# REMOVAL OF WATER VAPOUR FROM NATURAL GAS BY USING ZEOLITE 3A AND ZEOLITE 13X

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CERTIFICATION OF APPROVAL

# Removal of Water Vapour from Natural Gas by using Zeolite 3A and Zeolite 13X

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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# TABLE OF CONTENTS

## LIST OF FIGURES

## LIST OF TABLES

# ABSTRACT

This report basically discusses on the research done, work completed and understanding of the chosen topic, which is **Removal of Water Vapour from Natural Gas by using Zeolite 3A and Zeolite 13X.** In this study, zeolite is identified as the best adsorbent that capable to remove water vapour in natural gas. The working gas for separation of water from gas is methane as it been the major component in natural gas. In methodology section, the author discusses on the method of zeolite characterization, by using Surface Area Analyzer, X-Ray Flourescent (XRF), X-Ray Diffraction (XRD), Field-Emission Scanning Electron Microscope (FESEM) and Thermogravimetric Analyzer (TGA). The experimental procedure for evaluating the adsorbent performance is also included. Next is is results and discussion whereby result for characterization mentioned in methodology section and the dynamic performance of zeolite is been discussed. Two different pressure is used, at 40 barg and 60 barg in order to analyze the adsorbent performance. The objective of this study is to find the alternative way of removal water vapour from natural gas by using a solid desiccant method and to get the optimum operating conditions for the high performance of adsorbent. Experimental work is done to analyze the adsorbent performance and one parameter; pressure will be observed.

# CHAPTER 1
# INTRODUCTION

## 1.1 Background of Study

Natural gas is mainly composed of methane, the shortest and lightest hydrocarbon molecule. It also include varying amounts of heavier gaseous hydrocarbons such as ethane ($C_2H_6$), propane ($C_3H_8$), normal butane (n-$C_4H_{10}$), isobutane (i-$C_4H_{10}$), pentanes and even higher molecular weight hydrocarbons. The composition of natural gas can vary widely depending on the reservoir. **Table 1.1.1** below summarizes the typical composition of raw natural gas.

**Table 1.1.1:** Typical Composition of Natural Gas (NGA, 2009)

| Composition | Molecular Formula | Percentage |
|---|---|---|
| Methane | $CH_4$ | 70-90% |
| Ethane | $C_2H_6$ | 0-20% |
| Propane | $C_3H_8$ | |
| Butane | $C_4H_{10}$ | |
| Carbon Dioxide | $CO_2$ | 0-8% |
| Oxygen | $O_2$ | 0-0.2% |
| Nitrogen | $N_2$ | 0-5% |
| Hydrogen Sulphide | $H_2S$ | 0-5% |
| Rare gases | Ar, He, Ne, Xe | Trace |

In most cases, the water vapour and liquid water are also present. To meet the quality standards specified by the major pipeline transmission and distribution companies, the raw natural gas must be purified. One of the purification techniques is to remove acid gases (hydrogen sulfide and carbon dioxide) by membrane or amine treating. The next step involves of removal of water vapour from the gas either using regenerable absorption in liquid or a regenerable adsorption using a solid adsorbent.

The water vapour is the undesirable impurity. When water vapour in contact with the acid gases in natural gas, such as hydrogen sulfide and carbon dioxide, it will forms a corrosive mixture which reducing the life span of equipments. The presence of moisture in natural gas may cause pipelines and associated valves to freeze. Particularly at openings and bends in the pipeline, where pressure drop may occur, the expansion of gas followed by a temperature drop may result in the formation of hydrates, which restrict gas flow. Moisture also lowers the energy content (BTU) of the gas, thus lowering its quality and value. In general, the standards specify that the natural gas must be within a specific range of heating value (caloric value). In the United States, it should be about 1,035 ± 5% Btu per cubic feet of gas (DOE, 2009). P. Gandhidasan, Abdulghani A. Alfarayedhi, Ali A. Al-Mubarak (2000) posited that water is also removed to meet a water dew point requirement of a sales gas contract specification, which range from 32.8 to 117 kg/106 std $m^3$.

This research mainly focuses on the removal of water vapour from natural gas using a solid desiccant, particularly zeolite molecular sieve. Zeolite molecular sieves are crystalline structures that, on a molecular scale, are not unlike sponges. They have a solid framework, defined by large internal cavities where molecules can be adsorbed.

## 1.2 Problem Statement

Natural gas coming from the wellhead is usually formed with some water and is normally saturated with water vapour. The commonly used method for removal of water is to dehydrate the gas, which involves of two processes; either absorption or adsorption (NGA, 2009). For absorption dehydration, there are numbers of liquids that can be used to absorb water from natural gases such as calcium chloride, lithium chloride, and glycols (P. Gandhidasan et al., 2000).The typical technique is using triethylene glycol (TEG). The water vapour is removed from natural gas primarily by TEG dehydration towers. Glycol, the principal agent will serve to 'steal' the water out of gas stream when in contact with a stream of natural gas that contains water (NGA, 2009). Some disadvantages of TEG are; high pressure saturated operation has chances of gas leakage, therefore more space is required to comply with the hazardous area requirement (Arun, 2007) and glycol used is corrosive when contaminated. Overheating of the solutions for regenerating purpose also may produce both low and high boiling decomposition method. At low temperature, glycol solution tend to become viscous, therefore, they are hard to pump (P. Gandhidasan et al., 2000). Due to these limitations, the author would like to improve the water removal technique by using the solid desiccant method, specifically a molecular sieve type adsorbent. This technique is best suited for large volumes of gas under high pressure. The dynamic performance will be studied by varying the pressure.

### 1.3 Objectives

The main objectives of this study are:

1. To characterize zeolite 3A and zeolite 13X to know the properties and behaviour of samples.
2. To study the effect of varying pressure in removing water from natural gas using zeolite molecular sieves.

### 1.4 Scope of Study

The scope of work for this study is to do experimental work, specifically for adsorbent characterization and adsorbent performance. In adsorbent characterization, several equipments are used, such as Surface Area Analyzer, X-Ray Flourescent (XRF), X-Ray Diffraction (XRD), Thermogravimetric Analyzer (TGA) and Field-Emission Scanning Electron Microscope (FESEM). The importance of characterization in this study is to confirm and understand the physical and chemical properties of zeolite been used. For adsorbent performance, the author would investigate the effect of varying one important parameter; pressure toward the workability between two adsorbents, zeolite 3A and zeolite 13X. A few tasks and research need to be carried out by gathering all technical details regarding the suitability of chosen adsorbent and by studying their physical properties. A recommendation is to be made based on the findings of this study.

# CHAPTER 2
# LITERATURE REVIEW

## 2.1 Adsorbent

An adsorbent is a substance, which is usually porous in nature. It has a high surface area that can adsorb substances onto its surface using the intermolecular forces. The adsorption isotherm linear is only at very low concentrations, at higher concentrations the adsorption isotherm may be Langmuir or Freundlich in nature. Since solutes can be distributed between the adsorbent surface and a mobile phase, adsorbents are used as a stationary phases in gas-solid and liquid-solid chromatography (LS, 2009). H. Van Bekkum et al. (2001) found that in industry, adsorbents are also used for extraction purposes for removing traces of organic materials from large volumes of water very efficiently. For gas-solid chromatography, the typical adsorbents used are alumina, carbon, silica gel and bonded phases. These are widely used in the separation of the permanent gases and the low molecular weight hydrocarbon gasses. Adsorbents used in liquid solid chromatography are mostly silica gel and various types of bonded phases. Adsorbents in liquid-solid chromatography have a very wide variety of application areas

Adsorbents are usually in the form of spherical pellets, rods, moldings, or monoliths with hydrodynamic diameters between 0.5 and 10 mm (Wiki, 2009). To results in higher exposed surface area and hence high surface capacity for adsorption, the adsorbent must have high abrasion resistance, high thermal stability and small pore diameters. The adsorbents must also have a distinct pore structure which enables fast transport of the gaseous vapors.

Most industrial adsorbents are classes into three types:

- Carbon-based compounds – Are typically hydrophobic and non-polar, including materials such as activated carbon and graphite.

- Oxygen-containing compounds – Are typically hydrophilic and polar, including materials such as silica gel and zeolites.
- Polymer-based compounds - Are polar or non-polar functional groups in a porous polymer matrix.

### 2.2 Types of Adsorbent

Many type of adsorbent exist in petroleum industry. They are activated alumina, activated carbon, silica gel and molecular sieves. (David A. Zornes, 2004). Selection of dessicant for the desired process is very important since it will affect the efficiency of the adsorption unit.

#### 2.2.1 Activated Alumina

Activated alumina is made from aluminium hydroxide by dehydroxylating which produces a highly porous material. The surface area for this material can significantly over 200 $m^2/g$. It is made of aluminium oxide, $Al_2O_3$, the same chemical substance as sapphire and rubies (Wiki, 2009). It has a very high surface-area-to-weight ratio. That means it has a lot of very small pores, almost like tunnels, that run throughout it. They are also available in different forms, from rough granules to smooth uniform beads.

The uses of activated alumina vary from catalyst, dessicant and flouride adsorbent. Use as a desiccant, it works by a process called adsorption. The water in the air actually sticks to the alumina itself in between the tiny passages, as the air passes through them. Its ability to be shaped with well-defined pores defined as follows:

- Macropores (>1000Å) to enhance diffusion in pore system
- Mesopores (30-1000Å) to accomodate medium size molecules
- Micropores (<30Å) to accomodate small molecules like water

P. Gandhidasan et al. (2000) found that alumina is the cheapest among other adsorbent but it requires large towers for given water load, which increases capital cost and head load. The coadsorption of hydrocarbons will reduce its capacity for water and at the same time can lead to the loss of valuable hydrocarbon components to the fuel gas, and rehydration, which destroy its activities. Activated aluminas are more preferable when the adsorbent may be subjected to physical damage because they are among the thoughest adsorbents. **Table 2.1.1** below shows the typical properties for activated alumina.

**Table 2.1.1:** Typical properties of activated alumina

| **Description** | **Physical Properties** |
|---|---|
| Particle form | Sphere |
| Surface area ($m^2/g$) | 325-350 |
| Average crushing strength (lbs) | 35 |
| Average bulk density, packed ($lbs/ft^3$) | 48 |

### 2.2.2 Silica Gel

Silica gel is made synthetically from sodium silicate with the formula $SiO_2.nH_2O$. Silica gel has high surface area (around 800 $m^2/g$) and this properties allows it to adsorb water readily, making it useful as a desiccant (Wiki, 2009). The saturated gel then can be regenerated by heating it to 120 °C for two hours. Silica desiccant is effective when use in the dehydration of compressed air and natural gas. The desiccant silica gel bead shape, uniform particle size and high bulk density combine to ensure optimum air/gas flow without nesting or channeling. Minimal dusting occurs due to the hard, smooth, spherical shape of the silica desiccant beads.

Silica gel has an affinity for water. If a drop of liquid water touches a particle of it, it will adsorb the water so quickly that the silica gel will actually disintegrate. At low temperature, the ultimate capacity of silica gel for water is higher than the capacity on alumina or zeolites. P. Gandhidasan et al. (2000) stated that silica gel also can be regenerated at low temperature. Water molecules exhibits a lower vapour pressure than the surrounding air such that it will adhere to the gels surface. When an equilibrium of equal pressure is reached, no more adsorption occurs. Thus the higher the humidity of the surrounding air, the greater the amount of water that is adsorbed before equilibrium is reached. **Table 2.1.2** below summarizes the properties of silica gel.

**Table 2.1.2:** Typical properties of silica gel

| Description | Physical Properties |
|---|---|
| Surface area ($m^2/g$) | 650-750 |
| Average bulk density, packed ($lbs/ft^3$) | 48 |
| Pore size (nm) | 1-40 |
| Pore volume ($cm^3/gm$) | 0.42 |

P. Gandhidasan et al. (2000) posited that a problem with silica gel is its tendency to shatter when contacted with liquid water. If the adsorption flow is from top to bottom of the desiccant bed, then providing a layer of water-resistant desiccant on top of the bed can prevent this problem.

### 2.2.3 Activated Carbon

Activated carbon is produced by the partial burning of materials that contains a high content of carbon, such as coal, wood and coconut shells. The carbon surface is characteristically non-polar, that is, it is essentially electrically neutral. This non-polarity gives the activated carbon surface high affinity for comparatively non-polar adsorbates, including most organics. The porosity of activated carbon, which is classified by the size of the diameter of the pores, varies from micropores(2 nm), to mesopores (2-50 nm), to macropores(greater than 50 nm) (Isobel Parker & Donald Hughes, 2009). Activated carbon are frequently used to adsorb traces of organic impurities from gas and liquid streams and also used to adsorb heavy hydrocarbon from natural gas.

### 2.2.4 Zeolite Molecular Sieves

Molecular sieves are in the form of porous solids with pores of the size of molecular dimensions, 0.3-2.0 nm in diameter. The examples of molecular sieve types are zeolites, glasses, carbons and oxides. A few are crystalline with a uniform pore size delineated by their crystal structure, e.g., zeolites. Zeolite molecular sieves, which belong to the class of alumino silicates are crystalline, highly porous materials. These crystals are characterised by a three-dimensional pore system, with pores of precisely defined diameter. This diameter is in the dimension of the size of molecules such as water, $CO_2$ and $H_2S$. Chemically, they are represented by the empirical formula:

$$M_{\frac{2}{n}}O \bullet Al_2O_3 \bullet ySiO_2 \bullet wH_2O$$

where y is 2 to 10, n is the cation valence, and w represents the water contained in the voids of zeolite.

