



CHAPTER III EXPERIMENTAL

3.1 Materials

NaY and NaX zeolites used to exchange cation with metal ions were provided from Institut Français du Pétrole (IFP, France).

Ni(NO₃)₂ (99%), NiCl₂ (99%), and CuCl₂ (99%) used to exchange cation in NaY and NaX zeolites were purchased from CARLO ERBA.

3-methylthiophene (C₆H₆S, 99%), and benzothiophene (C₈H₆S, 97%), which represented sulfur compounds in transportation fuel models, were purchased from ACROS ORGANICS (New Jersey, USA). Their relevant properties are shown in Table 3.1.

Isooctane (C₈H₁₈, 99.5%) and Benzene (C₆H₆, 99%) and Toluene (C₇H₈, 99%) represented environmental transportation fuels were supplied by FAMITALIA CARLO ERBA (Milan, Italy) and ACROS ORGANICS (New Jersey, USA), respectively.

Table 3.1 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
Benzene	78.1121	80.1	0.8786
Toluene	92.1434	110.6	0.8669
3-Methylthiophene	98.612	114 at 738 mm Hg	-
Benzothiophene	134.195	221	-

3.2 Equipments

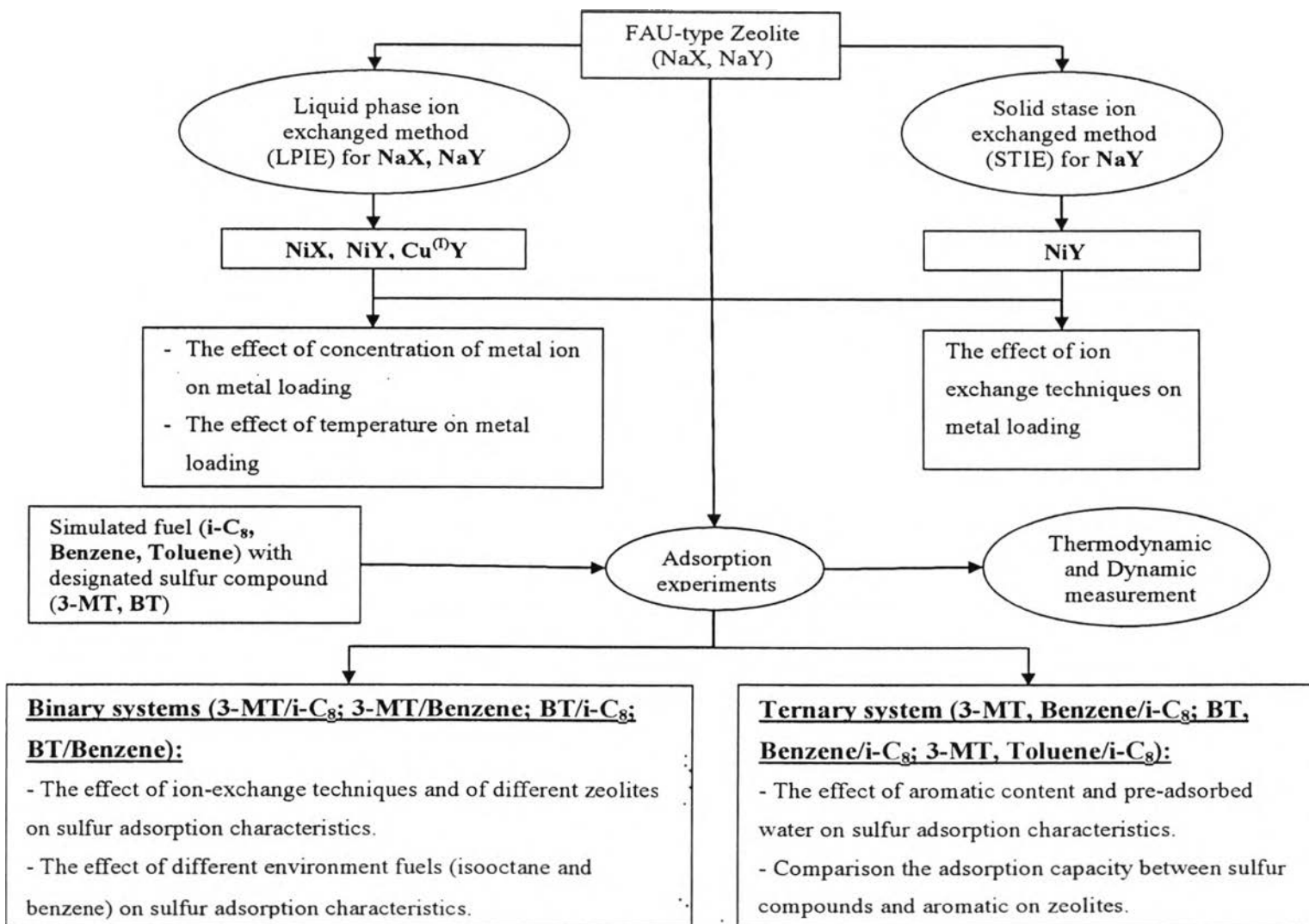
1. Gas Chromatography (HP 5890 Series2) with FID detector and HP-5 column (30 m*0.32mm*0.25mm film thickness)
2. Surface Area Analyzer (SAA) (Thermo Finnigan, Sorptomatic model)
3. Atomic Absorption Spectrometer (AAS) (Varian, SpectrAA 300 model)
4. X-ray Diffraction Spectroscopy (XRD) (Rigaku, Rint 2200 HV model)
5. Thermo Gravimetric Analyzer (TGA)
6. Thermo Gravimetric Analyzer (TGA) coupled to a Pfeiffer ThermoStar Mass Spectrometer (MS)
7. Vial 15 cm³
8. 10 µL Micro syringe
9. Magnetic stirrer
10. Stirring plate
11. Calcined equipment
12. Glassware

3.2 Methodology

3.2.1 Experimental Procedures

Overview of the experimental procedure covering the scope of the research is shown in Figure 3.1.

