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APPENDIX

1. Adsorption and Desorption of Cyclohexene and Cyclohexanol on ZSM-5 and Amberlyst-15

In the Chromatographic Reactor

The experiments were carried out to study the adsorption of cyclohexene, cyclohexanol and n-hexane on ZSM-5 and Amberlyst-15. The adsorption selectivity and capacity of cyclohexene and cyclohexanol were calculated from the experimental results. N-hexane and cyclohexane were used as the tracer to determine the void volume of the catalyst bed in the reactor. The experimental set-up is shown in Figure 2.

Adsorption on ZSM-5

The concentration of cyclohexene, cyclohexanol, and n-hexane in the eluted solution is illustrated in Figure A.1. The experimental conditions are listed in Table A.1.1. The results in the figure show that cyclohexene elutes from the reactor before cyclohexanol and n-hexane that almost simultaneously elutes. These results indicate that cyclohexanol is strongly adsorbed on ZSM-5 than cyclohexene and n-hexane. That also implies that n-hexane is not a suitable tracer for the void volume determination in the system because it is adsorbed more strongly than cyclohexene.

Adsorption on Amberlyst-15

Figure A.2 shows the concentration of cyclohexene, cyclohexanol and n-hexane in the eluted solution with the reaction conditions according to Table A.1.2. The results are approximately the same with those on ZSM-5. That is cyclohexanol is strongly adsorbed on Amberlyst-15 than cyclohexene and n-hexane is not a suitable tracer for the void volume determination.

Table A.1 The adsorption experiment conditions in the chromatographic system

<table>
<tr><th rowspan="3">Experiment</th><th rowspan="3">Tracer</th><th rowspan="3">Catalyst</th><th rowspan="3">Desor-bent</th><th colspan="3">Feed</th></tr>
<tr><th colspan="3">Concentration (wt%)</th></tr>
<tr><th>Cyclohe-xene</th><th>Cyclohex-anol</th><th>Tracer</th></tr>
<tr><td>1</td><td rowspan="4">n-hexane</td><td>ZSM-5</td><td rowspan="2">Water</td><td rowspan="4">85</td><td rowspan="4">10</td><td rowspan="4">5</td></tr>
<tr><td>2</td><td rowspan="4">Amberlst -15</td></tr>
<tr><td>3</td><td>Acetone</td></tr>
<tr><td>4</td><td>Methanol</td></tr>
<tr><td>5</td><td>Cyclo-hexane</td><td>Water</td><td>50</td><td>10</td><td>40</td></tr>
</table>

All experiments in this table were carried out at 120 °C.

Table A.2 The feed composition used for equilibrium the adsorption study in the batch system

Experiment	Concentration (wt%)		
	Cyclohexene	Cyclohexanol	n-hexane
1	5	5	90
2	10	10	80
3	20	20	60
4	30	30	40
5	40	20	40
6	10	50	40
7	0	20	80
8	20	0	80

All experiments in this table were carried out at 120 °C.

Using cyclohexane as a tracer with Amberlyst-15

The experiments were carried out with conditions from Table A.1.5. The results in Figure A.3 indicate that cyclohexane is also not a suitable tracer because it has the same adsorption behavior as cyclohexene.

In the Batch Reactor System

The batch adsorption experiments were performed to determine the exact adsorption capacity and selectivity of cyclohexene and cyclohexanol on Amberlyst-15. Table A.3 shows the concentration of each component in the feed compared those after the equilibrium was reached. From Experiment No. 7 in the table, it was clearly seen that cyclohexanol was converted to cyclohexene under the experimental condition in Table A.2. To confirm the conversion of cyclohexanol to cyclohexene, the amount of water in the solution was determined. The water in the batch solution of Experiment No. 7 was about 0.4 %, so it also confirms that cyclohexanol was converted to cyclohexene and water. However, the result in Experiment No. 8 shows that cyclohexene was not converted to cyclohexanol under this condition (without water). Because cyclohexene can be converted to cyclohexanol at 120 °C. The conversion of cyclohxene to cyclohexanol makes the error on cyclohexene and cyclohexanol concentration in the batch solution of Experiments No. 1 to 6, so the results could not be used for adsorption calculation.

