Computers and Chemical Engineering 67 (2014) 166–177

Contents lists available at ScienceDirect

Computers and Chemical Engineering

journal homepage: www.elsevier.com/locate/compchemeng

Design and control of distillation processes for methanol–chloroform separation

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ARTICLE INFO

Article history:
Received 25 October 2013
Received in revised form 6 March 2014
Accepted 31 March 2014
Available online 12 April 2014

Keywords:
Process design
Process control
Pressure-swing distillation
Extractive distillation
Pressure compensated
Azeotropes

ABSTRACT

The binary mixture of methanol–chloroform exhibits a minimum-boiling azeotrope with ~34 mol% methanol at 327 K under atmospheric pressure. In this paper, design and control of alternative distillation processes for separation of methanol–chloroform azeotropic mixture are explored. The steady-state and dynamic simulations are carried out with Aspen Plus and Aspen Dynamics. The comparison in terms of steady-state design is done between homogeneous extractive distillation and pressure-swing distillation processes. The pressure-swing distillation process is found significantly more economical than the homogeneous extractive distillation process. Based on results, a heat-integrated pressure-swing distillation process is considered, and found economically feasible. Thus, the dynamic comparison is done between pressure-swing distillation systems with and without heat integration. The pressure-swing distillation process without heat integration can be controlled using a basic control structure, while the heat-integrated pressure-swing distillation system requires a pressure-compensated temperature control structure. Results show that dynamic controllabilities of both processes are quite similar.

1. Introduction

In chemical process industry, desired product purities are obtained using separation processes, and distillation is by far the most widely used one of these processes. Distillation is based on differences in compositions between liquid and vapor phases. Thus, conventional distillation processes are used for mixtures with ideal or near-ideal vapor–liquid equilibrium behavior. If the mixture has a non-ideal vapor–liquid equilibrium behavior, it may form an azeotrope, which is a mixture of chemical components with identical compositions of liquid and vapor phases in equilibrium. At this point, some special distillation processes, including extractive distillation and pressure-swing distillation, has to be used to separate azeotropes.

Extractive distillation is a method where the relative volatilities of components to be separated are altered by using an additional component (called solvent or entrainer) with a higher boiling point. There are papers studied the design, synthesis and optimization of extractive distillation for different azeotropic systems (Langston et al., 2005; Kossack et al., 2008; Gil et al., 2009; De Figueiredo et al., 2011; Lek-utaiwan et al., 2011). Some of these papers also deal with entrainer selection techniques. The dynamic behavior and control of different extractive distillation processes are reported in several papers (Arifin and Chien, 2008; Gil et al., 2012; Luyben, 2013a; Qin et al., 2013; Fan et al., 2013). Recently, Ramos et al. (2013) proposed an optimal control strategy for an extractive distillation process.

On the other hand, pressure-swing distillation is based on the fact that at a simple change in pressure can alter the composition of the azeotrope, and two columns operating at two different pressures can achieve separation. Design, modeling and optimization of pressure-swing distillation processes are studied in several papers (Hamad and Dunn, 2002; Lee et al., 2011; Luyben, 2012; Kim et al., 2013). The dynamic controllability of pressure-swing distillation processes is considered in open literature for different binary azeotropic mixtures (Repke et al., 2005; Luyben, 2008a; Mulia-Sotoa and Flores-Tlacuahuac, 2011; Wei et al., 2013). Some of these papers deal with design and control of heat-integrated pressure-swing distillation systems. Recently, a study focusing on design and control of a new pressure-swing distillation process including an entrainer is reported in the literature (Li et al., 2013). There are also studies making a comparison between extractive distillation and pressure-swing distillation in terms of design and/or control for different chemical systems (Munoz et al., 2006; Luyben, 2008b, 2013b; Lladosa et al., 2011; Wang et al., 2012; Yu et al., 2012).

The binary mixture of methanol and chloroform is an organic waste of pharmaceutical and biotechnology industry. It is widely used as an effective solvent for bioactive substances' extraction from biological sources (Van Kaam et al., 2008). This binary mixture

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http://dx.doi.org/10.1016/j.compchemeng.2014.03.026
0098-1354/

