

Chapter 4

Experiment

4.1 Adsorbents

The activated carbons used in this research can be divided into 3 groups:

1. Activated carbons from coconut shell supplied by Carbokarn Company Limited.

Two grades of selected activated carbons are:

- 1.1. YAO 4/8 for air purification.
- 1.2. YAO 12/30 for water purification.

2. Carbon molecular sieves were supplied by Takeda chemical and industries, Ltd..

Selected activated carbon are:

- 2.1. MSC-3A with average pore diameter of 3 Å,
- 2.2. MSC-5A with average pore diameter of 5 Å,

3. Activated Carbon model LP (without information of type of raw materials and manufacture)

4.2 Manufacture of Activated Carbons

4.2.1 Activated Carbons

The typical manufacturing process for activated carbons can be divided into several steps, as illustrated in Figure 4.1 [30].

Raw Material Preparation Step

Generally, an activated carbon produced from a raw material which has low density and contain highly volatile matters, such as wood and lignin will yield high pore volume. In contrast, the coconut shell, of which density is relatively high and volatile matters will produce much small pore volume in which can be used for both liquid and gas purification processes. Raw materials that have been studied for the production of activated carbons are:

1. Cellulose materials, such as coconut shell, bagasses, sugar cane, corn-cobs and corn stalks.
2. Coals, such as lignite, peat, etc.
3. Production from animals, such as blood, bone, etc.

In this step, selected raw materials are grinding to the size of 100-325 mesh followed by screening in order to obtain desired particle size leading to uniform treatment. This research used coconut shell to be the raw material which has typical properties as summerized in Table 4.1.

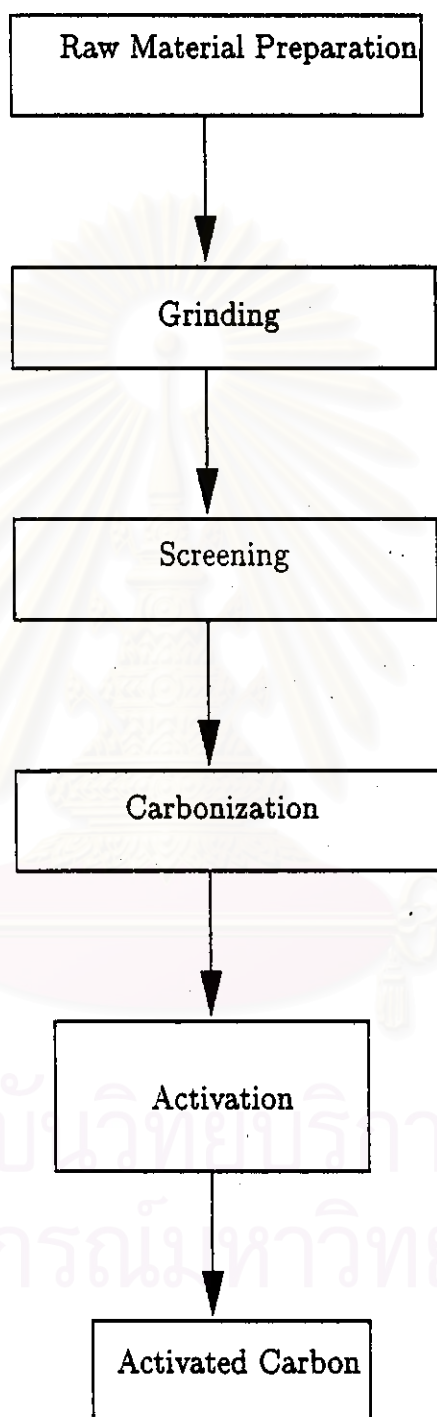


Figure 4.1: The basic manufacturing process for preparing activated carbon

Table 4.1: General properties of coconut shell

Physical properties		Component(%)
1	Fixed carbon	18.8
2	Volatile matter	80.8
3	Fine Ash	0.4

Carbonization Step

The raw materials are carbonized at temperature 200-500° C to remove most volatile from the raw materials.

Activation Step

Subsequently, the carbonized raw materials are activated with steam at temperature 700-1,000°C to increase porosity and specific surface area.

4.2.2 Carbon Molecular Sieves

Carbon molecular sieve is a special type of activated carbons with quite narrow pore size distribution within a range of micropore. Carbon molecular sieve are usually produced from coal, with specific treatment and precisely controlled manufacturing conditions. Manufacturing processes are similar to that for conventional activated carbons as shown in Figure 4.1 except raws materials particle size, carbonization temperature, activation temperature and oxidizing agent such as preparation from anthracite.

Raw Material Preparation step

Anthracite is gridded to 42-65 mesh.

