CERTIFICATION OF APPROVAL

Study on the Effect of Coal Drying in Adsorbing CO_2, CH_4 and N_2 at different Temperature and pH

by

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Approved by,

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CERTIFICATION OF ORIGINALITY

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

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ABSTRACT

Carbon Dioxide (CO_2) sequestration has become one of the attractive approaches to mitigate the high concentration of Carbon Dioxide in the atmosphere. CO_2 sequestration is the process where CO_2 is injected onto selected geological storage such as ocean, deep saline reservoirs, depleted oil and gas reservoir and sequestration in coal seams. However, this research will be focused on the sequestration in coal seams. The research has several objectives to be achieved. The objectives are to study on the reliability of this process to be implemented and to determine the suitable environment for the CO_2 adsorption to occur effectively. Then the research continues to recognize on the potential for CO_2 sequestration to be implemented in Malaysia. For this research, the scope has been narrowed to study on the effect of CO_2 adsorption onto coal in different temperature, pH and particle size. Then the scope moves to study on the coal adsorption preferential towards different types of gas which are CH_4 and CO_2. The coal used here is sub-bituminous. For the temperature variation, the temperatures are chosen from 30°C, 40°C, 50°C and 60°C. For pH variation, the pH is chosen between 2.4, 6.2 and 12 while for particle size variation, the sizes are 250μm and 1000μm. The experiment setup is done in low constant pressure. The adsorption is monitored based on either two observations, one is through the reduction of pressure in the closed coal sample cell and the other is to compare on the peak area ratio yielded by the Gas Chromatograph. From the experiments conducted, the following results are obtained. For temperature variation, the adsorption is low in higher temperature where it shows that relatively can cause the incomplete filled coal seams and time wasted for the coal to cool if the surrounding temperature is too high. For vary in pH, acidic coal (low pH) is preferable than neutral coal and base coal (high pH) for the adsorption to take place. This can further study on considering co-sequestering of acid gasses which technically can increase pore capacity. Between two different particle sizes, the adsorption is higher in the smaller particle size. For vary in type of gas, it shows that CO_2 has the highest adsorption onto coal compared to CH_4. This can be concluded where it can help to reduce cost by having CH_4 as the by product (sell or recycled energy) in the condition where the coal do adsorp CO_2 and let released CH_4 as the byproduct of the process.

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NOMENCLATURE

P	Pressure of the Cell (Pa)
V	Volume of the Cell (m^3)
N	Number of moles of gas in the cell (moles)
R	Universal Gas Constant = 8.314 kJ/ (kmol.K)
T	Temperature of the Cell (°C)
Z	Compressibility factor for Sample Gas
ΔP	Reduction of Pressure in the Cell (Pa)
P_o	Initial Pressure at t=0 (Pa)
P_i	Pressure at t=I (Pa)
i	time (min)
$-\Delta H_a$	Infinitesimal enthalpy change (kJ/kmol)
dH/dn	Infinitesimal enthalpy change (kJ/kmol)
dn	moles adsorbed is reduced (moles)
Mt	Unit of Production (metric tonne)
DM1	Digital Manometer (1)
DM2	Digital Manometer (2)
V1	Valve 1
V2	Valve 2
V3	Valve 3

ABBREVIATION

CH_4	Methane
CO_2	Carbon Dioxide
GHG	Greenhouse gas
HCl	Hydrochloric acid
NaOH	Sodium Hydroxide
He	Helium
EOS	Equation of State
GC	Gas Chromatography
O_2	Oxygen
K	Equilibrium Constant

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Excess of CO_2 emission to the atmosphere has been a major problem to the world today including Malaysia. CO_2 is one of the Greenhouse Gas that needs to be controlled. The concern is that this gas can lead to the global warming effect. This effect will cause a number of serious worldwide problems, including ozone depletion and desertification.

Other gaseous categorize in Greenhouse Gas include methane (CH_4), nitrous oxide (N_20), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and sulphur hexafluoride (SF_6). In Malaysia the main sources of CO_2 emission are motor vehicles, power stations, industrial fuel burning and processes, domestic fuel burning and the burning of municipal and industrial waste. Of the total emissions, CO_2 makes up 67.5% of the total, methane 32.4% and nitrous oxide 0.1% [17]

Malaysia's pollution problems have not been as severe as those of other Asian countries. However, as the urbanization and the industrialization become more intensified, the situation is going to be worsen unless there is high consideration is given to the incorporation of air pollution control measures. The government recognizes that it must pay particular attention to environmental management issues if Malaysia is to become a fully developed nation by 2020 and avoid severe industrial pollution.

Thus, Malaysia has done various solutions in order to control the rate of pollution emitted. One of them is to control the deforestation which is now in the implementation stage together with the cooperation from other countries. However, it does not control the emission of CO_2 that is already released by sources such as industrial sectors for instance. Thus this research proposes to reduce the amount of CO_2 by looking from totally different aspect which is to recycle the excess gas. This is also known as to restore CO_2 into a suitable storage and reduce the amount of CO_2 even more. CO_2 that has been focused here is absolutely the excess of CO_2 produced massively – the remaining gas from the stage of CO_2 utilization.

Storage of CO_2 is a new field to be explored [19]. This is called as the geological strategies to be considered to mitigate the increasing atmospheric concentration of CO_2. There are many kind of storages that theoretically practical to be implemented. Some of them are in the stage of trial and error to determine the possibility for them to be implemented widely. The storages mentioned here are ocean, deep saline reservoirs, depleted oil and gas reservoir and sequestration in coal seams. Among these storages, this research will be focused on the sequestration in coal seams. Sequestration in coal seam is easy to describe as the carbon dioxide injection and retention in coal. It applies the principle of adsorption between gas (CO_2) and solid (coal).

Coal is a combustible, sedimentary, organic rock formed from ancient vegetation, which has been consolidated between other rock strata and transformed by the combined effects of microbial action, pressure and heat over a considerable time period. This process is referred to as 'coalification'. Layered between other sedimentary rocks, coal is found in seams ranging from less than a millimeter in thickness to many meters. Coal is composed mainly of carbon (50-98%), hydrogen (3-13%) and oxygen, and smaller amounts of nitrogen, sulphur and other elements. It also contains a little water and grains of inorganic matter that remain as a residue known as ash when coal is burnt.

Coal has subsequently undergone changes in molecular physical structures during the transition where it becomes harder and more mature. Because of this, it can be divided into four major ranks: anthracite coal, bituminous coal, sub bituminous coal and lignite coal. Anthracite coal is coal of the highest metamorphic rank and it is known as 'hard' coal and has brilliant luster. Bituminous coal can be indicated by referring to the smoky flame when it burns and may contain 15-20wt% of volatile matter. Sub bituminous coal on the other hand is not as high on the metamorphic scale as bituminous and has often been called 'black lignite'. Lignite is the coal of the lowest metamorphic scale, vary in colour from brown to brown-black and have lower carbon content and higher moisture content than sub bituminous.

As for the gasses in coal seams, they exist either as free gas in cracks and fractures or is adsorbed on the internal surface of the microspores. The hydrocarbon type of gas is called as coal seam gas (CSG). Therefore coal seam gas can be defined as a naturally hydrocarbon compound that is formed as a by-product of the coal formation process. During this process, various hydrocarbons such as methane are released. Physically and chemically, coal seam gas is indistinguishable from conventional natural gas. The level of coal seams gas generated by and retained within the coal however depends on a number of factors including the rank of the coal.

TABLE 1.1: Coal Seam Gas potential for different rank of coal

Coal Rank	CSG potential
Anthracite coals	Low to zero
Bituminous coals	Moderate to high
Sub-bituminous	Moderate
Lignite	Zero to low

Based on the information above, this research touches on the possible for it to be implemented in Malaysia. The potential area in Malaysia is the unminable coal which is the coal in ex-mining coal areas. In Malaysia, the ex-mining coal areas is always been developed as the tourism place, for example, the ex-mining coal area in Tanjung Kubang, Labuan ,Batu Arang, Selangor and Bintulu, Sarawak. In Sabah, several areas with coal potential are now known, Maliau, Malibau, Silimpopon and Labuan (**TABLE 1.2**) while in Sarawak, coals are scattered around active areas such as Mukah, Sri Aman, Kapit and Sibu. The coal resource in Maliau and Malibau has been found to be suitable for future coal mining area. All of these areas can potentially become the suitable area to implement CO_2 Sequestration.

TABLE 1.2: Areas with coal potential, Sabah [18]

Area	Reserves (Metric tonne)	Quality
Maliau	215	High volatile bituminous
Malibau	44	High volatile bituminous
Silimpopon	14	Sub-bituminous
Labuan	9	Sub-bituminous
Total	282	

Basically, the overall process of CO_2 sequestration can involves several stages – identifying the sources of CO_2 release, capturing it and ready to be store. Referring to Figure 1.1, initially the solutions to reduce the amount of CO_2 are more focused on how to utilize the gas and how to improve the current system of CO_2 release. However, for the process of storing the CO_2, it needs to undergo the same steps undergone by the first two solutions.

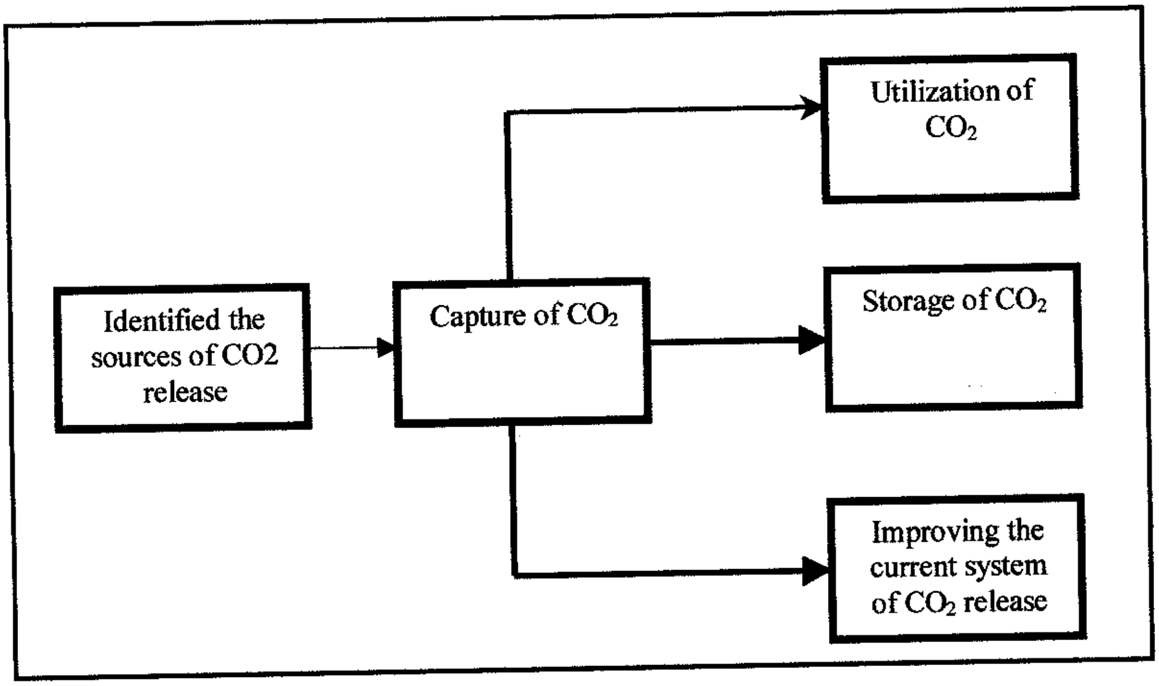

FIGURE 1.1: General Approach of Excess CO_2 Reduction in Atmosphere

1.2 PROBLEM STATEMENT

In order to determine the reliability of this process to be implemented here, there is a need to study on the adsorption characteristic of CO_2 onto coal with different parameters. Coal to be utilized here is the unminable coal. Since it is located underground thus the temperature involved here is the underground temperature. Underground temperatures tend to be constant overtime but increase with depth provided that there are no external influences. Furthermore, the adsorption itself is an exothermic which will provide a heat source. Realizing on these facts, thus it is important to know how temperature will affect the CO_2 adsorption onto the coal.

Water may exist in the coal because of the external physical operation such as drilling or the deposition of a combustion gas that may contain residual water of combustion. Existence of water is understood to affect the chemical property of the coal itself as it creates aqueous phase. The present aqueous phase will vary in composition according to its source and the nature of the coal bed and the surrounding minerals with which it is in contact. In other word the coal can be in acidic form or alkali form. Therefore there is a need to investigate whether it affects the CO_2 adsorption capacity of coals and how much extent it will be.

Pressure plays one of the main roles in implementing the sequestration process effectively. The adsorption can be significantly related to the external pressure implies. In addition the underground pressure may affect the ability of the coal to adsorb CO_2, as the pressure tends to be increase with depth. Thus similar to the temperature, it is important to know how pressure will affect the CO_2 adsorption onto the coal. However the experiment to study on this parameter is not practical to be done in the lab since the apparatus are mostly glass made. This means the study will be focused on two parameters out of three, which are temperature and pH.

One of the coal characteristics that need to be aware of is the ability for it to rapidly and irreversibly adsorb atmospheric oxygen. Irreversibly means adsorbed oxygen cannot be desorbed back. This will affect the whole experiment as the concern here is to study on the extent of CO_2 adsorption by coal in different parameters – temperature and pH. There is a need to make sure that the coal is absolutely free from the adsorbed gas. Thus the efforts needed to maintain an oxygen free environment so that the measured coal properties reflect the activity of the virgin coal as closely as possible under laboratory condition.

The idea of the overall process is to recognize the sources of CO_2 releases such as from the power plants, chemical plants and other CO_2 related industries. Then CO_2 is captured and stored by injecting it onto coal. Technically, when it involves injecting the gas, the cost consumes will be very high as the process is going to manipulate on the gas pressure. Thus realizing on the possibility of the process to be very costly, therefore any opportunity that can help to reduce this process should be considered thoroughly.

6	**Project Work continue**										▓	▓	▓	▓							
	~ List of References / Literature										░	░	░	░							
	~ Lab Equipment and Apparatus																				
	~ Sample Preparation										░	░	░	░							
	~ Practical / Laboratory Work										░	░	░	░							
7	**Submission of Dissertation Draft**														●						
8	**Submission of Project Dissertation**																	●			
9	**Oral Presentation**																				●

●	Suggested milestone
▓ ░	Process

CHAPTER 2

LITERATURE REVIEW AND/OR THEORY

2.1 THE PURPOSE OF THE PROCESS

CO_2 Sequestration also known as CO_2 injection into the coal seams has been recognized as one of the possible methods to mitigate the increasing concentration of CO_2 in atmosphere. It has long been recognized that, although the gas in coal seams can exists as free gas in cracks and fractures, most of the gas in coal is adsorbed on the internal surface of the micropores [3]. One of the most important advantages of coal seam sequestration is that CO_2 is stored in coals in an adsorbed state that is expected to be stable for geologically significant periods [9]. The principle of this sequestration is mainly due to the action of gas adsorption to the coal, therefore CO_2 injection into the coal seam is fixed firmly [2]. The injection of CO_2 may also enhance the production of coal bed methane to generate revenue to help offset sequestration costs [9]. Or in other word, methane can be recovered as a by-product. The fact will reduce the cost of sequestration [2]. Of fundamental interest is how this capacity of adsorption may change with a changing sequestration environment in order to determine which coal seams would be good disposal sites and under what environmental conditions the sequestered CO_2 would remain stable.

2.2 METHOD OF EXPERIMENT

There are several methods of doing the experiment proposed by several literature reviews. The methods are almost similar with each other. The differences are only on the type of apparatus used, the type of coal and the non-adsorbed gas used. These methods have been studied and the modified procedure based on these methods has been proposed for this research that fit to the availability of the equipments provided in the laboratory.

