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Separation of Diacteone Alcohol-Water Mixtures by Membrane Pervaporation

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Abstract: A study was conducted to evaluate membrane pervaporation for the separation of diacetone alcohol-water mixtures using commercially available membranes for organic enrichment and dehydration. Empirical correlations for the effect of the process parameters of feed concentration, feed temperature, permeate-side pressure, and scale-up were developed. The solvent-water mixture was successfully separated with a poly(vinyl alcohol) based Sulzer PERVAP 2210 dehydration membrane. Various dehydration membranes were evaluated and a comparison of the flux and separation factor was made. The membrane performance in separating acetone-water mixtures was also studied. An overall model to predict the membrane area needed for a scale-up was developed based on the results.

Keywords: Pervaporation, poly(vinyl alcohol) membrane, diacetone alcohol, solvent dehydration

INTRODUCTION

Pervaporation is a membrane separation with great versatility for application in the specialty chemical manufacturing industry for organic-water and organic-organic separations. Its versatility in a small-scale application makes it appropriate to consider for pilot-scale and batch operations for various separations. In particular, due to recent advances in membrane development, it can be applied to solvent dehydration applications that

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cannot be favorably accomplished through normal distillation and in the case of solvent recovery and reuse in green-engineered design (1).

Pervaporation operates with a liquid feed and produces a vaporous permeate and liquid retentate, either one may be the desired product depending on the application. Separation is accomplished by matching the membrane material type to the mixture to be separated and using a chemical potential driving force between the feed and permeate side of the membrane. This is typically maintained by keeping a very low partial pressure of the permeated species on the permeate side through either vacuum pervaporation, in which a vacuum pump is used to lower the total pressure on the permeate side, or by what is called sweeping gas pervaporation, in which an inert gas (such as nitrogen) is used to flush the permeate side of the membrane. In practice it is typical to use a chiller condenser to both trap the vapor and generate the permeate-side vacuum. A simplistic schematic of this process is shown in Figure 1.

While many traditional separations depend on the relative volatilities of the components in a mixture (distillation columns, flash drums, etc), the pervaporation separation capability is related to both relative diffusivities and solubilities of the components in the membrane. This means that, for example, a pervaporation process can be used to separate mixtures that have typically relied on entrainer-based azeotropic distillation. Depending on the membrane material and the components of the system, this could be a much more environmentally efficient separation (2).

Pervaporation has great utility in separating and purifying solvents in an overall process for mass integration in a green or sustainable designed manufacturing facility in industries ranging from specialty chemicals to petrochemicals. In this application pervaporation can be used in sequence with other processes to purify solvent waste and byproduct streams. For example pervaporation can be used to separate a solvent-water mixture after crystallization/filtration/washing operations. Mass integration techniques are used in an effort to recover and purify solvents and other unconverted materials in a

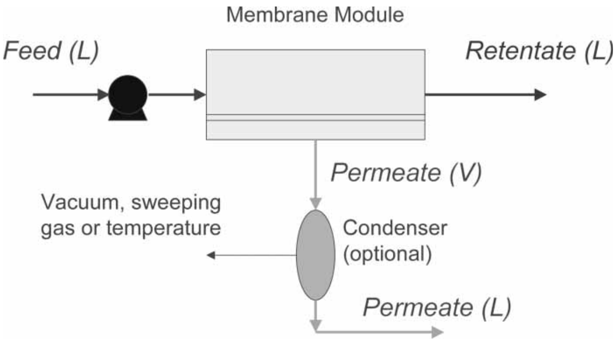

Figure 1. General schematic of a pervaporation process.

reaction and/or separation process sequence (3). The solvent can be purified by pervaporation and reused in the operation. By reusing these materials in the overall manufacturing scenario, the process is made more environmentally efficient, since the raw material costs (in this case fresh solvent) are reduced and the energy used to manufacture the fresh solvent is not expended. Through life cycle analysis this can be shown to reduce ecosystem impacts, e.g., green house gas emissions, etc (4).

The use of pervaporation in solvent dehydration has been shown to potentially be a much more efficient separation process than traditional separation processes like distillation, which depend on vapor-liquid equilibrium differences to separate components. This is especially useful in mixtures where azeotropes exist; rather than extreme operating conditions or adding more components to binary mixtures, a pervaporation unit in series with a distillation column or other separation unit can achieve much purer products at a lower cost (5). Also, because pervaporation can effectively separate components at essentially any temperature, it is also useful in flavor extraction and the purification of pharmaceutical products; these types of compounds tend to be extremely temperature sensitive, and may be damaged if heated or chilled excessively. Using appropriate membranes, good separations can be achieved without the need for significant alterations in the processing conditions.

Current pervaporation research that is the focus of this group's work is on two types of organic solvents widely used in specialty chemical manufacture: alcohols and ketones. Literature indicates that ethanol, for example, is probably the most widely studied of these compounds (6–10). Others include methanol (11, 12), methyl ethyl ketone (MEK) (13), butanol (14–16), acetone (17), and 2-propanol (18–22). Of interest to the topic of this paper, no information on pervaporation separation of diacetone alcohol-water mixtures appears in the literature.

Various membrane materials, e.g., polymeric and inorganic, have been evaluated and compared for the solvents mentioned above. Extensive work has been done on polymeric membranes since they were the first membranes looked at with pervaporation. Early membranes had a limited temperature and solvent stability; which has been improved to provide more reliable commercial units. Most of the dehydration membranes commercially available are poly(viny alcohol) based polymers (23, 24). Silica membranes (18, 19) usually give much higher water fluxes and separation factors than polymeric membranes made of poly(vinyl alcohol), and can withstand higher temperatures of up to 300 °C. Also, since the flux increases with temperature, the membrane surface area needed is less than that of the polymeric membranes (25). Chitosan membranes have good film forming properties, they are highly hydrophilic, and they have good chemical resistance properties (26). Chitosan may either be used by itself to form a membrane (12, 27), or it may be mixed with alginate (20, 22, 28), zeolites (29), or polysulfone (12), among others. Various other materials have been evaluated and compared with alcohol mixtures (30).

The following provides a brief introduction to the theory and relationships relevant to the work described. For a thorough review of pervaporation theory the reader is referred to the general membrane texts and handbooks that are available (31, 32). Transport parameters in this study were quantified by the accepted norms in the field. Permeate flow was measured and represented in terms of a mass flux of the total permeated and the individual components. Process stream concentrations were also quantified on a mass basis using weight (mass) percents of the component concentrations. Although with the lab-scale system used it was impractical to measure retentate concentrations, these were determined in the scale-up calculations. The feed and permeate process stream concentrations were used to determine separation factor to further quantify the separation effectiveness (for a binary '*i*' and '*j*' system). In the selective separation of water-organic mixture, the water is component '*i*' and organic is component '*j*.'

$$\alpha = \frac{y_i/y_j}{x_i/x_j} \tag{1}$$

where

α = separation factor of component i to j
y = mass fraction of component in permeate
x = mass fraction of component in feed

As stated earlier, the main driving force in pervaporation is determined based on the relative permeabilities of each component through the membrane. Each component will dissolve and diffuse through at a different rate; since this rate can be very different for different components in a mixture, separation can be achieved. In binary mixtures, the component flux can be described by Equation (2).

$$J_i = D_i c_i \left[\frac{d(\mu_i/RT)}{dz} \right] \tag{2}$$

where

J_i = component flux ($\mathrm{kg/m^2 - s}$)
D_i = diffusion coefficient ($\mathrm{m^2/s}$)
c_i = component concentration ($\mathrm{kg/m^3}$)
μ_i = chemical potential (J/mol)
R = universal gas constant (J/mol-K)
T = temperature (K)
z = distance through the membrane perpendicular to surface (m)

The most common description of the separation in pervaporation is the solution-diffusion mechanism. In this model, the molecules of the feed species must first sorb into the top layer of a membrane. They then diffuse through the membrane and, upon reaching the other side, evaporate. As such, there are usually two limiting factors in how well the two components separate. First, a component must sorb into the membrane material. If the species has a very low solubility limit in the polymer, then this step will most likely be hampered. Second, species must diffuse through the polymer material, hence any species with a low diffusivity in the polymer will usually result in a low permeate flux. The final step, evaporation, is generally not a significant source of resistance.

