STATIC STUDY OF MODIFIED MOFs WITH AMINES FOR CO_2 ADSORPTION

By

NATTHIKA SIRIWAT
14197

Dissertation submitted in Partial Fulfilment
of the Requirements for the
Degree Bachelor of Engineering (Hons)
(Chemical Engineering)

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Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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Approved by,

____

(Dr. MUHAMMAD AYOUB)
Project Supervisor

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
September 2014.

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the originality 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.

(NATTHIKA SIRIWAT)
Chemical Engineering Student

ABSTRACT

Nowadays, the emission of carbon dioxide (CO_2) is the most impact of global warming. Large amount of CO_2 is released from consumption of fossil fuels, transportation and many activities. To reduce the amount of CO_2 is can be achieved by many physical and chemical methods, for example, absorption, adsorption, CO_2 membrane filter and etc.

The development involved with nanotechnology, which selected the Metal Organic Frameworks (MOFs) as nano-material in order to enhance the CO_2 adsorption capability. This study is represented by modification of Isoreticular Metal Organic Frameworks (IRMOFs) and modification of IRMOFs with amines. Both of prepared IRMOF-3 and modified IRMOF-3-AMP were synthesized, characterized, investigated and compared for CO_2 adsorption capabilities. The IRMOFs is one of the modified MOFs, which is well-known of nano-porous materials. Their high pore volume and specific surface area properties support for CO_2 adsorption properties. Besides, the AMP has been selected to attach with IRMOF-3, since the amines-based used to support the CO_2 capture capability.

The prepared IRMOF-3 and modified IRMOF-3-AMP was well synthesized and characterized for CO_2 adsorption via Brunauer-Emmett-Teller (BET). Moreover, both of the modified MOFs were characterized by using Field Emission Scanning Electron Microscope (FESEM), Fourier Transform Infrared (FTIR), Transmission Electron Microscope (TEM), and Thermogravimetric Analysis (TGA) in order to support the BET analysis as well. The MOFs modifications were expected to achieve great results. However, the prepared IRMOF-3 has shown higher rate of CO_2 adsorption as compared with modified IRMOF-3-AMP due to AMP is not so effective after modification with IRMOF-3.The development of CO_2 adsorption in this study is important to the industrials regarding environmental concern, since this technology can be used to improve the pollution control and industrial operation hygiene.

ACKNOWLEDGEMENT

First of all, I would like to express my highest appreciation to my family for supporting any of my decision about study. I can’t be who I am today without them. They are the best contributor of my success and life.

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LIST OF ABBREVIATIONS

Mode	Abbreviation	Full name
Chemicals	AMP	2-Amino-2-Methyl-1-Propanol
	DEA	Diethanolamine
	DMF	Dimethylformamide
	$CHCl_3$	Chloroform
	IRMOFs	Isoreticular Metal Organic Frameworks
	MEA	Monoethanolamine
	MOFs	Metal Organic Frameworks
	$Zn(NO_3)_2 \cdot 6H_2O$	Zinc Nitrate Hexahydrate
Equipment	BET	Brunauer-Emmett-Teller machine
	FESEM	Field Emission Scanning Electron Microscope
	FTIR	Fourier transform Infrared Spectroscope
	TEM	Transmission Electron Microscope
	TGA	Thermogravimetric Analyzer

CHAPTER 1
INTRODUCTION

1.1 Project Background

Nowadays, innovation has been developed in every single thing in order to fulfill a better technology for new generations. At the same time, some of technologies continuously generate and release pollution to the environment. Besides, global warming is caused by the emission of greenhouse gases such as CO_2, CH_4, CFC, N_2O. The EPA (2014) revealed that, 82% of CO_2 was released to the atmosphere and it's considered as a highest impact on global warming. Thus, CO_2 gas is the most critical to be eliminated or captured as much as possible.

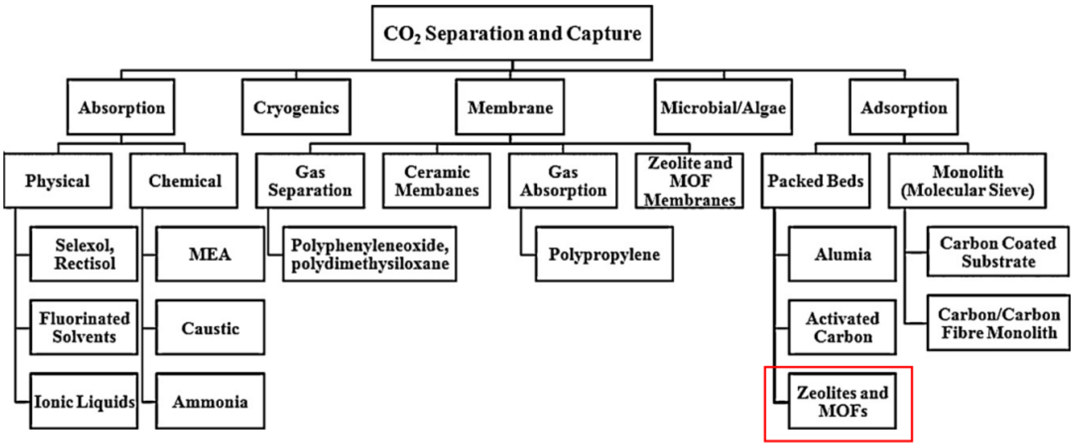


Figure 1: Different technologies and associated materials for CO_2 separation and capture (Thiruvenkatachari, 2009)

During the industrial processes, the CO_2 and another syngas are released to the atmosphere. Therefore, the CO_2 separation and capture seem to be the most effective method to reduce the amount of CO_2 from the processes. The CO_2 separation and capture technology is widely studying with different methods. Each method is used with different materials as shown in Figure 1.

This study aims to develop CO_2 capture with physical adsorption method by using modified Metal Organic Frameworks (MOFs), which is one of the broadly study of many researches nowadays.

The adsorption by using MOFs is excellently supported by many studies for their porous properties, which provides a higher pore volume as well as surface area for gas capture. Its capacity leads by its porosity which is controllable pore structures and tunable pore surface properties. The primary choices of porous material for gas separation are the shape and size of the pore (Yu et al., 2012; Li et al., 2011).

1.2 Problem Statement

Carbon dioxide is one of the greenhouse gases which give high impact for global warming crisis nowadays (EPA, 2014). Many researches aim to develop and modify the MOFs in order to increase the rate of CO_2 capture from the industrial processes.

The adsorption of CO_2 was focused in this study. The prepared IRMOF-3 and modified IRMOF-3-AMP are considered as new adsorbents. The IRMOF-3 contains high pore volume and surface area in previous studies. Furthermore, the alternative adsorbents are needed to develop for the active and economical material which provide higher CO_2 adsorption rate.

It has been found that the alkanolamine solvent such as MEA, DEA and AMP are given high absorption capability. These interested materials are brought to modification of IRMOF-3 with alkanolamine solvent to enhance CO_2 adsorption. It is rarely found to be attached with IRMOF-3. Therefore, AMP was selected as an amines-based for this study. The prepared IRMOF-3 and modified IRMOF-3-AMP were synthesized and studied in order to develop their capability for CO_2 adsorption.

1.3 Objectives

This study will be investigated the improvement of properties, characterization and investigated of prepared IRMOF-3 and modified IRMOF-3-AMP in order to enhance the CO_2 capture capability.

The objectives of this project are:

i. To synthesis of IRMOF-3 and modified IRMOF-3-AMP.
ii. To characterize the prepared IRMOF-3 and modified IRMOF-3-AMP via FESEM, FTIR, TEM, TGA.
iii. To analyze the capability of CO_2 adsorption of prepared IRMOF-3 and modified IRMOF-3-AMP via BET.

1.4 Scope of Study

This project was focused on main issues include;

i. To be familiar with synthesis procedure of modification of prepared IRMOF-3 and modified IRMOF-3-AMP.
ii. To be familiar with characterize procedure of prepared IRMOF-3 and modified IRMOF-3-AMP via FESEM, FTIR, TEM, TGA and BET.
iii. To analyze the CO_2 adsorption capacity of prepared IRMOF-3 and modified IRMOF-3-AMP via characteristic results.

1.5 Project Relevancy

Presently, the green technologies are attentive due to their lower pollutant releases to the environment as compared to the conventional technology.

Regarding some of the scientists believe that green technology will be applied in all manufacture areas by using green chemistry and green engineering principles in the future, in order to reduce any pollutants which can harm the environment (Green Technology, 2014).

This study could be applied with industrial process to reduce the amount of CO_2 that will be released to the environment during the production processes. This development involves with nanotechnology, since nano-materials were chosen to adsorb CO_2 in molecules level. Furthermore, performance of CO_2 capture will benefit to further development of CO_2 adsorption in order to improve the environment effects as well. Anyway, the prepared IRMOF-3 and modified IRMOF-3-AMP were expected to achieve great results on CO_2 adsorption capability.

1.6 Feasibility of the Project within the Scope and Time Frame

The first stage of this project is synthesis of MOFs which are prepared IRMOF-3 and modified IRMOF-3-AMP. Both of these synthesis were consumed a plenty of preparation time. Preparation of MOFs took a week to obtain the adsorbent. Then, the adsorbent were taken for characterisation and analysis via FTIR, TGA, FESEM, TEM and BET. These analyses took longer time to be completed.

Due to the time constraint of the Final Year Project, time management is very important to complete all activities within the semester. Moreover, this project needs guidance and suggestion from the expert like supervisor and co-supervisor during the progress. Although this project has been done with research and literature from FYP I, but the experiments take more time to completed within the FYP II time frames.

1.7 Organization of dissertation

This study focuses on development of CO_2 adsorption by using prepared IRMOF-3 and modify with amine (AMP).

Chapter *one* introduces the important of CO_2 impact to environment. The source which release flue gases and pollution impact are discussed.

Chapter *two* summarizes information from literature review, which related to CO_2 adsorption technology (e.g. separation, capture). The characteristic and function of Metal Organic Frameworks are discussed.

Chapter *three* focuses on research methodology. The project activities include of prepared IRMOF-3 & modified IRMOF-3-AMP synthesis procedure, Gantt chart & key milestones, reagent, equipment and characterization techniques.

Chapter *four* discussed the results after synthesis and characterization of both prepared IRMOF-3 and modified IRMOF-3-AMP. All characterization includes of FTIR, TGA, FESEM, TEM and BET.

Chapter *five* concludes the results and discussion throughout this study, and provides recommendation for future study of respective IRMOF and IRMOF-3 with amine modification research.

CHAPTER 2

LITERATURE REVIEW

2.1 The CO_2 Adsorption

This study aims to develop the MOFs adsorbent in order to capture and separate CO_2 gases by using their physical adsorption properties as shown in Figure 2.

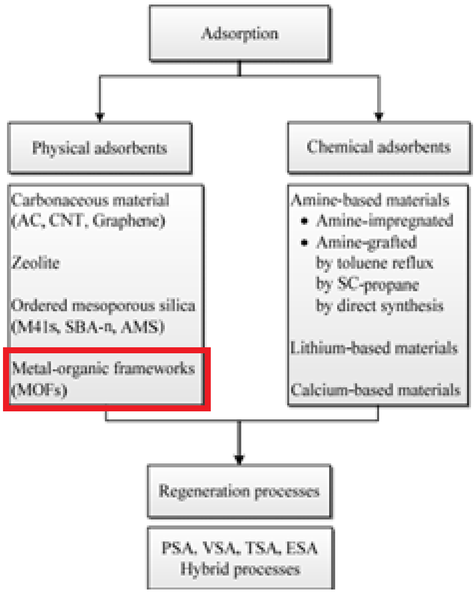


Figure 2: The post-combustion chart for Adsorption (Olajire, 2010)

The industrial processes gas stream lead of greenhouse gas release to atmosphere. The CO_2 are combined with those greenhouse gases and it is the highest impact to the environment. Nowadays, CO_2 separation and capture are widely study in order to enhance their performance.

The CO_2 capture can be applied to the industrial processes which require to remove or recovery of CO_2 such as post combustion flue gases from fossil fuel oxidation, Synthesis gas (e.g. CO_2, H_2, H_2O) from hydrogen production from natural gas etc. (Webley, 2014).

The CO_2 adsorbent is expected to meet these following criteria; Low-cost materials, low heat capacity, fast kinetic, high CO_2 adsorption capacity, high CO_2 selectivity and stability on thermal, chemical and mechanical (Olajire, 2010).

The development on this project combines with both physical and chemical properties of the adsorbent. The physical adsorbent is represented by IRMOF-3. It is a modified of MOFs that contains amine functional group, which provide a higher capacity of CO_2 adsorption. The chemical adsorbent is represented by Amines-based chemicals. The CO_2 capture is improved by Amines-based to approach the higher CO_2 adsorption rate (Olajire, 2010).

According to Li et al (2011), stated that the critical CO_2 capture capacity of MOFs is directly related to CO_2 measurement at room temperature and high pressure. It's been found that the total pore volume of MOFs is effectively correlated with CO_2 amount which could be adsorbed at high pressure. Hence, it's been concluded that the surface area directly related to CO_2 storage capability.

This study will be used BET method to determine the rate of CO_2 adsorption of modified MOFs. Since, many studies have been stated that Brunauer–Emmett–Teller (BET) method is related with isotherm adsorption analysis due to their pore volume and surface area of the adsorbents (Lili et al., 2012; Guo & Fang., 2014)

2.2 Isoreticular metal organic framework (IRMOFs)

Metal Organic Frameworks (MOFs) were introduced by Li et al (2011), that it is a class of crystalline porous material, which are constructed by organic linker molecules and metal joint (Tanabe et al., 2008). The remarkable of physical properties of MOFs are porosity structure which present of high pore volume - up to 90% of the crystal volume, and high specific surface area (Ma, 2011; Li et al., 2011;).

Zhou et al (2012) & Tanabe et al (2008) stated that Isoreticular metal organic frameworks (IRMOFs) are modified MOFs. The materials have been improved in order to increase their physical properties e.g. surface area.

High surface area of MOFs is devoted by many researches that, it improves CO_2 adsorption by chemical modification in order to increase the surface of the material (Yu et al., 2012). Nowadays, the MOFs have been developed more in terms of conceptual design, synthesis, and characteristic (Li et al., 2011).

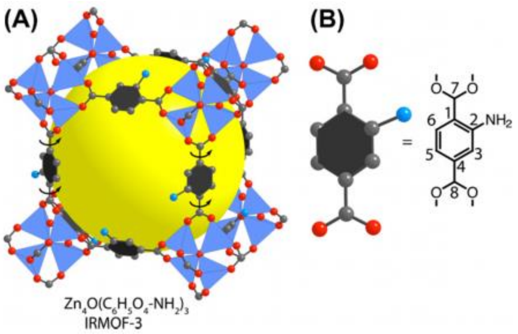


Figure 3: The structure of IRMOF-3 (A) represents the free volume within the framework with yellow sphere. (B) The ligand. (Morris et al., 2011)

This project focused on modification of IRMOFs and modification of IRMOFs with Amines. Moreover, its synthesis and characteristic were studied too. The Amines functional group is 2-amino-2-methyl-1-propanol (AMP). Many efficient researches claimed that MOFs has been developed into the most advantageous area of chemistry and material science (Ma, 2011). The improvement of the materials is important, especially, in terms of separation and gas storage e.g. hydrogen, methane and carbon dioxide (Yuan et al., 2010).

2.3 Amines-based

This study used Amines-based as a chemical to attach with modified MOFs in order to develop its capability of CO_2 capture.

Yu et al (2012) and Kim et al (2013), have acknowledged that basic organic group of amines, and inorganic metal oxide group of alkali-metal or alkali-earth metal, are interesting in terms of CO_2 capture development.

It is the most mature technologies for CO_2 capture by using alkanolamine solution, which is sub-ordinary of Amines group. Therefore, it is a challenge to improve CO_2 capture technology by using AMP as an additional agent with modified MOFs in this study.

2.4 Synthesis of MOFs

2.4.1 Synthesis of IRMOF-3

The prepared IRMOF-3 was adapted from Servalli et al., 2012 and Kim et al.,2013 synthesis that it was started by dissolving 2-Aminoterephtalic acid and $Zn(NO_3)_2 \cdot 6H_2O$ in DMF. The mixture was transferred to the autoclave and placed in the oven overnight with 105^{o}C. After it was cooled to the room temperature, the brown-amber crystals were washed with DMF for 3 times. The crystal IRMOF-3 were rinsed and soaked in $CHCl_3$ for 3 days. The crystal were dried and stored in dry keeper for the further characterization.

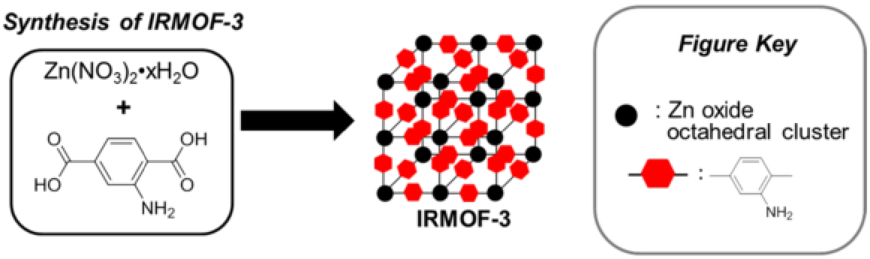


Figure 4: Synthesis of IRMOF-3 (Kim et al., 2013)

2.4.2 Synthesis of modified IRMOF-3-AMP

The synthesis of modified IRMOF-3-AMP was adapted from Cao et al. (2013). It was prepared with IRMOF-3, AMP and toluene.

