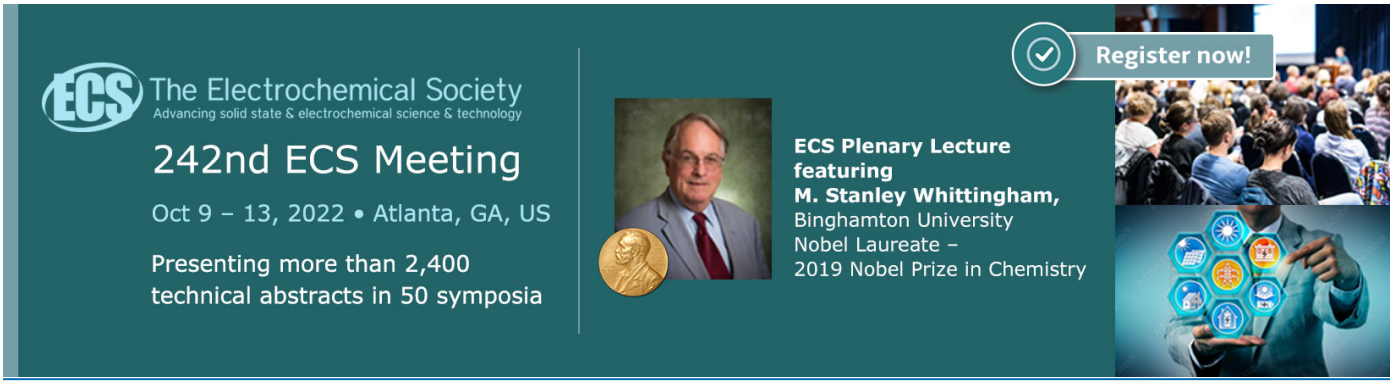
Preliminary Fractional Factorial Design (FFD) study using incorporation of Graphene Oxide in PVC in mixed matrix membrane to enhance CO_2/CH_4 separation



IOP Conf. Series: Materials Science and Engineering **702** (2019) 012041 doi:10.1088/1757-899X/702/1/012041

Preliminary Fractional Factorial Design (FFD) study using incorporation of Graphene Oxide in PVC in mixed matrix membrane to enhance CO_2/CH_4 separation

K R Raj, A R Sunarti*

Faculty of Chemical and Process Engineering Technology, College of Engineering Technology Universiti Malaysia Pahang, 26300 Kuantan, Pahang, Malaysia.

*E-mail: sunarti@ump.edu.my

Abstract. Mixed matrix membranes (MMMs) comprising of where polyvinyl chloride (PVC) and graphene oxide (GO) were employed in the membrane fabrication in order to improve the membrane characteristics. In this study of gas separation using mixed matrix membrane, gases such as CO_2 and CH_4 were used. The objectives of this research were to synthesize and develop MMMs PVC/GO, and also to carry out screening to determine best factors condition for membrane to function at high selectivity. The development of MMMs PVC/GO was based on 5 factors. Based on the screening tests, the run which was made up of factors PVC 20%, GO 4%, 1 bar of pressure during gas permeation, NMP solvent, and immersion time of 300s, shows to have the highest selectivity at 26.09 which was above the upper bound lines in the Robeson's Upper bound plot. Fractional Factorial Design (FFD) was applied to study the minimalization of influenced factors during MMMs preparation. Based on the FFD run, the R-squared (R^2) was 1.00. Factors that had less impact on the maximum selectivity were the time membrane immersed in water bath (s), and also gas pressure during gas permeation test.

1. Introduction

Polymer membranes are used commercially to separate air, to remove carbon dioxide from natural gas, and to remove hydrogen from mixtures with nitrogen or hydrocarbons in petrochemical processing applications. The fundamental parameters characterizing membrane separation performance are the Permeability, P, and the selectivity, $\alpha_{A/B}$. Gas selectivity is the ratio of permeability of two gases (P_A/P_B), where P_A is the permeability of the more permeable gas and P_B is the permeability of the less permeable gas in the binary gas pair. Polymers with both high permeability and selectivity are desirable. Higher permeability decreases the amount of membrane area required to treat a given amount of gas, thereby decreasing the capital cost of membrane units. A rather general trade-off relation has been recognized between permeability and selectivity: Polymers that are more permeable are generally less selective and vice versa.

The increasing global demand for energy-efficient separations in carbon capture has prompted international actions on searching for novel, high-performance separation membranes. Polymeric membranes offer advantages over inorganic membrane for their ease fabrication and low cost [1-2]. Unfortunately, the separation performances of polymeric membranes are limited by a trade-off between permeability and separation selectivity which is called the Robeson upper limit [3-4]. Therefore, mixed matrix membranes (MMMs), with hybrid advantages of both inorganic and polymeric membranes, are

developed combining polymeric materials with well-selected fillers. So far, a variety of inorganic materials, such as zeolites [5], silica [6], carbon nanotubes [7] and carbon molecular sieves [8] can be used as fillers of MMMs. However, owing to the intrinsic differences between the inorganic and polymeric phases, interface voids and rigidified polymer can easily appear in MMMs with inorganic fillers. Therefore, the synthesis of perfect MMMs with high separation performances is rather challenging. Mixed matrix membranes (MMMs) are considered a new-generation membrane for gas purification applications and have become a focus for research and development in both academic and industrial interests due to their unique properties combining inherent characteristics of polymer and inorganic fillers [9].

