

EFFICIENT APPROXIMATE METHOD FOR PACKED COLUMN SEPARATION PERFORMANCE SIMULATION

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ABSTRACT

Packed distillation and absorption columns are often modeled using equilibrium stages. However, determination of the packing height that corresponds to an equilibrium stage is not easy. For binary systems HETP values can be used, but these are not applicable to multicomponent systems because mass transfer rates of different components deviate from each other.

Rate-based non-equilibrium models can be used to overcome the problem of the HETP + equilibrium stage calculation method. Our efficient and approximate approach is different. It uses an equilibrium stage model with multicomponent efficiency factors for a certain packing height. These efficiencies are comparable to the multicomponent Murphree vapor phase efficiencies used for plate columns.

INTRODUCTION

The most common way to model and design packed distillation and absorption columns is to use ideal equilibrium stages. After achieving the required separation the packing height that corresponds to an equilibrium stage is estimated and the total required column height is calculated.

In case of binary systems HETP (Height Equivalent to a Theoretical Plate) values are used. These are available for many packing types and component pairs in the literature. For accurate results the component physical properties and flow conditions should be evaluated for each equilibrium stage used in simulation to get the corresponding HETP value for the equilibrium stage in question.

Multicomponent systems and binary systems in uncommon conditions could not be handled properly with HETP concept. In case of binary systems at uncommon conditions no experimental HETP values are available. On the other hand, multicomponent systems can not utilize HETP concept as such, because the mass transfer rates for different components in the system are not equal.

In order to overcome these HETP problems rate-based non-equilibrium models are used. In these models the mass transfer in vapor and liquid phases is taken into account. Thermodynamic phase equilibrium between vapor and liquid phases exists only in the phase interface. On both sides of the phase interface there are interfacial films that are the places where the mass transfer limitations exist. Further away from the phase interface there are bulk vapor phase and bulk liquid phase that are assumed to be perfectly mixed in each calculation segment. The rate-based non-equilibrium models are quite heavy to solve and a lot of physical property information that is not used by the equilibrium stage methods is required, e.g. viscosities, thermal conductivities, surface tension, diffusion coefficients etc. Also, mass transfer area and correlations for mass transfer rate for each type of packing are needed.

Our approach to model packed columns is different. We start from an equilibrium stage column model. For these models many efficient solution algorithms are available. We define the height of packing that is selected as a calculation segment. This segment height is then related to a mass transfer stage. We define multicomponent efficiencies for the selected packing height (mass transfer stage) that are used to correct the real mass transfer deviation from equilibrium stage solution in a similar way the multicomponent Murphree vapor phase plate efficiencies are used for plate columns. Therefore our calculation proceeds always in simulation mode, i.e. we do not directly calculate the height of packing needed to obtain the required separation. This is also the case with rate-based non-equilibrium model.

The model includes generalized Maxwell-Stefan multicomponent mass transfer calculations and thus we are able to predict for each component in each calculation segment its separation efficiency. Inversely, it is possible to calculate later the HETP value for each component in each calculation segment. The accuracy of the method is related to the number of calculation segments we specify for a certain packing height. As the calculation segment height decreases, i.e. the more segments we have for a certain packing height, the closer the solution gets to the rigorous integral solution of the column and at the same time more calculation effort is needed. Similarly, as in the case of rate-based models, a lot of physical property

information that is not used by the equilibrium stage methods is needed. Also, correlations for mass transfer rate and mass transfer area for each type of packing are needed.

We have implemented the packing calculation in flowsheeting program FLOWBAT [1] that already has similar multicomponent efficiency methods for plate columns (Ilme [2]). Thus we are able to calculate a column with any number of column sections having differing plate types, packing type and size, column diameter etc. Several correlations from literature have been implemented both for random and structured packing. Also, we have the capability in our program to evaluate column hydraulic performance, i.e. flooding, entrainment and pressure drops, simultaneously with the separation performance calculation. This allows us to evaluate the thermodynamic properties needed for separation performance simulation in real column conditions.

BACKGROUND

Mass Transfer Basics

The four simple and most commonly known theories for mass transfer in flows are film theory, penetration model, surface-renewal model and turbulent boundary layer model.

The whole mass transfer resistance in film theory is assumed to be in the thin stagnant volume at the interface of the turbulent phase. This stagnant volume is called film. The mechanism of mass transfer through the film is molecular diffusion (Holland [3]).

In separation processes usually two phases are present and both phases should be considered for total mass transfer resistances. Both phases then have a film at the interface and all mass transfer resistances are in these films. This two-film theory by Whitman [4] is much used for processes where the interface of the two phases is in equilibrium, the mass transfer rates are not too high and no surface-active components accumulate on the interface (Seader and Henley [5]).

The diffusion of component A from gas to liquid B in equilibrium conditions through gas film and liquid film is described with Fick's law as

$$N_A = \frac{(D_{AB})_G}{\delta_G} (c_{A_b} - c_{A_l})_G = \frac{(D_{AB})_L}{\delta_L} (c_{A_l} - c_{A_b})_L. \quad (1)$$

The determination of the film thickness is difficult and thus the mass transfer equation is written using mass transfer coefficients

$$N_A = k_L (c_{A_l} - c_{A_b}) = k_G (p_{A_b} - p_{A_l}). \quad (2)$$

Equation (2) holds when the system is dilute and equimolar counter diffusion can be assumed. There are numerous ways to calculate the mass transfer coefficients depending on the selection of driving force in the mass transfer equations.