The mixtures were condensed overnight for 75°C. Then, the products were filtered and dried it for 5 hours with 75°C. Then, it was stored properly in dry keeper.

2.5 The Materials characterization

Since the characterization of IRMOF-3 has been conducted from the previous case study, this table 1 is summarized the results of IRMOF-n type which had been analysed previously.

Table 1: The summary of modified MOFs results from previous studies

Characterization	**Adsorbents**	**Temp. (K)**	**Specific Surface area (m^2/g)**	**Specific volume (cm^3/g)**	**Authors**
NMR, XRD, BET	IRMOF-3C(amine)		IRMOF-3C(amine)=530		Britt et al., 2010
FTIR, H-NMR, XRD, BET	MOF 1-Me 1-Pr 1-Ph 1-PhCF$_3$	253-298	MOF= 4170 1-Me= 3550 1-Pr= 2900 1-Ph=3680 1-PhCF$_3$=3520		Ko & Kim, 2011
TGA, IR, BET	MOF-200 MOF-210 MOF-205 IRMOF IRMOF-3	298	MOF-200=4530 MOF-210=6240 MOF-205=4460 IRMOF=1430 IRMOF-3=2446	IRMOF=0.69 IRMOF-3=1.07	Suh et al., 2011
FTIR, Langmuir	IRMOF-3 IRMOF-3 [Mn]		IRMOF-3=2878 IRMOF-3[Mn]=2115	IRMOF-3=1.03 IRMOF-3 [Mn]=0.78	Bhattacharjee et al., 2011
FEM, XRD, BET	IRMOF-1	378	IRMOF-1=3800	IRMOF-1=1.55	Ma, 2011
H-NMR, BET	IRMOF-3	297	IRMOF-3=2163		Morris et al., 2011
XRD, IR, TEM, , BET	IRMOF-3	473	IRMOF-3=1212		Lili et al., 2012
XRD, TGA, BET	IRMOF-3 SI-IRMOF-3	423	IRMOF-3=2314 SI-IRMOF-3=362		Servalli et al., 2012
SEM, XRD, FTIR, XRF, TGA	IRMOF-3 IRMOF-3/TI		IRMOF-3=980 IRMOF-3/TI=870	IRMOF-3=0.47 IRMOF-3/TI=0.38	Kim et al., 2013
TGA, XRD, TEM, SEM, FTIR, AAS, BET	IRMOF-3	573-773	IRMOF-3=3295		Lien, 2013

Regarding the objective of study the capability of the modified MOFs and its characterization, therefore, the results of each characteristic had been obtained from this related equipment as follow;

Brunauer-Emmett-Teller (BET) Machine is introduced by Particle Analysis (2014), the machine based on BET method which will specify the surface area of particle by determine the physical adsorption of a gas on surface of the particle. Then, the amount of adsorbed gas will be calculated by a volumetric or continuous flow procedure. The results can be analyzed via the adsorption isotherm equation as shown in Appendix A.

Field Emission Scanning Electron Microscope (FESEM) is used to observe a structure in microscope on the surface of the materials. The visualized results can be achieved from this method (PhotoMetrics,Inc, 2012).

Fourier transform Infrared Spectroscope (FTIR) is used to define the organic or inorganic of the chemicals, which can be applied with solid liquid and gas analysis. Moreover, it will identify the type of chemical bond (Functional groups) of the materials by spectrum which is produced from infrared absorption. The spectrum will represent the molecular absorption, its transmission like a creation of a molecular fingerprint (WCAS, 2014; Thermo Nicolet, 2001).

Thermogravimetric Analyzer (TGA) is the equipment which uses to study the characterization, stability and composition of the materials analysis. The weight (mass) will be measured base on a function of temperature or time under atmosphere condition (PerkinElmer, Inc, 2014).

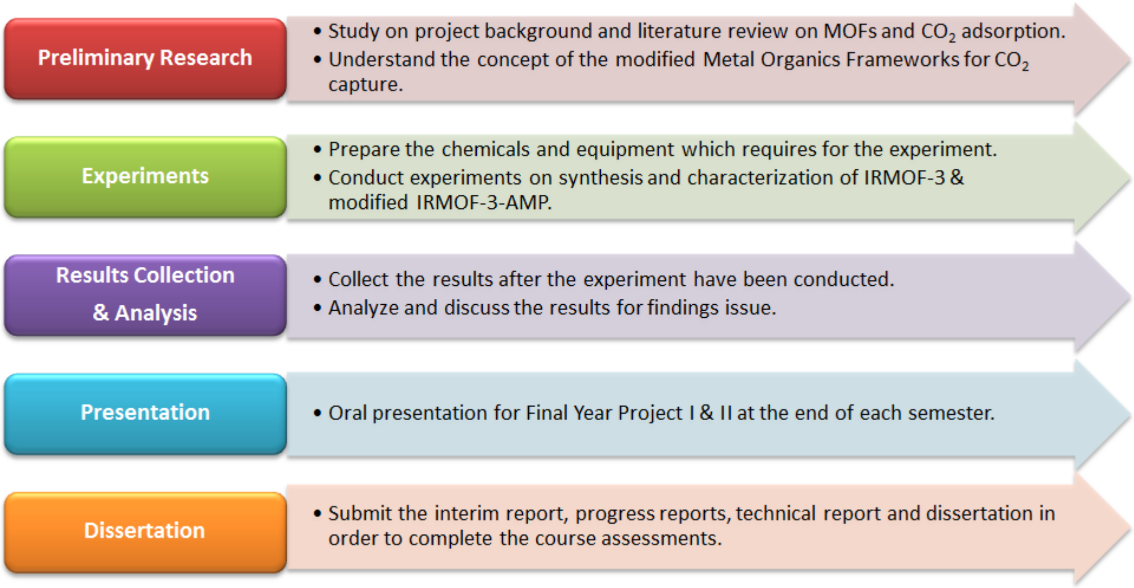
Transmission Electron Microscope (TEM) is a powerful which uses the electron diffraction through a thin material instead of light. This TEM can be observed the structure of crystal material, the growth of its layers and its composition. The high resolution of TEM supports to analyze the structure of the materials e.g. size, shape, quality etc. (David, 2014).

CHAPTER 3

METHODOLOGY

3.1 Research Activities

Figure 5 describes the sequence of work load expected to be performed in order to complete the project on time. The flow chart below are planned to perform during September 2014 semester during Final Year Project II.



Preliminary Research

- Study on project background and literature review on MOFs and CO_2 adsorption.
- Understand the concept of the modified Metal Organics Frameworks for CO_2 capture.

Experiments

- Prepare the chemicals and equipment which requires for the experiment.
- Conduct experiments on synthesis and characterization of IRMOF-3 & modified IRMOF-3-AMP.

Results Collection & Analysis

- Collect the results after the experiment have been conducted.
- Analyze and discuss the results for findings issue.

Presentation

- Oral presentation for Final Year Project I & II at the end of each semester.

Dissertation

- Submit the interim report, progress reports, technical report and dissertation in order to complete the course assessments.

Figure 5: The sequence of research activities flow.

3.2 Chemicals and Reagents Required

- 2-aminoterepthalic acid
- $Zn(NO_3)_2·6H_2O$
- DMF
- AMP
- Toluene
- $CHCl_3$

3.3 Apparatus and Equipment Required

3.3.1 Apparatus

Table 2: The apparatus required for the experiments

No	Apparatus	Function
1.	Beaker	To hold chemicals and reagents.
2.	Spatula	To transfer chemicals and reagents from bottle to beakers.
3.	Weighting machine	To measure the weight of chemicals.
4.	Measuring cylinder	To measure the weight of chemicals in liquid form accurately.

3.3.2 Equipment

Table 3: The equipment required for project analysis

No	Name of the equipment	Picture
1.	**BET** Brunauer-Emmett-Teller Machine	

No	Name of the equipment	Picture
2.	**FESEM** Field Emission Scanning Electron Microscope	
3.	**FTIR** Fourier transform Infrared Spectroscope	
4.	**TEM** Transmission Electron Microscope	
5.	**TGA** Thermogravimetric Analyzer	

3.4 Characterization Techniques

Brunauer-Emmett-Teller (BET) Method

The CO_2 isotherm adsorption was obtained from BEL Japan BELSORP-minill. This characterization needs pre-treatment of the sample, which was prepared by heating in vacuum condition overnight at 150^oC as followed by Servalli et al (2012) study.

Field Emission Scanning Electron Microscope (FESEM)

The crystal morphology of samples was observed by using Zeiss Supra55 Variable Pressure Field Emission Scanning Electron Microscope (VPFESEM), which analyzed the sample at 2000 voltages.

Fourier Transforms Infrared Spectroscopy (FTIR)

FTIR spectrum was obtained from Nicolet FTIR Impact 400 system. 15 mg of potassium bromide (KBr) and 2 mg of the solid sample was grinded and pressed as a small thin pellet. The pellet was placed into the FTIR scan to identify and analyze the materials, the components and the sample quality.

Thermogravimetric Analysis (TGA)

Thermogravimetric Analysis (TGA) was carried out in a 20ml/min flowing air atmosphere at a heating rate of 10˚C/min with temperature from 50˚C to 800˚C. The TGA result was obtained from Perkin Elmer Pyris 1 Thermal Gravimetric Analyzer, which provided the degradation temperature of the samples from the TGA profile.

Transmission Electron Microscope (TEM)

Zeiss Libra 200 Transmission Electron Microscope (TEM) was used to analyze the geometry and chemical of samples at atomic level. The TEM instrument operated at 200 kV. The MOFs are generally studied for morphology of individual nano-crystals.

3.5 Preparation for IRMOF-3

(Adapted from Servalli et al., 2012 and Kim et al., 2013)

a) 1.5 g of 2-Aminoterephtalic acid and 6 g of $Zn(NO_3)_2{\cdot}6H_2O$ are weighted and placed into the beaker. While a 150 ml of DMF is measured and placed into the previous beaker.

b) The beaker is covered with paraffin film and placed into sonication machine until the mixture is well dissolved.

c) The mixture is transferred into autoclave.

d) The autoclave filled with the mixture is placed in the oven for 24 hours with 105°C.

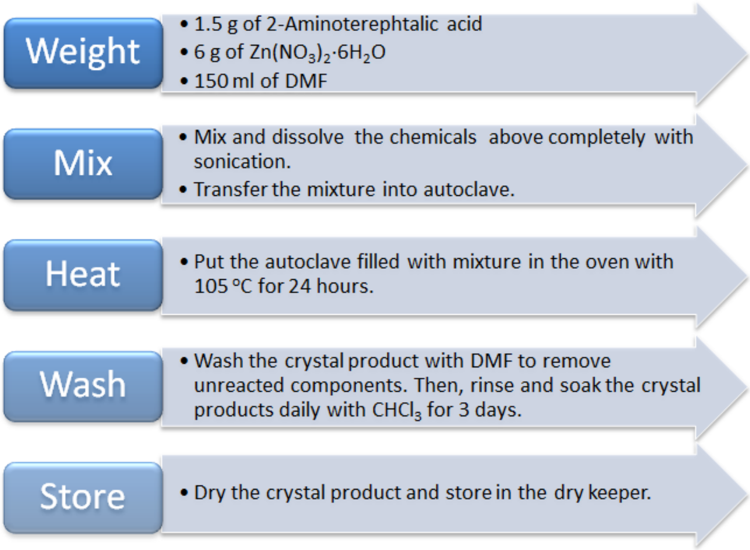
e) The autoclave is taken out from the oven and cooled down around 2 hours to reach room temperature.

f) The products appeared inside the autoclave as brown-amber crystal. It washed by DMF to remove unreacted component from the product.

g) The crystal products are rinsed and in $CHCl_3$ daily for 3days.

h) The crystal products are dried and stored in dry keeper.

3.5.1 Experimental Procedure Flowchart of IRMOF-3



- 1.5 g of 2-Aminoterephtalic acid
- 6 g of $Zn(NO_3)_2{\cdot}6H_2O$
- 150 ml of DMF

- Mix and dissolve the chemicals above completely with sonication.
- Transfer the mixture into autoclave.

- Put the autoclave filled with mixture in the oven with 105 °C for 24 hours.

- Wash the crystal product with DMF to remove unreacted components. Then, rinse and soak the crystal products daily with $CHCl_3$ for 3 days.

- Dry the crystal product and store in the dry keeper.

Figure 6: The procedure flowchart of prepared IRMOF-3.

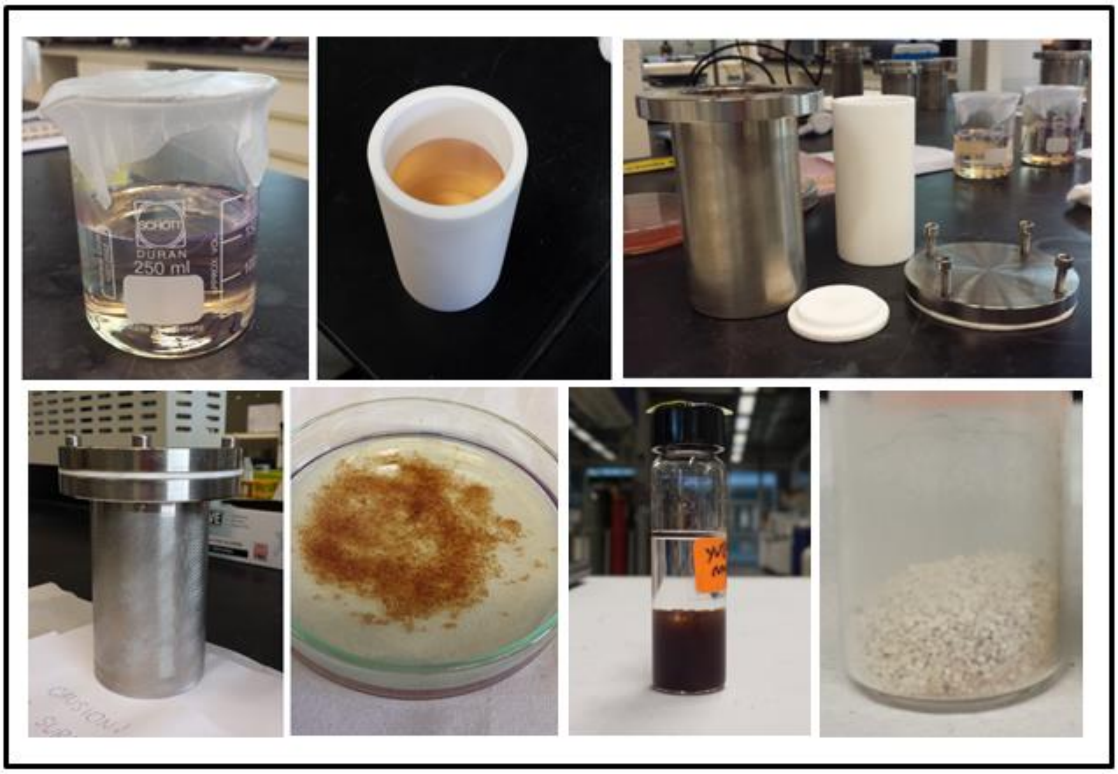


Figure 7: Synthesis of IRMOF-3

3.6 Preparation for modified IRMOF-3 with Amine

(Adapted from Cao et al., 2013)

a) 1.5 g of IRMOF-3 are weighted

b) The AMP:Toluene ratio are weight respectively 30wt%, 40wt%, and 50wt%.

**30wt% means to measure 30 ml of Amines (AMP) and 70 ml of Toluene.

c) The chemicals are mixed in the beaker and poured into the boiling flask for reflux condenser.

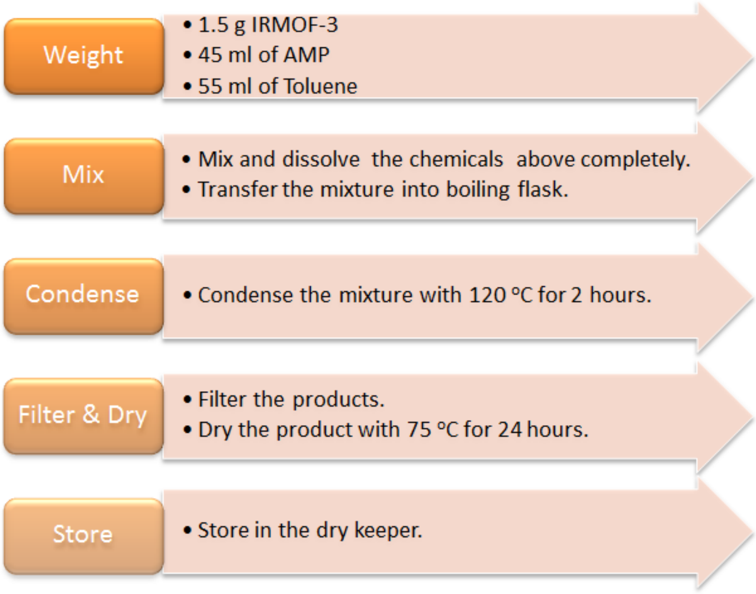
d) The reflux condenser is set at 75°C for 24 hours.

e) Cooled down the boiling flask to room temperature and filtered the product.

f) The products are collected and dried at 75°C for 5 hours.

g) Store the products in dry keeper.

