© 2006 IChemE

CONTINUOUS THREE PHASE DISTILLATION: A PROCESS FOR SEPARATING THERMALLY INSTABLE SUBSTANCES

Markus Ottenbacher, Hans Hasse
Institute of Thermodynamics and Thermal Process Engineering, University of Stuttgart
D-70550 Stuttgart, Germany, E-mail: hasse@itt.uni-stuttgart.de

In this work, the use of heteroazeotropic distillation for separation of thermally instable substances is discussed. A new process has been developed and analysed, which makes use of the fact that the boiling temperature of a heteroazeotrope is always lower that that of its constituents. Three phase distillation is characterised by the fact that two liquid phases and a vapour phase coexist in the entire column which ensures low temperatures in the entire apparatus. Experiments were carried out in a continuous laboratory scale distillation column equipped with structured gauze wired packing. The experiments prove the feasibility and operability of the new process and provide a sound data base for the development and the validation of process models. It is shown that the process can be successfully 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.

KEYWORDS: three phase distillation, heteroazeotropic distillation, thermally instable substances

INTRODUCTION

While distillation is the most important thermal separation process, its application for separating thermally instable substances is limited. The usual approach for preventing thermal decomposition or side reactions in distillation is to reduce the pressure and, hence, the boiling temperature. As this is limited by increasing volumetric flow rates and the overall pressure drop, alternative solutions are desirable. In addition to reducing the temperature, attempts are made to reduce negative effects by minimising exposition time to high temperatures. Because of lower residence times, continuous processes have advantages over batch processes in this respect.

It is well known that the boiling temperature of a heteroazeotropic mixture is always lower than that of its constituents. That effect has been used for a long time in carrier steam or heteroazeotropic batch distillation in pharmaceutical and specialty chemistry, often in batch processes.

Three phase distillation uses the same physical principle as these processes, but differs from them in the way the distillation is carried out: it is a continuous distillation in which two liquid and one vapour phase are present over the entire height of the column. The process is depicted in Figure 1. An entrainer W is chosen so that it forms heteroazeotropes with both components of the mixture to be separated, C1 and C2. This ensures the desired low temperature in the entire process, which is always lower than
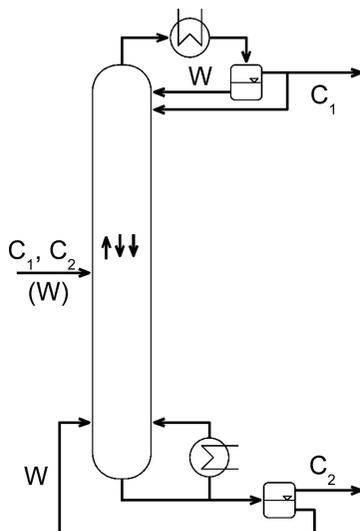
Figure 1. Continuous three-phase distillation for separating two compounds C1 and C2 by addition of an entrainer W

the boiling temperature of the lowest boiling pure component C1, C2, or W. Decanters are used both at the top and 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.

For a specified pressure and feed, the number of degrees of freedom of the process shown in Figure 1 is two, like in an ordinary distillation. This can be shown formally, e.g. using the method recommended by Henley and Seader [1], which is in good agreement with other methods tested. No degree of freedom is lost by introducing the additional liquid phase and the decanters. The entrainer make-up stream (supplied together with the feed in the flow sheet shown 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. Unlike other feed streams, is no degree of freedom.

ENTRAINER SELECTION

To explain the entrainer selection, it is assumed that the task is to separate a binary mixture of the components C1 and C2. Combining the mixture $C1 + C2$ with the entrainer W has to produce a ternary system with a phase behaviour that has been classified as "type two" by Sørensen et al [2], cf. Figure 2: The entrainer W forms binary heteroazeotropes with both compounds C1 and C2, the miscibility gaps these heteroazeotropes produce merge. No ternary azeotrope is allowed in the resulting system. To give an example: C1 and
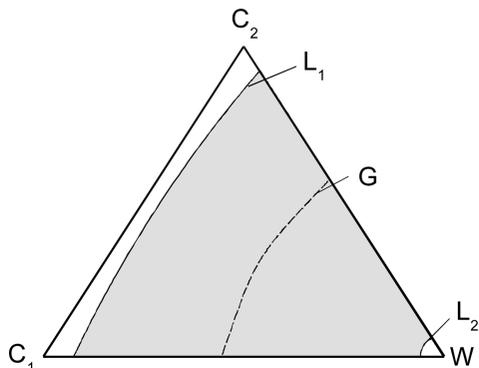
Figure 2. Schematic VLLE phase diagram for the process. C1, C2: organic components; W: entrainer; L1, L2: liquid phase; G: gaseous phase. p = const

