DEHYDRATION OF AQUEOUS APROTIC SOLVENT MIXTURES BY PERVAPORATION

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I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

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ABSTRACT

DEHYDRATION OF AQUEOUS APROTIC SOLVENT MIXTURES BY PERVAPORATION

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Aprotic solvents are organic solvents which do not easily react with a substance dissolved in it and they do not exchange protons despite of their high ion and polar group dissolving power. Therefore, this characteristic property makes aprotic solvents very suitable intermediates in many industries producing pharmaceuticals, textile auxiliaries, plasticizers, stabilizers, adhesives and ink. Dehydration of these mixtures and recirculation of valuable materials are substantial issues in industrial applications. The conventional method for recovery of aprotic solvents has been distillation, which requires excessive amount of energy to achieve desired recovery. Hydrophilic pervaporation, which is a membrane based dehydration method with low energy consumption, may become an alternative. Because of high dissolving power of aprotic solvents only inorganic membranes can be employed for this application.

In this study three types of inorganic membranes (NaA zeolite, optimized silica and HybSi) were employed. Main objective of this studys to investigate effect of membrane type and various operationg parameters (feed composition at a range of 50-5% and temperature at a range of 50-100^{o}C) on pervaporative dehydration of aprotic solvents; dimethylacetamide, dimethylformamide and n-methylpyrrolidone. During the experiments, feed samples were analyzed with Karl Fischer Titration Method; permeate samples were analyzed with Gas Chromatography.

Experiments showed that proper dehydration of aqueous aprotic solvent mixtures was succeded with all three membranes investigated. In the target feed water content range (50 to 20%wt), permeate water contents were higher than 98%wt which was quite acceptable for all membranes. Moreover, NaA zeolite membrane performed higher fluxes than optimized silica and HybSi in composition range of 50 to 15% water at 50^{o}C. It was also observed that HybSi membrane had higher fluxes and permeate water contents than optimized silica membrane for all solvents. On the other hand, the rates of decrease in permeate fluxes changed depending on the type of solvent for optimized silica and HybSi membranes. With both membranes, permeate flux of dimethylformamide decreased much slower than that of n-methylpyyrolidone. Furthermore, the results showed that permeate fluxes of HybSi membrane increased with increasing operation temperature due to the change of solvent activity in mixture. In addition, an Arrhenious type equation was used to describe changes in fluxes with changing temperature. It was also found that activation energy of water for diffusion through HybSi membrane was calculated as 8980 cal/mol.

Keywords: Pervaporation, Aprotic solvent, Inorganic membranes, NaA zeolite membrane, optimized silica membrane, HybSi membrane

ÖZ

SULU APROTİK SOLVENT KARIŞIMLARININ PERVAPORASYON İLE SUSUZLAŞTIRILMASI

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Şubat 2012, 94 sayfa

Aprotik çözücüler içinde çözündükleri maddelerle kolaylıkla reaksiyona girmeyen organik malzemelerdir ve bu çözücüler, yüksek iyonik ve polar grup çözücülüklerine rağmen, çözünürlerken proton değiş tokuş etmezler. Bu karakteristik özellikleri aprotik çözücüleri farmasotik ürünler, tekstil mamulleri, plastikleştiriciler, stabilizörler, katkı maddesi ve mürekkep gibi ürünleri imal eden endüstriel sektörler için çok uygun bir çözücü haline getirir. Bu karışımların susuzlaştırılması ve değerli çözücülerin üretime geri beslenmesi endüstriel faaliyetlerin önceliğidir. Bu amaçla kullanılan geleneksel metod distilasyondur ki bu yöntem istenilen geri kazanım için fazlasıyla enerji gerektirmektedir. Su-seven pervaporasyon, organik solüsyonların az enerji harcanarak susuzlaştırılmasını sağlayabilecek bir membran prosesi olarak alternatif olabilir. Aprotik çözücüler yüksek çözme güçleri sebebiyle sadece inorganik membranlar ile kullanılabilirler.

Bu çalışmada üç farklı inorganik membran ki bunlar NaA zeolit, optimize silika ve HybSi kullanılmıştır. Temel amaç membran tipinin (NaA zeolit, optimize silica ve

HybSi) ve çeşitli operasyon parametrelerinin (besleme su içeriği %50'den %5'e, sıcaklık 50'den 100°C'ye), bazı aprotik çözücü karışımlarının (dimethylacetamide, dimethylformamide ve n-methylpyrrolidone) pervaporasyonla susuzlaştırılmasına etkisini incelemektir. Deneyler sırasında, besleme numuneleri Karl Fischer Titrasyon yöntemi, süzüntü numuneleri ise Gaz Kromotografi kullanılarak analiz edilmiştir ve çözücü konsantrasyonları ölçülmüştür.

Çalışma sonuçları göstermektedir ki, sulu aprotik solvent karışımlarının uygun şekilde susuzlaştırılması üç membranla da sağlanmıştır. Hedeflenen su içeriği aralığında (%50'den %5'e), süzüntü su içerikleri üç membran için de %98'in üzerindedir. Bunun yanında, NaA zeolit membran %50'den %15'e kadar besleme suyu kompozisyonunda ve 50 °C'de, optimize silika ve HybSi membranlara göre daha yüksek süzüntü akısı ve süzüntü su içeriği sağlamıştır. Ayrıca, HybSi membran üç solvent için de optimize silikaya göre daha yüksek akı ve süzüntü su içeriği sağlamıştır. Öte yandan, optimize silika ve HybSi membranlar için süzüntü akısındaki düşüş hızı çözücünün türüne bağlı olarak değişiklik göstermiştir. İki membran için de dimethylformamide karışımının süzüntü akısı n-methylpyrrolidone karışımınınkinden daha yavaş düşüş göstermiştir. Dahası, elde edilen sonuçlar HybSi membrandaki süzüntü akılarının artan sıcaklıkla birlikte karışımlardaki çözücü aktivitelerinin değişimi sebebiyle arttığını göstermiştir. Bununla birlikte, akılardaki sıcaklığa bağlı değişimleri tanımlayabilmek için Arrhenious tipi bir denklemden faydalanılmıştır. Ayrıca, HybSi membrandan suyun difuzyonu için gereken aktivasyon enerjisi 8980 cal/mol olarak hesaplanmıştır.

Keywords: Pervaporasyon, Aprotik solvent, İnorganik membranlar, NaA zeolit membran, optimize silika membran, HybSi membran

To my beloved mother and father

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Symbols

x	mass fraction in feed
y	mass fraction in permeate
R	reflux ratio
D	debye
J	flux, g/m^2h
E	energy
N	permeation flux, g/m^2h
Q	quantity of permeate collected,g
Δt	time interval, min
A	area of selective layer
x_D	water composition in top product of distillation column
R_{min}	minimum reflux ratio

Abbreviations

DMAc	dimethylacetamide
DMF	dimethylformamide
NMP	n-methylpyrrolidone
THF	tetrahydrofuran
PV	pervaporation
wt	weigth
T1	feed tank 1

H1	heater 1
P1	pump 1
V1	valve 1
MM	membrane module

Greek Letters

α	separation factor

Subscripts

wat	water
sol	solution
min	minimum
act	activation
i	component ‘i’
j	component ‘j’

CHAPTER 1

INTRODUCTION

Sectors using different solvents have excessive amount of solvent recovery expenses which have a major contribution to overall production cost. [1] Recovery of those solvents are also important by considering their effect on environment after facility discharges. [2] Large share of used solvents are facilitated and recycled with the help of different methods. These solvent recovery methods are focused to develop due to their energy consumptions. By considering tremendous boost in membrane technologies in the last decade, membranes seem to be one of the most promising alternatives for process improvements.

With the high dissolving power characteristic, aprotic solvents are used in the production of pharmaceuticals, plasticizers, adhesives, synthetic leathers, fibers, films, surface coatings, inks and dyes. The main feature which distinguishes aprotic solvents from others having high dissolving power is that they do not share acidic hydrogen due to not having hydrogen bonding. So, they allow balancing ions in their solution without changing acidity. Dimethylacetamide (DMAc), dimetylformamide (DMF) and n-methylpyrrolidone (NMP) are three aprotic solvents commonly encountered in industrial applications. These are mixed with water at different steps of manufacturing with different compositions.

Dehydration of those mixtures is an important issue both by economical and environmental reasons. Beyond the economy of solvent recovery, environmental issues also impose proper solvent recovery processes. Distillation and extraction have been two main conventional methods for solvent recovery. [3] Especially, distillation comes forward for dehydration of aprotic solvents. Some domestic factories have used several distillation columns in series so that highly purified solvent stream could be recycled. However, energy consumption of distillation and additional solvent requirements of extraction are the major problems which encourages searches for alternative separation methods.

Membranes challenge these conventional techniques nowadays. Pervaporation (PV) implying ‘permeation’ and ‘vaporization’ is the most suitable membrane process for liquid mixtures.[4] While one side of membrane layer is in contact with mixture, other side is kept under very low total or partial pressure with the help of vacuum or a sweeping gas respectively. Molecules selectively passing through boundary layer due to their polarity, higher affinity and/or faster diffusivity are vaporized and removed from surface immediately. Therefore, desired species are enriched at permeate side during remaining ones are also enriched at retentate side simultaneously.[4] There are two crucial benefits of PV that makes it favorable among other solvent recovery applications. First, PV is relatively low energy consuming process. Required energy for the vaporization of the materials which are passing through the membrane, is supplied by latent heat of mixture. Therefore great amount of energy saving is achieved. Furthermore, the energy requirement of PV process to keep mixtures at certain temperature and permeate side at low pressure is much less than the energy requirement of the distillation process to boil mixture for a similar separation effeciency. [5,6] Moreover, since high boiling points and heat of vaporizations of aquatic aprotic solvent mixtures restrict the usage of distillation, advantage of PV over distillation escalates. [5,6] Second, PV membrane provides very high selectivities. [7,8] While, some thermodynamic limitations such as azeotrope formation may prevent reaching very high selectivities in distillation process, PV is an independent process from thermodynamics of mixture. [9] Additionally, desired selectivities can be achievable by using proper membranes so that this handicap of distillation can be overcomed with PV. [8] Moreover, PV is such a process that it can be easily integrated to process without interrupting continuity, and also easily scaled up to compete high flow rates. [10]

PV is performed in numerous studies and succeeded to the efficient separation. [10] Although, most of the studies have focused on polymeric membranes, increasing attention to inorganic ones is also undeniable. [11] There are some advantages of inorganic membranes over the polymeric membranes. While aprotic solvents are in contact with polymeric mebrane surface, almost all polymers dissolve and the membrane loses its characteristic of seperation features. However, inorganic membranes provide high chemical stability, so that these types of membrane can be used in PV of aprotic solvents. Van Hoof et al. [12] compare PV performances of NaA type zeolite membranes with polymeric membranes. Isopropanol/water, acetonitril/water and methylethylketon/water mixtures were examined for that purposes in composition range of 0-20%wt water in feed at 70°C. They concluded that NaA type zeolite membranes had higher thermal and mechanical stability than polymeric ones. On the other hand, Sommer et al. [13] investigated A-type zeolite membranes in the dehydration of industrial solvents including DMAc and DMF which are major interest in this study. The permate fluxes were 1.51 kg/m^{2}h and selectives for water over DMAc and DMF were 1600 and 2400, at 70°C, at 10.5 and 9.1%wt feed water content repectively. Sommer et al. [14] also studied on chemical stability of commercial A-type zeolite and amorphous silica membranes during PV for industrial organic solvents. Investigations on PV applications of aprotic solvents with inorganic membranes point out that both methodology and material meet expectations about dehydration of those solvents. Yet, available published data show that studies have been done with limited number of compositions, temperatures and membranes combinations, despite of the distinguishing potential of PV applications.

Although profitable applicability of PV processes of inorganic membranes have been already discovered, its integration to industry has still some obstacles. One of the most important concerns is the capital cost of commercial inorganic membrane systems. Fortunately; increasing operational cost of conventional separation methods due to their energy demand and decreasing fabrication cost of commercial inorganic membranes come to a point that, inorganic membranes conduce to increase in preference of PV systems. Another concern is operational fluxes. Industrial processes demand very high fluxes and achieving high fluxes is seem to be doubtful for now by using PV alone. Therefore, hybrid systems including both distillation and PV are investigated. Many studies [1,5,6,15] indicate the advantages of hybrid processes such as energy saving potentials and economic benefits. The most popular approach is placing a membrane after top stream of distillation column so that any azeotrope formation is exceeded. [5] This approach fits well to aqueous alcohol mixtures implying solvent rich top stream of distillation. It is probably valid for aqueous aprotic solvent mixtures having solvent rich bottom product of distillation. However, considering high boiling points and heat of vaporization of those mixtures, it is probably better to feed smallest amount of water to distillation column so that smallest amount of total mixture goes to boiler due to distillation dynamics; eventually, energy consumption in boiler is decreased. Therefore, both energy consumption of boiler is decreased and amount of solvent rich bottom product is increased simultaneously. This could be provided by placing a membrane before inlet stream of distillation which is an exceptional concept, since formations in literature usually propose integrating PV after distillation columns. [1,5,6,15] This approach was investigated by desing of an hybrid system and energy requirement calculataions. In previous PV studies show that almost all stayed in the range between 0% to 20% water content (w/w), and none of the PV studies investigated water content above 20% so far. One of the reasons of this might be that PV is still considered as polymeric membrane process. Since polymeric membranes have swelling problem and it is more effective at higher water contents [7], this common limit is accepted in time consequently. On the other hand, inorganic membranes are much more stable for high water contents than polymeric ones, yet they are not preferred beyond limits of polymeric membranes.

The possibility of removing water from inlet stream of distillation column by using hydrophilic inorganic membranes is examined in this study. Thus, energy consumption of distillation process of aprotic solvents can be reduced 10 or 20% decrease in water content of feed to distillation without losing any solvent is expected to save substantial amount of energy. Therefore, the water content of solution fed to PV system is kept between 10 to 50%wt water by considering industrial distillation applications that is completely unusual and new point of view. Most of the articles [4,7,11] offer PV applications after reaching 5% water where experiments in this study stops before that point. In this study; very new approach to separation techniques by advance use of commercial A-type zeolite, optimized silica and HybSi membranes with DMAc, DMF and NMP, is provided with experimental data. Experiments were conducted in composition range 10 to 50%wt water in feed and in temperature range 50 to 100^{o}C.

CHAPTER 2

LITERATURE SURVEY

2.1 Description of Pervaporation Process

Pervaporation is a common membrane process that is used for separation of liquid mixtures. First studies on PV [4] emerged in 1950s. It was commercialized in 1980s and its industrial applications were spread in 1990s. Jonquieres et al. [16] stated that industrialization of pervaporation rapidly increased with various purposes worldwide between early 1980s and late 1990s. Some examples of those industrial applications which were installed by GFT (today Sulzer Chemtech) were represented in Figure 2.1.

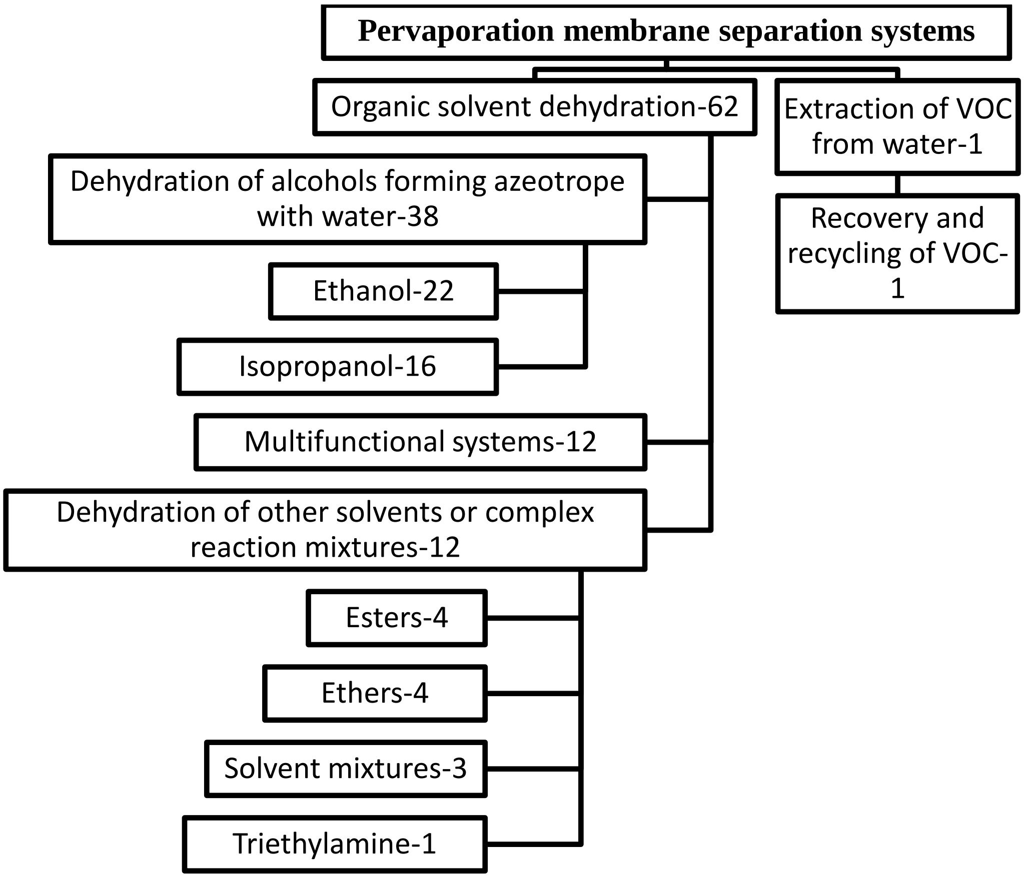


Figure 2.1.The 63 pervaporation membrane separation systems installed by GFT and associates within a period of time of 12 years between 1984 and 1996 [16]. The figure also shows the number of PV systems installed for a specific separation.

In pervaporation process liquid feed is in contact with one surface of membrane while other surface is kept under low pressure. Some molecules preferentially permeate through selective layer. The material passing through membrane is called as ‘permeate’ and the part of feed which is retained in other side is called as ‘retentate’. [4,11] The permeate evaporates due to low pressure which is a characteristic feature of pervaporation. [7] Low pressure can be created by either applying vacuum or using an inert purge gas which is usually nitrogen. Vacuum is generally preferred when permeate is desired product so that further separation of purge gas and permeate is avoided. [4] In some applications, retentate is recycled and given to feed to concentrate the feed. Accordingly, this method allows the enrichment of feed with the materials which are selectively sieved by the membrane. [8] Pervaporation with concentrated feed technique is simply illustrated in Figure 2.2.

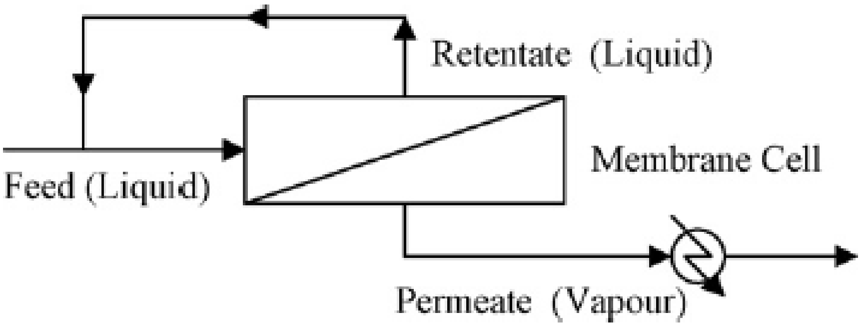


Figure 2.2. Pervaporation with concentrated feed technique [8]

There are some advantages of pervaporation systems over conventional separation techniques, which lead to an increase in demand of pervaporation applications. First of all, pervaporation is a selective sieving process that makes very high reachable concentrations at permeate side without any thermodynamic limitations. Consequently, any separation limitation due to azeotrope formation or close-boiling components can be handled with pervaporation. [11] Secondly, pervaporation requires relatively lower energy when it is compared with traditional separation methods, especially distillation method. During pervaporation process, only a fraction of feed (permeate) evaporates, while large amount of mixture has to be boiled in distillation. [17] Thirdly, no additional material, which contaminates product and necessitates further separation steps, is used in pervaporation. [4,11] Fourthly, pervaporation can be integrated into continuous systems and scaled up easily. [4,11]

Application areas of pervaporation are very wide (Figure 2.1). They are basically divided into three groups; dehydration of organic solvents, removal of organics from aqueous solutions and separation of organic-organic solutions. [10] Dehydration of organic solvents dominates both industrial applications and laboratory researches. [3,7,16] Recovery of organic solvents is a significant concern because of economic and environmental reasons. Accordingly, solvents may be recycled and reused with minimum waste production and energy consumption with a proper separation process.