Throughout the years there have been a number of researches done related to gas separation using mixed matrix membrane. In a research done by Adams et al. [10], Under both mixed feed conditions at 35 °C, substantial improvements in overall separation performance were observed. At low CO_2 partial pressures, CO_2 permeability roughly doubled with a nearly 50% increase in selectivity versus pure PVA under the same conditions. For the high CO_2 partial pressure feed, CO_2 permeability remained effectively unchanged with a 63% increase in selectivity versus pure PVA. Surprisingly, the performance of these PVA based MMMs approached the properties of current "upper bound" polymers. In another study done by Bao-Sheng et al. [11], GO loading increases from 1 to 3 wt.%. Based on the interaction of the GO and the polymer segmental chains, an increase in free volume of the polymer matrix resulted from the disruption of the polymer chains packing also demonstrates an ascending trend of the permeability. However, with 4 wt.% GO incorporated, the d-spacing of MMMs decreases slightly due to the poor dispersion of GO at higher loadings. A study done by Farahani et al. [12] shows that the effect of polymer concentration and solvent showed by the membranes fabricated using 15 wt% of PES concentration possessed greater fouling resistance and water flux compared to those of fabricated using 18 wt% of PES concentration. Also, membranes fabricated using DMA exhibited a more porous structure with considerably greater water flux as compared with those of fabricated using NMP as the solvent. Mixed matrix membranes are prepared in a dope solution where it is then heated at low heat for it to be casted on the casting machine via NIPS method [13]. However, NIPS method uses water in terms of water immersion of the produced membrane where the time for the membrane to be immersed is still not fixed. Ahmad et al. [14] study shows that MMM prepared with NIPS method shows the immersion time of the membrane in water for 60 minutes in the first immersion and left for another 24 hours for completing the process of removing excess chemicals. However, Farahani et al. [15] stated for the fabrication of NH2-MWCNT/P84 MMMs, the immersion time of the MMMs in water is around 2 days for removing excess chemicals. In another study by Qianyu et al. [16] shows the immersion time is only 1 hour for the fabrication of PVDF-AC MMMs using NIPS method.

Experimental designs are commonly performed in the study of empirical relationship, in terms of a mathematical model, between one or more measured responses and a number of variables or factors where these designs and modelling normally carried out in Design Expert software [17]. Experimental design and mathematical modelling techniques are mathematical tools normally used to optimize a process. Traditional methods of optimization involved changing one independent variable while fixing the others at a certain level. Experiment design techniques were developed to allow the gathering of maximum process information with reduced number of experiments. Experimental design techniques usually depend on empirical model structure in order to interpret experimental data and provide optimum process conditions. For the experimental design and response surface modelling for mixed matrix membrane by Kusworo et al. [18], mixed matrix membrane of PI/PES-Zeolite 4A was used for CO_2 separation. This research carried out experimental design via full factorial design (FFD) and central composite design (CCD) were systematically performed to investigate the main factor of fabrication parameters and the relationship with the mixed matrix membrane performance. A response surface methodology and central composite design were used in optimization experiments and iterative regression analysis to determine the maximum gas permeability and selectivity. Hence, the dominating factors that were likely to be the most important and influential could be diagnosed in order to optimise flat sheet mixed matrix membrane formation process. The effects and interactions of total solid/polymer concentration (X1), composition of polymer blending (X2) and zeolite content (X3) on carbon dioxide permeability and CO_2/CH_4 selectivity for PI/PES-zeolite mixed matrix membranes were investigated.

The experimental value and predicted responses for 16 trials runs. Another paper by Éva et al. [19], shows the full factorial design (FFD) performance based on the selected DOE procedure to evaluate the effect of every combination of the selected factors which are concentration of absorbent (X1), liquid volume flow (X2), and gas volume flow (X3) and hydrogen sulfide content of gas mixture (X4) with removal efficiency as its response. After the experimental work is finished and all the data is collected and systemized, a statistical modeling closes the procedure to compress the extracted information about the system applying the response surface methodology (RSM).

This study aims to prepare asymmetric PVC flat sheet MMMs using GO as a filler. A total of 5 factors have been selected to determine the to evaluate the significant factors towards the performance of the membrane during gas permeation test. Screening method via full factorial design (FFD) was used to determine the factor which provides the highest effect percentage. Factors used in this study are weight ratio of PVC, weight ratio of GO, pressure used during gas permeation (bar), time of membrane immersed in water (s), and type of solvent used. In this study, the response for the FFD would be selectivity of the MMMs.).

2. Methods

The materials that was used in this experiment were PVC with a melting temperature of 160ºC and also GO powder. Solvents such as DMF with 99.5% purity and NMP with 99.5% purity were used in this study. The boiling points of DMF and NMP are 153ºC and 202ºC respectively. There two gases used for gas permeation test were CO_2 and CH_4 gases. This research shows the usage of NIPS method for the fabrication of MMMs and gas permeation using MMMs for the separation of CO_2 and CH_4.

2.1. Fabrication of PVC/GO MMMs

The asymmetric flat sheet MMMs were fabricated using the NIPS technique [20]. Using the combination of PVC powder, GO powder, and NMP or DMF solution that formed a dope solution, the PVC/GO was stirred and dissolved in the solvents respectively. The dope solutions were prepared according to ratios of PVC, GO, and NMP or DMF, where for NMP or DMF will be constant at 80% of weight ratio of the solution. The dope solution was stirred for about 5 hours continuously at 130ºC for NMP mixed dope solution and 125ºC for DMF mixed dope solution, to ensure homogeneity. After completely dissolving, the dope solution was left and stirred for another 4 hours in order to remove trapped gas bubbles. In the production of asymmetric MMMs, phase inversion is considered to be a crucial method as it mainly focuses on polymer membrane which mainly goes through this method. Dry/wet phase inversion method is a process where the casted MMMs was left to vaporize and it was immediately immersed into a nonsolvent medium, normally water is used. The phase separation between solvent NMP or DMF, and nonsolvent such as water component, forms the membrane product. This is also assisting in the process of vaporization and polymer clotting. Using a glass plate or a polyester nonwoven fabric, the degassed dope solution was coated at room temperature at a knife gap of 0.3mm. After 10s of exposure in air, the casted film would be immediately immersed into a coagulation. The precipitated membrane was taken out of the coagulation bath and rinsed with running water to remove the residual solvent. The MMMs was then dried at room temperature.

