Continuous Three Phase Distillation: A Process for Separating Thermally Instable Substances

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Abstract

A new distillation process is presented for the separation of thermally instable substances. It can be used instead of or as an add-on to vacuum distillation. Unlike in vacuum distillation, reduction of the temperature is not achieved by lowering the pressure but by inducing a heteroazeotrope with an entrainer. Two liquid phases and a vapor phase coexist in the entire column. Extensive experimental studies show, that efficient separation is possible. The process can successfully be modeled using an equilibrium stage approach that accounts for the presence of two liquid phases. Convergence of the simulation model is not trivial. The homotopy continuation method was used for solving the model equations.

Introduction

Thermally instable substances play an important role in future markets like biosciences, pharmaceutics and specialty chemistry. Processing of mixtures containing such substances is a challenging problem.

Distillation is the most important thermal separation process. However, its application for separating thermally instable substances is limited. The usual approach to prevent thermal decomposition or side reactions in distillation is to reduce the pressure and, hence, the boiling temperature. As this is sometimes limited by increasing volumetric flow rates and the overall pressure drop, alternative solutions are desirable.

Besides from lowering the pressure, the boiling temperature of a mixture can be reduced by inducing a heteroazeotrope. The boiling temperature of a heteroazeotropic mixture is always lower than that of its constituents. In addition to reducing the temperature, negative effects can be reduced by minimizing the exposition time of thermally instable substances to high temperatures. Because of lower residence times, continuous processes have advantages over batch processes in this respect. A process utilizing these principles is presented in this work: Continuous three phase distillation.

Three phase distillation (cf. Figure 1) uses the same physical principles as carrier steam distillation or standard heteroazeotropic distillation, but differs from them in the way the distillation is carried out: it is a continuous distillation in which two liquid and one vapor phase are present over the entire height of the column. An entrainer E is chosen so that it forms heteroazeotropes with the compounds to be separated, A and B. This ensures the desired low temperature in the entire process. Decanters are used both at the top and at the bottom of the distillation column for recovery and recycling of the entrainer. The separated products are withdrawn as the second phase from the bottom and top decanter, respectively.

Figure 2 shows an example of the ternary mixture resulting from the addition of entrainer E to the original mixture AB. The entrainer has to be chosen so that it forms heteroazeotropes with both components A and B. The miscibility gaps these two binary heteroazeotropes form merge. This kind of topology has been classified as "type two" by Sørensen et al. [1]. Except for rare special cases, no ternary azeotrope is allowed in the
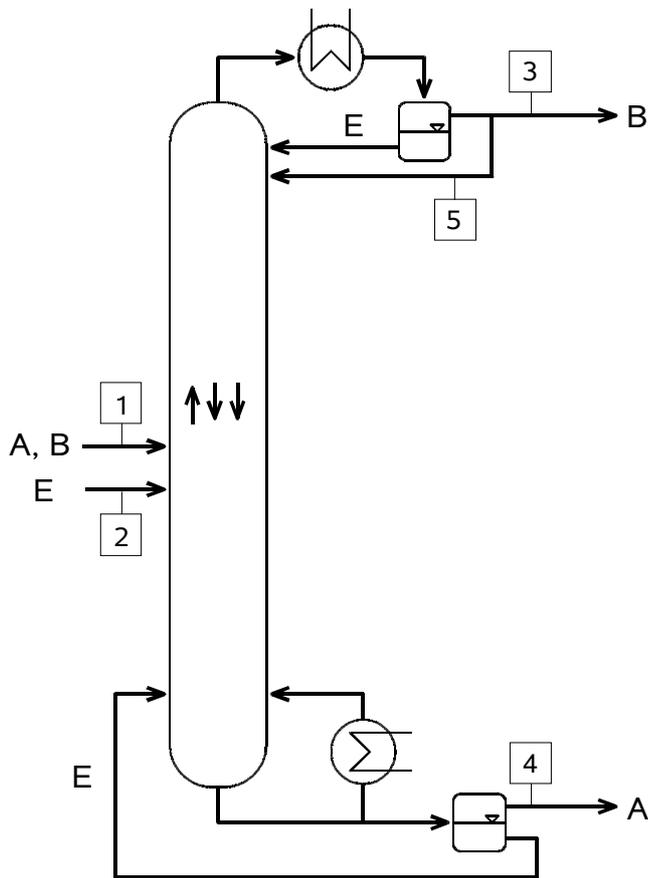
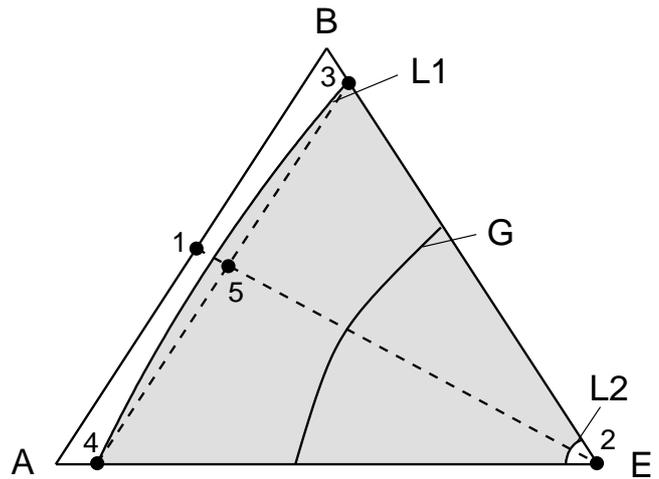**Figure 1:** Process flowsheet of the new process

