Perspective

Evolving Beyond the Thermal Age of Separation Processes: Membranes Can Lead the Way

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DOI 10.1002/aic.10330

Introduction

In 2003, the U.S. comprised 4.8% of the world's population and was responsible for a disproportionate 25% of the world's energy consumption (DOE, 2004). The industrial sector was responsible for 33% of our energy consumption, followed by transportation (27%), residential (22%) and commercial (18%) areas. Within the industrial sector some processes, such as raw material refining and polymer production intrinsically require high-temperatures to occur economically. Discounting these special cases, a significant fraction of industrial processes are currently carried out using thermally-driven methods, simply because installed capital investments provide inertia against change.

Electricity generation and separation devices based on *nonthermal processes* are especially attractive avenues to avoid thermodynamically imposed efficiency limitations on heat utilization. Membrane technology, important for nonthermal separation devices, will be the focus of this article. Opportunities offered by linking separation devices and fuel cells will also be considered. Replacing energy-inefficient separation processes requires confronting both materials and processing challenges to more broadly extend benefits available from first generation membranes. Indeed, despite many advantages, membranes have only recently emerged as a realistic platform for use in large scale processes. Since membrane technology is based on deceptively simple fundamentals, early work in this field overlooked the need to integrate four critical capabilities that are discussed later. The realization that membranes require treatment as a *cross-disciplinary specialty area* to allow this integration, has enabled movement of the technology from the laboratory into commercial reality. It is critical to maintain this perspective in order to position membranes to economically handle aggressive feed streams that must be treated to significantly improve the efficiency of global energy use in separations. This improvement is especially important as the world population expands and emerging economies develop.

This article also discusses large scale examples where *over an order of magnitude reduction in energy use* have been achieved by replacing thermally driven approaches with membrane processes. As such, this article should be of interest not only to potential creators of membrane devices, but also to those seeking to introduce energy-saving technology tools.

Membrane Technology-Four Essential Elements

(1) Development of high-efficiency modules with large amounts of area per volume was a necessary first step for the emergence of membranes in large-scale separations. The numbers are impressive: hollow fiber modules can contain 10,000 m^2/m^3 of module, which is over 100 times larger than early plate and frame units (Baker, 2004). Such high-efficiency modules provide the needed volumetric productivity to maintain compact system sizes for large scale applications with huge membrane area requirements.

(2) Creation of advanced materials with tunable capabilities to separate molecularly similar components has been a second key factor in the emergence of membranes as a broadly applicable technology platform. Gels, rigid thermally stable polymers, amorphous carbons, ceramics, zeolites, and metals provide a rich array of choices for forming functional high surface area units to perform separations (Kesting, 1985; Pinnau and Freeman, 1999; Pixton and Paul, 1994; Buxbaum, 1993; Langer and Peppas, 1993; Nair and Tsapatsis, 2003, Akin and Lin, 2002). These materials have applications running the gamut from processing of simple gases to complex biorelated feeds.

(3) Development of sophisticated capability to control microscopic transport phenomena by tailoring of *morphology* at multiple levels within a membrane cross-section has been a less obvious third factor in the emergence of membranes. For instance, in the thickness dimension of Figure 1, a submicrometer ultrathin selective skin region is supported atop low-resistance transition and microporous substrate layers (Carruthers et al., 2003). Within such an ultrathin top layer, additional structure with molecularly-selective and reactive features can exist.

As is the case in Figure 1, the scale of these critical features are truly molecular in nature and too fine to be imaged, even with the highest resolution microscopy. The detailed functional elements present in a membrane vary greatly depending on the

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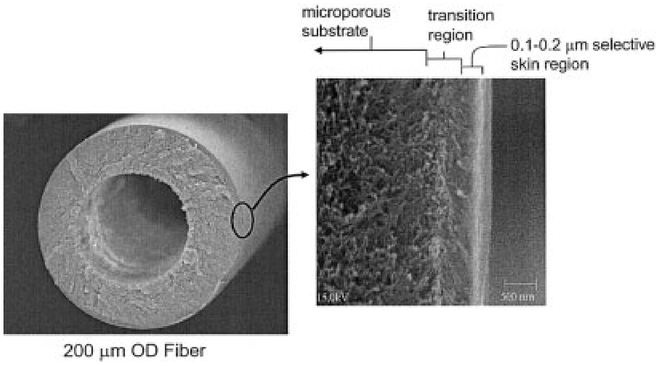

Figure 1. Asymmetric hollow fiber illustrating thin selective layer and an open porous substrate.

The selective layer may be dense, shown here here, or have tailored micro or nano pores that enable either molecular diffusion or viscous flow separation phenonmena to occur. For high-pressure operation, the fiber can be fed on the shell-side, but for low pressure cases bore-side feed is usually best (Carruthers et al., 2003).

particular application of interest. Recent examples of such morphology-engineering involves hybrid structures comprising *preassembled* micro or nanoscale functional entities dispersed in an engineered supporting matrix (Figoli et al., 2002; Mahajan and Koros, 2000). Such an approach allows efficient "offline" engineering of the functional selective entities without compromising rapid economical production of large surface area modules.

