CARBON DIOXIDE SEPARATION FROM BINARY GAS MIXTURE CONTAINING HIGH CARBON DIOXIDE CONTENT BY PRESSURE SWING ADSORPTION UTILIZING ORGANIC AND INORGANIC ADSORBENTS

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2019

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by

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Thesis submitted in fulfillment of the requirements
for the degree of
Master of Science

June 2019

ACKNOWLEDGEMENT

I would gladly like to convey my gratitude to my main supervisor, Prof. Dr. Mohd Roslee Othman and Dr. Iylia Binti Idris for their assistance and proper guidance for this research project.

Millions of thanks to my family for their love and support throughout this research especially to my spouse, Dr. Nur Hidayah Binti Abdull Jabbar to motivate me to further my research studies and to have strong believe in my academic passion.

I would like to thank the university staffs, lab assistants and library assistants for resources and guidance and provides necessary software and materials for my research project.

Also, I would like to express my gratitude to my colleagues especially to Ili Khairunnisa Binti Shamsudin for helping me out in research discussions and being supportive all the time.

I am gratefully acknowledging the support from the Universiti Sains Malaysia (USM) through the Bridging (304.PJKIMIA.6316102) and Research University (1001.PJKIMIA.8014115) grants. I acknowledge the support from the Fundamental Research Grant Scheme (FRGS) for Geran Sanjungan Penyelidikan (GSP), Ministry of Higher Education (MOHE), Malaysia.

Aman Abdullah
June 2019

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LIST OF ABBREVIATIONS

NBP	National Balancing Point
LNG	Liquefied Natural Gas
BABIU	Bottom Ash Upgrading
AwR	Alkaline with Regeneration
HPWS	High Pressure Water Scrubbing
As	Chemical Scrubbing
Cry	Cryogenic Separation
OPS	Organic Physical Scrubbing
MS	Membrane Separation
UiO66	Zirconium 1,4-dicarboxybenzene MOF
BDC	1,4-benzenedicarboxylic acid
PSA	Pressure Swing Adsorption
TSA	Temperature Swing Adsorption
VPSA	Vacuum Pressure Swing Adsorption
ppm	Parts Per Million
MOF	Metal organic framework
CCD	Central Composite Design
RSM	Response Surface Methodology
ANOVA	Analysis of variance
BET	Brunauer–Emmett–Teller
EDX	Energy dispersive x-ray
SCCM	Standard cubic centimeter per minutes
SEM	Scanning electron microscope
XRD	X-ray diffractometer
GC	Gas Chromatograph
IUPAC	International Union of Pure and Applied Chemistry

LIST OF SYMBOLS

Å	Interatomic distance
SA_{BET}	Specific surface area (Brunauer–Emmett–Teller)
tb	Breakthrough time
ts	Saturation time
Θ	Scattering angle
V	Voltage

PEMISAHAN KARBON DIOKSIDA DARIPADA GAS CAMPURAN BINARI YANG MEMPUNYAI KANDUNGAN KARBON DIOKSIDA YANG TINGGI MELALUI KAEDAH PENJERAPAN AYUNAN TEKANAN MENGGUNAKAN PENJERAP YANG ORGANIK DAN BUKAN ORGANIK

ABSTRAK

Proses penkayaan dan pemisahan gas karbon dioksida telah dikaji selama beberapa dekad dan pelbagai kaedah sedang digunakan dalam industri untuk mengurangkan dan menahan gas CO_2 akibat ciri-ciri pengakisan dan kesan-kesannya negatif terhadap alam sekitar. Gas rumah hijau seperti metana (CH_4) dan CO_2 adalah gas yang paling banyak dihasilkan dari telaga gas asli yang mempunyai kesan negatif yang signifikan terhadap pemanasan global. Dalam kajian ini, kaedah penjerapan ayunan tekanan digunakan sebagai mekanisme untuk menawan dan mengembalikan gas binari melalui proses pemisahan gas oleh penjerap. Penjerap yang digunakan dalam kajian ini ialah Zeolite 5A, Zirconium-benzene dicarboxylate (UiO-66) dan karbon teraktifk daripada Kenaf dan Kulit isirong sawit (PKS) menggunakan tahap tekanan sehingga 3 Bar. Penjerap telah disedia dan dicirikan menggunakan analisa Pembelauan Sinar-X (XRD), analisa Brunauer–Emmett–Teller (BET), analisa Mikroskopi Elektron Imbasan (SEM), analisa X-Ray Tenaga Sebaran (EDX) dan analisa saiz partikel. Pemilihan penjerap dan keupayaannya diuji melalui gas campuran binari sebanyak 70% CO_2 dan 30% CH_4 melalui kajian terobosan menggunakan cara volumetrik. Maklumat experimen telah dikumpulkan dengan memanipulasi julat masa penyerapan dan pelepasan sehingga 4 minit. Hasil kajian menunjukkan bahawa gas CO_2 mempunyai tarikan tinggi berbanding dengan CH_4 untuk penjerap-penjerap ini. Masa tepu penjerap merosot apabila peningkatan

tekanan berlaku dan sebaliknya. Maklumat eksperimen menggambarkan bahawa karbon teraktifk yang dihasilkan daripada PKS menghasilkan ketulenan dan pemulihan gas CH_4 dan CO_2 yang terbaik. Kadar ketulenan CH_4 dan CO_2 berjaya mencapai sekitar 85% dan 94% manakala pemulihan CH_4 dan CO_2 adalah hampir 94% dan 89%. Sebaliknya, penjerap yang lain mencapai masa tepu dalam waktu yang sangat singkat dan kurang berkesan untuk pemisahan kandungan karbon dioksida yang tinggi.

CARBON DIOXIDE SEPARATION FROM BINARY GAS MIXTURE CONTAINING HIGH CARBON DIOXIDE CONTENT BY PRESSURE SWING ADSORPTION UTILIZING ORGANIC AND INORGANIC ADSORBENTS

ABSTRACT

Carbon dioxide (CO_2) gas enrichment and separation process have been researched for decades and various methods are being applied in industries to reduce and resist CO_2 gas due to its corrosive characteristics and negative effects on environment. Greenhouse gases such as methane (CH_4) and CO_2 are the most abundant in natural gas wells. They contribute significant negative effects to global warming. In this research, Pressure swing adsorption method was utilized as a mechanism to capture and recover binary gas via gas separation process by adsorbents. The adsorbents used in this study were Zeolite 5A, Zirconium-benzene dicarboxylate (UiO-66) and activated carbons made from Kenaf and palm kernel shell (PKS) within the pressure differences of up to 3 bars. The adsorbents were prepared and characterized using X-Ray Diffraction (XRD) analysis, Brunauer–Emmett–Teller (BET) analysis, Scanning Electron Microscope (SEM) analysis, Energy Dispersive X-Ray (EDX) analysis and particle size distribution analysis. Adsorbents selection and their capability were tested using binary mixture gas of 70% CO_2 and 30% CH_4 via breakthrough studies using volumetric method. The experimental data were collected by manipulating the adsorption and desorption time ranging up to 4 minutes. The results show that CO_2 gas had higher affinity than CH_4 for these adsorbents. Adsorbent saturation period declined towards increasing pressure and vice versa. Experimental data showed that activated carbon made from palm kernel shell yielded the optimum purity and recovery of CH_4 and CO_2 gases. Purity of CH_4 and CO_2 of 85% and 94% respectively were successfully achieved at recovery of CH_4 and CO_2 of 94% and 89% respectively. The other adsorbents were saturated quickly and less effective for high carbon dioxide content separation.

