MAXIMIZING PURITY AND RECOVERY OF CARBON DIOXIDE FROM BIOGAS BY EQUALIZED PRESSURE SWING ADSORPTION USING UiO66 ADSORBENT

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MAXIMIZING PURITY AND RECOVERY OF CARBON DIOXIDE FROM BIOGAS BY EQUALIZED PRESSURE SWING ADSORPTION USING UiO66 ADSORBENT

by

TAN WERN KE

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LIST OF SYMBOLS

Symbol		Unit
Å	Interatomic distance	m
SA_{BET}	Specific surface area (Brunauer–Emmett–Teller)	m^2/g
tb	Breakthrough time	min
ts	Saturation time	min
Θ	Scattering angle	°
V	Voltage	V

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
SEM	Scanning electron microscope
XRD	X-ray diffractometer
GC	Gas Chromatograph
IUPAC	International Union of Pure and Applied Chemistry

ABSTRAK

Harga gas asli yang semakin tinggi disebabkan oleh keperluan tinggi dan isu-isu percemaran alam sekitar yang disebabkan oleh pelepasan metana dan karbon dioksida(gas rumah hijau) daripada biogas telah menyumbang kepada menaikkan taraf biogas. Dalam Kajian ini, penjerap UiO66 telah dipilih untuk menaikkan taraf biogas. Penjerap UiO66 telah disediakan dan dicirikan dengan 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. Ujian pencirian menunjukkan penjerap UiO66 ialah berliang-meso, kristal struktur dan bentuk celah serta mempunyai BET kawasan permukaan yang rendah. Kajian masa titik bolos dilakukan pada penjerap UiO66 dengan menggunakan komposisi gas(30%CH_4-70%CO_2) dalam tekanan 3 bar. CO_2 dibuktikan sedikit baik daripada CH_4 bila diserapkan ke dalam penjerap UiO66 kerana masa titik bolos CO_2 panjang sikit daripada titik bolos CH_4. Masa pelepasan dan penyerapan telah ditentukan berdasarkan pada masa titik bolos dan masa tepu untuk memperolehi ketulenan dan pemulihan gas karbon dioksida dan metana daripada penjerapan buaian tekanan. Maksimum ketulenan and pemulihan gas CO_2 ialah 82.70% dan 36.24%, maksimum ketulenan and pemulihan gas CH_4 ialah 38.22% dan 86.92% dalam 3.2 minit (masa penyerapan) dan 3minit (masa pelepasan) dengan menggunakan tekanan 3 bar.

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ABSTRACT

High price of natural gas due to high demand and environmental issues that caused by releasing methane and carbon dioxide (greenhouse gases) from biogas make biogas upgrading necessary. In this study, UiO66 adsorbent in pressure swing adsorption (PSA) processes was selected for biogas upgrading. The UiO66 adsorbent was 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 Analysis. The characterization tests showed that UiO-66 was mesoporous, slit-shaped, has low BET surface area and crystalline structure. Breakthrough study was carried out on the UiO66 adsorbent with feed gas composition (30%CH_4 - 70% CO_2) under 3 bar. CO_2 is the slightly strong adsorbed species compared to CH_4 in a UiO66 adsorbent which was proven by its slightly longer breakthrough time than CH_4 breakthrough time. Blowdown and adsorption time were selected based on breakthrough and saturated time and applied in PSA to obtain purity and recovery of CO_2 and CH_4. Maximum purity and recovery of CO_2 are 82.70% and 36.24% respectively whereas maximum purity and recovery of CH_4 are 38.22% and 86.92% respectively at 3.2 minutes of adsorption time and 3 minutes of blowdown time under 3 bar.

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

Natural gas well was first drilled in 1821 by William Hart and the gas, natural gas generate significant energy that bring great impact towards transport, industry, residential and power sector. Production and consumption on natural gas globally increase from low level in year 1989 to a yearly output of nearly 3500 Billion Cubic Meters in the year 2014 as illustrated in Figure 1.1.

