# PREPARATION AND CHARACTERIZATION OF CARBON MOLECULAR SIEVE PRODUCED FROM PALM SHELL

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To my beloved mother and father

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# ABSTRACT

Various types of microporous carbon gas adsorbents have been prepared from Malaysia carbonaceous solid waste, the palm shell as the precursor for further modification into carbon molecular sieve (CMS). It is an advantage to utilize the palm shell as starting material by converting into useful CMS since it can be obtained easily and abundantly in the country. The precursors were prepared in laboratory fluidized and fixed bed reactors by one-step physical treatments, which included carbonization in $N_2$ flow and directly followed by $CO_2$ activation. The effects of carbonization parameters, such as carbonization temperature, hold time and $N_2$ flow rate on the porosity development have been studied. The characterizations of precursors were carried out by constant volumetric physisorption analyzer to determine various characteristic parameters from the analysis of adsorption isotherm. Here, $N_2$ and $CO_2$ have been used as the adsorptive gas for analysis at 77 and 273 K, respectively. Although the entire precursor appeared to be highly microporous, only some precursors produced were considered suitable to be used as precursor of CMS for $O_2/N_2$ separation based on the literature survey finding. Then the precursors were modified into CMS using chemical vapor deposition (CVD) technique. The CVD technique involved deposition of pyrolytic carbon on the precursor by cracking of hydrocarbon gas substance. CVD parameters such as type of hydrocarbon gas substance, deposition temperature, deposition hold time and % v/v of hydrocarbon gas substance were manipulated to have pyrolytic carbon deposited on the pore mouth for improving separation selectivity with some trade-off in $O_2$ adsorption capacity. The characterizations of CMS were carried out by constant volumetric physisorption analyzer to determine the adsorption kinetic of $O_2$ and $N_2$ for determining the selectivity and $O_2$ adsorption capacity from isotherm at 298 K. The deposition mechanisms were proposed from the result obtained. By directly applied CVD to deposit carbon on precursor for modifying the pore mouth produced CMS which is not up to expected performance compared to commercial carbon molecular sieve (CCMS). It was due to the existence of a small portion of pore with bigger pore size. These pores could not be effectively lowered because further deposition of the pyrolytic carbon will close the smaller pore resulting in abrupt reduction in $O_2$ adsorption capacity. The conventional CVD involving pore blocking by pyrolytic carbon followed by control gasification in $CO_2$ atmosphere were used. In this experiment, the best samples from directly applied CVD and conventional CVD have selectivity of 8.00 and 5.00 respectively compared to the selectivity of 2.09 for the precursor.

