SEPARATION OF CO_2/CH_4 USING COVALENT ORGANIC POLYMER ADSORBENT

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CHEMICAL ENGINEERING

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by

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14637

Dissertation submitted in partial fulfilment of
the requirements for the
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Universiti Teknologi PETRONAS,

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CERTIFICATION OF APPROVAL

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Approved by

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(Dr. Nurhayati Bt Mellon)

UNIVERSITI TEKNOLOGI PETRONAS
BANDAR SERI ISKANDAR, PERAK
September 2015

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible of the work submitted in this project, that the original work is my own except as specify in the reference and acknowledgments, and that the original work contained herein have not been undertaken or done by unspecified sources or persons

GUADALUPE BINDANG MANGUE

ABSTRACT

Nowadays, natural gas is considered as one of the cleanest, safest gas and the most useful form of energy in our daily lives, its demand is increasing worldwide. One of the reasons the demand is still increasing is the presence of high amount of CO_2 in natural gas. Removing bulk amount of CO_2 from natural gas at high temperature, and low cost, it is still remaining as a major challenge for human beings. Different methods had been used such as membranes and others adsorbent such as zeolites but some of them are very expensive and limited. In 2012, Patel discovered an adsorbent called COP-1 which can capture CO_2 better than others material. Patel's COP-1 selectivity is 5616mg/g and it is stable at higher temperatures and higher pressures (200bars). Although COP-1 presents better characteristics patterns for CO_2 capture, the material is still under studies and it is limited because Patel concentrated only in CO_2/N_2 separation. The main objective of this paper was to synthesize and characterize COP-1 under ambient conditions for CO_2/CH_4 separation. In order to achieve that objective, different techniques (FT-IR, TGA, BET surface area, pore size, and SEM) were used to verify that the synthesized material is COP-1. In overall, the characterization results show similarities to Patel Results (2012) in terms of functional group, linkage and absence of crystallinity with some differences such as the surface area. The surface area of this paper ($11.944m^2g\text{-}^1$) was lower compared to Patel area($168m^2g\text{-}^1$). Using BELSORP pure gas adsorption of CH_4 (0.1176mmol/g) and CO_2 (0.6 mmol/g) were obtained. The selectivity obtained in this paper was 5.1g/g (CO_2/CH_4). Patel's COP-1 is stable at 360^0C in N2 environment and 285^0C in air while the synthesized COP-1 was stable at 220 ^0C in both environments. Based on the results obtained, the synthesized COP-1 is useful for liquefied natural gas (LNG) industries because LNG stack temperature(180^0C) is lower than 220^0C. The objective was achieved.

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CHAPTER 1

INTRODUCTION

1.1 Background Study

Nowadays, the manufacturers and the consumers of Natural Gas consider it as one of the cleanest and safest gas. Apart from being one of the cleanest and safest gases, it is also considered as one of the most useful forms of energy; by being so important and useful in our daily lives, the demand of natural gas is increasing all over the world.

In 2012, Malaysia became one of the major players in the natural gas industry and the second largest exporter of liquefied natural gas after Qatar. That year Malaysia exported 23.1 million metric tons of liquefied natural gas (LNG) (Prisecaru & Al Dulaimi, 2014). Rising domestic demand for natural gas as well as LNG export contracts puts great pressure for Malaysia to meet the needs in the coming years (Memon et al., 2014).

In 2012, Ali et al identified that, the proven natural gas reserves in Malaysia are the 3rd largest in Asia-Pacific region with around 83 trillion cubic feet, nevertheless some of these reserves contain high CO_2 gasses as part of the impurities, making the harvesting of natural gas with economic value a major challenge. In the same year, Shimekit and Mukhtar stated that, it is essential to remove the CO_2 gasses from the natural gas as it reduces the conversion rate and energy content of natural gas.

In 2010, Ahmed concluded that, CO_2 is capable of causing pipeline corrosion problems in the presence of traces of water during gas transportation during gas transportation. By removing CO_2 from natural gas that will optimize the volume of natural gas that is required to be transported without impurities.

CO_2 removal from natural gas is necessary to combat emission of greenhouse gasses to the atmosphere for environmental purpose as a step to combat global warming (Patel et al., 2013). In addition to that in 2012, Shimekit and Mukhtar stated that, removing CO_2 serves as compliance to quality standard specifications as a consumer fuel where CO_2 composition in fuel in most countries should be 2% and below.

In Malaysia, most of their offshore reserves contain CO_2. The range of CO_2 content in reservoirs is between 40 to 74 mole percent. It is required to remove the CO_2 from natural gas but unfortunately the current technology of CO_2 gas removal from natural gas has limitations. The current method can only remove CO_2 up to 40 mol %.

There are so many fields in Malaysia but K5 is the largest reserve in Malaysia and the second highest content of CO_2. K5 contains 4 trillion cubic feet of natural gas in reservoir but its natural gas contains 70% of CO_2 (Ahmad, 2010).

After several studies and research of CO_2 content in natural gas, it was found that Malaysia is not the only country that is suffering from having elevated amount of CO_2 in the natural gas. There are others countries that are suffering from the same problem such as South East Asia (SEA), Asia Pacific etc.

The problem of having CO_2 in natural gas reserves started long time ago. Since then, in order to remove CO_2 from natural gas there have been different approaches and people has used different technologies such as membrane, absorption and adsorption. All these technologies are facing serious limitations when it comes to large amount of CO_2 removal.

Currently, membrane technologies are known to be effective in CO_2 / gas separation between 5 to 40 mol% only and majority of the membranes are subject to gas losses, require pre-treatment of feed gas, sensitive to temperature and pressure variations (Ahmed, 2010). As for absorption, the most common solvent used is aqueous amine, which is only effective for removal of CO_2 concentration ranging of 20 to 50% with drawbacks such as lifetime of amine, vulnerable to degradation through oxidation, high equipment corrosion, high thermal regeneration cost and requirement of large absorber volume (Rufford et al., 2012). Since the current technology could not remove more than 50% of CO_2 from natural gas thus it is a grave situation to find new technologies which can remove bulk amount of CO_2 from natural gas. New advancement in adsorption technology attempted into new materials that could achieve the separation, which are Covalent Organic Framework (COF), Covalent Organic Polymer (COP) and metal-organic framework (MOF). Among these three different materials, COP has very high adsorption capacity of CO_2 (up to 5615 mg/g for COP-1) as well as high thermal and water stability (Patel et al., 2012). Therefore, COP-1 is considered as a promising material for the adsorption of CO_2. Therefore, the objective of this research is to synthesis and characterizes COP-1 to validate the material synthesized and then compare them to the results by Patel (2012) as well as to add on to the research library on morphology of COP-1 and fill the research gap on CO_2 adsorption capacity at ambient conditions. This paper will serve as a starting point for an extensive research on selectivity of CO_2 / CH_4 binary gas with high amount of CO_2 at high operating conditions similar to natural gas applications. This paper will not be able cover the wider scope due to time limitation.

1.2 Problem Statement

Currently, CH_4 is one of the most useful forms of energy in our daily lives and the demand of natural gas is increasing all over the world. Most of SEA countries such as Malaysia and Asia pacific countries reservoir are containing natural gas mixed with high amount of CO_2. Since the demand is worldwide and there are many gas reservoirs containing high amount of CO_2, for that reason it is required to develop new technologies that can separate bulk amount of CO_2 from natural gas. Based on the recent studies, COP adsorbent apparently shows favorable characteristics to achieve the removal of high amount of CO_2 from methane. Though COP is a new material and it is still under research stage.

There are many types of COPs but among all of them, COP-1 by Patel (2012) is still the best option for this research paper. COP-1 adsorption capacity of CO_2 is up to 5615 mg/g; apart from offering a high selectivity, COP-1 has the highest thermal and water stability compare to others COPs. Though COP-1 provides the best selectivity of CO_2 but the research information on this material was concentrated on CO_2 / N_2 separation (Patel et al., 2012).

1.3 Objective

The main objective of this research paper was to calculate the selectivity of CO_2/CH_4 separation using COP-1. In order to achieve that objective, COP-1 synthesizing and characterization under ambient conditions was required or it was done.

