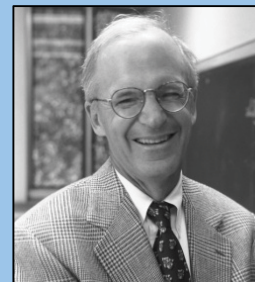# Can Separation Processes Be More Energy Efficient?

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1. Introduction

Chemical separations and chemical reactions are the two critical steps of today's chemical industry using roughly equal amounts of energy. Chemical separations are, at the moment, extremely inefficient. This paper will discuss ways in which their efficiency could be improved. For distillation, we should expect continuing evolutionary improvements, but not a dramatic change in paradigm. To improve energy efficiency by going beyond distillation, we should focus on absorption and membrane processing. This paper will first discuss why major improvements in distillation are unlikely. It will then explore two aspects of membrane processing which are suitable for non-cryogenic gas separation and for water ultrafiltration.

2. Key Features

Distillation. Chemical separations use about 10 percent of the total world's energy consumption. Distillation is the workhorse, requiring a million barrels of oil per day in the U.S. alone. Distillation typically has an efficiency of approximately 11 percent, although olefin-alkane separations like those of ethylene and ethane are still less efficient. The U.S. Department of Energy identifies these olefin-alkane separations as the greatest opportunity for improved energy efficiency.

The reason why distillation is so inefficient is a consequence of vapor-liquid equilibria and the second law of thermodynamics. The minimal energy required for distillation should be that of unmixing. After all, a distillation column simply uses heat to reverse mixing, splitting a feed into a distillate enriched in the more volatile component, and bottom streams depleted in that same component. However, the energy used in distillation is dramatically greater than the energy of unmixing. This energy, added to the distillation column as heat in the reboiler, must be sufficient to ensure significant liquid and vapor flows in the column. In common engineering terms, these flows ensure that the operating lines lie below the vapor-liquid equilibrium line. In more physical terms, these flows are required so that diffusion always occurs from high concentration to low concentration. These concentration differences are smallest at pinch points which occur either in the top of the bottom of the column or near the feed. The magnitude of the flow rates are a direct consequence of the second law of thermodynamics, reflected by the particular vapor-liquid equilibrium curve, and will not be overcome by any changes in equipment. Distillation is implicitly energy inefficient.

At the same time, we can hope that by changing column internals, we accelerate the mass transfer between liquid and vapor and at least come closer to the restrictions of the vapor-liquid equilibrium. Again, in common engineering terms, we expect that the height of distillation tower l is given by:

$$l = HTU \cdot NTU \tag{1}$$

where the height of the transfer unit, HTU, is a measure of the efficiency of the equipment, and the number of transfer units, NTU, describes the difficulty of the separation. When distillation columns are operated with a small NTU achieved by using a large reflux ratio, there is a large vapor flow per flow of distilled product, and hence a large heat load in the reboiler. This large heat load is a principal factor why distillation is energy inefficient. Our hope is that we can reduce the HTU, which is given by:

$$HTU = \frac{G}{k\,a} \tag{2}$$

where G is the vapor flux, k is the overall mass transfer coefficient, and a is the interfacial area per column volume.

We want to change the column internals to make the HTU as small as possible. In the past thirty years, improvements in the HTU have largely come from the use of structured packing, rather than random packing. Structured packings supply a larger interfacial area per volume. They also produce more even flows so that true countercurrent contacting is more completely approached. Even though they do not

supply significantly larger mass transfer coefficients, they do supply larger interfacial fluxes, smaller HTUs, and hence a closer approach to the limits of the second law.

We should expect modest gains in efficiency from the continued evolution of structured packing. Other innovations in distillation promise bigger gains but are much less likely. For example, experiments in the last few years suggest that we could make distillation dramatically more productive by extending structured packing to distillation in hollow fibers. Such hollow fibers have been shown to produce eighty or more times productive equipment than is possible even with the best structured packing. However, the hollow fibers are at the moment so fragile that they are very unlikely to find application in the petrochemical industry, although they might be useful for olefin-alkane separations.

Thus the situation for the efficiency of distillation seems clear. We can expect little improvement in the difficulty of the separation characterized by the NTU. We can expect continuing but minor improvements in the efficiency of distillation equipment as described by the HTU. However, we are unlikely to obtain dramatically improved energy efficiency for distillation simply because of the consequence of the vapor-liquid equilibrium.

Absorption. For large improvements in energy efficiency, we must look either to absorption or membrane processing. For absorption, we want to seek absorbents which show highly nonlinear isotherms. We are particularly interested in isotherms shaped like a step function, that is which absorb nothing at low solute concentrations but quickly saturate above a critical concentration. Such absorbents are known. The most common example is hemoglobin in blood. Examples of industrial relevance include zeolites and inorganic salts, which do show isotherms like this with carbon dioxide or ammonia. However, efforts at dramatically improved absorption require unsteady processes which are the antithesis of the normal operating procedures. Such processes are speculative.

Membrane Separations. A second, more developed option is membrane processing. Membranes are already used for the non-cryogenic separations of hydrogen from refinery gases and of nitrogen from air. In these processes, gas at high pressure is exposed to a membrane with a selective layer less than 0.5 μm thick. One component of the gas selectively permeates the membrane and is concentrated on the low pressure side. The energy efficiency of this process is claimed to exceed 50 percent. Such membrane processes have two major applications in hydrocarbon processing which have not been fully realized: the separation of carbon dioxide from methane, and the separation of olefins from alkanes.

