CHAPTER V

SECOND PHASE - PSA PILOT PLANT

Molecular sieves have become by far the most popular means to dehydrate ethanol to absolute or near absolute levels. Several factors have contributed to this efficiency including designing of the adsorbers, performance of the zeolite, and operating parameters. The key ingredient in this process, the pressure swing adsorption, is not well understood so this study has been prepared to give an understanding about what the PSA process is and how it can be used for alcohol drying.

5.1 Characteristic of the 3A zeolite

The molecular sieve 3A that was used in the PSA pilot plant was obtained from Zeochem AG, Switzerland. It was the same as the adsorbent used in the fixed bed experiment. Table 5.1 shows the specific surface area of 25.71 m^2/g analyzed by BET surface area analyzer. The specific surface area would be analyzed again at the end of the experiment to see how mechanical and thermal fatigue would affect the performance of the zeolite. It is expected that the surface area of an adsorbent would reduce after long period of operation, especially when working under changing pressure.

Table 5.1 BET surface area analyzer testing condition for the 3A zeolite before the experiments

Degas temperature	150°C
Degas time	60 minutes
Method	ISO 9277
Sample	Zeochem (Before)
Specific Surface Area (m^2/g)	25.71 ± 0.02

5.2 Two-level factorial designed experiment

This experiment studied different parameters that had the effect on the performance of the PSA pilot plant. Two-level factorial design experiment was used in this research work to preliminary screen the influence and interaction among each factor. In this work, the principal factors, which have an effect on the performance in terms of percentage of ethanol recovery and the enrichment of the product from the PSA system, are ethanol water mixture feed rate, adsorption pressure, cycle time, and the concentration of the feeding mixture. Table 5.2 shows the conditions of each experimental run and their subsequent answers of interest.

Carton *et al.* (1987) experimentally compared drying the ethanol-water azeotrope by vapor phase and liquid phase adsorption of the water onto 3A molecular sieve that the vapor phase process was more favorable since steeper breakthrough curve and that greater adsorptive capacities were obtained. Furthermore, it was indicated that an additional disadvantage of liquid phase adsorption is the retention of a substantial amount of feed in the void volume at the end of the adsorption stage. Hence, in this experiment, and initial bed temperature of 120 °C was considered to ensure condensation was avoided.

Table 5.2 shows the experimental conditions arranged by two-level factorial designs, which are widely used in experiments involving several factors where it is necessary to study the joint effect of the factors on a response. This section of the study involves 4 parameters resulting in 16 experimental runs. It can be seen that the enrichment of the ethanol product is not significantly affected by feed rate, cycle time or adsorption pressure. This could be explained by the fact that the PSA process was usually only operated at a fraction of the adsorbers' capacity and the duration of the adsorption step was much shorter than the time period needed for the breakthrough to occur to ensure high concentration product (Jain *et al.*, 2003).

At the same time, Table 5.2 shows that the percentage of ethanol recovery in the product stream is significantly affected by feed rate, feed concentration and cycle time. It can be seen that increasing cycle time or the feed rate also raises the percentage of ethanol recovery. However, the amount of ethanol in the product is a

reverse proportion to the feed concentration. In other words, the lower the ethanol concentration in the feed, the lower the percentage of ethanol recovery.

Table 5.2 2^k factorial designed experiment of the PSA pilot plant

Run No	Feed Rate (mL/min)	Feed Conc. (%vol)	Ads Pressure (bar)	Cycle Time (Min)	Enrichment (%vol)	Recovery (%)
1	80	92	2.0	10	99.56%	78.24%
2	80	92	2.0	15	99.64%	81.91%
3	80	92	2.4	10	99.61%	80.78%
4	80	92	2.4	15	99.64%	81.64%
13	80	95	2.0	10	99.58%	70.54%
14	80	95	2.0	15	99.50%	76.63%
15	80	95	2.4	10	99.53%	73.58%
16	80	95	2.4	15	99.54%	74.88%
9	100	92	2.0	10	99.64%	82.01%
10	100	92	2.0	15	99.64%	84.46%
11	100	92	2.4	10	99.56%	84.90%
12	100	92	2.4	15	99.66%	85.26%
5	100	95	2.0	10	99.59%	76.91%
6	100	95	2.0	15	99.60%	82.32%
7	100	95	2.4	10	99.57%	74.68%
8	100	95	2.4	15	99.58%	84.28%
AVG					99.59%	79.56%

It is important to notice that the cyclic steady state is approached after a few cycles of operation. Figure 5.1 shows the development of the product concentration profile as a function of operating time. The PSA system was able to produce high concentration of ethanol product after one or two cycles of operation thanks to the pre-heating system installed as the beds' jacket. Usually, PSA unit requires to start the operation with a pure ethanol feed stream and smoothly increase the concentration of

water until a required concentration of the ethanol-water mixture is achieved. Alternatively, process starts with a low flow of ethanol feed vapor. As the bed is being gradually preheated and preloaded with water, the feed flow is slowly increased. As soon as the wet ethanol vapor is introduced to the bed, a rapid water adsorption takes place accompanied by significant heat generation (Simo *et al.*, 2007). This strong temperature overshooting during the start-up of an exothermic catalytic reactor is well known fact; hence the preheating system was employed to shorten the start-up time.

