Distillation in Hollow Fibers

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Distillation in hollow fibers can give better, more productive separations than distillation in random or structured packing. Since the hollow fibers used have little resistance to mass transfer, the selectivity of the separation depends on the relative volatility, just as in conventional distillation. Because the fibers are nonporous, the distillation can operate at high flows which normally cause flooding, and at low flows which normally compromise loading. As a result, the turndown ratio is nearly infinite and the height of a transfer unit can be as small as desired. Experiments do give values consistent with correlations developed for other membrane modules, although the practical value of hollow fiber distillation is uncertain because of the materials limitations.

Introduction

Like many separation processes, distillation is normally regarded as a mature technology (Humphrey and Keller, 1991; Kister, 1992; Seader and Henley, 1998). As a result, few expect that major improvements are possible. Staged columns will probably continue to use trays 0.6 m apart. Columns with structured packing will perform better, with the height of a transfer unit (HTU) around 0.1 m, but even this innovation seems mature. Most working on distillation seem to feel that any asymptote in performance must be close at hand.

We feel that there is little experimental basis for this attitude. We feel that one possible analogy is the world record time for the one-mile run. Many may feel that humans have run the mile almost as fast as is possible, that is, after the four-minute barrier was broken, improvements would be minor. In fact, if we plot the record times for the past 150 years, we find a straight line, dropping 3 s every ten years. There are no discontinuities caused by faster running tracks or a truly exceptional athlete. Of course, an asymptote must exist: humans can presumably not run one mile in one minute. Still, there is nothing in the current world records to suggest that we are close to an asymptote.

More subjectively, we believe that no asymptote exists for separation processes. For example, we can imagine that the HTU is for gas absorption what the record time is for the one mile run. We then can plot the HTU for a particular tower packing vs. the year the packing was introduced. The results, like the guesses shown in Figure 1, again are without an obvious asymptote. We can dream about still smaller HTUs in more efficient or more rapid separation processes, even though these processes may turn out to be impractical. For now, being practical is not our goal; making the HTU as small as possible is our goal. After all, setting a world record in the one-mile run is not very practical either.

In this article, we want to explore using hollow fibers as a potential route to faster distillation. In this effort, we immediately acknowledge that any improvements which we find will not be of direct commercial value. Most obviously, our hollow fibers are made of polymers which will never stand the temperatures routinely used in distillation. They have small diameters and so are easily plugged with particulates, although this problem may be less severe for a vapor-liquid separation than for liquid-liquid extraction.

Still, we can expect that distillation in hollow fibers may have some significant advantages. To explore these advantages, we consider the system shown in Figure 2. The figure shows a conventional column, with a reboiler, a total condenser, and a column. The only difference is that the column is not staged or filled with packing, but is built with hollow fibers (Reed et al., 1995). These fibers are arranged like a conventional shell and tube heat exchanger, but the fiber "tubes" are typically less than 0.1 cm in diameter.

Such a hollow fiber column has three advantages over a conventional distillation tower. First, it offers a large interfa-

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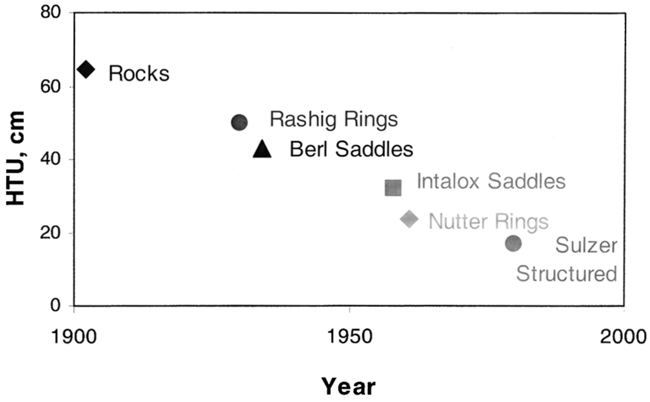

Figure 1. Height of a transfer unit has decreased over time.

These estimates imply that chemical separations have not yet reached maximum efficiency.

cial area per volume, typically around 50 cm^2/cm^3. All of this area is actively involved in the mass transfer between vapor and liquid. Second, because the liquid always fills the hollow fibers, this contact area is maintained, even at very low flows. There is thus no constraint of column "loading," and the turndown ratio of the column is infinity.

The third advantage of distillation in hollow fibers also results because the liquid and vapor flows are not in direct contact: there is no flooding caused by any two-phase flow. Indeed, we will routinely operate our experiments in regions which are not accessible to normal packed columns. Moreover, because the flows of liquid and vapor are now not around submerged objects, pressure drops in the column are more modest than in conventional equipment.