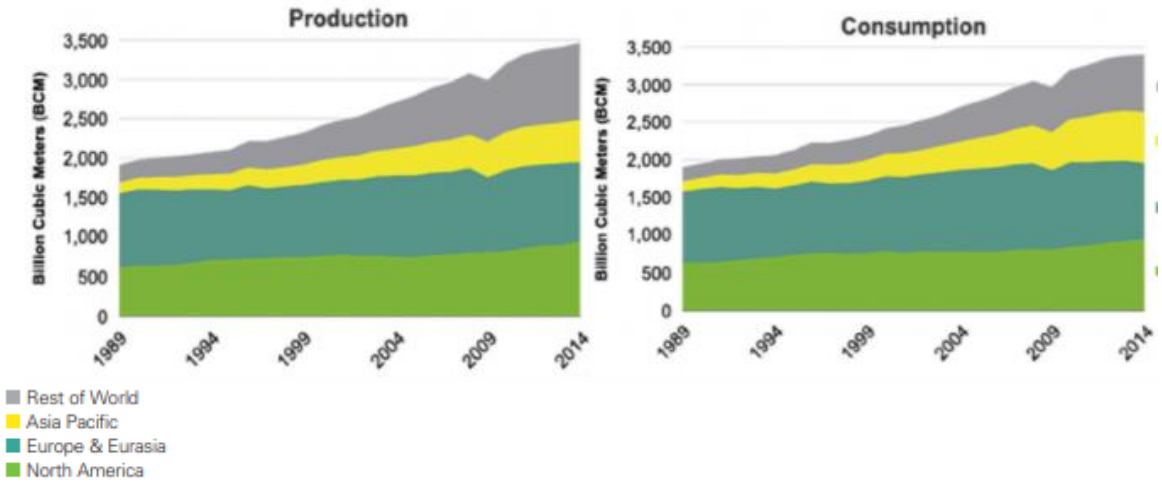


Figure 1.1: Global Production and Consumption of energy from natural gas from 1989 to 2014 (Faramawy *et al.*, 2016)

Consumption of natural gas resource can be distributed into 4 areas which are Asia pacific, Europe & Eurasia, North America and the rest of world with accounting for 19.9%, 29.6%, 28.3% and 22.2%. Almost the same, the percentage of production of natural gas in those areas just slightly higher than consumption of natural gas resource. Although there is enough supply of natural gas but the high demand of natural gas will be the key indicator to cause the raising in price. Figure 1.2 depicts the global price of natural gas.

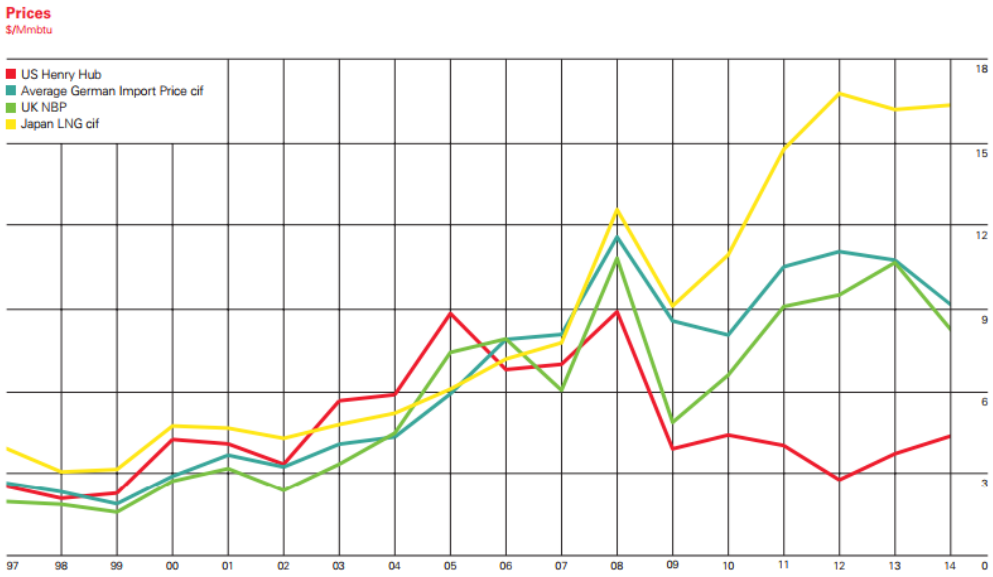


Figure 1.2: Global price of natural gas (Energy, 2015)

In 2014, the price of natural gas (US Henry Hub, Average German Import Price cif, UK National Balancing Point (NBP) and Japan Liquefied Natural Gas (LNG) cif still remain higher than the price in 1997.These hikes price of natural gas is the leading source in upgrading biogas. Biogas mainly consist of carbon dioxide and methane. Biogas upgrading can be act as substitution of natural gas by removing impurity carbon dioxide, CO_2 and increasing the methane rating (Petersson and WELLINGE, 2009).

