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R-2704

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MASTER

Separation of Water-Ethanol
Mixtures by Sorption,
Part 2

R. W. Hone
M. Lamarchand
W. Malaty

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CHEMICAL TECHNOLOGY DIVISION

SEPARATION OF WATER-ETHANOL MIXTURES BY SORPTION, PART 2

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ABSTRACT

As an alternative to distillation for concentrating fuel-grade ethanol from dilute aqueous solutions, adsorption from solutions at room temperature was studied using two sorbents: a Rohm and Haas copolymer resin (Amberlite XAD-4) and a proprietary molecular sieve. Both adsorption and desorption (in the latter case with N_2) were performed in a packed column. Breakthrough-curve analysis indicated that the adsorption capacities matched expectation at the higher flow rates (0.13 g EtOH/g XAD-4 and 0.1 g EtOH/g molecular sieve). The elution performance was disappointing in that the ethanol passed through a maximum concentration of only 43 wt % ethanol for XAD-4, and 65 wt % for the molecular sieve. Based on the low ethanol concentrations in the liquid condensed from the eluate, it was concluded that there was significant water adsorption on both sorbents and that the feasibility of the process is severely compromised by this fact.

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1. SUMMARY

As a part of the search for new fuels and fuel sources, ethanol is used in gasohol and is being proposed as a fuel in its own right. The ethanol is produced by fermentation of waste biomass and thus can be expected to produce 10% aqueous ethanol solutions. Several processes have been proposed for concentration of the solution to fuel grade (~99 wt %). Currently, distillation, which is costly and energy-intensive, is the most-often-used process.

A previous study investigated the equilibrium adsorption of ethanol from water by two sorbents: a Rohm and Haas copolymer (Amberlite XAD-4) and a proprietary molecular sieve (8). It was found that there was significant adsorption of ethanol in both materials, although the XAD-4 was probably preferable. This project tested the feasibility of a continuous separation of ethanol from water using these sorbents in a packed column.

A 10 wt % aqueous ethanol feed solution was pumped into a 25-cm-long, 1.9-cm-diam glass column packed with sorbent. A refractometer in the exit stream was used to monitor ethanol concentration, from which breakthrough curves were generated. Based on theoretical considerations and the equilibrium information gathered in a previous study, an ethanol loading of 0.13 g/g Amberlite resin and 0.08 g/g molecular sieve were anticipated. Experimental results for the former case varied from 0.13 to 0.09 g/g, depending on superficial velocity of the feed mixture. The molecular sieve yielded 0.098 g ethanol adsorbed per gram of sorbent. The errors and uncertainties in the experiments are such that these data are credible.

After adsorption, the ethanol in the columns was desorbed with pre-heated nitrogen (75°C). The ethanol concentration in periodic samples of eluted vapor was obtained by analysis with a centrifugal fast analyzer (CFA). The ethanol concentration passed through a maximum (43% for the Rohm & Haas sorbent, 65% for the other) and then dropped below the feed concentration (10%). The average ethanol concentrations for the desorbed vapors are perhaps the best indication of feasibility of the process. The desorbate from the Rohm & Haas resin had an average concentration of 26 wt % ethanol, while the molecular sieve yielded an average ethanol concentration of 12 wt % at a much lower N₂ temperature (35°C). Since both of these sorbents can be assumed to have some affinity for water, it is concluded that both probably have insufficient selectivity for ethanol to make the proposed process feasible. However, there was some evidence that the desorption process was nonuniform and that the apparatus should be modified and the sorbents be retested.

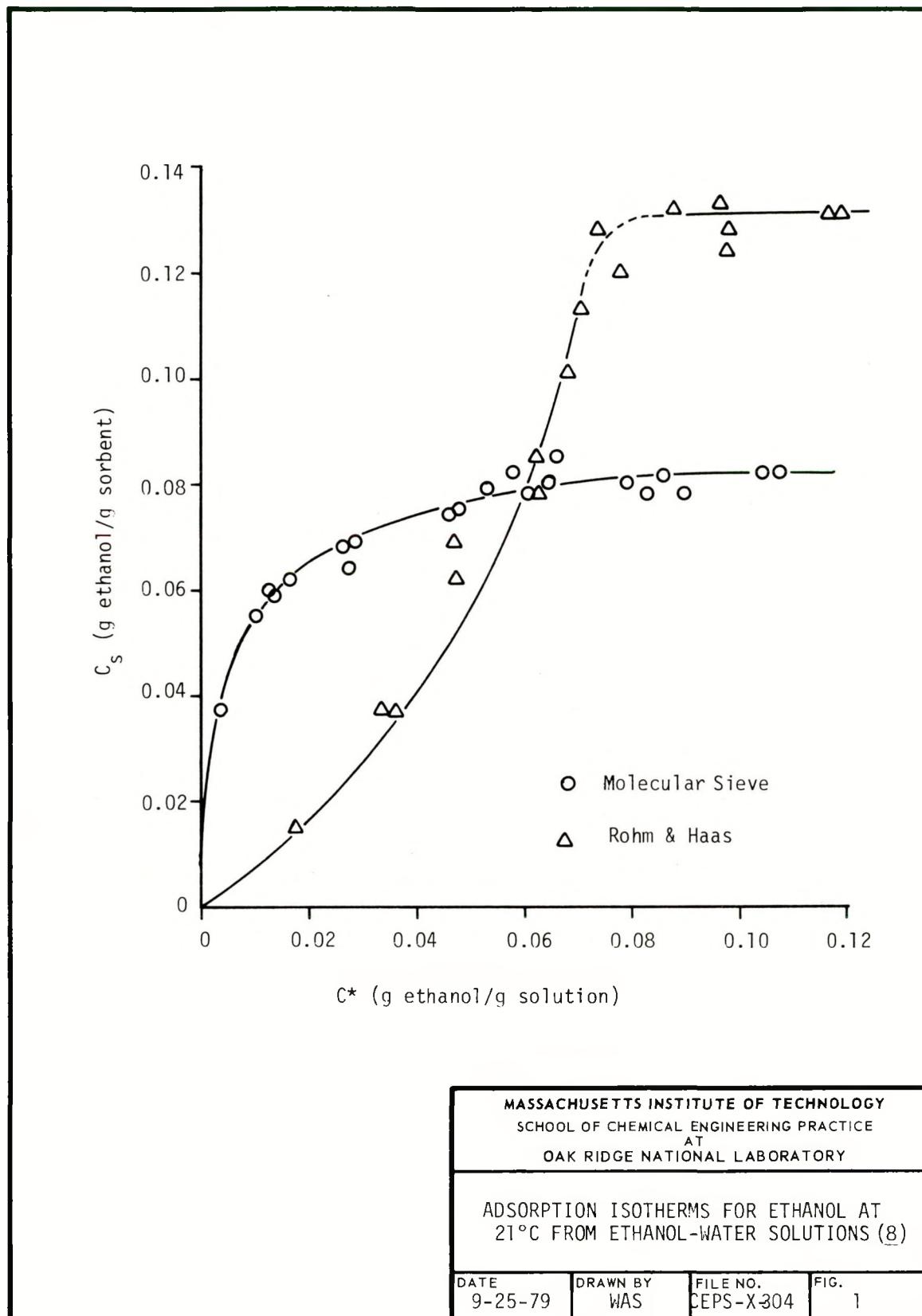
2. INTRODUCTION

2.1 Background

Recent proposals to reduce the consumption of gasoline in the U.S. include the use of gasohol (90 vol % gasoline, 10 vol % ethanol). The ethanol required for this application must contain less than 1% water (9). Other techniques suggest that near-azeotropic ethanol (95 wt %) could be used as a fuel with minor modifications to existing engines (4). Whether ethanol can be economically produced depends on the optimization of each step in the production process. Currently, most of the ethanol is produced by fermentation, which optimally yields a mixture of 90% water, 10% ethanol. Economics dictates that a low-cost material be used as a feed stock to fermentation. Rosen (7) describes a Danish plant in which molasses is used as the feed. Conventional separation of this mixture by distillation is particularly energy-intensive because of the water-ethanol azeotrope that forms at 95% ethanol and 1 atm. Conventional processes for breaking the azeotrope and recovering anhydrous ethanol are described by Robinson and Gilliland (6).

