Development of Covalent Organic Polymer for Carbon Dioxide Capture

By

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14839

Dissertation submitted in partial fulfilment of the requirements for the
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(Chemical)

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CERTIFICATE OF APPROVAL

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Approved by:

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TRONOH, PERAK

JANUARY 2015

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements and that the original work contained herein have not been undertaken or done by unspecified sources or person.

MUHAMMAD FIRDAUS BIN MD FAUZI

ABSTRACT

Natural gas has transformed to become one of the most important energy source globally surpassing w4orld's oil demand due to the increase in energy demand and decreasing of conventional energy. With this increasing in energy demand, the oil and gas industry are forced to reevaluate previous reserve that seems economically unfeasible for processing. These reserves are abandoned due to high carbon dioxide content. Motivation towards conducting this study is due the unfeasibility of current conventional method for carbon dioxide capture in natural gas stream where they are unable to cater the high CO_2 content from CO_2 rich natural gas reservoirs. Therefore, the development of new alternative materials and technology is needed to overcome this problem.

The objective of this study is to synthesis and characterize covalent organic polymer (COP-1) for CO_2 capture in natural gas stream. Development of COP-1 was chosen as the material due to its high CO_2 uptake and its ability to withstand harsh hydrothermal conditions. However, current studies for COP-1 development are mainly focused towards removal of CO_2 from flue gases. There are lack of information on its application in natural gas stream. Therefore, this study is focused on filling the gap for COP-1 application in natural gas industry.

Synthesis of COP-1in this study is done on a laboratory scale apparatus where the main raw materials for formation of COP-1 is by using Cyanuric chloride and Piperazine. Qualitative characterization of COP-1 conducted in this study is FTIR, XRD, and FESEM while the quantitative analysis includes the thermogravimetric analysis, BET surface area measurement, CO_2 and CH_4 uptake capacity and the hydrothermal stability.

Findings from this study shows promising outcome for the application of COP-1 in removal of CO_2 from natural gas stream. It's significantly high CO_2 uptake capacity and high stable under harsh hydrothermal conditions shows potential as alternative of current conventional method for CO_2 removal from natural gas stream.

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CHAPTER 1:
INTRODUCTION

1.1 BACKGROUND STUDY

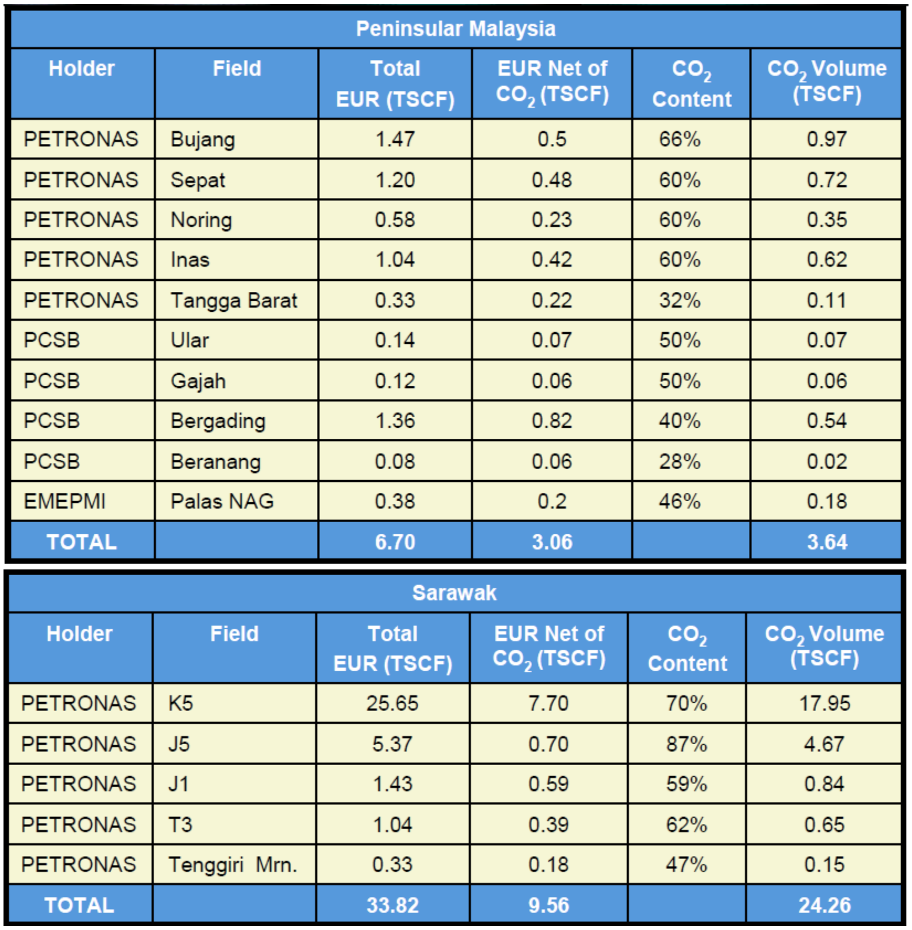
The global energy demand is growing exponentially due to the advancement of industrial development worldwide. From the report of United States Energy Information Administration (EIA), up to July 2014 natural gas remains as the top most energy source production with 2.238 Quadrillion BTU followed by Coal (1.723 Quadrillion BTU) and Crude Oil (1.535 Quadrillion BTU). Table 1 below presents the different energy production up to July 2014. On another note, BP Statistical Review of World Energy 2011 showed that 23.81% of world's energy in 2010 were supplied by natural gas. This is an increase of 7.4% natural gas consumption compared to the consumption in 2009.

Source	Production (Quadrillion BTU)
Coal	1.423
Natural Gas	2.238
Crude Oil	0.359
Nuclear Electric Power	0.754
Hydroelectric Power	0.231
Geothermal	0.018
Solar	0.039
Wind	0.115
Biomass	0.415

Table 1: Various Energy Production up to July 2014

In 2010, Malaysia ranks among the top 10 country with the largest holder of natural gas reservoirs with 83 trillion cubic feet reservoirs were proven to be in existence. 38% of these reservoirs can be found in the coast east peninsula, 48% located at offshore Sarawak, while the remaining 14% in offshore Sabah. These natural gas reservoirs are predicted to last for the next 36 years (Ali et al, 2012). A report from Prisecaru (n.d) and Dulaimi (2014) shows that Malaysia is the second largest liquefied natural gas (LNG) exporter next in line after Qatar with 23.1million metric tonne LNG exported in 2012.

