SIMULATION OF A NEW PRESSURE SWING BATCH DISTILLATION SYSTEM

Arpad Kopasz, Gabor Modla, Peter Lang

BUTE Dept. of Building Services and Process Engineering, H-1521 Budapest, Muegyetem rkp. 3-5

Abstract: *The operation and performance of a new pressure swing batch distillation configuration is investigated by rigorous simulation calculations. A maximum boiling point azeotrope is separated in a double column batch rectifier. We study the influence of the main operational parameters and determine the optimal value of these parameters. The calculation results are presented for the mixture water (A) – ethylene-diamine (B).*

Keywords: *batch rectification, pressure swing, maximum azeotrope, separation.*

1. INTRODUCTION

Distillation is the separation method most frequently applied in the chemical industry, which is based on the difference of volatility of the components of a liquid mixture. For the separation of the two components (*A* and *B*) forming an azeotrope a special distillation method must be applied either

-without applying a separating agent (pressure swing distillation (PSD)), or

-applying a separating agent (e.g. extractive or heteroazeotropic distillation).

Batch distillation (BD) has always been an important part of seasonal, uncertain or low capacity and high-purity chemicals' production. It is a process of key importance in the pharmaceutical and several other industries and in the regeneration of waste solvent mixtures.

The main advantage of batch distillation over continuous is that a single apparatus can process many different liquid mixtures. Even multicomponent mixtures can be separated by batch distillation in a single column.

Many mixtures form an azeotrope, whose position can be shifted substantially by changing system pressure, that is, a *pressure sensitive azeotrope*.

Lewis [8] was the first, who suggested to distill azeotropic mixtures by *pressure swing distillation*. This process has been suggested to separate azeotropic mixtures by e.g. Britton et al. [3], Black [2], Abu-Eishah and Luyben [1], Chang and Shis [4].

Knapp et al. [7] developed a new process, in which *pressure swing continuous distillation* was combined *with entrainer addition*. The possibility of the application of an entrainer for the separation of binary azeotropic mixtures increases to a large extent the number of mixtures separable by this process.

Phimister and Seider [11] were the first who studied first the batch application of the PSD. They investigated the separation of a minimum azeotrope (THF-water) by *semi-continuous PSD and reverse-batch operation* (batch stripping) by rigorous simulation. In the semicontinuous column better performance was achieved than in the batch stripper. They also investigated the control and other practical aspects of these configurations, and their performance was compared with that of a continuous system, as well. Wasylkiewicz et al. [14] developed an algorithm which allows the variation of compositions of azeotropes with pressure to be tracked, and all new azeotropes that appear within specified pressure range to be found.

To our knowledge Repke et al. [13] were the first, who investigated experimentally the application the *pressure swing distillation in batch*. They studied the separation of a minimum boiling, homoazeotropic mixture (acetonitrile-water) by pressure swing distillation in a batch rectifier and in a stripper with *pilot-plant experiments and rigorous simulations*. The aim of these authors was rather the experimental study of the pressure swing batch distillation than the exhausting theoretical study of the feasibility of the process.

Modla and Lang [10] studied the *feasibility* of pressure swing batch distillation (PSBD) of binary mixtures (forming minimum or maximum azeotrope) *in different column configurations assuming maximal separation.* They suggested *two novel configurations* having two rectifying (double column batch rectifier, DCBR) or two stripping sections (double column batch stripper, DCBS). They made rigorous simulation calculations for the different column configurations. They stated that these new configurations may provide a lot of advantages against the well-known simpler configurations (batch rectifier or stripper). The different configurations were compared for a given set of operational parameters without optimising their operation. The best results were obtained with the two new double column configurations. They did not investigate the influence of the operational parameters for the two new column configurations.

The aim of this paper

-to investigate the influence of the main operational parameters of the double column batch rectifier,

 -to determine the optimal value of these parameters.

The calculation results are presented for the mixture water (*A*) – ethylene-diamine (*B*) (forming a maximum boiling point azeotrope).

