralized water (specific conductivity is 5 µS/cm) produced by the Osmodemi 12 unit (Idrotecnica s.r.I., Italy) and DEG of grade A complying with the Russian national standard GOST 10136–77 and, therefore, having the following physicochemical properties: density at 20ºC is 1116–1117 kg/m^3; saponification number is less than 0.1 mg of KOH per 1 g of the product; mass concentration of DEG is more than 99.5%; mass concentration of water is less than 0.05%; and admixtures constitute less than 0.4 wt% including ethylene glycol in the amount of up to 0.15 wt% and organic acids in the amount of less than 0.005% in terms of acetic acid. Note that the Russian CGTP use DEG of a very similar composition. The initial mixture is poured to the feed tank *1* in the amount of 1.5 kg. The feed part of the unit is preliminarily purged with nitrogen to reduce the oxygen concentration. Switching on the recirculation pump and the feed tank's electric heater warms the feed to the desired process temperature and force it to circulate through the closed loop. Although the vacuum pump is still off at this time, a small portion of the feed permeates through the membrane pores and condenses on the permeate side of the membranes. Therefore, all the liquid collected at the bottom of the membrane module and inside the permeate collection vessel before the experiment begins are to be removed. After the vacuum pump is connected to the unit and the desired vacuum pressure is achieved in the permeate part of the unit, time reading begins. It takes less than 1 hour of unit operation to achieve adaptation of the membranes to temperature, feed composition and vacuum pressure (which is also

confirmed by the study (Mah et al., 2014)). Feed temperature in feed tank *1* and vacuum pressure in the intertubular space of membrane module *3* are kept constant during one experiment.

Collection of permeate and retentate samples is performed every 60 min with each sample being weighed on the AJ–1200CE scale (Shinko Denshi Co., Ltd., Japan) with accuracy ±0.01 g. All of the condensed permeate trapped inside the collection vessel *6* is poured into a separate vessel. A part of the sample is analyzed at 20ºC on a temperature-controlled IRF-454B2M Abbe refractometer (OJSC KOMZ-Baigish, Russia) measuring the refractive index of light of wavelength 589.3 nm with accuracy ±0.0001. DEG contents in the sample is determined from the measured refractive index using a piecewise-polynomial function of refractive index obtained by curve fitting to experimental data (Dyment et al., 1976). Retentate for analysis is collected through a sampler in line *2* into 1.5 ml vials and is also analyzed on the refractometer for determining its chemical composition. In periods between samplings, no attendance of the unit is required. After completing the experiment, leftovers from the feed and permeate parts of the unit are poured under nitrogen pressure into collecting tanks. The leftovers are weighed; the obtained values are summed with the weight of collected samples and the material balance is drawn from summary of the experiments. In all of the experiments, divergence from the initial amount of the feed constituted less than 3%, which may be considered satisfactory considering the volume of the unit. Each experiment is carried out several times for confirming stability and reproducibility of the results.

6. Results and discussions
6.1. Selection of feed DEG concentration ranges

According to requirements of the Russian Industrial Sector Norm for Process Designing "ONTP 1–86", level of saturation of DEG solutions with water at absorption does not exceed 2.5 wt%. However, saturation level up to 6 wt% is technically achievable and can be economically feasible in absorbers of CGTP of the Northern gas fields (Bekirov and Lanchakov, 1999) (saturation level is a difference between mass concentration of DEG in the rich and lean DEG solutions). The higher the saturation level is, the cheaper the natural gas dehydration at CGTP becomes due to energy savings on circulation and regeneration of DEG. In this regard, in (Akberov et al., 2014) an experimental study of PV dehydration of DEG by HybSi membranes was carried out for the DEG concentration ranges: 97–99.5 wt% and 93.5–99.5 wt% corresponding to saturation levels 2.5 wt% and 6.0 wt%, respectively. For convenience of reasoning, some results from (Akberov et al., 2014) in a somewhat changed form are given below for the DEG concentration range: 93.5–99.5 wt% (Fig. 4–6).

Fig. 4 shows a measured increase of DEG concentration in the feed from 93.5 wt% to 99.8 wt% for dehydration of ~1.5 kg of the feed solution at feed temperature T_f=90ºC and vacuum pressure in the permeate part of the unit p_p=20 mm Hg by HybSi membranes having the total surface area 0.04 m^2. It can be seen from the figure that dehydration of the mixture from 99.5 to 99.8 wt% consumes approximately 40% of the entire experimental time for dehydration in the DEG concentration range 93.5–99.8 wt%, which is comparable to time consumption on DEG dehydration in the DEG concentration range 97–99.8 wt% (about 48% of the entire experimental time). In view of this, it seems unreasonable from the economic point of view to dehydrate rich DEG at CGTP up to concentration of 99.8 wt%. Therefore, PV dehydration of the initial DEG/water mixture was carried out in our experiments only up to DEG concentration of 99.5 wt%, which is achievable at the existing Russian CGTP by feeding a stripping gas either to the evaporator or to the stripper bottom.

Fig. 4 also provides an embedded small plot comparing the curve for increase of DEG concentration in the feed from 98.5 wt% to 99.5 wt% for dehydration of ~1.5 kg of the feed solution by HybSi membranes of the total surface area 0.04 m^2 at T_f=90ºC and p_p=20 mm Hg with a similar curve for SepraTek membranes at T_f=90ºC and p_p=5 mm Hg. The latter curve is

adopted from (Yim and Kong, 2013) and adapted to conditions of our PV study, as testing of SepraTek membranes in (Yim and Kong, 2013) was carried out using the total membrane surface area 0.16 m^2 and a feed solution of weight ~2.5 kg. At that, the original values of DEG concentration in the feed from (Yim and Kong, 2013) were left unchanged, but the time axis was elongated by the factor of 2.4 (0.16·1.5/(0.04·2.5)=2.4). Differences in the value of p_p do not impede a comparison of the two curves, since DEG dehydration by means of HybSi membranes practically does not depend on p_p in the range of p_p from 5 to 20 mm Hg, as one can note from Fig. 6 below. It is easy to see from Fig. 4 that the curve for SepraTek membranes is less steep implying that SepraTek membranes yield to HybSi membranes at the feed temperature T_f=90ºC.

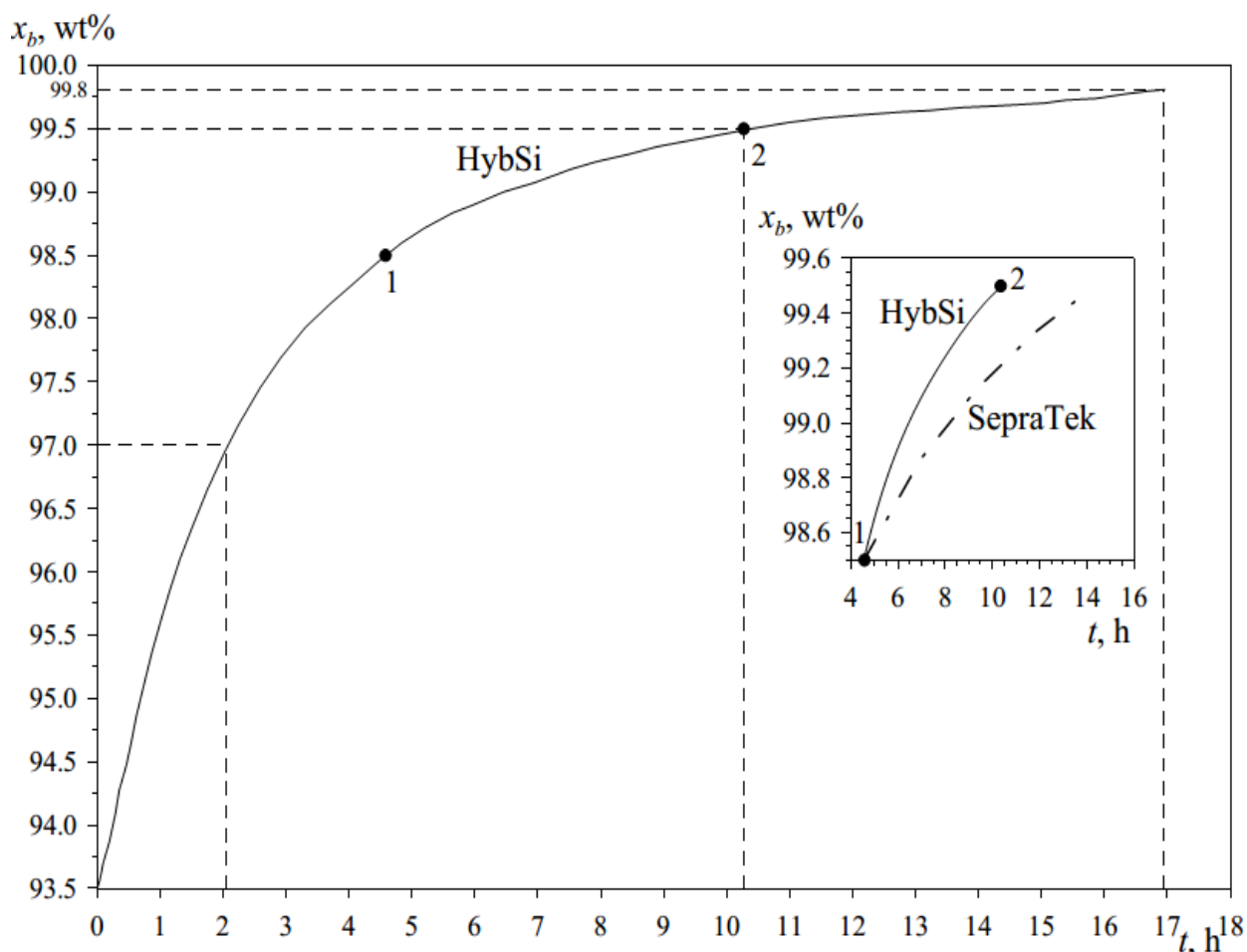**Fig. 4.** Increase of DEG concentration in the feed from 93.5 wt% to 99.8 wt% for dehydration of ~1.5 kg of the feed solution at feed temperature T_f=90ºC and vacuum in the permeate part of the unit p_p=20 mm Hg by HybSi membranes having the total surface area 0.04 m^2. The embedded small plot compares a curve for HybSi membranes (T_f=90ºC; p_p=20 mm Hg) with a curve for SepraTek membranes (T_f=90ºC; p_p=5 mm Hg) from (Yim and Kong, 2013) for increase of DEG concentration in the feed from 98.5 wt% to 99.5 wt%