# ABSTRAK

Pelbagai jenis karbon penjerap gas berliang-mikro telah dihasilkan daripada sisa pepejal berkarbon di Malaysia, iaitu tempurung kelapa sawit sebagai prekursor untuk pengubahsuaian seterusnya kepada pelbagai penapis molekul karbon (CMS). Ini merupakan satu kelebihan untuk menggunakan tempurung kelapa sawit sebagai bahan asas dan mengubahnya kepada CMS berguna kerana tempurung kelapa sawit dapat diperoleh dengan mudah dan banyak di negara kita. Prekursor telah dihasilkan dengan menggunakan reaktor-reaktor di makmal dengan rawatan fizikal satu-langkah dimana prosesnya termasuklah karbonisasi dalam aliran $N_2$ dan seterusnya diikuti dengan pengaktifan dengan $CO_2$. Parameter-parameter karbonisasi yang mempengaruhi pembentukan keliangan seperti suhu, masa penetapan dan kadar aliran $N_2$ telah dikaji dan dikenalpasti. Analisis penentuan sifat-sifat prekursor telah dijalankan dengan menggunakan peralatan penjerapan gas secara isipadu tetap untuk mendapatkan ciri-ciri struktur liang daripada isoterma penjerapan. $N_2$ dan $CO_2$ telah digunakan sebagai gas penjerap untuk analisis tersebut pada 77 K dan 273 K masing-masing. Walaupun semua prekursor yang terhasil menunjukkan struktur berliang mikro, hanya segelintir daripadanya didapati sesuai sebagai prekursor khas untuk CMS pemisahan $O_2/N_2$ berdasarkan kajian literature. Kemudian, prekursor diubahsuai kepada CMS menggunakan teknik pemendapan wap kimia (CVD). Teknik CVD melibatkan pemendapan karbon pirolitik ke atas prekursor melalui pemecahan molekul gas hidrokarbon. Parameter-parameter CVD seperti jenis gas hidrokarbon, suhu, masa penetapan dan %v/v gas hidrokarbon semasa pemendapan telah dikaji untuk memastikan karbon pirolitik termendap pada mulut liang agar dapat meningkatkan kepilihan dengan sedikit penurunan pada kapasiti penjerapan $O_2$. Analisis penentuan sifat-sifat CMS telah dijalankan dengan peralatan penjerapan gas secara isipadu tetap juga untuk menentukan kinetik penjerapan $O_2$ dan $N_2$ dan isoterma, khas untuk mendapatkan nilai kepilihan dan kapasiti penjerapan $O_2$ masing-masing. Mekanisme pemendapan juga dicadangkan berdasarkan data-data tersebut. Aplikasi CVD secara langsung untuk memendapkan karbon pada prekursor dengan tujuan untuk mengubahsuai mulut liang tidak berjaya mendapatkan CMS setanding dengan penapis molekul karbon komersial (CCMS). Ini kerana wujudnya sebahagian kecil liang dengan saiz yang lebih besar. Liang-liang tersebut tidak dapat dikecilkan kerana pemendapan karbon pirolitik yang selanjutnya akan menutup liang-liang yang kecil mengakibatkan penurunan mendadak pada kapasiti penjerapan $O_2$. Kemudian, CVD konvensional yang melibatkan penutupan semua liang dengan karbon pirolitik diikuti dengan pengaktifan dalam $CO_2$ secara terkawal telah dijalankan. Daripada eksperimen ini, sampel terbaik daripada CVD secara langsung dan CVD konvensional menunjukkan nilai kepilihan 8.00 dan 5.00 masing-masing berbanding nilai kepilihan 2.09 pada prekursor.

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$a$ - Radius of homogeneous sphere
$A$ - Adsorption potential
$A_a$ - Constant in Lennard-Jones potential for adsorbent
$A_A$ - Constant in Lennard-Jones potential for adsorbate
$A_t$ - Reactor cross sectional area
AC - Activated carbon
ASAP - Accelerated Surface Area and Porosimetry
ASU - Air separation unit
$b$ - Affinity constant
BET - Brunauer, Emmett and Teller
BJH - Barrett, Joyner and Halenda
CA - Chemical activation
CAU - Circulating Adsorption Unit
CCD - Chemisorbed carbon deposition
$CCl_4$ - Chloroform
$C_{d,or}$ - Orifice coefficient
$CH_2Cl$ - Dichloromethane
CMS - Carbon molecular sieve / molecular sieve carbon
$CMSN_2$ - CMS produced by Bergbau-Forschung for air separation.
$CO_2$ - Carbon dioxide gas
CVD - Chemical vapor deposition
$d$ - Diameter for the adsorbate molecule
$d_p$ - Particle size of raw palm shell
$d_t$ - Fluidized bed internal diameter
$d_{or}$ - Diameter of orifice of the tuyere
$D$ - Diffusivity constant
DA - Dubinin Astakhov

| | | |
|---|---|---|
| DD | - | Direct deposition |
| DFT | - | Density Functional Theory |
| DR | - | Dubinin Radushkevich |
| $E_o$ | - | Characteristic Energy – adsorption strength between adsorbate & adsorbent |
| FTIR | - | Fourier Transformed Infrared Spectroscopy |
| GC | - | Gas Chromatography |
| GCMS | - | Gas Chromatography Mass Spectroscopy |
| H-K | - | Horvath-Kawazoe |
| HTT | - | Heat treatment temperature |
| ID | - | Internal Diameter |
| ITM | - | Ion transport membrane |
| IUPAC | - | International Union of Pure and Applied Chemistry |
| K | - | Avogrado's number |
| $l$ | - | Distance between nuclei of two layers (slit width) |
| L | - | Nucleus to nucleus slit width |
| $L_{mf}$ | - | Minimum fluidization height. |
| $m_{shell}$ | - | Mass feed of raw palm shell |
| $M_{W,N2}$ | - | Molecular weight of $N_2$ |
| MSCs | - | Molecular sieve carbon |
| $M_t$ | - | Gas uptake at time, t |
| $M_\infty$ | - | Gas uptake at equilibrium |
| n | - | Surface heterogeneity in DA equation |
| $N_a$ | - | Number of atoms per unit area of adsorbent |
| $N_A$ | - | Number of molecules per unit area of adsorbate |
| $N_2$ | - | Nitrogen gas |
| $NH_3$ | - | Ammonia gas |
| $NO_2$ | - | Nitrogen dioxide gas |
| $N_{or}$ | - | The number of orifice of the tuyere |
| $O_2$ | - | Oxygen gas |
| P | - | Pressure |
| $P_o$ | - | Saturation pressure of the gas |
| PSA | - | Pressure swing adsorption |
| PT | - | Physical treatment |

