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Synthesis and Characterization of Covalent Organic Polymer (COP-1) Adsorbent for Carbon Dioxide Capture

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
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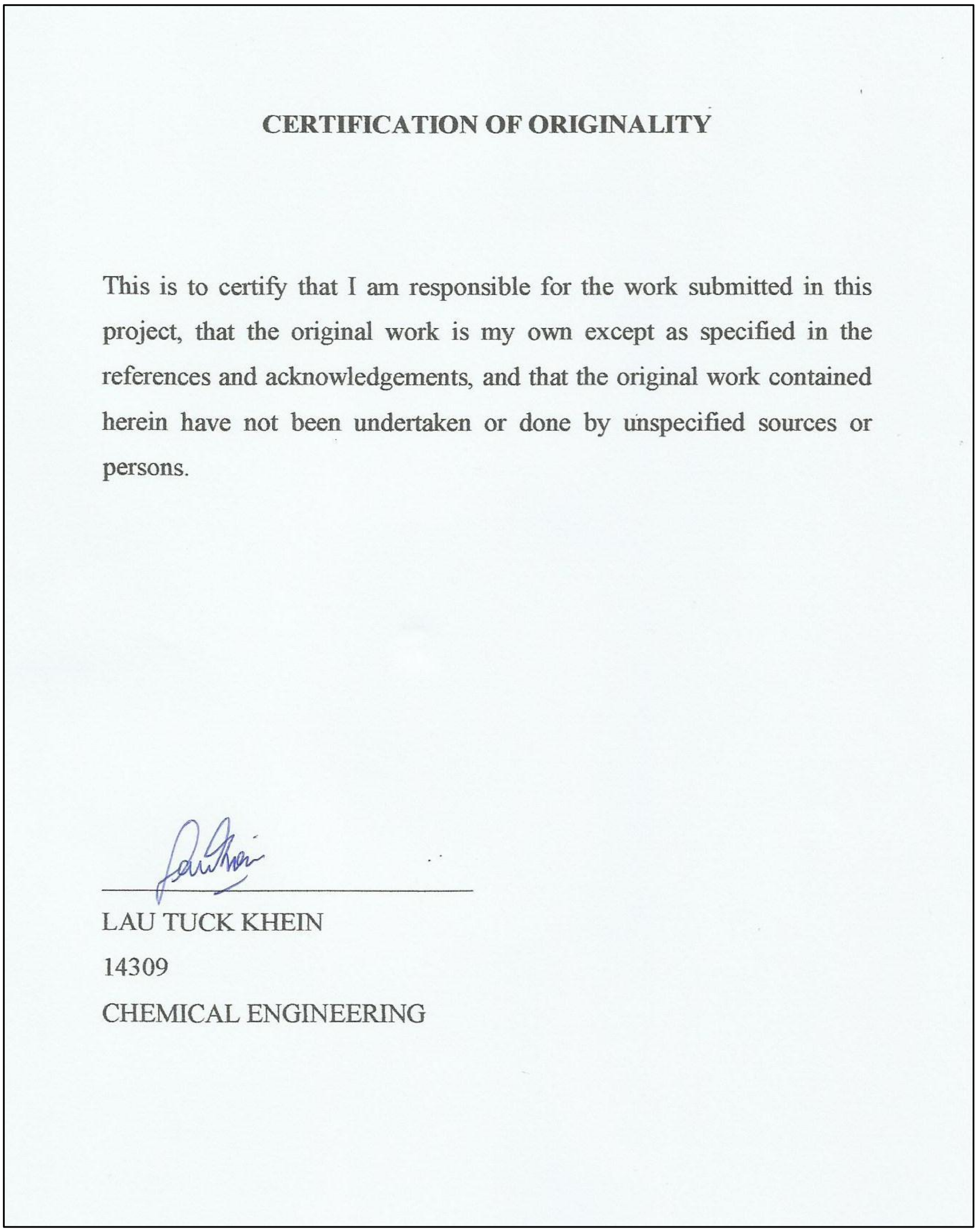

CERTIFICATION OF ORIGINALITY

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.

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ABSTRACT

Carbon dioxide (CO_2) capture from natural gas at high pressure conditions with high CO_2 capture ability as well as high selectivity of CO_2 over CH_4 at low cost remains a major challenge. Recently, covalent organic polymer (COP-1), an adsorbent discovered by Patel (2012) reports the highest carbon dioxide capture of all time of 5616 mg g^{-1} at 200 bar with high thermal stability and desirable characteristics promising for natural gas application. However, the current research information on COP-1 is limited where Patel (2012) only concentrates on CO_2 / N_2 separation and there is no data on CH_4 adsorption which remains a research gap. Besides, the synthesis methodology is not described in detail hence posing a major challenge to replicate the synthesis of COP-1 for further studies. The objective of this research is to synthesis and characterise COP-1 to validate the material synthesised and study on morphology of COP-1 as well as CO_2 / CH_4 adsorption capacity. COP-1 synthesised in this research are characterised using analysis of FT-IR, XRD, NMR, CHN, EDX, TGA, BET surface area, pore size, and FESEM. Pure gas adsorption of CO_2 and CH_4 has also been performed using BELSORP. Overall, the characterisation result shows similarities to Patel (2012) in terms of linkage, functional group and absence of crystallinity with difference such that both surface area and CO_2 capture using COP-1 in this research is about half of that obtained by Patel (2012). Pure gas adsorption of CO_2 and CH_4 using COP-1 in this research is found to be 0.59244 mmol g^{-1} and 0.11405 mmol g^{-1} respectively. A simple selectivity of CO_2 / CH_4 is calculated as 5.19. This research closed the research gap for CH_4 capture at low pressure as well as morphology of COP-1. Further study could be done on CO_2 / CH_4 binary gas selectivity with high amount of CO_2 at high pressure similar to natural gas application.

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LIST OF ABBREVIATIONS

UTP – Universiti Teknologi Petronas

USM – Universiti Sains Malaysia

NMR - Nuclear Magnetic Resonance

FT-IR - Fourier Transform Infrared Spectroscopy

XRD - X-ray Diffraction

CHN - Carbon Hydrogen Nitrogen Analysis

TGA - Thermal Gravimetric Analysis

BET - Brunauer-Emmett-Teller

FESEM - Field Emission Microscopy

EDX – Energy-dispersive X-ray Spectroscopy

CHAPTER 1

INTRODUCTION

1.1 Background

Natural gas is often described as one of the safest, cleanest and most useful forms of energy in our daily lives, hence the increase in demand for natural gas worldwide. In 2012, Malaysia exported 23.1 million metric tonnes of liquefied natural gas (LNG), thus became the world's second largest exporter of LNG after Qatar, and one of the major player in the natural gas industry (Prisecaru and 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).

Although the proven natural gas reserves in Malaysia are the third largest in Asia-Pacific region with around 83 trillion cubic feet, however 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 (Ali et al., 2012). 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 (Shimekit and Mukhtar, 2012). CO_2 also is capable of causing pipeline corrosion problems in the presence of traces of water during transport (Ahmed, 2010). Removing this gas optimises the volume of gas to be transported by eliminating the need for transport of gas impurities. Furthermore, removal of CO_2 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, 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 (Shimekit and Mukhtar, 2012).

It is known that most of the offshore gas reserves in Malaysia contain 50 to 74 mol% of CO_2, however the existing technology of CO_2 gas treatment system has capability limitations to treat natural gas with CO_2 up to only 30 to 40 mol% making the fields undeveloped so far (Ahmed, 2010). Among the fields, K5 which was discovered as early as the year 1970 is the largest recoverable reserve in Malaysia with 4 trillion cubic feet of natural gas in the reservoir; however its natural gas has the second highest CO_2 content of 70%. The unique scenario of high amount of CO_2 gas is not only suffered by gas reserves in Malaysia, but also common in Asia Pacific and SEA.

The technologies so far for CO_2 / natural gas separation such as membrane, absorption and adsorption, faces some limitations when it comes to bulk CO_2 separation. For instance, membrane separation are proven 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 separate natural gas with CO_2 composition of 50% and above, thus it is very critical to find a new technology capable of performing the separation. Recent advancement in adsorption technology ventured into new materials that could perform the separation, namely metal-organic framework (MOF), covalent organic framework (COF) and covalent organic polymer (COP). Among the three new materials, COP offers very high adsorption capacity of CO_2 (up to 5615 mg/g for COP-1) as well as having high thermal and water stability (Patel et al., 2012). Thus, COP is considered as a promising material for the adsorption of CO_2. The purpose of this research is to synthesis and characterise COP-1 to validate the material synthesised as compared 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 CH_4 gas adsorption capacity at atmospheric pressure. This research serves as a starting point for a wider research on selectivity of CO_2 / CH_4 binary gas with high amount of CO_2 at high pressure condition similar to natural gas applications. This research did not manage to cover the wider scope due to time limitation and equipment malfunction.

1.2 Problem Statement

In the coming years, there lies a dire need to cater for the increasing need of natural gas worldwide. For this reason, harvesting of natural gas from reservoirs in Malaysia containing high CO_2 content needs to be carried out and a technology to perform the separation needs to be developed. Recently, Covalent Organic Polymer (COP), a new adsorbent is discovered and shows seemingly promising characteristics to perform the separation of CO_2 / natural gas (for this research, natural gas is assumed to be CH_4) with high CO_2 content. COP however is a new material which is still in research stage, and there is no commercial COP available yet. Among the COPs, COP-1 by Patel (2012) is the most attractive option, hence used in this research. COP-1 offers very high adsorption capacity of CO_2 up to 5615 mg/g as well as having high thermal and water stability. However, the current research information on this material is limited and mostly concentrates on CO_2 / N_2 separation (Patel et al., 2012). There is also no data on CH_4 gas adsorption of COP-1. The synthesis methodology by Patel (2012) too does not publish the detail experimental set-up of equipment needed to perform the synthesis, hence causing the synthesis process to be challenging. This research on COP-1 would be able to contribute to the data on characteristics of COP-1 as well as the selectivity of CO_2 / CH_4 separation at atmospheric pressure.

