DEHYDRATION OF ALCOHOL SOLUTIONS OBTAINED FROM A SOLVENT RECOVERY PROCESS BY PERVAPORATION

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ABSTRACT

DEHYDRATION OF ALCOHOL SOLUTIONS OBTAINED FROM A SOLVENT RECOVERY PROCESS BY PERVAPORATION

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Solvent recovery is gaining importance in the chemical production processes to reduce the costs and because of environmental concerns. Therefore separation schemes for recovery and recycle of solvents used in printing and packaging industry were developed. However, a low value by-product, mainly ethyl alcohol and isopropanol, is obtained during the solvent recovery process. If the water concentration of this mixture is decreased below 0.1% by weight, the value of it increases significantly. To dehydrate this stream, a pervaporation-adsorption separation scheme is developed in this study.

The effect of pervaporation process parameters, such as temperature, feed flow rate, permeate side pressure, feed water and ethyl acetate concentration, on the performance of the PERVAP 2211 and 2201 membranes of Sulzer Chem-tech® using the real industrial by-product solution obtained from a local company are investigated. Pervaporation tests were conducted using a home made experimental setup equipped with 148 cm^2 rectangular shaped membrane module. Permeates obtained from these experiments were analyzed using a gas chromatograph equipped with FID and the water concentration of the feed solutions were analyzed using Karl-Fisher titration. Besides, adsorption studies were conducted using zeolite 3A in a fixed bed column.

As a result of this study, PERVAP 2201 membranes showed higher fluxes with a slightly lower permeate water concentration compared to PERVAP 2211 at the at ranges studied. The increase in the pervaporation performance was observed with an increase in the temperature, permeate side vacuum and feed flow rate over the membrane. Therefore, concentrated-mode experiments were conducted at 70°C, 2 torr permeate side pressure and 1.6 L/min of feed flow rate using the findings of the parametric studies and the retentate of this experiments were further dehydrated using liquid phase adsorption. Finally, the water concentration of the solution was decreased to 0.04% by weight.

Keywords: *Pervaporation, Adsorption, Solvent Dehydration, PERVAP 2211, PERVAP 2201*

ÖZ

ÇÖZÜCÜ GERİ KAZANIM SÜRECİNDE ELDE EDİLEN ALKOL ÇÖZELTİLERİNİN PERVAPORASYON YÖNTEMİ İLE SUSUZLAŞTIRILMASI

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Kimyasal üretim süreçlerinde ürün maliyetini düşürmek, çevreye zarar vermemek amacıyla çözücü geri kazanımı önem kazanmaktadır. Bu sebepten, baskı ve ambalaj sanayiinde kullanılan çözücülerin geri kazanımı ve tekrar kullanımını amacıyla yeni süreçler geliştirilmiştir. Ancak, çözücü geri kazanımı sırasında temel olarak etil alkol ve izopropil alkol içeren düşük değerde bir yan ürün elde edilmektedir. Bu yan ürünün değeri su miktarının kütlece %0.1'in altına düşürülmesi ile belirgin bir miktarda artacaktır. Bu çalışmada, bu ürünün susuzlaştırılması amacıyla pervaporasyon-adsorpsiyon ayırma şeması geliştirilmiştir.

Sıcaklık, besleme çözeltisi akısı, süzüntü tarafı basıncı, besleme çözeltisi su ve etil asetat miktarı gibi pervaporasyon parametrelerinin Sulzer Chemtech® firmasının üretimi olan PERVAP 2211 ve 2201 membranlarına etkisi yerel bir sanayiden elde edilen yan ürün kullanarak incelenmiştir. Pervaporasyon deneyleri 148 cm^2 membran alanına sahip bir membran modülü kullanılarak yapılmıştır. Deneylerde elde edilen süzüntü numuneleri FID donanımlı bir gaz kromatografisi ile, besleme çözeltisi su miktarı ise Karl Fischer titrasyonu analiz yöntemleri ile yapılmıştır. Adsorpsiyon deneyleri ise zeolit 3A dolgulu yatak kullanılarak yapılmıştır.

Bu çalışma sonucunda, PERVAP 2201 membranları kullanılarak PERVAP 2211 membranlarına göre incelenen paramatreler aralığında daha yüksek akı ve hafifçe daha düşük süzüntü su konsantrasyonu elde edilmiştir. Sıcaklık, süzüntü vakumu, besleme çözeltisi akış hızı gibi parametrelerin artışının pervaporasyon performansını artırdığı gözlemlenmiştir. Buna bağlı olarak, parametrik çalışma bulguları kullanılarak 70°C, 2 torr süzüntü basıncı ve 1.6 L/dakika besleme çözeltisi akış hızında konsantre modunda deneyler yapılmış ve elde edilen süzüntü sıvı faz adsorpsiyonu yöntemi ile susuzlaştırılmıştır. Sonuç olarak, çözelti su konsantrasyonu kütlece %0.04’e düşürülmüştür.

Anahtar sözcükler: *Pervaporasyon, Adsorpsiyon, Çözücü Susuzlaştırılması, PERVAP 2211, PERVAP 2201*

To my beloved family

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LIST OF SYMBOLS AND ABBREVIATIONS

Symbols

A	Area, m^2
J	Flux, g/m^2h
m	mass, g
t	Time, h
x	Mass Fraction in feed
y	Mass fraction in permeate

Abbreviations

EtOH	ethanol
EtOAc	ethyl acetate
IPA	isopropanol
THF	tetrahydrofuran

Greek Letters

α	Selectivity

Subscripts

a	alcohol
i	component ‘i’
j	component ‘j’
m	membrane
o	others
p	permeate
w	water

CHAPTER 1

INTRODUCTION

Recycling of the solvents is an important issue in chemical industry when low product cost is desired and also environmental concerns are considered.[1] Recovery of the solvents after use could be difficult since they could be contaminated with additional chemicals during either production or recovery processes and these impurities in solvents may decrease the product quality. Separation schemes must be developed for recovery and purification of these solvents in order to decrease the product cost and to be competitive in the market.[2] This is also the case in the solvent recovery of the packaging and printing industry.

In the packaging and printing industry, solvents are used to dilute and set the viscosity of the ink for further printing applications. These solvents are then separated from the package using steam after application (Figure 1.1). Therefore, water is mixed with the solvents. This mixture, containing mainly ethanol, isopropanol, water, ethyl acetate, and some other minor components are then sent to the recycling unit of the printing and packaging plant where it is dehydrated, fractionated and purified for reuse by employing conventional separation units such as adsorption and distillation.

In a local plant, the solvents and the water are separated from the stream using adsorption columns and the mixture obtained is then fed to the distillation unit composed of three distillation columns as illustrated in Figure 1.2. The bottoms products of the first two distillation columns are recycled directly to the process. But, a 300 tons/year by-product stream obtained from the bottoms stream of the third distillation column is sold at a very low value because of its water content. The value of this stream can significantly be increased if the water content is decreased below 0.1% by weight.

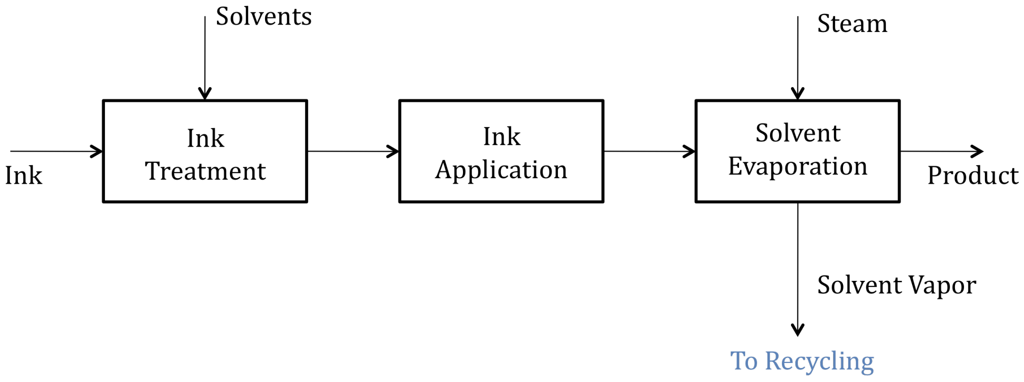


Figure 1.1. Ink application process in the packaging and printing plant

Solvent dehydration can be carried out with several different processes such as adsorption, distillation, pervaporation, extraction etc.[3-5] Each of these processes find use in the industry depending on the properties of the chemicals, concentrations of the solutions and the target chemical purity needed. Therefore, each of them is preferred depending on the expectation from the separation. To overcome the desired aim of separation, combination of these techniques with each other may be required rather than using single separation technique. Pervaporation has advantages, such as, low energy requirement, process continuity, easy scale up, no product contamination during separation as a result of additional components, no emissions and easy mounting to the current process over these processes as high solvent purity is desired.[4-9] It is an emerging technology in the industry when high chemical purity is required.[5,10-12] In addition, it is a useful method for the separation of azeotropic mixtures where traditional methods become insufficient because of the vapor-liquid equilibrium limitations.[13] About one hundred pervaporation plants were operating worldwide where four-fifths of these were used for the dehydration of the mixtures of ethanol and isopropanol with water. [10]

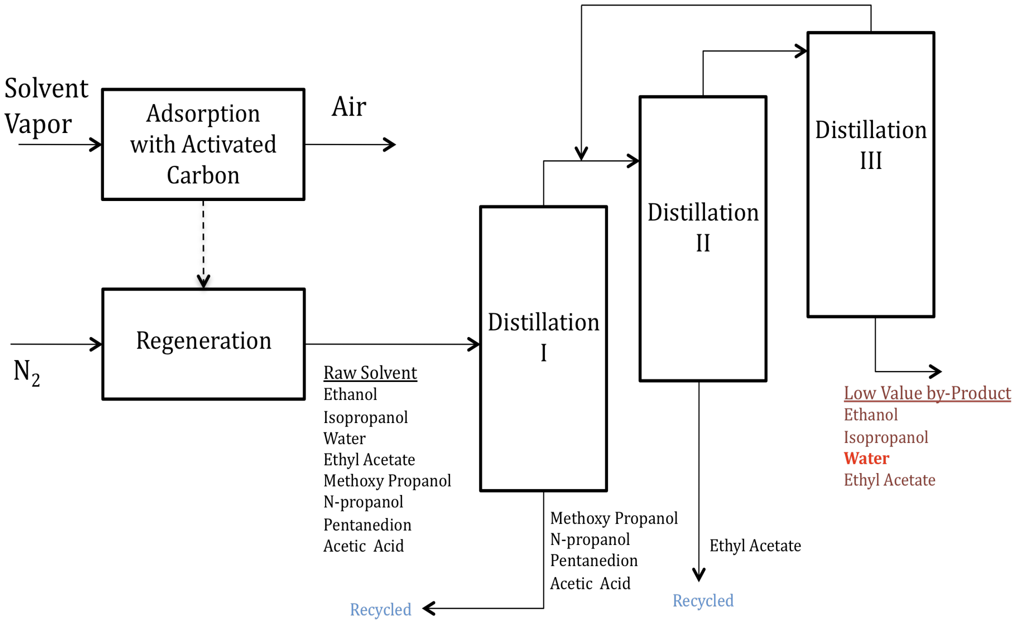


Figure 1.2. Solvent recovery process in the packaging and printing plant

Pervaporation is a membrane separation process where one or more of the components of the liquid feed are separated from the solution in vapor phase. The driving force of the mass transfer through the membrane is the chemical potential gradient across the membrane that is created using vacuum or inert purge gas.

There is a membrane in contact with the liquid feed in pervaporation. The separation of the desired components of the membrane starts with the selective sorption of the components from the feed solution, continues with the diffusion of these components through the membrane and finalizes with the evaporation from the permeate.[3,6,7] Based on the objective of separation, either permeated components (permeate) or the enriched feed solution (retentate) can be the valuable product of separation. Retentate will be the product in the dehydration of the solvents obtained from printing and packaging plant, and the water-rich permeate stream will be discarded without need of condensation.

Pervaporation is an advantageous method in the separation of the minor components from the liquid mixtures, especially for the dehydration of the solvents. Therefore, energy consumption is decreased when compared to the distillation process because only minor component of the solution consumes the latent heat. Additionally, it is also more feasible than the adsorption processes for the dehydration of the solutions containing minor amount of water that is costly using a single stage adsorption process.[7] The performance of separation is affected from the process parameters like temperature, feed flow rate, permeate side pressure and the feed components and the concentration. Therefore, detailed analysis on the effect of process parameters on the performance of the membrane should be conducted to run pervaporation more effectively.

The applicability of pervaporation to the dehydration of the industrial by-product solution obtained from a local packaging and printing company were investigated in this work. The effects of process parameters like feed flow rate, temperature, feed water and ethyl acetate content and permeate side pressure on the performance of hydrophilic PERVAP 2211 and PERVAP 2201 membranes of Sulzer Chem-tech® for the dehydration of the solvent mixtures containing mainly ethanol, isopropanol, water and ethyl acetate were investigated. The aim is to decrease the water content to 0.1% by weight in the retentate. To achieve this objective, pervaporation coupled with adsorption was considered to be useful for this dehydration purpose.

CHAPTER 2

LITERATURE SURVEY

2.1. Pervaporation

Pervaporation is a membrane separation technique that is used to separate liquid mixtures. The name “pervaporation” was derived from the combination of the words “permeation” and “evaporation” because the feed is in liquid phase and the molecules leave the membrane in vapor phase. The term was firstly used by Kober (1917) while introducing his work on permeation of water from aqueous solutions of albumin and toluene through collodion films. [6] However, it was 1956 that Heisler et. al. published the first quantitative work on pervaporation for the separation of ethanol/water solutions. Then, Binning et. al. were the researchers that highlighted the potential of pervaporation in the years 1958 - 1962. But, pervaporation was first commercialized about early 1980s for the separation of ethanol/water solutions just after Gesellschaft für Trenntechnic Co. developed the first commercial pervaporation membrane. After this breakthrough in pervaporation, there are numerous pervaporation plants that are installed in the world that counts about one hundred by the year 2001. [10]

Pervaporation is the only membrane separation technique where phase change occurs during separation. It uses the energy cleverly by evaporating only the permeated part of the solution. Therefore, the energy consumption is lower when preferentially permeating components are the minor one in the feed solution. In all cases, pervaporation uses energy more economically than the conventional distillation processes.

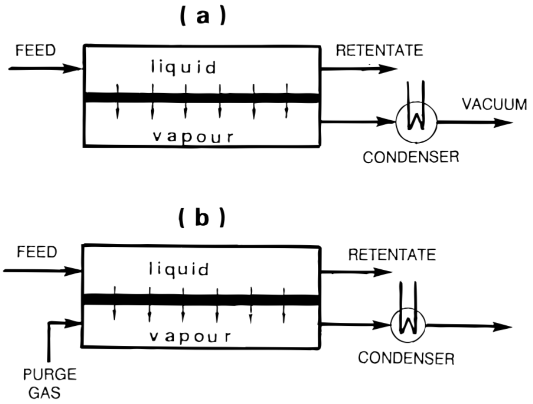


Figure 2.1. Schematic representation of the membrane pervaporation. (a) Vacuum pervaporation (b) Purge Gas Pervaporation [6]

In pervaporation process, membrane is in contact with the liquid feed and selectively permeates one or more of the components in the feed mixture. Molecules diffuse through the membrane with the presence of the potential gradient that is created by decreasing the chemical potential at the permeate side either by applying vacuum or by flowing purge gas from the permeate side. (Figure 2.1) The mass transport through non-porous membranes can best be described using solution-diffusion theory. According to this theory, the separation of the components of the feed components starts with the selective sorption of the components in the membrane matrix, continues with the selective diffusion through the membrane and finalizes with the desorption from the other side of the membrane. The type of the membrane determines which component is to be separated from the solution.[6] The selectivity of the membrane is higher if the selectively permeated components exist in small amounts in the feed solution. Otherwise, higher concentrations in the feed solution lead to excessive swelling of the membrane which decreases selectivity.

Pervaporation has advantages over the traditional separation methods when it is employed to separate azeotropic and close-boiling mixtures.[3,6,7] Since the separation of the components from the solution is independent from the vapor-liquid equilibrium in pervaporation, it is especially becoming a useful method in breaking the azeotrope of the solutions. Several possible candidates for the application of the pervaporation on mixtures are illustrated on Table 2.1.

Table 2.1. Azeotropic points of some mixtures [2,13]

Chemical	**Azeotrope Point** (wt%)
Ethanol/Water	95.6/4.4
Isopropanol/Water	87.8/12.2
n-Propanol/Water	71.7/28.3
2-Butanol/Water	73.2/26.8
n-Butanol/Water	57.5/42.5
t-Butanol/Water	81.1/11.8
Tetrahydrofuran/Water	94.1/5.9
Methanol/Acetone	12.0/88.0
Ethanol/Hexane	21.0/79.0
n-propanol/Cyclohexane	20.0/80.0

Pervaporation is a promising method having potential applications in the chemical industry.[5] The three types of application areas of pervaporation which are classified based on target minor component which will be selectively permeated, and some examples corresponding to these areas are listed in Table 2.2[4]. Solvent dehydration is the most developed area of pervaporation among these applications. About four-fifths of the pervaporation plants operating worldwide are used for dehydration purposes.[10] Although considerable research were conducted for dehydrations of the solvents such as THF, acetone, MEK etc., pervaporative dehydration is mostly concentrated on the separation of ethanol/water and isopropanol/water solutions as high purity is required for use as biofuel for the former and for pharmaceutical use for the latter. [2] Because, both ethanol and isopropanol forms azeotrope with water at the concentrations indicated in Table 2.1. Therefore, development of new methods for dehydration is important as the traditional methods for dehydration is insufficient to reach high purity or not suitable because mixing of additional components to the solution is inevitable that causes further problems with the purity of these chemicals.

Table 2.2. Application Areas of Pervaporation [4]

Application Area	Membrane	Examples
Dehydration of Organic Solvent	Hydrophilic	Dehydration of Ethanol, Isopropanol, Acetone, Acetic Acid, THF, MEK etc.
Removal of Organics from Aqueous Solutions	Hydrophobic	VOC removal from water, Separation of Biofuels from Fermentation Broths
Separation of Organic-Organic Solutions	Organophilic	Separation MTBE/Methanol, DMC/Methanol

Hydrophobic membranes are employed for the removal of organics in minor amounts from water that is important for the health and environmental concerns as the allowed discharge levels of the VOCs are getting lower everyday. [4] Some important components that are required to be removed from water include carbon tetrachloride, methyl t-butyl ether, etc. Removal of these materials can be accomplished also with other methods like air stripping, steam stripping, biological treatment, but most of them can generate secondary wastes that is also not desired because of the environmental and economical concerns. [4] Hydrophobic pervaporation is also an emerging membrane process in the separation of fermentation products such as ethanol from the fermentation broths.[14] With direct removal of product from the fermentation broths, the product inhibition effect can be reduced leading to higher productivity of the microorganisms.

Organic-organic separation with pervaporation is the most challenging application. But, it is gaining great importance in the chemical industry.[15] Although there are many membranes developed for the separation of polar/non-polar mixtures, aromatic/alicyclic mixtures, aromatic/aliphatic mixtures, aromatic isomers in the literature using organic and inorganic materials, applications of these membranes are limited because of the low performances of the organophilic membranes. [16]

2.2. Performance Criteria of Pervaporation

Performance of the membranes in pervaporation is generally reported as flux and selectivity. Flux is defined as the amount of material collected in unit time per unit area of a membrane and calculated using the formula,

$$J = \frac{m_p}{A.t} \qquad (2.1)$$

where m_p is the mass of permeate obtained in time t and from an active membrane transfer area of A.

Selectivity represents the ability of the membrane to separate the components from the feed solution and selectivity of the component i to the others is calculated using the formula,

$$\alpha_{i0} = \frac{y_i / (1 - y_i)}{x_i / (1 - x_i)} \tag{2.2}$$

where y_i is the mass fraction of the component i in the permeate whereas x_i is the mass fraction of the component i in the feed solution.

For a specific membrane, these performance parameters may depend strongly on the operation parameters such as temperature and feed concentration.[17] Besides, concentration of each component, especially the selective species of the membrane, in the feed solution affect the separation performance strongly, as well as the type of the chemicals included in the solution.

2.3. Effect of Membrane Type on Pervaporation

Pervaporation membranes can be classified according to the materials of construction. Inorganic and organic materials can be used to prepare membranes.[2,3,7,15] The selection of these can be made determining the properties and the components of the feed solution to be used. For instance, chemically and thermally stable membranes can be synthesized using zeolites and ceramics.[3,15] Zeolitic membranes are porous that have uniform, well-defined pores that create different transport rates for different species.[3] Similarly, ceramic membranes also have molecular-sized pores but have wider pore size distribution than zeolitic membranes.[15,18] Both inorganic membranes offer high permeability and selectivity when compared to the polymeric membranes in addition to their non-swollen behavior.[3,7,13,15,18,19] There are several studies published in the literature reporting high flux and high selectivity towards water using inorganic membranes for the dehydration of alcohols.[12,18-20] However, these membranes are more expensive and brittle than the polymeric membranes that limits their applications to laboratory use and only to specific purposes where polymeric membranes fail during operation.[3,19]

There is wide range of polymeric materials used to synthesize membranes for the removal of water from the solvent mixtures.[2] Polymeric membranes are cheaper to fabricate compared to the inorganic membranes. In addition, polymeric membranes could be used in different types of modules, such as, plate and frame, hollow fiber, spiral wound etc. that lead to higher membrane surface area to volume ratio than the modules used for the zeolitic membranes because of their flexible structure.[15,16]. However, polymeric membranes may suffer in selectivity at higher concentrations of the selectively permeated components in the feed solution.[7,13,15] Polymeric membranes swell as the concentration of the selectively permeated components in the feed is increased therefore creating additional routes for the larger molecules to diffuse through. However, the swelling of the membranes are minimized by cross-linking and additional increase in the selectivity of the membranes were observed for the composite membranes.[15]

Incorporating the inorganic materials into polymer matrix may lead to an improvement in the performance of the membranes. Increase in only flux without an effect on selectivity, increase in selectivity without an effect on flux and increase in both flux and selectivity were observed after the synthesis of the composite membranes.[15] However, these membranes were synthesized and tested at lab scale and are lacking in the application at industrial scale because of their difficult fabrication. They are synthesized unsupported at lab scale and synthesis at larger scale on a support for industrial application is costly when compared to the polymeric membranes currently.

