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DESULFURIZATION OF DISLE ISFAHAN OIL REFINERY COMPANY BY POLYDIMETHYLSILOXANE, POLY ETHYLENE GLYCOL, POLYETHERSULFONE AND POLY ACRYL NITRILE NANOCOMPOSITES

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ABSTRACT

In this research for fabricated the composite membranes usage a blend of polymers that are comprised of PDMS (polydimethylsiloxane), PEG (poly ethylene glycol), PES (polyether sulfone) and PAN (poly acryl nitrile) with crosslinking TMOS (tetramethyl orthosilicate) as crosslinking agent for decrease sulphur of diesel Isfahan oil Refinery company. Total sulphur of diesel as feed to membrane module is 6380ppm. In the research, four kinds of membrane including PDMS, blend of PDMS with PEG, blend of PDMS with PES and blend of PDMS with PAN are used. The process variables in this research are pump pressure of membrane module (5-9 Bar), crosslinking agent consumption (1.5 and 3 wt. %), crosslinking temperature (65-85ċ) and crosslinking time (0.5-2.5 hours). According to the research, it is observed that by increasing pump pressure, crosslinking agent consumption and crosslinking temperature, the sulfur content of retentate stream decreases if other variables remain constant. However, the conditions are different for the crosslinking time; when crosslinking time increases from 0.5 hours to 1.5 hour, the sulfur content of retentate stream decreases but when the time increases to 1.5 hours and other variables remain constant, sulfur content increases.

Keywords: poly dimethylsiloxane-crosslinking agent-crosslinking temperature-crosslinking time-retentate

INTRODUCTION

Sulfur limits of less than 30 ppm were introduced for gasoline in most developed countries to meet Environmental Protection Agency regulations, while new approaches for deeper desulfurization may become necessary in near future (<10 ppm sulfur)[1-5]. Commercial gasoline is a complex mixture composed of alkenes, C_5–C_{14}olefins, cycloparaffins, and aromatics. It is made up of products of isomerization, reforming and fluid catalytic cracking (FCC) units. FCC gasoline, which has ash are of 30–40%inthetotalgasolinepool, is the most important sulfur contributor in gasoline (up to 85–95%). Typical sulfur compounds in gasoline include mercaptane (RSH), sulfides (R_2S), disulfides (RSSR), thiophene, and the derivatives thereof [6].A basic method for removal of sulfur from gasoline is catalytic hydrodesulphurization (HDS). HDS of FCC gasoline is a straight forward way for reducing the sulfur to the levelsevenbelow1ppm.However, it needs high investment and operating costs, and also there is one big disadvantage; this technology suffers from a significant loss in the octane number caused by saturation of olefins. Therefore, more efforts are being made to develop novel non-HDS methodologies[7], such as bio-HDS, selective oxidation, selective extraction, catalytic extraction, alkylation-extraction, improved selective hydro processing[8], and membrane separation. Two main biochemical pathways in bio desulfurization have been reported: ring-destructive (degradation) and sulfur-specific (desulfurization). The former is not commercially useful for the petroleum industry because water-soluble sulfur compounds are produced and the carbon skeleton of sulfur compounds is used by the bacteria, which it reduces the fuel calorific value[9,10]. Oxidative desulfurization (ODS) combined with liquid extractions is considered one of the novel processes to reduce refractory sulfur-containing compounds. However, it is not successful with FCC gasoline due to the high olefinic content that tends to react with oxygen atoms to form epoxies. The oxidized and non-oxidized components must be separated from the feed by applying several extraction, washing, absorption, and distillation operations[11].these consecutive separation steps make the process complicated and expensive. As a non-HDS method, adsorption desulfurization has some problems to be solved. When the selectivity is low, the adsorbents are easy to be regenerated. As the selectivity increases, the spent adsorbents become more and more difficult to be regenerated[12-14]. Solvent extraction and calcinations in the air are two methods to regenerate the desulfurization adsorbents. Compared to the traditional and non-HDS separation processes, membrane separation offers many advantages including higher separation efficiency, lower energy consumption and operating cost, simple operation and control scheme, ease of scaling up, and adaptability to changes in process streams[15-17].These promising advantages make membrane separation an attractive process for many of research works in recent studies. As the work on membrane separations began in the early 1960s, a wide range of materials including Zeolite, polymers, dense metals, ceramics, and biological materials have been applied for manufacturing of the membranes. However, polymers are the most widely used materials for membrane manufacturing at present[18], because of significant advantages of the polymers including low cost, permeability, mechanical stability, and ease of process ability[19]. Three important features of chemical resistance, sorption capacity, and mechanical strength of the polymeric film are the main parameters in selection. Hence, solubility parameter [20] and membrane polarity are the two interesting indices in a development of the novel membrane materials. PDMS has been demonstrated as one of the most widely utilized membrane materials for liquid hydrocarbon desulfurization[21-24], owing to its outstanding aging resistance, thermal/chemical stability, good process ability, in particular, and its superior permeability to small molecules. Moreover, according to solubility parameter theory, the solubility parameter (Ә) of PDMS (Ә= ~ 21.0) is close to the solubility parameter of thiophene and its derivatives (Ә varied from ~ 19 to ~ 20[25].Consequently, PDMS polymer will display the priority in the selective dissolution of the sulfur components in liquid hydrocarbon. Pure PDMS membranes, however, have relatively poor mechanical strength due to the high flexibility of molecular chains. A number of strategies have been attempted to reinforce elastomeric PDMS in order to acquire better and wider applications. In recent years, elastomeric polymer–inorganic Nano composites have been the subject of a huge scientific interest. Theoretically, by introducing inorganic fillers into elastomers, the Nano composites will exhibit dramatically improved bulk proper- ties. However, the reinforcement of PDMS via physical incorporation of inorganic particles has severe challenges. On one hand, the significant difference in hydrophobicity makes it rather difficult to achieve homogeneous hybridization between the PDMS continuous phase and the inorganic dispersed phase via simple physical blending. The accompanying local stress and interface defects may substantially worsen the mechanical properties of the Nano composite membranes. On the other hand, since PDMS is usually dissolved in the non-aqueous oil-based solvent, it is quite difficult and even impossible to manipulate the simultaneous hydrolysis–condensation of silicon precursors and cross-linking of PDMS oligomers in a homogenous phase. In the present paper, the reverse osmosis membranes based on PDMS, PEG, PES, PAN/PES, PVP layers are designed to separate sulfur compounds from diesel of Isfahan oil Refinery Company.

