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APPENDICES

Appendix A Physical Properties of Ethanol and Water

Table A1 Physical Properties of Ethanol and Water (Benson, 2003)

Property	Ethanol	Water
Molecular Formula	CH_3CH_2OH	H_2O
Molecular Weight	46.07	18.016
Specific Gravity	0.789	1.00
Melting Point (°C)	-112	0
Boiling Point (°C)	78.4	100
Solubility	∞(in water)	

Appendix B Calculated Method

B.1. Single Component Adsorption Capacity

B.1.1 Moisture Adsorption Capacity (Sathupunya *et al.*, 2003)

The moisture adsorption capacity was determined as

$$Q_{ads} = \frac{W_2 - W_1}{M_{ads}} \quad \text{(B.1)}$$

where W_1 is the weight of the dried adsorbent (g).

W_2 is the weight of the wetted adsorbent (g).

W_2-W_1 is the mass of the water adsorbed (g).

M_{ads} is the mass of the adsorbent (g).

Q_{ads} is the mass of water adsorbed per unit mass of adsorbent ($g_{water}/ g_{adsorbent}$).

B.1.2 Ethanol Adsorption Capacity

The ethanol adsorption capacity was determined as

$$Q_{ads} = \frac{W_2 - W_1}{M_{ads}} \quad \text{(B.2)}$$

where W_1 is the weight of the dried adsorbent (g).

W_2 is the weight of the wetted adsorbent (g).

W_2-W_1 is the mass of the ethanol adsorbed (g).

M_{ads} is the mass of the adsorbent (g).

Q_{ads} is the mass of ethanol adsorbed per unit mass of adsorbent ($g_{ethanol}/ g_{adsorbent}$).

B.1.3 Ethanol Selectivity

The ethanol selectivity with respect to water was determined as

$$\alpha_{e/w} = \frac{X_e}{X_w} \qquad \text{(B.3)}$$

where X_e is the ethanol adsorption capacity of the adsorbent ($g_{ethanol} / g_{adsorbent}$).

X_w is the water adsorption capacity of the adsorbent ($g_{water} / g_{adsorbent}$).

$\alpha_{e/w}$ is the ethanol selectivity.

B.2. Competitive Component Adsorption Capacity

The adsorption uptake Q_{ads}, gram adsorbed solute per gram solid adsorbent, was found by a mass balance on the adsorbed species, assuming water was not significantly adsorbed. When using dry adsorbents, the mass balance yielded to the equation (Carton *et al.*, 1998):

$$Q_{ads} = \frac{(Wt_i\% - Wt_f\%)\, M_L}{(100 - Wt_f\%)\, M_{ads}} \qquad \text{(B.4)}$$

where $Wt_i\%$ is the initial mass fraction of ethanol in solution.

$Wt_f\%$ is the final mass fraction of ethanol in solution.

M_L is the mass of the solution (g).

M_{ads} is the mass of the dry adsorbent (g).

Q_{ads} is the mass of ethanol adsorbed per unit mass of adsorbent ($g_{ethanol}/ g_{adsorbent}$).

B.3. Dynamic Adsorption: Breakthrough Curves

A graphical method can be employed to determine an adsorbent's capacity to adsorb ethanol. A graphical presentation of data can be made, in which the normalized concentration of ethanol is plotted versus the total adsorbate volume of the experiment. As shown in Figure B1, the amount adsorbed is the area that exists above the curve. This area is estimated by creating a triangle from the linear portion of the curve up to the point of breakthrough, or threshold (Benson, 2003).

