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Computer Simulation of the Dartmouth Process for Separation of Dilute Ethanol/Water Mixtures

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ABSTRACT

High energy costs are associated with the recovery of ethanol from fermentation broths. This paper discusses a computer simulation of the Dartmouth Process, which aims to reduce these costs by the use of IHOSR distillation, extensive heat integration, and extractive distillation using a salt.

To resolve the uncertainty in modeling alcohol-water-salt vapor-liquid equilibrium, a new and more accurate activity coefficient model was used. An Aspen™ model was used to generate capital and energy costs for a range of ethanol concentrations in the feed. Simulation results show that the Dartmouth Process offers substantial economic advantages over benzene azeotropic distillation, particularly at low feed concentrations.

Index Entries: Ethanol separation; activity; coefficients; computer simulation.

INTRODUCTION

The recovery of ethanol from fermentation broths is responsible for a significant portion of the cost, and often the largest share of the energy requirements for yeast-based ethanol production (*3,5,13*). For processes where substrate concentration, fermentor design, or limitations of the fer-

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mentation agent require lower ethanol concentrations than those that can be produced by yeast, the incentive to develop energy-efficient alcohol recovery technologies is particularly great. Thermophilic bacteria represent a prominent example of alcohol-producing organisms that have potential advantages in comparison to yeast (*6*), but produce ethanol at relatively low concentrations.

Lynd and Grethlein (*7*) previously reported an energy-efficient distillation technique that combined IHOSR distillation (*8*), extensive heat integration, and extractive distillation using potassium acetate. In the previous report, energy requirements were presented for the process, hereafter called the Dartmouth Process. The present computer simulation study reports capital and operating costs for the Dartmouth Process, and compares these with the corresponding costs for conventional azeotropic distillation with benzene. In addition, an improved configuration of the elements of the Dartmouth Process is presented. This improved configuration was designed to operate at or near the temperatures of a fermentation broth. This feature reduces or eliminates the need for preheating the feed, with corresponding steam savings. In addition, it makes the Dartmouth Process compatible with ethanol removal applications with recycle of viable cells to a continuous fermentor.

THE DARTMOUTH PROCESS

Figure 1 shows a flowsheet representation of the Dartmouth Process. The two distillation columns that comprise the IHOSR section (columns C1 and C2), can be conceptually treated as one single column; the dilute ethanol solution (stream 1) is fed at the same stage where a portion of the vapor stream is taken out (stream 3). This vapor stream is sent to a compressor (VB1), where it is converted into superheated vapor at a higher pressure; the superheated stream (number 16) is then condensed in the column reboiler R1, and returned as reflux to the top of column C2 (stream 17). This condensation provides a substantial portion of the heat required by the reboiler. The bottoms of the IHOSR column contains essentially pure water.

The vapor distillate of the IHOSR section is condensed and fed as a saturated liquid into the extractive column C3, operated at a higher pressure, where extractive distillation using potassium acetate takes place. Potassium acetate, a nonvolatile component, leaves with essentially water only at the bottoms of the column (stream 7). It is later concentrated in evaporator E1, and dried in drum dryer D1, to be recirculated in solution with ethanol as reflux (stream 14). The column overhead stream, containing 99% weight ethanol, is condensed to provide the evaporator heat duty and the remaining part of the IHOSR reboiler duty. Thus, the energy consumption of the process is essentially a result of the heat duty of the