3.6.1 Experimental Procedure Flowchart of modified IRMOF-3-AMP



Weight

- 1.5 g IRMOF-3
- 45 ml of AMP
- 55 ml of Toluene

Mix

- Mix and dissolve the chemicals above completely.
- Transfer the mixture into boiling flask.

Condense

- Condense the mixture with 120 °C for 2 hours.

Filter & Dry

- Filter the products.
- Dry the product with 75 °C for 24 hours.

Store

- Store in the dry keeper.

Figure 8: The procedure flowchart of modified IRMOF-3-AMP.

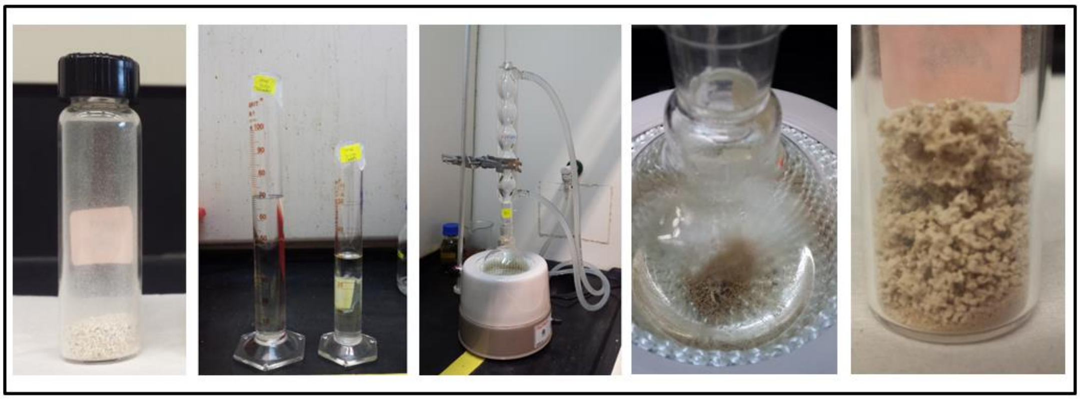
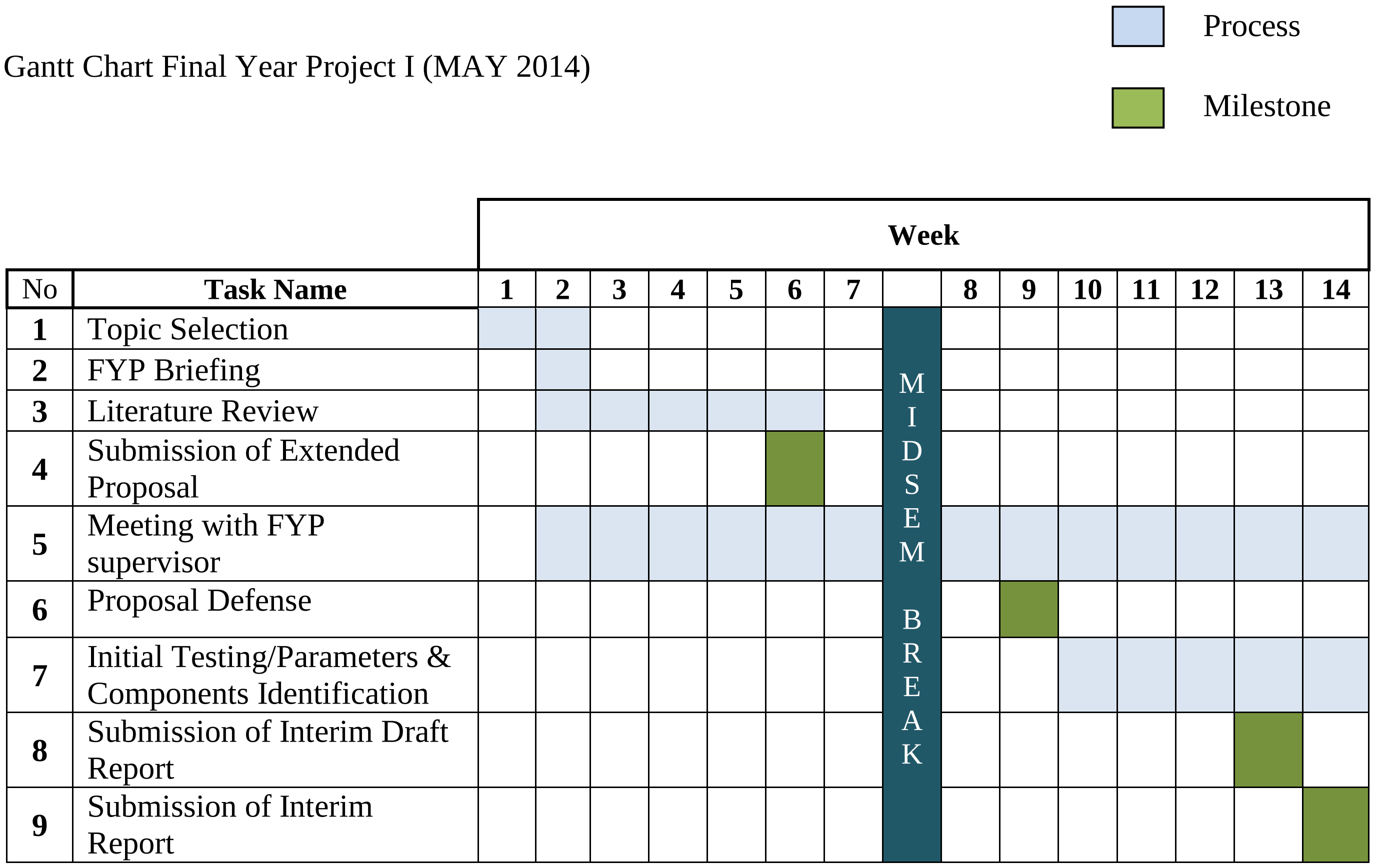


Figure 9: Synthesis of modified IRMOF-3-AMP

3.7 Gantt Chart and Key Milestones



Gantt Chart Final Year Project I (MAY 2014)

🟦 Process

🟩 Milestone

		Week														
No	**Task Name**	**1**	**2**	**3**	**4**	**5**	**6**	**7**		**8**	**9**	**10**	**11**	**12**	**13**	**14**
1	Topic Selection	🟦	🟦						MIDSEM BREAK							
2	FYP Briefing		🟦													
3	Literature Review		🟦	🟦	🟦	🟦	🟦									
4	Submission of Extended Proposal						🟩									
5	Meeting with FYP supervisor		🟦	🟦	🟦	🟦	🟦	🟦		🟦	🟦	🟦	🟦	🟦	🟦	🟦
6	Proposal Defense										🟩					
7	Initial Testing/Parameters & Components Identification											🟦	🟦	🟦	🟦	🟦
8	Submission of Interim Draft Report														🟩	
9	Submission of Interim Report															🟩

Figure 10: Gantt chart for FYP I

🟦 Process

🟩 Milestone

Gantt Chart Final Year Project II (SEPT 2014)

		Week															
No	**Task Name**	**1**	**2**	**3**	**4**	**5**	**6**	**7**		**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**
1	Designing the synthesis for modified MOFs	🟦	🟦	🟦	🟦	🟦	🟦	🟦	MID SEM BREAK	🟦	🟦	🟦	🟦	🟦			
2	Progress Report Submission									🟩							
3	Pre - SEDEX												🟩				
4	Submission of Draft Report													🟩			
5	Submission of Dissertation (Soft Bound)														🟩		
6	Submission of Technical Paper														🟩		
7	Oral Presentation															🟩	
8	Submission of Project Dissertation (Hard Bound)																🟩

Figure 11: Gantt chart for FYP II

CHAPTER 4
RESULTS AND DISCUSSION

4.1 Initial Assessment (prepared IRMOF-3 and modified IRMOF-3-AMP)

The prepared IRMOF-3 result was shown in small amber crystal in cube shape as shown in figure 12. The result is similarly with Britt et al (2010) and Flügel et al (2012). The synthesis of modified IRMOF-3-AMP was shown in figure 13. Both samples were dried as shown in figure 14 and prepared for characterization.

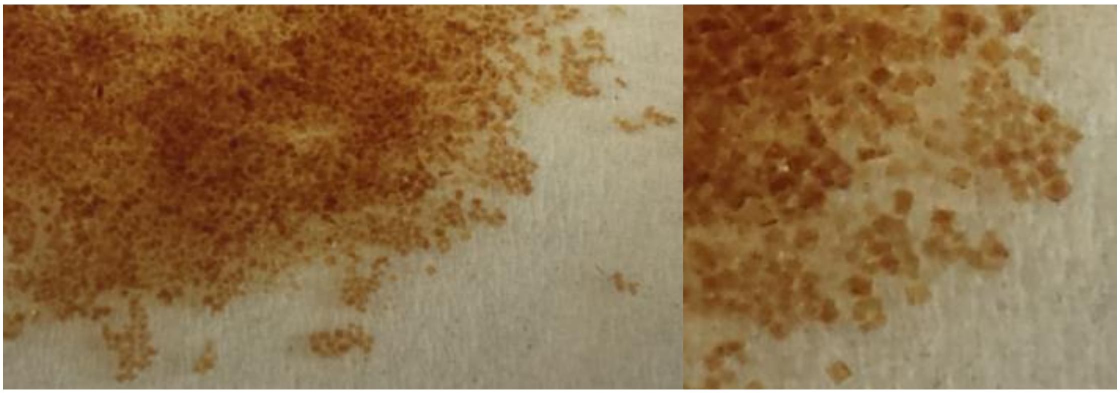


Figure 12: Synthesized IRMOF-3 amber crystal, Cube shape

Figure 13: Synthesized IRMOF-3-AMP

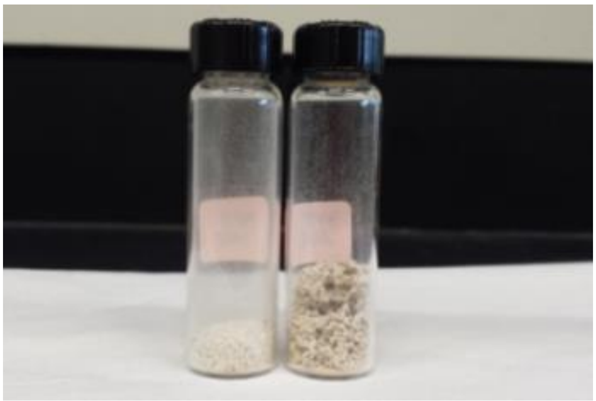


Figure 14: The sample of IRMOF-3(left) and modified IRMOF-3-AMP (right)

Table 4: The quantity of synthesized IRMOF-3

Batch	2-aminoterepthalic acid (g)	$Zn(NO_3)_2$ (g)	DMF (ml)	IRMOF-3 (g)
1	1.500	6.0055	150	2.5523
2	1.501	6.0050	150	2.3020
3	1.500	5.9995	150	2.1020
			Total/batch	**2.3188**

Table 5: The quantity of synthesized IRMOF-3-AMP

Batch	IRMOF-3 (g)	AMP (g)	Toluene (ml)	IRMOF-3-AMP (g)
1 (30wt%)	1.5102	30	70	1.202
2 (40wt%)	1.5001	40	60	1.329
3 (50wt%)	1.5014	50	50	1.266

4.2 Characterization of prepared IRMOF-3

4.2.1 FTIR

The FTIR method is important to identify the major characteristic of prepared IRMOF-3 infrared spectrum. The spectrums from synthesized IRMOF-3 were discussed according to the absorption peaks from Appendix B – FTIR spectra results. This study was not being discussed for the qualities of the features. The peaks from IRMOF-3 were listed below;

IRMOF-3: IR 3466.8–3419.16 cm^{-1} (s,b), 2931.19 cm^{-1} (m), 1619.10 cm^{-1} (m), 1499.27 cm^{-1} (m), 1379.67 cm^{-1} (m), 1107.29 cm^{-1} (m), 765.72 cm^{-1} (s), 584.03 cm^{-1} (s,b). **[strong (s), medium (m), broad (b)]

From the prepared IRMOF-3 graphs generated from FTIR analysis, was analyzed according to the table of Characteristic IR Absorptions. The first major peak at 3466.85 cm^{-1} indicated of H-bonded or O-H stretch that presented for functional group of alcohols or phenols.

The second major peaks at 1619.10 cm^{-1} indicates of N-H bend that presented for 1^{o} amines. The third major peak at 1379.67 cm^{-1} indicated CH$_3$ deformation. The last major peak at 765.72 cm^{-1} indicated C-H "oop" that presented aromatic or benzene ring. The rest of the minor peaks were indicated as follow discussion. At 2931.19 cm^{-1} indicated for C-H stretch that presents alkane, 1499.27 cm^{-1} indicated for C-C stretch in ring that presents aromatic, 1107.29 cm^{-1} indicates for C-N stretch, and 584.03 cm^{-1} indicated for C-H bend N-H wag of 1^{o}, 2^{o} amines.

4.2.2 TGA

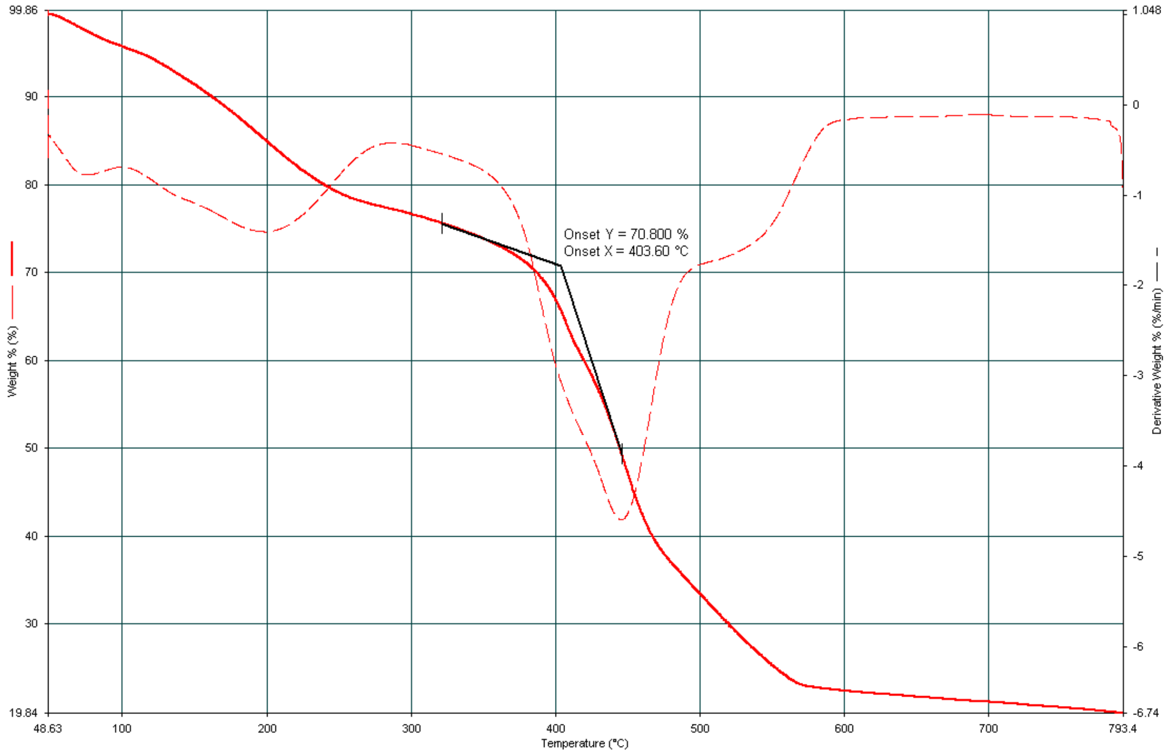


Figure 15: TGA of the prepared IRMOF-3

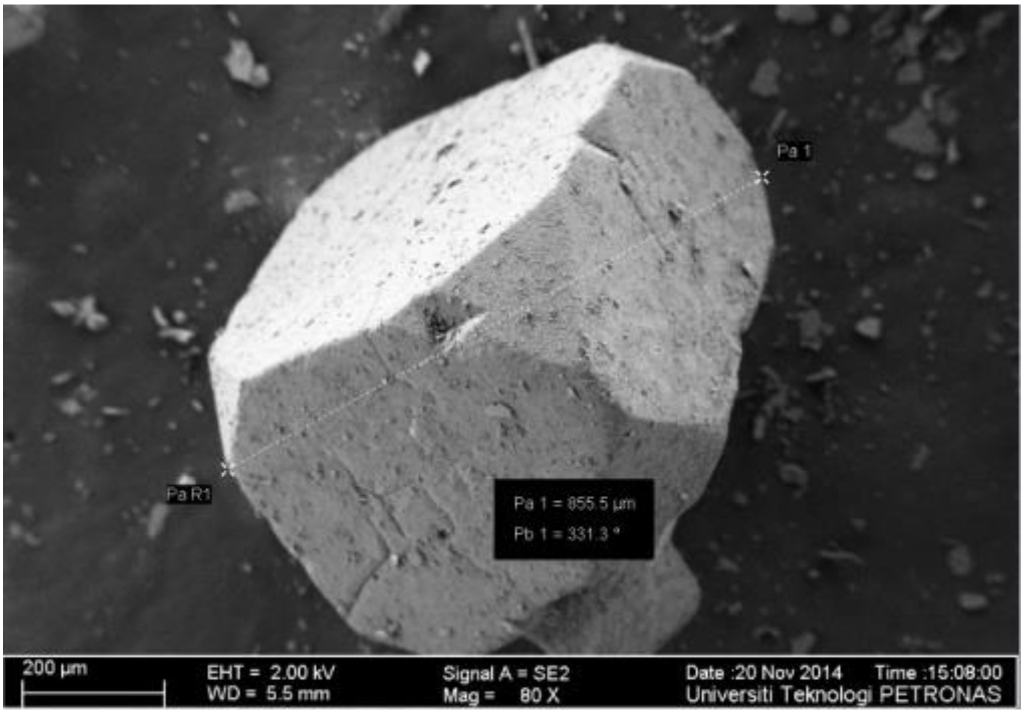
The TGA curve of synthesized IRMOF-3 is shown in Figure 15. It is clearly interpreted from the graph of derivative weight vs. temperature that the first weight loss produced around 100 ˚C to 200˚C. This might relate to the removal of the solvent which can be water and DMF.

