EFFECT OF MEMBRANE SELECTIVITY AND CONFIGURATION ON PURITY AND RECOVERY OF METHANE FROM SELECTED LANDFILL BIO-GAS

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UINVERSITI SAINS MALAYSIA

2021

EFFECT OF MEMBRANE SELECTIVITY AND CONFIGURATION ON PURITY AND RECOVERY OF METHANE FROM SELECTED LANDFILL BIO-GAS

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Project report submitted in partial fulfilment of the requirement for the degree— of

Bachelor of Chemical Engineering

2021

ACKNOWLEDGEMENTS

The final year project was completed to fulfil the requirement for the degree of Bachelor of Chemical Engineering. The completion of the final year project was done with many supports and commitments from some individuals. Hence, I would like to acknowledge the help from these individuals who help me in completing the final year project.

First and foremost, I would like to grab a golden chance to appreciate and express my sincere gratitude to my supervisor, Prof Dr. Mohd Roslee Othman who always gives his invaluable guidance, insightful supervision, endless encouragement and motivation throughout this project. Many thanks for his willingness to discuss the research problems and progress together and give some advice based on my progress. I could not have imagined that without his guidance and advice, this final year project will not be done completely on time.

Apart from that, I would also like to express my gratitude toward his PhD student, Masad Mezher Hasan for her kind cooperation. She is willing to sacrifice her time in helping me besides sharing her valuable knowledge. I would also like to give my special thanks toward graduate senior, Janice Ng Jia Yee who had lent me her hands in guiding me a right way in the final year project and sharing her knowledge and experience throughout the project.

Besides, I would also like to express my gratitude to my fellow friends and course mate. They always give me supports, encouragements, advices and laughter. I am grateful for being able to experience this moment of togetherness. Other than that, I very appreciate to School of Chemical Engineering, Universiti Sains Malaysia for giving final year students a chance to involve in research works and improved our soft skills.

Last but not least, I would not forget to express my appreciation to my family for their supports, motivations and encouragements throughout the years. I would like to thank all the people whom I might have missed out who have helped me directly or indirectly in accomplishment of this project. Thank you very much.

Hiew Yen Kei

July 2021

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LIST OF SYMBOLS

Symbol	**Description**	**Unit**
A	Area of membrane	cm^2
D	Diffusion coefficient of target gas	-
K_i	Permeability of CH_4	barrer
K_j	Permeability of CO_2	barrer
K_k	Permeability of N_2	barrer
K_l	Permeability of O_2	barrer
K_m	Permeability of H_2S	barrer
K_n	Permeability of H_2O	barrer
N	Flux through membrane	$cm^3/cm^2.s$
P_h	Feed Pressure	Pa
P_l	Permeate Pressure	Pa
q_f	Total feed flow rate	cm^3/s
q_o	Outlet reject flow rate	cm^3/s
q_p	Outlet permeate flow rate	cm^3/s
S	Solubility coefficient of the gas	-
t	Membrane thickness	cm
X_{oi}	Mole fraction of CH_4 in reject	-
X_{oj}	Mole fraction of CO_2 in reject	-
X_{ok}	Mole fraction of N_2 in reject	-
X_{ol}	Mole fraction of O_2 in reject	-
X_{om}	Mole fraction of H_2S in reject	-
X_{on}	Mole fraction of H_2O in reject	-

X_{pi}	Mole fraction of CH_4 in permeate	-
X_{pj}	Mole fraction of CO_2 in permeate	-
X_{pk}	Mole fraction of N_2 in permeate	-
X_{pl}	Mole fraction of O_2 in permeate	-
X_{pm}	Mole fraction of H_2S in permeate	-
X_{pn}	Mole fraction of H_2O in permeate	-

Greek Letters

α	Selectivity	-
θ	Stage cut	-
σ	Standard Deviation	-

Subscripts

i	Gas component CH_4	-
j	Gas component CO_2	-
k	Gas component N_2	-
l	Gas component O_2	-
m	Gas component H_2S	-
n	Gas component H_2O	-

LIST OF ABBREVIATION

Symbol	**Description**
ANOVA	Analysis of variance
CCD	Central composition design
CAGR	Compound annual growth rate
CH_4	Methane
CO_2	Carbon dioxide
DE	Design Expert
DOE	Design of experimental
GHG	Greenhouse gases
H_2O	Water
H_2S	Hydrogen sulfide
LPG	Liquefied petroleum gas
MMM	Mixed matrix membranes
N_2	Nitrogen
O_2	Oxygen
PDMS	Polydimethylsiloxane
PI	Polyimide
PSA	Pressure swing adsorption
PSf	Polysulfone
PVC	Polyvinyl chloride
RSM	Response surface methodology
SDGs	Sustainable Development Goals
VOC	Volatile organic compounds

