CHAPTER III
EXPERIMENTAL

3.1 Materials

The gases used in this research were hydrogen gas (99.999% purity), obtained from Praxair (Thailand) Co., Ltd., used as adsorbate and helium gas (99.99% purity), obtained from Thai Industrial Gas Public Co., Ltd., used as inert gas to determine manifold and sample cylinder volume of built constant volumetric isothermal adsorption apparatus. Activated carbon and carbon nanotubes both single wall and multi wall types were obtained from UOP LLC.

3.2 Experimental Apparatus

The constant volumetric adsorption apparatus built and used in these measurements is composed of a gas reservoir (150 cc) and a sample cylinder (50 cc), and both are connected by high-pressure bellow valves, Swagelok (Model SS-4-UK) and diaphragm valves, Swagelok (Model SS-DSS4), with ¼ inch stainless-steel Hylok tubings and fittings. The pressure transducer used in this system was purchased from Bourdon Sedeme (Model E913) which was capable of measuring gases in the range of 0-1500 psig with 0.2% global error. Its output signal is a direct current, 4-20 mA, which is necessarily to converted to a digital signal and recorded by a data logger (A/D). That data logger (Model AI200) was purchased from Wisco Co., Ltd. with OD95 Microsoft Excel program support, shown in Figure 3.1., for information management. To record the real-time pressure changes, the data logger was connected to a computer via port com 1. The pressure gauge was also a module from Bourdon Sedeme (Model MMX5), measuring in the range of 0-1500 psig.

Evacuation the manifold and the sample cylinder were accomplished with a Vacuubrand vacuum pump, model type RZ2 and monitoring with Edwards vacuum pressure sensor (Model AGD 101L). The volumetric adsorption apparatus was wholly immersed in water container connected with digital-temperature-controlling

