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Production of pure ethanol from azeotropic solution by pressure swing adsorption

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Abstract−Pressure swing adsorption (PSA) is attractive for final separation in the process of water removal especially for fuel ethanol production. Despite many researches on simulation and experimental works on adsorption of water on 3A zeolite in a fixed bed, none have studied a process with the actual PSA system. The purpose of this research was to study the PSA process with two adsorbers and effects of several parameters. The research also included analysis of kinetic and thermodynamic data of ethanol-water adsorption on commercial 3A zeolites in a single fixed bed. A two-level factorial design experiment was used in this research work to preliminarily screen the influence and interaction among the factors. Effects of important parameters such as initial temperature, feed concentration and feed rate were investigated. It was proven that the Langmuir isotherm could best predict the experimental results. In the PSA pilot test, the principal factors, which had effects on the performance, were feed rate, feed concentration, adsorption pressure and the cycle time. Prediction of the process efficiency in terms of ethanol recovery and enrichment was proposed in the form of regression models. The results of the study in a fixed bed adsorber could help designing a pilot-scale PSA unit. The experiments proved to be successful in terms of producing high concentration ethanol with high percentage of ethanol recovery. With further simulation work the process could be scaled up for an industrial use.

Key words: PSA, Adsorption, Separation, 3A Zeolites

INTRODUCTION

Conventionally, azeotropic distillation has been employed in production of fuel-ethanol. In azeotropic distillation, dehydration is carried out in the presence of an entrainer like benzene or cyclohexane. Although benzene has been banned in several countries for its carcinogenic effect, cyclohexane is still being employed. Moreover, this distillation method is very energy intensive.

To reduce energy consumption and to ensure a high level of dryness in the final ethanol product, zeolite has proved to be ideal. There have been several researches on adsorption of water from ethanol/water mixture, and they fall into two types: numerical simulation of dehydration of ethanol and water mixture [1-4] and experimental works to study the effects of its operating parameters in a single packed bed of 3A zeolite [5-7]. The effects of feed rate, feed concentration, adsorption temperature, and adsorption pressure are among the interesting factors that are examined. Through these studies, it is suggested that dehydration by adsorption on 3A zeolite has the advantage that the micropores are too small to be penetrated by alcohol molecules so that water is adsorbed without competition in the liquid phase. It requires little energy input and operates on cycles of short duration. Therefore, it has high adsorbent productivity and is often capable of producing very pure product. This latter feature is the interest of the present paper.

EXPERIMENTAL

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 different operating conditions. The zeolite was packed in a stainless steel column with inner diameter of 1.59 cm and a length of 45 cm placed in a tube furnace to maintain the temperature at desired values (Fig. 1). Carberry [8] 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 fed through the packed bed from the top. This avoided fluidization of the zeolite at higher feed rate. Once the adsorption column was saturated, the zeolite was removed and regenerated by heating in an oven at 220 °C. Prior to each run the regenerated zeolite was re-packed into the column and put under 300 °C with nitrogen gas flow through. The experiments studied the adsorption of water on 3A zeolite at a flow rate of 1-2 mL/min, temperature of 100 °C and 120 °C, and concentration between 85% v/v and 95% v/v.

In the second phase of testing, the pilot modeling of the cyclic PSA process was then designed along with its control system (Fig. 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. To shorten the time to steady state and prevent condensation, two sets of heaters were installed to maintain the initial temperature at 120 °C. The PSA cycle was divided into two stages: adsorption or production stage and desorption stage. During adsorption the water-ethanol vapor stream was fed to the bed from the top under high pressure. The product stream was collected at the bottom of the bed. Part of the product stream was used to re-pressurize and purge the bed during the desorption stage. The adsorption stage took about 600-900 sec-

