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A_m	active membrane surface area (m^2)
C_o	initial catalyst concentration charged to the pressure cell (mM)
C_p	final catalyst concentration in the permeate (mM)
C_r	final catalyst concentration in the retentate (mM)
Js	flux of solvent ($l\ m^{-2}\ h^{-1}$)
r	membrane rejection
t	time(h)
V_p	final volume of permeate (l)
V_r	final volume of retentate (l)

CHAPTER 1

INTRODUCTION

1.1 Background of study

1.1.1 Hydroformylation

Hydroformylation or known as oxo reaction is for the synthesis of aldehyde and alcohol from alkene. It is an important reaction from industrial and academic perspective. Approximately, 9 million metric tons per year of aldehydes and alcohols are produced using this reaction. These product is widely used in manufacturing of soaps, fragrances, detergents, adhesives,plasticizers and solvents[1-2]. Usually, a cobalt-or rhodium-based catalyst is often used. The advantages of the rhodium-catalyst system are mild reaction conditions and a linear aldehyde is always the desired product. However, the separation of the products and recovery of the precious catalyst remains a challenging problem. Molecular catalysts immobilized on different types of support have been explored. However, low catalytic activity and catalyst leach-out are difficult to overcome [3]. Water soluble rhodium catalyst is easily and almost completely separated from water insoluble products, however this technique is less efficient for higher olefins. The catalytic reaction occurs in aqueous phase, thus the success of the technique is limited to the solubility of the olefins in water phase [4]. The other way is by fluorous biphasic hydroformylation [5] but did not prove commercially successful.

A novel solvent system that itself reversibly changes from biphasic to monophasic at an elevated temperature, known as a thermomorphic biphasic or temperature-dependent multicomponent solvent system (TMS), has become interest in acting the reaction medium. The TMS system makes easy separation from the products on cooling of the reaction mixture [6, 7].

1.1.2 Membrane

Membrane technology has been widely used, due to its ability for a very selective, low cost and energy saving separation process. Rhodium is well known precious metals used for catalyst. Since the resources of this metal are limited, its worth has increased. Thus, by recycling this metal from secondary resources such as waste is essential. [8]. Thus, by using membrane technology, we are trying to recover Rh-catalyst from the hydroformylation process. The solvent that will be used is organic solvent by using nanofiltration process. Organic solvent nanofiltration is an emerging technology made possible by the recent development of solvent resistant nanofiltration (SRNF) membranes.

1.2 Problem statement

Catalyst play role in increasing the rate of reaction without consuming it. Rh-catalyst is useful in the synthesis of alcohols. Alcohols are important basic chemicals which find a wide variety of uses in industry such as synthetic rubbers, detergents, pharmaceuticals, beverages, etc. However, the frequent loses of the precious metal which may occur under process condition would be unbeneficial. The lost of only a trace amount of this precious metal making the process uneconomical to operate. In addition, it is overshadowing the attractive conversion rate and selectivity which is obtained when using this metal .The lost of the catalyst would be reducing the profit of the company as require a lot usage of the catalyst .However, we can try to recover it by using membrane process .From this way, it may help to maximize the profit and reduce the material cost. In addition, the Rh-catalyst is very high price and has poor resources. Thus, by using membrane technology; it is hope to be one of alternative way to recover the catalyst from waste and to increase the productivity. However, it is challenging to recover this metal.

Hopefully, by recovering the Rh-catalyst it would help in lower down the market price and maximize the usage of Rh-catalyst as we know that the resources of is very limited.

1.3 Objectives

The objectives of this project are:

1. To determine the stability of the membrane in the organic solvent.
2. To prove the stability of the membrane in respective pure solvent by varying operating pressure.
3. To study the effect of operating pressure and catalyst concentration on solvent flux and catalyst rejection

1.4 Scope of study

The project will cover about the organic solvent nanofiltration membrane. The membrane involve in this study is Duramem^{TM} membrane. It is modified polyimide based. From the literature, there are less information regarding the Duramem^{TM} membrane. This would give new information regarding that membrane especially stability in 1-4 dioxane,propylene carbonat, dodecane.

The flux study on those chemicals will also been conducted. This would be a way to confirm the stability of the membrane in respective solvent.

Besides that, this study emphasis on the recovery of Rh catalyst that has significantly impact in producing aldehyde. The variation of pressure would help in determining the effect on the process. This study also wants to demonstrate there is a way to recover back the catalyst in the process by introducing the membrane system in order to avoid the lost of catalyst during the process.

1.5 The relevancy of the project

This project is relevant to be conducted as it might help the industry by giving an idea of a way to recover of Rh-catalyst. This contribution would help the related industry increase the profit as we reduce the cost of the catalyst used. In addition, it is adding new application of membrane process. Besides that, it also widened the coverage of organic solvent in membrane process.

Besides that, the equipment used is available in the Universiti Teknologi PETRONAS (UTP). Thus, we should utilize the facilities provided in order to gain more information as well as to develop thinking skills and equip the students with research methodology and skills.

CHAPTER 2

LITERATURE REVIEW

2.1 Definition of membrane

Membrane processes have the potential to replace conventional energy-intensive separation techniques such as distillation and evaporation, to accomplish the selective and efficient transport of specific components. It provides reliable option for a sustainable industry growth. Membrane operation require low energy requirement, good stability under operative condition, environmental compatibility, easy control and scale up. Membrane is layer of material which serves as a selective barrier between two phases and remains impermeable to specific particles, molecules and substances when exposed to the action of a driving force .The driving force may be the temperature, pressure and concentration.

2.2 Overview on membrane separation

Basically there are three types of separation mechanism use in membrane which are size exclusion, solubility and charge. This project will involve regarding the size exclusion mechanism. The size exclusion differentiates the nano filtration, ultra filtration and micro filtration. The driving force for all these process is pressure.

Nanofiltration offers the smallest range of pores between range 1-10nm.This would not easily allow the catalyst to pass through the pore size. Nano filtration allows the permeation of low molecular weight (200-20.000 Daltons) substances. In general nanofiltration membranes are used to separate relatively small organic compounds and ions from a solvent.

Ultra filtration membranes have pore range between 5-100 nm. Micro filtration pore size is between 50 nm – 5µm.Both process has similar concept but different in pore size. The pore size of membrane can be examined by using Scanning Microscope Electron (SEM) [10].

2.3 Membrane material

In order to achieve a particular separation via a membrane process, the first step is to develop a suitable membrane. There are two types of membrane materials that basically use in industry which are polymeric and ceramic. Ceramic has excellent solvent solubility [10]. Thus, we have to identify the right organic solvent to be used in order to avoid any solvent stability problem. The advantage of using ceramic membrane does not absorb water and do not swell. Ceramics are thermally stable. Thus the membranes allow the process to be run at high temperature. In addition, ceramic membranes are wear resistance. This is beneficial for removal of particles or cake layer without damaging the membrane [11]. However, it is very expensive.

The polymeric membranes are membrane that can take the form of polymeric interphases, which can selectively transfer certain chemical species over other. It has limited chemical resistance and is not useful for solvent separations. Besides that, it can not operate at high temperature. However, it requires less cost of production [12].

2.4 The membrane filtration process

There are two types of the filtration which are dead-end filtration and cross flow filtration.

Dead-end filtration is the fluid flow is normal to the face of the filter .For the cross flow; the fluid to be filtered is pumped across the membrane and parallel to its surface.

One major difference in the operation is conversion per pass. In dead-end filtration, essentially all the fluid entering the filter is either retained by the cake or emerges as permeate. So, the conversion can approach 100%, all occurring in the first pass. For a cross flow filter, far more of the feed passed parallel the membrane than passes through it. The conversion per pass a long string of filter elements in series is generally <20%. Recycle permits the ultimate conversion to be much higher [12].

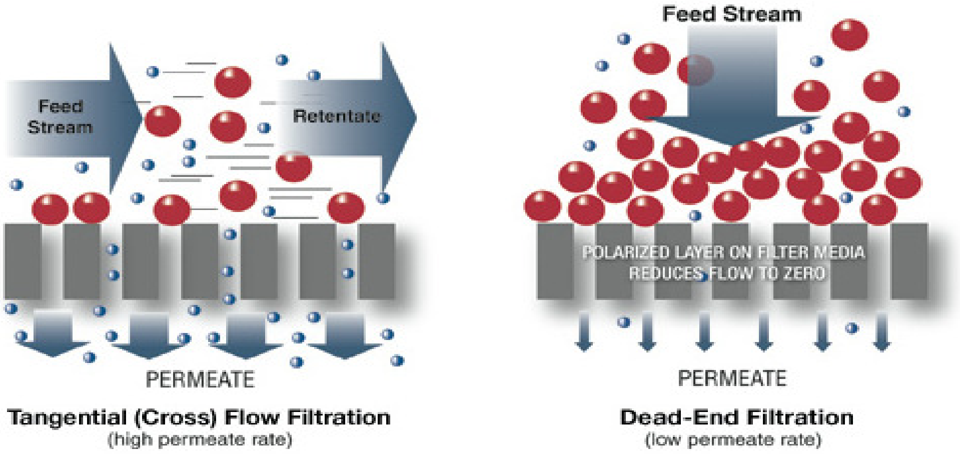


Figure 2.1: Cross flow filtration and dead end filtration.

2.5 Membrane fouling and concentration polarization

There also common problem face regarding the membrane which are membrane fouling and concentration polarization.

Membrane fouling is a major problem in all membrane operations. The process in which solute or particles deposit onto a membrane surface or membrane pores so that membrane performance is degraded. It will cause problems in measuring and interpreting pore size. The factors that contribute into this problem are membrane properties including pore size and membrane material, solution properties such as concentration and operating conditions.

Concentration polarization mostly leads to the formation of a concentrated layer near the membrane and this layer exerts a resistance towards mass transfer [12]. All the problems will lead to effect of flux. Flux can be signifying as the membrane performance.

During an actual separation, the membrane performance may change with time, and often a typical flux-time behavior may be observed as Figure 2.2 below [12]:

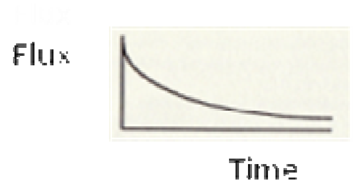


Figure 2.2: Flux behaviors as a function of time

From above, the flux through membrane decreases over time.

2.6 Nanofiltration (NF)

Nanofiltration (NF) is relatively new membrane process located between ultrafiltration (UF) and reverse osmosis (RO).

In recent years, NF has been proposed for uses in organic solutions. However, transport and retention data for NF membranes in organic solvents are very limited in the literature, and the mechanism of transport through NF membranes in organic solvent environment is not well understood [13].

NF membranes are effective over a molecular weight range that allows potential exploitation of the size difference between organic synthesis catalysts, which are usually relatively large (>600 Da), and products, which are often substantially smaller (<400 Da) [12, 13].

Nanofiltration performance has been observed that it is less predictable with organic solvents than with aqueous solutions [15-19]. Whu *et al.* [14] researched NF of larger organic microsolutes safranin O,brilliant blue R and Vitamin B_{12} in methanol solutions and reported that the manufacturer-specified molecular weight cut-off (MWCO) is an insufficient indicator of separation capabilities of the membranes. Yang et al. studied that lower rejections in organic solvents compare than in water for a wide range of commercial polymeric NF membranes including MPF membranes (MPF-44 and MPF-60) and Desal membranes(Desal-5 AND Desal-DK) [2]. Van der Bruggen *et al.* [17] reported that lower rejection in organic solvents (ethanol and n-hexane) compare than in water for N30F,NF-PES10,MPF-44 and MPF-50 Furthermore, Geens *et al.* [18] observed lower rejection of raffinose in methanol than in water for Desal membranes and N30F. After demonstrating that the membrane still stable after exposed to the organic solvent even though have lower rejection compare in water, Yang *et al.* [15] proposed that the higher rejection in water is likely due to large size of the solutes in water via the coordination of water molecules with the solute molecules. Van der Bruggen *et al.* [16] suggested an assumption which was the enhanced mobility of polymeric chains in organic solvents increased the effective membrane pore size, thus leading to lower rejection in organic solvents compare in the water. It is believed that the lower rejection in organic solvent than in water is a common scenario.

2.7 Organic solvent nanofiltration

Organic solvent nanofiltration is an emerging technology made possible by the recent development of solvent resistant nanofiltration (SRNF) membranes.
Recently,the advent of commercial organic solvent nanofiltration (OSN) has opened a wide potential applications[19]. OSN permit economic and efficient separation in the petrochemical,food and beverage, biotechnology and pharmaceutical industries for the separation of molecules in the range from 200-1000 gmol^{-1}[20,21]. The common of OSN are either composites comprising a polydimethylsiloxane (PDMS) separating layer on polyacrylonitrile (PAN) support, or integrally skinned asymmetric membrane made of polyimides[22]. Polyimides are unstable in some amines [23]. It also has generally poor stability and performance in polar aprotic solvent such as methylene chloride (DCM), tetrahydrofuran (THF), dimethyl formamide (DMF) and n-methyl pyrrolidone (NMP),in which most polyimides are soluble. However, this paper [24] report successful OSN in THF, DMF and NMP for the first time.

The mechanism of the separations with polymeric membranes in organic solvents is poorly understood. Performance of nanofiltration membranes in organic solvents is very different from that in aqueous solution; fluxes and rejection differ significantly. Prediction of the behavior of a membrane in organic solvents remains difficult [25].

Permeation through the membrane pores is only possible when the difference in surface energy between membrane and solvent can be overcome [26]. The less polar character causes a smaller difference in surface energy for hydrophobic membranes, so that the solvent flux will be larger. For hydrophilic membranes, the difference in surface energy increases when a less polar solvent is used, this causes a smaller solvent flux [25].

In addition, higher fluxes are evident in the case of relatively non-polar solvents, such as acetone and octane, while lower fluxes are indicated in the case of polar solvents, such as propanol and water [27].

According to experiment [27], the experimental data revealed a mark variation in the level of permeate flux among the various solvents. The flux of either pure or mixed solvents was mainly affected by surface tension and viscosity of the solvents.

2.8 Membrane stability

Most NF membranes, designed for aqueous system, lose their structural integrity and separation performance upon exposure to organic solvents. Membrane instability can result in surprisingly large fluxes due to swelling and/or cracking the membrane, or lead to negligible solvent permeation due to shrinking of the membrane matrix. Observation of membranes soaked for a period of time can give a preliminary insight into the membrane stability/durability [28].

Membrane swelling is a common phenomenon and may result in membrane deformation, particularly in organic solvent. Therefore, membrane stability has been a major concern with organic solvent [29].

2.9 Membrane pretreatment

A pretreatment of NF membrane is very important for obtaining reliable results. It is interesting that inconsistent membrane flux and rejection for the same membrane and organic solvent system have been observed. For example, under similar operating conditions, methanol fluxes across the MPF-50 membrane reported by different researchers [30-34] were in the range of 25-175$Lm^{-2}h^{-1}$ at 30 bar; rejection of 68% and for Safranine 0 (MW 350) with MPF-44 was reported by Whu *et al* [30] and Yang *et al* [31], respectively. Examination of these literature data showed that different authors employed different membrane pretreatment methods. It is well recognized that membrane pretreatment plays an important role in membrane performance of aqueous NF process.

Thus, membrane pre treatment is likely to be one of the reasons that result in inconsistent membrane performance in NF processes with organic solvents. However, no investigations into the effect of membrane pre treatment have been reported.

Pre treatment with organic solvents may wash the out of the preconditioning agents and/or additives used in the manufacturing processes. Polyamide, polyimide and polydimethylsiloxane (PDMS) membranes have been reported to be solvent resistant [32]. According to [32], the membrane pretreatment with methanol and acetone has a significant effect on solvent flux and membrane rejection properties in methanol solutions for polyamide and polyimide membranes and insignificant effect on a PDMS-based membrane. These show that polyamide- and polyimide-based membranes have strong interactions with acetone and methanol.

Membrane pre treatment could result in reorganization of membrane structure, changes in membrane pore size and hydrophobicity of the membrane.

2.10 Effect of pressure in catalyst rejection

Increasing pressure is found to beneficial in term of both flux and rejection.

The fact that an increase in the pressure result in increased rejection is consistent with the results of Whu.*et.al* for the SRNF of dyes from methanol [30].

Mass balances (MB) on the catalyst were evaluated at the end of each experiment in order to confirm than no catalyst was sticking to the membrane or absorbed into the pressure cell seal, using the equation (2.1):

$$\mathbf{MB = [(C_pV_p + C_rV_r)/ C_oV_o] \ x\ 100\%} \qquad \mathbf{(2.1)}$$

Where C_p is final catalyst concentration in the permeate,V_p is final volume permeate,C_r is final catalyst concentration in the retentate,V_r final volume retentate,C_o is initial catalyst concentration charged to pressure cell and V_o is initial volume charged to pressure cell.

Good agreement between input and output molar amounts of catalyst is obtained for the vast majority of the cases, with typical values of MB between 96 and 104% [35].