Ironically, the possible selectivity of the membrane will *not* be an advantage in our experiments. We will attempt to choose membranes which offer very little resistance to mass transfer, and so do not significantly alter the separation from that expected on the basis of the relative volatility. We are not trying to extend earlier efforts to stage selective membranes. Moreover, the membranes that we will use are nonporous, unlike those used earlier in the method called "membrane distillation" (Lawson and Lloyd, 2000; Courel et al., 2000).

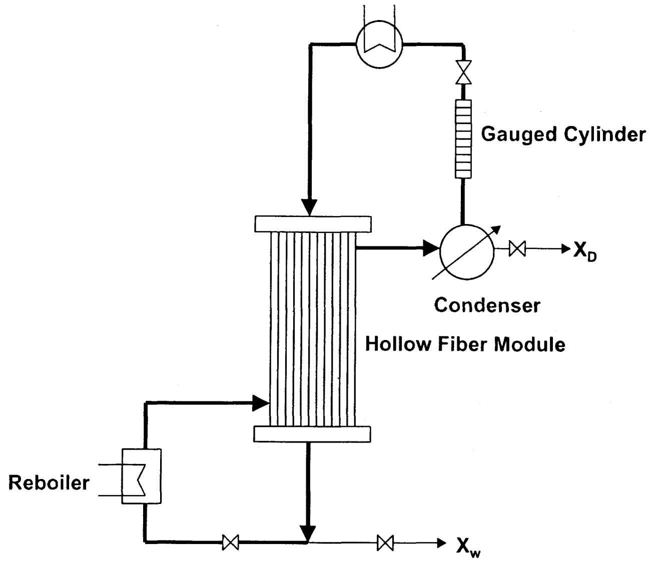

Figure 2. Process for hollow fiber distillation.

The hollow fiber module replaces the conventional packed tower used for differential distillation.

The distillation column shown in Figure 2 does have problems not encountered in more conventional equipment. For example, the pressure drop in the fibers is so small that the liquid tends to run directly out of the fibers. We stop this by adding the valve shown at the bottom of the fibers, but this can cause control problems. In addition, adding the feed directly to the reboiler will normally not be optimal, but adding a liquid feed as a central point to the inside of the fibers requires two hollow fiber columns separated by a feed port. Our focus here is on the simplest case, that in Figure 2.

Theory

We want to estimate the performance which we can expect from a typical hollow fiber module. To do so, we first establish as a benchmark a membrane module like those used in the past. We discuss its geometry, its mass balances, and its expected mass transfer. We will check these estimates in experiments later in this article.

Module geometry

In our experiments, we will use hollow fibers which have about 0.1 cm outer diameter, 0.067 cm inner diameter, and 20 cm length. We typically install 50 fibers in a module, giving a total cross-sectional area for the liquid flowing inside the fibers of 0.2 cm^2, and a cross-sectional area for the gas flowing outside the fibers of 1 cm^2. Our void fraction is about 0.8. Such a module has a membrane surface area per module volume a of 60 cm^2/cm^3 lumen.

Our test module is convenient for our experiments, but it is less effective than other commercial modules routinely built for practical separations. For example, one typical kidney module has 3,000 hollow fibers 400 μm in diameter and 30 cm long. The fibers, in a shell 4 cm in diameter, have total cross-sectional areas of 9 cm^2 and 2 cm^2 in the shell and in the lumens, respectively. This module has a membrane surface area per module volume a of 100 cm^2/cm^3 lumen. Our module has a smaller a, because we have fewer hollow fibers of larger diameter.

Our test module can be operated at flows greater than that which would cause flooding in normal distillation columns. To explore this, we first turn to estimates of flooding in conventional packed beds. Such flooding is normally calculated as a function of the flow parameter, defined as

$$\begin{bmatrix} \text{flow} \\ \text{parameter} \end{bmatrix} = \frac{L'}{G'}\sqrt{\frac{\rho_G}{\rho_L}} \tag{1}$$

where L' and G' are the mass fluxes of the liquid and vapor, respectively; and ρ_L and ρ_G are the corresponding densities. At total reflux in a distillation column, L' equals G'. In most cases, the ratio ρ_G/ρ_L is about 10^{-3}. Thus, the flow parameter is about $(10^{-3})^{1/2}$ or 0.03.

With this value of the flow parameter, we can estimate a capacity factor and a vapor velocity for a conventional packed column with an area per volume equal to that of our hollow fiber column. Making this estimate requires finding a packing factor. Because we have no data for fibers, we assume after Kister (1994) that the packing factor is proportional to the area per volume. Thus, for a column of Rashig rings with an area per volume of 16 cm^2/cm^3, we expect a packing factor of around 5,000. This leads to a vapor flux at flooding of around 0.03 g/cm^2 s, or a vapor velocity of 30 cm/s.

