CORRELATING PARAMETERS WITH HYDROGEN PURITY AND RECOVERY BY PSA IN HYDROGEN PURIFICATION FROM SYNGAS

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by

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Nurul Asyiqin Binti Zakaria
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LIST OF SYMBOLS

Symbol	Description	Unit
c_i:	molar concentrations of components	mol/m^3
C_{pai}	heat capacity of adsorbed phase	J/kg/K
C_{pw}	wall specific heat	J/kg/K
c_{ps}	particle specific heat	J/kg/K
d_b	bed inner diameter	m
d_p	particle diameter	m
D_L	axial dispersion coefficient	$W/m^2/K$
h_{gs}	gas/solid heat transfer coefficient	$W/m^2/K$
h_{in}	inner wall heat transfer coefficient	$W/m^2/K$
h_{out}	outer wall heat transfer coefficient	$W/m^2/K$
K_{Lg}	gas heat conductivity	W/m/K
K_{Ls}	solid heat conductivity	W/m/K
K_w	wall heat conductivity	W/m/K
L	bed length	m
N	number of components	-
$n_{\_i}$	molar flow rate of component	i
n^s_i	saturation adsorption amount of the ith component	mol/g
p	pressure of adsorbent bed	bar
R	universal gas constant, 8.314	J/mol/K
t	time	s
T_f	temperature of ambient	K

T_g	gas phase temperature	K
T_W	solid phase temperature	K
v_g	interstitial velocity of gases mixture	m/s
z	axial position in the bed	m

Greek symbols

Symbol	**Description**	**Unit**
ε_b	bed porosity	-
ε_p	particle porosity	-
μ	dynamic viscosity	m/s
ρ_g	gas phase density	kg/m^3
ρ_p	particle density of adsorbent bed	kg/m^3
ρ_s	skeletal density of adsorbent	kg/m^3
ρ_w	wall density	kg/m^3

LIST OF ABBREVIATION

Symbol	Description
ANOVA	Analysis of variance
CO_2	Carbon dioxide
Cu-BTC	Copper (ll)-benzene-1, 3,5-tricarboxylate
DE	Design expert
DOE	Design of experimental
EPA	United states environmental protection agency
GHG	Greenhouse gas
H_2	Hydrogen
IEA	International energy agency
MAPE	Mean absolute percentage error
NOx	Nitrogen oxide
PSA	Pressure swing adsorption
SMR	Steam methane reforming

MENGAITKAN HUBUNGAN ANTARA PARAMETER DENGAN KETULENAN DAN PEMULIHAN GAS HIDROGEN MENGGUNAKAN MODEL PENJERAPAN DALAM PROSES MENULENKAN HIDROGEN DARI GAS SINTETIK

ABSTRAK

Platform ASPEN dimanfaatkan dengan menggunakan model penjerap yang memilih Cu-BTC sebagai penjerap untuk mempelajari prestasi penulenan hidrogen (ketulenan dan pemulihan) dari gas sintetik yang mengandungi 80% H_2 dan 20% CO_2. Keputusan menunjukkan bahawa simulasi lengkung lolos dengan data eksperimen dari literatur adalah sesuai. Keputusan juga menunjukkan bahawa dengan meningkatkan tekanan penjerapan dan memanjangkan masa penjerapan, ia akan membawa kepada penurunan nilai untuk kedua-dua ketulenan dan pemulihan hidrogen. Sementara itu, peningkatan kepekatan awal hidrogen akan meningkatkan ketulenan hidrogen tetapi mengurangkan pemulihannya. Pengoptimunan juga dilakukan untuk mencari ketulenan dan pemulihan produk yang maksimum. Ketulenan dan pemulihan yang optimum masing- masing telah direkodkan pada 90.12% dan 93.22%, apabila tekanan penjerapan ialah 2 bar, masa penjerapan ialah 150s dan kepekatan awal hidrogen sebanyak 75% digunakan. Melalui bahagian pemaksimuman, model ini disahkan boleh mencapai standard ketulenan hidrogen untuk sel bahan api dengan menetapkan tekanan penjerapan, masa penjerapan dan kepekatan awal hidrogen masing-masing kepada 2 bar, 102.48s dan 80%.

CORRELATING PARAMETERS WITH HYDROGEN PURITY AND RECOVERY BY PSA IN HYDROGEN PURIFICATION FROM SYNGAS

ABSTRACT

The pressure swing adsorption model (PSA) on ASPEN Adsorption platform using Cu-BTC as the adsorbent was used to simulate the hydrogen purification performances (purity and recovery) from binary syngas feed (containing 80% H_2 and 20% CO_2). Results showed the simulated breakthrough curves from the Aspen simulation fit well with the experiment data from the literature. The results also showed that increasing adsorption pressure and prolonging adsorption time would lead to decrease of both hydrogen purity and recovery. Meanwhile, increasing hydrogen feed concentration, increased the hydrogen purity but reduced its recovery. The optimization was also carried out to find the maximum product purity and recovery. The optimized purity and recovery were recorded at 90.12% and 93.22% respectively when the adsorption pressure of 2 bar, adsorption time of 150s and hydrogen feed concentration of 75% were used. Through a maximisation section, this model was confirmed could meet the standard hydrogen purity for fuel cells by setting the adsorption pressure, adsorption time and hydrogen feed concentration to 2 bar, 102.48s and 80% respectively.

CHAPTER 1

INTRODUCTION

Chapter 1 introduces the overview of this research and problem on greenhouse gas emission due to the lack of utilizing sustainable energy. Generally, this chapter gives out the information on greenhouse gas problem, type of emission sources, problem statement and the objectives of this research paper.

