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Design and control of reactive distillation for ethyl and isopropyl acetates production with azeotropic feeds

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Abstract

Reactive distillations for the production of ethyl acetate (EtAc) and isopropyl acetate (IPAc) are classified as the type-II process where the first column consists of a reactive zone and a rectifying section followed by a stripper [Tang et al., 2005. Design of reactive distillations for acetic acid esterification with different alcohols. A.I.Ch.E. Journal 51, 1683–1699]. Instead of using pure alcohols and acetic acid as reactants, this paper studies the effects of reactant purity on the design and control of reactive distillation. This offers significant economical incentives (by reducing raw materials costs), because ethanol forms an azeotrope with water at 90 mol% and isopropanol/water has an azeotrope at 68%. The purities of the acid is set to 95% for acetic acid (industrial grade), 87% for ethanol, and 65% for isopropanol. The results show that the total annual costs (TAC) increase by a factor of 5% for EtAc and 8% for IPAc production using reactive distillation. Next, the operability of the reactive distillations with azeotrope feeds is explored. Three disturbances, feed flow, acid feed purity, and alcohol feed composition, are introduced to assess control performance using dual-temperature control and one-temperature-one-composition control. Simulation results indicate good control performance can be achieved for reactive distillation with azeotropic feeds.

Keywords: Ethyl acetate; Isopropyl acetate; Azeotrope; Reactive distillation; Control; Design

1. Introduction

Esters are of great importance to chemical process industries. Among them, acetate esters are important organic solvents widely used in the production of varnishes, ink, synthetic resins, and adhesive agents. They are produced from the reactions of acid and alcohols under an acidic condition. A key issue in the production of these esters is the low conversion from the reactions. As a result, heavy capital investments and high energy costs are inevitable. The reactive distillation is a very attract way to reduce these investments and energy costs.

Keyes (1932), among the first, studied an ethyl acetate (EtAc) process using a reactive distillation column which consists of a pre-esterification reactor, two recovery columns, and a decanter. Succeeding researches on this reactive distillation have been reported on either steady-state simulations (e.g. Chang and Seader, 1988; Simandl and Svrcek, 1991; Bock et al., 1997; Giessler et al., 2001), dynamic modelling (e.g. Alejski and Duprat, 1996), operation and control (e.g. Vora and Daoutidis, 2001; Georgiadis et al., 2002), and single column experiment (e.g. Klöker et al., 2004; Kenig et al., 2001). There is a common difficulty encountered in those studies due to the existence of a three-component azeotrope that has minimum boiling point. A conventional reactive distillation column will not be able to produce high purity of the acetate due to this fact. The resulting designs, as a consequence, still lead to heavy capital investments and high operational costs. Tang et al. (2003) change the typical reactive column configuration and developed a new process that consists of two columns (i.e., a column with a reactive zone and a rectifying section (the RD column) and one stripper) to produce high purity of EtAc with

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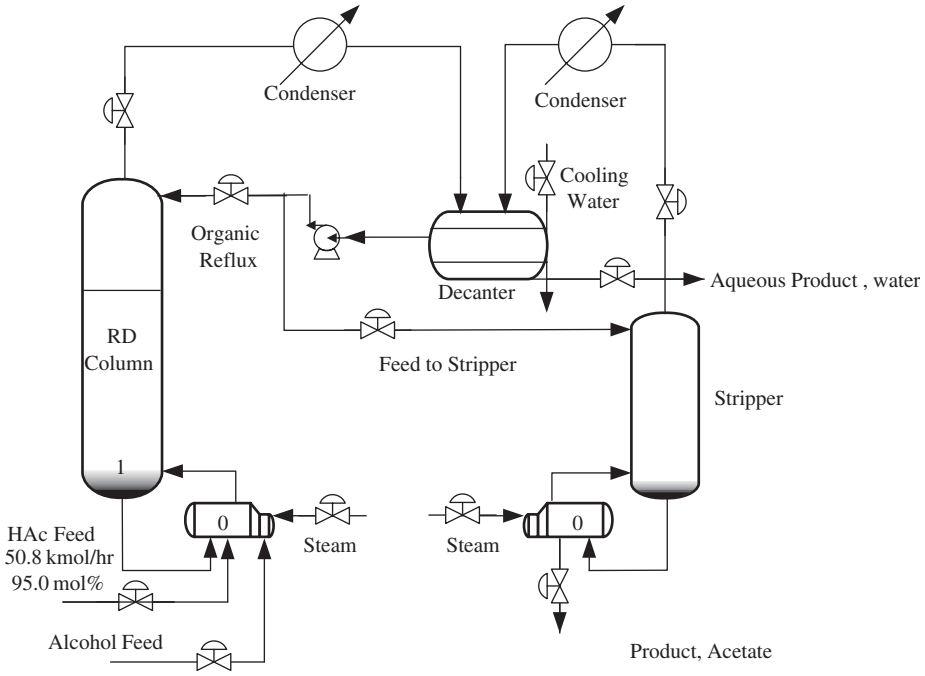

