

IDEAL DISTILLATION SYSTEMS

11

In this chapter we shall look at the synthesis of distillation-based separation systems. A separation system is a collection of devices to separate a multicomponent mixture in two or more desired final products. We shall start this chapter by designing a process to separate a mixture of three normal alkanes. We shall next look at separating a mixture of five alcohols, using insights from the first problem but adding a few as the problem has many more design alternatives. These mixtures display fairly ideal behavior and are much easier to consider than mixtures that display highly nonideal behavior. The heat integration of distillation processes is the subject of the next chapter while the separation of nonideal mixtures is the subject of Chapter 14.

11.1 SEPARATING A MIXTURE OF *n*-PENTANE, *n*-HEXANE, AND *n*-HEPTANE

In this example we assume we have an equimolar mixture flowing at 10 mol/s that is 20 mole % *n*-pentane, 30% *n*-hexane, and 50% *n*-heptane. Our goal is to separate this mixture into three products: 99% pure *n*-pentane, 99% pure *n*-hexane, and 99% pure *n*-heptane. Let us assume the feed and the products will all be liquids at their bubble points—that is, each is just ready to boil. If we were to decide to use distillation to accomplish this separation, Figure 11.1 shows two process alternatives that we should consider. In the direct sequence, we remove the most volatile species, pentane, in the first column and then separate the hexane and heptane in the second, while in the indirect sequence, we remove the heaviest species, heptane, first and then separate pentane from hexane. We might be interested in discovering which is less expensive to buy and operate. When we

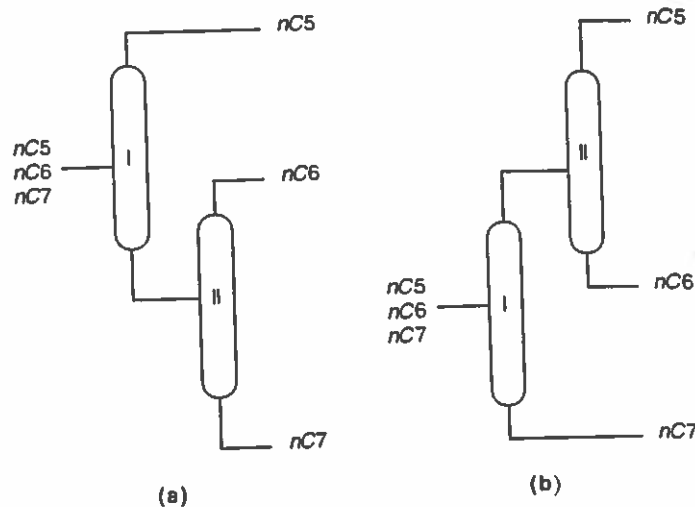


FIGURE 11.1 Two alternatives to separate $nC5$, $nC6$, and $nC7$ using distillation: (a) the direct sequence, and (b) the indirect sequence.

consider heat integrating columns—as we shall do in the next chapter—we can readily propose several other distillation-based separation schemes.

11.1.1 Do the Species Behave Ideally for Distillation?

We must first decide if these species display fairly ideal behavior during distillation. It does little good to design a system assuming ideal behavior if the mixture does not display it. For example, suppose we wish to separate toluene from water. We could assume ideal behavior and propose using distillation. However, these two species do not like each other at all. They will spontaneously separate into two fairly pure liquid phases: a toluene-rich phase and a water-rich phase. If the separation is complete enough for our needs, then the cost of separating is the cost of a decanter. A decanter will likely be much less costly than the column we would have designed assuming ideal behavior. Another possibility is that some of the species form azeotropes, as ethanol and water do. If any do, then we must design a very different process even if we can use distillation to accomplish the final separation. We will look at how to check for nonideal behavior in more detail in Chapter 14.

For species that are very similar—as are the n -alkanes we are considering here—we should expect close to ideal behavior. Table 11.1 contains some preliminary physical property data for these species. From this data we see there is quite a difference in normal boiling points, which should make the separation easier. All normal boiling points are above room temperature, although n -pentane is only just above. We include the critical properties so we have an idea of the extreme conditions we would dare to consider.

One of the first steps we might take is to compute several flash simulations for these species to see the volatility behavior they will display in a distillation column. In particu-

TABLE 11.1 Property Data for Alkane Example

Property	<i>n</i> -Pentane	<i>n</i> -Hexane	<i>n</i> -Heptane
<i>MW</i>	72.151	86.176	100.205
T_{boiling} , K	309.187	341.887	371.6
T_C , K	469.8	507.9	540.2
P_C , K	33.3	29.3	27.0

lar, we might wish to see what their relative volatilities are and how much they vary as composition varies. Table 11.2 shows the relative volatilities when we perform three flash calculations for the feed composition using a simulator: a bubble point flash, one where 50% of the feed exits as vapor, and a dewpoint flash. We used the Unifac method to evaluate liquid activity coefficients (as a precaution against surprising nonideal behavior). We see that the relative volatilities do not change too much. When we consider the behavior at infinite dilution (we did a bubble point calculation for each of three mixtures, each having a composition of a part per million for two of the species in the third), the relative volatilities range from 4.99 to 9.03 for *n*C5 relative to *n*C7 and from 2.25 to 3.02 for *n*C6 relative to *n*C7. These variations should not be ignored, but they do not indicate particularly nonideal behavior either.