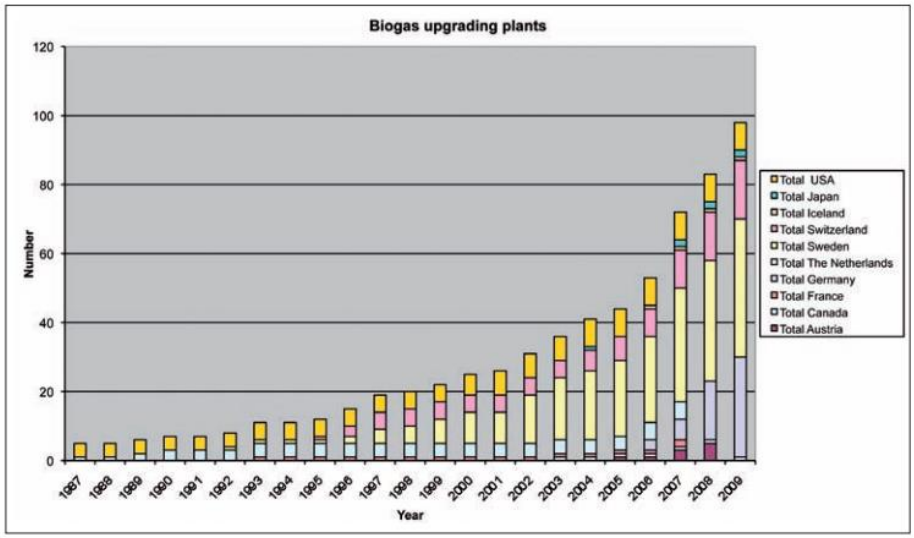


Figure 1.3:Total number of biogas upgrading plants (Petersson and WELLINGE, 2009)

From year 1987 to 2009, the importance of biogas upgrading have been widespread into many countries like Japan, Iceland, Switzerland, Netherlands, Germany, France and Austria. Therefore, figure 1.3 show clearly the trend, the total number of biogas upgrading plant have been increased drastically from 3 to 99.

Besides, not only reducing the price of natural gas, biogas upgrading also gain environment benefit of avoiding greenhouses gases methane and carbon dioxide emission to atmosphere. Carbon dioxide, CO_2 was separated and stored whereas the methane can be directly used as production of heat and steam, electricity, vehicle fuel and chemicals. Thus, importance of technologies separating between carbon dioxide and methane raise the attention worldwide (Starr Durany *et al.*, 2012). Figure 1.4 classifies the technologies of removing CO_2 from methane (biogas upgrading) and Figure 1.5 classifies the distribution of technologies applied in industrial.

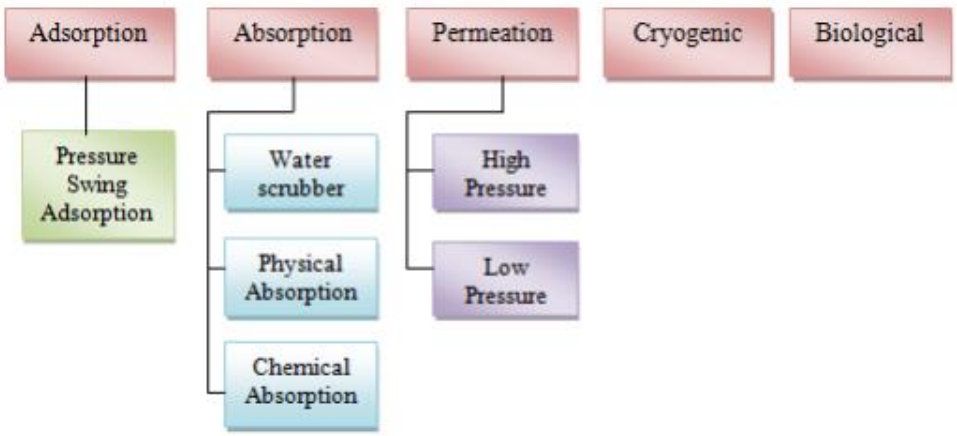


Figure 1.4: Classification of application technologies for separation of CO_2 from methane (biogas upgrading) (Warren, 2012)

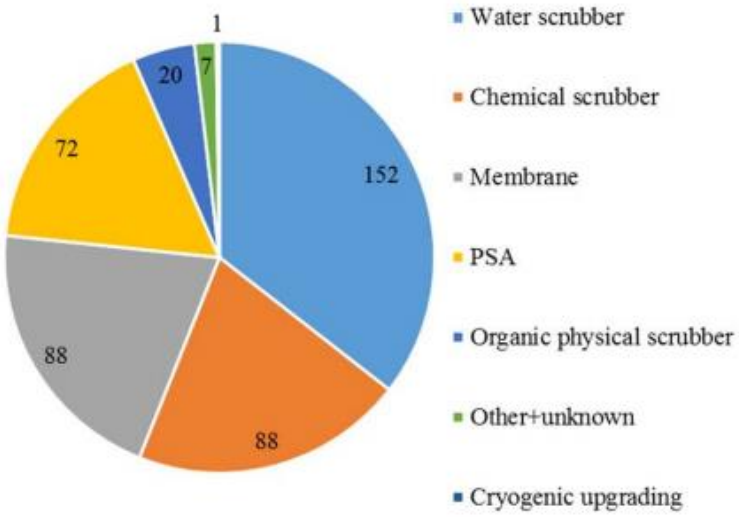


Figure 1.5: Classification of the distribution of technologies applied in industrial (HOYER *et al.*, 2016)

5 important technologies that can be applied to separate out CO_2 for biogas upgrading are adsorption, absorption, membrane, cryogenic and biological. Among these technologies, pressure swing adsorption have been acknowledged as third largest technology employed in biogas upgrading just behind the chemical scrubber technology which is 72 as stated in figure 1.5. PSA is a cyclic batch process where adsorptions are carried out at a comparatively higher pressure and desorption is accomplished at a lower pressure. In order to maximizing the purity and recovery of certain gas, type of adsorbent and the time evolution for gas adsorption play a vital role(Grande, 2012).