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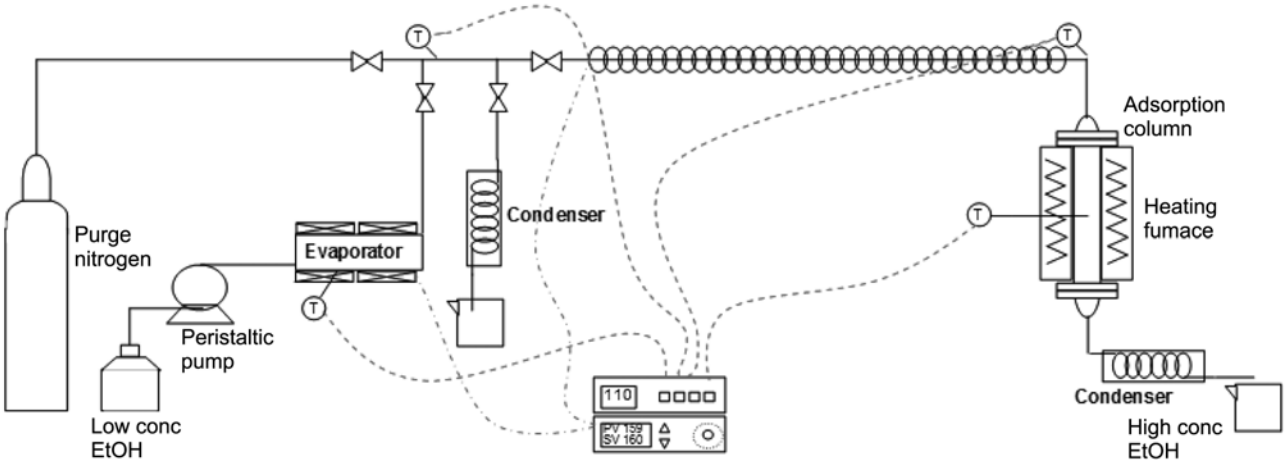

Fig. 1. Process flow diagram of the fixed bed adsorption column.

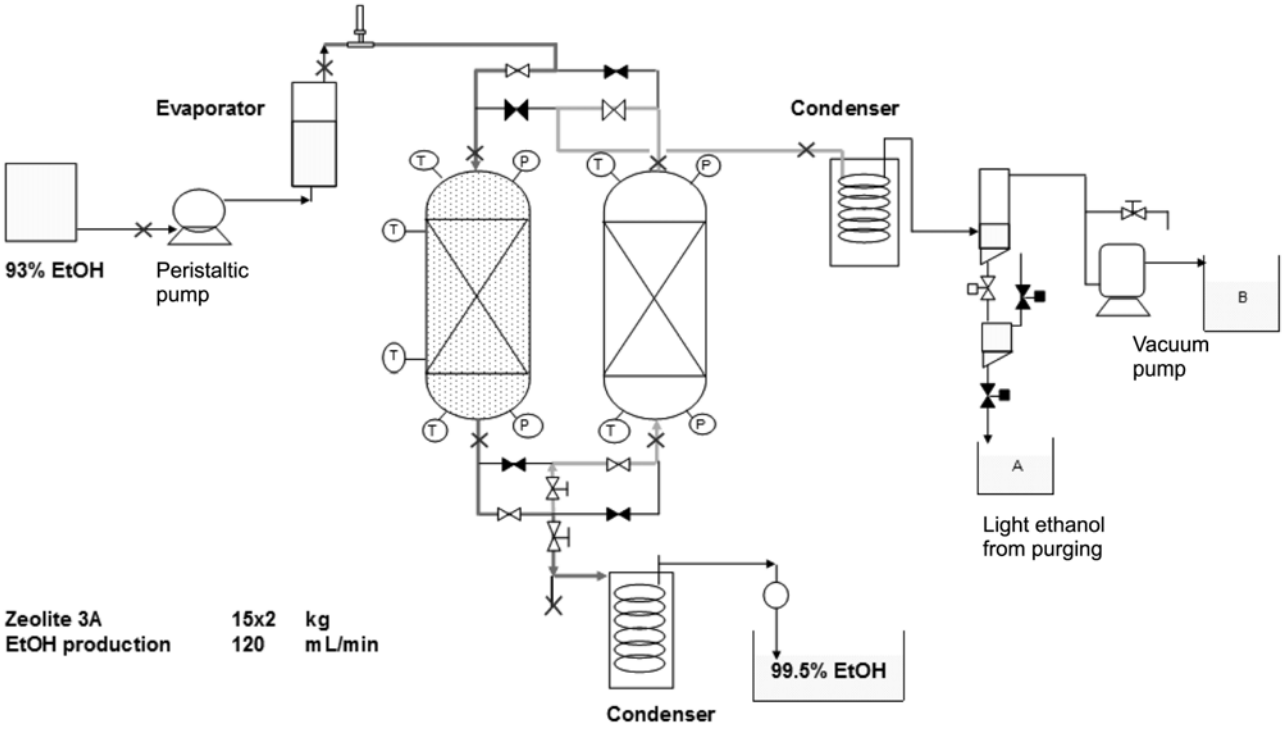

Fig. 2. Process flow diagram of the PSA pilot plant.

onds. The desorption stage followed after the production stage was completed. The bed then had to be depressurized, regenerated and re-pressurized to the adsorption pressure. The depressurization took place for approximately 400 seconds prior to being purged at 0.2 Bar from the bottom by using a portion of the product stream. This purging step took only 20 seconds. The bed was then continually repressurized by the product stream and then the feeding stream up to 2 or 2.4 Bar. All these steps were controlled by closing/opening of controlled valves through the use of the PLC system.