Mass Transfer in Binary Systems

Equation (2) can be written for a packed tower using mole fractions as the driving force

$$N_A = k_G (y_{A_i} - y_{A_b}) = k_L (x_{A_b} - x_{A_i}). \quad (3)$$

According to the two-film theory there is an equilibrium condition at the interface:

$$K_A = \frac{y_{A_i}}{x_{A_i}}. \quad (4)$$

Normally, only the bulk conditions and compositions are known, so equation (3) is combined with equation (4) to give

$$N_A = \frac{x_{A_b} - y_{A_b}}{\frac{1}{K_A k_G} + \frac{1}{k_L}}. \quad (5)$$

If we define $y_A^* = K_A x_{A_b}$, then equation (5) can be written as

$$N_A = K_G (y_A^* - y_{A_b}) = \frac{y_A^* - y_{A_b}}{\frac{1}{k_G} + \frac{K_A}{k_L}}. \quad (6)$$

HTU, NTU and HETP

For a dilute system in a packed column we can write mass balance for the gas phase using symbols of figure 1 and a_{eff} meaning the effective interfacial area of the packing:

$$\dot{G} dy = K_G a_{eff} (y^* - y) A_C dz. \quad (7)$$

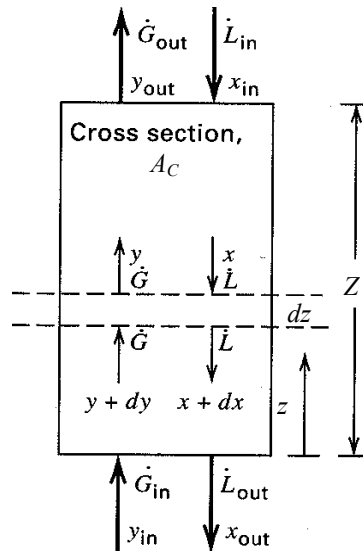


Figure 1. A section of a packed column.

By modifying and solving the equation (7) we get the height of the packing

$$Z = \frac{\dot{G}}{K_G a_{eff} A_C} \int_{y_{out}}^{y_{in}} \frac{dy}{y^* - y}. \quad (8)$$

It is commonly defined that

$$H_{OG} = \frac{\dot{G}}{K_G a_{eff} A_C} \quad (9)$$

and

$$N_{OG} = \int_{y_{out}}^{y_{in}} \frac{dy}{y^* - y}. \quad (10)$$

Equation (8) can then be written as

$$Z = H_{OG} N_{OG}. \quad (11)$$

H_{OG} is called the overall height of a transfer unit based on gas phase. Often it is called HTU for short. On the other hand N_{OG} is the overall number of transfer units based on gas phase, NTU for short.

When dealing with packed columns also the concept of equilibrium stages (ideal stages) is used (Stichlmair and Fair [6]):

$$Z = n H_{ETP}. \quad (12)$$

Here n is the number of equilibrium stages (ideal stages) and H_{ETP} is the height equivalent to a theoretical plate (HETP). HETP indicates the efficiency of the mass transfer. For binary systems the HETP value is the same for both components as the mass transfer efficiency is also the same for both components. According to Wesselingh [7] the HETP is almost constant for the whole packed column. HETP value can be used to evaluate the required height of packing for a column when equilibrium stage model is used to determine the number of equilibrium stages to obtain desired product qualities.

Methods for the Calculation of Binary Mass Transfer Coefficients and Specific Mass Transfer Area

The prediction of mass transfer coefficients using correlations is difficult because the mass transfer coefficients depend on the way the column packing is carried out and how well is the liquid distribution performed (Seader and Henley [5]). Often, when the height of a packed column is calculated the overall gas phase mass transfer coefficient K_G is used, as the mass transfer resistance lies usually in the gas phase:

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{m}{k_L}. \quad (13)$$

In distillation the vapor/liquid-equilibrium curve is not generally linear and thus m is the local slope of the equilibrium curve:

$$m = \frac{d y^*}{d x}. \quad (14)$$

In binary systems the slope of the equilibrium curve changes along the height of the column. On the hand, for multicomponent systems the slope is different for each component.

There are a number of correlations for the calculation of binary mass transfer coefficients and specific mass transfer area. Onda *et al.* [8], Bravo and Fair [9], Billet and Schultes [10] and Gualito *et al.* [11] have published correlations for random packing, while Bravo *et al.* [12], Fair and Bravo [13], Fair and Bravo [14], Billet and

Schultes [10] and Rocha *et al.* [15] have published methods for structured packing. Generally, it can be said that these correlations are based on rather small columns and a limited number of different component pairs. The applicability of a certain correlation should be evaluated for the system in question (Ilme [2]).

The HETP values can also be calculated for binary systems from some published correlations. Vital *et al.* [16] have reviewed HETP correlations published before 1984. Rules of thumb to estimate the HETP values have been presented by Kister [17]. Wagner *et al.* [18] and Lockett [19] have recently published correlations for HETP calculation of binary systems.

Mass Transfer in Multicomponent Systems

In ideal multicomponent systems the components present in the mixture do not have effect on each other. The components in such systems are of similar size and structure and they are not polar or just slightly polar. On the other hand in non-ideal systems there exist interactions between components that differ from other components in respect to size, character, polarity and hydrogen bonding tendency. Liquid/liquid-splitting and azeotropy are marks for heavy non-ideality.

In a thermodynamically ideal non-polar system the HTU or HETP values for different components are identical. On the contrary, in a thermodynamically non-ideal system the thermodynamic and physical properties in vapor and liquid are different for each component leading also to different HTU and HETP values for each component. In these systems the diffusion rate of a component does not depend only of the diffusivity of that component but also from the diffusivities of the other components in the mixture (Ilme [2]).

The diffusion in a multicomponent system is very complicated compared to binary systems. It is possible to have diffusion against concentration gradient (reverse diffusion); no diffusion although a concentration gradient exists (diffusion barrier) or diffusion while there is any driving force (osmotic diffusion). According to Seader and Henley [5] this can lead in multicomponent systems to HTU and HETP values in the range $[-\infty, +\infty]$. These strange phenomena are caused by the fact that the driving force is not the one used (concentration gradient) in calculations, but it is the gradient of chemical potential, see Wesselingh [7] or Khoury [20].

Multicomponent mass transfer is best described with Maxwell-Stefan diffusion equations. These are used in connection with film theory. Two classes of solution methods for Maxwell-Stefan equations have been presented: linearized theory and so called exact solution.

