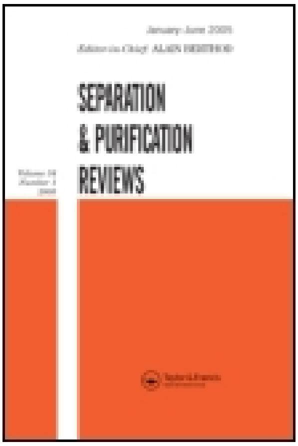

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Desulfurization of Gasoline by Pervaporation

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Worldwide concerns over the environment have stimulated increasing interest both in academic and industry for the deep desulfurization of gasoline. Due to some inherent disadvantages associated with the conventional hydrodesulfurization, several non-conventional techniques are being tried by researchers. Pervaporation is such a recently developed technology for gasoline desulfurization. Its efficiency has attracted worldwide attention. Compared with conventional sulfur removal technology for gasoline, pervaporation exhibits advantages of little reduction of octane number, low energy consumption, environmental benefits, simple operation, and easy scale-up. The advances of pervaporative operation for gasoline desulfurization are reviewed in this paper. The membrane materials used for desulfurization include polysiloxane, poly(ethylene glycol), polyimide, polyurethane and organic-inorganic hybrid membranes. Analysis of the selectivity–permeability with varying feed composition and operating parameters are investigated. Because of the attractive economic figures and high efficacy, the refiners expect that pervaporative desulfurization of gasoline shall soon become very important, either alone or coupled with presently available technologies.

KEYWORDS *Gasoline, desulfurization, pervaporation*

INTRODUCTION

The issue of gasoline desulfurization has gained importance during the past few years because today, on one hand, most refiners have to process denser

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TABLE 1 Evolution of The Sulfur Specification for Automotive Gasoline in the European Union

Gasoline specification	EURO III 2000	EURO IV 2005	EURO V 2009–10
Sulfur, ppm max.	150	50	10

and high sulfur crude oils (due to lack of availability of lighter, low sulfur crude), while the environmental regulatory limits on sulfur emissions are continually being lowered on the other. The recent sulfur specification of automotive gasoline in the European Union is given in Table 1. The present sulfur specification of gasoline i.e.,10 ppm may soon be reduced further in the near future, since the world is rapidly heading towards 'zero sulfur' (1).

Sulfur compounds in gasoline may be present as sulfides, thiols and mercaptans. These compounds are converted into sulfur dioxide during combustion of gasoline in automobile engines. Sulfur is controlled in finished gasoline to (2, 3).

- Limits emissions of sulfur oxides;
- Limits odor of certain sulfur compounds;
- Enhances storage stability;
- Improves conversion efficiency of conventional three-way exhaust catalysts, thereby reducing emissions of nitrous oxides (NOx), carbon monoxide (CO), hydrocarbons and volatile organic compounds (VOCs);
- Reduces emission of evil-smelling hydrogen sulfide gas during catalyst warm up;
- Reduces emission of sulfate particles that contribute to particulate matter emission.

Sulfur is conventionally removed from gasoline by

✓ Merox Extraction and
✓ Hydrodesulfurization

Low molecular weight mercaptans present in gasoline fractions are soluble in caustic soda and hence can be removed via merox extraction. In mercaptan extraction units, fresh feed is charged to an extractor, where mercaptans are extracted by a liquid countercurrent caustic stream and the treated product passes overhead to storage (4). However, the disadvantages associated with the merox process are:

- mercaptans present in gasoline fractions boiling above 100°C are insufficiently soluble in caustic soda,

- difficulty and cost of spent caustic waste disposal,
- the use of an expensive catalyst involving a chelate and possible contamination of the distillate with the catalyst (5).

In hydrodesulfurization (HDS) the chemically bound sulfur is converted to hydrogen sulfide. The H_2S gas is then removed in a gas scrubber. H_2S is converted to elemental sulfur in the downstream Claus process and yellow sulfur is sold off to the chemical industry (6). The traditional HDS process is highly efficient in removing thiols, sulfides and disulfides, but less efficient for thiophene and its derivatives; thereof for the very low reactivity of those refractory species under conventional conditions (7). However, the HDS process is expensive (4). Again the process faces an additional challenge, viz. to prevent the recombination of sulfur compounds. Recombination of H_2S and olefins can occur in the downstream part of the gasoline HDS process (1). Additionally, catalytic hydrodesulfurization results in a significant reduction of octane number due to olefins saturation (8).

Several non-conventional techniques have emerged, which include (1)

- ➢ Reactive Adsorption,
- ➢ Non-destructive adsorption,
- ➢ Alkylation,
- ➢ Physical separation methods,
- ➢ Precipitation,
- ➢ Polymerization,
- ➢ Extractive photochemical oxidation (9) and
- ➢ Sulfur reduction by additives (10)

Among the physical separation methods, the membrane based pervaporation process of sulfur removal from gasoline has gained much importance among researchers and refiners because of the inherent advantages associated with the process. Pervaporation is a separation process involving the partial vaporization of a liquid mixture through a selectively permeable membrane under a gradient of chemical potential (11).

Pervaporation separation technique has been successfully implemented for the following industrial applications (11):

- Treatment of wastewater contaminated with organics (pollution control applications),
- Separation and purification of valuable organic compounds from process streams (gasoline desulfurization),
- Azeotropic and close boiling liquid mixtures (separation of azeotropic ethanol-water mixtures),
- Separation of heat sensitive mixtures (fruit juice processing),

- Removal of one or more product species from reversible reaction systems (in esterification reactions).

Hence, pervaporation is one of the most active areas of current membrane research and has gained acceptance by the chemical industry as an effective tool for the separation and recovery of different liquid mixtures.

Pervaporation is considered to be a promising alternative to other separation techniques because the process (11):

i. is less energy intensive;
ii. is economical;
iii. is easily scaled-up;
iv. yields superior quality product – capable of reducing sulfur content of feed to about 10 ppm;
v. with little/no reduction of octane number;
vi. is clean and safe;
vii. has a high degree of flexibility regarding feed;
viii. is simple (no eluents, sorbents, additives or catalysts required);
ix. feed pretreatment is not needed;
x. no chemical transformations; and,
xi. is sturdy: the membrane elements have a long lifetime – minimum of 5 years.

These are the reasons why refiners are now considering pervaporation as a potential candidate to take up the increasing worldwide challenge of sulfur removal from gasoline which remains one of the important issues concerning public health. Sulfur removal from gasoline via pervaporation have been investigated and published by several researchers. Some refiners like Exxon Mobil Research & Engineering, Marathon Oil Company, Grace Davison have also published reports (12) on this new separation technique.