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 beds were made of stainless steel with a dimension of 50 cm in length and 20 cm inner diameter. 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 [9]. Each column was packed with 15 kg of 3A zeolite.

To measure the concentration of the fluid phase, an Anton Paar Density meter was used and data repeatability of 0.5% was obtained with the accuracy of ±0.001 g/cm^3. 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, feed concentration, adsorption pressure, and cycle time. The univariate experiment was then used to examine the in-

Table 1. Phase one testing. Adsorption of water on 30 g of 3A molecular sieve

3A						Theoretical		Experimental	
Run no.	T, °C	Flow rate, mL/min	Conc, %v EtOH	Breakthrough time, sec	Q, $g_{\cdot H2O}/g_{\cdot abs}$	LES cm	LUB cm	LES cm	LUB cm
1	100	1	95	3400	0.123	14.74	9.26	14.57	9.43
2	100	2	95	850	0.104	8.55	15.45	8.77	15.23
3	100	1	90	1950	0.163	12.91	11.09	11.77	12.23
4	100	2	90	540	0.135	8.54	15.46	6.86	17.14
5	120	1	95	2800	0.097	15.14	8.86	15.27	8.73
6	120	2	95	800	0.087	9.60	14.40	9.37	14.63
7	120	1	90	1800	0.148	13.02	10.98	11.08	12.92
8	120	2	90	480	0.127	8.09	15.91	6.40	17.60

fluence of each factor on the performance of the PSA system.

RESULTS AND DISCUSSION

1. First Phase-fixed Bed Adsorber

The main purpose of this experiment was to show the effects of flow rate, temperature and feed concentration on breakthrough time and water capacity. From Table 1, at 100 °C, a flow rate of 1 mL/min, and feed concentration of 95% vol gave the longest breakthrough time at 3,400 seconds. When compared at the same flow rate and feed concentration, lower initial temperature yielded higher breakthrough time and water adsorption capacity. This can be explained by the fact that adsorption is an exothermic reaction; hence it works better at lower temperature.

When adsorption process took place at the same temperature and same water concentration, a higher flow rate resulted in shorter breakthrough time. The higher feed rate meant higher vapor velocity and consequently resulted in a shorter contact time. Furthermore, by increasing the flow rate, the zeolite was exposed to a greater amount of water per unit of time.

Fig. 3 shows the amount of water that was adsorbed by different packing zeolite weights at a flow rate of 1 mL/min, 100 °C, and feed concentration of 95% vol. It can be seen that, for the same operating condition, water adsorption capacity is a direct proportion of the loading of the zeolite in the adsorber. Likewise, Fig. 4 shows that breakthrough time is highly dependent on the weight of the zeolite, given a particular adsorption condition.

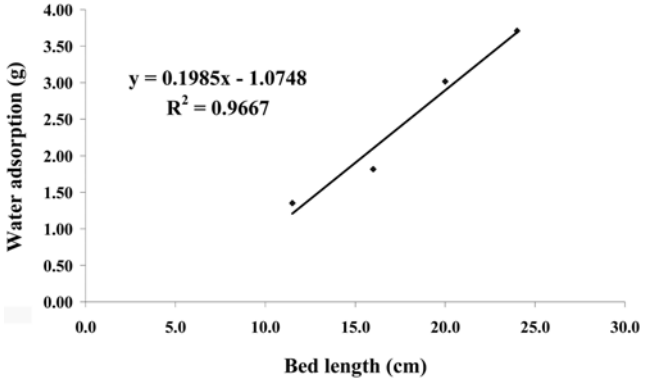

Fig. 3. Relationship between water capacity and bed length.

Fig. 5 illustrates fittings of the experimental result with different adsorption isotherms. In this case Langmuir isotherms could best predict the adsorption capacity of the 3A zeolite. Hence, monolayer adsorption of water from ethanol/water mixture on 3A zeolite can be expected.

