

# **Extraction of Organic Solvent (Ethanol) via Pervaporation using polyurethane Membrane: A simulation study**

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University of Engineering and Technology, Lahore**

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THIS PROJECT IS SUBMITTED TO THE DEPARTMENT OF CHEMICAL ENNGINEERING, UNIVERSITY OF ENGINEERING AND TECHNOLOGY, LAHHORE FOR THE PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE MASTER'S DEGREE IN CHEMICAL ENGINEERING.

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## Abstract

Hybrid distillation-membrane setups have caught much attention in recent years due to their less energy usage compare to conventional separation techniques such as extractive distillation for ethanol purification. Membrane separation processes operate without heating, therefore use less energy. Pervaporation and vapor permeation are the processing methods for the separation of liquid or vapor mixtures through a membrane. In this study, four different configurations of hybrid distillation-membrane setups are proposed. Both pervaporation and vapor permeation processes were modeled and simulated with the aid of solution diffusion model. The design of hybrid process has been performed by coupling the membrane model with a simulator of distillation column. In addition to this, the performance of ceramic, polymeric and composite membranes has also been investigated by evaluating the recovery and membrane area required for ethanol purification in a hybrid setup. The whole process was realized in Aspen plus. It was observed that distillation-membrane setups have great potential for ethanol purification since these setups exhibited relatively lower operating energy compared to art distillation. Furthermore, it was also found that the hybrid processes configured with a membrane exhibiting vapor permeation are less energy intensive than that of containing a pervaporation membrane.

**Keywords:** Hybrid Setup, Energy, Pervaporation, Vapor Permeation, Polymeric and Ceramic membranes, Membrane area and ethanol recovery.



## **CHAPTER 1: INTRODUCTION AND LITERATURE REVIEW**

## 1.1. Introduction

Energy consumption by chemical industry is increasing rapidly especially where the separation units such as distillation columns and evaporators are in operation. Continually diminishing reserves of natural gas, oil and coal have posed a big question mark on the fulfillment of future energy demand. It is predicted that global energy utilization in 2040 will be approximately 30% higher than the one in 2010 [1]. Although fossil fuels have been the major source of energy for several decades but their impact on the environment has always been an issue [2]. Therefore, an extensive amount of research is being conducted to find such alternative fuels that would not only meet the future energy demands but are also environment friendly. Ethanol is one such alternative that is readily available since one of its major sources is fermentation plant [3], [4]. Therefore, production and purification of ethanol has been a hot topic in recent years due to its emergence as a suitable alternative fuel source to conventional fossil fuels obtained from natural gas, oil and coal. Distillation is the most commonly used process to purify ethanol. However, it requires a large amount of energy, thus making it an energy intensive process. This problem is even magnified when it is required to get water free ethanol (purity>99 mol%). The problem arises due to the azeotropic nature of the water-ethanol mixture at higher concentrations of ethanol. Therefore, alternative techniques such as extractive distillation, pressure swing distillation, gas stripping [5]–[10] and membrane separations such as pervaporation and vapor [11] are employed to reduce the energy usage .

Membrane separation processes including pervaporation and vapor permeation operate without heating, therefore use less energy than conventional processes[11]. Although the feed to these processes is either pre-heated (pervaporation) or completely vaporized (vapor-permeation) but the heat utilization is much lower compared to the conventional processes and no additional heat is required during the specie transport. These processes are considered auspicious for the purification of organic solvents due to the fact that they are not only a suitable choice for breaking the azeotrop but also give high purity product. Low Energy requirements and better separation performance have made the membranes a perfect candidate for organic solvent dehydration. The membrane is carefully chosen such that only one the component of the feed is allowed to pass through the membrane,

whereas the other components should not have any affinity with the membrane. This selective nature of the membranes becomes the basis for the separation of a mixture without requiring any heat. In the pervaporation process a feed stream below its boiling point is first pre-heated in order to increase the partial pressure of the components and then sent to a membrane module. The component traveling across the membrane is vaporized on the permeate side by utilizing the heat from within the liquid. The partial pressure of the components is increased in order to enhance the driving force for mass transport. The permeate is condensed and collected at a lower vapor pressure on the permeate side. For the case of hydrophilic membrane in which water transports across the membrane, the high purity product is collected on the retentate side in liquid form. A standalone membrane unit or multiple membranes connected in series or parallel arrangements can yield the ethanol solution containing ethanol as high as 99.99 mol% [11]. However, ethanol recovery would be an issue due to the flux limitations of the

Membrane. Flux is the amount of mixture transported across a membrane per unit time per unit area. To get the desired purity of ethanol, multiple membranes may be installed that can be considered as number of stages (analogous to number of trays in a distillation column). However, in each of the membrane units a small amount of ethanol is also transported across the membrane due to which 100 % ethanol recovery becomes a tedious task. Membrane selectivity, which is the degree of separation, should also be very high in order to make sure that only small amount of ethanol travels across the membrane. However, a membrane with high selectivity yields overall lower flux and vice versa. Therefore, either high recovery or high purity can be achieved or a tradeoff must be made between them. It is due to this inherent feature of membranes that researchers are working on developing the membranes with high fluxes and favorable selectivities. On the other hand, a standalone distillation column is not sufficient to purify the organic solvent and the maximum separation cannot exceed the azeotropic composition of the mixture [10]. Therefore, the idea of integrating the distillation and membrane units together have caught much attention in recent years [12]. It was initially proposed that the top from the distillation column containing the azeotropic concentration of ethanol can be sent to the membrane unit for further purification. In this way, a relatively lesser number of membrane modules would be required due to the pre-concentration of the membrane feed by the

column. In addition to this, pre-heating required by pervaporation is also compensated as the top stream from the column is already at higher temperature. Therefore, by coupling the membrane and distillation units, the disadvantages of both units can be overcome. The coupling of these two units is usually termed as hybrid distillation-membrane setup. A significant amount of research has been conducted in order to optimize these hybrid process by either modifying the membrane module with higher selectivity or by using various configurations of the hybrid setups [13]–[18]. S. van Wyk et al. [13] investigated the viability of hybrid distillation-membrane setup for the concentration of organic solvents from Acetone-butanol-ethanol mixture to lessen the energy utilization of a downstream recovery from fermentation broth. The results of this work indicated that, in comparison to azeotropic distillation, about 53% of energy could be saved by employing hybrid setup. A. Rom et al. [14] investigated the energy saving potential of hybrid distillation-membrane setup for the recovery of butanol. The results of this work showed that about 53% of energy could be saved by employing hybrid setup in comparison to art distillation. G.R.Harvianto et al. [15] studied the feasibility of various configurations of the hybrid distillation-membrane setups for dehydration of isopropanol. In this study, it was found that, in comparison to azeotropic distillation, the use of hybrid setup saves energy. In another study the influence of heat integration with Hybrid Distillation-membrane setup was studied [16]. It was found that the separation cost is reduced by connecting the hybrid setup with heating source. M.A. Sosa et al.[17] compared various pervaporation membranes for the production of bioethanol. The results of this study indicated that feasibility of a membrane in a hybrid process can be best described when lab scale measurements are observed on a pilot scale and then ultimately on the commercial scale. D.A. Figueroa Paredes et al [18] investigated the feasibility of four different pervaporation membranes for the separation of methanolmethyl acetate mixtures. The analysis was based on the optimization of permeate pressure and it was found that permeate pressure plays a vital role in capturing trade-offs between the investment and operating cost of the pervaporation process.

