

CHAPTER III

EXPERIMENTAL PROCEDURE

3.1 Fixed bed experiment

This research focuses on water separation from ethanol-water solution under vapor phase with the use of 3A zeolite. The first phase testing was done in a fixed-bed adsorber under atmospheric pressure to study the optimum condition for adsorption and to compare the performance under difference operating conditions. The zeolite was packed in a stainless steel column with inner diameter of 1.59 cm and the length of 45 cm placing in a tube furnace to maintain the temperature at desired values (Figure 3.1). Carberry and Varma (1976) suggested a tube to particle ratio of less than 5-6 to avoid excessive radial temperature gradient, hence the ratio of 3.2-6.4 was used. Low concentration ethanol/water mixture was evaporated and superheated to avoid condensation before being fed through the packed bed from the top. This prevented fluidization of the zeolite at higher feed rate. The dried ethanol vapor at the bottom then passed through the condenser. Hence the final product was collected as liquid. Once the adsorption column was saturated, the zeolite was removed and regenerated by heating in an oven at 220 °C for 4 hours. Prior to each run the regenerated zeolite was re-packed into the column and put under 300 °C with nitrogen gas flow through for 2 hours. The bed is then cooled down to a desired temperature before the next experiment could begin.

The experiments studied the adsorption of water on 3A zeolite at a flow rate of 1-2 mL/min, initial bed temperature of 100 °C and 120 °C, and the concentration between 85 wt% and 95 wt%. The concentration of the dried ethanol as a product was constantly checked at every 2 minutes interval. Each experiment was run until the ethanol concentration of the product is equal to that of the feed mixture, i.e. the bed is fully saturated. This would allow the calculations of the water adsorption capacity of the zeolite and the length of equilibrium zone which would be helpful in designing the adsorption columns in PSA pilot plant.

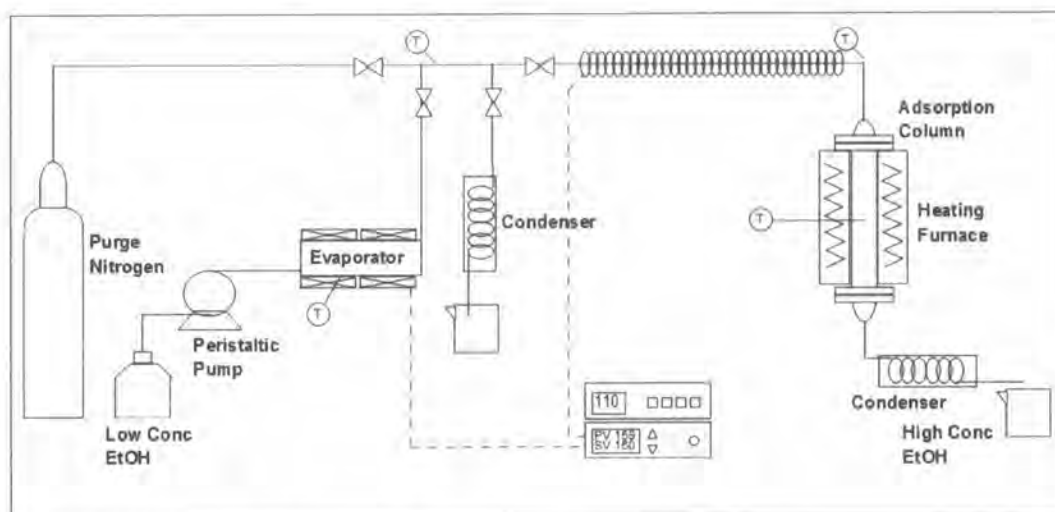


Figure 3.1 Schematic diagram of the fixed bed experiment.

3.2 PSA pilot plant

In the second phase of the study, the pilot modeling of the cyclic PSA process was then designed along with its control system (Figure 3.2). Operating conditions were similar to the industrial process. Normally, two or three beds PSA arrangements are used in the industry; in this study the two beds cycle was considered. The half cycle of ethanol PSA process, sequence of the operation and interactions between beds were also designed. The PSA cycle can be divided into two stages which were adsorption or production stage and desorption stage.

