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On Separation Efficiency

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Rising energy costs have renewed interest in energy efficient separations. Such efficiencies can be defined as the free energy of unmixing divided by the work done on and the heat added to the process. The greatest efficiencies occur when the energy cost far exceeds any capital cost. In this limit, rate processes are not important, and efficiency is governed by thermodynamics. Efficiencies for gas absorption and stripping are then typically around 50%. The efficiencies of liquid–liquid extractions are lower, especially when one solute is wanted at higher concentration. The efficiencies of membrane separations are higher, but these require high pressure, normally obtained mechanically. As a result, membrane efficiencies should be reduced by any Carnot efficiency of generating the mechanical energy. These results, which are consistent with earlier estimates for distillation, have implications for carbon dioxide capture as a route to mitigating global warming. © 2012 American Institute of Chemical Engineers *AIChE J,* 58: 3825–3831, 2012
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Introduction

The global recognition that fossil fuels are a limited resource has caused many to think about the energy used in chemical manufacturing, especially in chemical separations.[1] These separations, usually known to consume 30–80% of the energy used in making chemicals, are often targeted for improvement. They are a tempting target: distillation alone is estimated to consume about one million barrels of crude oil per day in North America alone, with an overall efficiency of around 11%.[2] This would seem to be a major opportunity for energy saving. Such a conclusion is endorsed by the National Academy of Engineering in reports written in part by established professors of environmental engineering and executives of major electricity companies.[3,4] The implication is that those actually involved in separation processes have, in their short-term thinking, neglected opportunities for energy saving.

In this article, we want to explore the maximum possible efficiency for isothermal chemical separations. In other words, we want to compare the free energy increase effected by separation with the minimum work required. Thus, we are looking at how the second law of thermodynamics constrains isothermal separation processes.

In making these estimates, we will assume that the cost of energy is much greater than the cost of capital. This is not true at present: the cost of energy is normally of the same magnitude as the cost of capital. Still, looking at this limit may have the same value as looking at the limit of the Carnot cycle. This Carnot limit is important, because it identifies how the second law of thermodynamics restricts the efficiency of heat engines. In exploring this limit, we assume two isoentropic steps and so implicitly neglect friction. We assume two isothermal steps and so implicitly assume heat transfer in large heat exchangers, whose capital cost is also ignored. Despite these assumptions, the Carnot efficiency is a useful limit for the efficiency of thermal engines.

Here, we seek similar efficiencies for isothermal chemical separations. We are concerned with the constraints of the second law of thermodynamics on the efficiencies of gas absorption, liquid–liquid extraction, and membrane separations. We want to compare these maximum possible efficiencies with those possible for distillation.[5] The results should help us to identify where opportunities for chemical manufacture with lower energy use actually exist.

Theory

We begin by defining the efficiency η of any separation. Commonly, two definitions have been used.[6,7] First, we can define

$$\eta = \frac{\Delta G(\text{unmixing})}{W + Q} \tag{1}$$

where ΔG (unmixing) is assumed to equal the negative of the free energy of mixing, and W and Q include any work or heat added to make the process run. A second common definition is

$$\eta = \frac{\text{minimum work}}{\text{minimum work} + \text{exergy loss}} \tag{2}$$

The exergy loss includes any Carnot efficiency and, hence, is especially valuable for nonisothermal systems. Because the

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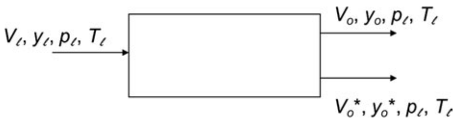

Figure 1. A general separation process.

The feed stream V_ℓ is unmixed to produce the product streams V_o and V_o^*.

separation processes considered here are nearly isothermal, we have chosen to use the first of these definitions.