In addition to the membranes synthesized and tested in the laboratory, there are various types of polymeric dehydration membranes commercialized by Sulzer Chem-tech® and Celfa Membrantechnic® where the products of Sulzer® are illustrated in Appendix A. Successful separations using these commercial membranes were observed in the literature. [21-34]

Selection of membrane type in pervaporation is an important decision. It should be selected while taking into account the components of the feed solution and operating conditions of the pervaporation process. Separation performance of the membrane and effect of operating conditions on the performance is strongly dependent on the structure of the membrane.

A study conducted by Qiao and his co-workers [21] illustrates how the two membranes PERVAP 2510 and PERVAP 2201 having different degree of cross-linking are affected by the changes in operation parameters. PERVAP 2201 membrane is more cross-linked than PERVAP 2510 and PERVAP 2510 has a lower contact angle than PERVAP 2201. PERVAP 2201 showed higher selectivities than PERVAP 2510 as a result of its higher cross-linking. Besides, the dependency of its flux and selectivity on temperature is more significant than PERVAP 2510 resulting from the loosened structure of the polymer with increasing temperature and the increase in the frequency of the diffusion jumps. The activation energies for water permeation across the membranes are 43.6 and 62.7 kJ/mol for PERVAP 2510 and PERVAP 2201, respectively. On the other hand, higher hydrophilicity and more freedom of the polymer chains in membrane matrix lead to a decrease in the ease of the passage of the molecules through the membrane. Therefore, the water flux through PERVAP 2510 is higher compared to PERVAP 2201 at the same process conditions and feed water concentrations. In addition, water flux of

PERVAP 2510 membrane increases more rapidly than PERVAP 2201 when the feed water concentration is increased.

Another study on the comparison of the commercial membranes was conducted by Atra et. al.[8] Comparison of the membranes CMC-CA-01, CMC-CE-01 and CMC-CE-02 of Celfa Membrantechnic® was studied on the dehydration of isopropanol/water mixtures. Variation of operating parameters such as temperature and feed concentration affected membrane performances similarly. It was found that, although each membrane showed potential for the dehydration of isopropanol, CE-01 membrane showed higher performance due to its higher PSI, which is the product of flux and selectivity, compared to the other membranes under investigation.

Van Hoof et. al. [22] are one of the groups that compared performances of zeolitic and polymeric membranes. The NaA type zeolitic membrane produced by Mitsui® and polymeric membranes PERVAP 2510 and CMC-VS-11V produced by Sulzer Chem-tech® and Celfa Membrantechnic®, respectively, for the dehydration of isopropanol was studied. As a result of this study, Celfa membranes showed higher fluxes for the feed water concentrations over 6 wt% although flux through each membrane increases with increasing water concentration of feed, zeolitic membrane showed higher fluxes below that concentration. On the other hand, the selectivity of zeolitic membrane is the highest for all concentration range where polymeric membranes showed comparable selectivities for relatively high feed water concentrations. As a result of this study, it was recommended that it is advantageous to use Celfa membranes if the purpose of dehydration is only to break the azeotrope. But, zeolitic membrane would be preferred if it is needed to dehydrate the mixture up to very low water concentration.

Another research group, McGinness et. al. [23] made comparison between Pervatech® silica membranes and PERVAP 2210 polymeric membranes for the dehydration of 95-5% THF-water mixture by weight. It was found that the trends of total flux vs. temperature graphs were similar for both membranes. Total flux through PERVAP 2210 membrane increased from 0.09 to 0.24 kg/m^{2}h whereas it increased from 0.21 to 0.67 kg/m^{2}h for Pervatech Silica membrane when the operation temperature is increased from 40 to 60°C. On the other hand, THF flux remained unchanged at 0.01 kg/m^{2}h in this temperature interval for PERVAP 2210 while from 0.0064 to 0.033 kg/m^{2}h was observed for Pervatech® Silica membranes as the temperature is increased from 20 to 60°C. In addition, the selectivities of each membrane increased with increasing temperature.

The dehydration performance of pervaporation depends significantly on the membranes used in the process. There are several different commercial membranes for the removal of water from solvents that give satisfactory results for different feed solutions. However, the performance of the membranes depends strongly on the operating conditions and the feed composition. Therefore, parametric studies should be conducted in order to design an effective pervaporation process for a specific feed solution.

2.4. Effect of Process Parameters on Pervaporation

Membrane performance depends on the parameters like operating temperature, permeate side pressure, feed flow rate and feed composition. Changes in these parameters alters the performance of the membrane resulting from the increase or decrease in the ease of transport of molecules through the membrane. The transport rate of the species through the membrane is affected from the changes in,

- Activity of the components in the feed
- Solubility of the feed components in membrane matrix
- Diffusivity of the components in membrane matrix
- Vapor pressure of the components in permeate side

Changes in each of the process parameters affect the pervaporation performance of a membrane. For instance, increasing the feed concentration could increase activity of the components in the feed. Solubilities and diffusivities of these components increase with temperature. In addition, applying higher vacuum to the permeate side decrease the partial pressures of the components in the permeate side therefore affecting the performance of the membrane. To observe the reaction of the membranes to the changes in the process parameters, several studies were conducted in the literature using commercial membranes.[20-33]

Generally, fluxes through the membranes are more sensitive to temperature change than the selectivity. Flux increases exponentially with temperature whereas selectivity may increase, decrease or remain constant depending on the behavior or the interactions between the components and membrane with temperature.[21,23,34] Flux increases with temperature exponentially because both solubility and diffusivity of the components in the membrane is affected by temperature. The combination of the increases in both solubility and diffusivity leads to an exponential increase of flux with temperature. On the other hand, the selectivity towards a component is affected by the individual sorption and diffusion in the membrane as well as the coupling effects occurring during the multicomponent transport through the membrane.[13] Therefore, the selectivity must be experimentally determined for each system.

The linear feed water concentration dependency of the flux is commonly observed on the dehydration membranes, as the driving force for mass transfer is linearly dependent on the activities of the species across the membrane. But, the permeate water concentration increases with feed water concentration at low feed water concentrations and is not affected by the feed water concentration change at higher feed water concentrations.[20,22,24-25] At high feed water concentrations, the driving force for water is dominant, therefore the permeate water concentration is the highest and practically is independent of feed water concentration. But at lower feed concentrations the transport components other than water come significant and decrease the permeate water concentration at lower feed water concentrations.[21]

The effect of permeate side pressure is not attracted much attention in the literature but may play significant role in the performance of the membranes. In some studies, the effect of permeate side pressure on dehydration performance was studied and strong dependency of permeate side pressure on flux and selectivity was observed. [23,35] Since it directly affects the driving force of mass transport, the decrease in total flux is inevitable with increasing permeate side pressure. In addition, the decrease in the selectivity of water with the increase in permeate side pressure may be attributed to the increase in the swelling of the membrane with permeate side pressure.[35] As the partial pressure of the components in the permeate side is increased, sorption of the components in the membrane increases therefore leading to more swelling of the membrane.

Hydrodynamic condition of the feed mixture over the membrane is important to run pervaporation more effectively because concentration polarization effects may come into significance at low feed flow rates. The flow of the liquid over the membrane should be in such a condition that the mass transfer resistance in the liquid phase is reduced.[36] This effect must be investigated experimentally.[26]

Pervaporation literature consists of some parametric studies on the dehydration using commercial hydrophilic membranes but large portion of the studies were conducted using synthetic binary feed solutions. For instance, Cséfalvay et. al.[24] illustrated that linear dependency of the flux to feed water concentration during permeation through PERVAP 2210 membranes were observed for the dehydration of IPA/Water mixtures.

When feed water concentration is above 10% by weight, the permeate concentration becomes constant at about 96% by weight at different temperatures. On the other hand, water concentration in permeate starts to decrease with feed water content, for low feed water concentrations, which is more drastic for operation at lower temperatures, i.e. permeate water concentration decreases to 40% and 80% at 2% feed water content at operation at 60°C and 80°C, respectively. In addition, the slope of the flux vs. feed water concentration graph increases as the operation temperature is increased.

An exponential increase in flux through the membrane is observed with respect to operation temperature by McGinness et. al.[23] They illustrated that for the separation of THF-Water mixtures at concentration of 95% THF by weight using PERVAP 2210, flux increased from 0.085 to 0.235 g/m^2h and permeate water concentration increases from 87% to 94% when operation temperature was increased from 40 to 60°C. This increase in selectivity of the membrane towards water was regarded as the result of the different dependency of the partial pressures of the components in the feed towards operation temperature.[23]

McGinness and his co-workers also observed a decrease in both total flux and selectivity with an increase in the downstream pressure. They related the decrease in total flux to the decrease in the driving force through the membrane.[23] Similarly, Okumuş et. al. [35] observed a decrease in total flux with increasing permeate side pressures in addition to a decrease in the selectivity from 256 to 143 with an increase in the permeate side pressure from 0.77 to 13.20 torr for the dehydration of the ethanol/water solution at 25 wt% by weight using homogenous PAN membranes. This decrease in selectivity with permeate side pressure was attributed to the increase in the swelling of the membrane.

Each process parameters of pervaporation was shown to affect the performance of pervaporation highly and detailed analysis on how membranes affect the performance analysis should be conducted before designing a pervaporation unit. Pervaporation literature consists of several works conducted on the dehydration of the solvents; each reported the influence of some of the process parameters on the performance of the commercial membranes. But the behavior of the membrane for the changes in each of the parameters affecting the performance should be known before designing a pervaporation system for a specific separation.

2.5. Effect of Feed Components on Pervaporation

The studies conducted for the dehydration using pervaporation can be classified as dehydration of binary and multicomponent feed mixtures. Being mostly binary solutions, feed solutions were generally prepared synthetically whereas some studies were also reported on the dehydration of the industrial feed mixtures. The components of the feed solution may play an important role in the separation behavior of the membrane in pervaporation. This effect results not only from the changes in the interaction of each component with the membrane but also from the interactions of components with each other in feed and in permeate.

The effect of the components on the performance of membrane is illustrated in a work conducted by van Baelen et. al. [27] They measured the flux and selectivity values of PERVAP 2201 membranes during the dehydration of binary solutions of methanol, ethanol and isopropanol with water at different feed water concentrations. The highest fluxes and the strongest dependency of flux on feed concentration were observed during methanol dehydration with PERVAP 2201. Methanol permeation increased linearly with methanol concentration in feed whereas the permeations of the other alcohols decrease with the concentrations of these alcohols in feed. The separation of methanol is governed by the sorption of the feed components to the membrane. But, ethanol and isopropanol fluxes are governed by the permeation of water through the membrane. This is explained using two theories by van Baelen et. al. First one is the permeation of alcohol molecules as solutions with the small pools of water molecules whereas the second theory is the formation of a superstructure of water with ethanol creating a new structure having enough polarity that permits transport through the membrane.[27]

When water selectivities are compared, a decreasing trend is observed for each solution having concentration above 20% water by weight as a result of swelling. But the trend is different of the methanol/water solution due to competition between methanol and water at low concentrations. Water molecules have higher tendency to be sorbed by membrane even at low concentration in ethanol and isopropanol. But, it is comparable with methanol at low water concentrations. Therefore, selectivity starts to decay as the water concentration in the feed is reduced from 20% by weight. But, that is not the case for the dehydration of ethanol and isopropanol. Membrane shows high selectivity to water even at low feed water concentrations.

Existence of additional components in the feed solutions may have significant effects on the pervaporation performance of the membranes even if they are in minor amounts. Van Baelen et. al.[28] studied on the dehydration of water/ethanol/methanol mixture using PERVAP 2201 membranes. They observed that, the partial water flux of the ternary mixtures is comparable with the ethanol/water dehydration whereas it is lower than that of methanol/water separation. Additionally, competition between water and methanol molecules occurs when the water activity is low and methanol activity is high in the feed for ternary mixtures.

The presence of ethanol in the solution also affected the separation performance of the membrane. For instance, keeping the activity of methanol in the solution at 0.3, addition of 5% of ethanol to the feed solution increased the methanol separation factor from 4 to 25. This effect is described by the increase in the polarity of the feed solution with the addition of ethanol to the solution. [28]

Another study to understand the effects of the feed components on pervaporation performance was carried out by Delgado and his co-workers [29]. They studied the effects of the chemicals that are present in the esterification of lactic acid with ethanol on dehydration using PERVAP 2201 membranes. Comparison between the dehydration performance of PERVAP 2201 for water/ethanol, water/ethyl lactate and water/lactic acid mixtures showed that the total flux depends strictly on the degree of swelling of the membrane at same process conditions and same water concentration in feed.

A step to understand the behavior of the performance of PERVAP 2201 during the dehydration of multicomponent mixtures, Delgado et. al. published study that reported the performance of the membrane for the removal of water from water/ethanol/ethyl lactate/lactic acid mixture. [30] As it was expected from the binary experiments, membrane showed comparable fluxes for the quaternary mixture with binary feed solutions. Furthermore, higher selectivities were obtained with the quaternary feed solutions. In addition, no effects on the membrane performance were obtained for a change in the feed lactic acid content although it is the component that caused most swelling to the membrane in binary mixtures.[29]

As a result of these researches published in the literature, the behavior of the membrane differs for the dehydration of the binary and multicomponent mixtures. The components may act different in multicomponent mixtures than the binary mixtures and the effect of the component to the separation may sometimes be difficult to predict by observing its behavior in binary separations.

2.6. Industrial Applications of Pervaporation and Pervaporation Based Hybrid Processes

Studies of Urtiaga et. al. illustrated that applying pervaporation for the following purposes could be a useful alternative to the current processes, [31]

- Separation of a waste ketonic mixture (acetone/water) into two streams, one is the concentrated ketone retentate whereas the other is the aqueous permeate solution that can further be treated,
- Dehydration of aqueous tetrahydrofuran solutions for recycling,
- Dehydration of isopropanol solutions obtained from pharmaceutical effluents for further usage,
- Dehydration of cyclohexane solutions for recycling back to synthetic rubber production unit.

CMC-CF-23 membranes produced by Celfa Membrantechnic® was used in the study of the dehydration of the pharmaceutical waste streams. Although the original waste stream is composed of 76.65% water, 17.0% IPA, 3.45% HCl and 2.9% NaCl by weight, the solution is pretreated before pervaporation using neutralization and distillation. The IPA enriched solution obtained was then sent to pervaporation and dehydrated successfully.

It took about 24 hours to decrease the water content of 2L of the distillate containing 35% water by weight to 0.3% water at operation temperature of 80°C, permeate side pressure of below 15 mbar using 145 cm^2 of membrane. Therefore, they claimed that, the dehydration of the pharmaceutical waste streams could successfully be achieved by employing neutralization, batch distillation and pervaporation process in series. [32] But detailed optimization of the process was not carried out. Two temperatures 50°C and 80°C were selected and it was observed that higher temperature operation is favorable both considering flux and selectivity.

Zeolitic membranes were used for the dehydration of the aqueous solutions of THF and acetone because of the higher chemical, mechanical and thermal stability than the polymeric membranes. 2L of each solution was dehydrated using NaA membranes produced by SMART Chemical Company LTD, UK. Water content of acetone was decreased to 0.2 wt% from 3.25 wt% at 48 °C in about 300 mins whereas THF was dried below 0.1 wt% water from 7.9 wt% initial water concentration in about 400 mins at 55°C and permeate side pressure of below 10 mbar. Therefore, the use of pervaporation for the removal of water from these solutions was found suitable. [33]

Although pervaporation is a promising separation alternative for the separation of the minor components from solutions as a stand alone process, it may also be an advantageous technique to use it as in combination with the traditional separation methods. Especially for the mixtures that are difficult to separate with the traditional methods, e.g. azeotropic or close boiling point mixtures, combination of pervaporation with traditional separation method is advantageous considering its lower cost and higher performance.

There are several different process designs for the combination of distillation with pervaporation is proposed in the literature. Sommer and Melin classified the hybrid process schemes and listed some use areas of these separation sequences as illustrated on Figure 2.2 and Table 2.3.

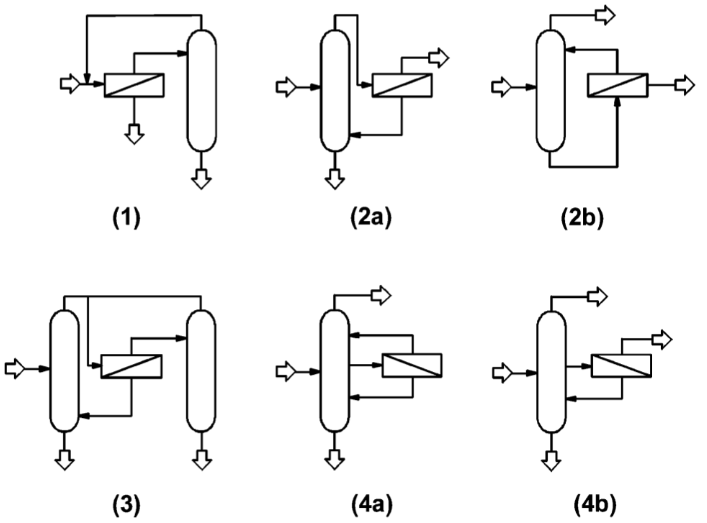


Figure 2.2. Possible distillation-pervaporation hybrid process schemes [37]

Table 2.3. Some preferred use areas and examples of distillation-pervaporation separation schemes [37]

Hybrid Separation Scheme	Use	Example
1	Feed mixture is close to azeotropic point and having high volatility after the azeotrope	Acetonitrile, Methyl Ethyl Ketone
2	Mixtures having a temperature minimum azeotrope	Ethanol, isopropanol dehydration
3	Mixtures having composition far from azeotrope but reaches azeotrope during separation	Isopropanol dehydration
4	Mixtures of low relative volatility and close boiling point mixtures	Separation of propane and propylene

As illustrated on Figure 2.2 and Table 2.3, the preferred flow scheme of the hybrid processes differs not only with the vapor-liquid equilibrium properties of the mixture but also with the concentration of the feed mixture to separation. For example, isopropanol-water mixture has a minimum temperature azeotrope therefore scheme (2) is preferred, but for the concentrations far from azeotrope point, scheme (3) can also be used.

Sommer and Melin [37] showed how combination of distillation and pervaporation in different combinations using silica membranes could affect the cost of the dehydration of isopropanol-water mixtures.

Dehydration of isopropanol-water mixtures was generally carried out using extractive distillation method employing ethylene glycol as an entrainer. Therefore, environmentally hazardous additional impurities is mixed with isopropanol that needs further purification. To overcome this difficulty in addition to a possible decrease in the cost of separation, Sommer and Melin [37] proposed three process schemes for this dehydration purposes type (3), type (4) hybrid processes and a single pervaporation unit.

Among the processes proposed by Sommer and Melin, type (4) and single pervaporation step can produce 99.9% isopropanol by weight but type (3) can produce 96.0% using silica membranes. For these separation purposes, detailed cost calculations were made and all of the distillation-pervaporation hybrid separation options found to be cheaper than the extractive distillation method. But, type (4a) hybrid system is shown to be the best choice among them because of its lowest investment and running costs. With the use of this technique, energy consumption decreased by 85% and investment and operation cost decreased more than 40%.

Further improvement on the process scheme (4) proposed by Sommer and Melin was made by Del Pozo Gomez et. al.[38] During the pervaporative dehydration of isopropanol by pervaporation, feed temperature was showed to decrease. As the most attractive operation is achieved by isothermal operation [38], the pervaporation module is heated with a heat exchanger in Sommer and Mellin's design. But, Del Pozo Gomez and his co-workers used heat integration and eliminated the need for an external heat exchanger for pervaporation module and condenser of the distillation. With the help of this small modification to the process, 44.7% of energy is saved and a maximum separation cost saving of 20% was achieved at the optimum conditions.

Van Hoof et. al.[39] studied on the use of polymeric (Pervap® 2510) and zeolitic membranes (Mitsui® NaA) in distillation-pervaporation hybrid process of type (3) and (4a). Similar to Sommer and Melin, they showed that option (4a) is economically more interesting because of its 49% lower total cost and 48% lower energy requirement. Besides, for each kind of processes costs of ceramic and polymeric membranes were shown to be similar. However, the lower resistance of the Mitsui membranes towards acidic solutions leads to the choice of these membranes for special uses.

