CARBON DIOXIDE SEPARATION FROM METHANE USING COVALENT ORGANIC POLYMER ADSORBENT

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CHEMICAL ENGINEERING

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by

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CERTIFICATION OF APPROVAL

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Approved by,

_____
(Dr. Nurhayati bt Mellon)

UNIVERSITI TEKNOLOGI PETRONAS

BANDAR SERI ISKANDAR, PERAK

September 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 reference and acknowledgements, and that original work contained herein have not been undertaken or done by unspecified sources or persons.

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AHMAD FARIDUDDIN BIN AB HAMID

ABSTRACT

In 21st century, many industrial area in the world trying to produce the technology which is low cost, easier to handle and user friendly. Basically this Final Year Project's objectives are to synthesis and characterize Covalent Organic Polymer as adsorbent for removal of carbon dioxide from methane. Besides that, the new synthesis Covalent Organic Polymer will be investigate its capturing ability in ambient condition. Previous research on the adsorbent for the capturing carbon dioxide had been widely executed. But there are different problem with different materials used. Metal based adsorbent had the problem with its weight thus polymer based is chosen to overcome weight problem. Besides that, use of amine solvent as the material had the flaws on its recyclability of the solvent. Thus, Covalent Organic Polymer has a great potential to overcome this problem. The scope of study of this project will covered the synthesis of new Covalent Organic Polymer, Characterization of new develop polymer and test the ability of material to capture carbon dioxide. For the characterization of this new polymer will use FTIR, SEM, TGA and BET.

ACKNOWLEDGEMENT

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LIST OF ABBREVIATION

BET   Brunauer-Emmett-Teller (BET) surface area

CH_4 Methane

CO_2 Carbon Dioxide

COF   Covalent Organic Framework

COP   Covalent Organic Polymer

DIPEA   N,N-diisopropylethylamine

SEM   Field emission microscopy

FTIR   Fourier transform infrared spectroscopy

HCP   Hypercrosslinked polymer

MOF   Metal Organic Framework

TGA   Thermal gravimetric analysis

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CHAPTER 1

INTRODUCTION

1.1   Background of Study

Combustion of fossil fuel, natural gas, biogas and landfill created the product of unwanted gas which is carbon dioxide gas. Approximately 30 billion tons of carbon dioxide gas was emitted for the past 5 years (Yuan Zhang, Sunarso, Liu, & Wang, 2013) contributing to the global warming, an irreversible increase of acidity in the ocean and rise of the sea level (Furukawa & Yaghi, 2009).

Carbon dioxide emission is considered as an environmental problem as it is associated with climate changes. The technologies to capture carbon dioxide can be separated into three different categories which are pre-combustion, post combustion and oxyfuel combustion. All different category will have different capability, criteria and condition for capture process (Xiang et al., 2012).

Carbon dioxide removal technique have been developed to meet the industries pipeline specification of carbon dioxide concentration less than 2% (Yuan Zhang et al., 2013). Thus, minimizing the emission of carbon dioxide is of utmost importance. The separation techniques that are available that can be group as follow based on figure 1.1 by (J.-R. Li et al., 2011; Tigabwa, 2010).
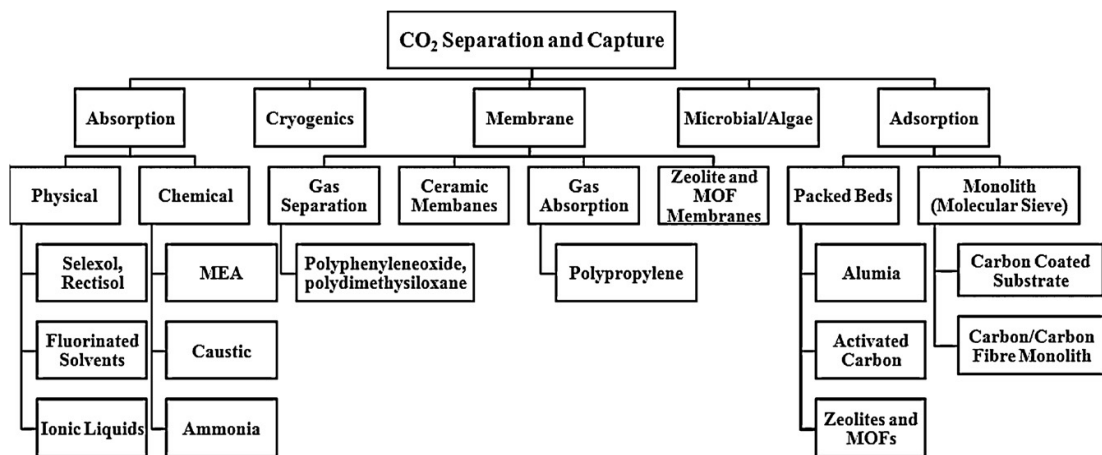
FIGURE 1.1   Different technologies and associated materials for CO_2 separation and capture.

Absorption technique by aqueous amines is one of the traditional technique but this technique require high energy and high operating cost. It also has low carbon dioxide capacities and lack stabilities over many cycles (Hicks et al., 2008). Other technologies are also being used in industries such as spray tower, pressure swing adsorption and cryogenic separation. All of this basically will complicated equipment and higher capital cost (Yuan Zhang et al., 2013).

The current challenge of developing the low cost technique for carbon dioxide separation has lead to the research in synthesizing new adsorbent materials. Adsorption based separation and multi scale porous solid sorbent material can be classify as low cost technique (Allen et al., 2015). According to the natural data of bonding between the solid surface and adsorbate molecule, adsorption can be separated into physical or chemical. Physical separation is more preferable than chemical adsorption (Martín et al., 2011).

Most of the porous material that is used in physical adsorption including activated carbon, metal organic framework and nanoporous polymeric networks are expected to meet the basic requirement which is based on (Byun, Je, Patel, Coskun, & Yavuz, 2014) have:

- ❖ Water and thermal stability
- ❖ High selectivity over other flue gases.
- ❖ Economic viability

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Nanoporous polymeric framework also has been studied extensively over the years. Covalent organic framework, microporous organic polymer, hypercrosslinked polymers and covalent organic polymer are the examples of nanoporous polymer framework. It is reported to have high gas permeability and selectivities for small molecules over large one such as methane (Byun et al., 2014).

Statistic in January 2008, 379 field have been explored and from those number it has 216 gas field and 163 oil field in Malaysia. Most of the reservoir in Malaysia contains high carbon dioxide content. Average carbon dioxide content varies from 40% to 66% (Tigabwa, 2010). Carbon dioxide can give the great impact to the environment when release to the atmosphere. Carbon dioxide also can react with water to produce corrosive compound that affect the pipelines in industries.

According to the earlier statement, carbon dioxide needs to be removed from natural gas as a priority importance in the industry based. In gas processing plant, these greenhouse gases are separated from gas before it can be use and transport for sale. Energy consumption for cryogenic processes in the industry normally use was very high, thus alternative technique need to be invented.

Carbon dioxide separation from methane can be separated using various membranes. Adsorbent based technology had become a competitive separation process nowadays. But, the biggest challenge to be the potential application in industry is that most adsorbent does not have the resilience in practical industries and quite quickly to fail. It also hard to maintain top performance for the long term operation in industries (Yuan Zhang et al., 2013).

Reported by (Xiang, Peng, Cheng, Li, & Cao, 2011), investigation of carbon dioxide capture in industry prefer using adsorption process because of its simplicity, ease of control and low cost. As a result, Covalent Organic Polymer will be used as the adsorbent for the separation process because it shows potential for carbon dioxide adsorption.

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The primary purpose in this research is to develop covalent organic polymer adsorbent as a material for carbon dioxide capture from methane because of the needed of capturing carbon dioxide in oil and gas industries.

1.2 Problem Statement

Carbon dioxide capture is a critical issues in oil and gas industries nowadays. The development of new type of adsorbent for capturing carbon dioxide has gain a wide interest in terms of research. Throughout all the research that had been done, there are many weaknesses in the previous developed material for carbon dioxide capture.

