Development of Covalent Organic Polymers (COP-4) Adsorbent Using Microwave Reactor for Carbon Dioxide Capture from Natural Gas

by

Mohammad Shamir Azmeir Bin Mohd Omer

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Dissertation submitted in partial fulfillment of
the requirement for the
Bachelor of Engineering (Hons)
(Chemical)

FYP II September 2014

Universiti Teknologi PETRONAS
Bandar Seri Iskandar,
31750 Tronoh,
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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Chemical Engineering Programme
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In partial fulfillment of the requirement for the
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(Chemical)

Approved by,

(DR NURHAYATI BT MELLON)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

September 2014

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 persons.

MOHAMMAD SHAMIR AZMEIR BIN MOHD OMER

ABSTRACT

The presence of carbon dioxide (CO_2) in natural gas stream become a problem since it brought negative impact to the heating value of the natural gas, as well as causing corrosion to pipelines and hydrate formation problem. Recently the new kind of adsorbent has been discovered to have the high capacity for CO_2 adsorption that includes Metal-Organic Framework (MOF), Covalent-Organic Framework (COF) and Covalent Organic Polymer (COPs). This research is concentrated to develop the COP-4 adsorbent using microwave reactor method. The main challenges in this research are the limitation information from literature regarding the COP synthesis using microwave reactor as well as longer time preparation by using conventional method. This method propose a faster synthesis method of COP-4 and theoretically will give higher yield and less reaction time. After synthesis, COP-4 sample undergo the characterization test included FTIR, TGA, SEM, XRD and BET. The results will be compared to the COP material developed using conventional method. Consequently, this study will contribute towards the development of sustainable CO_2 removal technologies.

ACKNOWLEDGEMENT

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Most important, a very special note thanks to my supervisor Prof Dr Nurhayati Mellon, who was always willing to assist and provided good support throughout the project completion. Your excellent support, patience and effective guidance have helped my project to completion. Nevertheless, I also would like to thank to my project partner, Sana Yaqub, Master Student in UTP doing the same project with me for guidances from the beginning of the project. I would like to thank to FYP1 and FYP2 coordinators, Dr Maziyar Sabet and Dr Asna respectively for arranging various seminars as support and knowledge to assist the group in the project. The seminars were indeed very helpful and insightful to us.

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CHAPTER 1

INTRODUCTION

1.1 Background

Gas demands is growing in every region in the world. International Energy Agency (IEA) forecasted that, gas demands will reach about 5.1 trillion cubic meters in 2035 and this is about over 1.8 trillion cubic meters from today. South East Asia has been viewed as one of the highest growth market for natural gas demands. Based on the quote from PETRONAS Gas and Power Business General Manager of Strategic Planning, Mr Ezhar Yazid Jaafar, "the demands is greater than supply even in the producing countries like Malaysia, Thailand and Indonesia." Based on the findings by IEA, the growing of demands of natural gas is driven by the power sector as gas replaces coal in power generation. This also indicates the increasing demand from the industrial, transports and building sectors. The high demand for natural gas as the alternative clean energy sources has been the shift in exploration trend of natural gas from conventional hydrocarbon reservoir to non-hydrocarbon reservoir containing CO_2 of up to 70% (AmResearch, 2014).

Based on the research conducted by Maybank Malaysia, Malaysia's geological gas reserves stood at about 82 million cubic feet (tcf) in 2011 and Malaysia is reputed to have the 15th largest reservoir in the world. From the production of natural gas overview, Malaysia's natural gas production stood at 2.0 tcf. Based on these statistics, it is estimated that the natural gas reserves in Malaysia is enough to sustain another 34 years of product cycle.
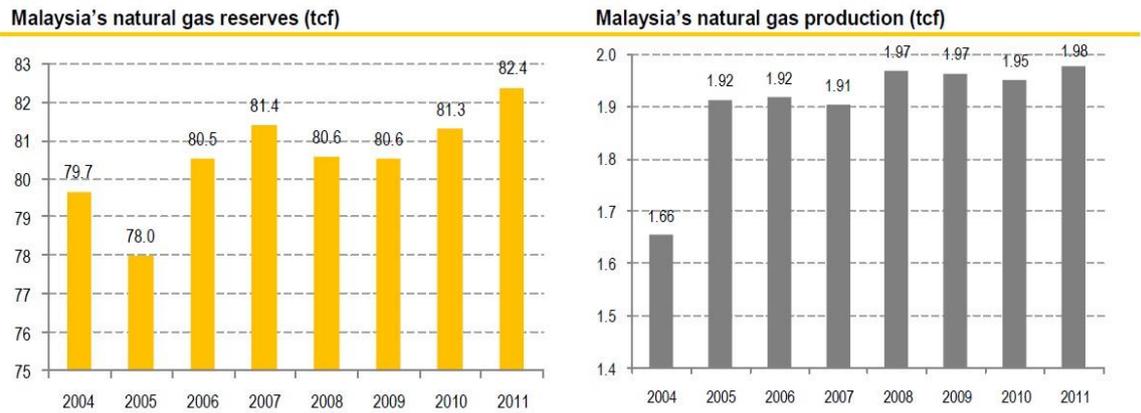
Figure 1. Statistics of Malaysia's natural gas reserves and production

Based on the facts, natural gas is one of the safest, cleanest, and most useful forms of energy. Natural gas is a hydrocarbon gas mixture that primarily consist of methane, but commonly has included the varying amount of other higher alkanes. Not only that, natural gas also commonly consist of less percentages of impurities like carbon dioxide, nitrogen and hydrogen sulfide. Carbon dioxide is a naturally occurring diluent in oil and gas reservoirs and it can react with hydrogen sulphide and water to make corrosive compounds that corrode pipelines. Apart from that, the presence of carbon dioxide reduces the energy content and the heating value of natural gas as well as causing hydrate formation problem. It is therefore critical that pipeline levels of carbon dioxide are no more that 2% - 3%. Well head natural gas can contain as much as 30% carbon dioxide (Fuller, n.d). The removal of the carbon dioxide from natural gas is very crucial to prevent the high amount of the carbon dioxide to emit to atmosphere as this emission can cause the greenhouse effect.

Since the concerns about the high carbon dioxide content in natural gas, many methods or applications have been developed to separate the carbon dioxide from natural gas. Most of these technologies are suitable for natural gas with up to 20% – 30% of carbon dioxide content. Thus, a new method for carbon dioxide capture that can separate CO2 from streams containing up to 70% CO2 at high pressure is important to ensure gas exploration from these fields are economically justified. Nowadays, there are four major technology involve in separation of carbon dioxide from natural gas that are:

1) Membranes separation

2

2) Cryogenics separation

3) Solvent separation

4) Adsorbent Separation

Membranes Separation

Gas separation membranes allow one component in a gas stream to pass through more quickly than others. There are many types of gas separation membranes, including the membranes of porous inorganic palladium membrane, the membrane polymer and zeolite. The limitation in using this method is membrane cannot usually achieve high degrees of separation, so multiple stages and / or recycling one flow is necessary (Davison, et. Al, 2001). This leads to increased complexity, power consumption and cost (Maqsood, et. Al, 2014). Several membranes with different characteristics are needed to separate high purity carbon dioxide. Two parameters that characterize the membrane performance are (1) permeability that measure of the volume of gas the membrane can process and (2) selectivity that measure of the membrane's ability to separate components. Currently, there are research carried out in developing the solvent that can assist the membrane separation process. Development is needed before the membrane can be used on a large scale for capture at power stations (Dortmundt, et. Al, n.d).
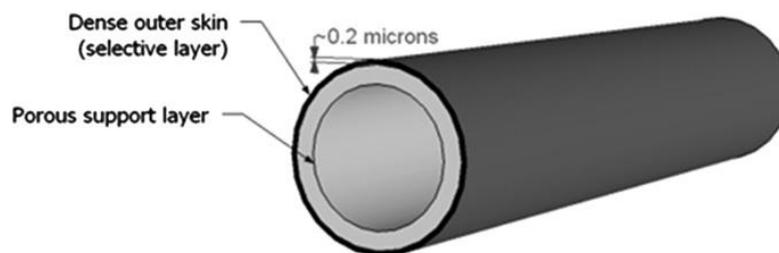
Figure 2. A symmetrical membrane morphology

Cryogenics Separation

Carbon dioxide can be separated from other gases by cooling and condensation. Cryogenic separation is widely used commercially for the flow that already has a high carbon dioxide concentrations typically higher than 90% but it is not used for more dilute carbon dioxide streams. A major disadvantage of cryogenic carbon dioxide separation is the amount of energy required to provide the necessary cooling for the

process, especially for the flow of liquid gas. Another drawback is that some components, such as water, should be removed before the gas stream is cooled, to prevent clogging. Cryogenic separation has the advantage that it allows for the direct production of liquid carbon dioxide, which is required for specific transportation options, such as transport by ship. Cryogenics is generally only used for high concentration, high pressure gas, such as in pre-combustion capture process or oxygen fired combustion (Sukanta, et. Al, n.d).

