A STUDY ON THE PURITY AND RECOVERY OF CARBON DIOXIDE GAS FROM BINARY FLUE GAS MIXTURE USING DIFFERENT ADSORBENTS IN PRESSURE EQUALIZED PRESSURE SWING ADSORPTION

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by

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LIST OF SYMBOLS

Symbol		Unit
P_{blow}	Blowdown pressure	bar
t_b	Breakthrough time	min
I	Electric current	mA
P_E	Electric power consumption	W
eV	Electronvolt	J
Å	Interatomic distance	m
t_s	Saturation time	min
Θ	Scattering angle	°
S	Specific surface area	m^2/g
θ	Surface angle	°
V	Voltage	V

LIST OF ABBREVIATIONS

APKS	Activated palm kernel shell
Ave	Average
BET	Brunauer–Emmett–Teller
C1	Adsorbent column 1
C2	Adsorbent column 2
EDX	Energy dispersive x-ray
MOF	Metal organic framework
MSDS	Material safety data sheet
Na-A	Na-A type zeolite
Na-X	Na-X type zeolite
PKS	Palm kernel shell
ppm	Parts per million
PSA	Pressure swing adsorption
PVSA	Pressure/vacuum swing adsorption
SEM	Scanning electron microscope
TGA	Thermogravimetric analyzer
TSA	Temperature swing adsorption
XRD	X-ray diffractometer
Z-13X	Zeolite-13X
Z-5A	Zeolite 5A
ZIF-8	Zeolitic imidazolate framework-8

KAJIAN MENGENAI KETULENAN DAN PEMULIHAN GAS KARBON DIOKSIDA DARI GAS SEROMBONG CAMPURAN DEDUA MENGGUNAKAN PELBAGAI PENJERAP DALAM PENJERAPAN BUAIAN TEKANAN BERTEKANAN SAMA

ABSTRAK

Pelepasan gas karbon dioksida (CO_2) kepada alam sekitar menyumbang kepada pemanasan global dan proses perubahan iklim. Untuk mengurangkan kesan pembebasan gas CO_2 kepada alam sekitar, kajian ini menjelajah penggunaan bahan penjerap tempurung isirung palma teraktif (APKS) dan Kerangka-Imidazolate-Zeolit-8 (ZIF-8) dalam proses penjerapan buaian tekanan (PSA) untuk memerangkap CO_2 daripada satu campuran dedua gas serombong mengandungi CO_2 dan gas nitrogen (N_2). CO_2 merupakan spesies lebih kuat terjerap berbanding dengan nitrogen dalam gas serombong. Bahan penjerap itu kedua-duanya disedia dan dicirikan menggunakan analisa Brunauer–Emmett–Teller (BET), analisa Mikroskopi Elektron Imbasan (SEM), analisa X-Ray Tenaga Sebaran (EDX), analisa Therma-Gravimetrik (TGA), analisa saiz partikel dan analisa Pembelauan Sinar-X (XRD). Kajian masa titik bolos dilakukan pada bahan penjerap dengan meyiasat kesan jenis-jenis bahan penjerap dan komposisi gas (15% - 25% CO_2). APKS terbukti bahan penjerap yang lebih baik dengan perkembangan besar pada kepekatan gas CO_2 yang diuji. Masa titik bolos kemudiannya diterima ke dalam PSA dan prestasi kedua-dua bahan penjerap dalam proses itu telah dinilai. Kesan jenis bahan penjerap dan komposisi gas dalam PSA telah disiasat. Ketulenan gas CO_2 telah dapat ditumpukan kepada 82.99% manakala pemulihan sebanyak 99.61% juga ditentukan. Keputusan yang didapati ini memberi sedikit harapan dalam aplikasi APKS dan ZIF-8 dalam

pemerangkapan CO_2 dalam PSA yang boleh jadi berguna untuk pemulihan alam sekitar dan penulenan nitrogen.

A STUDY ON THE PURITY AND RECOVERY OF CARBON DIOXIDE GAS FROM BINARY FLUE GAS MIXTURE USING DIFFERENT ADSORBENTS IN PRESSURE EQUALIZEDPRESSURE SWING ADSORPTION

ABSTRACT

Carbon dioxide (CO_2) gas emission to the atmosphere contributes to global warming and climate changes processes. To mitigate the effects of carbon dioxide release to the atmosphere, this study explores the usage of activated palm kernel shell adsorbent (APKS) and zeolitic imidazolate framework-8 (ZIF-8) in pressure swing adsorption (PSA) processes to remove carbon dioxide from a binary mixture of flue gas containing CO_2 and nitrogen (N_2) gas. CO_2 is the more strongly adsorbed species compared to nitrogen in a flue gas. The adsorbents were both prepared and characterized using Brunauer–Emmett–Teller (BET) Analysis, Scanning Electron Microscope (SEM) analysis, Energy Dispersive X-Ray (EDX) analysis, Thermogravimetric analysis (TGA), Particle Size Analysis and X-Ray Diffraction (XRD) analysis. Breakthrough studies were performed on the adsorbents with the effect of adsorbent types and feed gas composition (15% - 25% CO_2) investigated. APKS proved to be a better adsorbent with larger breakthroughs at the tested feed CO_2 concentrations. The breakthrough time was adopted into the PSA and the performance of both adsorbents in the process were evaluated. The effects of adsorbent type and feed gas composition in PSA were investigated. The purity of carbon dioxide gas was able to be concentrated to 82.99% and a recovery of 99.61% was also determined. These results provide some promising insight into the application of APKS and ZIF-8 in carbon dioxide capture in PSA which could be useful for environmental remediation and nitrogen purification.

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 from flue gas. In general, this chapter outlines the research background of carbon dioxide emissions and pressure swing adsorption, the problem statement and objectives of this study along with the scope of research. Next, a brief review of the study is provided through the organization of thesis.

1.1 Research Background

From the dawn of the industrial revolution in the 1760s, fossil fuels have been recognized as the driving influence behind the industrialized world and its economic growth. Energy from fossil fuels has grown from insignificant levels in 1800 to a yearly output of approximately 10 billion tons of oil equivalents in the year 2010 as illustrated in Figure 1.1.

