Effect of Different Synthesis Condition on the Covalent Organic Polymer-4 Properties as Adsorbent

by

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Dissertation submitted in partial fulfillment of
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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Chemical Engineering Programme
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Approved by,

Dr. Nurhayati Bt Mellon

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
JANUARY 2015

CERTIFICATION OF ORIGINALITY

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

RIFQI SANI BUDIAWAN

ABSTRACT

CO_2 content in some natural gas reserves is in high amount hence reduces the gas heating value. With the current high cost of separation technology, there is a need to separate the high CO_2 content from the natural gas by a cheaper means. Adsorption technology is known for its cost efficiency for separation when compared to another separation processes. In this paper, an effort to synthesize a new adsorbent COP-4 which has good CO_2 adsorption properties in high pressure is conducted. Review of recent literatures suggests that only a little research has been done in investigating the potential of adsorption to be used in the natural gas CO_2 separation. The adsorbent is investigated of its optimum production temperature in order to optimize the production costs by altering the reaction temperature and time. The adsorbent then are characterized by using VPFESEM, TEM, Surface area and Porosity Analyzer in order to investigate its preliminary properties. The COP-4 samples are made by using microwave reactor method, which is different than the conventional solvothermal method. The solvothermal method is the conventional method in the production of organic material using solvent that took relatively long reaction time. The microwave reactor method, potential reduction of the reaction time can be done to when compared to the original method. Characterization result indicates that the surface area and pore size of the COP-4 adsorbent decreases when produced in an increasing temperature, while still keeping its high pressure adsorption potential.

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CHAPTER 1

INTRODUCTION

In 2013, Malaysia is the world's second-largest exporter of liquefied natural gas after Qatar and the second-largest oil and natural gas producer in Southeast Asia. Malaysia has a relatively large reserve of natural gas. It has the 14th largest natural gas reserves in the world, estimated as of January 2008 to be 88 trillion standard cubic feet or 14.67 billion barrels of oil equivalent, and it is larger than its crude oil reserve of 5.46 billion barrels. However, some reserves have significant challenges to be developed since it has low gas permeability and a large CO_2 content (>20%) as well as low reservoir porosity ranging from 15% to 20%.

According to a study conducted by Darman in 2006, Malaysian natural gas fields have CO_2 contents ranging from 28% to 82%. Most of the reserve wells have CO_2 content ranging from 50% to 74%, with the second most 25% to 49% of CO_2, and the least is more than 75% CO_2. Malaysia is one of the few countries in the world to be a natural gas producer and net exporter which may turn to become a net importer if the production is not developed significantly to cover future needs due to high demand for energy from natural gas, as well as the feedstock for its petrochemical industry.

Low gas permeability of the reserves (1 to 10 mD) means the common method of extracting the well is not sufficient in drawing the gas out to the surface, hence needs to be supported with hydraulic fracturing of the reservoir, which increases capital requirement to develop such reservoir and due to high cost of the overall CO_2 removal system, developers would be discouraged to develop wells with high CO_2 content, or emit the CO_2 instead of storing due to the high cost involved.

Based from these reserve conditions, CO_2 removal technology from natural gas in Malaysia is important to ensure a viable well development as well as sustainable production.

1.1 Problem Statement

Carbon dioxide (CO_2) occurs naturally in natural gas reservoir; however, the presence of CO_2 causes many problems such as it reduces the energy contents and the heating value of the natural gas. In addition, CO2 mix with water in the wet condition of natural gas stream to become acid that may cause corrosion to the processing equipment. Furthermore, in the processing of Liquid Natural Gas (LNG) or Liquid Petroleum Gas (LPG), cold temperature in the operation can make the CO_2 to sublime into solids, forming hydrates that cause damages to the equipment or cause blockages in the pipelines. Thus, CO_2 need to be separated from natural to ensure an efficient and safe processing of natural gas as well as making a viable business. The level of CO2 in natural gas that is acceptable to be delivered to customers by pipeline is less than 3% (Ross and Cuellar, 2007).

Recent CO_2 capture technology using adsorbent material is an increasingly developed technology and has numerous studies in its application to the three separation conditions: pre-combustion, post-combustion, and oxy-fuel combustion. However, this creates application gap as only a little focus is given towards the natural gas processing that needs low cost CO_2 separation system in the development of high CO_2 gas fields, where new adsorbent materials have been developed to cater this need for example Covalent Organic Polymer (COP) which provides low cost solution with high performance for CO_2 separation. Development has been emphasized in improving the reliability, cost and performance of the adsorbent materials, CO_2 uptake, and hydrothermal stability.

1.2 Objectives and Scope of Study

The objectives of this project are:

1. To synthesize COP-4 by solvothermal method and using microwave reactor and characterize the COP-4
2. To perform adsorption capability study on the synthesized COP-4 adsorbent

The scopes of this project include:

1. Synthesis of 2 COP-4 samples using microwave reactor with reactor temperature of 105^0C for 4 hours and 145^0 C for 45 minutes;
2. Characterization & analysis of the COP-4 surface area, porosity and crystallinity;

CHAPTER 2

LITERATURE REVIEW

CO_2 separation from natural gas is important to the economic feasibility of the industry. Some of the technologies for CO_2 separation from natural gas are chemical absorption, adsorption, low temperature distillation, and membrane (Rufford, *et al.*, 2012). Current new technology of CO_2 removal is limited in its application in the natural gas processing, due to consideration of the operating conditions; with two main concern in the level of CO_2 to be captured and the CO_2 partial pressure involved (Rufford *et al.*, 2012).