The desulfurization technique is a one step operation, carried out at room temperature without use of any additional chemical, and at the same time the product specification of gasoline is duly maintained. Additionally, the importance of the process lies in the facts that the cost involved (in both capital and operating investments) is reduced compared to the Merox or HDS processes. The produced purified gasoline volume is high and the process is capable of handling any type of feedstock compared to the conventional HDS process (1). Hence, it is obvious that pervaporation offers tremendous economical advantage compared to the other sulfur removal techniques. Among the different liquid-liquid separation techniques, pervaporation is assessed to be the third highest in terms of its all round performance (13).

A sound knowledge about the sulfur components usually present in gasoline is absolutely necessary for the proper choice of membrane material. Typical sulfur compounds and corresponding refinery streams for gasoline

TABLE 2 Typical Sulfur Compounds Present in Corresponding Refinery Streams of Gasoline

Refinery streams (typical sulfur content)	Sulfur compounds weight %
Straight run naphtha (100–1000 ppm)	34 wt% of thiacycloalkanes, 38 wt% of thiols and sulfides, 12 wt% of thiophenes, 11 wt% of disulfides, and 5 wt% of unknown compounds. (14–16)
FCC naphta (300–5000 ppm)	46 wt% of thiophenes, 32 wt% of benzothiophenes, 14 wt% of thiols and sulfides, 4 wt% of thiacycloalkanes, 0.6 wt% of disulfides, 0.3 wt% of hydrogen sulfide and 3 wt% of unknown compounds. (16)
Coker naphtha (100–2000 ppm)	Mercaptan (0.5–2.5 wt %), Disulphide (0.15–3.3wt %), Sulfides (15–20 wt %) and others (80wt %) (17)

1 ppm is 1 μg/g or 1000 ppm is 0.1 wt%.

are outlined in Table 2 (14–17). It has been reported recently that thiophenic sulfur represents over about 80% of the total sulfur content in Fluidized Catalytically Cracked (FCC) gasoline (18). Again, it is more difficult to remove thiophenic sulfur compared to other sulfur compounds from gasoline fractions.

In this paper an attempt has been made to review the non-conventional approach of gasoline desulfurization using pervaporation technique by examining the following issues:

- Removal of sulfur compounds from gasoline by pervaporation,
- Commercial pervaporative desulfurization processes and its advantages over the conventional HDS process.

PERVAPORATIVE SEPARATION OF SULFUR COMPOUNDS FROM GASOLINE

As mentioned earlier, several organic-organic liquid mixtures have been separated successfully by using pervaporation separation technology. Hence, it is expected that sulfur containing species in hydrocarbon mixtures can also be separated using this technique. Like other pervaporation systems, the pervaporative gasoline desulfurization operation is guided by the nature of the membrane, the operating parameters and the characteristics of the separating species. These aspects have been discussed in detail in the following sub-sections.

The Pervaporation Process

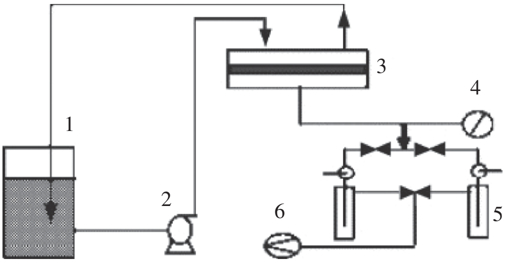
Pervaporation is a membrane separation process, involving the partial vaporization of a liquid mixture through a dense membrane for selective permeation of one or more components from a liquid mixture, whose downstream side is usually kept under vacuum (19).

The basic components of a pervaporative system include: a pervaporation cell with temperature control in which the membrane is housed, vacuum system, condensation usually cold traps maintaining cryogenic conditions and recovery systems of permeate and retentate, respectively (11). A schematic diagram of a continuous pervaporation unit is given in Figure 1. For gasoline desulfurization usually a non-porous polymeric membrane is chosen. When sulfur containing gasoline is subjected to pervaporation, sulfur compounds are expected to pass preferentially through the membrane producing desulfurized gasoline. For a continuous pervaporative mass transfer, the gasoline feed is kept in constant contact with the upstream side of the membrane and vacuum or a sweep gas is applied on the other side of the membrane. The sulfur components present in the gasoline feed absorb into the membrane, permeate through it and evaporate on the downstream side.

Pervaporation Characteristics

The performance of a pervaporative operation is evaluated in terms of permeate mass flux (J) and the membrane selectivity. The mass flux 'J' is the amount of the component permeated per unit area of the membrane per unit time for a specified system.

$$J = \frac{M_i}{at} \tag{1}$$



1. Feed tank from which the feed is pumped to the pervaporation cell and the desulfured retentate stream is concentrated by continuous pervaporation operation simultaneously.
2. Feed pump
3. Pervaporation cell
4. Pressure monitor
5. Cold trap to arrest the sulfur rich permeate stream
6. Vacuum pump

FIGURE 1 A schematic diagram of a continuous pervaporation unit reprinted from [18].

where M_i is the amount of the i^{th} component permeating through membrane area 'a' at time 't'. The mass flux J depends upon the operating temperature of the system. The relationship between the permeation flux and operating temperature can normally be expressed by the Arrhenius-type formula (20)

$$J = A\exp\left(-\frac{E_P}{RT}\right) \tag{2}$$

where A is the pre-exponential factor, E_P the activation energy of pervaporation, R the gas constant, and T the absolute temperature.

Selectivity can be represented by two ways, the separation factor and the enrichment factor. The former is specific for a binary mixture (21), while the latter is applicable for systems involving removal/recovery of target compound(s).

The Enrichment factor (E), being more relevant in this case, can be used to measure the separation selectivity of the sulfur compounds. For the desulfurization system it is defined as (22):

$$E = \frac{F_S}{P_S} \tag{3}$$

where F_S and P_S represent total sulfur content of feed (by weight) and the total sulfur content of the permeate (by weight) streams, respectively.

Since there is usually a tread-off between membrane permeation flux and selectivity, a composite parameter called Pervaporation Separation Index (PSI) has been widely accepted to evaluate the overall pervaporation performance (20–24). It is defined as:

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

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

Pervaporation Membranes for Gasoline Desulfurization

Membrane selection plays a key role in any pervaporative operation. Selection of the polymer materials for separation is based mainly on three important features, high chemical resistance, sorption capacity and good mechanical strength of the polymer film in the solution. The choice of membrane for the pervaporation process also depends highly on the components to be separated. Gasoline contains a large number of different compounds, hence material selection and material modification is very important to carry out pervaporative removal of sulfur containing compounds.

In most cases, a non-porous polymeric membrane is used to remove preferentially sulfur compounds from the gasoline feed. Poly dimethyl siloxane (PDMS) has been extensively used as membrane material for investigating the separation of various such hydrocarbon mixtures (25, 26), and attempts have been made to modify PDMS membranes in different ways to enhance the pervaporation performance (27, 28).

