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M.Sc. in Manager in Chemical Engineering

**PhD Thesis**

# Separation of highly non-ideal mixtures with batch heteroazeotropic rectification

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## 1. Introduction, backgrounds, aims of the thesis

Distillation is the most frequently separation method applied in the chemical industry based on the difference of volatility of the components of a liquid mixture. Because of its high demands of energy the optimal design and operation of the distillation columns is a very important issue.

In the chemical technologies large amount waste solvent mixtures are evolving. They frequently form azeotropic, low relative volatility ($\alpha$) mixtures.

For the separation of azeotropes and low $\alpha$ mixtures a special distillation method must be applied such as heteroazeotropic distillation. By this method a third component (entrainer) is added to the mixture in order to improve the separation, which forms heteroazeotrope with at least one component of the original mixture.

Batch distillation 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 industry and the regeneration of waste solvent mixtures.

The distillation can be performed as a continuous or batch operation. The advantages of the batch distillation are well known – flexibility, several products from one column, possibility of separation small amount mixtures.

The batch extractive (homoazeotropic) distillation has been investigated since 1991 in the Technical University of Budapest in collaboration with the INSA-Lyon University (France). Since that time a lot of studies were published about different types of mixtures and entrainers. The separation of minimum and maximum boiling point of azeotropes with heavy entrainers was studied by Lang et al. (1994), Lelkes et al. (1998a,b) and Lang, Modla et al. (2000a,b). Furthermore the separation of minimum boiling point of azeotropes with light entrainers was studied by Lelkes et al. (1998c), Lang et al. (1999) and Modla (1997). Then the investigation was continued with the study of separation of low reality volatility mixtures by heteroazeotropic batch rectification (Modla et al. 2001, 2003a). Finally other heterogeneous systems were also studied (Modla et al. 2003b, Modla et al. 2004, Lang, Modla et al 2004) which results are not presented in the thesis because of the limitation of its volume.

The aim of this thesis is to extend the former feasibility method published for the batch homoazeotropic distillation to batch heteroazeotropic distillation and to study the separation of a low relative volatility, zeotropic mixture (dichloromethane (DCM) (*A*)-acetone(*B*)) in a batch rectifier with a selective entrainer (water(*E*)) by feasibility and rigorous simulation calculations.

## 2. Investigation methods

I have investigated the batch heteroazeotropic rectification by feasibility method and rigorous process simulation.

The feasibility method is frequently applied at the research of distillation. I have developed a new feasibility method for the use of a heterogeneous entrainer the former methods published for the batch homoazeotropic distillation.

The feasibility method involves the following basic simplifying assumptions:

- negligible tray hold-up (excluding the decanter and the still),
- constant molar overflow,
- quasi-steady state in the column,
- separation of the heterogeneous liquid in the decanter at its boiling point.

Nowadays the distillation processes can be well simulated. In the research work and in the industry several different commercial process simulators (ASPEN, HYSIS, CHEMCAD) are applied. For the rigorous simulation calculations I have used the BATCHCOLUMN module of the CHEMCAD 5.0 professional flowsheet simulator (Chemstations, 2000) applying the simultaneous correction method. The solution method is based on quasi-steady state approximation.

When making the rigorous simulation the usual simplifying assumptions were applied:

- theoretical trays,
- negligible vapour hold-up,
- constant volume of liquid hold-up,
- negligible fluid dynamic lags.

In the calculations I have modelled real, pilot-plant rectification equipment and I have chosen real operation parameters.

## 3. Overview of new scientific results

### *3.1 Feasibility method*

<u>Thesis 1 - Definition of feasibility</u>

I was the first who has suggested the continuous feeding of the heterogeneous entrainer at the batch heteroazeotropic rectification (Modla et al. 2001). I have extended the feasibility method of Lelkes et al. (1998b) for the use of a heterogeneous entrainer and I have defined the notion of "instantaneous feasibility".

The separation is instantaneously feasible if from the actual still liquid (of composition ($x^o_S$) located on the still path) under the given operating conditions (for example R, F/V) a distillate of prescribed composition ($x^o_{D,spec}$) can be produced.

The necessary and sufficient condition of the instantaneous feasibility is to have at least one possible column liquid composition profile connecting the actual still composition ($x^o_S$)

- with the point $x^o_{D,spec}$ if $x^o_{D,spec}$ is located in the homogeneous region (excluding the heterogeneous liquid boiling envelope) or
- with the tie-line passing through $x^o_{D,spec}$ if $x^o_{D,spec}$ is on the heterogeneous liquid boiling envelope or in the interior of the heterogeneous region.