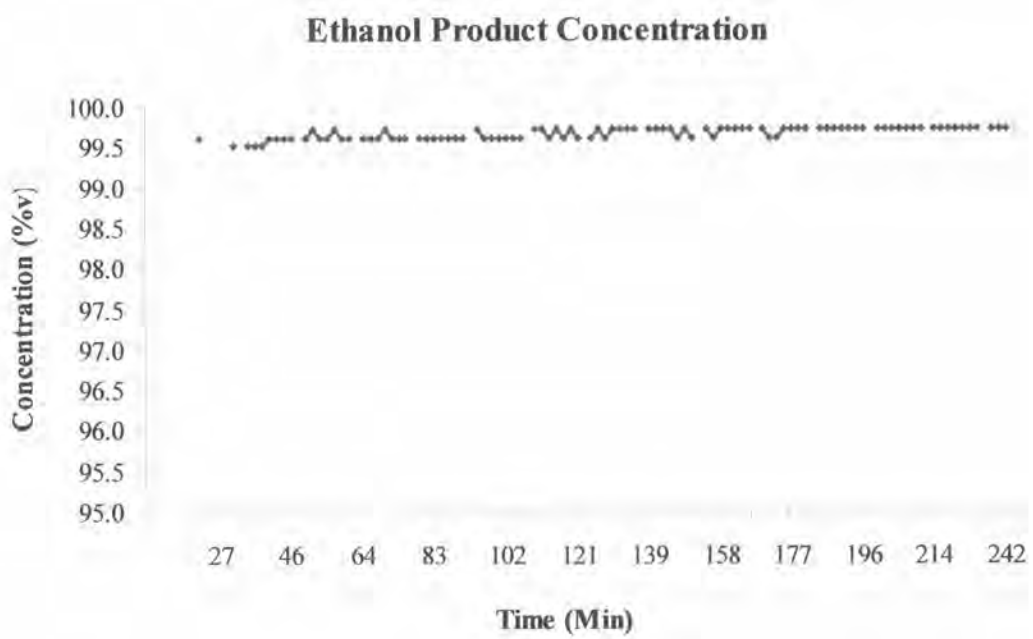

Figure 5.1 Illustration of the concentration of dry ethanol produced from a feed concentration of 92%vol, adsorption pressure of 2 bar, cycle time of 15 minutes, and feed rate of 100 mL/min.

The experimental data shown in Table 5.2 was then analyzed by "Design Expert" software to perform the analysis of variance (ANOVA) to find significant effects on an answer of interest, in this case percentage of ethanol recovery and the enrichment of ethanol in the product stream. Figure 5.2 illustrates that flow rate, feed concentration and cycle time significantly affect the recovery of ethanol while the quality of the ethanol as a product seems to only be affected by the ethanol concentration in the feed.

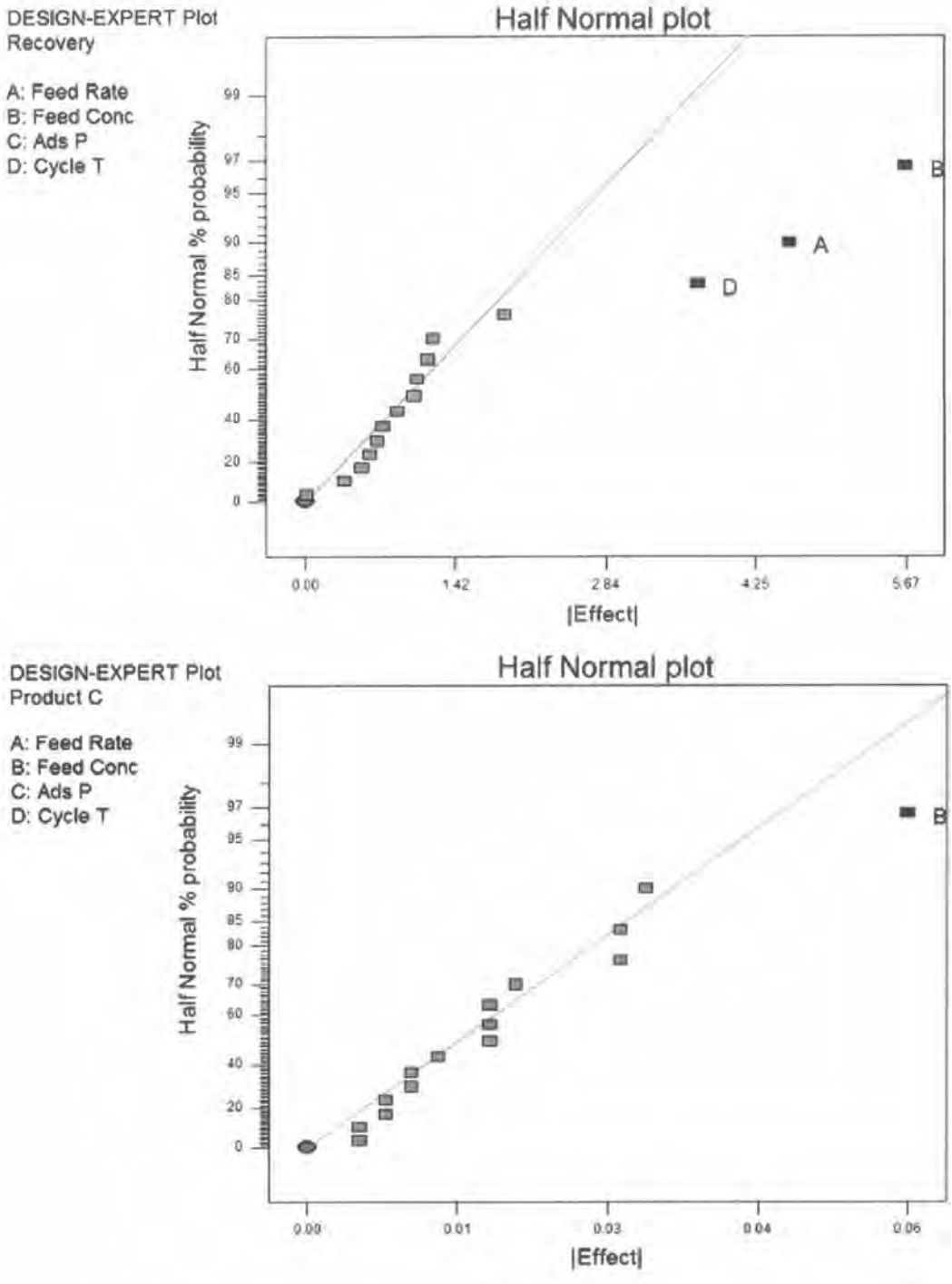

Figure 5.2 Design Expert normal plot of significant effects on percentage of ethanol recovery and concentration of ethanol product.