1.4 Scope of study

In order to achieve the main objective of this project the following sub-steps were required:

1.4.1 Synthesis of COP-1

The author had to develop and plan an experimental procedure that was able to perform synthesis and purification of COP-1.

1.4.2 Characterization of COP-1

According to Patel, it is necessary to validate COP-1 characteristics and to contribute the data for morphology as well as gas sorption measurements at atmospheric pressure to the research library. So in order to validate COP-1 characteristics the following techniques were required: NMR, FT-R, XRD, CHN, EDX, TGA, BET surface area and pore size. It is very important to ensure that the Morphology is studied through FESEM.

CHAPTER 2

LITERATURE REVIEW

2. 1 Adsorbent for CO_2 capture

Removing high amount of CO_2 from natural gas is still remaining as a major challenge for researchers and natural gas producers or industries. Different technologies such as membrane, absorbent, adsorbent, etc. has been developed in order to remove CO_2 from natural gas. Most of these techniques have some drawbacks and limitations when it comes to a bulk amount of CO_2. Recent adsorbent material advancement is providing possible solution for the limitation of the current technology in removing bulk amount of CO_2 from a gas mixture.

In 2012, Rufford and Yu stated that, the desirable characteristics of adsorbent for CO2 capture from natural gas are as follows:

I. High selectivity of CO_2 from N_2. Good adsorption capacity (gas capture and storage) for the target component, CO_2.
II. High surface area of adsorbent.
III. High hydro and thermal stability.
IV. Low cost of production, operational cost, capital cost and good sustainability.
V. Good physical and chemical stability through adsorption / desorption cycle.
VI. Generable by modest pressure or temperature swing to minimize operational cost.
VII. Robust performance in the presence of moisture and contaminant. Fast adsorption kinetics.

There are many types of adsorbents such as activated carbon, zeolites, covalent organic frameworks, metal organic framework, covalent organic polymer, etc. Zeolites can capture CO_2 easily with low energy but they are not stable in water.

Activated carbon can capture bulk amount of CO_2 than zeolites at high pressure but its CO_2/N_2 selectivity is low. Based on that reason, the most featured in CO_2 capture are Covalent Organic Polymer, Covalent Organic Framework and Metal Organic framework. These three different materials will be further discussed and compared in detail in order to show why COP is better than the rest adsorbent.

2.2 Adsorbent of CO_2 capture: COF, COP and MOF

2.2.1 Covalent Organic Framework (COF)

Covalent organic frameworks are linked together by strong covalent bonds; they are produced from organic monomer and they have a crystalline structure. In 2012, Dawson et al stated that, chemical tuning of covalent organic framework could alter the pore size to increase selectivity. In 2013, Chang et al stated that, the storage capacity of CO_2 can be determined by the porosity of the material.

According to Patel et al, COF is a light weight porous material but its CO_2 capacity does not meet the predicted theoretical performance of 9285mg/g. A relatively high CO_2 capacity achieved by COF-102 is 1200 mg/g at 55 bars and 25°C; COF-102 cost approximately $88598/kg (Ding & Wang, 2013). Apart from that, in 2012 Patel et al also stated that, the instability of covalent organic framework in water can only be slowed down by alkylating the organic struts. Referring to the cost, they also concluded that the production of material is higher as compared to conventional porous solids.

2.2.2 Covalent Organic Polymer (COP)

Covalent organic polymer is an amorphous porous polymer. Apart from being an amorphous porous polymer, it is also known as an adsorbent capable of being synthesized by extensive synthetic techniques or procedures. So, COP is capable of producing different structures for better characteristics improvement. From low density of material higher porosity was achieved. To continue lowering the density of COP, lighter elements of the periodic table are selected namely C, H and N (Chang et al., 2013). After doing all the analysis and test, Patel et al concluded that, COP-1 is the best CO_2 adsorbent among the COPs. COP-1 is selected as the best adsorbent of CO_2 capture because at 200 bar and 65°C its CO_2 adsorption capacities is up to 5616mg/g. Apart from having the highest selectivity, COP-1 is also stable in water at 100°C for at least one week without major loss of surface area or CO_2 capture capacities and cost approximately $ 9.8/kg

In 2012, Xiang Z, Han and Lu conducted and experiment and they concluded that the lithium decoration definitely improves H_2, CO_2, and CH_4 uptakes of the synthesized materials. In particular, at T = 77 K and ∼1 bar, the H2 uptake of lithium-modified COP material is 1.67wt%, which is increased by ∼70.4% compared with the unmodified compounds

In 2012, Patel et al has confirmed that it is possible to recycle COP up to at least five cycles using sample of H2 and CO_2. He also stated that modifying sorbents for improving carbon dioxide capture lead to surface area loss or accessibility of pores.

Since natural gas industries are operating at high pressures and high temperatures, studies have highlighted COP's ability to withstand high pressure and temperature conditions. For time being, pre-combustion applications require pressure up to 30 bars, post-combustion application at less than 6 bars and temperature of 40°C to 60°C (Patel et al., 2012). Therefore, the ability of COP to withstand pressure up to 200 bars and 100°C in water has opened the viability path for more application stages in the natural gas industry. According to Patel et al (2012), COP is also stable at temperature up to 350°C in air and 450°C in N2. Moreover, COP is easy for storage. COP does not show signs of degradation when stored under ambient atmospheric conditions even after several months with no care given (Patel et al., 2012).

In 2012, Xiang et al conducted an experiment on adsorption selectivity of COP-1 for CO_2/CH_4 separation. After conducting the test and analysis the selectivity of CO2/CH_4 was found to be between 4.1 and 5.0 at a CO_2: CH_4 ratio of 15: 85 at pressure range of 0 bar to 40 bars. Nevertheless, the experiment did not cover the ratio of CO_2: CH_4 at bulk amount of CO_2.

2.2.3 Metal Organic Framework (MOF)

In 2010, D’Alessandro et al stated that, metal organic framework is a microporous crystalline where organic bridging ligands are coordinated to metal-based nodes. The size of pore diameters is between 3 and 20 Å and the pore diameters are uniform. There are many types of metal organic framework (MOF) but according to D’Alessandro et al the MOF-177 has the highest adsorption capacity of CO_2 of 33.5mmolg-1 at 32 bars and surface area of 4500 m2g1.

In 2010 Jung et al carried out a study on MOF-177. Based on their results the CO2 adsorption of MOF-177 was 1315mg/g at 30bar and 298K.

The BET surface area of MOF was 4898 m2 g-1. MOF has some positive characteristics such as high void volume and high surface area for CO_2 capture capacity; yet, it has some disadvantages particularly for applications of CO2 removal in natural gas industry. One of the main MOF disadvantages is that MOF are less stable in oxygen and moisture due to metal clusters, where the condition is present in the natural gas industry. According to Xiang et al (2012) the performance of MOF in terms of CO_2 adsorption can decrease up to 50% in wet conditions Another disadvantage is that MOF are ideal in operation only at high pressure but low temperature conditions (Yu, 2012). MOF-117 cost approximately $65000/kg. From the literature screening the drawbacks of COF and MOF are clear stated. Based on these disadvantages the credibility of MOF and COF for CO_2 capture from natural gas industries was very low.

TABLE 2.1 Characteristics of best material that capture CO_2

	COF-102	COP-1	MOF-177
Cost	\$8898/kg CO_2 removed (10.1039/C2JM30761)	Cheap Only \$9.8/kg CO_2 removed (10.1039/C2JM30761H)	High \$65000/kg CO_2 removed (Yu,2012)
CO2 Adsorption capacity and pressure test feasibility	1200mg/g @ 55bars and 25°C (Ding & Wang, 2013 and Patel et al, 2012)	5616mg/g @200 bars, 65°C (10.1039/C2JM30761H)	1315 mg/g @ 30 bars, 25°C (Jung et al,2010)
Water stability	Not stable Its instability can only be slowed down by alkylating the organic struts (Patel et al,2012)	High stability Stable in boiling water for at least a week (Patel et al,2012)	Not stable performance decrease up to 50% in presence of moisture (Xiang et al,2012)
Pressure feasibility proven up to	55 bars. (J.Master.chem.,2012,22,8431)	200 bars (J.Master.chem.,2012,22,8431)	32 bars. (Yu,2012)
Thermal stability	Stable up to 450°C	In N_2 atmosphere it is stable up to 360°C but in air it is stable up to 285°C	Stable up to 25°C (Yu,2012)
Surface area	3620 m^2/g (J.Master.chem.,2012,22,8431)	168 m^2/g (Patel et al)	4898 m^2/g (Jung et al, 2010)

2.3 COP-1 Characterization techniques.

Currently COP-1 is known as the best adsorbent for CO_2 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:

2.3.1 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

2.3.2 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.