Absorption of CO_2 in gas stream by aqueous amine absorption (scrubbing) is a conventional method in the removal of CO_2 in the industrial scale, established by the application in the refineries, cement plant, and power plant. Mono-ethanolamine is the type of amine used as sorbent. The CO_2 loading capacity for the amines is in the range of 0.5–1 mol of CO_2 per mol of amine.

The chemical absorption process involves reactions of the CO_2 with the sorbent to form weakly bonded intermediate compounds, and these reactions can be reversed by the application of heat to release the CO_2 and regenerate the sorbent (Olajire, 2010). However, the main drawback of this process is that the process requires high money investment as the regeneration process of the sorbent requires a high amount of energy, and as its CO_2 loading capacity is relatively low, the process needs a high solvent circulation, large diameter and high pressure absorber which increase the capital requirements. In addition, the aqueous amine used as sorbent is corrosive in nature, hence may induce corrosion in the process equipment, and it may also degrade to form organic acids. Moreover the process also involves side absorption of hydrocarbon compound, such as benzene, toluene and ethyl benzene, which might be unintentionally removed with acid gases. Finally, the used sorbents cannot be recycled back to the process and are disposed of; hence cause environmental problems on disposal of such chemical (Cretier *et al*., 2004; Ebenezer and Gudmunsson 2006).

Another process that can be used to separate CO_2 is by cooling process. Lemmon *et al.* categorized the separation of CO_2 from natural gas by low-temperature processes (operating at temperatures below 1 ^{0}C) as gas–liquid phase separations operating at temperatures above the CO_2 triple point temperature of 56.6 ^{0}C and gas–solid phase separations where the de-sublimation of CO_2 occurs at temperatures below the triple point. Major drawback of this process is its energy intensive requirement, where a cryogenic low temperature is needed. It also needs additional process to remove moisture from the gas to prevent piping or equipment blockage due to solid ice formation. Impending issue of solid CO_2 formation that the effect of low temperature may pose, two technological approaches have been developed to overcome the issue in the form of extractive distillation by the addition of a heavier hydrocarbon to alter the solubility of components in the column (Ryan/Holmes process) and controlled freezing and re-melting of the solids (Controlled FreezeZone^{TM} and CryoCells processes). Even so however, these technologies have disadvantages that it uses toxic and flammable chemicals as the cooling fluids, such as acetylene and ethane (Ebenezer and Gudmunsson, 2006) and it has problems arising with the control of CO_2 freezing and CO_2 solid handling (Rufford *et al*., 2012). The advantage of this process is that it enables the production of liquid CO_2 which makes transportation easier, for example by ship.

Next method of separation, membrane separation has been applied since the 1980s in the natural gas industry to remove CO_2, N_2, H_2S and NGLs (Baker and Lokhwandala, 2008). It has also been applied to another industry, most successfully in the water purification technology (desalination). The technology is divided into three types: polymeric, inorganic and mixed matrix membrane. The commercial membrane technologies employed in the natural gas industry are predominantly nonporous polymeric membranes (Membrane Technology & Research, 2010).

In membrane separation, the transport method of gas molecules can be categorized into sorption–diffusion, solution-diffusion and molecular sieving (Koros and Mahajan, 2000). Transport of gas molecules through the membrane occurs first by absorption of the gas molecule into the membrane and then by diffusion, or permeation, of the molecule through the membrane material. Separation of gas components is therefore achieved by the differences in the solubility and mobility behaviors of the components of the natural gas feed.

The advantages of membrane technology are its ability to perform separation without phase change, low thermal energy requirement, simple operating equipment, and convenient start-up and shut down procedures. However, it has issues with the large volume application due to its low selectivity and capacity. Energy penalty and process complexity also relatively high, as it has low degree of separation the process needs multiple stages and recycles. This is due to loss of selectivity and separation performance due to degradation of the membranes; the presence of heavy hydrocarbon reduces its performance as it causes damage to the membrane (Shimekit and Mukhtar, 2012).

Alternatively, the adsorption-based separations are applied to remove water, sulphur, mercury and heavy hydrocarbon. The process has a high potential for use in the industry as it involves much less energy penalty than the absorption based separation hence the regeneration cost (Shimekit and Mukhtar, 2012), which is important due to the relative uneconomical nature of natural gas processing. In addition, it does not involve chemical solvent or sorbent which may be hazardous or toxic chemical. Moreover, adsorbent material has high stability and hence can be used in multiple cycles. However, current adsorbent technology is not considered attractive for large scale CO_2 removal operation due to the low capacity of the sorbent and low CO_2 selectivity (CO_2 capture project, 2008). Most of the current adsorbent technology only applied in processing natural gas feeds containing no more than 2% CO_2 and limited to natural gas flow rate of 15 MMscfd (Rufford *et al*., 2012) because the quantity of adsorbent required to capture greater volumes of CO_2 is large. Due to these conditions, more novel material with high CO_2 adsorption capacity, high gas selectivity, and high hydrothermal stability is needed for application in the industry.

Carbon dioxide exhibits a large quadripole moment, thus adsorbents with polar surfaces that have a high electric field gradient has more interaction to CO_2 than non-polar molecule such as CH_4. For selective adsorption of a non-polar molecule like CH_4, an adsorbent with a high surface area possessing a large number of sites for adsorption is a good material.

Current adsorption technology uses porous material as adsorbent such as activated carbon and zeolites with capacities up to 7.4 mmol g^{-1} (298 K at 32 bar) and 25 mmol g^{-1} (298 K at 30 bar) respectively (D'Allessandro *et al*., 2012). New nanoporous materials have also been developed and show promising potential in gas capture. To date, several crystalline and amorphous nanoporous organic materials with flexible design have been developed—namely, COF, PIM, HCP and CMP, CTF, PAF, PPN, POF, BILP, EOF, PECONF and COP (Patel *et. al*., 2012), MOF, and ZIF (Hao *et al*., 2011). These materials can provide alternatives to benchmark adsorbents such as the industrial standard zeolite 13X with CO_2 capacity of 3.3 mmol g^{-1} at 298 K and 100 kPa (Saha *et al*., 2010).