Experimental

Experimental setup

The experimental setup is shown in figure 1.

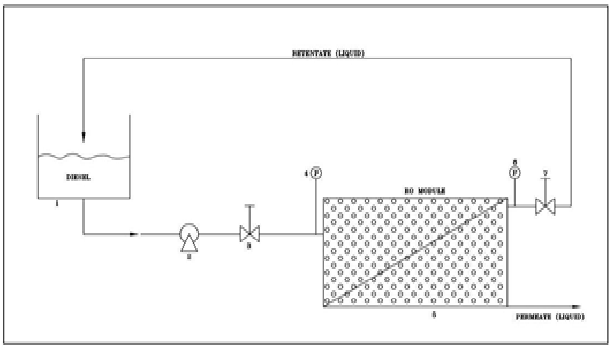

Figure 1
The schematic diagram of the reverse osmosis setup

The feed tank (position1) contains around 3 liters diesel with 6380 PPM total sulfur. The leftover diesel after every complete usage of related membrane is drained and after introducing fresh diesel into tank, test under determinate conditions is done by using fresh membrane in module. In position 2, there is a pump to build up pressure in the rig and to deliver diesel at different flow rates and defined pressure limit (5-9bar) to the membrane unit (position 5).A needle valve (position 3) was installed to determine and adjust the diesel flow to the membrane unit, the module was made of stainless steel and membranes with an active surface 85 cm^2 can be investigated. Pressure indicators (position 4 and 6) monitor the pressure of the diesel flow and that of the retentate flow respectively. The needle valve in position 7 was installed to control the flow of retentate. The membrane was pre-wetted by feed one hour before running the operation to achieve steady states in the system. The experiments were performed for 4 hours; the operational temperature was set in the range of 30-50ċ.

Membrane material

Tetramethyl orthosilicate (the corresponding average molecular weight was around 150,Merk,Germany),polydimethylsiloxane oligomer (the viscosity was 5000 mpa.sec and the corresponding average molecular weight was around 40000,Aldrich,USA),poly ethylene glycol (the corresponding average molecular weight was around 4000,BASF,Germany),polyethersulfone (the corresponding average molecular weight was around 58000,flakes,BASF,Germany),poly acryl nitrile (the corresponding average molecular weight was around 45000,Merk,Germany),polyvinylpyrrolidone as pore former(K90,the corresponding average molecular weight was around 360000,Merk,Germany),N,N-Dimethyl acetamide as solvent for fabricated of support layer (Merk,Germany),dibutyltin dilaurate (Fluka,Switzerland),ammonia as inducer (Merk,Germany),a symmetric poly ester ultra-filtration membranes used as support(PlasmaChemGmbH,Germany), n-heptane as solvent (Romil,UK),span80 as surfactant (Merk,Germany) and De-ionized water from a Millipore ultrapure water system as non-solvent was used in all the experiments.

Membrane preparation

Certain amount of Span 80 as surfactant, silicon precursor(TMOS)(1.5 and 3 wt.%), as well as PDMS and PEG oligomer were dissolved in n-heptane at room temperature to make a homogeneous solution. The weight ratio between solvent and polymer is amount 5.5 and weight ratio between all polymers in study is 1/1.Inducer aqueous solutions were suspended with a concentration of 0.5 molar (ammonia was dissolved in a 25 mill molar Tris-HCl buffer solution at neutral PH). And then specific amount of the above aqueous solution was drop wise added into the oil solution under vigorous mechanical stirring. Weight ratio between polymer, TMOS, dibutyltin dilaurate and Span 80 is 10/1/0.2/0.2.After stirring for 30 minute, small amount of dibutyltin dilaurate was added. After degassing, the solution was cast onto the support layer with casting knife; the solution for the support layer was prepared by precipitation via immersion technique. dissolving 15wt.% of PES and 3wt.% of PVP in DMAc, the homogeneous solution, cost on a symmetric poly ester ultra-filtration membranes, was immersed immediately in distilled water for remove the remaining DMAc. For prepare other support layer, dissolving 12wt. % PES, 3wt. % PEG, 3wt. % PVP in DMAc. The membranes were first dried in air for 24 hours and then thermally annealed at 65- 85ċ to accomplish Cross-linking and evaporate the residual solvent. After that, the membranes were washed by De-ionized water and finally placed between sheets of filter paper and dried. All samples were stored in dust free and dry environment before the performance of membranes were measurements. Another set of samples was done in parallel using the same procedure, except that PEG omitted from medium and replace with PES and PAN membranes.

