Review

# Pervaporative desulfurization of gasoline: A review☆

Aziz Fihri*, Remi Mahfouz, Abdullah Shahrani, Ihsan Taie, Gasan Alabedi

*Oil and Gas Network Integrity Division, Research & Development Center, Saudi Aramco, Dhahran 31311, Saudi Arabia*

## ARTICLE INFO

## ABSTRACT

The membrane based pervaporation process for sulfur removal from gasoline has evoked a great deal of attention due to its distinct advantages. Such advantages include: lower operating and energy costs, easier scale-up, as well as higher selectivity. The separation mechanism of pervaporative desulfurization is based on the sorption and diffusion differences between the components of the gasoline mixture. This review aims to provide insight into the state of the art research activities related to pervaporative desulfurization of gasoline using organic polymeric membranes. To obtain a comprehensive perspective about the pervaporative desulfurization, other techniques of desulfurization are discussed briefly in the introduction. The solubility parameter theory for membranes selection and the membranes material modifications are also examined in this review. The effects of various factors including feed sulfur content, operating temperature, permeate pressure and feed flow rate on desulfurization performance are discussed.

## Contents

☆ This article is dedicated to the memory of Bouchaib FIHRI, admirable father and an irreplaceable person.

* Corresponding author.
  *E-mail address:* Aziz.fihri@aramco.com (A. Fihri).

## 1. Introduction

Gasoline is a refined product of petroleum consisting of a mixture of alkanes, C5-C14 olefins and cycloparaffins, as well as aromatics compounds. Its composition depends on the crude oil used and is usually made up of different blending components coming from reforming, isomerization and fluid catalytic cracking (FCC) processes. Among them, FCC gasoline represents 30–40% of the total gasoline pool, making it the most important sulfur contributor in gasoline. Sulfur in gasoline can be found in different forms, such as sulfides, thiols and mercaptans. Many reports in scientific literature have confirmed that thiophenic sulfur represents over 80% of the total sulfur content in FCC gasoline after the alkali cleaning process [1]. These organosulfur impurities generate sulfur dioxide after combustion under high temperatures, which can contribute to acid rain as well as poison many of the catalytic converters used in automobiles [2]. A sulfur limitation of less than 10 ppm for gasoline is imposed now in many countries [3,4]. The catalytic hydrodesulfurization process (HDS) is traditionally used for gasoline desulfurization, but this conventional process requires high temperatures ranging from 300 to 400 °C and high pressures ranging from 30 to 130 atmospheres of absolute pressure as well as high hydrogen consumption. This process is very efficient for removing sulfides and disulfides but less effective toward thiophene and its derivatives such as dibenzothiophene and 4,6-dimethyldibenzothiophene. This process is strongly inhibited by the hydrogen sulfide generated from reactive sulfur compounds, and so shortening the catalyst's life [5,6]. Additionally, this catalytic process results in a significant reduction of octane number after treatment due to saturation of olefins molecules. Under these circumstances, many scientific papers have not only focused on improving HDS catalysts and processes but also on the development of alternative technologies. Many solutions have been proposed, such as alkylation-extraction, selective extraction, selective oxidation and membrane separation. The objective of this current study is to review the recent scientific and advanced technologies in the field of pervaporative desulfurization using the organic membranes, the factors affecting their performance and the different pathways used to enhance their separation properties. This will provide a better understanding of their performance and the gaps and challenges that still have to be overcome for large-scale use in industrial applications. We specifically choose to restrict our review efforts to polymeric membranes due to their wide accessibility to the entire chemist community including non-specialist of membranes synthesis and particularly to researchers involved in separating organic–organic liquid mixtures. The first section presents an overview of reported literature on the desulfurization methods that can replace the conventional hydrodesulfurization process. In the second section, basic principles on gasoline desulphurization by pervaporation and solubility parameter theory for membrane are discussed successively. The third section is devoted to membranes modifications and the factors affecting membrane performance. Finally, the review will provide remarks and recommendations on the topic.

## 2. Desulfurization methods

### 2.1. Desulfurization by alkylation

The catalytic alkylation reaction is based on increasing the molecular weight and the boiling point of the organosulfur compounds. This is done through alkylation reaction with olefins present in the feed, using acidic catalysts. Once the boiling temperature of the organosulfur species are shifted to a higher value, the alkylated heavy organosulfur species can be removed from gasoline by distillation. British Petroleum developed this process under the name olefinic alkylation of thiophenic compounds [7]. It can be handled under relatively mild conditions, with a minimal loss of octane number and without any hydrogen consumption. The desulfurization efficiency can be enhanced by increasing the alkylating agent/sulfur ratio [8–10]. The performance of this process is influenced by side reactions such as olefin polymerization and alkylation of aromatic hydrocarbons. In addition, the challenge of adopting olefinic alkylation of thiophenic compounds is the risk of corrosion and the toxicity produced by alkylation agents, which must be addressed before commercializing this process. Another disadvantage is the decrease in olefin concentration due to its reaction with the alkylating agents.

### 2.2. Desulfurization via extraction

The organosulfur compounds are more soluble in appropriate solvent than other hydrocarbons; therefore, it can be removed from gasoline via selective extraction using organic solvents. Afterward, the organosulfur compounds can be removed from the solvent by distillation to allow the solvent to recycle. This procedure is preferable due to the low operating temperature and relatively low pressure without hydrogen consumption. It also is performed without the use of any catalyst. The chemical structure of the gasoline compounds does not change during this process. However, the choice of solvent is crucial as it makes the process more efficient since the organosulfur compounds should be fully soluble in the organic solvent. To make this process feasible, the solvent should have a boiling temperature different than that of the organosulfur species. The solvent should also be non-toxic and cost effective to make the process economically viable and more sustainable. Experimental results revealed that desulfurization levels of 50–90% can be attained using polyethylene glycols, acetone, ethanol and nitrogen containing solvents [11–14]. It is worth mentioning that a mixture of solvent such as acetone-ethanol or a tetraethylene glycol-methoxytriglycol is usually used to enhance the solubility of sulfur impurities [11–14]. Unfortunately, the efficiency of this process is mainly influenced by the solubility of the organic sulfur species and the difficulty of making such a solvent mixture since its composition depends significantly on the spectrum of the organosulfur species present in the gasoline feed.

### 2.3. Oxidative desulfurization

Oxidative desulfurization combined with solvent extraction or distillation is considered as an alternative technology compared to the hydrodesulfurization process for effective desulfurization. During oxidative desulfurization, the sulfur species are oxidized using appropriate oxidants and converted to sulfoxides or sulfones. Afterward, they are preferentially extracted from gasoline due to their high relative polarity and high boiling point [15]. Several oxidants are reported in literature, such as $t$-butylhypochlorite, highly toxic $RuO_4$ and $H_2O_2$-$H_2SO_4$ systems [16–19]. However, oxidative desulfurization has several technical issues to overcome. First, some oxidants lead to undesirable reactions that can reduce the quantity and quality of the gasoline. Second, the selection of a suitable solvent for the extraction is serious issue and should be solved. Third, this process is not effective with FCC gasoline due to the high olefinic content, which can react with oxygen atoms to form epoxides. Lastly, the cost to treat sulfone waste should also be taken into consideration when evaluating oxidative desulfurization.

### 2.4. Biodesulfurization

Biodesulfurization is a process for reducing the organic sulfur content from fossil fuels using enzyme-catalyzed reactions. This

catalytic process occurs using water and oxygen at room temperature and without lowering the calorific value of the gasoline [20,21]. The microbial desulfurization involves a sequential oxidation of the organosulfur compounds and the break of the carbon-sulfur bonds. Many bacteria have been reported in the literature converting dibenzothiophene and alkyl sulfides, whereas fewer bacteria are found for benzothiophene and thiophene [22–25]. Biodesulfurization seems to offer several advantages compared to hydrodesulfurization. Importantly, this process does not decrease the octane number in gasoline and does not require high temperature or pressure. Despite impressive progress made to improve this process, a number of challenges remain untapped and many issues have to be solved before commercializing this technology. The stability and lifetime of bacteria under variable conditions in the refineries continues to pose difficulties as well as the amount of bacteria needed in this process. In addition, the rate of chemical reactions is faster when compared to the metabolism rate of sulfur compounds.

### 2.5. Desulfurization by ionic liquids

Ionic liquids are non-volatile organic liquid salt and have several advantages such as low vapor pressure in comparison to polar organic solvents. They are immiscible with gasoline, thermally stable and can be used in a wide range of temperature values [26]. The ionic liquids can also extract aromatic sulfur from gasoline at ambient temperature without any hydrogen consumption [27,28]. The removal of sulfur organic compounds from gasoline can be performed via a strong $\pi$–$\pi$ interaction with ionic liquids. The sulfides and alkylthiols are poorly extracted due to their weak interaction with the ionic liquids. Interestingly, the nitrogen compounds are found to be significantly better extracted when compared to organosulfur compounds [29]. Many studies confirm that the removal of sulfur compounds can modify the content of aromatics in gasoline, which can be problematic for maintaining octane number in gasoline [30–32]. Moreover, the regeneration of ionic liquid is expensive, and often several consecutive extractions are needed to reduce sulfur content from 300 to 10 ppm.

### 2.6. Desulfurization by reactive adsorption

Reactive adsorption, a process in which the sulfur organic species are converted into hydrocarbons, is an alternative process to reduce the sulfur content from gasoline [33,34]. The hydrocarbons can be returned to the final product without any structural modifications, whereas hydrogen sulfur is retained by the surface of sorbents. The zinc oxide modified with transition metals such as Nickel or Copper is the most important adsorbent mentioned in literature [35]. Petroleum Co., USA, used the principal of reactive adsorption to develop the so-called Phillips S Zorb process to remove sulfur from gasoline and diesel fuels [36,37]. The S-Zorb process consists of fluidized bed reactor technology conducted at high temperature and high hydrogen pressure. The used adsorbent is continuously removed from the reactor and transported into the regeneration reactor to be treated. Thus, he sulfur is removed from the surface of the adsorbent through burning and the formed $SO_2$ is sent to the sulfur plant. The adsorbent is then reduced with hydrogen and recycled back to the reactor.

