CORRELATING PARAMETERS WITH METHANE PURITY AND RECOVERY BY PRESSURE SWING ADSORPTION IN METHANE ENRICHMENT FROM BIOGAS

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by

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

Symbol	Description	Unit
Ci	gas phase concentration of component i	mol/m^3
D_L	axial mass dispersion coefficient	m^2/s
f	sphericity of the adsorbent	-
IPi	parameters of extended Langmuir isotherm	mol/kg, 1/bar, K
ksi	lumped mass transfer coefficient	1/s
Pi	partial pressure.	Pa
qi	adsorption capacity	mol/g
r_p	radius of the adsorbent particle	mm
T	temperature	K
t	time	s
Vz	physical velocity	m/s

Greek symbols

α	axial points	-
ε_b	total bed porosity	-
ε_i	interparticle voidage	-
ρ_s	adsorbent bulk density	kg/m^3
ρ_g	gas phase molar density	kg/m^3
μ	gas mixture viscosity	kg/m.s

LIST OF ABBREVIATION

Symbol	Description
ANOVA	Analysis of variance
CCD	Central composite design
CH_4	Methane
CMS	Carbon molecular sieve
CO_2	Carbon dioxide
DOE	Design of experimental
H_2S	Hydrogen sulphide
PSA	Pressure swing adsorption
SDG	Sustainable development goal
RSM	Response surface methodology
VPSA	Vacuum pressure swing adsorption

MENGHUBUNGKAN PARAMETER DENGAN KETULENANAN METANA DAN PEMULIHAN OLEH PENYERAPAN AYUNAN TEKANAN DALAM PENGAYAAN METAN DARIPADA BIOGAS

ABSTRAK

Model simulasi pengayaan metana daripada biogas melalui penjerapan ayunan tekanan (PSA) menggunakan Aspen Adsorption™ versi 11 telah dikaji dengan campuran binari biogas yang terdiri daripada komposisi berbeza CH_4 dan CO_2. Keluk terobosan data simulasi dan data eksperimen dibandingkan untuk mengesahkan model. Perbandingan itu mendedahkan bahawa lengkung terobosan metana dan karbon dioksida daripada eksperimen dan simulasi adalah dalam persetujuan yang baik. Kesan parameter reka bentuk seperti tekanan penjerapan, kepekatan CO_2 dalam suapan dan tempoh penjerapan, ke atas ketulenan metana dan pemulihan telah dianalisis. Peningkatan tekanan penjerapan membawa kepada jumlah CO_2 yang lebih tinggi terserap dan meningkatkan ketulenan CH_4 tetapi pemulihan CH_4 yang lebih rendah disebabkan oleh masa pengekalan yang lebih lama dalam lajur. Kepekatan CO_2 yang lebih tinggi dalam suapan dan masa penjerapan mengakibatkan pengurangan ketulenan metana manakala pemulihan biometana meningkat disebabkan masa tinggal yang lebih lama pada masa penjerapan yang meningkat. Dalam kerja ini, parameter operasi telah dioptimumkan untuk menghasilkan ketulenan CH_4 maksimum dan pemulihan daripada unit PSA. Ketulenan dan pemulihan CH_4 yang dioptimumkan direkodkan pada 99.996 % dan 98.785 % masing-masing pada tekanan penjerapan 3 bar, 50% kepekatan CO_2 dan 143 saat masa penjerapan. Kajian ini mengunakan gel silika sebagai penjerap yang berkesan dalam mengasingkan CO_2 untuk menghasilkan ketulenan biometana yang tinggi. Model yang dibangunkan mempunyai kecekapan yang tinggi untuk membuat ramalan prestasi menaik taraf biogas oleh PSA.

CORRELATING PARAMETERS WITH METHANE PURITY AND RECOVERY BY PRESSURE SWING ADSORPTION IN METHANE ENRICHMENT FROM BIOGAS

ABSTRACT

Simulation model of methane enrichment from biogas by pressure swing adsorption (PSA) using Aspen Adsorption™ version 11 was studied with binary mixture of biogas consisting of different compositions of methane and carbon dioxide. Breakthrough curves of simulated data and experimental data were compared to validate the model. The comparison revealed that methane and carbon dioxide breakthrough curves from experiment and simulation was in a good agreement. The effects of design parameters such as adsorption pressure, CO_2 concentration in the feed and adsorption duration, on methane purity and recovery were analysed. Increase in adsorption pressure led to higher amount of carbon dioxide being adsorbed and improved purity of methane but lower methane recovery due to longer retention time in the column. Higher CO_2 concentration in the feed and adsorption time resulted in the reduction of methane purity while biomethane recovery increased due to longer residence time at increased adsorption time. In this work, operating parameters were optimised to produce maximum methane purity and recovery from PSA unit. Optimised methane purity and recovery were recorded at 99.996 % and 98.785 % respectively at of 3 bar adsorption pressure, 50% carbon dioxide concentration and 143 seconds of adsorption time. This study presents silica gel as an effective adsorbent, competing other classes of carbon-based materials in separating CO_2 to produce high biomethane purity. The developed model has great competence for making prediction of biogas upgrading performance by PSA.

CHAPTER 1
INTRODUCTION

Chapter 1 introduces the overview of this research and significance of PSA for methane enrichment from biogas. In general, this chapter summarizes the research background of methane enrichment and application of PSA for methane enrichment, the problem statement and the objectives of this final year project.

