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APPLICATION OF PERVAPORATION IN GASOLINE DESULFURIZATION - VARIOUS SULFUR COMPOUNDS REMOVAL EFFICIENCY

ZASTOSOWANIE PERWAPORACJI DO ODSIARCZANIA BENZYNY - EFEKTYWNOŚĆ USUWANIA RÓŻNYCH ZWIĄZKÓW SIARKI

Abstract: In order to adapt to new and more rigorous requirements and to satisfy higher environmental expectations, specifications on sulfur content in gasoline demands a reduction of its level to 10 ppm. Sulfur in gasoline is a considerable source of sulfur oxides emissions. SO_x, which are formed during the combustion of sulfur-containing fuels, are sulfates precursors, which contributes to the formation of acid rains and further acidification of soils and surface water. Since sulfur is present in gasoline in a form of different compounds (such as thiophene and its derivatives, mercaptans and sulfides) and different sulfur species show different affinity with membrane materials, it is very important to investigate the efficiency of their removal separately. The aim of this research was to recognize the influence of typical chosen sulfur compounds present in gasoline on membrane pervaporation behavior and the efficiency of sulfur species separation. The influence of process parameters such as feed temperature, feed concentration and downstream pressure on the efficiency of thiophenes removal from model *n*-octane/sulfur compound mixtures by means of vacuum pervaporation method was also examined. During the test, the hydrophobic PDMS-based composite membrane were applied. Binary mixtures of thiophene/*n*-octane and 2-methylthiophene/*n*-octane were used as a model gasoline. The content of sulfur from thiophenes varied from 0.05 to 0.13 mas. %. Feed temperature was ranged from 30 to 50°C. The feed flow rate (80 dm³/h) was kept at constant level.

Keywords: vacuum pervaporation, desulfurization, thiophenes, gasoline

Introduction

Nowadays a lot of attention is being paid to the reduction of sulfur concentration in transportation fuels. In order to adapt to new and more rigorous requirements and to satisfy higher environmental expectations, specifications on sulfur content in gasoline demands a reduction of its level to 10 ppm [1].

Sulfur oxides, which are formed during the combustion of sulfur-containing fuels, are sulfates precursors which contributes to the formation of acid rains and further acidification of soils and surface water, as well as the formation of photochemical smog. Moreover, their presence in exhaust gases from vehicles contributes to the larger emission of NO_x and VOC's caused by the reduction of low-temperature catalytic converters activity.

Trade gasoline is a blend of gasoline fractions coming from various refinery processes such as light straight run, catalytic reforming, isomerization and fluid catalytic cracking (FCC). Streams derived from reforming and isomerization processes are generally characterized by low sulfur content, as feedstocks for those units are light fractions from the atmospheric distillation of crude oil [2]. Sulfur organic compounds tends to accumulate in higher-boiling fractions like atmospheric residue and fractions obtained from vacuum

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distillation, which are feedstocks for FCC units. Therefore, FCC gasoline is the main contributor of organosulfur compounds [3]. Although sulfur is present in gasoline in the form of different compounds, it occurs mainly in thiophenes, sulfides, mercaptans and disulfides [2, 3].

A lot of effort is now spent on developing novel and efficient hydrogen and non-hydrogen desulfurization technologies, such as selective extraction, catalytic extraction, selective oxidation, biodesulfurization, alkylation-extraction, improved selective hydroprocessing and pervaporative desulfurization (PVDS) [4, 5]. It should be noted, that some of them, including pervaporation, has already progressed beyond the lab-scale tests stage. In comparison with the traditional and other non-hydrogen separation processes, membrane separation offers many advantages including lower energy consumption and operating cost, simple operation and control scheme, easy scale up and adaptability to changes in process streams [6].

Pervaporation is a membrane technique, in which a first-order phase transition takes place. In pervaporation separation a dense non-porous membranes are applied. The liquid feed is contacted with the surface of the membrane and a specific compound is preferentially dissolved and transported across the membrane and then removed as vapour at the downstream side of the module. As a result of the separation, feed solution is divided into permeate and retentate streams. The vapour permeate is enriched in the component selectively transported through the membrane, while the liquid retentate in the component retained by the dense separation barrier. The vacuum pervaporation is carried out by maintaining the downstream pressure, lower than the saturation pressure of the permeating liquid solute at operating temperature [7]. The overall accepted mechanism explaining the mass transport across the dense membrane is solution-diffusion model [8].