The corresponding crystallographic structure is formed by tetrahedras of ($AlO_4$) and ($SiO_4$) (Ralph T. Yang, 2003). These tetrahedras are the basic building blocks for various zeolite structures, such as zeolites A and X. Due to the presence of alumina, zeolites exhibit a negatively charged framework, which is counter-balanced by positive cations resulting in a strong electrostatic field on the internal surface. These cations can be exchanged to fine-tune the pore size or the adsorption characteristics. For instance, the sodium form of zeolite A has a pore opening of approximately 4 Ångstrom (4 x 10–10 m), called 4A molecular sieve. If the sodium ion is exchanged with the larger potassium ion, the pore opening is reduced to approximately 3 Ångstrom (3A molecular sieve). On ion exchange with calcium, one calcium ion replaces two sodium ions.

### 2.2.4.1 Zeolite 3A

Zeolite 3A is the potassium formed of zeolite. It is formed by exchanging Na+ with K+, resulting in a smaller effective aperture size (of 3.0 A°) due to the larger K+. The aperture size of the sodium form can also be increased by exchanging Na+ with Ca+2 or Mg+2, because 2 Na+ are replaced by one divalent cation (Ralph T. Yang, 2003). The pore size of 3A molecular sieve is 3 Angstrom and does not adsorb any molecular larger than 3A. The formula presenting zeolite 3A:

$$0.4K_2O\ 0.6Na_2O\ Al_2O_3\ 2.0SiO_224.5H_2O$$

**Table 2.1.3** below summarizes the common properties of zeolite 3A.

**Table 2.1.3:** Typical properties of zeolite 3A

| Description | Physical Properties |
|---|---|
| Nominal pore size (A°) | 3 |
| Type of crystal structure | Simple cubic |
| Equilibrium water capacity (wt%) | 21 |
| Bulk density ($lb_s/ft^3$) | 44-46 |
| Crush Strength, beads ($lb_s$) | 10 |
| Heat of adsorption, max (BTU/lb $H_20$) | 1800 |

### 2.2.4.2 3A Molecular Sieve Typical Applications

- Dehydration of many kinds of liquids (such as ethanol)
- Dehydration of air
- Dehydration of refrigerant
- Dehydration of natural gas or methane
- Dehydration of cracked gas, ethylene, propylene or butadiene

### 2.2.4.3 13X Molecular Sieve

13X molecular sieve is a sodium form of type X crystal and has a larger pore opening than type 4A molecular sieve. 13X adsorbs molecules with a kinetic diameter of less than 9 Angstrom (0.9nm) and excludes larger molecules. Molecular sieve typical chemical formula;

- Silicon Dioxide: < 60 %
- Aluminum Oxide: < 40 %
- Sodium Oxide: < 20 %
- Magnesium Oxide: < 5 %

**Table 2.1.4** below summarizes the common properties of zeolite 13X.

**Table 2.1.4:** Typical properties of zeolite 13X

| Description | Physical Properties |
|---|---|
| Nominal pore size (A°) | 10 |
| Type of crystal structure | Body center cubic |
| Equilibrium water capacity @ 25 °C (%) | @ 10% RH, 19 |
| Bulk density ($lb_s/ft^3$) | 40.6 |
| Crush Strength ($lb_s$) | 7.7 |
| Heat of adsorption, max (BTU/lb $H_20$) | 1800 |

### 2.2.4.4 13X Molecular Sieve Applications

- Oxygen generators: medical or bulk oxygen production
- Air plant feed purification (simultaneous removal of $H_20$ and $CO^2$)
- Compressed air drying

## 2.3 Zeolite Characterization

### 2.3.1 Adsorption Isotherms

The experimental physical adsorption isotherms for pure gases have shapes, that are classified into FIVE types.

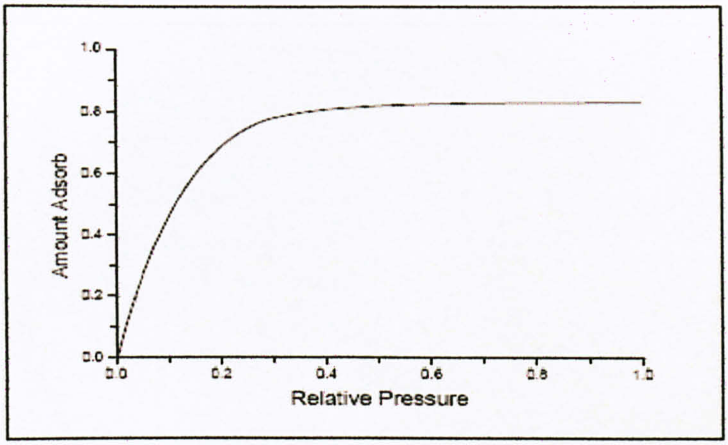


**Figure 2.1.1**: Type 1-microporous solid and chemisorption isotherm

For Type 1 isotherm, the adsorption is limited to the completion of a single monolayer of adsorbate at the adsorbent surface. Type I isotherms are observed for the adsorption of gases on microporous solids and chemisorption isotherms whose pore sizes are not much larger than the molecular diameter of the adsorbate. Complete filling of these narrow pores corresponds to the completion of a molecular monolayer.

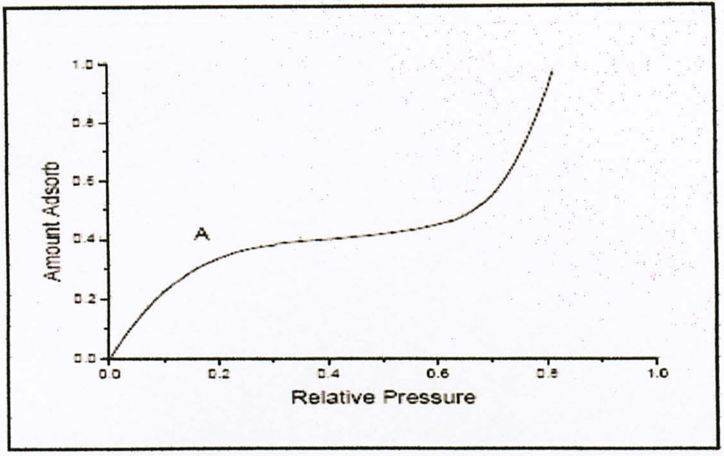


**Figure 2.1.2**: Type 2-non-porous solids

Type 2 isotherm shows an indefinite multi-layer formation after completion of the monolayer and generally found in adsorbents with a wide distribution of pore sizes. A monolayer is completed near to the first point of inflexion (point A), following which adsorption occurs in successive layers.

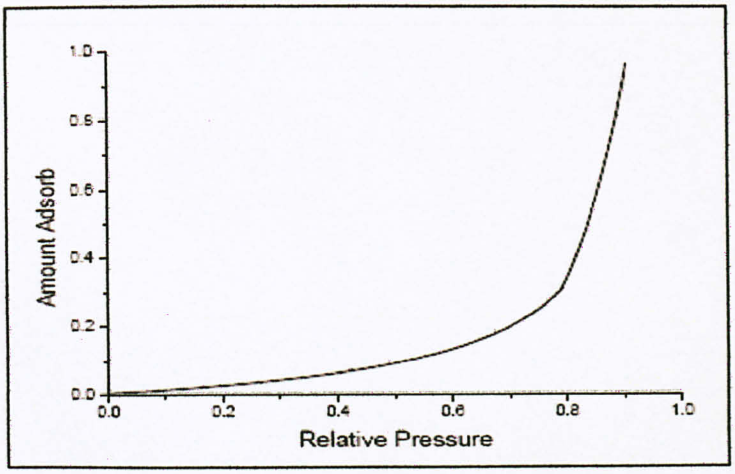


**Figure 2.1.3**: Type 3-non-porous and microporous

In Type 3 isotherm, the plot obtained is convex to the relative pressure axis is most commonly associated with both non-porous and microporous adsorbents. This class of isotherm is characteristic of weak adsorbate-adsorbent interactions. The weak interactions between the adsorbate and the adsorbent lead to low uptakes at low relative pressures. However, once a molecule has become adsorbed at a primary adsorption site, the adsorbate-adsorbate interaction, which is much stronger, becomes the driving force of the adsorption process, resulting in accelerated uptakes at higher relative pressure.

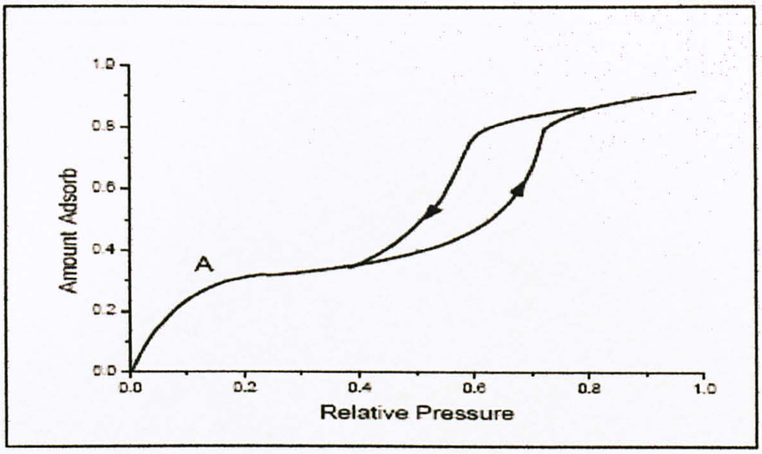


**Figure 2.1.4**: Type 4-hysterisis loop generated by capillary

Type 4 isotherm is a variation of Type 2, but with a finite multi-layer formation corresponding to complete filling of the capillaries. Capillary condensation gives rise to a hysteresis loop and these isotherms also exhibit a limited uptake at high relative pressures.

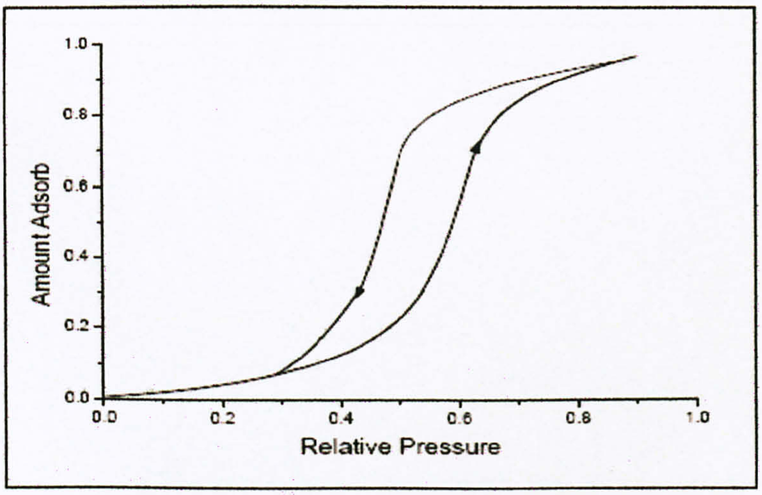


**Figure 2.1.5**: Type 5-microporous or mesoporous solids

Type 5 isotherm is similar variation of Type 3. These isotherms are indicative of microporous or mesoporous solids.

### 2.3.2 BET Surface Area

BET theory is a rule for the physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of a material. It is stressed that the B.E.T. equation should not be used for materials with very small pores, such as zeolites. As zeolites are crystalline, the possibility exists of measuring relative surfaces areas by X-ray crystallography

### 2.3.3 X-Ray Flourescent (XRF)

X-ray fluorescence (XRF) is one of the standard techniques used for the analysis of the elemental composition of zeolites. This method can analysis the major and trace elements in sample materials.

### 2.3.4 X-Ray Diffraction (XRD)

X-Ray diffraction is used for determining the long-range order and the phase purity of zeolites. The data is represented in a collection of single-phase X-ray powder diffraction patterns for the three most intense D values in the form of tables of interplanar spacings (D), relative intensities (I/Io), and mineral name. The XRD technique is by taking a sample of the material and places a powdered sample in a holder, then the sample is illuminated with x-rays of a fixed wave-length and the intensity of the reflected radiation is recorded using a goniometer. This data is then analyzed for the reflection angle to calculate the inter-atomic spacing (D value in Angstrom units - 10-8 cm). The intensity(I) is measured to discriminate (using I ratios) the various D spacings and the results are to identify possible matches.

### 2.3.5 Field-Emission Scanning Electron Microscope (FESEM)

Field emission scanning electron microscopy (FESEM) can provide high resolution secondary electron (SE) imaging capabilities at higher magnifications. (Refer to **Appendices A.2**). It has been a valuable technique for many years for characterizing the morphology, structure, and chemistry of microscopic particles and nanostructures. FESEM provides the opportunity to more fully and accurately characterize the overall shape, surface roughness, structure, and chemistry of particulate materials.

### 2.3.6 Thermogravimetric Analyzer (TGA)

Thermogravimetric analyzer (TGA) is a type of testing that is performed on samples to determine changes in weight in relation to change in temperature. The measurement is normally carried out in air or in an inert atmosphere, such as Helium or Argon, and the weight is recorded as a function of increasing temperature.

Such analysis relies on a high degree of precision in three measurements: weight, temperature, and temperature change. As many weight loss curves look similar, the weight loss curve may require transformation before results may be interpreted. A derivative weight loss curve can be used to tell the point at which weight loss is most apparent. Again, interpretation is limited without further modifications and deconvolution of the overlapping peaks may be required.