water bath, Polyscience model 9601. The schematic apparatus is shown in Figure 3.2. and the experimental set-up and the constant volumetric isothermal adsorption apparatus are shown in Figure 3.3. and Figure 3.4., respectively.
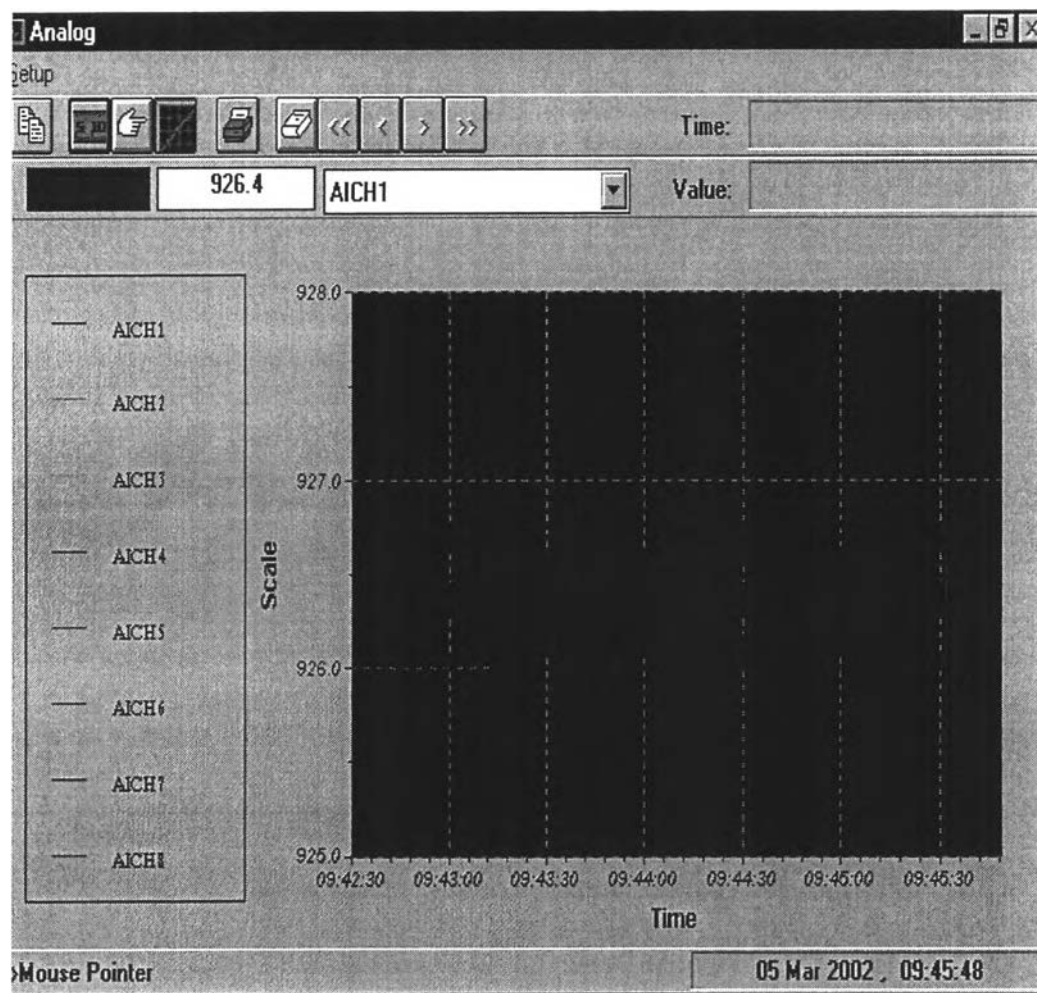
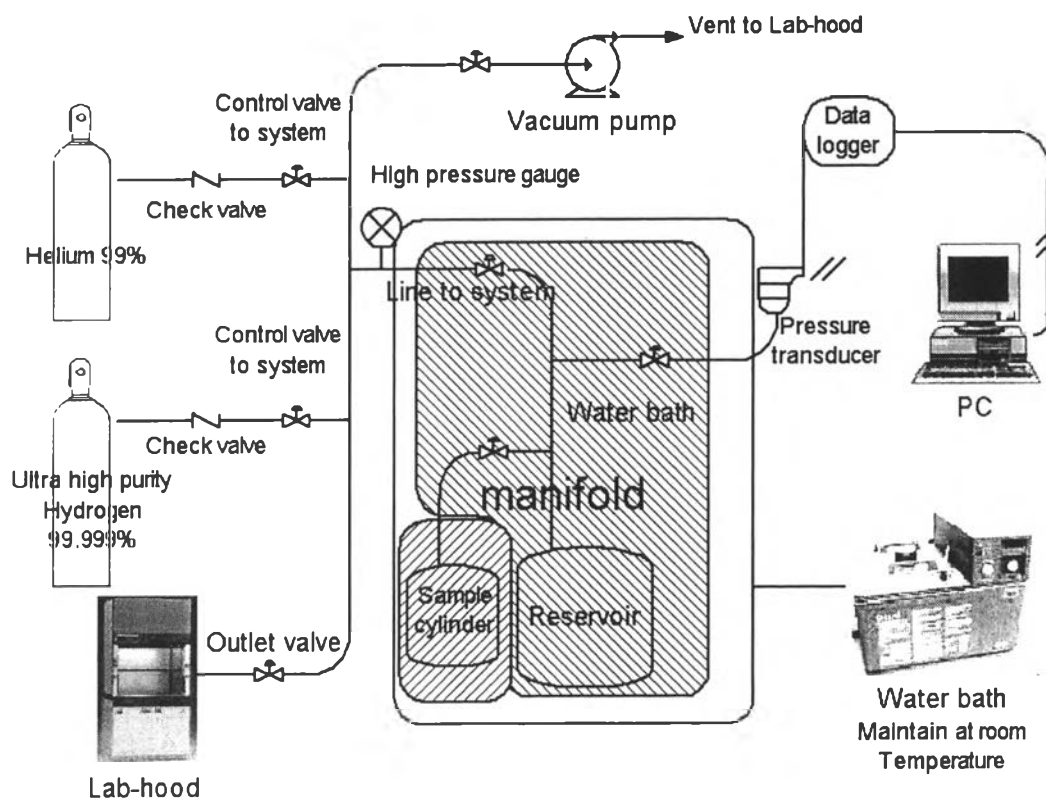

Figure 3.1 Display of OD 95 program.

Figure 3.2 Schematic of the adsorption apparatus.

