

Membranes Separation of 2-Ethyl Hexyl Amine/1-Decene

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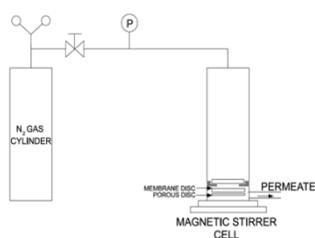
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Graphical abstract



Abstract

1-Decene is a valuable product in linear alpha olefins plants that is contaminated with 2-EHA (2-ethyl hexyl amine). Using organic solvent nanofiltration membranes for this separation is quite challengeable. A membrane has to be a chemically stable in this environment with reasonable and stable separation factor. This paper shows that Teflon AF 2400 and cellulose acetate produced interesting results in 1-decene/2-EHA separation. The separation factor of Teflon AF 2400 is 3 with a stable permeance of 1.1×10^{-2} L/(m²·h·bar). Likewise, cellulose acetate gave 2-EHA/1-decene separation factor of 2 with a lower permeance of 3.67×10^{-3} L/(m²·h·bar). A series of hydrophilic membranes were tested but they did not give any separation due to high degree of swelling of 2-EHA with these polymers. The large swelling causes the membrane to lose its diffusivity selectivity because of an increase in the polymer's chain mobility.

Keywords: Membrane; 1-Decene

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1.0 INTRODUCTION

Linear Alpha Olefins (LAO) products are essential components in producing a wide range of petrochemical products [1]. There is a large annual growth rate for LAO products worldwide per year. In 1999, 2.6 million tons were produced. Currently, the production rate is increasing by more than 3.5 wt% per year [2]. It reached up to 4.3 million tons in 2005. The main LAO products are 1-butene, 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene and 1-octadecene. These hydrocarbons are used in production of polyethylene, lubricants, detergents and surfactants, as shown in Table 1. About 6 wt% of the total LAO worldwide market is for 1-decene production [3]. The main application of 1-decene is in producing poly α -olefin synthetic lubricant (PAO) and detergent. Furthermore, 1-decene is used to make surfactants in a blend with higher linear alpha olefins [4].

There are mainly four different methods to produce LAO products. They can be produced by vapor thermo-cracking and high temperature dehydrogenation of n-paraffins. LAO is also produced via the oligomerization reaction of ethylene at high and low temperature. One of the most recent technologies to produce LAO is the ethylene oligomerization process through homogenous Ziegler-Natta catalysts composed of zirconium and alkylaluminum compounds. To avoid unwanted side products, 2-ethyl hexyl amine (2-EHA) is used as an additive in the reactor outlet to suppress any side reactions. Because the boiling point of 2-EHA is nearly identical to the boiling point of 1-decene, the amine contaminates the 1-decene product fraction

[1]. 1-Decene and 2-EHA are similar in their physical and thermodynamic properties. Therefore, conventional distillation is not feasible to separate 2-EHA from 1-decene. However, 2-EHA is soluble in aqueous solution which can be used for separation of 1-decene from 2-EHA by solvent extraction.

Table 1 Distribution of LAO product with their applications [3]

Polyethylene co-monomer	Oxo alcohols	Poly α -olefin	Others
C4-C8	C6-C16	C10-C14	C16-C20+
40%	19%	14%	27%

Membrane separation is a candidate unit operation that can possibly be used as a separation method of 1-decene and 2-EHA. The most promising organic/organic membrane separation processes are based on nanofiltration membrane or pervaporation. Organic-organic separation is one of the most demanding and energy intensive processes in the chemical process industry. Distillation and solvent extraction are commonly used to separate organics solutions. On the other hand, organic solvent nanofiltration (OSN) is a novel technology that could lead to reductions of capital and operation costs. For about 30 years, nanofiltration (NF) membranes have been commercially applied in water treatment [5]. OSN or solvent resistant nanofiltration (SRNF) for organic/organic

separation is currently limited by two factors: (i) membrane chemical stability and (ii) low flux [6].

Polyimide (PI) and polyacrylonitrile (PAN) are commonly used in OSN applications as either integral-asymmetric polymeric membranes or thin film composite membranes (TFC). A summary of OSN membranes is listed with their performance in Table 2 [7].

Currently, the only application which is commercially available in industry is lube oil dewaxing (MAX-DEWAX) in Mobil's Beaumont refinery in Texas, that started up in May 1998. The refrigeration and recovery units of a solvent-lube oil plant are debottlenecked via polyimide membrane (Matrimid-5218) with 300 g/mol molecular-weight cut-off (MWCO) which gives 99% rejection of lube oil filtrate. The plant capacity is 11.5 Km³ of solvent/day with a production increment of 25% and 3-5 vol% dewaxed oil yield. The capital cost pay-back of this process is less than one year. The success of this innovative unit is due to the aromatic selectivity of PI and the large difference of MW between lube oil and the solvents, a mixture of methyl ethyl ketone and toluene [8].

The closest application to 1-decene/2-EHA separation is the enrichment of aromatic such as benzene, toluene and xylene

from paraffins. By using Lenzing P84 PI membrane, these paraffins typically contain 7 to 8 carbons, such as ethyl hexane and dimethyl hexane and have a molecular weight difference with the aromatics of about 20 g/mol. The non-aromatic rejection for this application could reach up to 95%. Hence, it is proposed that for 1-decene/2-EHA separation, a membrane with either polar or nonpolar selectivity will be suitable regardless of the MW difference [7].

This study will analyze the feasibility of membrane separation of 2-EHA/1-decene in order to compete the current solvent extraction process. The target, in this work, is to find chemically stable membranes with high flux and minimum separation factor of 5. This separation factor will be barely able to use membranes as a bottleneck unit upstream of an existing plant to enrich 2-EHA stream. The enrichment criteria is to have a permeate stream that contains 80 wt% of 2-EHA and 20 wt% of 1-decene compared to a feed of 30 wt% of 2-EHA and 70 wt% of 1-decene. The enriched permeate can be recycle back to the LAO reactor unit as an additive without any further purification.