Figure 3.1 Schematic of the experimental procedures.



3.2.2 Preparation of the ion-exchanged zeolites using LPIE technique in a batch reactor

For the preparation by using the liquid-phase ion-exchange (LPIE) technique, the NaX and NaY zeolites were first dehydrated at 350°C for 2 hours to remove water adsorbed on zeolite. Secondly, the Ni²⁺ nitrate solutions (concentration was fixed at 0.01 mol/l) to zeolite ratio (S/A) was varied from 50:1, 100:1, 200:1 cm³/g-zeolite and exchanged at designated temperature for 48 hours (Xue *et al.*, 2005). The adsorbents were recovered by filtration and washed with deionized water 1000 cm³ to remove any salt or excess solution. After that, the sorbents were dried at 110°C overnight and then calcined at 350°C for 2 hours as shown in Figure 3.2. The dried samples of zeolites were be stored in air-tight bottles, and kept in the desiccators.

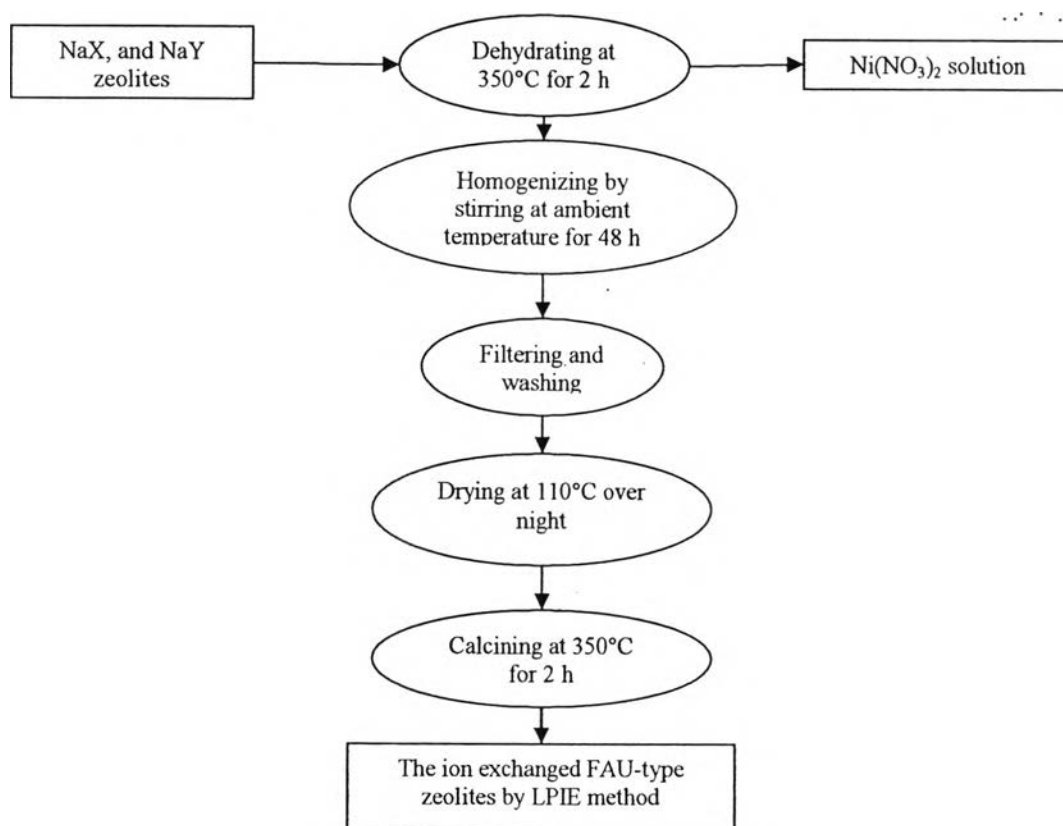


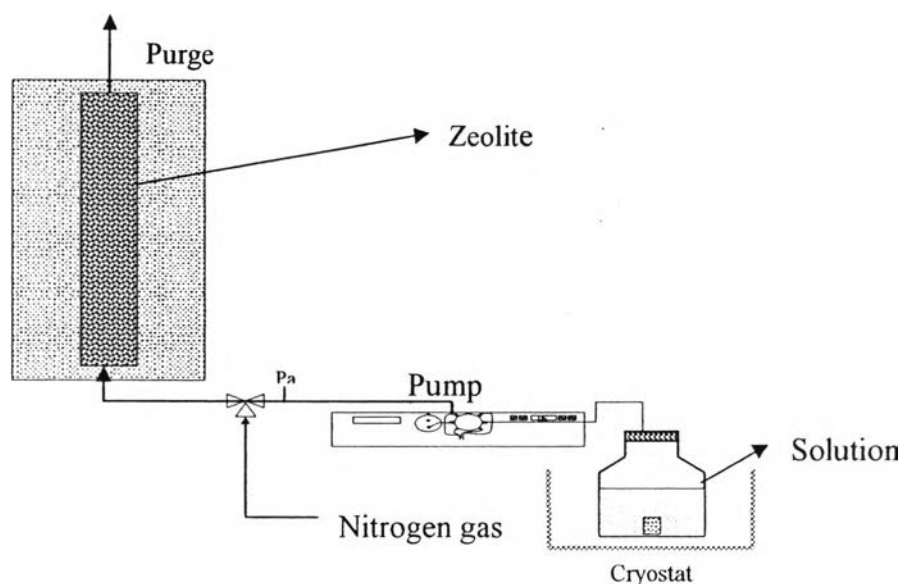
Figure 3.2 Schematic of the synthetic procedure of the ion exchanged FAU-type zeolites by LPIE method in a batch reactor.