CHAPTER 3

METHODOLOGY

3.1 Chemical and catalyst

The chemicals involve in this study are propylene carbonate (polar), dodecane (non polar) and 1-4 dioxane as well as temperature dependent multicomponent solvent (TMS) that consist mixture of those solvents. These solvents are all analar grades. In addition, acetone also will be used in order to wash out the coating on the membrane. The catalyst use is $RhH(CO)(PPh_3)_3$.

3.2 Membrane

The membranes uses are DuraMem^{TM} with molecular weight cut off (MWCO) of 200,300 and 500 membrane. All membranes are modified polyimide base. They are supplied in a “dry form” by Membrane Extraction Technology Ltd,UK.

3.3 Experimental set up

A METcell is used for the experiment. The cell is stainless steel high pressure stirred cell. It has capability to perform wide range of membrane separations. The METcell has a maximum working pressure of 69 bars and it can be used for nanofiltration separation using aqueous and non-aqueous solvents. The cell is set up by following way: a disc of desired membrane diameter is cut from membrane sheet by using a sharp knife. The membrane is inserted into the cell by ensure the active layer of membrane is facing down, to ensure it has contact with the solvent. After that, the porous stainless steel support disk can be placed on top of the membrane as to hold it in place. Before a METcell lid and stirrer assembly is placed inside the cell, about 250ml of acetone is poured into the cell to wash the membrane [35].

The cell is pressurized using nitrogen gas that allowed the pressure to the 20 bar. After the washing process has been done, the acetone is removed and the solution of catalyst is poured into the cell by varying the pressure from 12 to 20 bars [35].

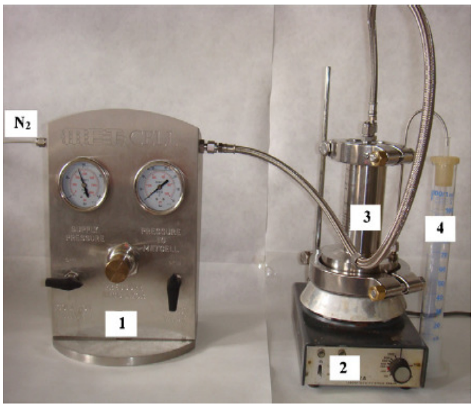


Figure 3.1: MET Cell set up:(1) pressure regulator, (2) Magnetic stirrer, (3) Nanofiltration MET Cell, and (4) Measuring cylinder

3.4 Experimental and analytical procedure

In order to assess the compatibility of the membrane with a given solvent, the membrane is soaking about 24 hours in respective solvent. The inspection after the period will give the preliminary insight of the membrane stability.

For further confirmation of the stability, flux study will be carried out. The 250ml of pure solvent will put in the cell at pressure of 20 bars. The time,t, taken for 20ml of permeate,V_p, to be collected will be recorded using stop watch. The solvent fluxes, J_s can be calculated by using equation:

$$\mathbf{J_s = V_p / A_m} t \qquad \mathbf{(3.1)}$$

Where A_m referred to the active membrane surface. The system is incompatible if zero flux is obtained under this condition. After getting 20ml of permeates, the pressure is changed to 16 bars and 12 bars.

The catalyst rejection is done for DuraMem^{TM} 300 with 1-4 dioxane. The 20ml of catalyst solution 0.5 mM is poured into the cell and varying the pressure from 12 to 20 bars. After half of the volume is collected, 10ml, keep the sample of the retentate and permeate for Uv-Vis analysis. The time taken for permeate to be collected must be recorded. The membrane rejection values,r, is calculated by using equation,

$$\mathbf{r = 1 - (C_p/C_r)} \qquad \mathbf{(3.2)}$$

Where C_p is final catalyst concentration of permeate (mM) and C_r is final catalyst concentration of retentate (mM) [35]. Experiment is repeated by using 0.1 mM and 0.15mM.

3.5 Tools

In order to conduct the experiment, two criteria have been chosen in selecting the equipment. The criteria are using for dead-end filtration and nanofiltration process. This has lead to the MET cell. The MET cell is a stainless steel-high pressure stirred cell that is capable of performing a wide range of membrane separations. Typically it is pressurized by using inert gas from a cylinder such as nitrogen gas.

Other than that, Ultraviolet Visible (Uv Vis) Spectroscopy will be used in order to determine the concentration of permeate and retentate. Uv Vis can be used to determine the concentration of a specific metal element, and in this case, determination of Rh catalyst. The concentration is to be used to calculate the rejection of catalyst.

Stopwatch also requires in order recording the time taken for completing the experiment.

CHAPTER 4

RESULTS & DISCUSSIONS

4.1 Compatibility test

Membrane compatibility test had been carried out. All the Duramem^{TM} 200,300 and 500 had been soaked with propylene carbonate, dodecane, 1-4 dioxane and TMS system. The physical observation of the membrane with naked eyes as below:

Table 4.1: Physical Observation on Duramem^{TM} 200

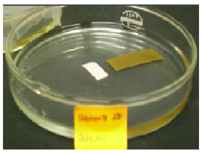
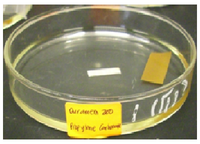
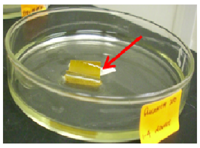
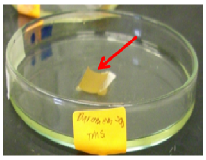
Chemical	*Physical Observation*		
	After 24 hours		Stability
Dodecane	*i) Remain Flat* *ii) a few fiber are damaged* *iii)do not crack*		Stable because not disintegrated
Propylene Carbonat	*i)Remain Flat* *ii)a few fiber are damaged* *iii)do not crack*		Stable because not disintegrated
1-4 Dioxane	*i) Curled* *ii)a few fiber are damaged* *iii)do not crack*		Stable because not disintegrated
TMS	*i)Curled* *ii)a few fiber are damage* *iii)do not crack*		Stable because not disintegrated

Table 4.2: Physical Observation on Duramem^{TM} 300

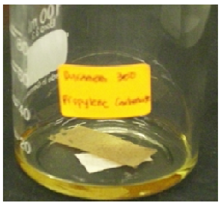
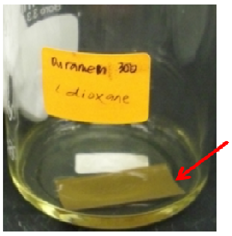
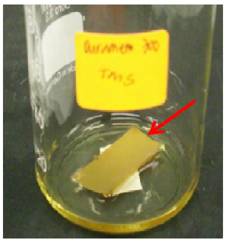
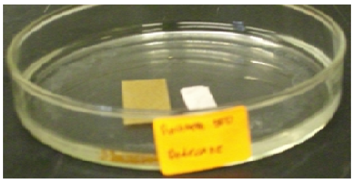
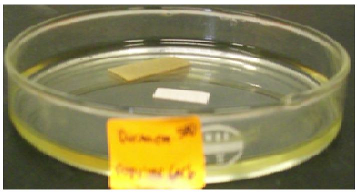
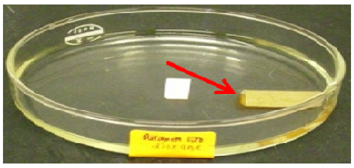
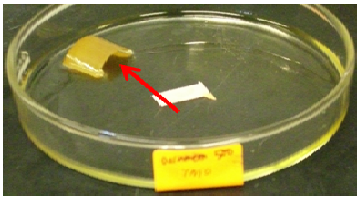
Chemical	Physical Observation		Stability
	After 24		
Dodecane	i)Remain Flat ii)no fiber damage ii)no crack		Stable because not disintegrated
Propylene Carbonat	i)Remain Flat ii)no fiber damage iii)no crack		Stable because not disintegrated
1-4 Dioxane	i)Curled ii)a few fiber are damaged iii)no crack		Stable because not disintegrated
TMS	i)Curled ii)a few fiber are damaged iii)no crack		Stable because not disintegrated

Table 4.3: Physical Observation on Duramem$^{\text{TM}}$ 500

Chemical	Physical Observation		
	After 24 hours		Stability
Dodecane	i)Remain Flat ii) a few fiber are damaged iii) do not crack		Stable because not disintegrated
Propylene Carbonat	i)Remain Flat ii)a few fiber are damaged iii)do not crack		Stable because not disintegrated
1-4 Dioxane	i)Curled ii)a few fiber are damaged iii)no crack		Stable because not disintegrated
TMS	i)Curled ii)a few fiber are damaged iii)no crack		Stable because not disintegrated

From table 4.1, 4.2 and 4.3, all membranes in respective solvent is not disintegrated. This shows that all membranes are stable. However, the stability of the membrane is not guide whether or not the solvent will pass through the membrane [35].