Separation in the case of pervaporation is based on the affinity between compound being removed and membrane material. According to the mass transport model, pervaporation process can occur only when a certain amount of a compound is dissolved in the membrane material in the first stage of pervaporation separation. In the second stage, diffusion through the membrane combined with plasticization of its amorphous parts takes place. Diffusion step with a step of the sorption determine the selectivity of the process. The permeated compounds are then removed on the opposite side. The driving force for the separation process *i.e.* the partial pressure gradient between feed and permeate site, is maintained by constant withdrawn of the permeated compounds from the membrane [8].

To ensure the efficient process performance, the material of an active layer needs to show high affinity toward removed component. Hence, solubility parameter δ ((MPa)^{1/2}) and membrane polarity are the two main factors used for the preliminary evaluation of the interaction between the polymeric membrane and components of the mixture, as well as development of the novel membrane materials. The more similar the solubility parameters of the polymer and solvent, the more soluble solvent in the polymer [9]. In order to remove a specific component or group of compound from a mixture, the polarity of those species must be close to the polarity of the polymeric material used [10].

The aim of this research was to recognize the influence of typical chosen sulfur compounds present in gasoline on membrane pervaporation behavior and the efficiency of sulfur species separation. The influence of process parameters such as feed temperature, feed concentration and downstream pressure on the efficiency of thiophenes removal from

model *n*-octane/sulfur compound mixtures by means of vacuum pervaporation method was also examined.


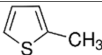
Experimental

Materials

To prepare the model gasoline, thiophene (99.5%, extra pure, benzene free) obtained from Acros Organics, 2-methylthiophene (98% purity) obtained from Sigma-Aldrich and *n*-octane (pure p.a.) obtained from Chempur were used. The physical and chemical characteristics of the investigated are listed in Table 1. Composite membranes consisting of a porous support with thin and dense poly(dimethylsiloxane) separating layer were obtained from PERVATECH, Netherlands.

Table 1

The physical and chemical characteristics of the investigated

Compound		Structural formula	Molecular weight [g/mol]	<i>B_p</i> [°C]	Vapour pressure [hPa]	δ [(MPa) ^{1/2}]
Hydrocarbon	<i>n</i> -octane	CH ₃ (CH ₂) ₆ CH ₃	114.23	125	14.7	15.5
Sulfur compound	thiophene		84.14	84	53 ^a	20
	2-methylthiophene		98.17	113	63.4 ^b	18.6

B_p - boiling point; δ - Hansen solubility parameter

Feed and permeate samples analysis

During studies, SRI 8610C Instruments Gas Chromatograph equipped with a dual FPD/ FID (flame photometric/flame ionization detector) detector and a Restek DB-1 MTX capillary column company (0.5 μ m, 0.53 mm \times 60 m) was used. The sample volume was 0.6 μ m³. Samples were injected manually using a SGE Analytical Science micro-syringe with a capacity of 5 μ m³. Retention time for thiophene was 3.45 min, for 2-methylthiophene was 6.73 min. The retention time for *n*-octane presented in samples from PV desulphurization process was 7.98 min. The temperature of the injector and detectors was 100 and 200°C, respectively. The column was conditioned each time before starting analysis. To ensure high purity of gases, additional air and hydrogen filters were installed.

Pervaporation experiments

The Sulzer lab-scale pervaporation setup, equipped with a test module with a diameter of 9 cm and a membrane effective area of 55 cm² was used for vacuum pervaporation measurements (Fig. 1). To prevent the mechanical damage of a membrane, it was kept on highly porous stainless steel support. The feed solution, maintained at a constant temperature by a thermostat (Thermo Electron Co., model Haake DC 30), was circulated to the upstream side of the cell using a recirculation pump. The permeated vapours were condensed by a cold traps cooled by immersion in Dewar flasks filled with liquid nitrogen,

while retentate was returned to the feed tank. Permeates were collected within a specified time interval. The cold traps were then brought to room temperature prior to measure their weight using a balance (RadWag PS 210/C/2). The membrane upstream side was kept at atmospheric pressure. A vacuum pump (Alcatel, model Pascal 2015 SD) was used to create a vacuum in the downstream side of the module and to ensure the pressure gradient across the membrane. The temperature was controlled through a PID controller device (Greisinger Electornics GTH 1100/2 DIF). Sufficient feed flow rate was maintained using a circulation pump. Total downstream pressure was measured by an electronic vacuum gauge (Vacuubrand DRV 2).

