Development of Bentonite Based Solid Support for CO_2 Removal

by

Muhammad Faiz Bin Mohd Fudzaili

Dissertation submitted in partial fulfilment of
the requirement for the
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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Chemical Engineering Programme
UniversitiTeknology PETRONAS
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BACHELOR OF ENGINEERING (Hons)
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Approved by,

(Assoc. Prof. Dr. Mohd Azmi B Bustam @ Khalil)

UNIVERSITY TEKNOLOGI PETRONAS
TRONOH, PERAK
September 2011

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.

(Muhammad Faiz Bin Mohd Fudzaili)

ABSTRACT

It is well known that the main contributor of greenhouse gases is CO_2. The increasing CO_2 concentration in the atmosphere has resulted in a lot of research finding ways to slow down this trend. Established traditional technologies to capture CO_2 use aqueous amines. However there are drawbacks to this method thus much attention has been given to solid support. Bentonite clays have high cation exchange capacity, swelling capacity, high surface areas, and consequential strong adsorption/absorption capacities. Moreover, Bentonite clays are cheap and have been proved as a suitable candidate in removing organic compounds such as benzene form water. Thus, the objective of this research is to develop bentonite clay into becoming an adsorbent for CO_2. Bentonite clays on its own are not effective adsorbents for organic compounds thus modifications to the surface chemistry can be done to enhance its capabilities by changing the surface form hydrophilic to organophilic (hydrophobic). This type of clays called as organoclays can be synthesized by exchanging the metallic cations on the surface of bentonite clays such as Mg^{2+}, k^+ and Na^+ with organic cations. Organic cations such as Tetramethylammonium (TMA) and Hexadecyltrimethylammonium (HDTMA) have been used to synthesize organoclays and have used successfully to treat water. Thus intercalation of bentonite clay with N-cetyltrimethylammonium bromide (CTMB) cations was done. The RAMAN spectroscopy results showed that the CTMB cations were successfully intercalated into the clays. Results from Transmission Electron Microscopy (TEM) showed that the organo bentonites had increased its basal spacing from 9.72 to 14.03 Å. CO_2 Adsorption were conducted and results showed the organo bentonite had the ability to adsorb CO_2 but at relatively low amounts.

ACKNOWLEDGEMENT

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

It is well known that the main contributor of greenhouse gases is CO_2. The increasing CO_2 concentration in the atmosphere has resulted in a lot of research finding ways to slow down this trend. CO_2 capture has attracted attention due to the potential of trapping and sequestering large amounts of CO_2 into geological reservoirs. This enables us to continue use fossil fuels as our main source of energy as changing to other energy alternatives is not possible in the immediate future without causing disruptions to the world economy (Murlidhar Gupta, 2003). Established traditional technologies in capturing CO_2 include absorption by aqueous amines. However this type of technology is energy intensive and expensive due to the high energy requirements to regenerate the adsorbents as water has high heat capacities and the use of temperature swings during desorption of CO_2 (Murlidhar Gupta, 2003). Another drawback of amine based absorption is the large physical footprint as well as corrosive problems due to oxidation. Therefore a lot of research has been done to find alternatives and in recent years much attention has been given into adsorption. It is widely reported that activated carbons, zeolites (P. D. Jadhav, 2007), pillared clays, metal oxides and their surface modifications for CO_2 capture (Diôgo P. Bezerra · Ronan S. Oliveira ·, 2011). In this study Bentonite clay has been selected to study its capability as a solid support for CO_2 adsorption as there are no current data available describing the above.

1.2 Problem Statement

Currently, there are no reports showing the capabilities of Bentonite clays to be used as a solid support by intercalation with functional amine groups as an absorber for the adsorption of CO_2.

1.3 Objective

The objectives of the project are:

1. To synthesise bentonite based solid support for the separation of CO_2 using amine groups.
2. To study and evaluate the characteristics of the synthesised solid support.
3. To study on the capabilities of the organoclay for CO_2 adsorption.

1.4 Scope of study

1. To research and study the characteristics of bentonite clays.
2. To search for suitable amines to intercalated into bentonite clays for CO_2 adsorption.
3. To study the effect of amine intercalation on the characteristics of the bentonite clay.
4. To study the effect of the intercalated amine on the adsorption of CO_2.

1.5 Feasibility of the Project

The time period for the project is 2 semesters, which is approximately 8 month to complete the project. There are also budget given to the student to purchase chemicals and each student is given RM 500 each. The apparatus for the experiment is available in block 5, UTP. Overall, based on the time period, budget and experimental apparatus, it is feasible to do the project.

CHAPTER 2

LITERATURE REVIEW

2.1 Literature Review

One of the main debates of the 21st century is global climate change. Global climate change or global warming has no doubt influenced our environmental and energy policies. Global warming which is caused by the accumulation of greenhouse gases (GHGs) in the atmosphere traps heat radiated from the sun by blocking outward radiation. One of the main contributors of the GHGs is carbon dioxide or CO_2. According to Intergovernmental Panel on Climate Change (IPCC) prediction, the worldwide energy demands will increase by 50% thus the energy related CO_2 emissions will rise by 52% in 2030 (Metz, 2005). The main reason of increasing CO_2 released into the atmosphere is because of burning of fossil fuels. As energy requirements will rise ever so high it is evident that the CO_2 released will escalate even further.

The technological options for cutting CO_2 emissions to the atmosphere are (i) to reduce energy consumption by increasing efficiency, (ii) to switch to less carbon intensive fuels, (iii) to increase the use of renewable energy sources or nuclear energy, (iv) to capture CO_2 by enhancing the biological absorption capacity of forests and soils, and (v) to capture and store CO_2 chemically or physically. Among these major options that are aimed at reducing anthropogenic CO_2 emissions the capture and storage of CO_2 offers several advantages. This is because it provides the time needed for renewable energies to mature and bring costs down as well as pave for more advances in technology. This enables of cleaner uses of fossil fuels during the transition period.

The goal in reducing CO_2 emissions on an industrial scale is the development of low cost means of capturing CO_2. However there are several points that should be discussed as to determine what sort of material shall be used to capture CO_2. One, if any chemical that is used in a once-through manner to capture CO_2 is deployed it will rapidly exhaust the supply of that said chemical. Second, chemicals produced from CO_2 as a reactant will rapidly saturate global markets for the chemical. This means that the capture material must regenerable which translates to energy requirements for regeneration must be taken into consideration (Murlidhar Gupta, 2003).

2.1.1 Amine Solutions as Carbon Dioxide Removal System

Among the alternatives for CO_2 capture, chemical absorption with amine aqueous solutions was demonstrated as one of the most mature and less expensive technologies to be applied to power plants

To date, almost all commercial chemical plants in the world use processes based on chemical absorption with alkanolamines such as monoethanolamine (MEA) solvent to capture CO_2. However this type of technology is energy intensive and expensive due to the high energy requirements to regenerate the adsorbents as water has high heat capacities. Another drawback of amine based absorption is the large physical footprint as well as corrosive problems due to oxidation (Murlidhar Gupta, 2003).

Other limitation of using liquid amines to capture CO_2 is the solubility of CO_2 in the liquid amines itself. With high viscosity of liquid amines the amount CO_2 adsorbed can't be maximized. To increase the absorption the footprint of the liquid amines must be increased but this in turn will increase costs.

To overcome these disadvantages, several other separation technologies, such as, adsorption, membrane and cryogenic separation have been studied. Because of the low energy requirement, cost advantage, and ease of applicability over a relatively wide range of temperatures and pressures, adsorption separation attracts much interest. The main target for adsorption separation is to develop an adsorbent with high CO_2 adsorption capacity and high CO_2 selectivity

2.1.2 Adsorbent for CO_2 Removal

It is without a doubt that if the surface area of amines contacted with CO_2 can be increased the absorption of CO_2 will also increase. A new concept called "molecular basket" is being discovered to develop a high capacity, highly selective CO_2 adsorbent. A novel type of solid adsorbent can serve as a "molecular basket" for "packing" CO_2 in condensed form in the porous channels.

Capturing large amounts of CO_2 can be done by the adsorbent having large pore channels filled with a CO_2 capturing substance acting as the "basket". In order to cause the "basket" to be a CO_2 "molecular basket", a substance with affinity towards CO_2 should be loaded into the pores of the support and as a result, the CO_2 adsorption selectivity and CO_2 adsorption capacity can be increased.

This is due to the adsorbents having large surface areas thus increasing the exposed amines to CO_2 as opposed to liquid amines where a large foot print will be needed to achieve the same effect which is not economically feasible.

2.1.3 Bentonite clays

The prospect of higher capture capacities of amines supported on "molecular baskets" has caught the attention to the development of solid supports with the introduction of functional amine groups on the active sites of adsorbent. Adsorbents like activated carbon and silica gels have been studied for this purpose.

Bentonite clays in recent years have gathered much attention as a sorbent for capturing organic compounds due to its high cation exchange capacity, swelling capacity, high surface areas, and consequential strong adsorption/absorption capacities. Moreover bentonite clays are widely available and relatively cheap. This, in theory suggests it has a high potential in supporting amines in capturing more CO_2 due to the large surface area. Bentonite clays have been widely used as an adsorbent in wastewater treatment as well as for dye removal (T.S. Anirudhan, 2006) (Gre´gorio Crini , 2006) (Yun-Hwei Shen*, 2002) (S.S. Tahir, 2007). Thus it is evident that bentonite clays has the capability to be used an adsorbent.

It is due to the reasons above that for this study bentonite clay is selected to be used as a sorbent. Bentonite is a natural clay mineral under the smectites family that is found in many places of the world. Clays of volcanic origin that contains montmorillonite is referred to as bentonite. Bentonite clays are characterised by having two siloxane tetrahedral sheets sandwiching an aluminium octahedral sheet (T.S. Anirudhan, 2006). Because of an isomorphic substitution within the layers (for example, Al^{3+}replaced by Mg^{2+} or Fe^{2+} in the octahedral sheet and Si^{4+} replaced by Al^{3+} in the tetrahedral sheet), the clay layer is negatively charged, which is counterbalanced by exchangeable cations such as Na^+ and Ca^{2+} in the interlayer (Yun-Hwei Shen*, 2002). The layered structure of the clay facilitates expansion after wetting. The hydration of the inorganic/metallic cations Na^+ and Ca^{2+} at the exchange sites results in a hydrophilic environment at the clay surface. This property makes natural bentonite as an ineffective sorbent for organic compounds such as CO_2.

