

A NEW PROCEDURE FOR YIELDING A RAPID SOLUTION BY USE OF THE MULTI- θ METHOD OF CONVERGENCE

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The definition of a new multiplier and the modification of the multi- θ method of convergence are developed for solving distillation problems. Furthermore, a procedure for stabilizing the numerical calculations and for yielding rapid solutions is proposed. It is found that an assumed value of a multiplier in each iterative computation can be assigned to an arbitrary number, and that it is better to be set equal to unity. To demonstrate the advantage of the proposed damping method, some numerical examples for distillation with hydrolysis of methyl acetate are presented. The reactive distillation problems are solved with the proposed procedure, and the results are compared with those by a conventional method. The proposed method constricts the large excursion resulting from the Newton-Raphson method. Then the corrected values can be confined within a region of convergence. The procedure proposed herein may be extended to other types of multistage separation processes.

Introduction

The multi- θ - η method of convergence proposed in the previous paper⁴⁾ has been developed and applied for solving reactive distillation problems involving steady state or unsteady state. An important aspect of the iterative computation method is to avoid over-correction and to achieve rapid convergence in obtaining a solution.

Holland²⁾ proposed the use of an appropriate weight factor to estimate the values of the variables for the next trial. Nelson⁶⁾ reported that, as the iterative number increases, the Newton-Raphson method becomes unreliable, often yielding large deviations in the estimation of the values of the variables for the next trial calculation; whereas by using the method of damped least square, convergence may be achieved. Also, Hirose¹⁾ demonstrated that a correction factor consisting of an exponential function may be used to avoid over-correction.

The purpose of this paper is to describe a new multiplier and a new damping method for solving problems involving reactive distillation.

1. Mathematical Model

A schematic diagram of a distillation column illustrating the material balances around the j th stage counted from the bottom is shown in Fig. 1. The transient component material balance enclosing stage j is expressed as follows⁵⁾:

$$\frac{H' dx_{ji}}{dt} = V_{j-1}y_{j-1i} - (L_j x_{ji} + V_j y_{ji}) + L_{j+1}x_{j+1i} + n_{Rj} + f_{ji} \quad (1)$$

The liquid holdup H' has been assumed to be constant and the vapor holdup has been assumed to be negligible. For steady-state operations, the first term on the left side in Eq. (1) becomes zero. Thus the material balance equation is expressed in the following functional form, where g_{ji} is equal to zero at convergence.

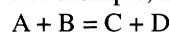
$$g_{ji} = V_{j-1}y_{j-1i} - (L_j x_{ji} + V_j y_{ji}) + L_{j+1}x_{j+1i} + n_{Rj} + f_{ji} \quad (2)$$

The corresponding equilibrium relation is given by

$$y_{ji} = K_{ji}x_{ji} \quad (3)$$

The vapor-liquid equilibrium ratio (K_{ji}) may be evaluated by use of the equations of state and other forms of the vapor-liquid equilibrium relationships.

For example, in the following reaction,



the resulting rate expression for the appearance of component A is expressed in the following form:

$$n_{RjA} = -(H_j/v_j^2)k_3 \{x_{jA}x_{jB} - (1/K_{Rj})x_{jC}x_{jD}\} \quad (4)$$

The rate of appearance of any component i by reaction is given by:

$$n_{Rji} = \epsilon_i n_{RjA} \quad (5)$$

where $\epsilon_i = 1$ for $i = A$ or B and $\epsilon_i = -1$ for $i = C$ or D .

