

**SEPARATION OF RHODIUM TRIS (TRIPHENYLPHOSPHINE)
CATALYST IN A HOMOGENEOUS SYSTEM BY USING
SOLVENT RESISTANT NANOFILTRATION (SRNF)**

by

Ahmad Kamil Bin Mustafa

**Dissertation submitted in partial fulfillment of
the requirements for the Bachelor of Engineering (Hons)
(Chemical Engineering)**

JAN 2012

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CERTIFICATION OF APPROVAL

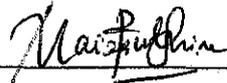
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Approved by,



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UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

JAN 2012

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or person.



AHMAD KAMIL BIN MUSTAFA

ABSTRACT

Advance technology show that nowadays nanofiltration can be used to separate main product from the catalyst for homogenous catalytic reaction. The purpose of writing this dissertation is to documentation the findings and research about the separation of tris(triphenylphosphine) rhodium catalyst in a homogenous solution by using solvent resistant nanofiltration. The objectives of the research are to determine the stability of solvent-membrane combination, to determine the solvent flux and membrane rejection of catalyst for the selected types of solvent-membrane combination and to assess the effect of pressure and catalyst concentration for the selected types of solvent-membrane combination.

The research has been done in four stages. Firstly, observing physical stability by soaking the cutting membrane in the pure ethyl acetate for 24 hours. Then the membrane will be dried out at 35°C until the membrane free from any solution. Before observing the membrane structure under Scanning Electron Microscopy (SEM), weight the drying membrane. Since the SEM equipment is not available due to broken and damaged, further discussion has been done and within the timeline, the result from physical changes has been neglected and solvent flux as well as catalyst rejection study has been carried.

Permeability study has been carried out in order for the membranes to reach its steady state flux rate. There are four membranes that have been used which are StarMem™ 122, StarMem™ 240, DuraMem™ 200 and DuraMem™ 500. The study is done by permeated 250mL of pure solvent as washing procedure to remove the coating layer. Then another 250ml will be permeated to observe the flux rate at 20 bar. Study only can be continued after the membranes reach its steady state.

METCell separation unit that has been used is one type of dead-end filtration. Extra care need to be applied while operating this unit since the experiment is carried out at high pressure up to 25bar. five reading for pressure variation (5,10,15,20,25 bar) has been used and four reading for catalyst concentration variation (0.2,0.5,0.8 and 1.0mM)

has been carried out throughout the research timeline. Solvent flux can be determined using formula given and catalyst rejection can be determined using UV-Vis Spectrophotometer which is available at 361nm wavelength.

Throughout the experiment, it was found that the solvent flux for pure solvent need more time to reach the steady state since the coating layer need to be removed first. As the experiment continued, it shows that DuraMem™ series has lower solvent flux rate and higher catalyst rejection compared to StarMem™ series when using ethyl acetate as the solvent. StarMem™ 122 unfortunately breaks during permeability study because of break during the study or the membrane was expired. From the result obtained, it was chosen that DuraMem™ 200 is the best combination with the solvent ethyl acetate in order to obtain high catalyst rejection and low solvent flux.

In conclusion, homogenous process can be utilized in the future since the catalyst can be separated from the product by using this solvent resistant nanofiltration. The membrane and solvent used must be compatible with the process since both of them are organic structure. So the process must be carried out without changes any of the structure. The green process can be achieved and industry can become economically since these expensive catalyst can now on be recycled using this process.

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LIST OF ABBREVIATIONS

1. UTP - Universiti Teknologi PETRONAS
2. Rh – Rhodium
3. MPa – Megapascal
4. SEM – Scanning Electron Microscopy
5. UV – UltraViolet
6. SRNF – Solvent Resistant Nanofiltration
7. MWCO – Molecular Weight Cut-off
8. MW – Molecular Weight
9. cP – centipoises
10. EA – Ethyl Acetate
11. WL – wavelength
12. SEDEX – Science, Education and Engineering Exhibition

CHAPTER 1

INTRODUCTION

1.1 Project Background

Industry used a metallic catalyst in order to increase the selectivity of the selected process. Nowadays, catalytic organic synthesis has become a point of interest because of its potential in developing environmentally processes within the world of green chemistry (G. Centi et al., 2003). However these catalysts are very expensive and sometimes difficult to recover and separate from the products since the reaction take place in a homogenous system.

Hydrofomylation process of alkenes basically is the addition of syn gas which is hydrogen and carbon monoxide into double bond carbon atom of alkenes to produce aldehydes in two forms which are linear product and branched product (D. Evans et al., 1968). In order to obtain high selectivity in linear product, the catalyst study has been done for years and the latest technology show that rhodium based catalyst is the most favorable than cobalt and others type of catalyst (F. Ungvary, 2007). The catalyst and all reactants are in solution which lead the process occurred in liquid phase. The overview of the hydroformylation process is shown below in Figure 1.

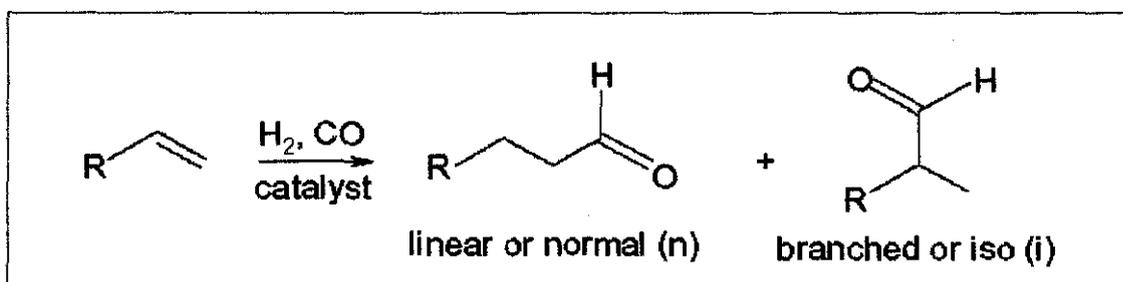


Figure 1: Hydroformylation of olefins

Hydroformylation of olefins has been used since 1950s to produce detergents and others product by using cobalt-based catalyst. However, in order to increase the selectivity of desired aldehydes, researched has been conducted to find a suitable catalyst. As years past, research found that rhodium based catalyst is more preferable but it was very

expensive to begin with. In order to use this catalyst economically to produce commercial product, a catalyst recovery system must be done.

The high selectivity of rhodium based catalyst process has made the manufacturers of n-butryna deyde favors this process. The high cost of rhodium catalyst has urge the researches to build near-complete catalyst recovery system for the process to be viable and the development of organometallic of rhodium catalyst using water soluble phosphines has assisted the process to be more feasible (Bhaduri et al., 2000). Below is the example of rhodium in its metallic form since it falls under transition metal and the organic structure of tris (triphenylphospine) rhodium.

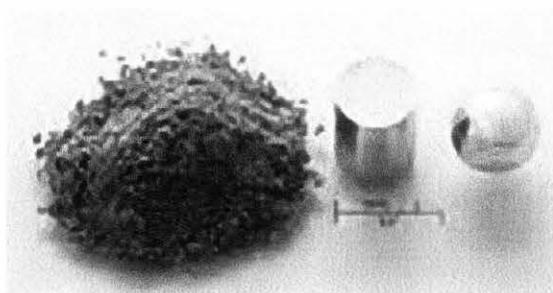


Figure 2: Rhodium metallic catalyst

A membrane process is defined as a process which feed stream is divided into two streams which are retentate and permeate streams. Any of the two can be considered as a product for conventional industry used. However for hydroformylation process of olefins, the desired product is in the permeate stream. Figure 3 below is the overview of membrane separation which use pressure difference as a driving force to let the permeate product stream go through the membrane.

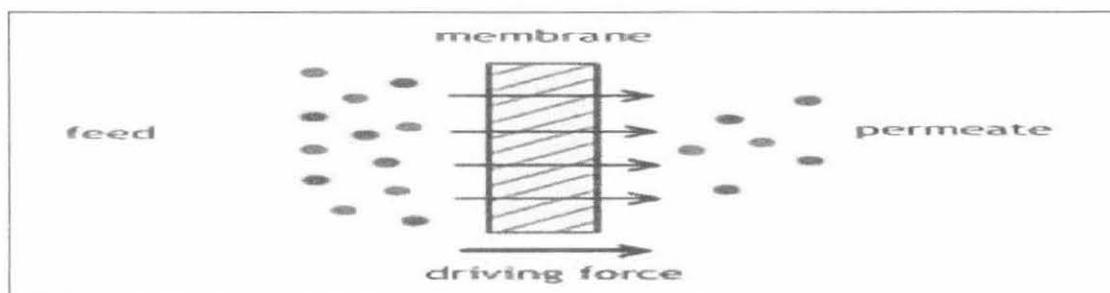


Figure 3: Membrane transport animation picture

Type of membrane used is a very critical criteria in order to recover most of the catalyst. Therefore, for liquid-liquid separation, an organic membrane is selected since the catalyst used also an organometallic catalyst where as the transition metal is bind with organic compound. The membrane performance can be classified into three main criteria which are the selectivity, the flux through membrane and also the recovery (Katleen Boussu, 2007).

Nanofiltration system has been widely used nowadays because it required lower operating pressure than reverse osmosis and therefore it saves more energy. This process can be defined as pressure driven process which using an organic semi permeable membrane which allowed a pore size less than one nanomone permeate through it (Eurodia). In addition, this process is one type of cross-flow filtration that fall in between ultrafiltration and reverse osmosis. As a pressure driven process, it uses a pressure difference to filtrate the catalyst between the feed (retentate) and the filtrate (permeate).