RESULTS AND DISCUSSION

In this research by using reverse osmosis module and by means of PDMS, PEG PES and PAN membranes and also by using TMOS as crosslinking agent and n-heptane as solvent, the total sulfur of finish diesel decreased from 6380 PPM to around 1600 PPM. Some of the membrane separation processes are based on the affinity of a specific compound or a class of compounds to the membrane. The permeated compounds are then removed on the opposite side. There are two common representations of selectivity: separation factor and enrichment factor. The sulfur enrichment factor (α) is defined as the ratio of the sulfur content in the permeate, C_P divided by the sulfur content in the feed C_F, [15,26]:

$$\alpha = \frac{C_P}{C_F} \qquad (1)$$

Solvent swelling measurements were carried out by using pre weighed dry membranes of the different weight of crosslinking agent (M_{dry}), immersing them in pure heptane until equilibrium swelling to be reached. The membranes were then pat dried and immediately weighted (M_{wet}). The swelling degree (M_{SD}) of the membranes was then calculated by[44]:

$$M_{SD} = \frac{M_{wet} - M_{dry}}{M_{dry}} \times 100 \qquad (2)$$

Two important parameters which contribute to separation performance in membranes are solubility parameter and membrane polarity. Solubility parameter, Ə $((\text{J/cm}^3)^{0.5})$, was firstly defined by Hilde-brand as the square root of cohesive energy, E_{coh} (J/mol) per molar volume, V $(\text{cm}^3/\text{mole})$: [27,28]

$$\text{Ə} = \sqrt{\frac{E_{coh}}{V}} \qquad (3)$$

This parameter, as an index of characterizing interaction intensity, can be used for selection of the membrane's material in the PV process. The relative permeating capability of the components, which mainly depends on the chemical and physical properties of the membrane, is a determinant parameter to achieve separation goals. Balance and dynamic state effects, i.e. the assignment of components in free solution and membrane phase as well as flow and diffusion of the components determine the permeation rate of a certain compound through a specific membrane. These two effects both are affected by the attraction and repulsion between permeation components and the membrane[29].The more proximity between solubility parameters of the two substances means better mutual solubility[18,30,31]. For a ternary system, including component ***'i'***, component ***'j'***, and the membrane, the component which is preferably transported needs to have strong dissolution performance and closer solubility parameter with the polymer molecule. Solubility parameters of PDMS, PEG, PES, PAN, thiophene species and most hydrocarbon species in the diesel are, 21.01,20.1,18.5,26.61,19-21 and 14-15 $(\text{J/cm}^3)^{0.5}$

respectively[27,32,33].The distinct difference in solubility parameter between the two typical species is just the key to fulfill the separation. The second parameter, which contributes to the separation performance, is membrane polarity. In order to separate a specific component in a feed mixture, the polarity of one of the components must be close to the polarity of the membrane[18].For example, the PEG membrane polarity (40.6kcal/mole)[34], is close to the polarity of thiophene (35.4kcal/mole). Therefore, thiophene permeates preferably through the membrane compared to the typical hydrocarbons in FCC gasoline with polarities in the range of 30–34 kcal/mole.[35]

The process variables in this research are

Pump pressure of membrane module (5-9 Bar), crosslinking temperature (65-85ċ), crosslinking time the range of which is 0.5-2 hours, and finally mass consumption of TMOS as crosslinking agent in fabrication of membrane in range of 1.5 and 3 wt. %.In fig.2 to fig.10, the purpose of the 'T', 'P' and ’t’ is crosslinking temperature, pressure of membrane module pump and crosslinking time respectively.

