

## CHAPTER IV

### EXPERIMENTS

#### 4.1 ADSORBENT PREPARATIONS

Three types of major materials for preparation of carbon adsorbents were composed of

1. stems of water hyacinth (excluding leaves and roots), sugarcane bagasse, and rice husk which were used as raw materials for preparation of carbon adsorbent,
2. 600 grams/liter zinc chloride solution which was used as a surface increasing reagent,
3. 100 grams/liter hydrochloric acid solution which was used as washing agent for the remaining reacting reagent, and
4. hot water for washing hydrochloric acid solution from the carbon adsorbent obtained.

The water hyacinth, sugarcane bagasse, and rice husk were dried and ground (except rice husk) to appropriate size for mixing with zinc chloride solution. The mass ratio of raw materials to the zinc chloride was four. The mixture was then prereacted

in an oven at temperature of 110°C for a few hours. Afterwards, they were carbonized and were reacted simultaneously in the muffle furnace at the temperature of 400°C for an hour. The obtained carbon adsorbent was cooled, and then was washed with the hydrochloric acid solution in order to eliminate the remaining surface increasing reagent. The adsorbent was washed with hot water and dried in the oven at the temperature of 110°C for a few hours. The dried adsorbent was sieved for the particle size in the range of 40–60 mesh for characterization. Other carbon adsorbents prepared from water hyacinth, sugarcane bagasse, or rice husk were produced with the same procedure, but at the temperatures of 500 and 600°C for reacting periods of 1, 2, and 3 hours, respectively. For comparison purpose, the raw materials were carbonized only at the temperature of 400°C for an hour.

Besides the yields of carbon adsorbents from 3 types of raw materials, the adsorbent characteristics were measured by nitrogen adsorption at the normal boiling point of nitrogen (77 K approximately) in order to obtain the pore size distributions and specific surface areas, as well as iodine adsorption. In addition, the surfaces of the adsorbent were monitored with scanning electron microscope (SEM).

However, in this research, the mechanism of the carbonization and activation process would be found out; thus, additional experiments for analyzed the problem were performed. By using 6 acidic solutions (including  $\text{ZnCl}_2$  solution) to react with the water hyacinth at the temperature of 400°C for an hour. The mixtures of water hyacinth and the acidic solutions were prereacted in an oven at the temperature of 110°C for 17 hours. During the prereaction process, the physical changes of the samples were observed.

The six acidic solutions used in this experiment is as following:

1. 425 grams/liter hydrochloric acid solution,
2. 600 grams/liter nitric acid solution,
3. 600 grams/liter sulfuric acid solution,
4. 600 grams/liter phosphoric acid solution,
5. 600 grams/liter zinc chloride solution, and
6. 300 grams/liter sodium chloride solution.

The physical properties of the chemical reagents were summarized in Table E.3 [Weast, 1968]. The experiments were carried out in the same manner as those for zinc chloride. The mixtures of water hyacinth and the surface increasing reagents were reacted in the oven at the temperature of 110°C for 17 hours to eliminate the water in the mixtures as much as possible. Afterwards, they were carbonized and reacted simultaneously in the muffle furnace at the temperature of 400°C for an hour. The carbon adsorbents were cooled, then were washed with hot water and were dried in the oven at the temperature of 110°C for a few hours. The dried carbon adsorbents were sieved for the particle size in the range of 40–60 mesh for characterization.

## 4.2 ADSORPTION EXPERIMENTS

### 4.2.1 Determination of Packed-Bed Characteristics

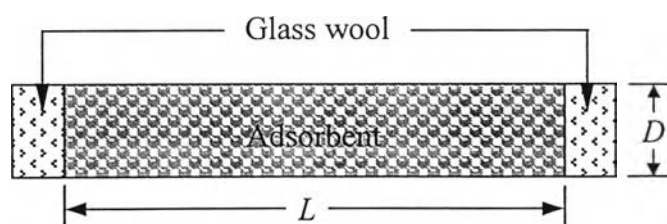


Figure 4.1 A typical packed column of an adsorbent for adsorption experiments

Each carbon adsorbent (particle size 40–60 mesh) was packed in a stainless steel tube with 1/4 inch in diameter. Both ends of the adsorbent were packed with inert material i.e. glass wool in order to prevent the entrainment of adsorbent, as illustrated in Figure 4.2. In addition, the inert material also provides transformation region for flow pattern within the column.