Material widely studied for CO_2 adsorbent is Metal Organic Framework (MOF), due to its controllable structural feature and high porosity. Moreover it has high internal surface areas high void volumes and low densities (D'Alessandro *et al*., 2010). Bao *et al*. reported that one type of MOF (Mg-MOF-74) has CO_2 adsorption capacity of 8.5 mmol g^{-1} at 298 K and 100 kPa where it is higher than the zeolite 13X of 3.3 mmol g^{-1}.

However, Dawson *et al.* reported that MOP(4) adsorption capacity is reduced by 50% when applied in realistic wet condition.

Among these new materials, Covalent Organic Polymer (COP) has a good hydrothermal stability due to its stable covalent bond (C-C, C-H and C-N bonds) and can be produced with a relatively low cost compared to another materials. Patel *et al.* reported that COP has a high CO_2 capture capacity, hydrothermally stable. Patel et al. have synthesized two COPs, with adsorption capacity up to 1.36 mmol g^{-1} (COP-1) and 0.91 mmol g^{-1} (COP-2) at 298 K and 1 bar. Xiang *et al*. have synthesized four COPs (COP-1, COP-2, COP-3, and COP-4) with adsorption capacity up to 0.91 mmol g^{-1} (COP-1), 1.43 mmol g^{-1} (COP-2), and 1.36 mmol g^{-1} (COP-3 and COP-4) at 298 K and 1 bar.

COP-4 made by Xiang *et al*. has a high CO_2 capacity due to its BET SSA (2015 m^2 g^{-1}) which is highest among the four COPs (594 mg g^{-1} at 298 K and 40 bar). Xiang *et al.* reported that it is higher than COF-5 (441 mg g^{-1}), COF-8 (502 mg g^{-1}) and COF-10 (412 mg g^{-1}) from the work of Furukawa *et al.*, PPN-1 (393 mg g^{-1}) and PPN-2(486 mg g^{-1}) reported by Lu *et al.* and BCMBP (100) (585 mg g^{-1}) reported by Dawson *et al.*

It is also has a high uptake of CH_4 (78 mg g^{-1}) which is reported to be higher than higher than the uptakes of COF-1 (40 mg g^{-1}, 35 bar) and COF-6 (65.6 mg g^{-1}, 35 bar) reported by Furukawa *et al.*,15 and HCP-2 (72 mg g^{-1}, 20 bar) reported by Wood *et al*.

CHAPTER 3

METHODOLOGY

The COP-4 is made according to the method described by Xiang et.al. It has a structure as follows:

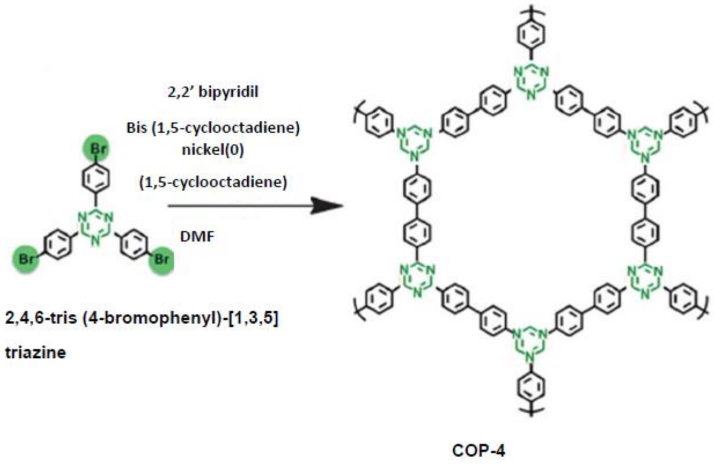

FIGURE 1.2.1 structure of COP-4

Under a nitrogen atmosphere, 1,5-cyclooctadiene (0.54 mL, 3.96 mmol, dried over CaH_2) is added to a solution of bis(1,5-cyclooctadiene)nickel(0) (0.956 g, 4.09 mmol) and 2,2′-bipyridyl (0.544 mL, 4.09 mmol) in dry dimethylformamide (55 mL), and the mixture is stirred until completely dissolved. 2,4,6-tris-(4-bromophenyl)-[1,3,5] triazine powder (0.363 g, 0.785 mmol) is subsequently added to the resulting purple solution to change it to deep-purple solution. The mixture is made for three samples namely COP4-conventional, COP4-105 and COP4-145. Conventionally, one of the sample solutions is heated at 105^0 C under a nitrogen atmosphere by solvothermal method overnight and the sample is designated as COP4-conventional. Inventively, another two of the sample solutions are put into a microwave reactor system Synthos 300. The reactor temperature and duration configuration are differentiated according to 2 samples to be made:

1. 105 ^{0}C for 4 hours with sample name COP4-105
2. 145 ^{0}C for 45 minutes with sample name COP4-145

After reaction is finished, the samples are cooled to room temperature and titrated by concentrated hydrochloric acid (4 mol) is added gradually to the suspension placed on top of a magnetic stirrer set to 1200 ppm until the black color of the suspension turn to off-white, and the solvent color to be light blue. Then the suspension is vacuum filtrated, and the solid particulate is washed with chloroform ($CHCl_3$, 5 × 15 mL), tetrahydrofuran (5 × 15 mL), and water (5 × 15 mL), respectively. Then the product is dried for 15 minutes in a 100 ^{0}C oven. Next, the product then immersed in absolute ethanol for 24 hours. The ethanol-contained sample is then filtrated and the dried in an oven for 1 hour at 100 ^{0}C with final yield of an off-white colored polymer powder.