The cost of the purification steps has a significant effect on the ultimate cost of the fuel-grade ethanol. Therefore, it is of interest to determine whether a process in which the selective adsorption of ethanol from a typical effluent from a biomass fermentation followed by a desorption cycle is technologically feasible. Schumacher and Hwa (8) investigated sorption as a means of purifying ethanol. Adsorption isotherms (Fig. 1) were obtained at room temperature for two hydrophobic sorbents: a high-surface-area Rohm & Haas styrene-divinylbenzene copolymer (Amberlite XAD-4) and a hydrophobic molecular sieve. Both sorbents reached equilibrium with a range of ethanol concentrations (0 - 12 wt %), and, as Fig. 1 shows, greater adsorption was observed for the Rohm & Haas material at higher ethanol concentrations. The method by which the isotherms were calculated involved a material balance on ethanol alone. Limitations in the experimental procedure prevented accounting for water. Although the reported hydrophobic nature of the sorbents may have justified this assumption, substantiation of that premise was required by an alternative experimental procedure.

The objective of this study was to investigate the feasibility of a bench-scale continuous adsorption process and to infer the accuracy of the isotherms reported previously. A process was carried out in a cyclically operated packed column in which the ethanol was selectively adsorbed and then recovered by desorption as an eluted vapor in preheated nitrogen carrier gas. Questions of rate of adsorption and desorption as well as product purity were answered by this study.



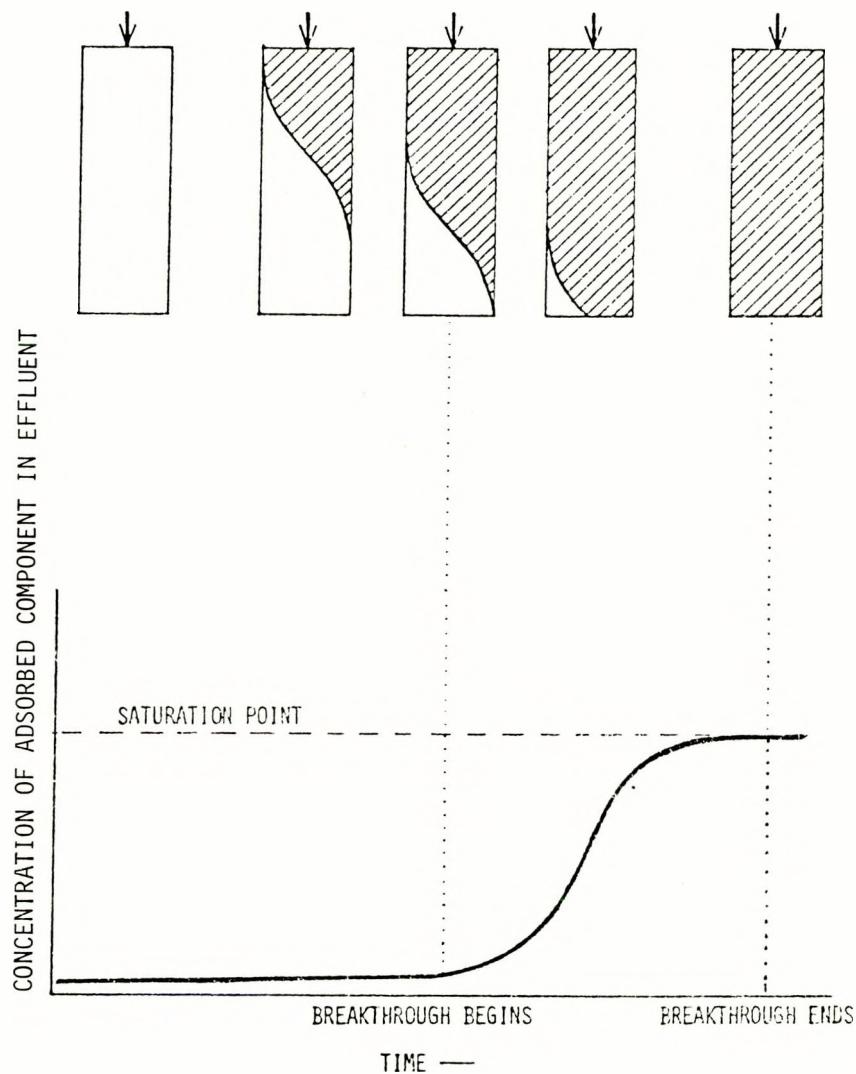
2.2 Column Sorption Theory

When a solution passes over particles in a packed bed, certain materials can adsorb some species preferably to others. This property can be used as the basis for a unit operation. If the selectivity for one of the species is strong, it will be essentially removed from the solution which is passing over the solid. This condition will continue until the solid becomes saturated, at which point the concentration of the solution exiting the bed is unchanged by its passage through the bed. The concentration-vs-time curve at the column exit for the adsorbed material is the breakthrough curve. A typical example is shown in Fig. 2. Before the leading edge of the front exits the bed, the concentration of adsorbable component in the effluent is the equilibrium value corresponding to the amount of component adsorbed on the saturated packing. Once this front reaches the bed exit, breakthrough is attained and the solute concentration rises to yield the breakthrough curve. The trailing edge of the front exits when the bed is saturated and the effluent composition is equal to that of the feed. The breakthrough curves are generally S-shaped, but their steepness and symmetry are influenced by a number of factors including sorption mechanisms and rates, sorption equilibria, fluid velocities, dispersion effects, and feed composition.

The adsorbed mixture is recovered by introducing an eluant into the column to shift sorption equilibrium. The eluant should either be an acceptable medium for containing the desorbed species or should be easily separable from them. In our system, preheated nitrogen gas served as a carrier while elevation of the temperature was used to shift the isotherm and cause desorption. A typical elution curve is shown in Fig. 3. The concentration of desorbed species passes through a maximum because the void spaces in the bed are initially filled with liquid from the previous adsorption step. A detailed analysis of adsorption and desorption is presented in Treybal (10).