### 2.7. Pervaporative desulfurization

Membrane technology applied to petrochemical field can be considered as an efficient approach for organic sulfur compounds removal [38]. This technology has gained an increasing interest attention during these last years because it offers many advantages compared to classical sulfur removal processes. This technology consists of process pervaporation and vapor permeation involving direct contact of the gasoline feed with the membrane processing good selectivity to separate the organic sulfur compounds from the sulfur enriched permeate fraction. The sulfur deficient retentate fractions can be used directly into the gasoline pool whereas the sulfur enriched permeate fractions need further treatment by conventional process. The membrane has often composed of a dense active layer and a porous support layer. Although the desulfurization by pervaporation has extensively studied but its has been little used industrially [39]. The main reason for that is the few number of available membrane material and their limited performance.

## 3. Pervaporative process

### 3.1. Basics of pervaporation

Gasoline desulfurization by a membrane-based pervaporation process is a newly emerging technology offering a number of potential advantages when compared to a non-HDS separation process [37,40]. This technology has gained increasing importance in recent years due to its distinct advantages, such as: lower operating and energy saving, ease of scaling up and manipulations, as well as greater selectivity toward thiophene over olefins without hydrogen consumption and the co-product of $H_2S$ gas. Using this technique, the feed treatment is not needed and the desulfurization can be achieved with little reduction of the octane number after sulfur removal. Moreover, the pervaporation process has been successfully used to separate liquid mixtures, which is difficult to achieve by usual distillation because of the close boiling point of liquid mixtures and its high sensitivity to heating. Presently, there are two commercial applications of pervaporation-one is the dehydration of alcohols and other solvents while the second application is the removal of trace volatile organic substances from water [41]. The pervaporative separation is a membrane processing of mixtures of liquid, by partial vaporization through a dense and nonporous membrane for selective permeation of one or more components from a liquid mixture [42]. As a result, the more permeable species in the permeate and the less permeable species in the feed can be concentrated. Basically, a typical pervaporative system includes a pervaporation cell where the membrane is held; a condensation system; and a vacuum system to recover the permeate (Scheme 1).

In this context, the S-Brane of Grace Davison Company and TranSep$^{TM}$ of TransIonics Corporation represents the successful membrane-dominated techniques for removal of sulfur from gasoline stream in which all costs only account for 20% of the conventional HDS process [42–45]. It is worth noting that the pervaporative desulfurization can be used alone or coupled with another desulfurization process.

The sulfur compounds pass preferentially through the dense polymeric membrane and can be removed from the feed due to their higher affinity and quicker diffusivity in the membrane. During the desulfurization process, the different organosulfur species of gasoline absorb into the membrane, diffuse through it, desorb out the membrane, then evaporate and condense at the cold permeate side of the membrane. For a continuous pervaporative process, the gasoline feed must be placed in direct contact with one side of the dense membrane, whereas a vacuum force must be applied from the other side of the membrane to maintain low absolute pressure at the downstream side of the membrane.

### 3.2. Pervaporation characteristics

The efficiency of a pervaporative operation can be evaluated in terms of permeate mass flux *(J)* and the membrane selectivity [46].
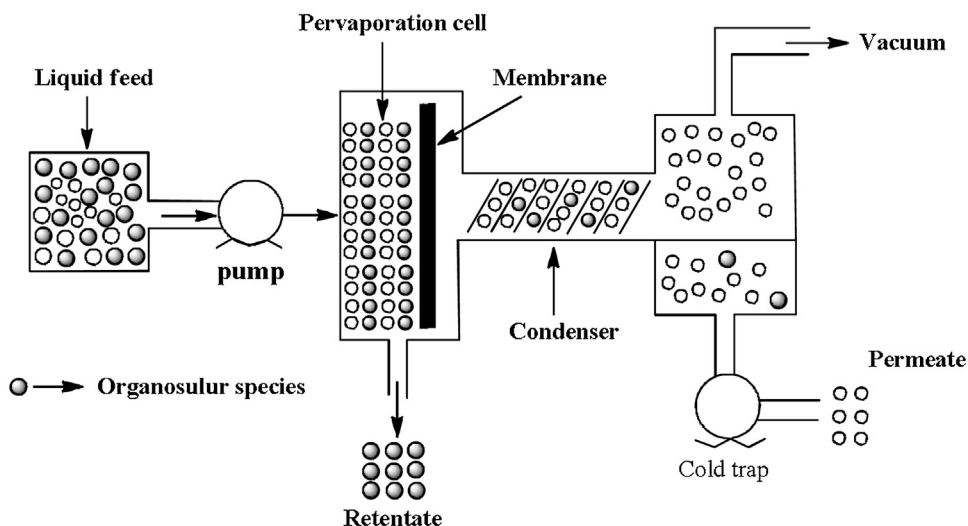
**Scheme 1.**

The flux can be expressed and calculated through Eq. (1):

$$(J = m/At) \tag{1}$$

The weight of permeate passing through the active membrane area A is represented by m, during the time t. Importantly, the mass flux J, depends strongly on the operating temperature conditions of the system [47]. The relationship between the permeation flux and operating temperature conditions can be expressed through the Arrhenius-type, following Eq. (2):

$$JP = Ap \exp\left(\frac{-E_p}{RT}\right) \tag{2}$$

In this equation, $J_P$ is the permeation flux, $A_P$ is a constant, $E_P$ represents the apparent activation energy for permeation, R is the gas constant and $T$ is the absolute temperature.

In general, there are two approaches to express selectivity: the separation factor and the enrichment factor. The separation factor is specific for a binary mixture, but the gasoline is a mixture of more than hundreds components. The sulfur enrichment factor can be used as an index of the separation selectivity for sulfur components [48]. In a desulfurization system, the enrichment factor is defined as the mass ratio of total sulfur content of feed (Gp) divided by the total sulfur in the permeate (Gs), as shown in Eq. (3).

$$(E = G_P/G_S) \tag{3}$$

As there is commonly a tread-off between the permeation flux and selectivity of membrane, another important parameter called pervaporation separation index (PSI) has been generally used by the scientific community to calculate the overall pervaporation efficiency [49–52]. It is expressed through Eq. (4):

$$PSI = J(E - 1) \tag{4}$$

when E = 1, no separation occurs; a PSI of zero means either zero flux or no separation.

## 4. Solubility parameter theory for membrane selection

Hildebrand first reported the solubility parameter (δ) as the square root of cohesive energy (Ecoh (J/mol) per molar volume, V (cm³/mol) as showed in Eq. (5) [53–55]. The solubility parameter is an effective way to characterize the interaction intensity between the solvent and membrane. Hildebrand solubility can provide

estimated information of the degree of interaction between materials. Accordingly, it can be used to select an appropriate membrane for pervaporation process. The solubility parameter provides essential information, allowing the selection of suitable polymer membranes to be able to achieve a particular pervaporative separation.

$$\delta = \left(\frac{E_{coh}}{V}\right)^{1/2} \tag{5}$$

Additionally, Hansen proposed an extension of the Hildebrand solubility parameter by dividing it in to its fractional components. The correlation can be expressed as shown in Eq. (6):

$$\delta = \delta^2{}_d + \delta^2{}_p + \delta^2{}_h \tag{6}$$

with $\delta_h$, $\delta_d$ and $\delta_p$ are solubility parameter, electrostatic and hydrogen bond components of the solubility parameter, and the dispersion, respectively. The Hansen solubility parameters are empirically determined based on multiple experimental solubility observations. It is an accurate tool to determine the suitable polymers that can be used to make an effective pervaporative separation [56].

The values of solubility parameters for some polymers and gasoline components are given in Table 1. The solubility parameters of thiophene species, which are the primary organosulfur species in FCC gasoline, is about 19–21 (J/cm³)^1/2. However, solubility of the most hydrocarbon species is in the range of 14–15 (J/cm³)^1/2. Additionally, the solubility parameters of most membrane materials reported in literature for pervaporative separation was about 20–26 (J/cm³)^1/2. Importantly, the solubility parameters of most membrane materials reported in recent literature were closer to the thiophene species than to the hydrocarbon species in gasoline, so they perform higher affinities to the thiophene species.

The composition of the membranes and their morphology are key elements that need to be addressed in any pervaporative process. Generally, the section of membranes is thought to be based on four important features, namely: high chemical resistance, high sorption capacity, good mechanical strength of the polymer film in the solution and low cost. In addition, a good interaction between the membrane and preferably one of the components in the mixture is required for the appropriate separation. Hence, the solubility parameter and the membrane polarity are the two interested indices in the design of news membranes [57,58]. The choice of membrane for the pervaporation

**Table 1**
Solubility parameters of polymeric membranes hydrocarbons and sulfur species in FCC [34,51].

| Gasoline components and polymers | $\delta$ (J/cm$^3$)$^{1/2}$ | Hydrocarbon | $\delta$ (J/cm$^3$)$^{1/2}$ | Typical sulfur species | $\delta$ (J/cm$^3$)$^{1/2}$ |
|---|---|---|---|---|---|
| Polypropylene | 21.93 | n-Pentane | 14.4 | Thiophene | 20 |
| polyethylene glycol | 20.1 | Isopentane | 13.8 | Methyl thiophene | 19.6 |
| Polyvinyl chloride | 26.49 | Hexane | 14.9 | Methyl thiophene | 19.5 |
| polyvinyl pyrrolidone | 20.56 | Heptane | 15.3 | Dimethyl thiophene | 19.3 |
| polyvinylbutyral | 23.12 | Octane | 15.5 | Trimethyl thiophene | 19.2 |
| PDMS | 21.0 | Isooctane | 14.2 | Diethyl thiophene | 19.2 |
| Polyurethane | 20.98 | Cyclopentane | 16.6 | Triethyl thiophene | 19 |
| Cellulose acetate | 25.06 | Cyclohexane | 16.7 | Thioether | 16.9 |
| Polyacrylonitrile | 26.61 | Methyl Cyclohexane | 16.0 | Dimethyl sulfone | 29.8 |
| Polystyrene | 18.5 | Benzene | 18.7 | Sulfide | 16.9 |
| Polyurea/urethane | 20.98 | Toluene | 18.2 | Disulfide | 17.4 |
| Polyimide | 32.3 | *m*-Xylene | 18.2 | *n*-Butyl sulfide | 28.1 |
| Polysulphone | 21.4 | *o*-Xylene | 18.5 | *n*-Butyl mercaptan | 18.4 |
| Polyvinyl alcohol | 39.15 | *p*-Xylene | 18.1 | Benzyl mercaptan | 21.1 |

process also depends strongly on the components to be separated. As the gasoline is a complex mixture, the selection and the modification of the membrane is very important to perform the desulfurization of gasoline bypervaporation.