Like other organic solvents, ethanol purification through the Hybrid Distillation-membrane setup has also been investigated previously [19]–[24]. These studies mainly focused on feasibility of hybrid distillation-membrane setups and the effect of hydrophobic and hydrophilic membranes, the effect of distillation column side stream and the effect of

pervaporation or vapor permeation on the membrane performance in a hybrid setup. However, there are no reports available concerning the performance of membranes of different types, including polymeric, ceramic and composite membranes, in various configurations of a hybrid distillation-membranes setup. The main questions that must be answered are as follows: (1) how different types of membranes including polymeric, ceramic and composites membranes would perform in hybrid distillation pervaporation or vapor permeation setup? (2) What is the effect of distillation column side stream on the total energy required and performance of each type of membrane mentioned previously ? (3) which type of process either hybrid distillation pervaporation or vapor permeation is feasible considering total energy requirement and ethanol recovery? Some configurations may yield high ethanol recovery but require high energy as well and vice versa. Therefore, further research is required for choosing the best configuration of a Hybrid Distillation-membrane setup in order to achieve both high Ethanol recovery and high purity by keeping the energy and material cost as low as possible.

Therefore, the aim of this work is to study the various configurations of a Hybrid Distillation-membrane setups for ethanol dehydration and to analyze and compare the performance of different membranes in each configuration. In addition to this, a comparative study between pervaporation and vapor permeation is also considered by employing different membranes for each configuration. The evaluation criteria is based on ethanol recovery, its purity, total membrane area required and total energy required. Furthermore, the results of this work are also compared with the results obtained from alternative hybrid processes which do not utilize membrane [10]. The hybrid process is realized in Aspen Plus which is a commercial software containing well established mathematical models for solving energy and material balance for unit operations such as distillation. Unit operations like membrane separations are not built in ASPEN Plus. Therefore, a mathematical model representing the membrane unit is developed in ASPEN Custom Modeler (ACM). ACM is then exported to ASPEN Plus and integrated with other unit operations. Highly concentrated ethanol is usually the demand on commercial scale. Therefore, in this study an ethanol purity of 99.99 mol% is set as target.

## **CHAPTER 2: MATERIALS AND METHODS**

## 2.1 Hydrophilic Membranes for Pervaporation

Hydrophilic membranes only allow the transport of water molecules due to the presence of hydrophilic (water loving) groups. Pervaporation process is best carried out by utilizing a hydrophilic membrane due to the presence of these polar functional groups within the membrane structure [25]. Hydrophobic membranes, on the other hand, favor the transport of organic part of the feed and exhibit low separation factors compared to the hydrophilic membranes when exposed to the dilute solution. Some of the key benefits of hydrophilic membranes include strength, hardness, extensive range of chemical and solvent resistance and the exhibition of barriers to some microbes. The main categories of hydrophilic membranes include polymeric membranes, ceramic membranes and hybrid membranes containing both polymeric and ceramic part.

Lab scale hydrophilic polymeric membranes of various selectivity have been prepared by many researchers for organic solvent dehydration [26], [27]. Their research showed that dehydration of ethanol by pervaporation is a feasible process as they were able to achieve high selectivity values. However, swelling problem and short life of polymeric membranes is a major concern which is why ceramic membranes have also been widely used for organic solvent dehydration due to their regular small pore size and strong hydrophilicity [28], [29]. In contrast to many polymeric membranes the ceramic membranes exhibit enormously high chemical and physical stability, exceptional separation features and long working life.

It is obvious from the above discussion that ceramic membranes have got much attraction for their favorable properties when compared to polymeric membranes. However, there are many other favorable factors including ease of processing and low fabrication cost that are associated to polymeric membranes. Ceramic membranes, on the other hand, are way too expensive. Therefore, the choice of either ceramic or polymeric membrane is still a challenge as both have some advantages and disadvantages. For this reason, many researchers have also developed hybrid membranes in which polymeric membranes have been prepared by either using a ceramic support or incorporating ceramic particles into a polymeric membrane to overcome the disadvantages of both types of membrane [30], [31]. Therefore, in this study, the performance of ceramic, polymeric and ceramic supported polymeric membranes have been taken into account by using data from various resources.

The Selection of various membranes was based on their ability to operate under the typical operating conditions of distillation column separating ethanol from water. Since the top from the column which will ultimately be fed to the membrane is azeotropic in nature and nearly at its boiling point, the membranes must have been experimented at various temperatures and higher ethanol fractions so that flux values could be interpreted at desired conditions. In addition to this, the chosen membranes must also withstand at higher temperatures. By considering these guide lines two polymeric membranes PI [26] and PVA [27], two ceramic membranes HybSi [28] and NaA zeolite [29], and two ceramic supported polymeric membranes Chitosan Ceramic supported [31] and PVA/Organosilica [30] have been selected for the investigation. The operating conditions and some peculiar features of these membranes are presented in the table 1. Pervaporation experiments and thermal characterization have shown that the six membranes selected in this study are thermally stable and can withstand under High vacuum.

**Table 1: Peculiar features of selected membranes of different types**

Membrane Type	Total Flux kg/m <sup>2</sup> .h	Separation Factor	T(°C)	Permate Pressure bar	Ref.
<b><u>Polymeric</u></b>					
PI	0.05 --- 0.13	130-300	40 --- 70	0.002	[26]
PVA	0.27 ---0.37	212-402	65 --- 75	0.03	[27]
<b><u>Ceramic</u></b>					
HybSi	0.80 --- 7.01	25-131	60 --- 80	0.0067	[28]
NaA Zeolite	3.62 --- 12.93	>100000	50 --- 75	0.002	[29]
<b><u>Polymeric-Ceramic Composite</u></b>					
Chitosan Ceramic-Supported	0.41 --- 0.57	302-638	30 --- 70	0.013	[30]
PVA/Organosilica	0.14 --- 0.18	231-1026	40 --- 80	0.003	[31]

## 2.2. Mathematical model for membrane separation

Many attempts have been made to develop general models for predicting the permeability of a component through a membrane but their validity is still a question as these models cannot predict the permeability through all types of membrane. This is due to the fact that with the passage of time, membranes with different characteristics are being synthesized,



thus requiring a new general model. The overall transmembrane mass transport is either diffusion controlled or sorption controlled and novel membranes can follow either of these phenomenon depending upon the interaction of components of the feed with the membrane material. F. Lipnizki & G. Trägårdh [32] wrote a comprehensive review on pervaporation models. According to F. Lipnizkia & G. Trägårdh sorption and diffusion through the membrane are the two main phenomenon that are responsible for specie transport via pervaporation or vapor permeation. Therefore, all the models developed previously mainly focused on the prediction of sorption and diffusion through membranes.

