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Nonequilibrium Modelling of Reactive Distillation: Multiple steady states in MTBE synthesis

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Abstract - We have developed a generic non-equilibrium (NEQ) model for packed reactive distillation columns. The important features of the model are the use of the Maxwell-Stefan equations for description of intraphase mass transfer and incorporation of a homotopy-like continuation method that allows for easy tracking of multiple steady states.

The interesting features of the developed NEQ model are demonstrated with a case study for production of Methyl-*tert*-butyl-ether (MTBE). Multiple steady states behaviour is observed when the bottom product flow rate of MTBE is varied. The results of the NEQ model show significant quantitative differences from an equilibrium stage (EQ) model. Furthermore, for the NEQ model counter-intuitive effects are observed for the low-conversion "branch". For example, increasing the mass transfer coefficient decreases the conversion of the low conversion branch. Decreasing the catalytic activity increases the conversion of the low conversion branch. The system is also found very sensitive to the amount of n-butenes (inerts) in the feed stream. With decreasing the n-butene feed, the phenomenon of multiple steady-states tends to disappear.

Keywords: reactive distillation, methyl tert-butyl ether synthesis, multiple steady states, non-equilibrium model, Maxwell-Stefan equations

INTRODUCTION

Currently there is considerable academic and industrial interest in multi-functional reactors, involving in-situ separation of products from the reactants (Krishna and Sie, 1994). Reactive distillation is one of the most common means of in-situ product removal (Agreda *et al.*, 1990; DeGarmo *et al.*, 1992; Doherty and Buzad, 1992). Both homogeneous and heterogeneous catalyzed chemical reactions can be carried out in a reactive distillation column (Sundmacher, 1995). There are three possible benefits of reactive distillation operation.

1. Higher conversions are obtained due to shifting of the equilibrium to the right. This is exemplified by the production of methyl acetate (Agreda *et al.*, 1990; Siirola, 1995) and tert-amyl ether (Bravo *et al.*, 1993)
2. Improved selectivity is obtained because of removal of products from the reaction zone. Such benefits are obtained for example in the production of propylene oxide from propylene chlorohydrins (Carra *et al.*, 1979) and for in the alkylation of benzene to produce cumene (Shoemaker and Jones, 1987).
3. Benefits of heat integration are obtained because the heat generated in the chemical reactions is used for vaporization. This is particularly advantageous for situations involving high heats of reaction such the hydration of ethylene oxide to ethylene glycol (Ciric and Gu, 1994).

A typical setup used for reactive distillation, using the MTBE process as example (Jacobs and Krishna, 1993), is shown at the left of Fig. 1. A column is usually split up in three sections: A reactive section, in which the reactants are converted into products and where, by means of distillation, the products are separated out of the reactive zone. The tasks of the rectifying and stripping sections depend on the boiling points of reactants and products. If the product is the lowest boiling component in the process, the rectifying section is used for product purification and reactant recycle, and the stripping section mainly for inert and by-product removal as well as reactant recycle. In case the product is the highest boiling component, the tasks of the sections are switched. With the setup as shown in Fig. 1, it is possible to virtually eliminate an entire post processing train in a process. One of the most spectacular examples of this kind is the Eastman process for production of methyl acetate (Siirola, 1995).

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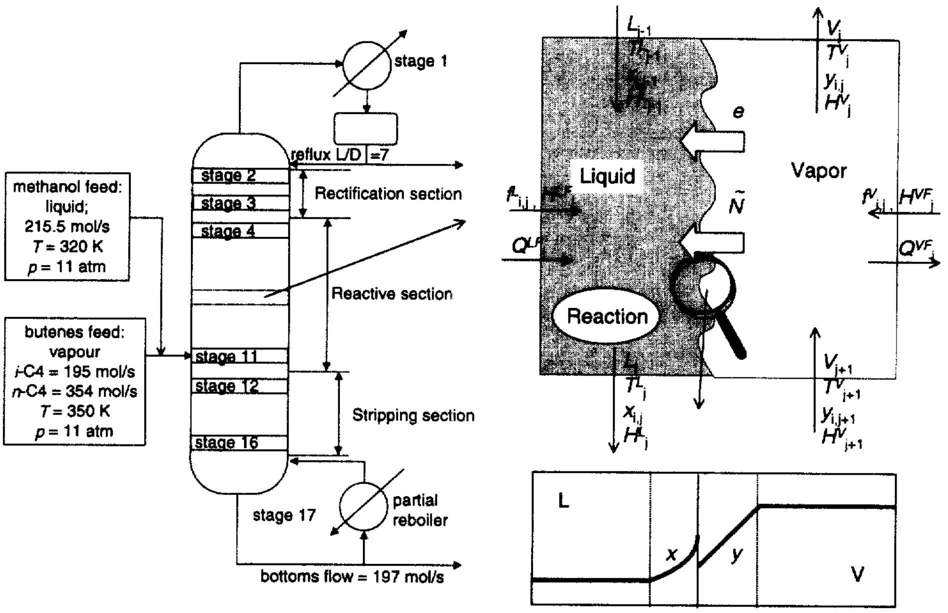