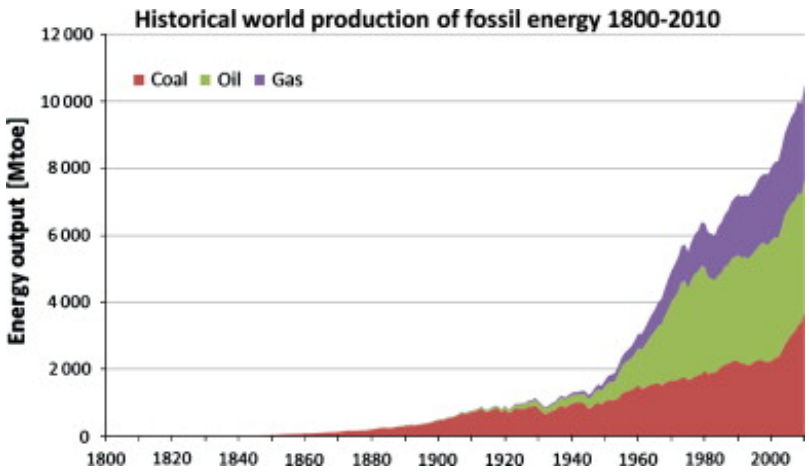

Figure 1.1: Global production of energy from fossil fuels from 1800 to 2010 (Höök *et al.*, 2012).

As of 2014, 81.1% of primary energy in the world is derived from fossil fuels with oil accounting for 31.3%, coal for 28.6% and natural gas for 21.2%. In the same year, only 1.4% of the world's primary energy is supplied from geothermal, wind, solar or other alternative energy sources (IEA, 2016). It is likely that fossil fuels will stay the spine of the world's energy system for some expected time, given their present dominance. However, global reliance on fossil fuels brings about a devastating yet associated problem, namely associated greenhouse emissions (Höök and Tang, 2013).

In fact, energy production is the leading source of carbon dioxide (CO_2) and other greenhouse gas emissions. Figure 1.2 shows the shares of global anthropogenic greenhouse gases in the year 2010.

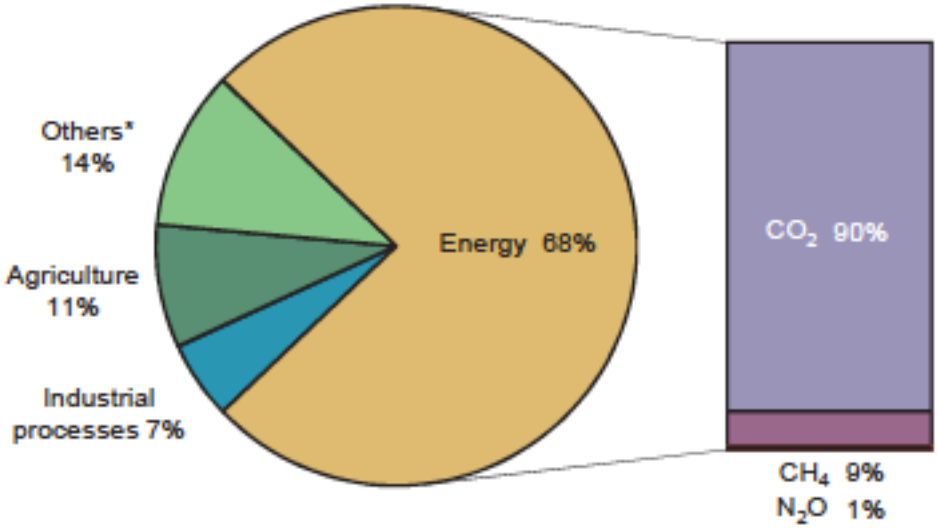

Figure 1.2: Global anthropogenic greenhouse gas emissions by type and source for the year 2010 (IEA, 2015).

Around 68% of all anthropogenic greenhouse gas emissions originate from the energy sector with CO_2 being the largest contributor through fossil fuel combustion. In 2013, nearly 32 billion tons of CO_2 were produced from fossil fuel consumption

and this number has since doubled since 1971. Figure 1.3 shows clearly the trends of CO_2 emission due to fossil fuel combustion over the years from 1971 until 2013.

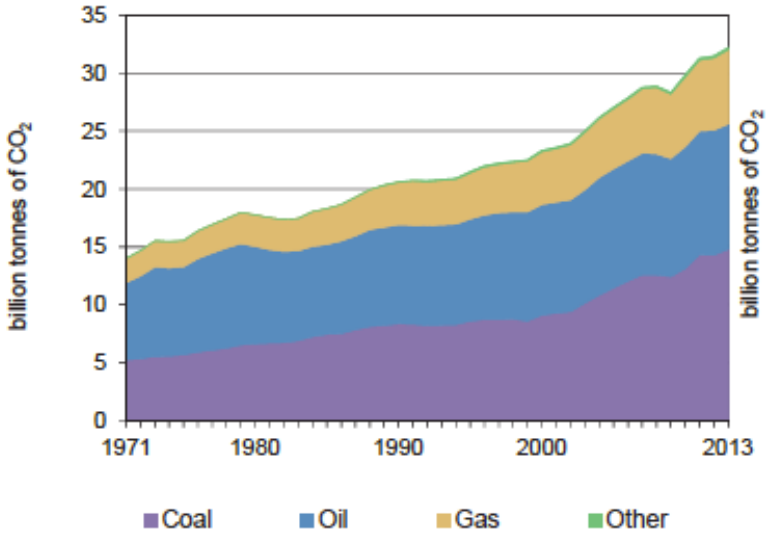

Figure 1.3: CO_2 emission trends from 1971 to 2013 by fuel (IEA, 2015).

Carbon dioxide emissions to the atmosphere have been acknowledged as a major contributor to global warming. Climate scientists have detected that carbon dioxide concentrations in the atmosphere have been increasing drastically over the past century. The 2014 concentration of CO_2 (397 ppm) was roughly 40% higher than in the mid-1800s, with an average growth of 2 ppm/year in the past few decades (Figure 1.4) (IEA, 2015).