2.3 Approach

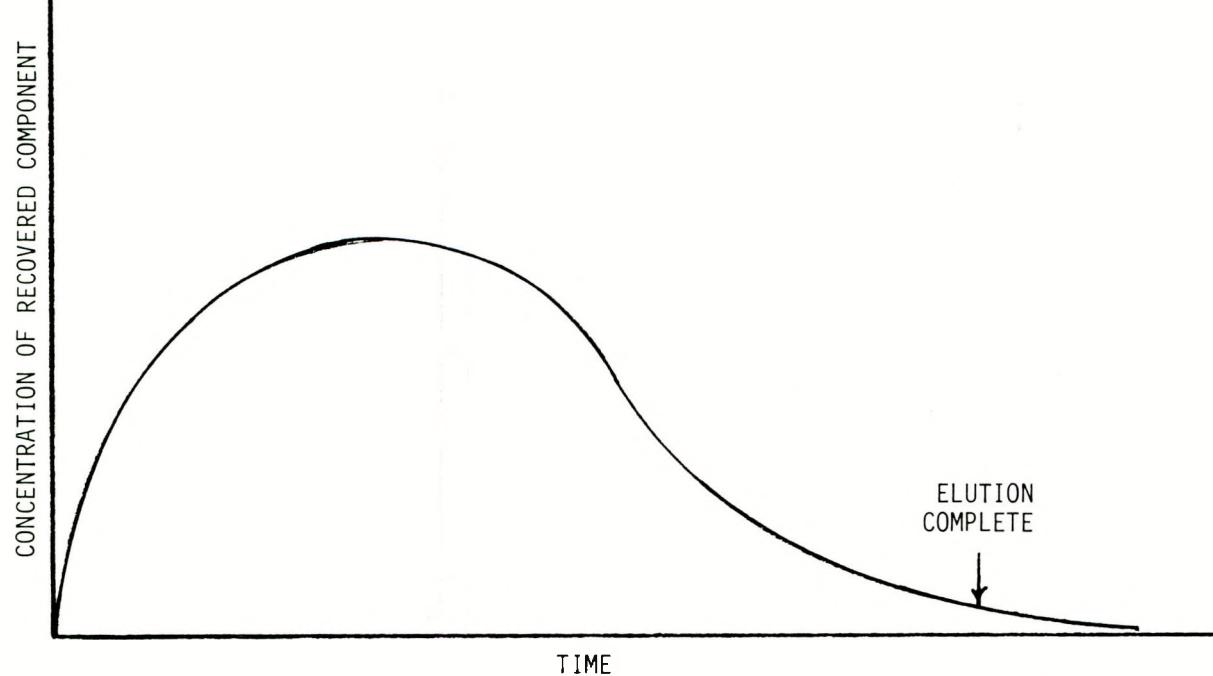
Adsorption and desorption experiments were conducted in separate columns, each packed with the Rohm & Haas or molecular sieve. The adsorption runs were designed to obtain breakthrough curves and to characterize their shape with respect to flow rate. The desorption steps were carried out with preheated nitrogen (75°C). The effect of gas temperature on elution curves was examined and provided a basis for evaluating the feasibility of the continuous adsorption-desorption process.



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MASS TRANSFER AND BREAKTHROUGH
IN ADSORPTION COLUMNS

DATE 11-24-79	DRAWN BY ML	FILE NO. CEPS-X-304	FIG. 2
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TYPICAL ELUTION CURVE

DATE 11-24-79	DRAWN BY ML	FILE NO. CEPS-X-304	FIG. 3
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3. APPARATUS AND PROCEDURE

3.1 Adsorption

The apparatus for the adsorption experiments is shown in Fig. 4. A piston pump with variable flow rate (0 - 180 cm³/h) was used to feed the adsorption column. The column was a 25-cm-long, 1.90-cm-ID, jacketed glass column packed with sorbent. Two pieces of hydrophilic porous Teflon frit (1.35- μ pore diameter), placed at the ends of the column, held the sorbent and also filtered the solution. The outlet stream was continuously analyzed by a refractometer which monitored the refractive index against a pure-water baseline.

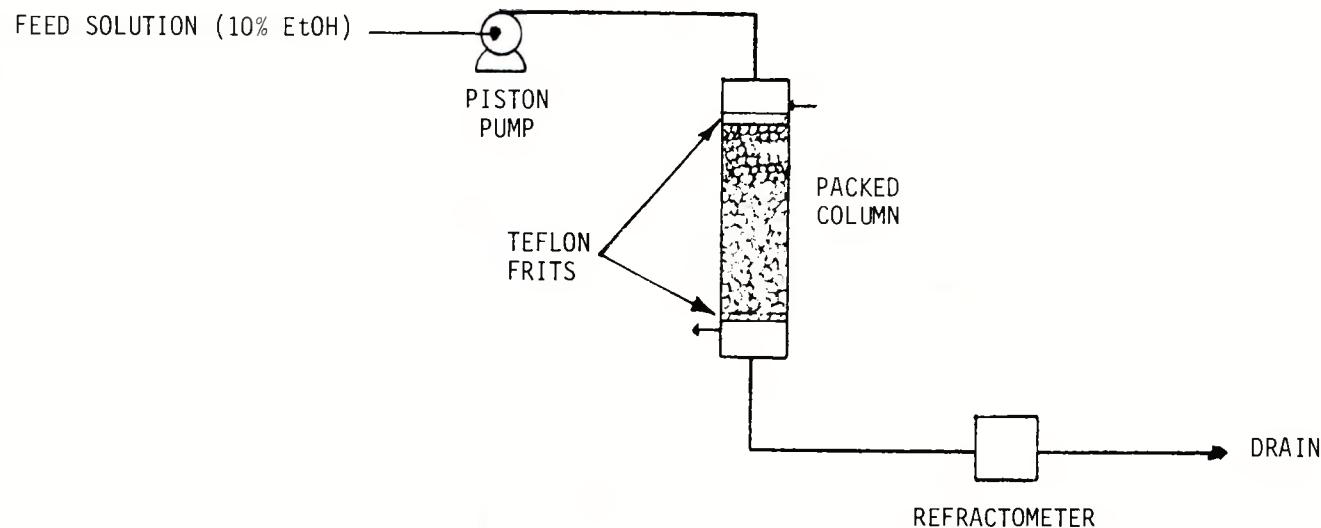
After drying and desorption, the entire apparatus was flushed with distilled water, which entered at the base of the column. Ethanol-water solution was then fed to the top of the column at a known flow rate. When the column appeared to be saturated, the feed solution was pumped directly to the refractometer to compare results for the effluent and the feed. For the molecular sieve an extra filter was used at the bottom of the column to remove fines from the solution attributable to sorbent abrasion under flow conditions.

3.2 Desorption

For the desorption experiment, two types of apparatus were successively used. In the original apparatus (Fig. 5), cool nitrogen (21°C) was heated to 35°C by passage through a hot-water bath and was further heated in the column by circulation of a 25% ethyleneglycol-water mixture through the jacket. The material desorbed from the packed sorbent was condensed in two acetone--dry-ice cold traps.

Cold-trap plugging and radial temperature gradients prevented efficient operation of the original apparatus. In the modified apparatus (Fig. 6), the temperature gradient was reduced by using a furnace to provide heated nitrogen to the column. At the exit of the column a chilled-water condenser was used to recover the desorbed material from the stripping gas. The condensed liquid was recovered in a burette which allowed sampling and monitoring of recovery rate. Finally, the residual material in the gas was recovered in an ice-water cold-trap followed by an acetone--dry-ice cold trap.

After adsorption the column was first flushed with cool nitrogen (21°C) and then dried for a variable time. The column was then heated to 75°C, and hot nitrogen (75°C) was used to desorb the ethanol-water mixture as a vapor. The condensate was removed from the burette at 10-min intervals, and concentrations were determined with a centrifugal fast analyzer (8). When no further condensate accumulated, the desorption was discontinued, and material in the cold trap was weighed and analyzed.