The high demand of natural gas requires the industry to reevaluate reservoirs which previously seems unconventional and economically unjustified. This includes the exploration of natural gas from reservoir with high content of Carbon dioxide (CO_2) and hydrogen sulphide (H_2S). Based on a study by Scott et al on natural gas reservoirs, CO_2 abundance may range from 10% - 90% from the same basin and occasionally in the same field. Another study was done by Nasir and Rahman (2006) on the carbon dioxide content in the gas reservoirs of Malaysia. From the report, it is summarized that the carbon dioxide content ranges from 28% to 87%. The tremendously high amount of CO2 are classified as sub-quality natural gas (SQNG) where gas fields contains more than 2% CO_2, 4% N_2 and 4ppm H_2S as stated by Kidnay and Parrish. This harsh content of impurities exceeds the pipeline specification which may cause corrosion to other equipment including the pipeline itself.



Peninsular Malaysia					
Holder	Field	Total EUR (TSCF)	EUR Net of CO_2 (TSCF)	CO_2 Content	CO_2 Volume (TSCF)
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

Table 2: Carbon Dioxide Content for Malaysian Natural Gas Reservoirs

Furthermore, the current conventional technology for CO2 separation from natural gas cannot cater these high CO2 natural gas streams, rendering these reservoirs as highly uneconomical. Thus, the search for new technology that is able to separate CO2 from CO2-rich natural gas stream is vital in ensuring the sustainability of the natural gas supply.

The most common conventional technology for CO2 separation form natural gas is through absorption using aqueous amine solution. However, several drawbacks were identified in the application of amine solution for CO2 separation. Among these drawbacks includes:

1. the large amount of energy required for regeneration of amine
2. relatively low CO_2 loading capacity of amines requires high solvent circulation rates and larger diameters
3. the corrosive amine solutions induce high equipment corrosion rates
4. degradation of amines to organic acids

To overcome this problem, research are conducted focusing on finding suitable adsorbent or hybrid adsorbent with the capability of high CO2 uptake that could withstand offshore operating conditions. Among development of adsorbents for carbon dioxide capture includes Metal Organic Frameworks (MOF), Covalent Organic Framework (COF), and Covalent Organic Polymers (COP). Each of these materials have their respective advantage and disadvantages in the study of CO2 capture.

Among these newly discovered technologies, COP seems to be most promising method due to its high CO2 uptake and very good hydrothermal stability. Thus the focus of this study us to evaluate the potential of COP adsorbent for CO2 capture from CO2 rich natural gas stream.

1.2 PROBLEM STATEMENT

Reports on the development of COP as adsorbent for CO2 capture showed highly promising findings due to its high CO2 uptake and good hydrothermal stability. However, since the development of COP adsorbent is fairly new, there is a lack of data available in literature on its capability for CO2 capture from natural gas stream. Most of the study reports the application of COP for post-combustion process where the operating conditions are near atmospheric in presence of high N2 gases.

Thus, this study is necessary to fill in the gap and evaluate the suitability of COP adsorbent for CO2 capture from CO2-rich natural gas stream especially at high operating pressure and temperature of 70 bar and 40^{o}C-180^{o}c that emulates the typical offshore operating condition.

1.3 OBJECTIVE

The objective of this study is:

1) To synthesis and characterize COP-1 for pre combustion CO_2 capture in natural gas industry
2) To study the low pressure CO_2 and CH_4 uptake capacity of COP-1
3) To study the hydrothermal stability of COP-1

1.4 SCOPE OF STUDY

1) Synthesis of COP-1 using laboratory scale reactor based on the method published by Patel (2012). Patel however does not specify the specific experimental setup for the synthesis of COP-1. Therefore, experimental design needed to be conducted for the synthesis of COP-1.Characterization of COPs are done with several test. FTIR is used to study the functional groups of the COP. Determination of amorphous or crystalline properties are done using the X-ray diffraction. The BET surface area of COP-1 is done through the adsorption of N_2 gas using BELSORP at low pressure.

Thermogravimetric analysis was conducted to study at what temperature COP-1 samples starts decomposing.

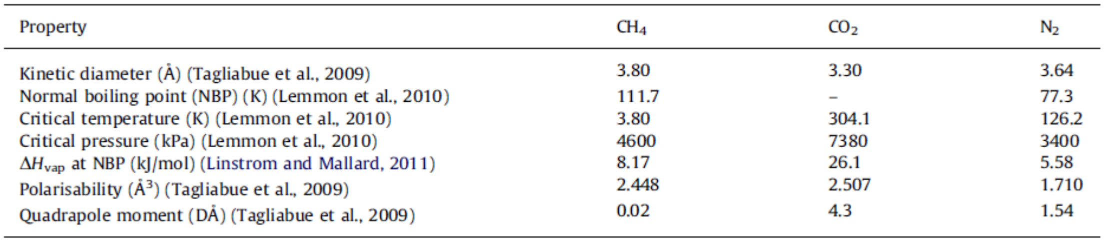
2) Low pressure adsorption capacity was done using BELSORP to measure the CO_2 and CH_4 uptake. The selectivity of COP-1 towards the adsorption of CO_2 could be identified from the adsorption capacity.
3) The hydrothermal stability of COP-1 was done by boiling COP-1 samples in water at 100°C for one week. A portion of samples were taken out at 3 days, 5 days and 7 days to measure it's BET surface area to study how COP-1 would withstand harsh conditions.

CHAPTER 2

LITERATURE REVIEW

2.1 CONVENTIONAL CARBON DIOXIDE CAPTURE

There are several molecular properties that could play an important role to achieve CO_2 separation. These properties includes differences in kinetic diameter, polarizability, quadrupole and dipole moments of the molecules Rufford et al, (2011). In the case of natural gas, the important element that should be taken into account is the separation of CO_2, N_2 and CH_4. Table 3 shows the molecular properties for each of these components. From the properties in Table 3, Kohl and Nielsen, (1997); Seader and Henly, (2006) listed five different methods that could achieve separation and purification of gasses which are (1) phase creation by heat transfer and/or shaft work to/or from the mixture, (2) absorption in liquid or solid sorbent, (3) adsorption on a solid, (4) permeation through membrane and (5) chemical conversion to another compound.



Property	CH_4	CO_2	N_2
Kinetic diameter (Å) (Tagliabue et al., 2009)	3.80	3.30	3.64
Normal boiling point (NBP) (K) (Lemmon et al., 2010)	111.7	–	77.3
Critical temperature (K) (Lemmon et al., 2010)	3.80	304.1	126.2
Critical pressure (kPa) (Lemmon et al., 2010)	4600	7380	3400
ΔH_{vap} at NBP (kJ/mol) (Linstrom and Mallard, 2011)	8.17	26.1	5.58
Polarisability (Å^3) (Tagliabue et al., 2009)	2.448	2.507	1.710
Quadrapole moment (DÅ) (Tagliabue et al., 2009)	0.02	4.3	1.54

Table 3: Molecular Properties of Methane, Carbon Dioxide and Nitrogen

Carbon dioxide are categorized as acidic gases content to natural gas production. In a conventional natural gas processing, CO_2 are removed together with H_2S content to produced sweetened natural gas by using aqueous amine absorption. This part of the natural gas processing is commonly called the Acidic Gas Removal Unit (AGRU) which is typically located upstream of the dehydration facilities. However, as discussed in the previous chapter, aqueous amine solutions introduce few negative effects towards the separation process and therefore, covalent organic polymers are introduced as an alternative for carbon dioxide capture.

