HETEROGENEOUS AZEOTROPIC DISTILLATION

Heterogeneous azeotropic distillation is a widely practiced process for the dehydration of a wide range of materials including acetic acid, chloroform, ethanol, and many higher alcohols. The technique involves separating close boiling components by adding a third component, called an entrainer, to form a minimum boiling, normally ternary azeotrope which carries the water overhead and leaves dry product in the bottom. The overhead is condensed to two liquid phases; the organic, "entrainer rich" phase being refluxed while the aqueous phase is decanted. Given the non-idealities, the phase splitting, the distillation boundaries present, and the possible existence of multiple steady states in such a system, columns like these can be extremely difficult to simulate and to operate. A systematic approach to the problem can save you many headaches.

When designing such systems, keep the following points in mind:

1. You need to start with two triangular plots: The residue curve map and the binodal plot. The residue curve map should have the liquid phase envelope superimposed. The binodal plot should be at anticipated condenser conditions.

2. The key feature of feasible heterogeneous azeotropic distillation is that entrainers and top tray vapor compositions are selected to generate liquid-liquid tie lines which straddle at least one of the distillation boundaries dividing the two regions containing the two components to be separated. In this way, the "jump effect" can be exploited, whereby each column is provided with a feed composition in the required (different) distillation regions. This is why the condenser must be two-liquid phase and we reflux the organic phase while decanting the aqueous phase.

3. Distillation boundaries in homogeneous mixtures cannot be crossed by residue curves, and for all practical purposes they cannot be crossed by the steady-state liquid composition profile in a distillation column either. Therefore, in order to isolate two pure components which lie in two different distillation regions, it is necessary to have two different feed compositions (one from each of the two regions) and two distillation columns. What Doherty and Caldarola (1985) show is that such an arrangement is impossible to construct by external recycles alone.

4. The distillate and bottoms product must lie on the same residue curve.

5. The feed, distillate, and bottoms product must be colinear; i.e., all lie on the same straight material balance line.

6. All feed to the column (reflux, makeup, and process feed) should be entered near the top of the column.

7. The composition of the vapor leaving the top tray must be near but not necessarily at the ternary azeotrope.

8. If at all possible (and it generally is possible) the column should be operated such that only one liquid phase exists on the stages. Since the condenser must be operated in the heterogeneous region, this means that the vapor coming from the top tray must be in equilibrium with a single liquid phase, but must condense to two liquid phases. This narrows

the selection of top tray vapor compositions considerably and in fact can only be achieved by careful manipulation of the condenser operating conditions and/or a mix of the decanter organic and aqueous phases in the reflux.

For minimum boiling, heterogeneous azeotropic systems, this can be accomplished by either adding water to the decanter in order to shift the overall composition into the two-liquid phase region, or by lowering the temperature of the condensate in order to enlarge the two-liquid phase region enough to encompass the distillate composition.

9. It is important to note that the liquid boiling envelope is not a simple liquid-liquid binodal curve at a fixed temperature, but the projection of the heterogeneous liquid boiling surface onto the composition base plane. This is critical because the top tray equilibrium liquid composition must lie outside the liquid boiling envelope. It is not enough to lie outside the condenser binodal plot heterogeneous envelope.

10. The composition of the two-liquid phases generated in the condenser must be taken from tie lines on a binodal plot calculated at condenser conditions, not top tray conditions.

11. The relative proportions of the two-liquid phases in the condenser, ϕ, is given by the lever rule;

$$ f = \frac{y_{e,i} - x_{aq,i}}{y_{e,i} - x_{org,i}} $$

12. The vapor composition in equilibrium with a (liquid) point on a residue curve must lie on the tangent to the residue curve. For homogeneous systems, each residue curve has an associated vapor boil-off curve, and they are related by this tangency condition. However, in the heterogeneous region there is only one vapor boil-off curve, namely, the vapor line. Therefore, the vapor composition in equilibrium with a point on a heterogeneous residue curve lies at the intersection of the tangent to the residue curve and the vapor line.