Based on articles by (Dawson, Adams, & Cooper, 2011), used of amine-containing solvent as the adsorbent shows quite impressive results but recycling this materials for the large scale will use 20-40% of the power plant energy produced. For the Metal Organic Framework, adsorption during pre-combustion capture reported gave excellent result. In post-combustion capture, Metal Organic Framework became problematic due relative hydrolytic instability. Besides that, using metal based material as the absorbent became problem because of its weight that will require expensive material for the storage. Thus, using the polymer as the lighter weight material will be the solution.

To overcome the previous problem in the adsorbent for capturing carbon dioxide, new develop material as adsorbent had been introduced, including covalent organic polymer. The advantage of this adsorbent is that it has high selectivity towards carbon dioxide. Besides that, post-combustion required adsorbent to withstand high temperature and pressure. Covalent Organic Polymer can withstand high temperature without losing any capability in capturing carbon dioxide. The recyclability of this adsorbent at high temperature also shows promising material to be use as adsorbent in industrial level (Patel et al., 2012).

Covalent Organic Polymer researched had been done earlier by (Patel et al., 2012) but the available research data on this topic is very scarce. Currently, the research on the use of the COP to remove carbon dioxide focus on post-combustion process in which natural gas is not of interest. In this research, the use of COP for carbon dioxide capture from natural gas will be explored.

1.3   Objective

The main objectives of this project are:

i.   To synthesis and characterize covalent organic polymer
ii.   To investigate carbon dioxide capturing capacity of the new synthesized COP-1 at ambient condition

1.4   Scope of study

The study will involve this following list:

i.   Synthesis of the covalent organic polymer using method based on research paper by (Patel et al., 2012).
ii.   Characterization of COP-1 using FTIR, SEM, TGA, and BET.
    a.   FTIR - To confirm chlorine atoms on Cyanuric Chloride had been replaced
    b.   SEM - Field emission microscopy
    c.   TGA - To test thermos stability
    d.   BET - To calculate specific surface area of material

Based on the subject that the author have learned throughout his undergraduate study, the relevancy of this project is suitable for him. It is achievable with the help of the supervisor. With the availability of the equipment in UTP, this project can be done and can be finish within the time frame planned. The scope of this project also can be covered all element during the laboratory analysis.

CHAPTER 2

LITERATURE REVIEW

The development of the separation of carbon dioxide in oil and gas industries is crucial from day to day to produce natural gas that has less carbon dioxide concentration. Earlier stage of separation using amine absorbent and it shows a lot of weaknesses. Same as cryogenic technique that used to separate carbon dioxide still use in industry in Malaysia nowadays. The step further is taken to have research and development in this separation. Researcher used membrane to separate and it use adsorption to separate carbon dioxide from methane.

2.1   Covalent Organic Framework (COF)

Porous crystalline macromolecule is one of the adsorbent for separation of carbon dioxide. One of the parts of this macromolecule is COF. The combination of light elements such as carbon oxygen and boron can create COF when they are linked together by strong covalent bond. The characteristic of COF is that it have rigid structure, high thermal stability and permanent porosity with high surface area (Croad, 2013).

Besides that, COF became an adsorbent material because of its porous material that come with package of low density and large BET surface area. It can become great potential in adsorption of carbon dioxide from methane (Zhu, Zhou, Hu, Liu, & Hu, 2011).

Boron can be classifying as hard Lewis acid and it has p-orbital. This bond is irreversible with oxygen atom. Thus, COF will have a firm structure and rigid (Di Carmine, 2014). In research paper by (Furukawa & Yaghi, 2009), they have done the research on COF. They have synthesis COF-1,-5,-6,-8,-10,-102 and -103. After the synthesis have complete, the report on result produce had been compared and rank among the other material with high performance based on gas capacities.

Using Gravimetric High Pressure Gas adsorption method, Low-Pressure Gas Adsorption Measurements and Estimation of Bulk Density, the result had been obtain by the author. Surface area of COF using BET had given value 750 m^2g^{-1} but carbon dioxide uptake only up to 230mgg^{-1} only. The methane uptake also is taken into consideration which was 40 mgg^{-1}. This make the ratio for carbon dioxide and methane ratio become 5.75 and still lower than ratio uptake for COP. Thus COP still more promising material.

2.2   Metal Organic Framework (MOF)

Metal organic framework (MOF) is in crystalline porous material which is formed from metal cation and organic electron donor linker. MOF have extremely high surface area and pore volume. The plus point of MOF is that it can be synthesize and it is not easy to collapse when solvent are removed from MOF. This can allow MOF to have the range of application in industry (Croad, 2013)

MOF is porous solid sorbent that have specialty to be highly tailorable (Allen et al., 2015). The nanoscale porosity of MOF shows the flexibility of the polymer. Thus, it can be specific over the wide temperature and pressure range. The versatility in structure of MOF provides it to be able to control the structure and micro structure of structural dynamic MOF. This can be one of the prospects to tailor this material for gas adsorption application.

The structure of MOF and its chemical composition of MOF can be tuned easily. This ability can be used to enhance their selectivity and adsorption capacity. This can be enhanced because they contain unsaturated metal sites, which is dominant

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interact with carbon dioxide materials. Reported in details study of carbon dioxide adsorption of MOF shows that unsaturated metals will have string affinity towards carbon dioxide thus it can absorb carbon dioxide over methane during dynamic separation (J. Li, Yang, Li, & Li, 2014).

There are few research paper for this material had been conduct in the past by (Allen et al., 2015). The sample of MOF were buy directly from Sigma-Aldrich but after the sample reach, they check the composition using TGA method to make sure same structure as they ordered. Besides that, they use characterization technique like powder X-ray diffraction, Neutron diffraction and Small-angle neutron scattering. From this characterization, the material was tested to know the adsorption capability of this material. In research done by (Furukawa & Yaghi, 2009), comparison on uptake ratio only 4.94 for the MOF. But the carbon dioxide adsorption higher than COF 32.5 compare with 27.3.

As conclusion, the MOF once was being the promising material for the adsorption of carbon dioxide but due to its weight which became the problem in industrial. Thus, all the research moves to the material using polymer for lighter weight.

2.3 Hypercrosslinked polymer (HCP)

The first HCP is known as 'Davankov resins', it were invented refer to crosslinked in polystyrene and it can only be synthesize by two simple step procedure. Amorphous organic material is the group where HCP is located that are made from light elements and crosslinked in polymer chain is one of its characteristic. It is consider a highly rigid network that hard to collapse because of the crosslinking in polymer. The other characteristic of HCP is that it has small pore sizes, micropore volumes and very high surfaces area (Croad, 2013).

Excellent textural development in HCP constitutes it in a family of low density porous materials. Microporosity and mesoporosity of HCP allow it to have large surfave area up to 1970 m^2g^1. These type of polymer also represent the low isoesteric

heats in carbon dioxide adsorption and it has a good selectivity towards carbon dioxide (Martín et al., 2011).

Robust micro porous organic can exhibit high surface area and HCP is one of the material that are in this family. Besides that, excellent chemical robustness in HCP made it to have strong acid base reaction that is used in carbon dioxide adsorption. These materials also have good thermal stability and quite readily to be produce in large scale. Other features of HCP, it is reported that their relative low heat of adsorption compare with other material (Martín et al., 2011).

In this section, the author will explain the previous research paper on HCP by (Martín et al., 2011; Yinghua Zhang et al., 2014). In the experiment, they prepare the chemical to synthesis the HCP. All this synthesis was conduct under nitrogen atmosphere. Carbon dioxide capture capacity had been evaluate at atmospheric and high temperature. Due to the low textural development of HCP material, capture capacity of carbon dioxide performance only 7wt%. Based on literature from (Yinghua Zhang et al., 2014), the selectivity of carbon dioxide ratio only 3.16 and still far compare to COP.

Hence, the previous material that had been research and tested have shown their own capability. From the auhor opinion, COP still the best polymer for adsorbent so far. That is why COP was chosen as the material for this research.

2.4 Zeolite

Application in industrial scale, zeolite have made massive attention because o fthe ability for the separation process and its low cost of production. Besides, zeolite materials can adsorp carbon dioxide in ambient temperature better (Y. Li, Yi, Tang, Li, & Yuan, 2013).

In many years back, zeolite have been extraordinarily produces in the form of powder. Using the technique of chitosanassisted to prepare binder less zeolite, the blockage in ore system have been overcome which this blockage was originated from the nanoparticle of zeolite powder (Yu, Gong, Zeng, & Zhang, 2013). Zeolite has the

characteristic which display reasonable mechanical strength, large BET surface area, high water adsorption capacity and lastly high adsorption in carbon dioxide over hydrogen particles.