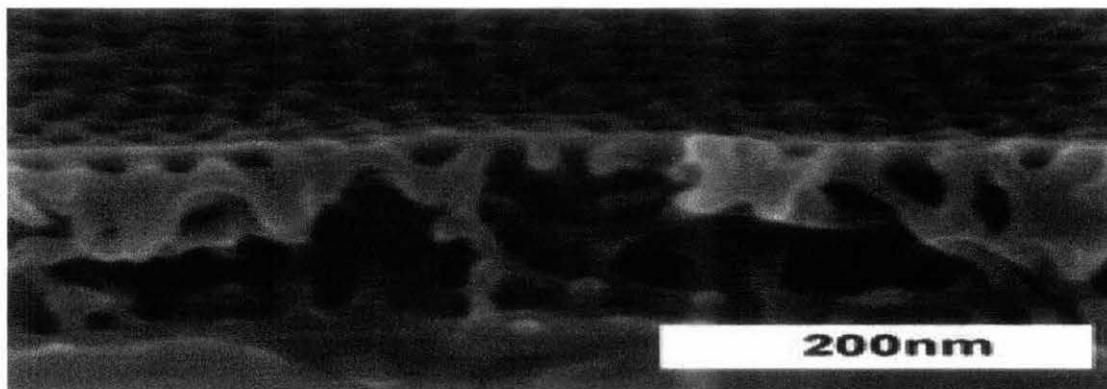


Figure 4: Membrane structure under microscope

This type of separation has found to be feasible for ideal rhodium recovery system which is relatively large compared to the reaction products which are smaller. However in order to be able to use nanofiltration separation method, a solvent stable nanofiltration membrane only can be applied due to the nature of catalyst that has organic outer layer and also the reaction take place. The solvent-membrane interaction gives a significant impact to have the optimum and ideal separation of this type of catalyst.

1.2 Problem Statement

Nowadays, the production of plastics and detergent product is widely manufactured by using the process hydroformylation of olefins. This process used a catalyst as a medium to increase the selectivity of desired product. Since 1950s, people used cobalt-based catalyst but the selectivity of desired product is low. After years of research, the used of rhodium catalyst slowly overtake the other catalyst. However this types of catalyst is very expensive.

An ideal catalyst recovery system must be constructed in order for this catalyst can be used economically in the industry. The catalyst must be recovered without affecting the main process and it still in the active form so that it can be used again for another reaction. Since this process is in homogenous solution, a liquid-liquid separation must be done and a membrane process is suitable for the recovery system. However, the study of solvent-membrane combination, effect of pressure and concentration and also the solvent flux must be conducted in order to clarified whether it was a good system or not.

Rhodium based catalyst is proved that gives high selectivity of desired product and operate in low operating temperature and pressure. However this catalyst is one type of water-soluble catalyst and it was difficult to recover the catalyst especially when dealt with high molecular weight of olefins. An ideal separation system must be conducted in order to recover most of the catalyst in the active form without distressing the main process.

Since the permeate product is the preferable one, we need to use solvent stable nanofiltration only based on the reaction and catalyst performance. The solvent used must be compatible with the membrane in order to reject most of the catalyst to permeate through membrane as well as does not damage the membrane itself. There are other criteria need to consider when choose the type of membrane such as operating temperature, pore size and catalyst concentration.

In this research, nanofiltration system is chose to separate the rhodium catalyst from its homogenous solution. However, the types of solvent-membrane used must be identified

and selected first in order to obtain the effect of pressure and catalyst concentration on the membrane used in this nanofiltration process.

1.3 Objectives

The objectives of the projects are:

- a) To study the compatibility of the solvent-membrane used by observing the membrane stability test in solvent at 2.0MPa.
- b) To determine the solvent flux and membrane rejection of catalyst for the selected types of solvent-membrane combination.
- c) To assess the effect of pressure and catalyst concentration for the selected types of solvent-membrane combination.

1.4 Scope of work

The scope of work for the project has been divided into three categories as below:

1.4.1 Compatibility of the solvent-membrane combination

The compatibility of solvent-membrane combination must be done prior to make sure the membrane is in good condition to proceed with separation module. The most common solvent used for nanofiltration membrane is toluene. We need to find the most compatible and economically solvent to use with the polyimide membranes other than toluene. Then the stability test should be conducted by soaking the membrane in the solvent for 24 hours at pressure 2.0MPa.

1.4.2 Solvent flux and membrane rejection of catalyst

At the same operating temperature and pressure, an experimental for solvent flux and membrane rejection must be conducted. Solvent flux show that how much of the solvent can flow through the membrane and the membrane rejection show that how compatible the membrane used for catalyst separation system.

1.4.3 Effect of pressure and catalyst concentration

In order to see how pressure and catalyst concentration affecting the catalyst recovery system, an experimental must be conducted by manipulated the pressure used and obtains the difference of reading in solvent flux and membrane rejection. The experiment will be repeated by manipulated the catalyst concentration and the graph will be draw to interpret the result.

CHAPTER 2

LITERATURE REVIEW

2.1 Homogenous Catalysis

In our current development of 21st century, catalytic organic synthesis has become a great focus in industry today. Homogeneous and heterogeneous catalysts are used widely for the conversion of any petrochemicals industry such as ammonia, methanol, urea and as well as natural gas. However, the number of homogeneously catalyzed processes has been steadily growing in the eighties and nineties (P. van Leeuwen, 2004). Homogeneously catalyzed process can be referred to as a catalytic process in which the catalyst and the substrates are in one phase, and for hydroformylation of olefins, it was in liquid phase.

Organometallic catalyst consists of a metal element at the centre which is surrounded by organic or inorganic ligands. The properties of the catalyst are determined by the metal and the ligands. The organometallic catalyst has organic ligands in it at the outer layer, which is affected the performance of catalyst if the ligands is changed resulting the changes in the rate of reaction as well as the selectivity of the products.

One of the commercial processes that have been using rhodium catalyst is hydroformylation of aldehydes to produce alkene. In this process, it was found that the industry has shifted the usage of cobalt-based catalyst into rhodium based catalyst before of the selectivity of main product is higher which is about 92-95%. Therefore the best recycle system need in order to use this expensive catalyst economically in the industry.

Davy Process Technology Limited in collaboration with The Dow Chemical Company has developed the 'Low Pressure Oxo' process (LP Oxo Process) a hydridocarbonyl coordination complex of rhodium, modified with triphenylphosphine ligand as catalyst and becomes the world leading position in low pressure of hydroformylation process which comprises two thirds of the world's production of butyraldehydes (R. Tudor, et al., 2007). P. van Leeuwen (2004) also agrees that rhodium catalyst does well in the

'Low Pressure Oxo' process as it is much faster and the feedstock utilization is much better compared to cobalt based catalyst.

The comparison between rhodium based process and cobalt based hydroformylation is shown in Table 1. The development of rhodium based catalyst favored by manufacturer due to the high selectivity and mild condition of the process.

Process Parameter	Cobalt	Cobalt + phosphine	Rhodium + phosphine
Temperature (°C)	140 - 180	160 - 200	90 - 110
Pressure (atm)	200 - 300	50 - 100	10 - 20
Alkane formation	Low	Considerable	Low
Selectivity of n-butyraldehydes (%)	75 - 80	85 - 90	92 - 95
Isolation of catalyst	Difficult; $\text{HCo}(\text{CO})_4$ is volatile	Less difficult	Less difficult; water soluble phosphine used

Table 1: Process Parameters of Hydroformylation Processes (Bhaduri et.al. 2000)

2.2 Membrane Separation for Catalyst Recovery

Current development of catalyst recovery can be achieved by combining the membrane separation with the chemical processing in the industry using solvent resistance nanofiltration membrane (SRNF) which the range of nominal molecular weight cut off (MWCO) are between 200 to 1000 Da (Luthra et al., 2002). The membranes should be effective in separating the organic synthesis catalyst with the product by the exploitation of the size difference between the catalyst (>600 Da) and the products (<400 Da) as stated by Scarpello et al. (2002).

For your information, the biggest problem that has been found on the catalyst system for homogenous system is the catalyst degradation which comes from the thermal separation process. This process will cause the enormous destruction of catalyst as it can precipitate onto the apparatus wall as a metallic rhodium because the organic ligands have been degraded. Therefore, Priske et al. (2010) proves that the solvent resistant nanofiltration (SRNF) membrane is possible to separate and recycle the homogeneous catalyst for hydroformylation process.

2.3 Effect of Molecular Weight Cut-off to Catalyst Rejection

Molecular weight cut off is the cut off value defined as that the lowest molecular weight value that 90% of the solute is retained by the membrane. In nanofiltration, the high MW of the catalyst compared to the MWCO of the membranes has assisted the catalyst separation.

The rejection of catalyst can be calculated using the formula below:

$$r = 1 - \frac{C_p}{C_r} \quad (2)$$

where r is the catalyst rejection, C_p is the concentration of permeate and C_r is the concentration of the retentate.

2.4 Membrane-Solvent Compatibility

Basically nanofiltration worked for aqueous system which has a solution contain of solutes and solvent. Thus, based on Yang et al,(2001),the membranes typically lose their structural integrity and separation performance upon exposure to organic solvent . Therefore, choosing the right solvent-membrane combination is the most important part that needs to be taken into consideration before applying the catalyst separation through nanofiltration system.. The compatibility of the membrane can be seen by observing the ability of the membrane to produce solvent flux, J_s at moderate pressure (Scarpello et al., 2002) and also by observing the physical changes and the active layer changes.

The solvent flux produced can be calculated using this equation:

$$J_s = \frac{V_p}{A_m t} \quad (1)$$

Where A_m is the active membrane surface area and t is the time taken for a certain volume of permeate to be achieved. The usage of polymeric membrane in organic system may cause an aggressive effect. The 'like dissolve like' rule of thumb is applicable since the polymeric membranes and also the transport properties are not affected due to swelling and plasticization (Descrocher, 2004).

The observation for ethyl acetate by Yang et al. (2001) for MPF-50 does not tally with the manufacturer's data regarding the stability of the membrane in a wide range of organic solvent including ethyl acetate and toluene. It also have different perspective with the observation made by Scarpello et al. (2002) since they have said that MPF-50 appears to be most flexible membrane due to its compatibility with all the chosen solvents including ethyl acetate.

Yang et al (2001) has mentioned that most of NF membranes, designed for aqueous system lose their structural integrity and separation performance upon exposure to organic solvent which cause membrane instability such as cracking, swelling and shrinking of membrane matrix that affect the solvent flux. Therefore, Yang has conducted an observation to see the stability of the membrane inside organic solvent for a few types of membrane and the result s as shown in Table 2 below.

