

**EFFECT OF MEMBRANE SELECTIVITY AND
CONFIGURATION ON PURITY AND RECOVERY OF
HYDROGEN FROM SYNGAS**

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**EFFECT OF MEMBRANE SELECTIVITY AND CONFIGURATION ON PURITY
AND RECOVERY OF HYDROGEN FROM SYNGAS**

By

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LIST OF SYMBOLS

Symbol	Description	Unit
n	Number of summation iteration occurred	-
A_t	Actual value	-
F_t	Simulated value	-
q_f	Feed flow rate	cm^3/s
q_p	Permeate flow rate	cm^3/s
q_o	Retentate flow rate	cm^3/s
x_f	Mole fraction of gas species in the feed	-
y_p	Mole fraction of gas species in the permeate	-
x_o	Mole fraction of gas species in the retentate	-
p_h	Feed Pressure	Pa
p_l	Permeate Pressure	Pa
K_i	Permeability constant of H_2	$(\text{cm}^3.\text{cm})/(\text{s}.\text{cm}^2.\text{cmHg})$
K_j	Permeability constant of CO_2	$(\text{cm}^3.\text{cm})/(\text{s}.\text{cm}^2.\text{cmHg})$
K_k	Permeability constant of CO	$(\text{cm}^3.\text{cm})/(\text{s}.\text{cm}^2.\text{cm}_\text{Hg})$

K_1	Permeability constant of CH ₄	(cm ³ .cm)/(s.cm ² .cm_Hg)
N	Flux through membrane	cm ³ /cm ² .s
A	Area of membrane	cm ²
L	Membrane thickness	cm
R ²	Coefficient of determination	-
Greek letter		
α	Selectivity	-
θ	Stage Cut	-
σ	Standard Deviation	-
Subscripts		
i	Gas Component H ₂	-
j	Gas Component CO ₂	-
k	Gas Component CO	-
l	Gas Component CH ₄	-

LIST OF ABBREVIATIONS

Abbreviation	Description
H ₂	Hydrogen
CO ₂	Carbon Dioxide
CO	Carbon Monoxide
CH ₄	Methane
ANOVA	Analysis of variance
CCD	Central Composite Design
RSM	Response Surface Methodology
MAPE	Mean Absolute Percentage Error
DE	Design Expert
PILM	Polyionic liquid membranes
CMSM	Carbon molecular sieve membrane
PSA	Pressure swing adsorption
SDG	Sustainable Development Goals
WGS	Water Gas Shift

KESAN SELEKTIVITI DAN KONFIGURASI MEMBRAN TERHADAP KETULENAN DAN PEMULIHAN HIDROGEN DARIPADA SINGAS

ABSTRAK

Dalam tesis ini, simulasi sistem pemisahan gas menggunakan membran untuk menuliskan hidrogen daripada singas telah dibincangkan. Simulasi ini dilakukan untuk mengkaji kesan selektiviti membran, konfigurasi aliran membran, nisbah kadar aliran dan tekanan input membran terhadap ketulenan dan pemulihan hidrogen daripada singas. Untuk memodelkan membran tersebut, model pencampuran lengkap telah digunakan. Pemodelan matematik yang terlibat dalam simulasi ini dilakukan dengan menggunakan perisian Mathcad dan hasilnya dianalisa menggunakan analisis varians (ANOVA) di bawah Kaedah Permukaan Tindak Balas atau kaedah yang dikenali sebagai *Response Surface Methodology* (RSM). Kami telah mengkaji dua jenis model konfigurasi aliran membran untuk menemui cara menghasilkan hidrogen berketulenan tinggi yang diterima sebagai hidrogen kelas komersial. Konfigurasi 1 melibatkan membran telap karbon dioksida manakala model konfigurasi 2 melibatkan membran telap hidrogen. Daripada kajian yang dijalankan, diperhatikan bahawa dalam konfigurasi pertama, pada nisbah kadar aliran 0.2, tekanan input 5 bar dan selektiviti CO_2/H_2 1500 diterapkan untuk mencapai ketulenan hidrogen yang tertinggi pada 52.24% dan kadar pemulihan 59.58% pada aliran meresap. Sementara itu, dalam aliran buangan, ketulenan dan kadar pemulihan karbon dioksida yang dicapai masing-masing adalah 52.21% dan 55.53%. Dalam konfigurasi kedua membran telap hidrogen digunakan. konfigurasi ini menghasilkan ketulenan hidrogen yang tertinggi iaitu 100% dengan kadar pemulihan 32.52%, ketulenan karbon dioksida dan kadar pemulihan masing-masing pada 27.35% dan 90.42% pada nisbah kadar aliran 0.2, tekanan input 25 bar dan selektiviti H_2/CO_2 500.

