

## Entrainer for batch distillation of acetic acid –water system

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Acetic acid–water system (AW) poses a challenge in reactive distillation, acetic acid purity and loss of acetic acid in aqueous solutions. Feasible separation of AW has been studied using entrainers but acetic acid loss in lean phase cannot be avoided. This study presents feasible region to operate column with toluene and benzene as entrainer for AW. Liquid–liquid equilibrium data and nature of tie line for ethyl acetate are given priority.

**Keywords:** Acetic acid, Batch distillation, Benzene, Entrainer, Toluene

### Introduction

Under batch distillation, to reduce further recovery of pure components, products are highly dependent on initial mixture compositions. Use of batch rectifier and stripper for heteroazeotropic systems has gained popularity<sup>1</sup>. Hillman<sup>2</sup> studied many process alternatives to achieve successful batch distillation operations. Distillation of heterogeneous mixture, which require decanter for handling liquid–liquid phase split, differs from ideal systems. Vapor condenses and condensate collects in decanter as entrainer rich phase and entrainer lean phase. Options are reported<sup>3-7</sup> for sending entrainer rich phase to column. Application of entrainer has smoothed process of complex heterogeneous systems. Efficiency of azeotropic batch distillation depends largely upon choice of suitable entrainer for the system.

Acetic acid–water (AW) system was studied with certain entrainer on lab scale in batch mode of operation and showed: a) decrease in loss of acetic acid from aqueous layer of distillate; and b) reduced reaction time to complete equilibrium controlled reaction with high conversion for a particular configuration of batch distillation assembly. Parameters (role of reflux, mode of operation, entrainer inventory, and feed position) for

feasible separation have been reported<sup>8</sup>. Simulations have been done to find out suitable entrainer for AW<sup>9-11</sup>.

This study presents toluene, benzene and ethyl acetate as an entrainer for AW to reduce amount of acetic acid loss in aqueous phase of distillate using Residue Curve Map (RCM).

### Experimental

#### Residue Curve Map (RCM)

RCM<sup>12</sup> is a geometrical tool to find feasible separation, column sequencing and optimum parameters for distillation operations. RCM are ternary diagrams displaying traces of liquid compositions remaining in a single batch still as a result of vaporization over a period of time. These liquid traces are known as residue curves. According to RCM technique<sup>13</sup>, any ternary diagram is divided into nodes (stable and unstable), saddles and distillation regions. A stable node is highest boiling vertex in a distillation region. All residue curves in a distillation region point towards a stable node. An unstable node is generally lowest boiling vertex in any distillation region, where all residue curves will originate from an unstable vertex. A saddle point, an intermediate point in a distillation region, has neither residue curves coming or going through it. Residue curve runs from unstable node to stable node via a saddle point. Distillation boundary is a hazy line joining a stable node to azeotrope present in system or formed by joining two

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Table 1—LLE data for AWT system<sup>13</sup> (experimental tie lines in mole% at 40°C)

| S No | Left phase |             | Right phase |             |
|------|------------|-------------|-------------|-------------|
|      | Water      | Acetic acid | Water       | Acetic acid |
| 1    | 95.371     | 4.574       | 0.507       | 1.369       |
| 2    | 90.923     | 8.959       | 0.753       | 3.465       |
| 3    | 88.869     | 10.982      | 0.997       | 4.863       |
| 4    | 85.859     | 13.959      | 1.232       | 7.687       |
| 5    | 82.310     | 17.468      | 1.469       | 8.816       |
| 6    | 79.243     | 20.466      | 1.687       | 12.722      |
| 7    | 72.854     | 26.519      | 2.129       | 16.675      |
| 8    | 62.796     | 35.572      | 2.775       | 21.091      |
| 9    | 58.320     | 39.517      | 4.066       | 24.126      |

azeotropes in the system. It divides ternary plot into distillation regions.

System was studied properly by vapor liquid equilibrium data for AW using toluene and benzene as entrainer. Tie line was compared for AW with toluene, benzene and ethyl acetate.