Firstly, the ethanol/water mixture was fed into the evaporator by the use of peristaltic pump. The feeding stream was then vaporized and superheated along the piping before entering into the first adsorbers. During adsorption in the first column the water-ethanol vapor stream was fed to the bed from the top under high pressure. Utilization of various on/off valves enabled the PSA system to direct the feed stream into a designated column. The product stream of dried ethanol could be collected at the bottom of the bed. Single tube condenser was used to condense the high concentration ethanol and the sample was collected as liquid to analyze its quality. Part of the product stream was used to purge and re-pressurize the other bed during and after the desorption stage. Desorption stage followed after the production stage was completed. The bed must then be depressurized, regenerated and re-pressurized to the adsorption pressure before next adsorption cycle could continue. The two

adsorbers were working simultaneously in different mode (adsorption and desorption) to allow continuous production of pure ethanol. To switch the mode of each adsorbers, the system operated the valves to direct the feeding stream into the second column and perform regeneration in the first column (see Figure 3.3). The operation continued in a cyclic batch. All these steps were controlled by closing/opening of controlled valves through the use of PLC system.

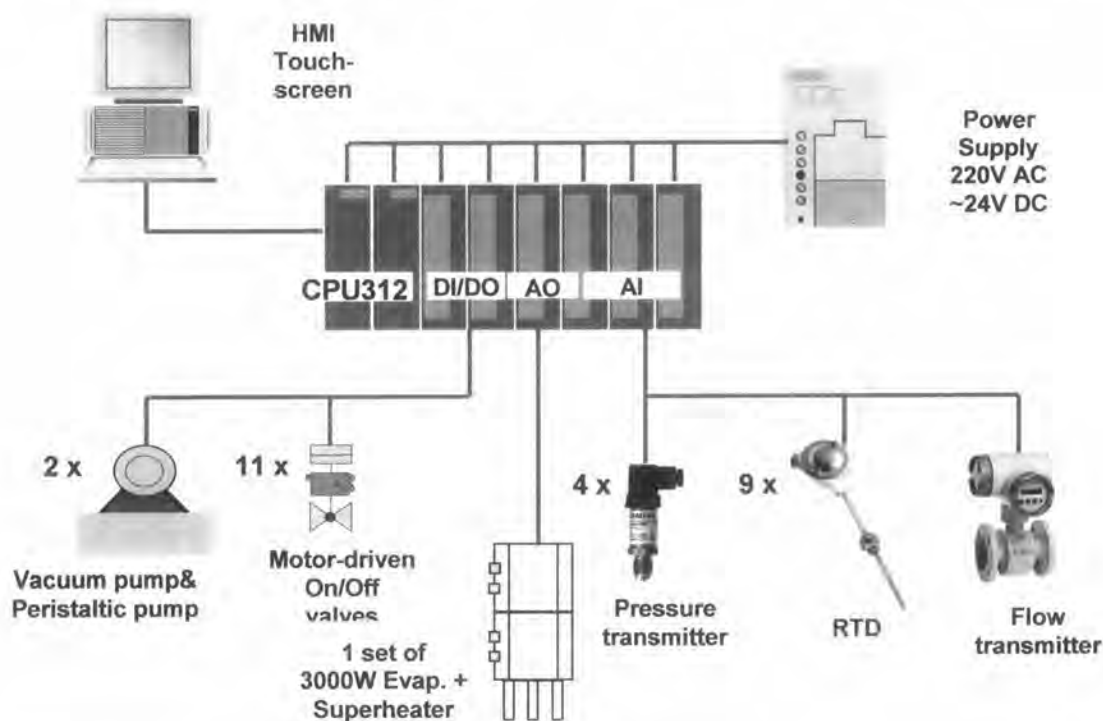


Figure 3.2 Control instruments for the PSA system.

The half cycle of the ethanol PSA process, sequence of steps and interaction between beds is presented in Table 3.1 and Figure 3.3. The control system was programmed such that the time interval between each step can be varied according to the process operator. Generally, the PSA system starts up at step T0 to heat up the evaporator before feeding of the ethanol-water can be made. The system then follows from step T1 until T6 and repeats again at step T1. But if any attempt to stop the system is made, then the control unit would direct the process through to step T9 before being shut down. However, it is also possible to run the PSA pilot plant in manual mode with a possibility of heating and purging the entire system with nitrogen gas. From Table 3.1, the PSA cycle can be divided into following stages:

1. Adsorption or production stage The water-ethanol vapor stream is fed to the bed from the top at 2.0 or 2.4 bar and 120 °C. The high pressure product stream is collected at the bottom of the bed (desirably dry ethanol). A part of the product stream is used to purge and re-pressurize the bed during the desorption stage. The adsorption stage takes about 600 to 900 seconds.