1.1 Background

Methane (CH_4) is an important greenhouse gas and has been identified as a significant contributor to global warming (Yusuf et al., 2015). Methane is used for a variety of purposes including industrial processes, heating, and electricity generation. It is also an important feedstock in the chemical industry. There are two types of methane produced namely, blue methane and green methane. Typically, methane is extracted from raw natural gas found in oil and natural gas reservoir. Methane derived from natural gas is called blue methane. Alternatively, methane can also be extracted from renewable energy resources like biogas which are produced from the decomposition of organic matter. This type of methane is called green methane or also known as biomethane. The production of blue methane however has reached a dilemma where natural gas resources are slowly depleting due to the high energy demand of growing human population and the industrial growth of developing countries. Therefore, advancement and utilization of renewable and sustainable energy resources are essential to mitigate the energy crisis as well as the environmental problems associated with methane emissions like global warming.

Biogas is one of the promising sustainable fuels as it is renewable and cheap. The United Nations adopted Sustainable Development Goal 7 (SDG7) as part of its

2030 development strategy, to ensure that modern energy becomes cheap, dependable, and sustainable for everyone (Munro et al., 2017). This fuel can be exploited to meet SDG7. Biogas which consists mainly of carbon dioxide and methane is commonly processed and purified to produce biomethane, which is more sustainable than the methane derived from natural gas.

In Malaysia, the supply of biogas generation such as landfills, agriculture waste, animal manure, wastewater treatment, and others are widely available. Landfills are the major source of methane release in Malaysia, accounting for 53%, followed by palm-oil mill effluent (38%), swine manure (6%) and industrial effluent (3%). (Abushammala et al., 2011). **Table 1.1** shows methane emissions from landfills in Malaysia which includes sanitary landfills and dump sites. The data was collected from a total of 226 landfills throughout Malaysia.

Table 1.1 Methane emissions from landfills in Malaysia (Abushammala et al., 2011).

Landfill type	Sanitary Landfills	Dump Sites
Total Methane emission (Gg)	141.6	177.2
Number of sites	14	212
Average methane emissions (Gg/site)	10.1	0.8

The implementation of biogas upgrading which utilises methane emissions from these sources can be used to compensate for the significant consequences of using fossil fuels to generate power. In addition, methane purification from biogas has great potential to prevent the occurrences of emission of greenhouse gases into the atmosphere and simultaneously reduce air pollution as well. According to the Sustainable Development Goal 13 (SDG 13), it urges us to take action to combat

climate change and its impacts. Therefore, by working towards methane enrichment from biogas, it is possible to accomplish SDG 13 in the near time.

1.2 Problem Statement

The global energy consumption is increasing exponentially due to the growing human population needs. This will present major challenges for the oil and gas industry sector, which is a major producer and consumer of energy. In the next 20 years, global energy demand is expected to increase by 48% with 80% of the energy demand being met by fossil fuels (Moodley and Trois, 2021). Fossil fuels however are not renewable resources resulting in an energy crisis and environmental issues. One of the major environmental problems linked with the usage of fossil fuels is the release of greenhouse gases such as methane. The energy sector is one of the largest contributors of global methane emissions which includes fuel production, coal mining and combustion of fossil fuels. The global methane emissions from the energy sector have increased drastically with a percentage change of 16.57% (Aydin et al., 2012).

Methane gas is one of the primary contributors to climate change and global warming. Methane accounts for about 20% of global warming. The comparative impact of CH_4 is 25 times greater than CO_2 over a 100-year period (Yusuf et al.,2015). Methane's lifetime in the atmosphere is much shorter than carbon dioxide (CO_2), but CH_4 is more efficient at trapping radiation than CO_2. Annual global methane emission is estimated to be around 570 million tonnes where 40% of emissions are from natural resources and the remaining 60% from human activity known as anthropogenic emissions (IEA, 2020). To solve the crisis of high energy demand, climate change as well as fossil fuel depletion, supply of alternate energy sources which are renewable

and eco-friendly is crucial. Therefore, the development of green and sustainable technologies that convert renewable resources into energy such as biomethane is augmented to accommodate the growing population's need for energy and a safer environment.

Biomethane also known as green methane is considered as a valuable renewable energy source that can generate electricity or heat (Chen et al., 2021). However, methane is never found in its pure form. In order to utilise the methane from its source, methane has to be separated from impurities and other gases such as carbon dioxide. To illustrate, methane from biogas can be cleaned to yield purified methane that can be readily incorporated into natural gas pipelines making it a promising renewable energy source (Holmes and Smith, 2016). It is important that impurities and other traces of gases to be separated from methane gas in order to produce high purity methane so that it can be injected in the natural gas grid or be directly used as vehicle fuel (Grande, 2011). A methane purity of 95% and above is needed to meet the pipeline grid specification (Qian and Rodrigues, 2021). Significant reduction of methane in the atmosphere and a potential renewable energy source can be achieved by using appropriate technologies to produce enriched methane gas with high purity and recovery.

Pressure swing adsorption (PSA) as a promising separation technology, is widely used in methane purification and proclaims it efficiency in carbon dioxide removal without the consumption of large amounts of water as in conventional physical methods such as water scrubbing (Niesner et al., 2013). PSA can be a very compact technology exploiting various adsorbents and process configurations. The lower energy consumption and flexibility of this method increases the potential for future expansion and modernization (Mersmann et al., 2000). Pressure swing adsorption has become an

attractive alternative for methane purification and recent study on the parameters that affect purity and recovery of methane gas is established to improve its performance.

