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Water and Beyond: Expanding the Spectrum of Large-Scale Energy Efficient Separation Processes

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Introduction

It is appropriate to begin any discussion of large-scale energy efficient separation processes by mentioning water purification. Membrane-based size discrimination between permeated water and nonpermeated species has undergone an impressive 3-4 order-of-magnitude refinement, while maintaining economically attractive productivities by engineering of materials, morphologies, and modules.[1–3] The ability to remove microsolutes differing in size by a few angstroms from water molecules also provides a useful starting point for the even finer-scale discrimination needed in large-scale nonaqueous applications. This Perspective illustrates principles needed for upstream purification of hydrocarbons encountered in the petrochemical industry, petroleum refining, and contaminant removal from flue gases related to oil-, coal- and natural gas-generated electrical power. Furthermore, separation issues related to shale gas, an emerging topic impacting both environmental and energy security issues will be considered to identify opportunities and further illustrate the potential of advanced separations as ''game-changers'' in the pursuit of global sustainability.

Widely-used large-scale purification and separation processes, generally, still rely largely upon thermally driven phase-change-based separations. This fact increases global energy consumption for separations in production of fuels, refined chemicals and electricity generation, in contrast to cases considered here that seek to minimize such phase-change-based separations. Energy costs and CO_2 emissions for processes, employed in the extraction and production of oil, natural gas and coal are largely ''invisible'' until these energy resources are passed to downstream processes. Needless to say, many of these processes involve extensive separations and are also quite energy intensive. As the world shifts increasingly to the use of natural gas as a low-carbon raw material, removal of acid gases and water comprise significant energy costs per unit of product. In downstream petrochemical and manufacturing processes, roughly 45% of production energy is associated with separations.[4,5] Finally, environmentally acceptable electrical power generation in the future is likely to not only be concerned with removal of SO_x and NO_x, but also CO_2, which are all heavily dependent on separation processes.

Therefore, while it is difficult to provide an exact amount of energy used by all these separation processes, it is clear that current separation energy costs are not only large already, but will continue to grow if ''business-as-usual'' scenarios are pursued in the future for capacity expansions to meet demand. With global population already passing 7 billion, and heading toward 10 billion by 2050, demands will accelerate as developing countries pursue higher standards of living. Various estimates of the fraction of global energy consumption associated with separations are difficult to assess, since the embedded energy cost for commodities can be accounted for in different ways. Whether the figure is 5, 10 or 15% on a 2012 basis*, business-as-usual approaches to carrying out these vital processes will place a major burden on energy resources and result in significant CO_2 emissions. If this scenario were unavoidable, like the second law of thermodynamics, it would be necessary to view the heavy cost of separations as nature's tax on our high standard of

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*To give a sense of scale, 5% of world energy consumption is equivlalent to approximately 25 quads (Energy Information Association). For comparison, total worldwide renewable energy (hydro, biomass, solar, and wind) production in 2008 was approximately 50 quads.

living. Fortunately this is not the case—we have a clear choice. In fact, the water purification case provides useful proof of this fact. Indeed, the ideal energy cost of producing pure water from a large source of typical ocean salt water via ideal demixing across a membrane is only approximately 1 kWhr-m^{-3},[6] while the heat of vaporization to distill the same amount of pure water is roughly 640 kWhr-m^{-3}. By clever heat management in optimized multistage flash processes, this energy cost can be cut to roughly 50 kwhr-m^{-3} in practical processes.[7,8] On the other hand, due to the realities of pumping fluids past membrane surfaces to minimize concentration polarization and the need for application of feed pressures beyond the osmotic pressure of the feed to provide economically attractive fluxes, the real cost energy cost for desalination is roughly 4.5 kWhr-m^{-3};[6,7] clearly more than an order of magnitude lower than that for optimized, heat integrated, thermally driven processes.

Expanding such savings to nonaqueous systems has proven to be challenging for reasons that will be discussed in later paragraphs. However, similar large potentials exist for diverse nonaqueous mixtures as well. Efficient heat management, as in the above thermally driven desalination, can help mitigate energy costs in nonaqueous cases as well. Major savings, however, require changing the paradigm in order to minimize phase transformations and thermally driven separations. Such a strategy can deliver the order of magnitude energy savings required to make advanced separations a powerful vehicle for reducing energy use and CO_2 emissions from large-scale processes. Besides benefitting global welfare in a general sense, adopters of low-energy intensive separations will also have competitive advantages by debottlenecking and ultimately replacing intrinsically more energy intensive methods that also have large CO_2 footprints.

Membranes and Sorbents: A Path Forward

Membranes are particularly attractive for cases in which high-to-medium contents of a desired component exist in a feed,[9] such as water purification cases, or the production of an inert, nitrogen-enriched stream from air for blanketing large drilling operations. Production of purified water, with return of the concentrated brine to the environment, is simple. In the case of water purification, the pressurized nonpermeate "reject" stream can be used in economical energy recovery turbines to reconvert the stored chemical potential back into mechanical energy.[10,11] This arrangement allows most of the consumed energy to be used only for the demixing process. Similarly, concomitant generation of a small O_2-enriched stream, which is subsequently sent back into the atmosphere, and a compressed nitrogen enriched product stream also minimizes the need for complex additional treatment of the product stream. For nitrogen enrichment, the pressurization of the feed need not be recovered, since this pressurization is useful to motivate delivery of the product to its point of use. In both cases, mechanical energy is transformed to chemical potential energy to allow the low-energy intensive demixing to achieve the desired product.