2.3.3 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.

2.3.4 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.

2.3.5 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).

2.3.6 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.

2.3.7 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.

2.3.8 FESEM - Field emission microscopy

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

TABLE 2.2 Patel Characterization tests results

Technique used	**Results Expected by Patel et al (2013)**
C-NMR H-NMR	C-chemical shift at 44.2ppm, Present at 164.7ppm of C-NMR spectra Chemical shift at 3.2ppm
FT-IR	Several strong bands in the 1200-1600 cm-1 region, Evident around 800cm-1 region. Absence of characteristic C-Cl stretching vibration at 850cm-1
BET surface area	168 m2 g-1
CHN	Theoretical C – 52.2 % H – 4.4% N – 43.5%
XRD	No crystallinity structure observed
TGA	Starts decomposing at 285°C in air and 360°C in N_2 atmosphere

CHAPTER 3

METHODOLOGY

In order to achieve the objective of this project, the author first synthesized COP-1. After synthesizing COP-1, the next step was to carry on the different characterization tests of COP-1.

3.1 Synthesis of COP-1

The synthesis of COP-1 is subdivided in two parts which are Synthesis part and Purification part.

3.1.1 synthesis of COP-1

The reaction below sows the chemical reaction used to synthesize COP-1.

$$\mathbf{2C3Cl3N3+\ 3C4N2H10} \longrightarrow \mathbf{C18N12H24+\ 6HCl} \qquad (1)$$

Where:

C3Cl3N3: is the cyanuric chloride

C4N2H10: is the Piperazine

C18N12H24: is the COP-1

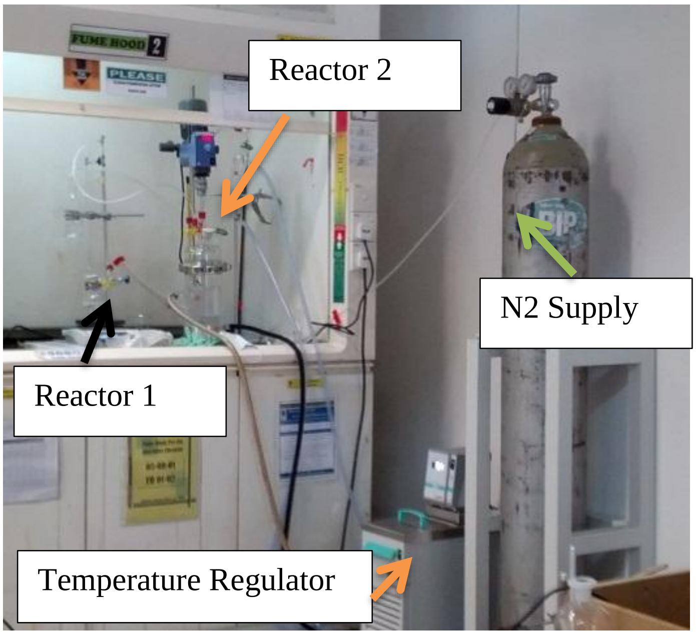

FIGURE 3.1 Experiment set-up

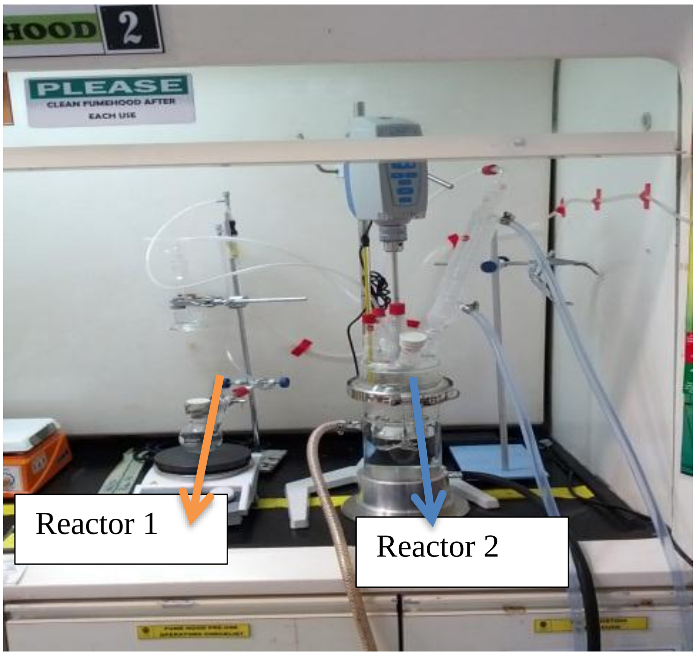

FIGURE 3.2 Reactor 1 and Reactor 2

1. For the experiment set-up, two different reactors were used which were Reactor 1 and Reactor 2. Nitrogen gas (N_2) was supplied to both reactors simultaneously to make sure that the reactor environment was filled with Nitrogen gas (N_2) and other gasses were displaced. After that, in Reactor 1, 5.0265 g (27.2mmol) of cyanuric

chloride was dissolved in 40 mL of 1,4-dioxane. In order to make sure that the cyanuric chloride solution in Reactor 1 was dissolved, a magnetic stirrer was used to stir the solution.

2. In Reactor 2, DIPEA (18.9 mL, 3 mmol) was added to piperazine (3.8326 g, 44.4 mmol) which has been dissolved in 160 mL of 1, 4-dioxane at 288 K. To ensure that the solution in the Reactor 2 is well mixed at 525 rpm, mechanical stirrer was attached to Reactor 2.

3. After that, in order to regulate the temperature in Reactor 2 to 15 °C, a temperature regulator was used. When the temperature reached 15 °C, cyanuric chloride solution from Reactor 1 was added dropwise to Reactor 2.

4. When cyanuric chloride reacted with piperazine, a white precipitate was formed. The white precipitate was stirred continuously at a constant stirring rate of 525 rpm at 15 °C for 1 h. After 1 hour, the temperature was increased to 25 °C for 2 hours. After 2 hours the temperature was increased to 85 °C for 21 h. The temperature in the reactor was regulated by the temperature regulator. The water channel was opened when the temperature was increased to 85 °C. The water channel was opened in order to maintain the temperature in the reactor at desired temperatures of 15 °C, 25 °C and 85 °C.

5. The reflux system connected at the top of Reactor 2 was used when the temperature was set at 85°C to ensure any vapor formed is condensed back into the reactor to ensure complete reaction. Reactor 2 had different nozzles. To ensure that the by-product (HCl) of the reaction was displaced out of the reactor into a conical flask, one of the nozzles of Reactor 2 was opened. The conical flask was containing water as waste to be disposed.

6. The white precipitate which is COP was then ready to undergo purification steps. Choosing the solvent was based on their properties because the needed solvent was required to be effective at temperature above 85°C for substitution of all three chlorides with their linkers to form COP-1. There are different types of solvents such as THF. THF could not be used because is considered ineffective (its boiling point is 68°C) (Memon et al., 2014).