Study conducted by Koczka et. al.[1] can be counted as an example on pervaporation based hybrid process of option (1) with real industrial solutions. They showed how hybrid processes including pervaporation decrease the cost of the separation of THF-water and THF-water-methanol mixture that are obtained from real industry. Total annual cost of the separation of the binary mixture can be reduced by 83% using PV+Distillation whereas ternary was reduced by 94% using Extractive Distillation+PV+Distillation hybrid processes by making improvements on the old recovery technology. In addition, utility costs are decreased by 84% and 60% for the dehydration of binary and ternary solutions, respectively. This study demonstrated the success of pervaporation on the dehydration of the real industrial solutions which are rarely studied in the literature.

With the construction of these improved separation schemes of both solutions, the process is also improved from batch system to continuous system. In addition, less material is lost during the separation. Therefore it can be concluded that, pervaporation not only created a cheaper way of separation but also an environmentally friendlier way of separation as a result of the minimum material loss, which is a requirement for a sustainable development. [1]

Another system having low energy consumption that composed of distillation and vapor permeation was proposed by Huang and his co-workers. [40] They proposed an improvement on the mechanical vapor compression, which is a known method used to decrease the energy consumption during separation. With the help of the installed membrane separation unit, the size of the distillation column is decreased since the membrane separation acts as an additional separation step therefore the energy consumption of the column is decreased. In addition to the lowered capital and working costs, the proposed separation system can produce ethanol with a purity of higher than 99% whereas it cannot be obtained from a single distillation system because of the equilibrium limitations. The distillation-membrane system is illustrated for use in ethanol-water separation, but it can be used for any kind of system if a suitable membrane is available.

For the comparison of the use of pervaporation and vapor permeation in the hybrid processes, Fontalvo et. al. [41] published a work for the separation of acetonitrile. It has been shown if membrane separation is to be used only to break the azeotrope in the hybrid process, vapor permeation is preferred, otherwise pervaporation is advantageous to use together with distillation. But, significant reduction in cost is obtained when both hybrid processes are used if it is compared with the conventional Acetonitrile separation process.

Several different successful process schemes including pervaporation were developed in the literature for dehydration of the solvent solutions especially creating azeotropes except for ethanol/isopropanol/water system. The separation schemes depend strictly on the characteristics of feed solution. Therefore, studies should be conducted for the solutions to be dehydrated. Also, the studies in the literature are generally lacking in optimization of the pervaporation unit, with some exceptions of temperature and feed concentration studies. Researchers did not report detailed analysis of the process parameters of pervaporation although it is needed for all systems to understand the behavior of the membrane to the possible changes in the process conditions.

Pervaporation seemed to be the best alternative for the dehydration of the by-product solution obtained from the solvent recycling unit of printing and packaging industry. Analysis on the effect of process parameters on the performance of the membranes should be carried out in order to design a dehydration scheme for the solvent mixture.

CHAPTER 3

EXPERIMENTAL

3.1. Pervaporation

3.1.1. Chemicals

The feed solution that was used in the pervaporation experiments was obtained from the solvent recovery process of a local packaging and printing industry. The main components of this by-product are ethanol, isopropanol, water and ethyl acetate and the composition is given in Table 3.1. In addition, chemicals like methoxypropanol can be found in the solution in trace amounts (much lower than 0.1%).

For the preparation of synthetic by-product mixtures, at a composition given in Table 3.1, ethanol, isopropanol and water were used. Alcohols were obtained from J.T. Baker® and of analytical grade having 99.5% purity and water was obtained from a RO system. In addition to the industrial and synthetic solutions, simulated by-product mixtures were prepared by changing the ethyl acetate content of the original by-product by adding ethyl acetate and water to the original industrial solution keeping the water concentration of the feed solution constant. Ethyl acetate used in the preparation of these solutions was obtained from J.T. Baker® having purity 99.5%.

Table 3.1. Composition of Industrial and Synthetic Solutions Used During The Experiments

Component	**Content (wt%)**	
	Industrial	**Synthetic**
Water	11.5	11.5
Ethanol	58.5	59
Isopropanol	29.3	29.5
Ethyl Acetate	0.7	-
Others	Trace	-

3.1.2. Membranes

The membranes used in this study are commercially available polymeric membranes that are purchased from Sulzer Chem-tech®, Germany. Among the dehydration membranes, illustrated at Appendix A, of the company, PERVAP 2211 and PERVAP 2201 membranes were chosen. Both membranes have been developed for the dehydration of volatile neutral organics and their mixtures. PERVAP 2201 membranes are capable of an operation at a maximum long-term temperature of 95°C and can tolerate up to 50% of water in feed mixture. Similarly, PERVAP 2211 can operate at a long-term temperature of 100°C and feed water content must be below 40%. In addition, the former is recommended to work at an organic acid content of 50% whereas the latter below 10%. More detailed specifications are listed in Appendix A.

Membranes were kept in the membrane module after experiments in order not to damage during installation to and removal from the module and module is filled with synthetic by-product mixture to avoid drying of membranes. The membranes were used until they are deteriorated or a significant performance deviation is observed in the experiments with fixed operation conditions, which are conducted periodically, when compared with results for new membranes.

3.1.3. Pervaporation Experiments

There are two pervaporation setups used in this study as illustrated in Figure 3.1 and 3.2 in addition to the three membrane modules which can be connected to these setups. The modules having 148 and 64 cm^2 active membrane areas illustrated in Figures 3.3 and 3.4 can be connected to the pervaporation set up A (Figure 3.1). One illustrated at Figure 3.5 having 12.6 cm^2 of active membrane surface area can be connected to the pervaporation set up B (Figure 3.2). The parametric experiments conducted using the rectangular shaped membrane module having 148 cm^2 but experiments with the circular modules having 64 and 12.6 cm^2 of membrane area were also conducted in order to understand the behavior of the membranes under different feed flow schemes over the membrane.

When novel rectangular shaped module having relatively higher active membrane area were used, higher permeate flow rate were achieved therefore steady-state can be observed faster in these experiments. In this configuration of the module, feed enters to the membrane module at an inclination which causes it to reach directly to the membrane surface and flows in longitudinal direction similar to the plate and frame modules. But in the case of the circular modules illustrated in Figures 3.4 and 3.5, feed enters to the module from the edge and it is assumed that well-mixing occurs over the membrane surface with the help of the high feed flow rates.

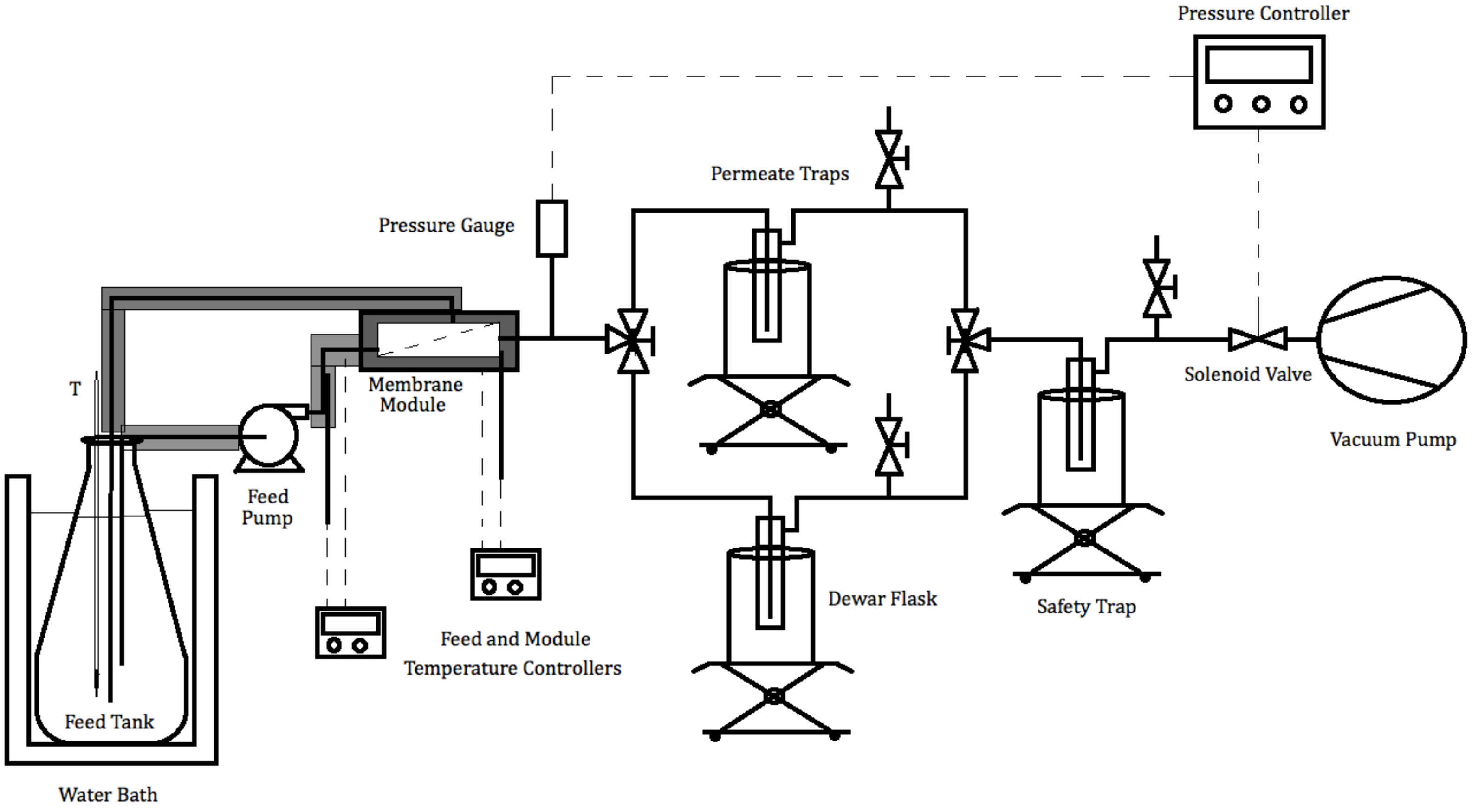


Figure 3.1: Pervaporation Experimental Setup A

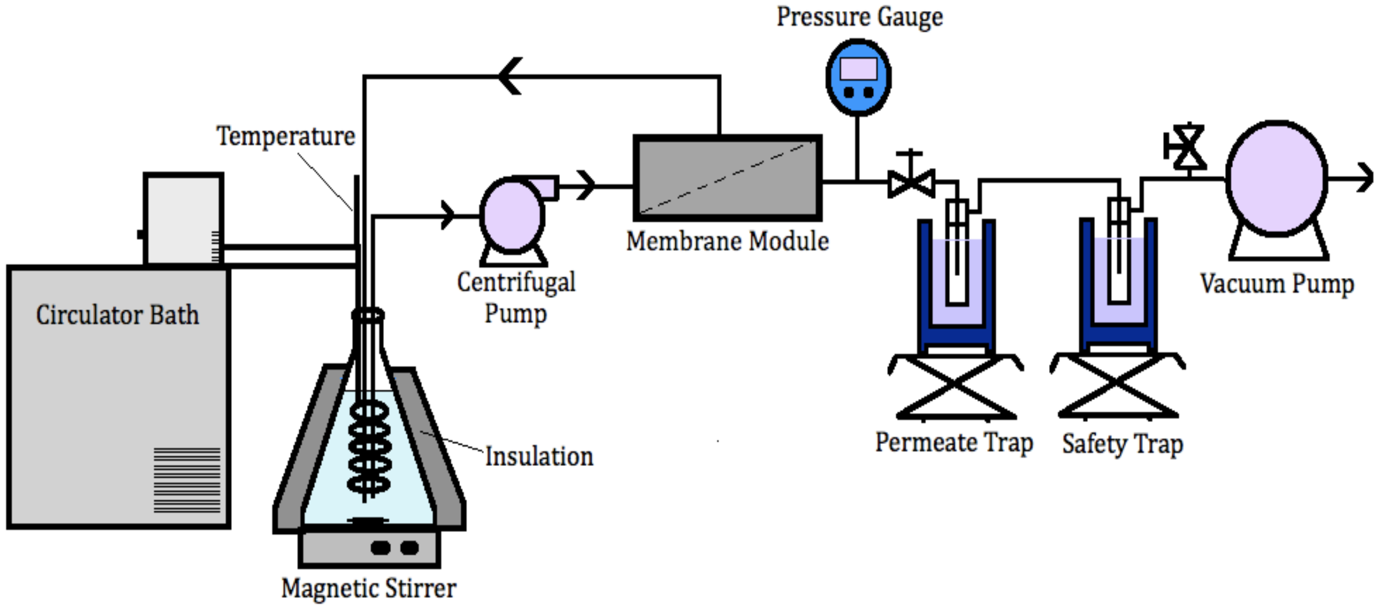


Figure 3.2: Pervaporation Experimental Setup B

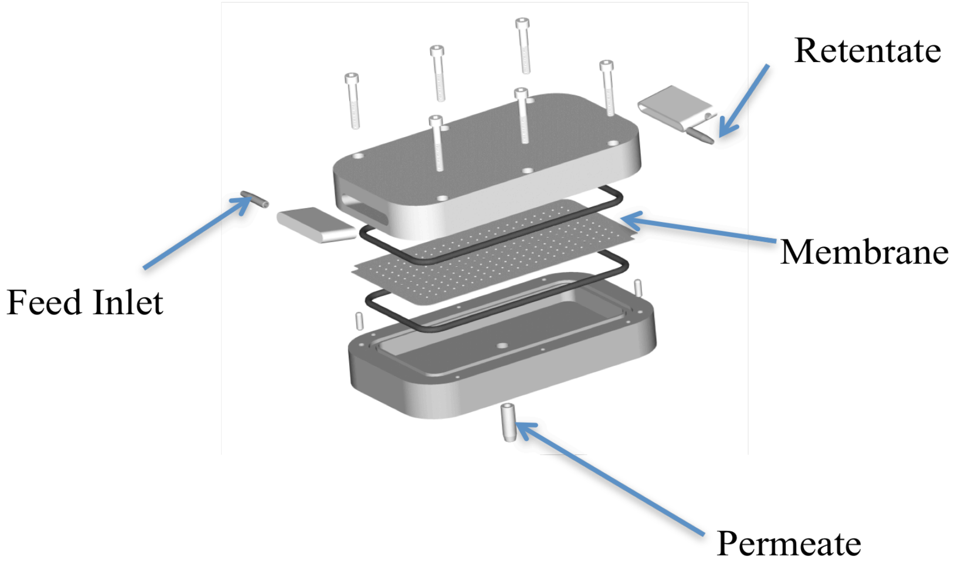


Figure 3.3. Rectangular shaped membrane module

The setup A is capable of working at feed temperatures between RT and 90°C, feed flow rates up to 1600 mL/min, permeate side pressure as low as 0.5 torr. The experimental parameters and parameter ranges used in this study are illustrated in Table 3.2.

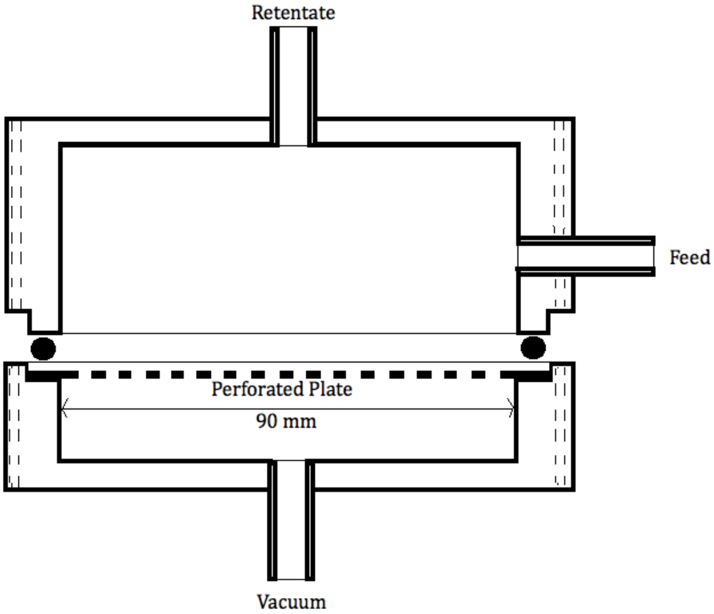


Figure 3.4. Circular membrane module having 64 cm^2 membrane area

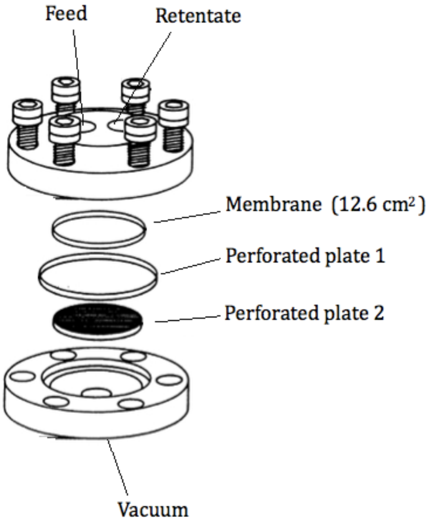


Figure 3.5. Circular membrane module having 12.6 cm^2 membrane area

Table 3.2. Parameter ranges used in the experiments

Parameter	Range
Temperature	40 - 77°C
Permeate Side Pressure	2 - 10 torr
Feed Flow Rate	250 - 1600 mL/min
Feed Water Content	1 - 11.5 wt%
Feed Ethyl Acetate Content	0.7 - 10 wt%

In the pervaporation set up A illustrated in Figure 3.1, a centrifugal pump (Cole Parmer® model 75225-05) having adjustable flow rate was used to circulate feed solution between feed side of the membrane module and the feed tank. Temperature of the feed solution is set using water bath (Polyscience® Model 8201) and temperature of the module was controlled using a home-made oven installed around the membrane module. All of the feed tubing is insulated and the temperature was set using heating tape and a controller unit applied around the tubing between feed tank and membrane module.

Vacuum was applied to the permeate side of the membrane using rotary vane pump (Edwards® RV3) where the pressure was controlled using Edwards® ADC Active Digital Controller having accuracy of ±15% equipped with Edwards Pirani Gauge and a solenoid valve.

There are two parallel permeate traps connected to the module in order to operate the system continuously and not to disturb the system before and after sampling. In addition, a safety trap is connected just before the vacuum pump in order to prevent it from any leakage from the permeate traps. The needle valve is connected just before the vacuum pump in order to adjust the pump suction rate and another needle valve is connected after the safety trap to create some leakage when it is needed.

The permeated vapor is collected in the permeate traps as condensed phase using liquid nitrogen. Samples were taken in one-hour period and weighed using glass traps. Each experiment lasted until steady state is reached, that is, three consecutive samples taken were having more or less the same flux. An amount of 3L of feed solution was used in the experiments unless otherwise is indicated. So, constant feed composition can be assumed during the experiments.

In the pervaporation set up B illustrated in Figure 3.2., a centrifugal pump (IWAKI® model 72010-25) was used to circulate feed solution between feed side of the membrane module and the feed tank. Temperature of the feed solution is set using circulator bath (Polyscience® Model 912) and glassware dipped into the solution where the solution is heated by circulating water between hot bath and the inside of the glassware. Vacuum was applied to the permeate side of the membrane using rotary vane pump (Edwards® RV5).

A permeate and a safety trap is connected to the membrane module at pervaporation set up B. Vacuum is applied to the membrane and the vapor is collected in the safety trap in the first 30 minutes. After that, the permeate trap was dipped into liquid nitrogen and vapor was collected for two hours. The flux measurements were made similar to those using set up A.

Flux was calculated using Equation 2.1 and the selectivity of water (w) to the organics (o) was calculated using Equation 2.2.

3.1.4. Sample Analyses

The water content of the feed solution was determined using KEM® Karl Fischer Moisture Titrator Model MKS-510. Depending on the amount of water in the mixture, 0.1 to 0.3 g of samples were injected into the medium, 3 chloroform-1 methanol using an injector and titrated with J.T. Baker®

Karl-Fischer Reagent 5. Firstly, mixture was taken into the syringe and weighed before injecting into the titration medium. It was also weighed again after the injection and recorded. The analyzer titrates the solution automatically using automatic unit and determines the end point using the signal obtained bye the potentiometer. After the titration, it calculates and gives the result using initial and final weight of the syringe and the amount of reagent used during the analysis.

The compositions of permeate samples were determined using Gas Chromatograph (Varian® CP-3800 Series) equipped with a Flame Ionization Detector and 50 m length and 0.32mm diameter Varian® CP-Wax 57 CB model capillary column working at an isothermal oven temperature program operating at 80°C, injector port temperature of 150°C and detector temperature of 200°C. During the analysis, 0.5 μL of samples were injected and it was splitted in 200:1 using Varian® 1177 injector. The accuracy of the GC analyses can be accounted as ±0.1% by weight of alcohols and the calibration curves for the analysis are illustrated at Appendix C.