2.2 ADSORBENTS FOR CARBON DIOXIDE CAPTURE

In the study of adsorption process for carbon dioxide capture, there are several criteria that should be satisfied. According to Rufford (2012), these criteria are;

1) High carbon dioxide capture selectivity
2) Significantly high adsorption capacity
3) High surface area for a more robust structure
4) High hydrothermal stability
5) Physical and chemical stability through adsorption and desorption process

There have been some discovery in the study carbon dioxide capture and storage schemes that shows metal-organic frameworks (MOFs) and covalent-organic frameworks (COFs) have the potential as CO2 capture alternative. Their high porosity and controllable structural features as well as their multi-chemical functionality makes them a perfect candidate for CO2 capture. (Venna and Carreon, 2014)

2.3 METAL ORGANIC FRAMEWORKS (MOF)

Metal Organic Frameworks (MOF) can be characterized by a crystalline structure network that consist of metal cations or metal-based-clusters that are linked by organic molecules which after removal of guest structures may result in three dimensional structure with permanent porosity as described by Venna and Carreon (2014). Due to the remarkably open porous networks and significantly high carbon dioxide uptake, MOFs are highly appealing for carbon dioxide capture technology. Perhaps one of the most promising MOFs development is MOF-177 by Millward A. R. and Yaghi O. M where the CO2 uptake reported were as high as 33.5mmol/g. However, some challenges that needs to take into account for the development of MOFs for CO2 capture according to Venna and Carreon (2014) are (1) poor MOFs reproducibility, (2) long term chemical instability, (3) high synthesis cost, and (4) limited separation selectivity.

2.4 COVALENT ORGANIC FRAMEWORK (COF)

The development of Covalent Organic Frameworks (COF) were pioneered by Yaghi and co-workers. While MOFs are constructed with metal cations, COFs materials are synthesized from organic monomers linked together by strong covalent bonds. However, both COF and MOF posses crystalline network structure. Commonly, COF were synthesized by reversible formation of B-O bonds where these Boroxine rings can be seen as analogues of metal centers in MOFs structure (Dawson et al, 2011).

In the development of COF for carbon dioxide capture, the highest recorded carbon dioxide uptake is 27.3 mmol/g at pressure of 55bar and temperature of 298K. Though the recorded uptake may not be highly significant, COF shows potential in pre-combustion carbon dioxide capture. One additional note to consider in the development of COFs are that their physiochemical stability may not be as strong as many other network structures.

2.5 COVALENT ORGANIC POLYMERS (COP)

A new class of high-capacity porous materials had been discovered with exceptionally high hydrothermal stability. These porous materials were constructed from a relatively stable covalent C-C, C-H and C-N bonds makes them a better alternative for CO2 capture. They are classified as covalent organic polymers (COPs). COPs are amorphous polymer networks with permanent pores.

In the study of CO2 capture, presence of water or water vapor is unavoidable. The impact of water co-adsorption may reduce the adsorption performance by 50% under a realistic “wet” conditions (Dawson et al, 2012). It is therefore crucial for the synthesis of porous materials have the ability of moisture-resistant especially for industrial applications.

There have been many discoveries in the development of COPs especially in the study of their carbon dioxide uptake. The highest carbon dioxide uptake of COP were recorded for COP-1 by Patel et al, where the carbon dioxide uptake reaches 5616mg/g at pressure as high as 200bar and temperature of 65ºC (Patel et al, 2012).

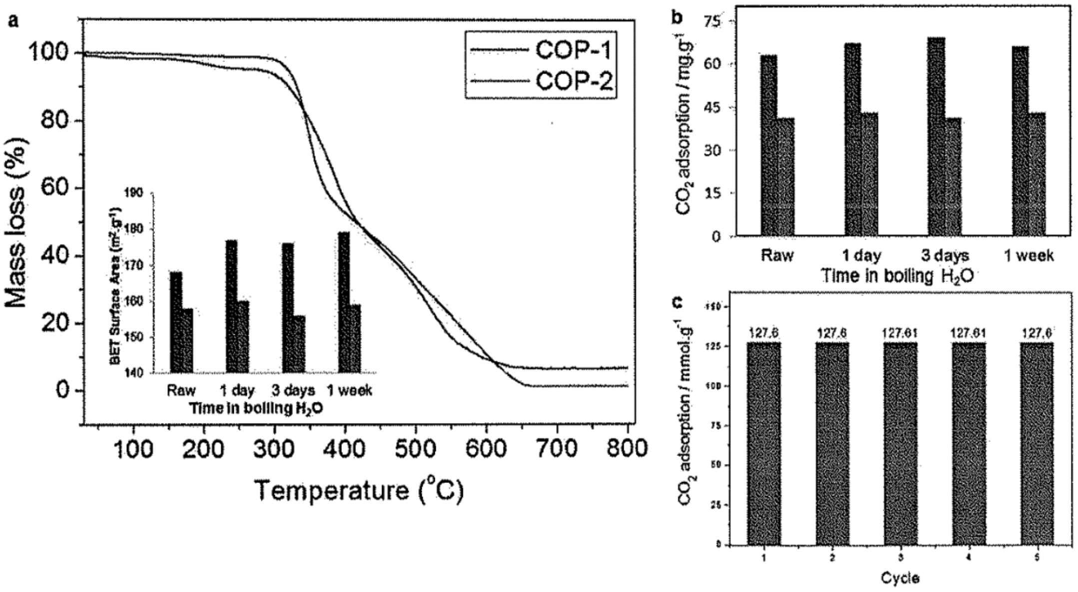


Figure 1: COP Hydrothermal Stability Test

Among other discovery in the development of Covalent Organic Polymers is that COP possesses very high hydrothermal stability. Patel et al presents that very minimal mass loss were recorded when COPs were left boiling at 100 ºC for a week. As for temperature degradation, only up to approximately 400 ºC significant mass loss can be seen for the COP networks. This robust structure also contribute to their consistent carbon dioxide uptake even after 5 cycles of adsorption/desorption process. Currently, COP-1 is being developed for post-combustion carbon dioxide capture which shows significant reliability. No current research is being conducted for its feasibility on pre-combustion carbon dioxide capture in natural gas processing.