(4) The development of manufacturing methods to rapidly link the earlier three elements into economical devices with minimal defects is the critically important "final factor" responsible for commercially successful large-scale membrane systems. Easily overlooked, this high speed processing capability is necessary to achieve cost-competitive modules (Eykamp, 1997). As new materials emerge, rethinking of the details in this "final factor" must also occur.

Figure 2 summarizes the earlier four key elements needed to introduce any new type of membrane process, or even a new generation of the same type of membrane process. The figure also emphasizes a lesson learned in the introduction of early membranes for energy efficient separations: *interlinkage* between these elements is also crucial. Poor connectivity at *interlinkage boundaries* between the four key elements can best be eliminated by viewing membrane technology holistically as an integrated subdiscipline within the chemical engineering paradigm.

Membrane Types and Terminology

This article focuses on synthetic (*man-made*) membranes, and is organized in terms of the "function" that a membrane provides in a particular application. Multiple phenomena, such as diffusion and fluid flow, or diffusion and reaction often occur simultaneously in membrane processes. Focusing on the *key* function to be performed by a membrane usually allows considering secondary effects as details that can be addressed during optimization of the structure within the framework of Figure 2 for each application.

In use, synthetic membranes typically involve transport of components from an "upstream" side to a "downstream" side that is defined by the preferred direction of movement of a specified component. Although microscopic details differ between the various applications, description of the transport process for a component i, across the membrane is possible in terms of the language of irreversible thermodynamics (Merten, 1966; Bird et al., 2002). This framework indicates that the flux of the ith component between upstream and downstream external phases is driven by the sum of the forces acting on the component. In principle, coupling of fluxes of one component to those of others may occur to complicate the description of transport. The negative gradient of chemical potential acting on component i as well as external forces, such as electrical and pressure gradients under different conditions, could all be at play in principle (Merten, 1966).

In fact, an almost unlimited number of net driving force terms $(\mathrm{DF})_i$ can be imposed on each penetrant between the upstream and downstream faces of a membrane. Fortunately, although coupling between effects can occur (Bird et al., 2002), a single driving force source, e.g., pressure, temperature, concentration, or voltage, is often sufficiently dominant in a given application to neglect the others. For such cases, which correspond to practical situations considered in this article, a simple expression given by Eq. 1 is useful to help organize the discussion of the broad membrane field, viz.

$$n_i = [(\text{Driving Force})_i]/(\text{Resistance})_i = [(DF)_i]/R_i \qquad (1)$$

where n_i is the flux of i, equal to the rate of transfer of component i per unit area per unit time. In Eq. 1, $(\mathrm{DF})_i$ is the net driving force acting on component i between the upstream and downstream membrane faces, while R_i is the net resistance retarding movement of i, across the membrane (Lee and Koros, 2002). Terminology for membrane types is summarized in Table 1 along with typical sources of driving forces used in each application and typical size discrimination limits. The resistance term in Eq. 1, $R_{i,}$ usually increases directly with the membrane thickness, so reducing thickness by some percentage generally increases flux by the same percentage. This generalization does have exceptions. For instance, reaction or complexation kinetics within the membrane or nonhomogeneous morphologies within the membrane may cause such exceptions in unusual cases (Crank, 1975, Cussler, 1997).

Most practical membrane processes indicated in Table 1 are continuous steady-state operations with a feed, permeate, and nonpermeate stream. Many types of membrane structures and modules exist, but the simple example in Figure 3 captures the essential features of all such processes. Since membrane pro-

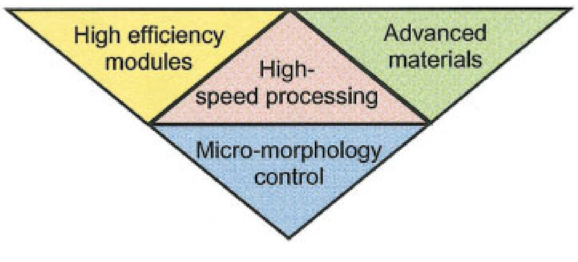

Figure 2. Enabling elements responsible for the emergence of modern synthetic membrane technology.

