

## CHAPTER III EXPERIMENTAL

### 3.1 Materials

The commercial zeolite X and Y in sodium form were provided by Institut Français du Pétrole (IFP), France. The properties of the zeolite are shown in Table 3.1 Diphenylmercury (99%) was purchased from ACROS ORGANICS, New Jersey, USA. The chemicals for condensate matrices; cyclohexane, ethylbenzene, n-heptane, *o*-xylene and toluene are 99% A.R. grade; 37% hydrochloric acid, 70% nitric acid and sodium hydroxide were purchased from Lab-Scan, Thailand. Heavy naphtha and condensate were provided by the Aromatics (Thailand) Public Company Limited (ATC), Rayong, Thailand. Mercury standard stock solutions ( $1000 \pm 3 \mu\text{g/ml}$  in 2%  $\text{HNO}_3$ ) was purchased from VARIAN, Australia. The stabilizing agent, potassium dichromate and reducing agent, sodium borohydride were obtained from CARLO ERBA REAGENTI, Italy.

**Table 3.1** Properties of commercial zeolites (Catalyst Analysis Laboratory, IFP, Lyon, France)

|   | Zeolite X | Zeolite Y |
|---|-----------|-----------|
| Si/Al                                       | 1.349     | 2.833     |
| Pellet diameter ( $\mu\text{m}$ )           | 641.624   | 726.217   |
| Pore volume ( $\text{cm}^3/\text{g}$ )      | 0.248851  | 0.271695  |
| Surface area ( $\text{m}^2/\text{g}$ )      | 681.026   | 651.015   |
| Crystalline size ( $\text{\AA}$ )           | 24.93     | 24.63     |
| Specific gravity of saturated pellet (g/ml) | 1.2036    | 0.9562    |
| Specific gravity of dried pellet (g/ml)     | 0.9358    | 0.8679    |

## 3.2 Experimental Equipments

### 3.2.1 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) technique was used to determine the phase transfer of adsorbents. The thermogravimetric analyzer (Du Pont TAG 2950, France) was programmed to heat up from room temperature to 700 °C with the rate of 10 °C/min for zeolite adsorbents under N<sub>2</sub> atmosphere (30 mL/min) The mass changes during temperature increase were monitored and recorded using the TA instrument thermal analyst system.

### 3.2.2 Cold Vapor Atomic Absorption Spectroscopy (CVAAS) Analysis

Cold vapor atomic absorption spectrometric analysis (CVAAS) technique was used to analyse Hg at the wavelength of 253.7 nm of mercury vapor. Each sample was measured by using the atomic absorption spectrometer (Varian model 300/400, Australia) equipped with a 10-cm-long path quartz cell and a mercury source lamp. The mercury was reduced to the elemental state by sodium borohydride reducing agent and aerated from solution into the absorption cell. All of the mercury in the sample solution placed in the reaction coil was chemically atomized and transported to the sample cell for measurement by collecting and integrating data over a 60 second time window while background correction was on. Absorbance (peak height) was measured as a function of mercury concentration.

#### 3.2.2.1 *Standard and Sample Preparation for CVAAS Technique*

A stock solution of mercury (II) nitrate Hg(NO<sub>3</sub>)<sub>2</sub> in 2% nitric acid containing  $1000 \pm 3$  µg/ml was diluted with deionized water to prepare standard solutions with mercury concentrations of 20, 50, 70 and 100 µg/l.

The organic sample of 0.5 ml was pipetted and transferred into a 60 ml PP type bottle. Five milliliters of concentrated nitric acid was added to decompose Hg-C bond. Then, ten drops of 1.33% (w/v) potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) solution was added to the oxidizing Hg. The solution mixture was left for 4 hours to ensure that all diphenylmercury was converted to mercury (II). Finally, the solution was diluted to 60 ml of distilled water.

### 3.2.2.2 Preparation of Reducing Agent for CVAAS Measurement

According to the operation manual of Varian instrument, sodium borohydride reducing solution (0.3% NaBH<sub>4</sub> in 0.5% NaOH) was prepared quantitatively by weighing 0.7500 g of NaBH<sub>4</sub> and transferring with water into a 250 ml volumetric flask. Thirty one milliliters of NaOH (12.5% v/v) was slowly added to the solution mixture and the solution was diluted to 250 ml with water. The solution was thoroughly mixed. The reducing solution was prepared freshly prior to the experiment.

