Application of poly(ether imide) membranes for the removal of the aromatic sulphur compounds from gasoline

Dragutin Nedeljkovic
American University of the Middle East, College of Engineering and Technology, Egalia, Kuwait
E-mail: Dragutin.Nedeljkovic@aum.edu.kw

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Abstract
Organic sulphur compounds are regularly present in the crude oil and natural gasoline, mostly as mercaptanes and heterocyclic sulphur compounds. Their combustion products have negative effects to both to the performance of the devices using gasoline and to the environment. Therefore, removal of the sulphur compounds in the pre-combustion process is of a great importance. One of the most promising method is application of the polymeric membranes. Suitable membrane should provide high permeability of sulphur compounds and low permeability of other hydrocarbons. In this work, several membranes based on the poly(ether imide) were tested for the sulphur organic compounds removal from the n-heptane. The membrane separation properties were measured for various concentrations of thiophene in heptane. It was found that increase of the amount of thiophene increases the flux of both thiophene and n-heptane. As the increase of the flux of the n-heptane was higher that the increase of the flux of the thiophene, the selectivity of the polyimide based membrane decreases with the increased concentration of thiophene in the feed. The possible reason is increased mobility of the polymer chains in the active layer.

1. Introduction

Purification of fuels has attracted significant focus from the scientific and engineering community in recent years. With more sophisticated engines, regulated and controlled by electronic equipment, their sensitivity and vulnerability to impurities in fuel increased as well [1]. Environmental concerns grew in parallel, as increased demand for energy caused increase in emission of common flue gases, and requirements for waste gas treatment became significant factor in design of the plants that use fossil fuel [2]. Therefore, requirements for reduction in emission of all types of pollutants that are commonly present in flue gases emerged as important task [3].

Sulphur, the element that is commonly present in fossil fuels is released in the atmosphere in the form of various oxides. Sulphur oxides (mainly SO₂) are toxic to the most of organisms and are one of the most abundant gas pollutants [4]. Additional negative effect of the sulphur oxide to the environment is that they are one of the main constituent of acid rains which further decrease the pH value of soil and water. The presence of the sulphuric oxides has also negative effect to the corrosion of metal (both in the vehicle’s engine and metals used in construction), concrete and plastic materials [5].

Effect of sulphur dioxide that cannot be neglected is that it rapidly ‘poisons’ the catalytic equipment of vehicle which further increase emission of nitrogen oxide [6]. Therefore, law regulations in most of the countries in the world are becoming more and stricter concerning the amount of sulphur that is allowed to be exhausted in combustion processes. According to currently active European Union regulation, maximal allowed amount of sulphur in exhausted gas is 10 ppm. The highest fraction of sulphur (around 90%) in the typical refinery fuel comes from fluid catalytic cracking (FCC) of gasoline, with the remaining fraction coming from reforming and isomerization [7]. Therefore, efforts are being made in the direction of reducing the amount of sulphur during the fuel refining inside the refinery. Traditional approach to this problem included selective extraction, catalytic extraction, selective oxidation, bio-desulphurization and alkylation-extraction [8]. In recent times, more efforts
are directed to the direction of treatment of the sulphur with various polymeric membranes [9, 10]. The idea is to synthesize the membrane that would be permeable for the sulphur compound, but not permeable for hydrocarbons that are mostly present in gasoline [11]. Advantages of this approach include higher efficiency, lower operational costs, adaptability to changes in process streams and low energy consumption [12, 13].

The amount of the sulphur in the gasoline mainly depends on the origin and type of the feedstock. Sulphur mainly appears in the form of thiophene, sulphides, mercaptanes and disulphides [14]. Ideal membrane for this application should have high permeability for sulphur compounds and low permeability for other hydrocarbons. Membrane techniques have been widely used in removal of various trace elements that have been observed as pollutants [15]. The vacuum membrane technology utilizes selective dissolution of sulphur compound in the suitable solvent, diffusion through the membrane, and evaporation on the permeate side. The key pre-requisite is to keep pressure at the downstream side lower than the saturation pressure or the permeating liquids [16]. In general, those processes are described by the solution—diffusion model [17]. Liquid solution is brought to the contact with the membrane at the feed side at atmospheric pressure. Components of the mixture are being dissolved with different rates in the bulk of the membrane and then they diffuse through the membrane with their respective rates. Permeated components are removed at the permeate side by the lower pressure at the permeate side. Constant removal of vapour at the permeate side maintains the driving force for the whole process.