Please note that in the two-liquid phase region, the vapor line lies very close to the heterogeneous distillation boundary. However, these two curves coincide exactly only when the distillation boundary is linear. In all other cases, the vapor line must lie to the convex side of the distillation boundary as required by the tangency condition.

All liquid compositions lying on the liquid boiling envelope will produce equilibrium vapor compositions on the vapor line. As the liquid composition moves away from the liquid boiling envelope, into the homogeneous region, the corresponding equilibrium vapor composition moves off the vapor line. However, the cusp in the vapor surface on either side of the vapor line is normally quite steep.

13. Within certain ranges of column specifications, heterogeneous azeotropic distillation systems exhibit multiple steady states. If these steady states are in close proximity, they frequently cause erratic behavior in the column. This of course makes the column hard to control.

14. Many heterogeneous azeotropic distillation systems show a very high sensitivity to small changes in the operating conditions or requirements. To mention just a few;

- Small changes in bottoms products purity specs can significantly impact the column temperature profile and entrainer requirements.
- Small changes in the reflux ratio can dramatically change the temperature profile.
- Small fluctuations in pressure can move the overhead composition outside the heterogeneous region, thus causing column failure.
- Small losses of decanter interface can cause the entire column sequence to shutdown.

ETHANOL-WATER-nPENTANE EXAMPLE

Consider the separation of ethanol and water using n-pentane as the entrainer. In this system all three binaries form minimum boiling azeotropes and a heterogeneous, minimum boiling azeotrope (low boiler) is formed by the ternary.

Assuming the thermodynamic model has been properly set up (the topic of another discussion), we should begin by looking at a residue curve map and a binodal plot for the system. The residue curve map should have the liquid boiling envelope superimposed. Together the two diagrams should look like this:

Residue Curve Map, N-Pentane/Ethanol/Water by NRTL
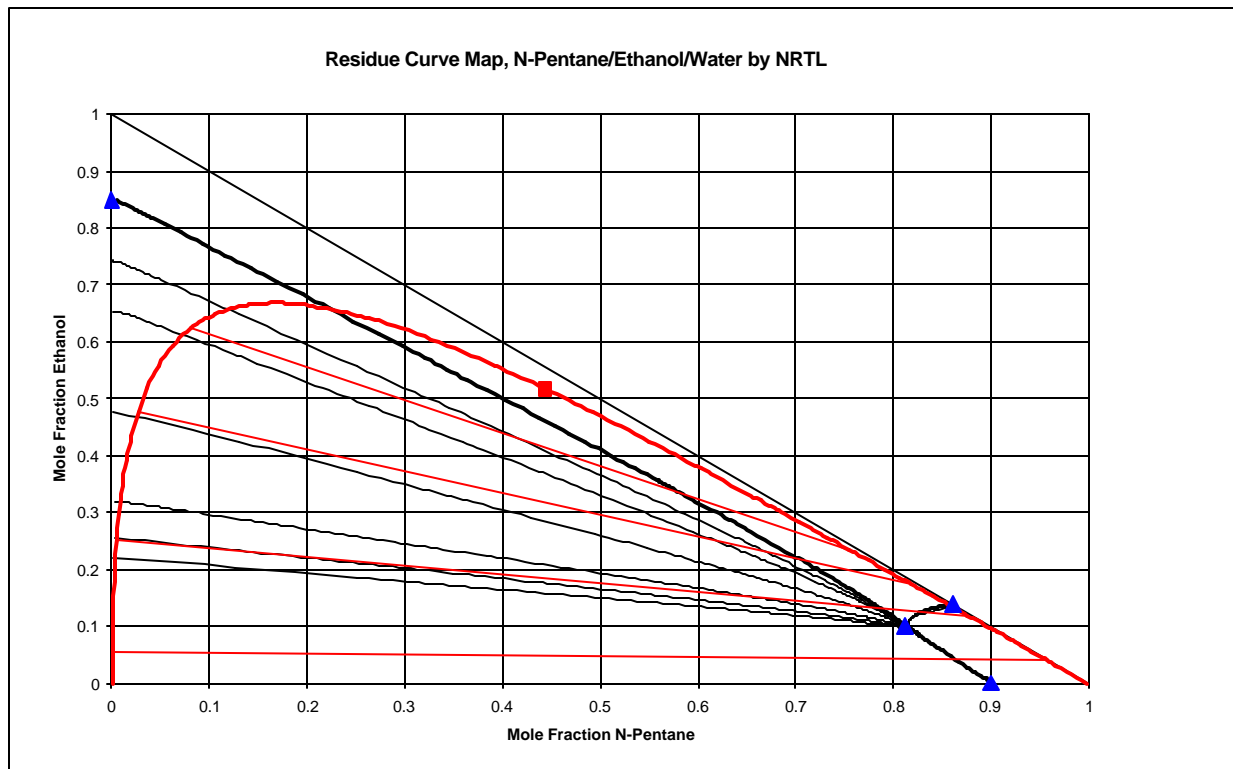
As you can see the map has distillation boundaries which cannot be crossed with conventional distillation. These boundaries partition the system into three regions. If the feed is in region one, a conventional distillation system will drive the ternary azeotrope to the top and pure water to the bottom. If the feed is in region two, the azeotrope will still go to the top but pure n-pentane will

