A Break-Even Analysis of Distillation–Membrane Hybrids

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The use of distillation–membrane hybrids is examined for the separation of two component mixtures exhibiting a tangent pinch, azeotrope, or low relative volatility. The merits of various process alternatives are discussed. A procedure for screening calculations is presented that allows the determination of the break-even cost for a membrane, above which the hybrid would be too costly to be competitive. This approach is applicable to the screening of all the types of membranes and can be used to target the desirable membrane properties. Screening calculations are performed for water–acetic acid, ethanol–water, and propylene–propane systems to demonstrate the inherent trade-offs of the hybrids and the effect of phase behavior on the performance.

Introduction

Distillation is the most commonly used method for separating mixtures of compounds with relatively low molecular weights. However, many industrially important liquid systems are difficult or impossible to separate by simple continuous distillation because the phase behavior contains an azeotrope, a tangent pinch, or an overall low relative volatility. One solution is to combine distillation with one or more complementary separation technologies to form a hybrid. The separations task is switched among the technologies in such a way that each operates in the region of the composition space where it is most effective.

Examples of such hybrids, combining distillation with stripping, absorption, and other techniques, abound (Stichlmair et al., 1989; Stichlmair and Herguijuela, 1992). In the manufacture of cellulose acetate, acetic acid is recovered with distillation, while water, the other component in the mixture, is recovered using extraction with diethyl ether as the solvent. In the separation of an ethanol–water mixture using benzene as the entrainer, decantation is used to effect a complete separation in the presence of a heteroazeotrope (Black, 1980; Stichlmair et al., 1989). Kumar et al. (1992) studied the use of an adsorption–distillation hybrid in the separation of the crude product stream from a propylene-ethylene plant and estimated a 50% savings in energy and a 15–30% savings in capital cost over the conventional distillation sequence. In this process, vacuum, thermal, and pressure swing adsorption are used to split the feed into an alkane stream and an alkene stream, while the distillation is used for the easy fractionation of each of these two streams. Ghosh et al. (1993) studied the use of another adsorption–distillation hybrid system for the separation of propane and propylene, but found that an adsorbent with a very high selectivity was required. In that study, distillation was used for a rough split while adsorption was used to achieve the final product purity. The use of combinations of membranes and extraction, and extraction and distillation in the recovery of carboxylic acids in water solutions have also been examined (Kramer and Al-Samadi, 1995; Gualy et al., 1996; Wytcherley et al., 1996).

Another example is in the dehydration of ethanol using a distillation–membrane hybrid. This example is of particular interest in that it does not require the addition of a separating agent or the incorporation of a semibatch process. Using a separating agent tends to make processes more complex and can be economically undesirable by increasing plant flows and inventories and usually requiring additional units for its complete removal and recovery. Another attractive feature of these hybrids is the relative youth of the membrane field, which results in a constant stream of new membrane technology. One study reported a 30% savings in production cost using a hybrid with a pervaporation membrane over distillation to separate a 50-50 wt % ethanol–water system (Pearce, 1989). A study by Goldblatt and Gooding (1986) found that using a membrane hybrid with a low separation factor was not economically attractive compared to using conventional azeotropic distillation. But, they concluded that using a membrane with a higher separation factor would most likely be

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competitive. Guerreri (1992) found that a 25% savings in operating costs could be achieved by using a hybrid with a pervaporation membrane over azeotropic distillation. Another work was a parametric study of the interaction of the membrane and the column in a hybrid for a specific configuration using the ethanol–water system as an example (Pettersen and Lien, 1995).

Other systems have been identified as potential applications of distillation–membrane hybrids. Stephan et al. (1995) and Morganti et al. (1994) found that a distillation–membrane hybrid could significantly reduce the number of trays and the reflux ratio in the separation of propylene and propane. This study presented an equation-based approach to sizing hybrids with facilitated transport vapor permeation membranes using a McCabe–Thiele analysis of the column. A pilot plant study of a distillation membrane hybrid demonstrated that a 20 to 50% savings in capital cost and up to 50% savings in operating cost was possible (Davis et al., 1993). Julka and Zanapalidou (1993), applying a hybrid that used a reverse osmosis membrane to a proprietary organic-water system with a tangent pinch, found a significant savings over using distillation. A design method for hybrids with reverse-osmosis membranes was formulated in that study. El-Halwagi (1993) examined the use of membrane hybrid systems for waste reduction.

It is highly desirable to develop a general framework for process synthesis in addition to the design methods for the specific membranes and hybrids seen in the preceding work. Experience shows that process synthesis occupies a relatively small fraction of the entire process development effort. However, a less than optimal flow-sheet decision can result in considerable economic penalty. The general framework should examine process alternatives, allowing many options to be quickly screened on cost comparisons and conceptual analysis. Thus, instead of requiring a reformulation of the design equations and a resimulation of the process for each of the many possible membranes being screened, this method should provide the minimum performance of membranes for which the economics of the hybrid is competitive. With the proliferation of new membranes, this will provide an effective screening tool as well as set targets for improvements in membrane performance.

As part of the new framework, this study presents a classification scheme for the distillation–membrane hybrids for binary mixtures based on the complexity of the configurations and the phase behavior. Three general types of systems are identified as candidates for hybrid application. Type I contains those systems with a difficult region near one of the pure components. This difficult region can either be a tangent pinch or an azeotrope. The acetic acid–water mixture that contains a tangent pinch at high water content is an example of this type. Type II includes systems with an azeotrope at an intermediate concentration. The ethanol–water system belongs to this system type, but also fits in type I because the azeotrope is not too far removed from pure ethanol. The last type of system (type III) has a difficult region that spans the whole composition space in the form of an overall low relative volatility, for example, the propylene–propane system. Note that water, ethanol, and propylene are the light components in the water–acetic acid, ethanol–water, and propylene–propane systems, respectively. For each of these system types, process configurations that are suited for the separation are identified. A break-even analysis described below provides the screening and targeting tool.

A Break-Even Analysis

For an economic evaluation of hybrids, a general cost model or procedure for both distillation and membrane units is needed. The costing procedure for distillation is well known and is outlined in Douglas (1988). Obtaining a general cost model for a generic membrane is difficult if the membrane is sized using physically meaningful equations. One problem is that different module configurations that have different transport patterns are possible, for example, a plate and frame pervaporation unit, a shell and tube reverse-osmosis (RO) unit, and a spiral-wound gas permeation unit. Another problem is the variety and availability of new and superior membranes, some of which exhibit new behavior, adding to the already wide range of behavior. This necessitates constant evaluation of any proposed distillation–membrane hybrids. It may even be difficult to determine the cost of the module casing and internal fixtures, which can be higher than the membrane itself. Users of membranes must work with a vendor to determine the cost of a specific membrane for their specific application.

In the absence of a general cost model, it is possible to calculate the maximum or break-even cost of the membrane that would make the hybrid cost as much as the conventional separation technique. The total annual break-even cost ($\mathrm{TAC_{BE}}$) is the difference between the cost of the conventional separation sequence ($\mathrm{TAC_C}$) and the cost of the distillation portion of the distillation–membrane hybrid ($\mathrm{TAC_D}$):

$$\mathrm{TAC_{BE}} = \mathrm{TAC_C} - \mathrm{TAC_D}. \tag{1}$$

The performance of a specific real membrane can then be determined from vendor quotes and compared to the break-even costs. If the quote is higher than the break-even cost, the conventional separation prevails. This approach is effective for all types of membranes, behavior, and costs because no assumptions are made about the membrane.

To calculate the cost of the distillation part, it is necessary to decouple the membrane from the distillation column by a certain selection of design variables. A generic membrane with one input stream and two output streams has six stream variables for two component systems. With two mass-balance equations around the unit, four degrees of freedom remain. Since the membrane feed flow rate and composition, or alternately the permeate flow rate and composition, are typically specified, two degrees of freedom are left. Using up these two degrees of freedom as the design variables by specifying the membrane performance, completely decouples the membrane. This choice allows an examination of the entire spectrum of membrane behavior, to which the performance of a real membrane can be compared. Before the calculations are explained in detail, we examine the hybrid process alternatives. A conceptual analysis is conducted on the interplay of distillation and membrane.