Table 2 Literature review for OSN membranes [7]

Membrane	Solute/Solvent	Permeance L/(m ² ·h·bar)	MWCO (g/mol)	Separation layer	Rejection (%) / Separation factor (-)	Reference
MPF-44 (Koch)	Safranin (0.01%) /methanol	0.3	250	Hydrophilic	67.6%	[9]
	Solvent blue (35mg/L) / methanol	0.2			85.0%	[10]
MPF-60 (Koch)	Safranin(0.01%) /methanol	0.5	400	Hydrophobic (PDMS)	81.0%	[9]
	Solvent blue (35mg/L) / methanol	0.1			89.0%	[10, 11]
MPF-50 (Koch)	Vitamin B12 (0.01%) / Methanol	1.2	700	Hydrophobic (PDMS)	89.0%	[9]
	Octane	11.6			—	[12]
	Methanol	5.8				
	Pentanol	1.0				
	Acetone (40% molar) / propanol	6.7			1.0 (-)	
	Pentane (40% molar) / acetone	16.7			1.0 (-)	
	Ethanol	6.4			—	[13]
n-Hexane	46.3	[13]				

Membrane	Solute/Solvent	Permeance L/(m ² ·h·bar)	MWCO (g/mol)	Separation layer	Rejection (%) / Separation factor (-)	Reference
Desal 5DL (GE Osmonics)	Xylose/Glucose (9:1)	2.5	150-300	Hydrophilic cross-linked aromatic polyamide	2.5 (-)	[6, 14]
Desal 5DK (GE Osmonics)	Xylose/Glucose (9:1)	0.8	150-300	Hydrophilic cross-linked aromatic polyamide	2.0 (-)	[6, 14]
N30F (Nadir)	Ethanol	5.6	400	Hydrophilic polyether-sulfone	8.7%	[15]
	2; 2 -methylenebis- (6-tert-butyl-4- methyl phenol)/ Ethanol	—				[13]
NFPE10 (Nadir)	Ethanol	11.0	1000	Hydrophilic polyether-sulfone	—	[15]
	2; 2 -methylenebis- (6-tert-butyl-4- methyl phenol)/ Ethanol	—				[13]
Matrimid- 5218	Lube-oil (20%)/methyl ethyl ketone-toluene	0.1	300	Hydrophilic Polyimide	99.0%	[8]
Lenzing P84	n-Decane (2%)	0.9	—	Hydrophilic Polyimide	44.0%	[16]
	1-Methyl naphthalene (2%)				1.0%	
	n-Hexadecane (2%)				79.0%	
	1-Phenyl undecane (2%)				66.0%	
	pristine (2%)				95.0%	
	n-Docosane (2%)/ toluene (88%)				92.0%	
STARMEM 122	Jacobsen catalyst (1.2mM) /THF	2.7	220	Polyimide semi-hydrophilic	96.0%	[17]
	Jacobsen catalyst (1.2mM) /EA	4.2			99.0%	
PDMS-PAN	n-Hexane	8.4	—	Hydrophobic (PDMS)	—	[18]
	n-Heptane	7.0				
	i-Hexane	7.8				
	i-Heptane	6.3				
	i-Octane	4.3				
	Cyclohexane	3.7				
	Xylene	4.9				
	Sunflower oil (0%)/hexane	3.7				
	Sunflower oil (8%)/hexane	2.4			88.0%	
	Sunflower oil (19%)/hexane	1.8			84.0%	

2.0 EXPERIMENTAL

2.1 Materials and Method

The thermodynamic interaction of a polymer toward a specific liquid can be measured by the swelling test. In the swelling test, a piece of polymer is immersed into the pure solvent (1-decene and 2-EHA), after weighting it in the dry state. Then, the difference in weight is measured which indicates the degree of swelling or solvent uptake. When the polymer is swollen, its dimensions increase. However, rigid glassy polymers with intrinsic microporosity only the weight changes while the dimensions are kept almost constant. This process is called solvent uptake. 2-EHA is more polar and more water soluble than 1-decene, so it was expected that hydrophilic polymers will be highly swelled with 2-EHA. Different types of polymers such as polyvinyl alcohol (PVA), poly (ether-block-amide) (PEBAX 1657), Nafion, Polyvinylpyrrolidone (PVP), Polymer of intrinsic microporosity (PIM-1) and polysulfone (PSE) were subjected to the swelling test.

Based on the swelling data, permeation tests were performed on the hydrophilic polymers which showed selectivity towards 2-EHA. PEBAX 1657, Nafion and PVA are nonporous hydrophilic polymers that are being used mainly in gas separation or water pervaporation. Utilizing these membranes in OSN has the disadvantage of a very low flux and, hence, high pumping energy required for the permeation. Despite that, if any of these polymers could give a selective separation of 2-EHA, it will be still a feasible process. This is because of the low concentration of 2-EHA in the feed which typically ranges between 20wt% to 30wt%. In contrast, a hydrophobic polymer, Teflon AF 2400, is selective to the hydrophobic 1-decene. However, using such a membrane will require high surface area module to accommodate the high concentration of 1-decene.

Two types of dead-end permeation cells were purchased from Sterlitech (Kent, USA); HP4750 and HP4750X which can withstand pressure up to 68 and 172 barg, respectively. Each cell is made of stainless steel and provided with a magnetic stirrer to minimize concentration polarization effect. The cell has a diameter of 49 mm and has an active membrane area of 14.6 cm² with 300 ml of liquid hold up, as shown in Figure 1 [18].

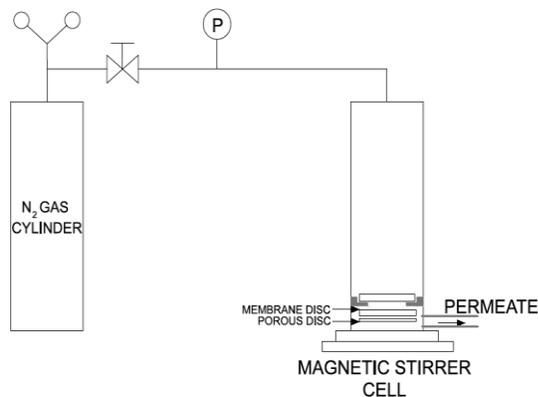


Figure 1 Dead-end permeation test set up

2.2 Characterizations

In the mixed feed permeation tests, it is required to check the composition of the feed, permeate and retentate. This can be done by using gas chromatography (GC) for liquid samples. The GC used in this work was an Agilent 7890A that contains a flame ionization detector (FID) which is sensitive to hydrocarbons. The GC is equipped with a split/split less injector and DB-WAX column (30 m x 0.32 mm x 0.25 µm film thickness). DB-WAX is applicable for organic and polar components. The GC is operated with the following conditions:

- A. Oven:
 1. Initial temperature: 60°C.
 2. Oven program:
 - a. 60°C for 1 min.
 - b. Then 35°C / min to 160°C for 1 min.
 - c. Then 70°C / min to 220°C for 1 min.
 3. Equilibrium time: 0.5 min.
 4. Holdup time: 20 min.
 5. Final temperature: 220°C.
 6. Run time: 6.7 min.
- B. Front detector FID:
 1. Temperature: 300°C.
 2. Hydrogen flow: 35 ml/min.
 3. Air flow: 300 ml/min.
 4. Make up (He): 5 ml/min.
- C. Front inlet (split):
 1. Split ratio: 50: 1.
 2. Temperature: 230.
 3. Total flow: 66.2 ml/min.
 4. Septum purge flow: 5 ml/min.
 5. Gas Saver: 20 ml/min after 2 min.
 6. Split flow: 60 ml/min.