TGA is commonly employed in research and testing to determine characteristics of materials such as polymers, to determine degradation temperatures, absorbed moisture content of materials, the level of inorganic and organic components in materials, decomposition points of explosives, and solvent residues. It is also often used to estimate the corrosion kinetics in high temperature oxidation.

# CHAPTER 3
# METHODOLOGY

This chapter focuses on characterization of zeolite 3A and zeolite 13X. The experimental procedure is also discussed as part of this methodology.

## 3.1 Adsorbent Characterization

The adsorption literature has reported tens of thosand of adsoprtion isotherms, of different systems and measured for many different tyes of adsorbent. The majority of these isotherms fall into five types and the first classification of physical adsorption isotherms were presented by Brunauer, Deming, Deming and Teller (BDDT). For this research, the author has characterize the adsorption isotherm of zeolite 3A and zeolite 13X by using Surface Area Analyzer, which also provides particle size analysis, surface area, pore volume and thickness. The analysis gas use is nitrogen, as the standard working medium.

The other method of zeolite characterization are X-Ray Flourescent (XRF), X-Ray Diffraction (XRD), Field-Emission Scanning Electron Microscope (FESEM) and Thermogravimetric Analyzer (TGA). The methods and purposes for each characterization is summarize in **Table 3.1.1.**

**Table 3.1.1:** Methods and procedures for zeolite characterization

| Method | Procedure | Purpose |
|---|---|---|
| X-ray Diffraction | The samples were grounded to powder form and the XRD of individual samples were recorded and were compared with the standard XRD pattern of molecular sieve available in the library of the system. | To identify the structure type of molecular sieves. |

| | | |
|---|---|---|
| FESEM | The samples were sputtered with a mixture of platinum and paradium before taking the images. The molar composition of silica and aluminum in the samples were measured by using FESEM equipped with an energy dispersive X-ray spectrometer (EDX). | To determine the morphology of the zeolite crystal. |
| Thermogravimetric Analyzer | The molecular sieve sample (100 mg) was ground and placed in a alumina crucible. The same weight of pre-calcined, ultrex grade aluminum oxide ($Al_2O_3$) was used as a reference sample in another crucible. The temperature was raised at a uniform rate of 10 ºC/min up to 900 ºC. The analyses were made in air atmosphere at a flow rate of 150 cm3/min. | To determine thermal stability for the zeolites. |

## 3.2 Experimental Procedure

Gas Dehydration Unit (GDU) is use to execute the experiment. (Refer to **Figure 3.1.1**). The adsorbent is inserted in an adsorption column which has a diameter of 150 mm and height at 300 mm. Only methane is use as working gas. In this research, the author only concerns on pressure manipulation.

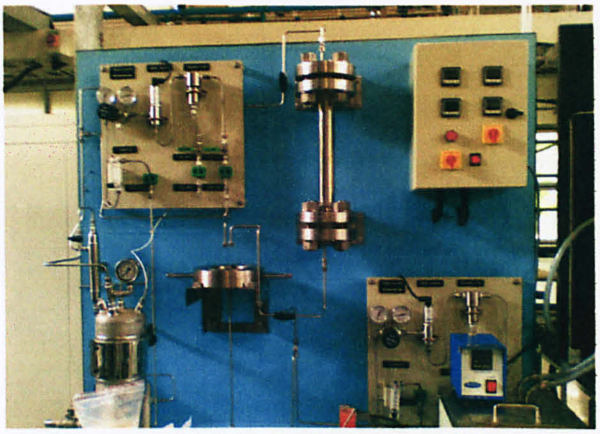


**Figure 3.1.1:** Gas Dehydration Unit (GDU)

The general procedures are presented as follows;

1. The working gas use is methane.
2. Parameter to be manipulated is pressure, varying from 40 barg to 60 barg.
3. Zeolite preparation to remove available moisture can be in two ways, either by increasing the temperature between 200-230°C or to insert the adsorbent into a vacuum oven.
4. For pressure manipulation, start from low pressure (40 barg) to high pressure (60 bars).
5. Wetting the gas by passing methane into saturation vessel filled with water vapour (water being heated first to form vapour).
6. Assume that the gas is saturated with water.
7. Moisture analyzer is use to measure the amount of adsorbed water. The analyzer is placed before the gas entering adsorption column and after it passes the adsorption column.
8. The adsorbed adsorbent is regent (by TSA). Increasing the temperature to 200°C. The water vapour is then being vented out.

Based on the literature review and some case study (Abdurrahman, 2006), the details procedures of the experiment are accomplish as following;

1. Adsorbent sample in adsorption column is heated up to 200°C by passing hot air for 30 minutes (to remove moisture).
2. The valve of the methane container is opened. The flow of methane gas in pipeline is set at 5 litre per minute (NLM) and the pressure is set at 40 barg.
3. The methane is wetted with water vapour by passing the gas into saturation vessel. (Note: The water in the saturation vessel is heated first up to 50°C to form water vapour)

4. The mixture of methane and water vapour exits from saturation vessel. The amount of water vapour in the outlet is measured by a moisture analyzer located at the inlet of adsorption column.
5. The mixture of methane and water vapour flows to adsorption column.
6. The amount of water in methane is determined by a moisture analyzer place at the outlet of the adsorption column.
7. The water vapour is ventilated out.
8. The adsorbent capacity and length for used and unused bed is calculated.
9. Procedures 1 to 8 are repeated for pressure of 60 barg (see **Table 3.1.2**) and the flow rate is remained at 5 NLM.

Table below shows the variation of pressure from 40 to 60 barg.

**Table 3.1.2:** Manipulated parameters

| Flowrate (NLM) | Pressure (bar) |
|---|---|
| 5 | 40 |
| | 60 |

# CHAPTER 4
# RESULTS AND DISCUSSION

## 4.1 Zeolite Characterization

### 4.1.1 BET Surface Area

The experimental work has been done to characterize zeolite 3A and zeolite 13X. In this characterization, the equipment used is Surface Area Analyzer and nitrogen is use as the analysis gas.

As defined by IUPAC, porosity has a classification system which gives a guideline of pore widths applicable to all forms of porosity. The widely accepted I.U.P.A.C. classification is as follows:

| | |
|---|---|
| Micropores: | < 2 nm diameter or <20 Angstrom |
| Mesopores : | 2-50 nm diameter or 20-500 Angstrom |
| Macropores: | >50 nm diameter or >500 Angstrom |

To study the adsorption isotherm that falls for zeolite 13X, a plot of volume adsorbed versus relative pressure is made. As shown in **Figure 4.1.1,** the trend follows type 1 isotherms, which indicates a microporous adsorbent whose pore sizes are not much larger than the molecular diameter of the adsorbate.

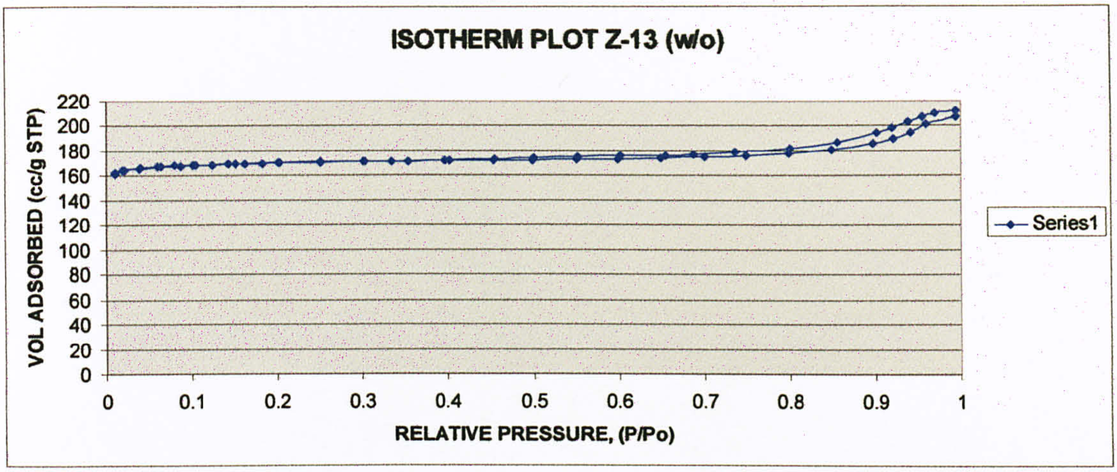


**Figure 4.1.1**: Isotherm plot for zeolite 13X

By using equation by DeBoer,

$$t = [13.990/(0.0340 - \log(P/P_o)]^{0.5}$$

a statistical thickness is calculated and a plot of volume adsorbed versus thickness is made. The basis of the t-plot is to compare the isotherm of an unknown, perhaps microporous, material with that of a non-porous reference material having similar surface characteristics. Until today, only the classical reference curves of Halsey, Harkins and Jura, or Broekhoff – DeBoer have been available. Referring to **Figure 4.1.2**, it demonstrates the relationship between volume of nitrogen adsorbed, and the average thickness of the adsorbed layer of nitrogen (t) on the adsorbent surface. From this plot, we obtain:

1. The intercept, which gives the micropore volume ($PV_{micro}$)
2. The slope of the straight line, giving the external surface area

The micropore volume for zeolite 13X is 0.251912 cc/g and the external surface area is 23.9567 sq. m/g.

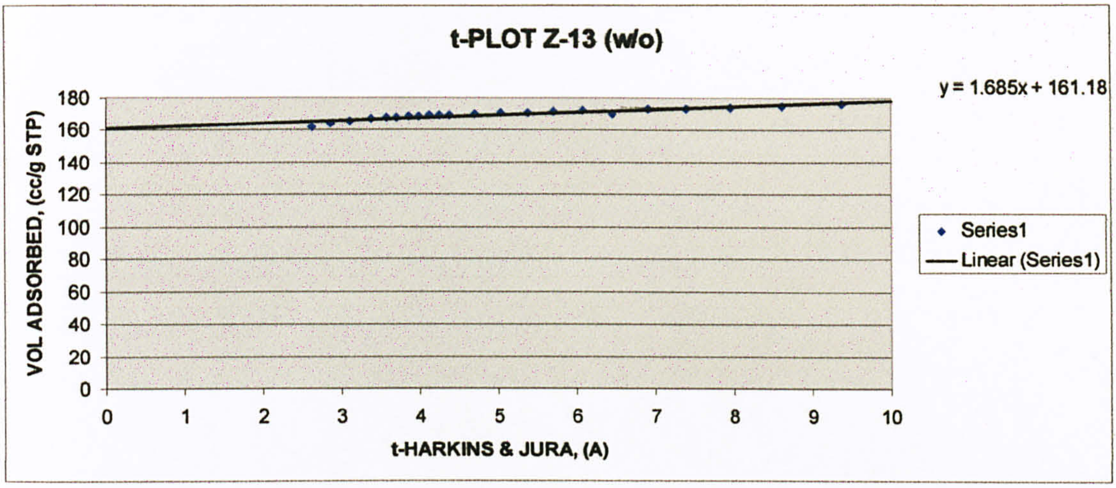


**Figure 4.1.2:** t-plot for zeolite 13X

The same study is performed for Zeolite 3A. A plot of relative pressure versus volume adsorbed is made. As shown in **Figure 4.1.3**, the trend is follows a type 2 adsorption isotherm which is a multilayer adsorption.

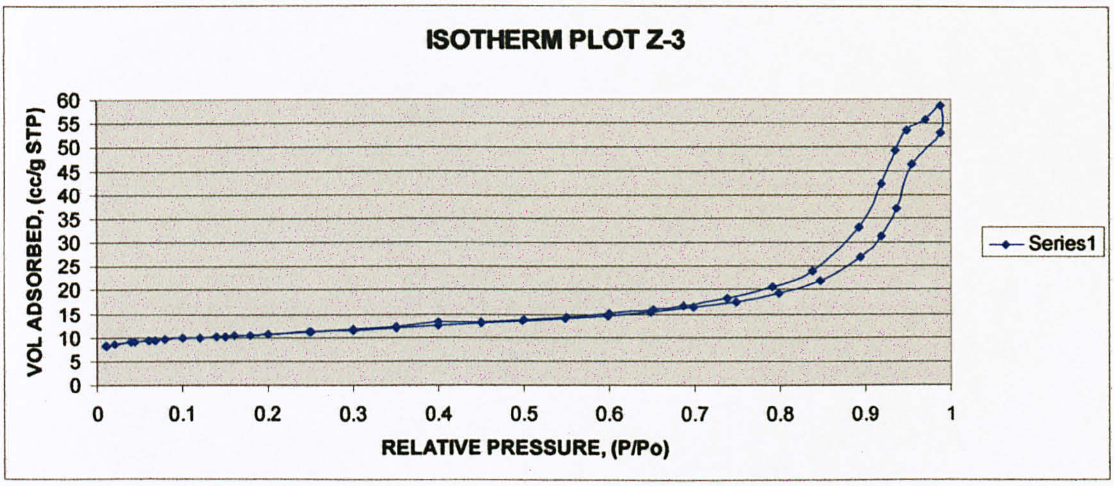


**Figure 4.1.3:** Isotherm plot for zeolite 3A

Based on the plot obtained as in **Figure 4.1.4**, the micropore volume for Zeolite 3A is 0.007303 cc/g and the external surface area is 21.2249 sq. m/g.