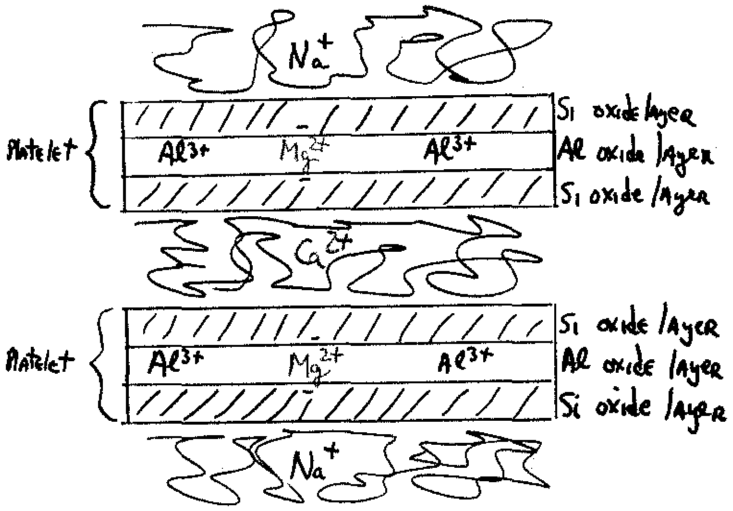

Figure 1: simple drawing describing the structure of bentonite clays

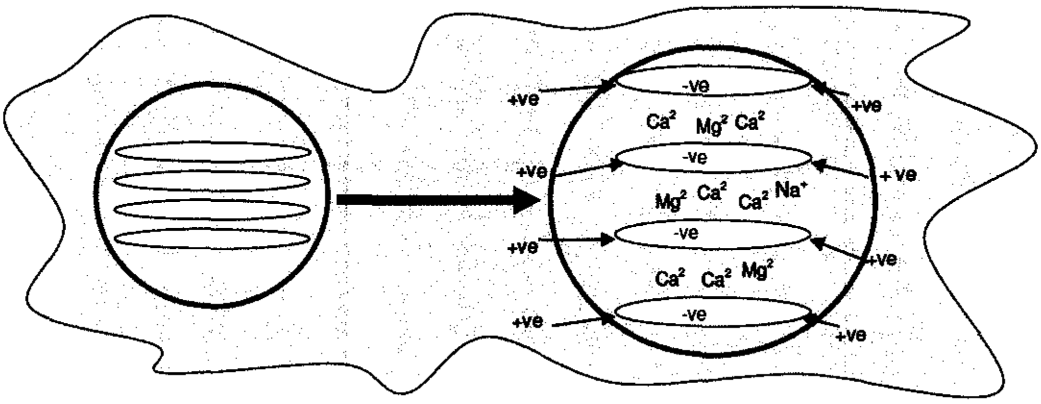

Figure 2: The negatively charged clay surface is balanced out by metallic cations

In 1969 a study was done on using montmorillonite without any modifications as adsorbent for CO_2 (L. A. G. Aylmore, 1970). The results obtained showed that little CO_2 was adsorbed on to the surface of montmorillonite. The ability of bentonite clays for sorption of organic molecules are greatly modified by replacing the exchangeable metallic cations with long chain or quaternary ammonium cations (Shmuel Yariv, 2002). The modified clays are commonly known as "organo-clays." Classification of organo-clays are divided into two with those saturated with large quaternary ammonium cations with one or two long alkyl chains and those saturated with small quaternary ammonium aliphatic and aromatic cations. The term "organophilic-clays" for the former and "adsorptive clays" for the later type are sometimes used by researchers (Shmuel Yariv, 2002).

2.2 Primary And Secondary Adsorption of Organic Matter

The replacement of metallic cations that is initially present at the exchange site of the clay by organic ammonium cations converts the clay into an organophilic (hydrophobic) clay that is capable of adsorbing polar and nonpolar molecules. The terms "primary adsorption" and "secondary adsorption" are used for the saturation of clay with organic cations (synthesis of organo-clays) and the adsorption of organic molecules by the modified clays respectively (Shmuel Yariv, 2002).

2.2.1 Organophilic Clays

One of the common ways of synthesizing effective organophilic clays is by replacing the metallic cations with quaternary ammonium cations of the type $[(CH_3)_3NR']^+$ or $[(CH_3)_3NR'R'']^+$, where R' and R" are aliphatic and aliphatic or aromatic substituents respectively (Shmuel Yariv, 2002). It is said that the adsorption of quaternary ammonium cation by cation exchange is independent of the pH of the system unlike the adsorption of primary, secondary, or tertiary ammonium cations which depend on pH of the system.

A study of the adsorption of several organic molecules by different clays treated with hexadecyltrimethylammonium (HDTMA) found that the adsorption of organic molecules such as benzene, naphthalene and bihenyl only increase relatively to the amount of adsorbed HDTMA. Another factor affecting adsorbability is relating basal spacing which depends on the charge density of the clay layers. Vermiculates treated with HDTMA had the highest charge resulting in a basal spacing of 2.8 nm shows alkyl-benzenes were preferably adsorbed while other smectites treated with HDTMA showed lower basal spacing of 1.37nm till >2.2nm had lower adsorption of alkyl-benzenes (Shmuel Yariv, 2002). It is concluded that the secondary adsorption of "organophilic-clays" for nonpolar molecules or molecules of low polarity increases with (1) increasing amounts of primary adsorbed organic ions, (2) increasing basal spacing.

2.2.2 Adsorptive Clays

Another method of adsorbing organic molecules is by using "adsorptive clays". The mechanism of the secondary adsorption by smectites saturated with small quaternary ammonium cations such as tetramethylammonium (TMA^+), tetraethylammonium (TEA^+), or trimethylphenylammonioum ($TMPA^+$) differs from smectites saturated with long chain quaternary ammonium cations ("organophilic-clays"). These smectites are characterized by their ability to adsorb various non-ionic organic compounds form water. The adsorption efficiencies are dependent on the size of the organic cation, the clay layer charge affect, the surface area and pore structure of the organoclays (Shmuel Yariv, 2002).

The ammonium cations play the role of pillars in these organoclays by holding the layers permanently apart without filling all the interlayer space preserving the distance between layers. Basal spacing of dehydrated montmorillonite increases from 0.95 nm to 1.36 nm and 1.40 nm after primary adsorption of TMA^+ and TEA^+ respectively (Shmuel Yariv, 2002). In the secondary adsorption the nonpolar molecules (for example CO_2) penetrate into the expended space between the pillars resulting on the sorption capacity greatly enhanced. These nonpolar molecules are not intercalated in the parent montmorillonite.

2.2.3 Homoionic Clays

It is reported that the adsorption of vapours are more effective by using TMA-clay than TMP-clays as TMA-clays has more surface area. Another way of increasing the surface area is by choosing the appropriate type of montmorillonite. It was discovered that more than 95% of the available sodium ions could be exchanged with quaternary ammonium cations (Z. Zhong Zhang, 1993). Potassium, on the other hand, was replaced at only 70-75% of the sites. This indicates that sodium montmorillonite was the preferred raw material. The sorption of quaternary amines on K-montmorillonite was generally less than that on Na-montmorillonite, probably due to the inability of amines with shorter alkyl chains to replace the tightly-held K^+ ions on clays (Z. Zhong Zhang, 1993).

CHAPTER 3

METHODOLOGY

3.1 Research Methodology

Research work

1. Study on bentonite.
2. Determine type of amine to be intercalated.
3. Determine the procedures to prepare organo bentonite.

Laboratory work

1. Characterisation of bentonite sample.
2. Preparation of Mg-bentonite
3. Characterisation of Mg-bentonite
4. Preparation of CTM^+ intercalation into bentonite clay
5. Characterisation of CTMB-bentonite

Data Interpretation

1. XRD analysis.
2. TEM analysis.
3. BET analysis.
4. RAMAN/FTIR analysis.

3.2 Methodology

The chemicals, equipment and tools required for this research are:

3.2.1 Chemicals

Chemicals required:

1. N-cetyltrimethylammonium bromide (CTMB), $C_{19}H_{42}BrN$
2. Magnesium chloride hexahydrate, $MgCl_2 \cdot 6H_2O$
3. Bentonite clay

3.2.2 Equipment/Tools

1. Fourier Transform Infrared Spectroscopy (FTIR)or
2. RAMAN spectroscopy.
3. BET Surface Area Analyser.
4. Transmission Electron Microscope (TEM).
5. X-ray diffraction (XRD).

3.3 Experiment Methodology

3.3.1 Preparation of Mg-Bentonite (homoionic-bentonite)

Homoionic bentonites were prepared by using suspensions of the clay (20 g) in magnesium chloride solutions 1 M. The mixtures were stirred overnight at 80 °C, to activate the ion exchange reaction. The resulting suspension was centrifuged and the supernatant discarded. This procedure was repeated several times and the excess salt is removed by washing repeatedly with distilled water until a negative $AgNO_3$ test. The product thus obtained is dried overnight at 80°C and converted into powder.

3.3.2 Preparation of Supported CTMB-Bentonite

Salt solutions of N-cetyltrimethylammonium bromide (0.1 M) at 250 mL were prepared and 5 g of Mg-Bentonite were added. The mixture is well stirred for 4 hrs.The resulting suspension is centrifuged and the supernatant discarded. The procedure is repeated several times with the clay being washed by centrifugation process using acetone: distilled water solution (9:1) to remove the excess ammonium cations adsorbed on the external surface of the clay till the washing solution is free from chloride ions. The washed clay is then dried overnight (80 °C) and made into powder.