T type zeolite for extraction fo carbon dioxide from methane during adsorption process also had been developed. Zeolite molecules sieves categorize as nanostructure crystalline material thus special technique as mention earlier need to be done to make sure the maximum performance of zeolite can be achieved. In research paper by (Rad, Fatemi, & Mirfendereski, 2012), BET surface area for T type zeolite only 369 and this consider very low.

According to (Yu et al., 2013), during their research on zeolite materials which comprising several types of its own kind. Some of the materials need to be synthesis using ion exchange like CaX and KX. For NaX only use normal synthesis method. Characterization of these materials was using XRD, FTIR, SEM and EDX technique.

Zeolite 5A shows the carbon dioxide adsorption capacity up to 4.73 but zeolite 13X only up to 4.5. It was better using MOF-177 which was 9.02. The best results for this research was using KX material to make zeolite because it adsorp more carbon dioxide.

2.5   Covalent Organic Polymer (COP)

MOF and COF is one of the most famous materials that use in adsorption technology to adsorb carbon dioxide due to their controllable structural features and their high porosity (Xiang et al., 2012). COPs multi-chemical functionality is widely study by the researcher around the world. This polymer is the polymer that suppress in amorphous porous polymer family. It shows high carbon dioxide capture capacity. In this journal, it is reported that COP can withstand high temperature water for weeks. Even it is in high temperature water, it cannot losing any capture capacity and can be recycle fully at high pressure and warm temperature (Patel et al., 2012).

The materials that are studied in membrane for adsorption of carbon dioxide basically have high carbon dioxide take. But carbon dioxide uptake is not the only

characteristic need to be analyzed, the excellent selectivity of carbon dioxide also important in this case to be good adsorbent. The selectivity that reported in the literature review is that COP have both of this elements (Xiang et al., 2012).

In previous research paper by (Patel et al., 2012), he carried out the research on COP. In their research, they explain on how to synthesis the COP material but the characterization data of COP quite insufficient. Only comparison of BET surface area and carbon dioxide adsorption was shown.

2.5.1   Expected Result Compare With (Patel et al., 2012) Research Paper

Using FTIR characterization for COP-1 based on figure below:
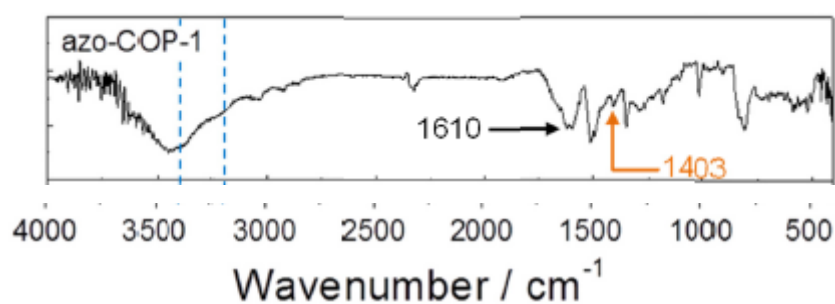
FIGURE 2.1   Expected FTIR COP-1

Lastly, in Patel's research paper. Data on TGA curve also shown as figure 4 below:
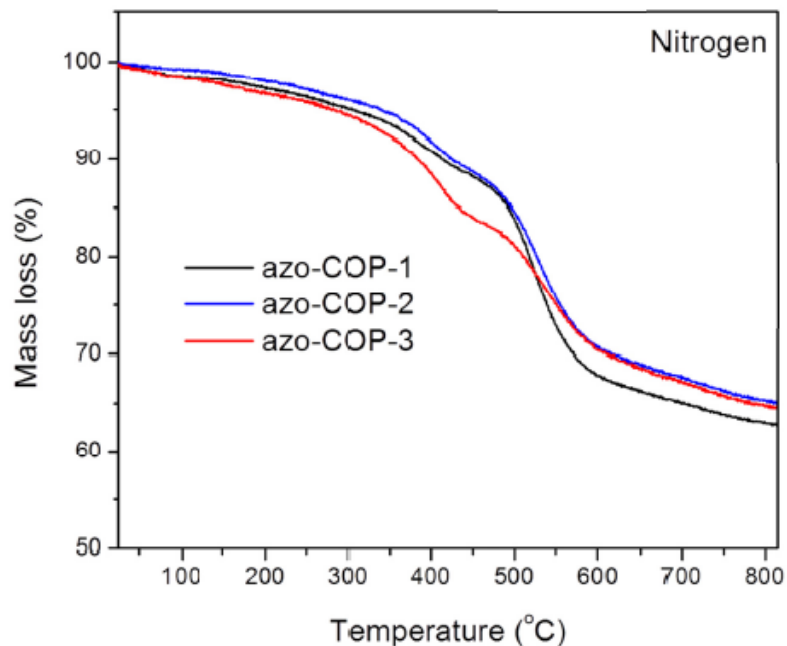
FIGURE 2.2   Expected TGA results of COP-1

2.6   Theory

2.6.1   COP-1 Characterization technique.

Currently COP-1 is known as the best adsorbent for CO2 capture from natural gas. According to Patel et al, there are different techniques in order to determine the characteristic of COP-1 adsorbent. The following are the techniques:

2.6.1.1   NMR - Nuclear magnetic resonance

Nuclear magnetic resonance is a technique used in order to determine the structure of organic compounds. From this technique we can observe or see the definite quantum mechanical properties of the atomic nucleus. Since COP-1 is synthesized in small amount this technique is suitable for COP-1 test because it has an advantage of testing even small amount of less than a milligram. For COP-1 characterization Patel et al (2012) stated that, C-NMR (which confirm the presence of

aliphatic CH$_2$ group and triazine ring carbons) and H-NMR (which confirm presence of methylene groups of piperazine are required

2.6.1.2   FT-IR - Fourier transform infrared spectroscopy

This technique is used to obtain infrared spectrum of absorption and Raman scattering of COP-1. The results of this technique will help to identity the compounds, the absence or presence of functional groups as well as the molecule structure. The mid region is the range of infrared regions where results are expected to arrive is at (670 – 4000 cm-1), which is the most widely used region. According to Patel et al (2012) FT-IR is also used to investigate the presence of typical stretching modes of CN heterocycles, characteristic breathing mode of triazine units, saturated carbons of piperazine as well as to confirm all three chlorine atoms on Cyanuric Chloride have been substituted.

2.6.1.3   CHN - Carbon hydrogen nitrogen analysis

This technique is used in order to analyze the elemental composition of a sample. COP-1 would be expected to show results where hydrogen, carbon, and nitrogen are all present in the sample. The composition of these elements will be investigate later in order to see if they are close or if they match the theoretical results from literature by Patel et al (2012) of 4.4% H, 52.2% C, and 43.5% N. The theoretical composition as proposed by Patel would also be re-calculated based on the chemical reaction of reactants.

2.6.1.4   EDX – Energy-dispersive X-ray Spectroscopy

This technique is used for chemical characterization or elemental analysis of a sample. It is able to sense the presence of more elements than CHN.

2.6.1.5   XRD - X-ray diffraction

This technique is used to identify the atomic and molecular structure of a solid. Solid with crystalline particles will cause the beam of incident X-rays to different diffraction into different specific directions. For COP-1 test, it is to check for presence of crystallinity in its structure (Patel et al., 2012).

2.6.1.6   TGA - Thermal gravimetric analysis

This technique is specially used for thermal analysis where sample physical and chemical properties changes are measured as a function of temperature. For COP-1, thermal gravimetric analysis (TGA) is used to test the thermos-stability at high temperature in air and N_2 atmosphere.

2.6.1.7   Brunauer-Emmett-Teller (BET) surface area

The main objective of this method is to explain the physical adsorption of gas molecules on a solid surface and it is used as the basis for an important analysis technique for the measurement of the specific surface area of a material. Apart from that, they also provide pore size as well as precise specific surface area evaluation of materials by nitrogen multilayer adsorption measured as a function of relative pressure using a fully automated analyzer.

2.6.1.8   FESEM - Field emission microscopy

This technique is used to investigate molecular surface structures and their morphology in material science.