2. Desorption stage follows after production stage is completed. The bed must be depressurized, regenerated, and re-pressurized to before next adsorption stage continues.

1st depressurization step: Initially, the pressure in the bed is 2.0 or 2.4 bar and declines to about 1.0 bar in 120 seconds or less. The flow through the valve is critical and the pressure decrease is linear.

2nd depressurization step: Pressure at the outlet (top of the bed) is 1.0 bar and it firstly declines linearly and at the end exponentially to 0.15 bar in about 200 seconds. The rate of the 2nd depressurization is governed by the cross section of the ball valve and the power of the vacuum pump.

Regeneration step with purge: The bed is purged at 0.15 bar from the bottom of the bed by using a portion of the product stream. This step is relatively short and only takes no more than 30 seconds in total.

Pressurization: Initially the bed is under vacuum at 0.15 bar and it is continually pressurized (from the bottom of the bed) by the product stream to approximately 0.6 to 0.8 bar in 140 seconds. Then the system switches and pressurization is continued by the feed stream all the way up to 2.0 or 2.4 bar in about 100 seconds.

Zeolite type 3A was used as adsorbent in the form of spheres with nominal diameter of 2.5-5 mm, as obtained from Zeochem® molecular sieve Z3-03. The bed was also characterized by determining some of its physical properties, which included the calculation of the porosity of the bed. A stainless steel vessels were used (57 cm in length; 20 cm i.d.) as packed bed. Its dimensions ensured good flow distribution since

the bed internal diameter was at least 10 times as much as the particle size and its length was at least 100 times as much as the particle size (Madson and Monceaux, 1999). Each column was packed with 16 kg of 3A zeolite.

The bed was also characterized by determining some of its physical properties, which included the calculation of the porosity and of the packing density of the bed. Under these conditions, the bed volume can be calculated from Equation 3.1.

$$V_{cs} = \frac{\pi \phi_{cs}^2 H_{cs}}{4} \quad (3.1)$$

To calculate the porosity of the bed, it was necessary to know the total mass of the particles that filled the bed. The process of bed filling started by placing the column in upright position and pouring the adsorbent at the top with the aid of a funnel. At the same time, moderate vibration was applied at the bottom of the column.

Table 3.1 Sequence of each equipment in the PSA system

	START	LHS Adsorption			RHS Adsorption			STOP		
	T0	T1	T2	T3	T4	T5	T6	T7	T8	T9
1 Peristaltic Pump	off	on	on	on	on	on	on	off	off	off
2 Heaters	on	on	on	on	on	on	on	off	off	off
3 On-off valve	off	on	on	on	off	off	off	off	off	off
4 On-off valve	off	off	off	off	on	on	on	off	off	off
5 On-off valve	off	off	off	off	on	on	off	on	off	off
6 On-off valve	off	on	on	off	off	off	off	on	on	off
7 On-off valve	off	off	off	off	off	on	on	off	off	off
8 On-off valve	off	off	on	on	off	off	off	off	off	off
9 On-off valve	off	off	on	on	off	off	off	off	off	off
10 On-off valve	off	off	off	off	off	on	on	off	off	off
11 On-off valve	off	on	on	off	on	on	off	on	on	off
12 On-off valve	off	off	off	on	off	off	on	off	off	on
13 On-off valve	off	off	off	on	off	off	on	off	off	on
14 Vacuum Pump	off	on	on	off	on	on	off	on	on	off

