PACKED COLUMN DISTILLATION SIMULATION WITH A RATE-BASED METHOD

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A simulation algorithm using a rate-based model is proposed for multicomponent packed column distillation. The packed column sections are divided into small segments for the modeling. For each packing segment, (6c + 7) MERQ equations are set up and solved by an equation-tearing method with two calculation loops. Calculation of the whole column consists of an iterative segment-wise algorithm with the correction of the bulk vapor composition by the overall normalized θ method for acceleration.

The numerical characteristics of the proposed algorithm and some remarks on its application are illustrated using numerical examples and experimental data obtained from a pilot-scale plant.

Introduction

Packed distillation columns with structured or regular packings are attracting more engineers' attention in retrofitting or improving the existing stage columns. Simulation of packed distillation columns has been done using equilibrium-stage calculation methods where considering HETP (the Height Equivalent to a Theoretical Plate) or numerical integration of differential equations of mass transfer (such as, Billingsley and Chirachavala, 1981 and Gorak, 1987). The value of HETP might depend on components like plate efficiency does for multicomponent distillation, and large simplification of the basic equations is required for a numerical integration approach. In order to meet the increasing demands on rigorous simulation methods, rate-based or nonequilibrium models have been developed considering heat and mass transfer between the bulk vapor and liquid phases (Krishnamurthy and Taylor, 1985a, b, c, d, 1987). Being based on the two-film theory, this model seems to be most suitable for modeling packed column distillation.

Krishnamurthy and Taylor established a set of equations consisting of heat and mass transfer rate equations, and equilibrium relationships at the interface; the so-called MERQ (Material balance, Energy balance, Rate, eQuilibrium) equations compared with the well-known MESH (Material balance, Equilibrium, Summation, Heat balance) equations for the equilibrium stage model.

Hints of successful application of the rate-based model are (i) precise evaluation of transport properties, such as heat and mass transfer coefficients, and interfacial area involved and (ii) effective solution of the strongly nonideal MERQ equations.

Many attempts have been made to correlate the transport properties and other characteristics for various packings. This is still in progress. As for solution methods, Krishnamurthy and Taylor (1985a, d) solved the MERQ equations simultaneously using Newton related methods to overcome the strong nonlinearity. As they mentioned, however, the only difficulty in applying the Newton related methods is to set up proper Jacobian matrix.

In the following, we apply a rate-based model to set up the MERQ equations. Then, we propose a solution algorithm using an equation-tearing technique. Also, the performance of the proposed method is discussed with numerical examples.

1. Assumptions and Models

1.1 Assumptions and basic equations

Figure 1 gives a schematic illustration of a small segment in a packed column. The model consists of bulk liquid flowing down on a packing surface, bulk vapor flowing up through the space between packings, and vapor-liquid interface. Heat and mass transfer occur only through this interface. The column is assumed to be adiabatic. Feeds and sidecuts are made between the segments using a collector-distributor device, where the vapor and liquid phases are mixed individually and completely before entering the next segments or sidecuts. The whole column is represented by the stack of the segments, and each segment is numbered from the top to the bottom (see Fig. 2). According to Fig. 1 the balance equations for the bulk liquid, bulk vapor and interface are given as follows:

Total material balances

$$L_{j-1} - L_j = -N_{j,i}^L a_j \quad (1)$$

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Fig. 1 Schematic model of j -th segment

$$-V_j + V_{j+1} = N_{j,i}^V a_j \quad (2)$$

$$N_{j,i}^L = N_{j,i}^V \quad (3)$$

where $N_{j,i}^L$ and $N_{j,i}^V$ are total mass fluxes in the liquid and vapor phases in the j th segment and have positive values for the transfer from the vapor to the liquid phase. a_j is the interfacial area for heat and mass transfer.

Component material balances

$$L_{j-1}x_{j-1,i}^L - L_jx_{j,i}^L = -N_{j,i}^L a_j \quad (i = 1, \dots, c-1) \quad (4)$$

$$-V_jy_{j-1,i}^V - V_{j+1}y_{j+1,i}^V = -N_{j,i}^V a_j \quad (i = 1, \dots, c-1) \quad (5)$$

$$N_{j,i}^L = N_{j,i}^V \quad (i = 1, \dots, c-1) \quad (6)$$

where c is the number of components, $x_{j,i}^L$ and $y_{j,i}^V$ are the bulk liquid and vapor compositions, and $N_{j,i}^L$ and $N_{j,i}^V$ are the component mass fluxes in the liquid and vapor phases. From the degrees of freedom, there are only $(c-1)$ independent equations.