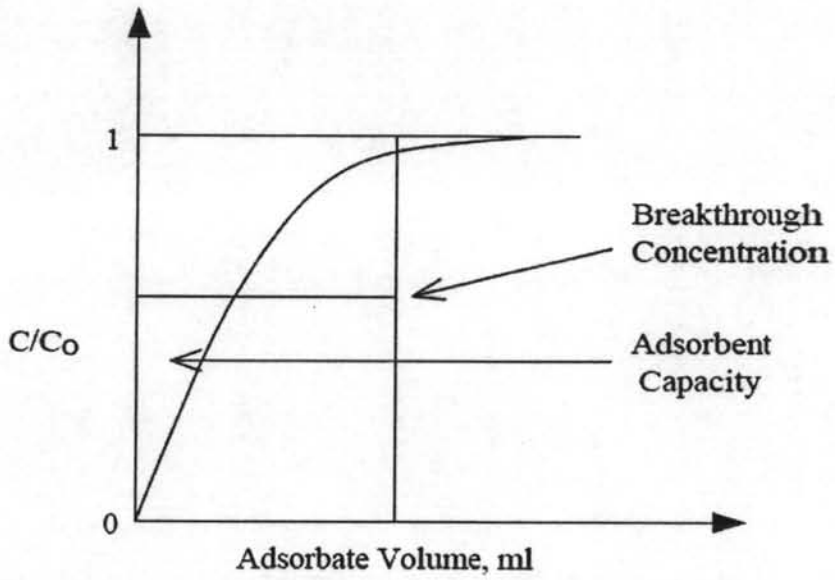

Figure B1 Graphical method for determining adsorption capacity (Benson, 2003).

The area of ethanol adsorption, which calculated from the breakthrough curve, is the unit of the normalized concentration of ethanol. Therefore, the mass ethanol adsorbed per unit mass of adsorbent ($g_{ethanol}/ g_{adsorbent}$) is that the area that exists above the curve multiply by the initial mass fraction of ethanol in feed then divided by mass of the adsorbent.

Appendix C Summary of Experimental Data

C.1. Summary of Experimental Data for Vapor Phase Experiments

Table C1 Experimental Data for Vapor Phase Experiments

Adsorbent	Ethanol Adsorption Capacity ($\%\ g_{ethanol} / g_{adsorbent}$)		Water Adsorption Capacity ($\%\ g_{ethanol} / g_{adsorbent}$)	
	25°C	40°C	25°C	40°C
Silicalite	19.03	9.93	15.75	15.82
Activated carbon	37.49	30.21	36.68	39.87
XAD-2	48.26	9.38	36.72	56.47
LZ-210	29.75	18.11	15.99	16.59
Silica gel	45.78	37.68	61.01	60.02
Silica gel treated with 3-aminopropyltrimethoxysilane	23.39	13.64	21.95	30.68
Silica gel treated with methanol	44.27	36.48	46.89	57.14
Silica gel treated with ethanol	46.61	32.05	39.74	58.01
Silica gel treated with propanol	45.21	36.41	38.85	61.52
Silica gel treated with butanol	48.56	33.51	32.14	55.61
Silica Hi-Sil®255	52.34	2.73	26.43	41.46
Silica Hi-Sil®255 modified with admicellar polymerization	55.36	1.32	12.23	22.12

C.2. Summary of Experimental Data for Batch Liquid Phase Experiments

Table C2.1 Experimental Data for Batch Liquid Phase Experiments Using Silicalite

Mass of Liquid (g)	Mass of Adsorbent (g)	Initial Ethanol Concentration (mass fraction)	Final Ethanol Concentration (mass fraction)	Ethanol Adsorption Isotherm ($g_{ethanol}/g_{adsorbent}$)
0.0000	0.0000	0.000	0.0000	0.0000
19.7809	2.0073	1.005	0.5610	0.0419
19.8181	2.0092	2.973	2.3350	0.0651
19.8599	2.0103	4.981	4.3110	0.0708
19.6460	2.0052	7.042	6.3480	0.0732
19.7048	2.0027	8.996	8.3180	0.0745
19.4423	2.0103	11.079	10.3580	0.0753
19.2658	2.0065	13.053	12.3640	0.0759

Table C2.2 Experimental Data for Batch Liquid Phase Experiments Using LZ-210

Mass of Liquid (g)	Mass of Adsorbent (g)	Initial Ethanol Concentration (mass fraction)	Final Ethanol Concentration (mass fraction)	Ethanol Adsorption Isotherm ($g_{ethanol}/g_{adsorbent}$)
0.0000	0.0000	0.000	0.0000	0.0000
20.3706	2.0046	0.901	0.9060	0.0019
20.0439	2.0051	3.010	2.9100	0.0058
19.8860	2.0027	4.990	4.8840	0.0094
20.1223	2.0055	6.977	6.8550	0.0127
19.8099	2.0053	9.014	8.7590	0.0156
19.9787	2.0029	10.987	10.7780	0.0185
19.6355	2.0027	13.019	12.7390	0.0211

Table C2.3 Experimental Data for Batch Liquid Phase Experiments Using Activated Carbon