(K.Schroeder et.al), on their study had implemented this method where it measures the pressure reduction as to indicate the extent of CO_2 adsorption on the sample coal. They has also mentioned on the pretreatment of the coal sample where to minimize surface oxidation, sample handling was performed in a He-flushed glove bag under a positive pressure of Helium and each sample was dried in-situ at 80°C under vacuum for 36 hr before the measurements were performed. Because coals rapidly and irreversibly adsorb atmospheric oxygen, efforts were devoted to maintaining an oxygen-free environment and ensured that the measured coal properties reflect the activity of the virgin coal as closely as possible under laboratory condition.

The apparatus consisted of a reservoir cell and a sample cell and both submerged within a temperature-controlled bath. They had identified the adsorption based on the pressure and temperature reading taken for each certain period. At equilibrium, the amounts of CO_2 within both the reference and sample cell were calculated using the real gas law and the Span and Wagner values for the gas compressibility. Using the change in pressure in the reference cell and accounting for the gas compressibility, the number of moles of gas transferred from the reference cell was calculated. Similarly, the number of gas-phase moles in the sample cell after the gas transfer was calculated from the post transfer sample-cell pressure. The missing moles of gas was accounted to the adsorption of CO_2 onto the coal

(Andreas Busch et.al) on the other hand had done a slightly different approach. They had conducted the volumetric gas adsorption experiments first to indicate the actual volume of the expanded gas. The procedure used for the experiment was quite similar to (K.Schroeder et.al). They had used the equation of state (EOS) to calculate the amount of substance (moles of gas) in the reference cell by computing from the pressure, the temperature and the volume of the cell.

(Andreas Busch et.al) has also suggested on the procedure for the adsorption measurements with methane/carbon dioxide mixtures. It requires an additional analysis step to determine the relative concentrations of the two compounds in the free (non-adsorbed) gas phase.

The corresponding experimental set-up was consisted of a flow-through measuring cell which is connected to a sample loop via a multiport valve. Free gas from the measuring cell was expanded into a previously evacuated sample loop. A small amount of this gas was then transferred to a gas chromatograph (GC) via a micro volume sampling valve and analyzed for its methane and CO_2 content by a thermal conductivity detector (TCD). In order to assess the source gas composition and to check for compositional fractionation effects due to gas transfer and expansion, blind experiments with an empty sample cell were conducted over the entire pressure range.

(K.Ohga et.al) offers the method by using the equipment consists of a reaction vessel to absorb gas on coal sample and a buffer tank to measure injection gas volume to the reactor. The injection gas volume into the reaction vessel and released gas were calculated from the change of the pressure in the buffer tank and absorption volume onto the coal sample was calculated from the change of the pressure in the reaction vessel. Coal sample was put into the reaction vessel. Released gas was analyzed by chromatography for every period.

2.3 RESULTS OBTAINED BY LITERATURE REVIEWS

The results from various literature reviews are presented in many ways. By knowing the results of each studied literature reviews, the output or result of the experiment can be determined to fit with the equipment used. The main purpose is that to have the comparison between the literature reviews and also between the results that obtained from the experiment. This will help to ensure that the results to be similar to the expectation. If not, the reasons or flaws of the research can be studied and discussed for further improvements. Below is the results obtained by previous conducted researches.

2.3.1 Effect of Temperature

(K.Schroeder et.al) had found that the effect of increasing temperature decreases the equilibrium adsorption capacity of the coal. They had made some justification on this finding. This was expected because higher temperatures increasingly favor the gas-phase due to the $T^{a}S$ entropy term in the free energy expression. This means deeper, warmer seams will adsorb less CO_2 at a given pressure than shallower, cooler ones. **FIGURE 2.1** shows the result obtained form the experiment they had conducted.

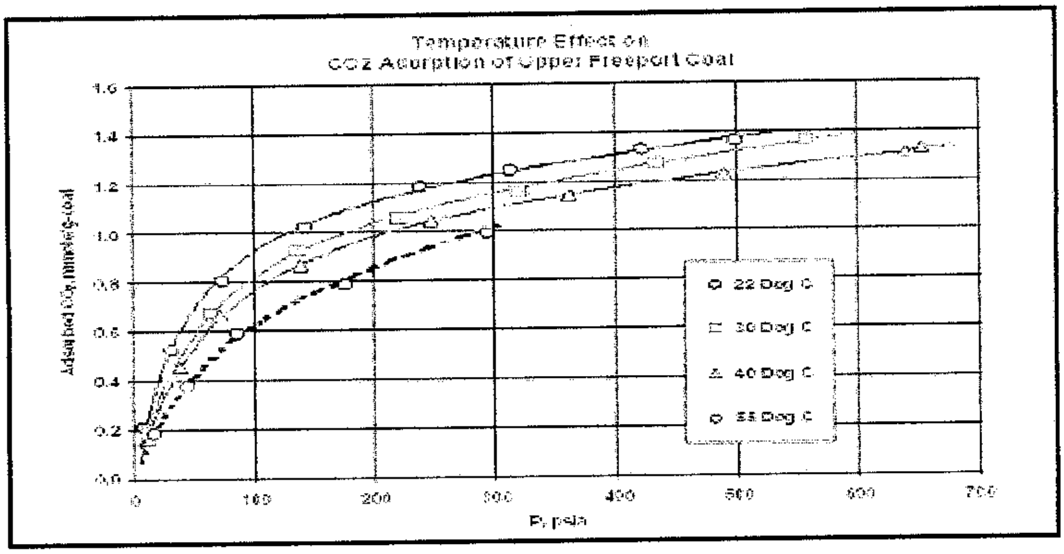

FIGURE 2.1: Temperature Effect on CO_2 Adsorption

2.3.1 pH Effect

(K.Schroeder et.al) had also conducted the experiment on pH effect on the CO_2 adsorption. They justified on the effect of pH on the chemistry of aqueous CO_2. At basic pH, dissolved CO exists as the carbonate ion and mineral carbonates are stable. At acidic pH, mineral carbonates dissolve, CO_2 that can remain dissolved exists as H_2CO_3 and CO_2 (aq) and CO_2 (gas) is produced. The pH of an aqueous solution also affects the surface of a material it is in contact with. In the case of coal, at the higher pH value, the carbonaceous surface, being in an environment above its isoelectric point, assumes a net negative charge. At the lower pH value, the carbonaceous surface assumes a net positive charge.

Both acid treatment and a base treatment results in an increase in adsorption capacity compared to the coal treated with only de-ionized water. If removal of acid-soluble minerals resulted in increased accessible pore volume, then increased CO_2 capacity would be expected. In this case it seems more likely that any increase in capacity would be due to surface-adsorbed base. If water is also present, alkali metal hydroxides react with CO_2 to form carbonates. Whatever the mechanism, the acid treatment appears to have a greater effect than the base or neutral treatments in these initial experiments. Below was the result obtained form the experiment they had conducted.

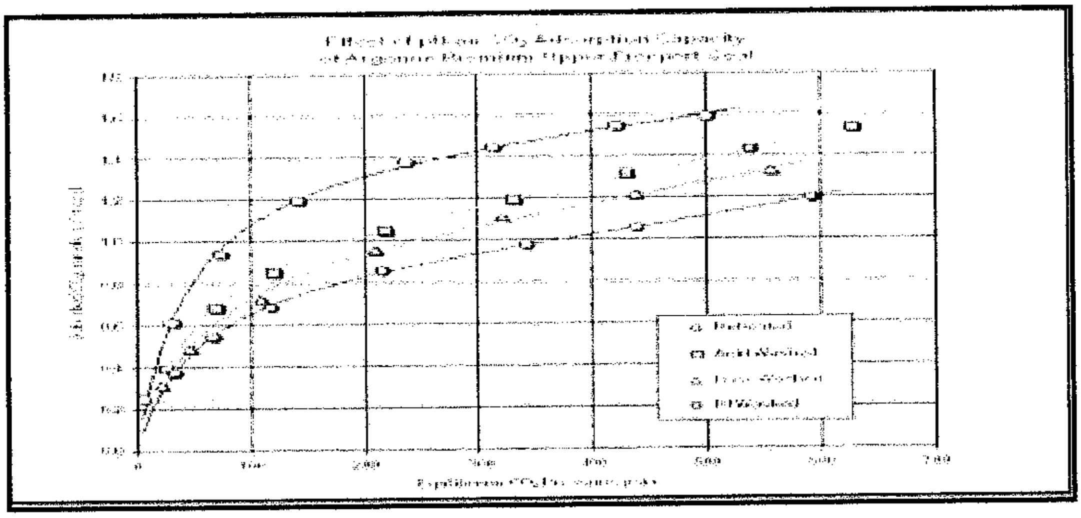

FIGURE 2.2: Effect of pH on CO_2 Adsorption

2.3.2 Comparison between CO_2 and CH_4 adsorption

(K.Ohga et.al) states on the approaches used to conduct the replacement experiment which is the comparison between adsorption of CO_2 and CH_4. From the result, when CO_2 concentration increases, the volume of CO_2 adsorption is increasing, the volume of methane adsorption is decreasing and nitrogen is not change.

(K.Schroeder et.al) agrees with the result obtained from (K.Ohga et.al). The experiment used Gas Chromatograph (GC) to measure the adsorption of CO_2 and CH_4. The expected conditions are stated below. In Adsorption experiment, if the result was obtained in such way that fraction of CO_2 as the free gas is more that CO_2 from the source gas, thus it can be indicated that the coal is preferred to adsorbed CO_2 more from the gas mixture. It will be the same as in Desorption experiment. If the result obtained where fraction of CO_2 as the free gas is less that CO_2 from the source gas, thus it can be indicated that the coal is preferred to adsorb CO_2 more from the gas mixture. Based on the result obtained, it can be seen that coal adsorbs more CO_2 than CH_4

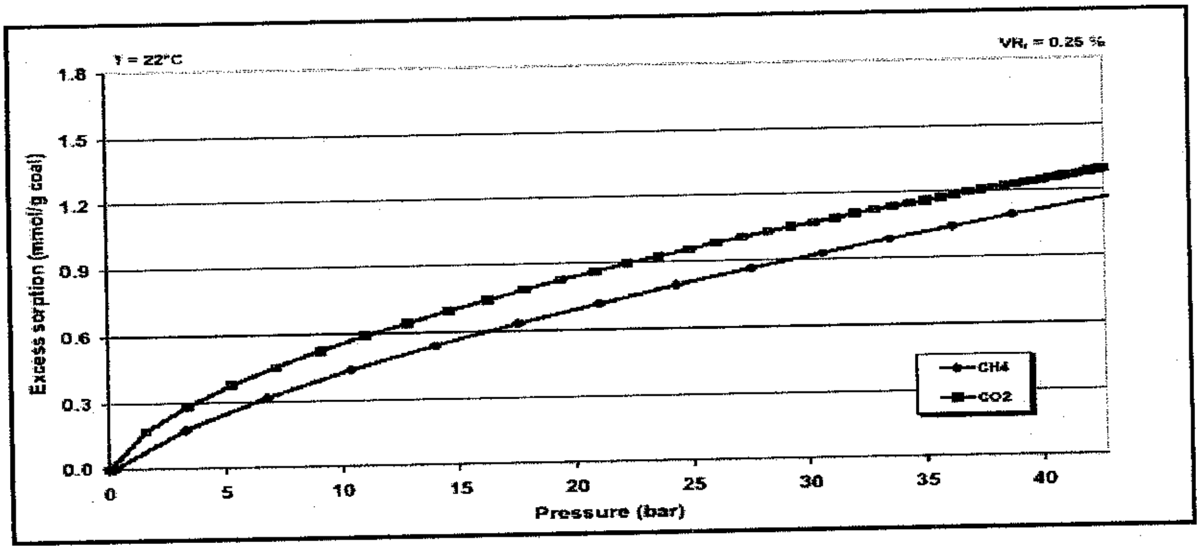

FIGURE 2.3: Comparison between CO_2 adsorption and CH_4 adsorption

(Andreas Busch* et.al) also agrees with the finding where they had also implemented the approach similar to (K.Schroeder et.al). However they found that it is not necessary that CO_2 will adsorb twice as much as CH_4 as the ratio is different for every different type of coal to be studied. They had studied for several types of coal and the result shows that some coal experiences on CO_2 preferential in low pressure and some experiences on CH_4 preferential. Further they were also expressed that for different pressure, it will lead to different preferential of adsorbing the gas. For low pressure, high rank coal prefers to adsorb CO_2 more than CH_4 compares to low rank coal but in high pressure, both low and high rank coals do prefer to adsorb more CO_2 compared to CH_4.

CHAPTER 3

METHODOLOGY/PROJECT WORK

3.1 PROCEDURE IDENTIFICATION

Generally the whole study touches on several stages. The initial stage covers on the related information and data gathering from various available resources such as books, research articles and online journal via internet access. Then after clearly define on the objective of the research, the analytical stage is proceeded. This involves the experiment and calculation based on the results obtained. The yields obtained then are discussed and further recommendations are proposed. Lastly the conclusion is stated based on the clarified objectives of research project.

The method chosen to conduct this research is through experimental study. The procedure is based on how to create the environment of experiment to be equal or almost similar to the actual environment of virgin coal. In order to prepare the procedure, lots of articles and literature reviews consist of related topics have been compared. However most of the articles and studies are concentrated on the effect of pressure on CO_2 adsorption. Because of the incompatible condition for the experiment on pressure effects to be conducted in our laboratory thus the research will be only concentrated on the effect of temperature and pH.

The idea is to vary in temperature and pH parameter and to study on the rate of CO_2 adsorption onto coals. Temperatures chosen are 30°C, 40°C, 50°C and 60°C while pH chosen are 2.4 (acidic coal), 6.2 (neutral coal) and 12 (alkali coal). Then the experiment continues on to study the comparison of CO_2 and CH_4.

Based on the objectives, the experimental work will be divided into two parts. First part touches on preparing the sample, lab apparatus, equipments and chemicals. Second part touches on conducting the main experiment in order to obtain the results. Procedure of preparing the samples and conducting the main experiment is repeated for every different parameter.

For sample preparation procedures, it can be subdivided into two parts which are preparing the chemicals and preparing the samples. Chemicals to prepare are 0.00398 M HCl (pH 2.4) and 0.10M NaOH (pH 12) in O_2 free environment.

Preparing the chemicals is not simply based on the normal procedures. In order to create O_2 free environment, the special equipment which is Controlled Nitrogen Flushed Box is chosen. It creates the environment filled with Nitrogen which is one of the non-adsorbed gases [3]. First step is to commission this equipment. When it is ready to be used, all the lab apparatus is transferred into the equipment. The lab apparatus must be in the size of the door of the Nitrogen Flushed Box. As the opening of door is not too wide, thus the size of the lab apparatus becomes the constraint in order to choose the suitable apparatus to prepare chemicals. Example, to prepare 5L chemicals, it is better to transfer five 1L beakers instead of 5L container.

Whenever the outer door is opened in order to transfer the related lab apparatus, the inner door must always be closed. The same application is implemented to transfer the apparatus into the antechamber, make sure that the outer door is closed, and then open the inner door. Then the equipment is purged with Nitrogen for 15 minutes before the chemicals preparation is started.

For this experiment, the coal sample is taken from the coal mines in Indonesia. Stated in Reference [2], the precautions had been taken during the collection, processing and packaging of the coal samples to avoid any exposure the atmosphere which is the non-oxygen free environment. However, for this research, the coal is assumed to have been exposed to such environment and thus several treatments must be conducted first for the experiment to be proceeded. Below are the physical properties of the coal sample used in this research.