Flory-Huggins Theory describes a general method used for the prediction of component profiles and to elaborate the sorption selectivity of membranes. Flory–Huggins theory takes account of the great differences in molecular sizes in adapting the usual expression for the entropy of mixing. Although it makes simplifying assumptions, it produces suitable outcomes for inferring experimental results. The free volume theory describes the specie transport through polymeric membranes based on molecular motion. The basis for this theory stems from Fick’s first law, which is usually restricted to ideal systems. The basic theme behind this theory is that an exterior molecule can only move in a polymer if suitable space exists. The reorganization of these spaces is due to the erratic fluctuation in the local density of the polymer. The Maxwell-Stefan theory deals with multi-component systems. This theory, when used for specie transport in membrane, gives better description for the permeability of more than two components.

Solution diffusion model [33] incorporates sorption, diffusion and desorption of the permeating component and therefore it is widely used for predicting the transport properties of species (in a binary mixture) through membranes. Sorption, diffusion and description together gives the overall mass transfer coefficient which is known as the permeability of the membrane. The dependence of flux on temperature and feed compositions is perfectly described by SDM which makes it easier to use especially when it comes to predicting the flux using a set of experimental data. Therefore, in this study, SDM have been chosen for pervaporation. The underlying assumptions of solution diffusion model used in this study are as follows:

- Permeability is constant throughout the membrane.
- Each stream has a constant pressure.
- Pressure drop from feed to retentate side is zero.
- Volume of the mixture in the membrane is constant.
- Retentate temperature is equal to the feed temperature.
- Permeate temperature is calculated by the simulator using permeate conditions.
- There are no polarization effects.

Solution diffusion model employs Fick's law of diffusion to predict the flux values. This model also allows us to use the experimental data for further calculations. According to the solution diffusion model the flux  $J_i$  ( $\text{kg m}^{-2} \text{h}^{-1}$ ) of a specie in permeate is given by equation (1).

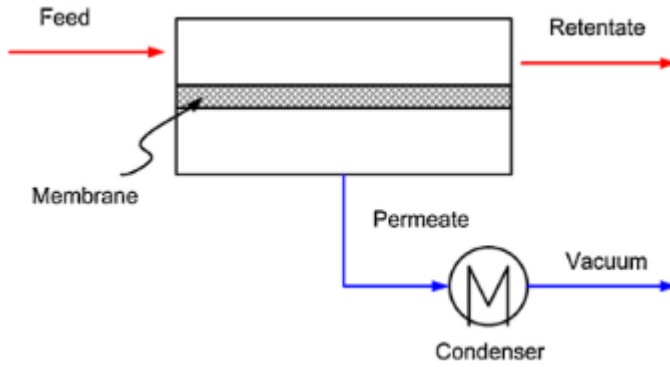
$$J_i = Q_i (x_i \gamma_i P_i^{\text{sat}} - y_i P_p) \text{ ----- (1)}$$

Where  $Q_i$  and  $\gamma_i$  represents the permeability ( $\text{kg m}^{-2} \text{h}^{-1}$ ) and activity coefficient respectively and  $P_p$  represents the permeate side pressure in bar. The activity coefficients can be approximated by using the Non-Random Two Liquid (NRTL) model. The saturated pressure ( $P_i^{\text{sat}}$ ) can be calculated by using the Antoine equation.  $Y_i$  which is the component mole fraction of a specie in permeate can be calculated by the following equation:

$$S = (y_i x_j) / [(1-y_i) x_i] \text{ -----(2)}$$

Where "S" is the membrane selectivity.

Pervaporation performance can be analyzed by observing the total flux (J) and selectivity (S) through the membrane. Feed at certain temperature ( $T_F$ ) and pressure ( $P_F$ ) containing a binary mixture is fed to the membrane with a certain flow rate (F) as shown in the Fig.1. Since the membrane is hydrophilic, pure ethanol is obtained in the retentae side and most of the water content becomes the part of permeate.



**Figure 1: A general schematic of membrane pervaporation or Vapor Permeation process.**

Temperature dependency of flux can be analyzed by the following relation:

$$J_i = Q_{i, \text{ref}} (x_1 y_i P_i^{\text{sat}} - y_i P_p) \exp [-E_i / R(1 / T - 1 / T_{\text{ref}})] \text{-----}(3)$$

Where  $Q_{i, \text{ref}}$  is the permeability at reference temperature,  $E_i$  is the activation energy of the specie and  $R$  is the general gas constant. Permeate flow rate ( $F_p$ ) can be calculated by the following equation.

$$F_p = J * A \text{-----}(4)$$

“A” in (4) represents the area ( $\text{m}^2$ ) of membrane.

Retentate flow rate ( $F_R$ ), and mole fractions of species ( $z_1$  &  $z_2$ ) in retentate can be calculated with aid of material balance as shown in equations (5 to 7).

$$F_R = F - F_p \text{-----}(5)$$

$$z_1 = (F x_1 - F_p y_1) / F_R \text{-----}(6)$$

$$z_2 = 1 - z_1 \text{-----}(7)$$

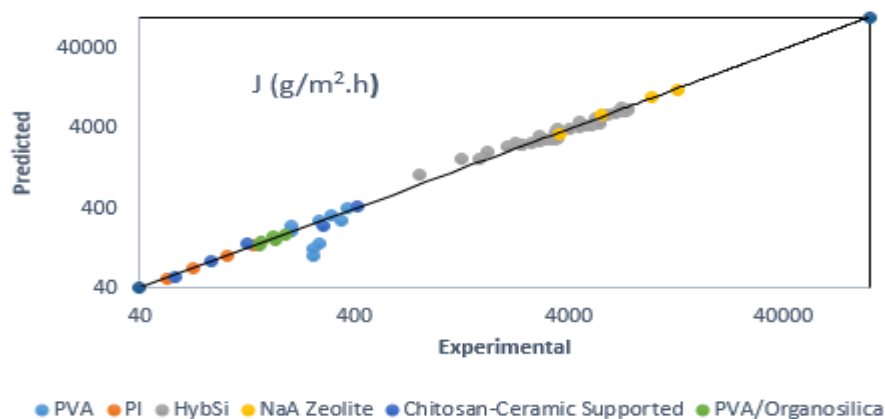
In this study, all the data have been taken from the pervaporation experiments. However, to predict the flux and separation factor for vapor permeation, the flux equation (3) is modified due the fact both permeate and feed are in vapor phase. The idea was taken from previous studies [34] in which it was shown that the activity coefficient in (3) should be replaced by the fugacity coefficient as shown in the equation (7).