3.2.3 Preparation of the ion-exchanged zeolites using LPIE technique in a fixed bed column

Experiments were done in pilot plant unit T169 at Institut Français de Pétrole (IFP), Lyon, FRANCE. The schematic of continuous system is shown in Figure 3.3. The adsorbent were prepared by twice exchanging.

The fixed-bed column was made of stainless steel tube (1cm, 100cm) which loaded with about 50g of zeolite. To ensure that all trapped gases expelled between and within the particles of zeolite, the column was first fully filled with deionised water for half an hour to wet the column. Since gases pockets inside the column could result in channeling, which would lower the bed utilization. Afterwards, CuCl_2 aqueous solution (0.5M) was pumped vertically upward at 5 ml/min – to avoid channeling due to gravity and ensure uniform distribution of solution throughout the column. The amount of copper in the ion-exchange solutions was equivalent to 4-fold cation-exchange capacity. The exchange temperature was set at 40°C . The exchange was finished after washing with deionsied water 1000 cm^3 , followed by drying at 110°C for 4 hours under N_2 gas at the flow rate $80\text{ cm}^3/\text{min}$.

The reduction of Cu^{2+} species to Cu^+ was carried out by activation at 450°C in pure helium for 12h at the flow rate $80\text{ cm}^3/\text{min}$.



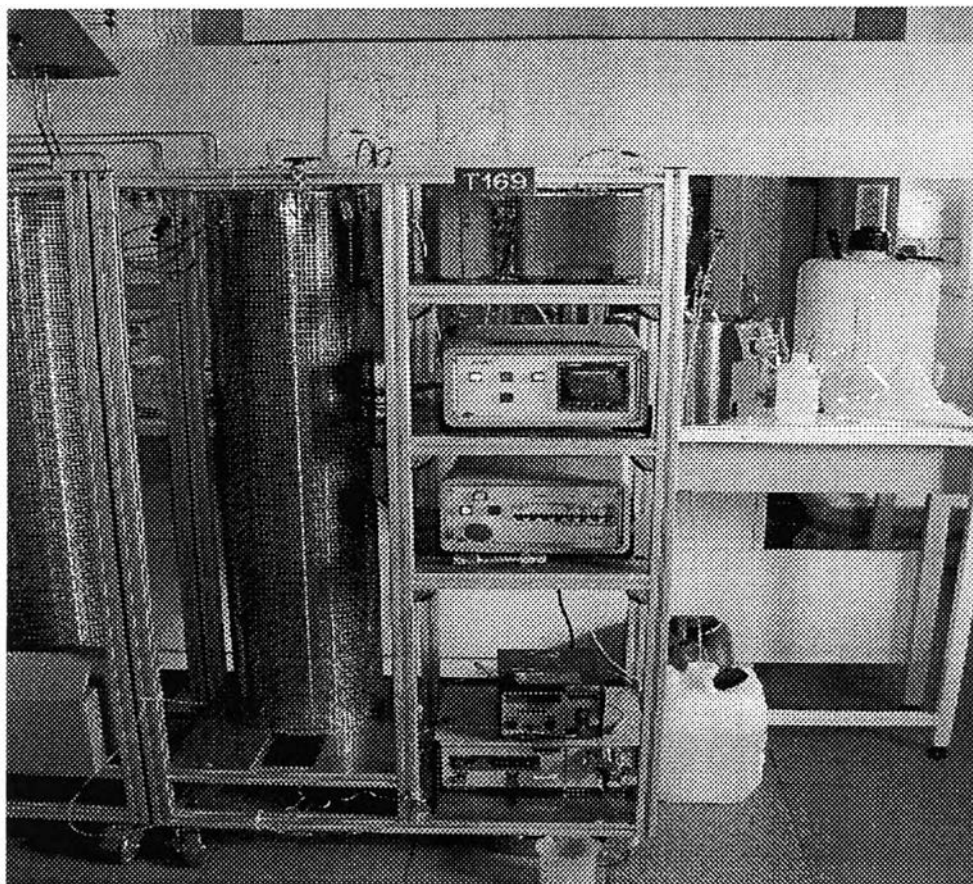


Figure 3.3 Schematic of the synthetic procedure of the ion exchanged FAU-type zeolites by LPIE method in a fixed bed reactor.

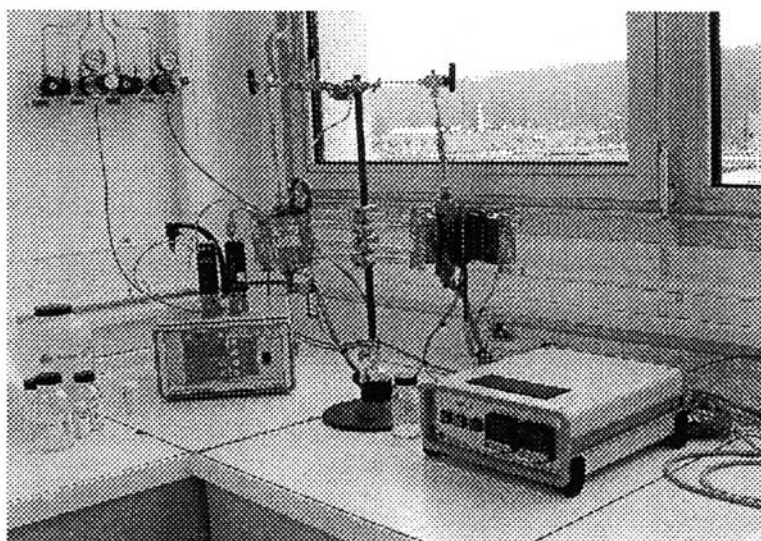


Figure 3.4 Furnace for activation.