Figure 1. Left figure shows the configuration of a 17-stage reactive distillation column for synthesis of MTBE following the work of Jacobs and Krishna (1993). The right figure shows the schematic representation of the NEQ model.

For design purposes, a variety of models is available in the literature. First, we have steady-state models in which the vapour and liquid phase are assumed to be in equilibrium and allowance is made for finite reaction rates (Abufares and Douglas, 1995; Alejski *et al.*, 1988; Carra *et al.*, 1979; Ciric and Gu, 1994; Eldarsi and Douglas, 1998; Hauan et al., 1995; Jacobs and Krishna, 1993; Nijhuis *et al.*, 1993; Pilavachi *et al.*, 1997; Simandl and Svrcek, 1991). Such models stem from conventional equilibrium-stage modeling of distillation columns. However, for reactive distillation the estimation of the height equivalent to a theoretical plate (HETP) or tray efficiencies for packed and tray columns is a much more difficult, if not impossible task. This is because in the presence of chemical reactions the concept of tray efficiency is devoid of any physical meaning and can have positive, zero or negative values with almost no change in the hydrodynamic conditions (Higler *et al.*, 1998).

In the second group of models, the column dynamic behaviour is taken into account while retaining the assumption of vapour-liquid phase equilibrium and finite chemical kinetics (Abufares and Douglas, 1995; Espinoza *et al.*, 1994; Ruiz *et al.*, 1995; Scenna *et al.* 1998; Schrans *et al.*, 1996).

The third group of models are the rate based models for reactive distillation, which follow the philosophy of rate based models for conventional distillation (Krishnamurthy and Taylor, 1985; Taylor and Krishna, 1993) and in some cases using rigorous Maxwell-Stefan theory for calculation of the interphase heat and mass transfer rates (Bravo *et al.*, 1993; Higler *et al.*, 1998; Kreul *et al.*, 1998; Sawistowski and Pilavakis, 1979; Sundmacher, 1995; Sundmacher and Hoffmann, 1996; Zheng and Xu, 1992).

In our earlier work (Higler *et al.*, 1999) we had developed a steady-state nonequilibrium model for reactive distillation tray columns. With the aid of a case study involving production of ethylene glycol, we had demonstrated the importance of column hardware design on selectivity and conversion. We had underscored the limitations of equilibrium stage modeling, especially as regards the realization of the phenomena of multiple steady states. In the present paper our objective is to consider the NEQ modeling of packed reactive distillation columns and to point out some hitherto unrecognized features concerning the influence of hydrodynamics and mass transfer on the phenomenon of multiple steady-states. We develop our arguments using the case study of synthesis of MTBE.

NONEQUILIBRIUM MODEL

A schematic representation of the NEQ model is shown at the right of Fig. 1. This NEQ stage may represent a section of packing in a packed column. The development of the material balances, component balances, interphase transport equations and reaction rate equations are the same as developed in our earlier paper (Higler *et al.*, 1999). Our model formulation caters for arbitrary number of reactions and the component molar balances for the vapour and liquid phases are

$$V_j y_{i,j} - V_{j+1} y_{i,j+1} - f^V_{i,j} + \tilde{N}^V_{i,j} = 0 \qquad (1)$$

$$L_j x_{i,j} - L_{j-1} x_{i,j-1} - f^L_{i,j} - \tilde{N}^L_{i,j} - \sum_{m=1}^{r} v_{i,m} R_{m,j} \varepsilon = 0 \qquad (2)$$