1.3 Objective

To synthesize and characterize COP-1 for CO_2 / CH_4 separation.

1.4 Scope of study

(i) Synthesis of COP-1

To plan and develop an experimental set-up that could perform synthesis and purification of COP-1.

(ii) Characterization of COP-1

To validate COP-1 characteristics as claimed by Patel (2012) and to contribute the data for morphology as well as gas sorption measurements at atmospheric pressure to the research library. Characterisation study for validation includes FT-IR, XRD, NMR, CHN, EDX, TGA, BET surface area and pore size. Morphology is studied through FESEM. Characterization on gas sorption measurements was done for pure gas adsorption capacity for both CO_2 and CH_4 at 101.3 kPa using BELSORP and the selectivity is calculated.

This project closes the gap of data for CH_4 adsorption capacity at low pressure and contributed the FESEM morphology of COP-1.

CHAPTER 2

LITERATURE REVIEW

2.1 Adsorbent for CO_2 capture

The recent advancement in adsorption promises a possibility for solution to the current technology limitation in separation of CO_2 with high concentration from a gas mixture. The desirable characteristics of adsorbent for CO_2 capture from natural gas as mentioned by Rufford (2012) & Yu (2012) include:

a) High selectivity of CO_2 from N_2.
b) Good adsorption capacity (gas capture and storage) for the target component, CO_2.
c) High surface area of adsorbent.
d) High hydro and thermal stability.
e) Low cost of production, operational cost, capital cost and good sustainability.
f) Good physical and chemical stability through adsorption / desorption cycle.
g) Generable by modest pressure or temperature swing to minimize operational cost.
h) Robust performance in the presence of moisture and contaminant.
i) Fast adsorption kinetics.

Among the mostly mentioned adsorbents from literature review are covalent organic framework (COF), metal organic framework (MOF) and covalent organic polymer (COP). These three materials are chosen to be elaborated and compared in detail as COF, MOF and COP are new adsorbents that show high CO_2 capture ability and is promising to perform CO_2 capture with high selectivity towards CO_2 from natural gas. Traditional adsorbents such as zeolites and activated carbon are not considered for this study as thorough research has been done on these materials over the years showing undesirable characteristics for CO_2 / natural gas separation. This is because zeolites could adsorb CO_2 quickly with low energy however it is unstable in water

(Liu et al., 2012). As for activated carbon, the ability to capture higher amount of CO_2 than zeolites at high pressure is desirable; however the selectivity of CO_2 / N_2 is low. Details about COF, MOF and COP is elaborated below.

Covalent organic framework (COF)

COF is synthesized from organic monomer and linked together by strong covalent bonds. It poses a crystalline structure. Chemical tuning of COF could alter the pore size to increase selectivity (Dawson et al., 2012). As for the storage capacity, it can be determined by the porosity of the material (Chang et al., 2013). COF is a light weight porous material; however its CO_2 capacity fails to meet the predicted theoretical performance of 9285mg g^{-1} (Patel et al., 2012). A relatively high CO_2 capacity achieved by COF-102 is 1200 mg g^{-1} at 55 bar and 25°C (Ding & Wang, 2013). Aside from that, the water instability of COF can only be slowed down by alkylating the organic struts (Patel et al., 2012). As for the cost, the production of material is higher as compared to conventional porous solids (Patel et al., 2012).

Metal organic framework (MOF)

MOF is a microporous crystalline where organic bridging ligands are coordinated to metal-based nodes (D'Alessandro et al., 2010). The pore diameters are uniform between sizes of 3 to 20 Å. Among many MOF, MOF-177 reported to have the highest adsorption capacity of CO_2 of 33.5 $mmolg^{-1}$ at 32 bar and surface area of 4500 m^2 g^{-1} (D'Alessandro et al., 2010). A study on MOF-177 by Jung et al (2010) shows CO_2 adsorption of 1315 mg g^{-1} at 30 bar and 298 K. The similar study by Jung et al shows BET surface area of MOF of 4898 m^2 g^{-1}. MOF has positive characteristics such as high void volume and high surface area-to-weight ratio for CO_2 capture capacity enhancement; however it has certain drawbacks especially for applications of CO_2 capture in natural gas industry. One major drawback is MOF is less stable in oxygen and moisture due to metal clusters, where the condition is present in the natural gas industry. The performance of MOF in terms of CO_2 adsorption can decrease up to 50% in wet conditions (Xiang et al., 2012). Another drawback is that MOF are ideal in operation only at high pressure but low temperature conditions (Yu, 2012). As COF and MOF have drawbacks that crucially affect their credibility to be applied in CO_2 capture from natural gas, the next part would focus on COP which seems to be a more promising material for the purpose based on literature screening.

2.2 Covalent organic polymer (COP)

COP is an amorphous porous polymer. Covalent organic polymer could be synthesised by a wide range of synthetic methods, hence able to produce a number of different structures for better characteristics improvement. Higher porosity could be achieved from a lower density material. To further lower the density of COP, lighter elements of the periodic table are selected namely C, H and N (Chang et al., 2013). Among the COP synthesised throughout the world, COP-1 by Patel et al shows the highest CO_2 adsorption capacities up to 5616 mg g^{-1} at high pressure of 200 bar and temperature as warm as 65°C (Patel et al., 2012). Another notable characteristic 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 CO_2 capture capacities. As for the recyclability ability of COP, a study by Patel et al has proven that it is possible to recycle COP up to at least five cycles using sample of CO_2 and H_2 (Patel et al., 2012).

There has been emphasis on the ability of COP to withstand high pressure and temperature condition as it is necessary to cater the industrial needs of natural gas processes. For instance, pre-combustion applications require pressure up to 30 bar, post-combustion application at less than 6 bar and temperature of 40°C to 60°C (Patel et al., 2012). Thus, the ability of COP to be robust at pressure up to 200 bar and 100°C in water has opened the feasibility path for more application stages in the natural gas industry. COP is also stable at temperature up to 350°C in air and 450°C in N_2 (Patel et al., 2012). In addition, COP is easy for storage. It does not show signs of degradation when stored under ambient atmospheric conditions even after several months with no care given (Patel et al., 2012).

Xiang et al (2012) performed test on adsorption selectivity of COP-1 for CO_2- CH_4 separation. It is found to be in the range of 4.1 to 5.0 at a CO_2: CH_4 ratio of 15: 85 at pressure range of 0 bar to 40 bar. However, the test did not cover CO_2: CH_4 ratio at higher CO_2 content. As for COP-1 by Patel et. al, no test had been done to study the selectivity of CO_2 from CO_2: CH_4 gas mixture of any composition.

COP are also cost effective due to low energy requirement and capital cost by utilising pressure swing adsorption rather than temperature swing adsorption due to the rapid CO_2 capture cycle of COP (Patel, H. A., et. al, 2012).There is also no need for post-processing or cross-linking in order for it to achieve permanent porosity. The material price for COP-1 is just \$9.8 kg^{-1} CO_2 removed (Patel, H. A., et. al, 2012).

2.3 Comparison between Different Adsorbents, COF, MOF and COP-1

The comparison between COF, MOF and COP-1 is shown in Table 1 below. From Table 1, it is seen that COP-1 offers the best characteristics among three adsorbents in terms of water stability, thermal stability, cost, and operating pressure tested. Besides, COP-1 shows good recyclability as well as great storage capability. The only characteristic of COP-1 that does not seem to be the best is the BET surface area. MOF is seen to be largest in terms of BET surface area. However, Patel et. al (2012) mentioned that in carbon capture and storage, the main and most important target is CO_2 capacity of sorbent compared to intrinsic properties such as surface area. Hence, the literature review supports the aim of this research to perform test on COP-1 as choice of sorbent as it seems to be the most promising material to perform CO_2 / CH_4 separation.

Table 1: Comparison of characteristics between COF, MOF and COP-1

	COF (COF-102) (Ding & Wang, 2013)	MOF (MOF-177) (Liu et al., 2012)	COP (COP-1) (Patel et al.,2012)
Water Stability	Not stable Instability can only be slowed down by alkylating the organic struts	Not stable Performance decrease up to 50% in presence of moisture	High stability Stable in boiling water for at least a week
Thermal stability	High Stability Stable up to 450°C	Ideal to operate at low temperature conditions 25°C	High stability Stable up to 360°C in N_2 atmosphere and 285°C in air
Cost	Very high \$88598 kg^{-1} CO_2 removed	Very High \$65000 kg^{-1} CO_2 removed	Very cheap Only \$9.8 kg^{-1} CO_2 removed
Pressure feasibility	Test proven up to 55 bar	Test proven up to 32 bar	Test proven up to 200 bar
CO_2	1200 mg g^{-1}@ 55 bar	1315 mg g^{-1}@ 30 bar	5616 mg g^{-1}@

adsorption capacity	and 25°C	and 25°C	200 bar, 65°C
BET surface area	3620 m^2 g^{-1}	4898 m^2 g^{-1}	168 m^2 g^{-1}
Recyclability	-	-	Recyclable up to at least five cycles
Storage	-	-	No degradation under ambient temperature up to several months

2.4 Test Used for Characterisation of COP-1

2.4.1 NMR - Nuclear magnetic resonance

NMR is a technique to determine the structure of organic compounds. This technique enables the observation of specific quantum mechanical properties of the atomic nucleus. One of the added advantage of this technique is that samples can be tested even in small quantities of less than a milligram. This advantage is well suited to test COP-1 samples, as they are only synthesised in a small amount. For characterisation of COP-1, C- NMR and H-NMR are used. C-NMR is used to confirm the presence of aliphatic CH_2 group and presence of triazine ring carbons while H-NMR to confirm presence of methylene groups of piperazine (Patel et al., 2012).

