REFERENCES

Ahn, H. and Brandani, S. 'A new numerical method for accurate simulation of fast cyclic adsorption processes' *Adsorption* 11 (2005): 113-122.

Al-Asheh, S., Banat, F., and Al-Lagtah, N. 'Separation of ethanol-water mixtures using molecular sieves and biobased adsorbent' *Chemical Engineering Research and Design* 82 (2004): 855-864.

Banat, F. A., Al-Rub, F. A., Simandl J. "Analysis of vapor-liquid equilibrium of ethanol-water system via headspace gas chromatography effect if molecular sieves" *Separation and Purification Technology* 18 (2000): 111-118.

Carberry, J.J. and Varma, A. 'Chemical and Catalytic Reaction Engineering' 1st Edition, McGraw-Hill, New York, 1976.

Carmo, M. J. and Gubulin, J. C. 'Ethanol-water separation in the PSA process' *Adsorption* 8 (2002): 235-248.

Carton, A., Gonzalez, G., Iniguez, T. A., and Cabezas, J. L. 'Separation of ethanol-water mixtures using 3A molecular sieve' *Journal of Chemical Technology and Biotechnology* 39 (1987): 125-132.

Chang, H., Yuan, X. G., Tian, H., and Zeng, A. W. 'Experiment and prediction of breakthrough curves for packed bed adsorption of water vapor on cornmeal' *Chemical Engineering and Processing* 45 (2006): 747-754.

Chahbani, M. H. and Tondeur, D. 'Mass transfer kinetics in pressure swing adsorption' *Separation and Purification Technology* 20 (2000): 185-196.

Charoonwattanalaoha, C. 'Simulation of effects of pressurization and depressurization methods on air separation by the pressure swing adsorption process' Thesis for

Master of Engineering, Chemical Engineering Department, Chulalongkorn University (1998).

Choong, T. S. Y., Paterson, W. R., and Scott, L. 'Development of novel algorithm features in the modeling of cyclic processes' *Computers and Chemical Engineering* 26 (2002): 95-112.

Chung, Y., Na, B. K., and Song, H. K. 'Short-cut evaluation of pressure swing adsorption systems' *Computer Chemical Engineering* 22 (1998): 637-640.

Crittenden, B. 'Selective adsorption – a maturing but poorly understood technology in Current Best Practice in Separations Technology' The R&D Clearing House, London: 1992.

Crittenden, B. and Thomas, W. J. 'Adsorption Technology & Design' 1st Edition, Butterworh Heinemann, Oxford: 1998.

Cruz, P., Santos, J. C., Magalhaes, F. D., and Mendes, A. 'Cyclic adsorption separation processes: analysis strategy and optimization procedure' *Chemical Engineering Science* 58 (2003): 3143-3158.

Ding, Y. and LeVan, M. D. 'Periodic states of adsorption cycles III. Convergence acceleration for direct determination' *Chemical Engineering Science* 56 (2001): 5217-5230.

Ding, Y., Croft, D. T., and LeVan, M. D. 'Periodic states of adsorption cycles IV. Direct optimization' *Chemical Engineering Science* 57 (2002): 4521-4531.

Farhadpour, F. A. and Bono, A. 'Sorptive separation of ethanol-water mixtures with a bi-dispersed hydrophobic molecular sieve, silicalite: determination of the controlling mass transfer mechanism' *Chemical Engineering and Processing* 35 (1996, a): 141-155.

Farhadpour, F. A. and Bono, A. 'Sorptive separation of ethanol-water mixtures with a bi-dispersed hydrophobic molecular sieve, silicalite: measurement and theoretical analysis of column dynamics' *Chemical Engineering and Processing* 35 (1996, b): 157-168.

Gales, L., Mendes, A., and Costa, C. 'Recovery of acetone, ethyl acetate and ethanol by thermal pressure swing adsorption' *Chemical Engineering Science* 58 (2003): 5279-5289.

Gomis, V., Pedraza, R., Frances, O., Font, A., and Asensi, J. A. 'Dehydration of ethanol using azeotropic distillation with Isooctane' *Industrial and Engineering Chemistry Research* 46 (2007): 4572-4576.

Gorbach, A., Stegmaier, M., and Eigenberger, G. 'Measurement and modeling of water vapor and adsorption on zeolite 4A – Equilibria and Kinetics' *Adsorption* 10 (2004): 29-46.

Guan, J. and Hu, X. 'Simulation and analysis of pressure swing adsorption: ethanol drying process by the electrical analogue' *Separation and Purification Technology* 31 (2003): 31-35.

Ingledew, W. M. 'The alcohol textbook: Continuous fermentation in fuel alcohol industry' 4th Ed., Nottingham University Press: Nottingham, 2003.

Jain, S., Moharir, A. S., Lo, P., and Wozny, G., 'Heuristic design of pressure swing adsorption: a preliminary study', Separation and Purification Technology, 33 (2003): 25-43.

Jiang, L., Biegler, L. T., and Fox 'Simulation and optimization of pressure swing adsorption systems for air separation' *AIChE Journal* 49 (2003): 1140-1157.

Jiang, L., Biegler, L. T., and Fox 'Design and optimization of pressure swing adsorption systems with parallel implementation' *Computers and Chemical Engineering* 29 (2005): 393-399.

Kearns, D. T. and Webley, P. A. 'Modeling and evaluation of dual-reflux pressure swing adsorption cycles: Part I. Mathematical models' *Chemical Engineering Science* 61 (2006, a): 7223-7233.

Kearns, D. T. and Webley, P. A. 'Modeling and evaluation of dual-reflux pressure swing adsorption cycles: Part II. Productivity and energy consumption' *Chemical Engineering Science* 61 (2006, b): 7234-7239.

Komarneni, S., Pidugu, R., and Menon, V. C. 'Water adsorption and desorption isotherms of silica and alumina mesoporous molecular sieves' *Journal of Porous Materials* 2 (1996): 99-106.

Kvarmsdal, H. M. and Hertzberg, T. 'Optimization of pressure swing adsorption (PSA) systems – studies on cyclic steady state convergence' *Computers and Chemical Engineering* 21 (1997): 819-832.

Kumar, R. 'Vacuum Swing Adsorption Process for Oxygen Production – A Historical Perspective' *Separation Science Technology* 31 (1996): 877-893.

Lalik, E., Mirek, R., Rakorczy, J., and Groszek, A. 'Microcalorimetric study of sorption of water and ethanol in zeolites 3A and 5A' *Catalysis Today* 114 (2006): 242-247.

Le Van, M. D. 'Fundamentals of adsorption' Proceeding of the 5th International Conference on Fundamental of Adsorption, Kluwer Academic Publisher, Boston, 1996.

Lu, L., Shao, Q., Huand, L., and Lu, X. 'Simulation of adsorption and separation of ethanol-water mixture with zeolite and carbon nanotube' *Fluid Phase Equilibria* 261 (2007): 191-198.

Lui, Y., Delgado, J., and Ritter, J. A. 'Comparison of finite difference techniques for simulating pressure swing adsorption' *Adsorption* 4 (1998): 337-344.

Luksamepicheat, P. 'Simulation of purge with strong adsorptive product in pressure swing reactor' Thesis for Master of Engineering, Chemical Engineering Department, Chulalongkorn University (1998).

Madson, P. W. 'The alcohol textbook: ethanol distillation: the fundamentals' 4th Ed., Nottingham University Press: Nottingham, 2004.

Madson, P. W. and Monceaux, D. A. 'The alcohol textbook: Fuel ethanol production' 3rd Ed., Nottingham University Press: Nottingham, 1999.

Michaels, A. S. 'Simplified method of interpreting kinetic data in fixed bed ion exchange' *Journal of Industrial & Engineering Chemistry* 44 (1952): 1922-1930.

