A Simple Method for Simulation of Stationary and Non-stationary Operation of Trayed Distillation Column

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A numerical method was developed for the analysis of the stationary and non-stationary operation of distillation columns, for mathematical model based on the concept of a theoretical tray and the ideal mixing of the phases on the tray. The approximation of the phase equilibrium equation by its Taylor polynomial is used for solving the system of equations representing the mathematical model of the column. The method was successfully applied in the analysis of the multi-component azeotropic mixtures distillation.

Keywords: azeotrope, distillation, mathematical modelling, phase equilibria

Non-linear nature of the equations that describe the operation of the distillation columns is the greatest problem in the simulation of their work for both stationary and non-stationary operating conditions. Various numerical methods were developed for purpose of column simulation i.e. for solving the system of equations that present the column mathematical model [1 - 3]. In case of stationary operation of the column the non-linearity of the mathematical model comes from the non-linearity of the phase equilibria equations. In case of the simulation of non-stationary column, non-linearity is also connected to the equation of fluid-dynamic characteristics of the trays [4, 5].

The assumption of constant relative volatility is often used in engineering practice, and the models that include this concept are frequently applied to the analysis of column operation. Main advantage of this concept is the significant simplification of the calculating procedure, especially for stationary operating conditions. Unfortunately, there is a large number of mixtures where the assumption of constant relative volatility is not applicable at all. Thus, nowadays the analyses based on the assumption of constant relative volatility are not often used, giving up the place to more complex numerical methods for calculation of the phase equilibrium.

The UNIQAC method is, according to [6], one of the often used methods for the design of new plants and the analysis of existing plants. This method yields excellent results, based on the physical behavior of multi-component two-phase systems. Regardless of whether the assumption of constant relative volatility or some more sophisticated mathematical procedures are used to determine the equilibrium composition, it is necessary to apply some of the numerical methods for solving complex systems of equations which describe the column operation. A number of methods is used for such calculations, for instance: the McCabe-Thiele method (applicable only for the two-component mixtures with the constant ratio of the molar flow rate of the vapor and the liquid phase; [7-9]), the Almost Band algorithm, the Theta method, the Newton-Raphson method described in [1]. These methods achieve good results for most azeotropic mixtures. However, for the analysis of azeotropic mixtures, especially in cases of distillation with the high reflux ratio, these methods often fail to provide the solution. The best results are usually obtained by using the Newton-Raphson method, but this method is also the most complicated one, requiring a significant amount of time for writing the programming code.

Stability of the Newton-Raphson numerical procedure depends on the evaluation precision of the Jacobian matrix, which makes application of this method even more difficult.

Nowadays many commercial software packages are developed such as HYSYS and ASPEN. HYSYS was used for testing the method described in this paper.

The concept of theoretical stage distillation has become widely accepted for the analysis of trayed distillation columns [7, 8]. The assumption of this concept simplifies the calculation, and the results are applicable in practice. The theoretical stage distillation assumption is abandoned once we move onto the phase of tray design, i.e. the design of the real column. It is only then that we adopt the concept of a real tray, and the tray efficiency is defined relative to the theoretical tray (Murphree tray efficiency [7]).

This paper describes a numerical method for simulation of the operation of trayed distillation columns under stationary and non-stationary operating conditions. The method enables rigorous calculation of the composition on each tray, and it can also be used for calculations under the assumption of the concept of the real stage. The basis for this numerical method is the linearized equation of the phase equilibrium. The linearization of the phase equilibrium equation is obtained using the Taylor series [2], [4, 10], which will be described in detail further on.

Authors used this method for analysis of complex distillation system for refined ethanol production, especially for optimization and automatic control purposes.

Mathematical Model of a Trayed Distillation Column for Stationary Working Conditions

Distillation tray columns are apparatuses working with counter-current fluid flow, and with direct phase contact on the column trays. A segment of a distillation column is schematically shown in figure 1. It is assumed that each

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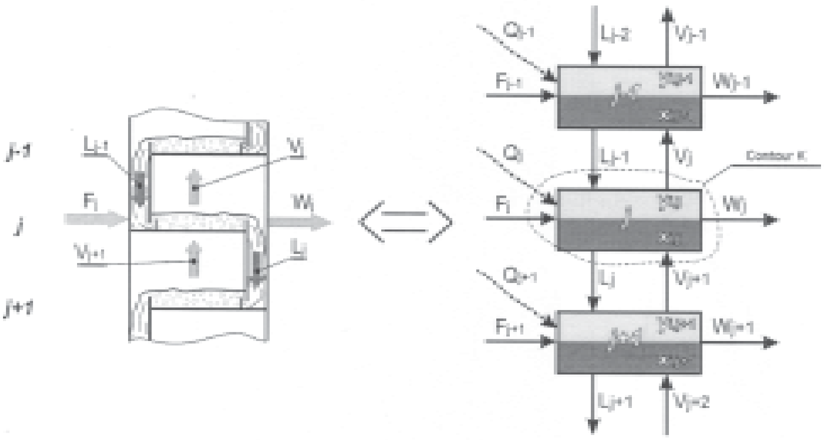