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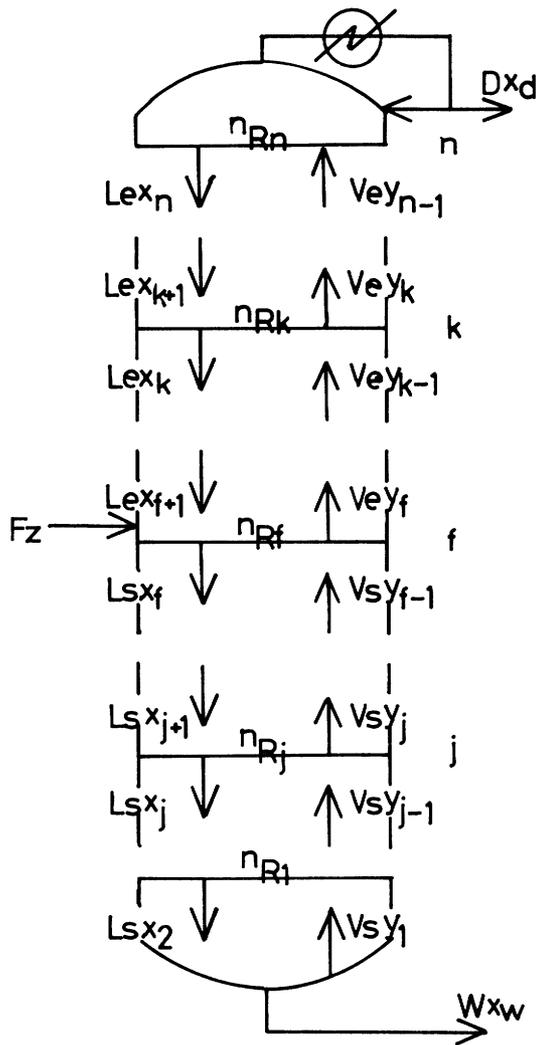


Fig. 1 Schematic diagram of distillation column.

2. Formulation of a Conventional Distillation Column in Steady-State Operation

For simplicity, consider the case of a column having one feed plate and constant molal overflow. For this case, the material balances are given by the following set of equations.

For $j = 1$ (bottom)

$$g_{1i} = -(W + V_s K_{1i}) x_{1i} + L_s x_{2i} + n_{R1i} \quad (6)$$

For $1 < j < f$ (stripping section)

$$g_{ji} = V_s K_{j-1i} x_{j-1i} - (L_s + V_s K_{ji}) x_{ji} + L_s x_{j+1i} + n_{Rj} \quad (7)$$

For $j = f$ (the end of the stripping section),

$$g_{ji} = V_s K_{j-1i} x_{j-1i} - (L_s + V_s K_{ji}) x_{ji} + L_s x_{j+1i} + n_{Rji} + q F z_{vi} \quad (8)$$

For $j = f + 1$ (the beginning of the enriching section),

$$g_{ji} = V_s K_{j-1i} - (L_e + V_e K_{ji}) x_{ji} + L_e x_{j+1i} + n_{Rji} + (1 - q) F z_{vi} \quad (9)$$

where $0 \leq q \leq 1.0$.

For $f + 1 < j < n$ (enriching section)

$$g_{ji} = V_e K_{j-1i} x_{j-1i} - (L_e + V_e K_{ji}) x_{ji} + L_e x_{j+1i} + n_{Rji} \quad (10)$$

For $j = n$ (top)

$$g_{ji} = V_e K_{n-1i} x_{n-1i} - (L_e + D K_{ni}) x_{ni} + n_{Rn} \quad (11)$$

where $x_{di} = K_{ni} x_{ni}$, $V_e = V_s + (1 - q)F$, $L_e = L_s - qF$, $V_e = L_e + D$ and $L_e = RD$.

3. The Definition of New Multipliers

New multipliers (θ_{ji} 's) are defined as follows:

$$x_{ji} = x_{ji}^a \theta_{ji} \quad (12)$$

$$\theta_{ji} = \theta_{ji}^a + \Delta \theta_{ji} \quad (13)$$

The superscript a refers to assumed values of the variables in a foregoing trial step. The definitions utilized in this procedure differ in form from those proposed in the previous paper⁴. Multipliers (θ_{ji} 's) are defined for every component and every plate. The new set of x_{ji} 's corrected for the next trial are found by use of the most recent set of θ_{ji} 's. Thus, the component material balance equations (the g_{ji} 's given by Eq. (2)) are expressed as a function of only the θ_{ji} 's for plates j and the plates adjacent to it, $j - 1$ and $j + 1$, as follows:

$$g_{ji} = F(\theta_{j-1i}, \theta_{ji} \text{ and } \theta_{j+1i}) \quad (14)$$

The values of θ_{ji} 's for the next trial are found by using the Newton-Raphson method. The complete set of Newton-Raphson equations is stated in the following matrix form for each component:

$$J(G/\Theta) \Delta \Theta = -G \quad (15)$$

where $J(G/\Theta)$ is the Jacobian matrix containing the partial derivative of g_{ji} 's with respect to θ_{ji} 's; $\Delta \Theta$ is a column vector including the increments of θ_{ji} 's; And G is a column vector including the values of the component material balance equations.

4. Evaluation of Elements of Jacobian Matrix

The elements of the Jacobian matrix are evaluated by use of the following equations of the g_{ji} 's.