In cases involving low-to-medium feed contents of a desired component, such as CO_2 capture from a flue gas feed—which has a low CO_2 chemical potential—sorbents are strong competitors to membranes.[9] For instance, selecting a sorbent with a strong affinity for CO_2 favors transport, despite the low-chemical potential of the CO_2, by providing a still lower chemical potential for CO_2 in the sorbed state. Unlike convenient steady-state membrane cases, where a constant chemical potential gradient moves water or oxygen permeate across a membrane, low-energy intensive sorbent systems are complicated by the need for a regeneration step. Nevertheless, by minimizing regeneration thermal penalties or by pressure reduction, low-energy intensity sorbent processes can compete effectively against membranes. Selecting between the membrane and sorbent options may also involve issues beyond strictly the energy intensity of demixing. For example, in novel cases where process integration is possible in flue gas capture approaches, membranes may still be the preferred option.[12,13]

Independent of whether membrane or sorbent options are pursued, the ability to economically manufacture and package surface area is key to economically deploying large-scale, low-energy intensive processes. This fact becomes clear from Eq. 1, where some measure of productivity (e.g., megaton per year, billion standard cubic feet per day, etc.) is represented as the product of flux and area

$$\begin{aligned}\text{Productivity} &= [\text{Flux}] \cdot [\text{Area}] \\ &= \frac{[\Delta\mu(\text{Chem. Potential})]}{[\text{Resistance}]} . [\text{Area}]\end{aligned} \tag{1}$$

The aforementioned relation applies whether the productivity measure involves steady state flux across a membrane or sorption/desorption fluxes ("swing capacity") into or out of a selective sorbent. For any *specified* productivity in either a sorbent or membrane, limits exist on the practical ability to reduce resistance (Eq. 1). To allow the minimum $\Delta\mu$ for the specified productivity, maximizing the contact area across which transport occurs remains the only option. This simple fact is analogous to the heat transfer case where the required ΔT across a heat-transfer device can be minimized by using a high-thermal contact area. The ability to configure membranes and sorbents to maximize the thermodynamic separation efficiency to a value approaching the free energy of demixing distinguishes them from less advanced separation approaches. Of course, creating high contact surface area modules requires balancing capital cost with operating cost advantages, so there is a critical need to create low-cost but effective high-surface area devices. Indeed, while special materials are critical to achieve the separations needed, it is module manufacturing, rather than specialty materials that are usually the limiting cost factors. This fact makes device engineering and fabrication more important in all advanced low-energy intensive processes by comparison to conventional thermally driven bulk separations[†]. Attractive approaches to address this need are the focus of much of the rest of this Perspective.

An Evolutionary Path for Membrane Development

To illustrate the aforementioned facts, membrane cases will be considered first, since the evolution of this

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[†] By analogy, advanced separation systems are as different from bulk separation systems as microelectronics are from traditional electronics (e.g., vacuum tubes).

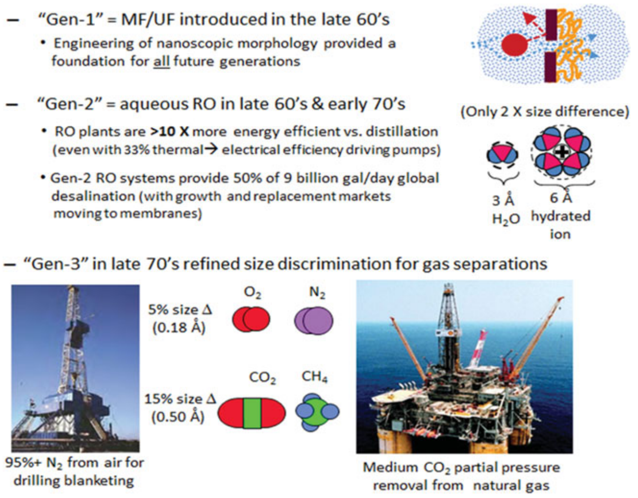

- "Gen-1" = MF/UF introduced in the late 60's
  - Engineering of nanoscopic morphology provided a foundation for all future generations
- "Gen-2" = aqueous RO in late 60's & early 70's
  - RO plants are >10 X more energy efficient vs. distillation (even with 33% thermal→ electrical efficiency driving pumps)
  - Gen-2 RO systems provide 50% of 9 billion gal/day global desalination (with growth and replacement markets moving to membranes)
- "Gen-3" in late 70's refined size discrimination for gas separations

Figure 1. Three generations of practical large-scale membrane processes have emerged since 1960.

technology platform shows a useful pattern that offers opportunities to be captured by the judicious design of sorbent systems as well. As indicated in Figure 1, broadly speaking, beginning in the 1960s, three well-defined generations of membrane systems have emerged over the last 50 years. The story started with water. The ability to remove progressively smaller particulates and eventually even solvated macromolecules from aqueous feeds by micro- and ultrafiltration comprised the first membrane generation (Gen-1). Despite impressive hydrodynamic membrane filtration capabilities in Gen-1, discrimination still involved separating 3 Å water molecules from entities that were orders of magnitude larger. Practical Gen-2 aqueous reverse osmosis membranes emerged in the late 1960s with the ability to reject microsolutes similar in size to 3 Å permeating water molecules. Specifically, these more advanced Gen-2 membranes could discriminate between free water and hydrated cations and anions with characteristic dimensions of roughly 6 Å, i.e., a 100% difference in size.

