

## CHAPTER III EXPERIMENTAL



### 3.1 Materials and Equipment

#### 3.1.1 Chemicals

Zeolite 4A ( $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:2\text{SiO}_2:y\text{H}_2\text{O}$ ) 1/16 inch extrudate was provided by Institut Français du Pétrole (IFP), France.

Calcium chloride dihydrate ( $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ) of 99%-102% purity was obtained from Carlo Erba Reagent Company.

Magnesium chloride hexahydrate ( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ) of minimum 99% purity was obtained from Scharlau Chemie.

Strontium chloride hexahydrate ( $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ ) of 99%-103% purity was obtained from Fluka Co., Ltd..

Normal decane ( $\text{C}_{10}\text{H}_{22}$ ) of 99+% purity was obtained from Acros Organics

#### 3.1.2 Equipment

Gas Chromatography (GC), Agilent technologies 6890N, situated at Institut Français du Pétrole (IFP), France.

Atomic Absorption Spectrometer (AAS), Varian, Model 300P, situated at the Petroleum and Petrochemical College (PPC), Thailand.

Thermogravimetric Analyzer, Setarum TAG 24, situated at Institut Français du Pétrole (IFP), France.

Water bath shaker, GFL 1086, situated at the petroleum and Petrochemical College (PPC), Thailand.

### 3.2 Molecular Sieve Preparation (work done at PPC)

Zeolite 4A or zeolite NaA was ion exchanged with different types of divalent cation ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Sr}^{2+}$ ) in order to give a pore size of zeolite suitable for paraffins extraction.

### 3.2.1 Molecular Sieve Preparation Procedure

The  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$  were mixed with deionised water to prepare various concentration solution of each cation. The ion exchange were carried out by pouring 50 ml of cation solution with known concentration into glass bottles containing 1 g of zeolite 4A and letting the system equilibrate in water bath shaker (calcium at 30°C, strontium at 30°C, magnesium at 30°C and 90°C). The equilibrium time was found by varying the contact time between the solid and the solution. The equilibrium was achieved when the concentration of the solution was relatively constant as the contact time still increase.

### 3.2.2 Cation Exchange Analysis

After the system reached its equilibrium, the glass bottles were removed from the constant temperature bath and filtered. The cation contents in the solution phase were determined by atomic absorption spectrometer. Calibration curves of AAS are shown in Appendix B. The amount of the cation exchanged into zeolite can be calculated by doing a mass balance of the cation in solution (see Appendix A). The level of exchange was rechecked by dissolution of zeolite after ion-exchange with acid (10% volume of conc  $\text{HNO}_3$  in water). The cation contents in the acid solution were also determined by atomic absorption spectrometer. Finally, the same level of exchanged zeolites of each divalent cation ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Sr}^{2+}$ ) was chosen as adsorbents for separation of normal paraffin and the efficiency of each adsorbent was then compared.

## 3.3 Paraffin Adsorption (work done at IFP)

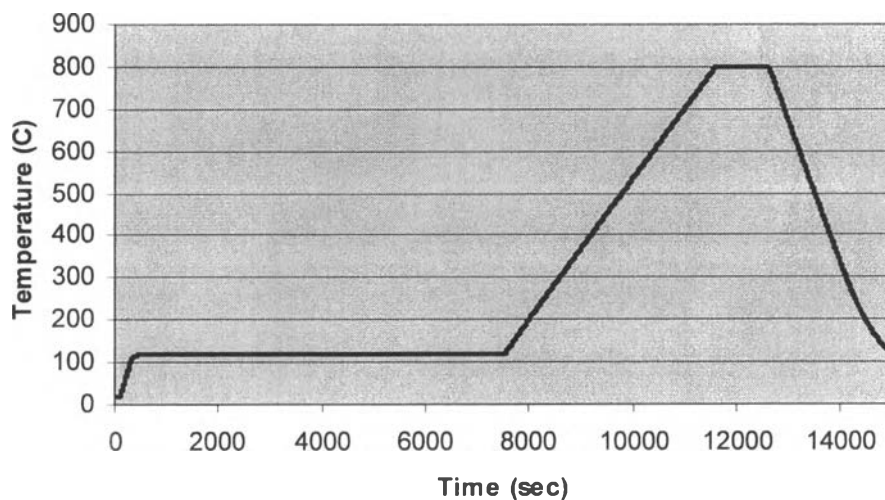
### 3.3.1 Feed Model

In this research, normal decane was used as a representative of normal paraffins in a carbon range of C10-C14.