EFFECT OF MEMBRANE SELECTIVITY AND CONFIGURATION ON PURITY AND RECOVERY OF HYDROGEN FROM SYNGAS

ABSTRACT

In this thesis, simulation of a membrane gas separation system for purification of hydrogen from syngas has been discussed. The simulation was done to study the effects of membrane selectivity, flow configuration, stage cut and feed pressure on the purity and recovery of hydrogen from syngas. In order to model the membrane, a complete mixing model was applied to study these effects. The mathematical modelling involved in the simulation was done in Mathcad and the results were analysed using the analysis of variance (ANOVA) under the Response Surface Methodology (RSM) method. In order to produce high purity hydrogen that is accepted as commercial industrial grade hydrogen, we studied two types of flow configuration models. Configuration 1 involves a carbon dioxide permeable membrane while configuration 2 model involves a hydrogen permeable membrane. As a result, it is noticed that in the first configuration, at the stage cut of 0.2, feed pressure of 5 bar and CO_2/H_2 selectivity of 1500, the highest purity of hydrogen at 52.24% and recovery of 59.58% at the permeate stream is achieved. Meanwhile in the retentate stream, the purity and recovery of carbon dioxide achieved is 52.21% and 55.53% respectively. The second configuration is when a hydrogen permeable membrane is applied. This configuration results in the highest possible purity of hydrogen of 100% with recovery of 32.52% and carbon dioxide purity and recovery at 27.35% and 90.42% respectively, at stage cut of 0.2, feed pressure of 25 bar and H_2/CO_2 selectivity of 500.

CHAPTER 1 INTRODUCTION

Chapter 1 is the introduction of this research and it presents the overview and significance of hydrogen purification via membrane separation. This chapter includes the background of hydrogen as emerging renewable energy, the sustainability aspect of the research, the problem statement and the objectives of this research.

1.1 Background

1.1.1 Hydrogen

Hydrogen is a simple element that is in abundance on earth. This element is well known for its property of being a very light, storable and energy dense material. However, hydrogen does not naturally found as an element on its own, it is always combined with other elements such as in water, organic compounds and biomass. The current industrial production of hydrogen is based on the extraction of hydrogen from natural gas and coal. Based on the statistics, the production of hydrogen is divided as such 48% is from natural gas, 30% from heavy oils and naphtha, 18% from coal and only 4% are from the electrolysis of water (Balat, 2008).

The demand for hydrogen has been increasing and is currently threefold of the demand back in 1975. This is due to its rise in applications. Hydrogen is used in metal working, flat glass production, oil refineries and as a source of energy. The application of hydrogen as an energy source is the least exploited field because the amount of energy required for its production is much more than the energy generated in return.

Hydrogen is seen as an upcoming energy carrier that is way cleaner and more environmentally friendly compared to fossil fuels. Usage of hydrogen as an energy source and fuel creates less pollution as the burning of pure hydrogen has no direct emission of pollutants or greenhouse gases. It also might help in reducing the depletion of fossil fuels as hydrogen is

very apt to be the fuel source of the era post-fossil fuels. Hydrogen can be used as an energy source in fuel cells and as a blending agent of natural gas to enhance its combustion properties. Furthermore, there is an increasing demand for commercially graded hydrogen with precise purity and impurity content due to a wide range of fast developing hydrogen uses as listed in **Table 1.1**.

Table 1.1 Commercial grade hydrogen and its purity and applications (Dawood *et al.*, 2020)

Form of Hydrogen	Grade	Purity (%)	Applications
Gaseous	A	98.00	Internal combustion engines for transport
	B	99.90	Industrial fuel used in power generation or heat energy source
	D	99.97	Fuel cells for vehicles
	E	50.0	Fuel cells for stationary applications
Liquid	A	99.995	Electrical energy requirements
Slush	-	99.995	Aircrafts and space vehicles on board propulsion system and

Utmost attention has been given to the research and development of hydrogen fuel technologies. The Malaysian government has started to prioritize research in hydrogen fuel cells since the Eighth Malaysia Plan. In Malaysia, RM 40 million has been invested and allocated for the research and development (R&D) by the Ministry of Science, Technology and Innovation (MOSTI) for hydrogen fuel technologies from 1997 to 2013 (Mah *et al.*, 2019).

However, hydrogen is not a primary source which means there is a need to produce hydrogen before supplying it as fuel. The conventional process of producing hydrogen is steam reforming of methane, electrolysis of water and coal or biomass gasification. In steam reforming of methane, methane or natural gas is reacted with steam producing a gaseous

mixture of hydrogen, carbon monoxide and carbon dioxide. The carbon monoxide will be further reacted in a Water Gas Shift (WGS) reaction to generate more hydrogen. As a final step, hydrogen is purified by removing other impurities (Palo *et al.*, 2007).

1.1.2 Syngas

Gasification of coal or biomass is a reaction where the coal or biomass is let to be burned in a gasifier with either steam or oxygen at high temperature. This reaction often produces syngas with various components and compositions. The components and the composition of the component in the syngas depend solely on the feed that is being used. Therefore, the gasification of biomass will require downstream processing to purify and recover high purity hydrogen. Electrolysis of water is by far the cleanest method to generate hydrogen as the only by-product that will be produced in the reaction is water. But this method is generally not used as the amount of electrical energy required to separate hydrogen from water molecule will be comparatively higher than the amount of energy being produced (Shiva Kumar *et al.*, 2019).

Syngas is a short name for synthesis gas which is a mixture of gas that contains mainly hydrogen, carbon monoxide, carbon dioxide and methane. It also might contain smaller amounts of nitrogen oxides, sulphur oxides, ammonia and hydrogen cyanide. Syngas is usually produced by the gasification of fossil fuels or biomass. Syngas is generally used as intermediates in the making of synthetic natural gas which then can be directly used as fuel. Other than that, it serves to produce other products such as methanol, nitrogen based fertilisers, transportation fuels and hydrogen.

The composition of syngas produced depends on the type of feedstock used and the operating parameters of the process. Syngas produced from biomass is the favourable choice since the production of hydrogen will solely depend on renewable sources which will be a great way to ensure the sustainability of the process.

