

## Simulation of Suspension Catalytic Distillation for Synthesis of Linear Alkylbenzene\*

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**Abstract** Suspension catalytic distillation (SCD) has been developed recently as an innovative technology in catalytic distillation. In this paper, a brief introduction to SCD is given and an equilibrium stage (EQ) model is developed to simulate this new process for synthesis of linear alkylbenzene (LAB) from benzene and 1-dodecene. Since non-ideality of this reaction system is not strong, EQ model developed could be applied to it successfully. Simulation results agree well with experimental data, and indicate some characteristics of SCD process as an advanced technology for the production of LAB: 100% conversion of olefins, low temperature (90–100°C) and low benzene/olefin mole ratio.

**Keywords** suspension catalytic distillation, equilibrium stage model, linear alkylbenzene

### 1 INTRODUCTION

In recent years, catalytic distillation has been receiving increasing attention as an alternative to conventional reactor-followed-by distillation processes<sup>[1–5]</sup>. It combines catalytic reaction and distillation in a single column, with a lot of advantages: (1) substantially capital savings due to simplification or elimination of the separation system; (2) improved conversion and selectivity; (3) reduced by-product formation; (4) benefits of heat integration; (5) avoidance of hot spot and runaways.

Installation, containment and removal of the catalyst are significant problems when applying catalytic distillation process to a large-scale industrial practice. In conventional catalytic distillation, envelope catalyst particles are most commonly within wire gauze envelopes due to the limitations of flooding<sup>[6–10]</sup>, so as to fix the catalyst in reaction section of catalytic distillation column. Although catalyst envelopes could minimize the potential of losing the catalyst particles in case the packing was damaged, it will substantially reduce catalyst effectiveness due to limiting the mass and heat transfer between the catalyst particles and the fluid around them. In addition, catalyst regeneration and prefabrication of catalyst envelopes in this configuration are very inconvenient.

A new catalytic distillation technology, suspension catalytic distillation (SCD), has been developed recently<sup>[11–14]</sup>, in which smaller catalyst particles (10–100  $\mu\text{m}$ ) are used while they are 1–3 mm for conventional catalytic distillation<sup>[5]</sup> and suspended in the liquid phase flowing downwards from the top to the bottom of reaction section. It is the most important characteristic compared with conventional catalytic distillation. SCD process over a tungstophos-

phoric acid supported catalyst has been already applied to the synthesis of linear alkylbenzene in bench scale and has demonstrated following promising results: 100% conversion of olefins, approximate 100% selectivity and high quality product with more 2-LAB isomer and less tetralins impurities, under very mild conditions:  $0.05 \times 10^6$  Pa, low temperature (90–100°C) and low benzene/olefin mole ratio (1.0)<sup>[14]</sup>. In addition, SCD process is being scaled up to a pilot plant.

A variety of models are available in the literatures for screening, analysis, design and optimization of reactive distillation systems<sup>[15–21]</sup>. In this paper, an equilibrium stage model is developed to simulate SCD process, in which the Murphree tray efficiency is used to deal with departures from thermodynamic equilibrium, and synthesis of linear alkylbenzene (LAB) over a tungstophosphoric acid supported catalyst is studied as a test case.

### 2 MODEL DEVELOPMENT

In SCD process for LAB synthesis, the size and concentration of catalyst particles suspended in liquid phase generally are very small, for example, 50–100  $\mu\text{m}$  and  $0.05 \text{ g}\cdot\text{ml}^{-1}$ , thereby it is not necessary to take internal diffusion into account. The liquid phase can be considered as a pseudo-homogeneous phase and the chemical reaction as a pseudo-homogeneous reaction. Some assumptions adopted in traditional stationary equilibrium stage (EQ) model are also used here: (1) The process has reached a steady state; (2) Vapor and liquid phases in each stage are perfectly mixed, respectively; (3) Reactions take place only in the liquid phase; (4) The vapor and the liquid leaving each stage are in thermodynamic equilibrium.