<u>Thesis 2- Application of profile maps and its equations</u>

**a.** The analysis of batch distillation by profile maps is named to „feasibility studies". The feasibility method is based on the analysis of the map of the possible overall liquid composition profiles. By the analysis of the (rectification and extractive) profile maps can be predicted the process of batch rectification.

I have derived the equations of (rectification and extractive) profile maps and I have presented the application of maps for batch heteroazeotropic distillation.

**b.** I have given a general form for equations of possible column liquid composition profiles. I have extended the equations by reducing the number of simplifying assumptions. Hence the feasibility method has become able for the analysis the "hybrid process" (Stichlmair 1998). We has already started to analyse this process (Láng et al 2003, Kótai et al 2004a,b,d,e).

The applied equations for the feasibility analysis are as follow:

*Operating line:* $y = g(x^o)$

Specified parameters: $x^o_{D,spec}, R, q_R, F/V, q_F, z$

*Upper (extractive)section profile:*

$$\frac{dx^o}{dh} = \frac{1 - \frac{R}{R+1}(1-q_R) - \frac{F}{V}(1-q_F)}{\frac{R}{R+1}q_R + \frac{F}{V}q_F}\left(y^* - g(x^o)\right)$$

*Lower (rectification) section profile:*

$$\frac{dx^o}{dh} = \frac{1 - \frac{R}{R+1}(1-q_R)}{\frac{R}{R+1}q_R}\left(y^* - g(x^o)\right)$$

*Equation of the still-path :*

$$\frac{dx_s^o}{d\xi} = \left(x_s^o - x_{D,spec}^o\right) - \left(x_s^o - z\right)\frac{F}{D}$$

where:

$D$ distillate flow [mol/s]

$dx^o/d\xi$ still composition changes (where $\xi$ dimensionless time)

$dx^o/dh$ liquid composition in the column (where $h$ dimensionless height)

$F$ entrainer feed flow [mol/s]

$q_F$ heat condition of feed

$q_R$ heat condition of reflux

$R$ reflux ratio [mol/mol]

$V$ column top vapour flow [mol/s]

$x^o$ overall liquid composition on the plate [mol/mol]

$x^o_{D,spec}$ specified distillate composition [mol/mol]

$x^o_S$ still-composition [mol/mol]

$y^*$ equilibrium vapour composition [mol/mol]

$z$ feed composition [mol/mol]

Thesis 3 - Estimation of the number of the theoretical plates

I have suggested a new method for the estimation of the number of ideal plates for batch heteroazeotropic distillation, which is based on the discrete profile-maps.

Thesis 4 - Determination of endpoints of rectification and extractive boundaries

I have suggested a new graphical method for the determination of the endpoints of rectification and extractive boundaries.

I have pointed out the endpoints of the boundaries the points of intersection of the equilibrium curve and operating line.

Thesis 5 - Results of feasibility analysis

I have studied several types of mixture by the new feasibility method (Modla 2003a, 2003b) and I have presented the results for one of them in the thesis. I have examined the reparability of the dichloro-methane/acetone mixture applying water as heterogeneous entrainer.

**a.** I have studied the heteroazeotropic rectification with batch and continuous entrainer feeding by feasibility method. I have stated that the separation is feasible with the both methods. Moreover, the separation is feasible with continuous entrainer feeding if we feed the entrainer to the top plate (without rectification section).

**b.** I have studied the influence of the operational parameters and determined their possible limits.

*The possible limits of the operational parameters at batch entrainer feeding:*

- minimum number of rectification plate ($N_{r,min}$),
- minimum reflux ratio ($R_{min}$),
- minimum of entrainer ($SF_{0,min}$),
- maximum amount of entrainer ($SF_{0,max}$).

Moreover:

- The more is amount of the entrainer the higher is the recovery.
- In this case the application of heterogeneous liquid reflux flow is necessary for the to feasible separation.
- The optimum amount of entrainer ($SF_{0,opt}$) can be expexted.

*The possible limits of the operational parameters at continuous entrainer feeding:*

- minimum reflux ratio ($R_{min}$),
- minimum entrainer flow ($(F/V)_{min}$),
- maximum entrainer flow ($(F/V)_{max}$).

Moreover:

- An additional batch entrainer feeding (mixed feeding, $SF_0>0$) increases the recovery.

