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Pervaporative desulfurization of gasoline – separation of thiophene/n-heptane mixture

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Abstract: This paper presents the recent advances in pervaporative reduction of sulfur content in gasoline. Methods of preliminary selection of membrane active layer material are presented. Interactions between gasoline components (typical hydrocarbon and sulfur species) and membranes are showed. Influence of pervaporation process parameters i.e. feed temperature, downstream pressure and feed flow rate on the separation efficiency is discussed. Investigations of the influence of sulfur concentration in fluid catalytic cracking (FCC) gasoline on membrane performance have been conducted. A series of PV tests was carried out to investigate the separation properties of the commercial composite membrane with an active layer made of poly(dimethylsiloxane) and to determine the efficiency of organic sulphur compound (thiophene) removal from model thiophene/n-heptane mixture depending on its concentration.

Introduction

Reduction of sulfur content in transportation fuels has received increasing attention with growing environmental awareness. Sulfur in gasoline is a considerable source of SO_x emissions. Toxicity of sulphur compounds, which by the combustion of motor fuel enters the atmosphere, are primarily associated with the formation of acid rain, which further contribute to the acidification of soil and surface water, as well as the formation of photochemical smog. It is impossible to mention the harmful effects of sulfur compounds in the increased concentration on the organisms. The negative effect of sulfur compounds during combustion of fuel, is also seen in the form of corrosion of metals and concrete, paper aging or destruction of plastics (Brunet et al. 2005, Leflaive et al. 2002, Song 2003). Moreover, the presence of sulfur oxides 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. Therefore, many countries adopt new and more rigorous regulations on sulfur content in gasoline. The specification in EU countries, demands a reduction of sulfur level in gasoline and Diesel fuels to 10 ppm (Directive 2009).

Nearly all of the sulfur (85–95%) in the typical refinery plant comes from Fluid Catalytic Cracking (FCC) gasoline, and a small amount originates from light straight run, reforming and isomerisation units. That is why, FCC gasoline is the natural substance to focus on sulfur reduction. The sulfur concentration of FCC gasoline depends on the sulfur type and its level in the FCC feedstock (Brunet et al. 2005). Although elemental sulfur, mercaptans, sulfides, disulfides, thiophene and its homologues are all present in petroleum or in petroleum fractions, sulfur occurs mainly in the form of thiophene, sulfides, mercaptans and disulfides (Leflaive et al. 2002).

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, bio-desulfurization, alkylation-extraction, improved selective hydroprocessing and pervaporative desulfurization (PVDS) (Ito et al. 2006, Song 2003). It should be noted that this new desulfurization technology has already progressed beyond the lab-scale tests stage. In comparison with the traditional and other non-HDS separation processes, membrane separation offers many advantages including lower energy consumption and operating cost, simple operation and control scheme, easy scale up, higher separation efficiency and adaptability to changes in process streams (Kujawski 2009, White 2006). Those promising advantages make membrane separation an attractive process for many of recent researches.

Theory

Pervaporation process principle

Pervaporation is a membrane technology utilizing a dense non-porous homogeneous polymeric film. The liquid solute selectively dissolves and diffuses in the membrane and is removed as vapour at the downstream side. The vacuum pervaporation is carried out by maintaining the downstream pressure, lower than the saturation pressure of the permeating liquid solute at that temperature (Huang et al. 2008).

Pervaporative separation is based on the affinity of a specific compound or a class of compounds to the membrane. The generally accepted mechanism explaining the mass transport across the dense membrane is solution-diffusion model (Kujawski 2009). According to this model, pervaporation process can occur only when a certain amount of solvent is dissolved in membrane material (Huang et al. 2008). The liquid feed solution is contacted with the membrane active surface at the upstream side, which is at atmospheric pressure. The components of a mixture are selectively dissolved and then diffuse through the membrane. The permeated compounds are then removed on the opposite side. The driving force for the separation process is maintained by constant withdrawal of the permeated compounds from the membrane.

Membrane material selection

The main parameters taken into account during the selection of a membrane material are sorption capacity, chemical resistance and mechanical strength of polymeric active layer. Good interaction between the polymeric membrane and preferably one of the components of the mixture is necessary for the appropriate separation. For good process performance, the material of active film needs to show high affinity towards removed component (Shao et al. 2007). Hence, solubility parameter (Hansen 1999) and membrane polarity are the two main interested factors in the development of the novel membrane materials (Lin et al. 2009).