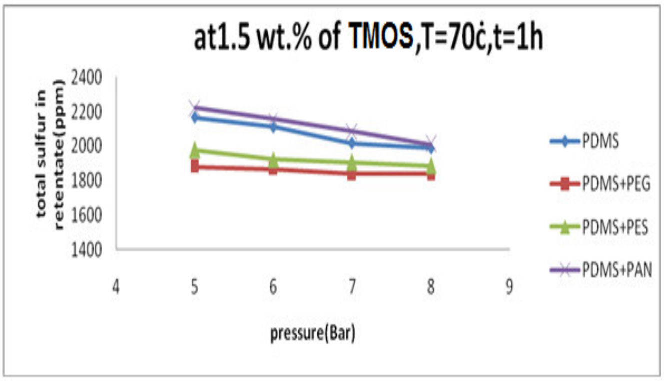

Figure 2
Variation of total sulfur in retentate with Pressure of membrane module

Fig.2 shows the changes of total sulfur in retentate stream by pump pressure of membrane module for a situation in which 1.5 wt.% of TMOS are used to make respective membranes as a crosslinking agent. According to this figure, the highest effect of membrane module pump pressure on the reduction of sulfur in retentate stream is for case of blending of PDMS and PEG polymers is used to make the membranes, and reason this is which usage of blending techniques of polymers cause improved properties of membranes which selectivity with respect to sulfuric compounds is significant. Due to the synergistic effect between the polymers, PDMS/PEG blended membrane shows excellent desulfurization performance with liquid hydrocarbons feed by exploiting properties of both PEG and PDMS (strong affinity to sulfur compounds and similar solubility parameter).[36,37]

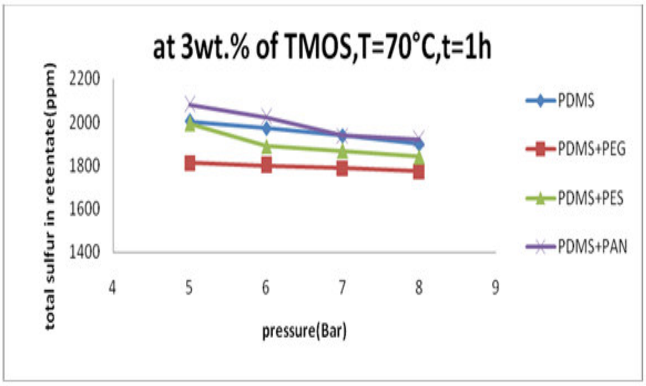

Figure 3
Variation of total sulfur in retentate with Pressure of membrane module

Fig.3 shows the changes of total sulfur in retentate stream by pump pressure of membrane module for a situation in which 3 wt. % of TMOS is used to make respective membranes as a crosslinking agent. Changes in fig.3 are relatively similar to fig.2, except that in this situation, changes occur more severely. Due to increasing the mass consumption rate of cross linking agent, swelling degree of membrane is reduced. As a result, the selectivity of membrane will be increased comparing to sulfuric substances, so, much more sulfur can be separated from input diesel (to membrane module) through permeate stream. Based on fig .3, (similar to fig. 2), the most significant effect of membrane module pump pressure on the reduction of available sulfur in retentate flow is for a situation in which a blending of PDMS and PEG polymers is used to make the membrane. Its reason was discussed previously.

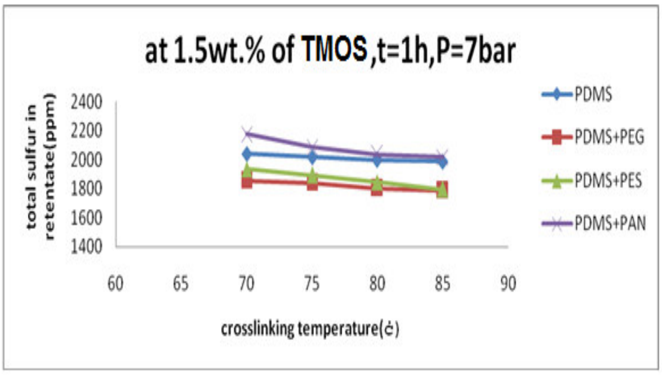

Figure 4
Variation of total sulfur in retentate
With crosslinking temperature

Fig.4 shows the changes of total sulfur in retentate stream by crosslinking temperature for a situation in which 1.5 wt. % of TMOS is used to make respective membranes as a crosslinking agent. According to fig.4, generally, by increasing crosslinking temperature in four membranes, total sulfur in retentate stream is decreased. According to this figure, the highest effect of crosslinking temperature on the reduction of sulfur in retentate stream is for the case of blending of PDMS and PEG polymers used to make the membranes. To interpret the reason, we can use fig. 9 and fig. 10, based on these figures, by increasing crosslinking temperature, swelling degree of membranes is decreases, as a result, the selectivity of membranes with respect to sulfuric compounds increases, so sulfur enrichment factor relating to the membrane increases. With all these interpretations, the quantity of available sulfur in retentate flow decreases.

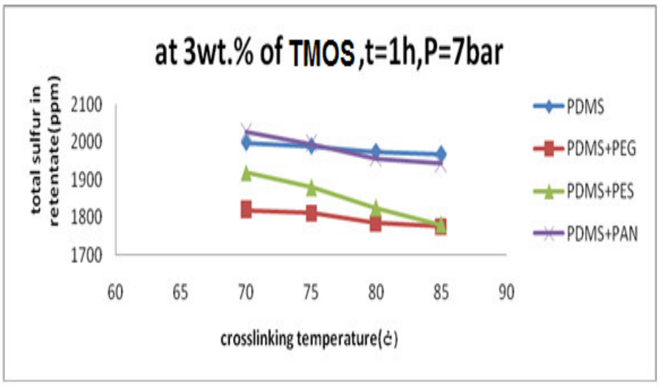

Figure 5
Variation of total sulfur in retentate
With crosslinking temperature

Fig.5 shows the changes of total sulfur in retentate stream by crosslinking temperature for a situation in which 3 wt. %of TMOS is used to make respective membranes as a crosslinking agent. Changes in fig.5 are relatively similar to fig. 4, except that in this situation, changes occur more severely than before. Its reason was discussed previously.