$Re_t$ - Vessel Reynolds number

$R_g$ - Gas constant

$S_{BET}$ - BET surface area

SEM - Scanning electron microscope

$S_E$ - External surface area by t-plot

$S_M$ - Micropore surface area by t-plot

sTPD - Production in Ton per day

T - Temperature

TEM - Transmission electron microscope

TSA - Temperature swing adsorption

$u_o$ - Velocity of gas in reactor tube

$U_o$ - Adsorbent-adsorbate interaction

$U_{or}$ - Maximum allowable jet velocity from holes

$U_a$ - Implicit function of the adsorbate-adsorbent interaction

V - Quantity of gas adsorbed at pressure P

$V_{DA}$ - Micropore volume by DA equation

$V_{DR}$ - Micropore volume by DR equation

$V_m$ - Quantity of gas adsorbed when entire surface is covered with a monomolecule layer

$V_T$ - Total pore volume

W - Volume of adsorbate in the microporous

$W_o$ - Maximum volume that the adsorbate can occupy

z - Distance of the adsorbate molecule from a surface atom in the slit wall

Greek symbol

$\beta$ - Coefficient of similarity (ratio of the liquid molar volume to that of the reference benzene vapor)

$\alpha$ - Degree of transformation

$\varepsilon$ - Potential energy of interaction

$\varepsilon_{mf}$ - void between particle during minimum fluidization

$\varepsilon^*$ - Minimum potential energy

$\sigma$ - Distance from a surface atom at zero interaction energy

$\rho_s$ - Density of raw palm shell

$\rho_{g,N2}$ - Density of nitrogen gas at 800°C, 1 atm

$\mu$ - nitrogen gas viscosity at 800°C, 1 atm

$\Delta P_b$ - Pressure drop across the bed

$\Delta P_d$ - Distributor pressure drop

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# CHAPTER 1

# INTRODUCTION

## 1.1 Typical Characteristics of Adsorbents

Adsorption process can be defined as when porous and discontinuity surface of a solid is exposed to a gas, the gas molecules will form bonds with it and become attached (Yang,1987). In another words, adsorption is a separation process in which certain components of a gaseous or liquid phase are selectively transferred to the surface of a solid adsorbent. There are four principles type of adsorption (Slejko, 1985):

(a) Exchange (ion exchange) – The electrostatic attachment of ionic species to site of opposite charge at the surface of the adsorbent, with subsequent displacement of these species by other ionic adsorbate of greater electrostatic affinity.

(b) Physical – The action of Van der Waals forces, which are comprised of both London dispersion forces and classical electrostatic affinity.

(c) Chemical – The reaction between an adsorbate and an adsorbent resulting in a change in the chemicals form of the adsorbate.

(d) Specific – The attachment of adsorbate molecules at functional groups on adsorbent surfaces can also result from specific interactions, which do not result in adsorbate transformation.

The physical adsorption is based on three distinct separation mechanisms (Do. 1998):

(a) Steric - The porous solid has pores with dimension such that it allows small molecules to enter while excluding large molecules from entry. Steric separation occurred unique with zeolite due to the uniform aperture size in the crystalline structure (Safarudin, 2000).

(b) Equilibrium - Solid has different abilities to accommodate different species that is the solid preferentially removes the stronger adsorbing species.

(c) Kinetic – Different species have different rates of diffusion into the pores. Thus by controlling the time of exposure, the comparable faster diffusing species is preferentially removed by the solid. Kinetic separation is possible only with carbon molecular sieve (CMS) because of the distribution of pore sizes and has found only one commercial application: the production of nitrogen from air (Yang, 1987).

