OPTIMIZING PURITY AND RECOVERY OF HYDROGEN FROM SYNGAS BY EQUALIZED PSA USING PALM KERNEL SHELL ACTIVATED CARBON ADSORBENT

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by

SHANTHINI GOBI

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LIST OF ABBREVIATIONS

AC	Activated Carbon
ACPKS	Activated Palm Kernel Shell
BET	Brunauer-Emmett-Teller
CMS	Carbon Molecular Sieves
EDX	Energy Dispersive X-Ray
KOH	Potassium Hydroxide
MOF	Metal Organic Framework
PKS	Palm Kernel Shell
PSA	Pressure Swing Adsorption
RSM	Response Surface Methodology
SEM	Scanning Electron Microscope
VPSA	Vacuum Pressure Swing Adsorption
XRD	X-Ray Diffractometer

PENGOPTIMUMAN KETULENAN DAN PEMULIHAN HIDROGEN DARI GAS SINTETIK OLEH PENJERAPAN BUAIAN TEKANAN BERTEKANAN SAMA MENGGUNAKAN PENJERAP TEMPURUNG ISIRUNG PALMA TERAKTIF

ABSTRAK

Tesis ini adalah berkenaan dengan penyediaan bahan penjerap, reka bentuk dan operasi unit penjerapan buaian tekanan (PSA) pada keadaan optimum untuk keberkesanan proses pemisahan gas. Tujuan tesis ini adalah ke arah mengoptimumkan ketulenan dan pemulihan gas hidrogen dari gas sintetik. Kajian terperinci pertama membentangkan penyediaan tempurung isirung palma teraktif dan kajian pencirian. Dalam penyedian penjerap, 800^{o}C suhu optimum pengaktifan telah digunakan. Manakala, kajian pencirian mendedahkan bahawa kawasan permukaan tertentu bahan penjerap adalah sekitar 697.67m^2/g dengan isi padu liang, 0.35m^3/g dan saiz liang pada 2.01nm. Purata saiz partikel penjerap direkodkan sebagai 0.11μm. Mikroskop Imbasan Elektron (SEM) dan Pembelauan Sinar-X (XRD) analisis mendedahkan struktur mampung ACPKS yang sangat amorfus. Kajian bulus pada pelbagai tekanan penjerapan telah dilaksanakan dan tekanan penjerapan pada 3 bar dipilih untuk kajian pengoptimuman yang berikutnya. Dengan menggunakan perisian Design Expert, satu kajian pengoptimuman mengenai masa penjerapan dan tiup-turun telah dibentangkan. Berdasarkan analisa perisian, keadaan operasi optimum unit PSA adalah diramalkan pada masa 5 minit penjerapan dan tiup-turun. Satu kaedah yang sistematik dan rapi dilaksanakan ke arah mencapai data sama seperti yang diramalkan oleh perisian. Kajian PSA yang beroperasi pada keadaan optimum operasi memberikan ketulenan hidrogen sehingga 99.978% dengan pemulihan 80.014%. Keputusan yang diperolehi menunjukkan hampir sama dengan data yang diramalkan oleh perisian.

OPTIMIZING PURITY AND RECOVERY OF HYDROGEN CAPTURE FROM SYNGAS BY EQUALIZED PSA USING PALM KERNEL SHELL ACTIVATED CARBON ADSORBENT

ABSTRACT

This thesis is concerned with the adsorbent preparation, design and operation of Pressure Swing Adsorption (PSA) unit at optimum condition for the effective syngas separation processes. The aim of the study is directed towards optimizing the purity and recovery of hydrogen gas from the syngas. The first detailed study presented in this work deals with the preparation of activated palm kernel shell (ACPKS) and its characterization study. In adsorbent preparation, optimum activation temperature of about 800ºC has been used. Whereas, the characterization study reveals that the specific surface area of the prepared adsorbent is around 697.67m^2/g with pore volume and pore size of 0.35m^3/g and 2.01nm respectively. The average particle size of the adsorbent sample is recorded as 0.11µm. Scanning Electron Microscope (SEM) and X-Ray Diffraction (XRD) analysis uncovers the spongy structure of the highly amorphous ACPKS. Breakthrough studies at varying adsorption pressure were executed and 3 bar adsorption pressure is chosen for the subsequent optimization study. Based on the software analysis, the optimum operating condition of the PSA unit is predicted at 5 minutes adsorption and blowdown time. A systematic and rigorous methodology are employed towards attaining the similar data as predicted by the software. The PSA study which operated at the optimum operating condition yielded hydrogen purity of up to 99.978% with recovery of 80.014%. The results obtained shows a close agreement with the predicted data given by the software.

CHAPTER ONE

INTRODUCTION

Chapter 1 briefly introduces on the necessity of utilizing Pressure Swing Adsorption (PSA) unit on capturing and separating carbon dioxide gas from syngas. Basically, this chapter outlines the research background of carbon dioxide recovery from syngas and the use of Pressure Swing Adsorption on optimizing carbon dioxide recovery, problem statement, and the objectives of the research study as well as the brief review regarding the study has been provided in this chapter.

1.1 Research Background

1.1.1 Syngas Production Technology

Steam methane reforming (SMR) process plays a major role in syngas production. It is a dominant industrial process that actively involved in producing hydrogen from syngas. Catalytic SMR process involves reaction between natural gas or other light hydrocarbons and steam. The subsequent reactions that areinvolved in the generation of syngas with effluent gas composition (in mole %) of about 76% H_2, 13% CH_4, 12% CO and 10% CO_2 on a dry basis (Barelli *et al.*, 2008) will occur as shown in the following equations:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad \Delta H^0_{298} = 206.2 kJ/mol \tag{1.1}$$

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 \quad \Delta H^0_{298} = 165 kJ/mol \tag{1.2}$$

The reforming reaction is actually enhanced by the use of nickel based catalyst. Then, the effluent gas from reforming unit will subsequently enter water gas shift (WGS) reactor to reduce the CO content in the syngas produced. The equation below represents the reaction within the WGS reactor (Barelli *et al.*, 2008).