1.1 Research Background

Global warming has been a talk issue for decades and its impacts are harming people around the world. Daily human activities have been contributed a lot of greenhouse gas (GHG) in the atmosphere. Based on the International Energy Agency (IEA) website, people are witnessing the increase of carbon dioxide gas (CO_2) emissions by 1.5 billion tonnes globally this year after the trend showing a decline during last year due to Covid-19 outbreak (IEA, 2021). As most sectors are opened again, humans' activities have been back on track and the report mentioned that, the global energy demand using coal is the reason for this increasing CO_2 emissions. This demand is expected to increase by 4.6% in 2021 (IEA, 2021).

As using coal has been a norm since past, people are trying to opt for a more sustainable way, by replacing it with hydrogen as energy carrier. The mentioned alternative can be categorised as renewable energy or known as clean energy because of its source is coming from natural resources. Hydrogen is the most abundant in the universe, containing the highest specific energy content (Balat, 2008). Moreover, it has many accessible storage methods (e.g., gaseous, liquid and solid) which makes it easy to handle (Abe et al., 2019). Aside from having important benefit in energy sector, hydrogen demand is increasing as it serves various field industries with the versatility of its uses. In medical sector, hydrogen can be used as a major physiological regulator of

antioxidant, anti-inflammatory, anti-apoptotic and other protective activities in cells and organs (Zhang et al., 2012). In chemical industry, there are few processes consuming hydrogen which are likely oil refining, ammonia production, methanol production and steel production. In the construction sector, the buildings need hydrogen to be blended into natural gas networks. In addition, hydrogen fuel cell car can be one of alternatives transportation nowadays to practice a more sustainable way of life (IEA, 2019). From the previous mentioned, it is proven that hydrogen has a lot of potential in different sectors, making the industry acknowledge its importance.

Based on the United States Environmental Protection Agency (EPA) website (n.d.), **Table 1.1** shows the transportation industry is a major source of greenhouse gas emissions, leading to 29% of 2019. Introducing hydrogen fuel cell to the automotive industry market does help to reduce the gas emission as fuel cells offer zero pollutant discharge (Du et al., 2021). Hydrogen fuel cell performs redox reaction producing current that can power the car engine. The first fuel cell with a mixture of hydrogen and oxygen was invented in 1806 meanwhile the first electric cars were produced 25 years later (WIPO, 2019).

Table 1.1 Total U.S. Greenhouse Gas Emission by Economic Sector in 2019(EPA.com, n.d.)

Economic Sector	**Percentage of GHG* emission**
Transportation	29%
Electricity	25%
Industry	23%
Commercial & Residential	13%
Agriculture	10%

Total Emissions in 2019 = 66,558 Million Metric Tons of CO_2 equivalent.
Percentage might not add up to 100% due to independent rounding.
*GHG = greenhouse gas

Combustion of hydrogen will form water and can be done either through direct combustion or consume it in fuel cell to produce electricity. Hydrogen as a transportation

fuel proves its energy yield amount to 2.75 times greater than hydrocarbon fuels (Kapdan and Kargi, 2006). The advantage of consuming fuel cell is that it has various primary resources can be used to produce pure hydrogen. As mentioned, zero pollution is claimed when driving an electric car as the only major oxidation product from the reaction is water vapour with a very small amount of nitrogen oxide (NOx) and no carbon dioxide is formed.

Despite of its large amount quantity in air, hydrogen is not readily available as it needs to go through a series of production processes due to its nature that is usually stored in water, hydrocarbons and other organic matter. The production process is carried out to efficiently extract the hydrogen from the compounds form then it must be issued to a purification process to get high purity hydrogen. Efficient usage of hydrogen in fuel cell needs to ensure it falls in a certain range of purity to avoid the contamination that can result in engine braking. The degree of hydrogen purity production is an important matter to achieve with the help of suitable advanced purification systems in industry such as pressure swing adsorption and membrane separation. Purification is needed to control the quality of gas over time and remove any impurity from the gas distribution system (Succi, Macchi and Riddle, 2017).

In the present work, Aspen Adsorption model is built and used to run the experiment. Next, the model must be proven valid by comparing simulation data from breakthrough curves with experimental results from other researchers' work. Subsequently, this study is continued by learning the effects of adsorption parameters (adsorption pressure, adsorption time and hydrogen feed concentration) on responses (hydrogen recovery and purity). Lastly, the analysis data establishes the optimum conditions in which maximum purity and hydrogen recovery are gained at the lowest operating condition applied.

1.2 Problem Statement

The growing demand for fossil fuels in many sectors such as heat and power generation is observed to increase due to the high population today. The issue of fossil fuel depletion has been a concern for past decades; thus, a new energy-driven system needs to be introduced. The primary source of air pollution, which is a part of the consumption of fossil fuels in Malaysia, comes from a mobile source that accounts for around 82% (Madhoun et al, 2012). Gasoline fuel cars produce a significant amount of greenhouse gas (GHG), mainly in the form of carbon dioxide and other gases such as carbon monoxide and nitrogen oxide, which produce during the combustion of fossil fuels to power the car. As the gases build up in the atmosphere, the heat will be trapped, thus contributing to what people call 'climate change' today. A proposed solution to reduce the GHG is to use the electric car driven by hydrogen fuel cell, also widely known as environmentally friendly transportation as it provides zero pollutant discharge.