The bed length ( $L$ ) of each adsorbent had to be adjusted in order to obtain suitable shape of chromatograms for analysis with moment method. Then the amount of adsorbent for each packed bed had to be recorded. If the adsorbent density were known, the corresponding bed porosity would be able to be determined from the volume ratio of the adsorbent to the packed bed. If the density of an adsorbent had not to be known, it was able to be determined from the Blake-Kozeny equation. In that circumstance, an additional packed column with sufficient length of packed bed (0.5, 1.0, and 6.0 cm for toluene, benzene, and o-xylene, respectively) might be required for measurement of the variation of pressure drops across the bed with the flowrates. With an appropriate form of linear plot, such as the expression in equation 4.2 in log-log scale, the bed porosity was able to be determined from the intercept.

$$\left(\frac{\Delta P}{L}\right)\left(\frac{D_p}{\rho_b v_0^2}\right) = 150 \left[\frac{(1-\epsilon)^2}{\epsilon^3}\right] \left[\frac{1}{D_p v_0 \rho_b / \mu}\right] \quad (4.1)$$

$$\log\left(\frac{\Delta P}{L}\right)\left(\frac{D_p}{\rho_b v_0^2}\right) = -\log\left[\frac{D_p v_0 \rho_b}{\mu}\right] + \log\left[\frac{150(1-\epsilon)^2}{\epsilon^3}\right] \quad (4.2)$$

This equation is generally good for void fractions less than 0.5 and is

valid only in the laminar region  $\left[\frac{D_p v_0 \rho_b}{\mu}\right] \left[\frac{1}{(1-\epsilon)}\right] < 10$  [Bird, Stewart, and Lightfoot,

1960]. Finally, the adsorbent density was also able to be determined from the relationship between the bed density and the bed porosity, as given in equation 4.3.

$$\rho_p = \rho_b / (1 - \varepsilon) \quad (4.3)$$

Subsequently, the resulted adsorbent density was used to determine the bed porosity of the corresponding packed bed for adsorption experiments. The characteristics of all packed column are summarized in Table E.4.

#### 4.2.2 Adsorbate-Vapour Preparation

An apparatus for preparing an adsorbate vapour is illustrated in Figure 4.2. The volumetric flask was filled with 200–250 ml of liquid adsorbate. The flask was sealed and kept in the room temperature for a few days to allow vapor-liquid equilibrium to be able to be reached. The mole fraction of the adsorbate can, therefore, be determined from the vapour pressure of the adsorbate at the given temperature [Breck, 1974; Reid, 1988; and Perry and Green, 1987]. Although the equilibrium has not been reached, a certain fraction of adsorbate vapour is sufficient for the experiments.

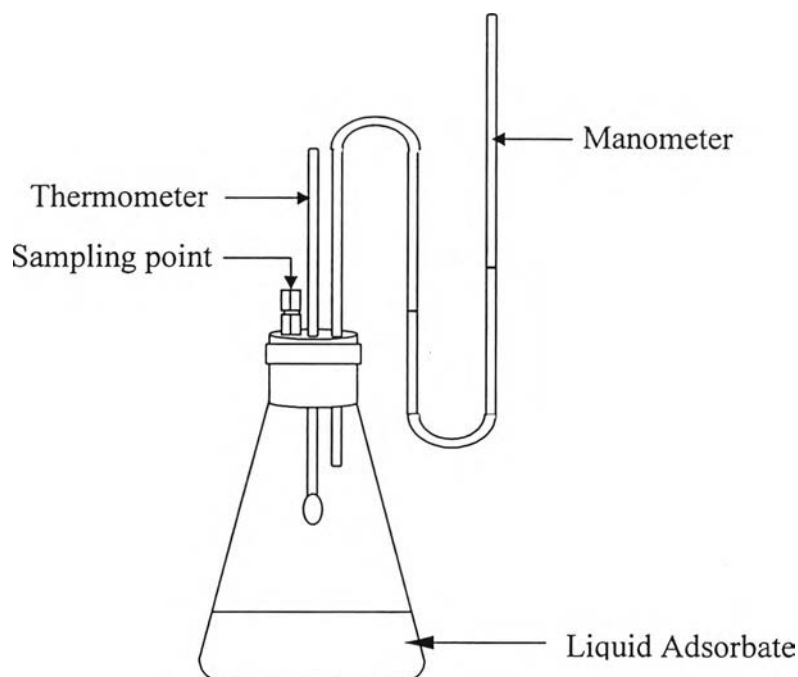


Figure 4.2 Adsorbate-vapour preparation apparatus

#### 4.2.3 Gas Chromatography Experiments

A Shimadzu gas chromatograph (model GC-8A) with a flame ionization detector (FID) was used to measure the adsorption equilibrium constants and mass-transfer coefficients. A carrier gas was nitrogen. Flowrates of carrier gas were measured by a soap-bubble flowmeter at the exit of the detector during each run. A conventional analysis column was replaced with another packed column containing a selected adsorbent. One end of the carbon adsorbent column was connected to the injector and the other end was connected to the detector. Each carbon adsorbent was purged with nitrogen at the temperature of 250°C and the flowrate of 50 cm<sup>3</sup>/min for 3–4 hr to ensure that no other adsorbate remained on the carbon adsorbent surface and then was brought to the desired temperature and flowrate. The injections of small pulse of adsorbates were carried out manually with a gas-tight syringe into the carrier