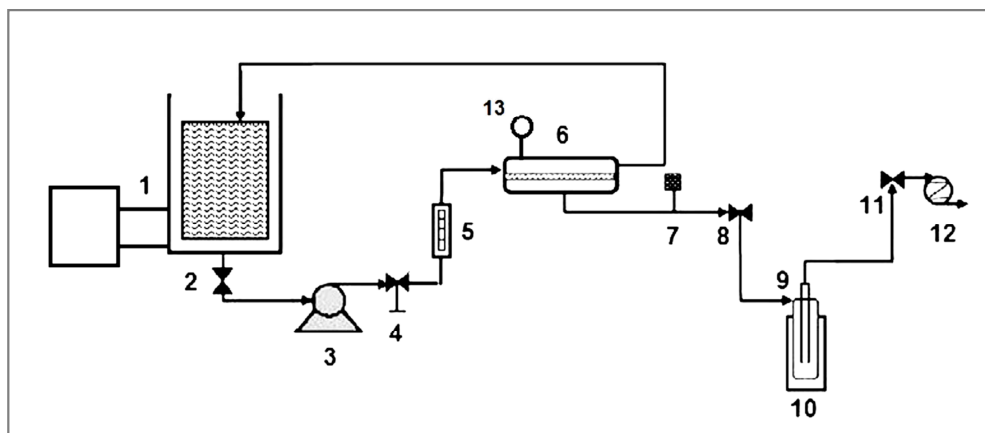


Fig. 1. Schematic diagram of the pervaporation system: 1 - thermostat, 2 - feed tank, 3 - circulation pump, 4 - pump regulator, 5 - rotameter, 6 - membrane module, 7 - vacuum pressure gauge, 8 - valve, 9 - cold trap, 10 - liquid nitrogen bath, 11 - valve, 12 - vacuum pump

Efficiency and selectivity of sulfur removal were evaluated basing on the dimensionless separation factor β (2). Yield of the pervaporation process was evaluated on the basis of the permeation flux determined as total and partial one:

$$J_m = \frac{m_p}{S_m \cdot t} \quad (1)$$

where: m_p - permeate weight [kg], S_m - membrane effective area [m²], t - time [h].

$$\beta = \frac{w_T^p/w_H^p}{w_T^f/w_H^f} \quad (2)$$

where: w_T^p, w_H^p - weight fractions of thiophenes and hydrocarbon, respectively, in the permeate [-], w_T^f, w_H^f - weight fractions of thiophenes and hydrocarbon, respectively, in the feed [-].

Results and discussion

Effect of sulphur content in feed

Differences in crude oil sulfur content mined from various sources made it very important to investigate the impact of the concentration of this element on membrane's

selectivity and transport properties and in consequence - on the efficiency of sulfur compound removal.

Two of typically presented in gasoline sulfur species, *i.e.* thiophene and 2-methylthiophene, were selected to investigate the different sulphur compound removal efficiency from *n*-octane/sulfur species mixtures with PDMS-based composite membranes. The effect of sulfur concentration in the feed on the pervaporation performance was investigated in the range of 0.05-0.13 mas. %.

The impact of thiophenes concentration in model gasoline on the total permeate flux for both binary *n*-octane/sulfur specie mixtures at the feed temperature of 30°C and permeate-side pressure of 100 Pa is shown in Figure 2. As it can be seen, the variation in thiophenes concentration in the feed had practically no influence on the transport of permeating compounds through the membrane. This relationship resulted most likely from the narrow scope of the concentration of thiophene and the fact, that the thiophene concentration was very low as compared to hydrocarbon content. Taking into account the solution-diffusion theory, the separation in pervaporation process is determined by the first two stages, *i.e.* the sorption and diffusion of mixture components [7]. Most likely the concentration of sulfur compound was beyond the range, where the effect of swelling caused by thiophene surpass the swelling phenomena resulted from hydrocarbon sorption in PDMS layer [10, 11]. Nonetheless, partial fluxes of sulfur compounds were proportional to the sulfur concentration, which leads to nearly unchanged values of thiophenes separation factor (Fig. 3).