MATERIALS AND METHODS

The objective for this separation was part of the engineering clinic at Rowan University (33, 34) where problems are provided by industrial clients for evaluation by faculty-student teams. This particular need emanated from a specialty chemical manufacturing stream that contains diacetone alcohol-water mixture with a temperature sensitive compound. Diacetone alcohol (4-hydroxy-4-methylpentan-2-one) is a colorless liquid that is completely miscible in water. Important physical and chemical properties of diacetone alcohol can be found in Table 1. Extraction was ruled out because of the

Table 1. Chemical and physical properties of diacetone alcohol

Property	Value
Boiling point	169–171 °C
Melting point	−47 °C
Density	0.93 g/mL
Solubility in water	∞
Health hazard	1
Fire hazard	2
Reactivity hazard	0
Threshold limit value	50 ppm
Lower flammability limit	1.8% (vol% in air)
Upper flammability limit	6.9% (vol% in air)
Flash point	58 °C
Vapor pressure at 25 °C	0.108 KPa
Surface tension @ 20 °C	30.9 mN/m
Hildebrand parameter	20.8 $(\text{cal/mL})^{1/2}$
Hansen parameter: dispersion	15.8 $(\text{cal/mL})^{1/2}$
Hansen parameter: polarity	8.2 $(\text{cal/mL})^{1/2}$
Hansen parameter: hydrogen bonding	10.8 $(\text{cal/mL})^{1/2}$
Log octanol/water partition coefficient	−0.3367

introduction of additional chemicals into the mixture. Due to this and other processing concerns, pervaporation was proposed as an alternative. The first attempt was to use organic selective pervaporation which was unsuccessful with the membranes utilized. The focused then turned to an analysis of the dehydration of the diacetone alcohol-water mixture.

A Zenon lab scale pervaporation unit was used for the experimental section of this study (35) (Fig. 2). This unit holds a rectangular membrane of 76 cm^2 in a permeation cell with a feed flow parallel to the membrane surface. Previous work by Mencarini et al (36) on this unit has shown that the conditions used in this study result in Reynolds numbers in excess of 19,000; this was previously shown to minimize the effect of any boundary layer formation and concentration polarization. The system is also capable of controlling the temperature of the feed stock, so as to allow for testing at a range of temperatures. A needle valve is installed directly before the vacuum pump; since the pressure gauges are located directly after the membrane housing, this allowed an operator to easily adjust the permeate pressure. After passing through the membrane, permeate vapors were collected in a collection jar immersed in a liquid nitrogen dewar. Another cold finger vapor trap was in place to ensure that all vapors were trapped. After 10–30 minutes of the collection, the samples were

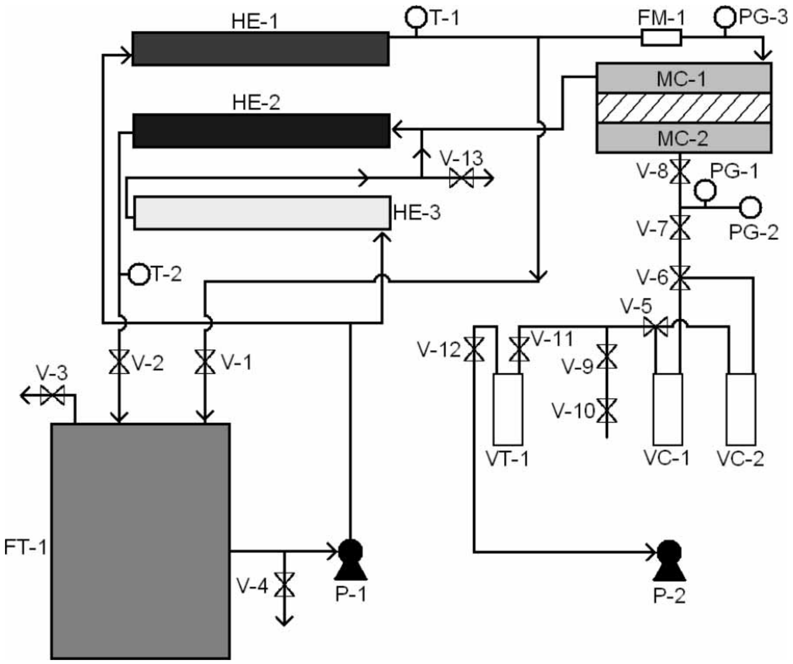

Figure 2. Schematic of Pervaporation Laboratory Unit (V – Valve, P – Pump, FT – Feed Tank, VT – Vapor Trap, PG – Pressure Gauge, T – Thermometer, HE – Heat Exchanger, FM – Flowmeter, VC – Vapor Collection Jar, MC – Membrane Cell Component).

removed; after warming up to room temperature, sample jars were massed and analyzed on a refractometer. Initial and final feed samples were also taken and analyzed to confirm that the feed did not change appreciably during the experiment. For each set of conditions, one to three runs were performed. For each run, four sample vials were collected to be sure that the system had reached steady state, and so that any problems with one sample would not affect the study. These samples were then analyzed and compared to ensure that the variability among the samples for each run was minimized. An analysis of membrane sheets at benchmark conditions was performed to verify membrane consistency. The refractometer used showed a variability of $\pm 0.009\%$ in its measurements.

Under recommendations from Sulzer Chemtech (Germany), Sulzer's PERVAP 2210 was chosen for this study. This membrane consists of a thin layer of poly(vinyl alcohol), PVA selective layer over a porous poly(acrylonitrile), PAN, support layer, and is recommended chiefly for use in the dehydration of neutral solvents. The three parameters tested were feed concentration, feed temperature, and permeate pressure. The benchmark conditions were as follows; feed concentration 90% w/w diacetone alcohol, feed temperature 50 °C, permeate-side pressure 2 torr(abs). The study examined feed concentrations ranging from 50–95% diacetone alcohol (a 25% diacetone alcohol run was also conducted but was not included in the regression fits). The variation in feed temperature was from 30 to 70 °C, and the permeate-side pressure from 2 to 25 torr(abs). For each set of data, a parameter was varied and its effects on both the flux and the concentration were measured. Both a linear regression and a data fit were completed for each parameter.