Solvent Separation

Amine scrubbing technology has embodied over the last 60 years in the oil and chemical industry, for the removal of hydrogen sulfide and carbon dioxide from gas flow. Mono-ethanolamine (MEA) is widely used amines for carbon dioxide capture. Carbon dioxide recovery levels as much as 98% and 99% may be achieved. However, there are questions about the level of degradation of the solvent in oxidizing environment of a flue gas and the amount of power needed for the regeneration. Improved solvents can reduce energy requirements by 40% compared with conventional MEA solvent. There is great interest in the use of sterically-hindered amines, which claims to have the good absorption and desorption characteristics (Xiang, et al., 2012).

Adsorbent Separation

Solid adsorbents, such as zeolites molecular sieve and activated carbon, can be used to separate carbon dioxide from gas mixtures. Zeolite molecular sieves are crystalline material with high porosity and belong to the class of aluminosilicates. Two important characteristics of zeolite molecular sieves are the selective adsorption due to the uniform pore size of the zeolite structure and high adsorption capacity for polar substances at low concentrations. These two advantages of zeolite molecular sieve has brought up to the ability of keep its high capacity at high temperature, which makes it the optimal material. Plus, synthetic zeolite that has pore size 0.9 m, can have maximum CO_2 sorption of 175 mg/g and moisture capacity 255 mg/g at 100 kPa and temperature of 298 K. Past studies report a CO_2/CH_4 selectivity for a new class of zeolitic materials known as zeolitic imidazolate frameworks (ZIFs) of 5.9 with 1.05 mmol/g CO_2 adsorbed at 800 torr and 298 K (Phan, et al., 2010).

Besides, activated carbon (AC) is a non-graphite form of carbon composed of carbonaceous material such as coal, lignite, wood, etc. Due to strongest physical adsorption forces or the highest volume of adsorbing porosity activated carbon are widely used now days. Surface area of activated carbon can be greater than 1000m²/g. Pressure range of AC mostly is between 100-1000 KPa at 298K.
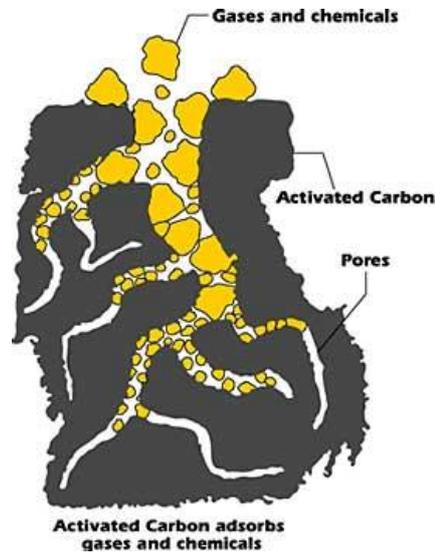
Figure 3. Activated Carbon (Google Image)

In pressure swing adsorption (PSA), the gas mixture flows through the packed bed of adsorbent at high pressure up to the desired concentration approaches equilibrium. The bed is regenerated by reducing the pressure. In temperature swing adsorption (TSA), adsorbent was regenerated by raising the temperature. PSA and TSA are commercially practiced gas separation method and used little in the production of hydrogen and the removal of carbon dioxide from natural gas. Adsorption is not yet considered attractive for large-scale separation of carbon from flue gas because the capacity and carbon dioxide selectivity of available adsorbents is low. However, it may be successful in combination with another capture technology.

Recently, the new kind of adsorbent has been discovered to have the high capacity for carbon dioxide adsorption that is metal-organic framework (MOF), crystalline covalent-organic framework (COF) and covalent-organic polymers (COP) (Xiang, et al., 2012). COP is a new class of crystalline porous materials has gained attention in the field of CO2 capture due to its low density, high hydrothermally stability, high surface area with high adsorption capacity of CO2. In all the study regarding COP, the preparation was using conventional method which is solvothermal synthesis. This

preparation method is usually lengthy and very time consuming. However, synthesizing adsorbent material using microwave synthesis method usually results in high yield, less reaction time and no side products is very attractive and has gained attention recently (Campbell, et. Al, 2009). In microwave synthesis there are two methods available, one is an open reaction vessel and second refers to sealed or closed reaction vessel with a reflux condenser. The yield in both cases were different. In order to achieve high yield of COP adsorbent, sealed reaction vessel is preferred currently, reported 200 times more heating than conventional synthesis (Campbell, et. Al, 2009).

1.2 Problem Statement

Current technology for CO2 capture is capable of separating Co2 from hydrocarbon reservoirs containing small percentage of Co2. It is not economically feasible for CO2 capture from non-hydrocarbon streams containing up to 70% CO2 (AmResearch, 2014). Currently, no commercial COP available in industries as the COP is a new adsorbent for separation of carbon dioxide from natural gas still under researches. Most of the current research of COP is focused on the separation between carbon dioxide and nitrogen. Most of the research concentrate on the carbon dioxide capture at low pressure. The purpose of this research is to investigate the feasibility of COP for carbon dioxide separation at high pressure conditions. As the research at different condition, limited data on carbon dioxide separation from natural gas using the COP available in the journal. Based on the several literature of COP screening, it was found that the COP-4 is the most attractive and suitable option at proposed conditions pressure and temperature for the deeper research. However, the preparation time of the COP adsorbent by conventional methods is very time consuming (72 hours) (Patel, et. Al, 2012). Hence this research proposes a new method to produce COP adsorbent using microwave reactor. Theoretically not only it will shorten the preparation time estimated about 2 – 8 hours synthesis, it will also enhance the CO2 uptake of the COP adsorbent (Campbell, et. Al, 2009).

1.3 Objective

The main objective of this study is synthesize and characterize covalent organic polymers (COP-4) using microwave reactor for carbon dioxide separation from natural gas.

1.4 Scope of Study

This research will focus mainly on two parts, which is the synthesis of COP-4, characterization of COP-4 and performance test of COP-4.

1.4.1 Synthesis of COP-4

The scope of the first part is to understand the methodology to synthesis COP-4 adsorbent using microwave reactor. All of the information from the methodology reported by Xiang, et. Al (2012), must be understand as it gives all the required data such as the raw materials (core and linker) needed as well as the amount required for each material, equipment, temperature and pressure conditions, time taken for each step of the synthesis process, and purification techniques to arrive at COP-4 that is ready for characterization study.

1.4.2 Characterization of COP-4

The scope of the second part of the project is to study structural as well as physical properties of covalent organic polymer required to separate carbon dioxide from natural gas. All the data must be recorded from all the test done to prove that COP-4 can be used to separate carbon dioxide from natural gas. Thus, several analysis are needed to identify the characteristics of the COP-4 adsorbent.

CHAPTER 2

LITERATURE REVIEW AND THEORY

The increasing CO2 concentration in the environment causing negative effects to the environment especially it will contributes high to the global warming issues. Many initiative has been taken including research to help reduce the global warming issue by considering the effective findings of capturing the high content of CO2 from many sources. Although at present, many conventional method has been developed and well established for CO2 capture from industrial processes but, the current challenges makes these conventional methods no longer effective and economical.

2.1 Key challenges in separating CO2 from Natural Gas Stream

Natural gas reserves commonly consist of mainly CH4, with contaminants such as CO2, N2 and water vapors. The CO2 content in natural gas stream can be as high as 80% and in certain cases, N2 gas is also present in significant amount depending on the type and location of the reservoir.

Among the main challenges in CO2 separation from the natural gas stream includes the high operating pressure, presence of water vapor in gas stream and N2 which can posed competitive adsorption to CO2. The higher content of CO2 in natural gas requires new technology that is robust in performance and able to handle the CO2 at high concentrations including the presence of water vapor and N2. Thus all the good adsorbent criteria need to be fulfilled in order to develop the new method to capture CO2 from natural gas. According to D'Alessandro, et. Al (2010), the close kinetic diameter of CO2 and N2 become one more challenge in separation hence separation base on molecular size may not be as effective as separation utilizing other chemical properties of the gases such as the moment and polarizability of the gases.