Process Configurations and Classifications

Since distillation is more economical for the bulk of the separation, the membrane is used only to aid the distillation column or to perform the part of the separation where distillation is difficult or impossible. Based on this premise, large numbers of configurations can be identified. Each configuration is classified according to system type and complexity as follows: $T - fmdL$, where T is the type of system as discussed earlier; f is the number of degrees of freedom for the configuration; m is the number of membranes; d is the number of distillation columns; and L is a letter designation for any configurations having the same number designation. It is assumed that four stream variables are specified: overall feed flow rate, overall feed concentration, and the two product concentrations. The degrees of freedom are calculated as the difference of the number of the stream variables, and the combined number of the specified variables, mass balance equations, and the constraints of equating concentration across any stream split. To simplify the counting, the liquid stream, the reboil stream, and the bottoms product off a distillation column can be treated as one stream because the reboil ratio is dependent on the reflux, which reduces the degrees of freedom in these three streams to two.

As an example of the classification scheme, the base-case configuration for system type I has a designation of I-311A (Figure 1). There are seven process streams producing 14 stream variables. With six mass balances, one stream split at the overhead and four specified variables, the degrees of freedom are three. The rest of the designation signifies that the configuration is applicable to system type I, that one column and one membrane are present, and that this is the first configuration with this number designation.

For simplicity, it is assumed in this and the other configurations that the membrane selectivity permeates the light component and that all of the feeds to the distillation column are saturated liquid streams. In the configurations for the systems with azeotropes, it is assumed that the overall feed is at a concentration below the azeotrope, that the azeotrope is minimum boiling, and that in system type I, the azeotrope is near the light component. These conditions only set the stream destinations in the flow sheet and do not affect the conceptual analysis. Also, throughout the article, all the concentrations refer to the concentration of the light component.

This base-case functions as follows. There is a tangent pinch at high concentrations of the light component as shown in the McCabe–Thiele plot (Figure 1). The heavy bottoms product with a composition of x_B is removed from the column, while the distillate with a composition of x_D is fed to the membrane. The membrane boosts the concentration so that the permeate stream is the light product with a composition of x_p. The retentate stream is returned to the column to the tray at the nearest liquid concentration. Obviously, there are three operating lines for this two-feed column. If a one-feed continuous distillation column was used instead of this hybrid, the operating lines would end at the light product concentration. With the hybrid, the operating lines end at the membrane feed concentration and terminate on the 45° line. This can then be thought of as a truncation, before the product concentration, and a lowering of the operating lines in the column.

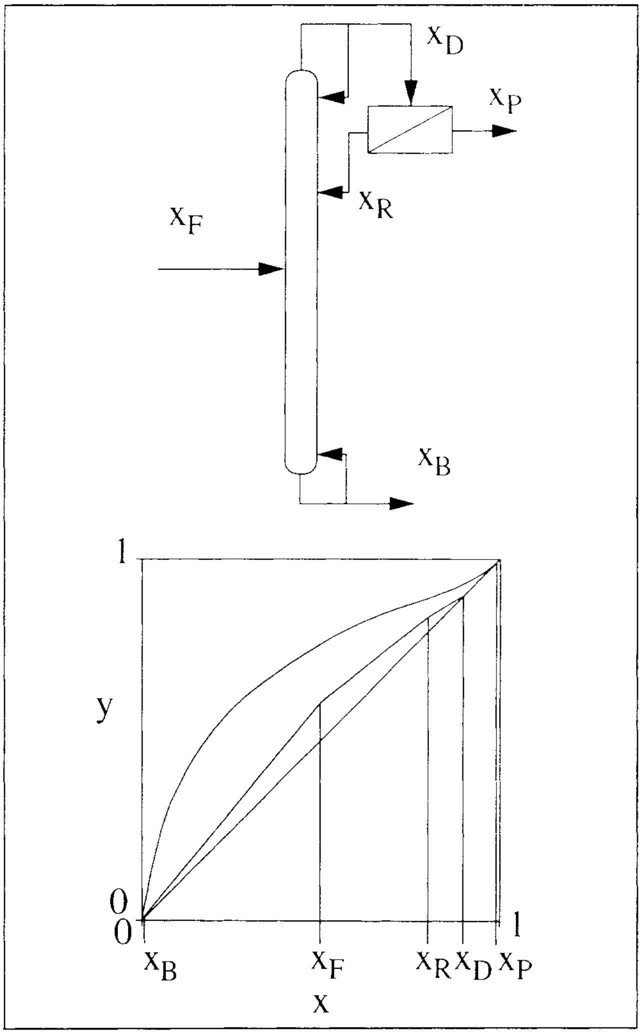


Figure 1. Configuration I-311A.

Figure 2 shows the base-case configuration, II-612A, for system type II where an azeotrope is sufficiently far from either product concentration that a membrane cannot take a stream at azeotropic concentration and provide the desired product. For this separation, two distillation columns are required to produce the products, while one membrane is needed to cross the azeotrope. The process operates in the following manner. The overall feed enters the first distillation column. The bottoms product from this column is the heavy product stream. The distillate is near the azeotropic concentration and is mixed with the distillate from the second column, then fed to the membrane. The retentate stream, which is below the azeotropic composition is returned to the first column, while the permeate stream, above the azeotropic composition, is the feed to the second column. The bottoms product from the second column is the light product stream. As a result, the first column operates totally in the region of compositions below the azeotrope, similarly to the column in I-311A. The operating lines are again truncated and lowered in this column. The second column is a standard one-feed column, which operates above the azeotropic concentration. As another example of the determination of the degrees of freedom, this configuration has 12 streams resulting in 24 stream variables, 12 mass-balance equations, two constraints

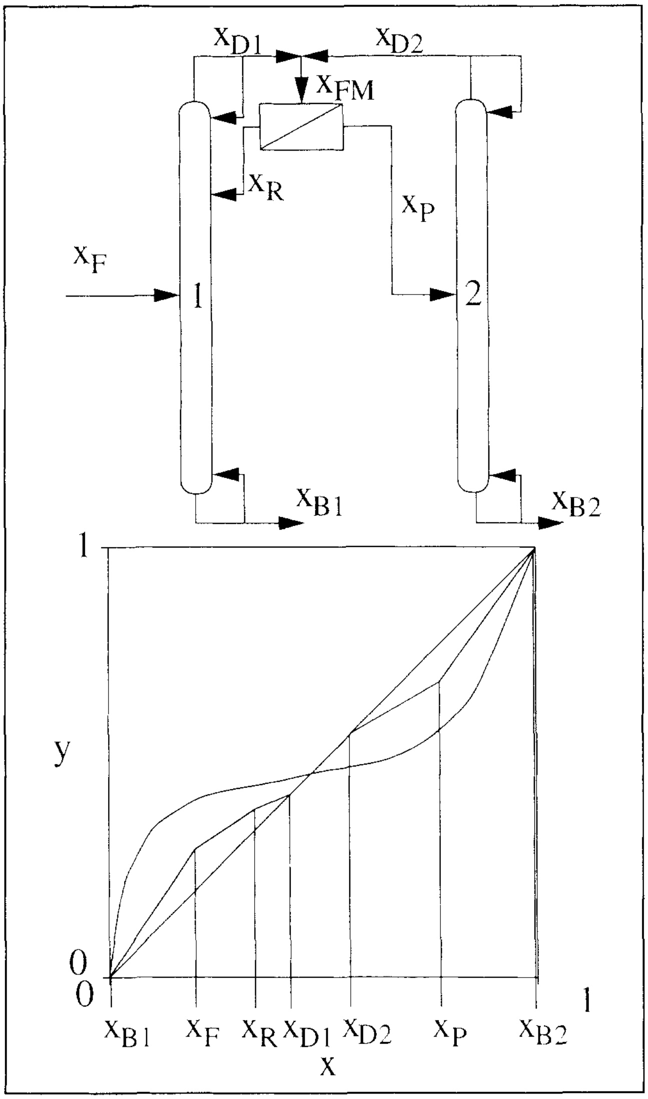


Figure 2. Configuration II-612A.