However, the problem when using hydrogen fuel cell cars is that, they need high-quality hydrogen to avoid the negative effects of impurities (Imamura et al., 2007). The purity of hydrogen fuel has to be in a standard range to ensure that the car's performance is in good condition. The fuel cell cars cannot tolerate any impurities in hydrogen fuel as they can lessen the car's performance and reduce the running life of fuel cells. Such as has been said, hydrogen purification from its source by utilizing pressure swing adsorption (PSA) technology will be discussed in this paper using Aspen built model. Pressure swing adsorption (PSA) is proposed to separate the hydrogen from the binary gas as hydrogen exists with other gas mixtures in this context; the other gas is carbon dioxide. The proposed feed gas is binary syngas containing hydrogen and carbon dioxide. Thus, the dilution effect of carbon dioxide will impact hydrogen if carbon dioxide cannot be removed to an allowable limit. This can cause catalyst poisoning during the reverse

water gas shift reaction when the high concentration of carbon dioxide converts to carbon oxide.

This simulation research focuses on finding the relationship between factors (adsorption time, adsorption pressure and concentration of H_2 feed) to responses (the purity and recovery of hydrogen product). A problem highlighted in this study is how to build a simulation model pressure swing hydrogen purification by utilizing the Aspen Adsorption software by considering many aspects. Based on the analysis study, the optimum condition of hydrogen adsorption is fixed to achieve the purpose of this study on harvesting the highest purity and recovery of hydrogen. Besides, enhancing the product H_2 recovery is also a significant aspect to gain high purity hydrogen as most previous studies will sacrifice recovery to have high purity hydrogen. Before the two mentioned studies can be carried out, the efficacy model will be tested with experimental studies.

Through this research, 2 out of 17 sustainable development goals (SDGs) which act as a call for action to promote a sustainable life are adopted. They are goals 7 (affordable and clean energy) and 13 (climate change). In this study also, a potential to support sustainable strategy under Key Economic Growth Activities 11 (KEGA 11), renewable energy can be carried out.

1.3 Objectives

1. To apply the Aspen model for hydrogen adsorption from syngas.

2. To relate adsorption parameters with purity-recovery of hydrogen.

3. To validate model efficacy with experimental results.

4. To optimize conditions for maximum purity and recovery of hydrogen.

CHAPTER 2

LITERATURE REVIEW

Chapter 2 presents various syngas sources and the type of available hydrogen purification methods. It also includes a brief explanation on pressure swing adsorption (PSA) as well as sections on past researchers' works (experimental and simulation). As in previous Chapter 1, hydrogen fuel cell has been introduced, thus, in this chapter, a more detailed information on hydrogen purity standard is reported. This work also supports sustainable ambition and few of related goals are mentioned.

2.1 Syngas

Syngas or synthetic gas, can be used as feed gas subjected to purification technologies. It is a mixture of gases largely composed of hydrogen, carbon monoxide, carbon dioxide, methane and nitrogen. The composition varies depending on the feedstock and gasification process involved; for example, as in **Table 2.1,** below is the summary of the composition of components by a few different gasification processes.

Table 2.1 Composition of syngas components from different gasification process (Du et al., 2021)

Compone-nts	**H2**	**CO**	**CO_2**	**CH_4**	**N_2**	**Ar**	**Total Sul-fur**	**H_2O**	**O_2**	**Others**	**Reference-s**
Coal gasification	25-35	35-45	15-25	0.1-0.3	0.5-1	-	0.2-1	15-20	-	-	27
Natural gas reforming	70-75	10-15	10-15	1-3	0.1-0.5	-	-	-	-	-	28
Methane reforming	75-80	0.5-2	20-25	-	-	-	-	-	-	-	29
Coke oven gas	45-60	5-10	2-5	25-30	2-5	-	0.01-0.5	-	0.2-0.5	2-5	30
Methanol purge gas	70-80	4-8	5-10	2-8	5-15	0.1-2	-	-	-	-	31
Synthetic ammonia tail gas	60-75	-	-	-	15-20	-	-	1-3	10-15	-	32
Biomass gasification	25-35	30-40	10-15	10-20	1	-	0.2-1	-	0.3-1	-	33

2.2 Steam Methane Reforming

Two types of hydrogen gas that have been produced today, known as blue hydrogen and green hydrogen. Green hydrogen is hydrogen formed during the electrolysis of water using electricity from solar cells of photovoltaic (PV) systems. It is a promising technology for hydrogen development because of 0 carbon emission during the process. Therefore, it helps in reducing the carbon footprint (Lehmann et al., 2021). At the same time, blue hydrogen is generated from fossil fuels in the form of a binary mixture of H_2 and CO_2 syngas through a steam methane reforming (SMR) process (Khan et al., 2021) that is widely commercialized today (ClarkeEnergy.com, n.d.).

Based on **Table 2.2,** it can be read that hydrogen mainly is produced from natural gas and oil. On (IEA, 2019) website, it was stated that 6% of global natural gas is for world hydrogen production, which is about 70 million tonnes.

Table 2.2 Annual Worldwide Hydrogen Production Share (Lipman, 2004)

Source	**Nm^3 (billions)/Year**	**Share**
Natural Gas	240	48%
Oil	150	30%
Coal	90	18%
Electrolysis	20	4%
Total	500	100%

Source: U.S. DOE, 2003
Note: Nm^3 are normal cubic meters of hydrogen

For a large scale hydrogen production, there are many possible ways of producing hydrogen, for example, using steam methane reforming, water electrolysis, coal gasification, pyrolysis, steam gasification, steam reforming of bio-oils, enzymatic decomposition of sugars and biomass gasification (Balat, 2008; Shabbani et al., 2021). Especially, steam methane reforming, more famously known as the SMR process, has

been favoured to meet the industry demand because of its abundance and affordability. The world's hydrogen production from SMR is over 95% as of 2020 (Rapier, 2020), and the reasons it is the most popular process are because it is the least expensive method and the most common route. The reaction of SMR is shown below (GBH Enterprise, 2013).