11.1.2 Goals for Our System Design

What might be the goals for our system design? One goal is to create the system having the least cost, but what do we mean by "cost"? As we saw in Chapter 5, we can measure the cost by modeling the cash flow caused by our design. In this case there will be an initial investment in purchasing and installing the equipment and then there will be annual costs in operating it. Operating costs will include utility and labor costs. The present worth of these cash flows can be the cost we then choose to minimize.

We also want our process to be safe. It should not needlessly employ hazardous chemicals. Indeed, if the species are sufficiently hazardous, we may choose not to build the process. It should not operate at extreme conditions of temperature and pressure if we can

TABLE 11.2 Example Relative Volatilities

	Percent of Feed Vaporized in Flash	Temperature (K)	Relative Volatility for <i>n</i> C5 Relative to <i>n</i> C7	Relative Volatility for <i>n</i> C6 Relative to <i>n</i> C7
Bubble Point	0	341.6	6.24	2.46
	50	351.3	5.51	2.32
Dewpoint	100	357.4	5.76	2.36

avoid it. It should also be environmentally benign. It should be flexible enough to operate at expected levels of production. From both a safety and an environmental point of view, not introducing any other species to carry out the separation would have its advantages.

For our original screening, we shall concentrate on minimizing costs, but we shall always watch out for safety and environmental issues as they arise.

11.1.3 Evaluating Cost

It will take us some effort to compute the costs for a column. We are trying at this point just to screen among alternatives; perhaps we can use a simpler evaluation. One we might consider is the vapor flow predicted within the column. The larger this flow, the larger the column diameter must be to accommodate it. Also, for a given feed, a larger vapor flow indicates a more difficult separation, which suggests there are more trays. Finally, the utilities consumed in a column create vapor in the reboiler and condense it in the condenser. Thus, the vapor flow directly reflects the utility use in a column. For this reason several authors have suggested its use in preliminary screening of design alternatives for separation systems consisting only of distillation columns. They suggest choosing the separation process that minimizes the sum of the vapor flows in its columns.

MINIMUM VAPOR FLOWS

How can we estimate vapor flow in a column? For nearly ideal behavior where we are willing to assume constant relative volatilities and constant molar overflow throughout a column, we can use Underwood's method to estimate minimum internal vapor and liquid flows. For preliminary design purposes, we may set the actual vapor flow to be a multiple, say 1.2, times the minimum vapor flow estimated for each column. If we do, then the total of the actual vapor flows in a column sequence will be 1.2 times the total of the minimum vapor flows for it. Thus, we can search for the better sequences using the total of their minimum vapor flows.

Underwood's method uses the following three equations:

$$\sum_i \frac{\alpha_{ik}}{\alpha_{ik} - \phi} f_i = (1 - q)F \quad (11.1)$$

$$(R_{\min} + 1)D = \sum_i \frac{\alpha_{ik}}{\alpha_{ik} - \phi} d_i = V_{\min} \quad (11.2)$$

$$\bar{R}_{\min} B = - \sum_i \frac{\alpha_{ik}}{\alpha_{ik} - \phi} b_i = \bar{V}_{\min} \quad (11.3)$$

where α_{ik} is the relative volatility of species i to k , f_i the molar flow of species i in the feed, q the fraction of the feed that joins the liquid stream at the feed tray, F the total molar flow of the feed, D the molar flow of the distillate, R_{\min} the minimum reflux ratio ($= L_{\min}/D$), d_i the molar flow of species i in the distillate, V_{\min} the minimum vapor flow possible in the top section of the column to accomplish the desired separation, \bar{R}_{\min} the

minimum reboil ratio ($= \bar{V}_{\min}/B$), b_i the molar flow for species i in the bottoms product, and \bar{V}_{\min} the minimum vapor flow in the bottom section of the column). The final variable in these equations is ϕ , which we shall define through its use in the next subsections.

Estimating Product Compositions. We wish to estimate the minimum vapor flows needed to separate our given feed mixture of 20% *n*-pentane, 30% *n*-hexane, and 50% *n*-heptane into one 99% pure product for each of the three feeds and products to a column. To use Underwood's equations we must estimate the compositions for the feeds and products to a column. To make these estimates, we need to make some assumptions about what exactly is contaminating each product. Let us assume that a product is contaminated only by species immediately adjacent to it in volatility. If there are two adjacent species—one more volatile and one less—let us further assume that they each supply half the allowed contamination. We assume, therefore, that the pentane product is contaminated only with hexane, that the hexane will be contaminated equally with both pentane and heptane, and the heptane is contaminated only with hexane. Thus, we start our problem by assuming that the product compositions are as shown in Table 11.3, where product I is the one rich in pentane, product II in hexane, and III in heptane. These product specifications are to hold no matter the distillation sequence we select.

We can write equations based on molar flows, μ , for our process as follows.

$$\mu_I(nC5) + \mu_{II}(nC5) = 2 \text{ mol/s}$$

$$\mu_I(nC6) + \mu_{II}(nC6) + \mu_{III}(nC6) = 3 \text{ mol/s}$$

$$\mu_{II}(nC7) + \mu_{III}(nC7) = 5 \text{ mol/s}$$

We note, from the initial product specifications, that we can also write:

$$\text{Product I: } \mu_I(nC5) = 99 \mu_I(nC6)$$

$$\text{Product II: } \mu_{II}(nC5) = \frac{5}{990} \mu_{II}(nC6), \mu_{II}(nC7) = \frac{5}{990} \mu_{II}(nC6)$$

$$\text{Product III: } \mu_{III}(nC7) = 99 \mu_{III}(nC6)$$

Substituting these latter four into the first three gives us three equations in the three flows for hexane that we can readily solve. Therefore, we can quickly compute the flows shown in Table 11.4.