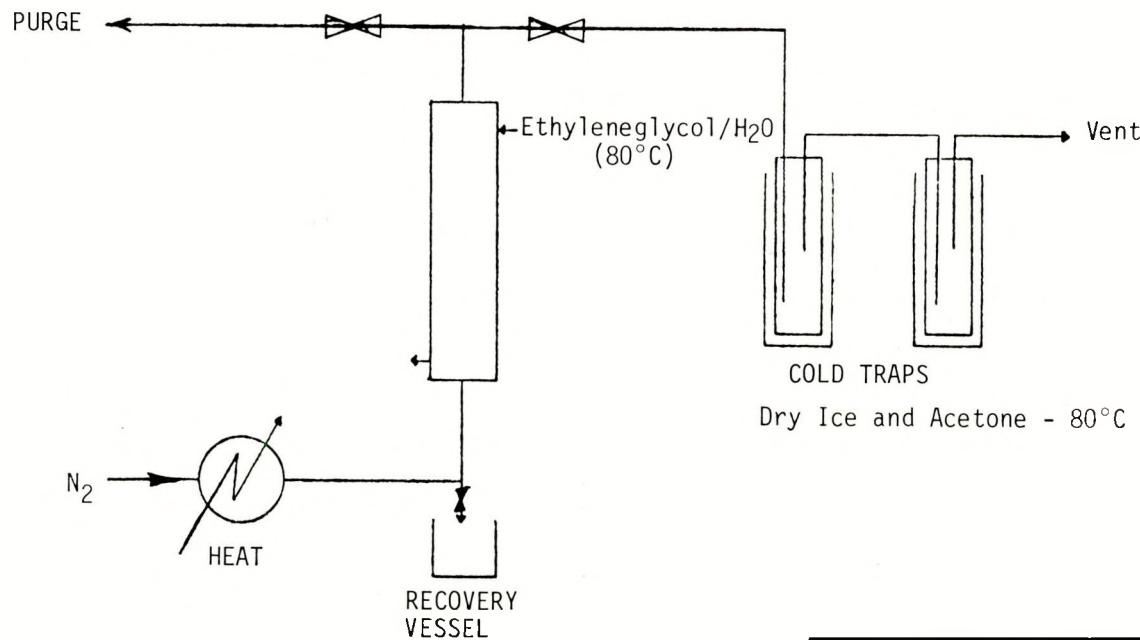


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ADSORPTION APPARATUS

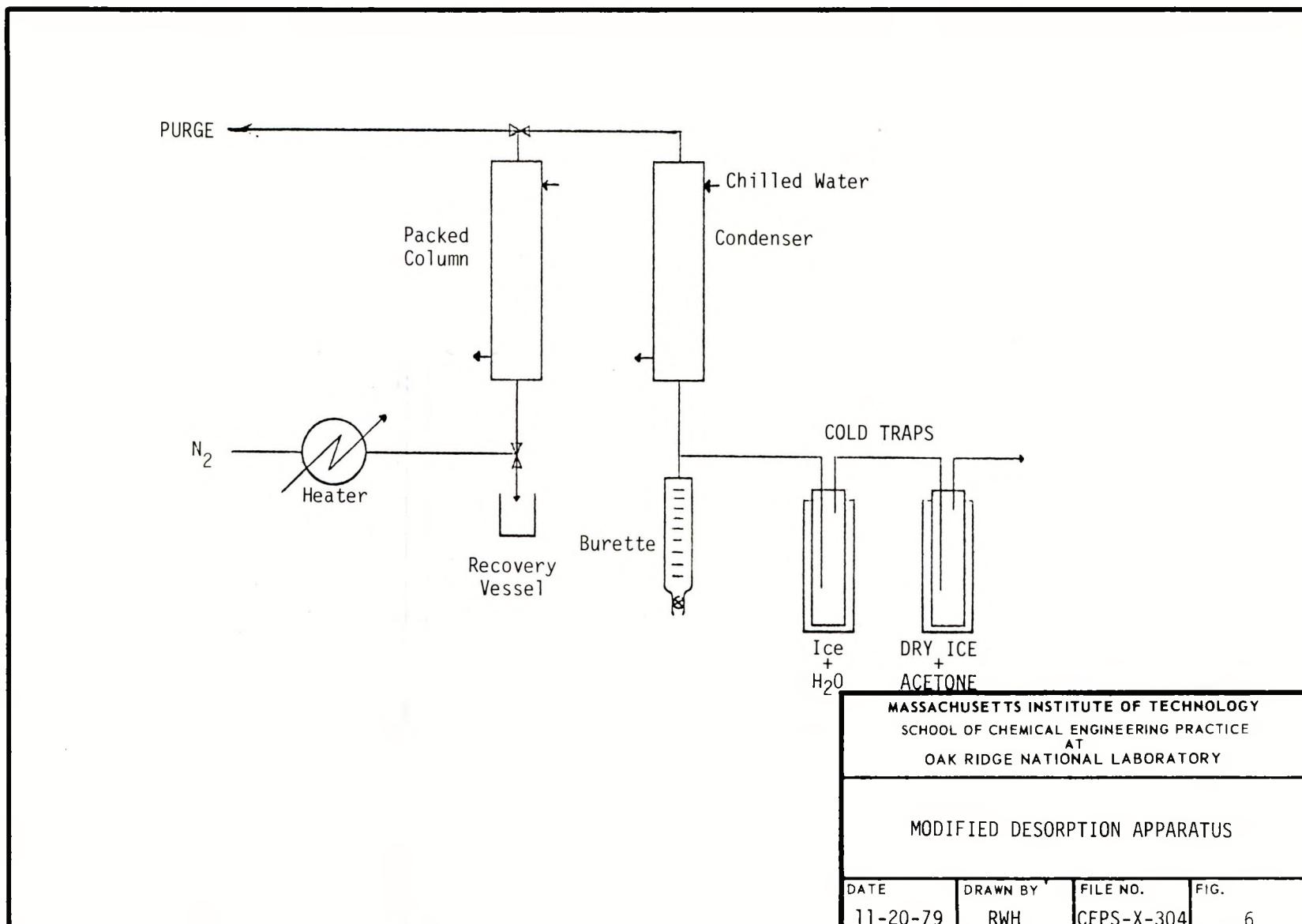
DATE 11-24-79	DRAWN BY ML	FILE NO. CEPS-X-304	FIG. 4
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ORIGINAL DESORPTION APPARATUS

DATE 11-24-79	DRAWN BY ML	FILE NO. CEPS-X-304	FIG. 5
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4. RESULTS AND DISCUSSION

4.1 Adsorption

4.1.1 Rohm & Haas Amberlite XAD-4 Resin

4.1.1.1 Breakthrough Curves. Breakthrough curves (Fig. 7) were obtained for superficial velocities of 0.77 and 1.12 cm/min. In both cases the slope appeared to be steep, which suggested a fast approach to sorption equilibrium. As the flow rate increased, the breakthrough curve became shallower, which may be explained by the increase of the mass-transfer limitation and possibly by increased axial dispersion.

The order of breakthrough was opposite to expectation. That is to say, the lower rate should be seen in the neighborhood of 180 ml cumulative volume. The most likely explanation for this is the possibility that complete desorption was not achieved on the previous run.