Practical gas separations such as O_2 removal from air or CO_2 removal from natural gas required another significant step to achieve discriminations that were up to 10 times finer in percentage size difference. Such membranes did not emerge as Gen-3 until the late 1970s due to their more advanced requirements. For instance, O_2 and N_2 differ by only 0.18 Å in effective minimum size. This small size difference is about 5% of the effective molecular diameter of the rejected N_2 and primarily enables the separation. Indeed, sorption (partition) selectivity only provides roughly a factor of 1.3 in favor of the more condensable O_2 vs. N_2, while the small size-dependent diffusion selectivity can be as high as a factor of 3-4, in favor of O_2 in Gen-3 membranes.[14] The two factors provide an overall intrinsic O_2 vs. N_2 "permselectivity" equal to the ratio of the permeabiliities of the two components or the product of the diffusion selectivity and partition selectivity, i.e., equal to $1.3 \times 4 > 5$ for a standard Gen-3 membrane. In general, the permeability of a component A provides an intrinsic measure of material productivity, which equals the flux of the component, normalized by the transmembrane driving force and effective membrane thickness L_m. This key parameter can also be expressed as the product of the penetrant diffusion coefficient (D_A), and sorption or partition coefficient (K_A), i.e.

$$\begin{aligned} P_A &= \frac{[\text{Flux of A}]}{[\text{transmembrane driving force of A}]/[L_m]} \\ &= [D_A][K_A] \end{aligned} \tag{2}$$

For asymmetric membranes with thin skins that are difficult to measure, another term, the so-called *permeance*, P_A/L_M, is commonly used. Independent of whether permeability or permeance is used, L_m is the same normalizing resistance for all components. So, intrinsic permselectivity equals either the ratio of permeabilities or ratio of permeances of component A and B. Furthermore, the product of the ratio of the diffusion coefficients and the partition coefficients for component A vs. B defines the intrinsic selectivity

$$\begin{aligned} \frac{P_A}{P_B} &= \frac{[\text{Flux of A}]}{[\text{Flux of B}]}\frac{[\text{transmembrane driving force of B}]}{[\text{transmembrane driving force of A}]}\frac{[L_m]}{[L_m]} \\ &= \frac{[D_A]}{[D_B]}\frac{[K_A]}{[K_B]} \end{aligned} \tag{3}$$

Equation 3 indicates that one can tune both "mobility selectivity" $[D_A]/[D_B]$ and "partitioning selectivity" $[K_A]/[K_B]$ through the judicious design of "advanced materials". However, an important example of a Gen-3 membrane illustrates the associated difficulties with the simple and broad implementation of this ideal approach. Specifically, CO_2 removal from natural gas to enable transport in low-cost carbon steel pipelines appears deceptively simple, since it has both a favorable size selectivity difference between CO_2 and CH_4 of 15% (vs. 5% for O_2 and N_2), and a favorable partitioning selectivity provided by the higher critical temperature of the CO_2 vs. CH_4. At low CO_2 partial pressures where membrane matrix swelling is low, this simple independent tuning strategy works fairly well. Unfortunately, the tendency for supercritical CO_2 to swell and soften rigid matrices of typical polymers, used for low CO_2 partial pressure feeds in Gen-3 membrane systems, presents a major new challenge.[15,16] For instance, natural gas feeds containing 40–50 mol % CO_2 at high pressures (~1000 psia) represent the demanding conditions that "Gen-4" membrane systems must face. The term "Gen-4" will be used in the rest of this discussion to mean membranes that are derived from polymers, but which address challenges not treatable via Gen 1-3 membrane systems *mentioned previously*.

A discovery enabling hyper-rigid defect-free selective layers via reactive interfacial polymerization to be packaged into spirally wound modules displaced the thicker skin fiber technology for Gen-2 reverse osmosis membranes. However, the technology to create ultrathin skins via reactive interfacial polymerization proved impractical for dry gas separations and fibers were rediscovered, since they also offer roughly 10 × higher surface-to-volume vs. spiral wound modules. These Gen-3 fibers also are more sophisticated than the earlier Gen-2 fibers, have thinner selective layers, approaching those of the reactively formed Gen-2 layers, and can be "caulked" to repair nanoscopic defects.[17]

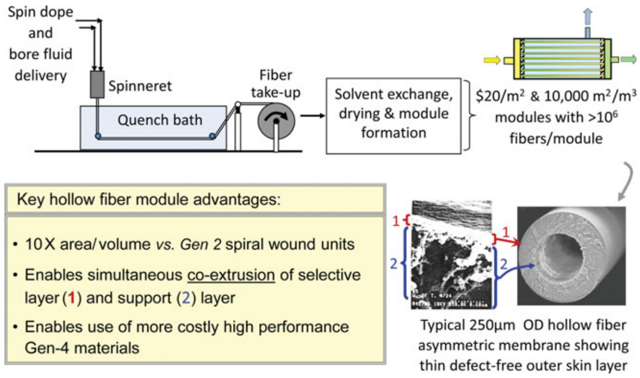


Figure 2. Gen-3 hollow fiber asymmetric membrane modules exceed capabilities of Gen-2 spiral wound flat sheet module technology.