Following the presentation by Taylor and Krishna [21] we arrive to equation (15) when the total mole flux is nearly to zero, the diffusion is equimolar and the mass transfer coefficients do not depend on the mole fluxes of the phases.

$$[K_{OG}]^{-1} = [k_G]^{-1} + \frac{c_G}{c_L} [M] [k_L]^{-1} \quad (15)$$

Taylor and Krishna [21] have defined the matrices $[R_G]$ and $[R_L]$ for gas and liquid phases, respectively, to calculate the mass transfer coefficients. Equations (16) and (17) give the elements of these matrices.

$$R_{i,i} = \frac{z_i}{\kappa_{i,nc}} + \sum_{\substack{k=1 \\ k \neq i}}^{nc} \frac{z_k}{\kappa_{i,k}} \quad (16)$$

$$R_{i,j} = -z_i \left(\frac{1}{\kappa_{i,j}} - \frac{1}{\kappa_{i,nc}} \right) \quad (17)$$

In equations (16) and (17) z_i is the mole fraction of component i in gas or liquid phase and $\kappa_{i,j}$ is the zero flux mass transfer coefficient for component pair i, j . Making another definition and equation manipulation Taylor and Krishna [21] finally arrive at

$$[K_{OG}]^{-1} = [R_G] + \frac{c_G}{c_L} [K][R_L]. \quad (18)$$

In case of non-equimolarity so called bootstrap matrices must also be included and they are calculated for nearly ideal system from the enthalpies of vaporization or in more non-ideal system using the differences between vapor and liquid partial molar enthalpies.

Multicomponent Mass Transfer in Packed Columns

Based on figure 2 by Taylor and Krishna [21] the mass balance for gas phase can be written:

$$\dot{G} \frac{dy_i}{dZ} = -J_{G,i} a_{eff} A_c. \quad (19)$$

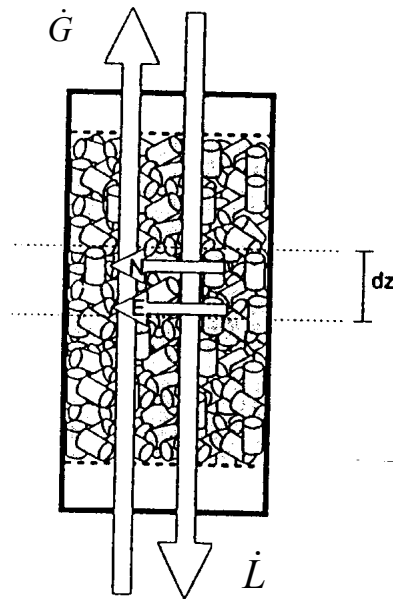


Figure 2. Packed column (Taylor and Krishna [21]).

Equation (19) can be given in matrix form

$$\dot{G} \frac{d(y)}{dZ} = -(J_G) a_{eff} A_c. \quad (20)$$

This leads to equation (21)

$$\dot{G} \frac{d(y)}{dz} = c_G [K_{OG}] (y^* - y) a_{eff} A_c. \quad (21)$$

Equation (21) can be expressed in dimensionless form (Taylor and Krishna [21]) as

$$\frac{d(y)}{d\zeta} = [N_{OG}] (y^* - y), \quad (22)$$

where $\zeta = z/Z$ dimensionless height of the packing and
 $[N_{OG}]$ matrix of overall numbers of mass transfer units.

The matrix of overall numbers of mass transfer units, $[N_{OG}]$, can be expressed as

$$[N_{OG}] = c_G [K_{OG}] \frac{a_{eff} Z A_c}{\dot{G}} = [K_{OG}] \frac{a_{eff} Z}{u_{SG}}. \quad (23)$$

When equation (18) is combined with (23) we get

$$[N_{OG}]^{-1} = [N_G]^{-1} + \frac{\dot{G}}{\dot{L}} [K] [N_L]^{-1}. \quad (24)$$

The inverse matrices $[N_G]^{-1}$ and $[N_L]^{-1}$ are defined by Taylor and Krishna [21] as

$$[N_G]^{-1} = \frac{[R_G] u_{SG}}{a_{eff} Z} \quad (25)$$

and

$$[N_L]^{-1} = \frac{[R_L] u_{SL}}{a_{eff} Z}. \quad (26)$$

The height of mass transfer unit for vapor phase is defined as

$$[H_G] = \frac{[R_G] u_{SG}}{a_{eff}}. \quad (27)$$

Similarly for liquid phase

$$[H_L] = \frac{[R_L] u_{SL}}{a_{eff}}. \quad (28)$$

The matrix of overall heights of mass transfer units, $[H_{OG}]$, can be expressed as

$$[H_{OG}] = [H_G] + \frac{\dot{G}}{\dot{L}} [K] [H_L]. \quad (29)$$

Ilme [2] has given the corresponding overall height of a transfer unit when the bootstrap matrices $[\beta_G]$ and $[\beta_L]$ are taken into account:

$$[H_{OG}] [\beta_G]^{-1} = [H_G] [\beta_G]^{-1} + \frac{\dot{G}}{\dot{L}} [K] [H_L] [\beta_L]^{-1}. \quad (30)$$

Finally the HETP matrix, $[H_{ETP}]$, can be calculated, analogously to binary systems, consisting of the elements (Taylor and Krishna [21]):

$$H_{ETP_{ij}} = \begin{cases} H_{OG_{i,j}} \frac{\ln \lambda_{ij}}{\lambda_{ij} - 1}, & \lambda_{ij} \neq 1 \\ H_{OG_{i,j}}, & \lambda_{ij} = 1 \end{cases} \quad i, j = 1, 2, \dots, nc-1 \quad (31)$$

Here the matrix of stripping factors $[\lambda]$ is defined as

$$[\lambda] = [M] \frac{\dot{G}}{\dot{L}} \quad (32)$$

EFFICIENCY OF PACKED COLUMNS

Murphree Vapor Phase Plate Efficiency

We shortly review Murphree vapor phase plate efficiency to better describe our definition of efficiency for packed columns. Based on figure 3 we can define the Murphree vapor phase plate efficiency as

$$E_{mv} = \frac{\bar{y}_n - \bar{y}_{n-1}}{y_n^* - \bar{y}_{n-1}} \quad (33)$$

where E_{mv} Murphree vapor phase plate efficiency,
 \bar{y}_{n-1} the average composition of vapor coming to plate n from plate below,
 \bar{y}_n the average composition of vapor leaving plate n to plate above, and
 y_n^* the vapor composition that is in equilibrium with the average composition of the liquid leaving from plate n .