Steam Reforming $CH_4 + H_2O \leftrightarrow CO + 3H_2$ (**Equation 2.1**)

Water Gas Shift $CO + H_2O \leftrightarrow CO_2 + H_2$ (**Equation 2.2**)

Equation 2.1 is a reaction between natural gas, specifically methane with steam at a higher temperature yielding carbon monoxide and hydrogen. **Equation 2.2** is the water shift gas reaction in which the additional steam reacts with carbon monoxide and converts the majority of it to give additional hydrogen and carbon dioxide with water as a by-product. Before CO_2/H_2 separation, water will usually be condensed out (Lively et al., 2012). Based on the chemical reactions above, products that form on a dry basis are on the order of 70-75% of hydrogen, 7-10% carbon monoxide and a trace of carbon dioxide (6-14%) as well as unreacted methane (2-6%). Due to the existence of hydrogen with other gases, a purification step must be added before it can be used. SMR has low production and maintenance costs, no oxygen consumption is needed in the catalytic reaction, and it is proven as a high-efficiency process (Shabbani et al., 2021).

2.3 H_2 Purification Technologies

Hydrogen purification technology acts as a connection between H_2 production and H_2 utilization. The development of the hydrogen energy industry drives the community to seek a high-efficient and low-power H_2 purification technology for fuel cell vehicles.

Many different purification technologies can be operated to separate hydrogen gas from other gases and are grouped into two, known as physical and chemical methods.

The physical method comprises adsorption, low temperature, and membrane separation methods (Du et al., 2021). On the other hand, metal hydride separation and catalysis methods are chemical methods (Du et al., 2021).

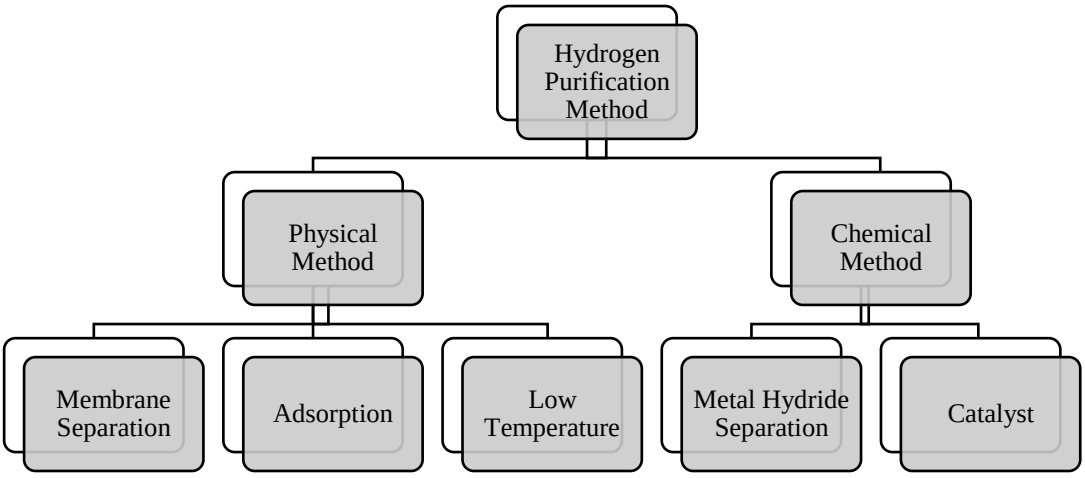

Figure 2.1 Type of hydrogen purification methods (Du et al., 2021)

According to **Figure 2.1**, one of many physical methods is membrane separation. One membrane-type separation method includes a metal membrane experiment which successfully produced H_2 with purity over 99.9999% in past studies. It is proved to be a reasonably effective separating method that comes with the drawback of high content of inert components (Du et al, 2021). This was achieved through Jo et al. (2018) research on utilizing the Pd/Ta composite membrane; however, adding a metal element such as Ta to Pd, costs the manufacturer another way around more on the modification of the membrane. Besides, hydrogen, which is separated using low-temperature separation known as cryogenic distillation, applies the difference of relative volatility to feed gas components, successfully yielding a high recovery and purity amount to 95% and 90-98%, respectively (Aasadnia et al, 2021). However, the standard H_2 purity in this method can only produce in a range of 85-99%, which does not satisfy the purity fuel cell requirements. The disadvantages of using this method are that they are high cost, high

requirement of energy consumption and hard to directly meet the purity standard for hydrogen gas (Du et al., 2021). Next, in the adsorption method, different processes existed, such as pressure swing adsorption, temperature swing adsorption and vacuum adsorption. PSA is widely chosen among other adsorption due to low operation cost and long service life with a disadvantage of not being cost-efficient because of too low requirements of one specific impurity removal, for example, CO<0.2ppm, which is not worth compared to the cost of the equipment and process itself.

The process requirement and operational performance are tabulated in **Table 2.3** to help visualize making proper choices on the appropriate purification process. The operational factors were compared by Miller and Stoecker (1989), Whysall and Picioccio (1999), such as flexibility and reliability.

Table 2.3 A reference guide on hydrogen purification processes (Liu and Zhang, 2004)

Properties	**PSA**	**Membranes**	**Cryogenic**
Process consideration			
Min. feed purity (vol. %)	>40	>25	15-80
Max. product purity (vol. %)	>99.9	>98	~97
Max. hydrogen recovery (%)	Up to 90	Up to 95	Up to 98
Inlet pressure (bar)	10-70	14-138	14-83
Outlet pressure (bar)	Similar to feed	Substantially less than feed	Similar to feed
Operational consideration			
Flexibility	Very high	High	Average
Reliability	High	High	Average

Alternatively, the purification of the hydrogen method through the chemical route can be explained by metal hydride separation and catalyst, referring to **Figure 2.1**. The

former way mentioned is suitable in separating desired gas from high inert components content of the sources, which uses H_2 storage alloys to adsorb and desorb H_2 reversibly. It can be grouped into its primary element alloy or based on its atomic ratio, for example, rare earth alloys and AB_5-type alloys. Dunikov et al. (2016) applied AB_5-type alloys to separate the H_2/CO_2 mixture and found that the H_2 purity produced was 59%, with a recovery of 94%. The drawback of using this process is that the purified material is easy to contaminate by impurity gas, reducing the purification efficiency.