In this study, a pressure swing adsorption simulation with silica gel as an absorbent is applied to purify methane from biogas. This model is designed using Aspen Adsorption and is used to separate the carbon dioxide gas from biogas to produce enriched methane gas. Also, the influence of absorption parameters such as adsorption time, CO_2 concentration in biogas feed and absorption pressure on purity and recovery of methane gas using PSA will be investigated. The study will outline the empirical relation between selected parameters and methane purity-recovery. The result of the breakthrough curve of PSA model is compared with experimental results to test the model efficacy. Lastly, optimization process of the PSA will be emphasised through sensitivity analysis to determine its optimum operating condition for maximum purity and recovery of biomethane.

1.3 Research Objectives

i. To apply Aspen Adsorption model for CO_2 adsorption and biomethane production from biogas.
ii. To validate model with experimental results from literature.
iii. To relate adsorption pressure, CO_2 feed concentration and adsorption time with purity and recovery of biomethane.
iv. To optimize conditions for maximum purity and recovery of biomethane.

CHAPTER 2

LITERATURE REVIEW

Chapter 2 presents the previous discoveries and reviews available from credible scientific records and references that are related to this final year project topic. This chapter covers the overview of methane purification technologies, pressure swing adsorption concepts and PSA technologies for methane enrichment.

2.1 Methane Gas

Methane (CH_4) is an odourless, colourless flammable gas and the simplest of all hydrocarbon molecules. Methane can be classified into two categories, namely blue methane and green methane. Blue methane is derived from natural gas which is a gaseous fossil fuel found in oil fields and natural gas fields. Natural gas consists primarily of methane with 85–95 mol%. Other components include carbon dioxide, nitrogen and small amounts of higher hydrocarbon, such as ethane, propane, and butane (Esteves et al., 2008). On the contrary, green methane also known as biomethane is produced from renewable energy source like biomass gasification or biogas upgrading. In biomass gasification, thermochemical conversion is used to convert biomass into a syngas, a gas mixture consisting of carbon monoxide, hydrogen, and methane. The high content of carbon monoxide and hydrogen can be converted into methane by methanation reaction (Shahbaz et al., 2016).

Biogas is a methane-rich gas consisting primarily of methane and carbon dioxide produced from microbial digestion of organic waste. One of the main sources of biogas are from landfills, waste-water treatment plants, manure fermentation and fermentation of energy crops where the organic matter is broken down by microorganisms in anaerobic conditions (Grande, 2011). **Table 2.1** shows the typical composition of biogas from three different sources.

Biogas produced from anaerobic digesters is usually a mixture of 50-75% methane and 50-25% carbon dioxide (Sangeetha et al., 2020). The overall biogas yield and methane content varies for different substrates, biological consortia, and digester conditions. Therefore, methane content in biogas can range from 40 – 70 vol % and the rest being carbon dioxide and traces of ammonia, hydrogen sulphide and hydrogen (Abbasi et al., 2012).

Table 2.1 Typical biogas composition (Chen et al., 2015)

Component	**Agricultural Waste**	**Landfills**	**Industrial Waste**
Methane, CH_4 (%)	50 – 80	50 – 80	50 – 70
Carbon dioxide, CO_2 (%)	30 – 50	20 – 50	30 – 50
Hydrogen sulphide, H_2S (%)	0.70	0.10	0.80

2.2 Methane Purification Technologies

Impurities like carbon dioxide, hydrogen sulphur and water must be separated from methane before it can be upgraded to a higher purity level in order to meet the quality standards for environmentally friendly fuels. The bulk removal of carbon dioxide is the most crucial and expensive step in the purification process; hence it will be the focus of this chapter. Various technologies have been developed to separate carbon dioxide from methane in biogas upgrading. The most common and widely used industrial applications is water scrubbing due to its simple, efficient, and low energy demand technology (Nock et al., 2014). However, the large consumption of water is considered as a drawback. Other technologies include chemical scrubbing, membrane separation, and pressure swing absorption (Xie et al, 2020; Ghasem, 2020). **Table 2.2** summarizes various physical and chemical methods for the removal of CO_2 in biogas.

Water scrubbing involves the physical absorption of carbon dioxide in water at high pressures as carbon dioxide is more soluble in water than methane. In most cases, water scrubbers are installed in a tall tower. Carbon dioxide is absorbed by the counter-current water sprayed from the top of the column. Typically, the column is filled with some material to increase the interface area, which aids in the absorption of carbon dioxide from the atmosphere. A regeneration column is used to release the carbon dioxide that has been dissolved in the water. Higher temperatures or lower pressures can be used to regenerate the water scrubbing process. At lower temperatures, carbon dioxide is more easily dissolved in water and pumping energy can be reduced (Islamiyah et al., 2015).

Chemical scrubbing is a technique that utilises a chemical solvent as an absorbent liquid Chemicals that have a high capacity for carbon dioxide absorption, such as amines, are better suited for upgrading methane with a low carbon dioxide content to a very high purity. Typically, the pressurised biogas in the column is scrubbed with a chemical solvent where the strong covalent bonds between the chemical solvent molecules and the carbon dioxide molecules make the chemical absorption process more efficient in absorbing carbon dioxide even at ambient temperature and pressure (Abdeen et al., 2016). In this absorption process, carbon dioxide present in the biogas is absorbed in the solvent and methane is recovered. This process may have higher energy costs due to the fact that carbon dioxide removal from biogas is a bulk process. On the other hand, physical solvents require less energy to remove bulk carbon dioxide and achieve a methane purity of 97-98 % (Grande, 2011).