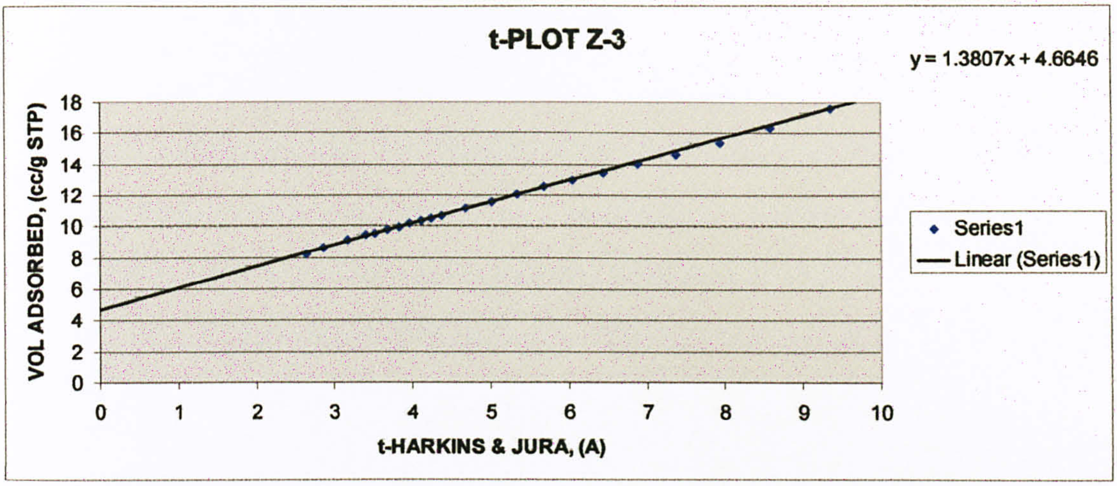


**Figure 4.1.4**: t-plot for zeolite 3A

### 4.1.2 XRF

Preparation of solid samples must be simple, rapid and reproducible. In this case, motar grinder is used to grind zeolite into the powdered form. (Refer to **Appendices A.1**).

Powdered samples of zeolite 3A and zeolite 13X are then been analyzed using X-Ray Flourescent (XRF). It was performed to know the chemical compositions of the minerals that are present in the zeolites. All samples are exposed to high energy X-ray radiation. The data given in **Table 4.1.1-4.1.2** shows that the silica, oxide and aluminium are present in major quantities while other minerals are present in trace amounts.

**1. Zeolite 3A**

**Table 4.1.1**: Chemical analysis of zeolite 3A

| Composition | Percentage (%) |
|---|---|
| O | 42.3 |
| Na | 4.67 |
| Mg | 1.53 |
| Al | 13.6 |
| Si | 20.2 |
| P | 0.111 |
| S | 0.0379 |
| K | 13.5 |
| Ca | 2.84 |
| Ti | 0.108 |

| | |
|---|---|
| Fe | 0.938 |
| Sr | 0.014 |

Compton=0.75, Rayleigh=1.31

**2. Zeolite 13X**

**Table 4.1.2:** Chemical analysis of zeolite 13X

| Composition | Percentage (%) |
|---|---|
| O | 46.1 |
| Na | 9.79 |
| Mg | 0.849 |
| Al | 15.5 |
| Si | 23.3 |
| K | 0.837 |
| Ca | 1.7 |
| Ti | 0.136 |
| Fe | 1.59 |

Compton=0.53, Rayleigh=0.89

### 4.1.3 XRD

This method is for determining the crystal structure of zeolite sodium A (zeolite NaA) and zeolite sodium X (zeolite NaX) using selected peaks from the X-ray diffraction pattern of the zeolite. X-Rays that strike certain crystallographic planes at specific angles are reinforced rather than annihilated. This phenomenon is called diffraction. The x-rays are diffracted when conditions satisfy Bragg's Law,

$$\sin\theta = \frac{\lambda}{2d_{hkl}}$$

The samples are first grind using motar grinder. (Refer to **Appendices A.1**) Grinding of course-textured samples is done gently. Over-grinding can lead to breaking up of fine crystals and destruction of the zeolite. The XRD patterns of the zeolite NaA containing sample and the reference sample (NaA) are obtained under the same conditions. **Figure 4.1.5-4.1.6** below shows the XRD pattern for both zeolite sample and reference sample.

The reference sample is as indicated by red line. For zeolite 3A, the best reference is potassium aluminum silicate. This reference indicates qualitatively the elements present in the sample. The crystal structure is cubic, with lattice parameters; a=12.30610, b=12.30610 and c=12.30610. The lattice parameters, which describe the size and shape of the unit cell, include the dimensions of the sides of the unit cell and the angles between the sides. In this case, the angle is at 90°.

The reference for zeolite 13X is sodium aluminum silicate hydrate whereas zeolite 13X with copper catalyst is potassium ethyl ammonium aluminium silicate hydrate. Both zeolite exhibits cubic crystal structure with slightly different lattice parameters value. The lattice parameters value for zeolite 13X; a=25.02800, b=25.02800, c=25.02800 and the lattice parameters value for zeolite 13X with copper catalyst; a=24.74000, b=24.74000, c=24.74000.

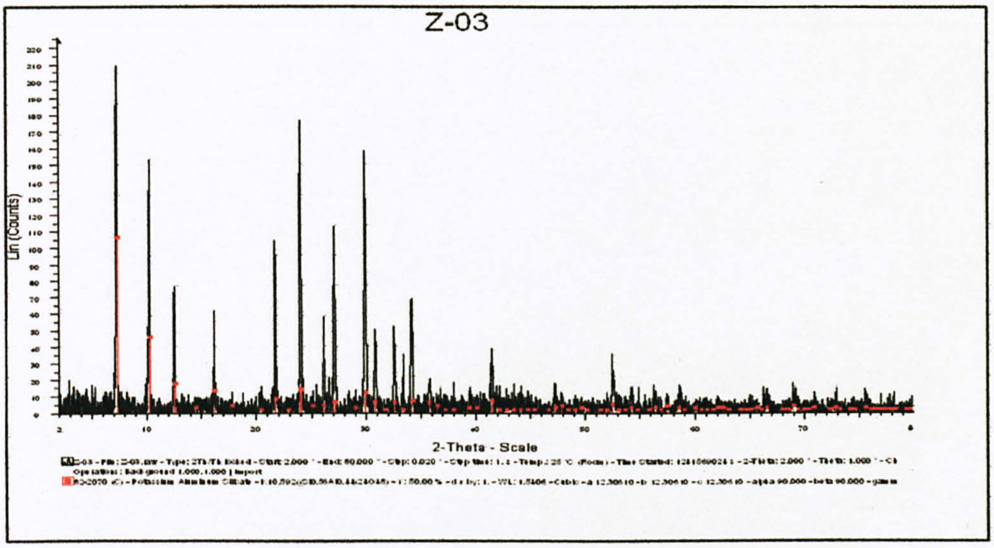


**Figure 4.1.5:** X-Ray diffraction pattern for zeolite 3A sample and reference sample (red)

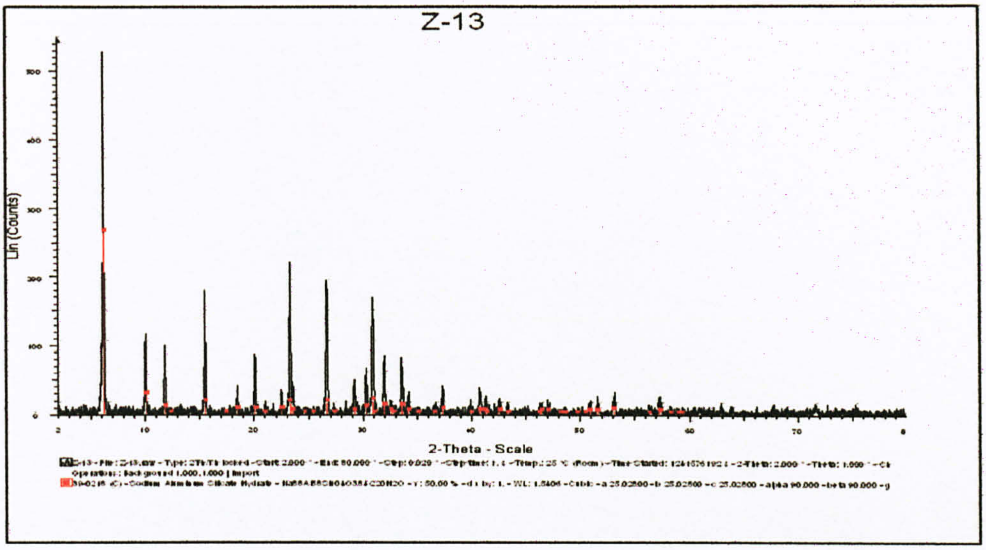


**Figure 4.1.6:** X-Ray diffraction pattern for zeolite 13X sample and reference sample (red)

### 4.1.4 FESEM Characterization

The morphology of the zeolites was studied fractionally for surface layer and for materials contains in it. **Figure 4.1.7-4.1.8** below represents the FESEM nanophotographs of zeolite particles at 100,000 magnification.

In **Figure 4.1.7**, for zeolite 3A, the crystallites were flat in shape. One can seen the porous structure on zeolite 3A with diameter between 11.72-21.51 nm (about 1-2 Angstrom).

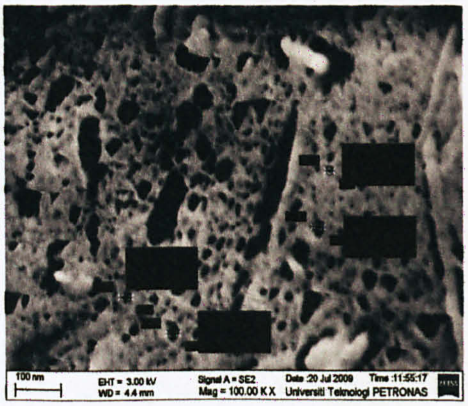


**Figure 4.1.7:** FESEM nanophotographs ($\times 100000$) of zeolite 3A

For zeolite 13X, the pore size are bigger than zeolite 3A and vary from 12.7-58.03 nm and for crystal morphology, we found a hollow rod like crystals.

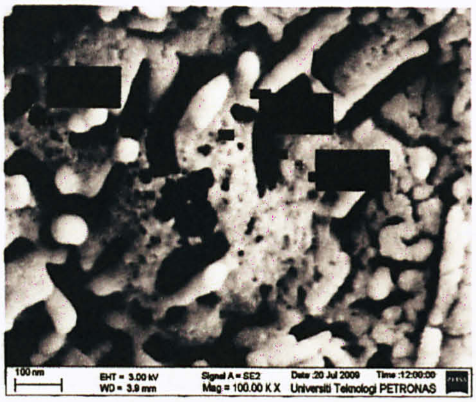


**Figure 4.1.8:** FESEM nanophotographs ( × 100000 ) of zeolite 13X

### 4.1.5 Thermogravimetric Analyzer (TGA) Characterization

Thermogravimetric analysis (TGA) is a useful tool for characterizing of zeolites. In general, thermal analysis describes a group of methods whereby the dependence of the parameters of any physical property of a substance on temperature is measured (F. Ramoa, 1983).

In this characterization, the technique used is changing of weight. The percent weight loss of a test sample is recorded while the sample is being heated at a uniform rate (10°C $\text{min}^{-1}$). Nitrogen gas is use and the flow rate is set at 150 $\text{cm}^3/\text{min}$. Next, the test material is placed in the specimen holder and the furnace is raised. The initial weight reading is set to 100%, then the heating program is initiated.

The gas environment is preselected for a thermal decomposition. **Figure 4.1.9-Figure 4.2.0** below shows the TGA analysis data which is in the form of percent weight loss versus temperature. The thermal anaylsis was carried out up to temperature of 900°C. The TGA curve of zeolite 3A up to temperature 290°C showed the liberation of water whereas zeolite 13X up to temperature of 340°C. As shown, the degradation temperature for both sample is more than 900°C.