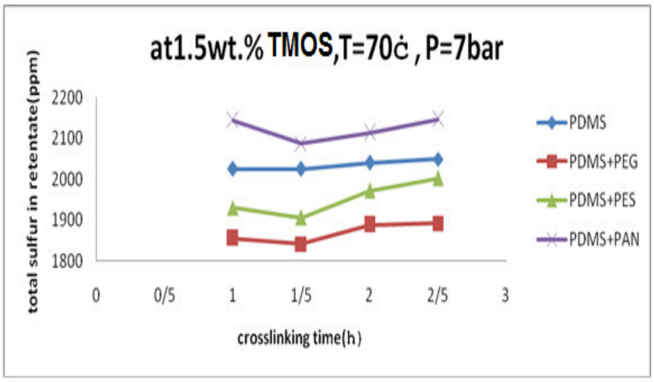

Figure 6
Variation of total sulfur in retentate with crosslinking time

Fig.6 shows the changes of total sulfur in retentate stream by crosslinking time for a situation in which1.5 wt. % of TMOS is used to make respective membranes as a crosslinking agent. The permeability coefficient, 'P' ($\frac{cm^2}{s.mol\%}$), can compute from the flowing mathematical expression which is the basic permeability equation for non-concentration dependent Fickian diffusion: [36,38,39,40]

$$P=D.S \qquad (4)$$

In equation (4), ‘P’ ($\frac{cm^2}{s.mole\%}$), ‘D’ ($\frac{cm^2}{s}$) and ‘S’ (mole %) are Permeability, diffusion and sorption coefficients respectively. According to fig.6, with increasing crosslinking time from 0.5 hour to 1.5 hours in fabrication of membranes, 'D', 'S' and 'P' coefficients related to hydrocarbon molecules of diesel decreased, while above coefficients for sulfur molecules of diesel increased, and thus further sulfur molecules separate from diesel by membrane or videlicet sulfur enrichment factor is increased. Now with the increase of this parameter from 1.5 hour to 2.5 hours, respective coefficients (D, S, and P) related to sulfur molecules of diesel decreased and thereupon less sulfur molecules from diesel separate by membrane or videlicet sulfur enrichment factor is decreased.

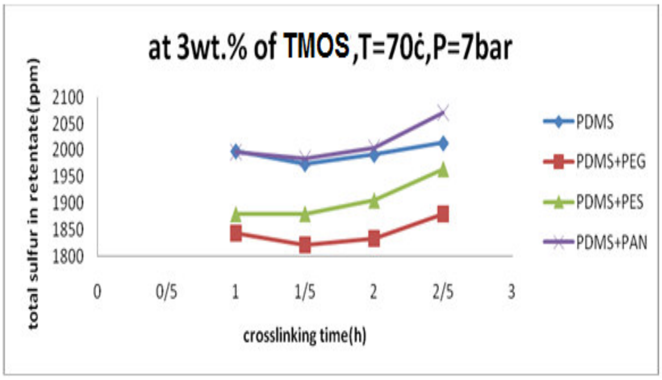

Figure 7
Variation of total sulfur in retentate
With crosslinking time

Fig.7 shows the changes of total sulfur in retentate stream by crosslinking time for a situation in which 3 wt. % of TMOS is used to make respective membranes as a crosslinking agent. Changes in fig.7 are relatively similar to fig. 6, except that in this situation, changes occur more severely than before. Its reason was discussed previously.

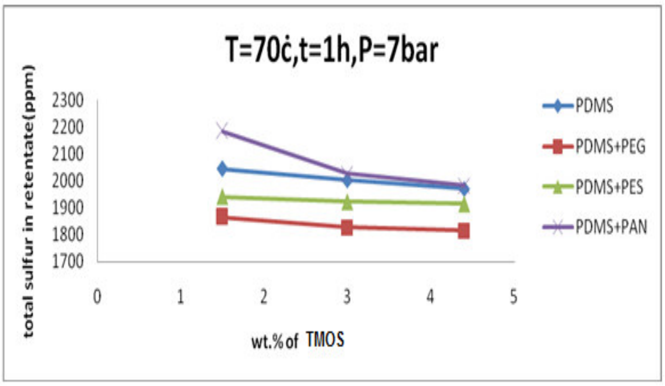

Figure 8
Variation of total sulfur in retentate with Weight of crosslinking agent