Choosing suitable purification technologies is usually based on hydrogen supply mode and its gas source (Du et al., 2021). Commonly, PSA is preferred when acquiring a large scale of hydrogen purification from natural gas reforming (Du et al., 2021). There are two types of PSA, which are adiabatic and non-adiabatic, and it has many good sides showing, for instance, having a low operational cost and a long service life (Du et al., 2021).

2.4 Pressure Swing Adsorption

Hydrogen greatly differs from other gas molecules regarding to static capacity, so it is very compatible with PSA separating and purification steps. The working process of 2 beds pressure swing adsorption comprises four common step cycles (Knaebel et al 2005). The four steps are adsorption, depressurization, purge and pressurization. Referring to **Figure 3.1,** F1 is the inlet feed gas (Ye et al., 2019). The high purity hydrogen is collected at P1 (outlet) at the adsorption step. In the depressurization step, the leftover hydrogen is pushed out of P1. Next, the purge step will purge the bed, and the waste gas will flow out through W1 (waste gas outlet). Lastly, in the pressurization step, the syngas is fed to make the adsorption bed in a high bed pressure state then the cycle is repeated (Zhang et al., 2019).

Investigating the pressure swing adsorption process can either be done by experimental studies or by Aspen Adsorption software. Experimental studies demonstrate the situation that happens as the experiment is conducted; meanwhile, the simulation is a prediction of how the result is supposed to be generated before the experiment is carried out. For a model developed in Aspen Adsorption to be proven to validate its correctness, the comparison of experimental data and the simulated breakthrough experiment are carried out. If the simulations serve a good agreement with the experimental result, the correctness of the model is verified thus the next experiment run will say to have credibility (Zhang et al., 2019).

2.5 Experimental studies of PSA

The PSA working is affected by the different types of adsorbents and applied technical processes. Various types of adsorbents and process cycles (e.g. a number of beds and steps) have been utilized in PSA experiments before, thus resulting in a different value of purity and hydrogen recovery for every experiment conducted. Below is the context of summary experimental research tabulated in **Table 2.4,** which explains the parameters studied, adsorbent applied and results of the experiment from other researchers' work.

In Lively et al. (2012) study, multi-layered hollow fibre adsorbent was packed into compact sections to provide a more efficient H_2 purification process and carbon dioxide removal using both isothermal and non-isothermal assumptions. In the experiment, feed of 25vol%CO_2/75%vol%He (H_2 surrogate) was fixed, and the results revealed a high purity of H_2 at 99.2% with a recovery of 88.1%.

Next, Shamsudin et al. (2019) have performed experiments in which the feed gas was set to 85vol% H_2 and 15vol% CO_2, as subjected to the inlet of the system that contained two stainless steel packed bed columns operated in six sequential modes

(pressurization, adsorption, depressurization, blowdown, purging and equalization). Hydrogen's purity achieved up to 100% with 88.43% recovery by applying microporous palm kernel shell-activated carbon (PCS) using the PSA system integrated with the pressure equalization. PKS exhibits a good trade as it retains CO_2 more effectively due to its higher adsorption affinity to that gas. The study covered the effect of adsorption and blowdown time on H_2 and CO_2 responses in which it concluded that the H_2 purity increases with increasing blowdown and adsorption time. Conversely, maximum H_2 recovery will be produced at the shortest blowdown time but adsorption time needs a longer period (Shamsudin et al., 2019).

In other research, Idris et al., (2019) prepared a palm kernel shell-activated carbon adsorbent to process 85%H_2 and 15% CO_2 gas binary mixture in a PSA study yielded an H_2 purity amount of 99.978% with 80.014% the recovery. In this experiment, a single adsorption column employed a six-step cycle was conducted by observing three effects (adsorption pressure, adsorption time and blowdown time) on hydrogen purity and carbon dioxide recovery at the blowdown line. Referring to the results documented, at high adsorption pressure, the purity and recovery of H_2 were similar and not affected much in PSA analysis. On the contrary, with a shorter specified adsorption time, H_2 purity will be increased but the recovery was recorded to have a lower value. Lastly, the longer the blowdown time, the better the purity of H_2 however the recovery of it will be lower

Moreover, Chou et al. (2013), applied a modified adsorbent of activated carbon AC5-KS and zeolite 13X-Ca to purify and recover hydrogen from the outlet stream in the water-gas-shift reactor (syngas). The design of a dual-bed eight-step process (feed pressurization (I), high-pressure adsorption (II), continuous adsorption (III), continuous adsorption (IV), counter-current depressurization (V), continuous depressurization (VI), counter current purge (VII) and product pressurization (VIII)) exhibited the H_2 purity

and recovery of 99.98% and 79% respectively. The performed experiment focused on the influence of feed pressure, bed length and step time in order to find the optimum operating conditions for H_2 and CO_2 purity and recovery. From the discussion, increasing the bed length will force the H_2 recovery to decrease; and on the contrary, the purity will increase at the top product. When the feed pressure was high, a lower recovery rate was produced; nevertheless the purity increased because other impurities decreased at the top.