CHAPTER 3

METHODOLOGY

3.1 Project Flow Chart

Project flow chart for this study is represented below in FIGURE 3.1:

Problem Statement & objectives
Purpose of conducting this project is identify

Literature Review	
Collecting information about the project	Analysed the source and represent it in the report.

Experiment Methodology
Deciding the best method to carry out the experiment based project.

Data Gathering Analysis
The experiment is carried out and the result obtained will be analysed and discussed

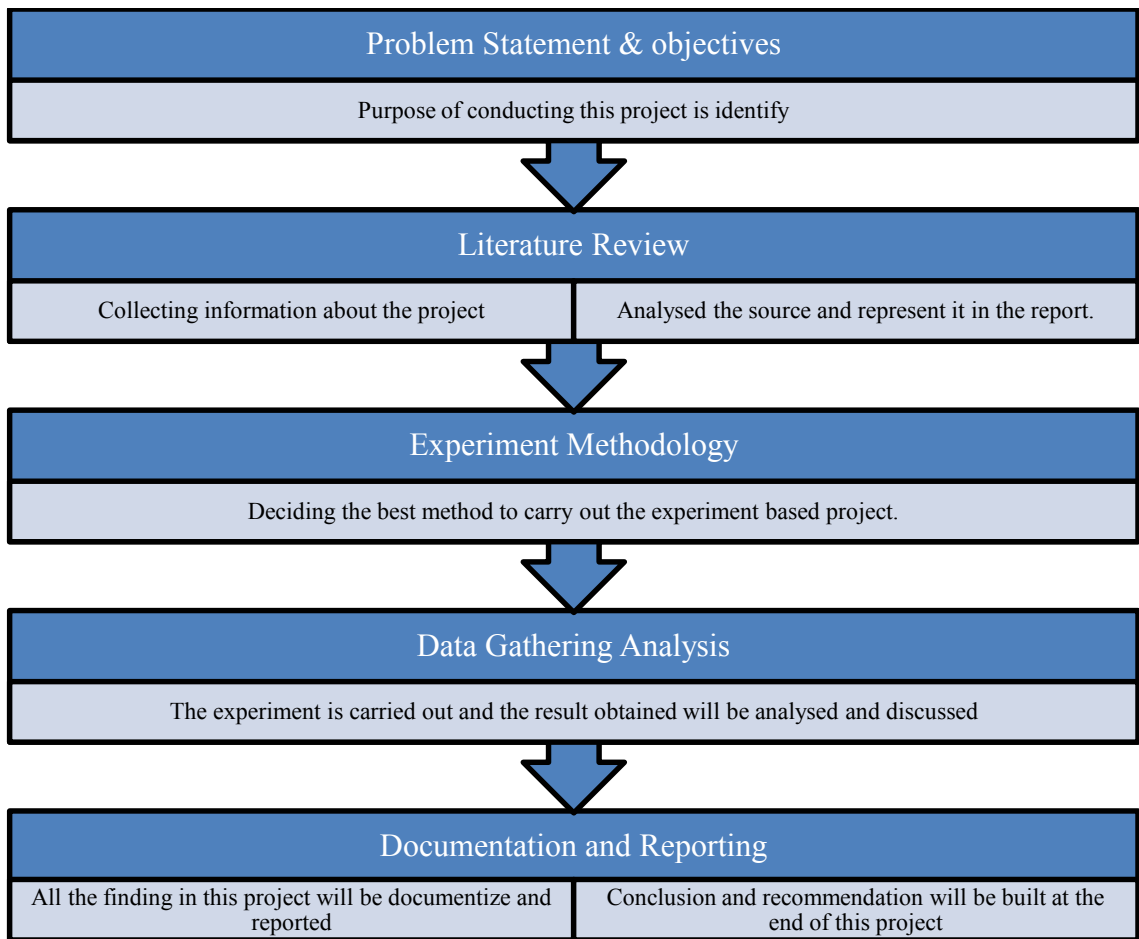| Documentation and Reporting	
All the finding in this project will be documentize and reported	Conclusion and recommendation will be built at the end of this project

FIGURE 3.1   Project Flow Chart

3.2 Gantt chart and Key milestones

Throughout the project, below in TABLE 3.1 and 3.2 are the planning and execution for the project:

TABLE 3.1   Gantt Chart for FYP

No	Detailed Work	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Selection of Project topic	■	■												
2	Preliminary Research Work			■	■	■	■								
3	Submission of Extended Proposal							■							
4	Proposal Defence								■	■					
5	Survey on available equipment and time for process										■				
6	Amendment on Research work											■	■		
7	Finalization of Interim Report													■	
8	Submission of Interim Report														■

TABLE 3.2   Gantt Chart for FYP II

No	Detailed Work	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Synthesis of COP														
	-Prepare the Apparatus	■													
	-Sythesis of COP-1	■	■	■											
2	Characterization of COP-1														
	-FTIR				■										
	-BET Surface Area					■	■								
	-SEM									■					
	-TGA										■				
3	Adsorption Isotherm Test														
	-BET CO$_2$ Analysis						■	■							
4	Progress Report							■	■						
5	Pre-Sedex											■			
6	Report Writing										■	■	■		
7	Draft Report Submission												■		
8	Final VIVA Presentation													■	
9	Hardbound Submission														■

3.3 Experiment Methodology

Materials that involve in synthesis of COP-1 as follow based on (Patel et al., 2012):

   i.   Cyanuric chloride

   ii.   N,N-diisopropylethylamine (DIPEA)

  iii.   Piperazine (anhydrous)

   iv.   1,4-dioxane

   v.   Ethanol

All solvent were dried and stored in anhydrous condition before used.

The chemical reaction involved in this reaction based on figure below:
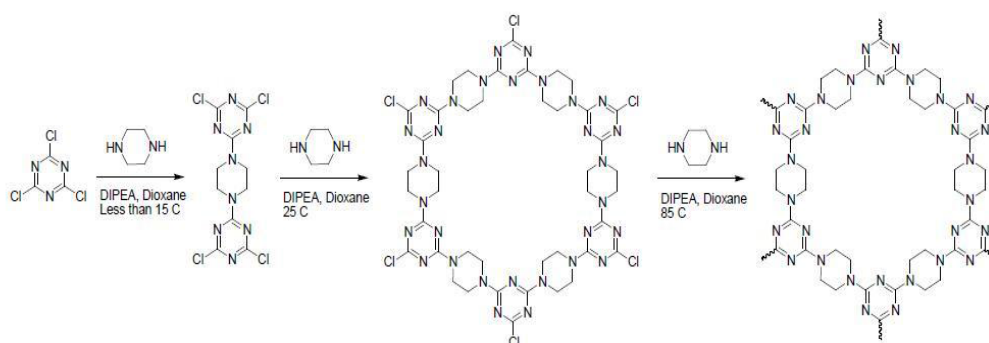
FIGURE 3.2   Chemical Reaction for COP-1

The H element of Piperazine will displace the Cl of cyanuric chloride to form a linkage between cyanuric chloride and piperazine. DIPEA dissolved in the solution enables the reaction to favour the formation of COP-1. At the end of the experiment with stirring of the reactants at 85 °C for 21 h in Reactor 2, all three Cl of cyanuric chloride will be substituted and linked up by piperazine to form a polymer called Covalent Organic Polymer-1.

Synthesis of COP-1 in this procedure follow these technique below based on (Patel et al., 2012):

i. In Reactor 1, channel N_2 supply to the reactor to ensure the reactor environment is filled with N_2 and displace out other gasses. Then, dissolve cyanuric chloride (5.00 g, 27.1 mmol) in 1,4-dioxane (40 mL) in Reactor 1. A magnetic stirrer is used to stir the solution in reactor 1 to ensure all the cyanuric chloride is dissolved

ii. In Reactor 2, also channel N_2 supply to the reactor to ensure the reactor environment is filled with N_2 and displace out other gasses. Then, add DIPEA (18.9 mL, 108.4 mmol) to piperazine (3.73 g, 43.3 mmol) which has been dissolved in 1,4-dioxane (160 mL) at 288 K. A mechanical stirrer is attached to reactor 2 to ensure that the solution in the reactor is well mixed.

iii. Using a syringe, add cyanuric chloride solution in reactor 1 dropwise to reactor 2 with continuous stirring at 15 °C in an N_2 environment.

iv. In Reactor 2, a white precipitate will form. Stir the white precipitate at 15 °C for 1 h. After that, continue stirring the white precipitate at 25 °C for 2 h and then at 85 °C for 21 h. Continuous stirring is done using a mechanical stirrer.

v. The temperature in the reactor is regulated by the temperature regulator which channels water at desired temperature to the outer wall of the double glass wall jacketed reactor, hence maintaining the temperature in the reactor at desired temperatures of 15 °C , 25 °C and 85 °C. One of the nozzles of reactor 2 is open to ensure that the by-product of the reaction, which is HCl is displaced out of the reactor into a conical flask containing water as waste to be disposed.