Before analyzing the samples obtained from the permeation tests, a calibration curve was generated by using standard mixtures of 1-decene and 2-EHA. Based on the area of the peaks for 1-decene and 2-EHA, which appear at retention times of 3.3 and 4.3 minutes, the concentrations were calculated.

3.0 RESULTS AND DISCUSSION

3.1 Swelling Test

Figure 2 and 3 show the degree of swelling for the tested polymers. According to the swelling data, permeation tests were started using a dead-end permeation cell, for PEBAX 1657, Nafion, Teflon AF 2400, cross-linked PVA and cross-linked PVA-SA, (SA is sodium alginate). It was found that hydrophilic polymer, such as PEBAX 1657 and Nafion showed very high degree of swelling for 2-EHA; 28% and 54%, respectively. On the other hand, low swelling was observed with 1-decene, only 3% in PEBAX 1657 and 6% in Nafion. This large difference in the degree of swelling of 2-EHA and 1-decene gives a pure component solubility selectivity of 9 for both polymers. Consequently, these two polymers were the first candidates for 2-EHA/1-decene separation test.

On the other hand, some polymers exhibited relatively low swelling towards both 2-EHA and 1-decene. Hence, these polymers can be considered as chemically stable. PVA and polysulfone swelled in 2-EHA 20% and 22%, respectively, giving a selectivity of about 2 over 1-decene. Therefore, PVA tested in the permeation cell under the assumption that this

polymer will have a very low flux but its separation will not be affected due to high swelling.

Finally, PVP and PIM-1 showed only a small difference in the swelling of 1-decene and 2-EHA. PVP swelled 9% in 2-EHA and 8% 1-decene. PIM-1 swelled 99% in 2-EHA and 67% in 1-decene.

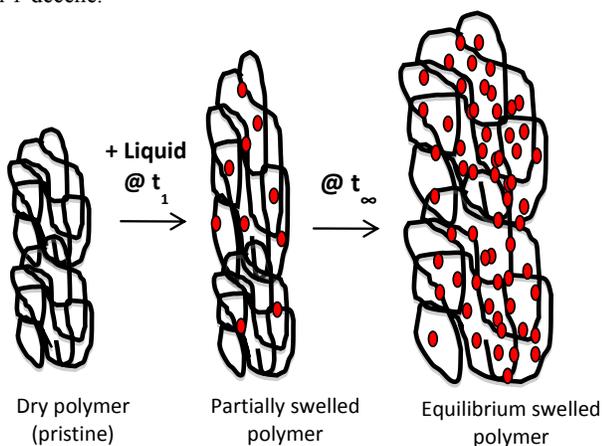


Figure 2 Swelling of polymers with solvents

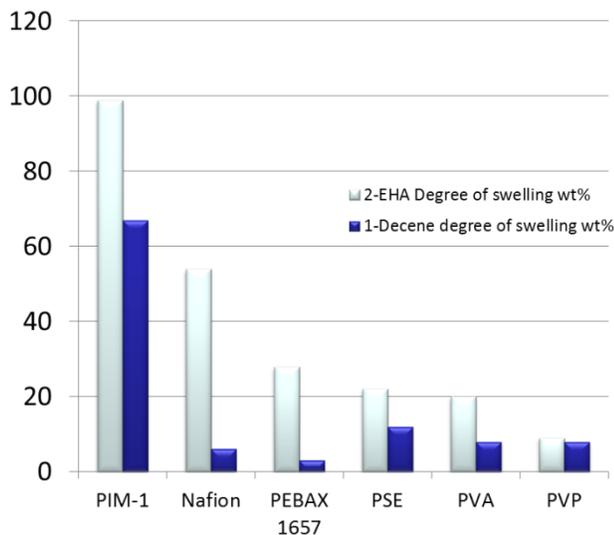


Figure 3 Degree of swelling of polymers with 1-decene and 2-Ethyl Hexyl Amine

3.2 Dead-end Permeation Tests

Pure 1-decene and 2-EHA or mixtures were filled into the cell and pressurized with N_2 , as shown in Figure 1. The permeate was collected in a graduated cylinder to measure the permeance and to take samples for GC analysis. A variety of polymers were tested as discussed below.

3.2.1 PEBAX 1657 Membranes

Poly(amid-6-*b*-ethylene oxide) (PEBAX 1657) is a block copolymer that has two segments; rigid crystalline polyamide (PA) and flexible polyether (PE) repeat units, as shown in Figure 4 [20]. The polyether block has high chain mobility; hence it is considered as the permeable site of the polymer. On the other hand, the polyamide phase is impermeable and gives

the polymer more chemical and mechanical stability. The polar ether linkage of the PE phase gives high polar/nonpolar selectivity. For example, PEBAX 1657 has a very high CO_2/N_2 selectivity [21]. The polarity of PEBAX 1657 and permeability can be enhanced by increasing the PE concentration which can be done by adding polyethylene glycol dimethyl ether as an additive [22].

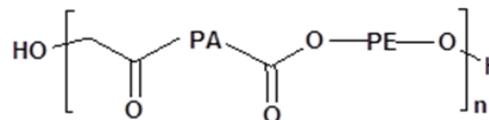


Figure 4 Chemical structure of PEBAX 1657 [23]

To make a PEBAX 1657 membrane, a solution was made by dissolving 1 wt% of PEBAX 1657 in a binary solution of 30 wt% water and 70wt% ethanol. Thereafter, the membrane was cast onto a porous PAN 350 support (Sepro, Oceanside, USA) by dip coating to get a thin film composite membrane (TFC). Isotropic dense PEBAX 1657 films were made by casting the polymer solution onto a glass plate and then evaporating the solvent. The dense film was used in the swelling test as mentioned earlier [24].

The PEBAX 1657 TFC membrane was subjected to a sustainability test to check whether it is stable in the 1-decene and 2-EHA environment. For that, CO_2 permeation test was carried out before and after immersing the membrane into the two organics which gives permeance between 75 and 87 GPU, as shown in Table 3. 1 GPU (gas permeation unit) is equal to $(1 \times 10^{-6} \text{ cm}^3(\text{STP})/\text{cm}^2 \cdot \text{s} \cdot \text{cmHg})$. After confirming the stability of the membrane, the selectivity of the PEBAX 1657 for CO_2/N_2 was checked and found to be 44 which is in close agreement with the reported literature selectivity of 61 [21].

