Development of Carbon Molecular Sieve for Gas Separation

by

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8185

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(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
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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.

MOHAMMAD SAIFULLAH BIN OTHMAN

ABSTRACT

Gas separation technology by adsorption processes has been widely applied in many related industries, such as petrochemicals, environmental technology, oil and gas industries.One of the typical applications of Carbon Molecular Sieve is as the separation barrier for separation of light gases. This application was known since 1950s. Recently as for gas separation, development carbon molecular sieve (CMS) has gained much attention by the engineers worldwide. One of the typical examples of gas separation is air separation. For the separation of air for nitrogen, N_2 and oxygen, O_2, it can be carried out by Pressure-Swing-Adsorption (PSA) over carbon molecular sieve. CMS adsorbent are widely used in gas separation process because it has effective micro pore diameter ranging from 0.14nm to 0.9nm which is comparable to the molecular diameter of adsorbates to be separated.

In this work, carbon molecular sieve was synthesized from commercial activated carbon. After synthesized process completed, these material were subjected to carbonization at 600^0C under an inert atmosphere. These materials then were analysed by Scanning Electron Microscopy (SEM) for structural analysis. The molecular sieve surface area and porosity will be estimated using BET method.

ACKNOWLEDGEMENT

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ABBREVIATIONS AND NOMENCLATURES

W = volume adsorbed at relative preesure P/Po

R = Gas constant

T = Absolute Temperature

Lm = Micropore width

Eo = Micropore size

CHAPTER 1

PROJECT BACKGROUND

1.1 BACKGROUND OF STUDY

Carbon Molecular Sieves (CMS) have gained a lot of attention by the researchers around the world as for their role in gas separations, adsorption and various catalytic applications. These ultra micro porous carbon or Carbon Molecular Sieves (CMS) are amorphous materials with narrow pores, similar in size to small molecules.

They have becoming centre of attention due to their commercial application in Pressure Swing Adsorption (PSA) process for the production of high purity Nitrogen from air.

Normally CMS are 3.7armstrong in size, depends on the preparation method that been used. It provides the sieving structure for small molecule separation. (Gil, 1998)

As for production preparing CMS that can produce high purity of Nitrogen, Selectivity and gas sorption rates are important. Based on the different kinetic adsorption characteristics of different gaseous in CMS, it is suitable for Pressure Swing Adsorption (PSA) process.

1.2 PROBLEM STATEMENT

1.2.1 Problem Identification

Molecular Sieves can be defined as substances with discrete pore structures that can separate the molecules on the basis on their size. Carbon Molecular Sieve is a special type of activated carbons. However, pore size distribution of these materials is not always strictly discrete and furthermore the, molecules are not hard spehes; they can sometimes squeeze in to narrow pores.

Despite from above, today's industries also demand for further research on Carbon Molecular Sieve to enhance the performance of CMS.

1.2.2 Significant of the Project

There are several methods to produce Carbon Molecular Sieve has reported and most of it is intend to slightly modify the pores created by carbonaceous materials whilst the pore structure is highly dependent on the starting materials. This study is significant to show the development of Carbon Molecular Sieve and to prove that the variation of temperature during carbonization could affect the pore size distribution of the CMS.

There are many ways to produces Carbon Molecular Sieve and they have used many template varied from Silica to Palm Shell and Walnut Shell. This experiment could show the performances of commercial Activated Carbons as template to produce CMS.

1.3OBJECTIVE

The objectives of the project are:

1.3.1 To develop Carbon Molecular Sieve for gas separation

1.3.2 To analyse the structural, pore size distribution, and surface area Characteristic of Carbon Molecular Sieve.

1.3.3 To assess the modified product behaviour for O_2/N_2 separation

1.4 SCOPE OF STUDY

The scope of study will be divided into two (2) sections:

1.4.1) Journal research

At first phase, journal research on related field is essential to give an overview on the FYP topic. Journal research has been done via internet on highly known website such as *sciencedirect.*

1.4.2) Laboratory work.

On the second phase, laboratory work will be done to produce carbon molecular Sieve (CMS) and others related test on the samples produced.

1.5 THE RELEVANCY OF THE PROJECT

The project is relevant to chemical engineer to find a solution or alternative product such as these CMS to enhance the performance of current Carbon Molecular Sieve. Since the performance of Molecular Sieve largely depends on pore size distribution, it is essential as recent industries always search for better technologies and findings that could give them more benefit in terms of boosting their productivity and selectivity.

1.6 FEASIBILITY OF THE PROJECT

The project is feasible within the time frame given (1 year) which divided into 2 sections; 1) Deep research/study of the project and 2) The production of carbon molecular sieve (CMS). For details timeline of the project, please refer to *Appendix 1: Key Milestone (applicable only for 1st section).*

CHAPTER 2

LITERATURE REVIEW

2.1 MOLECULAR SIEVES AND MICROPOROUS MATERIALS: A SERIES OF DEFINITIONS

With the discoveries of molecular sieve materials containing other elements in addition to, or in lieu of, silicon and aluminum, and the more recent discoveries of amorphous mesoporous materials (T.L. Thomas, 1986), the causal interchange of terms 'molecular-sieve' and 'zeolite' is in need of clarificatio. In 1932 McBain proposed the term 'molecular sieve' to describe a class of materials that exhibit selective sorption propoerties (D.P. Shoemaker, 1960). He proposed that for a material to be molecular sieve, it must separate components of a mixture on the basis of molecular size and shape. Two classess of molecular sieve were known when Mcbain put forward this definition: The natural zeolites and certain microporous charcoals. This list has now been expanded to include, in addition to the zeolites and carbon, microporous materials with pure silica, as well as vastly different elemental compositions. There are the silicas, metal silicates, metal aluminates, aluminophosphates and silico-and metal aluminophosphates. The continually expanding fields of molecular sieve are shown in the chart form figure below. All the materials represented in that figure are molecular sieves based on McBain's definition, as they will separate components of a mixture on the basis of size and shape. The difference lies not always within the structure of these materials, but their elemental composition. Therefore all are molecular sieves, but only aluminosilicates generally can be considered as classical zeolites.(M.Mitchell,R.Szostak,1997)

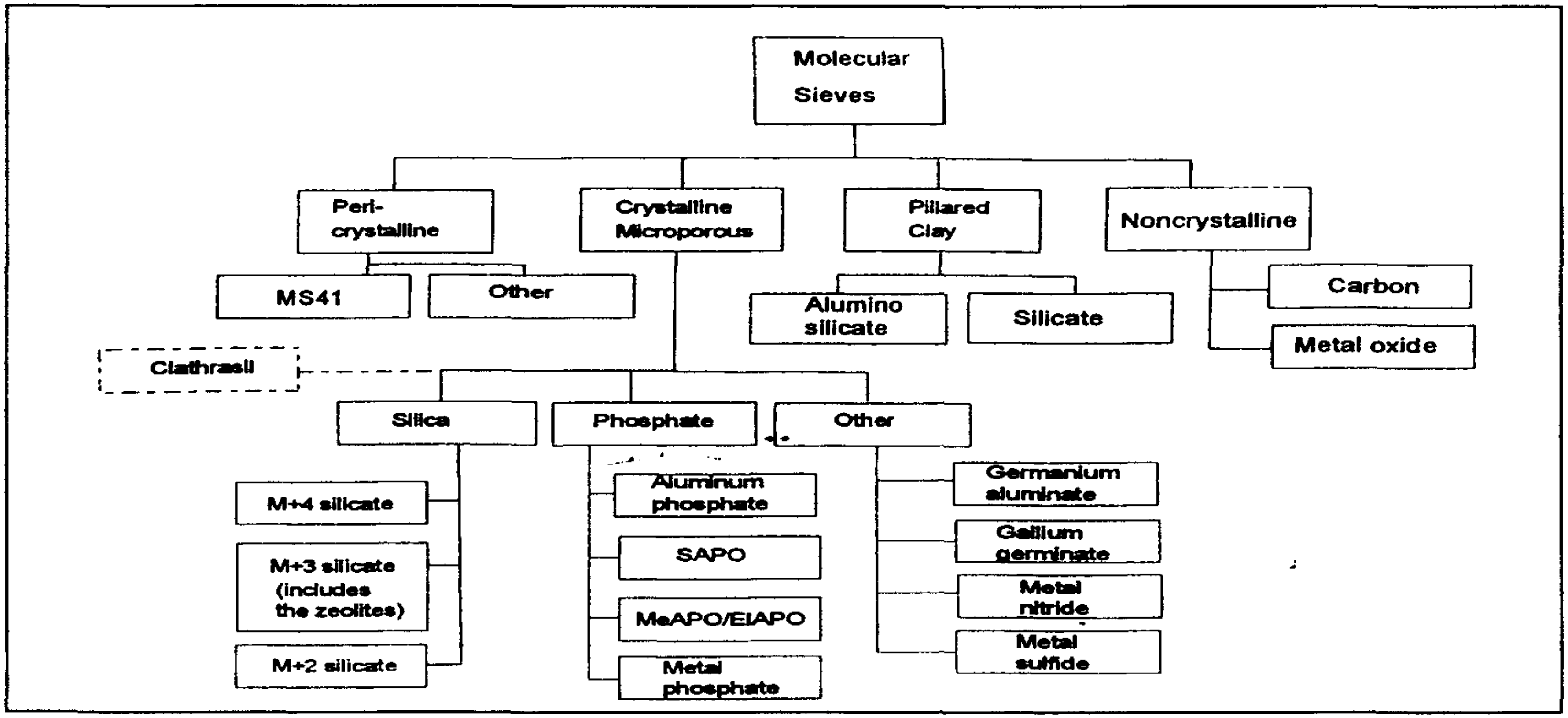


Figure 1: Classification of molecular sieves and related materials indicating the extensive variations in composition.

2.2ACTIVATED CARBON

2.2.1 Introduction

The term activated carbon in its broadest sense includes a wide range of amorphous carbon-based materials prepared to exhibit a high degree of porosity and an extended interparticulate surface area. These are obtained by combustion, partial combustion, and thermal decomposition of various carbonaceous substances. These materials may be granular or in powdered form. The granular form is characterized by a large internal surface and small pores, whereas the finely divided powdered form is associated with larger pore diameters but a smaller internal surface.

The use of activated carbon in the form of carbonized wood dates back many enturies. The Egyptians used it around 1500 B.C as an adsorbent for medicinal purposes and also as purifying agent. The ancient Hindus in India filtered their drinking water through charcoal. The basis for the industrial production of activated carbons, however, was established in 1900-1901 in order to replace bone char in the sugar refining process. This activated carbon was prepared by carbonizing a mixture of materials of vegetable origin in the presence of metal chlorides or by the action of carbon of carbon dioxide or steam on charred materials. Activated carbons with better decolorizing power were prepared by the action of zinc chloride on wood and other materials of high carbon content. The manufacturer of better quality gas-adsorbent carbons received fresh impetus during World War 1, when they were used in gas mask s for protection against poisonous gases. In the late 1930s the activated carbons were also manufactured, from sawdust by chemical activation with zinc chloride, for volatile solvent recovery and for the removal of Benzene from tower gas.