2.2 Adsorbent characteristics for carbon dioxide capture

The recent technologies in adsorption method become the new evaluation and solution to the current limitation technologies for separation of carbon dioxide form the natural gas. The good characteristics of the adsorbent are needed to enhance the efficiency in the carbon dioxide separation. All of the characteristics included:

a) High selectivity of CO2 from CH4

b) Good adsorption capacity for the target component, CO2

c) Fast adsorption kinetics

d) Good physical and chemical stability through adsorption / desorption cycle

e) Able to be regenerated by modest pressure or temperature swing to minimize operational cost

f) Robust performance in the presence of moisture and contaminant

g) Ordered structure is a priority

h) High gas capture and storage behavior

i) Low cost of solvent is always almost favored although overall capacity needs to be compromised, high surface area, Good sustainability (low cost) and high stability

2.3 Current research: Adsorbent type

At present, the effective carbon dioxide scrubbing without the big energy waste remains the crucial and big challenge for the fossil fuel burning industry (Patel, et al., 2012). Today the porous material have been promoted to be the long use of carbon dioxide adsorbent. The inexpensive porous polymers become the new feasible materials for capturing carbon dioxide from natural gas. The introduction of metal-organic framework (MOF) and crystalline covalent-organic framework (COF) have been rapidly developed as a gas storage and separation of carbon dioxide and natural gas because of the high specific surface area (Xiang, et. Al. 2012)

2.2.1 Covent-organic Framework (COF)

Covalent organic frameworks (COFs) represents exciting new type of organic porous materials, smart built with organic building units through strong covalent bonding. The crystal clear porous structure along with customized function of COF has offered superior potential in various applications, such as gas storage, adsorption, opto-

electricity, and catalysis (Peterson, et. Al, 2011). The reversibility of the covalent reaction dynamics, diversity of building blocks, and the retention of the geometry of three main factors involved in the design and synthesis of COFs reticular (Wissen, et. Al, 2005). Apart from that, COF is a light weight porous material; however its CO_2 capacity fail to meet the predicted theoretical performance of 9285mg g-1. Aside from that, the water instability of COF can only be slowed down by alkylating the organic struts. As for the cost, the production of material is higher as compared to conventional porous solids (Furukawa, et. Al, 2009).

2.2.2   Metal-organic Framework (MOF)

Metal-organic frameworks are a class of crystalline organic-organic hybrid compounds formed by coordination of metal clusters or ions with organic linkers. MOF have high surface areas and high pore volumes and are suitable for various kind of applications in energy storage, adsorption, hydrocarbon adsorption or separation, catalysis and others (Lee, et. Al, 2013). In terms of CO_2 separation, according to Figueroa, et. Al (2008), the high surface area to weight ration of MOF gives higher adsorption capacities towards CO_2 at moderate pressure. It is reported that the adsorption capacities of MOF may be up to 8.5 mmol/g at ambient conditions and 54.4 mmol/g at 50 bar and 25℃.
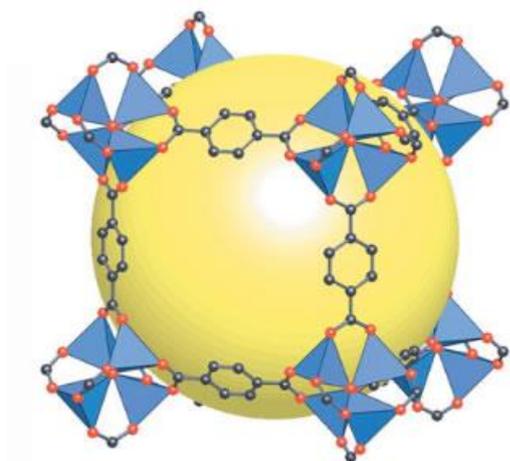
Figure 4. MOF, Porous structure

2.2.3   Covalent Organic Polymers (COP)

Generally, COP has cores and linkers that are bound via an organic coupling reaction. Most COPs are amorphous insoluble powders. The formation and structure of COP is shown in figure 2. The current research is about the porous covalent organic polymers

(COP) that have carbon dioxide adsorption capacities of up to 5616 mg/g that can stand at high pressure up to 200 bar and relevant industrial temperature (about 65 degree Celsius) (Patel, et al., 2012). Thus, the ability of COP to be robust at pressure up to 200 bar and 100℃ has opened the feasibility path for more application stages. Another significant feature of COP is that it is stable in boiling water at 100 ° C for at least one week without significant loss of surface area or CO2 capture capacity (Xiang, et. Al, 2012). This shows the exceptional capability of COP adsorbent for CO2 capture even in the presence of water vapors. Not only that, there is an emphasis on the ability of the COP to withstand high pressure and temperature conditions as it is necessary to meet the requirement in the natural gas industry. For CO2 separation from natural gas, the reported observed BET surface area was 2015 m2/g with CO2 adsorption of 594 mg/g at 18 bar and 298 K (Patel, et. Al, 2012). However, most of the reported literature shows the application of CO2 separation using COP for post-combustion process and few emphasize on application for separation CO2 from natural gas at high pressure condition. Xiang, et al, (2012) had research on CO2-CH4 separation using COP but the maximum pressure tested only up to 20 bars. Thus, this research focus on the investigation of CO2-CH4 separation with COP adsorbent at high pressure conditions.
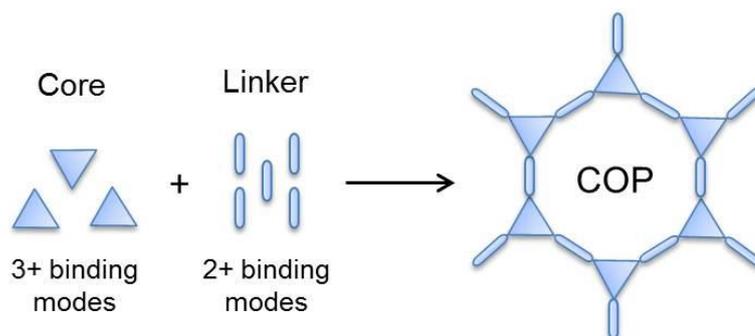
Figure 5. Covalent Organic Polymer (COP) formation

On the basis of the core, covalent organic polymers are classified as COP-1, COP-2, COP-3 and COP-4, shown in table 1:

Table 1: Table of type of adsorbent with respective cores

Adsorbent	Core
COP-1	1,3,5-tris(4-bromophenyl) ethynyl) benzene
COP-2	Tris (4-bromophenyl) amine
COP-3	1,3,5-tris (4-bromophenyl) benzene
COP-4	2,4,6-tris (4-bromophenyl)-[1,3,5] triazine

Source: Xiang, et. Al, (2012)

2.3 Characterization of Covalent Organic Polymers (COP-4)

In terms of characterization of COP-4, there are several tests assigned to confirm the structure of the COP-4 required and at the same the properties to separate the carbon dioxide from the natural gas. All the possible tests assigned based on literatures briefly shown below:

2.3.1 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is a technique used to obtain the infrared absorption spectrum, production or photoconductivity of solid, liquid or gas. FTIR technique is used in order to investigate several characteristics of the COP. Firstly FTIR is used to investigate the presence of typical stretching modes of CN heterocycles and characteristic breathing mode of triazine units. Plus, this technique used to confirm the absence of C-Br atoms in COP-4 to confirm all of three Br atoms on CC have been substituted (Patel, et. Al, 2012).

2.3.2 Scanning Electron Microscopy (SEM)

SEM basically practising in the surface, morphology and nature phase of sample. SEM is more preferred in order to know the amorphous surface of the sample due to their inferior details about the particular plane of phase impurities, defects in crystalline solid materials, and extended magnification range features. For the COP-4 synthesized, the SEM is used to confirm the nature phase of the sample either crystalline or amorphous.

2.3.3 X-Ray Diffraction (XRD)

XRD is a tool used to identify the crystal structure of atoms and molecules, which causes the crystal atoms incident X-ray beam to diffract into many specific directions. By measuring the angles and intensities of these diffracted beams, crystallographer can produce a three-dimensional picture of the density of electrons in the crystal. In this research, XRD is used to test the presence of crystallinity in the COP-4 structure. For this purpose, the angle must be set between 0.5 and 60 degree (Patel, et. Al, 2012).

2.3.4 Thermal Gravimetric Analysis (TGA)

According to information from Gnosys Global website (2013), Thermal Gravimetric Analysis or TGA is basically used to investigate the weight change of a material depending on the changes of temperature. All the changes both physical and chemical properties are measured as a function of increasing temperature with constant heat rate or as a function of time whereas with the constant temperature or mass loss. TGA is used in this research to test the thermo stability at high temperature. For test assigned to the COP-4, temperature condition must be set around 800℃ with constant heat rate at 10℃/min (Patel, et. Al, 2012). The result from the sample characterized need to be analysed in order to confirm the sample of COP-4 is hydrothermally stable.

2.3.5 Brunauer-Emmett-Teller (BET) Theory

BET theory aims to explain the physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique to measure the specific surface area of the material to explain the physical adsorption of gas molecules to solid surface. Thus, BET theory considering the multi-layered gas molecule adsorption, where it is not required for a layer to be completed before an upper layer formation starts.