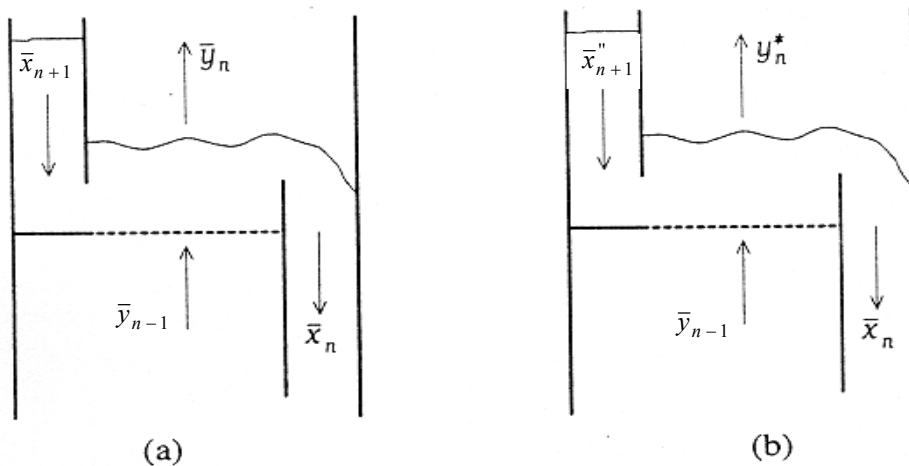


Figure 3. Definition of Murphree vapor phase plate efficiency. (a) A real plate. (b) A theoretical plate to define the Murphree vapor phase plate efficiency (\bar{x}_{n+1} is the liquid flow from plate above to the ideal plate). (Ilme [2])

If we take a look at the definition of the Murphree vapor phase plate efficiency in equation (33) we can see that in multicomponent systems in each plate of the column the efficiencies are different for each component. Additionally, when we have concentration maxima and minima inside the column the E_{mv} values can take values between $[-\infty, +\infty]$ as the divisor can be about zero. This does not pose a big problem

as in these situations no concentration changes for these components occur and the E_{mv} values can in practice be limited to a suitable interval.

Multicomponent Efficiency for Packed Columns

Equation (22) can be expressed as

$$\frac{d(y)}{dz} = [H_{OG}]^{-1} (y^* - y) \quad (34)$$

Figure 4 (Kister [17], p. 523 with modified symbols) shows the binary system equilibrium curve describing the mass transfer in a packed column.

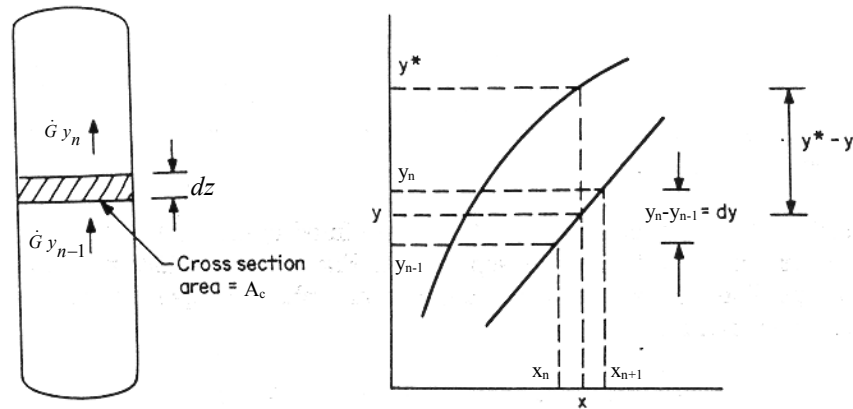


Figure 4. Mass transfer in a packed column.

The equilibrium vapor concentration y^* cannot be taken as a constant for a segment of the packing bed. This is due to the fact that liquid and vapor flow in opposite directions and thus the equilibrium vapor concentration y^* changes along the height of the packing according to the composition change of the liquid phase. Thus, if we like to calculate the vapor composition at a certain height of the packing we need to integrate the equation (34) numerically.

The numerical integration of equation (34) can be avoided when the term $(y^* - y)$ is approximated with arithmetic mean value for a limited segment height. Then for the segment number n we have

$$(y)_n - (y)_{n-1} = Z_n [H_{OG}]_n^{-1} \left(\frac{[K]_n (x)_n + [K]_{n+1} (x)_{n+1}}{2} - \frac{(y)_n + (y)_{n-1}}{2} \right), \quad (35)$$

- where y_n the vector of gas concentration leaving segment n ,
 y_{n-1} the vector of gas concentration entering segment n ,
 x_n the vector of liquid concentration leaving segment n ,
 x_{n+1} the vector of liquid concentration entering segment n ,
 Z_n the height of segment n ,
 $[H_{OG}]_n$ the matrix of overall heights of mass transfer units in segment n ,
 $[K]_n$ the diagonal matrix of (VLE) K values corresponding to liquid concentrations x_n , and
 $[K]_{n+1}$ the diagonal matrix of (VLE) K values corresponding to liquid concentrations x_{n+1} .

Now we define for packed columns the efficiency as, see figure 4 (similarly to the Murphree vapor phase plate efficiency of equation (33)):

$$E = \frac{y_n - y_{n-1}}{y_n^* - y_{n-1}}. \quad (36)$$

This definition can be applied for all components, so that all terms in equation (36) can have the component index. Now we define a diagonal matrix $[A]_n$ having as the diagonal elements the reciprocals of term $(y_n^* - y_{n-1})$ for $nc-1$ components.

$$[A]_n = \begin{bmatrix} \frac{1}{y_{1,n}^* - y_{1,n-1}} & 0 & \dots & 0 \\ 0 & \frac{1}{y_{2,n}^* - y_{2,n-1}} & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & \frac{1}{y_{nc-1,n}^* - y_{nc-1,n-1}} \end{bmatrix} \quad (37)$$

This leads to the following expression to calculate the efficiencies for each component in segment n of a packed column.

$$(E)_n = [A]_n \frac{Z_n}{2} [H_{OG}]_n^{-1} ([K]_n(x)_n + [K]_{n+1}(x)_{n+1} - (y)_n - (y)_{n-1}) \quad (38)$$

As an example the efficiency for component $i=1$ in a three component system for packing segment n we get by using equation (38):

$$E_{i,n} = \frac{Z_n}{y_{1,n}^* - y_{1,n-1}} \frac{2}{2} [H_{OG_{11}} (K_{11,n}x_{1,n} + K_{12,n}x_{2,n} + K_{11,n+1}x_{1,n+1} + K_{12,n+1}x_{2,n+1} - y_{1,n} - y_{1,n-1}) + H_{OG_{12}} (K_{21,n}x_{1,n} + K_{22,n}x_{2,n} + K_{21,n+1}x_{1,n+1} + K_{22,n+1}x_{2,n+1} - y_{2,n} - y_{2,n-1})]. \quad (39)$$

Description of the Method and Its Implementation

The method described in previous section has been implemented to in-house flowsheeting simulation program called FLOWBAT [1]. There are several column models in the program to describe distillation: distillation simulation module with rigorous plate efficiency calculation called DISTI (with inside out algorithm using Newton method or relaxation method), model for column/stripper/absorber COLUMN with a specific solution algorithm suitable for strippers and absorbers, reactive distillation column model RDISTI, reactive distillation column model combined with side reactor models RRDIST, and reactive rate-based distillation model DESIGNER. Aittamaa [22] originally started using multicomponent plate efficiencies in distillation calculation in DISTI. Later this approach was further developed by Ilme [2]. These methods have been extensively tested by Ilme [2], Klemola [23], Jakobsson [32] and also for industrial columns by Ilme *et al.* [24] and Jakobsson *et al.* [25].