C2 could be two unpolar high boiling thermally instable organic compounds, the entrainer W water. Generally, a wide miscibility gap and large temperature differences between the two binary heteroazeotropes are favourable properties for the suggested process.

The solubility of entrainer in the compounds C1 and C2 is especially important, as it determines the amount of entrainer present in the product streams leaving the decanters. The entrainer should thus be selected to be either tolerable or easily separable from the products.

EXPERIMENTAL SECTION
Continuous three phase distillation was studied in a laboratory scale distillation column (diameter: 50 mm). The glass column was equipped with 2.9 m of Sulzer CY structured wire gauze packing arranged in 6 sections. The sections have vacuum jackets, furthermore, each section and the connections were heated separately to minimize heat losses. The mass flow of all streams entering or leaving the column (cf. Figure 1) and the two reflux streams at the top of the column were measured, as well as temperature and pressure over the whole height of the column and in the peripheral equipment. Because of the comparably small hold up and thus shorter exposition time, packing is preferred over trays for the considered process. To obtain reproducible samples from the two-phase liquid mixture, special trays were used to ensure that *all* liquid passes through the sampling valve. Samples were analysed by gas chromatography. Based on the results of the analysis of the degrees of freedom, the D-G configuration [3] was chosen as basic concept for process control, i.e. the distillate flow rate and the reboiler heat duty were fixed to satisfy the two degrees of freedom of the column.

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. While they are by no means thermally instable and could easily be separated by conventional distillation, they are good test systems that allowed studying the basic features of continuous three phase distillation experimentally for the first time. They were chosen mainly because they show the desired phase behaviour, are fairly easy to handle and the chemicals are inexpensive and easily available in large amounts. The two test systems differ mainly in the boiling point difference between the two hetero-azeotropes and the width of the miscibility gap.

In the distillation experiments, the influence of all important process parameters like feed composition, heat duty and entrainer hold up in the column was studied for both test systems. Reflux was varied from minimal values to infinity. The full set of experimental results will be published elsewhere [4]. Two examples are presented and discussed in the section "Results" below.

While operation with two liquid phases turned out to be uncritical on the whole, some precautions are necessary to ensure proper operation of the reboiler. The reboiler of the laboratory column was a electrically heated vertical thermosyphon reboiler. While for the mixture ethyl acetate – 1-butanol – water the two liquid phases were dispersed well in the reboiler, for the mixture 2-methyl-4-pentanone – 1-butyl acetate – water two only poorly mixed layers formed. This lead to problems with product withdrawal at varying liquid levels in the reboiler. More critical, irregular periodic operation was observed in rare cases. We assume that nonuniform evaporation originating from unequal heat transfer to the two liquid phases was the cause for this behaviour. Cairns and Furzer [5] report similar observations, Repke and Wozny [6] report pressure shocks caused by erratic evaporation of the two liquid phases.

PROCESS SIMULATION

The process was simulated using an equilibrium stage model. Various attempts using commercial-grade process simulators, including Aspen Plus, as well as directly setting up the MESH-equations and solving them with Newton- and Levenberg-Marquardt-type solvers showed the need for a more robust calculation method. Apparently the combination of vapour-liquid-liquid equilibria with variable phase count (two or three, depending on whether a second liquid phase is present in the stage or not) and three recycle streams results in a system of equations that requires very accurate initial guesses to be solved with these locally convergent solver methods. This result is in accordance with the findings of Kovach and Seider [7] and others.

In contrast to the methods mentioned above, homotopy continuation is a globally convergent method. With homotopy continuation, the solution starts at a set of equations $g(x)$, which is easy to solve or the solution of which is known, and is gradually transformed to the original set of equations $f(x)$, which is difficult to solve.