From Table 5.3, the Model F-value of 24.00 implies the model is significant. There is only 0.01% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.05 indicate model terms are significant. In this

case, A, B, and D are significant model terms. Values greater than 0.1 indicate the model terms are not significant.

Table 5.3 Analysis of variance of significant effects on percentage of ethanol recovery

Source	Sum of Squares	DoF	Mean Square	F Value	Prob > F
Model	267.8	3	89.27	24.00	< 0.0001
A	83.81	1	83.81	22.53	0.0005
B	128.71	1	128.71	34.60	< 0.0001
D	55.28	1	55.28	14.86	0.0023
Residual	44.64	12	3.72		
Cor Total	312.44	15			

Table 5.4 Analysis of variance of significant effects on percentage of concentration of ethanol product

Source	Sum of Squares	DoF	Mean Square	F Value	Prob > F
Model	0.013	1	0.013	9.86	0.0072
B	0.013	1	0.013	9.86	0.0072
Residual	0.019	14	1.341E-003		
Cor Total	0.032	15			

From Table 5.4, the Model F-value of 9.86 implies the model is significant. There is only 0.72% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.05 indicate model terms are significant. In this

case, B is the only significant model term. Values greater than 0.1 indicate the model terms are not significant.

In addition to the analysis of variance to find significant effects on answers of interest like recovery and enrichment of ethanol, the Design Expert software also presents the regression models as following:

Recovery (%) = 226.46 + 0.23 Feed Rate (mL/min)
-1.89 Feed Conc. (%vol) + 0.74 Cycle T (min) (5.1)

Product C (%vol) = 101.38 – 0.019 Feed Conc. (%vol) (5.2)

5.3 Effects of different parameters

The previous section showed that there were three significant effects on the percentage of ethanol recovery which were flow rate, cycle time and feed concentration. It was also proven that the ethanol concentration in the product was significantly affected by the feed concentration. However, in the industrial scale operation, PSA process for water removal from ethanol only proceeds after the distillation process which typically gives around 92-95% vol of ethanol (Madson, 2004). This is a minute range and the author sees no important in varying the feed concentration apart from those presented in Table 5.2, hence further studies are made to thoroughly examine the effects of feed rate and cycle time.

5.3.1 Graphical models from Design Expert simulation

From the regression models given in Equation (5.1) and (5.2), the effects of different parameters can be illustrated graphically in Figure 5.3 to 5.6. From Figure 5.3, it can be seen that the feed rate at 100 mL/min gave an average of 81.5 % ethanol recovery when compared to around 77% from those of the feed rate at 80 mL/min. However, higher feed concentration tends to give lower percentage of ethanol recovery. As shown in Figure 5.4, feed concentration of 95%vol results in approximately 77% ethanol recovery as opposed to 82.5% recovery from the feed concentration of 92%vol.

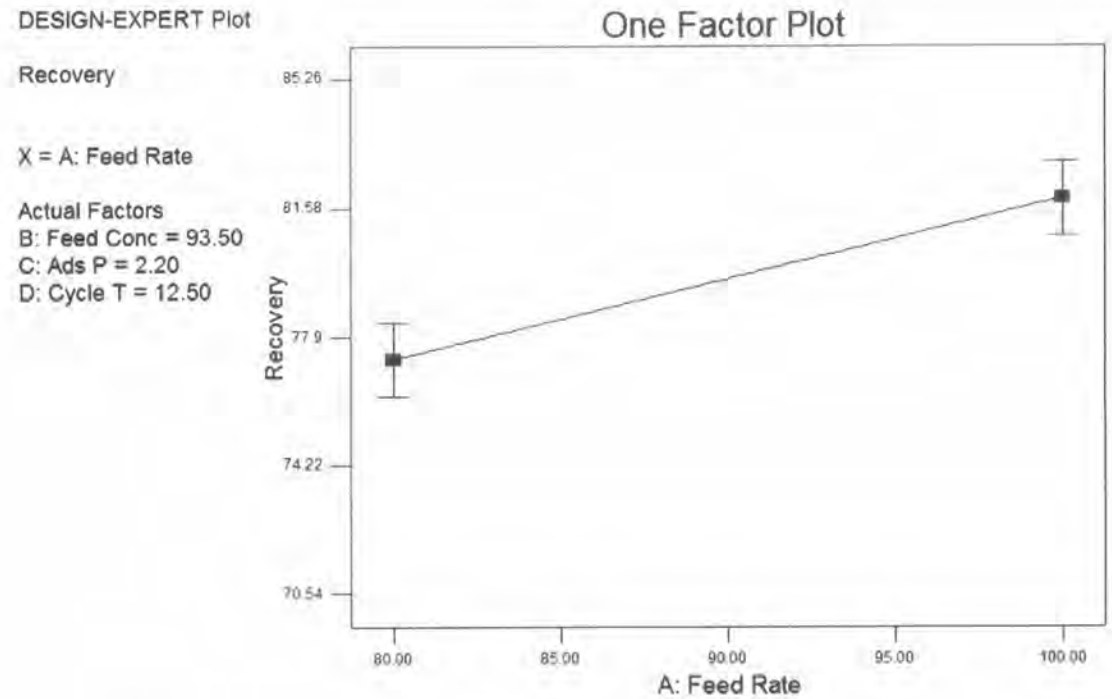

Figure 5.3 Graphical model of the effect of feed rate of ethanol-water mixture on percentage of ethanol recovery.