### 3.2.3 Mercury Analyzer (NIC SP-3D)

The analyzer includes three units: a mercury atomizer (MA), a controller (MA-1) and a mercury detector (MD-1). The principle is to pyrolyse a sample and separate the mercury it contains. The separated mercury is then sent to the detector through the use of cold atomic absorption spectrometry.

First, a sample boat was inserted into the sample-heating furnace, mercury was pyrolysed to Hg<sup>0</sup> at 700°C then collected (amalgamation with gold) by the first mercury collector. The other combustion products were exhausted then the first mercury collector was heated again, Hg was released and recollected at the second mercury collector. The other combustion products were exhausted again through the exhausted filter. Then Hg<sup>0</sup> was released after the second collector was heated and passed through the absorption cell together with the carrier gas. The mercury was then measured.

#### 3.2.3.1 Standard and Sample Preparation for NIC Mercury Analyzer

The standard solutions were prepared by dissolving diphenylmercury with mixed xylene in three concentrations, 10, 50 and 100 µg/l. The standards were then kept at 4°C.

A layer of additive B was added to the sample boat (made of ceramic), slowly drop 100 µl of sample onto additive B, other layers of additive B is added and filled up the sample boat with additive M.

### 3.3 Adsorption Study

#### PART I: Batch system

##### 3.3.1 Quantity of Appropriate Zeolite

The solution of 2000 ppb of DPM in n-heptane was prepared. The mass of zeolite adsorbents, 0.1, 0.2, 0.3, 0.4 and 0.5 g were loaded to determine the removal efficiency according to the equation shown below.

$$\text{removal efficiency} = \frac{Hg_{\text{content on entry}} - Hg_{\text{content on discharge}}}{Hg_{\text{content on entry}}} \times 100 \quad (3.1)$$

##### 3.3.2 Adsorption of DPM in n-Heptane Substitute Condensate

The adsorption isotherm was constructed from batch adsorption data to determine the DPM sorption on adsorbents at various DPM concentrations. The DPM concentrations in n-heptane solution were varied from 20 to 160 ppm (by weight). A 0.1 g of adsorbents was added into the solution of n-heptane in a 15 ml screw cap plastic bottles (polypropylene type) and was shaken for 12 hours at 30, 40 and 50 °C. The solution was then withdrawn for the analysis of mercury by CVAAS.

##### 3.3.3 Adsorption of DPM in Heavy Naphtha

DPM was spiked into heavy naphtha. The adsorption was also performed in batch system at 30, 40 and 50 °C and the procedure mentioned in 3.3.2 was repeated.

##### 3.3.4 Effect of Alicyclic and Aromatic Hydrocarbons on DPM Adsorption

Cyclohexane, toluene, ethylbenzene and *o*-xylene were selected as the representatives of alicyclic and aromatic present in heavy naphtha. Each of these was introduced into the n-heptane substitute condensate separately and its concentrations were varied between 0, 5, 10, 20 and 25 wt% as a typical composition in heavy naphtha (see Appendices A), 2000 ppb of DPM was also spiked. The adsorption of DPM in the solution was carried out at 30°C

### 3.3.5 Effect of Water Content in Zeolite to Adsorption of DPM

The water content of 0, 1, 3, 5 and 7 wt% in zeolite were prepared in the following manner. One hundred milligrams of evacuated zeolite was quickly weighed in a 15 ml bottle (PP type) using 5 digit digital balance, then it was exposed to air (zeolite can adsorb humidity in air) until the desired weight was reached. Fifteen ml of 2000 ppb DPM contaminated n-heptane was filled up immediately. The adsorption of DPM was carried out at 30°C.