Membrane type	Methanol	Ethyl acetate	Toluene
UTC-20	Curled	Immediately cracked	Immediately cracked
MPF-44	Flat	Curled	Rolled, translucent
MPF-50	Flat	Curled	Rolled, translucent
MPF-60	Flat	Curled	Curled, translucent
Desal-5	Flat	Flat	Flat
Desal-DK	Slightly curled	Immediately cracked	Immediately cracked

Table 2: Observation of membrane compatibility in organic solvent by Yang et al., (2001)

A few studies also have been done to observe the stability of membrane in the solvent system. The experiment using MPF-50 shows that non polar solvent has higher permeability than polar solvent (Machado et al., 1999). However, Scarpello et al. (2002) reported the level of flux of a given solvent through a given membrane cannot be simply predicted from physicochemical properties of the solvent such as the viscosity, molar volume and solvent hydrophobicity and air-liquid surface tension. This statement contradicts with the assumption of Machado et al. (1999) in their study saying that the decrease in viscosity leads to the increase in solvent flux and same trend observed for surface tension. Therefore, the solvent properties itself might affect the solvent flux as well as the membrane performance.

2.5 Membrane Pre-Treatment

Pre-treatment process is crucial part before using the membrane for the data experiment since we need to remove the coating layer as well as obtain a steady state flux rate. Different type of polymer made has different volume of solvent permeated before obtaining steady flux. It was because the function of the membrane as the universal refluxing volume cannot be defined as it is dependent on the polymer from which it is made. Each membrane should be pre-conditioned with pure solvent until a steady flux is obtained prior to using it to investigate the separation properties of the membrane (Gibbins et al., 2002).

Prior to reaction mixture separation, Luthra et al. (2002) also conduct the pre-conditioning by passing the pure toluene through membrane to allow benchmarking of the membrane status via the pure toluene flux. The flux was found to be decreased due to membrane compaction. Membrane compaction effect is agreed by Yang et al., (2001) in their experiment of determining the flux of pure solvent at steady state using MPF membranes as well as membrane compatibility effect.

Yang et al. (2001) make comparison between the methanol fluxes from Machado et al. (1999) and manufacturer value and find significant difference in value of flux of Machado et al. (1999) compared to theirs and the manufacturer's value. Different solvent flux value for the same membrane may due to insufficient of washing out of pre-conditioning agent or insufficient time to allow steady state flux.

Gryp et al., (2010) also pre-treat the STARMEMTM membranes with toluene in order to remove the preserving agent from the membrane. The cell was then washed out with the desired solvent that was used for steady state characterization. He also conducts the membrane break-in procedure after the pre-treatment in order to establish a steady state condition which is previously done by Scarpello et al. (2002). Membrane pretreatment could result in reorganization of membrane structure, changes in membrane pore size or free volume between the polymer chains and hydrophobicity of the membrane.

2.6 Effect of Operating Parameter to Solvent Flux and Catalyst Rejection

Scarpello et al. (2002) prove that solvent flux increases with the increase of pressure and the catalyst existence has no effect to the solvent flux. The catalyst rejections appear to increase with the increase of pressure due to a partially reversible, increasing compression of active layer when membrane subjected to higher pressure. Thus, pores were tightened or sealed (cylinder pore-based permeability) because of this membrane compaction.

Increasing surface and pore fouling resulting from building up of a layer of catalyst at the membrane surface acts to partially block the pores of the membrane. Because of that behaviour, the increase of catalyst concentration explains the reduction on solvent flux and also the increase of catalyst rejection reported by Scarpello et al. (2002) which is further confirmed by Luthra et al. (2002). There was also concentration polarization happened due to higher concentration when the solutes concentration is more than the bulk of the solution. Therefore another “active layer” has been produced by solutes concentration on the membrane surface itself.

Scarpello et al. (2002) find that the effect of initial catalyst concentration to rejection improves substantially for STARMEM™ 122- Wilkinson catalyst-tehrahydrofuran system from 0.971 to 0.995 by increasing the concentration from 0.785 to 5.0mM. Therefore at small range of data variation, we need to find the exact membrane solvent flux and catalyst rejection in order to obtain the accurate data. Rhodium based catalyst separation using a few compatible membranes solvent combinations will be used to study the catalyst rejection and the solvent flux by varying the operating parameters.

2.7 Current Research on the DuraMem™ development

Based on Siavash et al. (2011), he mentioned that solvent resistance nanofiltration (SRNF) has show promising performance as alternative tools to traditional separation units such as distillation columns for the recovery system. Research has been conducted for purification of residual solvent in the pharmaceutical industry. He mentioned that this SRNF process has found to be a major reduction in energy consumption by applying well chosen membrane process and the waste streams also can be reduced because of the recovery system.

Doorslaer et al. (2010) observed that the DuraMem membranes showed the highest rejection which up to 96% for the separation of reaction products from ionic liquid. Sereewatthanawut et al.(2010) studied that by using SRNF, large amount of solvent can be saved because of the solvent recovery system can be achieved well by using dual membrane diafiltration with DuraMem as the membrane module.

Siavash et al (2011) has mentioned that to determine membrane morphology, scanning electron microscopy (SEM) images were acquired with a Philips XL 30 FEG SEM, a semi-in-lens type of SEM with a cold field-emission electron source. Membrane cross-sections were obtained by breaking dry membranes under liquid nitrogen. Samples were coated with a gold layer using a high resolution sputter coater to reduce sample charging under the electron beam.

Siavash et al, (2011) has compared the performance of StarMem 122 and DuraMem 150 which have different molecular weight cut off (MWCO) of 220 and 150 respectively. The overall performance shows that DuraMem 150 was better than that of StarMem 122. The membrane is said that did not show any swelling effect because of the high degree of cross-linking of the polyimide structure. With exception of Donepezil in ethyl acetate, for all pharmaceuticals, the rejection given by DuraMem membranes was more than 90%. Therefore it was concluded that DuraMem give higher rejection of solutes compared to StarMem membrane.

CHAPTER 3

METHODOLOGY

3.1 Chemical and Membranes

The catalyst used is Carbonyl tris (triphenylphosphine) rhodium hydride, RhH (CO) (PPh₃)₃ with a molecular weight of 918.79 Da. It is a yellow solid that is soluble in chloroform and methylene chloride.

Ethyl acetate is the chosen since these solvents are able to dissolve the tested catalyst to produce homogenous solution and are commonly applied in organic synthesis. The other reason is the resources are quite good to be able to purchase and use it for the given one-year time to finish this project.

Solvent	Supplier	Purity (%)	MW (g/mol)	Water miscibility (% w/w)	Surface tension at 25°C (mN.m)	Viscosity at 20°C (cP)
Ethyl acetate	Merck	>99.9	89.00	7.9	23.9	0.440

Table 3: Physical parameters of the solvents.

Since there are limited time and resources, there is only four type of SRNF membranes that we can used to do the experiment which are STARMEMTM 122, STARMEMTM 240, DURAMEMTM 200 and DURAMEMTM 500 polyimide types. The active surface of these membranes are manufactured from polyimide with an active skin layer less than 0.2 mm in thickness and pore sizes that are less than 50 ANG (Scarpello et al., 2002). This membrane was found that having the maximum pressure and temperature is at 60 bar and 50°C. It is considered as hydrophobic membrane.

3.2 Equipments

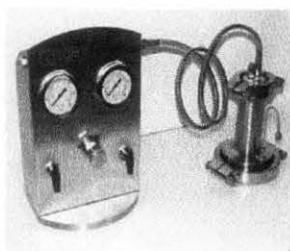


Figure 5: METcell Unit



Figure 6: UV-Vis Spectrophotometer



Figure 7: SEM unit

Equipments	METcell	UV-Vis	SEM
Functions	Nanofiltration process take places	Measure concentration of catalyst in solution	To see the surface structure of membrane
Max working pressure	69 bar	-	-
Availability	Yes	Yes	No

Table 4: Equipments used in the project

3.3 Experimental Procedure

The methodology for this experiment comprises of three parts. The first is to assess the compatibility of solvent-membrane, the second one is to determine the solvent flux and catalyst rejection and the last part to determine the effect of pressure and catalyst concentration for the homogenous system. Membrane solvent combination is prepared as shown in table 5 below.

Combination	Membrane	Solvent
1	DuraMem™ 200	Ethyl acetate
2	DuraMem™ 500	Ethyl acetate
3	StarMem™ 122	Ethyl acetate
4	StarMem™ 240	Ethyl acetate

Table 5: Membrane solvent combinations

Membrane sheet with 2cm wide and 2cm length each is soaked in the respective solution for 24 hours. The physical changes are observed after 24 hours. The sheet is dried using the oven at about 35°C in order to make sure that the membrane is free from solvent and coating agent. The membrane sheets are observed through Scanning Electron Microscopy (SEM) unit for microscopic view of the changes of membrane.

By using 82mm diameter of membrane disc, the membrane-solvent combination is tested in METcell to observe non-zero flux condition at pressure of 20bar. The stable combinations are used for the next sub-experiments. Membrane pre-treatment is crucial before starting an experiment. Permeation of the solvent in METcell at 20 bar is needed in order to reduce the influence of flux decline (Scarpello et al., 2002). The pre-treatment is stopped after 250ml of solvent is permeated and the permeability test is conducted. The time taken for 80 ml of solvent to be permeated is recorded. The permeability test is conducted for 1 hour.

The procedure in varying the pressure and catalyst concentration effect is the same. The only different is that each parameter is manipulated for five reading which are 5 bar, 10 bar, 15 bar, 20 bar and 25 bar for pressure variation while the catalyst concentration is analyzed at 0.2 mM, 0.5 mM and 0.8 mM, and 1.0 mM

As for pressure variation part, 30 ml of rhodium catalyst solution is prepared for each run. The solution is pressurized at the above mentioned pressure with stirred condition at 150 rpm. The permeation is stopped after half of the solution is permeated. Permeate and retentate are taken for UV-Vis spectrophotometer analysis.