KESAN SELEKTIVITI DAN KONFIGURASI MEMBRAN TERHADAP KETULENAN DAN PEMULIHAN METANA DARIPADA BIO-GAS TAPAK PELUPUSAN

ABSTRAK

Tesis ini membangunkan simulasi model membran untuk pengkayaan metana dari biogas tapak pelupusan terpilih. Simulasi ini digunakan untuk menyelidiki kesan kepekatan metana, tekanan suapan, dan nisbah kadar aliran pada ketulenan dan pemulihan metana, serta kesan kepemilihan terhadap ketulenan dan pemulihan metana dan karbon dioksida dalam biogas. Model pencampuran lengkap disimulasi menggunakan Mathcad dan prestasi dioptimumkan menggunakan kaedah tindakbalas permukaan dalam Design Expert. Penerapan teknologi membran dalam pengayaan metana dari biogas tempat pelupusan sampah dalam projek ini menghasilkan ketulenan dan pemulihan metana 100% pada kepemilihan CO_2/CH_4 sebanyak 623.12, nisbah kadar aliran sebanyak 0.43 dan tekanan suapan sebanyak 3.79 bar menggunakan konfigurasi membran jenis 1 pada kepekatan metana sebanyak 0.53, kebolehtelapan CO_2 sebanyak 3871.00 *barrer*, kebolehtelapan CH_4 sebanyak 6.21 *barrer* dan tekanan kemeresapan sebanyak 1 bar. Prestatsi tersebut telah meningkat naik berbanding dengan kerja-kerja sebelumnya tanpa memerlukan proses pemeringkatan. Pada kandungan metana sebanyak 0.60 dalam gas suapan, peningkatan pemotongan pentas ke 0.80 menyebabkan ketulenan metana dalam buangan menjadi lebih tinggi (100%), tetapi pemulihan metana lebih rendah (37.97%). Tekanan suapan nampaknya tidak mempengaruhi ketulenan dan pemulihan metana dalam buangan dengan ketara, tetapi ia menyebabkan ketulenan dan pemulihan karbon dioksida meningkat sedikit dari 29.72% ke 46.20% pada bahagian resapan. Apabila kandungan metana dinaikkan ke 0.60, ketulenan metana dalam buangan sebanyak 100% dicapai sedangkan pemulihan menurun ke 37.97%. Ralat kecil antara

kerja sebelumnya dan kajian ini adalah 7%, menunjukkan bahawa kaedah ini sangat tepat dalam meramalkan ketulenan dan pemulihan kedua-dua spesies gas menggunakan model pencampuran lengkap.

EFFECT OF MEMBRANE SELECTIVITY AND CONFIGURATION ON PURITY AND RECOVERY OF METHANE FROM SELECTED LANDFILL BIO-GAS

ABSTRACT

This thesis developed a simulation membrane model for methane enrichment from selected landfill biogas. The simulation was used to investigate the impact of methane feed composition, feed pressure, and stage cut on methane purity and recovery, as well as the impact of selectivity on methane and carbon dioxide purity and recovery in biogas. The complete mixing model was constructed in Mathcad and performance was optimized using Design Expert's Response Surface Methodology. The optimization of membrane technology in methane enrichment of biogas from a landfill in this project yield 100 % methane purity and recovery at CO_2/CH_4 selectivity of 623.12, stage cut of 0.43 and feed pressure of 3.79 bar using membrane configuration type 1 at methane concentration 0.53, CO_2 permeability of 3871.00 barrer, CH_4 permeability of 6.21 barrer, permeate pressure of 1 bar. This exceeded the performance of the previous work without staging the membrane process. At the methane composition of 0.60 in the feed gas, increasing the stage cut to 0.80 caused the purity of methane in retentate to be higher (100 %), but lower recovery of methane (37.97%). Feed pressure did not seem to affect the purity and recovery of methane in retentate significantly, but it caused carbon dioxide purity and recovery to slightly increase from 29.72 % to 46.20 % at the permeate side. When the methane composition in the feed was increased to 0.60, the 100 % purity of the methane in retentate was achieved whereas the recovery decreased to 37.97 %. The small error between previous work and the present study was 7 % and suggesting that the mode is highly accurate in forecasting the purity and recovery of the two gas species using the complete mixing model.

CHAPTER 1 INTRODUCTION

1.1 Background

The consumption of fossil fuel and energy in the world increase with rapid urbanization and population growth. This also increases the rate of organic waste production. The higher the consumption of fossil fuel, the higher the amount of greenhouse gases emissions to the atmosphere. Greenhouse gases (GHGs) contain carbon dioxide, methane, nitrous oxide and fluorinated gases, produced from burning of fossil fuels, agricultural and industrial activities that bring the negative impact on the environment and society. With this in mind, global warming would occur if GHG emission is not reduced. To overcome the environmental problem, sustainable development goal (SDG) must be achieved. Sustainable development goal is one of the main objectives that meets the needs of the present without compromising the ability of future generations to meet their own needs (Alayi et al., 2016). Renewable energy is showing a great potential to suit the energy demand in a sustainable way that can meet the SDG. Renewable energy resources such as biomass, solar, hydropower, wind and geothermal can be used to produce the green sustainable products. Thermal technologies that use heat to convert the biomass to an alternatives fuel such as gasification, liquid fraction and pyrolysis are also considered renewable including fermentation and anaerobic digestion (Korbag et al., 2020)**.** Therefore, biogas can be developed as a promising solution to pollution of the environment. Biogas as renewable energy is able to solve the problem of waste from industry, municipality and farm.

Biogas that is produced by the decomposition of organic matter in the absence of oxygen is through anaerobic digestion. Anaerobic digestion can be divided into four steps including hydrolysis, acidogenesis, acetogenesis and methanogenesis. Biogas can be produced from agricultural residual, sewage sludge and landfills. Solid wastes or wastewater are produced from the agri-food industry, beverage industry, alcohol distilleries, pulp and paper industry and other sectors (Chen et al., 2015). **Table 1.1** compares the compositions of biogas obtained from three different sources namely landfills, sewage digesters and farms during anaerobic degradation or combination of aerobic and anaerobic digestion. Methane (CH_4) and carbon dioxide (CO_2) are the two main components in the biogas from all the three sources. The other gases present in the biogas streams are hydrogen sulfide (H_2S), nitrogen (N_2), water vapor (H_2O) and traces of other volatile organic compounds (VOC) (Haider et al., 2016).

In this study, we used biogas from landfill source to purity methane. Since biogas from landfill contains methane, which is one of the greenhouse gases, purifying and capturing the gas from being release into the surrounding would be the aim of this project. Another greenhouse gas, carbon dioxide (CO_2) which is the second component of the biogas beside methane (CH_4) shall also be captured and purified simultaneously with methane.