2.2. Screening via Full Factorial Design (FFD)

Software usage, that is Design Expert is crucial for the evaluation the significant factors. Based on earlier journal studies, many factors affect the performance of the MMMs in gas separation process. A 2 Level Factorial Design has been carried out for this study where 5 factors have been chosen to determine the effects of the MMMs upon the performance of the MMMs in gas separation. These factors are weight ratio of PVC (A), weight ratio of GO (B), pressure used during gas permeation (bar) (C), type of solvent used (D), and time of membrane immersed in water (s) (E). From these 5 factors, 4 of these factors are numeric factors and another 1 is a categoric factor. The weight ratio of PVC was divided into 2 ratios which are 0.2% and 0.15%, whereas for GO the weight ratio was divided into 2 ratios also which are 0.02 and 0.04. The pressure that was set for gas permeation were 1 bar and 3 bar. The time the MMMs was immersed in the water was set to two different time which are 30s and 60s. Solvents that were used

in this study were NMP and DMF. Table 1 shows a brief explanation of the factors used in the screening process.

Table 1. Insertion of factor names and values according to types of factors in FFD

	Name	Units	Type	Low	High
A	Weight Ratio PVC	-	Numeric	0.15	0.20
B	Weight Ratio GO	-	Numeric	0.02	0.04
C	Pressure	bar	Numeric	1	3
D	Type of solvent	-	Categoric	NMP	DMF
E	Time of membrane in water	S	Numeric	300	600

Response values are inserted after taking note of conditions according to 5 factors with a total of 32 runs through experimental runs of experiment. From there, the R-squared will be examined where if it is more than 0.8 (>0.8), it is for bioprocess such as microbial fermentation and many more, while if it is more than 0.9 (>0.9), it is for chemical process. Coefficients will be checked, where for positive coefficients shows positive effect, while negative coefficients show negative effect. Final equation in terms of coded factors will be formed. Interaction graph for each factor interacting will be formed.

2.3. Gas Permeation Test using CO_2 and CH_4 gases

This study involves gas permeation test with a specific result from the performance of the MMMs. It is also to study whether the MMMs can separate the two gases without being ruptured. A gas permeation device was used in this study. Figure 1 shows the entire set up of the gas permeation experiment. Before the MMMs was put inside the device. The flat sheet MMMs was cut into 5cm in diameter circles. Pressure was set to according the runs provided from the screening table where some runs uses 1 bar of pressure while the rest were 3 bar of pressure. When the valve was opened for air flow at specific pressures, gases enter the device and through the MMMs for permeation and finally reaching the burette as gas bubbles. Time was started once the burette pipe is opened. Time was taken until it reached 0 ml reading at the top of the burette.

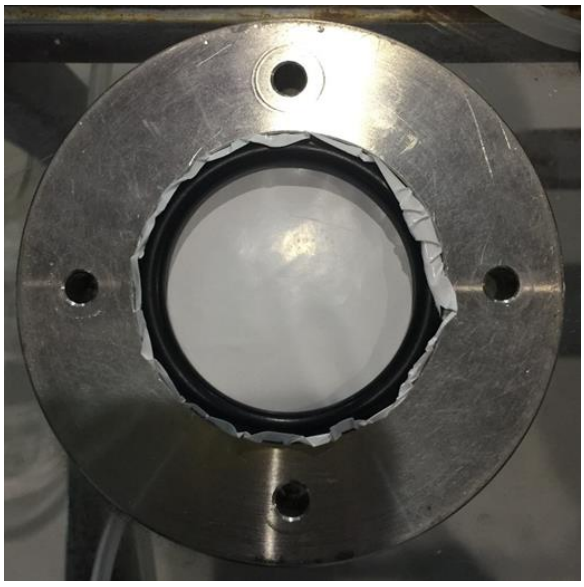


Figure 1. MMMs inside Gas Permeation Device.

Given below are equation (1) and equation (2), where equation (1) that was used for the calculation of the permeability of the MMMs, while equation (2) is the MMMs selectivity. Selectivity determines the ability of the MMMs to separate 2 gases, which were CH_4 and CO_2.

$$\frac{P}{l} = \frac{V}{At\Delta p} \quad (1)$$

$$\alpha_{CO2/CH4} = P_{CO2}/P_{CH4} \quad (2)$$

Where P is permeability ($cm^3/s.\ cm^2.cm\ Hg$), α is selectivity, l is membrane skin layer thickness (cm), Q is measured volumetric flow rate (cm^3/s), A is Effective membrane area (cm^2), ΔP is pressure differences across the membrane (cm Hg). Equation (2) is the selectivity of membrane to separate 2 gases. P_{CO2} represents the permeability of CO_2 whereas, P_{CH4} represents the permeability of CH_4.
[1 Barrer = 1X10-10 $cm^3/s.cm^2.cm\ Hg$]. Permeability should be converted into Barrer unit.

3. Results and Discussions

3.1. Screening using 2-Level Factorial Design

As stated earlier, MMMs has been produced according to 5 factors with specific criteria. These 5 factors have been inserted into the Design Expert software via 2-Level Factorial Design to achieve the experimental design table (table 2). From table 2, a total of 32 runs consisting of 5 factors in random arrangement has been distributed in the table. Each run has its own specific conditions according to all 5 factors introduced earlier. Experimental run was carried out via preparation of MMMs and gas permeation. Both permeability values from different types of gases were calculated to obtain the selectivity value which would then be added into the response section of the experimental table. Table 3 and 4 are the raw data and permeability values for each CO_2 and CH_4 gases respectively. A research done by Narenderan et al., six factors made up of volume of extracting solvent, the volume of dispersant/eluting solvent, extraction time, salt concentration, the flow rate of the sample, the volume of sample solution were considered in this study to determine the most significant factors. The results obtained were evaluated by ANOVA at 5 % significance level and it was observed that the factors, volume of dispersant/eluent solvent, volume of extraction solvent and flow rate of the sample showed statistical significance ($p = 0.05$) which was further investigated using CCD. The other factors (extraction time, salt effect and breakthrough volume in SPE) were not found to be significant ($p > 0.05$) [21].