TABLE 3.1: Parameters on the coal sample used

Source	PT.SUPERINTENDING COMPANY OF INDONESIA
Type of Coal	Bituminous
Total Moisture	13.3 wt%
Inherent moisture	9.1 wt%
Ash Content	4.5 wt%
Volatile matter	40 wt%
Fixed carbon	46.4 wt%
Total Sulphur	0.56 wt%
Gross Calorific Value	6663kCal/kg/a
Hardgrove grindability index	45
Ash Fusion Temperature, **(Reducing temperature)** **Initial deformation temperature**	1150°C

The second part of the research is to conduct the experimental work. There are five experiments that have been accomplished for this research. Experiment 1 is to study on the comparison of the rate of CO_2 and CH_4 adsorption onto coal at specific temperature and particle size. Gas Chromatograph is used for this experiment. Experiment 2 is to study on the effect of temperature variation on CO_2 adsorption for the similar particle size of untreated coal sample (30°C, 40°C, 50°C and 60°C). Then for Experiment 3, it is to check on the effect of pH variation on CO_2 adsorption for the similar particle size of coal sample at specific temperature (pH 2.4, 6.2 and 12).

Then the experiment continues on the effect of different particle size (250μm and 1000μm) of untreated coal sample on CO_2 adsorption at specific temperature. For the first four experiments the experiment is set up as in Figure 3.1 except that for Experiment 1 which is to study on the comparison of the rate of CO_2 and CH_4 adsorption onto coal at specific temperature and particle size, Gas Chromatograph (GC) is connected at the end of the experiment setup. Note that the experiment set up is at the external side of GC and does not include in the internal part of GC. The last experiment is more on the analysis of the metal components extracted by acid, distilled water and alkali in the filtered solution in Experiment 3. The equipment used is HACH Water Analysis.

Initially the coal sample needs to be grinded into several sizes. The reason is to standardize the particle sizes used in the experiment. The equipments used are mortar grinder and sievers. The sizes are 1000μm and 250μm. Before starting the experiment, the coal must be out gassed first to get rid of the gasses that exist in the coal seams in order to enhance the new adsorption. This is because, even though the gas in coal seams can exists as free gas in cracks and fractures but most of the gas in coal is adsorbed on the internal surface of the micropores [3].

For the experiment to compare between CO_2 and CH_4 adsorption onto coal, the procedure has to take into account on the initial pressure allowed in the experiment setup. Initially the experiment setup is flushed with nitrogen. For every 10 minutes the gas sample is taken to check the composition of nitrogen. Once it has reached 100% composition of nitrogen, carbon dioxide is released until it flushes all the nitrogen.

After it has reaches 100% composition of carbon dioxide, the flowrate of carbon dioxide to the experiment setup is reduced in order to avoid the sudden increment of pressure drop in the setup once the end-hose is connected to Gas Chromatograph. After the end-hose is connected, the CO_2 flowrate to the experiment setup is increased until the digital manometer (DM) shows 25kPa. Quickly valve 1 (V1) is closed and the sample gas is taken after 10 minutes. The sample gas is analyzed only at initial (t=0min) and at the end (t=10min).

The sample gas is only analyzed for 10 minutes because of the following reason. In order for the gas to be analyzed with Gas Chromatograph, there must be reasonable pressure in the sample cell to push the gas to Gas Chromatograph. Eventually the adsorption occurs in the sample cell reduces the pressure in it. Therefore if the studied period is too long, there will be no or less pressure in the sample cell to push the gas to Gas Chromatograph. As the result, the period time of 10 minutes is allowed for the adsorption to occur before the sample gas is fed into Gas Chromatograph. If more than that, it causes the gas fails to be fed into Gas Chromatograph for it to detect the gas components. The similar procedure is applied to CH_4 experiment.

For Experiment 2 which is to study on the effect of temperature variation on CO_2 adsorption for the similar particle size of untreated coal sample, the experiment is set up as such (**FIGURE 3.1**). Two cells, one is for reference cell and the other is for sample cell. Reference cell is remained as it is while the sample cell is filled with the sample coal. Reference cell is readied for the gas to be heat up at the studied temperature. It enhances the thermal equilibrium between the heat transfer provided by water bath heater and the gas in the reference cell. It is also to control the pressure and the amount of gas to be fed into the sample cell from the reference cell.

For the first step, the equipment is flushed with Nitrogen from the gas cylinder to get rid all the possible gas exists in the equipment. This is to eliminate the chance of pressure reading to be contributed by gasses other than CO_2 to be recorded. Then the nitrogen gas cylinder is closed and the pressure is released until it reached 0kPa. The step is repeated several times until all the possible Nitrogen gas has been released from the inner experiment apparatus.

Then CO_2 is released in order to flush the remaining Nitrogen Gas left. Then the water bath temperature is set up to be the desired temperatures which are 30°C, 40°C, 50°C and 60°C and the sample coal size is 1000μm. Valve 2 (V2) and Valve 3 (V3) are remained closed except Valve 1(V1). The gas is remained in the reference cell for 5 to 10 minutes to reach the thermal equilibrium.

Then, a portion of gas from the reference cell is transferred to the sample cell. It is important to note that the portion of gas must be the same for each experiment in one studied parameter. Thus, the pressure of the gas fed into the sample cell is 8kPa. After closing this valve a certain time (c. 1 minute) is allowed for pressure and temperature equilibration in the reference cell. The pressure reduction is recorded for every two minutes. For every experiment, the sample cell is changed, thus the weight of coal sample is recorded before the experiment.

As for the experiment for pH effect, it will be conducted similar to Experiment 2 (temperature effect); the difference is that the coal samples need to be treated first by soaking, filtering and drying overnight with 0.0328M HCl, 0.10M NaOH and distilled water in order to obtain the pH of 2, 12 and 6.2. The filtered solutions are analyzed to know the metal compound exist in it. This is where Experiment 5 is conducted. The filtered solution is taken to be analyzed via HACH Water Analysis. The expected metal compounds are listed by referring to the several literature reviews. Unfortunately, this analyzer needs specific reagent to detect certain metal. As the expected metal compounds such as Calcium, Magnesium and Aluminum are not available except for Silica, thus only Silica detection was proceeded.

For the experiment of different particle sizes, the procedures are similar with the experiment of the temperature effect. The particle sizes are 1000µm and 250µm. The difference is that the temperature must be constant for each particle size, which in this case is 40°C. Temperature is chosen as 40°C as it is set in the range of more than 30°C since logically the temperature underground is higher than at the ground surface which in the range of 30°C. However the temperature is chosen to be the lowest temperature of the temperature more than 30°C since it is affecting the rate of CO2 adsorption. This is discussed further in Chapter 4.

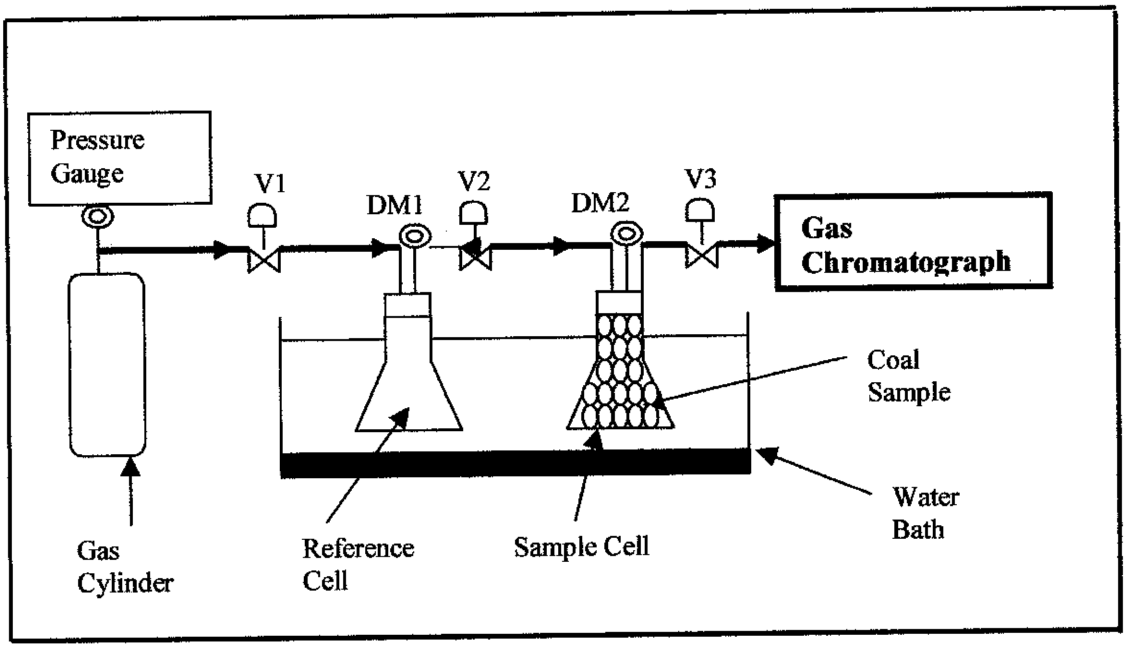

FIGURE 3.1: Experiment Set Up

CHAPTER 4

RESULT AND DISCUSSION

There are several of parameters to be studied for this research; temperature, particle size, pH and type of gaseous. Experiment 1 is to study on the comparison of the rate of CO_2 and CH_4 adsorption onto coal at specific temperature and particle size. Experiment 2 is to study on the effect of temperature variation on CO_2 adsorption for the similar particle size of untreated coal sample (30°C, 40°C, 50°C and 60°C). Then for Experiment 3, it is to check on the effect of pH variation on CO_2 adsorption for the similar particle size of coal sample at specific temperature (pH 2.4, 6.2 and 12).

Then the experiment continues on the effect of different particle size (250µm and 1000µm) of untreated coal sample on CO_2 adsorption at specific temperature. The last experiment is more on the analysis of the metal components extracted by acid, distilled water and alkali in the filtered solution in Experiment 3.

Here the data are taken as the peak area yielded by Gas Chromatograph, pressure reading for each two minutes and concentration in mg/L. Then the calculation and graphs are yielded based on the data taken.

4.1 RESULT

Experiment 1 is to study on the comparison on the rate of CO_2 and CH_4 adsorption onto coal at specific temperature and particle size. In order to make comparison between CO_2 and CH_4 adsorption onto coal, the suitable method is to compare on the concentration of gas at initial and concentration of gas after certain period. If the gas sample is the gas mixture, then the suitable method is to compare on the reduction gas fraction between initial and after certain period of process.

$$\text{Fraction } (CO_2 \text{ or } CH_4) = \frac{\text{Amount of the Gas Component}}{\text{Total Amount of the Gas Mixture}} \qquad [1]$$

$$\text{Reduction of Fraction } (CO_2 \text{ or } CH_4) = \frac{(\Delta \text{ Amount of the Gas Component})_{\Delta t}}{\text{Total Amount of the Gas Mixture}} \quad [2]$$

Higher adsorption is determined based on the larger reduction of fraction of gas component. It is analogous if the calculation is based on the peak area yielded from the Gas Chromatograph since the peak area here represents the amount of gas existing in the sample.

$$\text{Peak Area Ratio } (CO_2 \text{ or } CH_4) = \frac{\text{Peak Area of the Gas Component}}{\text{Total Peak Area of the Gas Mixture}} \quad [3]$$

$$\text{Reduction of Peak Area Ratio}(CO_2 \text{ or } CH_4) = \frac{\Delta \text{ Peak Area of the Gas Component}_{\Delta t}}{\text{Total Peak Area of the Gas Mixture}} \quad [4]$$

Thus the higher adsorption is determined based on the larger reduction of peak area ratio. The assumption to be made here is that there is no leakage occurs during the adsorption experiment. In other word, the amount of air at initial and final is remained the same.

TABLE 4.1: Reduction of Peak Area Ratio CH_4 Adsorption

Time	**CH_4**	**Air**	**Total Peak Area**	**Peak Area Ratio of CH_4**	**Reduction of Peak Area Ratio**
0	108456802	281962	108738764	0.997409	-0.000297
10	122669835	281962	122951797	0.997706	

TABLE 4.2: Reduction of Peak Area Ratio for CO_2 Adsorption

Time	**CO_2**	**Air**	**Total Peak Area**	**Peak Area Ratio of CO_2**	**Reduction of Peak Area Ratio**
0	135196113	3247508	138443621	0.976543	0.00148
10	126977924	3247508	130225432	0.975062	

Thus, it can be seen that the Reduction of Peak Area Ratio for CO_2 is positive which means adsorption occurs in CO_2 Experiments. On the other hand, Reduction of Peak Area Ratio for CH_4 is negative which means desorption occurs in CH_4 Experiments.

This experiment results gives the ratio of CO_2/CH_4 is 4.97, which means, for every 5 parts of CO_2 adsorbed, coal tends to desorp 1 part of CH_4.

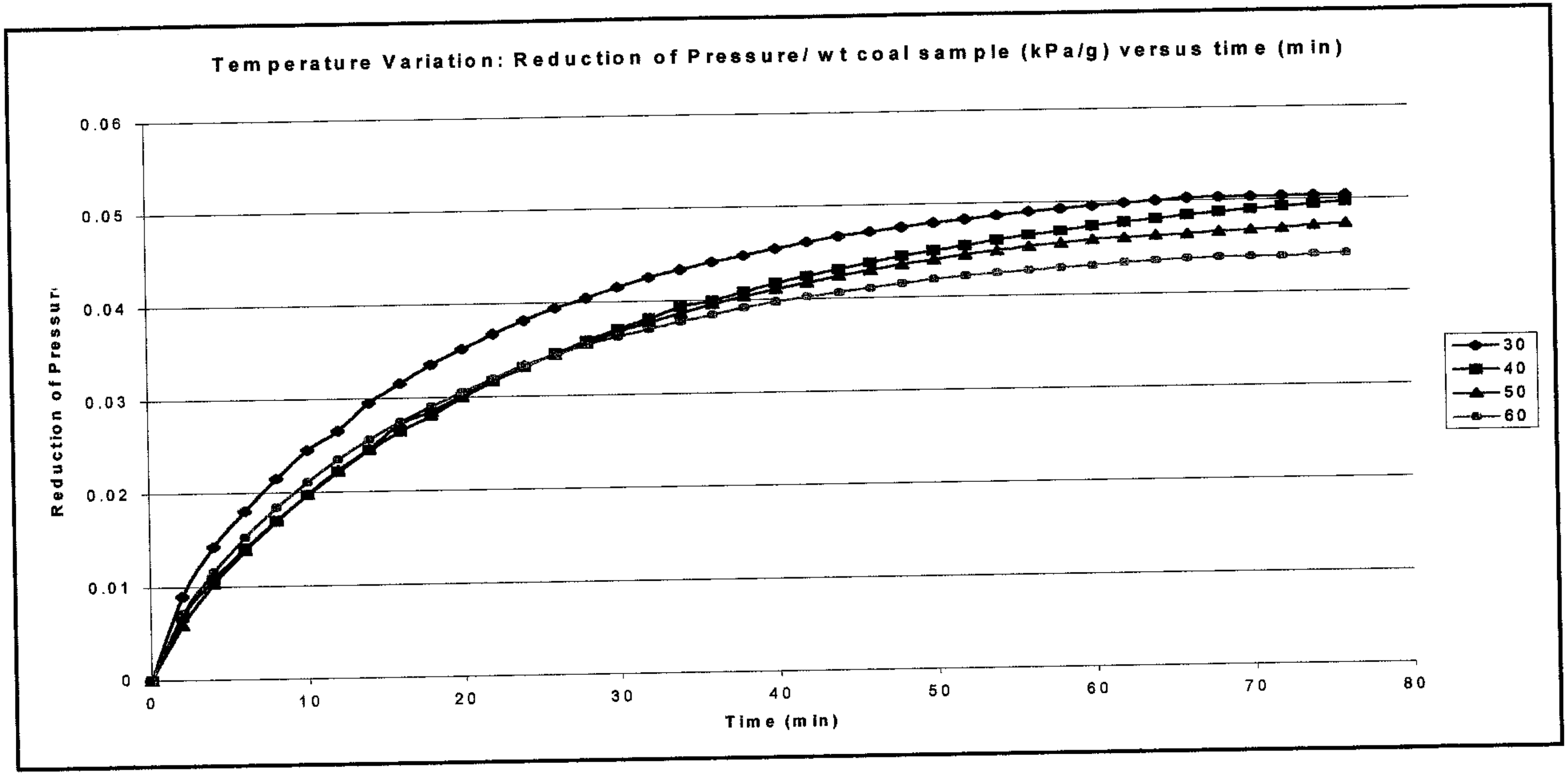

FIGURE 4.1: Graph on the study of the temperature variation effect on CO_2 adsorption for similar particle size of untreated coal sample (30°C, 40°C, 50oC and 60°C)