Table 1.1 Biogas composition from different sources (Haider et al., 2016)

Gas	**Composition (mol %)**		
	Landfill	Sewage digester	Farm
CH_4	47-57	61-65	55-58
CO_2	37-41	34-38	37-38
N_2	1-17	Trace	Trace
O_2	0-2	Trace	Trace
H_2S	<1	<1	<1
H_2O	4-7	4-7	4-7
Aromatic hydrocarbon	Trace	Trace	Trace

In general, the calorific value of biogas is 21.5 MJ/m^3 (Chen et al., 2015). After upgrading biogas into methane enriched gas, its calorific value rises to 35 - 45kJ/g meeting the energy standard of diesel, kerosene and LPG calorific values. Hence, the gas can be applied sustainably to generate heat, electricity and it can also be used as fuel for transport. Biogas is a renewable source of energy, it presents low carbon in biofuel resulting in emitting fewer greenhouse gases to the atmosphere, reducing the solid wastes and decreasing the odor released to the surrounding. This will drive the demand for biogas further to the point that it can becomes a substitute for conventional fuels. The enriched methane from biogas can also be to high quality fertilizer cosy effectively and ensure the safety of the manufacturing process by removal of the toxic gas such as H_2S that otherwise would be present if untreated biogas was used. As a result, the interest in developing biogas has rekindled especially during the pandemic and inflation.

Biogas in the global market was valued at USD 55.1 billion in 2019 and is anticipated to expand at a CGAR of 4.48 % over a few more years to come (Grand View Research, 2020). Major countries in the EU include Germany, UK, Italy and Spain are starting to develop biogas production to reduce the use of fossil fuel in transportation and reduce greenhouse gases emissions. The EU commitment to be independent of petroleum fuel by 2030 demonstrates the need to exploit biogas resources such as landfills. In Malaysia, landfills are the major source of methane emission of 53%, followed by the palm-mill effluent that generates 38%, swine manure of 6% and industrial effluent of 3% (Yong et al., 2019). The generation of methane from landfills in Malaysia is shown in **Figure 1.1**. Therefore, there is a potential to use methane gas to produce electricity sustainably in Malaysia.

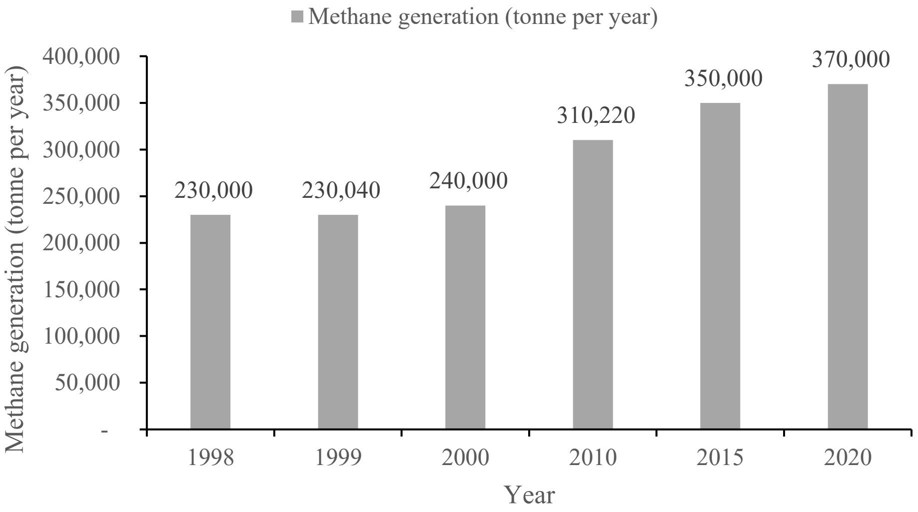


Figure 1.1 The generation of methane gas from 1998 to 2015 and the predicted value for 2020 (Yong et al., 2019)

The calorific power of biogas is directly proportional to methane content. The calorific value of pure methane is 38.1 MJ/m^3. The presence of carbon dioxide and the traces of impurities in the biogas cause the calorific value to decrease and corrosion to occur. Upgrading biogas needs to pass through two processes which are cleaning process and enrichment methane process (Masebinu et al., 2014). The cleaning process is to remove the traces of impurities such as acid gas from the biogas to reduce the corrosion of combustion engine, while the enrichment methane process is removing the carbon dioxide from biogas. The cleaning process and enrichment methane process not only increase the methane concentration in biogas, but it also improves the calorific value of the biogas. There are several technologies had been developed to separate the impurities from biogas and increase the calorific value of biogas to fulfil the demand for transportation and electricity generation as an alternative to fossil fuel. The common technologies are adsorption, absorption, cryogenic separation and membrane separation. Adsorption and absorption units generally have high energy demands and require relatively large equipment (Vrbová and Ciahotný, 2017).

Membrane separation technology has been interesting and attractive due to its simplicity, favourable economics, low energy demands, low carbon footprint and easy maintenance (Haider et al., 2016). Recently, membrane separation technologies have become very competitive as it involves many applications such as purification of wastewater, potable water production and gas separation (Vrbová and Ciahotný, 2017). There are many types of membrane materials used in enrichment the purity and recovery of methane from biogas like polymer membrane, mixed matrix membrane and inorganic membrane (Vrbová and Ciahotný, 2017). In this study, a hollow fiber membrane is used in improving the purity and recovery of methane from biogas produced from several countries’ landfills.