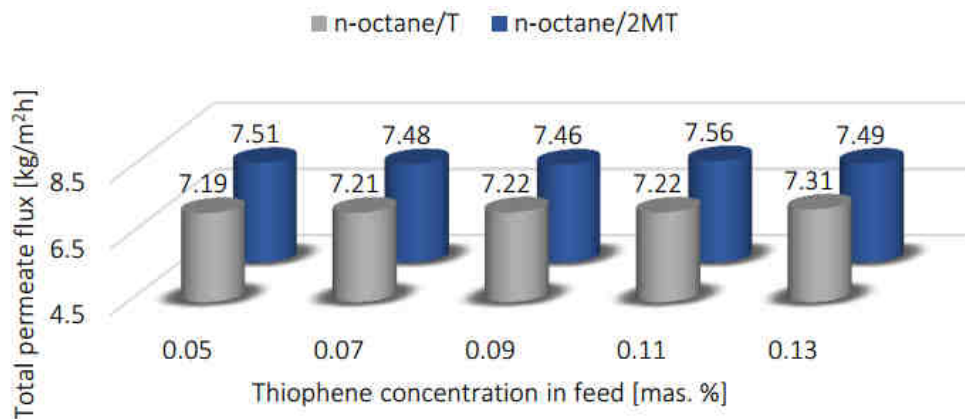


Fig. 2. Effect of feed concentration on the total permeate flux at feed temperature of 30°C and permeate pressure of 100 Pa

Experimental results also showed, that PDMS membrane is more selective to thiophene than to 2-methylthiophene (Fig. 3) and it may be mainly because of the difference in molecular size and structure but also due to the difference in partial vapour pressure, which is lower for 2-methylthiophene. Furthermore, thiophene shows higher chemical affinity to the poly(dimethylsiloxane), from which the membrane active layer was made (the solubility parameter for thiophene is $\delta = 20.0 \text{ (MPa)}^{1/2}$, for 2-methylthiophene is

$\delta = 18.6 \text{ (MPa)}^{1/2}$ and for PDMS is $\delta = 21.1 \text{ (MPa)}^{1/2}$). Obtained results correspond with results presented in the literature [11, 12].

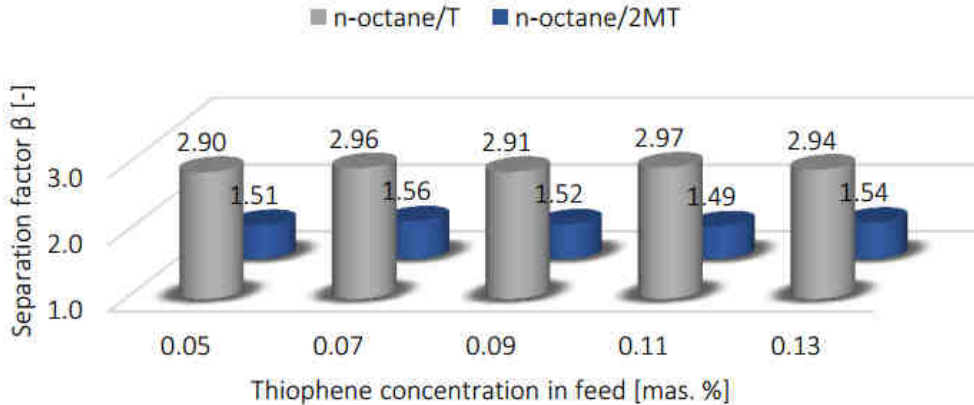


Fig. 3. Effect of feed concentration on the separation factor at feed temperature of 30°C and permeate pressure of 100 Pa

Effect of feed temperature

The effect of operating feed temperature on the efficiency of thiophene and 2-methylthiophene separation from model binary mixtures was investigated in the range of 30-50°C. Temperature dependence of total permeate flux and partial fluxes of individual compound for model mixtures are illustrated in Figures 4-6.