1.2 Problem statement

Biogas can be obtained during anaerobic digestion by breaking down organic material using different type of microorganism. In general, biogas composition consists of 40-70% methane, 30-60% carbon dioxide and small trace amount of hydrogen and hydrogen sulphide (Kossmann and Pönitz, 2007) whereas natural gas consist of 80-90% methane, 5% carbon dioxide and other gases (Faramawy *et al.*, 2016). Biogas and natural gas always have an unbreakable relationship. Both of them are renewable resources to generate electricity or act as fuel vehicle. However, natural gas seem to have more market value and high price when the demand increase yearly. In order to increase market value of biogas, researches were most likely to be conducted to reduce the CO_2 level because carbon dioxide reduce total energy calorific value of fuel gas.Moreover,CO_2 is an acidic gas. It can become carbonic acid upon contact with moisture such as shown by equation 1.

$$CO_2 + H_2O \rightarrow H_2CO_3 \quad (1)$$

This acid tends to corrode the pipeline and equipment which can increase the maintenance cost as well.

1.3 Research Objectives

The objectives of this research project are:

i) To prepare and characterize Zirconium-benzenedicarboxylate (UiO66) in terms of surface area, surface morphology and surface chemistry.

ii) To study the breakthrough analysis of carbon dioxide and methane gas using Zirconium-benzenedicarboxylate (UiO66).

iii) To obtain the highest CO_2 and CH_4 purity & recovery and by optimizing time of adsorption and blowdown using Design Expert software.

CHAPTER TWO
LITERATURE REVIEW

Chapter two briefly presents the previous discoveries and reviews available from credible scientific records and references that are related to this research topic. In general, this chapter outlines the overview of biogas, adsorption, and of significance, pressure swing adsorption (PSA) and adsorbent, specific UiO66. Then, a review on breakthrough studies involving UiO66 is presented to signify the importance of use in this research. Next, an extensive review of significance, pressure swing adsorption (PSA) is presented covering optimization and effect of the selected adsorption process variables.

2.1 Biogas

Biogas is one of the clean and renewable alternative energy that work as combustion fuel. Biogas main composition comprised of CH_4 and CO_2 and it is originated from feedstock agricultural, manure, crop residues, municipal waste (MSW) and industrial organics via anaerobic digestion process involving different types of microorganisms. Anaerobic process took place through 4 crucial steps which are 1) hydrolysis 2) Acidogenesis 3) Acetogenesis and 4) Methanogenesis. (Demirbas and Balat, 2009)

Specific emphasis also should be place on environment problems which is emission of greenhouses gases (CO_2 and CH_4) that contribute to global warming. Manure, sewage, waste water from livestock farm and industrial plant, as well as agricultural waste release biogas that contain of CO_2 and CH_4 which are not utilised and discharged to atmosphere, eventually causing environment issues. Therefore, there

must be some technologies to be applied. Table 2.1 showcase the biogas upgrading process in reducing global warming potential.

Table 2.1:Biogas upgrading process in reducing global warming potential (Starr Durany et al., 2012)

Upgrading Process	**Global Warming Potential(g of CO_2.Eqv)**
BABIU	-1977
AwR	-1794
HPWS	-1766
As	-1761
Cry	-1758
PSA	-1714
OPS	-1691
MS	-1489

Pressure swing adsorption (PSA) that recognised as mature technology requires more research and studies to improve the recovery and purity of CO_2 and then to be stored whereas high methane rating can be utilised to largely reduce the global warming potential.

2.2 Adsorption

Adsorption processes may be 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 may happen 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 sorbed molecules attach to the surface, the process is called adsorption whereas the sorbed 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 out the amount of solute adsorbed per unit mass of adsorbent at equilibrium. Adsorption is favoured at high pressure and low temperature. On the contrary, desorption is favoured at low pressure and high 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 illustrate the process of adsorption.

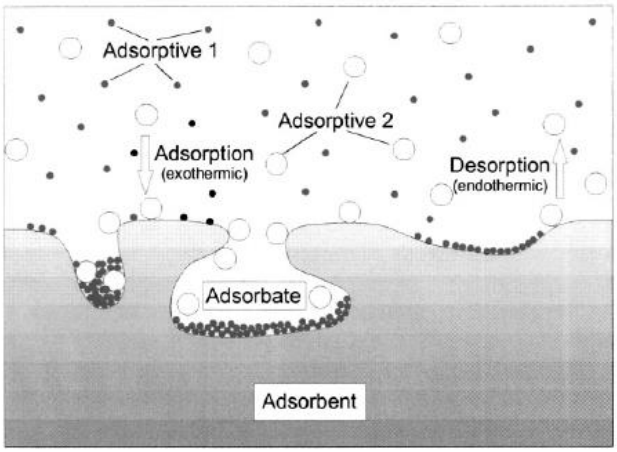


Figure 2.1: Adsorption system consisting of a two component sorptive gas, adsorbate and the adsorbent.(Keller and Staudt, 2005)

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 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 an endothermic process.

