

Separation of *n*-hexane–ethyl acetate mixtures by azeotropic batch distillation with heterogeneous entrainers

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Received 26 February 2004; received in revised form 4 May 2004; accepted 14 May 2004

Available online 2 July 2004

Abstract

In this article, a systematic study of the separation of the *n*-hexane–ethyl acetate mixture with an entrainer by heterogeneous azeotropic batch distillation is performed. Based upon the thermodynamic behaviour of the ternary mixtures, potential entrainers partially miscible with one or two original azeotropic components are chosen. In all cases, the entrainer adds a heterogeneous binary or ternary azeotrope that is the lowest boiling point in the ternary diagram. Therefore, it leaves the column by the overhead stream which is subcooled to get two liquid phases in the decanter. The phase with the highest amount of the original component is removed as distillate product whereas the entrainer-rich phase is continuously refluxed to the column. Considering methanol, acetonitrile, water and nitromethane as heterogeneous entrainers, screening was performed based on the composition of the unstable heteroazeotropic mixture, the ratio of both liquid phases in the condensed top vapour and the purity of the distillate product determined by the liquid–liquid envelope at the decanter temperature. The process feasibility analysis is validated by using rigorous simulation with the batch process simulator ProSimBatch. Simulation results are then corroborated in a bench experimental column for the selected entrainer, showing several advantages of heterogeneous batch distillation (HBD) compared to homogeneous systems. © 2004 Elsevier B.V. All rights reserved.

Keywords: Batch distillation; Heterogeneous entrainer; Azeotropic distillation

1. Introduction

Batch processes are again becoming important because of recent expansion of the pharmaceutical and speciality chemical industries in many developing countries. Besides, recycling of liquid waste streams is becoming a key issue in all processing plants to meet stricter environmental regulations. Batch distillation is a widely used separation method in batch processes because of its inherent operational flexibility due to some extent to its time dependent operation. The separation of azeotropic mixtures or close boiling components is a challenging task in many chemical processes as it is impossible using a single conventional column or as a pressure swing distillation is an uneconomical process. Alternative techniques based on the addition of an auxiliary

substance in the original mixture have been developed and are usually known as azeotropic and extractive distillation.

Process synthesis and design of these non-conventional distillation processes proceed in two steps. The first step—process synthesis—is the selection of one or more candidate entrainers along with the computation of thermodynamic properties like residue curve maps that help assess many column features such as the adequate column configuration and the corresponding product cuts sequence. The second step—process design—involves the search for optimal values of batch distillation parameters such as the entrainer amount, reflux ratio, boiler duty and number of stages. The complexity of the second step depends on the solutions obtained at the previous level, because efficiency in azeotropic and extractive distillation is largely determined by the mixture thermodynamic properties that are closely linked to the nature of the entrainer. Hence, we have established a complete set of rules for the selection of feasible entrainers for the separation of non ideal mixtures

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by homogeneous azeotropic batch distillation [1]. In contrast to batch homogeneous distillation processes, studies on heterogeneous batch distillation (HBD) were scarce [2–4] until a new method for the synthesis of heterogeneous distillation in a batch rectifier was defined and a complete set of rules for the selection of heterogeneous entrainers for the separation of non-ideal mixtures was established [5,6].

Simulation and experimental results have shown key differences between homogeneous and heterogeneous batch distillation [6]. Indeed, some advantages of heterogeneous batch processes compared to homogeneous systems are: (i) more suitable candidate entrainers and hence, more design alternatives for the separation of non-ideal mixtures, (ii) simplified distillation sequences thanks to the liquid–liquid phase split occurring in some parts of the column and in the decanter, (iii) the addition of a smaller amount of entrainer to the original mixture, (iv) the use of more flexible reflux policies through any combination of the entrainer-rich phase and the distillate-rich phase, (v) the still path can cross unstable separatrixes allowing the separation of components located in different basic distillation regions. The overall cost reduction generated by these advantages makes heterogeneous batch distillation an attractive option for the separation of non-ideal mixture generated by specialty industries.

The aim of this paper is to study the performance of heterogeneous batch distillation for the separation of the mixture *n*-hexane–ethyl acetate. This azeotropic mixture is often used in pharmaceutical industries for separating bioactive substances by liquid chromatographic processes. The separation of this mixture by batch distillation was first studied by Rodriguez-Donis et al. [7], by using acetone as a homogeneous entrainer. As the separation by using a single batch distillation process with acetone was not possible, a hybrid process was proposed involving a homogeneous azeotropic distillation column with acetone and a liquid–liquid extraction column with water. To circumvent this complex process, we propose in this paper a simpler process by using heterogeneous azeotropic batch distillation. Based on entrainer selection rules established by Rodriguez-Donis et al. [5], which consider the thermodynamic behaviour of multicomponent mixtures, an initial list of potential entrainers partially miscible with one or both original azeotropic com-

ponents are selected. From the analysis of residue curve map features, in particular the decanter phases composition and the distillation region separatrixes curvature, the sequence of products to be drawn from the rectifier column can be predicted. The number of distillation tasks in the whole process is set by the products targeted purity.

2. Selection of a suitable entrainer for the separation of *n*-hexane–ethyl acetate mixtures by heterogeneous azeotropic batch distillation

Liquid–vapour equilibrium data for the binary mixture *n*-hexane–ethyl acetate have been scarcely reported in the scientific literature [8]. Those authors reported a minimum boiling temperature azeotrope with an average mole fraction of *n*-hexane equal to 0.6565 and a temperature of 65.15 °C at 101.3 kPa. A more detailed experimental study, at atmospheric pressure, of liquid–vapour equilibrium was performed by Acosta et al. [9]. Their estimation of the azeotropic mixture corresponds to a temperature of 64.85 °C with a molar fraction of *n*-hexane of 0.657 with an average experimental error for the temperature and composition measurements of 0.02 °C and 0.003 mole fraction, respectively.

The candidate homogeneous and heterogeneous entrainers are investigated applying the rules reported by Rodriguez-Donis et al. [1,5]. The existence of binary and ternary azeotropes is sought by using literature data [8] and by simulating liquid–vapour and liquid–liquid–vapour equilibrium by using the BibPhyAddIn Macro in an Excel spreadsheet [10]. Confirming the need for a complex hybrid process in case a homogeneous entrainer like acetone is used [7], no homogeneous entrainer matching the reported rules has been found whereas some suitable heterogeneous entrainers have been identified; the composition and temperature of their azeotropic mixtures with the original components are displayed in Table 1 [8].

As seen in Table 1, the boiling temperature of the possible entrainers is either lower or higher than that of the original components. All candidates form a binary heterogeneous azeotrope with *n*-hexane. Methanol and acetonitrile

Table 1
Potential heterogeneous entrainers for the separation of *n*-hexane–ethyl acetate mixture with thermodynamics data from Gmehling et al. [8]

Entrainer	bp (°C)	Binary azeotrope with <i>n</i> -hexane (68.7 °C)		Binary azeotrope with ethyl acetate (77.1 °C)		Ternary azeotrope	
		x_{molar}^a	T (°C)	x_{molar}^a	T (°C)	x_{molar}^a	T (°C)
Methanol	64.7	0.5100 ^b	50.6	0.708	62.05	–	–
Acetonitrile	81.5	0.5755 ^b	54.4	0.6730	76.1	–	–
Water	100.0	0.7860 ^b	61.8	0.7000 ^b	70.5	0.5764 ^b 0.2558	60.7
Nitromethane	101.2	0.7271 ^b	62.0	Zeotropic	–	–	–

^a The mole fraction indicated is that of the lightest component in the mixture.

^b Heteroazeotrope.

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