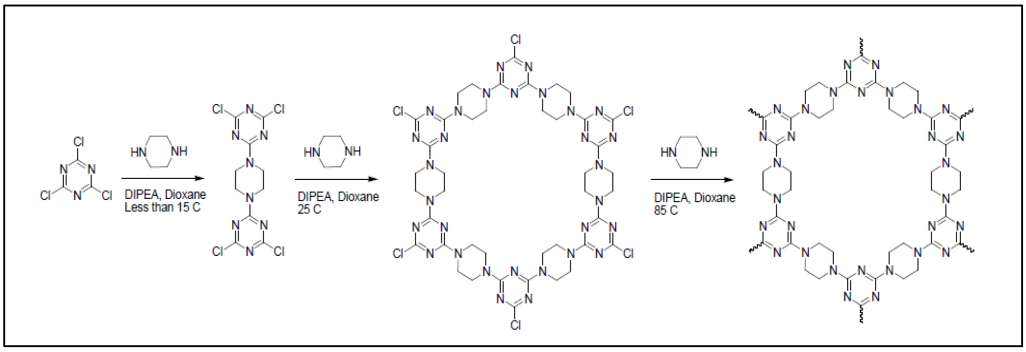

FIGURE 3.3 Chemical reaction to synthesize COP-1

$2C_3Cl_3N_3 + 3C_4N_2H_{10} \longrightarrow C_{18}N_{12}H_{24} + 6HCl$ (2)

Where:

$C_3Cl_3N_3$: is the cyanuric chloride

$C_4N_2H_{10}$: is the Piperazine
$C_{18}N_{12}H_{24}$: is the COP-1
HCl: is the hydrochloric acid

From figure 3.3, the chemical reaction to synthesis COP-1 can be seen. The linker of the above reaction was Piperazine while the Cyanuric chloride was acting as the base.

To form a linkage between cyanuric chloride and Piperazine, the H element of Piperazine was displaced the Cl of Cyanuric Chloride

In order to enable the reaction to favor the formation of Covalent Organic Polymer adsorbent (COP-1) formation, the N, N-Diisopropyletylamine (DIPEA) was added into the solution. After 21 hours the reaction was completed. Once the reaction was completed, all the 3 Cl of cyanuric chloride were substituted and linked up by piperazine to form a polymer called Covalent Organic Polymer (COP).

3.1.2 COP-1 Purification

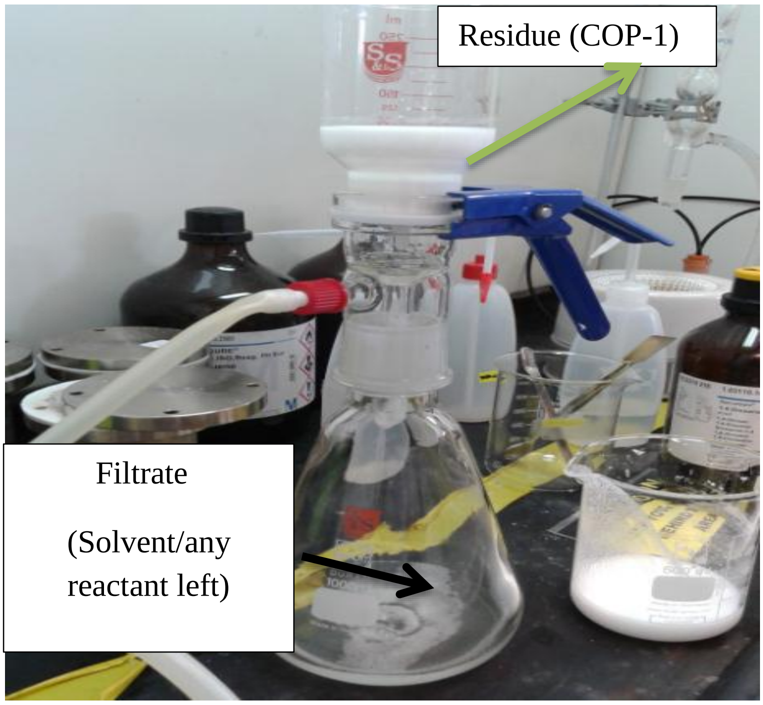

FIGURE 3.4 COP-1 Purification using Suction Filtration

1. COP-1 was filtered using suction filtration. The residue was the white precipitate designated as COP-1 while the filtrate was the solvent and/or any reactants left.
2. The white precipitate was washed by repeating the step of dissolving it in 1, 4-dioxane and performing filtration for three times. In order to make sure that most of the white precipitate was recovered, the filtrate was filtered too.
3. After the second step, the white precipitate recovered was soaked in ethanol for 12 hours. The total 12 hours were divided into three intervals where filtration was performed for each interval and dissolved in ethanol again.
4. The last step was to dry the white precipitate under vacuum for 2 h. In the oven, two different samples of 1.5 g of white precipitate were weighted and dried at different temperatures. One was dried at 28°C while the other one was dried at 120°C. The samples were dried at different temperatures to check if the temperature set at drying process could affect the surface area of the sample.

5. After the drying process, the sample which was designated as COP-1 was ready for characterization study.

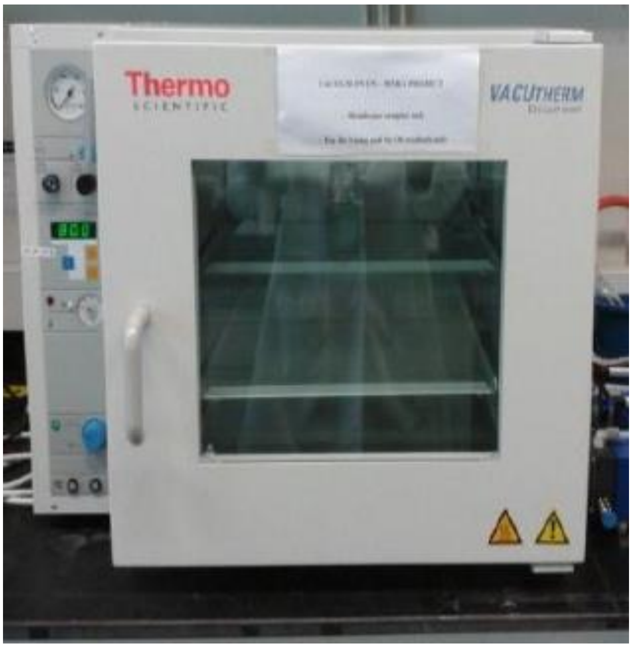

FIGURE 3.5 Vacuum Oven used to dry COP-1

3.2 Characterization of COP-1

In order to proceed with COP-1 characterization tests, first, the characterization on validate the material synthesized to be COP-1 was required. The second step is to conduct COP-1 morphology study using SEM and the final not least is to study the CO_2 and CH_4 adsorption capacities at atmospheric pressure in order to calculate selectivity**.**

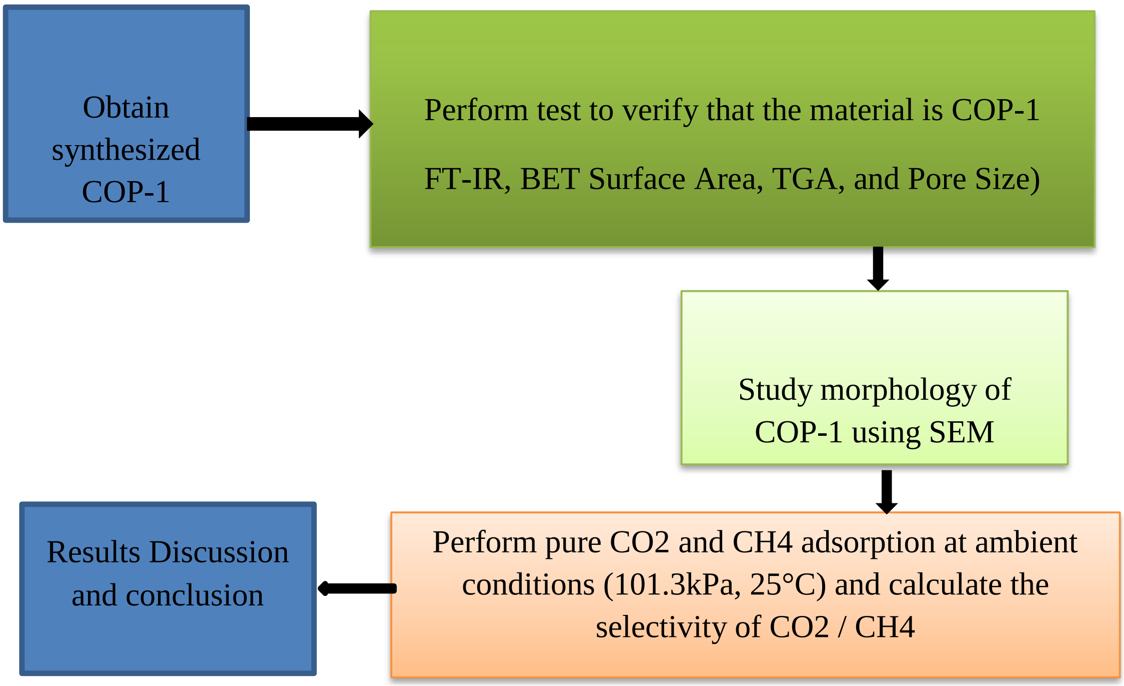

FIGURE 3.6 Methodology schematic diagram

In order to confirm that the product or material obtained from COP-1 synthesis was the desired product (COP-1), different characterization techniques were required. The characterization tests were required to investigate whether the synthesized product poses similar characteristics as the literature of COP-1 produced by Patel et al (2012).