## Results and Discussion

### 1. Acetic Acid –Water –Toluene (AWT) System

Liquid-liquid equilibrium (LLE) data (Table 1) for AWT was referred from DECHEMA<sup>14</sup>. In AWT, acetic acid is highest boiling vertex (BP 118°C) and becomes stable node (Fig. 1). There is presence of minimum boiling azeotropes between water and toluene at 84.4°C (Azeo 1) and acetic acid and toluene at 104.5°C (Azeo 2). Due to presence of azeotropes, entire ternary diagram is divided into three distillation regions (A, B and C). One of the distillation boundaries is formed between acetic acid and Azeo 1 and other between Azeo 1 and Azeo 2 (Table 2). In Region A, acetic acid is stable node, and water-saddle point and Azeo 1 is unstable node. In Region B, acetic acid is stable node, and Azeo 2-saddle point and Azeo 1 is unstable node. In Region C, toluene is stable node, and Azeo 2-saddle point and Azeo 1 is unstable node.

Under vapor-liquid equilibrium (VLE) data, there is no much difference in region A between liquid and vapor composition, suggesting that for feed in region A, time required will be more (Fig. 2). In region C, stable node is toluene, so nature of distillate will be richer in toluene, which is undesired (Fig. 1). Distillation in region B was found to be more superior to be operated. There were significant jumps between liquid and vapor compositions for points in region B, indicating that with minimum time and stages one can get desired output. Intensity of jump

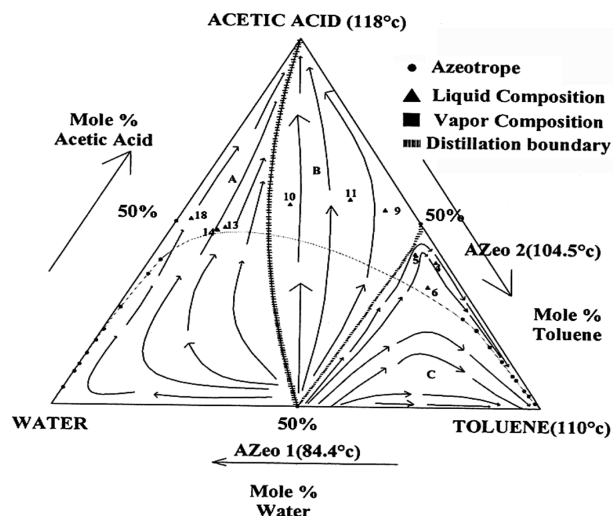


Fig. 1—Nature of residue curve for acetic acid-water-toluene system

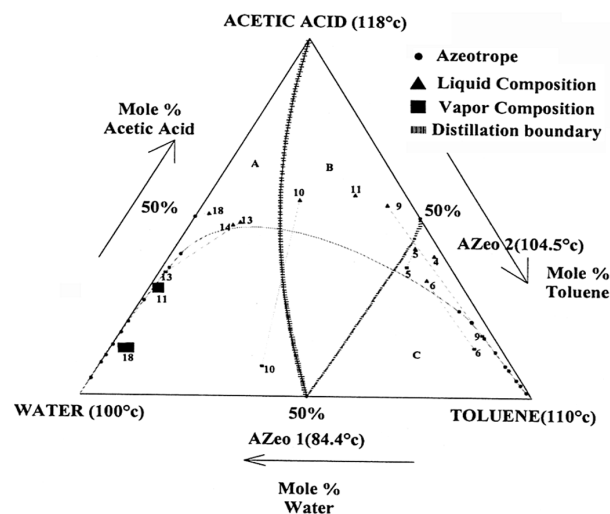


Fig. 2—Triangular diagram showing selected VLE along with bimodal curve

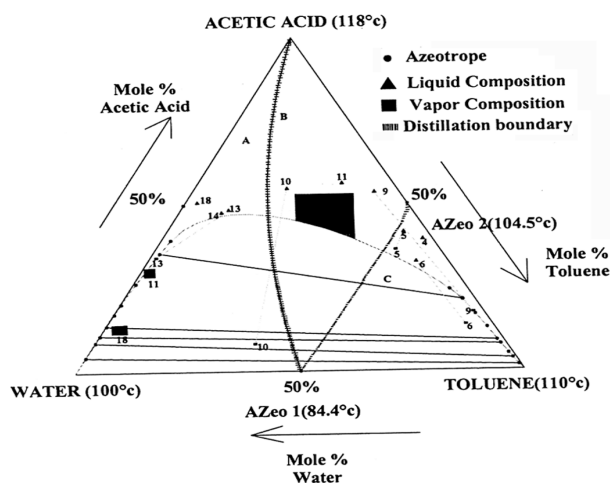


Fig. 3—Feasible reason to operate column (acetic acid-water-toluene system)