For $k = j - 1$ and at $1 < j \leq f + 1$,

$$\frac{\partial g_{ji}}{\partial \theta_{ki}} = V_s K_{j-1i} x_{j-1i}^a = A_{ji} \quad (16)$$

But, at $j = 1$, A_{ji} 's do not exist.

At $j + 1 < j \leq n$,

$$\frac{\partial g_{ji}}{\partial \theta_{ki}} = V_e K_{j-1i} x_{j-1i}^a = A_{ji} \quad (17)$$

For $k = j$ and $j = 1$ (bottom),

$$\frac{\partial g_{ji}}{\partial \theta_{ki}} = \frac{\partial n_{R1i}}{\partial \theta_{1i}} - (W + V_s K_{1i}) x_{1i}^a = B_{1i} \quad (18)$$

Table 2. Specification of examples

$$F = 1.00 \text{ mol}\cdot\text{min}^{-1}, z_1 = 0.019, z_2 = 0.021, z_3 = 0.500, z_4 = 0.460,$$

$$H_1 = 1.00 \text{ dm}^3, H_2 \sim H_{10} = 0.60 \text{ dm}^3, m = 0.023 \text{ kg}\cdot\text{catalyst}/\text{dm}^3$$

Example number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Number of plates	10	10	10	10	10	10	10	10	10	10	10	10	10	20	5
Feed plate	5	5	5	5	10	10	10	10	1	1	1	1	5	10	3
V [mol·min ⁻¹]	3.0	3.0	5.0	5.0	3.0	3.0	5.0	5.0	3.0	3.0	5.0	5.0	3.0	3.0	3.0
R [-]	8.0	10.0	8.0	10.0	8.0	10.0	8.0	10.0	8.0	10.0	8.0	10.0	20.0	8.0	8.0
D [mol·min ⁻¹]	0.333	0.273	0.625	0.455	0.333	0.273	0.625	0.455	0.333	0.273	0.625	0.455	0.333	0.333	0.333
W [mol·min ⁻¹]	0.667	0.727	0.375	0.545	0.667	0.727	0.375	0.545	0.667	0.727	0.375	0.545	0.667	0.667	0.667

Table 3. Profiles of θ_{ij} calculated without the proposed damping method for example 1

i	bottom				feed plate				top					
	1	2	3	4	1	2	3	4	1	2	3	4		
Iter. No.														
1	5.2	3.5	0.4	-0.9	-0.2	1.7	-0.6	-0.6	-0.7	1.6	0.0	0.5		
2	5.7	3.8	1.4	-0.6	0.1	2.3	-0.1	0.9	-0.9	2.5	3.9	2.0		
3	5.0	3.1	1.9	5061.	0.6	1.4	15560.	2.1	1.7	2.0	5.2	2.6		
4	4.2	2.4	3.4	5065.	5.4	0.6	15560.	3.1	11.7	1.6	5.8	3.0		
5	3.9	1.5	30.5	5064.	3547.	12.4	15560.	3.1	16.2	2.1	9.6	3.5		
6	841.9	44.3	3719.	5063.	19850.	13710.	15560.	6.1	18.6	3.6	14.2	3.9		
		divergence					divergence					divergence		

Table 4. Profiles of θ_{ij} calculated with the proposed damping method for example 1

i	bottom				feed plate				top				
	1	2	3	4	1	2	3	4	1	2	3	4	
Iter. No.													
1	6.170	4.516	1.422	0.077	0.814	2.700	0.398	0.414	0.132	2.592	0.005	1.539	
2	0.547	0.238	0.997	0.325	0.255	0.610	0.527	1.500	0.003	0.898	4.885	1.490	
3	0.705	0.493	1.911	1.203	0.732	0.493	0.962	1.566	4.972	1.374	1.833	1.373	
4	0.843	0.990	0.800	1.747	0.850	1.209	1.481	1.308	1.838	1.302	1.297	1.312	
5	0.850	1.152	0.821	1.848	1.325	1.265	1.334	1.203	1.297	1.216	1.334	1.207	
6	0.919	1.339	0.870	1.499	1.250	1.122	1.214	1.085	1.287	1.042	1.177	1.090	
7	1.000	1.094	0.988	1.045	1.046	0.984	1.017	0.991	1.046	0.931	0.975	0.996	
8	1.007	1.031	1.003	0.994	1.001	0.979	0.991	0.996	0.975	0.967	0.974	0.997	
9	1.002	1.000	1.003	0.991	1.002	1.000	1.003	0.991	0.975	0.996	0.991	1.000	
10	0.999	0.995	1.001	0.998	0.997	0.998	0.999	1.001	0.991	1.004	1.000	1.000	
11	0.999	0.998	1.000	1.001	1.000	1.001	1.001	1.000	1.000	1.002	1.001	1.000	
12	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	

ized as follows.