RESULTS AND DISCUSSION

The initial screening study attempted to enrich a dilute feed mixture of 5.0% diacetone alcohol and 95% water mixture using a silicone-based membrane, Sulzer PERVAP 1170. These studies conducted at feed temperature of 50 °C and 2 torr(abs) permeate-side pressure showed that minimal separation. The results produced a permeate diacetone alcohol concentration of 11.8% representing a 2.6 organic separation factor, and a total flux of $0.54\ \mathrm{kg/m^2h}$. This can be compared to the selective organic permeation of acetone-water mixtures with the same membrane and processing conditions. In the case of acetone, the permeate was greatly enriched, reaching 79.9% ($\alpha_{\circ} = 75.5$) with a $0.38\ \mathrm{kg/m^2h}$ permeate flux. Based on the results obtained for organophilic pervaporation, the research was directed to diacetone alcohol-water dehydration. Further analysis of the characteristics of this organic-water mixture that prevents the effective organic permeation with silicone-based membranes will be described in a subsequent paper.

Dehydration experimental parameters of feed concentration, feed temperature, and permeate-side pressure were analyzed and the results and correlations described in this section. The experimental results are depicted in terms of the total flux and the component flux of both water and organic. Concentrations are shown as weight percent (w/w %) of the organic in the feed and weight percent water in the permeate since for solvent dehydration purposes it is more meaningful to represent the information this way.

The effect of varying concentration on the flux of permeate is shown in Fig. 3 for process conditions of 50 °C and 2 torr(abs) using the Sulzer PERVAP 2210 membrane. As the concentration of diacetone alcohol increased from 50 and 95% (and feed water concentration decreased), the flux decreased from 1.63 to 0.089 kg/m^2-hr, respectively. This follows trends that would be expected for water selective membranes in solvent dehydration applications. The solvent flux remains relatively constant over the feed concentration range examined, varying slightly. The increase in the solvent permeation rate is most likely due to swelling effects in the membrane. The feed concentration's effect on the permeate concentration is shown in Fig. 4. This graph shows that as the feed concentration of diacetone alcohol was increased from 50 to 95 wt% (feed water concentrations decreasing from 50 to 5%), the water concentration in the permeate remains relatively constant, averaging 93.3%. This range of values represents water separation factors ranging from 11.5 to 333 (Fig. 5). The solution-diffusion model shows that both sorption and diffusion in polymeric membranes are important in predicting membrane performance, therefore feed concentration affects the sorption into the membrane on the feed side of the processes. Diffusion through the membrane is also governed by the concentration profile that exists. Desorption at the permeate-side is typically neglected in any analysis.

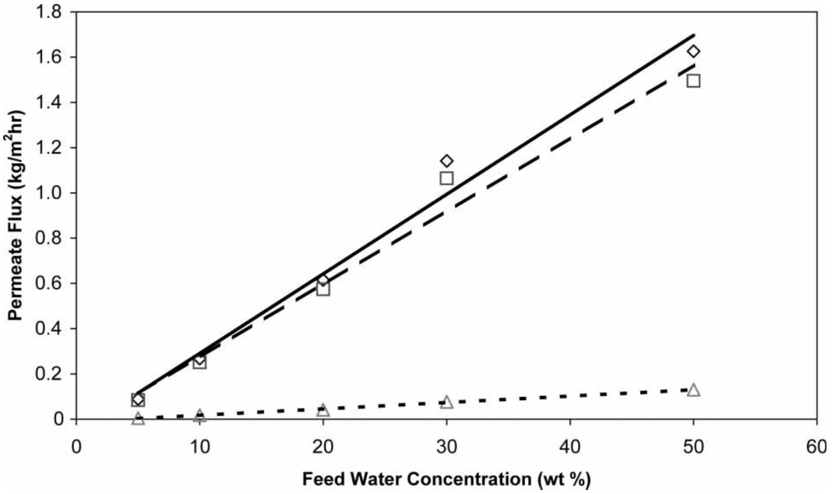

Figure 3. The effect of feed concentration on permeate flux for diacetone alcohol-water dehydration at 50 °C and 2 torr. Total flux (◇) and linear fit (—), water flux (□) and linear fit (– –), DAA flux (△) and linear fit (- - -).

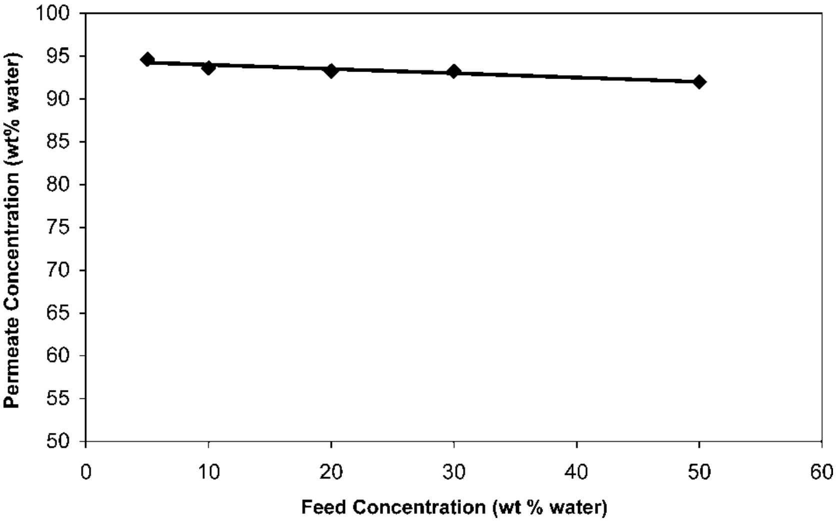

Figure 4. The effect of feed concentration on permeate concentration for diacetone alcohol-water dehydration at 50 °C and 2 torr.

The second parameter that was evaluated was the effect of feed temperature on permeate performance. An analysis, similar to the concentration analysis, was performed for the effect of temperature on the permeate flux and the separation factor. The total flux increases exponentially from 0.06 to 0.76 kg/m^2hr from 30 to 70 °C, respectively. Temperature variance's effect on permeate flux is shown with a plot of Ln(flux) *vs.* 1/T (Fig. 6), where temperature, T, is in Kelvin. This plot is a very common one performed in membrane analysis, since the activation energy can be calculated directly from the slope of the data and follows an Arrhenius-type relationship.

$$J_w = J_o \exp\left(\frac{E_a}{RT}\right) \tag{3a}$$

$$\mathrm{m} = \frac{-E_a}{R} \tag{3b}$$

m = slope of linear fit
E_a = Activation energy (J/mol)
R = Gas Constant (Joules/Mole*K)

This plot shows that the fluxes of both water and diacetone alcohol are affected by temperature in an exponential manner, and increase exponentially with an increase in the temperature. As the temperature increases, 1/T decreases, and the natural log makes the exponential trend of the data linear. The activation energy of this membrane for the 90% mixture of