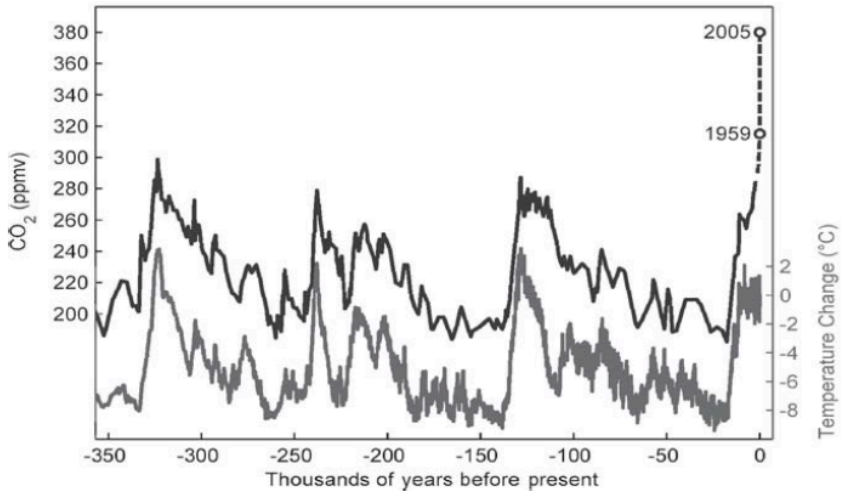

Figure 1.4: Climate history of the past 350,000 years (Petit *et al.*, 1999).

Sources of CO_2 emissions come from the combustion of fossil fuels that include coal, natural gas and petroleum, and industrial processes such as oil refining, production of cement, iron and steel. Concentrations of CO_2 in coal-fired power plants vary between 12.5-12.8% while in gas-fired power plants the concentrations of carbon dioxide can range from 7.4-7.7%. Thus, considering the abundant sources of CO_2 emissions, the strategic importance of post-combustion capture systems become evident (Dantas *et al.*, 2011). Figure 1.5 classifies technologies of post-combustion capture of CO_2.

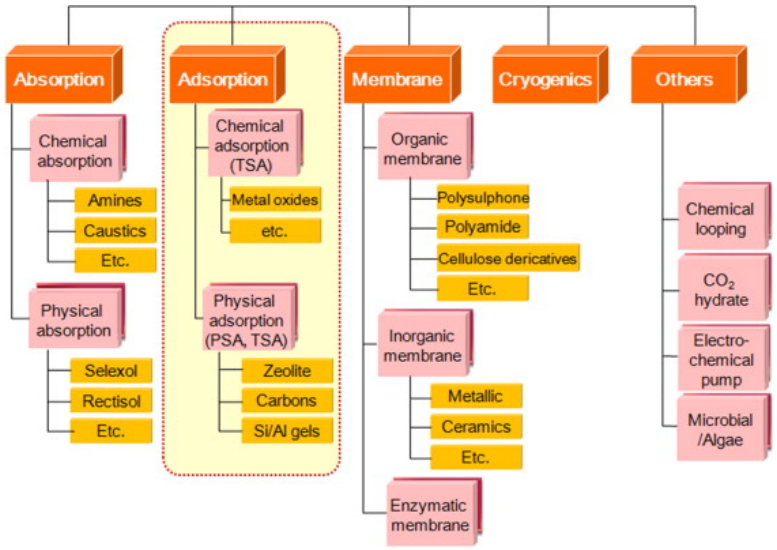

Figure 1.5: Classification of application technologies for post-combustion of CO_2 (Lee and Park, 2015).

The recovery of CO_2 from flue gases emitted by power plants, steel mills, cement kilns and fermentation processes is becoming increasingly viable (Chue *et al.*, 1995). Reduction of carbon dioxide emissions from flue gases can be achieved using post-combustion capture technologies such as adsorption (Dantas *et al.*, 2011). Pressure swing adsorption (PSA) is one of the most known industrial processes for gas separation. 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

any adsorption-based technology, the most important decision is the adsorbent selection. The adsorbent should be based on a material that has high affinity for the gas to be recovered with good sorption capacity as well as desorption capabilities (Gomes and Yee, 2002).

1.2 Problem Statement

While the transition towards a more sustainable energy economy is insistent, fossil fuels, which are understood to be the main contributor to global warming, are likely to remain the focal source of energy supply for the imaginable future. Power plants that burn fossil fuels emit CO_2 through the release of flue gases, which consequently becomes the major cause for the accumulation of CO_2 in the atmosphere, eventually causing long-term environmental problems. The composition of CO_2 in the flue gas is critical. In general, flue gases contain around 17% CO_2, 79% N_2 and the balance being O_2. Trace amounts of SO_2 and NO_x can also be found, but they are usually much less than 1% in total (Kikkinides *et al.*, 1993). It can be as low as 3 mol% from a gas-fired power plant and as high as 15 mol% from a usual coal-fired power plant (IEA, 2010). As CO_2 concentrations decrease, the energy for capture increases sharply. Post-combustion capture from a gas-fired power plant has not received much awareness so far. However, for countries like Singapore that generate more than 80% of its power from natural gas, it can be very crucial (Susarla *et al.*, 2015).

Adsorption based technology such as pressure/vacuum swing adsorption (PVSA) technology has been regularly researched because of the technology's low energy requirements and relative ease of use. Recognized as a mature technology, it is used to separate gas species from a mixture of gases according to the species'

molecular characteristics and affinity with regards to an adsorbent. The first and foremost important concern in any adsorption technology is to uncover the appropriate sorbent material for the proposed separation process. With regards to the current case, this sorbent material must possess a high selectivity for CO_2 over both N_2 and O_2, with fast exchange rates in order to achieve a sensibly high throughput. It is discovered that from previous literature, carbon has a much higher adsorption capacity for CO_2 than for N_2 and O_2 (Kikkinides *et al.*, 1993). Usual precursors used for the synthesis of activated carbons are organic materials that are rich in carbon. However, the high expense of activated carbon have restricted its applications and thus over the years, the focus of research has shifted to replace this commercially available activated carbon with suitable low cost alternatives (Gupta *et al.*, 2012). Therefore, the development of methods to reuse waste materials as activated carbons is greatly desired and offers a promising future. Activated carbon produced from palm kernel shell appear to be a flawless choice as the parent feed are abundantly available in Malaysia and have very low market value (Hidayu and Muda, 2016).