Fig. 1 Schematic of a distillation column

stage can have its feed flow outlet as well as side-stream product outlet. If a stage labeled j has no feed, then $F_j = 0$, and if it has no side-stream product outlet, then $W_j = 0$. In such way a uniform nomenclature is established for any stage and all the input and output streams.

Material balance equation for streams flowing over j - th tray is

$$L_{j-1} + V_{j+1} + F_j = L_j + V_j + W_j \qquad j = 1,\dots, Ns \quad (1)$$

General material balance equation for the j - th stage and i - th component for stationary operating conditions at the contour K is

$$\begin{aligned} & x_{i,j-1} \cdot L_{j-1} + y_{i,j+1} \cdot V_{j+1} + z_{i,j}^{F} \cdot F_j = \\ & = x_{i,j} \cdot L_j + y_{i,j} \cdot V_j + z_{i,j}^{W} \cdot W_j \qquad i = 1,.., Nc \end{aligned} \quad (2)$$

Finally, material balance equation for the same contour is

$$h_{j-1}^{l} \cdot L_{j-1} + h_{j+1}^{v} \cdot V_{j+1} + h_j^{F} \cdot F_j + Q_j = h_j^{l} \cdot L_j + h_j^{v} \cdot V_j + h_j^{W} \cdot W_j \quad (3)$$

Equations (1) and (2) represent generalizations of balance equations for all stages, including evaporator and condenser. An example of substituting the condenser with an equivalent schema is given in figure 2.

Phase composition which leaves a stage depends on the phase flow rate, composition of phases coming onto the tray and the phase contact surface and time on the tray. The problem of determining vapour phase composition can be simplified by adopting the concept of theoretical stage, with phases leaving the stage in equilibrium, which yields

$$\begin{aligned} y_{i,j} &= y_i^{r}\left(x_{1,j}, x_{2,j},\dots, x_{Nc,j}, p\right) \\ h_j^{v} &= h_R^{v}\left(x_{1,j}, x_{2,j},\dots, x_{Nc,j}, p\right) \\ h_j^{l} &= h_R^{l}\left(x_{1,j}, x_{2,j},\dots, x_{Nc,j}, p\right) \end{aligned} \quad (4)$$

Assuming the ideal mixing of phases on the tray, the composition and the temperature of the phase leaving the tray or the discharged side-stream is equal to the composition and the temperature of the corresponding phase on the tray.

Equilibrium phase composition is generally calculated by using complex mathematical procedures, such as NRTL, UNIQAC and UNIFAC methods. Due to complex dependence of the vapour phase composition on the liquid phase pressure and composition, the system of equations (1), (2), (3) and (4) cannot be solved explicitly, so the numerical method has to be used.

Mathematical Model of a Trayed Distillation Column for Non-Stationary Working Conditions

In addition to column calculations conducted for stationary working conditions it is of high importance to simulate the column operation under non-stationary working conditions for the automatic control systems design. Therefore, we are going to briefly define the equations which constitute the mathematical model of a non-stationary operation of a trayed distillation column. The concepts of theoretical stage distillation and the ideal mixing of phases on the tray were assumed, and the quantity of vapour on the tray was considered negligible.

A tray column with defined feed and discharge streams is shown in figure 1. The material balance equation for the j - th tray is

$$L_{j-1} + V_{j+1} + F_j = L_j + V_j + W_j + \frac{\partial M_j}{\partial \tau} \quad (5)$$

while the material balance equation for the same tray with respect to the i - th component is

$$\begin{aligned} & L_{j-1} \cdot x_{i,j-1} + V_{j+1} \cdot y_{i,j+1} + F_j \cdot z_{i,j}^{F} = \\ & = L_j \cdot x_{i,j} + V_j \cdot y_{i,j} + W_j \cdot z_{i,j}^{W} + \frac{\partial \left(M_j \cdot x_{i,j}\right)}{\partial \tau} \end{aligned} \quad (6)$$