where $\tilde{N}_{i,j}$ is the interfacial mass transfer rate and $R_{m,j}$ is the rate of reaction m on stage j. $v_{i,m}$ represents the stoichiometric coefficient of component i in reaction m and ε_j represents the reaction volume. For homogeneous reactions this is given by the total liquid holdup on stage j. For heterogeneous reactions (pseudo-homogeneous description), this is given by the total amount of catalyst present on the stage under consideration. The overall molar balances are obtained by summing eqs. (1) and (2) over the total number (c) of components in the mixture. The $\tilde{N}_{i,j}$ are related to the chemical potential gradients in either phase by the generalized Maxwell-Stefan equations (Krishna and Wesselingh, 1997; Taylor and Krishna, 1993)

$$\frac{y_{i,j}}{RT_j} \frac{\partial \mu^V_{i,j}}{\partial \eta} = \sum_{k=1}^{c} \frac{y_{i,j} \tilde{N}^V_{k,j} - y_{k,j} \tilde{N}^V_{i,j}}{c^V_{t,j} \left(\kappa^V_{i,k} a \right)_j} \qquad (3)$$

with a similar relation for the liquid phase. The $\kappa^L_{i,k}$ are mass transfer coefficients. Only *c - 1* of these equations are independent. The mole fraction of the *c-th* component is obtained by the summation equations for both phases. The enthalpy balances for both vapor and liquid phase are

$$V_j H^V_j - V_{j+1} H^V_{j+1} - F^V_j H^{VF}_j + e^V_j + Q^V_j \qquad (4)$$

$$L_j H^L_j - L_{j-1} H^L_{j-1} - F^L_j H^{LF}_j - e^L_j + Q^L_j \qquad (5)$$

where the interphase energy transfer rates e_j (equal in both phases) have conductive and convective contributions

$$e^V_j = -h^V_j a \frac{\partial T^V}{\partial \eta} + \sum_{i=1}^{c} \tilde{N}^V_{i,j} H^V_{i,j} \qquad (6)$$

with a similar relation for the liquid phase. h^L_j is the heat transfer coefficient in the liquid phase.

At the vapor liquid interface we assume phase equilibrium

$$y^I_{i,j} - K_{i,j} x^I_{i,j} = 0 \qquad (7)$$

where the superscript *I* denotes the equilibrium compositions and $K_{i,j}$ is the vapor - liquid equilibrium ratio for component i on stage j.

In addition to eqs (1) – (7), we have the summation equations for the mole fractions in the vapour and liquid phase and equations expressing the continuity of fluxes of mass and energy across the interface. Furthermore, in the NEQ model we take account of the pressure drop across a stage

$$p_j - p_{j-1} - \left(\Delta p_{j-1} \right) = 0 \qquad (8)$$

where p_j and p_{j-1} are the stage pressures and Δp_{j-1} is the pressure drop per tray from stage $j-1$ to stage j. The pressure drop over the stage is considered to be a function of the stage flows, the physical properties and the hardware design.

In the NEQ model hardware design information must be specified so that mass transfer coefficients, interfacial areas, liquid holdups can be calculated. To provide this information we have integrated a design methodology into the solution procedure for the model equations. During the calculations this design mode takes care of evaluating a design based on the calculated process variables, such as vapor and liquid flows and temperatures, and the physical properties, such as densities, surface tension, etc. During each iteration, the design is re-evaluated based on the design specification and modified if required. After convergence is achieved, we will then have a design that is consistent with the calculated process variables. When using this design mode, we need two additional specifications. These are the internals type, (sieve trays, valve trays, random packing, etc) and a design specification. For tray columns, this is normally a desired fraction of flooding. For packed columns, a desired pressure drop may also be used.

