CERTIFICATION OF APPROVAL

Adsorption of Carbon Dioxide Using Activated Carbon, Activated Alumina and Modified Activated Alumina

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.

TAN HEAN YEOW

ABSTRACT

The main objective of the project is to study the adsorption behaviour of carbon dioxide on different adsorbent varying in surface area, porosity and micropore characteristic. Beside, the study of modifying alumina with metal oxide is also conducted to observe any enhancement in adsorption. The last objective is to study the characteristic of the adsorbent used in terms of surface area, micropore volume and porosity.

The adsorption process is conducted experimentally using an simple adsorption column while the sample characterization is done using AutoSorb and Quanta-Chrome software. For adsorption, 4 types of adsorbent is used; 2.5mm activated carbon, 1.5mm activated carbon, activated alumina and modified alumina (added calcium oxide). Four pressures were used for adsorption ranging from 25kPa to 55kPa. After the data had been obtained, it is tabulated and graph using Microsoft Excel.

From the results, it is found that porosity, surface area and micropore volume have a big influence on the adsorption capacity of the adsorbent. The highest intake of carbon dioxide is by 1.5mm activated carbon and the least is activated alumina. From the BET and DR results, 1.5mm activated carbon has the largest surface area while alumina has the least. Granular size also plays and important part in adsorption. This project provides a basic for a better understanding in the adsorption process as this process in very important in the current industries.

ACKNOWLEDGEMENT

It had been a great pleasure to be able to complete the final year project which is partial fulfillment of the requirements for the Bachelor of Chemical Engineering (Hons). First and foremost, I would like to extend my most grateful appreciation to my supervisor, Ms. Anis Suhaila for her valuable time and effort to guide and assist me in my progress of the final year project by providing specific requirements that needed to achive the objectives of this final year project. Besides, she has given advices on the project for further improvement.

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CHAPTER 1
INTRODUCTION

1.1 BACKGROUND OF STUDY.

Carbon dioxide gas that are produced from the combustion of fossil fuels like petroleum and natural gases. To keep the environment safe from pollution, this gas is removed from the waste to be regenerate for the production of acid or industrial use. Adsorption technology is widely employed to remove CO_2 from the gas stream produced from the combustion. To improve adsorption of gas like CO_2, a study of CO_2 adsorption behavior on various adsorbent have to be conducted. Here, the all the factor that influence adsorption will be studied. Adsorption process is a process, which one or more component of a gas or liquid streams are adsorbed on the surface of a solid adsorbent and separation occurs. Among commercially used adsorbent nowadays are activated carbon and activated alumina.

1.2 PROBLEM STATEMENT

The green house effect is hitting the earth right now. For every increment of carbon dioxide concentration is the atmosphere, the temperature will rise. This will cause a lot of calamity to earth's population. The green house effect is caused by carbon dioxide that forms invisible layers that block the heat to be dissipated back to the space. So, this will cause the accumulation of heat at the earth's surface.

Due to all this, the world has come out with lots of solutions to reduce carbon dioxide in the atmosphere. All this have to be done at the unit itself that produces carbon dioxide. To reduce the emission of CO_2 to the air, the byproduct that contained CO_2 need to be filtered before released to the air. To filter, one of the ways is by adsorption. Adsorption is a process where continuous studies had been done to enhance the process.

Overall, this study is conducted to get a better understanding on the adsorption process.

1.3 OBJECTIVE AND SCOPE OF STUDY

1.3.1 Objectives

The study is conducted in an open ended manner where the progress depends on the availability of time. Hence, more progress beyond the scope of the project is feasible and this study sets the pioneering work related this topic. From the problem statement, the main objectives of the project are identified as follows:

- To determine the adsorption capacity of Carbon Dioxide in 2.5mm granular activated carbon, 1.5mm granular activated carbon, activated alumina and alumina modified with metal oxide
- To determine the effect of pressure on the adsorption capacity
- To study the effect of adding metal oxide on alumina
- To characterize adsorbent using BET, DR and T-Method to find the surface area and micropore volume

1.3.2 Scope of Study

As mention previously the study is an open – ended project. However the measure of success of the project depends on the achieved objectives within certain scope.

The scope of study is limited to only carbon dioxide. This is because carbon dioxide is readily available in the university and it is easier to obtain. This gas is also a non-hazardous gas. Besides, CO_2 is one of the common gases used for adsorption experiments because its diameter is widely accepted.

Next, there are only 2 types of adsorbent being used here, activated carbon and activated alumina. Activated carbon tested range from 1.5mm in granule size to 2.5mm. These 2 will be used to compare the effect of having different sizes of granules on adsorption. Activated alumina is to be compared with activated carbon to see which adsorbent can adsorbed more CO_2. The latest addition to the project is by adding metal oxides to alumina to enhance its adsorption. Here, the modified alumina will be compared with the unmodified alumina to see whether can the adsorption capacities increased with the addition of metal oxide.

This study only covers factors like surface area, pressure, pore volume, micropore surface area and particle size will be taken into account. All the thermodynamics properties involve enthalpy or entropy will not be covered in this study.

CHAPTER 2

LITERATURE REVIEW AND THEORY

2.1 ADSORPTION

2.1.1 Introduction

In adsorption processes one or more components of a gas or liquid stream are adsorbed on the surface of a solid adsorbent and a separation is accomplished. In commercial processes, the adsorbent is usually in the form of small particles in a fixed bed. The fluid is passed through the bed and solid particles adsorb components from the fluid. When the bed is saturated, the flow of the bed is stop and the bed is regenerated thermally of by other methods. So desorption occurs. The adsorbed material is then recovered and the solid adsorbent is ready to be used in another cycle again

Robert H.P (1997) stated that adsorption involves, in general, the accumulation (or depletion) of solute molecules at an interface (including gas-liquid interfaces, as in foam fractionation, and liquid-liquid interfaces, as in detergency). Here we consider only gas-solid interfaces, with solute distributed selectively between the fluid and solid phases. The accumulation per unit surface area is small; thus, highly porous solids with very large internal area per unit volume are preferred. Adsorbent surfaces are often physically and/or chemically heterogeneous, and bonding energies may vary widely from one site to another. We seek to promote physical adsorption or physisorption, which involves van der Waals forces (as in vapor condensation), and retard chemical adsorption or chemisorption, which involves chemical bonding (and often dissociation, as in catalysis). The former is well suited for a regenerable process, while the latter generally destroys the capacity of the adsorbent. Adsorbents are natural or synthetic materials of amorphous or microcrystalline structure. Those used on a large scale, in order of sales volume, are activated carbon, molecular sieves, silica gel, and activated alumina

Applications of liquid-phase adsorption include the removal of organic compounds from water or organic solutions, colored impurities from organics, and various fermentation products from fermentor effluents. Separations include paraffin from aromatics and fructose from glucose using zeolites. Application of gas phase include removal of water from hydrocarbon gases, sulfur compound from natural gases, solvents from air and other gases, and odors from air.

2.1.2 Adsorption Process

Robert H.P (1997) states that adsorption of a gas allows the probing of a solid surface hence the determination of its area. This includes surface irregularities and pore interiors. To some extend, the adsorption will always occur on a solid surface exposed to a gas or vapor. The amount adsorbed is a function of temperature, gas pressure and interaction potential between gas and solid.

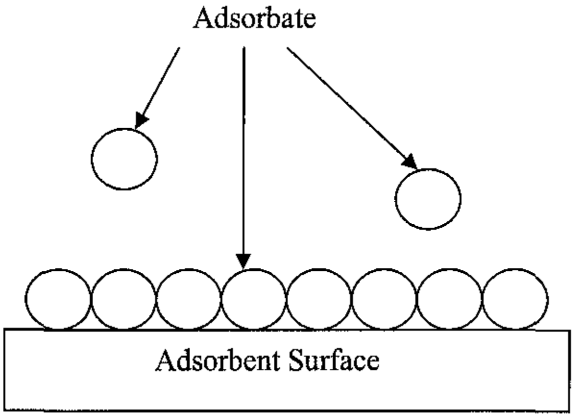

Figure 2.1: Adsorption process

The overall adsorption process consists of a series of steps in series (figure 2.1). When the fluid is flowing past the particle in a fixed bed, the solute first diffuses from the bulk fluid to the gross exterior surface of the particle. Then the solute diffuses inside the pore of the surface of the pore. Finally, the solute is adsorbed on the surface. Hence, the overall adsorption process is a series of steps.

Molecules are attracted to surfaces as the result of two types of forces: dispersion-repulsion forces (also called London or van der Waals forces) such as described by the Lennard-Jones potential for molecule-molecule interactions; and electrostatic forces, which exist as the result of a molecule or surface group having a permanent electric dipole or quadrupole moment or net electric charge.

Dispersion forces are always present and in the absence of any stronger force will determine equilibrium behavior, as with adsorption of molecules with no dipole or quadrupole moment on nonoxidized carbons and silicalite. If a surface is polar, its resulting electric field will induce a dipole moment in a molecule with no permanent dipole and, through this polarization, increase the extent of adsorption.

Similarly, a molecule with a permanent dipole moment will polarize an otherwise nonpolar surface, thereby increasing the attraction. For a polar surface and molecules with permanent dipole moments, attraction is strong, as for water adsorption on a hydrophilic adsorbent.

2.1.3 Factors Affecting Adsorption (Robert H.P, 1997)

2.1.3.1 Surface Area and Pore Structure

The adsorptive capacity of solid adsorbents generally proportional to the specific surface area, that is, the adsorption of certain solutes increases with an increase of surface area. However, the specific surface area alone is frequently inadequate to explain the adsorptive capacities of porous solids. The pore size distribution in activated carbon indicates the micropores contribute a major portion of the specific surface area. A solute molecule will readily penetrate into a pore having a certain critical diameter and will be excluded from pores smaller than this size.

2.1.3.2 Particle Size

The surface area of a nonporous adsorbent increases with decrease in particle size. However, the highly porous adsorbents such as activated carbon, most of the surface area resides in the internal pore structure and the adsorptive capacity is independent of the particle size. The particle size of activated carbon has no apparent effect on the adsorptive capacity for such solutes of small diameter micropores.

2.1.3.3 Nature of the Adsorbent

The physicochemical nature of the adsorbent can have profound effects on both rate and capacity for adsorption. Commercial carbons can be prepared from a variety of raw materials, including wood, lignite, coal, petroleum residues, and nut shells. The raw material is generally activated in an atmosphere of CO_2, CO, O_2, H_2O, vapor, air, or other selected gases, at a temperature between 300 and 100°C often followed by quenching in air or water. The most characteristic physical property of activated carbon is its extremely large surface area, which is composed mainly or surfaces bordering inner pore spaces.

2.1.4 Transport Mechanism (Perry's)

2.1.4.1 Pore diffusion in fluid-filled pores (Macropore Diffusions)

These pores are sufficiently large that the adsorbing molecule escapes the force field of the adsorbent surface. (Refer Figure 2.2) Thus, this process is often referred to as macropore diffusion. The driving force for such a diffusion process can be approximated by the gradient in mole fraction or, if the molar concentration is constant, by the gradient in concentration of the diffusing species within the pores.

2.1.4.2 Solid diffusion in the adsorbed phase (Micropore Diffusions)

Diffusion in pores sufficiently small that the diffusing molecule never escapes the force field of the adsorbent surface (Refer Figure 2.2). In this case, transport may occur by an activated process involving jumps between adsorption sites. Such a process is often called surface diffusion or, in the case of zeolites, micropore or intracrystalline diffusion. The driving force for the process can thus be approximated by the gradient in concentration of the species in its adsorbed state. Phenomenologically, the process is not distinguishable from that of homogeneous diffusion that occurs inside a sorbent gel or in a pore-filling fluid that is immiscible with the external fluid. The generic term solid diffusion is used here to encompass the general traits of these physically different systems.

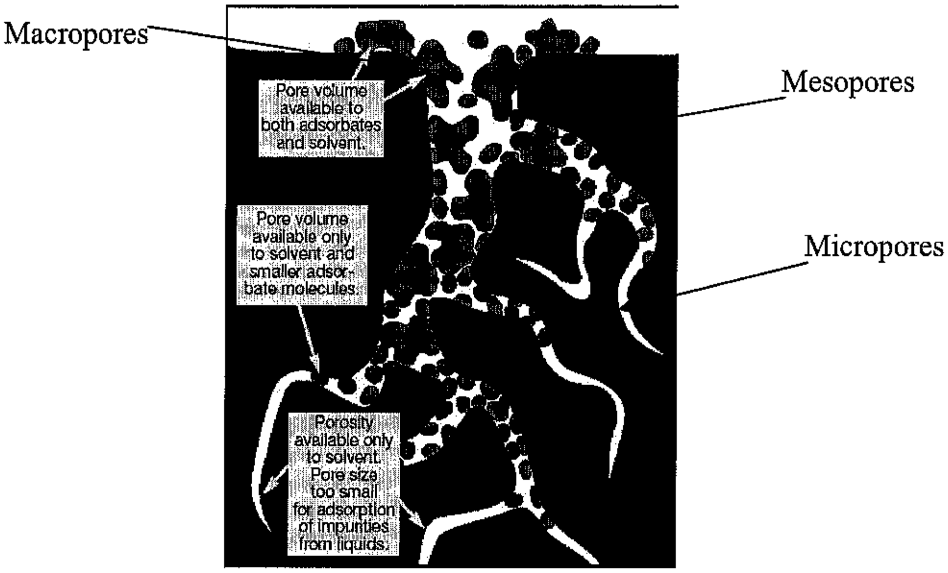

Figure 2.2: Cross Sectional View of a pore

2.1.4.3 Reaction kinetics at phase boundaries.

Rates of adsorption and desorption in porous adsorbents are generally controlled by mass transfer within the pore network rather than by the kinetics of sorption at the surface. Exceptions are the cases of chemisorption and affinity-adsorption systems used for biological separations, where the kinetics of bond formation can be exceedingly slow. Intraparticle convection can also occur in packed beds when the adsorbent particles have very large and well-connected pores. Although, in general, bulk flow through the pores of the adsorbent particles is only a small fraction of the total flow, intraparticle convection can affect the transport of very slowly diffusing species such as macromolecules.

The driving force for convection, in this case, is the pressure drop across each particle that is generated by the frictional resistance to flow experienced by the fluid as this flows through the packed bed. Intraparticle convection can also be significant when there is a total pressure difference between the center of the particle and the outside, such as is experienced in pressurization and depressurization steps of pressure swing adsorption or when more gas is drawn into an adsorbent to equalize pressure as adsorption occurs from the gas phase within a porous particle

2.1.4.4 External mass transfer

This process occurs between the external surfaces of the adsorbent particles and the surrounding fluid phase. The driving force is the concentration difference across the boundary layer that surrounds each particle, and the latter is affected by the hydrodynamic conditions outside the particles.

2.1.4.5 Mixing or lack of mixing

This process occurs between different parts of the contacting equipment. This may occur through the existence of a velocity distribution or dead zones in a packed bed or through inefficient mixing in an agitated contactor. In packed-bed adsorbers, mixing is often described in terms of an axial dispersion coefficient whereby all mechanisms contributing to axial mixing are lumped together in a single effective coefficient.

