

## Feasibility Study of Heterogeneous Batch Extractive Distillation

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### Abstract

Feasibility of batch heterogeneous extractive distillation is studied in the case where the heterogeneous azeotrope formed with the entrainer *is not* the most volatile point in the system. The composition profile maps based feasibility methodology is extended to this case, and demonstrated on the test problem of separating water from acetonitrile with butyl acetate as entrainer.

Whether the process is anyhow feasible and if one or two column sections are needed for feasible separation were questions answered by the feasibility study. The appropriate operation steps (i.e. the separation sequence) and the effect of the feed ratio and reflux ratio on the feasibility are also determined according to the short-cut calculated profile maps.

The results are verified by rigorous computation with ProsimBatch<sup>©</sup>.

**Keywords:** heterogeneous, extractive distillation, feasibility, azeotrope

### 1. Introduction

Extractive distillation is an efficient method for separating azeotropes in a rectifier. In this method an entrainer is fed continuously to the unit for enhancing the relative volatility of the mixture. The separation is called heterogeneous extractive distillation if the addition of the entrainer causes liquid phase split with heterogeneous azeotrope that *is not* the most volatile composition in the system.

Feasibility of continuous heterogeneous extractive distillation for separating minimum boiling azeotrope with maximum boiling entrainer that forms binary heteroazeotrope less volatile than the original homogeneous azeotrope has already been studied and published (Lelkes et al., 2003, Rodríguez et al., 2003). Feasibility of batch heterogeneous extractive distillation is discussed here.

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The candidate processes are operated in a distillation column with a heated (boiled) vessel at the bottom, and a condenser together with a decanter at the top. The entrainer is either (a) premixed to the charge (this is the solvent-enhanced batch distillation, SBD), or it can be continuously fed (b) into the still, (c) to some intermediate point in the column, or (d) to the top of the column, as are shown in Figure 1. The latter three cases are batch extractive distillation (BED) variants.

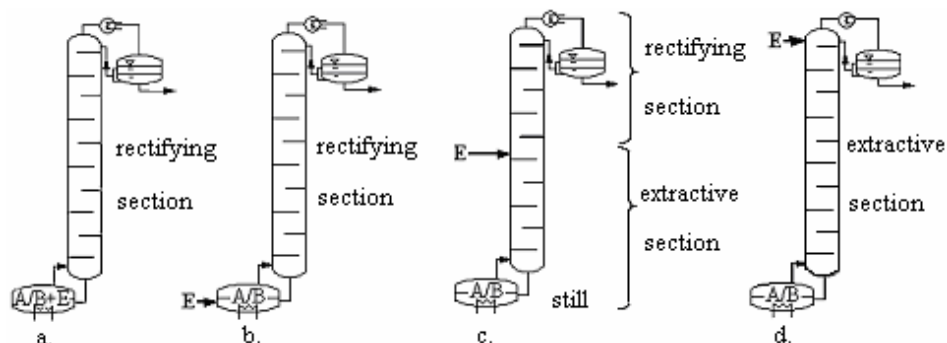


Figure 1. The entrainer is premixed (a), fed to the still (b) or to the column (c) or to the top (d).

## 2. Methodology

Feasibility study of the batch homogeneous extractive processes is based on short-cut calculated column profiles, as introduced by Lelkes et al., 1998abc. This methodology is extended to apply for the heterogeneous process. The column composition profile can be calculated with:

$$\frac{dx}{dh} = \frac{V}{L}(y - y^*) \quad (1)$$

where  $h$  is dimensionless column height;  $V$  and  $L$  are vapor and liquid flow rates, respectively;  $y^*$  is vapor composition in equilibrium with the liquid composition  $x$ ; and  $y$  is the actual vapor composition according to the component mole balance.

Equation (1) is an initial value problem forming a differential-algebraic equation with the actual component balance. The rectifying profile is computed top down; the extractive profile is computed bottom up.