The above articles present the method and its program implementation in quite detail. In order to handle all kinds of distillation and absorption columns further development on the use of efficiencies have been done for packed columns, both for random packing and structured packing. The correlations and calculation methods presented in literature for column hydraulics and pressure drops have been collected by Kleine [26]. Their program implementation has been completed with the realization of the packing efficiency method described in this paper. This work has

mostly been carried out by Kinnunen [27]. The mass transfer correlations currently implemented are given in references [8] to [15].

In FLOWBAT it is possible to define all distillation and absorption columns consisting of a number of sections. Each section can have its own plate type or packing type, column diameter etc. Thus it is possible to calculate columns with varying diameter and having both plates and packing. These calculations proceed in simulation mode. This means that the column internals have to be described in detail and then the column hydraulic and separation performances can be evaluated at the same time. If the result is not satisfactory, then modification to the column internals should be made and the column is recalculated.

The calculation for packing proceeds as follows. The whole height of packing is divided into a number of segments. Each of the segments corresponds then to a mass transfer stage in the distillation calculation. The obtained packing efficiencies are used to correct the compositions in the distillation solver in a similar manner as Murphree vapor phase plate efficiencies are used. The algorithm below is repeated for each of the segments to get the efficiency during that distillation solver iteration:

1. Evaluate the average conditions of the phases and their average compositions in addition to the properties of the packing.
 - Composition and properties of the phases.
 - Vapor and liquid flow rates.
 - Parameters of the packing.
2. Calculate the binary diffusion coefficients for all component pairs both for vapor and liquid phases.
3. Calculate the mass transfer coefficients for component pairs both for vapor phase and liquid phase using one of the methods of references [8] to [15].
4. Calculate the inverse matrices of mass transfer coefficients both for vapor phase and liquid phase using equations (16) and (17).
5. Evaluate the matrices of the heights of the mass transfer units both for vapor phase and liquid phase using equations (27) and (28).
6. Calculate the matrix of (VLE) K values.
7. Evaluate using equation (29) or (30) the matrix of overall heights of mass transfer units.
8. Finally calculate the efficiency defined by equation (36).

In step 7 above it is possible to use various methods. Equation (29) is simpler and suitable for thermodynamically quite ideal systems. When the mass transfer is non-equimolar and system non-ideal then bootstrap matrices should be used and equation (30) is selected.

It is possible to control the distillation calculation so that first the column is converged with fixed efficiencies, say 75 % for each component in each mass transfer stage. Then pressure drop calculation can be added if desired. As a final step the individual component efficiencies are brought in to the calculation. On the other hand, if the system is highly non-ideal and selected packing segment heights are not close to HETP values, it might be better to have the efficiencies in the calculation right from the beginning to ensure better convergence.

Approximations in the Model

We have already discussed about some of the approximations done in this method. If we inspect equations (22) and (34) and compare these to our basic equation (35), we can see that our method is closer to the integral solution of (34) when smaller segment heights we select. On the other hand, if the segment heights are too small and correspondingly the efficiencies for these segments are very low we have a large number of equilibrium stages in the distillation column solver and this might lead in to some numerical convergence problems.

If the selected packing segment height for the calculation is too high (say many times the approximated HETP value for the packing) then during the calculations numerical problems may easily arise and additionally the accuracy is not good. Some idea of the suitable segment height helps in getting good results.

It is possible to evaluate the bootstrap matrices if desired. This leads into a more accurate solution but more computational effort is needed. For non-ideal systems or systems having components of very different size the use of bootstrap matrices is recommended.

EXAMPLE CALCULATIONS OF LITERATURE TEST SYSTEMS

This kind of complex model requires comparison with real experimental data. Most of the published packed column data is from binary system with rather small columns. Recently, Pelkonen *et al.* [28] published multicomponent packed column data for structured packing. They also give a list of available published articles on other multicomponent structured packing experiments in which there are composition measurements along the packing height. This kind of data is most valuable for method validation.

Kinnunen [27] studied with the modeling approach we present in this paper the following multicomponent packed column systems:

- Acetone/methanol/methylacetate in a 79 mm diameter column where the packing height of 6.3 mm Raschig rings was varied from 0 to 680 mm and the column operated under total reflux, see Arwika [29].
- Methanol/2-propanol/water in a 100 mm diameter column where Sulzer CY packing height was 800 + 800 mm and the column operated under total reflux, see Górak and Vogelpohl [30].
- Methanol/acetone/water in a 100 mm diameter column where Rombopack 6M packing had a total of height of 3000 mm and two feeds were introduced into the column in different levels between the 1000 mm packing sections, see Pelkonen *et al.* [31].

Description of the Test Case

In this paper we deal only with the acetone/methanol/methylacetate case by Arwika [29]. This column had a diameter of 79 mm and it was operated in normal atmospheric pressure. The column was stabilized in total reflux conditions so that measured vapor and liquid flows were 0.019 mol/s. The height of the packing (6.3 mm Raschig rings) was changed between 0 and 680 mm. The concentrations have been measured from below and above the packing. Table 1 shows the experimental data of Arwika.

Table 1. Experimental data of Arwika [29] for liquid concentrations in system with components acetone/methanol/methylacetate, when the column in total reflux condition had vapor and liquid flows of 0.019 mol/s.

