CARBON DIOXIDE SEPARATION FROM BINARY GAS MIXTURE CONTAINING HIGH CARBON DIOXIDE CONTENT BY PRESSURE SWING ADSORPTION UTILIZING ORGANIC AND INORGANIC ADSORBENTS

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LIST OF ABBREVIATIONS

NBP	National Balancing Point
LNG	Liquefied Natural Gas
BABIU	Bottom Ash Upgrading
AwR	Alkaline with Regeneration
HPWS	High Pressure Water Scrubbing
As	Chemical Scrubbing
Cry	Cryogenic Separation
OPS	Organic Physical Scrubbing
MS	Membrane Separation
UiO66	Zirconium 1,4-dicarboxybenzene MOF
BDC	1,4-benzenedicarboxylic acid
PSA	Pressure Swing Adsorption
TSA	Temperature Swing Adsorption
VPSA	Vacuum Pressure Swing Adsorption
ppm	Parts Per Million
MOF	Metal organic framework
CCD	Central Composite Design
RSM	Response Surface Methodology
ANOVA	Analysis of variance
BET	Brunauer–Emmett–Teller
EDX	Energy dispersive x-ray
SCCM	Standard cubic centimeter per minutes
SEM	Scanning electron microscope
XRD	X-ray diffractometer
GC	Gas Chromatograph
IUPAC	International Union of Pure and Applied Chemistry

LIST OF SYMBOLS

Å	Interatomic distance
SA_{BET}	Specific surface area (Brunauer–Emmett–Teller)
tb	Breakthrough time
ts	Saturation time
Θ	Scattering angle
V	Voltage

PEMISAHAN KARBON DIOKSIDA DARIPADA GAS CAMPURAN BINARI YANG MEMPUNYAI KANDUNGAN KARBON DIOKSIDA YANG TINGGI MELALUI KAEDAH PENJERAPAN AYUNAN TEKANAN MENGGUNAKAN PENJERAP YANG ORGANIK DAN BUKAN ORGANIK

ABSTRAK

Proses penkayaan dan pemisahan gas karbon dioksida telah dikaji selama beberapa dekad dan pelbagai kaedah sedang digunakan dalam industri untuk mengurangkan dan menahan gas CO_2 akibat ciri-ciri pengakisan dan kesan-kesannya negatif terhadap alam sekitar. Gas rumah hijau seperti metana (CH_4) dan CO_2 adalah gas yang paling banyak dihasilkan dari telaga gas asli yang mempunyai kesan negatif yang signifikan terhadap pemanasan global. Dalam kajian ini, kaedah penjerapan ayunan tekanan digunakan sebagai mekanisme untuk menawan dan mengembalikan gas binari melalui proses pemisahan gas oleh penjerap. Penjerap yang digunakan dalam kajian ini ialah Zeolite 5A, Zirconium-benzene dicarboxylate (UiO-66) dan karbon teraktifk daripada Kenaf dan Kulit isirong sawit (PKS) menggunakan tahap tekanan sehingga 3 Bar. Penjerap telah disedia dan dicirikan menggunakan analisa Pembelauan Sinar-X (XRD), analisa Brunauer–Emmett–Teller (BET), analisa Mikroskopi Elektron Imbasan (SEM), analisa X-Ray Tenaga Sebaran (EDX) dan analisa saiz partikel. Pemilihan penjerap dan keupayaannya diuji melalui gas campuran binari sebanyak 70% CO_2 dan 30% CH_4 melalui kajian terobosan menggunakan cara volumetrik. Maklumat experimen telah dikumpulkan dengan memanipulasi julat masa penyerapan dan pelepasan sehingga 4 minit. Hasil kajian menunjukkan bahawa gas CO_2 mempunyai tarikan tinggi berbanding dengan CH_4 untuk penjerap-penjerap ini. Masa tepu penjerap merosot apabila peningkatan

tekanan berlaku dan sebaliknya. Maklumat eksperimen menggambarkan bahawa karbon teraktifk yang dihasilkan daripada PKS menghasilkan ketulenan dan pemulihan gas CH_4 dan CO_2 yang terbaik. Kadar ketulenan CH_4 dan CO_2 berjaya mencapai sekitar 85% dan 94% manakala pemulihan CH_4 dan CO_2 adalah hampir 94% dan 89%. Sebaliknya, penjerap yang lain mencapai masa tepu dalam waktu yang sangat singkat dan kurang berkesan untuk pemisahan kandungan karbon dioksida yang tinggi.