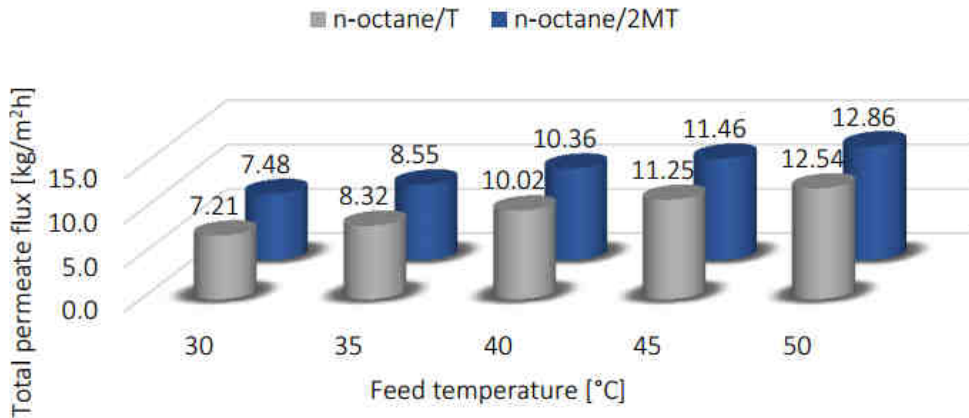


Fig. 4. Effect of feed temperature on the total permeate flux at feed concentration of 0.07 mas. % and permeate pressure of 100 Pa

Experimental data indicated an increase in the total flux (Fig. 4) and partial fluxes (Fig. 6) with the rise of the feed temperature. In Figure 5, separation factors decline with

the increase of feed temperature for both *n*-octane/sulphur compound mixtures. During the pervaporation experiments, a trade-off phenomenon between flux and selectivity was observed - as the feed temperature increased, the total flux increased but the sulfur separation factor shows a digressive trend.

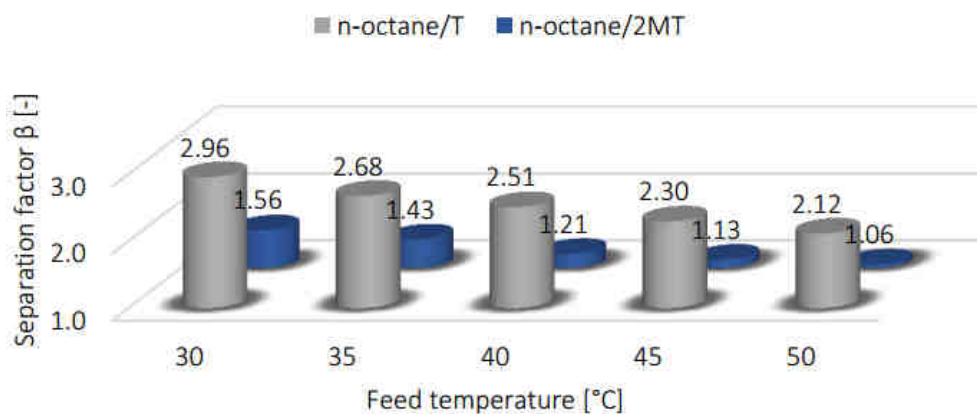


Fig. 5. Effect of feed temperature on the separation factor at feed concentration of 0.07 mas. % and permeate pressure of 100 Pa