The effects of linear velocity of feed, adsorption time and purge gas quantity were investigated by Yang et al. (2008) in the separation process of hydrogen from synthesis gas using layered beds of activated carbon and zeolite 5A. Different models were adopted and utilized, such as the non-isothermal and non-adiabatic models, linear driving models, and Dual-site Langmuir adsorption isotherm models. According to the result, high purity of H_2 (99.999%) and recovery (66%) was achieved by incorporating a 4-bed 9-step PSA process (adsorption, first pressure equalization, provide purge, second pressure equalization, blowdown, purge, second pressure equalization, first pressure equalization and backfill). Increasing the linear velocity and adsorption time will increase the H_2 recovery, but the purity was contrary. The purge gas quantity is the pressure difference between two steps (pressure equalization and purge steps). As purge gas quantity becomes smaller, the purity of hydrogen product decreases with increasing product recovery.

Besides, Shabbani et al. (2021) have published experimental data and achieved a high hydrogen recovery and a slightly lower purity of 99.3% and 92.5%, respectively, at a longer adsorption time by applying the non-adiabatic PSA, which makes use of amorphous microporous palm kernel shell activated carbon as adsorbent. The blowdown time was revealed not playing that important role in affecting the purity and recovery during the desorption process.

Syngas purification by a new adsorbent of porous amino-functionalized titanium terephthalate MIL-25 was carried out by Regufe et al. (2015) with a feed of 30%/70% of CO_2/H_2 mixture. In that work, a model was built to learn the curves' behaviour; from there, two designed PSA experimental tests were conducted. An H_2 purification test from a binary mixture was tested and managed to achieve H_2 purity at 100% and recovery of 23.5%.

Relvas et al. (2018) established the 4-beds 12-steps cycle including 8 elementary steps with a backfill and equalization step by using Cu-Ac-2 as the adsorbent. A design experiment was conducted in an in-house lab-scale PSA-built unit to determine the influence of pressure, product flow rate and adsorption time on PSA performance. Over 99.97% hydrogen purity with 76.19% recovery was attained in the product stream.

Table 2.4 Summary of experimental result studies utilizing PSA for hydrogen purification

Parameters Studied	**Type of Adsorbents**	**H_2 Purity**	**H_2 Recovery**	**Reference**
Applying both isothermal and non-isothermal assumptions on finding H_2 recovery and purity	Hollow fibers	99.2%	88.1%	(Lively et al., 2012)
Learning effect of adsorption and blowdown time on H_2 and CO_2 purity and recovery	Microporous palm kernel shell activated carbon	About 100%	88.43%	(Shamsudin et al., 2019)
Effects of adsorption pressure, adsorption time and blowdown time towards H_2 and CO_2	Palm kernel shell activated carbon	99.978	80.014	(Idris et al., 2019)
Effects of feed pressure, bed length and step time towards H_2 and CO_2 purity and recovery	Modified activated carbon AC5-KS and zeolite 13X-Ca	99.98	79	(Chou et al., 2013)

Table 2.4 Summary of experimental result studies utilizing PSA for hydrogen purification (continuation)

The effects of linear velocity of feed, adsorption time and purge gas quantity	Activated carbon and zeolite 5A	99.999	66	(Yang et al., 2008)
Effects of adsorption time and blowdown time on the purity and recovery of the gases	Microporous palm kernel shell	99.3	92.5	(Shabbani et al.,2021)
Designed experimental tests with different feed composition (single, binary and ternary)	MIL125(Ti)_ NH2	100	23.5	(Regufe et al., 2015)
Pressure, product flow rate and production time effects	Cu-AC-2	+99.97%	76.2%	(Relvas et al., 2018)

2.6 Simulation Studies of PSA

A simulation study is a way to predict how the system works in real life, and many researchers have shown their interest by researching using this method. Even though the results received are theoretical, they exhibit the potential benefits of using the condition preferred. Below is the discussion of summary simulated studies tabulated in **Table 2.5,** which explains the parameters studied, adsorbent applied and results of the experiment from other researchers' works.

Knaebel et al (2005) explored the effects of flow rates, bed pressures, step times and bed dimensions to maximize hydrogen recovery and had successfully produced 99.85% purity and 49.93% recovery of hydrogen by using activated carbon. He designed a bench-scale, single bed with a four-step PSA cycle consisting of (1) pressurization, (2) adsorption, (3) depressurization and (4) regeneration.

Zhang et al. (2019) developed the syngas treatment study using zeolite 5A for two models; a single-bed five-step and double-bed six-step PSA system. The results were

analysed concerning purity, recovery rate and yield of H_2. The influence of feed flow rate, and the adsorption time on hydrogen purity and recovery were investigated in the single bed model; meanwhile, in the dual-bed model, the effect of pressure equalization time was added to the previous parameters studies. The dual-bed process performance was superior to the former system, yielding a higher purity of H_2 at 99.9408% and an 11% higher recovery rate of H_2. The simulation outcome of a single bed gave an H_2 purity of 99.9097% and a recovery of 67.35%. Zhang et al. (2019) concluded that the decreased flow rate led to higher purity, whereas recovery became lower. Next, as the adsorption time is longer, the purity of H_2 can be seen as lesser. Nevertheless, the recovery was on the opposite side. Both purity and recovery were improved by inputting a longer pressure equalization time.

Moreover, Agueda et al. (2014) simulated the PSA process by taking advantage of UTSA-16 as an adsorbent producing H_2 purity of 99.99-99.999% and a recovery rate of 93-96%. A four-column PSA with a rinse step has been introduced after the feed step to separate the CO_2 impurities from SMR off-gas. The advantage of adding the rinse step to the system was that the higher concentration of CO_2 will be ended up in waste gas due to the higher adsorption affinity of CO_2 to the adsorbent, resulting in a higher H_2 recovery at the top.