Based on table 2, the highest selectivity is by Run 26 and the lowest selectivity is by Run 20. By comparing these 2 runs, we can see that in both Run 26 and Run 20 has the weight ratio of PVC and GO which are 20% and 4% respectively. However, when both runs are compared in factor 3 which is the pressure during gas permeation test, Run 26 used 1 bar of pressure whereas Run 20 used 3 bar of pressure. Another difference can be seen is in the categoric factor where Run 26 uses NMP whereas Run 20 uses DMF to prepare dope solution. Another difference was in the categoric factor where run 26 uses NMP whereas run 20 uses DMF to prepare dope solution. As stated earlier in Chapter 2 on the effects of solvent upon membrane performance, a study by Imtiaz Ali et al. shows PVDF homopolymer was blended with PVDF-co-HFP copolymer used different solvents, namely NMP, THF, and DMF solvents, were used to fabricate blended PVDF flat sheet membranes without the introduction of pore forming agent, via NIPS technique. Permeability of the membranes increased with the increase in overall content of PVDF. Mixed-solvents significantly improved permeability of membrane. This is because mixed-solvents undergo sonication where it is to ensure high degree of filler dispersion. [22]. The fifth factor was also the same in terms of the time of membrane immersed in water where both runs used 600s for immersion of MMMs inside water before left for drying. Table 3 is the calculation of selectivity based on the permeability values of both CO_2 and CH_4 gases from all 32 runs.

Table 2. Experimental Run Table (Design Expert using FFD)

Run	Factor 1 A: Weight Ratio PVC	Factor 2 B: Weight Ratio GO	Factor 3 C: Pressure (bar)	Factor 4 D: Type of Solvent	Factor 5 E: Water Contact of MMMs (s)	Response Selectivity
1	0.20	0.02	3.00	NMP	600.00	25.30
2	0.15	0.04	1.00	NMP	600.00	25.11
3	0.15	0.02	1.00	DMF	600.00	23.19
4	0.15	0.02	1.00	NMP	600.00	24.00
5	0.20	0.04	1.00	DMF	300.00	22.99
6	0.15	0.04	1.00	DMF	300.00	25.23
7	0.15	0.02	1.00	DMF	300.00	23.34
8	0.20	0.04	3.00	NMP	300.00	24.07
9	0.15	0.02	3.00	NMP	300.00	23.55
10	0.15	0.04	1.00	DMF	600.00	24.07
11	0.15	0.04	3.00	DMF	600.00	25.76
12	0.15	0.04	3.00	NMP	300.00	24.97
13	0.20	0.04	1.00	DMF	600.00	25.19
14	0.20	0.04	3.00	NMP	600.00	23.49
15	0.20	0.02	1.00	NMP	300.00	25.77
16	0.15	0.04	3.00	NMP	600.00	24.52
17	0.15	0.02	3.00	NMP	600.00	23.00
18	0.20	0.02	3.00	DMF	300.00	23.24
19	0.15	0.02	3.00	DMF	300.00	24.41
20	0.20	0.04	3.00	DMF	600.00	22.87
21	0.15	0.02	1.00	NMP	300.00	23.78
22	0.20	0.02	1.00	DMF	600.00	23.90
23	0.20	0.04	1.00	NMP	300.00	26.09
24	0.15	0.04	3.00	DMF	300.00	25.40
25	0.20	0.02	1.00	NMP	600.00	22.97
26	0.20	0.04	1.00	NMP	600.00	23.09
27	0.15	0.04	1.00	NMP	300.00	24.41
28	0.20	0.04	3.00	DMF	300.00	23.70
29	0.20	0.02	1.00	DMF	300.00	24.33
30	0.15	0.02	3.00	DMF	600.00	25.06
31	0.20	0.02	3.00	NMP	300.00	23.07
32	0.20	0.02	3.00	DMF	600.00	25.99

Table 3. Permeability and Selectivity for CO_2 and CH_4 gases.

Runs	Permeability of CO_2 gas. P_{CO2}	Permeability of CH_4 gas, P_{CH4}	Selectivity (P_{CO2}/P_{CH4}), α
1	455669.61	18009.58	25.30
2	409900.34	16319.89	25.11
3	406972.21	17548.78	23.19
4	501087.10	20876.28	24.00
5	577517.57	25115.46	22.99
6	396705.47	15718.76	25.23
7	614722.38	26331.06	23.34
8	625567.95	25987.80	24.07
9	320354.56	13600.91	23.55
10	248502.67	10321.25	24.07
11	282851.37	10978.46	25.76
12	385499.58	15437.89	24.97
13	225246.54	8938.56	25.19
14	502819.15	21403.29	23.49
15	361823.06	14035.35	25.77
16	711494.30	29005.30	24.52
17	375186.35	16310.81	23.00
18	508741.18	21887.27	23.24
19	422382.98	17302.83	24.41
20	488666.65	21365.93	22.87
21	188337.73	7919.30	23.78
22	274432.91	11479.57	23.90
23	419568.87	16078.45	26.09
24	470500.31	18518.60	25.40
25	256931.77	11184.80	22.97
26	225481.85	9764.62	23.09
27	647419.36	26515.10	24.41
28	434687.22	18336.20	23.70
29	321829.98	13225.03	24.33
30	405962.36	16196.31	25.06
31	633181.11	27438.35	23.07
32	408772.15	15726.84	25.99

Figure 2 shows the Robeson's plot of CO_2/CH_4 using MMMs. The dotted round circles are the experimental runs done during the screening phase of this study. All 32 runs have achieved high performance membrane as all are above the present and prior upper bound lines of the graph. A study done by Fang et al. shows membranes homopolymer poly (PFMMD) and copolymers poly (PFMMD-co-PFMD) with varied compositions was tested with N_2/CH_4, H_2/CH_4, He/CH_4, and CO_2/CH_4 gas separations where each upper bound, the points lie near the line hence, showing a promising performance from the membrane. Even though it does not show high performance, even more impressive results are obtained when PFMD is added to produce PFMMD–PFMD copolymers. These solution cast copolymers have He/CH_4 selectivity/permeability combinations that place them well above the 2008 upper bound [4], with selectivities higher than even the melt-pressed Hylon AD60 [23].