2. VLE CONDITIONS

The y-x equilibrium diagram and azeotropic data of the mixture studied are shown for the two different pressures in Fig. 1 and Table 1, respectively.
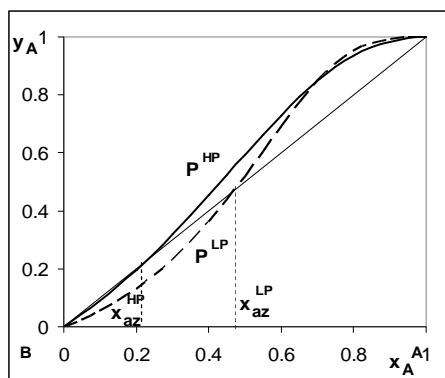

Fig. 1. *y-x* diagrams of the mixture water- EDA
(P^{LP}=0.1, P^{HP}=8.0 bar)

Mixture	P bar	x_{az} [%]	T_{az}[°C]	$T_{BP,A}$ [°C]	$T_{BP,B}$ [°C]
Water (*A*)-	0.1	47	62.2	45.8	50.8
EDA (*B*)	8.0	21	199.5	170.5	198.6

Table 1. Data of azeotropes

By varying the pressure the azeotropic compositions are shifted. For this mixture the difference of the two azeotropic compositions is more than 5%, and the difference of the two pressures applied is less than 10 bars, so the pressure swing process for the separation can be economical by Perry et al. [12].

3. Double column batch rectifier

The liquid streams flowing down from the two rectifying sections (Fig. 2) are mixed together in the bottom vessel operated at the higher pressure (P^{HP}).

The pressure of the liquid arriving from the column of lower pressure (P^{LP}) must be increased with a pump. The liquid leaving the vessel is divided into two parts. In the branch of light pressure there is a valve where the liquid is partially vapourised due to the decrease of pressure. In both branches there is a heat exchanger operated at P^{LP} and P^{HP}, respectively. The (saturated) vapours leaving these exchangers are introduced to the bottom of the columns.
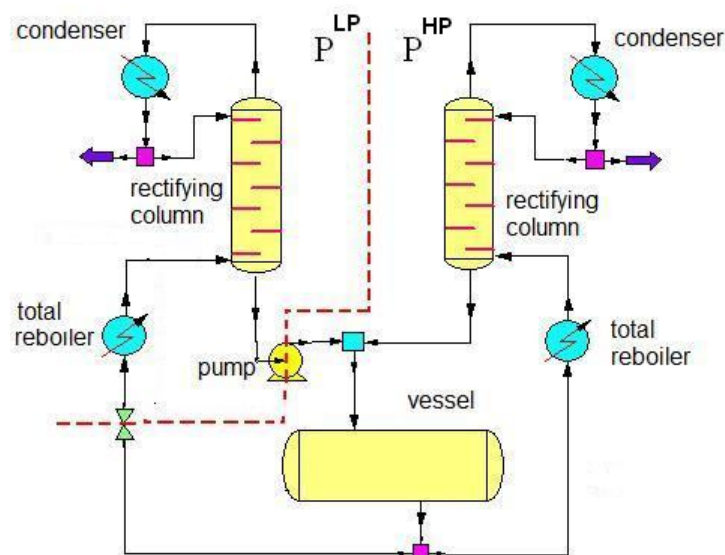

Fig. 2. Scheme of the double column batch rectifier

4. Rigorous simulation calculations

First the method then the results of the simulation calculations are presented.

4.1 Simulation method

The following simplifying assumptions were applied
- theoretical stages,
- negligible vapour hold-up,
- constant volumetric liquid plate hold-up.

The model equations to be solved are well known:
a. Non-linear differential equations (material balances, heat balances)
b. Algebraic equations (vapour-liquid equilibrium (VLE) relationships, summation equations, hold-up equivalence, physical property models).

For the calculations we used the CCDCOLUMN flow-sheet simulator of Chemstations [5].

The following modules were applied:
-DYNCOLUMN (column sections, simultaneous correction method),
-DYNAMIC VESSEL (vessel and product tanks),