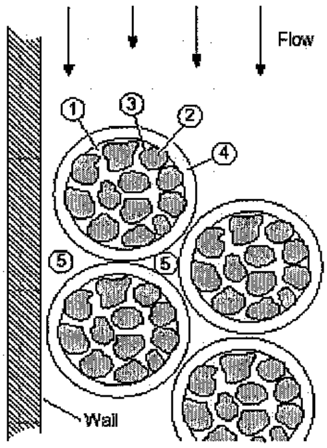

Figure 2.3: General scheme of adsorbent particles in a packed bed.

The figure 2.3 above shows the locations of mass transfer and dispersive mechanisms. Numerals correspond to numbered paragraphs in the text: 1, pore diffusion; 2, solid diffusion; 3, reaction kinetics at phase boundary; 4, external mass transfer; 5, fluid mixing.

2.1.5 Adsorbents

Many adsorbents have been developed for a wide range of separations. Typically, the adsorbents are in the from of small pellets, beads, or granules ranging from about 0.1mm to 12mm in size with the larger particles being used in the packed beds. A particle of adsorbent has a very porous structure with many fine pores and pore volumes up to 50% of total particle volume. The adsorption often occurs as a monolayer on the surface of the fine pores. However, several layers sometimes occur.

Most solids able to adsorb species from gases and liquids. However, only a few have a sufficient selectivity and capacity to make them serious candidates for commercial adsorbents, One of the important factor to be looked at is the large specific surface area (area per unit volume), which is achieved by adsorbent manufacturing techniques that result in solids with microporous structure. By definition of the International Union of Pure and Applied Chemistry (IUPAC), the diameter of micropore is <20Å, a mesopore is 20-500 Å and macropore is >500 Å.

There are a number of commercial adsorbents and some of the main of are described below. All are characterized by very large pore surface areas of 100 to over $2000m^2/g$.

2.1.5.1 Granular Activated Carbon

This is a microcrystalline material made by thermal decomposition of wood, vegetable shells, coal, etc and has surface areas of 300 to 1200 m^2/g with average pore diameters of 10 to 60Å. Organics are generally adsorbed by activated carbon. (See Figure 2.4). Activated carbon is mainly used in the adsorption industry and common processes are colour removal and gases adsorption due to the high porosity.

Figure 2.4: Porous Structure of Activated Carbon viewed using electron microscope

2.1.5.2 Activated Alumina

To prepare this material, hydrated aluminium oxide is activated by heating to drive off water. It is used mainly to gases and liquids. Surface areas range from 200 to 500 m^2/g, with average pore diameter of 20 to 140 Å. Common industries uses alumina to remove moisture and gases.

2.2 CARBON DIOXIDE (ADSORPTION GAS)

Carbon Dioxide is a widely distributed gas and it makes up 0.4% of the air. It is a colorless and odorless gas with acidic properties. It is about 50% heavier than air. It is possible because of its heavier molecular weight, 44. Carbon Dioxide might exist in crystalline or liquid under certain condition.

Carbon Dioxide is the major cause of greenhouse effect. It will form a shield that avoids the heat to dissipate out from the atmosphere. It is also corrosive in the presence of water and could solidify in the gas going to cryogenic plant thus will clog the pipes. The combustion of fossil fuels like petroleum supply more than 98% of the world energy needs. CO_2 exist as a non-polar molecule because the dipole canceled out each other.

$$O=C=O$$

Figure 2.5: Molecular structure of Carbon Dioxide.

2.3 SAMPLE CHARACTERIZATION

2.3.1 BET surface area analysis

The specific surface area of an adsorbent, S_g, measured by adsorbing gaseous nitrogen using the well-accepted BET method (Brunauer, Emmett, and Teller). Typically, the BET apparatus operated at the normal boiling point of N_2 (-195.8°C) by measuring the equilibrium volume of pure N_2 physically adsorbed on several grams of the adsorbent at a number of different values of the total pressure in the vacuum range of 5 to at least 250 mmHg.

Langmuir equation assumes monolayer capacity of the adsorbent while BET extend it to multiple layers. Thus the equation becomes

$$\frac{V}{V_m} = \frac{C\dfrac{P}{P_o}}{\left(1-\dfrac{P}{P_o}\right)\left(1-\dfrac{P}{P_o}+C\dfrac{P}{P_o}\right)} \text{ linearization gives } \frac{1}{V\left[\dfrac{P_o}{P}\right]-1} = \frac{1}{V_m C} + \frac{C-1}{V_m C}\left(\frac{P}{P_o}\right)$$

Po is the saturated vapor pressure of the gas over the solid

Po/P is the relative pressure

C is a constant which is related to the net heat of adsorption.

Adsorbate most commonly used is nitrogen because it is readily available in high purity. Besides, it has a widely accepted cross sectional area. It also have a strong gas-solid interaction

To calculate the total surface area, line $\dfrac{1}{V\left[\dfrac{P_o}{P}\right]-1}$ vs $\left[\dfrac{P_o}{P}\right]$ is plotted. Then, from the best fit line, the slope is equal to $s = \dfrac{C-1}{V_m C}$

Intercept is equal to $i = \dfrac{1}{V_m C}$

Thus the total surface area, $S_t = \dfrac{V_m L_{av} A_m}{M_v}$

2.3.2 Dubinin – Radushkevich (DR) Method.

Dubinin and Radushkevich posulated that the fraction of the adsorption volume V occupied by liquid adsorbate at various adsorption potential energies E can be express as a Gaussian function:

$$V = V_0 \, e^{-K(E/\beta)^2}$$

$$\beta = E / E_{ref}$$

where K is a constant based on the pore size distribution shape, V is an adsorption volume of liquid adsorbate and Vo is an adsorption volume of reference liquid adsorbate. Since

$$E = RT\ (\ln P_o / P)$$

Substitution and simplification yields

$$\text{Log } W = \log(V\rho) - k(\log P_o / P)^2$$

Where ρ is the liquid density.

2.2.3 Estimation of Micropores using T-Method

This method uses a mathematical representation of multi layer adsorption. The thickness of an adsorbate layer increases with increasing pressure. For every value of V_{STP} of adsorption is plotted against the corresponding value of t. If the model describes the experimental data, a straight line is produced on the t-plot.

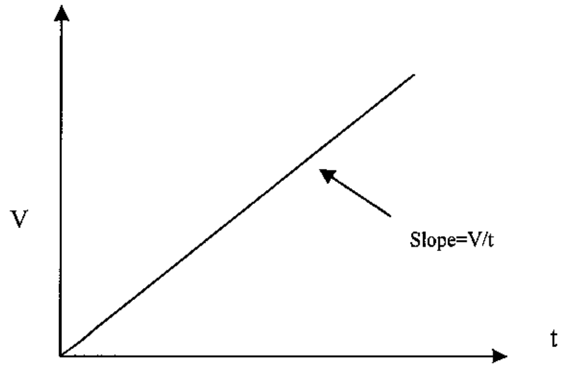

Figure 2.6: T-Plot Method for mesoporous only

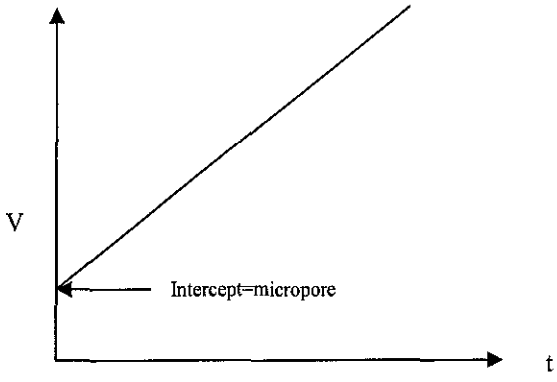

Figure 2.7: T-Plot Method in the presence of micropores

2.4 ADSORPTION OF CO_2 ON ACTIVATED CARBON AND MOLECULAR SIEVES

Ranjani (1997) from have conducted a study on adsorption of CO_2 on 3 adsorbents. They are molecular sieves 13X, molecular sieve 4A and activated carbon. The purpose of this study is to investigate the adsorption behavior of CO_2 on a porous adsorbent at high pressure and recovery of the gas at low pressure. Thus, the porous adsorbent can be used for subsequent adsorption. The adsorption isotherm at 25°C of pure CO_2 on the 3 adsorbent were obtained up to an equilibrium pressure of about 300psi using a volumetric adsorption apparatus.

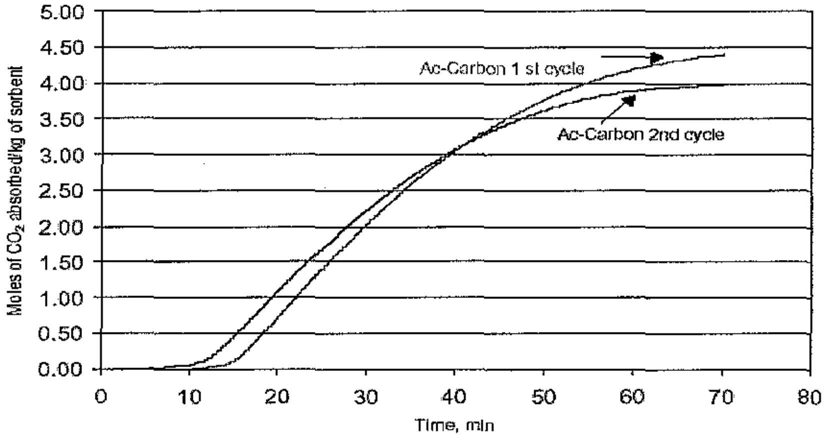

Figure 2.8: Adsorption of CO_2 on Activated Carbon, 250 psi, 25°C

From the figure above, the activated carbon saturation point is reached at the 70th minutes and the total mol adsorbed is around 4.50. The 1st cycle is done using new activated carbon and the 2nd cycle is done using the regenerated activated carbon. That explains why the saturation point for the 2nd cycle is lower than 1st cycle, due to the imperfect recovery of CO_2 at the regeneration point.

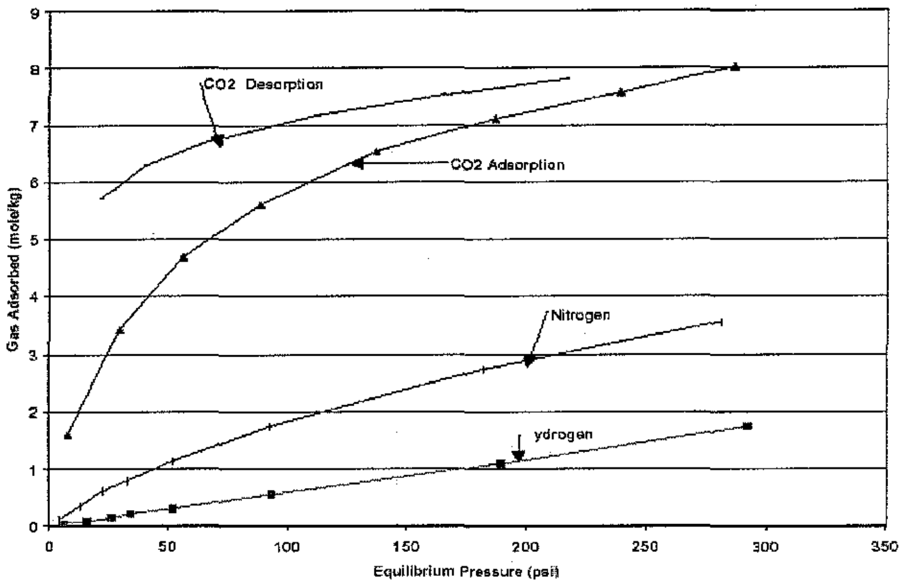

Figure 2.9: Adsorption Isotherm of activated carbon for different gases.

The CO_2 adsorption increased rapidly when the pressure was increased up to 50 psi but the CO_2 adsorption after 50 psi appeared to be gradual. The CO_2 adsorption for molecular sieve is higher at lower pressure but at higher pressure, the adsorption of CO_2 on activated carbon is significantly higher. This is because at high pressure, the activated carbon is utilized to the full capacity of the surface to form a close packed monolayer at the surface.

2.5 EFFECT OF SURFACE AREA AND MICROPOREVOLUME ADSORPTION IN CARBON

Weaver et. al (1994) did this research to monitor the effect of surface area and micropore volume on adsorption on carbon fiber. The main highlight in this paper is to know how can adsorption increase or decrease with variables like surface area and micropore volume. The initial part of this paper describes how BET analysis is done on carbon fiber. Nitrogen adsorption isotherms were measured at 77 K using our Autosorb-1 instrument. Micropore size analysis used a variety of methods, including the Brunauer, Emmett and Teller3 (BET) method for surface area and the Dubinin-Redushkevich (DR) method for micropore volume and micropore size.

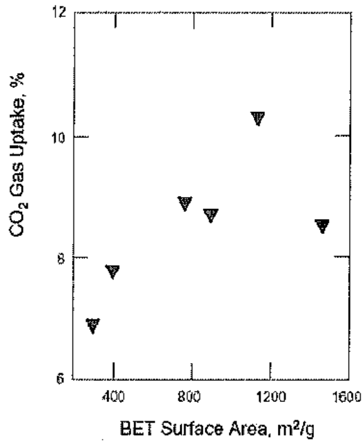

Figure 2.10: CO_2 uptake vs. BET surface area for carbon fiber.

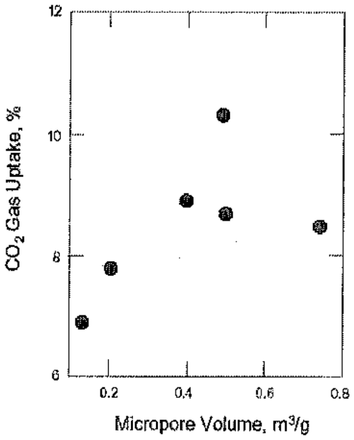

Figure 2.11: CO_2 uptake vs. micropore volume for carbon fiber.

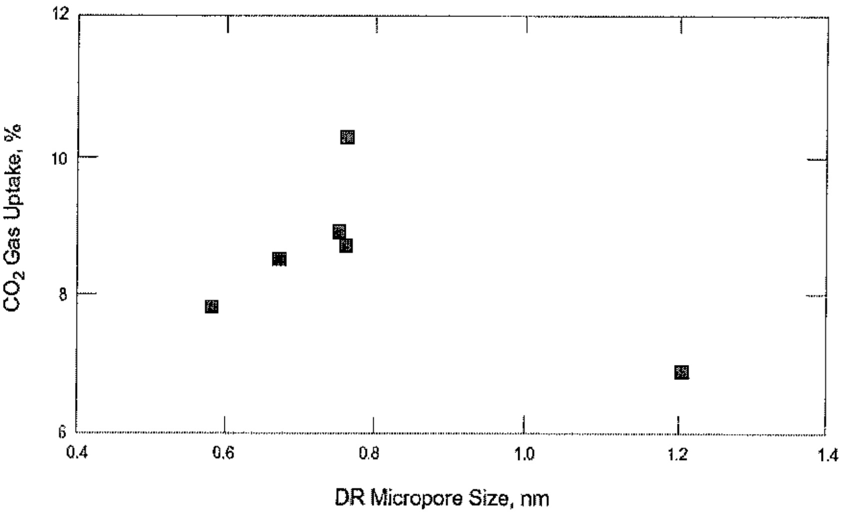

Figure 2.12: CO_2 uptake vs. mean micropore size.