6.2. Investigation of selectivity of HybSi membranes

Measured values of the DEG concentration in the permeate stream remained low throughout the entire experiment (T_f=90ºC; p_p=20 mm Hg) and did not exceed 1 wt% due to observed high selectivity of HybSi membranes to water for separation of the DEG/water mixture (water passes and DEG is rejected). Thus, based on expression (2), selectivity changes from 1500 (at water contents in retentate 6.5 wt%) to 20000 (at water contents in retentate 0.5 wt%) for DEG concentration in permeate 1 wt%. In view of such a high selectivity of HybSi

membranes to water for the DEG/water mixture separation, no investigation on behavior of membrane selectivity with a change in process conditions is performed.

For explaining the observed high selectivity of HybSi membranes to water at the DEG/water mixture separation, it is worth mentioning the study (Sekulic et al., 2005), in which ceramic membranes having a selective layer made of amorphous titania were used for deep dehydration of the EG/water mixture. The study showed that the titania membranes are not the best choice for dehydration of p-dioxane, ethanol, isopropanol and other organic matters, since they allow both water and organic substances to pass through the pores due to relatively large pore sizes (~0.9 nm) compared to sizes of molecules of both water (0.24 nm) and most organic substances (0.3–0.8 nm). However at dehydration of the EG/water mixture with the EG contents in the feed exceeding 85 mol%, the membranes showed extremely high values of selectivity to water owing to hydrogen binding of EG molecules by means of the hydroxyl functional groups (–OH) in pores of selective layers of the membranes. Therefore, the EG molecules happen not to be able to pass through the pores of the membranes. As a result, selectivity to water for the case of deep dehydration of EG turns out to be extremely high ($\alpha \gg 1000$). One can see similarities with HybSi membranes, whose selective layers have pores of sizes ~1 nm. Selectivity of the four HybSi membranes used in our study to water, based on data from the manufacturer, for dehydration of the isopropanol/water mixture (95/5 wt%) makes, on average, 639, whereas, according to our results, for dehydration of the DEG/water mixture (95/5 wt%) the value of selectivity becomes 2000–2500. Thus, one can assume that hydrogen binding of DEG molecules through hydroxyl groups (–OH) (all glycols have two (–OH) groups) in pores of the HybSi material really occurs, and it can be responsible for the observed high selectivity of the HybSi membranes to water for separation of the DEG/water mixture.

6.3. Dependence of permeate flux on feed temperature

Fig. 5 shows dependence of the total permeate flux J through HybSi membranes, evaluated using expression (1), on DEG contents in the feed and feed temperature T_f. The results indicate that the total permeate flux J increases essentially with increase in feed temperature T_f. This can be attributed to increase in water's saturated vapor pressure, increase in diffusion coefficient inside the membranes and change in the adsorption effects.

As it was mentioned in Section 1, at this point in time there exists information on possibility of PV dehydration of DEG using only HybSi membranes (Akberov et al., 2014) and SepraTek membranes (Yim and Kong, 2013). Fig. 5 also exhibits values of the water permeate flux J_{H2O} for SepraTek membranes obtained at the same values of feed temperature T_f: 70, 80 and 90°C. The values of the water permeate flux J_{H2O} for SepraTek membranes are chosen instead of the total permeate flux values J for the reason that the water permeate flux J_{H2O}, in the first place, affects the time of dehydration of the feed mixture of a given weight m_f from the initial concentration of DEG in the feed mixture to the final concentration. On the other hand, for HybSi membranes the values of the water permeate flux J_{H2O} approximately coincide with the values of the total permeate flux J due to smallness of DEG contents in the permeate stream (≤ 1 wt%), which allows comparing with each other values of the water permeate flux J_{H2O} for these two types of membranes.

As one can see from Fig. 5, dependence of the water permeate flux J_{H2O} on feed temperature T_f for SepraTek membranes is weaker compared to that for HybSi membranes. For explaining this phenomenon, it is necessary to analyze the structure of the selective layer of SepraTek membranes and compare it with that of HybSi membranes. However, according to (Yim and Kong, 2013), such information on the structure of the selective layer of SepraTek membranes is not yet available from the manufacturer of SepraTek membranes. The only information, which is available at this time, is that the selective layer is made of a hydrophilic PVA-based polymer material.
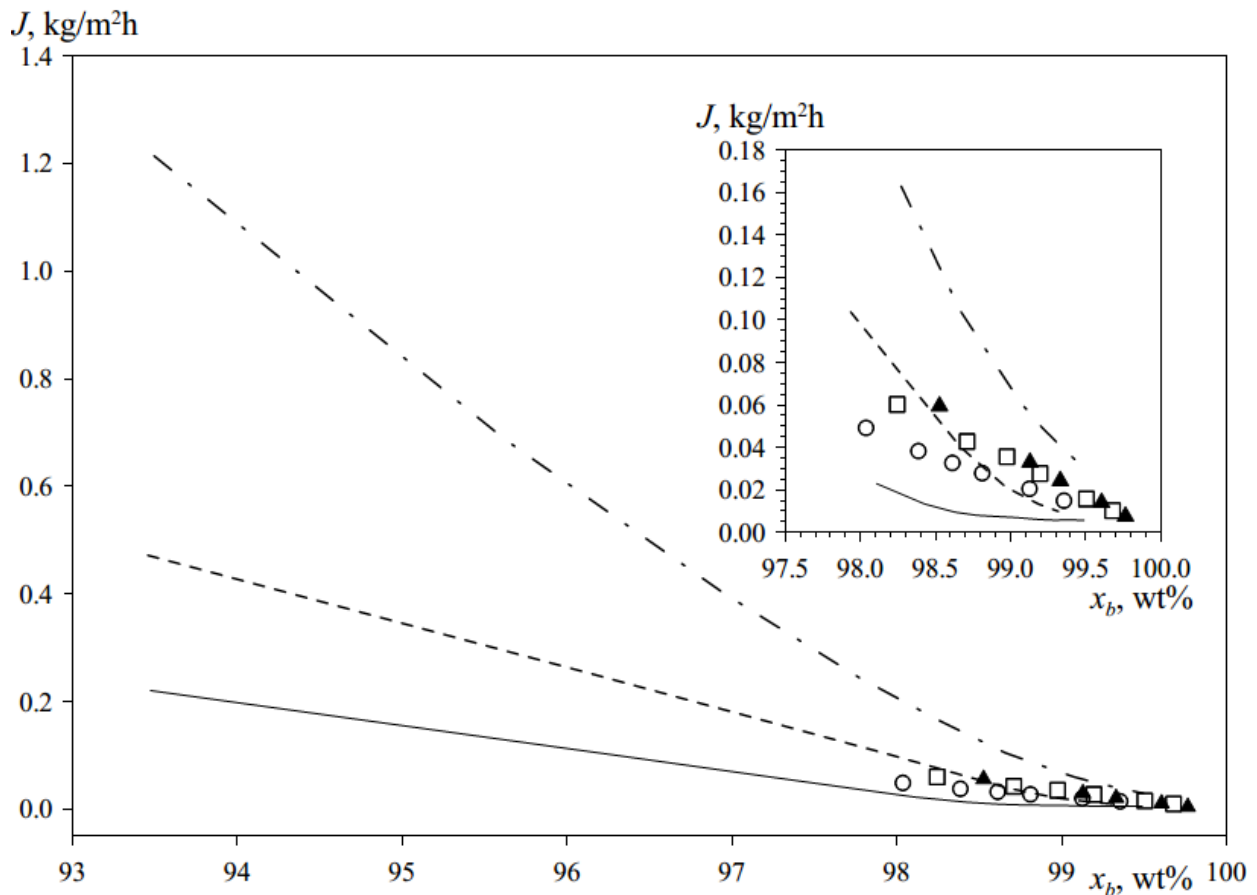
Fig. 5. Total permeate flux J through HybSi membranes at vacuum pressure in the permeate part of the unit p_p=20 mm Hg and feed temperature T_f 90°C (dash-dotted line), 80°C (dash line) and 70°C (solid line) for DEG concentration in the feed increasing from 93.5 wt% to 99.5 wt%. The embedded small plot is a zoom-in of the big plot's right end. Geometric figures denote values of water permeate flux J_{H2O} for SepraTek membranes at p_p=5 mm Hg from (Yim and Kong, 2013); ▲ − feed temperature 90°C; □ − feed temperature 80°C; ○ − feed temperature 70°C