TABLE 11.3 First Guess at Product Molar Percentages

	Feed	Product I <i>n</i> C5 rich	Product II <i>n</i> C6 rich	Product III <i>n</i> C7 rich
<i>n</i> C5	20	99	0.5	0
<i>n</i> C6	30	1	99	1
<i>n</i> C7	50	0	0.5	99

TABLE 11.4 Flows for Process in Figure 11.1a that Satisfy Composition Specifications Given in Table 11.3

Species	Product I mol/s	Product I mol%	Product II mol/s	Product II mol%	Product III mol/s	Product III mol%
<i>n</i> C5	1.985	0.99	0.015	0.005	0	0
<i>n</i> C6	0.020	0.01	2.930	0.99	0.050	0.01
<i>n</i> C7	0	0	0.015	0.005	4.985	0.99
total	2.005	1	2.960	1	5.035	1

Note that for high purity products (as here), one can readily estimate these flows using approximate computations. The contaminant flow for Product I is approximately 1% of the flow of pentane, i.e., 1% of 2 mol/s or 0.02 mol/s of hexane. The contaminants for Product II are each 0.5% of the flow of the heptane: 0.015 mol/s each of pentane and heptane. Finally, the contaminant flow for product III is 1% of 5 mol/s or 0.05 mol/s. We then correct the flow of pentane leaving in product I by reducing it by 0.015 mol/s, for hexane in Product II by removing 0.015 + 0.05 mol/s and for heptane in Product III by removing 0.015 mol/s.

Estimating Minimum Vapor Flows. For Underwood's method we start by using Eq. (11.1) to estimate the unknown variable ϕ . This equation involves only relative volatilities and information on the overall feed to the process. Thus, its value does not depend on the sequence we select to carry out the separation. We know from earlier that the relative volatilities are not constant, but they are nearly so. We need to use reasonable values; let us pick those we obtained when flashing 50% of the feed, as given in Table 11.2. For a bubble point feed, feed quality as indicated by q is equal to unity. Thus, we write:

$$\frac{5.51}{5.51 - \phi} \times 2 \text{ mol/s} + \frac{2.32}{2.32 - \phi} \times 3 \text{ mol/s} + \frac{1}{1 - \phi} \times 5 \text{ mol/s} = (1 - 1) \times 10 \text{ mol/s} = 0$$

Inspecting this equation, we will discover that it has three values for ϕ that satisfy it, one between $\alpha_{1,3} = 5.51$ and $\alpha_{2,3} = 2.32$, one between $\alpha_{2,3} = 2.32$, and $\alpha_{3,3} = 1.0$ and one at infinity. To see this behavior, let ϕ take a value just below 5.51, say 5.5099999999. The first term on the left-hand side will be very large and positive; it will dominate the left-hand side terms. As ϕ decreases and approaches 2.32 from above, the second term starts to dominate and move to negative infinity. The left-hand side thus decreases from plus infinity to negative infinity as ϕ moves from 5.51 to 2.32. At the same time, the right hand side remains at zero. Thus, there must be a solution between 5.51 and 2.32 where the left hand side crosses zero. The second and third terms on the left-hand side display the same behavior as ϕ moves from just below 2.32 to just above 1. Finally, the left-hand side asymptotically approaches zero as ϕ approaches either plus or minus infinity. We can use a root finder, for example, the goal seeking tool in Excel[®], to find the two finite roots, which are 3.806 and 1.462.

Specifications

Product III mol%
0
0.01
0.99
1

mate these flows is approximately 6.4 mol/s. The contaminants of pentane and hexane are 0.05 mol/s. We must separate 0.015 mol/s, for Product III by re-

method we start by using only relative volatilities. The value does not determine earlier that the minimum reasonable value in Table 11.2. Thus, we write:

$$0.015 - \phi = 0$$

ϕ that satisfy it, $\phi = 1.0$ and one other root. The minimum value of the left-hand term starts at $\phi = 1.0$, the right hand term is zero, where the left hand side is zero. We can use a quadratic equation to find two finite roots,

At this point we must select which of the two sequences we wish to analyze. For the direct sequence, the first column separates pentane from the other two species; its light key is pentane and its heavy key hexane. Its distillate product is product I, and its bottom product is everything else: the sum of products II and III. Underwood's method requires us to select the value for ϕ that lies between the volatilities for the key components for the column. Therefore, we select $\phi = 3.806$ and substitute this value into Eq. (11.2) to compute V_{min} , getting:

$$V_{min} = \frac{5.51}{5.51 - 3.806} \times 1.985 + \frac{2.32}{2.32 - 3.806} \times 0.020 = 6.4 \text{ mol/s}$$

Note we have used the distillate product flows for this column in this equation.