Heat balances

$$L_{j-1}H_{j-1}^L - L_jH_j^L = -E_j^L a_j \quad (7)$$

$$-V_jH_j^V + V_{j+1}H_{j+1}^V = -E_j^V a_j \quad (8)$$

$$E_j^L = E_j^V \quad (9)$$

where H_j^L and H_j^V are the molar enthalpies of the bulk liquid and vapor. E_j^L and E_j^V are the heat fluxes in the liquid and vapor side films.

Phase equilibrium is assumed to hold at the interface.

Equilibrium relationship

$$y_{j,i}^I = \gamma_{j,i} p_{j,i}^s x_{j,i}^I / P_j \quad (i = 1, \dots, c) \quad (10)$$

where $y_{j,i}^I$ and $x_{j,i}^I$ are the mole fractions on the vapor and liquid sides of the interface. $\gamma_{j,i}$ are activity coefficients. $p_{j,i}^s$ is the saturated vapor pressure of component i , and P_j is the total vapor pressure in the j th segment.

Stoichiometric relation gives the following equations for the compositions of the bulk phases and the interface.

Fig. 2 Packed distillation column

$$\sum_{i=1}^c x_{j,i}^L = 1 \quad (11)$$

$$\sum_{i=1}^c y_{j,i}^V = 1 \quad (12)$$

$$\sum_{i=1}^c x_{j,i}^I = 1 \quad (13)$$

$$\sum_{i=1}^c y_{j,i}^I = 1 \quad (14)$$

The mass transfer rates considering bulk flow terms are employed.

$$N_{j,i}^L = \sum_{k=1}^{c-1} k_{i,k}^L (x_{j,k}^I - \bar{x}_{j,i}^L) + \bar{x}_{j,i}^L N_{j,i}^L \quad (i = 1, \dots, c-1) \quad (15)$$

$$N_{j,i}^V = \sum_{k=1}^{c-1} k_{i,k}^V (\bar{y}_{j,i}^V - y_{j,k}^I) + \bar{y}_{j,i}^V N_{j,i}^V \quad (i = 1, \dots, c-1) \quad (16)$$

where $k_{i,k}^L$ and $k_{i,k}^V$ are multicomponent mass transfer coefficients which are determined from binary mass transfer coefficients $k_{i,k}^{bL}$ and $k_{i,k}^{bV}$ (Krishna and Standart, 1976), $\bar{x}_{j,i}^L$ and $\bar{y}_{j,i}^V$ represent average bulk compositions.

In the same way as above, the heat transfer rates are expressed as follows.

$$E_j^L = h_j^L (T_j^I - \bar{T}_j^L) + \sum_{i=1}^c N_{j,i}^L \bar{H}_{j,i}^L \quad (17)$$

$$E_j^V = h_j^V \frac{\epsilon^V}{e^{\epsilon^V} - 1} (\bar{T}_j^V - T_j^I) + \sum_{i=1}^c N_{j,i}^V \bar{H}_{j,i}^V \quad (18)$$

Table 1 Number of variables and equations in rate-based model

Variables		
Flow rate	L_p, V_j	2
Mole fraction	$x_{j,i}^L, y_{j,i}^V, x_{j,i}^I, y_{j,i}^I$	4c
Mass transfer rate	$N_{j,i}^L, N_{j,i}^V$	2c
Heat transfer rate	$E_{j,i}^L, E_{j,i}^V$	2
Temperature	T_p^L, T_p^I, T_j^V	3
		6c + 7
Equations		
Total material balance		3
Component material balance		3 (c - 1)
Heat balance		3
Interface VLE		c
Summation		4
Mass transfer rate		2 (c - 1)
Heat transfer rate		2
		6c + 7

where $\bar{H}_{j,l}^L$ and $\bar{H}_{j,v}^V$ are the partial molar enthalpies of component i of liquid and vapor. h_j^L and h_j^V are heat transfer coefficients in the liquid and vapor phases. The fraction term in the right hand side is a correction factor due to high mass flux (Bird et al., 1960), and ϵ^V is defined as follows.

$$\varepsilon^V = \sum_{i=1}^c N_{j,i}^V C_{pi}^V / h_j^V \quad (19)$$

Since the corresponding term for the liquid phase is usually close to unity, it is omitted in Eq. (17).