3.2.1 Characterization Techniques

The following are the techniques or tests that were performed as well as the purpose of each technique.

FT-IR TEST

i. To investigate the presence of typical stretching modes of CN heterocycles.
ii. To investigate characteristic breathing mode of thiazine units.
iii. To Investigate saturated carbons of piperazine and 4,4' –bipiperidine
iv. To confirm all three chlorine atoms on CC have been substituted

BET SURFACE AREA TEST

To obtain precise specific surface area evaluation of COP-1, the test was performed under mesoporous pore size (2-50 nm) category.

SEM TEST

To study the morphology of the sample expecting absence of crystalline

TGA TEST

To test the thermal stability of COP-1 at high temperature in air and N2 environment. Temperature range used is from room temperature, 25°C to 800°C with a heating rate of 10°C/min and repeated with 20°C/min.

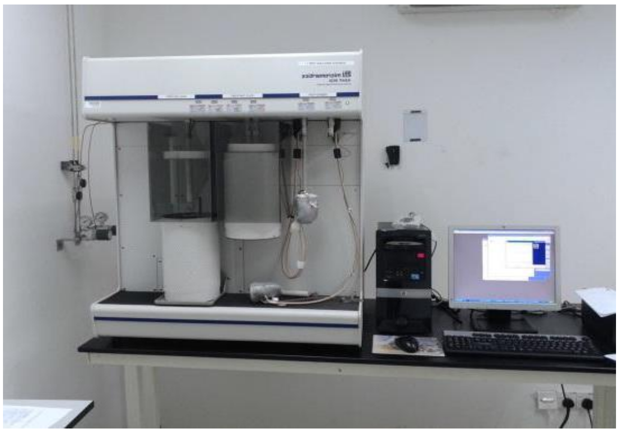

FIGURE 3.7 BET Analyzer

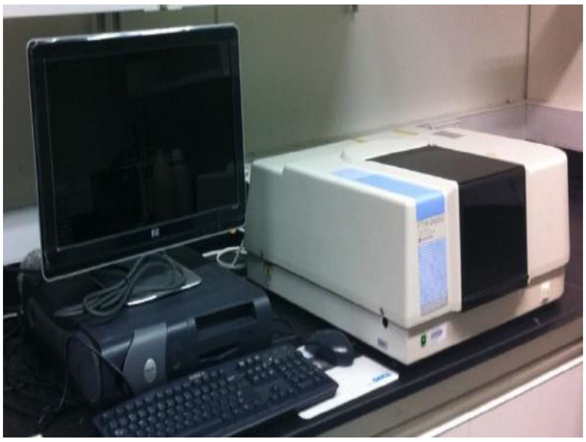

FIGURE 3.8 FT-IR SPECTROMETER

3.2.2 Gas Adsorption Analysis of COP-1

Two different type of gasses were investigated in order to investigate gas capture capacity of Covalent Organic Polymer one (COP-1). The gasses required investigations for this process were Carbon Dioxide (CO_2) and Methane (CH_4).

One of the objective was to have a high CO_2 adsorption capacity to capture high amount of CO_2 from natural gas and a low CH_4 capture to ensure that CH4 which is natural gas yield not be reduced through the CO_2 gas capture process. The apparatus used to perform the test was BELSORP at RCCO2C (located at Bock 05-00-01) Department, Universiti Teknologi Petronas. At the beginning it was stated that the experiment will be conducted under ambient conditions. Since two different gases were used, the experiment was conducted at the same conditions for both gases. The table below shows us the conditions at which the BELSORP was conducted for these two different gases.

TABLE 3.1 Adsorption Conditions

Number	Gas Capture Name	Pressure (atm.)	Temperature (°C)
1	CH4	1	25
2	CO2	1	25

BELSORP

Before proceeding with BELSORP part, the samples that were removed from vacuum oven was then placed in desecrator in order to cool down the sample.

After the cooling part, the sample was required to go under pre-treatment in order to perform BELSORP later.

For **Pre-Treatment part**, the vial was measured first without the sample (V). After that the vial was measure with 1/3 of the sample (VS). The mass (M) of the sample was then calculated by subtracting the value of the vial without sample from the value of vial with sample.

So $M= VS-V$. (3)

The sample underwent pre-treatment at 150°C and the time required to complete the pre-treatment was 5 hours. After the pre-treatment, the BELSORP was conducted using the M calculated.

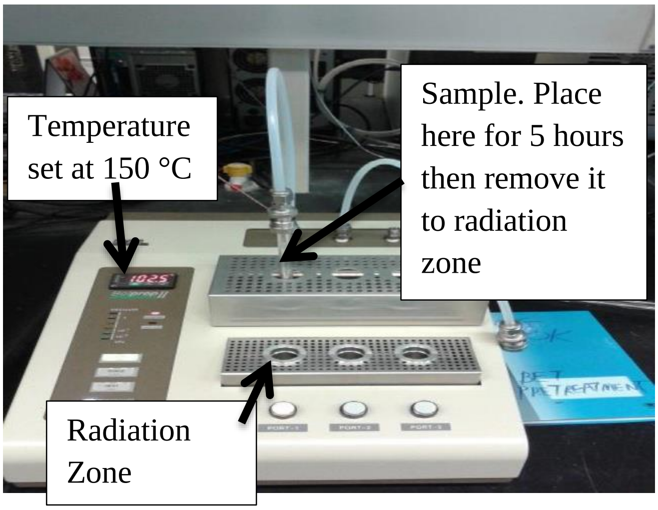

FIGURE 3.9 COP-1 Pre-Treatment Set-Up

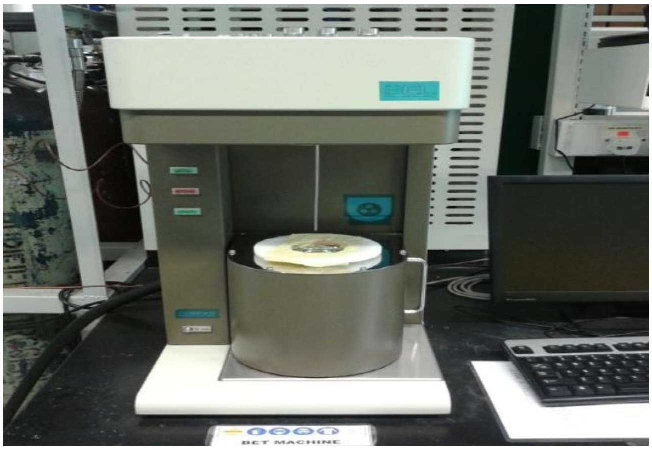

FIGURE 3.10 BELSORP Equipment

3.3 Key Milestone

Week 1-2

- ✓ COP-1 synthesizing
- ✓ COP-1 Purification.

Week 3-6

- ✓ Equipment booking for COP-1 characterization tests.
- ✓ Do the characterizations test to confirm the sample is COP-1
- ✓ Start writing the report based on the results obtained

Week 7-11

- ✓ Submission of progress report.
- ✓ Perform the characterization tests remaining.
- ✓ Finalize the results discussion
- ✓ Pre-SEDEX and Submission of draft report.