From the experimental plot, the Langmuir isotherm can be predicted as the following equation:

$$q = \frac{8.18c}{1+42.83c} \quad (1)$$

However, as shown in Fig. 6, breakthrough time significantly de-

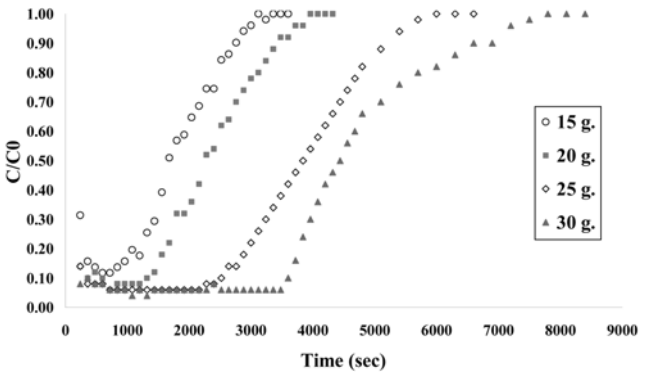

Fig. 4. Breakthrough time of different packing weight.

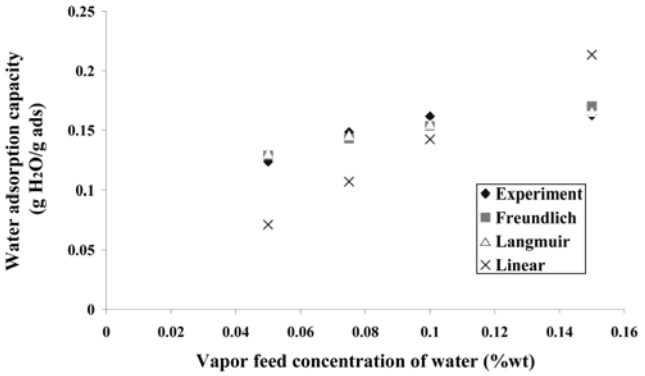

Fig. 5. Fitting of experimental data with various adsorption isotherms.

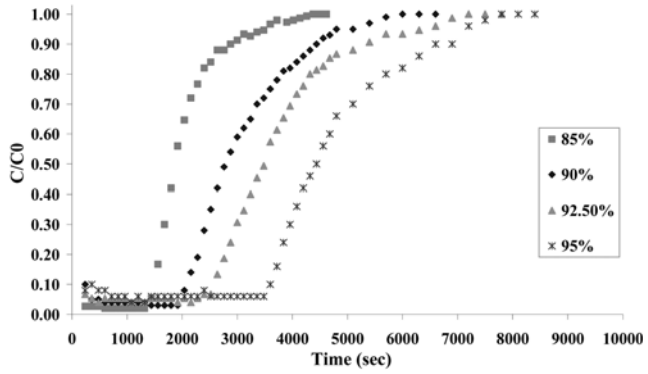

Fig. 6. Breakthrough time of difference feed concentration.

creases with lower ethanol feed concentration. Again, the main reason for earlier breakthrough times with increasing water concentration is that the adsorbent is exposed to more adsorbate per unit time [10].

2. Second Phase-PSA Pilot Plant

After some characterization and kinetics study of the 3A zeolite were completed, the PSA pilot plant was designed on the assumption of the predicted isotherm and the isotherm of the commercial grade zeolite used in this research. Factors that were taken into consideration were flow rate, feed concentration, adsorption pressure, and cycle time for each adsorption stage (Table 2). For each experimental run, the pilot plant was run until it reached steady state [11] and was run repeatedly as a cyclic batch operation.

From analysis of variance (ANOVA) using the Design-Expert

Table 2. PSA experimental conditions and results

Run	Feed rate, mL/min	Feed conc, %vol	Adsorption pressure, bar	Cycle time, min	Recovery, %	Product conc, %vol
1	80	92	2	10	75.48%	99.64%
2	80	92	2	15	81.91%	99.64%
3	80	92	2.4	10	80.78%	99.61%
4	80	92	2.4	15	81.64%	99.64%
5	80	95	2	10	76.91%	99.59%
6	80	95	2	15	82.32%	99.60%
7	80	95	2.4	10	73.58%	99.53%
8	80	95	2.4	15	84.28%	99.58%
9	100	92	2	10	82.01%	99.64%
10	100	92	2	15	84.46%	99.64%
11	100	92	2.4	10	84.90%	99.56%
12	100	92	2.4	15	85.26%	99.66%
13	100	95	2	10	70.54%	99.58%
14	100	95	2	15	76.63%	99.50%
15	100	95	2.4	10	74.68%	99.57%
16	100	95	2.4	15	74.88%	99.54%