1.2 Sustainability

Development and use of renewable energy have become important for long-term sustainability. Biogas development is considered as sustainable energy and many countries started to develop this sector to replace the usage of fossil fuel. This development can be done on a micro scale and on a macro scale. Biodegradable wastes derived from human social and industrial activities undergo anaerobic digestion to produce biomethane, which can increase the calorific value of biogas and reduce the GHGs emissions to the atmosphere. Biogas development can be used towards achieving the 17 Sustainable Development Goals (SDGs) promoted by the UN. This is because biogas development from landfills can reduce the total volume of waste entering the landfills, increase the lifespan of existing landfills and offsetting large repercussions associated with the burning of fossil fuels to generate electricity (Yong et al., 2019). One of the targets in 17 SDGs is the 7th SDG which is ensuring access to affordable, reliable, sustainable and modern energy for all (WBA, 2017). It can reduce the usage of fossil fuel-based energy sources by replacing with biogas and capturing waste heat from co-generating units linked to the biogas plants. Utilizing locally produced wastes and crops to generate energy for rural and remote communities. Besides, it also can be used to achieve the 11th SDG by making cities and human settlements inclusive, safe, resilient and sustainable by preventing the disease spread through collection and proper management of organic waste (WBA, 2017). Substituting fossil fuel with biomethane can improve urban air quality by using it in vehicles, domestic cooking and heating. Moreover, the implementation of biogas can divert away mixed wastes from entering landfills. This reduces the collective release of hazardous bad odor gases from landfills which result from the complex chemical reaction and degradation of waste within landfills (Yong et al., 2019). In addition, biogas development towards 13th SDG for taking urgent action to combat climate change and its impacts as biogas can reduce carbon dioxide emissions by replacing fossil-fuel-based energy sources with biogas and commercial fertilizers with digestate biofertilizer, reduction of methane and generation of renewable energy from food and other organic wastes, capturing emissions from landfills and reducing deforestation by replacing solid-biomass-based domestically (WBA, 2017).

In this study, enrichment methane and carbon dioxide from biogas to reach the natural gas standard by using the membrane gas separation are attempted. Process optimization which is critical for attaining improved purity and recovery while using the least amount of energy possible, is also performed. The mathematical model and simulation can be considered as one of the optimization processes which is implemented in membrane gas separation to reach 7th SDG by ensuring access to affordable, reliable, sustainable and modern energy for all. It is important in maximizing production while preserving the environment as anticipated from this project.

1.3 Problem Statement

Biogas is produced by anaerobic fermentation of biomass such as animal manures, sewage sludge and landfill. There are pretreatment process can be applied in biogas production which is aerobic pre-digestion that accelerates the hydrolysis step, reduce hydrogen sulfide concentration, prevent the accumulation of VFAs and increase the biogas production in anaerobic digestion (Rashvanlou et al., 2021). Biogas is renewable energy that has the potential to be a substitute for fossil fuel and to reduce the consumption of diesel in the transportation sector. It also reduces GHG emissions to the atmosphere. Municipal solid waste landfills generate biogas and leachate. Biogas can be used for heating and electricity production in many countries, however its use for vehicle fuel production is considered effective but unsafe because it contains trace compounds such as sulphur, chloride, carbon dioxide and silicon compounds which must be removed to meet the fuel quality standard.

The calorific value of biogas is low since the amount of carbon dioxide is high and there are some traces of hydrogen sulfide and volatile organic compounds. In order to increase the calorific value and reduce the unwanted components such as CO_2 and H_2S, membrane separation technology is introduced and applied to reduce the carbon dioxide and increase the purity and recovery of methane in biogas. The main objective of this thesis is to simulate the methane enrichment from closed landfill biogas by using the hollow fibre membrane in Mathcad. The simulated data generated by the Mathcad model will be validated with the experimental results. A process simulator can enhance the operating configuration and operating parameters to accomplish the desired purity and recovery. The study of parameters such as stage-cut, feed pressure, feed composition and membrane selectivity is employed to understand their effects on the enriched methane's recovery and purity.

1.4 Objectives

The objectives of the study are:

i. To study the effect of operating parameters such as stage-cut, pressure and feed composition on methane and carbon dioxide purity and recovery by using a statistical tool combined with complete mixing model.

ii. To study the effect of membrane parameters such as membrane selectivity and configuration on methane and carbon dioxide purity and recovery by using a statistical tool combined with complete mixing model.

iii. To determine the suitable membrane configuration for the optimum methane enrichment from biogas.

CHAPTER 2 LITERATURE REVIEW

Landfills are categorized into four types, which are industry waste landfill, municipal solid waste landfill, hazardous waste landfill and green waste landfill. Landfill undergoes anaerobic digestion to produce biogas. Biogas is a renewable fuel to reduce the environment of fossil fuels. Biogas produced from organic waste can be one promising solution. Therefore, the waste in the landfills consist of complex organic compounds that can undergo anaerobic digestion to produce biomethane and replace the fossil fuel. There is a pretreatment process that can be applied in biogas production which is aerobic pre-digestion. Aerobic digestion is a process through aerobic bacteria that break down organic matter including animal manure, landfill and food wastes in the presence of oxygen to produce carbon dioxide, water and some organic compounds. This process is implemented before anaerobic digestion can accelerate the hydrolysis step, reduce hydrogen sulfide concentration, prevent the accumulation of VFAs and increase the biogas production in anaerobic digestion (Rashvanlou et al., 2021). Anaerobic digestion consists of four steps namely hydrolysis, acidogenesis, acetogenesis and methanogenesis. The complex organic compounds from the wastes in landfills can be broken down into simple soluble molecules by hydrolytic microorganisms (Abdelgadir et al., 2014). For example, cellulose to sugars or alcohols and proteins to peptides or amino acids by using hydrolytic enzymes.