Hansen solubility parameter theory, δ $((J/cm^3)^{1/2})$, is the most effective method of preliminary selection of pervaporation membrane materials. The internal energy

change, ΔE (*kJ/mol*), for interaction of the solvent and polymer is defined as (Hansen 1999):

$$\Delta E = v_S v_P (\delta_S - \delta_P)^2 = v_S v_P |\Delta \delta|^2 \qquad (1)$$

where v is the volume fraction, and subscripts S and P correspond to the solvent and polymer, respectively.

The equation (1) shows, that the more similar solubility parameters of the polymer and solvent (i.e. lower ΔE), the more soluble solvent in the polymer (Smitha et al. 2004). Values of solubility parameters of polymers, hydrocarbons and sulfur species present in gasoline are listed in Table 1.

As the solubility parameters of many commercial membrane materials are more similar to the thiophene and its derivatives than to the hydrocarbon compounds, membranes show larger affinity to sulfur species (Mortaheb et al. 2012).

Polarity of membrane material also contributes to the separation performance. In order to remove a specific component from a mixture, the polarity of these components must be close to the polarity of the polymeric material of the active film (Lin et al. 2009).

The other way to determine the potential applicability of the membranes used in gasoline desulfurization is to investigate their swelling properties (Mortaheb et al. 2012). Swelling degree gives the information about membrane chemical resistance towards organic solvents. High swelling of the membrane induced by high concentrations of the permeating components results in the reduction of membrane selectivity. High membrane swelling can also result in the

Table 1. Solubility parameters of membrane materials, typical hydrocarbon and typical sulfur species present in gasoline [Qi et al. 2007]

Membrane material	δ $((J/cm^3)^{1/2})$	Sulfur species	δ $((J/cm^3)^{1/2})$	Hydrocarbon	δ $((J/cm^3)^{1/2})$
PP	21.93	Thiophene	20.0	*n*-pentane	14.4
PEG	20.10	2-methyl thiophene	19.6	isopentane	13.8
PVC	26.49	3-methyl thiophene	19.5	*n*-hexane	14.9
PVP	poly	Dimethyl thiophene	19.3	*n*-heptane	15.3
PVB	23.12	Trimethyl thiophene	19.2	*n*-octane	15.5
PDMS	21.01	Diethyl thiophene	19.2	isooctane	14.2
PU	20.98	Triethyl thiophene	19.0	cyclopentane	16.6
CA	25.06	Thioether	16.8	cyclohexane	16.7
PAN	26.61	Dimethyl sulfone	29.8	methyl cyclohexane	16.0
PS	18.50	Sulfide	16.9	benzene	18.7
PUU	20.98	Disulfid	17.4	toluene	18.2
PI	32.30	*n*-butyl sulfide	28.1	*m*-xylene	18.2
CTA	24.55	*n*-butyl mercaptan	18.4	*o*-xylene	18.5
PVA	39.15	Benzyl mercaptan	21.1	*p*-xylene	18.1

PP – polypropylene; PEG – poly(ethylene glycol); PVC – poly(vinyl chloride); PVP – poly(vinyl pyrrolidone); PVB – poly(vinyl butyral); PU – polyurethane; CA – cellulose acetate; PAN – polyacrylonitrile; PS – polystyrene; PUU – polyurethane-urea; PI – polyimide; CTA – cellulose triacetate; PVA – poly(vinyl alcohol)

increase of membrane pore space and enhances diffusion of molecules. This phenomenon contributes to the increased flux and decrease in sulfur enrichment factor (Kong et al. 2008). It is also the reason of the chemical degradation of active layer. According to literature (Mortaheb et al. 2012) the polymer material which gains less than 3% weight due to the sorption of feed components, is thought to be good. For example, CTA and PVP had swelling degree equal to 0 and 2.8%, respectively, whereas polystyrene was dissolved in gasoline (Lin et al. 2009).

The analysis of the sorption, diffusion and permeation coefficients is another way of preliminary membrane materials selection. By the comparison of dynamic sorption curves for gasoline component, it is seen that the time required to reach sorption equilibrium is different for various compounds (Mortaheb et al. 2012).

The permeation of a penetrant into a polymer depends on the diffusivity as well as on the solubility of the penetrant (Huang et al. 2008, Shao et al. 2007, Smitha et al. 2004). The sorption coefficient, S (g/g), also known as swelling degree, which is a measure of weight gained during sorption, is defined as the moles of solvent uptake by 100 g of the polymer membrane sample at sorption equilibrium (Lin et al. 2008a). The diffusion coefficient, D (cm^2/s), of gasoline components in membranes can be estimated based on the initial slopes of sorption curves (Sha et al. 2012a). The permeation coefficient, P (cm^2/s), is defined as (Sha et al. 2012a):

$$P = S \times D \qquad (2)$$

The temperature dependence of D, S and P can normally be expressed by Arrhenius-type equations (Feng et al. 1996).