Table 1. Primary Synthetic Membrane Application Types and Key Characteristics

Function or Application (Abbreviation)	Typical Source of Driving Force	Size Range of Entities Selectively Rejected from Feed*
Microfiltration (MF)	Trans-membrane pressure difference (10–25 psi)	100–20,000 nm
Ultrafiltration (UF)	Trans-membrane pressure difference (10–100 psi)	2–10 nm
Dialysis (D)	Trans-membrane solute concentration difference (1–20 mg/dl)	1–4 nm
Nanofiltration (NF)	Trans-membrane pressure difference (100–500 psi)	0.5–2 nm
Reverse Osmosis (RO)	Trans-membrane pressure difference (100–1500 psi)	0.3–0.5 nm
Pervaporation (PV)	Trans-membrane fugacity difference (5–20 psi)	0.3–0.5 nm
Gas separation (GS) or Vapor separation (VS)	Trans-membrane pressure difference (100–1500 psi)	0.3–0.5 nm
Electrodialysis (ED)	Trans-membrane voltage difference (1–2 volt per membrane pair)	0.3–0.5 nm

*Specific rejection depends upon details of selective layer morphology.

cesses involve separation of a permeated component A from a second, rejected component B, a measure of separation efficiency is useful. Due to the diversity of applications, many different measures of separation efficiency are used in the various membrane subareas in Table 1. Probably, the easiest measure to appreciate is the so-called “separation factor”, SF, given in Eq. 2, which shows the relative enrichment of component A vs. B due to the membrane process (Ho and Sirkar, 1992)

$$SF = \frac{\left(\dfrac{Composition\ of\ A\ downstream}{Composition\ of\ B\ downstream}\right)}{\left(\dfrac{Composition\ of\ A\ upstream}{Composition\ of\ B\ upstream}\right)} \qquad (2)$$

Since the SF is a “ratio of ratios”, any measure of composition (mole fraction, mass fraction, concentration, etc.,) can be used in Eq. 2, as long as one consistently uses the same measure for both upstream and downstream phases in contact with the membrane. Locally within a module, the ratio of compositions leaving the downstream face of a membrane equals the ratio of the transmembrane fluxes of A vs. B. Eq. 1 shows that each component flux is determined by its corresponding transmembrane driving force and resistance acting at that point. Therefore, for fixed feed composition and driving force conditions, a membrane with a high SF imposes a larger resistance on movement of B vs. A than does a membrane with a low SF. Selective restrictions arise from interaction of the membrane with each permeating component. The membrane acts as a “Maxwell’s demon”, with the only apparent moving parts being the penetrants undergoing separation. The ratio of upstream feed compositions in the denominator of Eq. 2 normalizes the SF to provide a measure of efficiency that is ideally independent of this variable.

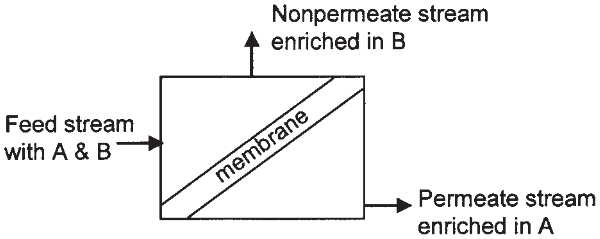

Figure 3. Idealized membrane process showing feed, nonpermeate and permeate streams.

The most permeable (A) component is enriched in the permeate stream, while the least permeable is enriched in the nonpermeate stream. Actual membranes can be flat sheets, spiral wound units, or hollow fibers.

To maximize flux for a given driving force, minimization of the membrane resistance R_i in Eq. 1 requires the smallest possible effective membrane thickness, ℓ. The ability to minimize ℓ without introducing defects relies upon the “micromorphology control” element in Figure 2, so this topic impacts virtually all of the applications in Table 1.

Hydrodynamic Sieving (MF & UF) Separations

Microfiltration (MF) and ultrafiltration (UF) (Table 1) involve contacting the upstream face of a porous membrane with a feed stream containing particles, or macromolecules (B) suspended in a low-molecular-weight fluid (A). The pores are simply larger in MF membranes than for UF membranes. In either case, a transmembrane pressure difference motivates the suspending fluid (usually water) to pass through physically observable *permanent pores* in the membrane. The fluid flow drags suspended particles and macrosolutes to the surface of the membrane where they are rejected due to their excessive size relative to the membrane pores. This simple process concentrates particles or macromolecules in the upstream nonpermeate stream, and produces essentially pure low-molecular-weight permeate downstream (SF→ ∞) if the pore-size distribution prevents any “B” from passage across the membrane.

