A new way of separating azeotropic mixtures in batch rectifier

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Abstract
Separation of a maximum boiling azeotrope (chloroform / ethyl acetate) with intermediate boiling entrainer (2-chlorobutane) in batch rectifier is studied in this paper with a new configuration variant (IBED) of batch extractive distillation (BED). Feasibility study is performed, then the two configurations are compared on the basis of theoretical considerations, short-cut estimations, and rigorous simulations. More than 20 % of the applied entrainer can be saved if IBED is applied instead of BED for separating the studied system.

Keywords: batch rectifier, batch extractive distillation, feasibility study

1. Introduction

Separation of azeotrope forming and low relative volatility components is infeasible with conventional distillation either in continuous or in batch way. Extractive distillation is one of the most widespread processes to separate such mixtures. In this process a third component (called entrainer or solvent), that strongly modifies the relative volatility of the components to be separated, is fed continuously to the column during the separation. Several researchers have published articles on extractive distillation of different mixture types, including minimum or maximum boiling azeotropes, or low relative volatility mixtures, with light, heavy, or intermediate boiling entrainer, in continuous process (e. g. Laroche et al., 1991) or in batch process either in rectifier (e. g. Lang et al., 1994, 2000; Lelkes et al., 1998, 2002; Rev et al., 2003) or in middle vessel column (e. g. Safrit et al., 1997; Warter and Stichlmair, 1999).

This article is written on the idea of applying a new configuration. In the conventional batch extractive distillation (BED) the mixture to be separated is charged to the still at the beginning of the process, and the entrainer is continuously fed to the column, or directly to the still vessel (pot), during the separation (Figure 1a). In the new configuration the pure entrainer is charged to the pot at the beginning of the process, and the mixture to be separated is fed continuously to the column or to the still

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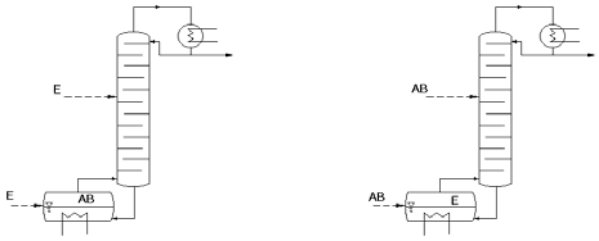
(Figure 1b). This new configuration is called inverse batch extractive distillation (IBED).



a) b)

Figure 1. BED (a) and IBED (b) configurations

We are mainly interested in the question if and how separation in the new configuration is feasible. This question is primarily answered with feasibility study based on short-cut calculations. On the other hand, the theoretical results are checked and confirmed with rigorous simulation.

Here we introduce IBED as applied for separating a system of maximum boiling azeotrope with intermediate boiling entrainer, a system suggested for batch distillation first by Bernot et al. (1991). However, the new configuration seems advantageous for different mixture types as well.

The feasibility study and the rigorous calculations for IBED are performed on a real mixture (chloroform / ethyl acetate / 2-chlorobutane). This mixture was applied by Lelkes et al. (2002) for studying the corresponding BED process. The results of both studies are applied for comparing the two process variants.

2. Feasibility study

The method of feasibility study published by Lelkes et al. (1998) was applied for the new configuration. Although this method was published specially for the study of BED, it can be applied for IBED as well. The composition of the continuous feed is equal to the azeotropic composition in the case of IBED, whereas it is usually near the pure entrainer vertex in the case of BED. Accordingly, the same tools and methodology can be applied for studying IBED and BED.

The separation is considered feasible if there is a composition profile which connects the specified distillate composition with the still composition. The column section above the feed is called rectifying section, whereas the column part below the feed is called extractive section. The composition profiles in these sections are, accordingly, called rectifying and extractive profiles.

If both an extractive profile and a rectifying profile are needed to connect the still composition to the distillate then the continuous feeding should be applied to the column itself. In this case the extractive profile starting from the still composition must intersect the rectifying profile starting from the specified distillate composition; thus, the calculation of both profiles is necessary for the feasibility study. If a single

rectifying profile connects the still composition to the distillate then no feeding to the column itself is needed. (However, feeding to the still is yet necessary.) In this case the feasibility study can be solely based on the calculated rectifying profiles.

2.1 Feasibility with infinite reflux ratio

Figure 2 shows simultaneously the extractive and rectifying profile maps with feed ratio F/V=0.1 and infinite reflux ratio (zero distillate withdrawal). Let the specified distillate composition lie near the vertex of pure component *A* (chloroform). Then the extractive profiles crossing the expected still compositions intersect the rectifying profile. Thus, the separation using IBED with infinite reflux ratio is feasible. (Expected still compositions are those on and to the left of the straight line connecting the azeotrope with the entrainer vertex.) This is so in spite of the presence of numerous fixed points of the extractive profile map (1 stable node (SN), 1 unstable node (UN) and 3 saddles (S)). The exact position of the saddle points were not determined, but the pointer of the dashed arrows mark possible places.