The weight percent of CO_2 adsorbed increases with increasing pore volume and BET surface area, apparently reaching peak adsorption capacity at micropore volumes of ~0.5 cm^3/g and BET surface areas of ~1000 m^2/g. Figure 2.12 shows CO_2 uptake plotted as a function of micropore size (DR method). The figures showed that the sample with the higher surface area do not necessarily have the highest loading. This is because its micropore volume is low. So, it can be concluded that micropore volume and surface area plays a big role in determining the adsorption capacity.

2.6 ADSORPTION OF CO_2 ON THE ALUMINA MODIFIED WITH BASIC METAL OXIDES

Tatsuro et al (1997) tried to examine the effect of basic metal oxides added to alumina on CO_2 adsorption at elevated temperatures. His finding are, by adding basic metal oxides to activated alumina, CO_2 is effectively separated from an N_2 containing mixture at elevated temperatures. Modifier examine were the oxides of rare earth metals (La, Ce, Nd, Pr), alkaline earth metals (Mg. Ca, Sr, Ba) and alkaline metals (Na, K, Rb, Cs).

Firstly, the alumina is impregnated in an aqueous solution of these metal nitrates, followed by drying at 383K overnight and calcinations at 1073K for 1 hour. The surface area is found to decrease.

Based on the results, the adsorption of CO_2 increase with the addition of metal oxides. The reason is the carbon atom of a CO_2 molecule should exhibit electrophilicity because the electron cloud is deviated in such a way that the electron density is enriched in the oxygen side. Oxygen anions will form a polar adsorption sites and it will induce an instantaneous dipole moment at the CO_2 molecules. Through electrostatic interaction, the bonding is formed between the CO_2 molecules and the oxygen anions of a metal oxide to form carbonate species. In short, the added metal oxides are the basic sites on this activated alumina.

CHAPTER 3
METHODOLOGY AND PROJECT WORK

3.1 PROJECT OVERVIEW

The study of carbon dioxide adsorption on various adsorbent is conducted via sets of experiments. Literature review is also done to get a better understanding on the topic. This is done by reviewing previous work done by researchers on carbon dioxide adsorption. To study the adsorption behavior of carbon dioxide on different adsorbent, several types of adsorbent have to be used. Due to time constraint, only four adsorbent is used.

The four adsorbent consist of two types of activated carbon and two types of activated alumina. The activated carbon varies in sizes while the activated alumina varies in their surfaces. The four adsorbent are 2.5mm granular activated carbon, 1.5mm granular activated carbon, activated alumina and alumina prepare in metal oxide. So, the sets of experiments will then be conducted to determine the adsorption loading of all 4 adsorbents.

Sample characterization will also be done for the adsorbent to obtain supporting information on the adsorption. The total surface area will be studied using BET method while micropore analysis is done using Dubinin Radushkevich (DR) method. Another method used for comparison of the surface area and micropore properties is the T-method. Autosorb and Quanta-chrome will be used to determine the characteristic on all 4 adsorbent.

After the data is obtained from the experiments, various graph are plotted using Microsoft Excel and the adsorption pattern is studied based on various conditions. The adsorption pattern can be studied on the basis of different adsorbent (different surface area, micropore volume) and also on the basis of different adsorption pressure.

3.1.1 Apparatus and tools used

All the material, tools and software used can be summarized in the tables below.

Table 3.1: Material used for project

Materials	Usage
2.5mm Granular Activated Carbon	Experiment sample
1.5mm Granular Activated Carbon	Experiment sample
Activated Alumina (1mm-3mm)	Experiment sample and to produce activated alumina with metal oxide
Carbon Dioxide	Adsorption gas for experiment
Nitrogen	Used with Autosorb to determine surface area and micropore analysis
Hydrated Sodium Hydroxide	Prevent adsorbent from moisture(storage)
Calcium Oxide	Modify activated alumina

Table 3.2: Tools and equipment used

Tools	Usage
Pressure Manometer	Monitor the inlet and outlet pressure of the adsorption column
Adsorption Column	Hold adsorbent while adsorption process occur
Digital Balance	Measure the weight change over adsorption time
Pipes	Provide passage for carbon dioxide to flow in and out the adsorption column
Gas Regulator	Regulates the air pressure
Vacuum Oven	Remove moisture from adsorbent

Table 3.3: Software Used

Software	Usage
Microsoft Excel	Plot graph and tables for interpretation
Quanta-Chrome	Determine surface area and micropore analysis using BET, DR and T method

3.2 EXPERIMENTAL PROCEDURE

3.2.1 Sample Preparation

3.2.1.1 Preparation of Adsorbent

The amount of adsorbent needed is weigh and placed in aluminium plate. The adsorbent is then placed in the vacuum oven. The temperature of the oven is set to be 110°C and outgassing is done for 24hrs. The oven compartment is also vacuumed so that all moisture is taken away. After 24hrs, the adsorbent is taken out and weigh again. The reduction in weight shows that moisture had been removed. This step is important to remove all the moisture trapped in the pore surface of the adsorbent.

3.2.1.2 Preparation of Alumina with Calcium Oxide.

An aqueous solution is prepared by dissolving 3g of calcium oxide in 300ml of distilled water to form calcium hydroxide solution. The aqueous solution is the mixed with Nitric acid and calcium nitrate is produce. Activated alumina is the impregnated in the aqueous solution for 15 minutes followed by drying at 110°C in vacuum oven for 24 hours.

3.2.2 Adsorption of Carbon Dioxide

The experimental setup is prepared based on Figure 3.1 below.

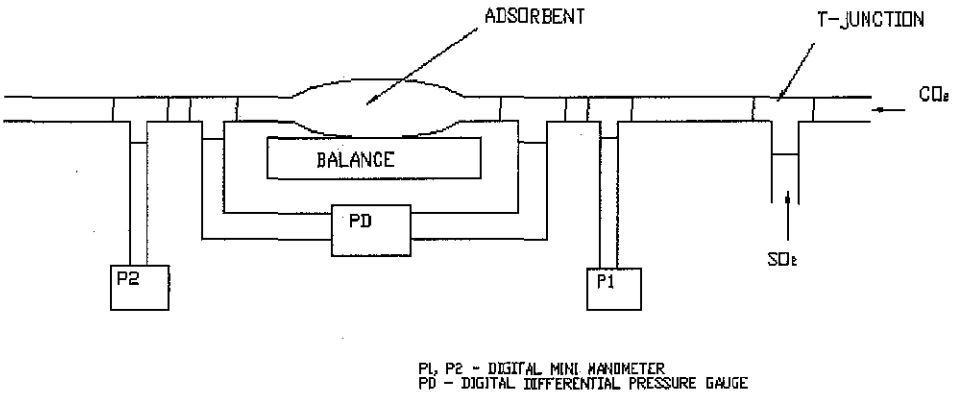

Figure3.1: Experimental Setup

88g of adsorbent is weight and placed in the adsorption column. Aluminium foil is then wrapped around the adsorption column to minimize any heat transfer to maintain the adsorption temperature. Carbon dioxide is regulated to 25kPa. The digital balance is reset as soon as the reading of the digital balance stops fluctuating and started to increase. The weight change is recorded every two minutes for 50 minutes. The steps are repeated for 35kPa, 45kPa and 55kPa.

In addition, the initial and final weight of the adsorbent must also be recorded to calculate the total amount of carbon dioxide adsorbed.

3.2.3 BET surface area and micropore analysis

About 0.1g of adsorbent to be analyzed is measured and placed in the tube. In the dialog box, physisorption is selected these settings below are applied

Table 3.4: AutoSorb Settings

Parameters	Settings
Degassed Temperature	150°C
Outgas Temperature	200°C
Outgas Time	1 hour
Number of data points	5 points BET
Adsorption	Yes
Desorption	Yes
P_o	1atm

For analysis, Quanta-Chrome is used. For micropore analysis, DR method and T-Method will be used while for surface area analysis, BET method and T-Method is used. T-method will provide the external surface area, micropore surface area and micropore volume. DR method will provide surface area, micropore width and micropore volume and lastly, multipoint BET will give the total surface area.

3.3 DATA MANAGEMENT AND ANALYZE

All data are keyed into tabular form. In order to analysis the data, those data have to be fit into graph .Both is done using Microsoft Excel. Graph of Carbon Dioxide Adsorbed vs. Time is plotted to monitor the weight change of the adsorbent as time passed as a proof that adsorption occur. Next, the adsorption isotherm is plotted (Carbon Dioxide Adsorbed vs. Pressure) to monitor the adsorption behavior at different pressure for different adsorbent. All the data obtained from Quanta-Chrome is put into bar chart to ease comparison on surface area and micropore data.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Surface Area and Physical Characteristic Data

Table 4.1: Micropore Characterization Data

Sample of Adsorbent	Micropore Analysis Data				Surface Area	
	Micropore Volume (cc/g)		Micropore Surface Area(m^2/g)		BET Total Surface Area (m^2/g)	T-Method External Surface Area (m^2/g)
	T-Method	DR	T-Method	DR		
2.5mm Activated Carbon	0	1.868	0	5255	41	41.02
1.5mm Activated Carbon	0.7606	1.073	1377	3021	1951	574.3
Activated Alumina	0	0.001	0	3.145	2.8	2.8