6.4. Dependence of permeate flux on vacuum pressure in the permeate part of the unit

Fig. 6 shows dependence of the total permeate flux J through HybSi membranes on DEG contents in the feed and vacuum pressure in the permeate part of the unit p_p. The results indicate that the total permeate flux J increases with decrease in vacuum pressure p_p. However, influence of vacuum pressure p_p on the total permeate flux J is not so strong as influence of feed temperature T_f. One can see that dependence of the total permeate flux J through HybSi membranes on vacuum pressure p_p is nonlinear. For instance, decreasing vacuum pressure p_p from 20 to 5 mm Hg leads to an insignificant increase in the total permeate flux J, which indicates existence of a certain limit, below which decrease in vacuum pressure is economically unfavorable. Thus, based on data for the total permeate flux J for PV dehydration of DEG up to 99.5 wt%, it can be concluded that the vacuum pressure in the permeate part of the unit p_p equal to 20 mm Hg is close to the optimum condition.

Fig. 6 also shows values of the water permeate flux J_{H2O} for SepraTek membranes at feed temperature T_f=90°C, but only at one value of vacuum pressure in the permeate part of the unit p_p=5 mm Hg, at which the study (Yim and Kong, 2013) was conducted.
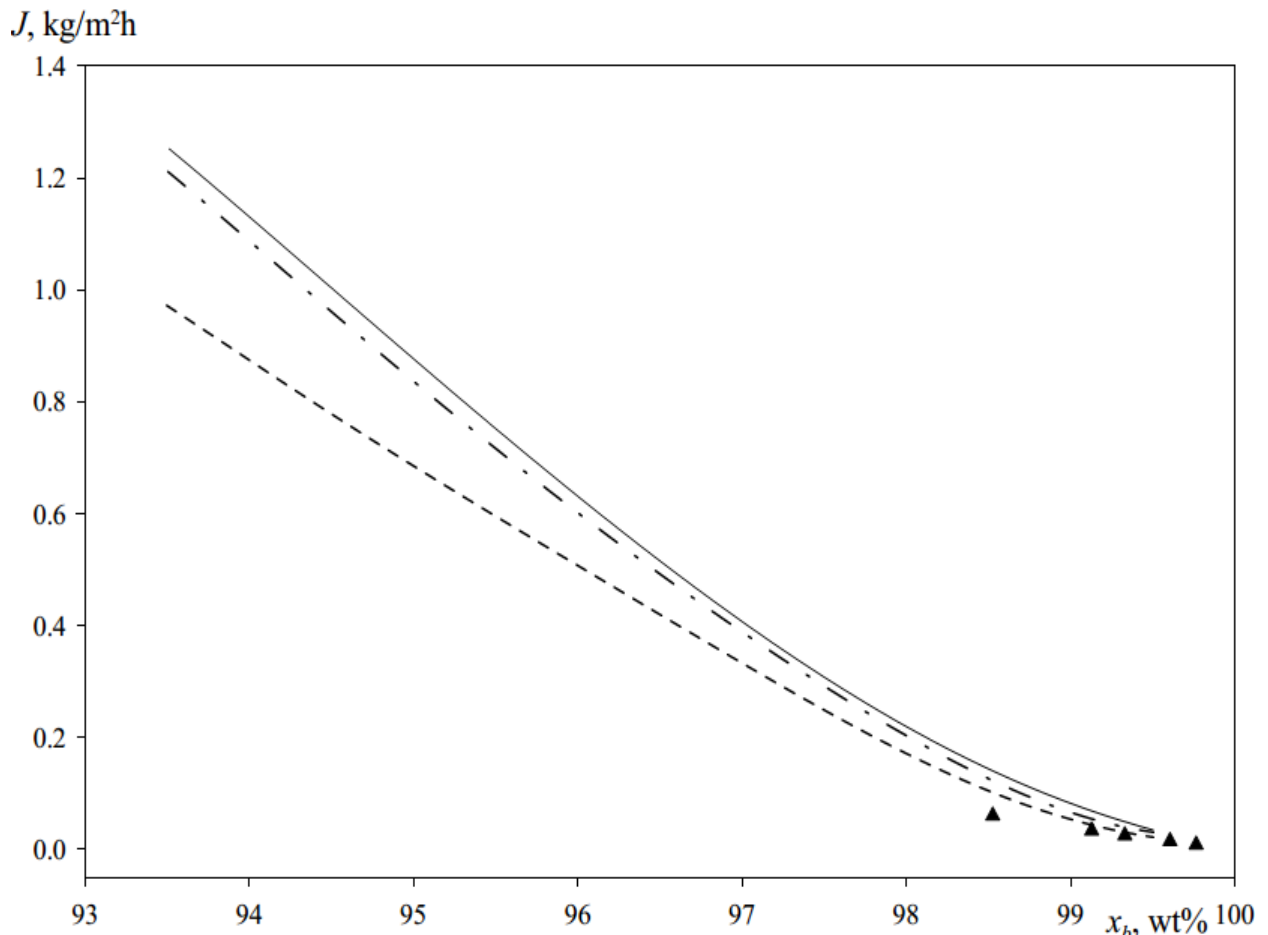
Fig. 6. Total permeate flux J through HybSi membranes at feed temperature T_f=90°C and vacuum pressure in the permeate part of the unit p_p 5 mm Hg (solid line), 20 mm Hg (dash-dotted line) and 30 mm Hg (dash line) for DEG concentration in the feed increasing from 93.5 wt% to 99.5 wt%. Geometric figures ▲ denote values of water permeate flux J_{H2O} for SepraTek membranes from (Yim and Kong, 2013) at T_f=90°C and p_p=5 mm Hg

6.5. Comparison of performance for dehydration of glycols by PV of our work with literature

When comparing data for HybSi membranes with literature data, one should keep in mind that, aside from our study (Akberov et al., 2014) and study (Yim and Kong, 2013), no other paper, to our knowledge, has ever reported results on dehydration of DEG by PV in the peer-reviewed literature. Of all glycols, EG has been the only glycol, whose dehydration by PV was studied thoroughly in laboratories. However, there exists some mentioning of PV dehydration of triethylene glycol (TEG) in (van Veen et al., 2001), but without any description of the used PV unit, experimental procedures, purity of the components and a type of the membrane module, which lowers practical importance of the result. It is worth noting that all of the three glycols (EG, DEG and TEG) can be potentially used for natural gas dehydration at CGTP (Zhdanova and Khalif, 1984).

In the peer-reviewed literature, numerous papers reported various results obtained using different glycols (EG, DEG and TEG), different ranges of feed glycol concentration, feed temperature and vacuum pressure in the permeate part of the unit, different PV units, membranes and experimental procedures. Therefore, it is nearly impossible to directly compare all the data sets from the peer-reviewed literature with each other. In addition, very few of the studies reported results on dehydration of glycols at their concentration in the feed exceeding 90 wt%, as they considered application of glycols, mainly, for deicing liquids. Since in our study we consider application of PV membranes for regeneration of DEG (and other glycols)

at CGTP of the Northern gas fields of Russia, we are interested only in those studies, which are devoted to PV dehydration of glycols at their concentration in the feed ≥90 wt%.