Table 3 Sustainability test for PEBAX 1657

Membrane condition	CO_2 permeance (GPU)
Before immersing in organics	75
After immersing in 1-decene	87
After immersing in 2-EHA	81

At this stage, the membrane was confirmed to be stable and selective to the polar component. Because 2-EHA is considered as a polar compound, it was hypothesized that the PEBAX 1657 will be selective to the amine over 1-decene. Subsequently, a mixture of 70 wt% of 1-decene and 30wt% of 2-EHA was prepared which is matching the actual LAO plant composition. Before starting with mixture feed permeation tests, pure component tests of 1-decene and 2-EHA were performed.

Using the dead-end permeation cell showed in Figure 1, 1-decene and 2-EHA were placed in two cells and the permeation tests were carried out in parallel. At 30 barg, the PEBAX 1657 permeated 2-EHA with a permeance of $6.35 \times 10^{-2} \text{ L}/(\text{m}^2 \cdot \text{h} \cdot \text{bar})$, while the permeance of 1-decene was $4.64 \times 10^{-4} \text{ L}/(\text{m}^2 \cdot \text{h} \cdot \text{bar})$. As a result, the pure-component 2-EHA/1-decene selectivity was 137. This was a very promising result. On the other hand, the mixture test gave a total permeance of $4.76 \times 10^{-3} \text{ L}/(\text{m}^2 \cdot \text{h} \cdot \text{bar})$. It was found that there is almost no separation using this membrane. The separation factor was 1.4 and after more than 200 hrs of operation it dropped to 1, as shown in Table 4. This enormous discrepancy between the selectivity of the pure and mixed feed tests can be attributed to the high degree of swelling of PEBAX 1657 in 2-EHA.

Table 4 PEBAX 1657 mixed feed permeation test

Time (hr)	Pressure (barg)	Volume (ml)	Total permeance L/(m ² ·h·bar) x 10 ⁻³	Separation factor
26.5	20	1.3	1.95	1.4
49.0	20	1.3	2.29	1.3
71.0	30	3.1	3.73	1.4
95.0	30	3.2	3.53	1.5
117.5	40	5.0	4.41	1.5
140.5	40	5.2	4.49	1.4
165.8	40	6.4	5.03	1.4
186.3	40	5.3	5.13	1.0

When the polymer swells, it becomes highly permeable. This is very clearly shown in Figure 5, where the flux of 2-EHA and 1-decene mixture increases with time for 60 hours at a constant feed pressure of 40 barg. In addition, Figure 6 shows linear relationship between the flux of the permeate with the pressure of the mix feed, taking into account the average flux at certain pressure.

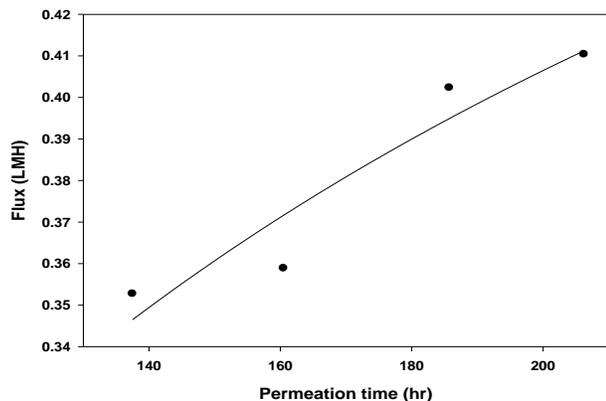


Figure 5 Flux (LMH) of mixed feed through PEBAX 1657 vs. permeation time (hr) at 40 barg

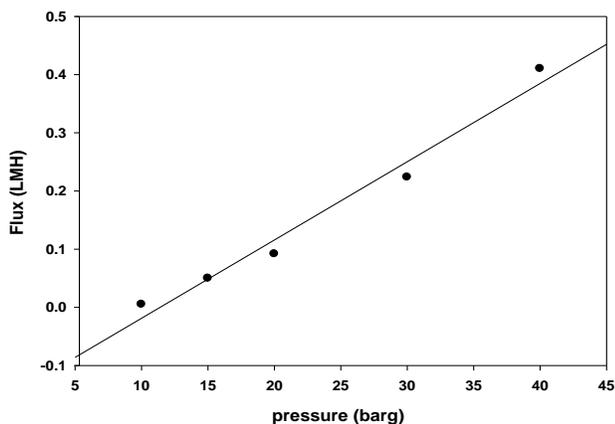


Figure 6 Relationship of flux (LMH) of mixed feed through PEBAX 1657 vs. pressure

3.2.2 Nafion Membrane

Nafion is an ion-exchange polymer invented by DuPont Company in the 1960's. It is a perfluorosulfonate ionomer

(PFSI) which is prepared by copolymerization of a perfluorinated vinyl ether comonomer and tetrafluoroethylene (TFE) [19]. Nafion has a sulfonyl fluoride group that is usually hydrolyzed to a sulfonic acid group (SO₃H). The sulfonic acid group can be exchanged with cations such as Na⁺. Figure 7 shows the chemical structure of Nafion. There are two segments in this polymer: (i) a hydrophobic PTFE backbone (poly(tetrafluoroethylene)) and (ii) hydrophilic site provided by the sulfonic acid group [25]. The group index *m* is between 1 to 3 and the index *n* is between 5 to 11. These indexes are indicating the ratio between the hydrophilic and hydrophobic phases and also represent the equivalent weight (EW) of the Nafion. EW is an indication for the weight of the dry Nafion in grams per mole of sulfonic acid groups by the acid form without changing the ether-linked sulfonated side [26]. This can be illustrated by the first two digits of the code followed by the trade name of Nafion. For example, Nafion 117 has an EW equal to 1100 g/mol-SO₃H and has a thickness of 7 mil (1 mil = 25.5 μm) [27].