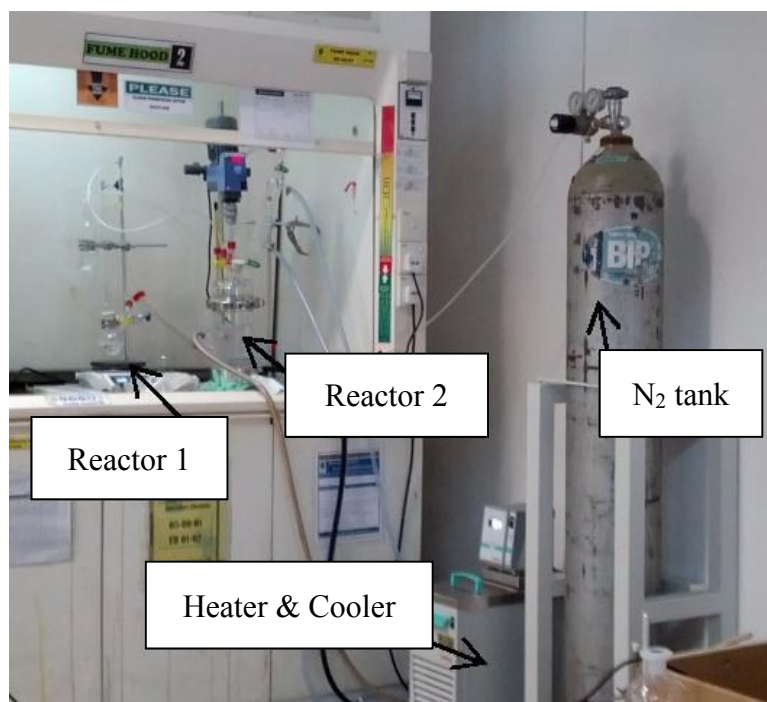vi. The white precipitate would be COP-1 and will then undergo purification steps.

FIGURE 3.3   Overall experimental setup for synthesis of COP-1
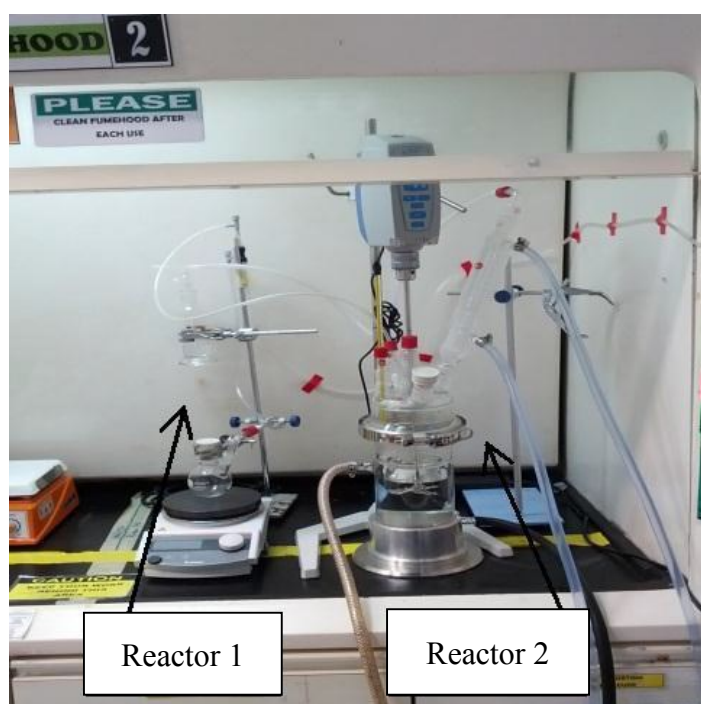
FIGURE 3.4   Closer view of Reactor 1 and Reactor 2

Purification of white precipitate.

i. After white precipitate is form in the synthesis method, white precipitate need to be wash off with 1,4 dioxane 3 times by using filtering method.

ii. Soak the precipitate in ethanol for 12 h, every 4 hours interval time the precipitate need to be washed with ethanol and soak back in ethanol.

iii. Finally, the precipitate form divided by two sample, first sample (sample 1) of COP-1 dry in room temperature under vacuum condition for 2h. The second sample (sample 2) dry in 120^OC under vacuum condition. All vacuum condition used the vacuum oven below.

FIGURE 3.5   Vacuum Oven

Characterization chosen to verify the synthesis element from the experiment earlier using several type of technique as per table below:

TABLE 3.3   Characterization parameter of interest

No	Test	Parameter of interest
1	FTIR	~ To investigate the presence of typical stretching modes of CN heterocycles ~ To investigate characteristic breathing mode of triazine units ~ Investigate saturated carbons of piperazine and 4,4' – bipiperidine ~ To confirm all three chlorine atoms on CC have been substituted
2	BET surface area	~ To obtain precise specific surface area evaluation of COP-1. The test was performed under mesoporous pore size (2-50 nm) category.
3	SEM	~ To investigate molecular surface structures and their morphology in material science
4	TGA	~ To test the thermos ability of COP-1 at high temperature in air and N_2 environment. Temperature range used is from room temperature to 800°C with a heating rate of 10°C/min.

All of the chosen test for the characterization for COP-1 is available in Universiti Teknologi Petronas (UTP) and the reliability of the equipment for the characterization is up to the university research level.

CO$_2$ adsorption experiments using volumetric gas sorption (BET). The investigation for gas capture capacity of the elements, we need to do two types of test which is CO$_2$ capture and CH$_4$ capture. The most successful adsorption is when the adsorption of CO$_2$ is high and the adsorption of CH$_4$ is low. The equipment uses is BELSORP at RCCO$_2$C Department, UTP. The test was done in ambient temperature and pressure.

Methodology for CO$_2$ adsorption are as follows:

i.   Each sample is out gassed at 408K for 5hours (under vacuum).
ii. The weight of each sample is recorded before and after out gassing to confirm the removal of guest molecules.
iii. About ~85-90mg of the out gassed samples are used for gas sorption measurements.
iv. The isotherms for CO$_2$ taken at ambient condition on the new synthesized COP-1.

FIGURE 3.6   Pre treatment

FIGURE 3.7   BELSORP

CHAPTER 4

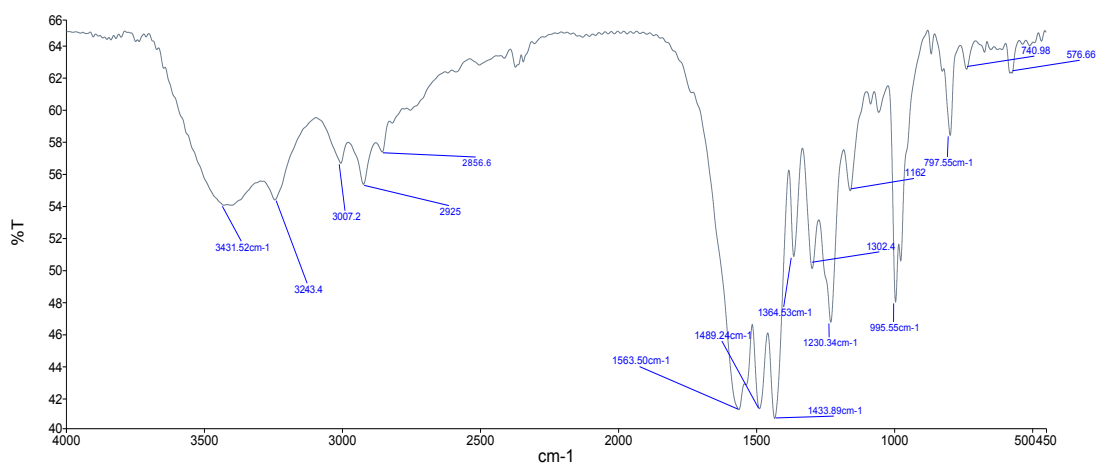# RESULT AND DISCUSSION

4.1   FTIR

FIGURE 4.1   FTIR curve

From the previous journal, they stated that functional group in COPs will show the presence of strong bonds. This strong bonds can be analyze from above graph by looking the peaks from 1200-1600 cm^{-1} region. The region will determine whether the typical stretching modes of CN heterocycles presence. The results shows that we have peaks from that region and shows the COPs has all the characteristic of strong bonds. This region basically shows the bond available in COPs such as C–C stretch (in–ring), C–H bend and C–N stretch