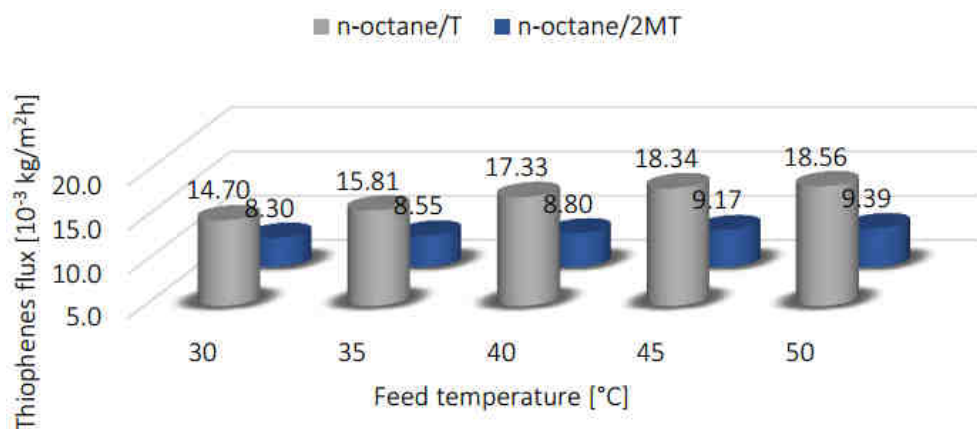


Fig. 6. Effect of feed temperature on thiophenes flux at feed concentration of 0.07 mas. % and permeate pressure of 100 Pa

Above mentioned relationships are thought to be a consequence of two simultaneously occurring phenomena [7]. First, operating temperature affects the driving force for the mass transfer - the increase in the temperature results in higher partial vapour pressure of components in the upstream side of the membrane and provide a greater driving force for the permeation of components since the downstream pressure remains practically unaltered. Secondly, rise of the temperature additionally enhance the swelling of the

membrane active layer, which, on the one hand is a “natural” consequence of feed components dissolution and on the other - can be responsible for the decrease in thiophene separation factor.

Effect of downstream pressure

Since the driving force of components permeation in pervaporation is the difference between the vapour pressure at feed and permeate side of the membrane, the downstream pressure is an important parameter that affects the performance of the PV process. On the basis of the above statement, it can be expected, that partial fluxes will increase with the decrease of the downstream pressure. It also determined the component concentration in the permeate stream and affected the membrane selectivity [7]. Downstream pressure impact on the total permeate flux and sulfur separation factor for model mixtures are illustrated in Figures 7 and 8.

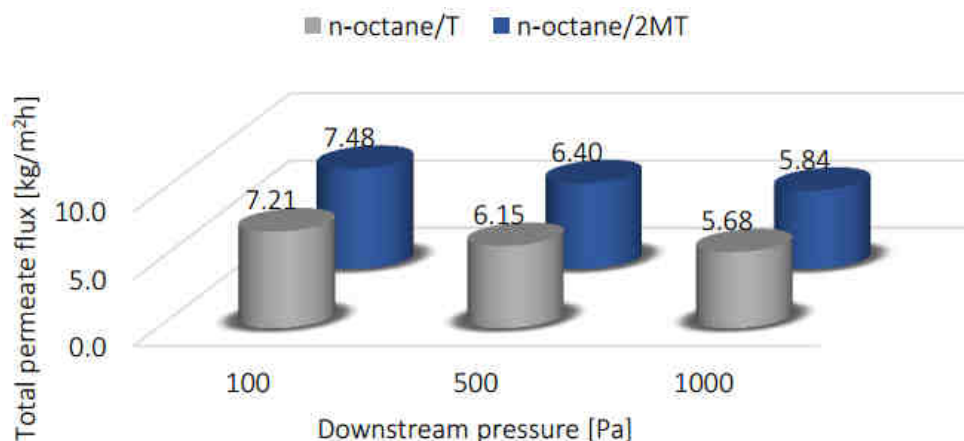


Fig. 7. Effect of downstream pressure on the total flux at thiophenes concentration of 0.07 mas. % and temperature of 30°C

The influence of permeate-side pressure on the pervaporation performance at 30°C and thiophenes concentration of 0.07 mas. % was investigated in the range of 100-1000 Pa. Experimental results indicated, that maximum partial pressure gradients obtained for the minimum downstream pressure was the most beneficial. As the permeate pressure of *n*-octane/thiophene and *n*-octane/2-methylthiophene mixtures was increased, the total flux decreased significantly. At the same time, the sulfur separation factor was declined more gently. Figures 7 and 8 indicates, that high vacuum (low downstream pressure) had a greater impact on total flux in comparison with sulfur separation factor.