The NEQ model requires thermodynamic properties, not only for calculation of phase equilibrium but also for calculation of driving forces for mass transfer and, in reactive distillation, for taking into account the effect of nonideal component behavior in the calculation of reaction rates and chemical equilibrium coefficients. In addition, physical properties such as surface tension, diffusion coefficients, viscosities, etc. for calculation of mass (and heat) transfer coefficients and interfacial areas. For each reaction we need to know the stoichiometric coefficients, reaction orders, and kinetic constants and whether the reaction is heterogeneous or homogeneous. A homogeneous reaction can also take place in the mass transfer film, the modelling of which requires additional equations for taking into account the effect of the reaction on the interphase mass transfer rate. Finally, we need to know the reaction volume. In EQ model simulations the reaction volume often is specified. In the NEQ model, is the reaction volume equal to the total liquid holdup on a stage; this is obtained directly from the packing specifications and hydrodynamic correlations. For a heterogeneous reaction there are two options for the description of the reaction term. The simplest way is to treat the reaction pseudo-homogeneously, whereby catalyst diffusion and reaction are lumped into an overall reaction term. In this case one only needs to specify catalyst weight and activity. This approach is adopted here. A more rigorous approach would involve a complete description of diffusion and reaction inside the catalyst particles. This approach is adopted by Sundmacher (1994). In this case one also needs information about the catalyst geometry (surface area, mean pore diameter, etc).

Table 1 (a). Tray Specifications

	Rectifying Section	Stripping Section	
	Sieve	Sieve	
Column diameter	5.595	5.019	m
Total tray area	24.58	19.78	m^2
Number of passes	5	5	-
Tray spacing	0.61	0.61	m
Flow path length	0.92	0.82	m
Active area	19.21	15.32	m^2
Total hole area	2.12	1.52	m^2
Downcomer area	2.68	2.23	m^2
Hole diameter	0.0047625	0.0047625	m
Weir length	22.95	20.62	m
Weir height	0.0508	0.0508	m
Weir type	Segmental	Segmental	-
Downcomer clearance	0.0381	0.0381	m
Deck thickness	0.00254	0.00254	m

Table 1 (b). Reactive packed section

	Randomly packed Raschig rings	
Column diameter	6.0	m
Total column area	28.27	m^2
Packing height	0.7	m
Specific packing surface	600	m^{-1}
packing size	¼	in
Void fraction	0.72	-
Nominal size	0.00635	m
Critical surface tension	0.061	$N\ m^{-1}$
packing factor	5249.34	-
Packing density	0.41	$kg\ m^{-3}$
Internal porosity	0.45	-
Exchange capacity	4.54	meq (H^+)/g

The steady-state model equations are solved using Newton's method as outlined in Taylor *et al.* (1994). In addition, we have equipped the program with a continuation method for analysis of multiple steady state behaviour. Continuation methods normally are used for finding solutions to 'hard' problems, where a very good initial guess is required in order for Newton's method to converge on that solution. In addition, it has proven to be a valuable tool for finding multiple steady states in distillation columns. The underlying idea of continuation methods is that of path following, whereby a mathematical path is traced from a problem $G(x)$ for which we can obtain a solution relatively easily to the 'hard' problem $(F(x))$, thereby keeping track of the changes in the variables. Such a path is implicitly defined by the homotopy equation

$$H(x,t)=(1-t)G(x)+tF(x) \qquad (9)$$

If our original problem is n-dimensional, this equation describes a curve in $(n+1)$-dimensional space. And since the solution to $H(x,0)=0$ coincides with $G(x)=0$, we have at least one point on this curve. We now have to evaluate how the variables change along the curve, and correct each accordingly as we walk along the curve. By differentiating the homotopy equation with respect to the arc length, and integrating the resulting system of differential equations, we can generate an estimate for a new point on the curve, which can then be corrected to give the next point on the curve. For more details about this method, the reader is referred to Wayburn and Seader (1987) and Kubicek (1976).

Multiple steady states are located using one of the operational specifications (e.g. reboiler duty, bottom product flowrate, feed rate) as the continuation parameter. This results in a system of n equations with $(n+1)$ variables, thereby implicitly defining a curve in $(n+1)$-dimensional space. If we have a converged solution for a fixed specification, we have a starting point on this curve, and we can then apply exactly the same algorithm as described previously to "walk" along the curve. By doing so we can follow the steady state solution of the model as a function of that specification. Thus, we can obtain valuable information about steady state column behavior and multiple steady state regions as will be shown later. An added benefit of this approach is that now we are following a solution that is at any point on the curve describing a physically meaningful situation and not a strictly mathematical artifact. In the latter case, the homotopy path in itself does not have a physical meaning and might go through regions of negative mole fractions etc. In these regions, the method may fail if, for instance, in activity coefficient calculations the logarithm of the mole fractions is required.