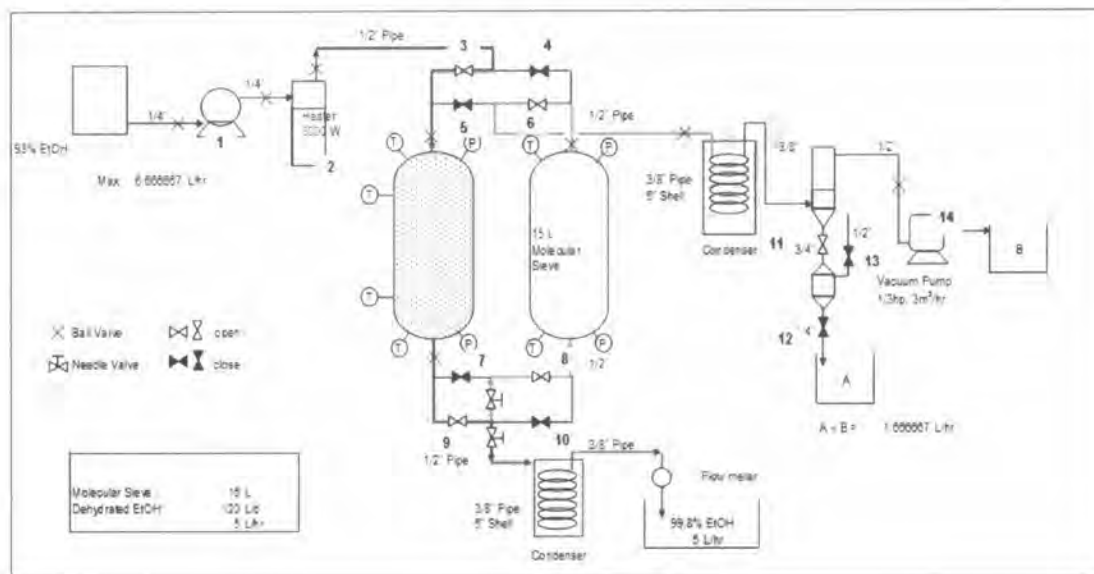


Figure 3.3a Schematic diagram of the PSA system while left column is under adsorption stage and right column is under desorption stage.

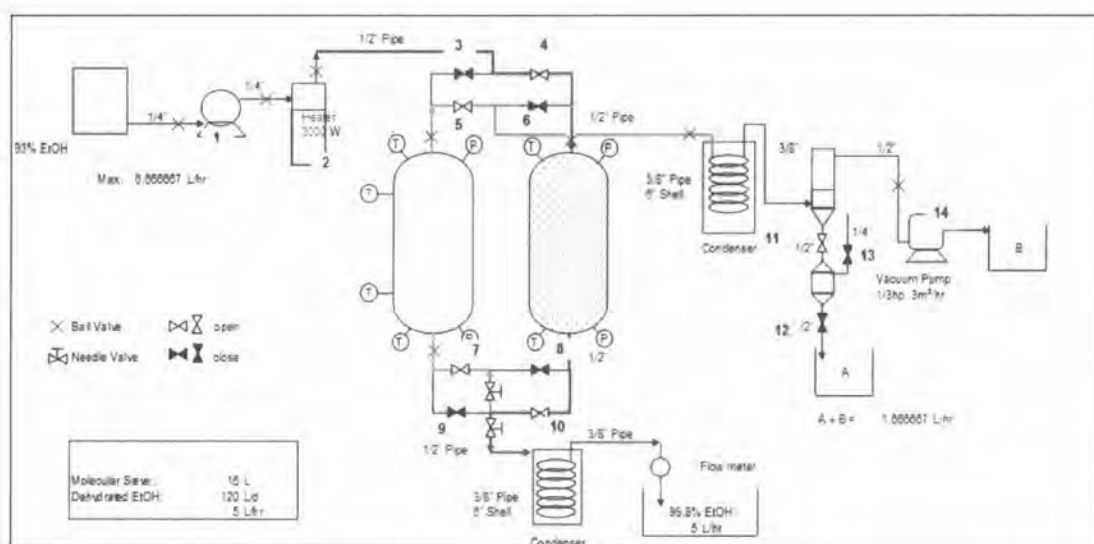


Figure 3.3b Schematic diagram of the PSA system while left column is under desorption stage and right column is under adsorption stage.

By weight difference, it was possible to determine the mass of particles loaded into the column and the porosity was calculated from Equation (3.2).

$$\varepsilon_l = 1 - \frac{M_s}{\rho_p V_{cs}} \quad (3.2)$$

Once the adsorbent mass contained in the bed and the total volume of the bed have been determined, the packing density was calculated from Equation (3.3). The characterization parameters of the bed are shown in Table 3.2.

$$\rho_b = \frac{M_s}{V_{cs}} \quad (3.3)$$

Table 3.2. Physical properties of the adsorption column.