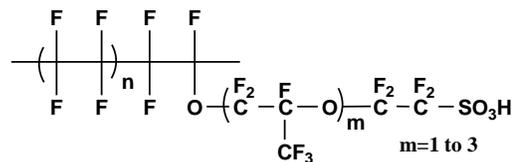


Figure 7 Chemical structure of Nafion [19]

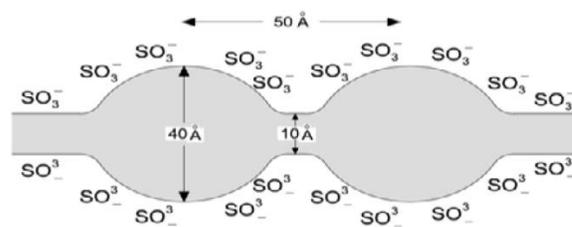


Figure 8 Proposed structure of Nafion [19]

The perfluorocarbon site gives the polymer chemical resistance towards solvents while the polar acid group provides ionic diffusional channels. These ionic are selective channels for the polar compound in the feed mixture. Figure 8 indicates the hydrophobic PTFE forming clusters of about 40 Å in diameter which is minimizing the interaction between the PTFE and polar compound such as water [19].

Based on the chemical resistance and the hydrophilicity of Nafion, it was assumed that Nafion will be more selective toward the polar 2-EHA. Hence, permeation tests were performed as discussed earlier for the pure components and mixture tests using dead-end permeation cells. It was found that Nafion is totally impermeable to 1-decene up to 125 barg while it permeated 2-EHA with a permeance of $1.33 \times 10^{-2} \text{ L}/(\text{m}^2 \cdot \text{h} \cdot \text{bar})$

at 70 barg. However, the mixed-feed permeation test revealed that Nafion is essentially non-selective to 2-EHA, as shown in Table 5. This confirmed that using a high swollen polymer will cause an increase in chain mobility of the polymer and, consequently, loss in selectivity.

Table 5 Nafion mixed feed permeation test

Time (hr)	Pressure (barg)	Volume (ml)	Total permeance $\text{L}/(\text{m}^2 \cdot \text{h} \cdot \text{bar}) \times 10^{-3}$	Separation factor
6.18	10	0.4	5.14	1.1
23.9	12	2.0	7.45	1.1
32.4	14	1.3	8.67	1.1
59.9	16	3.8	6.85	1.1
76.7	18	2.4	6.32	1.1
100.4	20	3.8	6.35	1.2
125.4	22	3.8	5.48	1.2
145.6	24	3.2	5.25	1.2
169.9	30	3.8	4.13	1.2
192.9	34	3.9	3.96	1.3
216.3	40	3.8	3.23	1.3
241.3	40	4.8	3.81	1.2
266.5	40	4.7	3.69	1.2

3.2.3 PVA and PVA-SA Membranes

Hydrophilic polymers, such as poly(vinyl alcohol) (PVA) and sodium alginate (SA), are usually utilized in pervaporation process for dehydration of organics [28]. PVA is highly hydrophilic polymer and is mechanically and chemically stable. However, it is considered to be a flexible polymer compared with a rigid one like SA. Furthermore, PVA has a lower separation factor and flux than SA in pervaporation of ethanol/water mixtures. Nevertheless, SA is suffering from very low polymer mobility that causing a noticeable drop in the flux. It was expected that, the combination of both polymers can produce a membrane with high separation factor and high flux for selective permeation of the hydrophilic solvent. PVA and SA have lower degree of swelling. Cross-linking these polymers could grant highly chemically resistance membranes [29]. Figure 9 and Figure 10 show the chemical structure for PVA and PVA-SA, respectively.

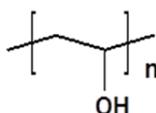


Figure 9 Chemical structure of PVA [29]

Two TFC membranes were cast onto porous PAN 350 support by dip-coating. These membranes were made from 2 wt% PVA and 1 wt% PVA-SA (1:1 ratio), each cross-linked for 1 minute. Each membrane solution was made by dissolving the polymer in hot water at 80 °C and then the TFC membranes were dried in the atmosphere for 1 day. Cross-linking was achieved by using a solution of 500 ml of DI water, 0.1 g of HCl and 8 wt% of 25 wt% glutaraldehyde as a cross linker.

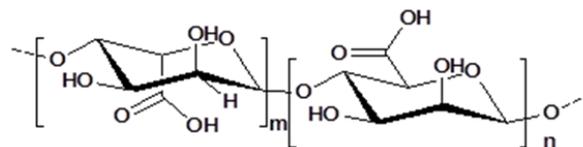


Figure 10 Chemical structure of alginic acid [28]

The pure 2-EHA/1-decene selectivity of a non-cross linked PVA was 16 with a permeance of $4.54 \times 10^{-2} \text{ L}/(\text{m}^2 \cdot \text{h} \cdot \text{bar})$ and $2.83 \times 10^{-3} \text{ L}/(\text{m}^2 \cdot \text{h} \cdot \text{bar})$ at 70 barg. Next, mixed feed tests were done for PVA and PVA-SA which have a cross-linking time of 1 minute. The permeation results are illustrated in Table 6 and 7. The first samples for both membranes had high separation factors of 9 in PVA and 4 in PVA-SA. However, the separation factor decreased dramatically to 1.5 for both membranes, as shown in Figure 11 and 12. The permeance through cross-linked PVA-SA was two-fold higher than cross-linked PVA which are $1.49 \times 10^{-3} \text{ L}/(\text{m}^2 \cdot \text{h} \cdot \text{bar})$ and $7.74 \times 10^{-4} \text{ L}/(\text{m}^2 \cdot \text{h} \cdot \text{bar})$, respectively.

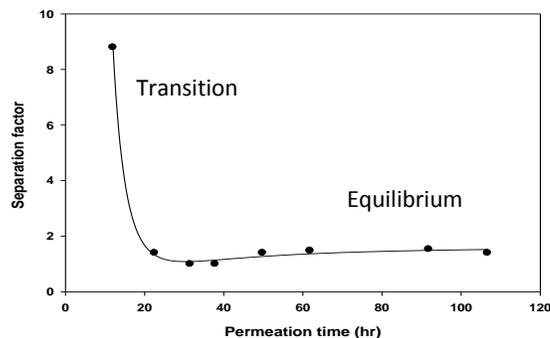


Figure 11 Separation factor of cross-linked PVA vs permeation time (hr)

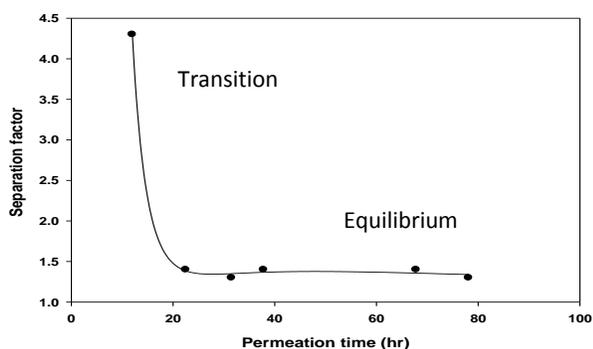


Figure 12 Separation factor of cross-linked PVA-SA vs. permeation time (hr)

This dramatic drop of separation factor for both membranes indicates the high influence of swelling in the polymer. This high degree of sorption dilates the polymer and decreases its diffusivity selectivity. When a polymer is highly swelled, it is undergoing an increase in chain mobility which is governing the diffusive transport. Therefore, the diffusion of the penetrants increase but the polymer will lose its diffusion selectivity [30].