Li et al. (2019) simulated the PSA model to separate H_2 from methane steam reforming off-gas by choosing activated carbon and zeolite 5A as adsorbents. A layered two-bed six-step PSA was designed to purify H_2 by theoretically investigating the effects of adsorption pressure, adsorption time, feed composition and purge-to-feed ratio (P/F ratio) on the process performance. They found the appropriate operating process parameters that gave a result of more than 99.95% H_2 purity and higher than 80% H_2 recovery. The results and discussions showed that further increasing the value of

adsorption pressure (3MPa), created a faint improvement in purity. However recovery suffered a significant drop. Increased adsorption time will affect the product purity, which became lower, whereas the recovery rose. Besides, a higher P/F ratio will cause the recovery to decrease in rate while the product purity increases steadily.

Production of high purity hydrogen of 99.9958% and hydrogen recovery of 52.11% was achieved through research by Ribeiro et al. (2008). The study reported using a four columns process filled by a dual-layer PSA by which the activated carbon is in the first bed followed by zeolite beds. It was conducted utilizing an eight step cycle to learn the influence of feed flow rate, purge to feed ratio and lengths of both adsorbent layers on the purity and recovery of H_2. Ribeiro et al. (2008) discussed that the higher feed flow rate, a smaller purge-to-feed ratio and a shorter beds used would induce a less purity and also showed a rise in recovery. In another statement, bed length's influence at the same total length was minor compared to other parameters.

Four-bed PSA processes were preferred from Ahn et al. (2012) study which was performed by simulation to separate hydrogen from coal gas. In PSA operation, process responses such as purity and recovery were affected by a few operating variables, namely P/F ratio, adsorption pressure, feed flow rate, adsorption step time, and carbon ratio. The results described a close to a linear variation with operating variables mentioned, excluding the adsorption step time. On the other hand, the higher the carbon ratio was set, the higher the recovery would be while the purity was sacrificed. In the four-bed PSA process, 96-99.5% H_2 purity and recovery of 71-85% was acquired.

A four-column PSA process with nine steps has been considered in the reported simulation by Delgado et al. (2014). From the research, the process has successfully

yielded more than 99.99% hydrogen with 90.3% recovery using an adsorbent called BPL activated carbon and 13X zeolite.

From Tao et al. (2019) research, using AC5-KS as an adsorbent yielded a hydrogen purity response of 99.17% and a recovery response of 58.94%. The simulated experiment was performed by a one-column VPSA that owns a vacuum pump with a 10-step cycle PSA model, which employed the effects of the P/F ratio and adsorption time studies. The documented results concluded that increasing the P/F ratio and decreasing the feeding time led to higher former response results and lower later responses.

Xiao et al. (2018) studied a different type of adsorbent from the previous mentioned, known as Cu-BTC, for hydrogen purification on Aspen Adsorption. The performance of hydrogen purification was evaluated by carrying out the parametric study on the influence of adsorption pressure, feeding time and feeding flow rate on hydrogen purity, recovery and productivity in a four-step PSA cycle. They concluded their research by reporting that higher adsorption pressure, shorter feeding time and lower feeding rate gave a good hydrogen purity result however it produced poor recovery.

In addition to utilizing the same kind of adsorbent, Cu-BTC, a study from (Ye et al., (2019) is comprehended. Based on the degree of affinity of CU-BTC towards components, it was reported that the adsorbent has a very low affinity to hydrogen thus only a small amount of it is adsorbed. The adsorption affinity of the adsorbent to binary components is CO_2>H_2. They carried out a series of experiments and assessed their simulation by the performance of hydrogen. The article covers the study of adsorption pressure, product flow rate and adsorption time on hydrogen purity and recovery. The same trend in the previous study is seen, which stated that increasing adsorption pressure,

lowering adsorption time and increasing product flow rate raise hydrogen purity and lower hydrogen recovery.

Table 2.5 Summary of simulation studies utilizing PSA for hydrogen purification

Parameters Studied	**Type of Adsorbents**	**H_2 Purity**	**H_2 Recovery**	**Reference**
Effects of flow rates, bed pressures, steps times and bed dimensions on purity and recovery of H_2	Activated carbon	99.85%	49.93%	(Knaebel, Ko and Biegler, 2005)
Effect of feed flow rate, the adsorption time on hydrogen purity and recovery	Zeolite 5A (single bed)	99.9097	67.35	(Zhang et al., 2019)
Effect of feed flow rate, pressure equalization time and adsorption time on H_2 purity and recovery	Zeolite 5A (double bed)	99.9408	78.85	(Zhang et al., 2019)
Adding a rinse step in cycle	UTSA-16	99.99-99.999%	93-96%	(Agueda et al., 2014)
The effects of adsorption pressure, adsorption time and P/F ratio on the purity and recovery were studied	Activated carbon and zeolite 5A	99.95	80	(Li et al., 2019)
The behaviour of both single column and four columns PSA processes (influence of feed flow rate, purge to feed ratio and lengths of both adsorbent layers)	Activated carbon and zeolite beds	1:99.9994 4:99.9958	1:51.48 4:52.11	(Ribeiro et al., 2008)
Effects of P/F ratio, adsorption pressure, feed flow rate, adsorption step time, and carbon ratio on product purity and recovery	Activated carbon	96-99.5	71-85	(Ahn et al., 2012)

Table 2.5 Summary of simulation studies utilizing PSA for hydrogen purification (continuation)

