

DESIGN OF AN EXPERIMENTAL PROCEDURE TO INVESTIGATE EFFICIENCY IN THE DISTILLATION OF AQUEOUS SYSTEMS

M. Caraucán, A. Pfennig

Department of Chemical Engineering, Thermal Unit Operations, RWTH Aachen
Lehrstuhl für Thermische Verfahrenstechnik, RWTH Aachen, Wüllnerstraße 5,
52062 Aachen, Germany
Phone: +49/241/80-9 54 90, Fax: +49/241/80-9 23 32
www: <http://www.tvt.rwth-aachen.de>

ABSTRACT

The efficiency of column internals for the distillation of aqueous systems is the result of the very complex interdependence of variations in the physicochemical properties due to concentration profiles and other factors like the internals geometry and the operating conditions. In this work we set out to derive a procedure which is able to account for these effects. In a first step the parameters which potentially have the strongest influence are identified. Then experiments are being planned with a carefully selection of test mixtures and experiments in order to discriminate the different effects in the complex interplay of parameters. In this paper, some first experimental results are presented. In a following publication, when the experimental phase of this investigation have been completely carried out, we will be able to present all the results as well as a model to determine efficiency of distillation in aqueous systems based on the experimental procedure here described.

Keywords: distillation; efficiency; aqueous systems; physicochemical properties; modelling.

INTRODUCTION

The principal methods for distillation-column design and for operating-column evaluation are based on engineering experience. It is a common practice in industry to use empirical correlations, obtained from industrial columns, to predict the efficiency. For example, the correlation graphics elaborated by O'Connell [1] were extensively used in industry for this task over a long period of time [2]. The study of O'Connell is especially based on hydrocarbon compounds, characterized by nearly ideal behaviour, for which this simplified model can be used with good accuracy. However, only limited information about aqueous systems, characterized by highly non-ideal behaviour, is there considered.

Most of the aqueous mixtures of commercial interest contain organic compounds ranging from small to moderate concentrations, which have to be separated by distillation. The presence of water in the mixture can change the physicochemical properties of the system extremely. Thus, the behaviour of the distillation column will depend on the local water concentration at a specific point. Additionally, it has been experimentally demonstrated that some physicochemical properties of water (e.g. relative volatility, surface tension, thermal conductivity, vapour pressure, viscosity, etc.) can change enormously in the presence of small amounts of organic compounds [3-8].

In the 90's, several authors (e.g. [9], [10]) presented design schemes, where limitations of thermodynamic models in predicting the liquid-vapour phase equilibrium (VLE) of some aqueous systems (e.g. system water + ethylene oxide [9]) at high purities of both components were taken into account. Experiments in laboratories and pilot plants should be conducted in order to obtain more detailed information on the systems and their behaviour in high-purity regimes.

In the last years, industry has made significant efforts to design columns for industrial applications using measurements performed on miniplant scale (30 to 80 mm column-diameter) and with more reliable thermodynamic data. These efforts have been especially focused on organic systems, but in reference to aqueous and viscous systems, much research work remains still to be done [11].

INFLUENCE OF PHYSICOCHEMICAL PROPERTIES OF AQUEOUS SYSTEMS ON DISTILLATION EFFICIENCY

To investigate the strong concentration dependence of distillation efficiency in aqueous systems, numerous authors have studied the influence of parameters such as concentration, physicochemical properties (density (ρ), viscosity (η), surface tension (σ), wetting ($\cos\theta$)), operating parameters (reflux ratio (v), liquid (L) and vapour (V) flow-rates), interfacial area, addition of surfactants, Marangoni effect (influences on the rate of mass or heat transfer caused by interfacial turbulence and/or destabilization or stabilization of the liquid film [17]), maldistribution, axial mixing, liquid and vapour phase resistance and behaviour and prediction of VLE (slope (m) and its curvature (dm/dx)) on the distillation efficiency [12-14, 16-35].

Thus, for example to explain the strong reduction of the efficiency of aqueous systems in the water-rich region in packed columns, some authors [33, 35] attribute it solely to changes in the wetting properties of the system with the composition, to maldistribution of the liquid phase and/or to reduction of the contact area for mass and heat transport between gas and liquid phase caused by the destabilisation of the liquid film (Marangoni effect, [17]) on the packing surface and break-up of it into rivulets of liquid due to local surface tension (concentration) gradients in negative systems. There are no doubts that the wetting degree in a packed column is a very important parameter for the efficiency. Nevertheless, this behaviour of the efficiency in aqueous systems is not an exclusive problem observed in packed columns but also in trayed columns [20, 27, 29, 31, 36], where the wetting properties play no role. Other investigations [27, 29, 31] have related the decrease of efficiency directly to the interfacial turbulence caused by the Marangoni effect. However, these authors have

examined only some parameters separately from all remaining ones. Additionally one column type was used during the experiments. This is however problematic due to the complexity and mutual dependency of the influencing parameters [17].

It is also well known, that common thermodynamic models have some limitations in predicting the VLE curve of aqueous mixtures, especially near azeotropic points and close to very high or very low concentrations [9, 13]. Hence, it is still necessary to generate a reliable experimental database in order to study aqueous systems. This would allow to improve efficiency predictions considerably [9, 13, 14].

In most literature, the characterization of aqueous systems does not take into account the effect of differences in the enthalpy of vaporization of organic compounds and water. For organic compounds, the enthalpy of vaporization ranges from 250 up to 1100 kJ/kg (Methanol), while for water it is 2257 kJ/kg at atmospheric pressure [15].

The variation of the enthalpy of vaporization with the concentration of the mixture has a strong influence on the local gas load within the column. Thus, in aqueous systems the internal flows of the column depend not only on the common operating parameters (e.g. reboiler duty, reflux, side-streams, pressure, etc), but also on the water concentration profile along the column. Column sections with a low water concentration will have a larger mass flow of vapour than the sections with a high water concentration.