Polymer membranes such as poly(ethylene-glycol), polyimide, and polyurea/urethane are commonly used for desulfurization [1,53,59–63]. Yet, the polydimethylsiloxane (PDMS) is the most preferred polymer as reported in the literature for pervaporative desulfurization of gasoline. It has superior permeability to small molecules, superior chemical and thermal stability, good processability and has a relatively low price [63]. The polydimethylsiloxane belongs to a group of silicones usually made of silicon, carbon and hydrogen as well as oxygen. PDMS consists of a flexible (Si–O) backbone and a repeating (Si(CH$_3$)$_2$O) unit where their number generally defines the molecular weight, and consequently many of the viscoelastic properties of the PDMS-based membranes.

According to solubility theory, the solubility parameter of PDMS is near to the solubility parameter of thiophene and its derivatives [63]. As a consequence, PDMS polymer will display priority in selective dissolution of the sulfur components in gasoline. Despite these remarkable properties, the pure PDMS membranes exhibit relatively poor mechanical strength due to the high flexibility of molecular chains. Although, various strategies have been attempted to reinforce elastomeric PDMS to acquire better and wider applications, requiring good mechanical properties.

## 5. Membrane material modifications

In general, differnts types of synthetic membranes are used in separation such as dense, porous and asymmetric membranes. During the separation process, the membranes can swell while in contact with the feed solution. Thus, membrane modification is necessary in order to reach high selectivity and high flux. Many approaches such as grafting, cross-linking, blending as well as the copolymerization have been reported in the literature to modify the properties of the membranes. Many efforts have been also made to incorporate the adsorptive fillers into polymeric membranes. It improves the polymer chain rigidity and the separation properties of the membrane by enhancing the sorption capacity for desired component. Consequently, the high sorption capacity of adsorbents and continuous operation of the membrane separation process are combined perfectly in the hybrid membranes. Many kinds of adsorbents have been used as fillers such as zeolites, metals oxide nanoparticles, etc [64,65].

Chen and co-workers prepared two polyimides containing fluorinated groups by condensation polymerization of 2,2′-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride with 4,4′-methylene diamine and diamino-3,3′-dimethyldiphenylmethane [61]. The flat asymmetric membranes of these materials were successfully prepared by phase inversion method and the inner structure was observed by method of SEM. The sulfur enrichment factor and the permeation flux were in the range of 3.12–2.24 and 0.56–1.68 kg/m$^2$ h for a feed with sulfur content from 720 to 802 ng/$\mu$m and operation temperature between 40 and 77 °C, respectively, for pervaporation n-heptane/thiophene mixtures. Unfortunately, the membrane performance deteriorated significantly with time.

White and co-workers used two polyurea/urethane multi-block copolymers as active layers on a polytetrafluoroethylene substrate for pervaporation desulfurization of refinery naphtha [66]. The first membrane was formed by a solution containing toluene diisocyanate terminated polyethylene adipate in 4-dioxane added to another solution containing 4-4′-methylene dianiline dissolved in 4-dioxane. The resulting gel was casted on a 0.2 μm pore size porous polytetrafluoroethylene membrane. The second membrane was synthetized using the same procedure by replacing 4-dioxane with a *N,N*-dimethylformamide solvent. The first membrane displayed an enrichment factor of 7.53 using a feed of 1065 μg/g thiophenic compounds, whereas an enrichment factor of 9.58 was observed when the second copolymer was usedwith a feed of 419 μg/g thiophenic compounds.

In 2006, Lin and co-workers reported important results in the field of desulfurization by pervaporation [53]. They investigated the swelling and pervaporation efficiency of a polyethylene glycol membrane (PEG) before and after cross-linking with maleic anhydride. They found that the flux and enrichment factor were 26.36 kg/(m$^2$h) and 1, respectively, for an unmodified membrane, whereas these values were 63 kg/(m$^2$h) and 3.05 for a cross-linked PEG membrane. The sulfur enrichment factor increased with the increase of the cross-linking agent loading and cross-linking time, while the total permeation flux decreased. Nevertheless, the decrease in the flux of sulfur components was slower due to their higher affinity to the PEG membrane. When the cross-linking agent loading increased to 18.18%, permeation flux decreased drastically to 0.4 kg/(m$^2$h); alternatively, the sulfur enrichment factor increased to 5.13. It should be noted that using 16% of maleic anhydride, the permeation flux and sulfur enrichment factor both exerted a higher level. In this study, the effect of the cross-linking time on pervaporation performance was also investigated. Indeed, when the cross-linking time increased, the permeation flux decreased firstly, then increased; opposite findings were observed for the sulfur enrichment factor. This may be due to excessive cross-linkingwhich shortens the length of chain links. At 60 min of cross-linking, both the sulfur enrichment factor and flux reached their highest values.

In another study, the same research group evaluated the deep desulfurization of FCC gasoline of a cross-linked polyethylene glycol membrane that was around $20\,\mu m$ thick [1]. Except at commencement, the flux and sulfur enrichment factor were almost always stable during the long operation of 500 h, indicating that this membrane possessed good resistance to pollution. The equilibrium values of the flux and sulfur enrichment factor vary in range of $0.5$-$0.6\,kg/(m^2 h)$ and $4.1$-$4.5$, respectively.

Qi and co-workers investigated the pervaporative desulfurization of model gasoline composed of $n$-octane and thiophenes, using $15$-$\mu m$ PDMS filled $Ag_2O$ [67]. The effect of several parameters such as $Ag_2O$ loading and feed temperature on the pervaporative were studied and evaluated. Transmission electron microscopy (TEM) measurements showed that $Ag_2O$ particles were highly dispersed in the polymeric phase and adhesive with the PDMS matrix. Moreover, the optimization studies showed that $Ag_2O$-filling leads to an increase in the selectivity of thiophenes due to the coordination of silver ion with C=C double bonds in thiophenes molecules. Due to the tortuosity effect of the impermeable $Ag_2O$ particles dispersed in the membranes, the total flux was also observed. When the feed temperature increased, the total flux increased, but the selectivity to thiophenes decreased simultaneously. Interestingly, the authors noted that when $Ag_2O$ content in the membranes increased from 0 to 5 wt%, the total fluxes decreased from 3.31 to $2.85\,kg\,m^{-2}h^{-1}$ at $50\,°C$, while the corresponding enrichment factors increased from 3.55 to 4.46 for thiophene and from 2.24 to 2.61 for 2-methylthiophene, respectively.

In a subsequent study, the same research group evaluated the $15$-$\mu m$ PDMS filled by AgY zeolite particles in the separation of thiopenes from mixture of $n$-octane, thiophene and 2-methyl-thiophene [68]. Scanning electron microscope (SEM) analysis of the membranes revealed that AgY zeolite particles were uniformly dispersed into the polymeric phase. The effect of zeolite loading and feed temperature on pervaporation process was investigated. Experimental results showed that AgY zeolite in PDMS membranes led to a significant increase in total flux with only a slight decrease in enrichment factor for both the thiophenes in the mixed matrix membranes. At $50\,°C$, with the AgY loading increment from 0 to 15 wt.%, the total flux increased from 3.31 to $8.15\,kg\,m^{-2}h^{-1}$, while the corresponding enrichment factors slightly decreased from 3.55 to 3.45 and from 2.24 to 2.14 for thiophene and 2-methylthio-phene, respectively. More importantly, the difference between enrichment factors of non-filled and filled membranes became unapparent at higher temperatures. However, at above 20% AgY loading, the zeolite particles caused more defects in the membranes, leading to low selectivity.

In a similar manner, Lin and co-workers studied the synthesis and the use of PDMS filled with $Ni^{2+}Y$ zeolite for the pervaporation removal of thiophene that was present in model gasoline composed of thiophene and $n$-octane [69]. SEM analyses revealed that zeolite particles were uniformly dispersed in the membrane and had an average size of approximately $1$-$2\,\mu m$. Interestingly, the permeation flux increased monotonically with the $Ni^{2+}Y$ content, and a considerable increase in the enrichment factor was found when the $Ni^{2+}Y$ content reached 5 wt%. When the $Ni^{2+}Y$ content varied from 10 to 20 wt%, the enrichment factor started to decrease, possibly due to the occurrence of defective voids within organic-inorganic interface region. For 500 ppm sulfur in feed at $30\,°C$, the PDMS membrane containing 5.0 wt% $Ni^{2+}Y$ zeolite exhibited the highest enrichment factor of 4.84 with a permeation flux of $3.26\,kg\,m^{-2}h^{-1}$. For comparison, it is noticeable that the enrichment factor and permeation flux for the unfilled PDMS were 2.9 and $2.3\,kg\,m^{-2}h^{-1}$, respectively. In addition, it was found that the interfacial morphology strongly influenced the separation performance of the hybrid membrane.

Kong and co-workers recently reported an exciting application of polyethylene glycol (PEG)/polyethersulfone (PES) composite membranes in the desulfurization of FCC gasoline by pervapora-tion [70]. The membranes were prepared using PEG as the active layer, PES as the support layer and in the presence of different amounts of maleic anhydride which was used as the cross-linking agent to reduce membrane swelling [71,72]. The experimental results revealed that increasing the amount of the cross-linking agent up to 25% led to a decrease of the permeation to less than $0.6\,kg/m^2 h$, which is an undesirable amount from a scale-up perspective of membrane technology. The authors further evaluated the long-term stability of PEG/PES membranes (500 h) with cross-linking agent amounts of 17% and 8%. When the cross-linking agent amount was 17%, the pervaporation performance of the composite membrane achieved a steady state for 6 h and changed slightly for the remainder of time. Nevertheless, when the cross-linking agent amount was 8%, the equilibrium was reached at only 3 h, but after 100 h the permeation flux incremented while the sulfur enrichment factor declined. These findings can be explained by the swelling of the low-cross-linked membrane by gasoline.

