

**Laboratory Investigation on the Effects of Acid and Surfactant on
Malaysian Coal for Coal Bed Methane (CBM) Study**

by

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14767

Dissertation submitted in partial fulfilment
of the requirements for the
Bachelor of Engineering (Hons)
Petroleum

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Petroleum Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfilment of the requirements for the
BACHELOR OF ENGINEERING (Hons)
PETROLEUM

Approved by,

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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 herein have not been undertaken or done by unspecified sources or persons.

(AFIF IZWAN BIN ABD HAMID)

ABSTRACT

Since the discovery of oil in Sarawak in 1910, Malaysian energy sector had been dependent on this resource. However the country's oil consumption has been steadily growing since then causes the long gone of easy-oil. So the government had to invest in enhancing recovery from existing oil or gas fields in order to meet energy need or find other alternative energy sources to replace the impending country's petroleum exhaustion, such as Coal Bed Methane (CBM). CBM is an unconventional reservoir thus it is hard to extract gas from them. CBM Production usually involves dewatering the formation to lower reservoir pressure. By lowering the reservoir pressure, it will allow the formation of free gas and raises the gas permeability thus allows the migration of gas into the wellbore. Hydraulic fracturing is the common method to stimulate CBM reservoir to produce methane gas. However, this method can cause formation damage. So the alternative to hydraulic fracturing is the acid fracturing technique. Several methods could be taken in optimizing the production of CBM to restore the gas porosity and permeability inside the coal seams thus increase the production of methane gas. The uniqueness of this project is how the coal will be stimulated. Starting from drying the coal samples in the oven for two hours, the project continues by weighing the dry coal samples, immerse them in the different mixture of acids with surfactants for 6 hours, weighing the wet coal samples until the process of calculating the porosity of the coal samples, which is the main factor that will determine the success of this project. Porosity test result shows different porosity values are obtained on each Malaysian coal samples after injected with the mixture of acid and surfactant. As a conclusion, mixture of HCl with THF and H₂SO₄ with Methanol are good candidates to be used for stimulation in coal formation having temperature of 100°C and 50°C respectively

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ABBREVIATIONS AND NOMENCLATURES

$Ash_{(wt\%,daf)}$	Ash Yield
BJH_d	Average pore diameter obtained by BJH equation
BET_s	Specific surface area obtained by the BET equation
$BJH_{mes.v.}$	Mesopore volume obtained by D-R equation
CBM	Coal Bed Methane
Coal (g)	Weight of Coal in gram
daf	Dry ash free
D-R mic.v.	Micropore volume obtained by the D-R equation
$E_{(wt\%,daf)}$	Extraction Yield
ECBM	Enhanced Coal Bed Methane
H_2SO_4	Sulfuric Acid
HCl	Hydrochloric Acid
HNO_3	Nitric Acid
M_{dry}	Weight of coal after being dried in oven, g
m_i	Mass fraction of acid/surfactant solution, wt%
m_{total}	Total mass fraction of acid/surfactant solution, wt%
M_{dry}	Weight of coal after being dried in oven, g
M_{wet}	Weight of coal after being taken out from solution, g
ρ_a	Density of acid solution, g/cm^3
ρ_b	Density of surfactant solution, g/cm^3
ρ_{Mdry}	Density of coal, g/cm^3
ρ_w	Density of acid and surfactant mixture, g/cm^3
Residue (g)	Weight of Residue in gram
THF	Tetrahydrofuran

wt%	Weight Percentage
X_a	Mass fraction of acid solution, %
X_b	Mass fraction of surfactant solution, %

CHAPTER 1

INTRODUCTION

1.1 Project Background

Since the discovery of oil in Sarawak in 1910, Malaysian energy sector had been dependent on this resource. This discovery had created opportunities for many oil majors to invest in the upstream and downstream sectors of the industry thus provide employment and skills transfer to Malaysians and changed the economic landscape of the country forever [1]. Most of the oil fields in Malaysia nowadays are considered as mature fields such as Bayan Field, which is located at Bintulu offshore, Sarawak [2]. The term mature field is not defined by their age but rather by where the field is with respect to its peak production, where the production has started to enter decline phase [3]. As of last year, Malaysia's daily production stood at 630,000 barrels, which is around 25% below the peak of 860,000 barrels per day achieved in 2004 [2]. Therefore, alternative energy must be found to replace the impending country's petroleum exhaustion.

Coal Bed Methane (CBM) is one of the alternative energy sources to replace petroleum. Methane have several advantages compared to oil such as it burns more cleanly than oil and also cheap. However, CBM is an unconventional reservoir, means that it is hard to produce gas from the reservoir without any recoveries. Enhanced Coal Bed Methane (ECBM) is one of the recoveries to boost the gas production from CBM reservoir. In recent years, CBM has been developed, modified and improved especially in United States, where they have discovered about 800 trillion cubic feet (Tcf) of methane in coal beds [4]. Figure 1.1 shows the worldwide CBM development activity respectively [5].

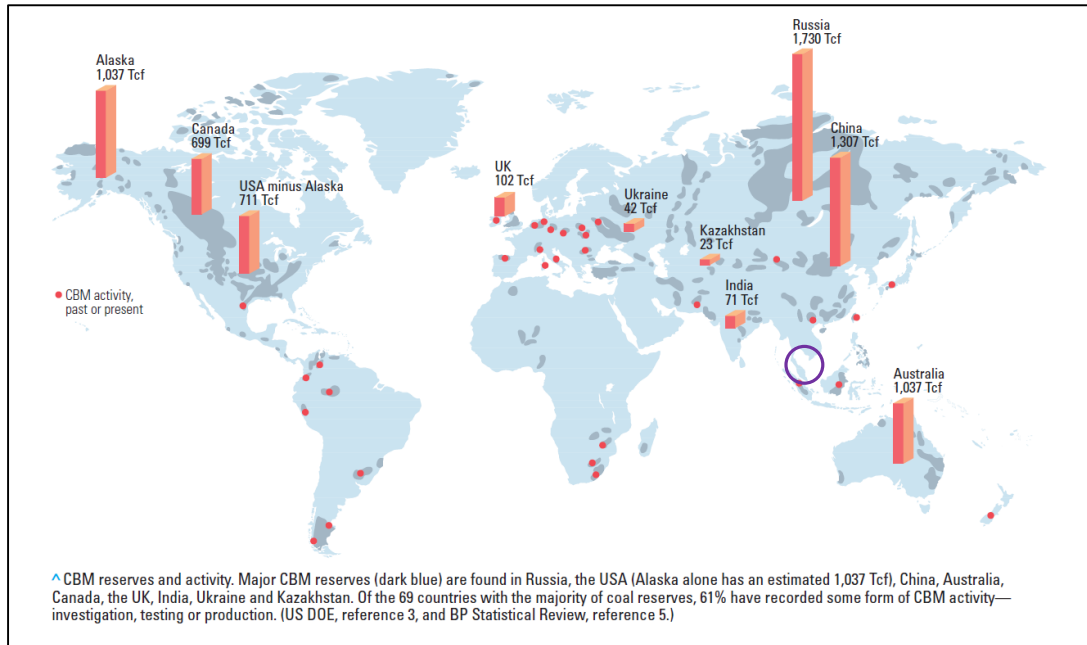


Figure 1.1 CBM reserves and activity
Source: Summer 2009, Oilfield Review, Schlumberger Magazine 2009

As shown in Figure 1.1, Malaysia (in circle) had no CBM production in 2009. Hence, CBM study in Malaysia is new. CBM process has also involved both of the oil and coal industry technologies. As example, methane that was produced for local use during preceding generation took along with other oilfield technology to fracture those coals and their dewatering in order to increase production rate to commercial levels [4].

Lastly, this project is the alternative to the method for CBM recovery. Its main focus is to investigate the effects of acids and surfactants on Malaysian coal for CBM study.

1.2 Problem Statement

CBM is a naturally fractured reservoir which contains natural gas that is stored in the coal seams. 90% of the storage contained methane gas and the remaining is the combination of water and carbon dioxide. However, at initial stage most of the CBM reservoir produce water because of cleats and at the same time the methane gas is adhered to the surface of the coal and deposited inside the pores.

Hydraulic fracturing is the common method to stimulate CBM reservoir to produce methane gas. However, this method can cause formation damage. So the alternative to hydraulic fracturing is the acid fracturing technique. However there is only a few researches had been done about stimulating the CBM reservoir using this technique.

Last but not least, this project will cover up several key points including:

- i) How does acid fracturing helps in optimizing the production of methane?
- ii) What is the substantial differences of using different mixture of acid and surfactant towards coal?

1.3 Objectives

In conducting this project, the main objectives has been identified:

- i) To increase the porosity of the Malaysian coal by acidizing with surfactant injection method

1.4 Scope of Study

There are several scopes of study will be focused in this project:

- i) Study the nature of the acid being used (Hydrochloric Acid (HCl), Sulfuric Acid (H₂SO₄) and Nitric Acid (HNO₃)) together with the surfactants (Acetone, Methanol and Tetrahydrofuran (THF)).
- ii) Study their effectiveness towards the stimulation process for porosity measurement.

The stimulation process will involve in drying process of coal samples at two different temperatures, 50°C and 100°C. Then they will be immersed in the mixture of acid and surfactant to investigate the effect on coal's porosity.

CHAPTER 2

LITERATURE REVIEW

2.1 Definition of Coal Bed Methane (CBM)

CBM is an unconventional natural gas that is stored in deeply buried coal seams [6]. These coal are drilled down into for the methane gas before being extracted and sold to the consumer. CBM consists of over 90% methane and the gas composition is normally stable. Hence, the gas can be fed directly into the natural gas network or a gas engine [7].

2.2 Formation of CBM and Its Potential in Malaysia

Coal is formed from peat, the deposited plant-derived organic material through coalification process [8]. Coalification process is initiated by the biochemical degradation but as the burial increases the overburden pressures and subsurface temperature, it causes the physiochemical process that continues coalification.

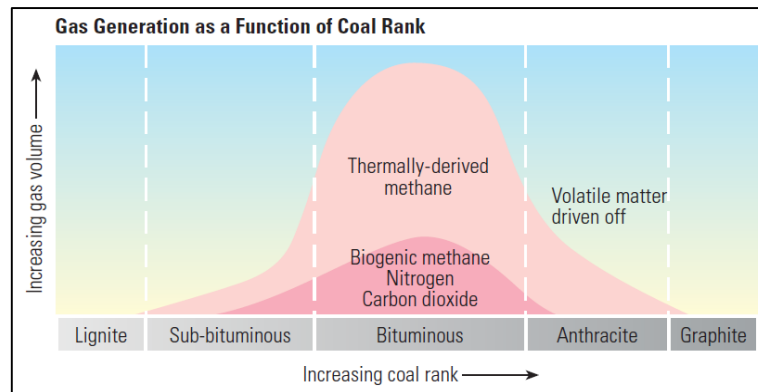


Figure 2.1 Gas Generation in Coal

Source: Autumn 2003, Oilfield Review, Schlumberger Magazine, 2003

As coalification progresses, the coal increases in rank, starting from lignite, sub-bituminous, bituminous, anthracite and graphite. As shown in the Figure 2.1 above, highest gas volume is contained in bituminous coal rank [5].

Next, dewatering process occur through time. It will cause the coal matrix to shrink and creation of endogenous cleats [5]. Coals cannot be economically produced without the presence of cleats to connect the pores. Next, CBM is not only been stored in coal matrices (primary storage), it is also been stored in cleats and natural fractures (secondary storage). There are two type of cleats (classified geometrically) which are face cleats and butt cleats. Face cleats is more continuous than the butt cleats which is less continuous [9]. In order for the gas to be produced, the coal needs to be depressurized. Then the adsorbed gas in the coal matrices diffused by Fick's Law and enter the cleat network and finally reaches the wellbore. [8]

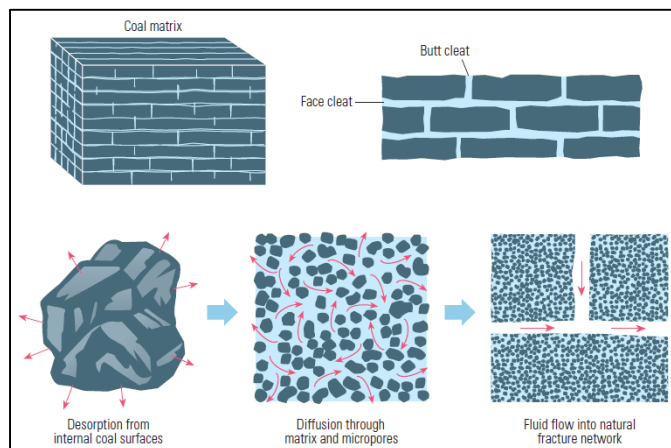


Figure 2.2 Adsorption and Desorption Process

Source: Summer 2009, Oilfield Review, Schlumberger Magazine, 2009

Based on the study conducted by Chen et al. (2011), CBM has a very good prospect in Malaysia since the highest recorded permeability is 46.17mD and the Balingian coalfields has the area of 6.0937km² which able to contain a resource of CBM of 95.37 Bscf [8].

2.3 Stimulation of CBM Production

CBM wells are often characterized as wells that have low production rates. In order to overcome this problem, CBM wells are commonly stimulated to contact the maximum drainage area to connect the cleats and natural fractures with the wellbore.

2.3.1 Fracture Stimulation for CBM Reservoirs

For CBM development, there are three primary categories for fracture stimulations which are polymer-base gel system, slickwater system and foamed [9]. However all of these fracture stimulations have their weaknesses. As example, crosslinked gel system can cause formation damage if the gel does not break, irreversibly plugging cleats. Next, slickwater systems will fail if the pumping rates is lower because the fluid has poor proppant-carrying capabilities. Last but not least, although foamed system is successfully reduces the potential for damage caused by interactions between the coal and the fracture fluids, the danger of formation damage still existed [9]. For example, the surfactants used by this system can negatively impact the wettability of the coal and reduce the rate of dewatering.