Non-carbonaceous adsorbents, such as zeolites, have high selectivity for CO_2 also. However, CO_2 adsorption on these materials especially zeolites is too strong, making desorption a difficult process (Kikkinides *et al.*, 1993). Zeolites are typically utilized at pressures above 2 bars and require very high regeneration temperatures, often above 573 K. Thus, CO_2 regeneration results in huge energy loss (Chue *et al.*, 1995, Harlick and Sayari, 2006). Furthermore, the performances of zeolite adsorptions decrease because they absorb moisture easily (Brandani and Ruthven, 2004). This issue however, can be mitigated with the utilization of an adsorbent material namely zeolitic imidazolate framework-8 (ZIF-8). ZIF-8, a metal organic framework (MOF) material shows unrivalled hydrophobicity and stability towards

moisture when compared with other adsorbents (Küsgens *et al.*, 2009). The utilization of activated palm kernel shell (APKS) and ZIF-8 in PSA allow the evaluation of their adsorption potential to separate CO_2 from N_2/CO_2 binary mixtures representative of flue gas.

1.3 Research Objectives

The objectives of this research project are:

i) To prepare and characterize activated palm kernel shell and ZIF-8 adsorbents in terms of surface area, surface morphology and surface chemistry.

ii) To study the breakthrough analysis of carbon dioxide and nitrogen gas using activated palm kernel shell and ZIF-8 adsorbents.

iii) To evaluate the performance of pressure swing adsorption by varying different operating parameters using activated palm kernel shell and ZIF-8 adsorbents.

1.4 Research Scope

In this study, activated palm kernel shells and ZIF-8 adsorbents were synthesized and prepared accordingly. After synthesis, both adsorbent materials were characterized using Particle Size Analyzer, Thermogravimetric Analyzer (TGA), Brunauer–Emmett–Teller (BET) analysis, Scanning Electron Microscope (SEM) and X-Ray Diffractometer (XRD). The characterizations were done to observe and study the adsorbent materials in terms of surface area, surface morphology and surface chemistry. Then, breakthrough studies were performed using both the adsorbent materials to observe adsorption breakthrough points. Lastly, the performances of the

adsorbent materials were evaluated through pressure swing adsorption by varying the binary gas compositions of CO_2/N_2.

1.5 Organization of Thesis

This thesis consists of five main chapters and each chapter contributes to the sequence of this study. The following are the contents for each chapter in this study:

Chapter 1 introduces the overview of this research and the significance of pressure swing adsorption in post-combustion carbon dioxide captures, problem statement, research objectives, research scope and the organization of thesis.

Chapter 2 discusses the literature review of this study. An insight into adsorbents in general and adsorbents used for carbon dioxide capture, a discussion on adsorption process, activated palm kernel shell, ZIF-8 and breakthrough studies involving the adsorbents are elaborated. Also, explanations on pressure swing adsorption and the influence of operating parameters are included as well.

Chapter 3 covers the experiment materials required for this study and the details of methodology from the start of this research project. It discusses on the description of equipment and materials used, characterization steps, breakthrough experiments, experimental procedures and description of parameters affecting the pressure swing adsorption process.

Chapter 4 refers to the experimental results and discussions of the data obtained. Further elaboration on the adsorbent characterization results, adsorbent breakthrough studies and effect of different factors on pressure swing adsorption are provided in this chapter.

Chapter 5 concludes all the findings achieved in this research study. Recommendations for future studies on this research topic are included as well.

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 and elaboration of adsorbents at large, adsorbents used in carbon dioxide capture and in particular, zeolitic imidazolate framework-8 (ZIF-8) and activated palm kernel shell (APKS). Then, a review on breakthrough studies involving ZIF-8 and activated palm kernel is presented to signify the importance of use in this research. Next, an extensive review of adsorption and of significance, pressure swing adsorption (PSA) is presented covering the selected adsorption process variables.

2.1 Adsorbents

An adsorbent is the solid or liquid on whose surface, adsorption occurs (Gopalan *et al.*, 2016). The first and foremost crucial concern in any adsorption process is to find the appropriate sorbent material for the proposed separation process (Kikkinides *et al.*, 1993). Solid adsorbents are porous media, which consist of voids, channels or spaces, which are deeper in dimension than they are wide. Typical commercial adsorbents, which may be in the form of granules, spheres, cylindrical pellets, flakes, or powders of diameter ranging from 50 mm to 1.2 cm, have specific surface areas within the span of 300 to 1,200 m^2/g. Thus, a few grams of adsorbent can represent a surface area equal to that of a football field (Seader *et al.*, 2010).

As shown in Figure 2.1, the large surface area of the adsorbent is due to the micropore and mesopore internal structures (Hassan *et al.*, 2015).

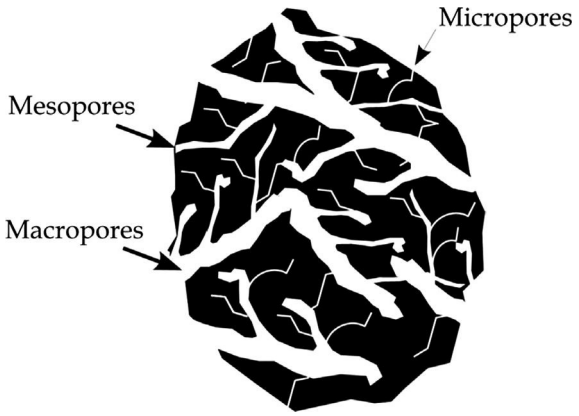

Figure 2.1: Schematic illustration of adsorbent pore structure (Hassan *et al.*, 2015).

The four most broadly used adsorbents in increasing order of commercial usage are activated alumina, silica materials, molecular-sieve zeolites and activated/molecular-sieve carbon (Seader *et al.*, 2010). Generally, fast adsorption and desorption kinetics, large adsorption capacity, limitless regenerability and stability and a wide yet tunable array of operating conditions might describe an ideal, hypothetical adsorbent (Choi *et al.*, 2009). The selection of adsorbent is amongst the crucial factors that influence adsorption, which eventually decides the economics, efficiency and flexibility of the adsorption process (Mittal *et al.*, 2016).

2.1.1 Activated Carbon Adsorbents

Activated carbon is a form of carbon that has been treated to become an extremely porous substance and to provide it with a very large surface area, which is highly preferable for adsorption or chemical reactions. Activated carbon is a member of a hierarchy of carbons ranging from carbon blacks to nuclear graphites, from carbon fibres and composites to electrode graphites, and many more. All of these carbons come from organic feed sources but with different carbonization and

manufacturing treatments (Marsh and Rodríguez-Reinoso, 2006). Generally, the parent materials used for the production of activated carbon are substances with high carbon content and low mineral matter content such coal, lignite, wood and peat (Wildman and Derbyshire, 1991, Karacan *et al.*, 2007, Ruiz *et al.*, 1993, Lozano-Castelló *et al.*, 2001, Mohan and Pittman Jr, 2006). Activated carbon is usually characterized by its large surface area (typically within the range of 800–1500 m^2g^{-1}), higher adsorption capacity, higher surface reactivity and suitable pore size. Activated carbon typically exists in the forms of granular and fiber materials. The activated carbon material in the form of fiber is desirable for its larger surface area, uniformly distributed pores and improved performance in heat and mass transfer processes as compared to the granular carbon (Ullah *et al.*, 2013). Activated carbon in the industry has a large number of applications such as in water treatment, air pollution control, and as a catalyst support (Marsh and Rodríguez-Reinoso, 2006).

2.1.2 Zeolite Adsorbents

Zeolites are naturally occurring microporous crystalline silicate framework materials that are widely used as catalysts in a variety of reactions as adsorbents (Breck, 1973, Szostak, 1998). Naturally occurring zeolites can be categorized into 40 different types with the most significant types being faujasite, cowlesite, chabazite and sodium chabazite. They are also synthesized in the laboratory with over 150 types of artificial zeolite synthesized worldwide already. These synthetic types are named with a single letter or a group of letters, such as type A, B, X, ZSM and so on (Ponec *et al.*, 1974). The adsorption capacity depends on the zeolite structure and usually occurs in the crystal pores or the center cages (Wang *et al.*, 2009). Zeolites have uniform pore sizes of 0.5–1.2 nm, forming networks of interconnecting

networks or cages for adsorbing and capturing gas molecules (Chester and Derouane, 2009). The microporosity on the interior of zeolites allows researchers to pioneer new innovative approaches to be introduced into majority of the catalytic and molecular sieving phenomena reviewed at the macroscopic level. Having being characterized with high selectivity zeolite also 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. This accounts for the substantial economic value of zeolites in adsorption applications (Dabrowski, 2001). Both naturally occurring and synthetic zeolites are considered essential materials that are widely used in the industry (Abdelrasoul *et al.*, 2017). Thus, zeolites have therefore been commonly used for gas separation and purification (Chałupnik *et al.*, 2013, Yang *et al.*, 2014, Choi *et al.*, 2009).

2.2 Adsorbents Utilized for Carbon Dioxide Capture

The process of carbon dioxide (CO_2) capture using an adsorbent, more often a dry adsorbent, encompasses selective separation of CO_2 based on gas–solid interactions. At large, common dry adsorbents such as activated carbons and molecular sieves are employed in packed columns (Balsamo *et al.*, 2013). A number of solid adsorbents to capture CO_2 have been reported in literature that includes zeolites, activated carbons, hydrotalcite-like compounds, as well as surface modified adsorbents, such as metal–organic frameworks (MOFs) and mesoporous silicas (Choi *et al.*, 2009, Goeppert *et al.*, 2011). Currently, the commercially available adsorbents in the market are activated carbons, zeolites, hollow fibers and alumina (Plaza *et al.*, 2010, Adelodun *et al.*, 2014, Ho *et al.*, 2008). Each material exhibits different pore

structures, specific surface area, surface functional groups and their application fields, which are highly specific. Table 2.1 lists and compares advantages and disadvantages of some typical non-carbonaceous adsorbents for CO_2 capture.

Table 2.1: Comparison between major non-carbonaceous adsorbents for CO_2 capture (Lee and Park, 2015).

Adsorbents	**Advantages**	**Disadvantages**
Zeolites, silica materials	• Low production cost • Large micropores and mesopores • Medium CO_2 adsorption (at 298 K and 1 bar)	• Poor performance of CO_2 adsorption due to easy moisture absorption • Heavy energy consumption during CO_2 desorption (poor economic feasibility) • Renewal difficulties
Metal organic frameworks (MOFs)	• Large specific surface area (over 10,000 m^2/g) and regular pore distributions • Ease of controlling pore sizes • Possible improvement in CO_2 selectivity according to various combinations of metal clusters and organic ligands	• Poor performance at the partial pressure of CO_2 • Poor economic efficiency due to high production cost • Complicated synthetic process • Possible structure failure due to moisture absorption during CO_2 capture • Unsuitable for use at high temperature.