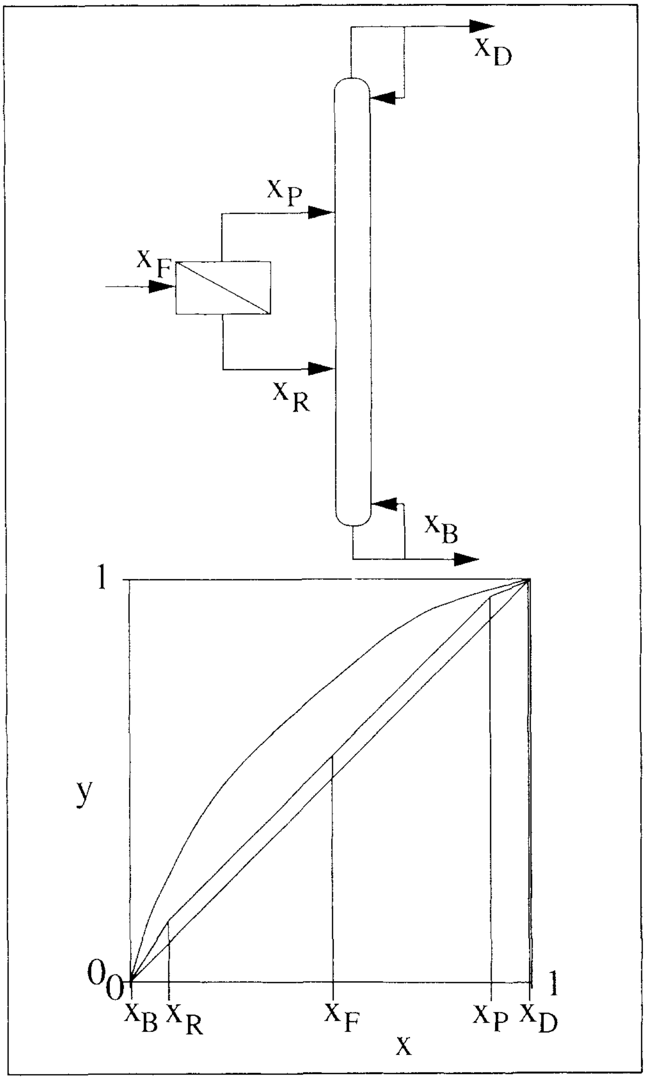


Figure 3. Configuration III-311A.

of equal concentrations at stream splits, and four quantities specified, all of which results in six degrees of freedom.

In system type III, the difficult region spans the whole range of compositions. Figure 3 shows the base-case configuration III-311A. One distillation column can produce both products, while one membrane is required to aid the column. The overall feed is the membrane feed. The permeate stream forms the upper feed to the column, while the retentate forms the lower feed. The operating lines are not truncated in this configuration, but are lowered in the region around the feed, resulting in a reduction in reflux ratio and the number of stages.

A list of twelve other possible configurations is presented in Table 1 along with a short description of the effectiveness for each configuration based on a conceptual analysis of the operating lines in the distillation columns. With the exception of two configurations (I-411A and III-411A), which have five specified variables, the number of specified variables are four for all cases. The configurations from Table 1 are displayed in Figure 4, in order of complexity. Configurations I-411A and III-411A have the same equipment configurations, but are applicable to two of the system types. The configuration presented as Pseudo I-311A is an example of how additional membranes can be added to the configuration I-311A, without changing the calculations. The two membranes inside the dotted box can be treated as one large membrane.

Some of the configurations in this table are only applicable to certain cases. For example, configuration I-311B, a modification of I-311A (Figure 1), is most effective if the distillate concentration is approximately the same as that of the feed to minimize mixing losses. This occurs only with a membrane having a high separation factor, defined in Eq. 4, or a concentrated feed (or a low light product concentration, of course). Configuration II-612B is appropriate for cases with a feed near the azeotrope, because the overall feed goes directly into the membrane. The membrane then splits the stream into a feed above the azeotrope and one below the azeotrope for the two columns. Each column has only one feed; thus, this configuration is not as well suited to large regions of low relative volatility around the azeotrope. Configuration III-511A, a modification of III-311A, greatly lowers the operating lines in the region near the feed pinch, by

Table 1. Additional Process Alternatives and Descriptions

Configuration	Effect and Merits
I-211A	Truncates operating line in the top section of the column
Pseudo I-311A	Similar to configuration I-311A; useful for membranes of low separation factor
I-311B	Truncates and lowers the operating lines; only effective for a concentrated feed or a membrane with a high separation factor
I-411A/III-411A	Lowers the operating lines in middle/top; not appropriate for azeotropic systems
I-521A	Truncates and lowers the operating lines; primarily for membranes of low separation factor
I-621A	Truncates and lowers the operating lines at the top and slightly below; the permeate from the lower membrane to the upper set at the same concentration as the distillate
II-512A	Truncates the operating lines at the top of the first column
II-612B	Only appropriate if the feed is near the azeotropic composition
II-822A	Similar to configuration II-612A, with the second column assisted by using another membrane to further truncate and lower the operating lines; good for systems with a large region of low relative volatility around the azeotrope
II-822B	Configuration II-822A with the retentate from the second membrane fed into the first column; again, good for a region of low relative volatility around the azeotrope
III-511A	Lowers the operating lines in the middle of the column greatly
III-521A	Lowers and truncates the operating lines on the top and bottom of the column

taking a side stream off the column and having three feeds to the distillation column.

More configurations can be developed for these systems than those listed in Table 1. Starting with a configuration, and choosing different stream destinations will produce another configuration. A more complex configuration can be constructed by generalizing a configuration or by adding units. For example, II-822A is essentially II-612A with another membrane unit to aid the second distillation column. Further modification of II-822A to II-822B results from changing a stream destination. The more complex units tend to have the more favorable operating lines. However, it should be remembered that the cost of the complexity may negate a savings from changes in the operating lines and that a complex configuration may reduce to a simpler configuration at the optimal operating conditions. For these reasons, investigating more complex configurations than those in Table 1 was not pursued in this work. More configurations have been examined and will be reported elsewhere (Pressly, 1998). The design calculations, used to show the trade-offs in the configurations, were performed for some of the simpler configurations.

Design Calculations

In the calculations below, no assumptions are made about the membrane unit. However, the phase of the distillation feed streams must be assumed. For this study, the assumption of saturated liquid feeds is made. Obviously, this condition will not be met without the addition of heat exchangers and condensers on the streams from the membranes. However, these equipment costs are not considered because of the screening nature of the calculations.

System type I, configuration I-311A

First, the flow rates of the two product streams, P and B, are determined using the overall mass-balance equations:

$$F = P + B \tag{2}$$

$$x_F F = x_P P + x_B B. \tag{3}$$

Then, the retentate flow rate, R, and composition, x_R, and the distillate flow rate, D, and composition, x_D, must be determined. These calculations are accomplished by defining a membrane separation factor, α, and cut, θ:

$$\alpha = \frac{x_P(1-x_D)}{(1-x_P)x_D} \tag{4}$$

$$\theta = \frac{P}{D}, \tag{5}$$

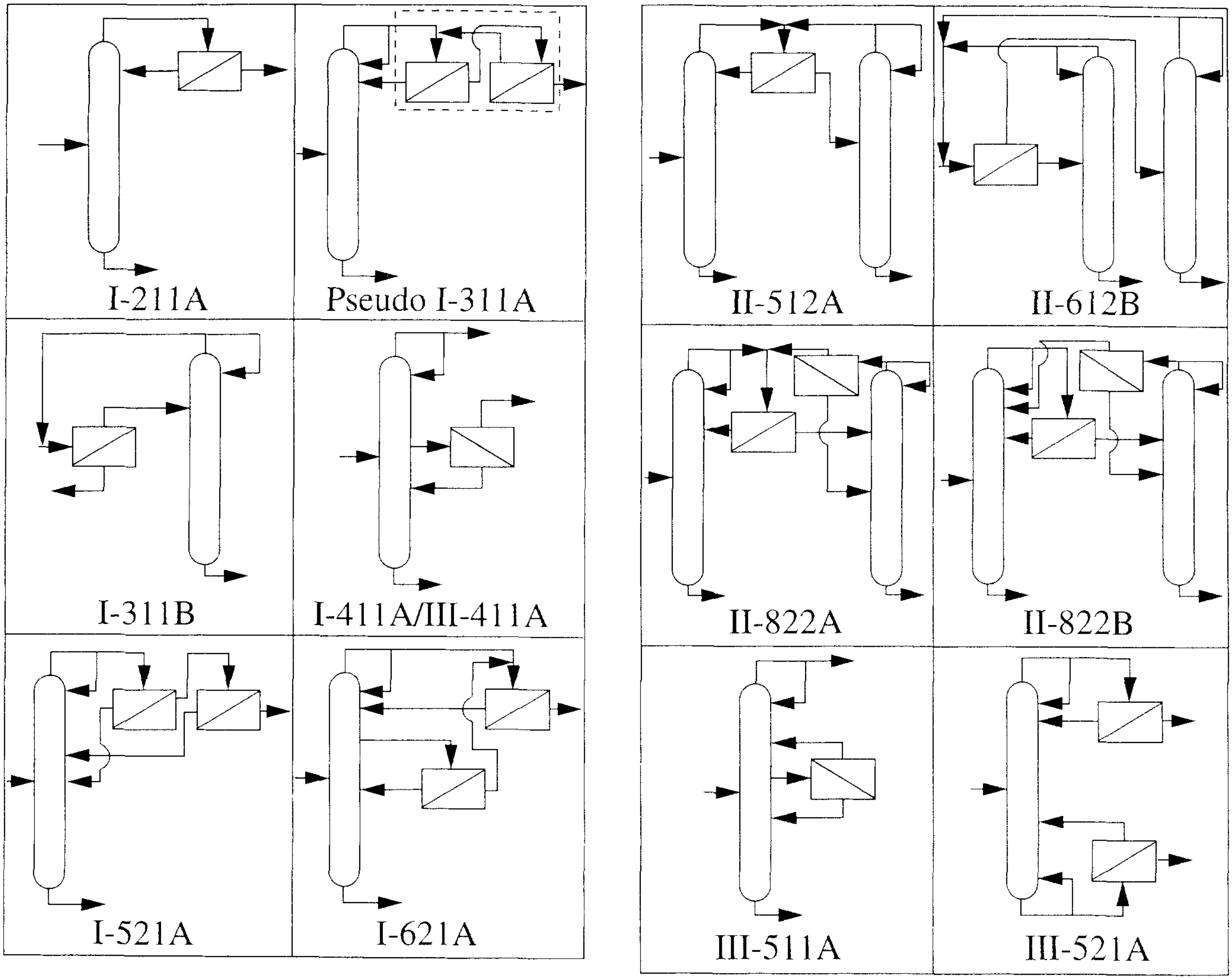
and using the mass-balance equations around the membrane:

$$D = P + R \tag{6}$$

$$x_D D = x_P P + x_R R. \tag{7}$$

The separation factor here, defined with mol fraction quantities, is equivalent to the usual separation factor defined with mass-fraction concentrations. The membrane cut is defined with molar flow rates.

The distillation column is now a fully specified two-feed distillation column that can be sized using the full phase behavior. For our case studies, a stage-by-stage method is used, starting at the bottom of the column and working up. The number of actual trays is calculated by dividing the theoretical number of stages by an overall efficiency; both overall efficiencies and Murphree vapor efficiencies were used initially and were found to produce similar results. The phase behavior is modeled with the Wilson equation for the activities and the Antoine equation for the vapor pressures. The assumption of constant molar overflow is made for the col-



(a) (b)

Figure 4. Additional process alternatives.

umn because of the screening nature of the calculations. The minimum reflux is calculated at the two feed locations and the largest value taken. The reflux ratio is then optimized for each combination of separation factor and membrane cut. The optimum refluxes were found to vary from practically the minimum reflux to up to over two times the minimum reflux. The reason for this is that the varying flow rate and composition of the membrane retentate feed has a large impact on the operating lines. After these calculations, the break-even cost data are plotted as curves of constant separation factor vs. membrane cut.

Experimental data for membrane performance are typically reported as separation factor, flux, feed, and permeate concentrations for a given temperature and membrane cut. A candidate membrane can be screened using the break-even plots as follows. First, a temperature and membrane cut are selected. Second, the separation factor at the permeate concentration, which is the light product concentration for I-311A, is determined. The membrane area is calculated as the permeate flow rate divided by the flux. The membrane cost can then be determined and compared to the break-even cost. The calculations can then be repeated for another membrane cut. If a change in separation factor or a decrease in flux is expected with the aging of the membrane, this concern may be addressed by examining the decrease in the break-even cost with a drop in separation factor or cut.

Obviously, in the screening calculations for this and the other configurations, for some values of the membrane cut and separation factor, the values of various calculated stream variables would either be physically impossible (for example, a stream concentration falling below zero) or undesirable for the flow sheet (for example, in configuration I-311A, the membrane feed having a lower concentration than the overall feed). For cases like these, calculations were stopped, as either an alternative hybrid configuration should be used or that membrane performance was not suitable for use in a hybrid.

System type II, configuration II-612A

Although the calculations for this configuration are more complex because of the additional units and design variables, the membrane can still be decoupled. The choice of design variables is as follows: the composition of the distillate stream from the second column, x_{D2}; the reflux ratios of the two columns; the separation factor; the membrane cut; and the composition of the feed to the membrane, x_{FM}. The reflux ratios, the separation factor, and the membrane cut are obvious choices. The membrane feed concentration is chosen so that it can be held constant throughout the study to allow easier comparisons of the separation factor, which as discussed earlier is a function of membrane feed concentration. Another of the stream variables could be used in place of x_{D2}. This variable is simply a convenient choice because it is bounded by the azeotropic concentration, which is known, and the concentration of the permeate stream, which is easily calculated. The calculations proceed by using the mass-balance equations and the equations for separation factor and membrane cut to step through and determine the flow rates and compositions of each stream, decoupling the membrane.

Each of the two reflux ratios is optimized individually for the columns. Then, x_{D2} is optimized for a fixed separation factor, cut, and membrane feed concentration. However, as the distillate concentration is changed, the membrane permeate flow changes. Obviously, a comparison of the break-even costs of two membranes with equal flux but different permeate flows would be unreasonable because the areas of the membranes would be different. A better comparison method for different permeate flow rates is to use the break-even cost per unit area of the membrane. This can be approximated by dividing the break-even cost by the permeate flow rate, which is directly proportional to the membrane area, given that the membrane flux is constant.

System type III, configuration III-311A

The design procedure for III-311A, used for the propylene–propane study, is fairly similar to the procedure for configuration I-311A because both configurations contain a two-feed column and the same number of design variables. For this configuration, the overall feed flow rate and composition is used with the two equations for separation factor and membrane cut to determine the retentate and permeate flow rate and composition, decoupling the membrane. Since many of these type III systems have a constant relative volatility, albeit low, a short cut method is sometimes appropriate for sizing the distillation column.

Results

The input parameters for all of the base-case studies are displayed in Table 2. In addition to the analysis of the base-case systems, the effects of the process variables on the break-even cost are studied. To evaluate these effects, the scaled break-even cost discussed earlier is used whenever the permeate flow rate changes, while the membrane feed concentration is constant. For the acetic-acid–water system, the membrane feed concentration is set by the light product concentration and the membrane separation factor. These two variables are constant in the case study except in the light product concentration study. For ethanol–water, except for the study on the effect of membrane feed concentration, it is held constant. For the propylene–propane system, the overall feed concentration is the membrane feed concentration. For all of these studies of the effects of the process variables, only the data for a constant separation factor of 50 are displayed to reduce the number of graphs presented.