There are two major parameters to evaluate the success of pervaporation process. First one is permeate flux which defines the permeate amount per unit area and time. It is calculated by using formula 2.1:

$$N = \frac{Q}{A.\Delta t} \qquad (2.1)^{[7]}$$

where N is permeation flux, Q is the quantity of permeate collected in time interval Δt and A is the area of selective layer. Second one is separation factor which is calculated with formula 2.2:

$$\alpha_j^i = \frac{{y_i}/{y_j}}{{x_i}/{x_j}} \qquad (2.2)^{[7]}$$

where x and y are compositions of species in feed and permeate respectively. [7] The high permeation flux represents quicker separation and less membrane area requirement. In addition, the higher separation factor becomes, the more selective process can be performed. Consequently, high permeation flux and separation factor are generally desired for pervaporation applications. These parameters are directly correlated with membrane and solvent properties, feed composition and operation temperature. [18]

2.2 Effect of membrane type on PV performance

Pervaporation membranes are categorized in to three major groups due to their application purposes. They are hydrophilic, hydrophobic and organophilic membranes. [10] Organophilic membranes are used for separation of organic-organic liquid mixtures and their application area currently is limited with lab-scale biological products. Hydrophobic ones are usually preferred for removal of volatile organic compounds (VOCs) from aqueous mixtures. On the other hand, almost 80% of pervaporation systems including large scale applications use hydrophilic membranes since dehydration of aqueous mixtures is the most common application of pervaporation worldwide. [10]

Membranes are subdivided into two groups which are organic and inorganic membranes according to their material. Membranes, which are made by numerous organic materials (polymers), are available and they are more widely used than inorganic ones due to several advantages. [4,7] The most important advantage is that fabrication of polymeric membranes is both easier and cheaper than fabrication of inorganic membranes more than acceptable. Furthermore, separation performances of polymeric membranes are more than enough for many applications. [4,7] Moreover, polymeric membrane modules have a great advantage of having higher area/volume ratio over inorganic membrane modules. It implies that polymeric membranes offers more compact operations with same membrane area than inorganic membranes. On the other hand, there are some handicaps of polymeric membranes which make inorganic ones favorable in last decade. [12,19] Polymeric membranes have operational limits of temperature and pressure, whereas inorganic membranes have relatively much higher thermal and mechanical stability. In addition, when compared to polymeric membranes, chemical stability and pH tolerance of inorganic membranes are much higher. Therefore, many mixtures, which are not possible to be separated with polymeric membranes, can be separated by inorganic membranes. [12–14,19] It is also important that swelling which is a serious problem for most of the polymeric membranes [7] is not an issue for inorganic membranes. [11] Moreover, many studies [20,21] conducted by using inorganic membranes show that selectivities and permeabilities of inorganic membranes are as high as those of polymeric membranes. The major disadvantage of inorganic membranes is manufacturing cost. In conclusion, application areas of inorganic membranes are broadened because of many advantages over polymeric membranes despite economic concerns.

There are basically two types of inorganic membranes, crystallized and amorphous membranes which are categorized due to their structures. [11] Zeolite membranes have uniform crystallized surface structure and they are called with the type of zeolite in their content such as; A type, T type, X type etc. Furthermore, their uniform and continuous structure result with an extensive molecular sieving and a high separation factor. [11] Mechanism of molecular transport through zeolite membranes can be explained in three steps. Initially, some molecules in the feed are adsorbed by membrane and interact with the active sites of zeolite crystals. Then, those molecules diffuse through zeolite pores by moving on one site to another due to chemical potential gradient. Finally, they are desorbed from membrane surface when they reach to permeate side. [4,11] It is considered that permeation flux of any material through selective layer depends on its adsorption-desorption rate and molecular interaction with active sites. It is also known that separation factor depends on the size of zeolite pores and the hydrophilic/hydrophobic nature of zeolite. [8,10,21,22] On the other hand, ceramic membranes have amorphous silica layers and they contain some cavities in certain extend. [24] They have similar thermal and mechanical resistance with zeolite membranes. There are many commercial silica membranes which are composed of several amorphous layers on top of each other so that their selective layers are optimized in different ways such as; pore size and thickness. Besides, some studies [13,20,25] showed that permeation fluxes of silica membranes were higher than zeolite membranes, while zeolite membrane had better separation factors at similar operation conditions. [20,25] Furthermore, another type of silica membrane which is known as hybrid silica membranes has recently emerged. These membranes are composed of both organic and inorganic material linked with each other to establish organic-inorganic bridges in selective layer.[24]

There are several ceramic based pervaporation membranes for use in dehydration processes. In order to determine which one is suitable for each specific application; content of mixture, desired product and operation conditions such as temperature, feed composition need to be considered. In this study, three commercial membranes; a NaA type zeolite, optimized silica and hybrid silica, were used. High chemical stability of these membranes is the main reason of this selection. Aprotic solvents (DMAc, DMF and NMP) cannot be separated by using any polymeric membranes because these solvents dissolve membrane polymers. High thermal stability of preferred membranes would also allow operation at higher temperatures so that higher permeate fluxes which were fundamental purpose of industrial applications could be achieved.

2.3 Effect of solvent type on PV performance

As it has already mentioned, permeation flux and separation factor are parameters, which depend on solvent-solvent and solvent-membrane interactions. [4,7,11,18] For binary aqueous mixtures, the interaction between water and solvent molecules are very important. The main criterion which is “activity” of a solvent in mixture must be considered to understand separation process. The higher the activity of solvent in the mixture mean the higher driving force for diffusion through membrane there will be. Correspondingly, permeation rate will depend on the solvent activity in mixture. [11,18] When the interaction between solvent and membrane is examined, it is seen that there are many parameters contribute on this interaction. First one is the hydrophilic/hydrophobic or organophilic nature of membrane. [4,11,18] Hydrophilicity of a membrane is a simple ratio of adsorption rates of water molecules over adsorption rates of solvent molecules. The inverse of this ratio gives hydrophobicity. [11] Moreover, higher hydrophilicity lead higher separation factor of water over solvent. [11] Moreover, activation energy for adsorption on membrane surface depend on both solvent and membrane characteristics. Solvents having smaller activation energies can penetrate through membrane relatively more easily than others. Extensive adsorption of one material on membrane surface may inhibit the permeation of other species. For instance, in hydrophilic inorganic membranes, adsorption strength of water molecules is much higher than the organic species in the mixture, thus water permeates faster than organic compounds, consequently, separation factor increases in favor of water. [9] Furthermore, kinetic diameters of solvent molecules and pore size distribution of selective layer are significant parameters. Solvent molecules having kinetic diameters that are smaller than pore sizes will diffuse through porous surface much more easily whereas larger molecules will pass more slowly or even will not pass. [7,11,18]

In the scope of pervaporation applications, almost all kinds of solvents are studied such as; ethers, aldehydes, ketones, esters, alcohols, glycols, amines, nitriles, halogenated hydrocarbons, carboxylic acids etc. Dehydration of alcohol mixtures dominates the studies about pervaporation. [3,16] On the other hand, aprotic solvents are rarely seen in pervaporation studies because of their basic characteristics. Aprotic solvents have high dissolving power in their mixture and do not contribute change in acidity because of not donating H^+. [26] This characteristic has made them common solvent in both industrial and laboratory applications, however it also has made them improper for pervaporation for a long period. They cannot be separated with polymeric membranes since they dissolve almost all polymeric material used in fabrication of those membranes. Fortunately, inorganic membranes having extensive chemical stability are promising materials in the separation of mixtures containing aprotic solvents by pervaporation.

Chapman et al. [27] examined dehydration of tetrahydrofuran (THF), which is a strong aprotic solvent, by applying pervaporation process. Dehydration of THF has a handicap of forming azeotrope at 5.3%wt water so that pervaporation separation of this mixture can compete with distillation, which is the most common conventional separation process. They studied the pervaporation performance of a composite membrane of a polymer and an inorganic substance, CMC-VP-31 supplied by CM Celfa. According to the results of this study, obtained permeation fluxes were 4 and 0.12 kg/m^2h for feeds with 10 and 0.3%wt water at 50^oC respectively. It was concluded that short term performance of the composite membrane CMC-VP-31 with THF was much better than polymeric membranes since inorganic material content of membrane increased its chemical stability.

Chapman et al. [8] reviewed studies performed on dehydration of tetrahdrofuran (THF) by using both polymeric and inorganic membranes. In this review article, various commercial polymeric membranes were compared with commercial inorganic membranes by their permeation fluxes, separation factors and short term performances in detail. They concluded that inorganic membranes had satisfactory separation performance for much longer period of applications than polymeric ones due to their chemical stability.

After the promising potential of inorganic membranes for dehydration of aprotic solvents was discovered, studies have mostly focused on comparing performances of different types of inorganic membranes. Sommer et al. [13] made a comprehensive investigation on five inorganic membranes and more than 30 different solvents including aprotics; dimethylacetamide (DMAc), dimethylformamide (DMF). A-, T-, Y-type zeolite membranes from Mitsui and two microporous silica membranes from ECN and Pervatech were used for many solvents. The results obtained from A-type zeolite membrane and microporous silica membrane from Pervatech for DMAc and DMF were given attention here due to the relativeness with the scope of present work. For A-type zeolite membrane, permeate flux and permeate water contents for DMAc were found as 1.51 kg/m^{2}h and 99.46%wt at 80^{o}C and at 10.5%wt water in feed; whereas for DMF, they were 1.51 kg/m^{2}h and 99.58%wt at 82^{o}C and at 9.1%wt water in feed respectively. For silica membrane from Pervatech, permeate flux and permeate water contents for DMAc were observed to be 2.21 kg/m^{2}h and 96.61%wt at 80^{o}C and at 9.4%wt water in feed; whereas for DMF, they were 1.14 kg/m^{2}h and 92.19%wt at 80^{o}C and at 9.1%wt water in feed respectively. With respect to the results, it is seen that permeation flux of DMAc at A-type zeolite membrane was lower than the one at silica membrane, while permeation flux of DMF at silica membrane was higher than the one in A-type zeolite membrane. On the other hand, permeate water contents of both solvents at A-type zeolite membrane were much larger than the ones at silica membranes, indicationg better selectivities. In addition, chemical stabilities of membranes were examined in this study and it was concluded that A-type zeolite membrane was less stable with acidic mixtures. In this study, aprotic solvent-water mixtures were separated at around 80^{o}C with a feed water content of approximately 10% by weight. However, more and systematic data should be obtained for dehydration of aprotic solvents for better applications of these processes.

Van Veen et al. [24] investigated solvent stability of recently developed hybrid silica membrane, HybSi. Dehydration of an aprotic solvent, n-methylpyrrolidone (NMP) was performed with HybSi membrane over forty-five days at 130^{o}C. According to results of this study, HybSi membrane was chemically stable enough against NMP, which was one of the most aggressive aprotic solvents, for a long term.

As can be seen from the literature sources, it is obvious that dehydration of aprotic solvents with inorganic membranes is not only possible but also essential by considering chemical stability concerns.

2.4 Temperature dependence of PV performance

Operation temperature is a critical parameter for pervaporation process. It has been clearly demostrated that there is a direct correlation between temperature and permeation flux. [7,8,13,18,19,28] This correlation has been explained with the temperature dependence of activity of solvents. [9,11,18] Increasing temperature resulted with the activity increase. Moreover, both adsorption and diffusion of molecules are defined with Arrhenius type equations. These equations refer that increasing temperature resulted with decreasing adsorption since it is an exothermic process. In addition, adsorption coverage decreases with increasing temperature. On the other hand, diffusivity increases with increasing temperature. Therefore increase in diffusion rate may compensate the decrease in adsorption rate so higher operation temperatures lead to higher permeation fluxes. [9,11,23,28] High permeation flux is always desired for pervaporation processes since required membrane area is reduced correspondingly. Therefore, operation temperature is set as high as possible. Inorganic membranes are preferable for high temperature applications over polymeric ones, since they have relatively much higher thermal stability. In addition, relatively higher cost of inorganic membranes can be compensated with decreasing membrane area by applying high temperature operations.

There are many studies investigating the effect of temperature on the performance of inorganic membranes, however, the ones focusing on aprotic solvents are very few. Chapman et al. [27] used a commercial composite membrane, CMC-VP-31 supplied by CM Celfa, for dehydration of tetrahydrofuran (THF). In this study experiments were conducted at three different temperatures, 25^{o}C, 40^{o}C, 55^{o}C. According to the results, both permeation flux and water flux increased with increasing temperature which was explained with increasing solubility of molecules on membrane surface and increasing diffusivity. Moreover, selectivity was also increased with increasing temperature. The reason was referred to be that solubility of water increased more relative to THF with increasing temperature so that number of penetrating water molecules became higher than number of THF molecules. Furthermore, change in water content of retentate with respect to time was also examined with changing temperature. It was concluded that temperature increase shortened the period of water removal from retentate.

Shah et al. [28] investigated pervaporation of dimethylformamide (DMF)-water mixture with a commercial NaA zeolite membrane. In order to understand the effect of temperature, experiments were carried on at 40, 60, 80^{o}C. Results showed that temperature increase leaded the increase of total flux. For instance, total fluxes at 50%wt feed water content were 0.5, 1.2, 1.8 kg/m^{2}h at 40, 60, 80^{o}C respectively. It was also observed that selectivities were not affected from changing temperature. This trend was explained with the Arrhenius type relation of diffusion through zeolite membrane.

Sommer et al. [14] also investigated the influence of temperature on pervaporation performances with inorganic membranes. With respect to their findings, diffusion through inorganic membranes was an activated process and it increased with increasing temperature. Furthermore, increasing temperature resulted with the decrease in saturation vapor pressure of materials. However, adsorption coverage of membrane surface got lower loading for those materials at higher temperatures. Yet, decrease in adsorption coverage is highly compensated with increase of diffusion rate. In addition, temperature dependences of NaA zeolite membrane and microporous silica membrane were also compared in this study. According to the conclusions of this study, same solvents had same activation energies for both membranes. Consequently, the temperature dependences of both membranes were close to each other.

2.5 Feed content dependence of PV performance

Feed content is one of the important parameters determining the pervaporation performance. Both permeation flux and separation factor depend on feed content. [4,18] When the concentration of species in feed decreases, its activity also diminishes which results in a decrease in permeation rate. Similarly, separation factor also depends on preferential adsorption of species. The membrane can be selective to a species with low concentration in the feed, if it is preferentially adsorbed by the membrane material. For very low concentrations of preferentially adsorbed compound, other species start to be adsorbed and separation factor falls down. [4,9,11,18,22] Furthermore, feed water content is usually around 5-10%wt for dehydration of aqueous organic solvent mixtures. There are two reasons of this. First of all, hydrophilic polymeric membranes dominate pervaporation applications, and they have swelling problem at high water contents. [7] Secondly, pervaporation is generally used for dehydrating the mixtures with very low water concentration, where the distillation is no longer profitable since the required number of trays increase substantially at low water concentrations where the operating and equilibrium lines approach each other. Furthermore, PV is commonly used to overcome azeotropes. On the other hand, in literature, there are also some studies done to investigate pervaporation at feed water contents higher than 20%wt. However, there are very few studies in literature, which have reported the effect of feed content for dehydration of aprotic solvents.

Shah et al. [28] examined a wide range of feed composition for dehydration of aqueous DMF composition with NaA zeolite membrane. in this study, separation performances were tested at 100, 70, 50, 30%wt water in feed at 40, 60, 70^oC. Results of this study showed that decline in feed water content resulted in decrease in total flux. Moreover, although a rapid decrease in total flux was observed with decreasing feed water content at 70^oC; it was slightly decreased at 40^oC. It was concluded that higher temperatures influenced the activity coefficient so that effect of feed content on total flux was enhanced. Moreover, it was seen that total flux was independent from feed content below 10%wt water.

Sommer et al. [14] also investigated the effect of feed content on dehydration of aqueous tetrahydrofurane (THF) mixture with A-type zeolite membrane. Permeation fluxes at 110^{o}C were found as 18, 17, 16, 12 kg/m^{2}h at 20, 15, 10, 5%wt water content in feed respectively. With respect to their results, it was stated that high water content leaded high permeation flux due to high activity coefficients. Furthermore, permeate water content was almost constant and above 99%wt water for whole composition range.

2.6 Hybrid Systems

Pervaporation gets more favorable over other traditional separation processes, especially distillation. [3] Unfortunately, pervaporation alone does not meet high flux requirements of industrial processes. Therefore, hybrid systems including pervaporation and distillation together are preferred commonly in industrial applications. Hybrid systems allow overcoming the basic problems of distillation processes such as; azetrope formation and close-boiling mixtures. [10] In addition, it was seen that pervaporation proposes not only improvements of separation performances but also economic benefits.

Van Hoof et al. [17] compared azeotropic distillation with hybrid systems including pervaporation and distillation with different configurations in terms of their cost effectiveness. In this study, dehydration of isopropanol was performed with both polymeric and inorganic membranes. According to the results, it was concluded that inorganic membranes were much favorable for hybrid systems. Moreover, their cost effectiveness analysis showed that hybrid systems had potential to save up to 49% of total cost when they were compared with azeotropic distillation.

There are very few studies in the literature which examined the hybrid systems for application on aprotic solvents. For instance, Koczka et al. [5] investigated industrial tetrahydrofurane (THF) recovery with distillation followed by pervaporation. According to their findings, azetrope point was effectively exceeded and considerable cost reduction was achieved.

There are many other studies [1,6,15] in literature explaining benefits of hybrid systems. On the other hand, different formations were proposed for various operations; yet, almost all of them suggest mounting pervaporation after distillation column for further dehydration of distillation product. Although, inorganic membranes have potential for pervaporation at high water compositions, there is no study done on integration of a pervaporation system before distillation column in literature yet. Potential energy saving of this formation which is still exceptional necessitates more attention.

CHAPTER 3

EXPERIMENTAL METHOD

3.1 Membranes and Modules

Three different commercial inorganic membranes; A-type zeolite, optimized silica and HybSi were used during experiments. A-type zeolite membrane was obtained from Fraunhofer-Gesellschaft, Munich, Germany. Inorganic-organic optimized silica and HybSi membranes were provided by Pervatech, Enter, Netherlands. These selected membranes have some common physical features. They are tubular, hydrophilic and have a membrane layer on the inner surface of an alumina tube. Dimensions of membranes are 250 x 10 x 7 mm, (L x Æout x Æin) and active area is 0.0056 m^2 approximately. Stainless steel membrane module designed for single membrane operations was used and membranes were sealed with silicon O-rings which are stable in aprotic solvent mixtures containing water above 3%. Illustration of membrane module is given in Figure 3.1. Each membrane was placed in module in order to provide parallel feed flow regime to the membranes.

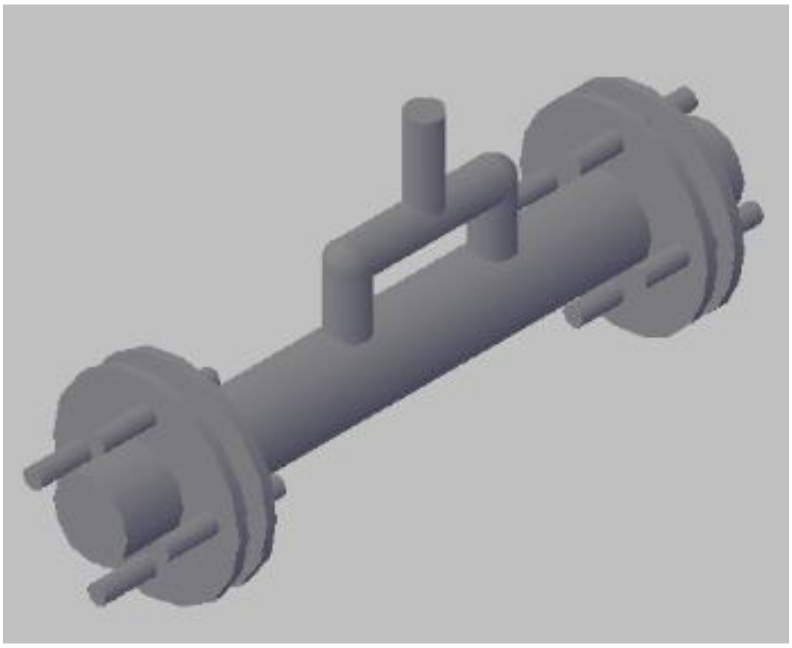
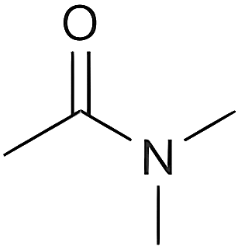
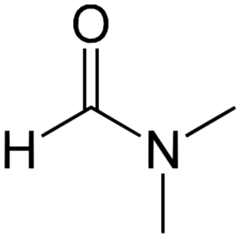
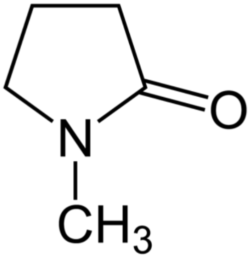
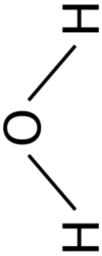


Figure 3.1. PV membrane module

3.2 Chemicals

Dimethylacetamide, dimethylformamide and n-methylpyrrolidone were provided from Merck and Sigma-Aldrich and used as received. De-ionized water was supplied by laboratory facilities. Properties of chemicals are tabulated in Table 3.1.

Table 3.1. Physical properties of aprotic solvents and water

Chemical Name	Dimethylacetamide (DMAc)	Dimethylformamide (DMF)	N-Methylpyrrolidone (NMP)	Water
Chemical Formula				
Molecular Formula	C_4H_9NO	C_3H_7NO	C_5H_9NO	H_2O
Boiling Point (^oC)	166	153	202	100
Heat of Vaporization (kJ/kg)	498	578	550	2257
Solubility in Water at 25^oC, δ_t ($MPa^{1/2}$)	22.7	24.8	22.4	-
Polarity (Debye)	3.70	3.86	4.10	1.85

3.3 Experimental Set-up and Procedure

A lab-scale pervaporation set-up was established and all membranes were performed in this unit which is schematically shown in Figure 3.2. Feed mixture was filled in glass feed tank (T1) and heated by an electrical heater (H1) placed bottom of T1. Temperature of mixture was controlled by a thermocouple which was stably placed into the T1. Feed was pumped through membrane module (MM) and recirculated to T1 by a reciprocating pump (P1). Silicon pipes connecting to T1, P1 and MM were kept as short as possible and covered with isolation in order to minimize the heat losses during liquid transportation. Feed flow rate was set to a 3000 cm^3/min, which corresponds to a linear velocity of 78 cm/min. This velocity was safe enough to avoid any concentration polarization on membrane surface. [4,11] Feed tank was open to air and pressure of T1 was at atmospheric pressure.

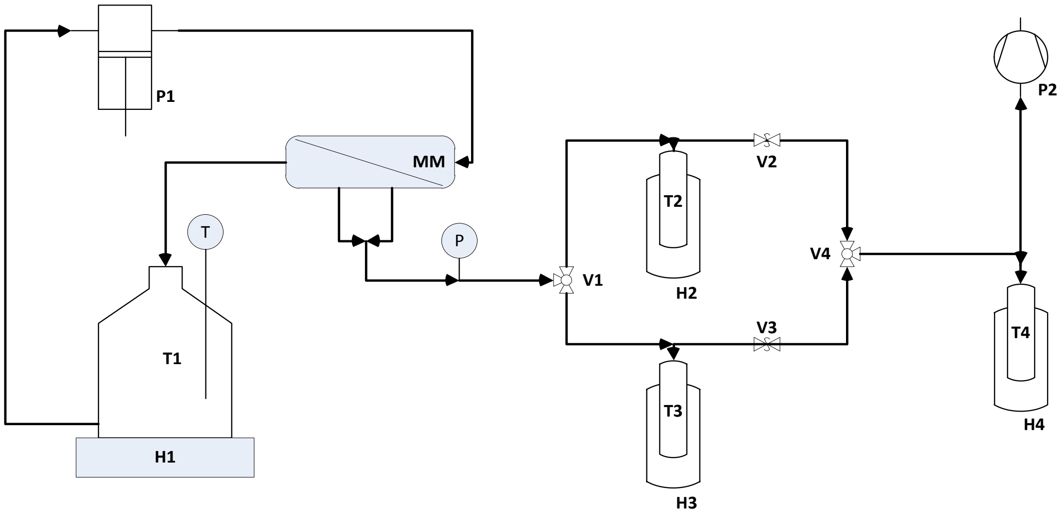


Figure 3.2. Pervaporation Set-up

Vacuum (0.055-0.100 bar) was provided by a pump P2 along whole path from P2 to MM. It was used to create low pressure, which is the driving force for material tranportation across the membrane, between feed and permeate sides of membrane. Species passing through membrane surface were vaporized and removed instantaneously. There were two parallel identical paths allowing periodic and continuous sampling of permeate. They were connected to each other with 3-way valves V1, V4 which were switched manually to take one line under vacuum at a time. When one line was closed, permeate passed through this line and came to collectors T2 or T3 that were dipped in coolers H2 or H3; and then it condensed and collected into a bottle. Simultaneously, other line was kept open without providing vacumming in order to weight and analyzed the collected permeate without any interruptions. Consequently, pseudo steady state data were collected. Pressure was measured by a vacuum gauge placed after MM. Glass lines were used in this system to detect any condensation problem due to vacuum loss immediately. Relief valves

V2, V3 were used to open lines to air. Coolers H2, H3 were dewar vessels filled with liquid nitrogen at 77K as a cooling agent. Collector T4 and cooler H4 were installed for safety considerations to prevent depredation of vacuum pump P2 if any liquid vapor pass from T2 or T3.

In this study, effect of membrane types and operations parameters such as; feed water content and operation temperature were investigated for three aqueous aprotic solvent mixtures. Feed was prepared with desired composition in the range of 30-50%wt water by adding solvent to water and then stirred until obtaining a homogenous mixture. This mixture was filled to T1 and heated by H1, while circulation was being maintained by P1. When temperature of mixture became stable, V1 and V4 were manually sencronized to take one line under vacuum. Meanwhile, P2 was operated and permeation began through closed line due to low pressure. After a certain period which was called as one ‘run’, V1 and V4 were switched and permeate flow was passed to the next path. Until next switch, collected material for a known time period was weighted and labeled for further analysis. Time intervals between runs were estimated inversely proportional with permeate flux from 10 to 90 minutes. Moreover, permeates were not returned to T1; therefore, mixture amount in T1 was depleted and composition was also altered depending on permeate content. Initial amounts of feeds were 500g and approximately 200g of mixtures were depleted in each set of experiments. In order to determine instantenous feed composition, samples were taken from T1 for analysis. Beetween different sets of experiments membrane module, liquid and vapour lines were washed, cleaned and dried properly in order to prevent any contamination altering the other experiments.

All experiments in this study were conducted as concentrated feed method which was the recycling of retentate to the feed tank while permeate was removed out of the system. The result was the depletion of water in feed with time the change of permeate flux with the composition of feed solution was investigated.Three different aspects were studied in described system. Initially, dehydration of aqueous dimethylacetamide (DMAc) mixture was performed with A-type zeolite, optimized silica and Hybsi membranes at $50^{o}C$ in composition range from 50 to 10% (w/w) water. This set of data was useful to distinguish different characteristics of membranes for the same solvent. Then, dehydration of binary DMAc-water, DMF-water and NMP-water were conducted with optimized silica and HybSi membranes at 50°C in similar composition range. So, behaviours of those mixtures at the same membrane were compared. Finally, aqueous DMAc mixture was investigated with HybSi membrane at 50, 70, 90, 100°C. Those temperatures were determined by considering real industrial applications and boiling points of mixtures; they were examined to be able to see temperature effect on PV outcomes such as permeate flux and separation factor. Materials and composition ranges above were selected by considering real industrial applications. Therefore, experiments illustrate estimation and comparison of:

- Reproducibility of pervaporation performances of NaA zeolite, optimized silica, HybSi membrane and stability of optimized silica
- Performances of three inorganic membranes with one aprotic solvent at same temperature and composition range.
- Dehydration of three aprotic solvents with one inorganic membrane at same temperature and composition range.
- Dehydration of one aprotic solvent with one inorganic membrane at different temperature and same composition range.

Those comparisons are crucial to design an aprotic solvent recovery system with inorganic membranes by PV, and they also allow comprehensive understanding of solvent-membrane relations. No experiments were carried out for separation by distillation column, yet calculations of energy and membrane area requirements were also presented in this study.

3.4 Analytical Methods

Feed water content was measured by using KEM Karl-Fisher Moisture Titrator MKS-520 during the experiments. Samples taken after each 3 runs were injected to Karl-Fisher Moisture Titrator. Permeate samples were analyzed in GC Spectroscopy from Varian CP-3800 series equipped with DB Wax column and FID detector.

Method details were given in Appendix D. Each sample was analyzed once. The separation factor was calculated with a formula given below:

$$\alpha_{wat}/_{sol} = \frac{({}^{y_{wat}}/_{y_{sol}})}{({}^{x_{wat}}/_{x_{sol}})} \qquad (3.1)$$ [4]

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Energy Calculations for Hybrid Process

Distillation columns with PV and without PV are visualized in Figure 4.1, in order to compare these two processes.

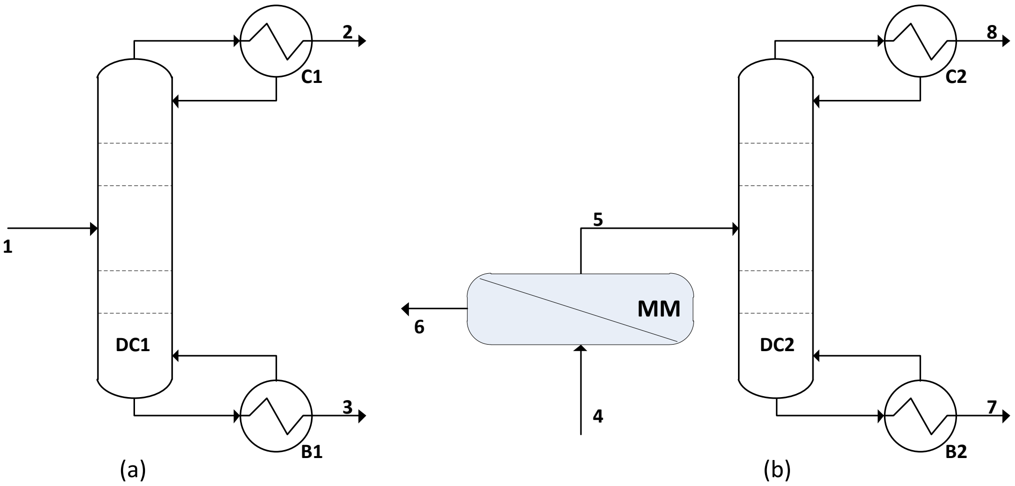


Figure 4.1. Distillation columns without PV (a) and with PV (b)

In Figure 4.1 (a) a separation process without PV is shown with a conventional distillation column (DC1), a condenser (C1) and a boiler (B1). Inlet stream of DC1 was aqueous aprotic solvent mixture; while top product stream (2) was water rich and bottom product stream (3) was solvent rich. In order to decrease energy consumption, PV system was mounted into the process, as shown in Figure 4.1 (b). Most of the previous studies [1,5,6,15] focused on placing a PV system right after the distillate for further dehydration, since the desired product was solvent rich stream and purity of this can be improved with the help of PV. On the other hand, in this study, a distillation system was used in which a membrane module (MM) was placed before the inlet stream (5) of column (DC2). DC2, C2, B2 were identical with DC1, C1, B1; and also compositions of streams 1, 2, 3 were same with 4, 8, 7. The difference coming with PV is the flow rate of feed to distillation column (stream 5) and its composition, in which solvent fraction is higher after pervaporation module. Hence, the heat duty in reboiler B2 is expected to be less then reboiler B1. In order to compare the heat duties of B1 and B2, water contents of streams 1 and 4 were kept the same and water content of stream 5 was derived. The heat duties of B1, B2 and the membrane area requirement with respect to the water content of stream 5 were the three main parameters which were investigated in this study. Three different cases were studied which are: (a) stream (1) having %50-50 water-DMAc without PV, (b) stream (5) having %40-60 water-DMAc with PV, (c) stream (5) having %30-70 water-DMAc with PV.

DMAc was chosen as a solvent for the design of distillation column since it is one of the common solvents which is recovered by employing distillation processes and also process conditions for distillation of aqueous DMAc mixtures are available in industry. Distillation of DMAc-water mixtures can be accomplished with high efficiency due to high relative volatility of DMAc that yields the x-y diagram as shown in Figure 4.2. However, it is a highly energy demanding process because of high heat of vaporization of DMAc. As the water content of feed stream to the distillation column is decreased by PV, amount of boil-up can be decreased; consequently, the reboiler heat duty of hybrid process will be lower than that of single distillation.

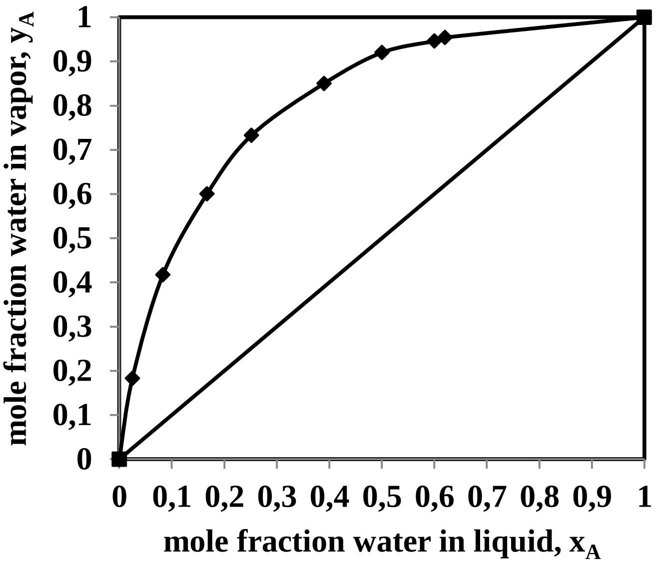


Figure 4.2. Vapor-liquid equilibrium for DMAc-water system

Required process conditions such as temperature and the compositions of stream 1, 2 and 3 (Figure 4.1)were selected based on the operation of a distillation column in a chemical plant producing synthetic fibers by using DMAc. Temperatures of streams 1 and 4 were 50^{o}C. Since PV was also performed at the same temperature of stream 5 so that temperature adjustment on stream before DC2 entrance was avoided. Flow rates of stream 1 and 5 were set to 100 kg mixture/hour as basis. Reflux ratio was set as 1.2 times of R_{min}, which was found as 2.6. Both columns were designed for 90%(w/w) water in the distillates and 90%(w/w) solvent in the bottoms. All intermediate stream compositions were calculated with McCabe-Thiele Method [29] by using vapor-liquid equilibria data of water-DMAc mixture. It was assumed that stream 6 was pure water which was also confirmed by PV results reported in Chapter 4.2. Required membrane areas were found by using permeate flux of HybSi membrane at defined conditions. Heat requirements of reboilers and PV were tabulated in Table 4.1 for single distillation and hybrid system with two different water contents in the feed to the column. The details of calculations were shown in Appendix B.

Table 4.1. Comparison of the required membrane areas and heat duties for a hybrid pervaporation-distillation system with different feed water contents to the distillation column

Case / Outcomes	**50%**wt water	**40%**wt water	**30%**wt water
Required membrane area (m^2)	-	91	182
Heat duty of boiler (W/kg of DMAc)	857	458	254
Heat duty of PV (W/kg of DMAc)	-	118	196
Total heat duty (W/kg of DMAc)	**857**	**576**	**450**

With respect to Table 4.1, it is seen that 10% reduction in water content of feed to distillation by PV caused a decrease in total heat duty from 857 to 576 W/kg of DMAc which corresponded to 33% decrease in total energy consumption of process. If the inlet water content is decreased to 30%, total heat duty will be 450 W/kg of DMAc, leading to a total energy saving of 48%. It is obvious that the energy consumption of the process was greatly diminished by hybrid design with this type of configuration.

The installed membrane areas were calculated 91 and 182 m^2 for cases (b) and (c) respectively. Larger membrane area was required to remove more water from the inlet stream, which increases the capital cost of an industrial scale PV process. The process should be optimized by balancing the membrane area requirement with the saving in heat duty. Although, cost calculation are not the scope of this thesis, benefits of PV, in terms of energy consumption, were validated.

4.2 Pervaporation experiments

The main focus of experiments is the comparison of membrane performances at different feed contents and temperatures for aqueous DMAc, DMF and NMP mixtures. Beside, reproducibility of experiments and membrane stability were also considered. In order to investigate reproducibility, PV of DMAc mixture for three membrane at 50°C was repeated sequentially. Obtained data in steady state experiments is represented in Figure 4.3.

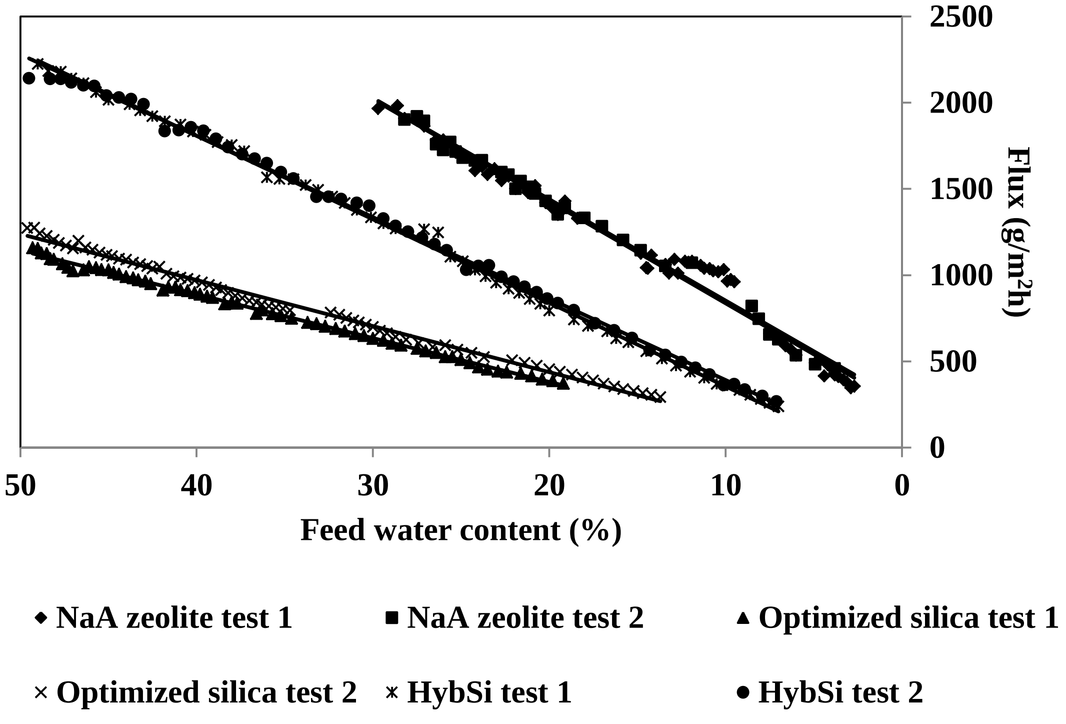


Figure 4.3. Fluxes with respect to feed water content with DMAc mixture at 50°C

It was observed that fluxes for sequential series were overlapped with NaA zeolite and optimized silica membranes, while HybSi membrane showed approximately 5% increase in second series than first series. Beside, separation factors in successive series of all membranes were close each other. NaA zeolite and optimized membranes performed repetative flux values in their series; thus their performances were reproducible. On the other hand, HybSi membrane showed sligth increase in fluxes yet its selectivities were close each other in both series. There might be slight expansion in porous selective layer resulting that flux increase, however this expansion did not lead any decrease in separation factor which implied a reproducible experiment series.

It was also important to estimate membrane stability for longer period. Pervaporation with pure water is a way to follow membrane performance. For that purpose, PV of pure water was performed before each experiment with aprotic solvent mixture with optimized silica membrane. This could not be experienced with NaA membrane since it was damaged earlier. It was not obtained for HybSi neither, since permeate fluxes were too high to get accurate results with our experimental set-up. Obtained data from optimized silica membrane for both pure water and aprotic mixtures were given together in Figure 4.4.

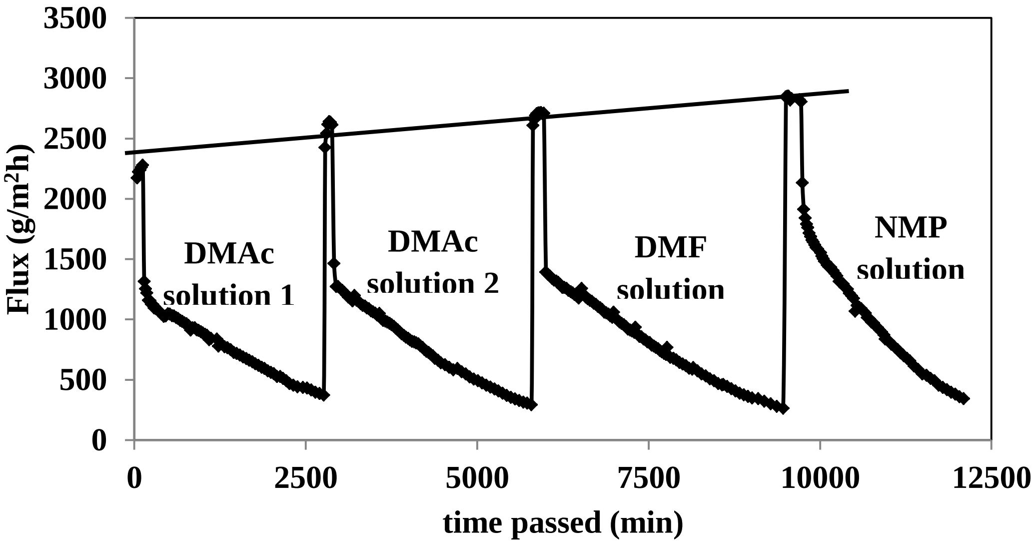


Figure 4.4. Fluxes of diffrenet solvent mixtures and pure water with respect to time at 50^{o}C with Optimized silica membrane. Feed amount 500g with 50-50% solvent-water solution

It was seen in Figure 4.4 that pure water fluxes displayed an approximately 5% increase. There might be a slow perminant disformation on selective membrane layer so that fluxes would increase while selectivity of membrane would decrease. It might be predicted that after a long period of usage, membrane would loose its selective structure and allow feed to pass through it.

4.2.1 Comparison of membrane performances in the separation of DMAC-Water mixtures

NaA type zeolite, optimized silica and HybSi membranes were used to separate aqueous DMAc mixture with initial water content of 50% by weight at 50°C. Experiments were carried on with concentrated feed method and pervaporation was continued until the water content of solution in the feed tank dropped from 50 to 20%. The initial water content of 50%(wt) in the feed is not usual for PV applications. Most PV systems are used to separate component with percent weight less than 15 from the mixture to achieve high purity products. In the present study, 10% reduction in water content of feed to the distilation column was shown to lead to a remarkable saving in energy consumption. Therefore, the PV process was aimed to decrease the water content of DMAc mixture by 10-20% before feeding to the distillation column, not to produce high purity DMAc by only pervaporation.

Three parameters to determine the performance of PV process were permeate flux, permeate water contents and time requirement for desired purity were investigated in this section. Permeate fluxes and permeate water contents with respect to feed water contents were given in Figure 4.5 and Figure 4.6.