We now want to choose conditions in the hollow fiber column which illustrate flows which would cause flooding or which would not give loading in a conventional column. For the limit beyond flooding, we choose a vapor velocity of 300 cm/s, ten times larger than the flooding velocity above. Because the ratio of gas to liquid cross sections is 5:1 and the ratio of vapor to liquid densities is 10^{-3}, this implies a liquid velocity of 1.5 cm/s. In the same spirit, we assume that for the limit below loading, we have a vapor velocity of 3 cm/s, ten times less than the estimated flooding velocity. This corresponds to a liquid velocity of 0.015 cm/s. We will use all these velocities in the estimates of mass transfer which follow.

Mass balances

We now turn to the mass balances basic to the operation of a differential distillation column. For simplicity, we consider only the case of total reflux, which for our module geometry implies

$$(1\ \text{cm}^2)G = (0.2\ \text{cm}^2)L \tag{2}$$

where G and L are the molar vapor and liquid fluxes in the column. We also assume constant molar overflow, so these flows are independent of position. Under these conditions, balances on the more volatile species in both vapor and liquid give the familiar operating line

$$y = x \tag{3}$$

where y and x are the mole fractions of the more volatile species in the vapor and the liquid, respectively. Finally, we can write a balance on the more volatile species in the liquid alone

$$0 = -L\frac{dx}{dz} - K_x a(x - x^*) \tag{4}$$

where K_x is an overall mass-transfer coefficient based on a liquid-side, mole fraction driving force, a is the fiber area per lumen volume, and z is the position in the column. These mass balances are easily integrated to find the number of transfer units NTU

$$NTU = \int_{x_0}^{x_t} \frac{dx}{x - x^*} = \left[\frac{K_x a}{L}\right]\ell \tag{5}$$

where ℓ is the length of the module. The number of transfer units is a measure of the difficulty of the separation. The reciprocal of the quantity in square brackets is often called the height of a transfer unit, or the HTU. It is a measure of the efficiency of the equipment.

The value of the NTU varies both with the fluid mechanics, represented by L, and with the overall mass-transfer coefficient K_x. This mass-transfer coefficient is complicated because of its units and because of the presence of the membrane. It can be shown to be given by (Cussler, 1997)

$$\frac{1}{K_x} = \frac{1}{mk_y} + \frac{1}{mk_m} + \frac{1}{k_x} \tag{6}$$

where k_y, k_m, and k_x are individual mass-transfer coefficients based on mole fraction driving forces in the vapor, across the membrane, and in the liquid, respectively; and the partition coefficient m is given by

$$y = mx^* \tag{7}$$

This form is that normally used to describe mass-transfer problems. However, in this case, we will find the physical meaning clearer if we use an overall mass-transfer coefficient K_L based on a concentration difference as a driving force

$$\frac{1}{K_L} = \frac{c_L}{K_x} = \frac{1}{Hk_G} + \frac{1}{Hk_M} + \frac{1}{k_L} \tag{8}$$

where k_G, k_M, and k_L are individual mass-transfer coefficients based on concentration differences as driving forces in the vapor, in the vapor adjacent to the membrane, and in the liquid, respectively. The new partition coefficient H is

$$c_{1G} = Hc_{1L}^* = \left(\frac{mc_G}{c_L}\right)c_{1L}^* \tag{9}$$

where c_{1G} and c_{1L} are the concentrations of the more volatile species in the gas and liquid, respectively. Note that both H and m are closely related to a Henry's law coefficient.

We can use past experiments on hollow fiber modules to make estimates of the individual mass-transfer coefficients and, hence, of the NTUs to be expected for distillation in hollow fibers. To do so, we return to the limits of high and low flow discussed above. For the high flow limit above flooding, we use a gas velocity of 300 cm/s, which gives a Graetz number given by (Cussler, 1997)

$$\frac{d_h^2 v_G}{D_G\,\ell} = \frac{(0.2\ \text{cm})^2\ 300\ \text{cm}^2/\text{s}}{\frac{0.1\ \text{cm}^2}{\text{s}}(20\ \text{cm})} = 12 \tag{10}$$

In this estimate, we have used the hydraulic diameter d_h of 0.2 cm for the shell side of the module described above. Under these conditions (Yang and Cussler, 1986)

$$\frac{k_G d_h}{D} = 1.25\left(\frac{d_h^2 v_G}{\ell v}\right)^{-0.93}\left(\frac{v}{D}\right)^{0.33} \tag{11}$$

Inserting the values used, we find a value for k_G of 6 cm/s.

From other experiments (Yang and Cussler, 1986; Nii et al., 2002; Kistler and Cussler, 2002; Wang et al., 2002), we obtain a mass-transfer coefficient k_M of 1 cm/s for transport across the membrane. Note that this value assumes mass transport from the vapor into the membrane and back into the vapor again. For the individual mass-transfer coefficient in the liquid, we again estimate the Graetz number

$$\frac{d^2 v_L}{D_L \ell} = \frac{(0.067\ \text{cm})^2 1.5\ \text{cm/s}}{\dfrac{10^{-5}\text{cm}^2}{\text{s}}(20\ \text{cm})} = 34 \tag{12}$$

Under these conditions, mass transfer is described by the familiar Leveque limit (Cussler, 1997)

$$\frac{k_L d}{D_L} = 1.62\left(\frac{d^2 v_L}{\ell D_L}\right)^{1/3} \tag{13}$$

Inserting the values given, we find k_L is about $8 \cdot 10^{-4}$ cm/s, a typical value.