Finally, when water represents the less volatile compound of the mixture, the local L/V ratio, i.e. the slope of the local operating line, can change along the column sections. The slope (L/V) of the local operating line in the rectifying section increases, which might promote liquid maldistribution in packed columns, whereas in the stripping section it decreases. Such variation in the operating line can cause the appearance of a pinch point, where the new operating line cuts the equilibrium curve and thus the separation in the column reduces significantly [16]. In some case, large variations of the local L/V ratio along of the column can occur, so the use of mixed beds with different packing types due to capacity limits or the design of two sections of the distillation tower with difference diameters might become necessary. However, it makes difficult to design the column internals.

This discussion shows that the behaviour observed for aqueous systems is a result of the very complex interaction of varying physicochemical properties due to concentration profiles and other factors like the internals geometry and the operating conditions of the column. Thus, a concept considering the interplay between different influences on the efficiency must be developed to be able to make a better prediction of the distillation efficiency of aqueous systems than the already existing ones. This integral view of the problem should be then compiled in an engineering model.

In order to develop a reliable engineering model for a better prediction of distillation efficiency for aqueous mixtures, the Department of Chemical Engineering, Thermal Unit Operations of the RWTH Aachen and the industrial partners BASF AG, Bayer AG, Degussa AG and Roche AG are working in a co-operation project.

The procedure developed in this collaboration to derive the desired engineering model is shown as a flow-sheet in Figure 1. The first steps of the concept illustrated in Figure 1 consists in collecting available engineering models that allow to predict the efficiency in distillation of aqueous systems. Based on these models, the principal parameters and variables affecting the efficiency are identified additionally taking information obtained from literature and industrial experience into account.

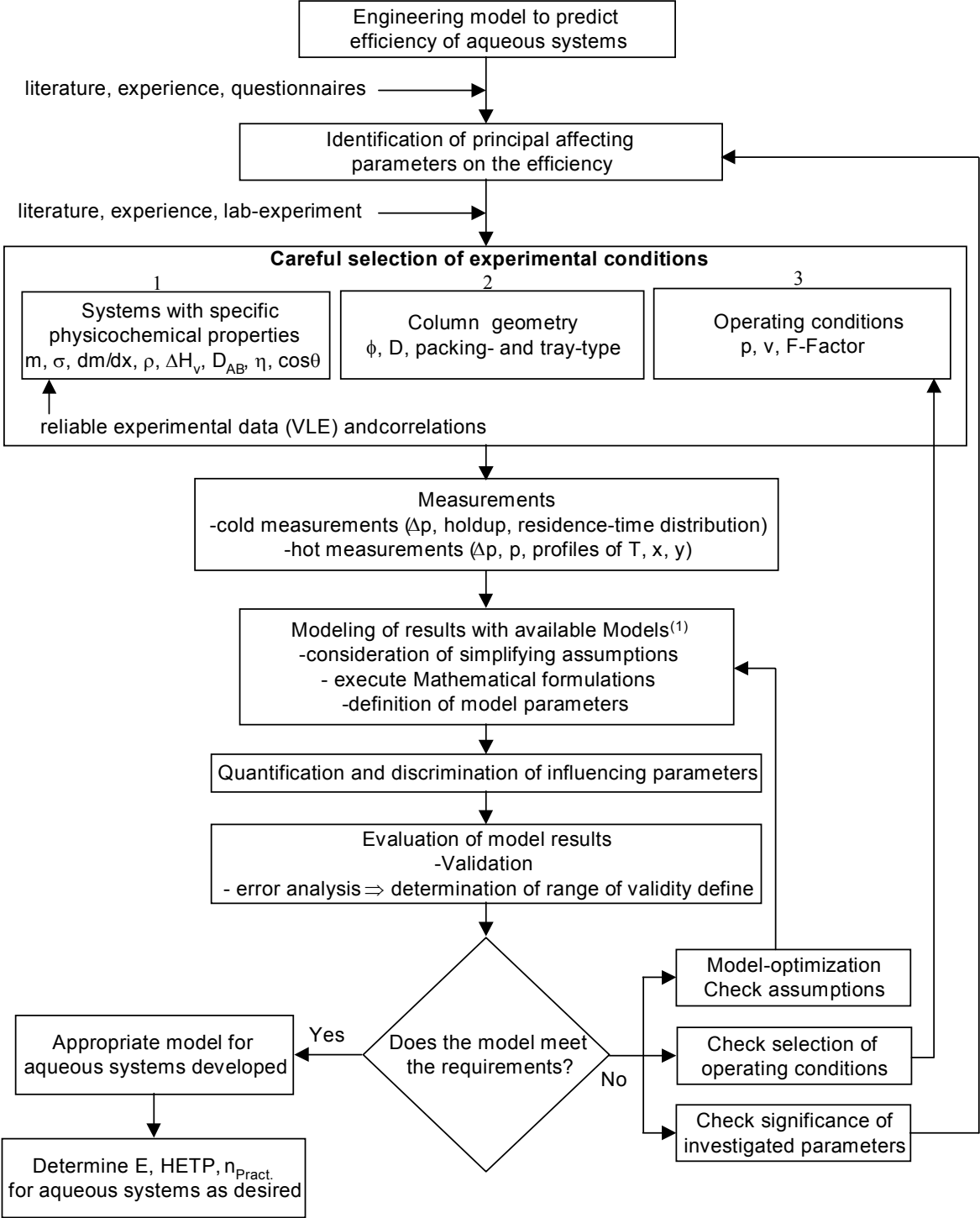


Figure 1: Flow-sheet of the investigation-concept

(1)Models from: [12, 29, 30, 31, 36-54].

In a next step experiments are planned to give insight into the interplay and mutual dependence of the parameters. This requires a careful selection of binary systems, column internals and operating conditions to be able to discriminate the individual influence of each parameter on column efficiency and to be able to later validate the derived model.