Step 1: Assume a set of temperatures (T_j) and a set of liquid compositions (x_{ji} 's). The set of vapor compositions (y_{ji} 's) corresponding to the set of assumed liquid compositions are found by use of the vapor-liquid equilibrium relationships accompanied by chemical reaction. Then normalize y_{ji} 's. Assume that each θ_{ji} is equal to 1.0. Calculate the reaction rate (n_{Rji}) for each component and on each plate.

Step 2: On the basis of T_j , x_{ji} , y_{ji} , K_{ji} and n_{Rji} assumed in step 1, calculate the elements of the Jacobian matrix in Eq. (26) by use of Eqs. (16) through (25).

Step 3: Calculate $\Delta \theta_{ji}$'s by solving Eq. (26). Apply the damping method by use of Eq. (32).

Step 4: Correct a set of liquid compositions by use of Eq. (12) and Eq. (13). Normalize the set of liquid compositions for each plate by Eq. (27).

Step 5: If $\Delta \theta_{ji}$'s and g_{ji} 's are within an acceptable tolerance, convergence has been achieved. If not, repeat steps 1 through 4 on the basis of the most recent set of values

of variables, until convergence has been achieved.

7. Vapor-Liquid Equilibrium Relationships

K -values are evaluated according to the correlations of the vapor-liquid equilibrium relationships accompanied by chemical reaction which occurs in the liquid phase³). For example, in the esterification of methylacetate, the K -values of methyl alcohol (2), water (3) and methyl acetate (4), except acetic acid (1), are evaluated by the following equation

$$\ln K_i = A_i/T + B_i \quad (33)$$

where $A_2 = -1.98 \times 10^3$, $A_3 = -2.20 \times 10^3$ and $A_4 = -1.69 \times 10^3$.

Also, B_i is restated in the polynomial equation of the hypothetical liquid compositions (X_i and X_k). These liquid compositions are restated by the stoichiometry as the following form:

For evaluating B_2 , if $x_3 > x_4$ ($i = 2$ and $k = 3$), set X_1

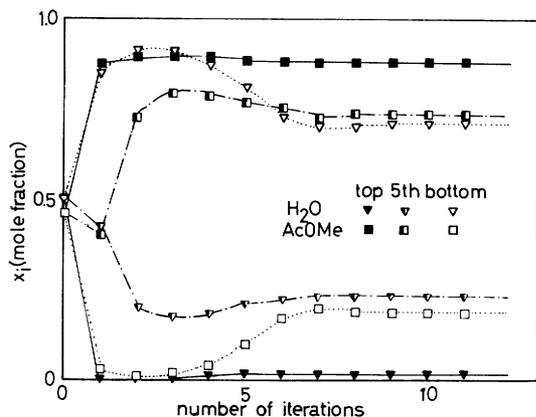


Fig. 2 Converging behaviours of liquid compositions of water and methylacetate

$$= x_1 + x_4, X_2 = x_2 + x_4, X_3 = x_3 - x_4 \text{ and } X_4 = 0$$

If $x_3 < x_4$ ($i = 2$ and $k = 4$), set $X_1 = x_1 + x_3$, $X_2 = x_2 + x_3$, $X_3 = 0$ and $X_4 = x_4 - x_3$.

Also, for evaluating B_3 and B_4 , if $x_1 > x_2$ ($i = 3$ or 4 and $k = 1$), set $X_1 = x_1 - x_2$, $X_2 = 0$, $X_3 = x_3 + x_2$ and $X_4 = x_4 + x_2$. If $x_1 < x_2$ ($i = 3$ or 4 and $k = 2$), set $X_1 = 0$, $X_2 = x_2 - x_1$, $X_3 = x_3 + x_1$ and $X_4 = x_4 + x_1$.