The activated carbons are excellent adsorbents and thus are used to purify, decolorize, deodorize, dechlorinate, filter, or remove or modify the salts, separate, and concentrate in order to permit recovery; they are also used as catalyst and catalyst supports. These applications of active carbons are of interest to most economic sectors and concern areas as diverse as the food, pharmaceutical, chemical, petroleum, mining, nuclear, automobile, and vacuum industries as well as the treatment of drinking water, industrial and urban waste water, and air and gas. Nearly 80% (220,000tonnes/year) of the total activated carbons is consumed for liquid phase applications where both the granuled and powdered form of active carbon is used. The used of powdered carbon is more ancient and generally involves processing of food and drinking water. The total consumption of activated carbons in gas phase applications is around 60,000 tonnes/year, which includes exclusively the granular form of the activated carbon, which may be extruded or pounded, the principal uses being in the purification of air, recovery of gold, and cigarette filters. The consumption of activated carbons is high in the US and Japan, which together consumes two to four times more active carbon than the Western European countries. The per capita consumption of active carbon per year is 0.5kg in Japan, 0.4kg in US, 0.2kg in Europe, and 0.03kg in the rest of the world

The adsorbent properties of activated carbons are essentially attributed to their large surface area, a high degree of surface area, a high degree of surface reactivity, universal adsorption effect, and favourable pore size, which makes the internal surface accessible, enhances the adsorption rate, and enhances mechanical strength. The most widely used commercial activated carbons have a specific surface area of the order of 800-1500 m^2/g. This surface area is contained predominantly within micropores, which have effective diameter smaller than 2nm. In fact, a particle of activated carbon is made up of a comples network of pores which have been classified into micropores (diameter<2nm), mesopores (diameter between 2 and 50nm), and macropores (diameters>50nm). The macropores do not contribute much toward surface area but act as conduits for the passage of the adsorbate into the interior mesopore and the micropore surface where most of the adsorption takes place. The pore size distribution in a given caron depends on the type of the raw material and the method of manufacture of the carbon as shown in figure below.

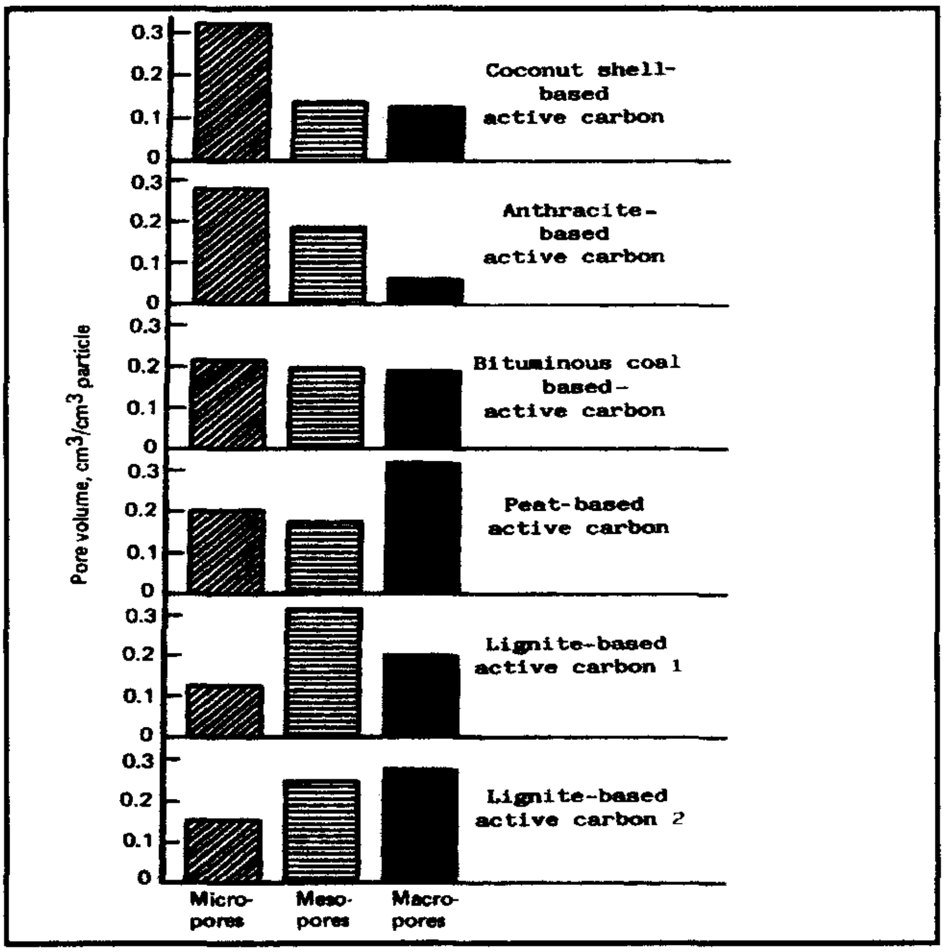


Figure 2: Pore size distribution in some activated carbons obtained by using different precursors.

The large surface area of the activated carbon is the rsult of the activation process in which a carbonaceous char with little internal surface is oxidized in an atmosphere of air, carbon dioxide, or steam at a temperature between 800^0C and 900^0C. This causes the oxidation of some of the regions within the char in preference to others so that as combustion proceeds a preferential etching occurs, resulting in the development of a large internal surface area, which in some cases may be as high as 2500m^2/g.

The structure of activated carbons has been repeatedly compared with that graphite and considered to be microcrystalline. However in recent year's transmission electron microscopy of carbonaceous materials has shown that the analogy with graphic is very poor and that the activated carbon structure can be visualized as stacks of flat aromatic sheets crosslinked in a random manner.

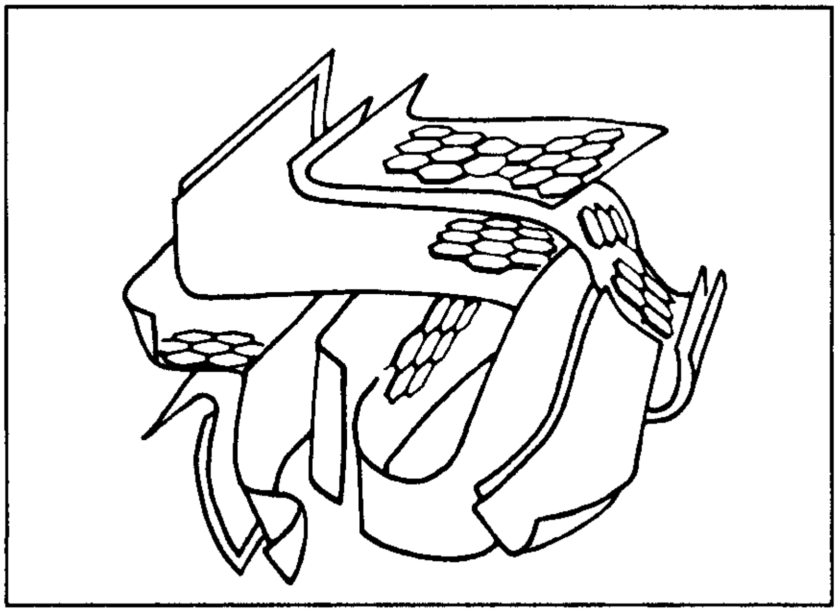


Figure 3: Schematic representation of the microstructure of activated carbons

Activation by carbon dioxide or steam at 800^0C-900^0C reduces the number of these aromatic sheets in the original stacks, leaving in some cases single and in general nonplanar layers.Electron spin resonance studies have revealed that the aromatic sheets in activated carbons contain free radical structures or structures with unpaired electrons. These unpaired electrons are resonance stabilized and are trapped during the carbonization process as a result of the breaking up of bonds at the edges of the aromatic sheets creating edge carbon atoms. These edge carbon atoms have unsatisfied valencies and can thus interact with the heteroatoms such as oxygen, hydrogen, nitrogen, and sulfur, giving rise to the different types of surface functional groups. The oxygen contents in the activated carbon can, however, vary between 1% and 25% depending on the type of raw material and the conditions of the activation process. The oxygen content of an activated carbon decreases with an increase in temperature of activation. At low temperature of activation the carbon-oxygen surface complexes formed are less stable and are removed as carbon dioxide on heat treatment in vacuum or in nitrogen. On the other hand, when the temperature of activation is high, the functional groups formed are more stable and could be removed only as carbon monoxide.

2.3 MANUFACTURE OF ACTIVATED CARBONS

2.3.1 Manufacture

The manufacture of activated carbons involves two main steps: the carbonization of the carbonaceous raw material at temperatures below 800^0C in the absence of oxygen and the activation of the carbonized product. Thus all carbonaceous materials can be converted into activated carbon, although the properties of the final product will be different, depending on the nature of the raw material used. The nature of activating agent, and the conditions of the activation process. During the carbonization, most of the noncarbon elements such as oxygen and hydrogen are eliminated as volatile gaseous products by the pyrolytic decomposition of the starting material. The residual carbon atoms group themselves into sheets of condensed aromatic ring systems with a certain degree of planar structure. The mutual arrangement of these aromatic sheets is irregular and therefore leaves free interstices between them which may become filled with the tarry matter or the products of decomposition or at least blocked partially by the disorganised carbon. These interstices give rise to pores, which make activated carbons as excellent adsorbents.