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Table 1 EQ model equations of stage  $j$  for SCD column

Equation	Equation description
total material balance	$M_{t,j} = (V_j + U_j^V) + (L_j + U_j^L) - V_{j+1} - L_{j-1} - F_j - \sum_{m=1}^r \sum_{i=1}^C v_{i,m} R_{m,j} \varepsilon_j = 0$
component material balance	$M_{i,j} = (V_j + U_j^V) y_{i,j} + (L_j + U_j^L) x_{i,j} - V_{j+1} y_{i,j+1} - L_{j-1} x_{i,j-1} - F_j z_{i,j} - \sum_{m=1}^r v_{i,m} R_{m,j} \varepsilon_j = 0$
energy balance	$H_j = (V_j + U_j^V) H_j^V + (L_j + U_j^L) H_j^L - V_{j+1} H_{j+1}^V - L_{j-1} H_{j-1}^L - F_j H_j^F + Q_j = 0$
equilibrium relation	$E_{i,j} = E_{mv,i,j} K_{i,j} x_{i,j} - E_{mv,i,j} y_{i,j+1} - y_{i,j} + y_{i,j+1} = 0$
summation equation	$S_j^V = 1 - \sum_{i=1}^C y_{i,j} = 0 \quad S_j^L = 1 - \sum_{i=1}^C x_{i,j} = 0$

Based on the assumptions mentioned above, model equilibrium stages can be summarized as MESH equations in Table 1, MESH is an acronym referring to the different types of equation. M, E, S and H denote respectively the material balance equations, the phase equilibrium relations, the summation equations and the energy balance equations. On each stage there are  $2C + 3$  independent iteration variables and functions,  $\mathbf{X} = (V_j, y_{1,j}, y_{2,j}, \Lambda y_{C,j}, T_j, x_{1,j}, x_{2,j}, \Lambda x_{C,j}, L_j)^T$  and  $\mathbf{F} = (M_{t,j}, M_{1,j}, M_{2,j}, \Lambda M_{C,j}, H_j, E_{1,j}, E_{2,j}, \Lambda E_{C,j}, S_j^{L,V})^T$ , respectively. Besides,  $S_j^{L,V} = \sum_{i=1}^C (x_{i,j} - y_{i,j}) = 0$ .

Some of these MESH equations should be modified slightly when used to describe column reboiler or overhead condenser because both have many flexible specifications in addition to heat load, and the energy balance equation, in most cases, is to be modified.

The last terms in total and component material balance equations represent the chemical reaction contributions in the liquid phase, in which  $v_{i,m}$  stands for the stoichiometric coefficient for component  $i$  in the  $m$ th chemical reaction,  $\varepsilon_j$  denotes the reactive volume of stage  $j$  (total liquid hold up), and the reaction rate equations  $R_{m,j}$  can be written in terms of concentrations of the relevant components as follows

$$R_{m,j} = \sum_{q=1}^2 k_{m,q} \prod_i c_{i,j}^{m_i} = \sum_{q=1}^2 A_{m,q} \exp\left(-\frac{E_{m,q}}{RT_j}\right) \prod_i c_{i,j}^{m_i}$$

where  $c_{i,j}$  is the concentration of component  $i$  in stage  $j$ ,  $A_{m,q}$  is the Arrhenius pre-exponential factor,  $E_{m,q}$  is the energy of activation,  $R$  is the universal gas constant and  $T_j$  is the temperature in stage  $j$ . This reaction model can deal with either irreversible or reversible reactions.  $q = 1$  indicates the forward reaction,  $q = 2$  the reverse reaction.  $k_1$  is positive and  $k_2$  is negative.

It is noticed that the energy balance equation does not include such terms representing the heat of reaction because the vapor and liquid enthalpies are re-

ferred to the element rather than to the components.