Table 2— Experimental VLE data for AWT ternary system

| Point number    | Liquid temp.<br>°C | Liquid composition<br>Mole% |             | Vapor composition<br>Mole% |             |
|-----------------|--------------------|-----------------------------|-------------|----------------------------|-------------|
|                 |                    | Water                       | Acetic acid | Water                      | Acetic acid |
| <i>Region C</i> |                    |                             |             |                            |             |
| 1               | 101.5              | 2.6                         | 35.35       | 7.88                       | 35.88       |
| 2               | 101                | 2.9                         | 25.97       | 2.55                       | 19.622      |
| 3               | 100                | 9.11                        | 35.40       | 9.4                        | 34.2        |
| 4               | 102.5              | 2.157                       | 39.289      | 8.88                       | 35.47       |
| 5               | 102                | 5.3                         | 41.5        | 9.75                       | 36.27       |
| 6               | 103                | 7.14                        | 32.55       | 5.911                      | 13.67       |
| 7               | 104                | 0.214                       | 13.3        | 1.7                        | 30.50       |
| 8               | 105                | 5.911                       | 13.67       | 6.904                      | 28.848      |
| <i>Region B</i> |                    |                             |             |                            |             |
| 9               | 98                 | 5.59                        | 53.47       | 2.3                        | 17.36       |
| 10              | 90.5               | 24.5                        | 54.71       | 55.82                      | 8.3         |
| 11              | 92.5               | 11.39                       | 56.23       | 68                         | 30.22       |
| <i>Region A</i> |                    |                             |             |                            |             |
| 12              | 103.5              | 24.05                       | 72.26       | 51.5                       | 43          |
| 13              | 101.5              | 40.80                       | 48.42       | 64.27                      | 34.31       |
| 14              | 102                | 42.80                       | 47.628      | 62                         | 36.9        |
| 15              | 92                 | 41.27                       | 52.45       | 62.19                      | 35.72       |
| 16              | 94                 | 34.5                        | 62.29       | 53.28                      | 34.09       |
| 17              | 100                | 63.02                       | 36.77       | 76.5                       | 22.35       |
| 18              | 101                | 46.6                        | 50.70       | 83.51                      | 15.90       |
| 19              | 100                | 62.34                       | 37.36       | 72.19                      | 27.39       |

for some points is such that it shows only 0-10% loss of acetic acid in aqueous phase.

Points 9 and 10 (Fig. 3) shows significant jumps with distillate composition below 8% tie line. Region B would be most favorable region for column operation since distillate collected in this region has shown some magnificent jumps, indicating efficient separation without much loss of acetic acid in aqueous solution. According to nature of VLE data in this region and conceptual methodology, feed position in shaded portion of region B would lead to negligible loss in acetic acid (0-2%) and may lead to less time in product separation.

## 2. Acetic Acid –Water –Benzene (AWB) System

LLE data for AWB system is given in Table 3. VLE data for some points are given in Table 4. In AWB system, acetic acid is highest boiling vertex and forms a stable node. There is presence of azeotrope between benzene and water at 70.5°C (Azeo 1) and acetic acid and benzene at 80°C (Azeo 2). Due to presence of azeotropes, entire ternary diagram is divided into three distillation regions (A, B and C). One of the distillation boundaries is formed between acetic acid and Azeo 1 and other between Azeo 1 and Azeo 2 (Fig.4). In Region A, acetic acid is stable node, water - saddle point and Azeo 1 is unstable node. In Region B, acetic acid is

Table 3— Experimental LLE data for AWB system (experimental tie line in mole%)

| S No. | Left phase |             | Right phase |             |
|-------|------------|-------------|-------------|-------------|
|       | Water      | Acetic acid | Water       | Acetic acid |
| 1     | 95.000     | 4.500       | 1.025       | 2.943       |
| 2     | 76.400     | 22.800      | 2.933       | 10.780      |
| 3     | 57.270     | 39.353      | 6.192       | 23.482      |
| 4     | 41.500     | 47.500      | 10.000      | 30.000      |
| 5     | 30.500     | 49.000      | 16.000      | 40.000      |

stable node, Azeo 2- saddle point and Azeo 1 is unstable node. In Region C, benzene is stable node, Azeo 2- saddle point and Azeo 1 is unstable node. One of the distillation boundaries is present between acetic acid and Azeo 1 and other distillation boundary is between Azeo 1 and Azeo 2. It is quite similar to AWT system. Nature of residue curves in region A is showing still path to be increasing and become richer in acetic acid (stable node). It is similar nature of residue curves in region B. Entire residue curves are approaching stable node acetic acid.