2. Experimental

2.1. Theoretical background

The choice of material suitable for making separation membrane is its chemical and mechanical resistance and adsorption capacity. The material used for making the membrane should have strong affinity towards component that is removed [18]. As the additional requirement is good contact between the polymeric membrane and the component of the mixture that should be separated. Therefore, two main parameters that should be taken in the consideration are solubility parameter and the polarity of the membrane [7, 19]. As proposed [7], solubility parameter theory is the most accurate method for the selection of the membrane material. The internal energy change ($\Delta E$) for polymer—solvent interaction is defined as:

$$\Delta E = v_S v_P (\Delta \delta)^2$$ \hspace{1cm} (1)

$$\Delta \delta = \delta_S - \delta_P$$ \hspace{1cm} (2)

In equation (1), $\Delta E$ is internal energy change in unit $\frac{kJ}{mol}$, $v$ is volume fraction of respective phase, and $\delta$ is the solubility parameter that is described elsewhere [20] in unit $\left( \frac{kJ}{cm^3} \right)^{1/2}$. Subscripts S and P correspond to solvent and polymer respectively. This equation directly implies that the solubility of the polymer in the polymer is directly proportional to the similarities in their solubility parameters [21]. Comparing the solubility parameters of various polymers that are used for commercial production of the membranes, it can be observed that their solubility factors are much closer to the solubility factors of thiophene in comparison to hydrocarbon species [22]. Therefore, the membranes are chosen for their good solubility of sulphur species, and bad solubility of hydrocarbons. According to one of the principal rules of solubility—similis similibus solvuntur—similar dissolves similar, the polarity of the active membrane film should be as close as possible to the polarity of the component that should be removed [23].

Another important issue about the potential application of membrane materials in desulphurization are its swelling properties. In general, the degree of swelling is defined as the chemical resistance of the membrane towards the organic solvents [24]. High swelling is induced my increased concentration of the permeating components, and usually results in decreased selectivity. If membrane swelling is high, the size of the pores is increased, and diffusion of all components of the mixture is enhanced. If the size of the pores is increased, fluxes of all components increase, resulting in decreased sulphur enrichment factor (ratio of sulphur in permeate and feed) [25]. It is assumed that suitable membrane should not gain more than 3% of its mass due to the swelling in order to prevent chemical degradation of the active layer [26]. The swelling degree is highly influenced by the degree of the cross-linking of the polymeric material that forms the membrane [27]. Just for comparison, swelling degree of poly(vinylpyrrolidin) is 2.8%, and polystyrene is soluble in most of the alkanes (C5–C9) [28]. Further criteria for the choice of the membrane material is the analysis of properties of adsorption, diffusion and permeation. It has been shown that the time to reach adsorption equilibrium is different for various compounds that are regularly present in gasoline [26, 29–31]. The adsorption coefficient $S$ (unit is $\frac{T}{L}$), also known as the swelling degree is defined as the weight gained during the adsorption, and it represents number of grams of solvent that can be adsorbed by one gram of the polymer, when adsorption equilibrium is reached [32]. The diffusion coefficient, $D$ \left[ cm^2/s \right]$ for different gasoline components can be estimated from the initial slope of the
adsorption curve when the amount of adsorbed gasoline component is presented versus time [33]. The permeation coefficient $P \left[ \frac{cm^2}{s} \right]$ is defined and calculated by equation (3):

$$P = S \cdot D$$

(3)

Dependence of $P$, $S$ and $D$ on temperature are usually given by the Arrhenius-type of the equation (equation (4))[34]

$$P = Ae^{-\frac{B}{RT}}$$

(4)

Where $A$ and $B$ are constants. Experimentally, $P$, $S$ and $D$ can be measured by analysis of dynamic adsorption curves for gasoline components. This can be done by plotting the graph $\frac{M}{M_\infty}$ versus $t$. $M$, and $M_\infty$ correspond to the weight gained at the time $t$ and weight gained when adsorption equilibrium is reached, respectively.