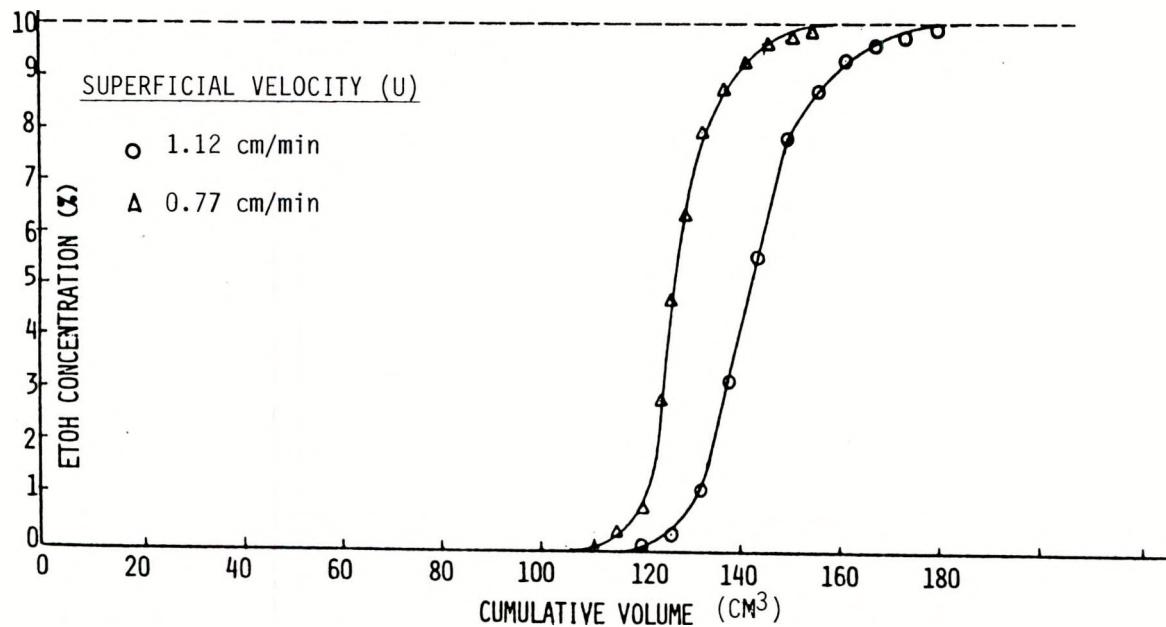
4.1.1.2 Weight of Adsorbed Ethanol. The weight of ethanol adsorbed was calculated by graphically integrating the difference between the solvent-front and the breakthrough curves (10). The solvent-front curve was a representation of the pumped volume needed for the solution to go through the column; it may be taken as the column holdup. The results of this integration are given in Table 1 in terms of g EtOH/g sorbent. Since the adsorption capacity of the sorbent is independent of the flow rate, the results should be constant. A comparison of these results with the theoretical value obtained from the isotherms suggests that the result of the first breakthrough curve is valid. The difference between the two curves may have arisen from a poor desorption of the packing material before adsorption, which would decrease the area of sorbent available for adsorption.

4.1.2 Molecular Sieve

4.1.2.1 Breakthrough Curve. One breakthrough curve (Fig. 8) was obtained for the molecular sieve at a flow rate of 1.12 cm/min. The steep slope of this curve again suggests a very fast equilibrium and reduced axial dispersion.

4.1.2.2 Weight of Adsorbed Ethanol. A comparison of the experimental and theoretical values showed a difference of 20% (Table 1), which may have been caused by experimental errors and incomplete desorption after the preceding experiment.

4.1.2.3 Comparison of the Two Sorbents. A comparison of Figs. 7 and 8 clearly indicates that the molecular sieve has a closer-to-ideal curve than does the Rohm & Haas resin. This much steeper curve might be attributable to a number of factors such as faster equilibration, less dispersion, and better mass transfer. Further study would be needed to elucidate the reasons for the differences. Since at least at high flow rates, both



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BREAKTHROUGH CURVES FOR ETHANOL
ON AMBERLITE XAD-4 RESIN

DATE 11-24-79	DRAWN BY WM	FILE NO. CEPS-X-304	FIG. 7
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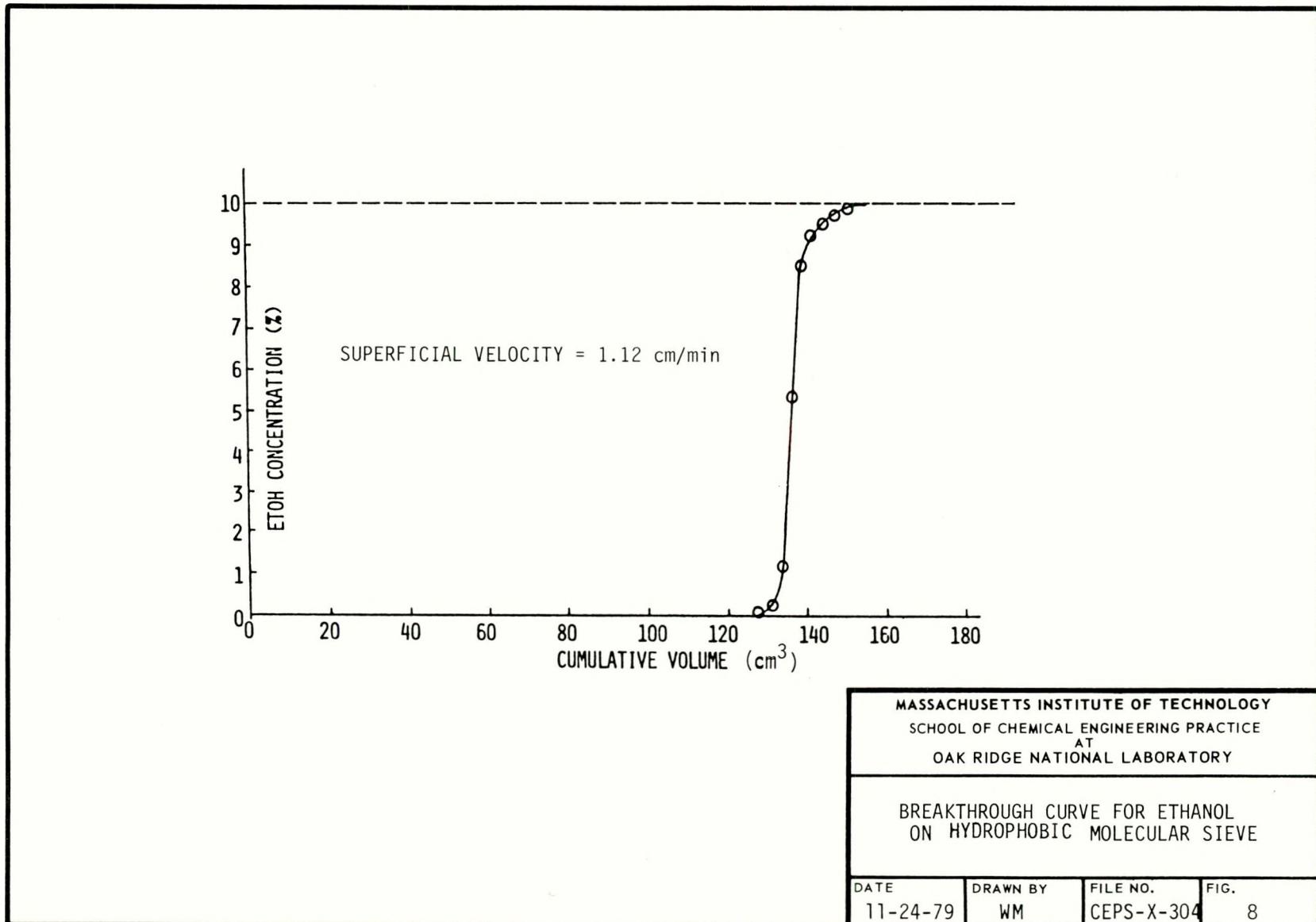


Table 1. Ethanol Loadings on Amberlite XAD-4 and Molecular Sieve Sorbents

<u>Sorbent</u>	<u>Superficial Velocity (cm/min)</u>	<u>Weight of Sorbent in Column (g)</u>	<u>Loading of EtOH in Column</u>		
			<u>Calculated from Isotherms (8) (g EtOH/g Sorbent)</u>	<u>Experimental (g EtOH/g Sorbent)</u>	<u>Difference (%)</u>
Amberlite XAD-4 Resin	1.12	35	0.13	0.126	3.0
Amberlite XAD-4 Resin	0.77	35	0.13	0.088	32.3
Molecular Sieve	1.12	40	0.08	0.098	19.0

sorbents showed good agreement with the calculated adsorption, credence is lent to the equilibrium data of the previous workers (8).