In Region C, space available is very small as azeotrope between acetic acid and benzene (98%) is near to benzene pure node. Distillate for feed points in this region may exhibit azeotropic composition. Presence of azeotrope in acetic acid and benzene (Azeo 2) makes

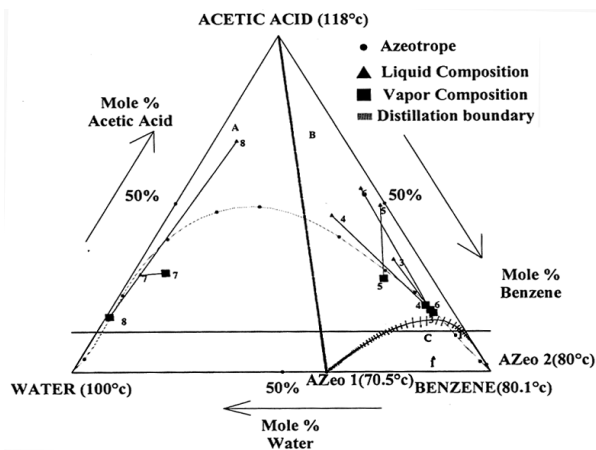


Fig. 4—VLE for some points of acetic acid-water-benzene system

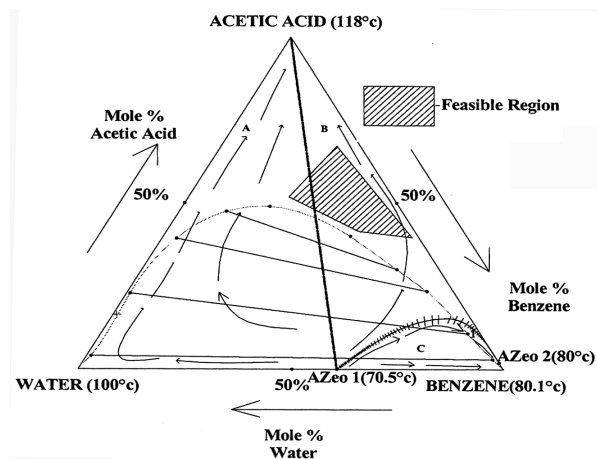


Fig. 5—RCM and feasible reason to operate column (acetic acid-water-benzene system)

Table 4: Experimental VLE data for AWB system

| Point number | Temp. °C | Liquid composition Mole% |             | Vapor composition Mole% |             |
|--------------|----------|--------------------------|-------------|-------------------------|-------------|
|              |          | Water                    | Acetic acid | Water                   | Acetic acid |
| 1            | 79.50    | 3.850                    | 11.760      | 0.970                   | 11.990      |
| 2            | 79.50    | 6.370                    | 33.310      | 6.910                   | 32.590      |
| 3            | 79.80    | 13.300                   | 42.780      | 4.910                   | 17.520      |
| 4            | 79.80    | 14.545                   | 46.362      | 5.540                   | 19.740      |
| 5            | 80.00    | 1.397                    | 49.330      | 11.598                  | 27.640      |
| 6            | 82.00    | 3.450                    | 54.400      | 5.150                   | 18.320      |
| 7            | 97.00    | 69.120                   | 28.820      | 62.870                  | 29.380      |
| 8            | 101.00   | 26.080                   | 68.500      | 82.800                  | 16.360      |