The transport mechanism of the gasoline component in membrane is presented by the empirical equation [35]:

$$\log \frac{M}{M_\infty} = K + n \log t$$

(5)

Masses in this equation are given in grams, and the time is given in seconds. Constant $K$ depends on the structure of the polymer and gives the information about the interactions between the polymer and the solvent. Higher value for the parameter $K$ indicate stronger interactions between the components of the gasoline and the polymer material. The value of the dimensionless parameter $n$ shows the type of the diffusion that is present in the system. For $n = 0.5$, diffusion obeys Fick’s law, while $n$ in range between 0.5 and 1 are characteristics of another diffusion mechanisms [35, 36].

Gasoline is a mixture of various hydrocarbons which are generally in one of the following groups: n-alkanes, iso-alkanes, cycloalkanes, aromatics and alkenes. The interaction of the functional groups of the mentioned classes is different with the different membranes, and therefore definition and understanding of those interactions is of essential importance for choice of the material [37, 38]. As the transport phenomena of various functional groups is different, the class of compounds significantly affects the performance of the membrane. In other words, the gradient of the chemical potential is not only determined by own chemical potential of the species, but also by chemical potential of other species present in the mixture. Therefore, it is important to study the synergistic effects of the gasoline components to the permeability properties of the membrane. In general, increase of the amount of aromatic compounds and alkenes increases the flux, but reduces the selectivity (enrichment of sulphur species) [39, 40]. This effect has been observed on typical hydrocarbon species present in gasoline on Polydimethylsiloxane (PDMS) based membranes [33, 39]. In the same study it has been observed that the addition of toluene and hexane (separately or in mixture) decreases both the enrichment factor and the total flux. In the hydrocarbon mixture chosen for simulating the properties of gasoline (of thiophene, n-heptane and toluene with addition of hexane) the increase of the swelling degree was measured (from 0.1149 (g g$^{-1}$) to 0.1571 (g g$^{-1}$)). In the same study, poly(ethylene glycol) membranes were tested, and their swelling degrees increased in the presence of toluene and hexane as well. For the feed mixture of n-heptane and thiophene, swelling degree changed from 0.0338 (g g$^{-1}$) to 0.1148 (g g$^{-1}$). This phenomenon is explained by the fact that the difference in affinity (δ) between toluene (δ$_{Toluene}$ = 18.2 cm$^{-3}$) and polymers

$$\left( \delta_{PEG} = 20.1 \text{ cm}^3, \delta_{PDMS} = 20.01 \text{ cm}^3, \delta_{STG} = 20.7 \text{ cm}^3 \right)$$

is smaller than the difference in the same parameter for n-alkanes (δ$_{n-alkanes}$ = 15.7 cm$^3$). It was also observed that the length of the chains of the n-alkanes is in opposite correlation with their partial fluxes. This was attributed to lower diffusivity of the alkenes with longer chains [40]. If thiophene is present in the mixture, coupling effect must be considered as partial fluxes and activation energy of thiophene and alkenes are different at the constant temperature. In general, lower alkenes cause higher permeation fluxes, but lower sulphur enrichment factor [22]. In the same study was observed that n-alkanes above the hexane (C-6) do not cause the swelling of the membrane which was attributed to the increased solubility by the plasticization degree [9]. Molecules of the shorter alkenes penetrate dense polymer membrane which causes decrease in the difference in activation energies for thiophene and alkenes [35]. Due to the shape of their molecules, cycloalkanes cause decrease in the flux and increase in enrichment factor for sulphur in comparison to n-alkanes ant aromatic compounds. It was also observed that increasing the amount of cyclohexane causes slight decrease in total flux and increase in enrichment factor, presumably by the effect of the reduction of the free volume in the bulk of polymer. The reason for this effect is low solubility of the cyclohexane in the polymer which reduced the swelling [36].