3.1 Sample Characterizations

3.1.1 Powder X-ray Diffraction Analysis

PXRD was performed with a X-ray diffactometer with Cu Kα line (λ = 1.54178 Å) as the incident beam. X-ray diffraction (XRD) patterns of the samples was acquired from angle of 0.5^0 to 60°.

3.1.2 Variable Pressure Field Emission Scanning Electron Microscopy

Structural imaging was done by using Variable Pressure Field Emission Scanning Electron Microscope (Zeiss Supra55 VP). Elements that were analyzed N, Br, Ni, C for EDX mapping and morphology analysis.

3.1.3 Transmission Electron Microscopy

Structural imaging was done by using Transmission Electron Microscope (Zeiss Libra 200). Sample was prepared by sonication.

3.1.4 X-Ray Photoelectron Spectroscopy

XPS data was obtained on X-Ray Photoelectron Spectrometer (Thermo Scientific, K-Alpha) equipped with twin anode Al Kα X-ray source. Because of the insulating nature of the samples, the charge shift was observed. The spectra was corrected based on C1s/285.0 eV without neutralization.

3.1.5 Surface Area and Porosity Analysis

BET SSA and Langmuir SSA was obtained using the Surface Area Analyzer and Porosimetry System (Micromeritics ASAP 2020). Prior to the analysis, the sample was degassed at 200 ^{0}C for 48 hours.

3.1.6 High Pressure Volumetric Analysis

The equipment was used to find the adsorption isotherm of CH_4 and CO_2 at 298 K. The volumetric technique consisted of introducing (dosing) a known amount of gas (adsorptive) into the chamber containing the sample to be analyzed. When the sample reached equilibrium with the adsorbate gas, the final equilibrium pressure was recorded. These data were then used to calculate the quantity of gas adsorbed by the sample. The equipment can represent high pressure condition up to 200 bar. The sample was degassed at ~ 10^3 Pa at 200 ^{0}C for 24 hours to remove unwanted adsorption of air and moisture.

3.1.7 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) data was collected on Perkin Elmer STA 6000 instrument, with the heating rate of 10 ^{o}C/min in nitrogen atmosphere.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Surface Area and Porosity

The surface area is measured by Micromeritics ASAP 2020, and the samples were degassed at 200 ^{0}C for 48 hours. The summary of the analysis is summarized in the table below. The surface area decreases as reaction temperature increases and shorter time taken. Similar reaction temperature was applied to both COP4-conventional and COP4-105 however in the second sample, the reaction time is reduced from overnight to only 4 hours. Large difference is observed from both surface areas, with -600 $m^2 g^{-1}$ reduction in the surface area when the reaction time is reduced. This magnitude in surface area reduction is similar to the third sample which is reacted at 145 ^{0}C in 45 minutes. The close value of the second and third sample means there is proportionality between reaction time and temperature. When the reaction temperature is increased while reaction time is decreased, both give the same effect to the surface area, hence the similarity in the magnitude.

TABLE 4.1.1 summary of COP samples properties

Sample	BET SSA (m^2g^{-1})	Langmuir SSA (m^2g^{-1})	Pore volume ($cm^3 g^{-1}$)
COP4-conventional	2015	3041	1.36
COP4-105	1461	2076	1.99
COP4-145	1380	1969	1.08

4.2 VPFESEM Image

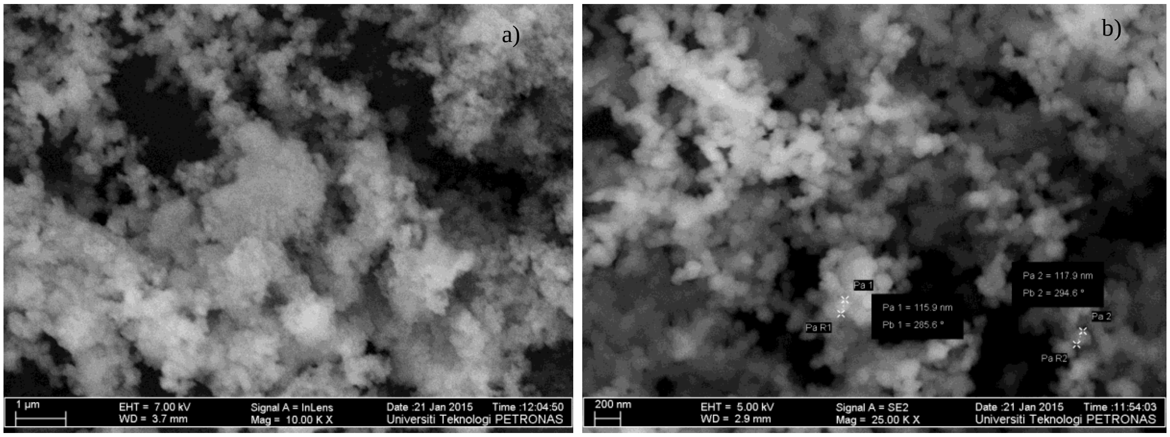

FIGURE 4.2.1 VPFESEM image of a) COP4-105 and b) COP4-145

VPFESEM image of the COP4-105 it reveals a rugged surface morphology with many closed pores and large open pores. The sample is reacted for 2 hours, and it shows that formation of large open pores is more vivid than the closed pores. The rugged morphology seems to show attachment of the molecules. The sample has lower BET surface area compared to COP4 from the literature, due to the former has much less large open pores than the latter. Large open pores might be the reason that it has larger surface area when compared to the COP4-145 sample, which has smaller large open pores. The COP4-145 image show an uneven surface with balls like agglomerate clumped together to form the surface. This might be due to incomplete formation of the short reaction time where particles are not been completely clumped and fused well. Higher temperature might also cause the open pore to close up hence forming smaller open pores.