Sorption, diffusion and permeation coefficients are determined based on the data obtained from systematic studies of dynamic sorption curves for gasoline components, i.e. the plots of M_t/M_∞ vs $t^{1/2}$. M_t and M_∞, (g), refer to weight gained due to sorption of feed component at time t (s), and at infinite time at equilibrium, respectively.

In order to investigate the transport mechanism of gasoline component in membrane the following empirical formula can be used (Qu et al. 2010):

$$log \frac{M_t}{M_\infty} = K + n log t \qquad (3)$$

In equation (3) constant K depends on the structural characteristics of the polymer and gives information about interaction between polymer and solvent. The value of n indicates the transport mode. The Fickian diffusion is characterized as n = 0.5, and non-Fickian or anomalous diffusion by n varying between 0.5 and 1 (Qu et al. 2010, Sha et al. 2012a). High K values indicate a strong membrane-gasoline component interaction.

Membrane materials used

Reported in literature membranes employed in pervaporative desulfurization of both, model and real gasoline are summarized in Table 2. In most of the cases polymeric membranes were used for the process. The main drawback of polymeric membranes is the high swelling and, as a consequence, decrease in membrane selectivity during the organic-organic mixtures separation caused by the high concentration of the permeating solvent. It can be seen that involved materials are hydrophobic polymers as well as hydrophilic ones. Hydrophilic properties of the polymer enhance the selectivity of sulfur compounds due to their higher polarity in comparison with the hydrocarbon species. Different results, which are reported by various researchers, might be due to either incorporating a particular additive in membrane preparation that largely reduces the swelling of the membrane, or the selected range of sulfur concentrations in their research.

Modifications including cross-linking, blending, filling, copolymerization, and treatment by charged ionic groups can improve performance of the membrane in two ways. First is to enhance the affinity to sulfur species based on the mentioned criteria and second to decrease the swelling degree to control permeation of the other species. The mixed matrix PDMS membranes (MMMs) filled with Ag_2O (Qi et al. 2007a), Ni^{2+}-Y zeolite (Li et al. 2008) and AgY zeolite (Qi et al. 2007b) were employed. The results indicate that the incorporation of zeolites leads to the increase in total flux. This phenomenon can be attributed to the Knudsen diffusion of permeating molecules in the macro- and mezo-pores of zeolites. The selectivity of the process was affected by two parallel factors. On the one hand, the interaction between thiophene and zeolite occurred and the transport of thiophene was favoured. On the other hand, the Knudsen diffusion in pores had negative impact on process selectivity. Addition of zeolites resulted in a slight decrease in sulfur enrichment factor.

Influence of hydrocarbons on the membrane performance

Since gasoline is a complex mixture composed of hundreds of compounds, in which five typical hydrocarbon groups are alkanes, isoalkanes, cycloalkanes, aromatics and alkenes, deep understanding of the solution/diffusion gasoline molecules on/in the membrane is essential. The above hydrocarbon groups have different interactions with the membrane, which influence the membrane performance significantly. It has been proven (Minhas et al. 2004, Scheatzel et al. 2001, Shao et al. 2007) that transport of one component across the membrane during the separation of organic-organic mixtures is composition--dependent. It means that permeability of a compound is not only driven by its own chemical potential gradient, but also by the gradient of chemical potential of other molecules present in the feed. Thus, it is very important to investigate also the synergetic effect of gasoline components on pervaporation behaviour of membranes.

Pervaporation results demonstrate that the increase in concentration of alkenes and aromatic compounds in the feed would yield a higher total flux but a lower enrichment factor for sulfur species. Kong et al. (2007) and Qi et al. (2006b) investigated the influence of typical hydrocarbon species presented in FCC gasoline on PDMS (Qi et al. 2006b) and PEG (Kong et al. 2007) membranes performance in pervaporative desulfurization. Reported data indicate that aromatics and alkenes have similar impact on membrane performance. Their studies showed that the addition of toluene and/or hexene into the feed resulted in the enrichment factor decrease and the increase of total permeate flux. Hexene added to the modal mixture