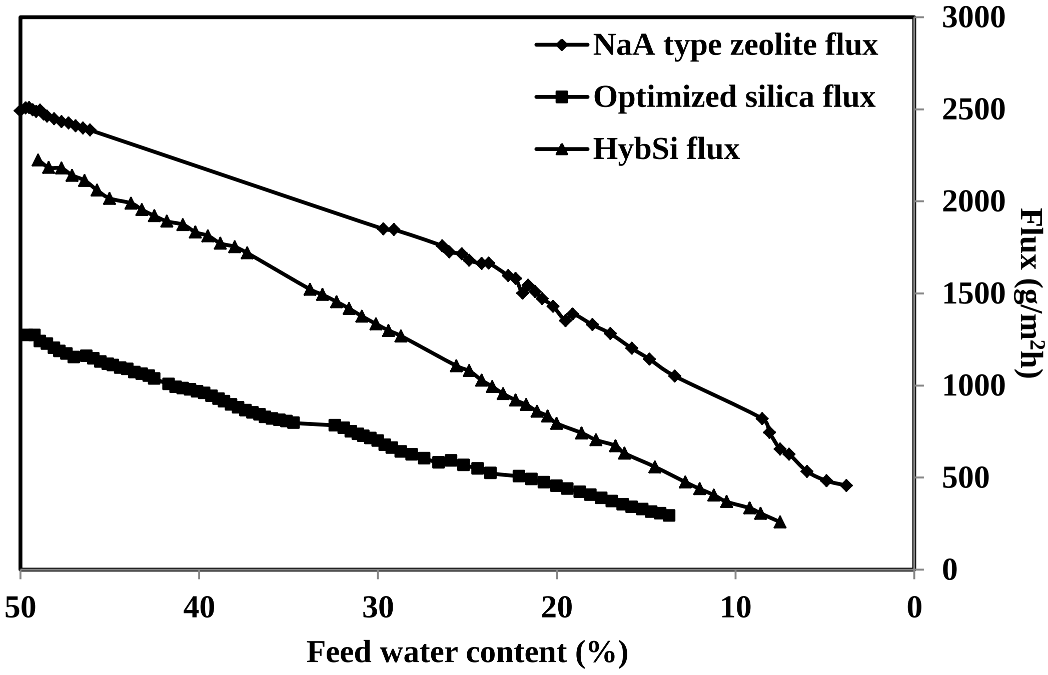


Figure 4.5. Flux with respect to feed water content at 50 ^{o}C

The permeate fluxes of all membranes decreased almost linearly with decreasing feed water content. The change of fluxes were 39.3, 27.4 and 47.4 g/m^{2}h.%feed water for NaA zeolite, optimized silica and HybSi membranes respectively. For hydrophilic membranes, permeate flux is proportional with the ratio of water to solvent molecules. [4,7,11] Adsorption of water molecules on membrane surface due to high affinity and diffusion of them through the membrane is more likely for high water to solvent ratio. Moreover, driving force of diffusion is directly proportional with diffusivity and feed composition. [9,18,21] Diffusion thorugh zeolite membranes is an activated process shown by Arrhenius type equation. [9,21] Diffusivity is likely to be affected mainly from temperature, which was constant throughout the separation process. Therefore, diffusion through the membrane depends essentially on the feed water content at constant temperature. A similar behavior is expected for silica membranes. [4,7,9,11]

The thickness and extend of hydrophilicity of selective layer are the key factors determining the permeances for a defect free and selective membrane [4,7,11] as well as the pore size distribution in the membrane. [11] Amorphous and optimized silica membranes are thinner than zeolite membrane, [8,11,13] but zeolite membrane is possibly more hydorphilic than the others. Thus, NaA type zeolite membrane had the highest permeate fluxes while optimized silica had the lowest ones along whole composition range. Besides, the NaA type zeolite membrane may have some non-zeolitic pores which allowed water molecules to pass through the membrane without any solvent transport due to hydrophilic character of surface of zeolite crystals. Sommer et al. [13] also investigated dehydration of aqueous DMAc and DMF mixtures with a commercial A type zeolite membrane of Mitsui. Corporation, the permeate flux and permeate water content of DMAc mixture (at 80°C and at 10.5%wt feed water content) were 1.51 kg/m^{2}h and 99.46% respectively, [13] that are comparable with the the flux and permeate water content obtained in this study, which were around 1 kg/m^{2}h and 98.5% at 50°C respectively.

Permeate water contents were used to calculate separation factors for all experiments. Some of them were given in Table 4.2. Rest of data were given in Appendix A.

Table 4.2. Separation factors of water over DMAc at 50 °C for three membranes

Feed water content (%)	A-type zeolite membrane		Optimized silica membrane		HybSi membrane	
	Perm. water content (%)	Separation factor	Perm. water content (%)	Separation factor	Perm. water content (%)	Separation factor
30.0	99.93	3225	98.99	230	99.17	276
27.5	99.97	7588	99.01	264	98.67	200
25.0	99.96	7210	98.83	253	99.24	392
22.5	99.95	6747	98.30	201	99.18	420
20.0	99.93	5877	98.40	249	99.15	465

As the permeate water concentrations are very high, a small increase in the permeate concentration appears as a large increase in sepearation factor, for instance for feed with 30% water, NaA zeolite and HybSi membranes have separation factors of 3225 and 276, respectively, although the difference between permeate water concentrations is only 0.76%. Therefore, slight changes in permeate compositions might be tolerated in industrial applications. Hence, the membrane performances were evaluated based on permeate compositions rather than separation factors. Since the permeate water contents were above 98% for all membranes and for all feed concentrations, they are acceptable for industrial processes. Reason of this is that desired product is not permeate but the retentate for dehydration processes. The permeate is the purge of the process, therefore 98% water is acceptable for facility discharges. Besides high water content in the permeate indicates that the lost amount of valuable solvent is low, which is important from economical point of view.

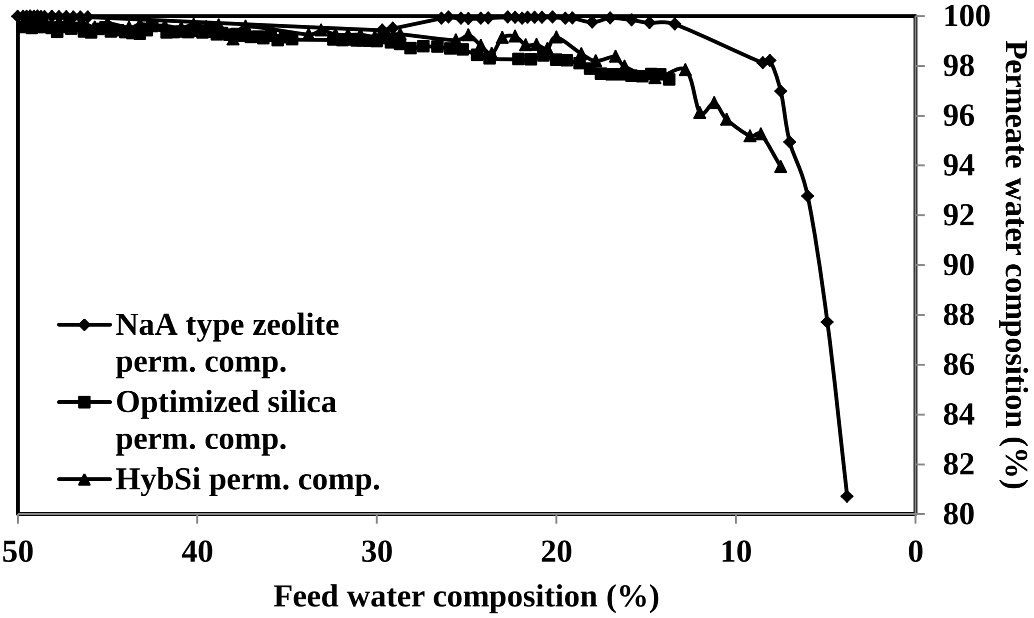


Figure 4.6. Permeate water content with respect to feed water content at 50 ^{o}C

Permeate water contents as a function of feed water content were shown in Figure 4.6. NaA type zeolite membrane produced over 99.9% permeate water content which was higher than other membranes, since pore size of NaA type zeolite membrane is much smaller than pore sizes of optimized silica and Hybsi. Hydrophilicity of NaA zeolite membrane was also higher than silica membranes so zeolite crsytals allowed mainly water molecules to pass through the selective layer; while other two were less selective for water molecules over DMAc molecules. Moreover, capillary condensation may significantly effect separation performance for zeolite membranes. [22] Capillary condensation is a situation that molecules in vapor phase are liquified in non-zeolitic pores. Consequently, porous pathways are blocked, other molecules can not fit into pores. As a result, an extra resistance layer is formed by occupied pores, thus selectivity of membrane layer increases. [22] In present experiments, although feed was already liquid, molecules were vaporised in porous medium due to low pressure. Yet, capillary condensation may occur even after this vaporization. Thus, it may also contribute the high selectivity of porous membrane layer. When optimized silica and HybSi were compared, it was seen that the Hybsi was more selective for water than the optimized silica. This was the expected result because of modified selective layer of the HybSi. While surface of the optimized silica was formed with amorphous silica layers, the HybSi had organic-inorganic molecule bridges in atomic level which secured its higher water selectivity over solvents. [24]

The permeate was above 99% water if the water content of feed is higher than 30%. Water content in permeate drastically decreased after 15% feed water content when NaA type zeolite membrane was used. Furthermore, for the case HybSi was used, it started to decrease when feed water content reached to 20% and decrease was more rapid after 15%. On the other hand, there was no sharp decrease for the optimized silica up to 13%, while there was a continuous slight decrease up to this composition. Number of active sites available for adsorption varied for different membranes. When there were enough water molecules in mixture, those sites were occupied by water molecules since they were preferentially adsorbed on hydrophilic surface; thus permeate water contents stayed over 98%. As composition reached at a certain point where number of water molecules were not sufficient to occupy all active sites, other molecules in mixture may permeate faster through the membrane. As a result, they diffuse through membrane and permeate water contents dropped. [9] It is very important to know where these decreases will start in order to be able to estimate when the application should be stopped. Since the decrease in permeate water content means an increase in solvent content and dehydration with minimum solvent lose should be aimed for industrial applications, the process should be ended before sharp decrease at the permeate water content. Selectivities (represented by permeate water content) were high and close to each other for all three membranes for target concentration range. Therefore, permeate fluxes become more important in membrane selection for this type of application.

Since our aimed product is retentate, operation times to reach targeted feed water contents of the three membranes were also compared. Figure 4.7 shows relation between feed water content and pervaporation period. Meanwhile, percent recovery refers the difference between two feed water contents in a limited period. Water amount in the feed is directly proportional with the operation time required and it determines the percent recovery rate. Accordingly, the same amount of water in the feed must be provided in each experiment in order to compare them with each other. Therefore, The feed was 500g with 50% initial water content for the separation by optimized silica and HypSi membranes, but the feed was 835 g with 30% initial water content for the separation by NaA-type zeolite membrane.

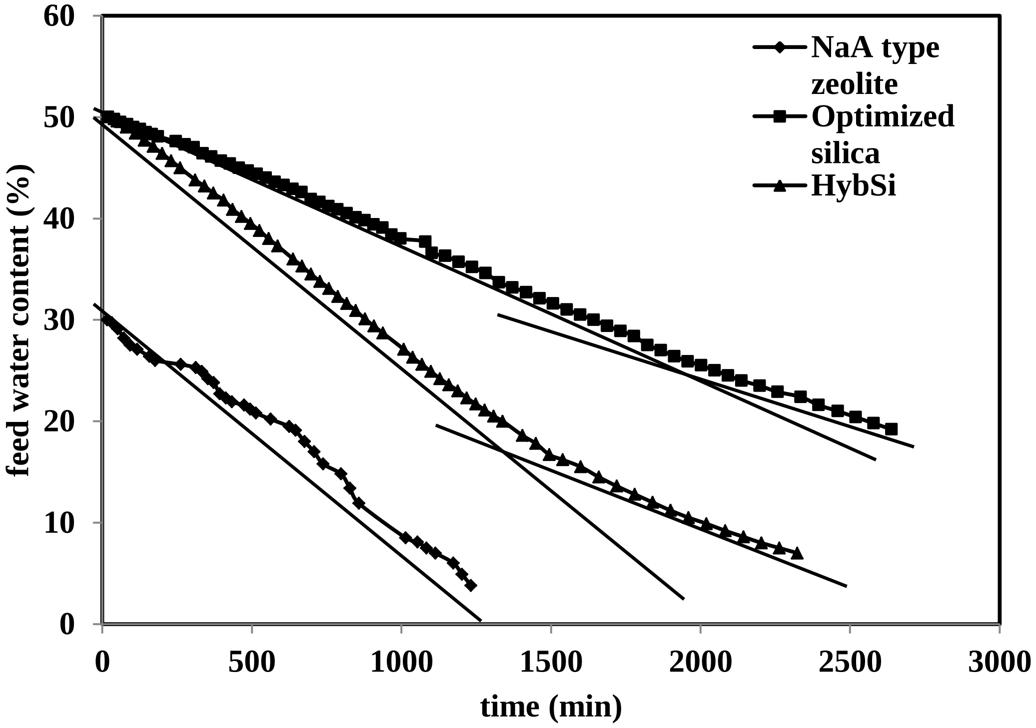


Figure 4.7. Feed water content versus time at 50 ^{o}C

As seen in Figure 4.7, the HybSi membrane reached from 50 to 30 feed water content in approximately 880 minutes, whereas the optimized silica recovered the same amount of water in 1640 minutes. The rate of decrease in feed water content was calculated by equation 4.1:

$$Rate\ of\ recovery = \frac{\Delta\%}{time} \qquad (4.1)$$

Rate of recoveries were calculated and given in Table 4.3.

Table 4.3 Rate of recoveries with DMAc-water mixture at 50°C

Feed water content (%wt)	Rate of recovery (Δ%/min)		
	NaA zeolite	Optimized silica	Hybrid silica
50	-	0.013	0.023
40	-	0.013	0.023
30	0.022	**0.013**	0.023
25	0.022	**0.008**	0.023
20	0.022	0.008	**0.023**
15	0.022	0.008	**0.011**
10	0.022	0.008	0.011

Rate of recovery was 0.013%/min up to 25%wt water in feed; afterwards, it was 0.008%/min for optimized silica membrane. It was 0.023%/min between 50 and 15%wt feed water content; then it became 0.011%/min below 15% for HybSi membrane. For, NaA zeolite membrane, rate of recovery was 0.022%/min from 30 to 3%wt water in feed. Although the rate of recovery was constant throughout the pervaporation process for NaA membrane, it dropped after 1900 and 1500 min of pervaporation for optimized silica and HybSi membranes, respectively. Recovery rate is related with the driving force. [9,18] The rate of recovery decreases after a certain time because the driving force, activity (or concentration) difference between feed and permeate, decreased by time. The decrease in activity of feed was more tolerated by the very hydrophilic zeolite A membrane than the others. The recovery rate for HybSi changed later than that for optimized silica membrane. NaA type zeolite, the optimized silica and the HybSi membranes required 560, 940 and 400 minutes to decrease feed water content from 30 to 20%, respectively. In addition, all membranes have similar separation factors. Based on these results, NaA type zeolite and HybSi membranes are more favorable than the optimized silica for large-scale applications.

4.2.2 Effect of solvent type on PV performance

PV performances of the optimized silica and the Hybsi membranes were investigated by separating aqueous solutions of three different aprotic solvents, DMAc, DMF and NMP mixtures at 50°C. A-type zeolite membrane was damaged during previous experiments, thus it was not used. Obtained results from optimized silica membrane were represented in Figure 4.8 and 4.9.

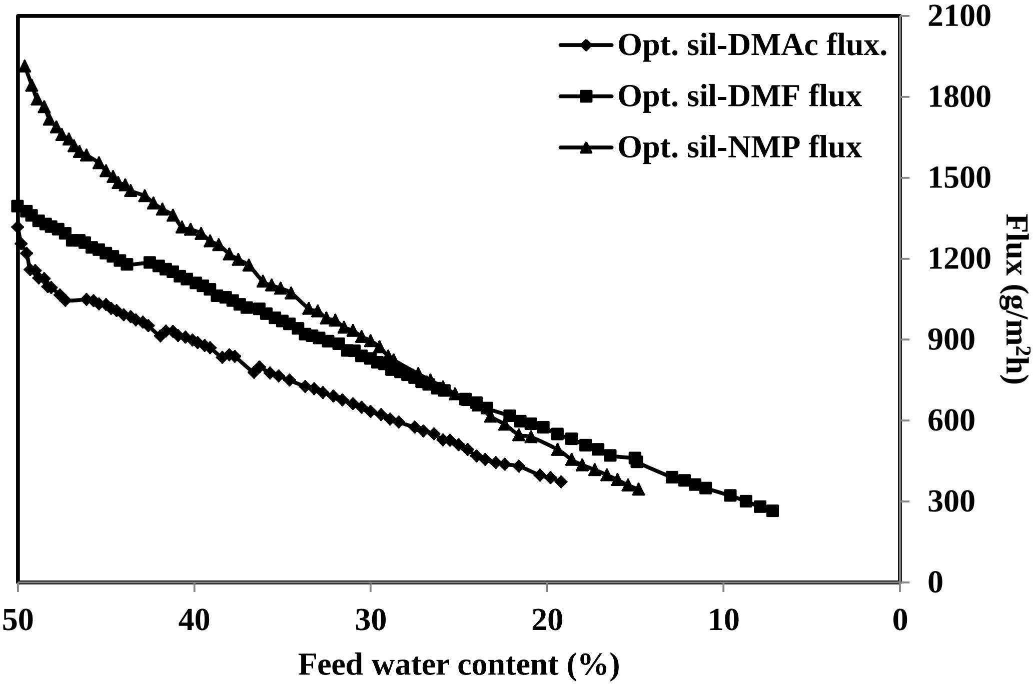


Figure 4.8. Permeate flux with respect to feed water content at 50°C

Figure 4.8 shows that, when the optimized silica was used, the permeate flux of NMP mixture was the highest while DMAc mixture was the lowest in the range from 50 to 30% feed water content. However, the permeate flux of DMF mixture decreased relatively slower than NMP mixture and became the highest one in the range below 30% feed water content.

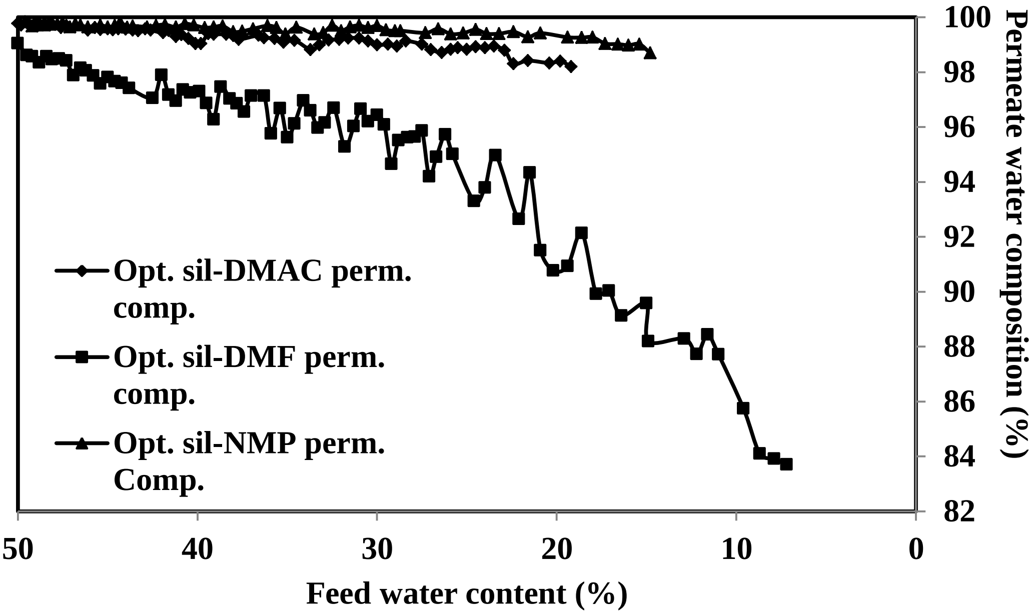


Figure 4.9. Permeate water content with respect to feed water content at 50°C

The permeate water content of NMP and DMAc mixtures were higher than 98%, whereas the permeate water content in the separation of DMF-water mixture decreased with increasing feed water content. Permeate fluxes through HybSi membrane of all mixtures overlapped between 50 and 35% feed water content and below these compositions, they started to split up slighlty (Figure 4.10). Furthermore, the permeate flux of DMF mixture became the highest one while that of NMP mixture was the lowest one up to 10% feed water content.

Permeate water contents were above 98% for all mixtures up to 20% water in feed (Figure 4.11). The behaviour of NMP and DMAC mixtures during the spearation by HypSi membrane was similar to those during the spearation by optimized silica membraneSharp decrease of permeate water content for DMAc mixture was also observed around 10% feed water content.The modified structure of HybSi membrane increased permeate flux compared with the optimized silica without losing its selectivity. Furthermore, it was seen that decrease in permeate water cs observed when the optimized silica was used, did not occur when the HybSi membrane was used in same content range(50-10%) for DMF.

