CHAPTER III
EXPERIMENTAL

3.1 Materials

Adsorbents (NaX, and NaY zolites) were provided from Institut Français du Pétrole (IFP, France).

3-methylthiophene (C_5H_6S, 99%), benzothiophene (C_8H_6S, 97%), dibenzothiophene ($C_{12}H_8S$, 99%), and decane ($C_{10}H_{22}$, 99%) were supplied by ACROS ORGANICS (New Jersey, USA).

Isooctane (C_8H_{18}, 99.5%) was supplied by FAMITALIA CARLO ERBA (Milan, Italy).

3.2 Experimental

3.2.1 Adsorbent Characterization

3.2.1.1 Surface Area Analysis

Surface area of adsorbents was determined by BET surface area analyzer (Thermo Finnigan, Sorptomatic 1990 SERIES). The surface areas of NaX and NaY zeolites were analyzed by using nitrogen gas adsorption. To eliminate adsorbed volatile compounds from micropore, adsorbents were dried and evacuated by turbo pump at 300 °C for at least 15 hrs.

3.2.1.2 Thermo Gravimetric Analysis

Thermo Gravimetric Analysis (TGA) technique was used to determine the phase transfer of adsorbents in order to minimize the effect of water adsorbed on adsorbents and limit the amount of water content in adsorbents not exceeded 5%. Weight losses in adsorbents upon temperature were investigated to indicate the proper temperature for treating the adsorbents before use. Each sample was measured by using Thermo Gravimetric Analyzer (Du Pont, TGA 2950). The specimen was heated up from 30°C to 800°C with the rate of 10°C/min for zeolite adsorbents. The mass changes

during temperature increase were monitored and recorded using the TGA instrument thermal analyst system.

3.2.2 Adsorption of Sulfur Compounds from Simulated Transportation Fuels

3.2.2.1 Preparation of Simulated Transportation Fuels

Simulated transportation fuels used in this study were decane and isooctane as a model for diesel and gasoline, respectively. The sulfur compounds used were benzothiophene (BT) and 3-metylthiophene (3MT) for simulated gasoline and dibenzothiophene (DBT) for simulated diesel. Thus, the simulated fuels were prepared by mixing benzothiophene or 3-methylthiophene with isooctane for simulated gasoline and dibenzothiophene with decane for simulated diesel.

3.2.2.2 Equilibrium Adsorption

Batch liquid adsorption experiments were carried out in a stainless steel cylindrical reactor with a volume of 100 ml and a top plate held in place with five bolts. The top plate has two ports: one for withdrawing the samples and another for inserting thermocouple into the reactor. The hollow rectangular basket containing an adsorbent was placed inside the reactor by screwing on the top plate. Heat was provided by electrical wired heater, which temperature was controlled by a PID controller. A Teflon o-ring was placed between the top plate and the reactor to prevent leak. The mixing was achieved by magnetic bar placed inside the reactor to constantly stir the solution in the reactor. The experiment set-up is shown in Figure 3.1. The experiment was started with adding the sulfur-containing feed into the reactor. The appropriate amount of the adsorbent was packed in the basket. The basket was then placed inside the reactor and the top plate was closed. The temperature was set at desired temperature using a PID controller. The equilibrium time was first determined for each system of 3-methylthiophene, benzothiophene, and dibenzothiophene. Once the system reached equilibrium, samples were withdrawn by using syringe and then analyzed by gas

chromatography (Agilent Technologies, 6890N) with FID detector and HP-1 Column (J & W Scientific).