A still composition  $x_S$  is feasible if there is a column profile connecting it to the top composition  $x_0$  that produces aqueous phase distillate with the needed purity after L/L phase split in the decanter. This may be reached by a single (either rectifying or extractive) column profile, or by a pair of profiles that meet at the feed stage. The process is in principle feasible if the feasible region (i.e. the region of feasible  $x_S$  compositions) can be reached from the charge composition  $x_{Ch}$ . For a practical process, the distillate purity should be maintained until reasonable recovery is achieved.

## 3. Feasibility study of acetonitrile / water / butyl acetate

Our problem here is separating acetonitrile from water with butyl acetate as entrainer, at atmospheric pressure. During the study, the phase equilibria are approximated by a

modified Raoult-Dalton equation with ideal vapour phase, and the non-ideality of the liquid mixtures is taken into account with activity coefficients from NRTL model. Excel add-in tool BibPhyAddIn<sup>®</sup> (ProSim SA, 2001) was used for computing equilibria. Table 1 shows the NRTL parameters, based on experimental data, applied for the calculation of the vapor/liquid (L/V) and the vapor/liquid/liquid (V/L/L) equilibrium:

Table 1. NRTL parameters

V/L	$A_{ij}$ [J/mol]	$A_{ji}$ [J/mol]	$\alpha_{ij}$	V/L/L	$A_{ij}$ [J/mol]	$A_{ji}$ [J/mol]	$\alpha_{ij}$
A – B	-236.4	1796.4	0.1	A – B	440.83	865.18	0.2
A – C	1710.94	-1180.02	0.1	A – C	-212.12	-177.67	0.2
B – C	4696.44	-1114.22	0.1	B – C	2865.4	477.67	0.2

Acetonitrile/water mixture forms a minimum boiling azeotrope. There is a heterogeneous azeotrope in the water / butyl acetate system, and no ternary azeotrope is formed. The original azeotrope is the lightest point of the ternary system. The characteristic boiling points, the residue curve map, and the isovolatility curve of acetonitrile/water are shown in Figure 2.

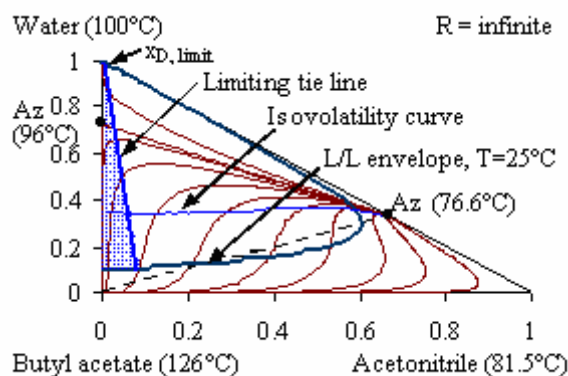


Figure 2. Residue curve map, L/L envelope, top destination region

Distillate purity is specified as  $x_{D,Water} \geq 0.99$ ; the actual distillate composition lies on the L/L envelope; thus, the top composition  $x_0$  of a feasible process should lie in the heterogeneous region to the left of a limiting tie line, with  $x_{D,limit} = [0.005895; 0.99; 0.004105]$ , at a decanter temperature 25 C. We name it as 'the top destination region'.

### 3.1. Analysis at total reflux

The residue curve map is shown in Figure 2. Each line starts from the neighborhood of the azeotrope, and runs towards butyl acetate or water, depending on at which side of the distillation boundary it is started. These lines approximate rectifying profiles at total reflux. The feasible region is the union of the top destination region and a small region below it, restricted from the right by the residue curve passing the counterpoint of  $x_{D,limit}$  on the limiting tie line.

SBD (Figure 1a) is feasible because the lower part of the feasible region can be reached by mixing the azeotrope with the entrainer, along the dashed line in Figure 2, even if a

huge entrainer ratio is needed. The same is true for the BED process with continuous entrainer feeding to the still (Figure 1b), after a huge entrainer pre-mix. **Below we study the feasibility of the separation without entrainer pre-mix.** Extractive profiles at total reflux are shown in Figure 3. There is a stable node moving first along the isovolatility line (see Safrit et al, 1995; Lelkes et al, 1998b) with increasing  $F/V$  ('feed ratio'), and then along the water / butyl acetate edge.