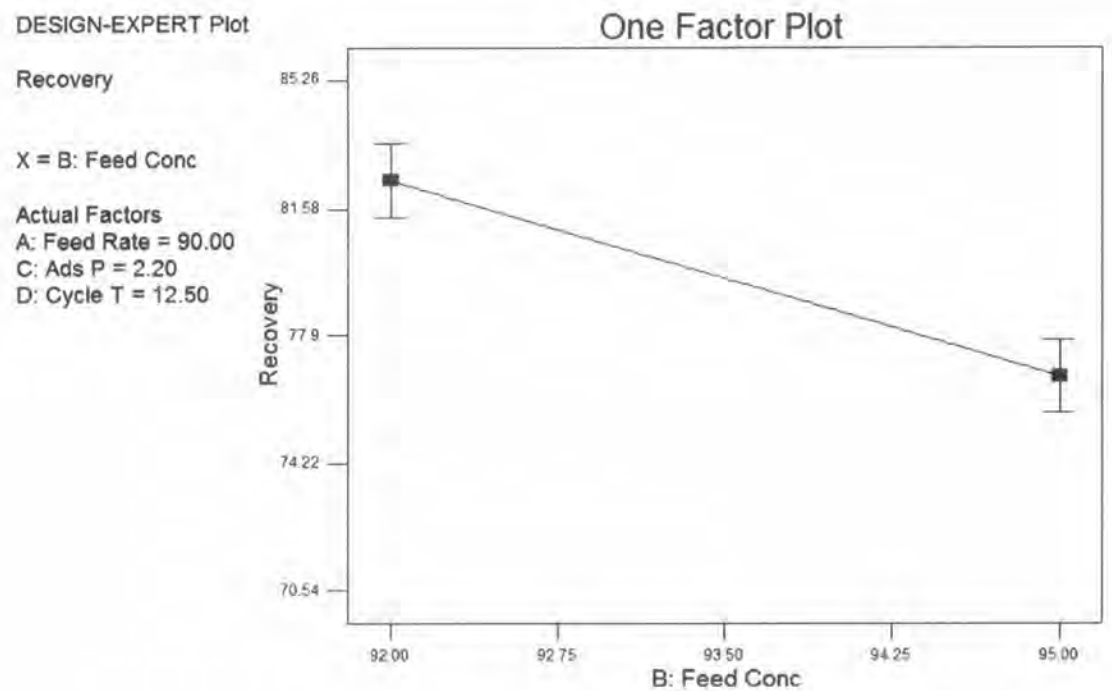

Figure 5.4 Graphical model of the ethanol feed concentration on percentage of ethanol recovery.

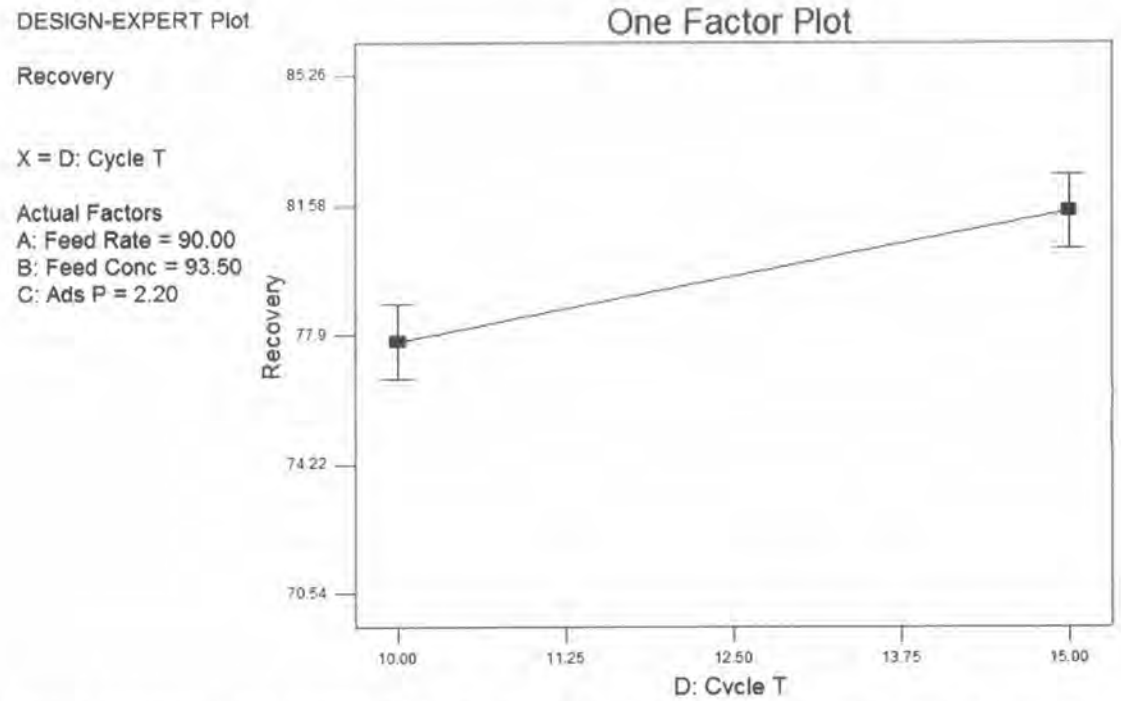

Figure 5.5 Graphical model of the effect of PSA cycle time on percentage of ethanol recovery.