3.2.4 Preparation of the ion-exchanged zeolites using SSIE technique

In the solid-state ion exchange process (SSIE), NaY was changed to acidic form after ion exchanging with a NH_4Cl solution (1M), drying overnight and calcining at 500°C . Then, 5 mol % of metal chloride salt was mixed with an aliquot of HY zeolite in a mortar under nitrogen atmosphere. Afterwards, the powder/salt mixture was placed in a tube reactor, heated in a linear ramp from room temperature to 150°C at $1^\circ\text{C}/\text{min}$, and held at that temperature for 4 h, all in an air-zero atmosphere. The temperature was then increased to 500°C also at $1^\circ\text{C}/\text{min}$ and held at that set point for 6h. The gas flow rate was kept constant at about $140 \text{ cm}^3/\text{min}$. After being heated, the zeolite was allowed to slowly cool to room temperature, again in air-zero shown in Figure 3.5.

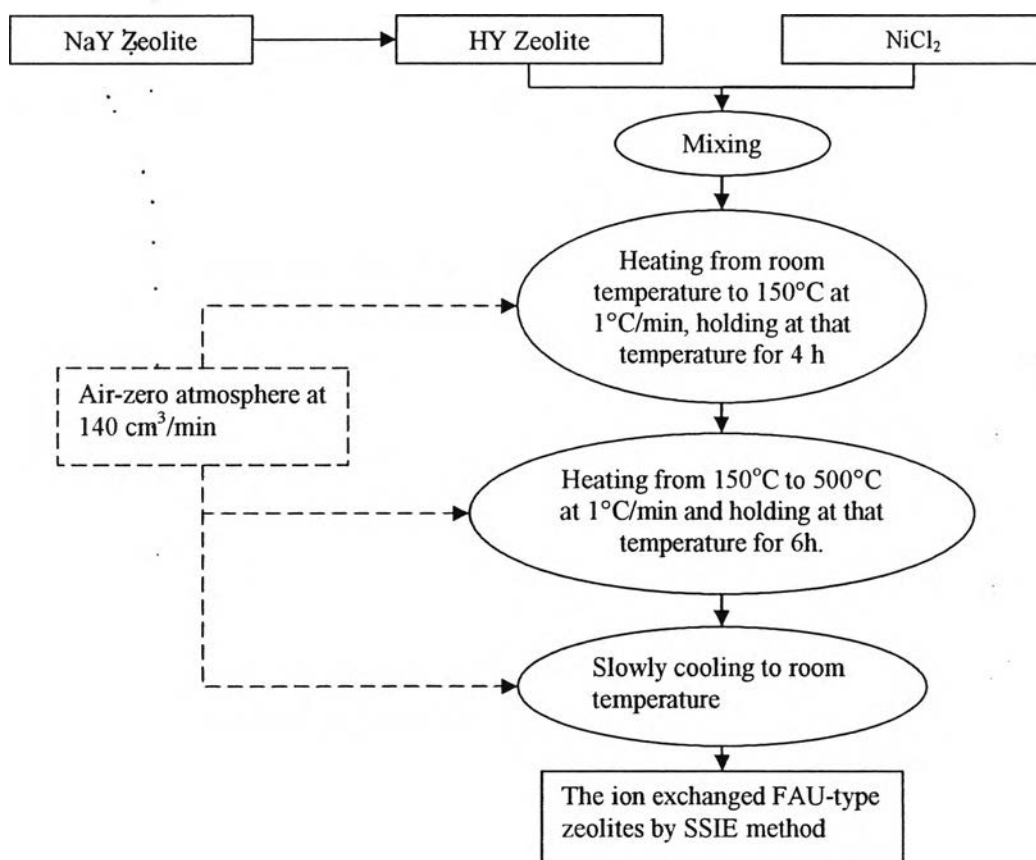


Figure 3.5 Schematic of the synthetic procedure of the ion exchanged FAU-type zeolites by SSIE method.

3.2.5 Characterization of adsorbents

Surface area and pore volume was determined by BET surface area analyzer – SAA (Thermo Finnigan, Sorptomatic model) and analyzed by using nitrogen gas adsorption and desorption. To eliminate adsorbed volatile compounds from the micropores, before being analyzed, adsorbents were dried and evacuated at 300°C for at least 3 hours.

X-ray diffraction (XRD) analysis was conducted by using a Rigaku, Rint 2200 HV model, so as to verify the structure of the zeolite after ion exchange and heat treatment (calcined at 350°C) compared with the original structure of the original zeolite before the modification.

The amount of metal loading was obtained by using an Atomic Absorption Spectrometer – AAS (Varian, SpectrAA 300 model). All the zeolite samples were dissolved in a Hydrogenfluoric (HF) solution to remove the zeolite framework. Then, the samples were mixed with aqua regia to dissolve the metal ions completely. An ion-exchange isotherm was constructed to measure a preference cation in the zeolite over another and the limitation of exchanging.

3.2.6 Preparation of the simulated transportation fuels

In this study, the simulated transportation fuels used were isooctane and benzene. The sulfur compounds used were 3-methylthiophene (3-MT) and benzothiophene (BT). The samples were prepared in binary system (by mixing sulfur compounds with isooctane and benzene) and in ternary system (by mixing sulfur compounds and benzene, toluene with isooctane).

3.2.7 Static adsorption experiment

Batch liquid adsorption experiments were carried out in a 15 cm³ vial in which ion-exchanged zeolites and simulated fuels. The ratio of fuel to adsorbent was fixed at 85 (Chansa, 2004) with constant stirring. The equilibrium time was set at 8h (Pringprayong, 2006). Once the system reached equilibrium, samples were withdrawn by using syringe and then analyzed by gas chromatography (HP 5890 Series2) with FID detector and HP-5 column (30m*0.32mm*0.25mm film

thickness). The conditions of gas chromatography used in this experiment are summarized in Table 3.2.