Simple carbonization does not give rise to products that have high adsorption capacity because of their less developed pore structure and low surface area. This pore structure is enhanced during activation process, which converts the carbonized raw material into a form that contains the greatest possible number of randomly distributed pores of various shapes and sizes giving rise to an extended and extremely high surface area of the product. (Roop Chand Bansal, 1998)

2.3.2 Raw Material

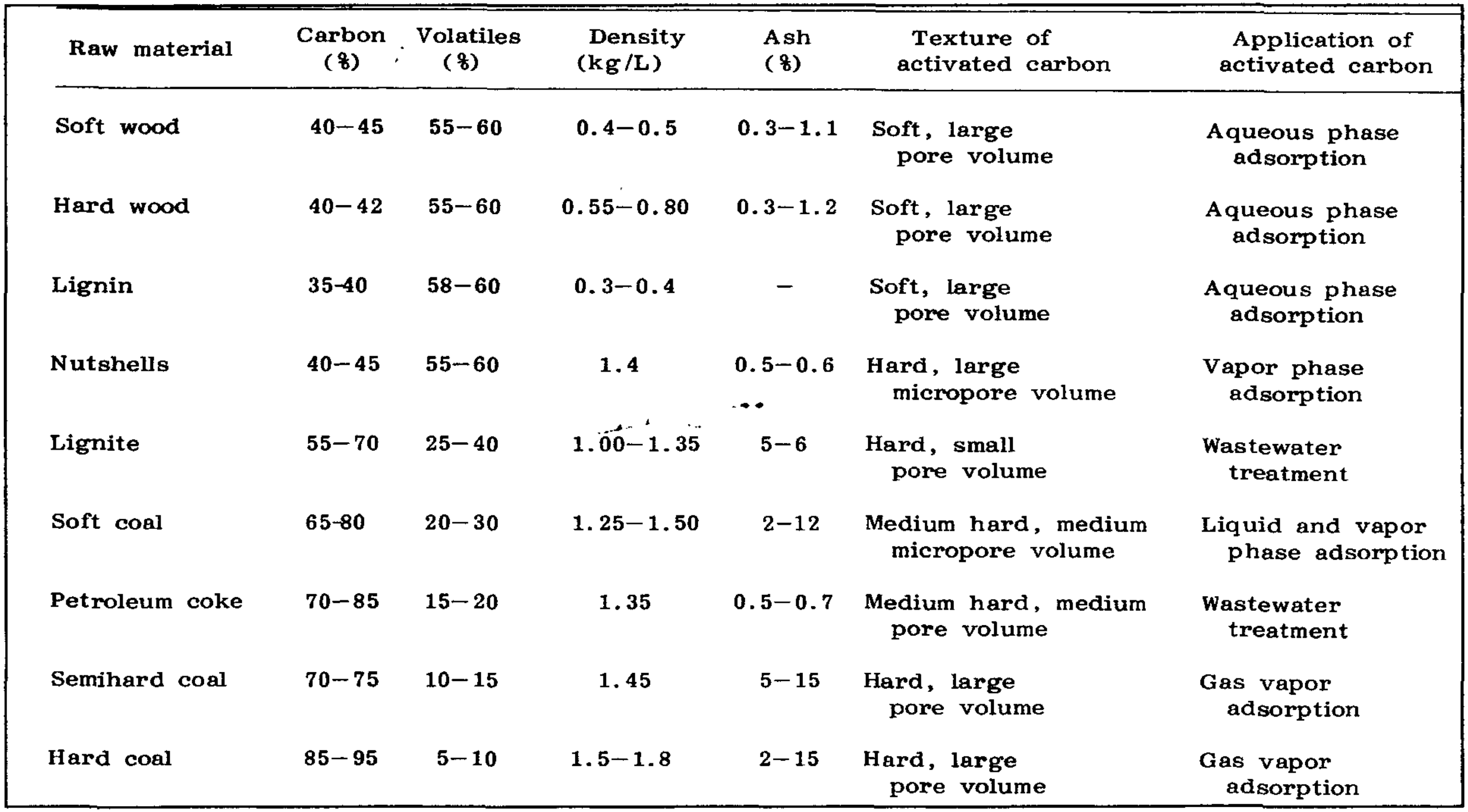
Any cheap material with high carbon content, low in inorganics can be used as raw material for the production of activated carbon. In early production procedures, preference was given to younger fossil materials such as wood, peat, and wastes of vegetable origin, which include fruit stones, nutshells, and sawdust. The chars obtained from them could be activated easily and produced reasonably high-quality activated carbons. The current trend, however, is to ward an increasing use of various kind of natural coal, hich are cheap and readily available. The following criteria are considered when choosing a carbonaceous raw material:

i) Potential for obtaining high-quality activated carbon.
ii) Presence of minimum inorganic
iii) Volume and cost of the raw material
iv) Storage life of the raw material
v) Wokability of the raw material

High density and sufficient volatile content of the raw material are of considerable importance. High density contributes to enhanced structural strength of the carbon so that it can withstand excessive particle crumbling during uuse. Low density material like wood and lignin, which also contain high volatile content, produce activated carbon with large pore volume but with low density. These carbons therefore are generally used for some liquid phase applications and are not very suitable for vapor adsorption applications. Coconut shell, fruit pits, and other nut shells which have higher densities than wood and have high volatile contents produce hard, granular carbons with large micropore volumes and are suitable for vapor as well as solution phase applications.

2.3.3 Carbonization

Carbonizzation involves thermal decomposition of the carbonaceous material, eliminating noncarbon species and producing fixed carbon mass and rudimentary pore structure. The process is usually carried out in rotary kilns or multiple heart furnaces at temperatures below 800^0C in a continous stream of an inert gas. The char produced in this manner is sometimes further calcinated at 1000^0C in the absence of any gas. The important parameters that determine the quality and the yield of the carbonized product are the rate of heating, the final temperature, and the nature and physical state of the raw material.



Raw material	Carbon (%)	Volatiles (%)	Density (kg/L)	Ash (%)	Texture of activated carbon	Application of activated carbon
Soft wood	40–45	55–60	0.4–0.5	0.3–1.1	Soft, large pore volume	Aqueous phase adsorption
Hard wood	40–42	55–60	0.55–0.80	0.3–1.2	Soft, large pore volume	Aqueous phase adsorption
Lignin	35–40	58–60	0.3–0.4	–	Soft, large pore volume	Aqueous phase adsorption
Nutshells	40–45	55–60	1.4	0.5–0.6	Hard, large micropore volume	Vapor phase adsorption
Lignite	55–70	25–40	1.00–1.35	5–6	Hard, small pore volume	Wastewater treatment
Soft coal	65–80	20–30	1.25–1.50	2–12	Medium hard, medium micropore volume	Liquid and vapor phase adsorption
Petroleum coke	70–85	15–20	1.35	0.5–0.7	Medium hard, medium pore volume	Wastewater treatment
Semihard coal	70–75	10–15	1.45	5–15	Hard, large pore volume	Gas vapor adsorption
Hard coal	85–95	5–10	1.5–1.8	2–15	Hard, large pore volume	Gas vapor adsorption

Figure4: Properties of Some Raw Used in the Manufacture of Activated Carbon

The carbonization involves two important stages that markedly determine the properties of the final product. The first stage is the softening-period, during which the temperature control has an important bearing on the type of char obtained. After the softening period the char begins to harden and shrink. The shrinkage of the char also plays a role in the development of porosity in the char. (Juhola, et. 1977)

2.3.4 Activation

The objective of activation process is to enhance the volume and to enlarge the diameters of the pores which were created during the crbonization process and to create some new porosity. The structure of the pores and their pore size distribution are largely predetermined by the nature of the raw material ane the history of its carbonization. Activation removes disorganised carbon, exposing the aromatic sheets to the action of activation agents in the first latter phases of the reaction the significant effect is the widening of the existing pores or the formation of the large-sized pores by complete burnout of the walls between the adjacent pores. This result in an increase in the transitional pores and the macroporosity, whereas the volume of the micropores decrease. Thus the extent of burnoff of the carbon material is a measure of the degree of activation.

According to Dubinin and Zaverina (1949), a microporous activated carbon is produced when the degree of burnoff is less than 50% and a macroporous activated carbon when the extent of burnoff is greater than 75%. When the degree of burnoff is between 50% and 75%, the product has a mixed porous structure and contains all types of pores.

Figure 4: Physical and adsorptive Properties of Wood-Base Activated before and after Compression and Extrusion.

Raw material	Bulk density (kg/L)	Total pore volume (cm^3/g)	CCl_4 adsorption capacity (%)
Wood	0.27	1.13	36.5
Compressed wood	0.47	0.81	81
Extruded wood	0.48	0.77	88
Coconut shell	0.48	0.75	72

Source: Juhola, 1977

2.3.5 Classification of Activated Carbons; Powdered form

Acyivated carbons are complex products which are difficult to classify on the basis of their behaviour, surface characteristics, and properties. For example, the BET surface area is in no manner a representative of the quality of the activated carbon because it does not indicate the surface accessibiltiy to larger molecules, which may be quite different. The only parameter that can give an idea of the quality of the carbon is its adsorption capacity and that only in case of particular application. Activated carbons are therefore classified on the basis of their particle size and particle shapes into powdered, granulated, spherical, or pelleted activated carbons.

Since this experiment objective to achieve activated carbons in the form of powdered activated carbons, we will focus on powdered activated carbons.

2.3.5.1 Powdered Activated Carbons

Powdered activated carbons have a fine granulometry less than 100μm with average diameter between 15 and 25μm. Thus they present a large external surface area and small diffusion distance. The rate of adsorption is very high and the problems related to the mass transfer are very low. (Johnson, 1977)

2.4 Application of Activated Carbon/ Carbon Molecular Sieve in Air Separation

One of the applications of Activated Carbons/CMS is for air separation. One of the current experiment conduscted to analyse this application was successfully conducted by R.F.P.M Moreira, H.J Jose, and A.E. Rodrigues. The separation of air for nitrogen can be carried out by pressure-swing adsorption over a carbon molecular sieve. The separation is kinetically controlled, since the equlibrium of both oxygen and nitrogen is very similar, but the adsorption kinetics for oxygen is faster than nitrogen. (R.F.P.M Moreira, H.J Jose, and A.E. Rodrigues 2000)

2.4.1PRESSURE SWING ADSORPTION (PSA)

2.4.1.1 Concept of swing adsorption

A swing adsorptionand desorption method is used for separation of one or more target components from mixed gases. A cycle of adsorption and desorption is practised by fluctuating parameters relating to adsorption. The parameters which dominate adsorption performance are temperature, total pressure, partial pressure of composing gases and adsorption velocity.
(www.jechem.co.jp)

2.4.1.2 PSA using Equilibrium Separation

Each adsorbate has its equilibrium adsorption for a certain adsorbent. Equilibrium separation PSA is a gas separation principle that makes use of this characteristic. The Hydrogen recovery technology using equilibrium separation CMS is well known as a typical example of this type of separation. As seen in adsorption isotherm of CMS in figure 5 below, equilibrium adsorption of Hydrogen is much smaller than that of methane and carbon dioxide. It can be considered that CMS does not absorb Hydrogen. Therefore, when raw gas mixtures rich in Hydrogen gas are passed through unit filled with CMS, concentrated hydrogen is obtained as a product gas.
(www.jechem.co.jp)