$$J_i = Q_{i, \text{ref}} (x_i \phi_i P_i^{\text{sat}} - y_i \phi_i P_p) \exp [-E_i / R(1 / T - 1 / T_{\text{ref}})] \text{-----}(8)$$

Once  $Q_{i,ref}$  and  $E_i/R$  are calculated, their values can be used to predict the flux for vapor permeation process with aid of equ(8). The above equations were coded in ACM by following the rules as described in Aspen Tech, Aspen Custom Modeler [35]. In ACM, steady state mode was active while solving the system of equations because the process is assumed to be continuous.

### 2.3. Model Validation

The accuracy of the model was investigated by comparing the predicted and experimental flux values. The model parameters  $Q_{i,ref}$  and  $E_i$  calculated by fitting the experimental data to the flux equation (3) for each type of membrane by minimizing the sum of standard deviations between predicted and experimental fluxes of both water and ethanol. The fitted parameters were used to predict the fluxes of both water and ethanol. It was observed that, the experimental data were in good agreement with the model predicted fluxes for all types of membranes. Figure 2 shows the comparison between experimental and model predicted fluxes for HybSi, NaA zeolite, PVA and PI membranes.



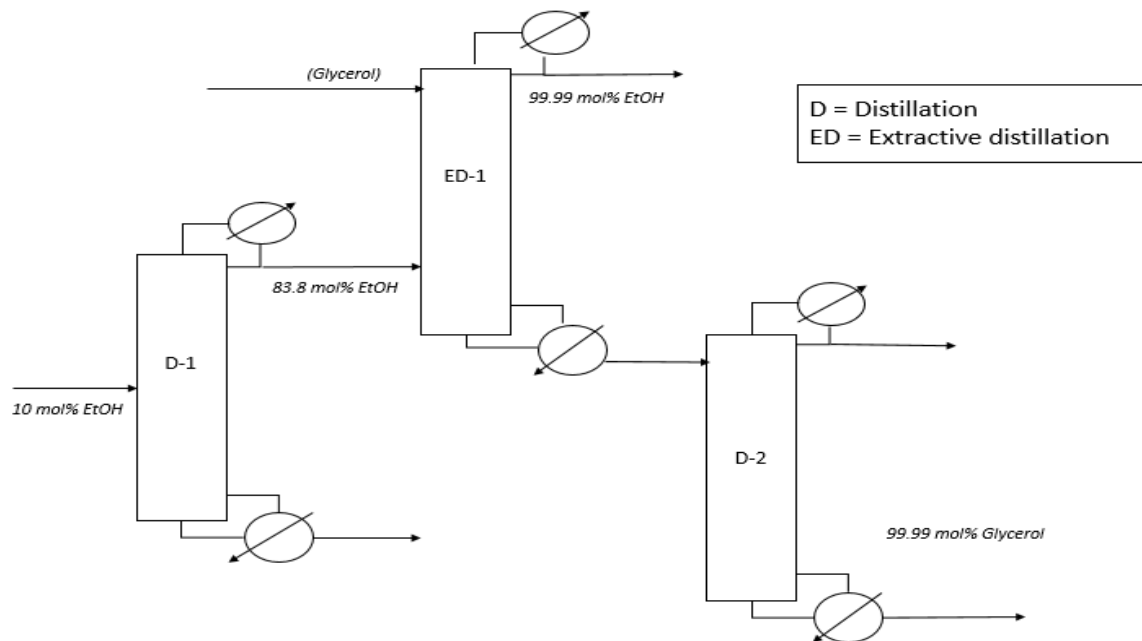
**Figure 2: A comparison between experimental and predicted total flux.**

$R^2$  value of 0.975 indicates that the flux values are accurately predicted. However there are few points corresponding to PVA membrane which are deviating from the main line. By increasing the ethanol concentration water flux is supposed to decrease but the water flux at 0.95 w% ethanol was greater compared to the flux at 0.925 w% ethanol.

## **CHAPTER 3: Simulations**

### 3.1. Conventional separation technique

In order to analyze the significance of pervaporation membranes for their ability to separate ethanol from water by utilizing least energy, their performance in terms of ethanol recovery and its purity has been compared with that of conventional separation technique. The conventional separation technique requires the pre-concentration of ethanol using conventional distillation until a maximum achievable purity is observed. One such conventional technique was studied by A. Avil et al [10] a schematic of which is shown in the figure 3. In this study it was found that the purification by conventional distillation (D-1) is not achievable due to azeotropic nature of the ethanol/water mixture at a purity of 96 wt % of ethanol, therefore the concentrated ethanol was further purified by employing an extractive distillation column (ED-1), using glycerol as entrainer, targeting for a purity of 99.99% in mole fraction of ethanol. The glycerol was recovered using an additional distillation column (D-2). In order to minimize the service cost. A. Avil et al also proposed alternative separating sequences (AS-1 and AS-2) and was able to minimize the service cost. The total energy requirement for each sequence is shown in the table 5. It may be noted that the addition of each column requires energy. Therefore, the idea of replacing these columns with membranes seems feasible due to fact that membranes operate without heating. In addition to this, very high ethanol recovery (>99%) can be expected using membranes there selective nature. Furthermore, the use of entrainer is also eliminated as the azeotrope can easily be broken due the hydrophilic nature of the membranes. Therefore, in this study, alternative designs of hybrid distillation-membrane setups have been considered. The ethanol purification column (ED-1) in CS-1 was replaced by the membranes in order to compare the significance of alternative CS-1 and alternative designs containing membranes.



