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Methane Purification Using PVC Membrane: Preparation, Characterization and Performance Study

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ABSTRACT : *Methane (CH4) gas stands as one of the most prevalent gaseous in the air. Global methane emissions from landfill are estimated to be between 30 and 70 million tonnes each year. Methane originating from landfill is vastly found in developed and populated countries, where the levels of waste tend to be the highest. A study was done at Kampung Sg. Ikan Landfill in Kuala Terengganu, Malaysia. In this study, wastes were segregated according to specific types of wastes, such as 3D plastics (bottles), 2D plastic (food wrappers), glasses, food wastes and so on. From this study, it is found that food waste contributes the highest collection of waste for the past three weeks of segregation activities in the landfill. The data and studies from the landfill motivated a method was needed to separate gas from wastes using a cheap and effective polymer and hence, usage of PVC was used to separate CH4 gas from the CO2/CH4 mixture. The PVC membrane is produced by the combination of Polyvinyl Chloride (PVC) and N-Methyl-2-pyrrolidone, (NMP) via dry/wet phase inversion technique. The production of PVC membrane is expected to improve the characteristics of the polymeric membrane, such as the permeability, selectivity and the pore size. PVC is introduced with ratio of NMP (solvent): PVC, 82:18, 80:20, 77:23, and 75:25. This ratio enables the desired selectivity and permeability of CO2/CH4 gas separation. The PVC membrane with composition 77:23 was the highest performance in terms of selectivity at 2 bars. The SEM images of the surface morphology were included with the pore diameter ranging from 9.87μm to 28.7μm.*

KEYWORDS: *Landfill; Methane; Permeability; Selectivity; Gas Separation*

I. INTRODUCTION

Annually, global methane emissions from landfill are estimated to be between 30 and 70 million tons. Most of this landfill methane currently comes from developed countries, where the levels of waste tend to be highest (GreenHouse Gas Online, 2002). A study was done at Kampung Sg. Ikan Landfill in Kuala Terengganu, Malaysia. Wastes from the city of Kuala Terengganu was collected, segregated into several categories within three weeks duration time as tabulated in Table 1.

Table 1: Waste collection data from Kg. Sg. Ikan landfill for three weeks

Categories/Week	1	2	3	Total
Total waste (kg)	11010.00	13500.00	7040.00	31550.00
Waste weighed (kg)	9926.95	12453.20	7007.90	29388.05
Waste weighed (%)	90.16	92.25	99.54	93.15
Plastic 3D (kg)	362.59	480.00	274.30	1116.89
Plastic 2D (kg)	869.10	1164.50	665.30	2698.90
Metal (kg)	7.96	33.70	33.20	74.86
Aluminum can (kg)	100.61	195.90	107.30	403.81
Paper (kg)	843.60	878.40	741.30	2463.30
Pampers (kg)	873.35	1631.00	889.40	3393.75
Glass (kg)	200.72	235.70	142.10	578.52
Wood/Landscape (kg)	1099.51	2179.20	1802.30	5081.01
Polystrene (kg)	118.90	219.70	81.10	419.70
Bed (kg)	9.48	0.00	10.00	19.48
Textile (kg)	108.94	289.50	146.40	544.84
Food waste (kg)	**4542.91**	**5227.60**	**2107.60**	**11878.11**
Others (kg)	1063.62	1046.80	66.50	2176.92

Dry/wet phase inversion method is introduced for membrane preparation, where the casting a wet film of polymer solution onto a porous non-woven polymeric support. The method to prepare the PVC based polymer was intensely reviewed by Ismail et al. [1]. Polymer solution concentrates on the top layer and then separates and solidifies throughout the film into two phases, one of which is a porous film with a denser, integrally skinned top layer. The progression of the precipitation process through the wet film increases the viscosity of the polymer-rich phase due to additional solvent depletion [2]. Flat sheet membrane configuration is introduced. It comprises of a selective membrane on top and a flat plate at the bottom, between which a net-like material is placed to provide space for the permeate removal, and on the other side of the flat plate, another sheet membrane and another net-like material are placed in mirror to form a sandwich-like module [3]. SEM and FTIR were used for examine the membrane morphology and was also used for chemical characterization of the membrane [2, 4] respectively.

