

CHAPTER III

EXPERIMENTAL

3.1 Equipment and Chemicals

The commercial activated carbon, granular activated palm shell based carbon was used as an adsorbent supplied by CARBOKARN Co., Ltd., (Thailand). Piperazine anhydrous ($\geq 99\%$, Merck) was dissolved in ethanol (AR grade, RCI Labscan, Thailand) for the impregnation of activated carbon. The actual piperazine loading on the activated carbon was determined by gas chromatography (PERICHROM PR2100, France) using a flame-ionization detector (FID) with a DB-5 column 0.53 mm id x 1 μm film thickness x 30 m length (J&W Scientific, USA). Thermal conductivity detector (TCD) with column, Rt®-Q-BOND 0.53 mm id x 20 μm film thickness x 30 m length (RESTEK, USA) was also installed in PERICHROM PR2100 gas chromatography for CO₂ adsorption experiment. To premix 4% CO₂, mass flow controllers (GFC 17) 0-200 STD mL/min for nitrogen (N₂) and carbon dioxide (CO₂), D-connect with LCD display, which were purchased from AALBORG, USA, to measure and control the gas flow. A relief valve (SS-RL3S4, Swagelok, USA) was used to control a fixed pressure for ventilation and enabling small quantity of 4% CO₂ gas to flow through a rotameter. The rotameter (PMR1-010266, Cole-Parmer) was used to adjust and controlled the volumetric flow (mL/min) but to ensure the actual volumetric flowrate before entering the adsorption column, a bubble flowmeter (Model 4068, Alltech) was used.

3.1.1 Experimental Setup

In Figure 3.1, the outlet flow rate released from the gas cylinders is controlled by mass flow controllers before mixing premixed 15 % CO₂/N₂ with pure N₂ in the mixing chamber to obtain 4 % CO₂. The mixed gas is then controlled to a fixed pressure for ventilation and enabling a small quantity of 4 % CO₂ gas to pass through the rotameter which the flow rate will be adjusted to 5 mL/min determined by a bubble flow meter. Before testing CO₂ adsorption through the adsorption column, the 4 % CO₂ gas is analyzed by a gas chromatography-thermal conductivity detector (GC-TCD) in comparison with the calibration curve of CO₂ gas shown in

Appendix D. The adsorption column is a tubular glass flow adsorber with an inner cell diameter of 4 mm, outer cell diameter of 6 mm, and 39 cm long. It is vertically oriented for the even distribution of adsorbent. The column, covered with a 40 cm long insulator wound with a heating tape, is used to maintain a stabilized temperature throughout the whole experiment. In the top 18.5 cm of the column, the adsorbent was packed and emplaced with glass wool at the top and the bottom to support the activated carbon, so the feed was running against gravity. The thermocouple was inserted at the bottom of the column to determine the temperature of internal column.

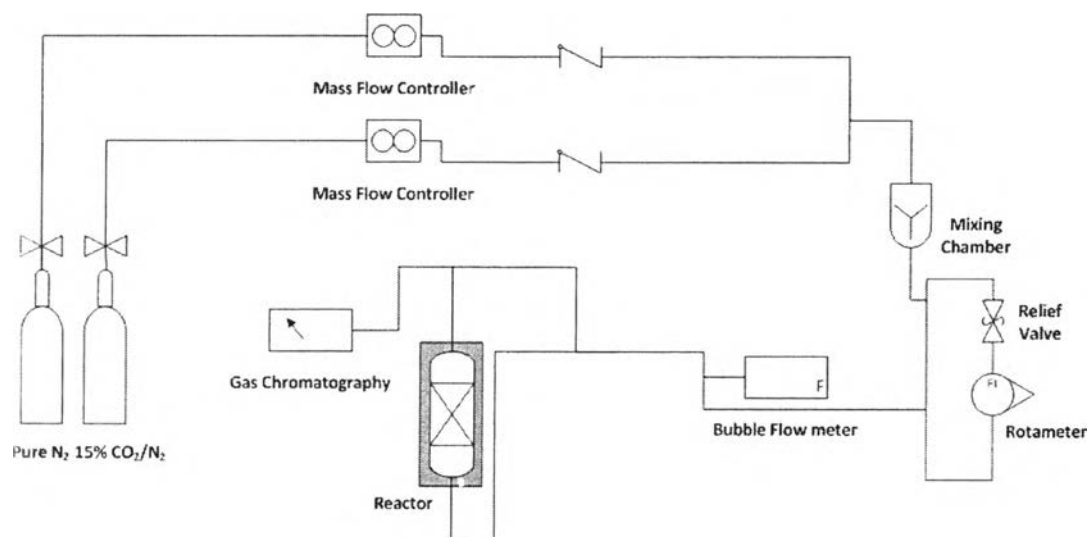


Figure 3.1 Schematic flow diagram for CO₂ adsorption.