Table 3.2 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 μ l

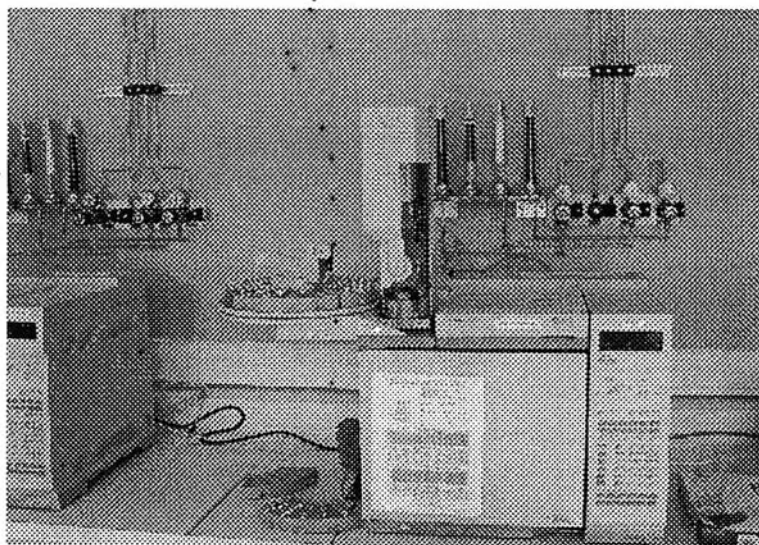


Figure 3.6 Gas Chromatography.

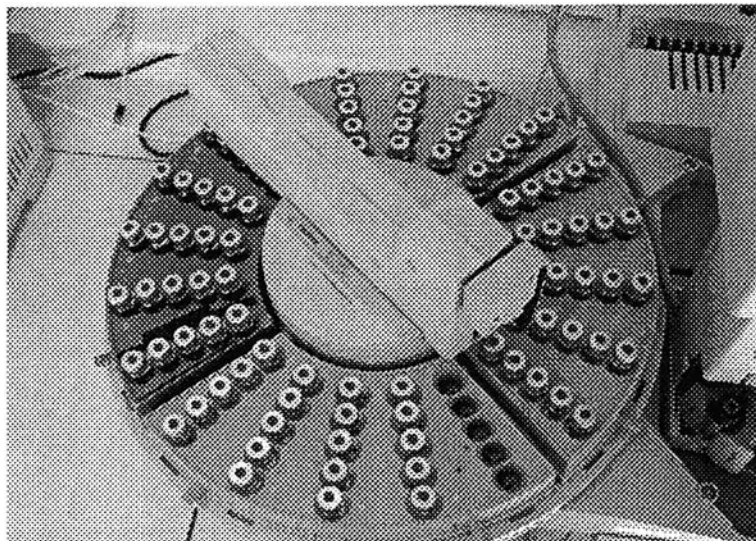


Figure 3.7 Support of Vials in Gas Chromatography.

3.2.8 Sulfur compounds analysis

Sulfur compounds were analyzed by using gas chromatography (HP 5890 Series2) with FID detector and HP-5 column (30 m*0.32mm*0.25mm film thickness). Concentration of sulfur compound in the liquid phase was determined before and after adsorption. Simple mass balance was performed to determine amount of sulfur adsorbed on the adsorbent. Then the adsorption isotherms were constructed to evaluate the adsorption capacity and selectivity of the adsorbent

3.2.9 Adsorption isotherm of sulfur compounds

Adsorption isotherms of sulfur compounds were constructed by plotting the adsorbed amounts of sulfur compound on the adsorbent versus metal loading on zeolites in batch reactor. At the beginning, the isotherms were constructed for the sulfur adsorption at 25°C. Fuel: adsorbent weight ratio was fixed at 85:1.

3.2.10 Model of adsorption isotherm on sorbents

After the adsorption, isotherms were constructed by varying the concentration of sulfur compounds and that isotherms were fitted with an appropriate model. The model adsorption isotherm used in this study is Langmiur isotherm which can be described as followed:

$$Q_s = \frac{Q_{\max} b C_s}{1 + b C_s}$$

Or the Langmuir isotherm is presented in the linear form:

$$\frac{C_s}{Q_s} = \frac{1}{Q_{\max} b} + \frac{C_s}{Q_{\max}}$$

Where: Q_s and Q_{\max} are the sulfur uptake (mmol-S/g-sorbent) and the maximum adsorption capacity (mmol-S/g-sorbent), respectively; C_s is the equilibrium sulfur concentration (mmol-S/g-fuel); b is a constant of sulfur adsorption (g-fuel/mmol).

3.2.11 Fixed bed adsorption

Experiments were done in pilot plant unit 179 at Institut Français de Pétrole (IFP), Lyon, FRANCE. The schematic of continuous system is shown in Figure 3.8.

A stainless steel tube (0.7 cm, 25 cm) loaded with about 2.5g of zeolite was used for adsorption experiments. Before packing, zeolite was dried at 400°C for 2 hours under N_2 gas at the flow rate 80 cm³/min to remove humidity and other impurities from the adsorbent, then weighed and packed to the columns. The columns were then placed in a tube furnace. Next, sulfur-free isooctane solution was allowed to flow through the sorbent at the rate of 2 ml/min to remove the trapped gasses. After wetting the adsorbent for about 15 min, the feed was switched to the simulated fuels at a flow rate of 2 ml/min. Effluent samples were collected in small vials (80 vials) at regular time intervals until saturation of the adsorbent was achieved. This could be observed similar the effluent total sulfur concentration and the influent total sulfur concentration. All the samples collected during the breakthrough experiments were analyzed by using gas chromatography.