Once the experimental strategy to discriminate the influence of the principal parameters affecting efficiency is established, the type of column has to be chosen and the ranges for the operating parameter have been established. The next step is to carry out the experimental work. In general two types of measurements must be conducted, i.e. cold and hot measurements. The cold measurements allow the characterization of the fluid dynamics (Δp , Holdup, and residence-time distribution) of the used column. These cold measurements are performed with water and air flowing in countercurrent. Hot measurements are then carried out with the systems previously selected to determine the efficiency of the distillation as a function of the concentration of the mixture and operating parameters.

After this, the available models are applied and their results compared to experimental data. Since the models generally contain simplifying assumptions their influence has to be evaluated. This includes a careful error analysis. If it is not possible at this stage to find an acceptable model or to discriminate between different models the choice of model assumptions and experimental condition (systems studied and operating condition) have to be re-inspected and adjusted. If finally a model is derived which is able to reproduce the experimental data with the desired accuracy the problem is solved and a more reliable method for distillation-columns design applicable to the separation of aqueous mixture is developed.

The following paragraphs describe the results of the first steps of this procedure that have been completed until today.

IDENTIFICATION AND QUANTIFICATION OF THE PRINCIPAL PARAMETER AFFECTING EFFICIENCY OF DISTILLATION IN AQUEOUS SYSTEMS

The parameters potentially affecting the efficiency of distillation of aqueous systems have been identified according to literature and industrial experience and classified in Table 1 in three groups. These will be now discussed in detail.

Table 1: Principal affecting parameters.

<p>1. Strong dependence of the physicochemical properties of the mixture on its composition</p> <p>Real behaviour of vapour-liquid equilibrium (VLE)</p> <ul style="list-style-type: none">• Slope and curvature of VLE of y-x curve• High relative volatility <p>Surface tension</p> <ul style="list-style-type: none">• Wetting• Maldistribution (local effects)• Marangoni Effect <p>Strong concentration dependence of heat and mass Transfer</p>
<p>2. Influence of the geometry of the internal column-fittings column internals</p> <ul style="list-style-type: none">• Hydraulics• Maldistribution (large scale effects)• Mixing behaviour in the column
<p>3. Operating conditions of the distillation column</p> <ul style="list-style-type: none">• F-Factor• Pressure (p)• Reflux ratio (v)

Strong Dependence of the Physicochemical Properties of the Mixture on its Composition

As mentioned before, aqueous systems are characterized by a highly non-ideal behaviour, which is sometimes difficult to describe sufficiently accurately with the existing thermodynamic models. Therefore, it is necessary to have reliable experimental VLE data and to carefully apply an appropriate thermodynamic model in order to study such systems. The influence of the composition on the relative volatility and on the slope and curvature of the VLE have been identified to be very important parameters affecting the distillation efficiency [12, 13, 14].

The influence of the surface tension on mass and heat transfer between vapour and liquid phase in a distillation column has been extensively investigated as well [2, 17, 21, 25, 26, 27, 29, 33, 55-60]. The high surface tension of water in comparison to that encountered in organic compounds and its strong concentration dependence (as it can be seen in Figure 3) influence some important effects such as: wetting, maldistribution, activated mass and heat transport area and Marangoni effect [2, 13, 17, 20, 25, 26, 27, 29, 30, 31, 33, 55, 56].

The dependence of heat and mass transfer properties on mixture composition is a particular characteristic of aqueous systems due to the chemical nature of the water molecule.

All the mentioned parameters must be considered in a high purity water region of a column, where small variations in organic-compound concentration can strongly change the physical properties of the mixture in these sections of the column, characterized by a strong decrease of the efficiency, as frequently reported in the literature [17, 20, 27, 31, 36].

Other properties such as diffusion coefficients, density, enthalpy of vaporization, viscosity and liquid and vapour phase resistance to mass transfer are affected by composition variations and can, therefore, affect the efficiency of the separation. Here, these parameters are to be considered during the analysis of the test results, however they are not systematically varied in order to simplify the complexity.

Influence of the Geometry of Column Internals

The objective of the internals of a distillation column is to induce an intimate contact between the vapour and liquid phases, which flow in countercurrent direction through the column. This produces a large contact area between both phases, and thus favours mass and heat transfer between the phases. Therefore, the geometry of the internals is an important parameter for the intensity and efficiency of contact between the phases in a distillation column. Additionally, the pattern of mixing of the vapour and liquid phase (plug flow, back mixing, stagnant zones or perfect mixing) as well as holdup and pressure drop of the column are also defined by the geometry and operating conditions.

Especially the mixing behaviour of a tray in combination with the curvature of the equilibrium curve influences the tray efficiency. If the liquid is perfectly mixed, the liquid composition on the tray is uniform. The Murphree efficiency (tray efficiency) will then coincide with the local efficiency (point efficiency) at any point on the tray [2]. However, if plug or cross flow is present on the tray, a concentration gradient in the liquid phase occurs. Due to the high relative volatility of aqueous systems at high purity water regions, the local efficiency will vary strongly from point to point on the tray. Thus, measurements using trays with and without cross flow allow to discriminate the effects on the distillation efficiency which are caused by changes of the curvature of the VLE, i.e. changes of the driving force with composition.

Operating Conditions of the Distillation Column

The operating conditions of a distillation column comprise mainly the vapour and liquid loads along of the column (side-streams and internal as well as external reflux), pressure of the column and overall concentration profile. These conditions affect directly and indirectly the pattern of mixing of the vapour and liquid phase, as well as the intensity of the contact between liquid and vapour.

DISCRIMINATION OF THE PRINCIPAL INDIVIDUAL PARAMETERS AFFECTING EFFICIENCY

After having identified the principal parameters, an experimental strategy to discriminate and quantify the different effects must be chosen. It can be determined based on industrial experience and literature.