CHAPTER ONE

INTRODUCTION

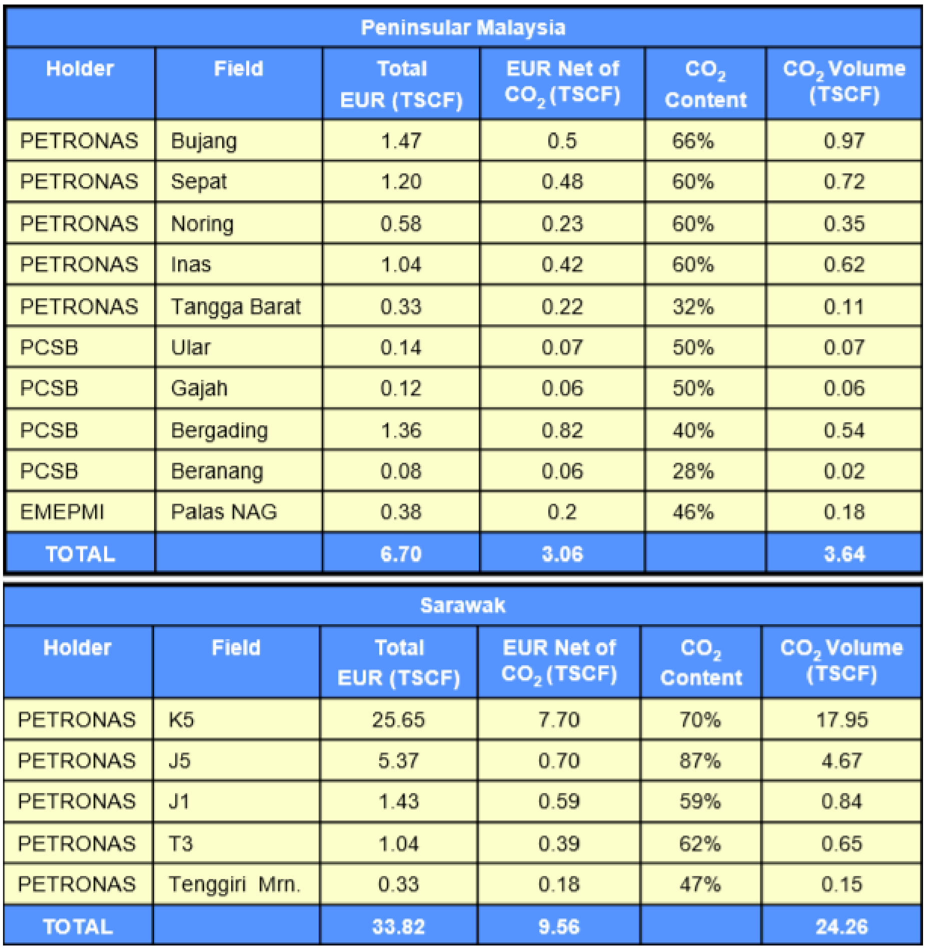
Chapter one introduces the overview of this research and how pressure swing adsorption (PSA) is significant for the capture of carbon dioxide (CO_2) gas for biogas upgrading. In general, this chapter outlines the research background of raising price of natural gas, environment problems and pressure swing adsorption for biogas upgrading, the problem statement and objectives of this study.

1.1 Research Background

Development of high CO_2 offshore gas fields reportedly significant challenges for all exploration and production (E&P) companies worldwide. PETRONAS reported that Malaysia has offshore gas field with high CO_2 content (Darman & Harun, 2006). High CO_2 content gas reservoirs make most of the gas field development uneconomical and it has remained undeveloped. As a developing country, Malaysia's resources must be developed timely to sustain supply to meet the increasing gas demand. In addition, the development of these high CO_2 gas fields requires prudent management of CO_2 capture, transportation, and storage and utilization to enable commercialization of these gas field.

Table 1.1 shows the list of high CO_2 content gas fields which range between 28 to 87 percentage of CO_2 content. The highest CO_2 content recorded as 87 percentage in J5 field from Sarawak. These high CO_2 content fields are not developed due to technology and facilities restrictions to deal with very high flow rate. In addition, capital expenses are astronomical to develop such large footprints and massive CO_2 separation requires sustainable production methods. Because, high CO2 fields requires high power and compression ratio with available current technology which would add more cost for gas separation and transportation.

Table 1.1: List of high CO_2 content gas fields in Malaysia (Darman & Harun, 2006)



Peninsular Malaysia					
Holder	**Field**	**Total EUR (TSCF)**	**EUR Net of CO_2 (TSCF)**	**CO_2 Content**	**CO_2 Volume (TSCF)**
PETRONAS	Bujang	1.47	0.5	66%	0.97
PETRONAS	Sepat	1.20	0.48	60%	0.72
PETRONAS	Noring	0.58	0.23	60%	0.35
PETRONAS	Inas	1.04	0.42	60%	0.62
PETRONAS	Tangga Barat	0.33	0.22	32%	0.11
PCSB	Ular	0.14	0.07	50%	0.07
PCSB	Gajah	0.12	0.06	50%	0.06
PCSB	Bergading	1.36	0.82	40%	0.54
PCSB	Beranang	0.08	0.06	28%	0.02
EMEPMI	Palas NAG	0.38	0.2	46%	0.18
TOTAL		**6.70**	**3.06**		**3.64**

Sarawak					
Holder	**Field**	**Total EUR (TSCF)**	**EUR Net of CO_2 (TSCF)**	**CO_2 Content**	**CO_2 Volume (TSCF)**
PETRONAS	K5	25.65	7.70	70%	17.95
PETRONAS	J5	5.37	0.70	87%	4.67
PETRONAS	J1	1.43	0.59	59%	0.84
PETRONAS	T3	1.04	0.39	62%	0.65
PETRONAS	Tenggiri Mrn.	0.33	0.18	47%	0.15
TOTAL		**33.82**	**9.56**		**24.26**

CO_2 is one of the major greenhouse gases, which contributes to global warming effect. The CO_2 emission to the atmosphere has been recognized to contribute to global warming (Zangeneh *et al.*, 2011). Carbon dioxide are released from natural and human sources. Carbon dioxide release from natural source is almost 20 times greater than the sources due to human activity; however, by years natural sources are overtaken by anthropogenic sources (Thiruvenkatachari *et al.*, 2009). The CO_2 released by human source is through the combustion of fossil fuels such as coal, natural gas or petroleum, and industrial processes such as power plants, oil refining and the production of cement, iron, and steel (Dantas, et al., 2011). Carbon dioxide has already been used in petrochemical industries for production of limited chemicals such as urea (Zangeneh *et al.*, 2011). Since the beginning of the industrial age in ca. 1800, the CO_2 concentration in atmosphere has increased from 280 to 390 ppm in 2010. Carbon capture and storage (CCS) will play a crucial role to attain the required greenhouse gas (GHG) emissions reduction (Riboldi & Bolland, 2016).