Height of packing [cm]	Acetone [-]	Methylacetate [-]	Methanol [-]
68.0 composition above the packing	0.196	0.373	0.431
43.0	0.198	0.315	0.488
26.0	0.181	0.270	0.548
23.0	0.185	0.280	0.535
15.0	0.169	0.252	0.579
10.0	0.165	0.234	0.600
5.0	0.154	0.213	0.633
0.0 composition below the packing	0.121	0.140	0.740
reboiler	0.073	0.070	0.856

Comparison of Model Results with Experimental Data

The column was simulated using the methods described in this paper using flow-sheeting program FLOWBAT. The total reflux situation was approximated by suitable means and thus the inner column vapor and liquid flows were adjusted to correspond to the experimental value 0.019 mol/s.

The component system acetone/methylacetate/methanol is quite non-ideal and thus the Wilson model was selected as the VLE model. Other physical property methods were selected to suit this ternary system from the methods available in FLOWBAT. The basic pure component parameters were retrieved from the databank of FLOWBAT. The VLE and other property calculation methods and parameters were not specifically tuned for this simulation and the Wilson parameters were taken from DECHEMA data books.

The first simulation was carried out using 430 mm total height of packing. This was divided into 20 segments of equal height, meaning 21.5 mm for a segment. In addition to that also the ideal reboiler and ideal condenser were used in simulation.

In the simulation model each of the segments correspond to an equilibrium stage whose concentrations are corrected using the efficiencies calculated by the method described in this paper.

The calculation used equation (29); i.e. no bootstrap matrices were included. The 6.3 mm Raschig ring asks for a suitable mass transfer calculation correlation and from the ones available the methods by Onda *et al.* [8] and Bravo and Fair [9] suited for this case and they also had published parameters available. For comparison we also simulated the same case using efficiencies equal to 1 for all components in all stages. This corresponds to the assumption of 21.5 mm for HETP and is marked as "ideal" in figure 5.

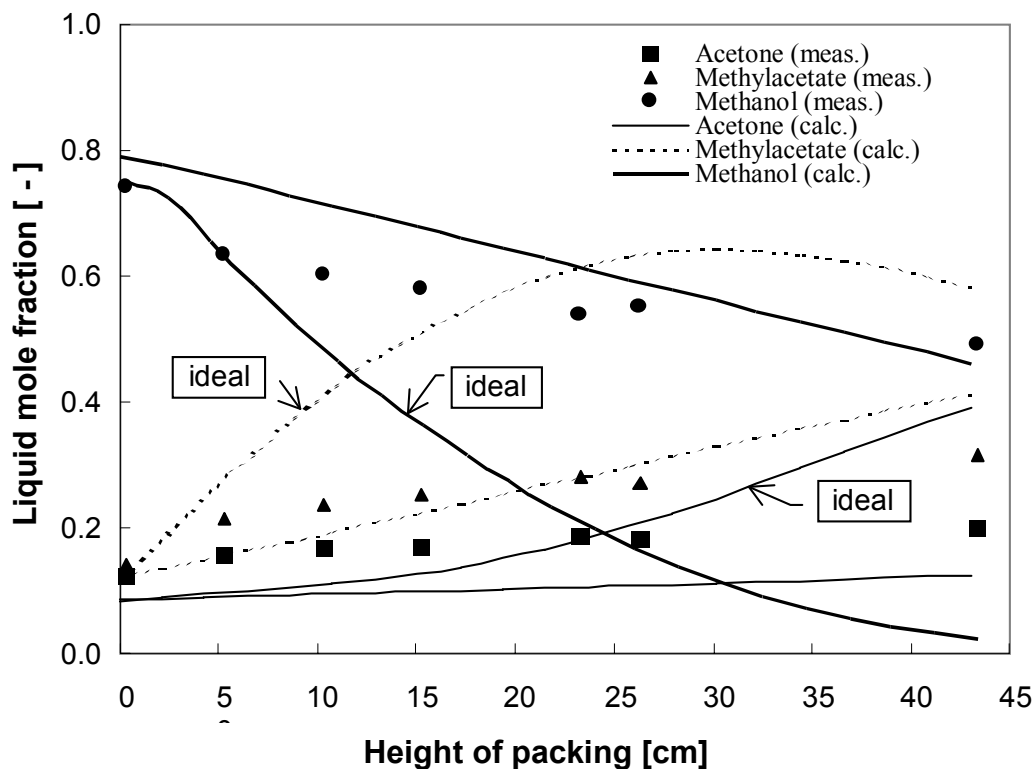


Figure 5. Measured and simulated liquid concentrations for the Arwika [29] case. Column had total reflux. The selected segment height was 21.5 mm and the Onda *et al.* [8] mass transfer model was used.

It is easy to see from figure 5 that for the "ideal" simulation case the guess of a HETP value of 21.5 mm was a too small value. Qualitatively the efficiency-based model gives reasonable accuracy in this case. We also changed the segment height and correspondingly the number of segments, but the concentration curves of the efficiency-based calculation practically overlapped with the ones in figure 5. This indicates that our method is not very sensitive for the selection of the segment height and the approximation of the rigorous integral method is good.

Table 2 shows the comparison of the same case as above but using the mass transfer correlations by Onda *et al.* [8] and Bravo and Fair [9]. It is easy to see that just the change of the mass transfer coefficient correlation and specific mass transfer area calculation method makes some difference in the results.

Table 2. Computed liquid concentrations for the Arwikar [29] case consisting of acetone/methylacetate/methanol.