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H^0_{298} = -41.2\ kJ/mol \quad (1.3)$$

After the completion of WGS reaction, high purity hydrogen able to be generated through application of downstream processing such as PSA process or amine scrubbing for CO_2 removal. Figure 1.1 below depicts the traditionally used stream methane reforming process in industries for syngas production (Barelli *et al.*, 2008).

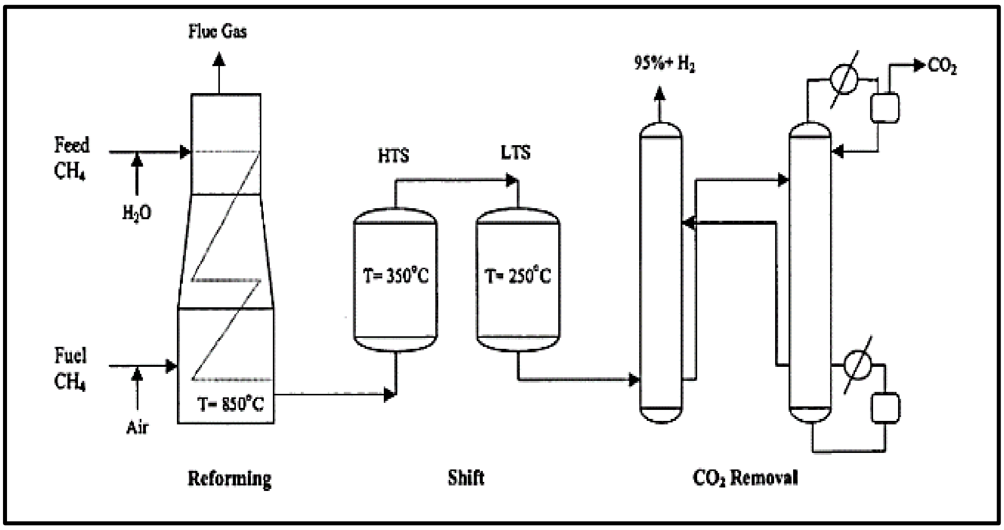

Figure 1.1: Typical Steam Methane Reforming Process (SMR)

In this research study, syngas derived from SMR off-gases has been a great concern due to its high percentage of carbon dioxide content. In the course of minimizing the impact of carbon dioxide release, PSA unit is utilized to optimize the purity and recovery of hydrogen. Based on the research journals, PSA is considered as one of the matured technology which is sustainably applicable in treating the SMR off-gases (Malek and Farooq, 1998; Yang *et al.*, 1995).

SMR off-gases comprises of multicomponent gas mixtures and they require detailed study in optimizing the recovery of hydrogen from syngas. A study by Barelli et al. (2008) proposed that SMR off-gas comprises of 76% H_2, 10% $C0_2$, 13% CH_4 and 12% CO. Another research analysis by Grande et al. (2017) states that SMR off gases consists of 76% H_2, 17% CO_2 and the remaining are methane and carbon monoxide.

1.1.2 Removal of Carbon Dioxide from Syngas

According to the recent conducted by Department of Energy (DOE) in US, nowadays, 95% of the hydrogen produced in the United States is made from methane steam reforming units (Collodi and Wheeler, 2010). Therefore, as depicted in figure 1.2 below, most of the CO_2 emitted from SMR plants have major contribution to the greenhouse effect.

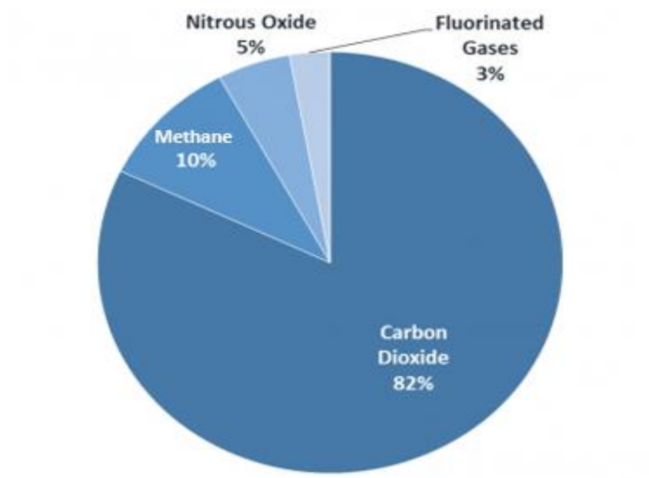

Figure 1.2: Unites States (US) Greenhouse Gas Emissions in 2015

In SMR plant, CO_2 is produced during the reforming and water-gas shift reaction as well as via the combustion of CO and natural gas in the SMR furnace. Hence, the removal of CO_2 from SMR plant has been a serious issue nowadays. This is because in a typical SMR plant, the raw H_2 (PSA inlet) has CO_2 concentration of about 15%, PSA tail gas generates about 45.1% CO_2 whereas steam reforming flue gas contributes about 19% CO_2 emission in overall (Collodi and Wheeler, 2010).

Hence, the utilization of PSA unit is a well-established technology in CO_2 capture from the syngas. Recently, large scale projects like Air Product's Port Arthur Project (Texas, USA) uses PSA/VPSA technology to capture CO_2. This projects is basically targeted to capture CO_2 up to one million tonnes/year (Collodi *et al.*, 2017).

1.1.3 Usage of Hydrogen Gas in Industries

In majority of the industrial applications, hydrogen is used as a reactant, such as in hydrogenation processes. Hydrogen is also used as a reactant in the chemical and petroleum industries. Among the major uses, ammonia production requires almost 50% of hydrogen as the main component, petroleum processing consumes about 37% whereas methanol accounts for almost 8% of hydrogen (Ramachandran, 1998). As mentioned earlier, in the petroleum industry hydrogen can be catalytically reacted with hydrocarbon in many ways such as in hydrocracking and hydro-processing. Hydrogen for this application is typically produced from an on-site plant either by steam reforming of methane (SMR) process or by partial pyrolysis of hydrocarbons in IGCC plants.