2.3.6 Water Stability Test

In order to confirm the COP-4 sample synthesized is hydrothermally stable in water, the water stability test need to be performed. According to the Patel, et. Al (2012), the COP sample need to be dispersed in water (15 mL) and kept under the temperature of 100℃ for the period of 1 day, 3 days and 1 week. Then, the sample are withdrawn after the specified period of time, filtered and dried at temperature of 100℃. Next, the surface area after the test need to be measured and compared to the before test measurement to observe the loss of surface areas. This activity are important to prove the robust performance of the COP material.

2.4 Gas Sorption Measurement

It is reported in Xiang, et. Al (2012), the CO2 uptake for COP-4 is higher than other CO2 due to the high BET surface area. It is analyzed that, the gas uptake is depends on the surface area of the sample. Based on table 2, it is reliable that the COP-4 is the most attractive in terms of adsorption capacity other than other COPs.

For this research it is proposed to have the test at high pressure around 80 bar with different temperature (50℃ and 70℃). It is expected that the adsorption capacity will be in range of 200 – 500 mg/g and 25 – 78 mg/g for CO2 and CH4 respectively. The value of the gas uptake may be or will be same in range as reported by Xiang, et. Al (2012) since the COP-4 sample is develop using the microwave reactor. Summary of porosity, adsorption and separation properties of COPs shown in table 2:

Table 2: Table of summary of porosity, adsorption and separation properties of COPs

Material	BET SSA m^2/g	CO2 uptake mg/g	CH4 uptake mg/g	O2 uptake mg/g	N2 uptake mg/g
COP-1	827	194	29	3.9	10
COP-2	1986	585	76	6.3	42
COP-3	1869	569	74	5.4	37
COP-4	2015	594	78	6.1	70

Source: Xiang, et. Al, (2012)

CHAPTER 3

METHODOLOGY / PROJECT WORK

3.1 Experiment Methodology

The experiment methodlogy consists of two parts whereby the synthesis of COP-4 and characterization of COP-4.

3.1.1 Synthesis of COP-4

For the COP-4 type adsorbent, the synthesis is done in microwave reactor. 1,5-cyclooctadiene (cod, 0.50 mL, 3.96 mmol, dried over CaH_2) was added to a solution of bis(1,5-cyclooctadiene) nickel(0) ([Ni(cod)2], 1.125 g, 4.09 mmol) and 2,20-bipyridyl (0.640 g, 4.09 mmol) in dry di-methylformamide (DMF, 65 mL), and the mixture was stirred until completely dissolved. Then 0.785 mmol of organic linker, 1,3,5-tris((4-bromophenyl) ethynyl)benzene, tris(4-bromophenyl)amine, 1,3,5-tris(4-bromophenyl) benzene, or 2,4,6-tris-(4-bromophenyl)-[1,3,5] tri-azine, was added to the resulting purple solution. The reaction vessels were heated to 145℃ in 45 minutes under a nitrogen atmosphere. After cooling to room temperature, concentrated HCl was added to each deep purple suspension, which changed into a transparent solution. After filtration, the residue was washed with $CHCl_3$ (5 x 15 mL), THF (5 x 15 mL), and H_2O (5 x 15 mL). The products were then immersed in absolute ethanol for 24 hours. The ethanol-contained samples were evacuated with supercritical CO_2 in a SFT-100XW critical point dryer (SepTech Co., Ltd.) Finally, the dried sample of COP-4 is obtained, by degassing in vacuum at 200℃.
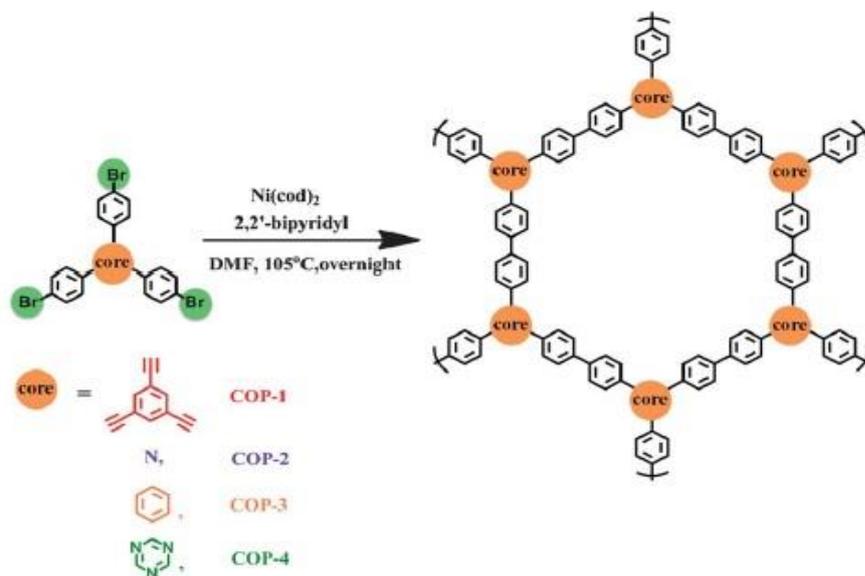
Figure 6. Formation and structure of COP-4 (core and linkers)

3.1.2 Characterization of COP-4

The characterization of COP-4 will be determined by undergo several test. The test will be conducted to determine the functional group in the COP-4, the total specific surface area, bonds and others. Several test need to be conducted are:

a) Fourier Transform Infrared Spectroscopy (FTIR)
b) Scanning Electron Microscopy (SEM)
c) X-Ray Diffraction (XRD)
d) Thermal Gravimetric Analysis (TGA)
e) BET Surface Area

3.2 Project Gantt Chart

Table 3: Gantt Chart and Key Milestone for FYP 1

No	Detail Work	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Project Title and Supervisor Allocation	■													
2	Understanding the Project	■	■												
3	Conducting Preliminary Studies on the Project			■	■										
4	Identifying Objectives and Scope of Study				■	■									
5	Investigating Synthesis Method of COP-4					■	■								
6	Investigating Equipment and Test required to verify synthesized COP-4 Characteristics						■	■							

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#	Task																
7	Plan Strategy to investigate COP-4 feasibility in CO2 separation from natural gas						🟥	🟥									
8	Preparation of Extended Proposal					🟥	🟥	🟥	🟥								
9	Submission of Extended Proposal								🟡								
10	Start of Project Work								🟥	🟥							
11	Proposal Defence									🟡							
12	Continuation of Project Work									🟥	🟥	🟥	🟥	🟥	🟥		
13	Preparation of Interim Reoprt									🟥	🟥	🟥	🟥	🟥			
14	Submission of Interim report															🟡	

Table 4: Gantt Chart and Key Milestone for FYP 2

No	Detail Work	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Continuation of Project Work – Investigating Synthesis Method of COP-4	■													
2	Conducting Test for the characterization of reactant and COP-4 sample	■	■												
3	Continuation of Project Work – Analyzing the results from several characterization test			■	■	■	■								
4	Preparation of Progress Report						■	■							
5	Submission of Progress Report								●						

No.	Task															
6	Preparation of other samples and conducting characterization tests						Red	Red	Red	Red						
7	Pre-Sedex									Yellow						
8	Preparation of Draft Final Report									Red	Red					
9	Submission of Draft Final Report										Yellow					
10	Submission of Dissertation (soft bound) and Technical Paper												Yellow			
11	Viva presentation													Yellow		
12	Submission of Project Dissertation (hard bound)														Yellow	

CHAPTER 4

RESULTS AND DISCUSSIONS

The sample of COP in white powder form is successfully synthesis using the microwave reactor. In order to confirm the sample is suitable before undergo the proposed test for the CO2 separation from natural gas (CH4), several characterization test need to be performed. Basically the characterization test will determine the sample is correct as COP-4 as compared to the literature by using different kind of characterization test including FTIR, SEM, XRD, TGA, and BET and Langmuir surface Area.

4.1 Fourier Transform Infrared Spectroscopy (FTIR) Test

FTIR test is required to determine the characteristic of the FT-IR absorptions of the functional groups that present in COP-4 sample. Several peaks need to be identified both in the spectra of triazine and COP-4. The peak in the region of 800 cm^{-1} shows the presence of triazine band. Whereas, the peak aroud the region of 500 to 690 cm^{-1} indicates the presence of the C-Br vibrations. In the triazine spectra, both peaks should be present in the spectra, while only the triazine peak should be present in the COP-4 spectra. This indicates the C-Br bond fully substitute during the reaction.