2.4.2 FT-IR - Fourier transform infrared spectroscopy

FT-IR is a technique that could be used to obtain infrared spectrum of absorption and Raman scattering of a solid, which is the state of COP-1. FT-IR results could give the identity of compounds, presence or absence of functional groups, as well as the structure of the molecule. The range of infrared regions where results are expected to arrive is at the mid region (670 – 4000 cm^{-1}), which is the most widely used region. For this research, FT-IR is 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 (Patel et al., 2012).

2.4.3 XRD - X-ray diffraction

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

2.4.4 CHN - Carbon hydrogen nitrogen analysis

A CHN analyses serves as a tool to analyse the elemental composition of a sample. COP-1 would be expected to show results where carbon, hydrogen and nitrogen are all present in the sample. The composition of these elements would then be investigated to see if they match or is close to the theoretical results from literature by Patel et. al, 2012 of 52.2% C, 4.4% H and 43.5% N. The theoretical composition as suggested by Patel would also be re-calculated based on the chemical reaction of reactants.

2.4.5 TGA - Thermal gravimetric analysis

TGA is a method of thermal analysis where changes in physical and chemical properties of a sample are measured as a function of temperature. For COP-1, TGA serves to test the thermo stability at high temperature in air and N_2 atmosphere.

2.4.6 Brunauer-Emmett-Teller (BET) surface area

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 for the measurement of the specific surface area of a material. BET analysis provides precise specific surface area evaluation of materials by nitrogen multilayer adsorption measured as a function of relative pressure using a fully automated analyzer. This analysis would be able to provide the pore size of the sample as well.

2.4.7 FESEM - Field emission microscopy

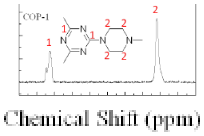
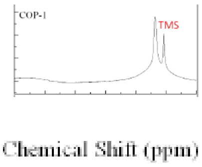
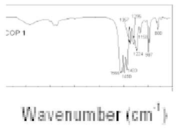
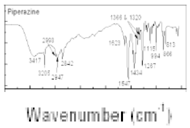
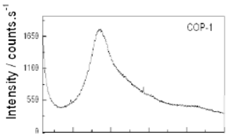
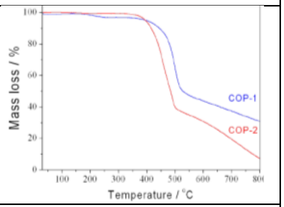
FESEM is an analytical technique used in materials science to investigate molecular surface structures and their morphology.

2.4.8 EDX – Energy-dispersive X-ray Spectroscopy

EDX is an analytical technique used for the elemental analysis or chemical characterization of a sample. While CHN could be used to determine the amount of carbon, hydrogen and nitrogen elements in the sample, EDX has the capability to sense the presence of major elements in the periodic table shall they be present.

2.5 Expected Results from Literature

Table 2: Expected result and explanation on verification of COP-1 tests (Patel et al., 2013)

No	Test	Expected result	Expected graph
1	NMR C-NMR H-NMR	C-chemical shift at 44.2ppm Present at 164.7ppm of C-NMR spectra Chemical shift at 3.2ppm	 
2	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 $850cm^{-1}$	 
3	XRD	No crystallinity structure observed	
4	CHN analysis	Theoretical %C – 52.2 %H – 4.4 %N – 43.5	
5	TGA	Starts decomposing at 285°C in air and 360°C in N_2 atmosphere	
6	BET surface area	$168\ m^2\ g^{-1}$	

Chapter 3

Methodology of Project Work

The methodology of this project is divided into two main parts to be approached. The first part would be on synthesis of COP-1 and the second portion on characterisation of COP-1.

3.1 Synthesis of COP-1

The synthesis of COP-1 is also divided into two parts, first synthesis and second purification of COP-1.

3.1.1 Synthesis

Figure 1: Overall experimental setup for synthesis of COP-1

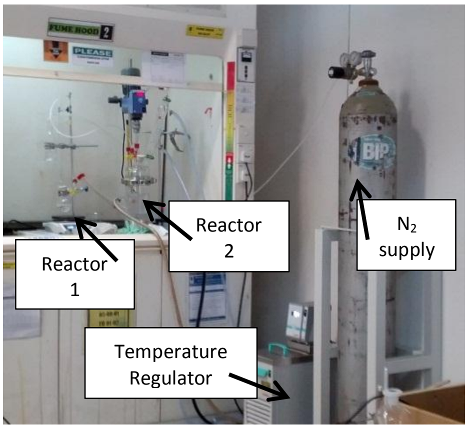


Figure 2: Closer view of Reactor 1 and Reactor 2

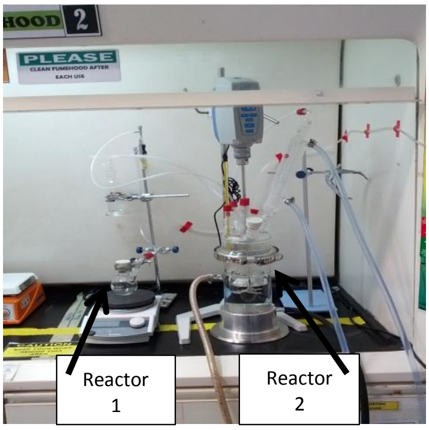


Figure 3: Adding of DIPEA to Reactor 2

Based on Figure 1 and Figure 2 showing the experimental setup:

1) Two reactors, Reactor 1 and Reactor 2 were used in this experimental set-up. In both reactors, N_2 gas was supplied simultaneously to the reactors to ensure the reactor environment was filled with N_2 and other gasses were displaced. Then, in Reactor 1 cyanuric chloride (5.00 g, 27.1 mmol) was dissolved in 1,4-dioxane (50 mL). A magnetic stirrer was used to stir the solution in Reactor 1 to ensure all the cyanuric chloride was dissolved.
2) In Reactor 2, DIPEA (18.9 mL, 108.4 mmol) as shown in Figure 3 was added to piperazine (3.73 g, 43.3 mmol) which has been dissolved in 1,4-dioxane (150 mL) at 288 K. A mechanical stirrer was attached to Reactor 2 to ensure that the solution in the reactor is well mixed at 190 rpm.
3) Next, a temperature regulator was used to regulate the temperature in Reactor 2 to 15 °C. When the temperature reached 15 °C, cyanuric chloride solution in Reactor 1 was added dropwise to Reactor 2.
4) White precipitate was formed when cyanuric chloride reacted with piperazine. The white precipitate was stirred continuously at a constant stirring rate of 190 rpm at 15 °C for 1 h. After that, stirring continued at 25 °C for 2 h and then at 85 °C for 21 h. The temperature in the reactor is regulated by the temperature regulator which channels water at desired temperature to the outer wall of the double glass wall jacketed reactor, hence maintaining the temperature in the reactor at desired temperatures of 15 °C , 25 °C and 85 °C.
5) A reflux system connected at the top of Reactor 2 is used when the temperature is set to 85°C to ensure any vapour formed is condensed back into the reactor to ensure complete reaction. One of the nozzles of Reactor 2

is open to ensure that the by-product of the reaction, HCl is displaced out of the reactor into a conical flask containing water as waste to be disposed.

6) The white precipitate was then ready to undergo purification steps.

Choice of solvent would prefer a solvent that is effective at temperature above 85°C for substitution of all three chlorides with their linkers to form COP-1. Dioxane is preferred over another popular solvent, THF as dioxane is still effective at 85°C while THF has a boiling point at 68°C hence making it ineffective (Memon et al., 2014).

Figure 4: Chemical reaction to synthesis COP-1

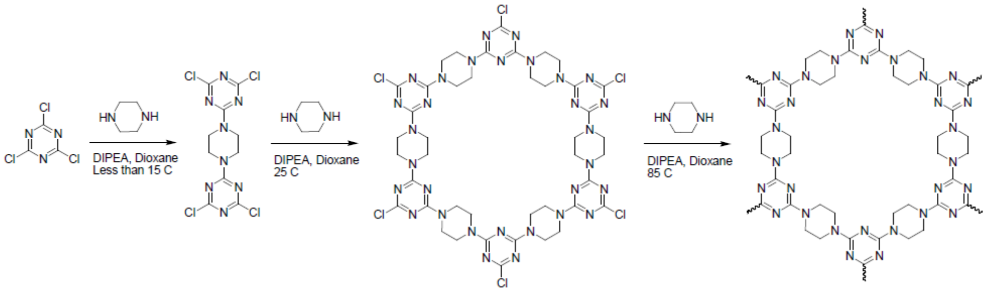


Figure 4 shows the chemical reaction to synthesis COP-1. Cyanuric chloride is the base and piperazine is the linker.

