

**HYDROGEN PURIFICATION FROM SYNGAS  
BY PSA USING MICROPOROUS MEDIA**

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**HYDROGEN PURIFICATION FROM SYNGAS BY PSA USING  
MICROPOROUS MEDIA**

**by**

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## LIST OF SYMBOLS

Symbol	Description	Unit
$C/C_0$	Concentration ratio	-
$C_e$	Concentration of adsorbate at equilibrium	mg/L
$C_0$	Adsorbate initial concentration	mg/L
$C_t$	Adsorbate concentration at any given time, t	mg/L
$k_1$	Pseudo-first order rate constant	$\text{min}^{-1}$
$k_2$	Pseudo-second order rate constant	$\text{g/mg}\cdot\text{min}$
$K_f$	Freundlich isotherm constant	$(\text{mg/g})(\text{L/mg})^{1/n}$
$K_{id}$	Intraparticle diffusion rate constant	$\text{mgg}^{-1}\text{min}^{-1(1/2)}$
$K_L$	Langmuir isotherm rate constant	L/mg
$m$	Mass of adsorbent	g
$M_w$	Molecular weight	g/mol
$n$	Heterogeneity factor	-
$P/P_0$	Partial Relative pressure	-
$P$	Pressure	bar
$P_1$	High pressure	bar

$P_2$	Low pressure	bar
$q_e$	Equilibrium adsorption capacity	mg/g
$q_{exp}$	Experimental adsorption capacity	mg/g
$q_m$	Maximum monolayer adsorption capacity	mg/g
$q_t$	Adsorption capacity at any given time	mg/g
$R$	Universal gas constant	J/mol.K
$R^2$	Correlation coefficient	-
$R_L$	Separation factor	-
$t$	Time	min
$t_b$	Breakthrough time	min
$t_s$	Saturation time	min
$T$	Temperature	°C
$\dot{V}$	Volumetric flowrate	mL/min
$W$	Energy flow	J/min
$\theta$	Theta	-
$\rho$	Density of inlet CO <sub>2</sub>	mg/L

## LIST OF ABBREVIATIONS

AC	Activated carbon
Ar	Argon
BIM	Benzimidazole
BET	Brunnauer-Emmet-Teller
CMS	Carbon molecular sieve
CCS	Carbon capture storage
CO <sub>2</sub>	Carbon dioxide
EDX	Energy dispersive X-ray
FTIR	Fourier transform infrared
GC	Gas chromatographer
GHG	Greenhouse gas
H <sub>2</sub>	Hydrogen
H <sub>2</sub> S	Hydrogen sulphide
H <sub>2</sub> O	Water
HFC	Hydrofluorocarbon
HNO <sub>3</sub>	Nitric acid



IGCC	Integrated gasification combined cycle (IGCC)
IUPAC	International Union of Pure and Applied Chemistry
KOH	Potassium hydroxide
MOF	Modified organic framework
MTZ	Mass transfer zone
N <sub>2</sub>	Nitrogen
N <sub>2</sub> O	Nitrous oxide
OFAT	One-factor-at-a-time
O <sub>2</sub>	Oxygen
PC	Pulse-chemisorption
PFC	Perfluorocarbon
PI	Performance indicator (Parameter indices)
PKS	Palm kernel shell
PSA	Pressure swing adsorption
PVA	Poly vinyl alcohol
SBU	Structural building unit
sccm	Standard cubic centimeters per minute

SEM	Scanning electron microscope
SF <sub>6</sub>	Sulphur hexafluoride
TGA	Thermogravimetric analysis
TG-DTG	Thermogravimetric - Derivative Thermogravimetric
TPD	Temperature programmed desorption
TSA	Temperature swing adsorption
VPSA	Vacuum pressure swing adsorption
wt. %	Weight percent
XRD	X-ray Diffraction
ZIF	Zeolitic imidazolate framework
ZIF-7	Zeolitic imidazolate framework-7
ZnCl <sub>2</sub>	Zinc chloride
Zr	Zirconium

# **PENULENAN HIDROGEN DARIPADA GAS SINTETIK MELALUI PSA MENGUNAKAN MEDIA BERLIANG MIKRO**

## **ABSTRAK**

Penggunaan tenaga yang boleh diperbaharui telah menjadi teknologi yang menarik dalam menangani masalah perubahan iklim sedunia dan penjanaaan tenaga masa depan. Hidrogen sebagai tenaga alternatif yang dicari telah mendapat sokongan yang meningkat untuk menjanakuaasa sistem sel bahan api atau bagi penggunaan manusia yang selamat. Terdapat keperluan mendesak untuk menulen gas hidrogen daripada gas sintetik ataupun pengeluaran singas daripada gasifikasi arang batu bagi memperoleh kembali hidrogen yang terbebas dan memerangkap CO<sub>2</sub> untuk menangani isu global perubahan iklim dengan lebih cekap. Salah satu teknologi penulenan singas utama iaitu unit penjerapan ayunan tekanan (PSA) digabung dengan langkah tindak balas anjakan air-gas (WGSR) bagi suapan gasifikasi (H<sub>2</sub> dan CO<sub>2</sub>) melalui penangkapan pra-pembakaran dapat memberikan perolehan semula hidrogen yang lebih bersih untuk aplikasi yang menguntungkan. Tesis ini memfokuskan kepada kajian penulenan hidrogen disamping penangkapan karbon (15 mol%), daripada 10 ml/min kadar aliran gas campuran H<sub>2</sub>/CO<sub>2</sub> singas dengan tekanan penjerapan yang berbeza-beza (1, 2 and 3 bar) dalam PSA dua lajur yang digabungkan dengan langkah penyamaan tekanan untuk penalti tenaga yang lebih rendah dan perolehan hidrogen yang lebih tinggi. Antara empat penyerap berliang yang telah disediakan, diaktifkan dan dicirikan, karbon teraktif tempurung sawit (PKS-AC) yang boleh digunakan semula dan kos rendah telah diketengahkan untuk menjadi memberikan penulenan hidrogen yang terbaik disebabkan oleh luas permukaan tertentu

yang tinggi iaitu sebanyak 697.67 m<sup>2</sup>/g dengan kapasiti penjerapan CO<sub>2</sub> yang agak tinggi iaitu sebanyak 422.64 cm<sup>3</sup> (CO<sub>2</sub>)/g pada STP. Masa penembusan adalah sehingga 35 min dengan kapasiti penjerapan sebanyak 7.9733 mg CO<sub>2</sub>/g. Nilai ujikaji sesuai dengan isoterma Langmuir jenis-I iaitu penjerapan selapis dan model tertib satu pseudo, menunjukkan jerapanfisi berbalik penuh melalui resapan sapat dan resapan intra-zarah sebagai mekanisma langkah penentuan kadar. Media PKS-AC berliang didapati berkesan dalam mencapai pemisahan optimum CO<sub>2</sub>/H<sub>2</sub> pada 2 bar, 5 minit masa penjerapan dan 5 minit masa tiup turun dengan 99.99% purata ketulenan H<sub>2</sub>, 99.99% purata perolehan H<sub>2</sub> dan 19.05% purata ketulenan CO<sub>2</sub>, 7.14% purata perolehan CO<sub>2</sub>.