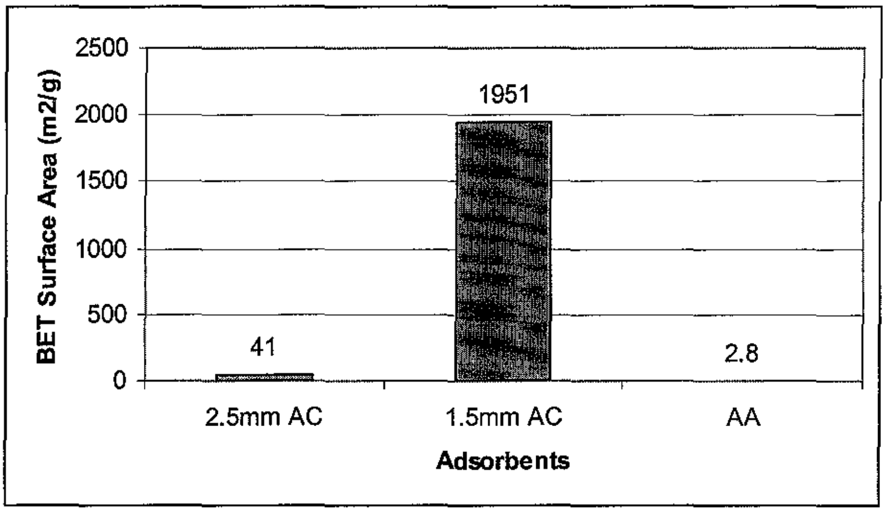

Figure 4.1: BET Surface Area for all 3 Adsorbents

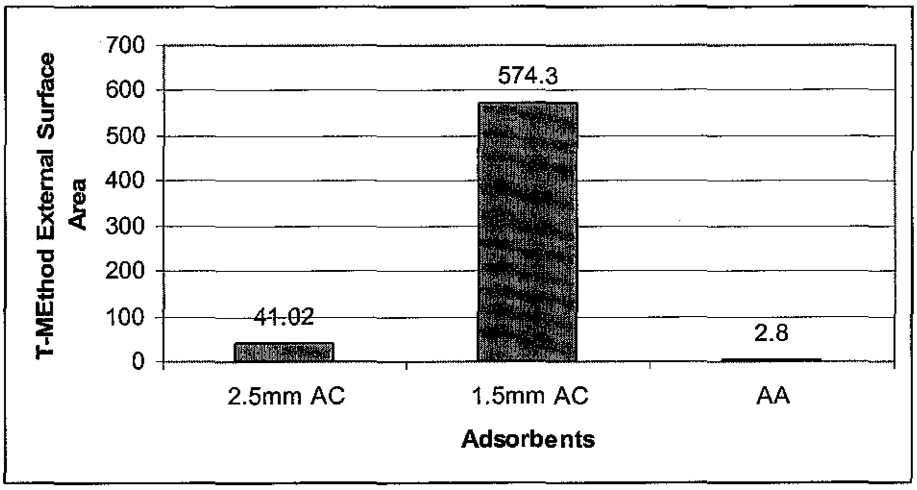

Figure 4.2: T-Method External Surface Area for all 3 Adsorbents

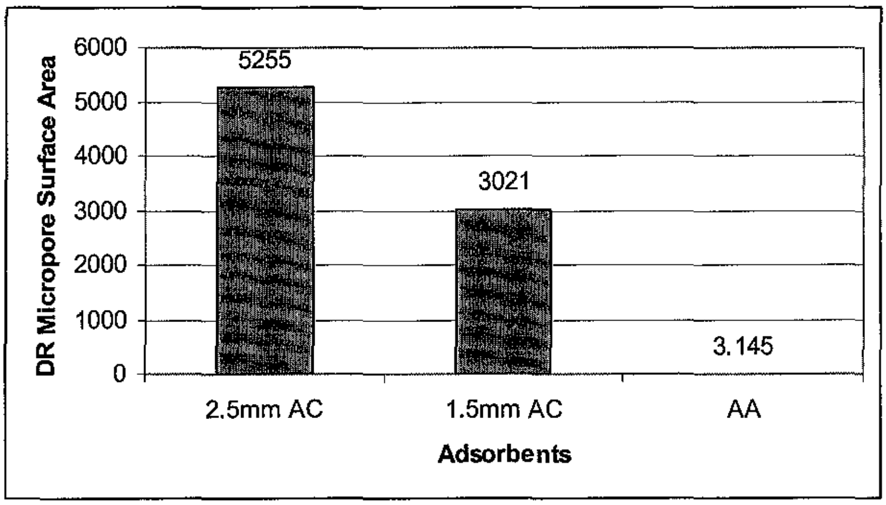

Figure 4.3: DR Micropore Surface Area for all 3 Adsorbents

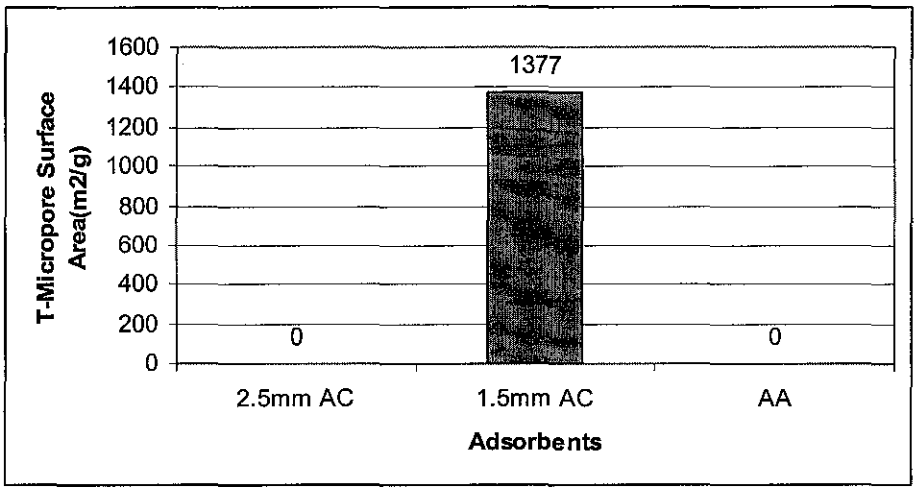

Figure 4.4: T Micropore Surface Area for all 3 Adsorbents

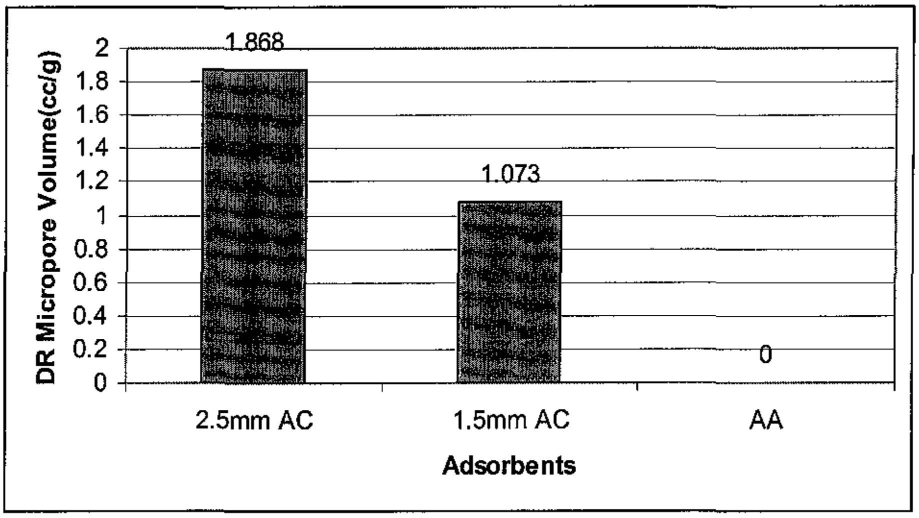

Figure 4.5: DR Micropore Volume for all 3 Adsorbents

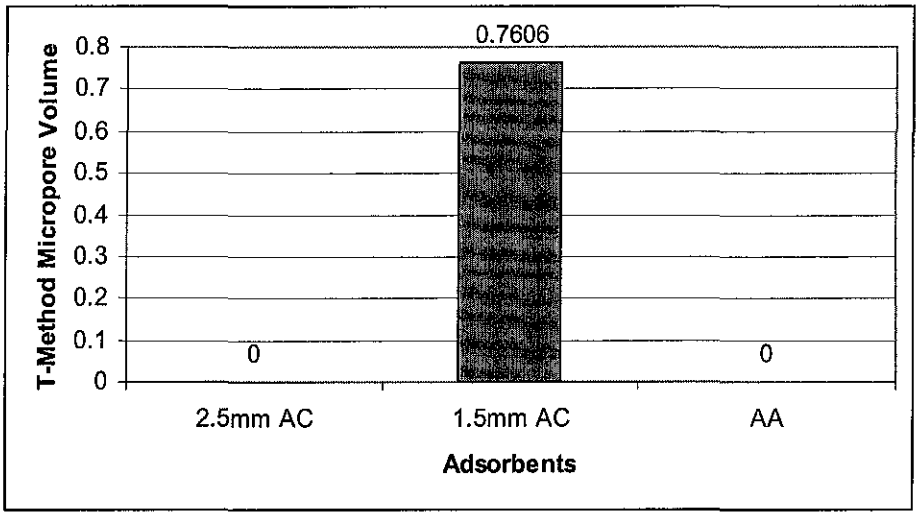

Figure 4.6: T Micropore Volume for all 3 Adsorbents

Figure 4.1 to Figure 4.6 above shows the surface area and micropore volume using BET, DR and T-Method. The BET total surface area gives good agreement with the T-Method external surface area in which the total surface area is equal to T-Method external surface area plus T-Method micropore surface area.

It is observed that activated alumina gives the lowest surface area and micropore volume. The value of the BET total surface area is only 2.8m^2/g and has an external surface area of 2.8 m^2/g also. External surface area is the surface area excluding the micropore surface area. Thus, this concluded that the activated alumina is a nonporous alumina. It only contains mesopore and macropore but very little micropore. This can be further proved by the T and DR micropore volume which gives the value 0 m^2/g.

However, there is a contradicting value given by T-Method and DR method on the micropore surface area. For T-Method, there micropore surface area given is 0 m^2/g while DR gives 5255 m^2/g. From these data, it is concluded that DR value is the sound value because it is not possible of having 0 m^2/g micropore surface area for activated carbon because the micropore volume is present and also experiment conducted shows adsorption on these sample. Its DR micropore volume is also close with 1.5mm activated carbon.

For 1.5mm activated carbon, it is shown that the BET total surface area is the highest. It also has the highest external surface area. This is because due to the smaller size of granule, 1.5mm has a higher surface area exposed. However, based on DR micropore surface area and volume, it has a lower value of both compared to 2.5mm activated carbon. It is suggest that 2.5mm activated carbon has a larger micropore compared to 1.5mm activated carbon. This might also caused by the longer effective length, L of the micropore.

Surface area analysis is not done for modified alumina due to the unavailability of the machine. However, Tatsuro (1997) findings shows that the surface area decrease from 160m^2/g to 130m^2/g for activated carbon.

4.2 Adsorption Capacity of Carbon Dioxide on 2.5mm and 1.5mm Activated Carbon, Activated Alumina and Modified Alumina at 55kpa

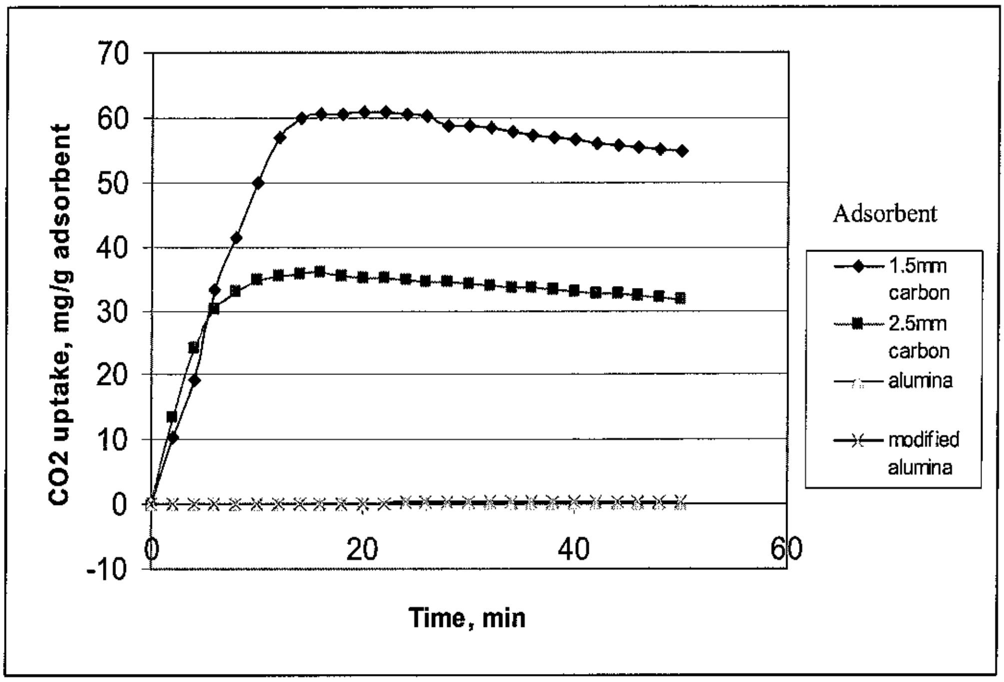

Figure 4.7: CO_2 uptake for different adsorbents

Based on the graph above, it can be concluded that 1.5mm granular activated carbon has the highest CO_2 uptake followed by 2.5mm activated carbon and lastly activated alumina and modified activated alumina (added metal iron). 1.5mm CO_2 uptake is 60.9mg/g carbon occurring at the breakthrough point (14th minutes) and the uptake for 2.5mm is 35.4mg/g carbon at the 14th minutes also. So, it can be concluded these activated carbon gets saturated at the 16th minutes at 55kPa. Based on the surface area data, 1.5mm activated carbon has the highest micropore surface area among all the adsorbent which means that there is more surface in the micropore carbon dioxide adsorption. Besides, this might also be due to the differences in terms of the pores. 2.5mm AC has a longer effective length that hinders diffusivity of CO_2 into the pores. The distance for the molecules to reach the interior surface is longer thus lower diffusivity occurs for the larger molecules.

However, the case is different from both activated alumina and modified activated alumina. The adsorption of CO_2 until the 50th minutes is still very low. Different adsorbent have different time to reach equilibrium. In this case, these adsorbents have not reached equilibrium. This may be due to the nature of the adsorbent itself. The pressures between 25kPa to 55kPa may not be a good range for activated alumina to reach equilibrium. More time or higher pressure has to set given in order to obtain the equilibrium data for these aluminas. Anyhow, it is predicted that even at equilibrium, the adsorption for CO_2 will still be lower than both activated carbon due to the lower amount of surface area.

4.3 The Effect of Adsorbent Size on the Adsorbent Capacity at 55kpa

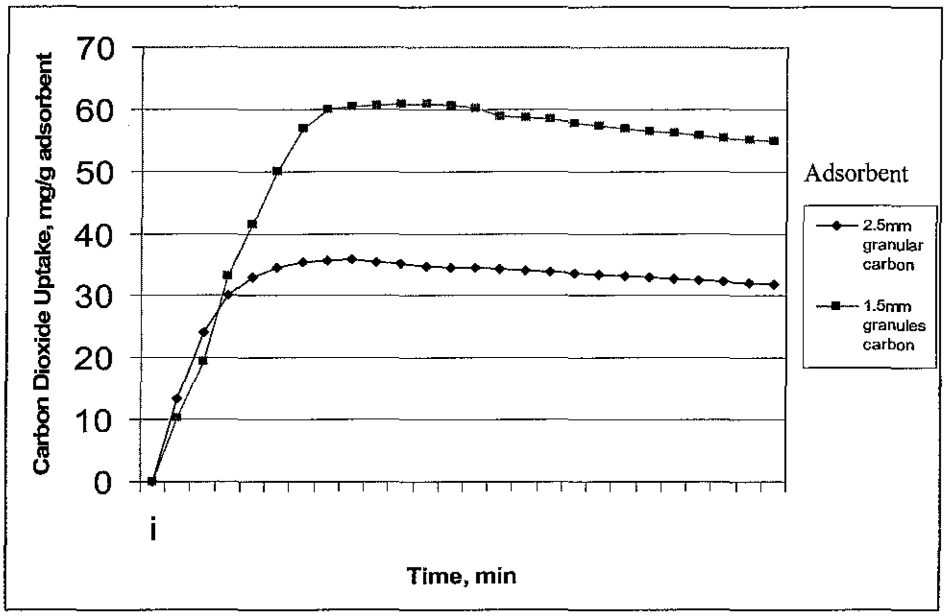

Figure 4.8: CO_2 uptake for activated carbon on different size

In terms of amount adsorbed, 1.5mm AC adsorbed more CO_2 compared to 2.5mm AC. This is because the large surface area combined with large micropore volume has a higher affinity to adsorbed more CO_2. 1.5mm activated carbon is reported to have a higher surface area because due to the smaller size, there is more surface areas exposed which enhances adsorption. Although 2.5mm AC has a higher micropore volume and surface area, its micropore surface area are not optimize due to larger resistance for CO_2 diffusions. If the experiments are conducted at lower temperature and higher pressure, a different set of results will be obtained. 2.5mm AC might have a higher CO_2 adsorption because the diffusivity resistances are minimizes. On the research done by Nakashima et. Al (2002), they stated that the optimum CO_2 adsorption temperature is around -10°C to 0°C. In short, the smaller the adsorbent size, the higher the CO_2 uptake due to higher surface area.

4.4 The Effect of Pressure Adsorption Capacity

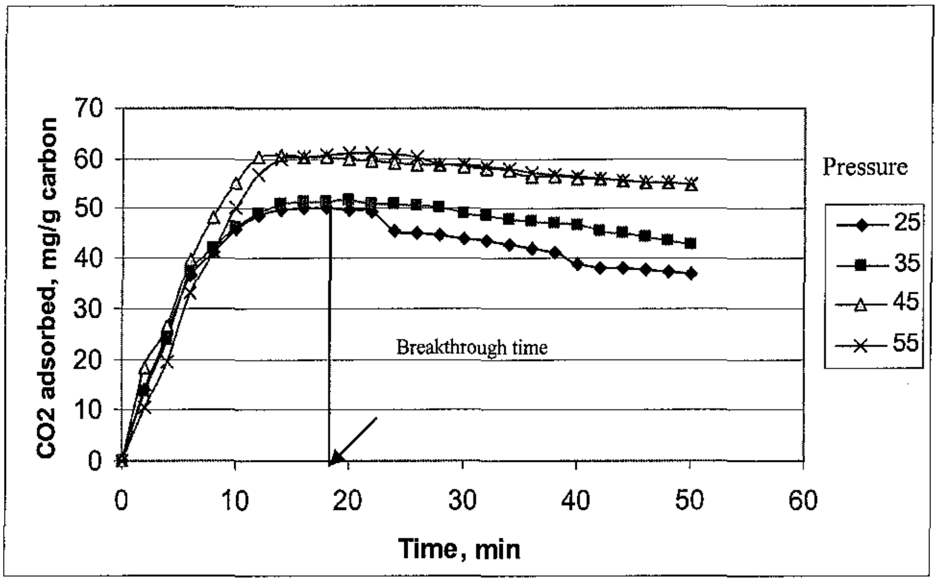

Figure 4.9: Adsorption on 1.5mm Activated Carbon

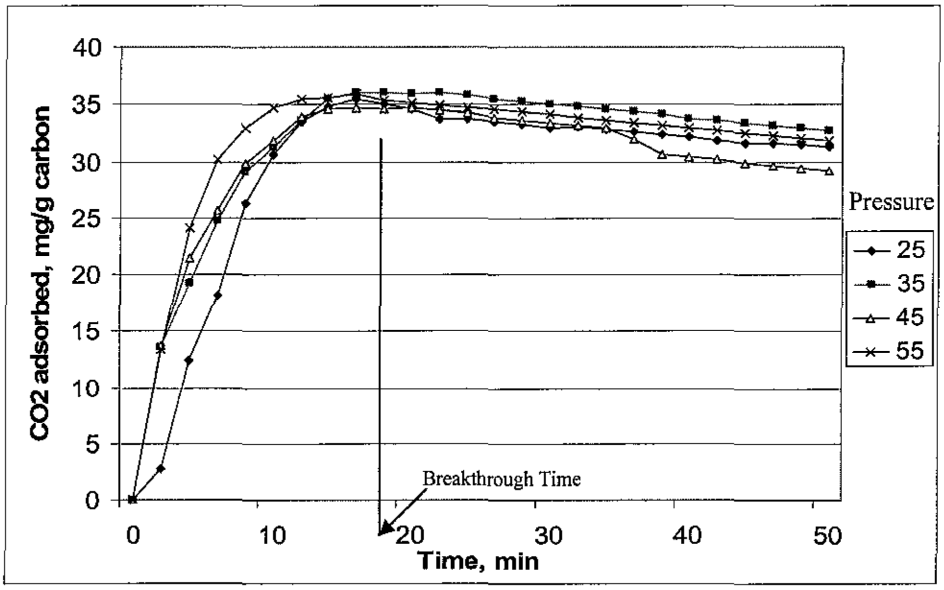

Figure 4.10: Adsorption on 2.5mm Activated Carbon

The figures above reported that higher pressure do not gives any clear effect on the CO_2 adsorption because the maximum points for 2.5mm activated carbon is not 55kPa. For 2.5mm activated carbon, the CO_2 uptake is the maximum for 35kPa while maximum CO_2 uptake for 1.5mm is 55kPa. 1.5mm activated carbon shows that increasing pressure of adsorption will gives higher adsorption rate (based on the slope) and a higher CO_2 uptake. The same conditions are expected for 2.5mm activated carbon also but the pressure range is just too narrow. The gap for each pressure is only 10kPa. So, due to the close value of pressure used, the correlations for 2.5mm activated carbon become unclear.