Table A.3 The results of equilibrium adsorption in the batch reactor

Experiment No.	Feed			Results		
	Cyclohex -ene	Cyclohex -anol	n-hexane	Cyclohex-ene	Cyclohex-anol	n-hexane
1	5.00	5.00	90.00	0.00	0.00	100.00
2	10.00	10.00	80.00	16.81	0.00	83.17
3	20.00	20.00	60.00	35.49	0.00	63.94
4	30.00	30.00	40.00	58.26	1.66	38.56
5	40.00	20.00	40.00	58.23	0.75	41.01
6	10.00	50.00	40.00	33.52	24.8	41.47
7	0.00	20.00	80.00	15.89	0.00	84.10
8	20.00	0.00	80.00	0.00	0.00	96.62

Table A.4 The results. of the chromatographic adsorption with acetone as a desorbent

No.	Time (min)	Concentration (wt%)				
		Cyclohexene	Cyclohexanol	n-hexane	Unknowns	Acetone
1	0	29.83	13.97	0.77	-	26.46
2	18	25.32	3.80	0.38	-	72.98
3	170	30.78	0.00	0.00	28.27	40.94
4	362	0.00	0.00	0.00	26.02	73.97
5	389	0.00	0.00	0.00	23.09	76.90

2. The Effect of Desorbents on Cyclohexene Hydration in a Chromatographic Reactor

To solve the desorption-limiting step of cyclohexanol, a suitable desorbent for the cyclohexanol desorption from Amberlyst-15 were carried out. The experiments were performed under the same condition of the cyclohexene hydration in the chromatographic reactor. Acetone or methanol was used as a desorbent because each of them can solubilize cyclohexanol.

Acetone

The concentration of the each component in the eluted solution from the reactor that uses acetone as the desorbent is shows in Table A.4 with the experimental conditions in Table A.1.3. A large fraction of unknown products were detected. That may result from reactions between the either cyclohexene or cyclohexanol with acetone. As a result, acetone is not a suitable desorbent for the cyclohexene hydration.

Methanol

Figure A.4 shows the concentration in the each component of the eluted solution following the condition in Table A.1.4. These results also indicate that methanol is not a suitable desorbent for the cyclohexene hydration because large amount of the unknown products were detected. That may result from reaction among cyclohexene or cyclohexanol with methanol.

3. Effects of the Operation Modes

Amberlyst-15 Saturated with Cyclohexene or Cyclohexanol

The cyclohexanol concentration from the cyclohexene with Amberlyst-15 saturated with cyclohexene or cyclohexanol is shown in Figure A.5. The experiments were carried out according to Tables A.1.2, A.1.8, and A.1.9. The cyclohexanol concentration decreases when Amberlyst-15 is saturated with cyclohexanol before the reaction; however, it increases when Amberlyst-15 is saturated with cyclohexene. The average cyclohexanol concentration with fresh Amberlyst-15, Amberlyst-15 saturated with cyclohexanol, and Amberlyst-15 saturated with cyclohexene is 0.75, 0.48, and 0.92 respectively. The results imply that Amberlyst-15 saturated with cyclohexanol has the effect on the thermodynamic equilibrium of the cyclohexene hydration. In addition, it can be further said that cyclohexanol is strongly adsorbed on Amberlyst-15 and that reduces the active size in the pore of Amberlyst-15. Moreover, the cyclohexanol concentration increases when Amberlyst-15 saturated with cyclohexene, imply that the active size of Amberlyst-15 could be lost by the internal diffusion step.

