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Separation of di-n-propyl ether and n-propyl alcohol by extractive distillation and pressure-swing distillation: Computer simulation and economic optimization

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ABSTRACT

Azeotropic mixtures are impossible to separate by ordinary distillation. Two of the most common methods for separating a binary homogeneous azeotrope are pressure-swing distillation (PSD) and extractive distillation (ED). The PSD process is effective if the azeotropic composition changes significantly with pressure. The ED process is effective if a suitable solvent can be found.

This paper compares these two alternatives to separate a mixture made up of 50 mol% of di-n-propyl ether and 50 mol% of n-propyl alcohol by means of a practical case of a plant to treat 12,000 Tm/year of this mixture.

The simulation has been carried out satisfactorily by mean of a package of commercial software (Aspen Hysys®) using the thermodynamic model UNIQUAC with binary parameters obtained experimentally by us in previous papers.

The two processes evaluated have been optimized independently from each other and the best configurations have been evaluated economically. Results show that, for this particular case, the PSD is more attractive than the extractive distillation.

1. Introduction

Distillation is the most widely used separation process in the chemical industries. In a typical chemical plant, distillation columns and their support facilities can account for about one-third of the total capital cost and more than half of the total energy consumption. Consequently, the design and optimization of the distillation train have a critical impact on the economics of the entire process. Moreover, when the problem is separate an azeotropic mixture, rigorous, robust and reliable thermodynamic models are crucial for the synthesis and design of these separation systems.

In this work, it has been studied the separation of binary azeotrope di-n-propyl ether (DPE) + n-propyl alcohol (PA). The aliphatic ethers are obtained normally by dehydration of the corresponding alcohol in the presence of an adequate catalyst. In this case, di-n-propyl ether can be prepared from n-propanol by dehydration with sulphuric acid. Final purification of ether in traditional technologies is a relative complex procedure due to the existence of a homogeneous minimum boiling point azeotrope at atmospheric pressure.

There are many techniques suitable for separation of azeotropic mixtures, such as pressure swing distillation [1], extractive and azeotopic distillation [2], liquid–liquid extraction [3], adsorption [4], pervaporation using membrane [5], salt addition [6], and some new coupling separation techniques and so on. Among the various techniques available for breaking azeotropes, how to select a suitable one, design and desired separation process, and optimize the separation sequences are a complex task. In this work, only pressure-swing distillation and extractive distillation have been considered.

Although these two alternatives are quite similar in process flow-sheet, the pressure-swing distillation is preferred because of the need of adding a solvent in the extractive distillation may rise to serious environmental concerns. Studies on the PSD processes have not received much attention so far, although it has been known since the 1920s.

Laboratory experiments in either pressure-swing distillation or extractive distillation are time-consuming and expensive because of the large number of parameters involved. It would be desirable to predict the experimental data with the help of available simulation programs.

The use of computer simulations for process modelling and design is an established best practice for rapid process

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development and optimization in the chemical and petrochemical industry. Such technology is also contributing to the development and optimization of process technologies and production plants. However, one of the challenges limiting the use of process modelling and design is the lack of proven models and databanks for estimating thermophysical properties. A major problem appears to be obtaining a reliable, consistent set of plant data. Nevertheless, in this case, it has been used consistent thermophysical experimental data determined by us in previous papers [7].

Aspen Hysys® v.2006.5 was selected as a process simulator for both its simulation capabilities and its ability to incorporate calculation using the spreadsheet tool.

In a previous paper, our research group [8] studied also these separation processes (extractive distillation and pressure-swing distillation) applied to the separation of isobutyl alcohol + isobutyl acetate azeotropic mixture.

1.1. Pressure-swing distillation

On the one hand, homogeneous azeotropic compositions that are pressure-sensitive can be separated using pressure-swing distillation (PSD), which utilizes two or more distillation columns operating at different pressures together with appropriate recycle strategies to achieve the desired separation.

Lewis [9] was the first, who proposed distilling the azeotropic mixtures by PSD. This process has been suggested by other authors to separate azeotropic mixture; e.g. Black [10], Abu-Eihah and Luyben [11], Chang and Shih [12]. Phimister and Seider [13] were the first who studied the batch application of binary PSD by simulation. They investigated the separation of a minimum azeotrope (THF-water) by semicontinuous PSD.