Table 1.2 Composition of syngas from various sources

Source of Syngas	Composition of gas components (mol%)			
	Gasification of rice husk*	Gasification of coal*	Pyrolysis of solar dried sewage sludge	Gasification of sawdust
Hydrogen	17.07	52.46	10.85	69.1
Carbon Monoxide	26.38	29.50	7.26	18.8
Carbon Dioxide	14.40	5.6	12.03	7.1
Methane	9.70	4.40	17.62	5.0
Nitrogen	20.99	1.50	-	-
Water	-	5.10	-	-
Hydrocarbon	-	-	4.3	-
Reference	(Khonde <i>et al.</i> , 2016)	(Sforza <i>et al.</i> , 2012)	(Trabelsi <i>et al.</i> , 2017)	(Xu <i>et al.</i> , 2018)

* The compositions in the literatures are given in volume fraction (vol%) and are being converted to mole fraction with the assumption the gas mixtures have the properties of ideal gas.

1.2 Sustainability

Sustainability has become a very important criterion to any research conducted in the science and technology field in recent years as an initiative to create a sustainable future. There is a set of 17 Sustainable Development Goals created to be implemented, in the name of United Nations' (UN) Transforming Our World: The 2030 Agenda to Sustainable Development. The 17 goals are outlined based on education, gender inequality, health, well-being and demography, energy carbonization, sustainable industry, food, lives on land and water, sanitation, cities and communities, and digital revolution for sustainable development.

This report contributes a small but impactful step towards achieving the Sustainable Development Goal (SDG) 13. The respective goal is to take urgent action to combat climate change. In order to limit the global average temperature rise below 2°C, a drastic reduction of anthropogenic carbon dioxide emissions is proposed. Usage of fossil fuels is known to be one of the main reasons for excessive anthropogenic carbon dioxide in the atmosphere. Hydrogen is an alternative renewable energy source if it is sourced from biomass gasification. The bio-hydrogen can be an excellent potential as an energy carrier due to its property of high energy density, zero emission of greenhouse gaseous and possibility of integration with the current fossil fuel technology for sustainability. Therefore, proposing an efficient purification membrane system for high purity hydrogen will make it possible to achieve the main aim of the respective goal.

Moreover, the conversion of hydrogen to heat end uses and electricity does not generate any polluting chemical or gaseous except water. Other than that, the infrastructural aspect of hydrogen as fuel can be resolved as hydrogen can be supplied using the existing technology with minimal changes. This research is a method to conduct a thorough study on the generation of high purity hydrogen from biomass syngas that can be used as an energy source. Thus, this

research also contributes to the sustainable development goal (SGD) 7 which is to ensure access to affordable, reliable, sustainable and modern energy for all.

1.3 Problem Statement

In order to exploit the capability of hydrogen to serve as an energy carrier, an enormous quantity of pure hydrogen must be produced. Purification of hydrogen from syngas will be essential. The current industrial process to produce hydrogen is energy extensive and dependent on fossil fuels. For instance, steam reforming of natural gas and gasification of coal. These processes will add up to amount of greenhouse gaseous emission into the atmosphere by which the main purpose of providing a clean energy source is disrupted.

In this study, hydrogen which is sourced from gasification of biomass will be purified from syngas to a commercial grade hydrogen. Syngas sourced from biomass will be an effective solution as it will maintain the carbon cycle rather than increasing the amount of carbon emission into the atmosphere, making it more sustainable. The purification method chosen is selectively permeable membrane system which is relatively simpler and not energy extensive compared to the current existing method such as pressure swing adsorption and cryogenic distillation. The membrane model is simulated using mathematical model to create a better understanding as a simulated model has better visualization and ability to handle uncertainty. This study is conducted to investigate the purity and recovery of hydrogen from syngas and the variables that affect the process such as membrane selectivity and configuration of the membrane model. The data obtained will be optimized to generate mathematical equations to simulate an optimum membrane model for the purification of hydrogen from syngas.

1.4 Objectives

- i. To study the effects of operating parameters such as stage-cut and feed pressure on the hydrogen and carbon dioxide purity and recovery from syngas by mathematical modelling simulation.
- ii. To study the effect of membrane selectivity and configuration on the hydrogen and carbon dioxide purity and recovery from syngas by mathematical modelling simulation.
- iii. To determine the suitable membrane configuration for the optimum purification of hydrogen from syngas by mathematical modelling simulation.

CHAPTER 2 LITERATURE REVIEW

Chapter 2 presents the reviews and basic concepts regarding this final year project topic that has been previously studied and experimented. Topics such as purification method used for hydrogen purification, overview of membrane technologies, the types of membranes and the key parameters of membrane gas separation will be discussed. Besides, overview of the Complete Mixing Model and the use of Design of Experiment will also be presented.

2.1 Purification Methods

The common industrial purification system of hydrogen from syngas is pressure swing adsorption (PSA) and cryogenic distillation. Purification of hydrogen from syngas by PSA is a dynamic process where the gas is channelled through adsorption column in a cyclic manner with the same sequence of steps. The advantage of the purification step using the PSA method is that the purified hydrogen has a high level of purity (99.999%)(Bernardo *et al.*, 2020). But the system is also known for its high energy demand and is not generally cost effective.