The simultaneous convergence (SC) method based on Newton-Raphson algorithm, which is very suitable for large nonlinear algebraic equations system, was used to solve the steady-state EQ model for SCD. We employ a by-stage grouping of the equations and variables so that for a single column the Jacobian matrix is block tri-diagonal in structure and this set of equations can be solved using a generalized form of the Thomas algorithm. After giving the column specifications, feed conditions and initial values for independent iterative variables, an iterative calculation is undertaken until reaching right results or failing in convergence. To improve convergence, some effective steps can be adopted as outlined by Lee and Dudukovic<sup>[22]</sup>, temperature changes are limited to a maximum (10 K) and flow changes are up to a maximum fraction of the old flows.

### 3 ACASE STUDY FOR LAB SYNTHESIS

Alkylation reaction of benzene with 1-dodecene to make LAB carried out in a laboratorial SCD sieve tray column is studied by means of simulation model developed above. The column configuration chosen for SCD process is shown in Fig. 1. The details of the experimental apparatus were described by Wen<sup>[14]</sup>. The total number of stages is 25, including a total condenser and a partial reboiler. Operation pressure is  $1.013 \times 10^5$  Pa. The reaction section is settled in the middle of the column, from stage 7 down to stage 17. The numbers of stages in rectifying section and stripping section are 5 and 8 respectively. After perfectly mixed in a vessel and preheated to its bubble point at feed tray pressure, benzene, industrial olefins and catalyst particles are pumped to the reaction section. Between the reaction and stripping sections, there is a catalyst sedimentation facility used to separate catalyst from the suspension and to recycle it to the reaction section. The sedimentated catalyst particles are pumped to the vessel where they are mixed with the fresh benzene and industrial olefins, or sent to regenerate elsewhere if needed. The liquid overflowing from the sedimentation facility flows to the stripping

section, where all unreacted benzene is removed and rises to the reaction section. The task of the rectifying section is to separate benzene from mixed aromatics so that benzene with an extremely high purity can be obtained in the overhead condenser.

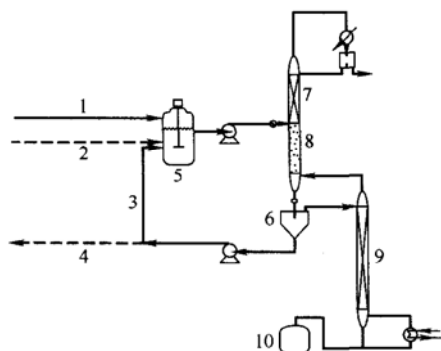


Figure 1 Experimental apparatus of SCD process for LAB synthesis

- 1—benzene and olefins; 2—supplemental catalyst;  
3—catalyst recycle; 4—catalyst regeneration;  
5—mixing; 6—liquid-solid separation;  
7—rectifying section; 8—reaction section;  
9—stripping section; 10—product

The composition of industrial olefins as hydrocarbon mixture is shown in Tables 2 and 3. In fact, it is very difficult to accurately simulate this system of LAB synthesis as a number of components and a series of reactions are involved. For the sake of simplification, some reasonable assumptions have to be adopted: *n*-dodecane is used to stand for the paraffin hydrocarbons ( $C_{10}$ — $C_{13}$ ) and 1-dodecene for the olefin hydrocarbons ( $C_{10}$ — $C_{13}$ ) in straight chain hydrocarbons due to their similar properties. A small amount of non-straight hydrocarbon, the products of some side reactions and unknown compounds are neglected. In other words, a four-component system composed of benzene, *n*-dodecane, 1-dodecene and LAB is discussed. The simplified feed conditions and other specifications are shown in Table 4.