II. EXPERIMENTAL

Materials and methods : The method is similar with the provided by Zhang [5].PVC powder and NMP solution is mixed to produce a homogenous dope solution. PVC will be stirred and dissolved in the solvent, according to the ratio of PVC and NMP mixed in the solution. For the membrane casting and dry/wet phase inversion method, a glass plate or a polyester nonwoven fabric was used to coat the degassed dope solution at room temperature at a knife gap of 0.3mm. After 30s of exposure in air, the cast film would be immediately immersed into a coagulation bath. The precipitated membrane will be taken out of the coagulation bath and rinsed with running water to remove the residual solvent. The product membrane from the coagulation bath will be dried at room temperature and thus, achieving a dry flat-sheet porous membrane.

Chemical and Physical characterization : Fourier Transform Infrared Spectroscopy, FTIR and a Scanning Electron Microscopy, SEM is used for the characterization of the PVC membrane. SEM device is to examine the membrane morphology [6]. The sample was fractured in liquid nitrogen and then inserted into the SEM device for cross sectional view of membrane. The size of pores on SEM micrograph that is scanned by a computer is calculated using the Sigma scan software. The FTIR was used for chemical characterization of the membrane [7]. It used to determine to functional group of PVC by locating the precise wavelength on the graph.

CO_2/CH_4 Separation Test : Gas permeation test is the method used for this separation test [8]. It is also to further understand the membrane involvement for both types of gases without being ruptured. Two gases are used for the gas permeation test, which are Methane, CH_4 and Carbon dioxide, CO_2 at a flow of 2 bars and it is measured by the bubble flow meter. The separation test for Methane, CH_4 and Carbon dioxide, CO_2, data were used to examine whether the created membrane has the ability to separate the two gases and differentiate the performances between membranes using different types of gases. Equation 1 is used to calculate permeance (GPU), while Equation 2 for selectivity using membranes and gases types as comparison. Both equations can be used to represent and show the ability to separate 2 gases (A and B), where in this case Methane, CH_4 and Carbon dioxide, CO_2[9].

$$\frac{P}{l} = \frac{(1X10\wedge6)Q}{(A\Delta P)} \qquad \text{Equation 1}$$

Where P/l is permeance (cm³/s. cm².cm Hg), α is selectivity, and P is permeability, where l is the membrane skin layer thickness (cm), Q is measured volumetric flow rate (cm³/s), A is Effective membrane area (cm²), ΔP is pressure differences across the membrane (cm Hg). Equation 2 is the selectivity of membrane to separate two gases.

$$\alpha = P2/P1 \qquad \text{Equation 2}$$

III. RESULT AND DISCUSSION

Characterization of the PVC Membrane : Fourier Transform Infrared spectroscopy (FTIR), is an important analysis as it provides the support data for the result obtain in this project. FTIR will demonstrate the bands that show the functional group of the membranes and provide information about the molecular interaction between the components contain inside the polymer solution. The significant peaks formed indicated the molecular orientation of the molecules.

After carrying our tests using the PVC membrane samples, data were collected from the FTIR spectroscopy usage. Figure 1 shows the results from FTIR using PVC membrane of different compositions.