To compute the minimum vapor flow for the second column in the direct sequence, we must first establish its feed, which, as we noted above, is the sum of products II and III in Table 11.4: 0.015, 2.98, and 5 mol/s respectively for species *nC5*, *nC6*, and *nC7* respectively. The light and heavy key components for this column are *nC6* and *nC7* respectively.

For this column Underwood's Eq. (11.1) becomes:

$$\frac{5.51}{5.51 - \phi} \times 0.015 + \frac{2.32}{2.32 - \phi} \times 2.98 + \frac{1}{1 - \phi} \times 5 = 0$$

and the root between the volatilities for the key components is 1.553. The minimum vapor rate is given by Underwood's equation II to be:

$$V_{min} = \frac{5.51}{5.51 - 1.553} \times 0.015 + \frac{2.32}{2.32 - 1.553} \times 2.93 + \frac{1}{1 - 1.553} \times 0.015 = 8.9 \text{ mol/s}$$

The total of the minimum vapor flows is, therefore, 15.3 mol/s for the direct sequence.

The two columns for the indirect sequence, as shown in Figure 11.1b, give minimum vapor flow of 10.7 and 5.5, respectively, for a total of 16.2 mol/s. According to the heuristic we should select the direct sequence.

MARGINAL VAPOR FLOWS

We introduce here an even less complicated evaluation function to compare sequences. Both of the sequences to separate *nC5*, *nC6*, and *nC7* split *nC5* from *nC6* and *nC6* from *nC7*. In the direct sequence, we carry out the *nC5/nC6* split in the presence of all of the *nC7* in the original feed, while the *nC6/nC7* split is without any *nC5* present. In the indirect sequence the reverse is true: The *nC6/nC7* split has all of the *nC5* present while the *nC5/nC6* has no *nC7* present.

Let us compare sequences by looking at how each is impacted by the presence of other species in carrying out a split between the key components for the column. Underwood's equations give us a possible way to make this estimate. Let us rewrite Eq. (11.1) in the form:

$$\sum \frac{\alpha_{i,k}}{\alpha_{i,k} - \phi} f_i = (1-q)F$$

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$$(R_{min} + 1)D = \sum \frac{\alpha_{i,k}}{\alpha_{i,k} - \phi} d_i = V_{min}$$

$$\sum_i \frac{\alpha_{i,k}}{\alpha_{i,k} - \phi} f_i = \sum_i \frac{\alpha_{i,k}}{\alpha_{i,k} - \phi} d_i + \sum_i \frac{\alpha_{i,k}}{\alpha_{i,k} - \phi} b_i = (1-q)F$$

Rearranging and using Eq. (11.2) gives:

$$V_{min} = \sum_i \frac{\alpha_{i,k}}{\alpha_{i,k} - \phi} d_i = (1-q)F - \sum_i \frac{\alpha_{i,k}}{\alpha_{i,k} - \phi} b_i \quad (11.4)$$

This equation relates V_{min} to a sum of terms for the presence of the species that exist in the distillate and to those that exist in the bottoms. Let us assume that the value of ϕ does not move very much whether the species other than the key species are in the feed or not for a column. Then the marginal contribution we might expect to V_{min} in the first column of the direct sequence caused by the presence of $nC7$ is approximately:

$$\Delta V_{min}(nC5/nC6, nC7) = - \frac{\alpha_{nC7, nC7}}{\alpha_{nC7, nC7} - \phi} = - \frac{1}{1 - 3.806} \times 5 \text{ mol/s} = 1.8 \text{ mol/s}$$

We note further that ϕ has a value somewhere between the relative volatilities of the two key species, $nC5$ and $nC6$. Let us assume it takes a value that is the average: 3.915. We would then estimate the extra vapor flow to be

$$- \frac{1}{1 - 3.915} \times 5 \text{ mol/s} = 1.7 \text{ mol/s}$$

For the indirect sequence we estimate the marginal vapor flow in the first column using the same type of argument to be

$$\frac{5.51}{5.51 - \frac{2.32 + 1}{2}} \times 2 \text{ mol/s} = 2.9 \text{ mol/s}$$

The indirect sequence shows a marginal flow that is 1.2 mol/s larger than the direct sequence. Our more accurate analysis above using Underwood's method gave a difference in total minimum flows of 16.2 - 15.3 or 0.9 mol/s. Both are estimates for the same differences, and both are telling us the direct sequence is better.

A SIMPLE MEASURE TO COMPARE SEQUENCES

We appear to have a very simple measure we can use to compare distillation sequences for separating relatively ideal mixtures using conventional distillation. It says to form the term

$$\left| \frac{\alpha_{i,k}}{\alpha_{i,k} - \frac{\alpha_{lk,k} + \alpha_{hk,k}}{2}} \times f_i \right| \quad (11.5)$$

for each species i that is not a key component for a column but is present in the feed to a column. The sum of such terms will indicate the increase in the minimum vapor flow

caused by the presence of these nonkey species for that column. We would prefer those sequences having the lowest total of marginal flows for all columns in them.

Looking at the form of this term we see that, the more the relative volatility differs from the volatilities of the key components, the larger the denominator and thus the lower the marginal flow. That is intuitively appealing. We also see that the marginal flowrate is directly proportional to the flowrate of the species in the feed, also intuitively appealing. A bit less obvious is that, the higher the volatility of the nonkey species present, the more it increases the marginal flowrate. It appears that the presence of the more volatile species is bad news. This suggests we should find ourselves preferring the direct sequence more often than the indirect one. The extra species for the direct sequence are always the less volatile ones in the mixture.