Figure 2: Schematic VLLE phase diagram for the process.
A, B: original components; E: entrainer; L1, L2: liquid phase; G: gaseous phase; dashed line: mass balances.

resulting system. A wide miscibility gap and large temperature differences between the two binary heteroazeotropes are favorable properties. The solubility of entrainer in A and B determines the amount of entrainer present in the product streams leaving the decanters. The entrainer should thus be chosen to be either tolerable or easily separable from the products.

Although discussed here for a binary mixture only, the process is without restriction applicable to mixtures containing more compounds, provided that the basic features of the mixture remain unchanged.

Like ordinary distillation, the process as shown in Figure 1 has two degrees of freedom for a given feed and pressure. This can be shown formally, e.g. using the method recommended by Henley and Seader [2]. No degree of freedom is lost or gained by introducing the additional liquid phase and the decanters.

The entrainer make-up stream (stream number 2 in Figure 1) which is necessary to account for entrainer losses in the outlet streams is determined by the global mass balance of the entrainer. This mass balance is shown schematically in Figure 2 for the case of complete separation of A from B: both balance lines for the mixing of the inlet streams (1-2) and for the splitting in the two outlet streams (3-4) intersect at the global mixing point (5). The amount of entrainer make-up needed is thus governed by the location of this global mixing point. Unlike other feed streams, this stream is no degree of freedom.

Experimental Work

Continuous three phase distillation was studied in a laboratory scale distillation column (diameter: 50 mm) equipped with 2.9 m of Sulzer CY structured gauze packing. Because of the comparably small hold up and thus shorter exposition time, packing is preferred over trays for the considered process. The mass flow of all streams entering or leaving the column and of the two reflux streams at the top of the column were measured. Temperature, pressure and liquid phase concentration profiles over the whole height of the column (subdivided in 6 sections) and in the peripheral equipment were measured. To obtain reproducible samples for the organic liquid phase and the two-phase liquid mixture, special sampling trays were used to ensure that all liquid passes through the sampling valve. Samples were analysed by gas chromatography.

Two different test systems were investigated: Ethyl acetate – 1-butanol – water (EAc – BuOH – W) and 2-methyl-4-pentanone – 1-butyl acetate – water (MIBK – BuAc – W). In both cases, water is the entrainer, whereas the two organic components are to be separated. The two test systems differ mainly in the boiling point difference between the top and bottom heteroazeotropes and in the width of the miscibility gap. Ethyl acetate – 1-butanol – water is easily separable, the temperature difference between head and bottom is more than 20 K. It has however a relatively narrow miscibility gap, that is, up to 0.2 g g^{-1} water are soluble in 1-butanol at 20 °C. 2-methyl-4-pentanone – 1-butyl acetate – water is more difficult to separate. The temperature difference between the two binary heteroazeotropes is only about 2.5 K. The miscibility gap in this second test system is large, only small amounts of entrainer are carried out with the product streams. These test systems are not thermally instable, but they form good examples that allowed studying the basic features of the investigated process.