Back diffusion and secondary flows near the membrane help return the rejected component B to the bulk (Mallubhotla and Belfort, 1997), so the process operates roughly at steady state, with only periodic cleaning. With proper surface pretreatment, nonideal fouling effects due to adsorption of macrosolutes or particles on the membrane can be minimized. Therefore, to a first approximation, one can consider that small solutes have free access to the membrane pore volume, while macrosolutes larger than a critical pore dimension have no access to internal pores. Essentially, the forces on low molecular weight suspending fluids in such membrane pores can be approximated as being equal to those experienced in a *bulk fluid* under equivalent applied fields. This approximation makes the driving force simply equal to the transmembrane pressure difference for MF & UF applications. Moreover, for the low-molecular-weight suspending fluid, the resistance term in Eq. 1 is simply proportional to bulk fluid viscosity, and the effective membrane thickness. Ideally, because macrosolutes larger than the effective pore diameter of the membrane cannot enter the pore, no macrosolute flux can occur ($R_B \rightarrow \infty$), so SF$\rightarrow \infty$. A few oversized pores in the selective layer can reduce observed separation factors; however, macrosolutes that are only slightly smaller than a pore still experience some rejection due to drag from the pore walls (Kulkarni et al., 1992). Therefore, for practical processes, the simplified picture of free passage of small molecules and rejection of macrosolutes larger than some characteristic membrane pore size captures the key aspects of MF and UF separations.

Removal of a bulk liquid often represents the major energy cost for processing suspended particles and macromolecular solutes including paints, foods, and myriad waste recycle streams. For dilute and semidilute feeds ($<$15 vol. %), both MF and UF enable large energy savings compared to evaporation approaches (Blume, 2004; Eykamp, 1997). Despite pumping expenses to drive permeation and minimize accumulation of a rejected component at the membrane surface, energy costs typically range between 0.15–5.0 (kw hr)/m^3 of water removed (Eykamp, 1997; Blume 2004). Generation of electricity using high-pressure steam gives typical efficiencies of 33% or less (Smith et al., 2002), thereby increasing the "thermal equivalent" energy cost for the membrane option. Using a median value of 2.5 (kw hr)/m^3 for such MF & UF membrane processes and accounting for 33% efficiency of steam generated electricity, a value of 2.5/(0.33)= 7.6 (kw hr)/m^3 results. Despite this "penalty", the membrane option offers roughly a *10-fold* savings over competitive thermal removal [$\sim$73 (kw hr)/m^3] by flash evaporation. Even if thermal energy input is needed in a final finishing step, using membranes in primary concentration steps can provide large overall processing cost savings.

Recently, UF processes have even been refined to enable passage of water "component A" and one macrosolute "component B" into the permeate while rejecting a second macrosolute "component C" into the nonpermeate (Figure 3). This fractionation of similarly sized proteins with different isoelectric points relies upon controlling the "effective" size of ionized ("C") vs. nonionized ("B") macrosolutes by adjustment of ionic strength and pH of the suspending fluid (Ebersold and Zydney, 2004). Controlling the local pH enables systematic adjustment of the state of charge of ionizable groups on the ultrafine pores in the membrane selective layer, and on macrosolute "C". This added degree of freedom enables the use of the feed pH to tune relative membrane resistances for a given pore-size membrane. A further extension of this approach enables even the separation of chiral compounds by using a large macroligand to selectively bind and retain one of the enantiomers (Romero and Zydney, 2002). This complexed entity can then be selectively retained in the nonpermeate stream. In these MF and UF cases, the driving force acting on every penetrant is effectively the same and equal to the full transmembrane pressure difference. Nevertheless, for the same transmembrane DF$_i$ and intrinsic pore-size distribution, the preceding case shows that the resistance ratio R_B/R_C, as well as R_B/R_A, can be adjusted by tuning various operating conditions.

Fractionation of Low-Molecular-Weight Mixtures (NF, D, RO, GS)

In Table 1, the size difference between the permeating component A vs. rejected components B, C, etc., decreases as one considers dialysis (D) → nanofiltration (NF) → reverse osmosis (RO) → gas separation (GS) processes. In these more subtle separations, strictly hydrodynamic sieving of a suspending low-molecular-weight solvent A (typically $<$ 3–5 Å) away from suspended B, is *no longer adequate* to achieve the desired fractionation. For the cases involving dialysis and finer discriminations, *intermolecular forces* become dominant determinants of the resistance R_i, acting on each penetrant.

Clearly, transmembrane pressure differences are not the only sources of driving forces (DF$_i$) to motivate separations. In hemodialysis, separate concentration differences can be applied to each penetrant by selecting the downstream "sweep stream" concentration relative to that in the upstream feed (Kessler and Klein, 1992). The feedstream (Figure 3) comprising blood (B) and urea (A), passes across the upstream face of a membrane. Simultaneously, solution (C) (not shown explicitly in Figure 3) without urea, but with an electrolyte concentration matched to that in the feed passes across the lower face of the membrane. A flux of urea (A) occurs into the downstream, and the purified blood (B) remains upstream and leaves as nonpermeate. In electrodialysis, a transmembrane voltage difference acts on mobile ionic species, but not the neutral water molecule (Eykamp, 1997). One can also imagine a similar process with a magnetic driving force if one of the components responds to magnetic fields. As a practical matter, however, the *pressure driven processes* (MF, UF, NF, RO, GS, and VS) in Table 1, are the most easily and economically applied in very large-scale systems that can impact global energy use.