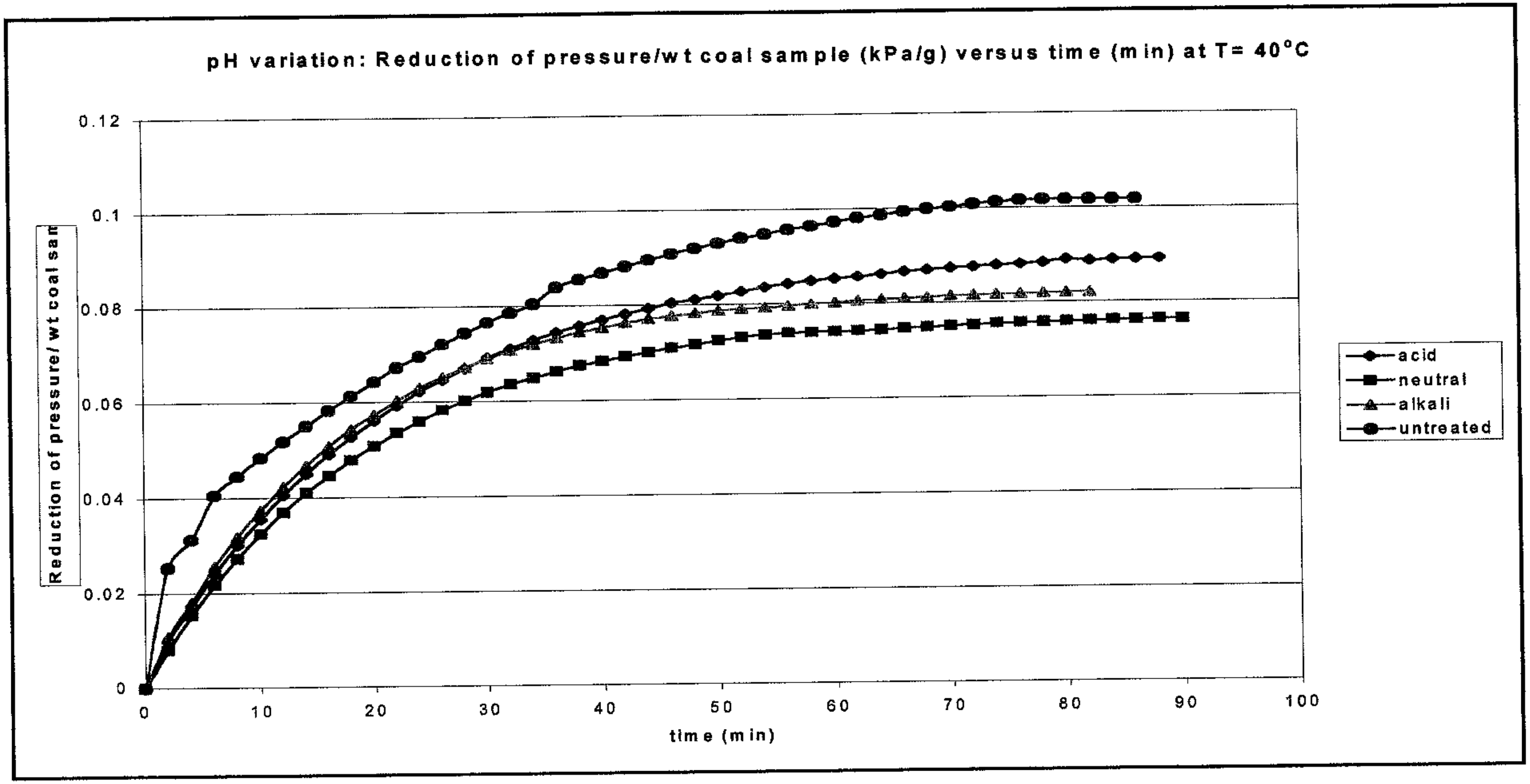

FIGURE 4.2: Graph on the study of pH the variation effect on CO_2 adsorption for similar particle size of coal sample at specific temperature, 40°C (pH 2.4, 6.2 and 12)

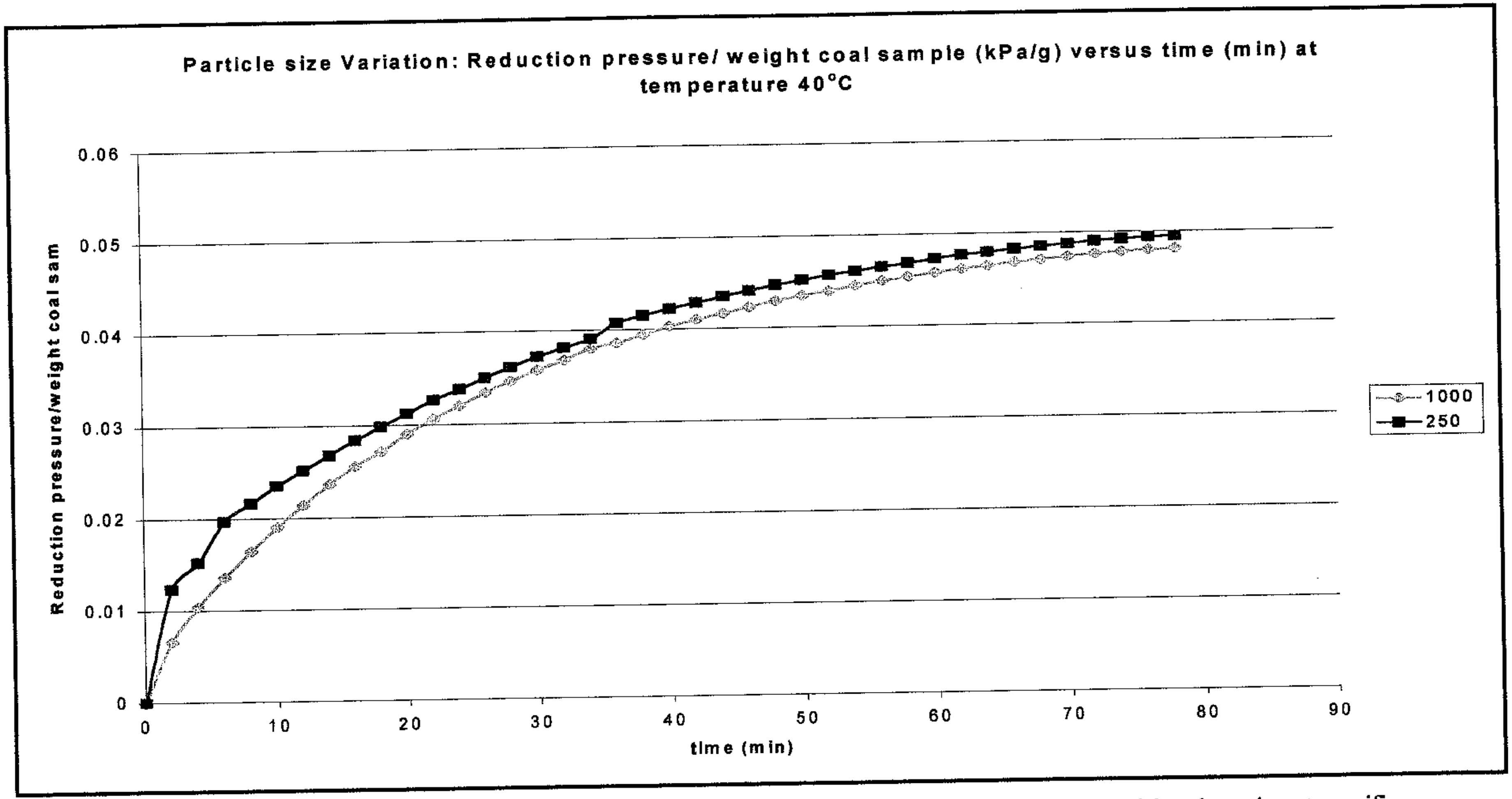

FIGURE 4.3: Graph on the study of different particle size (250μm and 1000μm) of untreated coal sample on CO_2 adsorption at specific temperature, 40°C

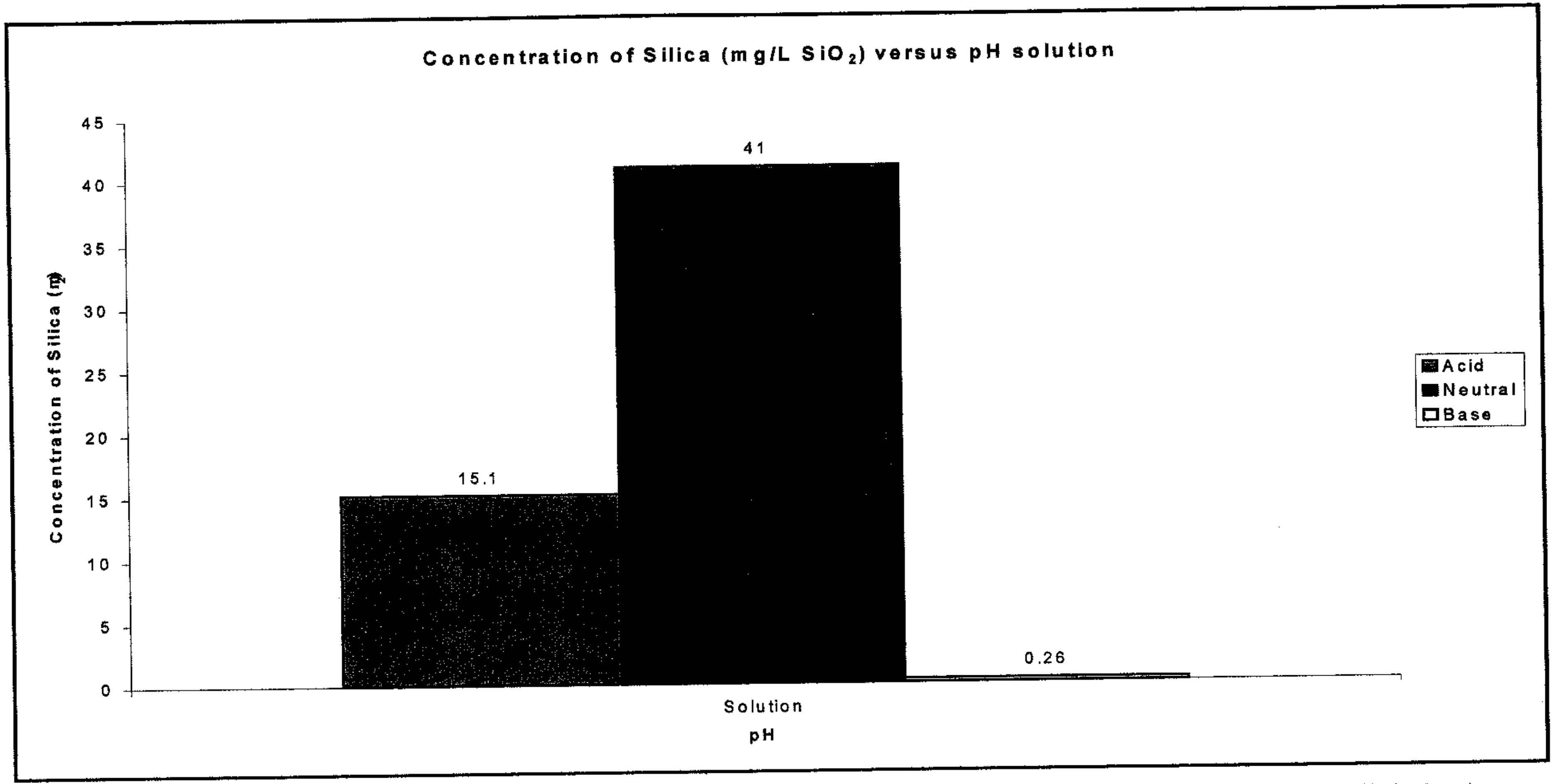

FIGURE 4.4: Graph on the concentration of metal compound, Silica (mg/L SiO_2) in different solution of acid (HCl), neutral (Distilled Water) and base (NaOH)

4.2 DISCUSSION

Adsorption refers to the condensation of gases on free surfaces. It is different compared to absorption where molecules penetrate into the mass of the absorbent. Basically the overall adsorption is a series of steps. Based on this study, the gas (CO_2 and CH_4) is the adsorbate (one which is being adsorbed) and coal is the adsorbent (one which is adsorbed). Initially the gas diffuses to the exterior surface of particle and then to the inside of coal pores. Then the gas is adsorbed on the surface of the pore.

Generally the adsorbate is attached to the adsorbent via physical adsorption and/or chemisorptions. Physical adsorption is also known as *van der Waals adsorption* while Chemisorptions is known as activated adsorption. Physical adsorption (physisorption) is when the intermolecular attractive forces between molecules of a solid (coal) and the gas (CO_2 and CH_4) are greater then those between molecules (CO_2 and CH_4) itself. Chemisorptions on the other hand are the formation of chemical bonds between the gas and coal. For this study, it has been identified that the type of adsorption occur between the coal and the gas is physical adsorption based on the definition above.

In detail, the net forces that exist between the gas and solid include repulsive forces (short term) as well as attractive forces (called coulombic forces). The repulsive forces are short term because of the nature of the electron clouds that exist around each molecule. When the degree of coverage (integration area point) is low, then the force between the adsorbent and adsorbate is important (low traffic), whereas once the surface begins to 'fill up' the adsorbate molecules begin to repel against each other. Chemisorptions involves chemical bonding, hence can only exist in one layer and the same sort of chemical bonding cannot exist between the adsorbent and the adsorbate. However, physisorption can exist on many layers although the forces involved are much weaker. [14]

The experiment is to study the extent of CO_2 adsorption onto coal in various possible environments. The experiments are to study on the comparison of CO_2 and CH_4 rate of adsorption onto coal at specific temperature and particle size, temperature variation for the similar particle size of coal sample, particle size variation of coal sample at specific temperature and pH variation for the similar particle size of coal sample at specific temperature. Besides that, there is an additional simple experiment conducted on the analysis of metal compound extracted in the filtered solution (acid, base and distilled water), continuation from the experiment of pH variation.

Before any experiments can be conducted, the physical properties of CO_2 must be determined first by referring on CO_2 phase diagram in Figure 4.4. It should be mentioned that the critical temperature and pressure CO_2 is about 31°C and 1070psia (73atm) [3]. These can be the reference to determine the choice of temperatures and pressures for the experiments.