Hydrolysis reactions is shown as below:

$$C_{24}H_{40}O_{20}{:}H_2O + 3H_2O \rightarrow 4C_6H_{12}O_6 \tag{2.1}$$

The acidogenesis stage is a fermentation stage, which converts the simple soluble molecules into short chain fatty acids, commonly known as volatile fatty acids or intermediates products, carbon dioxide and hydrogen and ammonia. Three types of acidogenesis reactions where glucose is transfer to ethanol, propionate and acetic acid respectively (Abdelgadir et al., 2014).

$$C_6H_{12}O_6 \rightarrow 2CH_3CH_2OH + 2CO_2 \tag{2.2}$$

$$C_6H_{12}O_6 + 2H_2 \rightarrow 2CH_3CH_2COOH + 2H_2O \tag{2.3}$$

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2 \tag{2.4}$$

The volatile fatty acids and ethanol produced during acidogenesis are metabolized to acetic acid, carbon dioxide and hydrogen. There are some examples such as propionate being converted into acetate which is only achievable at low hydrogen pressure and show as following (Abdelgadir et al., 2014).

$$CH_3CH_2COO^- + 3H_2O \rightarrow CH_3COO^- + H^+ + HCO_3{}^- + 3H_2 \tag{2.5}$$

Conversion of glucose and ethanol to acetate by acetogenic bacteria shown as below.

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2 \tag{2.6}$$

$$CH_3CH_2OH + 2H_2O \rightarrow CH_3COO^- + H^+ + 2H_2 \tag{2.7}$$

In the methanogenesis stage, bacteria convert CH_3COOH and H_2 into CO_2 and CH_4 (Abdelgadir et al., 2014).

$$CH_3COOH \rightarrow 2CH_4 + CO_2 \tag{2.8}$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \tag{2.9}$$

The general composition of biogas from landfill is 40 % to 57 % of methane, 37 % to 41 % of carbon dioxide and others are impurities components such as hydrogen sulfide, water vapor and volatile organic component (Haider et al., 2016). Raw biogas cannot use directly as vehicle fuel due to its big amount of hazardous impurities and carbon dioxide which reduces the heating value of biogas (Spitzer et al., 2018). **Table 2.1** illustrate the standard of the transportation sector for biogas in France and Sweden. Various technologies have been developed to enrichment the purity and recovery of methane from the biogas landfill and improve the calorific value of biogas, among these technologies are absorption and physical separation.

Table 2.1 Biogas quality standard for transportation sector in France and Sweden (Awe et al., 2017)

Compound	Unit	France	Sweden
Wobbe index (H)	MJ/Nm^3	48.2-56.5	44.7-46.4
Lower (L)	MJ/Nm^3	42.5-46.8	43.8-47.3
Methane	Vol %	≥ 86	≥ 97
Carbon dioxide	Vol %	≥ 2.5	≤ 3
Hydrogen	Vol %	≤ 6	≤ 0.5
Oxygen	Vol %	≤ 0.001	≤ 1
$CO_2+O_2+N_2$	-	-	≤ 5
Hydrogen Sulfide	ppm	≤ 5	≤ 15.2
Sulfur	ppm	≤ 30	≤ 23
Ammonia	ppm	≤ 3	≤ 20

2.1 Separation Technologies

One of the absorption processes to enhance the biogas to biomethane is water scrubbing. The principle of absorption is the carbon dioxide is more soluble than methane. For water scrubbing process, it consists of two columns absorption column and desorption column. When the biogas passes through the absorption column, the carbon dioxide is absorbed in the water at certain pressures. The water can be reused by decompressing water and by feeding a stripping gas at the desorption column. Based on Scholz et al. (2013), this process does not require heat to remove carbon dioxide from water. The pressurized water scrubbing process was using water as a solvent, which is safer than using chemical solvents. However, the water scrubbers operated at pressure not more than 10 bar, the gas must be compressed to grid pressure. The pressurized water also absorbs the H_2S component from biogas, but H_2S is hard to remove from water which leads to some of the water that must remove to prevent the accumulation of H_2S in it.

For the physical processes, such as pressure swing adsorption and membrane separation. Pressure swing adsorption (PSA) processes are based on the mechanism that gas molecules can be selectively adsorbed to solid particles' surface according to molecular size (Sun et al., 2015). This technology can separate CH_4 from other gas molecules such as N_2, O_2 and CO_2. This is because the molecular size of CH_4 is larger than other gas molecules. The concentration of CH_4 can reach about 96-98 % and CH_4 losses are about 2-4 % (Sun et al., 2015). However, this technology will lose more CH_4 at higher purity requirements cannot be avoided as some methane will adsorb on the solid surface (Scholz et al., 2013). The membrane process is used to separate the feed composition into two streams via a semipermeable barrier. The components that pass through the barrier are called permeate, while the others that do not pass through the barrier are called retentate (Baumgarner et al., 2009). The use of membrane has many advantages such as lower operating cost, easier maintenance, higher flexibility, no chemical substances required, the absence of phase change and most important is low energy consumption (Masebinu et al., 2014).

2.2 Membrane Separation Technology

In this study, we focus on membrane technology to improve the methane content in the biogas to fulfil the standard. Three types of processes can be considered depending on the membrane structure and permeation mechanism including Knudsen's diffusion via microporous barriers, molecular sieving with ultra-microporous membranes and diffusion through non-porous, dense membrane based on solubility diffusion mechanism (Harasimowicz et al., 2007). Gas separation through dense and non-porous membrane depends on differences in permeability of the gases through an appropriate membrane. The gas penetrates the nonporous membrane based on size, solubility and diffusivity. The performance of membrane depends on permeability and selectivity. Permeability is defined as the ability of membrane to allow the gas molecules to diffuse through the material of the membrane. Large molecule of gas consists of a low diffusion coefficient. The selectivity of the membrane is a measure of the ratio of permeability of the relevant gases for the membrane. The equation of permeability shown is given by (Jeon and Lee, 2015):

$$K = D \times S \tag{2.10}$$

Where, K is the permeability coefficient of the gas (Barrer), D is the diffusion coefficient of the target gas through the membrane and S is the solubility coefficient of the gas. The characteristic of gas separation membrane is determined by its selectivity with the Equation (2.11) (Jeon and Lee, 2015).