Cryogenic distillation is a process where the gas mixtures are partially condensed at low and high pressure to separate the gas mixture by distillation. This process in particular is not efficient as the purified hydrogen has a comparatively low purity level (95%) than the level of purity which is required by the standard application of hydrogen as fuel (Liemberger *et al.*, 2017). Cryogenic distillation is also considered an energy intensive process as there are numerous process equipment involved. Due to the characteristics of these processes, PSA and cryogenic distillation are more apt for large scale process but not appropriate for small scale or portable usage.

2.2 Membrane Technology

Membrane technology has been in the limelight as a very promising technology that will be able to produce products that are up to the standards of the traditional separation methods. Membrane separation system is where a solid selectively permeable barrier is used to separate a mixture of gaseous. The driving force of the system is usually the pressure difference from both sides of the membrane. The separation is accomplished by allowing selective molecules to permeate depending on the permeability of the molecule across the membrane while preventing the passage of other components. The membranes can separate the components by various sizes and molecular weight of the molecules. The membrane separation system possess certain advantages such as simpler operation, higher efficiency, lower operating and maintenance cost and much less impact on the environment (Bernardo *et al.*, 2020).

There are few types of membranes that have been developed by the membrane technology sector such as carbon molecular sieve membranes (CMSM), polyionic liquid membranes (PILM) and metal membranes. Carbon molecular sieve membranes are manufactured by carbonizing the polymeric precursors at high temperature under a controlled condition. These membranes are used extensively in gas separation due to their characteristics such as having excellent resistance towards corrosion, good thermal stability and higher permeability and selectivity compared to the polymeric membranes. The efficiency of the system is proven by He, 2017 who demonstrated a two stage carbon molecular sieve membrane system to purify hydrogen from biomass fermentation process. The system is energy efficient as it operates at the pressure and temperature of 20 bar and 20°C respectively and managed to recover 99.5% of hydrogen with high purity level.

Ionic liquid membranes are usually made up of salts that are either liquid at room temperature or solids that melt below 100°C. It is normally formed by an organic cation and an organic or inorganic anion. In the use of this membrane, the vapor pressure can be neglected,

the membrane is a non flammable membrane and it possesses physicochemical properties that can be altered by changing into different combinations of cations and anions. The ionic liquid membrane is a good choice of membrane for gas separation as it has a high carbon dioxide solubility and selectivity (Dai *et al.*, 2016). Ionic liquid membranes can be further categorised as supported ionic liquid, polymer ionic liquid composite, polymer ionic liquid gel and polyionic membranes.

In a metal membrane system, gas separation takes place via sorption diffusion mechanism. Hydrogen permeates from a region of high partial pressure to a region with lower partial pressure. Examples of metal membranes are niobium, vanadium, tantalum and palladium membranes. Even though the hydrogen permeation flux of the palladium membrane is the lowest, it is the most common metal membrane for hydrogen purification. This is because the dissociative adsorption of hydrogen on the gas metal interface of the palladium membrane requires the least or no activation energy (Nakatsuji *et al.*, 1985).

2.3 Membrane Separation System Parameters

There are few parameters that affect the purity and recovery of hydrogen from syngas by membrane separation such as permeability of the components, membrane selectivity, configuration of the flow direction across the membrane, stage cut and the pressure difference that exist across the membrane. The permeability of a gas component across the membrane is defined as the product of gas flux and membrane thickness divided by the differential pressure through the membrane. In general, it is the volume of gas component that pass through the membrane per unit area per unit time. Permeability of a gas component can be expressed using the following formula:

$$P_A = S_A D_A \quad \dots(2.1)$$

Where P_A = Permeability coefficient of gas A

S_A = Solubility coefficient of gas A

D_A = Diffusion coefficient of gas A

Next, the membrane selectivity is a ratio of permeability coefficient of gas A over permeability coefficient of gas B. Whereby the expression is as follow:

$$\alpha_{A/B} = \frac{P_A}{P_B} \quad \dots(2.2)$$

Where $\alpha_{A/B}$ = Membrane selectivity

P_A = Permeability coefficient of gas A

P_B = Permeability coefficient of gas B

In general when the membrane selectivity of gas A over B is more than unity, it defines as the gas A being more permeable towards the membrane while the gas B is less permeable. The configuration of direction flow across the membrane is another key parameter of membrane separation system that is being studied in this paper. The configuration of the membrane depends on the selectivity of the membrane. The membrane flow configuration is being divided by Configuration 1 and Configuration 2. In the Configuration 1, the model comprises of a carbon dioxide permeable membrane where the permeability of carbon dioxide across the membrane is higher than the permeability of hydrogen. The CO_2/H_2 selectivity of the membrane would be more than unity. While for the second configuration, the model involves a hydrogen permeable membrane which has higher hydrogen permeability compared to the carbon dioxide permeability across the membrane. Therefore, in the model of configuration 2, the H_2/CO_2 selectivity will be higher than one. The **Figure 2.1** and **Figure 2.2** below depicts both the membrane flow configurations.