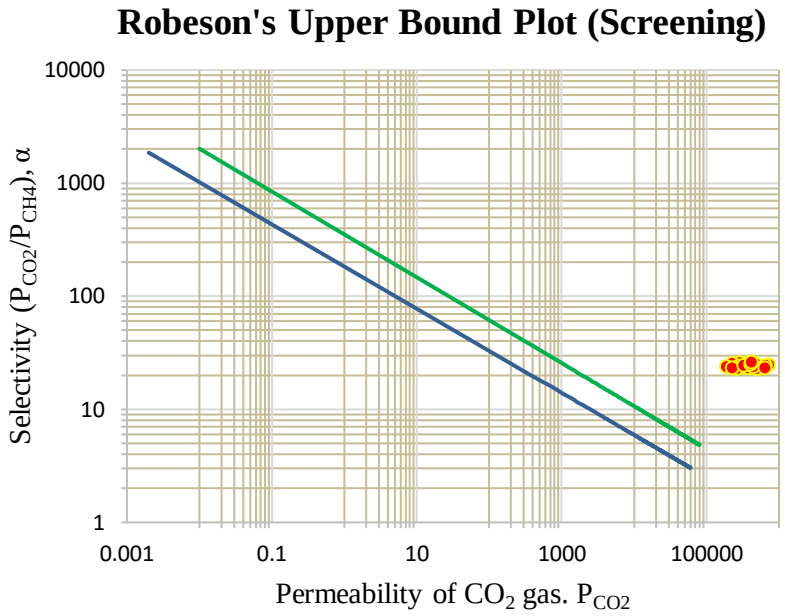


Figure 2. Robeson's Plot of CO_2/CH_4

3.2. Effect Lists of Factors and Pareto Chart

Even though all MMMs from the experimental runs are considered to be high performance via the Robeson's plot (figure 4), there are still more to study in terms of the factors affecting each run and how do they relate to each other. After calculating the permeability and selectivity of each runs, the experimental run table is further proceeded into the effects list of each factors individually and includes the interactions between factors. Table 6 shows the effect these factors individually and interactions between factors throughout the experiment and how they affect the experimental run.

Based on Table 4, as stated earlier where the 5 factors are weight ratio of PVC (A), weight ratio of GO (B), pressure used during gas permeation (bar) (C), type of solvent used (D), and time of membrane immersed in water (s) (E) interact among each other and contribute to each run in a certain percentage. When all 5 factors are compared individually, factor B shows the highest percentage of contribution at 3.66 %, and factor E shows the least percentage of contribution at 0.0072 %. When 2 factors interact, factor AB shows the highest at 14.83 and interaction of factor AE shows the least at $9.63X10^{-4}$ %. A study by Yanbin Cui et al., states that graphene layers in the polymer matrix are capable of producing a tortuous path, which acts as a barrier for gases. A high tortuosity leads to superior barrier properties and lower permeability of PNCs. The influence of the intrinsic properties of these fillers (graphene and its derivatives) and their state of dispersion in polymer matrix on the gas barrier properties of graphene/PNCs is discussed [24]. Hence this shows GO does affect the performance with the most significance.

Table 4. Effect List of Factors and Percentage Contribution (%)

Term	Percentage Contribution (%)
A - Ratio PVC	1.39
B - Ratio GO	3.66
C - Pressure	0.083
D - Type of Solvent	0.22
E - Water contact	0.072
AB	14.83
AC	3.74
AD	2.23
AE	9.63E-04
BC	1.39
BD	0.64
BE	2.15
CD	5.46
CE	6.34
DE	5.74

The effect of these 5 factors were analyzed with selectivity, where the Pareto chart is shown in figure 3. It is clearly seen that the interaction between weight ratio of PVC (A) and weight ratio of GO (B) shows the highest effect against selectivity, which is 93.11 while the lowest one is interactions of pressure used during gas permeation (bar) (C), type of solvent used (D), and time of membrane immersed in water (s) (E) (CDE), which is 24.86. From an individual standpoint, factor B shows the highest effect against selectivity at 46.54, while factor E shows the lowest effect against selectivity which lies slightly above the t-value limit line. The orange colored of bar shows that the effect possessed positive effects while the blue one has negative effects. A study done by Mah et al. [25] shows the Pareto chart where the bar lengths are proportional to the absolute value of the estimated effects, which helps to compare relative importance of the effects. The value of the Student's test parameter for p = 0.05 (95 % confidence level) and seven degrees of freedom (df) was 2.36. Thus, a t-value for the model coefficient which surpasses the critical value of 2.36 is considered to be statistically significant over the range of analytical response at the 95% confidence level. Four of the independent variables, namely TEOA concentration, TMC concentration, reaction time, and curing were statistically significant. Hence, these factors had major influence on the response within the limits of studied levels except pH of the aqueous solution. The interaction effect between TMC concentration and curing was the only two-way interaction effect that is statistically significant. The insignificance of effects does not mean that these factors are unimportant, but just implies a little influence on response. From the pareto chart, it is shows that more factors lead to negative effects compared the ones that lead to positive effect, however since all of the effect value of factors are all higher than the limits which is at 4.30, hence all factors are considered significant.