We now need only to estimate values of m. For many distillations, m is about one, so the partition coefficient H is about 10^{-3}. When we use these values and our other estimates in Eq. 8, we find

$$K_L = 4 \cdot 10^{-4}\ \text{cm/s} \tag{14}$$

We can use this to find an NTU of only about 0.3, but at a flow ten times above flooding. We will expect values like this in the experiments described below.

The overall mass-transfer coefficient estimated here is influenced significantly by resistances in the vapor, in the membrane, and in the liquid. The liquid is responsible for half of the total resistance. The contributions from both vapor and liquid are consistent with the results for many distillations (Kister, 1992; Bennett and Kovak, 2000). However, this result is different from that expected for gas absorption, where mass transfer is normally completely dominated by the resistance in the liquid. The reason for this difference comes from the partition coefficient m (or H). For distillation, m is normally of order one; for gas absorption, it is typically one-hundred times larger. It is the value of m, and not the value of any mass-transfer coefficient, which is responsible for the change in the rate-limiting step.

We can make estimates of the overall mass-transfer coefficient for the slow liquid flow of 0.015 cm/s in a way parallel to those for fast liquid flow of 1.5 cm/s. This slow flow is below that required for loading a packed column of equivalent area per volume, and so is the counterpoint to the fast flow limit, which was above the normal conditions for flooding. The only significant difference between these limits is that the Graetz number is now 100 times smaller, so the mass-transfer coefficients are now not given by Eqs. 11 and 13 but by (Kreith and Bohn, 1996)

$$\frac{kd}{D} = 4.36 \tag{15}$$

For the vapor, $d(=d_h)$ is 0.2 cm and D is 0.1 cm^2/s; for the liquid, d is 0.1 cm and D is 10^{-5} cm^2/s. This leads to the values summarized in Table 1. Again, the overall mass-transfer coefficient is significantly influenced by all three resistances: vapor, membrane, and liquid. The resistance in the liquid is still the most important.

The results in Table 1 illustrate the potential of distillation in hollow fibers, and they show how our current thinking about distillation may be constrained. The results at high flow show a mediocre HTU, one easily achieved with many types of tower packing. However, they do so at flows which are impossible to reach in these more normal packings. This implies that hollow fibers may provide a route to a more productive distillation. In contrast, the results at low flow give an attractive HTU of less than a centimeter. More interestingly, the results imply that cutting the velocity another factor of ten will reduce the HTU the same amount, because the mass-transfer coefficients are now independent of the velocities (cf. Eq. 15). Thus, we can have an HTU as small as we want.

While these estimates are intriguing, they do not have a firm experimental basis. We need to establish such a basis before we make any further speculations. Such an experimental basis is described in the following sections.

Experimental Methods

A feed solution with a mole fraction of isopropanol equal to 0.03 was prepared by adding the alcohol (Aldrich, 99.5+% ACS spectroscopic grade) to doubly distilled water. This solution was added to the reboiler of the distillation apparatus shown in Figure 2. The hollow fiber module, which is the only unusual part of this apparatus, was made with coated,

Table 1. Preliminary Estimates of Mass-Transfer Coefficients in Hollow Fiber Modules

Limiting Condition	Fast Flow ($v_L = 1.5$ cm/s)	Slow Flow ($v_L = 0.015$ cm/s)
Mass-Transfer Coefficient In:		
Gas ($D_G = 0.1$ cm^2/s)	$k_G = 6$ cm/s	$k_G = 2$ cm/s
Membrane (k_M from experiment)	$k_M = 1$ cm/s	$k_M = 1$ cm/s
Liquid ($D_L = 10^{-5}$ cm^2/s)	$k_L = 8 \cdot 10^{-4}$ cm/s	$k_L = 6 \cdot 10^{-4}$ cm/s
Partition Coefficient ($m = 1$)	$H = 10^{-3}$	$H = 10^{-3}$
Overall Mass-Transfer Coefficient	$K_L = 4 \cdot 10^{-4}$ cm/s ($K_x = 2 \cdot 10^{-5}$ mol/cm^2 s)	$K_L = 3 \cdot 10^{-4}$ cm/s ($K_x = 2 \cdot 10^{-5}$ mol/cm^2 s)
Height of a Transfer Unit [$L/K_x a$) or ($v_L/K_L a$)]	60 cm	0.8 cm

Table 2. Properties of Modules and of Structured Packing

Module Packing	Number of Fibers	Void Fraction ϵ	Area Per Volume a (ft^2/ft^3)	Packing Factor FP (a/ϵ^3)
Sulzer BX		0.90	150	206
Mellapak	250Y	0.95	76	89
1	25	0.85	201	327
2	50	0.71	484	1,352
3	75	0.56	916	5,216

microporous polyether fibers (Porous Media, St. Paul, MN). The fibers have an inside diameter of 0.067 cm, an outside diameter of 0.104 cm, and a 7 μm polydimethylsiloxane coating. This nonporous coating offers little resistance to diffusion, but it does stop convection.