Poly(ether imide) (PEI) was chosen as the active layer as it was applied in various systems where high purity of the organic components is required [38, 39]. Its application in fuel cells fabrication was taken as a good indicator of its durability under the application prolonged over significant periods of time [41, 42].
2.2. Materials and procedures
For experimental procedures, pure thiophene was used as received (>99.5% p.a. benzene free, supplied by Sigma Aldrich). As hydrocarbon component n-heptane (>99% supplied by Sigma Aldrich) was used as received. The concentration of solvent and the solute in streams were measured using the gas chromatograph with flame ionization detector (FID). Methanol (99% p.a. obtained by Sigma Aldrich) was used as received as GC solvent. The retention times for thiophene and toluene were 204 and 430 seconds, respectively. Membranes were with active layer of PEI on the porous support obtained from the Sefar, Switzerland.

The pervaporation test cell was made of the stainless steel with a diameter of 18 cm. membrane with the effective area of 227 cm² was placed on the porous steel support with the polymer—covered size orientated to the feed solution. The temperature was set at 45 °C by a thermostat and controlled by the PID device. The feed solution was brought to the upstream side of the membrane at the constant flow of 1 l min⁻¹, and the retentate was returned to the supply flask. The feed side was at atmospheric pressure, and the permeate side was kept at 10 kPa by the vacuum pump. The pressure was measured by vacuum gauge. Permeate vapour was condensed in the flask cooled by the liquid nitrogen. Samples of the solid permeate were taken at the time intervals, and brought to the room temperature to conduct the measurement of the mass. The measured mass was used for the calculation of the resulting mass flux. The concentration of thiophene in the feeding stream was between 0.5 and 2% by mass. The yield of the process was calculated and evaluated on the basis of both total and partial permeation flux (equation (6)):

$$J_m = \frac{m_p}{S_m t}$$  \hspace{1cm} (6)

In this equation, \(m_p\) is the weight of the permeate in grams, \(S_m\) is membrane effective area in m², and \(t\) is time in hours.

The efficiency of sulphur removal procedure was evaluated based on the enrichment coefficient (\(\beta\), dimensionless unit):

$$\beta = \frac{c_p}{c_F}$$  \hspace{1cm} (7)

Where \(c_p\) and \(c_F\) are concentrations in permeate and feed stream respectively.

3. Results and discussion
The main topic of the experiment was to test the influence of initial concentration of sulphur in the feed solution in order to test the efficiency of the process depending on source of the crude oil. Main measurements were conducted on the commercially available polymeric membranes with the active layer of poly(ether imide) and their efficiency and selectivity in removal of various initial concentrations of thiophene from n-heptane was tested. Results have shown that increase of the thiophene content in the feed solution in the range from 0.5 to 2 mass %cause increased flux for both thiophene and n-heptane flux. Increase of the flux for both components is followed by the decrease of the enrichment factor (selectivity) \(\beta\). The dependencies of fluxes were fitted by linear equations, estimated by the method of minimal squares. The obtained results are presented on figures 1 and 2.

Equations for fitting were obtained as:
For tiophene:

\[ y = 0.0757x + 0.0169 \]  

For n-heptane:

\[ y = 1.514x + 168.11 \]  

In both of cases, value for the x is mass percent of the thiophene in the feed stream, and y is flux of the respective substance in \( \frac{kg}{m^2 h} \). This behaviour can be explained by the increased activity of the thiophene as a consequence of increased concentration which enhances the solubility of thiophene in the active layer of the membrane. Accordingly, total flux of both components of the feed stream is increased as well. Due to the high affinity of the material used for the active layer of membrane towards thiophene, \( \delta_{PEI} \), the swelling of the membrane was increased, which further caused the increase of the flux. However, increase of the flux with the increase of the sulphur content is higher for the n-heptane in comparison with the thiophene which resulted in decrease of the total enrichment factor. For the fitting of the enrichment factor, quadratic function was used as it represents the changes better in comparison to linear function. The obtained data are presented on figure 3.