Segment number [-]	Height of packing [cm]	Method for mass transfer coefficients and specific mass transfer area: Onda <i>et al.</i> [8]			Method for mass transfer coefficients and specific mass transfer area: Bravo and Fair [9]		
		Acetone [-]	Methyl acetate [-]	Methanol [-]	Acetone [-]	Methyl acetate [-]	Methanol [-]
22 (condenser)	43.0 composition above the packing	0.1250	0.4133	0.4616	0.1337	0.4523	0.4140
21	40.9	0.1223	0.3999	0.4778	0.1300	0.4381	0.4319
20	38.7	0.1197	0.3862	0.4941	0.1266	0.4234	0.4500
19	36.6	0.1173	0.3722	0.5105	0.1234	0.4083	0.4683
18	34.4	0.1150	0.3580	0.5271	0.1204	0.3928	0.4869
17	32.3	0.1128	0.3435	0.5437	0.1176	0.3768	0.5056
16	30.1	0.1107	0.3289	0.5604	0.1149	0.3606	0.5245
15	28.0	0.1087	0.3141	0.5772	0.1124	0.3440	0.5435
14	25.8	0.1068	0.2992	0.5940	0.1101	0.3271	0.5628
13	23.7	0.1050	0.2841	0.6109	0.1079	0.3100	0.5821
12	21.5	0.1032	0.2690	0.6278	0.1058	0.2927	0.6015
11	19.4	0.1015	0.2538	0.6447	0.1037	0.2752	0.6210
10	17.2	0.0998	0.2386	0.6616	0.1018	0.2576	0.6406
9	15.1	0.0981	0.2234	0.6785	0.0999	0.2400	0.6601
8	12.9	0.0965	0.2083	0.6952	0.0979	0.2224	0.6796
7	10.8	0.0947	0.1934	0.7119	0.0960	0.2050	0.6990
6	8.6	0.0930	0.1787	0.7284	0.0940	0.1877	0.7183
5	6.5	0.0911	0.1642	0.7446	0.0920	0.1708	0.7373
4	4.3	0.0892	0.1501	0.7607	0.0898	0.1543	0.7560
3	2.2	0.0872	0.1364	0.7764	0.0875	0.1383	0.7742
2	0.0 composition below the packing	0.0851	0.1232	0.7917	0.0851	0.1229	0.7920
1 (reboiler)	Composition in the reboiler	0.0730	0.0689	0.8521	0.0730	0.0689	0.8581

HETP and HTU Values and Efficiencies

The calculated multicomponent HETP and HTU values for our test case are given in table 3. Again the results are for the Onda *et al.* [8] correlation. This information is also shown in figure 6. It is easy to see that even for this short column the HTU and HETP values for the components change quite much. The big difference between the components should also be noted.

The calculated efficiencies of the components as a function of the height of the packing bed are reported in table 4 and figure 7. Here also the same 21.5 mm segment height was used in simulation, i.e. efficiency for segment of 21.5 mm.

Table 3. Calculated HETP and HTU values for the components at different points of the packing height for the acetone/methylacetate/methanol case.

Height of packing [cm]	HETP [cm]			HTU [cm]		
	Acetone	Methyl acetate	Methanol	Acetone	Methyl acetate	Methanol
41.9	7.1	7.4	8.0	7.4	7.9	7.6
39.8	7.2	7.5	8.1	7.4	8.0	7.7
37.6	7.2	7.6	8.2	7.5	8.1	7.8
35.5	7.2	7.7	8.4	7.5	8.2	7.9
33.3	7.3	7.7	8.5	7.6	8.4	8.0
31.2	7.3	7.8	8.6	7.6	8.5	8.1
29.0	7.4	7.9	8.7	7.6	8.6	8.2
26.9	7.4	8.0	8.8	7.7	8.7	8.3
24.7	7.5	8.0	9.0	7.7	8.9	8.5
22.6	7.5	8.1	9.1	7.8	9.0	8.6
20.4	7.6	8.2	9.2	7.8	9.2	8.8
18.3	7.6	8.3	9.4	7.9	9.4	8.9
16.1	7.7	8.4	9.5	8.0	9.6	9.1
14.0	7.7	8.5	9.7	8.0	9.8	9.2
11.8	7.8	8.5	9.9	8.1	10.0	9.4
9.7	7.9	8.6	10.0	8.2	10.2	9.6
7.5	8.0	8.7	10.2	8.4	10.4	9.7
5.4	8.1	8.8	10.4	8.5	10.6	9.9
3.2	8.2	8.9	10.6	8.6	10.9	10.1
1.1	8.3	9.0	10.8	8.8	11.1	10.3

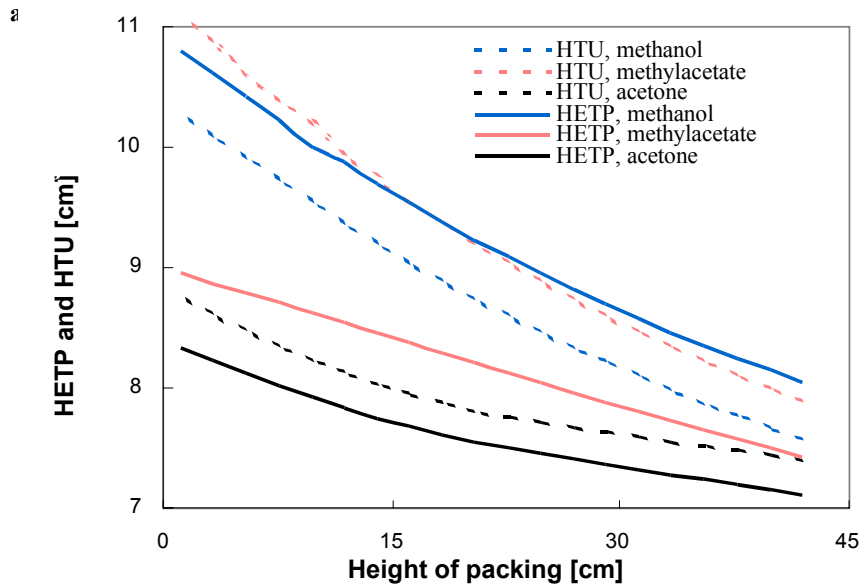


Figure 6. Calculated HETP and HTU values for the different components as functions of the height of the packing.

Table 4. The calculated efficiencies of the 21.5 mm packing segments.

Height of packing [cm]	Efficiency of different components for a 21.5 mm segment of packing [-]		
	Acetone	Methylacetate	Methanol
41.9	0.294	0.277	0.280
39.8	0.292	0.274	0.276
37.6	0.291	0.270	0.273
35.5	0.289	0.267	0.269
33.3	0.288	0.263	0.265
31.2	0.286	0.260	0.262
29.0	0.285	0.256	0.258
26.9	0.283	0.252	0.254
24.7	0.281	0.249	0.251
22.6	0.280	0.245	0.247
20.4	0.278	0.241	0.243
18.3	0.276	0.237	0.239
16.1	0.273	0.233	0.235
14.0	0.270	0.229	0.231
11.8	0.267	0.225	0.227
9.7	0.264	0.221	0.223
7.5	0.260	0.216	0.218
5.4	0.256	0.212	0.214
3.2	0.252	0.208	0.210
1.1	0.248	0.204	0.206