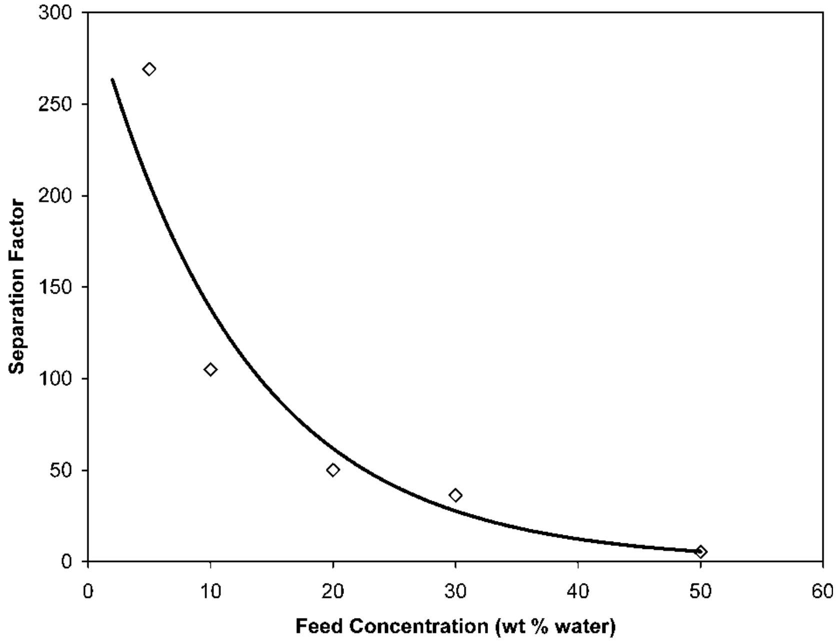

Figure 5. The effect of feed concentration on separation factor for diacetone alcohol-water dehydration at 50 °C and 2 torr.

diacetone alcohol-water was found to be 810.4 J/mol. Figure 7 shows that the temperature appears to have a small yet still significant effect on permeate concentration over the range of values studied. As the feed temperature was increased from 30 to 70 °C, the water concentration in the permeate increased slightly from 90.0 to 96.8%. Although the temperature affects the flux greatly, it does not have as great an effect on the separation factor. Solution-diffusion model parameters of solubility and diffusivity are also greatly affected by feed temperature. Therefore, the trends should follow those indicated by this study for other feed mixtures and membranes as well. Diffusion is increased by increasing feed temperature, which increases the permeation rate of the components being transported through the membrane.

The last process parameter tested was the effect of permeate-side pressure. The pressure range tested was 2 to 20 torr (abs) while the feed temperature and concentration were kept constant at 50°C and 90% diacetone alcohol, respectively. Flux dropped as the permeate-side pressure was increased as shown in Fig. 8. The values were tested from 2 torr (abs) (the lowest attainable pressure in the current system) to 20 torr (abs), after which the flux was so low that it could not be measured accurately within the time constraints on the project. A run was conducted at 25 torr (abs), and after half an hour there was not enough collected in a sample

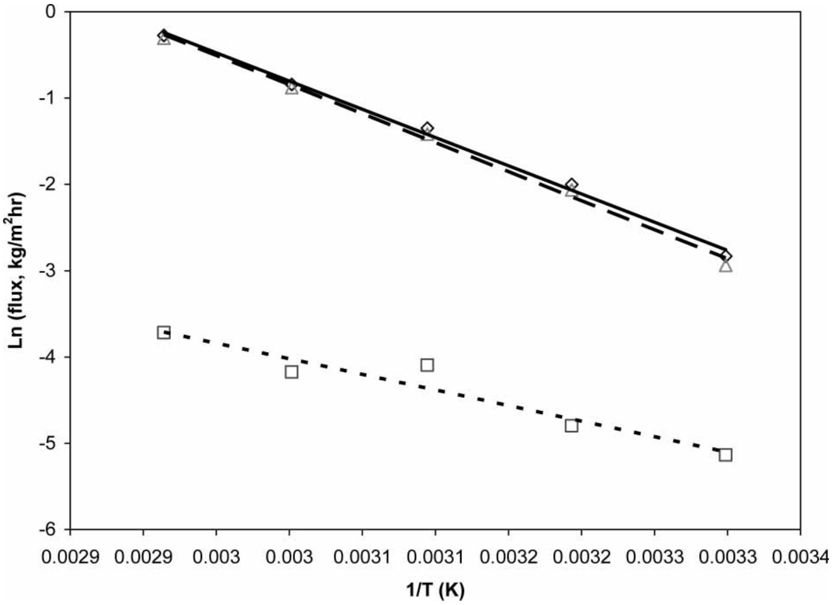

Figure 6. The effect of temperature on permeate flux for diacetone alcohol-water dehydration at 10% water feed and 2 torr. Total flux (◇) and linear fit (—), water flux (△) and linear fit (– –), DAA flux (□) and linear fit (- - -).

jar to perform a concentration analysis. The values for the total flux ranged from 0.26 kg/m^2 hr at 2 torr (benchmark condition) to 0.09 kg/m^2-hr at 20 torr. The effect of the permeate-side pressure on permeate concentration is shown in Fig. 9. The concentration of water slightly increases then decreases within the pressure range evaluated, although not significantly. The permeate-side pressure effects permeation rate since the activity of the permeating components is related to the permeate-side pressure. The maximum permeation rate should therefore be obtained at a zero permeate-side pressure. When the permeate-side pressure equals the saturation pressure, the activity gradient is zero and flux drops markedly. The effect of permeate-side pressure on the separation factor is a more complex phenomenon.

An initial attempt to provide preliminary scale-up calculations was performed with the data obtained. We recognize that other approaches and models exist for predicting pervaporation performance and scale-up (37). The three parameters were then correlated together into a model using a software package to generate an overall empirical expression. To do this, all data was placed into Statgraphics® (concentration) and Polymath® (flux) so that for each point a feed concentration, permeate pressure, and feed temperature along with the measured quantity were put in (flux or concentration). The overall expression can then predict permeate flux and concentration at any

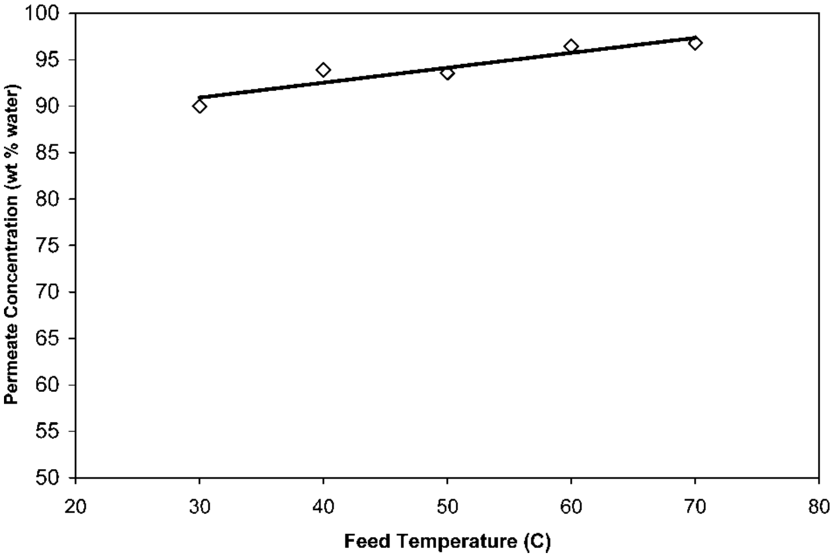

Figure 7. The effect of temperature on permeate concentration for diacetone alcohol-water dehydration at 10% water feed and 2 torr.