Important differences exist between the calculated adsorption and experimentally realized results. As may be seen from Table 1, the lower-flow-rate run with the Amberlite resin is at variance with theory by 32.3%. Experimental error can explain only a small part of this result. If we take the high-flow-rate run with this resin, long-term desorption had preceded that run. This was not the case with the second run. It is suspected that complete elution had not been achieved prior to the second run. On the other hand, the molecular sieve appeared to adsorb more ethanol than would have been predicted by theoretical calculation. More data would be required on both sorbents before a convincing argument could be made for the causes of the discrepancies.

4.2 Desorption

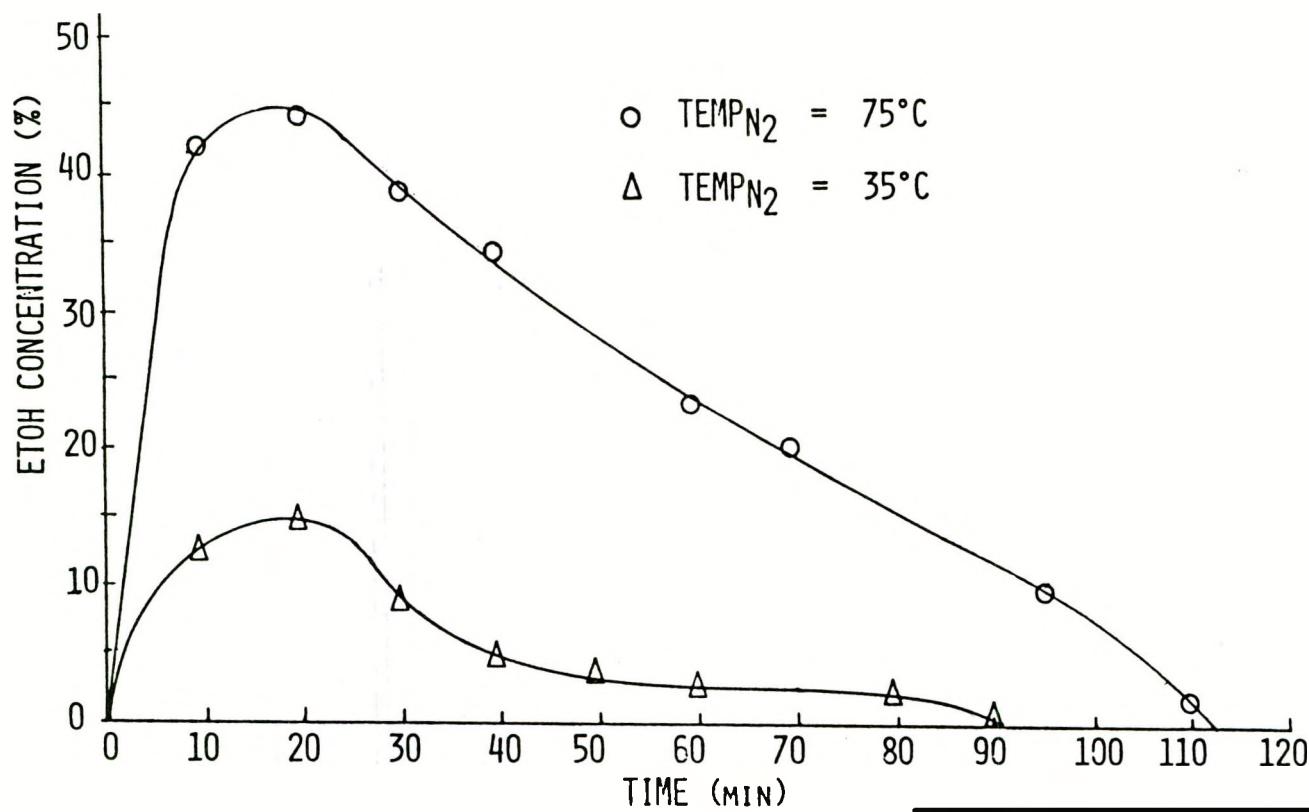
4.2.1 Rohm & Haas Amberlite XAD-4 Resin

Figure 9 shows the desorption results for the Rohm & Haas resin at 35 and 75°C. They are both typical elution curves and go through a maximum as predicted theoretically. Physically, this is due to the initial vaporization of the liquid in the void spaces of the packed column, which has a lower ethanol concentration than the adsorbed liquid. It is interesting to note the effect of temperature on the desorption curves. The curve at 75°C has a higher maximum and generally shows higher ethanol concentrations than the one at 35°C. This result implies that at the higher temperature the equilibrium strongly favors the desorption of the ethanol from the resin. At lower temperatures the primary thrust is probably the removal of physically held liquid from the pores and interstices. The obvious conclusion here is that desorption should be examined more closely at higher temperatures.

A detailed mass balance on the adsorption-desorption (at the higher temperature) process showed a column loading of 2.67 g adsorbed ethanol and an average ethanol concentration in the desorbed liquid of 26.2% (see Appendix 9.3 for calculations). The mass balance closes within 3.6%, which is within experimental error.

4.2.2 Molecular Sieve

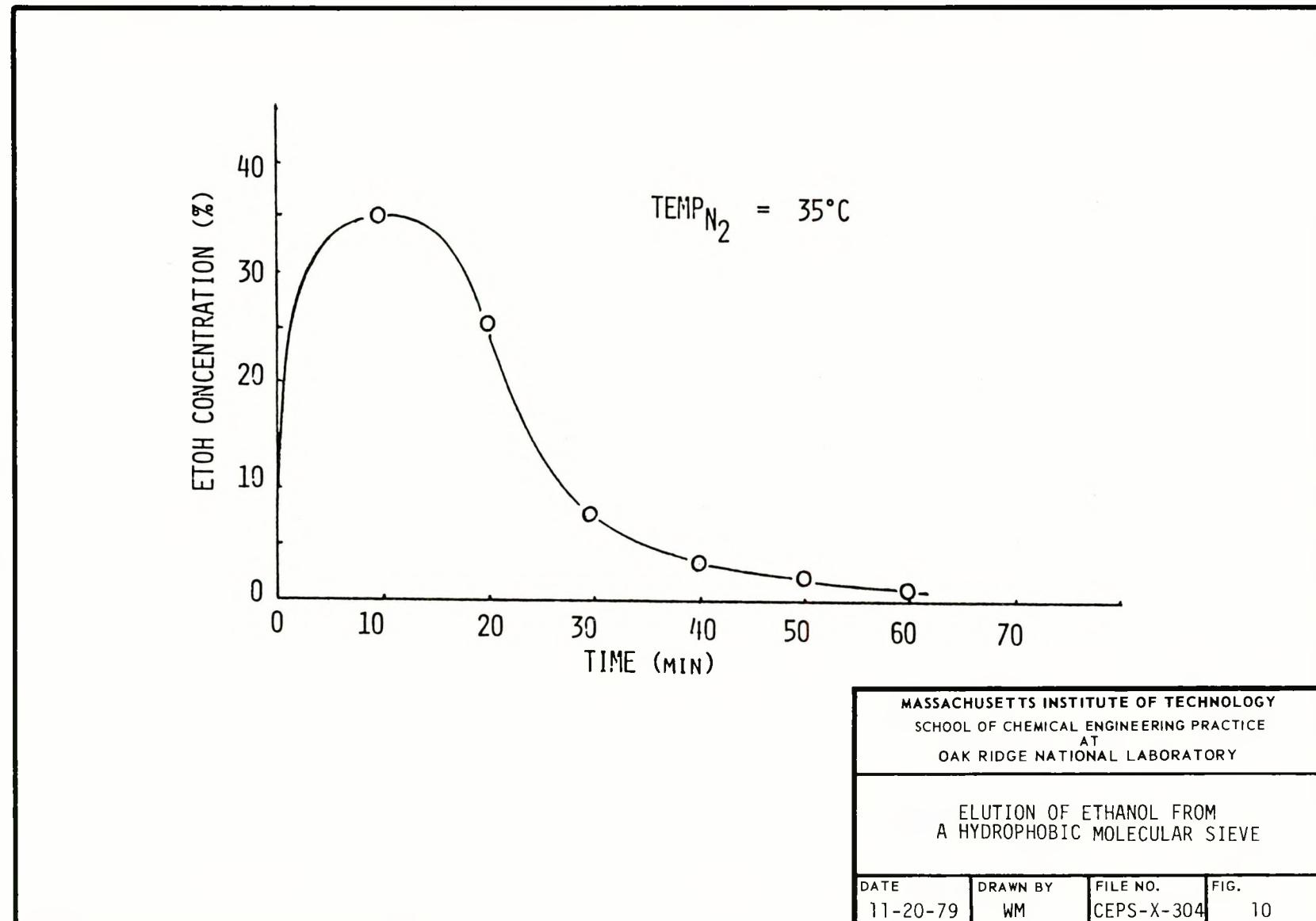
Figure 10 shows the desorption result for the molecular sieve at 35°C. This elution curve also follows the typical behavior of going through a maximum. Difficulties with the desorption apparatus prevented the development of a full desorption curve at the higher temperature (75°C). However, the three points that were obtained showed the same trend as the previous result: the concentration was high at early times and trailed off later. The higher nitrogen temperature yielded ethanol concentrations as high as 66%, contrasted to a corresponding 35% for the lower temperature. This further substantiates the conclusion that desorption is more efficient at higher temperature.