Carbonization Step

The volatile matter is removed by heating an anthracite prepared material in a tube furnace with a current of nitrogen. The heating rate was 5 ° C /min to reach the temperature of 950° C. The samples are heated for 2 hours and then cooled to room temperature.

Activation Step

The anthracite samples are activated in very thin layer by air at 425-430° C to the desired burn off. Then the samples are heated in nitrogen at temperature of 950° C, allowing 1 hour to remove the oxygen complex on the surface of the sample.

4.3 Characterization of Activated Carbons

4.3.1 Surface Characteristic

Shape and sizes of pores at the external surface of a selected activated carbon are monitored via a scanning electron microscope (SEM).

4.3.2 Pore Size Distribution

Large pore size distribution of a selected activated carbon can be measured with a mercury porosimetry which is based on the capillary law governing mercury penetration into pores. Subsequently, the pore diameters can be determined from

Washburn equation written as;

$$d = -(1/P)4\gamma\cos\theta \quad (4.1)$$

However, the resulted range of pore size is usually large than 1,000 Å

For small pore, the distribution is measured from the amount of nitrogen adsorbed at 77 K with assumption of monolayer or multilayer coverage described by Langmuir or BET isotherm respectively. The adsorption of nitrogen for BET method is carried on a micrometrics instrument (ASAP 2000).

4.3.3 Specific Surface Area

The iodine number is not only used to indicate the porosity of an activated carbon but also used to estimate the surface area. Standard test method for determination of iodine number is the adsorption of iodine from aqueous solution. Standard iodine solution is treated with three different weights of activated carbon under specified condition. The treated solution are filtered and measured iodine remaining in the filtrate by titration. The amount of iodine adsorbed per gram of carbon at a residual iodine concentration of 0.02 N is reported as the iodine number (ASTM D4607-94).

For small pore, at which the molecules of iodine can not penetrate, BET method is used to determined the surface area.

Table 4.2: The band of the functional group on activated carbon surface

No	Function group	Wave number (cm ⁻¹)
1	carboxylic	3,400-2,400
2	hydroxyl	3,650-3,500
3	carbonyl	1,850-1,650

4.3.4 Functional Groups

Most of activated carbons contain some functional groups on the surface which arise from either raw material or from pyrolysis or activation step. A selected activated carbon is verified the functional group by FTIR (Fourier-transform infrared spectrophotometer) which is sensitive to molecular bonding and has been used to draw inferences about activated carbon surfaces through chemical and pyrolytic studies [31]. In general, the functional groups on the surface exist mainly and the band of each group are shown in Table 4.2.

The complexes exist mainly in the following from;

4.3.5 Particle Density

The particle density ρ_p , a specific character of each type of activated carbon, was determined indirectly by using the Blake-Kozeny equation [29] for laminar flow;

$$\left(\frac{\Delta P}{L}\right) \left(\frac{d_p}{\rho v_0^2}\right) = \frac{150(1-\epsilon)^2}{\epsilon^3} \frac{1}{\frac{d_p v_0 \rho}{\mu}} \quad (4.2)$$

or

Table 4.3: The characteristics of packed columns for analysis the particle density

No	Types of activated carbon	Weight (g)	Volume of bed (cm ³)	Bulk density (g/cm ³)	length of column (cm)
1	CMS-3A	0.720	1.313	0.548	8.0
2	CMS-5A	0.647	1.313	0.493	8.0
3	LP814	0.782	1.470	0.532	6.2
4	YAO4/8	0.463	1.071	0.432	10
5	YAO12/30	0.913	1.641	0.557	9.0

$$\log \left(\left(\frac{\Delta P}{L} \right) \left(\frac{d_p}{\rho \bar{v}_0^2} \right) \right) = -\log \left(\frac{d_p \bar{v}_0 \rho}{\mu} \right) + \log \left(\frac{150(1-\epsilon)^2}{\epsilon^3} \right) \quad (4.3)$$

The bed porosity was determined by the plots of $\log \left(\left(\frac{\Delta P}{L} \right) \left(\frac{d_p}{\rho \bar{v}_0^2} \right) \right)$ versus $\log \left(\frac{d_p \bar{v}_0 \rho}{\mu} \right)$, the slope and the intercept of the line were equal to -1 and $\log \left(\frac{150(1-\epsilon)^2}{\epsilon^3} \right)$ respectively. The pellet density was found from this relationship;

$$\rho_p = \frac{\rho_b}{(1-\epsilon)} \quad (4.4)$$

The selected activated carbon is packed by using the same particle size and tube size as the adsorption experiment. The other characteristics of the packed column are shown in Table 4.3

The packed column is placed in the gas chromatography like the experimental procedure in order to find the relationship between pressure and carrier gas flow rate. Then the unpacked column has been replaced by a packed column and has been repeated in the same manner above. The pressure drop of the packed column is the difference in pressure of the packed and unpacked column.