Fig. 8 shows the changes of total sulfur in retentate stream along with the percent weight consumption rate of cross linking agent for a balanced and specific state at the pressure of membrane module with 7 bars, cross linking time with 1 hour and cross linking temperature 70ċ, for each four considered membrane. According fig.8, with increasing the consumption of crosslinking agent in the fabrication of membranes, total sulfur in the retentate stream is decreased and videlicet according equation (1), sulfur enrichment factor is increased. This conclusion could be observed in experimental work(fig.11),with consumption of TMOS as crosslinking agent, the mobility of macromolecules and chain segments are weakened and thus inter-chain free volume is diminished that discourages the permeation of small molecules. The phenomenon is more apparent with increase of crosslinking agent .[27,30,36,41] The effect of TMOS as crosslinking agent on the selectivity enhancement and also on restriction of swelling in the membrane with 8 micro meter PDMS active layer was investigated .[42] As expected, the sulfur enrichment factor increased by increasing the amount of crosslinking agent. However, it is necessary to avoid excessive crosslinking, as it makes the polymer membrane brittle with a loss in its dimensional stability, which spoils the membrane applicability for membrane process.[18]

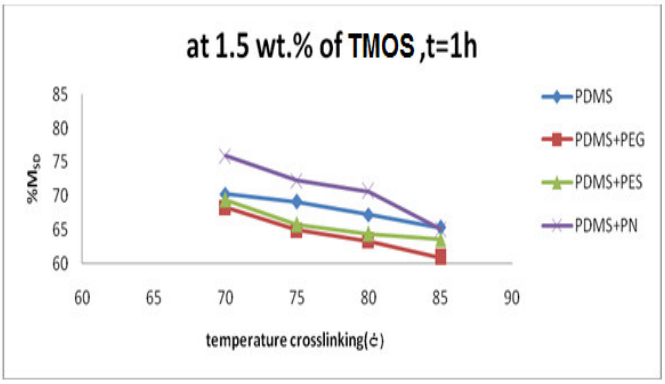

Figure 9
Variation of percent swelling degree With temperature crosslinking

Fig.9 shows the changes of swelling degree of the membranes by crosslinking temperature for a situation in which 1.5wt.% of TMOS are used to make respective membranes as a crosslinking agent.

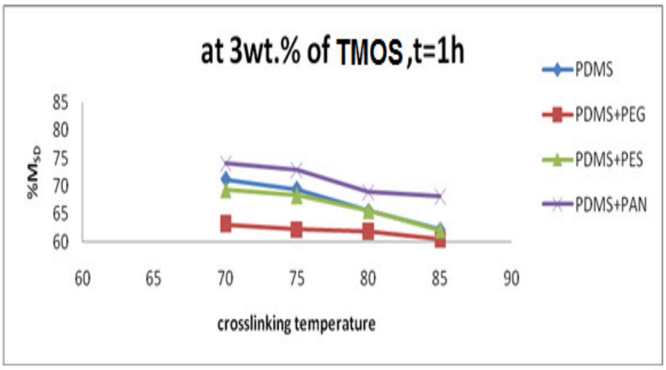

Figure 10
Variation of percent swelling degree with Temperature crosslinking

Changes in fig.10 are relatively similar to fig. 9, except that in this situation, changes are occurred more severely than before. Its reason was discussed previously.

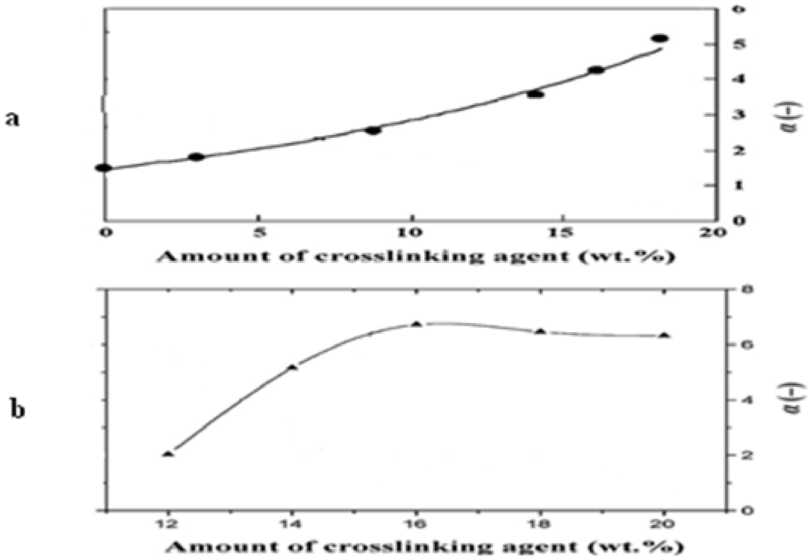

Figure 11
Variation of enrichment factor with amount of crosslinking agent (a)[37], (b)[44]

Fig. 11a shows the changes of enrichment factor by the consumption mass rate of cross linking agent for the separation of thiophene from the five element mixture by PEG membrane.Fig.11b shows the changes of enrichment factor by the mass consumption rate of crosslinking agent for separating ethyl thioether from heptane by PEG membrane. According to fig. 11a, by increasing consumption rate of crosslinking agent, thiophene enrichment factor increases. Due to increasing the mass consumption rate of cross linking agent, swelling degree of membrane is reduced so the selectivity of membrane will be increased compared to sulfuric substances. As a result, much more sulfur can be separated from input diesel (to membrane module) through permeate stream. Based on fig. 11b, it is concluded that by increasing the mass consumption rate of crosslinking agent, ethyl thioether enrichment factor increased ,but, in some part of the above diagram (over 16%wt.), the alteration diagram turns to be linear, which may be due to lower diffusion rate of ethyl thioether into the membrane compared to normal heptane.