To our knowledge, no experimental studies have ever been performed to compare dehydration of EG, DEG and TEG by the same PV membranes and under the same process conditions. When the three glycols interact with membranes, they affect the structure of the selective layer of the membranes differently depending on the glycol, as sizes of molecules of the three glycols and their physicochemical properties are different to a certain extent, which might be important for the PV process. The work (Uddin and Hagg, 2012) investigated influence of two glycols: EG and TEG on work of polymer-based gas separation membranes destined for separation of gases CH_4 and CO_2. The study showed that presence of the two glycols in the gaseous feed mixture CH_4/CO_2 affected the membranes differently. While presence of TEG in the feed mixture increased membrane selectivity, presence of EG gave quite an opposite effect leading to decrease in the membrane's life in service.

On the other hand, separations of gaseous mixtures can be essentially different from separations of liquid mixtures by PV even if the separations are carried out by exactly the same membranes. Therefore, it appears hardly possible to draw any practical conclusions from the aforementioned study in our case. In view of the facts, we present a comparison of our results with literature data on PV dehydration of various glycols without analyzing any distinctions related to the glycol's name, as it is out of the scope of the present study.

Table 1 provides a comparison of our data for the total permeate flux J and selectivity α obtained at PV dehydration of DEG by means of HybSi membranes with literature data on PV dehydration of EG, DEG and TEG at concentration of glycols in the feed ≥90 wt%. The data are sorted in ascending order with respect to glycol concentration in the glycol/water feed mixture (from 90 to 99 wt%). Abbreviations of names of polymer materials for selective layers of the membranes, such as PECM and SPEEK, are not expanded here to avoid excessive overloading. In all of the studies, feed pressure was atmospheric except for study (Sekulic et al., 2005) in which feed pressure was maintained at the level of two to three bars. In spite of the fact that feed pressure in most of the works was atmospheric, a statement was made in those works that feed pressure has no essential impact on the PV process, which is also confirmed by our study over HybSi membranes for the case of PV dehydration of DEG.

In Table 1 for study (Sekulic et al., 2005), we put selectivity of membranes equal to infinity, since its rigorous determination from their plot for water contents in the permeate is an impossible task, as water contents in the permeate nears 100 wt% (α>>1000). As it was mentioned Subsection 6.2, membranes used in (Sekulic et al., 2005) were ceramic with a selective layer made of amorphous titania. The membranes are not suitable at all for dehydration of p-dioxane, ethanol, isopropanol and other organic substances. However, the membranes were shown to be quite efficient for dehydration of the EG/water mixture with the EG contents in the feed exceeding 85 mol% owing to hydrogen binding of EG molecules in pores of the membrane's selective layer through their hydroxyl functional groups (–OH). Despite a possibility of separation of the EG/water mixtures by using these membranes, some additional studies over the membranes are needed to determine a possibility of separation of the DEG/water mixtures as well including a study on determining influence of various impurities contained in rich DEG at CGTP on selectivity of the membranes.

One can see from Table 1 that for separations of the glycol/water mixtures, various membranes were attempted including polymer, chitosan, zeolite, titania and silica membranes. In some of the studies rather high values of the permeate flux J and selectivity α were obtained. In comparing the data given in Table 1, it turns out that HybSi membranes may not represent the best option for the glycol/water mixture separations. However, the following two circumstances must be accounted for here. First, many of the membranes from Table 1 were developed in laboratories with the pursuit of a single purpose: PV separation of the binary EG/water mixtures. In case of presence of some other constituents in the feed, it is not

guaranteed that the values of J and α will be preserved. The same statement also applies to stability of the membranes. For example, many zeolite membranes have superior molecular-sieving properties and allow efficient separations of water molecules from molecules of organic substances even at feed temperatures of ~120 °C and higher. However, zeolite membranes disintegrate at low pH values of the feed mixture, which casts a doubt on their applicability for regeneration of rich DEG at CGTP. On the other hand, HybSi membranes can sustain pH values up to ~2. This restriction applies not to the selective layer made of the HybSi material, but to the ceramic support. By replacing the material of the ceramic support with a more acidproof material, chemical stability of HybSi membranes will increase. Second, in our study the highest feed temperature T_f was 90°C, which is definitely not the highest possible operating temperature for HybSi membranes (HybSi membranes can sustain high temperatures up to 150°C for long-term exposures, whereas zeolite membranes can sustain high temperatures only up to ~130°C, and polymer membranes − only up to 90°C). It can be seen from Fig. 5 given above in Subsection 6.3 that the permeate flux J for PV separation of the DEG/water mixture by means of HybSi membranes is very strongly dependent on feed temperature T_f. One can expect that if the feed temperature T_f is increased to 150°C, which is an inadmissible temperature for all remaining membranes of Table 1, the permeate flux J for HybSi membranes will increase significantly and exceed the values for the other PV membranes of Table 1. However, it must be kept in mind that feed temperature in points of heating of the feed cannot exceed glycol's thermal decomposition temperature (for DEG: 164°C). Range of operating temperatures for HybSi membranes is shifted towards higher temperature values.

It is worth noting that, of all the studies described in Table 1, only studies (Jehle et al., 1995; Nik et al., 2006; Yu et al., 2012; Yim and Kong, 2013; Akberov et al., 2014) are devoted to PV dehydration of glycols by means of commercially available membranes. The remaining studies are devoted to PV dehydration of glycols by membranes developed in laboratories for purely scientific purposes. At that, only study (Yu et al., 2012) is devoted to PV dehydration of a glycol (EG) using a pilot-scale unit with the total membrane surface area ~3 m². The study compared data obtained at the pilot-scale unit with data obtained at a small lab-scale unit and drew a conclusion that the total permeate flux values J measured during pilot testing turn out to be somewhat lower compared to values measured during lab testing, and concentration polarization is found to be stronger. It is also noteworthy that, except for HybSi membranes, no other membranes of Table 1 passed lab testing within several years of continuous operation (at least, for PV separation of glycol/water mixtures), and field data obtained at commercial PV plants are not public and have never been published in the open scientific literature. All remaining studies of Table 1 were carried out within several hours of experimental operation except for two studies reported in (Du et al., 2008; Wang et al., 2011) in which, in addition to short-term experiments, the membrane stability was investigated within ~1 month of continuous operation of a PV unit dehydrating the EG/water mixtures.

Table 1
Comparison of performance for dehydration of glycols (EG, DEG and TEG) by PV of our study with previous studies

Glycol/ conc., (wt%)	Material of selective layer	Membrane shape	T_f, °C	p_p, mm Hg	J, kg/m²h	α	Ref.
EG/90	PVA-PSF/TMC	Plate	60	≤ 2.3	0.360	987	(Hyder et al., 2009)
EG/90	Chitosan-PVA blend	Plate	70	≤ 2.3	0.460	663	(Hyder and Chen, 2009)
EG/90	PVA-GA	Plate	70	5.0	0.093	800	(Guo et al., 2007)

EG/90	PECM	Plate	70	5.0	0.065	150	(Hu et al., 2007)
EG/90	NaA zeolite	Tube, coated outside	70	≤ 3.8	0.630	1300	(Nik et al., 2006)
TEG/91	Silica	Tube, coated outside	80	6.0	0.184	2054	(van Veen et al., 2001)
EG/94	SPEEK	Plate	32	3.0	0.018	2220	(Huang et al., 2002)
EG/94	PDMAEMA/ PSF	Plate	30	10.0	0.222	600	(Du et al., 2008)
EG/95	Chitosan/PSF	Plate	35	0.5	0.200	112	(Feng and Huang, 1996)
EG/95	Chitosan coated zeolite	Plate	50	1.5–3.8	0.406	76	(Dogan et al., 2010)
EG/95	PAA/PVA/IPN (PAA/PVA:30/ 70)	Plate	50	1.0	0.225	360	(Burshe et al., 1998)
EG/95	Surface crosslinked chitosan	Plate	80	5.0	0.200	1248	(Nam and Lee, 1999)
EG/96	Crosslinked phosphorylated chitosan	Plate	30	0.3	0.378	234	(Rao et al., 2007)
EG/96	PVA/PAN GFT 1510	Plate	75	15.0–23.0	1.350	841	(Jehle et al., 1995)
EG/97	PAA-PEI polyelectrolyte	Plate	40	≤ 4.0	0.400	340	(Xu et al., 2010)
EG/97	Chitosan coated zeolite	Plate	75	4.5	0.245	101	(Kuila et al., 2011)
EG/98	NaA zeolite	Tube, coated outside	65	≤ 3.8	0.800	16000	(Jafari et al., 2013)
EG/98	Microporous titania	Tube, coated outside	80	4.5–6.0	0.227	∞	(Sekulic et al., 2005)
EG/99	PVAm-PVA/ CNT (2% CNT)	Plate	70	1.0	0.146	1160	(Hu et al., 2012)
EG/99	NaA zeolite	Tube, coated outside	100	7.5-15.0	0.030	1014	(Yu et al., 2012)
EG/99	PBI/PEI	Hollow fiber, coated inside	60	1.5	0.005	30000	(Wang et al., 2011)
DEG/99	PVA/acrylate (SepraTek)	Hollow fiber, coated inside	90	5.0	0.083	95	(Yim and Kong, 2013)

| DEG/99 | Hybrid silica (HybSi) | Tube, coated inside | 90 | 20.0 | 0.070 | 9800 | Our study (Akberov et al., 2014) |