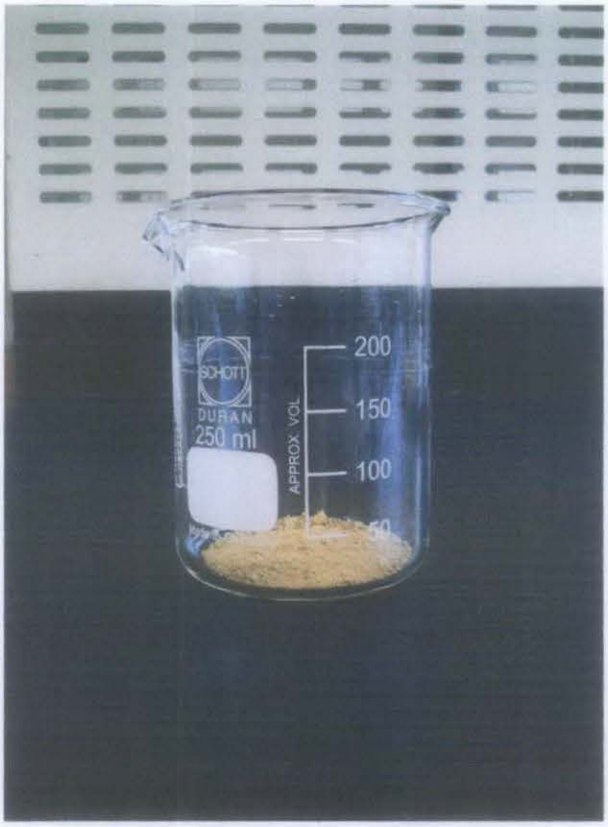

Figure 3: 5 g of Mg-Bentonite

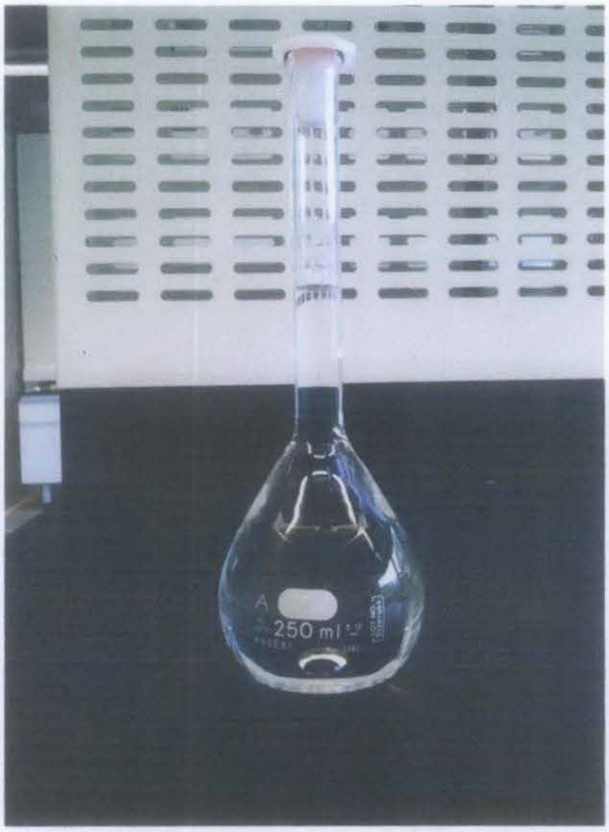

Figure 4: 250 mL of 0.1 M N-cetyltrimethylammonium bromide salt solution

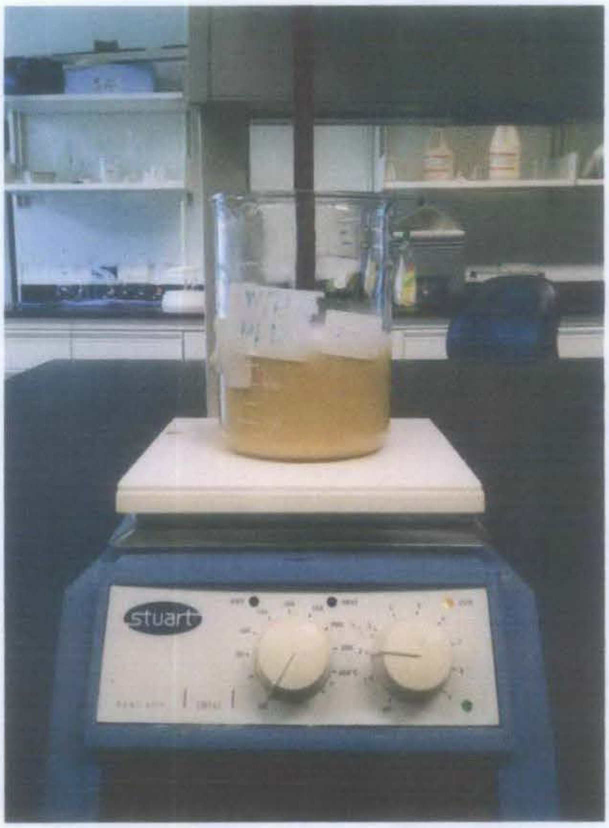

Figure 5: The mixture is stirred for 4 hours

3.3.3 Research Analysis/Characterization

The analysis that required in this research are:

1. RAMAN Spectroscopy.
2. BET Surface Area Analyser.
3. Transmission Electron Microscope (TEM).
4. X-ray diffraction (XRD).

3.3.4 Experimental Analysis for CO_2 adsorption

Solubility test will be conducted to measure the capturing capability of the CTMB-Bentonite clay. In brief, the sorption chamber is flooded with carbon dioxide from a gas cylinder and its pressure is manipulated. The mole of CO_2 absorbed by the CTMB-Bentonite can be calculated using ideal gas law, PV=ZnRT. The mole fraction versus time and mole fraction versus pressure was prepared and will be discussed in the result and discussion section. The procedures of CO_2 absorption test and setup are as shown below.

Figure 6: CO_2 adsorption shell

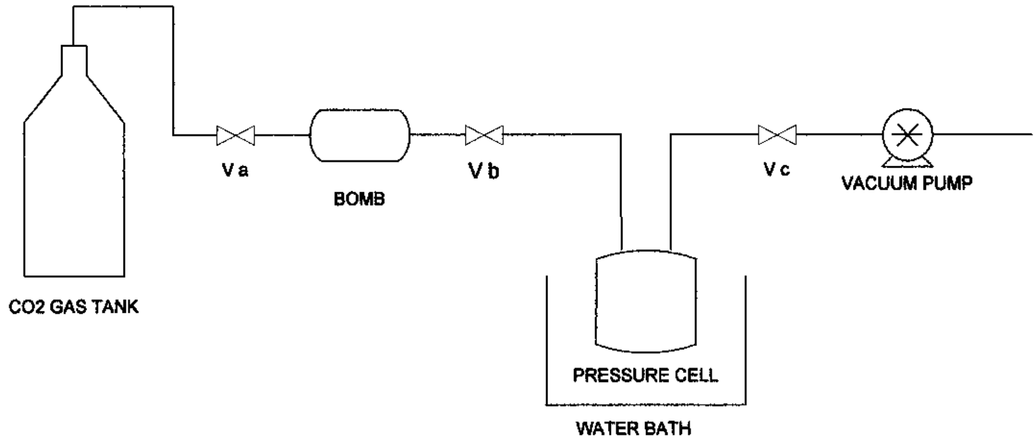

Figure 7: Schematic diagram of CO_2 adsorption test setup

Procedure:

1. Make sure Va, Vb and Vc are close tightly.

2. Open the regulator valve on the CO_2 gas tank.

3. Open Va until the desire pressure are achieved. Release pressure by opening Vb.

4. Insert the pressure cell with the CTMB-Bentonite clay.

5. Open Vb and start recording for 3 hours.

6. After 3 hours stop the timer and close Vb. The release slowly valve Vc and start the vacuum pump.

3.3.5 Calculation for Mole Fraction of CO_2 in CTMB-Bentonite

The amount of CO_2 gas is determined by the Ideal Gas Law. It is a good approximation for the behaviour of many gases under many conditions. The ideal gas law is a good approximation since the compressibility factor is assumed to be close to unity. The ideal gas law is as shown below

$$PV=ZnRT$$

Where

P is the absolute pressure of the gas (Pa)

Absolute Pressure = Gauge Pressure + Atmospheric Pressure

V is the volume of the gas (m^3)

Z is the compressibility factor, which depends on the temperature and pressure (dimensionless)

n is the amount of substance of the CO_2 gas (mol)

R is the gas constant (8.314 $JK^{-1}mol^{-1}$)

T is the absolute temperature (K)

The volume of CO_2 introduced into the system,

$$P_1V_1 = P_{initial}V_{initial}$$

The number of moles of CO_2 introduced into the system n_1 is calculated using ideal gas law.

$$n_1 = P_1V_1/RT$$

Number of moles of CO_2 gas that is absorbed into the ionic liquids, $n_{adsorbed}$ is calculated using the following equation.

$$P_1V_1/Z_1n_1 = P_2V_2/Z_2n_2$$

$$n_{adsorbed} = n2 - n1$$

Mole fraction of CO_2 absorbed, x_{CO2} is calculated using the following equation.

$$x_{CO2} = (n_{adsorbed} / na_{dsorbed} + n_{IL})$$

3.4 Project Timeline

Final Year Project 1

Table 1: FYP 1 Project Timeline

No.	Detail/ Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1	Selection of Project Topic	■	■						Mid-semester break							
2	Preliminary Research Work		■	■	■	■										
3	Submission of Extended Proposal Defence						●									
4	Proposal Defence									■	■					
5	Project work continues											■	■	■		
6	Submission of Interim Draft Report														●	
10	Submission of Interim Report															●

The important key milestone of this semester project is the submission of extended proposal defence, proposal defence and Interim Report.

Final Year Project 2

Table 2: FYP 2 Project Timeline

No.	Detail/ Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14	15
1	Project Work Continues	■	■	■	■	■	■	■	Mid-Semester Break								
2	Submission of Progress Report									●							
3	Project Work Continues									■	■	■	■	■			
4	Pre-EDX												●				
5	Submission of Draft Report													●			
6	Submission of Dissertation (soft bound)														●		
7	Submission of Technical Paper														●		
8	Oral Presentation															●	
9	Submission of Project Dissertation (Hard Bound)																●

The Key milestone for FYP 2 will be performing the experimental work and achieving the adsorption data for CO_2 in impregnated bentonite with AEPD and MEA and to submit the project dissertation at the end of week 15.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Powder X-Ray Diffraction

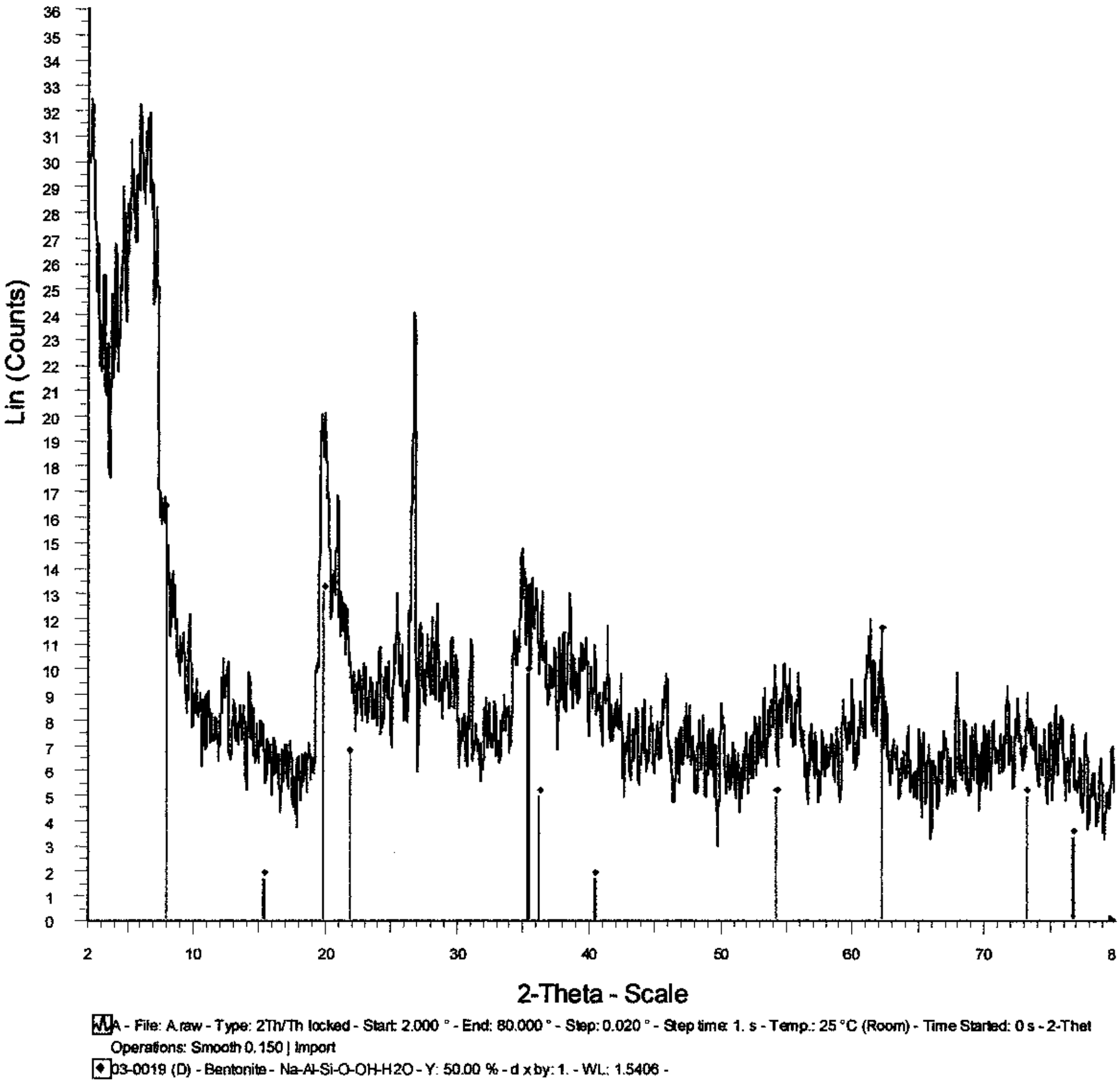

Figure 8: XRD pattern of Bentonite

The qualitative XRD analysis of bulk samples indicates the bentonite clay as bentonite.