An easy way to achieve this for arbitrary sets of equations is linear superimposition, cf. equation (1), where t is the so called homotopy parameter.

$$H(x, t) = tf(x) + (1 - t)g(x) \quad t \, \varepsilon \, [0 : 1] \tag{1}$$

The solution where $H(x, t) = 0$ holds is called the homotopy path. For more details, see e.g. [8] or [9]. While numerous generic suggestions are made in literature concerning the choice of $g(x)$, it was decided to define a new type of homotopy that makes use of the known structure of the underlying problem, which is in our case the equilibrium stage model. Only the feed stream to the equilibrium stage is subject to the homotopy. Thus only the mass and energy balance need to be transformed according to equation (1), as the feed stream only appears in those equations. The initialization of the algorithm was carried out using the same arbitrary starting point inside the miscibility gap for all equilibrium stages in the model. In the course of solving the problem, the "real" feed to the stages is gradually introduced, until at $t = 1$ the solution for $f(x) = 0$ is found. This approach was found to be even more robust than the widespread Newton homotopy [8,9,10,11].

The actual number of phases in an equilibrium stage in the process analysed here may vary in the course of following the homotopy path to the solution of the system of equations. To detect an equilibrium stage leaving the miscibility gap, a "negative flash"-criterion is used: As soon as one of the liquid streams leaving the equilibrium stage has to be negative to satisfy the MESH equations, this stream is set to zero and the system of equations is switched to the VLE case with only one liquid phase for this stage. Both the (now hypothetical) VLLE and the VLE are henceforth calculated simultaneously. The same criterion is then used to detect a transition of the miscibility boundary in the opposite direction. This method has worked very reliable and stable while requiring much less calculation effort than a fully-fledged phase stability test would, e.g. by tangent plane criterion. Eckert and Kubicek [12] have used a comparable approach, with different criteria however. The three phase distillation equilibrium stage model and the algorithm for its solution with the homotopy continuation method were implemented in the gPROMS process simulator.

It was found, that the vapour-liquid-liquid phase equilibria in the system ethyl acetate – 1-butanol – water are best described by UNIFAC and the Redlich-Kwong-Soave equation of state. Using only a single parameter set for both VLE and LLE calculations, the UNIQUAC model produced the best results for the second test system, 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 [13], parameters for the subsystem 2-methyl-4-pentanone – 1-butyl acetate were fitted to our own experimental data. The binary interaction parameters are tabulated in appendix A. The vapour phase of the second test system has been described using the Redlich-Kwong-Soave equation of state as well.

RESULTS

Figures 3 and 4 show the results of a typical experiment for the system ethyl acetate – 1-butanol – water that was carried out at ambient pressure and the corresponding simulation run. The temperature difference between the heteroazeotrope in the system ethyl acetate – water and that in the system 1-butanol – water is more than 20 K so that
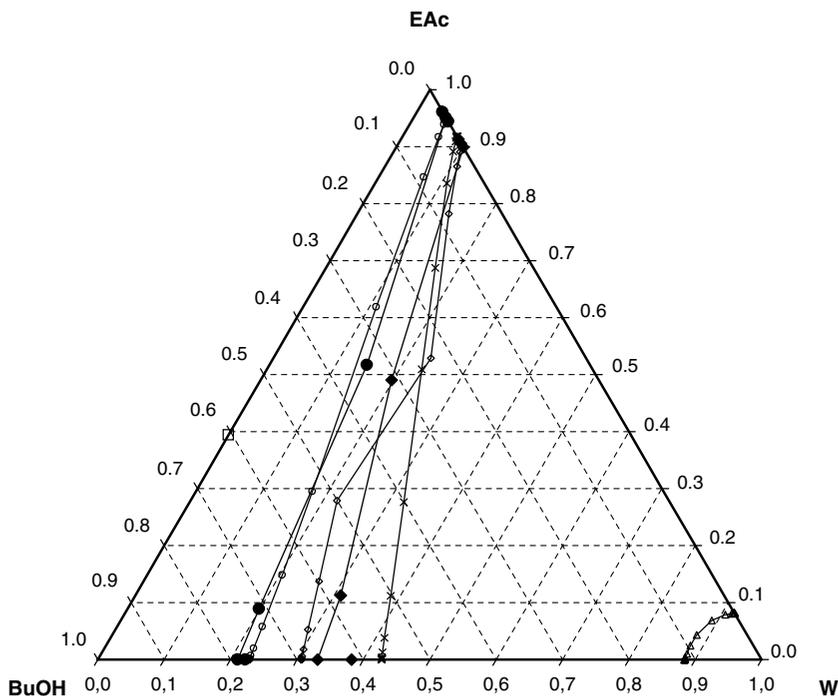
Figure 3. Typical result for the system EAc – BuOH – W. Circles: organic liquid phase; diamonds: mixture of both liquid phases; cross: gaseous phase; triangle: aqueous liquid phase; square: organic feed. Filled symbols: measurements; empty symbols + lines; simulation. All concentrations are given in g g^{-1}