In the respective FT-IR spectra of triazine (reactant), several strong bands in the region of 1250 – 1335 cm^{-1} were identified. This strong bands corresponding to the typical strong stretching modes of the C-N heterocycles. Apart from that, the same several bands in the respective region also present in the FT-IR spectra of the COP-4 sample with more intensity than the bands in the triazine. Whereby, the area of the peak in the triazine spectra is bigger than the area of the peak in the COP-4 sample spectra. Additionally, the characteristic breathing mode of the triazine units is evident around region of 800 cm^{-1}in both triazine and COP-4 spectra. Though, the intensity and the area of the peak of the characteristic of triazine unit in COP-4 FT-IR spectra is bigger than triazine spectra.

Based on the table of characteristic IR absorption, the characteristic of C-Br stretching vibration need to be confirmed around a region of $515 - 690\ cm^{-1}$. Both FT-IR spectra shown the presence of the C-Br stretching vibration around that region. With the presence of these vibrations, likely not all bromine atoms have been substituted. This phenomenon is likely because the reactant of sample is not fully converted to the COP-4 probably due to the too short reaction time.

Figure 8 and 10 show the important stretching vibrations around the respective region based on the characteristic IR absorptions reference.

	Peak	Intensity	Corr. Inte	Base (H)	Base (L)	Area	Corr. Are
1	408.91	21.249	0.436	435.91	397.34	25.704	0.197
2	482.2	16.371	7.181	520.78	447.49	52.193	6.113
3	617.22	21.149	6.34	748.38	555.5	114.007	8.128
4	767.67	30.592	0.499	775.38	752.24	11.855	0.085
5	802.39	19.708	11.051	829.39	779.24	31.038	5.361
6	844.82	28.172	4.309	867.97	833.25	18.025	1.258
7	972.12	32.879	0.585	979.84	887.26	43.011	0.369
8	1006.84	25.547	7.197	1033.85	983.7	27.6	3.281
9	1068.56	24.693	5.499	1091.71	1037.7	30.845	3.047
10	1103.28	27.275	1.134	1122.57	1095.57	15.023	0.264
11	1168.86	23.617	4.134	1195.87	1145.72	30.117	2.198
12	1280.73	22.547	1.471	1300.02	1199.72	61.251	1.822
13	1361.74	8.871	13.8	1427.32	1303.88	99.828	20.235
14	1519.91	4.058	13.547	1554.63	1431.18	115.131	25.619
15	1589.34	8.443	4.813	1608.63	1558.48	48.125	4.857
16	1631.78	9.892	3.102	1743.65	1612.49	106.836	3.268
17	2384.02	11.452	0.192	2395.59	1747.51	526.585	3.775
18	3421.72	0.382	0.257	3444.87	2399.45	1405.78	1.336
19	3460.3	0.384	0.109	3734.19	3448.72	562.245	9.269
20	3776.62	2.737	0.044	3788.19	3738.05	78.022	0.262

Figure 7. Data of triazine FT-IR spectra
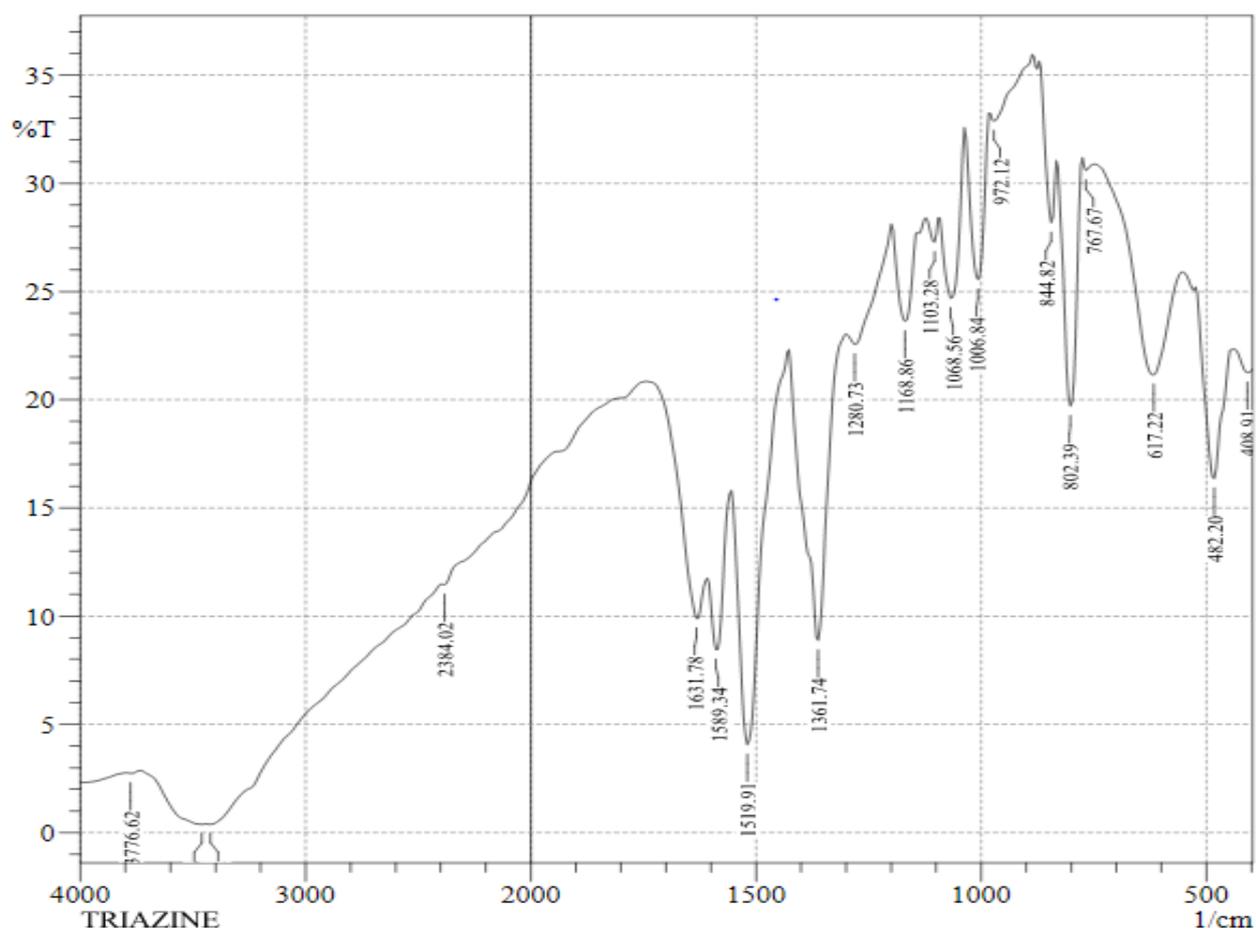
Figure 8. Graph of triazine FT-IR spectra

	Peak	Intensity	Corr. Inte	Base (H)	Base (L)	Area	Corr. Are
1	412.77	27.022	0.685	435.91	397.34	21.737	0.252
2	478.35	25.751	3.364	555.5	439.77	64.009	2.701
3	613.36	27.631	6.037	783.1	559.36	105.29	5.881
4	806.25	40.509	1.689	960.55	786.96	61.337	0.572
5	1014.56	44.513	0.599	1026.13	975.98	17.252	0.207
6	1145.72	40.952	0.144	1149.57	1029.99	44.836	0.8
7	1176.58	40.266	0.714	1203.58	1153.43	19.667	0.238
8	1373.32	26.888	7.94	1411.89	1207.44	92.015	4.82
9	1508.33	25.357	7.145	1539.2	1450.47	46.722	3.948
10	1627.92	16.061	15.99	1755.22	1543.05	127.65	23.125
11	2295.29	23.828	0.225	2306.86	1759.08	305.138	4.006
12	2384.02	22.123	0.421	2399.45	2310.72	56.694	0.261
13	3425.58	0.958	0.413	3444.87	2403.3	1031.875	1.042
14	3464.15	0.956	0.376	3734.19	3448.72	445.877	9.322
15	3772.76	7.309	0.172	3799.77	3738.05	69.798	0.356