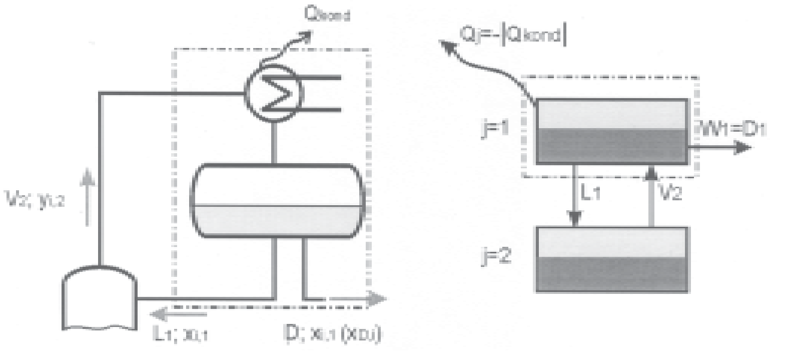

Fig. 2 Scheme of column - condenser connection

Finally, the material balance equation is

$$L_{j-1} \cdot h_{j-1}^{l} + V_{j+1} \cdot h_{j+1}^{v} + F_{j} \cdot h_{j}^{F} + Q_{j} =$$
$$= L_{j} \cdot h_{j}^{l} + V_{j} \cdot h_{j}^{v} + W_{j} \cdot h_{j}^{W} + \frac{\partial \left(M_{j} \cdot h_{j}^{l} \right)}{\partial \tau} \qquad (7)$$

These equations together with the equations which describe the fluid-dynamic characteristics of the trays and the phase equilibrium equations completely define the non-stationary operation of the column, assuming the theoretical stage distillation and the ideal mixing of liquid and vapour phases on the tray. The Francis weir formula is generally used to calculate fluid-dynamic characteristics of trays in such cases assuming the constant density of the binary mixture on the tray [7, 9]. In this way, only the qualitative analysis of the column operation can be performed. This means that, in addition to the equations describing the tray, further equations for the condenser and the evaporator should be defined. These equations are obtained in a similar way to those for the stationary model, and they generally represent a special case of equations (5), (6) and (7). For the purpose of concise presentation, these equations will not be further analyzed.

Linearization of the Phase Equilibrium Equation

Iterative methods are used for calculating compositions of mixtures on trays for stationary working trayed distillation columns. These iterative procedures simplify the phase equilibrium equation by using linear approximation, which yields results with a certain margin of error. After each iteration cycle, a correction of the simplified phase equilibrium equation takes place: complex mathematical methods (such as UNIQAC) are employed to calculate the equilibrium composition with a small margin of error. Simplified phase equilibrium equation is employed most frequently like in [1 or 7]

$$y_{i} = K_{i} \cdot x_{i} \qquad i = 1, 2, \ldots, Nc \qquad (8)$$

Phase equilibrium coefficients depend generally on the liquid phase composition and pressure. After each iteration cycle the phase equilibrium coefficients for each stage have to be re-calculated using the value of liquid phase composition as calculated in the previous iteration cycle. The big advantage of equation (8) lays in its linearity – by using this equation, subsystem (2) is transformed into a linear, usually tri-diagonal system of equations. Now, we are about to discuss an equation that can be used for numerical solving of the system of equations describing a stationary working distillation column. This equation can be used for simulation of non-stationary working distillation plants, too.

Equation (8) does not always yield a unit as a sum of vapour phase mole fractions, which creates a problem for its application in numerical calculations. However, we can use the following equation instead [7]

$$y_{i} = \frac{K_{i} \cdot x_{i}}{\sum\limits_{k=1}^{Nc} K_{k} \cdot x_{k}} \qquad (9)$$

Equation (9) yields an approximately correct solution for the vapour phase composition in the proximity of the liquid phase composition, for which the phase equilibrium coefficients have been calculated. Furthermore, the sum of vapour phase mole fractions calculated by using equation (9) is always equal to a unit. However, equation (9) is non-linear, so using it to solve a system of equations of the type (1), (2) or (3) would be too complicated. Linearization of equation (9) is performed by expanding it into a Taylor series in the vicinity of liquid phase composition for which the phase equilibrium coefficients have been calculated.

$$y_{i} = y_{i}^{*} + \sum_{j=1}^{N_C} \left(\frac{\partial y_{i}}{\partial x_{j}} \right)^{*} \cdot \left(x_{j} - x_{j}^{*} \right) +$$
$$+ \frac{1}{2!} \sum_{j=1}^{Nc} \sum_{k=j}^{Nc} \left(\frac{\partial^{2} y_{i}}{\partial x_{j} \partial x_{k}} \right)^{*} \cdot \left(x_{j} - x_{j}^{*} \right) \cdot \left(x_{k} - x_{k}^{*} \right) + \ldots \qquad (10)$$