-HEAT EXCHANGER, PUMP, VALVE,
-MIXER, DIVIDER,
-RAMP (for varying the reflux ratio at the end of the start-up (by changing the distillate flow rate.)
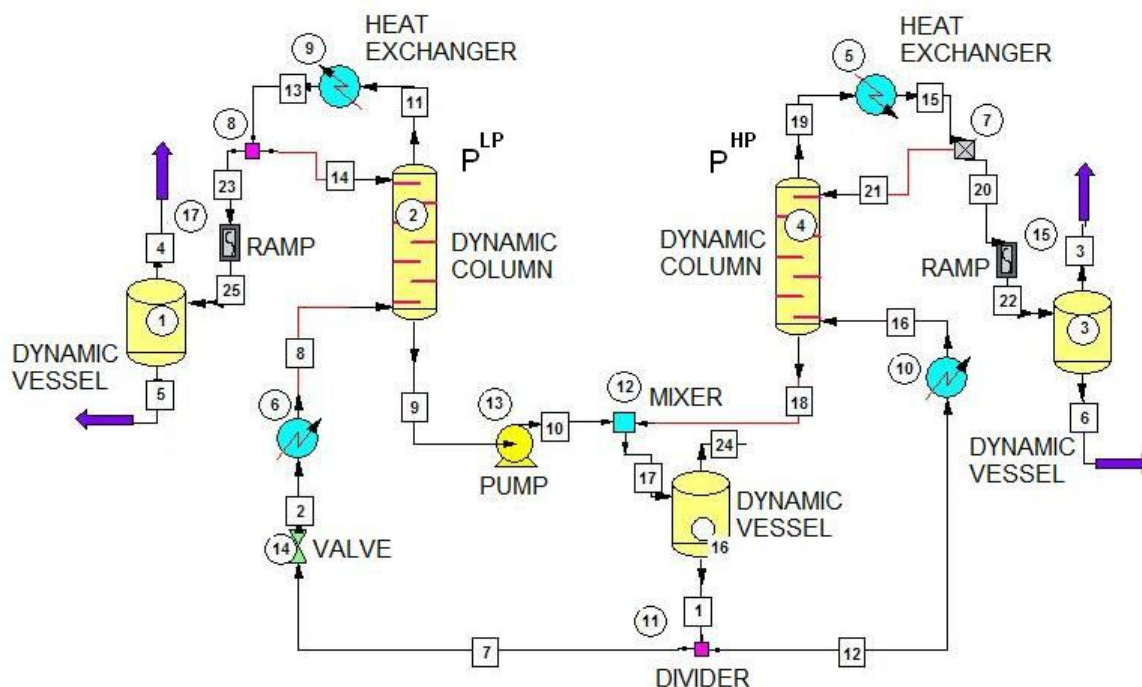The ChemCad model of the double column batch rectifier is shown in Fig. 3.

Fig. 3. The ChemCad model of the double column batch rectifier

4.2 Simulation results
The number of theoretical stages for each column sections is 20. (The total condenser and reboiler do not provide a theoretical stage.) The liquid hold-up is 25 cm^3/plate. The quantity of the charge is 10 dm^3. At the start plates of the columns are dry. The duration of the start-up period (purification without product withdrawal) is 30 min. The whole process is finished when the amount of liquid in the vessel decreases to 2% of the charge. The pressure of the columns does not change in time: $P^{LP}= 0.1$ bar and $P^{HP}=8$ bar.
The total vapour flow rate of the two column system (which equals to the total flow rate of liquid leaving the common vessel): $V_{total} = V^{LP}+V^{HP} = 340$ mol/h.
First the influence of the most important operational parameters will be investigated then the solution of a separation problem will be shown.

### 4.2.1 The influence of the most important operational parameters
The influence of the variation of the following parameters will be studied
- division of the total vapour flow rate between the two columns,
- reflux ratio of the low pressure column (R^{LP}),
- reflux ratio of the low pressure column (R^{HP}),
- charge composition.

The basic value of these parameters is as follows. The relative vapour flow rate of the LP column: $V^{LP}=V^{LP}/V_{total}$. The reflux ratios: $R^{LP}=R^{HP}=15$. The mole fraction of component *A* in the feed (charge): $z_A=0.34$.