The hollow fibers, installed in a glass shell with an inside diameter of 1.36 cm, were potted with epoxy (DP-460, 3M, St. Paul, MN), following the procedure described elsewhere (Dahuron and Cussler, 1988). Each module had an effective mass-transfer length of 20 cm. Other module properties are compared in Table 2 with two commercial structured packings—Sulzer Gauze BX and Mellapak (Sulzer Chemtech). The void fractions of the modules are lower than those of the structured packing, although the areas per volume are somewhat larger.

All distillation experiments were run at total reflux. In a typical experiment, 700 mL feed solution was poured into the round bottom flask, which serves as the reboiler. This reboiler was heated electrically to produce vapor which flowed up the shell side of the hollow fiber module to a water cooled condenser. The heating rate was adjusted by a variable transformer (Powerstat, Bristol, CT) and measured by both a multimeter (John Fluke, Everett, CA) and a power clamp meter (Extech, Gardena, CA). The condensate ran downwards through the hollow fiber lumens. Its flow was measured volumetrically. To minimize subcooling in the vapor condenser, we adjusted cooling water flow until the difference between vapor temperature and liquid temperature entering the module was below 2°C.

Solution concentrations were measured as 2 cm^3 samples taken from the reboiler and from the distillate. The concentrations were determined by injecting 2 μL samples into a Hewlett Packard GC-5790 gas chromatograph equipped with a flame ionization detector (FID) and a Super Q AT steel column (Alltech, IL). The carrier gas was nitrogen of purity 99.99%. Each concentration was measured at least in duplicate. We ran the column for at least 1 h to approach steady state, when the first sample was taken. Subsequent samples were then taken at about 60 min intervals to ensure steady state. Usually, the steady state was achieved within 2 h after a change in heat load.

The calculation of the number of transfer units from these data is complicated because the slope of the equilibrium line is not constant, so that m is not constant. We are especially interested in the concentration range of $0.13 < x < 0.68$. Over this range, the vapor-liquid equilibria fit the polynomials (Chu et al., 1956)

$$0.13 < x \leq 0.48 \qquad y^* = 0.4837 + 0.1464x + 0.1554x^2 \tag{16}$$

$$0.48 < x < 0.68 \qquad y^* = 0.6366 - 0.4923x + 0.8227x^2 \tag{17}$$

Using these relations and Eq. 5, we can find the NTUs for comparison with the estimates given in the theory. The results are in the next section.

Results

We want to see if our experiments support the expected behavior for hollow fiber distillation estimated above. These estimates included the effects of fluid flows and of NTUs. We consider first the effects of fluid flows.

We can routinely operate hollow fiber distillation at flows greater than that causing flooding, as shown in Figure 3. In this figure, we plot the normal flow parameter on the abscissa, and the common capacity factor on the ordinate (Kister, 1992; Stringle, 1987). The solid curve is the empirically determined limit of flooding. Points above this curve cannot be reached with conventional packing. In Figure 3, we also show as data points the conditions where we ran experiments. Almost without exception, these are above the limit where flooding normally occurs. In some cases, the data are almost one-hundred times above flooding. These data cover only a narrow range of flow parameters because we always ran at total reflux, so L and G were always equal. We plan

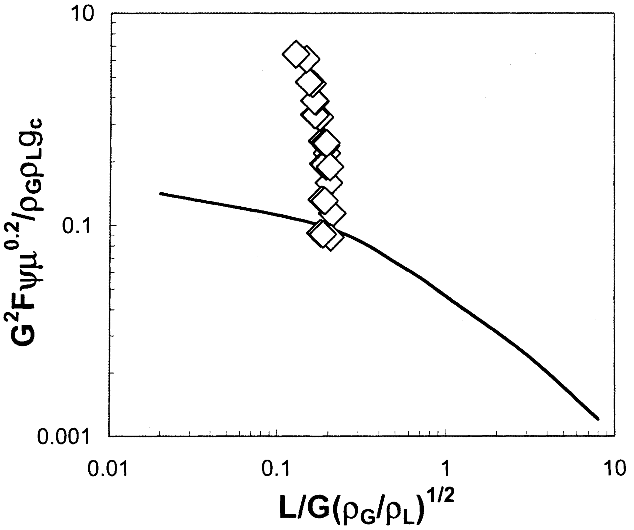

Figure 3. Hollow fibers operate above flooding.