Figure 1: FTIR using PVC membrane

Figure 2 shows the surface morphology of the cross section of the PVC membrane analyzed by SEM at 200X magnification. Figure 2a is the same membrane sample prepared with 18% PVC 82% NMP added has clearly showed that there is a different surface morphology compared to the others. The surface with finger-like structure and consistent pore diameter across the membrane can be clearly seen from this composition in Figure 4-3a. The structure is in agreement with the other study when using PVC[10]. Other three membranes were mixed in combination of 20% PVC 80% NMP (Figure 2b), 23% PVC 77% NMP (Figure 2c), and 25% PVC 75% NMP (Figure 2d). The surface morphology of these three membranes has also its significant changes among each other. Inconsistency in pore shape and also in diameter can be seen throughout Figure 2a, b, c, and d images of SEM.

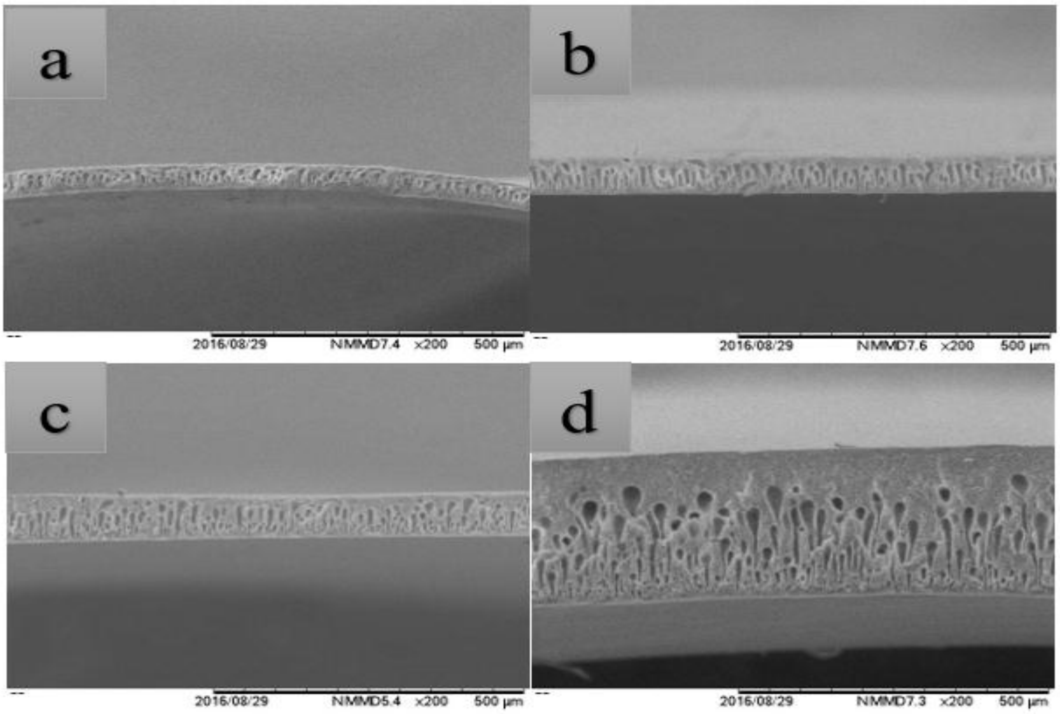

Figure 2: 200X Magnification of PVC Membrane Cross Sectional View, (a) 18:82, (b) 20:80, (c) 23:77, (d) 25:75

Membrane Performance : To the date, gas permeation is preferable to separate one gas from the gas mixture [3, 11–13].Table 1 shows the result of single gas permeation using Methane gas, CH_4 which the data has been utilized to calculate the Permeance, P/l and Permeability, P of PVC: NMP membranes which were in composition ratios of 18:82. 20:80, 23:77 and 25:75. On the other hand, Table 2 shows the result of single gas permeation using Carbon dioxide gas, CO_2 which the data has been utilized to calculate the Permeance, P/l and Permeability, P of PVC: NMP membranes which were in composition ratios of 18:82, 20:80, 23:77, and also 25:75 membranes. Both table carried out respective permeation test at a constant pressure of 2 bar (150.01231 cmHg), and at a volume of 50 cm3. After tabulating the permeability for each membrane according to its tested gas respectively, selectivity was calculated. From Table 1 and Table 2, both tables were used to tabulate each membrane PVC: NMP to calculate its respective selectivity which is shown in Table 3. In Table 3, membrane 23:77 shows the highest selectivity that is 5.75 followed by membrane 20:80, 18:82 and 25:75 by 3.35, 2.72, and 2.17.