4.3 EDX Analysis

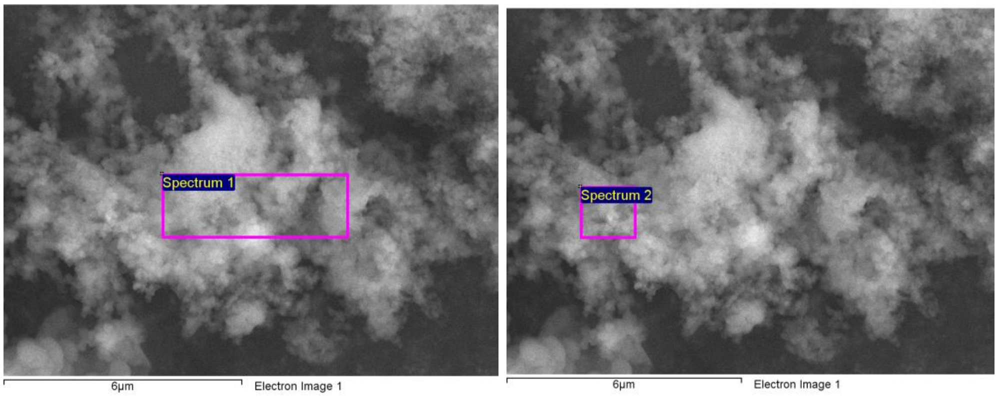

FIGURE 4.3.1 Spectrum 1 & 2 of VPFESEM image of COP4-105

TABLE 4.3.1 EDX analysis for spectrum 1&2 COP4-105

	Spectrum 1		Spectrum 2	
Element	Weight %	Atomic %	Weight %	Atomic %
C K	94.59	95.48	86.26	88.08
N K	5.18	4.48	13.59	11.9
Ni K	0.08	0.02	0.03	0.01
Br L	0.15	0.02	0.13	0.02
Total	100	100	100	100

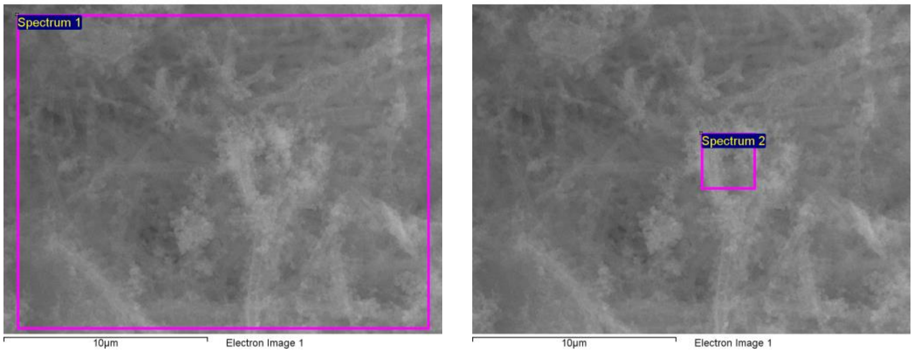

FIGURE 4.3.2 Spectrum 1&2 of VPFESEM image of COP4-145

TABLE 4.3.2 EDX analysis for spectrum 1&2 COP4-145

	Spectrum 1		Spectrum 2	
Element	Weight %	Atomic %	Weight %	Atomic %
C K	93.56	94.74	83.93	86.08
N K	5.97	5.18	15.76	13.86
Ni K	0.07	0.02	0.12	0.02
Br L	0.4	0.06	0.19	0.03
Total	100	100	100	100

The EDX analysis showed that in each sample, the elements that present correspond o a high number of percentage in weight and atom for carbon.

4.4 TEM imaging

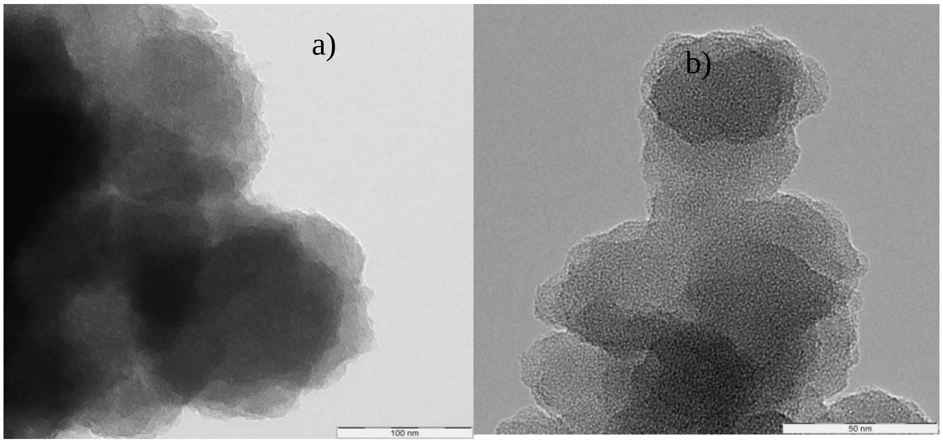

FIGURE 4.4.1 a) TEM image of COP4-105, and b) TEM image of COP4-145

TEM analysis shows 2-d image for each samples which were prepared by using isopropanol before the analysis. The images display dark and light regions. The darker regions represent the area where electrons are less likely to pass through when compared to the brighter area hence indicates the region with higher density and lower density. The rugged structure can be seen from the outer part of the structure in all the samples. The dotted particles in the image indicate pores that are distributed evenly throughout the material.