As usual, the flow parameter on the abscissa is plotted vs. the capacity factor on the ordinate. The data usually are at fluxes above the normal flooding limit, shown as the solid line.

to remove this assumption in later experiments where we will vary the reflux ratio.

The results clearly show how easily hollow fibers can operate above the normal flooding limit. In our experiments, we still kept the valve below the fiber bundle partly closed (cf. Figure 2), so that we could potentially operate at still higher flow rates. We can operate under these conditions because vapor and liquid are in contact only across the membrane walls. There is no resistance for a bubble rising through liquid because there are no bubbles. In the same sense, the falling liquid is not slowed by the rising vapor. We could operate the column horizontally, or in the absence of gravity. Such process intensification is in some ways an alternative to "HIGEE" contactors, which increase countercurrent vapor and liquid flow with centrifugal force (Stringle, 1987; Kellehar and Fair, 1996).

We can also operate hollow fiber distillation at flows below those commonly accessible in practice. For example, the data in Figure 4 show the number of transfer units per meter vs. the F-factor, a common variable for correlating results in structured packing. The data points in the figure are for hollow fibers; the curves are for two types of structured packing (Sulzer Chemtech). While the numbers are comparable, the flows with fibers can be much smaller than those in structured packing. Moreover, the contact area between liquid and vapor stays constant, independent of flow. In other types of packing, this area becomes smaller when the liquid starts to channel, running in rivulets or breaking into drops.

We should recognize that though we have reduced the fluid mechanical interactions between the liquid and vapor flows, we have not eliminated these. In particular, we find that we can easily operate only below a particular heating rate in any given module. This heating rate is small for a module with 12 fibers, reaches a maximum for a module with 50 fibers, and is smaller again for modules with 70 or more fibers. The reason for this behavior is a consequence of the equivalent of flooding. When the number of fibers is small, the valve at the bottom of the fiber bundle in Figure 1 is fully opened, but the pressure drop in the liquid-filled fibers is still not enough to insure adequate liquid flow. When the number of fibers is large, a corresponding effect occurs for the vapor flow rather than for the liquid flow. Our modules are made with a fixed diameter, so an increase in the number of fibers means a greater cross section for liquid flow, but a smaller cross section for vapor flow. At the largest number of fibers used, we believe that we must reduce the heating in order to insure even vapor flow. Of course, we can avoid these restrictions by installing pumps. Still, constraints in the current modules are the parallel to flooding in conventional equipment.

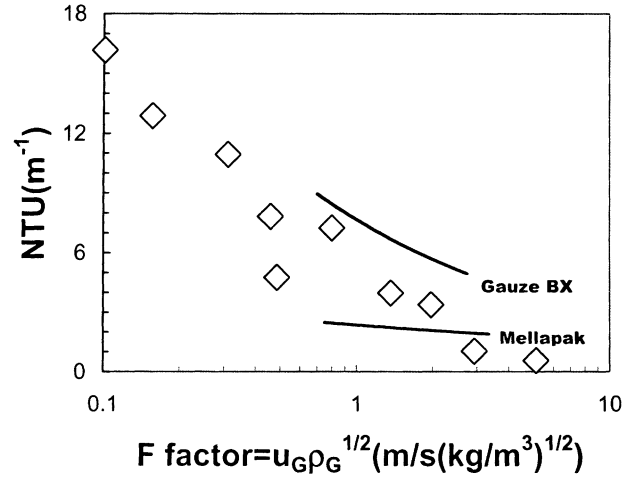

Figure 4. Hollow fibers operate below loading.

The F-factor is plotted vs. the number of transfer units. The data for hollow fibers are at lower flows than suggested for two structured packings, shown as the solid lines.

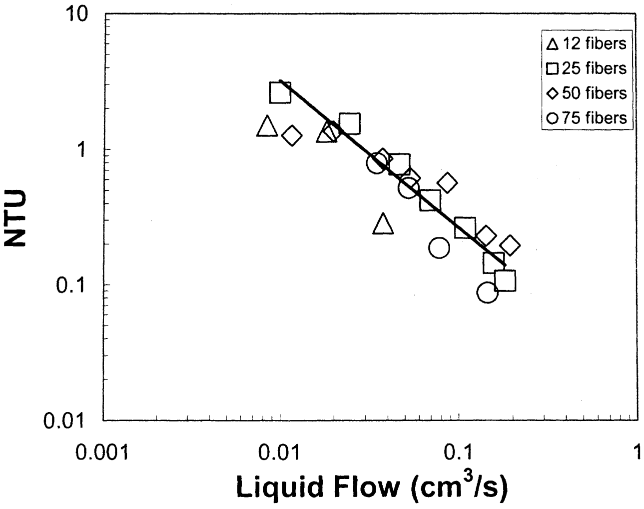

Figure 5. The number of transfer units (NTU) vs. liquid flow.