After the 21 hours stir of sample, all the chlorine will be replace by nitrogen from other ring. Results expected in this FTIR will be no pick at 850 cm^{-1}. From the results there are no pick at expected region shows that there are no C-Cl bonds present in the sample. All the C-Cl bond are confirmed to be replaced by C-C bond. Basically this conclude the molecules in the sample are having same characteristic as real COP.

Lastly, triazines molecules offer high nitrogen content in their structure. This feature are the desirable in capturing carbon dioxide. Coupling triazine with piperazine and 4,40-bipiperidine will develop COPs. So in FTIR results expected to have picks at region 2920-2930 cm^{-1} and the results show the expected results. The region shows presence of piperazine. The triazine is exists from the charts shows the peak at 800 cm^{-1}. Based on analysis done shows that the COPs develop by me basically match with the previous journal.

4.2 BET for CO_2 adsorption Sample 1

Sample 1 was test for CO_2 gas capture using BELSORP equipment. The result obtain are as follows:

TABLE 4.1 CO_2 gas capture

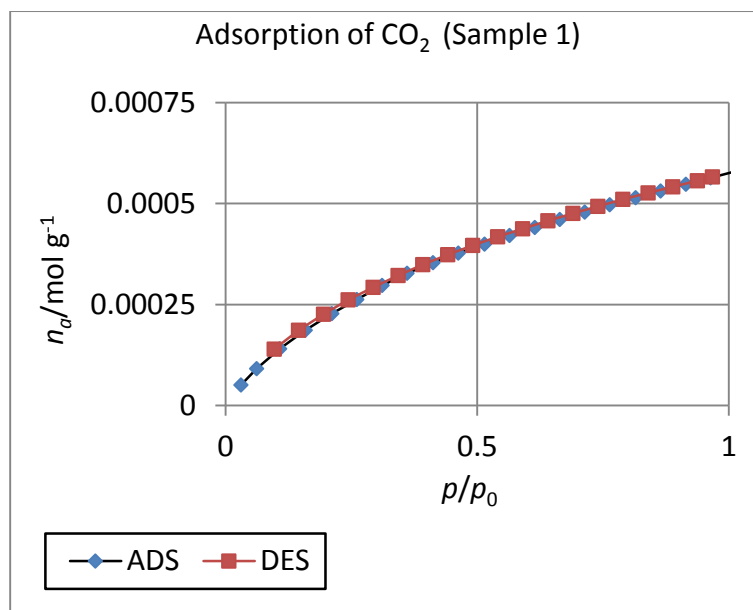| Sample	CO_2 Gas adsorption (mol/g)
COP-1 (28°C)	0.00057692

FIGURE 4.2   Adsorption of CO_2 (Sample 1)

From the graph, the system for characterization recorded the results for adsorption and desorption for sample 1 in adsorbing carbon dioxide. The adsorption at ambient temperature shows the reading 0.00057692 mol/g. This value had been converted into mg/g showing the value of 25.39 mg/g using certain calculation.

Comparing with previous journal, the results recorded still not reach their value. Our result recorded 25.39 mg/g compared to previous journal (Patel, 2012) which is 60 mg/g.

The different quite significant between this project and previous journal project. This different of the result obtain can be primer from the handling of the sample throughout the experiment going. Besides that, during some of the test going the sample had been left outside the desiccator resulting in the high content of moisture in COP sample. The active side had been reacted with air moisture because COP is very sensitive with moisture.

For the cooling of sample after stirring at $85^O C$, we used the cooler to make the sample cool faster and this sudden cooling had affected the result obtain compare to the previous journal.

4.3   BET for CO₂ adsorption Sample 2

Sample 2 was test for CO_2 gas capture and the result obtain are as follows:

TABLE 4.2 CO_2 gas capture

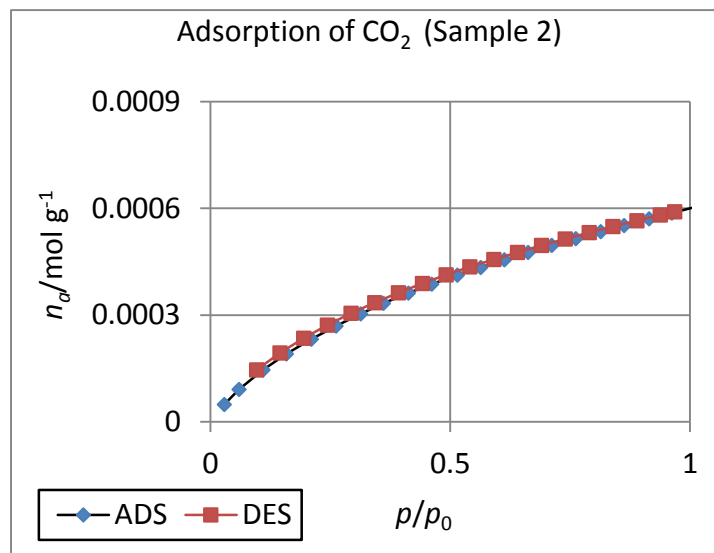| Sample	CO_2 Gas adsorption (mol/g)
COP-1 (120°C)	0.00060119

FIGURE 4.3   Adsorption of CO_2 (Sample 2)

From the graph, the system for characterization recorded the results for adsorption and desorption for sample 2 in adsorbing carbon dioxide. The adsorption at ambient temperature shows the reading 0.00060119 mol/g. This value had been converted into mg/g showing the value of 26.45 mg/g using below calculation

Comparing with previous journal, the results recorded still not reach their value. Our result recorded 26.45 mg/g compared to previous journal (Patel, 2012) which is 60 mg/g.

The different quite significant between this project and previous journal project. This different of the result obtain can be primer from the handling of the sample throughout the experiment going. Besides that, during some of the test going the sample had been left outside the dessicator resulting in the high content of moisture in COP sample. The active side had been reacted with air moisture because COP is very sensitive with moisture.

For the cooling of sample after stirring at 85^OC, we used the cooler to make the sample cool faster and this sudden cooling had affected the result obtain compare to the previous journal.

4.4 Comparison CO₂ adsorption rate between both sample

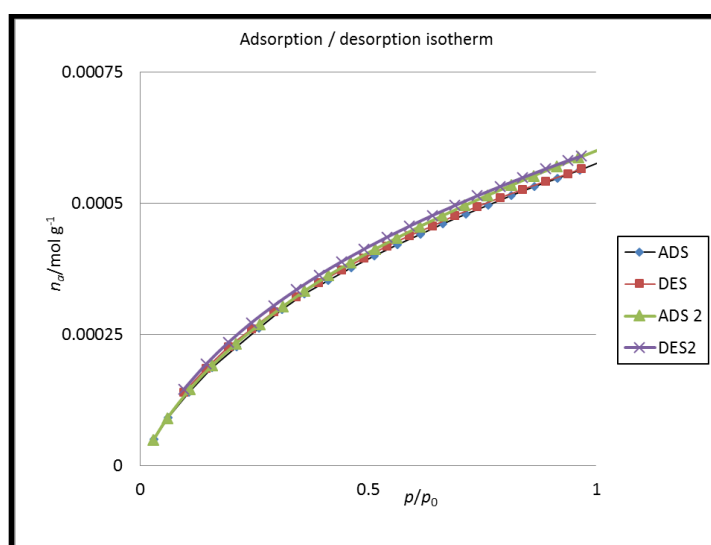Results obtain in previous section now will be compare and the result are as figure below.