come out the bottom. Likewise, a feed in region three will produce the azeotrope at the top and pure ethanol out the bottom. These are the best splits that can be produced.

Obviously, then to dehydrate ethanol we want to operate in region three. Ethanol and water will come in at the binary azeotrope (89.5% ETOH, 10.5% H_2O), but by controlling the amount of benzene used, and by grouping all feeds near the top of the column, we can force the combined feed into region three.

We don't actually need or even want the vapor leaving the top tray to be right at the azeotrope. Not only would this require unnecessary costs (stages and/or reflux), but it will cause multiple liquid phases to form on the top trays of the column. This can make operations difficult. Therefore, we want to produce a tops vapor which is close enough to the ternary azeotrope to phase split in the condenser but not on the trays. In other words, we want the composition of the vapor leaving the top tray to be such that its equilibrium liquid has a composition outside the two-phase region, but the vapor composition itself is <u>inside</u> the two-phase boundary. This leaves us with a narrow range of choices, all lying near the two-phase boundary on the binodal plot.

PRELIMINARY MATERIAL BALANCE:

Assume the following:

Column feed   =   242 lbmoles / hr. Ethanol and 40.58 lbmoles / hr. water
Column pressure   =   50 psia
Condenser Temperature =   saturated at 44 psia
Ethanol purity is to be 99.99%

We can now use the residue map and the binodal plot to do a preliminary material balance around the column.

Step 1.   Find the compositions of the top tray vapor, the condenser aqueous phase, and the condenser organic phase.

Given that we want essentially pure ethanol as a product, our first task is to "select" the vapor composition to go out the top tray. The composition must meet the following criteria:

(i.)   The liquid in equilibrium with the selected vapor must be single phase at system conditions.

(ii.)   The vapor must condense to two liquid phases at condenser conditions.

(iii.)   The composition of the two liquid phases which form in the condenser, must lie in different distillation regions; one aqueous (to be decanted), the other organic (to be refluxed).

Only those compositions in the region of the shaded box will meet these criteria (see figure 1). An exploded view of this area is shown in figure 2. The heavy black line represents the two liquid phase boundary. The dotted lines connect acceptable vapor-liquid equilibrium concentrations. The point in the two-phase region represents the possible top tray vapor composition, and the point in the one liquid phase region is the composition in equilibrium with that vapor.

In order to actually generate this vapor in the column, it will be necessary to reflux some of the decanter aqueous liquid.

Since these are preliminary calculations and criteria (i) has the smallest impact on the overall material balance, we will not try to satisfy this condition just yet. Instead we will focus on criteria (ii) and (iii). These can be satisfied by picking a tie line that passes through the shaded area of Figure 1.

As you can see such a tie line is not unique, so we must choose one that looks "best". The closer to the azeotrope we get, the harder it will be to satisfy criteria (i) later on and the more stages we will require. The closer to the two phase boundary we get, the greater the required reflux. To start let's pick tie line "A" shown. This means that any of the compositions from points 1 to 3 can be chosen as our top tray vapor compositions.