Modla, G. and Lang, P. 'Feasibility of new pressure swing batch distillation methods' *Chemical Engineering Science* 63 (2008): 2856-2874.

Monereau, C., Derive, N., and Petit, P. US Patent 5,951,694, assigned to L'Air Liquide, Societe Anonyme pour l' Etude et l' Exploitation des Procedes Georges Claude (1999).

Morigami, Y., Kondo, M., Abe, J., Kita, H., Okamoto, K. 'The first large-scale pervaporation plant using tubular-type module with zeolite NaA membrane' *Separation and Purification Technology* 25 (2001): 251-260.

Nomura, M., Yamaguchi, T., and Nakao, S. 'Ethanol/water transport through silicate membranes' *Journal of Membrane Science* 144 (1998): 161-171.

Nomura, M., Bin, T., and Nakao, S. I. 'Selective ethanol extraction from fermentation broth using a silicalite membrane' *Separation and Purification Technology* 27 (2002): 59-66.

Pozas, C., Cordero, R. L., Morales, J. A., Travieso, N., and Malherbe, R. R. 'Effect of pore diameter and acid strength in ethanol dehydration on molecular sieves' *Journal of Molecular Catalysis* 83 (1993): 145-156.

Quintero, J. A., Montoya, M. I., Sanchez, O. J., Giraldo, O. H., and Cardona, C. A. 'Fuel ethanol production from sugarcane and corn: Comparative analysis for a Colombian case' *Energy* 33 (2008): 385-399.

Rakshit, S. K., Ghosh, P., and Bisaria, V. S. 'Ethanol separation by selective adsorption of water' *Bioprocess Engineering* 8 (1993): 279-282.

Ruthven, D. M. 'Principles of Adsorption and Adsorption Processes' Wiley-Interscience, New York: 1984.

Ruthven, D. M., Farooq, S., and Knaebel, K. S. 'Pressure Swing Adsorption' VCH Publishers, New York: 1994.

Rutkai, G., Csanyi, E., and Kristof, T. 'Prediction of adsorption and separation of water-alcohol mixtures with zeolite NaA' *Microporous and Mesoporous Materials* 114 (2008): 455-464.

Salem, M. and Shebil, B. 'Effect of heat of adsorption on the adsorptive drying of solvents at equilibrium in a packed bed of zeolite' *Chemical Engineering Journal* 74 (1999): 197-204.

Sano, T., Yanagishita, H., Kiyozumi, Y., Mizukami, F., and Haraya, K. 'Separation of ethanol/water mixture by silicate membrane on pervaporation' *Journal of Membrane Science* 95 (1994): 221-228.

Seader, J. D. and Henley, E. J. 'Separation Process Principles' Wiley & Sons, New York: 1998..

Serbezov, A. 'Effect of the process parameters on the length of the mass transfer zone during product withdrawal in pressure swing adsorption cycles' *Chemical Engineering Science* 56 (2001): 4673-4684.

Simo, M., Brown, C. J. and Hlavacek, V. 'Simulation of pressure swing adsorption in fuel ethanol production process' *Computers and Chemical Engineering* 32(2007): 1635-1649.

Smith, O. J. I. V. and Westerberg, A. W. 'Acceleration of cyclic steady state convergence for pressure swing adsorption models' *Industrial and Engineering Chemistry Research* 31 (1992): 1569-1573.

Sowerby, B. And Crittenden, B. D. 'Vapour phase separation of alcohol-water mixtures by adsorption onto silicalite' *Gas Separation and Purification* 2 (1988): 177-183.

Sowerby, B. and Crittenden, B.D. 'An experimental comparison of type A molecular sieves for drying the ethanol-water azeotrope' *Gas separation and purification* 2 (1998): 77-83.

Swain, B. R. L. 'The alcohol textbook: Molecular sieve dehydrators. How they became the industry standard and how they work' 3rd Ed., Nottingham University Press: Nottingham, 1999.

Schweitzer, P. A. 'Handbook of separation techniques for chemical engineers' McGraw-Hill, New York, 1979 (pp3.21-3.38).

Tanaka, B. and Otten, L. 'Dehydration of aqueous ethanol' *Energy in Agriculture* 6 (1987): 63-76.

Teo, W. K. and Ruthven, D. M. 'Adsorption of water from aqueous ethanol using 3A molecular sives' *Industrial and Engineering Chemistry* 25 (1986): 17-21.

Thomas, W. J. and Crittenden, B. 'Adsorption Technology and Design' Butterworth-Heinemann: 1st Edition, Oxford; 1998.

Tien, C. 'Adsorption Calculations and Modeling' Butterworth-Heinemann: Boston 1994.

Todd, R. S. and Webley, P. A. 'Pressure drop in a packed bed under nonadsorbing and adsorbing conditions' *Industrial & Engineering Chemistry Research* 44 (2005): 7234-7241.

Tondeur, D. and Wankat, P. C. 'Gas purification by pressure swing adsorption' *Separation and Purification Methods* 14 (1985): 157-212.

Trent, R. E. 'Fundamentals of molecular sieves design' Presented at the *American Institute of Chemical Engineers Spring National Meeting*, Huston, Texas, April (1993).

Vareli, G., Demertzis, P. G., and Demertzi, K. A. 'Effect of regeneration thermal treatment of cellulosic and starchy materials on their capacity to separate water and ethanol' *Journal of Cereal Science* 31 (2000): 147-154.

Wankat, P. C. 'Separation Process Engineering' 2nd Edition, Prentice Hall: New Jersey 2007.

Yang, R.T. 'Gas Separation by Adsorption' Butterworth-Heinemann: Boston 1987.

APPENDICES

Appendix A

Some of the data from First Phase: Fixed bed experiment

In the factorial designed experiment, 8 runs were needed to analyze the 3 parameters involved in the study. Several more experimental runs were needed to further study the effect of each parameter. Due to the large amount of data obtained from the fixed bed experiment, only 4 sets of experimental data are shown in Appendix A.

1. Fixed bed experiment at 30 g zeolite, flow rate of 1 mL/min, initial bed temperature of 100 °C, and feed concentration of 95%.

Time (sec)	Temp.(°C)		%wt ethanol	C	C/C_0
	Bed	Ethanol			
0	101	31.8	95	5	1.00
240	107	31	99.6	0.4	0.08
360	109	31.1	99.5	0.5	0.10
480	110	30.9	99.6	0.4	0.08
600	112	31.2	99.6	0.4	0.08
720	114	31	99.7	0.3	0.06
840	115	31	99.7	0.3	0.06
960	117	30.8	99.7	0.3	0.06
1080	118	30.8	99.8	0.2	0.04
1200	119	30.5	99.7	0.3	0.06
1320	120	30.9	99.8	0.2	0.04
1440	120	30.9	99.7	0.3	0.06
1560	122	30.7	99.7	0.3	0.06
1680	122	30.7	99.7	0.3	0.06
1800	122	30.4	99.7	0.3	0.06
1920	121	30.4	99.7	0.3	0.06
2040	121	30.2	99.7	0.3	0.06
2160	120	30.7	99.7	0.3	0.06
2280	119	30.7	99.7	0.3	0.06
2400	119	30.5	99.6	0.4	0.08
2520	117	30.8	99.7	0.3	0.06
2640	116	30.4	99.7	0.3	0.06
2760	115	30.5	99.7	0.3	0.06
2880	114	30.4	99.7	0.3	0.06
3000	113	30.3	99.7	0.3	0.06
3120	112	30.4	99.7	0.3	0.06
3240	112	30.4	99.7	0.3	0.06
3360	111	30.2	99.7	0.3	0.06
3480	110	30.9	99.7	0.3	0.06
3600	109	30.3	99.5	0.5	0.10
3720	108	30.9	99.2	0.8	0.16
3840	108	30.5	98.8	1.2	0.24
3960	108	30.2	98.5	1.5	0.30
4080	107	31.6	98.2	1.8	0.36
4200	106	30.9	97.9	2.1	0.42
4320	106	31.2	97.7	2.3	0.46
4440	106	30	97.5	2.5	0.50
4560	105	30.7	97.2	2.8	0.56