Mass of Liquid (g)	Mass of Adsorbent (g)	Initial Ethanol Concentration (mass fraction)	Final Ethanol Concentration (mass fraction)	Ethanol Adsorption Isotherm ($g_{ethanol}/g_{adsorbent}$)
0.0000	0.0000	0.000	0.0000	0.0000
20.0849	2.0078	1.005	0.5340	0.0359
19.6840	2.0034	2.973	2.0350	0.0892
19.9846	2.0061	4.981	3.8590	0.1188
19.8108	2.0092	7.042	5.6190	0.1343
19.6783	2.0078	8.996	7.6790	0.1455
19.5920	2.0029	11.079	9.6720	0.1527
19.3871	2.0036	13.053	11.5900	0.1577

Table C2.4 Experimental Data for Batch Liquid Phase Experiments Using XAD-2

Mass of Liquid (g)	Mass of Adsorbent (g)	Initial Ethanol Concentration (mass fraction)	Final Ethanol Concentration (mass fraction)	Ethanol Adsorption Isotherm ($g_{ethanol}/g_{adsorbent}$)
0.0000	0.0000	0.000	0.0000	0.0000
17.5324	2.0013	1.038	0.974	0.0050
17.6921	2.0025	2.716	2.573	0.0132
18.2867	2.0037	5.027	4.793	0.0247
17.8360	1.9998	7.086	6.689	0.0347
18.0372	2.0080	9.085	8.640	0.0451
18.0935	2.0021	11.054	10.592	0.0567
18.5251	2.0024	13.179	12.551	0.0664

Table C2.5 Experimental Data for Batch Liquid Phase Experiments Using Silica Gel

Mass of Liquid (g)	Mass of Adsorbent (g)	Initial Ethanol Concentration (mass fraction)	Final Ethanol Concentration (mass fraction)	Ethanol Adsorption Isotherm ($g_{ethanol}/g_{adsorbent}$)
0.0000	0.0000	0.000	0.0000	0.0000
20.0736	2.0004	0.901	0.8720	0.0021
19.9643	2.0075	3.010	2.9010	0.0062
19.6983	2.0061	4.990	4.8960	0.0092
19.3860	2.0056	6.977	6.8540	0.0117
19.6319	2.0028	9.014	8.8610	0.0137
19.6490	2.0051	10.987	10.8630	0.0154
19.1750	2.0071	13.019	12.8650	0.0168

Table C2.6 Experimental Data for Batch Liquid Phase Experiments Using Silica Gel Treated with 3-aminopropyltrimethoxysilane

Mass of Liquid (g)	Mass of Adsorbent (g)	Initial Ethanol Concentration (mass fraction)	Final Ethanol Concentration (mass fraction)	Ethanol Adsorption Isotherm ($g_{ethanol}/g_{adsorbent}$)
0.0000	0.0000	0.000	0.0000	0.0000
19.9507	2.0021	1.901	0.9940	0.0074
19.8700	2.0021	3.090	3.0870	0.0099
19.7812	2.0029	4.990	4.9480	0.0106
19.8356	2.0049	6.977	6.9040	0.0109
19.4976	2.0081	9.014	9.0070	0.0111
19.5880	2.0035	10.987	10.9110	0.0112
19.5841	2.0042	13.019	13.0090	0.0113

Table C2.7 Experimental Data for Batch Liquid Phase Experiments Using Silica Gel Treated with Methanol

Mass of Liquid (g)	Mass of Adsorbent (g)	Initial Ethanol Concentration (mass fraction)	Final Ethanol Concentration (mass fraction)	Ethanol Adsorption Isotherm ($g_{ethanol}$/ $g_{adsorbent}$)
0.0000	0.0000	0.000	0.0000	0.0000
19.8561	2.0082	1.040	1.0140	0.0048
20.0092	2.0070	3.094	2.9920	0.0098
19.6132	2.0063	5.072	4.9610	0.0125
19.9910	2.0026	7.070	6.8950	0.0141
20.2025	2.0022	9.033	8.9040	0.0153
19.7908	2.0029	11.063	10.9260	0.0161
19.8850	2.0103	13.061	12.9240	0.0158

Table C2.8 Experimental Data for Batch Liquid Phase Experiments Using Silica Gel Treated with Ethanol

Mass of Liquid (g)	Mass of Adsorbent (g)	Initial Ethanol Concentration (mass fraction)	Final Ethanol Concentration (mass fraction)	Ethanol Adsorption Isotherm ($g_{ethanol}$/ $g_{adsorbent}$)
0.0000	0.0000	0.000	0.0000	0.0000
20.1497	2.0075	1.901	1.836	0.0066
20.0824	2.0097	3.374	3.261	0.0117
20.0383	2.0050	5.379	5.217	0.0171
19.3399	2.0037	7.377	7.218	0.0165
19.6939	2.0029	9.294	9.109	0.0200
19.5860	2.0082	11.267	11.089	0.0195
19.6208	2.0038	13.334	13.161	0.0195