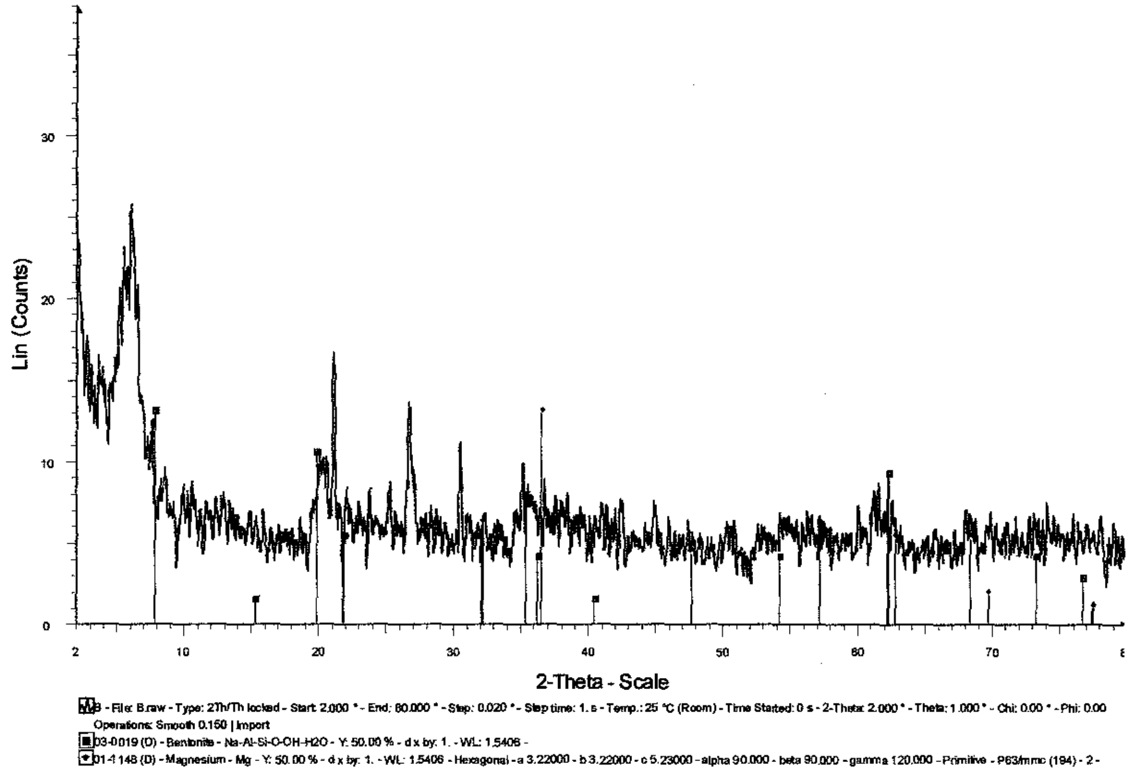

Figure 9: XRD pattern of Treated Mg-bentonite

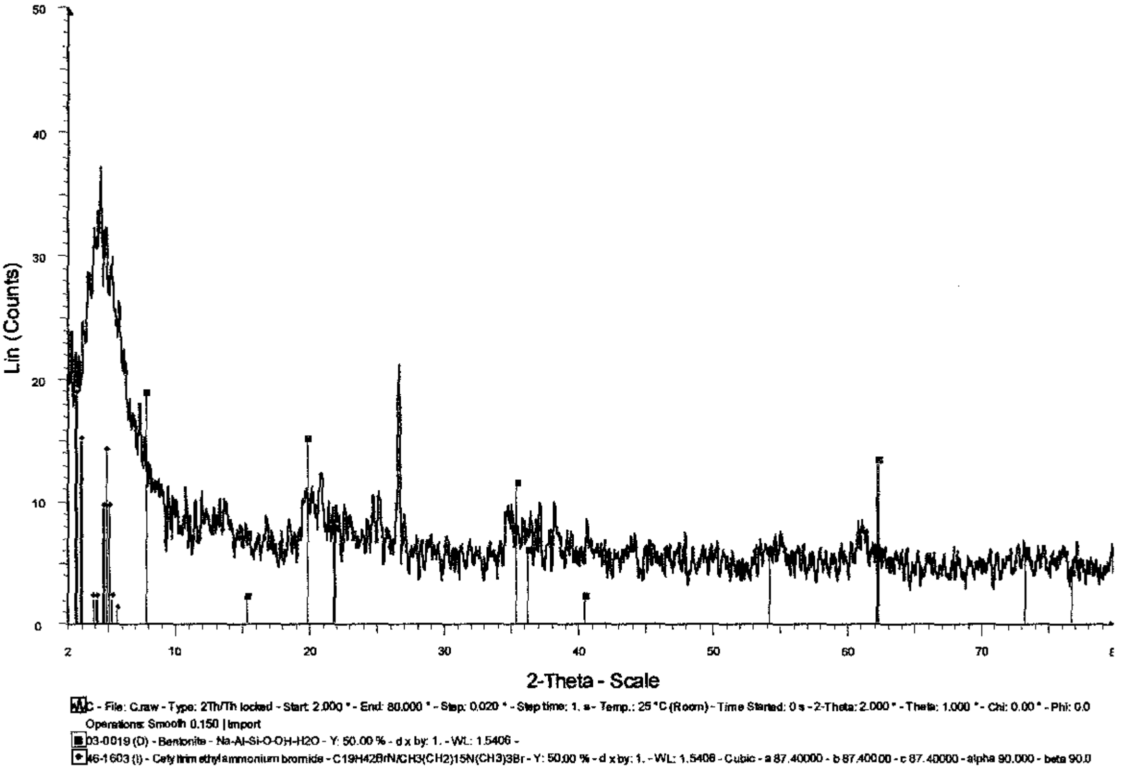

Figure 10: XRD pattern of synthesized CTMB-Bentonite

4.2 RAMAN Spectroscopy

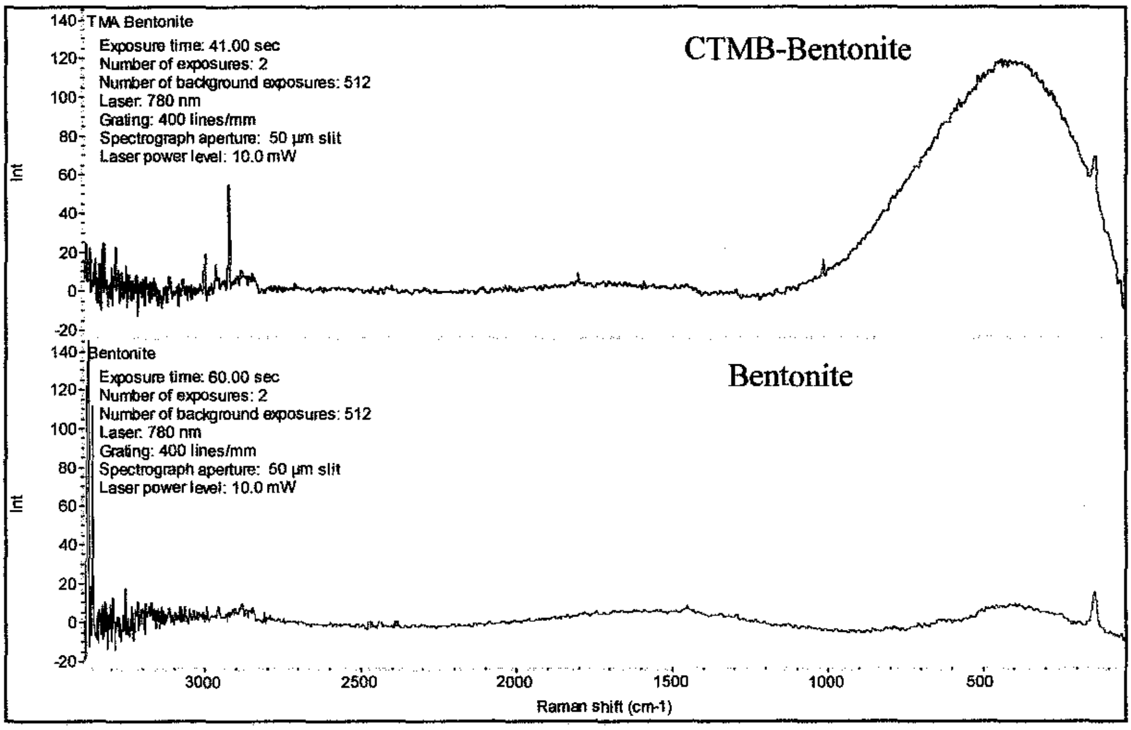

Figure 11: RAMAN spectra of original Bentonite and modified CTMB-Bentonite

The results of bentonite and bentonite intercalation with CTMB were evaluated by means of RAMAN spectroscopy. The IR spectra of the pure CTMB salts helped to better distinguish the visible absorption band in spectra of the modified bentonite (Jianxi Zhu, 2005). The stretching vibrations the C–H bonds occurring in the 2900 - 3000 cm^{-1} region reflect C_{19} chains of CTMB compounds. The adsorption band at 2900 - 3000 cm^{-1} corresponds to CH_2 stretching (Zuzana NAVRÁTILOVÁ, 2007). It is evident that CTMB cations are present in the modified bentonite. The huge peak on the right of the CTMB bentonite can be attributed to noise.

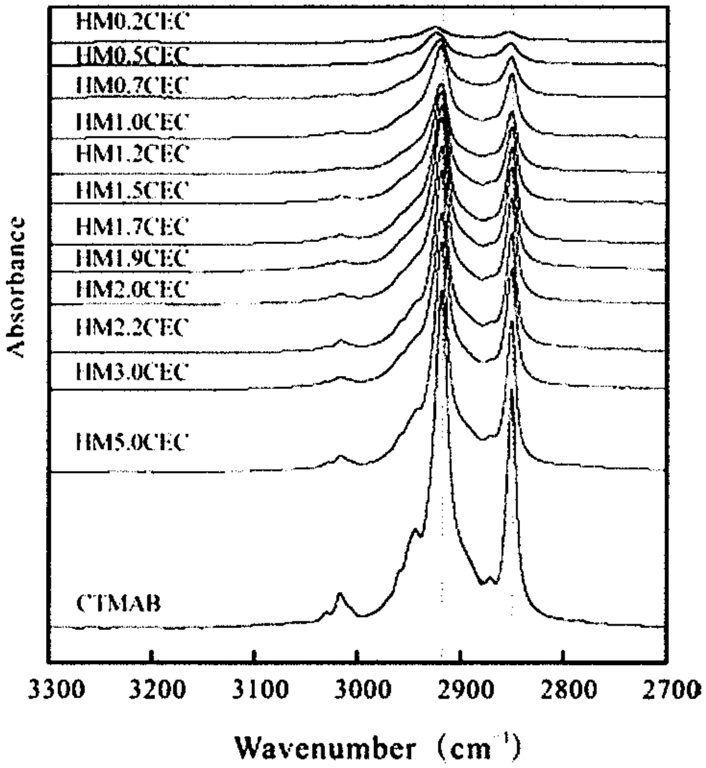

Figure 12: FTIR spectra of CTMB-Montmorillonite

A comparison was also done with a CTMB intercalated montmorillonite. The FTIR spectra of CTMB and surfactant-intercalated montmorillonite are shown in Figure 12 displays the C-H stretching vibration of the infrared spectrum (3300–2700 cm^{-1}) of the CTMB montmorillonite hybrid with different surfactant loading levels. The bands at ~2920 and ~2850 cm^{-1} correspond to the CH_2 stretching which is similar to our results (Jianxi Zhu, 2005).