Table 2.1: *continued*

Adsorbents	**Advantages**	**Disadvantages**
Alkali-based dry adsorbents (K-, Na-, etc.)	• Possible adsorption and desorption at a low temperature, i.e., 313-343 K (similar to amine-based absorption) • Possible CO_2 collection under wet conditions • Absorption and renewal under 473 K and possible operation at atmospheric pressure (high economic efficiency)	• Low adsorption capability (3–11 wt.%) • High-temperature reactions • Decrease in the collection ratio of CO_2 because of stable products (e.g., Na_2CO_3 and $NaHCO_3$) • Requires high temperatures during desorption (high energy consumption) • Complicated operation
Metal oxides-based adsorbents (CaO, MgO, etc.)	• Dry chemical absorbents • Adsorption/desorption at medium to high temperatures (>673 K) • Popular as a pre-combustion absorbent	• High consumption of energy due to adsorption/desorption at medium to high temperatures (>673 K) • High cost for regeneration • Demand for continuous addition of absorbents • Complicated process

Activated carbons are meso- or sometimes microporous carbonaceous structures that are well-known adsorbents and have an advantage over other adsorbents in terms of the cost of raw materials. A wide availability of feed sources for activated carbons make industrial-scale production relatively low-cost. Large differences in the physical properties of activated carbons, such as pore size distribution, pore structure and active surface area, makes activated carbon adsorption characteristics highly variable (Sircar *et al.*, 1996). However, in general, under ambient conditions and low pressure, it can be said that the CO_2 adsorption capacities on activated carbons are lower than that of zeolites or molecular sieves. On the contrary, at higher pressures, the CO_2 adsorption capacities of activated carbons are superior to those of zeolites. In terms of regenerability, the mild adsorption capability in the low-pressure region of activated carbons can be advantageous, considering that adsorbents must be regenerated in practice, and less energy is required making the adsorbent less energy intensive (Choi *et al.*, 2009). It has been reported that zeolitic adsorbents have a stronger physical interaction with CO_2 as compared to activated carbons, having higher heats of adsorption. This renders the desorption process more energy intensive (Kikkinides *et al.*, 1993).

Zeolites have been comprehensively investigated for CO_2 capture because of their molecular-sieving capability and the strong dipole–quadrupole (electrostatic) interactions between CO_2 and alkali-metal cations in the zeolite frameworks (Zhang *et al.*, 2008). The presence of aluminum atoms in these silicate-based molecular-sieve materials leads to negative framework charges that exchange with cations in the pore space. These structural characteristics of zeolites enable them to adsorb a wide-ranging variety of gas molecules, including acidic gas molecules such as CO_2 (Choi *et al.*, 2009). The cations present in zeolites, typically Li, Na, and Al, influence

the heat of adsorption of CO_2. Increasing monovalent charge density (of negative charges) increases the heat of adsorption (Dunne *et al.*, 1996). The CO_2 capture performances of zeolites are greatly manipulated by the temperatures and pressures of the operation. Zeolites are typically utilized at pressures above 2 bar and require very high regeneration temperatures, often above 573 K. Thus, CO_2 regeneration results in huge energy loss (Chue *et al.*, 1995, Harlick and Sayari, 2006). Zeolite 13X is by far the adsorbent most comprehensively studied in CO_2 separation processes, as a result of its high selectivity to CO_2 (Cavenati *et al.*, 2004).

Metal–organic frameworks (MOFs) are an emerging new class of crystalline solids, which have recently been investigated for use as CO_2 adsorbents. These materials consist of three-dimensional organic–inorganic hybrid networks formed by multiple metal–ligand bonds (Choi *et al.*, 2009). Various MOFs have been synthesized from permutations of inorganic (metal clusters) and organic units (ligands) through strong bonding (reticular synthesis). Due to the flexibility with which the geometries, dimensions and functionalities of the components can be varied, more than 20,000 different MOFs have been reported and studied. The typical specific surface areas of MOFs typically range from 1000 to 10,000 m^2/g (Furukawa *et al.*, 2010, Furukawa *et al.*, 2013). MOFs for CO_2 capture have structures that consist of available spaces at the center because the molecules are intertwined. Such a configuration provides a large body volume because the pores are attached to organic molecules and groups of metallic ions. MOFs are widely used as storage media for several gases because the pore diameters can be easily varied (Li *et al.*, 2011, Yang *et al.*, 2008, Sumida *et al.*, 2012, Keskin *et al.*, 2010, Simmons *et al.*, 2011). MOFs have improved CO_2 capture capacity at high pressure. However, compared to other solid physical sorbents, most MOFs have poor CO_2 capture

performances at low partial pressures of CO_2. Furthermore, the synthesis of MOF, a metal complex, from an organic ligand is cost intensive and complicated. This limits the use of MOFs in power plants. The maintenance of a high partial pressure condition is not economically feasible and thus, an economically viable MOF needs to be produced for the efficient storage and separation of large volumes of CO_2 (Lee and Park, 2015).

2.2.1 Activated Carbon from Palm Kernel Shell

Palm kernel shell (PKS) can be viewed as a flawless raw material used to prepare activated carbon with high surface area for CO_2 adsorption rate due to the abundantly available feed source in Malaysia that covers a very low market value. Studies previously done involved the adsorption of carbon dioxide via pressure swing adsorption using a binary gas mixture of 85% N_2 and 15% CO_2 representing a flue gas. Chemically activated palm kernel shell boasted the large surface areas and high number of pores as compare to activated carbon produced from coconut shells (Hidayu and Muda, 2016). Though not much work has been done on the capture of CO_2 using activated carbon made from palm kernel shell, methane adsorption has been tested regularly. Zaini and Hassan (2016) agreed that palm kernel shell is regarded as fitting precursors for production of low-cost activated carbon. The activation with $ZnCl_2$ under combination in sequence of CO_2 then followed by physical activation proved to be an efficient method for methane adsorption. Another study by Hidayu and Muda (2017) showed that PKS can be used as a flawless feed material to prepare activated carbon with high surface area for CO_2 adsorption capacity. Their recent study produced a CO_2 recovery of 99% and purity of 93%.

2.2.2 Zeolitic Imidazolate Frameworks (ZIF) - 8

Zeolitic imidazolate frameworks (ZIFs) come from a MOF sub-class which have tetrahedral networks analogous to zeolites but use imidazolate ligands linked-transition metal (Park *et al.*, 2006). ZIF's and in particular ZIF-8 show exceptional thermal, chemical and water stabilities under a range of conditions which indicates great promise for industrial adsorption applications (Huang *et al.*, 2011, Küsgens *et al.*, 2009, Nune *et al.*, 2010). While ZIF-8 is outdone by many other MOFs in terms of gas storage volume, its hydrophobicity and stability towards moisture is unrivalled when compared to most of the other MOFs (Küsgens *et al.*, 2009). A study by Pérez-Pellitero showed that the quantity of CO_2 adsorbed on ZIF-8 at low pressures were lower than that on ZIF-69. However, at higher pressures, ZIF-8 achieves a higher capacity. This phenomenon is explained by the fact that the total pore volume of ZIF-8 is bigger than that of ZIF-69. This indicates that ZIF-8 is a promising candidate for CO_2 capture at high pressures (Pérez-Pellitero *et al.*, 2010).