Same procedure is conducted for concentration variation but the pressure is fixed at 20 bar with stirred condition at 150 rpm. All the experimental procedure has been summarize in the chart below.

Physical Stability Study



Cut the membrane into 2cm width and 2cm length



weight the membrane before soaking



soaking the membranes into pure solvents for 24 hours



then, dry the membrane in the oven at 35°C



make sure the drying is complete before weight the membrane again



sent the dry membrane to Scanning Electron Microscopy unit to observe the inner changes

Permeability Study

Cut the membrane using the round disc given by supplier

Soaking the membranes into pure solvent for 2 hours

after that, place the membrane on the dead-end of the reactor

fill the reactor with 250mL of pure solvent

permeate all of the solvent and then once again fill the reactor with another 250mL of pure solvent

take time of each 30 mL of solvent permeate through membrane until reach steady state

Effect of pressure and catalyst concentration on solvent flux and catalyst rejection



flux can be calculated by taking time given by 15 mL of solution permeate through membrane



condition 1

at P=20bar, observe flux and catalyst rejection at 4 different catalyst concentration (0.2,0.5,0.8, 1.0mM)



condition 2

at C=1.0mM, observe flux and catalyst rejection at 5 different pressure reading (5,10,15,20,25 bar)



prepare the solution of 250 mL of 1.0mM using the formula $n=mV/1000$



produce the graph data and tabulated table from the data given through experiment

Quantitative Analysis



prepare standard solution of 0.2,0.4,0.6,0.8 and 1.0 mM of the solution



produce the calibration curve for UV-Vis analysis guided by Mr Jailani



take the absorbance peak at WL= 361nm



then, test all the permeate and retentate solution using UV-Vis to determine the absorbance



from the absorbance, determine the concentration and produce the graph and tabulated data

3.4 Gantt Chart

Activities	FINAL YEAR PROJECT 2/ WEEK NUMBER															
	1	2	3	4	5	6	7	M	8	9	10	11	12	13	14	
Membrane Stability test	█							MIDSEM BREAK								
Membrane Pre-treatment	█	█	█													
Effect of pressure and catalyst concentration on solvent flux				█	█	█	█									
Effect of pressure and catalyst concentration on catalyst rejection						█	█			█	█					
Submission of Progress Report												█				
Submission of Draft Report													█			
Submission of Dissertation and Technical Paper														█		
Oral presentation															█	
Submission of Project Dissertation (Hardbound)																█

Table 6: Gantt Chart for Final Year Project II

CHAPTER 4

RESULT AND DISCUSSION

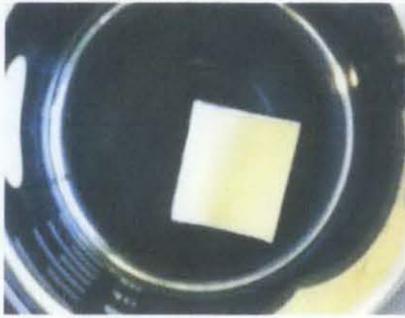
In this chapter, we will discuss on the experiment done and the result that has been obtained. Throughout these experiments, we need to clarify the effect of pressure and catalyst concentration on the solvent flux as well as catalyst rejection. For this project, four types of membranes have been used which are DuraMem™ 200, DuraMem™ 500, StarMem™ 122 and StarMem™ 240. All of these membranes is tested with organic solvents that has been clarified by supplier which is Ethyl Acetate. Therefore membrane stability test must be carried out before proceed to the main experiment.

4.1 Membranes Stability Test

Physical stability can be determined by observed the changes of the outer appearance of the membranes. According to Scarpello et al. (2002), if the membrane physical have changed, then the membrane are not compatible with the organic solvent itself. Thus as observation, all the membranes found that having physical changes except for StarMem™ 122. In the figure below, DuraMem™ 500 show the most changes by having curl shape, followed by DuraMem™ 200 by having medium curling. For StarMem™ series, only StarMem™ 240 was having slightly curl while for StarMem™ 122, it is confirm that there is no physical changes happened. The result can be summarized in the table below.

Membrane	Physical Changes Observation	
	Before soaking	After soaking
StarMem™ 240	Flat	Slightly curl
StarMem™ 122	Flat	Flat
DuraMem™ 200	Flat	Slightly curl
Duramem™ 500	Flat	Curl

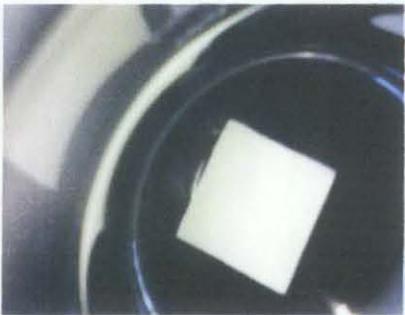
Table 7: Observation on the membrane after soaking



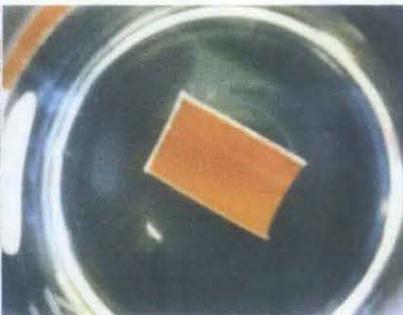
StarMem™ 122



DuraMem™ 500



StarMem™ 240



DuraMem™ 200

However, based on the supplier handout, it stated that the membranes all compatible with ethyl acetate. Since the physical changes only show the outer appearance of the membrane, we need to use Scanning Electron Microscopy (SEM) to see the changes at the active layer of the membrane. Unfortunately the equipments is not available because of broken. Then to clarify that this membrane is suitable or not with the organic solvent chosen, study has been carried out to disapprove the statement of Scarpello et. al (2002). Thus, this research has been continued to analyze the membrane rejection and solvent flux.

4.2 Permeability of DuraMem™ Membranes in Ethyl Acetate

The permeability study has been carried out before the main experiment can be conducted. It is because to remove the coating layer as well as to observe the ability of the membrane to permeate the solvent used. Since we are using two different series of the membrane, the graph also has been separated since the data is obviously at different range. The results of the DuraMem™ membranes are as per figure below.

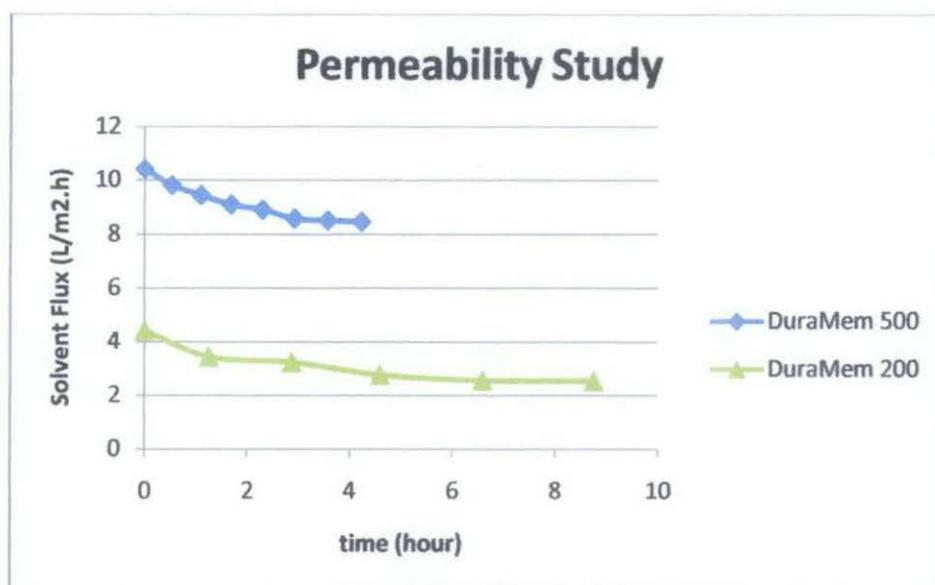


Figure 8: Permeability of DuraMem™ membranes over time

From the graph we can see that the membrane flux has reached steady state after a few hours. Since we used the dead end filtration, although the membrane has gone through physical changes, ultimately the membrane performance is not affected. The study show that DuraMem™ 500 reached stability after four hours while for DuraMem™ 200 is seven hour. The MWCO of DuraMem™ 200 is lower than DuraMem™ 500. The flux rate for DuraMem™ series is ultimately low which are below 12 L/m².h. Since we used pressure of 20 bar, the flux rate might be lower because the solvent permeate faster. Since there is no experiment done for DuraMem™ series, these data and figure can be the baseline for any future research and comparison if using another combination or solvents.

4.3 Permeability of StarMem™ Membranes in Ethyl Acetate

For StarMem™ series, as we can see in the figures above, StarMem™ 122 is more stable than StarMem™ 240 based on the physical changes. However during permeability study, the result comes out are obviously different. StarMem™ 240 has shown that increase in the flux permeability before reached it stability after 12 minutes. While for StarMem™ 122, the membranes break at pressure of 20 bar. The data can be observed from the graph below.