Later, Lin and co-workers investigated the desulfurization mechanism of typical gasoline composed of thiophene, $n$-heptane, cyclohexane, cyclohexene and toluene. The study used commercial polyethylene glycol membranes filled with various amounts of maleic anhydride as the cross-linking agent [73]. They found that the solubility, diffusion and permeation coefficients of typical gasoline components obviously declined when the cross-linking degree of polyethylene glycol increased.

In the same context, Chen and co-workers reported on the preparation of cross-linked polyethylene glycol/polyetherimide composite membranes (PEG/PEI) and their desulfurization perfor-mance in ethyl thioether/heptane mixtures [74]. The scanning electron microscope measurements revealed that thecross-sec-tional structureof PEG/PEI composite membrane consisted of a very thin layer and porous finger-like structure. The thickness of the PEG layer was found to be around $6\,\mu m$. The experimental data revealed that the flux and enrichment factor changedsignificantly in the range of 12–14 wt% of the cross-linker until the cross-linking agent reached its equilibrium saturation at 14 wt%. Moreover, the variations of the flux and enrichment factor were remarkably within 10 h of cross-linking time, while there wasalmost no change after 20 h of cross-linking as the cross-linking reaction was terminated.

It is worth noting that Lin and co-workers were able to prepare a CuY zeolite-filled polyethylene glycol hybrid membrane for sulfur removal from gasoline feed [75]. The sorption, diffusion, and permeation coefficients of gasoline components using filled membranes were significantly higher when compared to unfilled membranes. The zeolite filling led to an increase of flux due to zeolite porosity allowing more diffusion for smaller molecules through mixed matrix membranes. Additionally, the sulfur enrichment factor started to increase with zeolite loading and then declined at higher zeolite loading. This could be attributed to the combined influence of complexation force between zeolite and thiophenes, as well as the opposing effect between flux and selectivity. For instance, using 9 wt% CuY loading, a higher permeation flux of $3.19\,kg\,m^{-2}h^{-1}$ and sulfur enrichment factor of 2.95 were observed with a $1190\,\mu g/g$ sulfur content level in gasoline feed. This may be attributed to the combined influence of complexation force between CuY zeolite and thiophenes, as well as toopposing effects between flux and selectivity.

Kong and co-workers patented the preparation and the pervaporation performance of a polyacrylonitrile-grafted modified cellulose membrane for gasoline desulfurization [76]. The authors claimed that while the polyacrylonitrile side chain played a supporting role in the structure of a prepared membrane, the

cross-linked cellulose main chain inhibited the swelling of the membrane, and the cellulose chain segment controlled the permeation of the membrane. Additionally, the tuning of the permeability and the selectivity were found to depend on the change of contents of different chain segments.

In an interesting study, Qu and co-workers reported on the effect of cross-linking on desulfurization mechanisms. They investigated the sorption and diffusion behaviors of gasoline components through hydroxyethyl cellulose membranes using different amounts of 1,6-hexanediol diacrylate as the cross-linking agent [77]. The authors disclosed that the swelling degree of unmodified membrane in thiophene and toluene was infinite, meaning that these species can dissolve the unmodified membrane. Interestingly, an increase in the amount of 1,6-hexanediol diacrylate seemingly reduced the sorption and diffusion rates of gasoline components into the membrane and increased the difference of solubility/diffusion parameters between thiophene/hydrocarbon components. As was expected, the increase of cross-linking content led to a decrease in the permeation flux and an increase of the sulfur enrichment factor.

More recently, Liu and co-workers demonstrated that the copolymerization of polyimide with polyethylene glycol enhanced the permeation flux with a negligible effect on the sulfur enrichment factor [78]. In this study, the effect of weight loading of polyethylene glycol on the desulfurization performance was investigated using model gasoline that was prepared with $1000\,\mu g/g$ of sulfur content and membranes with a thickness around $10\,\mu m$. By increasing the weight loading of polyethylene glycol in the block copolymer, the permeation flux increased whereas the sulfur enrichment factor decreased.

Liu et al. also reported that the deposition of a thin layer of dopamine on $TiO_2$ microsphere ensured a high loading of $Ag^+$ on $TiO_2$ [79]. The dopamine was robustly anchored onto the $TiO_2$ microsphere surface via favorable coordination chemistry, allowing higher loading of $Ag^+$ ions with a strong coordination bond with amine groups of dopamine. Subsequently, the incorporation of modified $TiO_2$ microspheres into the PDMS matrix by physical blending improved the stability of thereof. The obtained results indicated that the $Ag^+$ loading amount notably increased in the presence of dopamine. The pervaporative desulfurization experiments showed that increasing the $Ag^+/TiO_2$ microsphere weight concurrently enhanced the normalized permeation flux and enrichment factor of the membranes. This could be attributed to the interfered polymer chain packing through the inorganic particle incorporation and specific reversible chemical reaction between $Ag^+$ and thiophene. The membrane exhibited an optimum desulfurization performance when the permeation flux, enrichment factor and the weight fraction of $Ag^+/TiO_2$ microsphere were attained $4.14\,kgm^{-2}h^{-1}$, 8.56, 5.0 wt%, respectively.

Zhang et al. fabricated a novel PDMS/poly(oligosilsesquioxanes) (POSS) composite membrane for the separation of thiophene/*n*-heptane, toulene/*n*-heptane and benzene/*n*-heptane mixtures [80]. By increasing the POSS loading into PDMS matrix, the sulfur enrichment factor of separation for thiophene/*n*-heptane increased. The enrichment factor of benzene and toluene displayed a similar trend to that of thiophene. The total flux of separation for thiophene/*n*-heptane increased up to 2 wt%, with the increase of the POSS loading in PDMS matrix, and then decreased at a higher POSS loading.

Jiang and co-workers synthesized PDMS–$SiO_2$ hybrid membranes *via* in situ biomimetic mineralization method [81]. It was found that use of silica precursors such as tetraethyl orthosilicate and tetramethylorthosilicate lead to the formation of a smaller silica nanoparticle. This happened through the synergy of polymerization of PDMS oligomers in the oil phase with silica precipitation in the reverse micro-emulsion. Consequently, the larger interfacial area engendered more hydrogen bonds between the silanol groups on the silica surface and the oxygen atoms on the polymer chains, leading to the improved mechanical strength of the membranes significantly. It was also reported that the incorporation of silica into the PDMS matrix increased the size and the number of free volume cavities that afford lower diffusion resistance for penetrant molecules. The as-prepared membrane exhibited an optimum desulfurization performance with permeation flux of $7.36\,kgm^{-2}h^{-1}$ and the selectivity of 4.98 toward thiophene in model gasoline.

Jiang and co-workers also synthesized different kinds of hybrid membranes possessing high separation performance by incorporating metal ion-chelated dopamine nanoaggregates into PDMS bulk matrix membrane [82]. The swelling-resistance and thermal stability of the resulting membranes were notably enhanced due to the improved cohesive energy and the chain rigidity accredited to the hydrogen-bond interaction between the dopamine nano-aggregates and PDMS. In this study, the $Cu^{2+}$ ion exhibited the best facilitated transporter compared to $Ni^{2+}$ and $Ce^{4+}$ ions, likely due to the high loading amounts of $Cu^{2+}$ ion and superior free volume properties of the PDMS-dopamine/Cu membrane. At $30\,^{\circ}C$ and 40 $Lh^{-1}$ of the feed solution, the membrane attained the permeation flux of $7.42\,kgm^{-2}h^{-1}$ and the enrichment factor of 4.81 when the dopamine/Cu loading reached 5.0 wt% exceeding the PDMS membrane.

In a recent report, Liu and co-workers developed dopamine (DA)-silver (Ag) nanoparticles and they subsequently embedded them into PDMS matrix to prepare PDMS-DAAg hybrid membranes for pervaporative desulfurization of model gasoline [83]. The authors indicated that the silver element played two crucial roles in the membranes. The first is that the $Ag^+$ facilitated the transport in the membrane due to continuous reversible interaction between $Ag^+$ and thiophene, leading to an increase of the overall selectivity of membranes. The second role is that silver nanoparticles rendered additional diffusion pathways for penetrants, which increased the permeation flux through the membranes. Moreover, the dopamine nanoparticles seemed to remove the voids of the interface between the silver nanoparticles and the polymer matrix through the formation of hydrogen bonds with hydroxyl of the PDMS chain, as well as with the amino groups of 3-amino-propyltrimethoxysilane (APTMS). Additionally, the dopamine nanoparticles reinforced the chain rigidity and led to a strengthened sieving effect and improved selectivity. The amine group of dopamine provided a lone electron pair to form coordinative bonds with silver ions. In the pervaporative desulfurization, the hybrid membrane with 5.0 wt% of DAAg nanoparticles exhibited an optimum separation performance with permeation flux of 8.22 $kgm^{-2}h^{-1}$, which is three times higher than that of PDMS. The enrichment factor reached 5.03, which is 50% higher than that of PDMS. The enhancement of separation performance was mainly due to the facilitated transport of thiophene by reversible interaction between $Ag^+$ and thiophene molecules, and the moderate fractional free volume tuned by DAAg nanoparticles. Moreover, the anti-swelling, mechanical properties and thermal stability of the membranes were also enhanced.

The main objective of cross-linking the polymer is to make it insoluble in the gasoline feed and to decrease its swelling in order to derive good selectivity. The chemical structure of the polymer is altered through the cross-linking process and different techniques may be used to create cross-linking. Such techniques include both a chemical reaction using a compound to connect two polymer chains, or irradiation using high-energy ionizing radiation. However, the cross-linkage and the degree of cross-linking should be controlled thoroughly to avoid excessive cross-linking as it makes the polymer membrane brittle with a loss in its dimensional stability, which spoils the membrane applicability for

pervaporation. Many research groups have reported on cross-linking modification of membrane material for gasoline desulfurization.