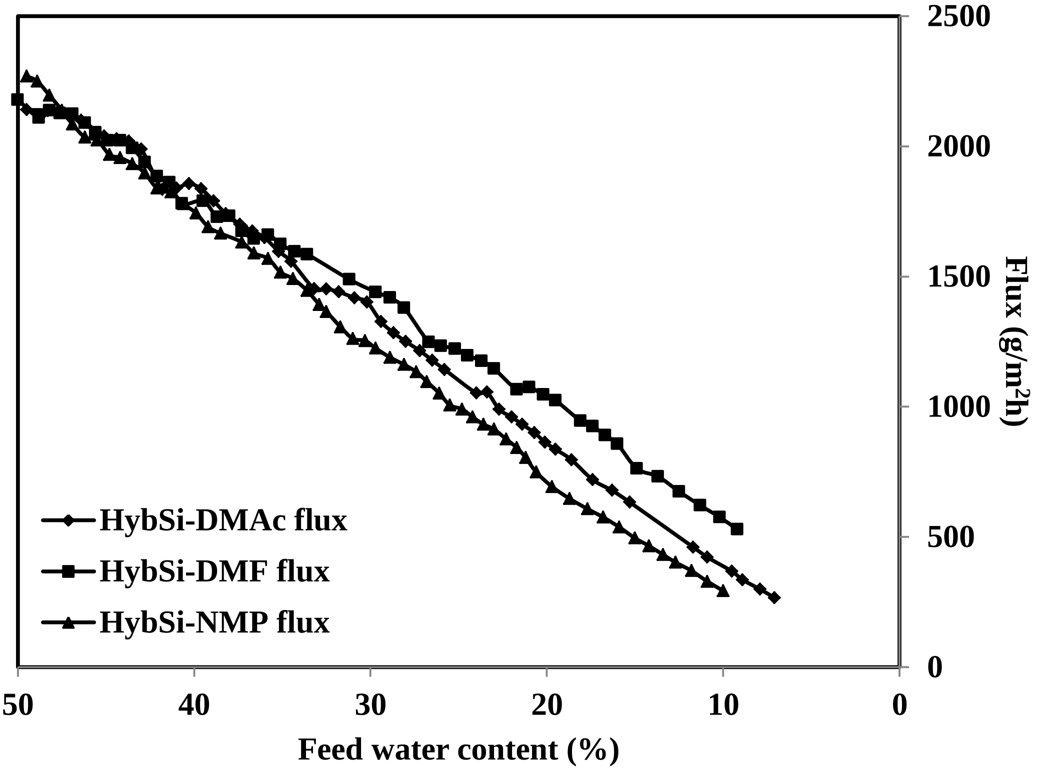


Figure 4.10. Permeate flux with respect to feed water content at 50^{o}C

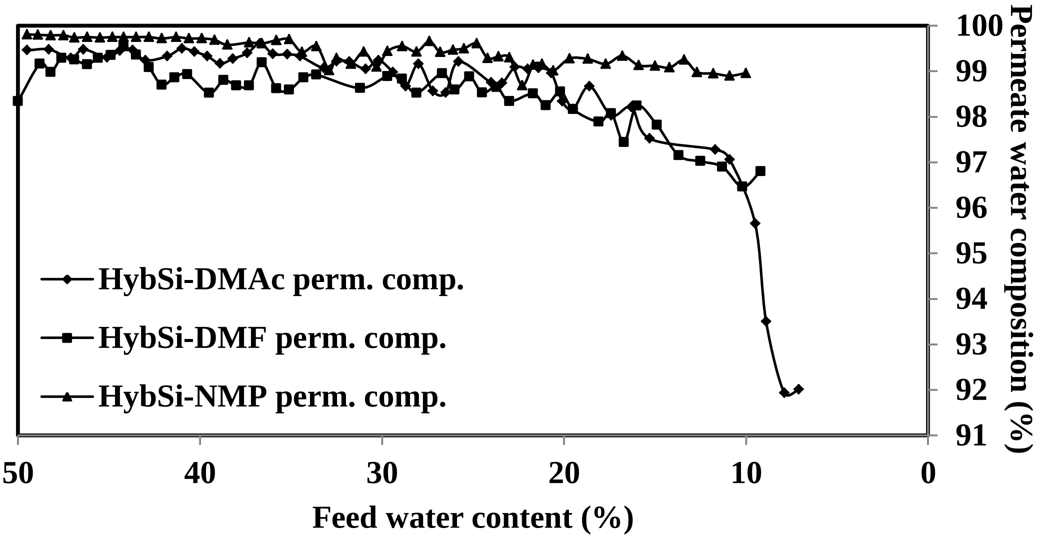


Figure 4.11. Permeate water content with respect to feed water content at 50^{o}C

The solvents exhibited different behaviours during the permeation through Optimized silica and HybSi membranes owing to differences in solvent-surface interactions or differences in activity changes of solvents in mixtures. [9,11,21] In order to understand the solvent-surface interactions and polarities of solvents might be considered. Polarity of NMP molecules are 4.1 Debye which is relatively higher than DMAc, 3.7 Debye and DMF, 3.86 Debye. Water has a high affinity with both membrane surfaces due to high hydrophilic character of surfaces. Polarity of water is 1.85 Debye which is the leading indicator property for molecule-surface interaction. It was expected that the molecules having similar properties with water would have had similar interaction with membrane surfaces. In other words, the solvent, whose polarity was more close to the one of water, would have had higher affinity with hydrophilic surfaces. This refers that the solvent, which was relatively more similar with water, would have liked by membrane surface which liked water. As it was seen in Table 3.1, DMAc has the closest polarity, 3.7 D; whereas, NMP has the highest one, 4.1 D. Thus, DMAc molecules adsorbed on surface relatively easier than NMP molecules did. Accordingly, adsorbed DMAc molecules blocked porous patways so that penetration of water molecules through membrane was reduced. Furthermore, those adsorbed molecules diffused through membrane layer and separation factor was also reduced. It was seen in Figure 4.9 and 4.11 that NMP molecules were rejected more than DMAc and DMF due to their high polarity. However, DMF molecules passed selectively layer more than DMAc molecules although polarity of DMAc molecules was closer to the one of water molecules. The reason was most probably the size of molecules. When molecular structures of DMAc and DMF were considered, DMF might have smaller size since it had one methyl group less. Therefore, size advantage of DMF molecules might compansate their disadvantage of polarity over DMAc molecules so that DMAc selectivity was higher than DMF selectivity for both memebranes.

When permeate fluxes (almost equal to water fluxes) was compared with same point of view, permeate flux of DMAc mixture was relatively lower than the ones of DMF and NMP. In Figure 4.8, permeate fluxes of mixtures with optimized silica membrane showed similar behaviour as expected; flux of DMAc mixture was the lowest while flux of NMP mixture was the highest. Moreover, in Figure 4.10, permeate fluxes with HybSi overlapped and flux of NMP mixture became the lowest one after a certain composition; in fact, they were still too close to each other. Rapid decrease of permeate flux of NMP mixture was observed with both membranes at different compositions. Trend of decrease in permeate fluxes were different for solvents due to their changing activities in mixture.

The rates of decrease in permeate flux changed depending on the type of solvent for both membranes. While, with the Hybsi this was barely distinguishable because of its high water permeance, it was clearly observed with the optimized silica. With the optimized silica, permeate flux of DMF decreased much slower than one of NMP. For better understanding of those trends, permeate fluxes were divided with feed water contents and obtained data was plotted for both membranes (Figure 4.12 and 4.13) and tabulated in Table 4.4. Both figures and table showed that permeate fluxes had different trends which were independent from feed water content in the range of interest. In order to explain these trends, activities of solvents in binary aquoeus mixtures were calculated by using UNIFAC and obtained data were represented in Figure 4.14.

Table 4.4. Permeate fluxes for optimized silica and HybSi membranes at 50°C

Feed water content (%)	Optimized Silica ($g/m^2h\%wt$ water)			HybSi ($g/m^2h\%wt$ water)		
	DMAc	DMF	NMP	DMAc	DMF	NMP
50	23.51	27.86	38.58	45.40	43.58	45.86
45	22.87	27.09	38.89	44.81	45.03	43.93
40	22.38	27.80	32.55	45.59	45.15	43.71
35	21.72	27.65	31.05	**45.11**	**46.27**	**43.19**
30	21.09	27.61	29.85	**44.33**	**48.32**	**41.32**
25	20.39	27.21	27.72	**43.39**	**48.61**	**39.94**
20	19.54	**28.41**	25.37	**39.73**	**51.92**	**35.17**
15	-	**29.91**	23.24	**38.92**	**53.81**	**33.03**
10	-	**33.10**	-	**36.24**	**56.48**	**29.32**

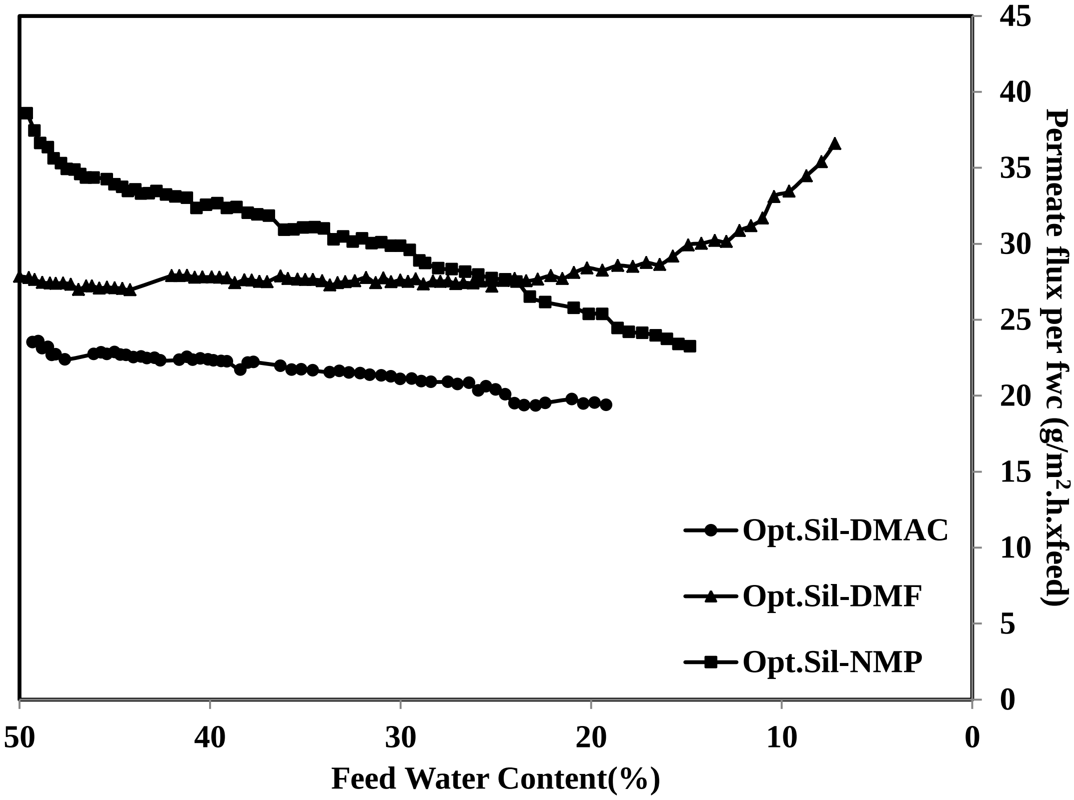


Figure 4.12. Permeate flux per feed water comp. vs feed water content with Optimized silica

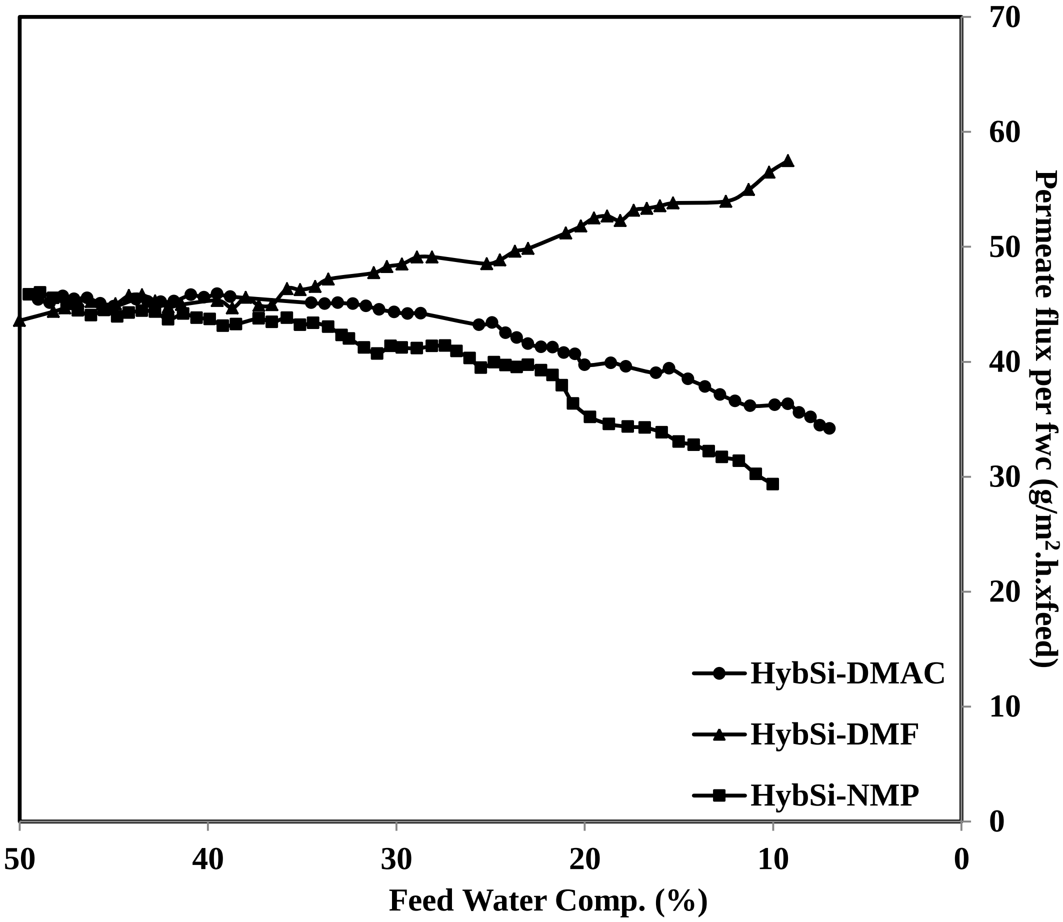


Figure 4.13. Permeate flux per feed water content vs feed water contentwith HybSi

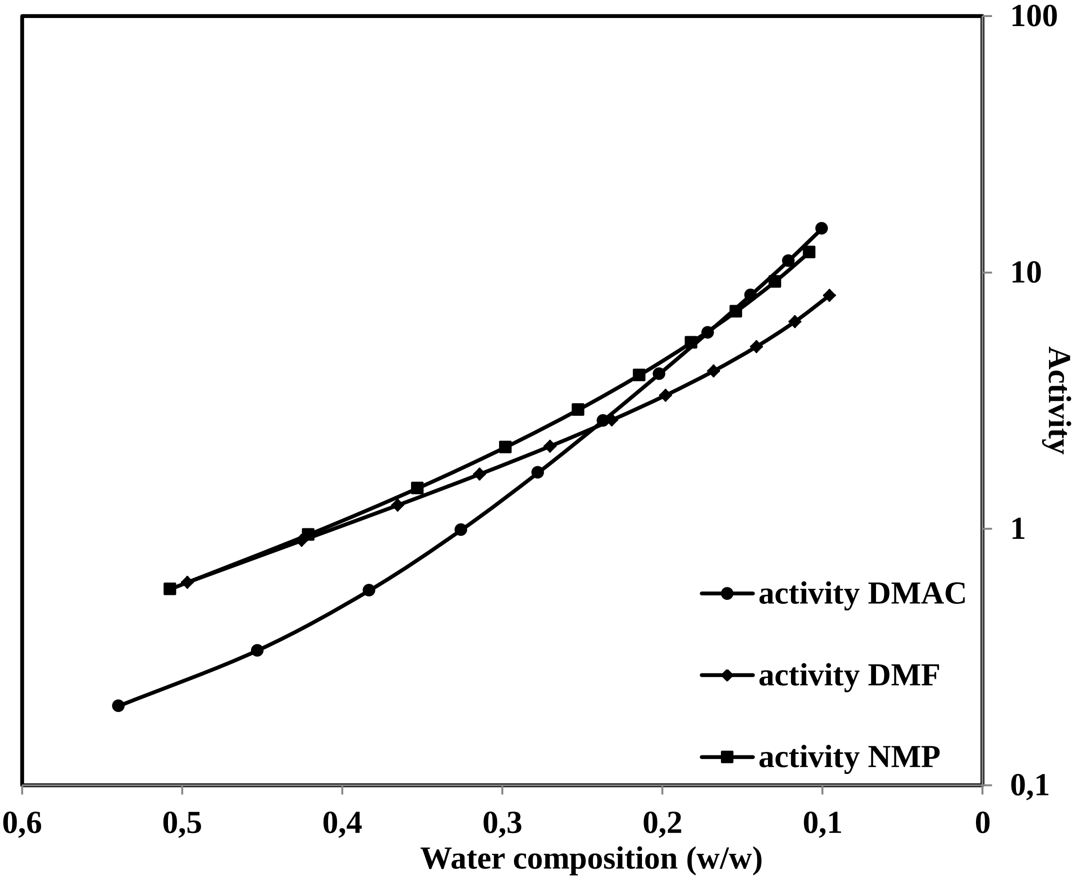


Figure 4.14. Solvent Activity versus water composition

Figure 4.14 showed the relation between changing activities of solvents with respect to water content of mixture. In order to calculate solvent activities, UNIFAC group contribution method was used as decribed in detail in Appendix C. Each molecular sub-group was taken separately to calculate interaction between other sub-groups in mixture. These interactions were calculated for pure components as reference point. Then, these calculations were repeated for aqueous mixtures. Permeate flux of a component in a mixture is directly proportional with its activity in mixture. [9,21] In all experiments explained above, water in mixture was depleated and its activity fell down while solvent activity increased. When permeate content that was mostly water was considered, it was expected to observe decreasing permeate flux with increasing solvent activity. However, these changes in solvent activities distincted from each other at different water contents (Figure 4.14). With respect to Figure 4.14, activity of DMAc was respectively lower above 20% feed water content. Accordingly, permeate fluxes were stable until that composition (Figure 4.12 and 4.13); then, it droped below 20%. Moreover, DMAc activity was so high that permeate flux started to fall down. Furthermore, when NMP and DMF activities were compared, it was investigated that NMP activity increased more rapidly than DMF and this resulted with much rapid permeate flux reduction of NMP mixture. From Figure 4.12 and 4.13, it was seen that permeate flux of NMP and DMF solutions became separated from each other at around 30% where their activities were distinguished in Figure 4.14. Moreover, permeate fluxes of DMAc and NMP mixtures went observably parallel below 20% where their activities got close to each other.

The permeances through optimized silica membrane for different aprotic solvent solutions were calculated from equation 4.2: [18]

$$\frac{P_i^G}{l} = j_i/(\gamma_i^L \times x_i^L \times P_i^{sat} - P_i) \qquad (4.2)^{[18]}$$

where γ_i is the activity coefficient calculated by UNIFAC model, P_i is the permeate side partial pressure, which was taken as 0.006 bar. The permeances was shown as P_i/l.

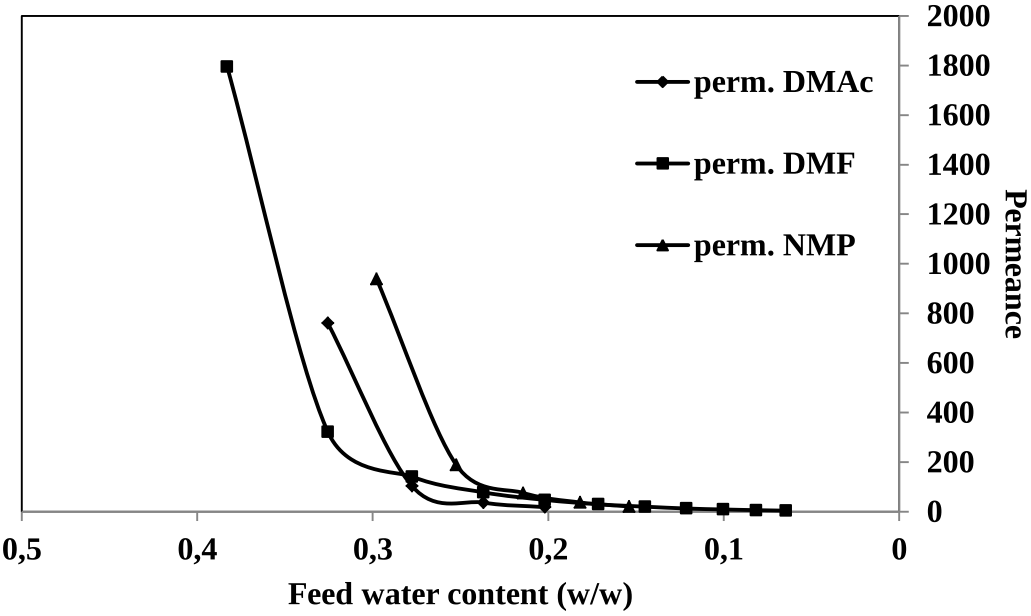


Figure 4.15. Permeance with respect to feed water content at 50°C for optimized silica membrane

Similar with Figure 4.12, decreases in permeances had different trends before and after 25%wt feed water content for optimized silica membrane. The reason is that permeance is a function of activity and it changes with a feed solvent content and solvent type.

4.2.3 Temperature Effect

As a significant design parameter, the effect of temperature on the separation performance of ceramic membranes was also investigated on this study. For this purpose, binary DMAc-water mixture was experienced with HybSi membrane at 50, 70, 90 and 100°C in the range of interest. Obtained data were represented in Figure 4.16 and 4.17.

