

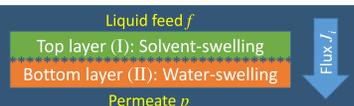
Efficient alcohol/water separation technologies needed

- The removal of water from organic solvents and alcohol biofuels is necessary for the production, blending, and reuse of those organic compounds.
- The EPA's New Definition of Solid Waste rule¹ contains a Remanufacturing Exclusion intended, in part, to promote the reuse/reprocessing of 18 industrial solvents, ranging from chlorinated hydrocarbons to lower alcohols.
- Water forms azeotropes with many hydrophilic organic solvents and biofuels, including 14 of the 18 industrial solvents targeted for reuse, complicating the separation of water/solvent mixtures.
- Conventional thermal separation technologies introduce significant material and energy demands, particularly when azeotropic mixtures are involved.
- Pervaporation and vapor permeation with water-selective membranes enable the removal of water from organic solvents, even when an azeotrope is present.

Rationale for studying multi-layer composite membranes

- Common hydrophilic polymer membranes often swell in water, resulting in permeances and selectivities that are dependent on the water content of the feed.
 - Operation of these membranes at high feed water concentrations may be unfeasible due to chemical or physical vulnerabilities.
- Recently, researchers at Membrane Technology and Research, Inc. demonstrated the benefit of overcoating a water-swelling hydrophilic membrane with a moderately water-selective, non-swelling perfluoropolymer (PFP) film.^{2,3} The non-swelling layer reduced the activity of water throughout the water-swelling hydrophilic polymer layer, resulting in:
 - reduced swelling in the hydrophilic bottom layer
 - increased water selectivity (α) of the multi-layer membrane relative to the base hydrophilic polymer, alone, under high water activities ☺
 - reduced water permeance relative to either layer individually. ☹
- The objective of this project was to assess whether overall multi-layer membrane performance could, theoretically, be improved by replacing the non-swelling top layer with a solvent-swelling, water-selective top layer.
 - Under low water activities in the feed, when solvent activity is the highest, a solvent-swelling top layer should exhibit maximum permeability, allowing the bottom layer to interact with a higher water partial pressure, resulting in:
 - increased water permeance and flux under low water conditions
 - protection of the bottom layer when water content of feed is high.

Multi-layer membrane model



The molar flux, J_i , through a multi-layer permselective membrane is calculated as:³⁻⁵

$$J_i = \bar{\pi}_i(p_i^f - p_i^p) = \bar{\pi}_i^I(p_i^f - p_i^*) = \bar{\pi}_i^{II}(p_i^* - p_i^p) \quad (1)$$

- $\bar{\pi}_i$ is the average permeance of species i in the multi-layer membrane
- $\bar{\pi}_i^I$ and $\bar{\pi}_i^{II}$ are the average permeances of the top (I) and bottom (II) layers
- p_i^f , p_i^* , and p_i^p are the partial pressures at the feed side of layer I, interface between layers, and permeate side of layer II, respectively.

Assumptions:

- The feed is an ethanol/water liquid mixture (e/w)
- Permeances in the top layer and bottom layer are only functions of ethanol partial pressure and water partial pressure, respectively
- The permeate pressure is negligible ($p_i^p = 0$)

If the permeances of layers I and II have been characterized separately as a function of feed partial pressures, also with negligible permeate pressure, then Equation 1 can be rewritten in the following form:³⁻⁵

$$p_w^f \bar{\pi}_w^I(p_e^f, 0) - p_w^* \bar{\pi}_w^I(p_e^*, 0) = p_w^* \bar{\pi}_w^{II}(p_w^*, 0) \quad (2a)$$

$$p_e^f \bar{\pi}_e^I(p_e^f, 0) - p_e^* \bar{\pi}_e^I(p_e^*, 0) = p_e^* \bar{\pi}_e^{II}(p_w^*, 0) \quad (2b)$$

- $\bar{\pi}_i^n(p_w^u, 0)$ is the average permeance of layer n as an individual membrane with an upstream water partial pressure of p_w^u and permeate pressure = 0.