4680	105	30.5	97	3	0.60
4800	105	30.9	96.7	3.3	0.66
5100	104	30.6	96.5	3.5	0.70
5400	103	30.8	96.2	3.8	0.76
5700	103	30.4	96	4	0.80
6000	103	30	95.9	4.1	0.82
6300	102	30.6	95.7	4.3	0.86
6600	102	31.1	95.5	4.5	0.90
6900	101	31	95.5	4.5	0.90
7200	101	31.2	95.2	4.8	0.96
7500	101	31	95.1	4.9	0.98
7800	101	30.5	95	5	1.00
8100	101	31.5	95	5	1.00
8400	101	30.1	95	5	1.00

2. Fixed bed experiment at 30 g zeolite, flow rate of 1 mL/min, initial bed temperature of 120 °C, and feed concentration of 95.1%.

Time (sec)	Temp.(°C)		%wt ethanol	C	C/C_0
	Bed	Ethanol			
0	119	31.5	95.1	4.9	1.00
240	126	30.7	99.5	0.5	0.10
360	127	30.1	99.5	0.5	0.10
480	129	30.4	99.5	0.5	0.10
600	132	29.8	99.5	0.5	0.10
720	136	30.3	99.5	0.5	0.10
840	137	30.1	99.5	0.5	0.10
960	139	29.9	99.5	0.5	0.10
1080	140	30	99.5	0.5	0.10
1200	141	29.7	99.5	0.5	0.10
1320	142	30.8	99.5	0.5	0.10
1440	142	30	99.5	0.5	0.10
1560	142	30.1	99.6	0.4	0.08
1680	142	30.3	99.6	0.4	0.08
1800	141	30.5	99.5	0.5	0.10
1920	141	30.5	99.6	0.4	0.08
2040	140	30.9	99.7	0.3	0.06
2160	139	30.5	99.7	0.3	0.06
2280	138	30	99.7	0.3	0.06
2400	136	30.3	99.6	0.4	0.08
2520	135	30.4	99.5	0.5	0.10
2640	134	30.5	99.5	0.5	0.10
2760	133	30.5	99.5	0.5	0.10
2880	132	30.5	99.2	0.8	0.16
3000	131	30.2	99.1	0.9	0.18
3120	130	30.3	98.8	1.2	0.24
3240	129	30.4	98.7	1.3	0.27
3360	128	30	98.4	1.6	0.33
3480	127	30.1	98	2	0.41
3600	126	30.8	97.9	2.1	0.43
3720	126	30.2	97.6	2.4	0.49
3840	125	30.3	97.4	2.6	0.53
3960	124	30.4	97.1	2.9	0.59
4080	124	30.4	97	3	0.61
4200	123	30.9	96.9	3.1	0.63
4320	123	30.6	96.6	3.4	0.69

4440	122	29.6	96.4	3.6	0.73
4560	122	30.2	96.2	3.8	0.78
4680	122	30.6	96	4	0.82
4800	122	30.4	95.9	4.1	0.84
5100	121	30.6	95.7	4.3	0.88
5400	121	31.2	95.5	4.5	0.92
5700	121	30.7	95.3	4.7	0.96
6000	120	30.2	95.1	4.9	1.00
6300	120	30.1	95.1	4.9	1.00
6600	120	31.5	95.1	4.9	1.00
6900	120	30.6	95.1	4.9	1.00

3. Fixed bed experiment at 30 g zeolite, flow rate of 2 mL/min, initial bed temperature of 120 °C, and feed concentration of 95.1%.

Time (sec)	Temp.(°C)		%wt ethanol	C	C/C_0
	Bed	Ethanol			
0	120	31.7	95.1	4.9	1.00
180	122	31.2	99	1	0.20
240	126	31.1	99.6	0.4	0.08
300	130	31.1	99.6	0.4	0.08
360	135	30.8	99.7	0.3	0.06
420	140	30.8	99.6	0.4	0.08
480	144	30.9	99.6	0.4	0.08
540	146	30.7	99.8	0.2	0.04
600	148	30.7	99.7	0.3	0.06
660	149	30.6	99.7	0.3	0.06
720	150	30.5	99.7	0.3	0.06
780	150	30.5	99.6	0.4	0.08
840	150	30.4	99.4	0.6	0.12
900	150	30.4	99.3	0.7	0.14
960	149	30.8	99.2	0.8	0.16
1080	148	30.8	98.9	1.1	0.22
1200	145	30.6	98.6	1.4	0.29
1320	143	31.2	98.2	1.8	0.37
1440	140	31.1	97.9	2.1	0.43
1560	138	30.9	97.6	2.4	0.49
1680	136	30.7	97.4	2.6	0.53
1800	134	31.4	97.1	2.9	0.59
1920	132	31.1	96.9	3.1	0.63
2040	130	31.3	96.7	3.3	0.67
2160	128	30.7	96.5	3.5	0.71
2280	127	31.3	96.3	3.7	0.76
2400	126	31.6	96.1	3.9	0.80
2520	125	31.3	96.1	3.9	0.80
2640	123	31.3	95.9	4.1	0.84
2760	122	30.8	95.7	4.3	0.88
2880	121	31.3	95.6	4.4	0.90
3000	121	31.6	95.4	4.6	0.94
3120	120	31.7	95.4	4.6	0.94
3240	120	31.5	95.3	4.7	0.96
3360	120	31.4	95.1	4.9	1.00
3480	120	31.2	95.1	4.9	1.00

4. Fixed bed experiment at 30 g zeolite, flow rate of 2 mL/min, initial bed temperature of 100 °C, and feed concentration of 95.1%.

Time (sec)	Temp.(°C)		%wt ethanol in water	C	C/C_0
	Bed	Ethanol			
0	100	31.4	95.1	4.9	1.00
240	107	30.2	99.7	0.3	0.06
300	114	30.5	99.7	0.3	0.06
360	122	30.8	99.8	0.2	0.04
420	128	30.8	99.8	0.2	0.04
480	132	30.9	99.8	0.2	0.04
540	136	31.1	99.8	0.2	0.04
600	138	31.1	99.8	0.2	0.04
660	140	31.1	99.8	0.2	0.04
720	140	31.1	99.8	0.2	0.04
780	141	31	99.8	0.2	0.04
840	140	31.1	99.8	0.2	0.04
900	140	31.2	99.7	0.3	0.06
960	139	31.1	99.6	0.4	0.08
1020	138	31.1	99.5	0.5	0.10
1080	137	31.3	99.3	0.7	0.14
1200	134	31.4	99	1	0.20
1320	132	30.8	98.7	1.3	0.27
1440	129	31.1	98.4	1.6	0.33
1560	127	30.4	98.1	1.9	0.39
1680	125	31.3	97.8	2.2	0.45
1800	122	31.2	97.5	2.5	0.51
1920	120	31	97.3	2.7	0.55
2040	118	31.1	97.1	2.9	0.59
2160	116	30.8	96.9	3.1	0.63
2280	114	31.6	96.7	3.3	0.67
2400	113	31.6	96.7	3.3	0.67
2520	111	31.6	96.5	3.5	0.71
2640	110	31.5	96.4	3.6	0.73
2760	108	31.6	96.2	3.8	0.78
2880	108	31.9	96.2	3.8	0.78
3000	107	32	96	4	0.82
3120	107	32.2	95.9	4.1	0.84
3240	106	32.1	95.8	4.2	0.86
3360	105	31.9	95.7	4.3	0.88
3480	105	32	95.5	4.5	0.92
3600	104	32	95.4	4.6	0.94
3720	105	32	95.2	4.8	0.98
3780	104	31.8	95.1	4.9	1.00
3840	104	32.1	95.1	4.9	1.00

Appendix B

Calculation of the water adsorption capacity of the zeolite

An example of the calculation of the water adsorption capacity of 30 g of zeolite is shown in Appendix B. The experiment was carried out under a flow rate of 1 mL/min, initial bed temperature of 100 °C, and feed concentration of 95%.