2.6 COMPARSONS BETWEEN MOFs, COFs, and COP-1

Characteristic	**COF (COF-102)**	**MOF (MOF-177)**	**COP-1**
BET Surface Area	**3620 m^2/g**	**4898 m^2/g**	**168 m^2/g**
High pressure CO_2 adsorption capacity	**1200 mg/ g** **At (55bar, 25 °C)**	**1315 mg/g** **At (30bar, 25 °C)**	**5616 mg/g** At (200bar, 65 °C)
Low pressure CO_2 adsorption capacity	**n/a**	**n/a**	**60mg/g at (1bar, 25 °C)**
Water Stability	**Unstable**	**Unstable** (Performance decrease by 50% in presence of moisture content)	**High** (stable after boiled for one week)
Thermal Stability	**Moderate**	**Ideal at low temperature 25 °C**	**Boiled up to 400 °C**
Recyclability	**n/a**	**n/a**	**5 recycles**

Table 4: Comparison between COF, MOF, COP-1, and COP-1

CHAPTER 3
METHODOLOGY

3.2 SYNTHESIS OF COP-1

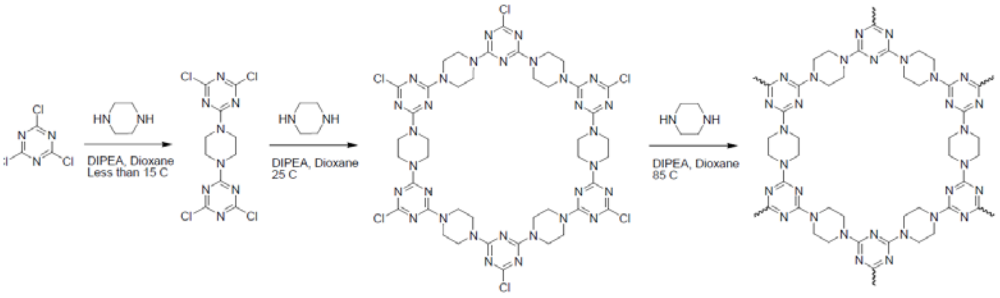
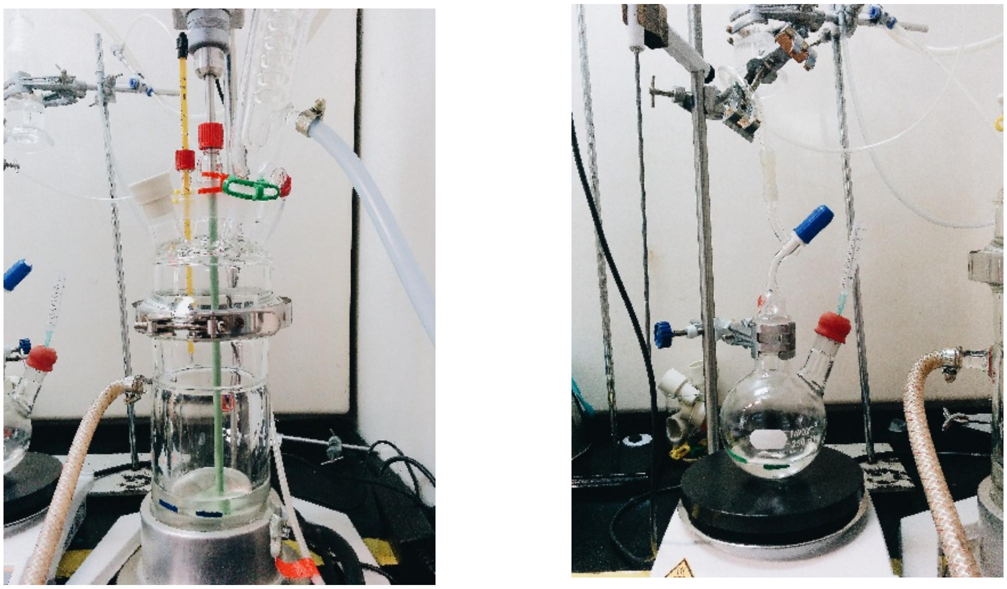


Figure 2: Synthesis COP-1 Chemical Reaction

1. Two reactors were prepared for the synthesis of COP-1 as shown in the figure above. 3.7g Piperazine was dissolved in 18.9 mL N,N-Diisopropylethylamine in Reactor 1 which is then added with 150 mL of 1,4-Dioxane.
2. 5.0g of Cyanuric Chloride was dissolved in 20 mL of 1, 4-Dioxane in reactor 2.
3. Mixture from reactor 2 was added into reactor 1 drop wise using a syringe. Reactor 2 is mechanically stirred at 15ºC for 1 hour.
4. Stirring of reactor 2 is continued at 25ºC for two hours and 85ºC for 21 hours.
5. After completion of synthesis, COP-1 produced is washed with 1, 4-Dioxane for 3 times in 12 hours for purification.

3.1 EXPERIMENTAL SETUP



Reactor 1

Reactor 2

Figure 3: Experimental Setup for COP-1 Synthesis

3.3 CHARACTERIZATION OF COP-1

3.3.1 Fourier Transform Infrared (FTIR) Spectroscopy

FTIR is conducted for the identification of functional group that made up the structure of COP-1. FTIR works on the principle where different chemical bonds absorbs infrared wave at different frequency. FTIR commonly works on frequency that ranges from 400cm^{-1} to 4000cm^{-1}.

Samples of COP-1 wafer is prepared to conduct the FTIR spectroscopy analysis. Potassium Bromide (KBr) powder is used for the making of sample wafer. 10% by weight of COP-1 was to the total mass of KBr used in the sample preparation. Mixture of KBr and COP-1 are well grinded to fine powder and compressed to a very thin sample wafer for the FTIR analysis.

3.3.2 X-Ray Diffraction (XRD) Spectroscopy

The XRD spectroscopy gives an interpretation on the structural information of the COP-1 samples. This is to show whether COP-1 has a crystalline or amorphous structure. The basic principle in the XRD analysis is that a continuous beam of X rays is incident on the sample cell. Highly intense radiation is diffracted in certain direction based on the sample cell tested in the XRD spectrometer. This diffraction corresponds to constructive interference from waves reflected from layers of crystals. A photographic film is then used to capture the diffraction pattern of the sample cell.

3.3.3 Field Emission Scanning Electron Microscopy (FESEM)

FESEM analysis provides the morphology studies of COP-1 sample. FESEM image is generated by focusing beam of electrons on the sample cell. From the image generated, sample structure can be analyzed.

3.3.4 Thermogravimetric Analysis

Through the Thermogravimetric analysis, we are able to analyze the thermal stability of COP-1 sample. In thermogravimetric analysis, COP-1 samples were heated at rate of 20^oC/min while the changes in mass of COP-1 sample are monitored. In this study, the thermogravimetric analysis is conducted under inert environment of N_2 gas. When decomposition happens, a decrease in mass can be observed in the sample of COP-1.

3.3.5 CO_2 and CH_4 uptake at low pressure

The CO_2 and CH_4 uptake of COP-1 at low pressure is measured using BELSORP located at UTP Research Centre for CO_2 capture. Pre-treatment of COP-1 should be conducted before the adsorption process is measured. Pre-treatment of COP-1 is done by heating the sample at 150^oC for 5 hours.