Table 6 One minute cross linked PVA mixed feed permeation test

Time (hr)	Pressure (barg)	Volume (ml)	Total permeance $L/(m^2 \cdot h \cdot bar) \times 10^{-3}$	Separation factor
12.0	120	2.2	1.21	8.8
22.5	120	2.0	1.26	1.4
31.5	120	2.6	1.91	1
37.8	120	1.8	1.89	1.0
49.8	124	1.8	0.96	1.4
61.8	124	2.6	1.39	1.5
91.8	124	3.2	0.68	1.5
106.7	124	1.8	0.77	1.4

Table 7 One minute cross linked PVA-SA mixed feed permeation test

Time (hr)	Pressure (barg)	Volume (ml)	Total permeance $L/(m^2 \cdot h \cdot bar) \times 10^{-3}$	Separation factor
12.0	80	3.5	2.89	4.3
22.5	80	2.9	2.74	1.4
31.5	80	3.6	3.97	1.3
37.8	80	2.2	3.46	1.4
67.8	80	3.0	0.99	1.4
78.1	124	2.4	1.49	1.3

3.2.4 Teflon AF Membranes

Teflon AF is an amorphous glassy perfluoropolymer. This hydrophobic polymer has high fractional free volume (FFV) [31]. There are two Teflon AF polymers commercially available, namely Teflon AF 1600 and Teflon AF 2400, which are produced by DuPont. They differ in the composition of tetrafluoroethylene (TFE) and 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole (BDD) segments [32]. Teflon AF 1600 is composed of 35 mol% of TFE and 65 mol% of BDD, while Teflon AF 2400 consists of 13 mol% of TFE and 87 mol% of BDD. Therefore, they have different FFV's which are 0.33 for Teflon AF 2400 and 0.29 for Teflon AF 1600 [33]. This high free volume is resulted from the combination of two bulky trifluoromethyl substituent groups linked to a dioxole ring, as shown in Figure 13. Teflon AF is a chemically stable polymer; only perfluorinated solvent can dissolve Teflon AF, for example perfluoro-Nmethyl morpholine [C5F11NO] [33].

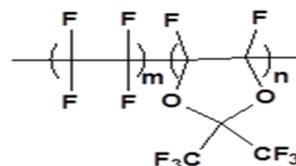


Figure 13 Chemical structure of Teflon AF 2400 [32]

Consequently, a permeation test was performed using a TFC membrane of Teflon AF 2400. It was found that the Teflon AF 2400 is selective to 1-decene with an ideal selectivity of 26 in the pure permeation test. Similarly, in the mixed feed test, the total permeance was $1.1 \times 10^{-2} L/(m^2 \cdot h \cdot bar)$ and the separation factor could reach up to 3, as shown Table 8.

Table 8 Teflon AF 2400 mixed feed permeation test

Time (hr)	Pressure (barg)	Volume (ml)	Total permeance L/(m ² ·h·bar) x 10 ⁻³	Separation factor
8.5	27	2.6	0.90	1.8
21.7	27	4.0	0.89	1.8
26.5	27	1.8	1.10	1.8
30.3	27	1.4	1.10	1.9
46.5	27	5.0	0.91	1.9
52.5	40	3.9	1.30	2.0
54.7	40	1.4	1.30	2.2
57.2	50	2.1	1.30	2.5
60.9	50	2.6	1.10	2.8
66.8	50	4.3	1.20	2.8
73.3	50	4.5	1.10	3.0
76.5	50	2.2	1.10	2.9

For Teflon AF-2400, a different behavior was observed. The separation factor for 1-decene/2-EHA is increasing exponentially with the time, as shown in Figure 14. During the permeation process the 1-decene concentration is increasing in the permeate while it is decreasing in the feed, for dead-end permeation cell, as shown in Figure 15. This could be because of the free volume in AF 2400 is preferentially sorbing 1-decene. Hence, the separation factor is increasing with the time. However, in order to know the steady-state separation factor, a higher volume of the feed is required with sufficient operation time.

The flux of 1-decene/2-EHA through the Teflon AF 2400 membrane is increasing linearly with increasing the feed pressure, as shown in Figure 16. However, the permeance through the membrane gave horizontal lines, to some extent, for 1-decene, 2-EHA and mixture permeance, as shown in Figure 17, 18 and 19. This indicates the stability of the polymer during the operation as it does not get affected with the swelling or compaction.

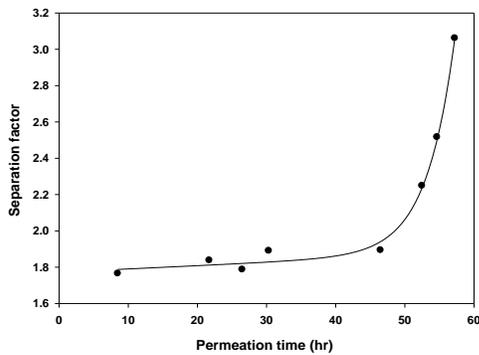


Figure 14 Separation factor for 1-decene/2-EHA through Teflon AF 2400 vs. permeation time (hr)

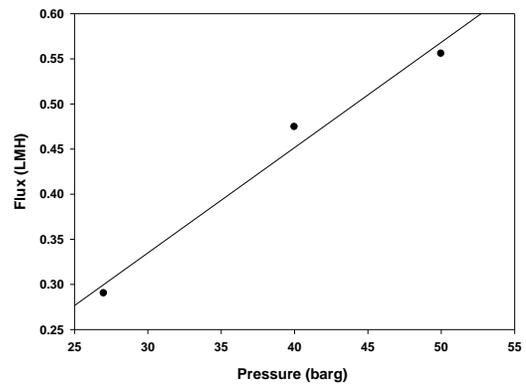


Figure 16 Flux through Teflon AF 2400 vs. Pressure (barg)

