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Separation of ethyl acetate–isooctane mixture by heteroazeotropic batch distillation

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ABSTRACT

This paper studies the separation of an ethyl acetate–isooctane mixture by heterogeneous azeotropic distillation in a batch rectifying column. An initial list of 60 candidates was studied but only methanol and acetonitrile were obtained as potential heterogeneous entrainers. These entrainers form a low boiling heterogeneous azeotrope with isooctane. Experimental verification of the miscibility gap with isooctane was performed at 25 °C for each entrainer giving a smaller region for methanol than for acetonitrile. Feasibility of the heterogeneous azeotropic batch distillation was carried out experimentally in a laboratory batch distillation column having 44 theoretical equilibrium stages and using a high reflux ratio. Several distillate fractions were taken as a function of the temperature at the top of the column. For both methanol and acetonitrile, the main fraction was defined by the condensed vapor providing a liquid–liquid split of the isooctane/entrainer heteroazeotrope into the decanter. Ethyl acetate impurity was detected in both decanted phases, but in much lower amount when using acetonitrile as entrainer. The process with acetonitrile also resulted in a shorter operating time and higher purity and recovery yield of isooctane as the main distillate product. Pure ethyl acetate remained into the boiler at the end of each process.

Keywords: Heteroazeotropic distillation; Solvent recovery; Batch distillation; Ethyl acetate–isooctane mixture; Entrainer selection; Methanol; Acetonitrile

1. Introduction

Solvent recovery is becoming a major issue in the pharmaceutical and specialty chemical industries. As waste regulations are becoming stricter, the economic benefits of having recovery systems for the reuse of solvents in processes are significant. Recovery of organic solvents is generally practiced because of increased solvent cost and potential solvent shortages. Pharmaceutical and chemical industries are using large amounts of solvents for production and cleaning operation that may end up as waste streams (Whim and Johnson, 1996; Stoye, 2000; Seyler et al., 2006). Batch processes have been the preferred operating mode in the manufacturing of high-value added chemicals, since the demand for high-value chemicals are seasonal and low in volume (Halim and Srinivasan, 2007).

Among all separation techniques, distillation is by far the most used technique for the separation of waste streams in their individual components. Unfortunately the use of conventional batch distillation is often limited by the frequent presence of azeotropes. Therefore, nowadays waste streams are often incinerated when azeotropes are involved (Van Baelen et al., 2010). Reducing incineration and increasing the

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recovery of these solvents by distillation will decrease emissions of greenhouse gasses in the air, lower the cost of waste incineration and will lead to a more efficient and sustainable use of raw materials (Seyler et al., 2006).

Advanced distillation techniques, like heteroazeotropic batch distillation on which we focus here, have to be applied to recover solvents from waste streams containing azeotropes. Although distillation requires also a lot of energy, there is still a benefit expected from an ecologic and economic point of view, especially in mixtures containing expensive solvents, like isooctane.

Most processes for the separation of azeotropic or low relative volatility zeotropic mixtures AB involve the addition of an entrainer E, leading to a homogeneous ternary mixture ABE or exhibiting a binary heterogeneous miscibility gap (Doherty and Malone, 2001). Simulation and experimental results have shown key differences between homogeneous and heterogeneous batch distillation and led to the publication of general feasibility rules (Rodriguez-Donis et al., 2001a,b; Skouras et al., 2005). 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) depending on the reflux policy, the typical unstable separatrices of residue curve map are not a limit anymore for the separation of components located in different basic distillation regions (Lang and Modla, 2006; Hegely et al., 2013).

In this study we are concerned with the separation of an organic waste composed of ethyl acetate (bp = 77.2 °C) and isooctane (bp = 99.1 °C), commonly used in the pharmaceutical industry. This binary mixture exhibits a minimum boiling temperature azeotrope at 76.3 °C under atmospheric pressure with 0.844 of ethyl acetate molar composition (Gmehling et al., 2004). According to the feasibility rules for batch azeotropic distillation (Rodriguez-Donis et al., 2001b; Skouras et al., 2005), non-conventional distillation processes such as heterogeneous azeotropic batch distillation (HABD) can be feasible to separate both components into high purity fractions. It requires the addition of an entrainer which has to form a heterogeneous binary azeotrope with one of the key components and having the lowest boiling temperature of the resulting ternary mixture. The formation of a ternary azeotrope should be avoided as it pollutes the main product distillate with unwanted compounds. However, good performance of the heteroazeotropic batch distillation is not limited by the presence of extra homogeneous binary azeotropes. Hence, feasible ternary diagrams for minimum boiling azeotropes are the 2.0-2b, 2.0-2c and 3.0-2 class diagrams according to Serafimov's classification having a physical occurrence of 21.1%, 0.9% and 8.4%, respectively (Hilmen et al., 2002; Kiva et al., 2003).