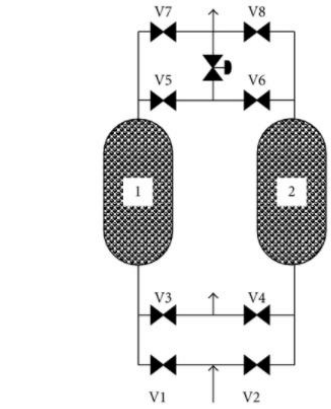
2.3 Pressure Swing Adsorption

Pressure Swing adsorption(PSA) is one of the separation technology can be 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 forth (Grande, 2012). Pressure swing adsorption technology always been selected to investigate due to its low energy, cost effective and ease of operation when compared with other technologies. For instance, cryogenic processes require the equipment and devices, like compressors, turbines, heat exchangers, insulators, and distillation columns in result of high capital cost (Sarkar, 2016).In biogas upgrading, amine scrubber need high heat temperature in associate to heat up the amine solvent about 150-170 ℃ for

regeneration and maintaining the adsorption efficiency. Undoubtedly, it will consume massive amount of energy in term of high cost and raise up the concern about safety issue (Miltner *et al.*, 2017).

Pressure swing adsorption, 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, impurities can be desorbed and discharged from the system. This shown that 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 depend on the suitable selection of adsorbent that well installed in PSA system and has matching pore size for the given adsorbate species to make it preferably to be adsorbed (Seader *et al.*, 2010).

Pressure swing adsorption consist of two or more beds that installed by adsorbents and operated by means of proper valves arrangement. The term ‘swing’ in PSA represent high pressure in feed change to low pressure while regeneration. PSA technology was firstly introduced by Charles Skarstorm, the four step of ‘Skarstrom cycle’ will be feed, blowdown, purge and pressurization. Figure 2.2 shows the schematic design of the PSA.



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)

If the pressure in the system replaced by temperature, which mean low temperature in feed and high temperature at regeneration process. It can be considered as temperature swing adsorption (TSA). Temperature swing adsorption (TSA) has its own benefit and drawback. TSA can be adopted during strong adsorption of mixture impurities to adsorbent in result good regeneration. However, TSA cycle time is much longer than PSA(Crittenden and Thomas, 1998). 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 converse 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. Longer the step time, the better of recovery and purity obtained.

2.4 Adsorbent

Selection of adsorbent always be the first consideration for the designation of 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. Micropores (<20Å diameter), mesopores (20-500 Å diameter) and macropores (>500 Å diameter) truly define the pore size of the adsorbents (DUTTA, 2007) .

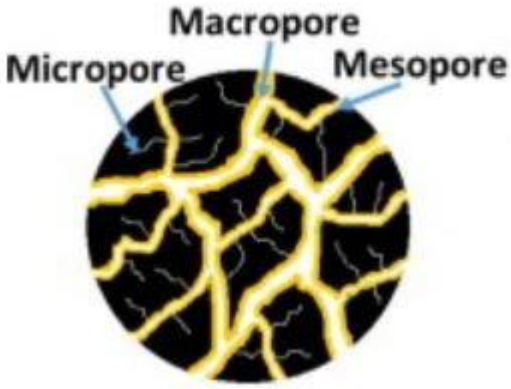


Figure 2.3: Schematic diagram of pore structure of adsorbent (Suresh Kumar *et al.*, 2017)

Activated carbon is a member of a family of carbons ranging from carbon blacks to nuclear graphites, from carbon fibres and composites to electrode graphites, 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}, larger the surface area, the better the performance of adsorption. Activated carbon also has larger working pressure (approximately 16 bar) and allows better performance in heat and mass transfer to decrease the bad smell and corrosiveness (Ullah *et al.*, 2013). (Rios *et al.*, 2013) studied on 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.

Zeolites are naturally occurring microporous crystalline silicate framework materials that have properties 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. 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 in order to remove CO_2.Adsorption capacity, thermal stability and regeneration rate in regard with different pore structure of adsorbents will be the benchmark for that researchers to figure out (Majchrzak and Nowak, 2017). The result of comparison of the selection criteria necessary for CO_2 capture can be concluded in Table 2.2.

Table 2.2 Result of comparison of the selection criteria necessary for CO_2 capture (Majchrzak and Nowak, 2017)

	Activated Carbon	**Zeolites**
Sorption capacity	Lower than zeolites (at ambient condition),higher at higher pressure	Higher than activated carbons(at ambient conditions),lower at higher pressures
Thermal Stability	Stable at multiple cycles	Stable at multiple cycles
Level of regeneration	The easiest to regenerate	Harder to regenerate than activated carbon
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
Impact of moisture	The least influence in compare to other adsorbents	High impact of moisture on sorption capacity.