There is another methods to reduce pressure through dewatering process in order to allow the methane gas to detach from the coal's surface and flow into the cleats and the wellbore. The first method is by using polymer-free CoalFRAC fluids [9]. It is proven that the wells that have been treated with the CoalFRAC system produced at a 38% higher rate than offset wells treated with other fluids [9].

Based on the below diagram, the average production for the wells treated with CoalFRAC fluid is compared with the offset wells treated with other fluid system. Although the rates were identical for both wells for the first two months, however, the wells treated with CoalFRAC fluid maintained higher rates over time than offset wells treated with other fluid.

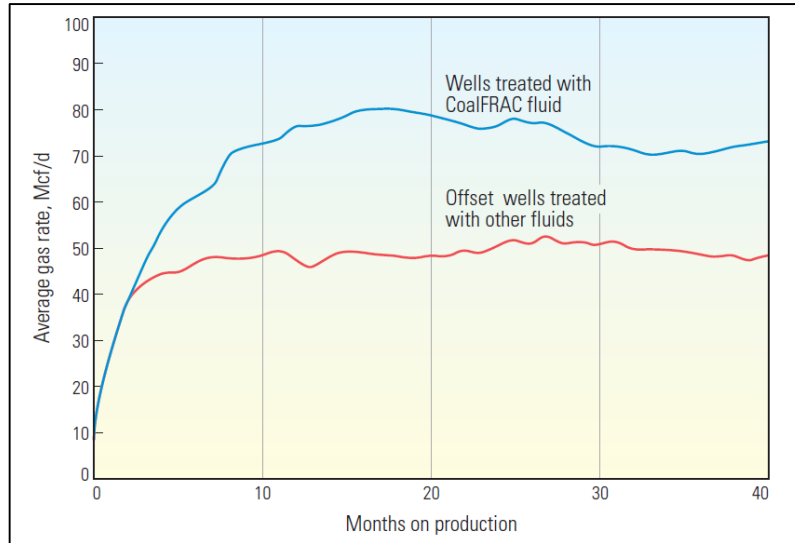


Figure 2.3 CoalFRAC Treatment Result

Source: Summer 2009, Oilfield Review, Schlumberger Magazine, 2009

2.3.2 Reaction between coal and acid

Acid is defined as any substances that tasted sour in water solution, changes the colour of acid-base indicator like litmus paper, reacts with some metals to yield hydrogen gas, reacts with base to form salt and promotes certain chemical reactions [10]. A research has been done to investigate the reactions of a bituminous coal with sulfuric acid. A reaction between concentrated sulfuric acid and bituminous coal produced useful ion-exchange materials. The reaction involves oxidation and sulfonation produce carboxyl and sulfonic acid groups and the chemical changes that occur in the coal substance can also be noticed [11].

An investigation on physical properties has been made. Large surface area is vital for ion exchangers. The experiment was conducted by using a raw coal with a surface area of $2.7\text{m}^2/\text{g}$. Then the raw coal will left to be react with different set of temperature of sulfuric acid for a few days. Below summarize the result of the experiment [11]:

Table 2.1 Sulfonation Data (Kinney & Gray, 1959)

	Temp. (°C)	Time (Days)	Surface Area (m ² /g)
Raw Coal (without react with acid)		-	2.7
Coal reacts with sulfuric acid	25	5	2.3
		10	0.002
		20	0.12
		31	1.5
	50	1	3.1
		3	16.0
	50	5	-
		8	54.0
		1	7.2
	100	2	101.0
		5	-
		8	222.0
		1	4.5
	110	3	158.0
		8	183.0
		1	178.0
150	3	272.0	

From Table 2.1, at 25°C, the surface area is smaller than the original size after been left for 24 hours. The report conclude that the reaction of the coal with acid is sealing off the coal pores. Then it can also be noted that at day 10 and day 20, the surface area are decreasing. At this temperature, coal pores are being closed off due to the reaction of coal with the acid and the acid molecules are still not widely dispersed [11]. Meanwhile, the surface areas of the original coal increase as the time increase at higher temperature (50°C, 100°C, 110°C and 150°C) [11].

The dispersion has increased and new surface areas are developed. Based on the observation made on the dispersion of sulfuric acid and the increment of surface area, a hypothesis had be deduced. During the dispersion process, the acid molecules exert their way between the coal lamella [11]. Besides, if the original coal is left for one (1) day at different higher temperature likes 50°C and 100°C, the effects of temperature on the surface area can be noticed. Hence, it can also be concluded that extending the duration of treatment at higher temperature can develop maximum surface area [11].

2.3.3 Roles of Surfactant in CBM Study

An experiment was conducted to study the pore structures and methane sorption characteristics of coal after extraction with tetrahydrofuran (THF). THF is a stable surfactant with relatively low boiling point, colourless, water-miscible organic liquid with low viscosity and is an excellent solvency [12]. It is classified as heterocyclic compound, specifically a cyclic ether and has odor similar to acetone.

Four Chinese coal samples were collected, where three of them were bituminous and one anthracite coals. They were extracted with THF solvent at 50°C and atmospheric pressure by microwave-assisted extraction. The extraction yield ($E_{(wt\%,daf)}$) is calculated by using the below formula [13]:

$$E_{(wt\%,daf)} = \frac{coal(g) - residue(g)}{1 - ash_{(wt\%,daf)} / 100} * coal(g) \times 100 \quad (\text{Equation 1})$$

The THF extraction is proven successful in this experiment where by the pore structure was changed by indifferent degrees. The extraction expands and dredges the pores, thereby increasing the ability of coal gas sorption. However, the degree of change of the pore structure is different due to their differences in coal rank, which results in either the increase or decrease of the micropore volume, along with the specific surface area [12].

Table 2.2 shows that Anthracite coal, CP No.3 does not change in volume after extraction and the increase of the mesopore volume results in the decrease of the specific surface area and a slightly increase in the average pore diameter. Meanwhile YZ No.5 shows an increment value for both micropore and mesopore volumes compared to raw coal, which leads to the obvious specific surface area increases and the average pore diameter reduces. However, ZJ No.9 and XG No.8 coals' micropore volume of the residues are less than the raw coal, which also led to the decrease value of their specific surface area. Meanwhile, the residues' average pore diameter increased greatly compared to the raw coals

for their high extraction yield which resulting in the increased mesopore volume [12].

Table 2.2 Average pore size, surface areas and micro/mesopore volumes of coal (Ji et al., 2014)

Coal Sample		BJH _d (nm)	BET _s / (m ² g ⁻¹)	BJH mes.v. / (cm ³ g ⁻¹)	D-R mic.v. / (cm ³ g ⁻¹)
CP No. 3 (Anthracite)	Raw coal	9.75	0.8718	0.0029	0.0004
	Residue	9.76	0.7144	0.0040	0.0004
YZ No.5 (Bituminous)	Raw coal	14.40	0.5915	0.0045	0.0003
	Residue	13.96	1.0171	0.0074	0.0004
ZJ No.9 (Bituminous)	Raw coal	8.55	0.4101	0.0028	0.0002
	Residue	17.73	0.2089	0.0359	0.0001
XG No.8 (Bituminous)	Raw coal	4.65	4.6476	0.0087	0.0019
	Residue	7.76	3.6706	0.0111	0.0015

Meanwhile, the expanding and dredging of pores is comprehensive after extraction. Extraction not only can expand the original hole (including macropore, mesopore and micropore) but can also dissolve some small molecules to form new micropore and mesopore structures. It is been concluded that the pore's structure degree is increasing after the extraction associated with the coal rank. Hence, THF surfactant proved that it can be used to stimulate the pore structure of the coals and extract methane gas from them [12].

2.4 Activated Carbon

Activated carbon is defined as a carbon that has been processed with oxygen to create millions of tiny pores between the carbon atoms. The process increases the surface area of the substance from 500 to 1500m²/g or 300 to 2000m²/g. The increased in surface area of activated carbon makes them suitable for adsorption process. Activated carbon is not only made up from charcoal but also wood, peat or coconut shells. Although it can be produced from almost any raw material, it is cost effective and environmentally friendly [14]. A study has shown that activated carbon made up from coconut shells have high volumes of micropores, thus making them as the most commonly used material for applications where high adsorption capacity is needed [15].

Activated carbon's production involves two main steps which are the carbonization of the carbonaceous raw material at temperatures below 800°C in an inert atmosphere and the carbonized product's activation [16]. Although all carbonaceous materials can change their form into activated carbon, their final products' properties may not be same because they depend on the raw material being used, the nature of the activating agent and the condition of the activation process [16]. Next, it is also important to choose the correct temperature during carbonization process in order to produce the desired product. High carbonization temperature increases resistivity but decreases the pore's volume at the same time because the product undergoes condensation process which yields an increase in mechanical strength. Therefore, adjusting the conditions of carbonization process can affect the final product entirely [15].

Next, the non-carbon elements such as oxygen and hydrogen are removed during the carbonization process as volatile gaseous products by the pyrolytic decomposition of the starting material. The residual elementary carbon atoms group themselves into stacks of flat, aromatic sheets cross-linked in a random manner, where by these sheets are irregularly arranged and leave free interstices. The interstices give rise to pores thus make activated carbons as excellent adsorbents. During carbonization process, tarry matter filled the pores. Then the pore structure in carbonized char is further developed and improved during activation process. The activation process is a process

where it converts the carbonized raw material into a form, where it contains greatest possible number of randomly distributed pores of various sizes and shapes. There are three types of pores and its diameter size [16]:

Table 2.3 Group of activated carbon's pores (Bansal & Goyal, 2005)

Type of Pores	Size of Pores (Diameter)
Micropores	< 2nm
Mesopores	2-50nm
Macropores	> 50nm

In activated carbon, about 95% of the surface area is constituted by the micropores and the remaining is mesopores. Macropores is considered not importance to the adsorption process in activated carbon because their contribution to surface area does not exceed 0.5m²/g. The macropores provide passage of adsorbate molecules into the micropores and mesopores [16].

2.5 Density of Coal

Density of coal is depending on the rank of coal itself. Kopp (2014) mentioned that coal has density ranges between 1.1 to about 1.5 g/cm³ [17]. This means that coal is just slightly denser than water and less dense than most rock [17]. As example, shale has a density of 2.7 g/cm³. This theory is supported by Gentzis (2013). By measuring coal densities of 590 coal cores of the sub-bituminous coal rank in the Powder River Basin, he found out that the coal density mostly occurs within a narrow range of 1.25 to 1.30g/cm³ [18].

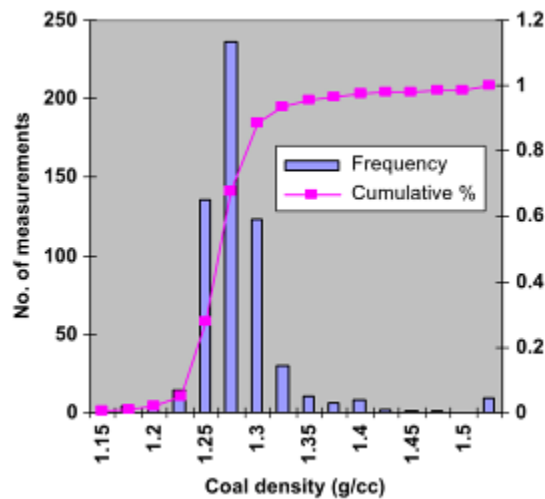


Figure 2.4 Frequency diagram of the density of the 590 sub-bituminous cores collected in the Powder River Basin, Wyoming

Source: Coal and Coalbed Gas: Fueling the Future, 2013

Meanwhile, the study done by Tunio & Ismail (2014), which is the Effect of Coal Rank and Porosity on the Optimization of ECBM Recovery also mentioned the density of coals in Table 2.4 [19]:

Table 2.4 Density of coal at different rank modified from (Tunio & Ismail, 2014)

CBM Basin	Coal Rank / Quality	Coal Depth (ft)	Coal Density (g/cm ³)
San Juan (United States)	Sub-bituminous	4,112.8	1.43
Powder River (United States)	Sub-bituminous C	557.0	1.33
Qinshui (China)	Anthracite	457.2	1.60
Zonguldak (Turkey)	High-volatile A bituminous	1,788.0	1.54
Upper Silesian (Poland)	High-volatile bituminous	3,280.0	1.30

Next, a study conducted by Gentzis (2013) mentioned that the coal rank of sub-bituminous to high-volatile C/B bituminous rank which are found at depths from <2000 to 6000ft (610 – 1579m) also have different density [20].

