

## RESIDUE CURVE MAPS

When an entrainer is added to a binary mixture, a ternary mixture results, and it is then necessary to consider the phase equilibria for this new mixture as well as to predict the ranges of possible overhead and bottoms compositions. Triangular diagrams are often used to describe the equilibrium relationships for ternary mixtures. Especially important are the residue curves on the diagrams. A residue curve represents the liquid residue composition with time as the result of a simple, one stage batch distillation. The results, when plotted on a triangular graph, are called a residue curve because the plot follows the liquid residue composition in the still. Different residue lines result from different starting compositions. A collection of these curves for a given ternary system is called a residue curve map. A residue curve map has the following characteristics:

1. If we assign the direction of the residue curves as being from the starting composition to the ending composition, then the arrow on each curve points from a lower boiling component or azeotrope to a higher boiling component or azeotrope.
2. The presence of azeotropes can create distillation boundaries which cannot be crossed by a residue curve. These distillation boundaries represent the residue curve on which the light or starting residue composition is a lower boiling pure component or azeotrope and the heavy or ending composition residue is a higher pure component or azeotrope. Any given pure component point or azeotrope will be connected to some but not all other pure component points and azeotropes on the graph. Those that are connected form distillation boundaries. These boundaries are thermodynamic in nature.
3. These distillation boundaries partition the map into distillation regions. The nature of these regions is such that two pure components which lie in different regions cannot be separated using conventional distillation.

Some definitions are in order before we explain how residue curve maps apply to enhanced distillation systems.

|                      |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |
|----------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <b>Node</b>          | Residue curves begin and end at nodes.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |
| <b>Stable node</b>   | The component or azeotrope with the highest boiling point in the region. All the residue curves in the region point to (terminate) at this point.                                                                                                                                                                                                                                                                                                                                                                                   |
| <b>Unstable node</b> | The component or azeotrope with the lowest boiling point in the region.                                                                                                                                                                                                                                                                                                                                                                                                                                                             |
| <b>Saddle</b>        | Residue curves move toward and then away from saddles. Pure components and azeotropes which have a boiling point between the stable and unstable nodes are saddles.                                                                                                                                                                                                                                                                                                                                                                 |
| <b>Vapor line</b>    | The vapor line is the line formed by those vapor compositions which are in equilibrium with the liquid compositions on the distillation boundaries. In other words, if you take all the compositions on a distillation boundary line as saturated liquid compositions; then determine the composition of the vapors which are in equilibrium with all these points; and plotted all these vapor compositions on the residue curve map, one line would be formed for each distillation boundary. That line is called the vapor line. |

**Vapor boilup curve**

The vapor boilup curve is the plot of the vapor compositions in equilibrium with any given residue curve.

**Binodal plot**

This is a constant temperature plot of all saturated liquid compositions. It is used to identify the liquid-liquid region of the mixture.

**Liquid boiling envelope**

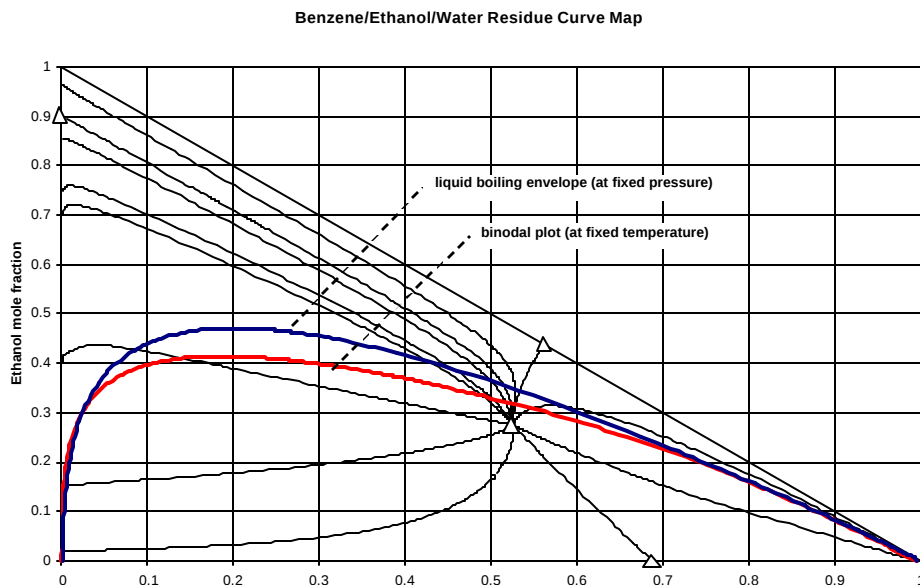
This is the constant pressure binodal like plot of the two liquid phase region of a ternary system.