For the micromolecularly selective processes in Table 1, an additional "partitioning" phenomenon also must be considered in the flux expression, to enable describing the process conveniently in terms of external phase conditions. In this case, the partitioning phenomenon can be accommodated as a factor contributing to R_i in Eq. 1 using a "partition coefficient" typically defined as

$$K_i = \frac{[\textit{Concentration of Component i in membrane}]}{[\textit{Concentration of Component i in external phase}]} \tag{3}$$

Since K$_i$ is expressed as a ratio, any consistent measure of composition in the membrane and external phases may be used in Eq. 3. When K$_i > 1$, the membrane acts as a "concentrator" that attracts component *i* from the external phase, and makes it available at the membrane surface for transmembrane movement. Intermolecular forces of solvation and mixing that are responsible for the partitioning process may be entropic, as well as enthalpic, in origin. The balance of these forces acting between the membrane and external phase can cause either a higher or lower concentration of a given solute inside the membrane relative to the external phase. If the tendency to enter the membrane is negligible, the partition coefficient approaches zero, *i.e.,* $K_i \rightarrow 0$.

Membranes with the ability to separate mixtures of low-molecular-weight solutes enable a whole new set of opportunities. Such membranes incorporate both thermodynamic partitioning and kinetic mobility discrimination phenomena within a single integrated unit. This combination of effects is a natural "*process intensification*"that distinguishes such membranes from all other steady-state separation devices. The synergistic action of these two discrimination phenomena permits adjustment of the relative compositions of different small molecules or ions in streams contacting the upstream and downstream faces of a membrane. Even in such complex micromolecular separations, an overall effective resistance R_i, can still be used to describe the inhibition to movement for each penetrant between the upstream and downstream external phases. The effective resistance in this case includes ξ_i, a *specific* mobility restriction coefficient per unit thickness, multiplied by the effective thickness of the membrane ℓ and divided by the partition coefficient K_i, viz.

$$R_i = \frac{[\ell]x[\xi_i]}{[Ki]} \tag{4}$$

Note that ξ_i reflects the full spectrum of factors retarding movement of component *i* across the membrane in response to the imposed driving forces. These factors can be diverse and include, for instance, local structural rearrangements, complexation events and electrostatic interactions between a moving penetrant, and the static membrane. While detailed specification of ξ_i may be complex in the presence of multiple types of forces, the use of such a generalized retardance factor within the membrane helps unify discussion of diverse membrane types. The membrane thickness ℓ scales this average specific mobility restriction coefficient ξ_i, thereby accounting for the extensive nature of the R_i term in Eq. 1. Moreover, the mobility restriction coefficient can be made very large ($\xi_i \rightarrow \infty$) by irreversible complexation (Cussler, 1994; Noble, 1990) or by large resistance to transport through a more densely packed morphology in the membrane (Park and Paul, 1997). Practically, if either $K_i \rightarrow 0$ or $\xi_i \rightarrow \infty$, then $R_i \rightarrow \infty$, so no flux of component *i* occurs, independent of the driving force acting across the membrane in the two external streams.

Adjusting Selectivity for Small Molecules

For a given pair of transmembrane driving forces *(*DF_A & DF_B), the ratio of the effective resistance acting on B *vs.* that acting on A in the membrane, *i.e.*, $R_\mathrm{B}/R_\mathrm{A}$, specifies the membrane-specific ability to separate this A-B pair. Since the thickness factor ℓ cancels: $R_B/R_A = \frac{[\xi_B]}{[K_B]} \Big/ \frac{[\xi_A]}{[K_A]} = \frac{[\xi_B]}{[\xi_A]}\frac{[K_A]}{[K_B]}$. This simple expression shows that the key ratio of resistances acting on component B vs. A is comprised of a product of a partitioning and mobility ratios. For most membranes, the mobility ratio ξ_B/ξ_A, can be approximated as $\xi_B/\xi_A = D_A/D_B$ since: $\xi_i \alpha (D_i)^{-1}$, where D_i is the average diffusion coefficient for component *i* within the membrane phase. In this common case, therefore

$$\frac{R_B}{R_A} \; \alpha \; \frac{[D_A]}{[D_B]}\frac{[K_A]}{[K_B]} \tag{5}$$

Equation 5 correctly suggests that one can tune *both* "mobility selectivity"D_A/D_B and "partitioning selectivity" K_A/K_B to develop "advanced materials" for every small molecule separation application in Table 1 (Koros et al., 1988). This strategy can be applied to virtually any type of membrane material ranging from gels to crystalline zeolites, metals, glasses or polymers. Moreover, *hybrid materials* comprised of combinations of more than one such material (e.g., a zeolite dispersed in a polymer) allow overcoming limitations associated with any specific pure component material type. For instance, intrinsic rigidity responsible for outstanding mobility selectivity in zeolites also causes brittleness and difficulties in their high speed processing. Polymers are processable, but lack the rigidity to perform fine mobility selectivity. Mixtures of zeolites and polymers or molecular sieve carbons and polymers are now being investigated to create highly selective hybrid materials amenable to economical high-speed fabrication (Ekiner and Kulkarni, 2003; Vu et al., 2003). As will be discussed in more detail, such materials are likely to be increasingly important for dealing with a broad range of future applications.