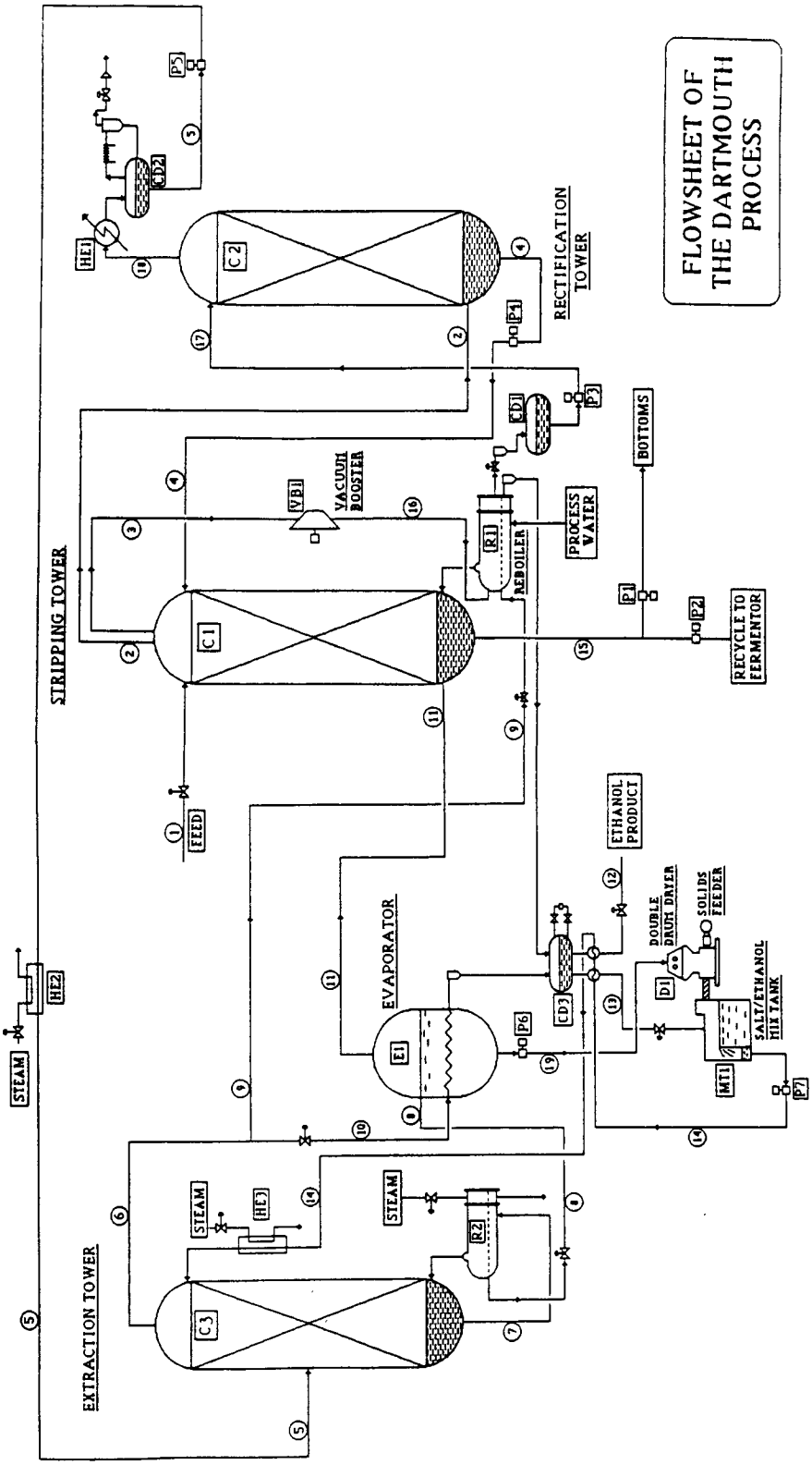

Fig. 1. Flowsheet representation of the Dartmouth Process.

extractive column reboiler R2 and the power requirements of the compressor VB1.

The configuration of the Dartmouth Process described above is an alternative to the previously presented version (*7*), in which the IHOSR column was operated at high pressure, using the heat of condensation of the vapor product to drive the extractive column.

Computer Simulation of the Dartmouth Process

A computer model to simulate the steady-state behavior of the Dartmouth Process was developed, with the following objectives: To facilitate the rapid estimation of equipment sizes and energy flows, for different feed concentrations, product qualities and ethanol production volumes; and to investigate the sensitivity of economic projections to ethanol concentration in the feed, assumed steam price and some economic parameters. The state-of-the-art flowsheet simulation package Aspen Plus™ (*2*) was chosen at simulation tool, because of its extensive simulation and costing capabilities.

The major source of uncertainty in the development of the computer model was the thermodynamic behavior of the ethanol-water-potassium acetate solutions. Although this particular mixture has been the subject of two previous pilot plant studies (*4,10*), a reliable thermodynamic model for the vapor-liquid equilibrium behavior of the solutions was not available. We have developed a new activity coefficient model, the NRS model, that is able to represent the behavior of the solutions with good accuracy (*12*).

The NRS model is proposed as an extension of the UNIQUAC activity cofficient model (*1*), by the inclusion of a third contribution term, the salt contribution, to express the activity coefficient of solvent i as follows.

$$\gamma_i = \gamma_i^C \gamma_i^R \gamma_i^S \tag{1}$$

The combinatorial and residual contribution terms to the activity coefficient, γ_i^C and γ_i^R, are calculated using the standard UNIQUAC binary parameters for ethanol and water. An important advantage of this approach is the availability of extensive tables of binary UNIQUAC parameters, which can be used by the NRS model without further regression.

The salt contribution term, γ_i^S, is calculated by an empirical expression based on a transformation of the three concentration variables in the solution. The molar concentration of solvent i is transformed to the salt-free mole fraction, as

$$\text{Xi} = \frac{\text{mole fraction of solvent } i \text{ in the mixture}}{1 - \text{mole fraction of salt in the mixture}} \tag{2}$$

The salt molar concentration is transformed in terms of the maximum salt mole fraction that can be attained in the particular ethanol-water

binary mixture at a pressure of one atmosphere, defining the normal relative saturation as

$$\zeta = X_3 / X_3^* = \frac{\text{mole fraction of salt in the mixture}}{\text{maximum salt mole fraction for the binary}} \quad (3)$$

Note that with the transformations described above, the composition of any liquid mixture of ethanol, water, and a salt is uniquely determined by an (X_1, ζ) pair. The range of possible values at atmospheric pressure is identical for both variables, $0.0 \leq X_1 \leq 1.0$ and $0.0 \leq \zeta \leq 1.0$.