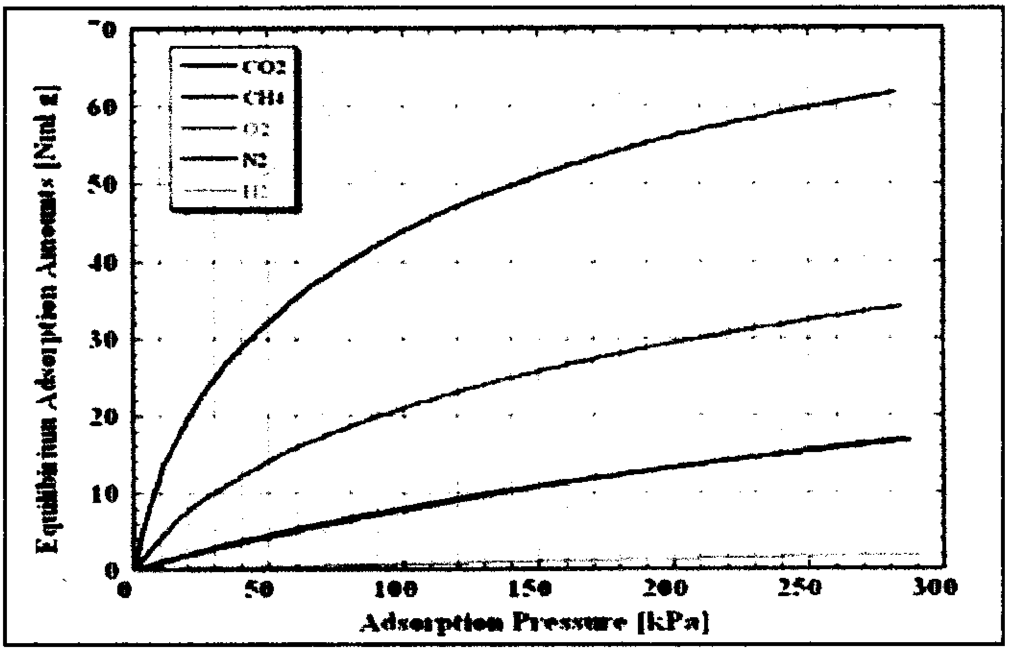


Figure 5: Adsorption Isotherm of Shirasagi CMS

Source: Japan EnviroChemical

2.4.1.3 PSA using Velocity Separation

An adsorbent with a certain pore diameter has unique adsorption velocity for each gas. Velocity separation PSA is a gas separation principle that makes use of this characteristic. It is most general that this type of PSA uses CMS as an adsorbent. The most famous example should be the PSA nitrogen generators. One of the most famous technologies in nitrogen generation by air separation is cryogenic separation, produces nitrogen gas by utilizing the difference of boiling points between nitrogen and oxygen. On the other hand, velocity separation PSA make use of the slight difference in their molecular size shown in figure 6. This mechanism can be achieved by fabricating CMS precisely so as to reflect the difference in adsorption velocity. In case of the separation between nitrogen and oxygen, from the adsorption velocity curves in figure 7, while oxygen reasces equilbrium in about five minutes after starting adsorption, the amount of nitrogen adsorbed reaches below 10% of equilibrium adsorption for the same period of time. Until then, only nitrogen gas comes out from the top of the vessel. (www.jechem.co.jp)

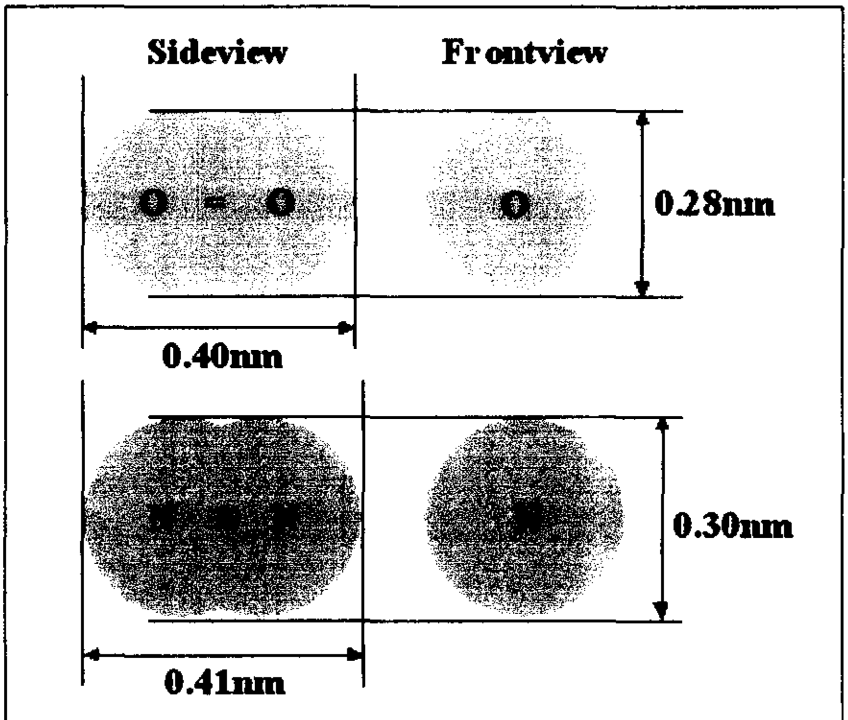


Fig.-4 Molecular Model of Oxygen and Nitrogen

Figure 6: Molecular Model of Axygen and Nitrogen

Source: Japan EnviroChemical

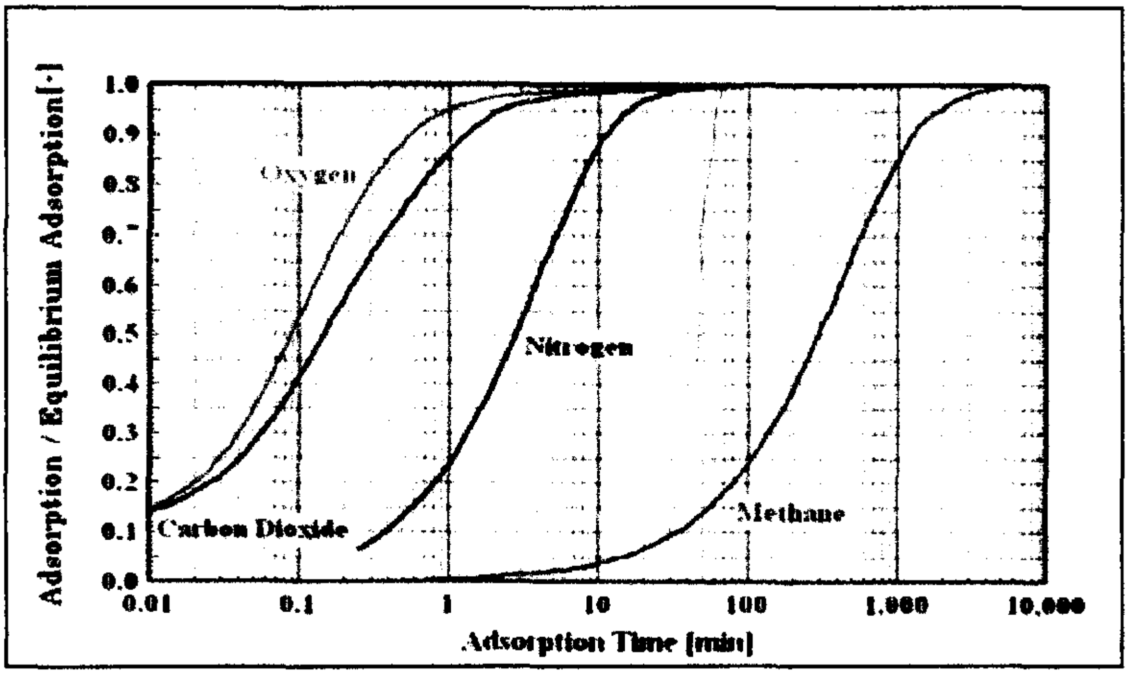


Figure 7: Adsorption Velocity Curves for Shirasagi CMS

Source: Japan EnviroChemical

CHAPTER 3

METHODOLOGY

3.1 FLOW OF WORK

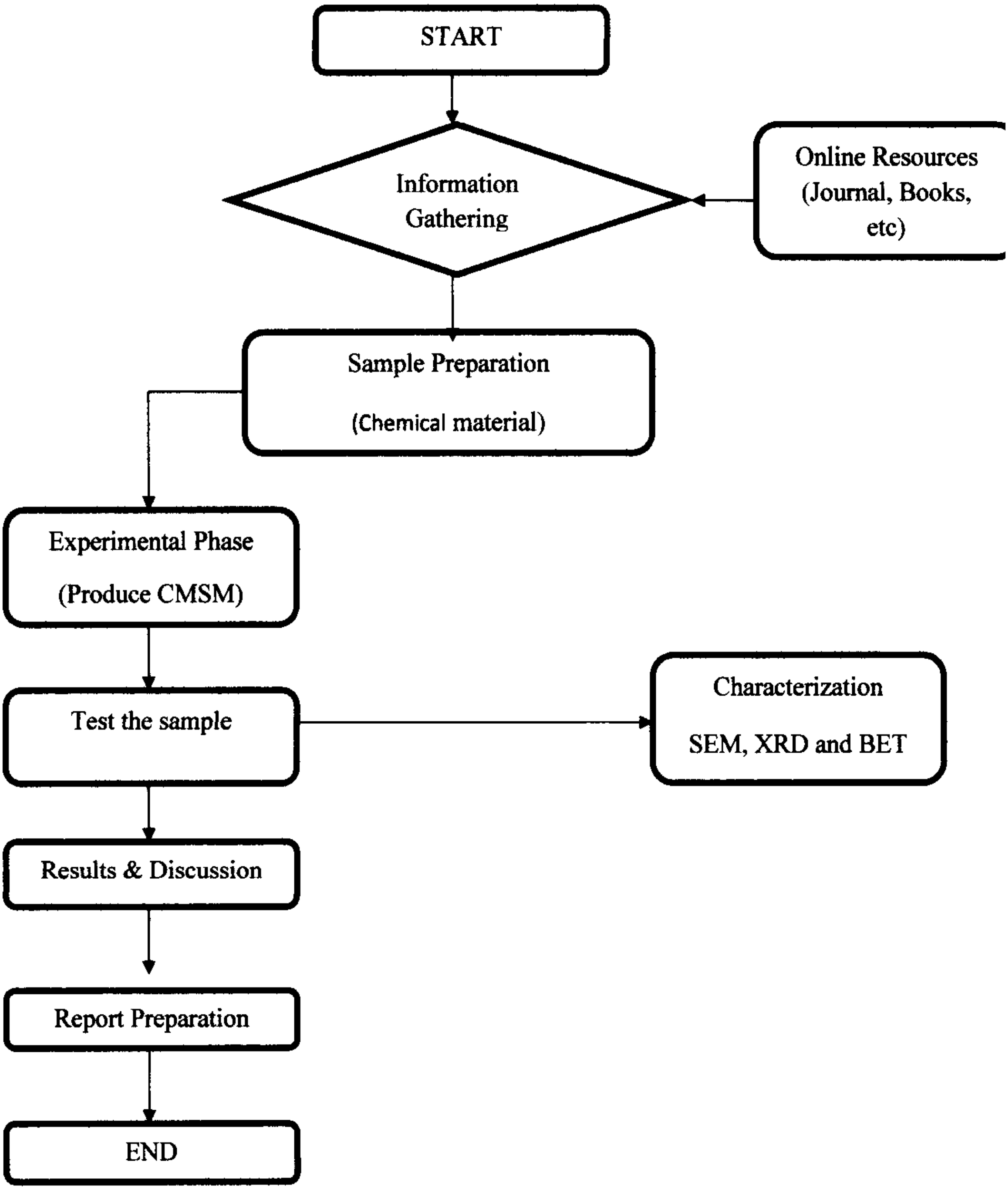


Figure 8: Flow of Work

3.2 SUMMARY OF PROJECT ACTIVITIES

3.2.1 Sample preparation (chemical materials)

Chemical preparation has been done last semester. The related chemicals are, Phosphoric Acid 5%, activated carbon (powder), and Formaldehyde.