Table 1: The Performance of the PVC Membrane Using Methane, CH_4

NMP (wt%)	PVC (wt%)	Time (s)						Average Time,	Volumetric Flow Rate,	Permeance,	Permeability
		1	2	3	4	5	6	t_{av} (s)	Q (cm^3/s)	P/l (GPU),(1x10^{-06})	P1(Barrer),(1x10^{-10})
82	18	211.43	292.55	281.90	260.61	308.26	302.88	276.27	0.19	6143.57	3004.21
80	20	398.11	378.15	350.23	391.76	388.12	396.50	383.82	0.13	4422.21	3095.54
77	23	772.77	773.21	769.35	778.82	787.23	789.24	778.41	0.06	2180.47	3013.41
75	25	511.43	492.55	581.90	510.61	508.26	502.88	502.29	0.10	3379.13	9731.90

Table 2: The Performance of the PVC Membrane Using Carbon Dioxide, CO_2

NMP (wt%)	PVC (wt%)	Time (s)						Average Time,	Volumetric Flow Rate,	Permeance,	Permeability
		1	2	3	4	5	6	t_{av} (s)	Q (cm^3/s)	P/l(GPU),(1x10^{-06})	P2 (Barrer),(1x10^{-10})
82	18	92.76	105.43	110.46	103.15	97.11	100.21	101.52	0.49	16718.81	8175.49
80	20	113.80	118.12	115.25	115.13	111.20	113.69	114.54	0.44	14819.43	10373.59
77	23	138.79	135.27	134.63	132.24	133.90	136.60	135.24	0.37	12550.39	17344.63
75	25	201.28	246.33	225.22	287.16	231.15	237.65	238.13	0.21	7127.54	20527.31

Table 3: Selectivity and Permeability of CO_2 gas using PVC membrane for Robeson's Upper Bound Comparison

NMP	**PVC**	**Permeability**	**Selectivity, α, (P2/P1)**
(wt %)	**(wt %)**	**P2, CO_2 (Barrer), (1x10^{-10})**	
82	18	8175.49	2.72
80	20	10373.59	3.35
77	23	17344.63	5.75
75	25	20527.31	2.17

From Figure 3, the orange line which indicates CO_2 gas shows higher permeability compared to the blue line which indicates CH_4 gas with lower permeability. For CO_2 shows the highest permeability with PVC composition of 25% in the membrane, followed by 23%, 20% and 18%. For CH_4 gas shows the highest permeability with PVC composition of 25% in the membrane, followed by 20%, 23% and 18%.

From Figure 4, the graph shows the relationship between selectivity versus the composition percentage of PVC membrane where 23% PVC 77% NMP membrane shows the highest selectivity, however, based on Table 2 and Table 3, 23% PVC and 77% NMP membrane showed the low permeability as it is not referred as the highest in terms of permeability. Membrane with a composition of 23% PVC and 77% NMP contains the suitable membrane to separate the CO_2 and CH_4 gas compared to the rest of the membranes as the selectivity of membrane 23% PVC and 77% NMP is 5.75. This result was supported by the fine or small pores diameter of the membrane which are 1.90µm to 1.97µm. The high performance of membrane 23% PVC and 77% NMP can be clearly seen in Figure 4 that shows the selectivity of CO_2 over CH_4 of the membrane.