The development of the NRS model is discussed elsewhere (*11*). The expression for the salt contribution term by the model is

$$\ln \gamma_i^S = \zeta [k_{oi} + k_{1i} \zeta + k_{2i} X_i] \quad (4)$$

The regression of the parameters required by the NRS model can be facilitated by defining an auxiliary variable:

$$\Gamma = \ln \gamma_i^S / \zeta \quad (5)$$

This auxiliary variable Γ is a linear function of X_i and ζ, and thus allows the use of simple least squares fitting for regression of k_{oi}, k_{1i}, and k_{2i}.

An important advantage of the NRS model is its ability to represent equilibrium curves at constant salt mole fraction, using parameters obtained from experimental data measured at the boundaries of the feasible region. These boundaries are: $\zeta = 0$ (salt-free binary), X_1 or $X_2 = 0$ (single solvent-salt solutions), and $\zeta = 1.0$ (boiling liquid mixtures in equilibrium with a solid salt phase). The experimental measurements taken at these boundaries require relatively simple laboratory procedures.

The evaluation of the computer model for the vapor-liquid equilibrium behavior of the ethanol-water-salt mixtures required the regression of parameters from the experimental data reported by Schmitt (*9*), using a multivariable linear regression program, and the calculation of a complete equilibrium curve, using a conventional bubble-point program.

In order to incorporate the NRS model into an Aspen simulation of the Dartmouth Process, a constant potassium acetate concentration in the liquid phase was assumed for each section of the column. This assumption, confirmed in the actual distillation runs reported by Schmitt (*9,10*), allows the use of pseudobinary distillation in the extractive column, where the presence of potassium acetate was not explicitly included.

The vapor-liquid equilibrium behavior of this pseudobinary for the entire range of salt-free compositions was calculated using the NRS model, in a separate bubble-point program. The equilibrium distribution variables (''*K*-values'') for ethanol and water obtained from the program were then incorporated into Aspen in tabular form with temperature; the simulation program uses nonlinear interpolation to calculate intermediate values. The enthalpies for the liquid streams were corrected to account for the presence of the salt.

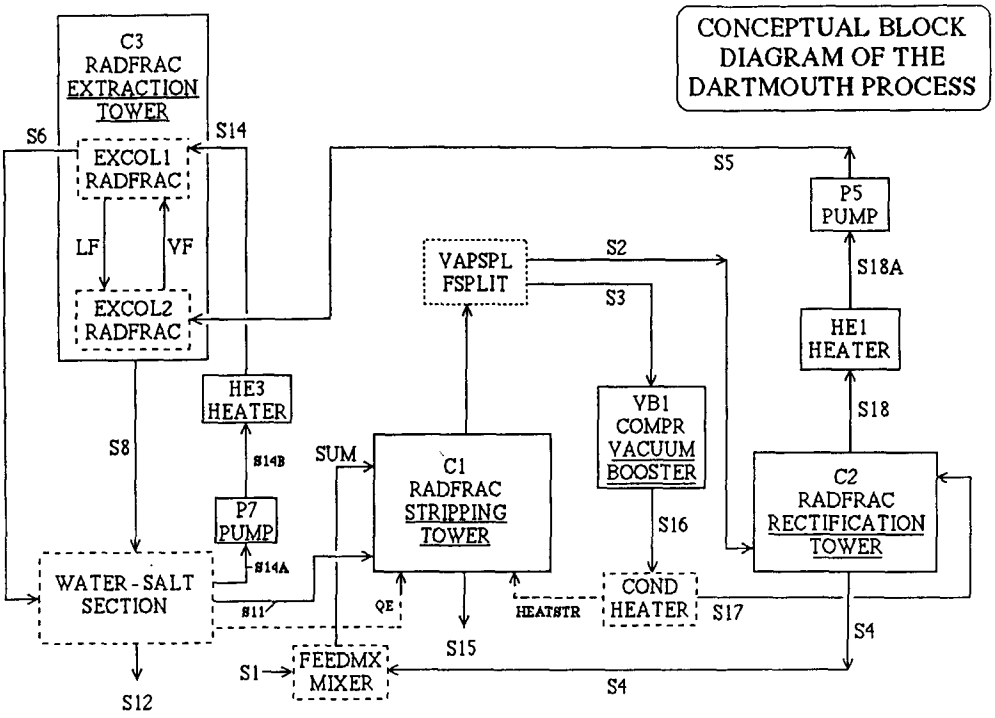

Fig. 2. Conceptual block diagram of the Dartmouth Process.