Then, the experiment will continue with the flux study to prove the stability of the membrane in the respective solvent.

4.2 Permeability test

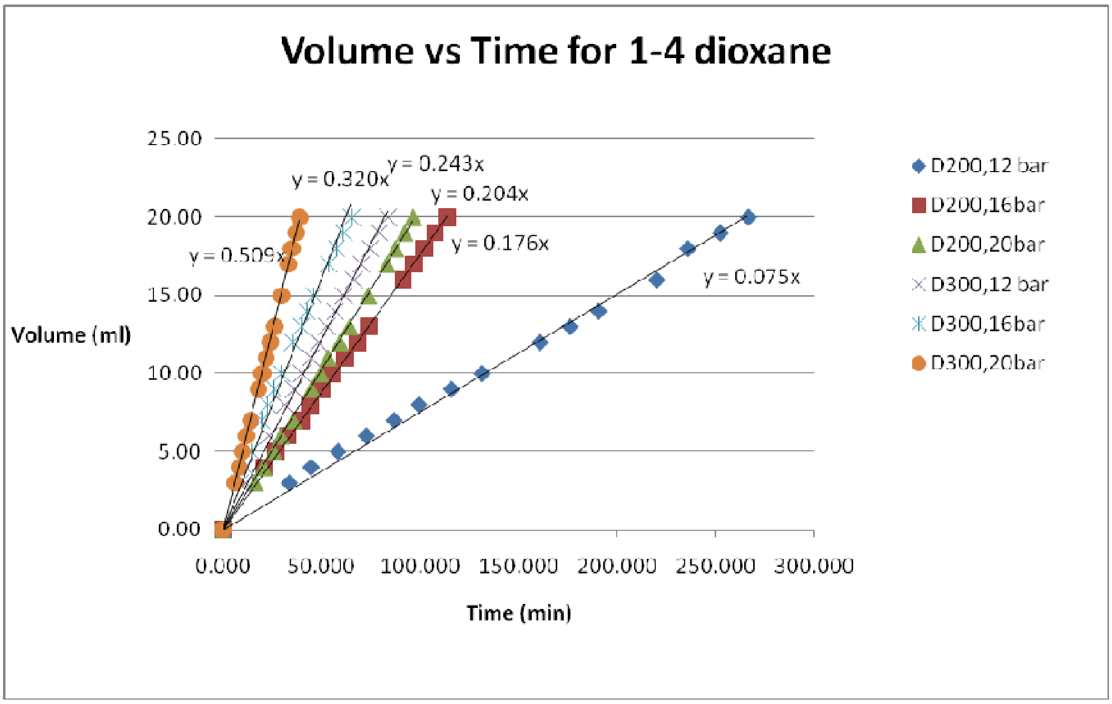


Figure 4.1: Volume of 1-4 dioxane collected versus time requires using Duramem^{TM} 200 and Duramem^{TM} 300 by varying operating pressure.

Figure 4.1 shows the volume of 1-4 dioxane collected versus time required across Duramem^{TM} 200 and 300 membranes. Based on the figure above, as volume collected increase, the time taken also increased. This shows that volume of 1-4 dioxane is linear with the time. Besides that, as operating pressure increase, the time required to collect the 1-4 dioxane become shorter. From above, by using Duramem^{TM} 300 at pressure 20 bars would give the shorter time. The increasing operating pressure will increase driving force inside the MET Cell, thus result in higher flow.

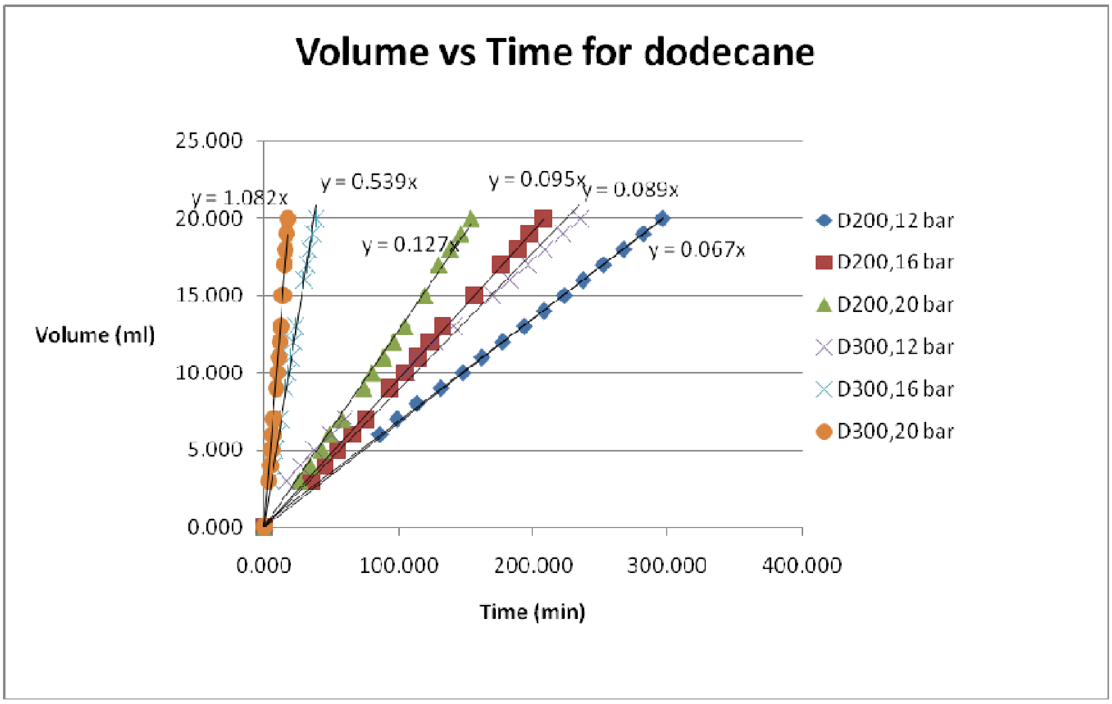


Figure 4.2: Volume of dodecane collected versus time requires using Duramem 200 and Duramem^{TM} 300 by varying operating pressure.

Figure 4.2 shows the volume of dodecane collected versus time required across Duramem^{TM} 200 and 300 membranes. Based on the figure above, as volume collected increase, the time taken also increased. This shows that volume of dodecane is linear with the time. Besides that, as operating pressure increase, the time required to collect the dodecane become shorter. By using Duramem^{TM} 300 at pressure 20 bars would give the shorter time. When operating pressure is increase, the driving force inside the MET Cell also increase, thus result in higher flow.

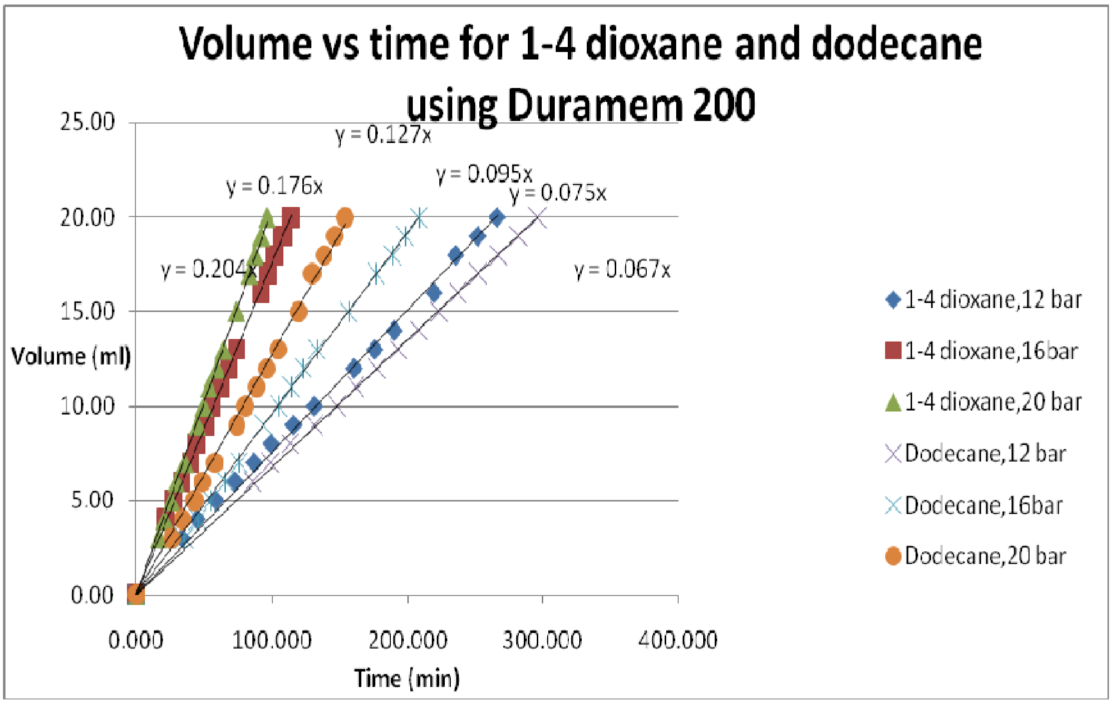


Figure 4.3: Volume of 1-4 dioxane and dodecane collected versus time require using Duramem^{TM} 200 by varying operating pressure.