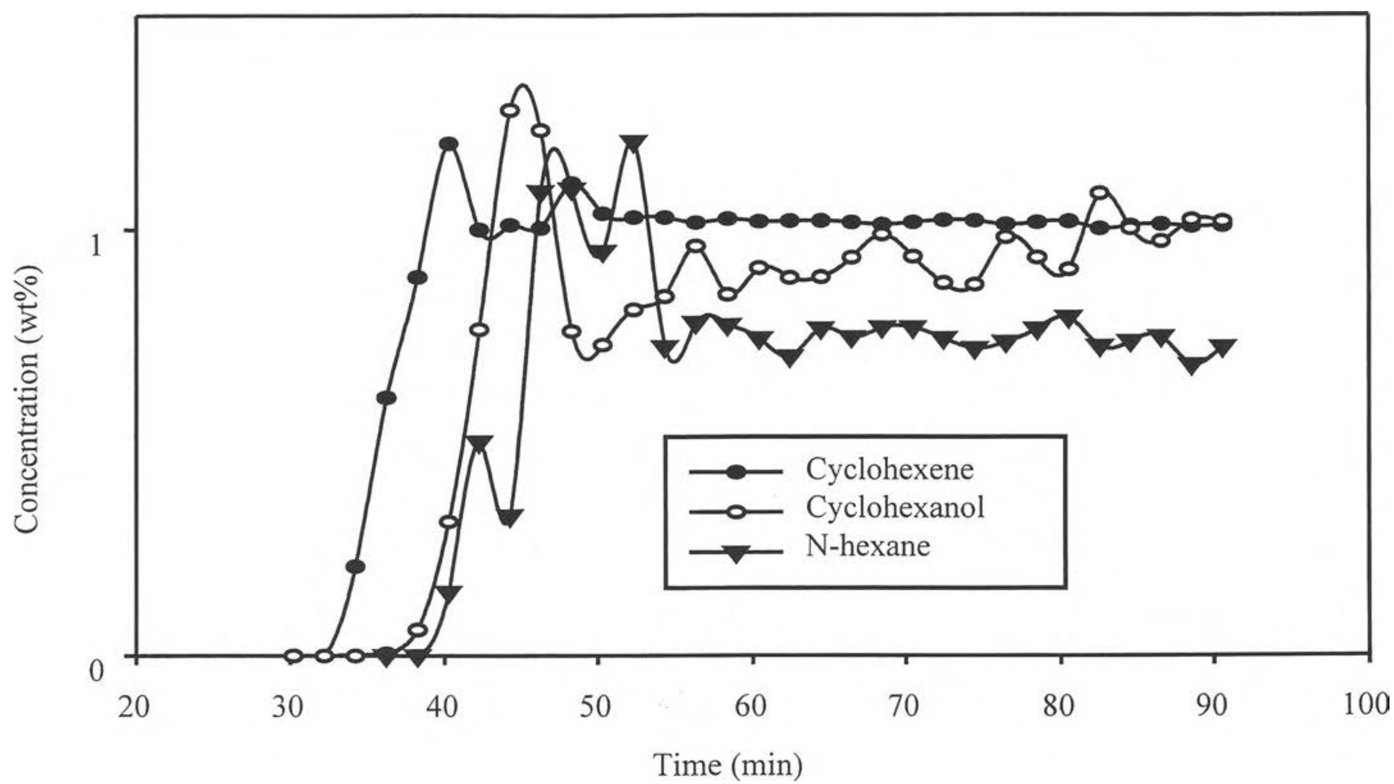

Figure A.1 The equilibrium adsorption of cyclohexene and cyclohexaol on ZSM-5 using n-hexane as a tracer at 120 °C