The Dartmouth Process was simulated in Aspen Plus™, following the conceptual block diagram shown in Fig. 2. The various blocks presented include the corresponding Aspen unit operation models used. The pseudo-binary approach used in the case of the extractive column required two separate distillation column models. The "water-salt section" block, which includes the evaporator E1, the dryer D1, and other equipment, was calculated manually, because of the lack of suitable models in the simulation package.

Economic Analysis Procedure

It is possible to evaluate the economic advantages of the Dartmouth Process and any other alternative processes for the separation of ethanol from dilute mixtures in water, by the use of a "cost-plus-return" approach, that incorporates the initial capital investment and the operating costs of each alternative into a single value. In this paper, the comparison is based on a Separation Cost Index, calculated by the following procedure.

1. The Aspen simulation runs report an "installed cost," or Direct Plant Investment (DPI). This corresponds to the equipment purchase costs (calculated for December, 1987), plus the installation materials (calculated in Aspen with built-in multipliers)

and installation labor costs (using a weighted average wage rate of $25/h).

2. The Allocated Power, General, and Services Facilities investment was calculated using the following factors.
   For steam generation and handling, $30 per 1000 pounds of steam used per h.
   For electrical power usage, $200 per kW used.
   For general facilities, 10% of the sum of Direct Plant Investment and Allocated Facilities.
   The allocated costs associated with process and cooling water usage or waste disposal were assumed to be relatively minor and also essentially constant for the various alternatives; therefore, they were not included in these calculations.
3. The Total Plant Investment (TPI) was then calculated as the sum of the direct plant investment and the allocated facilities investment. In order to incorporate both the initial and the operating costs in one single sum, the capital investment was included in the annual costs for each alternative process, by the addition of a statutory return on investment before taxes expressed as a percentage of TPI, as specified in each case.
4. The following operating costs were also calculated.
   Energy costs, reported directly in the simulation results (steam at a fixed price per 1000 lbs, and electrical power, at $0.06/kwh; the effect of various steam prices was separately studied).
   Direct operating labor, estimated as 0.35 manhours/ton of product. For a plant production of 25 MMgal/y, this translates to 26000 manhours, and using a wage rate of $20/manhour, results in a fixed operating cost of $520,000/y. Note that this cost will be the same for all alternatives, since it is a function only of total production rate.
   To this direct operating labor were added: the cost for supervisory labor (18% of the direct operating labor), the cost for labor supplies and services (6% of d.o.l.), and the cost of plant overhead including administration (60% of d.o.l.) for a total of $436,800/y, again constant for all alternatives.
5. The following capital-related annual costs were also added.
   Maintenance and repairs, estimated to be 3% of TPI.
   Depreciation, estimated to be 8% of DPI, plus 6% of allocated costs.
   Property taxes, estimated to be 2% of TPI.
   Insurance, estimated to be 1% of TPI.

The sum of the above contributions was defined to be the Total Separation Cost (TSC). Finally, a Separation Cost Index was defined in terms of added cost per gallon of ethanol produced, by dividing the resulting Total Separation Cost ($/y) by the plant production (gal/y).

RESULTS AND DISCUSSION

Thermodynamic Model

The predictive accuracy of the NRS model for the ethanol-water-potassium acetate represents a significant improvement over previously available models. In comparison to the experimental data reported by Schmitt (9), obtained at about the maximum constant salt mole fraction achievable at atmospheric pressure, the NRS model produced average deviations in the vapor phase composition of 0.0074 mole fraction units, and in the bubble-point temperature of 1.48 K. The vapor composition comparison is shown in Fig. 3, for two different salt concentrations and 3-phase saturation. The parameter values used in this comparison were obtained from boundary data, which did not include the experimental points shown in the two lower curves.

Process Simulation

Figure 4 shows the temperature and vapor composition profiles calculated by the simulation for the three distillation columns in the process, for the 1.5% wt ethanol feed. The observed discontinuity in the temperature profile of the extractive column at the feed tray is the result of a change in the salt molar concentration in the liquid, caused by the introduction of the salt-free feed stream.

The Aspen-based computer simulation of the Dartmouth Process also allowed the rapid calculation of capital and operating costs for several cases, which were then evaluated by the procedure outlined above. The design strategy of the Dartmouth Process involved a tradeoff between capital and energy costs to minimize energy usage, because the separation of ethanol from very dilute mixtures can be a highly energy-intensive operation. Figure 5 shows the relative contributions of various costs to the Separation Cost Index of the Dartmouth Process, for a feed concentration of 1.5% wt ethanol. The values shown were calculated using a statutory ROI of 20%, with steam priced at \$5.00/1000 lb. Total yearly production of ethanol was set at 25×10^6 gal.

An economic comparison with a more conventional extractive distillation with benzene was also carried out. An annual ethanol production of 25 million gallons was chosen for the comparison, and an Aspen computer model was developed for the concentrating section of the conventional process; the equipment and operating costs of the azeotropic distillation section were reported by Chem Systems (3). Figure 6 shows the comparison for the case of a statutory ROI rate of 20% and an assumed steam cost of \$5.00/1000 lb of steam, for ethanol concentrations in the feed in the 1.5–20% range. It can be observed that theDartmouth Process has a lower SCI for the entire concentration range shown; it also enjoys a significant economic advantage at the dilute end.