The amount of water adsorbed in 30g adsorbent = the sum of water trapped in the adsorber during each sample time

$$= \Sigma [(C_0-C) \times Q \times t]$$

where C_0 = feed concentration

C = product concentration

Q = flow rate

t = time during each sample

The amount of water adsorbed = [(0.05-0.004)*0.0166*240]
+ [(0.05-0.005)*0.0166*120] + [(0.05-0.004)*0.0166*120]
+ [(0.05-0.004)*0.0166*120] + [(0.05-0.003)*0.0166*120]
+ [(0.05-0.003)*0.0166*120].... + [(0.05-0.05)*0.0166*300]

= 3.71 g of water

= 3.71 g of water/30 g of zeolite

= 0.1235 g of water/g of zeolite

Hence, it can be concluded that the water adsorption capacity of the zeolite 3A under a flow rate of 1 mL/min, initial bed temperature of 100 °C, and feed concentration of 95% is 0.1235g/g of zeolite or 12.35%.

Time (sec)	Temp.(°C)		%wt ethanol	C	C/C_0	q
	Bed	Ethanol				
0	101	31.8	95	5	1.00	0
240	107	31	99.6	0.4	0.08	0.184
360	109	31.1	99.5	0.5	0.10	0.09
480	110	30.9	99.6	0.4	0.08	0.092
600	112	31.2	99.6	0.4	0.08	0.092
720	114	31	99.7	0.3	0.06	0.094
840	115	31	99.7	0.3	0.06	0.094
960	117	30.8	99.7	0.3	0.06	0.094
1080	118	30.8	99.8	0.2	0.04	0.096
1200	119	30.5	99.7	0.3	0.06	0.094

1320	120	30.9	99.8	0.2	0.04	0.096
1440	120	30.9	99.7	0.3	0.06	0.094
1560	122	30.7	99.7	0.3	0.06	0.094
1680	122	30.7	99.7	0.3	0.06	0.094
1800	122	30.4	99.7	0.3	0.06	0.094
1920	121	30.4	99.7	0.3	0.06	0.094
2040	121	30.2	99.7	0.3	0.06	0.094
2160	120	30.7	99.7	0.3	0.06	0.094
2280	119	30.7	99.7	0.3	0.06	0.094
2400	119	30.5	99.6	0.4	0.08	0.092
2520	117	30.8	99.7	0.3	0.06	0.094
2640	116	30.4	99.7	0.3	0.06	0.094
2760	115	30.5	99.7	0.3	0.06	0.094
2880	114	30.4	99.7	0.3	0.06	0.094
3000	113	30.3	99.7	0.3	0.06	0.094
3120	112	30.4	99.7	0.3	0.06	0.094
3240	112	30.4	99.7	0.3	0.06	0.094
3360	111	30.2	99.7	0.3	0.06	0.094
3480	110	30.9	99.7	0.3	0.06	0.094
3600	109	30.3	99.5	0.5	0.10	0.09
3720	108	30.9	99.2	0.8	0.16	0.084
3840	108	30.5	98.8	1.2	0.24	0.076
3960	108	30.2	98.5	1.5	0.30	0.07
4080	107	31.6	98.2	1.8	0.36	0.064
4200	106	30.9	97.9	2.1	0.42	0.058
4320	106	31.2	97.7	2.3	0.46	0.054
4440	106	30	97.5	2.5	0.50	0.05
4560	105	30.7	97.2	2.8	0.56	0.044
4680	105	30.5	97	3	0.60	0.04
4800	105	30.9	96.7	3.3	0.66	0.034
5100	104	30.6	96.5	3.5	0.70	0.075
5400	103	30.8	96.2	3.8	0.76	0.06
5700	103	30.4	96	4	0.80	0.05
6000	103	30	95.9	4.1	0.82	0.045
6300	102	30.6	95.7	4.3	0.86	0.035
6600	102	31.1	95.5	4.5	0.90	0.025
6900	101	31	95.5	4.5	0.90	0.025
7200	101	31.2	95.2	4.8	0.96	0.01
7500	101	31	95.1	4.9	0.98	0.005
7800	101	30.5	95	5	1.00	0
8100	101	31.5	95	5	1.00	0
8400	101	30.1	95	5	1.00	0
					Total	3.71

Appendix C

Calculation of the Length of Equilibrium Section (LES)

Length of equilibrium section (LES) can be found by Equation (2.11) or from the breakthrough curve. Appendix C shows how to find the LES of the 30g fixed bed adsorber under a flow rate of 1 mL/min, initial bed temperature of 100 °C, and feed concentration of 95%.

First method:

Equation (2.11) $$LES = \left(\frac{Q_F c_F t_b}{q_{ref} \rho_B \frac{\pi D^2}{4}} \right)$$

and $$LUB = L_B - LES$$

where Q_F is the volumetric flow rate of feed,

c_F is the concentration of the solute in the feed,

t_b is time to breakthrough,

q_{ref} is the loading per unit mass of adsorbent that is in equilibrium with the feed concentration,

S is the total mass of adsorbent in the bed,

ρ_B is the density of the bed,

D is bed diameter, and

L_B is the total bed length.

Second method:

Since the experiments were conducted the LUB could precisely be calculated from the breakthrough curves. To determine LUB from an experimental breakthrough curve, the front is located such that in Figure C1, area A is equal to area B. Then:

$$LUB = L_B \frac{t_S - t_b}{t_S} \qquad (2.13)$$

where L_B is the length of the experimental bed, t_s is time of the front that makes area A equal to area B, and t_b is breakthrough time.