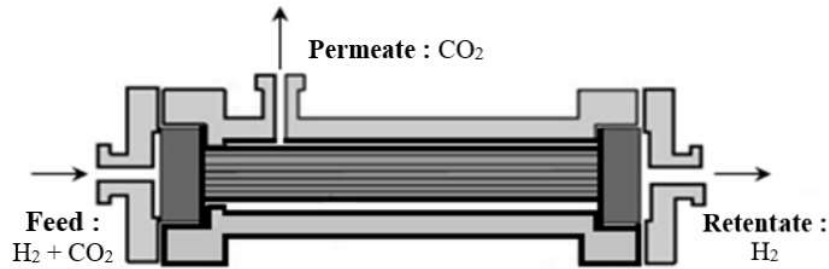


Figure 2.1 Direction of flow of gaseous across the membrane (carbon dioxide permeable membrane) in hydrogen purification system for configuration 1 model with CO₂/H₂ selectivity

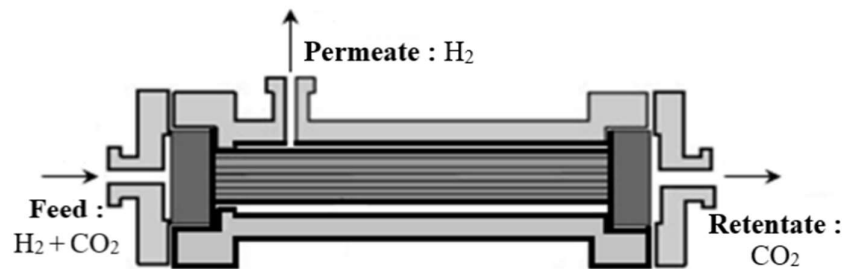


Figure 2.2 Direction of flow of gaseous across the membrane (hydrogen permeable membrane) in hydrogen purification system for configuration 2 with H₂/CO₂ selectivity

The purity of hydrogen recovered from membrane separation system is affected by stage cut variable. Stage cut the fraction of permeated flowrate from the total flowrate of the gas mixture. Poudel *et al.*, 2019 proved that the stage cut influences the selectivity and the permeability of the membrane through their work. When the stage cut is increased, it also indicates that the fraction of permeates gas flowrate is increasing. This is because when the stage cut is raised, the driving force of the system which is the differential pressure between both sides of the membrane is also increased.

Besides, the feed flowrate of the inlet gas mixture contributes to the performance of the membrane separation system. Generally, when there is an increment in the flowrate of feed into the system, the purity of the recovered hydrogen is said to be increasing too (Poudel *et al.*,

2019). This situation occurs due to the reason that the amount of gas particles in the system is more and will force the molecules that able to penetrate the membrane through selectively permeable membrane.

Another factor that affects the membrane permeability is the pressure applied on the membrane. The pressure applied on the membrane can be quantified by measuring the feed pressure and the permeate pressure of the gas. According to Roslan *et al.*, 2020, the permeability of a gas component through a membrane increases with the increment of the pressure. But one of the concerns regarding high pressure application, is that there is possibility for plasticization to occur. Plasticization is the changes when the interaction between the adjacent segment of polymer is disrupted due to high pressure applied. This disruption leads to permanent change in the structural integrity of the membrane and may alter the permeability of the membrane (Scholes *et al.*, 2010).

2.4 Complete Mixing Model

In a membrane separation system, gas is flowed through one side of the membrane which permeate in a perpendicular direction towards the membrane. The permeate that passes across the membrane accumulates at the low-pressure side of the system. The gas film resistance is negligible compared to the membrane resistance as the high gas diffusions coefficients causes the concentration gradient of the gas perpendicular to the surface of membrane to reduce as quite a small value. Therefore, the concentration of gas in a perpendicular direction to the membrane is uniform even when the gas stream is not flowing in a parallel direction to surface and vice versa. There are few numbers of idealized model of flow patterns where both the high-pressure feed side and the permeate side of the membrane to be operated at completely mixed phase or plug flow phase. The **Figure 2.3** shows the ideal flow patterns of a gas separation system using a membrane.

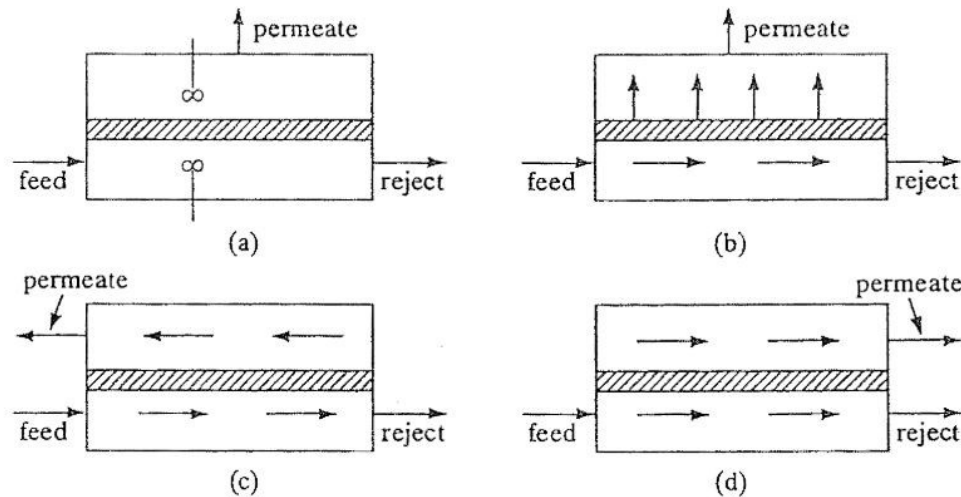


Figure 2.3 Examples of ideal flow patterns, a) complete mixing, b) cross flow, c) countercurrent flow and d) cocurrent flow (Geankoplis, 1993)

In this study, we are considering the complete mixing model, as it has the best approximation of the permeate purity. This is due to the mechanism of permeate flow rate as a small fraction of the feed which results to the minimalistic changes in the composition.