2.2 Feasibility study with finite reflux ratio and pure product

For a reliable pre-design the feasibility study must be applied for finite reflux ratio, as well. If the specified distillate composition lies near the vertex chloroform then a map similar to that in Figure 3 is obtained.

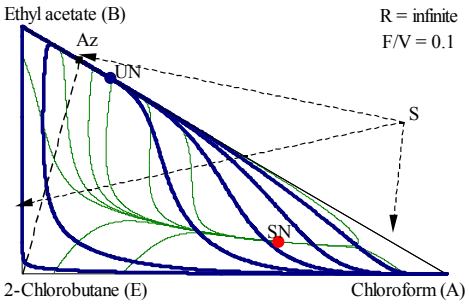


Figure 2. Rectifying and extractive profiles for infinite reflux ratio

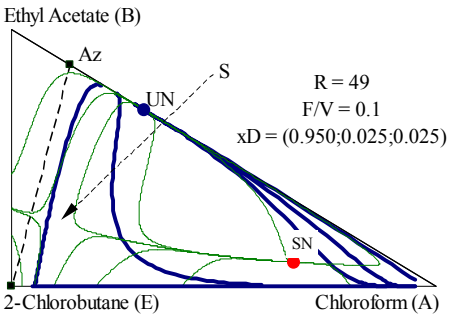


Figure 3. Rectifying and extractive profiles for finite reflux ratio and pure product

The rectifying profiles (bold lines) starting from a small triangle around the pure chloroform vertex, and calculated at a specified reflux ratio, cover a part of the composition triangle. This is called the rectifying region, valid at the specified reflux ratio. Some of those profiles belonging to R=49 are plotted bold in Figure 3.

There are an unstable (UN) and a stable node (SN) of the extractive profiles in the rectifying region, and there is a saddle (S) near the border of this region (its possible location is marked with the pointer of the dashed arrow in this figure as well). The separation is infeasible as is seen from the shape of the extractive profiles. The extractive profiles starting from the neighborhood of vertex *E* do not intersect any

rectifying profile and it is the same for the extractive profiles starting from the line connecting the entrainer and the binary azeotrope. Thus, the separation is infeasible in that case even if a part of the azeotropic mixture to be separated is charged together with the entrainer to the still at the beginning of the process.

2.3 Feasibility study with finite reflux ratio and binary product

According to the results of Lelkes et al. (2002), the separation of the studied mixture is infeasible with BED if the specified distillate is near pure component, but it is feasible if the specified product is a binary mixture of component *A* and the entrainer. Thus, components *A* and *B* are separated in a way that *A* is carried out by the entrainer in the distillate. For example, the rectifying and extractive profiles shown in Figure 4 are calculated for such a specification (distillate molfraction x_{DA}=0.4, and x_{AR}=0.95), where $x_{AR}=x_A/(x_A+x_B)$. The distillate composition is to be set in a long and narrow region along the base line (binary edge *A*-*E*) where the ratio of *B* to *A*, i.e. the entrainer-free composition of *B* is under a specified maximum, e.g. 5 %. A maximum of the entrainer molfraction in the distillate is also specified for avoiding too difficult recovery of *A* from *E*, and for avoiding application of too much entrainer in the process. Thus, the specified region of the acceptable distillate composition is a long, narrow triangle with a cut at its peek near the entrainer vertex. For checking the feasibility, the calculation of the rectifying profiles may be started from the limiting edge of the specified region.

The extractive profile map should be investigated together with the actual rectifying profile in the case of binary products because the position of the fixed points, and so the shape of the extractive profiles as well, depend on the value of x_{DA}, the molfraction of chloroform in the distillate. Figure 4 shows several rectifying profiles, but the extractive profiles belong to only one of them, the one drawn by bold.

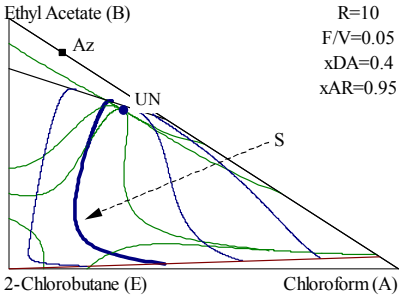


Figure 4. Rectifying and extractive profiles for finite reflux ratio and binary product

The extractive profiles starting from the neighborhood of vertex *E* do not intersect the corresponding rectifying profile (the one drawn by bold), but the rectifying region contains the initial still composition (i.e. a point near vertex *E*). Thus, the separation is feasible with a single rectifying section, and application of extractive stages is unnecessary.