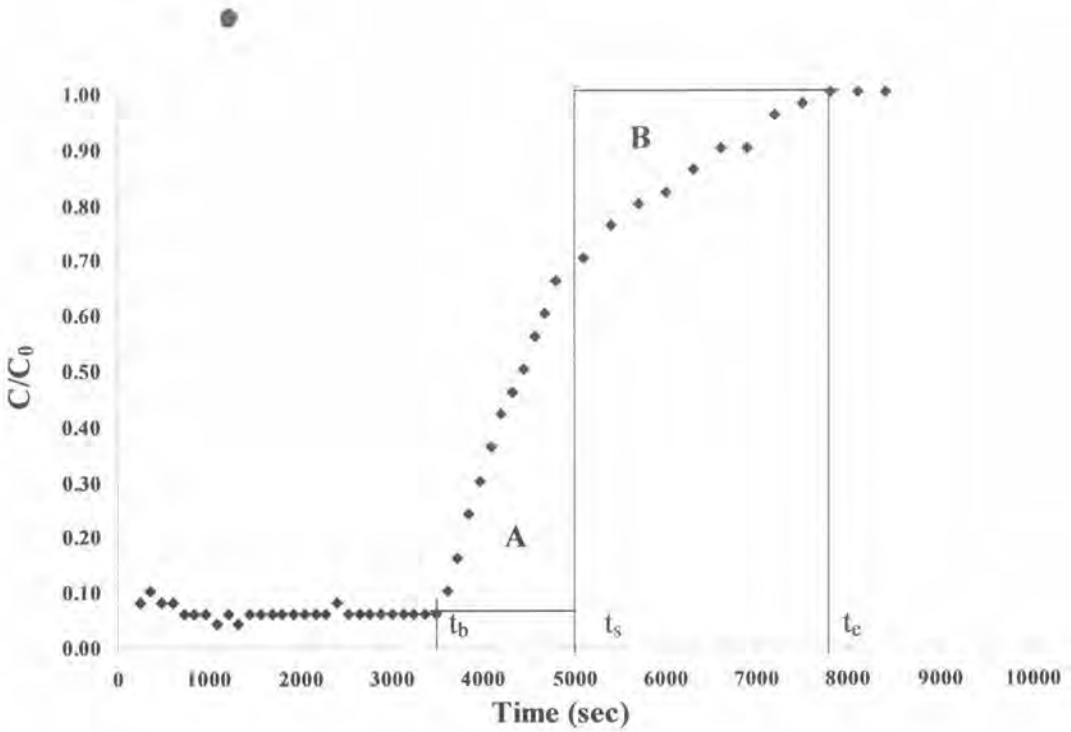

Figure C1 Breakthrough curve of the fixed bed experiment under a flow rate of 1 mL/min, initial bed temperature of 100 °C, and feed concentration of 95%.

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

$$LUB = 24 \times \frac{5000 - 3600}{3600}$$

LUB = 9.33 centimeters

LES = L_B – LUB

LES = 24 – 9.33

= 14.67 centimeters

Appendix D

Analysis of the property of Zeochem 3A

1. BET surface area

Zeochem 3A was analyzed by Micromeritics Surface Area Analyzer model Flow Sorb II 2300. The testing conditions and results are shown below:

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Metallurgy and Materials Science Research Institute Building, Chulalongkorn University Phyathai Rd., Bangkok, THAILAND 10330
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เลขที่ บรท. 035/2551

รายงานผลการวิเคราะห์/ทดสอบ

ตัวอย่าง	:	Zeolite
เจ้าของตัวอย่าง	:	ภาควิชาเคมีเทคนิค คณะวิทยาศาสตร์ จุฬาฯ
วัตถุประสงค์	:	ทดสอบหาพื้นที่ผิวจำเพาะ
เครื่องมือที่ใช้วิเคราะห์/ทดสอบ	:	SURFACE AREA ANALYZER ยี่ห้อ Micromeritics รุ่น FlowSorb II 2300
อุณหภูมิที่ใช้ในการ Degas	:	150°C
เวลาที่ใช้ในการ Degas	:	60 นาที
มาตรฐานที่ใช้ในการวิเคราะห์/ทดสอบ	:	ISO 9277
วันที่ทำการวิเคราะห์/ทดสอบ	:	6 ธันวาคม 2550

ผลการทดสอบ

จากการทดสอบหา SPECIFIC SURFACE AREA ของตัวอย่าง Zeolite ให้ผลการทดสอบดังนี้

SAMPLE	*SPECIFIC SURFACE AREA (m^2/g)*
3A ZeOChem coke	20.63 ± 0.01
3A ZeOChem before	25.71 ± 0.02
3A ZeOChem after	22.96 ± 0.03
3A Tosoh before	12.67 ± 0.01
3A Tosoh after	12.26 ± 0.03
New 3A Tosoh before	25.46 ± 0.03
New 3A Tosoh after	24.34 ± 0.04
4A Tosoh before	13.86 ± 0.02
4A Tosoh after	13.87 ± 0.02

ลงชื่อ ..... ลงชื่อ .....
(นางสาวสวดี สมาพิทักษ์) (ดร. สิริพรวณ นิลไพรัช)
ผู้วิเคราะห์/ทดสอบ ผู้รับรองผล

หมายเหตุ : ผลการวิเคราะห์ / ทดสอบ รับรองผลเฉพาะตัวอย่างที่ได้ทำการวิเคราะห์/ทดสอบโดย สถาบันวิจัยโลหะและวัสดุ จุฬาลงกรณ์มหาวิทยาลัย เท่านั้น

Figure D1 Results from the BET analysis of the 3A molecular sieve.

2. Thermogravimetric Analysis (TGA)

The TG/DTA (Thermal Gravimetric/Differential Thermal Analysis) model 851^e from Mettler Toledo was used to analyze the weight lost of the zeolite, which was found to

be approximately 4%, with changing temperature under a period of time. The analysis was carried out at 0-500 °C and air flow rate of 260 mL/min.

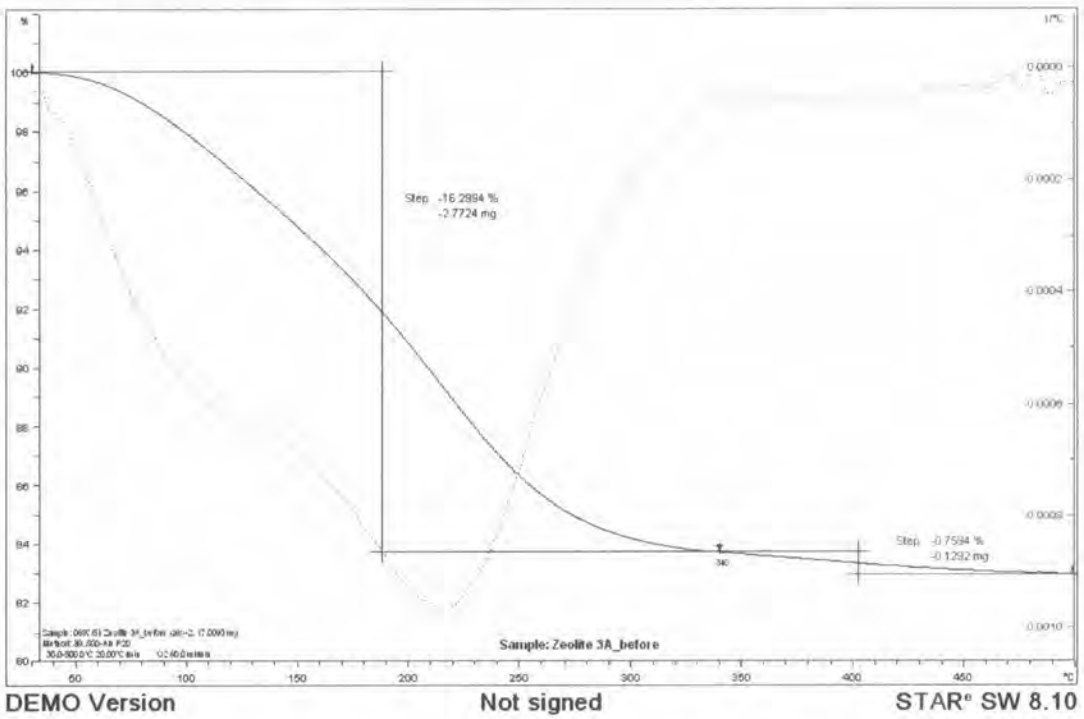

Figure D2 Thermogravimetric Analysis of Zeochem 3A before the experiment.