The solid line is predicted from published mass-transfer correlations.

We now turn to our measurements of NTUs in hollow fiber modules. These measurements, given in Figure 5, show that the NTU varies inversely with the $(-2/3)$ power of the liquid flow L. From Eq. 5, we see that the NTU is a function of both L and K_x; from Eq. 8, we see that K_x varies with k_L; and from Eq. 13, we see that k_L can vary with the cube root of v_L and, hence, of L. Thus, the variation of NTU with $L^{-2/3}$ is consistent with our expectations.

We can make these expectations more specific by predicting the NTUs for the 25-fiber module, as shown as the solid line in Figure 5. Here, we compare the NTU actually measured with those predicted from the equations given above. We assume that the membrane and the gas resistances combined are equivalent to about 1.4 s/cm, an average of the estimates in Table 1. Agreement is good. Thus, distillation in hollow fiber modules does behave as expected.

However, while the agreement between the experiment and prediction in Figure 5 is good, our results are considerably less reproducible than we had hoped. To illustrate this, we consider the distillate concentration plotted vs. heating rate, as shown in Figure 6. The data for different modules are overlapping, which might at first reassure us. However, the data include values for 12, 25, 50, and 75 fibers, which, of course, have areas per volume varying by a factor of six. Thus, we should have expected four sets of data for the four modules, and not the overlapping data sets which we observe.

The reason for this behavior is uneven flow on the shell side of the module. This uneven flow means that some rapidly

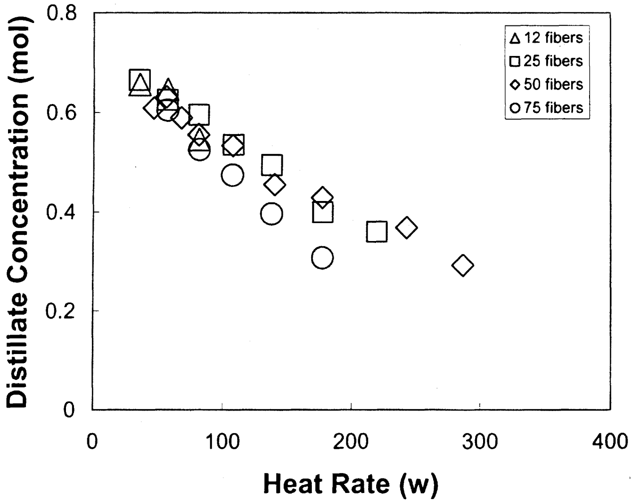

Figure 6. Distillate concentration vs. heating rate.

Because the heating rate is proportional to residence time in the column, the distillate concentration drops as the heating rate rises.

flowing vapor will pass through the module without any mass transfer, so that reported mass-transfer correlations vary widely (Lipnizki and Field, 2001). Some slowly flowing vapor will reach local equilibrium with the liquid, so its concentration will also be independent of mass-transfer rates. Under these conditions, Schlunder (1977) has shown that mass-transfer coefficients may vary nearly linearly with velocity. When we use our data to calculate mass-transfer coefficients, we sometimes observe a near-linear velocity variation, so we expect that this may be the case here. We will return to this point in the discussion which follows.

Discussion

The results above illustrate the advantages possible with hollow fiber distillation. The vapor and liquid flows are largely independent of the normal constraints of fluid mechanics, so that we can operate successfully at conditions which would normally cause flooding or not effect loading. The mass-transfer coefficients are typical values, but the interfacial area is high, so transfer rates are somewhat higher than normal. All these results are consistent with the estimates which we outlined earlier in the article.

We now want to explore three issues raised by these results. First, we want to know how much our module design can be improved. Second, we need to discuss how different separation equipment can be compared, especially because comparisons based on HTUs seem compromised. Third, we want to speculate about which distillations would be improved with hollow fibers.

We can improve the performance of our hollow fiber distillation by increasing either the membrane area per volume a or the overall mass-transfer coefficient K_G. If we use hollow fibers with half the diameter, we will double a, but we will increase the pressure drop in the hollow fibers by 16 times. At present, pressure drop is not a problem; indeed, we had to put a valve at the bottom of the hollow fiber bundle to *increase* the pressure drop. Still, the large increases in pressure drop caused by modest reductions in diameter suggest that we get a factor of two here, but not much more.

A more promising route to improved performance is to increase the overall mass-transfer coefficient K_L. As Eq. 8 shows, K_L includes contributions from the vapor, the membrane, and the liquid. As Table 1 shows, all three contributions are significant, so increasing any individual mass-transfer coefficient will help. In particular, we can most easily increase the individual mass-transfer coefficient inside the fibers by decreasing the fiber diameter, a change which is more significant at low flow. We can increase the membrane's coefficient k_M by reducing the thickness of the selective layer from around 7 μm to less than 1 μm, which will mean that the membrane's resistance should no longer contribute much to the overall coefficient. Both these changes are easily realized.