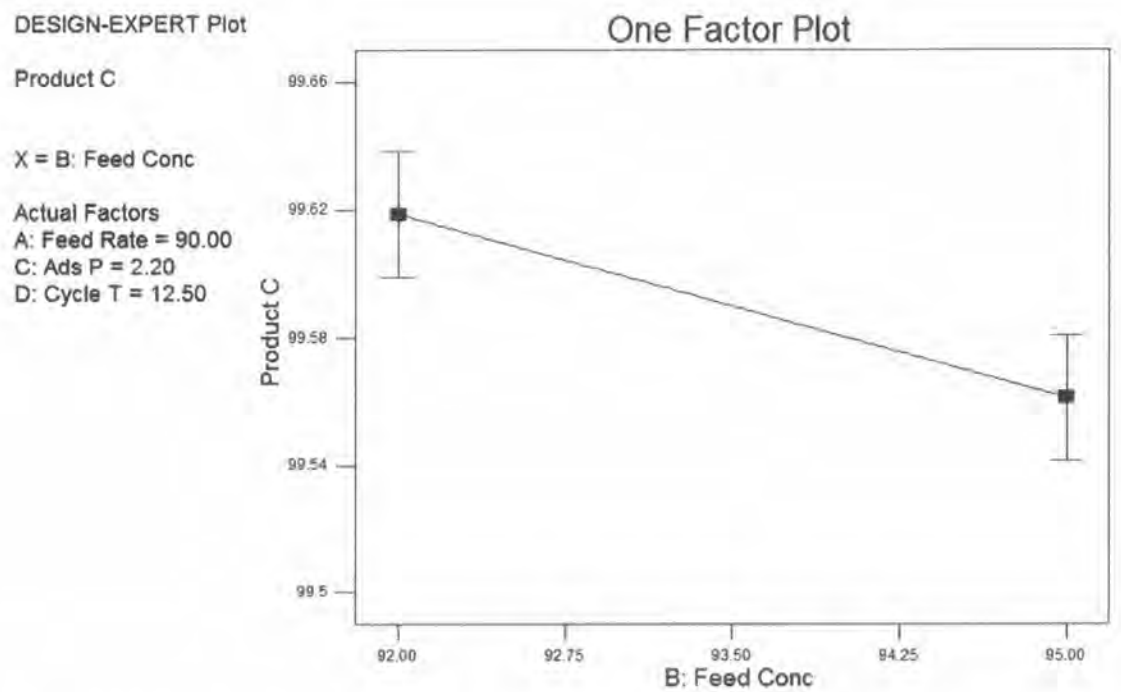

Figure 5.6 Graphical model of the effect of ethanol-water mixture feed concentration on concentration of ethanol product.

Adsorption is achieved due to the interaction forces between the adsorbing molecules and the adsorption surface. Although 3A molecular sieves were chosen to preferentially adsorb water, ethanol can still be trapped onto the surface of the adsorbent. According to Rakshit (1993), if the adsorber is loaded with higher mole fraction of water, it is less attract to ethanol and may be the reason that, in Figure 5.4, feed concentration of 92 %vol ethanol gave higher percentage of ethanol recovery.

Figure 5.5 shows that the cycle time of 15 minutes led to higher percentage of ethanol recovery at 81% while PSA pilot plant could only recover approximately 77% of ethanol when the cycle time of 10 minutes was employed. The effect of feed concentration on the enrichment of the product is shown in Figure 5.6. It is illustrated that higher enrichment of ethanol was achieved when the ethanol-water mixture concentration of 92% was fed into the system.

5.3.2 Effect of cycle time on the performance of PSA

From the analysis of effects of parameters in the previous section, further study was needed to clarify the role of cycle time on the performance of PSA. All experiments were performed at various cycle times (see Table 5.5) while adsorption pressure, feed concentration, and feed rate are maintained at 2.4 bar, 95%vol, and 100 mL/min, respectively.

From Figure 5.7, it can be seen that an increase in cycle time can improve the percentage of the ethanol recovery because the higher the cycle time, the higher proportion of the time during adsorption to the regeneration period (i.e. less number of regeneration step per hour). However, the effect of the cycle time on the product concentration cannot be clearly seen since the amount of zeolite packed in the adsorber was in abundant and the breakthrough had not yet occurred. The longest cycle time that was employed in this study was 35 minutes since the percentage of ethanol recovery seemed to converge at the value of around 90%. Furthermore, the longer the adsorption process was carried on, the higher the temperature surged in the column due to heat of adsorption. This temperature is naturally reduced once regeneration step takes places as energy is used to evaporate water during desorption (Salem and Sherbil, 1999).

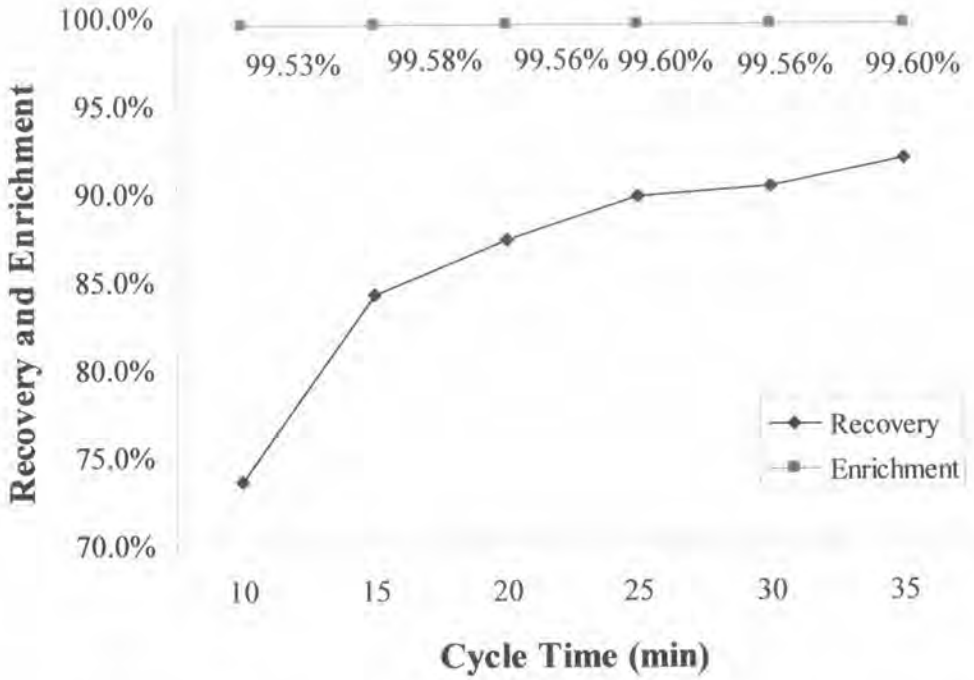

Figure 5.7 Effect of cycle time on product concentration and percentage of ethanol recovery.

