CHAPTER III
EXPERIMENTAL

3.1 Materials and Equipments

3.1.1 *Materials and Chemicals*

3.1.1.1 Raw Material

This experiment used coconut shells for the production of activated carbon by carbonization and chemical activation process. The coconut shells were crushed and sieved to size of 4-6 mesh.

3.1.1.2 Adsorbents

The adsorbents used in this study were commercial activated carbon (coconut-, palm-, and bituminous coal-based activated carbons).

3.1.1.3 Gases for adsorption experiment

Gases for methane adsorption were high purity grade helium, high purity grade nitrogen, and ultra high purity grade methane (99.999% purity) (from Labgaz Thailand Co., Ltd.).

3.1.1.4 Chemical

Potassium Carbonate (from Merck, Germany) was used in activation process for produced activated carbon.

3.1.2 Equipment

The equipment for this research were volumetric apparatus, BET Surface area analysis, and Field Emission Scanning Electron Microscope (FE-SEM).

3.2 Experimental Procedures

3.2.1 Characterization of adsorbents

The physical characteristic of adsorbents was carried out by using the followings:

- BET surface area analysis

BET surface area, micropore volume, total pore volume, and average pore diameter of the adsorbents were measured with the BET method on a Quantachrom/Autosorb1-MP instrument. Before analyzed, the adsorbent was removed the humidity on surface by out gassed under vacuum at 150 °C for approximately 20 hours. After that, the adsorbent was analyzed by nitrogen adsorption isotherms at -196°C.

- S_{BET} (BET surface area) was obtained from multiple point BET (Brunauer-Emmett-Teller) method which was derived from BET equation.

$$\frac{1}{W((P_0/P)-1)} = \frac{1}{W_m C} + \frac{C-1}{W_m C}\left(\frac{P}{P_0}\right) \tag{3.1}$$

Where: W = Weight of gas adsorbed at a relative pressure (P/P_0)

W_m = Weight of adsorbate forming a monolayer of surface coverage

C = A BET constant related to the energy of adsorption in the first adsorbed layer; its value is an indication of the magnitude of the adsorbent/adsorbate interactions.

- Micropore volume (V_{DR}) was obtained from DUBININ-RADUSHKEVICH (DR) method, which was calculated from the DR equation as followed.

$$V = V_0\left[-\left(\frac{A}{\beta E_0}\right)^2\right] \tag{3.2}$$

Where: V = Volume of gas adsorption

V_0 = Micropore volume

E_0 = Characteristic energy of adsorption

A = Free adsorption energy

β = Affinity coefficient

- Total pore volume was calculated from the amount of vapor adsorbed at a relative pressure close to unity, with the assumption that the pores were filled with liquid adsorbate.

- DR micropore was obtained DUBININ-RADUSHKEVICH (DR) method, which was calculated from the DR equation as followed.

$$W = W_0 \exp\left[-\left(\frac{RT\ln(P_0/P)}{\beta E_0}\right)^2\right] \tag{3.3}$$

Where: W = Weight of gas adsorbed at a relative pressure (P/P_0)

W_0 = Saturated weight of gas adsorbed

E = Characteristic adsorption energy

β = The affinity coefficient

- Average pore diameter

- Field Emission Scanning Electron Microscope (FE-SEM)

The morphology of activated carbon was investigated by using the Field Emission Scanning Electron Microscope (FE-SEM), Hitachi S-4800, with an accelerating voltage of 2 kV and platinum coated under vacuum condition.

3.2.2 Methane Adsorption by Activated Carbons

3.2.2.1 Samples Preparation: Activated Carbon

Activated carbons in this research were commercial activated carbons (coconut-, palm-, and bituminous coal-based activated carbons) and coconut-based activated carbons by chemical activation process from 3.2.3. The activated carbons were crushed and sieved to a size range of 20-40 mesh then, dried in the oven at 100°C for 24 hours. After degassing the activated carbons, put into the sample cell and weighed. Finally the sample cell was placed in the volumetric apparatus.