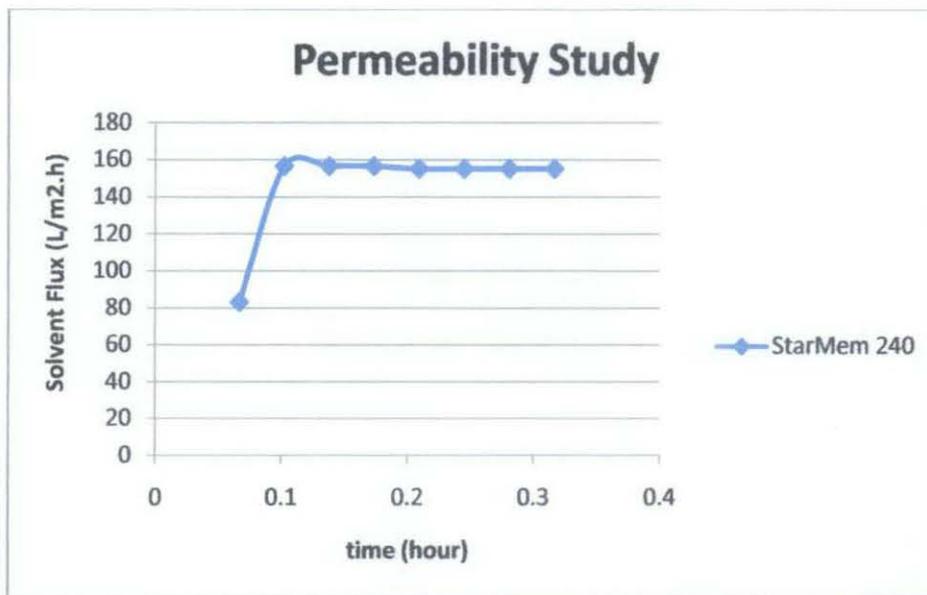


Figure 9: Permeability of StarMem™ 240 membrane over time

Flux decrease is common for permeability of pure solvent study in all literature. However for this case the flux has increased before it reached its stability. The main explanation for this situation is because the coating layer has not been fully removed yet. Thus the coating itself has build another active layer to increase the time of the pure solvent permeate through the membrane. Because of this situation might be found, in the future, more volume of pure solvent must be used in order to fully removed the coating layer before the permeability study can be continued at it stable state.

4.4 Solvent Flux Study of DuraMem™ Membranes in Ethyl Acetate

4.4.1 Solvent flux study at different concentration

At different concentration, the flux study has been observed by taking the time of 15 ml of the solution permeate through the membrane. From the figure, it shows that the initial concentration of the solution will reduce the solvent flux. For the information, the study has been carried out at 1.0mM then in decreasing order of 0.8mM, 0.5mM and 0.2mM. Scarpello et al (2002) confirmed that the increase in initial concentration is caused a reduction in flux value.

The study shown that increase of membrane fouling contributes of decrease in the solvent flux. It was because the catalyst particle stuck at membrane surface and pores hence the membrane performance is decreased. The other reason of this observation happened is the concentration polarization happened at initial concentration. This concentration of solutes particles becomes another active layer at the membrane surface since its concentration is higher than the bulk of solution. Thus, it will affect the permeability performance of the solution and decreasing in flux happened.

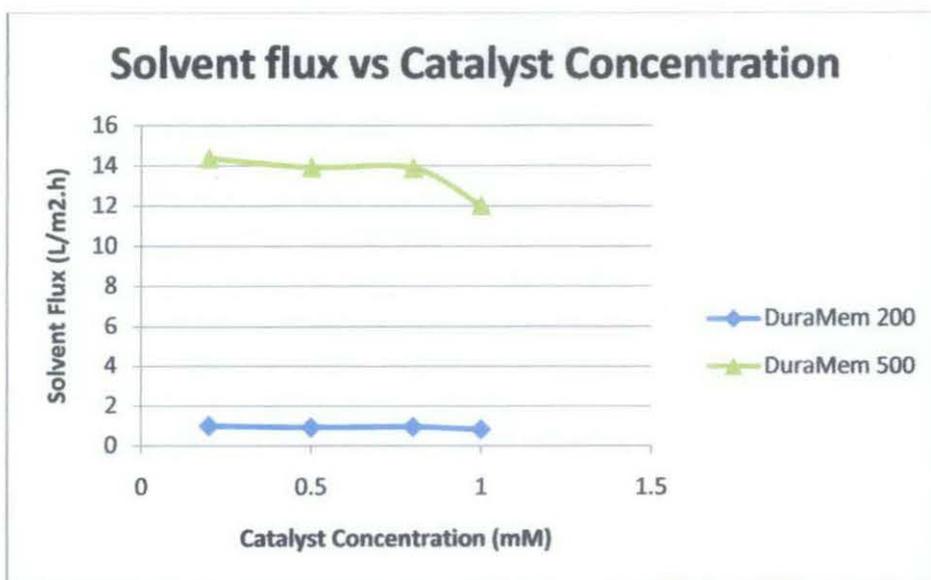


Figure 10: Solvent flux versus catalyst concentration for DuraMem™ Series

4.4.2 Solvent flux study at different pressure

For pressure variation, it was stated that by Scarpello et al. (2002) that when increase in the pressure, the solvent flux also increase. For DuraMem™ series, it found that the statement is also valid to be used. Obviously the solvent flux using catalyst solution and pure membrane are different because of the active layer of the membrane has been blocked by solute particles thus decrease in the flux rate. Since we are using solvent resistance nanofiltration, pressure driven force has been used in this type of process. So, increase in pressure ultimately will increase the solvent flux as well.

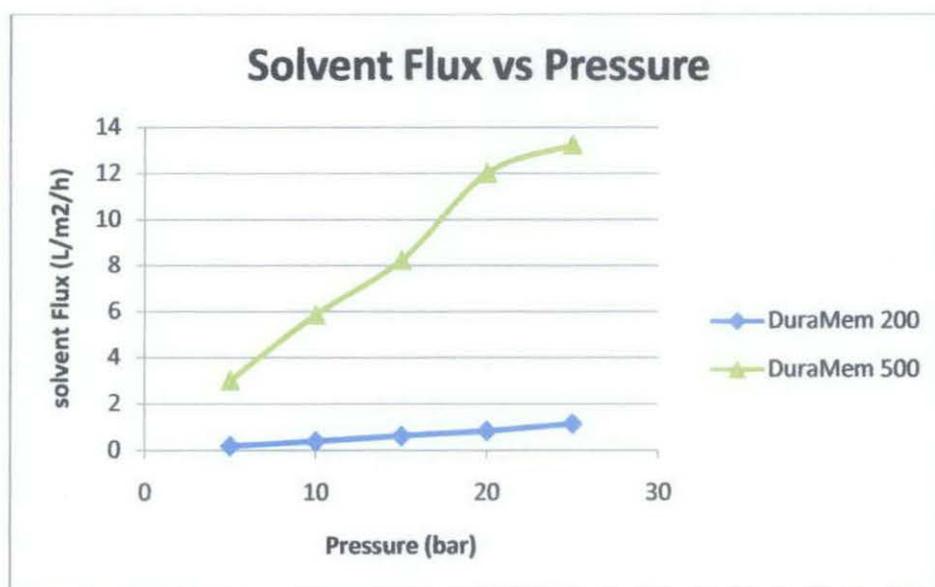


Figure 11: Solvent flux versus pressure for DuraMem™ Series

4.5 Solvent Flux Study of StarMem™ Membranes in Ethyl Acetate

4.5.1 Solvent flux study at different concentration

Since StarMem™ 122 has broken during permeability study hence the study for StarMem™ 122 has been stopped because of its instability with the organic solvent ethyl acetate or the other reason is because the membrane itself is expired. Thus for StarMem™ series, only StarMem™ 240 has been used to study the solvent flux as well as catalyst rejection. From figure above, we can see that the trend is obviously different from the existing trend. As we can see the flux rate at 0.2mM is so much greater than the flux rate at 0.4mM. Since the order of experiment is from higher to lower concentration, the only reason for this behavior is most of the pores of the membrane are filled with solutes particle. Therefore although at lower concentration, since there are membrane fouling happened, the flux rate also increase because the permeate time has been increased as well.

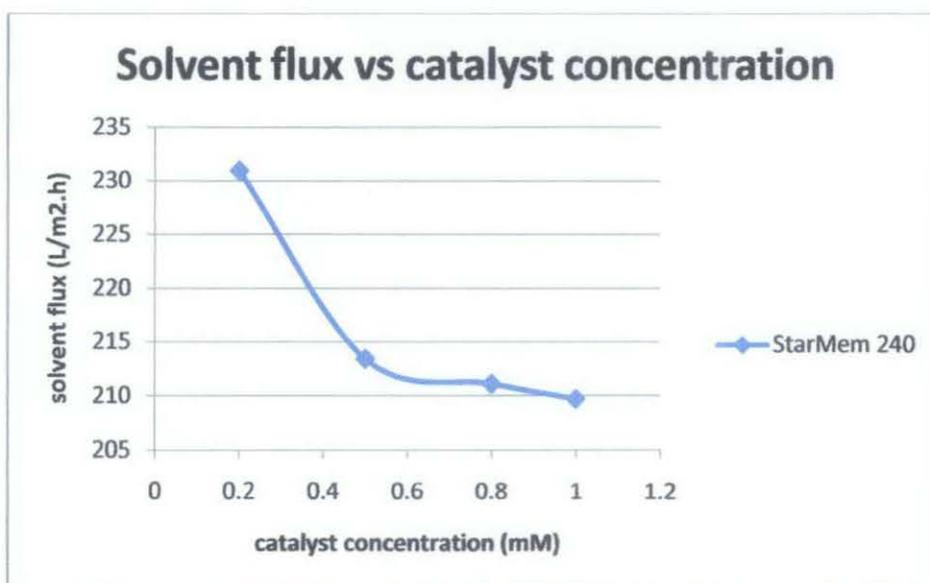


Figure 12: Solvent flux versus catalyst concentration for StarMem™ Series

4.5.2 Solvent flux study at different pressure

As mentioned in the previous by Scarpello et al (2002), when the pressure increase, the solvent flux also increase since nanofiltration is the pressure driven force process. However for StarMem™ 240 in ethyl acetate, the trend line of the graph is not really straight line based on the figure below. At intermediate pressure, the trendline is start to fluctuate because of the membrane fouling. From this behavior we can stated that StarMem™ 240 is not really compatible with ethyl acetate but still can be used as the membrane active layer for higher range of flux rate.