Table 5.5 The experimental results from the variation of cycle time

Feed Rate (mL/min)	Feed Conc. (%vol)	Ads Pressure (bar)	Cycle Time (min)	Recovery (%)	Enrichment (%vol)
100	95	2.4	10	73.58%	99.53%
100	95	2.4	15	84.28%	99.58%
100	95	2.4	20	87.38%	99.56%
100	95	2.4	25	89.72%	99.60%
100	95	2.4	30	90.33%	99.56%
100	95	2.4	35	91.89%	99.60%

5.3.3 Effect of flow rate on the performance of PSA

Experiments were carried out to investigate the effect of flow rate on the performance of the PSA pilot plant. The study was made at constant adsorption pressure of 2.4 bar, feed concentration of 95% vol ethanol, cycle time of 15 minutes

and initial bed temperature of 120 °C. It can bee seen in Figure 5.8 and Table 5.6 that the percentage of ethanol recovery is increasing with an increase of the flow rate.

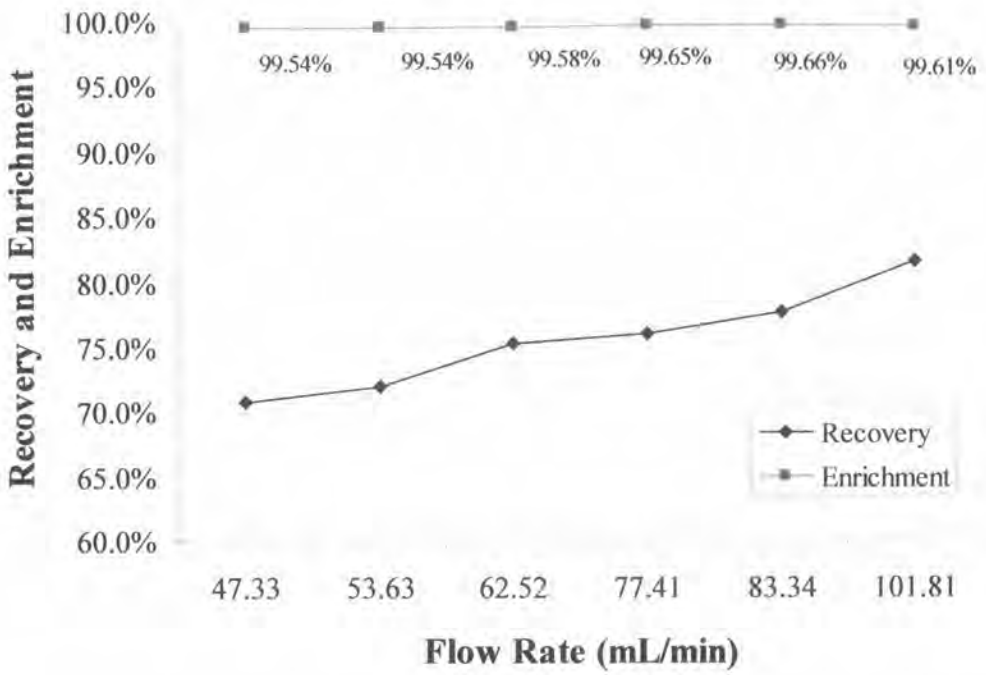

Figure 5.8 Effect of flow rate on product concentration and percentage of ethanol recovery.

Table 5.6 The experimental results from the variation of flow rate

Feed Conc. (%vol)	Ads Pressure (bar)	Cycle Time (min)	Flow Rate (mL/min)	Recovery (%)	Enrichment (%vol)
95	2.4	15	47.33	70.73%	99.54%
95	2.4	15	53.63	72.00%	99.54%
95	2.4	15	62.52	75.28%	99.58%
95	2.4	15	77.41	76.05%	99.65%
95	2.4	15	83.34	77.73%	99.66%
95	2.4	15	101.81	81.61%	99.61%

According to Fahardpour and Bono (1996a), external film mass transfer resistance, which is greatly affected by vapor velocity, may make small contribution to the behavior of a fixed-bed for the ethanol-water/zeolite system. Hence, it is fair to conclude that the higher recovery of ethanol was achieved mainly by high throughput of ethanol into the adsorber during adsorption period. However, the flow rate seemed to have no significant effect on the enrichment of the ethanol product. Again, under similar adsorption condition, the PSA pilot plant would produce dry ethanol so far as the bed length is longer than the LES.

5.4 Length of equilibrium section (LES)

As mention earlier, dry ethanol can be produced only when the length of equilibrium section (LES) is less than the bed length. Increasing the initial bed temperature decreases the time for breakthrough to occur. For ideal case, LES can be determined by a solute mass balance for a cylindrical bed of certain diameter. In this case the LUB, and consequently LES, can be determined from an experimental breakthrough curve. Table 5.7 shows the condition in which the experiment was carried to calculate the actual value of LES for the PSA pilot plant.