The percent weight loss for all samples are calculated using this equation:

$$\% \text{ weight loss} = \frac{\text{Initial weight - Final weight}}{\text{Initial weight}} \times 100$$

$$\% \text{ weight loss}_{\text{zeolite 3A}} = \frac{99.928 - 99.748}{99.928} \times 100 = 0.18$$

$$\% \text{ weight loss}_{\text{zeolite 13X}} = \frac{99.877 - 79.56}{99.877} \times 100 = 0.20$$

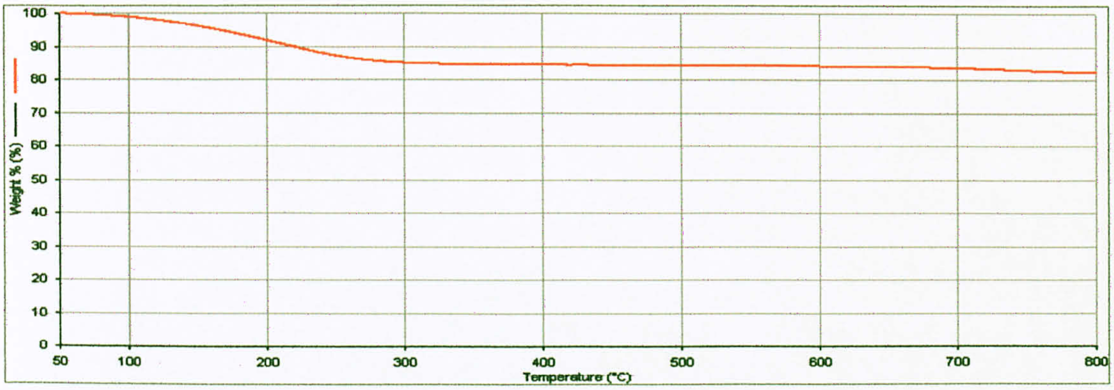


**Figure 4.1.9:** TGA curve for zeolite 3A

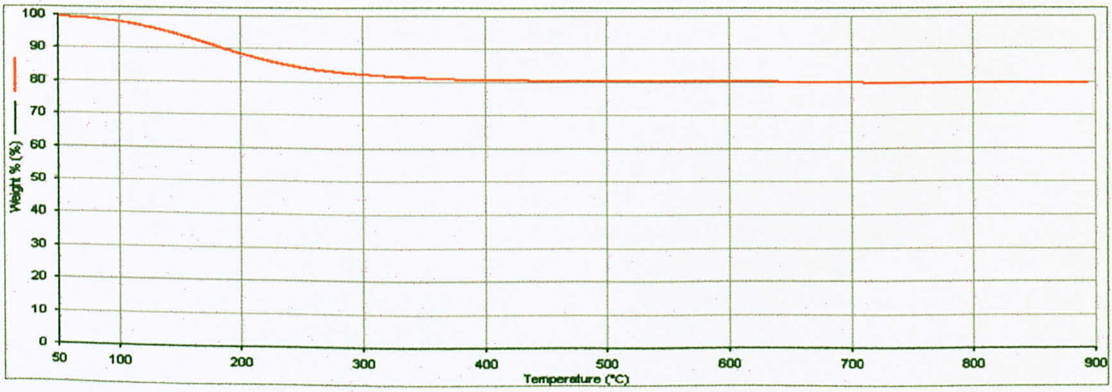


**Figure 4.2.0:** TGA curve for zeolite 13X

## 4.2 Parametric Analysis

### 4.2.1 Calibration Curve

The accuracy of flow meter used in the experiment is 1% of full scale. At 1 NLM, an error of 10% is introduced into the flow meter. Generally, the statistical acceptance criterion for the error introduced by measurement is only 5% (Montgomery, 2005). If the total flowrate exceeded 7 NLM, it would be difficult to analyze the methane purity since the breakthrough time would be tremendously fast. In this calibration a suitable flowrate that compromised between measurement error and ease of purity analysis need to be determined. It was found that at 4-6 NLM the measurement can be performed with good accuracy and the product purity can still be analyzed. Based on this, a flowrate of 5 NLM was determined as the most suitable flowrate with reasonable error of measurement.

To determine the best temperature of wetting methane gas, the pressure was varied form 20-60 bar and temperature from 40- 45 °C. From the data collected, a plot of moisture content (moisture concentration at inlet of adsorption column) versus pressure is made. From this, it is shown that pressure is inversely proportional with moisture content, which when the pressure increases the amount of moisture in methane is decreases. The trend is different with temperature, which increasing temperature will leads to higher moisture content. From this, it can concludes that the optimum temperature for wetting the methane gas is at 50 °C. **Table 4.1.3** below shows the data collected from the experiment.

**Table 4.1.3:** Inlet moisture content at various temperature and pressure

| Temperature °C | Pressure (bar) | Inlet Dew Point °C | Concentration (ppm) |
|---|---|---|---|
| 40 | 20 | 17.2 | 920 |
| | 40 | 15 | 410 |
| | 60 | 14.7 | 270 |
| 45 | 20 | 17.2 | 920 |
| | 40 | 15.7 | 428 |
| | 60 | 15.5 | 284 |
| 50 | 20 | 20 | 1096 |
| | 40 | 17.1 | 468 |
| | 60 | 17.2 | 317 |

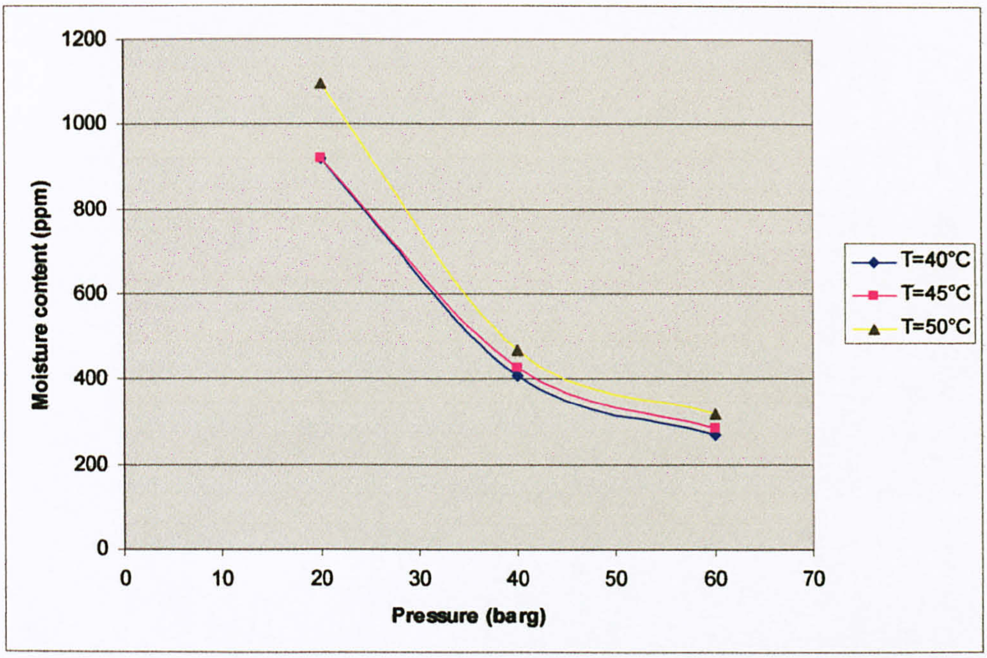


**Figure 4.2.1:** Calibration curve

### 4.2.2 Effect of Pressure

The methane gas is passed down through the packed bed at a constant flowrate (5 NLM). The concentrations of solute (water vapour) in the fluid phase and the solid adsorbent phase change with time and with position in the fixed bed as the adsorption proceeds. As the methane first comes in contact with the inlet of the bed, most of the mass transfer and adsorption takes place here. As the methane passes through the bed, the water vapour concentration in methane drops very rapidly with the distance in the bed and reaches zero well before the end of the bed is reached. After a certain period of time, the solid adsorbent near the entrance of the column is almost saturated, and most of the mass transfer and adsorption now takes place at point slightly farther from the inlet. At a later time, the profile or mass transfer zone where most of the concentration change takes place has moved farther down the bed. The outlet concentration remains nearly zero until the mass transfer zone starts to reach the column. Then the outlet concentration starts to rise, and at $c/c_o$=0.05, the outlet concentration has risen to a point called break point. The breakthrough concentration curve is shown in **Figure 4.2.2-4.2.3** where the concentration ratio $c/c_o$ is plotted versus time and time is taken for every 5 minutes. The fluid concentration $c_o$ is the inlet concentration and c is the outlet concentration.

The experiment is perform at two pressures; at 40 and 60 barg and the mass of zeolite 3A use to fill up the column is measure to be about 380 g. The result of the study is given in **Table 4.1.4** and from the calculated saturation capacity; it is preferable to perform adsorption at high pressure compare to at low pressure. The longer time for breakthrough at 60 barg compare to at 40 barg also verified that the high pressure is preferable.

**Table 4.1.4:** Result of pressure variation experiment for zeolite 3A

| **Pressure (bar)** | **Breakthrough Time (min)** | **Saturation Capacity (g water/g adsorbent)** | **Used Bed, $H_B$ (cm)** | **Unused Bed, $H_{NB}$ (cm)** |
|---|---|---|---|---|
| 40 | 140 | 0.001378 | 11.2 | 18.8 |
| 60 | 328 | 0.002304 | 18.2 | 11.8 |

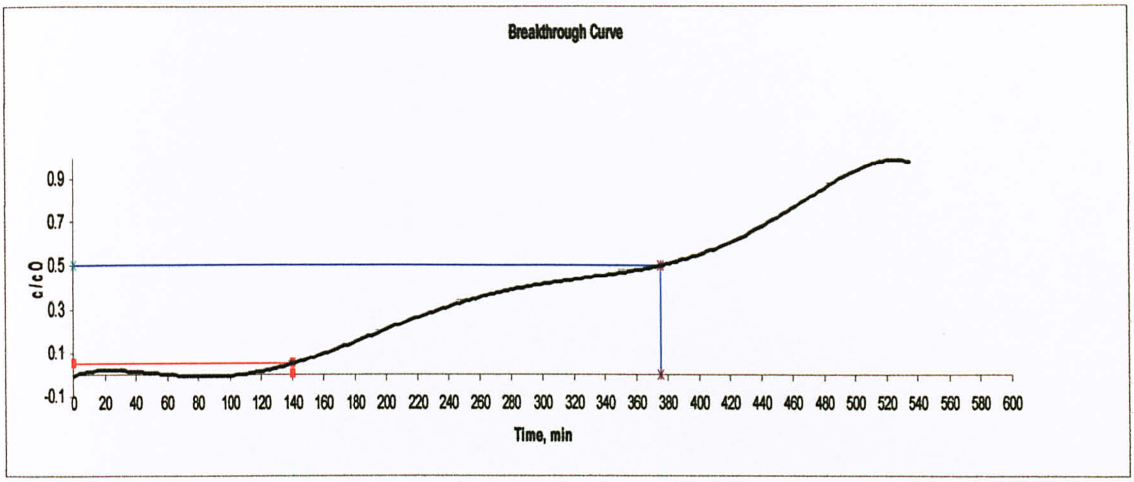


**Figure 4.2.2:** Breakthrough Curve for Zeolite 3A at 40 barg

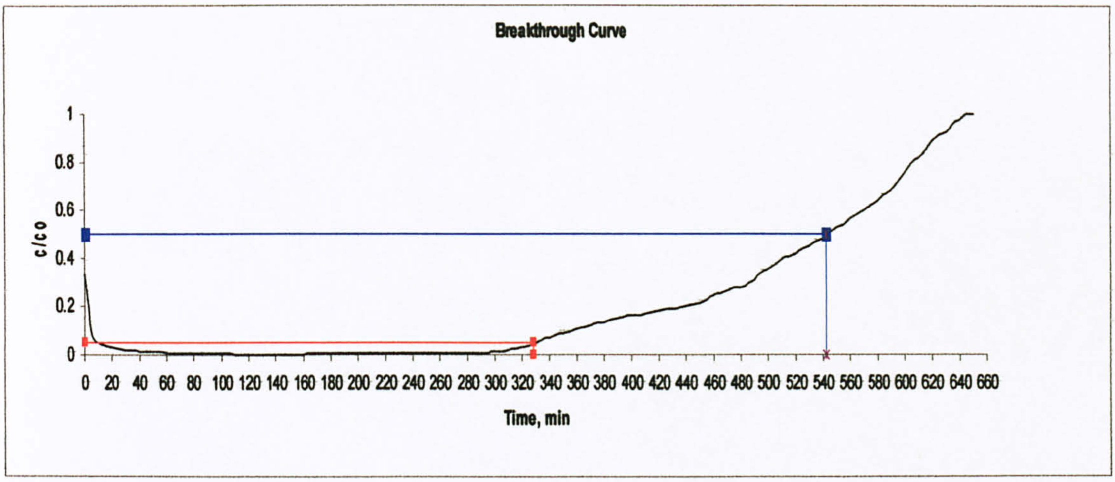


**Figure 4.2.3:** Breakthrough Curve for Zeolite 3A at 60 barg

The same study is also performs for zeolite 13X and 380 g of zeolite 13X is used. The result of the study is given in **Table 4.1.5.**

**Table 4.1.5:** Result of pressure variation experiment for zeolite 13X

| **Pressure (bar)** | **Breakthrough Time (min)** | **Saturation Capacity (g water/g adsorbent)** | **Used Bed, $H_B$ (cm)** | **Unused Bed, $H_{NB}$ (cm)** |
|---|---|---|---|---|
| 40 | 560 | 0.002940 | 20.5 | 9.5 |
| 60 | 580 | 0.003050 | 21 | 9 |

As shown in **Table 4.1.5**, the saturation capacity at 40 barg is slightly lower than at 60 barg. However this still indicates that high pressure will favor more adsorption. At higher pressure the diffusivity of the gas is faster thus ensure all the water vapour will be adsorbed in the adsorbent.