Figure 9. Data of COP-4 FT-IR spectra

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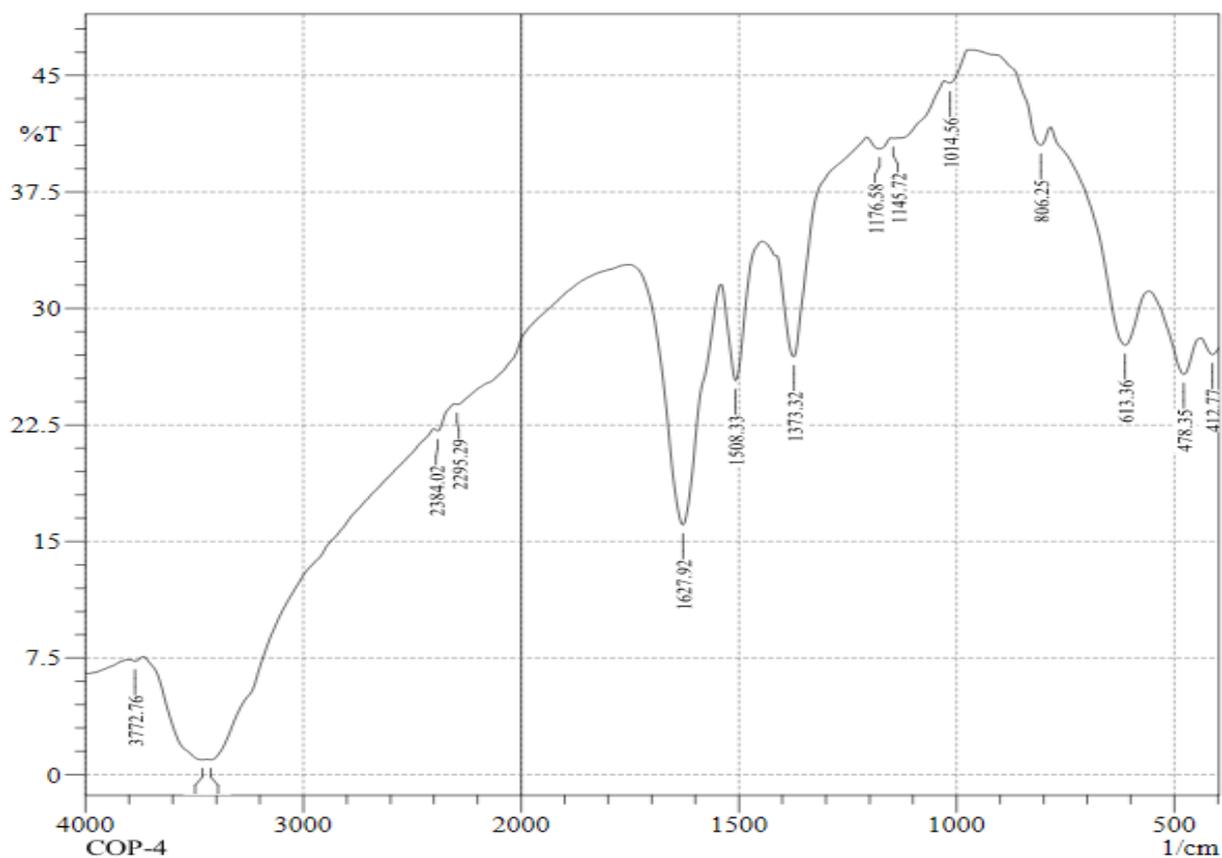
Figure 10. Graph of COP-4 FT-IR spectra

4.2 Scanning Electron Microscopy (SEM) Test

The SEM test is required to determine the phase structure of the triazine (reactant) and the COP-4 sample (product). Generally, most polymers from amorphous material. According to the result report from SEM test, the triazine is likely amorphous in phase as the arrangement of the structure of the molecules are complex and they cannot easily rearrange themselves to form the crystalline structure. As in crystalline matter, everything is generally oriented in identical repeating matter whereas the amorphous material structure everything is irregularly oriented and does not have spacing. Based on literature, some characteristic of the amorphous material included the arrangement of the long-chained molecules with no long-range order (as in figure 11).

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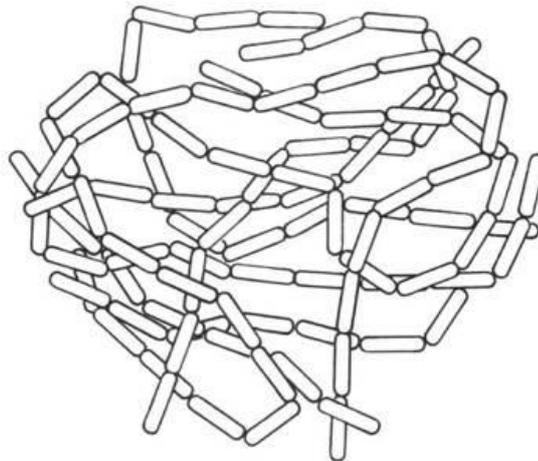
Figure 11. Amorphous long-chained arrangement molecules with no long-range order

SEM result reported that by varying the wavelength to determine the structure of the triazine and COP-4, the structure clearly indicates the characteristic of amorphous material. Likely, hypothesis can be made as the reactant of the COP-4 sample is amorphous, the product also is amorphous.

Wavelength Range (μm)	Structure
100	
40	

| 10 | |

Figure 12, SEM characterization of triazine

Wavelength Range (μm)	Structure
100	
40	

| 10 | |

Figure 13. SEM characterization of COP-4

4.3 X-ray Diffraction (XRD) Test

The powder of sample COP-4 synthesized is undergo the pattern test using the X-ray Diffraction (XRD) to analyze the nature phase of the sample either amorphous or crystalline. Pattern of COP-4 sample is acquired from 0.5 to 60° by a Rigaku D/Max-2500 Micro area X-ray diffractometer. Based on the result pattern, two sharp peaks has been observed indicates that the presence of the crystallinity in the sample around the region of 40 to 45°. Although the result from the SEM for the triazine confirm that the reactant used for synthesized the COP-4 sample is in amorphous phase, but the result of the XRD shows the product is semicrystalline as the existence of the crystal structure in the sample. This nature are likely has been affected by the mistakes in synthesized the sample. The most probably cause is the temperature for the synthesis is not suitable while preparing the sample. Temperature become the key role in determine the reaction is complete and all the raw materials is converted to the product required. As the temperature is not suitable, this will cause the decomposition of the several raw materials due to the poor ability to withstand to the certain high temperature.
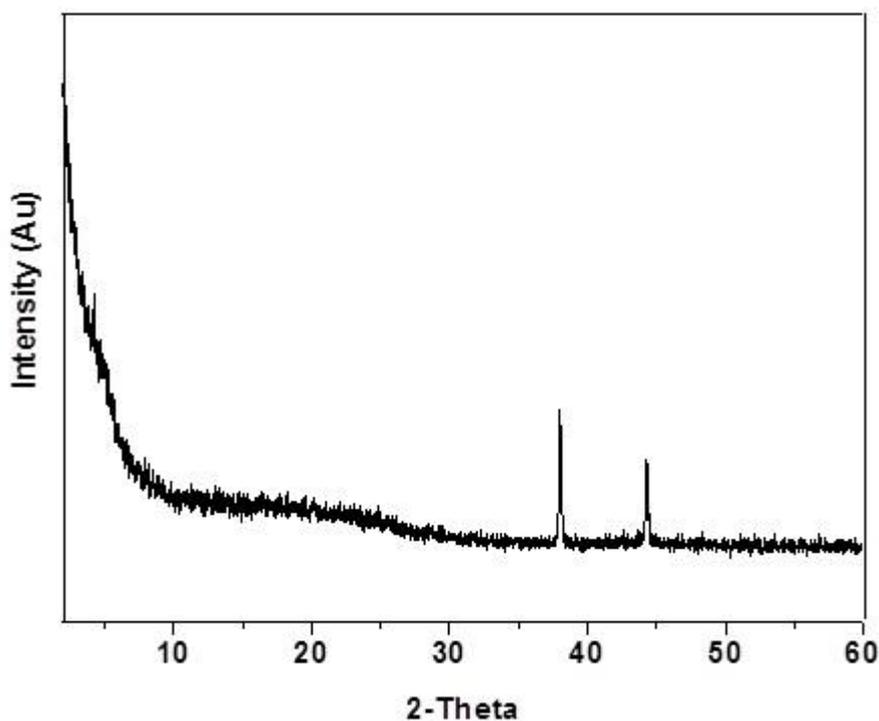
Figure 14. Powder X-ray diffraction (XRD) patterns of the COP-4 sample synthesized is acquired from 0.5 to 60°

If compared the X-ray diffraction pattern of COP-4 samples (figure 14), to the literature of the powder X-ray diffraction pattern of the COP sample (figure 15), there will be no crystallinity observed in the graph. Likely, the pattern of the COPs from literature is fully amorphous.
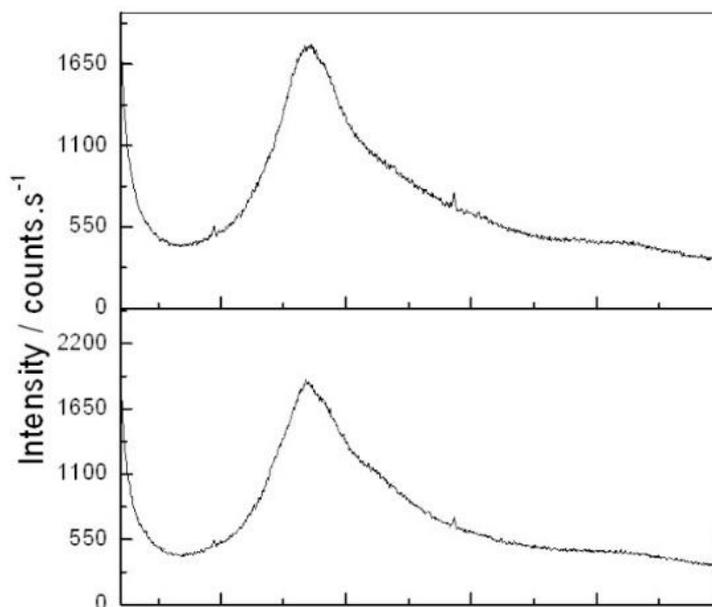
Figure 15. Powder X-ray diffraction (XRD) patterns of the COP samples from literature is acquired from 0.5 to 60°. No crystallinity was observed for both COP samples.