2.3 Breakthrough Study

Breakthrough studies allow the determination of adsorbent performance and characteristics. A typical breakthrough curve includes the ratio of effluent concentration to the influent concentration, C_0 against time. The shape of the equilibrium isotherm determines the shape of this curve and is influenced by the individual transport processes in the column and in the adsorbent. The most efficient adsorption performance will be obtained when the shape of the breakthrough curve is as sharp as possible. After some time, a breakthrough occurs at time, t_b with the breakthrough concentration, C_b determined.

The effluent concentration continues to increase with time until a saturation point, t_s is reached. This saturation point is the point at which the effluent concentration becomes equal to the feed concentration even with increase in time (Chu, 2004). Breakthrough times are normally assumed when C_b/C_0 reach 0.10 while ideally defined (usually 0.05-0.10), the saturation points indicate a value of 1.0 for C_b/C_0 (typically at 0.90-0.95) (Asberry *et al.*, 2014, Unuabonah *et al.*, 2010). Figure 2.2 shows a typical column breakthrough profile.

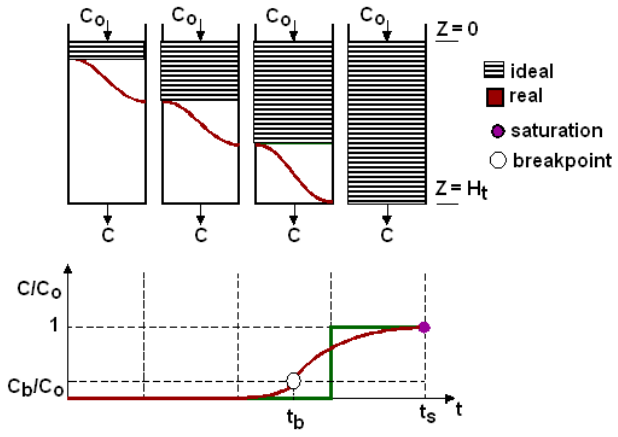

Figure 2.2: Typical breakthrough profile in column operation (Barros *et al.*, 2013).

2.3.1 Breakthrough Study of CO_2 Recovery Using Activated PKS

Chemically activated carbon produced from PKS achieved a breakthrough after 6 minutes into their study. The breakthrough time for PKS was two minutes longer than the other adsorbent studied. This suggests that the activated carbon produced from PKS is more efficient for CO_2 adsorption. Activated carbon produced from PKS has higher Brunauer, Emmett and Teller (BET) surface area and larger pore volume. CO_2 molecules are able to easily adsorb onto a bed of highly porous activated carbon and this allows a large CO_2 adsorption capacity (Hidayu and Muda, 2016).

2.3.2 Breakthrough Study of CO_2 Recovery Using ZIF-8

Previous work on CO_2 recovery involved the usage of membranes made from ZIF-8 to separate gaseous mixtures. Pérez-Pellitero *et al.* (2010) indicated that ZIF-8 is a promising candidate for CO_2 capture at high pressures as compared to other ZIF materials. The breakthrough curve for ZIF-8, however, is yet to be determined for CO_2 recovery.

2.4 Adsorption

Adsorption is a surface boundary phenomenon of accumulation of substance onto a liquid or solid phase from a bulk phase (Mehta *et al.*, 2015). Adsorption, generally can also be defined as a process where the molecules or atoms of a single or multi-component fluid system in liquid and gas tend to concentrate at the surface of a solid surface, under the effect of intermolecular interactions among the fluid (adsorbate) and solid phase adsorbent. If the strength of interactive forces between the adsorbent and the fluid structure is extremely strong, this results in an electron transfer driven bonding. The resultant phenomenon is called chemisorption.

On the other hand, physisorption, or in elaborate terms, physical adsorption occurs when the forces on the surfaces between the adsorbent and the fluid structure are rather weak and engage only with weak electrostatic interactions (Khajuria, 2011). Adsorption is a phenomenon that has been practiced since early times. Existing available literature dates it back to 1773 when Scheele carried out adsorption experiments of the uptake of gases by charcoal and clay (Dabrowski, 2001). Ever since then, the field of adsorption has seen a lot of research and development. Significant contributions to this field include the development of

isotherm models by Langmuir and Freundlich as well as the kinetic models developed by Lagregren and Ho. Figure 2.3 proves the process of adsorption.

The figure illustrates the interactions of adsorbate and the adsorbent with different concentrations of the gas phases evident. Adsorption is the transfer of molecules from a fluid phase to the surface of the solid phase. This transfer process is an exothermic one. Desorption, on the contrary, is transfer of molecules sticking to the surface of the solid back to the gas or liquid phase, usually an endothermic process (Keller and Staudt, 2005).

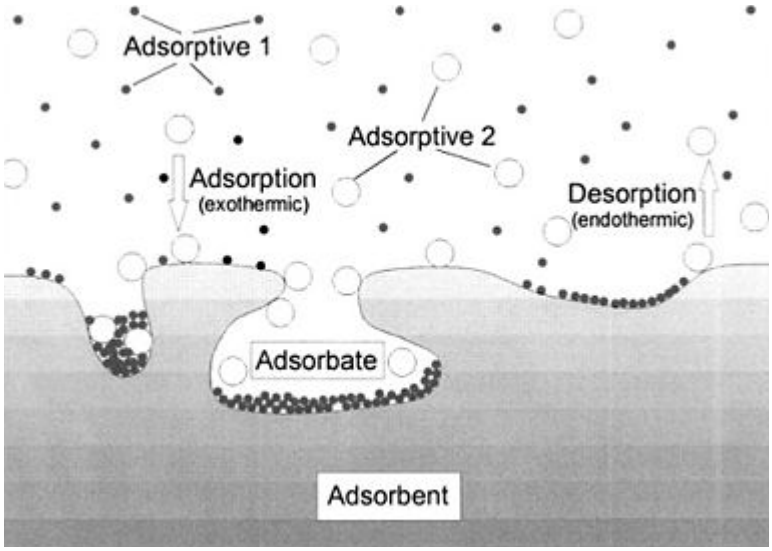

Figure 2.3: Adsorption system consisting of a two component sorptive gas, adsorbate and the adsorbent (Keller and Staudt, 2005).