3.1.5. ATR-FTIR and Contact Angle Measurements

To compare the degree of cross-linking of membranes, Shimadzu® FTIR Spectrometer equipped with attenuated total reflection was used with a scan number of 15. As it is illustrated in Figure 3.6, PERVAP 2211 membranes have larger peak at wavenumber of 1150 cm^{-1} that illustrates higher density of C-O bonds, therefore the higher degree of cross-linking than PERVAP 2201 membranes. [20]

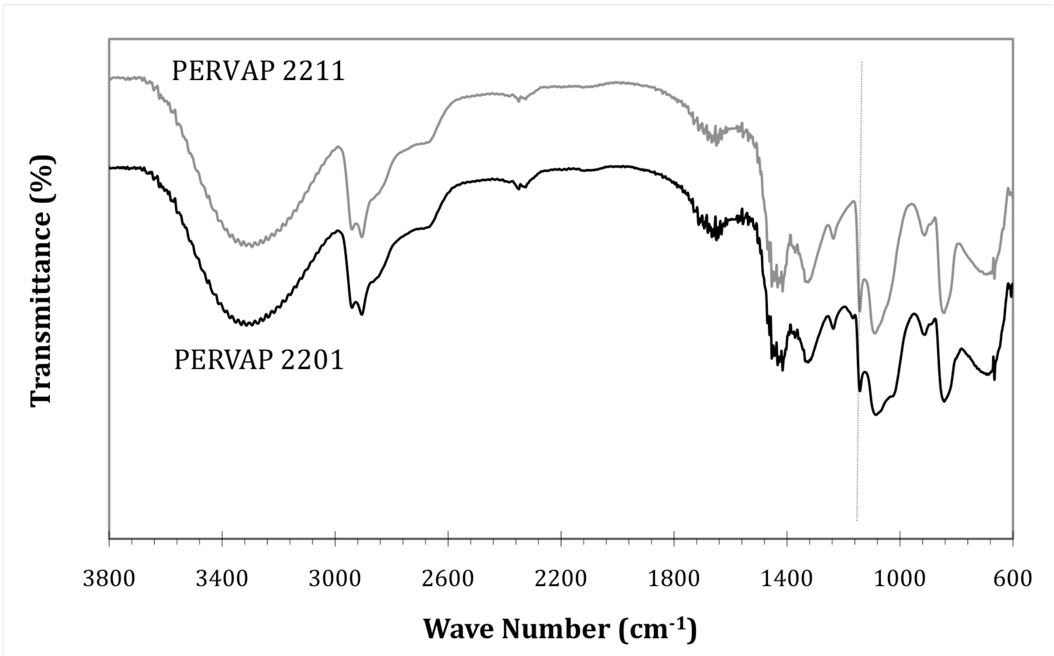


Figure 3.6: FTIR spectra of PERVAP 2201 and PERVAP 2211

Water contact angles on each membranes were measured using KSV® Contact Angle Measurement System and 1.3 mm diameter of deionized water droplets were put on the membrane using Hamilton® syringe. After making five measurements of each membrane, PERVAP 2201 was found to be slightly more hydrophilic than PERVAP 2211 because of its smaller water contact angle. (41° for PERVAP 2201 and 48° for PERVAP 2211)

3.2. Liquid Phase Adsorption

3.2.1. Chemicals

Ethanol and isopropanol were obtained from J.T. Baker® and of analytical grade having 99.5% purity and water used was the ultrapure water. A feed solution of 1.5% water, 32.8% isopropanol and 65.7% ethanol were prepared by weight.

1.6 mm diameter spherical shaped zeolite 3A was used in the experiments that were obtained from Merck®. It was calcinated at 250°C for 16 hours in aerated oven.

3.2.2. Liquid Phase Adsorption Experiments and Sample Analyses

The setup illustrated at Figure 3.7 was used in the adsorption experiments. 1.5 L of feed was prepared at a composition indicated above and filled into the feed tank. 72.8 g of activated zeolite 3A was filled into the 30 mm diameter column having at 20 cm height. Feed was pumped using Masterflex® Microprocessor Pump at a flow rate of 1.0 mL/min into the column entering from the bottom of the column. The outlet was collected from the top of the column at every 10 minutes for 20 seconds.

Samples were analyzed using HP 5890 Series II Gas Chromatograph equipped with a TCD detector and Porapak Q packed column. The injector is at 200°C, column oven operates isothermally at 150°C and detector is at 170°C. 1 μL of sample was injected to GC for the analysis.

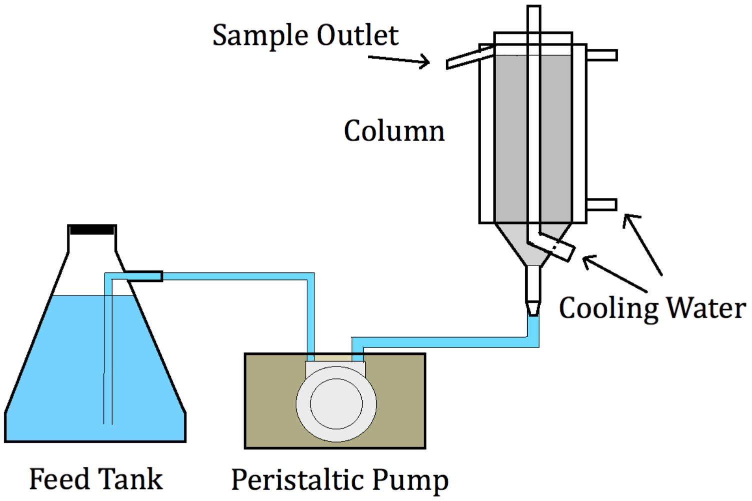


Figure 3.7. Liquid phase adsorption experimental setup

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1. Unsteady-State Pervaporation Experiments

Each experiment was repeated twice and the results were consistent with each other with a difference of 3%. The reported performances in this study are the averages of the repeated experiments at the same conditions.

Time dependent variation of the membrane performance obtained from a typical run at 50°C, 2 torr permeate side pressure, 1.6 L/min feed flow rate using PERVAP 2201 is illustrated in Figure 4.1. Total flux decreases and the permeate water concentration increases with time. The feed water concentration decreased to 11.2% by weight at the end. Both flux and permeate composition stabilizes together and reaches steady state at about fourth hour of the experiment. It takes shorter to reach steady state at higher temperatures. Similar trends for flux and permeate compositions were also observed in the other runs and were also reported by Okumuş et. al. in the separation of ethanol/water mixtures by synthesized PAN membranes.[35]

During the setting up the process conditions, stabilizing the feed and module temperatures without applying vacuum, feed solution is circulated between membrane module and the feed tank. Therefore, membranes may become saturated with the feed that may cause further swelling. This may lead to higher fluxes and lower selectivities at the beginning of the experiment than those obtained at steady-state.[35]

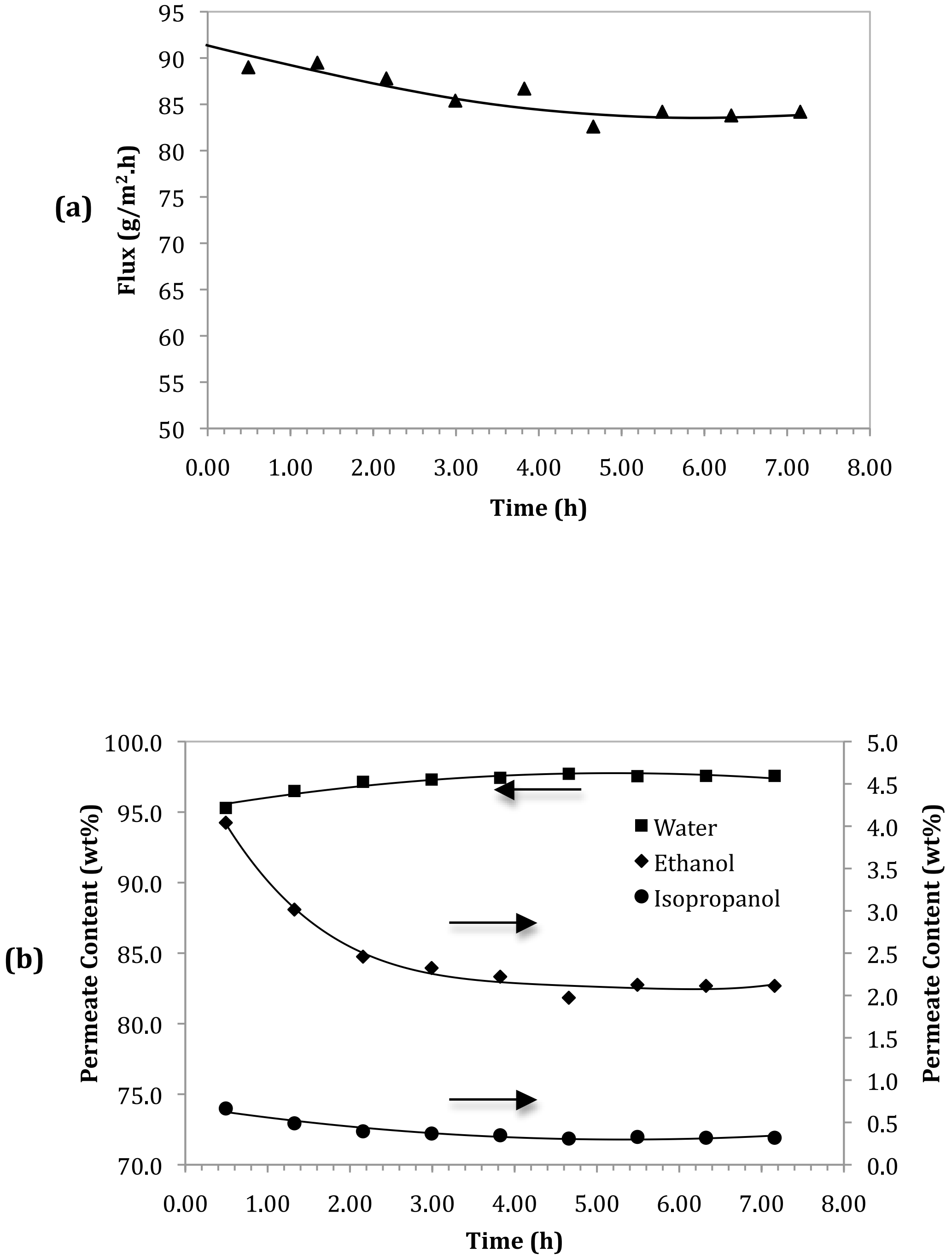


Figure 4.1: (a) Total flux and (b) permeate compositions with respect to time for an experiment conducted at 50°C and 2 torr permeate side pressure, 1.6 L/min feed flow rate using industrial feed. (after temperature stabilization, PERVAP 2201/1)

4.2. Effect of Feed Flow Rate

Figure 4.2 and 4.3 shows the effect of feed flow rate on the permeate composition and flux for PERVAP 2201 at 60°C and 2 torr permeate side pressure. The feed mass flux was defined as the feed mass flow rate over cross sectional area of the membrane module.

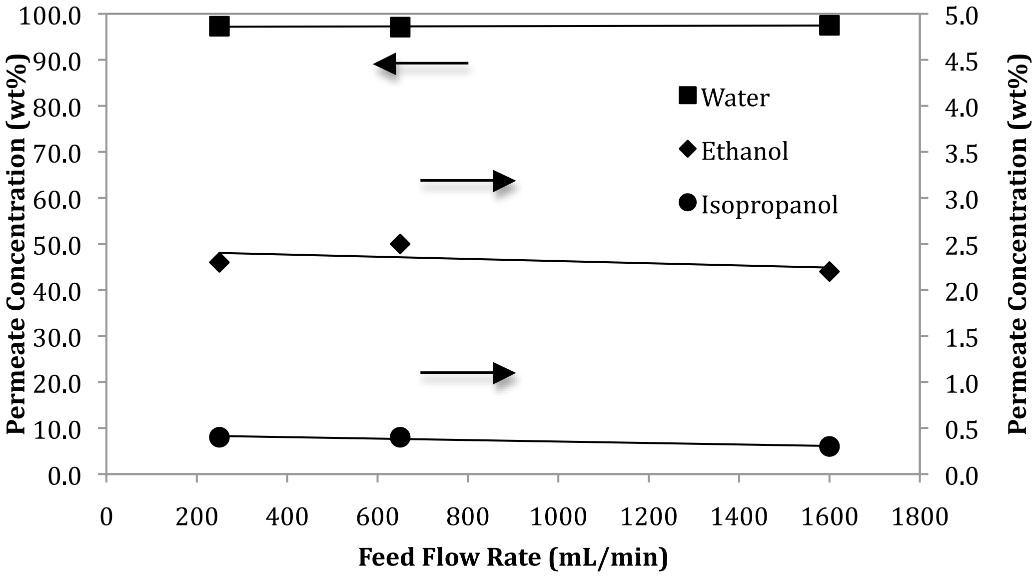


Figure 4.2. Effect of feed flow rate on the permeate composition of PERVAP 2201 (2201/1, 2 torr, 60 ^{o}C, after temperature stabilization)

Feed mass flux has almost no effect on the permeate composition in the range studied. On the other hand, permeate fluxes increases with increasing feed flow rates up to 600 mL/min then with further increases permeate flux remains constant. Below that value, permeate flux decreases. A decrease in the membrane performance at lower feed flow rates was also observed quantitatively by Urtiaga et al.[26] during the removal of chloroform from aqueous solutions.

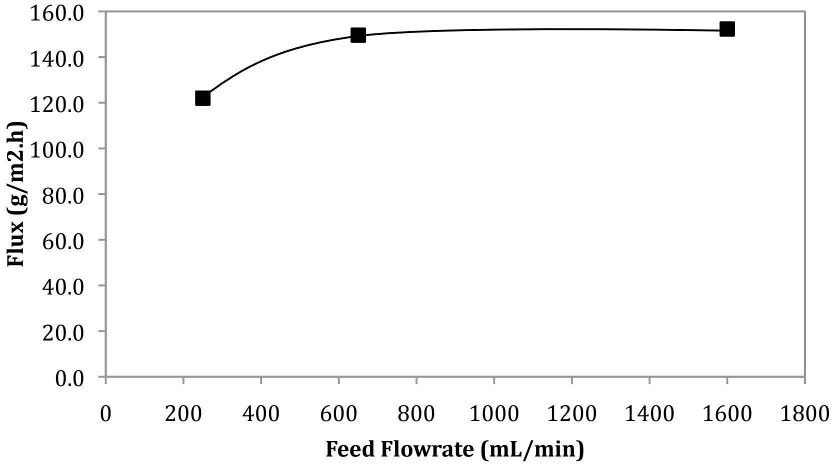


Figure 4.3. Effect of feed flow rate on the flux through PERVAP 2201 (2201/1, 2 torr, 60 °C, after temperature stabilization)

The decrease in the flux at lower feed flow rates, keeping the other variables constant, may result from the difference between the water concentration over the membrane surface and that of the bulk flow of the feed solution. This could be occuring at lower feed flow rates when transport resistance to water molecules in the feed solution may come into significance. Therefore, feed flow rate was decided to be set 1.6 L/min at further experiments to prevent lower fluxes due to concentration polarization. In addition, the existence of a limiting feed flow rate should be considered in the design of the pervaporation modules.

4.3. Effect of Permeate Side Pressure

The driving force for the mass transfer through the membrane is the chemical potential gradient which is strongly influenced by transmembrane pressure difference, therefore the pervaporation performance is likely to be affected by the permeate side pressure.[23,32,42] In a set of experiments using PERVAP 2211 membranes, the permeate pressure was varied between 2 to 10 torr. The results are shown in Table 4.1. The permeate side pressure significantly affects the separation performance of PERVAP 2211 membranes. Both flux and the permeate water concentration increases as the permeate side pressure is decreased. About one order of magnitude decrease in water flux whereas about two folds increase in ethanol and practically no change in isopropanol fluxes were observed as a result of the increase in permeate side pressure suggesting that permeate side pressure have different effects on the permeated components.

Table 4.1. Effect of permeate side pressure on performance of PERVAP 2211 (2211/3, 60°C, 1.6 L/min, after temperature stabilization)

P (torr)	**Total Flux** (g/m^2.h)	**Permeate** (Concentration: Mass Fraction, Flux: g/m^2.h)					
		Water		**Ethanol**		**Isopropanol**	
		Conc.	**Flux**	**Conc.**	**Flux**	**Conc.**	**Flux**
2	98.3	0.981	96.4	0.015	1.5	0.005	0.5
5	47.7	0.956	45.6	0.038	1.8	0.007	0.7
10	13.6	0.740	10.1	0.219	3.0	0.042	0.6

Similar trends illustrated in Table 4.1 were also observed in the literature for binary feed mixtures. McGinness et. al. [23] and Okumuş et. al.[35] reported an increase in both total flux and selectivity towards water when the permeate side pressure is lowered using dehydration membranes PERVAP 2210 and synthesized homogenous PVA membranes, respectively. Increase in the total flux with decrease in permeate side pressure is an expected result because driving force increases as the activity of molecules in the permeate side decreases.

Increase in the permeate water concentration with a decrease in permeate side pressure can be described using two schemes, first is the changes of the solubilities of the components in the permeate side of the membrane and second is the extent of swelling of the membrane.[35] The latter is more likely to affect the transport of the molecules through the membrane as ethanol, being a smaller molecule than isopropanol, is more affected from the swelling of the membrane.

Observing a significant increase in the membrane performance, both higher flux and selectivity towards water, at lower permeate side pressures, a pressure of 2 torr at the permeate side was used in the further experiments in this study.

4.4. Effect of Synthetic and Industrial Feed Solutions on the Performance of PERVAP 2211 and PERVAP 2201 Membranes

The industrial feed solution obtained from the packaging and printing industry includes some species at minor amounts, such as, ethyl acetate, 1-methoxy-2-propanol etc. The presence of an additional material to the feed mixture may affect the membrane performance as a result of the increase in the complexity of the interactions between membrane material and feed solution.[30] Experiments using the synthetic feed were, therefore, conducted at different temperatures to observe the effect of these minor components in the feed solution on membrane performance and to observe whether operation temperature has an effect on the interactions of these components with the membrane.

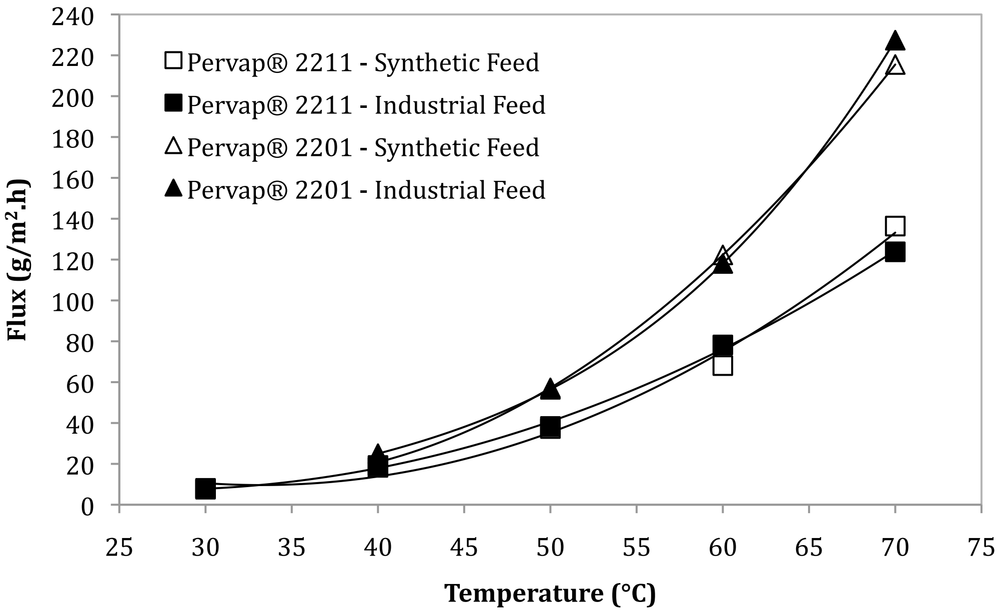


Figure 4.4. Comparison of the flux between synthetic and industrial feed solutions for dehydration using PERVAP 2201 and PERVAP 2211 (2211/2*, 2201/1, 2 torr, 1.6 L/min, before temperature stabilization)

The total flux obtained at different temperatures using industrial and synthetic solutions are illustrated in Figure 4.4. The minor components in the feed solution have no significant effect on the total fluxes through each membrane. Table 4.2 shows the effect of minor components on the permeate composition. PERVAP 2201 was not affected from the minor components. The permeate streams obtained from both industrial and synthetic solutions had nearly the same composition for PERVAP 2201 at all temperatures studied. However, the water concentration of the permeate is lower for industrial feed solutions than synthetic feed solutions especially at lower temperatures when PERVAP 2211 was used. These results suggested that PERVAP 2201 membranes can tolerate the existence of minor components more than PERVAP 2211. But, no difference observed between the experiments conducted at the same conditions using synthetic mixtures before and after the runs using industrial feed solutions. Therefore, these effects were reversible. As a result, it can be concluded that the minor components in the feed solution do not cause the membrane material to deform.

Table 4.2. Permeate compositions of the experiments conducted using industrial and synthetic solutions (2211/2*, 2201/1, 2 torr, 1.6 L/min, before temperature stabilization)

Temperature (°C)	**Permeate Water Concentration** (mass fractions) **PERVAP 2211**		**PERVAP 2201**	
	Industrial	**Synthetic**	**Industrial**	**Synthetic**
30	0.850	0.874		
40	0.892	0.948	0.949	0.971
50	0.959	0.973	0.965	0.952
60	0.959	0.981	0.974	0.976
70	0.984	0.976	0.976	0.977

4.5. Effect of Temperature on the Performance of PERVAP 2211 and PERVAP 2201 Membranes

Another factor affecting the membrane performance is the operation temperature. To observe the change in the pervaporation performance of PERVAP 2211 and PERVAP 2201 membranes, experiments were conducted at different temperatures.

Initially, cyclic temperature experiments were conducted using PERVAP 2201 to observe the operational stability of the membrane at varying temperatures. Duplicate experiments at temperatures 40 to 70°C were conducted at first as illustrated in Figure 4.5 in experimental order. Then, the temperature is decreased to 50°C and a significant increase in the flux from 55.9 to 75.6 g/m^{2}h was observed with a small increase in the selectivity when compared to the first experiment conducted at 50°C. The temperature is further increased to 60 and 70°C and higher fluxes and selectivities were also observed than the first experiments conducted at the same conditions. Then, long-run experiment, lasted about 12 hours, at 70°C were conducted at the second cycle. As a result of the long-run experiment conducted at 70°C, the performance of the membrane was stabilized and no change in the performance of the membrane observed at further cyclic temperature experiments.