Week 12-14

- ✓ Write Project dissertation.
- ✓ Submission of Project dissertation in soft copy.
- ✓ Oral presentation.
- ✓ Final Project submission in hard Bound

TABLE 3.2 Gantt Chart

No	Details	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	COP-1synthesis Purification	🟩	🟩	🟩											
2	Equipment booking			🟩	🟩	🟩									
3	COP-1test using FT-IR, BET surface, TGA, SEM, EDX					🟩	🟩								
4	Gas adsorption analysis CO_2/CH_4					🟩	🟩								
5	Writing and submission of Progress report						🟩	🟩	🟩						
6	Complete remaining tests rem									🟩	🟩				
7	Pre- SEDEX										🟩	🟩			
8	Submission of the report and Dissertation soft copy											🟩	🟩	🟩	🟩
9	Oral presentation and Submission of Report (hard copy)													🟩	🟩

CHAPTER 4

RESULTS AND DISSCUSION

As it was mention earlier, in order to verify that the sample obtained from the Synthesis is COP-1, different techniques were used. The techniques used in this research paper to determine if the sample is COP-1 were FT-IR, BET surface area, SEM, EDX and TGA. Under this section, the data obtained from COP-1 characterization test will be discussed in detail.

4.1 Characterization Techniques used and critical analysis of the data obtained

4.1.1 FT-IR Results

This technique was used to obtain infrared spectrum of absorption and Raman scattering of COP-1. The results of this technique helped to identity the compounds, the absence or presence of functional groups as well as the molecule structure. The mid region was the range of infrared regions where results were expected to arrive was at (670 – 4000 cm-1), which was 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. For this research paper, in this part, we used the dried COP-1 in order to perform the test. The results were then compared with the Patel (2012) results.

According to Patel (2012), 850 cm-1 wavelength number represents C-Cl stretching. As you can see from the figure 10, the FT-IR results for synthesized COP-1 show no peak at 850 cm-1(wavelength number). The results obtained from this technique for this research paper are similar to results obtained by Patel in 2012. So, from this technique it was concluded that, at 850 cm-1 wavelength number, the dried COP-1 was absent of characteristic C-Cl stretching vibration (absence of C-Cl bond from synthesized COP-1) and the expected or desired result was achieved. Apart from 850 cm-1 wavelength peak, another important peak that needed to be investigated was 800 cm-1 peak.

According to Patel (2012) the COP-1 peak at 800 cm-1 wavelength number represents the presence of Triazine in the sample. From figure 10 it is clearly seen that, there is still a peak at 800cm-1 which means the Triazine is still present in the synthesized COP-1. After analyzing 800 cm-1 wavelength number, another important region from FT-IR spectrum region was the region of 1200-1600 cm-1 wavenumber.

According to Patel (2012), in order to confirm that there is still stretching modes of CN in the sample (COP-1) there have to be several strong bands in the 1200-1600cm^{-1} region. As you can see from figure 10 there are strong bands in the region of 1200-1600cm^{-1} wavenumber; that means in the synthesized COP-1 the CN stretching modes are presents.

In overall, it could be concluded that, the results obtained for the synthesized COP-1 in tis research paper for this technique are similar to the results obtained by Patel in 2012. So, the desired results of this technique were achieved.

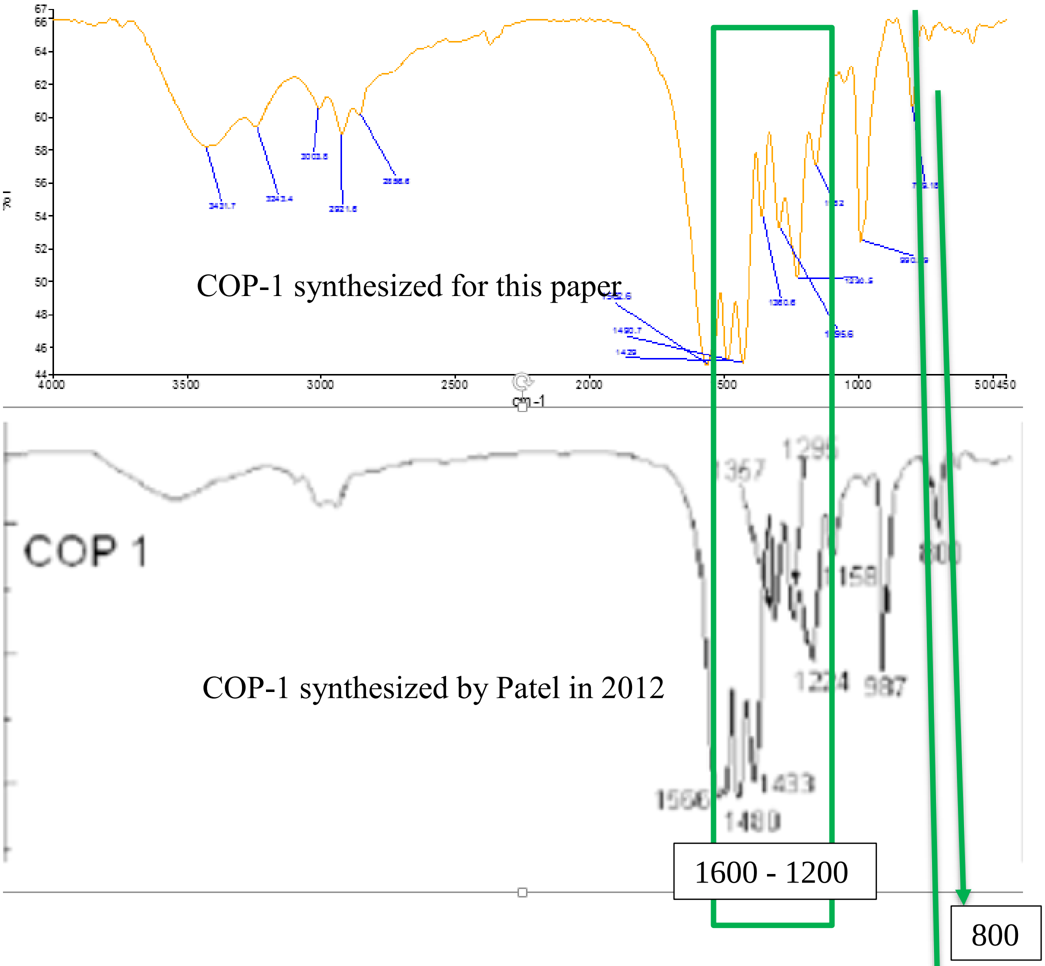

FIGURE 4.1 FT-IR Results Comparison

4.1.2 Bet surface area and pore size.

To know the pore size of the synthesized COP-1, Nitrogen gas (N_2) was the flow gas used in order to perform the test. The bet surface area obtained from this research paper was extremely smaller compared with the one obtained by Patel in 2012. The Bet surface area obtained in this research paper was 11.944m^2/g while the expected Bet surface area was 168 m^2/g (bet surface area by Patel). The pore size obtained from this paper was larger than the pore size obtained by Patel in 2012 which was the desired or expected size. Patel pore size is 6.6 nm while the pore size of this paper was 8.944nm. For a better capture of CO_2 gas, the sample required a large surface area and small pore size in order to have a better selectivity. According to

Rufford and Yu in 2012, small pore size would enhance the selectivity for CO_2 gas capture.

The reason why BET surface area obtained from synthesized COP-1 was smaller could be because the sample only undergo less than 24 hours of degassing. The sample only undergoes 12 hours of degassing. A longer time for degassing around one day and half (36 hours) could show a better result.

TABLE 4.1 BET surface area and pore size

Parameter	Patel Results, 2012 (Experiment expected Results)	Synthesized COP-1 Results (Results obtained from experiment)
Bet surface Area (m^2/g)	168	11.944
Pore size (nm)	6.6	8.98

4.1.3 SEM Results

In order to get images from SEM technique, different magnification numbers were used. For this paper the magnification used were 10KX, 30KX and 50KX. From SEM results (pictures below) it was conformed that there are not crystals present in the sample. So, from this technique it could be concluded that the synthesized COP-1 is amorphous and has pores.