We believe the best chance of increasing K_L and, hence, improving module performance comes from changing the flow outside the fibers. We suggest replacing the current parallel vapor flow on the shell side of the module with baffled liquid flow back and forth across the fibers. Past studies suggest that one baffle produces a large gain, but that more than four baffles are unnecessary (Wang and Cussler, 1993). These past studies also suggest that such flow will typically increase k_L about four times. With all these changes in a and in flow, we believe that the $K_L a$ can increase the mass-transfer coefficient by about ten times. We are going to try to do this.

The second issue raised by these results is to speculate on how different separation equipment can best be compared. In the past, this comparison was most often made in terms of a height of the transfer unit or HTU, defined as (cf. Eq. 5)

$$HTU = \frac{L}{K_x a} = \frac{v_L}{K_L a} \tag{18}$$

In the past, values of the HTU were often nearly constant, around 0.2 to 0.5 m. The reason for this constant value is probably the near linear variation of the apparent mass-transfer coefficient with velocity. This variation was often not a characteristic of mass transfer, but a consequence of uneven flows during the process (Schlunder, 1977).

In more modern distillation packing, flows are much more even, and the mass-transfer coefficient varies with perhaps the square root of velocity. As a result, we might expect that, as the velocity became small, the HTU would also become small, and the equipment would become very efficient. In practice, as the fluid velocity becomes small, the liquid no longer evenly coats the packing, so that the area a between liquid and vapor is also reduced. As a result, even as the velocity gets small, the HTU remains fairly constant. This is why the HTU has been such a successful figure of merit for separations.

For hollow fiber distillation, this is all changed. As explained above, we expect K_L to vary with the cube root of velocity at high flow (Eq. 13 and Figure 5) and to become independent of the velocity at low flow (Eq. 15). Moreover, the area per volume a will remain independent of flow. Thus, as flow becomes small, the HTU will get small. Indeed, we can have an HTU as near zero as we like.

Thus, with the advent of hollow fiber distillation, an HTU is no longer a good figure of merit for comparing separation processes. However, an HTU of near zero is for a useless process which produces nothing. However, this raises a different question: how should these processes be compared?

One possible alternative way to compare differential distillation processes is through their $K_L a$'s. For example, imagine we want to compare hollow fibers with structured packing. Hollow fibers will normally have a larger a. Structured packing may have a larger K_L for two reasons: it has no membrane resistance, and it constantly refreshes the vapor-liquid interface, approaching the penetration limit of the mass transfer. Which of these factors is more important under practical conditions is a challenge for future experiments.

Finally, we want to speculate on where this technology could be applied. Sure, the large value of $K_L a$ and the independence of liquid and vapor flows are assets, but where will this ever be practical? The membrane modules are made of carbon-based polymer thin films, glued together with epoxy resins, which are not that different than those from the hardware store. Could this type of system ever be valuable?

We do not know. On the one hand, we know our current modules would obviously not stand the conditions routinely present in a refinery's pipe still. We believe that the current membranes would also be ineffective for the cryogenic distillation of air. Both these situations will require membrane modules made of very different materials than those used here, and these materials at present are unidentified.

On the other hand, we believe that there may be commercially valuable systems which merit further study, even with modules close to those used here. One possible choice is distillation of ethylene-ethane, a major inefficiency in the manufacture of an important commodity chemical (Sundaram et al., 1994). This distillation, made under pressure at modest temperatures, is difficult to effect with structured packing, possibly because the density difference between liquid and compressed vapor is smaller than normal. Even the best sieve trays perform less well than with other separations where the density difference is larger (Reed et al., 1995; Lawson and Lloyd, 2000). While we do not argue that ethylene-ethane is a natural for hollow fiber distillation, we do feel that this is the type of system which merits further thought. We look forward to finding and learning of new studies of distillation using hollow fiber membranes.

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Notation

a = hollow fiber area per module volume
c = molar concentration
d = fiber diameter
d_h = hydraulic diameter in module
D = diffusion coefficient
G = molar flux of vapor
G' = mass flux of vapor
H = Henry's law coefficient
k_G, k_L, k_M = individual mass-transfer coefficients based on a concentration driving force
k_m, k_x, k_y = individual mass-transfer coefficients based on a mole fraction driving force
K_L, K_x = overall mass-transfer coefficients based on liquid concentration and mole fraction differences, respectively
ℓ = column height
L = molar flux of liquid
L' = mass flux of liquid
m = partition coefficient
v = velocity
x = mole fraction in liquid
x^* = mole fraction in liquid at equilibrium
y = mole fraction in vapor
z = distance
ϵ = void fraction
ν = kinematic viscosity
ρ_G, ρ_L = vapor and liquid densities, respectively

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