New double column system for heteroazeotropic batch distillation

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ABSTRACT

A new double column system (DCS) operated in closed mode is suggested for heterogeneous batch distillation. This configuration is investigated by feasibility studies based on the assumption of maximal separation and is compared with the traditional batch rectifier (BR). We study the configurations also by dynamic simulation based on a detailed model using a professional simulator. For the new configuration the minimal duration of the process is determined. The influence of the most important operational parameters is studied. The calculations and the simulations are performed for a binary (n-butanol–water) and for a ternary heteroazeotropic mixture (isopropanol–water + benzene as entrainer). One of the advantages of the DCS is that distillation of binary and ternary systems is performed in only one step. Furthermore the recovery of components is usually higher and the amount of byproducts is lower.

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1. Introduction

The recovery of organic solvents is performed mainly by distillation. In the pharmaceutical and fine chemical industries, batch processes are widely applied because of the low amount and the frequent change of the products. The azeotropic mixtures can be only separated into their pure components by the application of a special distillation method, such as pressure swing, extractive or heteroazeotropic distillation.

The *homoazeotropic mixtures* can be separated without the application of a separating agent by pressure swing distillation if the azeotrope is pressure sensitive. The semicontinuous and batch *pressure swing distillation* was investigated by simulation by Phimister and Seider (2000) and experimentally by Repke, Klein, Bogle, and Wozny (2007). Modla and Lang (2008) suggested two new double column configurations (double column batch rectifier and double column batch stripper) by modifying the middle vessel column. The two-column system was operated in open mode (with continuous withdrawal of products (distillate/bottoms)).

The *homogeneous batch extractive distillation* with the use of a heavy solvent in a rectifier was investigated among others by Lang, Yatim, Moszkowicz, and Otterbein (1994), Duessel and Stichlmair (1995), Lelkes, Lang, Benadda, and Moszkowicz (1998), Lang, Kovacs, Kotai, Gaal-Szilagyi, and Modla (2006), Kotai, Lang, and Modla (2007) and in a non-conventional configuration (mainly in middle vessel column) among others by Safrit, Westerberg,

Diwekar, and Wahnschafft (1995), Warter and Stichmair (1999), Cui et al. (2002), Low and Sorensen (2002), Warter, Demicoli, and Stichmair (2004), Steger et al. (2006).

If the components of a mixture form a *heteroazeotrope*, or by the addition of an entrainer a heteroazeotrope can be formed, it is possible to cross the azeotropic composition by decantation. The batch heteroazeotropic distillation (BHD) is a widespread industrial method. To our best knowledge so far the process was exclusively applied in the industry in batch rectifiers (equipped with a decanter) in open operation mode (continuous top product withdrawal).

Design and synthesis tools of batch distillation involve the analysis of residue curve maps. Pham and Doherty (1990) described the structure and properties of residue curve maps for ternary heterogeneous azeotropic mixtures. The residue curve map analysis and the subsequent determination of distillation regions consider only the phase equilibrium (VLLE) characteristics of the mixture. By extending the method of Pham and Doherty (1990), Lang and Modla (2006) suggested a new general method for the calculation of the residue curves and for the determination of batch distillation regions of the heteroazeotropic distillation. The method considers, in addition to the VLLE, operating parameters, such as withdrawal of the entrainer-lean or the entrainer-rich phase or any combination of them as distillate. The above method combines both VLLE information and material balances in the same map (still path map).

For the operation mode of batch heteroazeotropic distillation requiring the addition of the lowest amount of entrainer (E), the two separation methods (distillation and liquid–liquid phase split) of the hybrid process are applied simultaneously. This operation mode is named Mode II by Skouras, Kiva, and Skogestad (2005) and

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Nomenclature

D	distillate molar flow rate (kmol/s)
L	liquid molar flow rate (kmol/s)
R	reflux ratio
SD	amount of distillate (kmol)
T	temperature (°C)
t	time (h)
U	liquid holdup (kmol)
V	vapour molar flow rate (kmol/h)
v	relative vapour flow rate of a column (mol/mol)
x	liquid mole fraction
y	vapour mole fraction

Greek letter

τ	duration of the step (h)

Subscripts

A	more volatile component
AZ	azeotrope
B	less volatile component
b	beginning of the step
BAZ	binary azeotrope
ch	charge
E	entrainer
e	end of the step
i, j	components
ov	overall
res	residue at the end of the cycle
spec	specified value
TAZ	ternary azeotrope

Superscripts

1	first step of the operation
2	second step of the operation
Ar, Br	A-, B-rich phase
Er	E-rich phase
ir, jr	i-, j-rich phase
SD	amount of distillate in the product tank
α	A-producing column of the DCS
β	B-producing column of the DCS