The equation of dependency of the enrichment factor on the concentration of thiophene is given as:

\[ y = 862.87x^2 - 3448.6x + 4489 \]  

Where x represents mass % of thiophene in the feed stream, and y represents value of \( \beta \). The n-heptane has lower affinity to PEI \( \delta_{PEI} \), in comparison to thiophene is less soluble in non-swollen membrane. However, with the swelling diffusion is enhanced which results in the increase in total flux. This is supported by the observed decrease in enrichment factor with increase of thiophene concentration.

The value observed and measured for the PEI was compared to the available results for the membranes based on poly(ether sulfone) (PES) [16, 17]. Comparing two types of polymers, it was observed that results are comparable, and that use of PEI causes slight increase in overall flux with the decrease in selectivity of the membrane. Due to the structure and properties of PEI and PES, it is supposed that mixture of two polymers would obtain the best results that would include the best flux versus selectivity properties.

Figure 2. The dependency of the flux of n-heptane on the concentration of thiophene.

Figure 3. Dependence of the enrichment factor of Sulphur on the concentration of thiophene.
4. Conclusion

Removal of the sulphur and its compounds from the gasoline is one of the most important tasks, both economically and environmentally. Desulphurization might be obtained by various methods, and one of the most promising methods is application of the polymeric membrane processes driven by the difference in pressure between feed and permeate side. In this experiment, the influence of initial amount of sulphur compound (thiophene) in alkane (n-heptane) to the efficiency of sulphur removal process was investigated. It was observed that increase in the initial amount of sulphur in feed stream increases both flux of thiophene and the n-heptane. This behaviour is explained by the effect of swelling of the membrane as the high amount of thiophene is dissolved in active layer of membrane. The increase of the flux of n-heptane was higher in comparison with the increase of the flux of thiophene which caused decrease of the total enrichment factor. This is explained by the fact that higher concentration of dissolved thiophene in the active layer enhances solution and diffusion of n-heptane. During this process selectivity of the membrane decreases as a consequence of the increased mobility of polymer chains in the active layer. The desulphurization system which includes PEI as an active component has been observed as a good starting point for the future research and potential application. In the future research, attention will be paid to the construction of membrane with the active layer that would include the mixture of PEI and PES polymers.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