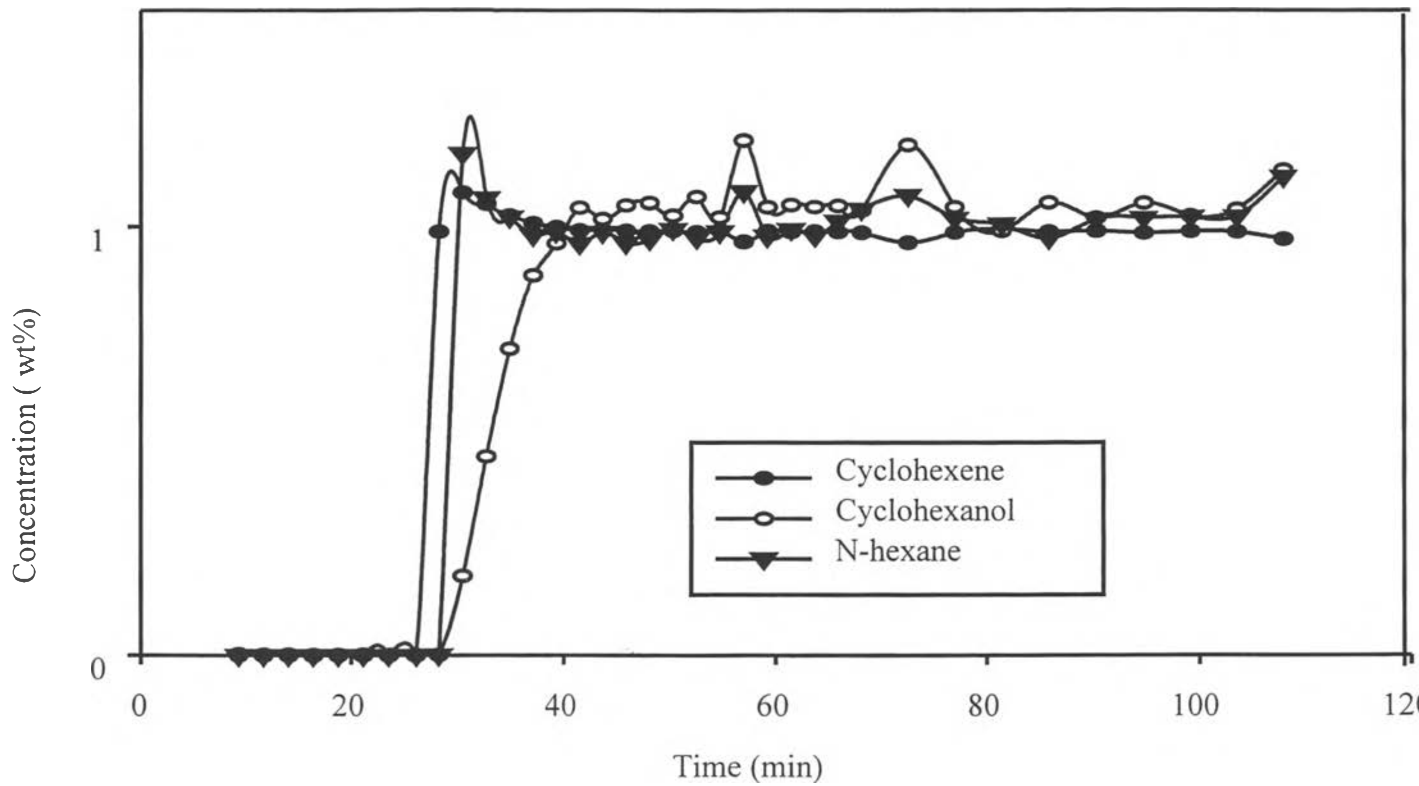

Figure A.2 the equilibrium adsorption of cyclohexene and cyclohexanol on Amberlyst-15 using n-hexane as a tracer at 120 °C