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

2 Cyanuric chloride + 3 Piperazine ⟶ COP-1 + 6 Hydrochloric acid

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

3.1.2 Purification

Figure 5: White Precipitate Solution before Filtration

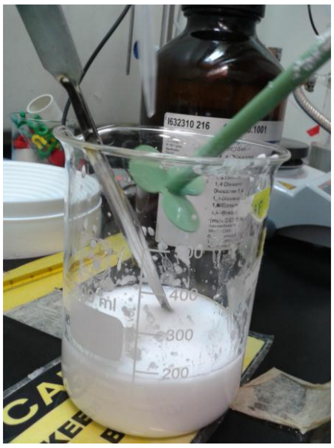
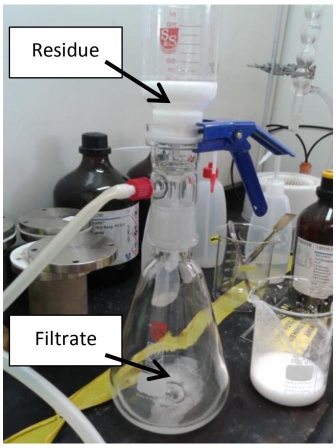


Figure 6: Suction Filtration

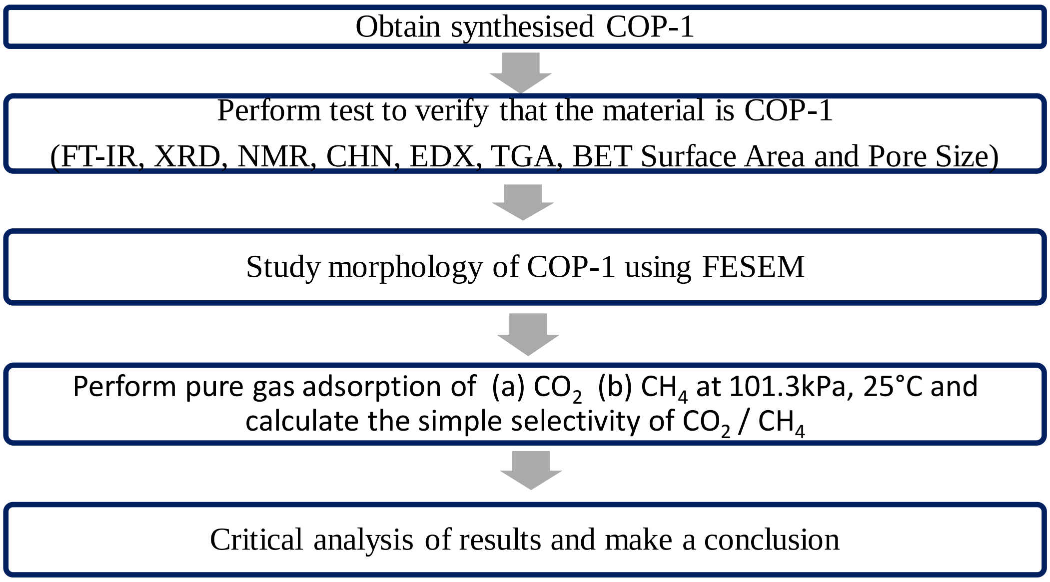


1) COP-1 was filtered using suction filtration. The residue would be the white precipitate designated as COP-1 while the filtrate would be the solvent and/or any reactants left.
2) The white precipitate was washed by repeating the step of dissolving it in 1,4-dioxane and performing filtration for three times. The filtrate was filtered also to ensure most of the white precipitate were recovered.
3) Next, the white precipitate recovered was soaked in ethanol for 12 hours. The 12 hours total time is divided into three intervals where filtration was performed for each interval and dissolved in ethanol again.
4) Finally, the precipitate was dried at room temperature under vacuum for 2 h. The sample was weighed between intervals until the mass is constant, signifying complete drying.
5) This sample is designated as COP-1 and was ready for characterization study.

Figure 7: Vacuum Oven

3.2 Characterisation of COP-1

The characterisation of COP-1 would be first on characterisation to validate the material synthesised to be COP-1, secondly study the morphology of COP-1 using FESEM and finally to study the CO_2 and CH_4 adsorption capacities at atmospheric pressure in order to calculate selectivity.



3.2.1 Characterisation Study on Synthesised Material (COP-1)

To investigate whether the synthesized material poses similar characteristics as the literature of COP-1 produced by Patel et al (2012), Table 3 shows the test to be performed as well as the purpose.

Table 3: Characterisation test used to verify the synthesised material

No	Test	Parameter of interest specification
1	NMR C-NMR H-NMR	To confirm the presence of aliphatic CH_2 group To confirm presence of triazine ring carbons To confirm presence of methylene groups of piperazine
2	FT-IR	To investigate the presence of typical stretching modes of CN heterocycles To investigate characteristic breathing mode of triazine units Investigate saturated carbons of piperazine and 4,4' –bipiperidine To confirm all three chlorine atoms on CC have been substituted
3	XRD	To test for presence of crystallinity in structure. The angle of diffraction is adjusted accordingly to view the clearest result at 2Theta = 0.5°-80°.
4	CHN analysis	To analyse the elemental composition of COP-1for carbon, hydrogen and nitrogen elements
5	TGA	To test the thermo stability of COP-1 at high temperature in air and N_2

		environment. Temperature range used is from room temperature, 30°C to 800°C with a heating rate of 10°C/min and repeated with 20°C/min.
6	BET surface area	To obtain precise specific surface area evaluation of COP-1. The test was performed under mesopore pore size (2-50 nm) category.
7	EDX	To investigate presence or absence of other elements aside from C,H and N
8	FESEM	To study the morphology of the sample expecting absence of crystalline

Figure 8: BET Analyser

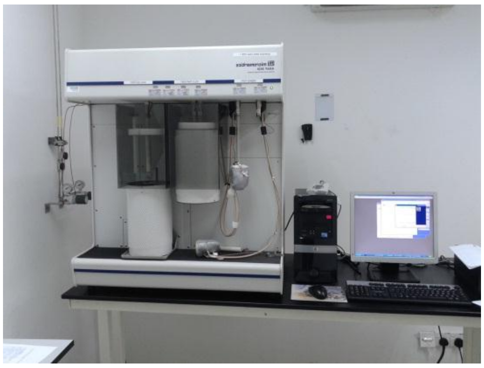


Figure 9: FTIR Spectrometer

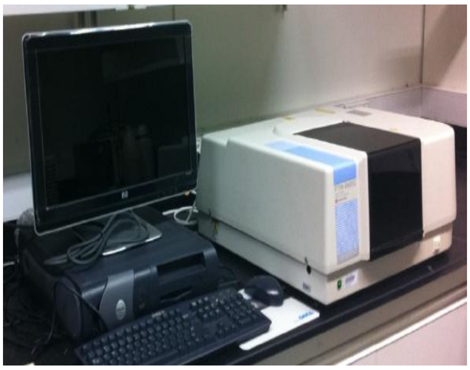


Figure 10: FESEM equipment SUPRA 55VP model manufactured by Carl Zeiss AG

Table 4: Location where characterisation test is done

No	Test	Location of Test
1	NMR C-NMR H-NMR	 Ionic Liquid Department, UTP Ionic Liquid Department, UTP
2	FT-IR	Chemical Engineering Department, UTP
3	XRD	SIRIM Berhad, USM
4	CHN analysis	SIRIM Berhad, USM
5	TGA	Chemical Engineering Department, UTP
6	BET surface area	Centralised Analytical Laboratory, UTP
7	EDX	Centralised Analytical Laboratory, UTP
8	FESEM	Centralised Analytical Laboratory, UTP

The samples are sent to the respective laboratories for analysis test where the analysis would be performed by competent technicians. The parameter of interest would be specified by the researcher as shown in Table 3 particularly for analysis test of XRD, TGA and BET surface area. Results which are presented in graphs such as FTIR and TGA are replotted again using Origin 8 software for better analysis.

In summary of methodology for characterisation, Fourier transform infrared spectroscopy (FT-IR) spectra was recorded as KBr pellet for cyanuric chloride, piperazine and COP-1 using Shimadzu FTIR-8400S over a range of 500 - 4000 cm^{-1} with a resolution of 4 cm-1 and 20 scans for signal accumulation. FT-IR spectrum is repeated for COP-1 after drying in vacuum oven for 2 hours. X-ray diffraction (XRD) was performed at 2-Theta = 0.5° – 80°, covering the range used by Patel (2012) of 0.5° - 60°. Then, the XRD curve is smoothened and replotted at 6° - 45° using Origin, to highlight the result. Nuclear magnetic resonance (NMR) spectra for COP-1 were recorded for ^{1}H NMR and ^{13}C NMR using Bruker Avance 500 MHz Spectrometer for solid NMR. Carbon hydrogen nitrogen analysis (CHN) was performed using 1.898g of COP-1 with a fill time of 18 seconds. Energy-dispersive X-ray Spectroscopy (EDX) was performed on Philips XL30/FEI ESEM. Thermal gravimetric analysis (TGA) was performed for COP-1 under N_2 and O_2 atmosphere which resembles air from 30°C to 800°C at a heating rate of 10°C min^{-1} and 20°C min^{-1}. Brunauer-Emmett-Teller (BET) surface area and pore size is analysed using Micromeritics ASAP 2020 Surface Area and Porosity Analyser using N^2 as analysis adsorptive. FESEM is done using SUPRA 55VP under magnifications of 10 KX, 20 KX, 31.71 KX and 50 KX. Pre-treatment of sample is done by degassing the sample under vacuum for 30 mins.

3.2.2 Gas Adsorption Analysis of Synthesised Sample (COP-1)

To investigate gas capture capacity of COP-1, two types of gasses are investigated, namely CO_2 and CH_4. It is desired to have a high CO_2 adsorption capacity to capture CO_2 from natural gas and a low CH_4 capture to ensure that CH_4 which is natural gas yield not be reduced through the CO_2 gas capture process. The equipment to perform the test is BELSORP at RCCO_2C Department, Universiti Teknologi Petronas. Table 5 shows conditions at which the gas adsorption measurement was done.

Table 5: Conditions at which Adsorption test was performed

No	Gas Capture	Temperature (°C)	Pressure (kPa)
1	CO_2	25	101.3
2	CH_4	25	101.3

Temperature range for test in Table 5 could suit post-combustion of natural gas conditions in accordance to Patel (2012). The post-combustion require less than 6 bar (600kPa) (Patel et al.,2012).

Figure 11: Pre-treatment of COP-1

Figure 12: BELSORP equipment

The COP-1 sample undergoes pre-treatment at 150°C under vacuum for 2 hours as seen in Figure 6 before adsorption test is carried out.