In some other applications, hydrogen can also be used as oxygen scavenger. In metallurgical processes, hydrogen mixed with nitrogen will be used in heat treating applications to remove oxygen as oxygen scavenger. Other than that, hydrogen is also used as fuel primarily in the Aerospace Industry. Hydrogen that has high burning efficiency than gasoline and its ability in producing clean emissions makes hydrogen as the ultimate fuel for automobiles. However, due to the deficient hydrogen storage facilities and its high maintenance costs, hydrogen as fuel for automobiles offers poor potential in its application as energy source (Air Products and Chemicals, 2011). In addition, there are also researches that interested in utilizing hydrogen as a fuel in fuel cells due to its clean burning characteristics.

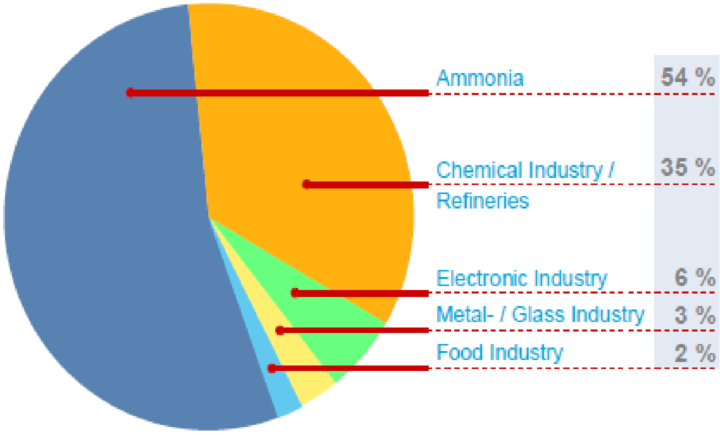

Figure 1.3: Industrial Hydrogen Market

The figure 1.3 above portrays the percentage of hydrogen consumption in various industrial applications. The highest percentage of hydrogen consumption is mainly focused on ammonia synthesis and in chemical industries or refineries. Hydrogen has high demand in industries in accordance with the increase in world oil consumption. Other than that, the decline in the overall crude oil quality, introduction of stringent environmental standards as well as establishment of new applications such as the use of hydrogen as automotive fuel and in fuel cells also leads to success economy in hydrogen production (Wawrzinek and Keller, 2007).

1.2 Problem Statement

Focusing on the current situation, control of anthropogenic CO_2 emission is a vital matter in order to prevent severe climate changes. A study by Lopes et al. (2011) states that typical syngas composition from steam-methane reformer off-gas mainly consists of 83% H_2 and 17% CO_2. Emission of carbon dioxide to the atmosphere is problematic because it may result in a severe greenhouse effect and will lead to life threatening consequences. Thus, there are some recent technologies which have shown undivided attention in producing high purity hydrogen via effective separation of carbon dioxide from syngas. Pressure Swing Adsorption (PSA) is one of the recognized technology in the field of gas separation. Generally, the PSA unit is used to separate the binary gas mixture based on the species' molecular characteristics and its affinity towards the adsorbent. PSA process is widely viewed as a promising way to recover hydrogen from various effluent gases because of its high efficiency (Moon *et al*,. 2016).

In the aim of minimizing the operational cost and to reuse the waste materials, palm kernel shell has been chosen as the most suitable adsorbent material in this study. In the recent research, Hidayu and Muda (2016) suggested palm kernel shell as the most satisfactory raw material in producing activated carbon with the high surface area for better carbon dioxide adsorption capacity. Consequently, the studies also state that the purity and recovery of carbon dioxide gas depend on the adsorption and blowdown time (Lopes *et al*,. 2012). Generally, this experimental study mainly focuses on the effect of hydrogen recovery and purity at varying adsorption and blowdown time with the aid of ACPKS as the CO_2 capture adsorbent. Moreover, optimization study on maximizing the product recovery and purity are analysed with the aid of the Design Expert Software.

1.3 Research Objectives

The objectives of this research project are;

i. To characterize and analyse the activated palm kernel adsorbent in terms of surface area, surface morphology and surface chemistry.
ii. To study the breakthrough analysis of carbon dioxide and hydrogen using activated palm kernel shell as the adsorbent.
iii. To evaluate the performance of Pressure Swing Adsorption (PSA) on the recovery and purity of hydrogen using activated palm kernel as the adsorbent by varying the adsorption and blowdown time.
iv. To optimize the recovery and purity of the gases using Design Expert Software.

1.4 Research Scope

In this study, activated palm kernel is synthesized and prepared according to the proposed activation method. Then the prepared adsorbent material is characterized to study on the surface morphology using Particle Size Analyzer, Scanning Electron Microscope (SEM), X-Ray Diffractometer (XRD), Energy Dispersive X-Ray Spectroscopy and Surface Area and Porosity Analyzer (SAPA). Consequently, breakthrough studies are performed using the activated palm kernel shell to predict the desirable adsorption and blowdown time. Using Design Expert software, a list of possible experiments at varying adsorption and blowdown time were investigated. Then, the performance of PSA is analysed by manipulating adsorption and blowdown time. Finally, an optimization study is performed to maximize the product recovery and purity with the aid of Design Expert Software.

1.5 Organization of Thesis

This thesis contains five main chapters and each chapter contributes to the understanding of this research study. The following briefly explains the overview of each chapter;

Chapter 1 outlines the research background, the significance of Pressure Swing Adsorption (PSA) in the pre-combustion carbon capture, problem statement, research objectives, research scope and the organization of the thesis.

Chapter 2 mainly discusses the literature review that relates to this research study. This chapter also explains the necessity of using activated palm kernel shell as the adsorbent, the PSA parameter study and the breakthrough studies as well as the Response Surface Methodology (RSM) studies are elaborated in detail.

Chapter 3 focuses on the methods and experimental set-up. It discusses on the type of materials and equipment needed, characterization studies, the experimental procedure in handling PSA unit and the steps in executing the breakthrough experiment as well as the methods in using Design Expert Software are well described.

Chapter 4 covers the core of this research project in which it examines the obtained experimental results and relates it to the pre-determined research objectives. A brief explanation is given on the adsorbent characterization data, adsorbent breakthrough studies and the effect of adsorption and blowdown time on the performance of PSA unit are investigated with the aid of Design Expert Software.