The polynomial equation has been obtained by use of a curve-fitting method from our data³) as follows:

$$B_i = \alpha_1 X_k^m (1 - X_i)^{3-m} + \alpha_2 X_k^p (1 - X_i)^{2-p} + \alpha_3 X_k^r (1 - X_i)^{1-r} + \alpha_4 (1 - X_i)^3 + \alpha_5 (1 - X_i)^2 + \alpha_6 (1 - X_i) + B_{oi} \quad (34)$$

where constants ($\alpha_1, \alpha_2, \alpha_3, \alpha_4, \alpha_5, \alpha_6, m, p, r$ and B_{oi}) in Eq. (34) are shown in Table 1.

The K -values of acetic acid are evaluated by the following equation.

$$t > 58^\circ\text{C}: K_1 = 1.63 \times 10^{-2} \times t - 0.936 \quad (t \text{ in } ^\circ\text{C}) \\ t < 58^\circ\text{C}: K_1 = 0.01 \quad (35)$$

8. Reaction Rate Equation

To solve the reactive distillation problems, the reaction rate equations are necessary, together with the vapor-liquid equilibrium relationships. Therefore, the reaction rate equation for the hydrolysis of methylacetate in the liquid phase has been studied from our experimental data over the temperature range 55°C to 70°C in a batch reactor with an ion-exchange resin fiber (Amberlite IR-120B) as the textile. The reaction rate for disappearance of methylacetate is presented in the following equation:

$$r_4 = m [k_m C_3 C_4 - k'_m C_1 C_2] = m [k_m x_3 x_4 - k'_m x_1 x_2] v^{-2} \quad (36)$$

where m is the concentration of the catalyst, the mass (kg) of the catalyst per unit volume (dm^3) of the liquid

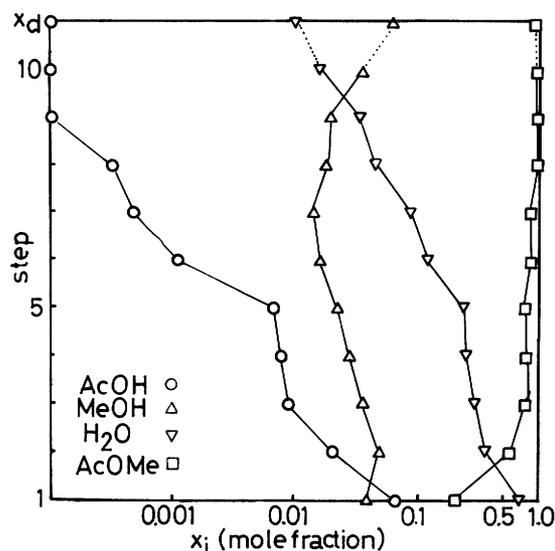


Fig. 3 Final profiles of liquid compositions

phase, and k_m and k'_m are the forward- and reverse-reaction rate constants at $m = 1 \text{ kg-cat./dm}^3$ respectively.

Two reaction rate constants may be restated as follows:

$$\ln k_m = -1.65 \times 10^3/T - 0.59 \quad (37)$$

$$\ln k'_m = -1.38 \times 10^3/T + 0.50 \quad (38)$$

If the reaction rate is negative, it is set to be zero.

9. Numerical Examples

To show the advantages of the proposed procedures, some numerical examples for reactive distillation problems in which the hydrolysis of methylacetate occurs in the liquid phase on each stage are given. Their specifications are presented in Table 2. Comparisons between results using of this damping method and those without it are made.

The values of the multipliers calculated without the proposed damping method diverged from unity in every example. These values of θ_{ij} 's for Example 1 are presented in Table 3 as a typical example.

However, the values of θ_{ij} 's corrected by use of the proposed damping method have been ensured to converge to unity at a trial number less than twenty in every example. These values of θ_{ij} 's for Example 1 are presented in Table 4 as a typical example. The convergence behaviours of the liquid compositions of water and methylacetate in the bottom, the feed plate and the top are shown in Fig. 2. The final profiles of the liquid compositions in each stage are shown in Fig. 3 for Example 1 as a typical example. The final calculated liquid compositions with the proposed damping method are presented in Table 5 for all examples in Table 2.

As shown in the tables and the figures, the proposed damping method has confined the corrected values within a region of convergence.