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ABSTRACT

Carbon dioxide (CO_2) gas enrichment and separation process have been researched for decades and various methods are being applied in industries to reduce and resist CO_2 gas due to its corrosive characteristics and negative effects on environment. Greenhouse gases such as methane (CH_4) and CO_2 are the most abundant in natural gas wells. They contribute significant negative effects to global warming. In this research, Pressure swing adsorption method was utilized as a mechanism to capture and recover binary gas via gas separation process by adsorbents. The adsorbents used in this study were Zeolite 5A, Zirconium-benzene dicarboxylate (UiO-66) and activated carbons made from Kenaf and palm kernel shell (PKS) within the pressure differences of up to 3 bars. The adsorbents were prepared and characterized using X-Ray Diffraction (XRD) analysis, Brunauer–Emmett–Teller (BET) analysis, Scanning Electron Microscope (SEM) analysis, Energy Dispersive X-Ray (EDX) analysis and particle size distribution analysis. Adsorbents selection and their capability were tested using binary mixture gas of 70% CO_2 and 30% CH_4 via breakthrough studies using volumetric method. The experimental data were collected by manipulating the adsorption and desorption time ranging up to 4 minutes. The results show that CO_2 gas had higher affinity than CH_4 for these adsorbents. Adsorbent saturation period declined towards increasing pressure and vice versa. Experimental data showed that activated carbon made from palm kernel shell yielded the optimum purity and recovery of CH_4 and CO_2 gases. Purity of CH_4 and CO_2 of 85% and 94% respectively were successfully achieved at recovery of CH_4 and CO_2 of 94% and 89% respectively. The other adsorbents were saturated quickly and less effective for high carbon dioxide content separation.

CHAPTER ONE

INTRODUCTION

Chapter one introduces the overview of this research and how pressure swing adsorption (PSA) is significant for the capture of carbon dioxide (CO_2) gas for biogas upgrading. In general, this chapter outlines the research background of raising price of natural gas, environment problems and pressure swing adsorption for biogas upgrading, the problem statement and objectives of this study.

1.1 **Research Background**

Development of high CO_2 offshore gas fields reportedly significant challenges for all exploration and production (E&P) companies worldwide. PETRONAS reported that Malaysia has offshore gas field with high CO_2 content (Darman & Harun, 2006). High CO_2 content gas reservoirs make most of the gas field development uneconomical and it has remained undeveloped. As a developing country, Malaysia's resources must be developed timely to sustain supply to meet the increasing gas demand. In addition, the development of these high CO_2 gas fields requires prudent management of CO_2 capture, transportation, and storage and utilization to enable commercialization of these gas field.

Table 1.1 shows the list of high CO_2 content gas fields which range between 28 to 87 percentage of CO_2 content. The highest CO_2 content recorded as 87 percentage in J5 field from Sarawak. These high CO_2 content fields are not developed due to technology and facilities restrictions to deal with very high flow rate. In addition, capital expenses are astronomical to develop such large footprints and massive CO_2 separation requires sustainable production methods. Because, high CO2 fields requires high power and compression ratio with available current technology which would add more cost for gas separation and transportation.

Table 1.1: List of high CO_2 content gas fields in Malaysia (Darman & Harun, 2006)

Holder	Field	Total EUR (TSCF)	EUR Net of CO_2 (TSCF)	CO_2 Content	CO_2 Volume (TSCF)
Peninsular Malaysia					
PETRONAS	Bujang	1.47	0.5	66%	0.97
PETRONAS	Sepat	1.20	0.48	60%	0.72
PETRONAS	Noring	0.58	0.23	60%	0.35
PETRONAS	Inas	1.04	0.42	60%	0.62
PETRONAS	Tangga Barat	0.33	0.22	32%	0.11
PCSB	Ular	0.14	0.07	50%	0.07
PCSB	Gajah	0.12	0.06	50%	0.06
PCSB	Bergading	1.36	0.82	40%	0.54
PCSB	Beranang	0.08	0.06	28%	0.02
EMEPMI	Palas NAG	0.38	0.2	46%	0.18
TOTAL		**6.70**	**3.06**		**3.64**
Sarawak					
Holder	**Field**	**Total EUR (TSCF)**	**EUR Net of CO_2 (TSCF)**	**CO_2 Content**	**CO_2 Volume (TSCF)**
PETRONAS	K5	25.65	7.70	70%	17.95
PETRONAS	J5	5.37	0.70	87%	4.67
PETRONAS	J1	1.43	0.59	59%	0.84
PETRONAS	T3	1.04	0.39	62%	0.65
PETRONAS	Tenggiri Mrn.	0.33	0.18	47%	0.15
TOTAL		**33.82**	**9.56**		**24.26**

CO_2 is one of the major greenhouse gases, which contributes to global warming effect. The CO_2 emission to the atmosphere has been recognized to contribute to global warming (Zangeneh *et al.*, 2011). Carbon dioxide are released from natural and human sources. Carbon dioxide release from natural source is almost 20 times greater than the sources due to human activity; however, by years natural sources are overtaken by anthropogenic sources (Thiruvenkatachari *et al.*, 2009). The CO_2 released by human source is through the combustion of fossil fuels such as coal, natural gas or petroleum, and industrial processes such as power plants, oil refining and the production of cement, iron, and steel (Dantas, et al., 2011). Carbon dioxide has already been used in petrochemical industries for production of limited chemicals such as urea (Zangeneh *et al.*, 2011). Since the beginning of the industrial age in ca. 1800, the CO_2 concentration in atmosphere has increased from 280 to 390 ppm in 2010. Carbon capture and storage (CCS) will play a crucial role to attain the required greenhouse gas (GHG) emissions reduction (Riboldi & Bolland, 2016).