Upper index * (asterisk) denotes terms corresponding to the liquid phase composition for which the phase equilibrium coefficients have been calculated so that $K_i = (y_i / x_i)^*$. Partial derivative of vapour phase with respect to the liquid phase is calculated by using equation (9)

$$\left(\frac{\partial y_{i}}{\partial x_{j}} \right)^{*} = \frac{\delta_{i,j} \cdot K_{i} \cdot \sum\limits_{k=1}^{Nc} \left(K_{k} \cdot x_{k} \right)^{*} - \left(K_{i} \cdot K_{j} \cdot x_{i} \right)^{*}}{\left(\sum\limits_{k=1}^{Nc} \left(K_{k} \cdot x_{k} \right)^{*} \right)^{2}} \qquad (11)$$

In the vicinity of the point for which function (9) was expanded into a Taylor series $y_{i}^{*} = K_{i} \cdot x_{i}^{*}$ and $\sum\limits_{i=1}^{Nc} (K_{i} \cdot x_{i})^{*} \equiv 1$, so equation (10) can be transformed into

$$\left(\frac{\partial y_{i}}{\partial x_{j}} \right)^{*} = \delta_{i,j} \cdot K_{i} - K_{i} \cdot K_{j} \cdot x_{i}^{*} \qquad (12)$$

Substituting equation (12) into (10), where all the higher order terms are neglected, finally yields

$$y_{i} = K_{i} \cdot x_{i} + y_{i}^{*} \cdot \left(1 - \sum_{k=1}^{Nc} K_{k} \cdot x_{k} \right) \qquad (13)$$

Equation (13) is linear and thus convenient for numerical solving of the system. Its solution in the vicinity of liquid phase composition for which the phase equilibrium coefficients have been calculated is more precise than the one obtained by using equation (8), especially if relative volatilities are generally constant. Vapour phase mole fractions sum obtained from equation (13) now becomes

$$\sum_{i=1}^{N_C} y_{i} = \sum_{i=1}^{N_C} K_{i} \cdot x_{i} + \sum_{i=1}^{N_C} y_{i}^{*} - \sum_{i=1}^{N_C} \left(y_{i}^{*} \cdot \sum_{k=1}^{N_C} K_{k} \cdot x_{k} \right) \qquad (14)$$

Since the equation

$$\sum_{i=1}^{N_C} y_{i}^{*} = \sum_{i=1}^{N_C} K_{i} \cdot x_{i}^{*} = 1 \qquad (15)$$

is always true, equation (14) can further be transformed into

$$\sum_{i=1}^{N_C} y_{i} = 1 + \sum_{i=1}^{N_C} K_{i} \cdot x_{i} - \left(\sum_{i=1}^{N_C} y_{i}^{*} \right) \cdot \left(\sum_{i=1}^{N_C} K_{i} \cdot x_{i} \right) =$$
$$= 1 + \sum_{i=1}^{N_C} K_{i} \cdot x_{i} - 1 \cdot \sum_{i=1}^{N_C} K_{i} \cdot x_{i} = 1 \qquad (16)$$

Consequently, the vapour phase mole fractions sum calculated by using linear equation (13) is always equal to a unit, as well as the sum of compositions calculated from equation (9).

Description of a Numerical Method for Calculating of Tray Compositions for Stationary Working Distillation Columns

Numerical method described in this paper which is employed for calculation of a stationary working distillation column is very simple, yielding satisfactory results even for the extremely complex distillation systems. The authors have been using it regularly for multicomponent azeotropic mixtures distillation analysis.

A simplified phase equilibrium equation (13) can be used for numerical calculations of phase compositions for stationary working trayed distillation columns. Using equation (13), subsystem of equations (2) can be transformed into the following system, which is linear for known phase flow rates

$$\begin{aligned} & x_{i,j} \cdot \left(L_j + K_{i,j} \cdot V_j\right) - V_j \cdot \\ & \cdot \sum_{k=1}^{Nc} K_{k,j} \cdot x_{k,j} - x_{i,j-1} \cdot L_j - \\ - & \left(K_{i,j+1} \cdot x_{i,j+1} - \overset{*}{y}_{i,j+1} \cdot \sum_{k=1}^{Nc} K_{k,j+1} \cdot x_{k,j+1} \right) \cdot \\ & \cdot V_{j+1} - z_{i,j}^{W} \cdot W_j = z_{i,j}^{F} \cdot F_j \end{aligned} \qquad (17)$$

Assuming the perfect phase mixture, and depending on whether liquid or vapour phase is discharged, term $z_{i,j}^{W} \cdot W_j$ becomes

$$z_{i,j}^{W} \cdot W_j = x_{i,j} \cdot W_j$$

if liquid phase is discharged, or

$$z_{i,j}^{W} \cdot W_j = \left[K_{i,j} \cdot x_{i,j} + \overset{*}{y}_{i,j} \cdot \left(1 - \sum_{k=1}^{Nc} K_{k,j} \cdot x_{k,j} \right) \right] \cdot W_j$$

if vapour phase is discharged.

Specific molar enthalpies of the liquid and vapour phase between two stages can be considered constant for each iteration cycle. At the end of each iteration cycle specific molar enthalpies are recalculated, using previously calculated liquid phase mole fractions. This assumption is quite common in calculations of this type, as specific molar enthalpy is generally constant for most solutions.

An algorithm which facilitates solving systems of equations describing a stationary working column is given below.

Liquid phase compositions are assumed for distillation column's each stage. These values are chosen arbitrarily, as long as their mole fractions sum equals one. In that case, we are able to employ a mathematical procedure (such as UNIQAC) to calculate equilibrium compositions.

Based on assumed liquid phase mole fractions, vapor phase equilibrium compositions and corresponding specific enthalpies $y_{i,j}, h_j^l, h_j^v, h_j^W \;\; i = 1,2,\dots,Nc \;\; j = 1,2,\dots,Ns$ are calculated using exact methods (e.g. UNIQAC). Using calculated vapour phase equilibrium compositions and assumed liquid phase compositions, phase equilibrium coefficients $K_{i,j} = y_{i,j} / x_{i,j} \;\; i = 1,2,\dots,Nc \;\; j = 1,2,\dots,Ns$ are obtained.

Phase flow rates are calculated by solving systems of equations (1), (3), assuming that specific phase enthalpies are equal to specific enthalpies calculated in step 2.

Liquid phase compositions for each stage are obtained by solving system of equations (17). This system (17) is equivalent to systems (2) and (13). Obtained liquid phase compositions are generally not equal to the assumed compositions. If the difference between assumed and calculated composition falls within the specified solution tolerance, the numerical computation is over, otherwise we proceed to step 5.

New corrected values are obtained from the following equation using calculated and assumed liquid phase compositions

$$\left(x_{i,j}^{co}\right)_{it+1} = \beta \cdot x_{i,j}^{ca} + (1 - \beta) \cdot \left(x_{i,j}^{co}\right)_{it} \qquad (18)$$

The procedure is repeated from step 2, where values $\left(x_{i,j}^{co}\right)_{it+1}$ take part of assumed values in the next iteration.

Numerical calculation coefficient β is assumed for each stage, according to the following rule

$$\begin{aligned} & [0 < \beta \leq 1] \vee \left[\beta \cdot x_{i,j}^{ca} + (1 - \beta) \cdot \left(x_{i,j}^{co}\right)_{it} > \right. \\ & \left. > 0 \;\; \forall \;\; j \in (1,2,..,Nc) \right| i = 1,2,\dots,Ns \end{aligned} \qquad (19)$$

For β = 0 corrected values of liquid phase mole fractions are equal to the initially assumed values. In such case, each following iteration cycle would be producing exactly the same values of liquid phase mole fractions over and over again, thus never reaching the desired solution.

For β = 1 iterative calculation becomes direct, i.e. assumed values of liquid phase mole fractions for the next iteration cycle are equal to the calculated values from the previous cycle. In this case a solution is obtained, usually with the fewest number of iteration cycles. However, the possibility of having an unstable calculation is also peaking, which means that the procedure may fail to produce a valid solution.

Equation (13) is a mathematical approximation of a real behavior of a multicomponent vapour-liquid system. It yields correct solutions only in the vicinity of liquid phase composition for which the phase equilibrium coefficients have been calculated. That is exactly the reason for numerical iteration with correction of phase equilibrium coefficient at each step of the iteration cycle. If liquid phase composition significantly varies from the composition for which the phase equilibrium coefficients have been calculated (assumed composition), negative vapour phase mole fraction can be obtained, which means that solving system of equations (17) can produce negative liquid phase compositions for a certain iteration cycle. Negative mole fractions can be corrected by choosing a suitable coefficient β . It is advisable to assume that β = 0.5 for each stage. If corrected liquid phase mole fractions still remain negative for a certain stage, we should keep dividing it by two until condition (16) is met. Increasing the number of iteration cycles improves the calculations for liquid phase mole fractions, thus making equation (13) more precise too, which means that we can assume larger values for β in order to speed up the calculation procedure.

Description of a Numerical Method for Calculating of Tray Compositions for Non-Stationary Working Distillation Columns

Non-stationary working column is described by a system of non-linear partial differential equations. For solving this system of equations we can use numerical methods which are similar to those used in fluid mechanics [11], or for non-stationary heat conduction problems. These methods are based on so-called hybrid numerical schemes. For instance, equation (6) is substituted by the following numerical approximation

$$\frac{\left(M_j\cdot x_{i,j}\right)_{\tau_n+\Delta\tau}-\left(M_j\cdot x^{*}_{i,j}\right)_{\tau_n}}{\Delta\tau}=(1-\beta)\cdot$$
$$\cdot\left(F_j\cdot z^F_{i,j}+L_{j-1}\cdot x^{*}_{i,j-1}+V_{j+1}\cdot y^{*}_{i,j+1}-W_j\cdot z^W_{i,j}-L_j\cdot x^{*}_{i,j}-V_j\cdot y^{*}_{i,j}\right)_{\tau_n}+$$
$$+\beta\cdot\left\{F_j\cdot z^F_{i,j}+L_{j-1}\cdot x_{i,j-1}+V_{j+1}\cdot\left[K_{i,j+1}\cdot x_{i,j+1}+y^{*}_{i,j+1}\cdot\left(1-\sum_{k=1}^{Nc}K_{k,j+1}\cdot x_{k,j+1}\right)\right]-\right. \tag{20}$$
$$\left.-W_j\cdot z^W_{i,j}-L_j\cdot x_{i,j}-V_j\cdot\left[K_{i,j}\cdot x_{i,j}+y^{*}_{i,j}\cdot\left(1-\sum_{k=1}^{Nc}K_{k,j}\cdot x_{k,j}\right)\right]\right\}_{\tau_{n+1}=\tau_n+\Delta\tau}$$

In equation (20), similar to the simulation of a stationary working column, asterisk (*) denotes mole fractions corresponding to the fractions for which the phase equilibrium coefficients have been calculated. As we are now dealing with a non-stationary problem, phase equilibrium coefficients are calculated using mole fractions from the immediately preceding moment. The entire calculation involves a time step $\Delta\tau$: given that in the moment τ_n all the mole fractions and flow rates are known, we are able to calculate mole fractions and flow rates in the moment $\tau_{n+1} = \tau_n+\Delta\tau$ Assuming that the difference in phase flow rate and enthalpy during the interval $\Delta\tau$ results in negligible changes in stream composition, the system of equations can formally be broken down into a system of equations describing tray composition and a system of equations describing phase flow rate. These systems can be solved separately to a certain degree, which additionally simplifies the calculation. This simplification is performed in a number of steps

Assuming that in the moment τ_n all the flow rates and compositions are known, phase enthalpies are calculated using these compositions. The adopted assumption is that at the moment of time $\tau_{n+1} = \tau_n+\Delta\tau$ enthalpies generally remain unchanged. Phase equilibrium coefficients are also calculated in the moment τ_n. These calculated phase equilibrium coefficients are used for calculating mole fractions in the next moment of time.

Flow rates in the moment τ_{n+1} are calculated based on the assumption from step 1. Balance equations from chapter 4 are used for these calculations.

Phase compositions are calculated using the calculated phase flow rates from step 2. This calculation is based on system of equations (20), using calculated flow rates in the moment τ_n and τ_{n+1}. Upon completing the phase composition calculation, the procedure for calculating phase compositions and flow rates is re-iterated for the next moment of time τ_{n+2}.

In equation (20) we assume that vapour and liquid phase composition dependence can be formulated as defined in equation (13). In such way we have linearized the entire system of equations; otherwise it might be very difficult to solve it. After each time step equation (13) is corrected by calculating new phase equilibrium coefficients for each tray.

Coefficient β defines a hybrid scheme. Its values must fall between 0 and 1. For extremely unstable calculations it is advisable to assume a value in diapason $0.5\div 1$. If β = 0.5, such scheme is referred to as Krank-Nicholson hybrid scheme.

Assuming that there are no changes in external flow rates (feed flow composition and flow rate, and discharge and reflux flow rate); each non-stationary problem after a long enough time tends to the stationary solution. Consequently, a non-stationary model can be used for stationary working columns.

An Example of Azeotropic Mixture Distillation Calculation

Numerical methods described in previous chapters were tested on a series of azeotropic and zeotropic mixtures, with side-by-side testing of the θ and Newton-Raphson methods.