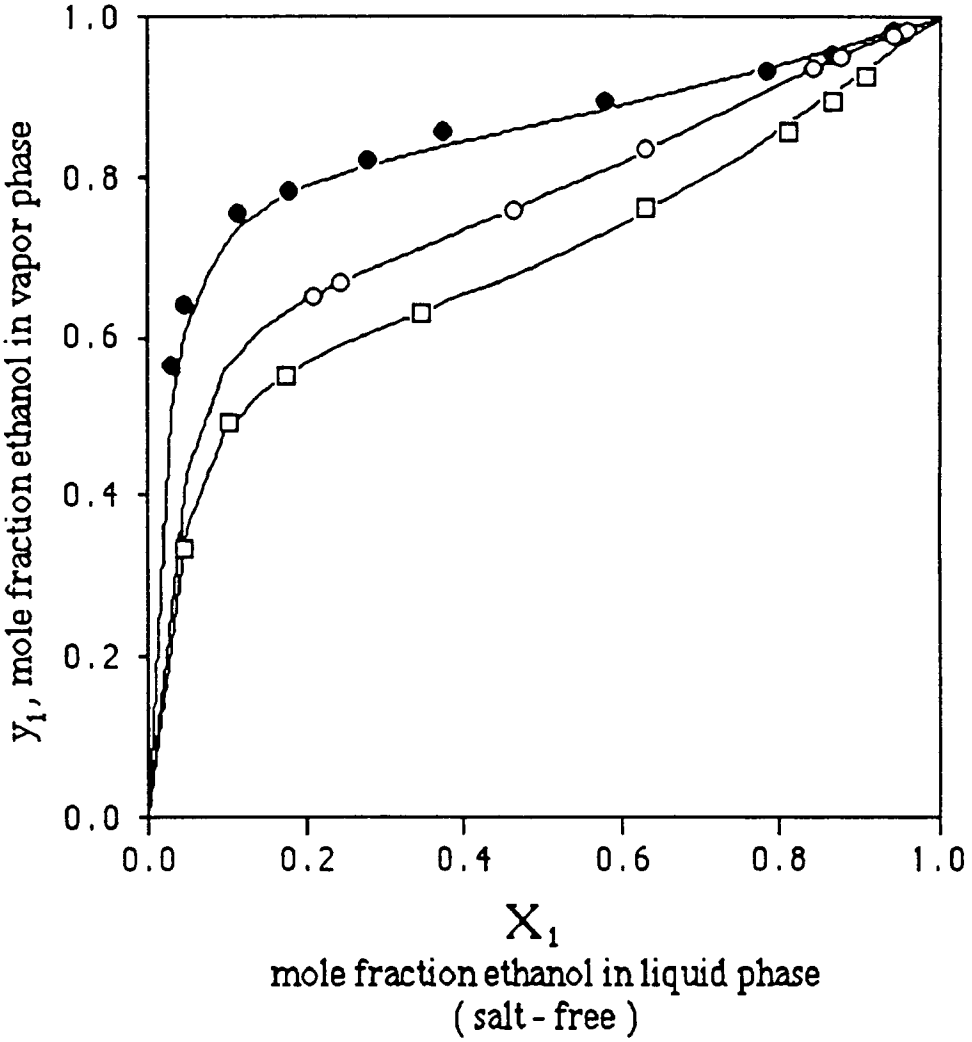

Fig. 3. Graphical comparison of the predicted vapor compositions for the system ethanol-water-potassium acetate at atmospheric pressure. Continuous lines: compositions predicted with the NRS model, using the parameters obtained from 3-phase boundary data. Experimental points reported by Schmitt (*9*), for $x_3 = 0.027$ [□], $x_3 = 0.104$ [○], and for 3-phase boundary points [●].

Figure 7 shows the energy requirements corresponding to the points plotted in Fig. 6. It may be seen that the total cost curve follows the general shape of the curve of energy requirements, which indicates that these costs (and not initial capital investment) may be the most important factor to be considered in economic comparisons between alternative ethanol separation processes. This consideration is inherent in the design strategy of the Dartmouth Process.