The next major weight loss in the range of 320˚C to 450˚C corresponds to the organic ligand decomposition. Therefore, it was specified the thermal stability of prepared IRMOF-3.

4.2.3 FESEM

The crystal morphology of samples was observed by using Variable Pressure Field Emission Scanning Electron Microscope (VPFESEM) at an accelerating voltage of 2kV and different magnifications.

The figures above show the cube-shaped crystal of prepared IRMOF-3 which agreed its previous synthesized results. The average particle size is given approximately 29-33.5 nm which close to the result of Low et al (2014), which is around 28 nm. The porous surface of prepared IRMOF-3 was captured clearly in figure 16(b) and 16(c).



(a)

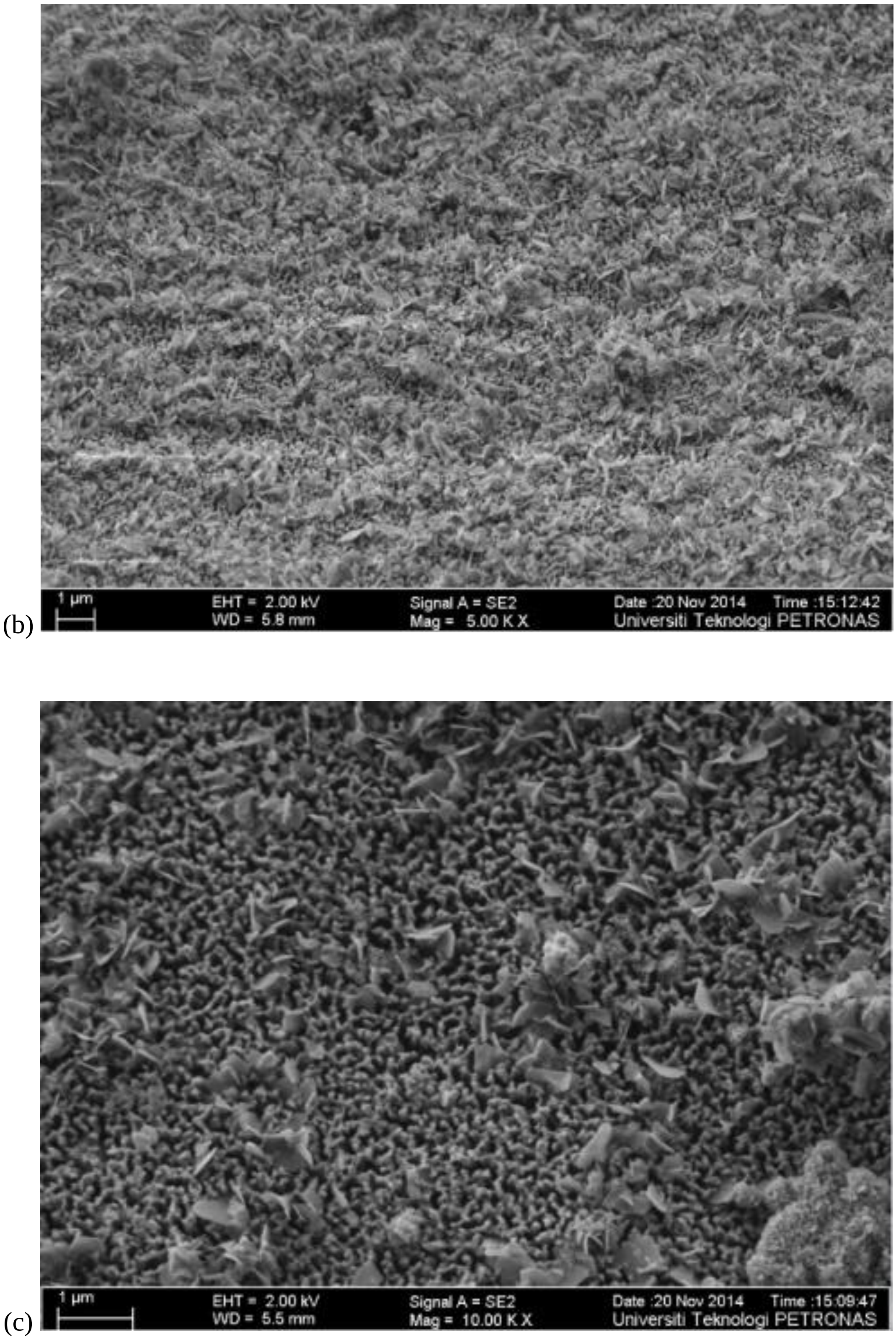
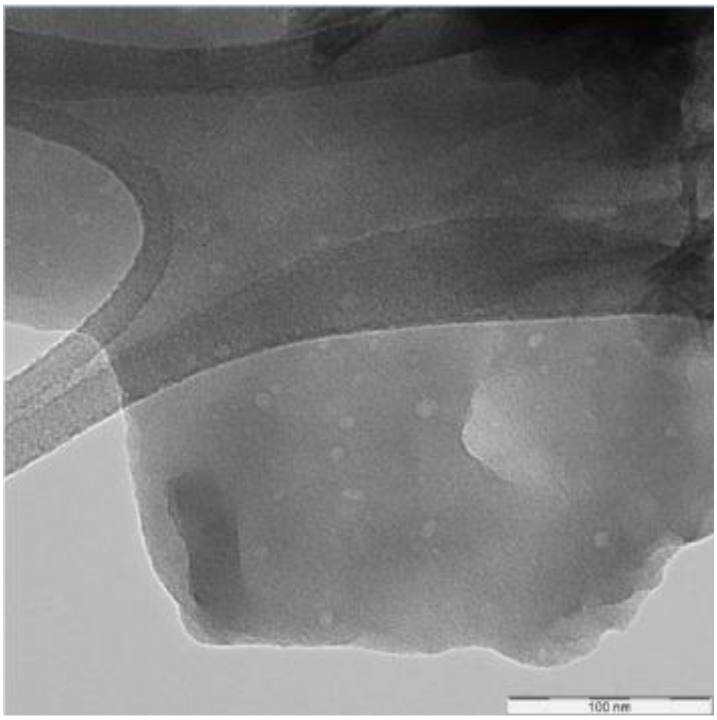


Figure 16: Prepared IRMOF-3 particle (a), Porous surface IRMOF-3 at 5 k magnification (b), and 10 k magnification (c)

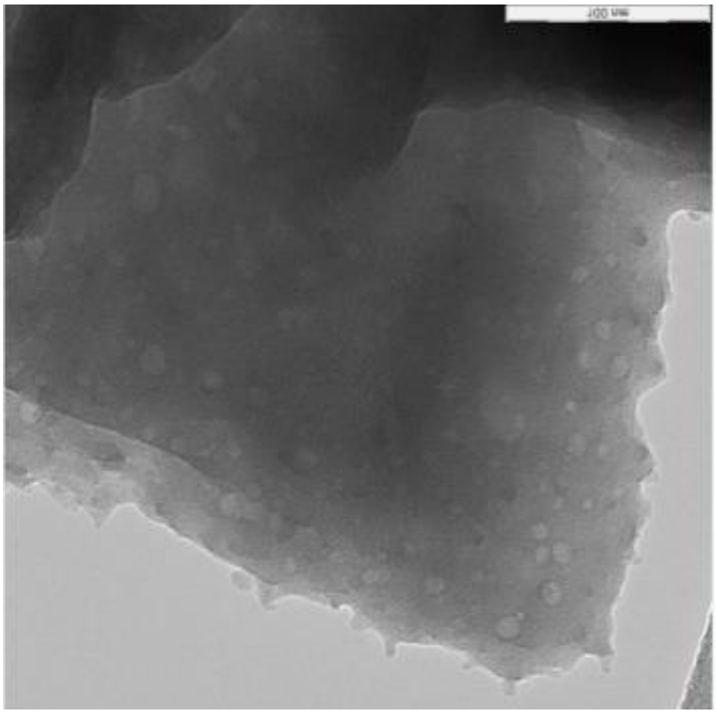
4.2.4 TEM

The Transmission Electron Microscope (TEM) results are obtained from Zeiss Libra 200 with an accelerating voltage of 200 kV.

(a)



(b)



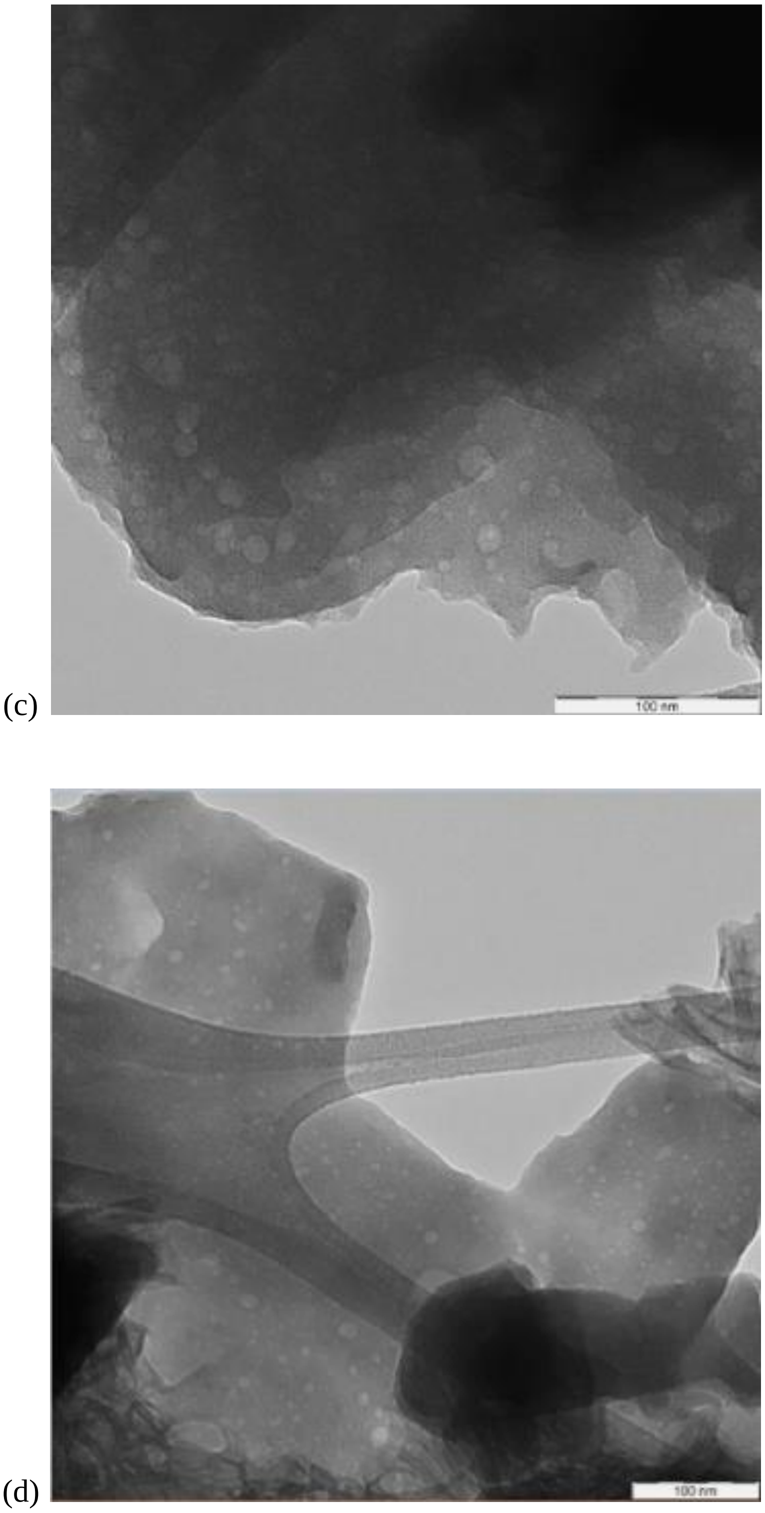


Figure 17: Prepared IRMOF-3 TEM results at different position (100 nm observation)

The figures above present of prepared IRMOF-3 physical structure, morphology, porosity in nano-crystal level in different side of particle. The result supports the FESEM result and CO_2 adsorption from BET result too.

At 100 nm observation, the average pore diameter of prepared IRMOF-3 is given around 8-10 angstroms which is similarly to Ranocchiari and Bokhoven (2011) result.

4.2.5 BET

Table 6: Sample weight for CO_2 isotherm adsorption of prepared IRMOF-3

	Weight (g)		
	Sample	**MP sample cell**	**Moisture removed**
Before Pre-treatment	0.54538	11.9166	0.1147
After Pre-treatment	0.4306		

Table 7: The results of prepared IRMOF-3 for CO_2 isotherm adsorption

Sample	IRMOF-3
Weight of sample after moisture removed (g)	0.4306
CO_2 gas Adsorption at 101.3 kPa (n_a/mol.g^{-1})	0.0016

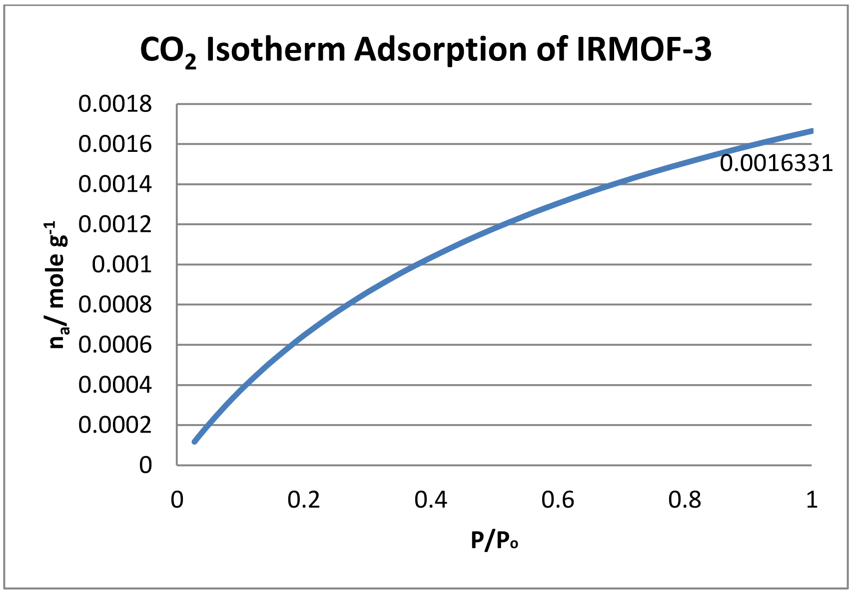


Figure 18 : Prepared IRMOF-3 CO_2 isotherm adsorption

The Figure 18 shows the CO_2 isotherm adsorption of prepared IRMOF-3 has been measured at 25°C is gradually increased in CO_2 uptake from 0 to 1 of P/P_o pressure ratio. The CO_2 gas adsorption capacity for prepared IRMOF-3 was given 0.0016 n_a/mole.g^{-1}, which is similar to Millward et al (2005) and Privalova et al (2012).

4.3 Characterization of modified IRMOF-3-AMP

4.3.1 FTIR

The result of modified IRMOF-3-AMP refer to Appendix C, is similarly with prepared IRMOF-3, but there is number of peaks are presented. The peaks from modified IRMOF-3-AMP are listed below;

IRMOF-3-AMP: IR 3443.72–3229.41 cm^{-1} (s,b), 2969.90-2884.05 cm^{-1} (m), 1610.52-1558.30 cm^{-1} (m), 1494.49-1419.50 cm^{-1} (m), 1376.27-1364.70 cm^{-1} (m), 1328.66-1253.20 cm^{-1} (s), 1192.28-1018.50 cm^{-1} (m), 958.76-924.49 cm^{-1} (m), 892.25-772.68 cm^{-1} (s), and 691.11-657.46 cm^{-1} (s,b).