In this paper, the choice of the entrainer is first discussed in order to find the best entrainer option for heterogeneous azeotropic batch distillation. Second, the topological and thermodynamics properties of the ethyl acetate–isooctane–entrainer mixture residue curve map are described. Feasibility of the heterogeneous azeotropic batch distillation (HABD) process is evaluated taking into account the extend of the liquid–liquid vapour equilibrium region into the residue curve map, the liquid–liquid split ratio at the binary heteroazeotrope and the purity of both decanted phases. Finally, experiments are run in a packed laboratory batch distillation column under high reflux ratio to validate the feasibility of the separation of ethyl acetate–isooctane mixture by heterogeneous batch azeotropic distillation. The purities of isooctane as distillate product and ethyl acetate as boiler product are then compared to the preliminary results given by the residue curve map analysis.

2. Entrainer selection for the separation of ethyl acetate–isooctane mixture

The overall performance of non-ideal mixtures separation strongly relies on the choice of a suitable entrainer E. Assessing feasibility requires the evaluation of the ability of E to form binary and ternary azeotropes with A or B. Azeotropic tendency can be approximately estimated via the study of chemical interactions (homologous series, polarity, hydrogen bonding aptitude) together with heuristics on boiling temperature differences (Berg, 1969; Perry et al., 1997; Doherty and Knapp, 1993; Gerbaud et al., 2006). Accurate prediction of azeotropic composition and temperature under the operating pressure requires either experimental data (Gmehling et al., 2004; Gmehling and Onken, 1982) or calculation using thermodynamic models of vapor–liquid and vapor–liquid–liquid phase equilibria, like activity coefficient models or equation of states or group contribution methods (Bossen et al., 1993; Gmehling and Möllmann, 1998; Thery et al., 2004).

First, the selection of potential feasible entrainers (E) for the separation of the minimum temperature boiling azeotropic mixture ethyl acetate (A)–isooctane (B) is performed using the RegsolExpert® wizard tool which combines chemical insight and thermodynamic calculations to find suitable entrainers (Gerbaud et al., 2006). A set of 60 components was selected as candidate entrainers belonging to several chemical families and having boiling temperature lower than ethyl acetate (light E), higher than isooctane (heavy E) and intermediate between both original components (intermediate E). The modified UNIFAC Dortmund version 1993 (Gmehling et al., 1993) was used for estimating the existence of binary azeotropic mixtures (A)–(E) and (B)–(E) and, also, the eventual occurrence of ternary azeotrope ABE. Predicted azeotrope occurrence was further verified against experimental evidence (Gmehling et al., 2004, this work).

Analysing all possible generic mixtures A–B separation with any entrainer E, Rodriguez-Donis et al. derived a completed set of necessary entrainer selection rules for batch azeotropic distillation were elucidated (Rodriguez-Donis et al., 2001a,b). Those rules were implemented into the decision making software RegSolExpert® for Regenerating Solvents by batch distillation, along with feasibility rules for classical and pressure swing batch distillation (Prosim S.A., 2012). In the batch rectification (resp. stripping) process, that usually starts with an infinite reflux (resp. reboil) operation followed by distillate (resp. bottom product) removal, the column overhead (resp. bottom) composition under infinite reflux (resp. reboil) is the least (resp. most) volatile component; an unstable (resp. stable) node; of the distillation region where the global mixture composition lies, enabling to recover it as distillate (resp. bottom product) (Bernot et al., 1990, 1991). Separation of minimum boiling azeotropic mixtures with homogeneous or heterogeneous entrainer is only feasible if: