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Separation of acetonitrile/methanol/benzene ternary azeotrope via triple column pressure-swing distillation

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ABSTRACT

Acetonitrile/methanol/benzene mixture forms more than one different azeotropes and its triangular diagram presents several distillation boundaries at atmospheric pressure. A process named as triple column pressure-swing distillation (TCPSD) was proposed to separate this complex ternary system. The feasibility of the process was confirmed using residue curve maps and rigorous steady-state simulations were implemented on Aspen Plus. On basis of minimum total annual cost, several operating parameters were optimized by pressure-swing optimization software using the sequential iterative optimization procedure and the economics of TCPSD were compared with four different separation configurations. The results demonstrated that the A-M-B separation configuration was the most optimal column sequence in global optimization to separate acetonitrile/methanol/benzene azeotropic mixture using TCPSD. TCPSD may arouse the interest of researchers in various fields and can assist engineers to select the optimal separating process.

1. Introduction

There is a common and complex ternary system containing acetonitrile, methanol, and benzene in the chemical and pharmaceutical industries. Methanol (CH_3OH), acetonitrile (CH_3CN), and benzene (C_6H_6) are commonly used as organic solvents in chemical and pharmaceutical industries due to their excellent physicochemical properties [1–3]. Therefore, it is attractive and necessary to separate and reuse acetonitrile, methanol, and benzene in order to protect environment and conserve resource. However, conventional separation process cannot separate ternary azeotropic mixture efficiently due to the complexity of acetonitrile/methanol/benzene system which has more than one different azeotropes and distillation boundaries in the ternary system. The boiling points of acetonitrile, methanol, and benzene are 354.63, 337.68, and 353.28 K under atmospheric pressure, respectively. The minimum-boiling azeotropes have compositions of 76.49 wt% (mass fraction) methanol at 336.55 K between methanol and acetonitrile, 38.53 wt% methanol at 331.39 K between methanol and benzene, and 31.66 wt% acetonitrile at 345.94 K between acetonitrile and benzene. Hence, the acetonitrile/methanol/benzene system belongs to the Serafimov class 3.0-2 [4,5], and Modla et al. [6] proposed some feasible methods using batch pressure-swing distillation for this classification. This paper studied the continuous pressure-swing distillation to separate the complex ternary mixture of acetonitrile/methanol/benzene into desired pure products with the minimum total annual cost (TAC).

Many published literatures focused on the separation of ternary mixture in recent years. There are some methods for separation of ternary azeotropic system such as membrane [7], continuous distillation [8,9], and batch distillation [6,10–13]. The concentration of water was improved at 94.9 wt% for the purification of ethyl acetate/ethanol/water ternary azetropic mixtures using membrane by Xia et al. [7]. Membrane separation has broken the azeotropic composition, however, the engineer should balance the economy and products' purities. Modla [11] introduced a new triple column configuration applied in pressure-swing batch distillation for separation of chloroform/acetone/toluene. Phimister and Seider [12] investigated the operation of a semicontinuous, middle-vessel column to separate a nearly-ideal ternary mixture. Huang et al. [8] studied direct and indirect sequence ideal heart-integrated distillation column to separate a simple close-boiling ternary mixture. As for the continuous distillation, Zong [9] studied the separation of acetonitrile/methanol/benzene system by the analysis of the distillation curves and distillation region characteristics via quintuple columns pressure-swing distillation, and the product purity was improved to 99.0 wt%. The continuous distillation can be

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Nomenclature

B	bottom flow rate [kg/h]
D	distillate flow rate [kg/h]
Feed	feed flow rate [kg/h]
ID	diameter of the column [m]
N_T	number of stages
N_F	number of feed locations
N_{REC}	number of recycle location
P	pressure [kPa]
REC	recycle flow rate [kg/h]
RR	reflux ratio
TAC	total annual cost [$/y]

Acronyms

ED	extraction distillation
PSD	pressure-swing distillation
PSDOS	pressure-swing distillation optimization software
RCMs	residue curve maps
TCPSD	triple column pressure-swing distillation

Indices

1, 2, 3	column index

competitively alternative in comparison with batch distillation due to the properties of larger throughput.

Pressure-swing distillation (PSD) [14–22] avoids the potential problem of introducing the third component and has gained lots of attention from researchers in recent years, by comparison with special distillation such as extractive distillation (ED) [23–28], azeotropic distillation [29–32], and reactive distillation [33–35]. Munoz [36] studied ED and PSD process for isobutyl alcohol/isobutyl acetate separation using the commercial simulator Aspen HYSYS while Lladosa et al. [37] investigated the separation of di-n-propyl ether and n-propyl alcohol and found that PSD was more attractive than ED using an entrainer. For separating ternary mixture containing azeotropes, Knapp and Doherty [38] introduced the method of the triple column pressure-swing distillation (TCPSD). The simulation and economic analysis for the ternary system, however, were not given in Knapp's paper. For a complex and special ternary azeotropic system which forming more than one different azeotrope and containing several distillation boundaries, one or two columns cannot achieve a desired separation, hence, TCPSD was proposed in this paper.

The influence of pressure on azeotropic composition and azeotropic temperature for binary system is always used to prove pressure-sensitivity [39–41] which is one of decisive factors for PSD, and triangular diagrams including residue curve maps (RCMs) [5,38,42–46] are usually used to analyze the feasibility of multicomponent separation. Fien and Liu [47] reviewed the design of separation processes and illustrated the use of ternary diagrams including RCMs for the feasibility analysis, flowsheet development, and preliminary design. Kiva and Krolikowski [4] presented different approaches to determine the product composition region for azeotropic mixture with different shaped distillation lines. Hence, pressure-swing distillation makes the separation possible by moving distillation boundaries that lie between the corresponding purity values of desired products at different pressures.

In this paper, a rigorous separation process of TCPSD was explored for the complex ternary system and four different separation sequences were analyzed. The optimum design of TCPSD to obtain more economically competitive process based on the minimization TAC was achieved by a sequential iterative method.

2. Basis of design

2.1. Property method

The quality of physical model parameters guarantees the accuracy of simulated results. The interaction parameters using the "Data Regression" function based on the vapor-liquid equilibrium data [9,48] was regressed to accurately calculate the thermodynamic property of acetonitrile/methanol/benzene system. The Wilson model with the regressed interaction parameters fits well with the vapor-liquid equilibrium of the acetonitrile/methanol/benzene system. The regressed interaction parameters for the Wilson model are shown in Table 1.

2.2. Economics

TAC consists of annual operating cost and capital investment and is used to evaluate different process design. Annual operating cost comprises annual steam and cooling water cost, while annual capital investment mainly includes cost of column vessel, plate, and heat exchangers. The capital investment usually ignores small items such as reflux drums, pumps, valves, and pipes because there are a large gap between major investment and small items costs. The total capital investment was divided by a five-year payback period and the operating time of designs was set at 8000 h/year. The column and sieve plate parameters were calculated via the "tray sizing" function in Aspen Plus. The overall heat transfer coefficients recommended by Luyben [49] are 0.852 kW/(K·m^2) for condensers and 0.568 kW/(K·m^2) for reboilers, respectively. The basis of the economics, the sizing relationships, and parameters are taken from Douglas [50].

3. TCPSD process

The feed flow rate is 1000 kg/h with 70.0 wt% methanol, 20.0 wt % acetonitrile, and 10.0 wt% benzene. The purity of three products was set as 99.9 wt%.

3.1. Process analysis using RCMs

Triangular diagram containing RCMs is used to describe the equilibrium relationships. The RCMs for the acetonitrile/methanol/benzene ternary system at 101.33 and 607.95 kPa are drawn and shown in Figs. 1a and b. That figures portray that all residue

Table 1
The regressed interaction parameters of the Wilson model.

	CH_4O/C_2H_3N	CH_4O/C_6H_6	C_2H_3N/C_6H_6
A_{ij}	0	−9.70	0
A_{ji}	0	5.07	0
B_{ij}	−97.08	2399.15	−233.59
B_{ji}	−262.83	−1965.61	−179.20
C_{ij}	0	0	0
C_{ji}	0	0	0