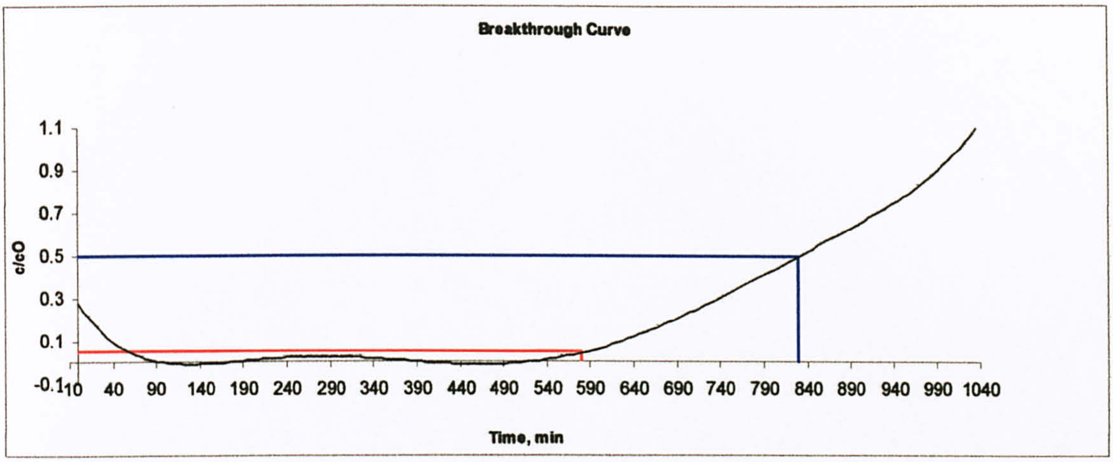


**Figure 4.2.4:** Breakthrough Curve for Zeolite 13X at 40 barg

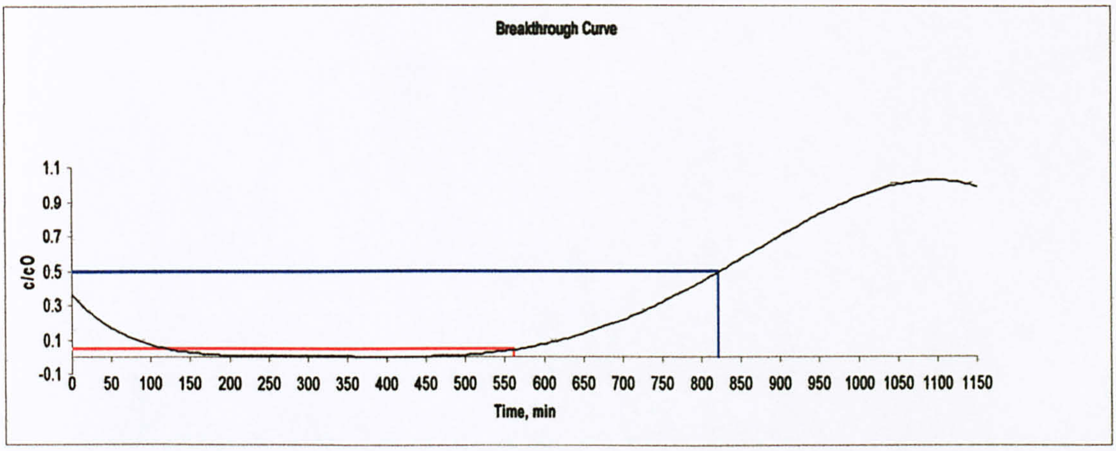


**Figure 4.2.5:** Breakthrough Curve for Zeolite 13X at 60 barg

To compare between two zeolites; zeolite 3A and zeolite 13X, the adsorbent capacity is plotted versus pressure. From **Figure 4.2.6**, it is shown that zeolite 13X have higher adsorbent capacity than zeolite 3A. The main reason why the adsorbent capacity for zeolite 13X is higher than zeolite 3A is due to high surface area of adsorbent. The higher surface area, the higher amount of water vapour will be adsorbed.

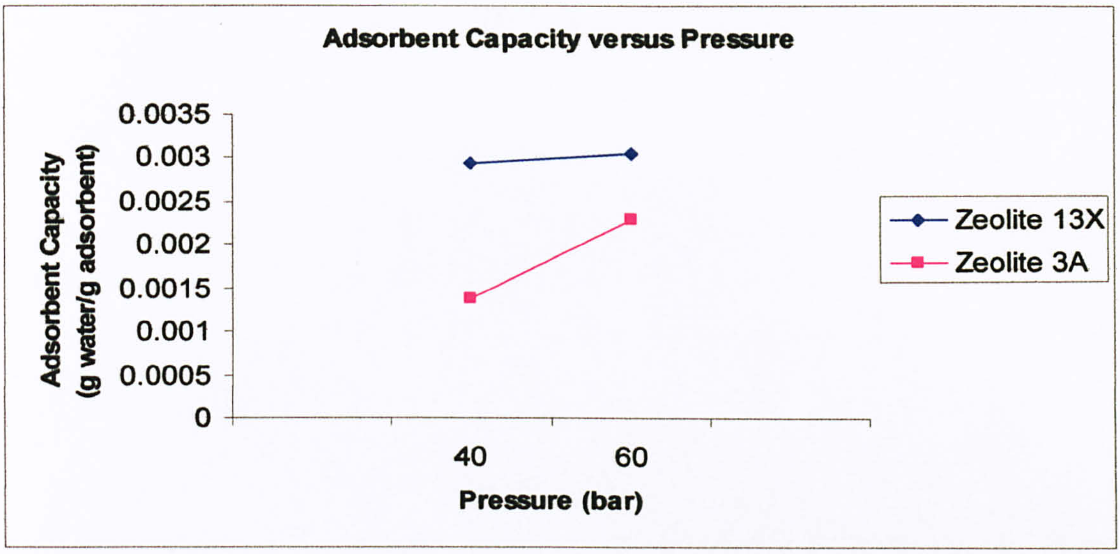


**Figure 4.2.6:** Adsorbent capacity

# CHAPTER 5

# CONCLUSION AND RECOMMENDATIONS

## 5.1 Conclusion

From adsorbent characterization and experimental, it is proven that the zeolites have a potential to become a good adsorbent in removing water from natural gas. Several general conclusions can be drawn as follows:

1. Results form surface area analyzer confirms that zeolite 3A is mesopore and zeolite 13X is micropore.
2. Zeolite 13X has higher surface area than zeolite 3A.
3. Zeolite 3A is potassium form and zeolite 13X is sodium form.
4. Both zeolites are crystalline phase but zeolite 13X is high in crystallinity compared to zeolite 3A.
5. Based on TGA analysis, both zeolites degrade at temperature higher than 900°C, thus it has high resistivity before fouling.
6. Comparing theory with actual, it is proven that zeolite 13X has bigger pore size and interconnecting pores than zeolite 3A.
7. For calibration, the ideal temperature to wet the methane is at 50°C and at 5 NLM.
8. High pressure will favour more adsorption compare to low pressure.
9. Zeolite 13X is preferable for removal of water vapour compare to zeolite 3A.

## 5.2 Recommendations

In this experiment, methane is wetted with water vapour in the saturation vessel. The exact amount of water vapour in the methane is unknown. The only measurement to know the amount of water been removed is by calculating the percentage of water, which is by measuring the amount of water before entering adsorption column and after entering the adsorption column by using moisture analyzer. For better estimation, it is recommended to do calculation or using any method to know the exact water that contains in the methane. A Karl Fischer titration is best recommended.

For TGA analysis, the constraint is on the equipment used. For better result, it is recommended to use TGA analyzer that can measure the temperature more than 900°C so that the degradation temperature of zeolite and copper catalyst can be determined precisely.

## REFERENCES

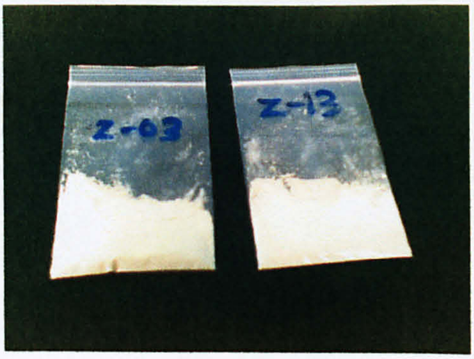
1. Abdurrahman (2006), *Parametric Analysis of $CO_2$ Separation from Natural Gas by Adsorption Process*
2. Arun Datta, 2007. *Process Engineering and Design Using Visual Basic,* p. 370.
3. David A. Zornes (2004), US Patent: *Molecular Separator Apparatus*, US 6, 706, 097 B2, p. 17
4. Department of Energy USA, Natural Gas Processing:The Crucial Link Between Natural Gas Production and Its Transportation to Market last updated 3 October 2009http://www.eia.doe.gov/pub/oil_gas/natural_gas/feature_articles/2006/ngprocess/ngprocess.pdf
5. F. Ramoa Ribeiro, 1984. *Zeolites: Science and Technology*. p. 185
6. H. van Bekkum, E.M. Flanigen, P.A Jacobs, and J.C. Jansen, 2001. *Introduction to Zeolite Science and Practice*. Vol. 137, 11-14
7. Isobel Parker, Donald Hughes, Activated Carbon last updated 2 October 2009 http://www.cee.vt.edu/ewr/environmental/teach/wtprimer/actcarbon/actcarbon.html
8. Library4Science, Adsorbent last updated 3 October 2009 http://www.chromatography-online.org/topics/adsorbent.html
9. Natural Gas Supply Association, Water Removal last updated 3 October 2009 http://www.naturalgas.org/naturalgas/processing_ng.asp
10. Natural Gas Supply Association, Typical Composition of Natural Gas last updated 3 October 2009 http://www.naturalgas.org/overview/background.asp
11. Natural Gas Supply Association, Glycol Dehydration last updated 3 October 2009 http://www.naturalgas.org/naturalgas/processing_ng.asp
12. P. Gandhidasan, Abdulghani A. Alfarayedhi, Ali A. Al-Mubarak (2000) *Dehydration of Natural Gas using Solid Dessicants*, 857-859
13. Ralph T. Yang (2003). *Adsorbents: Fundamentals and Applications*. John Wiley & Sons, Inc., Publication. p. 157

14. Wikipedia, Characteristics and General Requirements last updated 3 October 2009 http://en.wikipedia.org/wiki/Adsorption
15. Wikipedia, Activated Alumina last updated 3 October 2009 http://en.wikipedia.org/wiki/Activated_alumina
16. Wikipedia, Silica Gel Properties last updated 3 October 2009 http://en.wikipedia.org/wiki/Silica_gel

## APPENDICES A

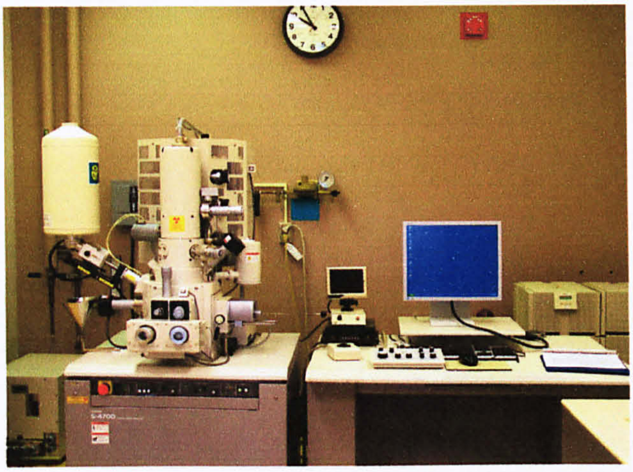
### A.1

Below are the pictures showing the equipment for making the powdered zeolite that be used in X-Ray Diffraction (XRD) to determine the crsytalline structure and X-Ray Flourescence (XRF) to know its composition. This equipment is called motar grinder and samples (Zeolite 3A and Zeolite 13X) are placed in a chamber before been crashed into powder.



## A.2

The pictures showing FESEM simulator. The computer is connected to FESEM simulator to take a look online at a number of microscopic objects.



## A.3

Below is Thermogravimetric Analysis (TGA). The zeolite sample is place on a platinum sample pan. Nitrogen gas is used as medium to heat sample.