If the *relative vapour flow rate* of the LP column is increased (by increasing in the LP branch the flow rate of the liquid coming from the common vessel) the distillate flow rate of this column (D^{LP}) increases to the detriment of that of the other column (D^{HP}) and so
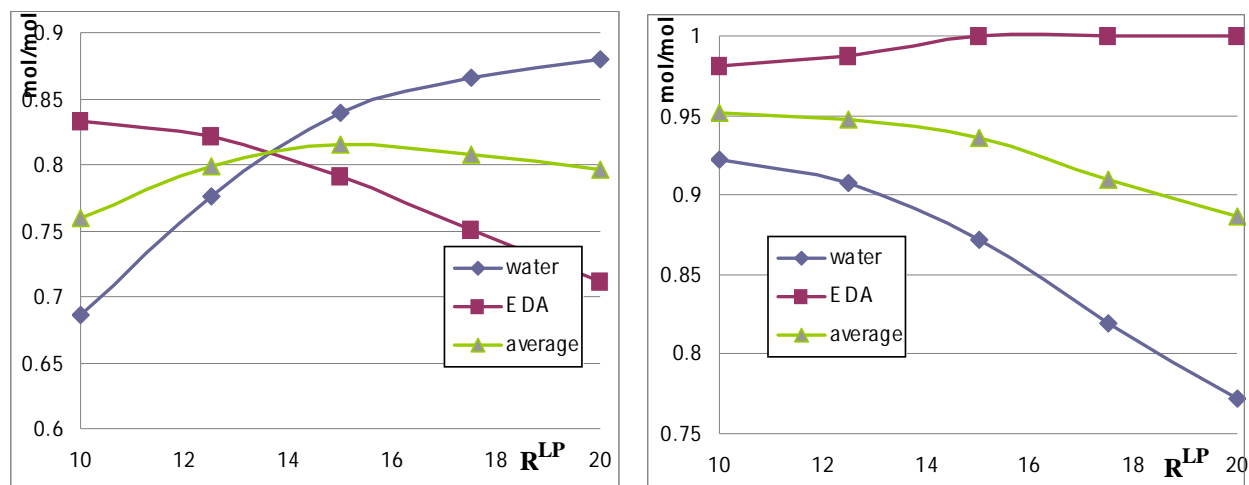
-the recovery of the component produced in this column (B, EDA) monotonously increases but its purity ($x_{D,B}^{LP}$) decreases (Fig. 4),

-the recovery of the other component (A, water) monotonously decreases since the quantity of A lost in D^{LP} rises, however its purity ($x_{D,A}^{HP}$) increases,

-both the average recovery ($\eta_{av}=(\eta_A+\eta_B)/2$) and the average purity (($x_{D,A}^{HP}+x_{D,B}^{LP}$)/2) has a maximum (at V^{LP}=0.6 and 0.65, respectively).
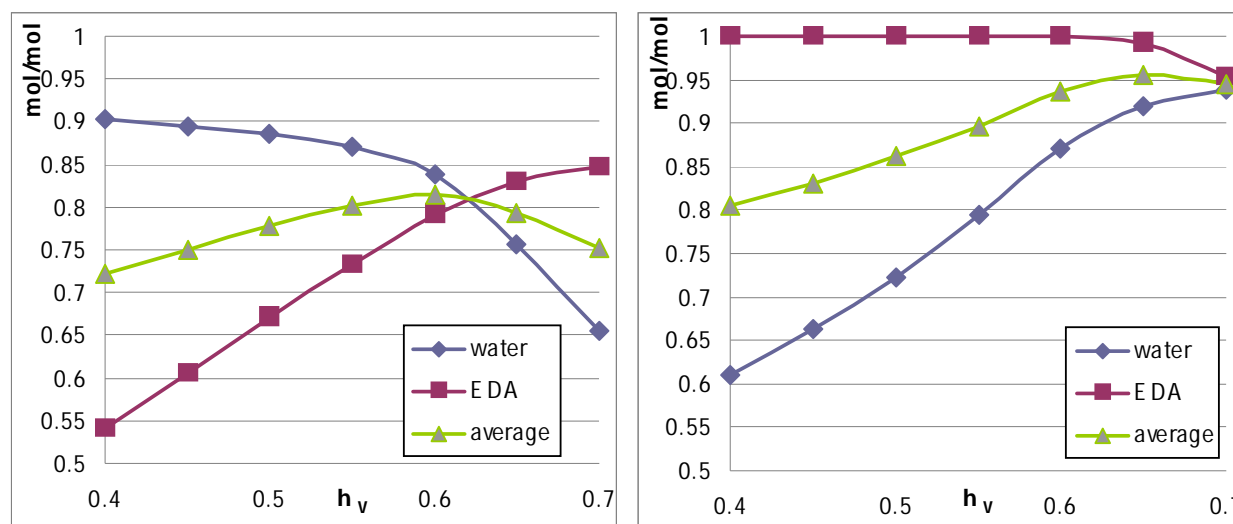
Fig. 4. Influence of the division of the total vapour flow rate on the recoveries and product purities ($R^{LP}=R^{HP}$=15, z_A=0.34)