# **HYDROGEN PURIFICATION FROM SYNGAS BY PSA USING MICROPOROUS MEDIA**

## **ABSTRACT**

Utilization of renewable energy has become attractive alternative in tackling the problem of global climate change and future energy production. Hydrogen as a sought-after energy substitute have received increasing support to power a fuel cell system or for safe human consumption. There is an urgent need to purify hydrogen gas from synthetic gas or syngas production of coal gasification in order to recover the spent hydrogen and capture CO<sub>2</sub> to address the global issue of climate change more efficiently. One of the main syngas purification technologies, i.e., pressure swing adsorption (PSA) unit coupled with water-gas shift reaction (WGSR) step of gasified feed (H<sub>2</sub> and CO<sub>2</sub>) via pre-combustion capture could provide cleaner hydrogen recovery for profitable applications.

This thesis focused on studying the purification of hydrogen in addition to carbon capture (15 mol%), from a 10 ml/min gas flowrate of H<sub>2</sub>/CO<sub>2</sub> mixture of syngas stream with varied adsorption pressures (1, 2 and 3 bar) in the two-column PSA incorporated with pressure equalization step for less energy penalty and higher hydrogen recovery. Amongst four porous adsorbents prepared, activated and characterized, the reusable and low-cost palm kernel shell activated carbon (PKS-AC) was highlighted to be the best in the hydrogen purification due to its high specific surface area of 697.67 m<sup>2</sup>/g with relatively high CO<sub>2</sub> adsorption capacity of 422.64 cm<sup>3</sup> (CO<sub>2</sub>)/g at STP. The breakthrough time was up to 35 min with adsorption capacity of 7.9733 mg CO<sub>2</sub>/g. The experimental values fitted a typical type-I Langmuir isotherm of a monolayer adsorption and pseudo-

one-order model, indicating fully reversible physisorption through film diffusion and intra-particle diffusion as the rate-determining step mechanisms. The porous PKS-AC medium was found effective in achieving CO<sub>2</sub>/H<sub>2</sub> optimum separation at 2 bar, 5 min adsorption time and 5 min blowdown time with 99.99% H<sub>2</sub> average purity, 99.99% H<sub>2</sub> average recovery and 19.05% CO<sub>2</sub> average purity, 7.14% CO<sub>2</sub> average recovery.

## **CHAPTER ONE**

### **INTRODUCTION**

This chapter familiarizes the research ideas by outlining the background and justification for the present study. It provides an overview on the evaluation of the current methods in the production of pure hydrogen (H<sub>2</sub>) from syngas by using Pressure Swing Adsorption (PSA) system and consequently program on the sequestration of carbon dioxide. The fundamentals of PSA process and the gas separation challenges are discussed providing framework for the objectives of this project. The chapter subsequently presents the problem statements, scope of the research and chapter by chapter summary of the thesis.

#### **1.1 Concern on anthropogenic carbon dioxide release**

The global climate change resulting from the release of anthropogenic carbon dioxide has been a global concern due to the close connection with human livelihood and the ecosystem (IPCC, 2018). The 2018 report states that the anthropogenic carbon dioxide triggered circa 1.0°C of global warming to exceed the pre-industrial levels about 0.8°C to 1.2°C. It also predicts that global warming would reach mean temperature up to 1.5°C in 2030 which would adversely affect the ecosystem and social order. The escalation of the greenhouse gas has been predominantly associated with the combustion of coal, livestock industry and fossil fuel in energy sector, deforestation and transportation sector.

The Kyoto Protocol specified methane (CH<sub>4</sub>), nitrous oxide (N<sub>2</sub>O), carbon dioxide (CO<sub>2</sub>), sulphur hexafluoride (SF<sub>6</sub>), hydrofluorocarbons (HFCs) and perfluorocarbons (PFCs) as the greenhouse gases. Amongst them, carbon dioxide contributed 76% to the greenhouse gas emission (IPCC, 2014) as illustrated in Figure 1.1. The greenhouse gas (GHG) has been known to cause climate change, extreme weather, rising of the sea level and marine population endangerment (Pires et al., 2011) leading to food supply disruptions, wildfires and loss of biodiversity. In addition, the increasing GHGs would lead to the depletion of ozone layer, thus the need to reduce the GHG emission especially from the anthropogenic origins.

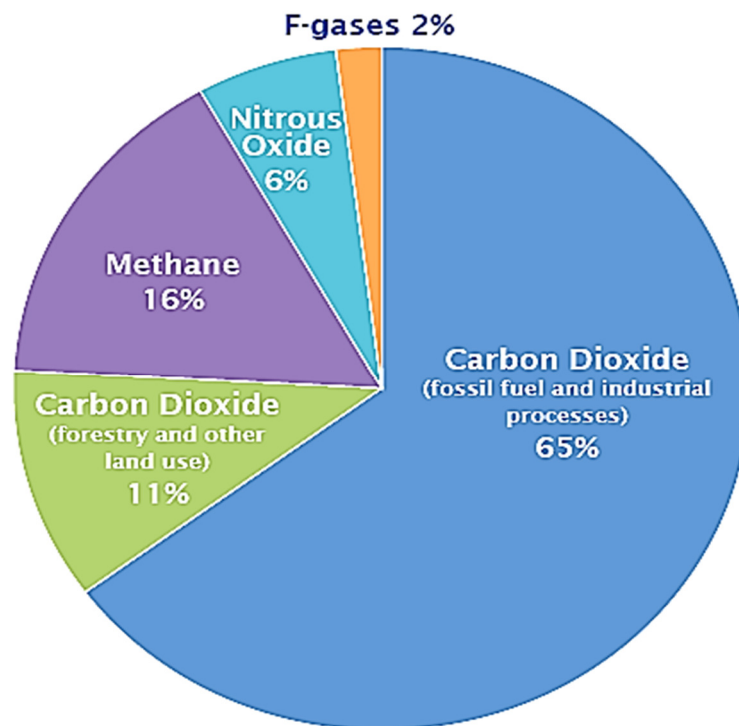


Figure 1.1: Global greenhouse gas emission  
(US Environmental Protection Agency, 2019)