Table 2.2 continued

	Carbon molecular sieves	Sorbents modified with amines
Sorption capacity	Lower than activated carbon and zeolites(at ambient condition)	Lower than physical adsorbents at 25 °C but higher at 70-90 °C
Thermal Stability	Stable at multiple cycles	Stable at multiple cycles
Level of regeneration	More difficult to regenerate than activated carbon, but much easier than zeolites	Easy to regenerate, but harder than activated carbon
Influence of other factors	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	Slight influence on moisture	Minimal or no impact of moisture on sorption capacity

2.5 Zirconium-benzenedicarboxylate UiO66 Adsorbent

UiO66 is 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 UiO66 has shown in Figure 2.4.

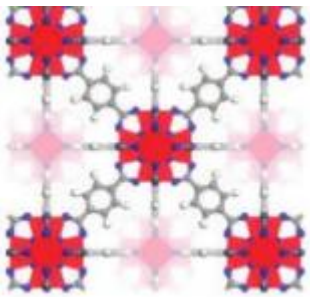


Figure 2.4: Cluster structure of UiO66 adsorbent with its linker 1,4-benzene-dicarboxylate (Cavka *et al.*, 2008)

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 indicate that UiO66 (SA_{BET}=1250m^2/g)(Huang *et al.*, 2017). Eventually, it exhibit that UiO66 has much better adsorption capacity than zeolite adsorbent.

Furthermore, UiO66 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 UiO66. The BET surface areas can change from 1175 m^2g^{-1} to 1777 m^2 g^{-1} that have been reported in recent research (Shearer *et al.*, 2016).

2.6 Breakthrough study

Breakthrough studies can act as guidance to evaluate the performance of bed which mean the adsorbent that installed in column. In pressure swing adsorption (PSA), it also allow 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).Breakthrough curve can be plotted by y-axis, C/Co which convey feed concentration after pass through the bed over concentration before feed in against x-axis, time. After injection of adsorbate, the process adsorption will start to occur and as the time pass three region will be established inside the bed at certain

length which are saturated zone, mass transfer zone and unused zone as shown in Figure 2.5.

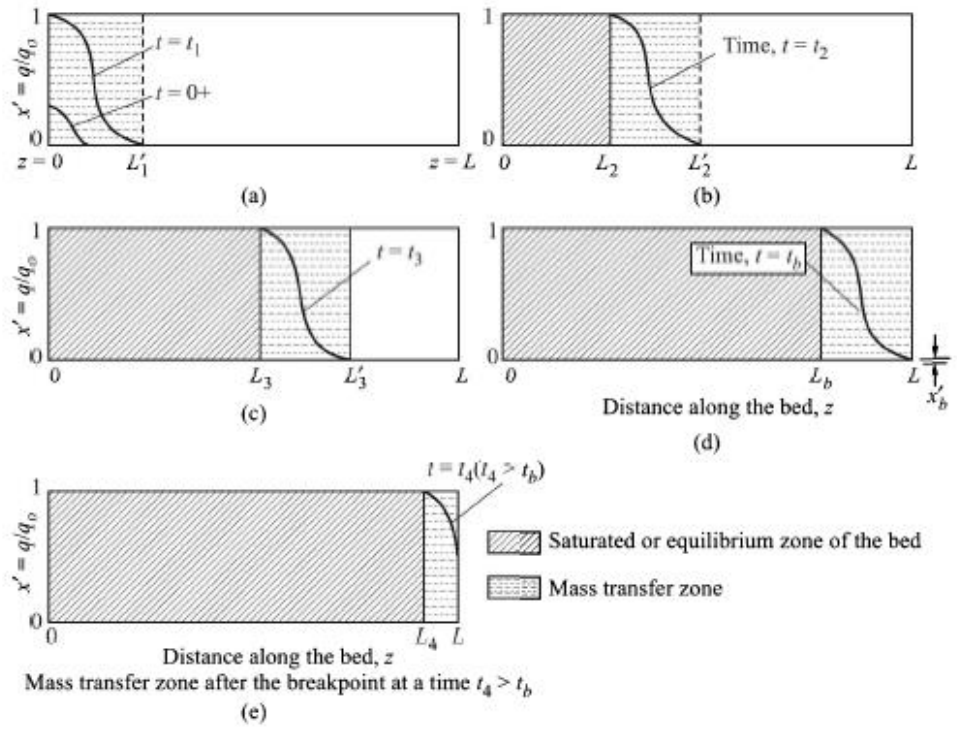


Figure 2.5: Solid concentration profile at different times

Once it reach the breakthrough time (t_b) concentration of effluent can be determined. Then concentration of effluent continues to increase until it meet 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 the longer breakthrough and saturated time (Chowdhury *et al.*, 2013).