Table 1 gives the summary of variables and equations involved. We must solve a set of $6c + 7$ nonlinear equations for each segment of packing.

1.2 Physical and transport properties and other parameters

Physical and thermodynamic properties of pure substances are available as functions of temperature from the literature, such as the work of Daubert and Danner (1989). Recommended mixing rules for predicting properties of mixtures can be found in Reid *et al.* (1988). The choice of mixing rules for transport properties, especially diffusivity, is critical and must be done with great care. The parameters for activity coefficients are available from the literature, such as the work of Gmehling *et al.* (1977ff). If the observed VLE data are not available for the mixtures involved, ASOG (Tochigi *et al.*, 1990) or UNIFAC (Fredenslund, 1977; Gmehling *et al.*, 1993) may be useful.

The correlations of binary mass transfer coefficients for several commercial packings have been reported in the literature; Billet and Schlutes (1993); Bravo *et al.* (1985); Fair and Bravo (1987, 1990); and Weiland *et al.* (1993). The Chilton-Colburn analogy (Bird *et al.*, 1960) is used to evaluate heat transfer coefficients.

The effective interfacial area per unit volume a_e is a complex function of various properties and operating conditions. Many attempts have been made to establish reliable

correlations for various packings; such as Billet and Schlutes (1993), Henriques de Brito *et al.* (1994), and Brunazzi *et al.* (1995). You may introduce an appropriate correlation according to the type of a packing used and the desired accuracy of the calculation. Specially defined dimensionless groups are usually used, close attention is also needed on application. In the following calculation, we will use an apparent specific surface area a_p as the effective interfacial area a_e for convenience. The interfacial area a_j is given as a product of a_e and the volume of the j th segment.

2. Calculation Algorithms

Krishnamurthy and Taylor (1985a, d) successfully applied a Newton related method for solving the MERQ equations after trying several other methods. Even though they emphasized the calculation efficiency of the Newton method, the proper formulation of the Jacobian matrix is a big issue to be solved, since evaluation of the transport properties involves many variables and correlations. Our attempt described below is based on the equation-tearing technique where two groups of equations and variables are solved alternatively, avoiding any cumbersome differentiation.

2.1 Algorithm for segments

The equations are divided into two groups; one for obtaining the bulk temperatures, T_j^I and T_j^V , the flow rates, L_j and V_j , and the heat and mass fluxes, $E_{j,i}^I$, $E_{j,i}^V$, $N_{j,i}^I$ and $N_{j,i}^V$, to satisfy the total material balances, Eqs. (1) - (3), and the heat balance at the interface, Eq.(9); the other for calculating the bulk compositions, $x_{j,i}^I$ and $y_{j,i}^V$ and the interfacial condition, $x_{j,i}^I$, $y_{j,i}^I$ and T_j^I , to satisfy the component mass balances, Eqs. (4) - (6).

All conditions of incoming streams, V_{j+1} and L_{j-1} , to the j th segment should be known during the calculation.

(a) Inner loop

During this calculation loop, the compositions, $x_{j,i}^L$, $y_{j,i}^V$, $x_{j,i}^I$ and $y_{j,i}^I$, are all kept constant. The calculation steps are as follows.

Step 1) Assume bulk temperature, T_j^L and T_j^V and total mass flux, $N_{j,t}^L$ and $N_{j,t}^V$. $N_{j,t}^L = N_{j,t}^V = 0$ is enough for the initial estimates.

Step 2) Evaluate binary mass transfer coefficients, $k_{i,k}^{bL}$ and $k_{i,k}^{bV}$, at zero mass flux using appropriate correlations with assumed compositions and temperatures.