We now consider the separation of a one-phase ideal binary solution. The general mass balance on such a system shown in Figure 1 gives

$$V_o = V_\ell \frac{(y_o^* - y_\ell)}{(y_o^* - y_o)} \tag{3}$$

$$V_o^* = V_\ell - V_o = V_\ell \frac{(y_\ell - y_o)}{(y_o^* - y_o)} \tag{4}$$

where the V's are flow rates in moles/time; and the y's are the mole fractions of the solute. The free energy of unmixing in such a system at constant pressure p_ℓ and temperature T_ℓ is

$$\begin{aligned}\frac{\Delta G(\text{unmixing})}{RT_\ell} = & -V_\ell[y_\ell \ln y_\ell + (1-y_\ell)\ln(1-y_\ell)] \\ & + V_o[y_o \ln y_o + (1-y_o)\ln(1-y_o)] \\ & + V'_o\left[y_o^* \ln y_o^* + \left(1-y_o^*\right)\ln\left(1-y_o^*\right)\right]\end{aligned} \tag{5}$$

This is, of course, the negative of the free energy of mixing the two product streams. This ideal mixing takes place at constant temperature and pressure. When one of the product streams is pure, this equation will have a simpler form. For example, if y_o^* equals one, then the third term on the right-hand side of this equation is zero. To measure the efficiency of the process, we must return any product streams to the original temperature, pressure, and composition that they had before mixing.

In some ways, this mixing and unmixing is reminiscent of a Carnot cycle. When used as an engine, this Carnot cycle involves a working fluid, which is heated, does work, and is cooled. The efficiency is the work divided by the heat. When used as a heat pump, the cycle provides heating or cooling in return for work. This second case is closer to the separations investigated here. The two product streams must be returned to the states that they had before mixing for the efficiency involved to meaningful. We now apply this to various separations.

Membrane separation of gases

In this case, shown schematically in Figure 2, the membrane is perfectly selective for solute, and the permeate is pure solute with a partial pressure equal to that in the retentate. The minimum work needed to reversibly compress the permeate back to the feed pressure p_ℓ is isothermal

$$W = V_o^* RT_\ell \ln\left(p_\ell / p_o^*\right) \quad = \quad -V_o^* \, RT \, \ln \, y_o \tag{6}$$

The maximum possible efficiency η is the free energy of unmixing divided by this work

$$\eta = \frac{(1-y_\ell)\,[y_o \ln y_o + (1-y_o)\,\ln(1-y_o)] \;-\; (1-y_o)\,[y_\ell \ln y_\ell + (1-y_\ell)\,\ln(1-y_\ell)]}{-\,(y_\ell - y_o)\,\ln(y_o)} \tag{7}$$

For a feed with $y_\ell = 0.21$ and $y_o = 0.01$, the efficiency will be less than 51%. For a feed with $y_\ell = 0.1$ and $y_o = 0.0001$, it will be about 35%. Similar results for specific systems have been reported by Mohr[8] and Reo et al.[9]

Gas absorption

We next estimate the heat and work required for the gas absorption process shown schematically in Figure 3. In this process, a gas flow rate of V_ℓ with a concentration of absorbable solute y_ℓ flows countercurrently through a packed tower to exit with flow rate V_o and concentration y_o. A reactive flow rate L, entering a concentration x_o and leaving at x_ℓ, absorbs solute. The exiting "loaded" liquid is heated to T_S in a heat exchanger to allow stripping of the absorbed solute. The stripped liquid, now with concentration x_o, returns through the heat exchanger to the top of the absorption tower.

To estimate the maximum possible efficiency, we assume the absorption is isothermal at temperature T_ℓ and that the

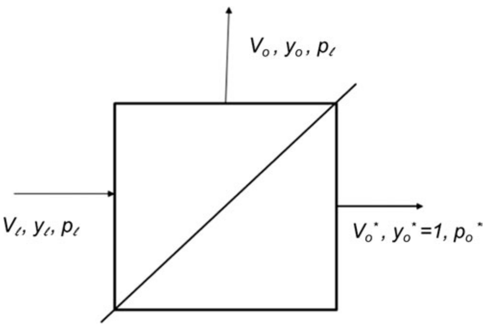

Figure 2. Membrane separation of gases.

A completely selective membrane produces a pure permeate at a flux of V_o*.

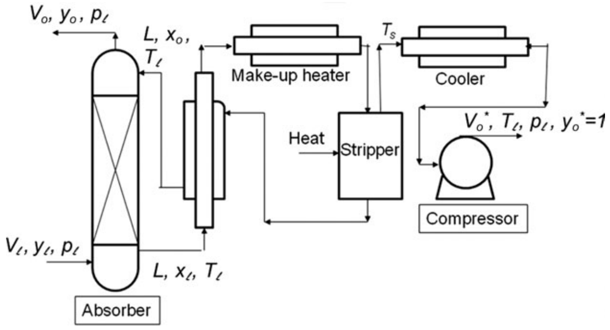

Figure 3. Gas absorption and stripping.