Membranes which show different permeabilities for these different gases are already known and are, in some cases, available as commercial skid-mounted systems. This is especially true for the separation of carbon dioxide from methane. However, these membranes perform often much less well than expected, because the selectivities claimed are frequently based on the ratio of the permeabilities of pure gases. For example, many have claimed that the permeability of pure carbon dioxide through a specific membrane is eighty times greater than the permeability of pure methane through that membrane. This is true for the pure gases. However, for mixed gases, the ratio of the two permeabilities drops dramatically to perhaps around four. This is illustrated in Figures 1 and 2 for the separation of ammonia, hydrogen, and nitrogen diffusing across perfluorosulfonate membranes (Nafion). Thus the energy efficiency of this type of separation is dramatically diluted.

We have been trying to recover these lost selectivities using membranes based on block copolymers. Such block copolymers self-assemble at a nanometer scale to make a variety of nanometer-sized structures. For example, some of these assemble to make monodisperse pores. When these pores are filled with polymer, their selectivity is less affected by having feeds of mixed gases. For example, the selectivity of ammonia through the block copolymer membranes is over eighty times the flux of the hydrogen and nitrogen, as shown in Figure 3. When the pores are empty, as shown in Figure 4, the ultrafiltration of water requires ten times less energy than with existing ultrafiltration membranes.

3. Conclusions

There are some opportunities for energy efficient separations. These are not in distillation where we should expect continued optimization but no dramatic breakthroughs. They may come from absorption and membrane processes. Though these clearly have risk, they merit investigation simply because the energy required is significantly less than in distillation.
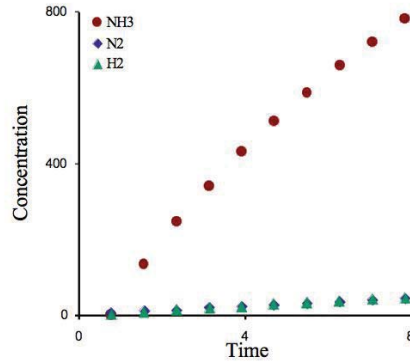
Figure 1. Diffusion of pure gases across Nafion. Ammonia is over one thousand times more permeable than hydrogen and nitrogen.
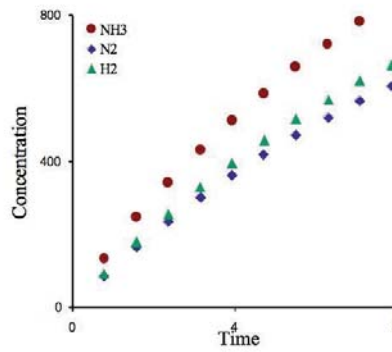

Figure 2. Diffusion of mixed gases across Nafion. The selective separation expected from Figure 1 is not observed; the separation process fails.
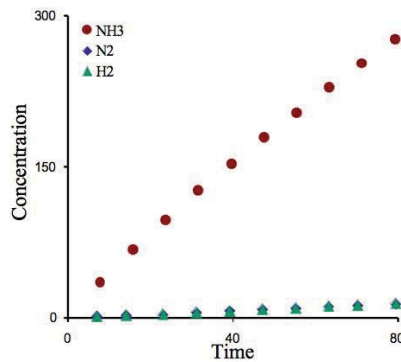

Figure 3. Diffusion of mixed gases across a block copolymer membrane. Ammonia is one hundred more permeable than either hydrogen or nitrogen, both for a mixed as feed (shown) and for pure gas feeds (not shown).
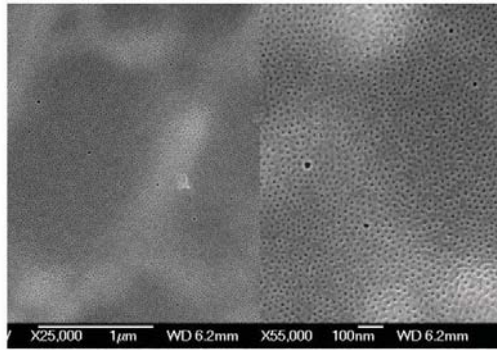
Figure 4. Monodisperse Nanopores Based on Etched Block Copolymer Membranes. Pores like these are especially valuable for remaining viruses from drinking water.

Speaker's Biography

Edward L. Cussler, currently Distinguished Institute Professor at the University of Minnesota, received the B.E. with honors from Yale University in 1961, and his M.S. and Ph.D. in Chemical Engineering from the University of Wisconsin in 1963 and 1965, respectively. After thirteen years teaching at Carnegie-Mellon University, Cussler joined the University of Minnesota in 1980. He has written over 200 articles and five books, including *Diffusion*, *Bioseparations*, and more recently, *Chemical Product Design*. Cussler has received the Colburn and Lewis Awards from the American Institute of Chemical Engineers (AIChE), for whom he served as Director, Vice President, and President. He has received the Separations Science Award from the American Chemical Society, the Merryfield Design Award from the American Society of Engineering Education, and honorary doctorate degrees from the Universities of Lund and Nancy. Cussler is a Fellow of the American Association for the Advancement of Science and a member of the National Academy of Engineering.