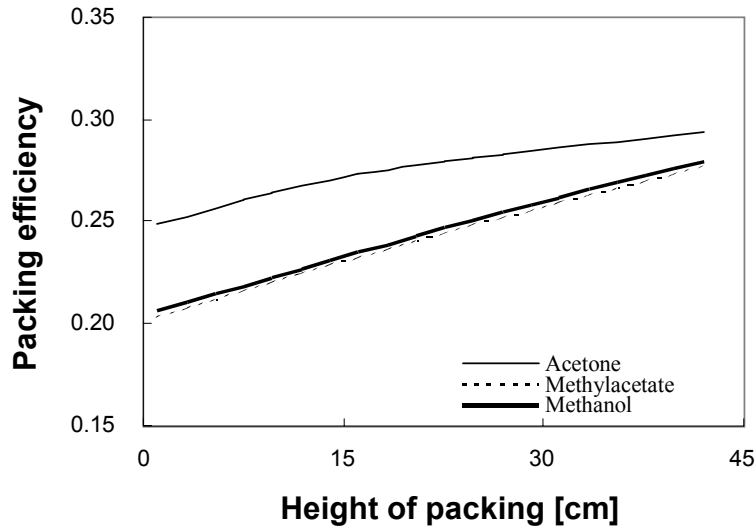


Figure 7. Efficiency of a 21.5 mm segment of packing as function of the location in the column. Efficiency of components is different.

When inspecting the results in table 4 and figure 7 it should be noted that these efficiencies are now given for 21.5 mm segment height of packing. These values are used to correct the mass transfer in the segment.

DISCUSSION AND CONCLUSIONS

Based on our test runs on the FLOWBAT flowsheeting program the column predictions are very realistic showing the success of the method presented in this paper. There are some discrepancies between experimental data and simulations, these might result from:

- Accuracy of the VLE-models.
- Accuracy of other physical properties: densities, viscosities, and especially diffusion coefficients.
- Our model has some approximations as discussed above.
- The mass transfer correlations of publications [8] to [15] implemented in the software. There is some deviation between simulation results with different mass transfer correlations. Many of the correlations are based on limited number of binary component pairs and it is possible that the physical properties are therefore not taken into account properly in the correlations.

The method has still to be verified using more experimental data. The data available for multicomponent systems in the literature is quite limited, especially if such data is sought that has measured compositions along the height of the packing.

The method can only be as accurate as are the methods used to calculate the binary mass transfer coefficients. This indicates that for different packing types the mass transfer correlations should be developed using as many different component pairs as possible to have fully the effect of physical properties on the models. Also, these binary mass transfer correlations should have as wide vapor and liquid loading conditions as possible.

Our calculations clearly show that each component can have different mass transfer characteristics inside one column as the composition and temperature change along the column. These leads to the conclusion that simple binary component system based HETP methods are not adequate enough for accurate absorption and distillation column design. Instead, our approach of using multicomponent mass transfer models to calculate the component efficiencies provides a more reliable way to estimate the real column performance. Another alternative to our model would be a rate-based non-equilibrium model that also takes into account the different mass transfer rates of the components. Our experience up to now shows that our method is fast because it uses the solution algorithms developed for the equilibrium stage distillation model that have been fine-tuned for fast calculation and robustness over the years.

NOMENCLATURE

$[A]$	diagonal matrix consisting of reciprocals of $(y_n^* - y_n)$, -
A_C	column cross-sectional area, m^2
a_{eff}	specific mass transfer area of the packing, m^2/m^3
c	concentration, mol/m^3
D	diffusion coefficient, m^2/s
d_i	driving force for component i in mass transfer, m^{-1}
E	packing segment vapor phase efficiency, -
E_{mv}	Murphree vapor phase plate efficiency, -
G_L	liquid mass flux, $kg/(s\ m^2)$
\dot{G}	gas mole flow, mol/s
$[K]$	diagonal matrix of vapor/liquid equilibrium K values, -
$[K_{OG}]$	gas phase zero flux overall mass transfer coefficient matrix, $mol/(s\ m^2)$
k	mass transfer coefficient, m/s
$[k_L]$	matrix of zero flux liquid phase mass transfer coefficients, $mol/(s\ m^2)$
$[k_G]$	matrix of zero flux gas phase mass transfer coefficients, $mol/(s\ m^2)$
H_{ETP}	HETP (Height Equivalent to a Theoretical Plate), m
H_G	height of mass transfer unit based on gas phase, m
H_{OG}	height of overall mass transfer unit based on gas phase, m
H_L	height of mass transfer unit based on liquid phase, m
J	diffusion flux, $mol/(s\ m^2)$
L	liquid mass flux, $kg/(s\ m^2)$
\dot{L}	liquid mole flow, mol/s
$[M]$	matrix of slopes of (VLE) equilibrium curves, -
m	slope of (VLE) equilibrium curve, -
(N)	vector of mole fluxes, $mol/(s\ m^2)$
N	mole flux, $mol/(s\ m^2)$
$[N_{OG}]$	matrix of overall numbers of mass transfer units, -
N_t	total mole flux, $mol/(s\ m^2)$
n	equilibrium stage number, -
n_i	mole amount of component i , mol
P	total pressure, Pa
$[R]$	inverse matrix of binary mass transfer coefficients, $m^2\ s/mol$
T	temperature, K

u_S	superficial velocity, m/s
x	mole fraction of component in liquid phase, -
y	mole fraction of component in gas phase, -
\bar{y}	average mole fraction of component in gas phase, -
Z	total height of packing, m
z	height of packing, m
z_i	mole fraction of component i in gas or liquid phase, -
$[\beta_G]$	bootstrap matrix for gas phase, -
$[\beta_L]$	bootstrap matrix for liquid phase, -
δ	film thickness, m
δ_{ij}	Kronecker delta (1, if $i = j$ and 0, if $i \neq j$), -
ζ	dimensionless height of packing ($= z / Z$), -
κ_{ij}	zero flux binary mass transfer coefficient for component pair ij , m/s
λ	stripping factor, -

Subscripts

b	bulk phase
G	gas or vapor
I	interface of phases
i	component i
j	component j
nc	total number of components present in system
L	liquid
n	segment n

Superscripts

* equilibrium

Abbreviations

HETP	H_{ETP}	height equivalent to a theoretical plate
HTU	H_{OG}	height of a transfer unit
NTU	N_{OG}	number of transfer units

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