$$\alpha_{AB} = {}^{K_A}\!/_{K_B} \tag{2.11}$$

Where, K_A and K_B are the permeability coefficient of gas A and B. The theoretical permeability can be determined by using Equation (2.12) (Ahmad et al., 2004; Jinsoo and Othman., 2019).

$$K = \frac{\varepsilon}{z\tau RT}\left\{\frac{P_{avg}r_p^2}{8\mu} + \left[\frac{2(r_p - r_g}{3}\sqrt{\frac{8RT}{\pi M}} + \frac{1}{\varepsilon}(D_s\rho_m f)\right]\right\}, for\ r_p \geq r_g \tag{2.12}$$

Where ε is the membrane porosity, z is the compressible factor, R is the gas constant in unit of kg $m^2s^{-2}kgmol^{-1}K^{-1}$, T is temperature in unit of K, P_{avg} is the average pressure in membrane pore in unit of $kgm^{-1}s^{-2}$, r_p is the radius of membrane pore in unit of m, μ is the viscosity of gas in unit of kg $m^{-1}s^{-1}$, M is the mass of molecule in unit of kg/kg mol, D_s is the surface diffusion in unit of m^2s^{-1}, ρ_m is the density of membrane in unit of kgm^{-3} and f is the equilibrium loading factor with unit of mol/kg.

Membrane separation technology is one of the techniques to remove carbon dioxide from the biogas and increase the purity of methane. Various membrane for CO_2/CH_4 separation has been studied by many researchers, such as chemical properties, physical properties, module configuration and membrane properties to develop more efficiency of carbon dioxide removal system. Membrane with high selectivity, and great permeability increases the purity of the product. The purity and recovery of CH_4 can be affected by the feed pressure, feed flow rate, membrane thickness, membrane area and module configuration.

There are many types of membrane materials such as polymeric, inorganic materials and mixed matrix membrane (MMM) have been investigated by many researchers. Cellulose acetate and polyimide membrane are commonly used in industry as they have the best combination of permeability and selectivity. The cellulose acetate membrane was preferred because of its high carbon dioxide permeability and selectivity 40-50 GPU and 15-37.2 respectively (Pan.C.Y, 1986).

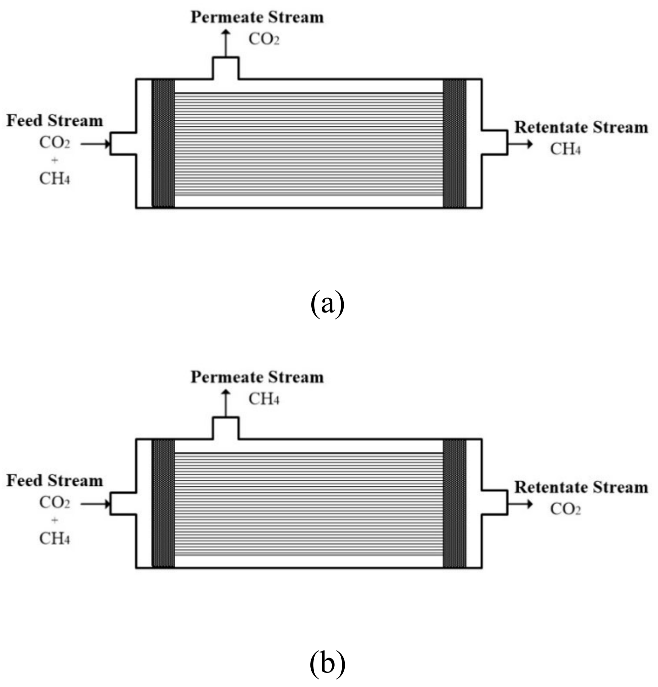
Selectivity is the most important parameter in the membrane process, which can affect the purity and recovery of methane and carbon dioxide. Many membranes reported that CO_2/CH_4 selectivity ranges from 8.6 to 37.2 for polyimide membranes (Kundu et al., 2013). The other type of membrane such as cellulose triacetate was used for gas separation. The permeability of carbon dioxide, nitrogen and methane are 60, 2.6 and 2.9 GPU (Kundu et al., 2013). The selectivity of CO_2/CH_4 is 20.7 (Kundu et al., 2013). Moreover, there is another type of membrane was fabricated from polysulfone (PSF) coated with polydimethylsiloxane (PDMS). The permeability of carbon dioxide and methane in this membrane are 5.96 and 158 GPU with selectivity of 26.5 (Shin et al., 2017). Different types of membrane materials consist of different permeability and selectivity of each gas species and it tabulated in **Table 2.2**. Increase the selectivity of carbon dioxide to methane is correlated with better carbon dioxide capture and removal.

Table 2.2 Permeability and Selectivity of different membrane material

Polymer	**Permeability (Barrer)**			**Selectivity**	**Reference**
	N_2	CO_2	CH_4	CO_2/CH_4	
Poly (4-methyl, 1-penten)	6.7	84.6	14.9	5.68	**(Harasimowicz et al., 2007)**
Polyimide TMPA-6FDA	35.6	440	28.2	15.6	
PPO	3.53	65.5	4.10	16.0	
Polysulphone	0.20	4.90	0.12	33.6	
Cellulose acetate	0.12	2.4	0.1086	22.1	**(Alqaheem et al., 2017)**
Polydimethylsiloxane (PDMS)	606.06	4000	1538.46	2.6	
Poly(trimethylsilylpropyne)	-	18,000	4,186	4.3	**(Jeon and Lee, 2015)**
Poly (methyl methacrylate)	-	0.50	0.003	140	
Polysulfone (PSF)	-	4.60	0.21	21.9	

Another factor that can affects the purity and recovery is stage cut. Stage cut is the ratio of the permeate flow rate to feed flow rate. The higher the stage cut, the higher the purity of methane at retentate, but the lower the recovery of methane. The driving force to push the molecules to the membrane cause the recovery of methane to decrease.