Table 2. Reported membrane material for gasoline desulfurization

Membrane	Feed	Sulfur content	Temperature, ºC	Flux, J, kg/m²h	Enrichment coefficient, β	Reference
PI (Matrimid 5218)	Model feed[1]	248 µg/g	71	6.2	2.18	White et al. 2004
Nafion RTM117(Na⁺)	Model feed[2]	4239 µg/g	-	0.58	63.64	Saxton and Minhas 2002
NF SR-90	Naphta	950 µg/g	-	0.23	5.26	Saxton and Minhas 2002
UF G-10	Model feed[2]	4239 µg/g	-	0.45	53.61	Saxton and Minhas 2002
PSU SEP-0013	Naphta	1750 ppm	21	-	1.0	Plummer and Bonelli 2002
PI (6FDA-MDA)	Naphta	1750 ppm	22	-	8.2	Plummer and Bonelli 2002
PDMS/PAN	Naphta	1750 ppm	23	-	16.8	Plummer and Bonelli 2002
PDMS/ceramic	Thiophene/n-octane	1000 µg/g	50	3.31	3.35	Qi et al. 2007
PDMS/PEI	Thiophene/n-heptane	500 ppm	30	3.26	4.48	Li et al. 2008
PES/Pluronic F127	Thiophene/n-octane	-	50	8.15	3.45	Qi et al. 2007
PDMS/PEI	Thiophene/n-octane	200 ppm	50	0.28	12	Chen et al. 2008
PDMS/PES	Thiophene/n-octane	500 mg/L	30	3.1	3.5	Li et al. 2009
PEG/PEI	Gasoline	900 µg/g	100	3.37	3.63	Kong et al. 2010
PEG/PU	FCC Gasoline	1227 µg/g	-	1.63	3.05	Lin et al. 2006
PEG-CuY	FCC Gasoline	1227 µg/g	-	2.33	2.10	Lin et al. 2010
PI-block-PEG	FCC Gasoline	1200 µg/g	110	283	1.7	Lin et al. 2008
HEC	Model feed[3]	1190 µg/g	-	3.19	2.95	Qu et al. 2010
PAN/cellulose	Rafinery naphta	805 µg/g	-	-	1.44	Kong et al. 2010
PUU/PTFE	Thiophene/n-heptane	1000 µg/g	-	-	1.7	Mortaheb et al. 2012
EC	Model feed[3]	-	85	1.5	8	Sha et al. 2012
EC-C₆₀	-	-	-	2.6	4	Sha et al. 2012
PBPP	Rafinery naphta	-	78	0.038	7.53	Yang et al. 2012
PTFEP	Model feed[4]	300 µg/g	80	0.70	3.75	Yang et al. 2012

[1] 1-pentene(12 wt.%)+2,2,4-trimethylpentane(33 wt.%)+methylcyclohexane(13 wt.%)+toluene(42 wt.%)+thiophene;
[2] methanol(10 wt.%)+toluene(48 wt.%)+1-octene(10 wt.%)+thiophene(1 wt.%);
[3] n-heptane/cycklohexene/cyclohexane/toluene/thiophene;
[4] n-heptane(40.5 wt.%)+cycklohexene(28.3 wt.%)+cyclohexane(8.63 wt.%)+toluene(27.7wt.%)+thiophene.
PEI – poly(ether imide); PES – poly(ether sulfone); HEC – hydroxyethyl cellulose; PTFE – poly(tetrafluoroethylene); EC – ethyl cellulose; PBPP – poly[bis(phenoxy)phosphazene]; PTFEP – poly[bis(trifluoroethoxy)phosphazene]

consisted of thiophene, *n*-heptane and toluene increased the swelling degree from 0.1149 (*g/g*) to 0.1571 (*g/g*). The addition of toluene or hexane into model feed composed of *n*-heptane and thiophene exacerbates the PEG membrane swelling degree (*SD*) from 0.0338 (*g/g*) for binary mixture (thiophene/*n*-heptane) to 0.1148 (*g/g*) for ternary mixture (thiophene/*n*-heptane/toluene). This phenomenon can be explained by the solubility parameter theory – the affinity between toluene [δ=18.2 ((J/cm³)^(1/2))] and PEG [δ=20.1 ((J/cm³)^(1/2))] or PDMS [δ=21.01 ((J/cm³)^(1/2))] membrane is stronger than between *n*-alkanes [δ~15 ((J/cm³)^(1/2))] and the aforementioned membranes.