Chapter 5 concludes all the findings resulted from this research study and also discusses the suggestion and recommendation in improvising the performance of the PSA unit.

CHAPTER TWO

LITERATURE REVIEW

Chapter 2 briefly discusses the previous discoveries and findings that presented by the experienced researchers on the factors affecting the PSA study and breakthrough analysis. The understanding on the operation of Pressure Swing Adsorption (PSA) unit as a matured technology as well as the utilization of Response Surface Methodology (RSM) in optimization studies is well explained in this section. This chapter also outlines the choice of activated palm kernel shell (ACPKS) as the most advantageous adsorbent material for improving the performance of PSA.

2.1 Adsorbent and Adsorption Process

Adsorbent is a solid porous material that used to adhere certain adsorbate that relatively has high selectivity towards the adsorbent. Adsorption is a phenomenon that occurs on the surface unlike absorption that refers to the phenomenon that occurs in volume. There are two types of adsorption process, namely physical adsorption (physisorption) and chemical adsorption (chemisorption). PSA unit applies physical adsorption process in separating gas species because only weak forces exists between the adsorbed molecules and the surface. Moreover, the adsorbed species can be easily removed by heating or decreasing the operating pressure of the PSA unit. “Adsorption” is a well-established and dominant technique for treating domestic and industrial gas effluents. The major advantages of adsorption technology are handy, acquires simpler method in treating acid gases, insensitive to hazardous substances, highly effective in its performance, environmentally friendly and economically feasible (Nouri *et al.*, 2007).

2.1.1 Types and Classification of Adsorbents

As mentioned earlier, the surface of the material upon which the adsorption takes place known as the adsorbent. In most industries, activated carbon is considered as the most famous adsorbent. Adsorbents are usually in the form of extrudes, spherical pellets and monoliths with an average diameter of 0.5 to 10 mm. It is necessary for adsorbents to possess a distinct pore structure for effective and fast transport of gas species. In relation to that, adsorbents must have high corrosion resistance, high thermal stability and small pore diameters to optimize the contribution towards the high surface area and large working capacity.

There are different kinds of adsorbents that are most widely used in industries for effective CO_2 capture. The Table 2.1 below depicts types of adsorbents that have been used in industries for optimizing CO_2 purity and recovery. Generally, there are some common adsorbents which are most frequently used for the removal of contaminants from the gases. Carbon based adsorbents, micro porous and meso porous silica and metal organic frameworks are the several type adsorbents that are popular in removing acidic gases like CO_2. Table 2.2 below shows the common classes of adsorbents and their respective advantages that aid in optimizing the CO_2 capture.

Table 2.1: Types of CO_2 Capture Adsorbents in PSA Technology

Types of Adsorbents	Findings/Studies	References
Zeolite 13X, AC, Cu-BTC	• Cu-BTC type adsorbent gives high CO_2 purity in PSA application than Activated Carbon and Zeolite 13X.	(Seongbin *et al*., 2016)
Zeolite 4A, AC	• AC has high thermal stability, much simpler to regenerate, improved adsorption capacity at higher operating pressure and it is also insensitive to impurities such as SO_X and NO_X. • AC is also well known for its wide range of availability, lower cost and low energy requirement for regeneration purpose.	(Majchrzak and Nowak, 2017)
AC and CMS	• AC gives much higher CO_2 purity in the blowdown product stream with better CO_2 recovery than the CMS.	(Kikkinides *et al*., 1993)
Raw PKS and ACPKS	• ACPKS has high CO_2 adsorption capacity than raw PKS, have good regeneration and better stability even after 10 cycles of adsorption-desorption process.	(Rashidi and Yusup, 2017)
(ACPKS) and Metal oxide impregnated PKS	• PKS is considered as the perfect raw material in preparing AC with high surface area for CO_2 adsorption. • Chemically activated PKS have higher CO_2 adsorption capacity than physically activated PKS.	(Hidayu and Muda, 2017)
USO-2-Ni MOF, UiO-67 and AC	• USO-2-Ni MOF adsorbents results in better separation and productivity than AC. • UiO-67exhibits worst separation performance but has better specific adsorbent productivity than AC.	(Casas *et al.*, 2013)
5A Zeolite and BPL Activated Carbon	• BPL Activated Carbon reported to have better adsorption and desorption ability in the removal of CO_2 than 5A Zeolite adsorbent. • BPL Activated Carbon considered as the most preferable adsorbent on CO_2 removal even CO_2 capacities and selectivity on the carbon is moderate than zeolite.	(Sircar and Golden, 2000)

Table 2.2: Classification of Adsorbents that are commonly used in CO_2 Capture

Adsorbent Types	Examples	Advantages
Carbon based adsorbents	• ACPKS • Coconut tree sawdust, silk cotton hull (Kadirvelu *et al.*, 2003) • Coconut Shell (Hidayu and Muda, 2017)	• Abundantly available and cheap (Hidayu and Muda, 2017). • Large surface area and pore volume (Abechi *et al.*, 2013). • Wider pore size distribution (Gu and Yushin, 2014) • AC is highly hydrophobic and it is also energy intensive material (Plaza *et al.*, 2010). • High CO_2 selectivity and adsorption capacity at moderate temperatures (Plaza *et al.*, 2007)
Micro porous and meso porous silica	• MCM-41 and MCM-48 (Hoffmann *et al.*, 2006) • SBA-15 (Liu *et al.*, 2011)	• Stable under acidic conditions (Luo *et al.*, 2008). • Meso porous material have good solid support due to good chemical and physical stability (Kumar and Guliants, 2010) • Have very high adsorption capacity for hydrocarbon molecules such as benzene (Bruzzoniti *et al.*, 2000).
Metal Organic Frameworks	• MOF-Mn (Bruzzoniti *et al.*, 2000) • Cu-BTC (Aprea *et al.*, 2010) • UiO-66, MOF-5, MOF-177 (Huang *et al.*, 2017)	• Have high degree of flexibility and able to control pore size and surface chemistry (Bruzzoniti *et al.*, 2000). High crystallinity, high specific surface area and pore volume (Aprea *et al.*, 2010). • Used for the CO_2 capture and most commonly in separation of N_2/CO_2 gas mixture (Aprea *et al.*, 2010; Huang *et al.*, 2017)

2.1.2 Activated Palm Kernel Shell (ACPKS)

Palm Kernel Shell (PKS) is considered as the most suitable compound in producing Activated Carbon (AC) due to its high carbon content (Shalna T and Yogamoorthi A, 2015). Most of the organic materials like cashew nut shells, coconut husk, wood sawdust, almond shells and oil palm wastes are most popularly used to convert into activated carbons (Nasri *et al.*, 2014). In recent researches, agricultural wastes are used as raw materials to produce activated carbons. The use of agricultural wastes for the sorption of acidic gases attract considerable attention because they are abundantly available and have very low market value (Ulfah *et al.*, 2016; Hidayu and Muda, 2017). Physical and chemical activation methods can be performed to generate activated carbon from agricultural by products.