Table 5— LLE data for acetic acid- water-ethyl acetate system<sup>13</sup> (experimental tie lines in mole% at 30°C)

| S No. | Left phase |             | Right phase |             |
|-------|------------|-------------|-------------|-------------|
|       | Water      | Acetic acid | Water       | Acetic acid |
| 1     | 18.547     | 3.091       | 97.329      | 0.899       |
| 2     | 22.391     | 5.892       | 96.236      | 1.762       |
| 3     | 26.777     | 8.368       | 94.975      | 2.666       |
| 4     | 31.513     | 10.504      | 93.791      | 3.490       |
| 5     | 34.457     | 12.332      | 92.804      | 4.294       |

separation tedious. Ultimate limit of residue curves in this region is entrainer via an azeotrope. For feed in region C, points 1 and 2 show vapor and still composition very near to each other, which is time consuming and not suitable for distillation operation. Even by having benzene as an entrainer, feed portion in region B is showing good jumps. Distillate collected was having very less loss of acetic acid in aqueous phase. Points 6, 5 and 4 are showing higher jumps, which were having feed

composition in region B, whereas when feed composition are falling in Region A, there is very small difference between vapor and liquid composition (point 7), indicating that large number of stages are required to bring desired separation. Nature of residue curves for this system and shaded portion, which may give best separation, are shown in Fig. 5. For feed lying in Region B and according to feed tendency, a wide gap is shown between distillate and bottom composition. It may be quite possible that when feed is in shaded region, distillate composition will exhibit only 1-2% loss of acetic acid at gain of minimum number of stages in the column.

AWT as an entrainer is same to results showing with AWB as an entrainer. In both systems, there is sure loss of acetic acid in aqueous phase. This loss of component B (acetic acid) in E-lean phase and falling liquid level in still may hamper amount of heat transferred and thereby vapor flow rate. Nature of tie line causes a loss of component B. In current work, selection of entrainer based on nature of tie line and decanter composition is given preference.

If an entrainer has reverse nature of tie line such as it is more towards water node and away from entrainer node, separation might be quite simpler. Such is the case of entrainer like acetic acid –water-ethyl acetate (AWE)<sup>15</sup> system (Table 5). In this system, there is only one minimum boiling azeotrope present between water and ethyl acetate at 70.4°C. Ternary plot is therefore divided into two distillation regions. As number of azeotropes increases, complexities in column increases, thereby reducing chances of feasible separations. From nature of residue curve for the system, it is found that in both distillation regions, residue curve approaches stable

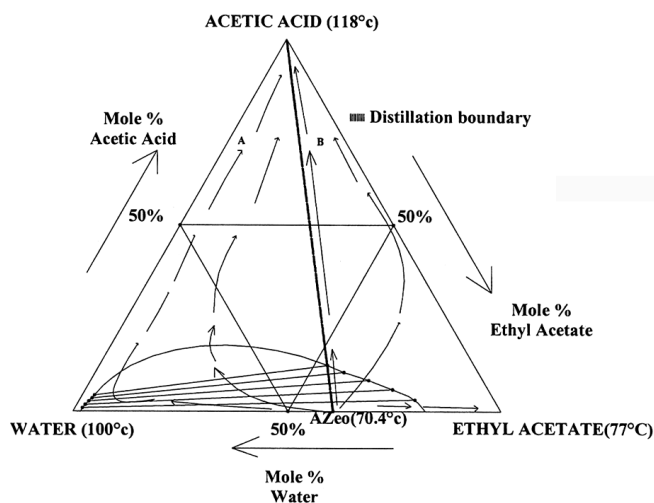


Fig. 6—Nature of tie line for acetic acid-water-ethyl acetate system

node acetic acid only. At heterogeneous region in AWE system, it covers approx. only 20%. Therefore, there are fewer chances of complexities in column. If one considers same feed positions of feasible region B for toluene and benzene as an entrainer in same position for ethyl acetate as an entrainer and compare with nature of tie line, one would find that in most of the cases there will be 0% loss of acetic acid in aqueous phase. This is purely due to opposite nature of tie line, which is more towards water node and away from ethyl acetate node (Fig. 6).

## Conclusions

AW system has mystery in much industrial processes. Proper experimental VLE study of the system to study nature of the bottom and distillation products is prerequisite, like for toluene and benzene, Region B was found to be favorable, yet acid loss was not completely eliminated. Working with these entrainers, three distillation regions, which add up to complexities in column, were found. Nature of tie line is important parameter to consider acid free disposal of water. Entrainer like ethyl acetate having tie line towards pure water node is considered a good option and may result in good separation and negligible loss of acetic acid in aqueous phase. This entrainer with acetic acid - water system leads to only two distillation regions. Entrainer

tendency to form azeotrope with acetic acid is also important factor; entrainer that does not form azeotrope with acetic acid should be preferred. In other words, less the number of distillation regions less is the amount of complexities in column and more is the tendency to achieve pure product.

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