A benzene-acetone-chloroform distillation column had 20 theoretical stages (trays), including evaporator and condenser, each providing a single stage. The tenth stage, counting from the condenser side, had a feed flow. Composition of the feed was z_F = [0.50 0.05 0.45], the reflux ratio was $R = 10$, and the distillate/feed ratio was D / F 0.3. The analysis showed the instability of the θ–method on the right-hand side of the azeotropic point (fig. 3).

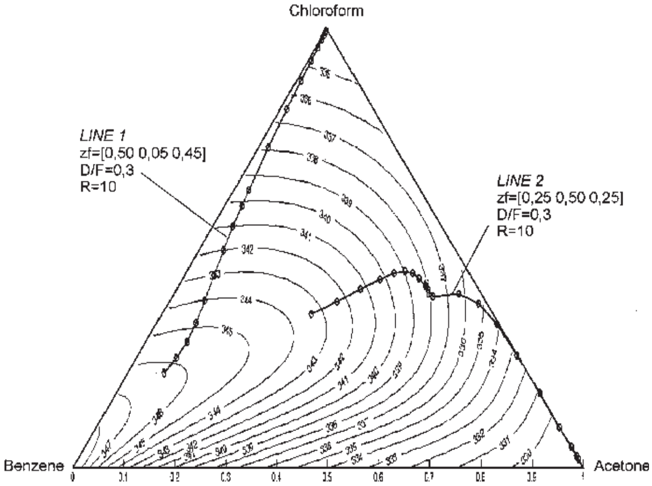

Fig. 3 An example of benzene-acetone-chloroform mixture distillation in a column with 20 theoretical trays

Consequently, the θ–method could not provide a valid solution for the described column, its operating conditions and feed composition. On the other hand, the method described in this paper led to a solution after 23 iteration cycles, which is reasonably fast. Initial (assumed) tray composition was [0.333 0.333 0.333]. Choosing other initial conditions made the application of the θ–method for the purposes of obtaining the solution completely futile. Another example was worked out with the following input data: z^F = [0.25 0.50 0.25], R = 10, D / F = 0.3 and number of stages was 20, the solution is shown in figure 3. This solution was achieved after 150 steps what takes less than minute of processor time. This example couldn't be solved nether with Newton-Raphson nor with θ method.

Methanol-acetone-chloroform mixture was used as another example of azeotropic mixtures distillation. The column had 10 theoretical trays, including condenser and evaporator, each representing one theoretical stage. The fifth tray (counting from the condenser) is the feed tray. The following results were obtained for several different

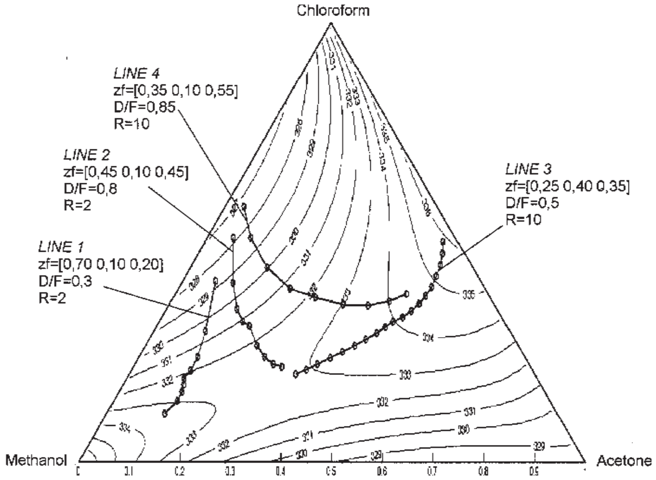

Fig. 4 An example of methanol-acetone-chloroform mixture distillation in a column with 10 theoretical trays

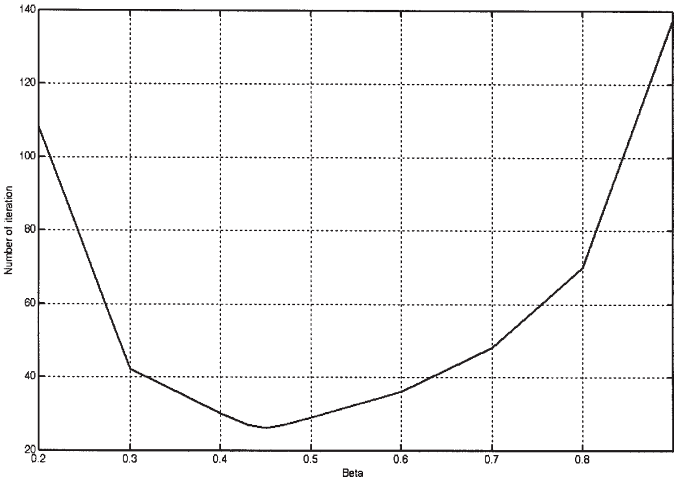

Fig. 5 Number of iterations vs. β - equations (18) and (19)

compositions of the feed flow as well as for various working conditions, results are shown in figure 4.