The heat transfer coefficients in liquid and vapor phase, h_j^L and h_j^V , are calculated from the averaged binary mass transfer coefficients using the Chilton-Colburn analogy. (Bird *et al.*, 1963)

Step 3) Calculate multicomponent mass transfer coefficients, $k_{i,k}^L$ and $k_{i,k}^V$, in the same way as Krishna and Standart (1976) (see also Appendix and Taylor and Krishna, 1994). When the thermodynamic factors are taken into account for evaluating liquid-phase mass transfer coefficients, the expressions are available for many activity coefficient models (Taylor and Kooijman, 1991; Mori *et*

al., 1995).

Then, calculate mass transfer fluxes, $N_{j,i}^L$ and $N_{j,i}^V$ ($i = 1, c - 1$), using Eqs. (15) and (16), and

$$N_{j,c}^L = N_{j,t}^L - \sum_{i=1}^{c-1} N_{j,i}^L \quad (20)$$

$$N_{j,c}^V = N_{j,t}^V - \sum_{i=1}^{c-1} N_{j,i}^V \quad (21)$$

Here the average compositions used, $\bar{x}_{j,k}^L$ and $\bar{y}_{j,k}^V$, are given as arithmetic averages.

$$\bar{x}_{j,i}^L = (x_{j-1,i}^L + x_{j,i}^L) / 2 \quad (22)$$

$$\bar{y}_{j,i}^V = (y_{j+1,i}^V + y_{j,i}^V) / 2 \quad (23)$$

This corresponds to a linear composition profile. Notes since $k_{i,k}^L$ and $k_{i,k}^V$ are the implicit functions of $N_{j,i}^L$ and $N_{j,i}^V$, this calculation becomes iterative.

After all mass fluxes are determined, evaluate the high mass flux correction factor e^V using Eq. (19).

Step 4) Solve Eqs. (7) and (8) for the bulk temperatures, T_j^L and T_j^V , respectively, with fixed L_j and V_j . The heat fluxes, E_j^L and E_j^V , are evaluated using Eqs. (17) and (18) at the same time. The average temperatures, $\bar{T}_j^L$ and $\bar{T}_j^V$, appearing in the equations are given as arithmetic average here.

$$\bar{T}_j^L = (T_{j-1}^L + T_j^L) / 2 \quad (24)$$

$$\bar{T}_j^V = (T_{j+1}^V + T_j^V) / 2 \quad (25)$$

Step 5) If Eq. (9) is satisfied, go to "Outer loop." If not, go to Step 6).

Step 6) Evaluate the enthalpies, H_j^L and H_j^V , and solve the total material balance and enthalpy balance equations below for the bulk flow rates L_j and V_j .

$$L_j + V_j = L_{j-1} + V_{j+1} \quad (26)$$

$$L_j H_j^L + V_j H_j^V = L_{j-1} H_{j-1}^L + V_{j+1} H_{j+1}^V \quad (27)$$

Step 7) Calculate the total mass fluxes $N_{j,t}^L$ from Eq. (1) and set $N_{j,t}^V = N_{j,t}^L$, then return to Step 3).

(b) Outer loop

During this calculation loop, the temperatures, T_j^L and T_j^V , the bulk flow rates, L_j and V_j , and the total mass flux, $N_{j,t}^L$ and $N_{j,t}^V$, are to be constant.

Step 1) Check the component material balance equations of liquid and vapor phases, Eqs. (4) and (5), with the results of "Inner loop." If they are satisfied, move to the next segment. Otherwise, correct the compositions in the following steps.

Step 2) Correct the bulk compositions $x_{j,i}^L$ and $y_{j,i}^V$ using the normalized θ method (Yamada *et al.*, 1984).

For the liquid phase,

$$(x_{j,i}^L)_{co} = \theta_j^L \phi_{j,i}^L (x_{j,i}^L)_{as} \quad (28)$$

where

$$\theta_j^L = \left[\sum_{i=1}^c \phi_{j,i}^L (x_{j,i}^L)_{as} \right]^{-1} \quad (29)$$

and

$$\phi_{j,i}^L = \frac{L_{j-1} x_{j-1,i}^L}{L_j (x_{j,i}^L)_{as} - N_{j,i}^L a_j} \quad (N_{j,i}^L < 0) \quad (30)$$

or

$$\phi_{j,i}^L = \frac{L_{j-1} x_{j-1,i}^L + N_{j,i}^L a_j}{L_j (x_{j,i}^L)_{as}} \quad (N_{j,i}^L \geq 0) \quad (31)$$