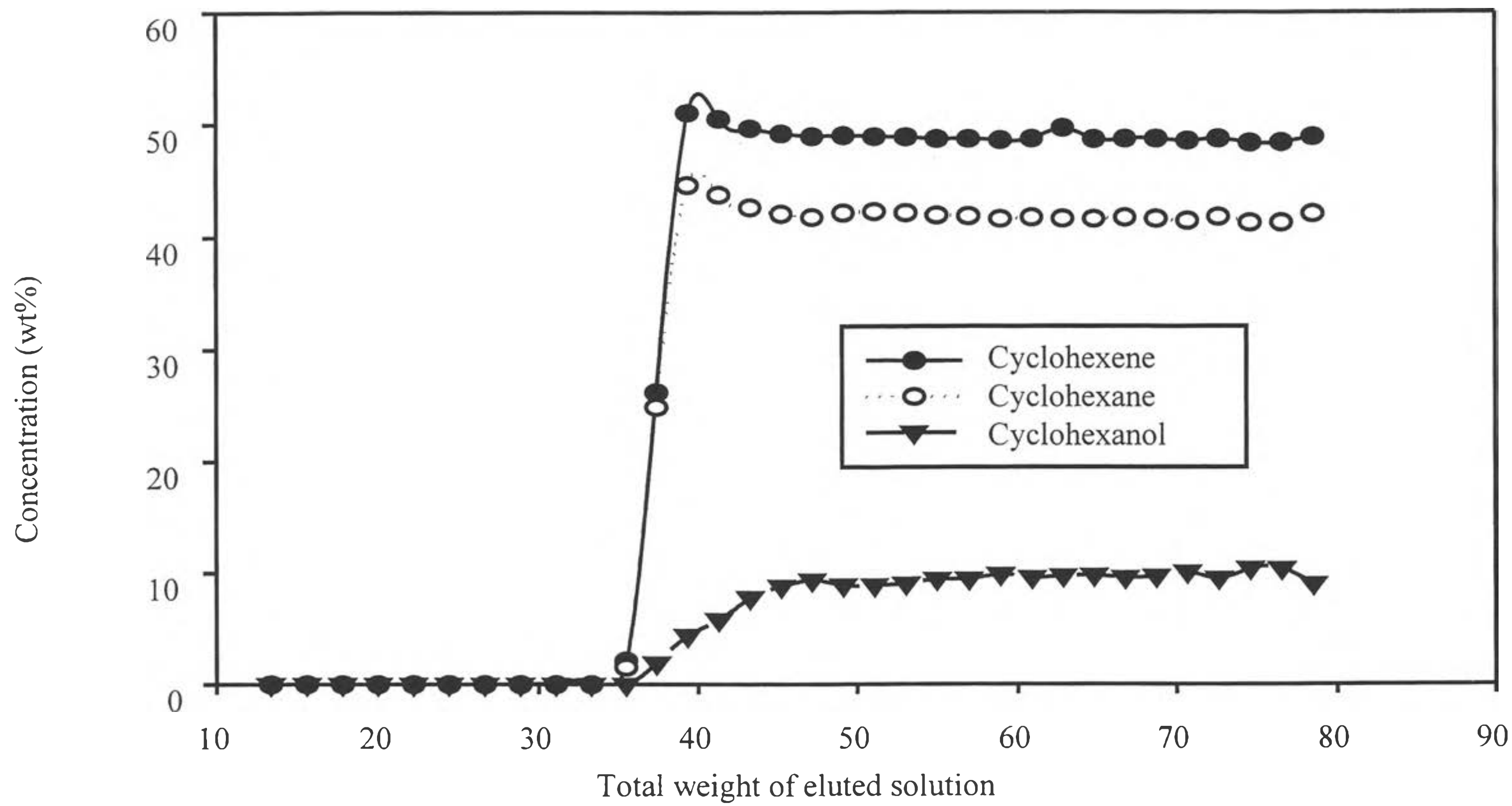

Figure A.3 The equilibrium adsorption of cyclohexene and cyclohexanol on Amberlyst-15 using cyclohexene as a tracer at 120 °C