3.3 Key Milestones

Week 1-4

- Synthesising the sample COP-1 and perform purification steps
- Booking of equipments for analysis
- Start with characterisation to verify the sample

Week 5-6

- Analysis of results and preparing progress report
- Sample characterisation analysis for remaining tests
- Performing analysis on gas adsorption

Week 7-9

- Progress Report Submission
- Continuation of remaining experiments and analysis of results
- Finalising results collected and preparation of Draft Report

Week 9-12

- Pre-SEDEX
- Submission of Draft Report
- Preparation of Technical paper and Project Dissertation

Week 13-14

- Submission of Project Dissertation (Soft Bound)
- Submission of Technical Paper
- Submission of Project Dissertation (Hard Bound)

3.4 Gantt Chart

No.	Detail	Week													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Synthesis of COP-1 and perform purification steps	■													
2	Booking of Analysis Equipment	■	■	■	■	■									
3	Performing Verification Characterisation of COP-1 (FTIR,XRD,TGA)		■	■											
4	Performing Verification Characterisation of COP-1 (NMR, CHN, EDX)				■	■									
5	Performing Characterisation Study of COP-1 (FESEM, BET)						■	■							
6	Gas Adsorption Analysis (CO_2)								■						
7	Finalising Progress Report & Submission								■						
8	Gas Adsorption Analysis (CH_4)									■					
9	Completion of remaining experiments & data analysis									■	■				
10	Pre-SEDEX											■			
11	Submission of Draft Report												■		
12	Submission of Technical Paper and Dissertation (Soft bound)													■	
13	Oral Presentation and submission of Project Dissertation (Hard bound)														■

CHAPTER 4

RESULTS AND DISCUSSION

This section on results and discussion will analyse results obtained through characterisation and gas sorption measurement. Characterisation analysis will discuss on results of FT-IR, XRD, NMR, CHN, EDX, TGA, BET surface area, pore size, and FESEM while gas sorption measurement will analyse the result obtained by pure gas adsorption of CO_2 and CH_4 using COP-1.

4.1 Characterisation Analysis

4.1.1 Fourier Transform Infrared Spectroscopy (FT-IR)

Figure 13: FT-IR Result using Dried COP-1 and COP-1 Before Drying

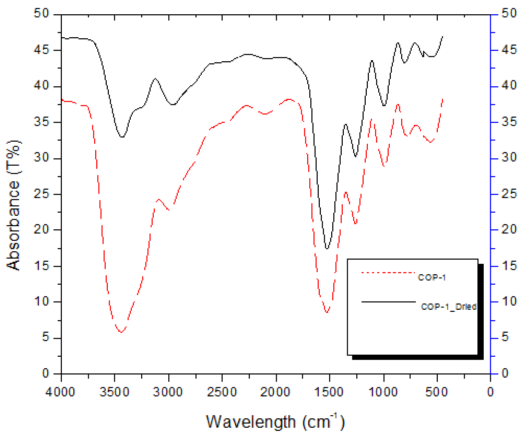


Figure 13 shows FT-IR analysis done on COP-1 samples under two conditions. The solid line shows the result of COP-1 that was tested after the sample has been dried in vacuum oven for 2 hours while the dashed line is COP-1 without drying. The COP-1 sample without drying was obtained from a bottle stored in a vacuum desiccator. The sample without drying and the dried sample show similar peaks except for the peak at 3500 cm^{-1}. The peak at 3500 cm^{-1} was very significant for the sample without drying. This denotes O-H stretching, hence representing presence of moisture. For sample after vacuum drying, the peak at 3500 cm^{-1} has reduced significantly. From the FTIR result, it could be concluded that COP-1 is very sensitive to air and will adsorb air very quickly and readily.

Figure 14: FTIR From This Research

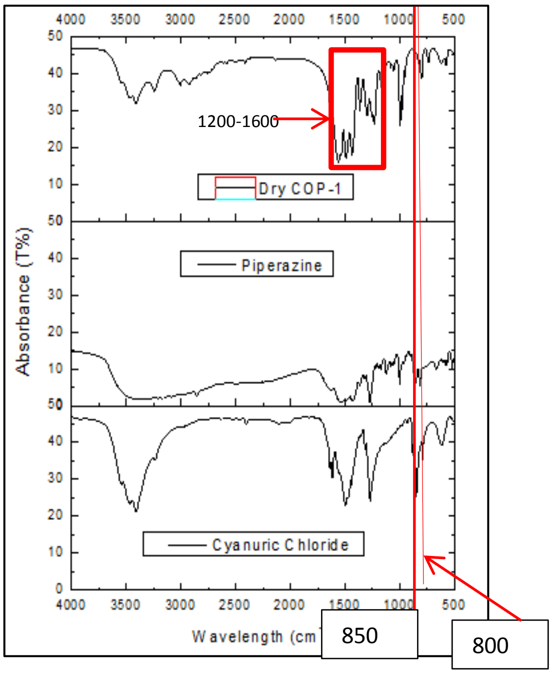
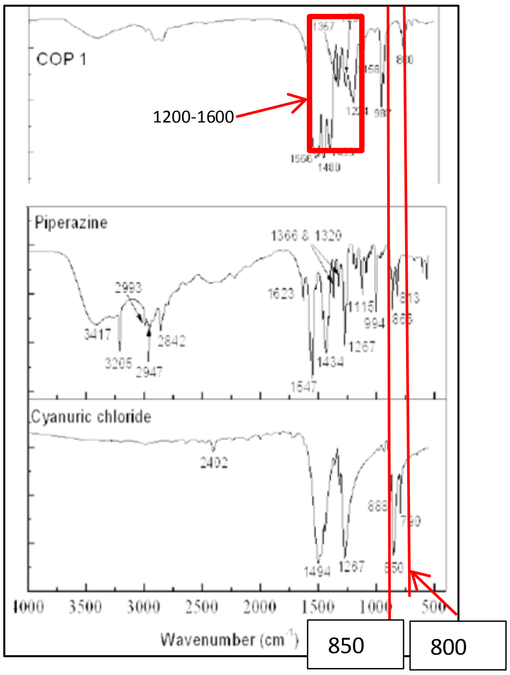


Figure 15: FTIR Result by Patel (2012)



FT-IR analysis done in Figure 14 is to investigate the functional groups of COP-1 with respect to cyanuric chloride and piperazine. The result was then compared with the results by Patel (2012) in Figure 15 for verification. The sample for COP-1 used was the dried sample as the graph by Patel (2012) also shows only a small peak at 3500 cm^{-1}. This is done for equal comparison.

The first crucial peak for investigation is the peak at 850 cm^{-1}. The peak at this wavenumber represents C-Cl stretching. It is noticed that cyanuric chloride sample have a significant peak at this wavenumber as cyanuric chloride has three chlorine atoms attached to it. After the reaction of cyanuric chloride with piperazine to form COP-1, it is expected that all three chlorine atoms of cyanuric chloride to be fully substituted by piperazine linkage. Hence, the FT-IR peak of COP-1 at 850 cm^{-1} should be absent. The result shown in Figure 2 is in accordance to the expected result and is similar to the result by Patel (2012) showing an absence of peak at the wavenumber of 850 cm^{-1}. Hence, it is concluded that the sample synthesised does not have C-Cl bond anymore and the results is desired.

The second crucial peak analysis would be at 800 cm^{-1}. This peak represents presence of triazine units. The triazine units are present in both cyanuric chloride and piperazine and would also be present in COP-1. It is expected that there will be a peak at 800 cm^{-1} for COP-1 hence proving that the triazine units are still present in the sample after the synthesis reaction. From Figure 2, it is verified that there is a peak at 800 cm^{-1} for COP-1 similar to result by Patel (2012), hence triazine units are present in COP-1.

The third analysis to the FT-IR spectrum is the region of 1200 cm^{-1} to 1600 cm^{-1} where it is expected to have several strong bands in COP-1 representing typical stretching modes of CN heterocycles. The presence of the CN heterocycles is evident in both the results obtained from this research with the result by Patel (2012). Hence, The FTIR results obtained from this research are all similar to the results by Patel (2012).

4.1.2 X-Ray Diffraction (XRD)

Figure 16: XRD raw data result from this research obtained from SIRIM Berhad

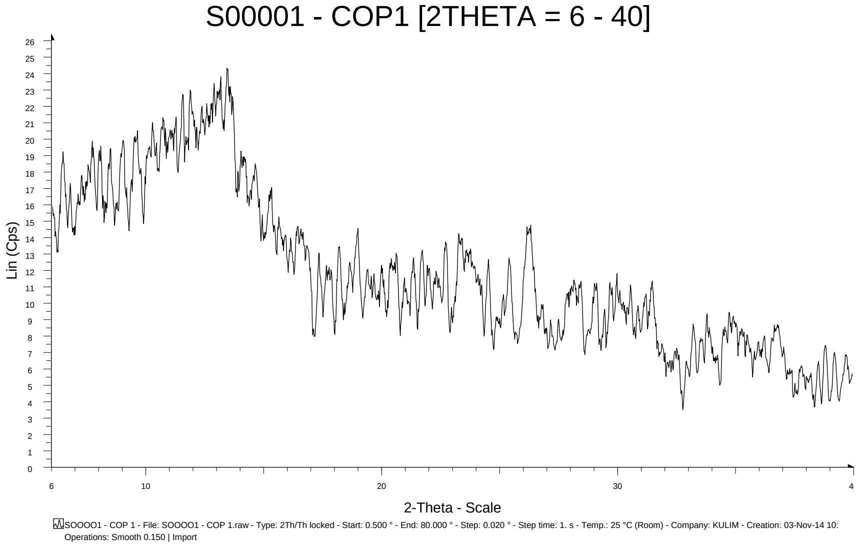


Figure 17: XRD From This Research

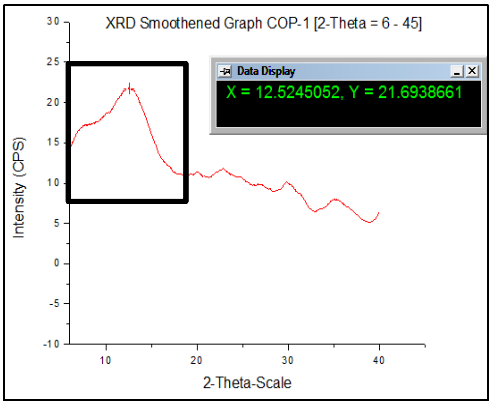
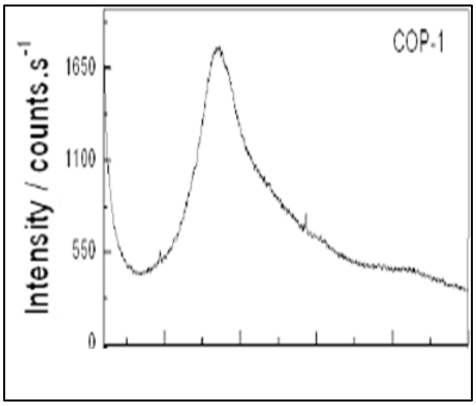


Figure 18: XRD Result by Patel (2012)



The raw data curve obtained directly from the XRD equipment (Figure 16) is smoothened after being replotted using Origin 8 software and displayed in Figure 17. The data in Figure 17 would be interpreted and compared with the literature result in Figure 18.