# APPENDICES B

## B.1

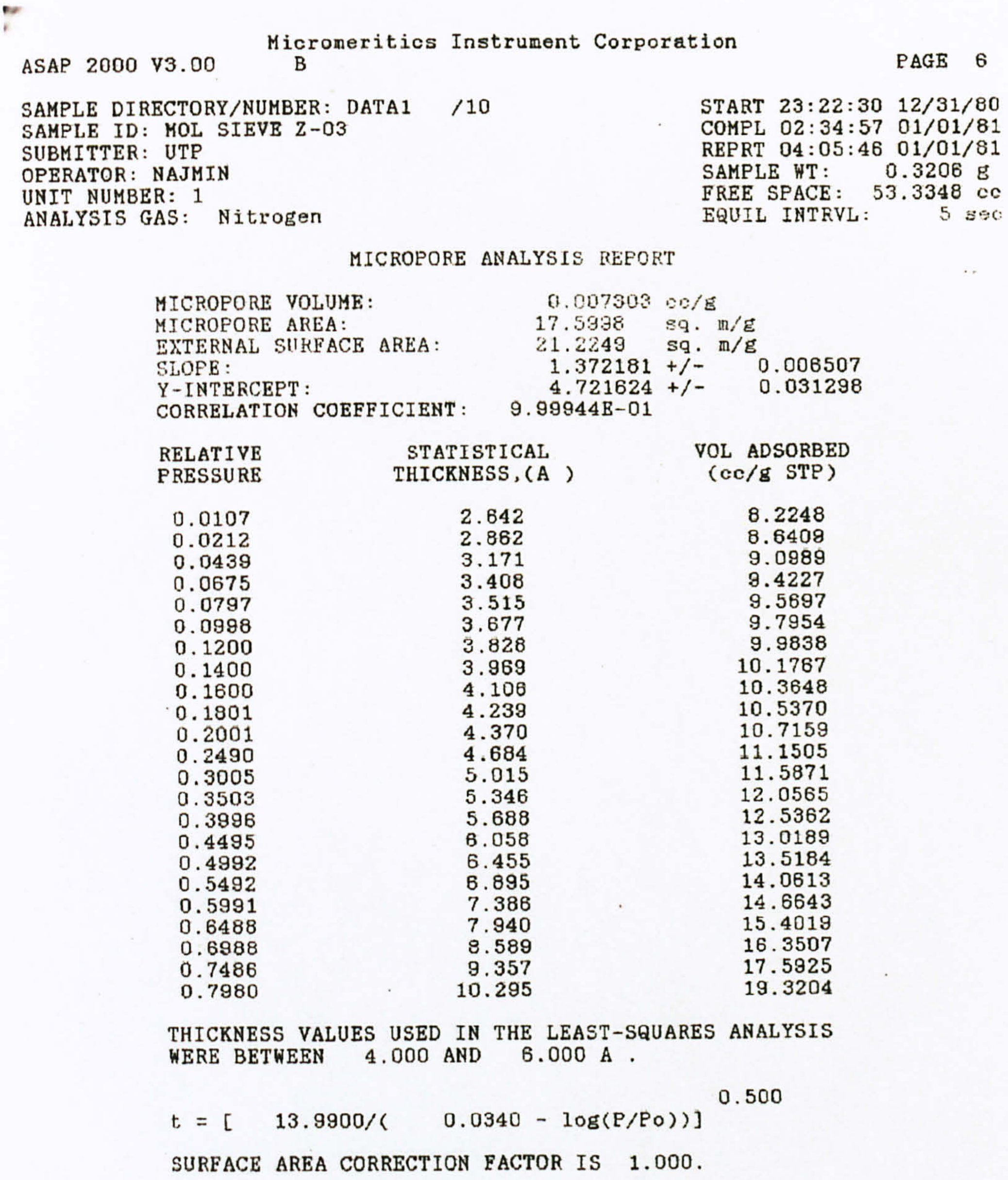
The data shown are the result from surface area analyzer for zeolite 3A. Analysis gas, nitrogen is been used as the working medium. The isotherm plot is then made as the result from volume adsorbed versus relative pressure.

```
                         Micromeritics Instrument Corporation
ASAP 2000 V3.00        B                                                 PAGE  1

SAMPLE DIRECTORY/NUMBER: DATA1    /10                     START 23:22:30 12/31/8
SAMPLE ID: MOL SIEVE Z-03                                 COMPL 02:34:57 01/01/8
SUBMITTER: UTP                                            REPRT 04:05:46 01/01/8
OPERATOR: NAJMIN                                          SAMPLE WT:      0.3206 g
UNIT NUMBER: 1                                            FREE SPACE:    53.3348 c
ANALYSIS GAS:   Nitrogen                                  EQUIL INTRVL:        5 se

                                  ANALYSIS LOG

   RELATIVE      PRESSURE     VOL ADSORBED    ELAPSED TIME      SATURATION
   PRESSURE       (mmHg)      (cc/g STP)        (HR:MN)        PRESS.(mmHg)

                                                  0:30            765.744
    0.0107         8.202        8.2248            0:38
    0.0212        16.207        8.6409            0:40
    0.0439        33.641        9.0989            0:43
    0.0675        51.715        9.4227            0:44
    0.0797        61.075        9.5697            0:46
    0.0998        76.497        9.7954            0:47
    0.1200        91.954        9.9838            0:49
    0.1400       107.262       10.1767            0:51
    0.1600       122.632       10.3648            0:52
    0.1801       138.038       10.5370            0:53
    0.2001       153.368       10.7159            0:55
    0.2490       190.834       11.1505            0:56
    0.3005       230.282       11.5871            0:58
    0.3503       268.504       12.0565            0:59
    0.3996       306.261       12.5362            1:01
    0.4495       344.572       13.0189            1:02
    0.4992       382.681       13.5184            1:04
    0.5492       421.007       14.0613            1:05
    0.5991       459.317       14.6643            1:07
    0.6488       497.390       15.4019            1:09
    0.6988       535.767       16.3507            1:11
    0.7486       573.964       17.5925            1:13
    0.7980       611.954       19.3204            1:16
    0.8469       649.515       21.9970            1:19
    0.8943       685.937       26.8579            1:25
    0.9191       705.088       31.3592            1:30
    0.9370       718.963       36.9976            1:37
    0.9541       732.284       46.3331            1:46
    0.9884       758.669       53.0480            1:48
    0.9888       759.037       58.6607            1:51
    0.9702       744.820       55.7676            1:52
    0.9481       727.982       53.3828            1:57
    0.9350       718.042       49.2210            2:03
    0.9194       706.194       42.3883            2:10
    0.8932       686.284       33.2375            2:18
    0.8388       644.586       24.0319            2:25
    0.7919       608.660       20.5783            2:29
    0.7377       566.998       18.2303            2:32
                                                  2:34            768.692
    0.6868       527.958       16.7897            2:36
    0.6519       501.103       16.0140            2:38
```

```
                          Micromeritics Instrument Corporation
ASAP 2000 V3.00              B                                          PAGE  2

SAMPLE DIRECTORY/NUMBER: DATA1    /10                     START 23:22:30 12/31/80
SAMPLE ID: MOL SIEVE Z-03                                 COMPL 02:34:57 01/01/81
SUBMITTER: UTP                                            REPRT 04:05:46 01/01/81
OPERATOR: NAJMIN                                          SAMPLE WT:     0.3206 g
UNIT NUMBER: 1                                            FREE SPACE:  53.3348 cc
ANALYSIS GAS:  Nitrogen                                   EQUIL INTRVL:      5 sec

                                    ANALYSIS LOG

   RELATIVE     PRESSURE      VOL ADSORBED     ELAPSED TIME      SATURATION
   PRESSURE      (mmHg)       (cc/g STP)        (HR:MN)        PRESS.(mmHg)

    0.6001      461.298         15.1254           2:40
    0.5503      423.024         14.4296           2:42
    0.5001      384.454         13.8262           2:44
    0.4501      345.984         13.2544           2:45
    0.4000      307.441         12.6995           2:47
    0.3498      268.866         12.1879           2:49
    0.2999      230.551         11.7036           2:50
    0.2499      192.075         11.2268           2:52
    0.1999      153.645         10.7600           2:54
    0.1499      115.231         10.2982           2:55
    0.1001       76.962          9.7910           2:58
    0.0799       61.386          9.5641           3:00
    0.0597       45.928          9.3190           3:01
    0.0400       30.765          9.0129           3:04
    0.0201       15.437          8.5646           3:08
    0.0104        8.016          8.1640           3:12
```

## B.2

The data from surface area analyzer for zeolite 3A which is then used to make a t-plot.



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                     Micromeritics Instrument Corporation
ASAP 2000 V3.00        B                                           PAGE  6

SAMPLE DIRECTORY/NUMBER: DATA1    /10                START 23:22:30 12/31/80
SAMPLE ID: MOL SIEVE Z-03                            COMPL 02:34:57 01/01/81
SUBMITTER: UTP                                       REPRT 04:05:46 01/01/81
OPERATOR: NAJMIN                                     SAMPLE WT:     0.3206 g
UNIT NUMBER: 1                                       FREE SPACE:   53.3348 cc
ANALYSIS GAS:  Nitrogen                              EQUIL INTRVL:       5 sec

                         MICROPORE ANALYSIS REPORT

        MICROPORE VOLUME:                 0.007303 cc/g
        MICROPORE AREA:                  17.5938    sq. m/g
        EXTERNAL SURFACE AREA:           21.2249    sq. m/g
        SLOPE:                            1.372181 +/-     0.006507
        Y-INTERCEPT:                      4.721624 +/-     0.031298
        CORRELATION COEFFICIENT:    9.99944E-01

        RELATIVE              STATISTICAL               VOL ADSORBED
        PRESSURE            THICKNESS,(A )               (cc/g STP)

         0.0107                  2.642                      8.2248
         0.0212                  2.862                      8.6408
         0.0439                  3.171                      9.0989
         0.0675                  3.408                      9.4227
         0.0797                  3.515                      9.5697
         0.0998                  3.677                      9.7954
         0.1200                  3.828                      9.9838
         0.1400                  3.969                     10.1767
         0.1600                  4.106                     10.3648
         0.1801                  4.239                     10.5370
         0.2001                  4.370                     10.7159
         0.2490                  4.684                     11.1505
         0.3005                  5.015                     11.5871
         0.3503                  5.346                     12.0565
         0.3996                  5.688                     12.5362
         0.4495                  6.058                     13.0189
         0.4992                  6.455                     13.5184
         0.5492                  6.895                     14.0613
         0.5991                  7.386                     14.6643
         0.6488                  7.940                     15.4019
         0.6988                  8.589                     16.3507
         0.7486                  9.357                     17.5925
         0.7980                 10.295                     19.3204

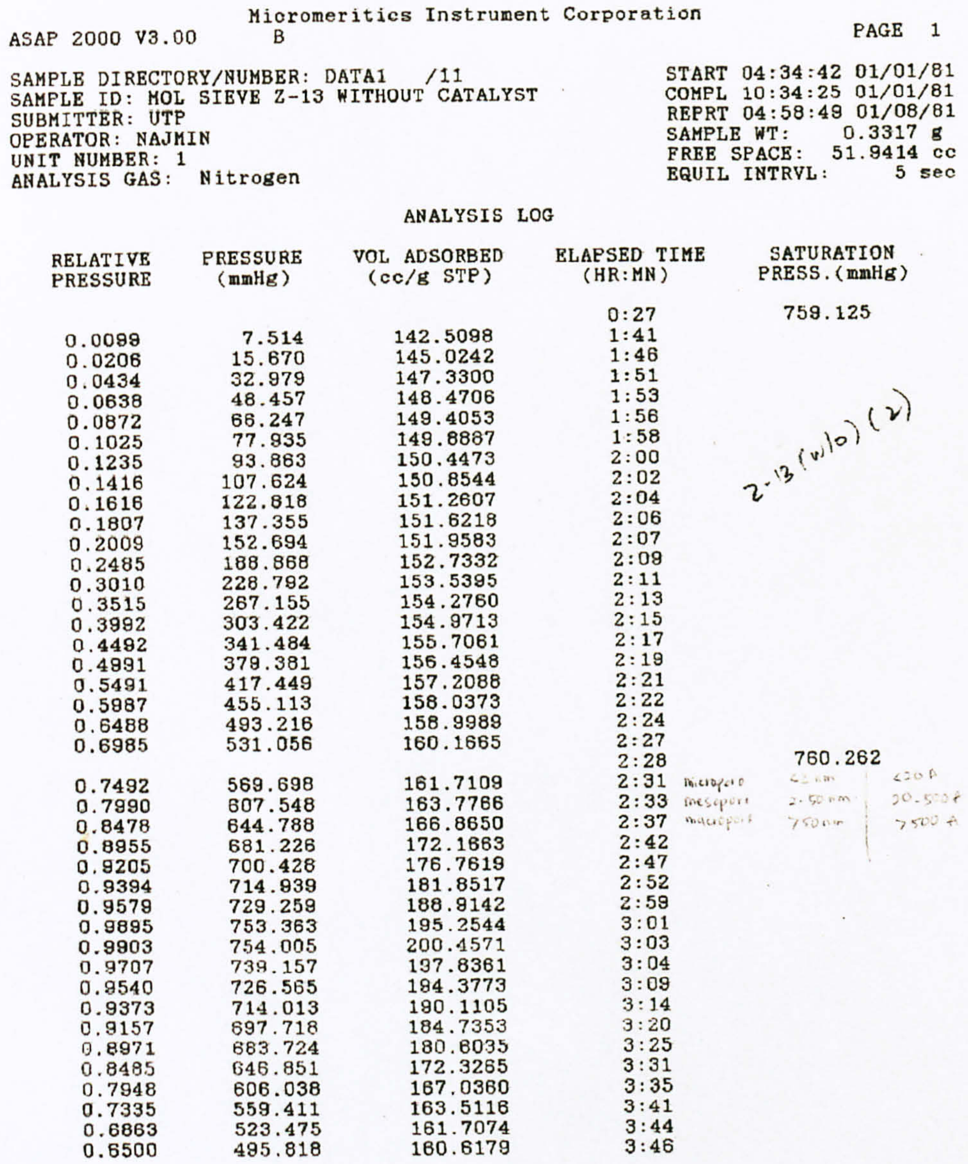
         THICKNESS VALUES USED IN THE LEAST-SQUARES ANALYSIS
         WERE BETWEEN   4.000 AND   6.000 A .