On the increase of *reflux ratio of the LP column* (R^{LP}) the distillate flow rate of this column (D^{LP}) decreases while that of the other column (D^{HP}) remains practically constant and
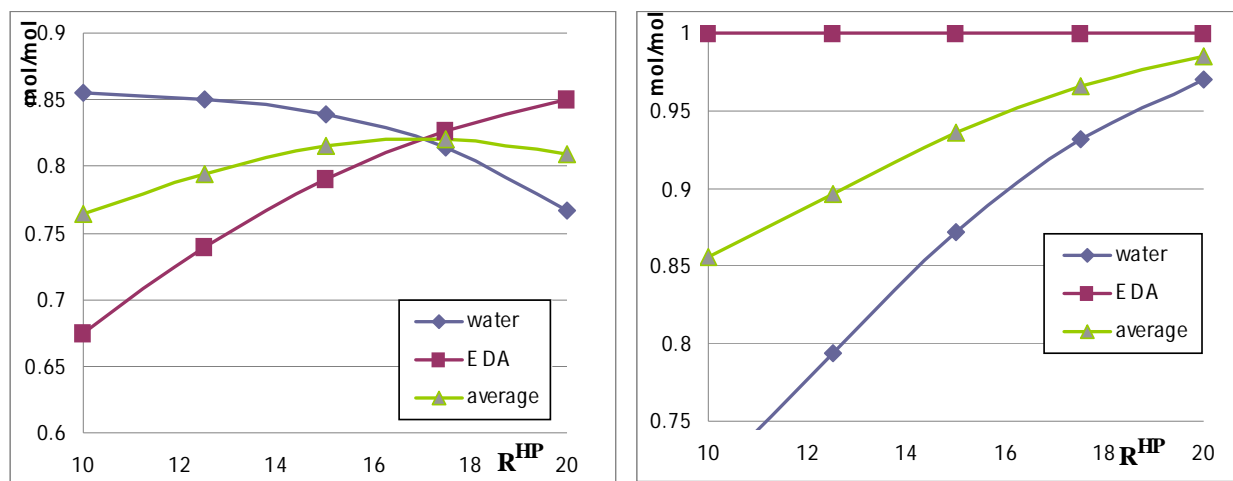
-the recovery of the component produced in this column (EDA) monotonously decreases while its purity increases (Fig. 5),

-the recovery of the other component (water) monotonously increases since its quantity lost in D^{LP} diminishes, however its purity decreases,

-the average recovery (η_{av}) has a maximum (at R^{LP}=15) but the average purity monotonously decreases since the purity of water product decreases to a greater extent than that of the EDA product increases (at R^{LP}=15 this product is quite pure).

Fig. 5. Influence of R^{LP} on the recoveries and product purities
(V^{LP}=0.6, R^{HP}=15, z_A=0.34)

On the increase of *reflux ratio of the HP column* (R^{HP}) the distillate flow rate of this column (D^{HP}) decreases while that of the other column (D^{LP}) remains practically constant and
-the recovery of the component produced in this column (water) monotonously decreases while its purity increases (Fig. 6),
-the recovery of the other component (water) monotonously increases since its quantity lost in D^{HP} diminishes, however its purity decreases,
-the average recovery (η_{av}) has a maximum (at R^{HP}=17.5) whilst the average purity monotonously increases since the purity of water product considerably increases while that of the EDA product hardly decreases.
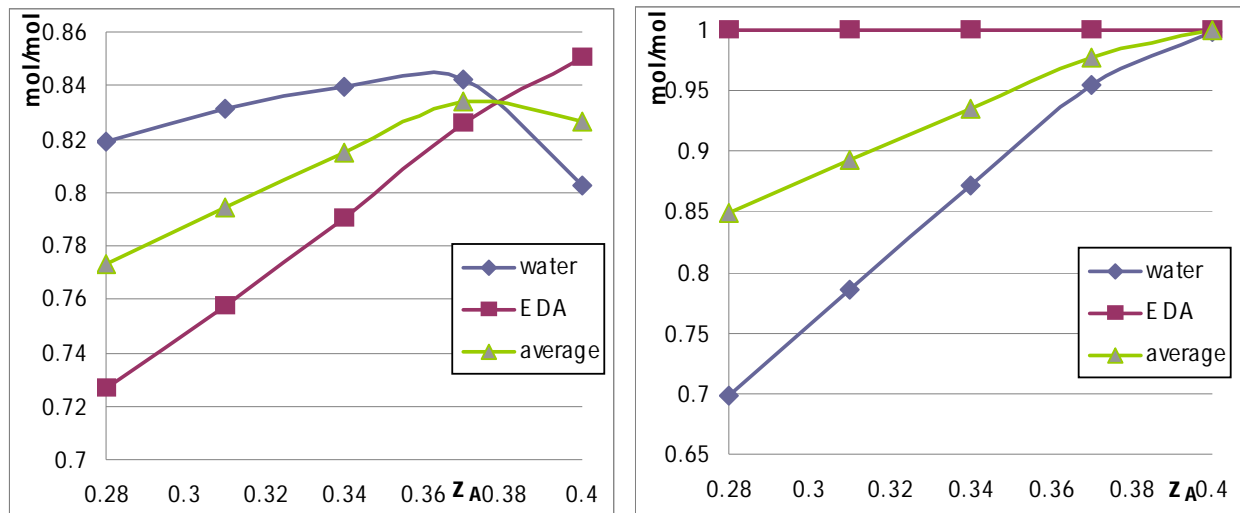