[Key: F-Gases (HFCs, PFCs, SF<sub>6</sub>)]



As indicated in “BP Statistical Review of World Energy 2019” report, the direct anthropogenic CO<sub>2</sub> released to the atmosphere triggered the escalation in world-wide temperatures recorded throughout the past decades (Dudley, 2019). CO<sub>2</sub> release is closely related to the energy demand such as illustrated in Figure 1.2 that shows energy demand and carbon emissions driven by industrial plants and fossil fuel power plants grew by 2.0% to 0.6 gigatonnes (Gt). As a result, the increase in CO<sub>2</sub> mitigation is needed to compensate for the global releases from 2 billion tonnes of CO<sub>2</sub> to over 36.8 billion tonnes due to the exponential growth in economic and population. The mitigation should come from fossil-fuel usage in power plants that contribute about 80% of the energy source worldwide and for decades to come (EIA, 2013). Coal-fired power plants alone, is generating about 38% of global electricity (“Coal & electricity, World Coal Association,” 2013)

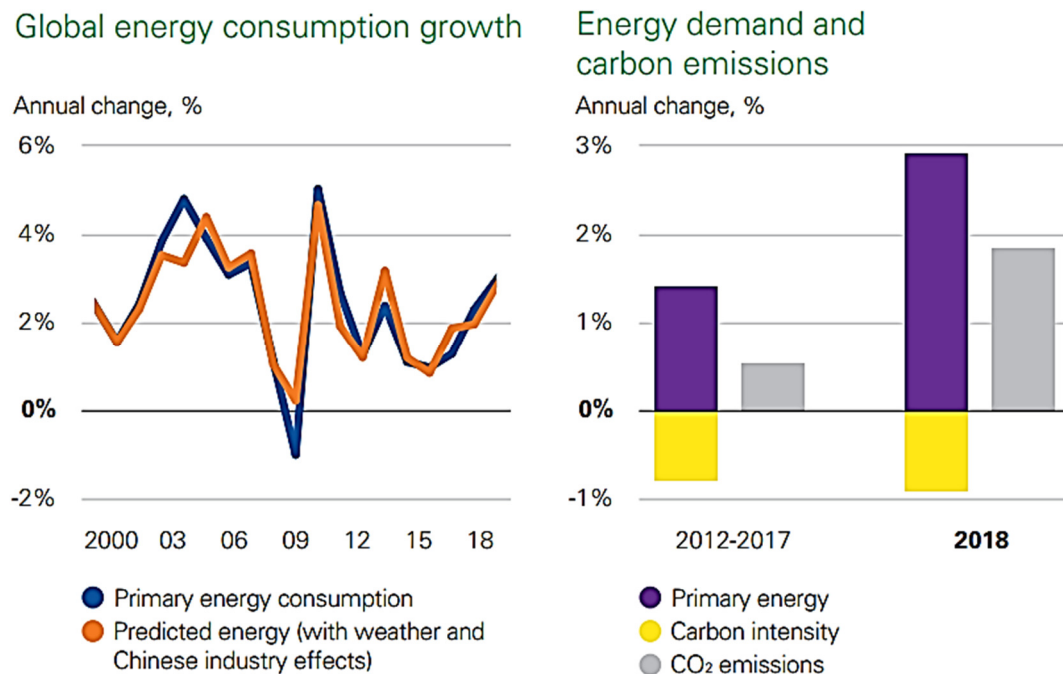


Figure 1.2: Global energy demand and carbon emission.

(Data source: “BP Statistical Review of World Energy 2019”)

The ever increasing anthropogenic CO<sub>2</sub> causes the heat to confine and increase in the overall tropospheric temperature (Charney et al., 1979). Removal of CO<sub>2</sub> can be done if CO<sub>2</sub> from fuel gas combustion is captured and prevented from being emitted to the atmosphere. In the effort to reduce the CO<sub>2</sub> footprints from the atmosphere, there are two main options available: (i) employment of renewable and alternatives energy, and (ii) application of carbon capture and sequestration or carbon capture and storage (CCS). The latter presently is the most practical near-term solution in tackling the challenges of climate change and therefore is applied industrially for a sustainable pathway in economic development and environmental benefits (Yang et al., 2008).

A CO<sub>2</sub> removal method can be categorized into three main methods including pre-combustion, post-combustion, or oxy-combustion. In the process energy generation, the pre-combustion CCS is a key in economical attempt to ease global warming to below 2°C relative to pre-industrial levels (IPCC, 2018). Pre-combustion capture method has been highlighted of late due to its low capital cost in comparison to post-combustion capture. The much higher partial pressure of CO<sub>2</sub> in the shifted syngas (15-60% concentration of total pressure of 2-7 MPa CO<sub>2</sub>) is sent to the separation stage for CO<sub>2</sub> separation using lower compression which allows for lower energy demanding separation process, and more effective use of pressure-driven systems compare to post-combustion capture (Lockwood, 2017). This method shall be able to alleviate the deterioration of environmental pollution, besides offering relatively affordable and practical means to produce hydrogen and capture CO<sub>2</sub> from syngas (CO<sub>2</sub>/H<sub>2</sub>) via a post-combustion capture (Chalmers et al., 2009) for electricity generation.

## 1.2 Syngas (synthesis gas)

Syngases are commonly obtained from the conventional partial oxidation of hydrocarbon in fossil fuels using oxygen (O<sub>2</sub>) in air or generated steam. In coal gasification process specifically, syngas is a mixture of gases (approximately 25-30% hydrogen (H<sub>2</sub>), 30-60% carbon monoxide (CO), 5-15% carbon dioxide (CO<sub>2</sub>) and about 5% methane (CH<sub>4</sub>) and other gases (Mondal et al., 2011). These are amongst the essential components used as industrial feedstocks for power generation, chemical processes and refineries which produce substantial amount of H<sub>2</sub> and CO<sub>2</sub> as wastes or by-products (Jordal et al., 2015). Table 1.1 shows the composition of syngas from various coal-gasification process.