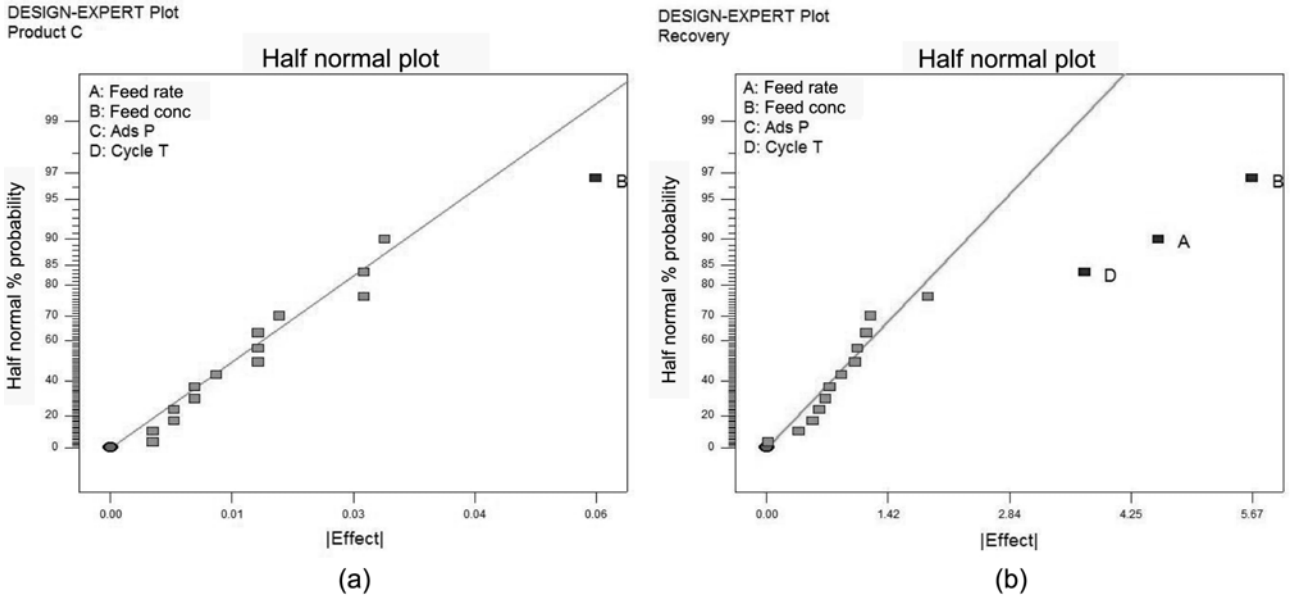

Fig. 7. Design-expert plots showing significant effects on production concentration and ethanol recovery.

software package (Fig. 7), it was proven that cycle time, feed concentration and feed rate significantly affected the performance of the PSA pilot plant in terms of ethanol recovery. On the other hand, the product concentration was largely dependent on feed concentration. It should be noted that during adsorption and regeneration the temperature increased and decreased in the range of 10-15 °C due to heat of adsorption and heat used to evaporate water during desorption, respectively [12,13]. The PSA unit maintained the temperature by slightly adapting the feed temperature so that it would compensate with heat released or consumed during adsorption or desorption, respectively.

Eqs. (2) and (3) show regression models used to predict the performance of the PSA pilot plant. From Eq. (2), recovery of ethanol can be increased by reducing feed concentration, increasing cycle time and feed rate. However, in the case of the concentration of the ethanol product, further study is needed to better explain the effects of each factor.

$$\text{Recovery}=226.46+0.23\ \text{Feed Rate}-1.89\ \text{Feed Conc}+0.74\ \text{Cycle Time} \quad (2)$$

$$\text{Product C}=101.38-0.019\ \text{Feed Conc} \quad (3)$$

From Eqs. (2) and (3), further experiments were done to study the effect of flow rate on product concentration and ethanol recovery. Fig. 8 shows that increasing the flow rate would significantly improve ethanol recovery.

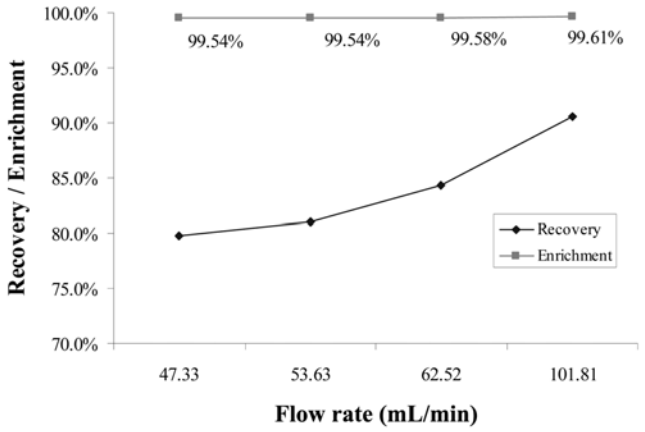

Fig. 8. Effect of flow rate on product concentration and ethanol recovery.