CCS can be defined as the separation and capture of CO_2 produced at stationary sources, followed by transport and storage in geological reservoirs or the ocean (Hauchhum & Mahanta, 2014). There are three major approaches for CCS: post-combustion capture, pre-combustion capture and oxyfuel process. In pre-combustion, the fossil fuel is reacted with air or oxygen and is partially oxidized to form CO and H_2 (syngas). Then in a gasification reactor, it is reacted with steam to produce a mixture of CO_2 and more H_2. CO_2 is then separated and resulting in a hydrogen-rich fuel which can be used in many applications. Oxy-combustion is when oxygen is used for combustion instead of air, which results in a flue gas that consists mainly of pure CO_2 and is potentially suitable for storage. The post combustion capture is based on removing CO_2 from flue gas after combustion. Instead of being discharged directly to the atmosphere, flue gas is passed through equipment which separates/captures most of the CO_2 (Dantas et al., 2011).

Post-combustion capture offers some advantages as existing combustion technologies can still be used without radically change them. This makes post-combustion capture easier to implement as a retrofit option (to existing power plants) compared to the other two approaches. Therefore, post combustion capture is probably the first technology that will be deployed in massive scales (Wang *et al.*, 2011).

Among the various separation technologies such as absorption, adsorption, cryogenic, membrane and micro algal bio-fixation, adsorption is considered as a competitive solution. Its major advantage is the ease of the adsorbent regeneration by thermal or pressure modulation (Thiruvenkatachari *et al.*, 2009). Flue gases of current power plants are a mixture of N_2, O_2, CO_2, SO_2, NO_2 and water plus other minor contaminants. The concentration of CO_2 in the flue gas is typically only 10 to 15% (around 12%) depending on the fuel used. Flue gases are normally at atmospheric pressure, but the temperatures might be between 320 K and 400 K, depending on the extent and type of contaminant removal. The flue gas conditions have created many problems for CO_2 capture (Álvarez-Gutiérrez *et al.*, 2017).

In addition to cryogenic process, absorption and membrane technology, adsorption is a separation technology that has the potential to reduce the cost and energy of post-combustion capture compared to other technologies. Adsorption processes for gas separation via selective adsorption on solid media are also well-known, and it can produce high purity streams with low energy consumption (Yang, 1997).

Several adsorption processes are used commercially for adsorbent process, including pressure swing adsorption (PSA), vacuum pressure swing adsorption (VPSA), and thermal or temperature swing adsorption (TSA). Some research works have been done using these processes on different types of adsorbent materials. Latest developments have proven that PSA is a promising option for CO_2 separation due to its ease of applicability over a relatively wide range of temperature and pressure conditions, its low energy requirements, and its low capital investment cost (Agarwal *et al.*, 2010)

1.2 **Problem Statement**

Almost 85% of the total world demand for energy is supplied by thermal power plants powered by fossil fuels, including coal, oil and gas. These fossil fuels account for about 40% of total CO_2 emissions (Metz et al., 2005).

The oil and gas industries are conducting many researches addressing the CO_2 concern as a threat of corrosion since 1940s via studies of carbon-methane (Unruh & Katz, 1949). An increase of pressure and temperature significantly increases the rate of corrosion and they could damage pipelines especially steel. Carbon dioxide have several reactions in the oil and gas field such as forming carbonic acid (H_2CO_3) while reacts with water and it also can reacts with minerals from reservoir. In carbonate reservoir, the reactions are relatively rapid whereas in silicate reservoirs its reactions are much slower and sometimes the CO_2 been trapped and being mineralized under high pressure (Overview of Greenhouse Gases, 2018).

Natural gas field also contains other compounds such as Sulphur dioxide (SO_2), water vapor (H_2O) and carbon compounds. Therefore, the most unwanted gas compounds which are corrosive and hazardous need to be controlled and removed from the early stage of gas processing system to avoid any major issues. In this case, CO_2 must be removed or reduced to optimum level from the overall amount of production via effective methods. Currently, Monoethanolamine (MEA) absorption method has been used by oil and gas to restrict the CO_2 from causing the problems.

The industries captured CO_2 is then used for enhanced oil recovery by injecting the gas into the reservoir for gas uplifting and reservoir pressure stabilization. Even though it is economical to reuse the produced gas such as CO_2 as injection gas, the purification using the current MEA absorption process for CO_2 gas is costly and complex. Therefore, separation method by adsorption should be effective and reliable for purifying, collecting and capture of CO_2 gas. Pressure swing adsorption method would be an effective way to capture and purify natural gases by selecting the appropriate adsorbents. This research is performed to study the effectiveness of PSA for CO_2 separation from high CO_2 content natural gas.

1.3 Objectives of Research Work

1. To analyze the organic and inorganic adsorbents for their physical characteristics.
2. To determine the breakthrough analysis of the adsorbents behaviour towards high CO_2 content natural gas.
3. To evaluate the effectiveness of the adsorbents for gas separation from high CO_2 content natural gas through PSA application.

1.4 Scope of Study

In this research, the focused area was pointed in using high content of CO_2 for binary gas separation. Previous findings show that PSA capability were not efficient if the CO_2 composition exceeds more than 50% and it would be causing troublesome to equipment. However, high CO_2 content separation performance can be achieved effectively by selecting suitable adsorbents and efficient methods. There are some limitations available in this research due to availability of equipment and technology. The maximum pressure used in this research were below 5 bar due to capability of equipment and prevent them from gas leaking. Maximum mixed gas flowrate controlled at 500 SCCM for testing binary gas. The sample used in this research weighed about 2 to 4 grams for each column. However, all the calculations were corrected for amount per gram for comparison purposes. Besides that, Gas Chromatography has its delaying period to synthesize results where the results only tend to be projected to that period frame and not able to test at any time randomly. All these limitations were considered while preparing results and calculations to avoid errors.

CHAPTER TWO

LITERATURE REVIEW

Chapter two briefly presents the preceding findings and reviews available from credible scientific records and references that are related to this research topic. In general, this chapter outlines the overview of natural gas, adsorption and its significance, pressure swing adsorption (PSA) and adsorbents. Then, a review on breakthrough studies involving organic and inorganic adsorbents were presented to signify the importance of uses in this research. In addition, an extensive review of significance and PSA were presented covering optimization and effects of the selected adsorption process variables.