In addition, advanced Gen-3 fibers were spun with composite structures, comprising more costly but more selective, thinner layers supported on low-cost polymers.[18,19] Such membranes, with ∼300 μm dia., yielded productive high surface-to-volume ratio modules that were a major step forward toward enabling separation of even relatively low-sorbing gas penetrants, e.g., O_2 and N_2. Figure 2 gives a schematic representation of the hollow fiber approach with highlights regarding the advantages it offers.

To significantly impact global energy use, a wide spectrum of separations must be addressed effectively. The CO_2/CH_4 case is only one of many that must be considered. To allow broad application, it is wise to select an approach capable of optimizing performance vs. cost across most of the large-scale energy-intensive molecular separations spectrum. Hollow fibers are key elements in such a strategy. In addition, one must select appropriate candidate ''advanced materials'' to enable evolutionary advancement of the technology base with minimal needs for disruptive changes in the existing manufacturing paradigm.

Linking the need for advanced materials and the need for minimal disruption to existing manufacturing approaches makes it questionable to consider even highly effective advanced materials such as zeolites, ceramics, metals and metal organic framework materials as monolithic selective layers in the design of Gen-4 membrane systems. Indeed, forming such advanced materials that offer higher selectivity performance currently requires a radically different manufacturing paradigm from that which has led to high surface-to-volume ratios in commercial Gen-1, -2 and -3 modules. This simple fact represents the major practical hurdle to using these advanced materials to address Gen-4 needs. Fortunately, the evolutionary fiber-based path discussed here enables development of increasingly sophisticated materials beyond Gen-3 polymers to create membranes with performance and cost to meet the diverse needs of Gen-4 membranes. The first step on this path begins with crosslinked polymers to overcome swelling-induced performance losses.[20,21] The next step involves hybrids, comprising polymer in a blend with inorganic or metal organic framework nanoparticles; thereby providing some of the separation advantages of hard-to-process advanced materials, while maintaining processing simplicity of polymer fiber spinning.[22] Finally, the most evolved form—comprising carbon molecular sieve (CMS) materials—offers extraordinary capabilities like other advanced materials, but with only a single pyrolysis step, using precursors derived from Gen-3 type polymer fibers.[23] This increasingly sophisticated family of materials offers the potential to address all but the highest temperature and most oxidizing feeds. This family of materials does address the needs of the most important large-scale separation needs of interest to current processes, as well as the needs of biobased and alternative feedstock processes. A workable strategy to implement this vision will be illustrated next through the examination of several representative cases. Moreover, opportunities to transfer advanced fiber-based membrane technology to enable advanced sorbent technology will also be illustrated using examples for CO_2 capture and possible processing of shale gas.

Generation 4 Membrane Example 1—High-Concentration Acid Gas Removal from Natural Gas

Cellulose acetate (CA), a derivative of natural cellulose with most of the available hydroxyl groups acetylated, is a classic Gen-3 membrane material. CA offers relatively good permselectivities for CO_2 vs. CH_4 (∼40 shown by the open green point in Figure 3)[24,25] when the CO_2 feed partial pressure is below 100 psi. At higher values of CO_2 partial pressure, swelling-induced softening of the glassy polymer matrix (''plasticization'') undermines the 0.5 Å size and shape discrimination needed to provide sufficient diffusion selectivity, which enables the high intrinsic permselectivity.[24] An increase in permeability due to the higher CO_2 diffusion coefficient, while seeming attractive, is quickly overshadowed in terms of overall performance by the selectivity loss shown by the green arrow in Figure 3. The change is drastic. For example, the low-partial pressure selectivity of 40 for CO_2/CH_4 is reduced 5-fold to 8 in the face of high CO_2 partial pressures. For a 50:50 feed this means that for every 8 molecules of CO_2 that permeate, 1 molecule of CH_4 also permeates and is reinjected into the reservoir in a dilute, economically unrecoverable form.

One concept that has been explored for preventing plasticization-induced selectivity loss relies on polymer crosslinking. While various approaches to crosslinking have been explored, an easily implemented example involving a highly selective copolyimide material can be considered to illustrate the evolutionary approach in the design of the requisite materials, noted earlier. Essentially, chemical crosslinks between two polymer chains act to reduce the amount of CO_2-induced chain swelling at high CO_2 partial pressures. It is first useful to review the so-called ''spinnable polymer upper bound tradeoff line'' shown in Figure 3. While various versions and generations of this line have been reported,[26] the most current one is shown in Figure 3. For equivalent packing of chain segments, for increasingly rigid chain backbone structures needed to enable diffusional jumps, higher selectivity but lower permeability polymers result. In terms of Eqs. 1 and 3, the lower CO_2 permeability and higher selectivity reflect lower values of D_{CO_2}, but higher values of $[D_{CO_2}]/[D_{CH_4}]$ to distinguish the 0.5 Å difference between

