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Feasibility of separation of ternary mixtures by pressure swing batch distillation

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ABSTRACT

Feasibility of the pressure swing batch distillation separation of ternary homoazeotropic mixtures in different single and double column configurations is investigated by assuming maximal separation. Feasibility regions where the ternary mixture can be separated into its pure components (by applying in at least one step pressure swing) and the separation steps for the recommended configurations are determined. The method is presented in details for the most frequent types of ternary mixtures with minimum azeotrope(s).

1. Introduction

Distillation is the separation method most frequently applied in the chemical industry, which is based on the difference of volatility of the components of a liquid mixture. For the separation of azeotropic mixtures a special distillation method must be applied such as the *pressure swing distillation* (PSD), extractive or heteroazeotropic distillation. The pressure swing distillation is the least studied from these three methods.

Batch distillation (BD) has always been an important part of seasonal, uncertain or low capacity and high-purity chemicals' production (Stichlmair and Fair, 1998; Mujtaba, 2004). It is a process of key importance in the pharmaceutical and several other industries and in the regeneration of waste solvent mixtures. The main advantage of batch distillation over continuous is that a single apparatus can process many different liquid mixtures. Even multicomponent mixtures can be separated by batch distillation in a single column. A comprehensive review of the computer-aided analysis, optimal design and control of batch distillation was published by Kim and Diwekar (2001).

The batchwise realisation of the special distillation methods with the application of a separating agent received great attention during the last decade. The *homogeneous batch extractive distillation* with the use of a heavy solvent in a rectifier was investigated among others by Lang et al. (1994), Duessel and Stichlmair (1995), Lelkes et al. (1998), Lang et al. (2006), Kotai et al. (2007) and in a non-conventional configuration (mainly in middle vessel column) among others by Safrit et al. (1995), Warter and Stichlmair (1999), Cui et al. (2002), Low and Sorensen (2002), Warter et al. (2004), Steger et al. (2006). Hua et al. (2007) proposed a modified operation mode of batch extractive distillation with two reboilers.

The different aspects of the *heterogeneous batch distillation* were studied among others by Modla et al. (2001, 2003), Rodriguez-Donis et al. (2002, 2005), Chien et al. (2004), Skouras et al. (2005a, b), Xu and Wand (2006). A general method for the calculation of residue curves and for the determination of batch distillation regions of heteroazeotropic distillation was suggested by Lang and Modla (2006). Pommier et al. (2008) developed a specific software architecture based on the BatchColumn® simulator and on both SQP and GA numerical algorithms for the optimisation sequential batch columns and heterogeneous batch distillation in open mode. Denes et al. (2009) suggested a new double column system operated in closed mode for heterogeneous batch distillation.

Many mixtures form an azeotrope, whose position can be shifted substantially by changing system pressure, that is, a *pressure sensitive azeotrope*. (At some pressure the azeotrope may even disappear.) This effect can be exploited to separate azeotropic mixtures without the application of a separating agent by the so-called pressure swing distillation.

Knapp and Doherty (1992) listed 36 pressure sensitive binary azeotropes as selected examples. The majority of the mixtures were taken from the book of Horsley (1973). The most complete collection of the azeotropic data was published by Gmehling et al. (1994), where the azeotropic compositions are given at different pressures and so their pressure sensitivity can be easily checked.

Lewis (1928) was the first, who suggested distilling the azeotropic mixtures by pressure swing distillation. This

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process has been suggested to separate azeotropic mixtures by e.g. Black (1980), Abu-Eishah and Luyben (1985), Chang and Shih (1989). More details about the pressure swing continuous distillation can be found in books of Van Winkle (1967) and Wankat (1988).

Knapp and Doherty (1992) developed a new process, in which continuous pressure swing distillation was combined with entrainer addition. The possibility of the application of an entrainer for the separation of binary azeotropic mixtures increases to a large extent the number of mixtures separable by this process. On the other hand the separation of the original components from the entrainer means an additional task.

By the above authors suitable pressure-swing entrainers cause distillation boundaries to move in one of three ways.

(i) The entrainer forms no new azeotropes at atmospheric pressure, but when the pressure is changed new azeotrope(s) appear which move rapidly with changing pressure (e.g. dehydration of ethanol with acetone).
(ii) The entrainer forms one or more new azeotropes whose composition(s) change rapidly with pressure.
(iii) The entrainer forms one or more new azeotropes at atmospheric pressure, but they disappear as the pressure is changed (e.g. separation of acetone and methanol with methyl ethyl ketone).