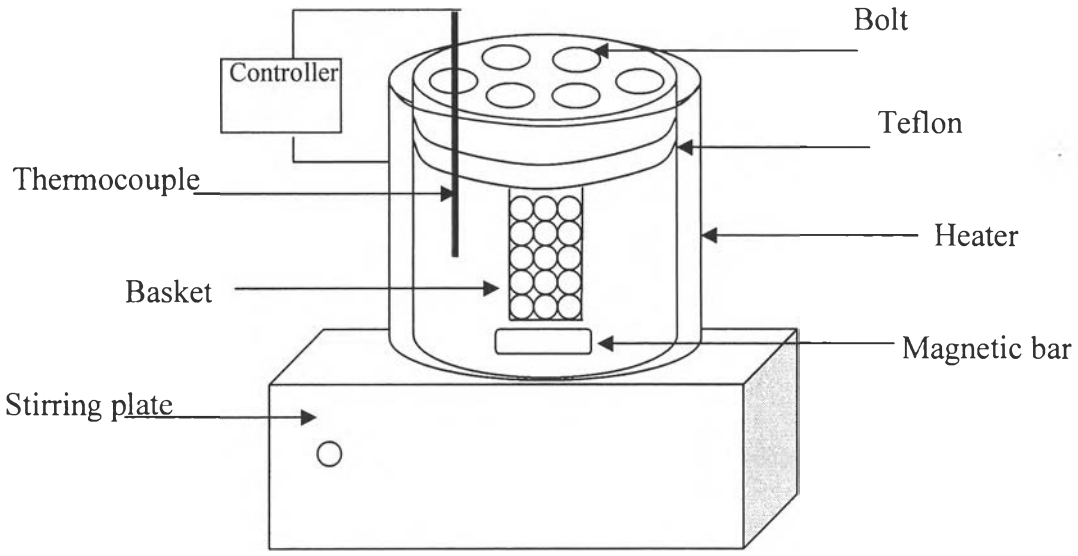

Figure 3.1 The experimental set-up for equilibrium adsorption experiments.

3.2.2.3 Sulfur Compounds Analysis

Sulfur compounds were analyzed by using gas chromatography (Agilent Technologies, 6890N) with FID detector and HP-1 Column (J & W Scientific). Concentration of sulfur compound in the liquid phase was determined before and after adsorption. A simple mass balance was performed to determine amount of sulfur adsorbed on the adsorbent. Then the adsorption isotherms can be constructed to evaluate the adsorption capacity and selectivity of the adsorbent.

3.2.2.4 Adsorption Isotherm of Sulfur Compounds

Adsorption isotherms of sulfur compounds were constructed by plotting the adsorbed amounts of sulfur compound on the adsorbent versus equilibrium concentration of sulfur compound in batch reactor. At the beginning, the isotherms were constructed for the sulfur adsorption at 25 degree centigrade. Fuel to adsorbent weight ratio used in this study was initially fixed at 85. The maximum of equlibrium concentration of sulfur compounds in the system was limited not higher than 2000 ppmw.

3.2.2.5 Model of Adsorption Isotherm on both Zeolites

After the adsorption, isotherms were constructed as described above, the adsorption data were fitted with an appropriate model. The model adsorption isotherm used in this study is Langmiur isotherm which can be described as follows:

$$Q = \frac{Q_{max} C_e}{k + C_e}$$

Q = adsorption capacity (mmol/g)

Q_{max} = maximum adsorption capacity (mmol/g)

k = adsorption affinity (μmol/g)

C_e = equilibrium concentration (μmol/g)

3.2.2.6 Effect of Temperature on Sulfur Compounds Adsorption

Effect of temperature on the adsorption of sulfur compounds was also examined at the temperatures of 25, 50, and 80 degree centigrade. Fuel to adsorbent weight ratio was fixed at 85. In addition, initial concentration of all sulfur compounds was set at 3000 ppmw.

3.2.2.7 Effect of Fuel to Adsorbent Weight Ratio on Sulfur Compounds Adsorption

Effect of fuel to adsorbent weight ratio on sulfur compounds adsorption was also detemined. Fuel to adsorbent weight ratio was varried at 85, 40, and 20, respectively. Temperature was kept at 25 degree centigrade whereas initial concentration of all sulfur compounds was fixed at 3000 ppmw.