To assess efficiency, we must heat the recycled stripping solution and recompress the removed gas.

absorbing liquid is completely selective, so that only the solute is absorbed. We also assume that the reactive liquid is nonvolatile, so the vapor released in the stripper is pure solute, that is, $y_o{}^* = 1$. Most importantly, we assume again that energy costs much more than capital. This has two effects. First, our heat exchanger has a very large area, so heat gained by the loaded liquid comes largely from cooling the hot, stripped liquid. Second, we will build a very tall absorption tower, so the liquid entering the absorption tower will be in equilibrium with the vapor leaving

$$p_o = y_o p_\ell = H_A x_o \tag{8}$$

where p_ℓ is the total pressure in the absorber, and H_A is the Henry's law constant for the absorbing solute at the absorber temperature. An alternative way to consider this limit is to recognize that the operating and equilibrium lines in the tall absorber intersect at x_o. This liquid is also in equilibrium with the vapor released in the stripper

$$p_S = H_S x_o = \frac{H_S}{H_A} p_o \tag{9}$$

The liquid from the stripper is recycled through that very large heat exchanger back to the absorber.

However, although the heat exchanger is large, energy is being lost in the system, because the pure stripped solute is being removed hot. To return this solute stream to the conditions that it had, hypothetically, before it was mixed, it is isobarically cooled from the stripper temperature T_S to the temperature T_ℓ. Finally, it is compressed from the pressure p_S to the pressure p_ℓ, the pressure that this stream would have before mixing.

We now calculate the minimum heat and work required to operate this process. Because we calculated the energy of unmixing V_ℓ to make V_o and V_o^*, so we must calculate the heat and work needed to return V_o^* from the pressure and temperature exiting the stripper (p_o, T_S) to the pressure and temperature that we assumed before mixing (p_ℓ, T_ℓ). This has two parts. First, there is the cooling from T_S to T_ℓ, which is energy lost to the system. As a result, we need to add to the stripper the makeup heat Q

$$Q = V_o^* \tilde{C}_p (T_S - T_\ell) \tag{10}$$

where $\tilde{C}_p$ is the molar heat capacity of the solute vapor being separated. This heat is positive. Second, we must isothermally recompress the vapor from the stripper pressure p_S to the original pressure of the feed, p_ℓ

$$\begin{aligned} W &= V_o^* \int_{p_S}^{p_\ell} \tilde{V} dp \\ &= V_o^* \int_{p_S}^{p_\ell} \frac{RT_\ell}{p} dp = V_o^* RT_\ell \ln \frac{p_\ell}{p_S} \\ W &= -V_o^* RT_\ell \ln \frac{H_S}{H_A} y_o \end{aligned} \tag{11}$$

This work is positive.

The efficiency of absorption η is thus

$$\begin{aligned} \eta &= \frac{\Delta G(\text{unmixing})}{W+Q} \\ &= \frac{(1-y_o)[-y_\ell \ln y_\ell - (1-y_\ell)\ln(1-y_\ell)] + (1-y_\ell)[y_o \ln y_o + (1-y_o)\ln(1-y_o)]}{(y_\ell - y_o)\left(-\ln \frac{H_S}{H_A} y_o + \frac{\tilde{C}_p}{RT_S}(T_S - T_\ell)\right)} \end{aligned} \tag{12}$$

This efficiency is reduced by a small raffinate concentration y_o. It is increased by a Henry's law constant that varies sharply with temperature but decreased by a large heat capacity. We turn now to corresponding limits for liquid separations.

Reverse osmosis

We next consider a liquid separation effected with a pressure difference, like reverse osmosis. Such a separation may operate either as a physical filtration or by a diffusion solubility mechanism. In either case, we assume the membrane's selectivity is very large. We also assume again that energy costs are much higher than membrane costs, so we are willing to use very large membrane areas.