4.5 Adsorption Isotherm

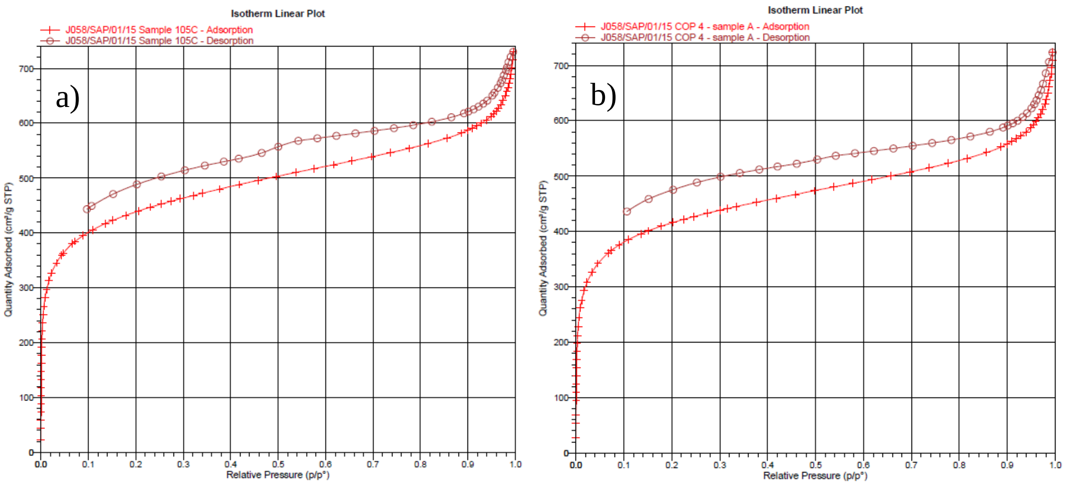

FIGURE 4.5.1 N_2 adsorption isotherms for a) COP4-105 and b) COP4-145

Using relative pressure to construct the isotherm eliminates changes in pressure from small changes in temperature. A small change in temperature changes the saturation vapor pressure considerably. For example, 0.1 K increase in temperature changes the saturation pressure of nitrogen from approx. 760 mm Hg to 800 mm Hg. The use of relative pressure is convenient and is scaled from 0 to 1. A relative pressure of 1 represents a completely saturated sample, i.e., all of the available surface structure is filled with liquid-like gas.

The adsorption isotherms for both samples show Type IV N_2 adsorption isotherms which have the property of good adsorbent in high pressure adsorption processes. At higher pressures the slope shows increased uptake of adsorbate as pores become filled. The graphs also show that the amount of pores are mainly mesopores, where below relative pressure of 0.2, the isotherm corresponds to micropore, while below 0.95 isotherm corresponds to mesopore and above 0.95 isotherm corresponds to macropore.

Type IV isotherms occurs on porous adsorbents with pores in the range of 1.5 – 100nm which is in accordance to the pore size obtained from the VPFESEM imaging.

4.6 Thermogravimetric Analysis

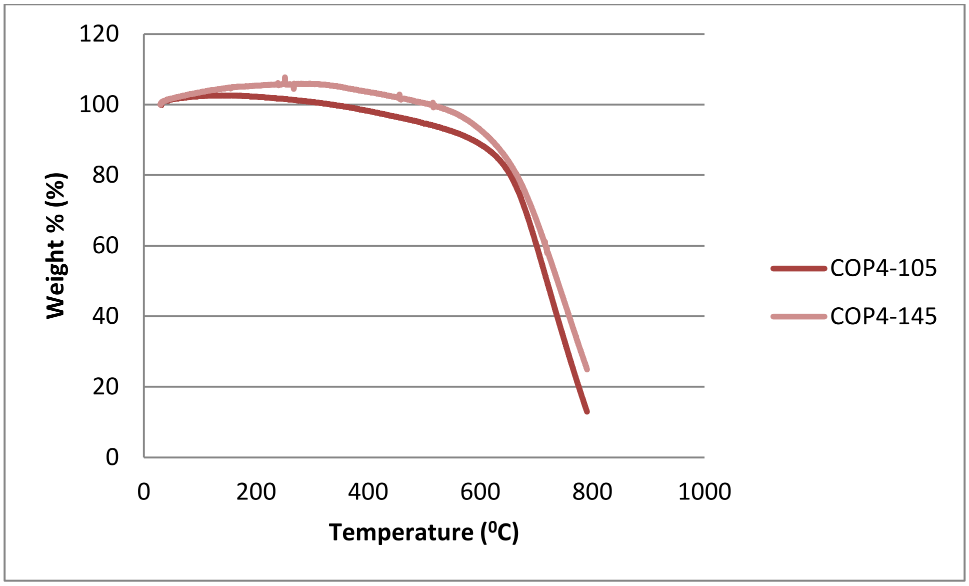

FIGURE 4.6.1 TGA graph of COP4-105 and COP4-145 samples

Thermogravimatric curve shows weight loss occurs for both samples. The sample COP4-105 undergoes weight reduction linearly to 90 wt% starting at temperature of 300 ^{0}C until 650 ^{0}C where it undergoes further steep reduction to 10 wt% at 800 ^{0}C. Similarly, the sample COP4-145 also undergo steep weight reduction at 650 ^{0}C to be 20 wt% at 800 ^{0}C. Hence the sample can withstand heating for up to 600 ^{0}C before it undergoes rapid mass degradation.

