CHAPTER III
EXPERIMENTAL

3.1 Equipment and Chemicals

In this study, two types of adsorbents were investigated, the commercial activated carbon which was granular activated palm shell based carbon supplied by CARBOKARN Co., Ltd., (Thailand). The other was the commercial silica gel, particle size 230-300 mesh, pore size 60 Å (technical grade) which was purchased from Sigma-Aldrich (Singapore). Piperazine anhydrous ($\geq$ 99%, Merck) was dissolved in ethanol (AR grade, RCI Labscan, Thailand) for the impregnation in activated carbon and silica gel. The actual piperazine loading on the adsorbents (activated carbon and silica gel) 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 CO_2 adsorption experiment. To feed 15% CO_2, mass flow controllers (GFC 17) 0-200 STD mL/min for nitrogen (N_2) and carbon dioxide (CO_2), 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 CO_2 gas to flow through a rotameter. The rotameter (PMR1-010266, Cole-Parmer) was used to adjust and controlled the volumetric flow (mL/min) however a bubble flowmeter (Model 4068, Alltech) was used to ensure the actual volumetric flowrate before entering the adsorption column. To maintain a constant pressure of CO_2 gas, back pressure regulator (GH30XTHAXXXG, Conoflow) was used.

3.1.1 Experimental Setup

Setup of CO_2 adsorption diagram is shown in Fig 3.1, the outlet flow rate released from the gas cylinders is controlled by mass flow controllers for line of 15 % CO_2/N_2 and line of pure N_2. The 15% CO_2 passed through the rotameter which

the flow rate is adjusted to 15 mL/min determined by a bubble flow meter. Before testing CO_2 adsorption in the adsorption column, the 15% CO_2 gas was analyzed by a gas chromatography-thermal conductivity detector (GC-TCD) in comparison with the calibration curve of CO_2 gas. The adsorption column was a tubular flow stainless steel adsorber with an inner cell diameter of 4 mm, outer cell diameter of 6 mm, and 31 cm long. It was vertically oriented for the even distribution of adsorbent. At the top and bottom 10 cm of the column, the adsorbent was packed and emplaced with glass wool to support the adsorbent and covered with glass bead at the top layer, and the feed was running against gravity. To maintain a constant pressure of CO_2 gas, back pressure regulator was used. A pressure gauge was used to monitor the column pressure. The concentrations of product stream were finally analyzed by a gas chromatograph. The thermocouple was inserted at the bottom of the column to determine the temperature of internal column.
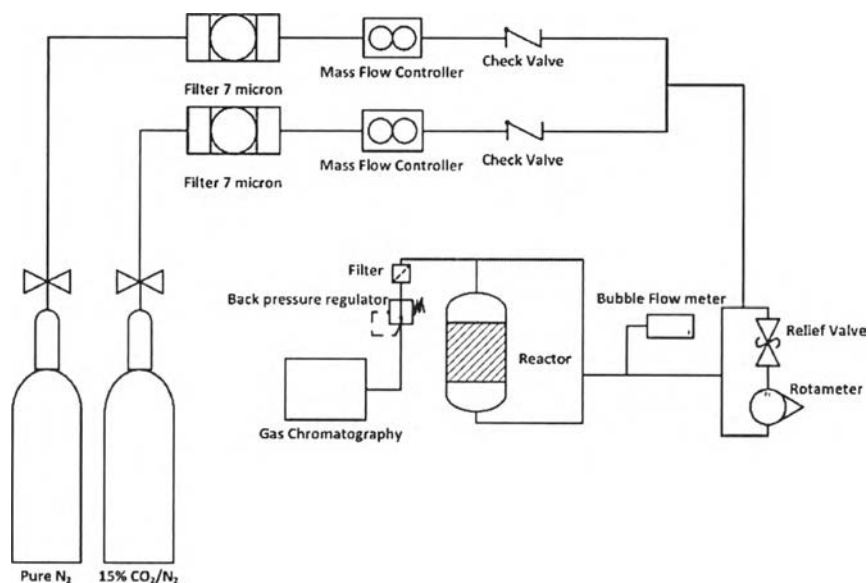

Figure 3.1 Schematic flow diagram for CO_2 adsorption.

3.2 Experiment procedures

3.2.1 Preparation of Adsorbents

To obtain a dry cleaned and proper size activated carbon, a granular size activated carbon was ground by milling jar and sieved to acquire a 20-40 mesh

size followed by heating in a 60 °C oven 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. For silica gel (230-300 mesh), it was used without further pretreatment.