The cyclic temperature experiments showed that a treatment lasting about 12 hours at 70°C could be applied to the membrane initially to stabilize the membrane. Therefore, further temperature studies were reported using the data collected from the experiments conducted after this treatment. It can be easily observed from Figure 4.6 that operation temperature strongly affects the total fluxes through each membrane. Exponential increase in the total flux with respect to operation temperature were observed for the membranes used in this study. In addition, only slight change in the water selectivity of PERVAP 2201 membranes was observed with temperature whereas considerable increase in the water selectivity with temperature was observed for PERVAP 2211 as illustrated in Figure 4.7. Similar trends for flux and water selectivities were also reported in the literature.[23,24,29,30] Delgado et. al. observed nearly constant water selectivities with respect to temperature for the dehydration of ethanol/water and ethanol/water/ethyl lactate/lactic acid systems using PERVAP 2201.[29,30] Besides, Csefalvay et. al.[24] and McGinness et. al.[23] observed increasing trends for water selectivities with temperature for the dehydration of isopropanol/water and THF/water systems, respectively, using PERVAP 2210. Although the dependency of the water selectivities shows differences with respect to temperature, exponential increase in the total flux with increasing temperature is the general case reported in the literature.

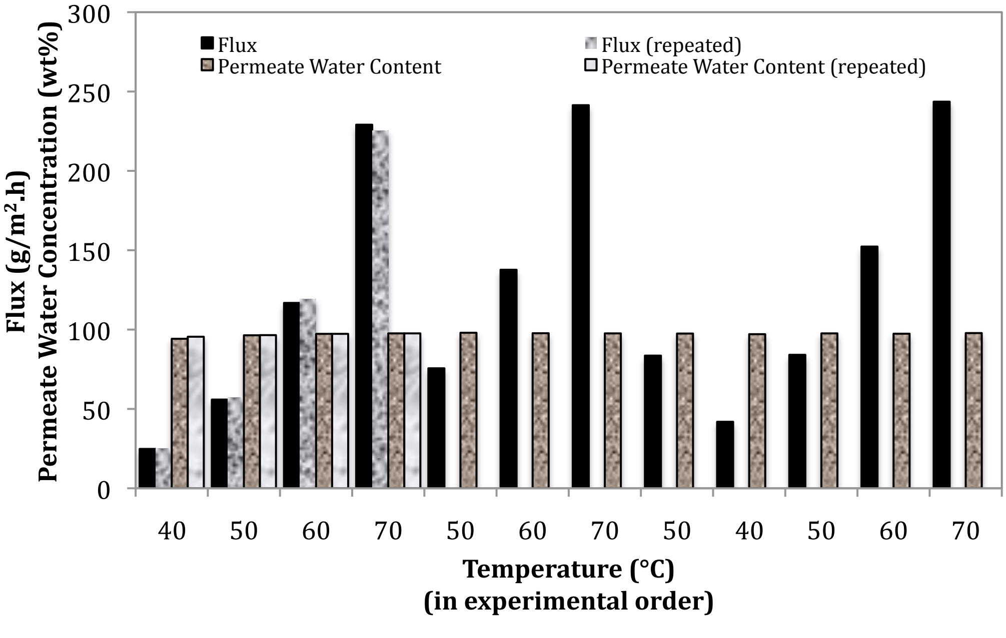


Figure 4.5. Cyclic temperature experiments (PERVAP 2201/1, 2 torr, 1.6 L/min)

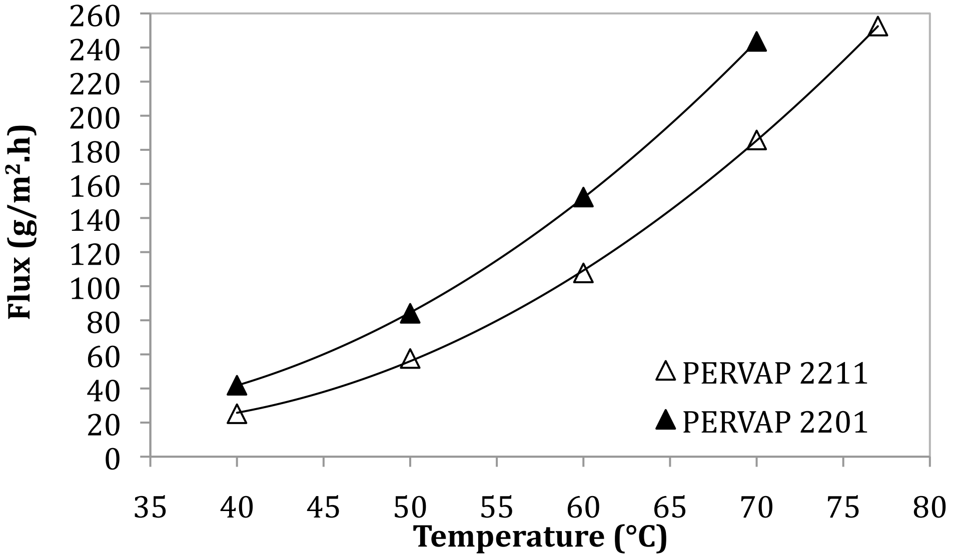


Figure 4.6. Effect of temperature on the total fluxes of PERVAP 2211 and PERVAP 2201 (2211/3, 2201/1, 2 torr, 1.6 L/min, after temperature stabilization)

Because of the increase in the diffusivity and solubility in the membrane in addition to an increase in the driving force of mass transport with temperature, total fluxes are increased with the operational temperature.[30] Diffusivity, being the dominant factor in the increase of the fluxes with temperature, is exponentially dependent on temperature.[23] Therefore, the fluxes were observed to be exponentially dependent on the temperature. However, the permeate composition is not that much dependent on the change in the temperature as illustrated in Table 4.3. The dependency of solubility and the diffusivity of the feed components in the membrane to the operation temperature may be the determining factor in the change of permeate compositions with temperature obtained from each membranes. PVA, which is the selective layer of both membranes, is a highly hydrophilic material[2] that may lead to high permeate water concentrations which may not be strictly dependent on temperature at the range studied.

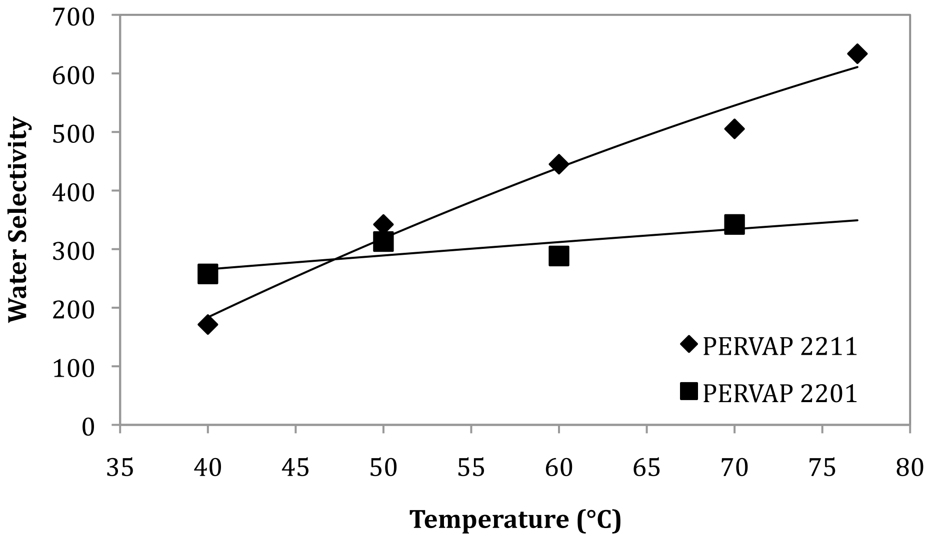


Figure 4.7. Effect of temperature on the water selectivity of PERVAP 2211 and PERVAP 2201 (2201/1, 2211/3, 2 torr, 1.6 L/min, after temperature stabilization)

In addition to the generally observed dependency of membrane performance on temperature, PERVAP 2201 was observed to have higher fluxes than PERVAP 2211; also the effect of temperature on total flux is more significant for PERVAP 2211 membranes.

The increase in the water selectivity of PERVAP 2211 may also be related to the higher cross-linking of the membrane. As the temperature is increased, water molecules could find more routes to diffuse through in PERVAP 2211 which may not have such effect on PERVAP 2201 membranes.

Table 4.3. Effect of temperature on the permeate compositions of PERVAP 2211 and PERVAP 2201 (2201/1, 2211/3, industrial feed, 2 torr, 1.6 L/min, after temperature stabilization)

Temp. (°C)	**Permeate Compositions**					
	PERVAP 2211			**PERVAP 2201**		
	Water	**EtOH**	**IPA**	**Water**	**EtOH**	**IPA**
40	0.957	0.034	0.009	0.971	0.025	0.005
50	0.978	0.018	0.004	0.976	0.021	0.003
60	0.983	0.015	0.002	0.974	0.022	0.003
70	0.985	0.014	0.001	0.978	0.019	0.003
77	0.988	0.012	BDL*			

* below detection limit

Change in the operation temperature of pervaporation also affected the selectivity of ethanol towards isopropanol. The effect of temperature on ethanol to isopropanol selectivity is illustrated at Table 4.4 for 2 torr permeate side pressure, 1.6 L/min industrial feed flow rate. Both membranes showed slightly higher selectivities towards ethanol in the temperature range studied. Higher selectivity of methanol to ethanol was reported in the literature on the dehydration of methanol/ethanol/water solutions using PERVAP 2201 membranes.[27] Hydrophilic membranes primarily transport the molecules that are more polar and smaller because of the higher sorption and diffusion of these molecules in the membrane compared to the other components. Therefore, ethanol, being a more polar and smaller molecule than isopropanol, is preferably transported through the membrane and it showed higher selectivity towards isopropanol.

Table 4.4. Effect of temperature on the selectivity of ethanol/isopropanol (2201/1, 2211/3, industrial feed, 1.6 L/min, 2 torr, after temperature stabilization)

Temp. (°C)	**Ethanol/Isopropanol Selectivity**	
	PERVAP 2211	**PERVAP 2201**
40	1.9	2.5
50	2.3	3.5
60	3.8	3.7
70	7.0	3.2

A drastic increase in the permeate flux coupled with no loss in the water selectivity signals that it is advantageous to use the membranes at higher temperatures. Each membrane is observed to achieve satisfactory removal of water from the industrial by-product since high permeate water concentration was obtained from both membranes. To choose between two types of membranes, fluxes should be considered since each show similar permeate water concentrations. However, if selectivity of water is crucial during the design of a pervaporation system, PERVAP 2211 would be advantageous for low temperature operation and PERVAP 2201 would be advantageous at higher temperatures than 50°C.

4.6. Effect of Module Type on the Performance of PERVAP 2211 and PERVAP 2201 Membranes

The flow scheme of feed on the membrane may effect the transport of the water molecules in the liquid phase, therefore may lead to a change in the performance of the membrane by creating an additional resistance to mass transport. The membrane module used in this study is a rectangular shaped module where liquid is flowing in the longitudinal direction. But, the generally used membrane modules in the literature are circular shaped.[43-44] In the circular modules, the feed enters from the edge of the module and leaves it after mixing over the membrane, which may cause different transport schemes of the molecules in the liquid phase. To clarify whether the newly designed module has differences from the circular modules as a result of this differences in the flow schemes, experiments were conducted using circular membranes. As it is illustrated in Figure 4.8, lower performance was obtained when circular module is used after observing lower water selectivity and same flux when compared to those of rectangular module, at first. But, additional work must be done in order to attribute this decrease in the performance to the different flow schemes of feed solution over the membrane by eliminating effect of other differences, such as usage of different membrane sheets, between two sets of experiments.

In order to clarify whether this difference in performance is resulting from the different flow schemes or from the possible non-homogeneities of the membrane, additional experiments were conducted using the rectangular shaped module and different membrane sheets and varying results were observed from these membranes. The observed flux of PERVAP 2211 changed in the range 101.8 - 185.8 g/m^{2}h and PERVAP 2201 in the range 168.8 - 241.4 g/m^{2}h. In addition, water concentration of the permeate varied in the range 0.979-0.995 and 0.932-0.976, respectively, at 70°C and 2 torr permeate side pressure and 1.6 L/min of industrial feed flow rate as illustrated at Table 4.5. Therefore, this signaled that membranes may have different performance characteristics. Furthermore, observed performance of a membrane is not uniform over the membrane surface.

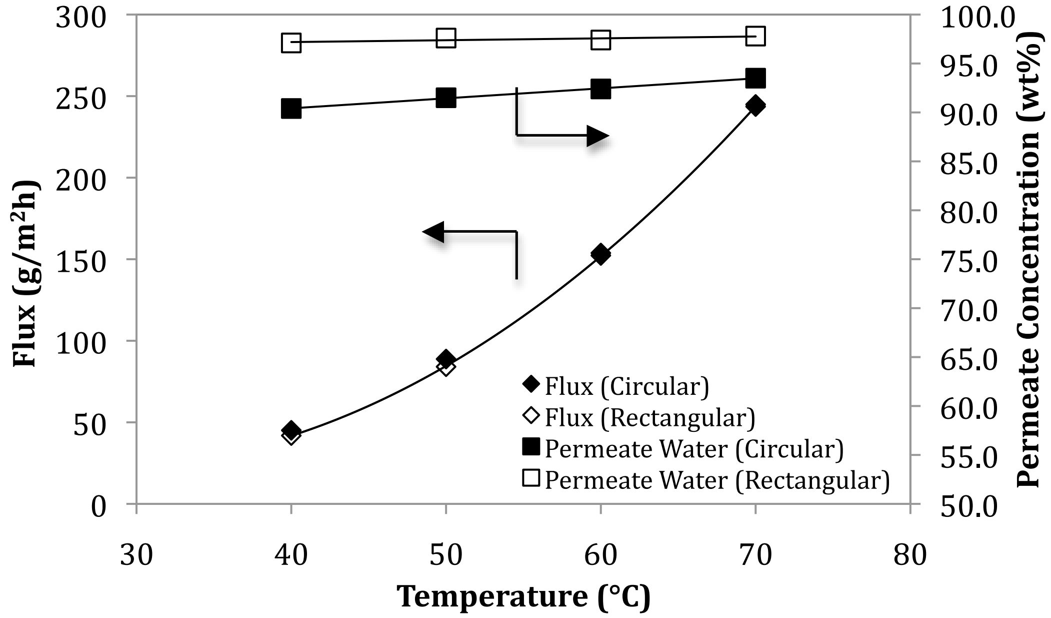


Figure 4.8. Performance of PERVAP 2201 membranes at different temperatures for circular and rectangular module (2201/1, 2201/1c, 2 torr, 1.6 L/min, after temperature stabilization)

To test the membrane homogeneity, the two rectangular shaped PERVAP 2201 membranes having 168.8 and 175.0 g/m^{2}h of fluxes together with 93.2% and 94.5% permeate water concentration by weight using rectangular module were cut into smaller pieces and coded as shown in Figure 4.9. To compare the homogeneity of the membrane, standard experiments were conducted at 70°C and the performance results of these pieces of membranes were tabulated at Table 4.6.

Table 4.5. Flux and permeate composition of different rectangular sheets of membranes (70°C, 1.6 L/min, 2 torr, industrial feed, after temperature stabilization)

Membrane	**Sheet**	**Flux** (g/m²h)	**Permeate Composition** (mass fraction)		
			Water	**EtOH**	**IPA**
PERVAP 2201	1	241.4	0.976	0.021	0.004
PERVAP 2201	2	188.2	0.943	0.049	0.009
PERVAP 2201	3	168.8	0.932	0.054	0.014
PERVAP 2201	3*	175.0	0.945	0.046	0.009
PERVAP 2211	1	124.3	0.983	0.016	0.001
PERVAP 2211	2	185.8	0.985	0.014	0.001
PERVAP 2211	3	115.9	0.989	0.008	0.003
PERVAP 2211	4	101.8	0.995	0.004	0.001
PERVAP 2211	4*	104.3	0.979	0.015	0.006

* second part of the membrane sheet.

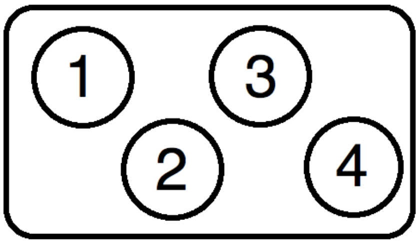


Figure 4.9. Cutting scheme of the rectangular membrane into small parts for testing using 12.6 cm² membrane module

Table 4.6. Performance of the membranes using 12.6 cm^2 circular module. (70°C, 1.6 L/min, 2 torr, industrial feed, after temperature stabilization)

Membrane	**Part**	**Flux** (g/m^{2}h)	**Permeate Composition** (wt%)		
			Water	**Ethanol**	**IPA**
2201/3	**1**	197.8	0.904	0.073	0.023
2201/3	**2**	208.5	0.939	0.052	0.009
2201/3	**3**	168.9	0.954	0.038	0.008
2201/3	**4**	182.0	0.967	0.027	0.006
2201/3	**Rectangular**	168.8	0.932	0.054	0.014
2201/3*	**1**	182.0	0.965	0.029	0.006
2201/3*	**2**	206.6	0.913	0.070	0.017
2201/3*	**3**	180.4	0.955	0.037	0.008
2201/3*	**Rectangular**	175.0	0.945	0.046	0.009

The results of the experiments conducted using 12.6 cm^2 of circular membranes showed that the membranes are not homogenous because of the differences of the fluxes and permeate compositions of each part. Since both fluxes and permeate water compositions varied at different directions for each part of the membrane, which can not be the result of only the membrane thickness change, there should be some structural non-homogeneities in the membrane.

Therefore, it can be concluded that, it is very difficult to compare the membrane performance at different feed flow schemes using these membranes since the differences in the pervaporation performances of membranes using each module are in the non-homogeneity range of the membrane. But, satisfactory separation of water from the solution, with permeate concentrations above 90% by weight, were obtained using the membrane modules introduced in this study. The effect of the possible local decreases of the membrane performance were minimized using the specially designed rectangular shaped pervaporation module during the experiments. As a result, the experiments were conducted using the rectangular module, having larger active membrane surface area. Also, steady state is reached faster as the result of this larger area of the rectangular module compared to the circular module, in addition, experimental errors were decreased since larger amounts of permeate collected in unit time.

4.7. Effect of Feed Water Concentration on Pervaporation Performance of PERVAP 2201 Membranes

The effect of feed water concentration on the flux and permeate composition of PERVAP 2201 is illustrated in Table 4.7. Total flux and permeate water concentration and the selectivity of water increased whereas permeate ethanol and isopropanol concentrations decreased as the feed water concentration is increased. Similar results were reported in the literature for the dehydration of ethanol, isopropanol and butanol isomers using PERVAP 2201 and PERVAP 2510 membranes.[21,22,27]

Table 4.7. Effect of feed water concentration on the peformance of PERVAP 2201 (2201/2, 70°C, 2 torr, 1.6 L/min, after temperature stabilization)

Feed Water Concentration (wt%)		**Exp. Time** (h)	**Flux** (g/m^{2}h)	**Permeate Composition** (weight fraction)			**Water Selectivity**
Initial	**Final**			**Water**	**EtOH**	**IPA**	
11.4	11.2	4	188.2	94.3	4.9	0.9	131.2
6.0	5.8	7	88.5	89.5	8.8	1.7	138.4
1.2	1.2	8	15.1	76.1	20.5	3.4	262.2

The swelling of the membrane and the driving force for the transport of water through the membrane increases with the feed water concentration. Therefore, flux increases with feed water concentration. At high feed water concentrations, the driving forces for the alcohol transport becomes negligible since the membrane is highly hydrophilic. As the concentration of water in the feed solution is decreased, transport of alcohol solutions comes into significance therefore leading to lower permeate water concentrations. But selectivity increases as the feed water concentration decreases. The increase in the water selectivity with a decrease in the feed water concentration may be regarded to the decrease in the swelling of the membranes. As the feed water concentration is decreased, swelling decreases therefore creating narrower routes for the molecules to pass through. As a result of this, membrane more selectively transports water molecules than alcohol molecules because it is a smaller molecule. The increase in the water selectivity at low feed water concentrations signals that PERVAP 2201 is capable of dehydrating the solvent solution to very low water concentrations.