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ELUTION OF ETHANOL
FROM AMBERLITE XAD-4 RESIN

DATE 11-20-79	DRAWN BY ML	FILE NO. CEPS-X-304	FIG. 9
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The mass balance for the molecular sieve showed a column loading of 2.7 g ethanol for the low-temperature desorption and an average ethanol concentration in the desorbate of 12.7%. It is reasonable to believe that the high-temperature result would yield a substantially higher ethanol concentration.

4.2.3 Comparison of XAD-4 and Molecular Sieve

Both of the two sorbents showed similar desorption features. The desorption curves both went through a maximum, as expected, and were more favorable at higher N₂ temperatures. Of particular importance is the observation that for both sorbents, the desorbed ethanol concentration at late times was lower than the feed concentration of 10%. This suggests that water as well as ethanol has been sorbed.

By comparing the amount of ethanol recovered by desorption with that adsorbed from the feed solution, the amount of nonadsorbed ethanol recovered in the desorption products was determined to be 0.67 g. The holdup material had a concentration of 10% EtOH; water held up in the column was 6.03 g. Therefore, in terms of column-to-resin loading, the physically held water amounted to 0.172 g/g Amberlite XAD-4 resin. Based on this premise and the fact that the total water removed from the bed during desorption was known to be 7.60 g, the total water adsorbed on the Amberlite resin was 1.57 g or 0.0045 g of water/g resin. Therefore, one of the major problems with the adsorption scheme which is proposed is the physical holdup of solution in the resin. Without any holdup, one could expect a 56 wt % ethanol concentration at exit. This is not attractive from the viewpoint of the energy industries.

Preliminary elution data on the molecular sieve at 75°C indicates that it is possible to increase the ethanol concentration to 65.9% at maximum, while the Amberlite was capable of only 44.8%. This indicates that there is some reason for pursuing this matter further.

4.2.4 Possible Contribution to Calculational Errors

Two areas of calculations were susceptible to error. The breakthrough-curve representations did not include the intermittent "noise" observed in the original breakthrough. This noise was omitted because it was caused by air bubbles and thus was felt to have no significance to the adsorption process.

The second area of possible error was the calculation of the column holdup volume. This volume was obtained by draining a full column and measuring the volume of fluid gathered. It is possible that liquid was held up in the column after draining and this would have two effects: (1) increase the calculated value of the ethanol adsorbed by increasing the area between the column holdup line and the breakthrough, and (2) increase the desorption product volume while diluting the product.

In the present apparatus, the desorption was not uniform over the length of the column. This may have led to a depression of the ethanol concentration maximums by dilution with held-up solution. A modification to provide a more uniform desorption is shown in Fig. 11. The distribution will provide a rapid access of the entire bed to the hot nitrogen and possibly more accurate results.

5. CONCLUSIONS

The following conclusions were reached:

1. The molecular sieve appears to be a more promising sorbent than the Rohm & Haas resin. It reached equilibrium faster and yielded purer ethanol.
2. Adsorption is not specific for either sorbent; water as well as ethanol is sorbed onto the surface.
3. For the sorbents studied, a separation process using adsorption does not appear very workable.

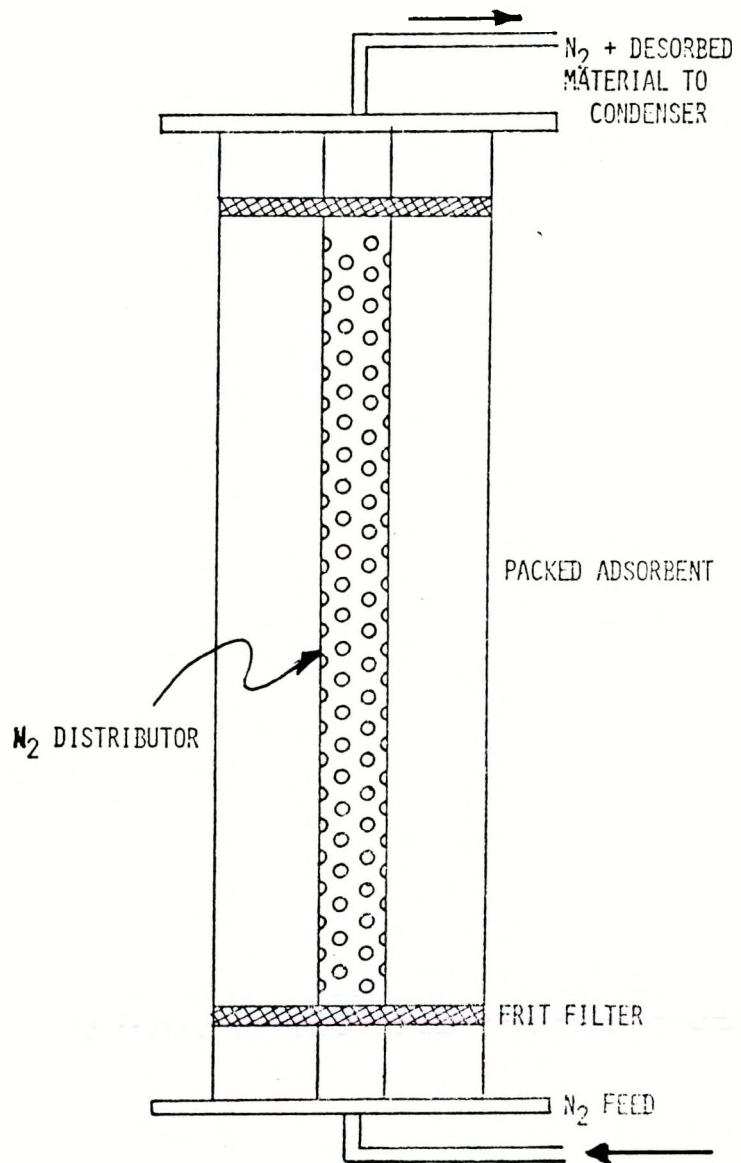
6. RECOMMENDATIONS

The results suggest the following recommendations:

1. Further study of molecular sieves requires the use of a stronger material that does not erode under flow conditions.
2. The desorption step should be studied carefully. This requires setting up a new apparatus to provide more-uniform desorption.
3. Other hydrophobic sorbents should be examined for the water-ethanol separation.