Figure 4.3 shows the volume of dodecane and 1-4 dioxane collected versus time required across Duramem^{TM} 200 membrane. Based on the figure above, as volume collected increase, the time taken also increased. This shows that volume of 1-4 dioxane and dodecane is linear with the time. By using Duramem^{TM} 200, 1-4 dioxane at pressure 20 bars would give the shorter time.

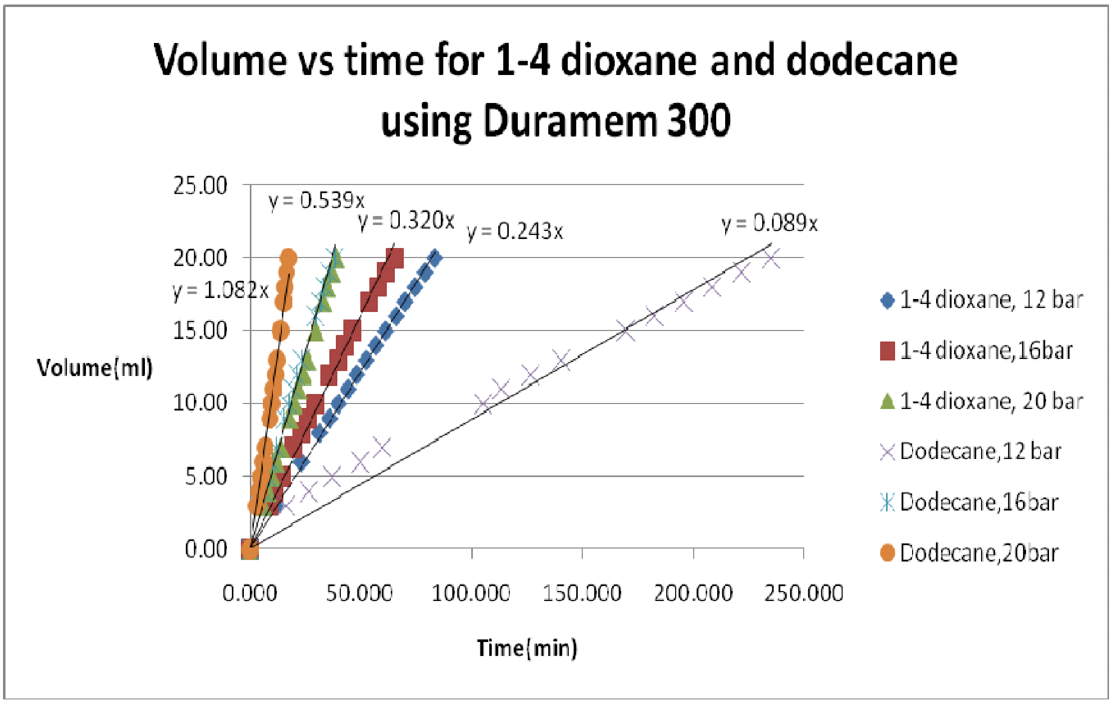


Figure 4.4: Volume of 1-4 dioxane and dodecane collected versus time require using Duramem^{TM} 300 by varying operating pressure.

Figure 4.4 shows the volume of dodecane and 1-4 dioxane collected versus time required across Duramem^{TM} 300 membrane. Based on the figure above, as volume collected increase, the time taken also increased. This shows that volume of 1-4 dioxane and dodecane is linear with the time. By using Duramem^{TM} 300, dodecane at pressure 20 bars would give the shorter time.

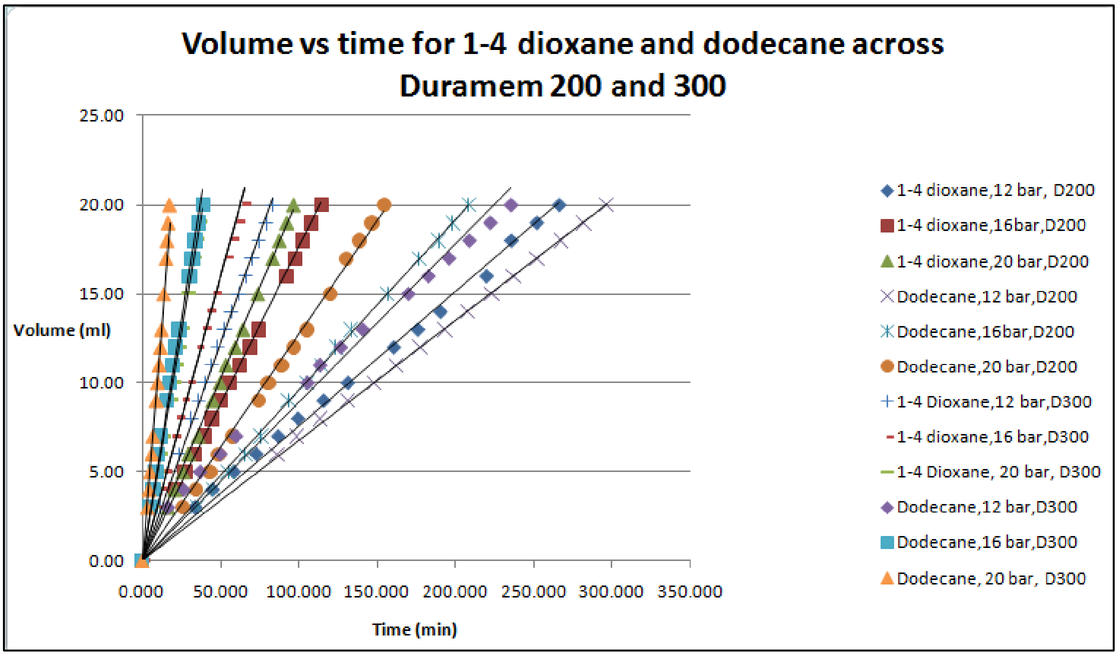


Figure 4.5: Volume of 1-4 dioxane and dodecane collected versus time require using Duramem^{TM} 200 and 300 by varying operating pressure.

Figure 4.5 shows the volume of dodecane and 1-4 dioxane collected versus time required across Duramem^{TM} 200 and 300 membranes. Based on the figure above, as volume collected increase, the time taken also increased. This shows that volume of 1-4 dioxane and dodecane is linear with the time. By using Duramem^{TM} 300, dodecane at pressure 20 bars would give the shorter time.

Table 4.4: Solvent flux data for 1-4 dioxane and dodecane

Membrane	Pure solvent	Pressure (bars)	Solvent flux,($lm^{-2}h^{-1}$)
D200	1-4 Dioxane	12	0.833
		16	1.956
		20	2.267
D200	Dodecane	12	0.744
		16	1.056
		20	1.411
D300	1-4 Dioxane	12	2.700
		16	3.556
		20	5.656
D300	Dodecane	12	0.989
		16	5.989
		20	12.022