The free energy of unmixing in reverse osmosis is still that in Eq. 5, with V_ℓ symbolizing the feed, V_o representing the retentate, and V_o^* describing the permeate. Because the membrane is perfectly selective, the solute concentration in the permeate $y_o{}^*$ is zero, so

$$V_\ell y_\ell = V_o y_o \tag{13}$$

$$V_o^* = V_\ell - V_o = V_\ell \left(1 - \frac{y_\ell}{y_o}\right) \tag{14}$$

For the separation to occur, the feed and retentate pressures must be very slightly above the osmotic pressure of the solution. Thus, the permeate, at a lower pressure, must be recompressed to the same, higher pressure to be in the state that it would have had before mixing. The work W required for this recompression is

$$\frac{W}{V'_o} = \int_{p_S}^{p_\ell} \bar{V} dp = \tilde{V} \Delta\pi = -RT \ln(1-y_o) \tag{15}$$

where the partial molar volume of the solvent $\bar{V}$ is assumed equal to its molar volume $\tilde{V}$, and $\Delta\pi$ is the osmotic pressure. Thus, the efficiency is

$$\eta = \frac{y_o[-y_\ell \ln y_\ell - (1-y_\ell)\ln(1-y_\ell)] + y_\ell[y_o \ln y_o + (1-y_o)\ln(1-y_o)]}{-(y_o - y_\ell)\ln(1-y_o)} \tag{16}$$

This limit for reverse osmosis is also useful in estimating the efficiency of liquid–liquid extractions, described in the following section.

Liquid–liquid extraction

The case of liquid–liquid extraction is more complex than the preceding cases, because it covers a broader variety of situations. Until now, we have separated a mixture into a pure component and a residual mixture. Now, we are separating a solution into two other solutions: an extract, which contains solvent and the target solute, and a raffinate, which contains residual target solute. We must choose the amount that we want to concentrate the target solute.

To illustrate the ideas involved, we consider two cases in more detail. In the first, we produce an extract, which is then separated by distillation to recover the original single solute. The case approximates the dewaxing of lubricants. In the second case, we use an extraction solvent to separate two different solutes, which are then processed to give two solutions, which if mixed would yield the original feed. We discuss these two cases sequentially.

The first extraction detailed here removes a single solute using a volatile extraction solvent, which we assume dissolves only the solute. The resulting extract is separated by evaporation to give a pure solute. In this case, the free energy of unmixing is again that given in Eq. 5 but with y_o* equal to one. The heat required for evaporation ΔH is

$$\frac{\Delta H}{RT} = \left[\left(\frac{\Delta\tilde{H}_{\text{vap}}}{RT}\right)\frac{L_o}{V_o^*}\right]V_o^* = [\beta]V_o^* \tag{17}$$

where $\Delta\tilde{H}_{\text{vap}}$ is the molar heat of vaporization of the extraction solvent, L_o is the flow of that solvent, and V_o^* is the amount of solute removed. For example, in the dewaxing of lubricants, V_ℓ would be the feed of untreated lubricants, L_o would be the flow of an ideal cresol-like extraction solvent, and V_o^* would be the amount of wax removed. The parameter β, normally much greater than one, is the dimensionless energy required for the amount of solvent used per wax recovered.

The efficiency of this extraction is

$$\begin{aligned}\eta &= \frac{\Delta G(\text{unmixing})}{\Delta H}\\ &= \frac{(1-y_o)\,[-y_\ell \ln y_\ell - (1-y_\ell)\ \ln(1-y_\ell)\,]\ +\ (1-y_\ell)\,[y_o \ln y_o + (1-y_o)\ \ln(1-y_o)\,]}{\beta(y_\ell - y_o)}\end{aligned} \tag{18}$$

The numerator in Eq. 18 is similar to those for membranes in Eq. 7, for gas absorption in Eq. 12, and for reverse osmosis in Eq. 16. The denominator, which is the heat required, is different.

In the second extraction case, we seek to separate two dilute, similar solutes from each other. This case, which approximates some pharmaceutical purifications, is more complex than the single solute case summarized by Eq. 18. Now, we consider a highly dilute solution containing solutes "1" and "2" in a stream entering with a flow of V_ℓ and concentrations $y_{1\ell}$ and $y_{2\ell}$, as shown in Figure 4. Because the solution is so dilute, the flow V_ℓ is nearly constant throughout the extractor. This feed solution could have been made by mixing a stream $(V_\ell - V_o)$ at concentrations $y_{1\ell}$* and $y_{2\ell}$* $= 0$ with a stream V_o at concentrations y_{1o}* $= 0$ and $y_{2\ell}$*. The best separation that we could hope for would use a solvent that is perfectly selective for species "1," so it removes species "1" but not species "2." This extract is then stripped with a flow V_ℓ of the original solvent in a very large stripper to give a final extract of V_ℓ and $y_{1\ell}$. To return the raffinate of the extractor to its original state, we use a reverse osmosis unit to reduce the solvent flow from V_ℓ to V_o. To return the stripped extract to its original state, we use a second reverse osmosis unit to reduce the solvent flow from V_ℓ to $(V_\ell - V_o)$. In these and other relevant flows, shown in Figure 4, species "1" and "2" are always dilute.