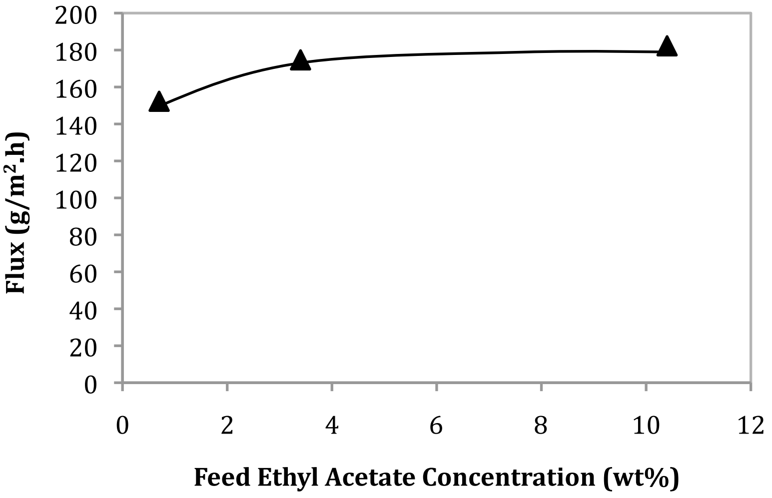
4.8. Effect of Feed Ethyl Acetate Concentration on Pervaporation Performance of Pervap 2201 Membranes

Ethyl acetate concentration of the feed solution may change due to the process conditions in the range of about 0% to 3% by weight because of the complex distillation column system and the multicomponent feed solution fed to distillation. To figure out how the change in feed ethyl acetate concentration affects pervaporation, experiments were conducted with simulated feed solution, prepared by changing ethyl acetate concentration at constant water concentration of the industrial feed solution, and the results are illustrated in Figure 4.10.

An increase in the total flux from 150 to 180 g/m^{2}h together with a slight decrease in the permeate water concentration from 97.4 to 95.9% by weight was observed when the feed ethyl acetate concentration is changed between 0.7 to 10.7% by weight. Membrane totally rejects ethyl acetate when its concentration in the feed is low since no ethyl acetate could be detected in the permeate at feed ethyl acetate concentrations of 0.7 and 3.7 wt%. But, small amount of ethyl acetate permeates through the membrane when concentration of it in the feed is relatively higher.

An increase in the flux with a loss in the selectivity of the membrane as a result of an increase in the feed ethyl acetate concentration of the feed signals that membrane may swell because of the presence of ethyl acetate in the feed. Increase in the ethyl acetate concentration will lead to a further decrease in the membrane performance. Also, standard experiments at 60°C, 2 torr and 1.6 L/min of industrial feed were conducted between each consecutive run of these experiments that are tabulated at Table 4.8. It was observed that exposure to ethyl acetate affected the membrane matrix irreversibly causing selectivity to drop and flux to increase. However, the decrease in the permeate water concentration was not very high that will need membrane replacement during the possible process.

(a)



(b)

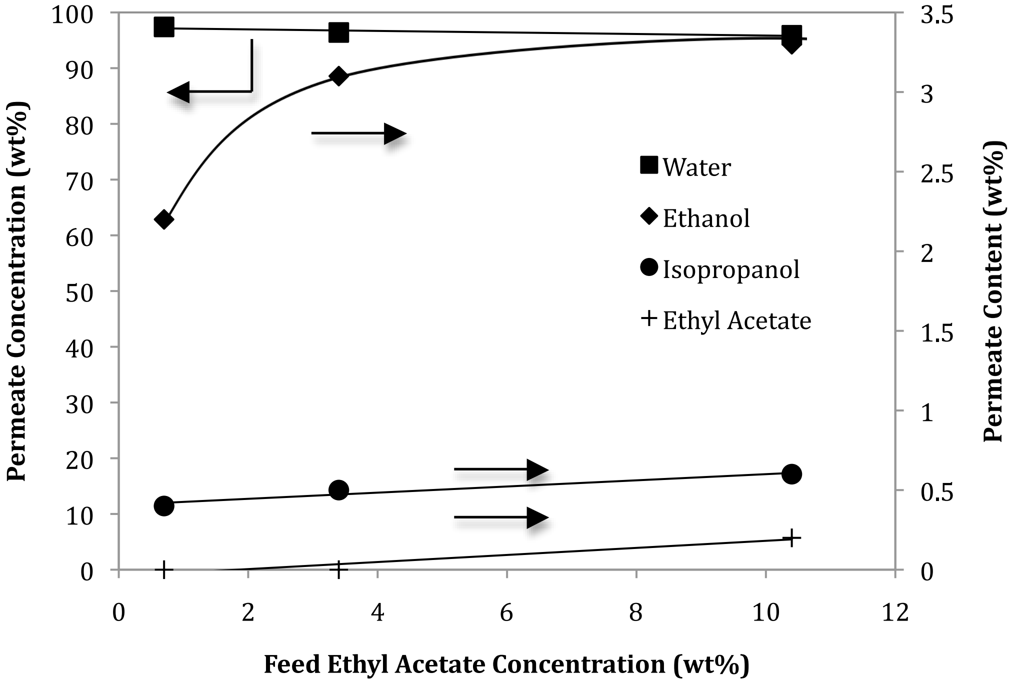


Figure 4.10. Effect of feed ethyl acetate concentration on performance of PERVAP 2201 membranes (a) flux (b) permeate composition (2201/1, 60°C, 2 torr, 1.6 L/min, after temperature stabilization)

Table 4.8. Membrane performance observed from standard experiments after exposure to ethyl acetate (2201/1, industrial feed, PERVAP 2201, 60°C, 2 torr, 1.6 L/min, after temperature stabilization)

Exposure to EtOAc (by weight)	**Flux** (g/m^2h)	**Permeate Composition** (mass fraction)			
		Water	**EtOH**	**IPA**	**EtOAc**
No exposure	157.5	0.974	0.022	0.004	-
After exposure to 3.3%	170.8	0.959	0.035	0.006	-
After exposure to 10.4%	171.3	0.958	0.035	0.006	-

4.9. Concentrated-Mode Experiments and the Effect of Feed Water Concentration on the Performance of Pervap 2211 and Pervap 2201 Membranes

Using the best conditions selected based on parametric studies, concentrated-mode experiments were conducted using each membrane as illustrated in Figures 4.11 and 4.12. 3L and 1.5L of industrial feed solutions were dehydrated by PERVAP 2201 and PERVAP 2211, respectively, at operation temperature of 70°C, permeate side pressure of 2 torr and feed flow rate of 1.6 L/min. The feed solution is recirculated between feed tank and the membrane module during the experiments and the change in flux, permeate composition and feed composition with respect to time was determined.

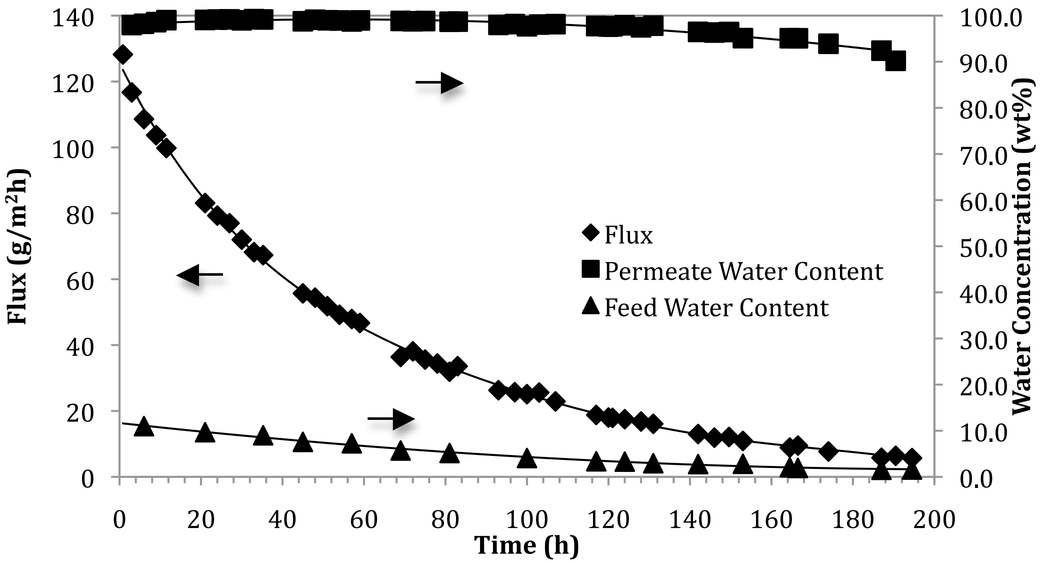


Figure 4.11. Flux, permeate water concentration and feed water concentration vs. time for PERVAP 2211 during concentrated-mode experiment. (2211/5, 1.5 L feed, 70°C, 2 torr, 1.6 L/min, after temperature stabilization)

The behavior of the membranes during the removal of water from the original industrial solution until 1.5% by weight is illustrated in Figures 4.11 and 4.12. The fluxes through each membrane decreased significantly with time. Permeate water concentration of PERVAP 2211 started to decrease faster after 120 hours whereas that of PERVAP 2201 was after about 50 hours run of the experiment. Since operating conditions such as, temperature, feed flow rate and permeate side pressure kept constant during the run of an experiment, the only factor affecting the changes in the flux and permeate water concentration is the changing feed composition.

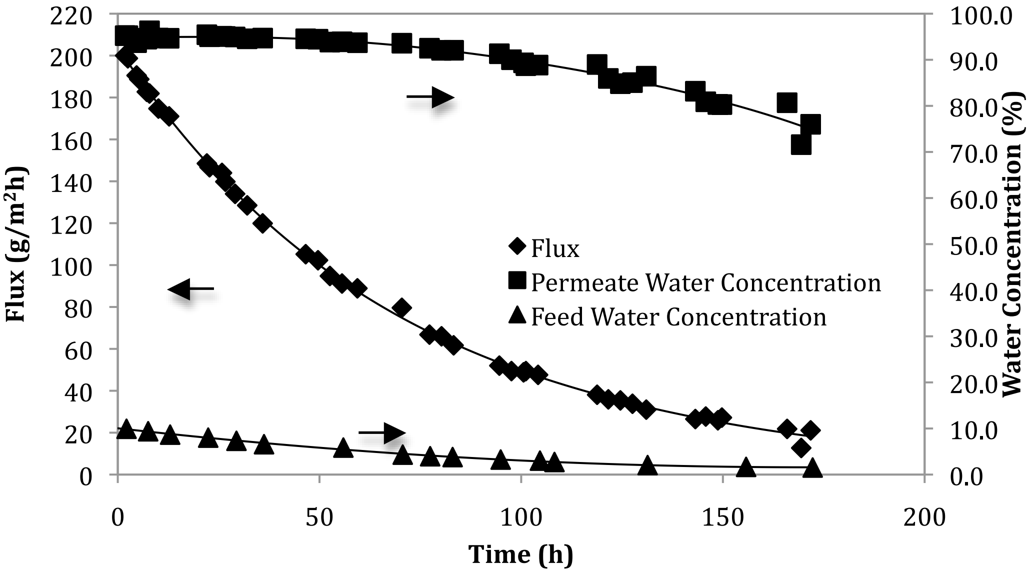


Figure 4.12. Flux, permeate water concentration and feed water concentration vs. time for PERVAP 2201 during concentrated-mode experiment. (2201/2, 3L feed, 70°C, 2 torr, 1.6 L/min, after temperature stabilization)

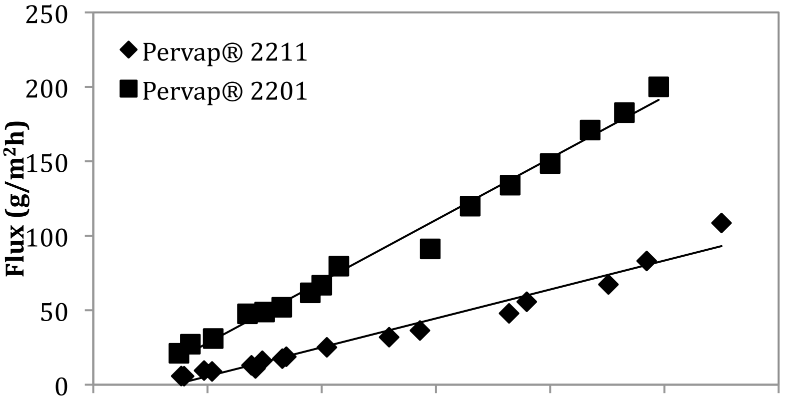


Figure 4.13. Change in flux with respect to feed water concentration during concentrated mode experiments (2201/2, 2211/5, 2 torr, 70°C, 1.6 L/min, after temperature stabilization)

To illustrate clearly how the performance of each membrane changed with respect to the change in the feed water concentration, fluxes and the permeate water concentrations of the experiments with respect to feed water concentrations were reported in Figures 4.13-15

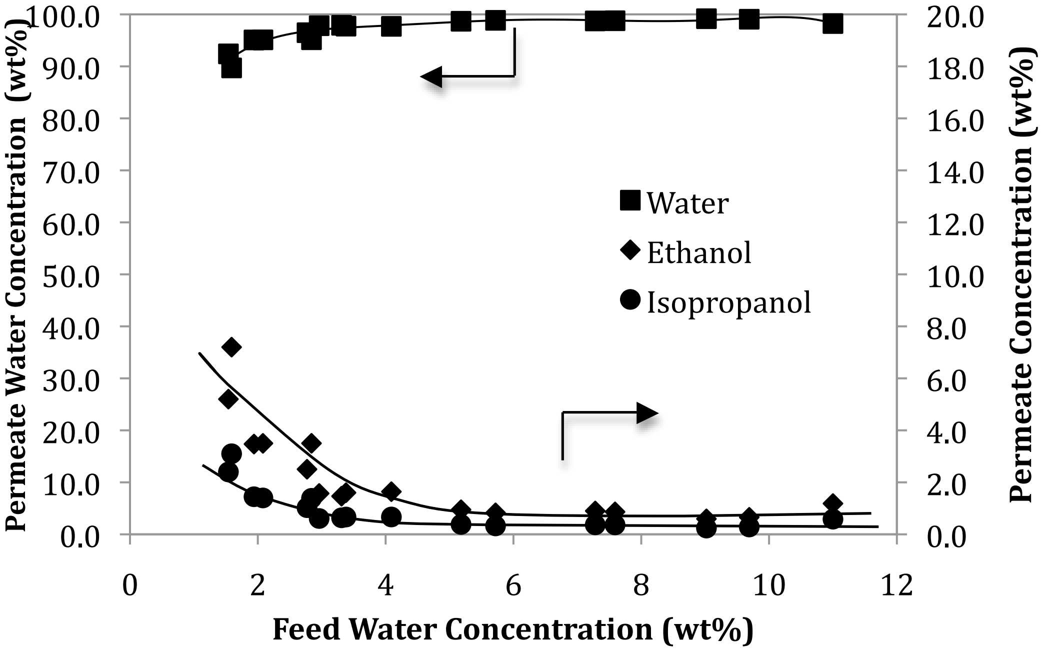


Figure 4.14. Change in permeate composition with respect to feed water concentration for PERVAP 2211 during concentrated mode experiments (2211/5,2 torr, 70°C, 1.6 L/min, after temperature stabilization)

The permeate fluxes through each membrane showed almost linear dependency to feed water concentration. The permeate water concentration of the membranes did not show strict dependency to feed water concentration at comparably higher water concentrations but started to decrease after feed water concentrations dropped below a certain value.

Similar trends were also observed in the literature. The permeate water concentrations were started to decrease at lower feed water concentration such as observed in this study and does not change with feed water concentration above that value. Qiao et. al. [21] studied dehydration of isopropanol and butanol isomers using PERVAP 2510 and 2201, van Baelen et. al.[27] studied isopropanol and ethanol dehydration using PERVAP 2201 and van Hoof et. al. [22] studied isopropanol dehydration using PERVAP 2510 membranes. Each group observed similar trends for the dependency of flux and permeate water concentration on the feed water concentration.

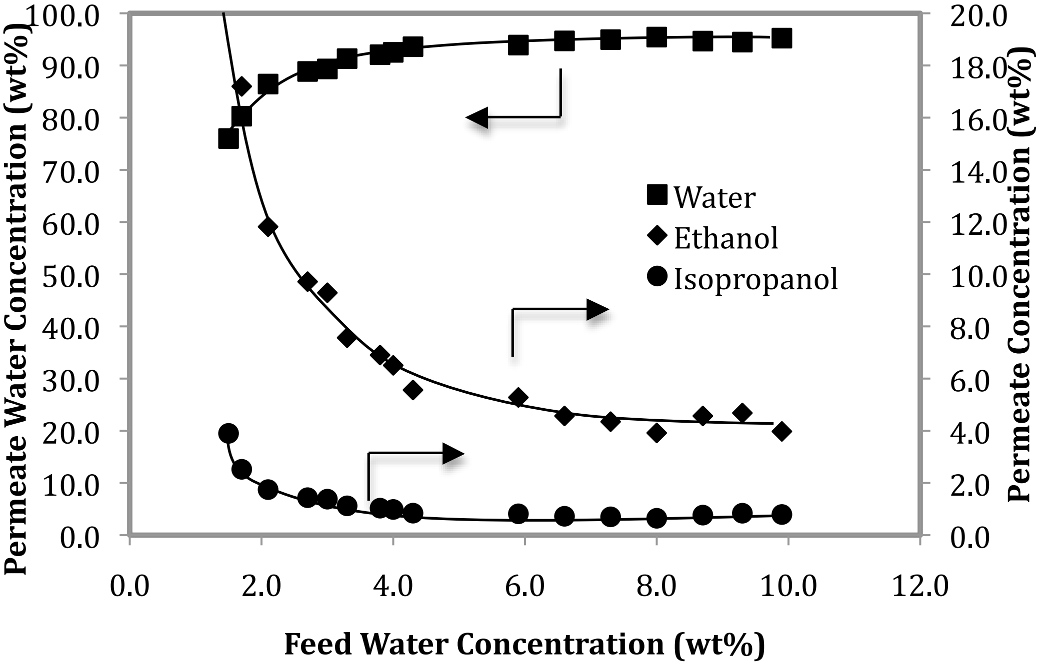


Figure 4.15. Change in permeate composition with respect to feed water concentration for PERVAP 2201 during concentrated mode experiments (2201/2, 2torr, 70°C, 1.6 L/min, after temperature stabilization)

Strict dependency of the permeate fluxes to the feed water concentration is an expected result since the swelling and the driving force through the membrane are both affected from the feed water concentration. Both swelling of membrane and the driving force of mass transport increases with the increase in the feed water concentration leading to an increase in the flux. The independency of the permeate water concentration from the feed water concentration may be regarded to the negligible potential gradient of the alcohol for transport through the membrane at higher feed water concentrations.[21] The increase in the permeate alcohol solutions in the permeate in lower water concentrations of the feed may be present as a result of the decrease in the water transport through the membrane therefore potential gradient of the alcohols came into significance.

The graph of flux vs. feed water concentration of PERVAP 2201 has higher slope than that of PERVAP 2211. Therefore, PERVAP 2211 showed lower dependency for a change in feed water concentration than PERVAP 2201. Increase in the water concentration of the feed may lead to higher swelling of PERVAP 2201 than PERVAP 2211. That is, water molecules can find more ways to transport to the permeate side of the membrane as the water concentration is increased with swelling. Similar trends were observed by Qiao et. al. during the dehydration of isopropanol using PERVAP 2510 and PERVAP 2201.[21]

The differences in the hydrophilicities of the membranes play role in the dependency of the selectivity of the membranes to feed water concentration. The permeate water concentration of PERVAP 2211 decreased from 99.0% to 90.0% when feed concentration of 3% is reached whereas that of PERVAP 2211 decreased from 94.0% to 75.0% after feed concentration of 5% by weight is reached. Having higher hydrophilicity and lower cross-linking, permeate composition of PERVAP 2201 was affected more from the change in the feed water concentration. As the water concentration is decreasing, other molecules in the feed solution can find more ways to diffuse through because of the lower packing density of PERVAP 2201. On the other hand, higher cross-linking of PERVAP 2211 leads the membrane to conserve the permeate water concentration until lower feed water concentrations than PERVAP 2201.

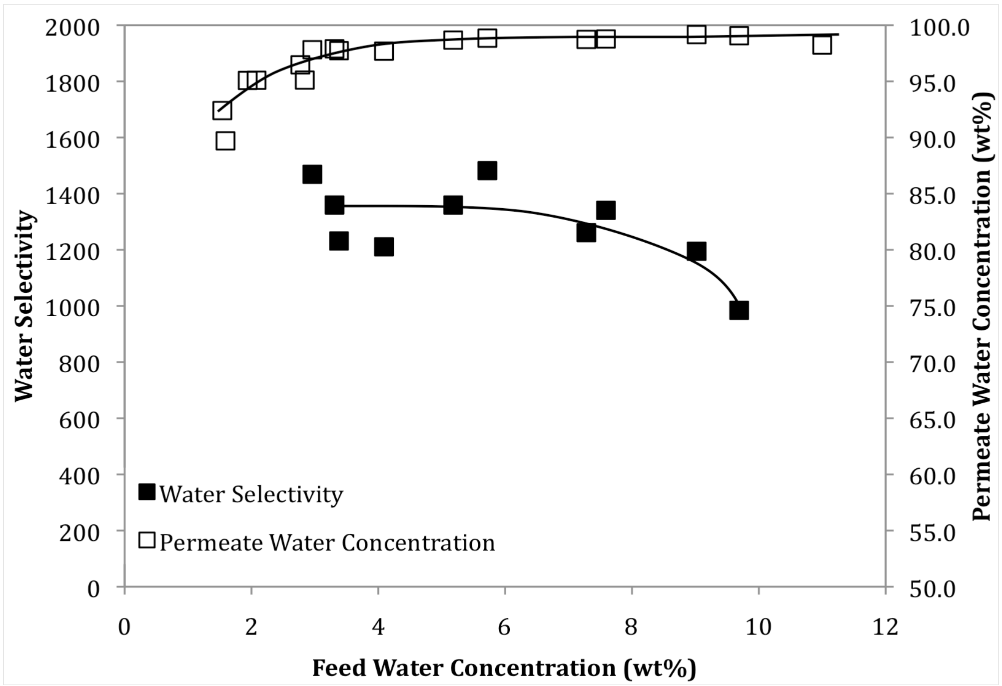


Figure 4.16. Water selectivity and permeate water concentration of PERVAP 2211 with respect to feed water concentration during concentrated mode experiments (2211/5, 2 torr, 70°C, 1.6 L/min, industrial feed, after temperature stabilization)

As the concentrations of the components of the feed mixture are changed, sorbed amount of each component in the polymer changes therefore influences the permeate composition. So, decreasing the water amounts of feed solutions leads to a decrease in permeate water concentration. But, this does not mean that the effectiveness of the membrane is decreased. As illustrated in Figure 4.16 and 4.17, membranes showed high selectivity towards water in the feed water concentration range studied in this work. As the feed water concentration decreases, the selectivity towards water is increased for both membranes resulting from the high hydrophilicity of the membranes.