ϕ_{cs}	20.8	cm
H_{cs}	57.0	cm
A_{cs}	339.9	cm ²
V_{cs}	19,376.1	cm ³
M_s	16,450	g
ρ_b	0.849	g/cm ³
ρ_p	1.25	g/cm ³
ε_L	0.321	

The ethanol-water solution was prepared from anhydrous ethanol and distilled water at concentrations of 92 to 95 % vol ethanol. In order to measure the concentration of the fluid phase, an Anton Paar Density/Specific Gravity/Concentration meter was used and data repeatability of 0.5% was obtained with the accuracy of $\pm 0.001\text{g/cm}^3$. The experimental setup was divided into four main parts: feed system (composed of a 20-liter tank, peristaltic pump, evaporator, valves, pipes and connections), central body (composed of two adsorption columns, heating system, valves, pipes, and vacuum pump), a product collection system (composed of collectors, two tube heat exchangers, and a cooling bath), and a control system with data collection and user interface units. Figure 3.4 illustrates the experimental system.

All experiments were organized by a 2^k factorial design which allowed fitting of models from a reduced number of experimental points, accomplishing interactions among the variables and the linear terms of each variable. The experiments investigated the effect of different operating parameters such as feed rate (80-100 mL/min), feed concentration (92-95% vol ethanol), adsorption pressure (2-2.4 Bar A),

and cycle time (10-15 mins) as shown in Table 3.3. The univariate experiment was then used to investigate the influence of each factor on the performance of the PSA system.

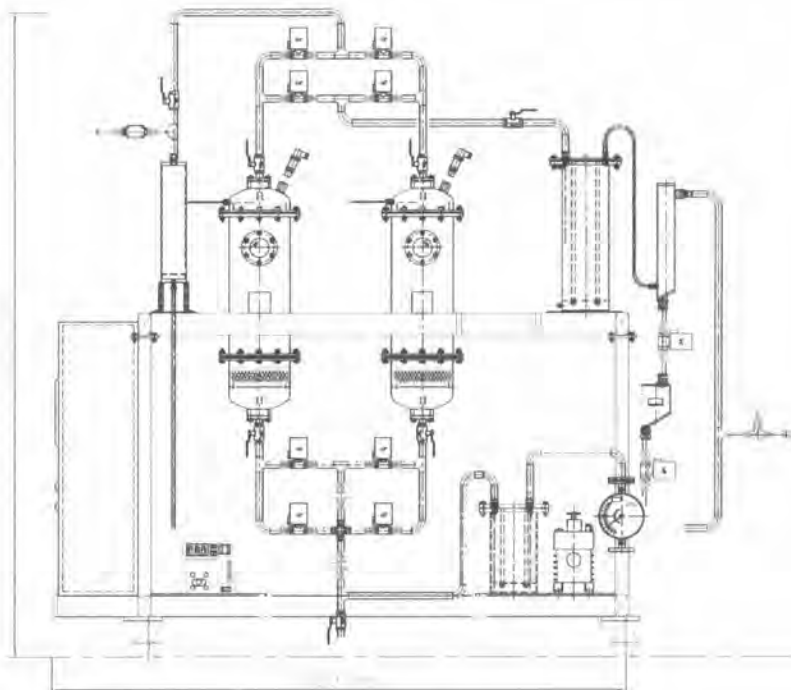


Figure 3.4 Illustration of the PSA experimental setup.

Answers of interest (enrichment of the fluid phase and the percentage of product recovery) were obtained from Equations 3.4 and 3.5, respectively, all of which were calculated at steady state.

$$E = X_f \quad (3.4)$$

$$R = \frac{M_f X_f}{M_0 X_0} \times 100 \quad (3.5)$$

E = Enrichment of the product (% in ethanol volume)

R = Percentage of ethanol recovery (%)

X_f = Concentration of the product in the recipient at steady state (% in ethanol volume)

X_0 = Concentration of the feeding fluid (% in ethanol volume)

M_0 = Amount of feeding fluid (mL)

M_f = Product amount in the recipient, for operation cycle (mL)

Table 3.3 Values of the variables for the preliminary experiments

Run	T (°C)	P _L (bar)	P _H (bar)	v (mL/min)	C (%vol)
1	120	0.15	2.4	80	95
2	120	0.15	2.4	80	95
3	120	0.15	2.4	80	92
4	120	0.15	2.4	80	92
5	120	0.15	2.4	100	95
6	120	0.15	2.4	100	95
7	120	0.15	2.4	100	92
8	120	0.15	2.4	100	92
9	120	0.15	2.0	80	95
10	120	0.15	2.0	80	95
11	120	0.15	2.0	80	92
12	120	0.15	2.0	80	92
13	120	0.15	2.0	100	95
14	120	0.15	2.0	100	95
15	120	0.15	2.0	100	92
16	120	0.15	2.0	100	92