For the vapor phase,

$$(y_{j,i}^V)_{co} = \theta_j^V \phi_{j,i}^V (y_{j,i}^V)_{as} \quad (32)$$

where

$$\theta_j^V = \left[\sum_{i=1}^c \phi_{j,i}^V (y_{j,i}^V)_{as} \right]^{-1} \quad (33)$$

and

$$\phi_{j,i}^V = \frac{V_{j-1} y_{j-1,i}^V + N_{j,i}^V a_j}{V_j (y_{j,i}^V)_{as}} \quad (N_{j,i}^V < 0) \quad (34)$$

or

$$\phi_{j,i}^V = \frac{V_{j+1} y_{j+1,i}^V}{V_j (y_{j,i}^V)_{as} - N_{j,i}^V a_j} \quad (N_{j,i}^V \geq 0) \quad (35)$$

Step 3) Calculate the interfacial compositions, $x_{j,i}^I$ and $y_{j,i}^I$, and temperature T_j^I as follows.

After replacing $N_{j,i}^L$ and $N_{j,i}^V$ of Eq. (6) with Eqs. (15) and (16), we may transpose the bulk flow term $\bar{x}_{j,i}^L N_{j,i}^L$ to the right hand side, and expand the summation of the liquid side diffusion term. This gives $(c - 1)$ simultaneous equations with respect to $(x_{j,i}^I - \bar{x}_{j,i}^L)$.

In a matrix form

$$[K] \cdot [\Delta x] = [w] \quad (36)$$

where the elements of the matrix $[K]$ and column vectors, $[\Delta x]$ and $[w]$, are given as follows.

$$K_{i,i} = k_{i,i}^L \quad (37)$$

$$\Delta x_i = x_{j,i}^I - \bar{x}_{j,i}^L \quad (38)$$

$$w_i = \sum_{k=1}^{c-1} k_{i,k}^V (\bar{y}_{j,k}^V - y_{j,k}^I) + \bar{y}_{j,i}^V N_{j,t}^V - \bar{x}_{j,i}^L N_{j,t}^L \quad (39)$$

As the average compositions, $\bar{x}_{j,i}^L$ and $\bar{y}_{j,i}^V$, and the interfacial vapor compositions $y_{j,i}^I$ are given, Eq. (36) is solved for Δx_i . Then $x_{j,i}^I$ ($i = 1, c - 1$) are obtained, and

$$x_{j,c}^I = 1 - \sum_{i=1}^{c-1} x_{j,i}^I \quad (40)$$

The vapor composition $y_{j,i}^I$ and temperature T_j^I at the interface are obtained from a bubble point calculation with $x_{j,i}^I$. If the component mass fluxes recalculated using Eqs. (15) and (16) satisfy Eq. (6), the values of $x_{j,i}^I$, $y_{j,i}^I$ and T_j^I are to be determined, and return to "Inner loop". Otherwise re-evaluate the elements of w_i (Eq. (39)) using the latest $y_{j,i}^I$ and repeat the calculation.

Table 2 Dimensions of packed column and packing element

Column	
Column height	3.00 m
Packed height	2.20 m
Diameter	0.21 m
Capacity of Still	0.30 m ³
Heat transfer area of reboiler	7.8 m ²
Heat transfer area of condenser	12.3 m ²
Packing (MC-250T*)	
Element diameter	0.199 m
Element height	0.183 m
Height of triangle	9.9 × 10 ⁻³ m
Base of triangle	25.4 × 10 ⁻³ m
Corrugation spacing	15.6 × 10 ⁻³ m
Specific surface area	250 m ² /m ³
Void fraction	0.98
Channel flow angle	45°
* Mitsubishi Co.	