The free energy of unmixing in this case is an extension of Eq. 5

$$\begin{aligned}\frac{\Delta G(\text{unmixing})}{RT} = {}& V_\ell[-y_{1\ell}\ln y_{1\ell} - y_{2\ell}\ln y_{2\ell} - (1-y_{1\ell}-y_{2\ell})\\ &\times \ln(1-y_{1\ell}-y_{2\ell})]\\ &+ (V_\ell - V_o)[y_{1\ell}^*\ln y_{1\ell}^* + (1-y_{1\ell}^*)\ln(1-y_{1\ell}^*)]\\ &+ V_o[y_{2\ell}^*\ln y_{2\ell}^* + (1-y_{2\ell}^*)\ln(1-y_{2\ell}^*)]\end{aligned} \tag{19}$$

This is subject to the mass balances

$$V_\ell y_{1\ell} = (V_\ell - V_o)y_{1\ell}^* \tag{20}$$

$$V_\ell y_{2\ell} = V_o y_{2\ell}^* \tag{21}$$

We will find it convenient to use these mass balances to define a dilution θ

$$\theta = \frac{y_{1\ell}}{y_{1\ell}^*} = 1 - \frac{y_{2\ell}}{y_{2\ell}^*} = \frac{V_\ell - V_o}{V_\ell} \tag{22}$$

The work required is that of the two reverse osmosis units

$$\frac{W}{RT} = -V_o \ln(1 - y'_{1\ell}) - (V_\ell - V_o)\ln\left(1 - y_{2\ell}^*\right) \tag{23}$$

Thus, the efficiency is

$$\begin{aligned}\eta = {}& \frac{[-y_{1\ell}\ln y_{1\ell} - y_{2\ell}\ \ln y_{2\ell} - (1-y_{1\ell}-y_{2\ell})\ln(1-y_{1\ell}-y_{2\ell})\,]}{-\ (1-\theta)\ \ln\left(1-\frac{y_{1\ell}}{\theta}\right) - \theta\ln\left(1-\frac{y_{2\ell}}{1-\theta}\right)}\\ &+ \frac{\theta\left[\frac{y_{1\ell}}{\theta}\ln\frac{y_{1\ell}}{\theta} + \left(1-\frac{y_{1\ell}}{\theta}\right)\ln\left(1-\frac{y_{1\ell}}{\theta}\right)\right] + (1-\theta)\left[\frac{y_{2\ell}}{1-\theta}\ln\frac{y_{2\ell}}{1-\theta} + \left(1-\frac{y_{2\ell}}{1-\theta}\right)\ln\left(1-\frac{y_{2\ell}}{1-\theta}\right)\right]}{-(1-\theta)\ln\left(1-\frac{y_{1\ell}}{\theta}\right) - \theta\ln\left(1-\frac{y_{2\ell}}{1-\theta}\right)}\end{aligned} \tag{24}$$

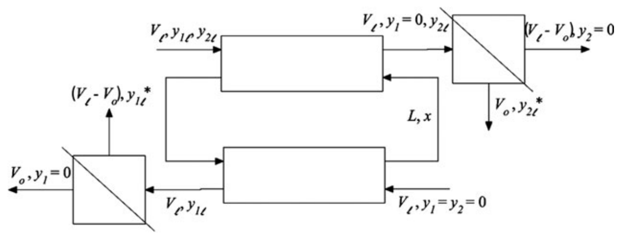

Figure 4. Liquid–liquid extraction.

Here, the efficiency depends on the amount of dilution.

where the dilution θ is also the fraction of the total flow V_ℓ exiting as $(V_\ell - V_o)$. The numerator in Eq. 24 is an analog to those in Eqs. 7, 12, 16, and 18. The denominator is different in each of these cases. These differences show that the maximum possible efficiency of these various separations is often significantly less than 100%, as detailed by the results discussed in the following section.