Adsorption capacity of the activated carbons highly depends on their porosity and surface area. There are studies shows that porous AC will usually have BET surface areas ranging from 541 to 622 m^2g^{-1} and total pore volume range from 0.254 to 0.297 cm^3g^{-1} (Ooi *et al*., 2017). Basically, the activated carbon pores are divided into three major groups based on their pore size diameter and the schematic diagram of the activated carbon pores is shown in the figure 2.1 below. Micropores have range of pore diameter less than 2nm, mesopores diameter range lies from 20-50nm and macropores pore diameter usually greater than 50nm (Nasri *et al.*, 2014). A large portion of AC which is about 95% is actually microporous and it is an important criteria in determining the adsorbent's adsorption capacity (Inagaki, 2009). Consequently, the microporous characteristics of the AC make it as the most appropriate adsorbent in gas separation and adsorption process.

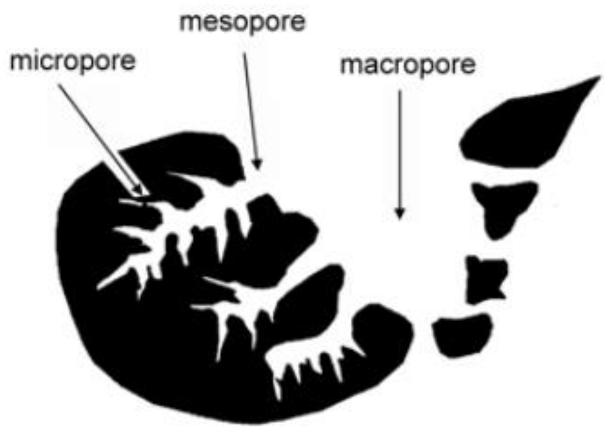

Figure 2.1: Schematic Diagram of the pores in Granular Activated Carbon (GAC)

Activated carbon will have better adsorption capacity than impregnated carbon. Recent research studies prove that AC will have better CO_2 adsorption capacity than amine impregnated carbon. This is because amine impregnated carbon only increases the actives sites but it reduces the pore size and pore volume (Nasri *et al.*, 2014). Since AC is one of the famous adsorbents that has been commonly used, the market value of the AC is also found to be kept increasing each year and is projected to increase around US$ 4 billion in 2019 (Rashidi and Yusup, 2017). The growing demand of this carbonaceous adsorbent is due to its novelty in effective removal of acidic gases in pre-combustion and post-combustion.

Activated carbon can be obtained in powdered, granulated and palletized forms. Powdered AC has the particle size less than 0.18mm with an average diameter of 0.15-0.25mm. In consequence, powdered AC will be mostly used in batch processes and mainly applicable in liquid and gas phase treatment. Whereas granular AC have the particle size ranging from 0.2-5mm and they also used in adsorption column for flue gas treatment. Palletized AC has particle size slightly similar to granulated AC but they are advantageous in terms of low-pressure drop, low dust content, and high mechanical strength (Rashidi and Yusup, 2017).

Total porosity and hardness of the activated palm kernel shell depend highly on the activation temperature. Increasing the activation temperature will optimize the porosity of AC due to the significant reduction in the volatile matter. However, the hardness of the AC is greatly affected since most of the carbon has been converted into the gaseous phase during high activation temperature process (Lua and Guo, 2001; Lua and Yang, 2004). Recently, studies have been proven that AC is a superior choice of adsorbent in carbon capture due to its highly developed porous structure (Pevida *et al.*, 2008). Momentarily, AC with micro and mesoporous structure is predominantly used in gas separation applications.

2.2 Breakthrough Study

Breakthrough curves are important for adsorptive separation technologies and it is a vital method for determining the dynamic response of an adsorption system (Chowdhury *et al.*, 2015). Relatively, the performance of fixed bed can be evaluated using the breakthrough study analysis. A breakthrough curve conveys the ratio of outlet concentration to inlet concentration (Cout/Cinlet) versus time. At a constant inlet gas concentration, the gas is allowed to pass through the adsorption column until the concentration at the outlet stream reaches approximately same concentration as in inlet concentration. Upon adsorption in a column, saturated zone, adsorption zone and fresh zone will be formed (Shahkarami, 2017).

Saturated zone exhibits inlet portion of the adsorption column that has high feed concentration of a particular gas species. The second portion is the adsorption zone which is also known as mass transfer zone (MTZ) that occurs along the operation. The MTZ basically indicates the degree of saturation of the adsorbate that decreases from 100% saturation point to zero. In short, graphical illustration for the movement of mass transfer zone (MTZ) along the column is called as the breakthrough curve (Chowdhury *et al.*, 2015). Subsequently, as soon as the major portion of the bed is saturated, the breakthrough point will occur. Lastly, the fresh zone shows that no adsorption process occurs in the adsorption column (Shahkarami, 2017).

Graphical representation of the three zones in adsorption column is clearly depicted in Figure 2.2 below. Whereas, Figure 2.3 portrayed the breakthrough curve characteristics in the fixed bed column adsorption process with respect to time (Chowdhury *et al.*, 2015).