In a recent study, Wu et al. reported that the interfacial stability between the PDMS active layer and the poly(ethersulfone) (PES) support layer, as well as swelling resistance of the membrane, can be improved by introducing a bifunctional aminosilane such as 3-aminopropyltrimethoxysilane [84]. The authors indicated that the introduction of APTMS lead to generate a cross-linked PDMS matrix through the condensation of the silanol end groups of PDMS with the methoxyl groups of APTMS as well as the anchoring PDMS to the PES support layer through formation of hydrogen bonds between the aminopropyl groups and the sulfone groups of PES. Additionally, the APTMS is acting as a sticker by its aminopropyl groups by the formation of van der Waals force and forming hydrogen bonds with the sulfone groups of PES. The PDMS-APTMS/PES membrane with an APTMS/PDMS weight ratio of 0.06 exhibited the highest permeation flux of 6.95 $kgm^{-2}h^{-1}$ with an enrichment factor of 3.15, for a feed concentration of 1300 ppm thiophene at 33 °C. The permeation flux decreased steadily by increasing cross-linker content from 0.06 to 0.4 while the enrichment factor first increased by increasing APTMS loading from 0.06 to 0.1, then decreased. This behavior could be attributed to an excess amount of cross-linker. This might be due to the fact that as excessive amount of the cross-linker was added, a portion of APTMS did not perform its cross-linking function but stayed in the PDMS active layer and enriched around the interface of PDMS and PES by forming hydrogen bonds between the amino groups of APTMS and the sulfone groups of PES support.

Chen and co-workers described the synthesis and the use of cross-linked polydimethylsiloxane-polyetherimide (PEI) composite membranes in pervaporative separation of n-heptane/thiophene mixtures [85]. SEM measurements revealed a clear boundary between the PDMS top layer and the PEI support layer. Meanwhile, the cross-sectional structure of the PDMS-PEI composite membrane consisted of an ultrathin skin layer and a porous finger-like structure. Additionally, the SEM images showed that the thickness of the PDMS top layer was approximately 4 μm. The effects of the amount of PDMS, cross-linking temperature, amount of cross-linking agent, and cross-linking time on the pervaporative efficiency were investigated. The authors concluded that the flux decreased when the amount of cross-linking agent increased. However, the enrichment factor increased when concentration of the crosslinking agent reached 20 wt% and then decreased. This could be attributed to a slower diffusivity speed of thiophene in the membrane in comparison to that of n-heptane [86]. They also indicated that increasing the cross-linking temperature in the range of 50–120 °C led to an increase of the permeation flux and the enrichment factor. According to the authors, the cross-linking performed from 80 to 100 °C during 10 h was more preferable, as almost no change in performance was observed for cross-linking reaction of more than 20 h.

Jin and Co-workers reported the preparation and the use of cross-linked PDMS/ceramic composite membrane for desulfurization of model gasoline composed of n-octane and thiophene [87]. The SEM measurements showed that the active PDMS layer uniformly coated uniformly the surface of the tubular ceramic supports. The surface of the composite membrane was dense and defect-free. In addition, the structures of $Al_2O_3$, $ZrO_2$ and PDMS layers were clearly observed. The PDMS layer was well adhered to the porous ceramic support layer and has a thickness of about 8 μm. In regard to the results described, the total flux increased with the increase of feed temperature and sulfur content, whereas the sulfur enrichment factor decreased. In addition, the total flux and sulfur enrichment factor improved with low permeate pressure and high feed flow rate. The membrane exhibited a high

total flux of 5.37 $kg/m^2h^{-1}$ and a corresponding sulfur enrichment factor of 4.22 for 400 $\mu g\,g^{-1}$ sulfur in feed under a pressure of 210 Pa at 303 K. These results indicate that the chosen membrane has high potential towards sulfur removal from gasoline at room temperature.

## 6. Factors affecting membranes performance

### 6.1. Operating temperature

Operating temperature is an important factor influencing the membrane performance for desulfurization. It is generally observed that increasing the operating temperature enhances the permeation flux but decreases the enrichment factor and the selectivity. This could be attributed two different factors as significant pressure difference and thermal stability of the membrane. The high vapor pressure difference between both sides of the membrane produced by elevated temperature enhanced the transport driving force [1]. Furthermore, the PDMS polymer chains became more flexible at an elevated temperature, leading to a larger free volume, and thus an increase in the mass transfer coefficients of penetrants in the membrane.

The effects of feed temperature on pervaporation performance using fluorinated polyimides membranes was also investigated [61]. The obtained results revealed that by increasing the feed temperature, both pervaporation flux and the sulfur enrichment factors increase. These findings can be explained by the mobility of polymer. Indeed, when the feed temperature was higher, the mobility of glassy polyimide chains increased in order that the high diffusion resistance of aromatic polyimide towards thiophene was reduced and thiophene can easily diffused through the fluorinated membranes. Therefore, the permeation of thiophene with large volume can be facilitated and both increased permeation flux and pervaporation selectivity are observed without trade-off behavior.

Lin and co-workers investigated the effect of the feed temperature on pervaporative desulfurization of model feed composed of thiophene and n-heptane using cross-linked PEG membranes [1]. As was expected, when the temperature increased in the range of 47–117 °C, the total permeation flux increased. The sulfur enrichment factor firstly increased then decreased subsequently. At 85 °C, the sulfur enrichment factor reached its high value. Indeed, the feed temperature improved the driving force of the source of mass transfer and the saturated vapor pressure of components at the permeated side and availed the components in permeating through the membrane. In a similar manner, the influence of the feed temperature on pervaporation performance of polyethyleneglycol/polyurethane blend was also investigated in a temperature range of 77–137 °C [88]. The same findings were observed-the permeation flux increased when the feed temperature increased, while the sulfur enrichment factor increased firstly and decreasedafterword.The results were similar with the conclusion for PEG membranes [53]. Also, similar conclusions were observed for the pervaporation performance of PEG membranes filled with CuY zeolithe. At 110 °C, the sulfur enrichment factor reached its highest value [75].

The research group of Li investigated the flux and the selectivity for thiophene/n-octane and

2-methylthiophene/n-octane mixtures under different feed temperatures between 30 and 70 °C, using PDMS-APTMS/PAN hybrid membranes [89]. The authors observed higher yield in total flux and lower selectivity towards thiophenes while increasing the temperature. For instance, the total fluxes for thiophene/n-octane mixture increased from 1.5 to 3.4 $kgm^{-2}h^{-1}$ when the temperature increased from 30 to 70 °C, whereas the selectivity decreased drastically from 4.9 at 30 °C to 3.9 at 70 °C. The same behaviors were observed on 2-methylthiophene/n-octane mixture while

increasing the temperature from 30 to 70 °C; the flux increased from 1.25 to 3.25 kgm$^{-2}$h$^{-1}$, but the selectivity decreased from 2.47 to 2.25. The increment of the total flux with temperature may be due to the increase of the mobility of individual permeating molecules and enhanced mobility of the polymer segments. The increase in the degree of swelling of the membrane with a steady increase in temperature resulted in more *n*-octane transport leading to decrease the selectivity to thiophenes.

Similar results are observed by Qi and co-workers on the effect of feed temperature on the pervaporative desulfurization efficiency using Ag$_2$O-filled PDMS membranes of model gasoline [67]. They revealed that the total flux and permeability increased with the feed temperature, but the selectivity to thiophenes decreased simultaneously.

Zhu and co-workers studied the PDMS–AgY for separation of thiopenes from the mixture of *n*-octane, thiophene and 2-methylthiophene, in the temperature range of 30–70 °C [68]. The experimental results indicated an increase in the total flux and a decline of enrichment factors by rising the feed temperature.

Li and co-workers investigated the flux and sulfur enrichment factor of PDMS-Ni$^{2+}$Y zeolite membranes for the pervaporative removal of thiophene from a model gasoline system under different feed temperatures of 30–70 °C [69]. As expected, they observed that the membrane exhibited increased permeation flux but decreased enrichment factor when the operating temperature increased.

Zhao and co-workers reported the separation of sulfur/gasoline mixture using PDMS/PEI composite membranes by pervaporation [90]. The effect of temperature on pervaporation performance with PDMS/PEI composite membranes was studied at different temperatures, ranging from 30 to 80 °C. They confirmed that a higher feed temperature yielded higher total flux and lower sulfur enrichment factor. An explanation for this result is that higher temperature enhances the mobility of polymer segments, which offers more free volume for permeating molecules to occupy, and thus facilitates their movement both in the bulk feed solution and within the membrane.

Xu and co-workers also investigated the effects of the operating temperature on the pervaporative desulfurization of model gasoline composed of *n*-octane and thiophene using PDMS/ceramic composite [87]. They reported that the total flux increased with the temperature, whereas the sulfur enrichment factor decreased. According to the authors, the improvement of the swelling degree of the polymer membrane weakened the difference of solubility and diffusion velocity; this resulted in more *n*-octane transport, which led to a decrease in the sulfur enrichment factor.

Using the model gasoline thiophene/*n*-octane binary mixture as the model system, the effects of the operating temperature on the desulfurization performance of the membranes were also investigated by the same research group [82]. At temperatures ranging from 27 to 42 °C, increasing the operating temperature enhanced the permeation flux of the PDMS, PDMS-dopamine-5.0 and PDMS-dopamine/Cu-5.0 membranes but reduced their enrichment factor.

Liu and co-workers studied the effect of operating temperature on the permeation flux and enrichment factor in pervaporative desulfurization of thiophene/*n*-octane mixtures using PDMS-DAAg hybrid membranes [83]. They confirmed that the permeation flux of the membranes augmented with higher operating temperature, but the enrichment factor was decreased.

Using PDMS/PEI composite membranes having a thickness of the PDMS layer of 7 μm, the research group of Li deeply studied the effect of feed temperature on permeate total flux, partial flux and enrichment factor for thiophene/*n*-heptane, 2-methylthiophene/*n*-heptane, 2,5-dimethylthiophene/*n*-heptane, *n*-butylmercaptan/*n*-heptane, *n*-butyl sulfide/*n*-heptane mixtures in the range of 50–90 °C [54]. The results of pervaporation performance revealed that as the feed temperature increased from 50 to 90 °C, the total flux and partial flux increased, whereas the enrichment factor decreased. The partial flux, total flux and enrichment factor of sulfur species had the same order: *n*-butylsulfide < *n*-butylmercaptan < 2,5-dimethylthiophene < 2-methylthiophene < thiophene, which is in the reverse order of their respective molecular weights.

## 6.2. Feed sulfur content

The sulfur level in gasoline varies from one refinery to another, depending on the crude source and the refining process. As such, it is essential to investigate the effect of varying feed sulfur content on the pervaporative proprieties.

