

CHAPTER III EXPERIMENTAL

This chapter explains the experimental setup to investigate the adsorption of various sulfur compounds from decane ($C_{10}H_{22}$) and isooctane (C_8H_{18}) solvents using NaX zeolite as adsorbents. Decane and isooctane were used to represent transportation fuels as diesel and gasoline, respectively. All adsorption experiments were conducted at ambient temperature whereas the desorption experiment was performed at 400°C .

3.1 Materials and Equipment

3.1.1 Materials

NaX zeolite used as adsorbent in this experiment was provided by Institut Français du Pétrole (IFP, France). The properties of this adsorbent are summarized in Table 3.1.

Table 3.1 Properties of NaX zeolite used in this experiment

Properties	NaX
Si/Al	1.349
Pellet Diameter (μm)	641.624
Pore Volume (cm^3/g)	0.248851
Surface area (m^2/g)	681.026
Crystalline size (A°)	24.93
Aperture (A°)	7.4

Three model thiophenic sulfur compounds used in this study which are 3-methylthiophene (C_5H_6S , 99%), benzothiophene (C_8H_6S , 97%) and dibenzothiophene ($C_{12}H_8S$, 99%) were purchased from ACROS ORGANICS from New Jersey, USA. Decane ($C_{10}H_{22}$, 99%) representing diesel was also purchased

from this company. Isooctane (C_8H_{18} , 99.5%) used to represent gasoline was supplied by FAMITALIA CARLO ERBA from Milan, Italy. The physical properties of sulfur compounds and simulated transportation fuels are listed in Table 3.2.

Table 3.2 Physical properties of sulfur compounds and simulated transportation fuels

Material	Molecular weight	Boiling point (°C)	Density (g cm ⁻³)
Isooctane	114.23	99	0.692
Decane	142.15	171-174	0.735
3-Methylthiophene	98.612	114 at 738 mm Hg	-
Benzothiophene	134.195	221	-
Dibenzothiophene	184.255	332-333	-

3.1.2 Equipment

- Gas Chromatography (HP 5890 Series2) with FID detector and HP-5 column (30 m*0.32mm*0.25mm film thickness)
- 10 µL Micro syringe
- Fixed bed column for adsorption in continuous process
- Peristaltic pump for control the solution flow rate
- Magnetic stirrer

3.2 Methodology

3.2.1 Preparation of the Adsorbents

NaX zeolite was dried at 400°C (Moise et al., 2001) with the rate of 10°C/min for 3 hours to eliminate water adsorbed on zeolite. Then, zeolite was placed in desiccator before used.

3.2.2 Preparation of the Simulated Transportation Fuels

Decane and isooctane were used as simulated transportation fuels to represent diesel and gasoline, respectively. Sulfur compounds used were 3-methylthiophene (3-MT) and benzothiophene (BT) for isooctane and dibenzothiophene (DBT) for decane. DBT is a heavy sulfur compound typically present in diesel oil. The samples were prepared by mixing 3-methylthiophene or benzothiophene with isooctane and dibenzothiophene with decane. The initial sulfur concentration was in the range of 200 – 1800 ppmw.

3.2.3 s Experimental Setup and Investigation

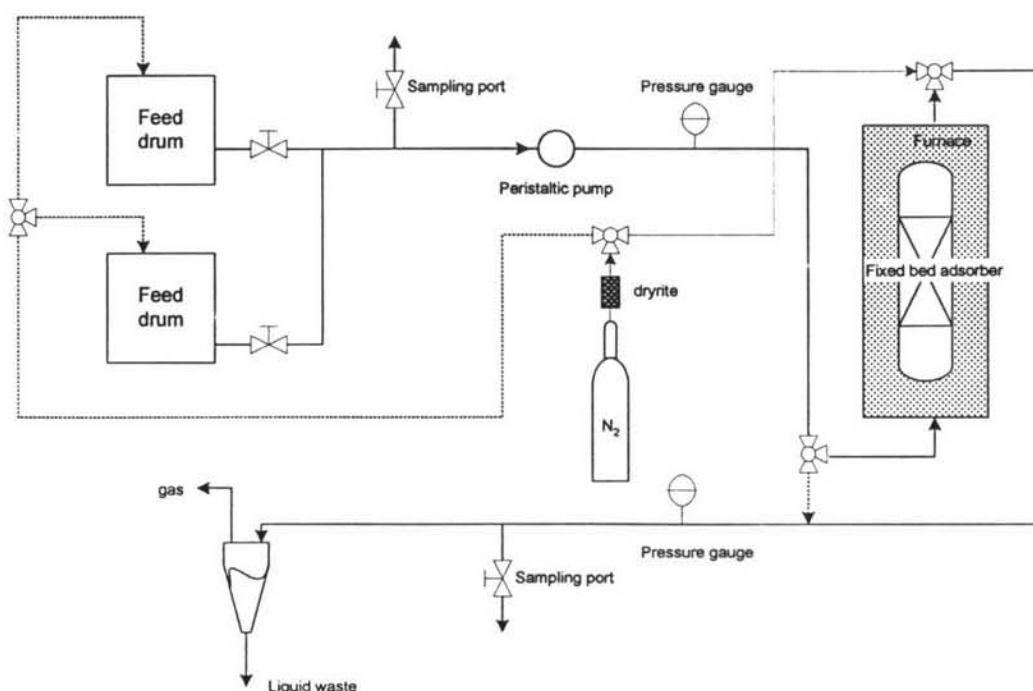


Figure 3.1 Schematic diagram of experimental setup.