Membrane separation is a highly selective process based on the different transport rates of chemical species through the membrane interphase. Membrane separations are particularly attractive for carbon dioxide removal because they consume

less energy, have high selectivity, are easily engineered, and thus cost less. A high recovery efficiency of methane can be achieved, while pure carbon dioxide can be obtained. However, the main drawback of membrane separation is that it requires multiple steps to achieve high purity. This biogas upgrading technology is based on the dissolution and diffusion of gases into polymer materials (membranes). When opposing sides of a polymer film are subjected to differential pressure, gas is transported across the film (permeation). The most frequently used membrane materials for biogas upgrading are polysulfide, polyimide, or polydimethylsiloxane (Chen et al., 2015).

Table 2.2 Summary of techniques for carbon dioxide removal principles.

Techniques	**Principles**
Water Scrubbing	A simple process to remove CO_2 since it has a higher solubility in water than methane
Chemical absorption	CO_2 reacting with special chemical substance including alkali solutions like sodium/potassium/calcium hydroxides, K_2CO_3, and amine compounds such as mono ethanol amine (MEA) and di-methyl ethanol amine
Membrane technology	Based on the different permeability of the component in the membrane material (hollow fibres, spiral wound modules, etc.), CO_2 can pass through the membrane driven by the high pressure while CH_4 are retained
Pressure swing adsorption (PSA)	Separating CH_4 and CO_2 from the biogas mixture based on their affinity to different adsorbent materials (active carbon, silica gel, molecular sieve, Al_2O_3, zeolite)

2.3 Pressure Swing Adsorption (PSA)

Pressure swing adsorption also known as PSA is a cyclic adsorption process mainly designed for gas separation and purification (Beck et al., 2012). PSA can be a very compact technology exploiting various adsorbents and process configurations which manipulates its behaviour. (Niesner et al., 2013). Due to the general compactness of the equipment, low energy requirements, low capital investment cost, and simplicity of operation, pressure swing adsorption (PSA) is one of the most renowned and recognised industrial processes for gas separation. (Augelletti et al., 2017). Adsorbent is the key factor of the PSA process (Xie et al., 2020). The adsorbent material used in PSA is subjected to pressure changes which selectively adsorb and desorb the undesired gas components. The selective adsorption occurs due to the difference in equilibrium capacities or by differences in uptake rates (Augelletti et al., 2017). Typical adsorbents are zeolite, activated carbon, carbon molecular sieve, silica gel, alumina, or synthetic resins.

PSA processes are classified as single-bed or multi-bed based on the number of adsorbers. Single-bed adsorptions typically have a shorter cycle time than multibed PSAs. As a result, single-bed PSA is also referred to as rapid PSA (RPSA). Additionally, RPSA has greater pressure drops than the multi bed systems. Multicolumn PSA units consist of two or more interconnected columns, allowing for continuous feed and product flow. At pressures close to atmospheric, the most frequently used PSA procedures rely on adsorbent regeneration below atmospheric pressure, a process known as vacuum pressure swing adsorption, VPSA. When compared to other types of PSA, this vacuum pressure swing adsorption method resulted in a significant reduction in energy consumption (Foukadi et al., 2020).

A pressure swing adsorption system typically involves two columns which acts as an adsorption and desorption column. There are 4 main operations in a PSA process, namely pressurisation of the inlet gas, adsorption of inlet gas at high pressure, depressurization to atmospheric pressure to release contaminant gas at the bottom of desorption column and lastly, desorption of contaminant gas from adsorbent with purging gas (Kwon et al., 2011). Both blue methane and green methane can be purified and recovered using PSA technology. For example, according to Bernades and Aurelio (2011), pressure swing absorption is the second most commercialised process for biomethane purification. Furthermore, the application of PSA unit for CO_2 removal from natural gas has been carried out by Xebec Inc with a methane recovery of around 62% with 1.42% of CO_2 (Grande and Blom, 2012).

2.4 Methane Enrichment using PSA

Numerous studies using pressure swing adsorption technology to enhance methane purity and recovery can be found in literature. Both experimental studies and simulation on PSA application to purify methane are reviewed. Cavenati et al. (2006) conducted an experimental study using a layered pressure swing adsorption process composed of a zeolite 13X to selectively remove carbon dioxide followed by a layer of carbon molecular sieve 3K to make the separation of nitrogen from methane. Overall unit performance was analysed using different operating temperatures and ratios of adsorbent layers. The results showed a methane purity of 86.0% with 52.6% recovery was obtained at ambient temperature while 88.8% purity with 66.2% recovery was obtained at 323 K using feed mixture of 60% CH_4, 20% CO_2, 20% N_2. Shen et al. (2018) studied the removal of CO_2 from biogas with silica gel as an absorbent. They

discussed the influence of adsorption step time, purge to feed ratio as well as desorption pressure in PSA. The purge to feed ratio was identified as a key factor which effects on all process performances. The experimental results revealed 98% methane purity and 85% recovery could be achieved.