In the residue map shown below (for the system Benzene/Ethanol/Water);

- The residue curves are represented by the light black curves,
- The distillation boundaries are represented by the heavy curves,
- The triangles indicate the azeotropes, and
- The two phase regions (at constant pressure and at constant temperature) are outlined by the liquid boiling envelope and the binodal plot as indicated.

For this system you will notice that;

- The binary azeotropes are all saddles. As a result the residue lines tend to move toward them at first and then at some point they turn away from them to the stable node.
- The ternary azeotrope, being a minimum boiling azeotrope, is an unstable node (in this case the only one in the system). This means that in any simple distillation, this azeotrope will always come out the top of the column.
- The pure components are all stable nodes. This means that in any simple distillation they will always come out the bottom of the column. Which component comes out the bottom depends on which region we are operating in.
- The liquid boiling envelope and the binodal plot are not the same. The condenser will generally operate at fixed temperatures so it is analyzed using the binodal plot. The top tray(s) of the column will be at the column pressure, so it must be analyzed using the liquid boiling envelope.



Please note the following properties of a residue curve map:

1. Based on experimental evidence, for ternary mixtures with very few exceptions, there are at most three binary azeotropes and restrictions that apply to a ternary system:

$$N_1 + S_1 = 3$$

$$N_2 + S_2 = B \leq 3$$

$$N_3 + S_3 = 1 \text{ or } 0$$

where,  $N_1$  = the number of pure single component nodes.  
 $N_2$  = the number of binary nodes.  
 $N_3$  = the number of ternary nodes.  
 $S_1$  = the number of pure component saddles.  
 $S_2$  = the number of binary saddles.  
 $S_3$  = the number of ternary saddles.

and

$$2N_3 - 2S_3 + 2N_2 - B + N_1 = 2$$

2. For homogeneous azeotropes the nodes may be either stable (maximum boiling) or unstable (minimum boiling). However, heterogeneous azeotropes can be either unstable nodes or saddles but not stable nodes (i.e. they cannot be maximum boiling).
3. The liquid temperature always increases along residue curves in the heterogeneous region. This property, coupled with fact that all singular points on heterogeneous residue curve maps are restricted to be either nodes or saddles, means that the entire topological methodology for analyzing and constructing homogeneous residue curve maps from boiling temperature data alone extends verbatim to heterogeneous mixtures.

### CONSTRUCTING A RESIDUE CURVE MAP BY HAND

To help in understanding residue curve maps, you can use the following procedure to construct a qualitatively accurate map by hand:

- Step 1: Label the ternary diagram, (names and boiling points) with the low boiling component at the top vertex; the high boiling component at the lower right vertex; and the intermediate at the lower left vertex. Plot compositions of all azeotropes and label the points with their boiling points. This determines the value of B.
- Step 2: Draw arrows on the edges of the triangle in the direction of increasing temperature for each pair of adjacent species (components and/or azeotropes).
- Step 3: Determine the type of point (node or saddle) that each pure component vertex is by using the arrows drawn in Step 2. This determines  $N_1$  and  $S_1$ .