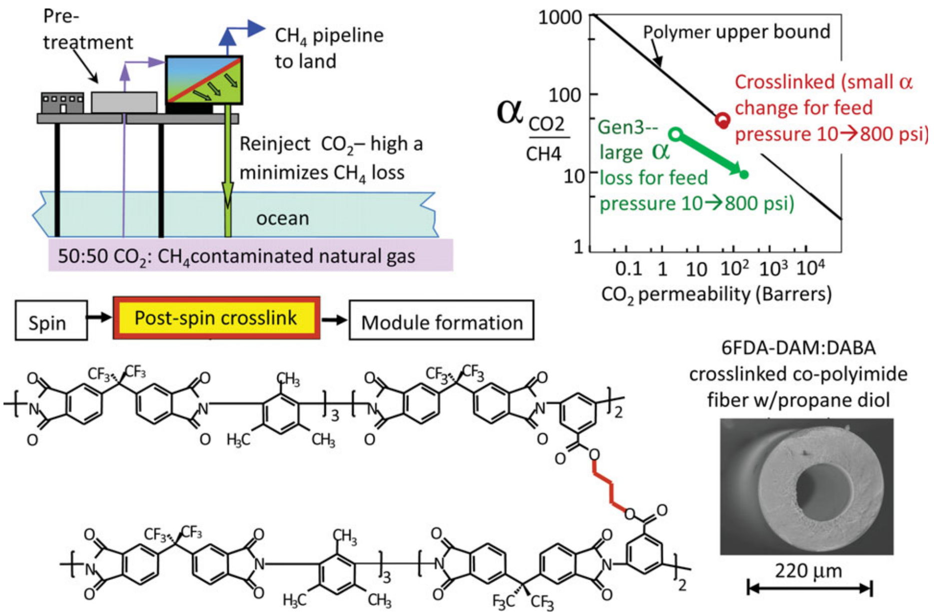


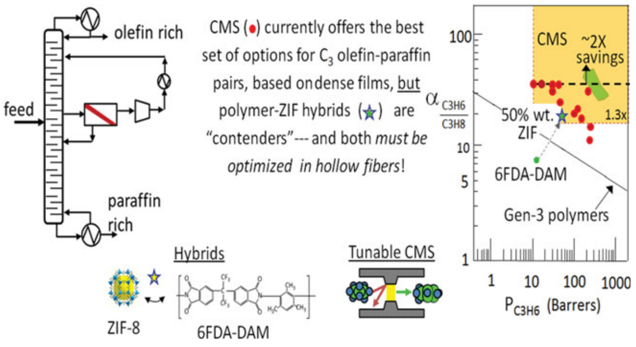
Figure 3. Gen-4 crosslinked membranes for high CO$_2$ content natural gas cleanup.

CO_2 and CH_4. Partition coefficient selectivities primarily reflect differences in critical temperatures between CO_2 (300 K) and CH_4 (191 K). Groups such as the acetates on cellulose acetate that interact with CO_2 can increase $[K_{CO_2}]/[K_{CH_4}]$.[24] While increasing partitioning selectivity is useful for low-partial pressure feeds like flue gases, stronger swelling at high CO_2 partial pressures undermines the all-important diffusion selectivity $[D_{CO_2}]/[D_{CH_4}]$ with a net loss in performance. Besides plasticization, which is associated with high-feed pressures, a high-transmembrane flux of CO_2 can carry some sorbed CH_4 by bulk flow in a nonselective mode across the membrane.[27] These facts make it questionable whether it is desirable to introduce strongly attractive groups in polymers meant to be used for industrially relevant, high CO_2 pressure membrane separations. Additional issues also arise in selecting polymers for such an application, since for hyper-rigid polymers, dissolution to make spinning solutions is impeded, and the economical hollow fiber spinning paradigm breaks down.

The copolyimide structure shown in Figure 3 balances the factors noted earlier and falls close to the upper bound line, defined in 2008, with a selectivity of roughly 45 for low-pressure feeds[28]. The intrinsic permeability and selectivity are somewhat higher than those of CA even for low feed pressures of a 50:50 mixture. More importantly, however, the copolymer, when crosslinked with a short chain diol (propane diol), maintains a high selectivity at very high-feed pressures of 50:50 mixtures. In contrast to the CA case, described earlier, for roughly every 45 CO_2 molecules that permeate, only 1 CH_4 permeates and is reinjected in the reservoir, which is roughly only a 2.2% product loss compared to the 1/8 or 12.5% loss in the case of CA. This excellent performance is indicated by the essentially unchanged selectivity and permeability for the open red point in relationship to the solid red point at low- and high-feed pressures, respectively, as shown in Figure 3. Not only is the membrane performance attractive, but also the process shown in Figures 2 and 3 to achieve this performance is attractive, requiring minimal changes in the manufacturing lines for the fabrication of Gen-3 materials to form a fully asymmetric crosslinked membrane. By tuning the dope composition and spinning conditions, monoesterified copolymer with at least one diol per two carboxylic acids can be spun as an asymmetric fiber via the approaches used for simple noncrosslinkable fibers shown in Figure 2.[28] The fibers then go through a solvent-exchange step in order to prevent capillary-force-induced pore collapse during drying. However, unlike a simple Gen-3 material, crosslinking can be achieved using the diol sidechains. To achieve this crosslinking, by performing the final drying stage at an optimized higher temperature, intersegmental crosslinking and rigidification occurs while the desired asymmetry is maintained. Indeed, the fabrication of the final membrane adds virtually no new processing steps and is effectively an "evolved Gen-3" (i.e., a Gen-4) material.