MTBE CASE STUDY

We analyze the MTBE process as described by Jacobs and Krishna (1993) using an equilibrium stage (EQ) approach. This column contains a total of 17 equilibrium stages: condenser, 2 rectifying stages, 8 reactive stages (containing 8000 kg of catalyst), 5 stripping stages and a reboiler; see Fig. 1. In our NEQ model, the non-reactive rectifying and stripping sections are configured as sieve trays. The reactive section is made up of Raschig ring shaped catalyst packing as used by Sundmacher and Hoffmann. (1994). In order to fix the column specifications for the NEQ calculations we first ran our model in the design model in order to fix the column diameter and catalyst packed section height and determine the hardware design for the non-reactive trays. The tray design procedure is that of Kooijman (1995) and Kooijman and Taylor (1995). The design specifications are given in Table 1.

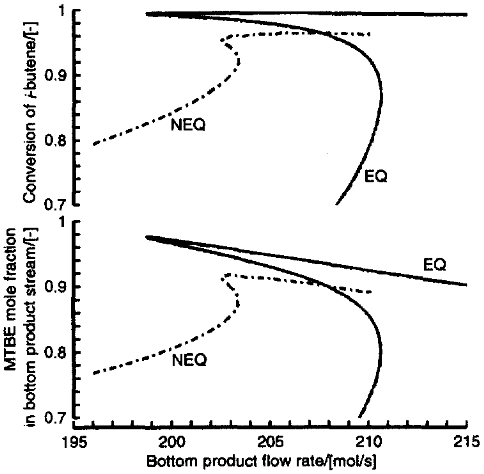

Figure 2. Comparison of EQ and NEQ models for MTBE synthesis.

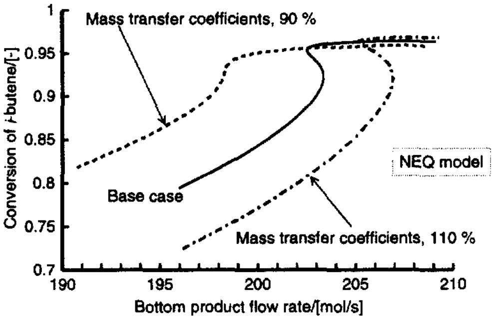

Figure 3. Sensitivity of NEQ model to mass transfer coefficients.

The UNIQUAC model was used for description of liquid phase nonideality, while the Soave-Redlich-Kwong equation was used for the vapor phase. The extended Antoine equation was used for calculation of the vapor pressure. Thermodynamic and kinetic data are taken from Rehfinger and Hoffmann, (1990).

From earlier work of Jacobs and Krishna (1993) and Nijhuis *et al.* (1993) we know that multiple steady states are to be expected for the chosen column configuration shown in Fig. 1. In order to track the steady states we chose the bottom product flow rate as the continuation parameter. Figure 2 compares the conversion and bottom product purity for the EQ and NEQ model calculations. In the EQ model implementation we have assumed a tray efficiency of 60% for the non-reactive stages. In the NEQ model sufficient number of "slices" in the reactive section are required for accurate calculations; our study shows that at least 90 slices are required for the 0.7 m high packed section for acceptable accuracy. For the packed section, mass transfer coefficients are calculated using Onda *et al*, (1968) correlation. The AIChE method was used for the sieve tray mass transfer calculations.

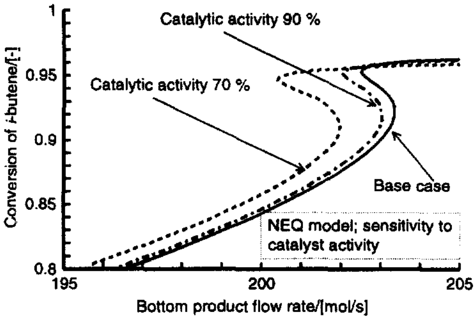

Figure 4. Sensitivity of NEQ model to catalyst activity.

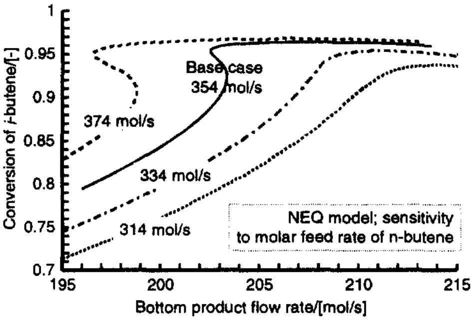

Figure 5. Sensitivity of NEQ model to n-butene feed flow rate.