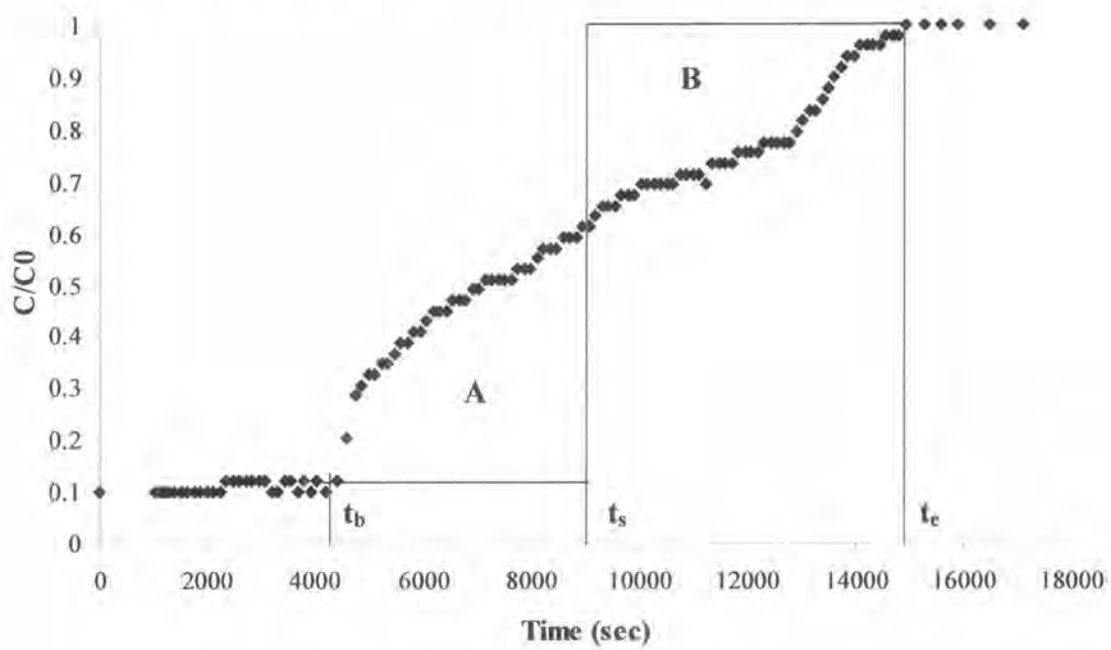

Figure 5.9 Breakthrough curve of one of the adsorber from PSA pilot plant.

From Figure 5.9, it can be seen that the breakthrough time and bed saturation occurred at 4380 and 14820 seconds, respectively, and hence giving t_s of 9200 seconds. Substituting all values, equation (2.13) yields:

$$LUB = L_B \frac{t_S - t_b}{t_S}$$

$$LUB = (57)\frac{9200 - 4380}{9200} = 29.86\,\text{cm}$$

and hence: $LES = L_B - LUB = 57 - 29.86 = 27.14$ cm.

As suggested earlier in this study, the length of equilibrium section (LES) can be reduced by increase the adsorption pressure, increase flow rate or decrease initial bed temperature while maintaining adsorption under vapor phase.

Table 5.7 Conditions for the breakthrough experiment

Weight of the zeolite	15	kg each column
Flow rate	100	mL/min
Initial bed temperature	120	°C
Adsorption pressure	2.4	bar
Feed concentration	95.1	%vol
Bed length	57	cm
Breakthrough time	4380	seconds

5.5 Comparison with models proposed in the literatures

Generally, the results obtained in this work have proven to be satisfied in terms of the performance of the PSA pilot plant. However, it is worthwhile comparing these results with some works proposed by other researchers. Carmo and Gubulin (2003) also carried out an investigation on ethanol-water separation employing PSA adsorption cycle with zeolite 3A as the adsorbent. However, the experiment was done in a single fixed bed but under similar operating conditions. The results obtained were

analyzed from fitted empirical equations for enrichment of the fluid phase of the ethanol product and the percentage of ethanol recovery in product steam, as shown in Equations (5.3) and (5.4):

$$E = 97.67 - (0.294\ P_H) - (1.294\ P_L) - (0.316\ v) + (0.392\ T) - (1.143\ P_H^2) + (0.704\ P_L^2) + (0.176\ P_L.v) \quad (5.3)$$

$$R = 67.481 - (0.56\ P_H) - (7.257\ P_L) + (4.483\ v) + (7.875\ T) + (8.994\ P_H^2) + (0.747\ P_L^2) + (0.245\ v^2) + (1.572\ T^2) + (1.275\ P_H P_L) + (2.504\ P_H.v) + (0.47\ P_H.T) - (0.813\ P_L.v) + (0.611\ P_L.T) + (0.203\ v.T) \quad (5.4)$$

where E is enrichment of the ethanol product, R is percentage of ethanol recovery, P_H is adsorption pressure, P_L is desorption pressure, v is flow rate, and T is initial bed temperature.

Since Carmo and Gubulin (2003) did not investigate the effect of feed concentration and cycle time, only adsorption pressure and feed rate can be compared directly to the work done by the current study. As seen in Table 5.8, it can be the enrichment of the product that was achieved by the PSA pilot plant in the current work is generally higher than that of the single fixed-bed from Carmo and Gubulin. However, it is shown that at lower flow rate of 80 mL/min, the percentages of ethanol recovery appear to be lower. It is important to notice that the enrichment and recovery percentage of ethanol product in Table 5.8 are derived from the model given in Equations (5.3) and (5.4). As proposed by Carmo and Gubulin, the experiments were organized by a three level factorial design which allowed fitting of second order models from a reduced number of experimental points, accomplishing interactions among the variables and the linear and quadratic terms of each inlet variable. Whereas, the experimental work done in this current study was organized by a two level factorial design giving only linear terms and the interactions among the variables.