3.2.2.2 Adsorption Experiment

- Volumetric Apparatus

The volumetric apparatus was used for study methane adsorption on activated carbons. This apparatus consists of a sample holder, a vacuum pump, and pressure transducer. Ultra high purity grade methane (99.999% purity) was used in the adsorption study. The schematic diagram of volumetric apparatus for this research is shown in Figure 3.1.

A gas reservoir was a high pressure stainless steel reactor and the pressure regulator with 4,000 psig maximum limit was installed to control a gas flow rate into the system. A K-type thermocouple was used for measuring the temperature of gas inside the reactor. The system pressure was measure by pressure transducer in the range of 0 to 3,000 psig with 0.13% error.

For each experiment, about 1.0-2.0 g of adsorbents was weighed and put into the sample holder. Next, the adsorbent was degassed by using a rotary vacuum pump prior to the methane adsorption. The temperature was controlled for each adsorption experiment. The pressures of gas were recorded before and after each gas expansion.

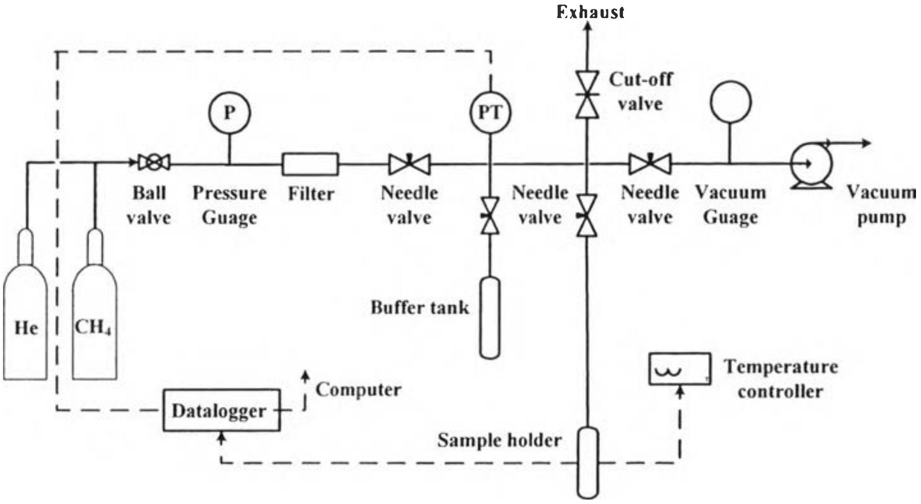

Figure 3.1 Schematic of the volumetric apparatus.

3.2.1.3 Measurement of methane adsorption and calculation

The pressure transducer was calibrated for every adsorption experiment. The vacuum pressure of -14.7 psi was used as the reference pressure. With this pressure, the relative was set to zero under vacuum condition.

- Determination of the Sample Holder Volume Using Helium

The volume of the sample holder was determined by helium expansion at 30°C, based on the assumption that no helium was adsorbed on the adsorbents. The pressures before and after each helium expansion were recorded.

To calculate the volume of instrument after helium expansion, V_2. Ideal Gas Law was used as followed.

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \tag{3.4}$$

Where: P_1 = Pressure of helium before helium expansion
V_1 = Volume of the system excluding volume of sample holder
T_1 = Temperature before helium expansion
P_2 = Pressure of helium after helium expansion

V_2 = Total system volume

= $V_1 + V_{\text{sample holder}}$

T_2 = Temperature after helium expansion

- Determination of the Methane Adsorption on Adsorbents

Determination of the methane adsorption was carried out at different constant temperatures; 35, 40, and 45°C; and pressure up to 1,000 psia. Temperature was heated up to the temperature at = 35, 40, and 45°C. At desired pressure, methane was introduced from a high pressure cylinder into a sample holder. During the experiment, the time to reach the equilibrium of methane adsorption was within approximately 20 min. The methane pressures were recorded before and after each methane expansion.