Table 2. Parameters for the Base Case Studies*

Feed concentration	0.5
Feed flow rate	100 lb mol/h
Light product concentration	0.995
Heavy product concentration	0.005
Cooling water cost	\$0.06/1,000 gal
Cost of steam at 25 psig	\$5/1,000 lb
Overall column efficiency	0.5
Marshall and swift index	1,028

*All concentrations in mole fraction of the light component.
SIunit: kg = lb × 0.454; L = gal × 3.79; kPa = psi × 6.89

System type I-A, water–acetic acid

The dependence of break-even cost on membrane cut and separation factor for configuration I-311A is displayed in Figure 5. The referenced conventional separation system for this base case is a single-feed distillation column, which has a TAC of \$398,000/yr. The family of monotonically increasing curves shows that the break-even cost increases with membrane cut and separation factor. At low separation factors, the annual break-even cost remains fairly constant at lower values of the membrane cut. At larger values of the membrane cut, the

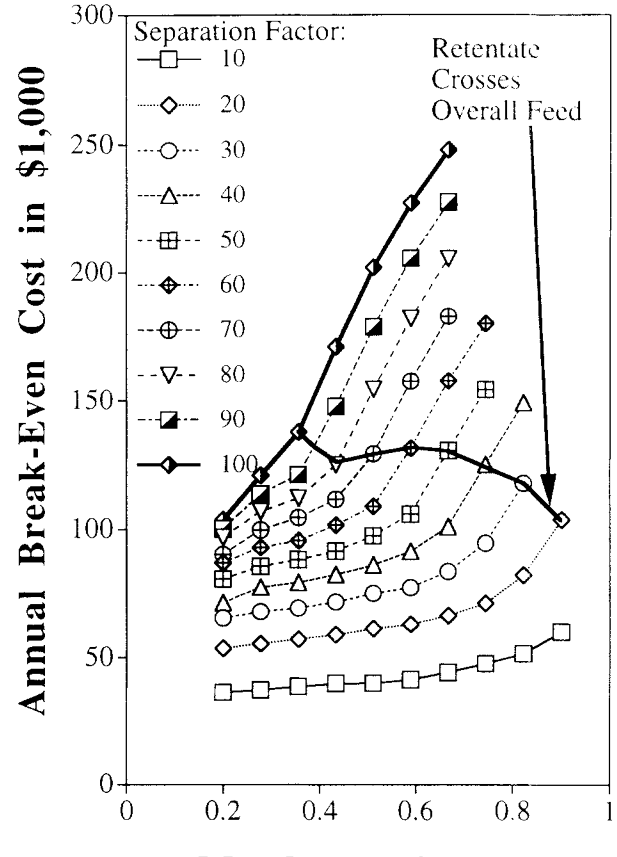


Figure 5. Base case for the water–acetic-acid system.

break-even cost exhibits an increase in slope. At the higher separation factors, this increase in slope occurs at such a lower membrane cut that the entire curve is highly sloped. We can conclude for the base case that a membrane with a very low separation factor (for example, 10) must either have a very low cost or operate at a high membrane cut to compete with a membrane with a moderate separation factor (for example, 20), even if the latter operates at a significantly lower membrane cut. The values of separator factor chosen for this plot are representative of the experimental values for the separation of water–acetic acid using poly(vinyl alcohol) membranes, which range from approximately 35 to 175 (Huang and Yeom, 1991).

This shape of the graphs can be explained by the placement of the retentate stream from the membrane. At the lowest membrane cut, the mole fraction of water in the retentate stream is near the light product concentration, resulting in the stream being fed near the top of the column. Because membrane cut is increased at a constant separation factor, the membrane retentate concentration is lowered, resulting in a lower retentate feed location. This raises the operating lines in the region just below the tangent pinch (see Figure 1), which still does not have a large relative volatility. This low relative volatility results in the minimum reflux ratio being set at the feed location of the retentate stream, the result being that the reflux ratio increases significantly as the membrane cut is increased in this region. Thus, even though increasing the membrane cut in this region improves the membrane performance, it has little effect on the economics. Once the membrane retentate stream crosses the overall feed concentration, marked with a curve in Figure 5, the minimum reflux ratio is set at the feed location of the overall feed, and thus remains constant. The retentate raises the operating lines in the bottom section of the column, but only slightly because of the low flow rate. With the effect of the increasing reflux ratio eliminated, the break-even cost rises much more steeply with the membrane cut. It should be noted that this shape is an effect of this particular phase behavior. The same configuration (I-311A) was applied to the system of ethanol–water, which can be treated as a type I or type II system; the break-even curves were concave downwards in the analysis of the base case because of the different phase behavior (Pressly, 1998).

The effect of the feed concentration on break-even cost is displayed in Figure 6. As can be seen, at a feed concentration of 0.1, the curve is very flat, but the scaled break-even cost is fairly high. At a low membrane cut, the break-even cost decreases with increasing water concentration. When the feed concentration is low, the amount of light product produced is small, resulting in a small vapor flow rate inside the column. This vapor flow rate increases with feed concentration. This effect leads to essentially a change in scale. Distillation cost, of course, scales with an exponent less than unity with vapor flow rate; membrane cost is proportional to area, which is proportional to permeate flow rate. This makes each curve start lower at small membrane cuts as the feed concentration is increased. However, as explained previously, the curves begin with a flat region followed by a more highly sloped region. The flat region decreases in length as the feed concentration is raised. Because of this, as the overall feed is increased above 0.4 mole fraction water, the scaled cost increases with feed concentration at large values of the membrane cut resulting in a crossover in the scaled cost.

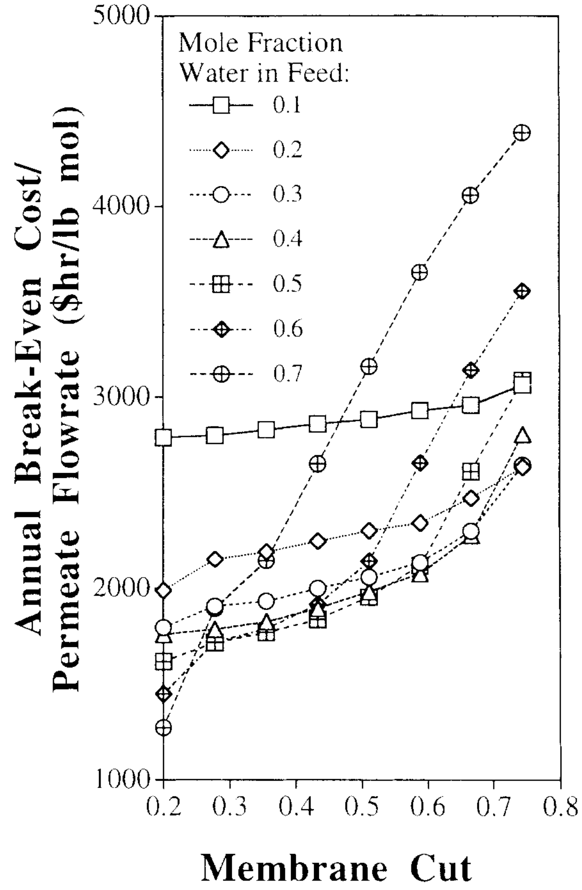


Figure 6. Effect of the overall feed concentration for the water–acetic-acid system.

Figure 7 displays the results of variations in the light product concentration on the break-even cost. The higher the top product specification is, the lower the annual break-even cost is. Achieving a permeate stream with a 0.999 mole fraction of water requires a membrane feed of 0.952 for a separation factor of 50. Thus, for a high top product concentration, it is very difficult for the membrane to keep the distillation column from having to operate in the region of the tangent pinch. The retentate stream is also higher in concentration for the higher product concentration and requires a larger membrane cut to cross the feed, which results in the flatter curves. In these cases, a configuration having more than one membrane unit might be more appropriate depending on the relative cost of the membranes compared to the column. The pseudo I-311A and I-521A both use an additional membrane to further boost the concentration at the top of the column. It should be noted that in this study the feed to the membrane (i.e., the distillate) changed in concentration for each new top product concentration. As mentioned, feed concentration can affect separation factor. The conclusion from this plot that a high product concentration tends to not favor the use of hybrid is weakened if the separation factor increases with light product concentration.

The effect of changing feed flow rate is displayed in Figure 8. Clearly, the lower flow rates favor the use of membranes.