**[strong (s), medium (m), broad (b)]

The first major peak at 3466.8–3419.16 cm^{-1} indicated of H-bonded or O-H stretch that presented for functional group of alcohols or phenols. The second major peak at 1610.52-1558.30 cm^{-1} indicated of N-H bend that presented for 1^{o} amines. The third major peak at 1376.27-1364.70 cm^{-1} indicates C-H rock that presented alkanes. The last major peak at 892.25-772.68 cm^{-1} indicates C-H “oop” that presented aromatic. The rest of the minor peaks are indicated as follow. At 2969.90-2884.05 cm^{-1} indicated for C-H stretch that presented alkane, 1494.49-1419.50cm^{-1} indicated for C-C stretch in ring that presented aromatic, 1328.66-1253.20 cm^{-1} indicated for C-N that presented aromatic amines which is an extra amine functional group as compared to the prepared IRMOF-3, 1192.28-1018.50 cm^{-1} indicated for C-N stretch that presented aliphatic amines, 958.76-924.49 cm^{-1} indicated for O-H bend that presented carboxylic acid, and 691.11-657.46 cm^{-1} indicated for -C≡C-H or C-H bend that presented alkynes.

According to both results are shown the similar functional group of modified IRMOF-3-AMP from the prepared IRMOF-3. From the additional amine functional group is proved that the AMP was bonded with prepared IRMOF-3 successfully. Besides, it possibly gained alkynes functional group or bonding structure.

4.3.2 TGA

The TGA curve of IRMOF-3 modified with AMP, named modified IRMOF-3-AMP. It is interpreted from the graph of derivative weight versus temperature that the weight loss due to the removal of solvent produced at around 180˚C. After that, the second range of weight loss occurs after 200˚C to 250˚C. Thus, thermal degradation of the as-synthesized material of IRMOF-3-AMP can be referred to this range. This result is indicated that amine modified IRMOF-3 possesses lower thermal stability.

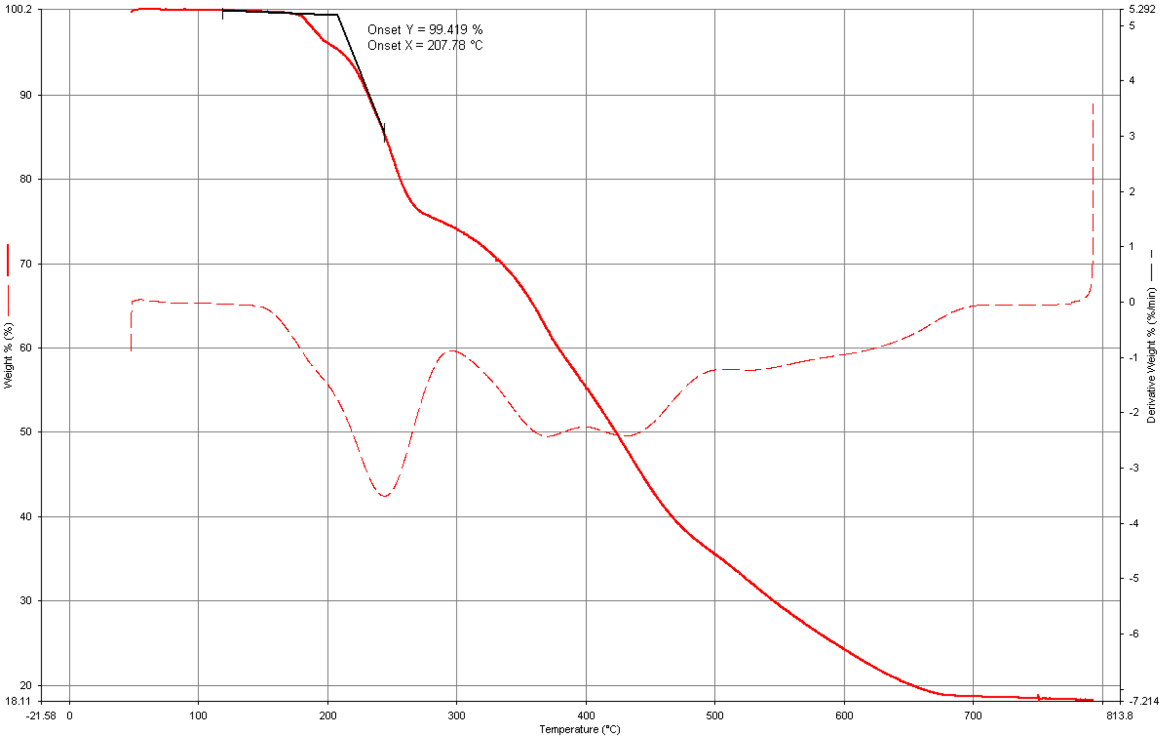


Figure 19: TGA of the modified IRMOF-3-AMP30%

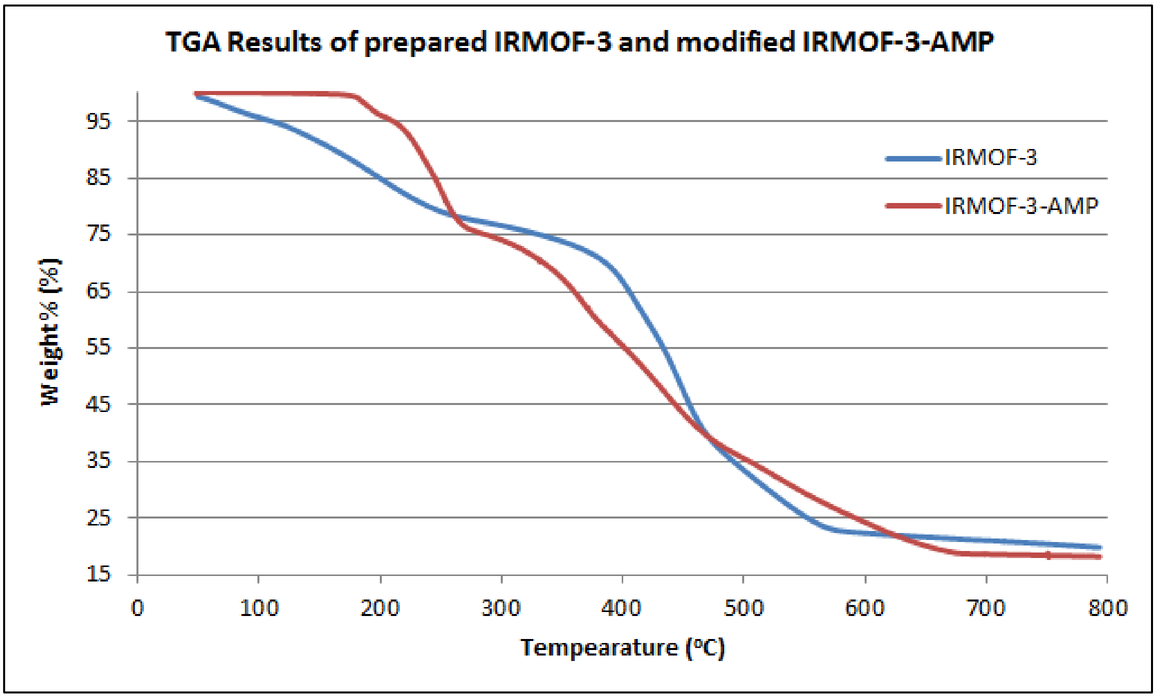
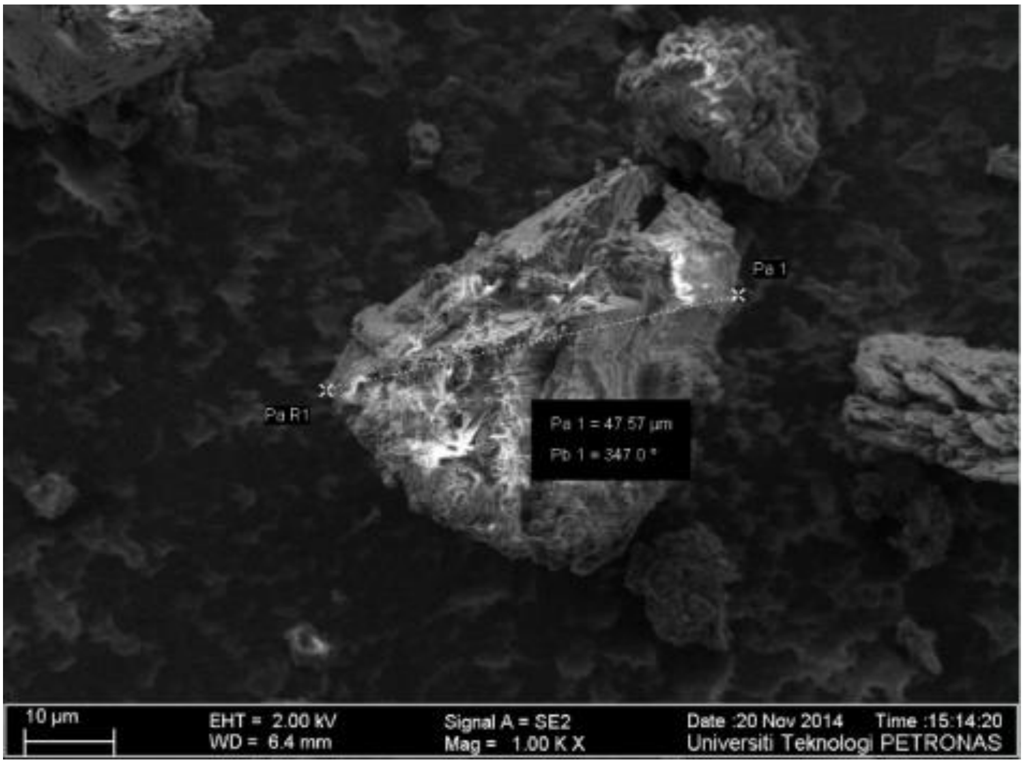


Figure 20: The comparison of TGA results between prepared IRMOF-3 and modified IRMOF-3-AMP

4.3.3 FESEM



(a)

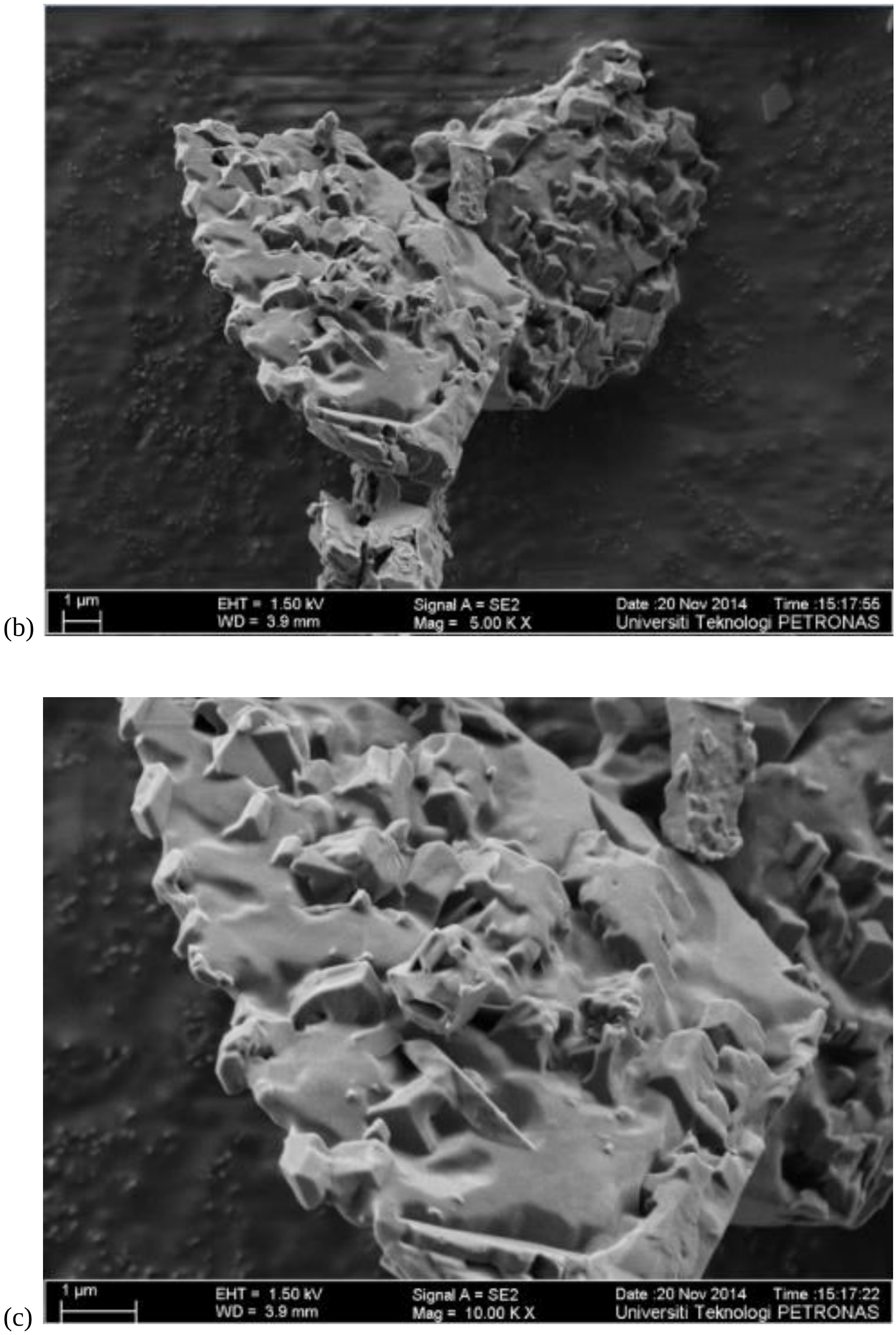
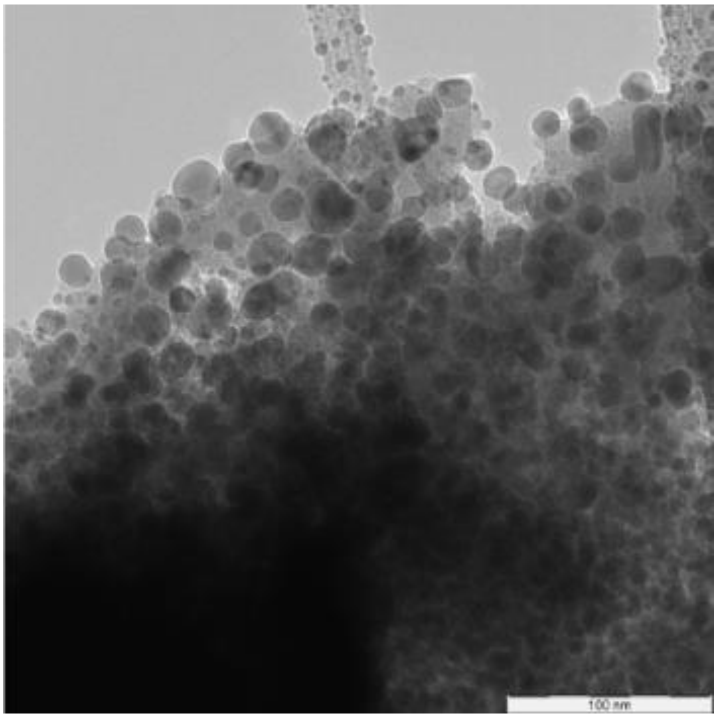


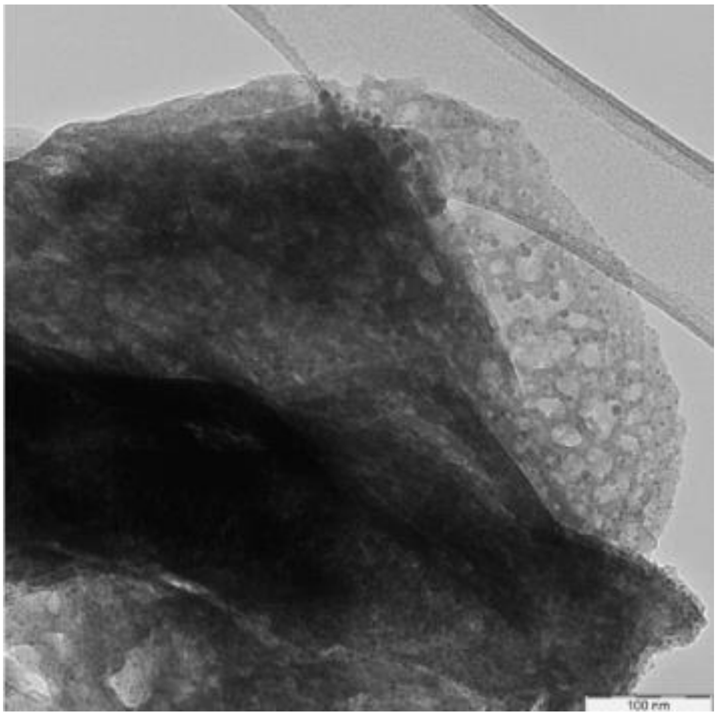
Figure 21: Modified IRMOF-3-AMP particle (a), Porous surface IRMOF-3-AMP at 5 k magnification (b), and 10 k magnification (c)

The morphology of modified IRMOF-3-AMP is differently from prepared IRMOF-3. The particle size provided closely with prepared IRMOF-3, which is around 28 nm. However, the porous property of prepared IRMOF-3 is much higher than modified IRMOF-3-AMP which was captured in Figure 21(b) and 21(c). Regarding this result was indicated that the cavity space of modified IRMOF-3-AMP to absorb CO_2 will be less than prepared IRMOF-3. Therefore, the lower porous properties will cause of lower CO_2 adsorption as well.