Table C2.9 Experimental Data for Batch Liquid Phase Experiments Using Silica Gel Treated with Propanol

Mass of Liquid (g)	Mass of Adsorbent (g)	Initial Ethanol Concentration (mass fraction)	Final Ethanol Concentration (mass fraction)	Ethanol Adsorption Isotherm ($g_{ethanol}$/ $g_{adsorbent}$)
0.0000	0.0000	0.000	0.0000	0.0000
20.0750	2.0081	1.059	1.0490	0.0052
20.0910	2.0056	3.062	2.9770	0.0103
19.5896	2.0027	5.136	4.9470	0.0130
19.5879	2.0085	7.075	6.9220	0.0148
19.6989	2.0051	8.971	8.9100	0.0159
19.5144	2.0065	11.007	10.8940	0.0168
19.6878	2.0022	12.948	12.8830	0.0174

Table C2.10 Experimental Data for Batch Liquid Phase Experiments Using Silica Gel Treated with Butanol

Mass of Liquid (g)	Mass of Adsorbent (g)	Initial Ethanol Concentration (mass fraction)	Final Ethanol Concentration (mass fraction)	Ethanol Adsorption Isotherm ($g_{ethanol}$/ $g_{adsorbent}$)
0.0000	0.0000	0.000	0.0000	0.0000
19.9392	2.0073	1.040	0.9910	0.0042
20.1264	2.0065	3.094	2.9760	0.0108
19.8488	2.0084	5.072	4.9330	0.0156
20.0750	2.0021	7.070	6.9010	0.0194
19.7829	2.0049	9.033	8.8470	0.0224
20.1441	2.0047	11.063	10.7940	0.0248
19.7367	2.0017	13.061	12.8440	0.0269

Table C2.11 Experimental Data for Batch Liquid Phase Experiments Using Silica Hi-Sil®255

Mass of Liquid (g)	Mass of Adsorbent (g)	Initial Ethanol Concentration (mass fraction)	Final Ethanol Concentration (mass fraction)	Ethanol Adsorption Isotherm ($g_{ethanol}$/ $g_{adsorbent}$)
0.0000	0.0000	0.000	0.0000	0.0000
15.6609	1.5083	1.038	0.9760	0.0038
15.1174	1.5028	2.716	2.6500	0.0064
15.4530	1.5004	5.027	4.9750	0.0080
14.9270	1.5037	7.086	7.0540	0.0087
15.1093	1.5068	9.085	8.9680	0.0091
15.0482	1.5019	11.054	11.0160	0.0094
14.8747	1.5014	13.179	13.0350	0.0096

Table C2.12 Experimental Data for Batch Liquid Phase Experiments Using Silica Hi-Sil®255 Modified with Admicellar Polymerization

Mass of Liquid (g)	Mass of Adsorbent (g)	Initial Ethanol Concentration (mass fraction)	Final Ethanol Concentration (mass fraction)	Ethanol Adsorption Isotherm ($g_{ethanol}$/ $g_{adsorbent}$)
0.0000	0.0000	0.000	0.0000	0.0000
15.1399	1.5024	1.038	1.0379	0.0007
15.2456	1.5095	2.716	2.7020	0.0019
14.9276	1.5094	5.027	5.0200	0.0037
15.4365	1.5049	7.086	7.0320	0.0056
14.8420	1.5007	9.085	8.9920	0.0077
14.9884	1.5079	11.054	10.9510	0.0102
15.3978	1.5026	13.179	13.0760	0.0121

C.3. Summary of Experimental Data for Column Dynamic Experiments

Table C3.1 Experimental Data for Column Dynamic Experiments Using Silicalite

Adsorbate Volume (mL)	C/C_0 (Concentration of Ethanol)
41.0	0.000
43.4	0.000
45.8	0.000
48.2	0.000
50.6	0.000
53.0	0.000
55.4	0.000
57.8	0.000
60.2	0.000
62.6	0.000
65.0	0.000
67.4	0.000
69.8	0.127
72.2	0.804
74.6	0.879
77.0	0.903
81.8	0.930
89.0	0.942
101.0	0.953