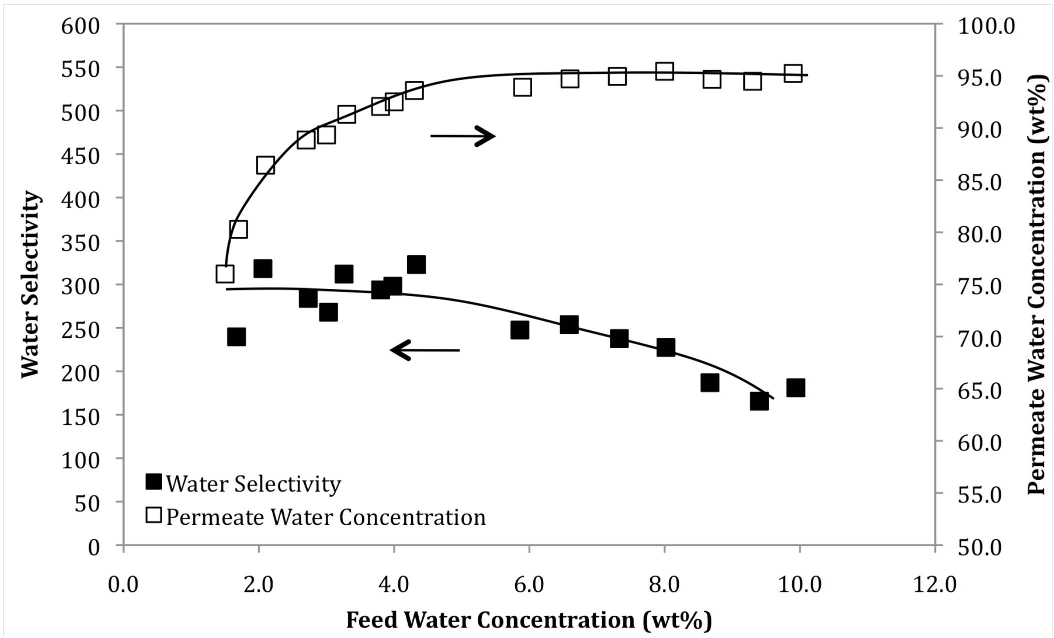


Figure 4.17. Water selectivity and permeate water concentration of PERVAP 2201 with respect to feed water concentration during concentrated mode experiments (2201/2, 2 torr, 70°C, 1.6 L/min, industrial feed, after temperature stabilization)

The decrease in the water concentration of the feed decreases also the swelling of the membranes. With lower swelling, the membrane becomes tighter creating narrower route for the transport of the molecules. Therefore the selectivity of the membrane is expected to increase at lower feed water concentrations as illustrated in Figure 4.16 and 4.17. Although the data of selectivity has some scattering because of the mathematical expression of selectivity, the trends showed a slight increase towards water selectivity at lower feed water concentrations.

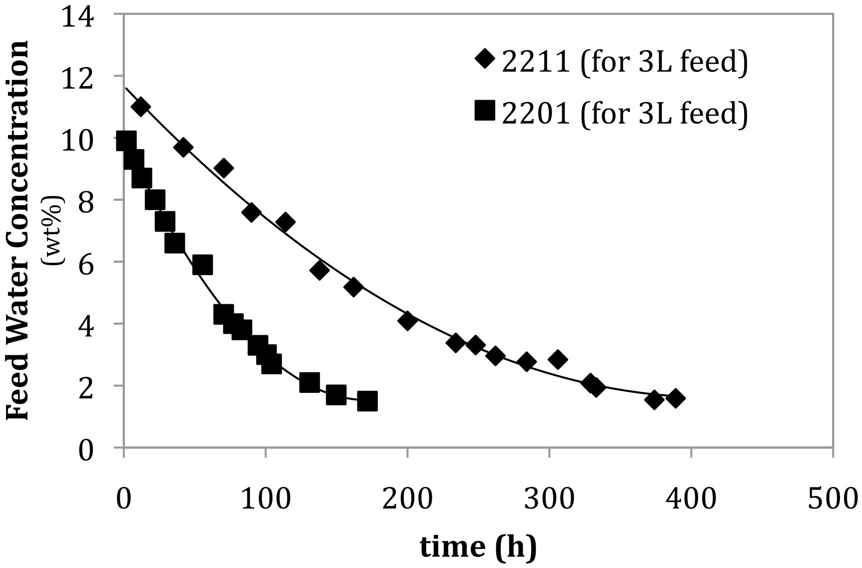


Figure 4.18. Change in feed water concentration during the concentrated-mode experiments (2201/2, 2211/5, 2 torr, 70°C, 1.6 L/min, after temperature stabilization)

Besides the analysis of the performance of the membranes at different feed water concentrations, the success of the pervaporation separation can best be investigated by observing the change in the water concentration of the retentates since the product of this process is the retentate and the objective of the separation is to lower the water concentration in the retentate. To observe this better and make comparison between use of each membranes, the time required for PERVAP 2211 to decrease the water concentration was calculated for 3L of feed and the trends are illustrated in Figure 4.18.

Although PERVAP 2211 is about two folds slower during the removal of water from the solution, both membranes were proved to be successful for the dehydration of the industrial feed solution as they perform satisfactory removal of water from the solution in the feed water concentration range studied. However exponential decay of the water concentration in the feed solution indicates that the rate of removal of water from the feed is efficient at higher feed water concentrations but lowers as the concentration in the feed decreases. For instance, the water concentration decreases from 8.0% to 4.0% at about 55 hours whereas decrease from 8.0% to 2.0% and 1.5% takes 110 and 150 hours, respectively, using a 148 cm^2 membrane and starting with a 3L of industrial feed solution. Therefore it would take very long time for the removal of the last 1% of the water from the feed solution.

4.10. Dehydration of the Alcohol Solution Using Liquid Phase Adsorption

It would take very long time to decrease the water concentration of the feed after 1.5% by weight with pervaporation only. Therefore, to shorten the time to decrease the water concentration to 0.1% by weight in the alcohol solution, liquid phase adsorption were conducted on the solution containing 1.5% water by weight at room temperature. The alcohol solution was synthesized to imitate the product of concentrated-mode pervaporation experiments. The result of this experiment is illustrated on Figure 4.19.

It can be observed that 600 mL of the solution was dehydrated to 0.04% water that corresponds to the removal of 6.9 g of water from the solution, that is the breakthrough capacity of 9.5%. In addition, the total capacity of the bed was found to be 18% by weight that is slightly lower than the capacity of 3A reported in the literature.[45] This may result from the use of binder to shape the zeolites to sphere.

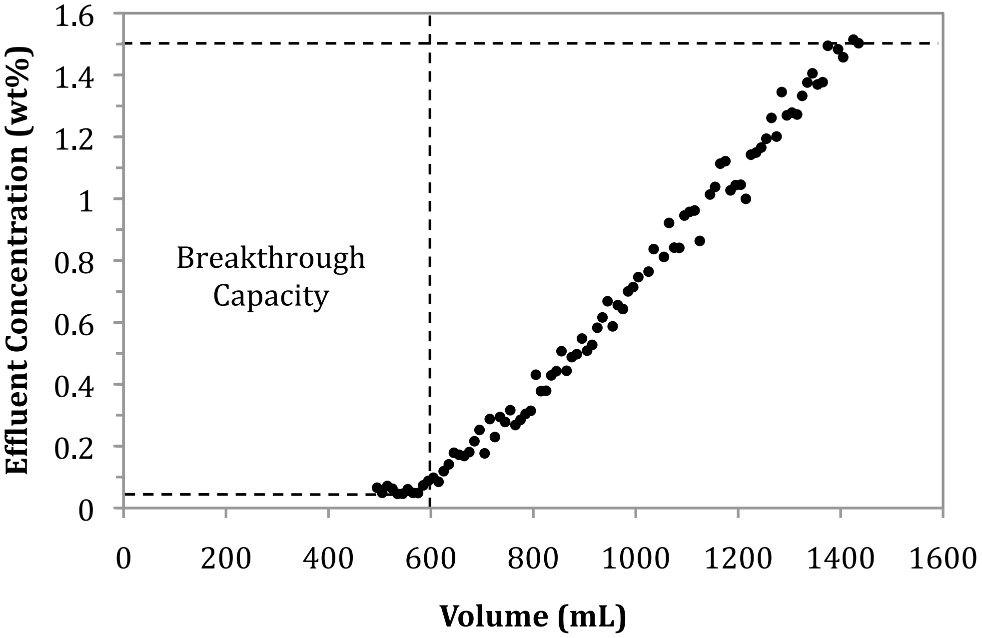


Figure 4.19. Breakthrough curve for dehydration of the 1.5% water/alcohol solution (72.8 g zeolite, 1.0 mL/min, RT, 1.5 wt% water in feed, after temperature stabilization)

As a result of the adsorption studies, the use of adsorption in combination with the pervaporation was found to be an advantageous alternative for the dehydration using a single stage pervaporation. Since the removal of water from the solution with pervaporation slows down at lower feed water concentrations, sequential scheme of pervaporation and adsorption would be a useful alternative. This novel separation scheme of distillation-pervaporation-adsorption system has advantages such as,

- Low cost of separation since pervaporation is an economical process, in addition, further reduction in cost could be possible by purging the permeate without condensation,
- Easy operation and control of the process parameters since the units were determined to be connected in series and no recycle stream is present.

Therefore the dehydration scheme for the solvent solutions could be a promising alternative over the traditional separation processes.

CHAPTER 5

CONCLUSIONS

The effect of operating parameters on the dehydration performance of pervaporation membranes PERVAP 2211 and PERVAP 2201 produced by Sulzer Chem-tech® for the industrial solution obtained from a domestic packaging and printing industry was investigated in this study. Feed temperature, feed flowrate, permeate side pressure, feed water concentration and feed ethyl acetate concentration was taken as the operation parameters.

The following conclusions were encountered during this study,

1. Both membranes were found to dehydrate the industrial feed solution and PERVAP 2201 was determined to be more successful in dehydration showing the industrial applicability of pervaporation for the dehydration of the solvent solution obtained from package printing.

2. Use of the novel sequential distillation/pervaporation/liquid phase adsorption separation scheme was shown to be successful in the dehydration of the solvent solutions below 0.1% by weight.

3. Operation of pervaporation at high temperatures is advantageous because flux increases significantly with an slight increase in the permeate water concentration as temperature is increased. It has greater effect on PERVAP 2211 that has more cross-linking.

4. Pervaporation separation performance is increased by keeping the permeate pressure as low as possible.

5. A feed flowrate higher than 0.6 L/min is sufficient to run pervaporation more effectively.

6. The minor components of the industrial feed solution has no significant effect on the performance of the membrane when they are in trace amount, but ethyl acetate may lead to swelling, i.e. increase in flux together with a decrease in selectivity, at higher concentrations.

7. The water concentration of the feed has more significant effect on permeate flux and composition through PERVAP 2201 due to its more hydrophilicity. Water selectivity of each membrane increased as the concentration of water in the feed solution is decreased.

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APPENDIX A

SPECIFICATIONS OF THE DEHYDRATION MEMBRANES PRODUCED BY SULZER CHEM-TECH®

The specifications of the polymeric dehydration membranes produced by Sulzer Chem-tech are illustrated at Table A.1.

Table A.1. Specifications of Sulzer Chem-tech® Polymeric Dehydration Membranes

Membrane Type	**Pervap™ 2200**	**Pervap™ 2201**	**Pervap™ 2211**	**Pervap™ 2216**
Main Application	for volatile organics and their mixtures	for volatile organics and their reaction mixtures	for volatile organics and their mixtures	for volatile organics and their mixtures
Max. Temperature, Long Term (°C)	95	95	100 (105 for EtOH)	100 (105 for EtOH)
Max. Temperature, Short Term (°C)	100	107	107	107
Max. Water Content in Feed, (wt%)	≤30	≤50	≤40	≤40
Major Limitations				
Aprotic Solvents (e.g. DMF, DMSO)	≤0.1 %	≤1 %	≤0.1 %	≤0.1 %
Organic Acids (e.g. acetic acid)	≤10 %	≤50 %	≤10 %	≤10 %
Formic Acid	≤0.1 %	≤0.5 %	≤0.1 %	≤0.1 %
Mineral Acids (e.g. H_2SO_4)	≤0.1 %	≤0.1 %	≤0.1 %	≤0.1 %
Alkali (e.g. NaOH)	excluded	≤ 10 ppm	≤ 10 ppm	≤ 10 ppm
Aliphatic Amines	≤0.1 %	≤50 %	≤1 %	≤1 %
Aromatic Amines (e.g. Pyridine)	≤0.1 %	≤50 %	≤50 %	≤50 %
Aromatic HCs, Ketones, Esters	no limitations	no limitations	no limitations	no limitations

Table A.1. *(cont'd)* Specifications of Sulzer Chem-tech® Polymeric Dehydration Membranes

Membrane Type	**Pervap™ 2510**	**Pervap™ 2210**	**Pervap™ 4101**	**Pervap™ 2255**
Main Application	for neutral alcohols, e.g. IPA, Butanols	for volatile neutral organics and their mixtures	for volatile neutral organics and their mixtures	Removal of MeOH from organics, low water cont. dehyd.
Max. Temperature, Long Term (°C)	95	95	100 (110 for EtOH)	85
Max. Temperature, Short Term (°C)	100	100	112	90
Max. Water Content in Feed, (wt%)	< 30	< 30	≤50	Upto 15
Major Limitations				
Aprotic Solvents (e.g. DMF, DMSO)	excluded	< 0.1 %	≤ 1 %	Excluded
Organic Acids (e.g. acetic acid)	< 0.1 %	< 0.1 %	≤ 10 %	< 100 ppm
Formic Acid	excluded	excluded	≤ 0.5 %	Excluded
Mineral Acids (e.g. H_2SO_4)	<0.1 %	< 0.1 %	≤ 1 %	Excluded
Alkali (e.g. NaOH)	excluded	excluded	≤ 10 ppm	Excluded
Aliphatic Amines	excluded	excluded	≤ 0.1 %	Excluded
Aromatic Amines (e.g. Pyridine)	excluded	excluded	≤ 0.1 %	Excluded
Aromatic HCs, Ketones, Esters	excluded	no limitations	no limitations	No limitations