Here, the first experiments are carried out on trays with an almost perfect liquid mixing pattern, a radial flow tray [36] which will be described in the experimental section. The influence of the wetting behaviour will be clarified with columns with random or structured packing. Measurements with a cross flow tray will be made to evaluate the effect of the curvature of the vapour-liquid equilibrium on the efficiency. The operating conditions chosen for the experiments with hot measurements are infinite reflux ratio and a constant pressure of 950 mbar. The F-factor will be varied systematically in all experimental runs. Few selected experiments will quantify the influence of pressure and finite reflux ratio.

It is crucial for the experiments that appropriate binary systems are carefully selected. According to our strategy, we have chosen three dominant parameters to be systematically varied in a first approach, namely VLE curve, surface tension and the presence or not of water in the mixture. To vary these parameters appropriate systems have to be determined. In an ideal case, the selection of the binary systems would be made in such a way that each one differs from the others only in one property. Then, the influence of this variable on the efficiency of distillation could be obtained individually. In reality, such systems can not be found. Therefore, after extensive comparison of the material properties of different mixtures three binary systems were selected for the investigation, two of which are aqueous:

System 1: methanol + water

System 2: water + morpholine

System 3: 1-propanol + 2-methoxyethanol

A summary of some physicochemical properties of these systems is shown in Appendix A in Table 2 and Figure 8.

The characteristics of these binary systems will now be discussed in the context of this project. Figure 2a shows the equilibrium curves of the three binary systems. In the system methanol + water, the equilibrium curve is strongly curved and very steep near the high purity water region. Contrary to this, the equilibrium curve of the system water + morpholine runs clearly flatter in the high purity water region. The equilibrium curve of the non-aqueous system 1-propanol + 2-methoxyethanol is almost identical to that of water + morpholine.

The difference between the equilibrium curves of the systems methanol + water and water + morpholine causes also a dramatic difference in the slope (m) of the equilibrium curves. Figure 2b shows m as a function of composition for each binary system. Here it is evident that in the system water + methanol, m is very steep close to pure water, whereas for the system water + morpholine m runs almost horizontal at the high purity water region. It is worthwhile noting, that the difference in m for the selected aqueous systems reaches a factor of 17 in the vicinity of pure water.

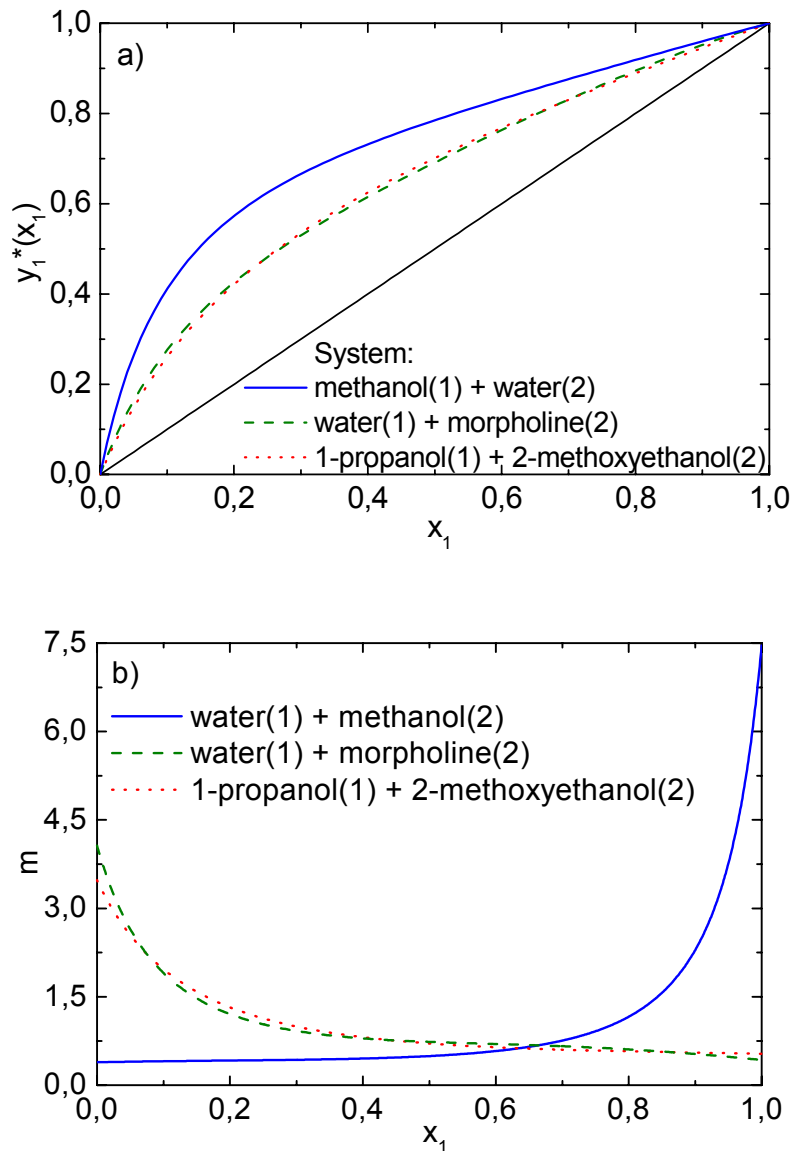


Figure 2: Vapour-liquid phase and slope (m) of the equilibrium curve of the selected binary system.

Figure 3 shows the variation of the surface tension (σ) for each system at its boiling point at atmospheric pressure. Extrapolation of σ to boiling temperature has been carried out with the correlation of Tamura et al. [61]. It is here interesting to observe the dramatic increase of σ approaching pure water in the aqueous systems, which is a consequence of the high value of σ for water compared to that of organic compounds.