- Step 4: (for ternary azeotrope, if present):  
Determine the type of point of the ternary azeotrope (if one exists). The point is a node if;
- $N_1 + B < 4$ , and/or
  - Excluding the pure component saddles, the ternary azeotrope has the highest, second highest, lowest, or second lowest boiling point of all the species. Otherwise, the point is a saddle. This determines  $N_3$  and  $S_3$ .
- Step 5: (for ternary saddle only, if present):  
Connect the ternary saddle, by straight lines, to all binary azeotropes and to all pure component nodes. Draw arrows on the lines in the direction of increasing temperatures. Using these arrows determine the type of point of each binary azeotrope. This determines  $N_2$  and  $S_2$ . If  $N_1 + B = 6$ , special checks should be made. If not, the sketch is complete.
- Step 6: (for a ternary node, if present, or for no ternary azeotrope):  
Determine the number of binary nodes,  $N_2$ , and saddles,  $S_2$ , by,
- $N_2 = (2 - 2N_3 + 2S_3 + B - N_1) / 2$
  - $S_2 = B - N_2$
- Step 7: Count the binary azeotropes that are intermediate boilers. Call that number  $B^1$ .  
Make the following checks:
- $B - B^1$  must equal  $N_2$ .
  - $S_2$  must be less than or equal to  $B^1$ . If these checks are not satisfied, one or more of the boiling points is probably in error.
- Step 8: If  $S_2 \neq B^1$ , no unique residue-curve map structure exists.  
If  $S_2 = B^1$ , a unique residue-curve map structure exists.
- Step 9: Draw the distillation boundaries (connections) as straight lines. The following rules are used:
- The number of distillation boundaries equals the number of binary saddles,  $S_2$ .
  - Each binary saddle must be connected to a node.
  - A ternary node must be connected to at least one binary saddle.
  - A pure component node cannot be connected to a ternary node.
  - An unstable node cannot be connected to a stable node.
  - A minimum boiling binary saddle connects to an unstable node that boils at a lower temperature.
  - A maximum boiling binary saddle connects to a stable node that boils at a higher temperature.
- This completes the connections.
- Step 10: Draw approximate residue curves in each region. These curves originate from unstable nodes and terminate at stable nodes. This completes the sketch.

## DISTILLATION CURVE MAPS

An alternative representation for distillation on a ternary diagram is a distillation curve for continuous, rather than batch, distillation. The curve is most readily determined for total reflux. The sequence of liquid-phase compositions, which corresponds to the operating line at total reflux, is plotted on a triangular diagram.

Distillation curve maps can be arbitrarily directed to increasing or decreasing temperatures. In the former case, they closely approximate residue curve maps.

## PRODUCT COMPOSITION REGIONS

Residue-curve maps and distillation-curve maps are used to make preliminary estimates of regions of feasible product compositions for distillation of non-ideal ternary mixtures. The product regions are determined by superimposing a column material balance line on the curve map diagram.

If a straight line is drawn that connects distillate and bottoms compositions, that line must pass through the feed composition at some intermediate point to satisfy overall and component material balances. For such a material balance line, the distillate and bottoms compositions must lie on the same distillation (residue) curve. Because of this, the feasible product region can be established like so:

- i. Find the limiting distillate composition point for the region. Draw a line from this point, through the feed composition, to the opposite side of the map. This point represents the bottoms composition with the lowest amount of low boiler possible for the limiting distillate composition. Call this material balance line  $M_1$ .
- ii. Find the limiting bottoms composition point for the region. Draw a line from this point, through the feed composition, to the opposite side of the map. This point represents the distillate composition with the lowest amount of high boiler possible for the limiting bottoms composition. Call this material balance line  $M_2$ .
- iii. Locate and draw the distillate curve which contains the feed composition. Call this curve  $D_F$ .
- iv. The areas on the convex side of  $D_F$ , and lying between  $M_1$  and  $D_F$  and between  $M_2$  and  $D_F$ , are the feasible product regions.

For azeotropic systems, where distillation boundaries are present, a feasible product region can be found for each distillation region.