A substantial reduction in the energy requirements of the Dartmouth Process is accomplished by a higher capital investment. Using reasonable

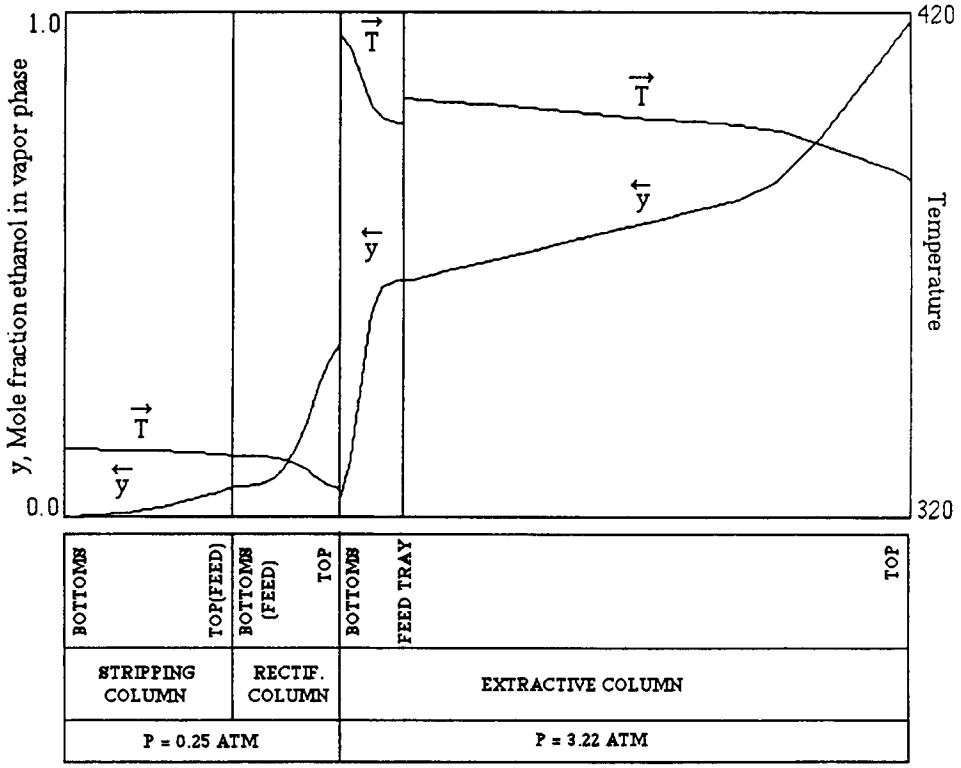

Fig. 4. Profiles of ethanol concentration in the vapor phase and temperature, for the three distillation columns in the Dartmouth Process. The profiles shown correspond to a feed concentration of 1.5% weight ethanol.

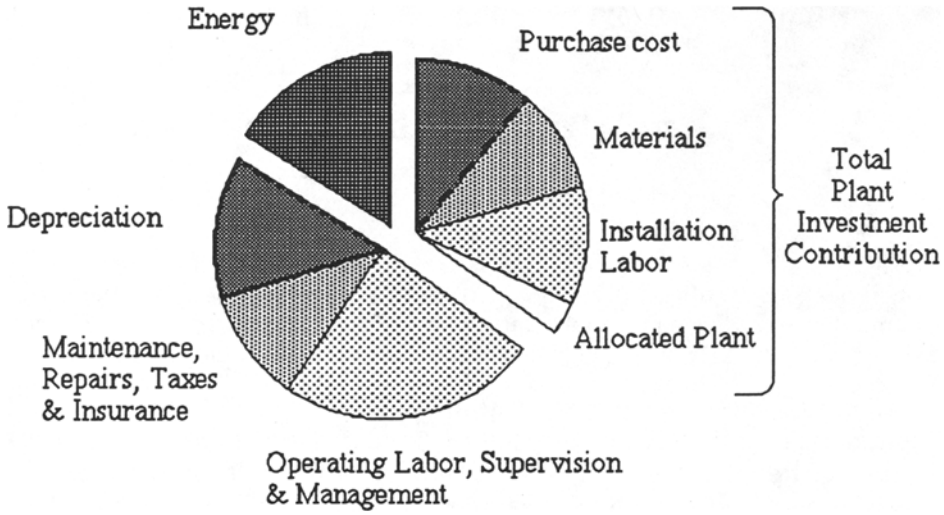

Fig. 5. Graphical representation of the relative contribution of major cost components of the Separation Cost Index for the Dartmouth Process. The following parameters were used in the calculations: for Total Plant Investment, a statutory ROI rate of 20%. For energy costs, steam at \$5.00/1000 lb, electrical power at \$0.06/kwh. Other assumptions as descrbed in the text. Note: the installation materials cost includes insulation, piping, electrical installation, concrete and steel structures, paint, and instrumentation.