ORCID iDs

Dragutin Nedeljkovic © https://orcid.org/0000-0003-3352-4452

References

[1] Brunet S, Mey D, Perot G, Bouchy C and Diehl F 2005 Applied Catalysis A: General 278 143–72
[2] Pourhashem G, Adler P, McAloon A and Spatari S 2013 Environ. Res. Lett. 8 025021
[3] Zhao L, Li K, Wu R, Zhang H and Jin J 2020 Mater. Res. Express 7 125502
[4] Chen J, Li J, Qi R, Ye H and Chen C 2008 Journal of Membrane Science 322 113–21
[5] Feng X and Huang R Y M 1996 Journal of Membrane Science 118 127–31
[6] Ti-Cai H, Zhao M, Xue-Feng Z and Qiong W 2019 Mater. Res. Express 6 055504
[7] Hansen C M 1999 Hansen Solubility Parameters: A User’s Handbook (Hoersholm, Denmark: CRC Press LLC)
[8] Huang J, Li J, Zhan X and Chen C 2008 Journal of Applied Polymer Science 110 3140–8
[9] Ito E and Veen R 2006 Catalysis Today 116 446–60
[10] Li L, Xu Z, Sun W, Chen J, Dai C, Yan B and Zeng H, 2020 Journal of Membrane Science 598 117661
[11] He S, Jiang X, Li S, Ran F, Long J and Shao L 2020 AIChE J. 66 e16543
[12] Jiang X, He S, Han G, Long J, Li S, Lai C H, Zhang S and Shao L 2021 ACS Appl. Mater. Interfaces 13 1296–305
[13] Kong Y, Lin L, Yang J, Shi D, Ou H, Xie K and Li L 2007 Journal of Membrane Science 293 36–43
[14] Kong Y, Lin L, Zhang Y, Lu F, Xie K, Liu R, Guo L, Shao S, Yang J and Shi D 2008 European Polymer Journal 44 3335–43
[15] Chandra N, Kumar K and Aravind U 2018 Mater. Res. Express 5 085504
[16] Kong Y, Lu F and Yang J 2010 Patent CN 101721924 A
[17] Kujawski W 2009 Pervaporation and vapors separation. Membranes Theory and Practice (Toruń: Zeszty III)
[18] Leiflaive P, Lemberton J L, Perot G, Mirgian C, Carriat J Y and Colin J M 2002 Applied Catalysis A: General 227 201–15
[19] Li B, Xu D, Jiang Z, Zhang X, Liu W and Dong X 2008 Journal of Membrane Science 322 293–301
[20] Li B, Zhao W, Su Y, Jiang Z, Dong X and Liu W 2009 Journal of Membrane Science 326 556–63
[21] Lin L, Kong Y, Wang G, Qu H, Yang J and Shi D 2006 Journal of Membrane Science 285 144–51
[22] Lin L, Kong Y, Xie K, Lai F, Liu R, Guo L, Shao S, Yang J, Shi D and Zhang Y 2008 Separation and Purification Technology 61 293–300
[23] Lin L, Kong Y and Zhang Y 2008 Journal of Membrane Science 325 438–45
[24] Lin L, Wang G, Qu H, Yang J, Wang Y, Shi D and Kong Y 2006 Journal of Membrane Science 280 651–8
[25] Lin L, Zhang Y and Kong Y 2009 Fuel 88 1799–809
[26] Morthere H R, Ghasemaghami F and Mokhtaran B 2012 Chemical Engineering Research and Design 90 409–32
[27] Basterra-Beroiz B, Rommel R, Kayser F, Westermann S, Valentin J I and Heinrich G 2018 eXPRESS Polymer Letters 12 731–9
[28] Plummer M A and Jonelli R F 2002 Removal of sulfur from a hydrocarbon through a selective membrane Patent US 0139713 Al
[29] Qi R, Wang Y, Chen J, Li J and Zhu S 2007 Separation and Purification Technology 57 170–5
[30] Qi R, Wang Y, Chen J, Li J and Zhu S 2007 Journal of Membrane Science 295 114–20
[31] Qi R, Wang Y, Li J, Zhao C and Zhu S 2006 Journal of Membrane Science 280 545–52
[32] Qi R, Wang Y, Li J and Zhu S 2006 Separation and Purification Technology 51 258–64
[33] Qu H, Kong Y, Lv H, Zhang Y, Yang J and Shi D 2010 Chemical Engineering Journal 157 60–6
[34] Saxton R J and Minhas B S 2002 Patent WO 000363822
[35] Sha S, Kong Y and Yang J 2012 Journal of Membrane Science 415–416 835–41
[36] Sha S, Kong Y and Yang J 2012 Energy & Fuels 26 925–9
[37] Schaeettel P, Vaucclair C, Luo G and Nguyen Q T 2001 Journal of Membrane Science 191 103–8
[38] Shariatinia Z, Mazloom Jalali A and Taromi F 2016 Modelling Simul. Mater. Sci. Eng. 24 035002
[39] Shao P and Huang R Y M 2007 Journal of Membrane Science 287 162–79
[40] Smitha B, Suhanya D, Sridhar S and Ramakrishna M 2004 Journal of Membrane Science 241 1–21
[41] Wang G, Weng Y, Xie D, Chu D and Chen R 2010 ECS Trans. 25 73
[42] McGrath J, Roy A, Lee H, Yu X, Badami A, Li Y and Wang H 2007 ECS Trans. 2 55