Reexamining our results for choosing between the direct sequence and the indirect for separating $nC5$, $nC6$, and $nC7$, we see that the lesser amount of $nC5$ favors the indirect sequence (it would be the better extra species present based on its flowrate of 2 mol/s versus 5 mol/s for $nC7$), but the higher volatility of $nC5$ (5.51 versus 1) favors the indirect sequence. The denominators are $3.9 - 1 = 2.9$ for the direct versus $5.5 - 2.2 = 3.3$ for the indirect suggesting their difference is not too important here in deciding. The higher volatility consideration dominates, and we choose the direct sequence.

11.2 SEPARATING A FIVE-COMPONENT ALCOHOL MIXTURE

We learned a lot from our previous example that will make this example much easier to analyze. Suppose we have a mixture of five alcohols that we shall label A , B , C , D , and E with flows in the feed of 1, 0.5, 1, 7, and 10 mol/s respectively, for a total of 19.5 mol/s. Suppose further that their relative volatilities are 4.3, 4, 3, 2, and 1 respectively. We note there is a lot of the heaviest species, which suggests we might prefer to remove it early in the best sequences.

We would like to find the preferred separation sequence based on the use of "simple" distillation columns. We use our approximate measure that estimates marginal vapor flows to choose among them. Table 11.5 gives the estimated marginal vapor flows we evaluate for each species over all possible key component pairs. For example, for a column to split D from E , having C present will increase the minimum vapor flow by 2.000

TABLE 11.5 Marginal Vapor Flows Estimated for Nonkey Species for Alcohol Example

	A	B	C	D	E
A/B	—	—	2.6	6.5	3.2
B/C	5.3	—	—	9.3	4.0
C/D	2.4	1.3	—	—	6.7
D/E	1.5	0.8	2.0	—	—

mol/s, having *B* present by 0.800 mol/s, and so on. Having both *C* and *B* present will add $2.000 + 0.800 = 2.800$ mol/s to the minimum vapor flow.

In Figure 11.2 we tabulate the total marginal vapor flows for all the columns that can exist in any of the separation processes possible based on simple distillation columns. They are placed in such a way that we can more easily see the total flows for each of the different sequences we can construct. For example, suppose we select the direct sequence. From this figure, the marginal flows should be for *A/BCDE*, *B/CDE*, and *C/DE* for a total of $12.3 + 13.3 + 6.7 = 32.2$ mol/s.

We wish to find the sequence with the minimum sum of marginal flows. We can readily do this from this figure by performing a *branch and bound* search. We start by comparing all the first separations we might make for the original feed: *A/BCDE*, *AB/CDE*, *ABC/DE* and *ABCD/E*. The one with the lowest marginal vapor flow is the split *ABCD/E* at 4.3 mol/s. With this split made, we next compare flows for *A/BCD*, *AB/CD* and *ABC/D*, choosing the split *ABC/D* for a total of $4.3 + 3.7 = 8.0$ mol/s. We have the mixture *ABC* to separate and compare *A/BC* and *AB/C*; we select *A/BC* to add another 2.6 mol/s for a total of 10.6 mol/s.

We now have a complete solution. We need to examine only solutions that can be less than 10.6 mol/s. Backing up to the decision among the alternatives *A/BCD*, *AB/CD* and *ABC/D*, we see that the second best decision, *A/BCD* with a flow total marginal flow of $4.3 + 9.1 = 13.4$ mol/s, will lead to a partial solution that exceeds 10.6 mol/s. Thus we

	13.3	6.7
	<i>B/CDE</i>	<i>C/DE</i>
12.3	8.0	2.0
<i>A/BCDE</i>	<i>BC/DE</i>	<i>CD/E</i>
18.6	2.8	9.3
<i>AB/CDE</i>	<i>BCD/E</i>	<i>B/CD</i>
10.4	9.1	1.3
<i>ABC/DE</i>	<i>A/BCD</i>	<i>BC/D</i>
4.3	14.6	2.6
<i>ABCD/E</i>	<i>AB/CD</i>	<i>A/BC</i>
	3.7	5.4
	<i>ABC/D</i>	<i>AB/C</i>

FIGURE 11.2 Total marginal flows for each of the columns making up all separation sequences for five components.

back up to our first decision. Only the decision *ABC/DE* could be less expensive but it has a marginal flow already of 10.4 mol/s. To complete this sequence we must add in the flows for separating *ABC*, a decision we already examined. The lowest marginal cost comes from using *A/BC* with a flow of 2.6 mol/s; it leads to too high a final marginal flow. Thus we now know that our solution—*ABCD/E*, *ABC/D*, and *A/BC*—must be the best solution based on the marginal flow estimates we have made to carry out our search.

We can easily enumerate the marginal vapor flows for the fourteen possible sequences for this example; we do so in Table 11.6. We see that marginal vapor flows range from a minimum of 10.6 mol/s to maximum of 32.3 mol/s.

11.2.1 Discussion

Selecting the best distillation-based separation sequence among those possible for separating relatively ideally behaving species has been the subject of many publications over the past quarter century. The emphases in these publications have been many: how to reduce the effort to search among the alternatives, the posing and testing of heuristics to select among the alternatives, how to evaluate alternatives. We shall start this section by exposing the size of the search problem.