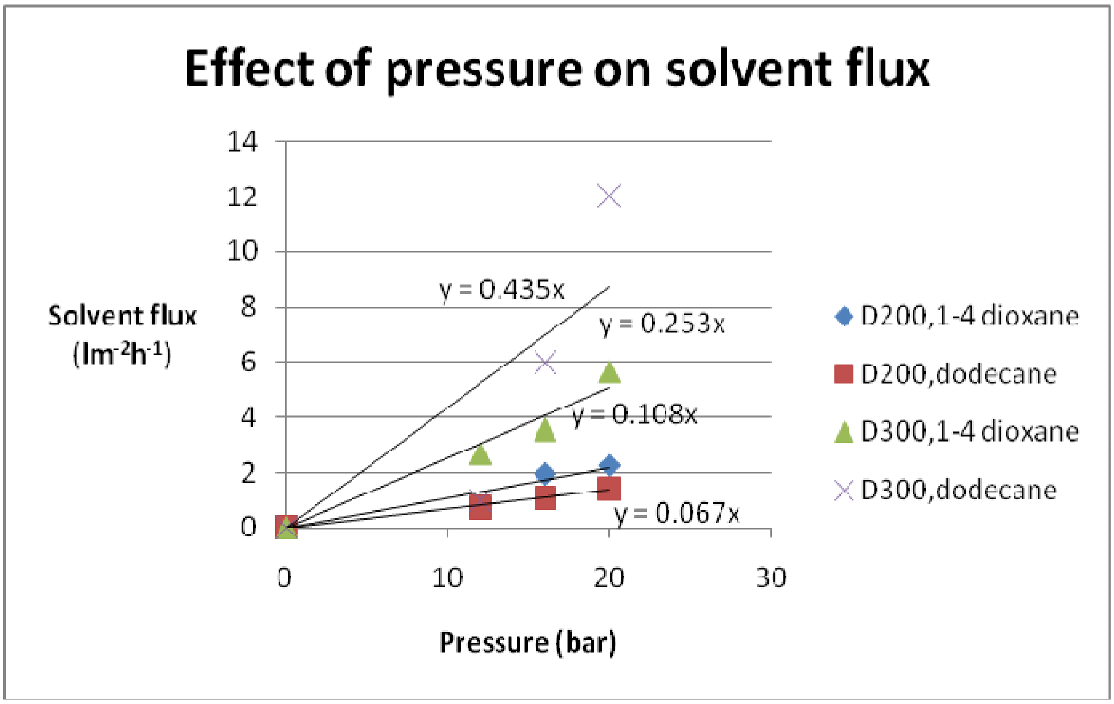


Figure 4.6: Solvent flux of 1-4 dioxane and dodecane versus operating pressure across the Duramem^{TM} 200 and Duramem^{TM} 300 membrane

Figure 4.6 shows that solvent flux of 1-4 dioxane and dodecane versus operating pressure across the Duramem^{TM} 200 and Duramem^{TM} 300 membrane. This figure shows that the solvent flux is almost proportional with pressure. As we increase the pressure, the solvent flux is also increased. By increase the pressure, the driving force inside the MET Cell also increase.

Based on figure 4.6, higher solvent flux of both dodecane and 1-4 dioxane are gained when using Duramem^{TM} 300 compared to Duramem^{TM} 200 . This shows that both solvent work well in Duramem^{TM} 300 compared to Duramem^{TM} 200. The difference of Duramem^{TM} 300 and Duramem^{TM} 200 is molecular weight cut off (MWCO). Thus, the MWCO also affect the solvent flux. Increasing the molecular weight cut off (MWCO) of membrane will increase the value of flux and take shorter time to permeate. Thus, the solvent will be more stable in the higher MWCO.

Comparing 1-4 dioxane and dodecane, it shows that dodecane exhibits higher flux in Duramem^{TM} 300 which is 12.022 lm^{-2} h^{-1}. The properties of chemicals also give effect on the solvent flux. This is due to non polar solvent. According to Machado *et.al* [27], the flux was found to be strongly dependent on the type of solvent. The non polar solvent shows higher permeability than polar solvent.

4.3 Catalyst rejection experiment

4.3.1 Effect of pressure on solvent flux using catalyst solution

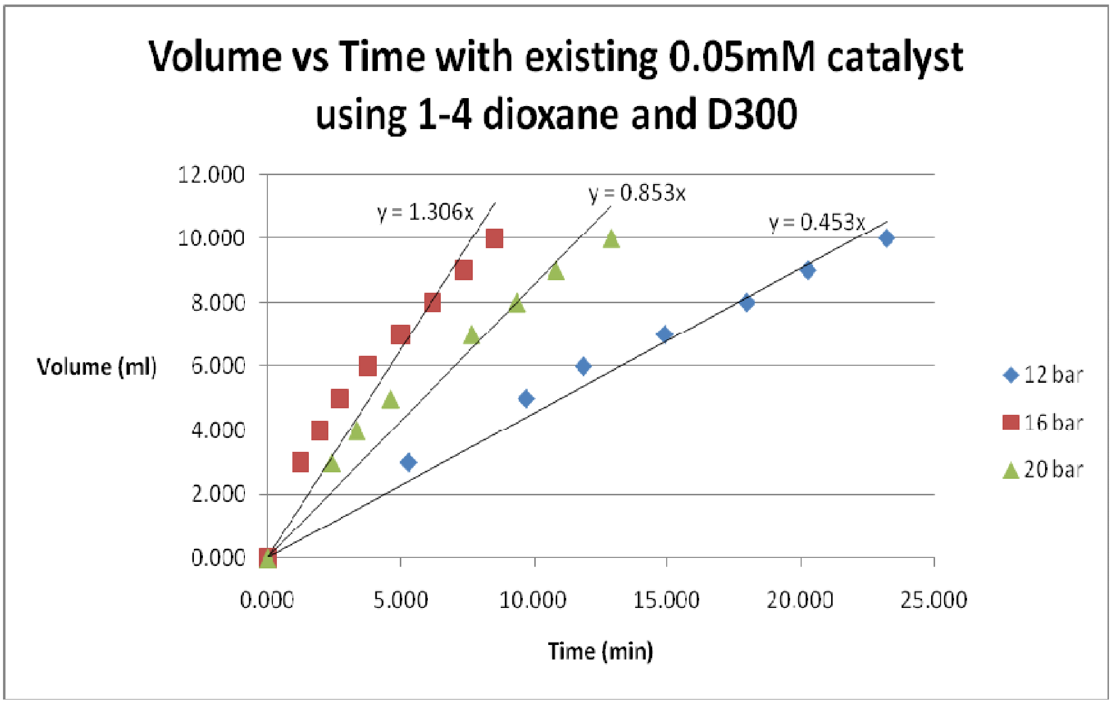


Figure 4.7: Volume of 1-4 dioxane with existing of catalyst collected versus time require using Duramem^{TM}300 membrane with initial catalyst concentration of 0.05mM by varying operating pressure .

Figure 4.7 shows the volume 1-4 dioxane with existing catalyst collected versus time required across Duramem^{TM} 300 membrane. Based on the figure above, as volume collected increase, the time taken also increased. Besides that, as increase in pressure, the time is shorter. However, this is not applicable at pressure 16 and 20 bars. This is may be due to the condition of membrane. Membrane is used repeatedly during the experiment is carried out at 20 bars; however it is used for the first time for 16 bars.

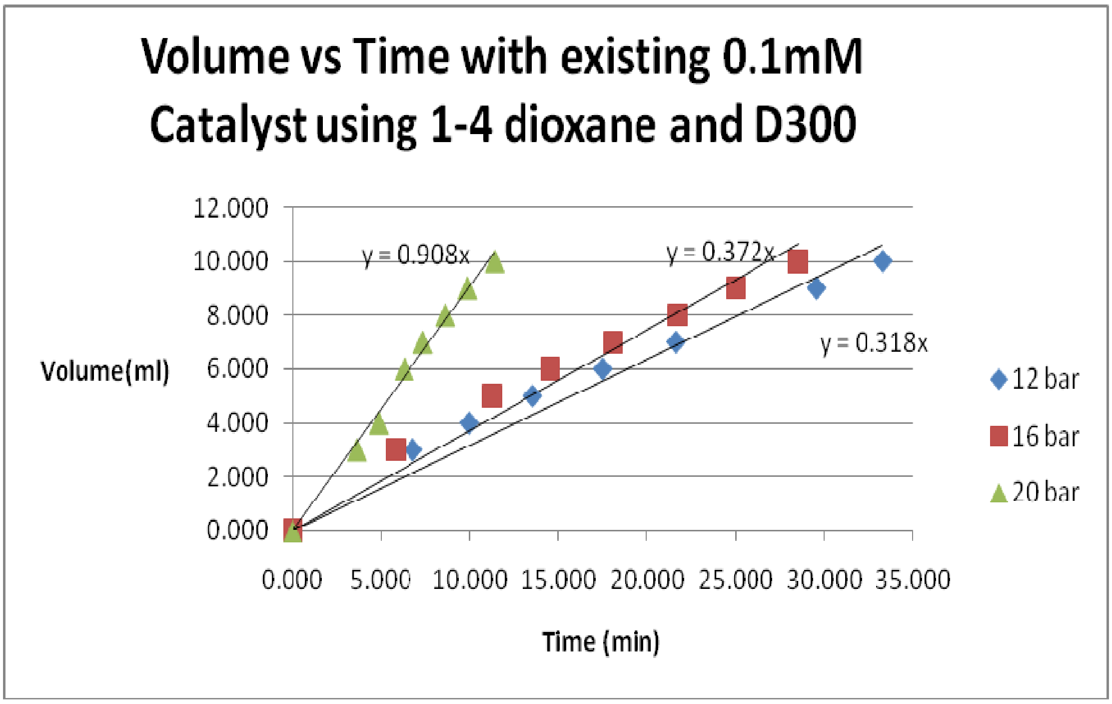


Figure 4.8: Volume of 1-4 dioxane with existing of catalyst collected versus time require using Duramem^{TM}300 membrane with initial catalyst concentration of 0.1 mM by varying operating pressure.