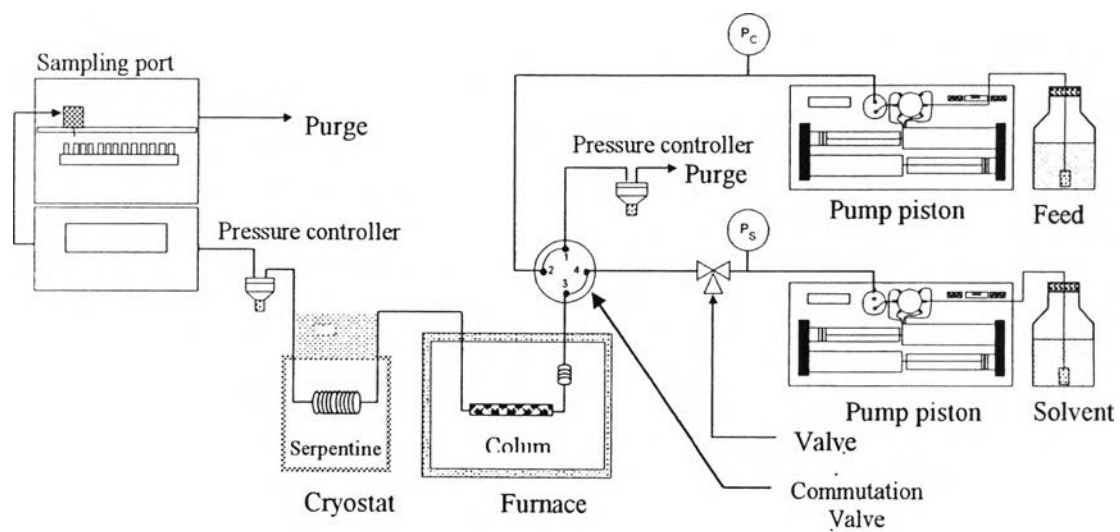


Figure 3.8 Schematic of the Fixed Bed Adsorption Breakthrough (Unit 179, IFP-LYON, FRANCE).

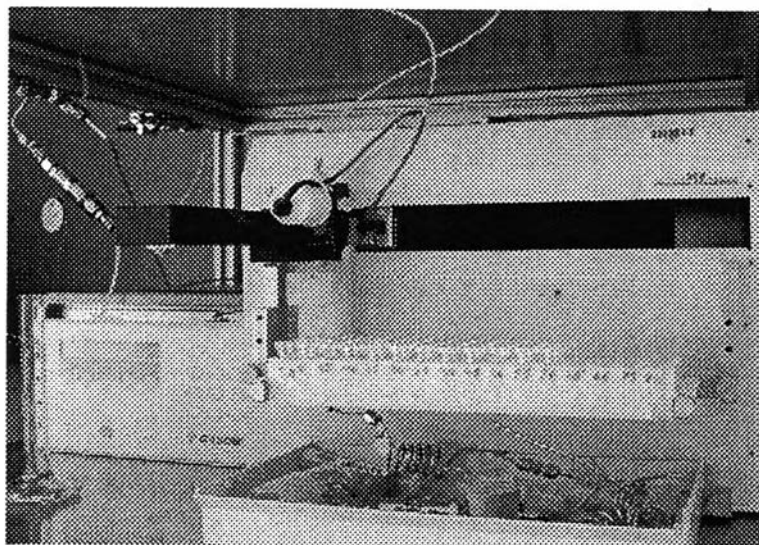


Figure 3.9 Collector in the fixed bed adsorption model.