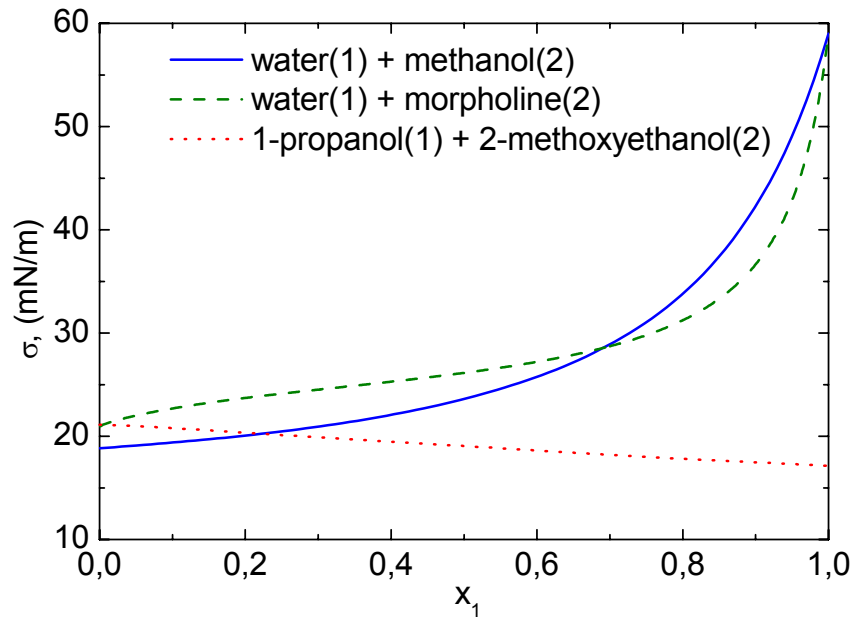


Figure 3: Surface tension at boiling point.

The selection of an organic system with a VLE curve similar to that of one aqueous system allows to discriminate the effect of the surface tension on the efficiency by comparing both systems.

MEASUREMENTS AND EXPERIMENTAL WORK

Figure 4 shows a drawing of the first type of tray selected for the experimental work. This radial flow tray was characterized by Reusch in his PhD-thesis [36]. A reason to choose this tray is that measurements done by Reusch show a total mixing of the liquid phase on the trays. This implies, that on the tray no concentration gradient exist in the liquid phase, i.e. the point efficiency coincides with the Murphree efficiency [2].

A plant for the experimental phase of this project was constructed with the support of the Bayer AG, Process Technology. The process flow diagram of the plant is shown in Figure 5. The column to be characterized is column C-1 in this figure. Three types of measurements can be carried out under this scheme: determination of the dry pressure drop (Δp) in column C-1 if no water is present, determination of Δp of each tray by countercurrent flow of water and air, and the holdup in the same experiments.

To carry out the measurements air is introduced into the system through a fan the flow of which is controlled and measured before it passes to the column C-2. In C-2 the air is saturated with water in order to avoid water losses in column C-1. The saturation of the air is achieved with a stream of water which cycles in a loop containing a thermostat that controls the temperature of the saturated air to 20°C. Finally, the air is introduced into column C-1 at the bottom, flows upwards through the trays of the column and is withdrawn at the top.

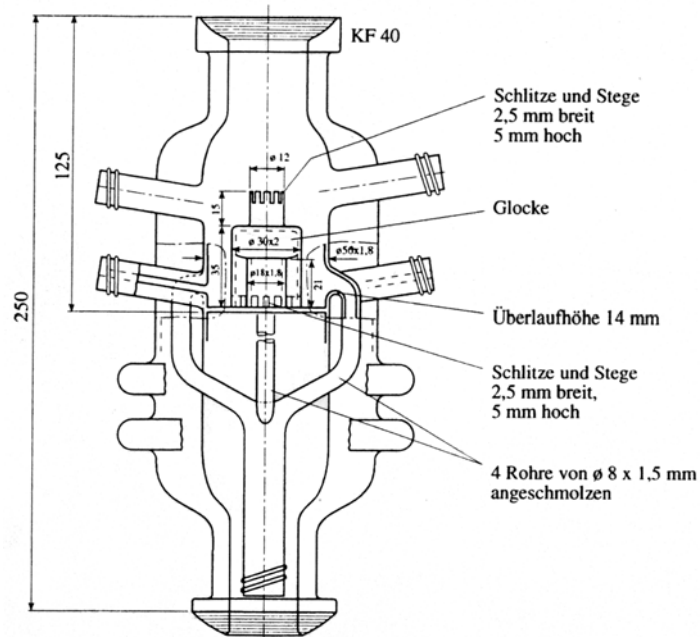


Figure 4: Radial flow tray (Reusch tray) [36].

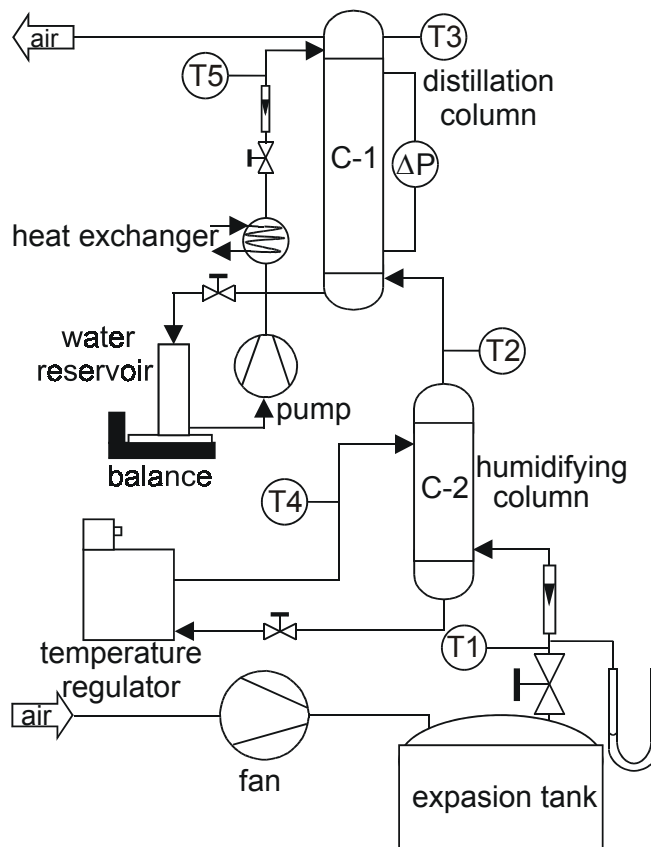


Figure 5: Process flow diagram of the plant for cold measurements.