Investigation of *n*-alkanes influence on the pervaporation efficiency and PDMS membrane performance conducted by Qi et al. (2006a) indicated that partial fluxes of tested linear alkanes were strictly related to carbon number of molecule – the longer the chain the less penetrating the alkane and the lower partial flux due to the decrease in diffusivity. It was also recognized that in the case of alkanes/thiophene mixtures the coupling effect had to be taken into account – partial fluxes and activation energy of thiophene and alkanes for different systems in constant temperature differed from each other. Desulfurization of ternary mixtures showed that

lighter alkanes content enhanced the total permeation flux. Simultaneously, the decrease in sulfur enrichment factor was observed. Kong et al. (2007) demonstrated that *n*-hexane practically did not induce the membrane swelling. Increase in the carbon number in the alkane enhanced the solubility caused by the increase in polymer plasticization degree (Kong et al. 2007). In addition, as the alkane molecule was shorter, it would penetrate into the dense polymer membrane and decrease in the difference between activation energies of the thiophene and alkane was observed (Qi et al. 2006a).

Cycloalkanes cause a slight decrease in permeation flux and increase in enrichment factor in comparison with alkenes and aromatic hydrocarbons. Kong et al. (2007) recognized that the addition of cyclohexane caused a small decrease in total flux due to the reduction of free volumes in the polymer and simultaneous increase in sulfur enrichment factor. This might have been due to the low solubility parameter of cyclohexane in the polymer. Cyclohexane weakened the swelling of the membrane material.

Gasoline sulfur species removal

Chen et al. (2008) and Zhao et al. (2008) investigated the impact of different sulfur species such as thiophene, 2-methyl thiophene, 2,5-dimethyl thiophene, *n*-butyl mercaptane and *n*-butyl sulfide on pervaporation behaviour of crosslinked PDMS/PEI membranes. Partial permeation flux and enrichment factor of sulfur compound in the same temperature were in the following order: *n*-butyl sulfide < *n*-butyl mercaptane < 2,5-dimethyl thiophene < 2-methyl thiophene < thiophene (Chen et al. 2008). Those experimental data were in the agreement with solubility parameter theory. *β* values of particular sulfur compounds decreased with the increase of ΔE. The higher was the difference between *δ* values of a sulfur organic derivative and membrane material the lower was the enrichments of the permeate in the removed compound. It was found that permeability of sulfur compound decreased with the increase of molecular size of permeating species (Chen et al. 2008).

Effect of operation conditions on pervaporation efficiency

Feed temperature is an important factor in the pervaporation process and affects all of the constituent steps of solute transport from feed solution to permeate side, as well as the driving force for mass transfer. During the PV process, a trade-off phenomenon exists between flux and selectivity – as the feed temperature increases, the total flux increases but the sulfur enrichment factor decreases. During the pervaporation process, permeating components diffuse through free volumes of the membrane. Thermal motions of polymer chains in amorphous regions produce free volumes. As temperature increases, frequency and amplitude of polymer jumping chains increase, resulting in the increase of free volume of the membrane. As a consequence, the diffusion rate of individual permeating components increases at higher temperatures leading to high permeation fluxes. Another reason for the increase of permeation flux with the increase in feed temperature is that with the increase of temperature, the vapour pressure of each component increases what results in high permeation flux of all components. Thus, feed temperature affects the feed/membrane characteristics and the driving force of the process (Lin et al. 2009, Mortaheb et al. 2012, Smitha et al. 2004). Generally, variations of total and individual fluxes are related by the Arrhenius-type equation *lnJ vs 1/T* which allows to estimate the activation energy of permeation. The lower the permeation activation energy, the lower the resistance force of mass transfer trough the membrane (Feng et al. 1996).

Permeate pressure is an important parameter that affects the performance of the PV process. Since the driving force for permeation of components in pervaporation is the vapour pressure difference between the feed and permeate side, the partial fluxes are expected to increase with the decrease of the downstream pressure. Permeate pressure greatly affects the operating cost of the process because the cost of maintaining vacuum is substantial. It also determines the component concentration in the permeate stream and affects the membrane selectivity (Lin et al. 2009, Mortaheb et al. 2012, Smitha et al. 2004).

The effect of feed flow rate can be attributed to the effect of concentration polarization in the liquid boundary layer adjacent to the membrane surface. Concentration polarization tends to decrease the permeation rate of the more permeable component (sulfur) and increase the permeation rate of the less permeable component (hydrocarbons), resulting in a lesser degree of separation. However, an increase in the feed flow rate could reduce the effect of concentration polarization (Mortaheb et al. 2012, Lin et al. 2009).