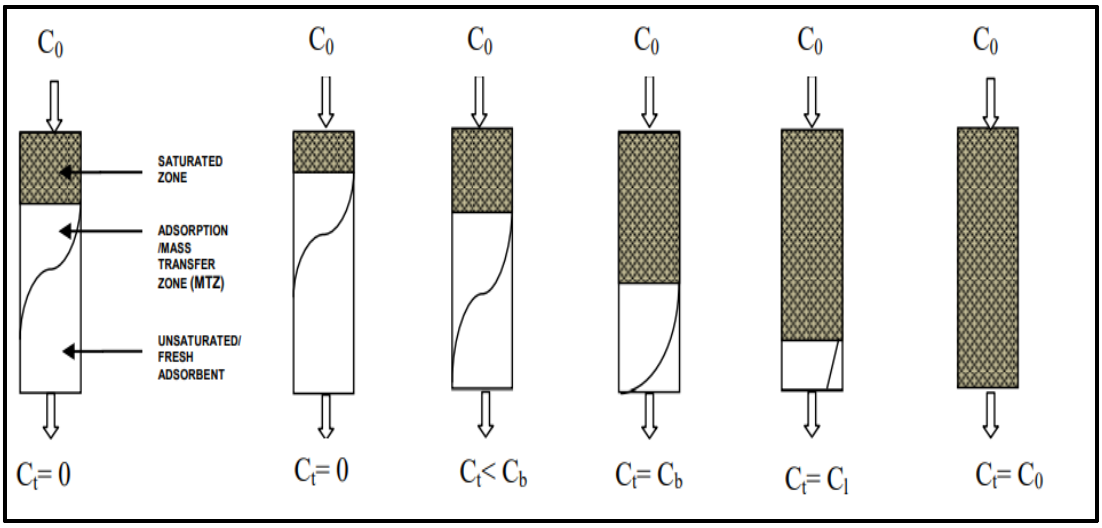

Figure 2.2: Schematic representation of Saturated, Mass Transfer and Fresh Adsorbent Zones in a fixed bed column.

From the breakthrough curve, the optimum working capacity of the adsorbent able to be identified (García *et al.*, 2011). Referring to the figure 2.3, when the breakthrough point becomes 0.05 (C_t/C_0) at the time $t_{0.5}$ (min), this exhibits that the adsorbent bed has been slightly used up. Usually, the adsorbent in the column will be changed when the breakthrough point is achieved in order to optimize the purity of product gas stream. Even after the breakthrough point, the column will continuously operate until C_t/C_0 becomes 0.90. The adsorbent is said to be completely exhausted when the predetermined concentration becomes almost equal to the initial concentration, C_0 = Ct at the time te (Chowdhury *et al.*, 2015; Shahkarami, 2017).

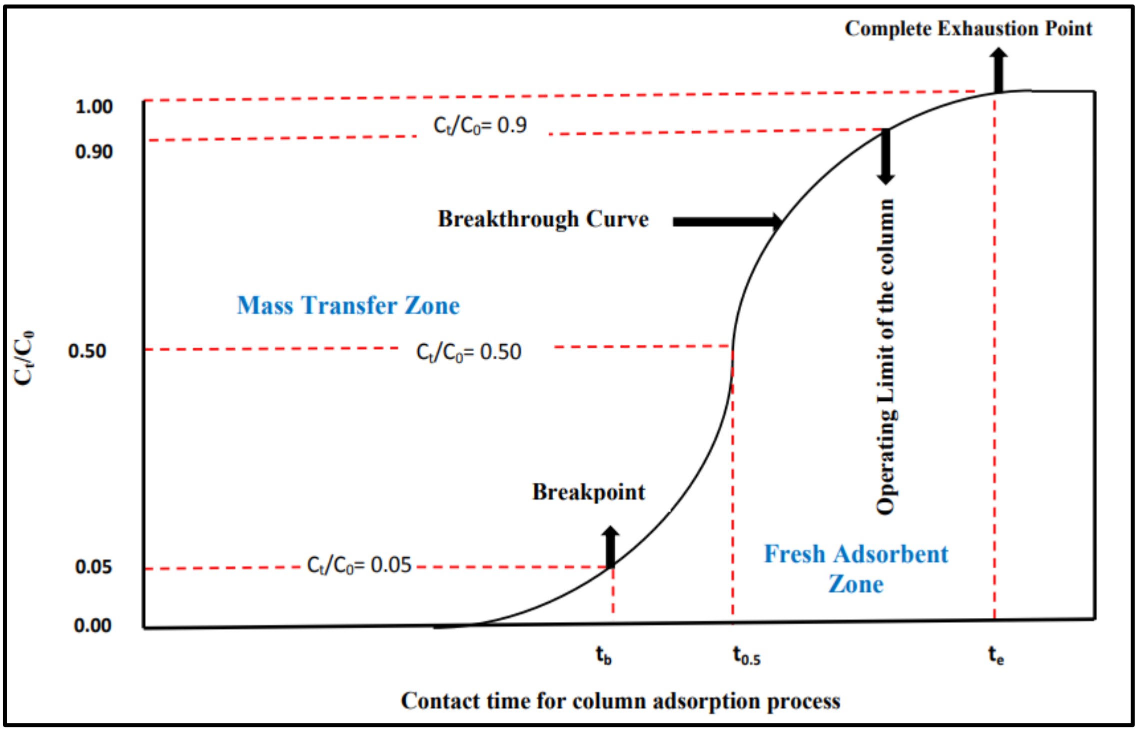

Figure 2.3: Typical Breakthrough Curve

2.2.1 Breakthrough study of CO_2 recovery using Activated PKS

Studies have proven that activated carbon has higher retention capacity for CO_2 than other gas species like N_2 (Malkoc and Nuhoglu, 2006). Next, there are also other studies reported that gas separation by activated carbon is much more desirable than the kinetic separation by carbon molecular sieves (Kikkinides *et al.*, 1993). In current research studies, breakthrough point for CO_2 has been evaluated at different adsorption pressures and the effect of gas mixtures at varying compositions are also been investigated (Na *et al.*, 2001; Siqueira *et al.*, 2017). Relatively, an experimental study is important to validate the data obtained.