The purpose of experimental setup in this research was to study adsorption and desorption of various sulfur compounds using adsorbent. The schematic diagram of experimental setup is depicted in Figure 3.1. This setup was mainly divided into two systems, those of which are liquid/gas feeding and

adsorption systems. The former consisted of feed drums, sampling ports, peristaltic pump and nitrogen cylinder while the latter comprised the fixed bed adsorber and furnace. The fixed bed adsorber was made by packing 0.5 g of the adsorbent in a vertical stainless steel tube located inside the furnace. The tube diameter and the length of adsorbent packing were 4.6 mm and 50 mm, respectively.

For the adsorber operation, the adsorbent packed inside the adsorber was initially treated with nitrogen gas at 400°C for 3 hours to remove trace water. Then, it was cooled down to room temperature in nitrogen flow. Nitrogen gas was pretreated inline prior to contacting the adsorbent using a drierite drying column. The bed was tapped to ensure proper packing and then simulated transportation fuels were fed to the adsorber from feed drum by peristaltic pump at flow rate of 0.5 cm³ min⁻¹. Effluent stream of transportation fuels were sampled at a regular time interval until saturation of the adsorbent was achieved. This could be observed by similar concentrations of sulfur compounds in inlet and exit streams. Afterwards, the sulfur contents in those samples were analyzed by using gas chromatography (HP 5890 Series II) with FID detector and HP-5 column. Concentration of sulfur compound in the liquid phase was determined before and after adsorption operation. A simple mass balance was performed to determine amount of sulfur adsorbed on the adsorbent each time interval. Finally, breakthrough curves were developed to evaluate the breakthrough capacity of the adsorbent. The conditions of gas chromatography used in this experiment were summarized in the Table 3.3.

Table 3.3 GC conditions for the analysis

Setting	Condition
Injection temperature	250°C
Oven temperature	50°C/5min, 10°C/min to 250°C, hold for 1 min
Detector temperature	280°C
Carrier gas	Helium 99.99% purity
Injection volume	1 µl

After the adsorbent was saturated with sulfur compounds, the adsorbent was subjected to desorption to study the capability of recovering sulfur compounds adsorbed on NaX zeolite. This was performed by feeding nitrogen to the adsorber to remove the simulated transport fuels left in the adsorber. Thereafter, the adsorber was heated to 400°C and hold about 1-6 hours while nitrogen was flown continuously through the adsorber. Finally, the adsorbent was cooled down to room temperature and then, the simulated transportation fuel was fed to the adsorber again to start the next adsorption cycle. The outlet concentration of sulfur compounds was also monitored as a function of time. This was used to develop the breakthrough curve for calculating the percentage of desorbing sulfur compounds from the adsorbent.

3.2.4 Calculation Method of the Breakthrough Curve

Breakthrough curve for adsorptive desulfurization of transportation fuels was developed by plotting sulfur concentration normalized by the inlet feed concentration of sulfur compound as a function of treated volume normalized by total bed weight as illustrated in Figure 3.2. The treated volume normalized by the total bed weight can be calculated from the following equation.

$$\frac{\text{Treated volume}}{\text{Total bed weight}} = \frac{tQ}{m_{\text{adsorbent}}} \quad (3.1)$$

The amount of sulfur adsorbed ($q_{\text{breakthrough}}$) in the bed can be determined by the following equation.

$$q_{\text{breakthrough}} = \left(\frac{v}{m_{\text{adsorbent}}} \right) \left(\frac{\rho_{\text{fuel}} X_i}{MW_{\text{sulfur}}} \right) \int_0^t \left[1 - \frac{C(t)}{C_i} \right] dt \quad (3.2)$$

where Q is the volumetric flow rate of feed stream ($\text{cm}^3 \text{min}^{-1}$), ρ_{fuel} the fuel density (g cm^{-3}) at room temperature, X_i the total sulfur fraction (by weight) in the feed, C_i

the total sulfur concentration in the feed (ppmw), $m_{adsorbent}$ the weight of adsorbent bed (g), MW_{sulfur} the molecular weight of sulfur, $C(t)$ the effluent total sulfur concentration (ppmw) at any time t (min). The integral on the right hand side of the equation is the area above the breakthrough curves at any time t as shown in the dark area of Figure 3.2. The breakthrough adsorption amount was obtained at the point where the sulfur concentration in the transportation fuel was less than 5 ppmw as recommended by Hernandez *et al.* (2005).

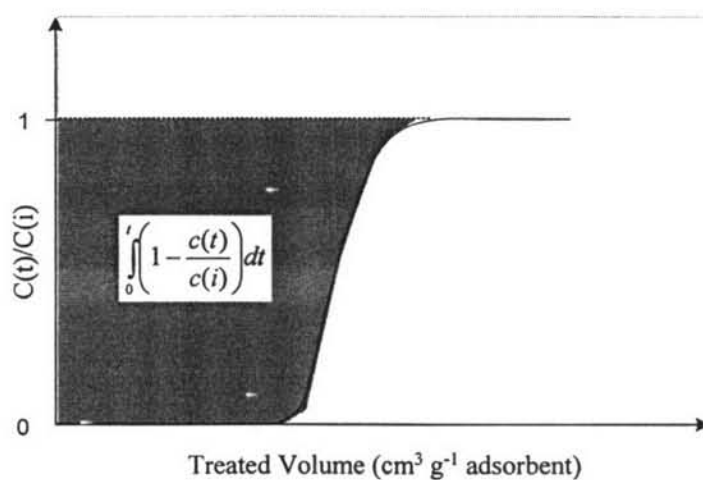


Figure 3.2 Breakthrough curve for adsorption process.