Fig. 6. Influence of R^{HP} on the recoveries and product purities
(V^{LP}=0.6, R^{LP}=15, z_A=0.34)

If the *mole fraction of water in the feed* (z_A) increases (the two distillate flows are practically unchanged and)
-the recovery of the other component (EDA) monotonously increases while its purity hardly varies (Fig. 7),
-the recovery of water has a maximum (at z_A=0.37) whilst its purity monotonously increases,

6 / 9

-the average recovery has also a maximum (at z_A=0.37) whilst the average purity monotonously increases.

Fig. 7. Influence of charge composition (z_A) on the recoveries and product purities
(V^{LP}=0.6, R^{LP}=R^{HP}=15)

4.2.2 Solution of a separation problem

The task is to find the value of the operational parameters (V^{LP}, R^{LP}, R^{HP}) -for the basic charge composition- satisfying the following criteria:

-Both product purities must be at least 98 mole% ($x_{D,av,B}^{LP} \geq 0.98$, $x_{D,av,A}^{HP} \geq 0.98$).

-Both recoveries must be at least 80 % ($\eta_B^{LP} \geq 0.8$, $\eta_A^{HP} \geq 0.8$).

The results obtained for the basic value of operational parameters clearly show that the above criteria are not satisfied for the basic case since

-the purity of water (0.795) is much lower and

-the recovery of EDA (η_B^{LP}=0.79) is also somewhat lower than their prescribed values.

On the basis of results of the parametric study the purity of water can be increased by decreasing D^{HP}, which can be made by

-increasing V^{LP} (which increases η_B^{LP}),

-decreasing R^{LP} (which increases η_B^{LP}),

-increasing R^{HP} (which increases η_B^{LP}).

However the results obtained for the basic value of operational parameters also show that -the

- the recovery of water (0.835) is higher and

- the purity of EDA (0.9999) is much higher

than their prescribed values. The closer are the values of these parameters to their prescribed values the more energy can be saved. (The energy consumption is nearly proportional to the duration of the process.)

On the basis of results of the parametric study the purity of EDA can be decreased by increasing D^{LP}, which can be made by

-increasing V^{LP} (which decreases η_A^{HP}),

-decreasing R^{LP} (which decreases η_A^{HP}),

-increasing R^{HP} (which decreases η_B^{LP}).

Modla and Lang [10] described that the two column system can be operated optimally if the vessel composition is kept constant, which means that the ratio of the production rate of the two components (($D^{LP} * x_{D,B}^{LP}$)/ $D^{HP} * x_{D,A}^{HP}$) must be equal to the ratio of the mole fraction of

the components in the charge $((1-z_A)/z_A)$. Assuming constant molar overflow and pure products and neglecting the column hold-up we can derive the following equation for the optimal operation, which gives the relationship between the 3 operation variables for a given charge composition:

$$\frac{1-z_A}{z_A} = \frac{R^{HP}+1}{R^{LP}+1}\frac{V^{LP}}{1-V^{LP}} \tag{1}$$

On the basis of the above results we decreased the value of R^{LP} to 10 (which remained unchanged) and from a much higher initial value ($R^{HP}=30$) we decreased progressively the value of R^{HP} until the duration of the process was minimal so that the prescribed criteria were still satisfied (Table 1). V^{LP} was considered as dependent variable and its value was calculated from Eq. 1 for the given R^{LP} and R^{HP} values.