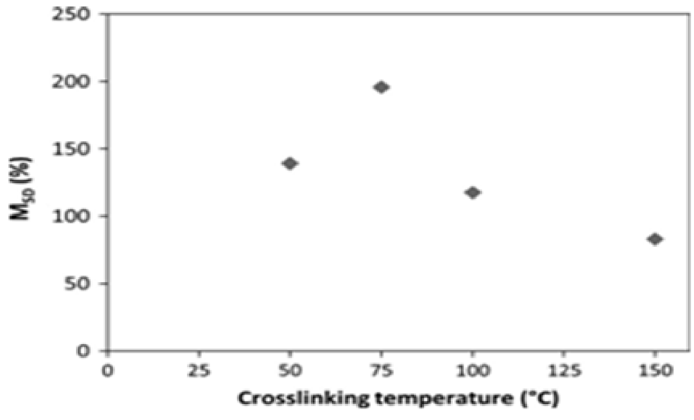

Figure 12
Variation of swelling degree with
Crosslinking temperature[44]

Fig.12 shows the changes of swelling degree of membranes by cross linking temperature in toluene. According fig.12, in general state, with increasing the temperature crosslinking, swelling degree of the membranes decreases. Such observations have been ascribed to a reduced chain length of the oligomers between cross-links[45], this shortening of the chains between cross-links enhances the elastic resistance to the swelling stress and therefore lowers the degree of swelling.[46,47] In the study on desulfurization mechanism of PDMD and PEI (poly ethylene imine) composite membranes with 4 micro meter active layers [43], they observed that enrichment factor is increased by increasing the crosslinking temperature in the range of 50ċ-120ċ

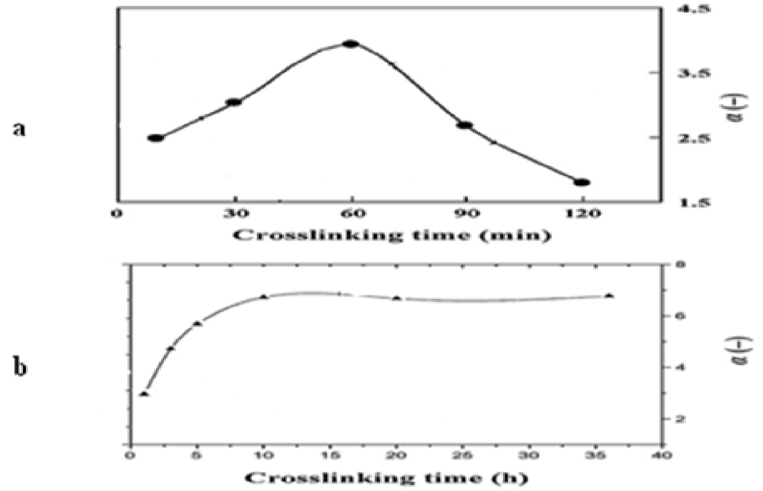

Figure 13
Variation of enrichment factor with crosslinking time (a)[27]*, (b)*[30]

Fig. 13a shows the changes of enrichment factor by the crosslinking time for the separation of thiophene from the five-element mixture.Fig.13b shows the changes of enrichment factor by the crosslinking time for separating ethyl thioether from heptane by PEG membrane. According fig.13a, by increasing crosslinking time to 60 minute, thiophene enrichment factor increases. This is due to this fact that' P',' D' and 'S' parameters relating to thiophene element increase. This means more amounts of thiophene can be separated by membrane, now, by increasing cross linking time from 60 minute to 120 minute, the thiophene enrichment factor decreases, because 'P', 'D' and 'S' parameters related to thiophene element decrease. According to fig.13 b, by increasing crosslinking time to 12 minutes approximately, the ethyl thioether enrichment factor increases, because as it was discussed before, 'P', 'D' and 'S' parameters related to ethyl thioether element increased. Now, by increasing cross linking time from 12 minute to 36 minute, the changes of ethyl thioether enrichment factor turn to be constant, because, 'P', 'D' and' S' parameters related to ethyl thioether element become constant and it will no longer follow cross linking time. Therefore, at t=36 minute, ethyl thioether enrichment factor is constant at its maximum state with the approximate quantity of 7.The driving force for any permeating component 'i' is μ_i (feed) - μ_i (permeate), where 'μ' is the chemical potential. This difference in chemical potentials is usually achieved by a permeate pressure much lower than the feed pressure. The resulting driving force causes each component to permeate with an individual velocity from the feed to permeate. Therefore, at steady state, the compositions of the feed and permeate differ from each other. In reverse osmosis, high pressure is applied to the liquid-feed side and, therefore, we have to take into account the pressure dependence of the chemical potential,