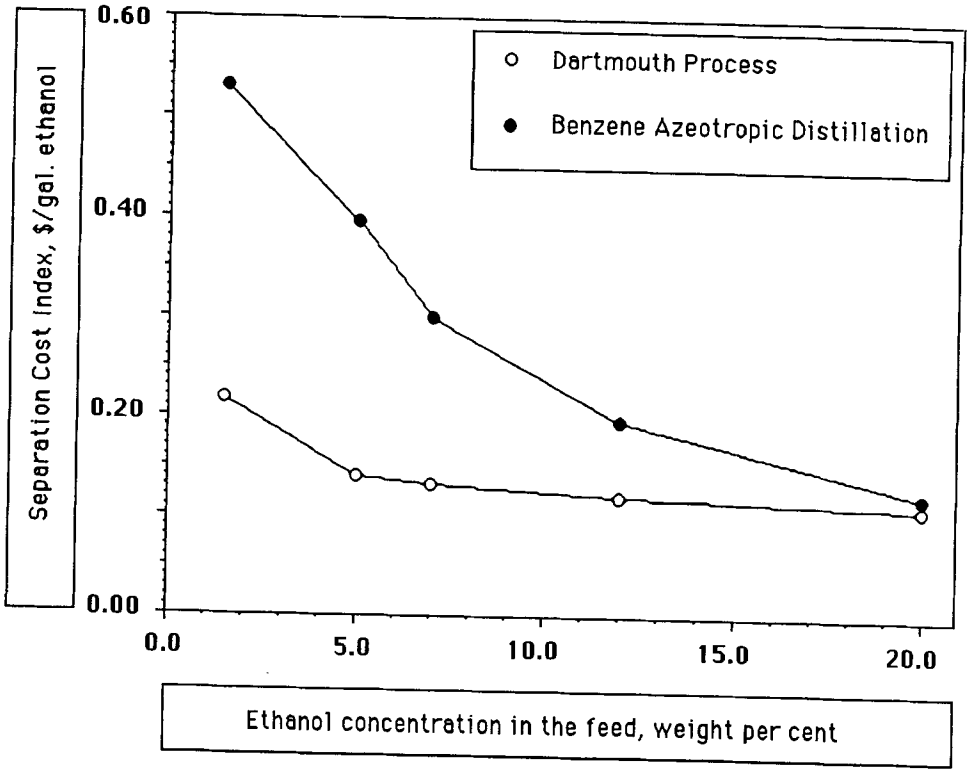

Fig. 6. Graphical comparison of the Separation Cost Index for the Dartmouth Process and a conventional benzene azeotropic distillation process. The values shown correspond to a statutory rate of return on investment of 20%, an assumed steam price of $5.00/1000 lb, and a total ethanol production of 25 million gal/y.

values for the statutory ROI and medium-pressure steam price, the Dartmouth Process offers substantial economic advantages. Conversely, it is possible to calculate the values of comparison parameters that would have to be used, in order to make the Dartmouth Process and a conventional benzene azeotropic distillation equally attractive. Figure 8 shows two of such comparison: (a) the required statutory rate of return on investment, using a steam price of $5.00/1000 lb, and (b) the required steam price, using a statutory ROI of 20%. The numerical value of these variables that match the SCI of both processes depend on the ethanol concentration in the feed; however, for the dilute concentrations typical of fermentation broths, very unrealistic values for ROI and/or steam price are required for the conventional process to be equally attractive.

CONCLUSION

In summary, the economic comparisons undertaken lead us to believe that the Dartmouth Process can potentially contribute to the economic feasibility of ethanol production from cellulosic substrates. Work is under