There are two sorts of membrane configurations that are dependent on the membrane's selectivity, the first of which is represented in **Figure 2.1 (a)** (membrane configuration of type 1) is used when carbon dioxide permeability across the membrane is greater than methane permeability. For this configuration, CO_2/CH_4 selectivity is greater than unity. The second membrane configuration is shown in **Figure 2.1 (b)** is used when permeability of methane across the membrane is greater than permeability of carbon dioxide. The selectivity of CH_4/CO_2 is higher than unity.



(a)

(b)

Figure 2.1 Hollow fiber membrane configuration in methane enrichment for membrane configuration of type 1 or CO_2/CH_4 selectivity and (b) membrane configuration of type 2 or CH_4/CO_2 selectivity(Li Chin Law et al., 2019)

Based on Pan's (1986) research, the cellulose acetate membrane was used to separate the CO_2 and H_2S from the sour natural gas. Cellulose acetate membrane contains an effective CO_2/CH_4 selectivity of 36 (Pan.C.Y, 1986). Methane enrichment and recovery in retentate stream, while carbon dioxide was removed in the permeate stream. **Table 2.3** shows that the parameters used in the membrane separation process. The feed pressure and permeate pressure were at 3528 kPa and 92.8 kPa respectively. Through the experiment, the purity of carbon dioxide on permeate side could be reached up to 95 % at the stage cut of 0.42. When the stage cut was increased to 0.61, the purity of carbon dioxide decreased to 80%.

Table 2.3 Parameters in membrane separation (Pan.C.Y, 1986)

Parameters		**Value**
Permeability (Barrer)	CO_2	1016.00
	CH_4	28.22
	C_2H_6	7.76
	C_3H_8	1.51
Feed gas (mole fraction)	CO_2	0.485
	CH_4	0.279
	C_2H_6	0.1626
	C_3H_8	0.0734

From the Kaldis (2000), the modelling of polyimide hollow fiber membrane module was used in separations of multicomponent gas mixtures. In this work, the module can be achieved a concentration of methane about 25 % and carbon dioxide about 14 % in the retentate stream with a stage cut of 0.22. As the stage cut increase, the concentration of methane in the retentate stream was increased to 39 %, while the concentration of carbon dioxide in the retentate stream was 12 % (Kaldis et al., 2000). The parameters used in the membrane separation was shown in **Table 2.4**.

Table 2.4 Parameters in membrane separation (Kaldis et al., 2000)

Parameters		**Value**
Permeability (Barrer)	CO_2	2362.20
	CH_4	93.98
	H_2	7366.00
	C_2H_6	16.26
Feed gas (mole fraction)	CO_2	0.115
	CH_4	0.167
	H_2	0.675
	C_2H_6	0.043
Pressure (bar)	Feed	20
	Permeate	1

Modelling of multicomponent gas with cellulose triacetate hollow fibre membrane was used in methane enrichment (Kundu et al., 2013). At 0.8 stage-cut the purity of methane at retentate was 93.85%, but at 0.2 stage-cut the purity of methane was 58.5% at a pressure of 600 kPa which was reported by Kundu et al. (2013). For a pressure of 400 kPa, the purity of methane at retentate was 91 % with a stage cut of 0.8, while at the stage cut of 0.2 the purity of methane at retentate was 56 %. **Table 2.5** illustrates the parameters in the membrane separation (Kundu et al., 2013).

Table 2.5 Parameters in membrane separation (Kundu et al., 2013)

Parameters		**Value**
Permeability (Barrer)	CO_2	1524
	CH_4	73.66
	N_2	91.44
Feed gas (mole fraction)	CO_2	0.40
	CH_4	0.40
	N_2	0.20

Shin et al.(2017) used the membrane that was fabricated from polysulfone (PSF) coated with polydimethylsiloxane (PDMS). For single stage of membrane separation, at 0.76 stage-cut the purity and recovery of methane at retentate were 98.53 % and 39.06 %, while the purity and recovery of carbon dioxide were 52.85% and 97.71% at a pressure of 7 bar with 40 % mole fraction of carbon dioxide and methane as a balance which was reported by (Shin et al., 2017). For double stage of membrane separation, at 0.76 stage-cut the purity and recovery of methane at retentate were 100% and 40.4%, while the purity and recovery of carbon dioxide were 52.70 % and 99.80 % at a pressure of 7 bar with 40 % mole fraction of carbon dioxide and methane as a balance which was reported by (Shin et al., 2017). **Table 2.6** illustrates the parameters in the membrane separation (Shin et al., 2017).

Table 2.6 Parameters in membrane separation (Shin et al., 2017)

Parameters		Value
Permeability (Barrer)	CO_2	3871
	CH_4	146
Feed gas (mole fraction)	CO_2	0.40
	CH_4	0.60

Based on Seman et al.(2019), the fluorinated polyimide (6FDA-TMPA) hollow fiber membrane was developed in Mathcad and used in the methane enrichment from closed landfill biogas. At stage cut of 0.3, the mathematical model has optimized the purity of methane in retentate from 87.26 % to 99.87 % and the recovery from 91.63 % to 99.49 %. The parameters were used in the membrane separation which can be seen in **Table 2.7**.