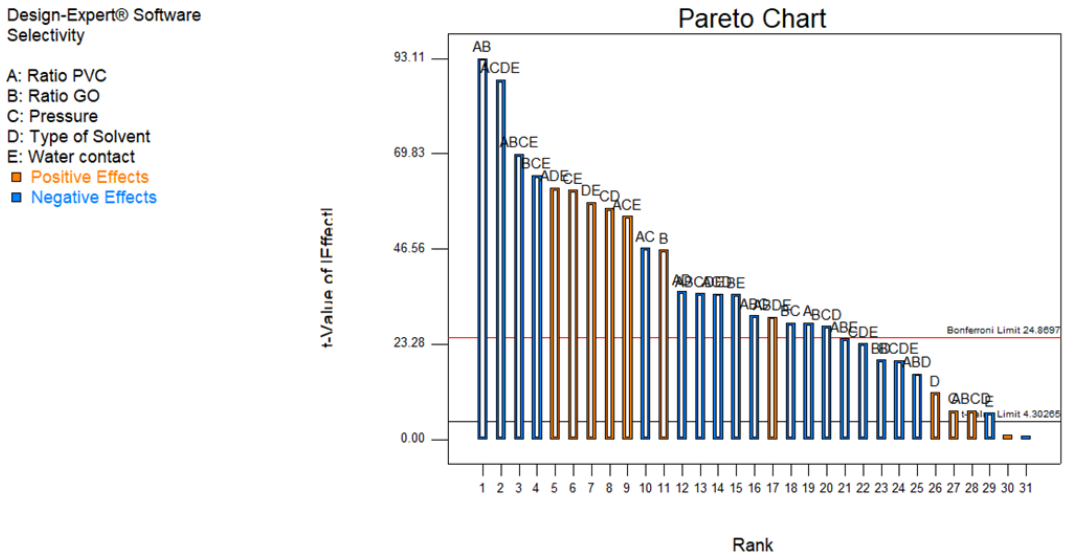


Figure 3. Pareto Chart from MMMs using 5 factors in FFD

3.3. Analysis of Variance (ANOVA) and Empirical Model Analysis

ANOVA is a statistical technique that separates the total variation in a set of data into component parts correlated with specific sources of variation. It is commonly for the purpose of testing hypothesis on the parameters of the model. In this experiment, ANOVA is used to test the statistical significance of the ratio of mean square variation which caused by regression and to test the mean square residual error. By using significance of factor (SOF) and R-squared (R^2) test, this research outlook two statistical point of view to analyse and asses the model of the experimental data. The goodness-of-fit is validated when the coefficient R^2 has the tendency to be closer to unity and when predicted is in agreement with the adjusted R^2. The R^2 for the analysed model must be more than 0.9 [26]. Table 5 show the result for SOF and the interaction for the selectivity of CO_2/CH_4 with the value of R^2. The R^2 for the analysed model must be more than 0.9. In table 5, the original value of R^2, adjusted R^2 and predicted R^2 are demonstrated after neglecting the insignificance terms of the design model. The predicted R^2 is 0.9912 is in reasonable agreement with adjusted R^2 because the value varied by 0.0088. In other words, the design model of the experiment is in an accurate description of experimental data which indicated the relationship between the variables and response data. The model result shows the tendencies for the model to form linear regression fit which showed that the experimental research range is adequate.

Table 5. R^2 statistic for the fitted model

Model Source	Selectivity of CO_2/CH_4
Std. Dev.	0.023
Mean	24.25
Coefficient of variation	0.096
R-Squared	1.0000
Adj R-Squared	0.9995
Pred R-Squared	0.9912
Adeq Precision	142.90

3.4. Interaction Factors, Model Graphs and Effect on Response (Selectivity)

One interaction factor only gives effect to the response (selectivity) and sometimes lack of interaction among another factor's information. However, based on earlier analysis and calculation, there are still interactions between other factors. Multiple interaction factors which requires further in-depth analysis and a better understanding can be seen from figure 4. Multiple interaction factors can sometimes relate two or more interaction factors for one response.

Based on figure 4, these multiple interaction factors can be divided into 5 parts. For the first part, the 3D graph is a plot for multiple interaction factors AB and response (selectivity), which are made up of both weight ratios of PVC and GO interaction factors. Other multiple interaction factors such as ABC and, ABD are also included in this graph section because 3D graph requires 3 axes where they are made up of factor A, B and response, so the rest of the factors which are linked to factors A and B which are also included in this part. From the 3D graph of part 1, the selectivity increases with an increase in weight ratio of PVC and GO. Further analysis shows the contour of 3D graph for part 1 where, more greenish color can be seen in the section where the weight ratio of PVC and GO are higher, and at that same greenish area was where the selectivity were higher. The second part of the table shows the multiple interaction factors AC and response (selectivity), which are made up of factors weight ratio of PVC (A) and pressure used during gas permeation (bar) (C). Other multiple interaction factors are also included in the AC to response plot, such as ACD and ACE, but as stated earlier, 3D graph requires 3 axes where they are made up of interaction factors A, C and response, so the rest of the factors which are linked to factors A and C which are also included in this part. The 3D plot in part 2 shows that even though there is an increase in weight ratio of PVC, an increase in pressure will reduce the selectivity. The contour of the 3D plot for part 2 shows that the bottom is right very yellowish because that area shows the highest response (selectivity), where in that area, the weight ratio of PVC is higher and pressure is low, hence, achieving higher selectivity compared to the upper part of the contour where the greenish area shows a higher pressure and lower selectivity, at increasing weight ratio of PVC. Part 3 shows the 3D plot of multiple interactions of BC and response (selectivity). Interaction factors BC are weight ratio of GO (B) and pressure used during gas permeation (bar) (C). In part 3, other than BC, the multiple interaction factors that come under this model graph are BCD and BCE. Only interaction factors B and C are in the 3D plot axes with response (selectivity) whereas the rest of the interaction factors are only linked to the stated interaction factors which B and C. Based on the 3D plot in part 3, an increase in GO effects the increase in selectivity. However, increase in pressure at low GO weight ratio shows lower selectivity. This can be seen in the contour plot of part 3, where the top left corner of the plot is blueish in color where that area has low selectivity. Even though the pressure is high, but when the weight ratio of GO is increased, the selectivity increases which can be seen on the top right of the plot where it is a bit greenish in color showing that the selectivity is much higher. The highest number of selectivity can be found at the bottom right of the plot where the plot looks slightly yellowish and it is at lower pressure and higher GO weight ratio. Part 4 of figure 4 shows model graph for the multiple interaction factors of BE with response (selectivity), interaction factors B and E are, weight ratio of GO (B) and time of membrane immersed in water (s) (E). Based on the 3D plot in part 4, at higher time of membrane immersed in water, the selectivity decreases. At the lowest weight ratio of GO, selectivity increases as time of membrane immersed in water decreases. Selectivity shows the highest at high GO weight ratio and low time of membrane immersed in water. From the contour plot of part 4, at low GO weight ratio, the top left corner shows high time of immersion but low selectivity. However, as selectivity does increase when time of immersion is reduced and weight ratio is increased where at the bottom right of the plot, the yellowish area represents high selectivity, high GO weight ratio and low time of immersion. Finally, part 5 is model graph for the multiple interaction factors of CE and response (selectivity). The interaction factors involved are pressure used during gas permeation (bar) (C) and time of membrane immersed in water (s) (E). From the 3D plot of part 5, at higher time of immersion in water and lower pressure, selectivity is low. At low pressure and time of immersion in water, selectivity is at its highest in the 3D plot. Based on the contour plot of part 5, the bottom left shows yellowish in color because that area shows the highest selectivity at low pressure and low time of immersion. On the top right of the plot where it is slightly blueish in color, selectivity is at its lowest when pressure and time of water immersion at its highest.