The success or failure of the process depends on how the solid performs in both equilibria and kinetics. A solid with good capacity but slow kinetic will take adsorbate molecules too long time to reach the particle interior. This means long gas residence times in a column, hence a long throughput. On the other hand, a solid with fast kinetics but low capacity will require large amount of solid for a throughput. To satisfy these two requirements, the following aspects must be satisfied (Do, 1998).

(a) The solid must have reasonably high surface area or micropore volume.

(b) The solid must have relatively large pore network for the transport of molecules to the interior.

The classification of pore size as recommended by International Unit of Pure and Applied Chemistry (IUPAC) (Sing, 1985) is often used to delineate the range of pore size (d is the pore diameter).

| | |
|---|---|
| Micropores | $d < 2$nm |
| Mesopores | $2 < d < 50$ nm |
| Macropores | $d > 50$ nm |

This classification is arbitrary and was developed based on the adsorption of nitrogen gas at its normal boiling point (77K).

Micropores can be further subdivided into ultramicroporosity and supermicroporosity (Marsh, 1987).

| | |
|---|---|
| Ultramicroporosity | $d < 0.5$ nm |
| Supermicroporosity | $1.4 < d < 3.2$ nm |

As ultramicroporosity has pore diameter equal or less than the diameter of the adsorbate molecule and activated diffusion effects and/or molecular sieve effects are the indication of the presence of ultramicroporosity. While for supermicroporosity, adsorption occurs by cooperative effects. The definitions and mechanisms of the above three effects will be discussed later in Chapter 3.

### 1.1.1 Molecular Sieve Carbon or Carbon Molecular Sieve

Since it is less hydrophilic than zeolite, carbon molecular sieve (CMS) can be used more efficaciously in separation processes involving wet gas stream. At present CMS is produced commercially by Bergbau-Forschung GmbH in West Germany and by Takeda Chemical Company and Kuraray Chemical Company in Japan. The raw material for Bergbau-Forchung's MSC is bituminous coal, 40 microns. Commercial CMS for air separation is produced by cracking hydrocarbon such as methane in order to deposit a thin layer of coke at the pore mouth. CMSN2 produced by Bergbau-Forchung GmbH was used in PSA for the production of dry and $CO_2$ free $N_2$ at 99.9% purity without the need to predry the air feed (Yang, 1987). Today, most commercial carbon sieves are prepared from anthracite or hard coal by controlled oxidation and subsequent thermal treatment. Subsequent treatments including controlled cracking of hydrocarbon within the micropore system and partial gasification under carefully regulated condition (Manzoor Zahur, 1991). Such a treatment is known as Chemical Vapor Deposition (CVD) and will be discussed in detail in Chapter 4. Table 1.1 shows the typical usage of different adsorbent in industrial processes nowadays.

**Table 1.1**: Typical process using adsorption technology (Do,1998)

| **Separation** | **Adsorbent** |
|---|---|
| Normal paraffin, iso-paraffin | Zeolite 5-A |
| Nitrogen / oxygen gas | Zeolite 5-A |
| Oxygen / nitrogen gas | Carbon molecular sieve |
| Ethylene / vent stream | Activated carbon |
| VOCs removal from air | Activated carbon |
| Carbon dioxide, ethylene from natural gas | Zeolite |
| Sulfur compound from natural gas | Zeolite |
| Drying of reactive gases | Zeolite 3-A, Silica gel, Alumina |
| Solvent removal from air | Activated carbon |
| Ordors from air | Activated carbon |
| NOx, SOx, from flue gas | Zeolite, Activated carbon |

### 1.2 Gas Adsorption Processes.

Large-scale adsorption processes can be divided into two broad classes. The first and the most important is the cyclic batch system, in which the adsorption bed is alternately saturated and then regenerated in a cyclic manner. The second is a continuous flow system, which involves a continuous flow of adsorbent countercurrent to a flow of feed (Geankoplis, 1993). For system where the separation factor is high and mass transfer resistance is small, cyclic processes are generally employed because of advantages of simplicity and cost. Continuous countercurrent operation is generally used only where selectivity are low and mass transfer resistance is high as it is only under these conditions that the additional capital cost of a countercurrent system can be justified (Manzoor Zahur, 1991).