6.6. Method for determining the required membrane surface area

An important parameter for engineering a PV unit is the value of required membrane surface area A_{req} depending on the unit's capacity, feed composition and process conditions (feed temperature T_f, vacuum pressure in the permeate part of the unit p_p, etc.). Most methods for determining the required membrane surface area utilize the assumption that the membranes have infinite selectivity to the desired component of the feed mixture meaning that only the desired component may permeate through the membranes (Akberov et al., 2014; Nunes and Peinemann, 2006). Unlike HybSi membranes, SepraTek membranes mentioned above do not have a sufficiently high selectivity to water for separation of the DEG/water mixture (selectivity to water is less than 150). At this time, there exists information on possibility of PV dehydration of DEG using only these two types of membranes (Akberov et al., 2014; Yim and Kong, 2013). Thus, for comparing the values of the required membrane surface area A_{req} for these two types of membranes under the same process conditions, feed compositions and the unit's capacities, some other approaches must be developed.

In the present work, a unit regenerating DEG at the rate 1000 kg/h is considered. The required membrane surface area A_{req} can be approximately determined through measuring the time of dehydration t_{deh} of the feed of initial weight m_f through the membrane surface area A_m used in the experiments from the initial mass concentration of DEG in the feed (retentate) to the final concentration via the formula: $A_{req} = 1000 A_m t_{deh} / m_f$. For HybSi membranes: m_f=1.5 kg, A_m=0.04 m^2; for SepraTek membranes: m_f=2.5 kg, A_m=0.16 m^2. The values of t_{deh} (in hours) are taken directly from the measured dependencies of the DEG concentration in retentate on time. In (Yim and Kong, 2013), dehydration of DEG was carried out by SepraTek membranes in the range of the DEG concentration 98–99.5 wt%. We extrapolated these data to the range 97–99.5 wt% having a greater practical importance for CGTP for making possible a comparison with data (Akberov et al., 2014) obtained for HybSi membranes. In view of difficulty of extrapolation of these data up to the DEG concentration of 93.5 wt%, results for SepraTek membranes are shown below only for the range of the DEG concentration: 97–99.5 wt%. For HybSi membranes, results obtained using this approach diverge from results obtained using the approaches from (Akberov et al., 2014) and (Nunes and Peinemann, 2006), which imply integrating the curves of Fig. 5–6, by not more than 5%.

Thus, data obtained via our lab-scale unit are scaled up to the pilot-scale unit that regenerates DEG at the rate 1000 kg/h. As it was mentioned in Subsection 6.5, in study (Yu et al., 2012), results obtained using a pilot-scale unit designed for dehydration of the EG/water mixture were compared with results obtained using a lab-scale unit for the same dehydration case. It was shown that the values of the total permeate flux J obtained during pilot testing are somewhat lower compared to values obtained during lab testing, which inevitably leads to some increases in the values of A_{req}. However, in our study, the differences between pilot and lab testing cases are neglected.

6.7. Dependence of the required membrane surface area on feed temperature

Fig. 7 shows the value of the required membrane surface area A_{req} as a function of feed temperature T_f for both HybSi and SepraTek membranes. It is noteworthy that for the identical range of the DEG concentration in the feed, i.e. 97–99.5 wt%, HybSi membranes yield to SepraTek membranes at feed temperatures of 70 and 80°C but surpass them at feed temperature T_f=90°C. For SepraTek membranes, the values of the required membrane surface area A_{req} are 1010, 710 and 680 m^2 at the values of the feed temperature T_f 70, 80 and 90°C, respectively, and for HybSi membranes, the values are 1820, 790 and 230 m^2 for the same values of the feed

temperature. It follows from the figure that the feed temperature T_f=80°C is close to the optimum feed temperature for SepraTek membranes. Note also that in our experiments the feed temperature T_f was limited from above by the value of 90°C due to risk of thermal decomposition of DEG in the feed tank in points of feed heating where the feed's local temperature achieves ~163°C upon increasing the process temperature T_f inside the PV module from 90 to 100°C and higher. This restriction applies only to the study described here and can be lifted for engineering a full-scale PV unit for CGTP in the future (HybSi membranes can sustain high temperatures up to 150°C for long term exposures and 190°C for short term exposures). Therefore, we consider temperature T_f =90°C as the value close to the optimum feed temperature for HybSi membranes, if the above temperature restriction applies to the PV unit. As a whole, dependence of the required membrane surface area A_{req} on feed temperature T_f in the temperature range 70–90°C is expressed more strongly for HybSi membranes than for SepraTek membranes, which can be related to the smaller size of pores of the selective layers of HybSi membranes (less than 1 nm).

It also follows from Fig. 7 that for HybSi membranes increase in the saturation level from 2.5 wt% to 6 wt% at CGTP leads to increase in the required membrane surface area A_{req} by 15, 15 and 22% at the feed temperature values 70, 80 and 90°C, respectively.

For these data, Table 2 provides quantitative assessment of the rate of increase of the required membrane surface area A_{req} (m²/°C) for decreases of feed temperature T_f 90°C→80°C and 80°C→70°C for a PV unit utilizing either HybSi or SepraTek membranes and regenerating DEG at the rate 1000 kg/h in the investigated DEG concentration ranges. Note that for HybSi membranes: p_p=20 mm Hg, and for SepraTek membranes: p_p=5 mm Hg. One can see from Fig. 6 shown in Subsection 6.4 that for HybSi membranes the total permeate flux J hardly changes with a change in p_p in the range of p_p from 5 to 20 mm Hg, which allows comparing the values of A_{req} for these two types of membranes despite differences in the values of p_p.

Table 2
Increase of required membrane surface area A_{req} (m²/°C) for decreases of feed temperature T_f 90°C→80°C and 80°C→70°C for a PV unit utilizing either HybSi or SepraTek membranes and regenerating DEG at the rate 1000 kg/h. For HybSi membranes: p_p=20 mm Hg, and for SepraTek membranes: p_p=5 mm Hg