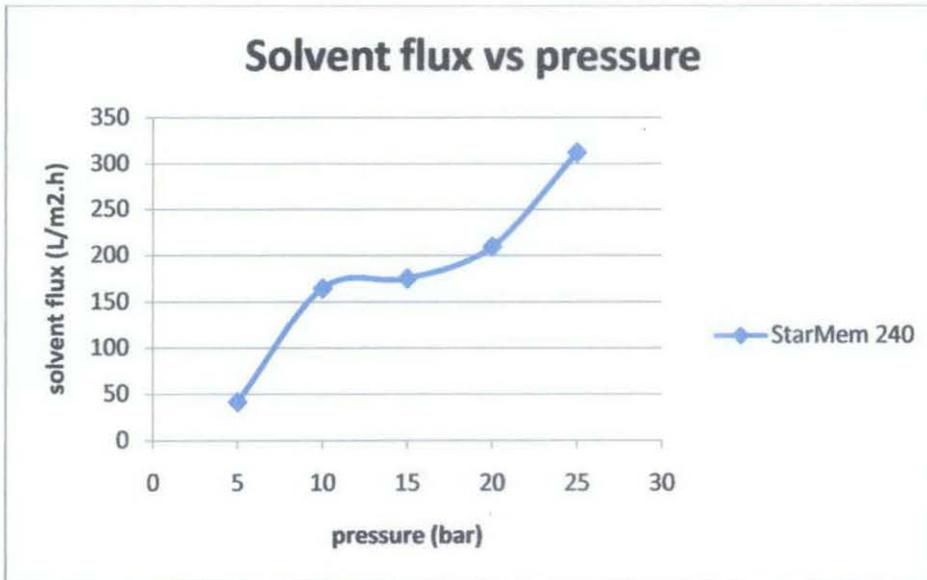


Figure 13: Solvent flux versus Pressure for StarMem™ Series

4.6 Catalyst Rejection Study of the Membranes in Ethyl Acetate

From the information given by supplier, it stated that the rejection of DuraMem™ membranes when using ethyl acetate is above 90%. Since these experiment is the baseline for DuraMem™ series, as we can see for both DuraMem™ membranes, the catalyst rejection is higher than 93% for both at different pressure and different concentration. It was because of the ability of the polyimide type of membrane to reject most of its solute particle to permeate through its membrane active surface layer. While for StarMem™ series, the rejection is obviously lower which is at range of 0.1 to 0.5 which 10% to 50%. Thus this data is enough to approve that StarMem™ series is not compatible used with ethyl acetate.

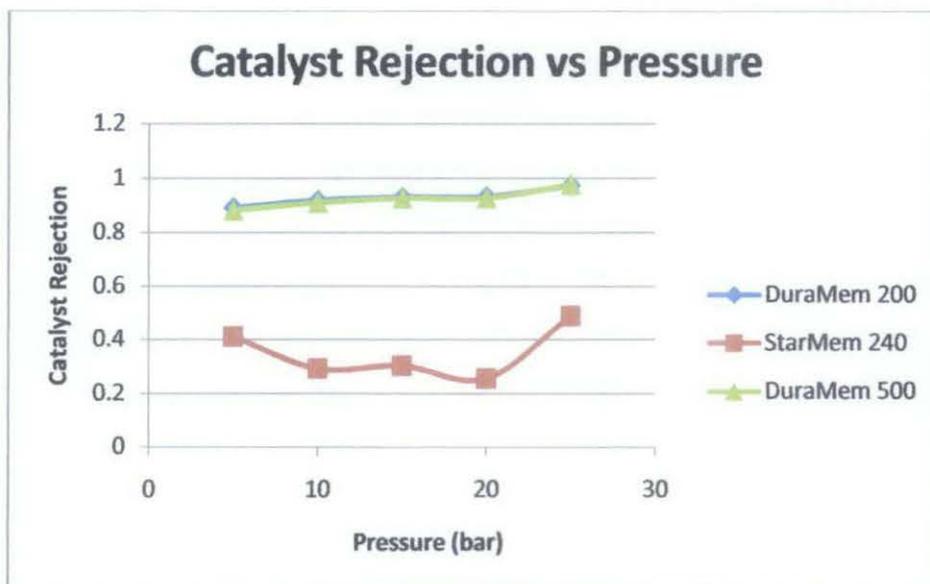


Figure 14: Catalyst rejection versus Pressure

From the figure above, as the pressure increase, the rejection also increases for DuraMem™ series. This is because of the membrane compaction happened when increased the pressure. Membrane compaction here meant that the active pores layer has decrease in size because of the increase in pressure has resulting into tighten the pores opening. While for the StarMem™ 240, the rejection is fluctuate because of its instability after a few runs with the solution. There is be possibility of membrane has break during the experiment which causes the performance to be lower.

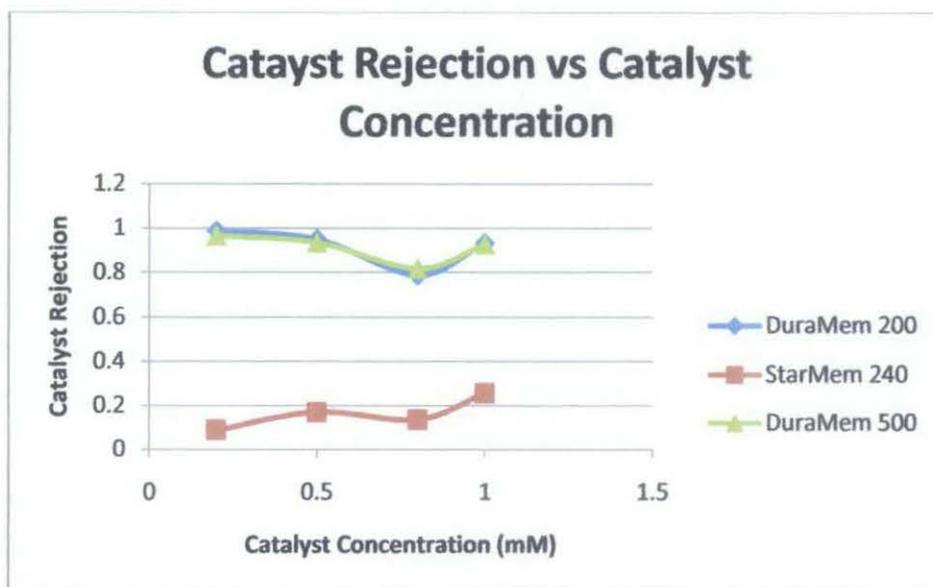


Figure 15: Catalyst rejection versus catalyst concentration

From the figure above, as we can see, although at different concentration, the rejection of DuraMem™ series is above 90% except for at 0.8mM. The only reason to explain this trend line is because of the analyzer used for catalyst rejection is UV-Vis Spectrophotometer. This equipment analysis shows the absorbance at low wavelength and the absorbance peaks are observed from many point. Because of this behavior, we decided to fix the absorbance peaks only at 361 nm which is based on the Scarpello et al (2002) as the baseline. Because of this, the trending may be affected as well as the rejection value. Therefore in future, we can decide the absorbance peak for DuraMem™ series whether it is suitable used at 361nm or not.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

From the data experiment, solvent resistant nanofiltration (SRNF) method is found to be able to separate rhodium catalyst solution from pure solvent with rejection rate above 90% for DuraMem™ series. It proves that the homogenous catalyst can be separated without affecting or break the active layer of the membranes when using appropriate organic solvent which is ethyl acetate. The compatibility of the membrane solvent combination is very important to have a good result whether for solvent flux as well as the catalyst rejection study. Therefore the organic membrane will not affect by the organic solvent used as well as not reacted with the outer behavior of the catalyst that has the organic structure.

A change of physicality of the membranes does not mean the membranes are not compatible with the solvent used. From this research, it was found that although DuraMem™ membranes had changed its outer appearance, but it was still stable to be carried out for filtration process as its given a good result for solvent flux as well as catalyst rejection. Although we cannot determine the inner changes on the active surface layer, the result itself can prove that the statement given by Scarpello et al. (2002) is invalid for DuraMem™ membranes.

Solvent flux is the pressure driven process when doing the filtration. Thus, when increase in the pressure, the solvent flux also increase since there are membrane compaction happened on the membrane pores. When using pure solvent, the solvent flux need a certain time before reach its stability. For DuraMem™ series, its need about 5 hours and above before the membranes solvent flux trending reaches it steady state behavior. However for different catalyst concentration, the trend is not really smooth and readable. However from the data research we can see that as the catalyst concentration increase, the solvent flux will decrease.

Catalyst rejection in this experiment gives a very good result for DuraMem™ series. As we can see the rejection is above 93% and therefore prove that the catalyst can be rejected using these membranes at this solvent using this nanofiltration process. However for StarMem™ series, it was found that the rejection rate is much lower and concluded that the StarMem™ series is not really compatible used with ethyl acetate. Since the trend for catalyst rejection is not really good for this research, the result may be affected by the analyzer used.

As recommendations, further research can be continued by using different solvents such as toluene, hexane, benzene and other organic solvents so that the data can be collected and comparison can be done to decide the solvent that give high compatibility when using with DuraMem™ and StarMem™ series. As well as for the membrane used, there are a lot of new membranes that has been produced lately, so these membranes also can be tested using the similar ethyl acetate as the solvent for comparison.