4.3 Surface Area Analysis

The nitrogen adsorption isotherms of Bentonite, Mg-Bentonite and CTMB-Bentonite are shown in Figure 13, Figure 14 and Figure 15 respectively. The surface area, pore volume and average pore diameter were 85.7717 m²/g, 0.114 cm^3/g and 7.88 nm respectively. After preparing homoionic form of bentonite, the pores were partially filled with Mg, further restricting the access of nitrogen into the pores at liquid nitrogen temperature. The residual pore volume of Mg-Bentonite is 0.112 cm^3/g while the surface area is estimated to be 103.2646 m^2/g and the average pore diameter was smaller at 5.76 nm.

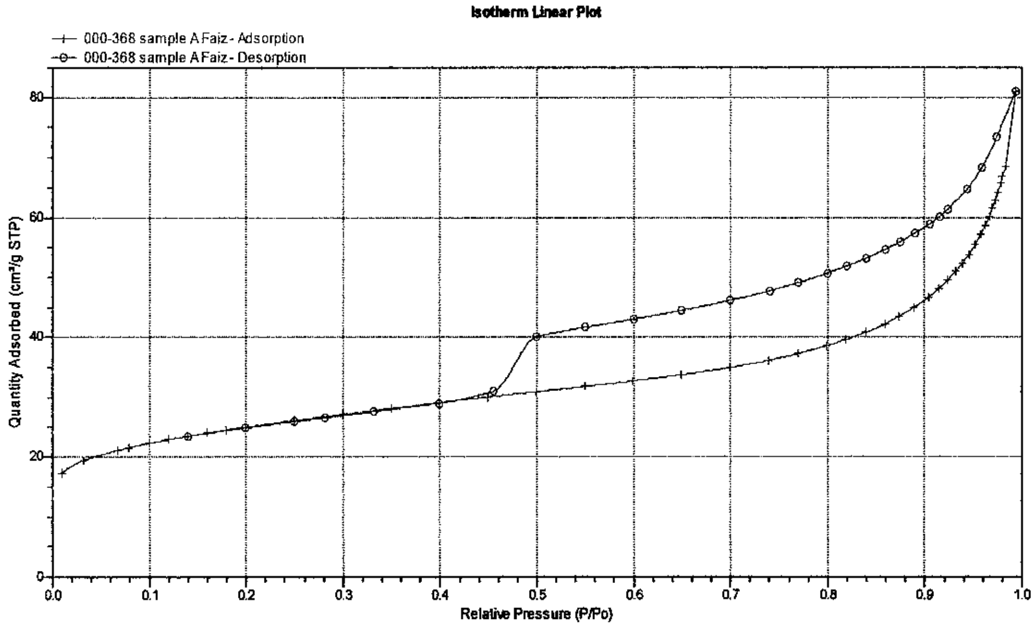

Figure 13: Nitrogen isotherm adsorption and desorption of Bentonite

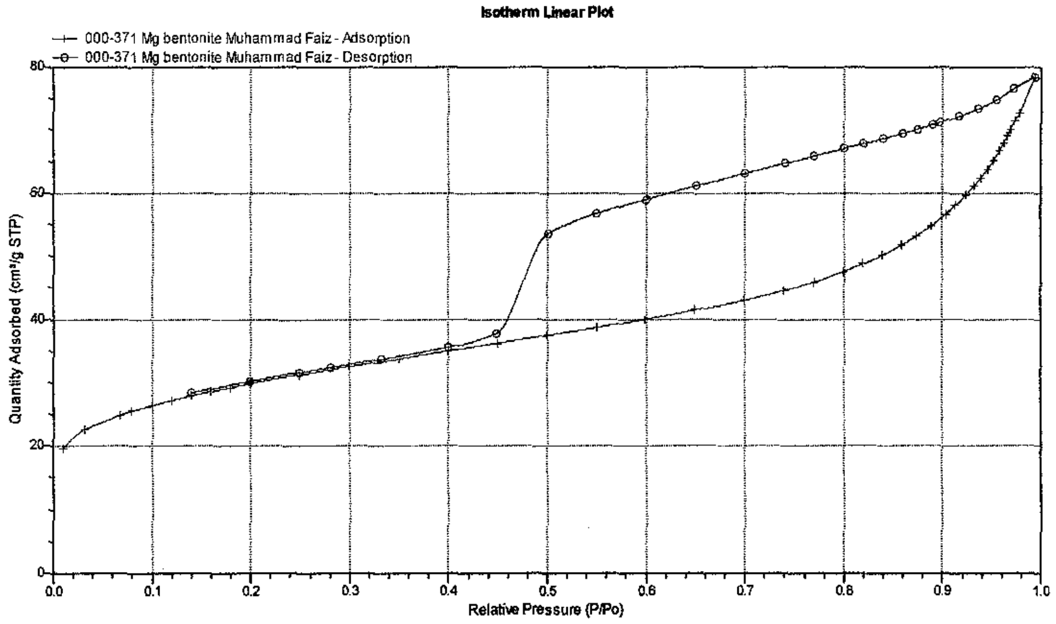

Figure 14: Nitrogen isotherm adsorption and desorption of Mg-Bentonite

In the physical properties characterization, the surface area and pore structure of bentonite and Mg-Bentonites before and after modification by amines were characterized using N_2 adsorption at 573 K. The nitrogen adsorption isotherms over the whole relative pressure for Mg-bentonite are shown in Figure 14. The abrupt increase of N_2 adsorption at relative pressure (P/P0 ~ 0.45) occurs because N_2 molecules are able to penetrate freely into the pores of bentonite without steric factor which capillary condensation and multilayer adsorption starting to occurs. Table 3 lists complete physical properties for the bentonites pore volume and pore diameter.

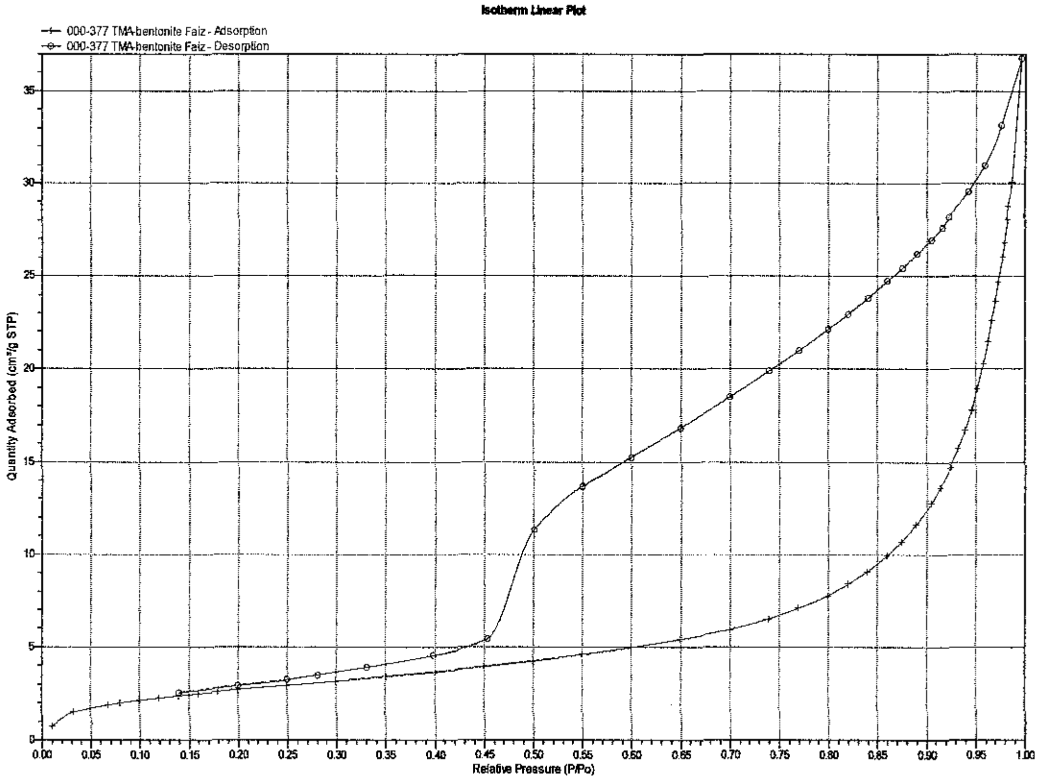

Figure 15: Nitrogen isotherm adsorption and desorption of CTMB-Bentonite

Table 3: Summary of N_2 adsorption properties for Bentonite Treated bentonite and amine modified bentonite

Properties	BET surface area (m^2/g)	Pore Volume (cm^3/g)	Average Pore Diameter (nm)
Bentonite	85.7717	0.114	7.88
Mg-Bentonite	103.2646	0.112	5.76
CTMB-Bentonite	10.4244	0.057	12.51

4.4 TEM Analysis

Transmission Electron Microscopy (TEM) images of the clays prepared using the ultrasonic and hydrothermal routes have been obtained. TEM permits the direct observation of microstructural features resulting from the transformation of clays to organoclays.

Unlike untreated Bentonite, both Mg-Bentonite and CTMB-Bentonite show very clear layer structures (Figure 7 and 8), and the *d*(001) basal spacing are 9.72 to 14.30 Å. In some places, there are some curved layers for both in the same samples. Meanwhile, some very large basal spacing can be observed as shown in Figure 18, but they are not prevalent.