Adsorption Henry's law constants and reciprocal diffusion time constants on hydrogen purity and recovery	BPL activated carbon layer with zeolite 13X	99.993	90.3	(Delgado et al., 2014)
The effects of P/F ratio and adsorption time in VPSA unit	AC5-KS	99.17%	58.94%	(Tao et al., 2019)
Effects of adsorption pressure, feeding time and feeding flow rate towards hydrogen purity, recovery and productivity	Cu-BTC	99.696%	47.753%	(Xiao et al., 2018)
Effects of adsorption pressure, adsorption time and product flow rate towards hydrogen purity and recovery		99.67%	34.70%	(Ye et. al., 2019)

2.7 Fuel Cells

The power source for a hydrogen fuel cell vehicle needs high-purity hydrogen to avoid ruining the running life of the car (Du et al., 2021). Based on the GB/T 3634.2-2011 standard, H_2 purity needs to achieve over 99.99% (Du et al., 2021). On the other hand, hydrogen fuel quality by the International Organization for Standardization (ISO) and the Society of Automotive Engineers (SAE) issued standards respectively in 2015 for road vehicles in which the same requirements for H_2 quality for a fuel cell are set (99.97%). After a few years, the ISO 14687-2:2012 and SAE J2719-201511 issued the new standard to extend the limit of few other impurities purposely; however, H_2 purity remained unchanged (Du et al., 2021). Many research articles also used the requirement of stated hydrogen with a purity of over 99.99% is needed for fuel cell applications as a goal for their hydrogen production (Lopes et al., 2011). In other study resources, hydrogen purity aims to reach the hydrogen quality of 99.97% for fuel cell application (Yang et al., 2019; VSL, 2019; Liemberger et al., 2017).

2.8 Sustainability

Influenced by a global commitment toward United Nations Sustainable Development Goals (UN SDGs) which are set to be fulfilled by 2030, signifies a determined effort to reduce inequalities globally and accomplish a sustainable future for all people. SDGs are a call for action for all countries – developed and developing – to end poverty while handling the climate change issue to preserve oceans and forests. There are 17 SDGs which are *no poverty, zero hunger, good health and well-being, quality education, gender equality, clean water and sanitation, affordable and clean energy, decent work and economic growth, industry, innovation and infrastructure, reduced inequalities, sustainable cities and communities, responsible consumption and production, climate action, life below water, life on land, peace, justice and strong institution and partnerships for the goals.* This present research solely aims to move towards utilizing new energy and reducing global warming by adopting 2 out of 17 goals, Goal 7 (*affordable and clean energy)* and Goal 13 (*climate change).*

Goal 7 is to ensure all access to affordable, reliable, sustainable and modern energy for all. Immediate action on finding suitable modern renewable energy is urged, especially in transport sectors, as in 2018, only 3.4% share of modern renewable energy out of total final energy consumption (UN, n.d.). In recent times, hydrogen fuel cell vehicles (HFCVs) have emerged and are newly developed as an option for change in transport sectors. Consuming hydrogen fuel cell energy has zero pollutants discharged except for how it is produced. Meanwhile, goal 13 is to take urgent action to fight against climate change and its impacts. Energy drives the transportation sectors has been known using fossil fuel-based in which it emits greenhouse gas thus resulting in blanketed Earth by GHG. Due to this, it helps encourage global warming by trapping the sun's heat and causing other problems such as glaciers melting and causing a rising sea level.

Nevertheless, hydrogen fuel cell cars could be one of the ways to reduce the GHG emission from transport sectors and head for a greener life. This study also has the potential to support the proposed Key Economic Growth Activities which has a total of 15 KEGAs and is defined as a demonstration of the rapid growth of future economic activity in line with the aspiration of obtaining high-value development in the economy. The chosen KEGA is KEGA 11 (Renewable Energy) that emphasizes by 2025, 20% of electricity generation will be contributed by renewable energy, and Malaysia has the potential to make development by assisting new technology (Epu.gov, n.d.).

2.9 Gaps in Knowledge

To highlight the gap analysis in this study, the hydrogen gas produced via traditional PSA often sacrificed the recovery rate and yield in terms of having a standard impurity content (Du et al., 2021). Moreover, their inherent drawback is that purified material can react with impure gas during the H_2 recovery, reducing the purification efficiency. Finding optimum operating conditions is important to increase both aspects mentioned earlier. Many kinds of technologies offered out there can produce large differences in the composition and impurity contents of H_2 based on different raw materials used. Thus, efficient H_2 purification technologies that support producing a higher recovery, higher removal of contaminants from H_2 and offer high-qualified H_2 for fuel cell vehicles are of the utmost importance for developing the H_2 fuel cell vehicle industry (Du et al., 2021).

CHAPTER 3

METHODOLOGY

This chapter describes the PSA setup design utilized in the separation process. The procedure and relevant software methods used for obtaining results are also described here.

3.1 Pressure swing adsorption model in Aspen Adsorption

Two models are built-in Aspen adsorption to study the breakthrough curves and PSA cycle respectively using the same model as in Ye et. al. (2019), which utilizes the adsorbent bed packed with Cu-BTC (copper (ll)-benzene-1, 3,5-tricarboxylate). Later the adsorption study will be carried out to determine the effects of adsorption pressure, adsorption time and hydrogen feed concentration on the purity and recovery of the hydrogen product.

3.2 Model assumptions and equations

In **Table 3.1,** lies the parameters for feed operating condition; meanwhile in, **Table 3.2** is listed the parameters for PSA bed and properties of adsorbent. The parameters of Extended Langmuir are shown in **Table 3.3**. The chosen feeding gas molar fraction is based on **Table 2.1,** which states the range for steam methane reforming is between 75-80% of hydrogen. They are the information needed during the process of building the model.

Table 3.1 Operating condition in PSA

Operating condition	**Value**
Feeding gas molar fraction	H_2/CO_2 = 80/20
Feeding temperature	303K
Ambient temperature	303K
Pressure	3.5bar
Feed flowrate	5e-7 kmol/s