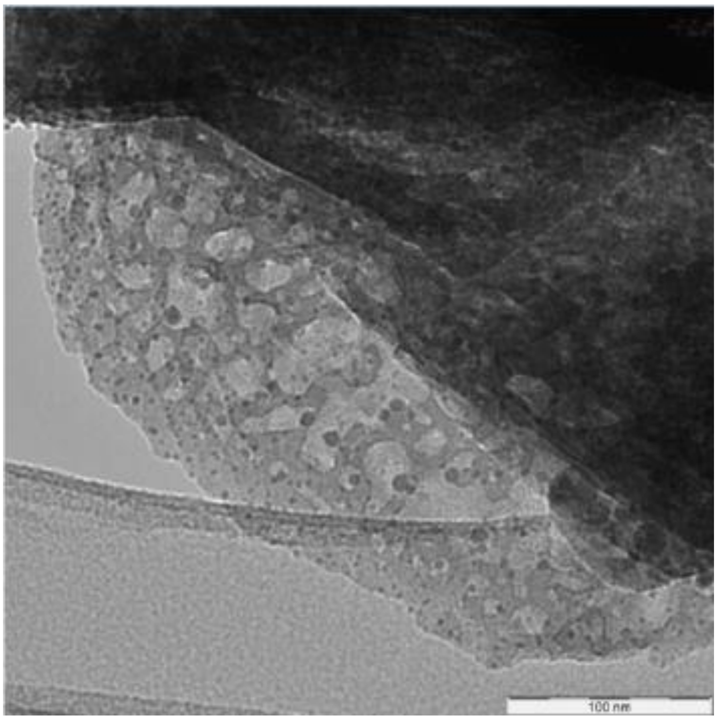
4.3.4 TEM



(a)



(b)



(c)

(d)

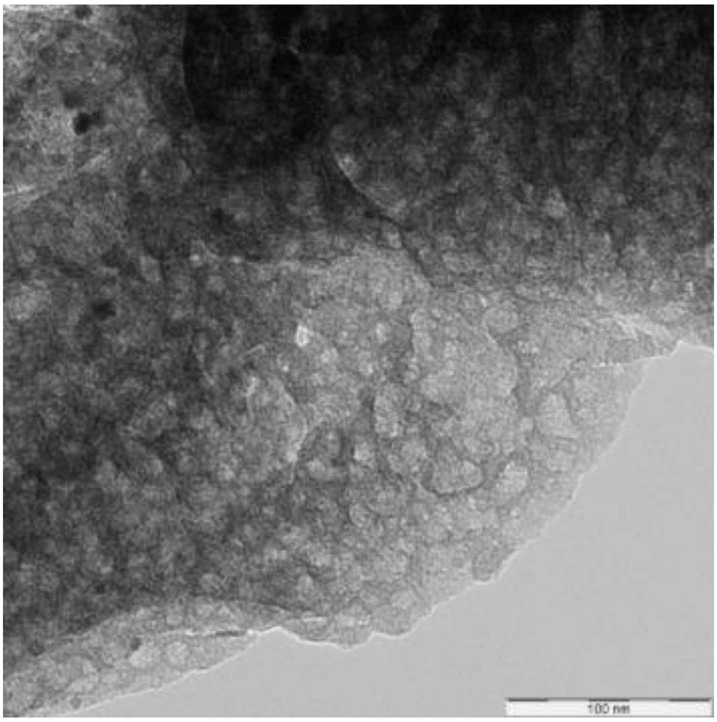


Figure 22: Modified IRMOF-3-AMP TEM results at different position

The figures above are presented of IRMOF-3-AMP physical structure, morphology, porosity in nano-crystal level in different side of particle. At 100 nm observation, the average pore diameter of IRMOF-3-AMP was given 26-29 angstroms which greater than prepared IRMOF-3 result. There are two suspects of this results which are;

1. There are pore blockages occupied over the pore of materials. or
2. The wider pore size is collapsing of the materials layer as shown in the figure 22.

4.3.5 BET

Table 8: Sample weight for CO_2 isotherm adsorption of modified IRMOF-3-AMP

	Weight (g)		
	Sample	**MP sample cell**	**Moisture removed**
Before Pre-treatment	0.6005	11.6761	0.0181
After Pre-treatment	0.5824		

Table 9: The results of modified IRMOF-3-AMP for CO_2 isotherm adsorption

Sample	IRMOF-3-AMP
Weight of sample after moisture removed (g)	0.5824
CO_2 gas Adsorption at 101.3 kPa (n_a/mol.g^{-1})	0.000028

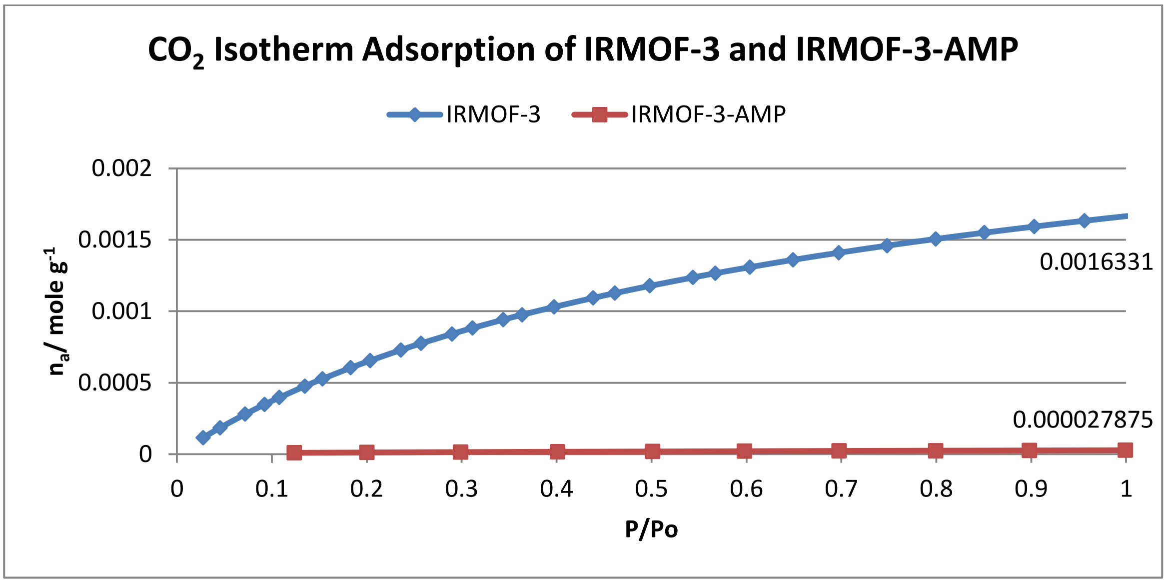


Figure 23: Comparison chart for prepared IRMOF-3 and modified IRMOF-3-AMP for CO_2 isotherm adsorption

The figure 23 shows the CO_2 isotherm adsorption of IRMOF-3-AMP that has been measured at 25°C. The adsorption is gradually increases in CO_2 uptake from 0 to 1 of P/P_o pressure ratio. The CO_2 gas adsorption capacity for IRMOF-3-AMP is 0.0000279 n_a/mole.g^{-1}. The result shows that capability for CO_2 isotherm adsorption of prepared IRMOF-3 is much higher than modified IRMOF-3-AMP, which proves the presumption of FESEM and TEM results that prepared IRMOF-3 provided higher porous property than modified IRMOF-3-AMP.

The prepared IRMOF-3 and modified IRMOF-3-AMP have presented the different of Thermal degradation, morphology and rate of CO_2 adsorption.The prepared IRMOF-3 gives higher adsorption rate results as compared with modified IRMOF-3-AMP. Several factors can be justified to declare the different of pore structure and lower CO_2 adsorption for modified IRMOF-3-AMP as discussed below.

1. The different pore structure of prepared IRMOF-3 and modified IRMOF-3-AMP leads the different of CO_2 adsorption capability. The pore structure of IRMOF-3 was reduced after amines modification.

As Rankine et al (2012) claimed for organic link and connectivity of the material can lead unwanted side reaction or hinder formation on the synthesis. The bonding of IRMOF-3 and AMP might not support a greater porosity. The IRMOF is the key of high porous surface, but the modification absolutely can change the structure and properties of materials. Therefore, both of main material and guest material need to be ensured with their capability, such as, integrate functionality or complexity. In order to predict the properties of modified material before synthesis.

In this case, the AMP was well attached with prepared IRMOF-3 as shown in FTIR result. But in term of porosity and pore structure, it was not supported to adsorb more CO_2 adsorption as much as prepared IRMOF-3 alone.

2. The humidity caused a higher content of water to be adsorbed by zinc nitrate hexahydrate during the synthesis of IRMOF-3. This water content affected the reaction time, the reaction temperature and the molar ratio of $Zn(NO_3)_2$ to 2-aminoterepthalic acid as similar case with Chen et al (2010) claimed on her study that the different molar ratios of reactant gave different product.

The result from prepared IRMOF-3 is more satisfied as compared to modified IRMOF-3-AMP. A great CO_2 adsorption has been notified for prepared IRMOF-3 in this study.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The prepared IRMOF-3 was well synthesized and well characterized. It was given the crystal with high porous surface. But the crystal was vanished after the additional amines have been added from the modification of IRMOF-3-AMP. Both of prepared IRMOF-3 and modified IRMOF-3 with AMP were characterized and prepared for each analysis as follow, FTIR, TGA, FESEM, TEM and BET.

The FTIR has been confirmed the functional groups that contain in each samples. The result of prepared IRMOF-3 is similar with previous study. However, modified IRMOF-3-AMP presented similarly with prepared IRMOF-3 but contain different structure. The TGA results present that the prepared IRMOF-3 has given higher thermal stability than modified IRMOF-3-AMP. Since degradation of modified IRMOF-3-AMP was occurred at early $200^{o}C$ while prepared IRMOF-3 was occurred at early $400^{o}C$. The FESEM results presented that prepared IRMOF-3 contains higher porous surface as compared with modified IRMOF-3-AMP. It's supported with the morphology results from TEM too. The modified IRMOF-3-AMP was suspected of being collapsed of the materials layer. Hence, it leads the lower capabilities of CO_2 isotherm adsorption. The BET results of modified IRMOF-3-AMP presented much different ability of CO_2 adsorption as compare with prepared IRMOF-3.

In conclusion, this study has been synthesized and characterized well for both prepared IRMOF-3 and modified IRMOF-3-AMP. The prepared IRMOF-3 has shown higher activity for CO_2 adsorption as compared to modified IRMOF-3-AMP due to higher porous surface.

5.2 Recommendation for Project Continuation

The study has been developed IRMOF-3 and modified IRMOF-3with AMP to enhance the capability of CO_2 adsorption. However, there are two recommendations from this study.

- The alternative chemical-based solution should be considered in future CO_2 capture study. The IRMOF-3 might be developed by modifying with metal-based, alcohol-based and etc.
- The main objective is to achieve a greater capability of CO_2 isotherm adsorption. Since the TEM results have been shown unclear results of being wider pore or the layer collapse. For the wider pore with blockage, the further study should find the solution to provide higher space of pore to capture CO_2.

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APPENDICES

APPENDIX A

The adsorption isotherm equation for BET;

$$\frac{1}{\left[V_a\left(\frac{P_0}{P}-1\right)\right]}=\frac{C-1}{V_mC}\times\frac{P_0}{P}+\frac{1}{V_mC}$$

Where P = partial vapour pressure of adsorbate gas in equilibrium with the surface at 77.4 K (b.p. of liquid nitrogen), in pascals,

Po = saturated pressure of adsorbate gas, in pascals,

Va = volume of gas adsorbed at standard temperature and pressure (STP) [273.15 K and atmospheric pressure (1.013 × 105 Pa)], in millilitres,

Vm = volume of gas adsorbed at STP to produce an apparent monolayer on the sample surface, in millilitres,

C = Dimensionless constant that is related to the enthalpy of adsorption of the adsorbate gas on the powder sample.

APPENDIX B - FTIR IRMOF-3

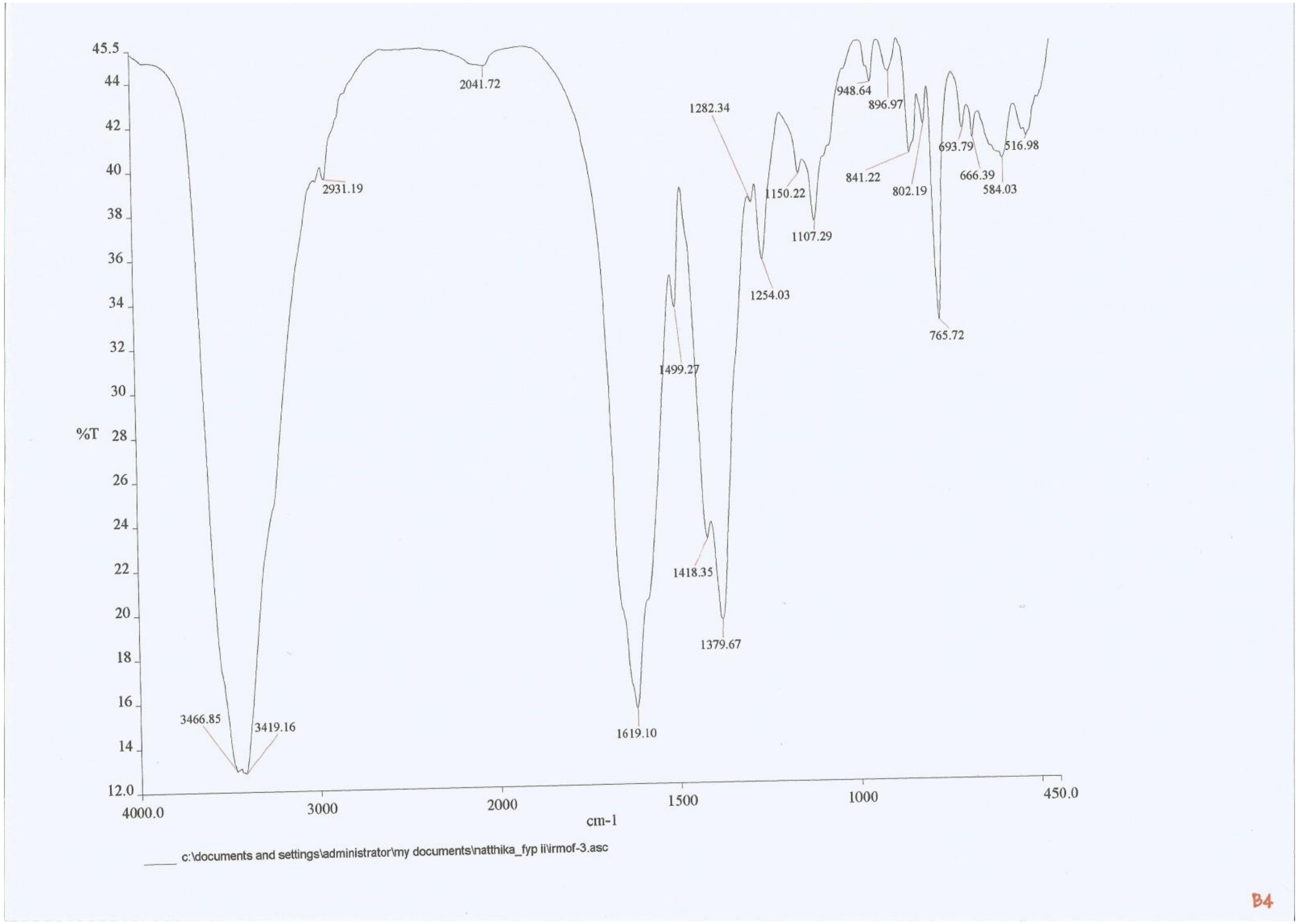


Figure 24: FTIR spectrum of prepared IRMOF-3 synthesized @ 105°C.