Table 1. The determination of the optimal value of R^{HP} ($z_A=0.34$, $R^{LP}=10$)

We can state that at $R^{HP}=24$ (where $V^{LP}=0.46$) the duration of the process is minimal and the prescribed criteria are still satisfied, that is, this value can be considered optimal. Below this value of R^{HP} the recovery of water is already too low.

5. CONCLUSION
The separation of a maximum boiling point azeotrope in a double column batch rectifier was studied by rigorous simulation. The calculations were performed for the mixture water (*A*) – ethylene-diamine (*B*) with the CCDCOLUMN professional dynamic flow-sheet simulator. We studied the influence of the main operational parameters (division of the total vapour flow rate between the two columns, reflux ratios and charge composition) and determined the optimal value of these parameters giving the highest average recovery and/or product purity. Finally the solution of a separation problem was presented.

ACKNOWLEDGEMENTS

REFERENCES
[1] Abu-Eishah S. I., Luyben W. L. (1985) „Design and Control of Two-Column Azeotropic Column Azeotropic Distillation system", Ind. Eng. Chem. Process. Des. Dev. 24, 132-140
[2] Black C. (1980) „Distillation Modelling of Ethanol Recovery and Dehydration Processes for Ethanol and Gasahol", Chem. Eng. Prog., 76, 78-85
[3] Britton E. C., Nuttiing H. S., Horley L. H. (1943) „Separation of Ketones and Monohydric Alcohols from Mixtures Thereof.", U.S. Patent, 2,324,255, July 13
[4] Chang T., Shih T. T. (1989) „Development of an Azeotropic Distillation Scheme for Purification of Tetrahydrofuran", Fluid Phase Equilib., 52, 161, 161-168
[5] Chemstations, "CHEMCAD User Guide" (2005).
[6] Duessel R. and J. Stichlmair. (1995) „Separation of Azeotropic Mixtures by Batch Distillation Using an Entrainer", Comp. Chem. Eng., Vol. 19, S113-118
[7] Knapp J.P. and M.F. Doherty (1992) „A new pressure swing-distillation process for separating homogeneous Azeotropic Mixtures", Ind. Eng. Chem. Res., 31, 346-357.
[8] Lewis W. K., (1928) „Dehydrating Alcohol and the Like", U.S. Patent, 1,676,700, July 10

[9] Luyben W. L., (2005) „Comparison of Pressure Swing and Extractive Distillation Methods for Methanol Recovery Systems…", Ind. Eng. Chem. Res., 44(15), 5715-25

[10] Modla G. and P. Lang (2008) „Feasibility of new pressure swing batch distillation methods", Chem. Eng. Sci. ,accepted for publication.

[11] Phimister, J.R.; Seider, W.D. (2000) „Semicontinuous, Pressure Swing Distillation", Ind. Eng.Chem. Res., 39, 122-130

[12] Perry R. H., D.W. Green, J.O. Maloney, (1998) „Perry's Chemical Engineer's Handbook", 7-th edition, McGraw Hill, New York

[13] Repke .J. U., Klein A., Bogle D., Wozny G., (2006) „Pressure Swing Batch Distillation for Homogenous Azeotropic Separation", Proceedings of Distillation and Absorption 2006, London, 709-718.

[14] Wasylkiewicz S. K., L. C. Kobylka, and F. J. L. Castillo. (2003) „Pressure Sensitivity Analysis of Azeotropes", Ind. Eng. Chem. Res., 42, 207-213.

Notation

D	distillate molar flow rate [mol/s]
N	number of theoretical stages
P	pressure [bar]
Q	heat duty [W]
R	reflux ratio
SD	amount of the top product [mol]
SQ	amount of heat [J]
t	time [s]
V	boil-up molar flow rate [mol/s]
x	liquid mole fraction [mol/mol]
z	feed/charge composition [mol/mol]

Greek letters

η	recovery

Subscripts

A	pure component A
av	average
az	azeotrope
B	pure component B
D	distillate product
V	vessel

Superscripts

HP	high pressure column
LP	low pressure column
vol	volumetric