### 3.3.2 Thermogravimetric Analyses

The temperature program desorption (TPD) of normal decane in each form of divalent metal zeolite A was performed in the thermobalance apparatus. This

experiment was divided into two sections: saturation of samples with normal decane and temperature program desorption in the thermobalance. First, the zeolites were activated by heating up to 400°C over a period of 2 hours under dry nitrogen flow and then placed directly into liquid normal decane for 24 hours. After each sample was saturated, approximately 50 mg of each sample were transferred into the thermobalance apparatus under dry helium atmosphere. Mass change of solids was detected as a function of temperature and time in this instrument. Samples were heated from room temperature to 120°C with a heating rate of 10°C/min and kept constant at this temperature for 2 hours in order to purge out normal decane which adsorbed only on the surface of solids and in the macropores. After 2 hours, the temperature was then increased again at the same rate to 800°C in order to see the temperature program desorption of normal decane which is adsorbed within the micropore of the molecular sieve. The temperature profile of the experiment is shown in Figure 3.1.



**Figure 3.1** Temperature profile used to study TPD of normal decane.

### 3.3.3 Breakthrough Curve Experiment

A schematic of the gas chromatography apparatus used in this study is presented on Figure 3.2. A stainless steel column ( $L=10$  cm and  $D=1$  cm) was filled with a known amount of activated adsorbent particles and placed into the chromatograph oven. Column temperature is thus regulated by the chromatograph

regulation system. An inert gas (nitrogen) was passed continuously through the column, so as to avoid adsorbent pollution by air. Nitrogen flowrate was controlled by a mass flowmeter, capable of delivering 0-120 cm<sup>3</sup>/min of gas.

After passing the flowmeter, the gas stream can either go directly to the chromatograph or pass through the saturator, where it is saturated with the selected hydrocarbon. The hydrocarbon concentration at the saturator was controlled by the saturator temperature, regulated by a cryostat. In this experiment, the temperature of the saturator was fixed at 18°C. With this system, it is possible to feed the column with a constant flow of hydrocarbon at controlled concentration, the lowest concentration being limited by the minimum temperature of the cryostat.

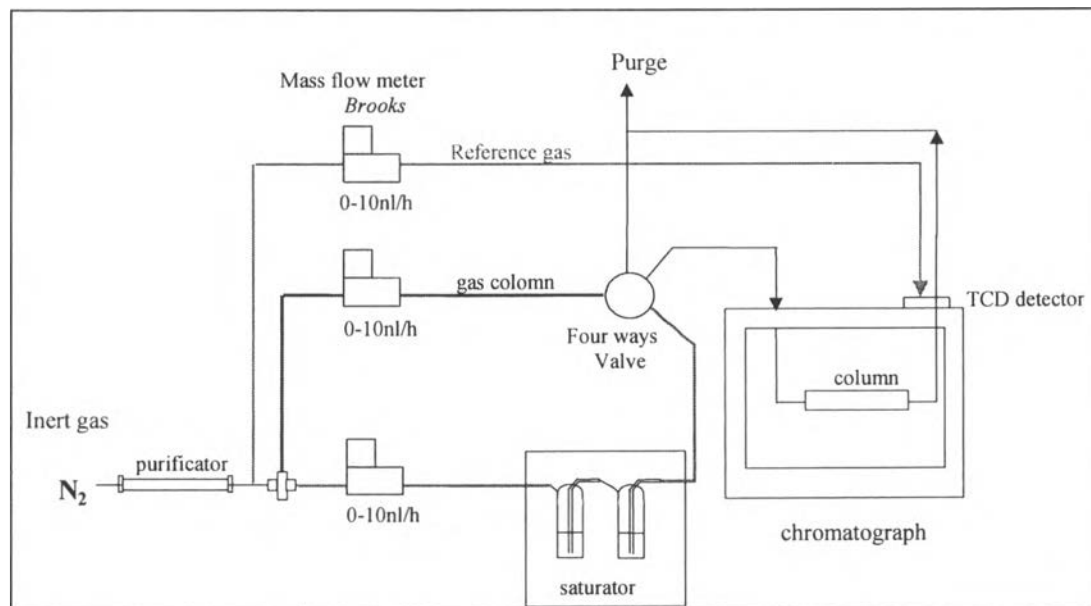
The efficiency of the saturator was checked: the measured concentration at the outlet of the saturator was in accordance with the theoretical value, calculated from the liquid-vapor equilibrium.

The signal at the output was measured every 1.2 seconds with a Thermal Conductivity Detector (TCD). The TCD was preferred to the Flame Ionization Detector (FID), which is usually used for hydrocarbon compounds, because of the flows of hydrocarbons to be detected: FID detector's saturation level is too sensitive. Pressure in the column was always at atmospheric pressure. There was no pressure regulation, and pressure drop through the column was found to be negligible.

Breakthrough curve is a plot of normalize concentration as a function of time. Normalize concentration can be calculated following Equation 3.1.

$$\text{Normalized concn.} = \frac{C_s(t) - C_i}{C_f - C_i} \quad (3.1)$$

where  $C_s(t)$  = the signal value at specific time (t).  
 $C_i$  = average base signal value of the breakthrough curve obtained.  
 $C_f$  = average final signal value of the breakthrough curve obtained.



**Figure 3.2** Breakthrough curve experimental set up.