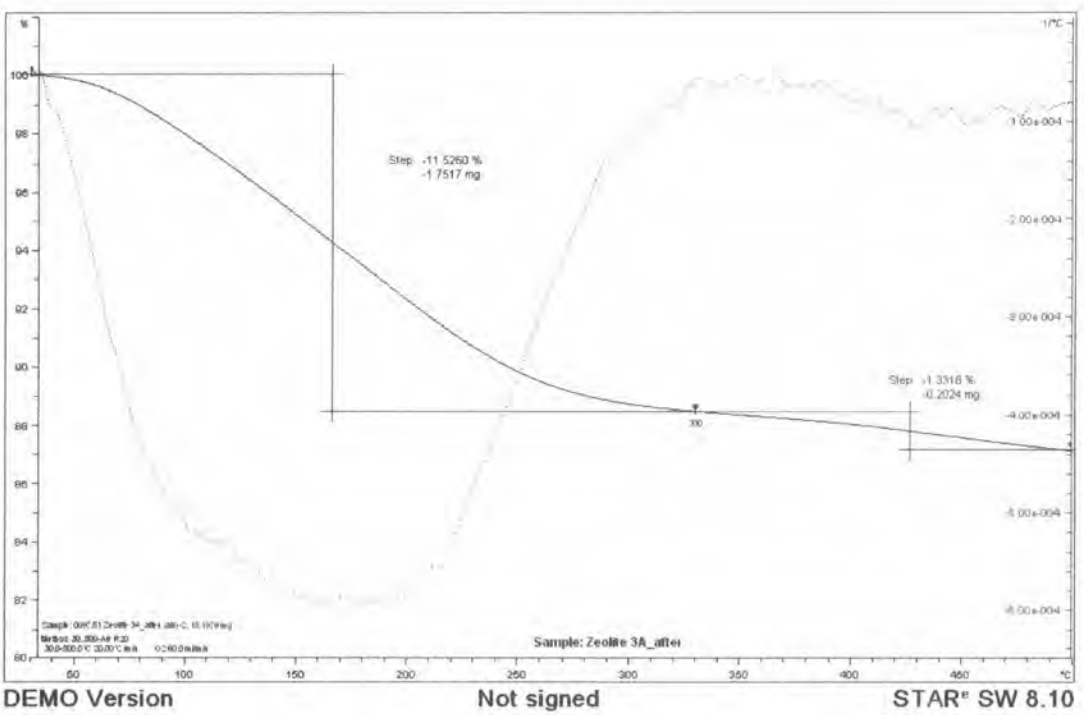

Figure D3 Thermogravimetric Analysis of Zeochem 3A after the experiment.

Appendix E

Some of the data from Second Phase: PSA pilot plant experiment

There were 16 runs in the 2^k factorial designed experiment plus more than 10 experimental runs in the univariate study. Due to the huge amount of raw data obtained from the PSA pilot plant, only 1 set of the data is shown in Appendix E.

Feed 29/1/2008

Feed Conc		92	% Vol Ethanol							
Pads		1	Bar G							
Feed Rate		80	mL/min							
Cycle time		10	min					Ethanol	Water	
	Total	17.176	L	Conc	92%	Vol		15.802	1.374	L
Product										
Nestle 6 L		5.424	L	Conc	99.5%	Vol		5.397	0.027	L
Product # 1		1.39	L	Conc	99.6%	Vol		1.384	0.006	L
Product # 2		1.374	L	Conc	99.6%	Vol		1.369	0.005	L
Product # 3		1.39	L	Conc	99.6%	Vol		1.384	0.006	L
Product # 6		1.37	L	Conc	99.6%	Vol		1.365	0.005	L
Product # 7		0.74	L	Conc	99.6%	Vol		0.737	0.003	L
Product # 9		0.73	L	Conc	99.6%	Vol		0.727	0.003	L
	Total	12.418	L	Max	99.7%	Vol				
				Avg	99.56%	Vol				
Regen										
Regen # 1		1.37	L	Conc	63.5%	Vol		0.870	0.500	L
Regen # 2		1.358	L	Conc	62.6%	Vol		0.850	0.508	L
Regen # 3		0.85	L	Conc	55.9%	Vol		0.475	0.375	L
	Total	3.578	L	Avg	61.35%	Vol				
				Total				14.558	1.438	L
Loss		1.18	L	Conc	105%	Vol		1.244	-0.064	L

Ethanol recovery 78.24%

Table E1 Concentration of the ethanol product measured on-line from PSA pilot plant

Time	Conc (%v)	Elapsed Time (min)
14.00		
14.11		11
14.16		16
14.18		18
14.19		19
14.20		20
14.22	99.5	22
14.24	99.5	24
14.25	99.4	25
14.27	99.5	27
14.29		29
14.30		30

Time	Conc (%v)	Elapsed Time (min)
16.17	99.6	137
16.19	99.6	139
16.20		140
16.22	99.6	142
16.24	99.7	144
16.25	99.7	145
16.27	99.6	147
16.29	99.7	149
16.30		150
16.32	99.7	152
16.34	99.6	154
16.35	99.6	155

14.32		32
14.34		34
14.36	99.5	36
14.38	99.5	38
14.39	99.4	39
14.40		40
14.42	99.5	42
14.44	99.6	44
14.47		47
14.48		48
14.49	99.6	49
14.50		50
14.52	99.5	52
14.53	99.5	53
14.55	99.5	55
14.57	99.5	57
14.59	99.5	59
15.00		60
15.02	99.5	62
15.04	99.6	63.5
15.05	99.5	65
15.07	99.5	67
15.09	99.5	69
15.10		70
15.12	99.5	72
15.13	99.5	73
15.15	99.5	75
15.17	99.5	77
15.19	99.5	79
15.20		80
15.22	99.5	82
15.24	99.6	84
15.25	99.6	85
15.27	99.5	87
15.29	99.6	89
15.30		90
15.32	99.6	92
15.33	99.6	93
15.35	99.6	95
15.37	99.5	97
15.39	99.6	99
15.40		100
15.42	99.6	102
15.43	99.6	103
15.45	99.6	105
15.47	99.6	107
15.49	99.5	109
15.50		110
15.52	99.6	112
15.54	99.6	114
15.55	99.6	115
15.57	99.6	117
16.37	99.6	157
16.39	99.7	159
16.40		160
16.42	99.7	162
16.44	99.7	164
16.45	99.6	165
16.47	99.6	167
16.49	99.7	169
16.50		170
16.52	99.7	172
16.53	99.6	173
16.55	99.6	175
16.57	99.6	177
16.59	99.7	179
17.00		180
17.02	99.6	182
17.04	99.7	184
17.05	99.7	185
17.07	99.6	187
17.09	99.6	189
17.10		190
17.12	99.7	192
17.13	99.7	193
17.15	99.6	195
17.17	99.6	197
17.19	99.6	199
17.20		200
17.22	99.7	202
17.23	99.6	203
17.25	99.6	205
17.27	99.6	207
17.29	99.6	209
17.30		210
17.32	99.7	212
17.33	99.7	213
17.35	99.7	215
17.37	99.6	217
17.39	99.6	219
17.40		220
17.42	99.7	222
17.43	99.7	223
17.45	99.7	225
17.47	99.6	227
17.49	99.6	229
17.50		230
17.52	99.7	232
17.53	99.6	233
17.55	99.6	235
17.57	99.6	237
17.59	99.6	239
18.00		240
18.02	99.7	242

15.59	99.6	119
16.00		120
16.02	99.6	122
16.04	99.6	124
16.05	99.6	125
16.07	99.6	127
16.09	99.6	129
16.10		130
16.12	99.6	132
16.13		133
16.14	99.6	134
16.15	99.5	135

18.04	99.7	243.5
18.05	99.6	245
18.07	99.7	247
18.09	99.7	249
18.10		250
18.13	99.7	252.5
18.16	99.7	256
18.19	99.7	259