The water in column C-1 is introduced at the top and withdrawn at the bottom. It comes from a closed system containing a valve, a rotameter, a heat exchanger operating with cold water, and a balance with a reservoir. The balance is used to

record changes of the amount of water in the reservoir which directly correspond to changes of the holdup in the column C-1. As a reference the value of the mass of water within C-1 is measured at the beginning of the experiment without air flow.

Figure 6 and 7 show results of measurements made to characterize the radial flow tray.

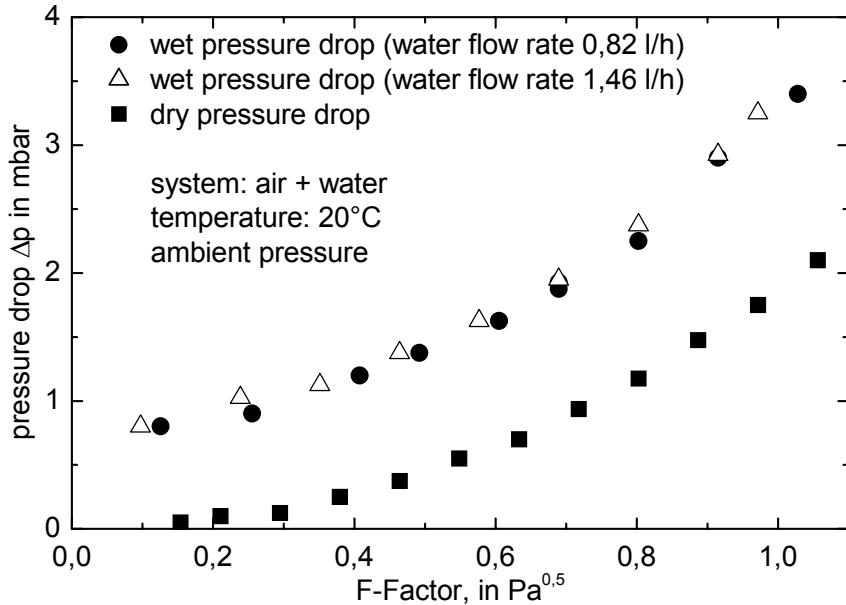


Figure 6: Pressure drop of the radial flow tray as function of air and water flow rates.

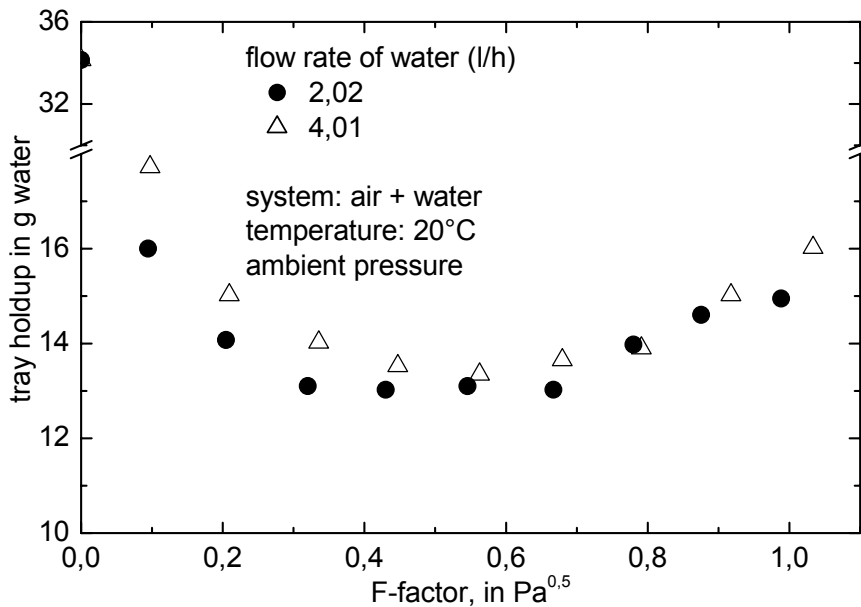


Figure 7: Holdup of the radial flow tray as function of air and water flow rates.

In order to investigate the nature of the liquid mixing pattern of the Reusch tray the residence-time distribution was determined with sodium chloride (NaCl) as tracer and conductivity measurements. The results are being analyzed right now and appear to confirm the results by Reusch [36], stating that good mixing of the liquid phase is guaranteed on the trays.

Hot measurements to determine the efficiency of distillation trays as function of concentration and operating conditions are currently being conducted. Experiments with the aqueous test system methanol + water [15] are carried out first. All these measurements will establish the basis for the modelling process. Results of the hot measurements will be presented at the International Conference on Distillation & Absorption 2002.

CONCLUSIONS

The efficiency of column internals for the distillation of aqueous systems is a result of the complex interrelation between the physicochemical properties of the mixture, the geometry of the internals, and the operating conditions of the distillation column. A procedure that allows discrimination and quantification of the principal affecting parameters by a careful selection of binary systems, geometry of the internals, and adequate operating conditions has been presented here and discussed in detail. Some first experimental results for a well mixed tray are shown in this paper. Further results of hot measurements will be presented at the conference. In a following publication, we will present all the results obtained during the experimental phase of this investigation. The procedure described here will be used to assist the model development for distillation of aqueous mixtures.

ACKNOWLEDGMENTS

The authors thank Dr. L. Deibele, Bayer AG, Process Technology, Dr. T. Adrian, BASF AG, Dr. A. Kobus, Degussa AG, Dr. R. Herguijuela, Roche AG for the financial and technical support of this research. M. Caraucán is grateful for financial support provided by FUNDAYACUCHO (Fundación Gran Mariscal de Ayacucho, Venezuela) and for administrative support in Germany by DAAD (Deutscher Akademischer Austausch Dienst).