Another experimental study by Cavenati et al (2005) discovered that purity of methane higher than 96% can be obtained with recovery higher than 75% using a single bed vacuum pressure swing adsorption technology with a kinetic adsorbent, carbon molecular sieve 3K. An experimental study using a feed mixture of 75 % methane 25 % carbon dioxide was conducted via 3-bed bench scale PSA set-up with 13-X zeolite. The study showed that the pipeline quality target of 97% methane purity with 90% recovery can be met by meticulously designing the PSA cycle and appropriate choice of operating parameters (Erden, 2016). Fatehi et al (1995) studied the effects of feed composition, cycle time, velocity, high to low pressure ratio and purge to feed ratio on methane purity. In this work, methane-nitrogen mixture was separated in a two-bed PSA unit using a carbon molecular sieve (CMS) adsorbent. A purity of 75 % was obtained for the 60%-40% mixture while 96% purity was obtained for the 92%-8% methane-nitrogen mixture. **Table 2.3** shows the summary of PSA experimental studies mentioned above.

Table 2.3 Summary of experimental studies using PSA for methane purification.

Parameters studied	Absorbent	CH_4 Purity	CH_4 Recovery	Reference
Different PSA cycles and effect of purge step	Carbon molecular sieve	97.5%	90%	Canevesi et al. (2019)
Effects of adsorption step time, purge to feed ratio and desorption pressure	Silica gel	98 %	< 85 %	Shen et al. (2018)
Effect of feed throughput and mixed binary gas adsorption isotherms	13X zeolite	97 %	90 %	Erden (2016)
Different operating temperatures and ratios of adsorbent layers	Carbon molecular sieve, 13X zeolite	88.8 %	66.2 %	Cavenati et al. (2006)
Co-current pressurisation with feed stream and counter-current pressurisation with product	Carbon molecular sieve, 3K	96 %	75 %	Cavenati et al. (2005)
Feed composition, cycle time, velocity, high to low pressure ratio and purge to feed ratio.	Carbon molecular sieve,	75 – 96 %	-	Fatehi et al. (1995)

A recent study by Chen et al. (2021) stimulated a dual-bed eight-step pressure swing adsorption process using zeolite 13X which obtained a top product CH_4 purity of 99.28% with 91.44% recovery and 0.015 ppm H_2S purity. The effect of 6 factors on methane purity and recovery were investigated. Among factors such as adsorption step time, purge step time, bed length, feed pressure, vacuum pressure and purge pressure,

methane purity is highly affected by purge pressure followed by vacuum pressure. In terms of methane recovery, the most significant factor is feed pressure and adsorption step time (Chen et al., 2021). Canevesi et al. (2018) evaluated the performance of a two-column PSA unit using composition feed of 60% CH_4 and 40% CO_2 at pressure swings between 5 to 0.1 bar. The stimulation resulted in 97.5% biomethane purity with recovery higher than 90%. Shen et al. (2018) demonstrated that silica gel was the promising adsorbent for CO_2/CH_4 separation. Their simulation results demonstrated that a dual vacuum pressure swing absorption (VPSA) process could produce an enriched methane gas with 98.01% CH_4 purity and 97.31% CH_4 recovery, as well as a concentrated CO_2 stream at 96.74% CO_2 purity and 97.58% CO_2 recovery.

A new VPSA configuration with a lead-trim concept was proposed by Santos et al. (2011) was evaluated through numerical simulation for further improving process performances. Two different adsorbents were employed in the process simulations: zeolites 13X (fast diffusion) and carbon molecular sieve (slow diffusion). Furthermore, the possibility of using less power in the purge step was considered. Using this process, both absorbents were able to achieve methane purity higher than 98%. Abd and Othman (2022) performed a parametric study to investigate the effects of process operation variables such as feed flowrate, adsorption step duration, axial mass dispersion coefficient, 5 different adsorbent properties, and adsorption bed dimensions on the purity and recovery of bio-methane. Among the 5 different adsorbents, CMS-3 K recorded the highest biomethane purity and recovery of 97.165% and 86.2% respectively. In addition, increasing the length and/or diameter of adsorption led to improved biomethane purity. However, higher feed flowrate and axial dispersion coefficient results in the reduction of methane recovery and purity. **Table 2.4** shows the summary of PSA simulation studies mentioned above.

Table 2.4 Summary of simulation studies using PSA for methane purification process

Parameters studied	**Absorbent**	**CH_4 Purity**	**CH_4 Recovery**	**Reference**
Adsorption step time, purge step time, bed length, feed pressure, vacuum pressure and purge pressure	Zeolite 13X	99.28 %	91.44 %	Chen et al. (2021)
Pressure swings from 5 to 0.1 bar	Carbon molecular sieve	97.5 %	90 %	Canevesi et al. (2018)
Adsorption step time, purge to feed ratio and desorption pressure	Silica gel	98.01 %	97.31 %	Shen et al. (2018)
Two types of PSA cycle configuration	Carbon molecular sieve, 13X zeolite	< 98 %	< 88 %	Santos et al. (2011)
Feed flowrate, adsorption step duration, axial dispersion coefficient, and adsorbent type and bed dimensions at an industrial scale	Silica gel, CMS-3 k, zeolite-NAUSY, Zeolite KZ10-04, zeolite 5A	97 – 90 %	81 – 86%	Abd and Othman (2022)

CHAPTER 3
METHODOLOGY

This chapter discloses the information on the methods applied in this final year project. It includes the general research flow diagram, Aspen Adsorption simulation and process optimization with software Design Expert Composite Design.