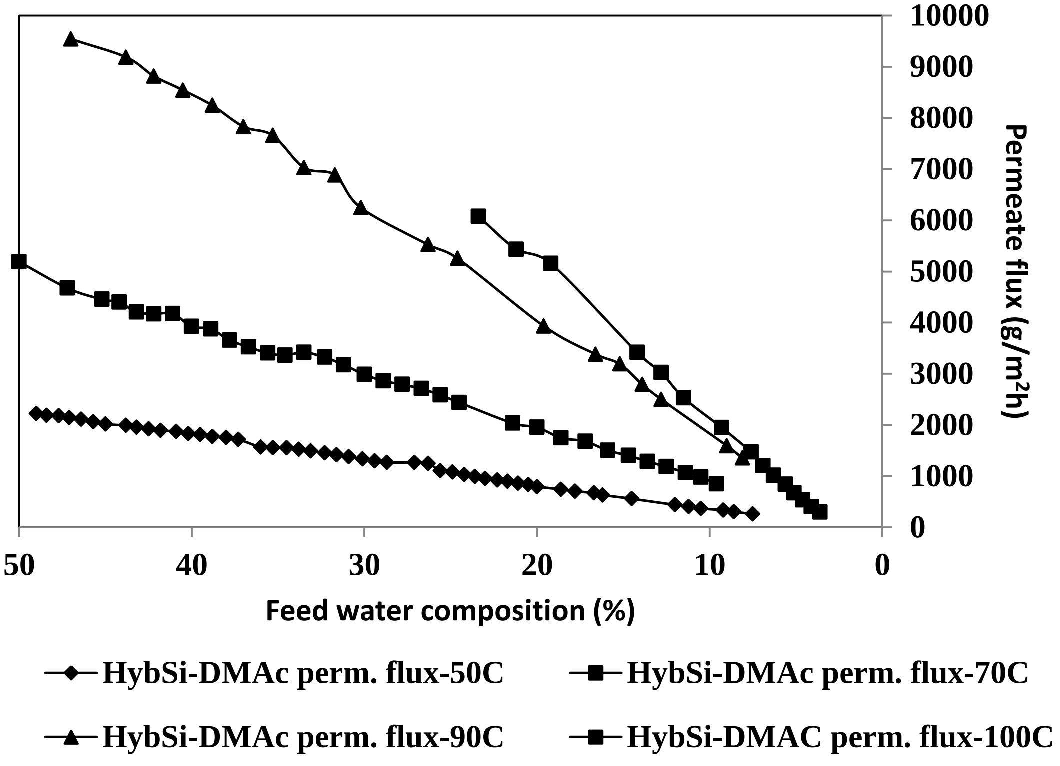


Figure 4.16. Permeate flux versus feed water content

Permeate fluxes displayed a great increase with increasing temperature especially for relatively high water contents. At 100°C, permeate fluxes became too high (for feed water contents above 25%) to conduct controlled experiments and to measure permeate fluxes accurately, for our experimental set-up. Shah et al. [28] investigated wide range of feed content for dehydration of aqueous DMF composition with NaA zeolite membrane. Separation performances were tested at 100, 70, 50, 30%wt water in feed at 40, 60, 70°C. The results showed that decline in feed water content resulted with decrease in total flux. It was observed that total flux decreases rapidly with decreasing feed water content at 70°C; however, it was slightly decreased at 40°C. It was concluded that higher temperatures influenced activity coefficient so that effect of feed content on total flux was extended.

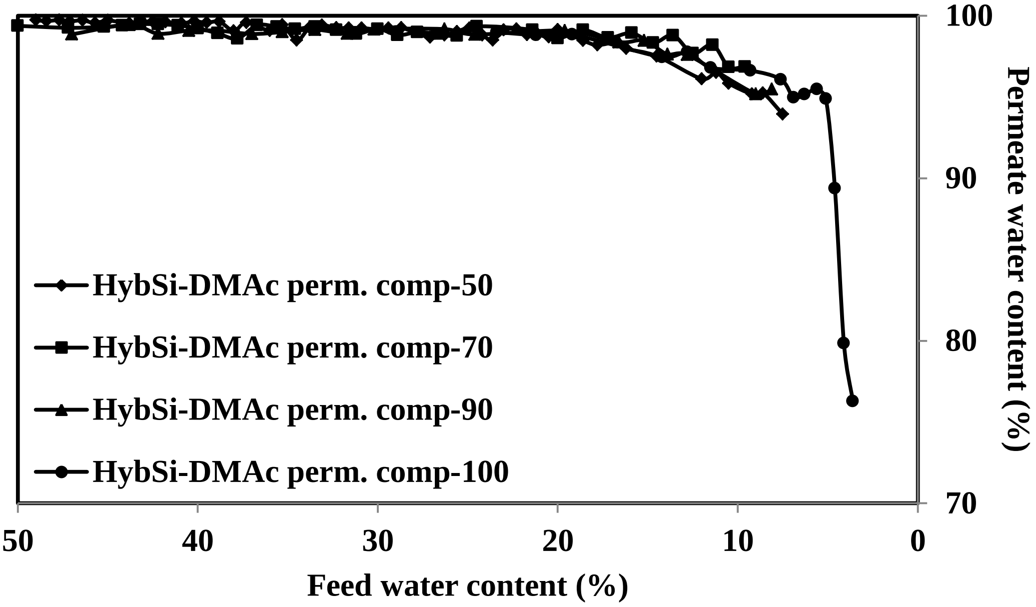


Figure 4.17. Permeate water content versus feed water content

It can be seen that permeate water contents overlapped and stayed over 98% until 20% feed water content and they started to drop afterwards which was very similar behaviour observed previously with HybSi (Figure 4.13). Therefore, it might be said that selectivity of HybSi membrane was independent from process temperature.

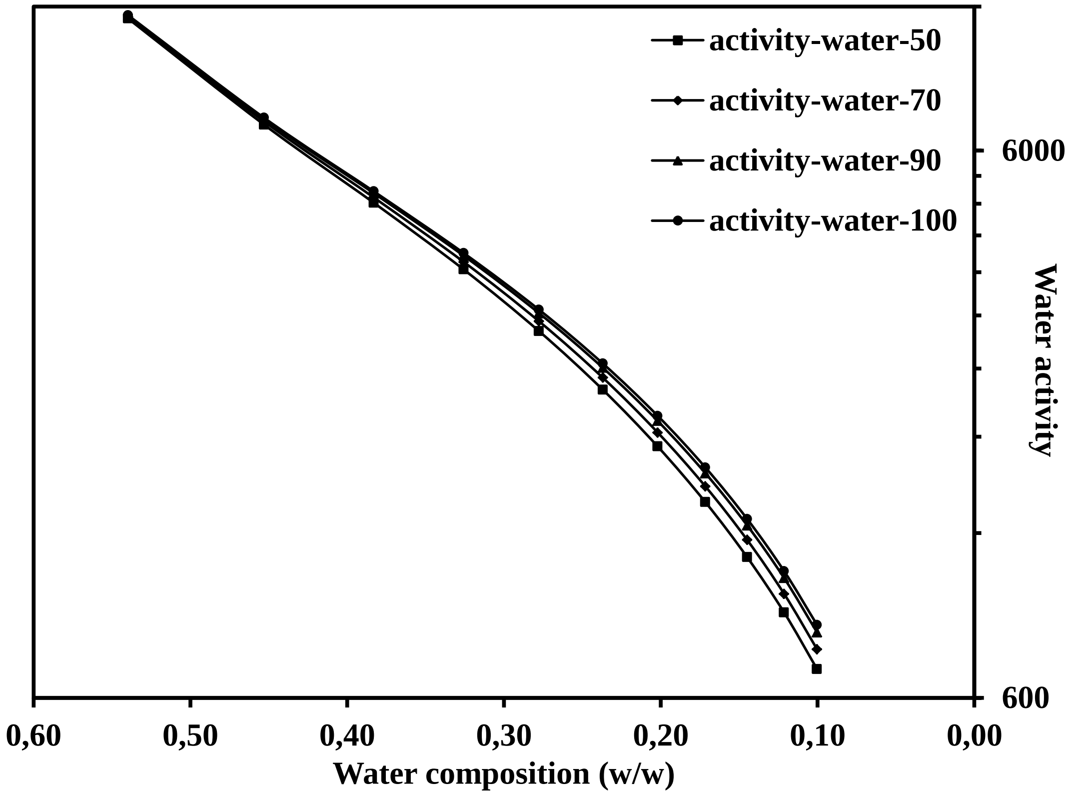


Figure 4.18. Water activity versus water composition

By considering the correlation between water activity in mixture and permeate flux, water activities were calculated in binary DMAc mixture in the range of interest and given in Figure 4.18. Those data were given in Appendix C. It was shown that water activities were almost the same when water content was high, whereas they separated with water content decreases and higher temperature, which then resulted with higher activity of the membrane. As a result, mixtures having higher temperatures had higher permeate fluxes. Casado et al. [21] investigated the effect of temperature on permeation flux for commercial silica membranes. Dehydrations of aqueous isopropanol and acetone mixtures were examined for this purpose. Flux was defined with the Arrhenius type equation:

$$LnJ_{0,wat}(T) = LnJ_{00,wat} - \frac{E_{act}}{RT} \qquad (4.3)^{[21]}$$

where $J_{0,wat}$ was permeate water flux, $J_{00,wat}$ was origin independent from temperature and E_{act} was activation energy required for mass transfer through membrane. Data obtained at 50, 70, 90 and 100°C for DMAc with HybSi membrane were fitted into equation 4.3 and Figure 4.19 was drawn. It could be seen that slopes of the lines at constant feed contents were constant an represented activation energy which was 8980 cal/mol.

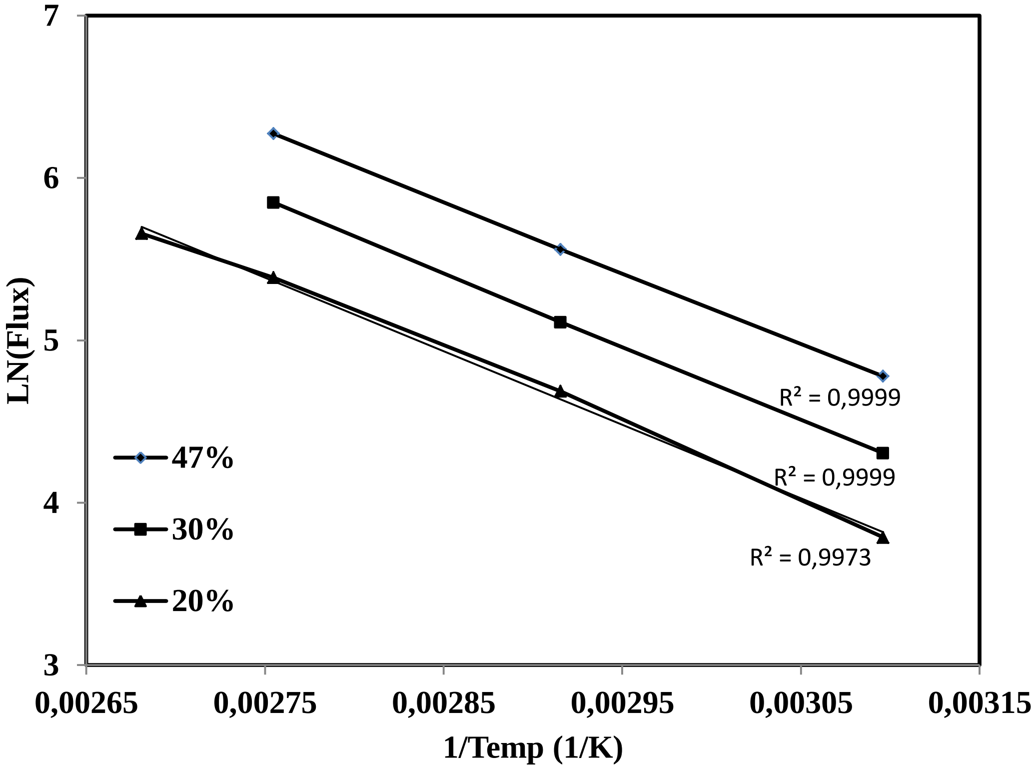


Figure 4.19. Ln(flux) versus 1/Temperature for HybSi membrane

When the increase in permeate fluxes were considered, it would be realized that, temperature adjustment might be beneficial option. Since increasing permeate flux will reduce membrane area requirement, there might be an optimization between cost of heat input and membrane area required.

CHAPTER 5

CONCLUSION

Performances of three commercial inorganic membranes; NaA zeolite, optimized silica and hybrid silica membranes, were investigated in this study. Dehydration of three commonly used aprotic solvent mixtures, which were dimeyhtlacetamide (DMAc), dimethylformamide (DMF), n-methylpyrrolidone (NMP), were performed with concentrated feed method in pervaporation experiments. All three membranes exhibited great chemical stability for DMAc, DMF, NMP.

With a designed hybrid system which included a membrane module mounted before a distillation column, it was ovserved that with 10% reduction in water content, total heat duty decreased from 857 to 576 W/kg of DMAc which was corresponded to 33% decrease in total energy consumption of boiler. Moreover, when the inlet water content was decreased to 30%, total heat duty became 450 W/kg of DMAc so total energy saving was 48%.

The change of fluxes for DMAc mixture were 39.3, 27.4 and 47.4 $g/m^2.h.\%$ feed water for NaA zeolite, optimized silica and HybSi membranes respectively at 50^{o}C. Moreover, NaA type zeolite membrane produced over 99,9% permeate water content, whereas optimized silica and hybrid silica stayed over 98% until 20% feed water content with DMAc mixture at 50^{o}C. Furthermore, rate of recovery for three membranes showed linear behaviour. The rate of recovery for optimized silica membrane was 0.013%/min up to 25%wt water in feed; afterwards, it was 0.008%/min . In addition, the rate of recovery for HybSi membrane was 0.023%/min between 50 and 15%wt feed water contents; then it became 0.011%/min below 15%.

For, NaA zeolite membrane, rate of recovery was 0.022%/min from 30 to 3%wt water in feed.

The dehydration data (obtained at 50^{o}C) of optimized silica and hybrid silica membranes for selected three aprotic solvent mixtures were compared. According to the results, when the optimized silica was used, the permeate flux of NMP mixture was the highest while DMAc mixture`s was the lowest in the range from 50 to 30% feed water content. However, the permeate flux of DMF mixture decreased relatively slower than NMP mixture and became the highest one in the range below 30% feed water content. Moreover, the permeate water content of NMP mixture was higher than 99% up to 15% feed water content, while DMAc mixture`s composition was over 98% despite of a slight decrease between 35% and 15% feed water contents. On the other hand, selectivity of DMF mixture dropped with an increasing trend. Accordingly, the solvent content in permeate of DMF mixture had increased continuously. For the HybSi membrane, permeate fluxes of all mixtures overlapped between 50 and 35% feed water content and below these contents, they started to split up. Moreover, the permeate flux of DMF mixture became the highest one while that of NMP mixture was the lowest one up to 10% feed water content. Furthermore, permeate water contents stayed above 98% for three mixtures up to 20% water in feed. In addition, NMP kept its profile which was almost the same with the profile at the optimized silica showed; whereas, the permeate water content of DMF mixture started to drop slightly. Furthermore, a sharp decrease of permeate water content of DMAc mixture was also observed around 10% feed water content.

Binary DMAc-water mixture was experienced with HybSi membrane at 50, 70, 90 and 100^{o}C in the range of 50 to 10%water in feed. According to the results, permeate fluxes displayed a great increase with increasing temperature. Futhermore, permeate water contents overlapped and stayed over 98% until 20% feed water content and they started to drop afterwards. In addition to all, permeate fluxes for HybSi membrane were defined with the Arrhenius type equation and activation energy for water permeation was calculated as 8980.2 cal/mol.

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APPENDIX A

EXPERIMENTAL DATA

Table A.1. Data obtained from experiments

Date: 09.05.11
Membrane: NaA type zeolite
Feed: 50-50%(wt) Water-DMAC
Temp: 50°C

Run Time (min)	Flux (g/m^2.h)	Feed Water Content (%wt)	Permeate Water Content (%wt)	Separation factor
15	2491.1	50.0	99,98	5280
30	2416.1	49.9	99,98	5163
45	2507.3	49.7	99,98	4536
60	2509.6	49.5	99,98	5962
75	2497.1	49.3	99,99	7756
90	2488.2	49.1	99,98	4783
105	2494.7	48.9	99,99	6880
125	2474.6	48.7	99.97	3510
150	2462.1	48.5	99.97	3539
180	2448.2	48.1	99.98	5394
210	2433.1	47.7	99.97	3654
240	2425.7	47.3	99.97	3713
270	2410.0	46.9	99.96	2830
300	2397.9	46.5	99.96	2875
330	2387.2	46.1	99.96	2922

Table A.2. Data obtained from experiments

Date: 26-30.05.11
Membrane: NaA type zeolite
Feed: 30-70%(wt) Water-DMAC series 1
Temp: 50^{o}C

Run Time (min)	Flux (g/m^2.h)	Feed Water Content (%wt)	Permeate Water Content (%wt)	Separation factor
16	1816.9	30.0	99.21	296
32	1849.9	29.7	99.43	410
52	1846.4	29.1	99.50	480
72	1901.1	28.2	99.58	602
93	1919.7	27.5	99.60	653
117	1894.0	27.1	99.72	910
157	1758.0	26.4	99.91	3168
177	1725.0	26.0	99.95	3743
262	1770.5	25.6	99.90	2892
313	1714.4	25.3	99.90	3065
333	1680.0	24.9	99.89	2607
353	1662.6	24.2	99.90	3273
373	1664.8	23.8	99.92	3852
393	1597.0	22.7	99.95	6906
413	1580.9	22.3	99.94	6148
433	1500.6	21.9	99.91	3829
474	1544.7	21.6	99.94	6310
494	1510.5	21.2	99.94	6114
514	1471.7	20.8	99.94	5765
563	1430.1	20.2	99.95	8381
625	1352.0	19.5	99.91	4699
646	1388.3	19.1	99.92	5589
676	1330.0	18.0	99.75	1832
708	1281.8	17.0	99.92	6007
738	1201.9	15.8	99.84	3336
798	1142.5	14.8	99.72	2037
828	1051.4	13.4	99.67	1951
858	1070.4	11.9	99.05	774
1014	819.7	8.5	98.12	560
1054	745.0	8.1	98.21	621
1084	654.0	7.5	96.98	396
1114	627.6	7.0	94.94	296
1174	533.7	6.0	92.77	201
1203	482.6	4.9	87.70	138
1233	457.1	3.8	80.71	106

Table A.3. Data obtained from experiments

Date: 26-30.05.11
Membrane: NaA type zeolite
Feed: 30-70%(wt) Water-DMAC series 2
Temp: 50°C

Run Time (min)	Flux (g/m^2.h)	Feed Water Content (%wt)	Permeate Water Content (%wt)	Selectivity
30	1914.9	30.0	99.93	3225
79	1966.9	29.7	99.95	4285
86	2062.3	29.1	99,97	7057
117	1983.6	28.6	99,95	4683
148	1908.1	28.2	99,96	6502
179	2022.4	27.9	99,95	4798
209	1897.0	27.5	99,97	7588
240	1863.5	27.1	99,94	4352
270	1990.5	26.7	99,95	5446
301	1783.5	26.4	99,97	8687
331	1784.0	26.0	99,93	3923
361	1590.3	25.6	99,96	6707
391	1711.7	25.3	99,97	8673
447	1590.5	24.9	99,96	7210
478	1606.4	24.2	99,96	8143
518	1629.7	23.8	99,95	6328
548	1583.1	23.5	99,94	5711
578	1617.3	23.1	99,96	8724
608	1548.8	22.7	99,96	7756
638	1574.2	22.3	99,95	6747
668	1502.2	21.9	99,93	5358
698	1533.7	21.6	99,96	8015
729	1477.4	21.2	99,96	8549
759	1518.5	20.8	99,96	10209
789	1419.3	20.2	99,95	7773
819	1386.6	19.8	99,93	5877
849	1350.4	19.5	99,93	6139
880	1429.2	19.1	99,93	5729
910	1328.1	18.4	99,91	4712
940	1367.9	18.0	99,95	9129

Table A.4. Data obtained from experiments

Date: 15-21.07.11
Membrane: Optimized silica
Feed: Pure water
Temp: 50^{o}C

Run Time (min)	**Flux (g/m^2.h)**	**Feed Water Content (%wt)**	**Permeate Water Content (%wt)**	**Separation factor**
24	2490.4	100	100	-
44	2174.1	100	100	-
64	2223.7	100	100	-
84	2240.5	100	100	-
104	2261.6	100	100	-
124	2279.8	100	100	-

Table A.5. Data obtained from experiments

Date: 15-21.07.11
Membrane: Optimized silica
Feed: 50-50%(wt) Water-DMAC series 1
Temp: 50^{o}C