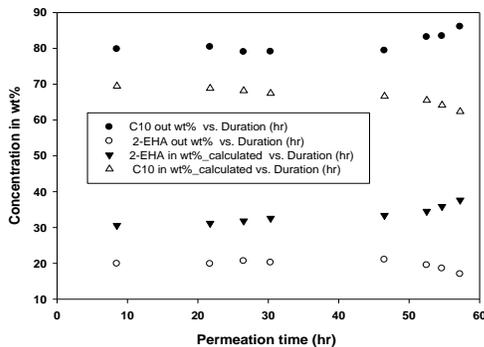


Figure 15 Concentration of 1-decene and 2-EHA through Teflon AF 2400 vs. permeation time (hr)

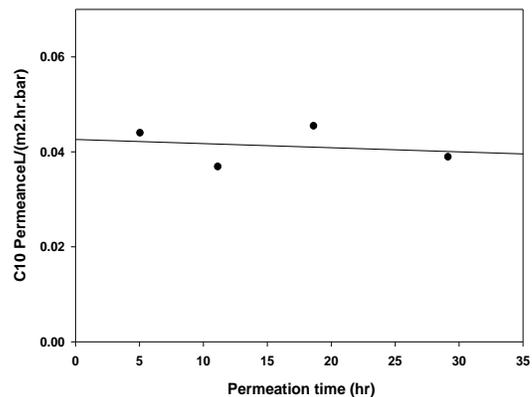


Figure 17 Pure 1-decene permeance through Teflon AF 2400 vs. permeation time (hr)

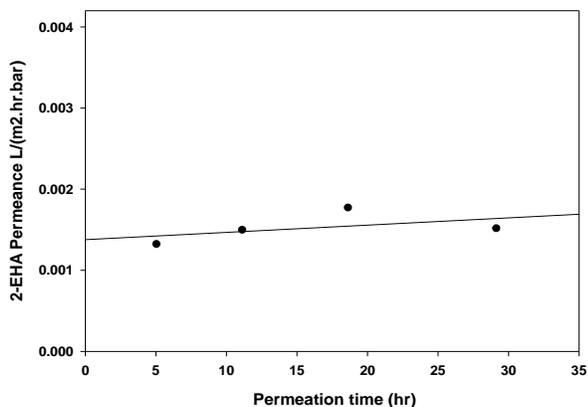


Figure 18 Pure 2-EHA permeance through Teflon AF 2400 vs. permeation time

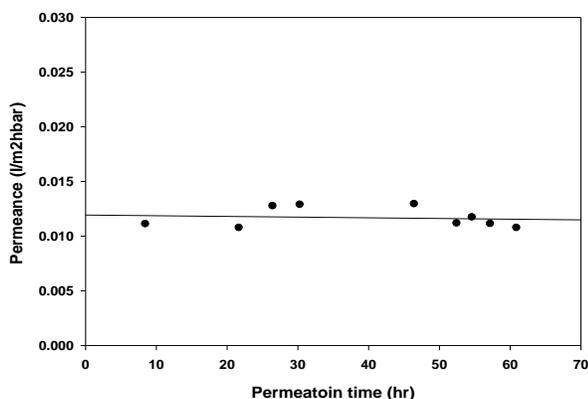


Figure 19 Mixed feed total permeance through Teflon AF 2400 vs. permeation time (hr)

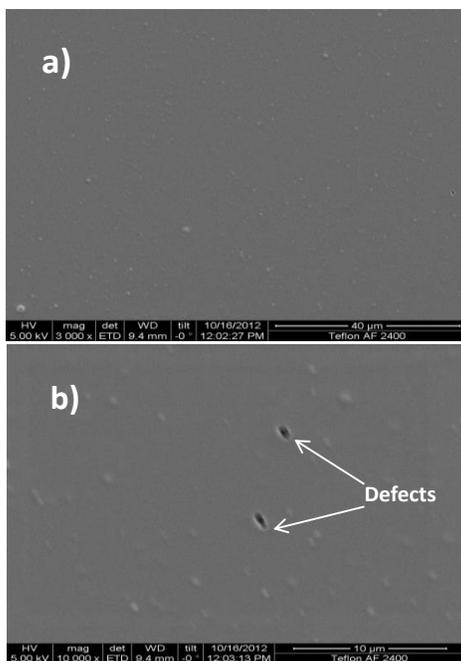


Figure 20 Surface SEM for Teflon AF 2400, a) without defects, b) with defects

Although, Teflon AF 2400 composite membrane showed interesting results for 1-decene/2-EHA separation, SEM images indicate some defects, as evidenced by Figure 20. A proper coating procedure is required for this type of polymer, in order to produce a defect-free membrane. If these defects are eliminated, a better separation factor is expected.

4.0 CONCLUSION

The separation of 2-EHA from 1-decene is very desirable process due to the high costs of compounds. The only proven technology to separate them is by HCl and caustic solvents extraction. Using polymeric membranes for 2-EHA and 1-decene separation is a difficult process because of two main reasons. First, they are almost identical in their physical properties except for the higher polarity of 2-EHA. Second, it is very difficult to find a polymer that can be chemically stable against 2-EHA. Several types of polymers were found to be stable in 2-EHA, namely are PEBAX 1657, Nafion, PVA and SA. These membranes had very high ideal selectivity in the pure component tests. However, these membranes suffered from high degree of swelling. As the polymer becomes highly swollen it exhibits high chain mobility. This causes dilation of the polymer chain which results in loss of diffusivity selectivity. Hence, the real selectivity of mixed feed experiment is significantly reduced. Furthermore, the flux through these nonporous polymers is very low to be applicable in the industry. Therefore, polymers with higher porosity can result better flux and make the process more feasible.

The only two membranes, which could maintain their separation factors for about 100 hours of operation, are Teflon AF-2400 and cellulose acetate. This is because these membranes do not have high degree of swelling with either 2-EHA or 1-decene. The 1-decene/2-EHA separation factor of the AF 2400 membrane was about 3. Similarly, CA NF membranes could give a constant separation factor for 2-EHA/1-decene between 1.7 and 2. However, these separation factors are too low to separate 2-EHA and 1-decene efficiently. Yet, membranes can possibly be used as a debottlenecking step upstream of an existing 1-decene/2-EHA separation unit. Consequently, a cost saving could be attained by reducing the equipment sizes. For that, future work needs to be done in this project to achieve a sustainable process with lower cost that can separate 1-decene from 2-EHA.

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I would like to dedicate the completion of this paper to my parents, for their blessing, love and encouragement. I also like to thank my brothers and sisters and special thanks to my beloved wife.