Table 2.7 Parameters in membrane separation (Seman et al., 2019)

Parameters		Value
Permeability (Barrer)	CO_2	440.0
	CH_4	28.2
	N_2	35.6
	O_2	111.0
	H_2S	1.0
	H_2O	1.0

Feed gas (mole fraction)	CO_2	0.38934
	CH_4	0.55000
	N_2	0.05000
	O_2	0.00400
	H_2S	0.00002
	H_2O	0.00664

There is a trade-off between purity and recovery. The higher the purity, the lower the recovery. Process optimization plays an important role to balance in achieving higher purity and recovery at the lowest possible energy consumption. Optimization is the essence of the latest industrial revolution (IR-4) in many modern industrial processes (Seman et al., 2019). It is important in maximizing production while preserving the environment. The mathematical model and simulation can be considered one of the optimization processes. Mathematical modelling had been reported by literature to investigate the gas transport through the hollow fiber membrane (Coker et al., 1998; Kaldis et al., 2000; Pan.C.Y, 1986). The Pan's model is accepted since the most practical representation of multicomponent gas transport via high-flux asymmetric hollow fiber membranes (Pan.C.Y, 1986). However, the model solution was using the trial-and-error method to estimate the initial pressure and concentration profiles along fiber length (Chu & Lindbråthen, 2019). There are some literature (Kaldis et al., 2000; Kundu et al., 2013) were reported to use the orthogonal collocation method to approximate nonlinear differential equations which yield fewer algebraic equations to improve the solution accuracy. In this study, the complete mixing membrane model considers pressure drop neglected in both feed and permeate sides, is developed to simulate gas transport through hollow fiber membrane modules. The process was simulated using Mathcad version 15 from MathSoft Incorporation. The simulation process surrounded by a single stage of membrane model. The mathematical model used and validated with previous work by using the mean absolute percentage error (MAPE). MAPE is used to assess the forecasting power of the model.

In a complete mixing model, the material balance of each gas species in the biogas was maintained and the permeability of each gas species was constant through the membrane (Seman et al., 2019). In the model, there is a relationship between purity-recovery and the membrane operation conditions. The purity and recovery of carbon dioxide in permeate and methane in reject was optimized by using a Response Surface Methodology (RSM). To generate the optimized result, Design Expert 12.0 will be used to generate the design matrix and responses. Finally, the mathematical model developed to study the effect of the operating parameters, membrane parameters and configuration of the membrane on the methane and carbon dioxide recovery and purity.

CHAPTER 3 METHODOLOGY

3.1 Research Methodology

Overall, of this report focused on the simulation of methane enrichment and recovery by membrane. **Figure 3.1** shows the activities of the research.

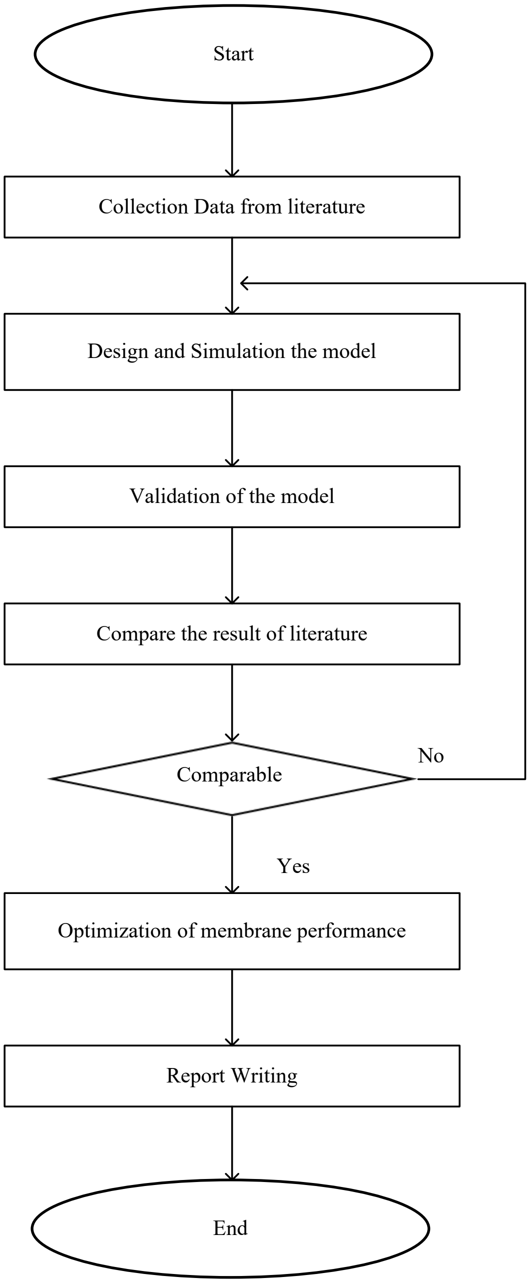


Figure 3.1 Activities of research

First, the process model of membrane for methane enrichment from closed biogas landfill is developed. Mathcad version 15 from MathSoft Incorporation is used for modelling and simulation of the process. Through the specify literature, the parameters, assumptions, and information such as operating conditions have been considered for the membrane. Next, validation of the model with the specify reference. In order to study the effect of operating parameters such as feed pressure, feed compositions, stage-cut, selectivity, simulation and design the response surface methodology (RSM) was employed. Design Expert 12.0 will be used to generate a design matrix and response. In this simulation, the responding variables are the amount of methane and carbon dioxide in the respective outlet stream. Response is simulated by using Mathcad model developed following the run number suggested by Design Expert 12.0. The performance index of methane enrichment by membrane is the purity and recovery of methane and carbon dioxide. In the working with complete mixing model, some assumptions are made as below:

i. Pressure drops in feed permeate side is neglected.
ii. Isothermal condition is applied in the whole membrane.
iii. Permeability of all the component gases is constant.
iv. Ideal gas behaviour is assumed.

Although the commercial membrane such as polysulfone (PSF), polyethersulfone (PES), polyamide (PA), polyimide (PI) and cellulose acetate could be used in gas separation, but most of them still have a limitation between permeability and selectivity (Roslan et al., 2020). In order to solve this limitation, multilayer-coated membrane was generated by forming a PDMS layer on the surface of PSF membrane which able to improve the membrane separation performance and improve the purity and recovery of methane from landfill biogas. This mixed matrix membrane is