There are four basic methods in common use for the cyclic batch adsorption system using fixed beds such as temperature-swing adsorption (TSA), pressure-swing adsorption (PSA), inert-purge gas stripping cycle and displacement-purge cycle. In general, these four basic methods operate with two or sometimes three fixed beds in parallel, one in adsorption cycle and the other two in a desorbing cycle to provide continuity of flow. After a bed has completed the adsorption cycle, the flow is switched to second newly regenerated bed for adsorption. These methods differ from each other mainly in the means used to regenerate the adsorbent after the adsorption cycle (Geankoplis, 1993).

For PSA cyclic batch adsorption the bed is desorbed by reducing pressure at essentially constant temperature and purging the adsorbate. This process for gases uses very short cycle time for regeneration compared to that for the temperature-swing cycle. However, the major limitation is that PSA cycles are restricted to components that are not too strongly adsorbed. For equilibrium system, usually high vacuum is not desirable for desorption process, but if the preferentially adsorbed species is too strongly adsorbed, an uneconomically high vacuum is required for an effective desorption. Thus, for this case, TSA is a generally preferred option due to modest change of temperature produces, in general, a significant change in the gas-solid adsorption equilibrium constant (Ruthven et al., 1994).

## 1.3 Air Separation Technologies.

Cryogenic separation that is liquefaction followed by distillation-remains the most frequently used process for large-scale application. Adsorption by PSA might be an alternative for $N_2/O_2$ separation as the cost required for a low temperature and high-pressure liquefaction during cryogenic separation is very expensive. While major cost for PSA is in the compressor costs and volume of the beds. The cost for adsorption is generally lower than distillation from small to medium throughput and when high purity products are not required (Yang, 1987). Basically for adsorption of air by PSA, bed size is the controlling factor in capital cost. Since production is proportional to bed volume, capital costs increase more rapidly as a function of production rate compared to cryogenic plants (Smith and Klosek, 2001). Moreover the compression power is also proportional to the volume bed size, causing proportional increase in utility cost. Currently there are many other air separation technologies available such as chemical processes, polymeric membranes and ion transport membrane and Table 1.2 presented the brief comparison among those technologies (Smith and Klosek, 2001).

**Table 1.2**: Technology comparison table (Smith and Klosek, 2001).

| Process | Status | Economic range (sTPD) | Byproduct capability | Purity limit (vol%) |
|---|---|---|---|---|
| Adsorption | semi mature | <150 | poor | 95 |
| Chemical | developing | undetermined | poor | 99+ |
| Cryogenic | mature | >20 | excellent | 99+ |
| Membrane | semi mature | <20 | poor | ~40 |
| ITM | developing | undetermined | poor | 99+ |

Note to Table1.2:
Status – degree to which the technology has been commercialized.
Economic range – typical production range where the technology is currently economically feasible.
Byproduct capability – is a measure of the ability of the process to produce relatively pure nitrogen or argon stream without add-on DEOXO or cryogenic systems.
Purity limit – maximum purity that can be economically produced using specific technology.
DEOXO process – the stoichiometric quantity of hydrogen required to oxide the residual oxygen is introduced, and the gas stream is then passed over a catalyst bed in which essentially all the oxygen is oxidized to water which is then removed by adsorption on a zeolite desiccant.
sTPD – Production in Ton per day.

For air separation by using CMS, the PSA cycle used is vacuum swing cycle. For sorption of oxygen and nitrogen on the CMS, it is apparent that there is the little difference in equilibrium but a large difference in diffusivity, with oxygen being more rapidly adsorbed species. The high pressure raffinate product in the PSA process is therefore nitrogen. In such a system purging with nitrogen to remove the faster diffusing oxygen from the bed is undesirable, since, as well as wasting product, a certain fraction of slowly diffusing nitrogen will adsorbed, thus reducing the capacity for oxygen during the next adsorption step. The kinetic PSA processes avoided this difficulty by using a vacuum to clean the bed rather than a purge (Ruthven et al., 1994). Adsorption and polymeric membrane process will continue to improve in both cost and energy efficiency through ongoing research and development of adsorbents and membrane materials. None of the technology is expected to challenge cryogenics for large tonnage production of high purity oxygen. ITM technology is currently foreseen as the best candidate to challenge cryogenics for the production of high purity, tonnage quantities of oxygen. The limitation for all the non-cryogenic processes is the requirement of liquid oxygen or nitrogen for system back up (Smith and Klosek, 2001).