Source: Patel, et. Al, 2012

4.4 Thermal Gravimetric Analysis (TGA) Test

Thermo gravimetric analyses of triazine and COP-4 sample is performed up to 800℃ at a heating rate of 10 ℃min^{-1} in N2 environment. From the analysed report, triazine and COP-4 sample started to decompose at around 350℃ and 370℃ in dinitrogen atmosphere. The decomposition rate is determine with the indicator of the loss on weight of the sample. These thermal decomposition is important to verify the ability of the triazine and the COP-4 sample is thermally stable. The almost same temperature for the decomposition of the triazine and COP-4 sample indicates that the triazine has almost completely react to form the COP-4 sample. According to the analysis, the COP-4 is reliable for the separation of the CO2 from natural gas stream below the temperature of its decomposition in natural gas stream.
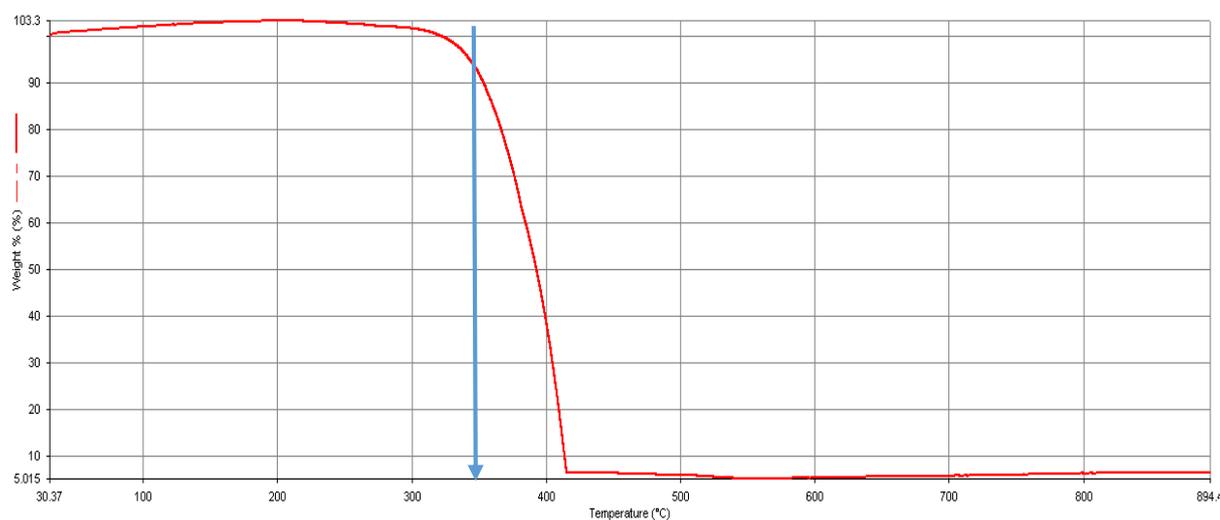
Figure 16. Thermogravimetric analysis of triazine (reactant) in dinitrogen environment

Note that the blue arrow color indicates the temperature of decomposition of the triazine (reactant) aprroximately at 350℃.
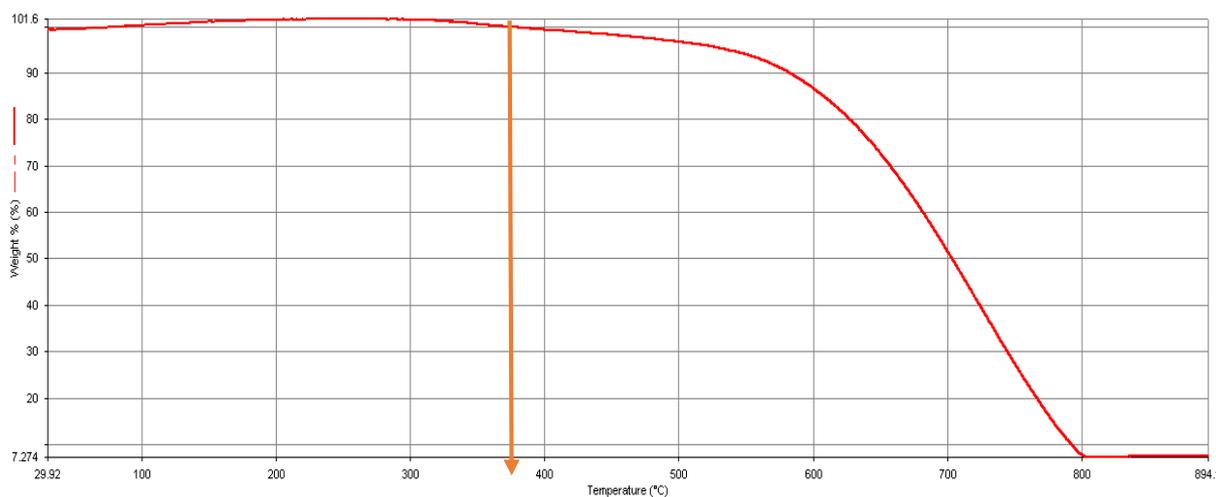
Figure 17. Thermogravimetric analysis of COP-4 sample (product) in dinitrogen environment

Note that the orange arrow color indicates the temperature of decomposition of the COP-4 sample (product) aprroximately at 370℃.

4.5 BET and Langmuir Surface Area Test

Generally, the BET surface area test aims to explain the physical adsorption of the gas molecules on a solid surface and server the important aspect to determine the specific surface area measurement of the material. In order to determine the porosity sample COP synthesized structure, nitrogen adsorption isotherm were obtained with a Micromeritics ASA 2020 that measured the surface area and porosimetry analyzer. The results from the analyzer are present in pore parameters that included the BET and Langmuir surface area, pore size and pore volume. The micropore surface area of the sample was determined by the t-method. Generally, the slope of the t-plot is directly proportional to the surface area of the sample. The capillary condensation inside the pores causes the upward deviation from the linearity of the plot while the initial slope is proportional to the micropore surface area. From the analysis, the sample of COP has the t-plot micropore area of 714.5421 m^2/g.
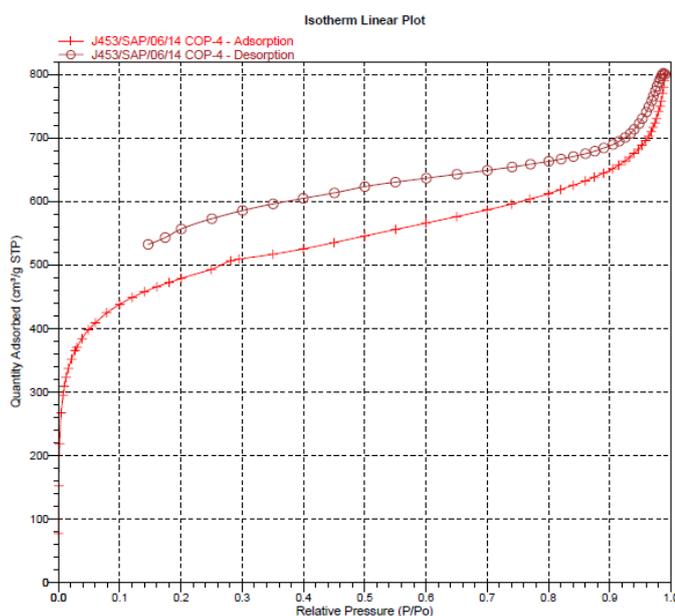
Figure 18. Isotherm Linear Plot

Based on Figure 18, it can be observed that, at low or initial $\frac{P}{P_o}$ the rounded knee plot indicates approximate location of the monolayer formation as the slope is proportional to the micropore surface area. Next, closure at $\frac{P}{P_o} \approx 0.4$, it indicates the presence of small mesopores as the hysteresis would stay open longer but for the tensile-strength-

failure of the nitrogen meniscus. From the point of $\frac{P}{P_o} \approx 0.7$ and above, the low slope region in middle of the isotherm indicates first few multilayer adsorption. The upward deviation from the linearity caused by the capillary condensation in mesopores and micropores.