Experimental

Materials

To prepare the model gasoline, thiophene (99.5%, extra pure, benzene free) obtained from Acros Organics and *n*-heptane (99% purity) (99%) obtained from J.T. Baker were used. Membranes with poly(dimethylsiloxane) active layer were obtained from PERVATECH, the Netherlands. These are composite membranes consisting of a porous support. On top of the porous support is a very thin but dense separating layer.

Analysis

The thiophene and *n*-heptane concentration in both, the feed and the permeate samples, were analysed using a gas chromatograph (SRI Instruments, USA) equipped with a flame ionization detector (FID) and Restek RTX-5 (0.53 μm, 0.53 mm × 30 m) capillary column. Methanol (pure p. a.) obtained from Avantor Performance Materials Poland S.A. was used as a GC solvent. Hydrogen was used as carrier gas. Retention time for thiophene was 3.40 min and that for toluene was 7.10 min.

Pervaporation experimental setup

The experimental setup, designed by Sulzer Chemtech, was used for the pervaporation measurements (Fig. 1). The pervaporation test cell with a diameter of 15.9 cm was made of stainless steel. The membrane with an effective area of 187 cm^2 was kept on highly porous stainless steel support with the shiny polymeric layer facing the feed solution.

The solution and feed cell was heated to desired temperature using a thermostat (Thermo Electron Co., model Haake DC 30). The temperature was controlled through a PID controller device (Greisinger Electornics GTH 1100/2 DIF). The feed solution was circulated to the upstream side of the membrane using a recirculation, while retentate was sent back to the flask. Sufficient feed flow rate was maintained. The membrane upstream side was kept at atmospheric pressure and the downstream side was maintained under vacuum

through the use of a vacuum pump (Alcatel, model Pascal 2015 SD). The total downstream pressure was measured by an electronic vacuum gauge (Vacuubrand DRV 2). The permeated vapours were condensed in the trap by keeping it in a flask, filled with liquid nitrogen. The frozen permeate was collected within a specified time interval. The cold traps were brought to room temperature prior to measurement of their weight using a balance (RadWag PS 210/C/2) to determine the mass flux. The concentration of thiophene varied from 0.8 *wt.%* to 1.6 *wt.%*. The feed temperature (40ºC), feed flow rate (75 L/h) and downstream pressure (100 hPa) were kept at constant level.

The yield of the pervaporation process was evaluated on the basis of the permeation flux J_m (4) determined as total and partial one. Efficiency and selectivity of sulfur removal were evaluated based on the dimensionless enrichment coefficient β (5).

$$J_m = \frac{m_p}{S_m \cdot t} \qquad (4)$$

where: m_p – pemreate weight, g; S_m – membrane effective area, m^2; time, h.

$$\beta = \frac{c'}{c} \qquad (5)$$

where: c – concentration of thiophene in feed sample, %; c' – concentration of thiophene in permeate sample, %;

Results and discussion

Taking into account the variable sulfur content in crude oil from different sources, it is very important to determine the effect of the concentration of this element in gasoline on selectivity of the membrane and the efficiency of the pervaporation process.

A series of pervaporation experiments were carried out to investigate the performance and separation properties of the commercial composite membrane with an active layer made of poly(dimethylsiloxane) and to determine the efficiency of organic sulphur compound removal (thiophene), depending on its concentration.

Research has shown that an increase in the sulfur content of model *n*-heptane/thiophene mixture simulating gasoline caused a slight increase in the total permeate flux (Fig. 2) and both, thiophene (Fig. 3) and *n*-heptane (Fig. 4) fluxes, while lowering the enrichment factor of the permeate (Fig. 5).

Such dependency can be explained by the fact that with increasing the concentration of thiophene, its activity increased, which, in turn, facilitated its dissolution in the active layer of the membrane. Accordingly, with the increase in thiophene concentration, the increase in the total permeate flux was observed.

Furthermore, due to the high chemical affinity of thiophene to the poly(dimethylsiloxane), from which the membrane active layer was made (the solubility parameter for thiophene is δ=20.0 $(J/cm^3)^{1/2}$ and for PDMS is $\delta = 21.1$ $(J/cm^3)^{1/2}$), increase in the content of thiophene in the model feed intensified membrane swelling phenomenon. As a result, the total flux increased due to the enhanced mobility of the polymer chains.