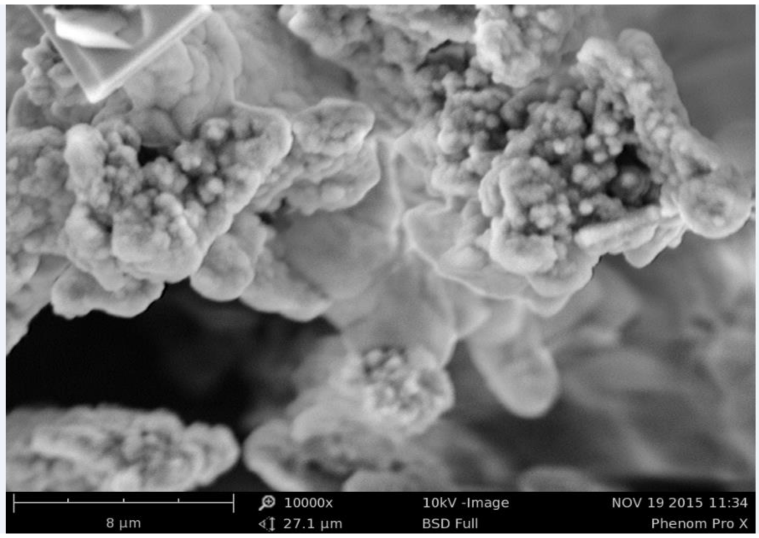

FIGURE 4.2 COP-1 image at 10 KX Magnification

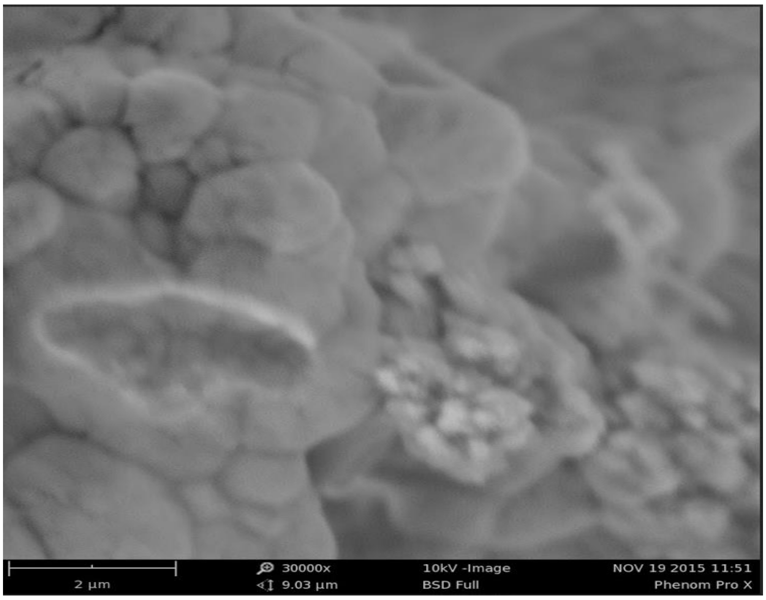

FIGURE 4.3 COP-1 Image at 30 KX magnification

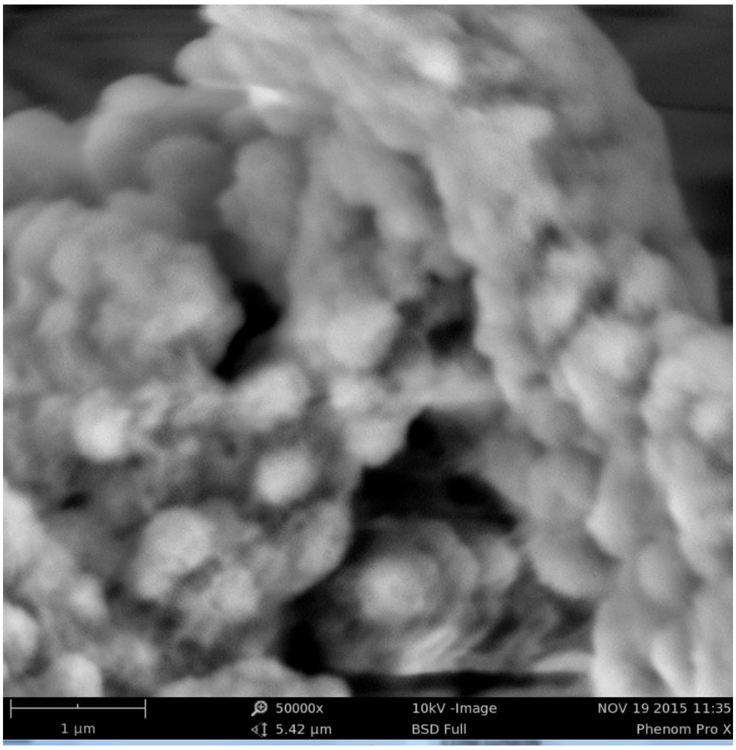

FIGURE 4.4 COP-1 Image at 50KX magnification

4.1.4 TGA Results

In order to know the thermal stability of the synthesized COP-1, TGA technique was used. The thermal stability test was conducted in two different environments; one was in N2 ambient and the other was in air. The heating rate used during the test was 10°C/min and 20°C/ min. According to Patel (2012), COP-1 is stable at 360°C in nitrogen ambient and 285°C in air. From this research paper the COP-1 started decomposing at 3100°C in N_2 environment. The decomposition temperature of synthesized COP-1 in air was 280°C.

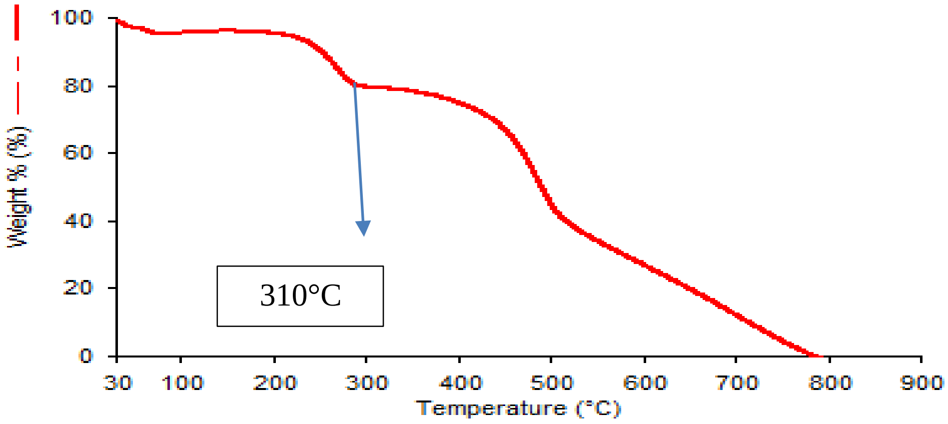

FIGURE 4.5 COP-1 Decomposition Temperature (310°C) in N_2 environment

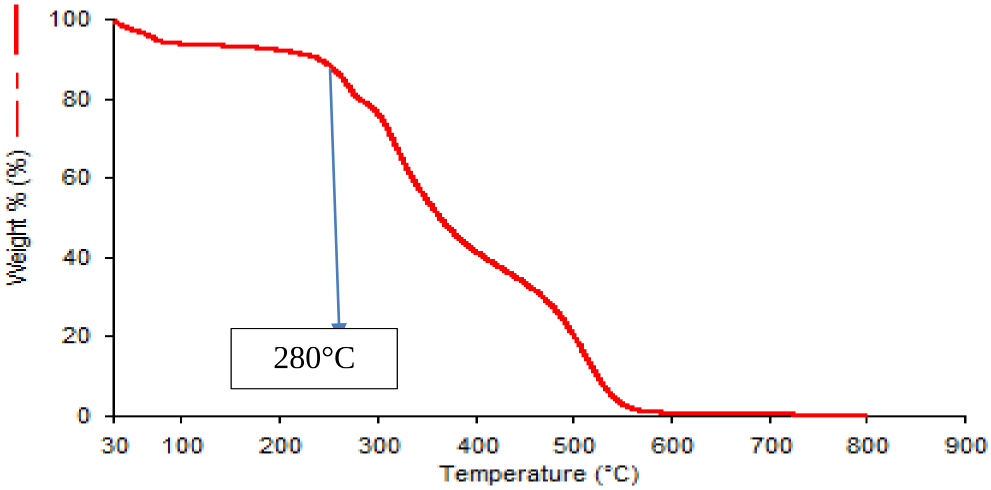

FIGURE 4.6 COP-1 Decomposition Temperature (280°C) in air environment

Based on the results obtained from the thermal stability test, it could be seen that the synthesized COP-1 is less stable compare to Patel COP-1; since the maximum stack temperature of liquefied natural gas is 180°C that means the COP-1 synthesized in this paper is still useful for natural gas applications or industries.