3.2.2 Preparation of Piperazine Impregnation onto Adsorbents

Piperazine (PZ) in adsorbent (activated carbon and silica gel) was prepared by wet impregnation. The dry activated carbon of 20-40 mesh size was impregnated by varying four different weight percent of piperazine, 2 wt %, 5 wt %, 10 wt % and 20 wt % to the total weight of piperazine and activated carbon. For example, 2 wt %, 0.02 g of piperazine crystals was dissolved in 5 mL of ethanol until finally dissolved then mixed with 1.0 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 filtered to dry in the oven at 60 °C for 1 ½ h to completely eliminate ethanol. The procedure was repeated for the preparation of the piperazine impregnated silica gel with 5 wt %, 10 wt % and 20 wt % i.e. 0.05 g, 0.10 g and 0.20 g of piperazine. The silica gel-PZ was prepared in the same way as the activated carbon. The actual piperazine impregnated on adsorbent was accurately analyzed by GC-FID.

3.3 Methodology

3.3.1 Characterization of Adsorbents

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 porous adsorbent. The specific surface area, S_{BET}, was determined from the linear part of the Brunauer-Emmet-Teller (BET) equation that is the most frequently used by assumed the adsorbent surface is uniform, all adsorption occurs through the same mechanism and the monolayer is formed. The different methods are suitable for the different pore sizes. To decide the amount of pores with the size, the shape of the pores is assumed to be homogenous for all pores. In this work, the micropore volume was estimated by using the t-plot

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) TM3000 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 40 to 20,000 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 adsorbent and impregnated adsorbent was determined in a nitrogen atmosphere by thermogravimetic 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 10 °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, and then the adsorbent (impregnated activated carbon and impregnated silica gel) was weighed and dissolved in 10 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 adsorbent. 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 adsorbent was filtered using filter paper No. 1. 0.04 μL of the filtrate was injected using a 1 μL syringe (SGC syringe) into the gas chromatography-flame ionization detector (GC-FID) via heated injection port at 200 °C with the split flow of 10 mL/min helium carrier gas. The DB® -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 °C, a ramp rate of 10 °C /min and isothermal temperature of 120 °C. The concentration of piperazine was quantitatively compared with a calibration curve of standard piperazine as presented in Appendix B.

3.3.2 CO₂ Adsorption-Regeneration

3.3.2.1 Preliminary Test for CO₂ Adsorption

In the CO_2 adsorption and regeneration experiments, adsorbent was tested in a stainless steel reactor. The conditions for each experiment performed were 15 mL/min of 15 % CO_2 feed gas flow at room temperature (25 °C). The effects of adsorption pressure were carried out at various pressures, i.e. 14.7, 30, 50, and 70 psi. To obtain the adsorption capacity and breakthrough curve for packed bed CO_2 adsorption, Rt®-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 °C. The GC-TCD injection port was heated to 100 °C with the spilt flow of 8 mL/min helium carrier gas.

After line cleaning-up, 1.0 g of adsorbent was filled into a tubular flow stainless steel adsorber column, while purging with N_2 gas at 113 mL/min. Then, 15% CO_2 of dry gas at 15 mL/min was allowed to flow into the packed bed adsorber to carry out the adsorption at room temperature and atmospheric pressure until the CO_2 concentrations of feed gas at the outlet of the adsorber reached equilibrium. The concentrations of CO_2 in the downstream in terms of chromatogram were continuously monitored using computer and WiniLab III V4.6 program in the computer.

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

$$Q_{ads} = \frac{F C_0 t_q}{W} \tag{3.1}$$

Where F (mol/min) is the total molar flow of feed gas, C_0 is the CO_2 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).

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

Where C_0 and C_A are the CO_2 concentrations of inflow and outflow gas stream of the column, respectively.

3.3.2.2 Effect of Adsorption pressure

The pressure effects on adsorption were studied at atmospheric pressure, 30 psi, 50 psi and 70 psi at the room temperature to find the optimum pressure that influences the most CO_2 adsorption capacity.

Table 3.1 Operating parameters of adsorption pressure system

Condition	Operation	Pressure (psi)
15%CO_2/N_2 15 mL/min	Feed	14.7 30 50 70
99.99% N_2 113 mL/min	Purge	14.7

3.3.2.3 Adsorbent Regeneration

To investigate the regenerability efficiency of the adsorbent, adsorption-regeneration cycle measurement were carried out. In this study, the column was first fed with 15% CO_2 at the constant pressure (e.g. atmospheric pressure, 30 psi, 50 psi and 70 psi). The flow rate was kept at 15 mL/min. After the CO_2 concentrations of feed gas at the outlet of adsorber reached equilibrium, the column pressure was released to the atmosphere, the adsorption bed was then continuously regenerated by purging with 113 mL/min pure nitrogen at atmospheric pressure and room temperature until the chromatogram showed no sign of CO_2 response during desorption. Then CO_2 adsorption was repeated and compared with the previous adsorption.