4.4 Adsorption Experiments

4.4.1 Column Preparation

1. To crush a selected activated carbon in order to yield particle sizes of 40-60 mesh.
2. To pack the crushed carbons into a stainless steel tube with 1/4 in. in diameter and with an appropriate length of carbon bed in order to obtain suitable chromatograms for analysis with the method of moment.
3. To measure the amount of carbons in the packed bed.
4. To measure the particle density and bed porosity.
5. Weigh the column again and plug the another end side.

Properties of all packed bed of selected activated carbons for each adsorbate vapor are summarized in Table 4.4.

Table 4.4: characteristics of all packed columns

Adsorbate-adsorbent	Length of packed bed (cm)	Bed porosity	Particle density (g/cm^3)
CMS-3A - Acetone	8.0	0.268	0.749
CMS-5A - Acetone	0.5	0.449	0.766
LP 814 - Acetone	0.2	0.601	0.760
YAO 4/8 - Acetone	0.2	0.308	0.538
YAO 12/30 - Acetone	0.3	0.706	0.809
CMS-3A - Toluene	2.0	0.368	0.749
CMS-5A - Toluene	0.2	0.315	0.766
LP 814 - Toluene	0.2	0.321	0.760
YAO 4/8 - Toluene	0.2	0.308	0.538
YAO 12/30 - Toluene	0.3	0.706	0.809

4.4.2 Adsorbate Vapor Preparation

Table 4.5: Physical properties of toluene and acetone

Physical properties	Toluene	Acetone
Molecular weight	92.13	58.08
Density (g/cm ³)	0.866	0.792
Boiling point (° C)	110.6	56.50
Heat of condensation (kJ/mol)	33.50	15.60
Critical temperature (T _c) (K)	593.6	508.0
Critical pressure (P _c) (atm)	41.6	47.0

An equipment for preparing adsorbate vapors is illustrated in Figure 4.2.

The volumetric flask is filled with 200-250 ml of liquid adsorbate. The flask is sealed and is kept in the room temperature for a few days to achieve vapor-liquid equilibrium. The mole fraction of the adsorbate can, therefore, be determined from the vapor pressure of the adsorbate at the given temperature. Other properties of selected adsorbates are summarized in Table 4.5.

4.4.3 Gas Chromatography Experiments

A gas chromatography model Perkin-Elmer 8700 with FID has been employed as an experimental equipment. The schematic diagram is shown in Figure 4.3.

An analysis column, which is placed in the oven of the gas chromatography, has been replaced with a packed column prepared in the previous section. The adsorbents are then purged with helium at temperature of 250° C at the flow rate of 50 cm³/min for 3-4 hours to remove all impurities. The flow rate of helium, as a carrier gas, is measured by a soap bubble flow meter.