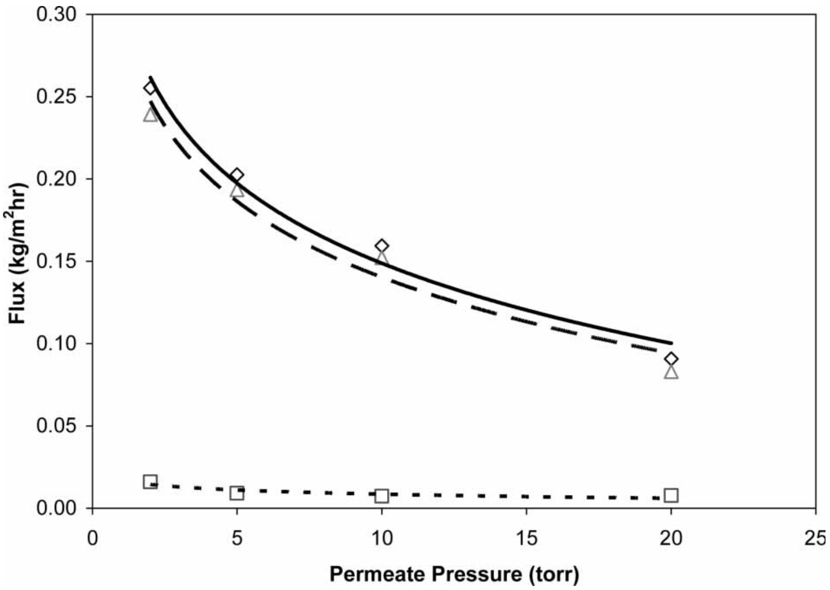

Figure 8. The effect of permeate-side pressure on permeate flux for diacetone alcohol-water dehydration at 10% water feed and 50 °C. Total flux (◇) and linear fit (—), water flux (△) and linear fit (– –), DAA flux (□) and linear fit (- - -).

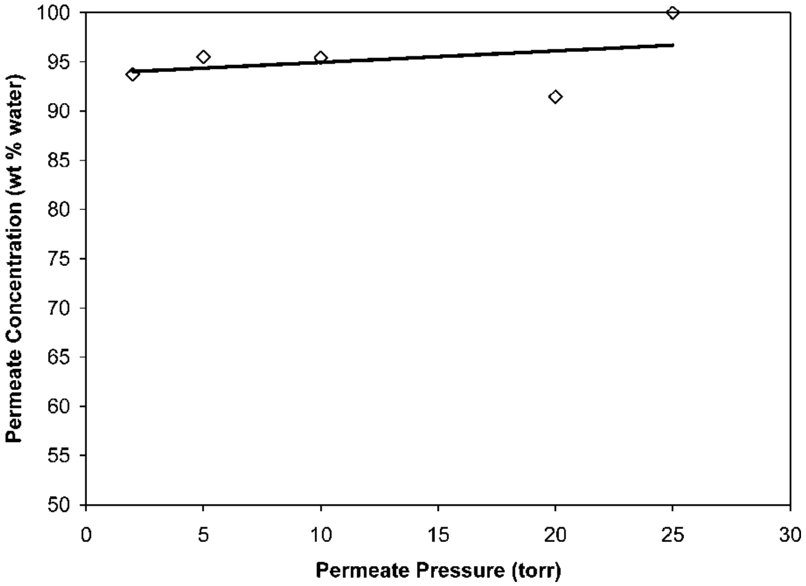

Figure 9. The effect of permeate-side pressure on permeate concentration for diacetone alcohol-water dehydration at 10% water feed and 50 °C.

feed concentration (5 to 50% water), feed temperature (30 to 70 °C), and permeate pressure (2 to 20 torr). This is shown in Equations (4) and (5).

$$J_{permeate} = -3.50(x_f) - 0.0118(P_p) + 0.398\exp\left(\frac{(1/303.15) - (1/T_f)}{3.845x10^{-4}}\right) + 2.78 \qquad (4)$$

$J_{permeate}$: Permeate flux (kg/m^{2}hr)
x_f: Feed concentration (wt fraction DAA)
P_p: Permeate pressure (Torr)
T_f: Feed temperature (K)

$$\mathrm{y_p} = 0.0256(x_f) - 0.0187(P_p) - 0.0641(1/T_f) + 0.950 \qquad (5)$$

y_p: Permeate concentration (wt fraction water)
X_f: Feed concentration (wt fraction DAA)
P_p: Permeate pressure (Torr)
T_f: Feed Temperature (K)

To show that the regression actually fits the data, it was compared to the experimental data from the concentration variance testing and agrees fairly well. A comparison of experimental flux data to the model is shown in Fig. 10.

The aforementioned correlations were used in a scale-up calculation to determine the system size needed for a particular dehydration. This is only a rough estimate since it does not take into account other design parameters or operational issues. For example others have explained how to incorporate module configuration and concentration polarization into design (37). To do this a hypothetical situation was created to determine a membrane area to perform the separation at a variety of operating conditions. For sake of the calculation shown, a feed concentration of 90.0% diacetone in the feed was used with a desired 99.0% diacetone in the retentate. A feed mass flow rate of 10.0 kg/min (600 kg/hr) was used. The analysis was performed by taking each pressure tested (2, 5, 10, and 20 Torr), and then varying the feed temperature from 30 – 70°C. Each set of conditions (temperature, pressure, and concentration) was then entered into Equations (4) and (5). This estimates the total flux and the flux composition. A system of equations can then be set up and iterated to find the membrane surface area that removes the appropriate amount of water. Some variation was required because at lower fluxes, the error in the flux regression resulted in negative predicted fluxes. In these cases, the temperature was adjusted to a value that would yield a positive

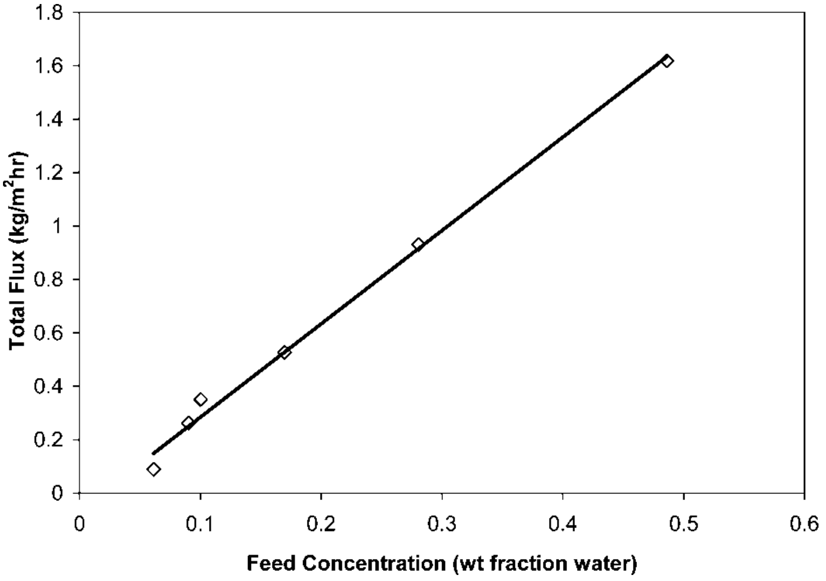

Figure 10. Permeate flux data comparison to model for diacetone alcohol-water dehydration. Experimental data (◇) and empirical model (—).

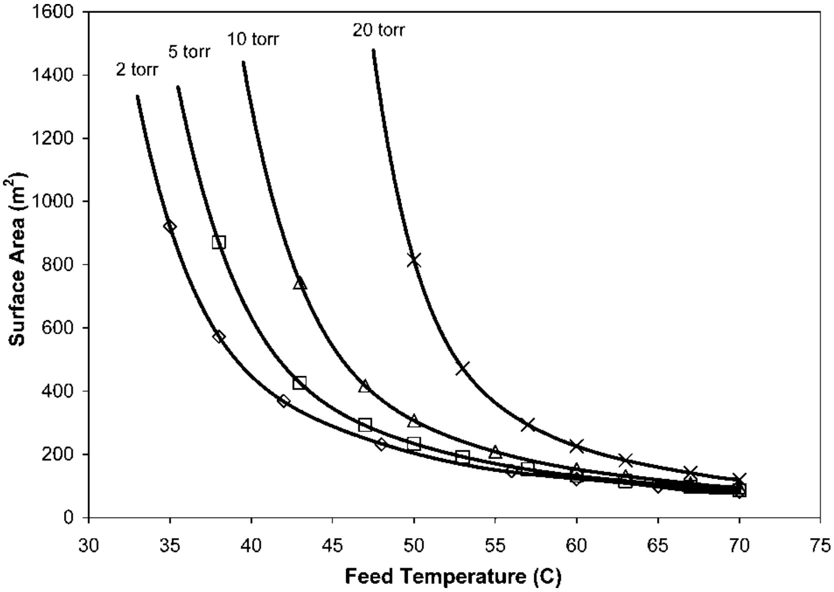

Figure 11. Model predictions for scale-up membrane area for various operating temperatures and permeate-side pressures for the case study. 2 torr (◇), 5 torr (□), 10 torr (△), and 20 torr(×).

flux, as well as a membrane area that could be solved for. Figure 11 shows the result of this analysis. The trends produced show how permeate-side pressure and feed temperature affect the required membrane area. As predicted, the best conditions are lower permeate pressure and higher temperature; this analysis could grant a user a rough estimate of how much surface area would be needed to perform a given separation at specific operating conditions.

A comparison study of various commercially available dehydration membranes was performed with the diacetone alcohol – water feed mixture. This is useful to gauge the effectiveness of these membranes in this and other applications. Nine membranes were studied in the lab unit at benchmark conditions (90.0% diacetone alcohol feed concentration, 2 torr(abs) permeate-side pressure, 50°C feed temperature). All of the Sulzer membranes consist of a PAN support with a PVA-based active membrane layer on top. A summary of the different membrane specifications can be found in Table 2.

Figure 12 shows the comparison between the overall permeate flux of the PERVAP 2210 that was used in this study and the other membranes available from Sulzer. The flux values ranged from a low of 0.05 kg/m^2hr with the PERVAP 2211D membrane to a high of 0.55 kg/m^2hr with a PERVAP 2255/50 membrane. Figure 13 shows the comparison between process separation factors of the membranes. These ranged from 7.3 with a PERVAP 2216

Table 2. Summary of Sulzer membrane properties (38)

Name	Application	Max water content (% wt)	Max operating temp (°C)
PERVAP 2210	Dehydration of neutral solvents (IPA, EtOH)	30	95
PERVAP 2200	Dehydration of neutral solvents	30	95
PERVAP 2201	Dehydration of neutral solvents and reaction mixtures	50	95
PERVAP 2201D	Dehydration of organic acids and reaction mixtures	80	100
PERVAP 2216	Dehydration of neutral solvents; separation of ethanol from other fermentation products	40	100
PERVAP 2510	Dehydration of neutral solvents (IPA)	30	95
PERVAP 2255/50	Removal of MeOH and EtOH from organics	3	85
PERVAP 2211	Dehydration of neutral solvents; separation of ethanol from other fermentation products	40	100
PERVAP 2211D	Dehydration of reaction mixtures and neutral solvents	40	110

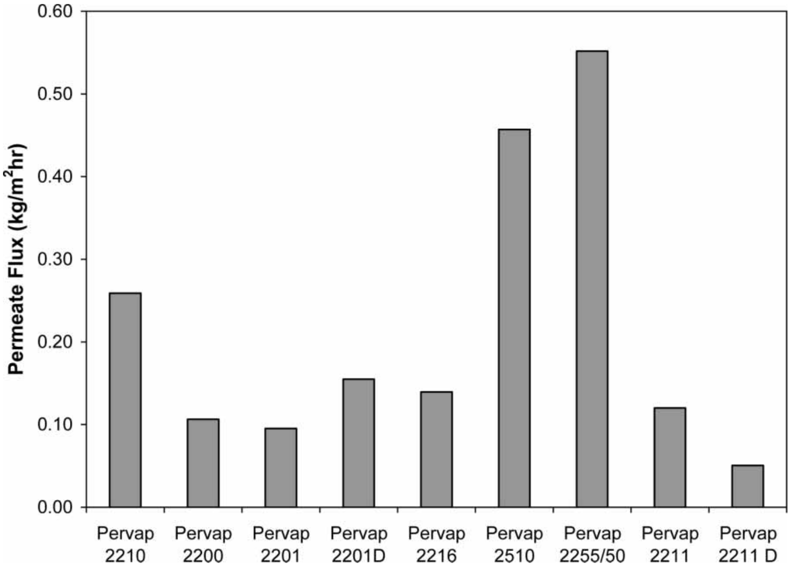

Figure 12. Comparison of permeate flux for various membranes for diacetone alcohol-water dehydration at 10% water feed, 50 °C and 2 torr.

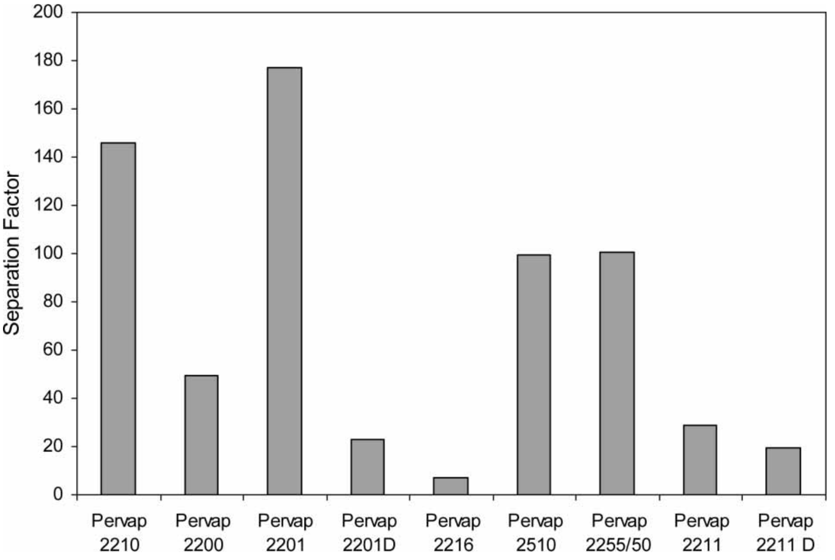

Figure 13. Comparison of water separation factor for various membranes for diacetone alcohol-water dehydration at 10% water feed, 50 °C and 2 torr.