They also mention that (continuous) pressure-swing distillation becomes rather complex, requires more than two columns when multiple boundaries lie between the pure components, and will only work if all boundaries shift with varying pressure. Therefore they do not suggest to use (continuous) pressure swing distillation when more than one boundary lies between the desired products.

Phimister and Seider (2000) were the first who studied the batch application of binary PSD by simulation. They investigated the separation of a minimum azeotrope (THF-water) by semi-continuous PSD and reverse-batch operation (batch stripping). In the semicontinuous column better performance was achieved than in the batch stripper. They also investigated the control and other practical aspects of these configurations, and their performance was compared with that of a continuous system, as well.

Wasylkiewicz et al. (2003) developed an algorithm which allows the variation of compositions of azeotropes with pressure to be tracked, and all new azeotropes that appear within specified pressure range to be found.

To our knowledge Repke et al. (2007) were the first, who investigated experimentally the application the pressure swing distillation in batch. They studied the separation of a minimum boiling, homoazeotropic mixture (acetonitrile-water) by pressure swing distillation in a batch rectifier and in a stripper with pilot-plant experiments and rigorous simulations. The aim of these authors was rather the experimental study of the pressure swing batch distillation than the exhausting theoretical study of the feasibility of the process.

Gerbaud et al. (2006) developed a systematic procedure enabling to find suitable process and eventually suitable entrainer for the batch separation of zeotropic or azeotropic binary mixtures. This algorithm takes into consideration also Matsuyama and Nishimura's and Serafimov's classification of ternary mixtures, respectively (if entrainer is applied). By the authors above pressure influence on azeotropic composition must be regarded first before considering any azeotropic or extractive distillation process. Besides, the example in this paper (water-acetonitrile) shows that lowering the pressure may induce the appearance of a LLV heterogeneous region while the homoazeotrope is kept. Lowering the pressure results in the decrease of condensation temperature of the top vapour. In the case of application of a very low pressure the condensation may require low temperature fluid which makes the PSD process costly.

Luyben (2005) compared the pressure-swing and extractive distillation methods for methanol recovery system in the TAME reactive distillation process. He presented a quantitative steady-state and dynamic comparison of the pressure-swing process (separation i-pentane/acetone) with an extractive-distillation process (by applying water as solvent). The extractive distillation process was found to be more economical. The plantwide dynamic controllability performances of the two systems were essentially equivalent.

Luyben (2008a) compared the continuous extractive distillation and pressure-swing distillation for the separation acetone/methanol. He presented that the extractive distillation system has a 15% lower total annual cost and the dynamic controllabilities of the two alternative processes are quite similar. Steady-state designs and control structures are also developed for the two methods when the columns are heat integrated.

Luyben (2008b) investigated the design and control of a fully heat-integrated pressure-swing azeotropic continuous distillation system for the separation THF/water.

Modla and Lang (2008) studied the feasibility of pressure swing batch distillation (PSBD) of binary mixtures (forming minimum or maximum azeotrope) in different column configurations assuming maximal separation. They concluded that the middle vessel column is not suitable for PSBD and suggested two novel configurations containing two rectifying (double column batch rectifier, DCBR) or two stripping sections (double column batch stripper, DCBS).

The above authors made rigorous simulation calculations for the different column configurations, as well. The different configurations were compared for a given set of operational parameters. The best results were obtained with the two new double column configurations equipped with a common bottom or top vessel, respectively. They stated that these new configurations may provide a lot of advantages against the well-known simpler configurations (batch rectifier or stripper). For separating minimum azeotropes they suggested the application of double column batch stripper or batch stripper and for maximum azeotropes double column batch rectifier or batch rectifier, respectively.

The aim of our work is

- to investigate the feasibility of the pressure swing batch distillation separation of ternary mixtures in different configurations by assuming maximal separation and straight boundaries,
- to determine feasibility regions where the ternary mixture can be separated into its pure components (by applying in at least one step pressure swing), and
- to determine the steps of separating azeotropic mixtures of different type in different (single and double) column configurations.

In this paper only the most frequent types of ternary mixtures are investigated (whose physical occurrence is more than 0.9% by Reshetov's statistics (1998).

Furthermore the following cases are not studied here:

- the volatility order of components varies, and
- the azeotrope disappears (excepted the case presented in Chapter 4.2.1), on the variation of pressure.