Semi-organic bonds in PDMS provide highly flexible backbone with large bond angle, long bond lengths and extreme freedom of rotation, which leads to an increasing free volume for the diffusion of the permeate molecules. Composite membranes with the barrier material on microporous Poly Acrylonitile (PAN) as support were also used (29) to solve the opposing effect of flux and selectivity in pervaporation operation. The advantage of the composite membrane is that each layer can be optimized independently to obtain optimal membrane performance with respect to selectivity, permeation rate, and chemical and thermal stability (30). The structure of the composite membrane makes the separation layer very thin resulting in higher flux even in presence of high degree of cross-linking (11).

Both ionic and non-ionic membrane materials have been used. For ionic membranes, the sulfur enrichment factor was much higher compared to that of their non-ionic counterparts. This might be due to the fact that sulfur compounds are generally more polar than the other hydrocarbon components present in gasoline fractions.

Solubility Parameter Theory for Membrane Selection

Transport across nonporous membranes in pervaporation is generally considered to follow the well-accepted solution-diffusion model (11, 31). The solution-diffusion model involves three successive steps (32) viz., dissolution of the preferentially permeable feed components on the swollen upstream surface layer of the membrane, diffusion of the components from the surface layer through the membrane, desorption of these components at the downstream surface of these membranes. Hence, permeation is dependent on the sorption and diffusion processes. In separation of hydrocarbon mixtures by pervaporation, selectivity is governed by the differences in solubility or diffusivity between the feed components in the membrane. In some cases, the difference in membrane solubility of the corresponding components plays an important role in determining the pervaporation selectivity.

The Hildebrand solubility parameter δ provides a numerical estimate of the degree of interaction between materials, and can be a good indication of solubility, particularly for non polar materials such as many polymers. δ, provides a framework for the selection of the polymer membranes able to achieve a particular pervaporative separation (33). Materials with similar δ values are likely to be miscible. Hansen proposed an extension of the Hildebrand solubility parameter concept by dividing it to its fractional components. The correlation can be expressed as:

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \tag{5}$$

where δ_d, δ_p and δ_h are the dispersion, electrostatic and hydrogen bond components of the solubility parameter, δ, respectively. The Hansen solubility parameters are determined empirically based on multiple experimental solubility observations (35). This solubility parameter approach has been successfully extended to polymer-solvent system and is an effective tool to identify polymeric membrane materials compatible with the target compounds in pervaporative separation (36).

The difference in Hansen solubility parameters (Δ) of the (i^{th}) component of the feed and that of the membrane material (3) is evaluated from the following equation (37):

$$\Delta_{i,\mathrm{z}} = \sqrt{\left[(\delta_{d,i} - \delta_{d,\mathrm{a}})^2 + (\delta_{p,i} - \delta_{p,\mathrm{a}})^2 + (\delta_{h,i} - \delta_{h,\mathrm{a}})^2\right]} \tag{6}$$

The greater the compatibility between the (i^{th}) component of the feed and the membrane material the smaller will be the magnitude of Δ (23).

The solubility parameters of the gasoline components, including both hydrocarbon and sulfur species and typical polymeric membrane materials are given in Table 3. Hence, from this table the membrane material suitable for the preferential removal of the sulfur containing compounds from gasoline can be selected.

On the contrary, in some cases, the difference in diffusivity of the feed components through the separating membrane might be the governing parameter. For such cases, a complementary approach should be adopted as proposed by Koros (38), which emphasizes primarily on the kinetic response of the membranes to the difference in shape and size of the components.

Membrane Material Modification for Improved Separation Properties

Membrane structures may be porous, dense and asymmetric. The choice for the selection of a good membrane requires a sound knowledge of membrane science. In the development of high performance membranes for organic mixtures separation, there arises a need to adjust the swelling extent occurring within the membrane, while in contact with the feed solution (20), since swelling increases diffusion coefficients of the penetrants (39). To achieve high selectivity and/or high flux, the membrane must be modified. Membrane modification can be achieved by any one of the following processes:

- Cross-linking,
- Grafting,
- Blending,
- Copolymerization

TABLE 3 The Solubility Parameters of the Gasoline Components, Including both Hydrocarbon and Sulphur Species and the Polymeric Membrane Materials

		Solubility parameter /$(J/cm^3)^{1/2}$			
Sl. No.	Components	(δ)	(δ_d)	(δ_p)	(δ_h)
1	n-Pentane	14.4	14.4	0	0
2	Isopentane	13.8	13.8	0	0
3	Cyclopentane	16.6	16.6	0	0
4	Hexane	14.9	14.9	0	0
5	Cyclohexane	16.7	16.7	0	0
6	Methyl Cyclohexane	16.0	16.0	0	0
7	Heptane	15.3	15.3	0	0
8	Octane	15.5	15.5	0	0
9	Isoctane	14.2	14.2	0	0
10	Benzene	18.7	18.4	0	2.0
11	Toluene	18.2	18.0	1.4	2.0
12	Thiophene	20.0	14.0	12.4	7.5
13	2Methyl Thiophene	19.6	15.1	12.1	2.6
14	3Methyl Thiophene	19.5	15.2	12.1	1.8
15	Thioether	16.9			
16	Dimethyl Thiophene	19.3	16.3	10.3	0.8
17	Diethyl Thiophene	19.2	16.2	10.3	0.7
18	Trimethyl Thiophene	19.2	16.2	10.3	0.8
19	Triethyl Thiophene	19.0	16.5	9.6	0.6
20	Sulphide	16.9			
22	Disulphide	17.4	17.0	3.1	2.1
24	n-Butyl Mercaptan	18.4			
25	Benzyl Mercaptan	21.1			
26	C5-Mercaptan	17.9			
27	Diethyl ether	15.8	14.5	2.9	5.1
28	Benzyl ether	18.6	16.3	8.9	0
29	Ethyl butyl ether	15.7	14.3	4.8	4.5
30	Polystyrene	21.4			
31	PolyDimethylSiloxane	21.0	19.2	0.1	5.7
32	Polyethylene glycol	20.1			
33	Polyurethane	21.0			
34	Polyetherimide	23.5			
35	Polyvinyl Alcohol	25.8	14.9	3.3	20.9
36	Polyacrylonitrile	26.6			
37	Polysulphone	21.4			
38	Polytetrafluoroethylene	13.99			
39	Polyimide	32.3			
40	Cellulose Acetate	25.1			
41	Polyvinyl chloride	26.5			
42	Polypropylene	21.9			
43	Polyvinylpyrrolidone	20.6			

Cross-linkage and the degree of cross-linking should be controlled thoroughly. Especially, in the case of a composite membrane it is rather difficult to ensure controlled cross-linking as composite membranes are produced by the usual coating-evaporation technique and chemical cross-linking is achieved during the evaporation period only. Hence, definite crosslinked polymer networks of appropriate chemical nature could be realized by means of “physical cross-linking”. Promising results concerning the separation of aromatics and saturates using physical cross-linking has been reported by Exxon (40).