3.2.2 Experimental Phase

Experimental Phase has been done on this semester to produce the product; CMS. A few samples of Carbon Molecular Sieves have been produced in the lab and now in a process of data analysing.

3.2.3 Characterization

The characterization of the samples will be using BET (Brauner-Emmet-Teller) Machine to estimate the surface area and porosity. Structure Analysis of Carbon Molecular Sieve are conducted using Scanning Electron Microscopy (SEM) while the diameter of pore size are characterised using X-ray Diffraction Machine (XRD).

3.2.4 Step by step procedure (current progress experiment)

1) 8g of powder activated carbon were prepared in a beaker

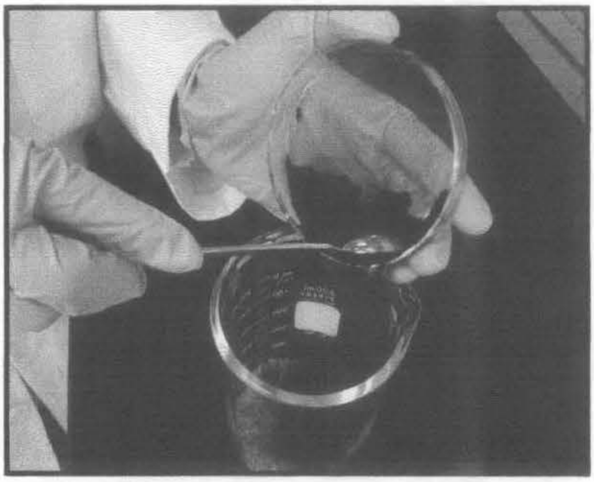


Figure 9: Weighing the activated carbon

2) 50 ml of Formaldehyde were mixed in the beaker containing activated carbon.

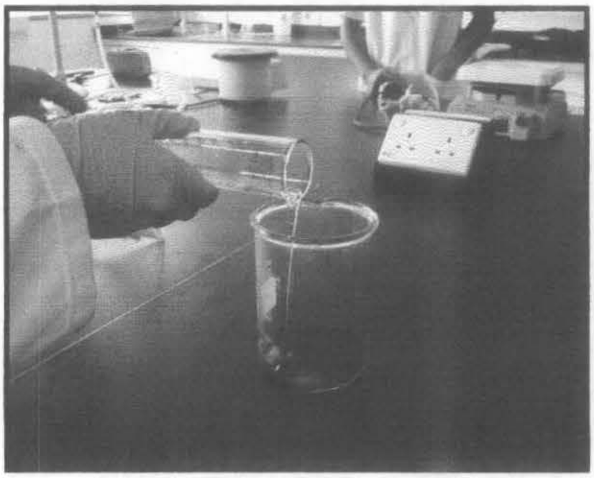


Figure 10: Mixed 50ml of Formaldehyde with avtivated carbon

3) The mixture then was heated up by using reflux heating until 80^0C

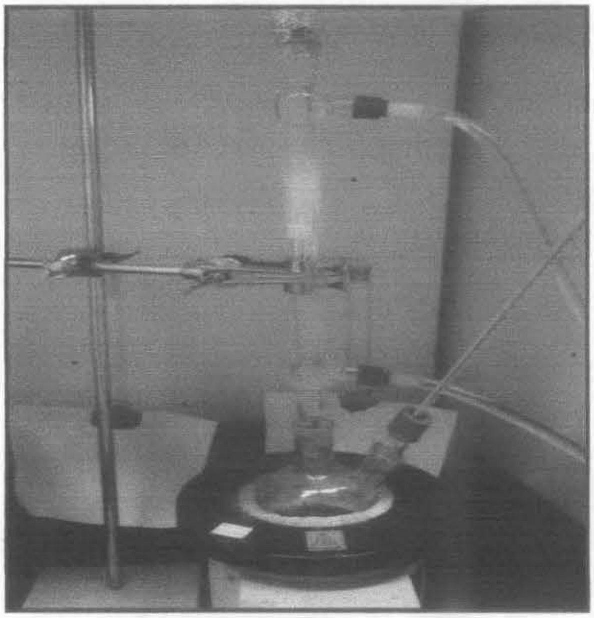


Figure 11: Heating sample

4) At 80^oC, 10 ml of H_3PO_4 were added to the mixture before temperature was increased to 100^0C.

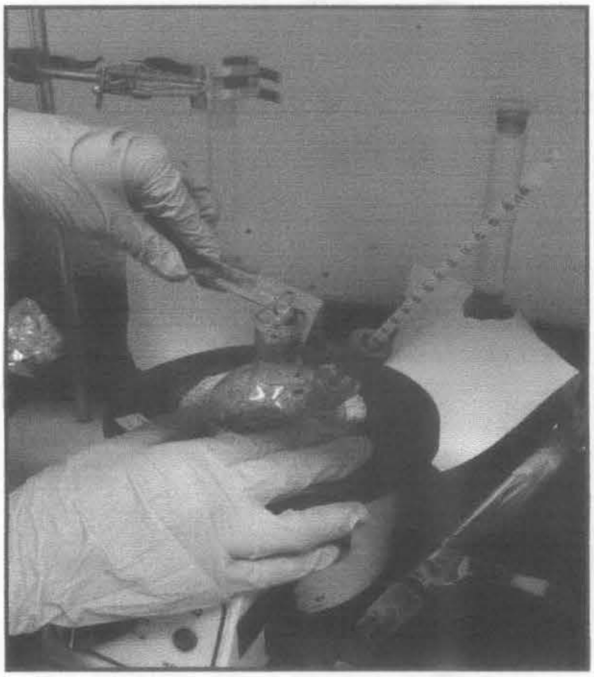


Figure 12: Adding 10ml of H_3P0_4

5) Following that the hot mixture then was filtered. The solid will be dried at 100^{0}C in the oven for 2 hours.

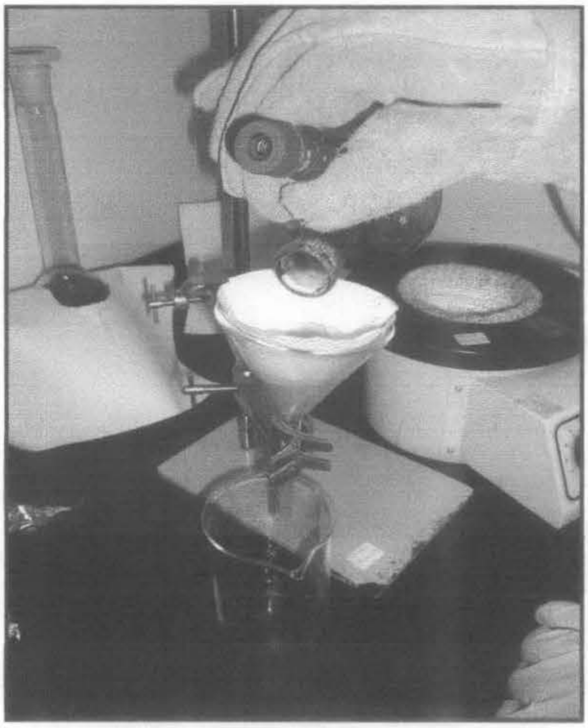


Figure 13: Filtering the sample

6) Samples are then carbonized under nitrogen flow for 1.5 hours at 800^{0}C in FBAU unit. Samples are ready for characterization.

3.3 TOOLS AND EQUIPMENT REQUIRED

1) Oven

   Oven are used in the production of speciment phase to dry the solid speciment at 100^0C

2) FBAU

   FBAU machine is used for carbonization process. For this experiment, the carbonization temperature is at 600^0C.

3) SEM

   SEM stands for Scanning Electron Microscopy machine. This machine produce structural image of the samples surface.

4) XRD

   X-Ray Diffraction Unit can measure the diameter size of the Carbon Molecular Sieve

5) BET

   Brunauer, Emmett and Teller (BET) method is the most widely used to estimate the surface area.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 RESULTS

4.1.1 Scanning Electron Macroscopy (SEM)

Scanning Electron Macroscopy (SEM) is able to produce a graphical image of the speciment surface at certain magnitude. From this image we can clearly see the pore size distribution. A standard optical microscope with 40x and 100x magnificient is sufficient to provide some visual information about the produts. A drop of the solution which contains the carbon molecular sieve powdered is palced on a glass slide. The presence of a crystalline phase is readily detected with a quick scan under the microscope.

Magnification in a SEM can be controlled over a range of up to 6 orders of magnitude from about 10 to 500,000 times. Unlike optical and transmission electron microscopes, image magnification in the SEM is not a function of the power of the objective lens. SEMs may have condenser and objective lenses, but their function is to focus the beam to a spot, and not to image the specimen

Scanning Electron Microscopy (SEM) can provide valuable information concerning the morphology of the crytalline phases obtained. A change in pore size are not obvious from X-ray powder diffraction pattern. SEM will provide the information concerning the pore structure and shape affected by the changing reaction conditions.

Figure below are the result from the SEM analysis.