                                                      0.500
         t = [   13.9900/(    0.0340 - log(P/Po))]

         SURFACE AREA CORRECTION FACTOR IS  1.000.
```

## B.3

The data shown are the result from surface area analyzer for zeolite 13X. Analysis gas, nitrogen is been used as the working medium. The isotherm plot is then made as the result from volume adsorbed versus relative pressure.



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                    Micromeritics Instrument Corporation
ASAP 2000 V3.00         B                                          PAGE  1

SAMPLE DIRECTORY/NUMBER: DATA1   /11                  START 04:34:42 01/01/81
SAMPLE ID: MOL SIEVE Z-13 WITHOUT CATALYST            COMPL 10:34:25 01/01/81
SUBMITTER: UTP                                        REPRT 04:58:49 01/08/81
OPERATOR: NAJMIN                                      SAMPLE WT:    0.3317 g
UNIT NUMBER: 1                                        FREE SPACE:  51.9414 cc
ANALYSIS GAS:  Nitrogen                               EQUIL INTRVL:     5 sec

                                ANALYSIS LOG

  RELATIVE     PRESSURE     VOL ADSORBED    ELAPSED TIME      SATURATION
  PRESSURE      (mmHg)      (cc/g STP)        (HR:MN)       PRESS.(mmHg)

                                                0:27           759.125
   0.0099         7.514       142.5098          1:41
   0.0206        15.670       145.0242          1:46
   0.0434        32.979       147.3300          1:51
   0.0638        48.457       148.4706          1:53
   0.0872        66.247       149.4053          1:56
   0.1025        77.935       149.8887          1:58
   0.1235        93.863       150.4473          2:00
   0.1416       107.624       150.8544          2:02
   0.1616       122.818       151.2607          2:04
   0.1807       137.355       151.6218          2:06
   0.2009       152.694       151.9583          2:07
   0.2485       188.868       152.7332          2:09
   0.3010       228.792       153.5395          2:11
   0.3515       267.155       154.2760          2:13
   0.3992       303.422       154.9713          2:15
   0.4492       341.484       155.7061          2:17
   0.4991       379.381       156.4548          2:19
   0.5491       417.449       157.2088          2:21
   0.5987       455.113       158.0373          2:22
   0.6488       493.216       158.9989          2:24
   0.6985       531.056       160.1665          2:27
                                                2:28           760.262
   0.7492       569.698       161.7109          2:31
   0.7990       607.548       163.7766          2:33
   0.8478       644.788       166.8650          2:37
   0.8955       681.226       172.1663          2:42
   0.9205       700.428       176.7619          2:47
   0.9394       714.939       181.8517          2:52
   0.9579       729.259       188.9142          2:59
   0.9895       753.363       195.2544          3:01
   0.9903       754.005       200.4571          3:03
   0.9707       739.157       197.8361          3:04
   0.9540       726.565       194.3773          3:09
   0.9373       714.013       190.1105          3:14
   0.9157       697.718       184.7353          3:20
   0.8971       683.724       180.6035          3:25
   0.8485       646.851       172.3265          3:31
   0.7948       606.038       167.0360          3:35
   0.7335       559.411       163.5116          3:41
   0.6863       523.475       161.7074          3:44
   0.6500       495.818       160.6179          3:46
```
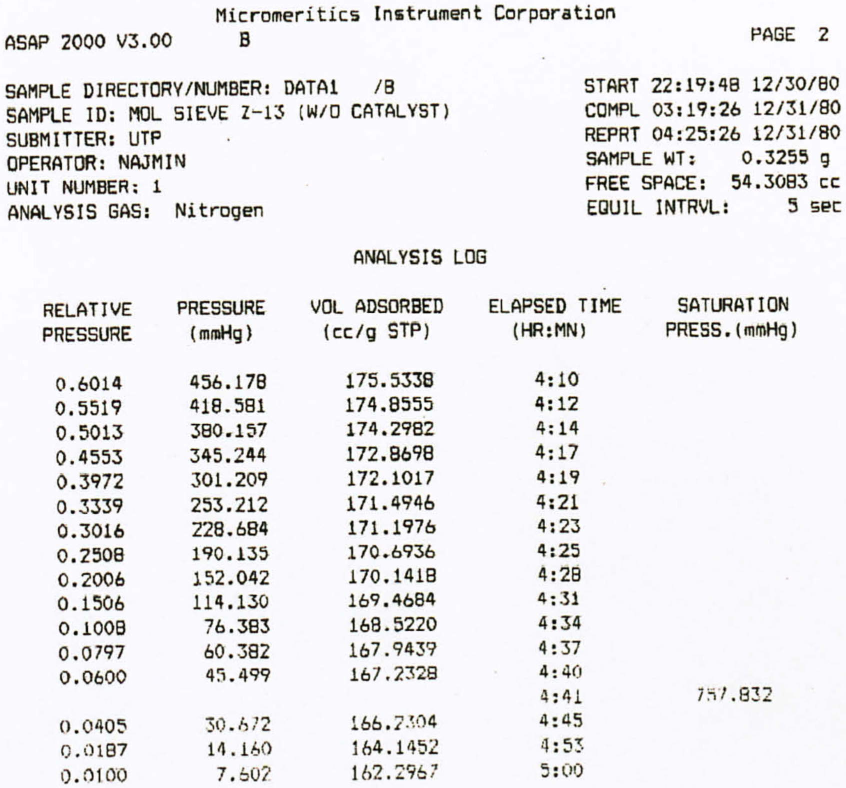

Z-13 (w/o) (2)

| | | |
|---|---|---|
| micropore | <2 nm | <20 Å |
| mesopore | 2-50 nm | 20-500 Å |
| macropore | >50 nm | >500 Å |



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                   Micromeritics Instrument Corporation
ASAP 2000 V3.00       B                                          PAGE  2

SAMPLE DIRECTORY/NUMBER: DATA1   /B                 START 22:19:48 12/30/80
SAMPLE ID: MOL SIEVE Z-13 (W/O CATALYST)            COMPL 03:19:26 12/31/80
SUBMITTER: UTP                                      REPRT 04:25:26 12/31/80
OPERATOR: NAJMIN                                    SAMPLE WT:     0.3255 g
UNIT NUMBER: 1                                      FREE SPACE:  54.3083 cc
ANALYSIS GAS:   Nitrogen                            EQUIL INTRVL:      5 sec

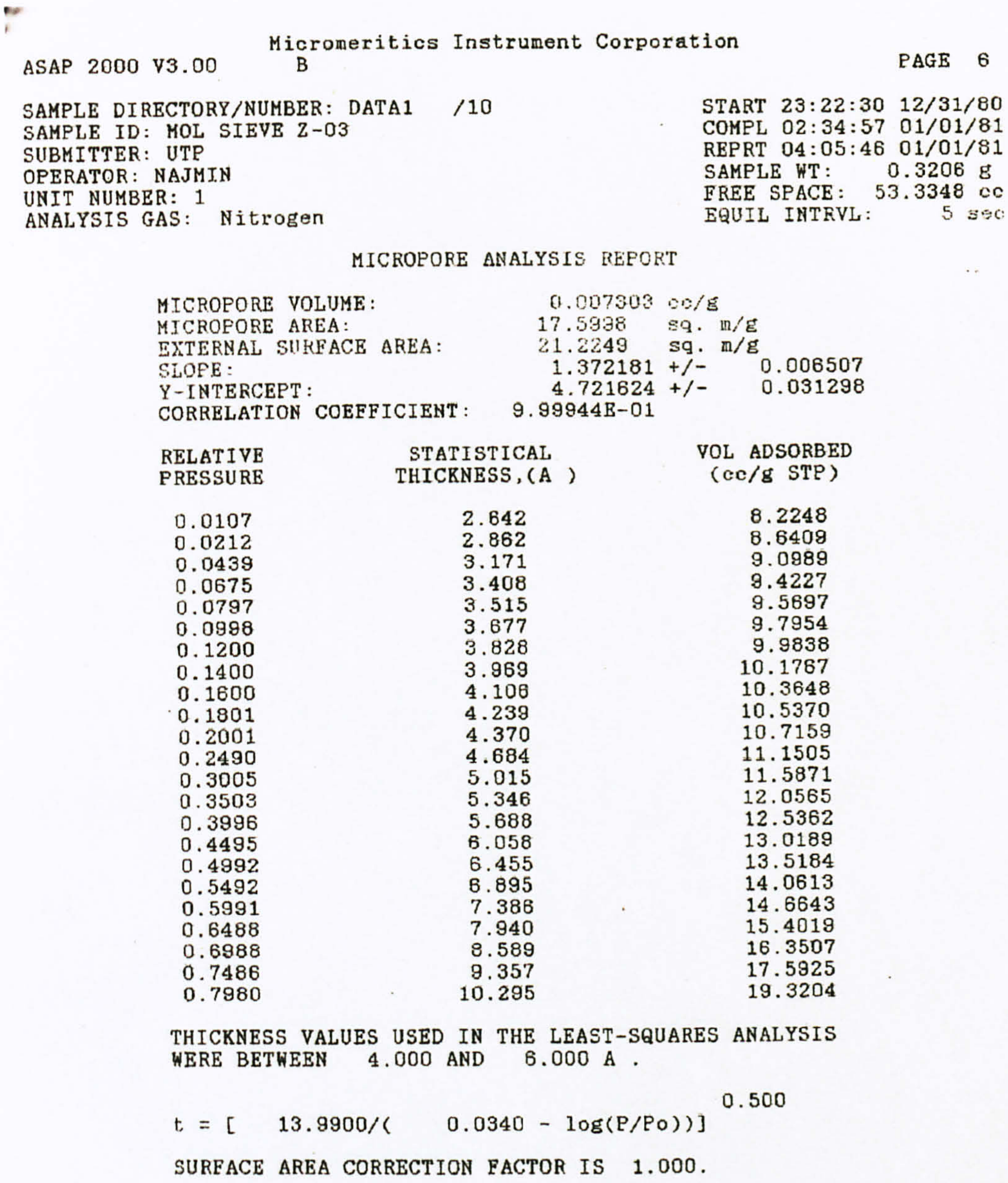
                               ANALYSIS LOG

  RELATIVE     PRESSURE    VOL ADSORBED   ELAPSED TIME     SATURATION
  PRESSURE      (mmHg)      (cc/g STP)      (HR:MN)       PRESS.(mmHg)

   0.6014      456.178       175.5338        4:10
   0.5519      418.581       174.8555        4:12
   0.5013      380.157       174.2982        4:14
   0.4553      345.244       172.8698        4:17
   0.3972      301.209       172.1017        4:19
   0.3339      253.212       171.4946        4:21
   0.3016      228.684       171.1976        4:23
   0.2508      190.135       170.6936        4:25
   0.2006      152.042       170.1418        4:28
   0.1506      114.130       169.4684        4:31
   0.1008       76.383       168.5220        4:34
   0.0797       60.382       167.9439        4:37
   0.0600       45.499       167.2328        4:40
                                             4:41          757.832
   0.0405       30.672       166.7304        4:45
   0.0187       14.160       164.1452        4:53
   0.0100        7.602       162.2967        5:00
```

## B.4

The data from surface area analyzer for zeolite 13X which is then used to make a t-plot.



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                    Micromeritics Instrument Corporation
ASAP 2000 V3.00         B                                             PAGE  6

SAMPLE DIRECTORY/NUMBER: DATA1    /10                     START 23:22:30 12/31/80
SAMPLE ID: MOL SIEVE Z-03                                 COMPL 02:34:57 01/01/81
SUBMITTER: UTP                                            REPRT 04:05:46 01/01/81
OPERATOR: NAJMIN                                          SAMPLE WT:     0.3206 g
UNIT NUMBER: 1                                            FREE SPACE:  53.3348 cc
ANALYSIS GAS:  Nitrogen                                   EQUIL INTRVL:       5 sec

                           MICROPORE ANALYSIS REPORT

          MICROPORE VOLUME:                   0.007303 cc/g
          MICROPORE AREA:                    17.5938   sq. m/g
          EXTERNAL SURFACE AREA:             21.2249   sq. m/g
          SLOPE:                              1.372181 +/-     0.006507
          Y-INTERCEPT:                        4.721624 +/-     0.031298
          CORRELATION COEFFICIENT:    9.99944E-01

          RELATIVE              STATISTICAL              VOL ADSORBED
          PRESSURE            THICKNESS,(A )              (cc/g STP)

           0.0107                  2.642                    8.2248
           0.0212                  2.862                    8.6409
           0.0439                  3.171                    9.0989
           0.0675                  3.408                    9.4227
           0.0797                  3.515                    9.5697
           0.0998                  3.677                    9.7954
           0.1200                  3.828                    9.9838
           0.1400                  3.969                   10.1767
           0.1600                  4.106                   10.3648
           0.1801                  4.239                   10.5370
           0.2001                  4.370                   10.7159
           0.2490                  4.684                   11.1505
           0.3005                  5.015                   11.5871
           0.3503                  5.346                   12.0565
           0.3996                  5.688                   12.5362
           0.4495                  6.058                   13.0189
           0.4992                  6.455                   13.5184
           0.5492                  6.895                   14.0613
           0.5991                  7.386                   14.6643
           0.6488                  7.940                   15.4018
           0.6988                  8.589                   16.3507
           0.7486                  9.357                   17.5925
           0.7980                 10.295                   19.3204

           THICKNESS VALUES USED IN THE LEAST-SQUARES ANALYSIS
           WERE BETWEEN    4.000 AND    6.000 A .

                                                         0.500
           t = [    13.9900/(      0.0340 - log(P/Po))]

           SURFACE AREA CORRECTION FACTOR IS   1.000.
```

## B.5

Sample of calculation for saturation capacity, used bed and unused bed length.

Zeolite 3A (40 barg)

methane flowrate=5 L/min=83.33 $cm^3/s$

methane density=0.717 $kg/m^3$=0.000717 $g/cm^3$

methane flowrate (mass)= $83.33 \times 0.000717 \times 3600 = 215.1$ g/hr

Total capacity of the bed, $t_t$=6.25 hr=375 min

Inlet water vapour concentration=389.55 ppm

Total water vapour adsorbed= $\frac{389.55}{1000000} \times 6.25 \times 215.1 = 0.5237$ g

Mass of adsorbent=380 g

Saturation capacity= $\frac{0.5237}{380} = 0.001378$

Total bed length, $H_T$=30 cm

Time equivalent to usable capacity, $t_u$=$t_b$=140 min

Usable bed length, $H_B$= $\frac{t_u}{t_t} \times H_T = \frac{140}{375} \times 30 = 11.2\,\text{cm}$

Unused bed length, $H_B$= $\left(1 - \frac{t_u}{t_t}\right) \times H_T = \left(1 - \frac{140}{375}\right) \times 30 = 18.8\,\text{cm}$