Table 1.1 Syngas composition from coal gasification.

References	Syngas composition (%)				
	CO	CO <sub>2</sub>	H <sub>2</sub>	H <sub>2</sub> O	Others (CH <sub>4</sub> , C <sub>2</sub> H <sub>2</sub> , N <sub>2</sub> )
(Chen et al., 2015)	42.36	9.81	29.38	16.34	2.11
(Lu & Wang, 2014)	52.00	8.00	15.00	19.00	6.00
(Li et al., 2020)	27.18	2.78	57.20	-	12.54
(Pinto et al., 2003)	17.30	20.40	39.40	-	22.90
(Cao et al., 2008)	31.12	17.29	45.60	-	5.99

Coal gasification is a key technology in the H<sub>2</sub> production (i.e. during the steam methane reforming reaction (SMR) and water gas shift reaction (WGSR) as shown in Equation 1.1 and Equation 1.2), in which gasification of carbon and steam are reacted to produce H<sub>2</sub> and CO, and the produced CO can accordingly shift to CO<sub>2</sub> while generating more H<sub>2</sub> via WGSR (Chimpae et al., 2019).

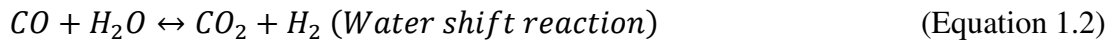
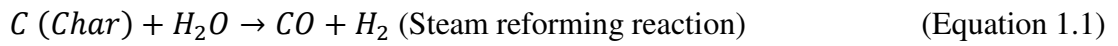


Figure 1.3 represents the schematic of H<sub>2</sub> production from coal gasification process. The production of hydrogen in this way is considered unsustainable in long term (Staffell et al., 2019) because of the consumption of a sizable amount of the coal resources.

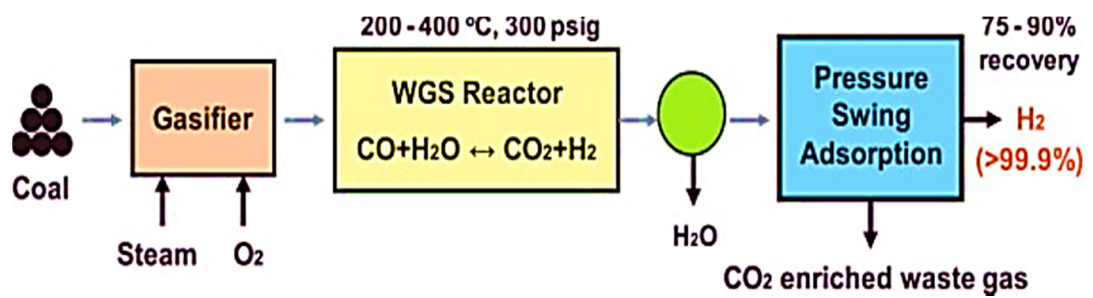


Figure 1.3: Process flow of H<sub>2</sub> production from coal gasification (Chou et al., 2013).

### 1.3 Technologies for H<sub>2</sub> purification from CO<sub>2</sub>

H<sub>2</sub> has been increasingly demanded by chemical production sector such as in production of methanol, ammonia and refineries (Golmakani et al., 2020). The gas is extracted mainly from fossil fuels, but now other renewable sources are also increasingly used. Half of the world H<sub>2</sub> demand is generated from steam reforming of natural gas, 30% from oil or naphtha refineries and off-gases, 18% from coal gasifier, 3.9% from electrolysis of H<sub>2</sub>O and 0.1% from other origins (Muradov & Veziroğlu, 2005).

H<sub>2</sub> energy has been an ideal candidate for providing a solution to the energy-related environmental problem (Acar & Dincer, 2014). Clean combustion of H<sub>2</sub> in fuel cells for power generation and also in transportation produces only energy and water thus making H<sub>2</sub> an alternative to fossil fuel replacement (García-Olivares et al., 2018). However, the present production of H<sub>2</sub> yields variety of unwanted by-products. Therefore, hydrogen needs to be purified before being utilized in power generation plants or fuel cells in vehicles for total zero emissions.

The performance and durability of H<sub>2</sub> fuel-cell is strongly dependent on the purity of the H<sub>2</sub> because contamination even with a minute CO or CO<sub>2</sub> can poison the catalyst in the fuel cell system and render the cell useless. This matured technology was further developed through prototype vehicles using H<sub>2</sub>-fuels cells and can be found all around European, Iceland, Japanese and North American cities (Brandon & Kurban, 2017; Haraldsson et al., 2005; Solomon & Banerjee, 2006). Thus, manufacturers have set high standards on the ultra-purity of commercial H<sub>2</sub> (“Hydrogen fuel quality — Product specification (ISO 14687:2019(E)),” 2020). H<sub>2</sub>

purity is specified to be at least 99.97% and other gases <300 ppm for commercial applications (Ohi et al., 2016).

By combining H<sub>2</sub> with oxygen (O<sub>2</sub>), a fuel cell could generate a sufficient electric power that emits only pure water as a by-product. The water produced by fuel cells was safe and clean enough to be consumed as drinking water for astronauts on the space shuttle (Hristovski et al., 2009). The potential of H<sub>2</sub> utilisation is further explored as a healing and preventive medicine against health disorder. H<sub>2</sub> infused in water reportedly could provide the health benefits (Nakao et al., 2010), but an ultra-purified H<sub>2</sub> is required for human safe consumption. In recent advances, the broaden potential use of hydrogen as preventive and therapeutic medical gas was proven to be advantageous (Huang et al., 2010).

Following our previous discussion, H<sub>2</sub> purification from syngas production is the key to solving the energy and environmental challenges via purification technologies applications such as cryogenic separation, chemical absorption, pressure swing adsorption (PSA) and membrane diffusion.