3.3 Density meter

In order to measure the concentration of the fluid phase, a portable density meter, DMA 35N from Anton Paar was used with the density accuracy of 0.001 g/cm^3 and the data reproducibility of 0.0005 g/cm^3 (Figure 3.5). Based on harmonic oscillator technology, the density meter could accurately measure density, specific gravity or ethanol concentration in % ethanol weight or % ethanol volume. It must also be noted that in the first phase of the experiment the enrichment of ethanol was measured in wt% similar to other literatures while % vol of ethanol was used in the second phase of the experiment which related to the industrial standard. It should be noted that at $30 \text{ }^\circ\text{C}$ the pure ethanol of 100 wt% concentration has a density of 0.78075 g/cm^3 and an inclusion of an undesired product, apart from ethanol and

water, could marginally change the density and consequently the concentration measurement.

Table 3.4 The specification of Anton Paar DMA 35N density meter

Measuring range	Density: 0 to 1.999 g/cm ³ Temperature: 0 to 40 °C (32 to 104 °F), filling at higher temperatures possible
Accuracy	Density: ±0.001 g/cm ³ Temperature: ±0.2 °C
Repeatability, s.d.	Density: 0.0005 g/cm ³ Temperature: 0.1 °C
Resolution	Density: 0.0001 g/cm ³ Temperature: 0.1 °C or 0.1 °F
Permanently stored tables and customer functions	°Brix, % Alcohol, Proof, °Baumé, °Plato, API gravity, API SG, API density, SG at ref.temp., %H ₂ SO ₄ , programmable customer functions
Data memory	1024 measuring values
Power supply	Two 1.5 V alkaline batteries (Micro LR03 AAA)
Sample volume	Approx. 2 ml
Dimensions	140 x 130 x 25 mm (5.5 x 5.1 x 1 inches)
Weight	275 g (10 ounces)



Figure 3.5 Anton Paar DMA 35N density meter.

3.4 Thermal Gravimetric Analysis (TGA)

Despite desorption and purging of the zeolite after each experimental run, there is some amount of water and ethanol remaining in the PSA system. Due to the fact that the adsorbers are preheated at high temperature before each operation with the absence of oxygen, there is a possibility of thermal cracking of ethanol to form coking on the surface of the zeolite. This could significantly affect the performance of the molecular sieve. Thermal gravimetric analysis will be used to study a presence of these undesired products. Figure 3.6 shows the TG/DTA (Thermal Gravimetric/Differential Thermal Analysis) model 851^e from Mettler Toledo that was used to analyze the weight lost of the zeolite with changing temperature under a period of time.



Figure 3.6 Thermal gravimetric analyzer model 851^e from Mettler Toledo.

3.5 BET

It is expected that after many operating cycles, with changes in temperature and pressure, the characteristic of the zeolite can be deteriorated. BET surface area and pore size diameter will be analyzed to study the effect of thermal and mechanical fatigue on the performance of the zeolite. The Flow Sorb II 2300 micro metric surface area analyzer (Figure 3.7) was used to detect the BET surface areas by nitrogen adsorption in a flow system.

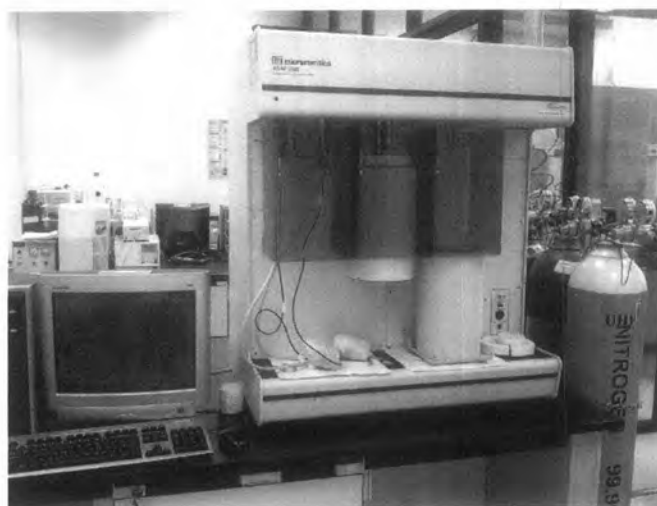


Figure 3.7 Micromeritics Surface Area Analyzer Flow Sorb II 2300.