2.7 Breakthrough Study of CO_2 Removal Using UiO66

In previous work, UiO66 has been applied for removal of CO_2 from N_2 at different pressure and the breakthrough curve is plotted. At pressure 3 bar, UiO66 achieved a breakthrough 400 second (6.67minutes) in their study. At pressure 4 bar, UiO66 achieved a breakthrough 500 second (8.3minutes) in their study. This reported

that as pressure increase, the adsorption capacity of adsorbent increase (Andersen *et al.*, 2013). Rather than using UiO66,the same class adsorbent (MOF) Cu-BTC tablets has been researched by studying the breakthrough curve in separation of 83% methane and 4.5% CO_2 at 1.1 bar and 308K,others will be helium gas. The breakthrough time for CO_2 removal was 1000 second (16.67 minutes) (Asadi and Ehsani, 2013). Other than that, 30PEI-impregnated UiO-66 has been characterized and explored by researchers to find out the breakthrough of binary mixture CO_2/CH_4 (ratio 1:9) at 308 K and compared with the UiO-66 without undergo process impregnation. The original CO2 breakthrough time for UiO-66 is 40s whereas 30PEI-impregnated UiO-66 for CO2 breakthrough time has been increased until 250s.(Xian *et al.*, 2015)

2.8 Effect of adsorption time and blowdown time in PSA

Adsorption time and blowdown time both are important parameters to affect the performance of pressure swing adsorption, PSA. (Rao *et al.*, 2010) examine on the optimization of combination adsorption time and blowdown time to maximize oxygen purity via stimulation COMSOL software by using adsorbent 5 Å and partially Ag exchanged-Li-substituted 13X zeolite adsorbents in two steps pulse pressure swing adsorption. From their findings, they discovered that very long adsorption time 0.24s will cause impurity like nitrogen penetrate through the bed and affect product oxygen purity at fixed desorption time 1.2 second. Same point have been reported in (Jain *et al.*, 2003) about the adsorption time cannot go beyond the breakthrough time of impurity. The adsorption time that stay within the limit also have to adjust to meet the high purity and recovery of product. It was discovered that 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 ($H_2/CO_2/CH_4/CO$).It showed that 0.2 ratio of blowdown time to adsorption time achieve highest recovery which exceeded 84% of recovery by using adsorbent ratio 60/60, 70/50 and 80/40 respectively.

2.9 Design Expert Response Surface Methodology (RSM) for optimization in PSA

RSM was introduced since 1951 and act as excellent platform to figure out optimum condition in experiments. It was set up by modelling techniques that involving mathematic and statistic theories which can provide robustness and flexibility in design system (Khuri and Mukhopadhyay, 2010). There were a few features inside RSM for example Central Composite, Box-Behnken,3 Level Factorial and so on. Among these features, one of commonly used feature will be Central Composite design (CCD). (Ribeiro Sant Anna *et al.*, 2015)adopted central composite design (CCD) for optimization of operational pressure to separate mixture gases (CH_4/N_2) in pressure swing adsorption. High pressure 6 bar, Intermediate 5.5 bar and low pressure 0.1 bar were the optimum condition to allow high N_2 purity 96.61% and N_2 recovery 89.81% to be produced. (Saberimoghaddam and Nozari, 2016) studied intensively on optimization purge/feed ratio and adsorption time for purification of hydrogen in an H_2/CO_2 mixture. Their result concluded that at intermediate condition purge/feed ratio 0.2 and desired adsorption time 10.42 minutes can obtain maximum of purity and recovery.

CHAPTER THREE

MATERIALS AND METHODS

This chapter covers the overall experimental aspects of the research project including the general research flow diagram, materials utilized, adsorbent preparation and characterization, experimental rig set-up for breakthrough studies and pressure swing adsorption along with optimization software Design Expert Central Composite Design (CCD).