The industrial cryogenic separation has made momentous progress since 1960s (Weinstock, 1969). It utilizes H<sub>2</sub> low boiling point of -252.9°C and phase change to separate other pollutants from H<sub>2</sub>. The H<sub>2</sub>-rich stream is cooled to a low temperature that turns H<sub>2</sub> into solid and separated from the remaining component gases. Cooled solid product is passed through a heat exchanger, then a compressor to final pressures of 100-200 atm in order to recover the purified hydrogen (Baxter et al., 2011). The benefit of the approach is that the H<sub>2</sub> is stored as a liquid due to the extreme cooling. This is considered ideal for a large-scale industry storage and application. The disadvantage however, comes from the expensive cooling process. The feed gas also

needs a prior purification step to remove CO<sub>2</sub>, H<sub>2</sub>S and water. This makes cryogenic separation less appealing than PSA or membrane processes (Liemberger et al., 2017). Apart from the cryogenic technology's energy extensiveness due to the extremely low temperature and high pressure requirement (Olajire, 2010), the purity of the hydrogen is also capped at 99% using this method (Al-Mufachi et al., 2015).

A chemical absorption process is carried out through a continuous scrubbing system consists of an absorber and a stripper occurred between 20 and 50°C, while desorption (regeneration) process occurs between 110 and 130°C (Kim et al., 2013). The reboiler is required in providing the heat of desorption and steam production for the stripping of CO<sub>2</sub> from the solvent. In the transition of CO<sub>2</sub> from gas phase to liquid phase, this process employs the CO<sub>2</sub> reversible chemical reaction using aqueous alkaline solvents. Adsorbents that are commonly used are monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA) and triethanolamine (TEA) (Shakerian et al., 2015). A strong bonded intermediate compound and kinetically faster is formed. Then, the absorbed CO<sub>2</sub> is stripped from the solution and a pure stream of CO<sub>2</sub> is compressed while the solvent recovered is pumped back to the absorber through a heat exchanger for subsequent cyclic application (Nwaoha et al., 2017). The weak binding of CO<sub>2</sub> and the solvent at high pressure is performed by a physical absorption process. In commercial applications, Purisol, Selexol, Rectisol and Fluor are commonly applied as the solvents. The disadvantages are flow problem (flooding) due to the increase of solvent viscosity, corrosion and high energy requirement for solvent regeneration (Islam et al., 2011).

Membrane diffusion is carried out using a selective barrier, separating gas stream through the membrane to permeate at various velocities. Among commercially attractive for membrane materials are dense and porous membranes, ion-conductive

and pervaporation membranes (Abanades et al., 2015). Differences in pressure are used to separate the feed gas components (Edlund, 2009). The mechanism for H<sub>2</sub> separation in polymeric and dense material membranes is solution-diffusion (Yin & Yip, 2017) which depends on both solubility and diffusivity. It is described in following steps: (i) Adsorption: H<sub>2</sub> molecules diffuse at one surface (feed side) of the membrane; (ii) Chemisorption and dissociation: The H<sub>2</sub> molecules split into atomic form of protons and electrons; (iv) Diffusion: The elementary components consists of proton diffuse through the membrane lattice; (v) Recombination: Protons and electrons re-associate to form molecular H<sub>2</sub>; and (vi) Desorption: The purified H<sub>2</sub> desorbs from the permeate. Membrane technology has unique advantages, including ease of operation, low energy demand as no phase transformation is involved, simple equipment and continuous operation (Bernardo et al., 2020). Since the H<sub>2</sub> needs to undergo a compression process for transport or storage, this separation method consumes much energy, yields low throughput, requires high operational and maintenance cost (Mondal et al., 2012) . Beside limited scale of use in the industry, polymer membrane diffusion also faces some issues with impurities of CO<sub>2</sub> and H<sub>2</sub>O requiring further stages of purification in the post-treatment (Sanders et al., 2013).

Adsorption of CO<sub>2</sub> is performed through physical (physisorption) or chemical (chemisorption) (Berger & Bhowan, 2011). In a physisorption process, a van der Waals bonding between the adsorbate and adsorbent exhibits dispersive forces or dipole interactions which allow rapid and reversible processes to occur during multiple adsorption and desorption. In a chemisorption process, the molecules of CO<sub>2</sub> fuse on surface of adsorbent to form chemical covalent bonds which are much stronger than the van der Waals's. Adsorption-based industrial processes main practises are H<sub>2</sub> purification (Sircar & Golden, 2000), air fractionation/separation (Arvind et al., 2002),



hydrocarbon (HC) separation (Grande & Rodrigues, 2004) and air drying (Subramanian & Ritter, 1998). Physical adsorption of CO<sub>2</sub> capture is most common method used due to its being cost effective and practical design for separation and purification of various gases. Various types of adsorbents for physisorption and chemisorption are zeolites, activated carbons, silica, aluminium oxide aluminosilicates impregnated with amines and metal oxides (Ben-Mansour et al., 2016). Moreover, CO<sub>2</sub> reutilization and exploitation are significant and beneficial in the downstream industries. Nevertheless, there has been insufficient effort in recycling of “after-capture” CO<sub>2</sub> to control the GHG release for economic gains and environmental benefits (Duraccio et al., 2015).

The other alternative for H<sub>2</sub> purification with CO<sub>2</sub> removal from a gas mixture is PSA (Riboldi & Bolland, 2017). PSA operates by exploiting the weak bonding between the adsorbate and adsorbent to benefit the rapid and reversible processes during multiple adsorption and desorption cycles. As such, the process of separating H<sub>2</sub> from CO<sub>2</sub> becomes more effective and efficient than the cryogenic separation, solvent absorption and chemical membrane separation discussed earlier. In this work, we propose the application of carbon-based and zeolite materials in CO<sub>2</sub> adsorption by PSA in order to improve the CO<sub>2</sub> capture so that CCS technology can be made more economical and efficient in the industry.

Table 1.2 enlists the three techniques for refineries off-gasses H<sub>2</sub> purification, summarized by Johnson Matthey Group Research Centre (Grashoff et al., 1983) including the eligible candidates for the present study. To date, the H<sub>2</sub> purification by effective CO<sub>2</sub> removal in about 10–15% composition from the syngas H<sub>2</sub>/CO<sub>2</sub> mixture remains a challenge (Lin et al., 2004). Nonetheless, palladium membrane diffusion and PSA technique are reported as compelling options to achieve ultra-pure H<sub>2</sub> quality

> 99.999% while the cryogenic separation (97% H<sub>2</sub> purity) and polymer membrane diffusion (98% H<sub>2</sub> purity) are having impurities of CO<sub>2</sub> and water which necessitate subsequent purification step (Rabiei, 2012).