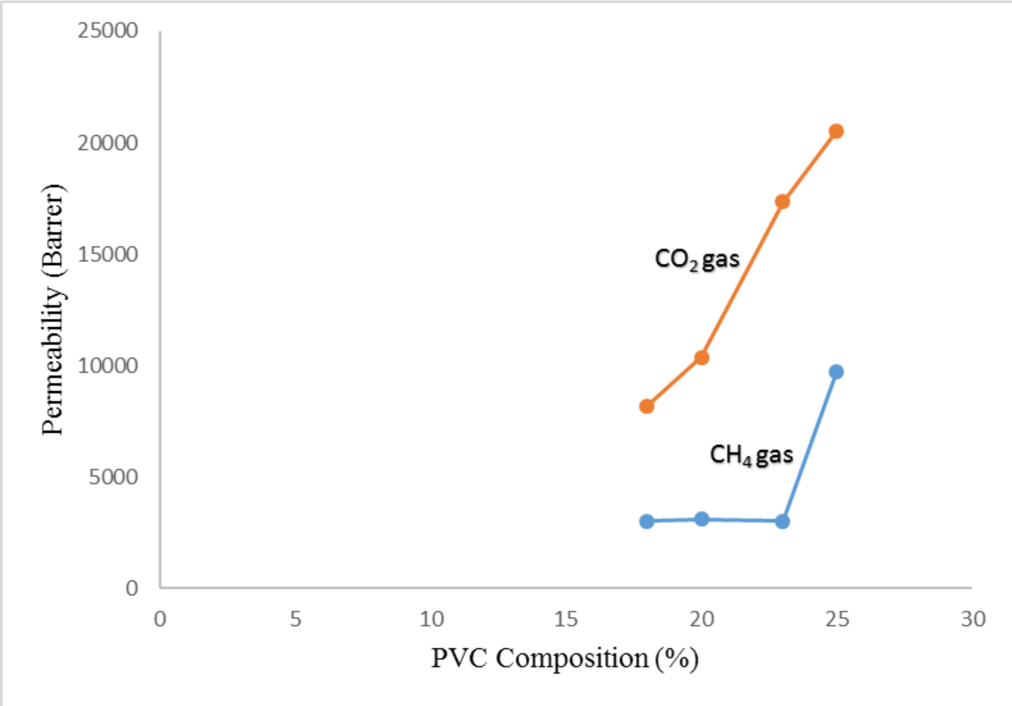

Figure 3: Permeability (Barrer) Vs PVC Composition (%)

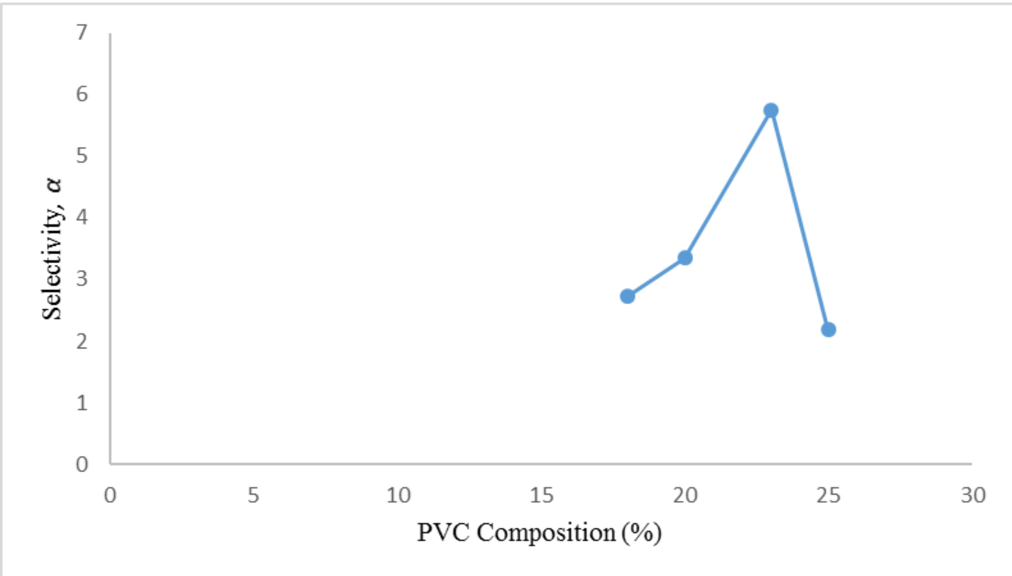

Figure 4: Selectivity, α Vs PVC Composition (%)