Lin and co-workers varied the sulfur content in a range of 100–1800 μg/g then studied its effect on pervaporation properties of a PEG membrane [59]. The experiment results demonstrated that increasing aromatics, alkenes and sulfur contentin the feed resulted in an increase of total flux and a decrease of the sulfur enrichment factor owing to extensive membrane swelling. However, alkanes and cycloalkanes had nearly negligible effects on membrane swelling and pervaporation performance. Additionally, the sorption selectivity decreased when the sulfur content decreased in the feed. However, the influence of increasing sulfur content on pervaporation performance reduced when the sulfur content was 600 μg/g.

Qi and co-workers investigated the impact of a range of 500–2500 μg/g sulfur content on pervaporation performance of model gasoline composed of *n*-octane/thiophene and *n*-octane/2-methylthiophene, using PDMS/PAN composite membrane [89]. They found that a variation of feed composition had nearly negligible influence on total fluxes and selectivity of PDMS membrane, while the partial fluxes of thiophenes were proportional to the concentrations of thiophenes present in the feed. This observation could be related to the ultra-low feed concentration and a narrow range of thereof. Importantly, the fluctuating concentration of thiophene in the feed yields very limited impact on the transport of *n*-octane through the membrane. On the other hand, the partial fluxes of thiophenes were still proportional to the concentrations of thiophenes in the feed.

Li and co-workers investigated the effect of sulfur content for a range of 500–900 ppm in the *n*-octane/thiophene feed on the pervaporation performance of PDMS-Ni$^{2+}$Y zeolite hybrid membranes [69]. The authors observed an increment of the permeation flux and a decrease of the enrichment factor occurred with an increase of the sulfur content in the feed. Interestingly, the influence of increasing sulfur content on pervaporation performance became less important when the sulfur content reached 800 ppm.

Wu and co-workers investigated the effect of thiophene loading in a PDMS/PES membrane on the permeation; the study was performed under the conditions of 33 °C on a range of 100–2300 ppm [84]. Surprisingly, research found that by increasing the thiophene content in the feed, the enrichment factor slightly increased and the permeation flux slightly decreased. The behavior could be attributed to the APTMS used as crosslinker of the top layer that largely reduced the swelling of the membrane.

Zhao and co-workers varied the sulfur content in the PDMS/PEI composite membranes with a range of 140–1200 ppm and studied its effect on pervaporation propertie [89]. Interestingly, they found a limited influence on the flux while varying the sulfur content in the feed. This finding would be attributed to the complexity of the gasoline, which is composed of alkanes, olefins, cycloparaffins, aromatics and sulfur species. The sulfur enrichment factor was at

first increased when the amount of thiophene was added in the gasoline, and then it varied slightly.

Cao and co-workers investigated the impact of sulfur content on pervaporation properties in the range of 1100–2300 ppm, using PDMS–DAAg [83]. As expected, the permeation flux increased while the enrichment factor decreased by increasing the sulfur content in the feed. According to the authors, this behavior might be attributed to the augmentation of saturated vapor pressure of thiophene on the upstream side.

The effect of sulfur content on the permeate partial flux and enrichment factor for thiophene/$n$-heptane, 2-methylthiophene/$n$-heptane, 2,5-dimethylthiophene/$n$-heptane, $n$-butyl mercaptan/$n$-heptane, $n$-butylsulfide/$n$-heptane mixtures in a range of 50–250 ng/$\mu$l was deeply investigated by Chen and co-workers, using PDMS/PEI composites membranes [54]. The experimental results revealed that increasing of the content from 50 ng/$\mu$l to 250 ng/$\mu$l had only negligible influence on total fluxes, while the partial fluxes of organic sulfur were proportional to the concentrations of organic sulfur in the feed. However, the curve of the enrichment factor declined slightly as the sulfur content increased, and then the curve was nearly invariable. Partial flux of organic sulfur species in the same organic sulfur content held the following order: $n$-butylsulfide < $n$-butylmercaptan < 2,5-dimethylthiophene < 2-methylthiophene < thiophene. The enrichment factor of organic sulfur species in the same organic sulfur content held the following order: $n$-butylsulfide < $n$-butylmercaptan < 2,5-dimethylthiophene < 2-methylthiophene < thiophene.

### 6.3. Permeate pressure

The potential chemical difference between the permeate-side and the feed side created by the vacuum or the sweep gas to the permeate-side of the membrane, is critical mass transfer driving force for pervaporation process. The effect of permeate pressure on pervaporation desulfurization performance is an important factor to investigate for understanding membrane performance and to provide necessary design data for technology scale-up.

Lin and co-workers studied the effects of permeate pressure on the desulfurization performance of cross-linked polyethylene glycol membranes [1]. They mentioned that at a lower permeate pressure, the flux decreased when the permeate pressure rose and as the driving force for the transport of components was reduced. This finding is similar to that which was reported for polyethylene glycol/polyurethane blend membranes and polydimethylsiloxane/ceramic composite [59]. At a higher permeate pressure, the flux decreased for the same reason mentioned above. Nevertheless, the sulfur enrichment factor was sensitive to permeate pressure as it increased firstly and decreased afterword. At a permeate pressure of 10.5 mmHg, the sulfur enrichment factor showed its highest value.

The effects of permeate pressure on pervaporation performance of PEG/PU blend membranes was evaluated by Lin and co-workers [68]. The experimental data obtained with 1200 $\mu$g/g of sulfur content level in FCC gasoline feed at 110 °C of feed temperature demonstrated that the flux and sulfur enrichment factor decreased when the permeate pressure rose and as the driving force for transport of the components was reduced. Contradictory results were observed with fluorinated polyimides membranes [61].

To date, there are relatively few studies describing the effect of permeate pressure on the performance of polydimethylsiloxane/ceramic composite membranes. Xu and co-workers investigated the effect of permeate pressure from 500 to 8200 Pa on membrane performance [87]. Due to the reduction of the driving force of for the transport of components, the study showed that the total flux decreased significantly by increasing the pressure. In contrast, the sulfur enrichment factor declined gently. The obtained results revealed that low permeate pressure was beneficial to improve the total flux and sulfur enrichment factor.

### 6.4. Feed flow rate

The increase of the feed flow rate was favorable to reduce the concentration polarization and thickness of the liquid boundary layer. The mass transfer resistance of the boundary layer was lowered. Meanwhile, a reduction of concentration polarization meant that thiophene concentration near the membrane surface was close to that in the bulk, which could enhance sorption and swelling of thiophene in the membrane. Consequently, both total flux and sulfur enrichment factor rose slightly.

Lin an and co-workers reported that the flux and sulfur enrichment factor both increased with the increase of the feed flow rate from 0.03 to 1 L/h, owing to the decrease of concentration of polarization and temperature polarization at 100 °C, 1 mmHg permeate pressure and 1397.2 $\mu$g/g sulfur content level in the model compounds feed composed of thiophene and $n$-heptane [1].

An original work of Xu and co-workers described the effect of feed flow rate on pervaporation performance for desulfurization of $n$-octane/thiophene using PDMS/ceramic composite membrane, with a the feed flow rate ranging from 10 to 30 L/h [87]. They found that the total flux and sulfur enrichment factor increased slightly with an increase in the feed flow rate.

Similar effects on the permeation flux and enrichment were observed by Wu and co-workers who used the PDMS/PES membrane with the feed flow rates ranging from 30 to 60 L/h, for a model gasoline feed with 1300 ppm thiophene [84].

Li and co-workers reported the impact of feed flow rate on pervaporation performance for desulfurization in the range of 32–62 L/h [69]. Using PDMS–5 wt% Ni$^{2+}$Y zeolite, and contrary to the above findings, the permeation flux increased from 2.9 to 4.4 kgm$^{-2}$h$^{-1}$, whereas the separation factor decreased from 4.90 to 3.65. Additionally, the enrichment factor was found to be decreasing slightly with the increase of the feed flow rate. This could be attributed to the significant influence of reduction in concentration polarization on the penetrating of the solvent in the membrane.

Additionally, Li and co-workers investigated the impact of the feed flow rate on the on pervaporation efficiency of thiophene/$n$-octane model gasoline in the range of 20–50 L/h, using PDMS-SiO$_2$ nanocomposite membranes [81]. They found also that the total flux increased slightly by increasing the feed flow rate. According to the authors, the increasing of the feed flow rate rendered the boundary layer to be thinner. Therefore, the mass transfer resistance of the boundary layer on the upstream decreased, which caused an increase in permeation flux. Importantly, the increase of the permeation flux promoted the thiophene when compared to $n$-octane molecules, which increased the enrichment factor consequently. The enrichment factor decreased by increasing the feed flow rate, it was probably due to the thickness reduction of the boundary layer by decreasing the permeability difference between thiophene and $n$-octane. Similar results were reported by Cao and co-worker for the feed flow range of 20–50 L/h, using PDMS-DAAg/5-5.0 and PDMS-dopamine/Cu for model gasoline-thiophene/$n$-octane binary mixture [82,83].

### 7. Concluding remarks and outlook

As shown throughout this review, a noticeable progress has been made during the last few years on the desulfurization of gasoline by pervaporation. This process offers many advantages such as operating at a lower temperature and thus saving energy, the ease of scaling up and ability to manipulate and higher selectivity. Another advantage is that the pervaporation process

can offer the possibility of removing sulfur from gasoline without hydrogen consumption and can produce a slight reduction of octane number. The current research on desulfurization of gasoline by pervaporation is a newly introduced research subject and is mainly focused on the process introduction, membrane materials and optimization of operating parameters. However, despite impressive progress in research, a number of issues should be resolved in order to promote and deploy this technology for industrial application. The optimization and improvement of separation properties for the pervaporative desulfurization process based on PDMS membranes still needs to be improved. An in-depth understanding of the solution-diffusion mechanism of the gasoline molecules is necessary to design an ideal membrane with high separation efficiency. Additionally, the effect of the concentration of the sulfur species on separation flux is still unclear in research, and many studies should be performed in order to overcome this issue by using different kinds of gasoline that originate from different refineries. Thus, the coupling of pervaporative with catalytic hydrodesulfurization for gasoline desulfurization is another option to produce low sulfur and high octane number gasoline. Also, in-depth studies based on larger scale experiments should be performed in order to evaluate this combination in terms of practical circumstances of various refineries, total octane number loss, the economic feasibility and practicability, as well as cost assessment. Although there have been many advances dealing with pervaporative desulfurization of gasoline in the last few years, there is still a long way to go before achieving the optimized procedure. With these present challenges combined with growing interest in the desulfurization of gasoline by pervaporation, it is certain that this new process will continue to be a fast-moving topic for the next several years.