3.1 Research Methodology

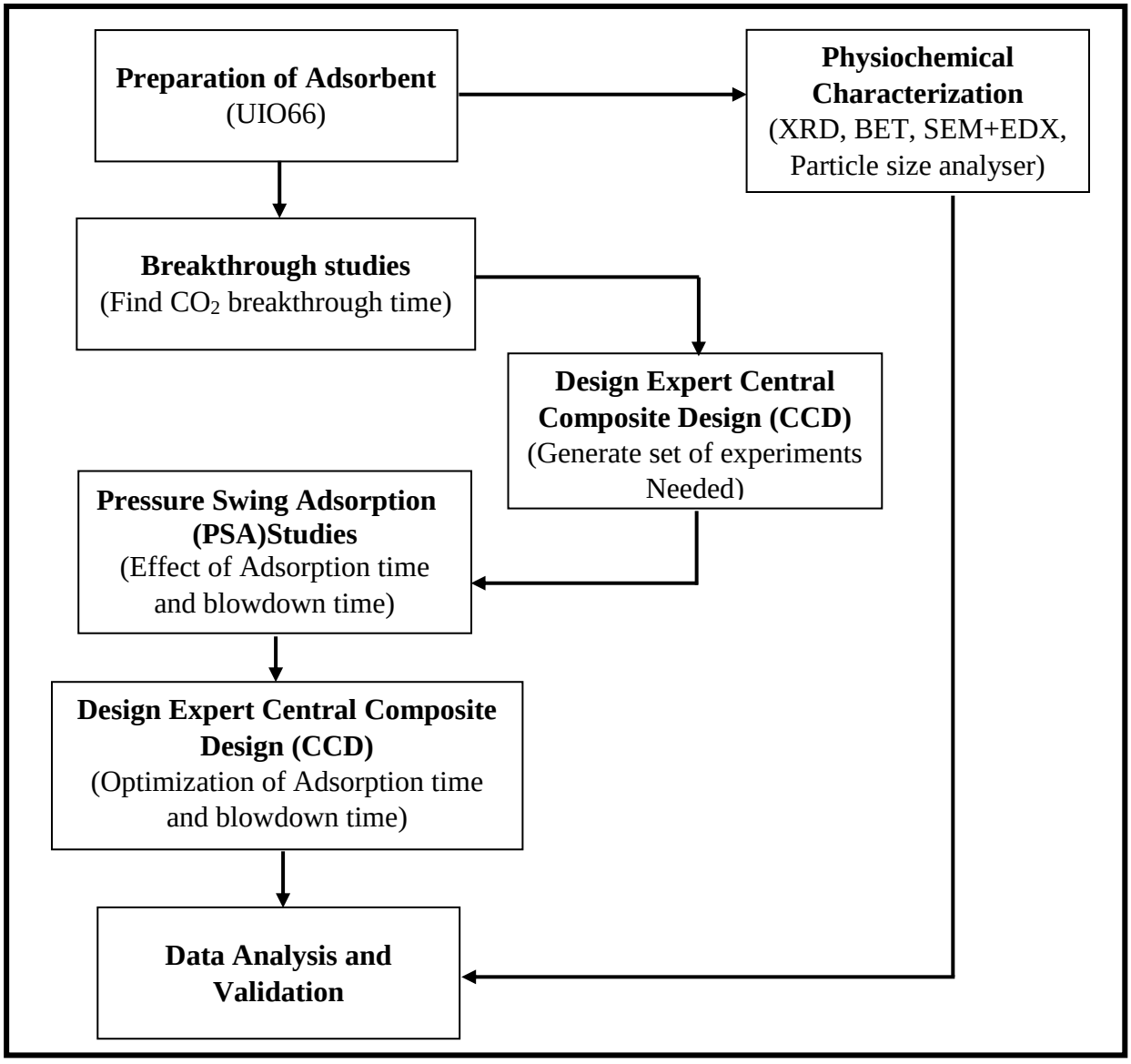


Figure 3.1: General layout of research flow diagram.

3.2 Materials and Chemicals Required

The list of materials and chemicals used in this research are shown in 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 UiO66
Dimethylformamide (DMF)	$HCON(CH_3)_2$,	99.8	Sigma-Aldrich	Preparation of adsorbent UiO66
1,4 benzenedicarboxylic acid (BDC)	C_9H_6	-	Sigma-Aldrich	Preparation of adsorbent UiO66
Ethanol	CH_3CH_2OH,	99.8	Sigma-Aldrich	Preparation of adsorbent UiO66

3.3 Equipment Required

Different types of equipment were used for different purposes in this research such as preparation of adsorbents, breakthrough study and PSA studies. The list of equipment used in the study are shown in Table 3.2.

Table 3.2: List of equipment.

Equipment	Model	Application
X-Ray Diffractometer (XRD)	Bruker XRD D8 Advance	➢ To study the crystallinity and atomic spacing of sample. ➢ To analyse the crystalline phases and orientation.
Surface Area and Porosity Analyser (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 Analyser	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.

Table 3.2 continued

Equipment	Model	Application
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 analyser	AALBORG	➢ Binary mixture flow rate checking

3.4 Adsorbent Preparation

3.4.1 Zirconium-benzenedicarboxylate (UiO-66)

Firstly, 1.06 g of zirconium (IV) chloride (ZrCL4) was dissolved with 30 ml of dimethylformamide (DMF) and follows with 30 minutes of stirring. After that, 0.78 g of 1,4 benzenedicarboxylix acid (BDC) was dissolved into 30 ml of DMF at 25 °C in a volumetric flask. Both dissolved solutions were mixed and stirred together with 2 ml of deionized water and placed in an oil bath. The mixture was then go through thermal treatment process in furnace at 120 °C about 30 minutes. After the process, the solution was then cooled down to room temperature for 2 hours. Finally, precipitate was obtained as expected. Absolute ethanol was then used to washed the resulting precipitate repeatedly for 3 times. The washed precipitate was then dried at 70 °C for overnight.