(c) Feeds and Sidecuts

When the feed is introduced between the j th and $j + 1$ st segments, the liquid and vapor flow rates and compositions must be corrected as follows.

$$L_{j,co} = L_j + F_j^L \quad (41)$$

$$x_{j,i,co}^L = \frac{L_j x_{j,i}^L + F_j^L x_{j,i}^F}{L_j + F_j^L} \quad (42)$$

$$H_{j,co}^L = \frac{L_j H_j^L + F_j^L H_j^{FL}}{L_j + F_j^L} \quad (43)$$

$$V_{j+1,co} = V_{j+1} + F_j^V \quad (44)$$

$$y_{j,i,co}^V = \frac{V_{j+1} y_{j+1,i}^V + F_j^V y_{j,i}^F}{V_{j+1} + F_j^V} \quad (45)$$

$$H_{j,co}^V = \frac{V_{j+1} H_{j+1}^V + F_j^V H_j^{FV}}{V_{j+1} + F_j^V} \quad (46)$$

For sidecuts only flow rates are corrected.

$$L_{j,co} = L_j - S_j^L \quad (47)$$

$$V_{j+1,co} = V_{j+1} - S_j^V \quad (48)$$

2.2 Algorithm for whole column

The algorithm for solving an operation type problem is described below, where column dimension, packing height, and the geometry of the packing should be specified as well as feed and operating conditions.

The outline of the algorithm is basically the same as the authors previously proposed for multistage distillation calculations (Mori *et al.*, 1994). The stagewise calculation based on the equilibrium stage model is replaced by the segmentwise calculation described above.

Step 1) Assume bulk liquid and vapor compositions, $x_{j,i}^L$ and $y_{j,i}^V$ interfacial compositions, $x_{j,i}^I$ and $y_{j,i}^I$, bulk flow rates, L_j and V_j , and temperatures T_j^L , T_j^V and T_j^I .

Table 3 Estimation of mixture properties

Vapor Diffusivity	Brokaw (Reid <i>et al.</i> , 1987)
Liquid diffusivity	
(at infinite dilution)	Raddy and Doraisway (Reid <i>et al.</i> , 1987)
(at finite dilution)	Vignes (Reid <i>et al.</i> , 1987)
Vapor viscosity	Brokaw (Reid <i>et al.</i> , 1987)
Vapor thermal conductivity	Lindsay-Bromley (Reid <i>et al.</i> , 1987)
Liquid thermal conductivity	Li (Reid <i>et al.</i> , 1987)
Others	molar average
Activity coefficient model	ASOG (Tochigi <i>et al.</i> , 1990)
Mass transfer coefficient	Bravo <i>et al.</i> , 1985
Heat transfer coefficient	Chilton-Colburn (Bird <i>et al.</i> , 1963)

Step 2) Calculate each segment from the top to the bottom.

Step 3) Check the total component material balances around the column; if they are satisfied, terminate the calculation. Otherwise go to the next step.

Step 4) Correct the calculated bulk vapor composition $y_{j,i}^V$ using the overall normalized θ method described below, then return to Step 2)

$$(y_{j,i}^V)_{co} = \Theta_j \Phi_i (y_{j,i}^V)_{ca} \quad (49)$$

where

$$\Theta_j = \left[\sum_{i=1}^c \Phi_i (y_{j,i}^V)_{ca} \right]^{-1} \quad (50)$$

and

$$\Phi_i = \frac{(input)_i}{(output)_i} \quad (51)$$

The term $(input)_i$ represents the total molar flow rate of component i into the column due to feeds, and the term $(output)_i$ the total molar flow rate of component i leaving the column due to a distillate, bottoms and sidecuts.

3. Numerical Examples and Discussion

The algorithm described above is coded in Fortran 77 and the program is executed on a HP715/50 (Hewlett Packard Co.) work station with double precision. The judgement of convergence are set as; a maximum relative error $< 10^{-10}$ for VLE calculation; $< 10^{-1}$ (beginning) to 10^{-10} (last) for inner and outer loop calculations; and $< 10^{-6}$ for total component material balances.

The dimension of the column and the geometry of the packing are listed in **Table 2**. The feed is introduced at the middle of the column using a collector-distributor device which is considered not to work as a separation element. The enriching and stripping sections consist of six packing elements. The structure of the packing used is similar to other commercial corrugated sheet-type packings, but with sheet sandwiched by gauze. Thus, the wetting characteristic is close to that of gauze-type packings. The assumptions and calculating conditions are shown in **Table 3** and **Table 4**. The bottoms rate for Example 3 is determined as a balance of the feed and distillate rates in the experiment. There is no other adjusting parameter used in the following calculation.