2.3 Pressure Swing Adsorption (PSA)

There are various gas separation technologies which have been ultimately used in the industries. Absorption, cryogenic distillation, membrane separation and adsorption are the readily available gas separation technologies (Siqueira *et al.,* 2017). However, it has been found that adsorption using PSA is the most promising technology due to its lower cost of maintenance and energy intensive (Mondal *et al.*, 2012; Leung *et al.*, 2014). The main industrial applications of the PSA unit are air separation, air drying and hydrogen purification (Ruthven *et al.*, 1994). Thus, PSA has been denoted as one of the economically advantageous processes in separating gas species. PSA is a superior technology that actively utilized in industries for efficient CO_2 capture and storage. PSA is operated by periodic changes of pressure aiming to optimize the removal of acid gases from specific gas mixtures, like syngas or flue gas.

The PSA unit will operate in a cyclic manner to upgrade the product purity until the adsorbent is exhausted. The behaviour of the PSA unit highly depends on the type of adsorbent employed in the process. However, the engineering working criteria of the PSA unit is also a crucial factor that needs to be considered in its designing methodology. To improvise the PSA performance, adsorption time, blowdown time, number of cycles to be operated, type of adsorbents to be used, feed gas flow rate and its composition, as well as the column length, plays a decisive role (Na *et al.*, 2001; Siqueira *et al.*, 2017). Comparatively, the performance of PSA can be appraised by recovery and purity of the product gas stream attained.

The outstanding benefits of PSA unit over the other gas adsorption technologies like cryogenic distillation are lower operating costs, efficient product purity for other applications can be achieved, reduce the emission CO_2, no risk of explosion, easier maintenance, in-house placement and production. Basically, the PSA technology is presented by the typical Skarstrom Cycle (Grande, 2012). Skarstrom Cycle represents the operation of the PSA unit that utilizes one of the most basic configuration procedures which comprises of pressurization, depressurization, blowdown and desorption (Delgado and Rodrigues, 2008; Grande, 2012; Siqueira *et al.*, 2017)

Yet, due to certain drawbacks, some modifications have been introduced to upgrade the Skarstrom Cycle. Therefore, the improvements that imposed on the typical PSA unit are the introduction of vacuum for column regeneration, proposed by P. Guerin de Montgareuil and D.Daniel (1964) and the installation of pressure equalization step is suggested by the ESSO Research Group (Stark, 1966; Berlin, 1966). The establishment of vacuum in regeneration process helps to remove adsorbed gas molecules more effectively and also able to boost the product purity at blowdown. The equalization step is aimed for direct improvement in the recovery of light product (Warmuzinski and Tanczyk, 2003; Delgado and Rodrigues, 2008). Further exploration on pressure equalization step draws the attention of research area on the designing of multiple column (Polybed) PSA units that could benefit the industry in terms of enhanced hydrogen recovery, unlimited capacity in the CO_2 capture and increased unit utilization due to the operation of the multi-bed system at reduced cycle times. (Stöcker *et al.*, 1998)

A typical PSA unit comprises two or more columns loaded with adsorbents that specifically interconnected to each other. PSA unit basically comprises two general steps in separating gas which is adsorption and desorption process. As shown in the Figure 2.4, during the adsorption process heavier components will be retained in the adsorbent. To allow effective adsorption process to occur, feed gas mixture will be subjected into the adsorption column at high pressure (Siqueira *et al.*, 2017;

Abdeljaoued *et al.*, 2018; Moon *et al.*, 2018). During the adsorption mechanism, heavier molecules will be adsorbed on to the adsorbate that acts as size-selective sieving whereas the lighter species will be excluded from the column. Subsequently, the bed that concentrated with adsorbate species will undergo regeneration or desorption process via lowering the gas phase partial pressure within the column (Perez, 2015). After this procedure, the adsorbate will be fresh enough to be employed with next batch of gas mixtures. Referring to Figure 2.4, Δq that known as working capacity, hereby represents the difference in the solid phase loadings between the high pressure adsorption step and the low pressure desorption step for a single gas species.

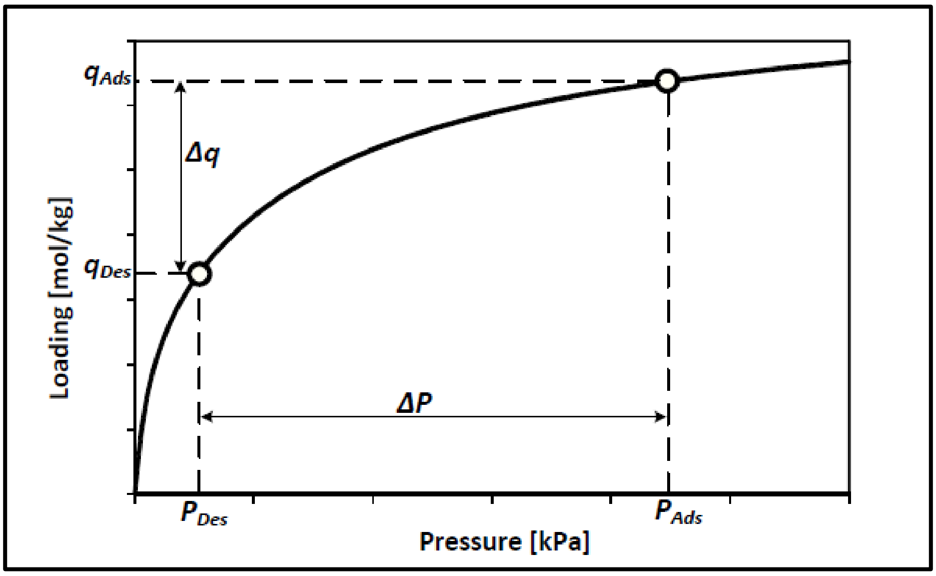

Figure 2.4: Pressure Swing Adsorption (PSA) Description

2.3.1 Utilization of Pressure Swing Adsorption on H_2 purification

Over the years it has been demonstrated that PSA technology is most widely used in hydrogen purification, preferentially in steam methane reforming industries (Grande, 2012). On the other hand, PSA is a matured technology for acidic gas removal such as CO_2 which is the major contributor to global warming.