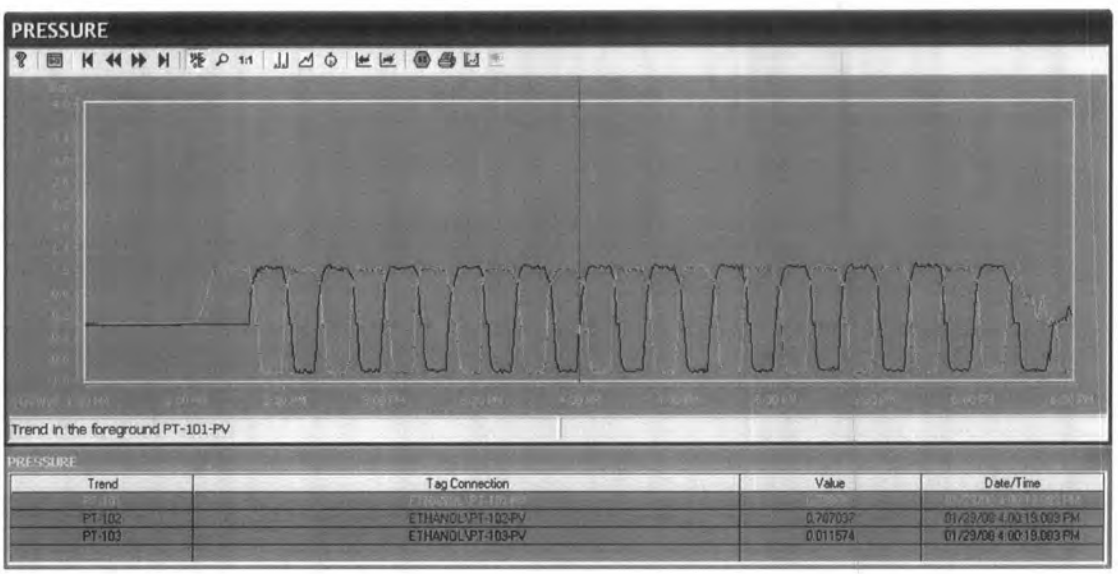

Figure E1 The pressure inside the two adsorbers during adsorption and desorption.

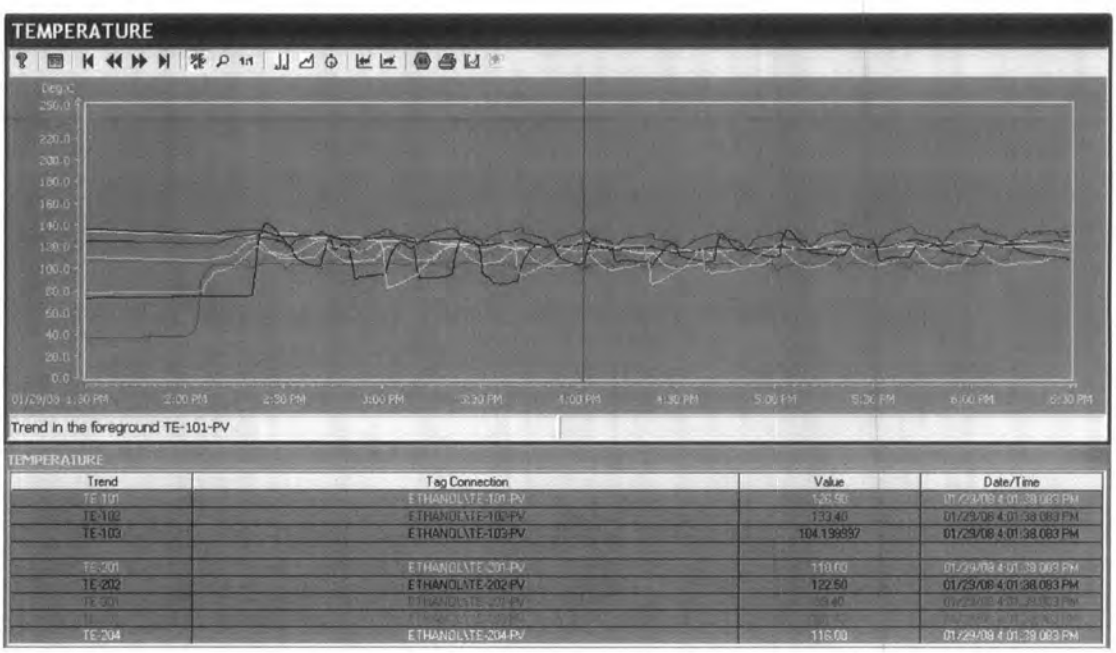

Figure E2 The temperature inside the two adsorbers during adsorption and desorption.

Appendix F

Prediction of the ethanol concentration in the product stream from PSA pilot plant

As explained in Chapter 2, the concentration of the product can be predicted by Equation 2.36.

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

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

All parameters to be substituted in β_{strong} are given in Table F1. Most of the parameters are from operating conditions and bed characteristic of the PSA pilot plant. However, the values of K'_{strong} and K'_{weak} must be further investigated.

Table F1 parameters to be substituted in β_{strong}

PSA system		
Column Height	0.5	m
Feed concentration	0.144	mole fraction water
Superficial velocity	0.945216	m/s
High P	2.4	bar
Low P	0.15	bar
Operation at	393	K
Purge feed ratio	1.1	
Zeolite property		
Density	2.1	g/cc
K_d	1	
Particle porosity, ε_p	0.56	
External porosity, ε_e	0.32	
R	8.314	$m^3Pa/(mol.K)$
q_{max}	8.547009	mmol/g
K_m	0.337955	$(kPa)^{-1}$
K'_{mp}	2.888504	mmol/(g.kPa)
K'_{weak}	0.4	K'_{strong}

To be able to find K'_{strong}, the adsorption equilibrium constant is needed. In this case the isotherm of the Zeochem 3A (Figure F1), given by the manufacturer, is used. Four specific operating conditions are assumed to obtain their corresponding water adsorption capacity of the adsorbent (as shown in Table F2).

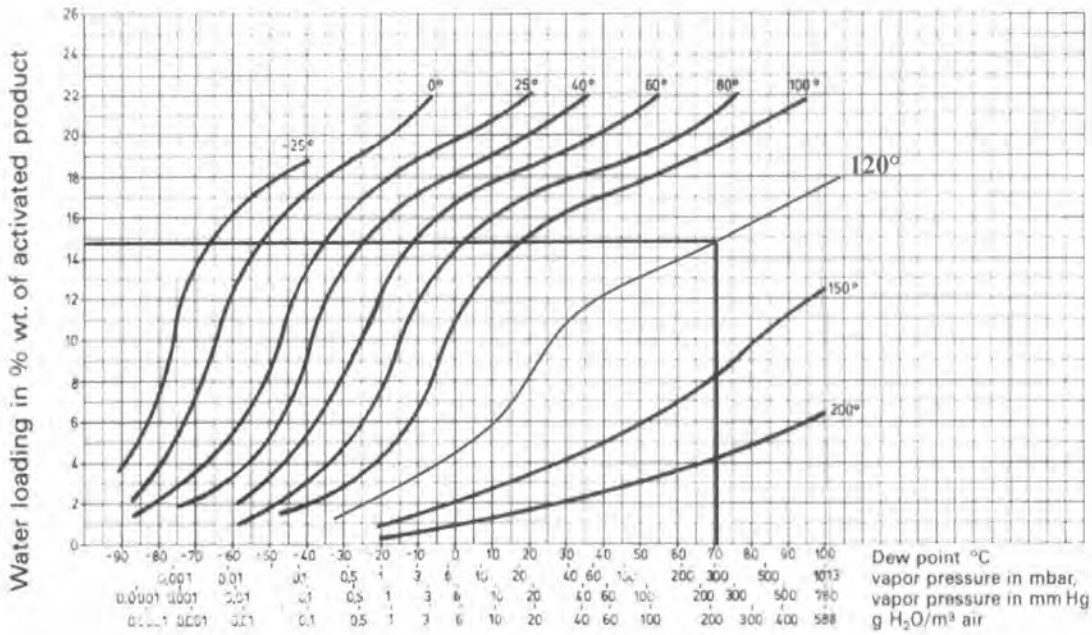

Figure F1 Equilibrium data from the zeolite 3A manufacturer (Source: Zeochem AG).