CCS can be defined as the separation and capture of CO_2 produced at stationary sources, followed by transport and storage in geological reservoirs or the ocean (Hauchhum & Mahanta, 2014). There are three major approaches for CCS: post-combustion capture, pre-combustion capture and oxyfuel process. In pre-combustion, the fossil fuel is reacted with air or oxygen and is partially oxidized to form CO and H_2 (syngas). Then in a gasification reactor, it is reacted with steam to produce a mixture of CO_2 and more H_2. CO_2 is then separated and resulting in a hydrogen-rich fuel which can be used in many applications. Oxy-combustion is when oxygen is used for combustion instead of air, which results in a flue gas that consists mainly of pure CO_2 and is potentially suitable for storage. The post combustion capture is based on removing CO_2 from flue gas after combustion. Instead of being discharged directly to the atmosphere, flue gas is passed through equipment which separates/captures most of the CO_2 (Dantas et al., 2011).

Post-combustion capture offers some advantages as existing combustion technologies can still be used without radically change them. This makes post-combustion capture easier to implement as a retrofit option (to existing power plants) compared to the other two approaches. Therefore, post combustion capture is probably the first technology that will be deployed in massive scales (Wang *et al.*, 2011).

Among the various separation technologies such as absorption, adsorption, cryogenic, membrane and micro algal bio-fixation, adsorption is considered as a competitive solution. Its major advantage is the ease of the adsorbent regeneration by thermal or pressure modulation (Thiruvenkatachari *et al*., 2009). Flue gases of current power plants are a mixture of N_2, O_2, CO_2, SO_2, NO_2 and water plus other minor contaminants. The concentration of CO_2 in the flue gas is typically only 10 to 15% (around 12%) depending on the fuel used. Flue gases are normally at atmospheric pressure, but the temperatures might be between 320 K and 400 K, depending on the extent and type of contaminant removal. The flue gas conditions have created many problems for CO_2 capture (Álvarez-Gutiérrez *et al*., 2017).

In addition to cryogenic process, absorption and membrane technology, adsorption is a separation technology that has the potential to reduce the cost and energy of post-combustion capture compared to other technologies. Adsorption processes for gas separation via selective adsorption on solid media are also well-known, and it can produce high purity streams with low energy consumption (Yang, 1997).

Several adsorption processes are used commercially for adsorbent process, including pressure swing adsorption (PSA), vacuum pressure swing adsorption (VPSA), and thermal or temperature swing adsorption (TSA). Some research works have been done using these processes on different types of adsorbent materials. Latest developments have proven that PSA is a promising option for CO_2 separation due to its ease of applicability over a relatively wide range of temperature and pressure conditions, its low energy requirements, and its low capital investment cost (Agarwal *et al*., 2010)

1.2 **Problem Statement**

Almost 85% of the total world demand for energy is supplied by thermal power plants powered by fossil fuels, including coal, oil and gas. These fossil fuels account for about 40% of total CO_2 emissions (Metz et al., 2005).

The oil and gas industries are conducting many researches addressing the CO_2 concern as a threat of corrosion since 1940s via studies of carbon-methane (Unruh & Katz, 1949). An increase of pressure and temperature significantly increases the rate of corrosion and they could damage pipelines especially steel. Carbon dioxide have several reactions in the oil and gas field such as forming carbonic acid (H_2CO_3) while reacts with water and it also can reacts with minerals from reservoir. In carbonate reservoir, the reactions are relatively rapid whereas in silicate reservoirs its reactions are much slower and sometimes the CO_2 been trapped and being mineralized under high pressure (Overview of Greenhouse Gases, 2018).

Natural gas field also contains other compounds such as Sulphur dioxide (SO_2), water vapor (H_2O) and carbon compounds. Therefore, the most unwanted gas compounds which are corrosive and hazardous need to be controlled and removed from the early stage of gas processing system to avoid any major issues. In this case, CO_2 must be removed or reduced to optimum level from the overall amount of production via effective methods. Currently, Monoethanolamine (MEA) absorption method has been used by oil and gas to restrict the CO_2 from causing the problems.