According to the analysis report too, the pore size of adsorption and desorption by BET are 29.7121 A and 31.2540 A respectively. According to these number, it can be concluded that the sample of COP is mesopore surface area same as reported in literature by Patel, et. Al (2012) . The analysis report gives the information included the relative pressure range that used in the test that is $0.06 - 0.28$ approximately. Using the available information in the result report, the BET surface area can be measured using the BET equation.

Table 5: BET Surface Area Report

Relative Pressure ($\frac{P}{P_o}$)	Quantity Adsorbed (cm^3/g STP)	$\dfrac{1}{\left[V\left(\frac{P_o}{P}\right) - 1\right]}$
0.060049419	408.2751	0.000156
0.078918747	424.1403	0.000202
0.100193231	437.7226	0.000254
0.120232983	448.4433	0.000305
0.140417172	457.3775	0.000357
0.160653530	465.3307	0.000411
0.180846730	472.1036	0.000468
0.200630945	478.4647	0.000525
0.249377566	492.5921	0.000674
0.281115141	506.1849	0.000773
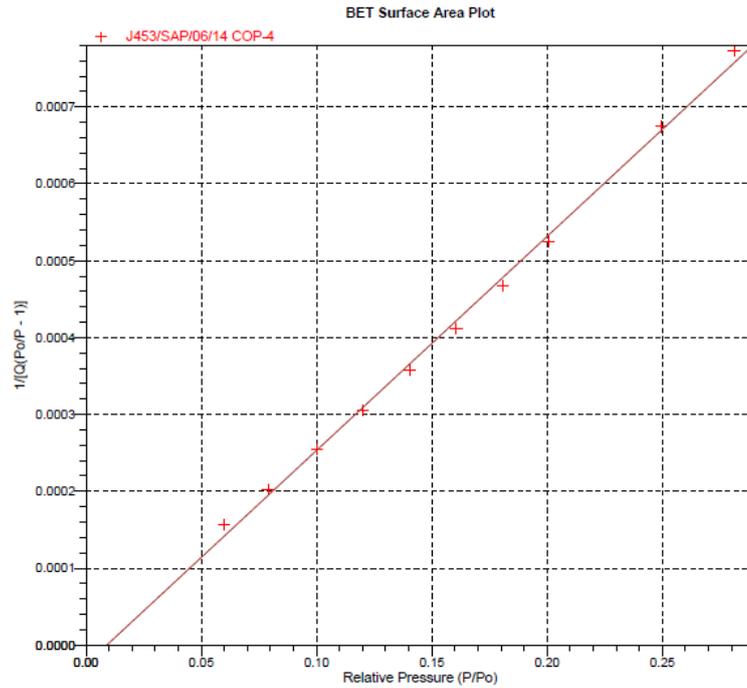
Figure 19. BET Surface Area Plot

$$\frac{1}{V\left[\left(\frac{P_o}{P}-1\right)\right]} = \frac{c-1}{v_m c}\left(\frac{P}{P_o}\right) + \frac{1}{v_m c}$$

Whereby,

P and P_o indicates the equilibrium and saturation pressure of adsorbates at the temperature of adsorption respectively.

V is the adsorbed gas quantity

v_m is the monolayer adsorbed gas quantity

c is the BET constant

By the application of the BET theory equation, the value of v_m and c need to be determined first by using the equation of;

$$v_m = \frac{1}{A+I}$$

$$c = 1 + \frac{A}{I}$$

Whereby,

A indicates the slope of the BET linear plot graph and,

I is the y-intersection on the plot

According to the result report, the value of $A = 0.002784 \ g/cm^3$ while $I = -0.000025 \ g/cm^3$. After the calculation using the equation sated above, the value of $v_m = 362.5165 \ cm^3/g$ and $c = -109.520007$. Using the BET equation by substituting all available information, the value of adsorbed gas quantity, $V = 506.1849 \ cm^3/g$ at $\frac{P}{P_o} = 0.28$. A total surface area S_{Total} and a specific surface area S_{BET} are evaluated using following equation:

$$S_{Total} = \frac{(v_m N S)}{V}$$

$$S_{BET} = \frac{S_{Total}}{a}$$

Whereby,

N = Avogadro's Number

S = Adsorption cross section of the adsorbing species $= 0.1620 \ nm^2$

V = molar volume of adsorbent gas

a = mass of adsorbent (g) $= 0.0193 \ g$

Based on calculation the $S_{BET} = 1578.1066 \ m^2/g$

Table 6: Summary of BET Surface Area analysis

Sample	BET SSA (m^2/g)	Langmuir SSA (m^2/g)	t-Plot Micropore Area (m^2/g)	Pore Volume (Adsorption) (cm^2/g)	Pore Volume (Desorption) (cm^2/g)	Pore Size (Adsorption)	Pore Size (Adsorption)
COP-4	1578.0796	2344.8204	714.5421	1.172221	1.233052	29.7121 A	31.2540 A

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

The aim of this research is to investigate the adsorbent capacity of the COP-4 prepared in a microwave reactor. In order to achieve the objective of this project, 2 major parts need to be focused consist of the synthesis and characterisation of COP-4. For the synthesis of COP-4, all the steps in methodology need to be followed in order to achieve desired product. For this purpose, the reaction takes place by using the microwave reactor instead of using the conventional method as reported in available literature. Secondly, the characterisation of the COP-4 using several characterisation tests included FTIR, TGA, SEM, XRD, and BET surface area. These tests are required to confirm the COP-4 has been correctly synthesis.

There are some deviations from the results reported in literature due to the mistakes in preparing the sample. Not only that, due to the time constraint and the availability of the gas adsorption test equipment, the last part of the project cannot be done using the COP-4 sample developed. Hence, this project required a lot of time and it is dealing with the advanced equipment in order to achieve full results. But, based on the results in this project, it is reliable that COP-4 has been developed as the characterisation test results are tally with the literature.

It is recommended to run the gas adsorption capacity test using a Rubotherm Magnetic Suspension Balance. This advanced equipment was utilized for high pressure CO_2 adsorption capacity determination. In a typical high pressure CO_2 adsorption-desorption isotherm measurement, approximately 0.25 g of COP need to be placed on a holder. The proposed test will take place at 80 bar for 50℃ and 70℃ respectively.

1) Pure gas adsorption of CO_2 (Percentage Ratio of CO_2:CH_4 – 100:0)
2) Pure Gas adsorption of CH_4 (Percentage Ratio of CO_2:CH_4 – 0:100)

3) Binary gas adsorption of CO_2/CH_4 at different composition, temperatures and pressures

Based on these three characteristics, different composition of CO_2 and CH_4 are selected based on the several temperatures and pressures conditions as shown in table 7:

Table 7. Table of test composition ratio of CO2 to CH4

Composition Ratio (%)	
CO2	**CH4**
70	30
55	45

By taking into account of the time constraint and the feasibility of the students in handling the project, hopefully, this adsorbent development manage to give even small contribution in oil and gas industries in future.

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APPENDICES

Figure 20. Microwave reactor

Figure 21. Sample mixture before HCl addition
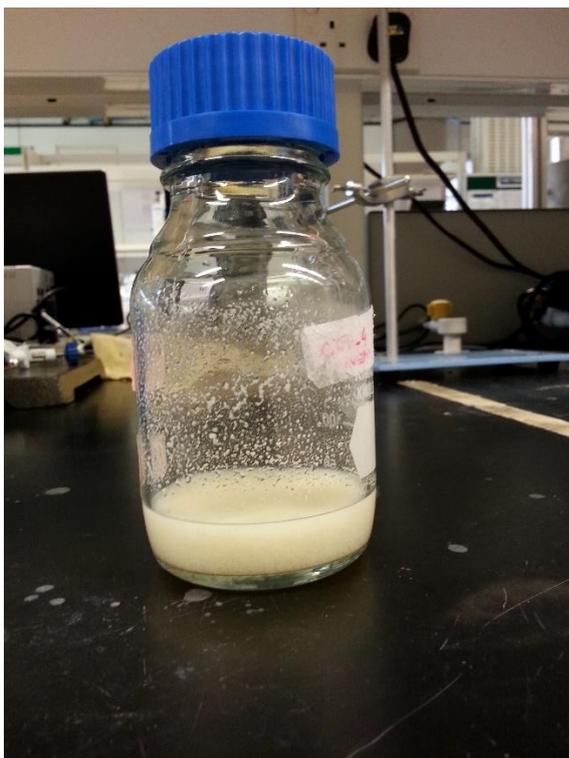
Figure 22. Sample mixture after HCl added (before filtration)

Figure 23. COP-4 sample