Cross-linking modification of membrane material for gasoline desulfurization was done by several researchers. Lin et al. (41) studied and analyzed pervaporation performance and membrane preparation based on the solubility parameter theory, and determined polyethylene glycol (PEG) as the promising membrane material for gasoline desulfurization. In spite of its desulfurization capacity (42, 43), they reported that PEG needed modification for its easier swelling and unstable pervaporation performance.

They used maleic anhydride as the cross-linking agent and reported that the degree of cross-linking, which is adjusted by the concentration of cross-linking agent and the cross-linking reaction time, has important influence on membrane pervaporation performance. They also reported (41) that cross-linking modification of PEG decreased the solubility of gasoline components (especially for thiophene, toluene and cyclohexene) and improved the solvent resistant performance of PEG. These properties were important for membrane life in field application.

Cross-linked PDMS–polyetherimide (PEI) composite membranes were produced by Chen et al. (44), in which phase inversion technique was used to prepare asymmetric microporous PEI membrane which acted as the microporous supporting layer. They investigated the effect of the amount of PDMS, cross-linking temperature, amount of cross-linking agent and cross-linking time on the separation efficiency of *n*-heptane–thiophene mixtures. Experiment results demonstrated that optimum flux and sulfur enrichment factor were achieved with 80–100°C of cross-linking temperature and amount of cross-linking agent up to 20 wt.%, and 25 wt.% of PDMS amount. The degree of swelling and stability of the composite membrane during long-time operation were also studied.

Qi et al. (45) prepared mixed matrix membranes of PDMS with silver oxide (Ag_2O) as the solid filler and used them for desulfurization of model gasoline composed of n-octane and thiophenes. Ag_2O-filling leads to an increase in selectivity to thiophenes because of the physico-chemical interaction between Ag_2O particles and thiophene molecules, as well as a decrease in total flux owing to the tortuosity effect of the impermeable Ag_2O particles. With the rise of feed temperature, the total flux increases but the selectivity to thiophenes decreases simultaneously. They reported that when Ag_2O loading was increased from 0 to 5 wt%, the total fluxes decreased from 3.31 to 2.85 kg/m^2 h at 50°C, while the corresponding enrichment factors increased from 3.55 to 4.46 and from 2.24 to 2.61 for thiophene and 2-methyl-thiophene, respectively.

Desulfurization via pervaporation using hybrid membranes was performed by some researchers (46, 47). PEG–CuY zeolite hybrid membranes were fabricated for sulfur removal from gasoline feed by Lin et al. (46). The sorption, diffusion, and permeation coefficients of gasoline components in filled membranes are higher than the corresponding unfilled membranes. There was a significant increase in flux due to the CuY zeolite filling because the porous zeolite allows for more diffusion for small molecules in mixed matrix membranes. The sulfur enrichment factor increased first and then decreased with the increasing zeolite content. This result was attributed to the combined influence of complexation force between CuY and thiophenes as well as the opposing effect between flux and selectivity. Similar observations were reported by Li et al. (47) and Qi et al. (48) who used PDMS-NiY zeolite hybrid membranes and PDMS–AgY zeolite mixed matrix membranes, respectively, for the same purpose.

Polyethyleneglycol/polyurethane (PEG/PU) blend membranes were effectively used by Lin et al. (12) for catalytically cracked FCC gasoline desulfurization by pervaporation under various conditions. Higher sulfur enrichment factor and permeation flux were obtained for PEG/PU blend membranes, which was due to the synergistic effect between the polymers. It was also observed that the thiophene species were efficiently removed by the PEG/PU membranes, which once again verified the applicability of the solubility parameter theory in complex organic mixture separation by pervaporation.

Composite membranes prepared from different polymers allow a combination of properties that may not be available in a single material (11). Separation of sulfur/gasoline mixture with PDMS/PEI composite membranes by pervaporation was performed by Zhao et al. (49). From the **e**xperimental results it was inferred that higher feed temperature yielded higher total flux and lower sulfur enrichment factor. With the increase of sulfur content in the feed, the total flux varied very little, but the sulfur enrichment factor first increased with the amount of thiophene added into the gasoline, and then reached a maximum. The increase in thickness of the PDMS layer in the membrane resulted in a smaller flux but a higher sulfur enrichment factor.

Desulfurization of model gasoline composed of n-octane and thiophene was done by Xu et al. (50) with cross-linked PDMS/ceramic composite membrane. The structural morphology and thermal stability of the composite membranes were characterized by scanning electron microscope (SEM) and thermogravimetric analysis (TGA), respectively. Experimental results indicated that an increase of sulfur content in feed resulted in a higher total flux but a lower sulfur enrichment factor whereas increasing the feed temperature, had the reverse effect. Total flux and sulfur enrichment factor improved with low permeate pressure and high feed flow rate. The composite membrane exhibited a high total flux of 5.37 kg m^{-2} h^{-1} and corresponding sulfur enrichment factor of 4.22 for 400 $\mu g\ g^{-1}$ sulfur in feed under 210 Pa at 303 K indicating that the chosen membrane has high potentiality towards sulfur removal from gasoline at room temperature.

Kong et al. (51) prepared a PEG/polyethersulfone (PES) composite membrane using pre-wetting combined with double-layer coating methodology, that can be applied on a commercial plant for FCC gasoline desulfurization. The pre-wetting method prevents the process of pore penetration (the intrusion of the separating layer into the porous support layer) that may occur in a composite membrane (52). This phenomenon of pore penetration can increase the effective thickness of the separating layer, thereby decreasing the permeation flux.

The results also indicated that the pre-wetting method effectively confined the intrusion of PEG solution to porous PES support layer in coating process. Pervaporation experiments indicated that the membrane, with the crosslinking agent amount of 17% and solids content in active layer solution of 16%, had a stable performance for FCC desulfurization. It was found that the pervaporation performance of the composite membrane changed slightly when the thickness of active layer varied from 4.25 μm to 33.26 μm.

However, Ying Kong et al. (51) tentatively put forward that the pervaporation performance of the composite membrane is chiefly determined by the crosslinking degree of active layer, and the increase of active layer thickness has little effect on flux and sulfur enrichment factor but only prolongs the equilibrium process of the composite membrane. Furthermore, surface deficiency occurred more frequently on the composite membrane with ultrathin active layer, which led to an unstable pervaporation performance or even the gasoline leaked through the membrane with huge flux but no selectivity. To summarize, the active layer of the composite membrane should maintain a proper thickness for practical application.