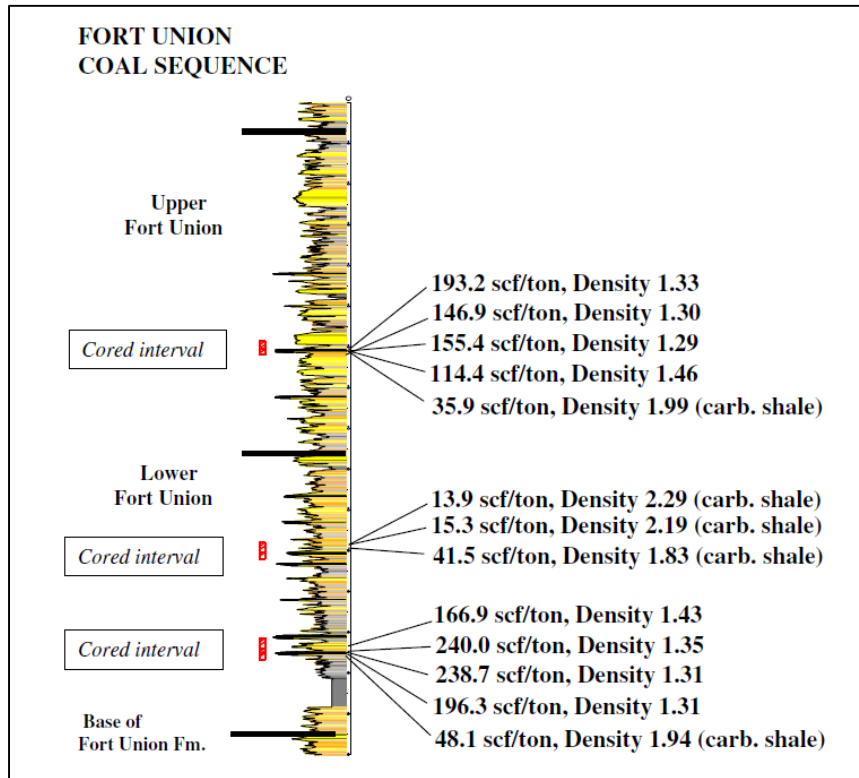


Figure 2.5 Density of coal of the Paleocene Fort Union coals in south-central Wyoming, USA

Source: Coalbed Methane Potential of the Paleocene Fort Union Coals in South-Central Wyoming, USA, International Journal of Coal Geology 108, 2013

CHAPTER 3

METHODOLOGY

3.1 Project Activities

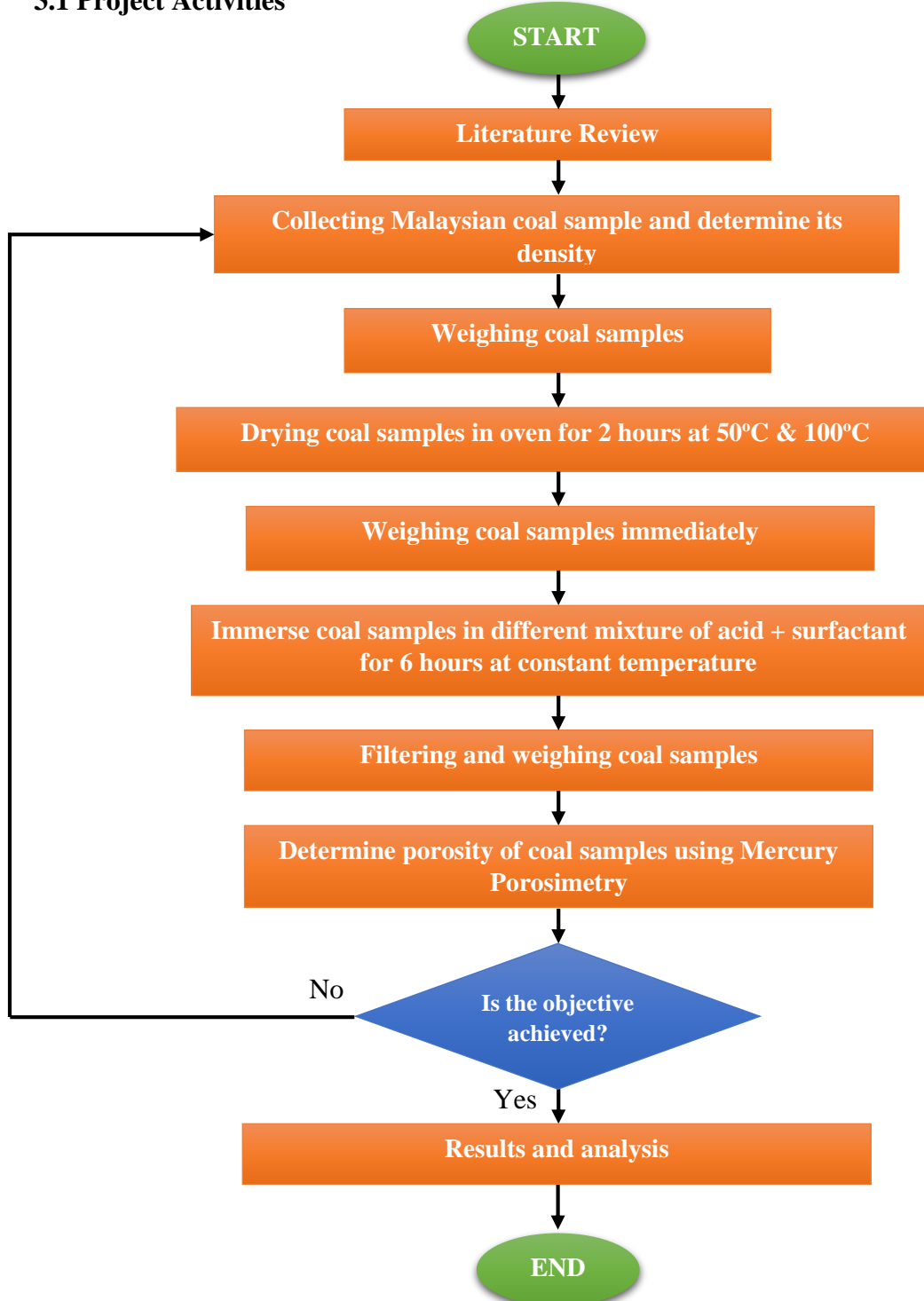


Figure 3.1 Steps in carrying out the project

Methodology of this project involved in conducting an experiment by using chemicals to study their effects on Malaysian Coal for CBM study. Three different acids and surfactant are used to stimulate the coal samples separately. The results of this experiment will be observed and recorded.

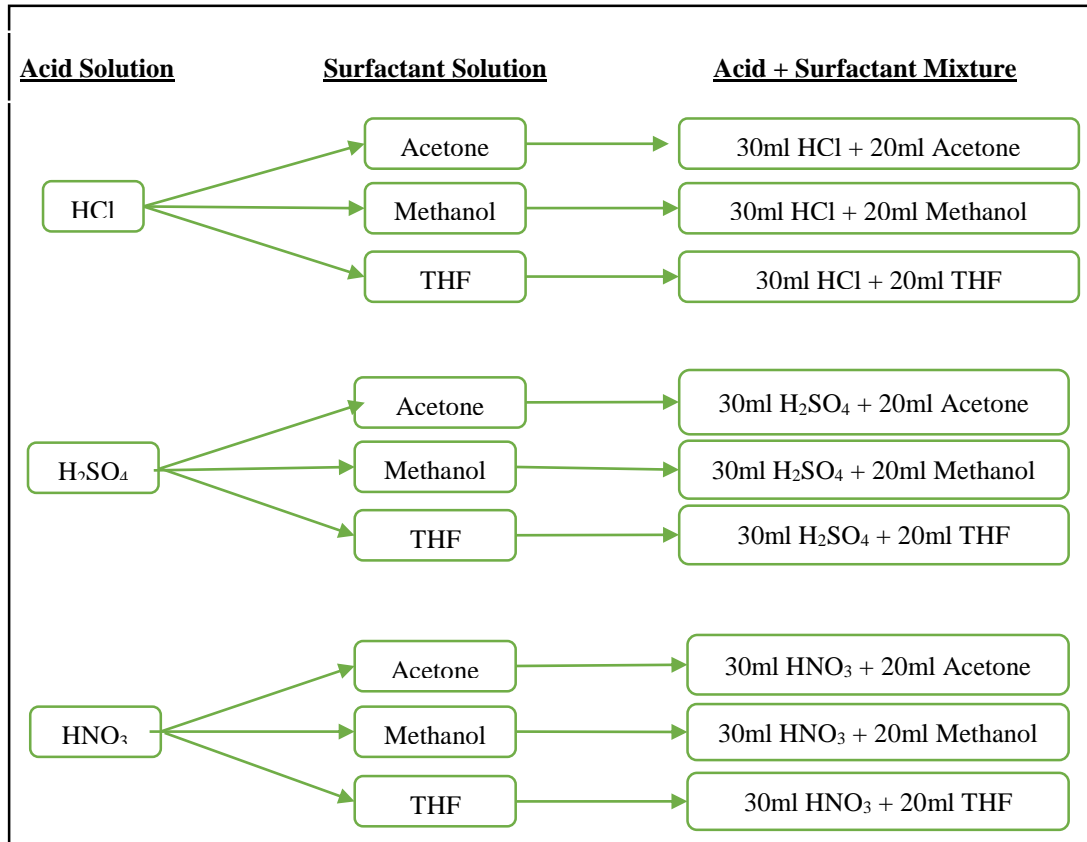


Figure 3.2 Mixture of Acid and Surfactant Solution

Based on Figure 3.2 above, three (3) acids and three (3) surfactants are mixed together. A total of nine (9) 50ml solutions will be used to immerse coal samples inside them.

3.1.1 Experimental Procedure for Density Measurement

Step 1: Prepare three (3) small size of coal samples in range of 2.60g to 3.00g.

Step 2: Pour 50cm³ of water into the beaker / measuring cylinder, or making sure there is enough to cover the coal sample completely.

Step 3: Measure the weight of the coal sample (Sample 1).

Step 4: Immerse one of the coal samples in the water.

Step 5: Measure the volume of water being displaced.

Step 6: Measure the density of the coal sample by using below formula [21]:

$$\rho_{Mdry} = \frac{\text{Mass of the Dry Coal Sample}}{\text{Volume of Water being Displaced}} \quad (\text{Equation 2})$$

Step7: Tabulate all results in Table 3.1 below.

Step 8: Repeat the process (Step 3 until Step 5) with the other two (2) coal samples and take the average value.

Table 3.1 Example of Table Result for Density Measurement

Sample No.	Weight of Dry Coal, g	Initial Volume of Water, ml	Volume of water being displaced, ml	Density of the Coal, g/ml
1				
2				
3				

3.1.2 Experimental Procedure for Porosity Measurement

Step 1: Prepare nine (9) small size of coal samples in range of 2.60g to 3.00g.

Step 2: All of the coal samples are weighed using weighing scale. Record their weight.

Step 3: Heat all of the coal samples in the oven at 100°C for two (2) hours.

Step 4: Prepare 9 measuring cylinders with different solution (Refer to Figure 3.2).

Step 5: After two hours, take out the coal samples from the oven and directly weighing them to obtain their dry weight accurately.

Step 6: Immerse all of the coal samples into their respective solution for 6 hours at room temperature.

Step 7: After 6 hours, take out all the coal samples from the measuring cylinder using tong and wipe them using filter paper.

Step 8: Weigh the wet coal samples using weighing scale and record the value. Tabulate all the data into the table below.

Table 3.2 Example of Table Result for Porosity Measurement

Sample No.	Weight of Coal before heating, g	Dry Weight / Weight after Heating, g	Type of Solution (Acid + Surfactant)	Volume of Acid, ml	Volume of Surfactant, ml	Wet Weight, g	Porosity of Coal Sample, %

Step 9: Analyze the result.

Step 10: Repeat the experiment from Step (1) until Step (9) for temperature at 50°C.

3.1.3 Experimental Procedure for Porosity Measurement by using Mercury Porosimetry Equipment

Step 1: Take all the samples from the previous experiment.

Step 2: Dry them for one day.

Step 3: Take Sample 1 (without injection of acid and surfactant) and put in the equipment.

Step 4: Handle the flow of mercury into the sample with care as it is dangerous.

Step 5: After about 3 hours in the equipment, the sample is taken out and the result is obtained from the computer interface.

Step 6: Repeat Step 3 until Step 5 for next coal sample.

Step 7: Record and tabulate the measurement data.

Step 8: Analyze the result from the equipment.