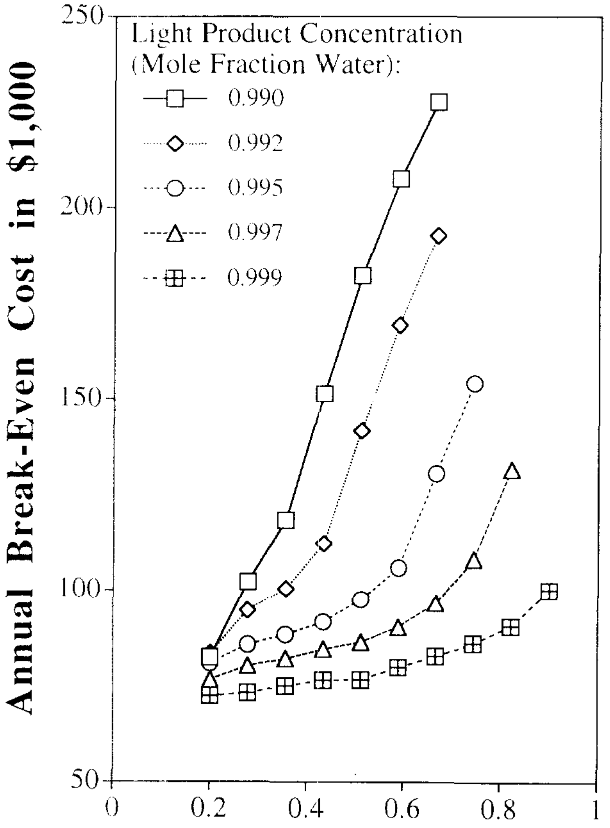


Figure 7. Effect of the light product concentration for the water–acetic-acid system.

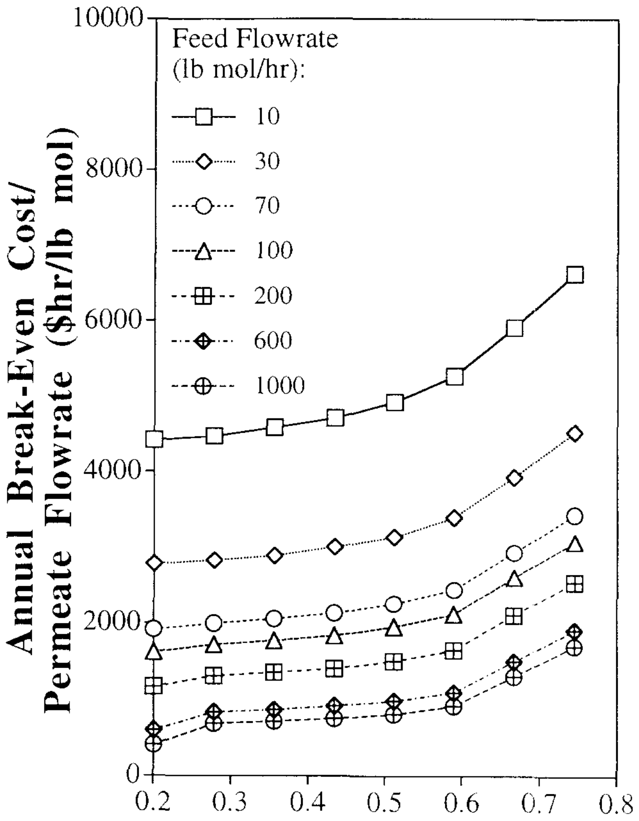


Figure 8. Effect of the overall feed flow rate for the water–acetic-acid system.

This result is expected because distillation scales with vapor flow rate with an exponent less than unity, while membranes scale linearly with flow rate. The relative differences in the break-even cost across the range of flow rates are quite large. For example, the scaled cost for a feed flow rate of 10 lb mol/h is over twice as large as for a flow rate of 100 lb mol/h. The effect of flow rate was also examined for the ethanol–water and propylene–propane system; exactly the same effect was observed for these systems, too. These data are reported elsewhere (Pressly, 1998). For these systems, small-scale processes greatly favor the use of this hybrid.

System type II, ethanol–water

Extractive distillation with ethylene glycol serves as the reference separation system for this case study. Using a set of parameters (Table 3) adapted from Knight (1986), who found the approximately optimal operating conditions, the TAC for this separation was calculated (using Mayflower for the sizing calculations) to be $517,000/yr. In applying configuration II-612A to this system, several possible membrane feed concentrations are possible for the base case, as discussed earlier. For reasons discussed below, a base case of a membrane feed composition of 0.70 mol fraction ethanol was used. Figure 9 shows that the curves of break-even cost vs. membrane cut are close to being linear in membrane cut, but are slightly concave down. It was found that for a given separation factor, the optimal distillate concentration from the second column remains approximately constant. As a result, the feed flow rate and composition to the second column remain approximately constant as membrane cut is varied. Thus, for a given separation factor, the change in cost is governed pri-

Table 3. Data for the Extractive Distillation of Ethanol–Water with Ethylene Glycol

Pressure	1 atm
Reflux ratio	0.42
Ratio of entrainer to feed	1.0
Ethanol–water feed	
Ethanol mol fraction	0.8564
Water mol fraction	0.1436
Ethylene glycol mol fraction	0.0
Ethylene glycol feed	
Ethanol mol fraction	0.0
Water mol fraction	0.001
Ethylene glycol mol fraction	0.999
Distillate	
Ethanol mol fraction	0.995
Water mol fraction	0.0049
Ethylene glycol mol fraction	0.0001
Bottoms	
Ethanol mol fraction	0.0001
Water mol fraction	0.1232
Ethylene glycol mol fraction	0.8767

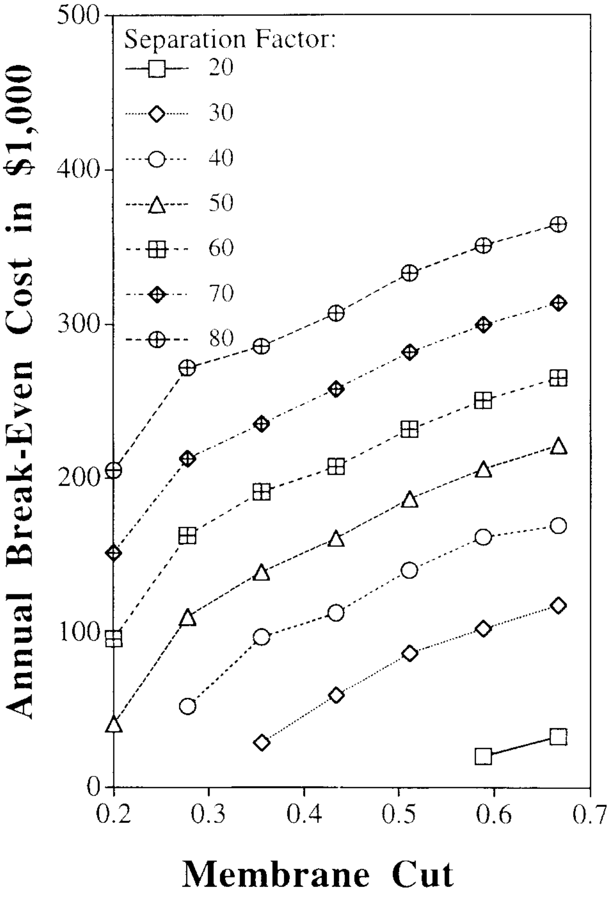


Figure 9. Base case for the ethanol–water system.

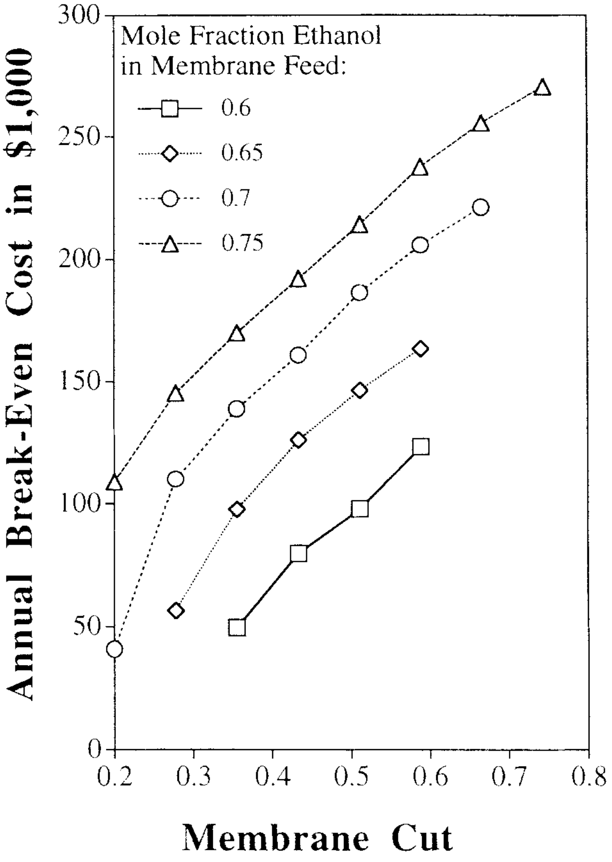


Figure 10. Effect of the membrane feed concentration for the ethanol–water system.

marily by the changes of the cost of the first column. As the membrane cut is increased, the retentate stream decreases in ethanol concentration and total flow rate. Recall that a similar situation occurred in the water–acetic-acid system; when the retentate composition dropped from near the light product concentration to the overall feed concentration, a significant increase in reflux resulted. In the ethanol–water system, the relatively fast transition from a relative volatility of unity at the azeotrope to reasonably large relative volatilities as the ethanol concentration is decreased, results in the reflux in the first column not changing greatly as the membrane cut is increased. This results in the cost for this column depending mainly on the retentate flow rate. At a small membrane cut, a small increase in cut causes a larger decrease in the retentate flow rate than at large cuts. As a result, the break-even cost increases more quickly with membrane cut for low membrane cuts, resulting in the observed behavior.