Cryogenic process is currently the most efficient and cost-effective technology to produce large quantities of oxygen, nitrogen, and argon products. However, it requires stringent air pretreatment section to remove process contaminants, including water, $CO_2$ and hydrocarbons. Van Hardeveld et al. (2001) have analyzed the cause of a serious explosion in an air separation unit (ASU) in Bintulu (Malaysia) on 25 December 1997. Ultimately, conclusive evidence was obtained that combustible airborne particulates had passed the main purification section of the air separation unit. These combustible contaminants had accumulated on the aluminium main vaporizers of the distillation column. Once hydrocarbon combustion was triggered, it led to aluminium combustion, which generated heat and vaporized the cryogenic liquids.

### 1.4 Adsorption Mechanism

Forces of adsorption of relevant interest here is the van der Waals forces, which exists between all atoms and molecules and can be classified into three groups (Do, 1998).

a) Dipole-dipole forces
b) Dipole-induced dipole forces – in this case one molecule having a permanent dipole will induce a dipole in a non-polar atom.
c) Dispersion forces.

The dispersion force is the most important force in physical adsorption. It has an origin in the quantum mechanics. Non-polar atom such as neon or helium, the time average of its dipole moment is zero. But at instant time “t” there is an asymmetry in the distribution of electrons around the nucleus and this generates a finite dipole. This so generated dipole will polarize any nearby atom (that is it distorts the electron distribution) so that the nearby atom will acquire a dipole. These two dipoles will attract and the time average of this attractive force is finite (Do,1998). As a result, our characterization was solely based on physical adsorption with dipole-dipole and dipole-induced dipole forces is neglected as these forces were proved not playing an important role in air separation by CMS which will be further described in Chapter 3.

## 1.5 Research on Palm Oil Wastes for Carbon Adsorbent Preparation

Malaysia palm oil industries are producing about 27.6 million tons of solid wastes, including 14.8 million tons of empty palm oil fruit bunches, 2.7 million tons of fruit fibers and 7.7 million tons of palm shells in year 2000 (Wong and Nasir Ani, 2002). Palm kernel shells have long been used as fuel in boiler to produce steam and electricity for mill. Palm kernel shell is the hard portion of the oil palm fruit that is broken to extract oil from the kernel. Generally, the palm oil mills have excess shells that are unutilized and contribute to environmental pollution (Puad, Hamami and Zaihan, 2002).

The principle commercial activated carbon feed stocks and proportions in which they are used were summarized by Bansal et.al. at 1988 as wood,35%; coal,28%; lignite,14%; coconut shell,10%; peat,10% and others, 3% (Guo and Lua. 2002). As the price of commercial activated carbon has dropped continually over the last decade or so, agricultural by-products are gaining great importance as precursors to active carbon production. First, they lost their role as a major fuel and source of energy; second, they are ever accumulating renewable sources; and third, they are low-ash materials (Pastor-villegas and Duran-Valle. 2002).

There are two factors contributing to the properties in activated carbon produced that are raw material and processing method. The selection of the precursor essentially determines the range of adsorptive and physical properties that can be attained in the activated carbon products (Guo. and Lua. 2002). Asiah (1992) has conducted the experiment on several local agricultural by-products suitable for producing active carbon. She carbonized sugarcane fibre, rice husk, fiber and shell of palm at 450 °C. The first two precursor produced chars showing standard isotherm of type II with hysteresis loop are closed in the pressure range near saturation. This shape reveals that the adsorbing solid contains mesopores with an upper size restriction whilst palm fiber char sample adsorption isotherm is mixed type I and IV. This isotherm showed that char is mixed of micro and mesopore. Palm shell char however showing type I isotherm indicating microporous property. As char will be further activated to activated carbon it is important to ensure the quality of char prior to the further process. Generally, the activation reaction rate is dependent on the transient pore structure of char during the activation process (Lua and Guo, 2001). Guo and Lua (2000) in his experiment have drawn the conclusion that the shell activated carbon was predominantly microporous whilst activated carbon derived from fibre predominant mesopore and macropore because of severe reduction of carbon-$CO_2$. Furthermore, hardness is an important property of the activated carbon and experimental result obtained by Lua and Guo (2001) has proven that the lowest Rockwell Hardness of activated carbon carbonized at 873K for 3h and activated at 1173 K for 30 min for palm shell is 19.0, which was sufficiently high to minimum hardness required. Hardness or durability of individual adsorbent particles is an important property to be considered, for granular type adsorbent application as a result of attrition during regeneration (Slejko, 1985).