The sensitivity of azeotropes to changes in pressure has been known and studied for years. The magnitude of pressure effects depends on the mixture. Sometimes, composition of azeotropes change very little (e.g. the ethanol–water azeotrope). However, there are mixtures where compositions of some azeotropes change rapidly with pressure and even azeotropes that appear and disappear as pressure varies. In our case, the DPE + PA azeotropic composition is pressure-sensitive.

From the viewpoint of green chemical principles, additional solvents should be avoided as much as possible in chemical process. Following these principles, PSD seems to be more attractive and should be preferentially selected, compared to the azeotopic/extractive distillation. However, it is not often exploited commercially, because in many case the relative volatility remains close to 1.0 at the top of the column (for minimum-boiling azeotrope) or at the bottom (for maximum-boiling azeotrope). In such cases, a high reflux ratio and a large number of equilibrium stages are required to achieve complete separation, so the intensity of energy consumption may lead to be a process economically noncompetitive.

To investigate how the PSD works with the DPE + PA azeotropic system, we have done a computer simulation of the vapour–liquid equilibrium using ComThermo® Aspen v.2006.5 at different pressures with the interaction parameters obtained from experimental VLE data obtained by us [7]. Based on these results we have decided to carry out the design and optimization of the pressure-swing distillation process.

1.2. Extractive distillation

On the other hand, extractive distillation (ED) can be used to separate the components of an azeotropic mixture adding a solvent (entrainer) that is capable of strongly modifying the relative volatility of the mixture. The synthesis and design of extractive distillation processes take place in two steps [14]. The first one involves the selection of one or more candidate solvents (which facilitate the separation by changing the relative volatilities in the mixture through physical or chemical interactions with the original components), and the choice of one or more column configurations. The second step, process design, involves the search for optimal process parameter values. The success of the second step depends on the solutions obtained for the first one because efficiency in extractive distillation is largely determined by the choice of a suitable entrainer.

In this work, based on the guidelines for the solvent screening, initially, it had been chosen five solvents: 1-pentanol [15], n-butyl propionate [16], N,N-dimethylformamide [17] and 2-ethoxyethanol [18]. Therefore, in order to be able to select the best solvent among them, we have carried out simulations with Aspen Hysys® v.2006.5 of Aspen Technology Inc., using the binary interaction parameters correlated from experimental data obtained for all binaries involved and determined by our research group.

After all, the aim of this work is to study the influence of the operation variable values a column configuration on the performance of the DPE + PA separation by extractive distillation using an entrainer and by swing-pressure distillation with the help of a commercial simulator (Aspen Hysys® v.2006.5 of Aspen Technology Inc.). Finally, we have chosen the best alternative for the separation of the azeotropic mixture under study from the economic point of view. The results from the study will provide basic design information in applications associated with extractive distillation.

Table 1
UNIQUAC binary interaction parameters.

Component *i*	Component *j*	A_{ij} (J/mol)	A_{ji} (J/mol)
Di-n-propyl ether	n-Propyl alcohol	3426.70–2.187*T*[a]	2209.81–3.487*T*[a]
Di-n-propyl ether	2-Ethoxyethanol	1984.08	−692.81
n-Propyl alcohol	2-Etoxyethanol	123.54	17.48

[a] *T* is the temperature in Kelvin.

2. Simulation

2.1. Problem definition

The two alternatives considered in this study (PSD and ED) were simulated starting from the same initial data. The feed is a mixture made up of 50 mol% of di-n-propyl ether and 50 mol% of n-propyl alcohol, with a flow rate of 12,000 Tm/year; we took 8000 working hours per year, which is a mass flow of 1500 kg/h (≅18.49 kmol/h).

2.2. Property package

Computer simulation using commercial process simulators is a useful tool to predict qualitatively the influence of the operating variables on the column performance, provided that the interaction binary parameters for the studied mixture are available in their own databank. The accuracy of the simulated results is strongly dependent on the quality of the binary parameters from the liquid-phase activity coefficient models.

In this case, UNIQUAC activity model [19] was chosen and we have used the binary interaction parameters published by us in previous papers [15–18]. The parameters used are listed in Table 1.

2.3. Pressure-swing distillation

It is well known that, in some cases, changing the system pressure can affect the vapour–liquid equilibrium (VLE) of a mixture. This effect can be used to separate a binary mixture containing a minimum boiling azeotrope, provided that this mixture significantly changes composition over a moderate pressure range.