As stated above, membrane composed of 23% PVC and 77% NMP shows the highest selectivity. For further studies in depth, Robeson Upper Bound Correlation was used in order to understand further the selectivity of CO_2/CH_4 with Permeability of CO_2 in PVC membrane for comparison with the standard data provided by previous studies [14, 6]. The present upper bound shows the most recent studies from other research involving the selectivity of CO_2/CH_4 of membranes.

Membranes of composition ratio PVC: NMP of 18:82. 20:80, 23:77, and also 25:75 were used in this upper bound correlation. From Figure 5, which is based on L.M Robeson's journal of The Upper Bound Revisited, where his research and reference values were used for comparison with other research in order for better improvement for further future research. Based on Figure 6, membrane 23:77 is close to the prior upper bound line, while membrane 18:82, 20:80 and 25:75 were located at lower selectivity values ranging between selectivity values of 2 to 4. This shows membrane 23:77 can be accepted to be suitable for this research as its reading was considered to be almost equivalent to prior upper bound values.

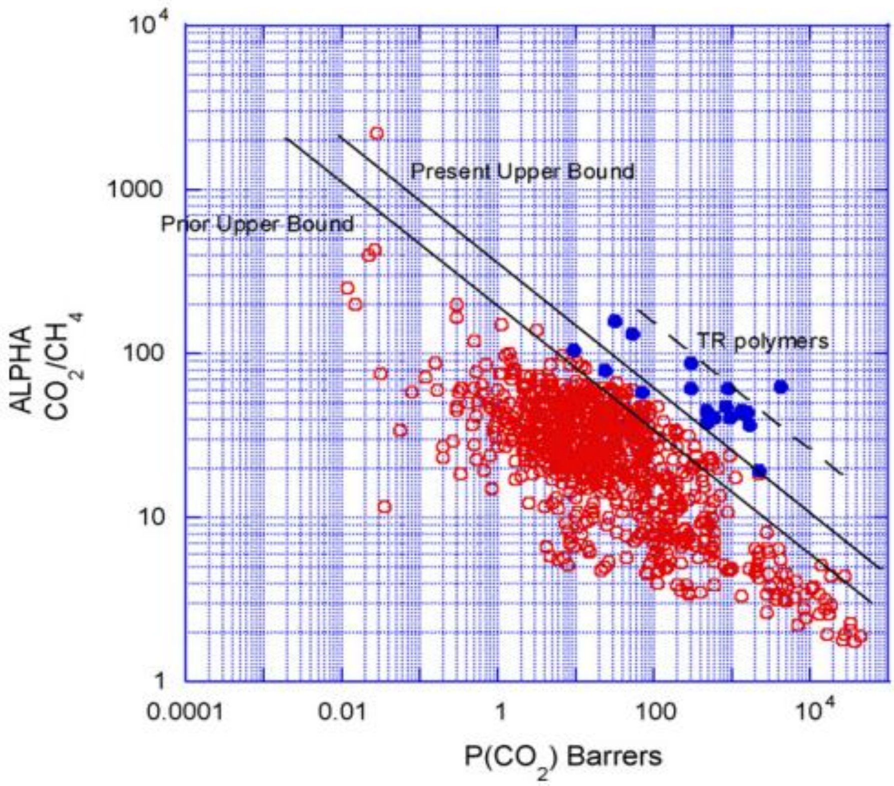

Figure 5: Upper bound correlation for CO_2 /CH_4 separation (L.M. Robeson, 2008)