Run Time (min)	**Flux (g/m^2.h)**	**Feed Water Content (%wt)**	**Permeate Water Content (%wt)**	**Selectivity**
20	1316.7	50	99.77	440
40	1254.6	49.8	99.71	341
60	1219.0	49.5	99.81	529
84	1158.9	49.3	99.69	328
104	1155.3	49.0	99.78	472
126	1128.0	48.8	99.76	436
146	1125.1	48.5	99.76	445
166	1095.4	48.3	99.73	400
186	1092.1	48.1	99.75	422
246	1065.3	47.6	99.62	291
276	1045.2	47.3	99.69	356
306	1025.0	47.0	99.68	352
336	1029.6	46.4	99.67	349
365	1048.2	46.1	99.53	246
397	1043.5	45.7	99.62	315
427	1031.8	45.4	99.55	263
457	1029.1	45.0	99.57	280
487	1014.5	44.7	99.54	270
517	1006.5	44.4	99.58	299
547	990.8	44.0	99.56	287
577	984.2	43.6	99.53	272
607	972.5	43.3	99.51	265
637	964.5	42.9	99.58	315
667	950.4	42.6	99.53	285
698	912.8	41.9	99.43	243
727	930.3	41.6	99.52	290
757	929.2	41.2	99.30	203
787	914.1	40.9	99.36	224
817	908.7	40.5	99.22	186
847	897.5	40.1	99.04	154
877	888.1	39.8	99.04	156
907	877.8	39.4	99.40	255
937	869.6	39.1	99.38	251
967	833.4	38.4	99.38	257
997	842.6	38.0	99.33	241
1081	837.2	37.7	99.19	201
1102	778.0	36.6	99.34	259

Table A.5 (cont'd). Data obtained from experiments

1147	797.3	36.3	99.25	233
1192	775.0	35.7	99.23	231
1237	764.6	35.2	99.08	199
1282	749.2	34.6	99.16	223
1327	725.8	33.7	98.82	165
1372	717.6	33.2	98.99	197
1418	703.5	32.7	99.17	244
1463	689.5	32.1	99.19	258
1508	675.3	31.6	99.24	282
1553	661.0	31.0	99.24	290
1598	648.5	30.5	99.13	260
1643	632.7	30.0	98.99	230
1688	620.7	29.4	99.01	239
1733	605.0	28.9	98.95	231
1778	593.6	28.4	99.13	287
1823	574.5	27.5	99.01	264
1868	560.6	27.0	98.82	227
1913	550.2	26.4	98.71	271
1958	526.8	25.9	98.83	242
2003	525.7	25.5	98.89	261
2048	509.7	25.0	98.83	253
2093	491.8	24.5	98.92	281
2138	467.6	24.0	98.89	281
2198	455.0	23.5	98.94	304
2258	442.9	22.9	98.79	276
2335	437.2	22.4	98.30	201
2395	430.3	21.6	98.42	226
2459	414.9	21.0	94.08	60
2519	397.2	20.4	98.33	230
2579	386.8	19.8	98.40	249
2639	372.1	19.2	98.20	229

Table A.6. Data obtained from experiments

Date: 06-10.08.11
Membrane: Optimized silica
Feed: Pure water
Temp: 50^{o}C

Run Time (min)	**Flux (g/m^2.h)**	**Feed Water Content (%wt)**	**Permeate Water Content (%wt)**	**Separation factor**
20	2425.4	100	100	-
40	2543.0	100	100	-
60	2617.7	100	100	-
80	2641.5	100	100	-
100	2634.5	100	100	-
120	2615.1	100	100	-

Table A.7. Data obtained from experiments

Date: 06-10.08.11
Membrane: Optimized silica
Feed: 50-50%(wt) Water-DMAC series 2
Temp: 50^{o}C

Run Time (min)	**Flux (g/m^2.h)**	**Feed Water Content (%wt)**	**Permeate Water Content (%wt)**	**Separation factor**
30	1465.4	50.0	99.70	336
60	1273.4	49.6	99.54	222
90	1274.2	49.2	99.51	210
150	1241.0	48.9	99.54	228
180	1226.2	48.5	99.54	228
210	1204.5	48.1	99.51	218
240	1186.4	47.8	99.35	167
270	1172.0	47.4	99.55	243
300	1154.0	47.0	99.48	214
330	1199.3	46.7	99.20	142
360	1159.8	46.3	99.37	182
390	1147.3	45.9	99.32	173
420	1129.6	45.5	99.47	223
450	1116.4	45.1	99.53	256
480	1109.8	44.8	99.37	193
510	1095.3	44.4	99.42	215
540	1088.9	44.0	99.34	190
570	1072.4	43.6	99.30	184
600	1063.0	43.2	99,27	179
630	1052.3	42.8	99.42	231
660	1037.2	42.5	99.58	319
690	1049.0	42.1	98.85	118
720	1007.1	41.7	99.33	207
750	992.3	41.3	99.34	213
780	985.3	40.9	99.37	227
810	977.2	40.5	99.34	222
840	968.0	40.1	99.39	243
870	958.0	39.7	99.32	221
900	943.3	39.3	99.35	238
930	927.2	38.9	99.25	207
960	913.3	38.6	99.30	224
990	896.9	38.2	99.24	211
1020	880.0	37.8	99.26	219
1050	865.7	37.4	99.20	207
1080	852.2	37.0	99.15	198
1110	841.8	36.6	99.16	204
1140	829.1	36.3	99.10	194

Table A.7 (cont’d). Data obtained from experiments

1170	820.2	35.9	99.20	222
1200	812.9	35.5	99.02	184
1230	806.1	35.1	99.14	213
1260	796.8	34.7	99.06	199
1290	782.8	32.4	99.04	215
1320	769.7	31.9	99.02	216
1350	750.9	31.5	99.05	227
1380	736.3	31.1	99.01	221
1410	725.5	30.8	99.01	224
1440	713.1	30.4	98.99	225
1470	699.3	30.0	98.98	227
1500	677.2	29.6	99.10	262
1545	661.8	29.2	98.93	225
1590	641.5	28.7	98.86	216
1650	624.8	28.1	98.70	194
1710	604.6	27.4	98.78	215
1770	581.8	26.6	98.76	219
1830	592.9	25.9	98.69	216
1890	567.7	25.2	98.65	217
1950	549.2	24.4	98.43	195
2010	523.8	23.7	98.29	185
2070	506.6	22.1	98.26	199
2130	491.3	21.4	98.25	206
2190	474.0	20.7	98.40	236
2250	454.7	20.0	98.23	221
2310	438.9	19.4	98.21	228
2370	421.9	18.7	98.09	223
2430	406.1	18.1	97.88	209
2490	388.2	17.5	97.67	197
2550	371.1	16.9	97.65	204
2610	354.0	16.3	97.65	214
2670	339.8	15.8	97.59	216
2730	328.0	15.2	97.57	224
2790	314.7	14.7	97.66	242
2850	305.2	14.2	97.65	251
2910	293.3	13.7	97.44	240

Table A.8. Data obtained from experiments

Date: 16.08.11
Membrane: Optimized silica
Feed: Pure water
Temp: 50°C

Run Time (min)	**Flux (g/m^2.h)**	**Feed Water Content (%wt)**	**Permeate Water Content (%wt)**	**Separation factor**
20	2610.2	100	100	-
40	2657.9	100	100	-
60	2692.2	100	100	-
80	2707.1	100	100	-
100	2713.1	100	100	-
120	2713.1	100	100	-
140	2714.8	100	100	-
160	2704.6	100	100	-
180	2711.2	100	100	-

Table A.9. Data obtained from experiments

Date: 17-22.08.11
Membrane: Optimized silica
Feed: 50-50%(wt) Water-DMF
Temp: 50^{o}C

Run Time (min)	Flux (g/m^2.h)	Feed Water Content (%wt)	Permeate Water Content (%wt)	Separation factor
30	1393.0	50.0	99.05	104
60	1374.6	49.5	98.62	73
90	1359.6	49.2	98.57	71
120	1339.3	48.8	98.35	62
150	1326.5	48.4	98.57	74
180	1317.4	48.1	98.47	69
210	1307.6	47.7	98.49	71
240	1292.4	47.3	98.42	69
270	1266.1	46.9	97.88	52
300	1266.1	46.5	98.15	61
330	1257.8	46.2	98.06	59
360	1240.2	45.8	97.87	54
390	1231.7	45.4	97.58	48
420	1219.0	45.0	97.81	54
450	1207.0	44.6	97.66	52
481	1192.3	44.2	97.61	52
511	1177.8	43.8	97.42	48
550	1258.4	43.4	96.16	33
580	1209.1	42.9	97.59	54
610	1184.7	42.5	97.06	45
640	1171.7	42.0	97.90	64
670	1160.1	41.6	97.17	48
700	1149.8	41.2	96.95	45
730	1133.8	40.8	97.36	53
760	1123.3	40.4	97.25	52
790	1109.3	39.9	97.30	54
820	1097.5	39.5	96.87	47
851	1085.3	39.1	96.27	40
881	1061.5	38.7	97.46	61
911	1055.3	38.2	97.03	53
941	1043.4	37.8	96.86	51
971	1028.9	37.4	96.55	47
1001	1017.5	37.0	97.14	58
1016	1060.4	36.5	92.88	23
1046	1012.1	36.3	97.14	60
1076	994.9	35.9	95.76	40
1106	979.6	35.4	96.68	53

Table A.9 (cont'd). Data obtained from experiments

1136	967.6	35.0	95.62	41
1169	956.6	34.6	96.12	47
1199	939.8	34.1	96.96	62
1229	919.3	33.7	96.60	56
1259	913.2	33.3	95.97	48
1289	904.4	32.9	96.16	51
1319	892.6	32.4	96.69	61
1334	934.6	32.0	93.58	31
1364	883.1	31.8	95.28	43
1394	858.3	31.3	96.03	53
1424	857.4	30.9	96.66	65
1454	838.5	30.5	96.21	58
1484	828.3	30.0	96.44	63
1514	814.3	29.6	96.09	58
1544	808.2	29.2	94.65	43
1574	787.4	28.8	95.52	53
1604	779.1	28.3	95.62	55
1634	767.6	27.9	95.64	57
1664	757.3	27.5	95.87	61
1694	741.8	27.1	94.20	44
1724	732.5	26.7	94.91	51
1754	718.1	26.2	95.73	63
1784	710.6	25.8	95.01	55
1799	768.5	25.4	90.46	28
1844	685.5	25.2	92.81	38
1888	678.3	24.6	93.30	43
1934	664.7	24.0	93.79	48
1979	644.7	23.4	94.97	62
2027	630.9	22.8	95.63	74
2072	616.5	22.1	92.65	44
2118	595.7	21.5	94.34	61
2163	587.2	20.9	91.51	41
2178	601.1	20.4	87.89	28
2238	573.8	20.2	90.77	39
2301	548.3	19.4	90.93	42
2361	531.2	18.6	92.13	51
2421	507.5	17.8	89.92	41
2481	491.6	17.1	90.04	44
2541	469.6	16.4	89.13	42
2601	458.1	15.7	92.03	62
2616	459.6	15.0	89.58	49
2676	445.7	14.9	88.19	43
2736	426.3	14.2	84.53	33

Table A.9 (cont'd). Data obtained from experiments

2796	407.8	13.5	90.64	62
2856	388.9	12.9	88.29	51
2916	376.6	12.2	87.73	51
2976	361.6	11.6	88.44	58
3036	348.6	11.0	87.72	58
3127	344.2	10.4	80.00	34
3217	321.1	9.6	85.74	57
3309	299.9	8.7	84.10	55
3399	279.7	7.9	83.91	61
3489	263.5	7.2	83.70	66

Table A.10. Data obtained from experiments

Date: 25.08.11
Membrane: Optimized silica
Feed: Pure water
Temp: 50^{o}C

Run Time (min)	**Flux (g/m^2.h)**	**Feed Water Content (%wt)**	**Permeate Water Content (%wt)**	**Separation factor**
21	3107.8	100	100	-
41	2845.5	100	100	-
61	2851.6	100	100	-
81	2849.8	100	100	-
102	2817.8	100	100	-
122	2831.3	100	100	-
241	2820.4	100	100	-
261	2805.6	100	100	-

Table A.11. Data obtained from experiments

Date: 07-12.09.11
Membrane: Optimized silica
Feed: 50-50%(wt) Water-NMP
Temp: 50^{o}C

Run Time (min)	**Flux (g/m^2.h)**	**Feed Water Content (%wt)**	**Permeate Water Content (%wt)**	**Separation factor**
20	2134.7	50.0	99.74	377
40	1913.4	49.6	99.83	585
60	1841.5	49.2	99.68	324
80	1790.7	48.9	99.71	355
100	1762.3	48.5	99.72	376
120	1716.1	48.2	99.74	406
140	1687.2	47.8	99.75	433
160	1658.7	47.5	99.80	548
180	1642.6	47.1	99.65	319
200	1617.8	46.8	99.76	468
220	1596.8	46.5	99.71	390
242	1583.6	46.1	99.65	332
284	1554.8	45.4	99.71	408
304	1525.0	45.0	99.64	335
324	1504.2	44.6	99.70	413
344	1481.8	44.3	99.82	717
364	1473.2	43.9	99.63	345
384	1451.8	43.6	99.68	409
405	1438.8	43.2	99.27	178
435	1432.2	42.8	99.65	379
466	1405.5	42.3	99.70	449
496	1383.1	41.8	99.73	511
526	1360.5	41.2	-99.64	390
556	1316.4	40.7	99.76	613
586	1308.5	40.2	99.71	511
616	1293.2	39.6	99.62	399
646	1264.8	39.1	99.64	432
676	1250.8	38.6	99.68	494
706	1216.8	38.0	99.47	308
739	1196.8	37.5	99.49	322
769	1174.7	36.9	9958	406
789	1068.5	36.4	99.41	296
819	1115.4	36.1	99.69	577
849	1101.0	35.6	99.62	470
879	1089.8	35.1	99.39	301
909	1072.4	34.5	99.63	508
939	1053.8	34.0	98.84	165

Table A.11. Data obtained from experiments

969	1014.5	33.5	99.39	322
999	1005.3	33.0	99.43	357
1029	979.0	32.5	99.70	696
1059	970.6	32.0	99.51	433
1089	945.5	31.5	99.65	619
1119	932.7	31.0	99.70	734
1149	910.7	30.5	99.62	591
1179	895.4	30.0	99.69	740
1209	872.8	29.5	99.54	514
1229	837.6	29.0	99.50	492
1274	824.2	28.7	99.51	506
1319	794.6	28.0	98.80	212
1364	772.8	27.3	99.43	465
1409	749.0	26.6	99.58	657
1454	724.2	25.9	99.39	466
1499	698.6	25.2	99.42	513
1544	677.4	24.5	99.55	689
1589	656.9	23.9	99.40	529
1649	614.8	23.2	99.40	550
1709	585.9	22.4	99.47	645
1769	546.8	21.6	99.28	500
1829	538.6	20.9	99.42	654
1889	510.0	20.1	98.29	229
1949	492.3	19.4	99.27	566
2009	454.4	18.6	99.26	586
2069	435.2	18.0	99.27	618
2129	417.5	17.3	99.04	491
2191	397.8	16.6	99.02	510
2251	379.6	16.0	98.98	510
2311	360.1	15.4	99.02	553
2371	344.0	14.8	98.70	436

Table A.12. Data obtained from experiments

Date: 18-26.10.11
Membrane: HybSi
Feed: 50-50%(wt) Water-DMAC series 2
Temp: 50^{o}C

Run Time (min)	**Flux (g/m^2.h)**	**Feed Water Content (%wt)**	**Permeate Water Content (%wt)**	**Separation factor**
52	2140.1	49.5	99.46	188
82	2078.3	48.9	99.41	177
112	2137.4	48.3	99.48	207
142	2137.8	47.7	99.28	150
172	2117.4	47.1	99.29	157
202	2100.5	46.4	99.48	222
232	2096.5	45.8	97.14	40
262	2039.5	45.1	99.30	174
293	2028.5	44.4	99.45	227
323	2019.8	43.7	99.46	238
353	1989.6	43.0	99.24	174
403	1833.9	41.8	99.33	207
435	1838.9	41.0	99.50	289
465	1857.1	40.3	99.43	260
495	1836.6	39.6	99.33	225
525	1790.3	38.9	99.17	189
555	1741.5	38.2	99.27	221
585	1701.0	37.4	99.40	279
615	1674.7	36.7	99.61	446
645	1648.8	36.0	99.38	286
675	1596.2	35.2	99.37	292
705	1558.4	34.5	99.33	282
755	1453.3	33.2	99.07	214
785	1452.6	32.5	99.22	263
820	1440.9	31.8	99.21	271
850	1418.3	30.9	99.05	233
880	1402.2	30.2	99.24	303
910	1326.3	29.4	98.98	234
940	1284.3	28.7	98.67	184
970	1250.4	28.0	99.16	302
1000	1214.9	27.2	98.56	183
1030	1178.3	26.5	98.53	186
1060	1142.8	25.8	99.21	363
1110	1029.9	24.7	98.64	221
1140	1053.0	24.0	98.75	250
1170	1056.1	23.4	98.74	257
1200	989.9	22.7	99.09	370

Table A.12 (cont'd). Data obtained from experiments

1230	960.7	22.0	99.05	370
1261	932.3	21.4	99.07	389
1291	900.4	20.7	98.96	365
1321	863.1	20.1	98.34	236
1351	836.3	19.5	98.17	221
1431	796.0	18.6	98.67	325
1491	719.5	17.4	98.03	236
1551	678.7	16.3	98.21	282
1611	633.6	15.3	97.52	218
1671	563.9	14.3	95.18	118
1731	535.7	13.4	92.48	80
1791	495.1	12.5	96.25	180
1851	460.8	11.7	97.28	270
1911	422.4	10.9	97.06	270
1971	361.6	10.1	93.09	120
2031	367.7	9.5	95.65	210
2091	335.4	8.9	93.50	147
2151	299.0	7.9	91.93	133
2211	266.8	7.1	92.01	151

Table A.13. Data obtained from experiments

Date: 18-26.10.11
Membrane: HybSi
Feed: 50-50%(wt) Water-DMAC series 2
Temp: 50^{o}C

Run Time (min)	**Flux (g/m^2.h)**	**Feed Water Content (%wt)**	**Permeate Water Content (%wt)**	**Separation factor**
52	2140.1	49.5	99.46	188
82	2078.3	48.9	99.41	177
112	2137.4	48.3	99.48	207
142	2137.8	47.7	99.28	150
172	2117.4	47.1	99.29	157
202	2100.5	46.4	99.48	222
232	2096.5	45.8	97.14	40
262	2039.5	45.1	99.30	174
293	2028.5	44.4	99.45	227
323	2019.8	43.7	99.46	238
353	1989.6	43.0	99.24	174
403	1833.9	41.8	99.33	207
435	1838.9	41.0	99.50	289
465	1857.1	40.3	99.43	260
495	1836.6	39.6	99.33	225
525	1790.3	38.9	99.17	189
555	1741.5	38.2	99.27	221
585	1701.0	37.4	99.40	279
615	1674.7	36.7	99.61	446
645	1648.8	36.0	99.38	286
675	1596.2	35.2	99.37	292
705	1558.4	34.5	99.33	282
755	1453.3	33.2	99.07	214
785	1452.6	32.5	99.22	263
820	1440.9	31.8	99.21	271
850	1418.3	30.9	99.05	233
880	1402.2	30.2	99.24	303
910	1326.3	29.4	98.98	234
940	1284.3	28.7	98.67	184
970	1250.4	28.0	99.16	302
1000	1214.9	27.2	98.56	183
1030	1178.3	26.5	98.53	186
1060	1142.8	25.8	99.21	363
1110	1029.9	24.7	98.64	221
1140	1053.0	24.0	98.75	250
1170	1056.1	23.4	98.74	257
1200	989.9	22.7	99.09	370

Table A.13 (cont'd). Data obtained from experiments

1230	960.7	22.0	99.05	370
1261	932.3	21.4	99.07	389
1291	900.4	20.7	98.96	365
1321	863.1	20.1	98.34	236
1351	836.3	19.5	98.17	221
1431	796.0	18.6	98.67	325
1491	719.5	17.4	98.03	236
1551	678.7	16.3	98.21	282
1611	633.6	15.3	97.52	218
1671	563.9	14.3	95.18	118
1731	535.7	13.4	92.48	80
1791	495.1	12.5	96.25	180
1851	460.8	11.7	97.28	270
1911	422.4	10.9	97.06	270
1971	361.6	10.1	93.09	120
2031	367.7	9.5	95.65	210
2091	335.4	8.9	93.50	147
2151	299.0	7.9	91.93	133
2211	266.8	7.1	92.01	151

Table A.14. Data obtained from experiments

Date: 16-23.11.11
Membrane: HybSi
Feed: 50-50%(wt) Water-DMF
Temp: 50°C

Run Time (min)	**Flux (g/m^2.h)**	**Feed Water Content (%wt)**	**Permeate Water Content (%wt)**	**Separation factor**
21	2179.0	50.0	98.34	59
42	2030.5	49.6	99.12	114
62	2087.1	49.2	99.19	127
92	2109.6	48.8	99.16	124
122	2138.5	48.2	98.98	104
152	2127.2	47.6	99.29	154
183	2124.6	46.9	99.25	150
213	2089.8	46.2	99.15	137
243	2052.7	45.6	99.29	167
274	2022.0	44.9	99.35	186
304	2022.8	44.2	99.54	271
334	1992.8	43.5	99.36	203
364	1938.9	42.8	99.08	144
394	1884.5	42.1	98.70	105
424	1862.0	41.4	98.86	122
454	1780.3	40.7	98.93	135
504	1790.6	39.5	9852	102
534	1729.4	38.7	98.80	130
564	1732.3	38.0	98.68	122
594	1675.2	37.3	98.68	126
625	1645.8	36.6	99.19	212
655	1659.8	35.8	98.62	128
685	1624.1	35.1	98.59	129
715	1596.1	34.3	98.86	167
745	1585.5	33.6	98.92	182
802	1495.6	32.2	90.54	152
832	1489.2	31.2	98.63	149
862	1472.4	30.5	-	-
893	1440.4	29.7	98.89	210
924	1419.1	28.9	98.83	207
954	1380.3	28.1	98.52	170
1004	1248.4	26.7	98.95	259
1034	1233.5	26.0	98.59	199
1064	1222.8	25.2	98.88	262
1094	1197.1	24.5	98.53	206
1124	1176.0	23.7	98.65	236
1154	1146.6	23.0	98.34	198