4.7 FT-Ir spectra

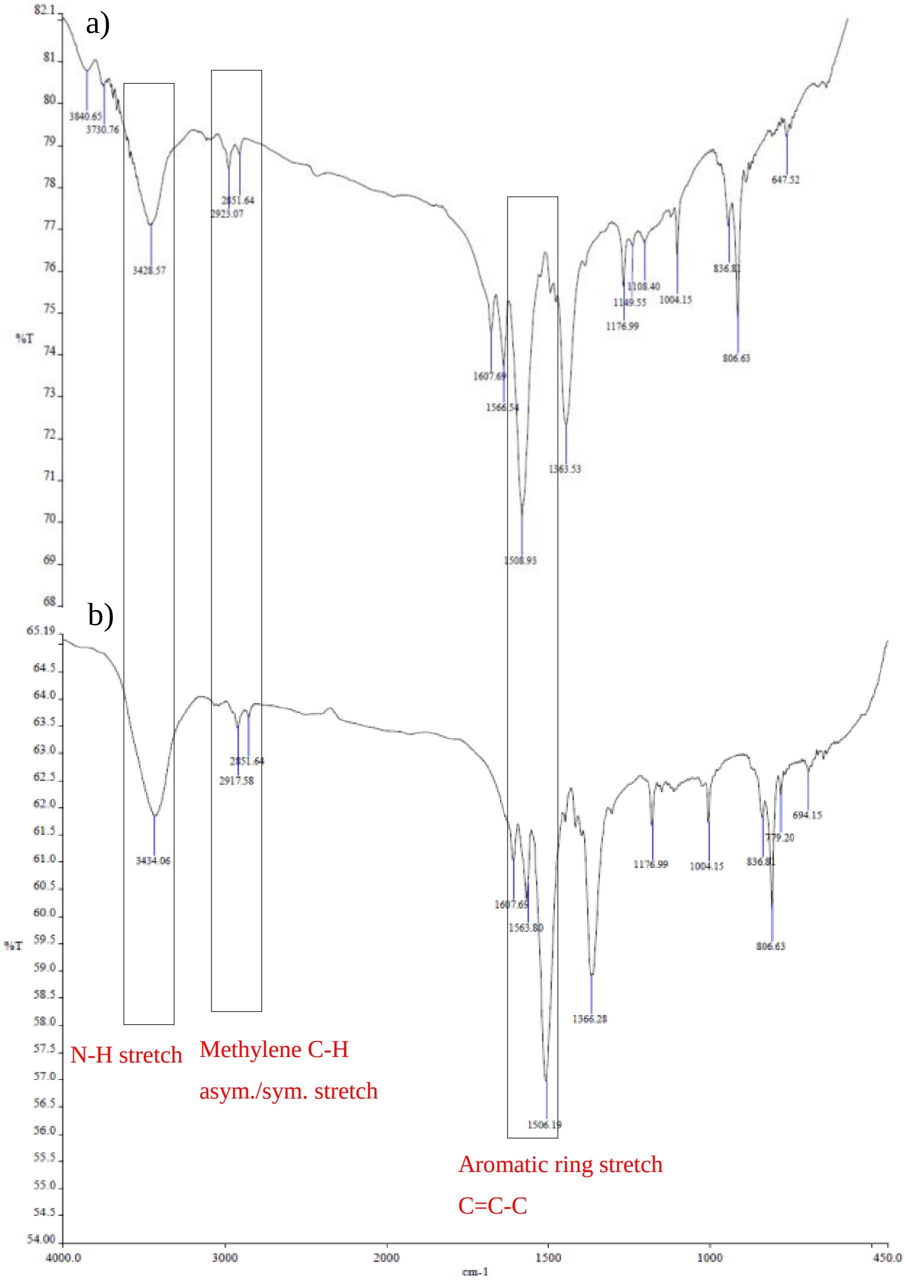

FIGURE 4.7.1 FT-Ir spectra of a) COP4-145 and b) COP4-105 samples

The spectra shows similarity on the overall spectral make-up in both samples, with the difference being the magnitude of the overall spectrum where COP4-145 has a lower transmittace peaks than the COP4-105. From the spectra, there is an indication of an aromatic primary amine compound N-H stretch in the region of 3510-3380 cm^{-1} which is similar to triazine, which is used as the monomer. Further aromatic compound indicaton is present in the region 1410-1450 cm^{-1} as aromatic ring stretch C=C-C.