membrane to 177 with the PERVAP 2201 membrane. From Fig. 12, it can be seen that the PERVAP 2210 used in this study, was above average (and third highest) in terms of the overall permeate flux; and second best in terms of the water separation factor. The membrane with the best water separation factor (PERVAP 2201) also had the second lowest overall permeate flux (0.10 kg/m^{2}hr), so this membrane would probably only be useful (in a binary aqueous diacetone alcohol system) when a very low water content diacetone alcohol stream was required. The two membranes with the highest overall permeate fluxes (PERVAP 2255/50 and 2510) also had separation factors only slightly below that of the 2210; these membranes would probably be best for industrial use, especially if they performed comparably at higher temperatures (and were chemically stable at those elevated temperatures). Overall, these results also show that there can be a large variation in pervaporative performance even among one membrane material. Even though all of the Sulzer membranes were polyvinyl alcohol, the different treatments, modifications, and processing methods of the membranes resulted in a wide variety of flux and separation factor.

A final study was conducted to compare the pervaporative performance of a more common solvent, acetone, with that of diacetone alcohol at the benchmark process conditions (10% feed water concentration, 50 °C and 2 torr). The purpose of this study was to give some insight into the dependence of the water flux on the organic solvent present. Figure 14 shows three comparisons between the acetone and the diacetone alcohol runs for the flux, the

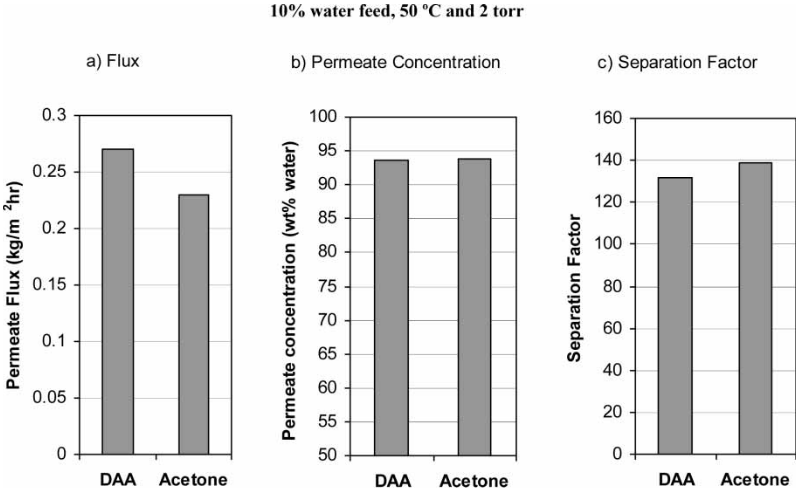

Figure 14. a, b, c Comparison of diacetone alcohol separation with acetone with PERVAP 2210 membrane at 10% water feed, 50 °C and 2 torr.

permeate concentration, and the separation factor. It appears that the separation performance is not affected by the solvent swap of diacetone alcohol with acetone. The permeate concentration of the resultant separation with acetone feed produces a permeate concentration of 93.9% water and a 0.23 kg/m^{2}hr total flux. These results appear similar to what was obtained from the diacetone alcohol runs, although the flux is slightly lower with the acetone dehydration. This shows that experimental studies are useful in predicting pervaporative performance in translating results form one particular chemical system to the other.

CONCLUSIONS

Pervaporative separation of diacetone alcohol-water mixtures can be effectively accomplished. Studies were conducted to examine the effect of feed concentration, feed temperature, permeate-side pressure, and membrane type on separation performance. Data correlations were performed to develop a scale-up model to size a commercial unit.

As the feed concentration of water was decreased, the flux decreased. The separation factor of the water increased as the water content decreased. As the temperature of the feed was increased, the membrane separation performance was enhanced, since permeate flux and concentrations of water increased. The total flux increased with increasing temperature, following an exponential relationship. The best flux and separation appear at the highest temperature studied, 70 °C. The permeate concentration of water increased slightly as the permeate-side pressure increased, while the flux quickly decreased to essentially zero at 25 torr. The highest fluxes occurred at low permeate pressures. While higher pressures did give a slightly better separation, the flux difference was much more significant than the change in concentration achieved by using a higher pressure and therefore it appears most desirable to operate the system as a low permeate-side pressure.

The experimental results were correlated over the range of parameters examined and produced acceptable simplified models. These were useful in predicting the performance at any concentration, temperature and pressure within the study limits and also for scale-up purposes. A simplified model was proposed to scale-up the process and produced correlations for the effect of the process parameters on the membrane area. Feed specifications of the organic solvent concentration and flow rate, and desired permeate purity provide input conditions to the model, which then can be used to see how the operating temperature and permeate-side pressure at these conditions effect required area for the intended separation efficiency.

Various Sulzer dehydration membranes were examined for the diacetone alcohol-water dehydration. In this comparison it was shown that both the permeate flux and the water separation factor must be taken into account when selecting a proper membrane for the separation. For example, the 2201 membrane had a water separation factor 40% higher than the 2210, but had a much lower flux. Conversely, membranes with higher fluxes than the 2210 membrane exhibited lower separation factors. The 2210 membrane used for the process parameter study is quite acceptable in terms of balancing flux and the separation factor.

REFERENCES

1. Slater, C.S. and Schurmann, T. (2005) Membrane pervaporation: an experimental experience in novel separations for green engineering. Proceedings of the 2005 American Society for Engineering Education Annual Conference.
2. Nicol, W. (2003) Comparing catalytic distillation to separate reaction and distillation for production of diacetone alcohol. *Chemical Engineering Research and Design*, 81: 1026–1032.
3. Allen, D. and Shonnard, D. (2002) *Green Engineering: Environmentally Conscious Design of Chemical Processes*; Prentice Hall: Upper Saddle River, New Jersey.
4. Shonnard, D., Lindner, A., Nguyen, N., Subamatram, R., Fichana, D., Hesketh, R., Slater, C.S., and Engler, R. (2006) Green Engineering–Integration of Green Chemistry, Pollution Prevention, and Risk Based Considerations. In *Handbook of Industrial Chemistry and Biotechnology*; Springer Publishers.
5. Van Hoof, V., Van den Abeele, L., Buckenhoudt, A., Dotremont, C., and Leysen, R. (2004) Economic comparison between azeotropic distillation and different hybrid systems combining distillation with pervaporation for the dehydration of isopropanol. *Separation and Purification Technology*, 37: 33–49.