The performance of different pervaporation systems, reported by researchers, for sulfur removal are listed in Table 4. From the Table 4 listed data, it is evident that modified membranes exhibited higher enrichment factor compared to their unmodified counterparts.

Effect of Operating Parameters on Pervaporative Desulfurization

The operating parameters have a remarkable influence on the overall pervaporation separation operation i.e., both flux and enrichment factor.

Operating Temperature

As discussed earlier, it is generally observed that the permeation flux increases with temperature with other operating parameters remaining constant due to the Arrhenius-type exponential relation between temperature and diffusivity. According to this relation, diffusivity will increase with temperature when the activation energy has a positive value, which is mostly observed in the pervaporation of liquid mixtures (11). This increase in diffusion coefficient may be attributed to the fact that at elevated temperature

TABLE 4 The Performance of Different Pervaporation Systems for Sulphur Removal from Gasoline

System	Membrane material	Thickness (μm)	Temp. (°C)	Downstream pressure (Pa)	S content (μg/g)	Flux (J) (kg/m^{2}h)	Enrichment factor (E)	Ref
Model Gasoline	PDMS with Ag_2O filled	15	50	500	500	3.31	3.55	(45)
Gasoline	PDMS-Ni^{2+}Y zeolite hybrid	–	30	–	500	3.26	4.84	(47)
FCC Gasoline	Polyethylene glycol/ polyethersulfone composite	16	100	4666	900	3.37	3.63	(52)
Ethyl thio-ether/ heptane	Polyethylene glycol/ polyetherimide composite	150	80	200	–	1.8	6.7	(53)
n-octane/ thiophene	PDMS/ polyacrylonitrile composite	0.1	30	500	500	1.5	4.9	(27)
FCC Gasoline	Polyethylene glycol/ polyurethane blend	10–20	110	1400	1200	2.50	4.03	(12)
n-heptane/ thiophene	Fluoro-polyimide	–	60	2000	0.785	1.35	2.86	(54)
Refinery naphtha	Polyimide	10	85	120	807	3.25	1.44	(42)
Thiophene/ heptane	Polyurethane	10	85	133.3	–	10.81	1.51	(42)
Gasoline	Polyvinylpyrrolidone	50	115	10666	4000	12–3600	–	(55)

the polymer chains of the membrane material become more flexible thereby increasing the available free volume for diffusion through the polymeric matrix. Hence, it can be inferred that both hydrocarbon and sulfur fluxes are expected to increase with temperature. On the other hand, the change in sulfur enrichment factor will depend on the relative change of the hydrocarbon and sulfur fluxes.

Investigators (18, 27) have reported that for pervaporative desulfurization of FCC gasoline using cross-linked PEG membranes, when temperature was increased, the total permeation flux increased, but sulfur enrichment factor increased firstly and decreased then. At 358 K (95°C), the sulfur enrichment factor reached its peak value. Increase of feed temperature enhanced the driving force source of mass transfer and the saturated vapor pressure of components at permeate side and availed components in permeating through the membrane.

However, the continuous increase of feed temperature weakened the difference of solubility and diffusion velocity of sulfur and hydrocarbon species, and caused the decrease of sulfur enrichment factor. The influence of feed temperature on pervaporation performance of PEG/PU blend membranes (12) and the effect of feed temperature on pervaporation performance of PEG/CuY hybrid membranes were also studied (46). The results were similar with the conclusion for PEG membranes.

Cross-linked polydimethylsiloxane (PDMS)/ceramic composite membranes were prepared and employed by Xu et al. (50) for desulfurization of model gasoline composed of n-octane and thiophene. Separation of sulfur/gasoline mixture with PDMS/PEI composite membranes by pervaporation was also conducted (49). They also observed that when the temperature increased, the total flux increased due to similar reasons, whereas the sulfur enrichment factor decreased. The increasing degree of swelling of the membrane material with temperature resulted in more hydrocarbon flux thereby decreasing the selectivity towards the sulfur species.

Downstream Pressure

In pervaporation operation, increasing the downstream pressure will decrease the pressure difference between the feed-side and the permeate side thereby reducing the driving force of mass transfer (chemical potential gradient). Hence a decrease in permeating flux is generally observed with increasing permeate pressure, all other parameters remaining constant (11).

Under lower permeate pressure, flux decreased with increasing permeate pressure since there was a reduction of driving force for transport of components during the desulfurization of FCC gasoline (18). Similar results were reported by a number of researches (12, 50, 56). The sulfur enrichment factor increased initially when the permeate pressure increased. Since the saturated vapor pressure or partial vapor pressures of *n*-heptane is lower than that of thiophene, an increase of permeate pressure slowed down evaporation of *n*-heptane relatively and caused an increase of sulfur enrichment factor.

However, sulfur enrichment factor was susceptible to the increase of permeate pressure. It increased firstly and then decreased. At permeate pressure of 10.5 mm Hg, 0.014 kg cm^{-2} or 0.2 p.s.i., sulfur enrichment factor met its peak value. A decrease in the speed of flux of sulfur species compared to that of hydrocarbon species, at 10.5 mm Hg particularly, was observed (18). But with the continuous increase of permeate pressure, the difference between evaporation and permeation capacity is weakened. Due to higher concentration on the feed side, heptane's permeation amount increased relatively thereby causing a decrease of sulfur enrichment factor.

The effect of permeate pressure on pervaporation performance of PEG/PU blend membranes was studied by Lin et al. (12). The experiments were conducted at about 383 K (110°C) of feed temperature with 1200 μg/g sulfur content level in FCC gasoline feed. Both the flux and sulfur enrichment factor decreased with the increasing permeate pressure since there was a reduction of driving force for transport of the components.

Feed Sulfur Composition

Since the sulfur content of gasoline varies from refinery to refinery depending on the nature of the crude being processed and the process of refining, it is necessary to study the influence of varying feed sulfur content on the pervaporative performance. It has been observed by some researchers that a higher feed sulfur content resulted in a higher total flux but a lower sulfur enrichment factor (18, 50, 51). When the sulfur content in feed increased, an extensive swelling of the membrane occurred due to more dissolution of sulfur components in the membrane.

The increasing swelling of the membrane would weaken difference of sorption and diffusion characteristics of the individual component. Consequently, both the sulfur and hydrocarbon components permeated the swollen membrane easily, and the membrane had high permeation flux but the sulfur enrichment factor declined. However, the influence of increasing sulfur content on pervaporation performance weakened after some time (18) when sulfur content come to 600 μg/g. Since the occurrence of swelling balance in the membrane and the saturated sulfur concentration on the surface of the membrane, flux and sulfur enrichment factor changed little with the increasing sulfur content level of feed.