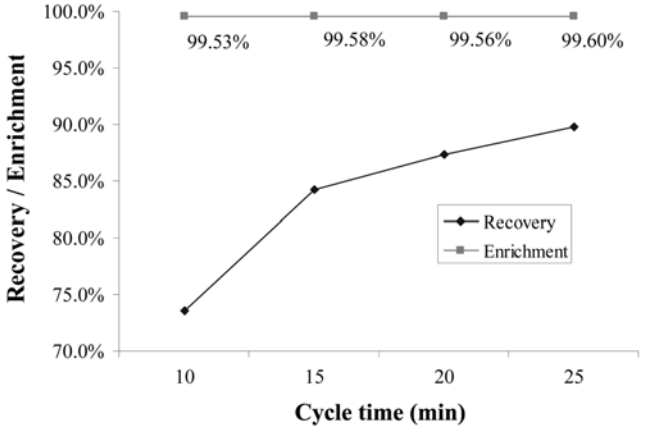

Fig. 9. Effect of cycle time on product concentration and ethanol recovery.

From Fig. 9, 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 and regeneration. 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 abundance and the breakthrough had not yet occurred.

CONCLUSION

The process of ethanol-water separation in the PSA process was studied. The research included analysis of kinetic and thermodynamic data of ethanol-water adsorption on commercial 3A zeolites. The first phase of the testing was done in a fixed-bed adsorber under atmospheric pressure to study preferable conditions for adsorption. The experiment showed that increasing initial temperature of the bed would reduce water capacity of the zeolite and that breakthrough time was decreased as ethanol-water solution feed rate was increased. Furthermore, it can be suggested that the lower the concentration of the feed solution, the sooner the bed saturated. In addition, the results of the experiment showed the water adsorption capacity of the zeolite which could help in the process of designing a PSA system.

It was also shown that by increasing the feed concentration in a PSA process the quality of the product (enrichment of ethanol) increased marginally. At the same time, increased flow rate provided a significant increase in the ethanol recovery. On the other hand, increasing feed concentration led to a reduction of the recovery. Furthermore, for similar adsorption and desorption conditions, a shorter cycle within each operation gave a high-quality product but at a lower quantity. It was also proven that the designed PSA system was capable of continuously producing high concentration ethanol product.

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REFERENCES

1. W. K. Choi, K. Ti, Y. K. Yeo, H. Lee, H. K. Song and B. K. Na, *Korean J. Chem. Eng.*, **20**, 617 (2003).
2. S. Jain, A. S. Moharir, P. Lo and G. Wozny, *Separation and Purification Technology*, **33**, 25 (2003).
3. Y. M. Kim and S. S. Suh, *Korean J. Chem. Eng.*, **16**, 401 (1999).
4. M. Simo, C. J. Brown and V. Hlavacek, *Computers and Chemical Engineering*, **31**, 1635 (2008).
5. M. J. Carmo and J. C. Gubulin, *Adsorption*, **8**, 235 (2002).
6. C. Pozas, R. L. Cordero, J. A. Morales, N. Travieso and R. R. Malherbe, *Journal of Molecular Catalysis*, **83**, 145 (1993).
7. W. K. Teo and D. M. Ruthven, *Industrial and Engineering Chemistry*,

25, 17 (1986).
8. J. J. Carberry, *Chemical and catalytic reaction engineering*, McGraw-Hill, New York (1976).
9. P. W. Madson and D. A. Monceaux, *The alcohol textbook: Fuel ethanol production*, Wiley & Sons, New York (1994).
10. B. Sowerby and B. D. Crittenden, *Gas separation and Purification*, **2**, 77 (1988).
11. H. M. Kvarmsdal and T. Hertzberg, *Computers and Chemical Engineering*, **21**, 819 (1997).
12. E. Lalik, R. Mirek, J. Rakorczy and A. Groszek, *Catalysis Today*, **114**, 242 (2006).
13. M. Salem and B. Shebil, *Chemical Engineering Journal*, **74**, 197 (1999).