However, based on the rate of adsorption (slope), 2.5mm activated carbon data shows that for higher pressure, the adsorption rate is higher. In short, the uncorrelated results for the CO_2 uptake for 2.5mm activated carbon are due to noises like temperature, moisture or human errors.

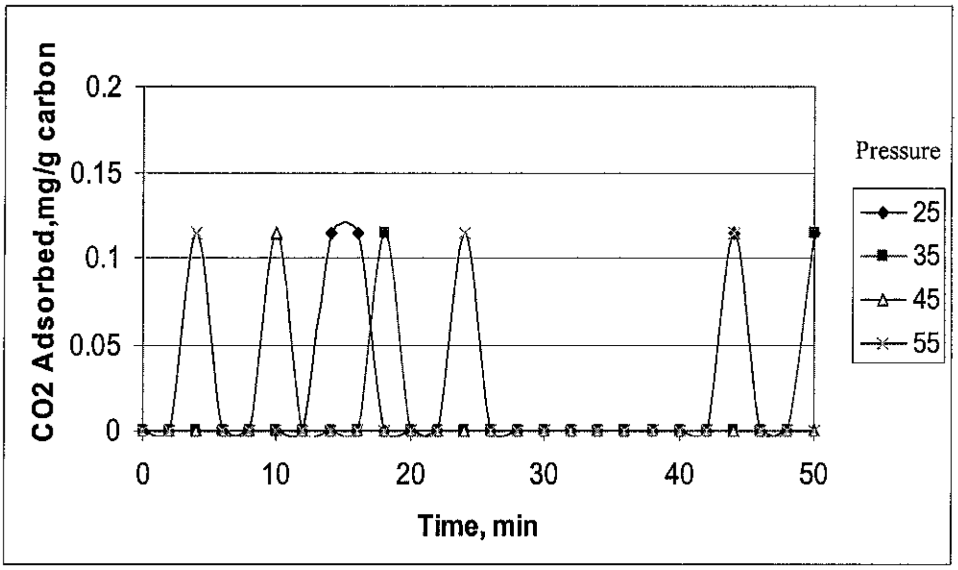

Figure 4.11: Adsorption on Activated Alumina

For activated alumina, due to the non-equilibrium conditions, the results do not show any trend except the fluctuating curves. However, for the modified alumina, it is shown that the maximum point for adsorption of CO_2 is at 55kPa, followed by 45kPa until 25kPa.

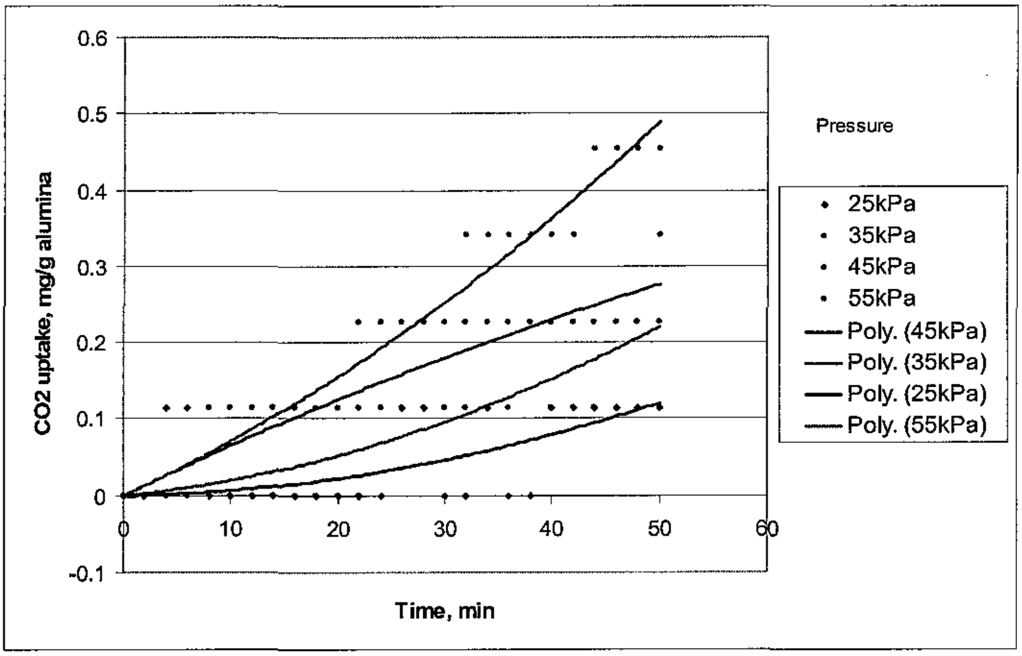

Figure 4.12: Adsorption on Modified Activated Alumina

The best line is plotted to get a clearer picture on the effect of pressure on modified activated alumina. A clearer trend on the effect of pressure can be seen. As the pressure increase, the CO_2 uptake is found to increase too.

All these strongly prove that pressure is an important factor in adsorption where higher pressure gives higher adsorption rate and higher CO_2 uptake. This is because the driving force for the molecules diffusions into the pores is higher at higher pressure. Anyhow, the results for the effect of higher pressure can be better demonstrated if the pressure range is higher up to MPa range.

4.5 The Effect of Adding Metal Oxide to Activated Alumina at 55kpa

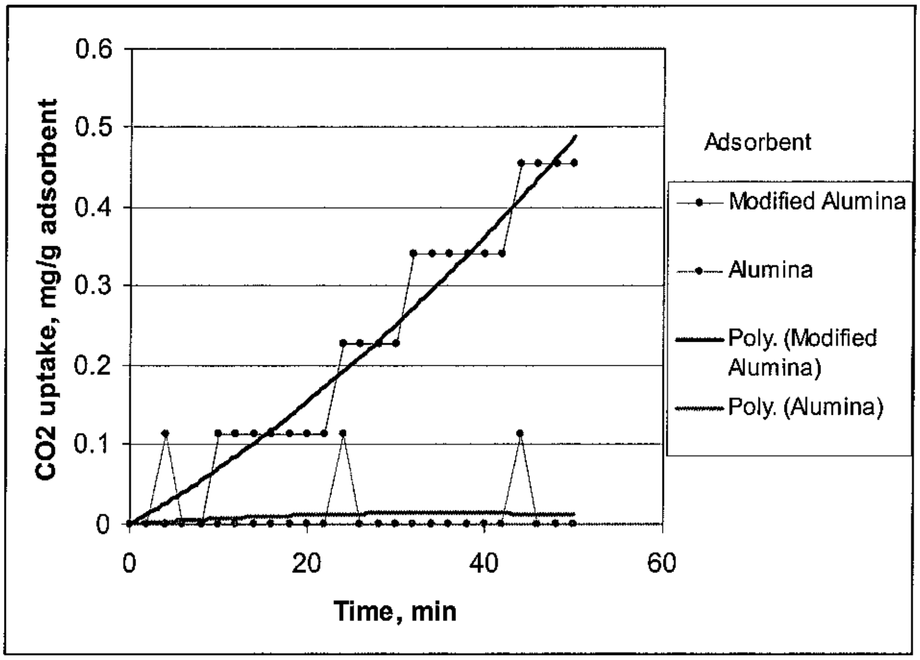

Figure 4.13: CO_2 uptake for activated alumina and alumina with metal oxide

The purpose of adding calcium oxide is to enhance the adsorption of CO_2. So, figure 4.13 proved that the adsorption really enhance for the modified alumina although the increment is only 0.4mg/g alumina. Despite having a small surface area (2.8m2/g), the presence calcium oxide manage to increase the adsorption by forming bonds with the molecules. Tatsuro et. Al (1997) research on this addition effect states that the interactions happens between the carbon atom of a CO_2 molecule and the oxygen anion of the added metal oxide and between an oxygen atom of a CO_2 molecule and the cation (in this case, Ca^{2+})of the metal oxide.

Carbon atoms of a CO_2 molecule exhibit electrophilicity, because the electron cloud is deviated in such a way that the electron density is enriched in the oxygen side. Oxygen anions of a metal oxide are basic sites on the alumina. The polar sites will induce the dipole moment at the CO_2 molecules and attraction can happen. Through electrostatic interaction, the bonding is formed between the CO_2 molecules and the oxygen anion of a metal oxide to form carbonate species (CO_3^{2-}). So, the added adsorption sites enhance the adsorption of alumina despite having small surface area.

4.6 Adsorption Isotherm for All Adsorbent

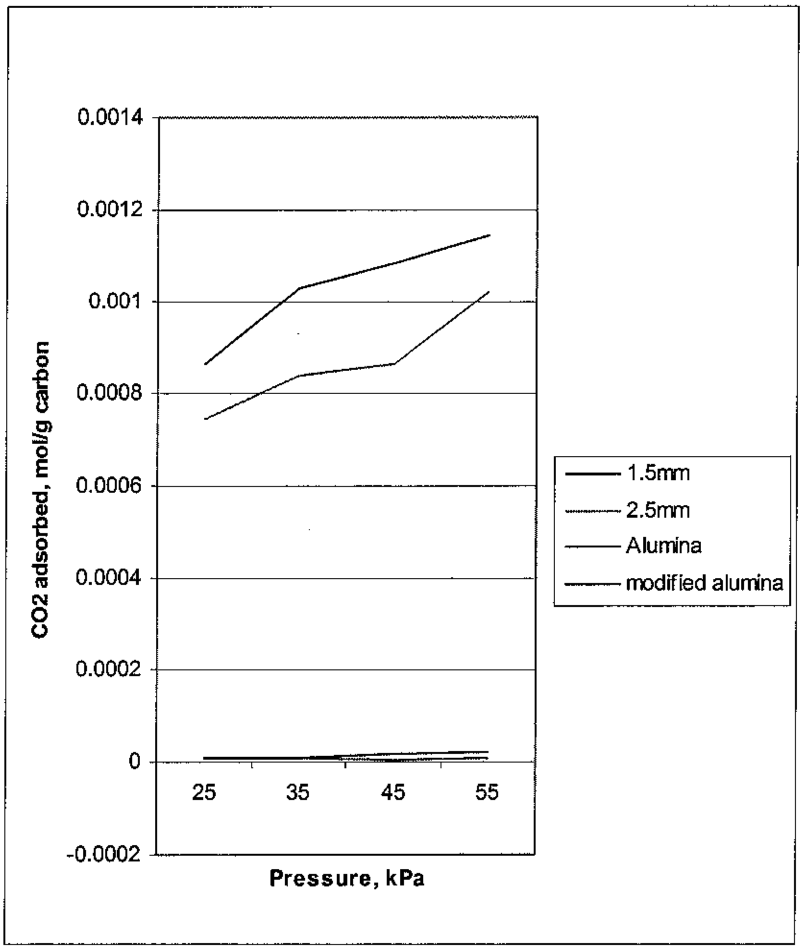

Figure 4.14: Adsorption Isotherm for 3 adsorbents

The graph above shows the adsorption isotherm for all 4 adsorbent used; 2.5mm activated carbon, 1.5mm activated carbon, activated alumina and alumina with metal oxide. We can see that as the pressure increase the CO_2 adsorbed is higher for all adsorbent except activated alumina. The higher pressure will exert more forces for the pore diffusivity.

For activated alumina, different case is reported. Apparently, there is only very little adsorption of $CO_2$where the maximum amount adsorbed is 0.04g and the least is 0.01g. This value is relatively small compared to the amount adsorbed by activated carbons (2-5g). The low adsorption amount is logical based on the data from micropore characterization where the alumina is concluded as nonporous adsorbent.

Its low porosity caused it to have very little pores thus having a much lower total surface area compared to activated carbon. Besides, the time set for an adsorption is only 50 minutes per adsorbent. Based on the results from section 4.2, 50minutes is too short for both activated alumina because they are unable to reach equilibrium by that time. They needed more time to reach equilibrium.

In addition, those four points is not sufficient enough to determine which type of is the best fit for the results obtained. From the plots obtained (not available), the best fit for the data is similar for all linear, freundlich and langmuir isotherm where the regression is more than 0.92. So, the conclusion made is the four points are just a small part in the isotherm curve. It requires a bigger range of pressure, says 25kPa to 50Mpa, to obtain a clearer isotherm so that the isotherm fitting can be done properly.

CHAPTER 5:
CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

Overall, the study of carbon dioxide adsorption on activated carbon and activated alumina of various types and sizes have been successfully conducted. The four types of adsorbent give different results in adsorption capacity thus providing a base to analyze the different between the 4 adsorbents that caused the adsorbent's loading to differ.

1.5mm activated carbon has the highest loading followed by 2.5mm activated carbon and lastly activated alumina. One of the main factors the contributed to the differences is the total surface area. The higher the total surface area, the higher the adsorption capacity because there are more surface for the CO_2 molecules to adsorb. However, although 2.5mm activated carbon has a higher micropore surface area due to larger pore volume, it is suspected that the lower adsorption happen due to the low diffusivity to the internal pores. The diffusivity to the internal micropore surface is a function of the pore's effective length, L. The longer the length, the higher the resistance for the molecules to get to the surface.

The almost null adsorption of CO_2 on both alumina and the modified alumina is because the adsorption of CO_2 has not reach equilibrium. So, the adsorption capacity of activated alumina cannot be concluded However, it is expected that the adsorption capacity will still be lower than activated carbon due to the low porosity (low surface area and 0 pore volume) of the alumina surface. Thus, this adsorbent is concluded to be non-porous. Due to that, calcium oxide is added to this alumina to enhance its adsorption. By adding metal oxide, the oxygen anion will act as a basic surface of chemisorption with the carbon dioxide molecules to form a carbonate. After adsorption process is done on this modified alumina, it is found that compared to the normal alumina, the amount of CO_2 adsorbed increase by about 0.4mg/g alumina. The increment is due to the presence of more adsorption sites for the molecules to interact and form bonds.

Overall, all the objectives is achieved and a greater understanding of CO_2 adsorption, physical characteristic of adsorbent, and the certain factors that affects adsorption is achieved.