3.1 Overview of Research Methodology

This study is focused on the optimization of methane enrichment from biogas by pressure swing adsorption process. **Figure 3.1** shows the overall flowchart which outlines the major plan and procedure to conduct the research study. The process starts with simulation model implementation of Aspen Adsorption model, followed by validating breakthrough curves of methane and carbon dioxide using developed model with experimental data. The experimental design and statistical analysis utilizing response surface methodology (RSM) to study the effect of adsorption pressure, CO_2 concentration in biogas feed and adsorption time on the purity and recovery were discussed. The well fitted model will be used for optimization of biomethane purity and recovery via RSM followed by data analysis. Final report will then be written to complete the research paper.

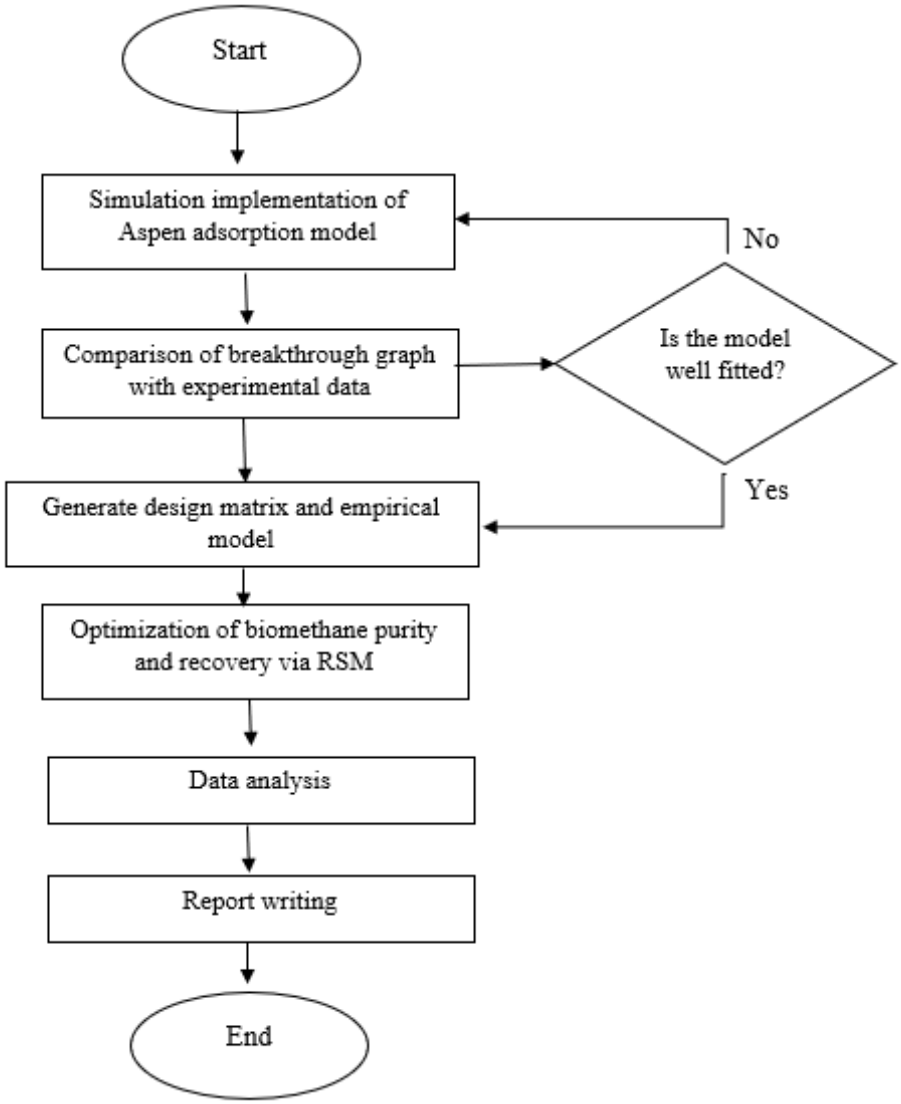

Figure 3.1 Overall research methodology flowchart.

3.2 Model Assumptions and Implementation

Simulation of a two bed four step PSA process model with silica gel as an absorbent is used to conduct the study. This design of the PSA unit for biomethane upgrading from raw biogas was modelled using Aspen Adsorption ™ version 11 by AspenTech. This simulator is a comprehensive flowsheet for the ideal simulation, design, and optimization of the gas/liquid adsorption processes. Therefore, Aspen Adsorption is a suitable software to stimulate the adsorption model of a PSA unit.

Figure 3.2 shows the pressure swing adsorption model from Aspen Adsorption simulator. To reduce the complexity of the simulation, some assumptions are made. The relevant equations and assumptions are discussed in the next subsections.