Skouras, Skogestad, and Kiva, (2005). In Mode I the two separation methods are realised in sequence. For Mode II two separation strategies can be realised as presented by Koehler, Haverkamp, and Schadler (1995) and Skouras, Kiva, et al. (2005) and Skouras, Skogestad, et al. (2005). In Strategy A (in the first dehydration step) the *E*-rich phase is totally refluxed and in Strategy B only partially refluxed. Obviously Strategy B requires greater amount of entrainer since a considerable part of the entrainer is also withdrawn as distillate. Therefore it provides a competitive alternative to Strategy A only where *E* is already present in sufficient quantity in the original (*A–B–E* ternary) mixture. For both strategies of operation Mode II, Lang and Modla (2006) suggested to distinguish two versions: (1) the *E*-lean phase is not refluxed and (2) the *E*-lean phase is also refluxed partially (in order to increase the reflux ratio, if necessary).

The batch rectifier (BR) was investigated with variable decanter holdup by Rodriguez-Donis, Gerbaud, and Joulia (2002) and with continuous entrainer feeding by Modla, Lang, and Molnar (2001) and Modla, Lang, Kotai, and Molnar (2003) and Rodriguez-Donis, Equijarosa, Gerbaud, and Joulia (2003), respectively. Recently the closed operation mode for the BR and also for multivessel columns was extensively studied by Skouras, Kiva, et al. (2005) and Skouras, Skogestad, et al. (2005). Pommier et al. (2008) developed a specific

software architecture based on the BatchColumn® simulator and on both SQP (Sequential Quadratic Programming) and GA (Genetic Algorithm) numerical algorithms for the optimisation of sequential batch columns and heterogeneous batch distillation in open mode.

The goals of this paper are:

- to suggest a new double column system (DCS) for the batch heteroazeotropic distillation,
- to investigate this configuration first by feasibility studies then by dynamic simulation based on a more detailed model,
- to compare its performance with that of the traditional BR.

For both configurations we investigated the simultaneous realisation of distillation and liquid–liquid phase split (Mode II). Furthermore we studied only the cases where one-phase streams are led to the top of the column(s) from the decanter.

We compared the optimal operation of the two configurations. The total duration of the process was minimised ($\min(\Delta t)$) by repeated simulations. Since the (total) heat duty was kept constant this means practically minimising the operation costs ($\min(C_{op})$).

The calculations and the simulations were performed for a binary (n-butanol (A)–water (B)) and for a ternary heteroazeotropic mixture (isopropyl-alcohol (A)–water (B) + benzene as entrainer (E)). For the simulation we used the dynamic simulator of CHEMCAD 5.6 (module CC-DCOLUMN, Chemstations, 2007).

2. The column configurations studied

First the operation of the BR then that of the new double column system (DCS) will be presented. For the sake of simplicity we assume maximal separation for both configurations, that is, in each column the top vapour has always azeotropic composition.

2.1. Batch rectifier

First the separation of the binary then that of the ternary mixture is presented.

2.1.1. Separation of the binary mixture (Fig. 1)

If the feed (charge) composition $x_{ch,A}$ is in the heterogeneous region ($x_{AZ,A}^{Br} < x_{ch,A} < x_{AZ,A}^{Ar}$), it is worth to separate it by decantation into an *A*-rich ($x_{AZ,A}^{Ar}$) and a *B*-rich ($x_{AZ,A}^{Br}$) phase before the start of the distillation.

One production cycle consists of two distillation steps. We select the phase to be distilled in the first step so that the overall quantity of the two products in the first cycle be maximal. By assuming
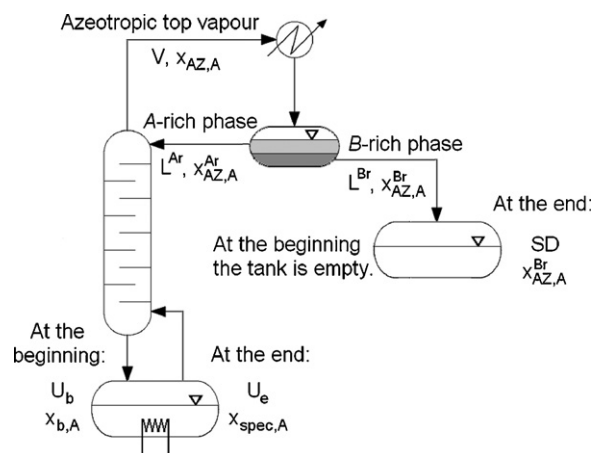

Fig. 1. Batch rectifier producing A from a binary mixture.