ethyl acetate and 1-butanol are readily separated. The mutual solubilities in the liquid phase are fairly large (up to 0.2 g/g for the solubility of water in 1-butanol at 20 °C) so that comparatively large amounts of the entrainer water are carried out together with the product streams. Ethyl acetate (top product) and 1-butanol (bottom) are completely separated, except for trace amounts. This is due to the high installed separation capacity (approx. 24 theoretical stages) and reflux ratio (R = 2.6 ≈ 4R$_{min}$). The number for HETP was taken from the SULZER data sheet assuming an overall column efficiency of 70%. Feed position and composition are indicated in Figures 3 and 4 respectively. Figure 3 shows that the concentration profile in the organic and aqueous liquid phase in the column follows the binodal curves of the system (aqueous phase not shown). The gas phase concentration follows the vapour line, which connects the two binary heteroazeotropes. This is similar to conventional heteroazeotropic distillation (see e.g. [14]).

845
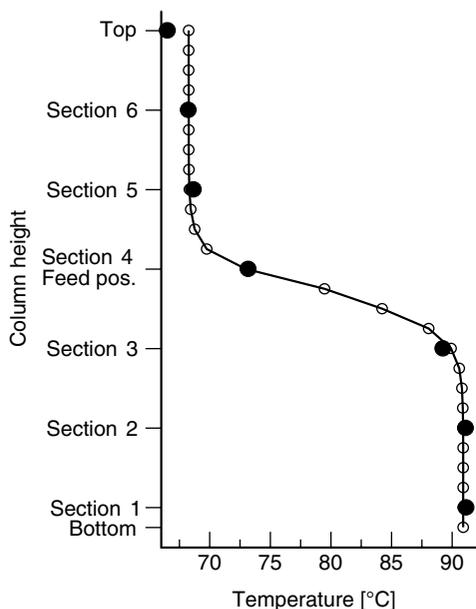
Figure 4. Temperature profile for EAc – BuOH – W. Filled symbols: measurement; empty symbols + lines: simulation. Each section corresponds to 0.48 m of Sulzer CY packing

It has to be noted, that the average concentration of the liquid phases follows this line as well, shifted however by the addition of feed and reflux streams. Because of the withdrawal of overhead product at the top of the column, the reflux is rich in entrainer causing a corresponding shift of the average liquid concentration and the liquid phase ratio in the rectifying section to the entrainer side. Below the feed, the average liquid concentration is shifted markedly to the other side of the vapour line, as the feed is comparatively poor in entrainer. The experiment is well described by the model over the entire height of the column, as can be seen from the comparison of the concentration data presented in Figure 3 and the temperature profile in Figure 4. Note that the temperature is below 100 °C everywhere in the column. The remaining differences between experiment and simulation can be fully explained by the experimental uncertainties and the limited accuracy of the thermo-physical property model.