APPENDIX B

DETAILED DRAWINGS OF MEMBRANE MODULES USED IN THE STUDY

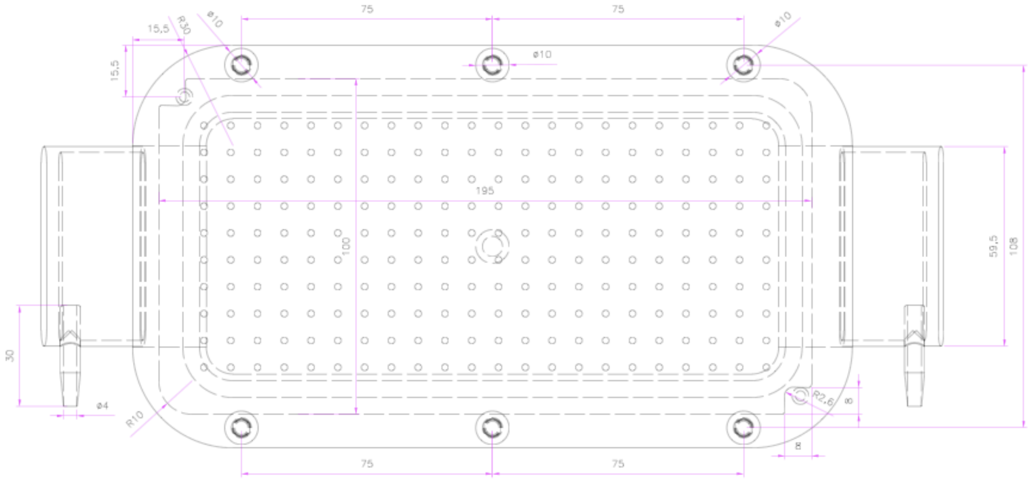


Figure B.1. Top view of the rectangular membrane module

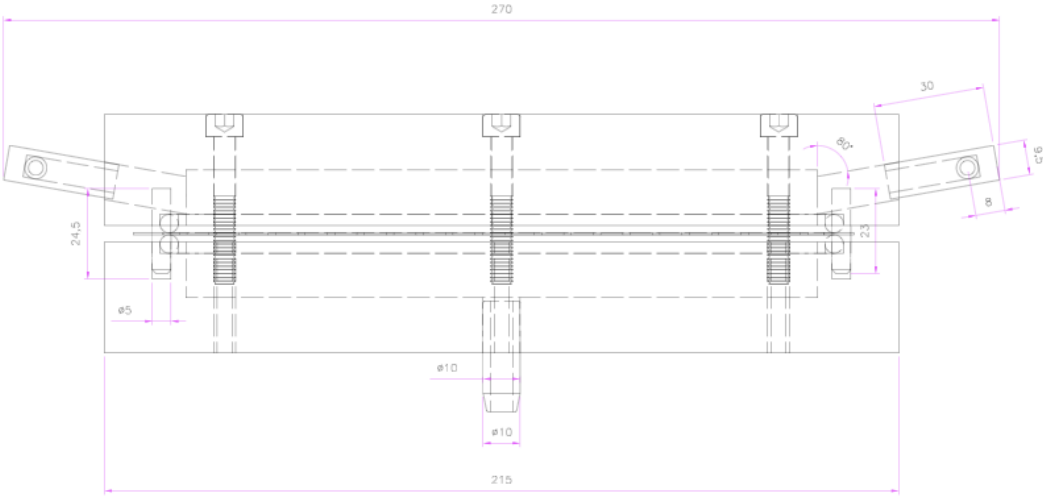


Figure B.2. Width view of the rectangular membrane module

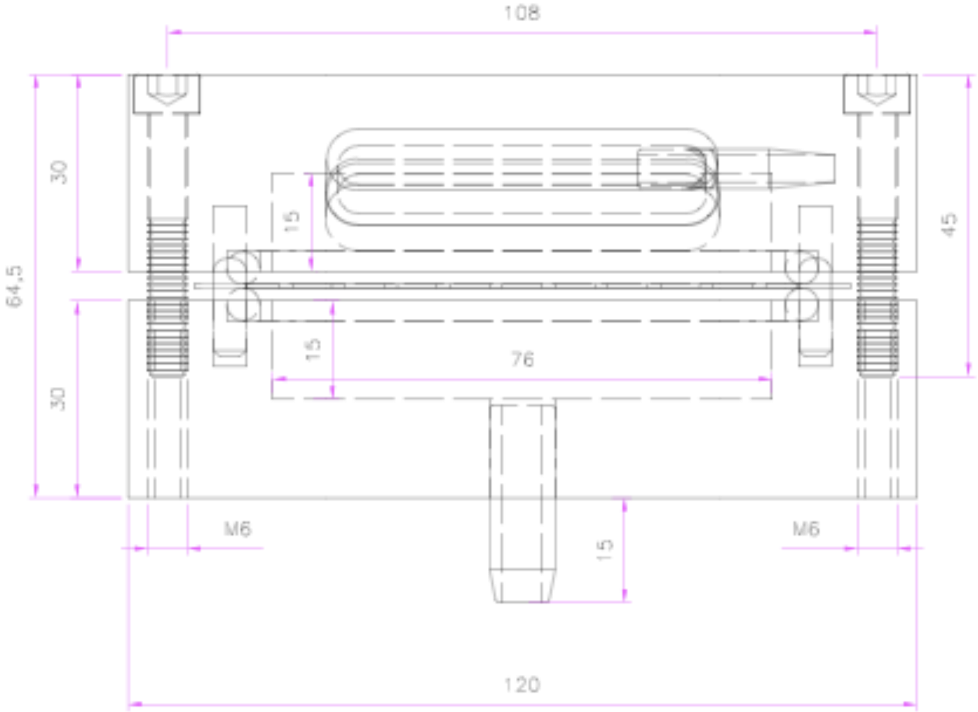


Figure B.3. Depth view of the rectangular membrane module

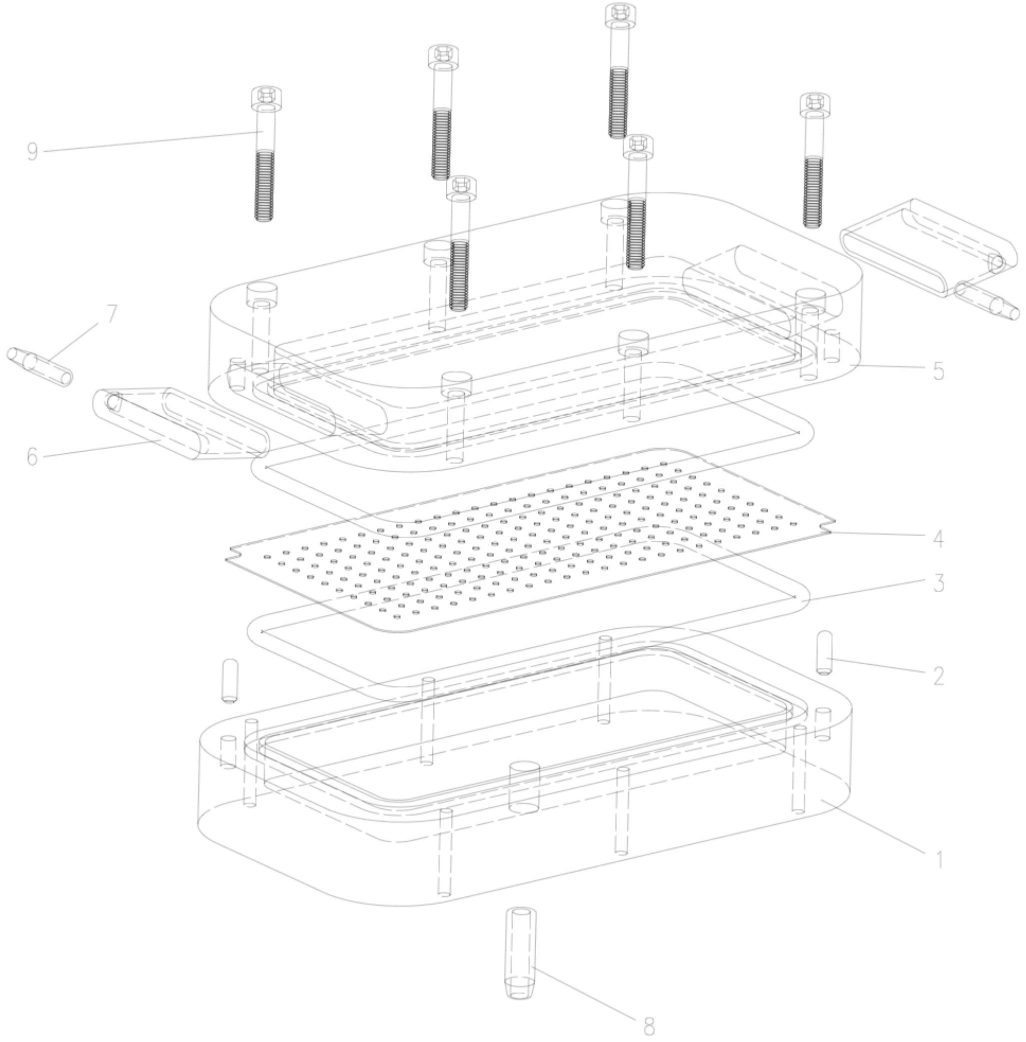


Figure B.4. Detailed parts of the rectangular membrane module

APPENDIX C

GAS CHROMATOGRAPHY CALIBRATION CURVES

Table C.1. Calibration data for gas chromatography analysis

Standard	Composition			Area			Mean Area		
	Ethanol	**IPA**	**EtOAc**	**Ethanol**	**IPA**	**EtOAc**	**Ethanol**	**IPA**	**EtOAc**
ST1	0.01			135467 124898			130183		
ST2	0.02			261604 249409			255507		
ST3	0.04			564538 533536 515974			538016		
ST4	0.06			838707 802944			820826		
ST5	0.08			1154780 1090740			1122760		
ST6	0.10			1362582 1310586			1336584		
ST1		0.01			143758 140483			142121	
ST2		0.02			299153 292410			295782	
ST3		0.04			616769 624797			620783	
ST4		0.06			964777 967898			966338	
ST5		0.08			1368189 1280120			1324155	
ST6		0.10			1594800 1723476			1659138	
E1			0.02			213381 243375 229573			228776.3333
E2			0.04			424064 426363			425213.5
E3			0.06			622116 642099			632107.5
E4			0.07			827859 822732			825295.5
E5			0.09			1048728 1042380			1045554

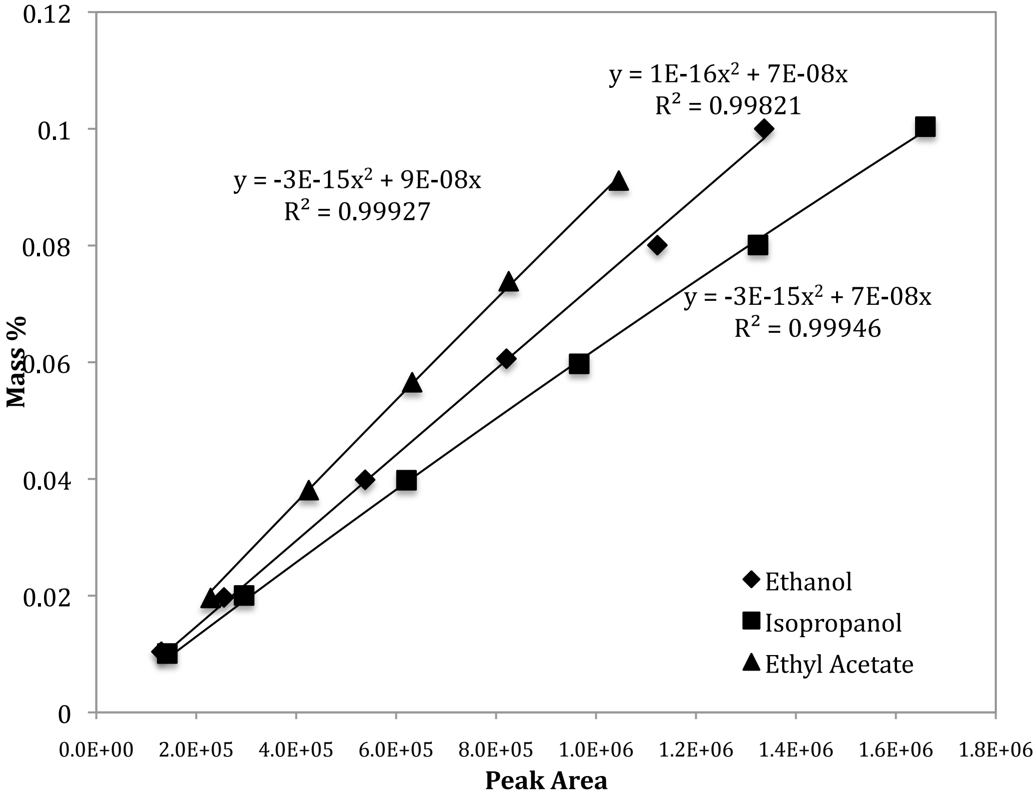


Figure C.1. Gas Chromatography calibration curve

APPENDIX D

EXPERIMENTAL DATA OBTAINED FROM THE EXPERIMENTS

Table D.1: Data obtained from the experiments

Pressure	2 torr
Module	Rectangular
Membrane	Pervap 2211

		Temp.	**Flux**		**Permeate Composition**			
Feed	**Membrane**	**(°C)**	**(g/m²h)**		**Water**	**EtOH**	**IPA**	**Date**
industrial	2211/2*	30	8.1	7.6	72.7	21	6.4	July 29,2009
industrial	2211/2*	30	7.6		85	10.6	4.4	July 30,2009
industrial	2211/2*	30	7		85	10.8	4.2	August 5,2009
industrial	2211/2	40	19.4	19.2	89.9	7.4	2.8	July 9,2009
industrial	2211/2	40	19		88.5	8.6	2.9	July 11,2009
industrial	2211/1	50	38.7	38.3	95.4	3.2	1.4	June 19,2009
industrial	2211/2	50	38.7		95.7	3.1	1.2	June 24,2009
industrial	2211/2*	50	37.3		96.3	3.1	0.6	August 24,2009
industrial	2211/2*	50	38.5		95.5	3.6	0.9	August 28,2009
industrial	2211/2*	60	80	78.2	95.7	3.6	0.8	August 26,2009
industrial	2211/2*	60	78.3		96.1	3.2	0.7	August 29,2009
industrial	2211/2*	70	124.3	123.8	98.3	1.6	0.1	August 1,2009
industrial	2211/2*	70	123.2		98.4	1.5	0.1	August 8,2009
industrial	2211/2*	77	142.2	142.2	98	2	-	September 8,2009
Synthesized	2211/2*	30	8	8	87.4	8.8	3.8	August 11,2009
Synthesized	2211/2*	40	18.3	18.3	94.8	3.6	1.6	August 12,2009
Synthesized	2211/1	50	33.8	34.9	95.2	3.3	1.5	June 20,2009
Synthesized	2211/1	50	33.6		95	3.5	1.5	June 25,2009
Synthesized	2211/2*	50	37.3		97.3	1.9	0.7	August 15,2009
Synthesized	2211/2*	60	68.1	68.1	98.1	1.4	0.5	August 19,2009
Synthesized	2211/2*	70	136.4	136.4	97.6	2	0.5	August 22,2009

Table D.1 (cont'd): Data obtained from the experiments

Pressure 2 torr
Module Circular
Membrane Pervap 2211

Feed	Membrane	Temp. (°C)	Flux (g/m^2h)		Permeate Composition			Date
					Water	EtOH	IPA	
industrial	2211/3c	50	22.8	23	99.1	0.9	0	October 19,2009
industrial	2211/3c	50	23.1		99.4	0.6	0	October 20,2009
industrial	2211/3c	60	59.4	59.5	99.8	0.2	0	October 21,2009

Temperature 50 C
Module Rectangular
Membrane Pervap 2211

Feed	Membrane	P (torr)	Flux (g/m^2h)	Permeate Composition			Date
				Water	EtOH	IPA	
Synthesized	2211/3	2	47.8	96.3	2.5	1.2	October 30,2009

Temperature 60 C
Module Rectangular
Membrane Pervap 2211

Feed	Membrane	P (torr)	Flux (g/m^2h)	Permeate Composition			Date
				Water	EtOH	IPA	
Industrial	2211/3	2	93.6	98.3	1.3	0.4	November 2,2009
Industrial	2211/3	2	103	97.8	1.7	0.5	November 10,2009
Industrial	2211/3	5	51.1	96.4	3	0.6	November 4,2009
Industrial	2211/3	5	44.3	94.7	4.5	0.8	November 13,2009
Industrial	2211/3	10	14.1	69.8	25.3	4.9	November 6,2009
Industrial	2211/3	10	13	78.1	18.5	3.4	November 14,2009

Pressure 2 torr
Module Rectangular
Membrane Pervap 2211

Feed	Membrane	Temp.	Flux (g/m^2h)	Permeate Composition			Date
				Water	EtOH	IPA	
Industrial	2211/3	40	25.2	95.7	3.4	0.9	November 18,2009
Industrial	2211/3		33	92	6.3	1.7	December 4,2009
Industrial	2211/3	50	57.6	97.8	1.8	0.4	November 20,2009
Industrial	2211/3		63.6	95	4.1	0.9	December 5,2009
Industrial	2211/3	60	107.8	98.5	1.5	-	November 21,2009
Industrial	2211/3	70	185.8	98.6	1.4	-	November 24,2009

Table D.1 (cont'd): Data obtained from the experiments

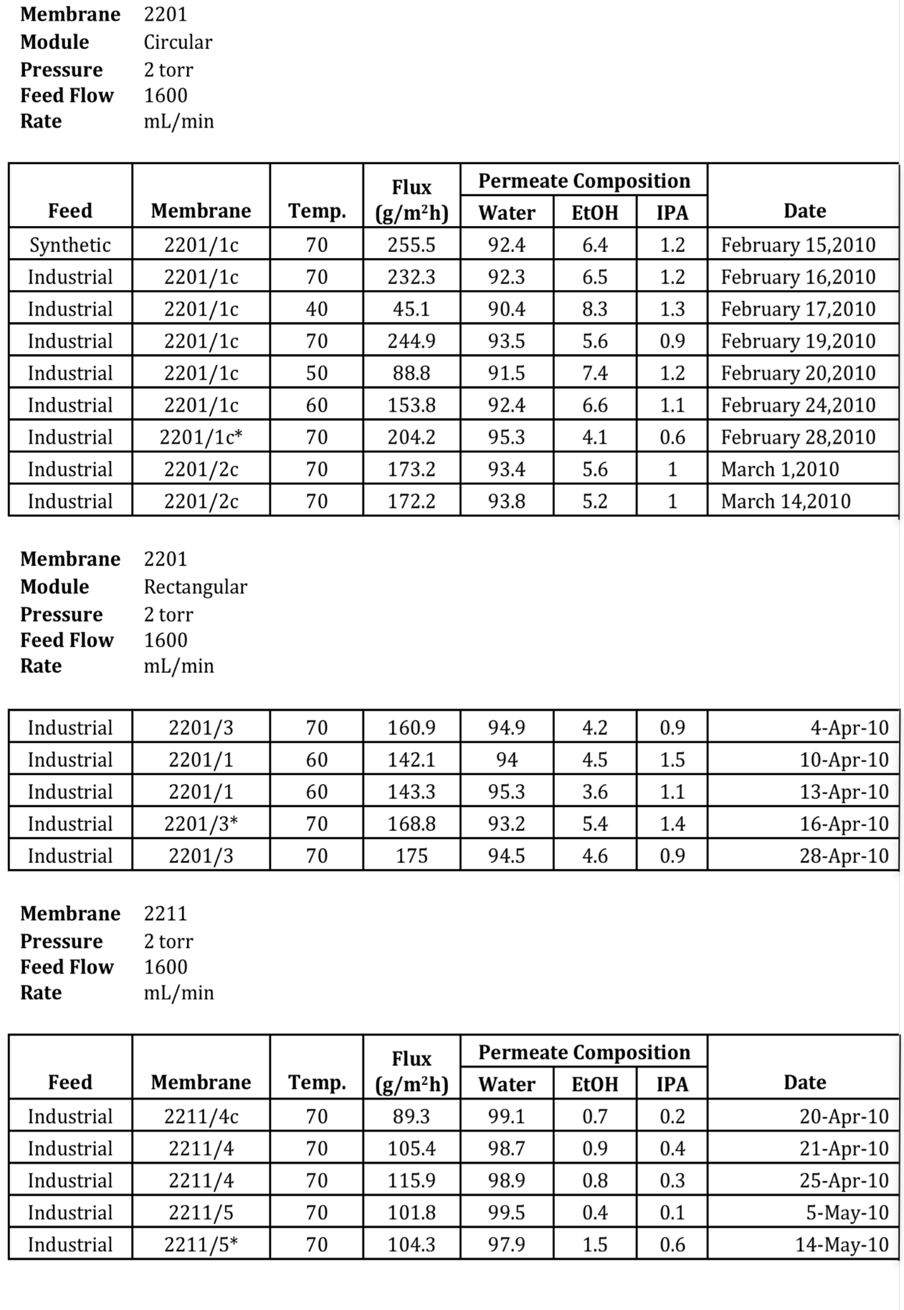
Pressure 2 torr
Module Rectangular
Membrane Pervap 2201

Feed	Membrane	Temp.	Flux (g/m^{2}h)	Permeate Composition			Date
				Water	EtOH	IPA	
Synthetic	2201/1	40	20.8	97.1	1.7	1.2	December 9,2009
Industrial	2201/1	40	24.8	94.2	5	0.8	December 11,2009
Industrial	2201/1		25.1	95.5	4	0.5	December 12,2009
Synthetic	2201/1	50	57.2	95.2	4.1	0.7	December 14,2009
Industrial	2201/1	50	55.9	96.4	3.1	0.5	December 16,2009
Industrial	2201/1		57.1	96.5	3	0.5	December 18,2009
Synthetic	2201/1	60	122.3	97.6	2.1	0.3	December 19,2009
Industrial	2201/1	60	116.8	97.3	2.3	0.4	December 22,2009
Industrial	2201/1		119.4	97.5	2.2	0.3	December 23,2009
Synthetic	2201/1	70	215.5	97.7	2	0.3	December 26,2009
Industrial	2201/1	70	229.1	97.6	2.1	0.3	December 27,2009
Industrial	2201/1		225.5	97.6	2.1	0.3	December 29,2009
Industrial	2201/1	50	75.6	98	1.7	0.3	December 30,2009
Industrial	2201/1	60	137.7	97.7	2	0.3	January 2, 2010
Industrial	2201/1	70	241.4	97.6	2.1	0.4	January 12, 2010
Industrial	2201/1	50	83.6	97.5	2.1	0.4	January 15, 2010
Industrial	2201/1	40	41.9	97.1	2.5	0.5	January 19, 2010
Industrial	2201/1	50	84.1	97.6	2.1	0.3	January 20, 2010
Industrial	2201/1	60	152.3	97.4	2.2	0.3	January 21, 2010
Industrial	2201/1	70	243.6	97.8	1.9	0.3	January 16, 2010

Membrane 2201/1
Module Rectangular
Temperature 60°C
Pressure 2 torr

Feed	Feed Flow	Permeate Composition			Flux (g/m^{2}h)	Date
		Water	EtOH	IPA		
Industrial	1600	97.4	2.2	0.3	152.3	January 21,2010
Industrial	650	97.6	2.1	0.3	140	January 21,2010
Industrial	650	97.1	2.5	0.4	149.6	January 25,2010
Industrial	250	97.5	2.2	0.3	113.8	January 25,2010
Industrial	250	97.1	2.5	0.4	121.3	January 28,2010
Industrial	250	97.7	2	0.3	122.6	January 29,2010
Industrial	1600	95.9	3.5	0.6	170.8	February 6,2010
Industrial	1600	95.8	3.5	0.6	171.3	February 12,2010

Table D.1 (cont'd): Data obtained from the experiments



Membrane 2201
Module Circular
Pressure 2 torr
Feed Flow Rate 1600 mL/min

Feed	Membrane	Temp.	Flux (g/m^2h)	Permeate Composition			Date
				Water	EtOH	IPA	
Synthetic	2201/1c	70	255.5	92.4	6.4	1.2	February 15,2010
Industrial	2201/1c	70	232.3	92.3	6.5	1.2	February 16,2010
Industrial	2201/1c	40	45.1	90.4	8.3	1.3	February 17,2010
Industrial	2201/1c	70	244.9	93.5	5.6	0.9	February 19,2010
Industrial	2201/1c	50	88.8	91.5	7.4	1.2	February 20,2010
Industrial	2201/1c	60	153.8	92.4	6.6	1.1	February 24,2010
Industrial	2201/1c*	70	204.2	95.3	4.1	0.6	February 28,2010
Industrial	2201/2c	70	173.2	93.4	5.6	1	March 1,2010
Industrial	2201/2c	70	172.2	93.8	5.2	1	March 14,2010

Membrane 2201
Module Rectangular
Pressure 2 torr
Feed Flow Rate 1600 mL/min

Industrial	2201/3	70	160.9	94.9	4.2	0.9	4-Apr-10
Industrial	2201/1	60	142.1	94	4.5	1.5	10-Apr-10
Industrial	2201/1	60	143.3	95.3	3.6	1.1	13-Apr-10
Industrial	2201/3*	70	168.8	93.2	5.4	1.4	16-Apr-10
Industrial	2201/3	70	175	94.5	4.6	0.9	28-Apr-10

Membrane 2211
Pressure 2 torr
Feed Flow Rate 1600 mL/min

Feed	Membrane	Temp.	Flux (g/m^2h)	Permeate Composition			Date
				Water	EtOH	IPA	
Industrial	2211/4c	70	89.3	99.1	0.7	0.2	20-Apr-10
Industrial	2211/4	70	105.4	98.7	0.9	0.4	21-Apr-10
Industrial	2211/4	70	115.9	98.9	0.8	0.3	25-Apr-10
Industrial	2211/5	70	101.8	99.5	0.4	0.1	5-May-10
Industrial	2211/5*	70	104.3	97.9	1.5	0.6	14-May-10

Table D.1 (cont'd): Data obtained from the experiments

Membrane 2201/3
Module Milipore
Pressure -13.0 psig
Feed Flow 1600
Rate mL/min

Feed	Membrane	Temp.	Flux (g/m²h)	Permeate Composition			Date
				Water	EtOH	IPA	
Industrial	2201/3-1	70	182	96.5	2.9	0.6	30-Apr-10
Industrial	2201/3-2	70	206.6	91.3	7	1.7	1-May-10
Industrial	2201/3-3	70	180.4	95.5	3.7	0.8	1-May-10

Membrane 2211/4
Module Milipore
Pressure -13.0 psig
Feed Flow 1600
Rate mL/min

Feed	Membrane	Temp.	Flux (g/m²h)	Permeate Composition			Date
				Water	EtOH	IPA	
Industrial	2211/3-1	70	112.5	98.9	0.8	0.3	7-May-10
Industrial	2211/3-2	70	129.5	99.3	0.5	0.2	8-May-10
Industrial	2211/3-3	70	123.5	99.2	0.6	0.2	8-May-10
Industrial	2211/3-4	70	127.4	98.9	0.8	0.3	9-May-10

Membrane 2201/3*
Module Milipore
Pressure -13.0 psig
Feed Flow 1600
Rate mL/min

Feed	Membrane	Temp.	Flux (g/m²h)	Permeate Composition			Date
				Water	EtOH	IPA	
Industrial	2201/3*-1	70	197.8	98.9	7.3	2.3	16-May-10
Industrial	2201/3*-2	70	208.5	99.3	5.2	0.9	16-May-10
Industrial	2201/3*-3	70	168.9	99.2	3.8	0.8	16-May-10
Industrial	2201/3*-4	70	182	98.9	2.7	0.6	17-May-10