NUMBER OF POSSIBLE SEQUENCES

As we have seen in the alcohol example above, we can readily generate many different separation sequences to separate a given mixture into desired products. A formula exists to estimate the number of sequences for separating n species into n pure component prod-

TABLE 11.6 Total Marginal Vapor Flows for all Fourteen Possible Sequences for Alcohol Example

Seq. No.	Separations in Sequence	Marginal Vapor Cost	Rank
1	<i>A/BCDE</i> , <i>B/CDE</i> , <i>C/DE</i> , <i>D/E</i>	32.3	14
2	<i>A/BCDE</i> , <i>B/CDE</i> , <i>CD/E</i> , <i>C/E</i>	27.6	13
3	<i>A/BCDE</i> , <i>BC/DE</i> , <i>B/C</i> , <i>D/E</i>	20.3	8
4	<i>A/BCDE</i> , <i>BCD/E</i> , <i>B/CD</i> , <i>C/D</i>	24.4	11
5	<i>A/BCDE</i> , <i>BCD/E</i> , <i>BC/D</i> , <i>B/C</i>	16.4	6
6	<i>AB/CDE</i> , <i>A/B</i> , <i>C/DE</i> , <i>D/E</i>	25.3	12
7	<i>AB/CDE</i> , <i>A/B</i> , <i>CD/E</i> , <i>C/D</i>	20.6	9
8	<i>ABC/DE</i> , <i>A/BC</i> , <i>B/C</i> , <i>D/E</i>	13.0	2
9	<i>ABC/DE</i> , <i>AB/C</i> , <i>A/B</i> , <i>D/E</i>	15.8	5
10	<i>ABCD/E</i> , <i>A/BCD</i> , <i>B/CD</i> , <i>C/D</i>	22.7	10
11	<i>ABCD/E</i> , <i>A/BCD</i> , <i>BC/D</i> , <i>B/C</i>	14.7	4
12	<i>ABCD/E</i> , <i>AB/CD</i> , <i>A/B</i> , <i>C/D</i>	18.9	7
13	<i>ABCD/E</i> , <i>ABC/D</i> , <i>A/BC</i> , <i>B/C</i>	10.6	1
14	<i>ABCD/E</i> , <i>ABC/D</i> , <i>AB/C</i> , <i>A/B</i>	13.4	3

ucts using simple sharp separators. In this section we shall first define and illustrate what a simple sharp separator is and then present the formula.

Simple Sharp Separators. A simple sharp separator splits its feed into two products, each having no species in common with the other. A simple distillation column that splits its feed containing species A , B , C , and D into the two products A and BCD is an example of a simple sharp separator.

There are other separation processes that act as simple sharp separators. For example, an extractive distillation column immediately followed by a column to recover the extractive agent is a simple sharp separator. Consider, for example, using an extractive agent to separate propylene from propane, as illustrated in Figure 11.3. We feed propane and propylene into this two-column process and remove a pure propane and a pure propylene product from it. Thus, the two columns together act like a sharp separator. The extractive agent simply recycles. (Of course some of the agent is lost with the products and must be made up using a small makeup solvent stream.)

The relative volatility between propylene and propane varies from about 1.06 to 1.09, with propylene being the more volatile. Using distillation to separate propylene from propane requires a very large column, 150 or more stages, and a reflux ratio of 20 or

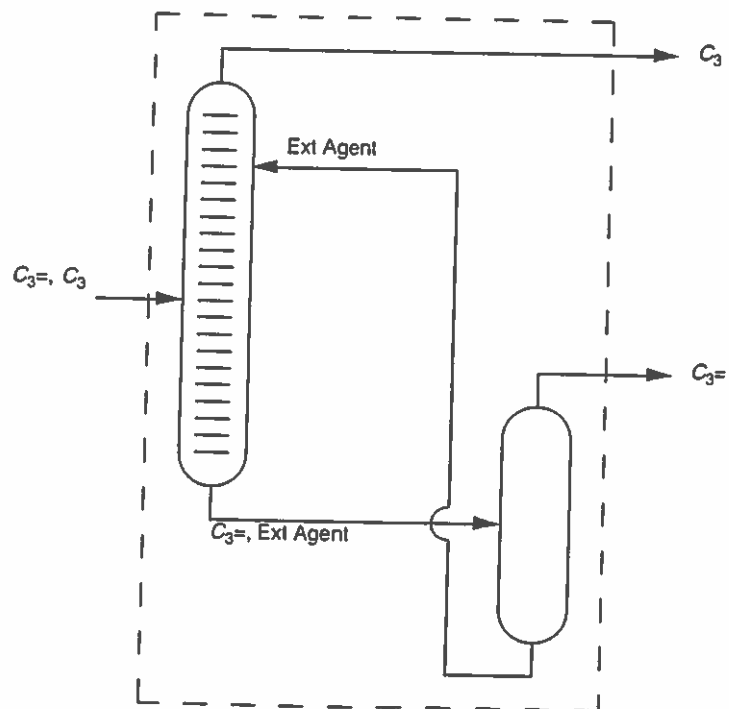


FIGURE 11.3 Separating propylene and propane using an extractive agent.

more. This reflux ratio says we must condense 20 moles of top product (propylene) and reflux it for every mole of propylene product we remove from the column. Thus, it requires the expenditure of a lot of utilities for each mole of product.