FIGURE 4.4   Adsorption of CO_2

There are no significant changes between this two samples. The adsorption rate for sample 2 only show the different of 1 mg/g compared to sample 1. This amount of difference cannot be prove of the significant changes in the experiment.

4.5 BET for CH₄ adsorption Sample 1

Sample 1 was test for CH_4 gas capture using BELSORP equipment. The result obtain are as follows:

TABLE 4.3   CH$_4$ gas capture

Sample	CH$_4$ Gas adsorption (mol/g)
COP-1 (28°C)	0.00012346

FIGURE 4.5   Adsorption of CH$_4$ (Sample 1)

From the graph, the system for characterization recorded the results for adsorption and desorption for sample 1 in adsorbing methane. The adsorption at ambient temperature shows the reading 0.00012346 mol/g. This value had been converted into mg/g showing the value of 1.98 mg/g using below calculation.

The calculation is done to develop the ratio of the selectivity between carbon dioxide and methane. The higher ratio will be the better results.

4.6   BET for CH4 adsorption Sample 2

Sample 2 was test for CH$_4$ gas capture using BELSORP equipment. The result obtain are as follows:

TABLE 4.4 CH$_4$ gas capture

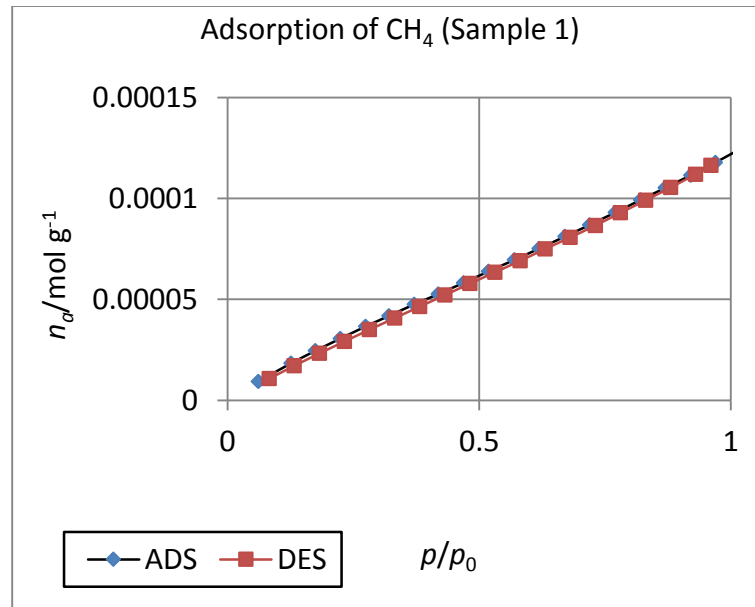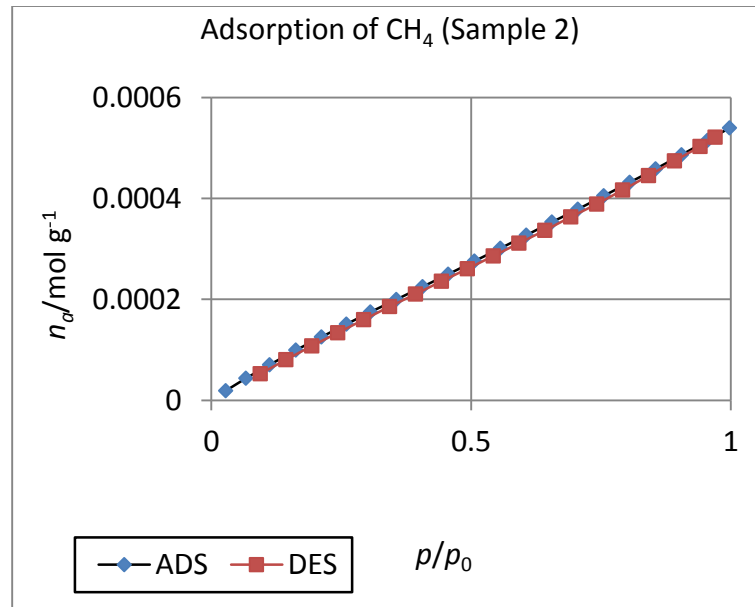| Sample	CH$_4$ Gas adsorption (mol/g)
COP-1 (120°C)	0.00053962

FIGURE 4.6 Adsorption of CH$_4$ (Sample 2)

From the graph, the system for characterization recorded the results for adsorption and desorption for sample 2 in adsorbing methane. The adsorption at ambient temperature shows the reading 0.00053962 mol/g. This value had been converted into mg/g showing the value of 8.633 mg/g using certain conversion calculation.

The calculation is done to develop the ratio of the selectivity between carbon dioxide and methane. The higher ratio will be the better results.

4.7 Comparison CH₄ adsorption rate between both sample

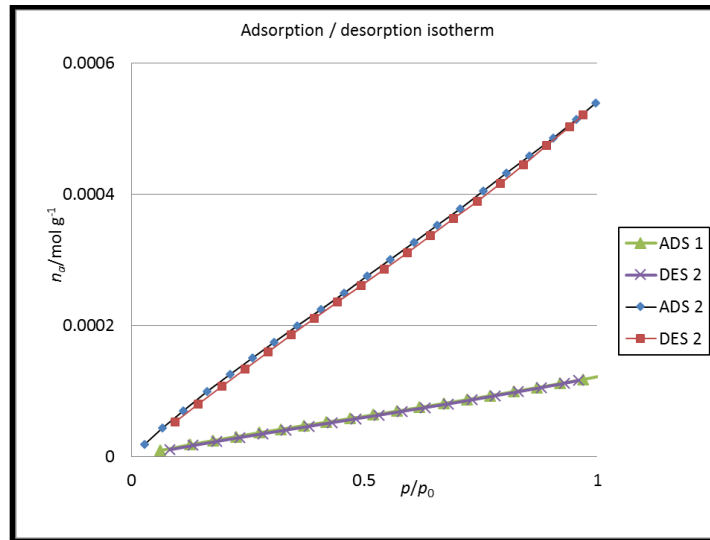Results obtain in previous section now will be compare and the result are as figure below.

FIGURE 4.7   Adsorption of CH₄

There are significant changes between this two samples. The adsorption rate for sample 2 show the different of 6.65 mg/g. This amount of difference can be prove of the significant changes in the experiment.

4.8 Selectivity of adsorption

The selectivity is calculated using below approach. The calculation below is for sample 1.

$$Adsorption\ rate\ of\ CO_2 = 0.00057692\ \frac{mol}{g} \times 1000\ \frac{mmol}{g}$$

$$Adsorption\ rate\ of\ CO_2 = 0.57692\ \frac{mmol}{g}$$

$$Adsorption\ rate\ of\ CH_4 = 0.00012346\ \frac{mol}{g} \times 1000\ \frac{mmol}{g}$$

$$Adsorption\ rate\ of\ CH_4 = 0.12346\ \frac{mmol}{g}$$

After the adsorption of both gasses is calculated, the ratio of both gasses will represent the selectivity of the COPs.

$$Selectivity = \frac{Adsorption\ rate\ of\ CO_2}{Asorption\ rate\ of\ CH_4}$$

$$Selectivity = \frac{0.57692\ mmol/g}{0.12346\ mmol/g}$$

$$\boldsymbol{Selectivity = 4.67}$$

The selectivity is calculated using below approach. The calculation below is for sample 2.

$$Adsorption\ rate\ of\ CO_2 = 0.00060119\ \frac{mol}{g} \times 1000\ \frac{mmol}{g}$$

$$Adsorption\ rate\ of\ CO_2 = 0.60119\ \frac{mmol}{g}$$

$$Adsorption\ rate\ of\ CH_4 = 0.00053962\ \frac{mol}{g} \times 1000\ \frac{mmol}{g}$$

$$Adsorption\ rate\ of\ CH_4 = 0.53962\ \frac{mmol}{g}$$

After the adsorption of both gasses is calculated, the ratio of both gasses will represent the selectivity of the COPs.

$$Selectivity = \frac{Adsorption\ rate\ of\ CO_2}{Asorption\ rate\ of\ CH_4}$$

$$Selectivity = \frac{0.60119\ mmol/g}{0.53962\ mmol/g}$$

$$\boldsymbol{Selectivity = 1.11}$$

From the calculation above, it shows that sample 1 shows higher selectivity which is 4.67 compare to sample 2 only 1.11. The previous journal recorded that the ratio is 5.616. There are a gap in the results, the justification are because of the different gasses use in the experiment. They use ratio between CO_2 and N_2 but in our experiment the author use CO_2 and CH_4.