Baseline: Non-swelling layer on top of water-swelling layer

Guided by the assumptions of Huang *et al.*³, permeances of the individual layers were modeled using the following expressions:

$$\text{Top Layer} \quad \bar{\pi}_i = \bar{\pi}_i^0 \exp(\Lambda_{1,i} p_e^f + \Lambda_{2,i} (p_e^f)^2) \quad (3a)$$

$$\text{Bottom Layer} \quad \bar{\pi}_i = \bar{\pi}_i^0 \exp(\Lambda_{1,i} p_w^f + \Lambda_{2,i} (p_w^f)^2) \quad (3b)$$

The baseline case is that of a multi-layer membrane composed of a PFP top layer and a cellulose ester bottom layer with parameters for equations 3a/3b as shown in the table below for pervaporation of ethanol/water mixtures at 75 °C.

	Non-swelling Layer I Water	Non-swelling Layer I Ethanol	Hydrophilic Layer II Water	Hydrophilic Layer II Ethanol
$\bar{\pi}_i^0$ (GPU)	1000	15.4	5060	12.8
$\Lambda_{1,i}$ (cmHg ⁻¹)	0	0	-0.02	-0.009
$\Lambda_{2,i}$ (cmHg ⁻²)	0	0	0.00327	0.00856

Using these parameters and values of p_i^f calculated with the NRTL thermodynamic model (ChemCAD v7.1), along with equations 2 and 3, the permeances and water/ethanol selectivities of the individual layers as membranes and of the multi-layer composite were calculated as a function of feed water concentration (Figure 1).

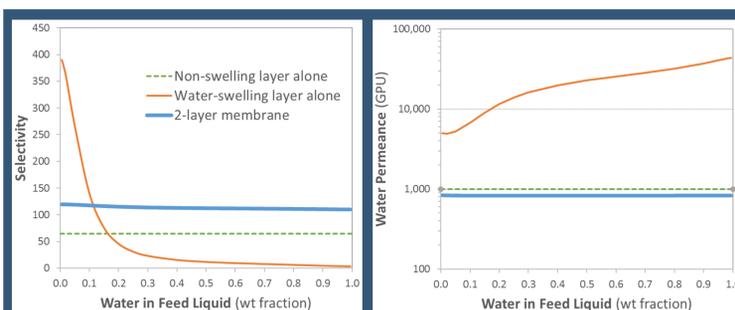


Figure 1. Performance of the baseline multi-layer membrane and of the PFP and cellulose ester layers as individual membranes as a function of feed composition.

The calculated effect of layering the materials is consistent with that reported by Huang *et al.*³: the highly variable selectivity of the water-swelling bottom layer is moderated by the non-swelling top layer yielding selectivities higher than that of the top layer, but permeances below that of the top layer for the entire range of feed compositions.

Achieving increased permeance in multi-layer membranes

- Under the low water levels that may be necessary to meet biofuel or solvent specifications, the partial pressure gradient driving force for water permeation will be quite small.
 - the membrane area required to accomplish water removal at trace levels can be quite significant, even dominating the total membrane area required in a dehydration process.
- As indicated in equation 1, a higher water permeance would counter low water partial pressure differences.
- Assuming the properties of the hydrophilic bottom layer are fixed and represented by those of the cellulose ester layer described above, two options for increasing permeance under low water conditions were considered:
 - Increasing the constant permeance of the non-swelling top layer (Figure 2)
 - Replacing the non-swelling top layer with a material that swells in ethanol such that water permeance increases as ethanol activity increases.

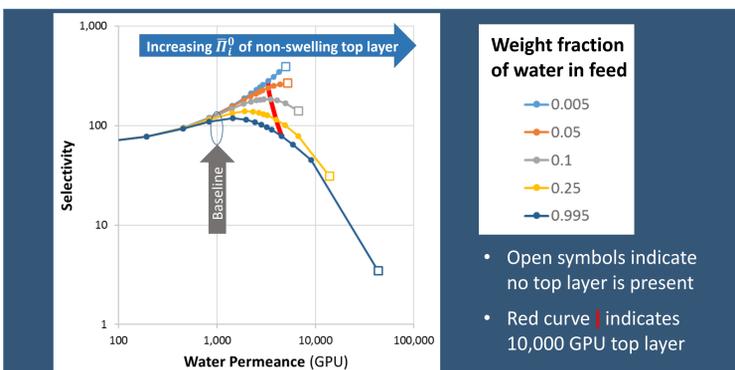


Figure 2. Effect of varying top layer water permeance on selectivity and water permeance of multi-layer membrane (top layer selectivity fixed at 65).