**c.** I have determined the steps of the processes.
*In the case of batch entrainer feeding:*

0. Addition of the whole quantity of E (SF) to the binary charge A-B.
1. Start up ($R=\infty$).
2. Production/withdrawal of one component of the binary charge (A or B).
3. Separation (purification) of the remaining component (B or A) from the entrainer.

*In the case of continuous (and mixed) feeding of the entrainer:*

0. Addition of a small quantity of E ($SF_0$) to the binary charge A-B (optional; mixed feeding).
1. Start up ($R=\infty$, $F=0$).
2. Production/withdrawal of one component of the binary charge (A or B) under continuous feeding of E ($F>0$).
3. Separation (purification) of the remaining component (B or A) from E ($F=0$).

### *3.2 Rigorous simulation calculations*

I have presented some rigorous calculation results for the separation of the mixture of DCM-acetone with water as entrainer by batch and continuous entrainer feeding. The rigorous simulation calculations were made by a professional flowsheet simulator.

Thesis 6 - Boundaries, influence of the column holdup

I have obtained that the boundaries (rectification and extractive) really exist and that their location can be determined by rigorous calculations. These boundaries limit the recovery. I have shown that the column holdup influences the location of boundaries. The increase of the column holdup the decreases recovery decreasing at considerable amounts of entrainer.

Thesis 7 - Influence of the operational parameters

I have analysed an industrial problem by rigorous simulation calculations in order to determine the optimum of operational parameters.

By binary batch distillation the removal of DCM was not possible since the relative volatility ($\alpha_{A,B}$) is very near to unity at low concentrations of acetone. Hence the application of an entrainer was necessary.

**a.** Batch addition of entrainer

First the traditional batch heteroazeotropic distillation was studied where the whole amount of entrainer is added in batch. I have concluded that two-phase reflux had to be applied and that the separation of the top condensate by decantation was not necessary since in this case the benefits of the phase separation were lost by the increase of the hold-up caused by the decanter.

I have studied the influence of the reflux ratio and the entrainer/charge ratio. I have established that there is an optimum of reflux ratio at higher entrainer/charge ratios.

**b.** Continuous entrainer feeding

I have verified also by rigorous simulation calculations that the separation is feasible even without rectification section (entrainer feeding to the top plate of the column). I have stated that from the point of view of the separation DCM-acetone in each case the optimum feed stage was the top plate of the column.

I have studied the effects of the variation of reflux ratio under different conditions (for example: constancy of entrainer and heat consumptions, constancy of entrainer consumption and distillate quantity).

I have found an optimum of reflux ratio under constant of entrainer and heat consumptions.

Thesis 8 - Mixed feeding

I was the first who has suggested the mixed feeding of the heterogeneous entrainer. I have combined the batch addition and continuous feeding of the entrainer by adding one part of entrainer to the charge (in Step 0; $SF_o$) in batch and the other part continuously (during Step 2; $SF_2$). For this mixed addition of entrainer I have studied the influence of the variation of the ratio $SF_o/(SF_o+SF_2)$ under constant overall entrainer and energy consumption. At the medium values of $SF_o/SF$ (e.g. at $SF_o/SF=0.5$) both the recovery of DCM and the loss of acetone was significantly more favourable than at the extreme values of $SF_o/SF$.

Comparing the batch addition, continuous feeding and mixed addition of the entrainer under constant energy and entrainer consumptions I have obtained the best results (highest recovery of DCM and lowest loss of acetone) by the mixed addition.

## 4. Application of the results

Not only the low-relative volatility mixture but also the azeotropes can be studied by the extended feasibility method. Moreover the „hybrid process" can be studied by this method.

In the thesis I have suggested solution for an industrial problem, which solution can be applied in the industry.

The batch heteroazeotropic rectification process presented can be applied for the solution other separation problems, mainly in the pharmaceutical industry, the production of the fine-chemicals and the regeneration of waste solvent mixtures.

The existing batch rectification equipment can be easily modified (with low cost) for the application of continuous and mixed entrainer feeding rectification. (It is enough to create a feeding facility and to apply a dosing pump.)

## 5. The continuation of the research

In the thesis I have studied the separation of a low relative volatility mixture by batch heteroazeotropic rectification (with batch and continuous entrainer feeding). In the future we will study the separation of minimum and maximum boiling point azeotropes.

We have already started to study the „hybrid process" by the new extended feasibility method.

In the last few years the more sophisticated configurations such as the middle vessel and multi-vessel columns were intensively studied. Our research group (Lang, Modla and Kotai) has already begun to study these sophisticated batch column configurations. It is worth to study the application of these column configurations for heteroazeotropic rectification.

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