The curve in Figure 17 shows a very broad peak at 2 - theta-scale of 6° to 17° and no peaks at other regions. The peak of the curve is identified at 12.52° giving an intensity value of 21.69 counts per second. The results by Patel (2012) in Figure 18 also show a broad peak. Hence, from this XRD test, it could be concluded that there is absence in crystallinity in the structure of COP-1 as the peak is very broad. Shall there be signs of crystallinity, the peak observed shall be very sharp. Therefore, XRD analysis proved the expected result of COP-1 to show absence of crytallinity.

4.1.3 Nuclear Magnetic Resonance (NMR)

NMR on COP-1 was performed for both C-NMR and H-NMR. C-NMR done in this experiment is shown in Figure 19 while C-NMR done by Patel (2012) is shown in Figure 20. H-NMR is shown in Figure 21.

Figure 19: C-NMR in this Research

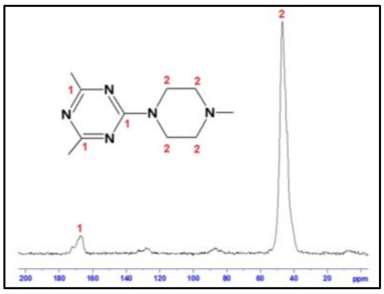
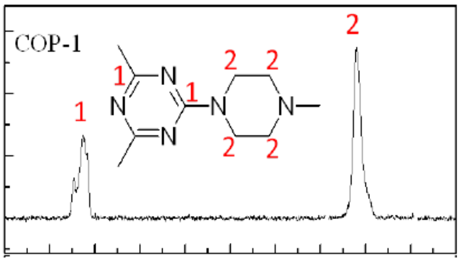


Figure 20: C-NMR by Patel (2012)



C-NMR of COP-1 shown in this research as seen in Figure 19 shows two main peaks at 46.82 ppm and 167.12 ppm. The peak at 46.82 ppm represents aliphatic CH_2 group of COP-1 as labelled in Figure 19. As for the second peak at 167.12 ppm, it represents triazine ring carbons. Hence, C- NMR confirms the theoretical linkages that should be present in COP-1. The C-NMR peaks identified by Patel as seen in Figure 20 were 44.2 ppm and 164.7 ppm which were close to what is obtained in this research.

Figure 21: H-NMR in this Research

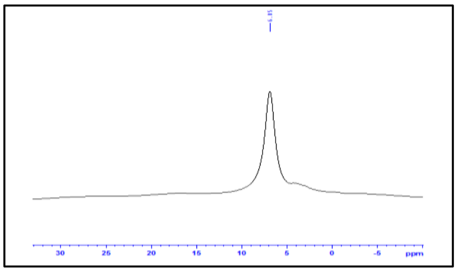
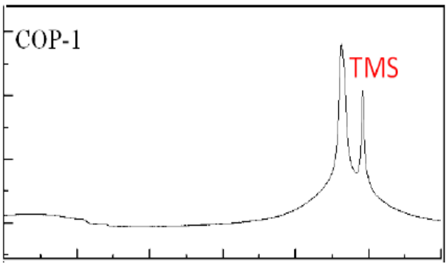


Figure 22: H-NMR by Patel (2012)



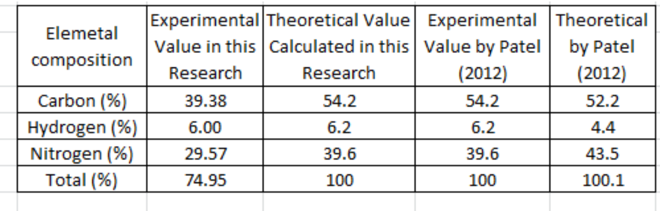
H-NMR in this research shown in Figure 21 for COP-1 also confirms the theoretical chemical shift corresponding to methylene groups of piperazine at 6.85 ppm in this research and at 3.2 ppm in the research by Patel (2012) in Figure 22.

Thus, NMR managed to show the linkages that are supposed to be present in COP-1.

4.1.4 Carbon Hydrogen Nitrogen Analysis (CHN)

CHN analysis serves to investigate elemental composition of COP-1 in terms of carbon, hydrogen and nitrogen present in the sample.

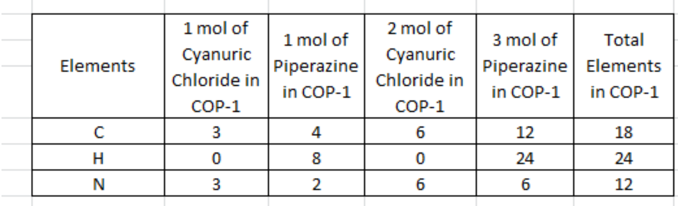
Table 6: CHN Analysis and Theoretical value of COP-1



Elemetal composition	Experimental Value in this Research	Theoretical Value Calculated in this Research	Experimental Value by Patel (2012)	Theoretical by Patel (2012)
Carbon (%)	39.38	54.2	54.2	52.2
Hydrogen (%)	6.00	6.2	6.2	4.4
Nitrogen (%)	29.57	39.6	39.6	43.5
Total (%)	74.95	100	100	100.1

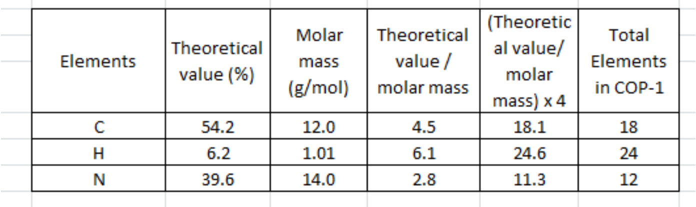
The theoretical values calculated in this research suggest that the experimental result and theoretical value by Patel (2012) should be swapped. The experimental value as claimed by Patel (2012) of 54.2 % C, 6.2% H and 39.6% N should be the theoretical value according to calculation from this research as shown in Table 7 and Table 8.

Table 7: Theoretical Total Elements of Carbon, Hydrogen and Nitrogen in COP-1



Elements	1 mol of Cyanuric Chloride in COP-1	1 mol of Piperazine in COP-1	2 mol of Cyanuric Chloride in COP-1	3 mol of Piperazine in COP-1	Total Elements in COP-1
C	3	4	6	12	18
H	0	8	0	24	24
N	3	2	6	6	12

Table 8: Validated Theoretical Percentage of Elements in COP-1



Elements	Theoretical value (%)	Molar mass (g/mol)	Theoretical value / molar mass	(Theoretical value/ molar mass) x 4	Total Elements in COP-1
C	54.2	12.0	4.5	18.1	18
H	6.2	1.01	6.1	24.6	24
N	39.6	14.0	2.8	11.3	12

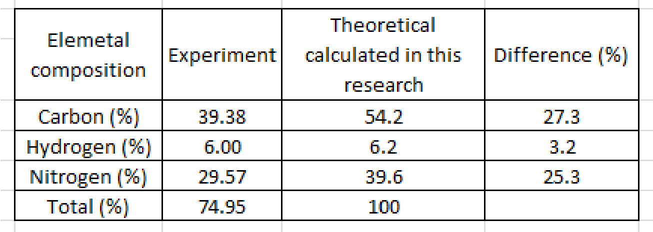
The balanced equation for synthesis of COP-1 is:

$$2\,C_3Cl_3N_3 + 3\,C_4N_2H_{10} \rightarrow C_{18}N_{12}H_{24} + 6\,HCl$$

Two moles of cyanuric chloride reacts with three moles of piperazine to form one mole of COP-1 and six moles of hydrochloric acid. The elemental composition of the COP-1 formed is calculated by first calculating the theoretical amount of elements in COP-1 as shown in Table 7. Then, in Table 8, the theoretical percentage of elements was verified to be 54.2% C, 6.2% H and 39.6% N by taking into consideration the molar mass of C, H and N. The theoretical percentage of element composition sums up to 100%.

As for the experimental value found for the CHN analysis as shown in Table 9, it is found to be 39.38% C, 6% H and 29.57% N.