APPENDIX C - FTIR IRMOF-3-AMP

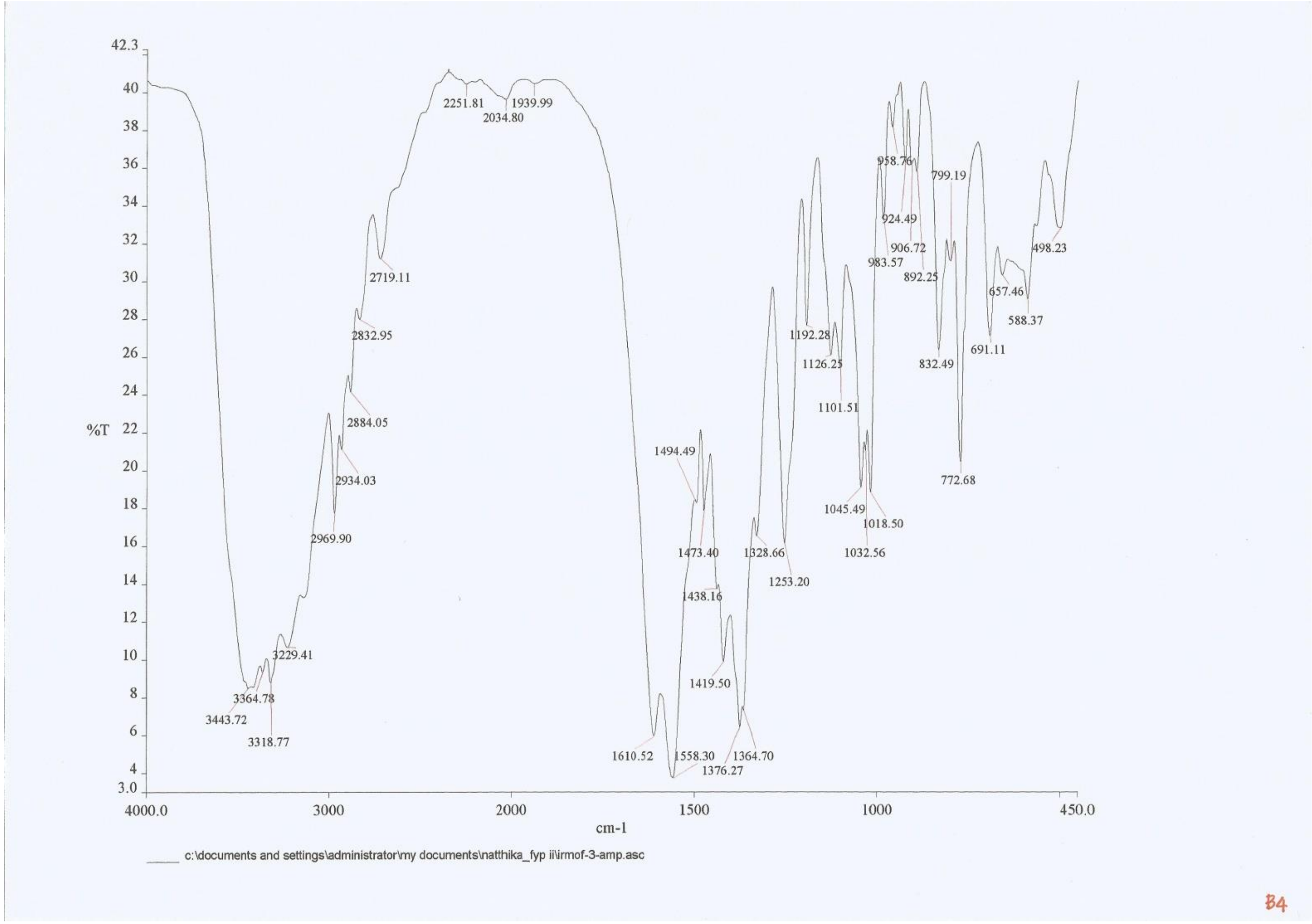
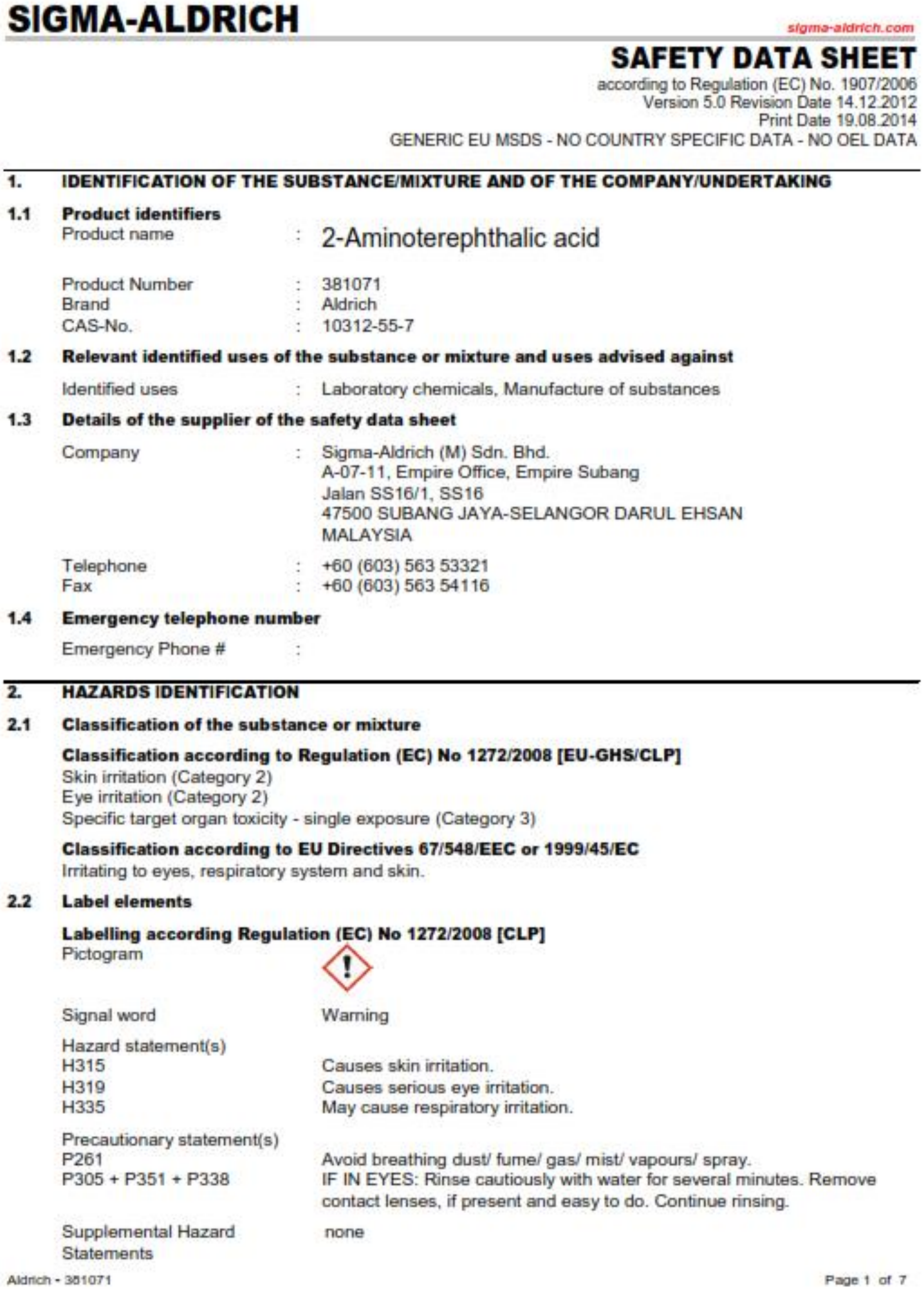


Figure 25: FTIR spectrum of modified IRMOF-3-AMP synthesized @ 75°C

APPENDIX D - 2-AMINOTERPHTHALIC ACID MSDS



SIGMA-ALDRICH

sigma-aldrich.com

SAFETY DATA SHEET

according to Regulation (EC) No. 1907/2006
Version 5.0 Revision Date 14.12.2012
Print Date 19.08.2014
GENERIC EU MSDS - NO COUNTRY SPECIFIC DATA - NO OEL DATA

1. IDENTIFICATION OF THE SUBSTANCE/MIXTURE AND OF THE COMPANY/UNDERTAKING

1.1 Product identifiers

Product name	:	2-Aminoterephthalic acid
Product Number	:	381071
Brand	:	Aldrich
CAS-No.	:	10312-55-7

1.2 Relevant identified uses of the substance or mixture and uses advised against

Identified uses	:	Laboratory chemicals, Manufacture of substances

1.3 Details of the supplier of the safety data sheet

Company	:	Sigma-Aldrich (M) Sdn. Bhd. A-07-11, Empire Office, Empire Subang Jalan SS16/1, SS16 47500 SUBANG JAYA-SELANGOR DARUL EHSAN MALAYSIA
Telephone	:	+60 (603) 563 53321
Fax	:	+60 (603) 563 54116

1.4 Emergency telephone number

Emergency Phone # :

2. HAZARDS IDENTIFICATION

2.1 Classification of the substance or mixture

Classification according to Regulation (EC) No 1272/2008 [EU-GHS/CLP]
Skin irritation (Category 2)
Eye irritation (Category 2)
Specific target organ toxicity - single exposure (Category 3)

Classification according to EU Directives 67/548/EEC or 1999/45/EC
Irritating to eyes, respiratory system and skin.

2.2 Label elements

Labelling according Regulation (EC) No 1272/2008 [CLP]

Pictogram	❗
Signal word	Warning
Hazard statement(s)	
H315	Causes skin irritation.
H319	Causes serious eye irritation.
H335	May cause respiratory irritation.
Precautionary statement(s)	
P261	Avoid breathing dust/ fume/ gas/ mist/ vapours/ spray.
P305 + P351 + P338	IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.
Supplemental Hazard Statements	none

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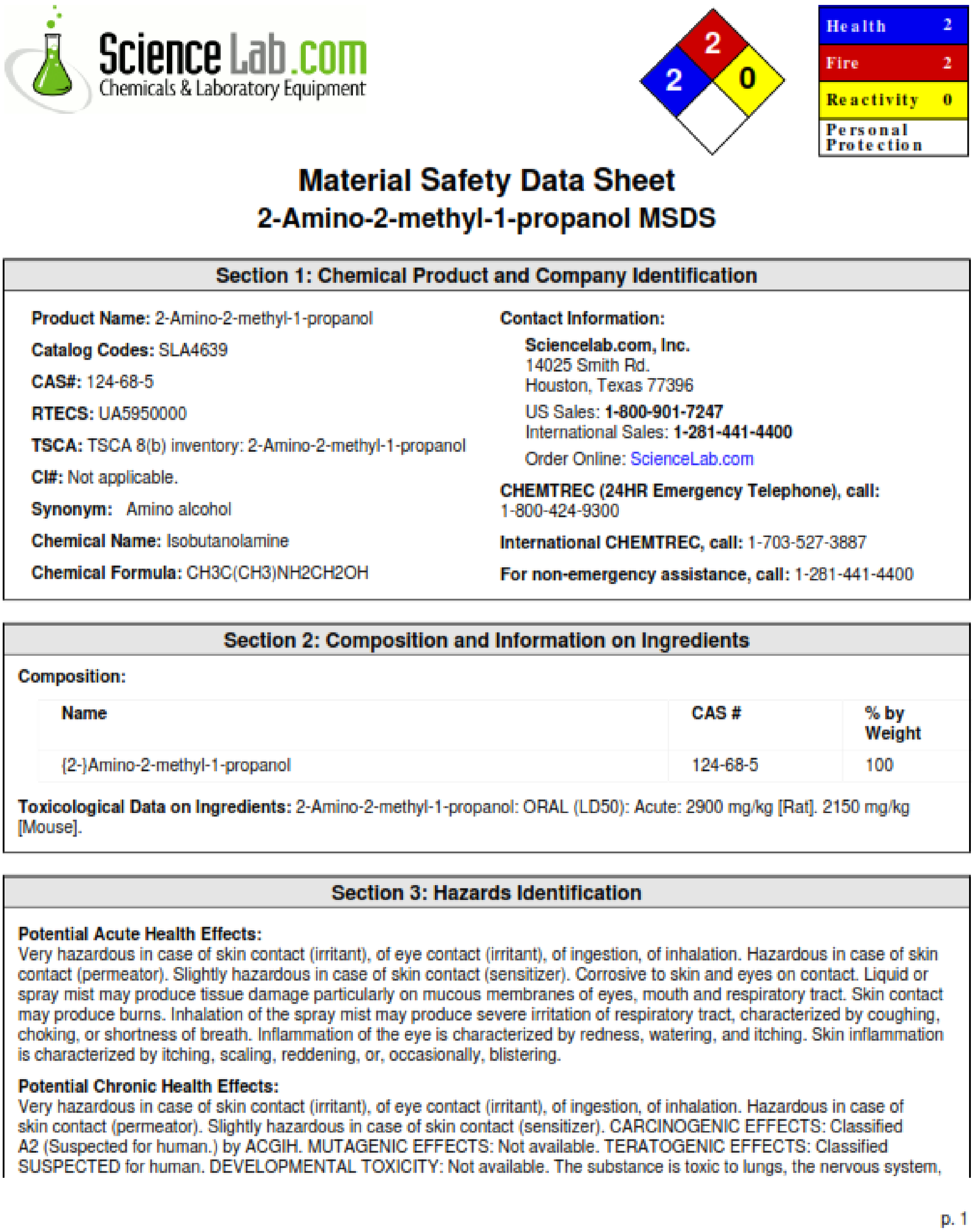
APPENDIX E- 2-AMINO-2-METHYL-1-PROPANOL MSDS



Science Lab.com
Chemicals & Laboratory Equipment

Health	2
Fire	2
Reactivity	0
Personal Protection	

Material Safety Data Sheet

2-Amino-2-methyl-1-propanol MSDS

Section 1: Chemical Product and Company Identification

Product Name: 2-Amino-2-methyl-1-propanol

Catalog Codes: SLA4639

CAS#: 124-68-5

RTECS: UA5950000

TSCA: TSCA 8(b) inventory: 2-Amino-2-methyl-1-propanol

CI#: Not applicable.

Synonym: Amino alcohol

Chemical Name: Isobutanolamine

Chemical Formula: CH3C(CH3)NH2CH2OH

Contact Information:

Sciencelab.com, Inc.
14025 Smith Rd.
Houston, Texas 77396

US Sales: **1-800-901-7247**
International Sales: **1-281-441-4400**

Order Online: ScienceLab.com

CHEMTREC (24HR Emergency Telephone), call:
1-800-424-9300

International CHEMTREC, call: 1-703-527-3887

For non-emergency assistance, call: 1-281-441-4400

Section 2: Composition and Information on Ingredients

Composition:

Name	CAS #	% by Weight
{2-}Amino-2-methyl-1-propanol	124-68-5	100

Toxicological Data on Ingredients: 2-Amino-2-methyl-1-propanol: ORAL (LD50): Acute: 2900 mg/kg [Rat]. 2150 mg/kg [Mouse].

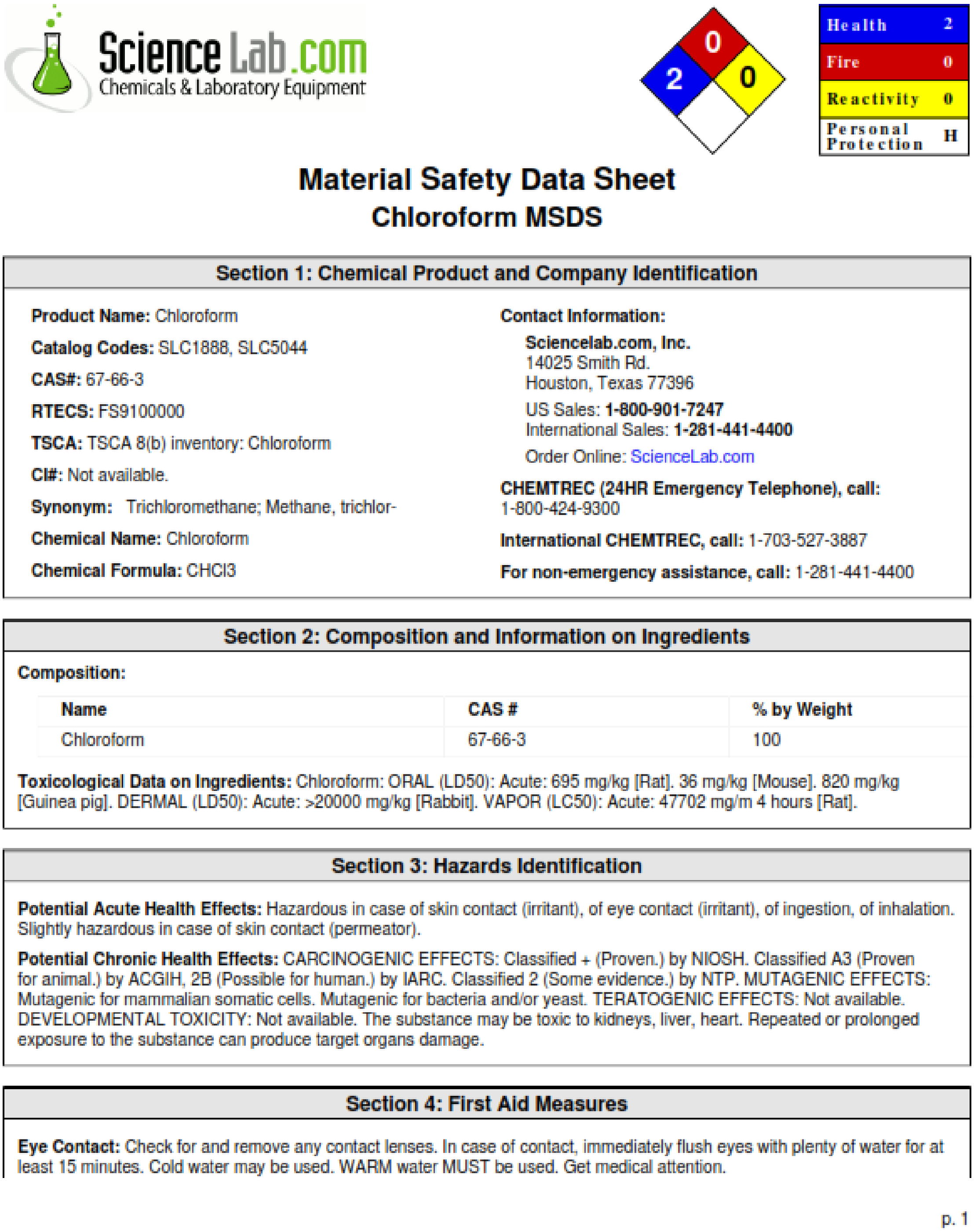
Section 3: Hazards Identification

Potential Acute Health Effects:
Very hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation. Hazardous in case of skin contact (permeator). Slightly hazardous in case of skin contact (sensitizer). Corrosive to skin and eyes on contact. Liquid or spray mist may produce tissue damage particularly on mucous membranes of eyes, mouth and respiratory tract. Skin contact may produce burns. Inhalation of the spray mist may produce severe irritation of respiratory tract, characterized by coughing, choking, or shortness of breath. Inflammation of the eye is characterized by redness, watering, and itching. Skin inflammation is characterized by itching, scaling, reddening, or, occasionally, blistering.