The extraction of oil production from the reservoir is not an easy process due to various factors including reservoir pressure changes, multi-phase flow production, petrophysical properties and well behavior. At one stage, the production recovery for mature wells declined significantly and may cause the well to be idle or restrict the oil from flowing to the surface. Therefore, recovery system plays an important role to extract optimum amount of resources from the reservoir by altering the flow assurance and improve the reservoir properties. This phase is called as tertiary phase. The tertiary phase is also known as Enhanced Oil Recovery (EOR) phase (Olarjire, 2014).

EOR is a collection of methods that allow for more effective oil extraction when the primary and secondary phases are not sufficient. It is also useful in wells that contain heavier oil that is evidently more difficult to extract. Typical EOR methods can yield up to three times more oil than primary or secondary phase methods. The most popular EOR methods available in industry are thermal recovery, chemical injection, and gas injection. Chemical injection has various methods which includes the uses of CO_2, polymer and surfactants (Zerpa *et al*., 2005).

The utilization of CO_2 by means of CO_2 injection after water-flooding is an EOR method that is of great potential in reducing residual oil saturation in oil reservoirs. It has been approximated that CO_2 flooding would produce an additional 7 to 15% of the initial oil in place (Matthiasen, 2003). CO_2 has been used for decades in EOR to liberate residual oil, including water-alternating-gas (WAG) operations (Sohrabi et al., 2004). However, there is still a need for improved practices in EOR because significant amount of oil is still left behind, even after EOR attempts (Maugeri, 2004).

CO_2 has built a reputation as being one of the main concerns worldwide in the recent years due to the increasing amount of greenhouse gases in the atmosphere as well as issues related to global warming which poses harmful effects to the environment. The utilization of CO_2 for a good cause such as in this proposed research for oil recovery would hopefully be of some help in battling the issues caused by CO_2. Carbon capture and storage (CCS), as means of storing the CO_2 for useful purposes such as for use in water aquifers, has also been researched with great effort in recent years (Ntiamoah *et al*., 2015).

CO_2 is a corrosive gas which affects many facilities while producing oil through EOR especially pipelines and trunk lines. Well producing CO_2 needs corrosive inhibitors to suppress the negative effects. However, nowadays application of CO_2 in EOR to enhance the production is more ideal for wells which has a pressure greater than minimum miscibility pressure (MMP) and its typically about deeper than 2500ft. Meanwhile, EOR application using CO_2 from natural gas reduces the burning of unwanted gas which is considered environmentally friendly in some countries. Therefore, the enrichment of CO_2 gas from natural gas and reinject the gas in EOR process reduces the carbon released to environment (Dodds *et al.*, 2015).

2.1 Adsorption

Adsorption processes is classified as purification or bulk separation, depending on the concentration in the feed of the components to be adsorbed (Seader *et al.*, 2010). The solid that adsorbs a component is called the adsorbent, and the component adsorbed is called adsorbate. Adsorption happens on the surface of liquid, but it is less practical importance than adsorption in solid. The adsorption process occurred because of the interaction between the adsorbate molecules and the surface of the adsorbent. If the adsorbed molecules attach to the surface, the process is called adsorption whereas the adsorbed molecules are distributed throughout a liquid phase, the process is called absorption. The reverse of adsorption is called desorption. Pressure and temperature both are important factor to be used to determine the amount of solute adsorbed per unit mass of adsorbent at equilibrium.

Adsorption is favored at higher than atmospheric pressure and ambient temperature below 30^oC. On the contrary, desorption is favored at lower than atmospheric pressure and higher then ambient temperature.

Other than that, the strength of attachment between adsorbate and adsorbent is relied on the chemical or physical bonds that formed. For the strong chemical bond that formed between them can be known as chemisorption whereas the weak Van der Waal’s force and electrostatic force that promote the physical bond is called as physical adsorption (Dutta, 2007). Figure 2.1 illustrates the process of adsorption occurred at exothermic reaction and desorption occurred at endothermic reaction.

The interaction between adsorbent and adsorbate in terms of transferring of molecules from the gas or liquid phase to the surface of the solid phase, normally is an exothermic process. Conversely, desorption is the transfer of molecules sticking to the surface of the solid back to the gas or liquid phase, normally is an endothermic process.

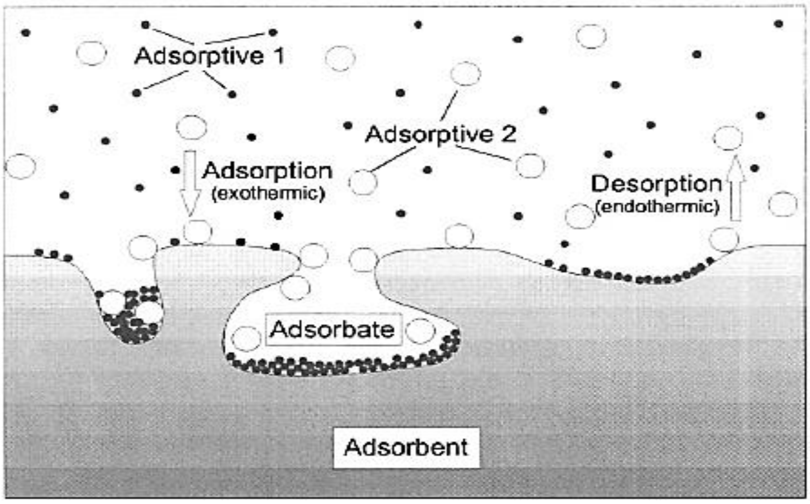


Figure 2.1: Adsorption system consisting of a two component adsorptive gas, adsorbate and the adsorbent (Keller & Staudt, 2005)

2.2 Pressure Swing Adsorption

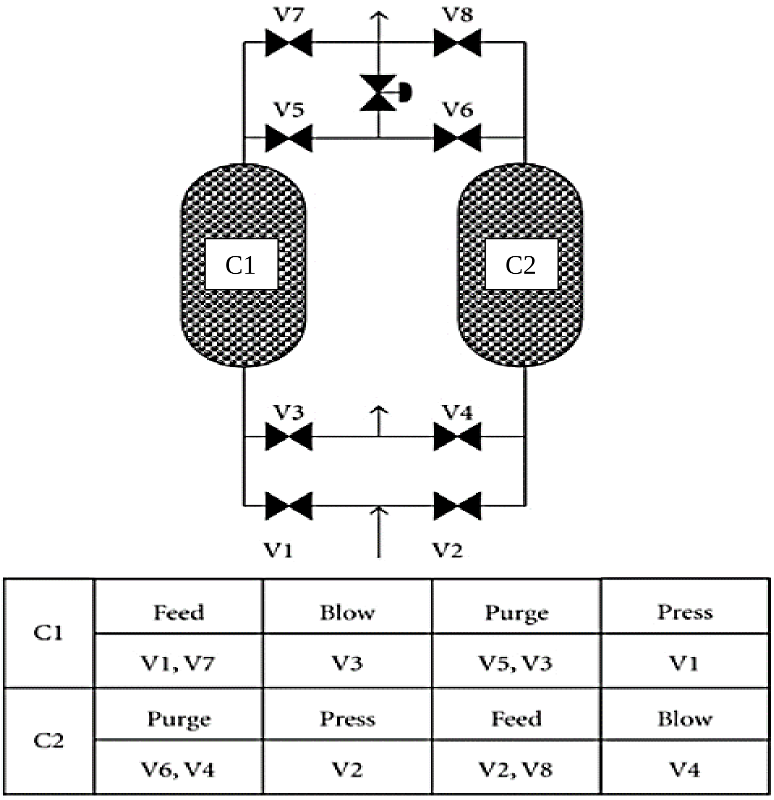
PSA is one of the separation technologies that is widely applied in different applications for example hydrogen purification, air separation, OBOGS (on-board gas generation system) CO_2 removal, noble gases (He, Xe, Ar) purification, CH_4 upgrading, n-iso paraffin separation, and so on (Grande *et al.*, 2017). PSA is normally selected due to its low energy, cost effective and ease of operation when compared with other gas separation technologies such as cryogenic separation. Cryogenic processes require the equipment and devices, like compressors, turbines, heat exchangers, insulators, and distillation columns resulting high capital cost (Riboldi & Bolland, 2017).