Table 9: Percentage Difference between Experimental Composition and Theoretical Value



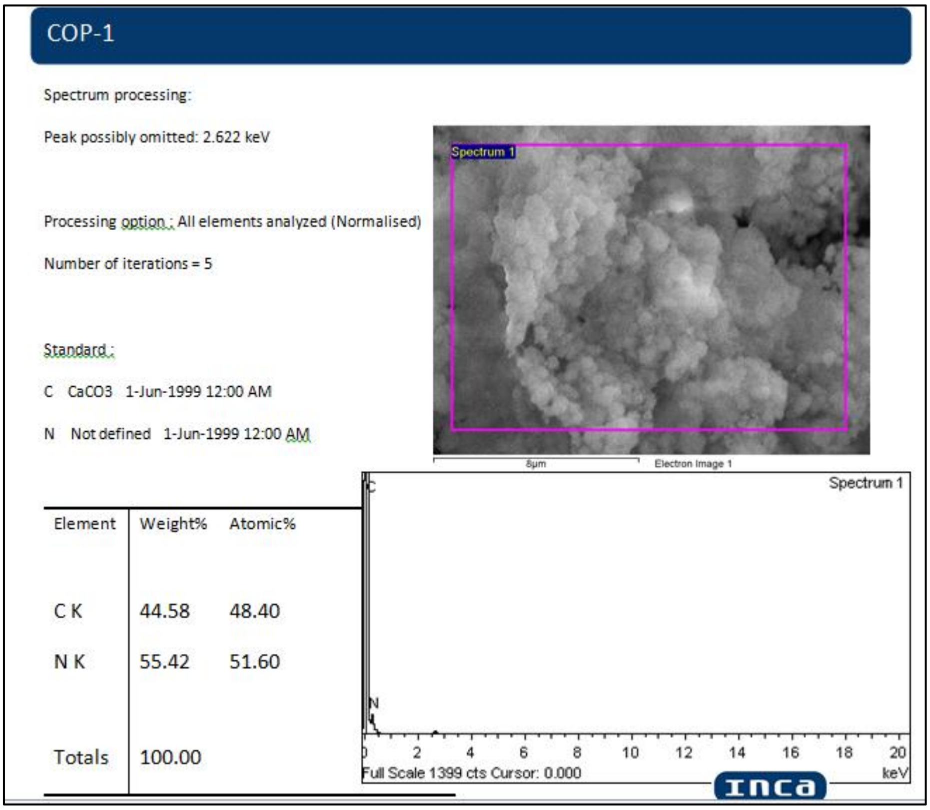
Elemetal composition	Experiment	Theoretical calculated in this research	Difference (%)
Carbon (%)	39.38	54.2	27.3
Hydrogen (%)	6.00	6.2	3.2
Nitrogen (%)	29.57	39.6	25.3
Total (%)	74.95	100	

In Table 9, it is observed that the experimental CHN percentage of elements present sums up to less than 100%. Also, the differences are huge for carbon and nitrogen composition. The reason behind this is there might be other impurities in the COP-1 synthesised. The impurities which are neither C, H nor N could not be detected by the analyser. The impurities might be present when the CHN test is done due to improper pre-treatment or impurities might be present in the sample during synthesis. The CHN analysis needs to be repeated to be more certain on the cause. If the repeated analysis still shows the same result, it may be caused by incomplete reaction of the reactants. The white precipitate which is COP-1 is filtered out and designated as the sample; however the excess reactants are disposed. This may cause the experimental composition less than theoretical. The amount of elements in COP-1 ($C_{18}N_{12}H_{24}$) are more than cyanuric chloride and piperazine.

Since CHN analysis showed that impurities might be present in the sample, EDX is done to further investigate if elements other than carbon, hydrogen and nitrogen are present in the sample.

4.1.5 Energy Dispersive X-ray Spectroscopy (EDX)

Figure 23: Elements Present in COP-1 from EDX Analysis



COP-1

Spectrum processing:

Peak possibly omitted: 2.622 keV

Processing option : All elements analyzed (Normalised)

Number of iterations = 5

Standard :

C CaCO3 1-Jun-1999 12:00 AM

N Not defined 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
C K	44.58	48.40
N K	55.42	51.60
Totals	100.00	

The EDX analysis can detect all elements from carbon (atomic number = 6) upwards; this means that it cannot detect elements with the atomic numbers 1-5, namely, hydrogen, helium, lithium, beryllium and boron. Hence, if there is no impurity present in COP-1 sample, the result would expect to show detection of C and N elements only with the absence of other elements such as Cl. The results for the EDX analysis were indicated as follows as Figure 23. The results for EDX indeed does not detect other impurities and is consistent with FT-IR that all three chlorine atoms of cyanuric chloride was fully substituted by piperazine linkage. Piperazine $C_4N_2H_{10,}$ however only consist of the elements C, H and N so this test could not tell if piperazine has completely reacted but could verify that the sample does not contains element other than C and N.

4.1.6 Thermal Gravimetric Analysis (TGA)

TGA is used to study the thermal stability of the sample to investigate when the sample starts to decompose.

Figure 24: TGA Curves in this Research Under N_2 and O_2 Atmosphere at 10°C / min Heating Rate

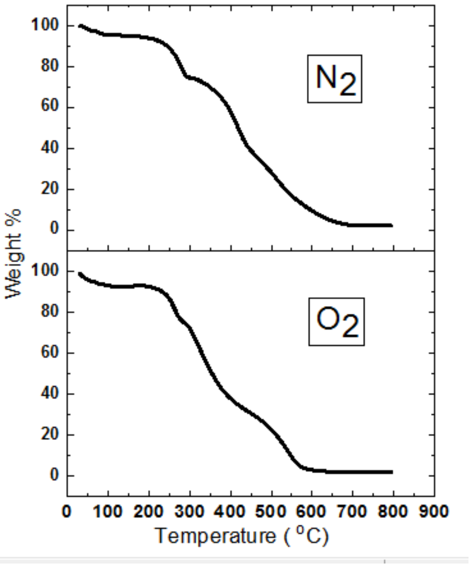
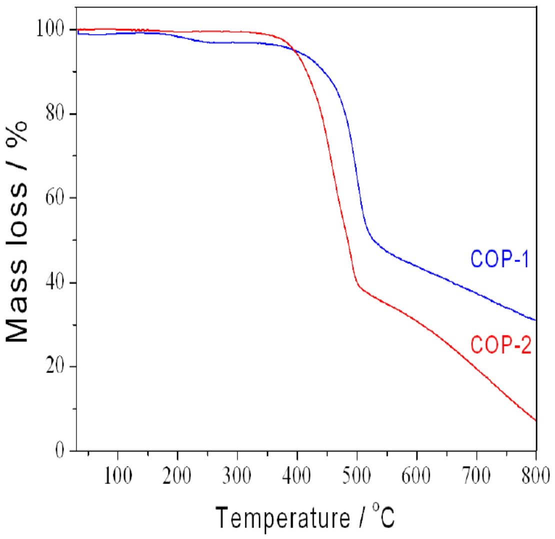
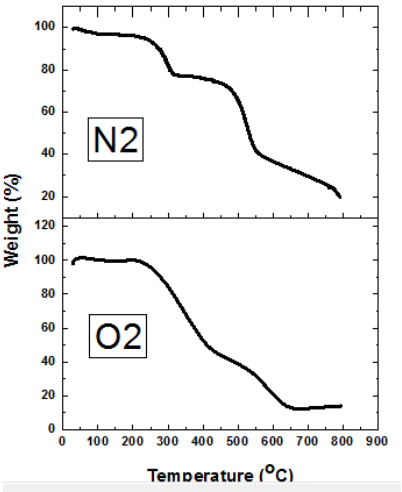


Figure 25: TGA by Patel (2012) Under N_2 Atmosphere at 10°C / min Heating Rate



The TGA result in this research is shown in Figure 24 for a heating rate of 10°C / min, similar to the condition used by Patel (2012) as shown in Figure 25. The curve in Figure 24 showed that COP-1 starts decomposing at 210°C under both N_2 and O_2 atmosphere. In comparison, the results by Patel (2012) states that COP-1 started to decompose at 360°C in N_2 atmosphere and 285°C in air which in this research resembled by $O_{2.}$ The thermal stability of this sample is less than the COP-1 synthesised by Patel (2012), however this thermal stability is already sufficient to cater for the natural gas scrubbing industry operating at ideal temperature of 40°C to 70°C. The maximum stack temperature of LNG operation is also limited to 180°C. Thus, this sample synthesised shown high thermal stability to suit all condition for natural gas applications. The TGA is repeated for heating rate of 20°C / min to investigate the improvement in thermal stability as seen in Figure 26.

Figure 26: TGA Curves Under N_2 and O_2 Atmosphere at 20°C / min heating rate



The curve in Figure 26 showed that COP-1 starts decomposing at 230°C under N_2 atmosphere and 220°C under O_2 atmosphere. The thermal stability improved as accordance to theory that the sample will degrade less under higher heating rate hence less heating time. However, the thermal stability of this sample is still less than that synthesised by Patel (2012).