Reverse Osmosis- A Prototype Large Scale Success

Reverse osmosis purification of water was the first large scale commercially viable membrane fractionation of *low-molecular-weight* liquid mixtures. Like all of the cases involving low-molecular-weight fractionation in Table 1, RO purification of potable water from brine relies upon "partitioning selectivity" and "mobility selectivity" contributions in Eq. 5. Optimization of the membrane material and structures for this application took place over two decades, but membranes are now rapidly displacing thermal desalting (Marks et al., 2004; Pankratz and Toner, 2003). By understanding how and why RO has displaced distillation in this large-scale application, one can see how to help expand the energy-efficient membrane paradigm more broadly.

Both gas separation and RO require high feed pressures to achieve useful fluxes. Nevertheless, the *utility* of having a *high-pressure* nonpermeate stream leaving the module in Figure 3 differs greatly for GS vs. RO cases. For gases, the energy used to compress feed streams is valuable in subsequent processing and product storage. On the other hand, for liquids, after the RO separation is completed "excess pressure" in the nonpermeate is not needed. Reclaiming this energy is now standard procedure in state-of-the-art RO systems. "Pervaporation" is a variant of reverse osmosis that uses a low-pressure liquid feed with a *vapor permeate* under vacuum. Effectively, pervaporation involves permeation and evaporation of a portion of the feed, thereby requiring significant thermal energy input (Eykamp, 1997). While overcoming the need for high-pressure feed and nonpermeate energy recovery, pervaporation still requires the input of considerable thermal energy. Because it eliminates this thermal inefficiency associated with pervaporation, reverse osmosis became the favored process for water desalination.

The "effective" driving force in Eq. 1 for reverse osmosis permeation of water is proportional to the difference in applied transmembrane pressure,ΔP, and the transmembrane osmotic pressure $\Delta \Pi$, viz, $DF_i = [\Delta P - \Delta \Pi]$ (Merten, 1966). For 50% recovery of feed entering with 34,000 ppm of total dissolved salts in seawater, the stream leaving the module has a very large osmotic pressure. This osmotic pressure must be overcome to produce the last increment of potable water product leaving the module. As noted earlier, providing a large transmembrane ΔP *without* paying an excessive energy cost is commonplace in state-of-the-art reverse osmosis operations with compact energy recovery turbines (Marks et al., 2004). This practice of recovery of unused energy in compressed nonpermeate streams (Figure 3) should be transferable to organic systems as well.

A state-of-the-art RO seawater system produces over *100 million gallons per day* with 50% feedwater recovery as potable water product using a 940 psi (~65 bar) feed pressure (Marks et al., 2004). These high pressures and flows are now routinely accommodated economically with compact vessels and high productivity membranes. An optimized thermal distillation plant with the same feedwater requires 1014 Btu/gal [73 (kw hr)/m^3] of water produced (Pankratz and Tonner, 2004), while the state-of-the-art seawater RO system has an energy cost of only 2.2 (kw hr)/m^3) (Marks et al., 2004, Pankratz and Tonner, 2004). Using the current paradigm of steam cycle generation of electricity with an efficiency of only 33%, the effective "thermal equivalent" energy cost for the membrane process is (2.2/0.33)(kw hr)/m^3) = 6.7 (kw hr)/m^3). Thus, even with a "penalty" factor, the membrane option is over *10 fold more efficient* than the thermal approach.

It is well-known that electrochemical oxidation of a fuel to extract power can theoretically be performed in a fuel cell much more efficiently than is possible via a heat cycle. For example, a H_2/O_2 fuel cell reaction at 25°C has an ideal efficiency of 83% at 25°C, as compared to 30–33% in optimized heat cycles. Current fuel cells still require improvement, and rarely exceed 50-60% efficiency; however, this already surpasses the 33% efficiency for optimized thermal systems (Brandon et al., 2003). Using a conservative 50% efficiency limit, a fuel cell coupled to a reverse osmosis unit would show an improvement of $73/(2.2/0.50) > 16$ fold better than the thermal alternative**!** Whether one considers the already achievable 10-fold reduction without fuel cell integration or the 16-fold reduction achievable by eventually coupling this membrane process with a fuel cell, the numbers are impressive. These numbers also give a vision of a much more energy efficient future if the membrane platform is extended to *nonaqueous applications*. More advanced dual cycle (gas turbine plus steam turbine) thermal systems can increase thermal efficiencies to 50–60%, thereby matching those of many existing fuel cells. Clearly, however, complex thermal systems are nearing the end of their technology optimization development curve, while fuel cell are only at the beginning of theirs. Moreover, by operating at low-temperatures fuel cells naturally overcome NOx generation problems, which complicate operating at the higher-temperatures needed to benefit from the advantages of such dual cycle thermal system.