## Acknowledgments

## References

[1] L. Lin, G. Wang, H. Qu, J. Yang, Y. Wang, D. Shi, Y. Kong, Pervaporation performance of crosslinked polyethylene glycol membranes for deep desulfurization of FCC gasoline, J. Membr. Sci. 280 (2006) 651–658.

[2] H.M. Li, L.N. He, J.D. Lu, W.S. Zhu, X. Jiang, Y. Wang, Y.S. Yan, Deep oxidative desulfurization of fuels catalyzed by phosphotungstic acid in ionic liquids at room temperature, Energy Fuels 23 (2009) 1354–1357.

[3] C.S. Song, An overview of new approaches to deep desulfurization for ultra-clean gasoline, diesel fuel and jet fuel, Catal. Today 86 (2003) 211–263.

[4] I.V. Babich, J.A. Moulijn, Science and technology of novel processes for deep desulfurization of oil refinery streams: a review, Fuel 82 (2003) 607–631.

[5] K.G. Knudsen, B.H. Cooper, H. Topsoe, Catalyst and process technologies for ultra low sulfur diesel, Appl. Catal. A Gen. 189 (1999) 205–215.

[6] X. Ma, K. Sakanishi, I. Mochida, Hydrodesulfurization reactivities of various sulfur compounds in diesel fuel, Ind. Eng. Chem. Res. 33 (1994) 218–222.

[7] G.A. Huff, O.S., Owen, B.D, Alexander, D.N., Rundell, W.J., Reagan, J.S. Yoo, (1999), WO 9909 117.

[8] M. Arias, D. Laurenti, V. Bellière, C. Geantet, M. Vrinat, Y. Yoshimura, Preparation of supported $H_3PW_{12}O_{40} \cdot 6H_2O$ for thiophenic compounds alkylation in FCC gasoline, Appl. Catal. A: Gen. 348 (2008) 142–147.

[9] X. Wu, Y. Bai, Y. Tian, X. Meng, L. Shi, Gasoline Desulfurization by catalytic alkylation over methanesulfonic acid, Bull. Korean Chem. Soc. 34 (2013) 3055–3058.

[10] P.T. Burnett, G.A. Huff, V.R. Pradhan, M. Hodges, J.A. Glassett, S.G. McDaniel, P. Hurst, The European Refining Technology Conference, Rome, Italy, November 13–15, 2000.

[11] C. Song, X. Ma, New design approaches to ultra-clean diesel fuels by deep desulfurization and deep dearomatization, Appl. Catal. B-Environ. 41 (2003) 207–238.

[12] I. Funakoshi, T. Aida, Process for recovering organic sulfur compounds from fuel oil, US5753102 A (1998).

[13] P. Forte, Process for the removal of sulfur from petroleum fractions, US 5 582 714. (1996).

[14] Y. Horii, H., Onuki, S., Doi, T., Mori, T., Takatori, H., Sato, T., Ookuro, T. Sugawara, Desulfurization and denitration of light oil by extraction, US5494572A, (1996).

[15] M. Ali, A. Al-Malki, B. El-Ali, G. Martinie, M.N. Siddiqui, Deep desulphurization of gasoline and diesel fuels using non-hydrogen consuming techniques, Fuel 85 (2006) 1354–1363.

[16] J. Williams, The thermal decomposition of hydrogen peroxide in aqueous solutions, Trans. Faraday Soc. 24 (1928) 245–255.

[17] L. Skattebol, B. Oulette, S. Solomon, Reactions of sulfides with tert-butyl hypochlorite, J. Org. Chem. 32 (1967) 3111–3114.

[18] J.L. Courtney, K.F. Swansborough, Ruthenium tetroxide oxidations, Rev. Pure Appl. Chem. 22 (1972) 47–54.

[19] E. Ahnonkitpanit, P. Prasassarakich, Coal desulphurization in aqueous hydrogen peroxide, Fuel 68 (1989) 819–824.

[20] J.R. Gallagher, E.S. Olson, D.C. Stanley, Microbial desulfurization of dibenzothiophene: a sulfur-specific pathway, FEMS Microbiol. Lett. 107 (1993) 31–35.

[21] M. Kobayashi, K. Horiuchi, O. Yoshikawa, K. Hirasawa, Y. Ishii, K. Fujino, H. Sugiyama, K. Maruhashi, Kinetic analysis of microbial desulfurization of model and light gas oils containing multiple alkyl dibenzothiophenes, Biosci. Biotech. Biochem. 65 (2001) 298–304.

[22] Y.K. Chang, S.K. Rhee, J.H. Chang, H.N. Chang, Desulfurization of dibenzothiophene and diesel oils by a newly isolated gordona strain, CYKS1, Appl. Environ. Microbiol. 64 (1998) 2327–2331.

[23] P. Wang, S. Krawiec, Desulfurization of dibenzothiophene to 2-hydroxybiphenyl by some newly isolated bacterial strains, Arch. Microbiol. 161 (1994) 266–271.

[24] D.J. Boron, W.R. Deever, R.M., Atlas, B.L., McFarland, J.A., Meyer, A.R., Johnson, NPRA, meeting, San Antonio, (1999), AM-99-54.

[25] W.E. Kleinjan, A. de Keizer, A.J.H. Janssen, Biologically produced sulphur, in: r steudel (Ed.), Top. Curr. Chem. 230 (2003) 167–188.

[26] N.V. Plechkova, K.R. Seddon, Applications of ionic liquids in the chemical industry, Chem. Soc. Rev. 37 (2008) 123–150.

[27] S. Zhang, Z.C. Zhang, Novel properties of ionic liquids in selective sulfur removal from fuels at room temperature, Green Chem. 4 (2002) 376–379.

[28] J. Eber, P. Wasserscheid, A. Jess, Deep desulfurization of oil refinery streams by extraction with ionic liquids, Green Chem. 6 (2004) 316–322.

[29] A.R. Hansmeier, G.W. Meindersma, A.B. de Haan, Desulfurization and denitrogenation of gasoline and diesel fuels by means of ionic liquids, Green Chem. 13 (2011) 1907–1913.

[30] L. Alonso, A. Arce, M. Francisco, O. Rodríguez, A. Soto, Liquid–Liquid equilibria for systems composed by 1-Methyl-3-octylimidazolium tetrafluoroborate ionic liquid, thiophene, and *n*-Hexane or cyclohexane, J. chem. eng. data, 5 2 (2007) 1729–1732.

[31] L. Alonso, A. Arce, M. Francisco, A. Soto, Solvent extraction of thiophene from n-alkanes ($C_7$ $C_{12}$, and $C_{16}$) using the ionic liquid [C8mim][BF4], J. Chem. Thermodyn. 40 (2008) 966–972.

[32] L. Alonso, A. Arce, M. Francisco, O. Rodríguez, A. Soto, Gasoline desulfurization using extraction with [C8mim][BF4] ionic liquid, AIChE J. 53 (2007) 3108–3115.

[33] K. Tawara, T. Nishimura, H. Iwanami, T. Nishimoto, T. Hasuike, New hydrodesulfurization catalyst for petroleum-fed fuel cell vehicles and cogenerations, Ind. Eng. Chem. Res. 40 (2001) 2367–2370.

[34] H. Reza Mortaheb, F. Ghaemmaghami, B. Mokhtarani, A review on removal of sulfur components from gasoline by pervaporation, Chem. Eng. Res. Des. 90 (2012) 409–432.

[35] J. Fan, G. Wang, Y. Sun, C. Xu, H. Zhou, G. Zhou, J. Gao, Research on reactive adsorption desulfurization over Ni/ZnO-SiO₂-Al₂O₃ adsorbent in a fixed-fluidized bed reactor, Ind. Eng. Chem. Res. 49 (2010) 8450–8460.

[36] K. Dennis, S-Zorb – advances in applications of phillips S-Zorb technology, Presented at the NPRA Q & A Meeting, October, 2000.

[37] P.S. Kulkarni, C.A.M. Afonso, Deep desulfurization of diesel fuel using ionic liquids: current status and future challenges, Green Chem. 12 (2010) 1139–1149.

[38] M.A. Plummer, Jr. RF. Bonelli Removal of sulfur from a hydrocarbon through a selective membrane, Patent US 0139713 A1; (2002).

[39] G. Krishnaiah, J. Balko, Reduce ultra-low sulfur gasoline compliance costs with Davison clean fuels technologies, NPRA Annual Meeting, San Antonio, TX, 2003.

[40] X. Zhao, G. Krishnaiah, T. Cartwright, Membrane separation for clean fuels, Refining PTQ Summer Q3 (2004) 21–27.

[41] A. Jonquieres, R. Clement, P. Lochon, J. Néel, M. Dresch, B. Chretien, Industrial state-of-the-art of pervaporation and vapour permeation in the western countries, J. Membr. Sci. 206 (2002) 87–117.

[42] A.C.M. Franken, M.H.V. Mulder, C.A. Smolders, Pervaporation process using a thermal gradient as the driving force, J. Membr. Sci. 53 (1990) 127–141.

[43] X. Zhao, G. Krishnaiah, C. Todd, Membrane separation for clean fuels, Petrol. Technol. Q. 9 (2004) 21.

[44] X. Zhao, G. Krishnaiah, T. Cartwright, S-Brane technology brings flexibility to refiners' clean fuel solutions, NPRA annual meeting, San Antonio, TX, 2004.

[45] J.W. Balko, Method of reducing sulfur in hydrocarbon feedstock using a membrane separation zone US Patent 7, 267, 761, (2007).

[46] C. Zhao, J. Li, R. Qi, J. Chen, Z. Luan, Pervaporation separation of n-heptane/sulfur species mixtures with polydimethylsiloxane membranes, Sep. Purif. Technol. 63 (2008) 220–225.