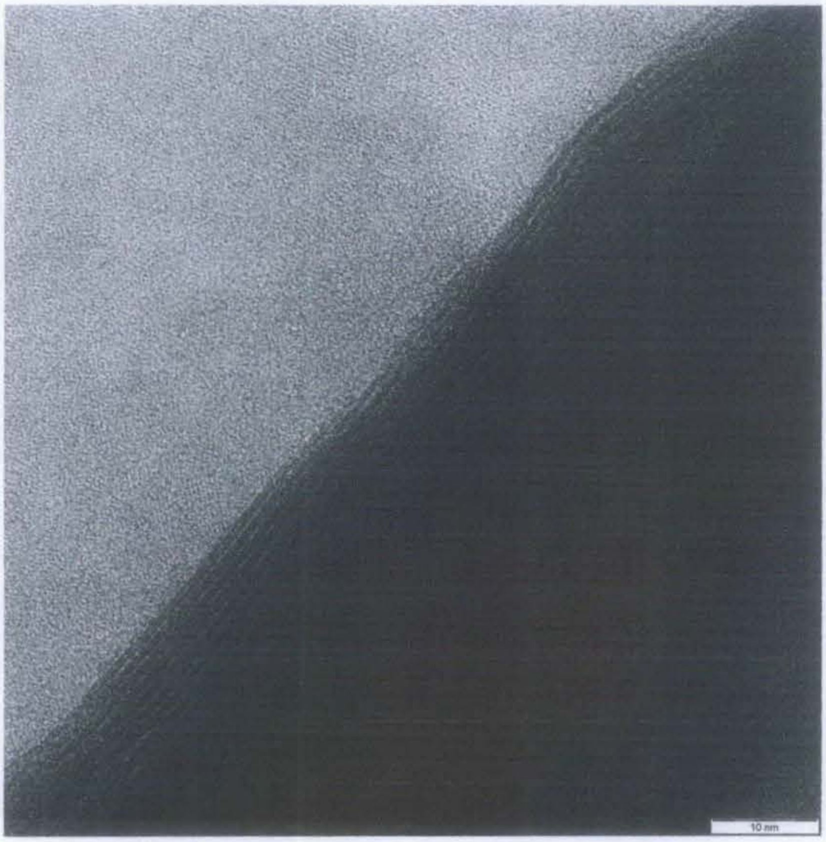

Figure 16: Bentonite

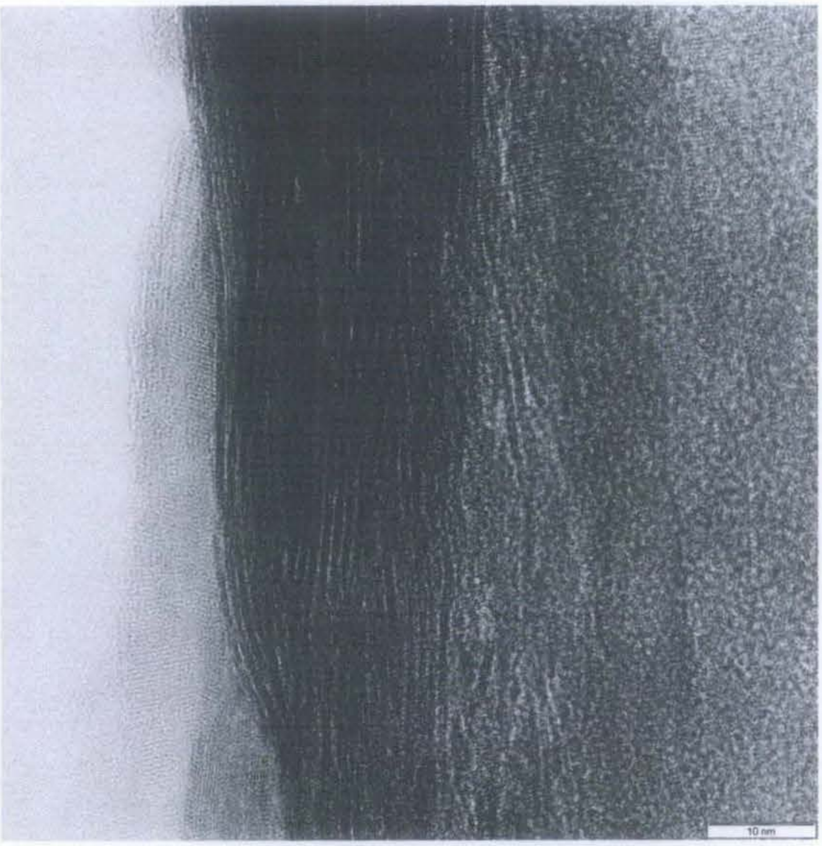

Figure 17: Mg-Bentonite

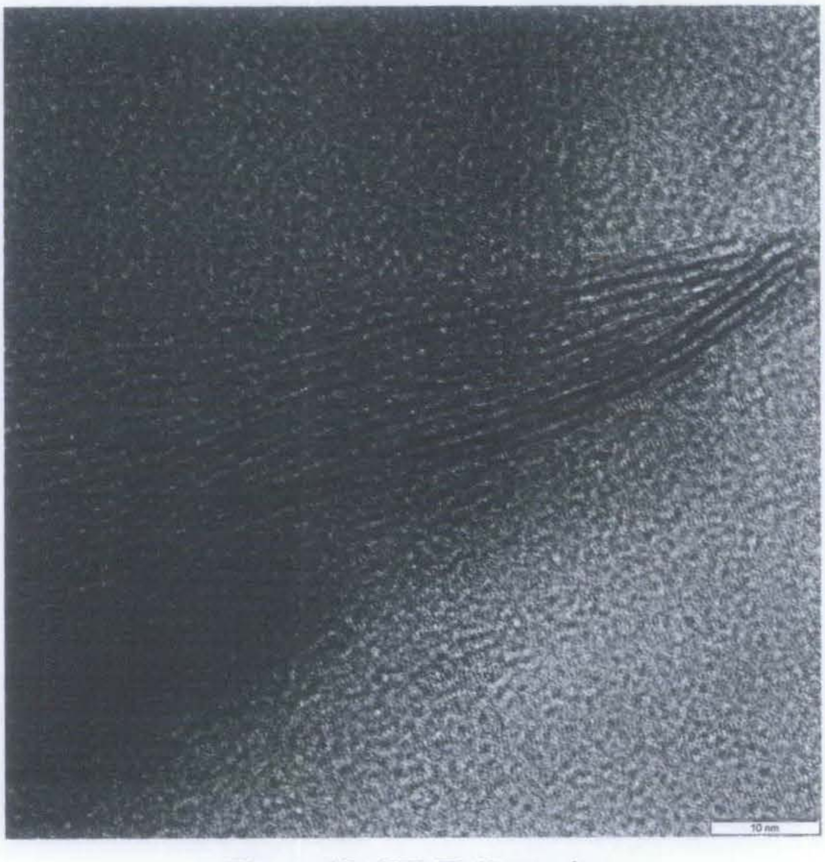

Figure 18: CTMB-Bentonite

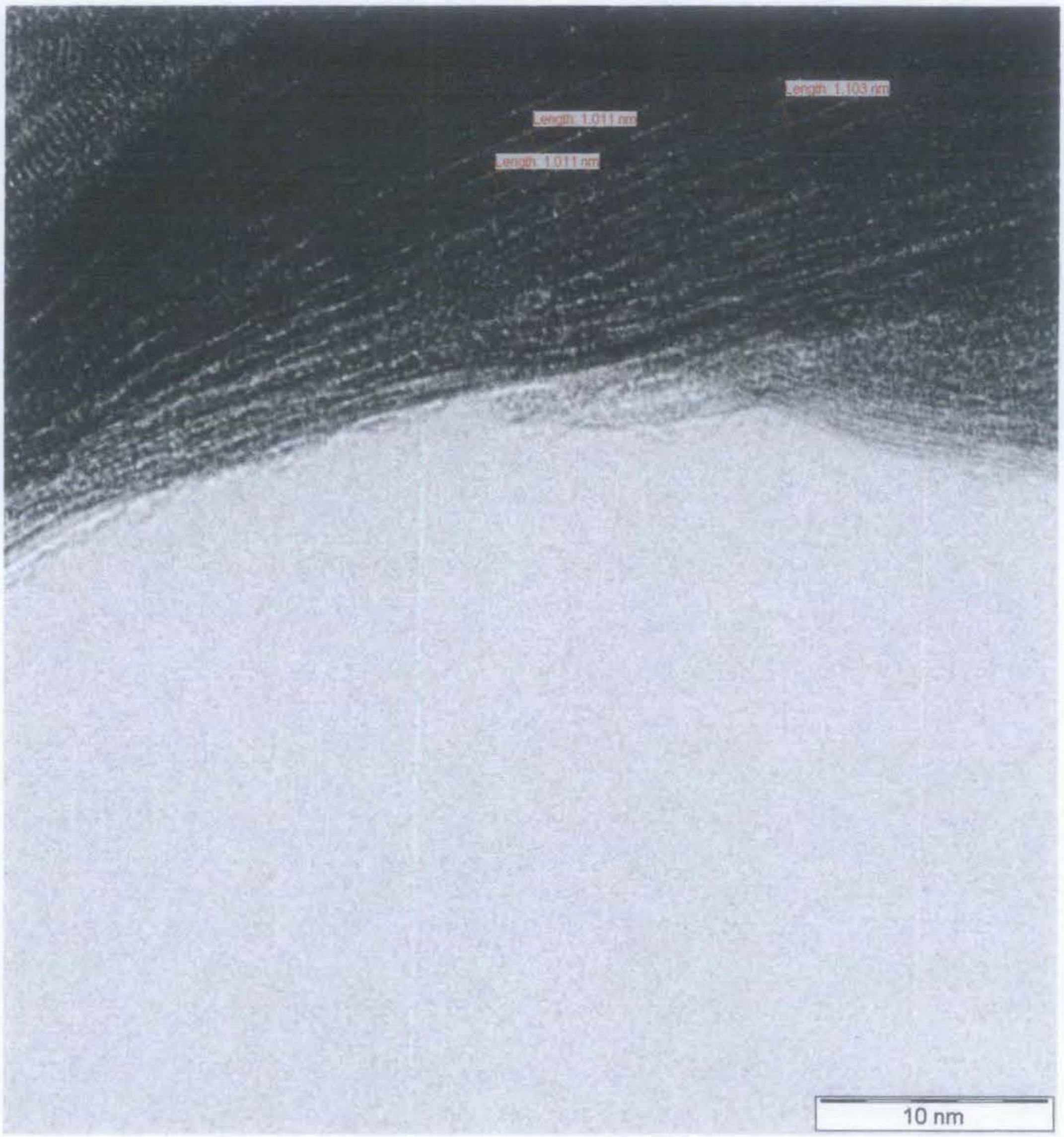

Figure 19: Basal spacing for Bentonite

The basal spacing of bentonite as shown in figure 19 can be calculated by taking the average:

$$(1.059 + 0.873 + 0.951 + 1.005)/4 = 0.972 \text{ nm or } 9.72 \text{ Å}$$

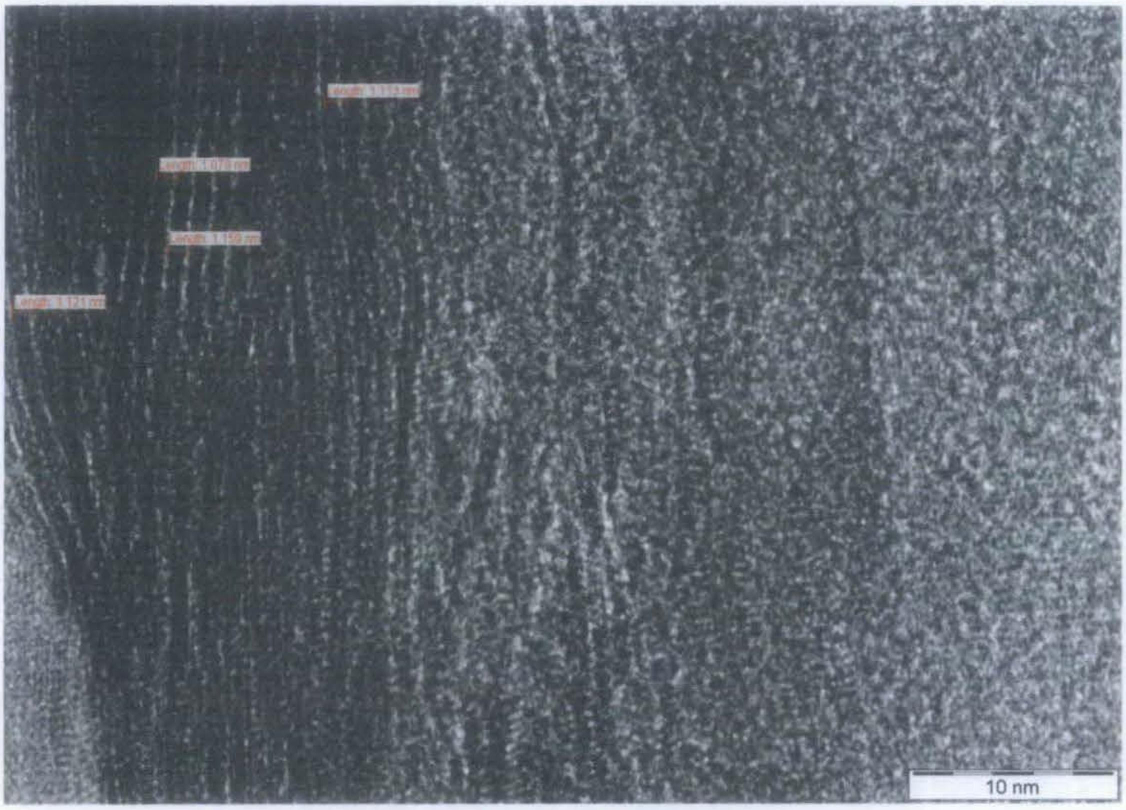

Figure 20: Basal spacing for Mg-Bentonite

The basal spacing of Mg-bentonite as shown in figure 20 can be calculated by taking the average:

$$(1.113 + 1.078 + 1.159 + 1.121)/4 = 1.118 \text{ nm or } 11.18 \text{ Å}$$

Figure 21: Basal spacing for CTMB-Bentonite

The basal spacing of CTMB-bentonite as shown in figure 21 can be calculated by taking the average:

$$(1.487 + 1.505 + 1.211 + 1.408)/4 = 1.403 \text{ nm or } 14.03 \text{ Å}$$

The TEM images of CTMB-Bentonite reveal that the *d*(001) basal spacing increased further to 14.03 Å. For Mg-Bentonite, as shown in Figure 10, the basal spacing are mainly from 10.78 to 11.59 Å. The increase in basal spacing of CTMB-Bentonite can be explained as ammonium cations play the role of pillars in these organoclays by holding the layers permanently apart without filling all the interlayer space preserving the distance between layers thus increasing the basal spacing.