SAMPLE #1

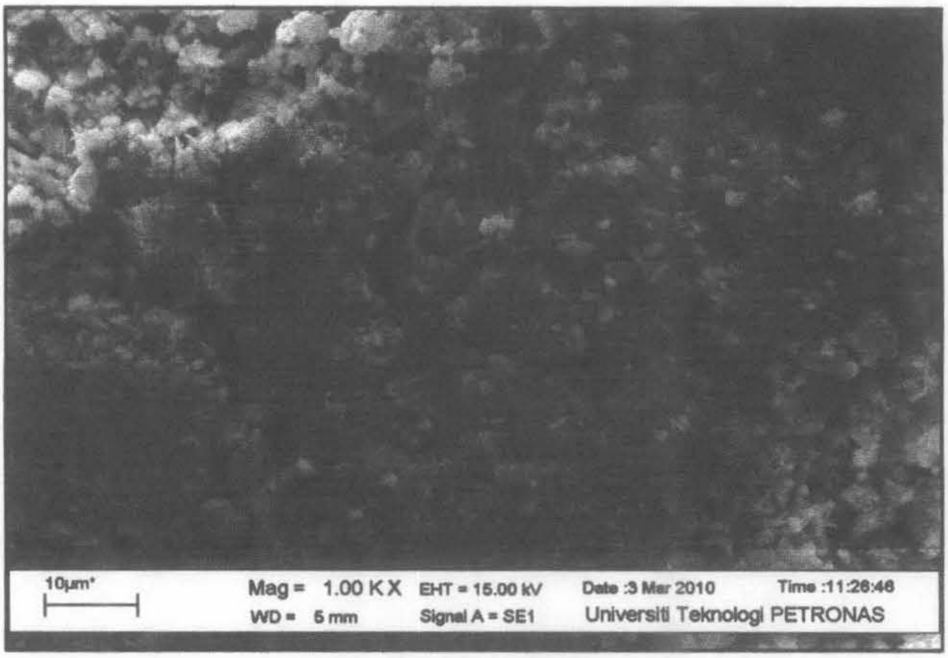


Figure 14: Scanning at magnitude 1.00 KX

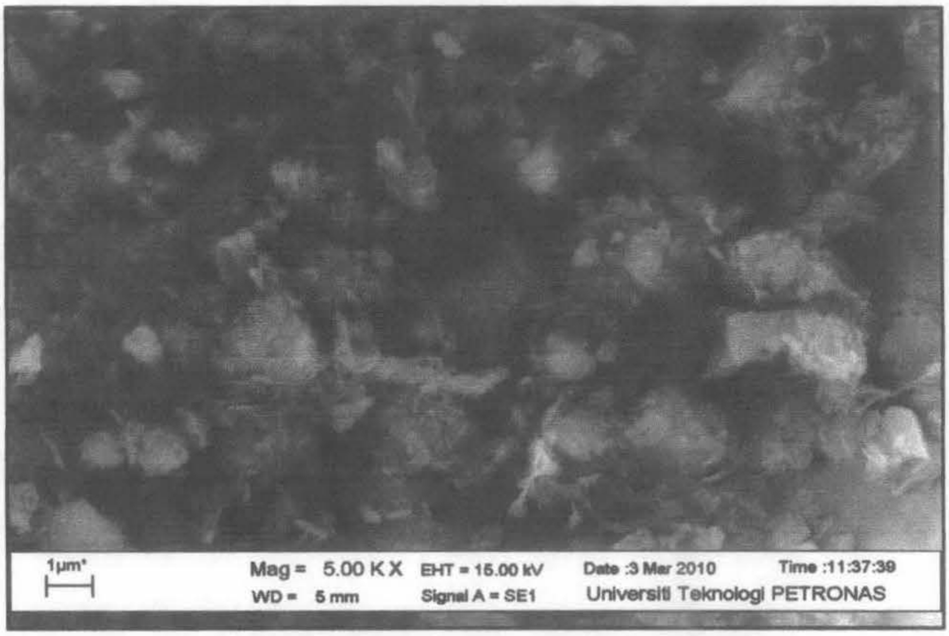


Figure 15: Scanning at magnitude 5.00 KX

SAMPLE #2

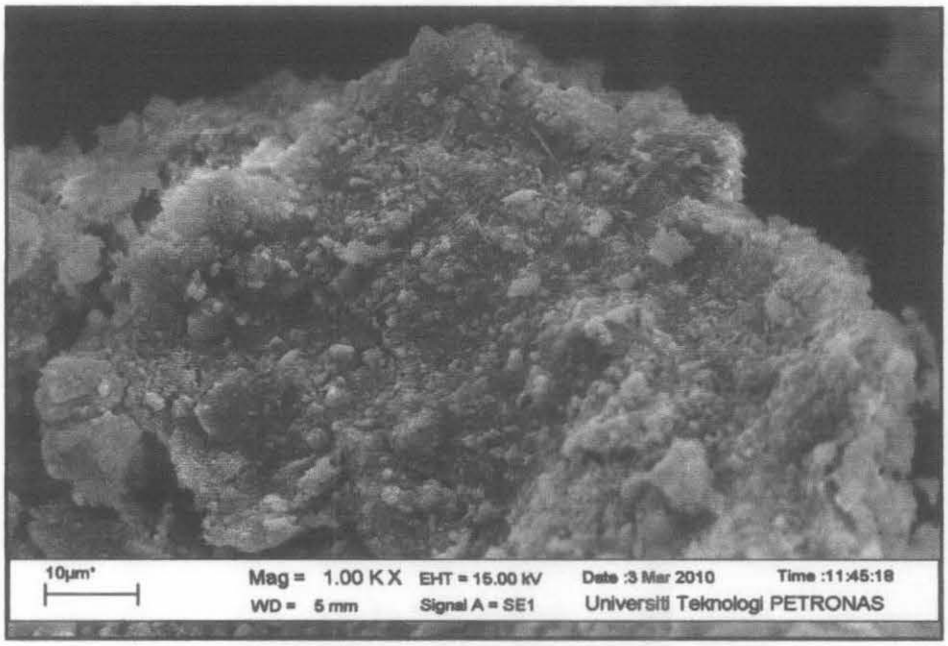


Figure 16: Scanning at magnitude 1.00 KX

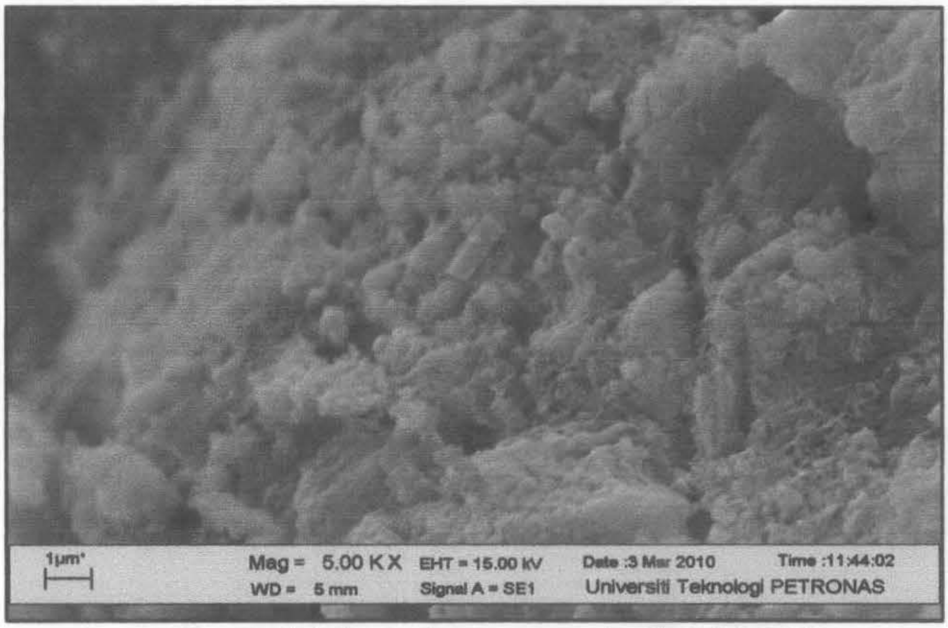
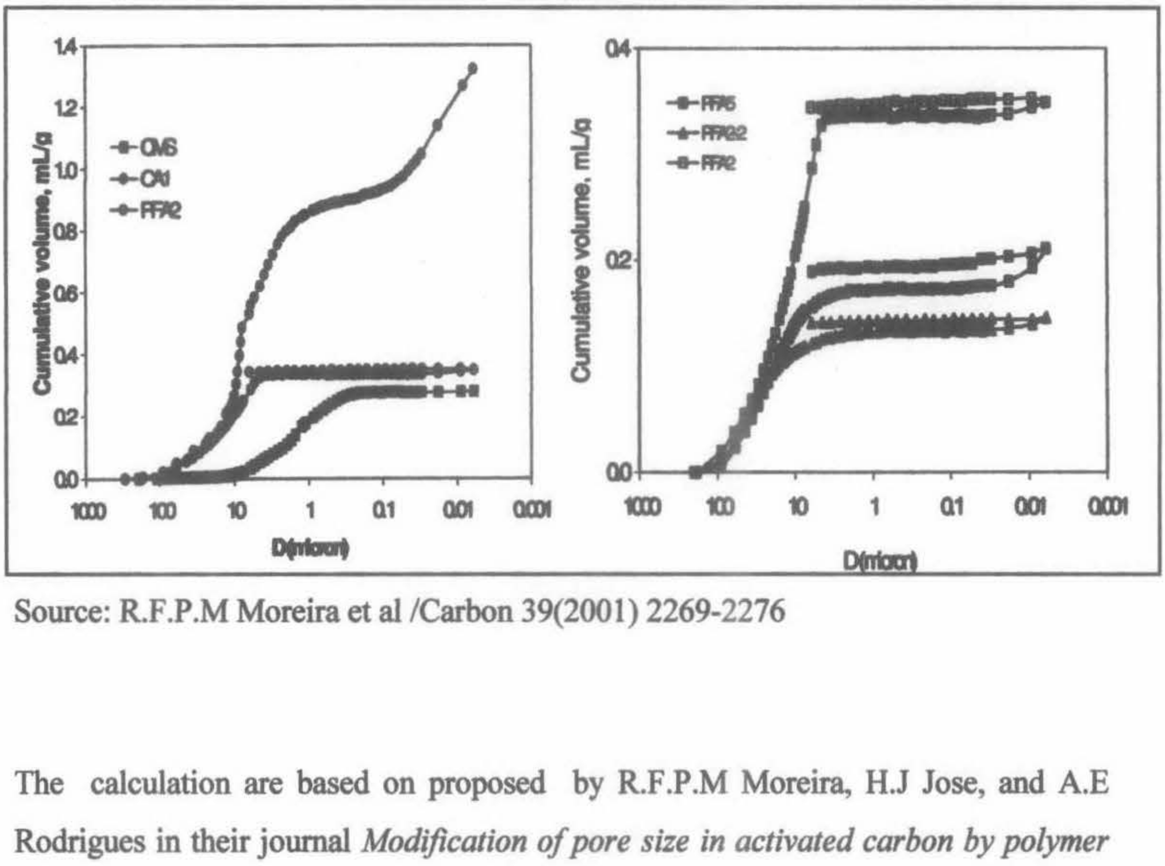