**Figure 3: CS-1 conventional separation sequence (A. Avil et. al.)**

**Table 2: Design Characteristics of Columns in the CS-1 Sequence**

	D-1	ED-1	D-2
number of stages	20	26	6
feed stage	10	24	5
entrainer feed stage		4	
feed molar flow (kmol/h)	45.36	5.41	4.15
entrainer molar flow (kmol/h)		3.18	
distillate flow (kmol/h)	5.41	4.44	0.99
bottoms flow (kmol/h)	39.94	4.15	3.15
temperature, top (K)	351.35	351.47	361.05
temperature, bottoms (K)	101.35	101.35	101.35
design pressure (kPa)	6.19202	1.1341	0.3863
heat duty (GJ/h)	1.78	0.27	0.15

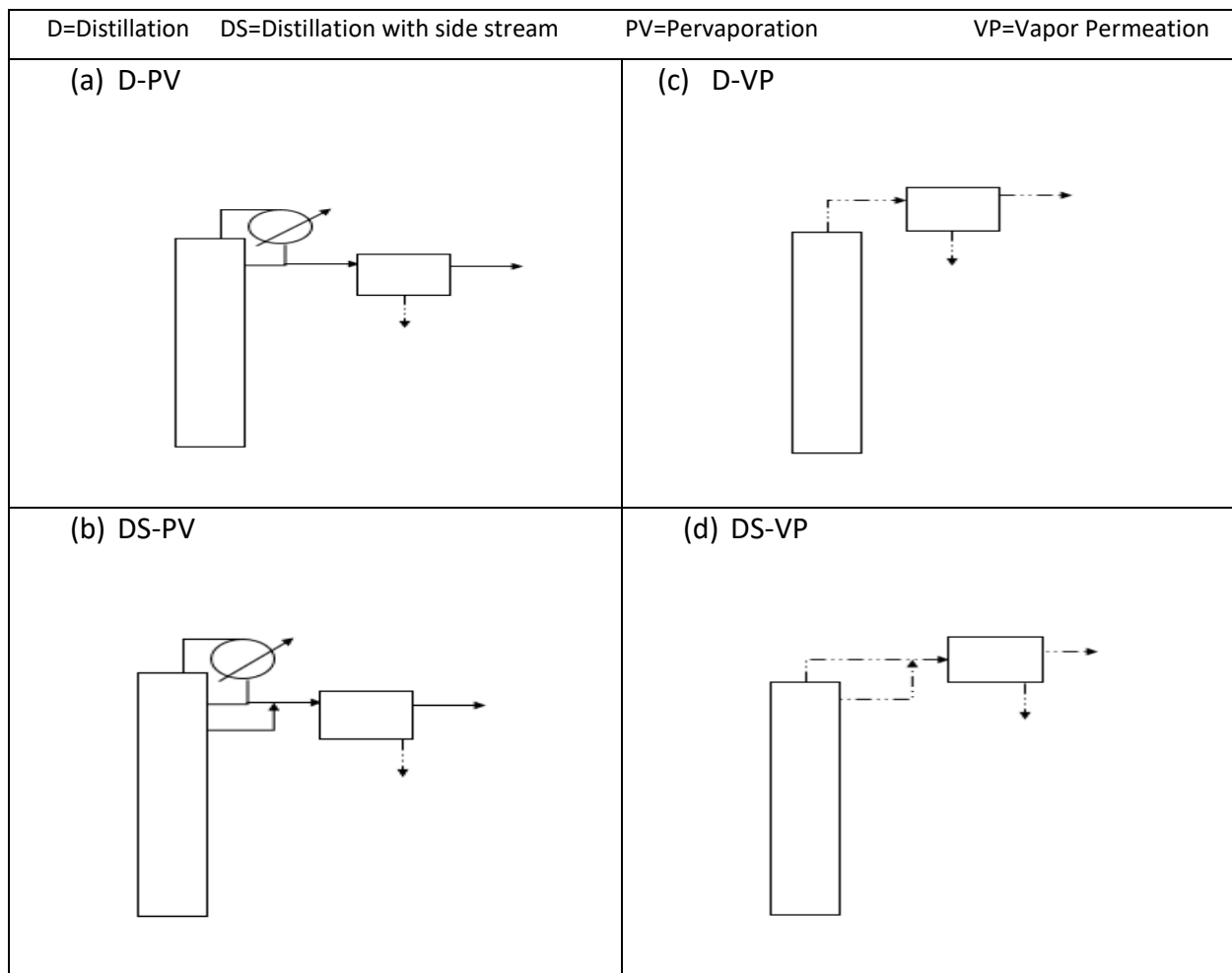
### 3.2. Alternative designs for ethanol purification

A Hybrid Distillation-membrane setup can have various configurations depending upon the specific role of the membrane [11]. For example, if distillation is used as a final step to get high purity of organic solvent, pervaporation is employed before the column to pre-concentrate the organic solvent from low concentration (< 1 wt%) to about 10 to 15 wt%. If

membrane is used as a final step to get high purity organic solvent then it is configured after the column. On the other hand, if the distillation column is not configured with the condenser then top from the column is in vapor form and vapor permeation is employed in that case. However, the decision of integrating a condenser with the column is based on the feasibility of vapor permeation. Vapor permeation is favorable if the feed mixture consists of non-volatile or undissolved species and any of its constituents that have the tendency to precipitate out can be eliminated as bottom product in the evaporator. However, the final product which is in the vapor form must be condensed to room temperature in order to store it in liquid form thus requiring some additional cooling duty. Pervaporation on the other hand doesn't require condensation of the final product since the product is already in liquid form. However, the final product is still hot due to the pre-heating of feed and must be cooled to room temperature. Therefore, a tradeoff must be made between pervaporation and vapor permeation by studying the performance and economy of both processes. In addition to this, reboiler duty of the column can be reduced by minimizing the reboiler load, which can be done by the removal of side stream from the column. The side streams drawn from the column either in liquid or vapor form contain ethanol and must be sent to the membrane units for further purification. However, by doing so a relatively larger membrane area might be required due to the higher membrane feed. Furthermore, the organic solvent mole fraction is different in vapor and liquid side streams due to thermodynamic limitations originated by vapor-liquid equilibrium in the column. When these streams would enter the membrane for further purification, one may observe different membrane areas and organic solvent recovery for both liquid and vapor feeds. Therefore, the effect of feed phase on membrane performance seems to be an interesting topic for discussion. All the parameters discussed so far including, reboiler duty, cooling duty, organic solvent recovery and membrane area required are interlinked and must be optimized in order to reduce the total energy demand and material cost. In order to meet this target four alternative designs have been proposed and the effect of side stream, feed phase and the type of membrane on the reboiler duty, cooling duty, organic solvent recovery and membrane area required have been investigated. The six membranes chosen in this study were investigated at higher ethanol concentrations. Therefore, in this study all the configurations of hybrid pervaporation-distillation setups are chosen in such a way that in each configuration, membrane is configured after the column as shown in the fig.4. First, a distillation column is



configured the membrane (D-PV) as shown in the fig 4 (a) in which ethanol mixture leaves the top of the column and a part of it is sent back to the column as a reflux after its condensation whereas the remaining ethanol mixture is fed to the membrane for further purification. In the Second configuration (DS-PV), a side stream is withdrawn from the column, which is then mixed with the top stream and sent to the membrane unit for further purification as shown in the fig.b. The other two alternate configurations D-PV and DS-VP as shown in the fig.1(c) and fig.1(d) are different in from D-PV and DS-PV in way that the streams drawn from the column are in vapor phase.