The greater energy efficiency of membranes for performing separations, and of fuel cells for conversion of chemical bond energy into electrical energy clearly makes their combination especially attractive. On the other hand, the well-known thermodynamic *inefficiency* in generation of electricity using high-pressure steam can be linked to the unfortunate widespread acceptance of the inefficiency of doing thermally-driven separations. Specifically, generation of electricity using high-pressure steam produces excess low-pressure steam: this fact is often used to justify continuation of inefficient separation processes driven by this excess low value steam (Steinmeyer, 1997). In fact, discussions of thermal separation efficiencies are sometimes based on the efficiency of an ideal heat engine operating between the reboiler and condenser temperatures. Such an approach overlooks the intrinsic limitations of *all* thermally driven processes and perpetuates the unnecessary linkage between thermal energy conversion processes and separation processes.

Energy Efficiency Increases-No Need to Wait for the "Ultimate" Membrane

It is *not necessary* to wait for perfection of nonaqueous reverse osmosis systems to begin benefiting from savings associated with membrane separations. Meaningful savings are possible using available gas and vapor separation membrane units, while aggressively pursuing development of nonaqueous RO and its larger energy payoffs over the next decade. Vapor separation processes are operationally similar to gas separation units but often use a light vacuum downstream, depending on the vapor pressure of the components at the feed temperature. Reconfiguring existing thermally driven processes to produce vapor feeds to membrane units for targeted fractionations of valuable component could be an attractive evolutionary strategy. As economical nonaqueous RO capability develops, these processes should phase out the older thermal units in the same rapid evolutionary manner that is currently occurring in the aqueous RO arena. Even rapid evolution takes time (10–15 years), as it did for aqueous systems. Such a process should begin now to avoid further proliferation of additional energy inefficient separation units to meet expanding capacity needs.

In fact, capacity expansions of existing thermally-driven separation units are ideal ways to introduce membranes more broadly into large-scale use while minimizing risks and building familiarity with this relatively new technology. This approach leverages existing investments without the need to build entirely new thermally-driven separation units. Within an existing integrated plant, valuable compounds within a vapor feed stream currently sent to another thermally driven separation unit could be *membrane-fractionated* into higher value products, with minimal expense and significant energy savings. Consider, for instance, the 515 Btu/lb (0.151 kwhr/lb) reboiler energy inputs for the propylene/propane separation using cryogenic distillation (Humphrey and Keller, 1997). With a typical 50/50 feed and recovery of a 99.5% propylene product, this corresponds to roughly 0.302 kw hr/lb propylene product. A recent vapor permeation membrane process patent cites an energy cost of roughly 0.050 kw hr/lb propylene product for

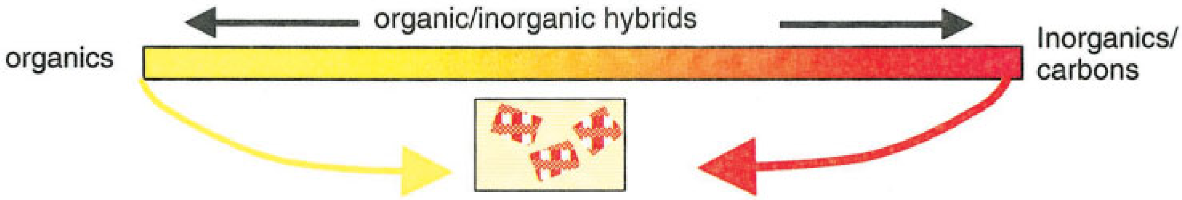

Figure 4. Advanced materials spectrum, including not only the extremes of organic polymers and inorganic or carbon materials, but also hybrids of these materials to provide property and processing advantages.

this separation, with a membrane having intrinsic properties similar to those currently reported in the literature (Collings et al., 2004). As in the water RO case, accounting for the current paradigm of steam cycle generated electricity with a typical efficiency of only 33% gives the effective "thermal equivalent" energy cost of (0.05/0.33)Btu/gal = 0.151 Btu/gal-still greatly superior than the thermal option. Moreover, as in the RO example, integrating such a process with a 50% efficient fuel cell shows an improvement of 0.302/(0.05/0.5) > 3-fold better than the thermal alternative**!** First generation membranes have been reported with properties that suggest this separation can be achieved (Yoshino, 2003), so this type of application is likely to develop over the next few years.