REFERENCES

1. H. E. O'Connell (1946), Trans. AIChE 42, 741-755.
2. H. Z. Kister (1992), Distillation: Tray Efficiency, Design, McGraw-Hill, New York, pp. 365-419.
3. T. D. Ling and M. Van Winkle (1958), Ind. Eng. Chem., 3, 88-95.
4. M. W. Biddulph and M. A. Kalbassi (1988), Ind. Eng. Chem., 27, 2127-2135.
5. B.I. Konobeev and V. V. (1970), Zhurnal Prikladnoi Khimii, 43 (4), 803-811.
6. J.J. Jasper (1972), J. Phys. Chem. Ref. Data, 1, 872-1010.

7. J. Gmehling, U. Onken and W. Arlt (1981): Vapor-Liquid Equilibrium Data Collection: Aqueous-Organic Systems, Vol. 1 (Parts 1, 1a and 1b), Frankfurt/Main.
8. K. Stephan and H. Hildwein (1987), Recommended Data of Selected Compounds and Binary Mixtures, Vol. IV, Parts 1+2, Dechema, Frankfurt am Main, pp. 537-567.
9. S. Zeck (1990), Chem. -Ing. -Tech., 62 (9), 707-717.
10. U. Eiden, R. Kaiser (1997), Distillation and Absorption '97, Inst. Chem. Engs., Symposium Series No. 142.
11. L. Deibele, R. Goedecke, H. Schoenmakers (1997), Distillation and Absorption '97, Inst. Chem. Engs., Symposium Series No. 142.
12. H. A. Mostafa (1979), Trans. IChemE, 57, 55-59.
13. F. P. Moens (1972), Chem. Eng. Sci., 27, 275-283.
14. D. P. Kurtz, K. J. McNulty and R. D. Morgan (1991), Chem Eng. Prog., 87, 43-49.
15. U. Onken and W. Arlt, (1990), Recommended Test Mixtures For Distillation Columns, Institution of Chemical Engineers, Rugby, pp. 4-61.
16. D. P. Kurtz, K. J. McNulty and R. D. Morgan (1991), Chem. Eng. Prog., 87, 43-49.
17. F. J. Zuiderweg and T. Yanagi (1992), I. Chem. E. Symposium Series N° 128 Distillation and Absorption 1992, Rugby, Uk., A181-A191.
18. A. B. Ponter and P. H. Au-Yeung (1984), Chem. -Ing. -Tech., 56 (9), 701-703.
19. V. D. Veen, and A. A. H. Drinkenburg, and F. P. Moens (1974), Trans. Instn. Chem. Engrs., 52, 228-233.
20. G. Anderès (1962), Chem. -Ing. -Tech., 34 (9), 597-602.
21. T. D. Koshy and F. Rukovena (1986), Hydrocarbon Processing, 65,1 , 64-66.
22. S. R. M. Ellis, M. J. Hardwick (1969), I. Chem. E. Symposium Series N° 32 (Distillation Symposium Brighton 1969), 1:29-36
23. F. Kaštánek and G. Standart (1967), Sep. Sci., 2 (4), 439-486.
24. E. R. Gilliland (1940), I & EC, 32 (9), 1220-1223.
25. F. J. Zuiderweg and A. Harmens (1958), Chem. Eng. Sci., 9 (2/3), 89-108.
26. F. J. Zuiderweg (1964), Chem. -Ing. -Tech., 36 (3), 290-295.

27. F. J. Zuiderweg (1983), Chem. Eng. Res. Des., 61, 388-390.
28. F. J. Zuiderweg (1953), Chem. -Ing. -Tech., 25 (6), 297-308.
29. G. X. Chen, A. Afacan, K. T. Chuang (1994), Can. J. Chem. Eng., 72, 614-621.
30. F. J. Zuiderweg (1982), Chem. Eng. Sci., 44, 1441-1464.
31. Z. P. XU, A. Afacan, K. T. Chuang (1994), Can. J. Chem. Eng., 72, 607-613.
32. L. Deibele, and H. Brand (1985), Chem.-Ing.-Tech 57, 439-442
33. R. C. Francis and J. C. Berg (1967), Chem. Eng. Sci., 22, 685-692.
34. R. J. Mangers and A. B. Ponter (1980), Ind. Eng. Chem. Proc. Des. Dev., 19 (4), 530-537.
35. S. J. Procter, M. W. Biddulph and K. R. Krishnamurthy (1998), AIChE Journal, 44 (4), 831-835.
36. Reusch, D. (1996), Entwicklung und Überprüfung eines pragmatischen Modells für die Reaktivdestillation. PhD Thesis, Universität zu Köln.
37. Ronge, G. (1994), Überprüfung unterschiedlicher Modelle für den Stoffaustausch bei der Rektifikation in Packungskolonnen. PhD Thesis, University RWTH-Aachen.
38. R. Zarzycki, and A. Chacuk (1993), Absorbtion: fundamentals & applications. 1st Edition, Pergamon Press Inc, New York.
39. H. Chan, and J. R. Fair (1984), Ind. Eng. Chem. Process Des. Dev. 23, 820-827.
40. W. K. Lewis (1936), I & EC, 28, 399-402.
41. E. F Wijn (1996), Chem. Eng. J., 63, 167-180.
42. A. G. Fane and H. Sawistowski (1969), I. Chem. E. Symposium Series N° 32 (Distillation Symposium Brighton), 32, 1:8-1:17.
43. G. X. Chen and K. T. Chuang (1994), Ind. Eng. Chem. Res., 33, 907-913.
44. G. X. Chen and K. T. Chuang (1993), Ind. Eng. Chem. Res., 32, 701-708.
45. F. Kašánek (1970), Collect. Czech. Chem. Commun., 35 1170-1187.
46. M. J. Lockett, and I. S. Ahmed (1983), Chem. Eng. Res. Des., 61, 110-118.
47. M. J. Lockett, and T. Plaka (1983), Chem. Eng. Res. Des., 61, 119-124.
48. R. Krishna (1985), Chem. Eng. Res. Des., 63, 312-322.

49. H. Chan, and J. R. Fair (1984), *Ind. Eng. Chem. Proc. Des. Dev.*, 23, 814-819.
50. C. Soares, A. A. Barros, and M. R. Wolf-Maciel, Simulation of a sieve plate column with ethanol/water system using the nonequilibrium stage model. *ECCE* 2001.
51. D. L. Bennett, D. N. Watson, and M. A. Wiescinski (1997), *AIChE Journal*, 41, 1611-1625.
52. Z. P Xu, A. Afacan and K. T. Chuang (1996), *Trans. Instn. Chem. Engrs.*, 74, 893-899.
53. A. Vogelpohl (1979), *Distillation*, EFCE publication, 2.1/25-2.1/31.
54. P. H. Calderbank, J. Pereira (1979), *Distillation*, EFCE publication, 2.3/27-2.3/42.
55. N. Kolev and KR. Semkov (1991), *Chem. Eng. Process.*, 29, 83-91.
56. C. V. Sternling and L. E. Scriven (1959), *A.I.Ch.E Journal*, 5 (4), 515-523.
57. G. S. Bainbrigdge and H. Sawistowski (1964), *Chem. Eng. Sci.*, 19, 992-993.
58. H. W. van der Klooster, A. A. H. Drinkenburg (1979), *Distillation*, EFCE publication, 2.5/21-2.5/37.
59. H. Sawistowski (1973), *Chem.-Ing.-Tech* 45 (18), 1093-1140.
60. J. Hovestreyjdt (1963), *Chem. Eng. Sci.*, 18, 631-639.
61. R. C. Reid, J. M. Prausnitz, and B. D. Poling (1987), *The Properties of Gases and Liquids*, McGraw-Hill, New York.
62. N. B. Vargatik (1983), *Handbook of Physical Properties of Liquid and Gases*. Hemisphere Publishing Corporation, Amsterdam.
63. J. Timmermans (1965), *Physico-Chemical Constants of Pure Organic Compounds*, Vol 1-2, Elsevier Publishing Corporation, Washington.

APPENDIX A

Table 2: Some physicochemical properties of the selected binary systems [61-63].

Parameter	System		
	methanol + water	water + morpholine	1-propanol + 2-methoxyethanol
Relative volatility (α)	2,6 – 7,5	2,3 – 4,0	1,9 – 3,5
Slope of the vapour-liquid equilibrium curve (m)	0,38 – 7,5	0,43 – 4,0	0,53 – 3,5
Value of m at high purity water regions	7,5	0,43	----
Difference of surface tension ^(a) ($\Delta\sigma$) (mN/m)	(+) 39,9 (boiling point)	(-) 34,16 (T = 20°C)	(+) 8,88 (T = 20°C)
Max. or Min. of the stabilizing M-index ^(b) (mN/m) (at boiling point)	10,5 ^(c) ($x_w \cong 0,85$)	-8,1 ($x_w \cong 0,85$)	1 ^(d) ($x_p \cong 0,54$)
critical concentration region ^(e)	$x_w \in$ (0,6 – 1,0)	$x_w \in$ (0 – 0,4)	$x_p \in$ (0 – 0,4)

^(a) (+): Positive System (heavy component has higher surface tension [25])

(-): Negative System (light component has higher surface tension [25])

^(b) Maximal or minimal value of the stabilizing index M-index, which is responsible for the onset of Marangoni convection:

$$M - index = (x - x^*) \frac{d\sigma}{dx}; [13, 27]$$

x: mole fraction of the light component in liquid phase

x^* : x in equilibrium with y

y: mole fraction of light component in vapour phase

σ : surface tension

^(c) x_w : liquid-phase mole fraction of water

^(d) x_p : liquid-phase mole fraction 1-propanol

^(e) Concentration zone of the liquid-phase in which the curvature of the vapour-liquid phase equilibrium changes especially strongly.

Cont. Appendix A

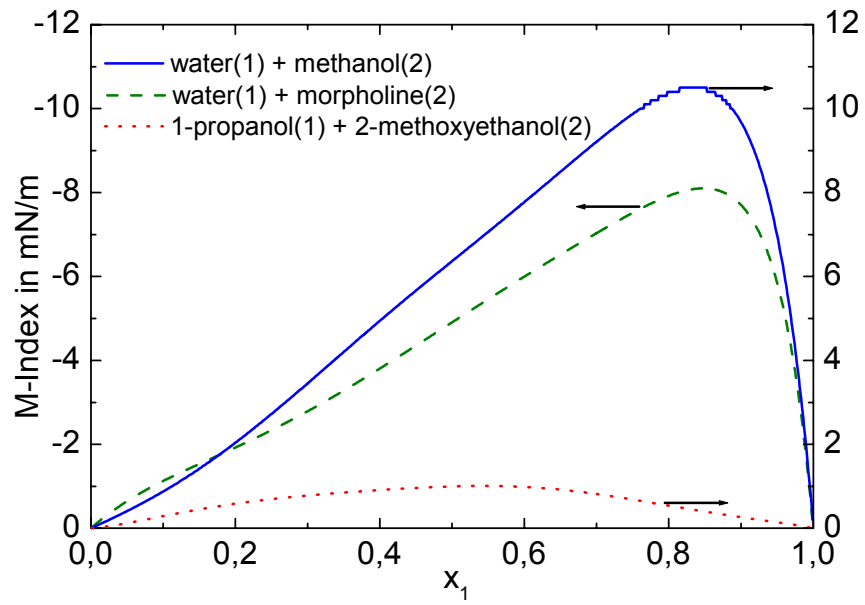


Figure 8: M-Index at boiling point.