Figure 17: Scanning at magnitude 5.00 KX

4.1.2 BET (Brannauer-Emmet-Teller)

This BET method is the most widely used technique to estimate the surface area and to determine the larger pores such as macropores of the activated carbons. The size distributions and densities from the literature review can be seen in the figure 18 below:

Figure 18: Cumulative pore size distribution for CA1, PFA2, PFA2-2, and PFA5



Source: R.F.P.M Moreira et al /Carbon 39(2001) 2269-2276

The calculation are based on proposed by R.F.P.M Moreira, H.J Jose, and A.E Rodrigues in their journal *Modification of pore size in activated carbon by polymer deposition and its effect on molecular selectivity.*

According to their journal:

4.1.2.1 Equilibrium isotherm

Nitrogen adsorption on CMS materials is difficult to measure, due to the high resistance to nitrogen duffusion or adsorption. Adsorption in micropores does not take place by successive build-up of molecular layers, as supposed by BET theory. The microporous properties were calculated from Dubinin-Astakhov (DA) formalism and the DA equation was applied to obtaine the micropore volume (W_O) and the characteristic energy (E_O). The DA formalism was applied in the range of relative pressure S of $0<P/Po<0.2$

$$W=W_O \exp [-(\varepsilon/Eo)^2] \text{ ---------------- -- } (1)$$

Which;

W = volume adsorbed at relative pressure P/Po

ε = RT ln (Po/P) = adsorption potential

Where;

R= gas constant

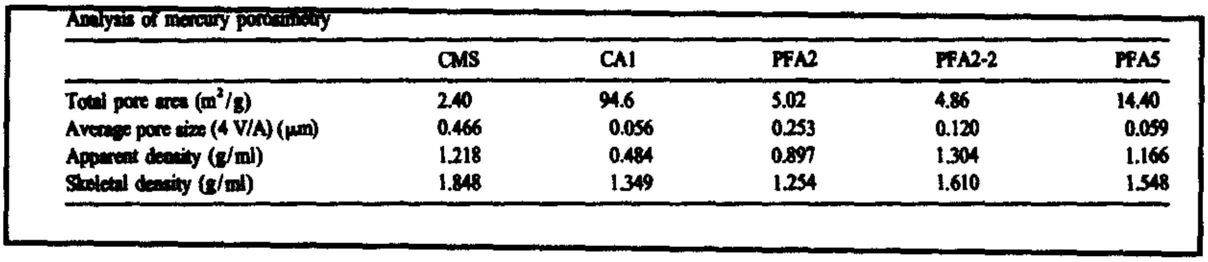
T= absolute temperature

To estimate the micropore size, McEnaney has proposed that Eo and Lm, the micropore width, can be related by followed equation where Lm is in the nanometers

$$Lm=4.691 \exp (-0.0666Eo) \text{ ------------------ } (2)$$

Table form below shows the analysis of porosimetry.

Figure 19: Analysis of porosimetry



Analysis of mercury porosimetry

	CMS	CA1	PFA2	PFA2-2	PFA5
Total pore area (m^2/g)	2.40	94.6	5.02	4.86	14.40
Average pore size (4 V/A) (μm)	0.466	0.056	0.253	0.120	0.059
Apparent density (g/ml)	1.218	0.484	0.897	1.304	1.166
Skeletal density (g/ml)	1.848	1.349	1.254	1.610	1.548

Source: R.F.P.M Moreira et al /Carbon 39(2001) 2269-2276

4.1.3 XRD (XRAY-DIFFRACTION)

It is one of the primary techniques used by mineralogists and solid state chemists to examine the physico-chemical make-up of unknown solids. This 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/I_0), and mineral name.

The XRD technique takes 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.

Figure below are the result from the XRD analysis:

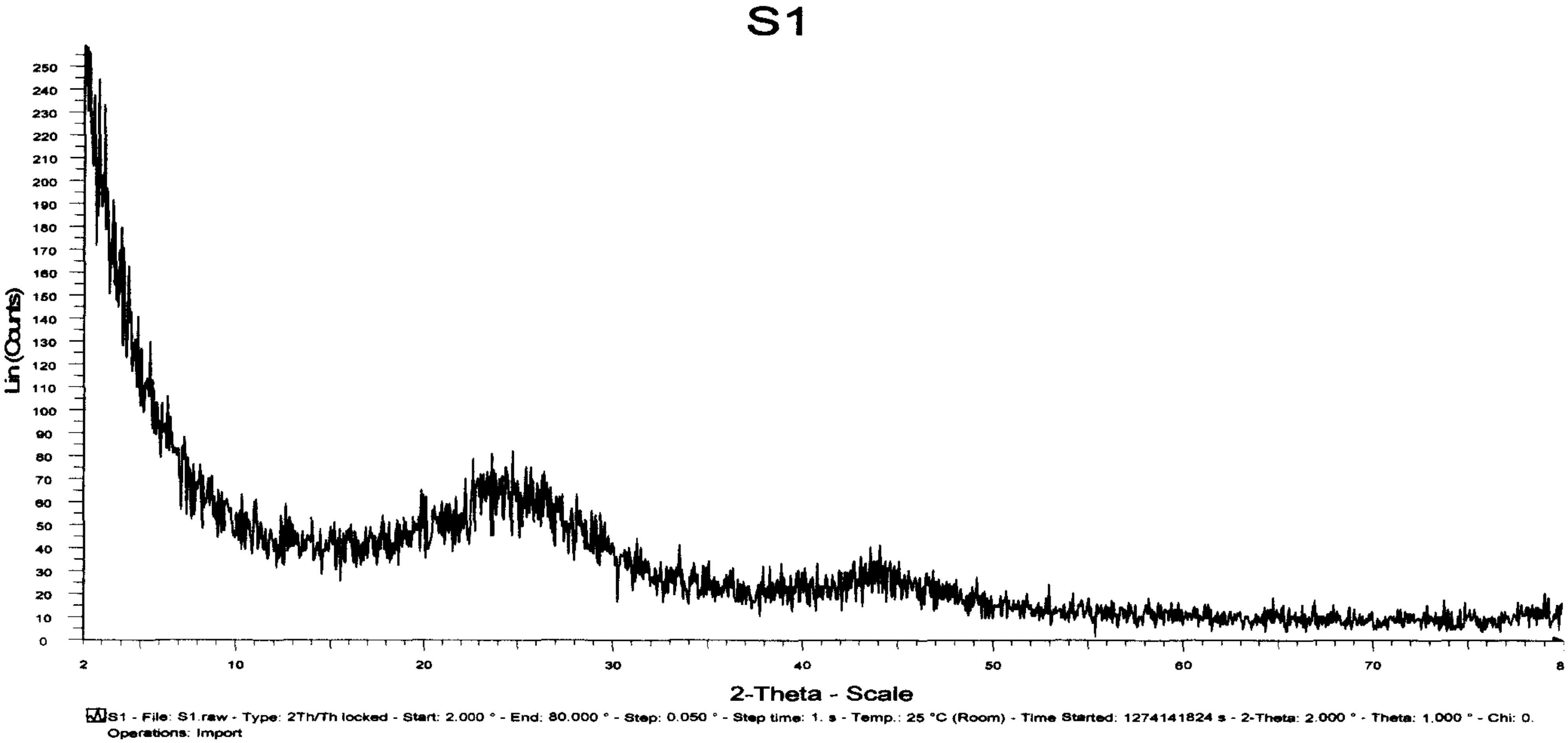


Figure 20: XRD for sample 1 (powder activated carbon)

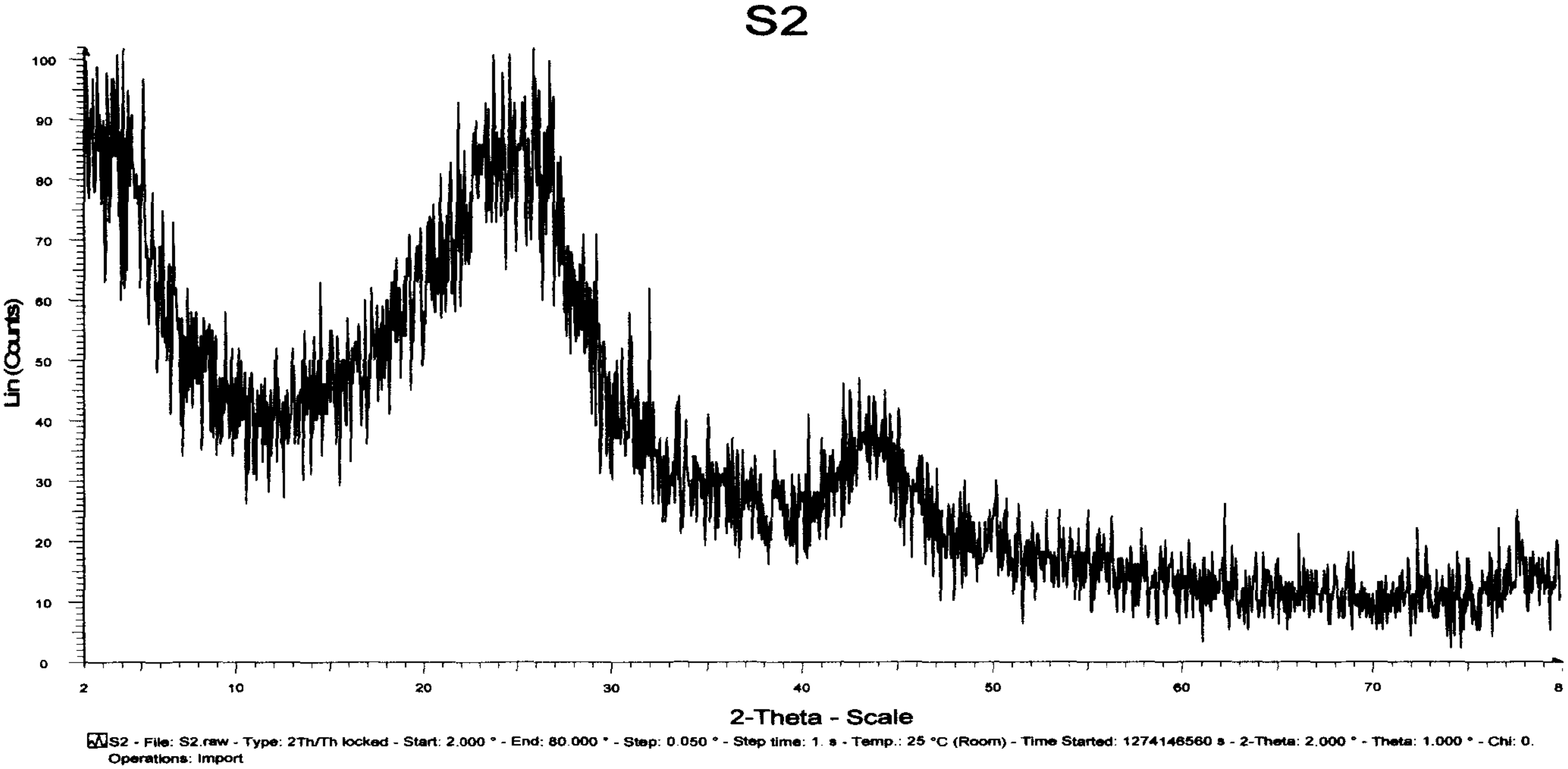


Figure 21: XRD for sample 2 (with chemical before carbonization)