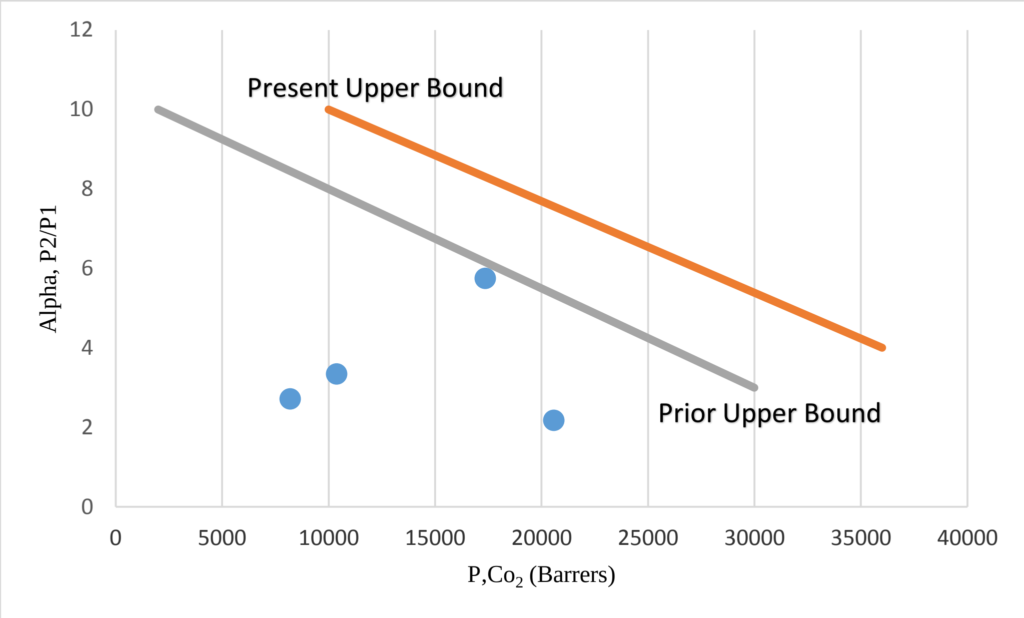

Figure 6: Robeson Upper Bound Correlation

PVC membrane show significant improvement when the concentration percentage was increased to certain amount. From the FTIR result, it was noticeable PVC appearance for all membrane samples are around 1728 cm^{-1}. From the performance view, the PVC membrane with composition PVC: NMP of 23:77 is the most suitable for the ability to separate the two gases. The permeability of the membrane of composition 23:77 has a high permeability of CO_2 and CH_4 were recorded at 17344.63 Barrer and 3013.41 Barrer respectively. Even though the membranes with composition PVC:NMP of 25:75, 20:80, and 18:82 showed higher readings at certain permeability values, composition of 23:77 is the best in terms overall when compared to the selectivity and also the Robeson's Upper Bound Correlation (Figure 5 and Figure 6). The selectivity of CO_2/CH_4, α for membrane 23:77 was the highest which is 5.75. All values of selectivity for each membrane were compared with the Robertson Upper Bound Correlation (Figure 5 and Figure 6). Membrane 23:77 was the closest to the prior upper bound line in the Robertson Upper Bound Correlation. These high-performance membrane samples were proved by the SEM image of the surface morphology itself. The pore diameter ranged from 1.90μm to 1.97μm. Even though membrane 23:77 is still below the Robeson's prior upper bound plot, there is still a bigger role in the future for improvement in terms of polymer concentration and solvent-nonsolvent pair so that a better flat sheet membrane can be produced as discussed in the literatures [6, 15].

IV. CONCLUSION

A conclusion section must be included and should indicate clearly the advantages, limitations, and possible applications of the paper. Although a conclusion may review the main points of the paper, do not replicate the abstract as the conclusion. A conclusion might elaborate on the importance of the work or suggest applications and extensions.

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