Table 1.2 Separation techniques for purification of H<sub>2</sub> and CO<sub>2</sub> removal.

(Ref.)	Principle	Typical feed gas	Hydrogen output %		Scale of use	Comments
			Purity	Recovery		
Cryogenic Separation (Weinstock, 1969)	Partial condensation of gas mixtures at low temperatures	Petrochemical and refinery off-gases	90–98	95	Large scale	Pre-purification step necessary to remove CO <sub>2</sub> , H <sub>2</sub> S and H <sub>2</sub> O
Chemical absorption (Zhang et al., 2011)	CO <sub>2</sub> solubility and recovery	Any CO <sub>2</sub> containing gas stream	85-98	Up to 95	Large scale	High energy requirement for solvent regeneration
Palladium Membrane Diffusion (Boon et al., 2016)	Selective diffusion of H <sub>2</sub> through a palladium alloy membrane	Any H <sub>2</sub> containing gas stream	≥99.99 99	Up to 99	Small to medium	Sulphur-containing compounds and unsaturated hydrocarbon impair permeability
Pressure Swing Adsorption (Siqueira et al., 2017)	Selective adsorption of impurities from gas stream	Any H <sub>2</sub> rich gas	99.999	70–85	Large scale	The recovery is relatively low as H <sub>2</sub> is lost in the purging step

#### **1.4 Pressure Swing Adsorption (PSA) unit for H<sub>2</sub> purification**

Several other techniques for CO<sub>2</sub> separation from syngas has been discussed in previous section. However, they are insufficiently feasible for CCS approach, they do not reach an acceptable separation performance, or do not fulfil the requirements for current economic conditions (Al-Mamoori et al., 2017).

Pressure swing adsorption (PSA) is a viable energy, cost-efficient option and widely applied in industrial processes for gas separation from flue, fuel and syngas. PSA is a novel method to facilitate home medical oxygen generators and airbrake drying systems for small, medium and large-scale industrial applications for H<sub>2</sub> purification. In a cyclical process, adsorption is performed during pressurization while, desorption for adsorbent regeneration is performed during blowdown to produce high-purity outputs (Riboldi & Bolland, 2017). The PSA is considered as a favourable option, in comparison to the absorption method which likely to suffer a few drawbacks resulted from high energy requirement and corrosion problem in process equipment. The selection of PSA approach is further supported by the adsorbent regenerability potential intended for lowering the energy penalty, hence the capital cost reduction in CO<sub>2</sub> capture (Hongjun et al., 2011) and least environmental impact (Glier & Rubina, 2013).

PSA processes are operated with a pressure elevated feed, whereas vacuum swing adsorption (VSA) processes are driven by vacuum control. In temperature swing adsorption (TSA) processes, they are operated at alternating bed temperature to achieve the swing effect between adsorption columns. Among the adsorption processes mentioned, TSA is found to be productively and economically unattractive due to the heating requirement in regeneration step. In the latest development of PSA,

a vacuum pressure swing adsorption (VPSA) processes are also applied for CO<sub>2</sub> capture, CH<sub>4</sub> separation and H<sub>2</sub> purification (Lopes et al., 2011) and solid adsorbents such as zeolites, metal organic frameworks, poly aspartamide, metal oxides, activated carbon, porous silicates, and chitosan are being used (Mondal et al., 2012). Solid adsorbent is indisputably an alternative to physical solvents, due to its accessibility and non-corrosiveness (Ebner & Ritter, 2009; Yong et al., 2002). For large-scale operations using solid adsorbents, among the known challenges are, a large volume of adsorbents is required, complicated synthesis process, limited adsorption capacity due to adsorbent exhaustion and heating requirement for adsorbent regeneration (Lee & Park, 2015).

Liu et al. (2009) reported that the commercially utilised 13X zeolite suffers drawbacks from co-adsorption with water causing reduction in adsorption capacity. In the work, there were also problems in implementing the rapid change of pressure and temperatures on a large-scale level and the influence gas impurities on capacity, selectivity and stability of the adsorption process. In the study, they also mentioned the importance of developing and recognizing the practicality in regeneration methods intended for large-scale operation. Yang et al., (1997) studied on gas separation via one column PSA process using zeolite 5Å for H<sub>2</sub>/CO<sub>2</sub> and H<sub>2</sub>/CO binary mixtures at 70/30 volume % composition via both experimental and simulation. The H<sub>2</sub> achieved a purity up to 70% to 99.99% (recovery 67.5%) in the H<sub>2</sub>/CO<sub>2</sub> and up to 97.09% purity (recovery 67.5%) in the H<sub>2</sub>/CO system. A low pressure range (below 10 bar) was proposed in H<sub>2</sub> enrichment for coke oven gas and melting incinerator gas through PSA processes (Ahn et al., 2001; Moon et al., 2014). Similarly, Divekar et al. (2020) reported on an experiment which was also being conducted at a low pressure ranging

from 2 to 0.1 bar resulted in CO<sub>2</sub> purity of 95 mole% and at least 90 mole% for H<sub>2</sub>/CO<sub>2</sub>, respectively.

## 1.5 Problem statement

Fossil fuels are likely to remain as major contributor to energy production and global warming. However, H<sub>2</sub> recovered from H<sub>2</sub>-rich off-gas streams as a byproduct in petrochemical facilities, power plants or refineries and residual gas (Benson & Celin, 2018) may be able to help alleviate the global warming concern. H<sub>2</sub> recovery system becomes an interesting alternative for significant cost effective and productivity improvement. Here, H<sub>2</sub> must be purified and CO<sub>2</sub> must be removed from the syngas stream in order to benefit economically (Figueroa et al., 2008) and conserve the environment.

Among the techniques developed for gas separation in a power plant, most do not fulfill the requirements for acceptable separation performance from an economic standpoint. It is also important to acknowledge that upon the H<sub>2</sub> extraction, purification and refining will further increase the total cost due to requirement of ultra-high purity supply particularly in semiconductor industry, H<sub>2</sub> fuel cells and H<sub>2</sub> infused drinks in therapeutic alternative for human consumption. The previous advances in the PSA process were mainly driven by motivation to improve the separation performance in terms of the purity and the recovery of the output streams. In this work, the challenge is to achieve a targeted value for pure-H<sub>2</sub> purity in H<sub>2</sub>-enriched gas stream that is set to be over 99.99% while for CO<sub>2</sub>-enriched gas stream the desired value of CO<sub>2</sub> purity should be above 95%.