Generation 4 Membrane Example 2—Propane-Propylene Debottlenecking

One of the most energy intensive petrochemical processes involves the so-called "thermal cracking of hydrocarbons", which creates mixtures of light olefins and paraffins for a very broad range of diverse applications.[4] Current global ethylene production comprises over 253 billion pounds/yr, while propylene comprises 84 billion pounds/yr worldwide. These large capacities, coupled with the great similarity between the C_2 olefin and paraffin and the C_3 olefin and paraffin molecules require highly energy intensive separation trains. The largest column on petrochemical sites is usually the so-called "C_3 splitter".[29] This large C_3 distillation unit creates a purified propylene distillate for



CMS (●) currently offers the best set of options for C_3 olefin-paraffin pairs, based on dense films, <u>but</u> polymer-ZIF hybrids (☆) are "contenders"--- and both *must be optimized in hollow fibers*!

Figure 4. Generation 4 hybrids and carbon molecular sieve (CMS) materials are attractive olefin-paraffin "debottleneckers".

use in the production of polypropylene and other higher value products, plus a propane product that can be recycled for additional cracking to propylene. While both C_2 and C_3 olefin-paraffin pairs are important, the C_3 pair is more amenable to membrane separation due to slightly greater difference in diffusion coefficients between propylene and propane vs. ethylene and ethane. The effective size difference between C_3H_6 and C_3H_8 is only about 0.1 Å (roughly 5%); compare it to the the 15% difference for CO_2/CH_4 and the 100% size difference between water and hydrated ions in Gen-2 aqueous reverse osmosis (RO). Thus, the C_3H_6/C_3H_8 case is effectively 3 × more difficult than the CO_2/CH_4 case and 20 × more difficult than the Gen-2 RO case on the basis of size discrimination alone. Moreover $[K_{C_3H_6}]/[K_{C_3H_8}]$, the partitioning selectivity based on critical temperatures is very low, so Gen-3 polymers typically produce overall permselectivites less than two.[30] Required performance for debottlenecking shown in the gold region of Figure 4 lies above the spinnable polymer upper bound line. Moreover, crosslinking like that used for CO_2/CH_4 is unlikely to be helpful, since maintaining intrinsic properties is insufficient in this case—so actual boosts above the upper bound are needed. Although approximate, one can infer the required permeability and selectivity to allow a roughly 1.3 × and 2 × increase in productivity at equivalent energy cost.[31] This performance domain is shown in Figure 4 via dashed lines with the assumption that a selective layer of 2 μm or less can be achieved in the final asymmetric membrane used.

In the past, extensive carrier facilitated transport and complexation work sought to avoid confronting the challenging small-size difference, noted earlier.[32] Trace reactive impurities and carrier instabilities undermine these approaches, so more robust, but highly challenging, sized-based diffusion selectivity is likely to be the preferred path to the Gen-4 membranes for the C_3H_6/C_3H_8 debottlenecking goal. A finely tuned molecular sieve carbon can, in fact, be used to reach this goal, reflecting the end point on the evolutionary fiber-based path mentioned earlier in relationship to Figure 2. Dense carbon films with mixed gas selectivities in the target range have already been reported,[33] and translating these properties into a 1-2 μm asymmetric membrane would provide the required debottlenecking solution. Attractive properties have also been reported for carbon molecular sieve (CMS) composites supported on alumina[33] and the metal organic framework material ZIF-8, and as such, these materials offer alternative paths for this application.[34] In one reported case, a pure ZIF-8 selective layer on a flat sheet silica support had high permeability and selectivities in the range of the dense carbon film and the composite carbon on alumina[35] (green swath in Figure 4). A second ZIF-8 option involving incorporation of ZIF-8 into a mixed matrix hybrid at 50 wt % loading in the 6FDA-DAM polymer matrix also provides properties within the desired property zone. Even at a 50 wt % loading, however, the hybrid showed less selectivity than the pure ZIF-8 on alumina or the CMS[34] in Figure 4. Costs are likely to be lower and tailorability may be greater for CMS compared to metal organic frameworks, based on the known tunability of CMS.[36] At this early stage, however, pure CMS fiber, hybrid polymer-ZIF-8, and composite ZIF-8 or composite CMS each have attractive aspects, and these candidates need processing optimization prior to real implementation. The hybrid polymer-ZIF-8 fiber and CMS fiber options offer advantages of scalability consistent with the existing fiber spinning platform as indicated in Figure 5.

Without processing breakthroughs, composite pure ZIF-8 or CMS layers on porous alumina will be much more expensive than hybrid polymer-ZIF-8 or pure CMS fibers. Moreover, high-quality supports needed for such composites are expensive and not easily scaled-up. To be cost-competitive with pure CMS fibers, much lower-cost supports would be needed for composite membranes.