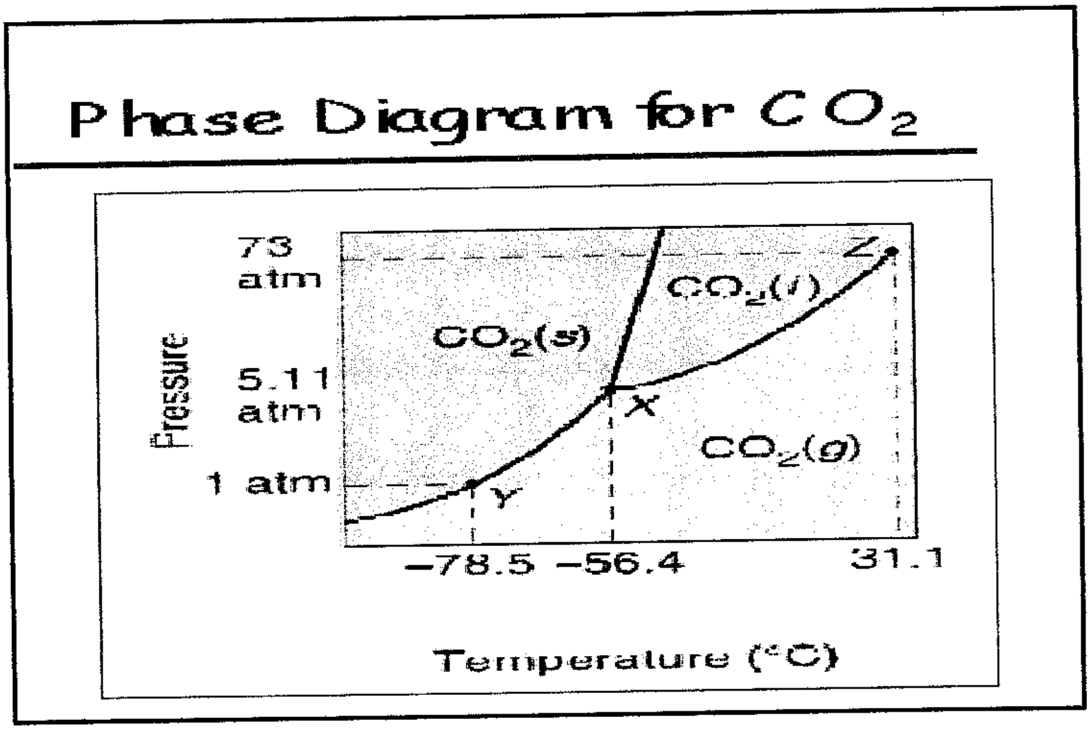

FIGURE 4.5: Phase Diagram for CO_2

At temperature below the critical temperature and pressure of CO_2, increasing pressure will ultimately result in condensation of CO_2 and the apparent amount 'adsorbed' CO_2 would rapidly increase [3]. Thus the measured data will be the condensed CO_2 which is inaccurate since CO_2 in the study must be in gas phase region.

At temperatures and pressures above the critical point, CO_2 exists as supercritical fluid [3]. This is also the avoided region since the supercritical fluid actually has physical properties somewhere between those of a liquid and a gas. Supercritical fluids are able to spread out along a surface more easily than a true liquid because they have lower surface tensions than liquids. At the same time, a supercritical fluid maintains a liquid's ability to dissolve substances that are soluble in the compound, which a gas cannot do [13]. Thus it is important to ensure that CO_2 used in the experiments must be in the region of gas phase of the CO_2 phase diagram. [3].

The experiments implement low pressure which is 8kPa (0.08atm) to 25kPa (0.25atm) for the temperature ranges from 31°C to 60°C. It is in the gas phase region of CO_2 referring to the CO_2 phase diagram in Figure 4.5. The pressure implemented is low because of the unreliability of the lab apparatus toward the high pressure. A trial experiment was conducted to determine the extent of pressure that the experiment setup can stand before the stopper that closes the cell blows up. From the trial experiment, the pressure is only allowed to be up until 0.3kPa, thus the choice of pressure is determined based on this limitation.

Based on the procedure of Experiment 1 (the study on the comparison of CO_2 and CH_4 rate of adsorption onto coal at specific temperature and particle size), the experiment setup is flushed with N_2 and the studied gas (CO_2 or CH_4) for a few minutes. Within this period, the sample gas is taken for every 10 minutes and analyzed using Gas Chromatograph to ensure that only desired gas exists in the experiment setup. N_2 is flushed to get rid all the gasses that exist initially in the cell. Then it is replaced with CO_2 or CH_4, depending on the studied gas at that time.

For the purpose of adsorption (adsorption experiment), the sample gas is taken at t_0 and t_{10}. For each sample, it is analyzed with Gas Chromatograph and the result is obtained in term of peak area. The adsorption is taken based on the reduction of Peak Area yielded by this equipment within 10 minutes. The gas that has the higher reduction of peak area within 10 minutes can be conclude as having the higher rate of adsorption compared to the other gas.

For the experiments of temperature variation for the similar particle size of coal sample, particle size variation of coal sample at specific temperature and pH variation for the similar particle size of coal sample at specific temperature, based on the procedures approaches, the data of pressure measurements have been recorded for every two minutes. The result targeted is number of moles adsorbed CO_2 per gram coal sample versus pressure at various parameters. This represents the adsorption of CO_2 onto coal in different condition or environment. However instead of calculating the number of moles per adsorbed CO_2 per gram coal sample, the result is changed to be reduction of pressure per gram coal sample versus time.

They represents to each other by referring on the Non-Ideal gas equation.

$$PV=ZnRT \qquad [5]$$

P = Pressure of the Cell (Pa)
V = Volume of the Cell (m^3)
n = Number of moles of gas in the cell (moles)
R = Universal Gas Constant = 8.314 kJ/ (kmol.K)
T = Temperature of the Cell (^oC)
Z = Compressibility factor for Sample Gas

Here the difference of pressure in certain period of time in the cell is equivalent to the number of moles adsorbed by coal sample in that particular period of time provided that the remaining parameters are constant throughout the experiment. For the adsorption to occur, the pressure is seen to be reducing as time goes.

Assuming that ZRT/V is constant;

At t=0min;

$$P_o\ V=Zn_oRT \qquad [6]$$

At t=Imin;

$$P_i\ V=Zn_iRT \qquad [7]$$

Therefore, for the pressure reduction;

$$P_i V - P_o V = Zn_iRT - Zn_oRT$$

$$P_o - P_i = (ZRT/V)\ (ni - n_o)$$

$$\Delta P = (ZRT/V)\ \Delta n \qquad [8]$$

Where;

ΔP =Reduction of Pressure in the Cell (kPa)

P_o = Initial Pressure at t=0 (kPa)

P_i = Pressure at t=I (kPa)

i = time (min)

Δn = Number of mol adsorbed

Comparison between CO_2 and CH_4 Adsorption onto Coal

The first experiment is to study on the comparison of CO_2 and CH_4 adsorption onto coal at specific temperature and particle size. It is analyzed based on the reduction of peak area ratio of the sample gas mixture. The gas samples are the mixture of CO_2 and N_2 and the mixture of CH_4 and N_2. Here nitrogen gas exists as the remaining gas that is not fully flushed by the studied gas (CO_2 and CH_4). Initially the gas sample is tended to be CO_2 and CH_4 mixture but it cannot be proceeded due to the lack of lab apparatus supply. However the modification has been made especially on the calculation verification.

Here the calculation is made based on the reduction of peak area ratio of each gas sample. Peak area ratio represents the fraction of the gas. The procedure that had been undertaken is based on the comparison between the gas sample taken at t=0min and t=10min. Each of these was analyzed with Gas Chromatograph and yielded the peak area of each gas components.

Based on the result, the peak area is reduced as the experiment was conducted which represents there is adsorption occurs. Thus, if it is intended to calculate the reduction fraction of gas component, the usual way is to deviate the initial amount of gas with the final amount of gas, and the value is divided with the total amount of gas mixture.

However, Gas Chromatograph here does not provide the value of concentration; instead the peak area is given. Therefore it can however be calculated by using the reduction of peak area ratio since from the observation, the peak area of the studied gas reduces during the adsorption experiment. In addition, the peak area yielded; represents the gas component existing in the sample. Hence, the calculation is conducted as above in Chapter 4. The focus here is to determine which one of the studied gases is preferably to be adsorbed by the coal.

From the result of the experiment, the reduction of peak area of CO_2 is 5 times larger than the increment of peak area of CH_4. This value is obtained by considering the assumption to neglect the increment of the peak area of air that possibly indicates the leakages of the equipment when the experiment was conducted (adsorption occurs). Thus it shows that for this type of coal (bituminous), it prefers to adsorb CO_2 than CH_4. This result agrees with the result obtained by (Busch and Bergen, 2003) where they have also obtained the same for the high rank coals (bituminous and anthracites).

From (Busch and Bergen, 2003), it has mentioned that this experiment outcome is depending on the type of the coal whether it is high rank coal or low rank coal. In low pressure experiment, for high rank coal, CO_2 is preferable than CH_4 while for low rank coal, it is CH_4 that is preferable, not CO_2. For high pressure, CO_2 is always preferable than CH_4 for all rank of coal. As the experiment here is conducted in a very low pressure, the possibility of CH_4 not to be adsorbed or the possibility of CO_2 to be adsorbed by coal is rather high. Thus the result shows that the desorption of CH_4 had occurred. Here, it shows that for 5 parts of CO_2 adsorbed, the coal tends to desorb 1 part of CH_4 out.

From this result, it can be implemented in sequestrating CO_2 onto coal bed methane area. For every coal mining area, there is always a portion of abandoned mining area where the coal there cannot be collected because of several reasons such as unsafe geographical area for people to get it and others. Thus by having this as the possible future CO_2 Sequestration area, it can help in reducing the cost of this process by having a side income.

Coal bed methane is the coal bed that contains CH_4. CH_4 here is also known as natural gas and was created through a process called *coalification* which converts organic plant matter into coal over millions of years. The natural gas is attached or adsorbed to the coal itself, instead being trapped in the pore pace of the rock like most conventional natural gas (other type of coal seam gas components). Pressure from overlying rock and water within the natural fracture system of the coal seam keeps CH_4 bound to the coal. CH_4 here is indistinguishable from the natural gas where it can be used for home heating, gas-fired electricity generation, and industrial fuel.

Therefore as for the coal in the condition where CO_2 is preferable than CH_4, it can be said that by injecting CO_2 onto the coal bed methane, the coal will desorp CH_4 that is already contains in the coal. CH_4 is collected by reducing the pressure in the coal seam so that CH_4 flows through fractures in the coal into the well bore. The gas would then flow up to the surface. If few natural fractures exist, producers may use hydraulic fracturing to create channels in the coal. When the natural gas reaches the surface, it is compressed and transported through natural gas pipelines. It is then can be sold to cover up or reduce the cost of CO_2 sequestration.

Effect of Different Temperature

The second experiment is the temperature variation for the similar particle size of untreated coal sample. The temperature dependence of CO_2 adsorption onto coal sample is shown in Figure 4.1. The graph shows the adsorption rate of CO_2 onto coal in different temperature. The temperatures in study are 30°C, 40°C, 50°C and 60°C. Here it can be seen that as the temperature increases, the adsorption rate/ wt coal sample decreases.

Adsorption is a dynamic equilibrium [13]. When the temperature of the system increases, it creates greater ratio of gas phase medium. In other word, average time spent by molecule on the surface (residence time) is lower compare for the molecule in the release condition (gas phase that is not bonded with the solid). This is because high temperatures increasingly favor the gas–phase due to the T°S entropy term in the free energy expression [3].

Here it can be explained through Le Chatelier's principle. From Le Chatelier's principle, changes temperature cause shifts in equilibrium without changing the value of the equilibrium constant, *K*. In contrast, almost every equilibrium constant changes in value as the temperature changes. Thus by applying this principle, the rules for the temperature dependence of this equilibrium constant can be deduced. It can be applied by treating heat as if it were a chemical reagent. In an endothermic reaction, heat is considered as a reactant whereas in an exothermic reaction, heat is considered as a product.

Endothermic: Reactants + *heat* ↔ products

Exothermic: Reactants ↔ products + *heat*

Gas adsorption is nearly always exothermic. In the exothermic process, heat is considered as a product which is at the right hand side of the equation. It means that the process tends to produce heat towards the right hand side. The principle says that for the exothermic process, when the temperature of the surrounding increases, the equilibrium tends to shift in the direction that adsorbs heat and less favor in producing heat. Therefore, the equilibrium will shift to the left.

Magnitude of K indicates the extent to which an adsorption will proceed. Usually in the context of chemical reaction, large K will tend to proceed far to the right which means to the product (producing more heat, favor in exothermic). Since the adsorption is exothermic, and increasing the temperature tends to shift the equilibrium to the left (towards adsorbing the heat), thus it shows that the adsorption is not favored in high temperature as compared to the low temperature. Here it can be seen the magnitude of *K* is low.

The experiment was suggested to increase the temperature until the temperature that caused the equilibrium to shift to the left is obtained. It means that the temperature that caused no adsorption to occur, instead desorption is favored. However the water bath is limited until 60°C because of the evaporation of water had started to occur at that temperature. Evaporation condition is not in favor for the water bath heater especially in order to maintain the constant temperature to the gas in the cells as the phase of water is kept changing.

The temperature effect can also be seen from Clausius-Clapeyron equation

$$(\partial \ln P / \partial T)_\theta = -\Delta H_a / RT^2 \qquad [9]$$

P = Pressure
T = Temperature
$-\Delta H_a$ = Infinitesimal enthalpy change

$-\Delta H_a$ is the differential of molar enthalpy of adsorption, equals dH/dn, where dH is the when dn moles are adsorbed at coverage, θ. After integration, the relationship can be found as such,

$$\ln P = \Delta H_a / RT \qquad [10]$$

Since it can be said that $-\Delta H_a = dH/dn$, thus;

$$\ln P = (dH/dn) / RT \qquad [11]$$

P = Pressure
T = Temperature
dH/dn = Infinitesimal enthalpy change
dn = moles adsorbed
Θ = integrated surface area

As dH/dn is perpendicular with T, therefore as the temperature increases, dn moles adsorbed is reduced.

Effect of Different Particle Size

The first experiment is the particle size variation of untreated coal sample at specific temperature, 40°C. The particle size dependence of CO_2 adsorption onto coal sample is shown in Figure 4.3. The graph shows the adsorption rate of CO_2 onto coal in different particle size. The particle sizes in study are 250μm and 1000μm. Here it can be seen that smaller particle size leads to increment of the adsorption rate/ wt coal sample.

The reason behind this is because smaller particles enhance the rate of adsorption by exposing more entrances to the coal pores which means larger surface area. This will increase the rate of diffusion to the surface of the coal.

Notably, the size of the particle has little effect on adsorptive capacity as expressed by total surface area. While it is well known that smaller particles of a given mass of coal would have a greater surface area than larger particles, the huge internal surface area of coal dominates so much that the particle size essentially has no effect on the capacity [15]

Effect of Different pH

The third experiment pH variation for the similar particle size of coal sample at specific temperature. The pH dependence can be seen in Figure 4.2. The graph shows the adsorption rate of CO_2 onto coal in different pH. The pH in study is 2.4, 6.2, and 12. Together, they are compared with the adsorption rate of CO_2 onto untreated coal. Here it can be seen that, the adsorption rate/ wt coal sample decreases from untreated, acidic, alkali, and neutral condition.

Different pH is created by adding HCL (acid), NaOH (alkali) and Distilled Water (neutral) slowly onto coal sample. From Figure 4.2, the adsorption rate of CO_2 / gram coal sample of the acid treated and base treated coal sample are higher that the coal treated with only de-ionized water. Treating with acid however leads to higher adsorption rate of CO_2 / gram coal sample compared to treating with base.

The filtered solutions are then analyzed with HACH Water Analyzer. The expected metal compounds to be extracted by the filtered solution are listed based on the literature reviews. The metal compound such as Calcium, Magnesium, Aluminum and Silica are expected to be in the coal. Thus, after implementing the standard HACH reagents, the treated solutions are analyzed using HACH Water Analyzer. As the reagents are only available to detect the presence of Silica, thus the experiment was only done for Silica compound only. Because of this reason, the experiment conducted is only to prove that the filtered solution do extract some metal compound which in this case is Silica.