In the distillation experiments, the influence of all important process parameters like reflux ratio, feed composition, heat duty and entrainer hold up was studied for both test systems. The experimental results are discussed below together with the results of modeling and simulation.

Process Simulation

The required complexity of a model to reliably describe a process is always a concern, especially when dealing with two liquid phases on packing in a distillation process (see for example [3], [4]). The process was simulated using an equilibrium stage model to test its fitness for use with this problem.

It was found, that even this simple model can only be solved with considerable numerical effort. This is due to the combination of vapor-liquid-liquid equilibrium stages with variable phase count (two or three, depending on whether a second liquid phase is present in a stage or not) and, compared to ordinary distillation, two additional recycle streams. Note that, depending on the curvature of the binodal line and on the temperature dependence of the miscibility gap, not all equilibrium stages necessarily show a liquid-liquid phase split. While all stages in the distillation column of course do, some parts of the plant like preheaters and feed mixers (not shown in Figure 1) are located inside or outside the miscibility gap, depending on which of the aforementioned experiments is analyzed. Several process simulators were tested, that is, several numerical solver methods. It turned out that a sequential solver has big problems with convergence. Setting up the MESH-equations and solving them equation oriented with Newton- and Levenberg-Marquardt-type solvers requires very accurate initial guesses. Furthermore the number of phases in each stage usually has to be preassigned for the problem to be solved with these locally

convergent solver methods. Thus, the globally convergent homotopy continuation method (see e. g. [5], [6]) was implemented in the gPROMS process simulator. Details on the implementation will be published elsewhere [7]. This proved to be a very reliable method, all results presented below were produced this way. Furthermore, the process simulator OPEN CHEMASIM [8], which has lately become available to the academic community, was briefly tested for the simulation of the new process. Using the standard initialization and solver implemented in OPEN CHEMASIM, correct solutions were obtained. OPEN CHEMASIM uses an equation oriented Newton-Raphson-algorithm and special algorithms to produce initial values for the calculation.

Several activity coefficient models (among them NRTL, UNIQUAC, UNIFAC) were evaluated for the test systems used in the experiments. The UNIQUAC model was used for 2-methyl-4-pentanone – 1-butyl acetate – water. For the subsystems 2-methyl-4-pentanone – water and 1-butyl acetate – water, UNIQUAC parameters were derived from published data [9], parameters for the subsystem 2-methyl-4-pentanone – 1-butyl acetate were fitted to our own experimental data, to be published in [7]. It was found that the available experimental literature data on vapor-liquid and liquid-liquid phase equilibria in the system ethyl acetate – 1-butanol – water are accurately described by UNIFAC, eliminating the need for UNIQUAC parameters.