3.2 Experiment procedures

3.2.1 Preparation of activated carbon

To obtain a dry purified and proper size activated carbon, a granular size activated carbon was crushed and sieved to obtain a 20-40 mesh size followed by heating in a 60 °C oven at for 6 h and kept in the desiccators at room temperature to avoid the moisture effect. The constant mesh size was controlled throughout the experiments to fulfill the adsorption column, as well as to optimize the pressure drop.

3.2.2 Preparation of impregnated activated carbon

The dry activated carbon of 20-40 mesh size was impregnated with piperazine by varying three different weight percent, 23.07 wt %, 28.57 wt % and 33.33 wt % to the total weight of piperazine and activated carbon. For 23.08 wt %, 0.15 g of piperazine crystals were dissolved in 5 mL of ethanol until completely dissolved then mixed with 0.5 g of activated carbon. The mixtures were mixed in a 50 mL beaker at 500 rpm using a magnetic bar on a stirring hot plate (C-MAG HS10 IKA®, USA) for 2 h by sealing the top with the parafilm, after that it was filtered using a suction pump. The impregnated piperazine then was shifted to dry in the oven at 60 °C for 1 ½ h to completely remove ethanol. The procedure was repeated for the preparation of 28.57 wt % and 33.33 wt % with 0.2 g and 0.25 g of piperazine. The actual piperazine impregnated on activated carbon was accurately analyzed by GC-FID.

3.2.3 Preparation of moisturized activated carbon and impregnated activated carbon

The dry activated carbon and impregnated activated carbon kept in the desiccators were equilibrated in a moisturized and close system for 20 h at room temperature.

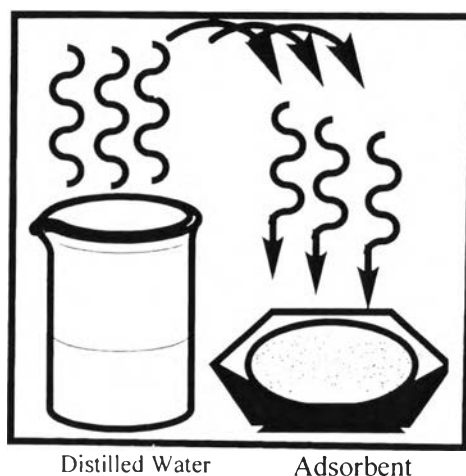


Figure 3.2 Moisturized adsorbent at room temperature.

3.3.1 Characterization of activated carbon

3.3.1.1 Surface area characterization of adsorbents

Surface area analyzer (Autosorb-1MP, Quantachrome, USA) was used to analyze the surface area of the adsorbent. The specific surface area, S_{BET} , was determined from the linear part of the Brunauer-Emmett-Teller (BET) equation and the calculation of pore size distribution was performed using Barret-Joyner-Halenda (BJH) equation using the full isotherms method. These parameters were calculated to identify the effects before and after piperazine loading via the impregnation method.

3.3.1.2 Surface morphology characterization

Scanning electron microscope (SEM; S-4800, Hitachi, Japan) was used to analyze the surface morphology of the adsorbent. The sample was placed on the carbon tape which was coated with platinum under vacuum. The SEM images were captured at a magnification of 2,000 and 100,000 to distinguish the pore site distribution of the activated carbon before and after piperazine loading via the impregnation method.

3.3.1.3 Measurement of thermal stability

The thermal stability of pure activated carbon and impregnated activated carbon was determined in a nitrogen atmosphere by thermogravimetric differential analysis (TG-DTA, Perkin Elmer Thailand Co., Ltd). 4–20 mg of sample was weighed on the heating pan in the chamber which was heated at a ramping rate of 5 °C/min at room temperature with 90 mL/min of N_2 flow to a final temperature of 900 °C.