Close the point f just inside region three as our top tray composition. This composition is 82.665% n-pentane, 12.33% ethanol, and 5.01% water.

The end point compositions of tie line "A" (from Table 1) are:

Aqueous phase = (0.43% P, 23.81% E, 75.76% W)
Organic phase = (87.88% P, 11.6% E, 0.52% W)

Thus,

	Top Tray	Left Phase	Right Phase
Pentane	82.756%	0.43%	87.88%
Ethanol	12.326%	23.81%	11.60%
Water	5.018%	75.76%	0.52%

(mole percents)

Step 2: Find the flowrates of the top tray vapor, the reflux, and the distillate (decant).

Since all the water must go out the top of the column, we can use the aqueous phase composition to determine the distillated flowrates.

DISTILLATE FLOWRATES:

Water Flow Out = 40.58 lbmoles / hr.

Ethanol Out = $\dfrac{23.81}{75.76} * 40.58 = 12.753$ lbmoles / hr.

n-Pentane Out = $\dfrac{0.43}{75.76} * 40.58 = 0.23$ lbmoles / hr.

Total Distillate Flow = 40.58 + 12.753 + 0.23 = 53.563 lbmoles / hr.

The lever rule says:

$$f = \frac{\text{Reflux Flow}}{\text{Distillate Flow}} = \frac{\text{Reflux Flow}}{40.58 \ \text{lbmoles / hr.}} = \left| \frac{y_{e,i} - x_{aq,i}}{y_{e,i} - x_{org,i}} \right|$$

Graphically, this means that:

$$f = \frac{\text{flow}}{\text{Distillate flow}} = \frac{\text{the distance}}{\text{the distance}} \quad \frac{\text{point 1} \quad \text{point f}}{\text{point f} \quad \text{point 4}}$$

Where point _ is the location of the feed composition.

Using the n-pentane concentrations we get

$$f = \left| \frac{.82656 - .0043}{.82656 - .8788} \right| = \left| \frac{.82226}{.05224} \right| = 15.74$$

We can check this using the ethanol concentrations:

$$f = \frac{.12326 - .2381}{.12326 - .116} = \left| \frac{-.11484}{.00726} \right| = 15.82 \quad \text{OK.}$$

Therefore,

Total Reflux Flow = 53.563 x 15.74 = 843.08162 lbmoles / hr.

Pentane	=	843.08 ∗ .8788	= 740.90 lbmoles / hr.
Ethanol	=	843.08 ∗ .116	= 97.80 lbmoles / hr.
Water	=	843.08 ∗ .0052	= 4.58 lbmoles / hr.
			843.08 lbmoles / hr.

Flow to condenser = 843.08 + 53.563 = 896.643 lbmoles / hr

Now check top tray compositions:

896.643 ∗ .8266 = 741.17 lbmoles / hr. vs. 740.9 + 0.23 = 741.13 lbmoles / hr.
896.643 ∗ .1232 = 10.56 lbmoles / hr. vs. 97.8 + 12.753 = 110.55 lbmoles / hr.
896.643 ∗ .0502 = 45.01 lbmoles / hr. vs. 4.38 + 40.58 = 44.96 lbmoles / hr.

n-Pentane makeup = n-Pentane out in distillate = 0.23 lbmoles / hr.

Step 3: Calculate the ethanol out the bottom:

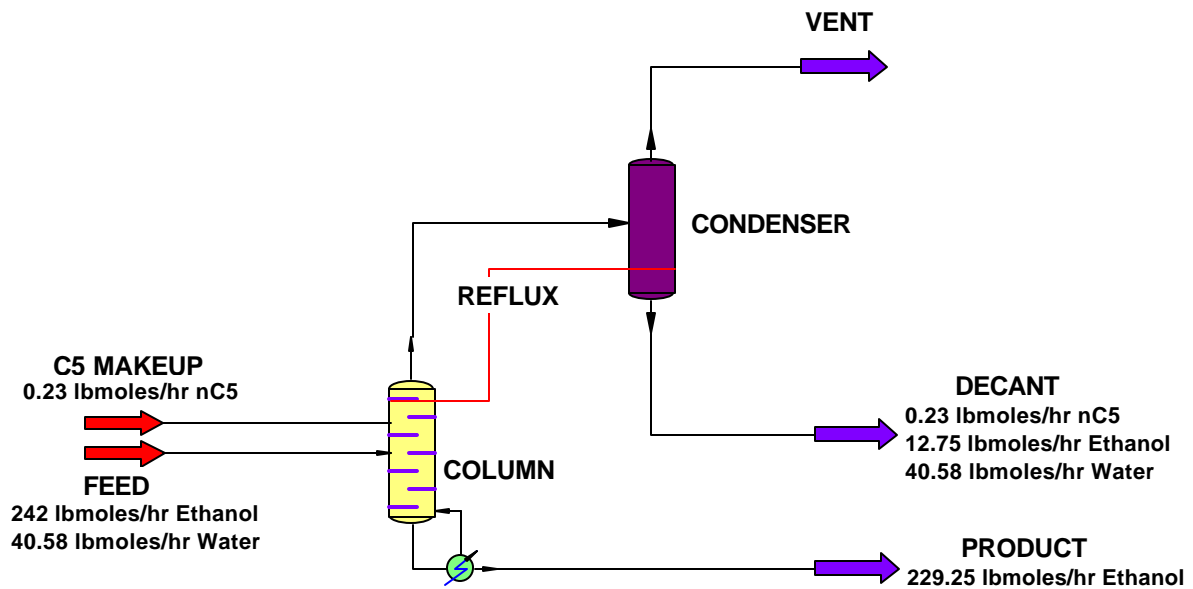Ethanol in bottoms = 242 - 12.753 = 229.247 lbmoles / hr.

Step 4: Calculate the overall material balance.

Computed Binodal Curve in Mole Percent:

(1) = Water
(2) = Ethanol
(3) = N-Pentane

Left Phase			Right Phase		
(1)	(2)	(3)	(1)	(2)	(3)
99.976	0.000	0.024	0.180	0.000	99.820
94.500	5.445	0.055	0.272	4.046	95.682
89.500	10.395	0.105	0.352	6.827	92.821
84.500	15.315	0.185	0.423	8.938	90.639
79.500	20.195	0.305	0.484	10.577	88.938
74.500	25.023	0.477	0.538	11.910	87.552
69.500	29.786	0.714	0.586	13.064	86.350
64.500	34.466	1.034	0.633	14.128	85.239
59.500	39.046	1.454	0.679	15.169	84.152
54.500	43.499	2.001	0.728	16.236	83.036
49.500	47.797	2.703	0.781	17.369	81.851
44.500	51.898	3.602	0.839	18.604	80.556
39.500	55.751	4.749	0.907	19.982	79.111
34.500	59.281	6.219	0.985	21.553	77.462
29.500	62.378	8.122	1.080	23.384	75.535
24.500	64.873	10.627	1.200	25.585	73.215
19.500	66.479	14.021	1.359	28.344	70.296
14.500	66.649	18.851	1.596	32.046	66.358
9.500	64.091	26.409	2.028	37.683	60.289
6.832	60.403	32.765	2.504	42.500	54.996
5.010	55.866	39.124	3.167	47.500	49.333
3.923	51.748	44.329	3.938	51.748	44.315

THEREFORE,

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CONDENSER

REFLUX

C5 MAKEUP
0.23 lbmoles/hr nC5

FEED
242 lbmoles/hr Ethanol
40.58 lbmoles/hr Water

COLUMN

DECANT
0.23 lbmoles/hr nC5
12.75 lbmoles/hr Ethanol
40.58 lbmoles/hr Water

PRODUCT
229.25 lbmoles/hr Ethanol

MASS BALANCE

Stream	Moles In	Moles Out
C5 Makeup	0.23 nC_5	
Feed	242.00 ETOH 40.58 H_2O	
Decant		0.23 nC_5 12.75 ETOH 40.58 H_2O
Product		229.25 ETOH
Total	282.81	282.81