An extractive agent is typically a heavy species that preferentially "likes" one of the two species. Here acrylonitrile with its double bonds is a candidate. The extractive agent is fed into the column a few trays below the top so it will be present in the liquid phase on all stages below where it is fed. The propylene/propane feed enters the column well below the extractive agent. The agent alters the activity coefficients for propylene and propane in such a way that propylene becomes much less volatile than propane, thus the stages between the two feeds remove the propylene from the propane in the presence of the extractive agent. Only propane makes it to the tray where we feed the extractive agent. Being much more volatile than the extractive agent, a few additional trays above that feed allows us to separate the propane from the agent. Propylene and agent become the bottoms product. We then have to separate the propylene and agent in a second column, recycling the agent back to the first column.

The Thompson and King Formula to Compute the Number of Sequences. Thompson and King (1972) developed the following formula to compute the number of sequences that can be developed based on simple sharp separators to separate a mixture containing n components into n pure component products:

$$\text{no. sequences} = \frac{(2(n-1))!}{n!(n-1)!} S^{n-1}$$

Table 11.7 lists the number of sequences for different numbers of species in the mixture and for up to three separation methods. While the numbers of sequences grow large quite quickly as a function of the number of species, they grow almost explosively when one allows different types of separators to carry out each task. Thus, many efforts in the synthesis of separation processes have emphasized how one can search these large spaces and/or how one can quickly find good solutions among the large number of alternatives.

TABLE 11.7 Number of Sequences to Separate n Components into n Single Component Products Using S Different Separation Methods

nS	1	2	3
2	1	2	3
3	2	8	18
4	5	40	135
5	14	224	1134
6	42	1344	10,206
7	132	8448	96,228
10	4862	2,489,344	95,698,746

HEURISTICS

One approach to finding good separation processes quickly is to use heuristics. These are guidelines based on experience that aid a designer to find the better solutions for the type of problem at hand. If we have a good solution to our separation problem, we know we need not look further at any other solution that we can prove will cost more. We used such a bounding idea in the branch and bound search we carried out in the alcohol example above. We can also use heuristics in a negative way where we eliminate any part of a solution that we believe will be much too expensive to be in any solution. Not allowing certain separation steps in any solution can often dramatically reduce the size of a search.

We list in Table 11.8 a set of commonly used heuristics for designing separation sequences (for example, see Seader and Westerberg, 1977). Note that the last heuristic states that we have listed these heuristics in order of importance in our decision making.

Let us apply these heuristics to find a separation process for the example in section 11.2, the example to separate five alcohols. To remind ourselves, we have a mixture of five alcohols that we labeled *A*, *B*, *C*, *D*, and *E* with flows in the feed of 1, 0.5, 1, 7, and 10 mol/s respectively, for a total of 19.5 mol/s. These species have relative volatilities of 4.3, 4, 3, 2, and 1 respectively.

Heuristic 1 is not applicable as we are treating none of these alcohols as dangerous or corrosive. For heuristics 2 and 3, we need first to compute relative volatilities for each possible pair of key components. These relative volatilities are simply the ratio of the relative volatility for the light key divided by that for the heavy key: $4.3/4 = 1.075$ for *A/B*, $4/3 = 1.333$ for *B/C*, $3/2 = 1.5$ for *C/D* and $2/1 = 2$ for *D/E*. While one is only just larger than 1.05, none is less so we skip to heuristic 4. Heuristic 4 tells us to make the easiest split first, suggesting we make the split between *D* and *E* where the relative volatility between the key components is the largest with a value of 2. Heuristic 5 also suggests we make a split that leads to the removal of species *E*. Heuristic 6 proposes we remove species *A* first (the direct sequence). For heuristic 7, we note that all species are desired

TABLE 11.8 Heuristics for Designing Separation Processes

Heuristic 1:	Remove dangerous and/or corrosive species first.
Heuristic 2:	Do not use distillation when the relative volatility between the key components is less than 1.05.
Heuristic 3:	Use extractive distillation only if the relative volatility between the key components is much better than for regular distillation—say 6 times better.
Heuristic 4:	Do the easy splits (i.e., those having the largest relative volatilities) first in the sequence.
Heuristic 5:	Place the next split to lead to the removal of the major component.
Heuristic 6:	Remove the most volatile component next (i.e., choose the direct sequence).
Heuristic 7:	The species leading to desired products should appear in a distillate product somewhere in the sequence if at all possible.
Heuristic 8:	These heuristics are listed in order of importance.

Exercises

products. The direct sequence would maximize the number of them that would appear in a distillate somewhere in the sequence.

The last heuristic says to carry out the decision supported by the heuristic with the lowest number. So we elect to remove species *E*, as supported by both heuristics 4 and 5. A similar set of arguments leads us to remove species *D* next. The *B/C* split is much easier than the *A/B* split so we elect it next, leaving us with the *A/B* split last. This solution is the third best among the fourteen possible based on marginal vapor flows (see Table 11.6). It is only slightly worse than the second best. Using these heuristics, the effort we took to find it was minimal.

With a little thought it is possible to develop a variety of different search strategies using just these heuristics. For example, one might enumerate all sequences where at least one heuristic supports each decision leading to it. We will not examine any of the others.