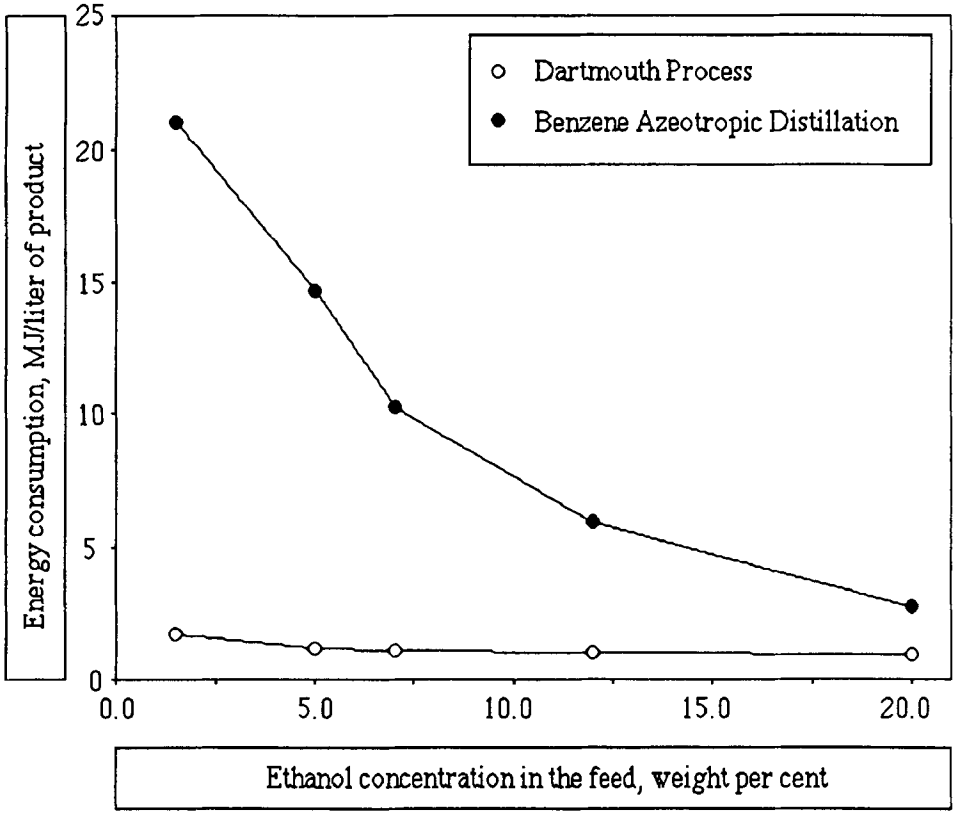

Fig. 7. Comparison of the energy consumption of the Dartmouth Process and a conventional benzene azeotropic distillation. Plant size corresponds to 25 million gall of ethanol/y.

way at the Thayer School, to extend these economic comparisons to include other alternative processes for the separation of ethanol and water.

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REFERENCES

1. Abrams, D. S. and Prausnitz, J. M. (1975), *AIChE J.* **21**(1), 116.
2. Aspen Technology, Inc., 251 Vassar Street, Cambridge, MA 02139.
3. Chem Systems, Inc. (1984), "Economic Feasibility Study of an Enzymatic Hydrolysis Based Ethanol Plant with Prehydrolysis Pretreatment," SERI Subcontract No. XX-3-03097-2, New York.
4. Cook, R. and Furter, W. F. (1968), *Can. J. Chem. Eng.* **46**, 119.

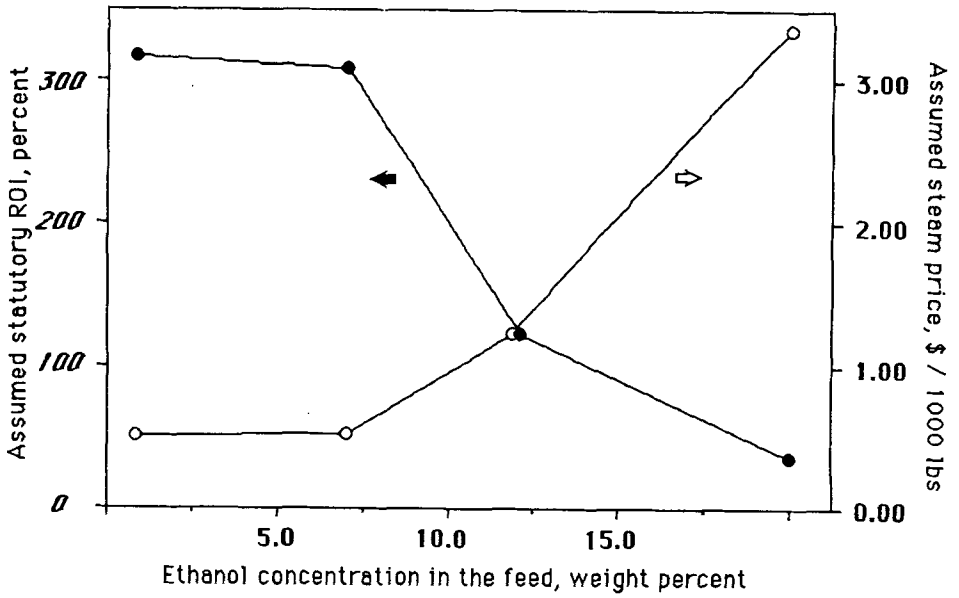

Fig. 8. Parameter values required to match the separation cost indices of the Dartmouth Process and a conventional benzene azeotropic distillation, as a function of ethanol concentration in the feed. The statutory ROI calculations [black data points] correspond to an assumed steam price of $5/1000 lb. The Steam price calculations [white data points] were obtained using a statutory ROI of 20%.

5. Katzen, R. and Associates (1978), US Dept. of Commerce, HCP/J6639-01.
6. Lynd, L. R. (1988), *Advances in Biochemical Engineering/Biotechnology*, Fiechter, A., ed., Springer/Verlag.
7. Lynd, L. R. and Grethlein, H. E. (1984), *Chem. Eng. Prog.*
8. Lynd, L. R. and Grethlein, H. E. (1986), *AIChE J.* **32**(8).
9. Schmitt, D. (1979), *Dr. Ing. thesis*, University of Karlsruhe, West Germany.
10. Schmitt, D. and Vogelpohl, A. (1983), *Sep. Sci. Technol.* **18**(6), 547.
11. Torres, J. L. (1988), *D. Eng. thesis*, Thayer School of Engineering, Dartmouth College, Hanover, NH.
12. Torres, J. L., Lynd, L. R., and Grethlein, H. E. *AIChE J.*, submitted.
13. Venkatasubramanian, K. and Keim, C. (1985), *Starch Conversion Technology*, van Beynum, G. M. A. and Roels, J. A., eds., Dekker, NY.