5.2 RECOMMENDATION

A few recommendations had been proposed for a better performance network. First of all, to get the most accurate and reliable data, it is better is a high technology equipment being used instead of a self assembled equipment. This is because from the self assembled equipment, a lot of problem arises. Among them are leaks. Leak will cause the pressure of the adsorption to be not accurate thus causing errors. Besides, temperature of the adsorption cannot be well controlled too. Adsorption is a temperature sensitive process. That is why is the temperature is not kept constant; the experiments will be less accurate. So, AutoSorb is used for more accurate, less erroneous data and also to get the full isotherm for adsorption and desorption.

One more is to use column that has a uniform hollow to prevent large pressure drop. The pressure recorded at the inlet of the column is higher that the pressure recorded at the outlet by 3 to 5 folds. This is because the diameter where the pressure is recorded is smaller (0.5cm) compared to the diameter of the column (4cm). This difference will cause large pressure drop in the column.

Besides, more samples needed to be used for clearer comparison of data. With more samples, more properties can be look into. If powdered activated carbon is used, there will be 3 sizes of activated carbon; 2.5mm, 1.5mm and powdered. However, the experiment setup cannot be used to conduct adsorption for powdered activated carbon because there is no filter to trap the powder from escaping from the adsorption column.

Besides, for alumina modified with metal oxides, if the experiments is conducted many types of metal oxides like K, Mg or Na, a comparison can be made to investigate the effect of different metal oxide to adsorption. Also, if the concentration of metal nitrates is varied, how it will affect the adsorption capacity. All this can be possibly done if more time is given for this study.

Besides, conducting the experiment for a wider range of pressure can lead to a better graph because 25kPa to 55kPa cannot give a clear data for the effect of pressure. So, if the pressure conducted is further apart, the amount of CO_2 adsorbed will differ greatly too, thus a clear correlation can be seen.

More CO_2 can be adsorbed also if higher pressure is used due to the higher driving forces. Another thing is the adsorbents are not fully loaded yet because the high surface area given by the BET is capable to adsorb more CO_2. However, as stated by K. Kaczmarski1, and J. Ch. Bellot (1998) in their research on particles porosity effect on adsorbent, "*Effective mass-transfer kinetics depends on particle-size distribution (PSD) and particle porosity (among other complex phenomena). The pore-diffusion flux can vary with adsorbate loading – if the amount of adsorbed species is sufficiently large it can lead to hindrance effects that substantially change particle porosity*". This proves that the surface areas are not optimized due to hindered effects by the adsorbed species.

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CHAPTER 6:

APPENDIX

Table 6.1: Gantt Chart of Progress so far

Activities	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Topic Selection	■														
Preliminay Research		■	■												
Submission of preliinary Report			■												
Experiment				■	■	■	■								
Mid Semester Break								■							
Submission of Progress Report							■								
Analyzing Results / Research				■	■	■	■	■	■	■	■	■			
Preparing Final Report											■	■			
EDX												■			
Submission of Final Report													■	*	***
Oral Presentation														■	■

*** current week

* progress so far

Table 6.2: Results for adsorption of 2.5mm AC

	Weight			
	25	35	45	55
0	0	0	0	0
2	13.97727	13.63636	18.18182	10.34091
4	24.77273	23.63636	26.47727	19.31818
6	36.47727	37.5	39.77273	33.18182
8	41.25	42.04545	48.06818	41.36364
10	45.79545	46.36364	55.22727	50
12	48.52273	48.97727	60.34091	56.81818
14	49.65909	51.13636	60.56818	60
16	50.22727	51.36364	60.11364	60.45455
18	50.11364	51.47727	60.22727	60.68182
20	49.88636	51.59091	59.88636	60.90909
22	49.31818	51.13636	59.54545	60.90909
24	45.34091	50.90909	59.09091	60.56818
26	45.22727	50.68182	58.86364	60.22727
28	44.88636	50	58.63636	58.86364
30	44.09091	48.97727	58.29545	58.63636
32	43.40909	48.63636	57.84091	58.40909
34	42.61364	47.84091	57.61364	57.84091
36	42.04545	47.5	56.47727	57.27273
38	41.36364	46.93182	56.25	56.93182
40	38.86364	46.47727	56.02273	56.47727
42	38.29545	45.56818	55.90909	56.13636
44	38.06818	45	55.68182	55.79545
46	37.72727	44.31818	55.34091	55.34091
48	37.27273	43.63636	55.11364	55.11364
50	36.93182	42.95455	54.88636	54.88636

Table 6.3: Results for adsorption of 1.5mm AC

T(min)	Weight(g)			
	25kPa	35kPa	45kPa	55kPa
0	0	0	0	0
2	2.7272727	13.636364	13.75	13.409091
4	12.386364	19.204545	21.477273	24.090909
6	18.068182	24.772727	25.681818	30.113636
8	26.25	29.090909	29.886364	32.954545
10	30.568182	31.25	31.818182	34.659091
12	33.522727	33.636364	33.977273	35.454545
14	34.772727	35.454545	34.545455	35.568182
16	35.454545	36.022727	34.659091	35.909091
18	35	36.022727	34.545455	35.340909
20	34.545455	35.909091	34.659091	35.113636
22	33.75	36.022727	34.431818	34.886364
24	33.75	35.795455	34.204545	34.659091
26	33.522727	35.454545	33.863636	34.545455
28	33.295455	35.227273	33.636364	34.318182
30	32.954545	35	33.409091	34.090909

32	33.068182	34.772727	33.181818	33.863636
34	32.840909	34.545455	32.954545	33.636364
36	32.613636	34.318182	31.931818	33.409091
38	32.386364	34.090909	30.568182	33.181818
40	32.159091	33.75	30.340909	32.954545
42	31.818182	33.636364	30.113636	32.727273
44	31.590909	33.409091	29.886364	32.5
46	31.590909	33.181818	29.659091	32.272727
48	31.477273	32.954545	29.431818	32.045455
50	31.25	32.727273	29.204545	31.818182

Table 6.4: Results for adsorption alumina

T(min)	Weight (g)			
	25kPa	35kPa	45kPa	55kPa
0	0	0	0	0
2	0	0	0	0
4	0	0	0	0.114
6	0	0	0	0
8	0	0	0	0
10	0	0	0.114	0
12	0	0	0	0
14	0.114	0	0	0
16	0.114	0	0	0
18	0	0.114	0	0
20	0	0	0	0
22	0	0	0	0
24	0	0	0	0.114
26	0	0	0	0
28	0	0	0	0
30	0	0	0	0
32	0	0	0	0
34	0	0	0	0
36	0	0	0	0
38	0	0	0	0
40	0	0	0	0
42	0	0	0	0
44	0.114	0	0	0.114
46	0	0	0	0
48	0	0	0	0
50	0.114	0.114	0	0

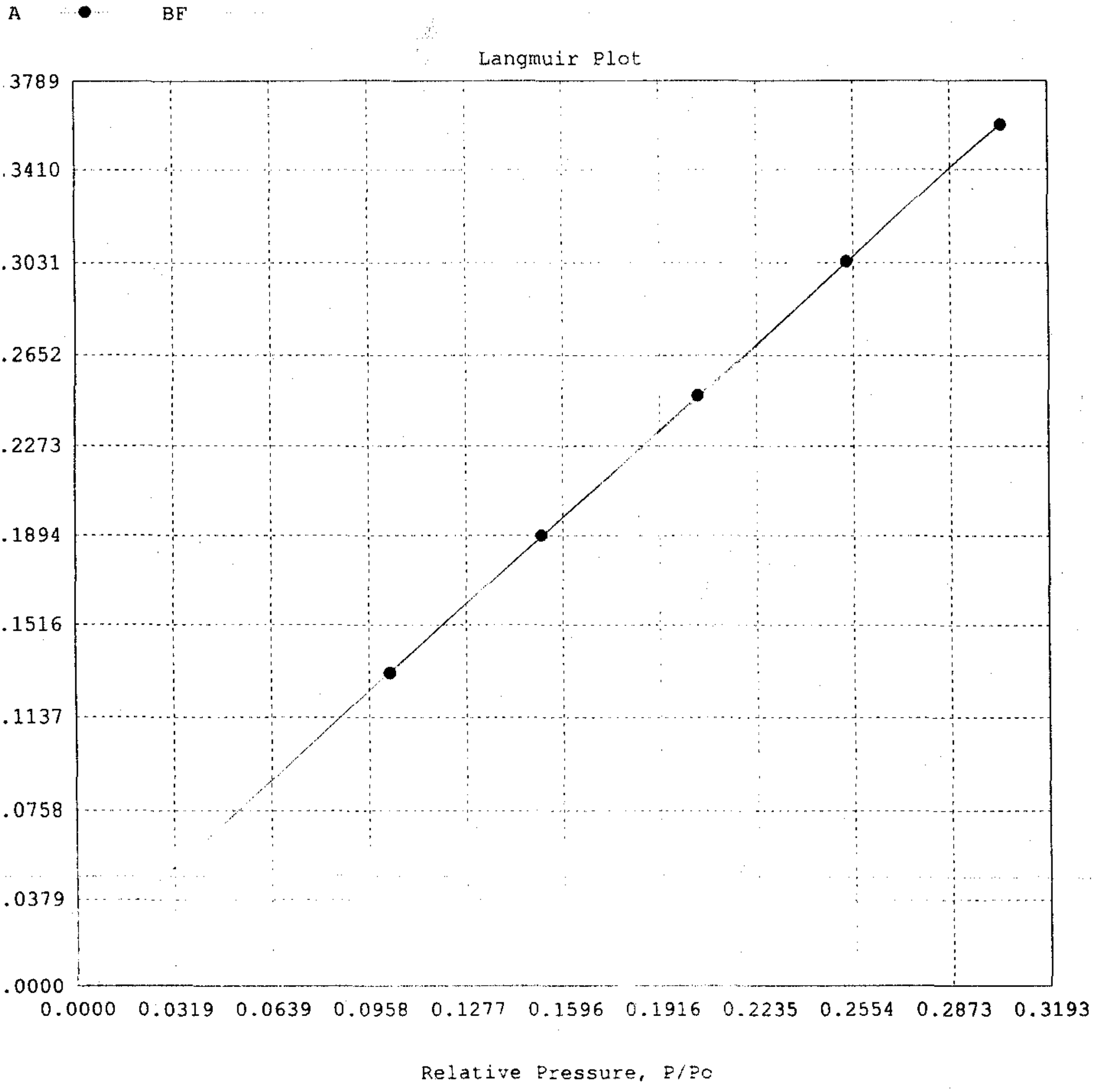
4.1.4 Total CO2 uptake for all 4 adsorbent.

Sample of Adsorbent	CO2 uptake (g)			
	25kPa	35kPa	45kPa	55kPa
2.5mm Granular Activated Carbon	3.01	3.12	3.18	3.22
1.5mm Granular Activated Carbon	4.66	4.89	5.09	5.3
Activated Alumina	0.03	0.03	0.02	0.04
Activated Alumina with Calcium Oxide	not yet	not yet	not yet	not yet

Table 4.4: Net CO2 uptake of 4 adsorbents

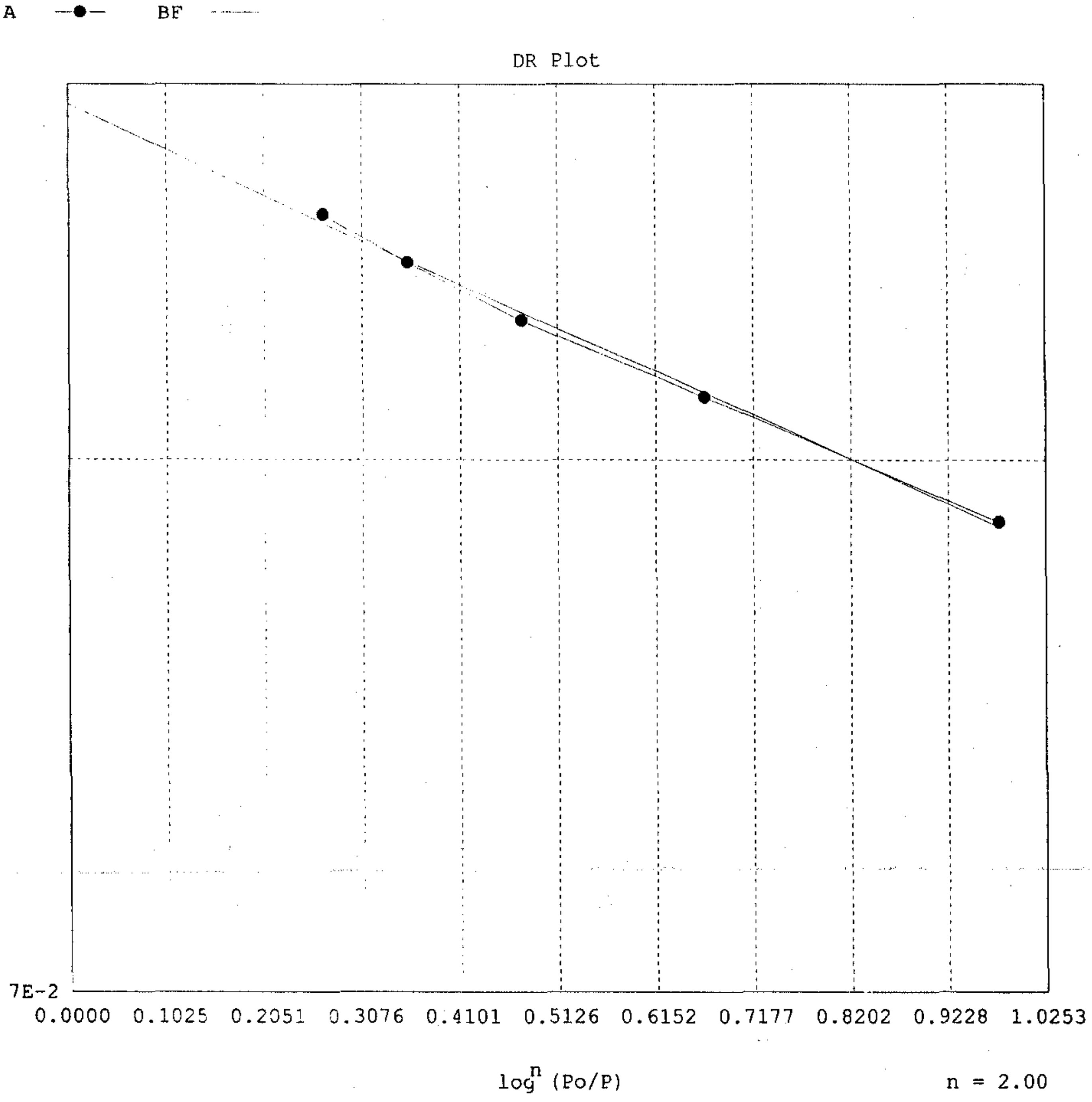
Quantachrome Corporation
Quantachrome Autosorb Automated Gas Sorption System Report
Autosorb for Windows® Version 1.20

```
 ID           1.5mm granular activated carbon
ption         Degassed at 150 deg.
ts
 Weight       0.1008 g
ate           NITROGEN              Outgas Temp    200.0 °C     Operator          YEOW
Sec Area      16.2 Å²/molecule      Outgas Time    1.0 hrs      Analysis Time     243.8 min
ality         6.580E-05             P/Po Toler     1            End of Run        04/08/2004 16:03
lar Wt        28.0134 g/mol         Equil Time     3            File Name         15MMAC.RAW
n #           1                     Bath Temp.     77.40        PC SW Version     1.20
```