It was found by Qi et al. (27) that variation of feed (n-octane and 2-methyl-thiophene) composition had nearly negligible influence on total fluxes and selectivity, while the partial fluxes of thiophenes are proportional to the concentrations of thiophenes in the feed. They attributed such behavior to the ultra low feed concentration and the narrow range thereof.

On one hand, the change in thiophene concentration in feed yields very limited impact on the transport of *n*-octane through the membrane. On the other hand, the partial fluxes of thiophenes are still proportional to the concentrations of thiophenes in the feed. The former resulted in nearly unchanged total fluxes, while the latter led to nearly unchanged selectivity to thiophenes.

Feed Flow Rate/Speed of Agitation

It is expected that with increasing feed flow rate (for continuous operation)/speed of agitation (for batch operation) permeate flux tends to increase (11). This behavior may be due to the decrease in mass transfer resistance by the thinning liquid-boundary layer effect as turbulence of the system is increased. Sulfur enrichment factor may increase or decrease depending on the relative fluxes of the sulfur and hydrocarbon species. However, beyond a certain value of the feed flow rate/agitator speed such positive effect on pervaporation efficiency is expected to level off as the liquid-boundary layer thickness becomes practically constant (11).

It has been reported (18, 50) that total flux and enrichment factor increased with increasing flow rate. In general, the concentration of sulfur compounds which were the more permeable components was lower on the membrane surface than that in the bulk phase. The increase in feed flow rate reduced the effect of concentration polarization and thickness of the liquid boundary layer. A reduction in concentration polarization indicated that sulfur species concentration near the membrane surface was close that in the bulk, which enhanced sorption and swelling of the sulfur species in the membrane leading to a rise in sulfur enrichment factor.

Effect of the Hydrocarbon Components of Gasoline on the Pervaporation Performance

Usually commercial gasoline is made up of different blending components coming from reforming, coking, isomerization and FCC processes. Among them, FCC gasoline, which represents 30–40% of the total gasoline pool, is by far the most important sulfur contributor. Hence, gasoline is a rather complex mixture of various hydrocarbons ranging from C_5 to C_{14} (7). Typical hydrocarbons that are present are paraffins, cycloparaffins, olefins and aromatics.

Thus, it is obvious that these different components interact differently with the membrane material and within themselves and hence influence the pervaporative operation significantly. The compositional changes of gasoline components during membrane treatment should be investigated for analyzing the octane number loss. PDMS membrane has been extensively investigated for the separation of various mixtures (25, 26) and attempts have been made to modify PDMS membrane in different ways to enhance pervaporation performances.

Qi et al. reported (27, 57) that the PDMS/PAN composite membranes that were prepared to separate alkane/thiophene mixtures exhibited thiophene selectivity. Semi-organic bonds in PDMS provide highly flexible backbone with large bond angle, long bond lengths and extreme freedom of rotation, which leads to an increasing free volume for the diffusion of the permeate molecules.

Different hydrocarbons and sulfur components making up the model gasoline, PDMS membrane was used for sulfur removal from gasoline by pervaporation and the impact of different hydrocarbon species on the desulfurization efficiency was investigated experimentally by Qi et al. (7).

Experimental results of a series of alkane/thiophene mixtures indicated that, the total fluxes decrease with increase of carbon number in the alkane, while the enrichment factor of thiophene increases simultaneously. With the membrane having a normalized PDMS layer of 15 μm, the total flux for *n*-octane/thiophene mixture was measured to be about 1.04 kg m^{-2} h^{-1}, with the corresponding enrichment factor of thiophene 4.4 at 31°C.

Compared with alkanes, the olefins are characterized by one or more double bonds and have therefore a plane geometry, which favors their transport through the dense membrane. Pervaporation results of *n*-hexene/*n*-hexane/thiophene demonstrated that, the rise of concentration of *n*-hexene in the feed leads to a larger total flux, but a smaller enrichment factor for thiophene at the same time. Additionally, the similar framework and electronic properties of aromatics and the coexisting aromatic sulfur heterocycles results in negative influence for this desulfurization process. With the increase of the content of toluene in toluene/*n*-octane/thiophene model mixtures, the total flux increased while the enrichment factor of thiophene decreased. For such system, the coupling effect should be taken into consideration for the further understanding or mathematical simulation of the transport process.

Detailed investigations of the influence of FCC gasoline components on membrane performance were also conducted by Kong et al. (58). Typical hydrocarbon and sulfur components were studied for their effect on pervaporation performance and swelling degree through polyethylene glycol (PEG) membranes. The results demonstrated that the increasing aromatics, olefins and sulfur content in feed led to the increased flux and decreased sulfur enrichment factor due to the enhanced membrane swelling. However, alkanes and cycloalkanes had little influence on membrane swelling and pervaporation performance.

Membrane performance comparison for model compounds and gasoline feed was also conducted to examine the above conclusion. Hydrocarbon group, sulfur species distribution and octane number of feed and permeate sample were obtained by gas chromatography (GC) analysis, and the results suggested that aromatics content increased and other hydrocarbon groups content changed little through pervaporation process. Additionally, the overall analysis indicated that higher sulfur enrichment factor and lower flux were usually achieved with lower sulfur level feed.

Sorption and transport behavior of gasoline components in PEG membranes were investigated by Lin et al. (42). The sorption, diffusion and permeation coefficients were calculated by the systematic studies of dynamic sorption curves of gasoline components such as thiophene, *n*-heptane, cyclohexane, cyclohexene and toluene in PEG membranes.

Furthermore, the temperature dependence of diffusion and solubility coefficients and the influence of crosslinking degree on sorption and diffusion behaviors were conducted to elucidate the mass-transfer mechanism. The dynamic sorption curves, transport mode, activation energy and thermodynamic parameters all indicated that the thiophene species were the preferentially permeating components. Li et al. (47) calculated the diffusion coefficients of small penetrants (thiophene, n-octane) in the PDMS polymer matrix by molecular dynamics simulation using Materials Studio Software®. Here also results indicated that the diffusion coefficient of n-octane is lower than that of the thiophene species. Researchers all over the world have recognized the potential of pervaporative desulfurization and efforts are going on to commercialize this new technology.

COMMERCIAL PERVAPORATIVE DESULFURIZATION PROCESSES

A commercial hydrodesulfurization (HDS) unit uses hydrogen under high pressure and temperature to convert the sulfur embedded in the sulfur compounds to hydrogen sulfide which is a cost and energy intensive technology.

Aiming at capital-avoiding technology for sulfur removal without significant octane rating loss and without high consumption of limited hydrogen supply, novel non-HDS methodologies are rapidly developed and moving toward commercial levels. Investigations on the pervaporative desulfurization of gasoline by several researchers stimulated the scaling-up of the process for industrialization. Considerable efforts are being expended by refiners and other organizations to develop this technology that will allow them to meet the mandated sulfur specifications on time. The reported commercial processes are discussed below.