In biogas upgrading, another separation technology such as amine scrubber needs a lot of heat to heat up the amine solvent about 150-170 °C for regeneration and maintaining the adsorption efficiency. This could consume massive amount of energy in term of high cost and the concern about safety issue (Miltner, Makaruk, & Harasek, 2017).

PSA is a cyclic process which employs equilibrium establishment in separation and mass transfer rate driven among adsorbate and adsorbent. When high pressure is applied, adsorption will occur and increase the amount of adsorbed impurities leading to high purity of product. Whereas, when the pressure is reduced and reached back to atmospheric pressure, regeneration will occur the impurities can be desorbed and discharged from the system. Thus, there is a relationship of equilibrium concentration of adsorbed impurities with the pressure. If the pressure is significantly reduced below the atmospheric pressure it is called as vacuum swing adsorption (VSA). For the mass transfer rate, it is greatly dependent on the suitable selection of adsorbent installed in PSA system and the pore size for the given adsorbate species (Seader *et al.*, 2010).

PSA consists of two or more beds that contain adsorbents and is operated by means of proper valves arrangement. The term ‘swing’ in PSA represents high pressure in feed change to low pressure while regeneration. PSA technology was firstly introduced by Charles Skarstrom, with the four steps of ‘Skarstrom cycle’; feed, blowdown, purge and pressurization. Figure 2.2 shows the schematic design of the PSA which consists of two-bed columns (C1 and C2), feed valves (V1, V7, V2 and V8), purge system and blowdown valves (V3 and V4).

If the pressure in the system is replaced by temperature, which mean low temperature in feed and high temperature at regeneration process, it can be considered as temperature swing adsorption (TSA). TSA has its own benefit and drawback where it can be adopted during strong adsorption of mixed impurities. However, TSA cycle time is much longer than PSA because temperature affects molecular reactions towards adsorptive characteristics whereas higher pressure lowering the cycle time and reduces energy needed for adsorption than TSA (Crittenden & Thomas, 1998).



C1	Feed	Blow	Purge	Press
	V1, V7	V3	V5, V3	V1
C2	Purge	Press	Feed	Blow
	V6, V4	V2	V2, V8	V4

Figure 2.2: Schematic design of the first two-column pressure swing adsorption unit and valve sequencing for different steps in the cycle (Grande, 2012)

In the years after Skarstrom invention, pressure equalization step was introduced to modify Skarstrom cycle to improve energy recovery. Chua *et al.*, (2013) employed formula equations to evaluate energy conservation by using pressure equalization step whereas Yang *et al.*, (1997) studied effect of pressure equalization time on H_2 purity and recovery for H_2/CH_4 separation. They found that the longer the step time, the better of recovery and purity obtained.

2.3 Adsorbent

Proper selection of adsorbent is the first consideration prior to PSA (Jain *et al.*, 2003). Different type of solid adsorbents like zeolites, molecular sieve, silica gel and activated carbon all of them have their own attributes that pose a strength in binding toward their selective separation of mixture. It is noted that selectivity, adsorption capacity and reversibility of adsorption mainly depend upon adsorbent characteristics like particle size, porosity, specific surface area, structure strength and stability. Figure 2.3 shows the adsorbents pore size which were classified into micropores (<20Å diameter), mesopores (20-500 Å diameter) and macro-pores (>500 Å diameter). These pore sizes were used as an important tool in PSA system for binary gas separation (Dutta, 2007). Pore size of adsorbent acts as a physical separator by filtering larger gas particles than pore size and allowing smaller gas particles to flow through during adsorption process.

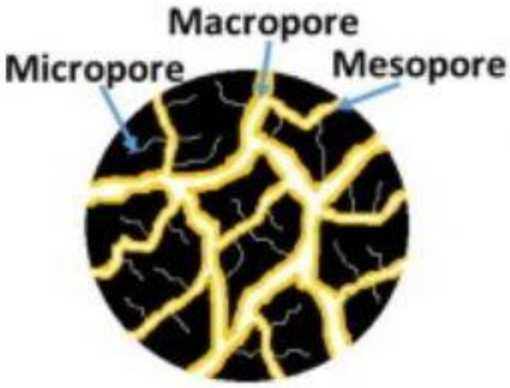


Figure 2.3: Schematic diagram of pore structure of adsorbent. (Suresh Kumar *et al.*, 2017)

2.3.1 Activated Carbon

Activated carbon is a member of a family of carbons ranging from carbon blacks to nuclear graphite, from carbon fibers and composites to electrode graphite, and many more. Mostly, activated carbon production are made of peat as well as woods, fruit stones and nutshells, as with coconut shells, as well as some synthetic organic polymers. Activated carbon is treated to enhance the porosity which become preferable for adsorption or chemical reactions (Marsh and Rodríguez-Reinoso, 2006).

Activated carbon can be applied in refrigerator application. Their surface area typically within the range of 800–1500 m^2g^{-1}. The larger the surface area, the better the performance of adsorption. Activated carbon also has larger working pressure (approximately 16 bars) and allows better performance in heat and mass transfer to decrease the bad smell and corrosiveness (Ullah *et al.*, 2013). Rios *et al.*, (2013) performed experimental binary equilibrium isotherms for CO_2-CH_4 mixtures on an activated carbon at 293K. CO_2 presented at highly adsorbed amounts on activated carbon with respect to CH_4. A maximum selectivity of around 8.7 was observed for a nearly equimolar mixture at 0.1 MPa.

2.3.2 Zeolite

Zeolites are naturally occurring microporous crystalline silicate framework materials that have been used in adsorption and ion exchange. Natural zeolite crystals can be found from volcanic sediments in closed alkaline and saline lake-systems. Naturally occurring zeolites can be categorized into 40 different types. In order to fulfill the huge demand of industrial, they are also synthesized in the laboratory by using hydrothermal synthesis techniques at temperatures of around 25–150 ° C (usually 100 ° C) (Xu *et al.*, 2009).