Figure 3.3 Experimental set-up.

Figure 3.4 The constant volumetric isothermal adsorption apparatus.

3.3 Adsorbent Characterization

3.3.1 BET Surface Area Measurement

The surface areas of all adsorbents were measured by the five-point BET method using a Quantachrome Corporation Autosorb I. Before measurement, an adsorbent sample was outgassed by heating at 523 K for 4 hours under vacuum to eliminate volatile adsorbates on the surface. BET surface area were determined by measuring the quantity of gas adsorbed onto or desorbed from a solid surface at 5 equilibrium vapor pressure (P/P$_o$) values (0.1115, 0.1615, 0.2115, 0.2615 and 0.3115) by the static volumetric method. The data were obtained by admitting or removing a known adsorbate gas, nitrogen, into or out of a sample cell containing the solid adsorbent maintained at a constant temperature below critical temperature of the adsorbate, that is 77 K for nitrogen.

The adsorption data were calculated using the Brunauer-Emmett-Teller (BET) equation as shown in equations 3.1 and 3.2.

$$\frac{1}{W\left(\frac{P_o}{P}-1\right)} = \frac{1}{W_mC} + \frac{C-1}{W_mC}\frac{P}{P_o} \tag{3.1}$$

where W =   weight of gas adsorbed at relative pressure P$_o$;

W_m =   weight of adsorbate constituting a monolayer of surface coverage;

C =   constant that is related to the energy of adsorption in the first adsorbed layer and magnitude of adsorbate/adsorbent interaction.

The surface area can be obtained from the following equation.

$$Surface\ area\ of\ sample\ = \frac{W_m A_{nitrogen}(6.02 \quad 10^{23})}{M_{w,nitrogen}} \qquad (3.2)$$

where $A_{nitrogen}$ =   cross-sectional area of one molecule nitrogen

=   0.162 nm^2 (at 77K);

$M_{w,nitrogen}$ =   molecular weight of nitrogen (28)

3.3.2 Raman Spectroscopy

In case of carbon nanotubes, there are three modes that are of importance, namely Radial Breathing Mode (RBM) Band, Disordered Carbon Band, and Graphitic Band. In this study, the Raman spectroscope has been used to test on two different samples of carbon materials – single-walled carbon nanotubes and multi-walled carbon nanotubes. The Raman measurements were performed with a LabRam JY Horiba Raman microscope equipped with a CCD (charge-couple device). The laser power used was a 632.8 nm.

3.4 Calibration of Manifold and Sample Cylinder Volume

The volumes of the manifold (V_m) and the sample cylinder (V_{sc}) were determined from helium expansions at a pressure range of 140-1040 psia. The mass balance was taken over two system states. The first state was the initial state, before expansion, where helium gas was only present in the manifold volume, and no gas was present in the outgassed cylinder. The second state, after expansion into the outgassed cylinder, where gas was present in both the manifold and the sample cylinder. If the mass balance is equal to zero, it indicates that the system was free of leakage and of adsorbed gas on an apparatus. To determine V_m, the following steps are required:

a. Material balance over manifold and the sample cylinder

$$V_m \rho_1 = (V_m + V_{sc})\rho_2 \tag{3.4}$$

where V_m = volume of the manifold, cc

V_{sc} = volume of the sample cylinder, cc

ρ_1 = density of the gas in the manifold at pressure P1, g/cc

ρ_2 = density of the gas in the manifold + sample cylinder at pressure P2,

g/cc

One mass balance equation was not enough to be solved for determining 2 parameters, volume of manifold and sample cylinder. Thus, the known volume materials were put into the sample cylinder for another mass balance equation. The material used for the known volume was 158.5438 g of 99.48 %steel kindly donated by Sahaviriya Steel Industries Public Company Limited. Knowing the density of this steel (7.7728 g/cc, generously carried out by Metallurgy and Materials Science Research Institute, Chulalongkorn University), a very precise value of its volume can be obtained.