PSA is one of the most developed method for gas purification. It is highly relevant for the effectiveness and optimization of CCS process. However, there are limited system analyses reported in the literature that is related to CO<sub>2</sub>/H<sub>2</sub> separation using PSA. Also, despite the apparent advantages of PSA in gas separation, the H<sub>2</sub> purification by effective removal of CO<sub>2</sub> of about 10–15 mole% from the syngas remains a challenge. This is worsen by the fact that most adsorbents that are used are costly to produce and regenerate. Thus, there is a need for high quality adsorbent that is produced from a low-cost material such as recycled agricultural wastes (Ochedi et al., 2020). Activated carbon (AC) made from organic waste of palm kernel shell (PKS) turned up to be an impeccable choice, considering Malaysia is facing problems in handling the disposal of the waste from palm oil industries (Singh et al., 2010). Wrong technique of waste disposal and open burning could be avoided by recycling of the wastes in order to benefit the economy and environment. To harness the full potential of this waste material, porous PKS AC is chosen as an adsorbent material and the adsorption performance must be made to compete well with the commercial adsorbents. This material will help in tackling the pollution problems and global CO<sub>2</sub> mitigation through proper handling of waste.

The aim of this thesis is to close the knowledge gap and, consequently provide contribution on the development of CCS via PSA for syngas pre-combustion carbon capture from gas mixture (containing H<sub>2</sub> and CO<sub>2</sub>). This work proposes a process in which 15 mol% of CO<sub>2</sub> is adsorbed from a H<sub>2</sub>/CO<sub>2</sub> gas mixture approximating a syngas stream via PSA process in the effort to achieve ultra-pure H<sub>2</sub>. In evaluating the proposed material's performance, selected solid adsorbents will be tested in a 2 unit fixed-bed PSA unit for CO<sub>2</sub> removal. While for the design aspect, the integrations of equalization step in the “Skarstrom steps” is proposed as a measurement of energy

gains leading to operating cost reduction in achieving the low energy requirement for industrial application. Additionally, in this comparative study of carbonaceous and modified organic frameworks (MOF) adsorbents for H<sub>2</sub> purification is carried out in the dynamic condition of two fixed bed adsorption focusing specifically on continuous improvement of PSA performance.

## **1.6 Objectives of the Research**

The objectives of this research are:

1. To synthesize adsorbents from palm kernel shell (PKS-AC), carbon molecular sieve (CMS) and MOF-based adsorbents (ZIF-7 and UiO-66).
2. To characterize the adsorbents for their physical and chemical properties.
3. To study the effects of fixed bed operating pressure and type of adsorbents on the breakthrough and saturation time.
4. To determine the adsorption equilibrium isotherms, kinetics and mechanisms of the adsorption process.
5. To identify the PSA operation parameters (initial adsorption pressure, adsorption time and blowdown time) that affect the purity and recovery of H<sub>2</sub>/CO<sub>2</sub>.

## 1.7 Scope of research

This work involves synthesis of palm kernel shell activated carbon (PKS-AC), carbon molecular sieve (CMS) and metal–organic framework (ZIF and UiO-66) through physical and chemical activation for pressure swing adsorption. The as-synthesized adsorbents were characterized by X-ray diffraction (XRD), Fourier transform infra-red (FTIR) spectroscopy, thermogravimetric (TG) analysis, nitrogen adsorption, temperature-pressure desorption (TPD), scanning electron microscopy (SEM) and energy dispersive X-ray (EDX). This study is an essential effort toward the development of adsorbents porous systems by combining the benefits of thermal, mechanical and structural stability material for diversified future applications.

The investigation of CO<sub>2</sub> breakthrough curves was performed using different adsorbents and initial pressure of gas mixtures (1, 2 and 3 bar). Adsorption isotherms based on Langmuir and Freundlich models, kinetic models of pseudo first and second order, including mechanism such as intra-particle diffusion model were used to analyse the equilibrium of the adsorption process.

Furthermore, the work also assesses the characteristics of the prepared adsorbents in terms of the adsorption capacity, gas separation performance and aging of the adsorbent under a rapid cyclical PSA process within a typical cycle time of 10 minutes (Grande, 2012). A lower range of pressure (1-3 bar) was chosen to address a more economical approach in PSA. Separation studies were carried out via the previously mentioned PSA unit using a varied initial adsorption pressure of 1, 2 and 3 bar, adsorption time of 0.5, 1, 3 and 5 minutes and blowdown time of 0.5, 1, 3 and 5 minutes. The selected range of the adsorption and blowdown time of 1-5 minutes was used based on the breakthrough analyses. The manipulation of variables and their



effects on purity and recovery for H<sub>2</sub> purification with CO<sub>2</sub> removal are investigated. The feed concentration of CO<sub>2</sub> is kept constant at 15 mol% to replicate the composition of actual syngas in the industry. PSA processes with adsorption, pressure equalization, desorption and re-pressurization operating modes are performed.

## **1.8 Organization of the thesis**

There are five (5) chapters in the thesis that gives informative contents about the research.

Chapter One presents the general background on global issues, CO<sub>2</sub> emission, H<sub>2</sub> purification as well as CO<sub>2</sub> capture and sequestration of syngas, viable gas purification and separation technologies and its potential adsorbents. The statement of research problem, objectives and thesis organization are included in this chapter.

Chapter Two presents the literature on the previous researches. This chapter is written to provide details and ideas to move the project forward. The first section presents the definitions of adsorbents, previous applications, materials, preparation methods and expected characterization results. It also covers the analysis of adsorption isotherms, kinetics and mechanisms of a fixed bed breakthroughs, fundamental of PSA processes and its parameter performance indicators.

Chapter Three covers the material and method. This chapter presents the materials, chemicals and equipment used throughout the experiments. It also provides the detailed description of the experimental procedures and the equipment used in characterizing the samples, preparation methods of adsorbents, fixed bed breakthrough studies and regenerations of adsorbents.