Artificial zeolites can be synthesized and distributed as 150 types which are named by one letter or a group of letters, such as type A, type X, type Y, type ZSM and so on (Nagah *et al.*, 2013). The internal modification of zeolites like pore opening, pore size and thermal stability allow researchers to focus on new innovative approaches to be introduced so that high selectivity zeolite has the capacity to separate substances based on differences in sizes and shapes of particles (refer to Figure 2.4).

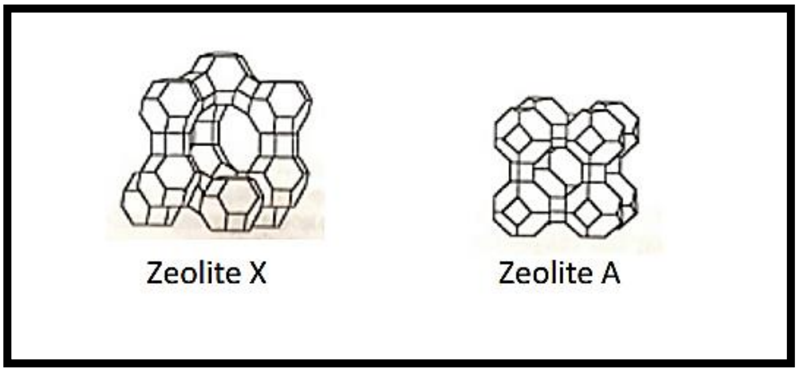


Figure 2.4: Schematic diagram of Zeolites structures
(Bartholomew & Farrauto, 2006)

Adsorption processes are normally reversible in practice. This permits the zeolite to be reused many times, swinging between adsorption and desorption steps (Dąbrowski, 2001).

Moreover, from previous works, researchers have carried out certain experiment by using different appropriate adsorbents to remove CO_2. Adsorption capacity, thermal stability and regeneration rate in regard with different pore structure of adsorbents will be the benchmark for researchers to base their researches on (Majchrzak and Nowak, 2017). The comparison of the selection criteria necessary for CO_2 capture is given in Table 2.1 which were used as standard criteria to choose an adsorbent for CO_2 bulk separation.

Table 2.1: Result of comparison of the selection criteria necessary for CO_2 capture (Majchrzak and Nowak, 2017)

	Activated carbon	Zeolites	Carbon molecular sieves	Sorbents modified with amines
Sorption capacity	Sorption increases at pressure above 1 bar	Sorption recorded decreasing at pressures above 5 bars	At ambient condition depicted very low sorption	Optimum sorption occurred at 70-90 °C
Thermal Stability	All adsorbents are stable at multiple cycles			
Level of regeneration	Easy to regenerate by heating in oven	Harder to regenerate than activated carbon	Difficult to regenerate	Easy to regenerate
Influence of other factors	The least influence of NO_X and SO_X (level of ppm)	Greater impact of other compounds: SO_X and NO_X than for AC	The least influence of NO_X and SO_X (level of ppm)	The largest effect of SO_X and NO_X on sorption capacity.
Impact of moisture	Less influence on moisture	High impact on moisture	Slight influence on moisture	Minimal or no impact of moisture

According to Majchrzak and Nowak (2017), higher sorption capacity is preferred to allow more gas particles to be adsorbed at one time and low pressure and temperature were prior to reduce energy consumption. Besides that, adsorbents that were capable of multiple cycles and easier to regenerate are ideal to select. Less impacts towards sour gases and moisture would results better in adsorption process.

2.3.3 Zirconium-Benzene dicarboxylate (UiO-66) Adsorbent

UiO-66 is a synthetic porous solid adsorbent that coordination via zirconium and its linker 1,4-benzene-dicarboxylate. It can be grouped as metal-organic framework (MOF) adsorbent (Cavka *et al.*, 2008). The cluster structure of UiO-66 has shown in Figure 2.5.

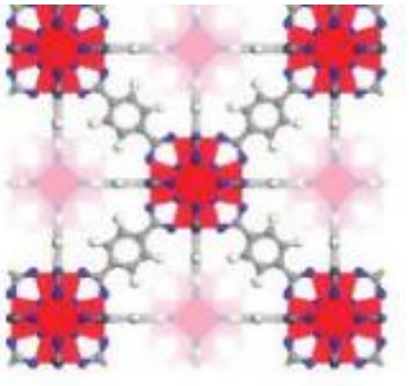


Figure 2.5: Cluster structure of UiO-66 adsorbent with its linker 1,4-benzene-dicarboxylate (Cavka *et al.*, 2008)

Commonly, zeolite is the good adsorbent to be employed in capturing CO_2 owing to its high surface area (SA_{BET} =726m^2/g), small pore volume (0.25cm^3/g) and high thermal and chemical stability. But, interestingly, recently metal-organic framework (MOFs) are an emerging new class of solid crystalline and decided to be investigated by many researchers because of its high specific surface area and adsorption capacity leading to large capacity of CO_2 to be adsorbed (Sumida *et al.*, 2012). From previous research, it indicated that UiO-66 has larger surface area than many types of zeolites (SA_{BET}=1250m^2/g) (Huang *et al.*, 2017). Eventually, it exhibits that UiO-66 has much better adsorption capacity than zeolite adsorbent due to higher capability of surface area.

Furthermore, UiO-66 metal-organic framework can undergo development and alter the pore size to achieve higher adsorption capacity. Different kind of modulator the acid solvents can be added to compensate the ligand of the structure UiO-66. The BET surface areas can change from 1175 m^2g^{-1} to 1777 m^2 g^{-1} that have been reported in recent researches (Shearer, et al., 2016).

2.3.4 Palm Kernel Shell (PKS)

In this study, palm kernel shell that has been principally found in Malaysia has been utilized as the preliminary material for activated carbon production. More than 270 oil palm mills in this country were available and the total amount of palm kernel shell is equivalent to more than 2.4 million tons per annum (Abnisa, *et al.*, 2011). Comparing palm kernel shell to other solid residues from oil palm industry such as mesocarp fiber and empty fruit bunch, palm kernel shell is more competent as precursors due to its porous surface, high mechanical strength, high chemical stability, various surface functional groups, and insolubility in water (Bakar, et al., 2016). Besides, poor disposal procedure of these palm kernel shell including open burning and dumping at sites stimulates further utilization of these solid residues.

Moisture content in kernel shells is low compared to other biomass residues with different sources suggesting values between 11% and 13%. Palm kernel shells contain residues of Palm Oil, which accounts for its slightly higher heating value than average lignocellulosic biomass. Compared to other residues from the industry, it is a good quality biomass fuel with uniform size distribution, easy handling, easy crushing, and limited biological activity due to low moisture content (Zafar, Bioenergy Consult, 2019).