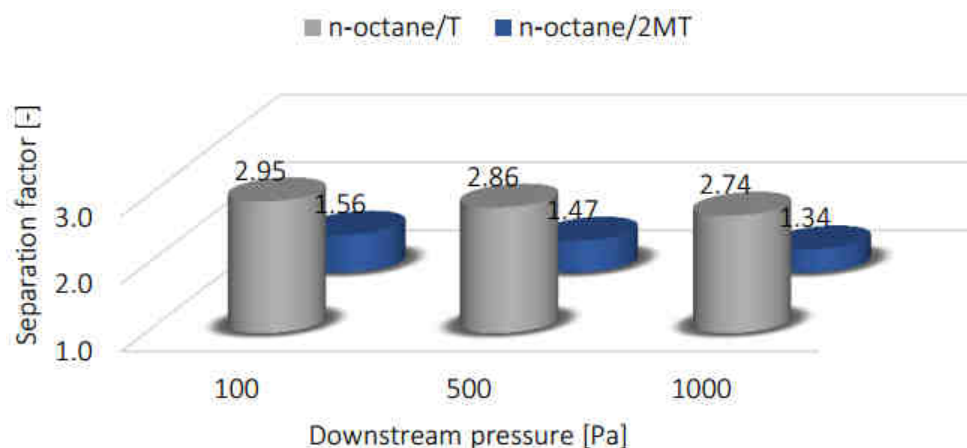


Fig. 8. Effect of downstream pressure on the separation factor at thiophenes concentration of 0.07 mas. % and temperature of 30°C

Conclusions

- Experimental results indicated, that higher feed temperature yielded higher total flux and lower sulfur separation factor.
- Simultaneously, the increase in total permeation flux resulted in the separation factor decrease, which was caused by the decrease in the selectivity of the active layer resulted from its enhanced swelling.
- Partial fluxes of thiophenes were proportional to its concentration in the feed. However, the variation of thiophenes concentration had almost imperceptible impact on the total flux and selectivity.
- Differences of chemical affinity of the investigated thiophenes to poly(dimethylsiloxane) led to various selectivities thereof within PDMS membrane for both separated mixtures.
- As the permeate pressure in desulfurization of *n*-octane/thiophenes using a PDMS was increased, the total flux was decreased significantly while the sulfur separation factor was declined gently.

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ZASTOSOWANIE PERWAPORACJI DO ODSIARCZANIA BENZYNY - EFEKTYWNOŚĆ USUWANIA RÓŻNYCH ZWIĄZKÓW SIARKI

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Abstrakt: Ze względu na rosnącą świadomość ekologiczną dużą uwagę poświęca się jakości paliw transportowych, w tym zawartości siarki. Spalanie związków siarki obecnych w benzynie stanowi źródło emisji SO_x . Co więcej, obecność tlenków siarki w spalinach przyczynia się do zwiększonej emisji NO_x i lotnych związków organicznych (VOC), spowodowanej obniżeniem się niskotemperaturowej aktywności katalizatorów. Dlatego regulacje prawne wprowadzone w krajach UE wymagają redukcji poziomu siarki w benzynie do 10 ppm. Jako że siarka występuje w benzynie w postaci różnych związków (takich jak tiofen i jego pochodne, merkaptany i siarczki) oraz różne związki siarki wykazują różne powinowactwo względem materiału membrany, bardzo ważne jest, aby zbadać efektywność ich usuwania oddzielnie. Celem badań było określenie wpływu typowych wybranych związków siarki obecnych w benzynie na selektywność membrany oraz wydajność separacji związków siarki w procesie perwaporacji próżniowej. Zbadano również wpływ parametrów procesu, takich jak temperatura nadawy, stężenie usuwanych zanieczyszczeń i ciśnienie po stronie odbioru permeatu na skuteczność usuwania tiofenów z modelowych mieszanin *n*-oktan/związek siarki. W czasie badań stosowano hydrofobowe membrany kompozytowe na bazie poli(dimetylosiloksanu). Nadawę stanowiły dwuskładnikowe mieszaniny *n*-oktan/tiofen i *n*-oktan/2-metylotiofen. Zawartość siarki obecnej w tiofenach wahała się w granicach od 0,05 do 0,13% mas. Wpływ temperatury nadawy zbadano w zakresie 30-50°C. Przepływ nadawy (75 dm³/h) utrzymywano na stałym poziomie.

Słowa kluczowe: perwaporacja próżniowa, odsiarczanie, tiofeny, benzyna