**Figure 4: Various configurations of hybrid distillation-membrane setups.**

### 3.3. Formulation of the optimization problem

Ethanol recovery, its purity, reboiler duty, condenser duty and membrane area are the parameters used in the evaluation of a hybrid distillation-membrane setup. Since both distillation and membrane units operate side by side therefore, the influence of each

parameter on the overall performance of hybrid setup is considered. The effect of reboiler duty on ethanol recovery and membrane area, the effect of feed phase on the ethanol recovery and membrane area, the effect of side stream on the reboiler duty, ethanol recovery and membrane area and the effect of the type of membrane on ethanol recovery and membrane area were studied by using ASPEN Plus software. The feed for all the configurations was the same as that of conventional setup. The optimized parameters for each configuration (Table 2) containing different types of membranes were found with aid of iterative procedure.

**Table 3 : Optimized parameters of distillation column in various configurations of hybrid setups.**

Configuration	D-PV	D-VP	DS-PV	DS-VP
Q h (GJ/h)	1.79	0.66	0.70	0.64
Q c (GJ/h)	-1.54	0.00	-0.43	0.00
Reflux Ratio	6.02		0.97	
Ethanol Cooling duty (GJ/h)	-0.03	-0.21	-0.03	-0.21
Permeate Cooling Duty (GJ/h)	-0.04	-0.21	-0.09	-0.25
Distillate rate (Kmol/h) / Ethanol (mol%) / T (C)	5.42 / 0.837 / 77.86	9.1 / 0.5 / 84	5.41 / 0.72 / 78.18	9 / 0.5 / 84.31
Side stream flow (kmol/h) / Ethanol (mol%) / T (C)			1 / 0.63 / 78.50	1 / 0.117 / 85.083
Membrane Feed (Kmol/h) / Ethanol (mol%) / T(C)	5.42 / 0.837 / 77.86	9.1 / 0.5 / 84	6.41 / 0.707 / 78.23	10 / 0.453 / 84.38

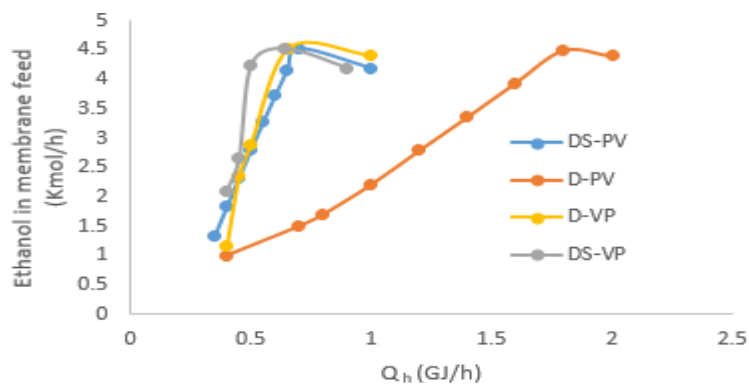
## **CHAPTER 4: Results and Discussion**

In this section first, the results obtained from both distillation and membrane units have been discussed separately, and then the effect of coupling the membrane unit with the distillation column has been described.

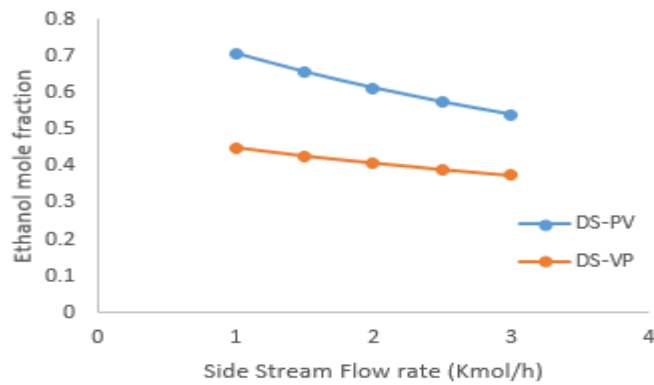
## 4.1. Distillation unit

### 4.1.1 The effect of reboiler duty and side stream flow rate on ethanol recovery

Typical fermentation broth contains 4.536 mol/h of ethanol (Table 2) and to recover this quantity reboiler duty is adjusted accordingly. The variation of reboiler duty with ethanol flow rate is shown in the figure 5. It may be noted that after a certain point ethanol flow starts decreasing due the increased vaporization of water molecules in the reboiler. In addition to this, the optimum side stream flow rate in line with the reboiler duty and ethanol fraction in the membrane feed is another important factor. The variation of ethanol mole fraction with side stream flow rate is shown in the figure 6. By increasing the flowrate of side stream ethanol mole fraction decreases due to the fact that more water accompanies the side stream as the flowrate is increased.



**Figure 5 : Effect of reboiler duty on ethanol flow rate in the membrane feed.**



**Figure 6: Effect of side stream flow rate on the ethanol mole fraction in the membrane feed.**

#### 4.1.2. The effect of Side stream on reboiler duty and condenser duty

Reboiler duty required for each configuration is shown in the table 3. Compared to the other configurations reboiler duty for D-PV was highest (1.79 GJ/h). It was due the fact that no side stream was drawn in this configuration and all the reflux coming back from the condenser combines with the feed and falls into the reboiler, thus increasing the reboiler load. A significant decrease ( $\sim 61\%$ ) in the reboiler duty was observed for the case of DS-PV compared to D-PV. This observation was attributed to the extraction of side stream from 2<sup>nd</sup> stage (from top) of the column. The extraction of side stream from the column reduced the reboiler duty because of relatively lesser flow of the downcomer. On the other hand, the reboiler duty for DS-VP was only 3% less than that of D-VP. It was due to the fact that the extraction of vapor side stream doesn't reduce the liquid downcomer significantly and as a result reboiler load is not reduced to a certain degree compared to the extraction of a liquid side stream. Condenser duties for D-PV and DS-PV were -1.54 and -0.43 GJ/hr respectively. This variation was attributed to the variation in the reflux ratios. The optimized reflux ratios for D-PV and DS-PV were 6.02 and 0.97 respectively. Since condenser duty varies directly with reflux ratio, a higher value of reflux ratio results in relatively higher condenser duty.