3.3.6 BET Surface Area

The BET surface area of COP-1 is measured through adsorption of pure nitrogen gas. Adsorption of N2 gas is conducted using BELSORP located at UTP Research Centre for CO_2 capture. Pre-treatment of COP-1 is done by drying at 150°C for 5 hours. This is important as improper drying of COP-1 could affect the adsorption of N2 gas thus resulting in lower BET surface area.

3.3.7 Hydrothermal Stability Test

Figure 4: Hydrothermal Stability Experimental Setup

For the test of COP-1 hydrothermal stability, a sample of COP-1 is boiled in water as set up in figure below. Sample of COP-1 is boiled for a period of one week. A portion of COP-1 sample from the round bottom flask is taken out to measure its BET surface area. From analyzing the changes in the COP-1 surface area, it gives a general idea on COP-1 hydrothermal stability.

3.3 PROJECT FLOW CHART

Preliminary Studies

- Literature Review on existing studies from books and journals
- Understading of Adsorption process
- Understanding the concept of Covalent Organic Polymer for CO_2 adsorption
- Understanding the conventional method for CO_2 capture

Experimental Tests

- Identifying experimental procdures for COP sysnthesis
- Conduct sysnthesis of COP-1
- Characterization of COP-1
- Measurement of CO_2 uptake

Data Collection

- Compilation of datas
- Analyze feasibility of COP-1 in natural gas indutry.

Conclusion

- Concluding the outcome and findings
- Project report preparation

3.2 PROJECT MILESTONES

Activity		FYP1														FYP2													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1.0 COP Selection																													
1.1	Comparisons of COPs								■																				
1.2	Conforming COP								■																				
2.0 Synthesis of COP-1																													
2.1	Design of experimental setup									■	■																		
2.2	Purchasing of chemicals										■	■	■	■															
2.3	Conducting COP-1 synthesis														■														
2.4	COP-1 synthesis complete														■														
3.0 Qualitative Characterization of COP-1																													
3.1	FTIR															■													
3.2	X-ray Diffraction																	■											
3.3	BET Surface Area																		■										
3.4	FESEM + EDX																												
3.5	CHN Analysis																												
4.0 Quantitative Characterization of COP-1																													
4.1	Adsorption Analysis																			■									
4.2	Thermogravimetric Analysis																			■									
4.3	Hydrothermal Stability																					■	■						
4.4	Regenerative Cycle Study																												

CHAPTER 4

RESULTS AND DISCUSSION

4.1 QUALITATIVE CHARACTERIZATION TEST

4.1.1 Identification of Functional Groups

Identification of functional groups for COP-1 is conducted by using FTIR analysis. From the COP-1 FTIR Spectra in figure 4, firstly we could identify that the drying pretreatment was successful where no significant stretching can be observed at range of 3000 cm^{-1} to 3500 cm^{-1}. Broad stretching may be observed when there are presence of moisture content in the sample.

While comparing spectra of COP-1 to its raw materials, there are several important peaks that should be taken into observation. Among the important peak is those at 850 cm^{-1} which is present in the spectra of Cyanuric chloride. This peak represent the presence of C-Cl bonding where three of this bonding can be found in the structure of Cyanuric chloride. However, after the synthesis of COP-1, these C-Cl bonding are broken and linked to Piperazine. Therefore, the peak at 850cm^{-1} should not be present. The absence of this peak can be observed from the spectra of COP-1 conforming the success of COP-1 synthesis.

Another peak that plays an important presence is those that proves the presence of triazine unit that is part of the structure of Cyanuric chloride and Piperazine that remains in the formation of COP-1. All three spectra proves the presence of triazine unit with peak approximately in the region of 800 cm^{-1}. One last important peak to characterize COP-1 is the presence of CN heterocycles peak that ranges from 1200 cm^{-1} to 1600 cm^{-1}. These peaks were confirmed to be presence from the spectra of COP-1. Figure 4 below shows the comparison between COP-1 spectra synthesized in this study and by Patel (2012). In general, both FTIR spectras shows similar important peaks that proves the success in formation of COP-1.

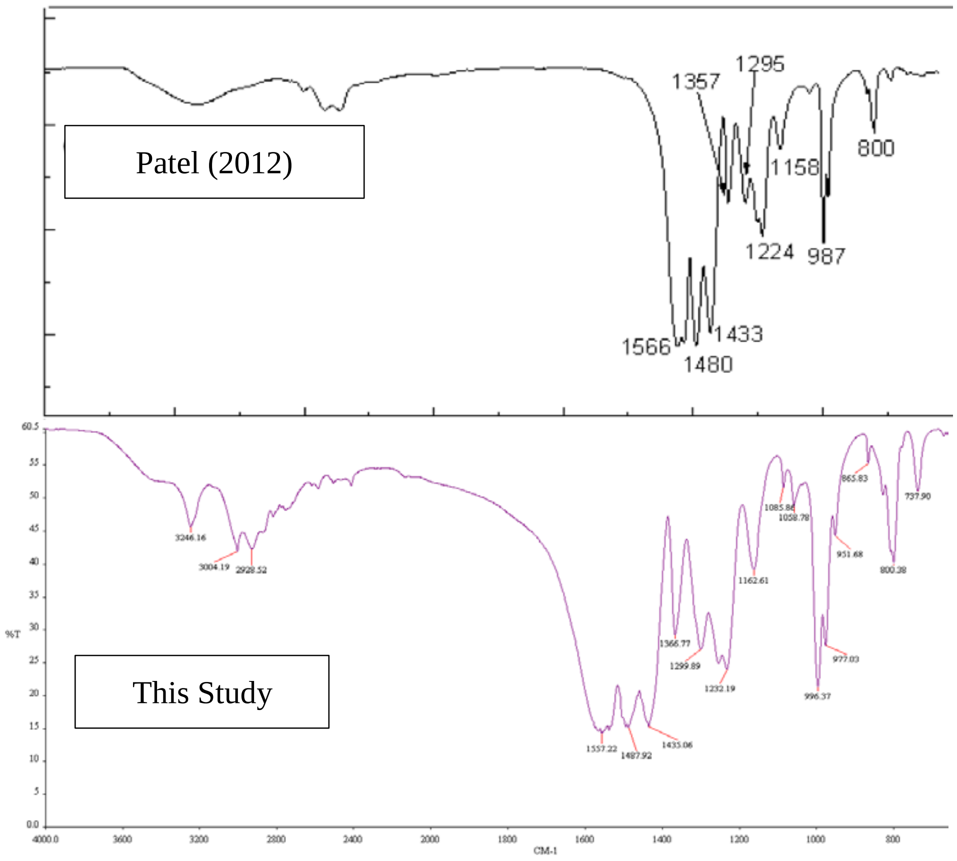


Figure 5: Comparisons between COP-1 FTIR spectras between literature and synthesized