Table 4 Calculation conditions for examples

Ex. 1				
System	Methanol (1) / Ethanol (2) / Water (3)			
Pressuer	101.4 kPa			
Feed	1.11 mol/s	$T^F = 353.65$ K (b.p.)	(center feed)	
	(1) 0.185	(2) 0.045	(3) 0.770	
Distillate	0.19 mol/s			
Bottoms	0.92 mol/s			
Reflux ratio	$R_D = 6.42$	$T_1^L = 339.15$ K (b.p.)		
Number of division	100			
Ex 2				
System	Methanol (1) / Water (3)			
Pressuer	101.3 kPa			
Feed	1.00 mol/s	$T^F = 298.65$ K	(center feed)	
	(1) 0.500	(2) 0.500		
Distillate	0.50 mol/s			
Bottoms	0.50 mol/s			
Reflux ratio	$R_D = 5.00$	$T_1^L = 298.15$ K		
Ex. 3				
Same as Ex. 1 except for $T^F = 333.15$ K and $T_1^L = 312.55$ K				

3.1 Segment size

The size of the segments, and the number of division, directly affects the total computation time required for convergence. Example 1 is solved with changing the size of the segment and the CPU time required for convergence is summarized in **Fig. 3**. The overall normalized θ method proves able to reduce the computation time to a reasonable level.

For faster calculation a large segment size is preferred, but sometimes this results in numerical instability due to large changes in the process variables, especially temperature, across the segment. This unfavorable situation, however, may be avoided by changing the segment size through the column.

The operation of Example 2 undergoes a large temperature disturbance due to introducing the cold feed and reflux. The temperature profiles in **Fig. 4** show that a properly chosen segment size can give consistent results with a lesser number of division.

3.2 Vapor phase diffusivity

Among the properties involved in the calculation, estimation of the binary diffusivity in the vapor phase seems to be most important. The specifications of Example 3 is taken from one of the experimental data obtained by the pilot-scale packed distillation column. The simulation has been done using three correlations for predicting vapor phase diffusivities; Neufeld (Reid *et al.*, 1987), Brokaw (Reid *et al.*, 1987), and Fuller *et al.* (Reid *et al.*, 1987). In **Fig. 5** not much difference can be seen between the methods of Brokaw and Fuller *et al.*. Only Neufeld gives largely deviated results, since the polarity is not accounted for in the correlation. The observed data and calculated results with Brokaw (Reid *et al.*, 1987) are given in **Table 5**.

The correlations of binary mass transfer coefficients for packings are not widely established. We employ the ones by Bravo and Fair (1985) in our simulations, since the geometry and material is very close to that of the pack-

Fig. 3 Effect of overall normalized θ method on calculation time **Fig. 4** Effect of segment size on temperature profiles

ing we used. The calculated results (solid lines) in **Fig. 5** show fairly good agreement with the experimental results. Using inadequate correlations may produce erroneous simulation results.

Conclusion

A simulation algorithm using a rate-based model is proposed as the equation-tearing method with iterative segment-wise calculations. Comparison of the simulation results show good agreement with the experimental results. Besides the characteristics of the proposed method are found as follows.

- Computation time can be reduced greatly without any numerical instability by using irregular segment sizes and by applying the overall normalized θ method for the bulk vapor-phase composition.

- Prediction of the diffusivities, especially of vapor mixtures, has a large influence on the calculation results. The models or correlations must be selected properly

(a) Composition profiles (see Fig. 5 (b) for keys)

(b) Temperature profiles

Fig. 5 Observed data and calculated results with different estimation methods of vapor phase diffusivity

considering the nature of mixtures and the type of packings. This closely relates the effective interfacial area as well.

New structured packings are being developed for exploring higher efficiency. As mentioned above the successful application of the rate-based model strongly depends on the accuracy of predicting transport properties. The authors hope for more active investigation on this field.