Moving the pervaporation process from laboratory experiment to pilot plant operations and/or a economically sound demonstration unit is extremely complicated. Each step brings an increase in membrane area requirement, equipment, quantity of required feedstocks, time for execution, analytical facilities, technical issues, and operating personnel.

Until recently the detailed report about the scale-up of pervaporation for gasoline desulfurization is very scarce.

A detailed study was carried out by Lin et al. (59) to optimize the pervaporative gasoline desulfurization by process simulation. The different operating parameters of the desulfurization process, of the membrane area required as well as of the retentate flux were taken into account. Equations derived from experimental data on a laboratory scale using the process simulation model were applied to design the scale-up units.

S-Brane® is a successful commercial process developed by Grace Davison Company. S-Brane® is a simple physical separation process that separates sulfur containing molecules from FCC gasoline. Primary advantages of this technology are: (60)

a. a substantial reduction in the amount of octane-sensitive high olefin gasoline that requires capital-intensive hydrodesulfurization;
b. low capital cost;
c. simplicity in design and safe operation;
d. modular design allowing for simple unit expansions and revamps for future regulations change;
e. low operating cost;
f. an inherently safer sulfur removal process asset, since the operating temperatures and pressures are much lower than traditional processes and
g. since the membrane is very selective for aromatics benzene precursors in the reformer, feeds are minimized.

S-Brane operates as a pervaporation mode membrane process. The overview of this separation process is illustrated in Figure 2 (60). The feed stream is passed over a specifically formulated polymeric membrane that selectively allows permeation of sulfur-containing molecules. The feed gasoline stream is separated into two product streams. The relatively sulfur-free stream (typically about 75% of the total volume) can be blended directly into the gasoline pool, while the other stream (25%) containing most of the sulfur requires hydrotreating before it is blended back into the gasoline pool.

An S-Brane pilot plant (1 barrel per day (BPD) capacity) and an S-Brane Demonstration Plant (300 BPD capacity) has been constructed and installed in 2001 and 2003, respectively (61). During the test runs, different FCC gasoline feed streams were treated releasing sulfur levels below 30 ppm. The demonstration plant installed at ConocoPhillips Bayway refinery, was designed to process light and intermediate cut naphtha streams (LCN & ICN) (60). Employing a single stage design, the plant processed both LCN and ICN over a wide range of operating conditions. Gasoline was circulated over the membrane on the tube-side of the module.

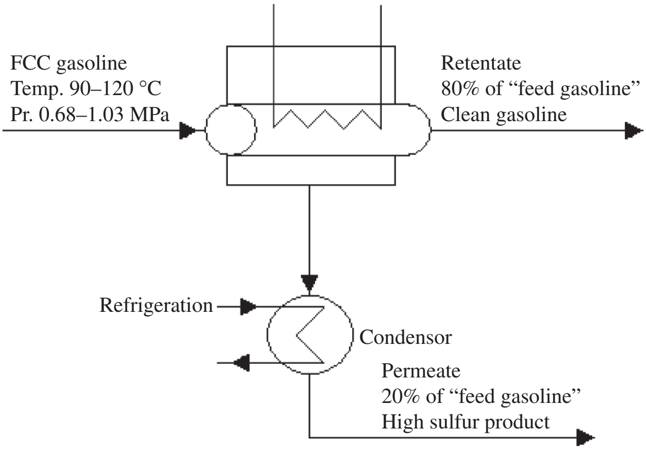


FIGURE 2 Schematic overview of the S-Brane process redrawn from (60).

The driving force causing the preferential permeation of sulfur molecules across the membrane was created by the tube-side temperature (66–121°C) and shell-side vacuum (6.9–20.7 kPa). Gasoline was raised to the processing temperature by exchanging heat with the low sulfur product (retentate) and a steam heater. Low pressure steam was used for maintaining the module at the operating temperature. The permeate was recovered in the condensation section. Steam ejectors provided the initial evacuation of non-condensable gases in the Demonstration Plant. During normal operation, the vacuum was maintained by permeate condensation.

A chiller-based refrigeration system was used to condense the permeate vapors. The results from the demonstration plant confirmed their expectation based on pilot plant and laboratory results. For a range of actual refinery naphtha feeds, they have demonstrated over 90% sulfur reduction of both ICN and LCN feed. In addition, they have also demonstrated 20 ppm or lower sulfur with LCN feed.

In case of commercial pervaporative desulfurization technology, S-Brane decouples the olefins and aromatics to separately deal with the octane issue. For an olefins-rich refinery stream, the sulfur can be effectively concentrated in the permeate stream and then hydrotreated. The clean stream will retain the olefins and result in minimum ultimate octane loss.

The S-Brane process complements existing and new hydrotreating facilities. S-Brane produces a gasoline stream capable of complying with low sulfur specifications, unloads existing hydrotreating facilities, and results in an overall increase in the gasoline blending pool octane value. The unit can be modularized and installed with minimal impact to existing refinery infrastructure and minimal operations downtime.

Commercial systems for S-Brane have been proposed from 5000 to 40,000 BPD. These large-scale systems could require 10,000 m^2 of membrane. The needed actual membrane area is dependent on feed stream composition, feed volume, target purities, and capabilities of available splitters and hydrogenation units. Given the successful scale-up from lab to pilot to demonstration scale, commercial installations should expect similar performance, with additional cost savings from economy of scale. Capital costs can be 20–25% of that for other gasoline desulfurization technologies (61).

The report on S-Brane (61) revealed that the permeate can also be collected at atmospheric conditions in order to avoid loss of non-condensable light hydrocarbons, and allow complete permeate recycle. The vacuum pump exhausted to atmospheric pressure, and a glycol chiller condensed the permeate into a liquid. On all accounts, condensing the permeate at atmospheric conditions is a necessary consideration for the large-scale applications of pervaporation to reduce refrigeration duty.

The biggest issue of this process would, however, appear to be the ‘stage-cut’ (related to the ratio of S-rich to S-poor product) to be applied. The typical stage cut of the present S-Brane process is high at around 30%, which means that only 70% of the stream can be desulfurized to, for instance, 30 ppm w sulfur, while the remaining 30% is the sulfur-rich stream, to be routed to hydrodesulfurization or other processes. Such a high stage cut is possibly also connected with the necessity of retaining the olefins in the low-S stream, selectivity always being a problem. Maybe the process is only suitable to treat certain boiling-range fractions, in which case integration with hydrotreating is still required when full-range FCC gasoline is treated (1).