Chapter Four elucidates the experimental results together with the analyses. In the first stage, the characteristics of synthesized adsorbents are explained according to the data obtained from TGA, XRD, FTIR, SEM-EDX, particle size analyzer, nitrogen adsorption studies in Autosorb, CO<sub>2</sub>-PC and CO<sub>2</sub>-TPD analysis. Second stage involves the transient breakthrough study in defining the adsorption isotherms, kinetics and mechanisms for adsorbents at different pressures. Third stage explains the assumptions made for the idealization of PSA process which aided the fundamental performance indicators (PI). Fourth stage provides the utilization of performance indices for evaluation of the synthesized adsorbents via a PSA unit. Fifth stage is to evaluate and maximize the performances of a CO<sub>2</sub>/H<sub>2</sub> gas separation. Cycle repetitions and adsorbent recyclability are also studied. In summary, proper PSA process and material engineering are described in correlation to the separation performance at specific ranges of operating conditions.

Chapter Five presents the conclusion and recommendations for future consideration derived from the thesis based on the project's findings.

## **CHAPTER TWO**

### **LITERATURE REVIEW**

This section is written to arrange the details on the idea of the project by presenting the previous findings and reviews available from reliable scientific databases with references. Herein, the theories of adsorption are elucidated to demonstrate the importance of the adsorbent selection for PSA application. The backgrounds of carbon based and modified organic framework (MOF) based adsorbent, in relation to their adsorption properties, operating parameters and conditions are reviewed and highlighted. A brief discussion of PSA technology is also included. It also elaborates on the basic principles and analysis of breakthroughs curves, adsorption isotherms, kinetic and mechanism, basic principles of PSA processes and its performance in terms of its purity and recovery.

#### **2.1 Adsorbents in PSA**

The function of the adsorbent is to offer the surface area of adsorption for molecules interaction. Adsorbents can allow molecules of a gas or liquid mixture to make contact and adhere to its surface in a process called “adsorption”. It is an occurrence of molecular attraction between an adsorbate phase and the adsorbent surface of a solid in a monolayer or multilayer diffusion (Langmuir, 1918; Myers & Prausnitz, 1965; Polanyi, 1932). Solid adsorbents are permeable media consist of voids, channels or spaces, which are deeper in dimension, compositions and structures. This characteristic for adsorbent is defined by their specific area, commonly related to porosity which is chosen according to the requirement for substantial adsorption capacity of the heavier component. In order to be considered as

a good adsorbent, the following factors are considered: (a) good selectivity between the adsorbing molecule and the adsorbent surface, (b) higher capacity with larger surface area of adsorbent; and (c) durability of adsorbent, which mainly depends on the fabrication process of the adsorbents (Egídio Rodrigues et al., 2017).

Generally, the pore size is significant in defining the physical features of the adsorbent in the typical adsorption and desorption rates. Adsorption processes allow the interaction between the solid and the fluid phase according to the equilibrium pressure and temperature of adsorbents. High surface area and highly porosity (meso and macro pores) in the adsorbent medias are needed to permit the entrance of gas molecules into the porous structure. The diffusion rates of the adsorbates through the pores structure of adsorbent will result in different types of diffusional resistance (Ruthven, 1984). In micropores, the adsorbates are having higher affinity towards the adsorbent surface. Conversely, in mesopores and macropores, the adsorbed molecules experience less or no attractive force allowing the adsorbate to penetrate faster through the material (Beyzavi et al., 2015). While in other circumstances, if the diffusional resistance in bulk component is substantial, this will result in unreasonably longer time to separate the gas (Weber & Chakravorti, 1974). In typical commercial adsorbents, the materials are grouped into organic, hybrid and inorganic adsorbents. They can be in cylinders, spheres, granules, flakes, or powders with varying sizes of 50 nm to 1.2 cm and surface areas of 300 to 1200 m<sup>2</sup>/g (Seader & Henley, 2010). Alternatively, the adsorbent can also be shaped into spherical pellets or extruded as the honeycomb monolithic structures in attempt to reduce pressure drop in the typical fixed bed adsorption system (Rezaei & Webley, 2009).

In order to achieve the higher attractions of porous adsorbents towards certain gas components at various working conditions, material engineering and synthesis have been exploited in the recent years. In the material engineering, the main interest is to discover a newly improved adsorbents that could improve the overall adsorption performance (Siqueira et al., 2017; Sircar et al., 1996) which eventually increase the efficiency of the adsorption unit, product purity, product recovery, energy intake and economics of the adsorption unit (Mittal et al., 2016).

The knowledge on both adsorption equilibrium and kinetics are critically dependent on the selection of promising material adsorbent with high selectivity, rapid adsorption kinetics, unlimited regenerability and adsorption capacity, along with the desorption ability and a wide-ranged operating conditions (Shi et al., 2016). The adsorption capacity generally increases with increase in BET surface area. Usually, a BET surface area larger than 500 m<sup>2</sup>/g is preferable (Song et al., 2015) . These factors are the key to adsorbents ideal for application of pre-combustion carbon capture (Wang et al., 2017). A variety of porous adsorbents can be utilized for CO<sub>2</sub> capture commercially such as supported carbons, molecular sieves, zeolites, silica gel, hydrotalcites, aluminosilicate zeolite, activated calcium oxides, amines, mesoporous materials, polymer and metal-organic framework (MOF) materials (Younas et al., 2016)

Table 2.1 lists and compares the characteristics of solid adsorbents in the previous study. The adsorbents that shall be used in the current study are classified into carbon-based and modified organic framework (MOF) based, so the work will be focused more on these types of media.

Table 2.1: Characteristics of solid adsorbents (Yuan et al., 2016).

	Optimal operating condition		Mechanism	Main application	Advantages	Disadvantages
	P (bar)	T (°C)				
Carbon adsorbent	0.1-10	25-75	Physisorption	CO <sub>2</sub> /CH <sub>4</sub>	cheap raw materials; rapid carbonation kinetics; low desorption temperatures low CO <sub>2</sub> capacity at mild conditions	low CO <sub>2</sub> capacity at mild conditions
Modified organic framework (MOF) adsorbent	high	low	Chemisorption	CO <sub>2</sub> /CH <sub>4</sub> CO <sub>2</sub> /H <sub>2</sub>	high surface area; tailorable pore metrics; high density of active sites; adjustable chemical functionality; huge and accessible pore volumes	unclear regenerability; expensive synthesis route; low CO <sub>2</sub> capacity under mild conditions