Hollow Fiber Membrane-Inspired Sorbents for CO_2 Recovery from Flue Gas

Dealing with CO_2 emissions from use of hydrocarbon resources is one of the large challenges facing the globe in this century. CO_2 management requires global strategies to avoid hampering long term economic sustainability and welfare. Even more than water, CO_2 management is a global issue due to facile atmospheric mixing between sources from both responsible low CO_2-intensive emitters and less responsible high-intensity CO_2-emitters. Replacement of coal by natural gas, precombustion CO_2 capture, oxycombustion, chemical looping, cellulosic biofuels and advanced algae can offer some long term mitigation.[37] More rapid CO_2 reductions via postcombustion capture and sequestration from more than 5,000 world-wide large-scale coal-fired power stations is also possible, but the only "ready" approach appears to be based on aqueous amines of various types.[38] These aqueous amine approaches are energy

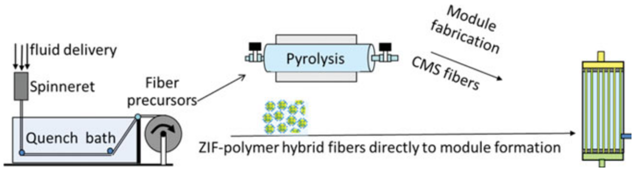


Figure 5. Process advantages exist for both hybrid ZIF-polymer fibers and CMS materials.

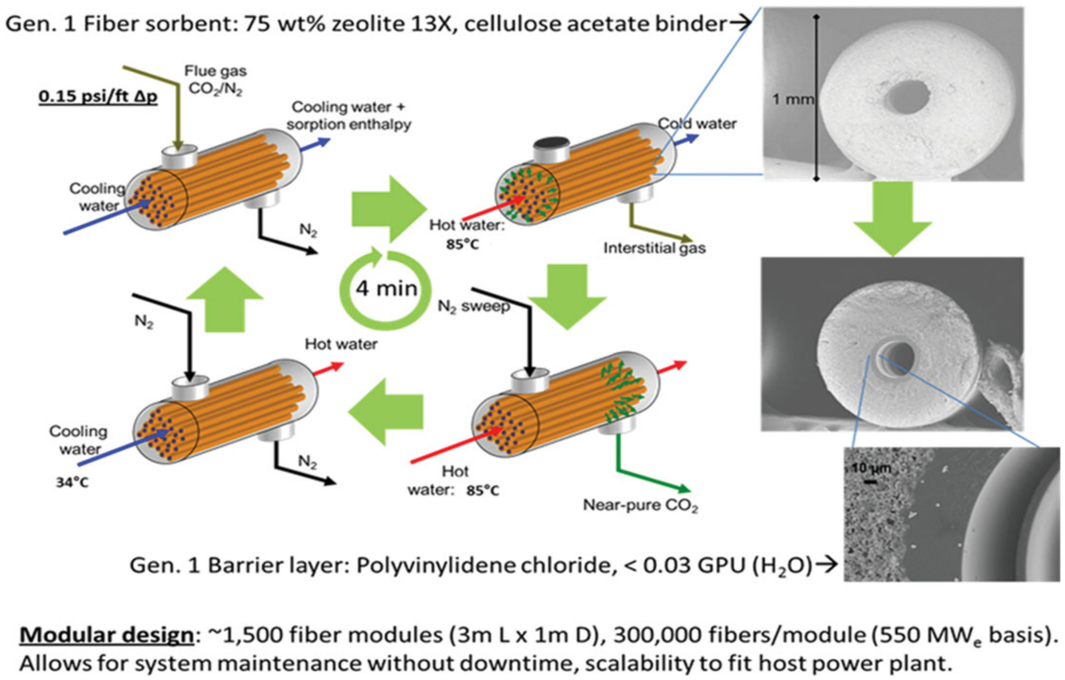


Figure 6. Fiber sorbents in "rapid thermal swing adsorption" mode for post-combustion CO$_2$ recovery.

intensive, even with heat integration, as indicated in various technoeconomic estimates for typical 550 MW$_e$ coal fired power stations.[39–41]

A less energy intensive approach based on engineered fiber sorbents, using the same basis guidelines, result in more attractive estimates of 15–25% parasitic load and $39/tonne CO$_2$.[39,42] Efficient packing of large-fiber sorbent surface areas into low-pressure drop contacting modules, containing engineered amine sorbents,[43] shown in Figure 6, is the enabling feature of this approach. The fibers comprise 1,200 μm dia. highly porous sorbents with a 400 μm bore lined with highly impermeable lumen layers (shown in Figure 6),[42,44] which allow for these fibers to be high-efficiency "adsorbing heat exchangers". Such devices allow integration options that are unavailable to pellets or monoliths, and feature characteristics borrowed from the membrane paradigm that include modularity, spinnability, and post-treatment protocols.[44,45] To process 10^6 SCFM of 13% CO$_2$ atmospheric pressure feed flue gas, 1,500 modules (3 m L $\times$ 1 m D) containing 300,000 fibers/module are being considered.[46] The modular approach allows for system maintenance without downtime and easy scalability to fit different size host power plants. Moreover, relatively easy module design modifications and manufacturing platforms from current large-scale hollow fiber modules can minimize costs. Heat integration[42,47] is also enabled by the adsorbing heat exchange concept that permits capture and reuse of sorption enthalpy in addition to simple sensible heat exchange used in traditional aqueous amine absorption processes. Several variants on this approach, including nanoparticle solid supported amines and sorption of task-specific high capacity ionic liquids into the interconnecting porous walls of the fibers are under active development.[48,49]

The impermeable lumen layers[44] allow for temperature control. Specifically, during sorption, water flows in the fiber bores for efficient utilization of the selective sorption centers. Moreover, subsequent rapid desorption can be achieved for regeneration of the fiber using only hot water.[50] By avoiding the use of steam, which is typically used in aqueous amine absorption processes,[38] more heat integration options become available. Moreover, the highly porous fiber walls allow high diffusional exchange rates with the selective sorbent entities and the external shell-side flue gas.[42,51] Rapid 2–4 min cycles of the modules between sorption and desorption stages shown in Figure 6 are also enabled by the small fiber wall dimensions.