On the other hand, as it can be seen in Figs 3 and 4, *n*-heptane flux increased more rapidly with increasing the sulfur compound concentration comparing to thiophene flux. Although *n*-heptane has a relatively low affinity towards PDMS (the solubility parameter for *n*-heptane is $\delta = 15.3$ $(J/cm^3)^{1/2}$), and harder than thiophene is dissolved in unswollen membrane, the swelling enhanced its diffusion, which also was not without influence on the total flux of the permeate.

Previously mentioned phenomenon explains the decrease in permeate enrichment factor β (Fig. 5) with the increase of thiophene concentration. As a result of the selective layer swelling and enhanced dissolution of n-heptane in the active layer material, a decline in the selectivity of thiophene sorption process occurred.

Conclusions

Separation of sulfur species from gasoline represents one of the most challenging applications of pervaporation process.
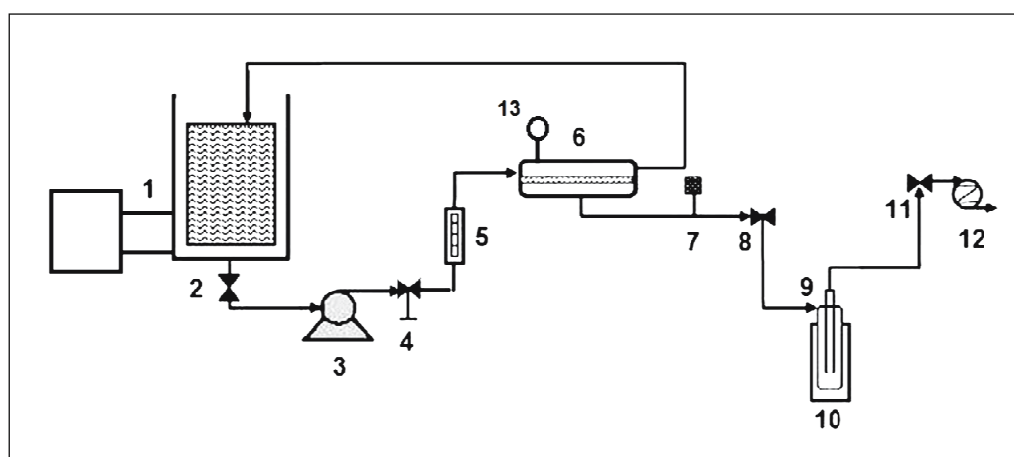

Fig. 1. Schematic diagram of the pervaporation system: 1 – thermostat, 2 – feed tank, 3 – circulation pump, 4 – pump regulator, 5 – ratameter, 6 – membrane module, 7 – vacuum pressure gauge, 8 – valve, 9 – cold trap, 10 – liquid nitrogen bath, 11 – valve, 12 – vacuum pump
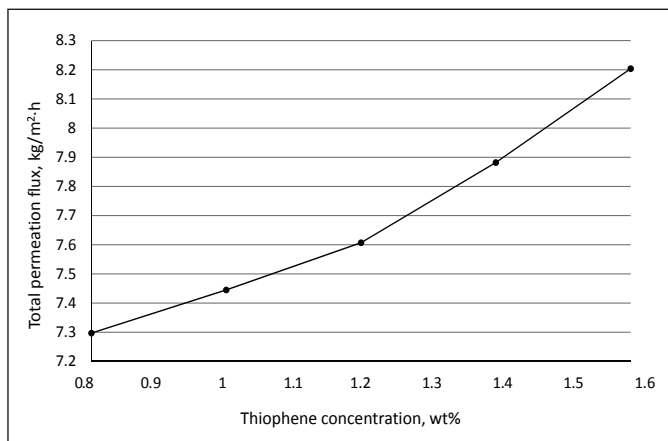
Fig. 2. Effect of sulfur content in the feed on the total permeate flux
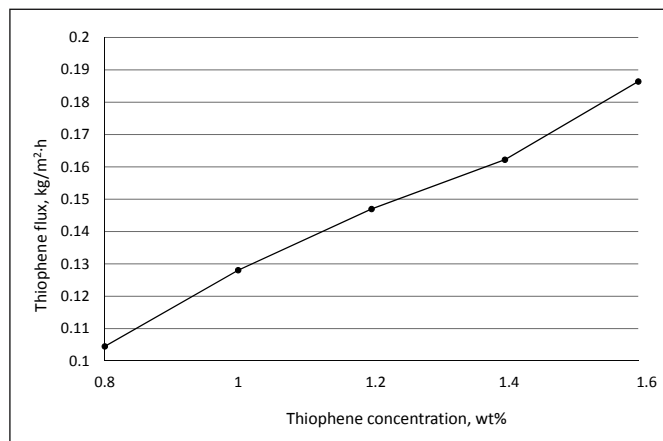