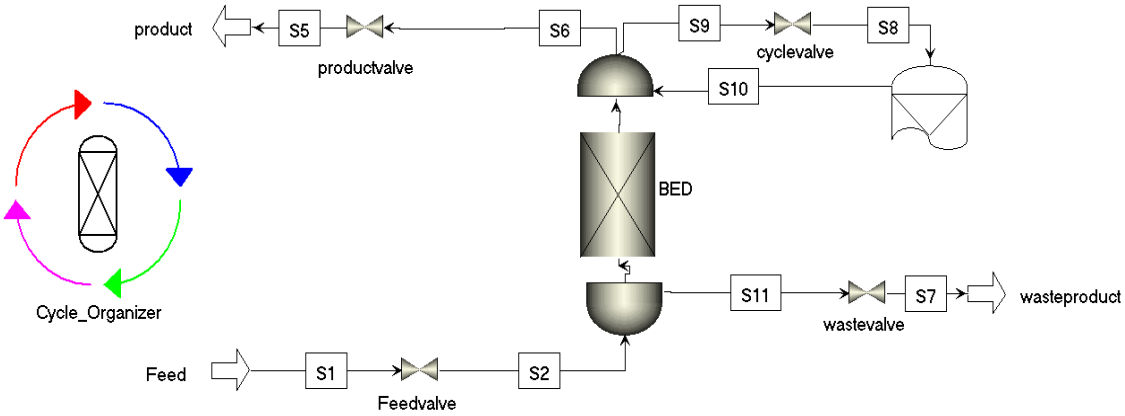

Figure 3.2 Pressure swing adsorption model set up from Aspen Adsorption

3.2.1 Adsorption bed configuration

The configuration of the model bed includes the assumption of material/momentum balance, kinetic model, isotherm, energy balance and reaction. The pressure swing adsorption model in this research is established following the model assumptions of Abd. and Othman (2022).

During model development, the material balance assumption is selected to be convection with estimated dispersion that changes along the adsorption bed. For momentum balance, the pressure drop along the column bed is calculated using Ergun equation. In this case, the gas obeys ideal gas law.

As for the kinetic model assumption, linear lumped resistance with estimated mass transfer coefficient is selected to consider the mass transfer resistances with linear shape. The kinetic model specifications are essential to handle various mass transfer resistances in the gas phase adsorption such as resistance between the bulk gas and the gas/solid interface, and resistance related to the surface morphology of the adsorbent (Abd and Othman, 2022). For this work the mass transfer coefficient is considered constant.

The equilibrium of both CH_4 and CO_2 was simulated by multicomponent extended Langmuir isothermal with partial pressure dependency. In Aspen Adsorption, this model is called Extended Langmuir 2. The mass transfer coefficients, heats of adsorption, and the isothermal parameters of CH_4 and CO_2 in the silica gel adsorbent are shown in **Table 3.1.**

The energy balance assumption in this case is that the model is presumed to be isothermal. The heat loss to the surrounding is neglected as the bed height is small causing the heat transfer to be insignificant. Lastly, there is no reaction taking place throughout the adsorption process.

Table 3.1 Fitting parameters of extended Langmuir 2 model (Shen et al, 2018).

Adsorbate	**Carbon dioxide**	**Methane**
Adsorption capacity, mmol/g	6.006	3.278
Langmuir isothermal parameter, (1/bar)	8.609 e-6	7.538 e-5
Heat of adsorption, kJ/kg	24.967	14.873
Mass transfer coefficient, (1/*s*)	0.0643	0.356

The above assumptions are used in the following equations (Abd et al., 2022). The partial differential equations describe the model, including, mass balance for component, momentum balance, mass transfer rate and adsorption isotherm.

Component mass balance equation,

$$-D_L \varepsilon_i \frac{\partial^2 C_i}{\partial z^2} + \frac{\partial (V_z C_i)}{\partial z} + \rho_s \frac{\partial C_i}{\partial t} + \varepsilon_b \frac{\partial C_i}{\partial t} = 0, i = 1, \ldots\ldots, n \quad (1)$$

Momentum balance equation,

$$-\frac{dp}{dz} = \frac{150 \mu V_z (1-\varepsilon_b)^2}{4 {R_p}^2 {\varepsilon_p}^2} + 1.75 \frac{\rho_g {V_z}^2 (1-\varepsilon_b)}{4 {R_p}^2 {\varepsilon_p}^2} \quad (2)$$

Mass transfer rate,

$$\frac{\partial q_i}{\partial t} = k_{si}(q*_i - q_i) \quad (3)$$

Langmuir adsorption isotherm,

$$q_i = \frac{\left[IP_{2i} \exp\left(\frac{IP_{3i}}{T}\right)\right] P_{yi}}{1 + \sum\left\{\left[IP_{2i} \exp\left(\frac{IP_{3i}}{T}\right)\right] P_{yi}\right\}} \quad (4)$$

PSA technology performance is commonly assessed based on the purity, and recovery of methane which can be calculated using the following relationships, (Abd and Othman, 2022).

$$CH_4\ Purity = \frac{Amount\ of\ CH_4\ in\ enriched\ biogas\ stream}{Amount\ of\ CH_4\ and\ CO_2 in\ species\ stream} \quad (5)$$

$$CH_4\ Recovery = \frac{Amount\ of\ CH_4\ in\ enriched\ biogas\ stream}{Amount\ of\ CH_4\ in\ feed\ stream} \quad (6)$$

3.2.2 Adsorbent

Silica gel was selected as an adsorbent for the PSA model. It has been known that the interactions between adsorbate and adsorbent are influenced by the pore size distribution, specific surface area and surface heterogeneity, as well as the adsorbate properties. Therefore, the characterization of adsorbent was necessary to incorporate in the bed configuration. Shen et al. (2018) had performed standard nitrogen gas adsorption desorption isotherms on the silica gel to obtain its characteristics. **Table 3.2** represents the characteristics of adsorption bed and silica gel.