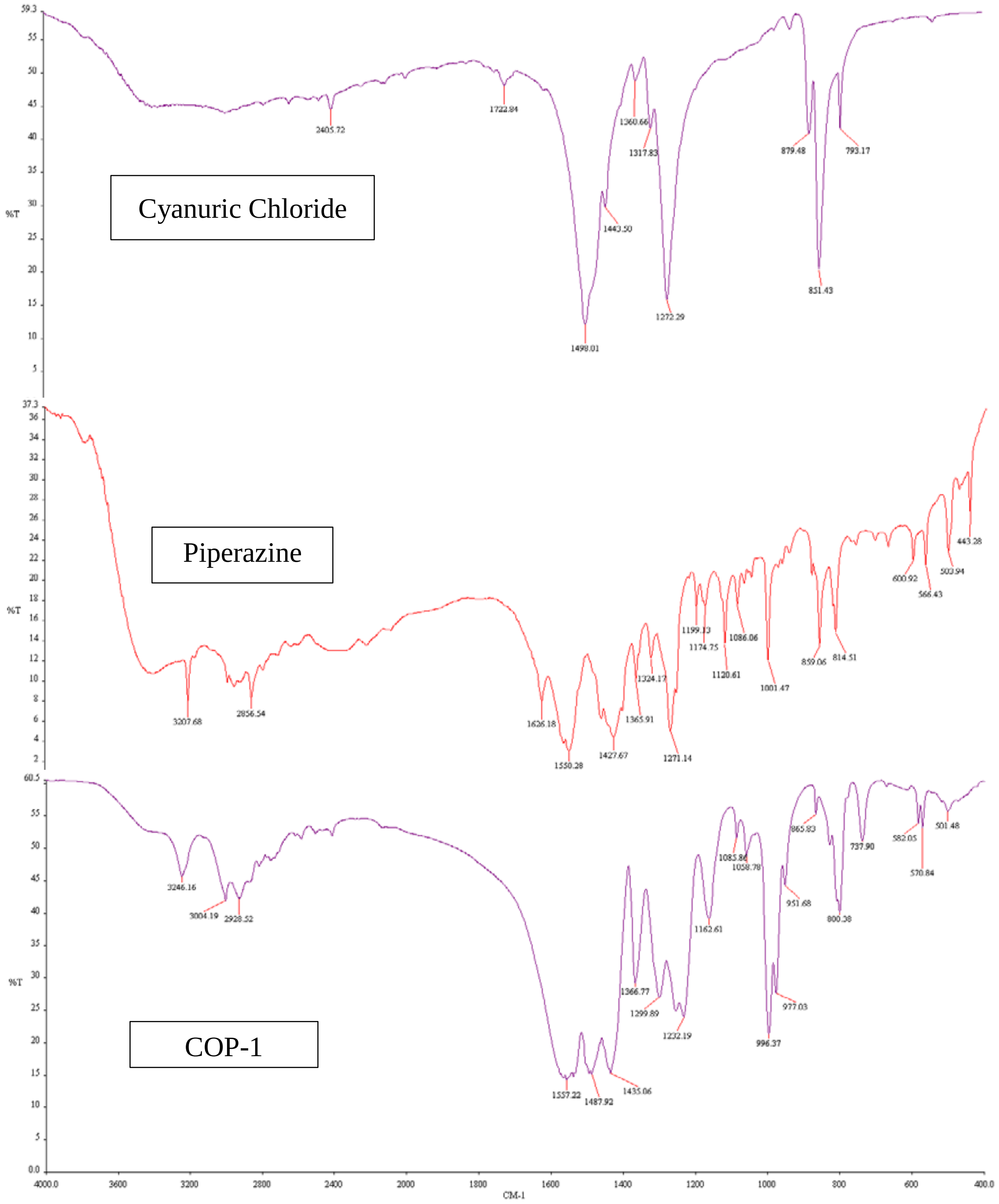


Figure 6: FTIR Spectra for Cyanuric Chloride, Piperazine and COP-1

4.1.2 X-ray Diffraction (XRD)

The X-ray Diffraction analysis is to study the morphology of COP-1 in order to test whether the sample is in amorphous or crystalline structure. Based on the study done by Patel, COP-1 shows the properties of amorphous structure. X-ray diffraction was done at angle of 0.5° to 80° in order to obtain a more significant trend of amorphous structure. Figure 6 below presents the XRD results obtained for COP-1 in this study.

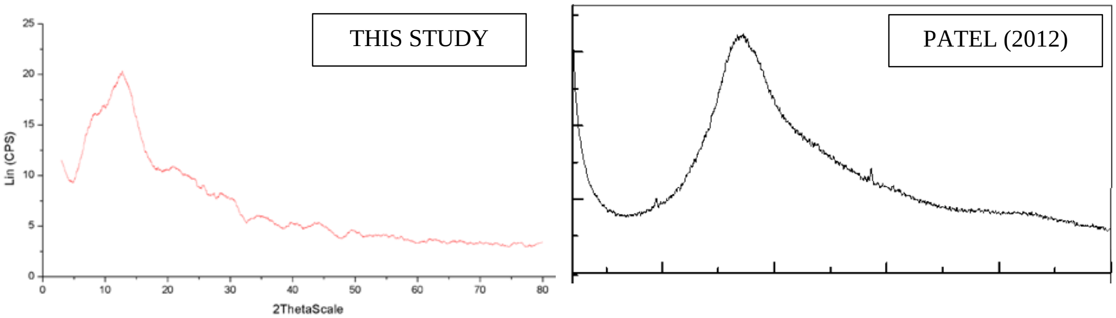


Figure 7: X-ray Diffraction Result

From the XRD curve by Patel (2012), broad range curve is seen which is similarly seen in the XRD result obtained from this study where broad curve ranges from 5° to 17° on the 2 theta scale. This broad range of curve in both studies conforms the absence of crystalline structure in COP-1 samples.

4.1.3 BET Surface Area

In the study of nanoporous materials for gas adsorption, the measurement of its BET surface area is highly crucial as it affects the amount of gaseous molecules it could uptake. Surface area also plays an important role in providing the robust structure for the nanoporous materials under harsh conditions.

The BET surface area of COP-1 was measured using N_2 adsorption curve at low pressure. Patel (2012) reported in his study that COP-1 achieved BET surface area of 168 m^2/g. However, in this study the BET surface area measured is only at 107.95 m^2/g. BELSORP mini measurement is highly off may due to the uncallibrated equipment. The lower measurement if surface area could be due to the failure to maintain synthesis temperature at 85^{o}C. Patel (2012) tabulated that a significant reduce in surface area when COP-1 was synthesized at 70^{o}C where the surface area measured is at 66 m^2/g.

4.1.4 Field Emission Scanning Electron Microscope (FESEM)

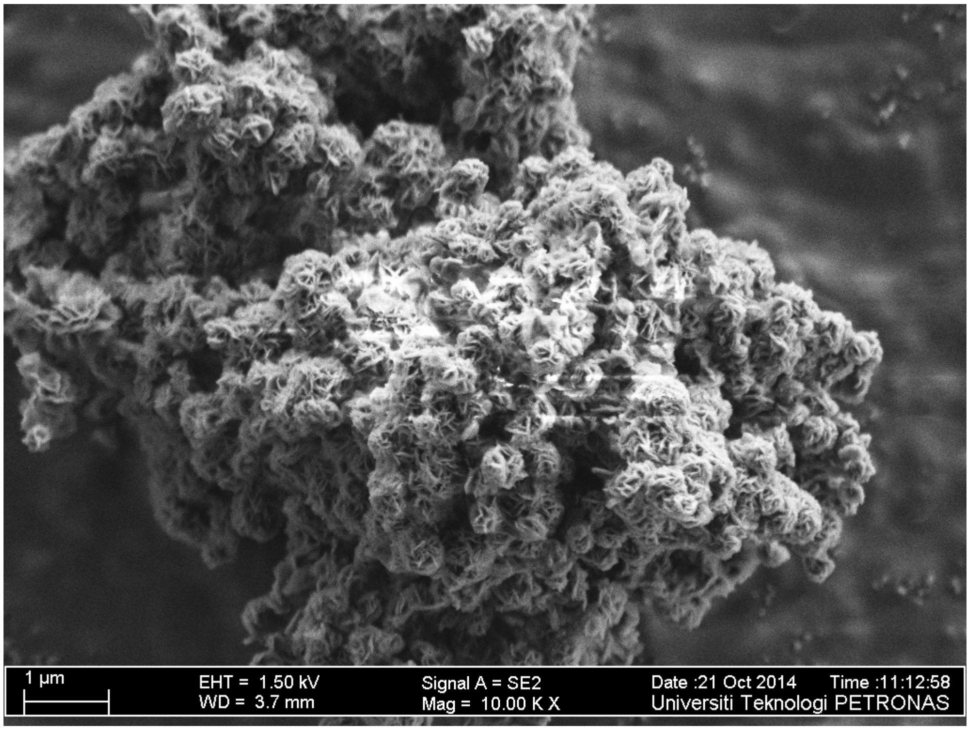


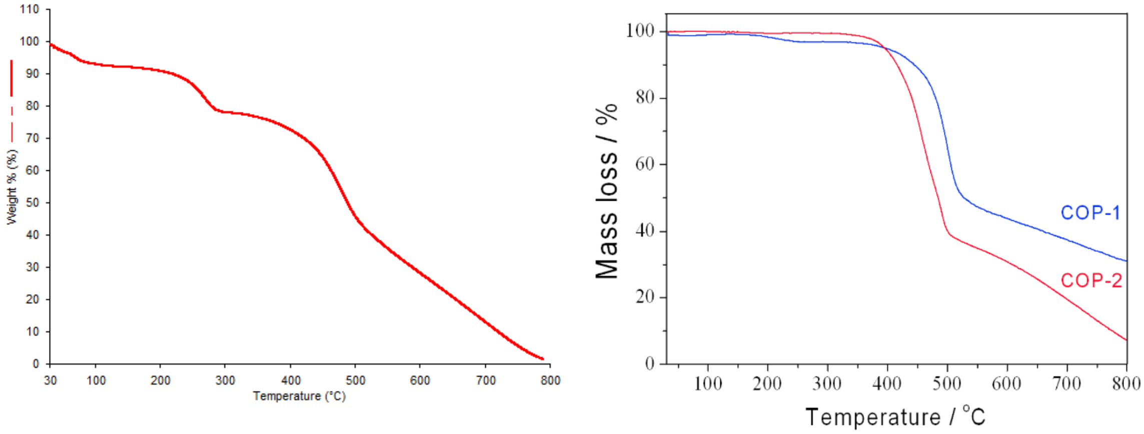
Figure 8: FESEM result for morphology study of COP-1

Figure above presents the surface structure of COP-1 generated from FESEM analysis. From the image, we can see that COP-1 does not show signs of crystalline structure. It could also be observed that structure of COP-1 consists of many pores. These presence of pores shows feasibility for adsorption process. Therefore, COP-1 would be very promising in adsorption of carbon dioxide in natural gas industry.

4.2 QUANTITAIVE CHARACTERIZATION TEST

4.2.1 Thermogravimetric Analysis (TGA)

The Thermogravimetric analysis was conducted to study to what extend the COP-1 sample is able to withstand high thermal exposure. The COP-1 was heated from room temperature of 30°C up to 800°C at the rate of 20°C/min. Figure 7 below shows the comparison between TGA curve in this study and Patel (2012).



THIS STUDY

PATEL (2012)

Figure 9: Thermogravimetric Analysis curve

It could be observed that there are quite significant differences in the curve from both studies. A drop of 20% by mass of sample could be observed at temperature of 270°C whereby the TGA results by Patel (2012) does not show this trend. This mass loss could be due to the lower BET surface area obtained in the synthesis of COP-1 in this study. Though mass loss is observed in the TGA results, this measurement is still highly reliable in the application of natural gas industry. The conventional method of removing carbon dioxide content in natural gas pipeline conducted using an absorber and stripper is operated at temperature of 40°C at the absorber while 180°C at stripper. Therefore, a Temperature Swing Adsorption system may be applied for COP-1 regeneration.

Though some differences are observed in the TGA curve, same trend could be seen when the sample is heated up to 500°C where 50% of the sample are still available in the sample. But, at 800°C all samples were completely gone whereby when compared to the results obtained by Patel (2012) 40% of the overall samples remains. This is again could be related to the lower surface area of COP-1 obtained in this study as lower surface area may reduce the robustness of COP-1.