4.4 CO2 Adsorption of CTMB-Bentonite

The mole fraction of CO_2 adsorbed versus time in minutes (figure 22) and pressure versus time in minutes (figure 23) was plotted. The effect of pressure towards CO_2 adsorption in CTMB-bentonite can clearly be seen. As the pressure increase, the mole fraction absorbed also increases. Since CTMB-bentonite is a physical solvent, it tends to prefer to adsorb CO_2 in high pressure. From the results obtained, the time taken for to achieve equilibrium is roughly 30 minutes for 10 bar, 2.20 hours for 20 bar, and it did not achieve equilibrium for 30 bar and 40 bar as the adsorption was still going on though at relatively low rate.

As we can see the adsorption of CO_2 only increased with increased operating pressure. But increasing pressure can only force the adsorption to a certain extent as we can see at 40 bar where the adsorption drops in a small fraction. An explanation that could be given is that at 40 bar the optimum pressure at which the adsorption could take place has been exceeded whereby the desorption rate of CO_2 is higher causing the adsorption to be less.

The low adsorptions of CO_2 or can be attributed to the layers of the bentonite have been occupied by the large C_{19} CTMB molecules. With the basal spacing of roughly 14 Å the layers will surely be filled and less space is present to facilitate the CO_2 adsorption whereby the size of CO_2 is roughly at 3 Å. Thus this explains the low adsorption of CO_2. Had it been intercalated with a smaller amine such as tetramethylammonium the results would be more encouraging.

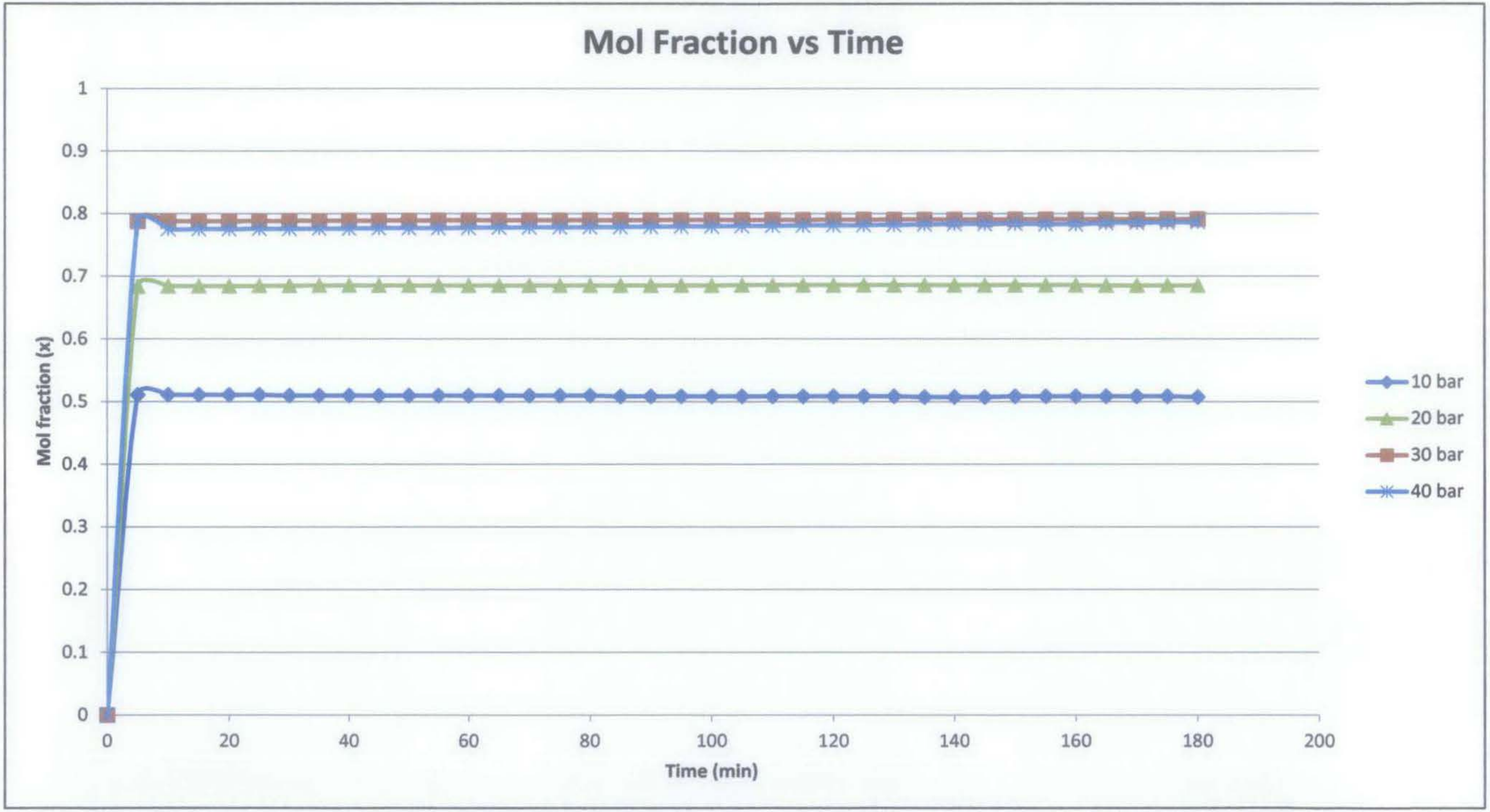

Figure 22: Mole Fraction versus Time of CO_2 Adsorption

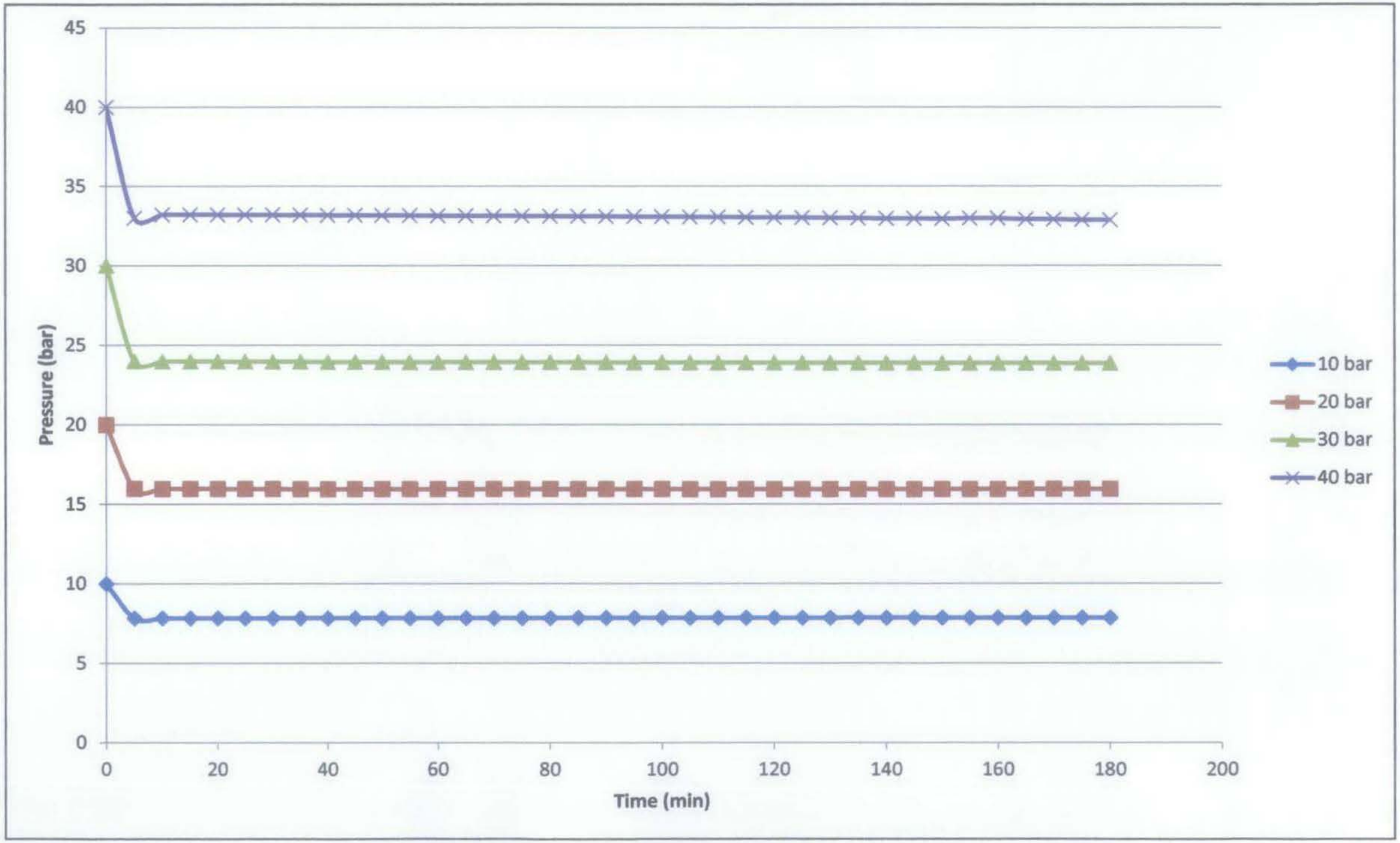

Figure 23: Pressure versus Time of CO_2 Adsorption

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The bentonite intecalated with CTMB was synthesized with haivng a surface area of 10.42 (m^2/g) and basal spacing of 14.30 Å. The adsorption of CO_2 showed that the CTMB-Bentonite was not an effective CO_2 adsorbent due to the large size of C_{19} molecules of CTMB hindering the adsorption process. A smaller amine will produce a better adsorbing organoclay.

5.2 Recommendations

A few recommendations can be proposed in order improve the study and achieve better results. They are:

a) A smaller quaternary ammonium cation is used such as tetramethylammonium as smaller amines will facilitate better adsorption capabilities for CO_2.
b) Magnetic Suspension Bed or MSB should be used to measure the capabilities of CO_2 solubility. MSB also can determine the effectiveness of the products by measuring the ability of the products to be regenerated.
c) All reagents that are used need to be kept in drying agent to avoid the reagents interact with the moisture which will alter the chemical properties of the reagents.