Figure 2 shows that multiple steady-states exist for both EQ and NEQ models and the differences between these implementations are significant. It is interesting to note that the low conversion branch of the NEQ model lies above that of the EQ model. In the low conversion branch of the curve, the reaction proceeds in the reverse direction; incorporation of a mass transfer resistance (as in the NEQ) model hinders this and improves conversion and bottom product purity.

To reinforce the above observation we carried out a sensitivity analysis for the NEQ model in which the mass transfer coefficient was taken to be 90% and 110% of the base case. Figure 3 shows that the 90% case leads to *higher* conversions in the low conversion branch, whereas the 110% case leads to *lower* conversions. This counter-intuitive effect is because in the low conversion branch the reaction is proceeding in the "wrong" direction and decreasing the interphase transfer facility helps by mitigating a bad situation. The results of Fig. 3 emphasize the need for accurate estimation of mass transfer coefficients and the importance of ensuring operating conditions to stay in the high conversion branch; in the latter case the sensitivity to the estimation of the mass transfer coefficients is minimal.

The effect of decreasing catalyst activity, due to catalyst aging or deactivation, on the overall process performance are shown in Fig. 4. With decreasing catalyst activity, the conversion does not change substantially in the high conversion branch. This is because the reaction in the case under consideration is fast enough to come close to chemical equilibrium. In the low conversion branch decreasing catalyst activity improves the conversion, another counter-intuitive effect.

Calculations were done in which the flowrate of "inert" n-butene was chosen to be 354 (base case), 314, 334, and 374 mol/s and results are presented in Fig. 5. It is interesting to note that a certain minimum amount of n-butene is required for good operation of the given column. Normal butene serves as a 'coolant' of the reactive zone, thereby keeping the temperature of the reactive zone at a level where the equilibrium constant is favorable for the production of MTBE; reducing the feed of n-butene results in loss of conversion. We also note that the phenomenon of multiple steady states tends to disappear for low values of n-butene feed to the column. This role of "inerts" has not been stressed earlier in the literature on reactive distillation for MTBE.

CONCLUDING REMARKS

We have developed a non-equilibrium (NEQ) model for reactive distillation, and used the model to study a reactive distillation process as presented by Jacobs and Krishna (1993) for the production of MTBE. Such a NEQ model is indispensable for design because there is no simple procedure for estimation of HETP for the reactive packed section; such HETP values are required for use in EQ model based designs. We have demonstrated that the phenomenon of multiple steady states is also found for the NEQ model. Furthermore, our study has revealed the sensitivity of conversion to mass transfer coefficients, catalyst activity and n-butene feed flow rate.

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NOTATION

a	interfacial area, m^2
c	number of components, -
c_t	total concentration, mol m^{-3}
e	energy transfer rate, J s^{-1}
$F(x)$	Function vector
F^V	Vapor feedstream, mol s^{-1}
F^L	Liquid feedstream, mol s^{-1}
f	component feed stream, mol s^{-1}
$G(x)$	alternative function vector,-
H	molar enthalpy, J mol^{-1}
$H(x,t)$	Homotopy function vector, -
h	heat transfer coefficient, W m^{-2} K^{-1}
K	vapour-liquid equilibrium constant, -
L	Liquid flowrate, mol s^{-1}
$\tilde{N}$	Mass transfer rate, mol s^{-1}
p_j	stage pressure, Pa
Q	Heat duty, J s^{-1}
$R_{m,j}$	Reaction rate, mol m^{-3} s^{-1}
R	Gas constant, J mol^{-1} K^{-1}
r	number of reactions, -
T	Temperature, K
t	homotopy parameter,-
V	Vapor flowrate, mol s^{-1}
x	mole fraction in the liquid phase, -
y	mole fraction in the vapor phase, -

Greek

ε	reaction volume, m^3
η	dimensionless coordinate, -
κ	mass transfer coefficient, m s^{-1}
μ	Chemical potential, J mol^{-1}
ν	stoichiometric coefficient, -

subscripts

i	component index,-
j	stage index, -
k	alternative component index, -
m	reaction index,-
t	total,-

superscripts

F	Referring to feed stream
I	Referring to interface
L	Referring to liquid phase
V	Referring to vapor phase

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