Table 3.2 Bed and adsorbent characteristic (Shen et. al., 2018)

Parameter	**Value**
Adsorbent type	Silica gel
Bed length (m)	1
Bed diameter (m)	0.06
Bed wall thickness (m)	0.002
Bed void (m)	0.37
Particle void (m)	0.35
Particle radius (m)	0.002
Bulk solid density (kg/m3)	750
Adsorbent shape factor	0.83
Specific heat capacity of adsorbent (J/kg.K)	0.902
Adsorbent thermal conductivity (w/m.K)	0.3

3.2.3 Pressure swing adsorption cycle steps

The PSA cycle includes different steps in which the operating pressure swings along the adsorption bed layer. Typically, four different steps are executed in each cycle. In this work, the raw biogas is compressed to reach the designated pressure for the adsorption step. The targeted pressure of the adsorption step in this study is 4 bar at 303 K and 1 bar for the regeneration step. The PSA cycle simulated by Aspen adsorption using single adsorption column, whereas the other steps of the cycle have been modelled and controlled using cycle organizer. The cycle steps operation is shown in **Figure 3.3.**

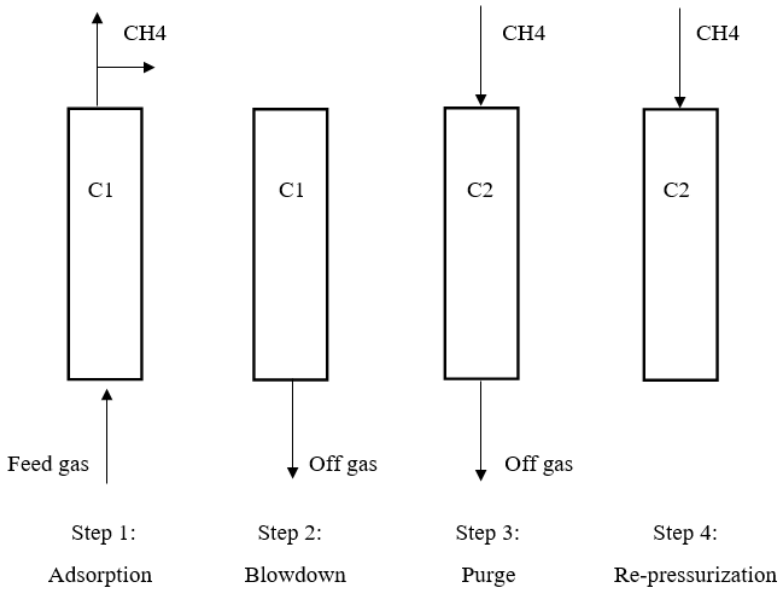

Figure 3.3 Pressure swing adsorption cycle steps

During the adsorption step, the biogas is fed to the column through the bed reaching the column head. In the adsorption step, the feed and product valves were opened, whereas the intermediate and the waste valves were closed. For the next step which is blowdown, the pressure of the adsorption column was reduced to 1.1 bar by opening the waste valve product and close all the other valves. Then, in the purge step,

part of the upgraded gas was fed in the column for the regeneration of the bed by opening the intermediate valve and closing all the other valves. The time of this step equals to the time of the adsorption step minus re-pressurization and pressurization durations. Lastly, the adsorption layer was re-pressurized to reach 4 bar by opening feed valve and closing all the other valves.

3.3 Model validation

Validation of model was performed to test the model capability in reproducing the experimental results. Breakthrough curves response was plotted from Aspen Adsorption simulator to compare the obtained results with experimental data from Shen et. al. (2018).

3.4 Design of Experiment (DOE)

Design of experiment which is a systematic method to determine the relationship between factors affecting a process and the output of that process was established. In this study, response surface methodology (RSM) was used for optimization of process parameters and in identifying the optimal conditions for methane enrichment from biogas. Response Surface Methodology (RSM) is a group of statistical and mathematical techniques utilised to improve and optimize a process by analysing the influence of the independent variables on the responses. This method is chosen to be used in this research because it can provide reasonable distribution of data points, allows model adequacy with internal estimate of errors and able to build up higher order model.

In this study, the DOE method of central composite design was used. The central composite design method with statistical analysis is used to determine the number of runs to be evaluated for the optimization of the variables and responses. The axial points are located at ($\pm\alpha$, 0, 0), (0, $\pm\alpha$, 0) and (0, 0, $\pm\alpha$) where α is the distance of the axial point from centre and makes the design rotatable. The axial points were set as face centred ($\alpha = 1$) in order to obtain more precise estimate error and at the same time prevented the parameters go beyond limit boundary. **Table 3.3** displays the high- and low-level setting values for each factor. The minimum, and maximum values of each variable are labelled as −1 and +1, respectively.

Table 3.3 The high- and low-level setting values for each factor in DOE

Variable	**Unit**	**Coded variable level**	
		-1	**+1**
A. Adsorption pressure	bar	3	6
B. CO_2 concentration	%	35	50
C. Adsorption time	s	120	180

Design-Expert version 13.0.5.0 was utilised to generate a design matrix for a total of 20 simulation runs. **Table 3.4** shows the design matrix generated from the Design Expert. After incorporating the response (CH_4 purity and recovery) from Aspen model into the design matrix, the design expert software will generate the correlations between the 3 factors and 2 which is represented by a polynomial equation. Using these correlations, respective figures and tables are constructed to analyse the collected data.