The result obtained in term of mG/L of SiO_2. From Figure 4.4, the graph on the concentration of metal compound of Silica (mg/L SiO_2) in different solution of acid, neutral and base, it can be seen that the solution from neutral solution had extracted the highest amount of Silica which is 41mg/L, followed by acid with 15mg/L and base with only 0.26mg/L.

Silica presence is proved by the change of color from yellow to blue. Note that the filtered solution must be in clear solution for HACH Water Analysis to detect any presence of desired metal compound. Based on this observation, all the solutions do contain Silica compound extracted from the coal. This result comes with the explanation. Coal does not consists of 100% carbon and do have some metal compounds attached to it. Coal itself is an organic compound and formed from ancient vegetation which obviously must have at least Calcium and other metal compound in it.

However, based on Reference [15], the best outcome is to check on every possible metal compound exist and the solution that has the highest total amount of metal compound extracted will have the highest adsorption. This is because, when the coal is pretreated with the aqueous solution, whether the solution is acidic, basic or neutral, it tends to dissolve certain minerals that exist in the coal. When the coal were filtered and dried overnight, it tends to remove and outgas the dissolved mineral whether it is acid-soluble mineral, base-soluble mineral and etc. Removal of these minerals resulted in increased accessible pore volume and hence the increased capacity of CO_2

would be expected, so does the adsorption rate of CO_2 per gram coal sample of each sample.

Reliability of Implementing the Process in Malaysia

In order to implement CO_2 Sequestration in Malaysia, there are several factors that need to be considered. The factors are such as suitable location, type of coal, financial support and others. In term of possible area, Malaysia has several unminable coal areas, for instance in Batu Arang , Selangor. In addition, there are a lot of active areas and newly found areas scattered in Sabah and Sarawak which in the future will be the areas that contain only unminable coal. These are the possible areas that can be considered for the trial implementation of CO_2 Sequestration.

For this experiment the type of coal used is bituminous. Here in Malaysia, the type of coal is ranked between bituminous and sub-bituminous. Based on the experiment results and related articles, all coal is suitable for the sequestration to be implemented onto it, but for each type of coal and different conditions, it gives different rates and preferences. Therefore, before any further trial implementation, the coal must undergo some experiments to estimate the extent of adsorption of CO_2 and CH_4.

One of the advantages of this process is that it can store CO_2 in the coal for years. Malaysia has taken seriously in handling the air pollution problem and readily invested on the possible solutions that can help in order to reduce the problem in becoming a fully developed nation by 2020 and avoid severe industrial pollution. One of the projects that Malaysia has invested is on the deforestation control which is now in the implementation stage together with the cooperation from other countries.

However in the initial stage of implementing this process, it cannot avoid in facing high cost for the new technology and equipment to be used as for instance; the pressure plays crucial role in the process in term of gas injection and gas collection. Realizing this matter, it can be said that, there is possibility for this process to be implemented in Malaysia if there is a strong financial support.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

CO_2 Sequestration has the possibility to be implemented in Malaysia as there are many ex coal mining area and newly –explored coal mines area especially in Sabah and Sarawak. Several experiments have been conducted to study on the suitable environment for this process to be implemented in Malaysia. Experiment 1 is to study on the comparison of the rate of CO_2 and CH_4 adsorption onto coal at specific temperature and particle size. Experiment 2 is to study on the effect of temperature variation on CO_2 adsorption for the similar particle size of untreated coal sample (30°C, 40°C, 50°C and 60°C). Then for Experiment 3, it is to check on the effect of pH variation on CO_2 adsorption for the similar particle size of coal sample at specific temperature (pH 2.4, 6.2 and 12). Then the experiment continues on the effect of different particle size (250µm and 1000µm) of untreated coal sample on CO_2 adsorption at specific temperature. The last experiment is more on the analysis of the metal components extracted by acid, distilled water and alkali in the filtered solution in Experiment 3.

From the experiments conducted, the following results are obtained. For temperature variation, the adsorption is low in higher temperature. For vary in pH, acidic coal (low pH) is preferable than alkali coal (high pH) for the adsorption to take place. Between two different particle sizes, the adsorption is higher in the smaller particle size. For vary in type of gas, it shows that CO_2 is has the highest adsorption onto coal compared to CH_4.

With these result obtained, the suitable environment for the sequestration of CO_2 onto coal can be considered. In the temperature dependence experiment, it shows that the temperature can seriously affect the sequestration capacity. High temperature favors less in adsorption and leads to the incompletely filled coal seams. Hence, to wait for a seam to cool caused the time constraint and eventually affects the cost of sequestration. In the pH dependence experiment, it can be assisted in considering adding or co-sequestering together with acid gasses so that it helps in increasing the pore volume of the coal sample. This will eventually help in overcoming the increasing cost of the sequestration process. However a lot of studies such as on the indication of the most suitable and effective gas and the possible chemical reaction must be conducted in future.

In the experiment to compare adsorption of CO_2 and CH_4, it shows that CO_2 is preferable to be adsorbed compared to CH_4. Thus it will come to the solution to overcome the cost of the whole process of sequestration. By injecting CO_2 it helps to desorp the existing CH_4 contains in the coal, here, by selling CH_4 it will reduce the cost of sequestration.

5.2 RECOMMENDATION

The recommendations are made based on several aspects in order to further complete the current research. There are several improvements that can be made on the experiment setup. The current experiment setup is only available to study on the trend of the rate of adsorption of each parameter variation. It is better to obtain the extent of adsorption of each parameter variation. This will help to enhance the study to the next step which is the modeling.

Therefore the improvements are recommended on the lab apparatus used. Currently the lab apparatus used is made of glassware which is obviously cannot withstand high pressure. For this experiment setup, the highest pressure that it can go is only 0.30kPa which is too low if it is to obtain the extent of adsorption of each parameter variation. Instead, it is only suitable if it is to recognize the trend of adsorption of each parameter variation. The suggestion is to have the apparatus that can be able to withstand the pressure at least more than 0.3kPa.

Although the experiment does not varies in pressure because of the same reason which is no suitable lab apparatus to be used, but even the experiment varies in other parameters, temperature for instance, the adsorption is still observed from the reduction of pressure indicated by digital manometer. If the amount of coal is too much with the small pressure injected onto it, thus logically there will be no excess of gas left to indicate the extent of adsorption. Thus it is difficult to indicate the difference of adsorption for each variation of parameters.

In order to enhance the research, there are several explorations of other aspects can be conducted such as the extent of adsorption for difference type of coal. Currently there is only one type of coal used for this research and it is obtained from Indonesia. It is assumed that the coal obtained form Indonesia is not varies much the coal in Malaysia. However several literature reviews has studied that the extent of adsorption is different for each type of coal collected from different area. Thus the research will become more complete if the sample coal is obtained locally from different area. The area suggested are the ones that have the potential for this process to be implemented there. For the initial start, the coal can be collected from the areas mentioned under the research. Additional recommendation is to study on the binding mechanism of CO_2 by coal where it can be further analyzed on the BET surface area of coal in order to determine on how much the area of the particular coal has be taken by CO_2. This can assist in explaining further on the effect of adsorption caused by every studied parameter.

Other than that is to improve further on experiment pH variation. The reason why acidic treated coal has the highest rate of adsorption compared to basic and neutral condition is that the total amount of metal compound extracted by acid is high compared to the other two. Although it is mentioned in the literature reviews but there is no specific experiment conducted is indicated. Thus for this research, HACH Water Analysis is used to analyze the metal compounds that is extracted by the solution. Unfortunately the reagent to study the metal compound is not readily available to analyze the intended metal compound such as Calcium, Magnesium and Aluminum. Therefore, this experiment is suggested to be done in the next study in order to strengthen the discussion part of the research. In addition to the equipment used, it is also recommended to use Atomic Absorption Spectrometers (AAS) and Ion Chromatograph (IC) for further verified analysis.

This process even though it is recognized as one of the possible way to reduce the concentration of excess CO_2 in the atmosphere, but it is also very costly since it deals a lot with pressure and pumping process. Therefore, the initial stage to overcome the cost of the process has been identified which is to recover CH_4 as CO_2 is injected onto the coal. However it is better if there are several alternatives to be considered in order to reduce the cost and make this process to be economically wise. For instance, the method used by several established companies where it is suggested that instead of focusing on how to reduce the operational cost, it is wiser to cut on the management cost. Thus, instead of implementing the project alone, it is more economically wise if it is done in term of business shares and cooperation from other companies where the cost and profits are shared together.

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APPENDICES

PENDIX A: Experiment Data on the study on the effect of temperature variation on CO_2 adsorption for the similar particle size of untreated

l sample (30°C, 40°C, 50°C and 60°C)

Time	Temperature Variation															
	Raw Data				Corrected Data				Reduction of Pressure (kPa)				Reduction of Pressure/wt coal sample (kPa/g)			
°C / min	30	40	50	60	30	40	50	60	30	40	50	60	30	40	50	60
0	16.04	15.25	16.09	14.56	16.09	16.09	16.09	16.09	0	0	0	0	0	0	0	0
2	13.32	13.25	14.14	12.21	13.37	14.09	14.14	13.74	2.72	2	1.95	2.35	0.00900215	0.00689655	0.00594911	0.0071212
4	11.72	12.11	12.69	10.74	11.77	12.95	12.69	12.27	4.32	3.14	3.4	3.82	0.01429753	0.01082759	0.01037281	0.0115758
6	10.58	11.16	11.54	9.51	10.63	12	11.54	11.04	5.46	4.09	4.55	5.05	0.01807049	0.01410345	0.01388126	0.015303
8	9.53	10.3	10.51	8.46	9.58	11.14	10.51	9.99	6.51	4.95	5.58	6.1	0.02154559	0.01706897	0.01702361	0.0184848
10	8.62	9.52	9.59	7.58	8.67	10.36	9.59	9.11	7.42	5.73	6.5	6.98	0.02455734	0.01975862	0.01983037	0.0211515
12	8	8.81	8.75	6.79	8.05	9.65	8.75	8.32	8.04	6.44	7.34	7.77	0.0266093	0.0222069	0.02239307	0.0235455
14	7.12	8.15	8.02	6.1	7.17	8.99	8.02	7.63	8.92	7.1	8.07	8.46	0.02952176	0.02448276	0.02462017	0.0256364
16	6.49	7.58	7.16	5.49	6.54	8.42	7.16	7.02	9.55	7.67	8.93	9.07	0.03160682	0.02644828	0.02724388	0.0274848
18	5.9	7.1	6.73	4.96	5.95	7.94	6.73	6.49	10.14	8.15	9.36	9.6	0.03355949	0.02810345	0.02855574	0.0290909
20	5.4	6.54	6.17	4.47	5.45	7.38	6.17	6	10.64	8.71	9.92	10.09	0.0352143	0.03003448	0.0302642	0.0305758
22	4.93	6.06	5.64	4	4.98	6.9	5.64	5.53	11.11	9.19	10.45	10.56	0.03676982	0.03168966	0.03188114	0.032

62	0.98	1.4	0.98	0.23	1.03	2.24	0.98	1.76	15.06	13.85	15.11	14.33	0.04984279	0.04775862	0.04609799	0.0434242
64	0.92	1.3	0.91	0.17	0.97	2.14	0.91	1.7	15.12	13.95	15.18	14.39	0.05004137	0.04810345	0.04631155	0.0436061
66	0.85	1.2	0.88	0.12	0.9	2.04	0.88	1.65	15.19	14.05	15.21	14.44	0.05027304	0.04844828	0.04640308	0.0437576
68	0.84	1.12	0.8	0.09	0.89	1.96	0.8	1.62	15.2	14.13	15.29	14.47	0.05030614	0.04872414	0.04664714	0.0438485
70	0.83	1.04	0.76	0.08	0.88	1.88	0.76	1.61	15.2	14.21	15.33	14.48	0.05033924	0.049	0.04676917	0.0438788
72	0.82	0.96	0.71	0.09	0.87	1.8	0.71	1.62	15.2	14.29	15.38	14.47	0.05037233	0.04927586	0.04692172	0.0438485
74	0.82	0.9	0.62	0.03	0.87	1.74	0.62	1.56	15.2	14.35	15.47	14.53	0.05037233	0.04948276	0.04719629	0.0440303
76	0.81	0.84	0.57	0	0.86	1.68	0.57	1.53	15.2	14.41	15.52	14.56	0.05040543	0.04968966	0.04734883	0.0441212

APPENDIX B: Experiment Data on the effect of pH variation on CO_2 adsorption for the similar particle size of coal sample at specific emperature (pH 2.4, 6.2 and 12).

pH Variation																
Time	**Raw Data**				**Corrected Data**				**Reduction of Pressure (kPa)**				**Reduction of Pressure/wt coal sample (kPa/g)**			
°C / **min**	**2.4**	**6.2**	**12**	**Untreated**	**2.4**	**6.2**	**12**	**Untreated**	**2.4**	**6.2**	**12**	**Untreated**	**2.4**	**6.2**	**12**	**Untreated**
0	15.32	14.81	13.8	15.69	15.7	15.69	15.69	15.69	0	0	0	0	0	0	0	0
2	13.63	13.25	11.98	11.88	14	14.13	13.87	11.88	1.69	1.56	1.82	3.81	0.01	0.0081	0.011	0.0254
4	12.38	11.85	10.75	10.99	12.8	12.73	12.64	10.99	2.94	2.96	3.05	4.7	0.0173	0.0153	0.018	0.031333
6	11.23	10.62	9.49	9.61	11.6	11.5	11.38	9.61	4.09	4.19	4.31	6.08	0.0241	0.0217	0.026	0.040533
8	10.2	9.54	8.45	9.01	10.6	10.42	10.34	9.01	5.12	5.27	5.35	6.68	0.0302	0.0273	0.032	0.044533
10	9.28	8.55	7.53	8.43	9.65	9.43	9.42	8.43	6.04	6.26	6.27	7.26	0.0356	0.0324	0.037	0.0484
12	8.43	7.67	6.69	7.92	8.8	8.55	8.58	7.92	6.89	7.14	7.11	7.77	0.0406	0.037	0.042	0.0518
14	7.67	6.88	5.94	7.42	8.04	7.76	7.83	7.42	7.65	7.93	7.86	8.27	0.0451	0.0411	0.047	0.055133
16	6.97	6.19	5.27	6.93	7.34	7.07	7.16	6.93	8.35	8.62	8.53	8.76	0.0492	0.0447	0.051	0.0584
18	6.36	5.56	4.67	6.48	6.73	6.44	6.56	6.48	8.96	9.25	9.13	9.21	0.0528	0.0479	0.054	0.0614
20	5.78	4.99	4.16	6.04	6.15	5.87	6.05	6.04	9.54	9.82	9.64	9.65	0.0562	0.0509	0.057	0.064333
22	5.24	4.48	3.67	5.59	5.61	5.36	5.56	5.59	10.08	10.3	10.13	10.1	0.0594	0.0535	0.06	0.067333