2.4.1 Pressure Swing Adsorption

Numerous adsorption processes are used commercially for adsorbent process. Some of them include pressure swing adsorption (PSA) and thermal or temperature swing adsorption (TSA) (Hauchhum and Mahanta, 2014). Pressure swing adsorption technologies have been frequently investigated because of its low energy

consumptions and relative ease of operation. Recognized as a mature technology, it used to separate gas species from a mixture of gases according to the species' molecular characteristics and affinity with regards to the adsorbent material. It is widely considered a highly effective process if highly selective adsorbents with high capacity are utilized (Huang and Eić, 2013). PSA processes are usually employed for gas-solid system displaying physisorption, where both fast adsorption and desorption at the adsorbent surface is accomplished by varying the pressure levels inside the adsorbent bed.

Generally, PSA separation processes are classified into two categories. The categories include equilibrium-based separation and mass transfer kinetics driven separation, depending upon which of these mechanism is playing the limiting role. Equilibrium based PSA separations use the equilibrium adsorbed phase concentration relationship of the impurity with its bulk phase partial pressure. The adsorbent material is meant to have the least affinity for the product component. In order to increase the adsorbed amount of impurities, the pressure during the adsorption step is kept highest leading to the enrichment of product component in the gas phase. Regeneration is performed at significantly lower pressure allowing the impurities to desorb back to the gas phase and be taken out of the bed for disposal. It is essential to note that the mass transfer rate of all the species can be quite similar in pure equilibrium driven separation. On the other hand, in kinetic driven separation, the mass transfer rates of the components from the bulk phase to the adsorption site are performed through the suitable selection and development of adsorbent pore characteristics for the given gaseous species. This allows for an effective separation (Khajuria, 2011).

A PSA system typically comprises of two or more adsorbent-filled beds interconnected to each other via a system of switch valves. These valves in turn control the simultaneous operation of product purification and adsorbent regeneration steps. Thus, a multiple bed arrangement is required to ensure continuous purification, while the other beds enter the regeneration mode. While employing exactly the same cyclic steps of a Skarstrom cycle, a vacuum swing cycle differs from it in terms of operating vacuum to regenerate the exhausted adsorbent bed in the purge step, instead of the product itself. During the purge step, the product end remains closed while the feed end is connected to vacuum in order to remove the strongly adsorbed component as shown in Figure 2.4. The exclusion of a product side stream for purging purpose, enhances the product recovery as well (Khajuria, 2011).

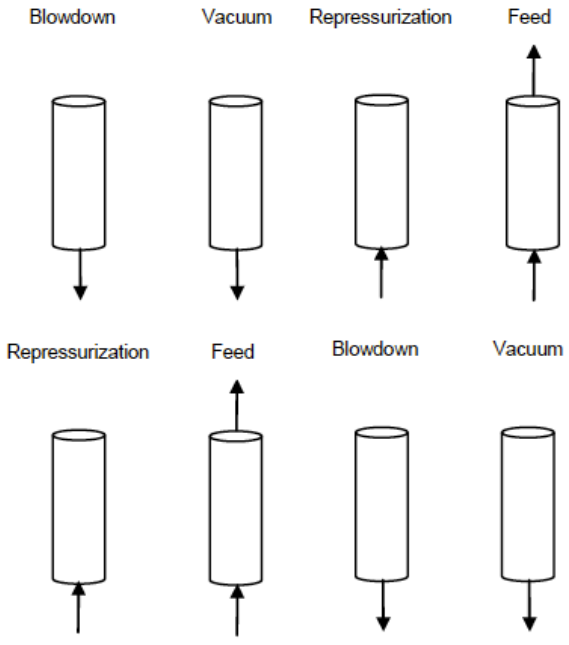

Figure 2.4: Two-bed, four-step vacuum pressure swing adsorption cycle (Khajuria, 2011).

In previous PSA studies and literature, the combination of product recovery and purity, outlined in equations 2.1 and 2.2, has been extensively used to target different processes. Product purity is usually fixed by the customer requirements while substance recovery is to be maximized at the specified purity levels.

$$\text{Product recovery} = \frac{\text{Amount of component in the product stream}}{\text{Amount of component in the feed stream}} \quad \text{Eq. (2.1)}$$

$$\text{Product purity} = \frac{\text{Amount of component in the product stream}}{\text{Total amount of product stream}} \quad \text{Eq. (2.2)}$$

2.4.2 Pressure Swing Adsorption on CO_2 Recovery from Flue Gas

With the concern of increased global warming, more and more attention has been paid to the capture of CO_2 from flue gases emitted by power plants. These emissions account for a large chunk of overall CO_2 emission. CO_2 capture by pressure swing adsorption is a promising option for separating carbon dioxide from flue gas since it has a high number of advantages. Those advantages include low energy requirements, low capital investments costs and easy to achieve automated operations. PSA processes in particular with the use of novel adsorbent materials have attracted much research effort (Shen *et al.*, 2011). Flue gases from power plants typically have CO_2 concentrations of 15% and the balance of the gas composition occupied by N_2. A study done using a three-bed PSA cycle has indicated that with a vacuum pressure of 10 kPa, CO_2 can be purified up to 95.3% with a recovery of 98.2% (Ling *et al.*, 2016). Izumi, on the other hand, used a two-stage pressure swing adsorption (PSA) process that could concentrate CO_2 from 15% up to 99%. The first stage was a dual-bed process, while the second stage was a four-bed process (Izumi,