gas at a given flowrate, several injections were repeated at other flowrates within a range of 20 to 100 ml/min. For each column of carbon adsorption, the temperature of the column was altered in the range of 180–270°C. Each injected volume of the adsorbate vapour was about 100  $\mu$ l. For another adsorbate, the same experiment was repeated except the injected gas contained another type of selected adsorbates. Similarly, the adsorption experiments on another type of carbon adsorbents were also carried out in the same procedure except the packed column contained the desired adsorbent that was changed in the block of column as illustrated in Figure 4.3.

From an obtained chromatogram, in Figure 4.4, adsorption-equilibrium constants, overall mass-transfer coefficient were able to be determined with the first absolute moment and the second central moment of the chromatogram, respectively. In addition, the effects of temperature on the equilibrium constant and on the mass-transfer coefficient were investigated.

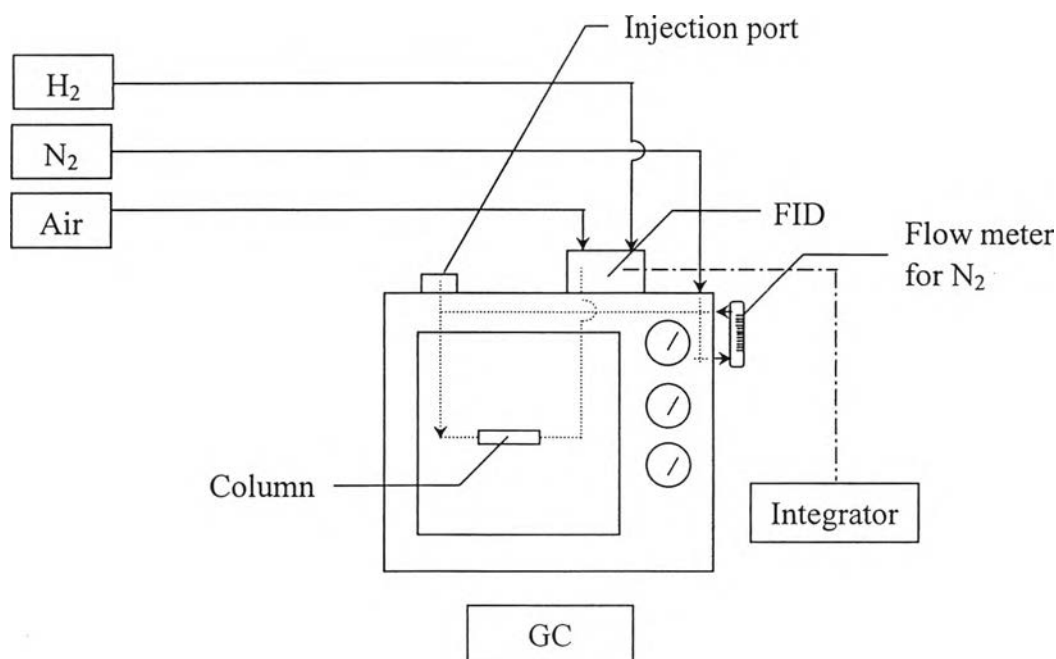


Figure 4.3 Schematic diagram of GC experiment

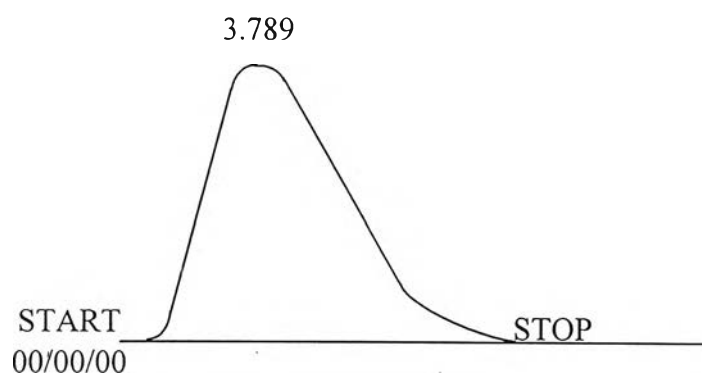


Figure 4.4 A chromatogram from the experimental result