4.1.7 BET Surface Area and Pore Size

Table 10: BET Surface Area and Pore Size

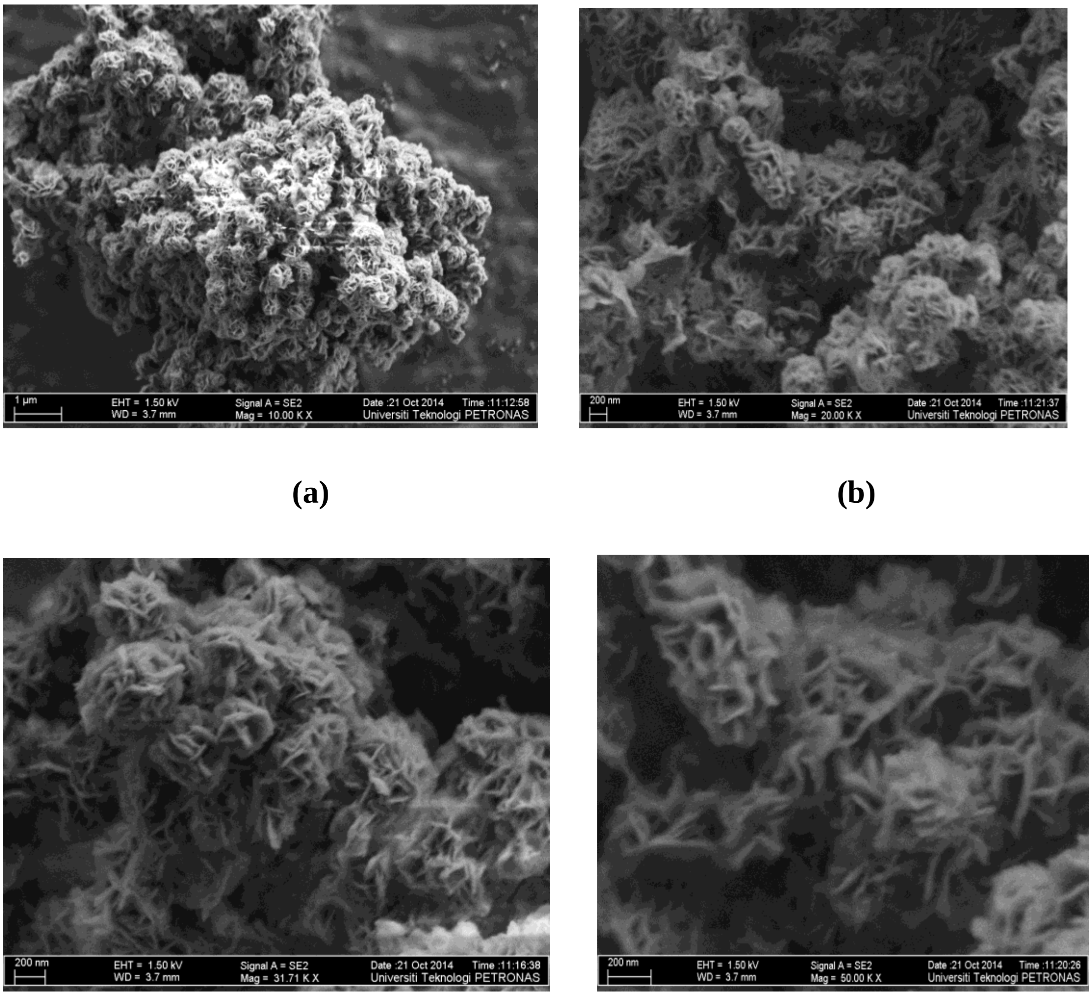
BET Surface Area (m^2/g)	
Experimental	Patel (2012)
75.4746	168

Pore Size (nm)	
Experimental	Patel (2012)
7.9819	6.6

The BET surface area found in this research as shown in Table 10 is half of the surface area obtained by Patel (2012). The pore size of the sample in this research of 7.9819 nm is mesoporous and is slightly larger than the pore size reported by Patel (2012). Desirable properties for CO_2 gas capture would be high surface area and small pore size would enhance selectivity for CO_2 gas capture Rufford (2012) & Yu (2012). The flow gas for the test is the commonly used N_2 gas. The reason behind less BET surface area is probably because the sample only undergo around 12 hours of degassing. A longer time for degassing around 24 hours could show a better result. The sample should also be dried in vacuum oven before analysis. Besides, another reason is the reaction was incomplete during synthesis and requires a repeat in synthesis for the second batch of COP-1 synthesis. Pore size might be disrupted during arrangement of the polymer which is incomplete in reaction.

4.1.8 Field Emission Microscopy (FESEM)

Figure 27: FESEM images of COP-1 at magnification of (a) 10 KX (b) 20 KX (c) 31.71KX and (d) 50KX



(a) **(b)**

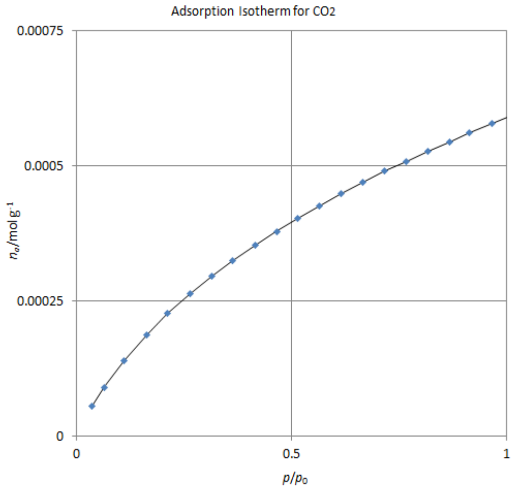
(c) **(d)**

The COP-1 morphology is observed to be non-crystaline, flaky in nature and looks like petals of a flower. It has many pores available and is very promising for gas capture.

4.2 Gas Adsorption Measurement

4.2.1 CO_2 Pure Gas Adsorption Measurement

Figure 28: CO_2 Adsorption Isotherm for COP-1



The CO_2 gas capture capacity for COP-1 at 1 bar, 25°C is taken at the highest value at $p/p_o = 1$ of 26 mg g^{-1}. The unit conversion is shown in Table 11 as well as comparison with results from Patel (2012).

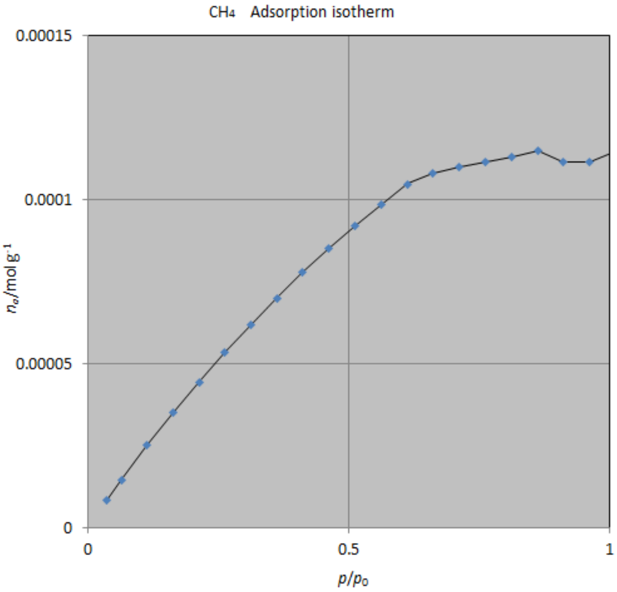
Table 11: Gas Sorption Measurement of CO_2 from this Research and by Patel (2012)

Gas	Experiment Adsorption Capacity		Adsorption Capacity (Patel et al., 2012)
	mmol g^{-1}	mg g^{-1}	mg g^{-1}
CO_2	0.59244	26	60

The adsorption capacity as shown in Figure 28 increases as p/p_o increases till it reaches the maximum of 1. The CO_2 gas capture of COP-1 synthesised in this research is half of that published by Patel (2012). It is seen that there is relationship between the BET surface area of COP-1 and the corresponding CO_2 adsorption capacity. When the surface area found in this research to be half of that shown by Patel (2012), the CO_2 gas capture is half as well.

4.2.2 CH_4 Pure Gas Adsorption Measurement

Figure 29: CH_4 Adsorption Isotherm for COP-1



The CH_4 gas capture capacity for COP-1 at 1 bar, 25°C is taken at $p/p_o = 1$ of 1.8 mg g^{-1}. The unit conversion is shown in Table 12. For methane gas capture of COP-1, it has not been studied and this result narrows the research gap.

Table 12: Gas Sorption Measurement of CH_4 from this Research and by Patel (2012)

Gas	Experiment Adsorption Capacity	
	mmol g^{-1}	mg g^{-1}
CH_4	0.11405	1.8

The CH_4 adsorption capacity of 1.8 mg g^{-1} is relatively low compared to gas adsorption of CO_2 of 26 mg g^{-1}. It is a desirable result as the objective of the sample is to capture high amount of CO_2 and low CH_4 capture.

4.2.3 CO_2 / CH_4 Gas Adsorption Selectivity

Table 13: CO_2 / CH_4 Selectivity

Gas	Adsorption Capacity (mmol g^{-1})	Selectivity of CO_2 / CH_4
CO_2	0.59244	5.19
CH_4	0.11405	

The selectivity of CO_2 / CH_4 of 5.19 could not be compared with other COPs as there is no study on the selectivity of COP for CO_2 / CH_4 separation. When compared with materials as shown in Table 14 such as MOF and zeolites, it is seen that the COP-1 produced in this research shows relatively high selectivity at similar pressure condition at atmospheric pressure. However, for material with high selectivity, the selectivity can be as high as 257 using MOF (Liu et al.,2012).

Table 14: Selectivity of CO_2/ CH_4 of Various Materials at Atmospheric Pressure

Material	CO_2/ CH_4 Selectivity at Atmospheric Pressure
COP-1	**5.19**
ZSM-5 (Salmasi et al.,2013)	1.7
β-zeolite (Salmasi et al.,2013)	4.63
MCM-41 (Salmasi et al.,2013)	4.5
MOF - Al(OH)(NDC) (Liu et al.,2012)	4.4
MOF - Zn2(BPDC)2(BPEE) (Liu et al.,2012)	257

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

In conclusion, this research managed to synthesise a material that shows similar characteristics to COP-1 in terms of functional groups, linkage, absence of crystallinity, and thermal stability sufficient to cater for natural gas applications. However, some differences are noted such that the elemental composition of COP-1 does not tally with Patel (2012). A possible reason is there might be impurities in the sample, but EDX analysis showed that no elements other than C and N are present in the sample. Another difference is that both surface area and CO_2 capture using COP-1 in this research is fell short of that obtained by Patel (2012). The pure gas adsorption capacity of CO_2 and CH_4 in this research is found to be 26 mg g^{-1} and 1.8 mg g^{-1} respectively. A simple selectivity of CO_2 / CH_4 is calculated as 5.19. The morphology of COP-1 is observed to be porous, non-crystaline, flaky in nature and looks like petals of a flower. This research closed the gap for CH_4 capture data at low pressure as well as the morphology of COP-1. All the objectives are achieved.

For recommendations, to improve this research, the synthesis methodology would be improved by ensuring that N_2 atmosphere is provided at its best during weighing of reactants and transferring of reactants from one reactor to another. The preparation of reactants should also be quick to avoid the interference of air since the materials are very sensitive to air. The synthesis should also be repeated with different stirring rates to ensure the reactants are fully reacted. Synthesis of COP-1 with excess of reactants in different proportions can also be investigated. As for analysis, all samples should be degassed and undergo drying prior to analysis test. Further study on this research could be on CO_2 / CH_4 binary gas selectivity with high amount of CO_2 at high pressure condition similar to natural gas applications.

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