Potential Chronic Health Effects:
Very hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation. Hazardous in case of skin contact (permeator). Slightly hazardous in case of skin contact (sensitizer). CARCINOGENIC EFFECTS: Classified A2 (Suspected for human.) by ACGIH. MUTAGENIC EFFECTS: Not available. TERATOGENIC EFFECTS: Classified SUSPECTED for human. DEVELOPMENTAL TOXICITY: Not available. The substance is toxic to lungs, the nervous system,

p. 1

APPENDIX F - CHLOROFORM MSDS



ScienceLab.com
Chemicals & Laboratory Equipment

Health	2
Fire	0
Reactivity	0
Personal Protection	H

Material Safety Data Sheet
Chloroform MSDS

Section 1: Chemical Product and Company Identification

Product Name: Chloroform

Catalog Codes: SLC1888, SLC5044

CAS#: 67-66-3

RTECS: FS9100000

TSCA: TSCA 8(b) inventory: Chloroform

CI#: Not available.

Synonym: Trichloromethane; Methane, trichlor-

Chemical Name: Chloroform

Chemical Formula: CHCl3

Contact Information:

Sciencelab.com, Inc.
14025 Smith Rd.
Houston, Texas 77396

US Sales: **1-800-901-7247**
International Sales: **1-281-441-4400**

Order Online: ScienceLab.com

CHEMTREC (24HR Emergency Telephone), call:
1-800-424-9300

International CHEMTREC, call: 1-703-527-3887

For non-emergency assistance, call: 1-281-441-4400

Section 2: Composition and Information on Ingredients

Composition:

Name	CAS #	% by Weight
Chloroform	67-66-3	100

Toxicological Data on Ingredients: Chloroform: ORAL (LD50): Acute: 695 mg/kg [Rat]. 36 mg/kg [Mouse]. 820 mg/kg [Guinea pig]. DERMAL (LD50): Acute: >20000 mg/kg [Rabbit]. VAPOR (LC50): Acute: 47702 mg/m 4 hours [Rat].

Section 3: Hazards Identification

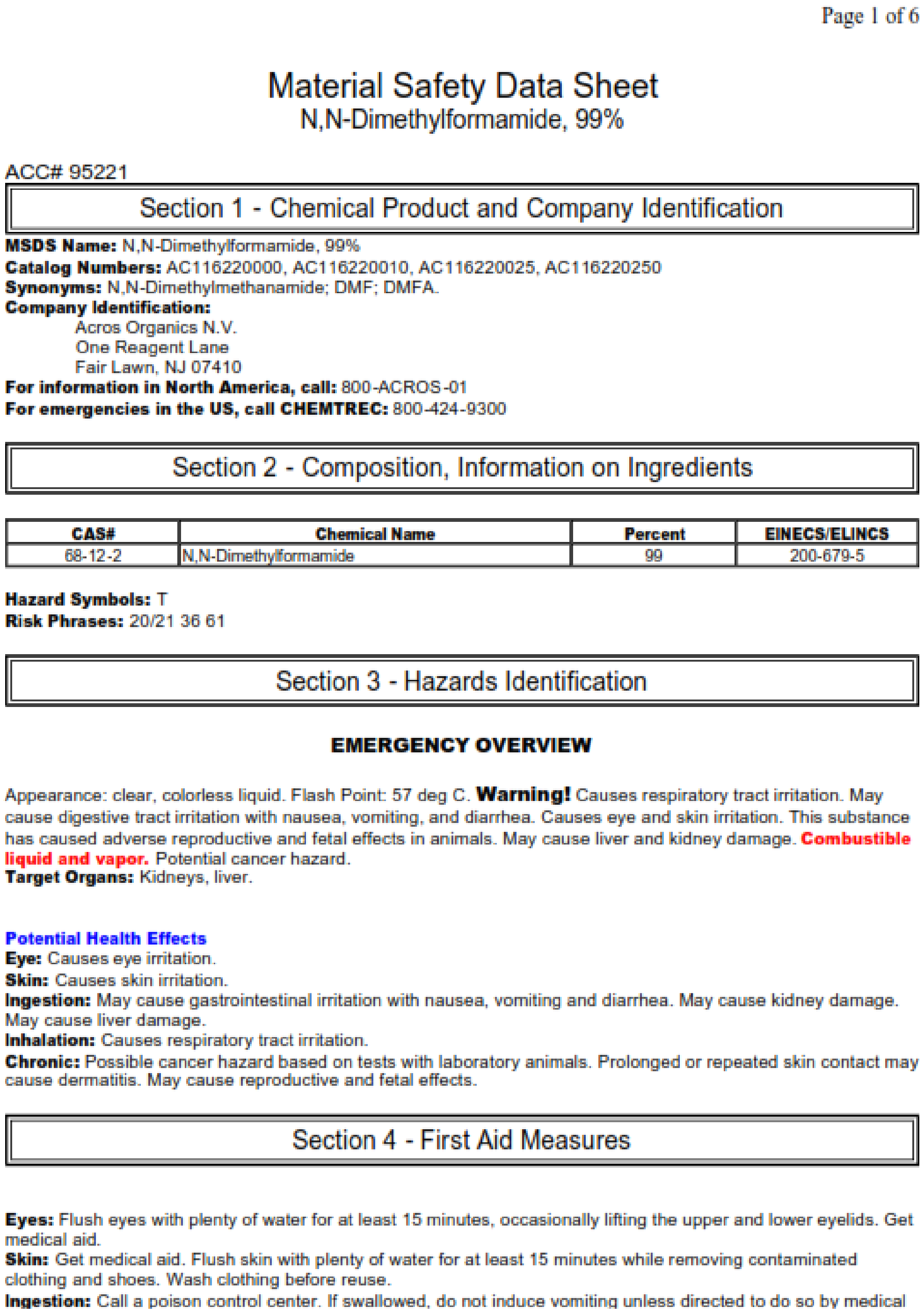
Potential Acute Health Effects: Hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation. Slightly hazardous in case of skin contact (permeator).

Potential Chronic Health Effects: CARCINOGENIC EFFECTS: Classified + (Proven.) by NIOSH. Classified A3 (Proven for animal.) by ACGIH, 2B (Possible for human.) by IARC. Classified 2 (Some evidence.) by NTP. MUTAGENIC EFFECTS: Mutagenic for mammalian somatic cells. Mutagenic for bacteria and/or yeast. TERATOGENIC EFFECTS: Not available. DEVELOPMENTAL TOXICITY: Not available. The substance may be toxic to kidneys, liver, heart. Repeated or prolonged exposure to the substance can produce target organs damage.

Section 4: First Aid Measures

Eye Contact: Check for and remove any contact lenses. In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Cold water may be used. WARM water MUST be used. Get medical attention.

APPENDIX G – N,N-DIMETHYLFORMAMIDE MSDS



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Material Safety Data Sheet

N,N-Dimethylformamide, 99%

ACC# 95221

Section 1 - Chemical Product and Company Identification

MSDS Name: N,N-Dimethylformamide, 99%
Catalog Numbers: AC116220000, AC116220010, AC116220025, AC116220250
Synonyms: N,N-Dimethylmethanamide; DMF; DMFA.
Company Identification:

Acros Organics N.V.
One Reagent Lane
Fair Lawn, NJ 07410

For information in North America, call: 800-ACROS-01
For emergencies in the US, call CHEMTREC: 800-424-9300

Section 2 - Composition, Information on Ingredients

CAS#	Chemical Name	Percent	EINECS/ELINCS
68-12-2	N,N-Dimethylformamide	99	200-679-5

Hazard Symbols: T
Risk Phrases: 20/21 36 61

Section 3 - Hazards Identification

EMERGENCY OVERVIEW

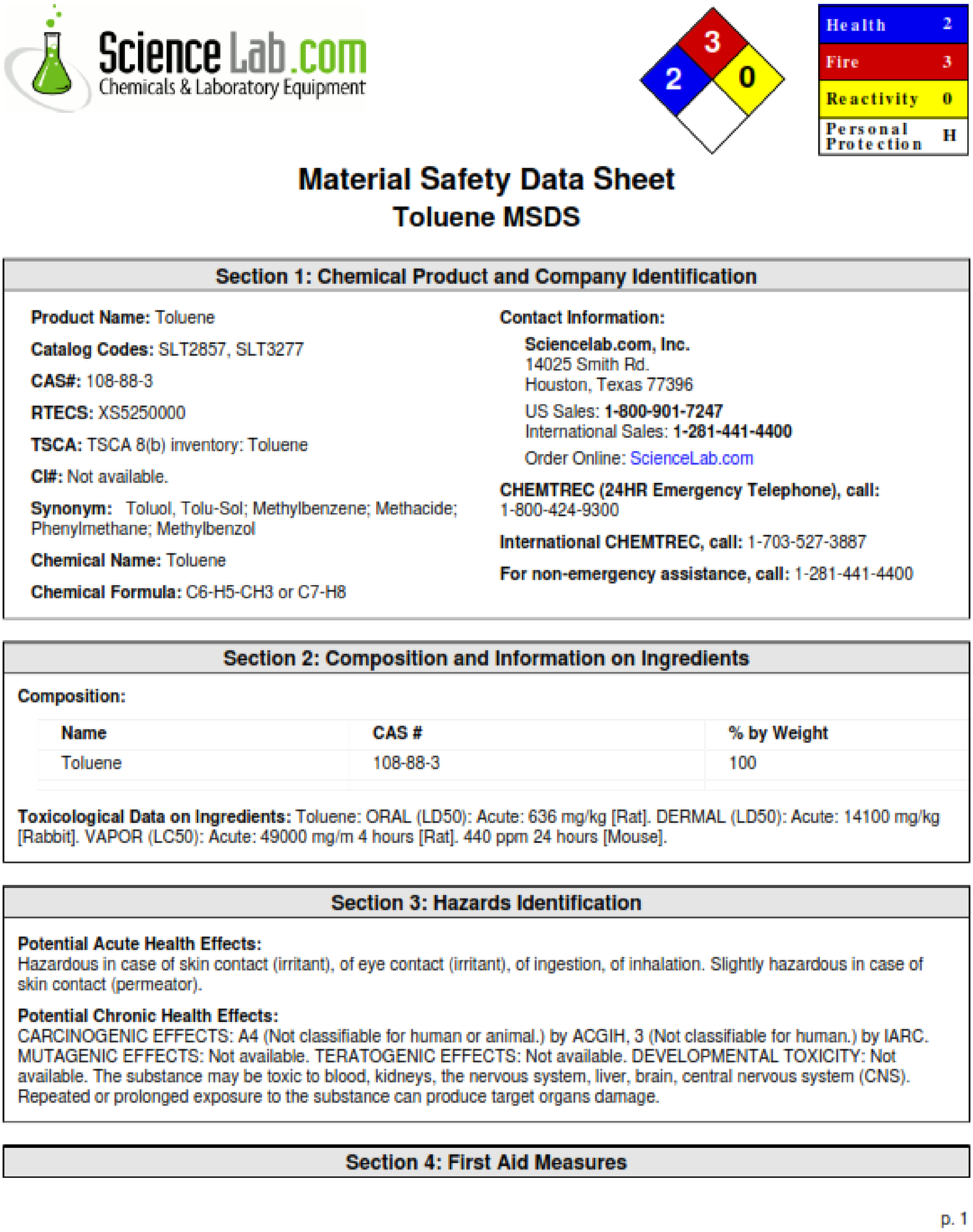
Appearance: clear, colorless liquid. Flash Point: 57 deg C. **Warning!** Causes respiratory tract irritation. May cause digestive tract irritation with nausea, vomiting, and diarrhea. Causes eye and skin irritation. This substance has caused adverse reproductive and fetal effects in animals. May cause liver and kidney damage. **Combustible liquid and vapor.** Potential cancer hazard.
Target Organs: Kidneys, liver.

Potential Health Effects
Eye: Causes eye irritation.
Skin: Causes skin irritation.
Ingestion: May cause gastrointestinal irritation with nausea, vomiting and diarrhea. May cause kidney damage. May cause liver damage.
Inhalation: Causes respiratory tract irritation.
Chronic: Possible cancer hazard based on tests with laboratory animals. Prolonged or repeated skin contact may cause dermatitis. May cause reproductive and fetal effects.

Section 4 - First Aid Measures

Eyes: Flush eyes with plenty of water for at least 15 minutes, occasionally lifting the upper and lower eyelids. Get medical aid.
Skin: Get medical aid. Flush skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Wash clothing before reuse.
Ingestion: Call a poison control center. If swallowed, do not induce vomiting unless directed to do so by medical

APPENDIX H – TOLUENE MSDS



Health	2
Fire	3
Reactivity	0
Personal Protection	H

Material Safety Data Sheet

Toluene MSDS

Section 1: Chemical Product and Company Identification

Product Name: Toluene

Catalog Codes: SLT2857, SLT3277

CAS#: 108-88-3

RTECS: XS5250000

TSCA: TSCA 8(b) inventory: Toluene

CI#: Not available.

Synonym: Toluol, Tolu-Sol; Methylbenzene; Methacide; Phenylmethane; Methylbenzol

Chemical Name: Toluene

Chemical Formula: C6-H5-CH3 or C7-H8

Contact Information:

Sciencelab.com, Inc.
14025 Smith Rd.
Houston, Texas 77396

US Sales: **1-800-901-7247**
International Sales: **1-281-441-4400**

Order Online: ScienceLab.com

CHEMTREC (24HR Emergency Telephone), call:
1-800-424-9300

International CHEMTREC, call: 1-703-527-3887

For non-emergency assistance, call: 1-281-441-4400

Section 2: Composition and Information on Ingredients

Composition:

Name	CAS #	% by Weight
Toluene	108-88-3	100

Toxicological Data on Ingredients: Toluene: ORAL (LD50): Acute: 636 mg/kg [Rat]. DERMAL (LD50): Acute: 14100 mg/kg [Rabbit]. VAPOR (LC50): Acute: 49000 mg/m 4 hours [Rat]. 440 ppm 24 hours [Mouse].

Section 3: Hazards Identification

Potential Acute Health Effects:
Hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation. Slightly hazardous in case of skin contact (permeator).

Potential Chronic Health Effects:
CARCINOGENIC EFFECTS: A4 (Not classifiable for human or animal.) by ACGIH, 3 (Not classifiable for human.) by IARC. MUTAGENIC EFFECTS: Not available. TERATOGENIC EFFECTS: Not available. DEVELOPMENTAL TOXICITY: Not available. The substance may be toxic to blood, kidneys, the nervous system, liver, brain, central nervous system (CNS). Repeated or prolonged exposure to the substance can produce target organs damage.

Section 4: First Aid Measures

APPENDIX I – ZINC NITRATE HEXAHYDRATE MSDS

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SAFETY DATA SHEET

according to Regulation (EC) No. 1907/2006
Version 5.0 Revision Date 14.09.2012
Print Date 19.08.2014
GENERIC EU MSDS - NO COUNTRY SPECIFIC DATA - NO OEL DATA

1. IDENTIFICATION OF THE SUBSTANCE/MIXTURE AND OF THE COMPANY/UNDERTAKING

1.1 Product identifiers

Product name : Zinc nitrate hexahydrate

Product Number : 228737
Brand : Sigma-Aldrich
CAS-No. : 10196-18-6

1.2 Relevant identified uses of the substance or mixture and uses advised against

Identified uses : Laboratory chemicals, Manufacture of substances

1.3 Details of the supplier of the safety data sheet

Company : Sigma-Aldrich (M) Sdn. Bhd.
A-07-11, Empire Office, Empire Subang
Jalan SS16/1, SS16
47500 SUBANG JAYA-SELANGOR DARUL EHSAN
MALAYSIA

Telephone : +60 (603) 563 53321
Fax : +60 (603) 563 54116

1.4 Emergency telephone number

Emergency Phone # :

2. HAZARDS IDENTIFICATION

2.1 Classification of the substance or mixture

Classification according to Regulation (EC) No 1272/2008 [EU-GHS/CLP]
Oxidizing solids (Category 2)
Acute toxicity, Oral (Category 4)
Skin irritation (Category 2)
Eye irritation (Category 2)
Specific target organ toxicity - single exposure (Category 3)

Classification according to EU Directives 67/548/EEC or 1999/45/EC
Contact with combustible material may cause fire. Harmful if swallowed. Irritating to eyes, respiratory system and skin.

2.2 Label elements

Labelling according Regulation (EC) No 1272/2008 [CLP]
Pictogram

Signal word Danger

Hazard statement(s)	
H272	May intensify fire; oxidiser.
H302	Harmful if swallowed.
H315	Causes skin irritation.
H319	Causes serious eye irritation.
H335	May cause respiratory irritation.

Precautionary statement(s)	
P220	Keep/Store away from clothing/ combustible materials.

Sigma-Aldrich - 228737 Page 1 of 6