2.5 Numerical Simulation

The developed equations of the model for the prediction of composition of gas components in the permeate and retentate stream as well as the material balance of gas components across the membrane needs to be solved numerically to simulate the membrane separation process. In order to solve the system equation, the Mathcad software is used in which the simultaneous equation with two unknown method is utilized. The mathematical modelling simulation has become the new interest as it possesses few advantages. The first is that the simulation process is a risk free environment as the simulation modelling provides a safe path to test and explore different what if scenarios. The effect of changing a factor in a process can be predicted without putting the production at risk. Thus, this also leads to saving money and time. The virtual experiments with simulation models are less expensive and consumes shorter time in comparison with experiments with real assets (Pelalak *et al.*, 2018).

2.6 Design of Experiment

One of the most widely utilized experimental designs for process optimization is response surface methodology (RSM). It is a collection of statistical and mathematical tools that are used to design, improve and optimize processes. It is a method of fitting a polynomial equation to experimental data to describe the behaviour of a data set in order to make statistical predictions. RSM is also known as an empirical modelling method which is mainly used to figure out the relationship between a collection of experimental factors and the observed results (TaHERi Afarani *et al.*, 2019). Multiple regression analysis is used in this experimental design method, which allows for fewer experimental runs. RSM has several features including Central Composite, Box-Behnken and 3 Level Factorial. Central Composite Design (CCD) is one of the most widely used aspects among all of them. CCD has been used to optimize membrane processes in recent years because it is a dependable model that requires less experimental experiments and takes into accounts of interaction between factors (Meng *et al.*, 2013). The potential of the CCD approach for modelling of hydrogen purification from syngas by membrane separation has been studied in this research, given the growing interest in the CCD approach in membrane gas separation. It is also applicable to research the interactions between the various parameters that affect the process.

2.7 Mean Absolute Percentage Error

Mean Absolute Percentage Error (MAPE) is a method to validate the suggested model. This method shows the error of the predicted value compared relative to the actual value. Thus, it demonstrates the forecasting power of the suggested model. Therefore, validation of the model by calculating the MAPE value ensures the accuracy of the membrane model proposed.

The mean absolute percentage error is calculated using the following formula:

$$MAPE = \frac{1}{n} \sum_{t=1}^n \left| \frac{A_t - F_t}{A_t} \right| \quad \dots(2.1)$$

Where:

n: number of summation iteration occurred

A_t: the actual value

F_t: the simulated value

The forecasting power of the model is based on the MAPE percentage list which is shown in the **Table 2.1**.

Table 2.1 MAPE forecasting power (Montaño Moreno *et al.*, 2013)

MAPE	Forecasting Power
<10%	Highly accurate forecasting
10% - 20%	Good forecasting
20% - 50%	Reasonable forecasting
>50%	Weak and inaccurate forecasting

The purity error and recovery error are calculated as follow:

$$\text{Purity Error} = \left| \frac{\text{Purity from previous work} - \text{Simul purity in the present work}}{\text{Purity from previous work}} \right| \quad \dots(2.2)$$

$$\text{Recovery Error} = \left| \frac{\text{Recovery from previous work} - \text{Simulate recovery in the present work}}{\text{Recovery from previous work}} \right| \quad \dots(2.3)$$

CHAPTER 3 Methodology

This chapter contains details on the methodologies used in this research. This section includes the general research flow diagram with the schedule of the research activity, the procedures in the Mathcad simulation and the analysis of the results in the Design Expert software.

3.1 Overview of Research Methodology

Figure 3.1 shows the flow of activity of research.