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APPENDICES

Average weight of the membrane before soaking and after drying

Membranes	weight before soaking(g)				weight after drying(g)			
	1	2	3	average	1	2	3	average
StarMem™ 240	0.0667	0.0672	0.0668	0.0669	0.0521	0.0522	0.0522	0.0522
StarMem™ 122	0.0725	0.0724	0.0724	0.0724	0.0589	0.0587	0.0588	0.0588
DuraMem™ 200	0.0923	0.0929	0.0929	0.0927	0.0568	0.0569	0.0569	0.0569
DuraMem™ 500	0.0767	0.0769	0.077	0.0769	0.052	0.0522	0.0522	0.0521

Permeability study of the membranes

Membrane used	t (min)	t (hour)	Vp (L)	Vp(L)	Js(L/m ² .hr)
DuraMem™ 200	0.00	0.00	0	0	0.00
	75.39	1.26	0.03	0.03	4.42
	96.83	1.61	0.06	0.03	3.44
	103.00	1.72	0.09	0.03	3.24
	120.00	2.00	0.12	0.03	2.78
	130.00	2.17	0.15	0.03	2.56
	131.00	2.18	0.18	0.03	2.54
StarMem™ 240	0.00	0.00	0	0	0.00
	4.00	0.07	0.03	0.03	83.33
	2.13	0.04	0.06	0.03	156.49
	2.13	0.04	0.09	0.03	156.49
	2.13	0.04	0.12	0.03	156.49
	2.15	0.04	0.15	0.03	155.04
	2.15	0.04	0.18	0.03	155.04
	2.15	0.04	0.21	0.03	155.04
	2.15	0.04	0.24	0.03	155.04
DuraMem™ 500	0.00	0.00	0	0	0.00
	32.00	0.53	0.03	0.03	10.42
	33.97	0.57	0.06	0.03	9.81
	35.32	0.59	0.09	0.03	9.44
	36.68	0.61	0.12	0.03	9.09
	37.46	0.62	0.15	0.03	8.90
	38.89	0.65	0.18	0.03	8.57
	39.20	0.65	0.21	0.03	8.50
	39.40	0.66	0.24	0.03	8.46

For DuraMem™ 200,

No	Pressure(bar)	Concentration(mM)	t (min)	t (hour)	Vp (mL)	V (L)
4.1	20	1	0	0	0	0.000
			66	1.1	5	0.005
			66	1.1	5	0.005
			69	1.15	5	0.005
4.2	20	0.8	0	0	0	0.000
			63	1.05	5	0.005
			57	0.95	5	0.005
			56	0.933333	5	0.005
4.3	20	0.5	0	0	0	0.000
			57	0.95	5	0.005
			61	1.016667	5	0.005
			62	1.033333	5	0.005
4.4	20	0.2	0	0	0	0.000
			55	0.916667	5	0.005
			55	0.916667	5	0.005
			56	0.933333	5	0.005

No	Pressure(bar)	Concentration(mM)	t (min)	t (hour)	V (L)	Js (L/m ² .hr)
4.1	20	1	201	3.35	0.015	0.829187396
4.2	20	0.8	176	2.933333	0.015	0.946969697
4.3	20	0.5	180	3	0.015	0.925925926
4.4	20	0.2	166	2.766667	0.015	1.004016064

No	Pressure(bar)	Concentration(mM)	t (min)	t (hour)	Vp (mL)	V (L)
			0	0	0	0.000
			49	0.816667	5	0.005
			49	0.816667	5	0.005

For StarMem™ 240,

No	Pressure(bar)	Concentration(mM)	t (sec)	t (hour)	Vp (mL)	V (L)
7.1	25	1	0	0	0	0.000
			10	0.002778	5	0.005
			11	0.003056	5	0.005
			11	0.003056	5	0.005
7.2	20	1	0	0	0	0.000
			12.13	0.003369	5	0.005
			17.56	0.004878	5	0.005
			18	0.005	5	0.005
7.3	15	1	0	0	0	0.000
			12.47	0.003464	5	0.005
			21.5	0.005972	5	0.005
			23.3	0.006472	5	0.005

No	Pressure(bar)	Concentration(mM)	t (sec)	t (hour)	Vp (mL)	V (L)
8.1	20	0.8	0	0	0	0.000
			13.24	0.003678	5	0.005
			13.92	0.003867	5	0.005
			20.21	0.005614	5	0.005
8.2	20	0.5	0	0	0	0.000
			12.69	0.003525	5	0.005
			13.88	0.003856	5	0.005
			16.29	0.004525	5	0.005
8.3	20	0.2	0	0	0	0.000
			12.56	0.003489	5	0.005
			14.25	0.003958	5	0.005
			16.49	0.004581	5	0.005

No	Pressure(bar)	Concentration(mM)	t (sec)	t (hour)	V (L)	Js (L/m ² .hr)
8.1	20	0.8	47.37	0.013158	0.015	211.104074
8.2	20	0.5	46.86	0.013017	0.015	213.401622
8.3	20	0.2	43.3	0.012028	0.015	230.946882

For DuraMem™ 500,

No	Pressure(bar)	Concentration(mM)	t (min)	t (hour)	Vp (mL)	V (L)
11.1	25	1	0	0	0	0.000
			3.4	0.056667	5	0.005
			4.15	0.069167	5	0.005
			5.03	0.083833	5	0.005
11.2	20	1	0	0	0	0.000
			3.87	0.0645	5	0.005
			4.76	0.079333	5	0.005
			5.24	0.087333	5	0.005
11.3	15	1	0	0	0	0.000
			5.66	0.094333	5	0.005
			6.99	0.1165	5	0.005
			7.57	0.126167	5	0.005
11.4	10	1	0	0	0	0.000
			8.53	0.142167	5	0.005
			9.49	0.158167	5	0.005
			10.43	0.173833	5	0.005
11.5	5	1	0	0	0	0.000
			16.68	0.278	5	0.005
			18.35	0.305833	5	0.005
			20	0.333333	5	0.005

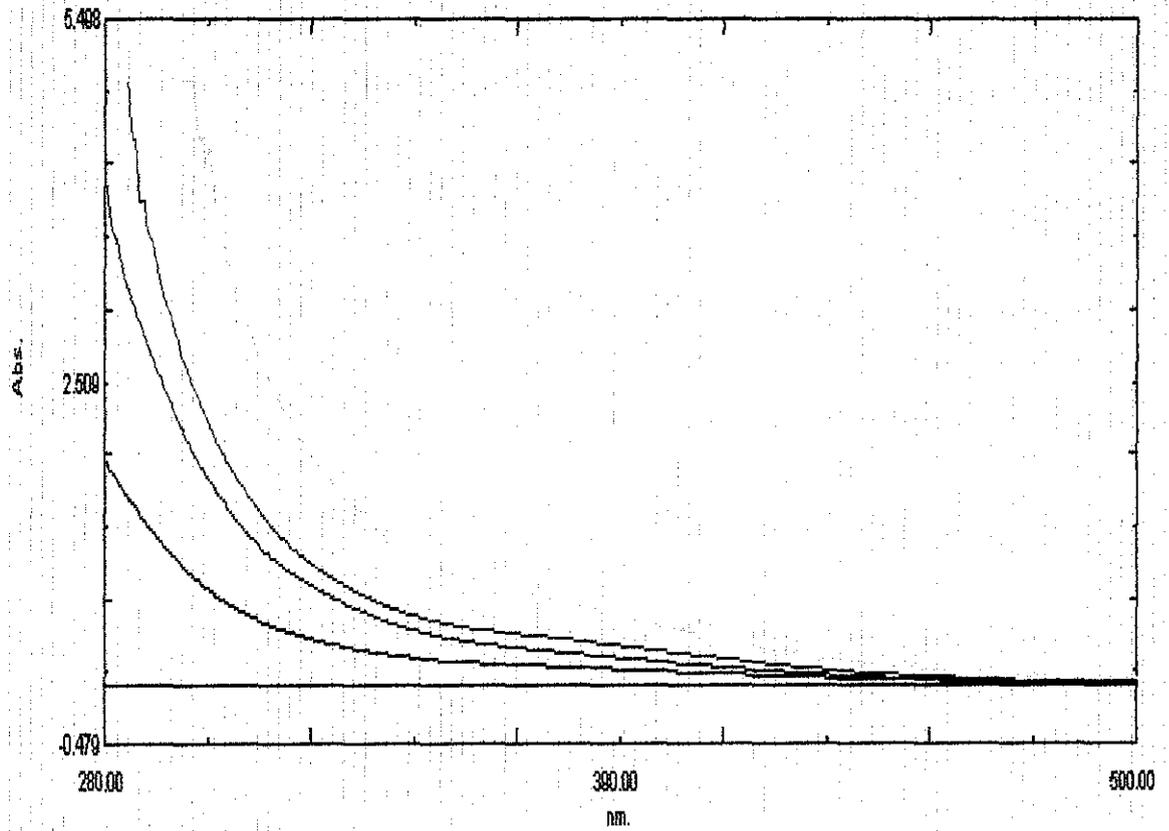
No	Pressure(bar)	Concentration(mM)	t (min)	t (hour)	V (L)	Js (L/m ² .hr)
11.1	25	1	12.58	0.209667	0.015	13.2485427
11.2	20	1	13.87	0.231167	0.015	12.0163422
11.3	15	1	20.212	0.336867	0.015	8.24592651
11.4	10	1	28.45	0.474167	0.015	5.85823081
11.5	5	1	55.03	0.917167	0.015	3.02865104

No	Pressure(bar)	Concentration(mM)	t (min)	t (hour)	Vp (mL)	V (L)
12.1	20	0.8	0	0	0	0.000
			3.3	0.055	5	0.005
			4.27	0.071167	5	0.005
			4.43	0.073833	5	0.005
12.2	20	0.5	0	0	0	0.000
			3.3	0.055	5	0.005
			4.15	0.069167	5	0.005
			4.52	0.075333	5	0.005
12.3	20	0.2	0	0	0	0.000
			3.42	0.057	5	0.005
			4.04	0.067333	5	0.005
			4.14	0.069	5	0.005

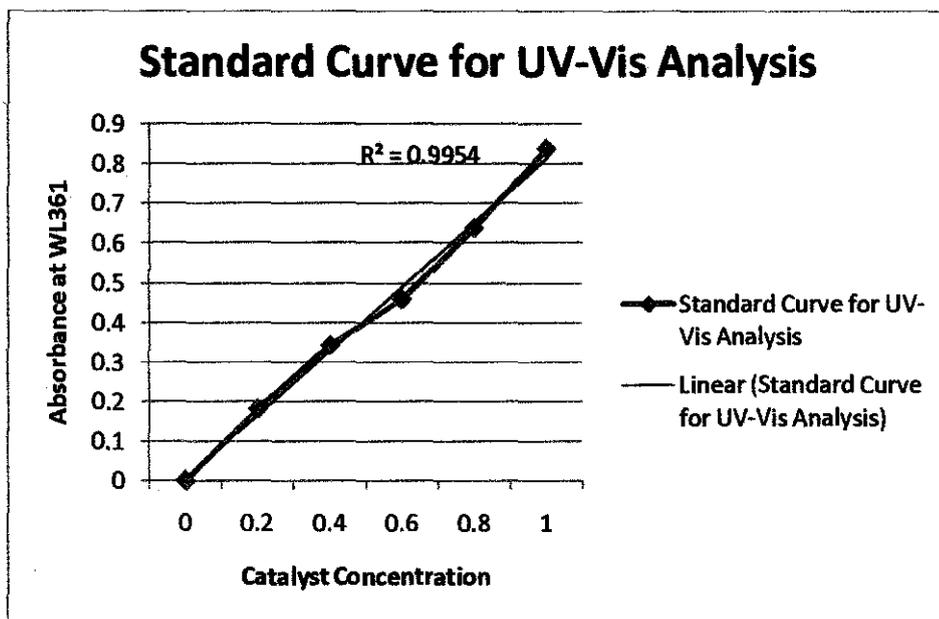
No	Pressure(bar)	Concentration(mM)	t (min)	t (hour)	V (L)	Js (L/m ² .hr)
11.2	20	1	13.87	0.231167	0.015	12.0163422
12.1	20	0.8	12	0.2	0.015	13.8888889
12.2	20	0.5	11.97	0.1995	0.015	13.9236981
12.3	20	0.2	11.6	0.193333	0.015	14.3678161