In another study related to screening of MMMs using DoE can be seen in Back et al. research. In that research, seven-channel capillary membranes were fabricated in a steam–dry–wet spinning process, while varying the composition of the polymer solution and the process temperatures in a three-level fractional factorial linear screening design. The polymers PVDF was the chemically resistant main polymer and PVP was added as hydrophilic co-polymer. In the model graph with interaction factors, it showed that the concentration of the main polymer PVDF and the molecular weight of the co-polymer

PVP showed linear relations with both permeability and retention. The obtained membranes may be suitable for micro/ ultra-filtration and, together, demonstrate the merits and limitations of DoE for multi-channel membrane screening. The permeability could be increased using sodium hypochlorite post-treatment, although retention was slightly compromised [26].

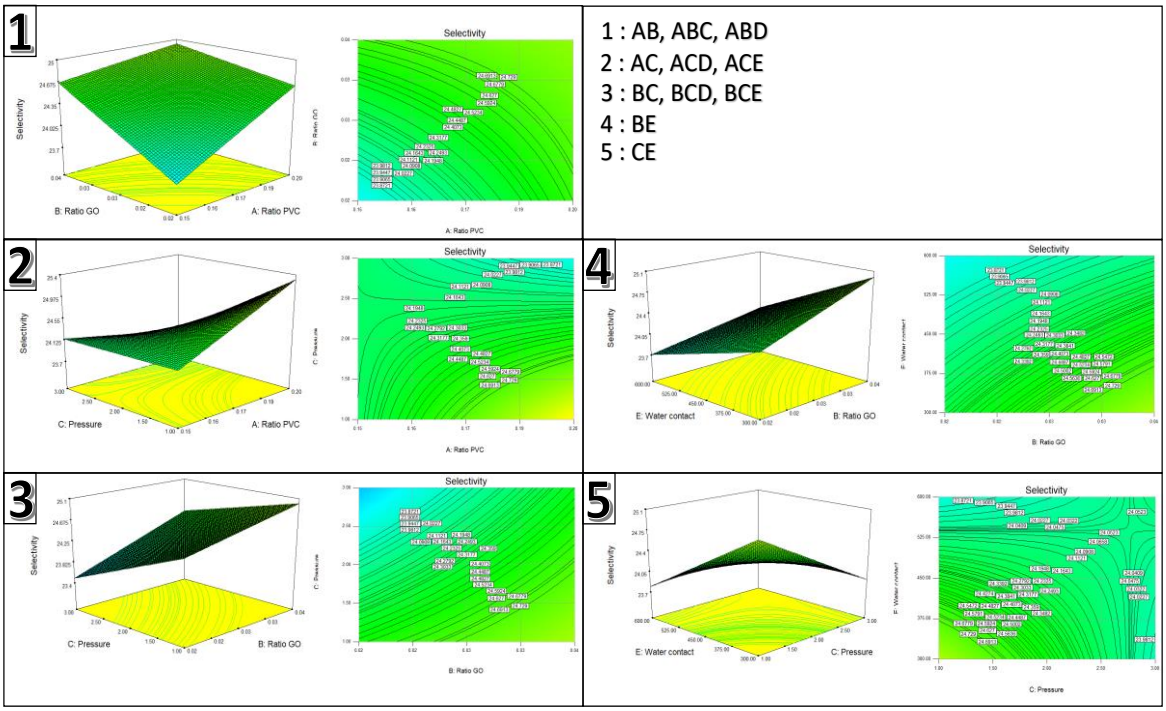


Figure 4. Model Graphs using Interaction Factors from Screening (3D Plot)

4. Conclusion

Based on this study, MMMs with factors of weight ratio of GO and PVC shows the most contribution and highest in the effect list. The interaction between both factors also show the highest in terms of contribution. Type of solvent which are NMP and DMF also show the third most contribution. Based on the 3D plot without considering the categoric factor which is type of solvents, weight ratio PVC and GO show to have the highest selectivity when both have the higher weight ratio, followed by lower pressure and shorter time of membrane immersed in water. From the screening table, run 23 shows the highest selectivity while run 20 shows the lowest selectivity at 26.0951 and 22.8713. In both runs, run 23 has lower pressure at 1 bar while run 20 is carried out at 3 bar of pressure. Run 23 uses solvent NMP while run 20 uses DMF. Run 23 immersed MMMs at 600s in water while run 20 at 300s in water. However, both runs use weight ratio PVC of 20% and weight ratio GO of 4%. Hence, factors weight ratio of PVC, weight ratio of GO and type of solvents contribute to the highest selectivity and also shows highest response during interaction among factors.

Acknowledgement

The authors would like to thank Universiti Malaysia Pahang for funding this project using university grant RDU1803113.