Table 5. Final liquid compositions calculated with the proposed damping method

example	bottom				feed plate				top				n_R	No. of trial
NO. \ i	1	2	3	4	1	2	3	4	1	2	3	4		
1	0.065	0.038	0.709	0.188	0.007	0.022	0.232	0.739	0.000	0.035	0.016	0.949	0.024	12
2	0.061	0.043	0.635	0.261	0.007	0.024	0.246	0.723	0.000	0.048	0.057	0.895	0.025	11
3	0.068	0.000	0.932	0.000	0.023	0.012	0.917	0.048	0.000	0.042	0.125	0.833	0.015	9
4	0.074	0.026	0.831	0.069	0.005	0.026	0.208	0.761	0.000	0.058	0.058	0.884	0.026	8
5	0.066	0.051	0.638	0.245	0.006	0.027	0.175	0.792	0.000	0.024	0.153	0.823	0.019	13
6	0.081	0.073	0.641	0.205	0.011	0.037	0.203	0.749	0.000	0.017	0.131	0.852	0.023	14
7	0.079	0.000	0.921	0.000	0.026	0.030	0.931	0.013	0.000	0.064	0.127	0.809	0.017	9
8	0.079	0.051	0.767	0.103	0.006	0.051	0.195	0.749	0.000	0.033	0.129	0.838	0.018	8
9	0.058	0.023	0.698	0.221	0.001	0.019	0.095	0.885	0.000	0.070	0.048	0.882	0.019	8
10	0.053	0.024	0.645	0.278	0.001	0.019	0.092	0.888	0.000	0.077	0.046	0.877	0.018	13
11	0.077	0.001	0.920	0.002	0.022	0.045	0.696	0.237	0.000	0.073	0.065	0.862	0.017	8
12	0.069	0.014	0.843	0.074	0.001	0.017	0.104	0.878	0.000	0.066	0.050	0.884	0.018	9
13	0.047	0.035	0.558	0.360	0.006	0.019	0.212	0.763	0.000	0.051	0.012	0.937	0.021	6
14	0.080	0.056	0.700	0.164	0.007	0.016	0.226	0.751	0.000	0.030	0.001	0.969	0.033	13
15	0.058	0.038	0.700	0.204	0.007	0.036	0.263	0.694	0.000	0.033	0.080	0.887	0.019	6

n_R = Total reacted moles

Conclusion

The definition of new multipliers and the modification of the multi- θ method of convergence have been developed for solving distillation problems.

Since the Newton-Raphson method may not always assure convergence in the computation of a separation system exhibiting highly nonideal behaviour, damping methods must be used to avoid divergence and achieve rapid convergence.

In the proposed procedure, a set of initial values of the multipliers at each trial step is assigned to unity. The proposed method can confine the corrected values by use of the Newton-Raphson method within a region of convergence.

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Nomenclature

A	= constant for each component of Eq. (33)	[-]
	= or element of Jacobian matrix	
B	= constant for each component of Eq. (33)	[-]
	= or element of Jacobian matrix	
C	= molal concentration	[mol-dm ⁻³]
	= or element of Jacobian matrix	
D	= distillate rate	[mol-min ⁻¹]
F	= total feed molal rate	[mol-min ⁻¹]
f	= component feed molal rate	[mol-min ⁻¹]
H	= liquid holdup on each plate	[dm ³]
H'	= molal liquid holdup on each plate	[mol]
K	= vapor liquid equilibrium ratio	[-]
K_R	= reaction equilibrium constant	[-]

k	= forward-reaction rate constant	[dm ³ ·mol ⁻¹ ·min ⁻¹]
k'	= reverse-reaction rate constant	[dm ³ ·mol ⁻¹ ·min ⁻¹]
L	= overflow liquid molal rate	[mol-min ⁻¹]
n_R	= reacted moles	[mol-min ⁻¹]
q	= feed thermal condition	[-]
r	= reaction rate	[mol-dm ⁻³ ·min ⁻¹]
T	= temperature	[K]
t	= time	[min]
W	= waste rate	[mol-min ⁻¹]
v	= liquid molal volume	[dm ³ ·mol ⁻¹]
X	= hypothetical mole fraction in liquid compositions	[-]
x	= mole fraction in liquid	[-]
y	= mole fraction in vapor	[-]
z	= overall feed composition in mole fraction	[-]
z_L	= liquid-phase feed composition in mole fraction	[-]
z_v	= vapor-phase feed composition in mole fraction	[-]
ϵ	= stoichiometric coefficient	[-]

<Subscripts>

d	= distillate
e	= enriching section
f	= feed plate
i	= component number
j	= stage number counted from bottom
k	= component number
s	= stripping section

<Superscripts>

a	= assumed values
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