The data for calibration curve of UV-Vis Analysis

No	Sample ID	Type	Conc	WL361.0	Wgt.Factor
1	Std6	Standard	0	0.001	1
2	Std1	Standard	0.2	0.183	1
3	Std2	Standard	0.4	0.344	1
4	Std4	Standard	0.6	0.461	1
5	Std5	Standard	0.8	0.64	1
6	Std3	Standard	1	0.839	1



Standard Curve for UV-Vis Analysis



The absorbance and concentration data from UV-Vis Spectrophotometer

Membrane	Sample ID	Type	Conc	WL361.0
DuraMem™ 200	4.1P	Unknown	0.164	0.139
	4.1R	Unknown	2.453	1.996
	4.2P	Unknown	0.19	0.16
	4.2R	Unknown	0.894	0.731
	4.3P	Unknown	0.028	0.028
	4.3R	Unknown	0.557	0.457
	4.4P	Unknown	0.003	0.008
	4.4R	Unknown	0.273	0.227
	5.1P	Unknown	0.048	0.045
	5.1R	Unknown	1.806	1.471
	5.2P	Unknown	0.122	0.105
	5.2R	Unknown	1.13	0.922
	5.3P	Unknown	0.162	0.137
	5.3R	Unknown	2.338	1.903
	5.4P	Unknown	0.154	0.131
	5.4R	Unknown	1.903	1.55

StarMem™ 240	7.1P	Unknown	0.482	0.397
	7.1R	Unknown	0.943	0.771
	7.2P	Unknown	0.835	0.683
	7.2R	Unknown	1.122	0.916
	7.3P	Unknown	0.821	0.672
	7.3R	Unknown	1.178	0.961
	7.4P	Unknown	0.834	0.683
	7.4R	Unknown	1.179	0.963
	7.5P	Unknown	0.76	0.622
	7.5R	Unknown	1.292	1.054
	8.1P	Unknown	0.544	0.447
	8.1R	Unknown	0.479	0.395
	8.2P	Unknown	0.328	0.272
	8.2R	Unknown	0.395	0.326
	8.3P	Unknown	0.175	0.148
	8.3R	Unknown	0.192	0.162
DuraMem™ 500	11.1R	Unknown	1.528	1.246
	11.1P	Unknown	0.036	0.035
	11.2R	Unknown	1.624	1.323
	11.2P	Unknown	0.119	0.102
	11.3R	Unknown	1.626	1.325
	11.3P	Unknown	0.121	0.104
	11.4R	Unknown	1.606	1.308
	11.4P	Unknown	0.144	0.122
	11.5R	Unknown	1.546	1.26
	11.5P	Unknown	0.183	0.155
	12.1R	Unknown	0.862	0.705
	12.1P	Unknown	0.158	0.134
	12.2P	Unknown	0.04	0.038
	12.2R	Unknown	0.608	0.499
	12.3P	Unknown	-0.008	-0.001
	12.3R	Unknown	0.241	0.201

The computed rejection for different experiment

Membranes	No	Pressure(bar)	Concentration(mM)	V (L)	Js (L/m ² .hr)	Cp	Cr	cp/cr	Rejection
DuraMem™ 200	4.1	20	1	0.015	0.8291874	0.164	2.453	0.066857	0.933143
	4.2	20	0.8	0.015	0.9469697	0.19	0.894	0.212528	0.787472
	4.3	20	0.5	0.015	0.92592593	0.028	0.557	0.050269	0.949731
	4.4	20	0.2	0.015	1.00401606	0.003	0.273	0.010989	0.989011
	5.1	25	1	0.015	1.13378685	0.048	1.806	0.026578	0.973422
	4.1	20	1	0.015	0.8291874	0.164	2.453	0.066857	0.933143
	5.3	15	1	0.015	0.61957869	0.162	2.338	0.06929	0.93071
	5.4	10	1	0.015	0.38314176	0.154	1.903	0.080925	0.919075
	5.2	5	1	0.015	0.18335167	0.122	1.13	0.107965	0.892035
StarMem™ 240	7.1	25	1	0.015	312.5	0.482	0.943	0.511135	0.488865
	7.2	20	1	0.015	209.6875655	0.835	1.122	0.744207	0.255793
	7.3	15	1	0.015	175.1620249	0.821	1.178	0.696944	0.303056
	7.4	10	1	0.015	164.6903821	0.834	1.179	0.707379	0.292621
	7.5	5	1	0.015	41.61984434	0.76	1.292	0.588235	0.411765
	7.2	20	1	0.015	209.6875655	0.835	1.122	0.744207	0.255793
	8.1	20	0.8	0.015	211.1040743	0.544	0.479	1.135699	0.135699
	8.2	20	0.5	0.015	213.4016219	0.328	0.395	0.83038	0.16962
	8.3	20	0.2	0.015	230.9468822	0.175	0.192	0.911458	0.088542

DuraMem™ 500	11.1	25	1	0.015	13.2485427	0.036	1.528	0.02356	0.97644
	11.2	20	1	0.015	12.0163422	0.119	1.624	0.073276	0.926724
	11.3	15	1	0.015	8.24592651	0.121	1.626	0.074416	0.925584
	11.4	10	1	0.015	5.85823081	0.144	1.606	0.089664	0.910336
	11.5	5	1	0.015	3.02865104	0.183	1.546	0.11837	0.88163
	11.2	20	1	0.015	12.0163422	0.119	1.624	0.073276	0.926724
	12.1	20	0.8	0.015	13.8888889	0.158	0.862	0.183295	0.816705
	12.2	20	0.5	0.015	13.9236981	0.04	0.608	0.065789	0.934211
	12.3	20	0.2	0.015	14.3678161	0.008	0.241	0.033195	0.966805

Calculation of solvent flux

For combination of DuraMem 200-ethyl acetate,

Volume of solution, $V = 0.015 \text{ L}$

Time taken, $t = 3.35 \text{ hour}$

Active membrane surface area, $A_s = 0.0054 \text{ m}^2$

Solvent flux by formula;

$$J_s = \frac{V_p}{A_m t}$$

$$J_s = \frac{0.0015}{0.0054 \times 3.35}$$

$$J_s = 0.829 \text{ L/m}^2 \cdot \text{h}$$

Calculation of mass of catalyst for solution preparation

To prepare 250ml of 1.0mM;

$$n = \frac{MV}{1000}$$

where n= mole of catalyst,g/mol

M= concentration of solution, mM

V= volume of solution, mL

$$n = \frac{1.0 (250)}{1000}$$

$$Js = 2.5 \times 10^{-4} \text{ mole}$$

Mass of catalyst = n x MW

where MW of catalyst =918.79

$$\begin{aligned} \text{Mass of catalyst} &= (2.5 \times 10^{-4})(918.79) \\ &= 0.2300\text{g} \end{aligned}$$

Calculation for preparation of standard solution

Standard solution is made by preparing 250 mL of 1mM of rhodium catalyst solution and to be diluted to get the concentration at desired value. Solution is prepared 10 mL for each concentration.

For 0.4mM

$$M_1V_1 = M_2V_2$$

$$(1.0 \times 10^{-3})V_1 = (0.4 \times 10^{-4})10$$

$$V_1 = 4 \text{ mL}$$

4 mL of the 1.0mM solution need to be diluted in 6 mL of pure ethyl acetate to get the solution at 0.4mM concentration.

By using the same formula, the volume of 1.0mM need to use for dilution is as per below;

Concentration (mM)	V1 (mL)	Volume of pure ethyl acetate (mL)
0.2	2	8
0.4	4	6
0.6	6	4
0.8	8	2
1.0	10	0

DAVISON MEMBRANES

Data Sheet: Grace Davison Organic Solvent Nanofiltration Membranes

STARMEM™ 122; STARMEM™ 240

Membrane Material	Polyimide
Sheets	215 x 280 mm
Modules	Spiral Wound (2.5" x 12"; 2.5" x 40"; 4" x 40"; 8" x 40")
Maximum Pressure	60 bar
Maximum Temperature	50 °C
Stable in Solvents ¹	Alcohols (e.g. Butanol, Ethanol, Iso-propanol) Alkanes (e.g. Hexane, Heptane) Aromatics (e.g. Toluene, Xylene) Ethers (e.g. Methyl- <i>tert</i> -Butyl-Ether) Ketones (e.g. Methyl-Ethyl-Ketone, Methyl- <i>iso</i> -Butyl-Ketone) Others (e.g. Butyl Acetate, Ethyl Acetate)

Membrane Code: STARMEM™	<u>122</u> <u>240</u>
Permeability ² / L m ² h ⁻¹ Toluene at 55 bar	30 20
Molecular Weight Cut-Off / Dalton ^{3,4}	220 400

1. Data referring to pure solvents. If you intend to use a different solvent please contact us for further advice.
2. Performance Data are approximate.
3. Based on rejection of normal alkanes dissolved in toluene. MWCO = molecular weight cut-off, defined as MW at which 90% rejection is obtained from a curve of rejection versus molecular weight of n-alkanes dissolved at 2 wt% in toluene.

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