References

[1] Jusoh N, Yeong Y F, Chew T L, Lau K K and Shariff A M 2016 Current development and challenges of mixed matrix membranes for CO_2/CH_4 separation *Separ. Purif. Rev.* 45 321-44
[2] Nasir R, Mukhtar H, Man Z and Mohshim D F 2013 Material advancements in fabrication of mixed-matrix membranes *Chem. Eng. Technol.* **36** 717-27
[3] Robeson L M 1991 Correlation of separation factor versus permeability for polymeric membranes

J. Membr. Sci. **62** 165-85
[4] Robeson L M 2008 The upper bound revisited *J. Membr. Sci.* **320** 390-400
[5] Goh P S, Ismail A F, Sanip S M, Ng B C and Aziz M 2011 Recent advances of inorganic fillers in mixed matrix membrane for gas separation *Separ. Purif. Technol.* **81** 243-64
[6] Khan A L, Klaysom C, Gahlaut A, Khan A U, Vankelecom I F J 2013 Mixed matrix membranes comprising of Matrimid and -SO3H functionalized mesoporous MCM-41 for gas separation J. *Membr. Sci.* **447** 73-79
[7] Vu D Q, Koros W J and Miller S J 2003 Mixed matrix membranes using carbon molecular sieves - I. Preparation and experimental results *J. Membr. Sci.* **211** 311-34
[8] Ebadi Amooghin A, Mashhadikhan S, Sanaeepur H, Moghadassi A, Matsuura T and Ramakrishna S 2019 Substantial breakthroughs on function-led design of advanced materials used in mixed matrix membranes (MMMs): A new horizon for efficient CO_2 in separation *Progress in Materials Science* **102**
[9] Yong W F, Li F Y, Xiao Y C, Li P, Pramoda K P, Tong Y W and Chung T S 2012 Molecular engineering of PIM-1/Matrimid blend membranes for gas separation *J. Membr. Sci.* **407–408** 47-57
[10] Ryan T A, Lee J S, Bae T -H, Jason K W, Johnson J R, Christopher W J, Sankar N, and William J K 2011 CO_2–CH_4 permeation in high zeolite 4A loading mixed matrix membranes *Journal of Membrane Science* **367**(1–2) 197-203
[11] Bao-Sheng G, Wang T, Hai-Xiang S, Gao W and Hao-Ru Z 2018 Preparation of mixed matrix membranes based on polyimideand aminated graphene oxide for CO_2 separation *Polymer Advanced Technology* **29**(4) 1334-43
[12] Farahania M H, Rabieeb H and Vatanpour V 2019 Comparing the effect of incorporation of various nanoparticulate on the performance and antifouling properties of polyethersulfone nanocomposite membranes *Journal of Water Process Engineering* **27** 47-57
[13] Ahmad A L, Ramli W K W, Fernando W J N and Daud W R W 2012 Effect of ethanol concentration in water coagulation bath on pore geometry of PVDF membrane for membrane gas absorption application in CO2 removal *Separation Purification Technology* **88** 11-18
[14] Ahmad N A, Mohd Noh A N, Leo C P and Ahmad A L 2017 CO_2 removal using membrane gas absorption with PVDF membrane incorporated with POSS and SAPO-34 zeolite *Chemical Engineering Research and Design* **118** 238-47
[15] Farahani M H, Dan H and Tai-Shung C 2018 Cross-linked mixed matrix membranes (MMMs) consisting of amine-functionalized multi-walled carbon nanotubes and P84 polyimide for organic solvent nanofiltration (OSN) with enhanced flux *Journal of Membrane Science* **548** 319-31
[16] Qianyu L, Shaobin H, Yongqing Z and Shuaifei Z 2018 Comparing the antifouling effects of activated carbon and TiO_2 in ultrafiltration membrane development *Journal of Colloid and Interface Science* **515** 109-18
[17] Nele M, Vidal A, Bhering D L, Pinto J C and Salim V M M 1999 Preparation of high loading silica supported nickel catalyst: Simultaneous analysis of the precipitation and aging steps *Applied Catalysis A: General* **178**(2) 177-89
[18] Kusworo T D, Ismail A F and Mustafa A 2015 Experimental Design and Response Surface Modelling of Pi/Pes-Zeolite 4a Mixed Matrix Membrane for CO_2 Separation *Journal of Engineering Science and Technology* **10** 1116 – 30
[19] Molnár É, Varga T, Rippel-Pethő D, Bocsi R, Bobek J and Horváth G 2017 Optimization of the Sodium Hydroxide–Assisted Hydrogen Sulfide Selective Removal from Natural Gas *Chemical Engineering Communications* **204**(8) 974–81.
[20] Rabiee H, Farahani M H and Vatanpour V 2014 Preparation and characterization of emulsion poly (vinyl chloride)(EPVC)/TiO2 nanocomposite ultrafiltration membrane *J. Membr. Sci.* **472** 185–193
[21] Narenderan S T, Meyyanathan S N and Karri V V S R 2019 Experimental design in pesticide extraction methods: A review *Food Chemistry* **289**
[22] Ali I, Bamaga O A, Gzara L, Bassyouni M, Abdel-Aziz M H, Soliman M F and Albeirutty M 2018 Assessment of blend PVDF membranes, and the effect of polymer concentration and blend

composition *Membranes* **8**(1)
[23] Fang M, He Z, Merkel T C and Okamoto Y 2018 High-performance perfluorodioxolane copolymer membranes for gas separation with tailored selectivity enhancement. *Journal of Materials Chemistry A* **6**(2) 652–658
[24] Cui Y, Kundalwal S I and Kumar S 2016 Gas barrier performance of graphene/polymer nanocomposites *Carbon* **98** 313–333.
[25] Mah K H, Yussof H W, Abu Seman M N and M A W 2018 Polyester thin film composite nanofiltration membranes via interfacial polymerization: influence of five synthesis parameters on water permeability *Journal of Mechanical Engineering and Sciences* **12**(1) 3387–3398
[26] Back J O, Brandstätter R, Spruck M, Koch M, Penner S and Rupprich M 2019 Parameter screening of PVDF/PVP multi-channel capillary membranes *Polymers* **11**(3) 1–17