3.2.12 Calculation method of the Breakthrough Curve

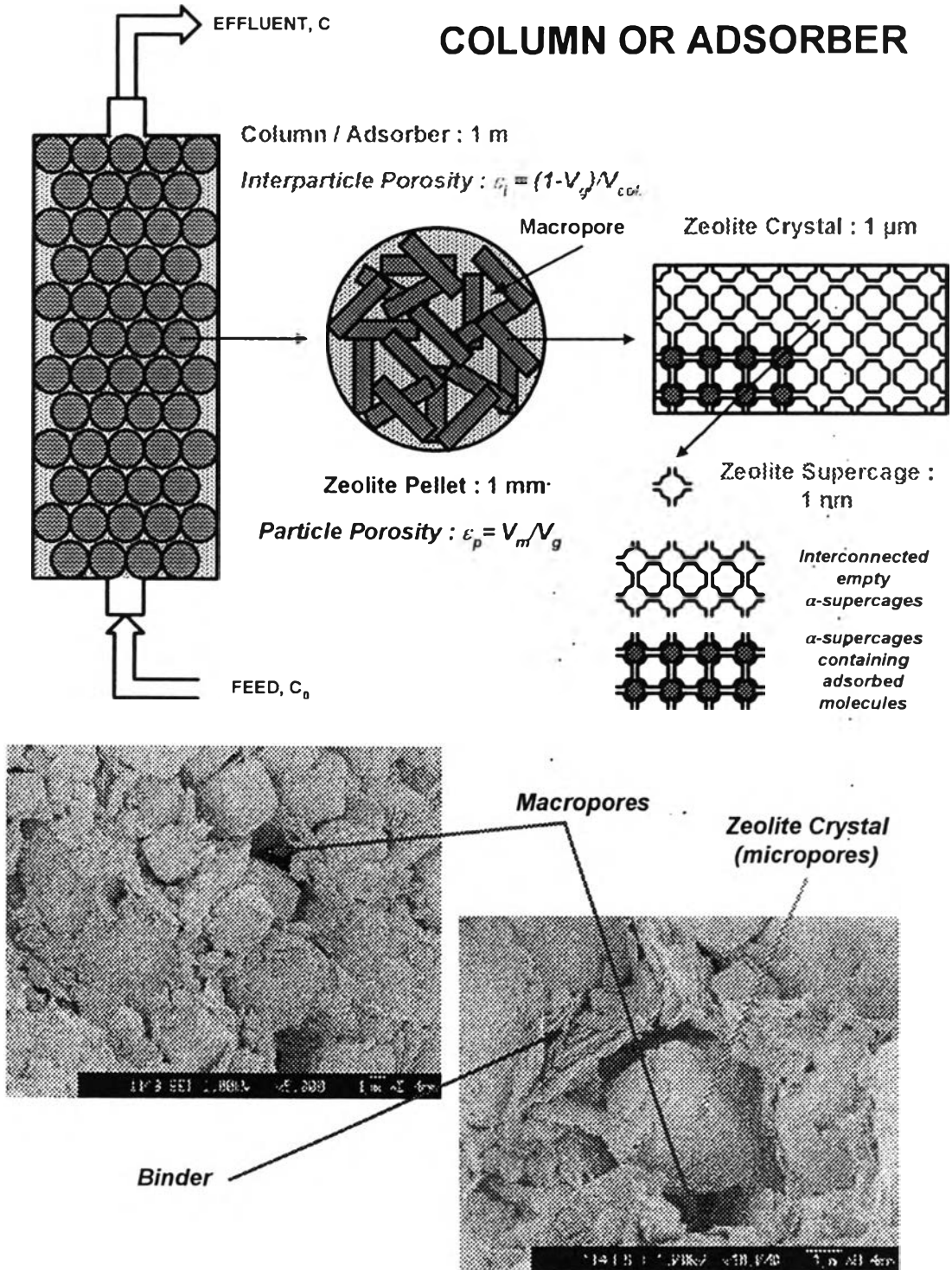


Figure 3.10 The adsorber geometry.

The adsorber geometry is schematically depicted in Figure 3.10. Transportation fuel is fed to the fixed bed adsorber packed with zeolites having a biporous structure. The void between the crystals creates macropores. These pores act as conduit for transportation of the sulfur compound molecules from bulk phase to the interior of the crystal. Once the sulfur compounds molecules are inside the particle, they are adsorbed at the pore- mouth of the micropores and hence, the adsorbed specific diffuse into the interior of the crystal through micropores of the crystal. The diffusion process in the macropores and micropores follows the molecular diffusion mechanisms while that inside the crystal follows an intra crystalline diffusion mechanism. Thus, in case of former, adsorption is usually controlled by intra crystalline diffusion.

3.2.12.1 Definitions of the different Volumes in the Column

The total volume of the column:

- The total volume of the column: V_C
- The total Inter-particle volume = The void volume between the particles: V_I
- The total volume of the adsorbent particles: V_P

⇒ Volume balance:

$$V_C = V_I + V_P$$

The total Adsorbent Particle Volume can be divided into:

- The Macro porous Volume (Void between the zeolite crystals within the particle): V_M
- The Micro porous Volume (α -cages of the zeolite = calculated from "Dubinin Volume" form $N_2@77K$ adsorption): V_μ
- The Volume of the Solid (Si, Al, O, cations, binder): V_S

⇒ Volume balance:

$$V_P = V_M + V_\mu + V_S$$

3.2.12.2 Porosity Levels in the Column

- Inter-particle porosity: ε_i
= Void between the particles (beads, extrudates) of adsorbent

- Particle porosity: ε_p
= Macro porous void in the particles (beads, extrudates) of adsorbent
- Total Bed porosity: ε_B
= Void between particle + macro porous void in the particles = volume occupied by the fluid (liquid) phase

$$\varepsilon_I = \frac{V_I}{V_C} \qquad \varepsilon_P = \frac{V_M}{V_P}$$

$$\varepsilon_B = \frac{V_I + V_M}{V_C} = \frac{V_I}{V_C} + \frac{V_M}{V_P} \frac{V_P}{V_C} = \frac{V_I}{V_C} + \frac{V_M}{V_P} \frac{(V_C - V_I)}{V_C} = \varepsilon_I + (1 - \varepsilon_I) \varepsilon_P$$

Determination of ε_i and ε_p : by "density measurements"

- "Bulk" density: ρ_B
= Mass M_S of solid / Bulk volume occupied V_C
- "Particle" density: ρ_P
= Mass M_S of solid / Volume of Particles (from Hg porosimetry at low pressure) V_P
- "structural" density: ρ_S
= Mass M_S of solid / Volume of Particles, macro porosity excluded (from Hg porosimetry at high pressure) $V_S + V_\mu$
- Macroporous volume: v_M
= Macroporous volume per gram of solid (Hg porosimetry at "high pressure")

$$\rho_B = \frac{M_S}{V_C} \qquad \rho_P = \frac{M_S}{V_P} \qquad \rho_S = \frac{M_S}{V_S + V_\mu}$$

$$\varepsilon_I = \frac{V_I}{V_C} = \frac{V_C - V_P}{V_C} = 1 - \frac{V_P}{V_C} \frac{M_S}{M_S} = 1 - \frac{\rho_B}{\rho_P}$$

$$\varepsilon_P = \frac{V_M}{V_P} = \frac{V_P - (V_S + V_\mu)}{V_P} = 1 - \frac{(V_S + V_\mu) M_S}{M_S V_P} = 1 - \frac{\rho_S}{\rho_P}$$

$$\varepsilon_P = \frac{V_M}{V_P} = (v_M M_S) \frac{\rho_P}{M_S} = v_M \rho_P$$

3.2.12.3 First Moment of the Breakthrough Curve (μ)

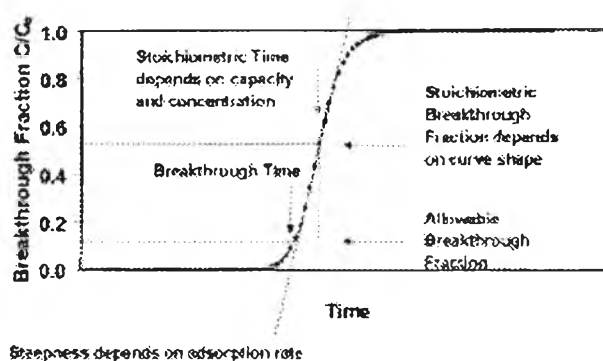


Figure 3.11 Characteristics of a typical adsorption breakthrough curve.