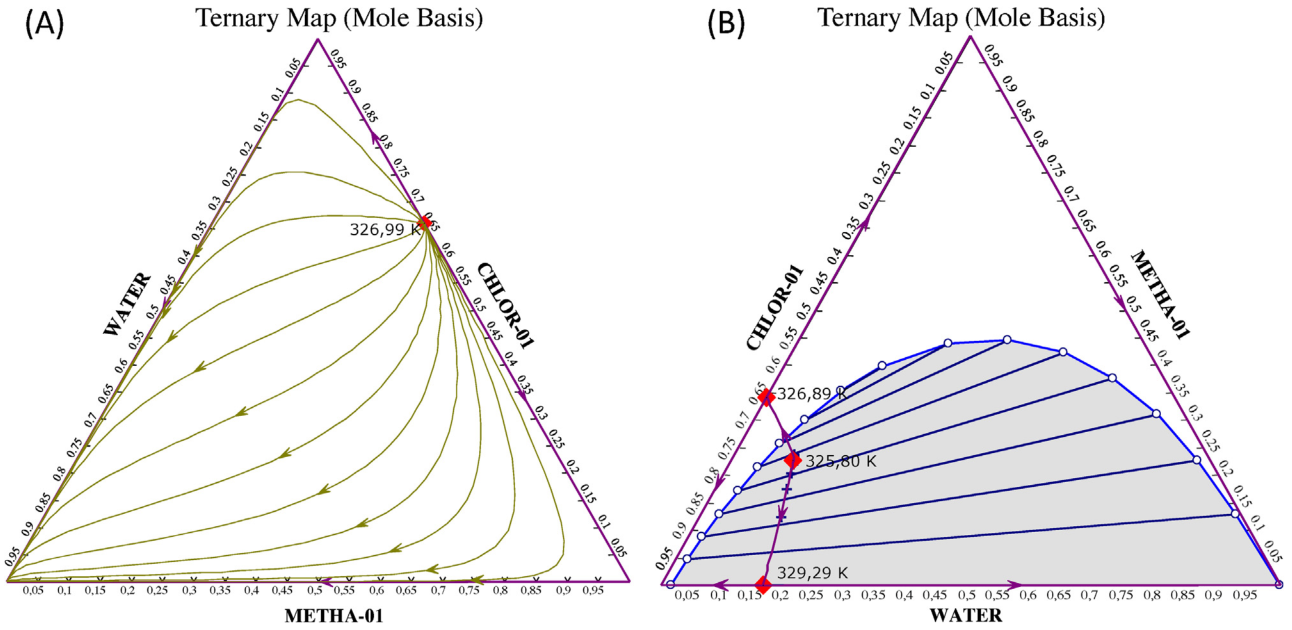

Fig. 1. Ternary map for methanol–chloroform–water system using: (A) Wilson, (B) NRTL.

exhibits a minimum boiling azeotrope with ~0.34 methanol molar composition at 327 K under atmospheric pressure. Thus, chloroform cannot be separated from methanol by using conventional distillation columns. For that reason, the steady-state design of methanol–chloroform extractive distillation process with water as the solvent has been studied by Langston et al. (2005). However, they have not considered the dynamic control of this process. On the other hand, no work has been found in the open literature on the separation of this azeotropic mixture using a pressure-swing distillation process.

The aim of this paper is to compare alternative separation processes for the methanol–chloroform system. Two alternatives, homogeneous extractive distillation and pressure-swing distillation in continuous columns, are compared in terms of steady state design. A heat-integrated pressure-swing distillation system is also considered. It will be indicated that the design of pressure-swing distillation systems with and without heat integration results in lower total annual cost (TAC) compared to homogeneous extractive distillation process. Thus, the comparison in terms of dynamic control is done between pressure-swing distillation systems with and without heat integration.

2. Steady-state designs

2.1. Extractive distillation process

The first issue in the extractive distillation is the choice of a suitable entrainer. In the study of Langston et al. (2005), water was suggested as the entrainer for a methanol–chloroform binary azeotropic system. They also claimed that the Wilson package was found to be the most suitable thermodynamic model. The ternary diagram for the mixture of methanol–chloroform–water using Wilson model is shown in Fig. 1A. It is seen that water does not induce any new azeotrope with the original mixture, and the only binary minimum-boiling point azeotrope is between methanol and chloroform.

However, two experimental studies reported that the mixture of methanol–chloroform–water has two binary (methanol–chloroform and chloroform–water) and one ternary minimum-poiling point azeotropes (Hilal et al., 2001; Van Kaam et al., 2008). These results are examined and validated using the NRTL model of Aspen Plus, and given in Fig. 1B.

In this study, we would like to investigate the feasibility of a homogeneous extractive distillation process for the separation of chloroform–methanol mixture. Selection of the entrainer is made from a list of candidate entrainers given in Table 1, which do not induce any new azeotrope with the original mixture. This list is based on a study published in open literature (Van Kaam et al., 2008). Toxic and polluting affects besides the infinite dilution activity coefficient ratio are taken into account, and 1-propanol is selected as the most suitable entrainer among the candidates. Since no termodynamic model suggestion is found for 1-propanol in the open literature, several reasonable candidates such as NRTL, UNIQUAC, WILSON and UNIFAC are explored using Aspen Plus simulation. Since there is almost no difference between the results of illustrated models, NRTL is selected as the thermodynamic model in this study.

The steady-state flowsheet of the homogeneous extractive distillation process including an extractive column and a recovery column is given in Fig. 2. The extractive column has two feed streams. Since the boiling point of the entrainer is higher than that of the original mixture, it is fed in the upper part of the column. This stream is a mixture of the recycled and make-up entrainer. The recycled stream is essentially pure 1-propanol, but it also keeps a very small amount of original mixture. A small amount of make-up stream is required to account for the small losses of 1-propanol in the product streams. The mixture of methanol and chloroform is fed from a lower section of the column as a fresh feed stream. The fresh feed flowrate is 100 kmol/h of 50 mol% chloroform and 50 mol% methanol. The distillate of the first column is 99.5 mol% chloroform, and the bottoms stream is essentially a binary mixture of methanol and 1-propanol. The bottoms stream of the extractive column is fed into the recovery column to easily separate these components. The amount of the chloroform presented in the bottoms of first column leaves the systems essentially from the top of the second column. Thus, the mol fraction of chloroform in the bottoms of first column is calculated from material balance, and used as the second specification of the extractive column. Methanol is taken from the top of second column with a purity of 99.5 mol%, while 1-propanol is recycled back to the extractive column leaving from the bottoms. It is assumed that the impurity in the bottoms of