3.2 Key Milestone

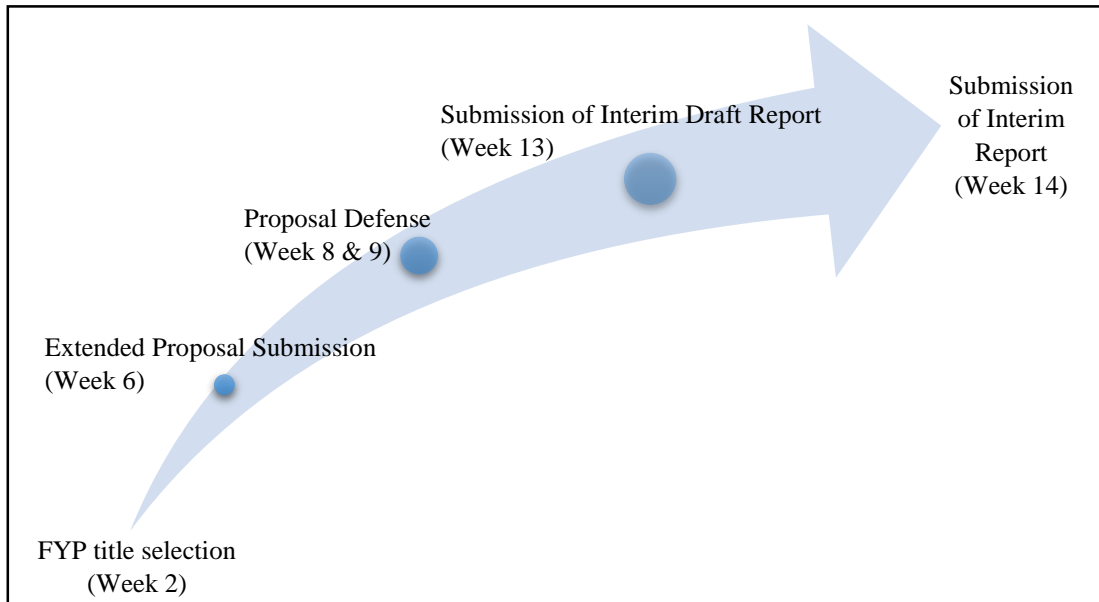


Figure 3.3 The key milestones of the FYP I

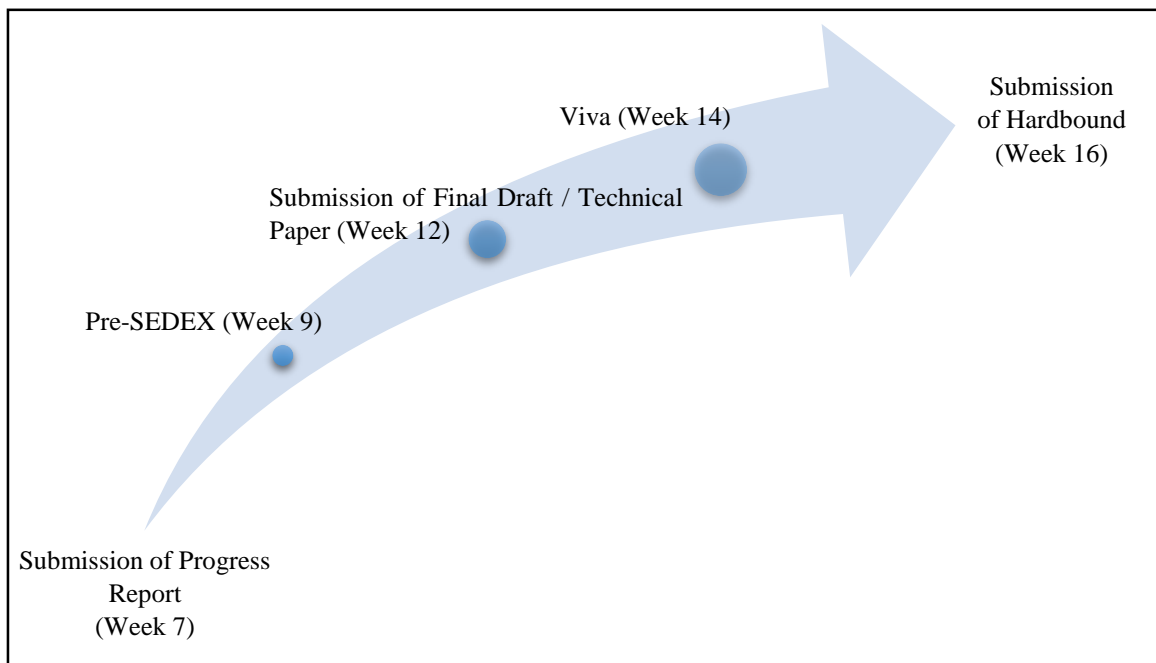


Figure 3.4 The key milestones of the FYP II

3.3 Tools, Software, Apparatus & Materials Required

The main tools and software required to complete this project are as follows:

Table 3.3 List of tools, software, apparatus and materials required to complete the project

Tool/Apparatus	Function
Hammer	To crush coal samples into finer sizes
Weighing Scale	To weight the coal samples
Oven	To dry the coal sample at 50°C and 100°C
Mercury Porosimetry	To measure the porosity of the coal samples
Filter Paper	To filter coal samples from the acid and surfactant solution
Measuring Cylinder	Used to stirred and mixing liquid
Software	Function
Microsoft Office	The software is used to record all data regarding the project as well as the documentation
Microsoft Power Point	The software is used to prepare for the presentation along the project
Materials	
1. Coal Samples	
2. Acid Solution (Hydrochloric Acid, Sulfuric Acid & Nitric Acid)	
3. Surfactant (Acetone, Methanol & Tertahydrofuran)	

CHAPTER 4

RESULTS & DISCUSSION

4.1 Experiment 1: Density Measurement

Before proceeding with porosity calculation, the density of coal must be determined first. For density measurement experiment, it is conducted by using Archimedes' principle. From equation (2), density of coal can be measured by calculating the two important parameters, mass of the coal and volume of the coal. Below is how the experiment is conducted:

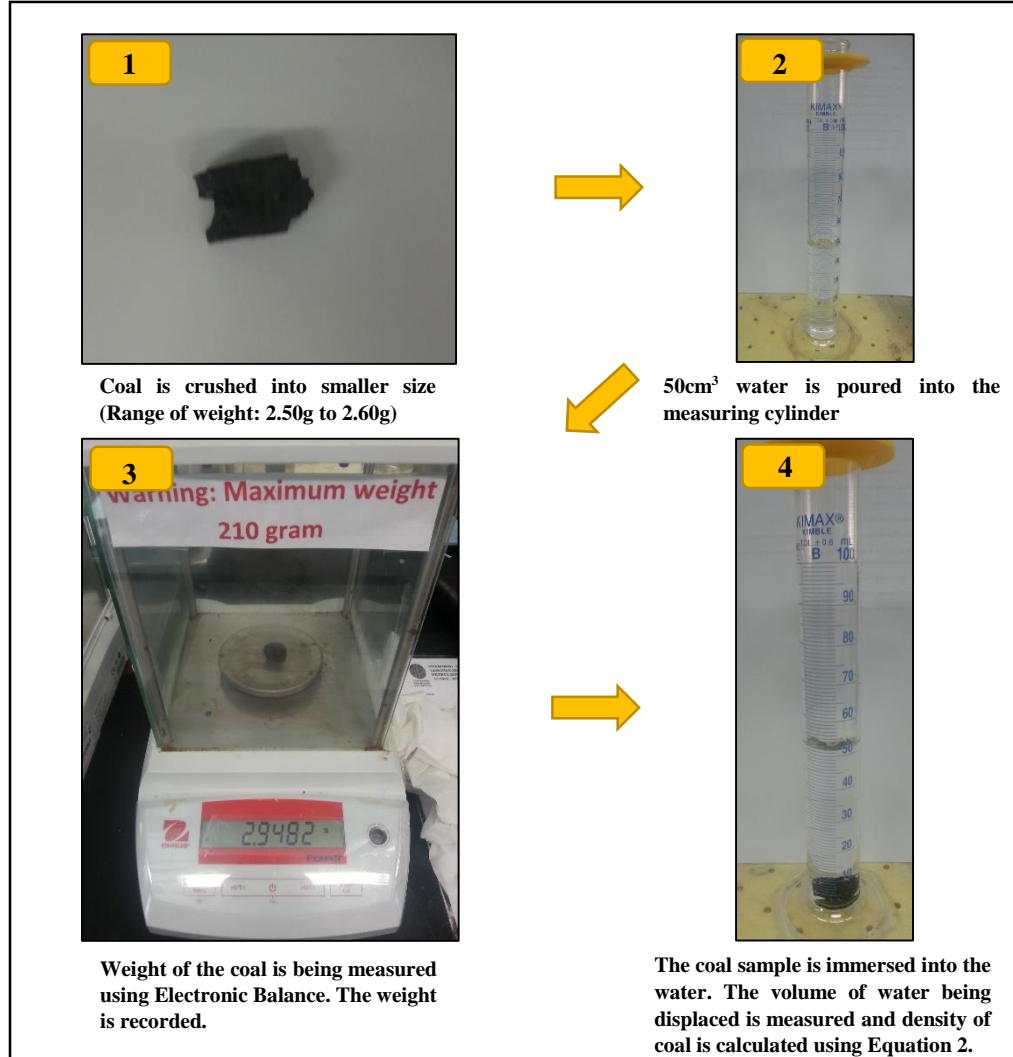


Figure 4.1 The experimental procedure for density measurement experiment

Next, below is the result of the experiment:

Table 4.1 Calculation for Density of Coal

Sample No.	Weight of Dry Coal, g	Initial Volume of Water, cm ³	Volume of Water Being Displaced, cm ³	Density of the Coal, g/cm ³
1	2.9482	50	2.7	1.09
2	2.9299	50	2.6	1.13
3	2.9480	50	2.7	1.10
			Average Density of the Coal	1.11

Below is the example of the calculation for the coal's density:

Sample 1

By using Equation 2 in the previous section;

$$\begin{aligned}\rho_{coal} &= \frac{2.9482g}{2.7cm^3} \\ &= 1.09g/cm^3\end{aligned}$$

Hence, the average of the coal is:

$$\begin{aligned}\text{Average Density of the Coal, } \rho_{coal} &= \frac{(1.09 + 1.13 + 1.10)g/cm^3}{3} \\ &= 1.11 g/cm^3\end{aligned}$$

From the result above (Table 4.1), the average of the density of the Mukah's Sub-bituminous coal is 1.11 g/cm³. The result for this experiment complies with the result as stated by Kopp (2014) where he mentioned that coal usually has density of 1.1 g/cm³ to 1.5 g/cm³, depending on its rank [18]. Although Kopp, Tunio & Ismail (2014) and Gentzis (2013) emphasize that the density of Sub-bituminous coal is in between 1.25 g/cm³ to 1.50 g/cm³ in their studies, this differences is caused by the geological factor [18][19][20]. A study conducted by S. Shu-xun et al. (2009) shows that geologic

control is one of the critical factors which controls productivity of CBM well. Researchers analyzed that the difference of the porosity, permeability and adsorption capacity of the coal in research area are affected by geologic structure and tectonic stress field. These are the main affecting factors that affect productivity of the CBM well [22].

Therefore, it is concluded that the density of Mukah's Sub-bituminous coal is 1.11 g/cm³.

4.2 Experiment 2: Porosity Measurement

After the density of the coal is measured, the project is continued by investigating the effects of acids and surfactant towards Malaysian coal. One of the parameters being investigated is the coal's porosity. Porosity measurement experiment is conducted by using the below materials:

1. Sub-bituminous coal sample from Mukah Field, Sarawak
2. 300ml Hydrochloric Acid Solution (wt 37%)
3. 300ml Sulfuric Acid Solution (wt 95% - 97%)
4. 300ml Nitric Acid Solution (wt 69%)
5. 200ml Acetone Solution
6. 200ml Methanol Solution
7. 200ml Tetrahydrofuran Solution

Next, below is the procedure in conducting this experiment:

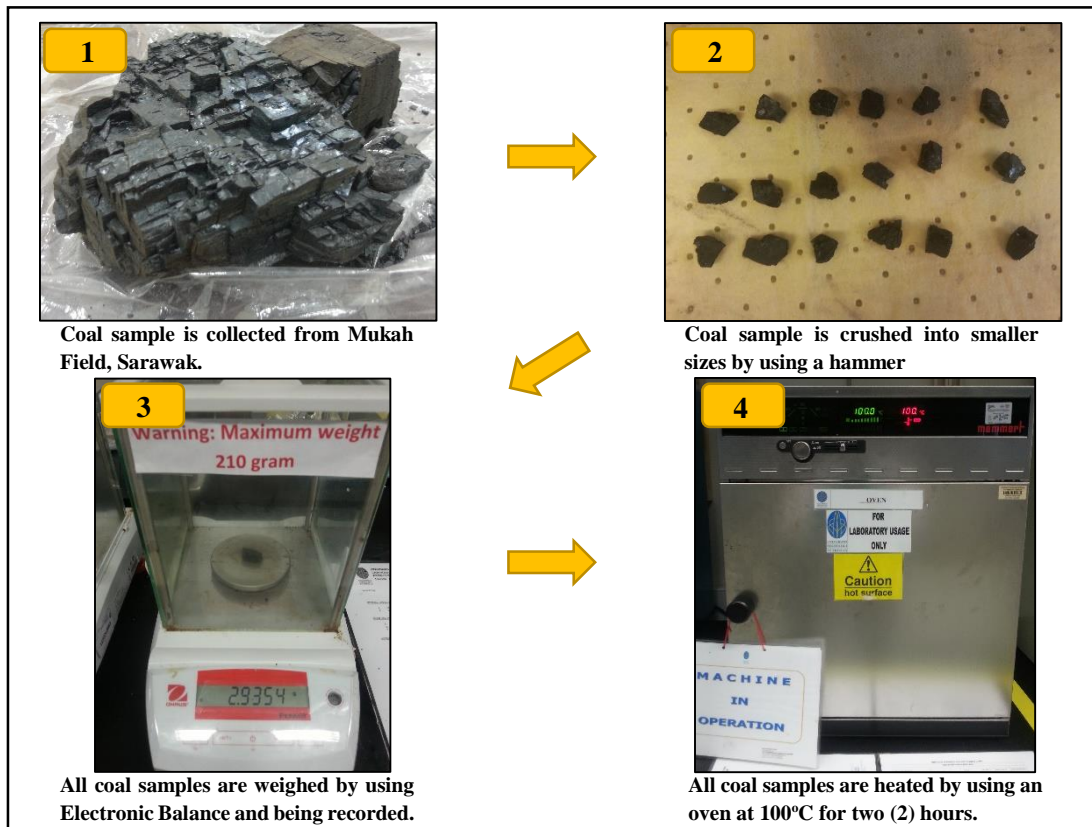


Figure 4.2a The experimental procedure for porosity measurement experiment (Part a)