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Nomenclature

a = Interfacial area of liquid and vapor [m²]

Table 5 Observed and calculated results

		Methanol (1)	/	Ethanol (2)	/	Water (3)
Distillate	obs.	0.851		0.110		0.039
	cal.	0.864		0.113		0.023
Bottoms	obs.	0.036		0.031		0.933
	cal.	0.043		0.030		0.926

a_e	=	Effective interfacial area per unit volume	[m ² /m ³]
a_p	=	specific surface area of packing	[m ² /m ³]
C_p	=	specific heat at constant pressure	[J/mol K]
c	=	number of components	[-]
D	=	Fick diffusivity	[m ² /s]
E	=	heat transfer rate	[W/m ²]
F	=	molar flow rate of feed	[mol/s]
H	=	molar enthalpy	[J/mol]
h	=	heat transfer coefficient	[W/m ² K]
$K_{i,l}$	=	matrix elements defined in Eq. (37)	
k	=	multicomponent mass transfer coefficient	
k^b	=	zero flux binary mass transfer coefficient	[mol/(m ² ·s)]
L	=	molar flow rate of the liquid	[mol/s]
N	=	mass transfer rate	[mol/(m ² ·s)]
N_s	=	number of division in packed column	[-]
P	=	total pressure	[Pa]
p^s	=	saturated vapor pressure	[Pa]
S	=	molar flow rate of sidcut	[mol/s]
T	=	temperature	[K]
t	=	time	[min]
V	=	molar flow rate of vapor	[mol/s]
w_i	=	vector element defined in Eq. (39)	
x	=	mole fraction in liquid phase	[-]
Δx_i	=	vector elements defined in Eq. (38)	
y	=	mole fraction in vapor phase	[-]
Z	=	position in distillation column	[m]
z	=	feed composition	[-]
γ	=	activity coefficient	[-]
Θ	=	Correction factor in overall normalized θ method	[-]
θ	=	correction factor in normalized θ method	[-]
π	=	circular constant (= 3.141592)	[-]
Φ	=	component material balance around whole column	[-]
ϕ	=	component material balance around segment	[-]

<Subscripts>

i	=	component number
j	=	segment number
L	=	referring to liquid phase
m	=	mean value
t	=	referring to total
V	=	referring to vapor phase

<Superscripts>

I	=	referring to interface
L	=	referring to liquid phase
V	=	referring to vapor phase
-	=	average or partial molar value

Appendix: Estimation of multicomponent mass transfer coefficient k_{ij} from binary mass transfer coefficient k_{ij}^b

Liquid phase multicomponent mass transfer coefficients are obtained by the following matrix operation.

$$[k^L]_a = [B^L]^{-1} a [I^L] [\Xi^L] \quad (\text{A.1})$$

where $[I^L]$ is a thermodynamic factor matrix and $[\Xi^L]$ is a finite flux correction factors given by

$$[\Xi^L] = [\theta^L] \{ \exp [\theta^L] \} \{ \exp [\theta^L] - [I] \}^{-1} \quad (\text{A.2})$$

and

$$[\phi^L] = [\Gamma^L]^{-1} [\Phi^L] \quad (\text{A.3})$$

$[I]$ is the identity matrix, and $[B^L]$ and $[\Phi^L]$ are defined by the same general matrix $[M]$ whose elements are given below.

$$M_{ij} = \frac{m_i}{k_{ic}^{bL} a} + \sum_{j \neq i}^c \frac{m_j}{k_{ij}^{bL} a} \quad (i = 1, \dots, c-1) \quad (\text{A.4})$$

$$M_{ij} = -m_i \left(\frac{1}{k_{ij}^{bL} a} - \frac{1}{k_{ic}^{bL} a} \right) \quad (i = 1, \dots, c-1) \quad (\text{A.5})$$

and each matrix is obtained as follows.

$$\frac{[B^L]}{a} = [M] \quad \text{with} \quad m_i = \bar{x}_i \quad (\text{A.6})$$

$$[\Phi^L] = [M] \quad \text{with} \quad m_i = N_i^L \quad (\text{A.7})$$

For the vapor phase, the corresponding equations are derived by replacing x with y and the superscript L with V in the equation above. Note that $[\Gamma^V]$ in the vapor phase can be approximated by the identity matrix. Thus, the equations corresponding to Eqs. (A.1) and (A.2) becomes

$$[k^V] a = [B^V]^{-1} a [\Xi^V] \quad (\text{A.8})$$

and

$$[\Xi^V] = [\Phi^V] \{ \exp [\Phi^V] - [I] \}^{-1} \quad (\text{A.9})$$

$[B^V]$, $[\Phi^V]$ are defined by the same way as in Eqs. (A.4) - (A.7).

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