Option 1 – Increase permeance of non-swelling top layer

From Figure 2: Increasing the permeance of the non-swelling top layer yields both higher selectivity *and* higher permeance for the lowest feed water concentrations. However, at higher feed water concentrations, swelling of the bottom layer causes a deterioration in overall selectivity for higher permeance top layers.

- the top layer water permeance delivering maximum selectivity for a given feed composition increases with decreasing feed water concentration

Conclusion: a top layer that naturally increases permeance as feed water concentration decreases (i.e. as ethanol activity increases) should be able to achieve maximum selectivity while still increasing overall permeance and controlling swelling in the hydrophilic layer at higher water concentrations.

Option 2 – Permeance of top layer increases with ethanol

The effect of various ethanol swelling properties of the top layer on performance of the multi-layer membrane, keeping the water swelling characteristics of the bottom layer the same as before, were evaluated.

The properties of the top layer for three scenarios are shown in the table below:

Ethanol-swelling scenario	Max. Water Selectivity (at $p_e^f=0$)	Min. Water Selectivity (at $p_e^f=66.6$ cmHg)	Min. Water Permeance (at $p_e^f=0$)	Max. Water Permeance (at $p_e^f=66.6$ cmHg)
1 [†]	65	65	1,000 GPU	10,000 GPU
2 [†]	65	32.5	1,000 GPU	10,000 GPU
3 [†]	130	65	1,000 GPU	10,000 GPU

[†]The 2nd exponential coefficients in the permeance expressions, $\Lambda_{2,i}$, for the top layer were set to 0.

In Figure 3, the selectivities and permeances of multi-layer membranes with these three ethanol-swelling properties are compared to those of the baseline multi-layer membrane | (top layer constant water permeance = 1,000 GPU and $\alpha = 65$) and a membrane with top layer of constant $\alpha = 65$ but with constant water permeance of 10,000 GPU (| the same as the red curve in Figure 2).

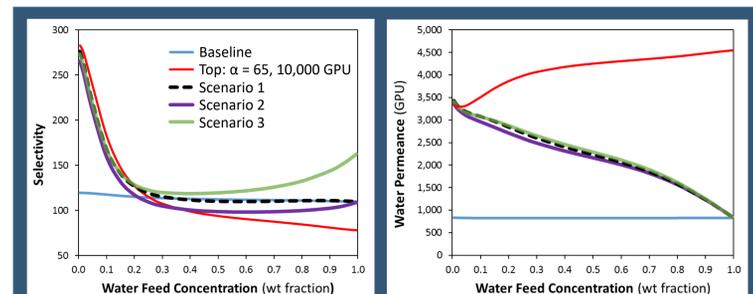


Figure 3. Effect of ethanol-swelling properties of top layer on overall selectivity and water permeance of multi-layer membrane (bottom layer is that of the baseline).

- All of the solvent-swelling scenarios, as well as the non-swelling 10,000 GPU example |, yielded significant enhancements in both selectivity and permeance relative to the baseline | for feeds of less than 20 wt% water.
- The constant 10,000 GPU example | maintained high water permeance over all water concentrations, but exhibited the lowest α for feeds with > 30 wt% water due to high interface water activities and bottom layer swelling.
- If α of the ethanol-swelling top layer under low ethanol activities is higher than that of the baseline (| vs. |), then higher α and permeances are possible.

Conclusions

- Adding a non-swelling top layer to a water-swelling film reduces solvent and water activities in the swelling layer, thereby moderating the properties of the resultant multi-layer membrane, confirming prior literature analyses.
- Increased overall permeance can be most easily accomplished by increasing the permeance of the non-swelling top layer (e.g. a thinner top layer).
- A solvent-swelling top layer may be advantageous, depending on the effect of the solvent-swelling characteristics on permeances and selectivity.
 - Ideally, the top layer would “disappear” at low feed water levels but would provide sufficient water mass transfer resistance to protect the bottom layer from damaging water activities under high water concentrations.

References/Acknowledgements/Disclaimers

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