Quantachrome Corporation
Quantachrome Autosorb Automated Gas Sorption System Report
Autosorb for Windows® Version 1.20

ID	1.5mm granular activated carbon				
ption	Degassed at 150 deg.				
ts					
Weight	0.1008 g				
ate	NITROGEN	**Outgas Temp**	200.0 °C	**Operator**	YEOW
Sec Area	16.2 Å²/molecule	**Outgas Time**	1.0 hrs	**Analysis Time**	243.8 min
ality	6.580E-05	**P/Po Toler**	1	**End of Run**	04/08/2004 16:03
lar Wt	28.0134 g/mol	**Equil Time**	3	**File Name**	15MMAC.RAW
n #	1	**Bath Temp.**	77.40	**PC SW Version**	1.20



```
                        Quantachrome Corporation
        Quantachrome Autosorb Automated Gas Sorption System Report
                    Autosorb for Windows®  Version 1.20

        1.5mm granular activated carbon
on      Degassed at 150 deg.

ight    0.1008 g
        NITROGEN           Outgas Temp    200.0 °C    Operator         YEOW
 Area   16.2 Å²/molecule   Outgas Time    1.0 hrs     Analysis Time    243.8 min
ty      6.580E-05          P/Po Toler     1           End of Run       04/08/2004 16:03
 Wt     28.0134 g/mol      Equil Time     3           File Name        15MMAC.RAW
        1                  Bath Temp.     77.40       PC SW Version    1.20


                            AVERAGE PORE SIZE

                 Average Pore Diameter = 1.977E+01 Å
```

Quantachrome Corporation
Quantachrome Autosorb Automated Gas Sorption System Report
Autosorb for Windows® Version 1.20

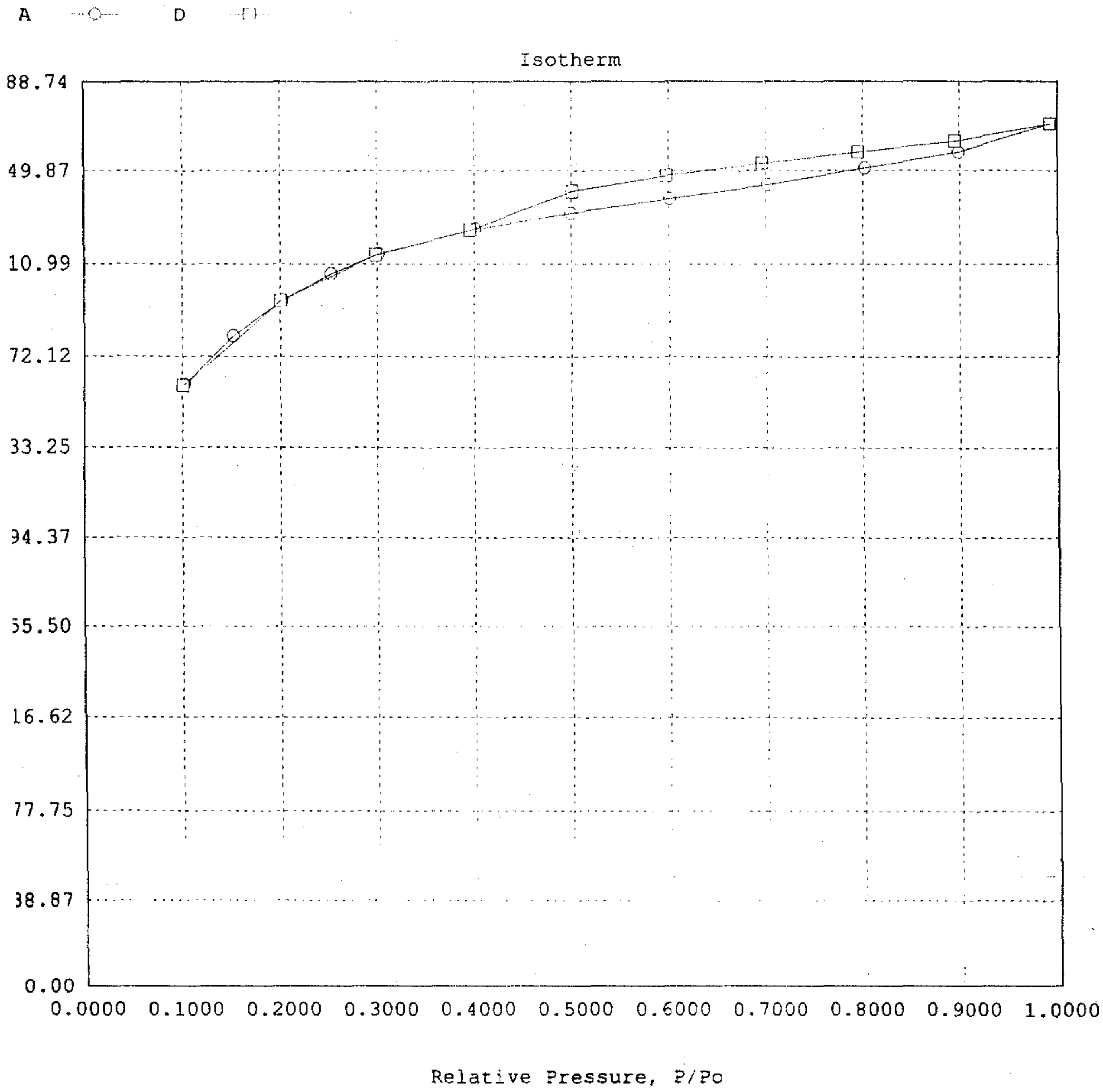
```
)          1.5mm granular activated carbon
ion        Degassed at 150 deg.

eight      0.1008 g
e          NITROGEN            Outgas Temp    200.0 °C    Operator         YEOW
: Area     16.2 Å²/molecule    Outgas Time    1.0 hrs     Analysis Time    243.8 min
ity        6.580E-05           P/Po Toler     1           End of Run       04/08/2004 16:03
r Wt       28.0134 g/mol       Equil Time     3           File Name        15MMAC.RAW
#          1                   Bath Temp.     77.40       PC SW Version    1.20
```

DA Method Micropore Analysis

eter .]	Dv(r) [cc/Å/g]	Diameter [Å]	Dv(r) [cc/Å/g]	Diameter [Å]	Dv(r) [cc/Å/g]
0E+00	9.24857E-44	1.4600E+01	1.41639E+00	2.3200E+01	2.95374E-01
0E+00	4.14594E-36	1.4800E+01	1.39530E+00	2.3400E+01	2.84330E-01
0E+00	5.90886E-30	1.5000E+01	1.36989E+00	2.3600E+01	2.73758E-01
0E+00	5.64761E-25	1.5200E+01	1.34093E+00	2.3800E+01	2.63638E-01
0E+00	6.41034E-21	1.5400E+01	1.30912E+00	2.4000E+01	2.53948E-01
0E+00	1.33991E-17	1.5600E+01	1.27510E+00	2.4200E+01	2.44670E-01
0E+00	7.24210E-15	1.5800E+01	1.23942E+00	2.4400E+01	2.35783E-01
0E+00	1.31870E-12	1.6000E+01	1.20256E+00	2.4600E+01	2.27271E-01
0E+00	9.95620E-11	1.6200E+01	1.16494E+00	2.4800E+01	2.19115E-01
0E+00	3.67240E-09	1.6400E+01	1.12693E+00	2.5000E+01	2.11300E-01
0E+00	7.53947E-08	1.6600E+01	1.08882E+00	2.5200E+01	2.03809E-01
0E+00	9.56203E-07	1.6800E+01	1.05088E+00	2.5400E+01	1.96629E-01
0E+00	8.14677E-06	1.7000E+01	1.01332E+00	2.5600E+01	1.89744E-01
0E+00	4.98974E-05	1.7200E+01	9.76312E-01	2.5800E+01	1.83142E-01
0E+00	2.32134E-04	1.7400E+01	9.40001E-01	2.6000E+01	1.76808E-01
0E+00	8.57996E-04	1.7600E+01	9.04501E-01	2.6200E+01	1.70732E-01
0E+00	2.61413E-03	1.7800E+01	8.69898E-01	2.6400E+01	1.64901E-01
0E+00	6.76785E-03	1.8000E+01	8.36261E-01	2.6600E+01	1.59305E-01
0E+00	1.52672E-02	1.8200E+01	8.03636E-01	2.6800E+01	1.53932E-01
0E+00	3.06417E-02	1.8400E+01	7.72057E-01	2.7000E+01	1.48773E-01
0E+01	5.56749E-02	1.8600E+01	7.41543E-01	2.7200E+01	1.43817E-01
0E+01	9.29214E-02	1.8800E+01	7.12103E-01	2.7400E+01	1.39057E-01
0E+01	1.44207E-01	1.9000E+01	6.83736E-01	2.7600E+01	1.34483E-01
0E+01	2.10251E-01	1.9200E+01	6.56435E-01	2.7800E+01	1.30087E-01
0E+01	2.90502E-01	1.9400E+01	6.30186E-01	2.8000E+01	1.25862E-01
0E+01	3.83194E-01	1.9600E+01	6.04970E-01	2.8200E+01	1.21799E-01
0E+01	4.85590E-01	1.9800E+01	5.80764E-01	2.8400E+01	1.17891E-01
0E+01	5.94325E-01	2.0000E+01	5.57544E-01	2.8600E+01	1.14132E-01
0E+01	7.05772E-01	2.0200E+01	5.35279E-01	2.8800E+01	1.10516E-01
0E+01	8.16383E-01	2.0400E+01	5.13943E-01	2.9000E+01	1.07035E-01
0E+01	9.22943E-01	2.0600E+01	4.93503E-01	2.9200E+01	1.03685E-01
0E+01	1.02274E+00	2.0800E+01	4.73929E-01	2.9400E+01	1.00460E-01
0E+01	1.11367E+00	2.1000E+01	4.55188E-01	2.9600E+01	9.73542E-02
0E+01	1.19423E+00	2.1200E+01	4.37250E-01	2.9800E+01	9.43627E-02
0E+01	1.26351E+00	2.1400E+01	4.20083E-01	3.0000E+01	9.14807E-02
0E+01	1.32111E+00	2.1600E+01	4.03656E-01	3.0200E+01	8.87036E-02
0E+01	1.36704E+00	2.1800E+01	3.87938E-01	3.0400E+01	8.60270E-02
0E+01	1.40170E+00	2.2000E+01	3.72899E-01	3.0600E+01	8.34468E-02
0E+01	1.42569E+00	2.2200E+01	3.58511E-01	3.0800E+01	8.09590E-02
0E+01	1.43981E+00	2.2400E+01	3.44745E-01	3.1000E+01	7.85597E-02
0E+01	1.44498E+00	2.2600E+01	3.31574E-01	3.1200E+01	7.62454E-02
0E+01	1.44216E+00	2.2800E+01	3.18972E-01	3.1400E+01	7.40125E-02
0E+01	1.43231E+00	2.3000E+01	3.06914E-01	3.1600E+01	7.18578E-02

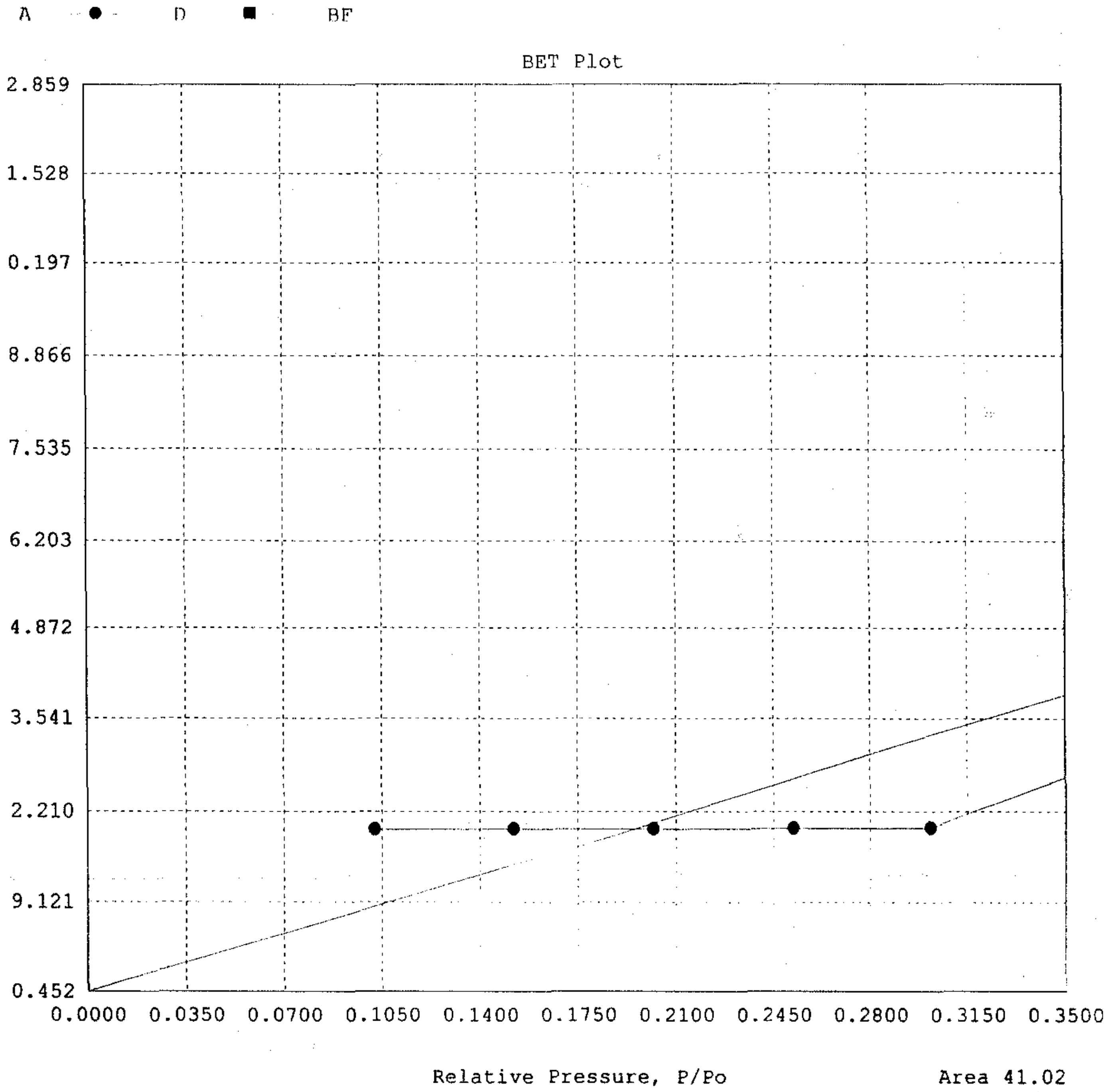
Quantachrome Corporation
Quantachrome Autosorb Automated Gas Sorption System Report
Autosorb for Windows® Version 1.20

e ID	2.5mm granular activated carbon				
iption	Degassed at 150 deg.				
nts					
e Weight	0.1080 g				
bate	NITROGEN	**Outgas Temp**	200.0 °C	**Operator**	YEOW
-Sec Area	16.2 Å²/molecule	**Outgas Time**	1.0 hrs	**Analysis Time**	369.1 min
eality	6.580E-05	**P/Po Toler**	1	**End of Run**	04/07/2004 21:15
ular Wt	28.0134 g/mol	**Equil Time**	3	**File Name**	AS4471.RAW
on #	1	**Bath Temp.**	77.40	**PC SW Version**	1.20