Results

Two from 27 available experiments and their associated simulation results are shown in Figures 3 and 4. Both show a conventional ternary concentration diagram and a temperature profile as well as an entrainer free concentration profile over the height of the column. Graphic elimination of the entrainer corresponds to a projection of all concentration
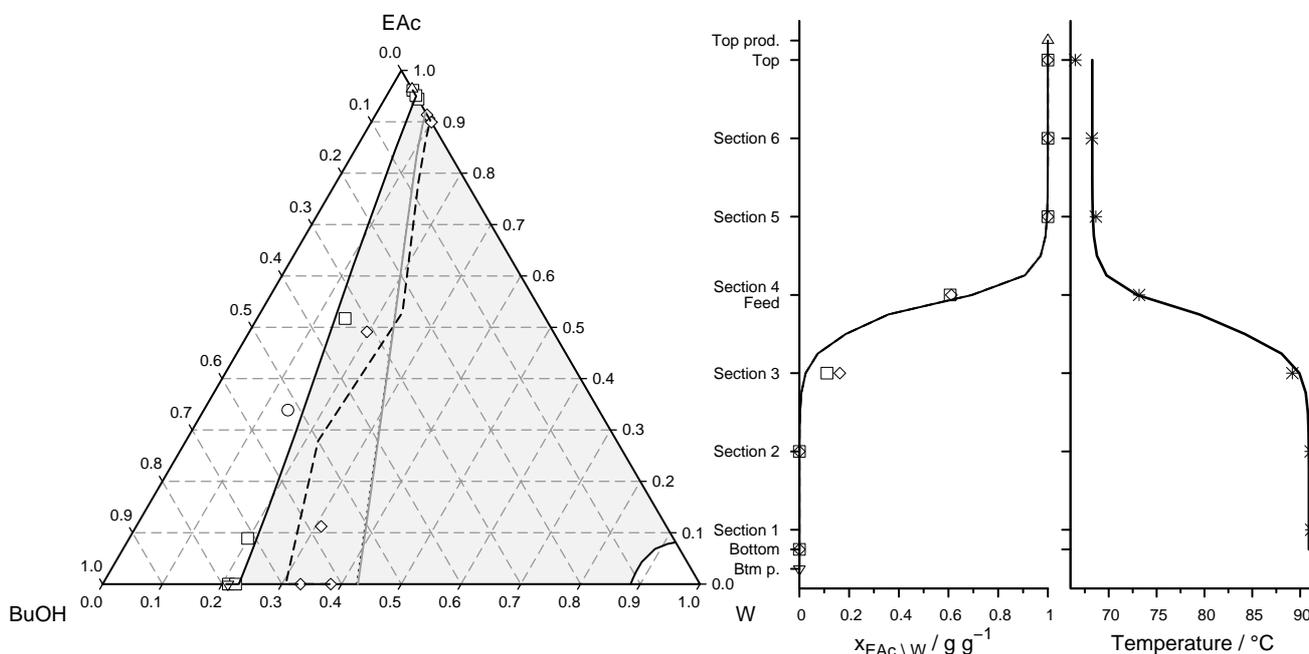

Figure 3: Typical result for ethyl acetate – 1-butanol – water (EAc – BuOH – W).
Left: ternary concentration diagram, middle: entrainer free concentration profile, right: temperature profile.
Measurements: square: organic liquid phase; diamond: mixture of both liquid phases; circle: feed. Simulation: black line: liquid phases; dashed line: mixture of both liquid phases; gray line: vapor phase; shaded area: miscibility gap. All concentrations are given in g g^{-1}.

points in the ternary diagram to the upper left base of the triangle. This rendition is suitable for judging the separation progress over the height of the column, that is, the purification of light- and heavyboiler. It is complementary to the temperature profile.

Figure 3 shows an example for the system ethyl acetate – 1-butanol – water with feed positioned in the middle of the column, as indicated in the diagrams. Ethyl acetate (top product) and 1-butanol (bottom) are completely separated, except for trace amounts. This is due to the high separation capacity of the laboratory column (approx. 26 theoretical stages) and high reflux ratio (R = 2.6 ≈ 4Rmin), the reflux ratio being defined as ratio of reflux stream of the organic phase (stream 5) to top product stream (stream 3). See Figure 1. The number for HETP was taken from the Sulzer data sheet assuming an overall column efficiency of 75%.