## **PART II: Continuous system**

### 3.3.6. Pilot Operations

The work carried out on the pilot plant unit U844, IFP, Lyon, in a continuous system was studied in different means:

- Effect of acidity
- Effect of hydrocarbon matrix

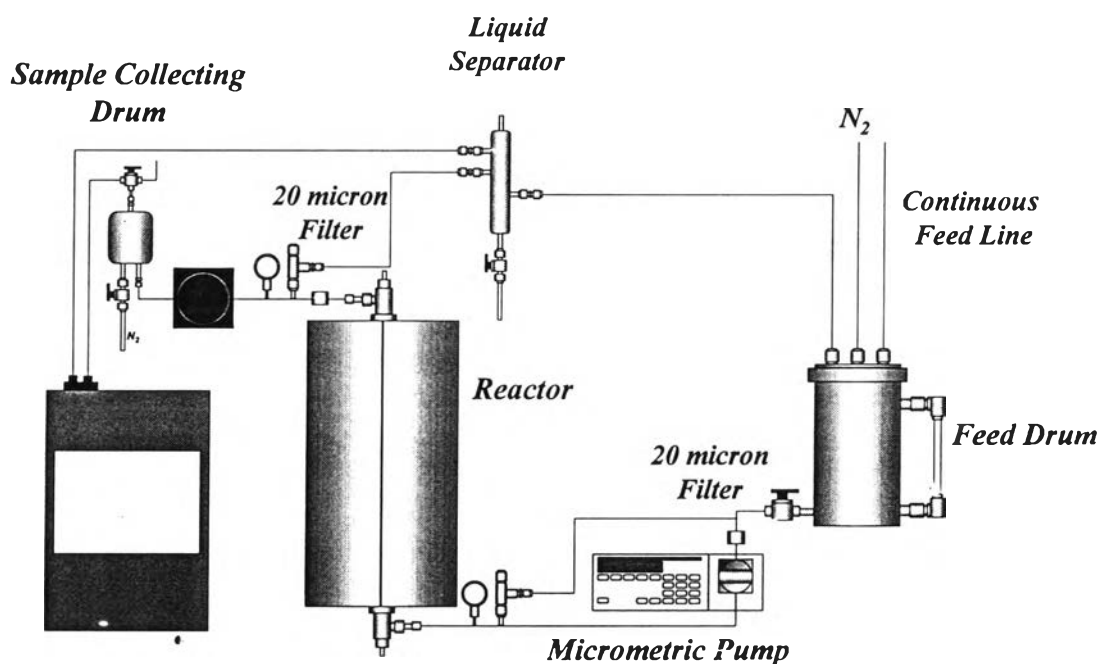
Three adsorbents were tested, NaX (micro balls), NaY (microballs) and CMG273 (by Axens). Two different kinds of feedstocks were used in this test, heavy naphtha and condensate. In addition, ASTM grade n-heptane was used for desorption phases and cleaning of the unit.

The solutions of 2000 ppb DPM in heavy naphtha and real condensate containing 180-200 ppb of total mercury were tested in the small pilot scale of unit number U84. In general, these tests were performed using a reactor (9 mm I.D., 32.6 cm height) in which the trapping mass was loaded and diluted with 1 ml of inert material (SiC, with an average particle size of 1.19 mm), to maintain a ratio of the volume of trapping mass to that of diluent at a constant value of 0.5. The experiments were operated at 70°C to maintain the system in liquid phase by using heated circulating oil and the pressure of the unit was set to 5 bars for mechanical maintenance reasons. The feedstock was pressurized under a light nitrogen pressure of 5 ml/min for pushing the solution throughout the process line. The feed flow rate was set to 7 ml/min. The adsorbent was packed between two inert packing materials of SiC. Prior to the actual testing, the adsorbent was pretreated ex-situ at 400°C under nitrogen atmosphere for 12 hours, then loaded inside the reactor and heated up to

200°C with passing nitrogen through to remove moisture, air and oil for at least 8 hours. Then, the unit was cooled down to 70°C and stopped the passing of nitrogen before injecting the feed for the experiment. The effluent was collected every hour by stocking in plastic HDPE, 60 ml bottles, and then analyzed by mercury analyzer (model NIC SP-3D, Japan).

### 3.3.6.1 Experimental Setup

This unit composed of a feed stock drum pressurized under a slight nitrogen flow. A micrometric pump injects the feedstock into a reactor containing the adsorbent. This reactor is heated by heated circulating fluid system. A sample collecting system. A waste disposal system and a liquid separator for environmental concerning reasons. The experimental setup is shown in Figure 3.1.



**Figure 3.1** Experimental setup (pilot unit 844, IFP, Lyon, France)