Thus, the application of PSA unit in treating reformer off-gases mainly focuses on improving the H_2 purity as well as to optimize the recovery of CO_2. Effluent from SMR off-gases primarily comprises of 75-85% of H_2 and the balance gas composition occupied by CO_2 (Collodi and Wheeler, 2010). A study executed using a poly bed system with 10 parallel columns indicated that H_2 can be purified up to 99.999% with recovery of 86.0% (Sircar and Golden, 2000).

Another study performed by Lopes et al. (2011) shows that H_2 purity of 99.981% could be reached with the recovery of 81.6%. In the same study, simulation analysis has been accomplished to study the effect of feed pressure on the purity of H_2. It has been found that, increasing the feed pressure will results in H_2 purity over 99.99% with CO_2 contamination lower than 10ppm in product stream.

Other than that, there is also demand in capturing CO_2 using pressure swing adsorption. Based on Kim experimental evaluation, it has been stated that adsorption step time does not give significant effect on the CO_2 purity, however, reducing the adsorption time will enhance the recovery of CO_2 up to 92.70% and reduces H_2 recovery to about 67.50% (at bottom product). Thus, at shorter adsorption time the purity of H_2 in the product stream will be improved (Kim *et al.*, 1995).

In accordance with the aim of producing high purity H_2, choice of adsorbents to be used plays a major role in optimizing CO_2 capture and improving H_2 recovery in the product stream. Recent researches use activated carbon as the main choice of candidate to capture CO_2 and to generate high purity of H_2 in product stream (Sircar *et al.*, 1996; Sircar and Golden, 2000; Lopes *et al.*, 2011).

2.3.2 PSA Performance Analysis on the Recovery and Purity of the gases

Most researchers have been studied the effects adsorbent type, the adsorption and desorption pressure on the PSA performance. But, the effect of the adsorption and blowdown time on the PSA performance has attracted little attention from the researchers. In this present study, effects of these variables on the product purity and recovery as well as on the performance of PSA were identified through experimental analysis.

2.3.2.1 Effect of Adsorption time on the Purity and Recovery of the gases

Choi et al. (2003) explored the effect of adsorption time on the recovery of CO_2 through both experimental and simulation analysis. The study explained that increasing the adsorption time will relatively improve the CO_2 concentration in the waste gas stream. The effect of adsorption time on the CO_2 concentration data is further confirmed when the simulation results show good agreement with the experimental study. When the adsorption time increases, product purity will increase since most of the CO_2 will be adsorbed on the adsorbent material. Thus, the recovery of CO_2 will be inversely proportional to the adsorption time. This is because, at longer adsorption time, the adsorbent bed is nearly occupied causing a portion of CO_2 to be lost in product stream when the bed breakthrough and relatively it will reduce the CO_2 recovery in product stream but will optimize the CO_2 recovery in the bottom product. At shorter adsorption time product purity will be improved since the product stream will not be contaminated with CO_2. By taking these factor into consideration, the study able to identify the optimal operating condition of PSA that can give CO_2 purity of 99.5% and recovery of 69% through experimental evaluation. Another study by Na et al. (2001) also states that at longer adsorption time, the CO_2 purity in waste stream improved but its recovery greatly affected due to significant loss of CO_2 in product the stream. This research study also states that CO_2 purity of 99.8% is achieved with the recovery of about 34% for adsorption time of 480 seconds and blowdown time of 509 seconds. Thus, as aforementioned, longer adsorption time is not favourable to optimize the product purity. Next, an experimental investigation by Hayashi et al. (1996) founds that 60 seconds as the optimum adsorption time to obtain a high CO_2 concentration in the waste gas stream.

2.3.2.2 Effect of Blowdown time on the Purity and Recovery of the gases

Lopes et al. (2011) in his research investigated the effect of blowdown time on the recovery and purity of H_2 as well as on the concentration of CO. The study shows that at longer blowdown time (200 seconds) the H_2 purity recorded is slightly higher than the purity data given at lower blowdown time (150 seconds). However, the recovery of H_2 at 200 seconds is 74.17% whereas at 150 seconds it gives slightly higher recovery data of about 74.34%. In relation to this, decreasing the blowdown time causes the CO concentration to be enhanced from 5.0 to 6.4ppm. This phenomenon indicates that when the blowdown time increases, the recovery of H_2 is affected due to the presence of CO in the waste stream.

In general, the blowdown time and adsorption time are interrelated to each other in optimizing the product recovery and purity (Hayashi *et al.*, 1996). Santos et al. (2011) studied experimentally the performance of PSA in improvising the purity and recovery of CH_4 at varying pressurization and blowdown time. At 60 seconds pressurization and 310 seconds of blowdown, the CH_4 purity is obtained around 99.34% whereas at minimum pressurization and blowdown time of 43 and 293 seconds respectively, the CH_4 purity obtained is 98.03%. However, CH_4 recovery has been increased from 77.95% to 88.24% when the pressurization and blowdown time are reduced.

2.4 Response Surface Methodology

Response surface methodology (RSM) is a collection of mathematical and statistical techniques for an empirical model building which is useful for developing, improving and optimizing the process (Carley *et al.*, 2004; Bezerra *et al.*, 2008). Relatively, RSM explores the relationship between several independent variables (input variables) and the response factors (output variables). The main objective of RSM is to optimize the system performance that influenced by the two or more input variables. In consequence, RSM analysis can be utilized to approximate both experimental and numerical responses (Gunst, 1996).

The response of RSM model will be represented in graphical form, either in the three-dimensional space or as contour plots that helps to visualize the shape of the response surface. Design Expert Software is one of the simple and promising technique that used in the RSM for process optimization. In the previous experimental analysis, optimization test is performed by manipulating one parameter while the others kept at the constant level. This type of traditional optimization technique known as one-variable-at-a-time (Bezerra *et al.*, 2008). The major drawbacks of this technique are the increase in operational expenses, failure in evaluating the effect of different variables on the process output simultaneously (Lundstedt *et al.*, 1998), increase the number of experiments to be conducted, time-consuming procedure and it also might result in the waste of raw materials (Bezerra *et al.*, 2008).

RSM has gained immense popularity in wide range industrial applications due to its simplicity in handling. RSM result investigation is done by employing regression analysis based on data obtained from the experiments carried out and the analysis method can be used as well to find the approximate minimum or maximum response