4.9 BET Surface Area.

The graph below show the BET surface area that are generated from the sample 1 and sample 2.
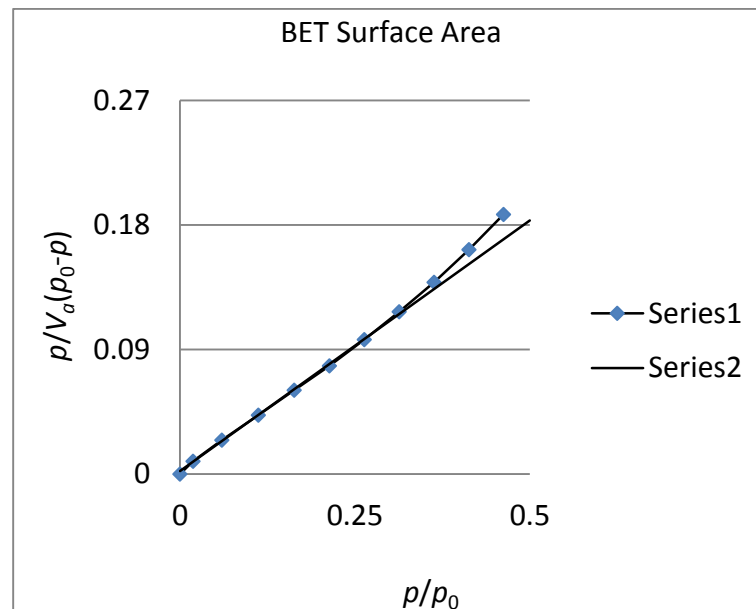

FIGURE 4.8   BET Surface Area

From the BET surface area analysis, the surface area for our sample only 11.944 m^2g^{-1} compare to the previous journal which is 168 m^2g^{-1}(Patel, 2012).

The different quite significant between this project and previous journal project. This different of the result obtain can be primer from the handling of the sample throughout the experiment going. Besides that, during some of the test going the sample had been left outside the dessicator resulting in the high content of moisture

in COP sample. The active side had been reacted with air moisture because COP is very sensitive with moisture.

For the cooling of sample after stirring at 85°C, we used the cooler to make the sample cool faster and this sudden cooling had affected the result obtain compare to the previous journal.

4.10   SEM Analysis.

SEM analysis basically to test the morphology of the sample. The picture showing sharp edge and has arranged structure basically has the properties of crystalline. The other type of picture that showing the irregular shape type basically contain round shape or inconsistent saying that the sample is amorphous.

The expected results from this SEM is that to get the amorphous and the results recorded shows that our sample are amorphous and porous as per below at 10000x magnification and 20000x magnification.
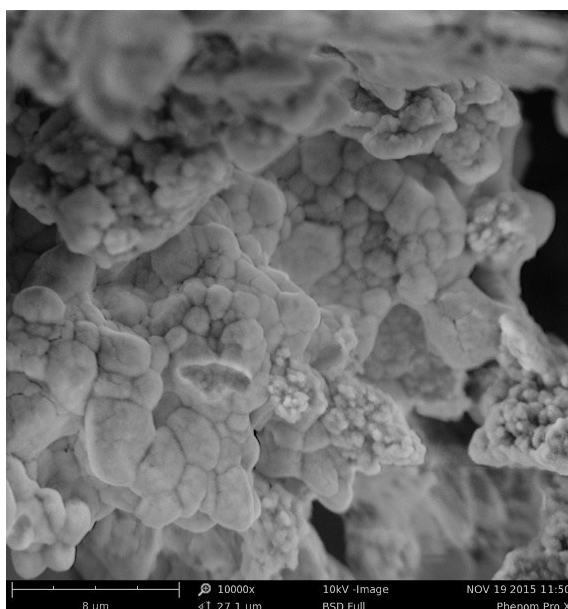

FIGURE 4.9   SEM result (10000x)
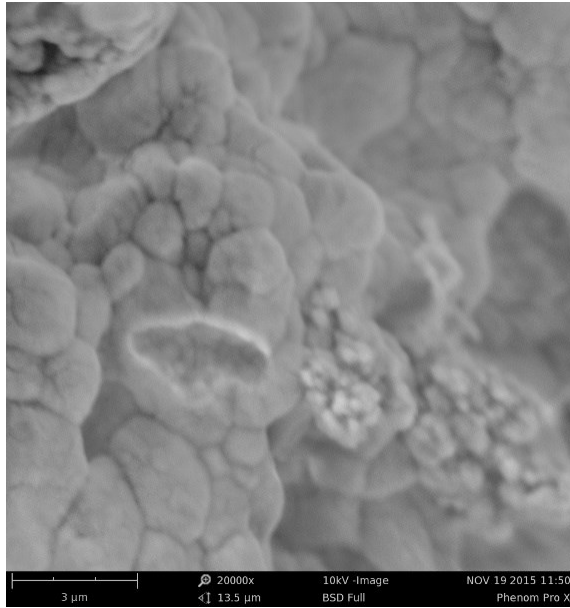
FIGURE 4.10   SEM result (20000x)

4.11   TGA results

TGA basically to test the heat resistance of the sample. This test will show the temperature that sample can stand comparing with the weight loss of sample. the test basically will perform up to 800 ^{O}C at a heating rate of 10 ^{O}C per minute. The results obtain from this test as per figure below:
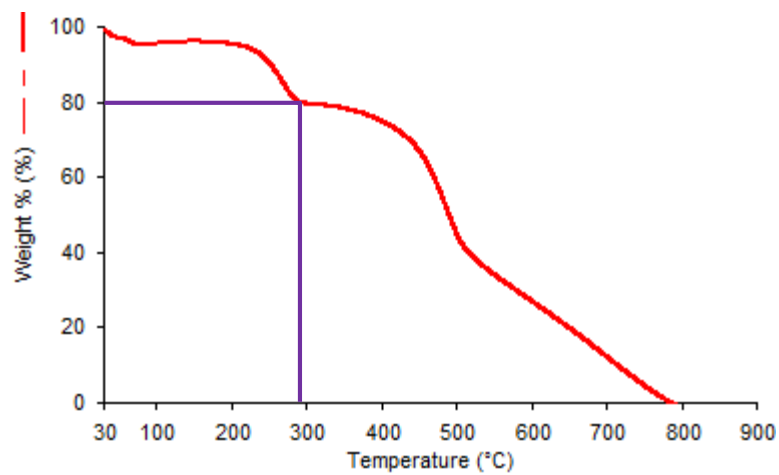

FIGURE 1.8   TGA results

The results had shown the sample start to decompose at the temperature 278-290 ºC. From the Patel journal, his sample start to decompose at 285-290 ºC. The different between our samples do not show any significant changes compare to the previous journal.

For the TGA result, the sample had been successfully synthesized and meet the expected results.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

This project is the research on the separation of carbon dioxide from methane. It is important project because this alternative route to separate carbon dioxide from methane provides us with less capital cost, less energy used and high selectivity over carbon dioxide. Covalent Organic Polymer will be the great potential to fulfill the entire requirement.

The objective of this project is to synthesis and characterize covalent organic polymer and to investigate carbon dioxide capturing capacity of the new synthesized COP-1 at ambient condition. Basically, the objective had been achieved and successfully delivered in this report.

The results achieved in this project compare to the results from previous journal which is (Patel, 2012) still need to have improve in term of handling of chemical and storing the sample. The surface area obtain had been show most significant different and based on TGA, the results are almost the same. For the adsorption rate, the result of this experiment obtain half value from the previous journal.

As recommendation for this project, the stirring at 85ºC need to be cool naturally and not using the cooler. The sudden cooling of the sample had showed the decreasing in the performance of COP. The storing of the sample also need to be in desiccators all the time due to the sensitivity of sample to the air moisture. This recommendation will basically increase the performance of COP.

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