#### 4.1.3. The effect of the phase of the outlet streams on reboiler duty

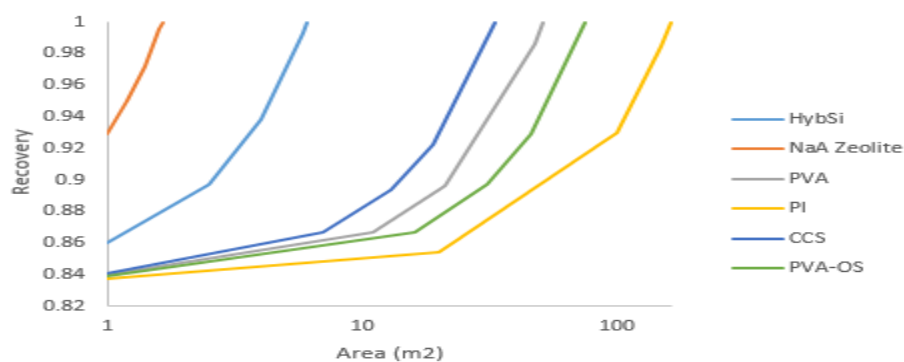
It may be noted from the table.3 that reboiler duties for the configurations exhibiting the extraction of vapor streams are less than the reboiler duties of the configurations exhibiting the extraction of liquid streams. It was due to fact that the prior configurations doesn't

contain a condenser therefore reflux is zero and the only load to the reboiler is the liquid feed stream coming down the column. Therefore, to this point, it seems like vapor permeation is a feasible process if we take into account the reboiler duty only. However, ethanol recovery its purity and membrane area required for each configuration would give us a better idea about the feasibility of pervaporation or vapor permeation.

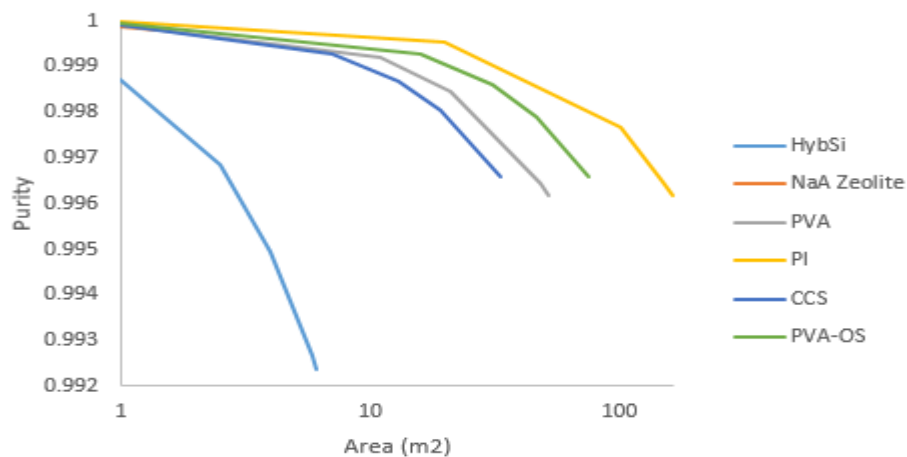
## 4.2. Membrane Unit

### 4.2.1. The effect of membrane area on ethanol recovery and purity

In order to see the effect of membrane area on the ethanol recovery and its purity, Ceramic membrane HybSi has been chosen as an example and the feed to membrane is the one with typical outlet stream conditions of a conventional column such distillate of D-1 column in CS-1. The variation of ethanol recovery and it's purity with membrane area are shown in the fig.7 and fig.8 respectively. It can clearly be seen from these figures that like any other separation process recovery and purity are inversely related. As we go on to increase the area ethanol recovery is also increased. It is due the fact that by increasing the area more the membrane can accommodate larger volumes thus increasing the product recovery. Ethanol purity on the other hand decreases with as we go on to increase the area. It is due the fact that by increasing the area there are more chances for the ethanol molecules to accompany the water molecules in the permeate side. That is why the membranes are carefully fabricated by making sure that the selectivity is on the higher side. The six membrane chosen in this study where if good selectivity which is why all the membranes resulted higher ethanol recovery with 99.99 mol% pure ethanol.



**Figure 7 : The effect of membrane area on the ethanol recovery**



**Figure 8 : The effect of membrane area on the ethanol Purity**

#### 4.2.2. The effect of membrane type on the ethanol recovery and membrane area

A comparison between membrane areas required for each configuration to get 99.99 mol% ethanol is shown in the table 4. It was observed that membrane area have very strong dependency on water flux. Membranes with high water flux such as ceramic membranes exhibited low membrane area and those with low water flux such as polymeric and composite membranes exhibited relatively high membrane area. The high water flux of a hydrophilic membrane indicates that most of the water content move across the membrane leaving behind the ethanol which is collected on the retentate side. If water flux of a hydrophilic membrane is low than relatively larger area is required for maximum water transportation across the membrane. Average flux through PI membranes was least among all the membranes used in this study thus resulting in higher membrane areas ranging from 162.94 to 307.55 m<sup>2</sup> for various configurations. Water flux through PVA membranes was higher compared to that of PI membrane thus resulting in relatively lower membrane areas ranging from 51.55 to 89.3 m<sup>2</sup>. In addition to this, ceramic membranes exhibited relatively lower membrane areas ranging from 6.03 to 10.57 m<sup>2</sup> and 1.64 to 2.89 m<sup>2</sup> for HybSi and NaA zeolite membranes respectively. Composite membranes also followed the same trend, as polymeric and ceramic membranes. On the other hand, ethanol recovery showed great dependency on the separation factor. It can observed from the table 3 that ethanol recovery is highest for NaA Zeolite membrane due to its highest separation factor among all

types of membranes. Therefore, the membranes exhibiting higher flux and separation factors gives favorable performance than those with lower flux separation factors.

**Table 4: Optimized parameters of membrane unit in various configurations of hybrid setups.**

Membrane Type	Area (m <sup>2</sup> ) / % Recovery			
<b>Ceramic</b>				
HybSi	6.02 / 99.25	9.62 / 99.31	8.14 / 99.09	10.57 / 99.31
NaA Zeolite	1.64 / 99.99	2.62 / 99.99	2.18 / 99.99	2.89 / 99.99
<b>Polymeric</b>				
PVA	51.54 / 99.63	80.96 / 99.66	64.60 / 99.52	89.30 / 99.67
PI	162.94 / 99.63	278.47 / 99.65	217.60 / 99.54	307.55 / 99.65
<b>Composite</b>				
C-C-S	33.41 / 99.67	60.12 / 99.9	44.90 / 99.85	69.90 / 99.89
PVA-OS	75.28 / 99.67	165.69 / 99.73	101.38 / 99.59	165.69 / 99.60

### 4.3. Hybris Distillation-Membrane setup

#### 4.3.1. Effect of side stream on membrane area, ethanol recovery

The extraction of side stream exhibited very strong influence on the membrane area, and ethanol recovery. When the top stream was combined with the side steam drawn from the second stage of the column, relatively larger membrane areas were observed compared to the configurations without side streams. This observation was attributed to the larger feed flow rate and relatively lesser ethanol fraction in the membrane feed for the case of D-PV and D-VP compared to DS-PV and DS-VP (Table 4). Ethanol fraction in the membrane feed in D-PV and D-VP is higher compared to that of in DS-PV and DS-VP and as a result lower surface area is required for the transportation of water molecules across the membrane. On the other hand, ethanol recovery was high (>99 %) for all configurations with or without side steam due the selective nature of the membranes.