Results

The calculations above give the maximum efficiencies possible for some separations using membranes, gas absorption, or liquid extraction. They center on simple forms of these separations. They do not include more elaborate schemes, like membrane separations with large numbers of stages, or partial extractions giving incomplete separations. In addition, the maximum efficiencies possible depend on the details of the particular separations. However, because these efficiencies are often less than 50%, they are important limits. To examine this assertion in greater detail, we consider specific cases.

The efficiencies for the membrane separation of gases are shown in Figure 5. These efficiencies, for the perfectly selective single membrane shown in Figure 2, are calculated from Eq. 7. The results are shown as a function of the feed concentration y_ℓ and the relative concentration y_o/y_ℓ. Lower values of the feed concentration give higher efficiencies, because the work of recompression is smaller. Higher values of the retentate over feed concentration, which imply a smaller stage cut, also give higher efficiencies.

The efficiencies for gas absorption for a feed concentration $y_\ell = 0.1$ are shown vs. heating and effluent concentration y_o in Figure 6. This figure assumes that H_S/H_A equals three, a ratio typical of that for carbon dioxide absorption using aqueous amines as chemical solvents.[10,11] The efficiency is lower if the exiting gas concentration y_o is lower. It is lower if heating is larger.

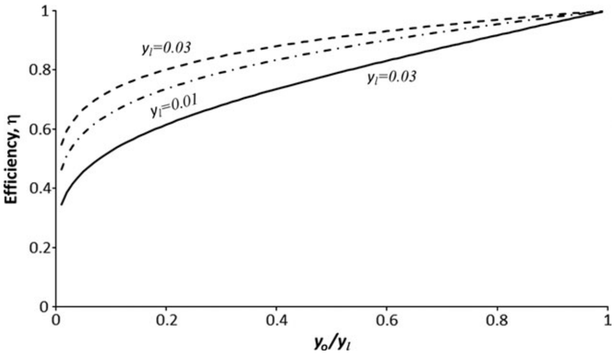

Figure 5. Maximum efficiency for membrane-based gas separations.

The efficiency drops as the feed concentration of the more permeable species rise, but it changes less with the fraction removed $(1 - y_o/y_\ell)$.

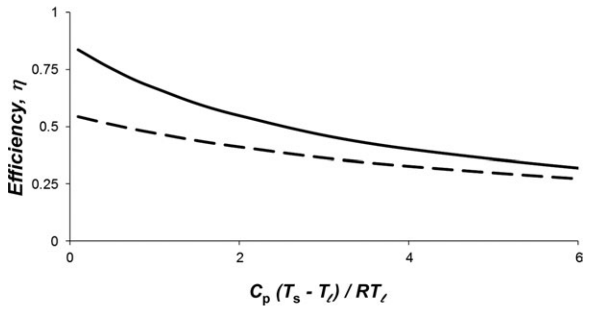

Figure 6. Maximum efficiency for gas absorption for $y_\ell = 0.1$.

The ratios of the Henry's law constant, H_S/H_A, is taken as close to that observed for carbon dioxide stripping between 300 and 370 K.

This efficiency, found with infinitely large equipment, may make us wonder if high efficiencies can ever be achieved for gas absorption. They can, as shown in Figure 7. This figure plots the efficiency η as a function of y_o/y_ℓ, which is a rough measure of the amount removed. The figure shows this efficiency for several values of the feed concentration y_ℓ. In these cases, the efficiency is high when very little is separated. When we seek 90% removal, efficiencies will always be smaller.

The efficiencies of reverse osmosis, shown in Figure 8, are also high when very little is separated. For example, imagine the feed concentration y_ℓ is 0.01, close to that of salt in seawater. If the retentate concentration is only slightly higher, perhaps 0.0101, the efficiency estimated from Eq. 16 is near 100%. On the other hand, if the retentate concentration is 10 times greater than the feed, the efficiency drops to about 25%. Moreover, in reverse osmosis, the pressure difference required to operate the process is normally generated with electrically driven pumps. The electricity will often be made with a heat engine. Such heat engines, normally fired by coal or another fossil fuel, typically have an efficiency of between half and a one-third. This compromises the overall efficiency of reverse osmosis.

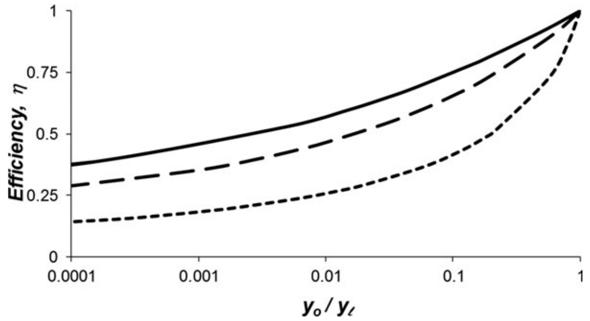

Figure 7. Absorption efficiency vs. product removed.

The efficiency, shown here for no heating, drops as the concentration in the feed y_ℓ rises or as the fraction removed $(1 - V_o/y_\ell)$ increases.

Next, we turn to liquid–liquid extraction. In this case, the maximum efficiency possible varies strongly with the concentration desired in the extract. In the theory above, we

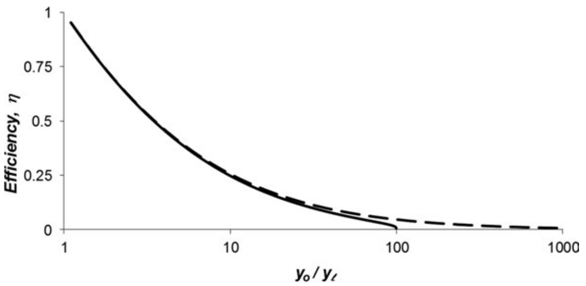

Figure 8. Maximum efficiency η of reverse osmosis.

The efficiency drops as the retentate concentration y_o rises, almost independently of the feed concentration y_ℓ.

have expressed this choice not as a concentration increase, but as its reciprocal, a dilution θ defined $y_{1\ell}/y^*_{1\ell}$. The maximum efficiency possible is shown as a function of θ in Figure 9. When we seek only to double the concentration, the efficiency is high, up to 70%, though this is again subject to the efficiency of the pumps driving the reverse osmosis units shown in Figure 4. When the solute concentration is increased 10 times so θ is 0.1, the efficiency is lower, around 25%.

Discussion

Energy policy studies conclude that industry is the largest energy-consuming sector in the world economy. About one-third of the total U.S. energy consumption is due to four energy-intensive industries: chemicals, petroleum, iron and steel, and pulp and paper. Within the chemical and petroleum industries, separations (especially distillation and gas treating) are frequently said to offer opportunities to improve energy efficiency.[3,4]

This article explores the feasibility of this goal. It considers the maximum efficiency possible for gas absorption, liquid–liquid extraction, and different membrane separations. It defines efficiency as the free energy of unmixing divided by the minimum work and the minimum heat necessary to effect the process. It assumes every possible chemical advantage: exquisitely selective liquid absorbents for gas treating, completely selective extraction solvents, infinitely selective membranes, and heat exchangers with huge areas for heat recovery. It seeks to discover the highest possible efficiencies for these separations. It seeks the separation efficiencies that are analogous to those achieved by the Carnot cycle for heat engines.

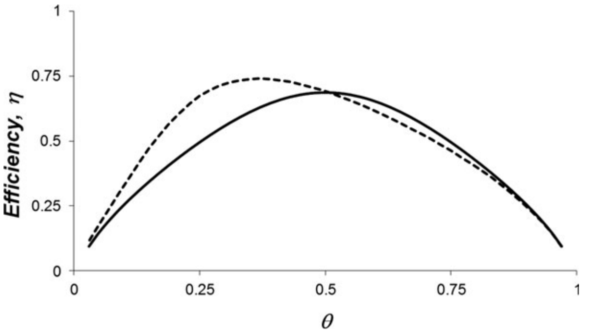

Figure 9. Maximum efficiency of solvent extraction.

The efficiency drops, if either solute is significantly concentrated during the separation.

The results show maximum efficiencies that are considerably less than 100% for most separations. Those for gas absorption with a feed containing 10% solute are about 65% for 90% recovery ($y_o/y_\ell = 0.1$) and about 50% for 99% recovery. Those for liquid–liquid extraction can be lower, especially when the solute of interest is concentrated significantly from its concentration in the feed. The efficiencies of membrane processes, especially reverse osmosis, can approach 100%, but this occurs only when a small fraction of the feed passes through the membrane. All these processes—absorption, extraction, and membranes—show inefficiencies like those found for the efficiency of distillation.[5]

The point benefits from examples. Those struggling to set energy policy often contrast distillation and membrane processing. They correctly point out distillation is 11% efficient. Surely, we are collectively smart enough to improve this. Those advocating membrane processing often correctly assert that membranes do not require major latent heat effects. Surely, we are collectively smart enough to discover how this smaller heat requirement can yield higher separation efficiency.