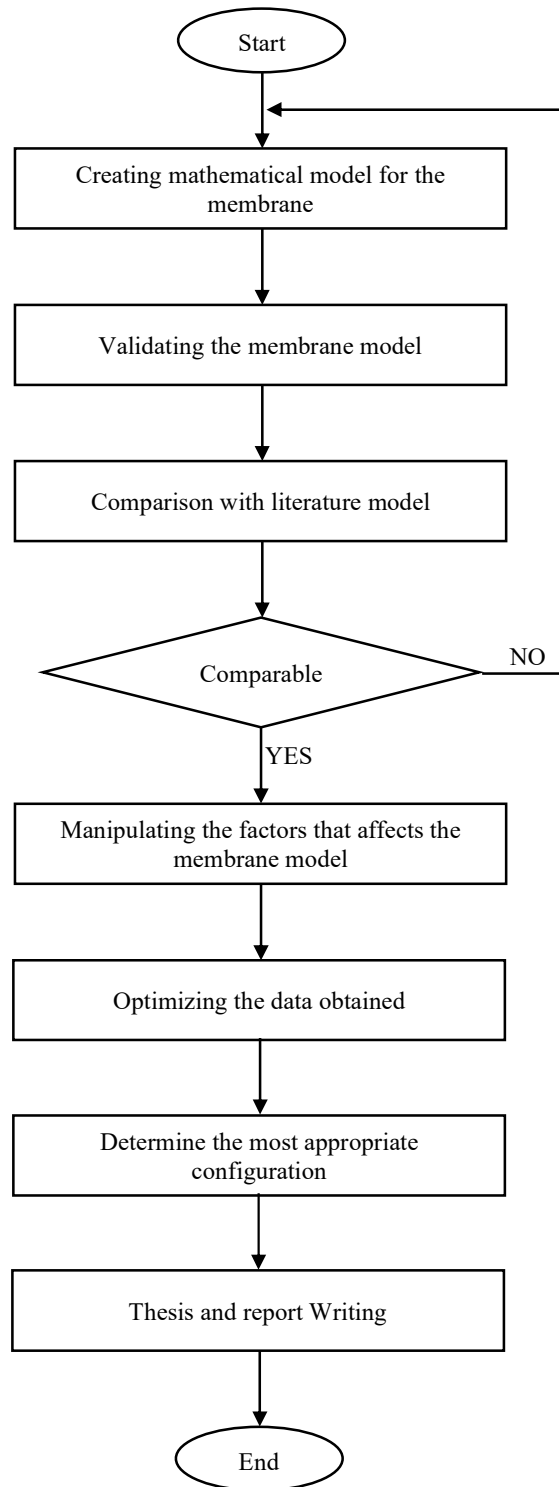


Figure 3.1 Flow of research activities

3.2 Complete Mixing Model

The research is started by creating a simulation program in Mathcad 15 MathSoft by using the complete mixing model equations. The simulation is used to calculate the concentration of gas component species in the retentate and the permeate of the membrane, and the purity and recovery of hydrogen and carbon dioxide from the syngas. The calculations were made based on some assumptions:

- i. The model of gas separation is completely mixed
- ii. The condition of model is isothermal
- iii. The pressure drop in the retentate and permeate stream is negligible
- iv. No interactions between the different component of gas

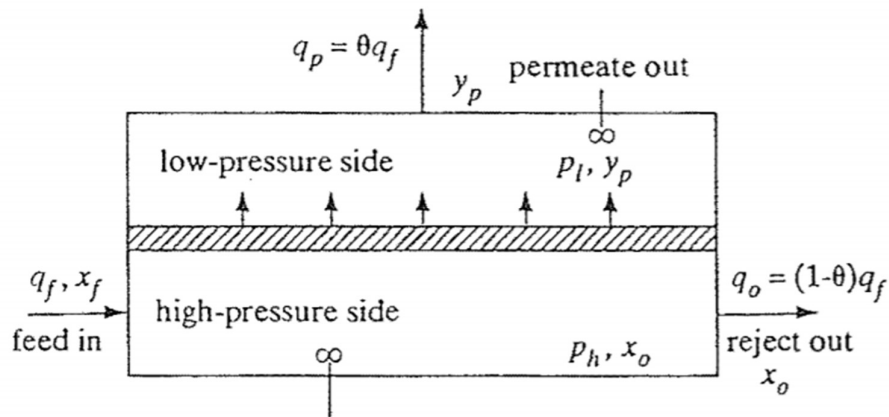


Figure 3.2 Schematic diagram of a complete mixing model for gas separation (Geankoplis, 1993).

The parameters in the **Figure 3.2** represents:

q_f = total feed flowrate (cm^3/s)

q_p = outlet permeate flowrate (cm^3/s)

q_o = outlet retentate flowrate (cm^3/s)

x_f = mole fraction of gas component in the feed

y_p = mole fraction of gas component in the permeate

x_o = mole fraction of gas component in the retentate

P_h = feed pressure cm Hg

P_l = permeate pressure cm Hg

θ = stage cut = $\frac{q_p}{q_f}$

Table 3.1 Properties of the gas components used in the simulation for configuration 1 (carbon dioxide permeable membrane) model

Gas Component	Molecular Weight (g/mol)	Permeability, K $(\frac{\text{cm}^3 \cdot \text{cm}}{\text{s} \cdot \text{cm}^2 \cdot \text{cmHg}})$	Selectivity (Yin <i>et al.</i>, 2017)
Hydrogen	2.016	7.66×10^{-9}	7.7
Carbon dioxide	44.01	5.86×10^{-8}	1
Carbon monoxide	28.01	0.609×10^{-10}	962
Methane	16.04	0.583×10^{-10}	1005

Table 3.2 Properties of the gas components used in the simulation for configuration 2 (hydrogen permeable membrane) model

Gas Component	Molecular Weight (g/mol)	Permeability, K $(\frac{\text{cm}^3 \cdot \text{cm}}{\text{s} \cdot \text{cm}^2 \cdot \text{cmHg}})$	Selectivity (Yin <i>et al.</i>, 2017)
Hydrogen	2.016	1.4×10^{-9}	1
Carbon dioxide	44.01	5.6×10^{-10}	2.5
Carbon monoxide	28.01	0.609×10^{-10}	23
Methane	16.04	0.583×10^{-10}	24

Table 3.3 Parameters of the membrane model

Parameters	
Membrane Area (cm²)	3800
Effective thickness (cm)	0.005
Feed Flowrate (cm³/s)	10000
Stage cut	0.2-0.8
Feed Pressure (bar)	5-30
Permeate Pressure (bar)	1

Table 3.1, **Table 3.2** and **Table 3.3** are properties of gas component and parameters of the membrane used in the simulation of the membrane model.