#### 4.3.2. Effect of feed phase on membrane area

In order see the effect of pervaporation and vapor permeation on the membrane performance, each type of membrane was exposed to liquid and vapor feed phase separately. It was found that the membrane area is higher for vapor permeation compared

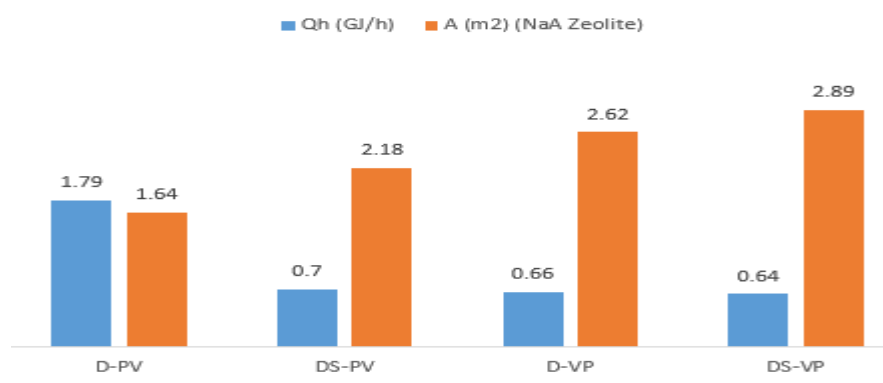


to pervaporation for each type of membrane and for all four configurations. This observation was attributed to the larger feed flow rate and relatively lesser ethanol fraction in the membrane feed for the case of vapor permeation Table 4. Compared to lower ethanol fraction in vapor feed, ethanol fraction in the liquid feed is higher and as a result lower surface area is required for the transportation of water molecules across the membrane. On the other hand, ethanol recovery was favored by both pervaporation and vapor permeation due the fact all membranes chosen in this study possessed favorable selectivity values. It can clearly be observed from the table that ethanol recovery is more than 99% for all types of membranes configured in all four configurations. However, it may be noted that the ethanol recovery for vapor permeation is slightly higher than that of pervaporation due the fact that in vapor permeation feed temperature is higher than that of pervaporation. In addition to this, in pervaporation process feed is first vaporized and then travel across the membrane due to which some of the water molecules may accompany ethanol on the recovery side. .

#### **4.4. Selection of the most feasible configuration and membrane type**

The most feasible configuration is the one that exhibit least heating duty and the membrane type that exhibit the least area and highest recovery. Total heating duty required for each configuration recommended in this study and for each configuration recommended by A Avil et al [10] are shown in the table 3 . It can clearly be observed from the table that alternative configurations suggested by A.Avil et al [10] exhibited low %age savings in energy compared to the one recommended in this work, with DS-VP the most energy efficient (Table 5) process for the purification of ethanol originating from a typical fermentation broth. In order to select the most suitable membrane for ethanol purification the criteria of observance is the least area and highest recovery. It can be observed from the table 3 that NaA Zeolite exhibited the least area highest recovery therefore one can easily categorized this membrane as the best. However, many other important factors including, ease of fabrication, thermal stability and mechanical stability must also be considered while selecting the membranes for commercial separation. Ceramic membranes are thermally and

mechanical strong but are not easy to manufacture, whereas polymeric membranes can be manufactured easily in such a way that the final membrane prepared is thermally and mechanically stable. On the other hand, polymeric membranes also exhibit the swelling problem due to which their life is less than that of ceramic membranes and may cost more than ceramic membranes considering the long run operations. Composite membranes, which contains both ceramic and polymeric part can be optimized to such conditions that all difficulties mentioned above are minimized. Therefore, while selecting the membrane for ethanol purification all factors discussed above must be considered before recommending one feasible membrane. Therefore, if we take into account only the ethanol recovery, membrane area, and its thermal and mechanical stability then ceramic membranes are the best compared to polymeric and composite membranes out of which NaA Zeolite is the best among all types of membranes chosen in this study due to its least area and highest recovery. It is also worth mentioning here that when NaA zeolite was configured in different configurations, it exhibits different areas. The configurations with low reboiler duties exhibit relatively higher membrane areas as shown in the Fig.9.



**Figure 9 : A comparison between membrane area reboiler duty for various configurations.**

**Table 5 . Heating duty of various configurations.**

Configuration	Ref.	Total heating duty (GJ/h)	% Savings
CS-1	A. Avil et al	2.20	0%
AS-1	A. Avil et al	3.02	-37%
AS-2	A. Avil et al	1.54	30%
D-PV	This work	1.79	19%
D-VP	This work	0.66	70%
DS-PV	This work	0.70	68%
DS-VP	This work	0.64	71%

## Conclusion

In this study, four different configurations of hybrid distillation-membrane setup are proposed. Both pervaporation and vapor permeation processes were modeled and simulated with the aid of solution diffusion model. The design of hybrid process has been performed by coupling the membrane model with a simulator of distillation column. It was found that the extraction of side streams from the column reduced the reboiler duty because of relatively lesser flow of the downcomer. Total heating duty was least for DS-VP. It was due to the absence of condenser and relatively lesser reboiler duty compared to the other configurations. It was also found that hybrid setups including membranes are less energy intensive compared to that of without membranes. It was also observed that membrane area have very strong dependency on water flux. Membranes with high water flux such as ceramic membranes exhibited low membrane area and those with low water flux such as polymeric membranes exhibited relatively high membrane area. In addition to this, the membrane areas were found to be higher for vapor permeation compared to pervaporation for each type of membrane and for all four configurations. This observation was attributed to the larger feed flow rate and relatively lesser ethanol fraction in the membrane feed for the case of vapor permeation. Furthermore, relatively larger membrane areas were observed for configurations with a side stream compared to the configurations without a side stream. This observation was attributed to the larger feed flow rate and relatively lesser ethanol fraction in the membrane feed for the case of D-PV and D-VP compared to DS-PV and DS-VP. Finally, it was concluded that hybrid processes containing a membrane are less energy intensive compared to the conventional ethanol purification process. .

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