Table C3.2 Experimental Data for Column Dynamic Experiments Using Activated Carbon

Adsorbate Volume (mL)	C/C_0 (Concentration of Ethanol)
46.0	0.000
48.4	0.169
50.8	0.000
53.2	0.000
55.6	0.000
58.0	0.000
60.4	0.000
62.8	0.000
65.2	0.000
67.6	0.000
70.0	0.000
72.4	0.000
74.8	0.000
82.0	0.724
86.8	0.909
94.0	0.957
106.0	0.969
118.0	0.972

Table C3.3 Experimental Data for Column Dynamic Experiments Using XAD-2

Adsorbate Volume (mL)	C/C_0 (Concentration of Ethanol)
25.0	0.000
27.4	0.000
29.8	0.000
32.2	0.000
34.6	0.000
37.0	0.000
39.4	0.000
41.8	0.000
44.2	0.002
46.6	0.057
49.0	0.234
51.4	0.563
53.8	0.822
56.2	0.914
58.6	0.950
61.0	0.961
65.8	0.970
73.0	0.977
85.0	0.982
97.0	0.979
109.0	0.979
121.0	0.983

Table C3.4 Experimental Data for Column Dynamic Experiments Using LZ-210

Adsorbate Volume (mL)	C/C_0 (Concentration of Ethanol)
44.0	0.000
46.4	0.097
48.8	0.303
51.2	0.562
53.6	0.760
56.0	0.873
58.4	0.931
60.8	0.959
63.2	0.971
65.6	0.978
68.0	0.980
70.4	0.981
72.8	0.985
80.0	0.986
84.8	0.984
92.0	0.984
104.0	0.979
116.0	0.987

Table C3.5 Experimental Data for Column Dynamic Experiments Using Silica Gel

Adsorbate Volume (mL)	C/C_0 (Concentration of Ethanol)
46.0	0.000
48.4	0.002
53.2	0.276
58.0	0.984
62.8	0.974
67.6	0.974
72.4	0.970
77.2	0.968
82.0	0.970
86.8	0.970
91.6	0.971
96.4	0.972
101.2	0.976
106.0	0.974
110.8	0.974
115.6	0.975
120.4	0.974
125.2	0.971
130.0	0.974
134.8	0.975
139.6	0.973
144.4	0.973
149.2	0.973
154.0	0.969

Table C3.6 Experimental Data for Column Dynamic Experiments Using Silica Gel Treated with 3-aminopropyltrimethoxysilane

Adsorbate Volume (mL)	C/C_0 (Concentration of Ethanol)
40.0	0.000
42.4	0.081
44.8	0.844
47.2	0.937
49.6	0.993
52.0	0.987
54.4	0.973
56.8	0.973
59.2	0.973
61.6	0.967
64.0	0.970
66.4	0.973
68.8	0.969
76.0	0.970
88.0	0.969
100.0	0.968
112.0	0.968
124.0	0.967
136.0	0.969

Table C3.7 Experimental Data for Column Dynamic Experiments Using Silica Gel Treated with Methanol

Adsorbate Volume (mL)	C/C_0 (Concentration of Ethanol)
46.0	0.000
48.4	0.255
50.8	0.793
53.2	0.954
55.6	0.982
58.0	0.982
60.4	0.992
62.8	0.991
65.2	0.989
67.6	0.988
70.0	0.972
72.4	0.973
74.8	0.987
82.0	0.990
86.8	0.986
94.0	0.991
106.0	0.990
118.0	0.962

Table C3.8 Experimental Data for Column Dynamic Experiments Using Silica Gel Treated with Ethanol

Adsorbate Volume (mL)	C/C_0 (Concentration of Ethanol)
42.0	0.000
44.4	0.325
46.8	0.861
49.2	0.971
51.6	0.984
54.0	0.990
56.4	0.986
58.8	0.981
61.2	0.993
63.6	0.994
66.0	0.993
68.4	0.994
70.8	0.990
78.0	0.984
82.8	0.995
90.0	0.977
102.0	0.977
114.0	0.985

Table C3.9 Experimental Data for Column Dynamic Experiments Using Silica Gel Treated with Propanol

Adsorbate Volume (mL)	C/C_0 (Concentration of Ethanol)
43.0	0.000
45.4	0.289
47.8	0.584
50.2	0.891
52.6	0.956
55.0	0.968
57.4	0.973
59.8	0.975
62.2	0.979
64.6	0.979
67.0	0.978
69.4	0.978
71.8	0.977
79.0	0.979
83.8	0.980
91.0	0.980
103.0	0.983
115.0	0.984