2.3.5 Kenaf

Kenaf is a prehistoric crop and has an extensive history of being planted and utilized by human beings. It is considered as an alternative crop that provides a good source for cellulose. The usage of kenaf has enlarged due to its biodegradability and environmental compatibility (Yusof, et al., 2015). Kenaf (*Hibiscus cannabinus* L.) has similar types of morphological structures like cotton and jute and is currently grown in Malaysia profusely. Kenaf is a good biomass candidate for activated carbon production because of its fast growth rate and large biomass production. Kenaf is a warm season annual herbaceous crop that grows best in the tropics and subtropics without need of special care (Meryemoglu, *et al*., 2016)

In Malaysia, the National Kenaf Research and Development Program has been on track to produce kenaf due to its prolonged application in diverse sectors. The government has allocated around 12 million RM for further development of the kenaf-based industry under the 9th Malaysia Plan (2006-2010) (Chowdhury, et al., 2012). Kenaf, which is known to be renewable, inexpensive and easily grown plant was selected in this work as a precursor to synthesize active porous material for CO_2 adsorption.

2.4 Breakthrough study

Breakthrough studies can act as guidance to evaluate the performance of adsorbent bed installed in the column. PSA allows the determination of duration of adsorption in order to control the purity of product. Beyond the duration of adsorption, the purity of product will decrease significantly (Warren, 2012). A breakthrough curve can be plotted by values of C/Co at y-axis (concentration) after passing through the bed concentration before feed, against time in the x-axis. After injection of the adsorbate, the adsorption will start to occur and as the time passes the three regions will be established inside the bed at certain length designated as saturated zone, mass transfer zone and unused zone such as shown in Figure 2.6.

Once it reaches the breakthrough time (t_b), the concentration of effluent can be determined. Then the concentration of effluent continues to increase until it meets the saturated point at the time (t_s) (Dutta, 2007). On the other hand, if the bed height is increased, mass transfer zone will be extended, causing longer breakthrough and saturated time (Chowdhury, *et al.*, 2013).

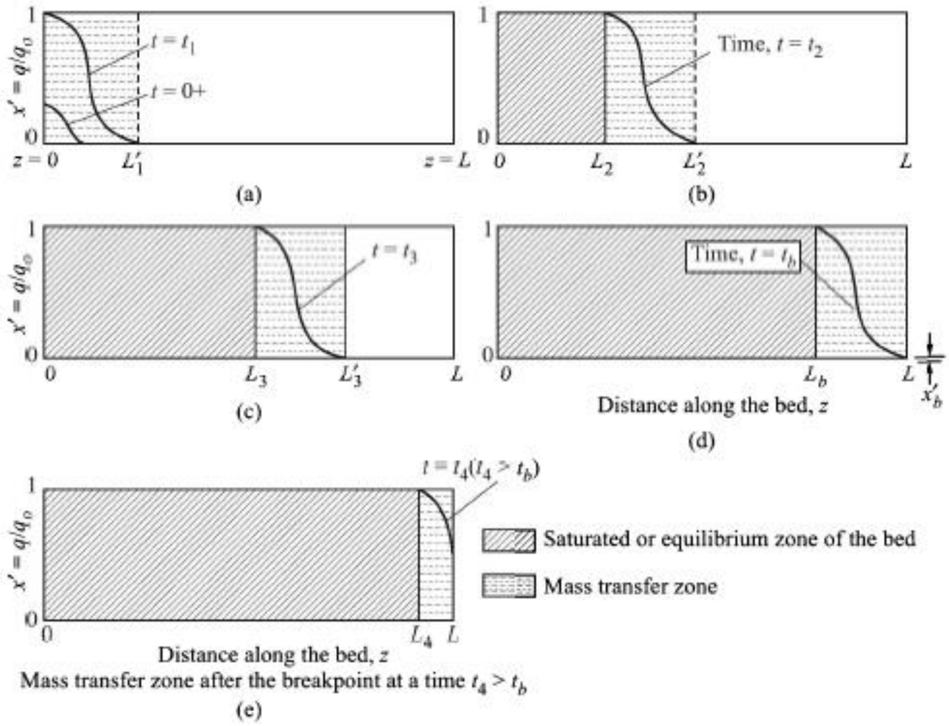


Figure 2.6: Solid concentration profile at different times (Dutta, 2007)

2.5 Effect of adsorption time and blowdown time in PSA

Adsorption time and blowdown time both are important parameters that affect the performance of PSA. Rao *et al.*, (2010) examined the optimization of combined adsorption time and blowdown time to maximize oxygen purity via simulation of COMSOL software. They used adsorbent 5Å and partially Ag exchanged-Li-substituted 13X zeolite adsorbents in two steps pulse PSA. From their findings, they discovered that brief adsorption time of 0.24s will cause impurity like nitrogen to penetrate through the bed and affect the oxygen purity at fixed desorption time of 1.2s. Similar results have been reported previously by Jain *et al.*, (2003) about the adsorption time that cannot go beyond the breakthrough time of impurity.

The adsorption time that stays within the limit also must be adjusted to meet the high purity and recovery of the product. It was discovered that by increasing total adsorption time, at the same time the purity of product will increase but recovery of product will decrease. Kim *et al.*, (2000) studied experimentally about blowdown time ratio to the adsorption time using double layer bed of activated carbon and zeolite 5A to separate gas mixture of H_2/CO_2 and CH_4/CO. It showed that 0.2 ratio of blowdown time to adsorption time achieved the highest recovery exceeding 84% by using adsorbent ratio of 60/60, 70/50 and 80/40 respectively.

Overall, PSA tends to optimize purity and recovery output by utilize energy efficiently. Adsorbents that has high surface area, optimum pore size and ability to regenerate were preferred to separate binary gas. Adsorbents made from organic sources were estimated to show higher surface area and larger working pressure due to its internal structure arrangement. The selected adsorbents were also selected based on availability and sustainable development needs. In this research, organic adsorbents selected were activated carbon made from palm kernel shell and kenaf whereas inorganic adsorbents were UiO-66 and Zeolite 5A for natural gas separation. Effects of adsorption time and blowdown time of adsorbents reflects their capability to separate natural gas.

CHAPTER THREE

MATERIALS AND METHODOLOGY

In this chapter materials and methodology used in this research were described. It includes the general research flow diagram, specific preparation of adsorbents methods and types of characterization of adsorbents. Besides that, the types of materials utilized in the experiments, experimental rig set-up for natural gas mixture, breakthrough studies for each sorbent and proses of PSA system were elaborated in detail.

3.1 Research Methodology

Overall the research focused on two important outcomes which were the feed gas mixture composition and the sorbents behavior on adsorption and desorption behaviour of adsorbate. The PSA rig has been designed and set-up earlier to run the experiments smoothly. It has been tested for gas leaking by applying high pressure (up to 4 Bar) of argon gas and soap to see if there was bubbles to ensure all parts were joined tight and secured from gas leakage.

Figure 3.1 shows the general research flow chart for selection of adsorbents to separate natural gas efficiently by using PSA system. Physiochemical characterization acted as an important factor to selecting desirable adsorbents for binary gas separation.