4.2.2 Low Pressure CO_2 and CH_4 adsorption capacity

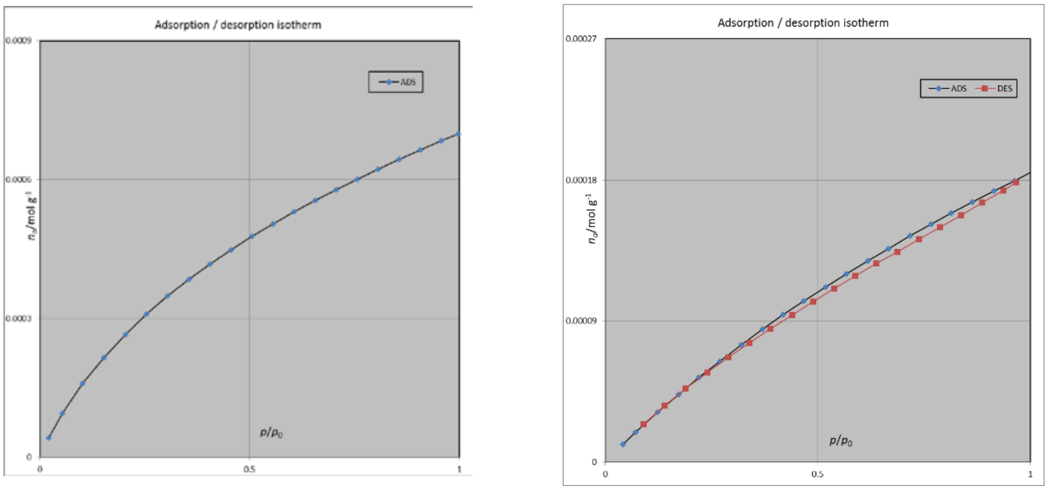


Figure 10: Low Pressure CO2 Adsorption Curve

The low pressure CO_2 and CH_4 adsorption measurement was conducted using BELSORP mini where 0.69921 mmol/g is measured for CO_2 and 0.18505 mmol/g for CH_4. This measurement is significantly low compared to the adsorption capacity measured by Patel (2012). This measurement is approximately half to the record by Patel. This may be related to the lower BET surface area measured where the BET surface area measured using the BELSORP mini is 88.476 m^2/g. This proves the correlation between the surface areas of nanoporous materials to the amount of gas adsorbed. Although there is a significant difference in the measurement of CO_2 and CH_4 adsorption capacity, we can clearly see that COP-1 prefers adsorption of CO_2 compared to CH_4 with a ratio of 3.78. However, binary mixture gas adsorption study should be conducted to study on a more accurate selectivity of CO_2/CH_4 mixture on COP-1 adsorption.

4.2.3 Hydrothermal Stability Test

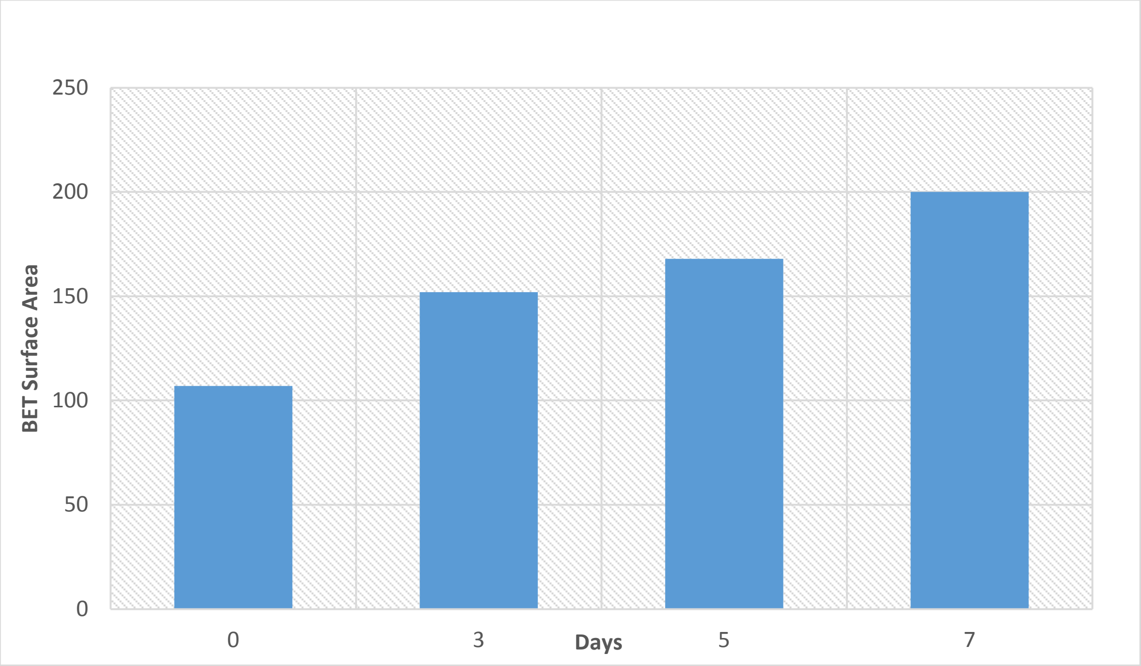


Figure 11: BET Surface Area after Hydrothermal Stability Test

Samples from the hydrothermal stability test were taken out and dried for the measurement of their BET surface area using BELSORP. Figure above displays the changes in surface area of COP-1 when boiled in water. From the figure above, we can see that the longer the COP-1 is boiled in water, their surface area increases. Although the surface area changes by time, this is not a negative sign for the COP-1 hydrothermal stability as instability pattern would show a reduction of surface area for COP-1 sample. From the pattern observed above, increase in the surface area could the result of pore expansion when boiling happens and also clearing of clogged pores in the COP-1 structures. From the results of the hydrothermal stability test, we could conclude that COP-1 shows high feasibility for the operation of natural gas industry where the stream may contain moisture content at high pressure.

CHAPTER 5

CONCLUSION

From the characterization results, it is concluded that the synthesis of COP-1 using lab scale apparatus was successful. Analysis of the functional groups of from the FTIR spectra proves the presence of several important functional groups that made up the structure of COP-1. The XRD analysis of COP-1 also confirms the amorphous structure of COP-1 when compared to the results from Patel (2012).

However, the measurement of BET surface area was not met up to the surface area measured by Patel (2012). The surface area of COP-1 measured in this study was only up to 107m^2/g while Patel (2012) was able to measure up to 168 m^2/g. This deviation in surface area measurement could be due to the result of temperature deviation during the synthesis of COP-1. Therefore, optimization of COP-1 synthesis should be done to meet the measurement of surface area of COP-1.

From the quantitative analysis of COP-1, it could be seen that COP-1 shows high feasibility for its application in the removal of CO_2 from natural gas industry. The thermogravimetric analysis shows that COP-1 are able to withstand the operating temperature in the upstream natural gas industry where the adsorption process is conducted at 40^{o}C while desorption is conducted at 180^{o}C. The hydrothermal stability test for COP-1 also shows that the COP-1 structure are robust enough to withstand harsh conditions that resembles the natural gas stream.

COP-1 also shows significant selectivity towards CO_2 compared to CH_4. At low pressure adsorption, the selectivity of CO_2/CH_4 is measure to be approximately 4.0. This is highly important for COP-1 application in the natural gas stream so that no CH_4 are adsorbed in the separation process. However, adsorption of CO_2 and CH_4 in binary mixture gas system should be conducted to have a more accurate selectivity study for COP-1.

From the quantitative analysis of COP-1, it could be seen that COP-1 shows promising outcome for its application in the removal of CO_2 content from natural gas stream.

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