The plot of the effect of variations in the membrane feed concentration from 0.60 mol fraction ethanol to 0.75 is displayed in Figure 10. As can be seen, at the lower membrane feed concentrations, the break-even cost is smaller, while maintaining the same ethanol production rate results in the membrane permeate flow rate being larger. Thus, the lower feed concentrations of the membrane feed are likely to be less economical. Conversely, the larger feed concentrations to the membrane resulted in larger break-even costs and lower permeate flow rates. At these largest feed concentrations, the configuration is only suited economically to membranes with small separation factors, so that the permeate concentration remains above the light product concentration. The configuration became close to I-311A for large values of the membrane feed. A membrane feed composition of 0.70 mol fraction ethanol was thus chosen as the base-case configuration, because it produced a reasonable level of economic feasibility while allowing a wide range of separation factors to be examined.

The effect of the overall feed concentration variations is displayed in Figure 11. The curves for the larger ethanol concentrations are more highly sloped, while the curves for the lower ethanol concentrations are flatter. The curve for the overall feed concentration of 0.1 mol fraction ethanol has the highest scaled break-even cost overall except the very highest value of the membrane cut, when it is crossed by the curve for a concentration of 0.7 mol fraction ethanol. This is similar to the result observed in the water–acetic-acid study, except much less pronounced. As discussed in the water–acetic-acid case, the scaling of the membrane and the distillation column as the feed concentration changes results in the lower overall feed concentrations having a larger break-even cost at low membrane cuts.

The effect of changing the light product concentration from 0.992 mol fraction ethanol to 0.999 mol fraction ethanol is displayed in Figure 12. As the ethanol concentration of the light product is increased, the hybrid becomes less attractive.

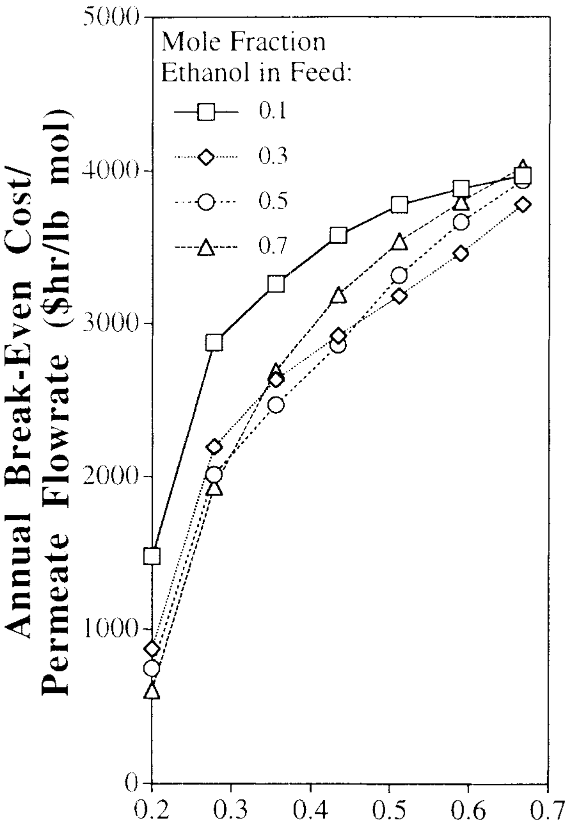


Figure 11. Effect of the overall feed concentration for the ethanol-water system.

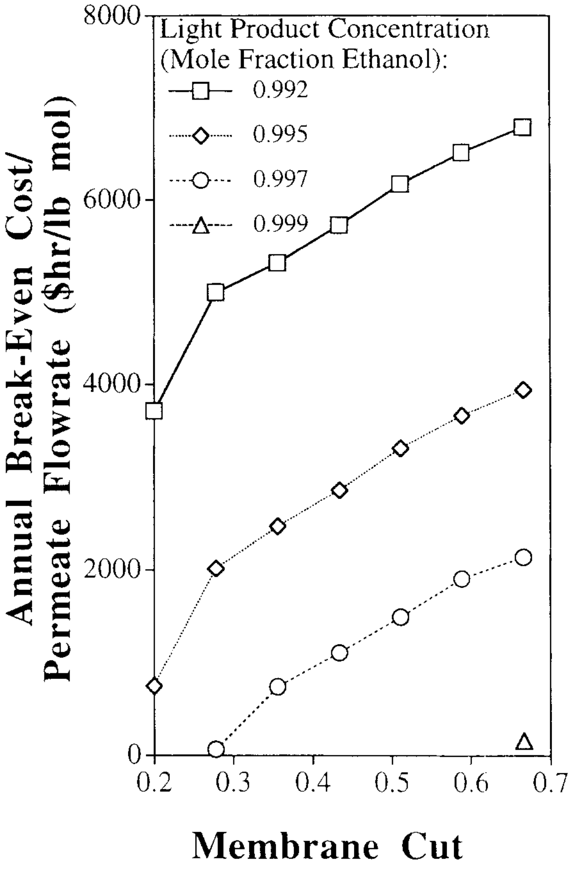


Figure 12. Effect of the light product concentration for the ethanol-water system.

At a product concentration of 0.999 mol fraction ethanol, a membrane with a separation factor of 50 operating at a membrane cut of about 0.7 would practically have to be free to operate and maintain. At low product concentrations, the maximum cost per unit area is increased, resulting in a hybrid looking much more attractive.

System type III, Propylene - Propane

The TAC calculated for the one-feed distillation used as the referenced separation technique for this system was $811,000/yr. The base case for this system is displayed in Figure 13. The curves for different membrane separation factors lie very close together on the graph, especially at the lower membrane cuts, and to a lesser extent at the higher membrane cuts. The curves display a region only slightly concave upwards, followed by a small region with a larger slope at high membrane cuts. This increase in slope becomes more pronounced as the separation factor is increased. As the membrane cut is increased, the retentate composition drops more and more quickly until it reaches zero. The observed increase in slope at large membrane cuts is a result of the retentate stream dropping quickly to being very close in concentration to the bottoms product stream, which causes a larger drop in the number of stages in the column.

The effect of the overall feed concentration is displayed in Figure 14. The curves are very close to being colinear The deviations from this colinearity are some increases in slope, again caused by the sudden drop in retentate concentration, as the cut is increased if the retentate concentration is low. Thus, essentially no effect on the break-even cost is observed as the overall feed concentration is varied.

The effects of the light product concentration on the break-even cost are displayed in Figure 15. Again, the curves are almost colinear. As is the trend in the first two studies, the highest light product concentration results in the break-even cost being lower. However, this difference is slight. The reason for this is that the membrane is operating in the middle region of the distillation column for this configuration and does not have a strong effect on the top of the column. Thus, changing the product concentration for a hybrid has nearly the same effect on the cost of the hybrid as on the reference distillation column, which results in no significant change in the break-even cost.