Simo *et al.*, (2007) developed a mathematical model for the two bed PSA process to study a five step PSA cycle with a counter-current depressurization and a counter-current pressurization with the product. The model was used to study the dynamics and performance of an industrial PSA process used to break the ethanol-water azeotrope and deliver a fuel grade ethanol product. The cyclic steady state was reached after 350 cycles. Temperature front sensing was used to monitor the concentration front since the two waves propagate together. Online plant data was used to verify the simulation results and parametric study has examined the effects of the feed stream temperature, duration of the purge step, feed water concentration, and pressure ratio on the performance of the de-watering process.

Unfortunately, the current study and the work proposed by Simo *et al.* were undergone at completely different operating conditions; hence, direct comparison can not be made. However, both studies found that the increase of feed stream temperature can improve the quality of the product. Further process intensification can be achieved by operating at higher pressure ratio by increasing the feed stream pressure and/or decreasing the regeneration pressure.

Table 5.8 Comparison between the current study and Carmo and Gubulin (2003)

					Carmo and Gubulin (2002)		Current study	
P_H (bar)	v (mL/min)	P_L (bar)	T (°C)	Conc (%vol)	E (%vol)	R (%)	E (%)	R (%)
2.4	100	0.15	120	95	98.68	80.31	99.58	84.28
2.4	80	0.15	120	95	98.88	79.14	99.54	74.88
2	100	0.15	120	95	98.49	82.22	99.60	82.32
2	80	0.15	120	95	98.70	81.15	99.50	76.63

5.6 Prediction of the enrichment of the product for pressure swing adsorption

As explained in Chapter 2, during adsorption the mole fraction of the water decreases but when under blowdown step the mole fraction of adsorbate in the gas increases because of desorption as pressure drops. During repressurization the opposite occurs and the adsorbate mole fraction in the gas is again decreased. Determining the mole fraction changes from the feed to the product concentration requires solution of the partial differential equations for the system. Wankat (2007) defined parameter β_{strong} for the strongly adsorbed component as:

$$\beta_{strong} = \frac{\varepsilon_e + (1-\varepsilon_e)\varepsilon_p K_{d,i} + (1-\varepsilon_e)(1-\varepsilon_p)\rho_s K'_{weak} RT}{\varepsilon_e + (1-\varepsilon_e)\varepsilon_p K_{d,i} + (1-\varepsilon_e)(1-\varepsilon_p)\rho_s K'_{strong} RT} = 0.4 \qquad (2.35)$$

This parameter measures the ratio of the amount of weakly adsorbed to the amount of strongly adsorbed adsorbate in a segment of the column. Here it is assumed that $K'_{weak} = 0.4\ K'_{strong}$ (see Appendix F). Hence, Equation (2.36) predicts a decrease in mole fraction y_A for an increase in pressure.

$$\frac{y_{A,after}}{y_{A,before}} = \left[\frac{p_{after}}{p_{before}}\right]^{\beta_{strong}-1} \qquad (2.36)$$

$$y_{A,after} = 0.144 \times \left[\frac{2.4}{0.15}\right]^{0.4-1} = 0.027$$

Suppose the PSA pilot plant was operated at the feed concentration of 95% vol of ethanol under atmospheric pressure and a temperature of 30 °C or at the mole fraction of water in the feed of 0.144 (see Table 5.9). In the experiment, the regeneration of the molecular sieve took place under the pressure of 0.15 bar. After pressurization of the adsorber, the adsorption process was carried out at 2.4 bar resulting in a decrease of mole fraction of water at the outlet to 0.027 as shown in Equation 2.36. This is equivalent to 99.13% vol of ethanol in the liquid phase under atmospheric pressure and a temperature of 30 °C. It can be seen that the model yields a fairly accurate prediction of the enrichment of ethanol when compared to the actual experimental result of 99.57 and 99.58%vol at the same operating condition with cycle time of 10 and 15 minutes, respectively.

Table 5.9 Parameter for calculating the enrichment of the ethanol product

Bulk density	ρ_b	0.849	g/cm^3
Internal or pore porosity	ε_p	0.56	
External porosity	ε_e	0.32	
Water mole fraction in feed (95%vol ethanol at 1 atm, 30°C)	$y_{A,before}$	0.144	
Adsorption pressure	p_{after}	2.4	bar
Desorption pressure	p_{before}	0.15	bar
K'_{strong} (Appendix F)	$K'_{M,p}$	2.89	mmol/(kPa.g)
Particle density	ρ_p	1.25	g/cm^3

5.7 Property of the zeolite after pressure and thermal fatigue

The adsorbent life in a well-designed alcohol plant has an average life of five years (Crittenden, 1992). The mass transfer rate and the equilibrium capacity will drop as the adsorbent deteriorates resulting in early breakthrough with the consequent higher water content in the product. Obviously the cycle times can be reduced until it reaches an impractical time where a bed can not be depressurized and repressurized in the allotted time. Then the adsorbent must be replaced.

Table 5.10 BET surface area analyzer testing condition for the 3A zeolite after several experimental runs

Degas temperature	150°C
Degas time	60 minutes
Method	ISO 9277
Sample	Zeochem 3A (After)
Specific Surface Area (m^2/g)	22.96 ± 0.03

The life of the adsorbent primarily depends on the feed composition and the efficiency of the inlet separators to keep solids off the bed. Degradation of molecular sieves is due to many factors. The thermal and physical stresses of each regeneration

can eventually break some of the crystal. Furthermore, the regular temperature and pressure changes tend to produce attrition between the individual adsorbents. An obvious way to increase the adsorbent's life is to run longer cycles, i.e., to water breakthrough each cycle thus minimizing the number of regenerations.

Table 5.10 shows the BET surface area analyzer testing condition for the 3A zeolite and its specific surface area after several experimental runs. It can be seen that the specific surface area was reduced by 10.69 percents from 25.71 $\pm$ 0.02 m^2/g to 22.96 $\pm$ 0.03 m^2/g.