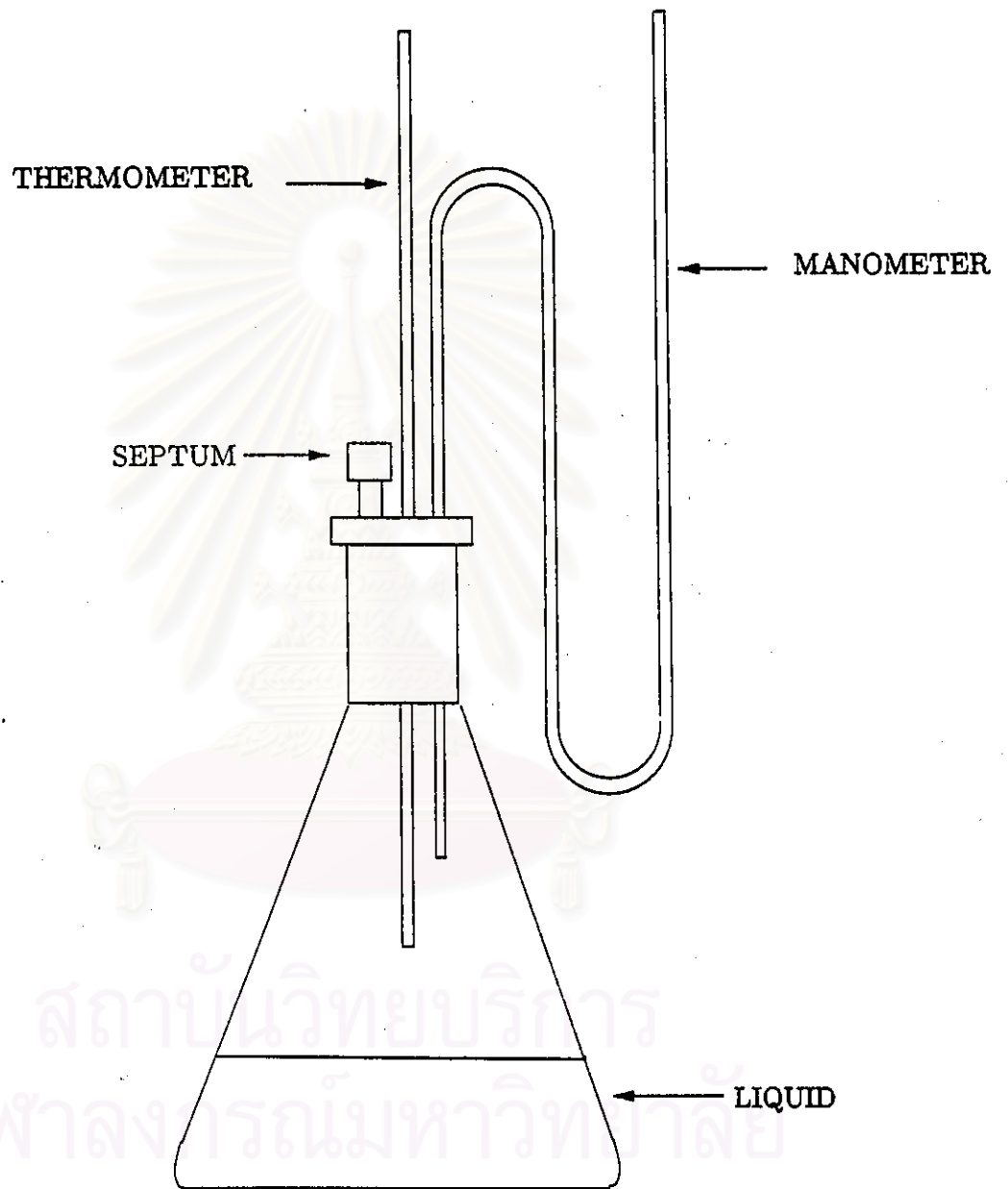


Figure 4.2: Closed volumetric flask used for vapors preparation.

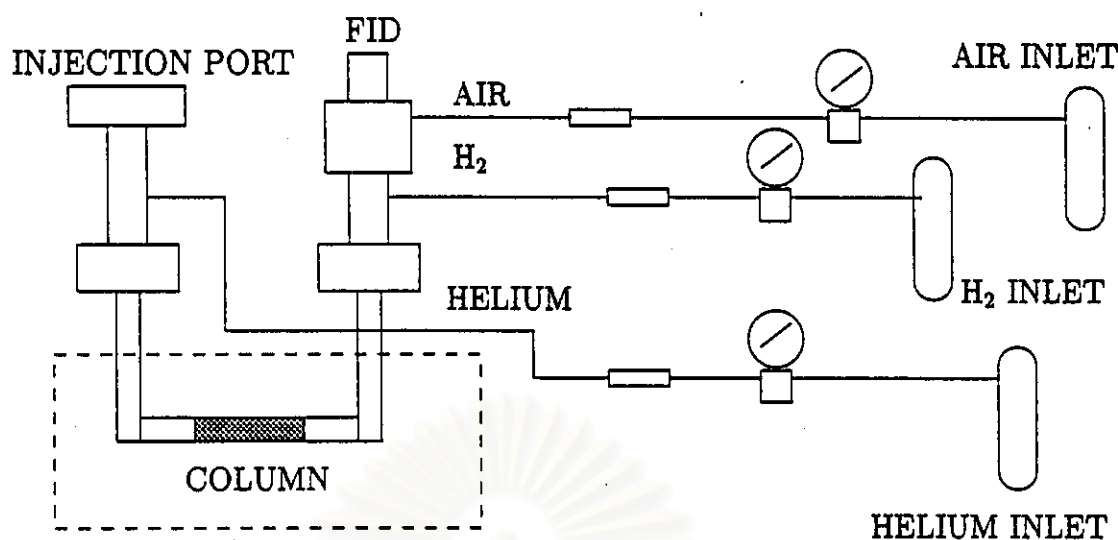


Figure 4.3: Schematic diagram of gas chromatography experiment

Adsorption experiments are carried out with pulse injection as a conventional chromatographic condition. In order to ensure dilute solution, an injected volume of the adsorbate vapor is less than $100 \mu\text{l}$. While the flow of carrier has been varied in a range of $20\text{-}100 \text{ cm}^3/\text{min}$ at a given temperature. The adsorption experiments are repeated at another temperature, which is in a range $50\text{-}250^\circ \text{C}$. Again, the experiments are repeated with another type of adsorbate.

A resulted chromatogram for each injection has been recorded for determination adsorption equilibrium constant, heat of adsorption, and overall mass transfer coefficients.