However, when we consider the analysis of these separations in more detail, our conclusions are less definite. The efficiency of distillation involves both a temperature-dependent, Carnot term, and an unmixing term. Once the Carnot term is removed, distillation is perhaps 50% efficient, comparable with other processes. Alternatively, if the pumps used in membrane separations are electrically driven and the electricity is generated from coal combustion, then the reverse osmosis process as a whole has efficiency like other separations.

Further improvements in membranes may not lead to additional gains in membrane efficiency. This already seems to be happening, as shown in Figure 10. In this figure, the power consumed to purify one cubic meter of seawater by reverse osmosis is plotted over the last 40 years.[12–15] This power is approaching the limit of Eq. 16, shown as the dashed horizontal line. Improvements in reverse osmosis membranes and module designs do seem to be approaching the limits calculated here.

The results in this article can be used to estimate the minimum cost increases caused by specific environmental strategies. To illustrate this, imagine burning a coal with the formula CH

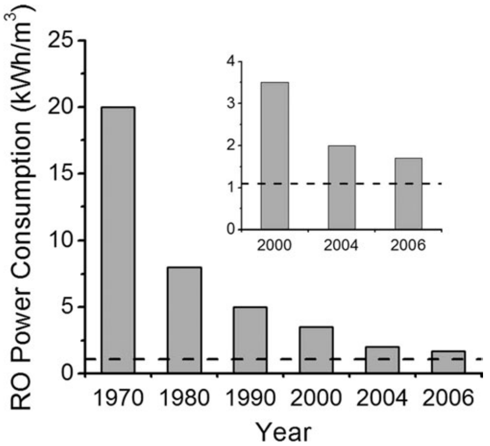

Figure 10. Reverse osmosis efficiency over 40 years.

The energy used in reverse osmosis is approaching the limit in Eq. 16.

$$4CH + 5O_2 \rightarrow 4CO_2 + 2H_2O$$

We burn this coal discharging a flue gas containing 10% CO_2. If we do not separate the flue gas, we produce about 337 kJ/mol CH.[16] If the Carnot efficiency of this combustion is 40%, we get (0.4) (337) = 135 kJ/mol of useful work.

Now imagine, we want to capture the carbon dioxide and recompress it to one atmosphere, the total pressure of the flue gas. The heating required, given by Eq. 10, involves increasing the temperature 70°C. If the heat capacity of the CO_2 is $3.5R$, then the amount of heat used is [3.5 (8.31 J/mol K)] = 2 kJ/mol CH. Thus, we have left (337 – 2) = 335 kJ/mol CH, which, after power generation, leaves [0.4 (335 kJ/mol)] = 134 kJ/mol CH. As H_S/H_A equals about 3 for the amines used now and the product temperature is about 300 K, the recompression of the carbon dioxide product is found from Eq. 11 to be at least {(−8.31 (J/mol) K) (300 K) ln [(3) (0.010)]} = 9 kJ/mol CH. Thus, we have 125 kJ/mol CH of work left, which is about 8% less than without carbon dioxide capture.

This result implies that capturing and sequestering carbon dioxide will increase power generation costs by a minimum of 8%. Operating costs average about three times energy costs,[17,18] so that operating with carbon dioxide capture would increase these costs about 24%. Capital costs roughly equal energy costs,[17,18] another rise of 8%. Thus, carbon dioxide capture including energy, operating, and capital costs increases bills for electricity by over 30%. In making these estimates, we do not advocate any particular policy, but we feel arguments like those advanced in this article can help choose between alternative policies.

Why even after any constraints of the Carnot cycle are removed are separation processes so inherently inefficient? The answer, of course, is that entropy is a cruel master, that the entropy of unmixing requires considerable work to overcome. If entropy is too abstract a concept, then we can say separation processes are hard to reverse, because diffusion in one phase spontaneously occurs from high concentration to low concentration. Reversing diffusion will always be inefficient. Alternatively, we can say that overcoming dilution will always be hard. We can do so by recompression of gases, by reverse osmosis of liquid solutions, or by other separations, but each case takes a lot of work. This is why separation efficiencies will always be limited.

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