The industries captured CO_2 is then used for enhanced oil recovery by injecting the gas into the reservoir for gas uplifting and reservoir pressure stabilization. Even though it is economical to reuse the produced gas such as CO_2 as injection gas, the purification using the current MEA absorption process for CO_2 gas is costly and complex. Therefore, separation method by adsorption should be effective and reliable for purifying, collecting and capture of CO_2 gas. Pressure swing adsorption method would be an effective way to capture and purify natural gases by selecting the appropriate adsorbents. This research is performed to study the effectiveness of PSA for CO_2 separation from high CO_2 content natural gas.

1.3 **Objectives of Research Work**

1. To analyze the organic and inorganic adsorbents for their physical characteristics.
2. To determine the breakthrough analysis of the adsorbents behaviour towards high CO_2 content natural gas.
3. To evaluate the effectiveness of the adsorbents for gas separation from high CO_2 content natural gas through PSA application.

1.4 **Scope of Study**

In this research, the focused area was pointed in using high content of CO_2 for binary gas separation. Previous findings show that PSA capability were not efficient if the CO_2 composition exceeds more than 50% and it would be causing troublesome to equipment. However, high CO_2 content separation performance can be achieved effectively by selecting suitable adsorbents and efficient methods. There are some limitations available in this research due to availability of equipment and technology. The maximum pressure used in this research were below 5 bar due to capability of equipment and prevent them from gas leaking. Maximum mixed gas flowrate controlled at 500 SCCM for testing binary gas. The sample used in this research weighed about 2 to 4 grams for each column. However, all the calculations were corrected for amount per gram for comparison purposes. Besides that, Gas Chromatography has its delaying period to synthesize results where the results only tend to be projected to that period frame and not able to test at any time randomly. All these limitations were considered while preparing results and calculations to avoid errors.

CHAPTER TWO

LITERATURE REVIEW

Chapter two briefly presents the preceding findings and reviews available from credible scientific records and references that are related to this research topic. In general, this chapter outlines the overview of natural gas, adsorption and its significance, pressure swing adsorption (PSA) and adsorbents. Then, a review on breakthrough studies involving organic and inorganic adsorbents were presented to signify the importance of uses in this research. In addition, an extensive review of significance and PSA were presented covering optimization and effects of the selected adsorption process variables.

The extraction of oil production from the reservoir is not an easy process due to various factors including reservoir pressure changes, multi-phase flow production, petrophysical properties and well behavior. At one stage, the production recovery for mature wells declined significantly and may cause the well to be idle or restrict the oil from flowing to the surface. Therefore, recovery system plays an important role to extract optimum amount of resources from the reservoir by altering the flow assurance and improve the reservoir properties. This phase is called as tertiary phase. The tertiary phase is also known as Enhanced Oil Recovery (EOR) phase (Olarjire, 2014).

EOR is a collection of methods that allow for more effective oil extraction when the primary and secondary phases are not sufficient. It is also useful in wells that contain heavier oil that is evidently more difficult to extract. Typical EOR methods can yield up to three times more oil than primary or secondary phase methods. The most popular EOR methods available in industry are thermal recovery, chemical injection, and gas injection. Chemical injection has various methods which includes the uses of CO_2, polymer and surfactants (Zerpa *et al*., 2005).

The utilization of CO_2 by means of CO_2 injection after water-flooding is an EOR method that is of great potential in reducing residual oil saturation in oil reservoirs. It has been approximated that CO_2 flooding would produce an additional 7 to 15% of the initial oil in place (Matthiasen, 2003). CO_2 has been used for decades in EOR to liberate residual oil, including water-alternating-gas (WAG) operations (Sohrabi et al., 2004). However, there is still a need for improved practices in EOR because significant amount of oil is still left behind, even after EOR attempts (Maugeri, 2004).

CO_2 has built a reputation as being one of the main concerns worldwide in the recent years due to the increasing amount of greenhouse gases in the atmosphere as well as issues related to global warming which poses harmful effects to the environment. The utilization of CO_2 for a good cause such as in this proposed research for oil recovery would hopefully be of some help in battling the issues caused by CO_2. Carbon capture and storage (CCS), as means of storing the CO_2 for useful purposes such as for use in water aquifers, has also been researched with great effort in recent years (Ntiamoah *et al*., 2015).

CO_2 is a corrosive gas which affects many facilities while producing oil through EOR especially pipelines and trunk lines. Well producing CO_2 needs corrosive inhibitors to suppress the negative effects. However, nowadays application of CO_2 in EOR to enhance the production is more ideal for wells which has a pressure greater than minimum miscibility pressure (MMP) and its typically about deeper than 2500ft. Meanwhile, EOR application using CO_2 from natural gas reduces the burning of unwanted gas which is considered environmentally friendly in some