Fig. 1. Configuration of Type II process for the production of Ethyl and isopropyl acetates.

a very stringent specification on the remaining HAc. Later, it was found (Tang et al., 2005) that the production of isopropyl acetates (IPAc) encountered the same difficulty when reactive distillation is involved. Thus, Tang et al. (2005) provides a generalization from their studies of esterifications from acetic acid with different alcohols. They classified the reactive distillation column for the productions of EtAc and IPAc as a type II configuration (Fig. 1). The process configuration of this type is very different from what is known as a typical reactive distillation column. That is, instead of having reactive, rectifying, and stripping sections in one column, reaction and rectifying take place in the RD column and the further purification of acetate is carried out in a downstream stripper while recycling organics with a composition close to ternary azeotrope back to the decanter.

The objective of this work is to investigate the effects of feed purity to the design and control of type II reactive distillation for EtAc and IPAc productions. This has important economical implications, because ethanol forms an azeotrope with water at 90 mol% and isopropanol–water has an azeotrope at 68 mol% isopropanol. In addition to impure alcohol composition, the industrial grad HAc is used. Thus, without further purification on these raw materials, significant cost reduction can be achieved. The catalysts in use are Purolite CT179 in the production of EtAc system, and Amberlyst 15 in the production of IPAc. For the feed purity changes, it is important to study the possible changes in design, variations in the total annual cost (TAC), and control, disturbance rejection capability for feed flow and feed composition changes.

The remainder of this paper is organized as the follows. First, the physical properties and reaction kinetics of these two systems are investigated. Next, qualitatively, process flowsheets are generated based on the thermodynamic behaviors of these two systems. Then, design procedures are proceeded to determine, quantitatively, the numbers of trays in each of sections in the reactive distillation column and the stripper. An improved design is sought by minimizing the TAC. Finally, two control schemes (dual-temperature control and one-temperature-one-composition control) are devised and disturbance rejection capability is evaluated for flow as well as composition variations.

2. Phase equilibrium and reaction kinetics

Both the EtAc and IPAc systems exhibit non-ideal phase behaviors and, as will be shown later, each system has four azeotropes. In order to represent accurately the phase equilibriums of the systems, the selection of the form of the thermodynamic model and the determination of the parameters are essential. To account for the non-ideal vapor–liquid equilibrium (VLE) and possible vapor–liquid–liquid equilibrium (VLLE) for these quaternary systems, the NRTL (non-random two-liquid) activity coefficient model is adopted by Aspen Plus (2001).

The NRTL model parameter sets as shown in Table 1 are taken from the literature. The vapor phase non-ideality such as the dimerization of acetic acid is also considered. The second viral coefficients of Hayden-O'Connell (1975) are used to account for vapor phase association of acetic acid due to dimerization and trimerization. The Aspen Plus built-in association parameters are used to compute the fugacity coefficients.

The thermodynamic model predicts three binary and minimum boiling azeotropes and one ternary minimum boiling