24	4.76	4	3.22	5.25	5.13	4.88	5.11	5.25	10.56	10.8	10.58	10.44	0.0622	0.056	0.063	0.0696
26	4.34	3.56	2.85	4.87	4.71	4.44	4.74	4.87	10.98	11.3	10.95	10.82	0.0647	0.0583	0.065	0.072133
28	3.94	3.19	2.51	4.52	4.31	4.07	4.4	4.52	11.38	11.6	11.29	11.17	0.067	0.0602	0.067	0.074467
30	3.56	2.84	2.21	4.19	3.93	3.72	4.1	4.19	11.76	12	11.59	11.5	0.0693	0.062	0.069	0.076667
32	3.25	2.53	1.94	3.9	3.62	3.41	3.83	3.9	12.07	12.3	11.86	11.79	0.0711	0.0636	0.071	0.0786
34	2.95	2.27	1.72	3.62	3.32	3.15	3.61	3.62	12.37	12.5	12.08	12.07	0.0729	0.065	0.072	0.080467
36	2.68	2.03	1.5	3.1	3.05	2.91	3.39	3.1	12.64	12.8	12.3	12.59	0.0745	0.0662	0.073	0.083933
38	2.45	1.79	1.31	2.86	2.82	2.67	3.2	2.86	12.87	13	12.49	12.83	0.0758	0.0675	0.074	0.085533
40	2.24	1.6	1.15	2.65	2.61	2.48	3.04	2.65	13.08	13.2	12.65	13.04	0.0771	0.0685	0.075	0.086933
42	2.04	1.43	0.99	2.45	2.41	2.31	2.88	2.45	13.28	13.4	12.81	13.24	0.0782	0.0693	0.076	0.088267
44	1.85	1.27	0.85	2.25	2.22	2.15	2.74	2.25	13.47	13.5	12.95	13.44	0.0794	0.0702	0.077	0.0896
46	1.66	1.1	0.76	2.07	2.03	1.98	2.65	2.07	13.66	13.7	13.04	13.62	0.0805	0.071	0.078	0.0908
48	1.53	0.97	0.66	1.89	1.9	1.85	2.55	1.89	13.79	13.8	13.14	13.8	0.0812	0.0717	0.078	0.092
50	1.4	0.82	0.57	1.74	1.77	1.7	2.46	1.74	13.92	14	13.23	13.95	0.082	0.0725	0.079	0.093
52	1.26	0.69	0.53	1.59	1.63	1.57	2.42	1.59	14.06	14.1	13.27	14.1	0.0828	0.0732	0.079	0.094
54	1.13	0.6	0.49	1.46	1.5	1.48	2.38	1.46	14.19	14.2	13.31	14.23	0.0836	0.0736	0.079	0.094867
56	1.01	0.54	0.43	1.33	1.38	1.42	2.32	1.33	14.31	14.3	13.37	14.36	0.0843	0.0739	0.08	0.095733
58	0.91	0.51	0.38	1.22	1.28	1.39	2.27	1.22	14.41	14.3	13.42	14.47	0.0849	0.0741	0.08	0.096467
60	0.82	0.49	0.33	1.09	1.19	1.37	2.22	1.09	14.5	14.3	13.47	14.6	0.0854	0.0742	0.08	0.097333

62	0.76	0.47	0.28	0.97	1.13	1.35	2.17	0.97	14.56	14.3	13.52	14.72	0.0858	0.0743	0.081	0.098133
64	0.68	0.44	0.23	0.89	1.05	1.32	2.12	0.89	14.64	14.4	13.57	14.8	0.0862	0.0745	0.081	0.098667
66	0.6	0.39	0.19	0.79	0.97	1.27	2.08	0.79	14.72	14.4	13.61	14.9	0.0867	0.0747	0.081	0.099333
68	0.55	0.35	0.17	0.71	0.92	1.23	2.06	0.71	14.77	14.5	13.63	14.98	0.087	0.0749	0.081	0.099867
70	0.49	0.29	0.13	0.64	0.86	1.17	2.02	0.64	14.83	14.5	13.67	15.05	0.0874	0.0752	0.081	0.100333
72	0.44	0.27	0.1	0.56	0.81	1.15	1.99	0.56	14.88	14.5	13.7	15.13	0.0877	0.0753	0.082	0.100867
74	0.38	0.22	0.09	0.5	0.75	1.1	1.98	0.5	14.94	14.6	13.71	15.19	0.088	0.0756	0.082	0.101267
76	0.36	0.19	0.07	0.45	0.73	1.07	1.96	0.45	14.96	14.6	13.73	15.24	0.0881	0.0758	0.082	0.1016
78	0.31	0.18	0.05	0.43	0.68	1.06	1.94	0.43	15.01	14.6	13.75	15.26	0.0884	0.0758	0.082	0.101733

APPENDIX C: Experiment Data on the effect of different particle size (250μm and 1000μm) of untreated coal sample on CO_2 adsorption at specific temperature

Particle Size								
Time	**Raw Data**		**Corrected Data**		**Reduction of Pressure (kPa)**		**Reduction of Pressure/wt coal sample (kPa/g)**	
oC / **min**	**1000μm**	**250μm**	**1000μm**	**250μm**	**250μm**	**1000μm**	**250μm**	**1000μm**
0	15.25	15.69	15.69	15.69	0	0	0	0
2	13.25	11.88	13.69	11.88	3.81	2	0.012344879	0.006666667
4	12.11	10.99	12.55	10.99	4.7	3.14	0.015228591	0.010466667
6	11.16	9.61	11.6	9.61	6.08	4.09	0.019699964	0.013633333
8	10.3	9.01	10.74	9.01	6.68	4.95	0.02164404	0.0165
10	9.52	8.43	9.96	8.43	7.26	5.73	0.023523313	0.0191
12	8.81	7.92	9.25	7.92	7.77	6.44	0.025175777	0.021466667
14	8.15	7.42	8.59	7.42	8.27	7.1	0.02679584	0.023666667
16	7.58	6.93	8.02	6.93	8.76	7.67	0.028383501	0.025566667
18	7.1	6.48	7.54	6.48	9.21	8.15	0.029841558	0.027166667
20	6.54	6.04	6.98	6.04	9.65	8.71	0.031267213	0.029033333
22	6.06	5.59	6.5	5.59	10.1	9.19	0.03272527	0.030633333

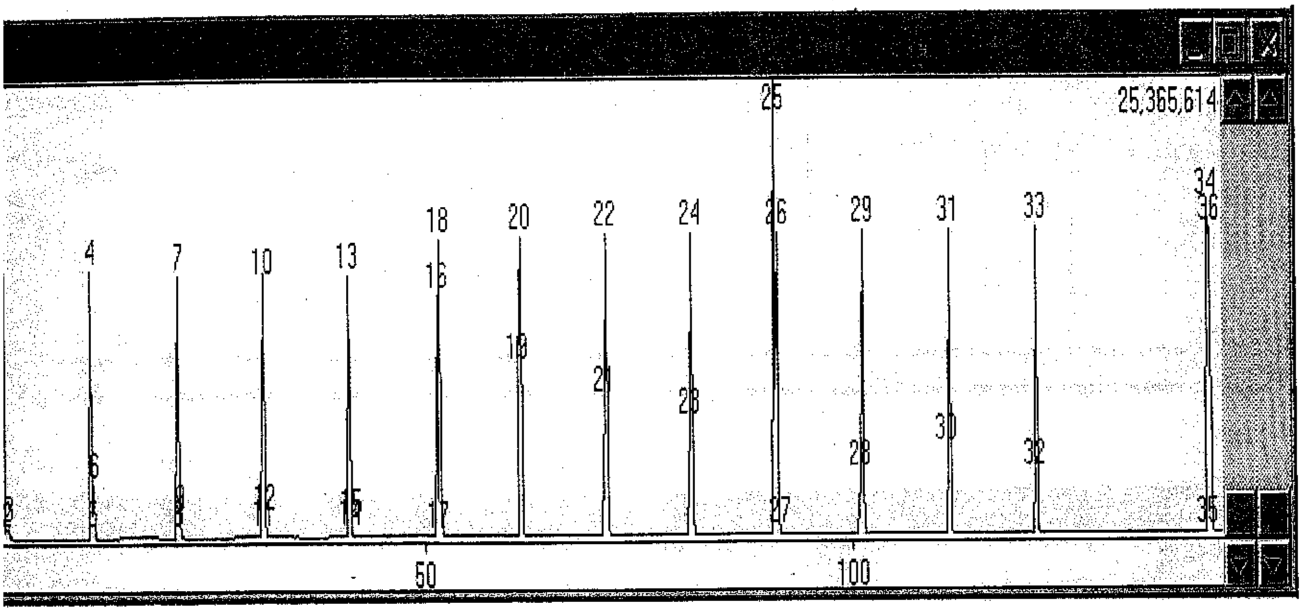
24	5.63	5.25	6.07	5.25	10.44	9.62	0.033826912	0.032066667
26	5.22	4.87	5.66	4.87	10.82	10.03	0.03505816	0.033433333
28	4.85	4.52	5.29	4.52	11.17	10.4	0.036192204	0.034666667
30	4.5	4.19	4.94	4.19	11.5	10.75	0.037261446	0.035833333
32	4.19	3.9	4.63	3.9	11.79	11.06	0.038201082	0.036866667
34	3.83	3.62	4.27	3.62	12.07	11.42	0.039108317	0.038066667
36	3.65	3.1	4.09	3.1	12.59	11.6	0.040793183	0.038666667
38	3.4	2.86	3.84	2.86	12.83	11.85	0.041570813	0.0395
40	3.14	2.65	3.58	2.65	13.04	12.11	0.042251239	0.040366667
42	2.93	2.45	3.37	2.45	13.24	12.32	0.042899264	0.041066667
44	2.74	2.25	3.18	2.25	13.44	12.51	0.04354729	0.0417
46	2.55	2.07	2.99	2.07	13.62	12.7	0.044130512	0.042333333
48	2.36	1.89	2.8	1.89	13.8	12.89	0.044713735	0.042966667
50	2.2	1.74	2.64	1.74	13.95	13.05	0.045199754	0.0435
52	2.06	1.59	2.5	1.59	14.1	13.19	0.045685773	0.043966667
54	1.9	1.46	2.34	1.46	14.23	13.35	0.046106989	0.0445
56	1.76	1.33	2.2	1.33	14.36	13.49	0.046528205	0.044966667
58	1.64	1.22	2.08	1.22	14.47	13.61	0.046884619	0.045366667
60	1.51	1.09	1.95	1.09	14.6	13.74	0.047305835	0.0458

62	1.4	0.97	1.84	0.97	14.72	13.85	0.047694651	0.046166667
64	1.3	0.89	1.74	0.89	14.8	13.95	0.047953861	0.0465
66	1.2	0.79	1.64	0.79	14.9	14.05	0.048277873	0.046833333
68	1.12	0.71	1.56	0.71	14.98	14.13	0.048537083	0.0471
70	1.04	0.64	1.48	0.64	15.05	14.21	0.048763892	0.047366667
72	0.96	0.56	1.4	0.56	15.13	14.29	0.049023102	0.047633333
74	0.9	0.5	1.34	0.5	15.19	14.35	0.04921751	0.047833333
76	0.84	0.45	1.28	0.45	15.24	14.41	0.049379516	0.048033333
78	0.82	0.43	1.26	0.43	15.26	14.43	0.049444318	0.0481

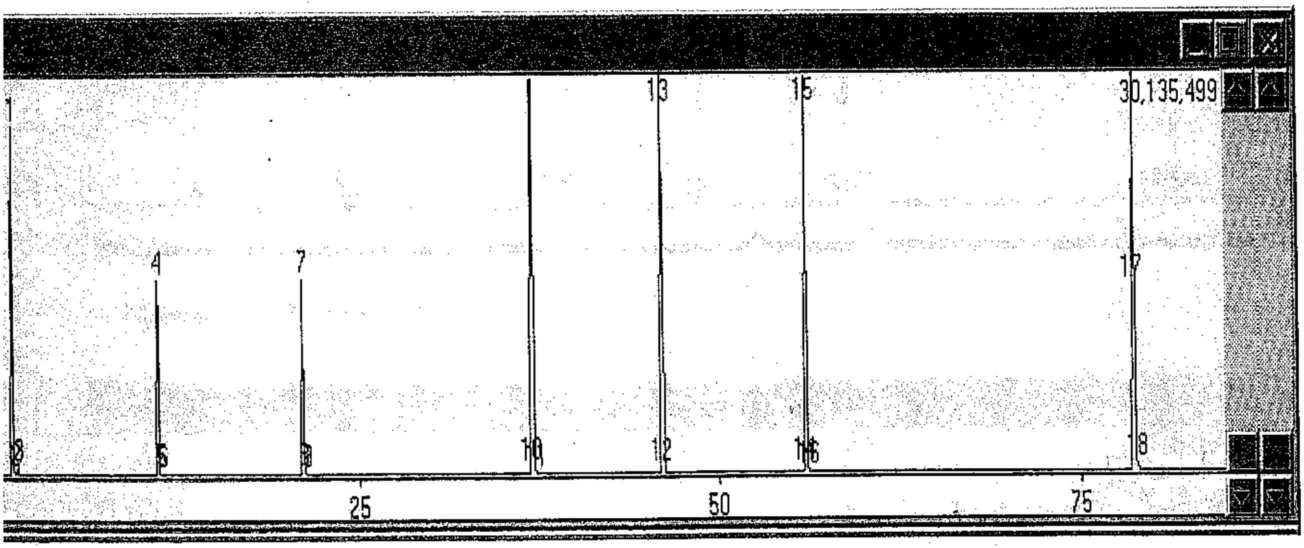
APPENDIX D

Data obtained from Gas Chromatograph

(i) Carbon dioxide

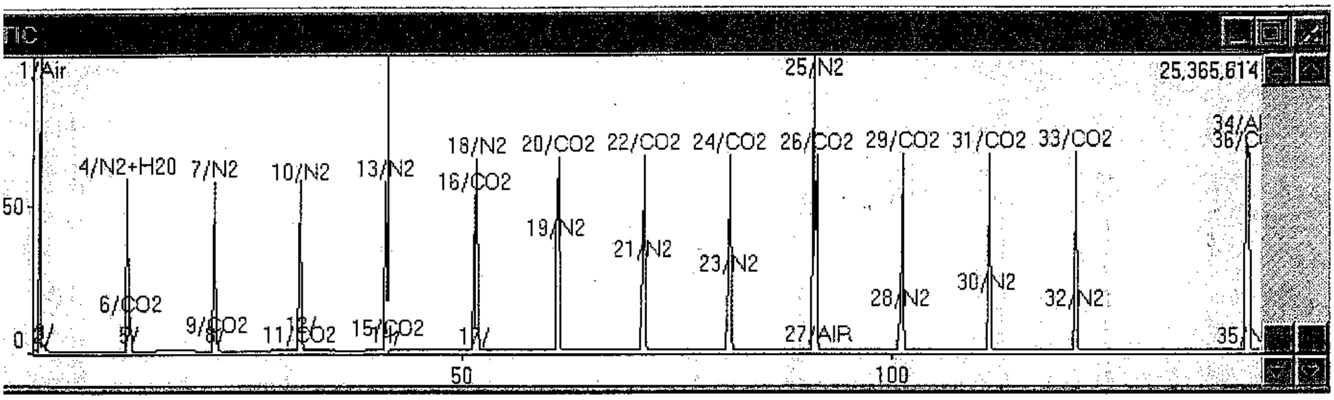


(ii) Methane

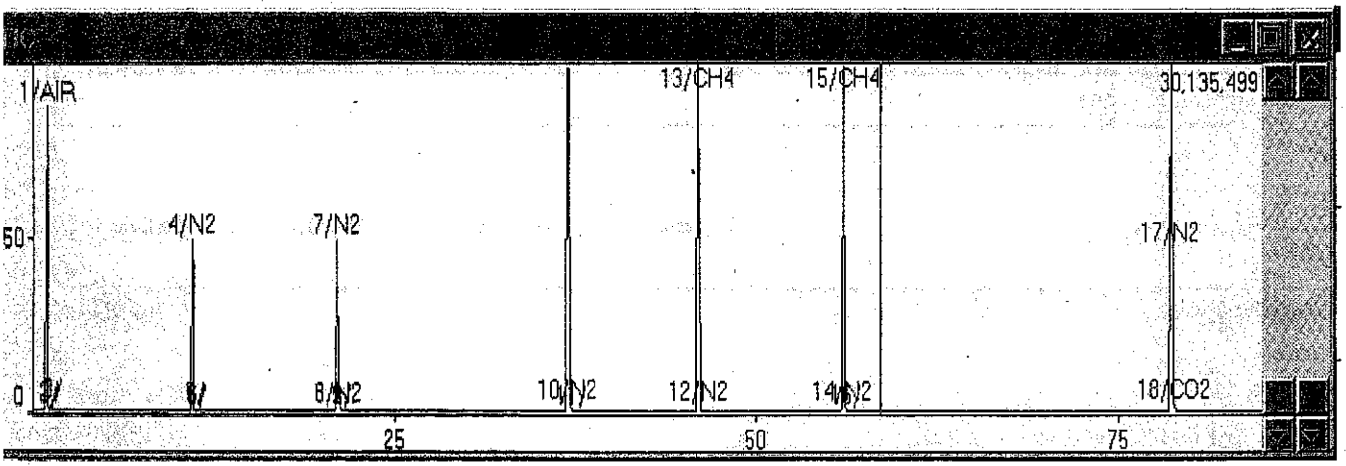


Data obtained from Gas chromatograph (Name of the component) (Width*Slope)