Table C3.10 Experimental Data for Column Dynamic Experiments Using Silica Gel Treated with Butanol

Adsorbate Volume (mL)	C/C_0 (Concentration of Ethanol)
44.0	0.000
46.4	0.321
48.8	0.667
51.2	0.897
53.6	0.958
56.0	0.973
58.4	0.978
60.8	0.978
63.2	0.980
65.6	0.983
68.0	0.983
70.4	0.983
72.8	0.981
80.0	0.986
84.8	0.986
92.0	0.984
104.0	0.988
116.0	0.982

Appendix D Liquid Chromatograph Calibration and Operating Conditions

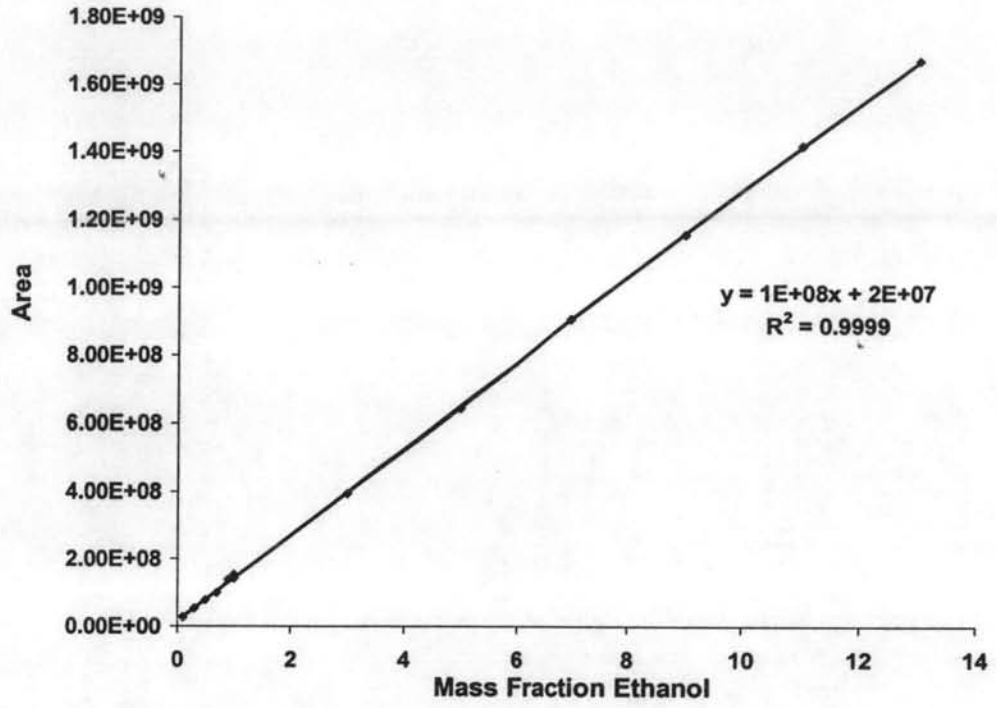

Figure D1 Liquid chromatograph calibration curve for measuring concentrations of ethanol

The operating conditions that have been set on the Liquid chromatograph (LC) for the analysis of ethanol are given below.

Series:	Waters 2695 Separation Module combined with a Waters 2414 Refractive Index
Column:	BioRad HPX-87H (300x7.8 mm) "ion-exclusion"
Detector:	RI sensitivity setting 8 polarity
Detector Temperature:	40°C
Mobile Phase:	0.0089N of H_2SO_4 (1 mL conc. H_2SO_4 in 4 L H_2O)
Mobile Phase Flow Rate:	0.8 mL/min.
Injection Volume:	10 μL
Injection Temperature:	60°C
Analysis Time:	~ 20 min.
Retention Time of Ethanol:	~ 15 min.

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1. Piriyasurawong, K., Rangsunvigit, P., and Kulprathipanja, S. Ethanol Production: Applicability of Reactive Separation. Poster presentation at AIChE Annual 2005 National Meeting, Cincinnati, Ohio, USA.

Award:

1. Piriyasurawong, K., Rangsunvigit, P., and Kulprathipanja, S. Ethanol Production: Applicability of Reactive Separation. The Best of Poster Presentation at AIChE Annual 2005 National Meeting, Cincinnati, Ohio, USA.