The ideal gas law and conservation of mass were also used for determining the amount of methane adsorbed on the adsorbents. The amounts of methane adsorbed by activated carbons can be obtained by the following equation.

$$n_{ad} = n_{ad-1} + \frac{P_i V_1}{zRT_i} - \frac{P_{f-1} V_2}{zRT_{f-1}} - \frac{P_f (V_1 + V_2)}{zRT_f} \tag{3.5}$$

Where: n_{ad} = Total amount methane adsorbed by activated carbons (mole)

n_{ad-1} = Amount methane adsorbed at previous stage (mole)

P_i = Initial pressure of methane before methane expansion into the sample holder (psia)

P_{f-1} = Final pressure of methane after methane expansion into the sample holder in the previous stage (psia)

P_f = Final pressure of methane after methane expansion into the sample holder (psia)

V_1 = Volume of manifold excluding volume of sample holder (cm^3)

V_2 = Volume of the sample holder (cm^3)

Z = Compressibility factor of methane

T_i = Initial temperature of methane before methane expansion into the sample holder (K)

T_f = Final temperature of methane after methane expansion into the sample holder (K)

T_{f-1} = Final temperature of methane after methane expansion into the sample holder in the previous stage (K)

R = Gas constant, 82.0578 atm cm^3/mol K

3.2.3 Production of activated carbons

3.2.3.1 Carbonization process

20 g of raw coconut shell was weighed and then put into the stainless steel reactor which was then placed in the furnace. Next, the coconut shell was heated up at the rate of 10 °C/min to final temperature at 400, 500, and 600 °C and held for 30, 60, 90, 120, and 150 min while the nitrogen flow passing it at the flow rate 150 ml/min. The product from this process called "char".

3.2.3.2 Activation process (Chemical activation process)

Approximate 10 g of char (400 °C, 60 min) was impregnated with potassium carbonate solution with ratio 1:1 by weight and dried in the oven at 100°C for 24 hours. The chars was then placed in a stainless steel reactor and then put in the furnace. After that, the reactor was heated up at the rate of 10 °C/min to a final temperature at 600 °C and held at this temperature for 60 min, 120 min, and 180 min under nitrogen flow rate at 100 ml/min. The carbon product was washed with DI water until pH $\approx$ 7. Finally, the coconut shell activated carbons were characterized by BET Surface Area Analysis, and Field Emission Scanning Electron Microscope (FE-SEM).

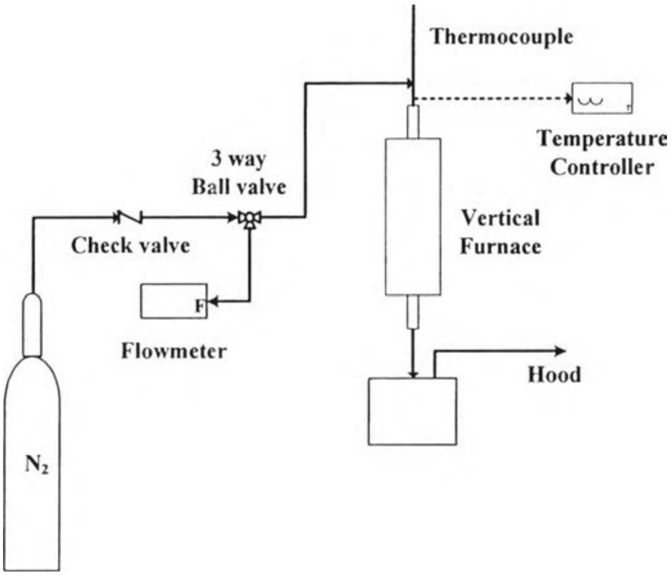

Figure 3.2 Schematic diagram of apparatus to produce activated carbon.

The burn-off, θ (%wt), is calculated as follows:

$$\theta = \frac{W_i - W_t}{W_i} \times 100\% \tag{3.6}$$

Where: W_i is the initial mass of the char (or activated carbon), (g)

W_t is the mass of the char (or activated carbon) after carbonization (or activation), (g)

The yield is calculated as follows:

$$\text{yield}(\%) = \frac{W_t}{W_i} \times 100\% \tag{3.7}$$

Where: W_i is the initial mass of the char (or activated carbon), (g)

W_t is the mass of the char (or activated carbon) after carbonization (or activation), (g)