b. Material balance over the manifold and the sample cylinder with a standard sample material with known volume, V_k (e.g. steel sheet)

$$V_m \rho_3 = (V_m + V_{sc} - V_k)\rho_4 \tag{3.5}$$

where V_k = volume of steel that is used, g/cc

ρ_3 = density of the gas in the manifold at pressure P3, g/cc

ρ_4 = density of the gas, at pressure P4, in the remaining space of the

manifold and the sample cylinder

Both the above equations are solved to get V_m,

$$V_m = \frac{V_k}{\dfrac{\rho_1}{\rho_2} - \dfrac{\rho_3}{\rho_4}}$$
(3.6)

Hence,

$$V_{sc} = \frac{-V_k \rho_4}{\dfrac{\rho_2 \rho_3}{\rho_1 - \rho_2} - \dfrac{\rho_2 \rho_4}{\rho_1 - \rho_2} - \rho_4}$$
(3.7)

Experimental gas density data calculated at any pressure and temperature from Beattie-Bridgeman Equation of State (Cengel, 1994), which is accurate for density, ρ of not greater than 0.8 critical ρ, were used in measuring adsorption isotherms for all gases evaluated in this study.

$$P = \frac{R_u T}{\upsilon^2} \left(1 - \frac{c}{\upsilon T^3}\right)(\upsilon + B) - \frac{A}{\upsilon^2}$$
(3.8)

where

$$A = A_0 \left(1 - \frac{a}{\upsilon}\right)$$
(3.9)

and

$$B = B_0 \left(1 - \frac{b}{\upsilon}\right)$$
(3.10)

when   P = pressure in kPa

   υ = specific volume in m^3/kmol

   T = temperature in Kelvin

$$R_u = 8.314 \ kPa \cdot m^3 / (kmol \cdot K)$$

A_0, B_0, a, b and c are the five constants in the Beattie-Bridgeman Equation for gas of interest as given in Table 3.1.

Table3.1 Five constants in the Beattie-Bridgeman Equation

Constant	H_2 gas	He gas
A_0	20.0117	2.1886
B_0	-0.00506	0.05984
a	0.02096	0.01400
b	-0.04359	0.0
c	504	40

3.5 Data Collection with Adsorbents

After the parameters V_m and V_{sc} have been determined, it is ready to proceed to H_2 adsorption studies. It is crucial that the pressure transducer must be calibrated for each adsorption experiment. Atmospheric pressure, 14.7 psia can be used as a reference pressure to set the zero span on the transducer to vacuum or set it to 14.7 psig. After this step, the adsorbent was first placed in the sample cylinders and being outgassed at 0.01 Torr for at least 14 hours. The manifold was initially pressurized with the H_2 gas at 140 psia. Hence, the valves on both sides of manifold were closed. The manifold pressure was then allowed to reach the equilibrium, before the pressure was recorded. Usually, this step took about 5-10 minutes. This was done to ensure that the manifold did not leak. The gas was consequently expanded into the sample cylinder by opening valves, which was initially under vacuum, containing the adsorbent. After the pressure equilibrated in the manifold and sample cylinder, the final pressure was then recorded. This process required 5-30 minutes to reach equilibrium time. The pressures were recorded every 10 seconds until the pressure in the manifold and the sample cylinder became constant. In order to check variations of equilibrium pressures, pressurizing the system with the adsorbent for about 6 hours was conducted to check the variability of equilibrium

pressure. The background leakages and standard deviation of data were taken into account in the analysis of the hydrogen sorption results.

The relationships governing the adsorption procedure can be derived from a mass balance around the constant volume apparatus. In practice, the manifold volume, V_m, was used to contain the adsorbate being emitted via a valve into a constant sample cylinder volume, V_{sc}. The volume of manifold plus sample cylinder was consequently the total volume of the system as the following equation;

$$V_s = V_m + V_{sc} \tag{3.11}$$

For purpose of the mass balances, the mass of the pure gas in the manifold was calculated by multiplying manifold volume, V_m, by the gas density, ρ, at that temperature and pressure. The mass in the gas phase in the cylinder with the adsorbent, was simply the gas density, ρ, multiplied by the volume of the cylinder, V_{sc}, subtract the volume occupied by the adsorbent, dead space volume, V_{ds}. This volume was the only available volume, V_a, which the gas phase molecules could occupy. The space occupied by the adsorbent is unavailable to the gas and is easily considered as dead space. The available volume, V_a, in the cylinder can then expressed as the following equation;

$$V_a = V_{sc} - V_{ds} \tag{3.12}$$

The carbon materials can be regarded in theirs graphitic form. Its density is equal to 2.25 g/cc, although in its disorder crystal state it probably is closer to 2.1g/cc (Patel, 2000). The volume occupied by MWNTs and activated carbon in the experiment were then calculated based on density of 2.20 g/cc (Park, 1999).