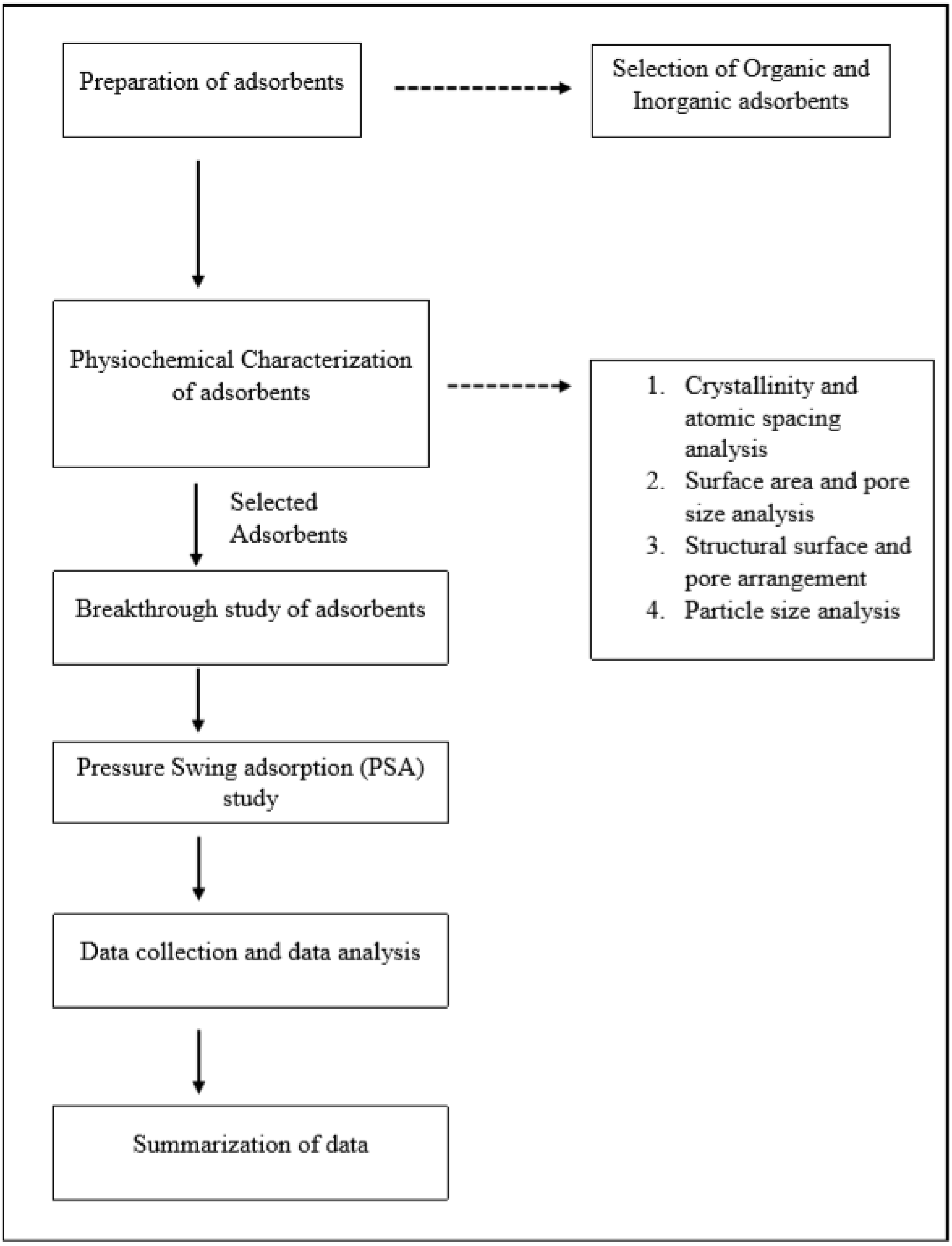


Figure 3.1: General Research Flow Diagram

3.2 Materials and Chemicals Required

The materials and chemicals were required in this research are listed in the Table 3.1.

Table 3.1: List of materials and chemicals

Chemical	Molecular Formula	Purity (%)	Supplier	Usage
Methane	CH_4	99.9	Araztech - Engineering	PSA and Breakthrough studies
Carbon dioxide	CO_2	99.9	Araztech - Engineering	PSA and Breakthrough studies
Zirconium (IV) Chloride	$ZrCl_4$, anhydrous powder	99.99	Sigma-Aldrich	Preparation of adsorbent UiO-66
Dimethylformamide (DMF)	$HCON(CH_3)_2$,	99.8	Sigma-Aldrich	Preparation of adsorbent UiO-66
1,4 – Benzene dicarboxylic acid (BDC)	C_9H_6	-	Sigma-Aldrich	Preparation of adsorbent UiO-66
Ethanol	CH_3CH_2OH	99.8	Sigma-Aldrich	Preparation of adsorbent UiO-66
Zeolite 5A	Sources obtained from Universiti Sains Malaysia (USM) Petroleum lab.			
Activated Carbon (Palm Kernel Shell)	Precursor purchased from Tenaga Nasional Berhad; modified and activated in USM Petroleum lab			
Activated Carbon (Kenaf)	Precursors purchased from Universiti Teknologi Malaysia (UTM); modified and activated in USM Petroleum lab			

3.3 Preparation of Synthetic Natural Gas with High CO_2 Content

The synthetic natural gas containing high CO_2 composition was made in the laboratory by mixing 70wt.% CO_2 with 30wt.% CH_4 per volume basis. The binary gas composition has been checked constantly using GC to ensure the feed gas amount.

3.4 Equipment Required

There are different types of equipment used in this research to synthesize adsorbents components and characterize them. The list of equipment and their uses are listed in the Table 3.2.

Table 3.2: List of equipment required and their applications

Equipment	Model	Application
X-Ray Diffractometer (XRD)	Bruker XRD D8 Advance	To study the crystallinity and atomic spacing of sample. To analyze the crystalline phases and orientation.
Surface Area and Porosity Analyzer (SAPA)	ASAP 2020	A surface area analysis conducted to determine the surface area (BET) of the adsorbents.
Scanning Electron Microscope (SEM)	Quanta FEG450	To determine a better view and clear understanding on the structural surface and pore arrangement of the adsorbent samples. Different magnification power was used to show the most suitable image.
Energy Dispersive X-Ray Spectroscopy	Quanta FEG450	To identify chemical composition of the adsorbent sample.
Particle Size Analyzer	CILAS 1180	To study the size of particle based on diffraction pattern obtained
Gas Chromatograph (GC)	Agilent Technologies 7890A	To determine the composition of binary gas mixture and adsorption capacity.
Furnace	GSL-1100x, MTI Corp	To provide thermal treatment to increase pore area of adsorbent.
Oven	Heraeus	For drying purpose. To regenerate the adsorbent by removing moisture and impurities.
Flow Meter Analyzer	AALBORG	Gas flow rate checking

3.5 Adsorbent Preparation

Preparation of adsorbents involves three samples which are UiO-66, activated carbon made from Kenaf and activated carbon made from Palm Kernel Shell whereas Zeolite 5A was obtained from USM Petroleum lab and used as received and went through degassing treatment by applying heat at 80-100^{o}C.