Conclusions

Three types of systems that are difficult to separate by distillation were identified as being candidates for distillation-membrane hybrids: system type I—tangent pinch or azeotrope near a pure component; system type II—azeotrope at an intermediate concentration; system type III—overall low relative volatility. Alternative configurations were compiled for each type of system and conceptually analyzed by examining the effect of the membrane(s) on the dis-

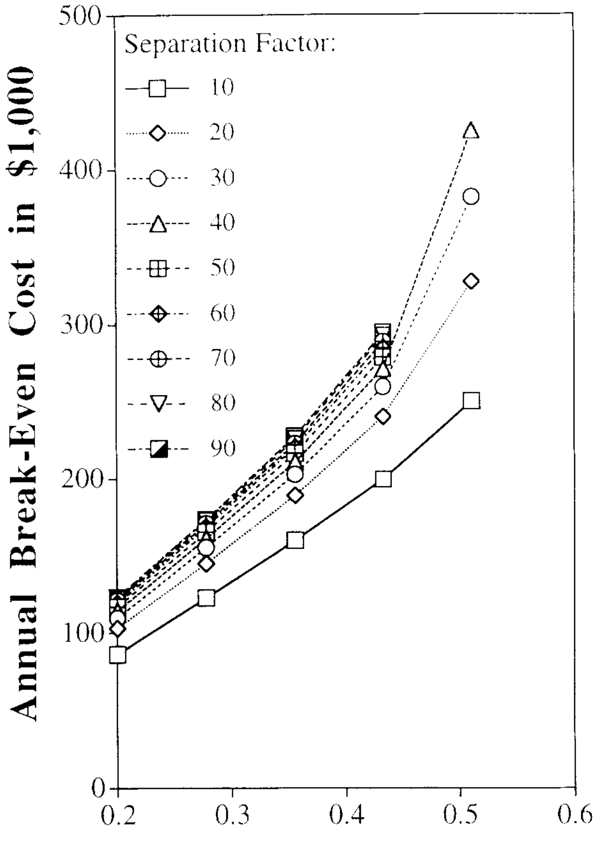


Figure 13. Base case for the propylene–propane system.

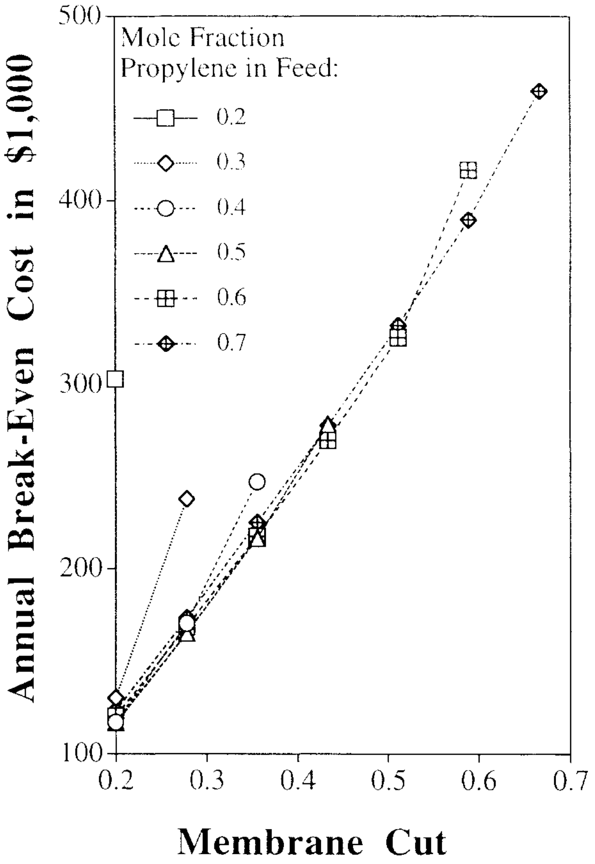


Figure 14. Effect of the overall feed concentration for the propylene–propane system.

tillation column(s). The merits and characteristics of each process were organized into a table, which can be used in selecting an initial group of process alternatives for screening calculations. A new classification scheme was developed that allows these configurations to be compared on complexity.

A design method was developed to screen hybrid alternatives by calculating a break-even cost or maximum cost of the membrane for the hybrid to be as economical as a referenced conventional separation technique. This is a general procedure that requires only one set of calculations to be performed for the screening of all possible membranes instead of requiring a reformulation of the design equations and simulation for each new alternative membrane.

Using the design method, one case study on each of the system types was performed using one configuration from each set of that system type:

Water–acetic acid	System type I	Configuration I-311A
Ethanol–water	System type II	Configuration II-612A
Propylene–propane	System type III	Configuration III-311A

For these systems, the inherent trade-offs in these hybrids were examined. It was found that in all of the systems except for the propylene–propane system, a membrane with a high separation factor but a significantly lower permeability, that is, having a lower membrane cut for the same sized area, almost always had a higher break-even cost. For the propylene–propane system, permeability was observed to be as significant if not more so than separation factor.

The effect of the major process variables on the economics of these hybrids was examined to determine what cases these hybrid systems are most appropriate for. It was found that low flow rates strongly favored the use of the hybrid systems due to the economics of scale between the conventional separation techniques (distillation) and the membrane in the hybrid. For the water–acetic acid and the ethanol–water systems, the break-even cost per unit area was larger at low membrane cuts for low overall feed concentration, but rose less with membrane cut. Conversely, at high overall feed concentration, the break-even cost per unit area was lower at low membrane cuts, but rose more steeply with increasing membrane cut. Thus, a membrane that can operate at a high membrane cut was found to be most effective if the overall feed concentration was high. The effect of variations in the light product concentration demonstrated that a lower product concentration favors the use of a hybrid in the water–acetic-acid and ethanol–water systems. In these two studies with the propane–propylene system, very little effect on break-even cost was observed with variations in overall feed concentration and light product concentration. For this

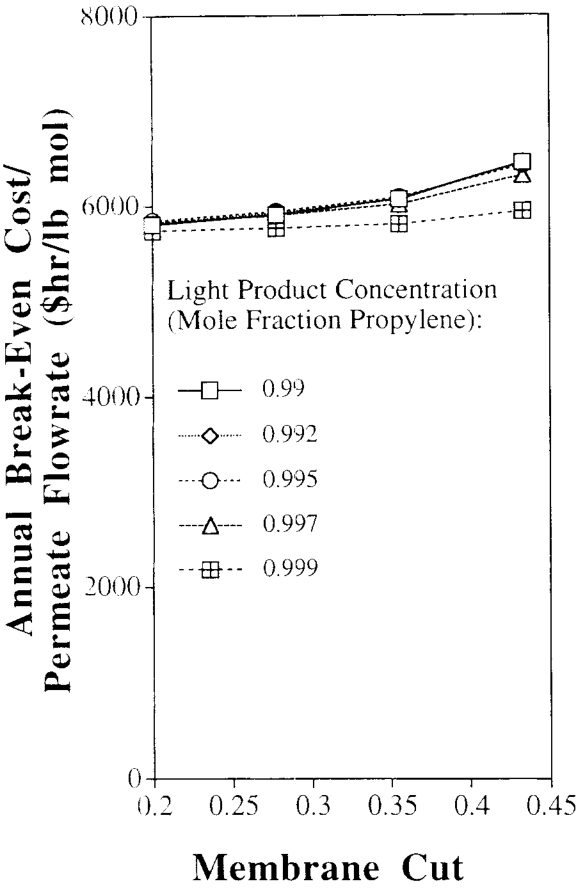


Figure 15. Effect of the light product concentration for the propylene–propane system.

system, separation factor and membrane cut had the largest impact.

Distillation has been the mainstay of separation processes for a long time. Membranes for the separation of liquid systems are one of the newer technologies. The result of combining these technologies is a process that can cost less than using distillation alone. Indeed, hybrid systems have already been put into use industrially for ethanol dehydration. With the development of cheaper and more effective membrane materials and the accumulation of applications experience, the use of hybrid systems is expected to increase. Hopefully, this break-even analysis procedure will help accelerate this effort.

Acknowledgment

Financial support from the National Environmental Technology Institute and from the National Science Foundation fellowship awarded to one of the authors (T.G.P.) is gratefully acknowledged. We thank V. Julka and H. R. Zanapalidou for helpful discussions on this work.

Notation

B = bottoms flow rate of the distillation column (lb mol/h)
F = overall feed flow rate (lb mol/h)
P = permeate flow rate (lb mol/h)

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