In addition to emerging applications like that noted above, hydrogen separation units with excellent reliability records have proven valuable in petrochemical applications, and their popularity continues to grow (MacLean and Graham, 1980; Zolandz and Fleming, 1994). Membrane-based monomer recovery units have also been installed recently for propylene polymerization vent gas streams (Baker, 2003). Finally, membranes are being deployed for large-scale sites, especially offshore where their compact size and light weight is attractive and growing (Gall and Sanders, 2002; Sanders, 2003). While the above trends are desirable, to significantly impact the global energy efficiency picture, a realistic strategy is needed to accelerate them.

Key Hurdles to Overcome for Nonaqueous Separations

Despite the previous examples for large-scale (>10 million SCFD) gas separations noted above, these applications represent a small fraction of potential membrane-based applications inside refineries and chemical complexes. Three related hurdles exist to broadly extending existing membrane separation successes to other low-molecular-weight organic compounds: these hurdles are the lack of economical materials, membranes and module fabrication methods. Indeed, large osmotic pressures, higher temperatures and more aggressive organic feeds in these systems will require even more robust membranes and modules than are currently available for water feedstreams. These are real, but surmountable, hurdles that can be addressed in the context of Figure 2. For instance, at 25°C an osmotic pressure of roughly 79 atm (1161 psi) must be overcome to cause forward flux of propylene from a 75/25 molar mixture to produce a 95/5 molar downstream mixture of propylene and propane. Such pressures can even now be contained within a compact membrane vessel, and some gas separation modules already operate with higher-feed pressures. Such an RO system would even further increase the energy savings below those cited for the propylene/propane vapor separation case mentioned previously.

Much of the technology for gas and vapor separation materials, membranes and modules that are now emerging as large-scale units were derived from work supported on reverse osmosis in the early 1960's (Lonsdale, 1982). This program by the Office of Saline Water (OSW) targeted energy-efficient processes based on the promising, but unproven (*at the time*) membranes for aqueous separation. These early membranes were, at that time, in a similar state to those for current organic systems, and many problems had to be overcome (Merten, 1966; Lonsdale, 1982). While sharing some aspects with aqueous feeds, nonaqueous feeds present new challenges that must be attacked holistically within the framework of Figure 2. A program similar to the OSW initiative, but aimed at organic feeds and high-pressure gases and vapors, would be a positive step in this direction and an investment in the future. Such a sea-changing undertaking probably requires government initiation as it did in the visionary OSW case. Despite demanding requirements for selectivity and robustness in this next generation of applications, membranes, and modules *must retain their attractive cost advantages.* Realistically, therefore, any program to introduce truly new high- performance membranes should incorporate hybrid materials within its enabling vision. A complete picture of membrane materials includes the spectrum ranging from purely inorganics and carbons to purely organic polymers shown in Figure 4. Current work has really only explored the two extreme ends of this spectrum, plus a few hybrids containing 10–15% inorganic or carbon dispersed phases in a polymer continuous phase. For future demanding applications, it is likely that the optimum position in the materials spectrum in Figure 4 may be even past the "midpoint" in hybrid composition. Indeed, very high percentages of inorganic or carbon solids, compatibly bound within an appropriate polymer matrix, could be the preferred membrane material of the future for many applications. Such hybrids have the potential to provide the selectivity and strength of inorganics and carbons, and the processability and flexibility of polymers.

Some Concluding Thoughts

The earlier illustrations show that major, even revolutionary, energy savings are possibly relative to competitive thermal options by introducing membrane processes for separations. Nevertheless, the discussion also clarifies the need for a large-scale integrated systematic approach to greatly broaden the economical application of membranes to more aggressive feed streams. This information highlights the need for modeling and analysis that starts at megascale plant systems and ranges down to the molecular scale where most separations ultimately occur. Materials science is a critical component; however, technologies to engineer supermolecular membrane morphologies and economical modules are equally critical to build such an expanded platform. In addition to its central role in advanced separation devices considered here, aspects of membrane technology impact fuel cells, advanced batteries used in hybrid vehicles, and low cost flexible solar energy cells. Applying all of these related energy saving devices across the various sectors of society mentioned in the introduction of this article would motivate rational change toward energy efficiency. The special opportunities for synergistic combination of fuel cells and membrane separation technologies should be vigorously pursued to break the unnecessary current linkage between inefficacies in thermal energy conversion processes and separation processes. The U.S. has taken action to promote the introduction of fuel cells, advanced batteries, and solar cells; however, much less aggressive action is apparent to promote energy efficient separations. A concerted program focused on developing the membrane platform beyond its current state to enable rapid replacement of energy-inefficient separation processes is needed badly. If emerging economies outside the US with fewer installed thermal processes ultimately make investments in these more efficient approaches, our economy based on thermal dinosaurs stands to be the biggest loser– *natural selection works!*

Acknowledgments

Support is acknowledged from the Georgia Research Alliance, the DOE, under grant DE-FG03-95ER14538, and the National Institute of Standards and Technology, ATP Project Number 00-00-3968.

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