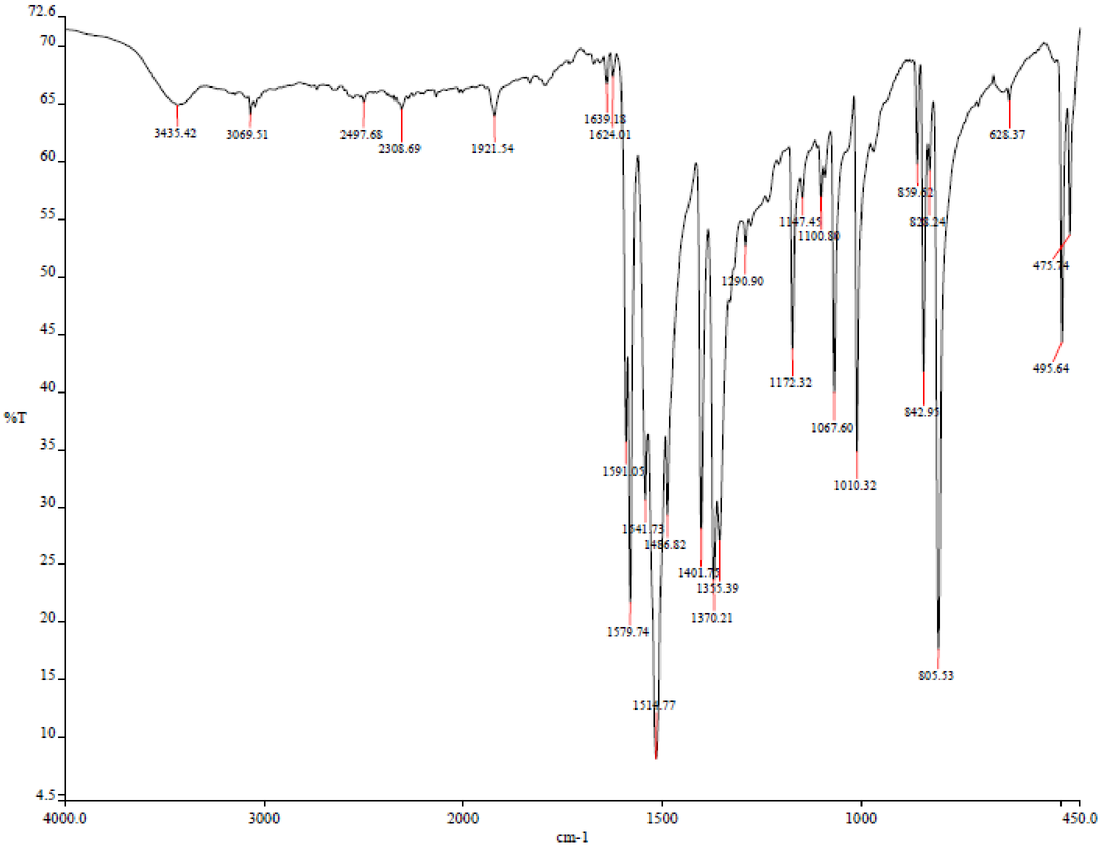

FIGURE 4.7.2 FT-Ir spectra of triazine

CHAPTER 5

CONCLUSION AND RECOMMENDATION

In conclusion, characterization of COP-4 synthesized by using microwave reactor in different reaction configuration has been achieved. VPFESEM and TEM imaging shows the effect of different reaction condition to the pore size of the COP-4 and the pore distribution on the sample. Surface area measurement shows that higher reaction temperature and shorter time from the literature condition produce less surface area and porosity compared to the literature COP-4. The EDX analysis indicates the main composition of carbon in the samples and the adsorption isotherm shows type IV isotherm which has good property in application on high pressure adsorption. TGA analysis shows that the COP-4 samples can withstand temperature for up to 600 ^{0}C before degraded. FT-Ir analysis confirmed the aromatic ring structure of the COP-4 samples which is similar in the literature.

The author recommends further research in investigating disproportionality of reaction time and temperature, where samples should be made with the same reaction time but increasing temperature or vice versa, and then be compared to obtain its relationship. Further research should also be done in determining the CO_2 adsorption isotherm and high pressure adsorption capacity for the potential application in CO_2 separation in a high pressured environment due to its adsorption characteristic which shows good adsorption capacity in high pressure.

REFERENCES

1. Xiang, Z., X. Zhou, C. Zhou, S. Zhong, X. He, C. Qin and D. Cao (2012). “Covalent-organic polymers for carbon dioxide capture.” Journal of Materials Chemistry 22(42): 22663.
2. Patel, H. A., S. H. Je, J. Park, D. P. Chen, Y. Jung, C. T. Yavuz and A. Coskun (2013). “Unprecedented high-temperature CO2 selectivity in N2-phobic nanoporous covalent organic polymers.” Nat Commun 4: 1357.
3. Xiang, Z., D. Cao, W. Wang, W. Yang, B. Han and J. Lu (2012). “Postsynthetic Lithium Modification of Covalent-Organic Polymers for Enhancing Hydrogen and Carbon Dioxide Storage.” The Journal of Physical Chemistry C 116(9): 5974-5980.
4. Martin, R. L., C. M. Simon, B. Medasani, D. K. Britt, B. Smit and M. Haranczyk (2014). “In SilicoDesign of Three-Dimensional Porous Covalent Organic Frameworks via Known Synthesis Routes and Commercially Available Species.” The Journal of Physical Chemistry C 118(41): 23790-23802.
5. Hu, J.-X., H. Shang, J.-G. Wang, L. Luo, Q. Xiao, Y.-J. Zhong and W.-D. Zhu (2014). “Highly Enhanced Selectivity and Easy Regeneration for the Separation of CO2over N2on Melamine-Based Microporous Organic Polymers.” Industrial & Engineering Chemistry Research 53(29): 11828-11837.
6. Leung, D. Y. C., G. Caramanna and M. M. Maroto-Valer (2014). “An overview of current status of carbon dioxide capture and storage technologies.” Renewable and Sustainable Energy Reviews 39: 426-443.
7. D’Alessandro, D. M., B. Smit and J. R. Long (2010). “Carbon dioxide capture: prospects for new materials.” Angew Chem Int Ed Engl 49(35): 6058-6082.
8. Rufford, T. E., S. Smart, G. C. Y. Watson, B. F. Graham, J. Boxall, J. C. Diniz da Costa and E. F. May (2012). “The removal of CO2 and N2 from natural gas:

A review of conventional and emerging process technologies." Journal of Petroleum Science and Engineering 94-95: 123-154.

9. Shimekit, B., Mukhtar, H., (2012). "Natural Gas PurificationTechnologies – Major Advances for CO2 Separation and Future Directions."
10. Ross, P. F., Cuellar K. T., Economical Option for CO_2/Methane Separation in Produced Gas Containing High CO_2 Fraction.

APPENDICES

A. Project Milestone & Gantt Chart

No	Detail/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	Experimental work	🟥	🟥	🟥	🟥	🟥	🟥	🟥								
2	Progress report submission								X							
3	Experimental work								🟥	🟥	🟥	🟥	🟥			
4	Pre-EDX											X				
5	Draft report submission												X			
6	Analysis and report												🟥	🟥	🟥	
7	Softbound submission													X		
8	Techncal paper submission													X		
9	Oral presentation														X	
10	Hardbound submission															X

X=Milestone