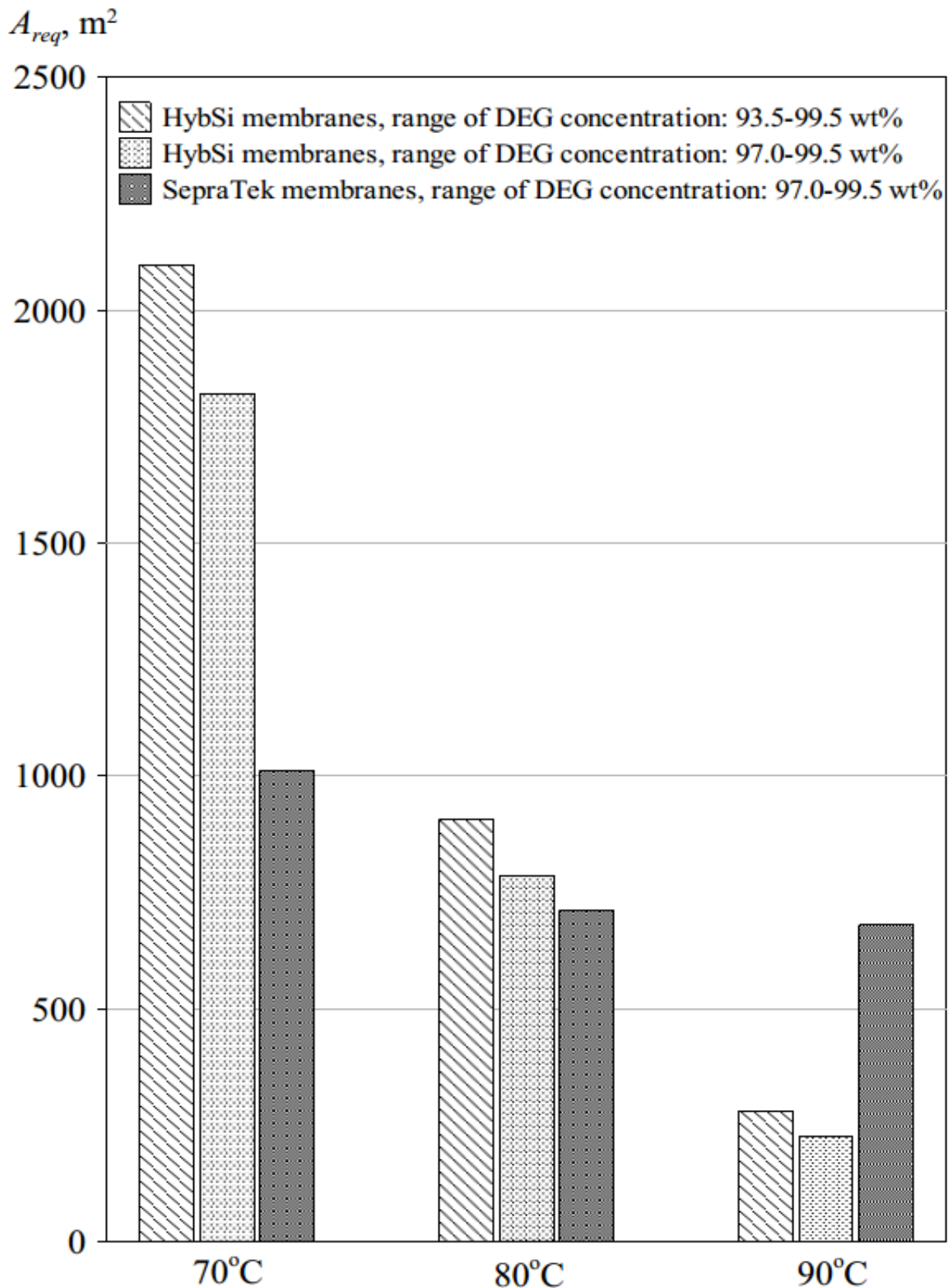| Decrease of T_f	Increase of A_{req}, m²/°C		
	HybSi		SepraTek
	97–99.5 wt%	93.5–99.5 wt%	97–99.5 wt%
90°C→80°C	56	63	3
80°C→70°C	103	119	30

Fig. 7. Dependence of required membrane surface area A_{req} on feed temperature T_f for a PV unit utilizing either HybSi membranes or SepraTek membranes and regenerating DEG at the rate 1000 kg/h. For HybSi membranes: $p_p=20$ mm Hg, and for SepraTek membranes: $p_p=5$ mm Hg

6.8. Dependence of the required membrane surface area on vacuum pressure in the permeate part of the unit

Fig. 8 shows the value of the required membrane surface area as a function of vacuum pressure in the permeate part of the unit p_p for feed temperature T_f=90°C for a PV unit utilizing HybSi membranes and regenerating DEG at the rate 1000 kg/h. For dehydration in the range of the DEG concentration 97–99.5 wt%, the values of the required membrane surface area A_{req} are 195, 230 and 280 m^2 at the values of vacuum pressure in the permeate part of the unit p_p 5, 20 and 30 mm Hg, respectively, and for the DEG concentration range 93.5–99.5 wt%, the values of the required membrane surface area A_{req} are 240, 280 and 340 m^2 at the same values of vacuum pressure in the permeate part of the unit p_p. Thus, it follows for HybSi membranes that increase in the saturation level from 2.5 wt% to 6 wt% at CGTP leads to increase in the required membrane surface area by 23, 22 and 21% at values of vacuum pressure in the permeate part of the unit p_p equal to 5, 20 and 30 mm Hg, respectively, for feed temperature T_f=90°C.

Table 3 provides quantitative assessment of the rate of increase of the required membrane surface area A_{req} (m^2/mm Hg) for increase of vacuum pressure in the permeate part of the unit p_p for a PV unit utilizing HybSi membranes and regenerating DEG at the rate 1000 kg/h. It follows from these data that the value of vacuum pressure in the permeate part of the unit p_p=20 mm Hg is close to the optimum value, which can be regarded as an additional proof of a conclusion made in Subsection 6.4 at consideration of data for the total permeate flux *J*. As to SepraTek membranes, tests of the membranes were carried out only at one value of vacuum pressure in the permeate part of the unit equal to 5 mm Hg.

Table 3

Increase of required membrane surface area A_{req} (m^2/mm Hg) for increases of vacuum pressure in the permeate part of the unit p_p for a PV unit utilizing HybSi membranes and regenerating DEG at the rate 1000 kg/h at temperature T_f=90°C

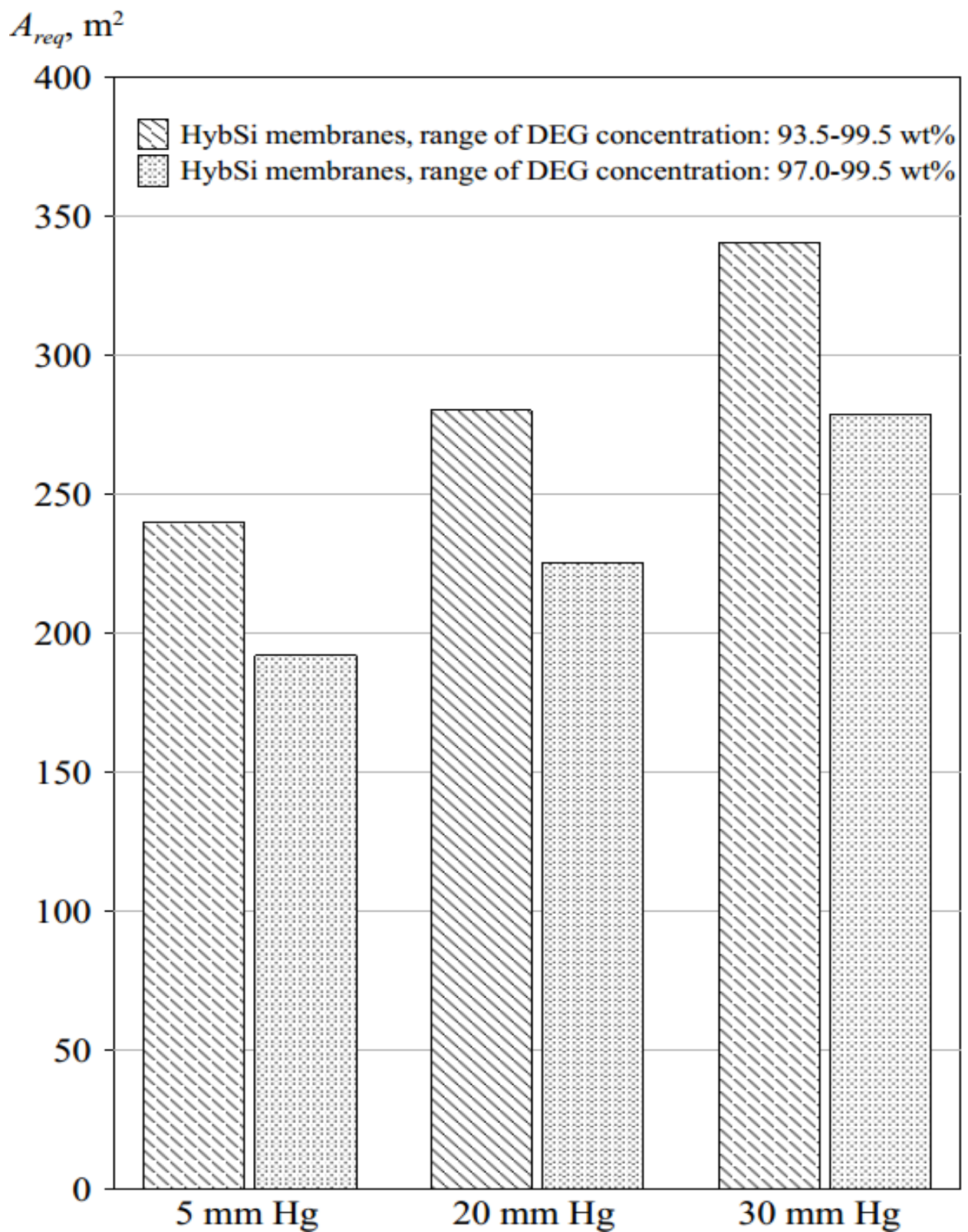| Increase of p_p	Increase of A_{req}, m^2/mm Hg	
	HybSi	
	97–99.5 wt%	93.5–99.5 wt%
5 mm Hg→20 mm Hg	2.3	2.7
20 mm Hg→30 mm Hg	5.0	6.0

Fig. 8. Dependence of required membrane surface area A_{req} on vacuum pressure in the permeate part of the unit p_p at feed temperature T_f=90°C for a PV unit utilizing HybSi membranes and regenerating DEG at the rate 1000 kg/h

6.9. Losses of DEG for DEG regeneration by PV and stripping

For HybSi membranes, DEG contents in permeate was roughly 1 wt% for all process conditions (Akberov et al., 2014), and for SepraTek membranes, DEG contents in permeate was 63, 55 and 51 wt% for feed temperatures T_f 70, 80 and 90°C, respectively, for the residual water contents in the feed equal to 1 wt% (Yim and Kong, 2013). Table 4 provides assessment of DEG losses for a unit regenerating DEG at the rate 1000 kg/h by PV with the use of HybSi and SepraTek membranes and by stripping.