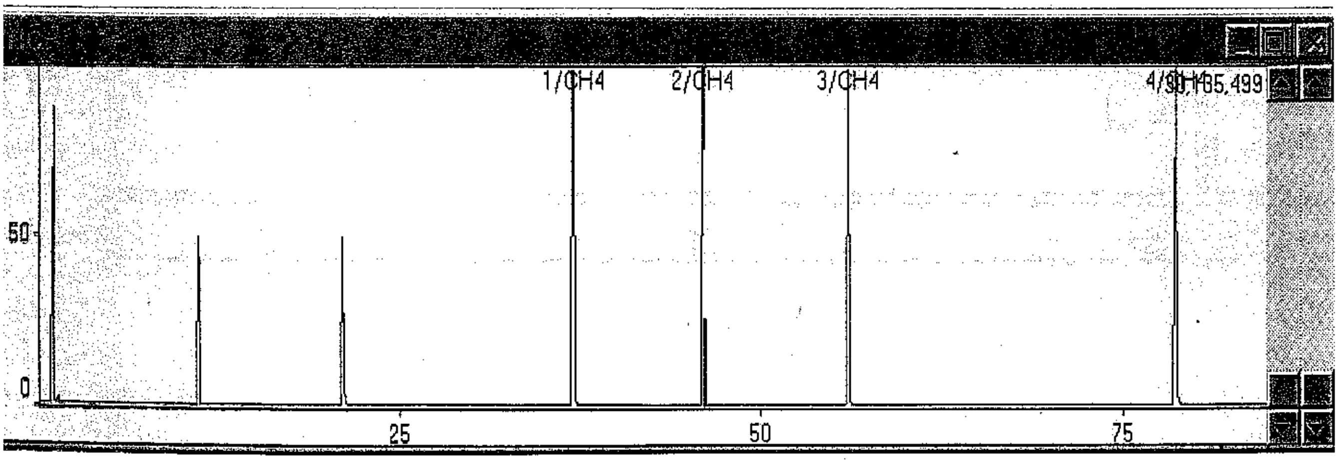
(i) Carbon Dioxide (3*1000)



(ii) Methane (2*800)

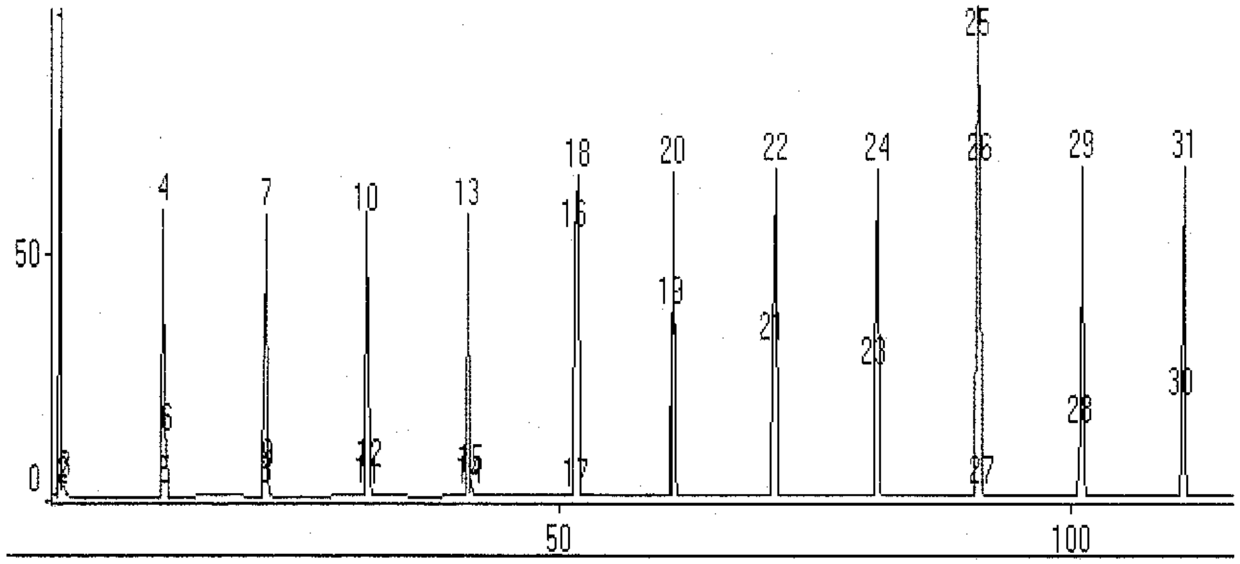


(iii) Methane (10*10000)

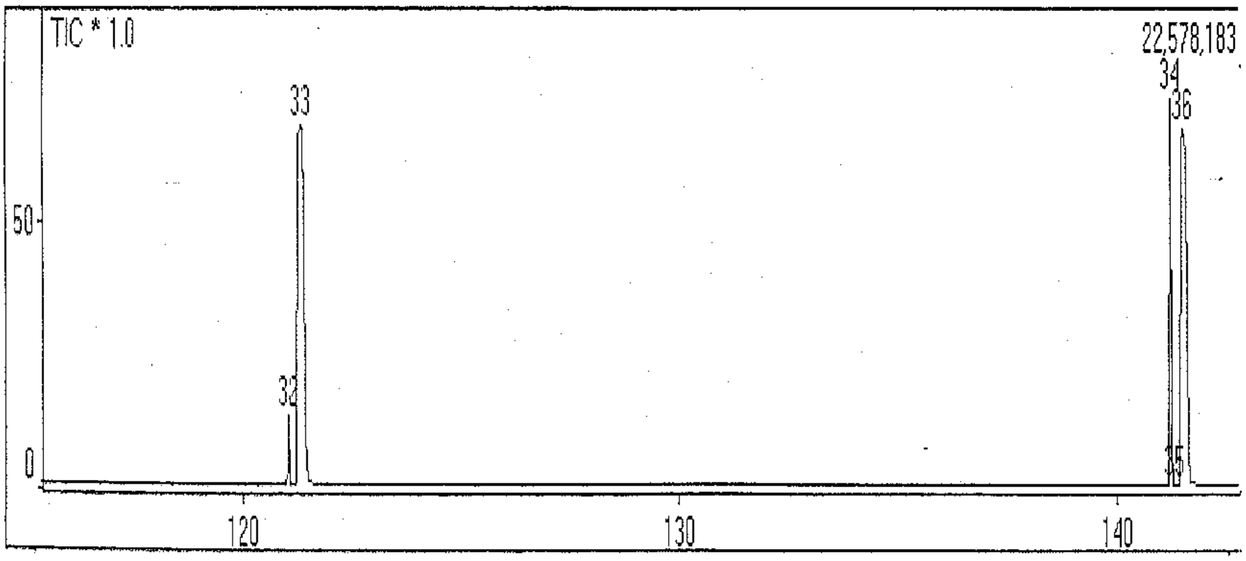


Carbon dioxide (3*1000)

(i) Flushing



(ii) Adsorption Experiment (period of 10 minutes)



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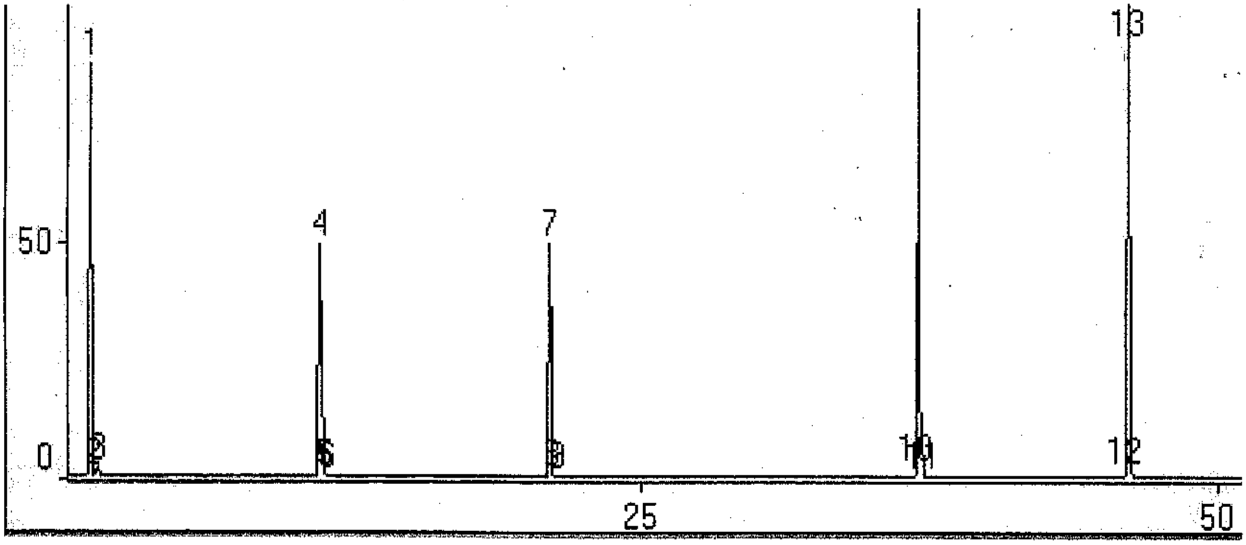
 SITI.D04  04/04/12 15:57:55
           : air - N2 (purge)
           :
or         : Mohd FAB
 File Name : SITI.MET

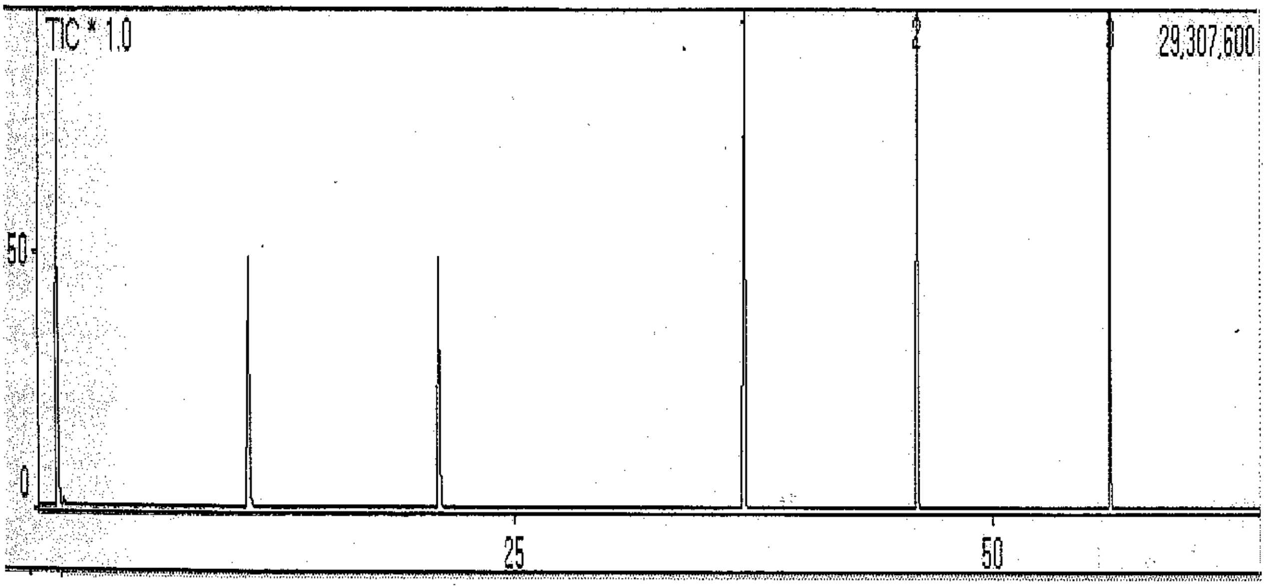
eak Report ****
 R.Time  I.Time - F.Time         Area      Height A/H(sec)    MK %Total Name
  1.027   0.983 -   1.433    66877869    25092080    2.665    S     4.43 Air
  1.158   1.142 -   1.225       72655       41859    1.736    T     0.00 N2+H2O
  1.356   1.333 -   1.425      444072      431098    1.030    T     0.03 CO2
 11.051  11.017 -  11.358    45385385    14556238    3.118    S     3.01 N2+H2O
 11.192  11.167 -  11.267       49854       38423    1.297    T     0.00 N2
 11.384  11.358 -  11.475     3478292     2883214    1.206     V    0.23 CO2
 21.059  21.033 -  21.467    45351258    14323467    3.166    S     3.00 N2
 21.192  21.175 -  21.267       55877       36617    1.526    T     0.00 H2O
 21.393  21.367 -  21.450     1145612     1027215    1.115    T     0.08 CO2
 31.033  31.008 -  31.442    45556734    14017030    3.250    S     3.02 N2
 31.183  31.167 -  31.258       64510       42671    1.512    T     0.00 CO2
 31.380  31.350 -  31.425      971727      963179    1.009    T     0.06 N2(MIX)
 41.040  41.017 -  41.433    47678633    14226023    3.352    S     3.16 N2
 41.171  41.158 -  41.258       82388       41249    1.997    T     0.01 CO2
 41.374  41.350 -  41.425      861019      737322    1.168    T     0.06
 51.551  51.533 -  51.625    13650506    13106264    1.042          0.90 CO2
 51.642  51.625 -  51.675       26290       19639    1.339     V    0.00 N2(MIX)
 51.838  51.675 -  52.242   127631612    16219076    7.869          8.45 N2
 61.055  61.025 -  61.125     7263315     9303228    0.781          0.48 N2
 61.344  61.283 -  61.708   127804164    16317371    7.832          8.46 CO2
 71.063  71.025 -  71.133     5625317     7462038    0.754          0.37 N2
 71.353  71.275 -  71.742   135136524    16455435    8.212          8.95 CO2
 81.052  81.025 -  81.117     5988989     6097629    0.982          0.40 N2
 81.340  81.275 -  81.742   130126718    16464511    7.903          8.62 CO2
 91.065  91.025 -  91.325    49823524    25005081    1.993          3.30 N2
 91.347  91.325 -  91.733    90664883    16482158    5.501    SV    6.00 CO2
 91.533  91.517 -  91.608       23129       19380    1.193    T     0.00 AIR
101.051 101.017 -101.100     3407282     3271121    1.042          0.23 N2
101.341 101.267 -101.725   130767380    16567865    7.893          8.66 CO2
111.062 111.042 -111.117     3890425     4549609    0.855          0.26 N2
111.352 111.283 -111.692   132782944    16641353    7.979          8.79 CO2
121.063 121.025 -121.125     2563068     3247508    0.789          0.17 N2
121.354 121.283 -121.717   135196113    16692043    8.099          8.95 CO2
141.234 141.192 -141.350    22486702    17963018    1.252    S     1.49 AIR
141.317 141.300 -141.342       19661       21227    0.926    T     0.00 N2
141.522 141.350 -141.858   126977924    16536373    7.679          8.41 CO2
---------------------------------------------------------------------------
al                         1509932348                             100.00
```

Methane (different integration of width and slope)

(i) Flushing (2*800)



(ii) Flushing (10*10000)



(iii) Adsorption (10*10000)