The breakthrough curve can be defined as the “S” shaped curve that typically results when the effluent adsorbate concentration is plotted against time or volume (as seen in Figure 3.11). Breakthrough curves can be constructed for full scale, dynamic, or pilot testing. The breakthrough point is the point on the breakthrough curve where the effluent adsorbate concentration reaches its maximum allowable concentration, which often corresponds to the treatment goal. The treatment goal is usually based on regulatory or risk based numbers. The main aim when sizing adsorptive columns is the ability to predict the service time (or total effluent volume) until the column effluent exceeds breakpoint concentration.

A breakthrough curve is defined by three characteristics: geometric midpoint (stoichiometric time and corresponding relative concentration), steepness, and shape. The midpoint is determined by the flow rate, the concentration, and the capacity of the adsorbent bed and temperature. The steepness of a breakthrough curve is related to the rate (speed) at which the sulfur compounds are removed from the simulated fuels as it flows through the bed. In the simplest case, steepness is described by an overall mass-transfer (adsorption) rate coefficient, which is larger for larger adsorption rates. If this rate coefficient is constant throughout the breakthrough process, the shape of the breakthrough curve will be symmetrical. However, it has often been observed that breakthrough curves are skewed (asymmetrical), usually steeper at the beginning of breakthrough than at the end.

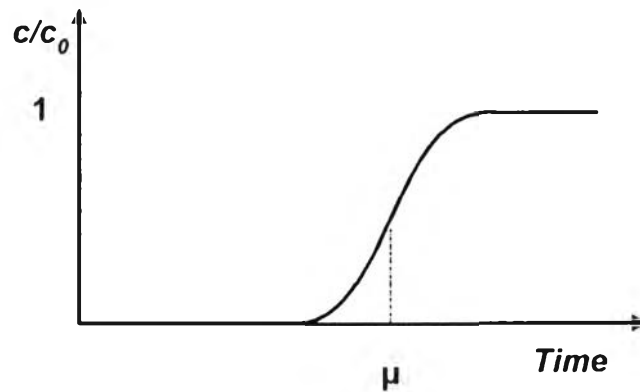


Figure 3.12 The first Moment of the Breakthrough Curve (μ).

In order to apply moment analysis to a pulse response curve to estimate linear adsorption constants and mass transfer parameters, the following assumptions are made:

- ❖ The mobile phase is a dilute solution.
- ❖ Velocity is constant throughout column cross-section. This assumption is valid due to the fact change in concentration of adsorbing species is occurred at trace level which does not contribute to a significant change in local velocity inside the bed.
- ❖ No chemical reactions occur.
- ❖ Temperature is uniform throughout the bed and the pellet.
- ❖ Intra-particle diffusion is described by pore diffusion. For a linear isotherm system, the flux due to surface diffusion, if important, can be lumped together with the pore diffusion flux.
- ❖ External mass transfer from the bulk liquid to the pores is described by film mass transfer.
- ❖ Axial dispersion effects are considered.

First Moment of the Breakthrough Curve (μ) (Figure 3.12):

$$\mu_1 = \mu = \int_0^{\infty} (1 - y) dt \quad y = \frac{c(t)}{c_0}$$

For a given adsorbed component (sulfur compounds), at $t = \mu$, all the sulfur compounds introduced in the column is in the column. So, the total amount of thiophene in the column:

$$Q^{TOT} = \mu FC = \mu S_c uC = \mu \frac{V_c}{L_c} uC \quad (1)$$

Where Q_{TOT} : total amount of sulfur compounds in the column (mole or g)
 μ : mean breakthrough time (experimental determination or calculation)
 C : concentration of sulfur compounds in the feed (mole or g)
 F : feed flow rate (cm^3/min)
 V_c, S_c, L_c : volume, section and length of the column (adsorbent bed)
 u : superficial liquid velocity in empty column (cm/min)
 $=$ ratio flow rate / column section

Sulfur compounds in the column is partially adsorbed in V_μ , and partially adsorbed in solution (at feed concentration) in $V_I + V_M$. So:

$$Q^{TOT} = \varepsilon_I V_c C + (1 - \varepsilon_I) V_c Q \quad (2)$$

Where Q : total amount of sulfur compounds in the particle (in $V_M + V_\mu$)
 By comparing the two expressions (1) and (2) for Q_{TOT} , we have:

$$Q^{TOT} = \mu \frac{V_c}{L_c} uC = \varepsilon_I V_c C + (1 - \varepsilon_I) V_c Q$$

$$\mu = \frac{L_c}{u} \left[\varepsilon_I + (1 - \varepsilon_I) \frac{Q}{C} \right] = \frac{L_c}{v} \left[1 + \frac{(1 - \varepsilon_I) Q}{\varepsilon_I C} \right]$$

Where v : "real" liquid velocity ($v = u / \varepsilon_I$)

We have also:

$$Q = \varepsilon_p C + (1 - \varepsilon_p) q \quad \text{Or} \quad \frac{Q}{C} = \varepsilon_p + (1 - \varepsilon_p) \frac{q}{C} = \varepsilon_p + (1 - \varepsilon_p) K$$

Where q : amount of sulfur compounds adsorbed in the micropores only.
 K : the equilibrium constant.