Figure 4.8 shows the volume 1-4 dioxane with existing catalyst collected versus time required across Duramem^{TM} 300 membrane. Based on the figure above, as volume collected increase, the time taken also increased. Besides that, as increase in pressure, the time is shorter.

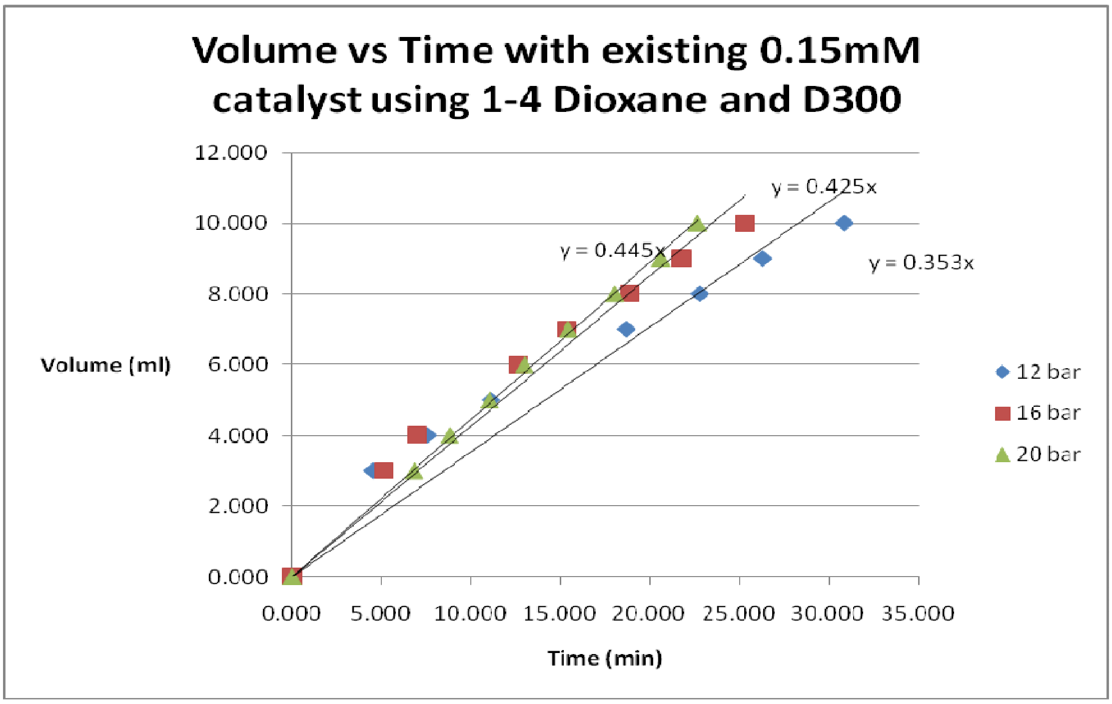


Figure 4.9 : Volume of 1-4 dioxane with existing of catalyst collected versus time require using Duramem ^{TM}300 membrane with initial catalyst concentration of 0.15 mM by varying operating pressure.

Figure 4.9 shows the volume 1-4 dioxane with existing catalyst collected versus time required across Duramem^{TM} 300 membrane. Based on the figure above, as volume collected increase, the time taken also increased. Besides that, as increase in pressure, the time is shorter.

Table 4.5: Solvent flux data with existing of catalyst

Membrane	Solvent	Concentration (mM)	Pressure (bars)	Solvent flux,J_s ($lm^{-2}h^{-1}$)
Duramem 300	1-4 dioxane	0.05	12	5.033
			16	14.511
			20	9.478
		0.1	12	3.533
			16	4.133
			20	10.089
		0.15	12	3.922
			16	4.722
			20	4.944

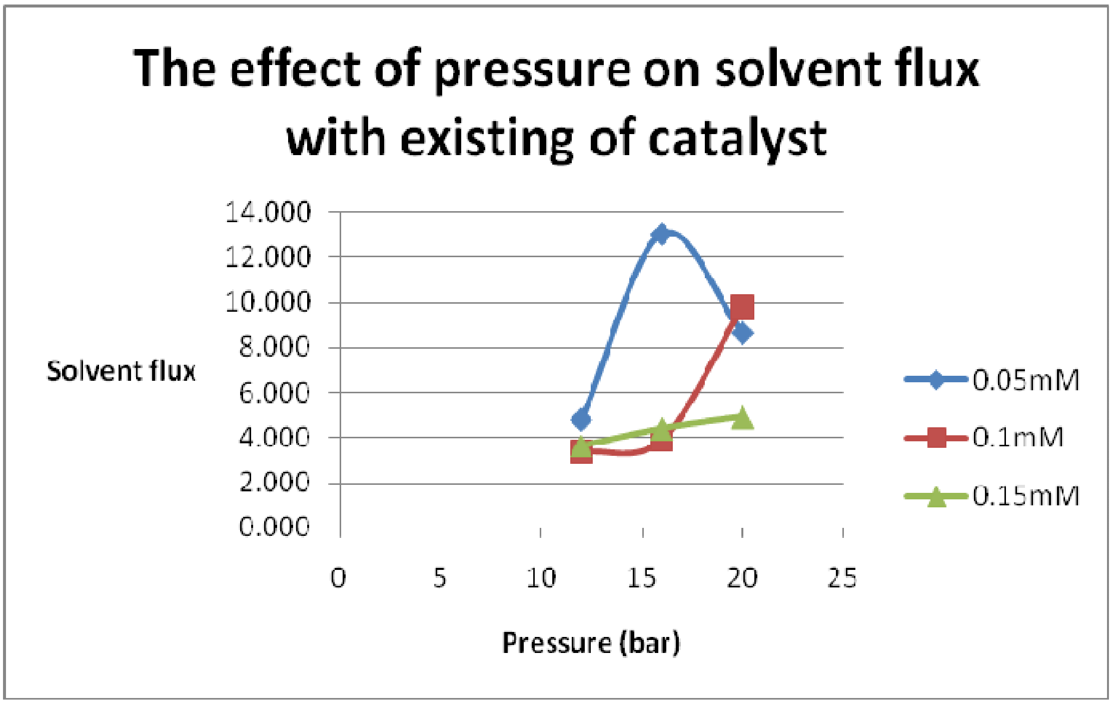


Figure 5.0: Solvent flux of 1-4 dioxane with existing of catalyst versus operating pressure across Duramem ^{TM}300 membrane.

Figure 5.0 shows solvent flux versus pressure across Duramem^{TM} 300 membrane. Based on the figure above, as pressure increase, solvent flux also increases. As pressure increase, the driving force inside the MET Cell also increases. This would lead to increasing of solvent flux. The fact that an increase in pressure results in increase of solvent flux is consistent with the result J.T.Scarpello *et al* [35].

4.3.2 Effect of catalyst concentration on solvent flux

Figure 5.0 shows solvent flux versus pressure across Duramem^{TM} 300 membrane. From the figure, it shows that as increasing in concentration of catalyst solution, the solvent flux is decreased.

The dependency of flux on catalyst concentration observed during this study is consistent with the earlier published data [30].

The decreasing of solvent flux may be due to the increase of concentration polarization effect. Concentration polarization creates a layer near the membrane that exerts a resistance towards the mass transfer. In addition, the pore fouling also would explain the decreasing of the solvent flux. The membrane does not perform 100% due to these two factors.