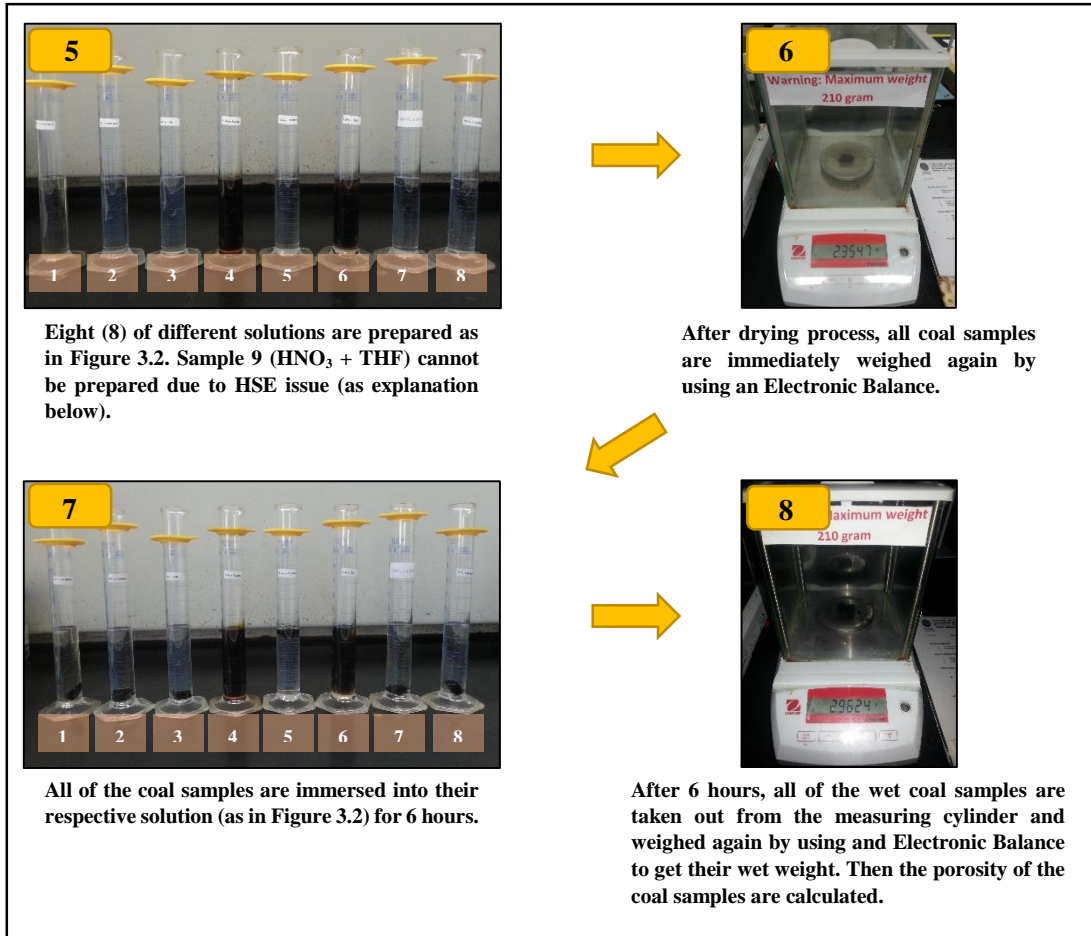


Figure 4.2b The experimental procedure for porosity measurement experiment (Part b)

The porosity measurement of the coal samples can be calculated by using the below formula [23]:

$$Porosity(\%) = \frac{\rho_{Mdry} (M_{Wet} - M_{dry})}{\rho_{Mdry} (M_{Wet} - M_{dry}) + \rho_w \times M_{Dry}} \times 100\% \quad (\text{Equation 3})$$

Where;

ρ_w = Density of acid and surfactant mixture, g/cm³

- Hydrochloric Acid (wt 37%) = 1.190 g/cm³
- Sulfuric Acid (wt 95% - 97%) = 1.840 g/cm³
- Nitric Acid (wt 69%) = 1.410 g/cm³

Source: <http://www.merckmillipore.com>

- Acetone = 0.791 g/cm³
- Methanol = 0.7918 g/cm³
- Tetrahydrofuran = 0.889 g/cm³

Source: <https://pubchem.ncbi.nlm.nih.gov/>

Meanwhile, the density of acid and surfactant mixture is calculated by using the below formula [24]:

$$\rho_w = \frac{1}{\left(\frac{X_a}{\rho_a} + \frac{X_b}{\rho_b} \right)} \quad (\text{Equation 4})$$

Next, the mass fraction of the acid and surfactant can be calculated by using the below formula [24]:

$$X_a = X_b = \frac{m_i}{m_{total}} \quad (\text{Equation 5})$$

Due to Health, Safety and Environment (HSE) issue, only eight (8) samples were prepared. The mixture of HNO_3 and THF produced a vigorous reaction thus cause the chemicals to spill out from the measuring cylinder (Figure 4.3). Table 4.2 and Table 4.3 below shows the porosity results for drying coal samples at 100°C and 50°C respectively.

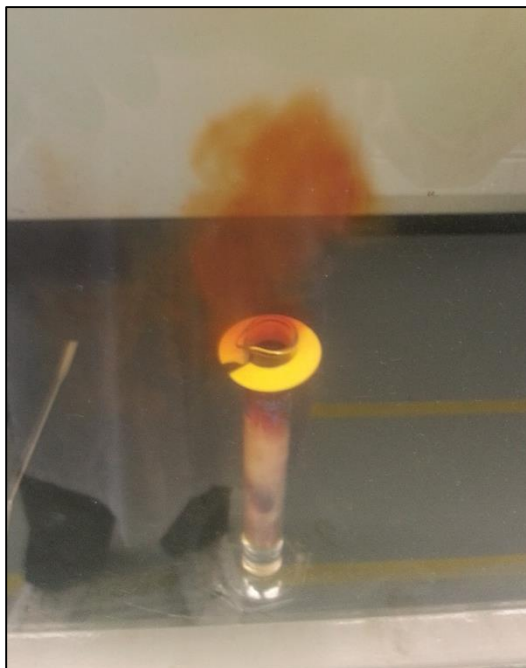


Figure 4.3 Shows that the mixture of HNO_3 with THF produces a vigorous reaction

Table 4.2 Results for drying coal samples at 100°C

Sample No.	Weight of Coal before heating, g	Dry Weight / Weight after Heating, g	Type of Solution (Acid + Surfactant)	Volume of Acid, ml	Volume of Surfactant, ml	Density of Solution, g/cm³	Wet Weight, g	Porosity, %
1	2.9301	2.3547	HCl + Acetone	30	20	0.99	2.9624	22.44
2	2.9816	2.3598	HCl + Methanol	30	20	0.99	3.0941	25.85
3	2.9390	2.5017	HCl + THF	30	20	1.05	3.4231	28.06
4	2.9695	2.4218	H ₂ SO ₄ + Acetone	30	20	1.20	2.9626	17.09
5	2.9515	2.3106	H ₂ SO ₄ + Methanol	30	20	1.20	3.1957	26.11
6	2.8994	2.2975	H ₂ SO ₄ + THF	30	20	1.29	2.5436	8.45
7	2.9317	2.5713	HNO ₃ + Acetone	30	20	1.07	Dissolve	N/A
8	2.9209	2.3493	HNO ₃ + Methanol	30	20	1.07	4.7196	51.04
9	N/A	N/A	HNO ₃ + THF	30	20	1.14	N/A	N/A

*Note that 1cm³ = 1ml

*Note that for Sample 7, N/A is Non Applicable because result cannot be obtained due to the coal sample that was immersed in the mixture of HNO₃ and Acetone is dissolved

*Note that for Sample 9, N/A is Non Applicable because the experiment cannot be conducted due to a reaction that was taken place when HNO₃ mixed with THF

Table 4.3 Result for drying coal samples at 50°C

Sample No.	Weight of Coal before heating, g	Dry Weight / Weight after Heating, g	Type of Solution (Acid + Surfactant)	Volume of Acid, ml	Volume of Surfactant, ml	Density of Solution, g/cm³	Wet Weight, g	Porosity, %
1	2.7293	2.4042	HCl + Acetone	30	20	0.99	2.9502	20.29
2	2.7143	2.4239	HCl + Methanol	30	20	0.99	2.9626	19.94
3	2.6068	2.3102	HCl + THF	30	20	1.05	2.9405	22.42
4	2.9030	2.5454	H ₂ SO ₄ + Acetone	30	20	1.20	2.7679	7.47
5	2.6478	2.4024	H ₂ SO ₄ + Methanol	30	20	1.20	4.1907	40.72
6	2.9845	2.7073	H ₂ SO ₄ + THF	30	20	1.29	3.0269	9.23
7	2.6783	2.4128	HNO ₃ + Acetone	30	20	1.07	Dissolve	N/A
8	2.9413	2.6610	HNO ₃ + Methanol	30	20	1.07	4.1711	36.96
9	N/A	N/A	HNO ₃ + THF	30	20	1.14	N/A	N/A

*Note that 1cm³ = 1ml

*Note that for Sample 7, N/A is Non Applicable because result cannot be obtained due to the coal sample that was immersed in the mixture of HNO₃ and Acetone is dissolved.

*Note that for Sample 9, N/A is Non Applicable because the experiment cannot be conducted due to a reaction that was taken place when HNO₃ mixed with THF

From the results in Table 4.2 and Table 4.3, the graphs of Weight of Coal after being taken out from the Solutions vs Type of Solutions were plotted for both of the temperatures, 100°C and 50°C.

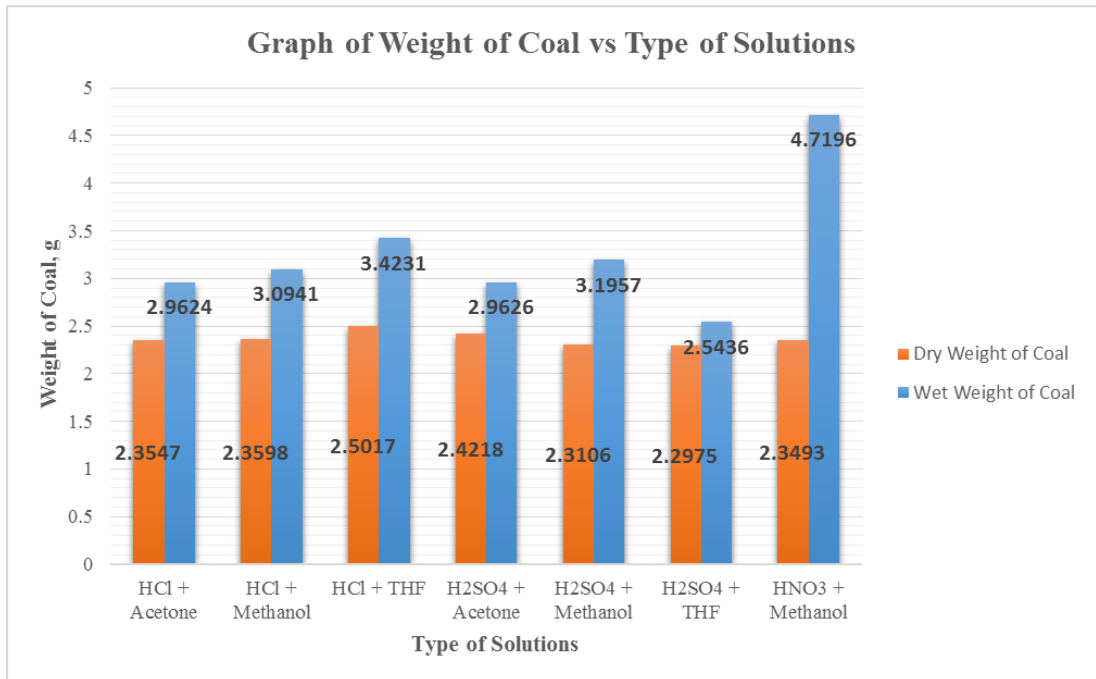


Figure 4.4 Graph of Weight of Coal after being taken out from the Solutions vs Type of Solutions (at 100°C)

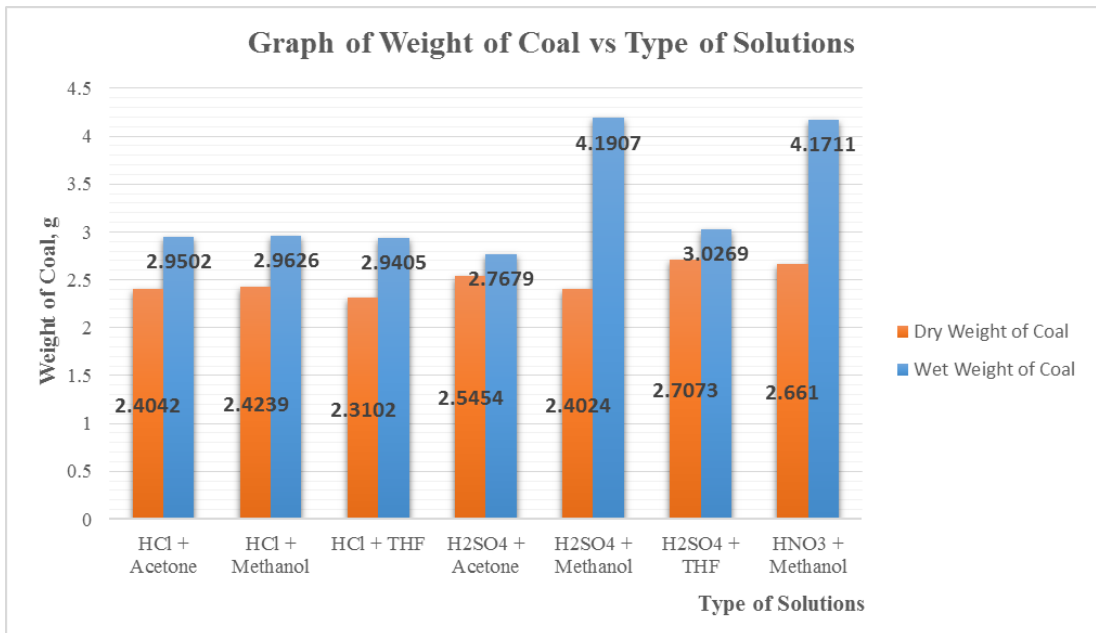


Figure 4.5 Graph of Weight of Coal after taken out from the Solutions vs Type of Solutions (at 50°C)

Figure 4.4 and Figure 4.5 show the graph of Weight of Coal vs Type of Solutions. Two graph is plotted representing the dry weight of the coal and wet weight of coal. From the above graphs, the results showing that the weight of coal after being taken out from the solutions are increased.

Figure 4.4 shows that at 100°C, the coal that was immersed in Sample 3 (HCl + THF), Sample 5 (H₂SO₄ + Methanol) and Sample 8 (HNO₃ + Methanol) were able to adsorb the solution greatly. This is because, weight of the samples taken out from these (3) samples are heavier compared to the weight of the samples taken out from other solutions at 100°C. It means that the coal samples that have been stimulated by the solution of HCl + THF, H₂SO₄ + Methanol and HNO₃ + Methanol have better adsorption compared to coal samples that have been stimulated by other mixtures of acids and surfactants.

Meanwhile, at 50°C, the result is slightly different. The graph shows that the coal that was immersed in Sample 6 and Sample 8 are only able to adsorb the solution greatly compared to the coal dried at 100°C. Thus it proves that the temperature of the coal is an important parameter in this experiment.

As mentioned before, the first solution (Sample 9), HNO₃ and THF cannot be mixed together because a vigorous reaction took place immediately (Figure 4.3). Meanwhile, for the second solution (Sample 7), when a coal is immersed into the HNO₃ and Acetone solution, a reaction was taken place too.

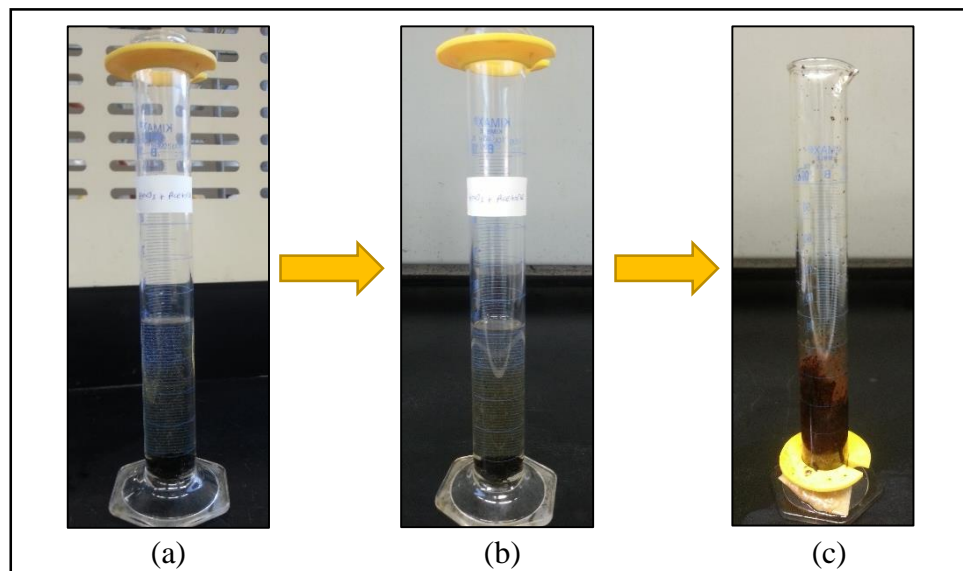


Figure 4.6 A reaction was taken place after a coal is immersed into the solution of HNO_3 and Acetone

As in Figure 4.6, Figure 4.6(a) shows that after a coal is immersed into the solution for 2 minutes, the bubbles are produced indicating that the coal is reacting with the solution. After 5 minutes, the solution changed colour into brownish as in Figure 4.6(b). After 30 minutes, Figure 4.6(c) shows that coal is reacting with the solution, causing the coal to dissolve completely. The experiment is repeated by immersing the coal samples (which was heated at 50°C) into the solutions. The results obtained for Sample 7 is same. The coal is dissolved completely in the solution of HNO_3 and Acetone after 30 minutes (Figure 4.7).



Figure 4.7 Mixture of coal and solution of HNO₃ and Acetone caused a reaction took place thus cause the coal to dissolve completely.

Based on a case study “Explosion at U. Maryland: Another Nitric Acid Oopsie”, two students were injured in an explosion + fire that was caused by the addition of nitric acid into a bottle with an organic reagent in it [25]. Bracher (2011) emphasized that whoever taught orgo lab must remind students not to mix HNO₃ with acetone or other oxidizable solvent. He added that the lab instructor should add a warning label at organic waste bottle stated that adding HNO₃ can cause bottle to explode [25].

These results can be seen clearly by calculating the percentage of adsorption capacity of coal at 100°C and 50°C. The percentage of adsorption capacity of coal can be calculated by using the below formula:

$$\text{Percentage of Adsorption Capacity of Coal, \%} = \frac{M_{Wet} - M_{Dry}}{M_{Wet} + M_{Dry}} \times 100\% \quad (\text{Equation 6})$$

Hence, the results are tabulated as follows:

Table 4.4 The results for the percentage of adsorption capacity of coal (at 100°C & 50°C)

No. of Sample	Type of Solution (Acid + Surfactant)	Percentage of Adsorption of Coal @ 100°C, %	Percentage of Adsorption of Coal @ 50°C, %
1	HCl + Acetone	11.43	10.20
2	HCl + Methanol	13.46	10.00
3	HCl + THF	15.55	12.00
4	H ₂ SO ₄ + Acetone	10.04	4.19
5	H ₂ SO ₄ + Methanol	16.07	27.12
6	H ₂ SO ₄ + THF	5.08	5.57
7	HNO ₃ + Acetone	Dissolve	Dissolve
8	HNO ₃ + Methanol	33.53	22.10
9	HNO ₃ + THF	N/A	N/A

*Note that N/A is Non Applicable because the experiment cannot be conducted due to a reaction that was taken place when HNO₃ mixed with THF

Table 4.4 shows that the percentage of adsorption of coal at 100°C is higher than the percentage of adsorption of coal at 50°C except for Sample 5 (H₂SO₄ + Methanol), Sample 6 (H₂SO₄ + THF) and Sample 8 (HNO₃ + Methanol). This may be due to the suitability of the solution with the temperature of the coal samples.

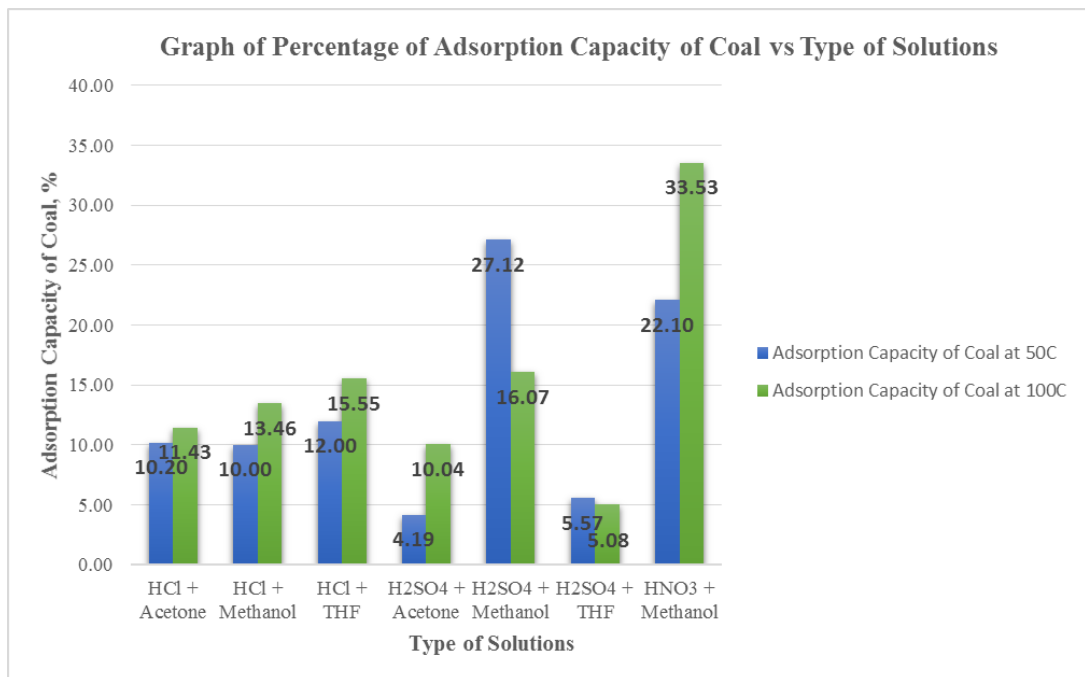


Figure 4.8 Graph of Adsorption Capacity of Coal vs Type of Solutions (at 100°C & 50°C)

Figure 4.8 above shows a comparison of the percentage of adsorption capacity of coal based on the results obtained. Sample 5 (H₂SO₄ + Methanol) and Sample 8 (HNO₃ + Methanol) have the highest adsorption by coal samples, followed by Sample 3 (HCl + THF) and others. In addition, it can be seen that Methanol is a good surfactant to be mixed with acid solutions as it results in better adsorption since the coal samples were increased greatly in term of weight after being immersed in different type of solutions.

For porosity measurement, below is the example of the calculation for porosity of coal drying at 100°C:

Sample 1 (HCl + Acetone)

$$\text{Mass Fraction of HCl, } X_{HCl} = \frac{m_i}{m_{total}} = \frac{0.30}{0.50} = 0.60$$

$$\text{Mass Fraction of Acetone, } X_{Acetone} = \frac{m_i}{m_{total}} = \frac{0.20}{0.50} = 0.40$$

$$\text{Density of the Solution, } \rho_w = \frac{1}{\frac{X_a}{\rho_a} + \frac{X_b}{\rho_b}} = \frac{1}{\frac{0.60}{1.190} + \frac{0.40}{0.791}} = 0.99 \text{ g/cm}^3$$

$$\begin{aligned} \text{Porosity (\%)} &= \frac{1.11(2.8273 - 2.3547)}{1.11(2.8273 - 2.3547) + (0.99 \times 2.3547)} \times 100 \\ &= 18.37\% \end{aligned}$$

Sample 5 (H₂SO₄ + Methanol)

Since the volume of acid and surfactant being used in this experiment are same which are 30ml and 20ml respectively, the mass fraction of acid and surfactant are also same (0.60 and 0.40 respectively). Hence;

$$\begin{aligned} \text{Density of the Solution, } \rho_w &= \frac{1}{\frac{0.60}{1.840} + \frac{0.40}{0.7918}} \\ &= 1.20 \text{ g/cm}^3 \end{aligned}$$

$$\begin{aligned} \text{Porosity (\%)} &= \frac{1.11(3.1957 - 2.3106)}{1.11(3.1957 - 2.3106) + (1.20 \times 2.3106)} \times 100 \\ &= 26.11\% \end{aligned}$$

Sample 8 (HNO₃ + Methanol)

$$\begin{aligned} \text{Density of the Solution, } \rho_w &= \frac{1}{\frac{0.60}{1.410} + \frac{0.40}{0.7918}} \\ &= 1.07 \text{ g/cm}^3 \end{aligned}$$

$$\begin{aligned} \text{Porosity (\%)} &= \frac{1.11(4.7196 - 2.3493)}{1.11(4.7196 - 2.3493) + (1.07 \times 2.3493)} \times 100 \\ &= 51.04\% \end{aligned}$$

Meanwhile, below is the porosity value for a coal sample without injection of the mixture of acid and surfactant.

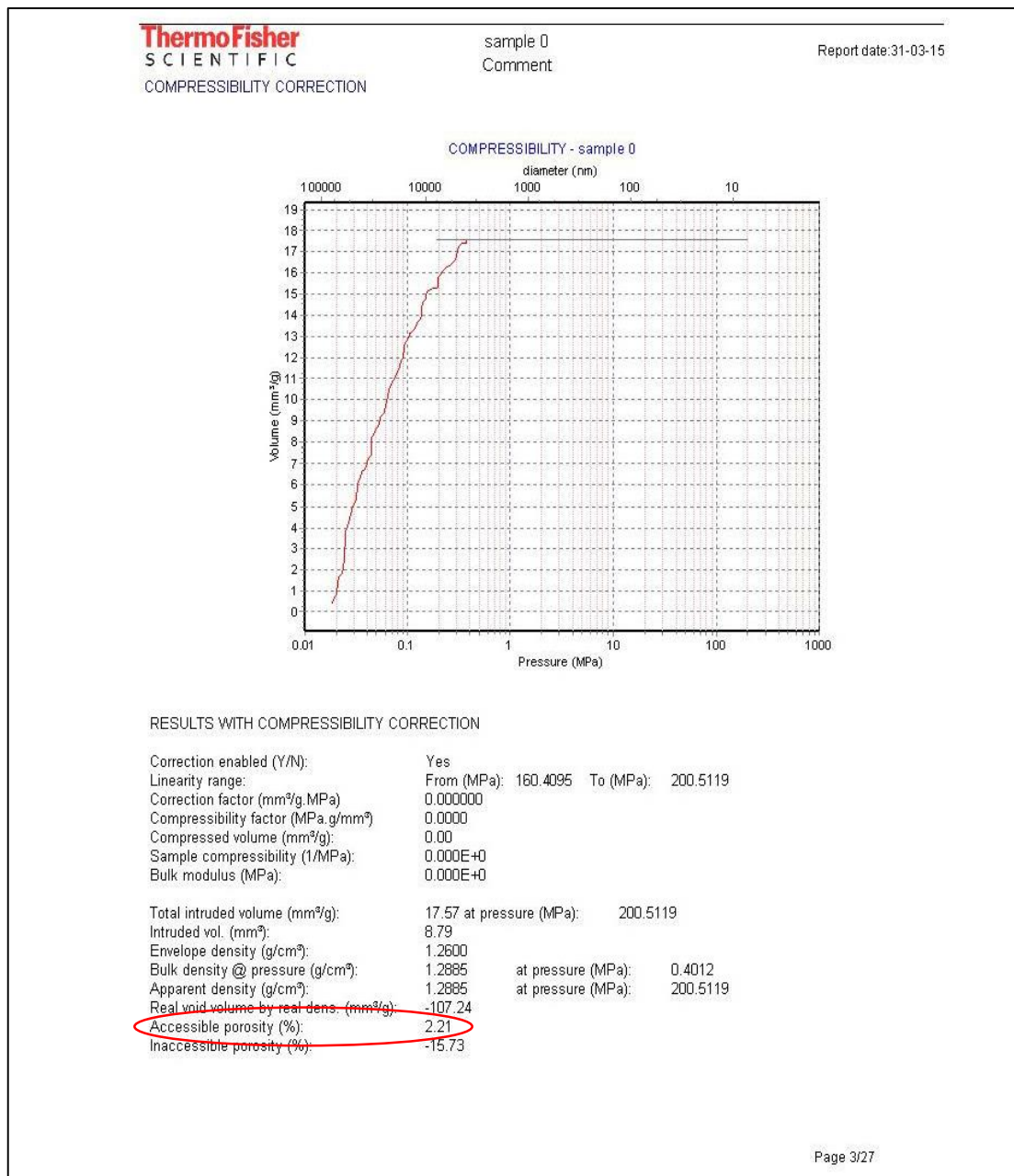


Figure 4.9 Porosity value for a coal sample without injection of the mixture of acid and surfactant

Based on the figure above, the coal sample has porosity value of 2.21% without injection of acid and surfactant.

From the results in Table 4.2 and Table 4.3, the graph of Porosity of Coal vs Type of Solution for coal samples dried at 100°C and 50°C is plotted.

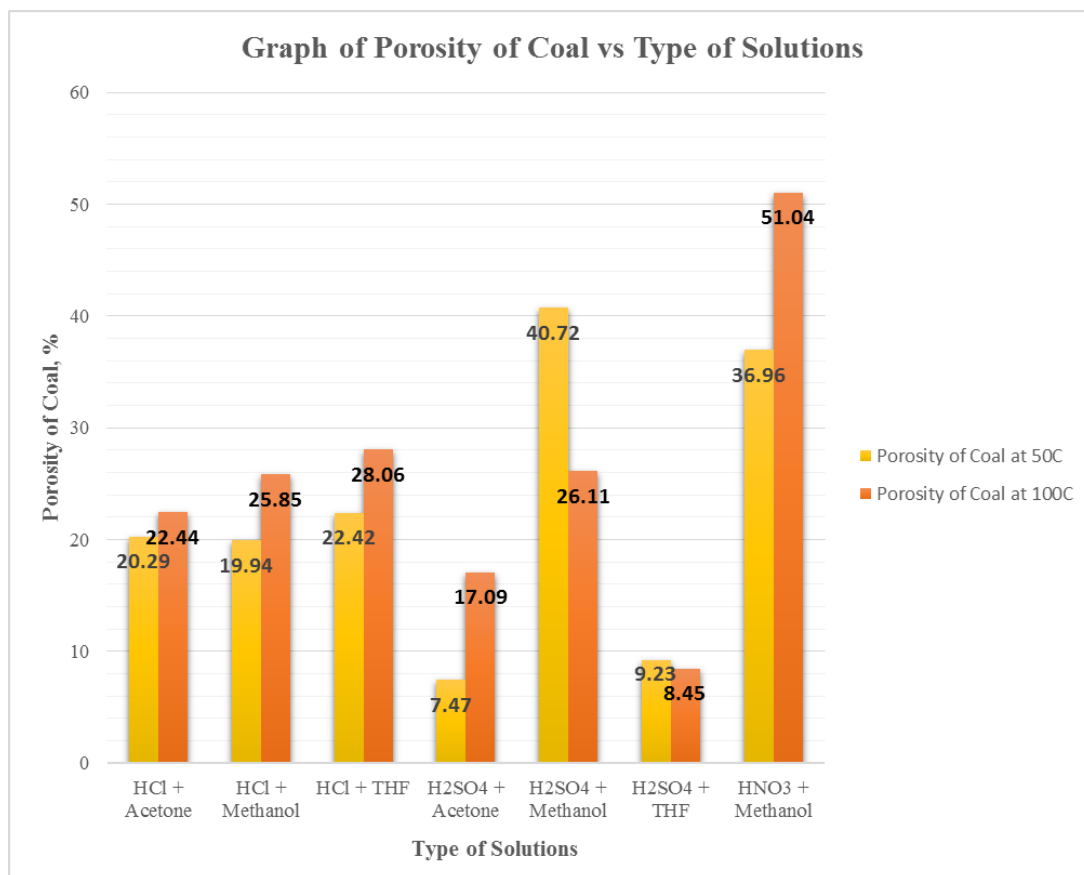


Figure 4.10 Graph of Porosity of Coal vs Type of Solutions (at 50°C & 100°C)

Based on the results obtained in Figure 4.9 and Figure 4.10, it can be seen that the mixtures of acid and surfactant are able to alter the porosity of the coal samples.

From Figure 4.10, at 50°C, Sample 5 (H₂SO₄ + Methanol) gave the best results on porosity percentage, followed by Sample 8 (HNO₃ + Methanol), Sample 3 (HCl + THF) and others. Meanwhile, Sample 4 (H₂SO₄ + Acetone) showed the lowest performance to alter the porosity of coal samples at 50°C.

On the other hand, at 100°C, coal samples that have been stimulated by the mixture of HCl + THF (Sample 3), H₂SO₄ + Methanol (Sample 5) and HNO₃ + Methanol (Sample 8) show better result on porosity percentage. Between these samples, Sample 6 (H₂SO₄ + THF) show the lowest performance to alter the porosity of the coal samples.

Comparing the results in both conditions (drying coal sample at 100°C and 50°C), it can be seen that the results obtained depend on the suitability of the mixture of acid and surfactant with the temperature. Most of the coal samples that have been dried at 100°C able to give the better increment on the porosity percentage. But at 50°C, coal samples that have been immersed in the solution of H₂SO₄ + Methanol (Sample 5) and H₂SO₄ + THF (Sample 6) gave encouraging results compared to coal samples that have been dried at 100°C.

From the analysis made, it can be concluded that, the higher percentage of porosity can be obtained by drying the coal samples at higher temperature. However it also depends on the type of the acids and surfactants used. For the mixture of HCl with surfactants, the mixture of HCl with THF gave the best porosity percentage for both of the temperatures. Meanwhile, for the mixture of H₂SO₄ with surfactants, the mixture of H₂SO₄ with Methanol for both temperatures are able to give the better increment on the porosity percentage. Last but not least, an encouraging result is obtained for the mixture of HNO₃ with methanol for both of the temperature.

Thus it can be concluded here that the mixture of HCl with THF and H₂SO₄ with Methanol are good candidates to be used for stimulation in coal formation having temperature of 100°C and 50°C respectively. Although the mixture of HNO₃ with Methanol gave high porosity value, it is better to avoid using HNO₃ with surfactant considering the HSE issue.

4.3 Porosity Measurement by using Mercury Porosimetry Equipment

After analyzing the porosity measurement by using manual calculation, this project proceed with the measurement of porosity by using Mercury Porosimetry equipment. As mentioned before, the porosity value of the coal sample without injection of acid and surfactant is 2.21% (Figure 4.9). Below are the results of the other coal samples.

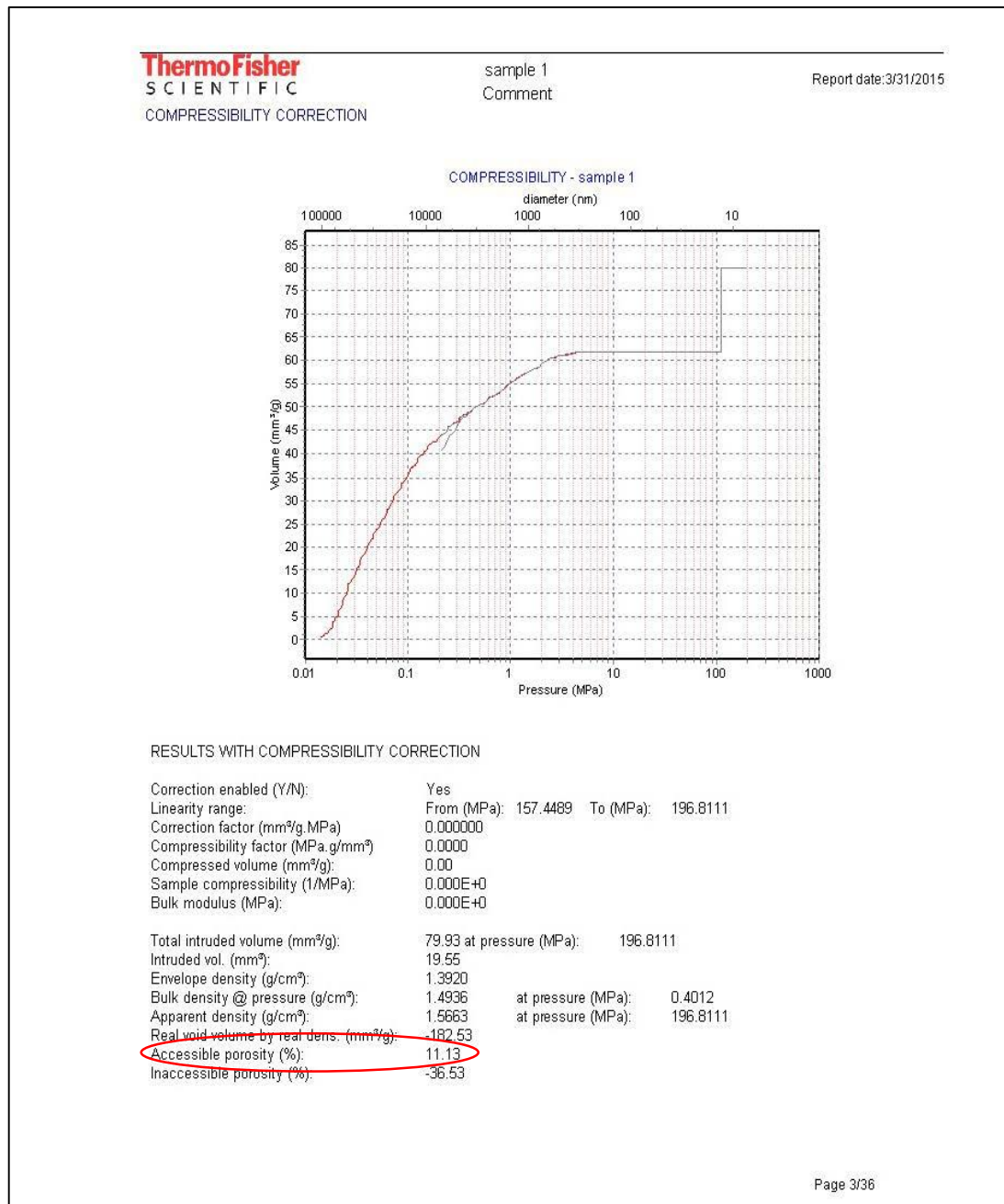
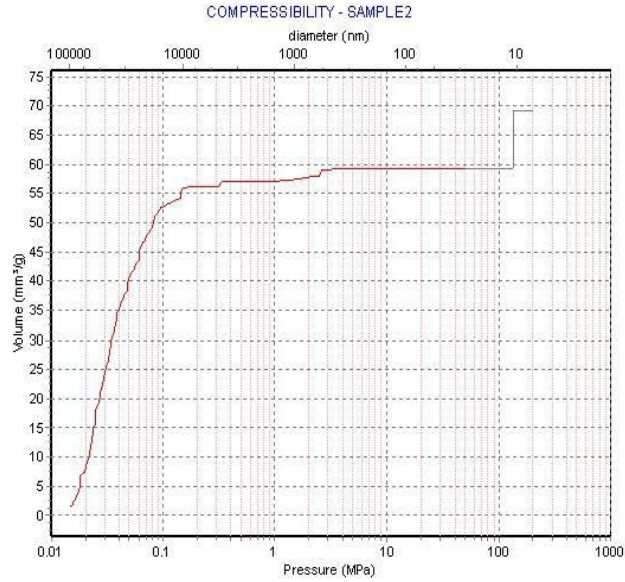


Figure 4.11 Porosity value for a coal sample with injection of HCl and Acetone

COMPRESSIBILITY CORRECTION

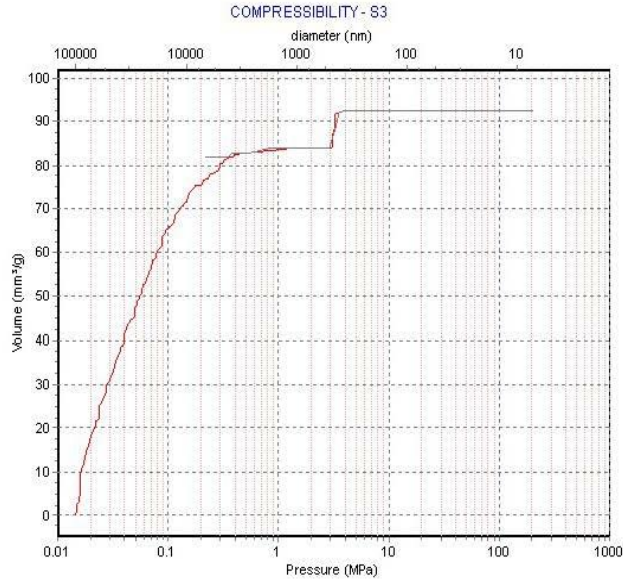


RESULTS WITH COMPRESSIBILITY CORRECTION

Correction enabled (Y/N):	Yes		
Linearity range:	From (MPa): 160.4901	To (MPa): 200.6126	
Correction factor (mm³/g.MPa)	0.000000		
Compressibility factor (MPa.g/mm³)	0.0000		
Compressed volume (mm³/g):	0.00		
Sample compressibility (1/MPa):	0.000E+0		
Bulk modulus (MPa):	0.000E+0		
Total intruded volume (mm³/g):	69.08	at pressure (MPa):	200.6126
Intruded vol. (mm³):	11.40		
Envelope density (g/cm³):	1.1391		
Bulk density @ pressure (g/cm³):	1.2182	at pressure (MPa):	0.4012
Apparent density (g/cm³):	1.2364	at pressure (MPa):	200.6126
Real void volume by real dens. (mm³/g):	-7.10		
Accessible porosity (%):	7.87		
Inaccessible porosity (%):	-8.68		