3.3.1.4 Measurement of degree of piperazine loading (wt %) on the adsorbent using GC-FID (PR2100)

The impregnated activated carbon was crushed into fine particles, which was then weighed and dissolved with 5 mL of ethanol. The solution was heated at 60 °C and stirred at 250 rpm for an hour to complete dissolution of piperazine from the activated carbon. After 1 h, the solution was cooled to room

temperature then the volume was made up to 10 mL with ethanol. The fine particle of activated carbon was filtered using filter paper No. 1. 0.04 μL of the filtrate was injected using a 0.5 μL syringe (SGC syringe) into the gas chromatography-flame ionization detector (GC-FID) via heated injection port at 200 $^{\circ}\text{C}$ with the split flow of 10 mL/min and helium as a carrier gas. The DB $^{\circ}$ -5 column with 0.53 mm id x 1.0 μm film thickness x 30 m length was used to operate at an initial temperature of 50 $^{\circ}\text{C}$, a ramp rate of 10 $^{\circ}\text{C}$ /min and isothermal temperature of 120 $^{\circ}\text{C}$. The concentration of piperazine was quantitatively compared with a calibration curve of standard piperazine as presented in Appendix D.

3.3.1.5 Measurement of degree of piperazine loading (wt%) using CHN Analyzer

CHN Analyzer (Truespec CHNSO, LECO, Thailand) was used. In this technique, 0.15 g of impregnated activated carbon was weighed and wrapped with the CHN foil to be combusted in order to break down the substances into simple compounds for elemental analysis. Then the 3 elemental compositions including Carbon (C), Hydrogen (H) and Nitrogen (N) were quantified by the device software.

3.3.2 CO₂ Adsorption-Desorption Experiment

3.3.2.1 Preliminary test for CO₂ adsorption

To obtain the adsorption capacity and breakthrough curve for packed bed CO₂ adsorption, Rt $^{\circ}$ -Q-BOND column with 0.53 mm id x 20 μm film thickness x 30 m length was used to operate at an isothermal temperature of 40 $^{\circ}\text{C}$. The GC-TCD injection port was heated to 100 $^{\circ}\text{C}$ with the split flow of 8 mL/min and helium as a carrier gas. In typical CO₂ adsorption, 0.5 g of adsorbent was filled into a tubular flow glass adsorber column that was heating tape wounded around and covered with an insulator. For line cleaning, the column without the adsorbent (blank adsorber) was installed into the line, and then pure N₂ gas was purged along the adsorption line for 30 mins. Preliminary test runs were undertaken into 2 separate sets that was dry and saturated unmodified adsorbents and impregnated adsorbents.

After line cleaning-up, 0.5 g of adsorbent (pre-dried at 60 °C for 1 h or moisturized adsorbent) was loaded in the column, while purging with N₂ gas at 113 mL/min. Then, 4 % premixed CO₂ of dry gas at 5 mL/min was allowed to flow into the packed bed adsorber to carry out the experiment at room temperature and atmospheric pressure until the CO₂ concentrations of feed gas at the outlet of adsorber reached equilibrium. The concentrations of CO₂ in the downstream in terms of chromatogram were continuously monitored using WiniLab III V4.6 program in the computer.

The dynamic adsorption capacity of the adsorbent (Q_{ads}) was calculated by Eq. (3.1),

$$Q_{ads} = \frac{FC_0t_q}{W} \quad (3.1)$$

Where F (mol/min) is the total molar flow of feed gas, C_0 is the CO₂ concentration of the inlet stream, W is the mass of solid adsorbent loaded in the column, and t_q (min) is the stoichiometric time which was determined from the breakthrough curve according to Eq. (3.2) via MATLAB software version 7.10.0.499 (Guerreero *et al.*, 2010).

$$t_q = \int_0^{\infty} \left(1 - \frac{C_A}{C_0}\right) dt \quad (3.2)$$

Where C_0 and C_A are the CO₂ concentrations of inflow and outflow gas stream of the column, respectively.

3.3.2.4 Effect of Adsorption Temperature

The temperature effects on adsorption were studied at 298 K, 316 K and 326 K at atmospheric pressure to find the optimum temperature that influences the most CO₂ adsorption capacity.

3.3.2.2 Adsorbent regeneration

To investigate the regenerability efficiency of the adsorbent, adsorption-desorption cycle measurement were carried out. After the CO₂ concentrations of feed gas at the outlet of adsorber reached equilibrium, the adsorption bed was then continuously regenerated by sweeping with 113 mL/min pure nitrogen at room temperature until the chromatogram showed no sign of CO₂ response during desorption. Then CO₂ adsorption was repeated and compared with the previous adsorption.