7. ACKNOWLEDGMENTS

We wish to thank W.W. Pitt and J.E. Mrochek for their guidance. Special thanks are due M.S. Denton for his helpful suggestions and good humor, and to J.B. Overton for his valuable aid through the experimental work.



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PROPOSED MODIFICATION
TO THE DESORPTION COLUMN

DATE 11-20-79	DRAWN BY ML	FILE NO. CEPS-X-304	FIG. 11
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8. APPENDIX

8.1 Physical Properties of Rohm & Haas XAD-4 Resin

The following physical properties of the Rohm & Haas copolymer (Amberlite XAD-4) were provided by the vendor:

appearance	hard, hydrated, opaque beads
average particle diameter	0.30 to 0.45 mm
true wet density in distilled water	1.02 g/ml
bulk density	44 lb/ft ³
porosity of dry beads	0.50
surface area	725 m^2/g
average pore diameter	40 \AA

8.2 Sample Calculations

8.2.1 Maximum Theoretical EtOH Adsorption

A widely accepted method of determining the volume of a monolayer on the surface of a porous particle is:

$$S_g = \left(\frac{V_m N_0 \rho}{M} \right) \alpha \quad \text{or} \quad V_m = \frac{M S_g}{N_0 \rho \alpha}$$

$$\alpha = 1.09 \left(\frac{M}{N_0 \rho} \right)^{2/3}$$

where

$$M = \text{molecular weight} = 46 \text{ g/mol}$$

$$\rho = \text{density} = 0.8 \text{ g/cm}^3$$

$$N_0 = \text{Avogadro's number} = 6.02 \times 10^{23} \text{ mol}^{-1}$$

$$\alpha = 1.09 \left[\frac{46}{(6.02 \times 10^{23})(0.8)} \right]^{2/3} = 2.28 \times 10^{-15} \text{ cm}^2/\text{molecule}$$

$$V_m = \frac{(46 \text{ g/mol})(7.0 \times 10^6 \text{ cm}^2/\text{g sorbent})}{(6.02 \times 10^{23} \frac{\text{mol}}{\text{mol}})(0.8 \frac{\text{g}}{\text{cm}^3})(2.28 \times 10^{-15} \text{ cm}^2/\text{molecule})}$$

$$= 0.293 \text{ cm}^3/\text{g sorbent} = 0.23 \text{ g EtOH/g sorbent}$$

8.2.2 Desorbed Ethanol

The following is a calculation of the amount of ethanol desorbed in the high flow-rate Amberlite run.

$$W_{\text{total}} = (\Sigma W_{\text{B.S.}}) + W_{\text{C.T.A.}} + W_{\text{C.T.B.}}$$

where

$W_{\text{B.S.}}$ = weight of ethanol in burette samples

$W_{\text{C.T.A.}}$ = weight of ethanol in cold trap A

$W_{\text{C.T.B.}}$ = weight of ethanol in cold trap B

Burette Samples

Sample No.	Time (min)	Volume (ml)	EtOH Concentration (g/ml)	$W_{\text{B.S.}}$ (g)
1	10	1.5	0.42	0.63
2	20	1.7	0.44	0.75
3	30	0.5	0.39	0.20
4	40	0.3	0.34	0.10
5	60	0.2	0.34	0.07
6	95	1.8	0.10	0.18
7	110	1.5	0.02	0.03
8	125	0.6	0.03	0.02
9	140	1.2	0.03	0.04
		9.3		$\Sigma W_{\text{B.S.}} = 2.02$

$$W_{\text{C.T.A.}} = (C_{\text{EtOH}})(V_{\text{C.T.A.}}) = (0.793 \text{ g/ml})(0.4 \text{ ml}) = 0.32$$

$$W_{\text{C.T.B.}} = (C_{\text{EtOH}})(V_{\text{C.T.B.}}) = (0.668 \text{ g/ml})(0.5 \text{ ml}) = 0.33$$

$$W_{\text{total}} = 2.02 + 0.32 + 0.33 = 2.67 \text{ g}$$

8.3 Mass Balance

The following is a material balance check on the Amberlite XAD-4 adsorption and desorption process (see Fig. 12).

$$\text{input} = \text{output} + \text{losses}$$

$$W_{\text{feed}} = W_{\text{analyzer}} + W_{\text{flushed}} + W_{\text{desorbed}} + W_{\text{vent}}$$

where

$$\begin{aligned} W_{\text{feed}} &= (173 \text{ ml})(0.10 \text{ ml EtOH/ml solution})(0.8 \text{ g/ml EtOH}) \\ &= 13.8 \text{ g} \end{aligned}$$

$$W_{\text{analyzer}} = (166 \text{ ml solution})(0.026 \text{ g EtOH/ml solution}) = 4.3 \text{ g}$$

$$W_{\text{flushed}} = (79 \text{ ml solution})(0.08 \text{ g EtOH/ml solution}) = 6.3 \text{ g}$$

$$W_{\text{desorbed}} = 2.7 \text{ g}$$

Therefore,

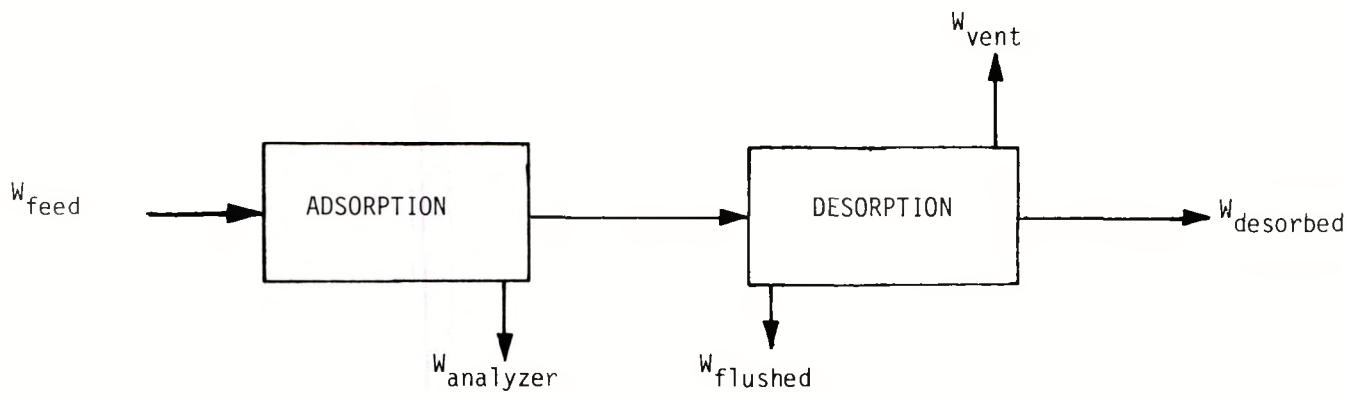
$$W_{\text{vent}} = 13.8 - (4.3 + 6.3 + 2.7) = 0.5 \text{ g}$$

$$\% \text{ loss} = 3.6$$

The material which is assumed to be vented (W_{vent}) accounts for the non-closure of the material balance and therefore is the loss.

8.4 Literature References

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MATERIAL BALANCE FLOW DIAGRAM FOR
AMBERLITE ADSORPTION-DESORPTION PROCESS

DATE 11-20-79	DRAWN BY LM	FILE NO. CEPS-X-304	FIG. 12
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