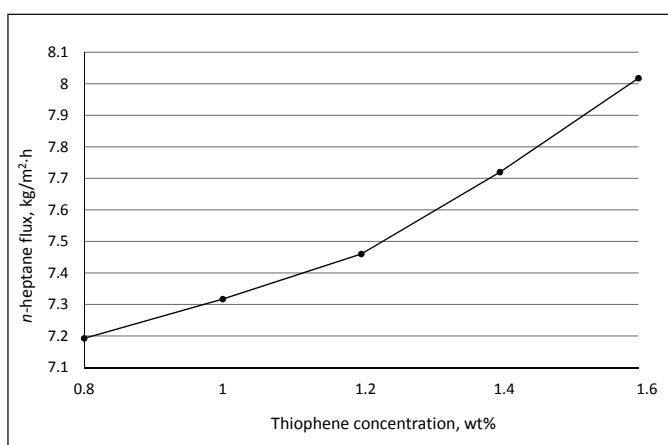**Fig. 3.** Effect of sulfur content in the feed on thiophene flux

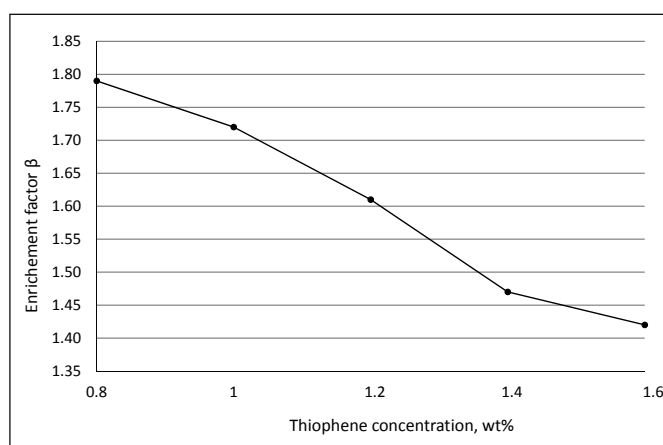**Fig. 4.** Effect of sulfur content in the feed on n-heptane flux

Fig. 5. Effect of sulfur content in the feed on the permeate enrichment factor

Research performed in this field has already gained a number of successes but there is still a number of studies to be done. Subsequent investigations on new membranes application for gasoline desulfurization by means of vacuum pervaporation process will be helpful for creating final solutions to this interesting, but also very challenging problem.

Experiments have shown that the sulfur content in gasoline has a significant impact on the selectivity of the membrane, and hence, the efficiency of PV desulfurization process.

With the increase in the sulfur content in the feed, an increase in the total permeate flux was observed. This is due to the increase in the swelling degree of the membrane as a result of dissolution of larger amounts of thiophene in active layer material.

The increase in n-heptane flux with increasing the concentration of sulphur was more rapid in comparison with thiophene flux. The reason is that the enhanced membrane swelling phenomenon, caused by higher concentration of dissolved in active layer thiophene, facilitated the dissolution and diffusion of n-heptane.

Simultaneously, the increase in total permeation flux resulted in the enrichment factor decrease, which was caused by the increase in the mobility of the polymer chains and a decrease in the selectivity of the active layer.

Acknowledgements

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Perwaporacyjne odsiarczanie benzyny – separacja mieszanin tiofen/n-heptan

W pracy zaprezentowano dotychczasowe osiągnięcia w perwaporacyjnym odsiarczaniu benzyny krakingowej. Przedstawiono kryteria wstępnego doboru materiału warstwy aktywnej membran. Omówiono ponadto wpływ typowych węglowodorów oraz związków siarkoorganicznych obecnych w benzynie krakingowej na selektywność i właściwości transportowe membran jak również wpływ parametrów procesowych (temperatury nadawy, ciśnienia po stronie permeatu oraz szybkości przepływu nadawy) na efektywność procesu perwaporacyjnego odsiarczania. W pracy przedstawiono możliwość zastosowania komercyjnych membran kompozytowych z warstwą aktywną wykonaną z poli(dimetylosiloksanu) (PDMS) w procesie perwaporacyjnego odsiarczania benzyny pochodzącej z fluidalnego krakingu katalitycznego (FCC). Określono wpływ stężenia organicznych związków siarki na efektywność ich usuwania z organicznych mieszanin tiofen/*n*-heptan metodą perwaporacji próżniowej.