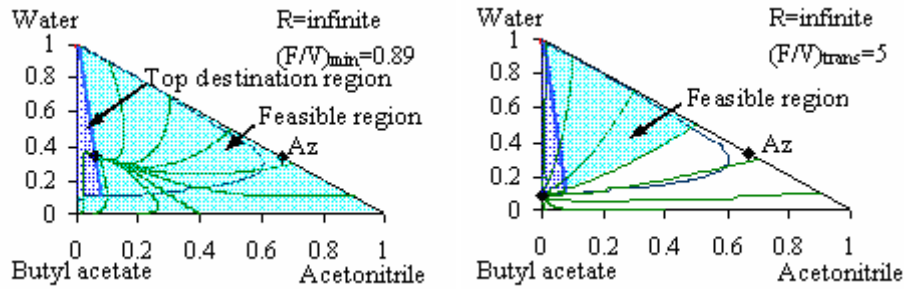


Figure 3. Profile map just above  $(F/V)_{min}$  and above  $(F/V)_{trans}$

There is a minimum feed ratio below which the vapour extractive profiles arriving from right do not reach the top destination region. In that case the feasible region of BED is approximately the same as without extractive section. As a conservative estimate, the liquid profile is computed, instead, see Figure 3 left with here  $(F/V)_{min} \approx 0.9$ . Above this value, however, all the extractive profiles reach the top destination region; and the whole triangle is feasible. In this case, BED is feasible with extractive section alone, feeding the entrainer to the top (Figure 1d). The stable node leaves the top destination region if the feed ratio exceeds a certain value (here  $(F/V)_{trans} \approx 5.0$ , Figure 3, right). Above this feed ratio, only a limited region in the upper right part of the triangle is feasible without rectifying section (that is, with the arrangement in Figure 1d); and just those compositions at the lower right part are infeasible that would be important for governing the still composition in an appropriate direction. Above this feed ratio, therefore, both extractive and rectifying sections are needed; thus, the entrainer is to be fed to an intermediate stage, as in Figure 1c. That is why we call it 'transition feed ratio'.

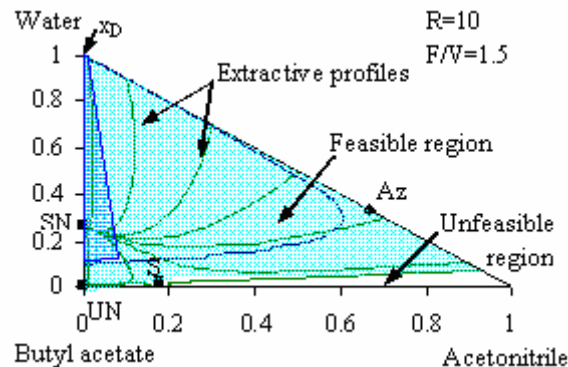


Figure 4a. Reflux ratio above minimum

### 3.2. Analysis at finite reflux ratio

With decreasing reflux ratio, and a feed ratio a little bit above  $(F/V)_{\min}$ , the stable node shifts a little bit nearer to the water / butyl acetate edge, and to the butyl acetate vertex, but remains in the top destination region.

A more important effect is the appearance of a saddle at the acetonitrile / butyl acetate edge, that moves to the interior of the triangle with decreasing  $R$ , see Figures 4ab. The separatrix pair stretching approximately parallel to the acetonitrile / butyl acetate edge form a borderline to the feasible region. There is a reflux ratio  $R_{\min}$  at which the straight section of mixing the azeotrope with the entrainer is tangent to the borderline. Below this minimum reflux ratio we cannot enter the feasible region by premixing.