The mass balance was taken over two system states. If the mass balance was not equal to zero, the difference was taken as the amount adsorbed.

$$(M_m)_{before} + (M_{sc})_{before} = (M_m)_{after} + (M_{sc})_{after} + M_{ad} \tag{3.13}$$

where M_m = mass of gas in manifold

M_{sc} = mass of gas in the sample cylinder available volume, V_a

M_{ad} = mass adsorbed on the substrate, also to the total change of mass in the system, ΔM

Therefore:

$$M_{ad} = [(M_m)_{before} + (M_{sc})_{before}] - [(M_m)_{after} + (M_{sc})_{after}] \tag{3.14}$$

This equation could be rewritten in terms of the gas densities and known volumes.

$$M_{ad} = [(\rho V_m)_{before} + (\rho V_a)_{before}] - [(\rho V_m)_{after} + (\rho V_a)_{after} \tag{3.15}$$

where ρ_{before} = density of the gas before expansion, g/cc

ρ_{after} = density of the gas after expansion, g/cc

There are two measuring methods that were employed in this thesis, the stepwise and continuous adsorption. The stepwise adsorption was begun with initial pressure about 140 psia and repeated until the adsorbate had come to a final pressure of ~1040 psia with increment equal to 100 psia. In each increment, the system and the adsorbent were vacuumed at 0.01 Torr for at least 14 hours. The continuous adsorption was also begun with same initial pressure at 140 psia and repeated until the adsorbate had come to a final pressure of ~1040 psia with the same increment, 100 psia, without outgassing in each increment. These two processes were employed ten equilibrium adsorption pressures to record. Many data points could be measured over this pressure range by adjusting the increment of the manifold pressure between each equilibrium step. The amount adsorbed (wt.%) was calculated as the adsorbed hydrogen mass divided by the mass of carbon nanotubes.

3.6 Data Collection with Blank Test

Blank test must be employed to check the reliable of the set-up apparatus and to check the leak of the system. If the system has leakage, the amount of leaking gas must be taken in to account to correct the reported results.

The collection methods were divided into two manners subtraction method and leaking factor. First, the adsorption amount was calculated from pressure data by using the calculation that has been mentioned previously. The hydrogen adsorption was corrected by using adsorption data from blank test (no specimen in the sample cylinder) subtracting from the actual adsorption data. This method was called subtraction method. The second method was the correction by taking the leaking factor into account. The leaking factors were the ratio of pressure at that time to the initial pressure of that blank test experiment. To the correct the amount of adsorbed hydrogen, the hydrogen pressure was recalculated by multiplying leaking factor with original pressure data.

3.7 Experimental Conditions

The adsorption of hydrogen was performed at 298 K. A refrigerated water-bath was used to maintain the thermal equilibrium of gas in the manifold, valves and sample cylinder immerged in temperature-controlled bath with a high precision (+/- 0.1 °C) temperature control set-up. A pressure transducer, as described previously, was used to record the initial and final equilibrium pressure in the manifold. The standard amount of carbon materials sample used in these experiments was about 1.0 - 4.0 grams, depending on the adsorbent's density.

In order to perform a new experimental run, the sample was pretreated by degassing under vacuum at about 0.01 Torr and 298 K for at least 14 hours. The use of high vacuum pressure helped in the regeneration of the substrate. The degassing procedure was carried out to remove pre-adsorbed gases.

3.8 Data Analysis

The manifold and sample cylinder were calculated from helium test. Then, the adsorption of hydrogen can be calculated by using manifold and sample void volumes with the density of hydrogen gas at each equilibrium pressure. The real adsorption data were corrected with the ratio obtained from the blank test. All specimens have been tested in the same manner to plot the number of hydrogen adsorbed as a function of equilibrium pressure.