1. Feed = 95%v ethanol @1atm, 30 °C = 5%vol at 2.4 bar and 120 °C = water partial pressure = 91.2 mmHg (12 kPa) = water loading in %wt = 0.124 g $_{water}$/g $_{ads}$ = 6.89 mmol/g

2. Feed = 92.5%v ethanol @1atm, 30 °C = 7.5%vol at 2.4 bar and 120 °C = water partial pressure = 136.8 mmHg (18 kPa) = water loading in %wt = 0.132 g $_{water}$/g $_{ads}$ = 7.34 mmol/g

3. Feed = 90%v ethanol @1atm, 30 °C = 10 %vol at 2.4 bar and 120 °C = water partial pressure = 182.4 mmHg (24 kPa) = water loading in %wt = 0.136 g $_{water}$/g $_{ads}$ = 7.57 mmol/g

4. Feed = 85%v ethanol @1atm, 30 °C = 15%vol at 2.4 bar and 120 °C = water partial pressure = 273.6 mmHg (36 kPa) = water loading in %wt = 0.142 g $_{water}$/g $_{ads}$ = 7.91 mmol/g

From these four sets of parameters, the water partial pressures are then plotted against p/q in Figure F2 to find the Langmuir isotherm.

Table F2 Four specific operating conditions and their corresponding water adsorption capacities

P (kPa)	q (g_{water}/g_{ads})	q (mmol/g)	p/q
12	0.124	6.89	1.7419
18	0.132	7.34	2.4521
24	0.136	7.57	3.1701
36	0.142	7.91	4.5497

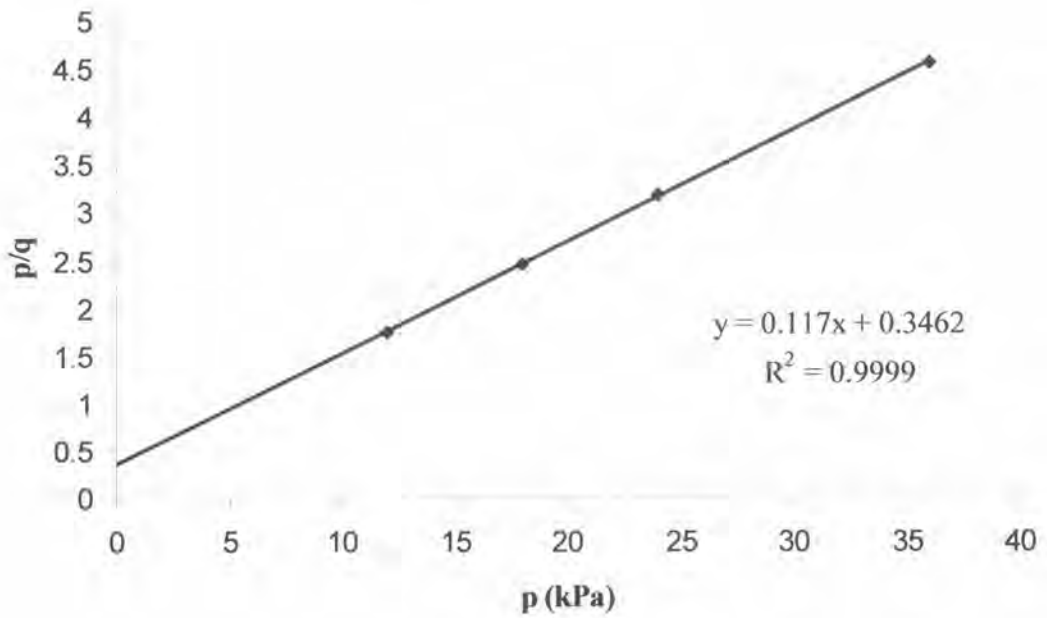

Figure F2 Plot to give straight line for Langmuir isotherm.

From Figure F2, Slope = $0.117 = 1/ q_{max}$

$q_{max} = 8.547$

Intercept = $3.462 = 1/(q_{max}K_A)$

$K_m = 0.338$

$K'_{mp} = q_{max} K_m$

$= 8.547 \times 0.338 = 2.889$

K'_{weak} is assumed to be approximately 40% of K'_{strong} or K'_{mp}. This can be supported by the breakthrough experiment of the pilot plant adsorber. The amount of water and ethanol trapped in the bed is compared in Table F3. It can be seen that although the zeolite adsorbed most of the water feeding into the fixed bed, part of the ethanol is also trapped. This amount of ethanol trapped is found to be approximately 40% of the water adsorption.

Table F3 The amount of ethanol and water adsorbed in the adsorption column

Ads P	2.4	bar		
Feed C	95.10%	vol		
Feed rate	100	mL/min		
Actual flow	95.257	mL/min		
	Product(L)	%vol	Ethanol (L)	Water (L)
	5.65	99.4	5.6161	0.0339
	1.39	98.3	1.36637	0.02363
	1.344	97.9	1.315776	0.028224
	1.37	97.7	1.33849	0.03151
	1.42	97.5	1.3845	0.0355
	1.39	97.3	1.35247	0.03753
	1.45	97.1	1.40795	0.04205
	1.37	96.8	1.32616	0.04384
	1.35	96.7	1.30545	0.04455
	1.385	96.5	1.336525	0.048475
	2.684	96.1	2.579324	0.104676
	1.14	95.4	1.08756	0.05244
	0.95	95.1	0.90345	0.04655
Total	22.893	-	22.32013	0.572875
Feed	23.719	95.1	22.55677	1.162231
Trapped in bed			0.236644	0.589356
%ethanol/water trapped in bed			40.153%	

Appendix G

Experimental setup

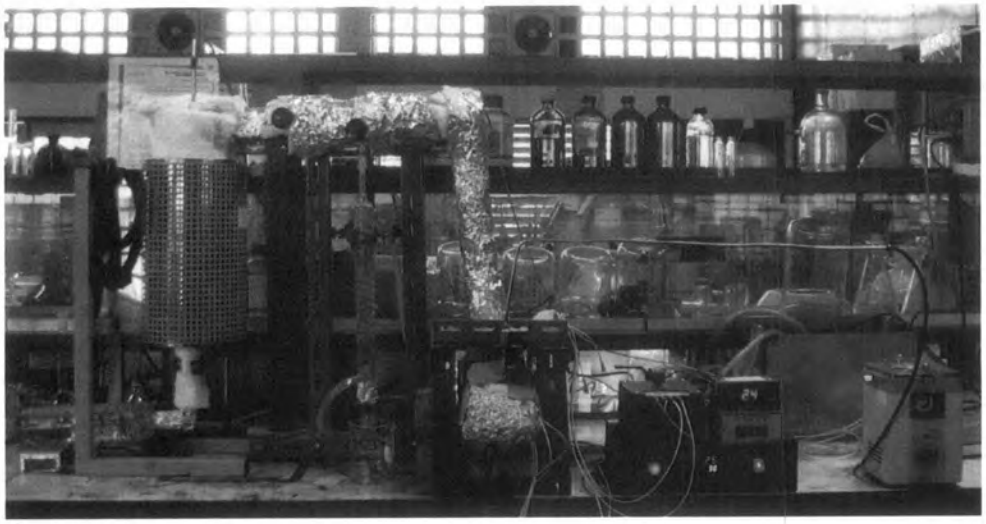

Figure G1 Setup of the fixed bed experiment.

Figure G2 PSA pilot plant.

VITA

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