Figures 5 and 6 show results of a typical experiment for the second test system, 2-methyl-4-pentanone – 1-butyl acetate – water (MIBK – BuAc – W). In contrast to the first test system, the temperature difference between the heteroazeotropes in the binary water-containing subsystems is only about 2.5 K and the mutual solubilities are low. Despite high separation capacity (same as above) and reflux ratio, only incomplete
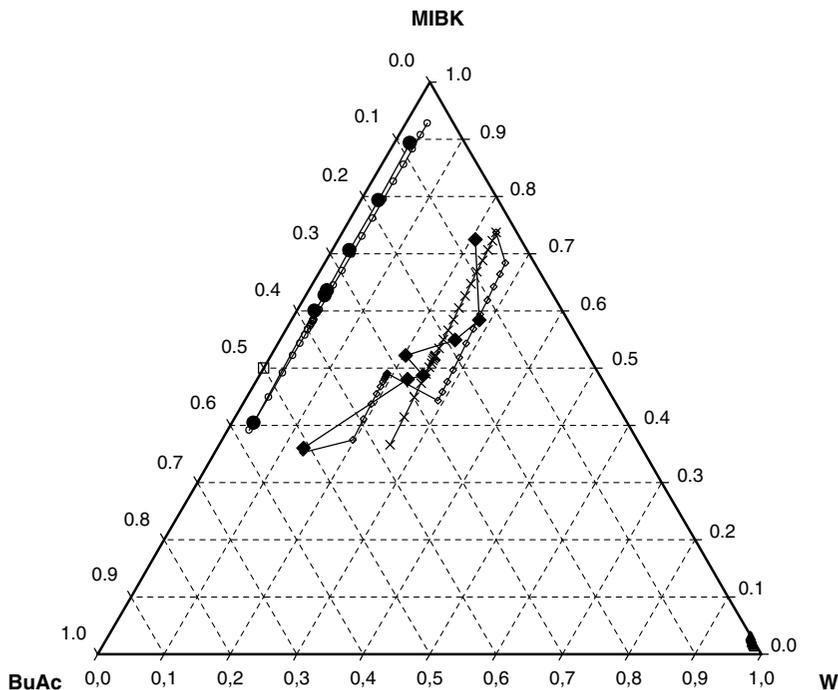
Figure 5. Typical result for the sytem MIBK – BuAc – W. Circles: organic liquid phase; diamonds: mixture of both liquid phases; cross: gaseous phase; triangle: aqueous liquid phase; square: organic feed. Filled symbols: measurements; empty symbols + lines; simulation. All concentrations are given in g g^{-1}

separation of MIBK and BuAc is achieved. However, basic features of the three phase distillation are the same as in the first example. This includes a similar behavior of the overall liquid phase concentration profile related to the vapour line. Again, the experimental results are well described by the equilibrium stage model.

FLUID DYNAMICS
Qualitative investigations into the behaviour of the two liquid phases formed by the test systems have been carried out. For that purpose the Sulzer CY gauze packing was installed in a thermostated double jacket glass tube and the liquid two phase feed was supplied by two metering pumps at flow rates similar to those in the column. Both test systems were examined at temperatures similar to those in the distillation
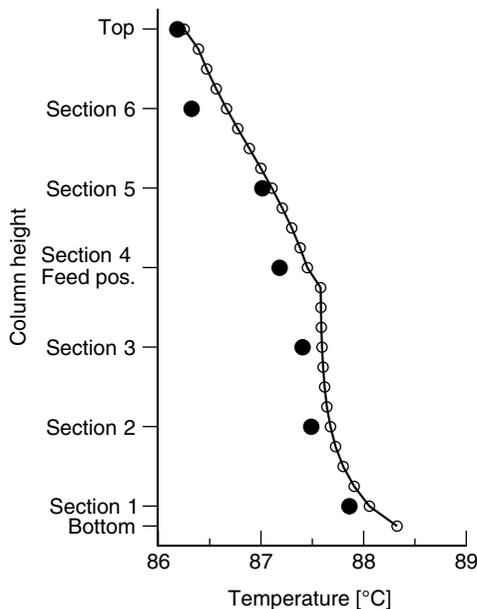
Figure 6. Temperature profile for MIBK – BuAc – W. Filled symbols: measurement; empty symbols + lines: simulation. Each section corresponds to 0.48 m of Sulzer CY packing

experiments. The observation of the flow pattern was made visually after adding small amounts of suitable colouring agents to the two liquid phases. It was found, that the flow patterns of the two test systems on the gauze packing differ considerably. While for the system ethyl acetate – 1-butanol – water both liquid phases behave similarly, the liquid phases of the system 2-methyl-4-pentanone – 1-butyl acetate – water show a behaviour that is similar to that of pure water together with a typical unpolar organic liquid. However, in both cases and for all studied liquid phase flow ratios, it was always found that the two phases did either flow more or less independently or that the aqueous phase was covered by the organic phase.