[47] B. Li, W. Zhao, Y. Su, Z. Jiang, X. Dong, W. Liu, Enhanced desulfurization performance and swelling resistance of asymmetric hydrophilic

pervaporation membrane prepared through surface segregation technique, J. Membr. Sci. 326 (2009) 556–563.

[48] B. Smitha, D. Suhanya, S. Sridhar, Separation of organic?organic mixtures by pervaporation-a review, J. Membr. Sci. 241 (2004) 1–21.

[49] P. Sampranpiboon, R. Jiraratananon, D. Uttapap, X. Feng, R.Y.M. Huang, Pervaporation separation of ethyl butyrate and isopropanol with polyether block amide (PEBA) membranes, J. Membr. Sci. 173 (2000) 53–59.

[50] K. Rychlewska, K. Konleczny, Reduction of sulfur content in FCC gasoline using vacuum, Monogr. Environ. Eng. Committee Polish Acad. Sci. 118 (118) (2014) 39–53.

[51] R.Y.M. Huang, X. Feng, Dehydration of isopropanol by pervaporation using aromatic polyetherimide membranes, Separ. Sci. Techno. 28 (1993) 2035–2048.

[52] M.G. Nawawi, R.Y.M. Huang, Pervaporation dehydration of isopropanol with chitosan membranes, J. Membr. Sci. 124 (1997) 53–62.

[53] L. Lin, Y. Kong, G. Wang, Selection and crosslinking modification of membrane material for FCC gasoline desulfurization, J. Membr. Sci. 285 (2006) 144–151.

[54] J. Chen, J. Li, R. Qi, H. Ye, C. Chen, Pervaporation performance of crosslinked polydimethylsiloxane membranes for deep desulfurization of FCC gasoline I. Effect of different sulfur species, J. Membr. Sci. 322 (2008) 113–121.

[55] M. Pei-sheng, Z. Xing-min, Petrochem. Technol. 23 (1994) 593–597.

[56] X. Feng, R.Y.M. Huang, Liquid separation by membrane pervaporation: A review, Ind. Eng. Chem. Res. 36 (1997) 1048–1066.

[57] T. Shimidzu, M. Yoshikawa, alkali metal Ions selective transport membrane and an evaluation of membrane property, Nippon Kagaku Kaishi 6 (1983) 958–960.

[58] M. Yoshikawa, H. Yokoi, K. Sanui, N. Ogata, T. Shimidzu, Polymer membrane as a reaction field. II. Effect of membrane environment on permselectivity for water-ethanol binary mixtures, Polym. J. 16 (1984) 653–666.

[59] Y. Kong, L.G. Lin, J.R. Yang, FCC gasoline desulfurization by pervaporation: effects of gasoline components, J. Membr. Sci. 293 (2007) 36–43.

[60] L.G. Lin, Y. Kong, J.R. Yang, D.Q. Shi, K.K. Xie, Y.Z. Zhang, Scale-up of pervaporation for gasoline desulphurization Part 1. Simulation and design, J. Membr. Sci. 298 (2007) 1–13.

[61] L.H. Wang, Z.P. Zhao, J.D. Li, C.X. Chen, Synthesis and characterization of fluorinated polyimides for pervaporation of n-heptane/thiophene mixtures, Eur. Polym. J. 42 (2006) 1266–1272.

[62] L.S. White, R., Franklin, W., Dayton, M. Lesemann, Membrane separation for sulfur reduction US Patent, 7048846 B2, (2006).

[63] D. Mitra, Sep desulfurization of gasoline byPervaporation, Purif. Rev. 41 (2012) 97–125.

[64] L. Lin, Y. Zhang, Y. Kong, Recent advances in sulfur removal from gasoline by pervaporation, Fuel 88 (2009) 1799–1809.

[65] Z. Yang, W. Zhang, T. Wang, J. Li, Improved thiophene solution selectivity by $Cu^{2+}$, $Pb^{2+}$ and $Mn^{2+}$ ions in pervaporative poly[bis($p$-methyl phenyl) phosphazene]desulfurization membrane, J. Membr. Sci. 454 (2014) 463–469.

[66] L.S. White, R.F. Wormsbecher, M Lesemann Membrane separation for sulfur reduction, Patent US 0211706 A1; (2004).

[67] R. Qi, Y. Wang, J. Chen, J. Li, S. Zhu, Pervaporative desulfurization of model gasoline with $Ag_2O$-filled PDMS membranes, Sep. Purif. Technol. 57 (2007) 170–175.

[68] R. Qi, Y. Wang, J. Chen, J. Li, S. Zhu, Removing thiophenes from n-octane using PDMS?AgY zeolite mixed matrix membranes, Sep. Purif. Technol. 295 (2007) 114–120.

[69] B. Li, D. Xu, Z. Jiang, X. Zhang, W. Liu, X. Dong, Pervaporation performance of PDMS-$Ni^{2+}$Y zeolite hybrid membranes in the desulfurization of gasoline, J. Membr. Sci. 322 (2008) 293–301.

[70] Y. Kong, L. Lin, Y. Zhang, F. Lu, K. Xie, R. Liu, L. Guo, S. Shao, J. Yang, D. Shi, Studies on polyethylene glycol/polyethersulfone composite membranes for FCC gasoline desulphurization by pervaporation, Eur. Polym. J. 44 (2008) 3335–3343.

[71] R.Y.M. Huang, J.J. Shieh, Crosslinked blended poly(vinylalcohol)/N-methylol nylon-6 membranes for the pervaporation separation of ethanol-water mixtures, J. Appl. Polym. Sci. 70 (1998) 317–327.

[72] F.E. Duprez, E.J. Goethals, R. Schue, H. Qariouh, F. Schué, Segmented network structures forthe separation of water/ethanol mixtures by pervaporation, Polym. Int 46 (1998) 117–125.

[73] L. Lin, Y. Kong, Y. Zhang, Sorption and transport behavior of gasoline components in polyethylene glycol membranes, J. Membr. Sci. 325 (2008) 438–445.

[74] J. Chen, J. Li, J. Chen, Y. Lin, X. Wang, Pervaporation separation of ethyl thioether/heptane mixtures by polyethylene glycol membranes, Sep. Purif. Technol. 66 (2009) 606–612.

[75] L. Lin, Y. Zhang, H. Li, Pervaporation and sorption behavior of zeolite-filled polyethylene glycol hybrid membranes for the removal of thiophene species, J. Colloid Interface Sci. 350 (2010) 355–360.

[76] Y. Kong, F., Lu, J. Yang, Process for preparing polyacrylonitrile-grafted modified cellulose membrane for gasoline desulfurization, C.N. Patent 101721924A, (2010).

[77] H. Qu, Y. Kong, H. Lv, Y. Zhang, J. Yang, D. Shi, Effect of crosslinking on sorption, diffusion and pervaporation of gasoline components in hydroxyethyl cellulose membranes, Chem. Eng. J. 157 (2010) 60–66.

[78] F. Lu, Y. Kong, H. Lv, J. Ding, J. Yang, The pervaporation performance of polyimide-block-polyethylene glycol membranes for gasoline desulphurization: effect of PEG groups, Adv. Mater. Res. 150 (2011) 317–320.

[79] W. Liu, B. Li, R. Cao, Z. Jiang, S. Yu, G. Liu, H. Wu, Enhanced pervaporation performance of poly (dimethyl siloxane) membrane by incorporating titania microspheres with high silver ion loading, J. Membr. Sci. 378 (2011) 382–392.

[80] Q.G. Zhang, B.C. Fan, Q.L. Liu, A.M. Zhu, F.F. Shi, A novel poly(dimethyl siloxane)/poly(oligosilsesquioxanes) composite membrane for pervaporation desulfurization, J. Membr. Sci. 366 (2011) 335–341.

[81] B. Li, W. Liu, H. Wu, S. Yu, R. Cao, Z. Jiang, Desulfurization of model gasoline by bioinspired oleophilic nanocomposite membranes, J. Membr. Sci. 415–416 (2012) 278–287.

[82] W. Liu, Y. Li, X. Meng, G. Liu, S. Hu, F. Pan, H. Wu, Z. Jiang, B. Wang, Z. Li, X. Cao, Embedding dopamine nanoaggregates into a poly(dimethylsiloxane) membrane to confer controlled interactions and free volume for enhanced separation performance, J. Mater. Chem A. 1 (2013) 3713–3723.

[83] G. Liu, T. Zhou, W. Liu, S. Hu, F. Pan, H. Wu, Z. Jiang, B. Wang, J. Yang, X. Cao, Enhanced desulfurization performance of PDMS membranes by incorporating silver decorated dopamine nanoparticles, J. Mater. Chem. A 2 (2014) 12907–12917.

[84] H. Wu, X. Zhang, D. Xu, B. Li, Z. Jiang, Enhancing the interfacial stability and solvent-resistant property of PDMS/PES composite membrane by introducing a bifunctional aminosilane, J. Membr. Sci. 337 (2009) 61–69.

[85] J. Chen, J. Li, R. Qi, H. Ye, C. Chen, Pervaporation separation of thiophene-heptane mixtures with polydimethylsiloxane (PDMS) membrane for desulfurization, Appl. Biochem. Biotechnol. 160 (2010) 486–497.

[86] J. Wang, R. Latz, J. Dahl, Pasel R. Pasel, Liquid phase desulfurization of jet fuel by a combined pervaporation and adsorption process, Fuel Process. Technol. 90 (2009) 458–464.

[87] R. Xu, G. Liu, X. Dong, W. Jin, Pervaporation separation of $n$-octane/thiophene mixtures using polydimethylsiloxane/ceramic composite membranes, Desalination 258 (2010) 106–111.

[88] L. Lin, Y. Kong, K. Xie, Polyethyleneglycol/polyurethane blend membranes for gasoline desulphurization by pervaporation technique, Sep. Purif. Technol. 61 (2008) 293–300.

[89] R. Qi, C. Zhao, J. Li, Y. Wang, S. Zhu, Removal of thiophenes from $n$-octane/thiophene mixtures by pervaporation, J. Membr. Sci. 269 (2006) 94–100.

[90] Z. Changwei, L. Jiding, C. Jian, Q. Rongbin, L. Zhaokun, Separation of sulfur/gasoline mixture with polydimethylsiloxane/polyetherimide composite membranes by pervaporation, Chin. J. Chem. Eng. 17 (2009) 707–710.