Figure 4.12 Porosity value for a coal sample with injection of HCl and Methanol

COMPRESSIBILITY CORRECTION

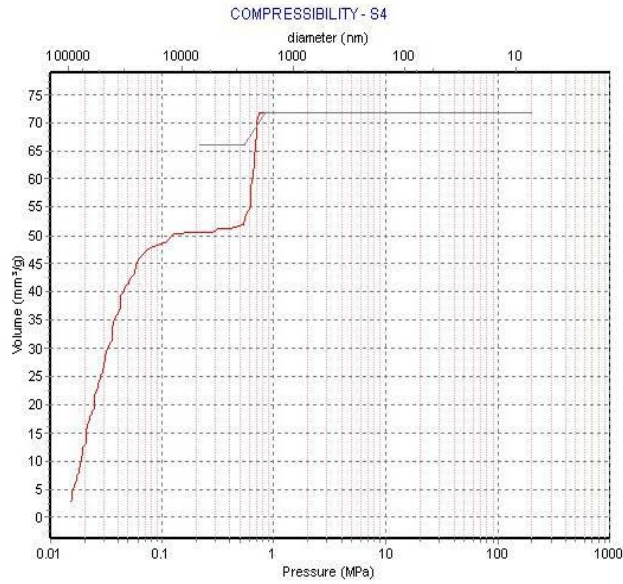


RESULTS WITH COMPRESSIBILITY CORRECTION

Correction enabled (Y/N):	Yes		
Linearity range:	From (MPa):	160.7302	To (MPa): 200.9127
Correction factor (mm³/g.MPa)	0.000000		
Compressibility factor (MPa.g/mm³)	0.0000		
Compressed volume (mm³/g):	0.00		
Sample compressibility (1/MPa):	0.000E+0		
Bulk modulus (MPa):	0.000E+0		
Total intruded volume (mm³/g):	92.41 at pressure (MPa):		200.9127
Intruded vol. (mm³):	16.47		
Envelope density (g/cm³):	1.5110		
Bulk density @ pressure (g/cm³):	1.7258	at pressure (MPa):	0.4012
Apparent density (g/cm³):	1.7562	at pressure (MPa):	200.9127
Real void volume by real dens. (mm³/g):	-299.09		
Accessible porosity (%):	13.96		
Inaccessible porosity (%):	-50.09		

Figure 4.13 Porosity value for a coal sample with injection of HCl and THF

COMPRESSIBILITY CORRECTION

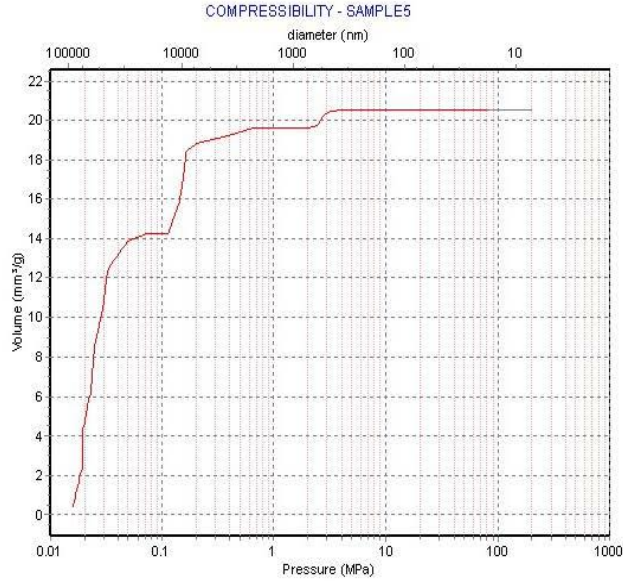


RESULTS WITH COMPRESSIBILITY CORRECTION

Correction enabled (Y/N):	Yes		
Linearity range:	From (MPa):	160.8097	To (MPa): 201.0121
Correction factor (mm³/g.MPa)	0.000000		
Compressibility factor (MPa.g/mm³)	0.0000		
Compressed volume (mm³/g):	0.00		
Sample compressibility (1/MPa):	0.000E+0		
Bulk modulus (MPa):	0.000E+0		
Total intruded volume (mm³/g):	71.84 at pressure (MPa):	201.0121	
Intruded vol. (mm³):	9.75		
Envelope density (g/cm³):	1.5913		
Bulk density @ pressure (g/cm³):	1.7328	at pressure (MPa):	0.4012
Apparent density (g/cm³):	1.7966	at pressure (MPa):	201.0121
Real void volume by real dens. (mm³/g):	-272.47		
Accessible porosity (%):	11.43		
Inaccessible porosity (%):	-54.79		

Figure 4.14 Porosity value for a coal sample with injection of H₂SO₄ and Acetone

COMPRESSIBILITY CORRECTION

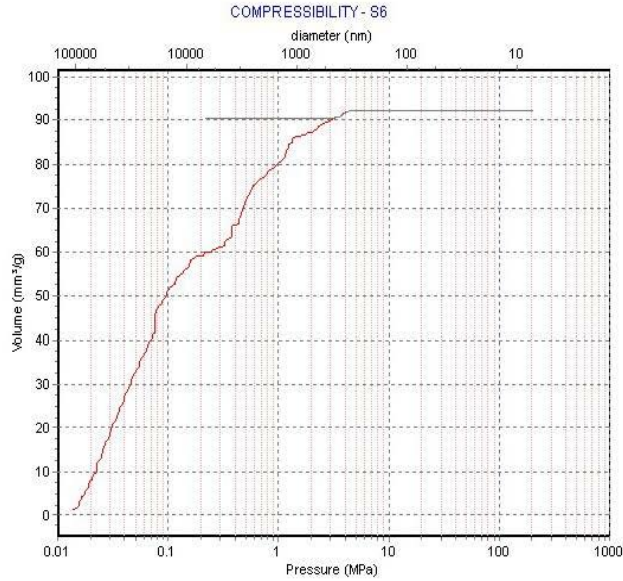


RESULTS WITH COMPRESSIBILITY CORRECTION

Correction enabled (Y/N):	Yes		
Linearity range:	From (MPa):	160.4893	To (MPa): 200.6116
Correction factor (mm³/g.MPa)	0.000000		
Compressibility factor (MPa.g/mm³)	0.0000		
Compressed volume (mm³/g):	0.00		
Sample compressibility (1/MPa):	0.000E+0		
Bulk modulus (MPa):	0.000E+0		
Total intruded volume (mm³/g):	20.53 at pressure (MPa): 200.6116		
Intruded vol. (mm³):	5.01		
Envelope density (g/cm³):	1.3119		
Bulk density @ pressure (g/cm³):	1.3459	at pressure (MPa):	0.4012
Apparent density (g/cm³):	1.3482	at pressure (MPa):	200.6116
Real void volume by real dens. (mm³/g):	-138.64		
Accessible porosity (%):	2.69		
Inaccessible porosity (%):	-20.88		

Figure 4.15 Porosity value for a coal sample with injection of H₂SO₄ and THF

COMPRESSIBILITY CORRECTION



RESULTS WITH COMPRESSIBILITY CORRECTION

Correction enabled (Y/N):	Yes		
Linearity range:	From (MPa):	160.4895	To (MPa): 200.6119
Correction factor (mm³/g.MPa)	0.000000		
Compressibility factor (MPa.g/mm³)	0.0000		
Compressed volume (mm³/g):	0.00		
Sample compressibility (1/MPa):	0.000E+0		
Bulk modulus (MPa):	0.000E+0		
Total intruded volume (mm³/g):	92.22 at pressure (MPa): 200.6119		
Intruded vol. (mm³):	18.49		
Envelope density (g/cm³):	1.3508		
Bulk density @ pressure (g/cm³):	1.4831	at pressure (MPa):	0.4012
Apparent density (g/cm³):	1.5430	at pressure (MPa):	200.6119
Real void volume by real dens. (mm³/g):	-160.60		
Accessible porosity (%):	12.46		
Inaccessible porosity (%):	-34.15		

Figure 4.16 Porosity value for a coal sample with injection of HNO₃ and Methanol

From the figures above, the graph of porosity value using Mercury Porosimetry equipment can be plotted.

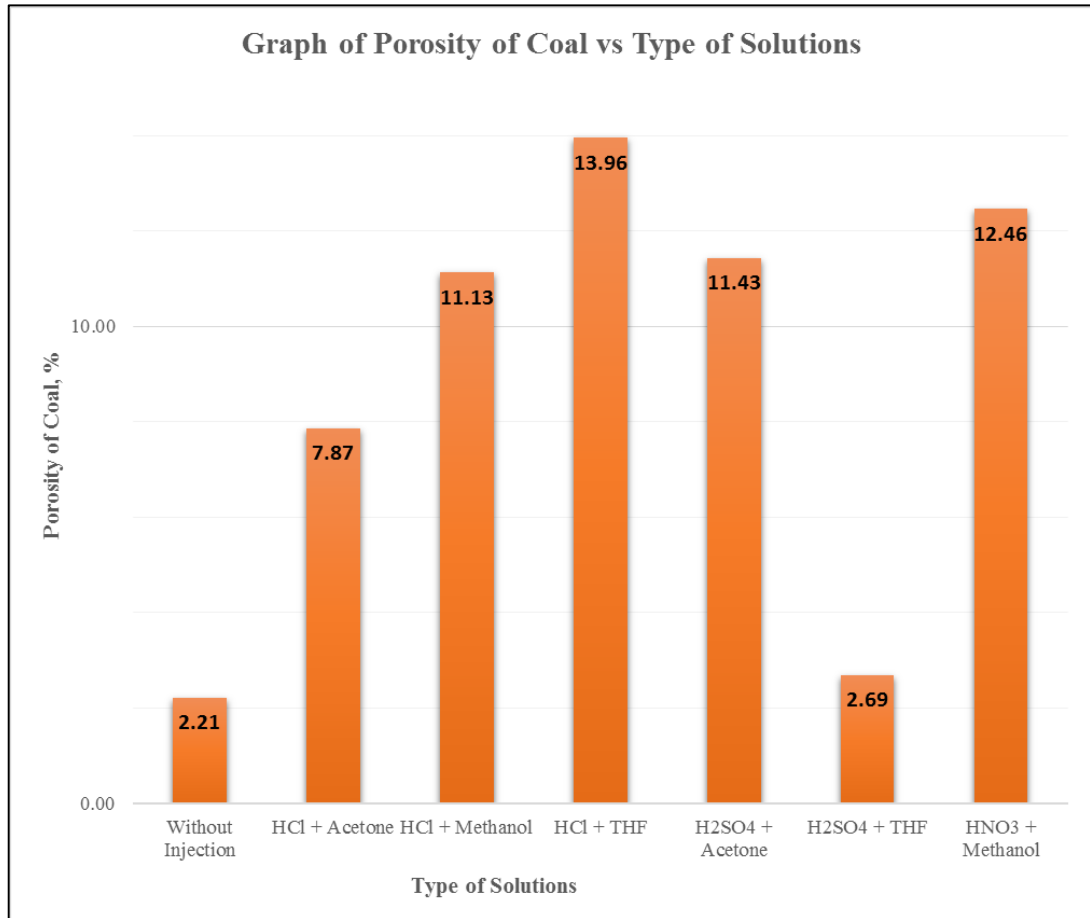


Figure 4.17 Graph of Porosity of Coal vs Type of Solutions (using Mercury Porosimetry)

However, an error is occurred when determining the porosity for coal sample that was immersed in the mixture of H₂SO₄ and Methanol. From Figure 4.17, it can be observed that the different porosity values are obtained by using the Mercury Porosimetry equipment. But it can be seen that the porosity values for this experiment are lower compared to the previous experiment. This is may be due to the effects of acid and surfactant towards the coal became weaker. It can concluded that the mixture of HCl and THF is the best candidate when determining by using mercury porosimetry.

CHAPTER 5

CONCLUSION & RECOMMENDATION

This research is focused to investigate the reaction of coal samples with different mixtures of acid and surfactant can result in higher porosity at two different temperature. From the first experiment, it is proved that the density of the Mukah's sub-bituminous coal is 1.11 g/cm^3 . It can be seen when the coal samples were immersed in the solutions. The coal samples sunk when being immersed the mixture of acid and surfactant having density ranging 0.99 to 1.07 g/cm^3 but floated when being immersed in the mixtures having density of 1.20 g/cm^3 .

For the next experiment, the results were analyzed based on the porosity calculation. It is proved that the use of the mixtures of acid and surfactant can result in higher coal's porosity at higher temperature but it also depends on the type of the mixture itself. For the last experiment, all of the coal samples were able to increase in porosity. However, an error had occurred when running the coal sample that was immersed in mixture of H_2SO_4 and Methanol in the equipment. Based on the analysis made from both experiment, the mixture of Hydrochloric Acid with Tetrahydrofuran and the mixture of Sulfuric Acid with Methanol can be concluded as the best candidates for acid stimulation in coal formation having temperature of 100°C and 50°C respectively.

Although the mixture of Nitric Acid with Methanol can result in higher porosity, it is recommended to avoid using the mixture as stimulating agent for coal formation due to HSE issue. It is recommended to study the compatibility and concentration of acid and surfactant first before carrying out the experiment. Last but not least, increasing porosity does not automatically increasing the permeability. Hence a further detail study can be done by taking porosity and permeability parameters into account.

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