Safaruddin (2000) has also characterized both palm shells after pyrolysis (char) and (activated carbon) activation after pyrolysis. He found that palm char has surface area higher than coal char and average pore diameter was smaller than coal char. Furthermore, compared to coal, palm shell has another merit of high carbon but low ash contents, which are associated with the feasibility of highly porous structures within the carbon matrix. The characterization came out with conclusion that palm shell can be used to prepare microporous adsorbent as a starting material for carbon molecular sieve. He also proposed that the suitable method for developing carbon molecular sieve from microporous adsorbent is by deposition of carbon or Chemical Vapor Deposition (CVD).

CMS exists for air separation by using PSA system in industry. In this experiment, we are aimed to diverse the sources studied for the production of CMS. As the commercial carbon molecular sieve available in the market now is produced from hard coal (anthracite) with methane deposition as stated in 1.1.1. The above statement has supported our research objective to convert the palm oil waste especially palm shell into carbon molecular sieve. Besides being value added to the waste palm shell, the environmental problem of ever accumulating waste will be solved. Palm shell was chosen in view of its suitability as precursor and the processing parameter and method will be manipulated to obtain the CMS suitable for air separation by PSA.

## 1.6 Research Objectives

1. To develop microporous carbon from palm shell as a precursor for further pore mouth modification by using CVD method.
2. To characterize the microporous carbon with appropriate calculation method by physisorption technique.
3. To modify the microporous carbon by one-step CVD process by directly applying of CVD and conventional CVD involving pore blocking by pyrolytic carbon followed by careful gasification in $CO_2$ atmosphere.
4. To characterize the CMS after CVD with appropriate calculation method by Rate of Adsorption technique.

## 1.7 Research Scopes

This research is the preliminary study of the conversion of palm shell into CMS capable for the separation on $O_2/N_2$. The procedure is first to fabricate microporous carbon with high micropore volume to serve as precursor for further pore mouth modification by using CVD method. Selection of appropriate starting material and various kind of processing method of microporous material is essentially important to produce the microporous carbon with narrow pore size distribution and relatively small pore size suitable for further modification. The microporous carbon is then undergoes the CVD process which mainly deposits carbon on the pore entrance until the desired pore size and distribution is obtained. Only one step CVD with direct deposition (DD) is explored in this research although two steps CVD and other type of one step CVD technique are available due to some constraint. The CVD research here involved two different approaches that are first direct deposition the carbon on the precursor until narrow pore size is reached and second closure of the pore of the precursor at the pore entrance followed by pore reopening by activation with $CO_2$. The mechanism of CVD and the development of carbon deposit at different parameters is discussed and compared with the existing literature survey available.

## 1.8 Contribution

The research on CMS and particularly CVD method for pore modification is of interest of local researcher in the recent years although Bergbau Forchung manufactured CMS for PSA process in 1973. From the literature survey, there is no journal published on fabricating CMS for $O_2/N_2$ separation using CVD method particularly using palm shell as starting material. Even though, there are published journal on fabricating CMS for $O_2/N_2$ separation using CVD method using different starting material such as coconut shell (Braymer et al., 1994, Cabrera et al., 1993), walnut shell (Hu and Vansant, 1995), carbon fiber from petroleum pitch (Casa Lillo et al., 2002) and coal (Hu and Vansant, 1995, Chagger et al., 1995), there are no complete formulation on CVD process and the parameters used are differ from one to another due to different precursor and gas or liquid substances used for carbon deposition. The contribution of the research is summarized as followed:

- Establishing the detail on fabricating CMS for $O_2/N_2$ separation from palm shell waste which involved a series of processes. Appropriate analysis methods developed are used for the adsorbent for the intermediate products and the end product also included.
- The ever accumulating palm shell is possible to be solved by converting it into high value added product as their role as fuel is still not attractive although oil prices have surged high recently due to some problem (STAR, 17 Jul. 2004).
- Served as preliminary research and finding for complete understanding of CVD process. Some useful recommendation was suggested for further research direction.

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