Table A.14 (cont'd). Data obtained from experiments

1204	1066.3	21.7	98.51	238
1234	1075.3	21.0	98.25	211
1264	1046.4	20.2	98.55	269
1294	1024.0	19.5	98.16	221
1324	990.3	18.8	95.14	85
1354	946.4	18.1	97.89	210
1384	925.4	17.4	98.07	242
1414	890.8	16.7	97.44	190
1454	857.0	16.0	98.24	294
1474	823.2	15.3	95.95	131
1534	762.8	14.9	97.82	257
1594	732.2	13.7	97.15	214
1654	674.5	12.5	97.02	228
1714	621.2	11.3	96.90	245
1774	576.1	10.2	96.46	240
1834	529.0	9.2	96.80	298

Table A.15. Data obtained from experiments

Date: 30.11.11-03.12.11
Membrane: HybSi
Feed: 50-50%(wt) Water-NMP
Temp: 50^{o}C

Run Time (min)	**Flux (g/m^2.h)**	**Feed Water Content (%wt)**	**Permeate Water Content (%wt)**	**Separation factor**
20	2583.7	50.0	98.96	95
50	2269.9	49.5	99.81	529
80	2250.0	48.9	99.80	530
110	2195.6	48.2	99.79	510
140	2138.6	47.5	99.79	535
170	2085.0	46.9	99.74	428
200	2035.2	46.2	99.75	474
230	2023.5	45.5	99.74	458
260	1967.9	44.8	99.75	501
290	1956.5	44.2	99.75	495
320	1932.9	43.5	99.75	512
350	1897.4	42.8	99.75	531
381	1839.0	42.1	99.72	488
411	1824.4	41.3	99.75	563
441	1778.6	40.6	99.72	530
471	1744.0	39.9	99.72	535
501	1690.5	39.2	99.69	504
531	1665.8	38.5	99.58	382
581	1632.1	37.3	99.63	448
611	1590.0	36.6	99.61	444
641	1568.5	35.8	99.68	557
671	1516.1	35.1	99.70	618
702	1492.1	34.4	99.42	328
731	1446.1	33.6	99.55	438
751	1391.9	32.9	99.02	206
782	1365.5	32.5	99.29	291
812	1306.6	31.7	99.16	253
843	1261.2	31.0	99.43	386
873	1253.6	30.3	99.10	254
917	1224.3	29.7	99.44	421
950	1189.8	28.9	99.55	544
980	1162.0	28.1	99.43	449
1000	1134.0	27.4	99.66	785
1030	1096.4	26.8	99.42	470
1060	1051.8	26.1	99.47	535
1090	1006.4	25.5	99.50	586
1120	990.5	24.8	99.61	766

Table A.15 (con't). Data obtained from experiments

1150	960.3	24.2	99.29	436
1180	932.6	23.6	99.32	475
1210	913.5	23.0	99.30	476
1240	875.4	22.3	98.69	263
1270	842.6	21.7	99.14	416
1300	804.4	21.2	99.16	437
1330	749.0	20.6	99.01	386
1410	692.9	19.7	99.28	561
1470	646.6	18.7	99.27	592
1530	607.9	17.7	99.16	548
1590	575.6	16.8	99.34	745
1650	538.0	15.9	99.13	601
1710	495.5	15.0	99.12	637
1770	465.3	14.2	99.08	651
1830	431.6	13.4	99.25	850
1906	402.5	12.7	98.98	668
1996	370.1	11.8	98.95	704
2086	329.3	10.9	98.90	738
2176	293.2	10.0	98.96	860

Table A.16. Data obtained from experiments

Date: 07-09.12.11
Membrane: HybSi
Feed: 50-50%(wt) Water-DMAc
Temp: 70°C

Run Time (min)	**Flux (g/m^2.h)**	**Feed Water Content (%wt)**	**Permeate Water Content (%wt)**	**Separation factor**
20	5189.7	50.0	99.38	159
40	4495.2	49.0	99.48	200
60	4576.6	48.1	99.41	183
80	4673.8	47.2	99.26	150
100	4342.1	46.2	99.41	195
120	4453.9	45.2	99.32	178
140	4397.7	44.2	99.41	212
160	4206.5	43.2	99.49	259
180	4171.2	42.2	99.48	261
200	4174.3	41.1	99.41	241
220	3925.8	40.0	99.23	192
240	3876.4	38.9	98.92	143
260	3654.9	37.8	98.60	116
281	3522.0	36.7	99.42	294
301	3405.6	35.6	99.32	264
321	3360.4	34.6	99.18	228
341	3419.7	33.5	99.33	292
361	3322.5	32.3	99.12	236
381	3175.8	31.2	98.88	195
401	2986.5	30.0	99.19	284
421	2859.4	28.9	98.81	216
441	2790.6	27.8	98.99	269
461	2708.4	26.7	98.89	259
481	2584.4	25.6	98.77	248
501	2437.9	24.5	99.34	489
521	2244.8	23.5	97.77	121
571	2033.8	21.4	99.13	421
601	1952.9	20.0	98.62	286
630	1748.6	18.6	99.12	491
660	1678.9	17.2	98.65	352
690	1501.9	15.9	98.94	496
720	1401.5	14.7	98.33	341
750	1287.5	13.6	98.80	525
780	1183.9	12.5	97.69	296
810	1069.4	11.4	98.21	427
840	977.8	10.5	96.85	262
870	848.7	9.6	96.87	291

Table A.16. Data obtained from experiments

900	773.8	8.8	97.63	428
930	694.6	8.1	97.84	514

Table A.17. Data obtained from experiments

Date: 10.12.11
Membrane: HybSi
Feed: 50-50%(wt) Water-DMAc
Temp: 90^{o}C

Run Time (min)	**Flux (g/m^2.h)**	**Feed Water Content (%wt)**	**Permeate Water Content (%wt)**	**Separation factor**
10	11560.0	50.0	99.02	101
30	9625.6	48.9	97.83	47
45	9541.4	47.0	98.86	98
60	9810.6	45.5	99.32	176
75	9186.7	43.8	99.45	234
90	8818.2	42.2	98.90	123
105	8542.3	40.5	99.09	160
120	8243.1	38.8	99.08	171
135	7828.5	37.0	98.88	150
150	7656.5	35.3	99.00	182
165	7028.6	33.5	99.15	231
180	6884.5	31.7	98.91	195
195	6242.9	30.2	99.17	275
210	6329.9	28.2	98.37	154
225	5522.7	26.3	99.18	388
240	5255.4	24.6	98.85	264
256	4425.6	22.9	98.83	283
271	4682.5	21.3	96.23	94
286	3932.1	19.6	99.08	441
301	4153.9	18.2	96.80	136
317	3381.9	16.6	98.38	306
332	3192.4	15.2	98.48	362
347	2791.8	13.9	97.62	254
367	2500.9	12.8	97.60	277
387	2111.8	11.4	94.99	147
407	1809.5	10.1	98.29	512
427	1593.2	9.0	95.19	200
447	1354.5	8.1	95.48	240

Table A.18. Data obtained from experiments

Date: 15.12.11
Membrane: HybSi
Feed: 50-50%(wt) Water-DMAc
Temp: 100°C

Run Time (min)	**Flux (g/m^2.h)**	**Feed Water Content (%wt)**	**Permeate Water Content (%wt)**	**Separation factor**
10	9407.9	25.4	94.11	47
26	6078.4	23.4	98.99	321
41	5432.5	21.2	98.82	310
56	5158.9	19.2	98.85	360
71	3958.4	17.3	97.39	178
86	3835.0	15.8	96.63	153
101	3418.1	14.2	97.46	232
116	3023.9	12.8	97.77	298
131	2529.8	11.5	96.81	234
146	2211.4	10.3	97.91	408
161	1949.4	9.3	96.63	280
176	1695.8	8.4	98.36	653
191	1471.9	7.6	96.08	298
206	1201.5	6.9	94.98	255
227	1017.8	6.3	95.16	293
247	840.5	5.6	95.48	356
267	672.1	5.1	94.89	345
297	533.3	4.6	89.37	174
327	404.0	4.1	79.85	93
357	295.3	3.6	76.28	86

APPENDIX B

DISTILLATION COLUMN CALCULATIONS

B.1 Calculation of minimum reflux ratio

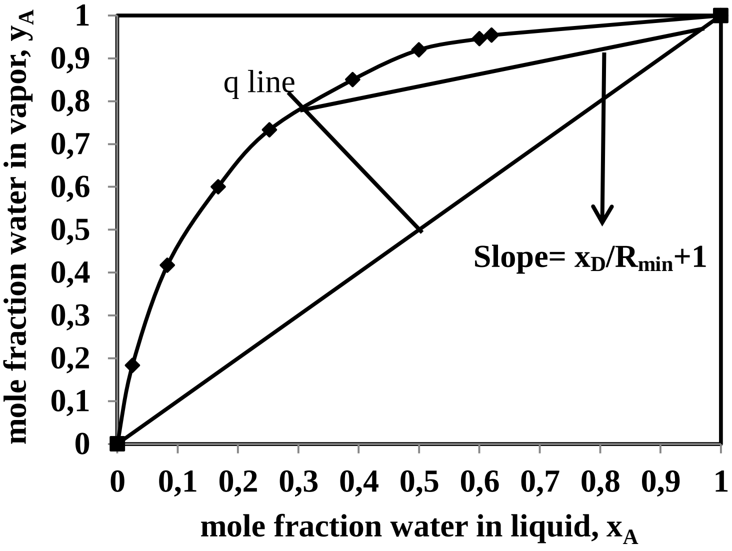


Figure B.1. Vapor-liquid equilibrium for DMAc-water system

x_D = 0,98%mole (0,9%wt)

Slope = 0,2727 = x_D/ (R_{min}+1)

R_{min} = (0,98/0,2727)-1 = **2.6**

B.2 Calculation of heat duty of reboiler

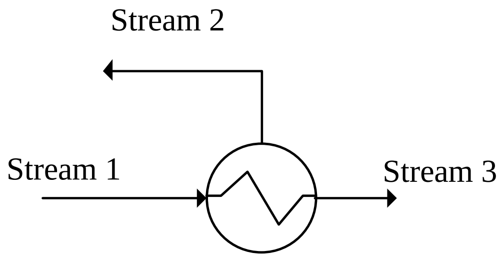


Figure B.2 Reboiler of distillation column

Feed of distillation column was taken 100kg/hour as basis for calculations.

Content of stream 1, 2 and 3 were calculated by using vapor-liquid equilibrium data for DMAc-water mixture and tabulated in Table B.1.

Table B.1. Content of streams around reboiler

	%mole		%weigth	
	DMAc	Water	DMAc	Water
Stream 1	1,17 kmol (28%)	3,06 kmol (72%)	101,6 kg (35,2%)	55,2 kg (64,8%)
Stream 2	2,79 kmol (19%)	0,65 kmol (81%)	50,2 kg (90%)	56,6 kg (10%)
Stream 3	0,52 kmol (66%)	0,27 kmol (34%)	45 kg (90%)	5 kg (10%)

$$Q = n_w \times \Delta H_w^{vap} + n_{DMAc} \times \Delta H_{DMAc}^{vap}$$

$$Q = 2{,}79kmol \times \frac{39543kj}{kmol} + 0{,}65kmol \times \frac{43825kj}{kmol}$$

$$Q = 138811kj\ for\ 45\ kg\ DMAc\ recovery$$

$$Q = \frac{3085kj}{kgDMAc} \times \frac{1000}{3600s} = \frac{\boldsymbol{857W}}{\boldsymbol{kgDMAc}}$$

APPENDIX C

UNIFAC GROUP CONTRIBUTION METHOD CALCULATIONS

Activity coefficient was calculated by combining two contents; combinatory and residual. [30]

$$ln\gamma_i = ln\gamma_i^c + ln\gamma_i^r \qquad (C.1)\ [30]$$

C.1 Calculation of combinatorial content

$$ln\gamma_i^c = ln\frac{\phi_i}{x_i} + \frac{z}{2}q_i ln\frac{\theta_i}{\phi_i} + L_i - \frac{\phi_i}{x_i}\sum_{j=1}^{n} x_j L_j \qquad (C.2)[30]$$

Parameters in equation C.2 were calculated with: [30]

$$\theta_i = \frac{x_i q_i}{\sum_{j=1}^{n} x_j q_j}\ ;\ \phi_i = \frac{x_i r_i}{\sum_{j=1}^{n} x_j r_j}\ ;\ L_i = \frac{z}{2}(r_i - q_i) - (r_i - 1)\ ;\ z = 10$$

$$r_i = \sum_{k=1}^{n} \nu_k R_k\ ;\ q_i = \sum_{k=1}^{n} \nu_k Q_k \qquad [30]$$

C.2 Calculation of residual content

$$ln\gamma_i^r = \sum_k^n \nu_k^{(i)} \left[ln\Gamma_k - ln\Gamma_k^{(i)}\right]$$ (C.3)[30]

Parameters in equation C.3 were calculated with:

$$ln\Gamma_k = Q_k \left[1 - ln\sum_m \Theta_m \Psi_{mk} - \sum_m \frac{\Theta_m \Psi_{km}}{\sum_n \Theta_n \Psi_{nm}}\right]$$ (C.4)[30]

$$\Theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n}$$ (C.5)[30]

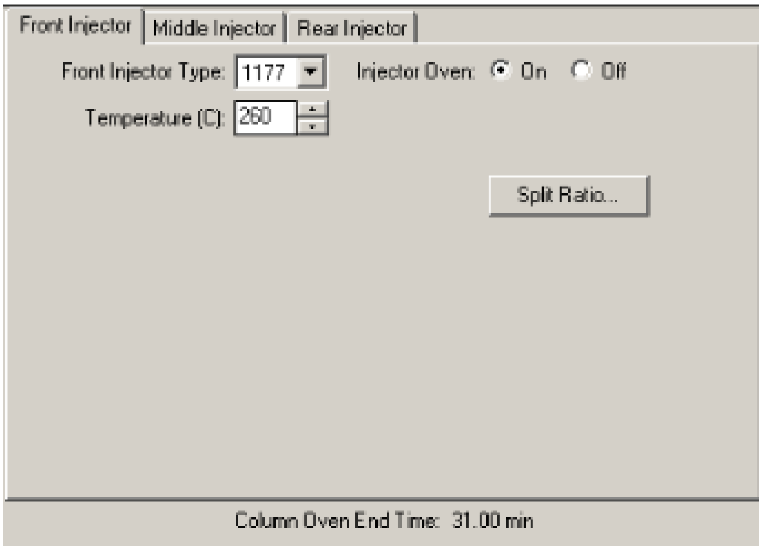
$$\Psi_{mn} = \exp - \left[\frac{U_{mn} - U_{nm}}{RT}\right] \; ; \; X_m = \frac{\sum_j \nu_m^j x_j}{\sum_j \sum_n \nu_n^j x_j}$$ [30]

$$\Psi_{mn} = \exp \frac{-a_{mn}}{T}$$ [30]

Parameters for UNIFAC structural groups were taken from tables in literature. [30]

APPENDIX D

GAS CHOROMATOGRAPHY METHOD



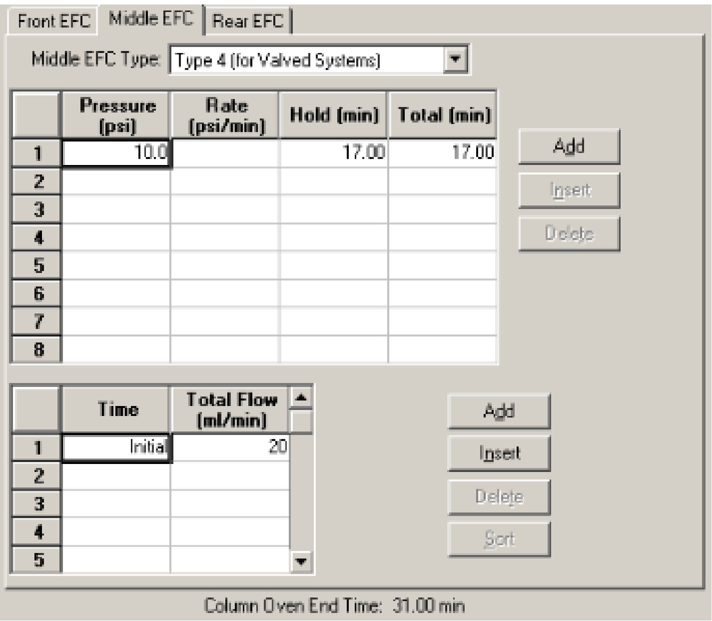
Front Injector Type: 1177

Injector Oven: ● On ○ Off

Temperature (C): 260

Column Oven End Time: 31.00 min

Figure D.1. Injector conditions of GC



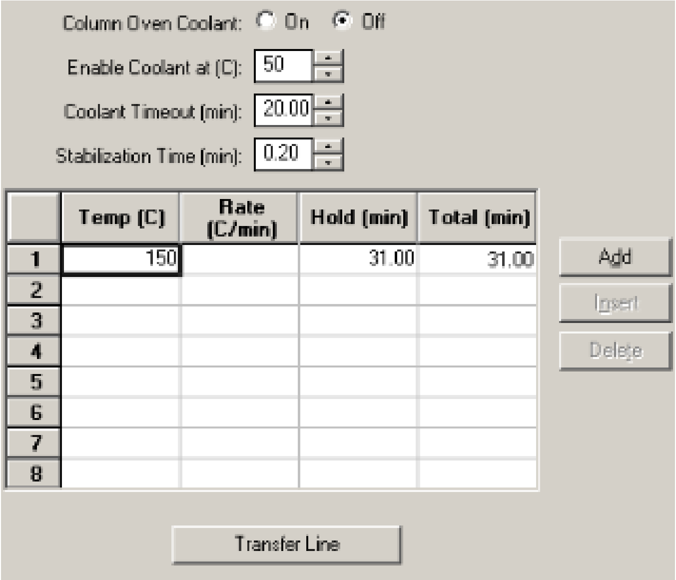
Middle EFC Type: Type 4 (for Valved Systems)

	Pressure (psi)	Rate (psi/min)	Hold (min)	Total (min)
1	10.0		17.00	17.00
2				
3				
4				
5				
6				
7				
8				

	Time	Total Flow (ml/min)
1	Initial	20
2		
3		
4		
5		

Column Oven End Time: 31.00 min

Figure D.2. Flow conditions of GC



Column Oven Coolant: ○ On ● Off

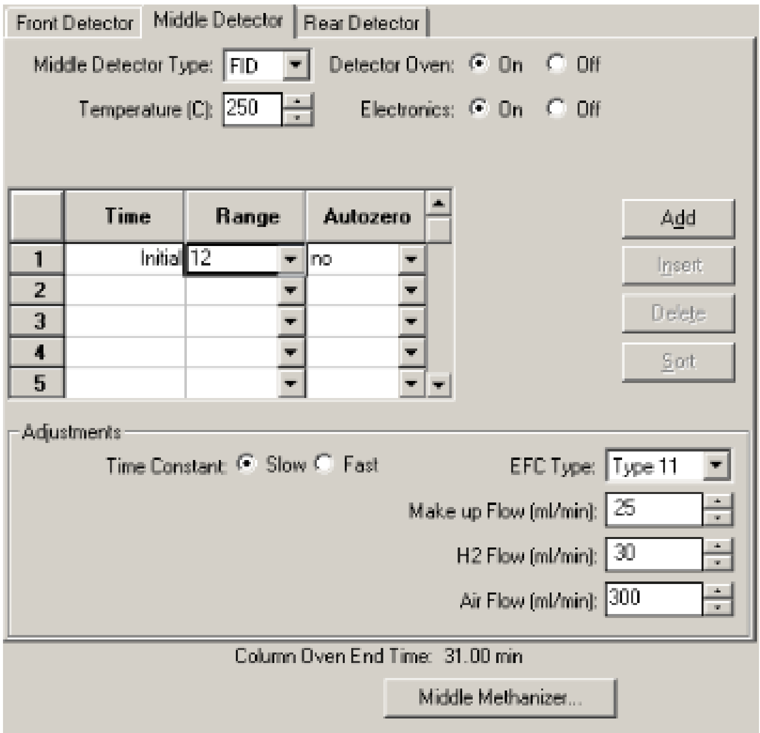
Enable Coolant at (C): 50

Coolant Timeout (min): 20.00

Stabilization Time (min): 0.20

	Temp (C)	Rate (C/min)	Hold (min)	Total (min)
1	150		31.00	31.00
2				
3				
4				
5				
6				
7				
8				

Figure D.3. Oven conditions of GC



Middle Detector Type: FID

Detector Oven: ● On ○ Off

Temperature (C): 250

Electronics: ● On ○ Off

	Time	Range	Autozero
1	Initial	12	no
2			
3			
4			
5			

Adjustments

Time Constant: ● Slow ○ Fast

EFC Type: Type 11

Make up Flow (ml/min): 25

H2 Flow (ml/min): 30

Air Flow (ml/min): 300

Column Oven End Time: 31.00 min

Figure D.4. Detector conditions of GC