6. Li, L., Xiao, Z., Tan, S., Pu, L., and Zhang, Z. (2004) Composite PDMS membrane with high flux for the separation of organics from water by pervaporation. *Journal of Membrane Science*, 243: 177–187.
7. Mora Molina, J., Vatia, G., and Bekassy-Molnar, E. (2002) Comparison of pervaporation of different alcohols from water on CMG-OM-101 and 1060-SULZER membranes. *Desalination*, 149: 89–94.
8. Van der Bruggen, B., Jansen, J.C., Figoli, A., Geens, J., Van Baelen, D., Drioli, E., and Van Decasteele, C. (2004) Determination of parameters affecting transport in polymeric membranes: parallels between pervaporation and nanofiltration. *Journal of Physical Chemistry B*, 108: 13273–13279.
9. Fadeev, A.G., Kelley, S.S., McMillan, J.D., Selinskaya, Y.A., Khotimsky, V.S., and Volkov, V.V. (2003) Effect of yeast fermentation by-products on poly[1-(trimethylsilyl)-1-propyne] pervaporative performance. *Journal of Membrane Science*, 214: 229–238.
10. Kanti, P., Srigowri, K., Madhuri, J., Smitha, B., and Sridhar, S. (2004) Dehydration of ethanol through blend membranes of chitosan and sodium alginate by pervaporation. *Separation and Purification Technology*, 40: 259–266.
11. Bowen, T.C., Wyss, J.C., Noble, R.D., and Falconer, J.L. (2004) Measurements of diffusion through a zeolite membrane using isotopic-transient pervaporation. *Microporous and Mesoporous Materials*, 71: 199–210.
12. Ghazali, M., Nawawi, M., and Huang, R.Y.M. (1997) Pervaporation dehydration of isopropanol with chitosan membranes. *Journal of Membrane Science*, 124: 53–62.
13. Elabd, Y.A. and Barbari, T.A. (2001) Separating solvation from molecular diffusion in polymers. *AIChE Journal*, 47: 1255–1262.
14. Guo, W.F., Chung, T-S., and Matsuura, T. (2004) Pervaporation study on the dehydration of aqueous butanol solutions: a comparison of flux vs. permeance, separation factor vs. selectivity. *Journal of Membrane Science*, 245: 199–210.
15. Urtiaga, A.M., Casado, C., Aragoza, C., and Ortiz, I. (2003) Dehydration of industrial ketonic effluents by pervaporation. Comparative behavior of ceramic and polymeric membranes. *Separation Science and Technology*, 38: 3473–3491.
16. Guo, W.F., Chung, T-S., and Matsuura, T. (2004) Pervaporation study on the dehydration of aqueous butanol solutions: a comparison of flux vs. permeance, separation factor vs. selectivity. *Journal of Membrane Science*, 245: 199–210.
17. Huang, C., Ng, F.T.T., and Rempel, G.L. (2000) Application of catalytic distillation for the aldol condensation of acetone: the effect of the mass transfer and kinetic rates on the yield and selectivity. *Chemical Engineering Science*, 55: 5919–5931.
18. Gallego-Lizon, T., Ho, Y.S., and Freitas dos Santos, L. (2002) Comparative study of commercially available polymeric and microporous silica membranes for the dehydration of IPA/water mixtures by pervaporation/vapour permeation. *Desalination*, 149: 3–8.
19. Verkerk, A.W., Van Male, P., Vorstman, M.A.G., and Keurentjes, J.T.F. (2001) Description of dehydration performance of amorphous silica pervaporation membranes. *Journal of Membrane Science*, 193: 227–238.
20. Moon, G.Y., Pal, R., and Huang, R.Y.M. (1999) Novel two-ply composite membranes of chitosan and sodium alginate for the pervaporation dehydration of isopropanol and ethanol. *Journal of Membrane Science*, 156: 17–27.
21. Yu, J., Lee, C.H., and Hong, W.H. (2002) Performances of crosslinked asymmetric poly(vinyl alcohol) membranes for isopropanol dehydration by pervaporation. *Chemical Engineering and Processing*, 41: 693–698.

22. Huang, R.Y.M., Pal, R., and Moon, G.Y. (2000) Pervaporation dehydration of aqueous ethanol and isopropanol mixtures through alginate/chitosan two ply composite membranes supported by poly(vinylidene fluoride) porous membrane. *Journal of Membrane Science*, 167: 275–289.
23. Neto, J.M. and Pinho, M.N. (2000) Mass transfer modeling for solvent dehydration by pervaporation. *Separation and Purification Technology*, 18: 151–161.
24. Gallego-Lizon, T., Edwards, E., Lobiundo, G., and dos Santos, L.F. (2002) Dehydration of water/t-butanol mixtures by pervaporation: comparative study of commercially available polymeric, microporous silica, and zeolite membranes. *Journal of Membrane Science*, 197: 309–319.
25. van Veen, H.M., van Delft, Y.C., Engelen, C.W.R., and Pex, P.P.A.C. (2001) Dewatering of organics by pervaporation with silica membranes. *Separation and Purification Technology*, 22-23: 361–366.
26. Nawawi, M., Ghazali, M., and Huang, R.Y.M. (1997) Pervaporation dehydration of isopropanol with chitosan membranes. *Journal of Membrane Science*, 124: 53–62.
27. Won, W., Feng, X., and Lawless, D. (2002) Pervaporation with chitosan membranes: separation of dimethyl carbonate/methanol/water mixtures. *Journal of Membrane Science*, 209: 493–508.
28. Kanti, P., Srigowri, K., Madhuri, J., Smitha, B., and Sridhar, S. (2004) Dehydration of ethanol through blend membranes of chitosan and sodium alginate by pervaporation. *Separation and Purification Technology*, 40: 259–266.
29. Kittur, A.A., Kulkarni, S.S., Aralaguppi, M.I., and Kariduraganavar, M.Y. (2005) Preparation and characterization of novel pervaporation membranes for the separation of water–isopropanol mixtures using chitosan and NaY zeolite. *Journal of Membrane Science*, 247: 75–86.
30. Semenova, S.I., Ohya, H., and Soontarapa, K. (1997) Hydrophilic membranes for pervaporation: an analytical review. *Desalination*, 110: 251–286.
31. Baker, R.W. (2004) Pervaporation. In *Membrane Technology and Applications*; 2nd Ed.; John Wiley & Sons, Ltd: Chichester, England.
32. Fleming, H.L. and Slater, C.S. (1992) Pervaporation. In *Membrane Handbook*; Ho, W.S.W. and Sirkar, K.K. (eds.), Van Nostrand Reinhold Publishers: New York, NY.
33. Slater, C.S., Hesketh, R.P., Newell, J.A., Farrell, S., Gephardt, Z.O., Savelski, M.J., Dahm, K.D., and Lefebvre, B.G. (2005) ChE at Rowan University. *Chemical Engineering Education*, 39: 82–87.
34. Farrell, S., Hesketh, R.P., Savelski, M.J., Dahm, K.D., and Slater, C.S. (2003) Membrane projects with an industrial focus in the curriculum. *Chemical Engineering Education.*, 37: 68–73.
35. Slater, C.S. and Lipski, C. (1997) Development of experimental methodology in pervaporation. *International Journal of Engineering Education*, 13: 210–219.
36. Mencarini, J., Coppola, R., and Slater, C.S. (1994) Separation of tetrahydrofuran from aqueous mixtures by pervaporation. *Separation Science and Technology*, 29 (4): 465–481.
37. Rautenbach, R., Herion, C., and Meyer-Blumenroth, U. (1991) Engineering aspects of pervaporation: calculation of transport resistances, module optimization and plant design. In *Pervaporation Membrane Separation Processes*; R.Y.M. Huang (ed.), Elsevier Science: Amsterdam, The Netherlands.
38. Sulzer Chemtech (2004) Information brochure.