4.3.3 Effect of catalyst concentration on catalyst rejection

After getting data by using Uv Vis, the rejection is calculated and presented below:

Table 4.6: Rejection data

Catalyst concentration (mM)	Pressure (bar)	Final catalyst concentration in permeate,C_p(mM)	Final catalyst concentration in retentate,C_r(mM)	Rejection,r (%)
0.05	12	0.552	0.552	0
	16	0.552	0.552	0
	20	0.552	0.552	0
0.1	12	0.313	0.428	26.87
	16	0.282	0.428	34.11
	20	0.180	0.428	57.94
0.15	12	0.467	0.552	15.40
	16	0.232	0.428	45.79
	20	0.191	0.467	59.10

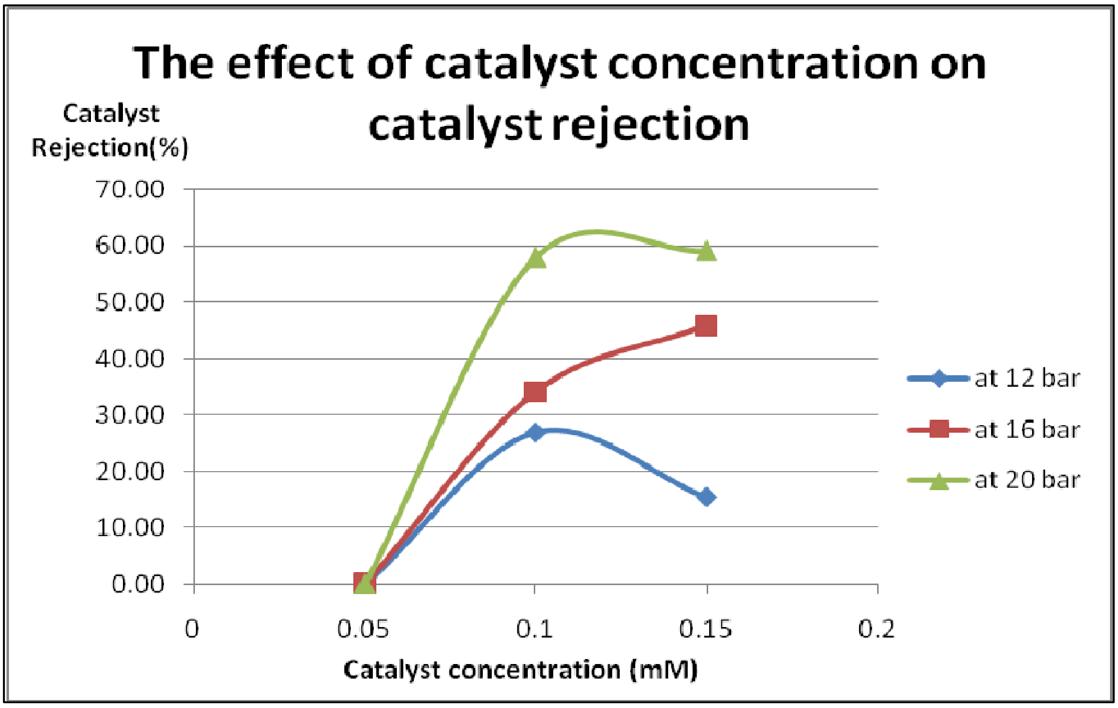


Figure 5.1: Percentage of catalyst rejection versus catalyst concentration using Duramem 300 membrane by varying pressure.

Figure 5.1 shows the percentage of catalyst rejection versus catalyst concentration across Duramem^{TM} 300 membrane. From the figure, it shows that as catalyst concentration increase, the rejection also increase too. This observation is consistent with previous published data [35]. Increasing C_o from 0.05mM to 0.15 mM improved catalyst separation from 0% to 45.79% at 16 bars and from 0% to 59.1% at 20 bars. However, at 12 bars, the separation is increased from 0% to 26.87%, however decrease later to 15.4 %. This is due to less membrane effectiveness during conducting the experiment at 12 bars with concentration 0.15 mM.

4.3.4 Effect of pressure on catalyst rejection

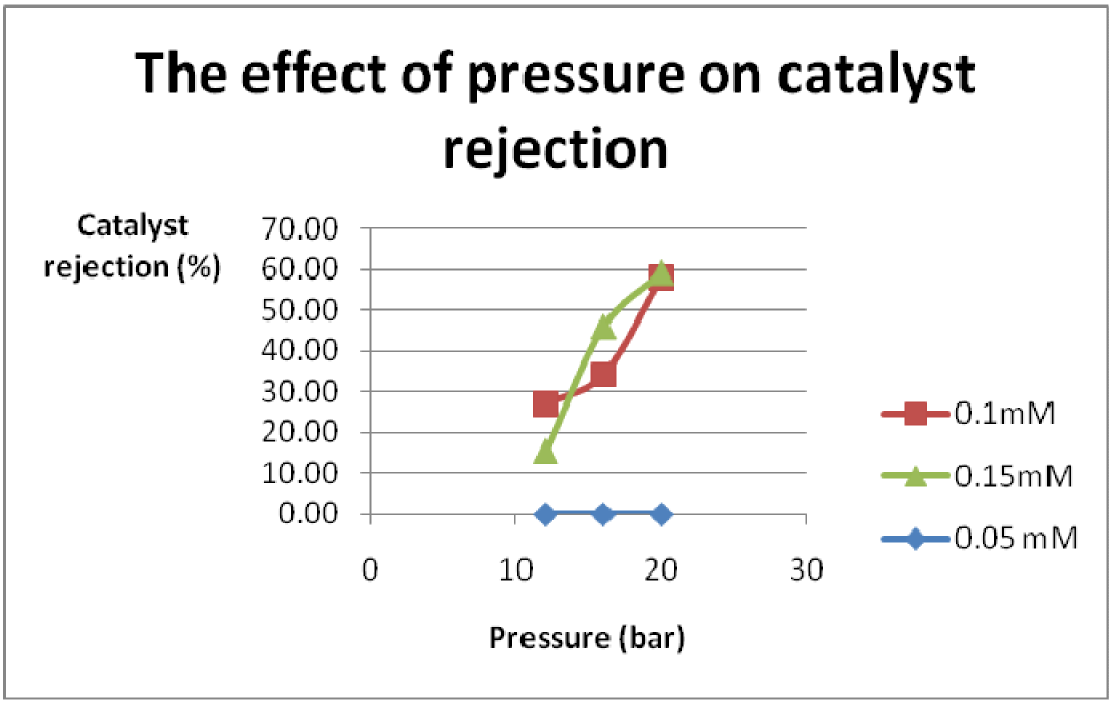


Figure 5.2: Percentage of catalyst rejection versus operating pressure using Duramem 300 membrane by varying catalyst concentration.

Figure 5.2 shows the percentage of catalyst rejection versus pressure across Duramem^{TM} 300 membrane. From the figure, increasing pressure was found beneficial in the catalyst rejection. As pressure increase, rejection is increased too. The increasing of driving force inside the MET Cell leads to the increase of rejection. From the table 4.5, the rejection increase from 15.4 % to 59.1%.The fact of increase in pressure results in increased rejection is consistent with the result of Whu *et al.* [15] for the SRNF of dyes from methanol. They suggested that this observation is due to partially reversible, increasing compression of the active layer when the membrane is subjected to increasingly higher pressures, resulting in a tightening or sealing of the pores. As a consequent, better catalyst separation occurs. However, small concentration of catalyst would not affect the rejection whether conducting in small or high pressure.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The membrane-solvent combination tested in this study was examined via physical stability and solvent flux study. The physical stability does not guarantee that the membrane is stable with the respective solvent. Thus, it is important to determine the solvent flux in order to ensure the membrane can work with the solvent. The non polar solvent shows higher permeability. From the experiment, dodecane was non polar solvent and has high solvent flux across Duramem^{TM} 300 which was 12.022 lm^{-2} h^{-1} at 20 bars. The molecular weight cut off (MWCO) also affected the value of solvent flux gains. From the result, solvent flux across Duramem^{TM}300 was higher compared by using Duramem^{TM}200.Thus, the higher MWCO, and the higher solvent flux was gained.

Apart from that, the solvent flux was examined had affected by variations in parameters which are pressure and catalyst concentration. Based on the experiment conducted, increasing pressure will increase the solvent flux. This was due to increase of driving force exerted in the MET Cell. However, increasing catalyst concentration had resulted in the decreasing of solvent flux. This was due to concentration polarization effect.

Next, the catalyst rejection was shown to be affected by factor of pressure and catalyst rejection. By increasing pressure, the catalyst rejection also increases. Increasing catalyst concentration also will increase the catalyst rejection. The rejection of Rh catalyst at operating pressure 20 bars and at 0.15mM was increased from 15.4 % to 59.1%. In general, both parameters used were beneficial in getting higher rejection.

These results establish the potential of recovery of Rh catalyst for hydroformylation process by varying operating pressure and catalyst concentration by using membrane process.

5.2 Recommendations

For further research, the study of the effect of temperature also would be good in order to have the best parameter in getting the maximum catalyst rejection.

In order to expand the research, the experiment should involve variety type of membrane as well as variety type of chemical groups can be used. Besides that, the use of different catalyst also would expand the research.

Besides that, the experiment also can be conducted using cross flow nanofiltration.

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