Table 4
Losses of DEG at PV using HybSi and SepraTek membranes and at stripping for a unit regenerating DEG at the rate 1000 kg/h. DEG flux through membranes J_{DEG} is taken for the case of water contents in retentate (in the feed) equal to 1 wt%

T_f, °C	A_{req}, m^2		J_{DEG}, kg/m^{2}h		Losses of DEG at PV, ton/year		Losses of DEG at stripping, ton/year
	HybSi	SepraTek	HybSi	SepraTek	HybSi	SepraTek	
70	1820	1010	8E-5	0.040	1.3	353.9	
80	790	710	2E-4	0.041	1.4	255.0	2.1
90	230	680	7E-4	0.043	1.4	256.1	

In Table 4: $J_{DEG}=y_b J/100\%$. For HybSi membranes: J=0.008, 0.020, 0.070 kg/m^{2}h for feed temperatures T_f 70, 80, 90°C, respectively; y_b=1 wt%. For SepraTek membranes: J=0.063, 0.075, 0.083 kg/m^{2}h; y_b=63, 55, 51 wt% for the same feed temperatures T_f. Losses of DEG at PV are determined by the following expression: $A_{req}J_{DEG}\cdot24\cdot365/1000$ (ton/year). Losses of DEG at stripping constitute 3.5 g per 1000 standard cubic meters of dehydrated natural gas based on data from (Zhdanova and Khalif, 1984) (similar values are also found in (Bekirov and Lanchakov, 1999)). Here it is considered that for dehydration of natural gas at the rate 68000 standard cubic meters per hour during the cold period of the year, a unit regenerating rich DEG at the rate 1000 kg/h is required in line with calculations performed with the use of methods described in (Bekirov and Lanchakov, 1999) and (Lanchakov et al., 2000). It follows from Table 4 that DEG losses through HybSi membranes are of the same order of magnitude as DEG losses at stripping and they are smaller by two orders of magnitude than DEG losses through SepraTek membranes.

6.10. Additional operational costs for DEG regeneration by PV and stripping

At regeneration of DEG by stripping, on flame tubes of the evaporator a part of DEG decomposes into carboxylic acids, aldehydes, ketones, etc. leading to destruction of a material of the flame tube walls (Russian steel grades equivalent to AISI 321) as well as of a material of the lean-rich DEG exchanger and of the stripper internals. Some alkalies are added to the system to reduce corrosion of the equipment. At the same time, formation of resins on contact surfaces of the flame tube walls results in significant reduction of their heat transfer coefficient. In line with (Elistratov, 2004), repairs of evaporators of the fired heaters at CGTP occur every 3–4 years, and a CGTP, processing 25 billion standard cubic meters of natural gas per year, requires a replacement of 14 tons of the used flame tubes by the new ones during those repairs. Then, a natural gas dehydration plant, processing 68000 standard cubic meters of natural gas per hour, requires, roughly, a replacement of 0.381 kg of the used flame tubes by the new ones. The amount of works and equipment downtime, associated with those repairs, are also quite important. In addition, the stripper internals must also be periodically replaced with the new internals.

In line with data (Jonquières et al., 2002), energy expenditures for carrying out the PV process can be up to 60% lower than energy expenditures for carrying out the distillation

process for dehydrating organic solvents at industrial plants. In case of DEG regeneration by stripping, the greatest energy expenditures are associated with heating the rich DEG by means of burning a wellhead gas or a stripping gas. As to vacuum stripping for regenerating DEG at the rate 1000 kg/h, a column of the packed type would be a preferred option due to a small capacity of the unit and, hence, to a small diameter of the column. A variety of column internals can be used in this application, such as the Montz-pak B1-250 block-structured packing (Olujic et al., 1999). For a vacuum pressure in the column as small as 300 mm Hg (a typical vacuum pressure for vacuum strippers) in case of DEG dehydration in the range of the DEG concentration 97–99.3 wt%, diameter and height of the column filled with the above internals will be 0.12 m and 6.2 m, respectively. At that, energy consumption for heating the rich DEG from 20°C (the assumed temperature of natural gas dehydration in the absorber of CGTP) up to the required process temperature will be about 91.0 kW. For comparison, energy consumption for carrying out PV, i.e. for heating the rich DEG from 20°C up to the optimum process temperature 90°C, will be 40.7 kW, which is lower by ~55% than energy consumption for vacuum stripping.

In case of using a stripping gas in the stripping column (instead of vacuum), regeneration of the stripping gas (methane: ~99%, other hydrocarbons: ~1% with possible presence of N_2, CO_2, H_2S, etc. in trace concentrations in most of the Northern gas fields (Bekirov and Lanchakov, 1999; Gritsenko et al., 1999; Vyakhirev et al., 2002)) represents certain technical difficulties. Hence, some additional capital and operational costs must be borne to reduce a risk of the stripping gas exiting to the atmosphere, which would result in environmental pollution, contribution to the Earth's greenhouse effect, emergencies during explosions and other complications.

6.11. Proposed system of natural gas dehydration by absorption with DEG regeneration in the PV unit

Fig. 9 shows a simplified schematic of a proposed natural gas dehydration system by absorption for CGTP with regeneration of DEG in the PV unit. The PV unit works in the continuous regime regenerating rich DEG up to a required concentration within one pass. In case of using SepraTek membranes in place of HybSi membranes, recovery of DEG from the permeate stream is needed. For that, either a stripping column or a supplementary PV unit with organophilic or molecular-sieving membranes must be used (Li et al., 2007; Khachonbun, 2013). Lifetime of HybSi membranes is 5-6 years. Lifetime of SepraTek membranes is not yet known at this time. Exact parameters of the regeneration equipment are to be clarified after completing all pilot tests with genuine samples of rich DEG from CGTP. Also, laboratory studies on thermal stability, durability and chemical stability of the membranes with respect to broad temperature fluctuations, solid particles and substances absorbed by DEG from natural gas during absorption (e.g., salts: NaCl, $MgCl_2$, $CaCl_2$, etc.) are needed along with investigations on erosive wear, attrition and leaching (for HybSi membranes) in selective layers of the membranes. At the Russian CGTP, a variety of filters, sediment tanks, cyclones and other apparatuses for purification of DEG are already used today quite efficiently (Andreev et al., 2010).

The proposed schematic may also be used at those CGTP, in which TEG is used as a liquid absorbent instead of DEG. Our preliminary tests with HybSi membranes have shown that the values of selectivity α and permeate flux J for TEG dehydration are comparable to those observed for DEG dehydration. TEG is a much more commonly used absorbent for natural gas dehydration elsewhere in the world, and a trend to replace DEG by TEG at CGTP has come forward in recent years in Russia's Northern gas fields as well as (e.g., Zapadno-Tarkosalinskoe field). TEG has many advantages over DEG including a higher thermal degradation temperature of 206°C (i.e. regeneration can be carried out in the stripper without applying vacuum or a