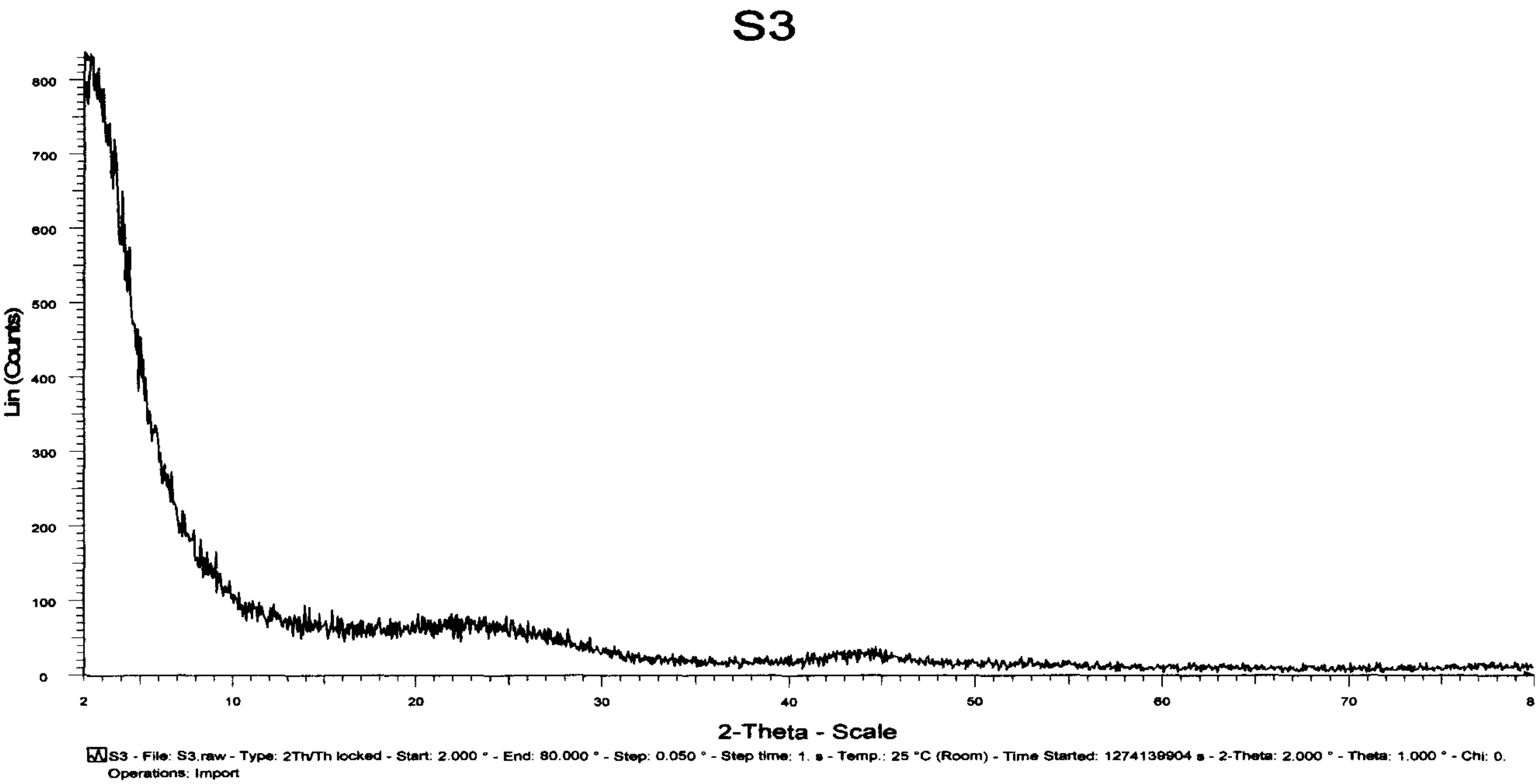


Figure 22: XRD for sample 3 (with chemical after carbonization)

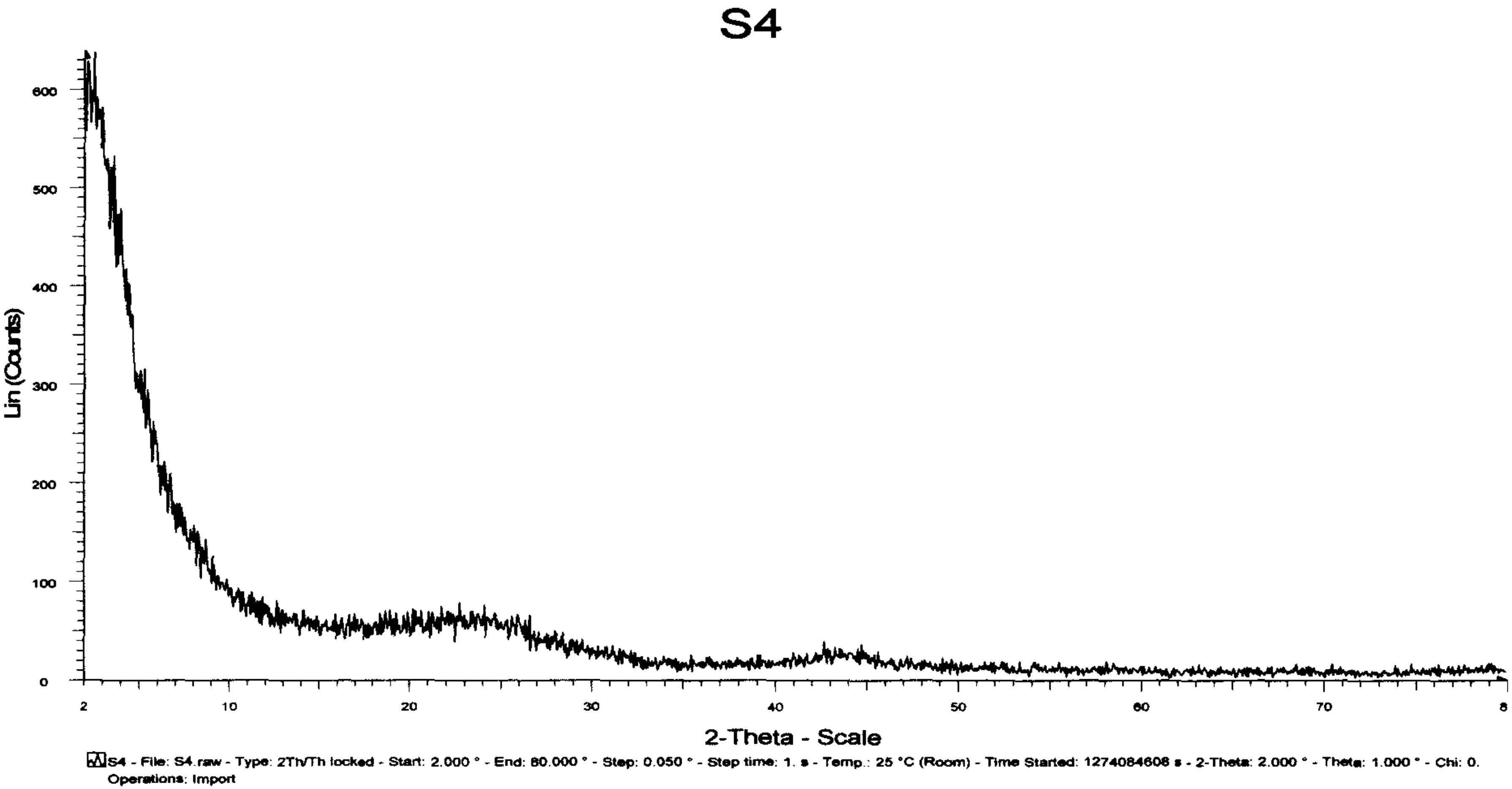


Figure 23: XRD for sample 4 (with chemical after carbonization)

4.2 DISCUSSION

Based on the result from the SEM analysis, at magnitude =1.00KX shows the surface image of the Carbon Molecular Sieve (CMS). Sample #1 and sample #2 at magnitude =1.00KX clearly shows the image of the surface of the carbon molecular sieve produced. The macropores of the products can be analysed from the image.

Based from the image, the pore size are well distributed and yet it can be seen that most of the pores are not relatively equal in size.The earlier justification from literature review have early indicates that the pore size distribution are depends on how the CMS itself manufactured.

Most of the possibility that affects the arrangements of the pores occurs during carbonization of the product. The temperature is not regulated well on 800^0C affect the pore size distribution.

At magnitude = 5.00 KX, shows more details on the surface of both samples. The result also showed the undistributed pore size of CMS.

This project is not complete yet as there are a few analysis using XRD and BET machine is on the queue.

CONCLUSION

The research/ analysis are done based on industrial application needs nowadays. In order to produce a high quality gas separation membrane (CMS), the selection of the starting material is important as the pore structure dependent on it. Overall the current result is not fully according to the expected result. Since the pore size distribution are depends on how it produced, a little changes should be made, in this case the variation of temperature during carbonization. Current carbonization temperature is at 800^0C.On next experiment, the temperature will be varying from 700^0C to 900^0C.

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APPENDICES

APPENDIX 1: KEY MILESTONE FYP 2

Activity	1	2	3	4	5	6	7		8	9	10	11	12	13	14
Project Work Continue	▨	▨	▨					Mid Semester Break							
Submission of Progress Report 1				■											
Project Work Continue				▨	▨	▨	▨								
Submission of Progress Report 2									■						
Seminar (compulsory)										▨	▨	▨			
Project Work Continue									▨	▨	▨	▨			
Poster Exhibition											■				
Submission of Dissertation Report (Soft Bound)													■		
Oral Presentation and Hard Bound														■	■

APPENDIX 2:KEY MILESTONE FYP 1

Activity	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Selection of topic	■	■								Mid Semester Break						
Preliminary Research Work		■	■	■												
Submission of Preliminary report							■									
Project Work							■	■	■							
Submission of Progress report									■							
Seminar									■							
Project Work continues											■	■	■	■	■	■
Submission of Interim Report														■		
Oral Presentation															■	