Quantachrome Corporation
Quantachrome Autosorb Automated Gas Sorption System Report
Autosorb for Windows® Version 1.20

e ID	2.5mm granular activated carbon				
iption	Degassed at 150 deg.				
nts					
e Weight	0.1080 g				
bate	NITROGEN	**Outgas Temp**	200.0 °C	**Operator**	YEOW
-Sec Area	16.2 Å²/molecule	**Outgas Time**	1.0 hrs	**Analysis Time**	369.1 min
eality	6.580E-05	**P/Po Toler**	1	**End of Run**	04/07/2004 21:15
ular Wt	28.0134 g/mol	**Equil Time**	3	**File Name**	AS4471.RAW
on #	1	**Bath Temp.**	77.40	**PC SW Version**	1.20



```
                    Quantachrome Corporation
      Quantachrome Autosorb Automated Gas Sorption System Report
                 Autosorb for Windows®  Version 1.20

)        2.5mm granular activated carbon
ion      Degassed at 150 deg.

eight    0.1080 g
e        NITROGEN          Outgas Temp   200.0 °C   Operator        YEOW
c Area   16.2 Å²/molecule  Outgas Time   1.0 hrs    Analysis Time   369.1 min
ity      6.580E-05         P/Po Toler    1          End of Run      04/07/2004 21:15
r Wt     28.0134 g/mol     Equil Time    3          File Name       AS4471.RAW
#        1                 Bath Temp.    77.40      PC SW Version   1.20


                t-Method Micropore Analysis (de Boer)

         P/Po              Thickness          Volume
                              Å             [cc/g] STP

      1.0249e-01             3.70             929.380
      1.5224e-01             4.05            1003.028
      2.0210e-01             4.38            1057.204
      2.5246e-01             4.71            1096.954
      3.0191e-01             5.02            1125.454

                     Slope =  1.475E+02

             Y - Intercept =  3.974E+02 cc/g

         Micro-pore volume     =  0.000E+00 cc/g

         Micro-pore area       =  0.000E+00 m²/g

         External Surface Area =  4.102E+01 m²/g

     Correlation Coefficient   =  0.987221
```

```
                    Quantachrome Corporation
        Quantachrome Autosorb Automated Gas Sorption System Report
                  Autosorb for Windows®  Version 1.20

D         2.5mm granular activated carbon
ion       Degassed at 150 deg.

eight     0.1080 g
e         NITROGEN            Outgas Temp    200.0 °C   Operator         YEOW
c Area    16.2 Å²/molecule    Outgas Time    1.0 hrs    Analysis Time    369.1 min
ity       6.580E-05           P/Po Toler     1          End of Run       04/07/2004 21:15
r Wt      28.0134 g/mol       Equil Time     3          File Name        AS4471.RAW
#         1                   Bath Temp.     77.40      PC SW Version    1.20


                          MULTIPOINT BET

            P/Po              Volume            1/(W((Po/P)-1))
                            [cc/g] STP

        1.0249e-01           929.3796             9.831E-02
        1.5224e-01          1003.0278             1.433E-01
        2.0210e-01          1057.2037             1.917E-01
        2.5246e-01          1096.9537             2.463E-01
        3.0191e-01          1125.4537             3.075E-01
        9.9313e-01          1322.6111             8.746E+01

                         Area =  4.102E+01 m²/g

                        Slope =  1.054E+02

                Y - Intercept = -2.045E+01

      Correlation Coefficient =  0.977373

                            C = -4.151E+00
```

```
                              Quantachrome Corporation
                Quantachrome Autosorb Automated Gas Sorption System Report
                          Autosorb for Windows®  Version 1.20

D         2.5mm GAC
ion       Degassed at 150 deg.

eight     0.1080 g
e         NITROGEN               Outgas Temp    200.0 °C    Operator        SHEEMA
c Area    16.2 Å²/molecule       Outgas Time    1.0 hrs     Analysis Time   369.1 min
ity       6.580E-05              P/Po Toler     1           End of Run      04/07/2004 21:15
r Wt      28.0134 g/mol          Equil Time     3           File Name       AS4471.RAW
#         1                      Bath Temp.     77.40       PC SW Version   1.20


                             DA Method Micropore Analysis

meter       Dv(r)           Diameter      Dv(r)           Diameter      Dv(r)
Å]        [cc/Å/g]            [Å]       [cc/Å/g]            [Å]       [cc/Å/g]

00E+01  1.63968E-01
00E+01  1.59473E-01
00E+01  1.55124E-01
00E+01  1.50915E-01
00E+01  1.46842E-01
00E+01  1.42899E-01
00E+01  1.39082E-01
00E+01  1.35387E-01
00E+01  1.31808E-01
00E+01  1.28341E-01
00E+01  1.24983E-01
00E+01  1.21730E-01
00E+01  1.18577E-01
00E+01  1.15522E-01
00E+01  1.12561E-01
00E+01  1.09690E-01
00E+01  1.06907E-01
00E+01  1.04207E-01
00E+01  1.01590E-01
00E+01  9.90505E-02
00E+01  9.65872E-02
00E+01  9.41970E-02
00E+01  9.18776E-02
00E+01  8.96265E-02
00E+01  8.74414E-02
00E+01  8.53200E-02
00E+01  8.32602E-02
00E+01  8.12600E-02
00E+01  7.93173E-02
00E+01  7.74303E-02
00E+01  7.55970E-02
00E+01  7.38158E-02
00E+01  7.20849E-02
00E+01  7.04026E-02
00E+01  6.87674E-02
00E+01  6.71778E-02

                         Best E =  5.50 kJ/mol
                         Best n =  1.90
            Pore Diameter (Mode) =  1.6800E+01 Å
```

```
                        Quantachrome Corporation
         Quantachrome Autosorb Automated Gas Sorption System Report
                   Autosorb for Windows®  Version 1.20

D         2.5mm GAC
ion       Degassed at 150 deg.

eight     0.1080 g
e         NITROGEN           Outgas Temp   200.0 °C   Operator        SHEEMA
c Area    16.2 Å²/molecule   Outgas Time   1.0 hrs    Analysis Time   369.1 min
ity       6.580E-05          P/Po Toler    1          End of Run      04/07/2004 21:15
r Wt      28.0134 g/mol      Equil Time    3          File Name       AS4471.RAW
 #        1                  Bath Temp.    77.40      PC SW Version   1.20


                       DA Method Micropore Analysis

meter     Dv(r)          Diameter     Dv(r)          Diameter     Dv(r)
Å]        [cc/Å/g]         [Å]        [cc/Å/g]         [Å]        [cc/Å/g]

00E+00    1.20512E-43    1.5800E+01   1.63246E+00    2.4400E+01   6.24694E-01
00E+00    3.68247E-37    1.6000E+01   1.66977E+00    2.4600E+01   6.03898E-01
00E+00    9.33846E-32    1.6200E+01   1.69801E+00    2.4800E+01   5.83836E-01
00E+00    3.11214E-27    1.6400E+01   1.71768E+00    2.5000E+01   5.64485E-01
00E+00    1.97057E-23    1.6600E+01   1.72938E+00    2.5200E+01   5.45826E-01
00E+00    3.18343E-20    1.6800E+01   1.73375E+00    2.5400E+01   5.27834E-01
00E+00    1.66316E-17    1.7000E+01   1.73147E+00    2.5600E+01   5.10489E-01
00E+00    3.40366E-15    1.7200E+01   1.72320E+00    2.5800E+01   4.93768E-01
00E+00    3.18841E-13    1.7400E+01   1.70963E+00    2.6000E+01   4.77651E-01
00E+00    1.55255E-11    1.7600E+01   1.69138E+00    2.6200E+01   4.62117E-01
00E+00    4.36177E-10    1.7800E+01   1.66907E+00    2.6400E+01   4.47144E-01
00E+00    7.70462E-09    1.8000E+01   1.64329E+00    2.6600E+01   4.32713E-01
00E+00    9.18744E-08    1.8200E+01   1.61455E+00    2.6800E+01   4.18804E-01
00E+00    7.84590E-07    1.8400E+01   1.58336E+00    2.7000E+01   4.05398E-01
00E+01    5.04070E-06    1.8600E+01   1.55016E+00    2.7200E+01   3.92477E-01
00E+01    2.53888E-05    1.8800E+01   1.51536E+00    2.7400E+01   3.80022E-01
00E+01    1.03786E-04    1.9000E+01   1.47932E+00    2.7600E+01   3.68017E-01
00E+01    3.54530E-04    1.9200E+01   1.44237E+00    2.7800E+01   3.56443E-01
00E+01    1.03730E-03    1.9400E+01   1.40479E+00    2.8000E+01   3.45285E-01
00E+01    2.65453E-03    1.9600E+01   1.36683E+00    2.8200E+01   3.34527E-01
00E+01    6.04833E-03    1.9800E+01   1.32873E+00    2.8400E+01   3.24154E-01
00E+01    1.24580E-02    2.0000E+01   1.29066E+00    2.8600E+01   3.14151E-01
00E+01    2.35002E-02    2.0200E+01   1.25280E+00    2.8800E+01   3.04504E-01
00E+01    4.10537E-02    2.0400E+01   1.21528E+00    2.9000E+01   2.95199E-01
00E+01    6.70596E-02    2.0600E+01   1.17822E+00    2.9200E+01   2.86223E-01
00E+01    1.03274E-01    2.0800E+01   1.14174E+00    2.9400E+01   2.77563E-01
00E+01    1.51024E-01    2.1000E+01   1.10589E+00    2.9600E+01   2.69208E-01
00E+01    2.11021E-01    2.1200E+01   1.07077E+00    2.9800E+01   2.61145E-01
00E+01    2.83245E-01    2.1400E+01   1.03641E+00    3.0000E+01   2.53363E-01
00E+01    3.66940E-01    2.1600E+01   1.00287E+00    3.0200E+01   2.45852E-01
00E+01    4.60676E-01    2.1800E+01   9.70172E-01    3.0400E+01   2.38601E-01
00E+01    5.62494E-01    2.2000E+01   9.38342E-01    3.0600E+01   2.31600E-01
00E+01    6.70069E-01    2.2200E+01   9.07397E-01    3.0800E+01   2.24840E-01
00E+01    7.80894E-01    2.2400E+01   8.77344E-01    3.1000E+01   2.18311E-01
00E+01    8.92450E-01    2.2600E+01   8.48186E-01    3.1200E+01   2.12005E-01
00E+01    1.00234E+00    2.2800E+01   8.19923E-01    3.1400E+01   2.05912E-01
00E+01    1.10842E+00    2.3000E+01   7.92549E-01    3.1600E+01   2.00026E-01
00E+01    1.20884E+00    2.3200E+01   7.66052E-01    3.1800E+01   1.94337E-01
00E+01    1.30209E+00    2.3400E+01   7.40423E-01    3.2000E+01   1.88839E-01
00E+01    1.38704E+00    2.3600E+01   7.15645E-01    3.2200E+01   1.83525E-01
00E+01    1.46288E+00    2.3800E+01   6.91702E-01    3.2400E+01   1.78387E-01
00E+01    1.52916E+00    2.4000E+01   6.68576E-01    3.2600E+01   1.73419E-01
00E+01    1.58567E+00    2.4200E+01   6.46247E-01    3.2800E+01   1.68615E-01
```

```
                              Quantachrome Corporation
              Quantachrome Autosorb Automated Gas Sorption System Report
                           Autosorb for Windows®  Version 1.20

D         2.5mm granular activated carbon
ion       Degassed at 150 deg.

eight     0.1080 g
e         NITROGEN             Outgas Temp    200.0 °C    Operator         YEOW
c Area    16.2 Å²/molecule     Outgas Time    1.0 hrs     Analysis Time    369.1 min
ity       6.580E-05            P/Po Toler     1           End of Run       04/07/2004 21:15
r Wt      28.0134 g/mol        Equil Time     3           File Name        AS4471.RAW
#         1                    Bath Temp.     77.40       PC SW Version    1.20


                                 AVERAGE PORE SIZE

                       Average Pore Diameter = 1.995E+03 Å
```

```
                    Quantachrome Corporation
      Quantachrome Autosorb Automated Gas Sorption System Report
                 Autosorb for Windows®  Version 1.20

D          2.5mm granular activated carbon
ion        Degassed at 150 deg.

eight      0.1080 g
e          NITROGEN             Outgas Temp    200.0 °C    Operator         YEOW
ec Area    16.2 Å²/molecule     Outgas Time    1.0 hrs     Analysis Time    369.1 min
ity        6.580E-05            P/Po Toler     1           End of Run       04/07/2004 21:15
r Wt       28.0134 g/mol        Equil Time     3           File Name        AS4471.RAW
#          1                    Bath Temp.     77.40       PC SW Version    1.20


                         TOTAL PORE VOLUME

            Total pore volume = 2.046E+00 cc/g for

            pores smaller than 2808.9 Å (Diameter),

            at P/Po = 0.99313
```

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                         Quantachrome Corporation
          Quantachrome Autosorb Automated Gas Sorption System Report
                    Autosorb for Windows®  Version 1.20

:D          2.5mm granular activated carbon
:ion        Degassed at 150 deg.
;
Ieight      0.1080 g
.e          NITROGEN            Outgas Temp    200.0 °C   Operator        YEOW
:c Area     16.2 Å²/molecule    Outgas Time    1.0 hrs    Analysis Time   369.1 min
.ity        6.580E-05           P/Po Toler     1          End of Run      04/07/2004 21:15
ir Wt       28.0134 g/mol       Equil Time     3          File Name       AS4471.RAW
 #          1                   Bath Temp.     77.40      PC SW Version   1.20


                    DR Method Micro-Pore Analysis

               log^2.00(Po/P)               Weight Adsorbed
                                               [grams]

                 9.78760E-01                  1.254E-01
                 6.68241E-01                  1.354E-01
                 4.82253E-01                  1.427E-01
                 3.57378E-01                  1.481E-01
                 2.70530E-01                  1.519E-01

                             Slope = -1.175E-01

            Y - Intercept (anti-log) =  1.630E-01

             Correlation Coefficient =  0.999015

                  Average Pore Width =  5.641E+00 nm

              Adsorption Energy (Eo) =  4.608E+00 kJ/mol

                   Micro Pore Volume =  1.868E+00 cc/g

             Micro Pore Surface Area =  5.255E+03 m²/g
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