Trans Ionincs Corporation of the Woodlands, has developed a commercial non-hydrotreating desulfurization process. The process, TranSep-G™, is a patented membrane pervaporation process for the removal of sulfur-containing aromatics from gasoline streams without also removing the olefins, thereby allowing the high-sulfur product to be nonselectively hydrotreated without significant loss in octane (62). TranSep-G™, apart from other pervaporation processes is simpler and uses a unique venturi nozzle and special working fluid with which to pull the vacuum required to recover permeate from the downstream side of the membrane. Permeate is recovered from the Venturi liquid at atmospheric pressure thus eliminating expensive refrigeration systems generally required to condense light hydrocarbons at high vacuum. This reduces both the capital and operating costs substantially over conventional pervaporation systems that use vacuum pumps (or steam ejectors) and refrigeration units (62).

S-Brane® and TranSep-G™ processes are the pioneers of industrial gasoline desulfurization via pervaporation. Their work shall definitely instigate further development towards better commercial membrane processes for desulfurization.

Commercial Process Economics

Researchers at the Davison Catalysts division of W. R. Grace have developed a pervaporation membrane process that removes sulfur from gasoline during manufacturing more economically than currently practiced methods. In parallel with the technical feasibility efforts the economic feasibility of the process has been substantiated. The cost estimate process carried out by Grace Division and CBI Howe-Baker confirmed low capital and operating costs with improved energy efficiency compared to the HDS counterparts.

The S-Brane technology also allows maximizing crude processing flexibility to implement the solution quickly and safely (60). The investment requirement of a S-Brane unit is a third to a sixth of that required for a similar-sized hydrotreater. The potential investment savings using a configuration exploiting the synergy of two technologies is about US $30 million for a 35,000 BPD gasoline desulfurization facility. The operating costs also compare favorably. The technology's operating costs are about 0.5 cents to 1.5 cents per gallon of product lower than costs for other post-treating technologies, such as hydrotreating. This is because S-Brane operates at lower temperatures and pressures than the alternatives, and significantly reduces overall hydrogen requirements.

Maintaining the octane number in commercial gasoline desulfurization is another important issue. Refiners do not have the option to spare octane quality to stay in the premium gasoline market. The conventional hydrotreating technologies for meeting sulfur regulations result in a significant reduction of gasoline octane (by 3 to 4 units) via olefins saturation. On the contrary, gas chromatographic analysis of both feed and permeate samples carried out by Kong et al. (58) reveals that the major octane contributors (isoalkanes, alkenes and aromatics) are more or less retained during pervaporation using PEG membranes.

Detailed investigation on octane number loss was also carried out by Grace Division (60). The sulfur molecules are concentrated (20–30% by volume) in the permeate stream leaving a retentate with low sulfur level. Only the permeate stream is subjected to HDS, keeping aside the retentate, to preserve the octane number. The existing naphtha hydrocracker can be utilized for this purpose at a much lower throughput thereby lowering operating costs by reducing hydrogen consumption. By using a membrane system to bypass a large fraction of the feed around the HDS unit, the total quantity of naphtha that can be treated is increased.

Additionally, this results in a reduced octane number (by 20–30%) compared to the process hydrotreating the entire stream. The octane number loss of the combined retentate and permeate streams is about 0.5–1.0. Hence, by employing S-Brane Technology better preservation of octane index is achieved. Such octane number savings translates to about $5 million for a unit having capacity 3000 BPD. Thus the octane number loss during conventional HDS is clearly the economic incentive to consider installing an S-Brane pervaporation unit.

The process can be installed in combination with other gasoline desulfurization steps, such as after a main fractionator or downstream of a naphtha splitter. Capital costs range from $100 to $500 per BPD of installed capacity. Other sulfur removal techniques can cost from $1,000 to $2,000 per BPD (63). Again, the construction being modular, it gives some flexibility to the refiner. Additional membrane area in stages or modules can always be added later as per future requirements. This allows the refiner to spread an investment over the compliance period (61).

CONCLUSION AND FUTURE PROSPECTS

Today's refineries are processing low grade crudes with high sulfur content and doing more bottom-of-the-barrel conversions to gasoline, gas oil, etc. The need for new sulfur management facilities is expected to grow as demand for cleaner fuels increase. The importance of the relatively simple pevaporative desulfurization process of gasoline has been recognized by refiners. A lot of effort is still being spent on this aspect, both in industry and in academia during recent times. A review of these investigations can present a clear knowledge and valuable suggestions to related researchers.

From the above study it is quite evident that sulfur removal from refinery gasoline streams via pervaporation is a promising alternative to the conventional hydrodesulfurization technology and bears the potential of achieving commercial status. Pervaporative desulfurization did achieve commercial status, e.g., S-Brane® & TranSep-G™ but their popularity is yet to approach that of the commercialized desulfurization alternatives. However, apart from cost benefits and reduced loss of octane number, the other advantages of this alternative technology can possibly convince the refiners towards adoption of this technique.

The separation efficiency of the process, as mentioned earlier, depends on the combined effect of flux and sulfur enrichment factor. Deep understanding of the solution/diffusion mechanism of the gasoline molecules through the membrane is necessary for the selection of suitable membrane. Membrane material modification might be useful for improving separation efficiency. Investigations using composite membranes might help to solve the contradictory behavior of flux and enrichment factor. Further investigations using mass transfer resistance model of composite membranes can provide useful guidance on the control of ultra-thin thickness of the separation layer resulting in flux enhancement. Detailed investigations on the effect of concentration polarization of the sulfur species influencing the separation flux are yet to be done.

Optimization of the operating parameters like temperature, feed flowrate, downstream pressure and feed sulfur composition can be performed to influence the separation efficiency of the pervaporative desulfurization process. The techno-economic factors for the selection, design and operation of membrane modules include cost of the supporting materials, power consumption in pumping and ease of replacement. Development, selection, design and operation of new membrane modules may lead to easy scaling-up and industrialization of the process. Further discussion on membrane selection based on solubility parameter theory for sulfur removal from gasoline may be beneficial in choosing more efficient membrane materials.

The pervaporative desulfurization unit may be coupled with the existing conventional desulfurization units to produce a product stream of greatly improved quality (both in terms of sulfur removal and retention of octane number) than can be achieved by applying a single technology. Moreover, the present hydrodesulfurization units and their supporting facilities need not be dismantled abruptly by such process integration. Such an alternative might be attractive to the refiner because of the economical advantages associated with it.

In spite of the successful example involving coupling of S-Brane with permeate gasoline HDS, there are many problems that need to be addressed. Significant investigations, including the discussion on octane value of retentate gasoline, more detailed performance study for different FCC gasoline from various refineries, optimization of pervaporation units, cost assessment based on practical results and design for gasoline desulfurization on larger scale, both single and coupled with existing units, are yet to be done.

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