4.2 Gas adsorption measurement from pure gas

4.2.1 CH_4 pure gas adsorption measurement

The methane gas (CH4 gas) capture capacity for COP-1 at ambient conditions is taken at P/Po = 1 of 1.888 mg g-1. Refer to table 6 to see the unit conversion.

TABLE 4.2 Unit Conversion for CH_4 Pure Gas Adsorption

Gas Name	Experimental Adsorption capacity value of the gas
CH4	0.00011768 mol./g= 0.1176mmol/g

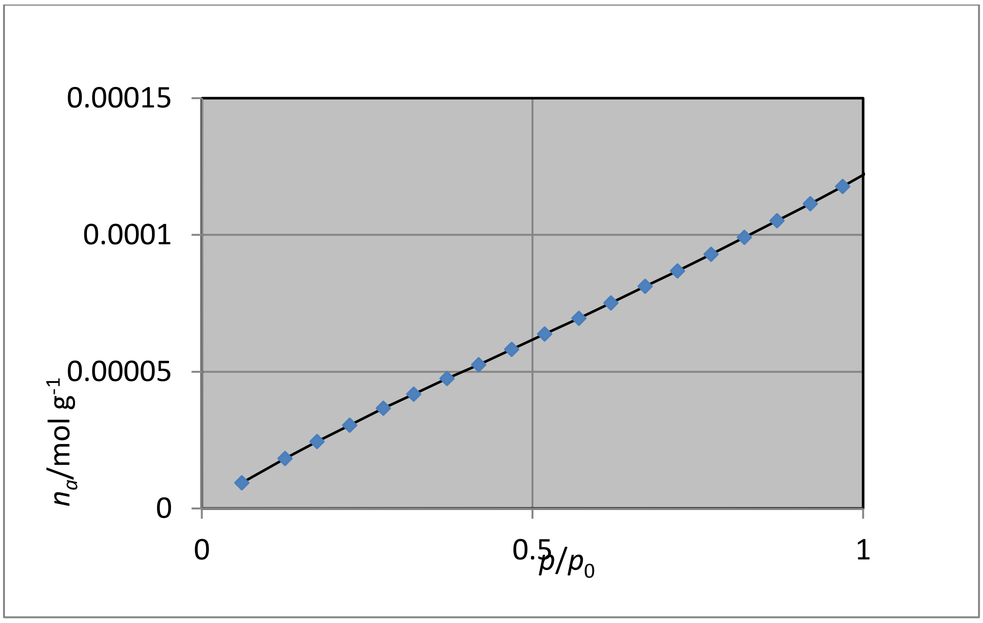

FIGURE 4.7 CH4 Adsorption Isotherm

4.2.2 CO_2 pure gas adsorption measurement

The Carbon dioxide gas (CO_2) capture capacity for COP-1 at ambient conditions (1 atm. 25°C is taken at P/Po = 1 of 26.4 mg g-1. Refer to table 4.3 to see the unit conversion.

TABLE 4.3 Unit conversion for CO_2 Pure Gas Adsorption

Gas Name	**Experimental Adsorption capacity value of the gas**
CO2	0.0006 mol/g=0.6mmol/g

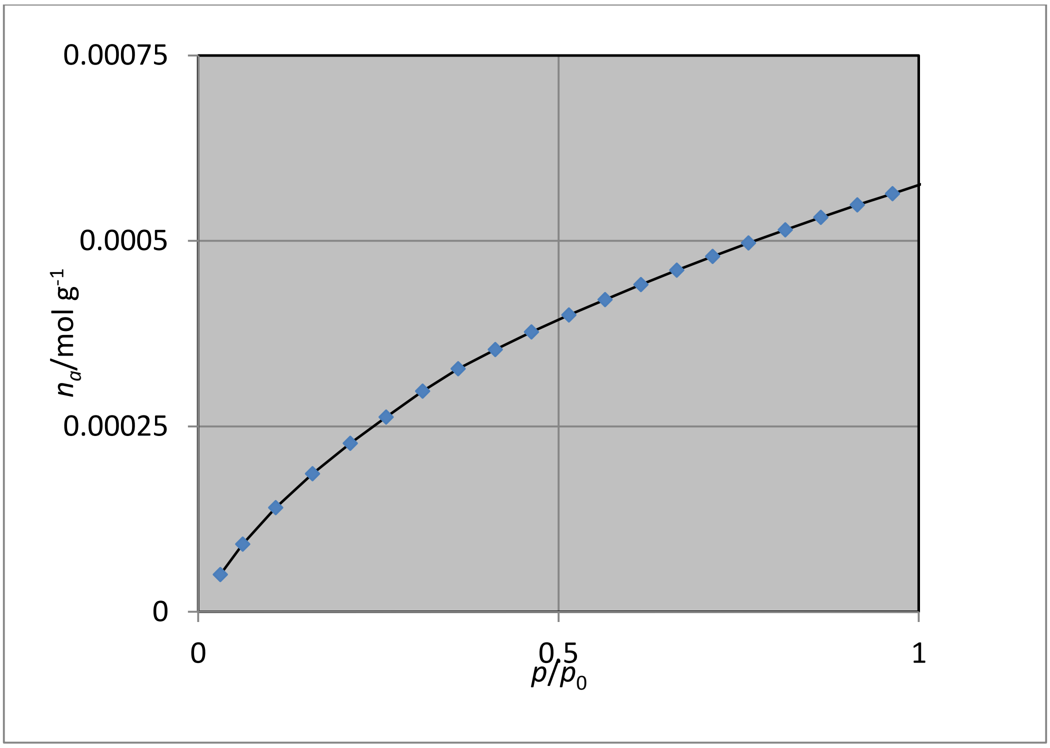

FIGURE 4.8 CO_2 Adsorption Isotherm

4.2.3 Selectivity of CO_2/CH_4

After calculating the adsorption capacity of CO2 and CH4, the selectivity between these two gases was then calculated. The selectivity obtained from this research paper was 5.1mg/g which were lower than the expected value (5.616mg/g) calculated by Patel in 2012 although Patel results were based on CO_2/N_2 separation.

TABLE 4.4 CO_2/CH_4 selectivity result

Gas Used	Adsorption capacity (mmol/g)	CO_2/CH_4 Selectivity
▪ CO2 ▪ CH4	▪ 0.6 ▪ 0.1176	5.1

From this part it could be observed that, the smaller the pore size the better the selectivity. As the pores size increase, the selectivity decrease. So, from this characterization technique we could conclude that, the selectivity and the pore size of the sample are inversely.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

In conclusion, this research paper managed to synthesize a product that shows similar characteristics to COP-1 in terms of functional groups, linkage, and absence of crystallinity. However, some differences are noted such as the surface area. The surface area obtained in this research paper (11.944m^2/g) was lower than the results obtained by Patel in 2012(168m^2/g). The thermal stability of synthesized COP-1(220°C) was the same in N_2 environment as well as in air environment but lower than Patel results (360°C in N2 and 285°C in air). Although the synthesized COP-1 was less stable than Patel's COP-1, the sample obtained from this paper is still useful and sufficient for natural gas application or industries because it is still stable at temperature(280°C) higher than LNG stack temperature (180°C). The pure gas adsorption capacity of CO_2 and CH4 in this research paper was found to be 26.4 mg/g and 1.9 mg/g respectively. The selectivity of CO_2 / CH_4 calculated in this paper was 5.1mg/g. The morphology of synthesized COP-1 was observed to be non-crystalline and porous.

Since this paper focused in synthesizing COP-1 for CO_2/CH4 separation under ambient conditions, for future studies is recommended to do the COP-1 synthesis at pressures and temperatures higher than ambient conditions.

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