References

- [1] Belov, G. and P. Matkovsky. 2010. Processes for the Production of Higher Linear α -olefins. *Petroleum Chemistry*. 50(4): 283–289.
- [2] Samsel, E.G. and F.N. Brooks. 2002. Process for Linear Alpha Olefins, Google Patents.
- [3] Forestière, A., H. Olivier-Bourbigou, and L. Saussine. 2009. Oligomerization of Monoolefins by Homogeneous Catalysts Oligomérisation des mono-oléfines par des catalyseurs homogènes.
- [4] Le, Q. N. and J. Shim. 1997. Lubricant Compositions of Polyalphaolefin and Alkylated Aromatic Fluids. Google Patents.

- [5] Darvishmanesh, S., *et al.* 2011. Performance of Nanofiltration Membranes for Solvent Purification in the Oil Industry. *Journal of the American Oil Chemists' Society*. 88(8): 1255–1261.
- [6] Vandezande, P., L. E. M. Gevers, and I. F. J. Vankelecom. 2008. Solvent Resistant Nanofiltration: Separating on a Molecular Level. *Chem. Soc. Rev.* 37(2): 365–405.
- [7] Silva, P., L. Peeva, and A. Livingston. 2008. Nanofiltration in Organic Solvents. *Advanced Membrane Technology and Applications*. 451–467.
- [8] White, L. S. and A. R. Nitsch. 2000. Solvent Recovery from Lube Oil Filtrates with a Polyimide Membrane. *Journal of Membrane Science*. 179(1): 267–274.
- [9] Whu, J., B. Baltzis, and K. Sirkar. 2000. Nanofiltration Studies of Larger Organic Microsolute in Methanol Solutions. *Journal of Membrane Science*. 170(2): 159–172.
- [10] Yang, X., A. Livingston, and L. Freitas dos Santos. 2001. Experimental Observations of Nanofiltration with Organic Solvents. *Journal of Membrane Science*. 190(1): 45–55.
- [11] Peeva, L. G., M. Sairam, and A. G. Livingston. 2010. 2.05-Nanofiltration Operations in Nonaqueous Systems. In *Comprehensive Membrane Science and Engineering*, D. Editor-in-Chief: Enrico and G. Lidietta, Editors. Elsevier: Oxford. 91–113.
- [12] Machado, D. R., D. Hasson, and R. Semiat. 1999. Effect of Solvent Properties on Permeate Flow Through Nanofiltration Membranes. Part I: Investigation of Parameters Affecting Solvent Flux. *Journal of Membrane Science*. 163(1): 93–102.
- [13] Van der Bruggen, B., J. Geens, and C. Vandecasteele. 2002. Fluxes and Rejections for Nanofiltration with Solvent Stable Polymeric Membranes in Water, Ethanol and n-hexane. *Chemical Engineering Science*. 57(13): 2511–2518.
- [14] Sjöman, E., *et al.* 2007. Separation of Xylose from Glucose by Nanofiltration from Concentrated Monosaccharide Solutions. *Journal of Membrane Science*. 292(1): 106–115.
- [15] Boussu, K., *et al.* 2006. Characterization of Commercial Nanofiltration Membranes and Comparison with Self-made Polyethersulfone Membranes. *Desalination*. 191(1): 245–253.
- [16] White, L. S. and C. R. Wildemuth. 2006. Aromatics Enrichment in Refinery Streams Using Hyperfiltration. *Industrial & Engineering Chemistry Research*. 45(26): 9136–9143.
- [17] Scarpello, J., *et al.* 2002. The Separation of Homogeneous Organometallic Catalysts Using Solvent Resistant Nanofiltration. *Journal of Membrane Science*. 203(1): 71–85.
- [18] HP-4750 and HP-4750X data sheets, <http://www.sterlitech.com>.
- [19] Baker, R. 2012. *Membrane Technology and Applications*. Wiley.
- [20] Bondar, V., B. Freeman, and I. Pinnau. 2000. Gas Transport Properties of Poly (ether-b-amide) Segmented Block Copolymers. *Journal of Polymer Science Part B: Polymer Physics*. 38(15): 2051–2062.
- [21] Kim, J. H., S. Y. Ha, and Y. M. Lee. 2001. Gas Permeation of Poly (amide-6-co-ethylene oxide) Copolymer. *Journal of Membrane Science*. 190(2): 179–193.
- [22] Yave, W., A. Car, and K.V. Peinemann. 2010. Nanostructured Membrane Material Designed for Carbon Dioxide Separation. *Journal of Membrane Science*. 350(1): 124–129.
- [23] Le, N. L., Y. Wang, and T. S. Chung. 2011. Pebax/POSS Mixed Matrix Membranes for Ethanol Recovery from Aqueous Solutions Via Pervaporation. *Journal of Membrane Science*. 379(1): 174–183.
- [24] Louie, J. S., *et al.* 2006. Effects of Polyether–polyamide Block Copolymer Coating on Performance and Fouling of Reverse Osmosis Membranes. *Journal of Membrane Science*. 280(1): 762–770.
- [25] Jiang, J. S., D. Greenberg, and J. Fried. 1997. Pervaporation of Methanol from a Triglyme Solution Using a Nafion Membrane: 1. Transport Studies. *Journal of Membrane Science*. 132(2): 255–262.
- [26] Mauritz, K. A. and R. B. Moore. 2004. State of Understanding of Nafion. *Chemical Reviews*. 104(10): 4535–4585.
- [27] Costamagna, P., *et al.* 2002. Nafion[®] 115/zirconium Phosphate Composite Membranes for Operation of PEMFCs above 100°C. *Electrochimica acta*. 47(7): 1023–1033.
- [28] Yeom, C. and K. H. Lee. 1998. Characterization of Sodium Alginate and Poly (Vinyl Alcohol) Blend Membranes in Pervaporation Separation. *Journal of Applied Polymer Science*. 67(5): 949–959.
- [29] Praptowidodo, V. S. 2005. Influence of Swelling on Water Transport through PVA-based Membrane. *Journal of Molecular Structure*. 739(1): 207–212.
- [30] Sanders, E. 1988. Penetrant-induced Plasticization and Gas Permeation in Glassy Polymers. *Journal of Membrane Science*. 37(1): 63–80.
- [31] Pinnau, I. and L.G. Toy. 1996. Gas and Vapor Transport Properties of Amorphous Perfluorinated Copolymer Membranes based on 2, 2-bistrifluoromethyl-4, 5-difluoro-1, 3-dioxole/tetrafluoroethylene. *Journal of Membrane Science*. 109(1): 125–133.
- [32] Bernardo, P., E. Drioli, and G. Golemme. 2009. Membrane Gas Separation: A Review/State of the Art. *Industrial & Engineering Chemistry Research*. 48(10): 4638–4663.
- [33] Zhang, H. and S. Weber. 2012. Teflon AF Materials. *Fluorous Chemistry*. 307–337.