A New Direction: Separation Challenges in Water-free Shale Gas Development

Disposal vs. treatment and ultimate reuse of the significant amounts of water used in hydrofracturing of shale gas reservoirs is currently receiving considerable attention,[52–54] with a variety of approaches under discussion. Shale gas reserves clearly have enormous potential to provide energy and raw material resources for the US extending into the next century. Despite this benefit, the unconventional methods currently needed to access these resources also have potentially large environmental costs that require attention.[55] Membranes could assist greatly in allowing concentration of wastewater for disposal and even allowing recycle and reuse of a major portion of the water used in the process. Here we consider a possibly even more attractive option.

In principle, water use in so-called "hydraulic fracking" of freshly drilled wells to enable the flow of gases to the wellhead can be eliminated by a new technology, called "gas fracking".[56] This technology is less environmentally disruptive, since it eliminates the need for aqueous fracking fluids and their subsequent processing. Gas separation is relevant to this new approach since, as outlined below, gas fracking can be complemented with sorbent technology to capture and recycle propane, the main component in the gas fracturing fluid, rather than considering it a waste. Specifically, gas fracking uses gelled propane with stabilized proppant particles (usually fine sand) to hold the fractured reservoir formation open for easy gas flow to the well head for collection after fracturing. Since propane is miscible with natural gas, its backflow to the well-head occurs naturally after the gel is broken by depressurization. Moreover, gas collection efficiency can be higher than with conventional methods.[56] By offering a compact on-site option for separating the gas mixture at the wellhead, the propane can be reconstituted with the required fresh proprietary gelling agent and proppant particles for local and onsite reuse. This strategy eliminates the need for hauling fresh water to the site and hauling and disposal of contaminated waste "flow-back" water. A separation process, related to the fiber-sorbent approach described earlier, can be envisioned to separate the miscible propane-methane mixture at the wellhead, which reduces the already low-environmental impact of gas fracking by allowing for onsite recovery of propane. Furthermore, this fiber sorbent process could be used for recovery of naturally occurring C_2-C_4 in gas wells with high "condensable" content. There are many complications such as particulate flow, entrained water, and other volatile organics such as benzene, toluene and xylene. Nonetheless, the flexibility, adaptability and compactness of the fiber sorbent platform make it well-suited for this ultra-challenging application. Specifically, the use of conventional filtration and microfiltration as well as the use of guard beds for feed pretreatment prior to the fiber sorbent unit are details requiring attention.

Traditional packed beds could, in principle, also be used in such a process. Nevertheless, the higher bed pressure drops, particle fluidization, particle attrition and bed heat management difficulties associated with traditional pellet beds can be mitigated with the fiber sorbent approach outlined previously. While some of these benefits can be captured by monolith sorbent designs, only hollow fiber sorbents can provide such intimate contact with a thermal moderator.[50] Moreover, fiber sorbents offer tunable options to minimize overall mass-transfer resistances and unutilized bed lengths in comparison to traditional packed beds, thus greatly reducing the total column length and system footprint. Finally, rapid fiber sorbent cycling promotes efficient sorbent utilization and overall system downsizing relative to traditional pellet packed beds for easy mobility to inconvenient sites.[58]

Summary and Outlook

Large-scale separation processes present both challenges and opportunities for CO_2 emission reductions and energy efficiency improvements. The challenges are associated with replacing traditional, energy inefficient, phase change-based separation devices with those that approach the thermodynamic demixing limit. The opportunities exist from the anticipated growth in world-wide demand for commodity products, and the possibility of performing the separations needed in a much more efficient manner than traditional methods. Examples in the upstream and downstream hydrocarbon processing sectors have been illustrated in this article. Additional examples could also be presented for diverse alternative feedstock systems as well. In fact, these alternative hydrocarbon sources are more challenging than those for the traditional petrochemical industries.

We have shown that membrane and sorbent devices are key elements for enabling major reductions in energy intensity and CO_2 emissions in a representative group of these industries. Nevertheless, for these devices to become a widespread reality, not only are advanced materials critical, but significantly more advanced manufacturing processes are needed for the fabrication of these devices. Analogous to the microelectronics revolution, the fabrication cost of advanced separation devices must be reduced sufficiently to enable their broad use. Separation device cost can decrease dramatically by more broadly relying on the readily scalable fiber manufacturing platform, which has served the large volume textile fiber industry well. Clearly membranes and sorbents described here are much more complex than simple textile fibers; in the same way as micro- or nanolithographically produced components are more complex than components produced from traditional macroscale lithography. This fact notwithstanding, in manufacturing of both microelectronics and advanced separations, chemical engineering skills are crucial for transforming specialty materials into high-value-added devices. Moreover, in the case of separations, the combination of capabilities within our discipline also makes it uniquely well-suited to integrate such next generation separation systems into existing processes based on hydrocarbon as well as future alternative feedstocks. Our community, therefore, truly "owns" this area, and promoting its advancement must be one of our key priortiies.

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