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,x} = v_i \qquad (5)$$

Where, v_iIs the partial molar volume of component 'i' in the mixture. Integration of equation (5), from the standard pressure (P^0= 1 bar) to P_F (pressure at feed side) and assuming that $v_i$is independent of pressure gives:

$$\mu_{iF}^{L} = \mu_{iF}^{L}(P^0 = 1\,bar) + v_{iF}(P_F - P^0) = \mu_{iF}^{0L} + RT\,Ln(\delta_{iF}^{L} x_{iF}^{L}) + v_{iF}(P_F - P^0) \quad (6)$$

The chemical potential $\mu_i^M$of component 'i' inside the membrane must also be determined at P_F:

$$\mu_i^M = \mu_i^{0M} + RT\,Ln\left(\delta_i^{c,M} c_i^M\right) + v_i^M(P_F - P^0) \quad (7)$$

The above equation, $\delta_i^{c,M}$and c_i^M , activity coefficient is based on molar concentration and molar concentration respectively. Assuming that $v_{iF} = v_i^M = v_i$and taking into account that $\mu_{iF}^{0L} = \mu_i^{0M}$, the equilibrium condition $\mu_{iF}^{L} = \mu_i^M$,gives $S_i^L = S_{iF}^L$.(where S_i^L is the liquid solubility coefficient of component i).

In reverse osmosis, the pressure drop from the feed side to the permeate side is located at the phase boundary between the membrane and the liquid permeate. Therefore, equality of the chemical potential requires:

$$RT\,Ln(\delta_i^{c,M} c_i^M) + v_i^M(P_F - P^0) = RT\,Ln(\delta_{iP}^{L} x_{iP}^{L}) + v_i(P_F - P^0) \quad (8)$$

Or

$$\delta_{iP}^{L} x_{iP}^{L} \exp\left[-\frac{v_i(P_F - P_P)}{RT}\right] = \delta_i^{c,M} \qquad (9)$$

Where P_P is the pressure in the liquid permeate (usually 1 bar) and subscript P denotes the permeate. Assuming that Fick's law is valid inside the membrane,

$$J_i = \frac{D_{iM}}{z_M}(c_{iF}^M - c_{iP}^M) = \frac{D_{iM}}{z_M}\left\{S_{iF}^L x_{iF}^L - S_{iP}^L x_{iP}^L \exp\left[-\frac{v_i(P_F - P_P)}{RT}\right]\right\} \qquad (10)$$

Where D_{iM} is the diffusion coefficient of 'i' component in membrane (with units m^2s^{-1}) ,J_i is the flux (with units mol m^2 s^{-1}) and z_M is thickness of top layer of the membrane (with units meter).If$S_{iF}^L \approx S_{iP}^L = S_i^L$, an acceptable approximation for many cases,[48]

$$J_i = \frac{D_{iM} S_i^L}{z_M}\left\{x_{iF}^L - x_{iP}^L \exp\left[-\frac{v_i(P_F - P_P)}{RT}\right]\right\} \qquad \textbf{(11)}$$

Equation (11) shows that J_i is enhanced as P_F becomes larger than P_P.According fig.2 and fig.3, with increasing pump pressure of module membrane, total sulfur in the retentate stream is decreased. According to equation (11), with increasing P_F (pressure at feed side), J_i (flux at permeate side) is increased and thus further sulfur molecules separates from diesel and weight fraction of sulfur in retentate stream is decreased. The specification of finish diesel of Isfahan oil refinery (general diesel) and diesel from retentate stream of membrane module (processed diesel) at P=7bar, T=85ċ, t=1 hour with 3wt. % of TMOS is shown in table 1.

Table1
Specification of general diesel and processed diesel

Specifications	dimensions	general diesel	processed diesel
IBP	Ċ	155	157
10%	Ċ	190	193
20%	Ċ	211	209
30%	Ċ	226	221
40%	Ċ	246	225
50%	Ċ	270	246
60%	Ċ	288	269
70%	Ċ	307	289
80%	Ċ	326	320
90%	Ċ	348	348
FBP	Ċ	381	381
Cetane index	-	50.9	52.6
Specific gravity(60F^0/60F^0)	-	0.8840	.8316
Flash point	Ċ	62	60
Viscosity at 40ċ	mm^2/sec	2.4	2.4
Cloud point	Ċ	-2	-4
Total Sulfur content	PPM	6380	1702

By comparing Specification of general diesel and processed diesel, it is observed that the main specifications of processed diesel, such as Cetane index, cloud point, and total sulfur are better than general diesel.

CONCLUSIONS

Crosslinking the polymer in the membrane technology makes it insoluble in the feed mixture and decreases its swelling in order to derive a good selectivity. The effect of the pump pressure of membrane module, crosslinking agent consumption, crosslinking temperature, and crosslinking time in decreasing sulfur of finish diesel Isfahan oil refinery by PDMS, PEG, PES and PAN membranes was investigated. It was found out that by increasing module pump pressure, crosslinking agent consumption, and crosslinking temperature, the sulfur content of retentate stream decreases if other variables remain constant. However, for crosslinking time, the conditions are different; when crosslinking time increases from 0.5 hour to 1 hour, sulfur content of retentate stream decreases but when the time increases to 1.5 hour and other variables remain constant, sulfur content increases.

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