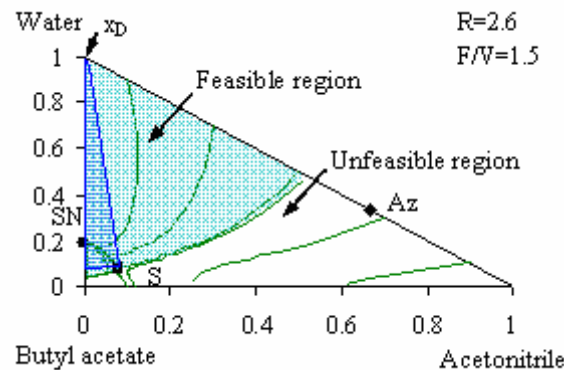


Figure 4b. Reflux ratio below minimum

### 3.3. Suggested separation process, and rigorous simulation

Use of BED with an enriching section (Figure 1c) may result in overstepping the limit tie line from below. Thus, the entrainer is most expediently fed to the top, and the feed ratio is kept between  $(F/V)_{\min}$  and  $(F/V)_{\text{trans}}$ . The process steps are as follow:

1. Heat-up; done with total reflux, and no feed. The top composition is near the binary homogeneous azeotrope.
2. Run-up; with total reflux, and entrainer feeding. A new column profile forms with a top composition in the top destination region. The still composition moves to the interior of the triangle.
3. Production of water. Entrainer feeding is maintained; water is distilled out; the still composition approaches the acetonitrile / butyl acetate edge.
5. Production of acetonitrile. Acetonitrile is distilled out; the entrainer remains in the still. Since the product purity is practically constant in step 3, the still path belonging to a given pair of  $R$  and  $F/V$  can be well estimated. Such an estimation, together with the still path computed with rigorous simulation using ProsimBatch<sup>®</sup> (ProSim SA, 2001) are shown in Figure 5.

A distillation unit with 30 theoretical stages (including the boiler) was assumed with a boiler power 1.5 kW, and a very small hold-up (5 ml) per stage. The charge was 2000 ml only, with composition  $x_{\text{Ch}}=[0.667; 0.333; 0]$ . The decanter temperature was constant 25 C, its hold-up was 30 ml. The water production step, after a 21 second run-

up, was 1.1 h long with  $R \approx 10$ , and  $F = 225$  mol/h pure butyl acetate feed entering the top stage, that roughly corresponds to  $F/V = 1.5$ .

Approximately 83.4 % of the water content in the charge is recovered with high purity ( $x_{\text{water}} = 0.9916$ ) in this way, according to the simulation results. The final entrainer to charge ratio is approximately 5.

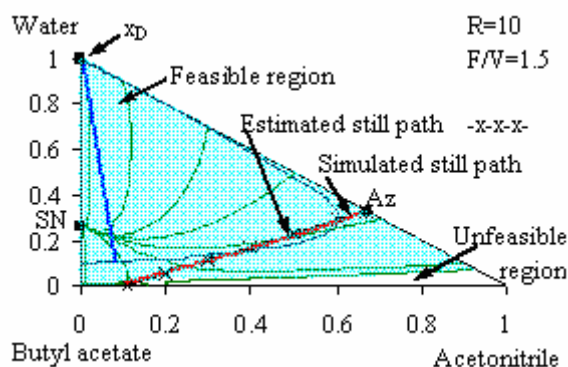


Figure 5. Estimated and simulated still paths at  $F/V = 1.5$  and  $R = 10$

#### 4. Conclusions and recommendations

The feasibility methodology originally developed for homogeneous extractive distillation is successfully extended to the heterogeneous case. Batch heterogeneous extractive distillation is feasible even if the new heteroazeotrope is less volatile than the original homogeneous azeotrope between the components to be separated.

The process is feasible even without extractive section, but with great mixing or pre-mixing of the entrainer to the charge. A top destination region is assigned by the liquid phase split region at the temperature of the decanter and by the limiting tie line according to the minimum product purity. There is a minimum entrainer feed ratio and a minimum reflux ratio. The process is feasible without enriching section with a feed ratio below a so-called transition feed ratio. Feasibility of the BED process with feeding to the top of the column is validated by simulation with ProsimBatch and BibPhyAddIn.

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