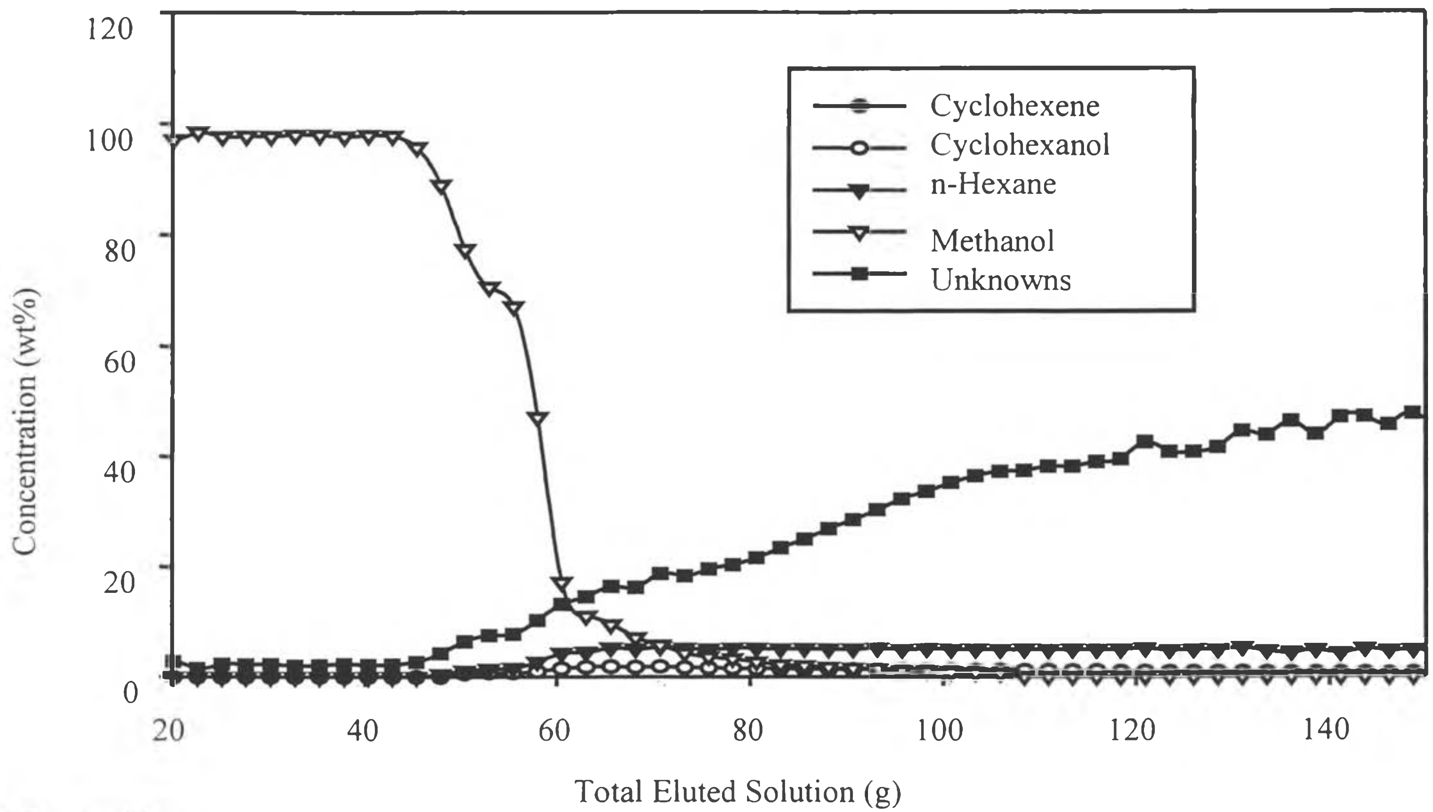

Figure A.4 The equilibrium adsorption of cyclohexene, cyclohexanol, and n-hexane on Amberlyst-15 in the chromatographic reactor using methanol as desorbent

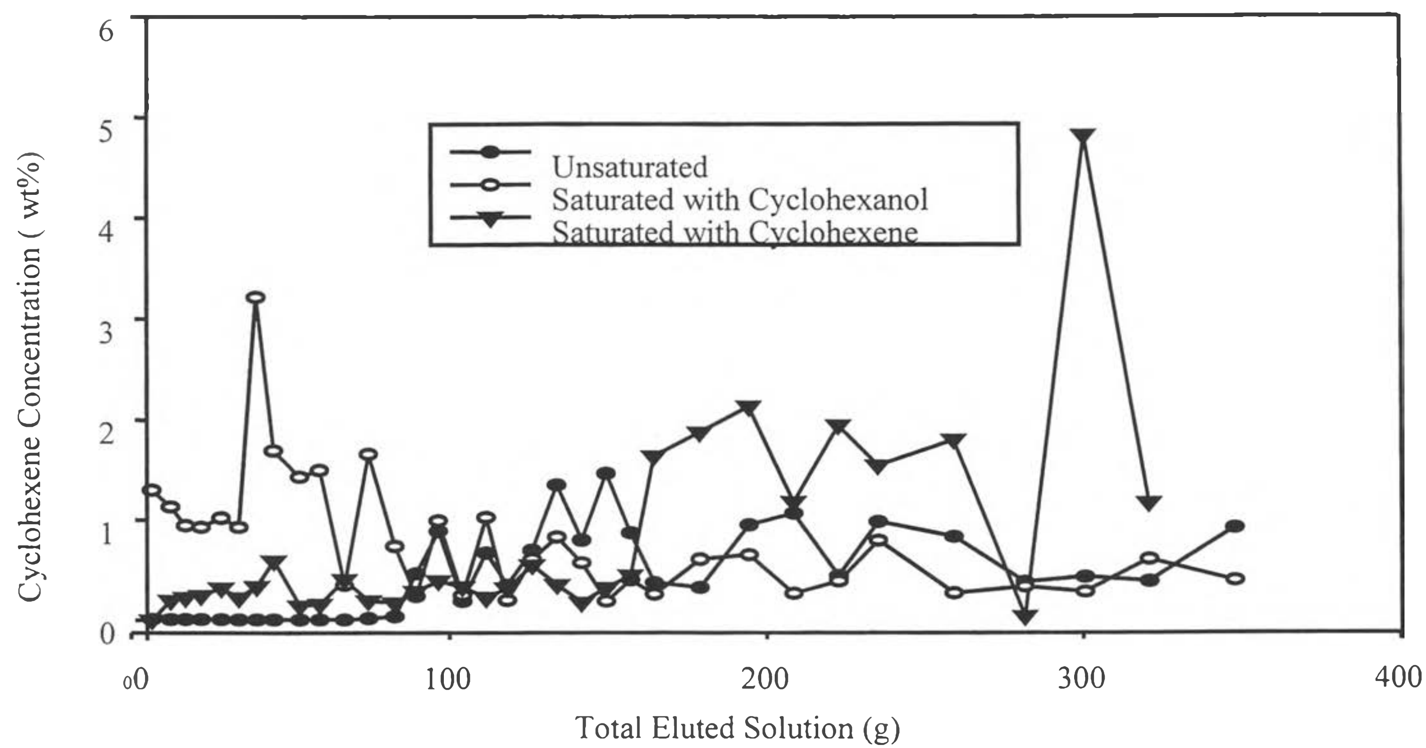

Figure A.5 The effect of cyclohexene and cyclohexanol loaded on Amberkyst-15 on the cyclohexene hydration in the chromatographic reactor

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