The next chapter (Chapter 12) will look at heat integrating distillation columns. Chapter 14 looks at the synthesis of separation processes for species that behave highly nonideally. In Chapter 17 and part of Chapter 18 we shall look again at the search problem for distillation sequences for relatively ideally behaving species, but this time we shall propose search algorithms that use mixed integer programming.

REFERENCES

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- Seader, J. D., & Westerberg, A. W. (1977). A combined heuristic and evolutionary strategy for synthesis of simple separation sequences. *AIChEJ*, 23, 951.
- Thompson, R. W., & King, C. J. (1972). Systematic synthesis of separation systems. *AIChEJ*, 18, 941.

EXERCISES

The first four problems are a review of undergraduate distillation concepts. Students who cannot do these should review appropriate undergraduate textbook material on distillation.

1. Consider a column to separate acetone from ethanol. The equilibrium data for acetone in ethanol at one atm are in Table 11.9 (Perry, 1950).
The feed has a flowrate of 0.1 kgmol/s. It is 50 (mole)% acetone and is liquid at its bubble point ($q = 1$). Products are liquids at their respective bubble points. Assume 99% of the ethanol and 96% of the acetone are recovered in their respective products. The column operates at one atm.

TABLE 11.9 Acetone Vapor/Liquid
Equilibrium Compositions
for Acetone/Ethanol Mixtures

x	y	x	y
0	0	40	60.5
5	15.5	50	67.4
10	26.2	60	73.9
15	34.8	70	80.2
20	41.7	80	86.5
25	47.8	90	92.9
30	52.4	100	100
35	56.6		

- Using a McCabe-Thiele diagram, determine the number of stages to separate acetone from ethanol.
 - Should the column have been designed for one atm? If not, how would you choose the pressure? Explain your answer.
 - Compute the condenser and reboiler duties for the column. How close are they to being equal? Can you guess why they are this close?
 - Should you preheat the feed to the column when it is running at one atm? Explain. You can answer this question without doing any computations. Look at the impact of preheating the feed on the construction of the McCabe-Thiele diagram to make your argument.
- A column is a passive piece of equipment once it is designed and built. Assuming it is properly designed, how is it that one can "make" a column carry out the separation desired? For example, consider separating a mixture of *ABC* into two products *A* and *BC*. Explain how to operate a column so it gives one 99% of species *A* in the distillate product (top product) while forcing 99% of species *B* and virtually all of species *C* to the bottom product. What would you control? Assume *A* is most volatile and *C* least.
 - Using all that you know about the use of the McCabe-Thiele diagram for analyzing binary distillation columns, demonstrate that the number of degrees of freedom is five plus the total of those associated with completely specifying the feed.
 - Show that the mole fraction averaged relative volatility

$$\bar{\alpha}_k \equiv \sum_j \alpha_{jk} x_j$$

- is equal to $1/K_k$, the reciprocal of the K -value for the selected key component.
- You are to separate the following relatively ideally behaving mixture of *A*, *B*, and *C*. The feed is at its bubble point of 345.8 K at 1 bar.

Component	feed, kmol/hr	VPA, unitless	VPB, K	VPC, K
A	50	11.1	3000	-70
B	100	10.2	2800	-70
C	30	10	3000	-70

The last three columns are the Antoine constants for evaluating vapor pressure, using the following formula:

$$P_i^{\text{sat}} \text{ (bars)} = \exp(VPA_i - \frac{VPB_i}{T(K) + VPC_i})$$

- Show that the bubble point temperature for the feed is 345.8 K when pressure is 1 bar.
- The Underwood roots for the original feed are 1.116 and 2.826. Show that the minimum vapor flow in the top of the column for the *A/BC* column should be approximately 828 kmol/hr. What assumptions do you need to make to do this computation?
- The minimum vapor flows for the following columns are similarly computed to be:

$$V_{\text{min}}(AB/C) = 254 \text{ kmol/hr}$$

$$V_{\text{min}}(A/B) = 830$$

$$V_{\text{min}}(B/C) = 183$$

Which sequence is to be preferred: *A/BC*, *B/C* or *AB/C*, *A/B*? Why?

- Compute marginal vapor flows using the very approximate method developed in this chapter. Are they in rough agreement with numbers that can be computed from the information given above? Do they predict the same sequence?
6. You have a mixture of 35 mole % *n*-heptane, 30% *n*-hexane, 10% isobutane, and 25% *n*-pentane.
- Determine the bubble and dewpoint temperatures for the above mixture. Pressure is one atmosphere. Assume Raoult's law for expressing vapor-liquid equilibrium.
 - You want to run a flash unit for the above mixture in which 50% of the *n*-hexane leaves in the vapor product. Determine the fraction of the other species that leave in the vapor product. The pressure is one atmosphere. Repeat this computation for a pressure of two atmospheres. Do you notice anything interesting here? (Hint: Note first that

$$\frac{v_i/l_i}{v_k/l_k} = \frac{y_i V/x_i L}{y_k V/x_k L} = \frac{y_i/x_i}{y_k/x_k} = \frac{K_i}{K_k} = \alpha_{ik}$$

$$y_i = K_i x_i = \frac{\alpha_i}{\bar{\alpha}} x_i = \frac{P_i^{\text{sat}}(T)}{P} x_i \Rightarrow \frac{P_i^{\text{sat}}(T)}{P} = \frac{\alpha_i}{\bar{\alpha}}$$