The concentration profiles of the organic and aqueous liquid phase in the column follow the binodal curves of the underlying mixture. The gas phase concentration follows the vapor line, which connects the two binary heteroazeotropes. This is similar to conventional heteroazeotropic distillation (see e. g. [10]). The concentration of the mixture of both liquid phases follows this line as well, shifted however by the addition of the feed and reflux streams. Because of the withdrawal of organic product at the top of the column, the reflux is rich in entrainer causing a shift of the average liquid concentration and the liquid phase ratios in the rectifying section to the entrainer side. Below the feed, the average liquid concentration is moved to the other side of the vapor line, as the feed is comparatively poor in entrainer. The temperature in the entire column is below 100 °C, which is the boiling temperature of the entrainer used. The temperature decrease in the bottom of the column is approx. 26 K.
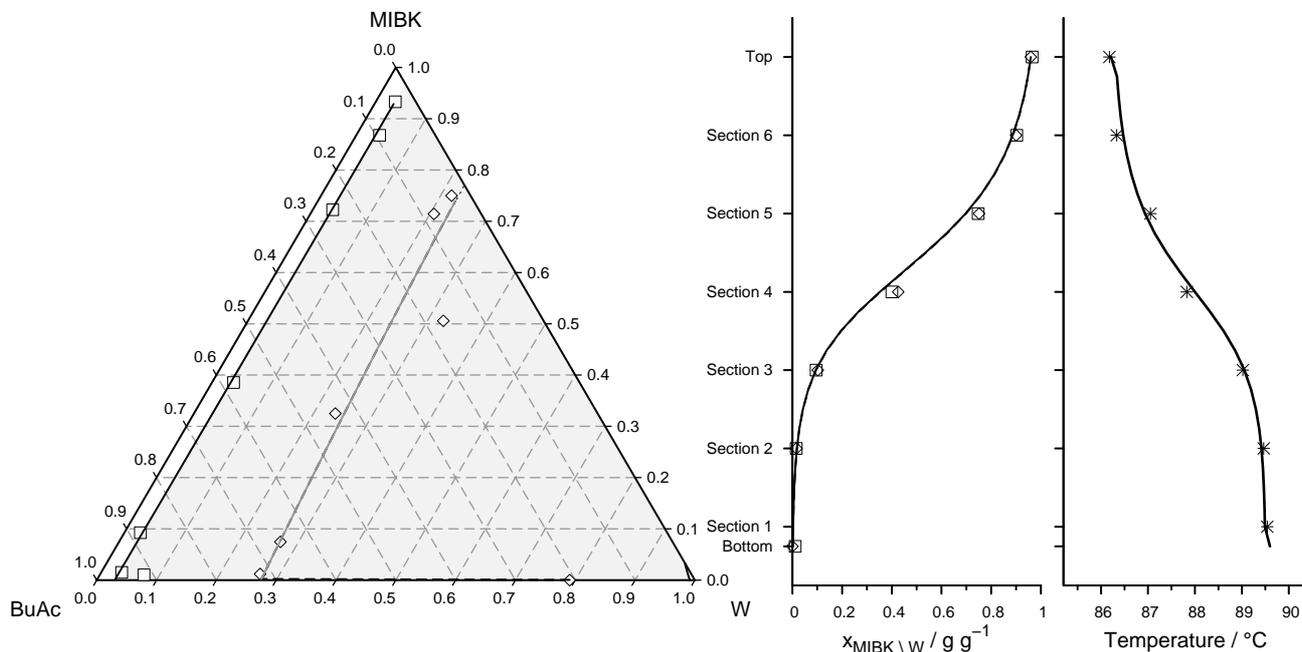

Figure 4: Example for 2-methyl-4-pentanone – 1-butyl acetate – water (MIBK – BuAc – W) at infinite reflux.
Left: ternary concentration diagram, middle: entrainer free concentration profile, right: temperature profile.
Measurements: square: organic liquid phase; diamond: mixture of both liquid phases; circle: feed. Simulation: black line: liquid phases; dashed line: mixture of both liquid phases; gray line: vapor phase; shaded area: miscibility gap. All concentrations are given in g g^{-1}.

The second test system, 2-methyl-4-pentanone – 1-butyl acetate – water, is difficult to separate. So despite high separation capacity (same as above) and reflux ratio, only incomplete separation of MIBK and BuAc has been achieved in the experiments. Figure 4 shows an example at infinite reflux. However, basic features at finite and infinite reflux are the same as in the first example. This includes a similar behavior of the overall liquid phase concentration profile related to the vapor line. The temperature decrease achieved in this example is approx. 35 K.

All experiments are well described by the equilibrium stage model over the entire height of the column, as can be seen from the comparison of the data presented in Figure 3 and Figure 4. The average absolute deviation between simulation and experiment is between 1.5 and 3.8 weight% for experiments with infinite and finite reflux. Temperatures are predicted as accurate as 0.2 K. The agreement can be even improved by about 1 weight% if the measurement data are consolidated using a maximum-likelihood estimation taking into account the measurement uncertainties. The differences between experiment and simulation can be fully explained by the experimental uncertainties and the limited accuracy of the thermo-physical property model.

Conclusion

A new distillation process for continuous separation of thermally instable substances is presented. An efficient lowering of the temperature in the entire column is achieved by using an entrainer that forms heteroazeotropes with the compounds to be separated. The experimental and theoretical studies presented show that the new process is feasible and is a promising alternative or addition to state of the art processes like vacuum distillation. The experimental data for two test systems and the simulation results agree very well and show that three phase distillation can safely be evaluated using readily available data and simulation methods.

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