As a summary, the separation applying IBED is feasible if the specified distillate composition is the binary mixture of component *A* and component *E*, and the mixture of *A* and *B* is to be fed to the still.

3. Comparison

The same essential results are obtained for IBED as the ones published by Lelkes et al. (2002) for BED. Therefore, the two configuration variants can be compared according to their efficiency.

3.1 Preliminary short-cut calculations and theoretical considerations

The same average distillate (collector) composition at the end of the process, and equal final still compositions are applied in the comparison of the two processes. The data are collected in Table 1. The two compared processes have the same operation time, and both of them needs the same amount of entrainer to separate the same amount of azeotrope. They differ only in the number of stages necessary to produce the same product. In all the studied cases, IBED can be run with less number of theoretical stages. Why it is so is explained by comparing Figure 5 and Figure 6.

Table 1 – Results of the preliminary calculations

	R	D	F/D	ΣAz	ΣE/ΣAz	$x_D^{average}$	T	$N^{\#}$
BED	10	1 kmol/h	0.878	85.4 kmol	0.973	(0.150;0.017;0.833)	78 h	$N^{I}(t)$
IBED	10	1 kmol/h	0.214	85.4 kmol	0.973	(0.150;0.017;0.833)	78 h	$N^{II}(t)$

$^{\#}N^{I}(t) > N^{II}(t)\ \forall t$

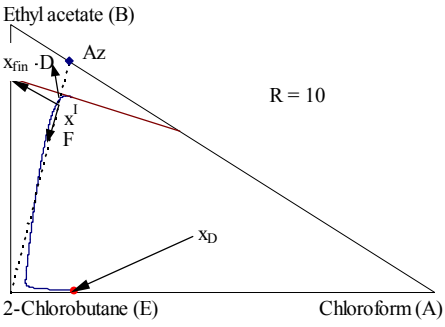


Figure 5. Predicted still-path of the BED process

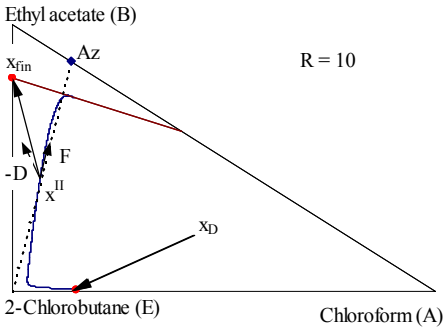


Figure 6. Predicted still-path of the IBED process

Figure 5 shows the estimated still-path for the BED process, and Figure 6 shows that for the IBED process. The initial still compositions lie on the same rectifying profile, so the two still-paths intersect the rectifying profiles of the same bundle (not shown in the figures) during the process. The predicted direction of the still-path is computed according to summing the vectors, shown in the figures, directed by the product removal and by the feed. The position of $\mathbf{x}_D$ is also pointed by an arrow.

The still-path of IBED runs nearer to the *AE* edge, and the necessary number of stages is in relation with the length of the rectifying profile. Thus, a smaller column is sufficient for the same separation with IBED than with BED. This conclusion can be turned out: IBED can produce better product than BED in the same column with the same operation parameters.

3.2 Rigorous calculations

Rigorous calculations are performed with ChemCAD® 5.11 software. The simulations for the two different processes were run with the same parameters (see Table 2). The simulation results are also compared in Table 2. Nearly the same product (entrainer free product purity, x_{AR}) was produced with IBED and with BED, and the recovery of the chloroform (η_{CHCl3}) are almost the same in the two processes. However the solvent demand of the IBED is significantly less than that of the traditional BED. More than 20 % of the entrainer can be spared if the applied process is IBED instead of BED.

Table 2. Simulation results comparing the new scheme and the traditional BED

	BED	IBED
N	45	
R	20	
Q [kWh]	15	14,985
Amount to be separated [mol]	68	
Initial composition of the still [mol]		
$CHCl_3$	34	21
EtOAc	34	21
2-ClBu	0	70
Applied amount of entrainer [mol]	90	70
x_{AR}	0,995	0,997
η_{CHCl3}	92,0 %	91,2 %
F [mol/h]	9	7,8

4. Conclusion

A new configuration, the inverse batch extractive distillation (IBED), as a variant of batch extractive distillation (BED) is introduced in this article. The entrainer, instead of the mixture to be separated, is charged into the still of the batch rectifier at the beginning of the process, in this new configuration. The mixture is fed continuously into the system during the separation. The feasibility study published by Lelkes et al (1998) for BED process is used to investigate the feasibility of the new configuration. The results of the feasibility study and other short-cut calculations are supported by rigorous simulation. The new configuration is beneficial because more than 20 % of the applied entrainer can be saved for the studied system if IBED is applied instead of BED.

Acknowledgement

This study has been supported by OTKA T037191 and F035085.

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