stripping gas), less toxicity and fewer losses at absorption due to smaller vapor pressure, which compensate a slightly higher cost of TEG compared to the cost of DEG.
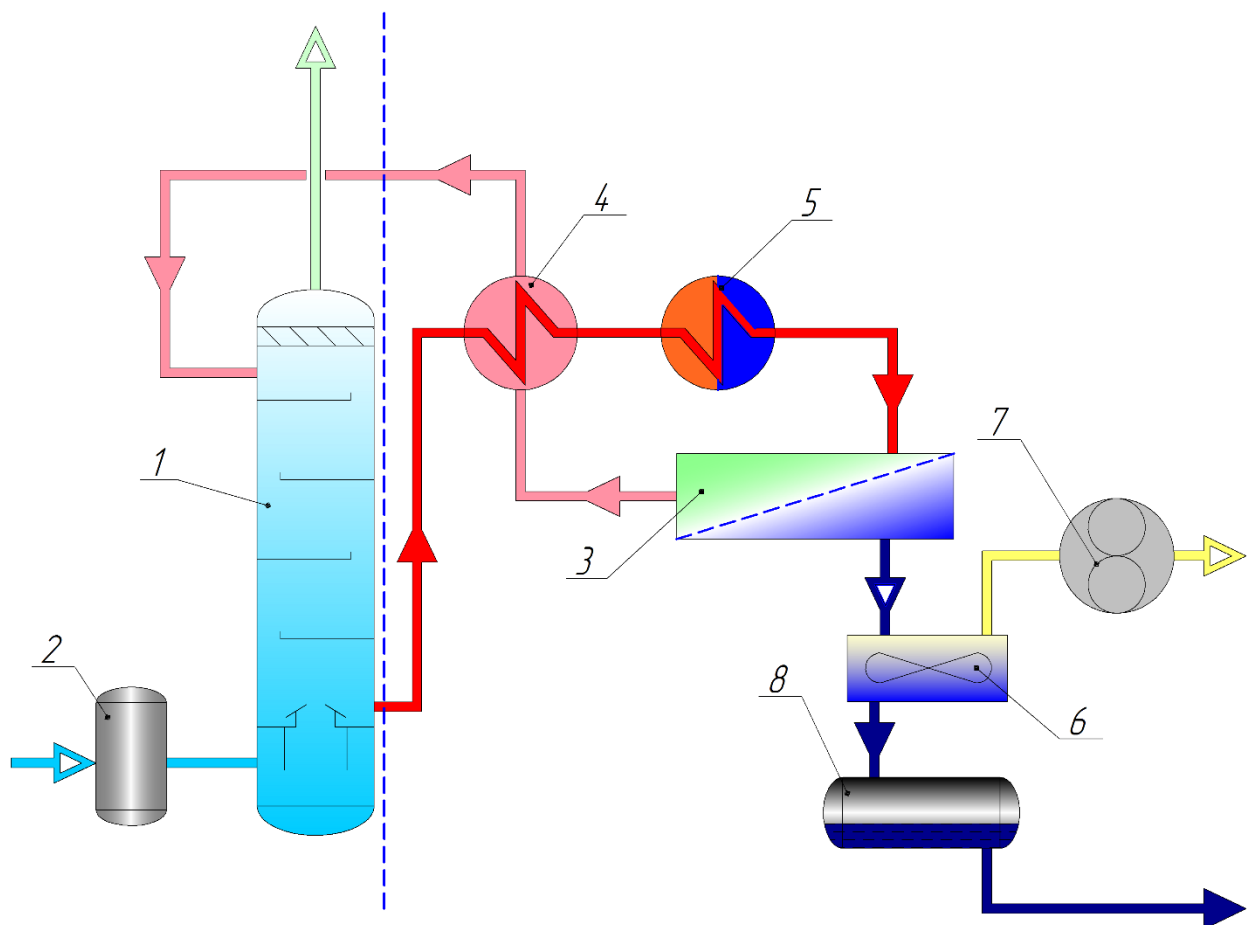

Fig. 9. Proposed natural gas dehydration system by DEG absorption for CGTP with regeneration of DEG in the PV unit: *1* – absorber; *2* – inlet scrubber; *3* – PV membrane module; *4* – lean-rich DEG heat exchanger; *5* – fired heater; *6* – condenser; *7* – vacuum pump; *8* – permeate collection vessel.

6.12. Limitations of the DEG regeneration technology by PV with the use of HybSi membranes

Based on data from manufacturer of the HybSi membranes (Pervatech BV), data from developer of the HybSi material (Energy Research Centre of the Netherlands) and our own data, limitations for a PV unit destined for DEG regeneration at CGTP with the use of tubular ceramic membranes coated on the inside with the HybSi material, are given in Table 5. The limitations apply to the membrane tubes having the inner and outer diameter equal to 7 mm and 10 mm, respectively.

Table 5
Limitations of the DEG regeneration technology by PV with the use of ceramic membranes coated on the inside with the HybSi material and having the inner and outer diameter equal to 7 mm and 10 mm, respectively

Name of parameter	Range of admissible values
Feed part	
- feed temperature, °C	70 … 150
- feed pressure, atm (absolute)	1 … 7
- linear speed in membrane, m/s	1 … 7
- feed composition	Mainly, DEG and water. Absence of inorganic salts, solid particles, resins. 2<pH<8
Permeate (vacuum) part	
- cooling agent temperature (water), °C	1 … 5
- vacuum pressure, mm Hg	~0 … 30
Membrane module	
- Location of membrane tubes inside the membrane module	In-series, if pressure drop on the feed side between entrance and exit from the membrane module, caused by hydraulic resistance, exceeds several bars, which is related to membrane fragility. Otherwise, location is either in-parallel or combined: in-series + in-parallel

Limitations for feed composition were mentioned above in Section 3. The lower limitation for feed temperature is related to absence of pervaporation at feed temperatures lower than the limiting value (i.e. pervaporation rate is inappreciable for membrane surface area of 0.04 m^2). The upper limitation for feed temperature is related to thermal stability of HybSi membranes. The lower and upper limitations for feed pressure are related to prevention of a risk of cavitation of the feed pump and fragility of the membrane tubes, respectively. The lower and upper limitations for linear speed of the feed mixture in the membrane tubes are related to prevention of concentration polarization and erosion of the selective layer, respectively. The lower and upper limitations for temperature of the cooling agent (water) in the condenser of the permeate part of the unit are related to prevention of cooling agent freezing and possibility of vacuum creation, respectively. The upper limitation for vacuum pressure in the permeate part of the unit is related to a sharp decrease in driving force for PV through HybSi membranes when this limitation value is exceeded.

The number of membrane modules and location of the membrane modules with respect to each other (in-series or in-parallel) will be determined, mainly, by the available spacing for the PV unit at CGTP. The final operating parameters of the PV unit equipped with HybSi membranes will be determined after completing all pilot tests with genuine samples of rich DEG from CGTP. As to SepraTek membranes, no information on such limitations is available in the open literature.

7. Conclusions
The study showed that HybSi membranes produce a positive effect upon dehydration of a DEG/water mixture in the DEG concentration range 93.5–99.8 wt%. DEG dehydration up to 99.8 wt% requires a membrane surface area, which is roughly twice as much as a required membrane surface area for DEG dehydration up to 99.5 wt%.

Based on the conducted experimental study of PV dehydration of DEG up to 99.5 wt %, it can be concluded that the following operating conditions for a PV unit working on HybSi membranes are close to optimum conditions: vacuum pressure in the permeate part of the unit p_p=20 mm Hg and feed temperature T_f=90°C. Increase in the saturation level from 2.5 wt% to 6 wt% at CGTP leads to inessential increase in the required membrane surface area A_{req} (by not more than 25%). DEG losses through HybSi membranes do not exceed DEG losses at stripping (due to high selectivity of HybSi membranes to water for the DEG/water mixture separation) and they are smaller by two orders of magnitude than DEG losses through SepraTek hollow-fiber polymer membranes. Use of PV instead of stripping for diethylene glycol regeneration leads to more than two-fold energy saving. Studies on PV dehydration of genuine samples of rich DEG from CGTP as well as laboratory studies on thermal stability, durability and chemical stability of the membranes are needed for determining parameters of the proposed pilot unit for regeneration of rich DEG by HybSi membranes.

The PV technology with the use of HybSi membranes can become an alternative to conventional stripping technologies: stripping under vacuum and stripping with the use of a stripping gas, which are widely used today for deep regeneration of DEG at the Russian CGTP. Results of the study can be used for designing a pilot-scale PV unit for DEG dehydration working on HybSi membranes and for developing theoretical models of separation.

Symbols used

A_m membrane surface area, m^2
A_{req} required membrane surface area, m^2
J total permeate flux through the membranes, $kg/(m^2\,h)$
m_p weight of collected permeate, kg
m_f initial weight of feed, kg
p_p vacuum pressure in the permeate part of the unit, mm Hg
T_f feed temperature, ºC
t time, h
t_{deh} time required for dehydration, h
x mass concentration of a component in retentate (in the feed), wt%
y mass concentration of a component in permeate, wt%
α selectivity
Δt sampling time, h

Subscripts

a, b components of the binary mixture (a is water; b is DEG)
DEG DEG
deh dehydration
f feed
$H2O$ water
m membrane
n number of the (–CH_2–) groups in the molecular structure of HybSi
p permeate
req required

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