These observations agree with those of Siegert [15]. In that situation, no decrease of separation efficiency due to the introduction of the second liquid phase is expected. Because the aqueous liquid phase contains only small amounts of the substances to be separated, gas-liquid mass transfer limitations for that phase that might be caused by reduced transfer areas should be of little account. Siegert concludes from his experiments, that the transfer area of the (in this case) organic phase remains either unchanged or even increases because of the formation of ripples.

This explains why the simulations could be carried out successfully with HETP numbers taken from the Sulzer data sheet.

CONCLUSION

A new process for continuous separation of thermally instable substances by distillation has been presented. It has been shown that an efficient lowering of the temperature in the entire column can be achieved by using an entrainer that forms heteroazeotropes with the compounds to be separated. The experimental studies and modelling and simulation work presented here show that the new process is feasible and represents a promising alternative or addition to state of the art processes like vacuum distillation. The experimental data obtained in the present work 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.

REFERENCES

1. Henley, Ernest J. and Seader, J. D.: Equilibrium-Stage Separation Operations in Chemical Engineering, John Wiley & Sons, New York, 1981.
2. Sørensen, Jens M. and Magnussen, Thomas and Rasmussen, Peter and Fredenslund, Aage: Liquid-liquid equilibrium data: their retrieval, correlation and prediction, *Fluid Phase Equilibria* **2** (1979) 297–309.
3. Stichlmair, Johann and Fair, James R.: Distillation: principles and practice, Wiley-VCH, New York, Weinheim, 1998.
4. Ottenbacher, Markus: PhD Dissertation, University of Stuttgart, 2006.
5. Cairns, Brett P. and Furzer, Ian A.: Multicomponent Three-Phase Azeotropic Distillation. 1. Extensive Experimental Data and Simulation Results, *Industrial & Engineering Chemistry Research* **29** (1990) 1349–1363.
6. Repke, Jens-Uwe and Wozny, Günter: A Short Story of Modeling and Operation of Three-Phase Distillation in Packed Columns, *Industrial & Engineering Chemistry Research* **43** (2004) 7850–7860.
7. Kovach III, J. W. and Seider, W. D.: Heterogeneous Azeotropic Distillation: Experimental and Simulation Results, *AIChE Journal* **33** (1987) 1300–1314.
8. Allgower, Eugene L. and Georg, Kurt: Numerical continuation methods. An introduction, Springer, Berlin, Heidelberg, 1990.
9. Wayburn, T. L. and Seader, J. D.: Homotopy continuation methods for computer-aided process design., *Computers & Chemical Engineering* **11** (1987) 7–25.
10. Vickery, D. J. and Taylor, Ross: Path-Following Approaches to the Solution of Multicomponent, Multistage Separation Process Problems, *AIChE Journal* **32** (1986) 547–556.
11. Kovach III, J. W. and Seider, W. D.: Heterogeneous azeotropic distillation - Homotopy-continuation methods, *Computers & Chemical Engineering* **11** (1987) 593–605.

© 2006 IChemE

12. Eckert, E. and Kubicek, M.: Multiple liquid-vapor-equilibrium flash calculation by a global approach., *Computers & Chemical Engineering* **17** (1993) 879–884.
13. DDB - Dortmund Data Bank, Version 2003, DDBST GmbH, Oldenburg,
14. Pham, Hoanh N. and Doherty, Michael F.: Design and synthesis of heterogeneous azeotropic distillations - I. Heterogeneous phase diagrams, *Chemical Engineering Science* **45** (1990) 1823–1836.
15. Siegert, M.: Dreiphasenrektifikation in Packungskolonnen, VDI-Verlag, Düsseldorf, 1999.

APPENDIX A

Table 1. UNIQUAC binary interaction parameters for 2-methyl-4-pentanone (1) – 1-butyl acetate (2) – water (3)

A12 = 506.49	A21 = −395.49	A31 = 472.165
A13 = 4164.193	A23 = 2979.09	A32 = 1790.6