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APPENDICES

CO_2 adsorption at 10 bar

Time	Pressure	Z	Mol CO_2	Mol adsorb	Fraction adsorbed (x)
0	10	0.9483	0.115281462	-	0
5	7.83	0.9598	0.089183855	0.02609761	0.5107402941
10	7.83	0.9598	0.089183855	0.02609761	0.5107402941
15	7.83	0.9598	0.089183855	0.02609761	0.5107402941
20	7.83	0.9598	0.089183855	0.02609761	0.5107402941
25	7.83	0.9598	0.089183855	0.02609761	0.5107402941
30	7.84	0.9598	0.089297755	0.02598371	0.5096472630
35	7.84	0.9598	0.089297755	0.02598371	0.5096472630
40	7.84	0.9598	0.089297755	0.02598371	0.5096472630
45	7.84	0.9598	0.089297755	0.02598371	0.5096472630
50	7.84	0.9598	0.089297755	0.02598371	0.5096472630
55	7.84	0.9598	0.089297755	0.02598371	0.5096472630
60	7.84	0.9598	0.089297755	0.02598371	0.5096472630
65	7.84	0.9598	0.089297755	0.02598371	0.5096472630
70	7.84	0.9598	0.089297755	0.02598371	0.5096472630
75	7.84	0.9598	0.089297755	0.02598371	0.5096472630
80	7.84	0.9598	0.089297755	0.02598371	0.5096472630
85	7.85	0.9597	0.089420972	0.02586049	0.5084593132
90	7.85	0.9597	0.089420972	0.02586049	0.5084593132
95	7.85	0.9597	0.089420972	0.02586049	0.5084593132
100	7.85	0.9597	0.089420972	0.02586049	0.5084593132
105	7.85	0.9597	0.089420972	0.02586049	0.5084593132
110	7.85	0.9597	0.089420972	0.02586049	0.5084593132
115	7.85	0.9597	0.089420972	0.02586049	0.5084593132
120	7.85	0.9597	0.089420972	0.02586049	0.5084593132
125	7.85	0.9597	0.089420972	0.02586049	0.5084593132
130	7.85	0.9597	0.089420972	0.02586049	0.5084593132
135	7.86	0.9597	0.089534884	0.02574658	0.5073559400
140	7.86	0.9597	0.089534884	0.02574658	0.5073559400
145	7.86	0.9597	0.089534884	0.02574658	0.5073559400
150	7.85	0.9597	0.089420972	0.02586049	0.5084593132
155	7.85	0.9597	0.089420972	0.02586049	0.5084593132
160	7.85	0.9597	0.089420972	0.02586049	0.5084593132
165	7.85	0.9597	0.089420972	0.02586049	0.5084593132
170	7.85	0.9597	0.089420972	0.02586049	0.5084593132
175	7.85	0.9597	0.089420972	0.02586049	0.5084593132
180	7.86	0.9597	0.089534884	0.02574658	0.5073559400

CO_2 adsorption at 20 bar

Time	Pressure	Z	Mol CO_2	Mol absorb	Fraction absorbed (x)
0	20	0.8924	0.245005402	-	0
5	15.99	0.9154	0.190960165	0.054045237	0.6837254083
10	15.98	0.9154	0.19084074	0.054164662	0.6842025280
15	15.98	0.9154	0.19084074	0.054164662	0.6842025280
20	15.98	0.9154	0.19084074	0.054164662	0.6842025280
25	15.97	0.9155	0.190700483	0.054304919	0.6847610415
30	15.97	0.9155	0.190700483	0.054304919	0.6847610415
35	15.96	0.9155	0.190581071	0.05442433	0.6852349923
40	15.96	0.9155	0.190581071	0.05442433	0.6852349923
45	15.96	0.9155	0.190581071	0.05442433	0.6852349923
50	15.96	0.9155	0.190581071	0.05442433	0.6852349923
55	15.96	0.9155	0.190581071	0.05442433	0.6852349923
60	15.96	0.9155	0.190581071	0.05442433	0.6852349923
65	15.96	0.9155	0.190581071	0.05442433	0.6852349923
70	15.96	0.9155	0.190581071	0.05442433	0.6852349923
75	15.96	0.9155	0.190581071	0.05442433	0.6852349923
80	15.96	0.9155	0.190581071	0.05442433	0.6852349923
85	15.96	0.9155	0.190581071	0.05442433	0.6852349923
90	15.96	0.9155	0.190581071	0.05442433	0.6852349923
95	15.96	0.9155	0.190581071	0.05442433	0.6852349923
100	15.96	0.9155	0.190581071	0.05442433	0.6852349923
105	15.95	0.9156	0.190440858	0.054564544	0.6857896906
110	15.95	0.9156	0.190440858	0.054564544	0.6857896906
115	15.95	0.9156	0.190440858	0.054564544	0.6857896906
120	15.95	0.9156	0.190440858	0.054564544	0.6857896906
125	15.95	0.9156	0.190440858	0.054564544	0.6857896906
130	15.95	0.9156	0.190440858	0.054564544	0.6857896906
135	15.95	0.9156	0.190440858	0.054564544	0.6857896906
140	15.95	0.9156	0.190440858	0.054564544	0.6857896906
145	15.95	0.9156	0.190440858	0.054564544	0.6857896906
150	15.95	0.9156	0.190440858	0.054564544	0.6857896906
155	15.95	0.9156	0.190440858	0.054564544	0.6857896906
160	15.95	0.9156	0.190440858	0.054564544	0.6857896906
165	15.96	0.9155	0.190581071	0.05442433	0.6852349923
170	15.96	0.9155	0.190581071	0.05442433	0.6852349923
175	15.96	0.9155	0.190581071	0.05442433	0.6852349923
180	15.96	0.9155	0.190581071	0.05442433	0.6852349923

CO_2 adsorption at 30 bar

Time	Pressure	Z	Mol CO_2	Mol adsorb	Fraction adsorbed (x)
0	30	0.8309	0.394709629	-	0
5	23.99	0.8687	0.301901765	0.092807864	0.7877900582
10	23.98	0.8687	0.30177592	0.092933709	0.7880165034
15	23.98	0.8687	0.30177592	0.092933709	0.7880165034
20	23.98	0.8687	0.30177592	0.092933709	0.7880165034
25	23.97	0.8688	0.301615355	0.093094274	0.7883047237
30	23.96	0.8688	0.301489525	0.093220105	0.7885300465
35	23.96	0.8688	0.301489525	0.093220105	0.7885300465
40	23.95	0.8689	0.301329011	0.093380618	0.7888167812
45	23.94	0.8689	0.301203195	0.093506434	0.7890409901
50	23.94	0.8689	0.301203195	0.093506434	0.7890409901
55	23.93	0.869	0.301042733	0.093666896	0.7893262505
60	23.93	0.869	0.301042733	0.093666896	0.7893262505
65	23.93	0.869	0.301042733	0.093666896	0.7893262505
70	23.93	0.869	0.301042733	0.093666896	0.7893262505
75	23.93	0.869	0.301042733	0.093666896	0.7893262505
80	23.92	0.869	0.300916932	0.093792698	0.7895493539
85	23.92	0.869	0.300916932	0.093792698	0.7895493539
90	23.91	0.8691	0.300756521	0.093953109	0.7898331512
95	23.91	0.8691	0.300756521	0.093953109	0.7898331512
100	23.91	0.8691	0.300756521	0.093953109	0.7898331512
105	23.9	0.8691	0.300630734	0.094078896	0.7900551573
110	23.9	0.8691	0.300630734	0.094078896	0.7900551573
115	23.9	0.8691	0.300630734	0.094078896	0.7900551573
120	23.89	0.8693	0.30043581	0.09427382	0.7903982613
125	23.89	0.8693	0.30043581	0.09427382	0.7903982613
130	23.88	0.8693	0.300310052	0.094399578	0.7906190250
135	23.88	0.8693	0.300310052	0.094399578	0.7906190250
140	23.88	0.8693	0.300310052	0.094399578	0.7906190250
145	23.88	0.8693	0.300310052	0.094399578	0.7906190250
150	23.87	0.8694	0.300149766	0.094559863	0.7908997277
155	23.87	0.8694	0.300149766	0.094559863	0.7908997277
160	23.87	0.8694	0.300149766	0.094559863	0.7908997277
165	23.87	0.8694	0.300149766	0.094559863	0.7908997277
170	23.87	0.8694	0.300149766	0.094559863	0.7908997277
175	23.86	0.8694	0.300024022	0.094685607	0.7911194116
180	23.86	0.8694	0.300024022	0.094685607	0.7911194116

CO_2 adsorption at 40 bar

Time	Pressure	Z	Mol CO_2	Mol adsorb	Fraction adsorbed (x)
0	40	0.7612	0.534840559	-	0
5	33.02	0.8176	0.441510882	0.093329678	0.7887258674
10	33.22	0.8096	0.448574265	0.086266294	0.7753138074
15	33.22	0.8096	0.448574265	0.086266294	0.7753138074
20	33.22	0.8096	0.448574265	0.086266294	0.7753138074
25	33.21	0.8096	0.448439234	0.086401326	0.7755861532
30	33.21	0.8096	0.448439234	0.086401326	0.7755861532
35	33.2	0.8097	0.448248836	0.086591724	0.7759690487
40	33.19	0.8097	0.448113821	0.086726738	0.7762397760
45	33.18	0.8098	0.447923487	0.086917073	0.7766203190
50	33.18	0.8098	0.447923487	0.086917073	0.7766203190
55	33.17	0.8098	0.447788489	0.087052071	0.7768894423
60	33.16	0.81	0.447542959	0.087297601	0.7773772558
65	33.15	0.81	0.447407994	0.087432565	0.7776444934
70	33.14	0.8101	0.447217817	0.087622742	0.7780199669
75	33.14	0.8101	0.447217817	0.087622742	0.7780199669
80	33.13	0.8101	0.447082869	0.08775769	0.7782856319
85	33.12	0.8102	0.446892756	0.087947803	0.7786588204
90	33.11	0.8102	0.446757825	0.088082735	0.7789229268
95	33.1	0.8104	0.446512671	0.088327889	0.7794011672
100	33.09	0.8104	0.446377772	0.088462787	0.7796634414
105	33.08	0.8105	0.446187817	0.088652743	0.7800317054
110	33.07	0.8105	0.446052935	0.088787624	0.7802924511
115	33.05	0.8106	0.445728178	0.089112381	0.7809177259
120	33.04	0.8106	0.445593313	0.089247246	0.7811763447
125	33.03	0.8107	0.445403501	0.089437058	0.7815392988
130	33.02	0.8107	0.445268653	0.089571906	0.7817964214
135	33	0.811	0.444834345	0.090006214	0.7826204417
140	32.98	0.8112	0.444455142	0.090385417	0.7833348391
145	32.98	0.8112	0.444455142	0.090385417	0.7833348391
150	32.96	0.8113	0.444130862	0.090709697	0.7839420498
155	32.99	0.8111	0.44464472	0.090195839	0.7829782723
160	32.99	0.8111	0.44464472	0.090195839	0.7829782723
165	32.93	0.8115	0.443617257	0.091223302	0.7848968362
170	32.92	0.8116	0.443427899	0.09141266	0.7852467256
175	32.9	0.8117	0.443103905	0.091736654	0.7858427568
180	32.88	0.8119	0.442725455	0.092115104	0.7865347924