example 1: z^F= [0.70 0.10 0.20]; reflux ratio R =2; distillate flow ratio D / F = 0.3
example 2: z^F = [0.45 0.10 0.45]; reflux ratio R =2; distillate flow ratio D / F = 0.8
example 3: z^F = [0.25 0.40 0.35]; reflux ratio R = 10; distillate flow ratio D / F = 0.5
example 4: z^F = [0.35 0.10 0.55]; reflux ratio R = 10; distillate flow ratio D / F = 0.85

Calculations for examples 1 and 3 were conducted using both θ -method and the method described in this paper (based on linearized phase equilibrium equation). The results were identical. On the other hand, θ-method failed to produce valid results for examples 2 and 4. Example 2 was obtained with relative ease using the method described in this paper. Example 4 was also obtained using this method, although it took a large number of iteration cycles and coefficient β =0.1. Stability of the proposed numerical method depends on the value of β. We haven't consider stability of method in mathematical point of view, but we have tested stability with a number of different mixtures (solutions), compositions and column design. Figure 5 presents the dependency of the number of iterations on β for described example.

It can be seen that the minimal number of iteration is obtained for β=0.45.

Conclusions

Numerical methods presented in this paper enable relatively simple simulation of stationary and non-stationary working distillation columns with multiple stages. Apart from the exact phase equilibrium equation (e.g. UNIQAC method), all the other equations are linear, which makes writing of the programming code a relatively easy task. Results obtained using the numerical methods described in this paper are identical to the results obtained from some more frequently employed methods, such as the θ-method and the Newton-Raphson method. The method described in this paper is proving to be stable in a number of cases. In the case of instability, numerical stability can always be reached by decreasing the maximum value of coefficient β, which leads to obtaining a valid result. Decreasing the value of β increases the number of iteration cycles necessary to obtain a solution with satisfactory precision. The method can readily be applied to distillation refineries with multiple columns, too. The core part of this method is the approximated phase equilibrium equation, which can also be used for simulation of a non-stationary working distillation plant, single-step distillation with a high pressure drop, etc. Due to the linearization procedure that was applied to the phase equilibrium equation, the method always yields valid solutions for calculations of distillations assuming constant coefficients of relative volatility, which is a common case in the industry. Correction of mole fractions on trays is performed in a very simple manner at the end of each iteration cycle.

For simulation of non-stationary working distillation columns, a so-called hybrid method is suggested, and linearization of the phase equilibrium equation was also applied. Non-stationary model and the corresponding numerical method can also be applied to simulation of continuous and batch distillation processes, and also in cases of plants with multiple columns.

The advantage of this method lies in the fact that the algorithm is simple, and easy to be programmed. We have used this method for optimizing of complex ethanol distillation system (for 7 component mixture) with great success. Method was also successful used for calculations necessary for batch rectification of ethanol-water mixture.

Nomenclature

x - liquid phase component mole fraction, mol/mol
y - vapor phase component mole fraction, mol/mol
z - feed flow or side-stream product mole fraction, mol/mol
L - liquid phase, mol/s
V - vapor phase leaving the tray flow rate, mol/s
F - feed flow rate, mol/s
W - side-stream product flow rate, mol/s
M - liquid phase quantity (on a tray or in condensers), mol
h - specific mole enthalpy of the stream, J/mol
Q - heat entering a stage, W
$\delta_{i,k}$ - the Kronecker delta term; $\delta_{i,k}$ =1 for i = k, in other cases $\delta_{i,k}$ =0
β - numerical calculation coefficient
τ - time, s
Ns - number of stages
N_c - number of components in the mixture

Subscripts

i, k - index denoting component (i = 1,2,..., Nc k = 1,2,...,Nc))
j - index denoting stage (j = 1,2,...,Ns))
it - iteration cycle number (it = 1,2,...)
R - specific equilibrium enthalpy

Superscripts

r - equilibrium composition

W - side-stream product
F - feed flow
l - liquid phase
v - vapor phase
ca - calculated values
co - corrected value

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Manuscript received: 12.10.2010