The overall material balance of the system and material balance of each gas species is as follow:

$$q_f x_f = q_p y_p + q_o x_o \quad \dots(3.1)$$

$$q_f x_{fi} = q_p y_{pi} + q_o x_{oi} \quad \dots(3.2)$$

$$q_f x_{fj} = q_p y_{pj} + q_o x_{oj} \quad \dots(3.3)$$

$$q_f x_{fk} = q_p y_{pk} + q_o x_{ok} \quad \dots(3.4)$$

$$q_f x_{fl} = q_p y_{pl} + q_o x_{ol} \quad \dots(3.5)$$

Where, x_{fi} = mole fraction of H₂ in feed

x_{fj} = mole fraction of CO₂ in feed

x_{fk} = mole fraction of CO in feed

x_{fl} = mole fraction of CH₄ in feed

y_{pi} = mole fraction of H₂ in permeate

y_{pj} = mole fraction of CO₂ in permeate

y_{pk} = mole fraction of CO in permeate

y_{pl} = mole fraction of CH₄ in permeate

x_{oi} = mole fraction of H₂ in retentate

x_{oj} = mole fraction of CO₂ in retentate

x_{ok} = mole fraction of CO in retentate

x_{ol} = mole fraction of CH₄ in retentate

The flux through the membrane was given by:

$$N = \frac{K}{L}(P_h - P_l) \quad \dots(3.6)$$

Where N = flux through the membrane (cm³/cm².s)

K = Permeability of the gas species (cm³.cm/s.cm².Hg)

L = membrane thickness (cm)

P_h = feed pressure (cm Hg)

P_l = permeate pressure (cm Hg)

Since, the flux of membrane is also represented by the following equation:

$$N = A \times q_p \quad \dots(3.7)$$

Where A= membrane area (cm²)

$$\frac{K}{L}(P_h - P_l) = A \times q_p \quad \dots(3.8)$$

$$q_p = \frac{KA}{L}(P_h - P_l) \quad \dots(3.9)$$

The rate of diffusion of each gas component is represented by:

$$q_p \cdot y_{Pi} = K_i \frac{A}{L}(p_h \cdot x_{oi} - p_l \cdot y_{Pi}) \quad \dots(3.10)$$

$$q_p \cdot y_{Pj} = K_j \frac{A}{L}(p_h \cdot x_{oj} - p_l \cdot y_{Pj}) \quad \dots(3.11)$$

$$q_p \cdot y_{Pk} = K_k \frac{A}{L}(p_h \cdot x_{ok} - p_l \cdot y_{Pk}) \quad \dots(3.12)$$

$$q_p \cdot y_{Pl} = K_l \frac{A}{L}(p_h \cdot x_{ol} - p_l \cdot y_{Pl}) \quad \dots(3.13)$$

Where, K_i = Permeability of H_2

K_j = Permeability of CO_2

K_k = Permeability of CO

K_l = Permeability of CH_4

The purity and recovery of H_2 and CO_2 were calculated using equations as follow:

$$H_2 \text{ purity in permeate} = \frac{q_p y_{pi}}{q_p} \times 100 \quad \dots(3.14)$$

$$H_2 \text{ recovery in permeate} = \frac{q_p y_{pi}}{q_f x_{fi}} \times 100 \quad \dots(3.15)$$

$$H_2 \text{ purity in retentate} = \frac{q_o x_{oi}}{x_o} \times 100 \quad \dots(3.16)$$

$$H_2 \text{ recovery in retentate} = \frac{q_o x_{oi}}{q_f x_{fi}} \times 100 \quad \dots(3.17)$$

$$CO_2 \text{ purity in permeate} = \frac{q_p y_{pj}}{q_p} \times 100 \quad \dots(3.18)$$

$$CO_2 \text{ recovery in permeate} = \frac{q_p y_{pj}}{q_f x_{fj}} \times 100 \quad \dots(3.19)$$

$$CO_2 \text{ purity in retentate} = \frac{q_o x_{oj}}{x_o} \times 100 \quad \dots(3.20)$$

$$CO_2 \text{ recovery in retentate} = \frac{q_o x_{oj}}{q_f x_{fj}} \times 100 \quad \dots(3.21)$$

Detailed calculations and mathematical simulations are attached in the Appendix.

3.3 Validation and Comparison

The complete mixing model suggested is validated by comparing the results simulated with the experimental values from published literature. These input parameters are maintained from the values adapted from the respective literature. The **Table 3.4**, **Table 3.5**, **Table 3.6** and **Table 3.7** shows the input parameters of membrane models adapted from the literature and validated by simulating the models by using the complete mixing model.

Table 3.4 Input parameters used in the simulation adapted from Pan, 1986

INPUT PARAMETER	
Feed Flowrate (cm³/s)	500
Feed Pressure (cm Hg)	5223.4
Permeate Pressure (cm Hg)	842.3
Hydrogen Permeability ($\frac{\text{cm}^3 \cdot \text{cm}}{\text{s} \cdot \text{cm}^2 \cdot \text{cmHg}}$)	8.1452×10^{-6}
Membrane Area (cm²)	5.03×10^{-5}
Effective Length (cm)	8×10^{-3}

Table 3.5 Input parameters used in the simulation adapted from Chiappetta *et al.*, 2006

INPUT PARAMETER		
Membrane	A	B
Feed Flowrate (cm³/s)	8	8
Feed Pressure (cm Hg)	380, 760, 1900	380, 760, 1900
Permeate Pressure (cm Hg)	83.5	83.5
Hydrogen Permeability ($\frac{\text{cm}^3 \cdot \text{cm}}{\text{s} \cdot \text{cm}^2 \cdot \text{cmHg}}$)	2.0012×10^{-4}	9.9761×10^{-5}
H₂/CO₂ Selectivity	10	5
Membrane Area (cm²)	0.7854	0.7854
Effective Length (cm)	0.02	0.02