Table 2 Composition of industrial olefins

Constitution	Mass fraction, %
straight chain hydrocarbons	96.0
non-straight chain hydrocarbon	2.6
aromatic hydrocarbon	1.2
diolefins	0.04
water	0.002
unknown	0.18
total	100

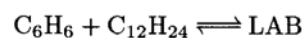
Table 3 Distribution of straight chain hydrocarbon

Straight chain hydrocarbons	Paraffin hydrocarbon	Olefin hydrocarbon
$C_9$	0.2	
$C_{10}$	16.7	1.4
$C_{11}$	32.2	3.2
$C_{12}$	24.9	3.0
$C_{13}$	12.3	2.1
Total	86.3	9.7

Table 4 Column specifications for simulation

number of components	4
feed temperature, K	388
feed pressure, Pa	$1.013 \times 10^5$
component flow rates in feed, mol·h <sup>-1</sup>	
benzene	0.448
1-dodecene	0.48
LAB	0.0
<i>n</i> -dodecane	4.2
reflux flow rate, mol·h <sup>-1</sup>	8.961
liquid hold up, m <sup>3</sup>	5.1
bottom flow rate mol·h <sup>-1</sup>	4.77
tray (Murphree vapor) efficiency	0.7

The alkylation reaction of benzene with 1-dodecene for LAB synthesis is



which is an exothermic and irreversible reaction due to its large value of reaction equilibrium constant. Other side reactions in this system also include further alkylation reactions of LAB with olefin and dimerization of olefins.

The rate equation for this reaction has little been cited in the literatures, in particular for the tungstophosphoric acid supported catalyst, so it has to be measured experimentally. In this paper, the following reaction rate equation applicable for high ratio of benzene to olefin and obtained by Wen<sup>[14]</sup> is adopted

$$-\frac{dc_{1,2}}{dt} = k_s c_{1,2}$$

$$k_s = 4.89 \times 10^4 \exp(-36000/RT)$$

where  $c_{12}$  represents concentration of 1-dodecene in liquid phase.

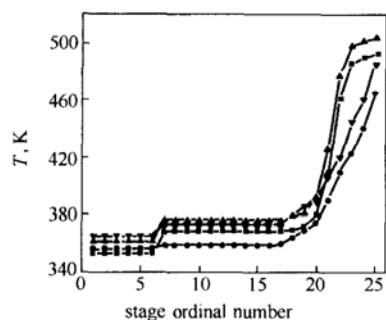
Calculation of vapour-liquid equilibrium constant of this system is based on two simplifications: (1) The vapour phase is an ideal gas due to low operation pressure; (2) The fugacity of pure liquid is insensitive to pressure, with the compressibility equal to one.

Hence

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i p^{sat}}{p}$$

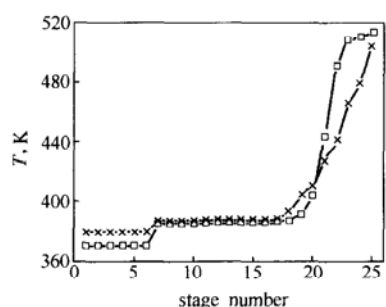
UNIFAC (universal quasi-chemical functional-group activity coefficients) group method is used for computing the activity coefficients of liquid phase and the vapour pressure is calculated by Antoine's equation.

Simulation results based on the EQ model of SCD process for LAB synthesis are shown in Figs. 2—8. For comparison with experimental observation, some data obtained by Wen<sup>[14]</sup> are also added.



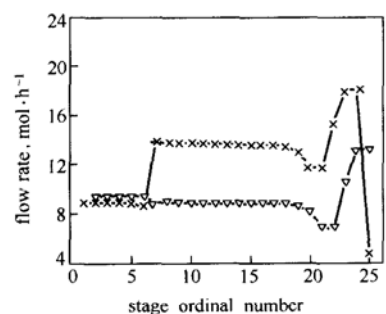
**Figure 2** Comparison of temperature profile predicted by EQ model and experimental data (operation pressure:  $1.013 \times 10^5$  Pa and  $1.317 \times 10^5$  Pa; mole ratio of benzene to olefin in feed: 1.0)

—■— EQ model at  $1.013 \times 10^5$  Pa;  
 —●— experimental value at  $1.013 \times 10^5$  Pa;  
 —▲— EQ model at  $1.317 \times 10^5$  Pa;  
 —▼— experimental value at  $1.317 \times 10^5$  Pa



**Figure 3** Comparison of temperature profile predicted by EQ model and experimental data (operation pressure:  $1.621 \times 10^5$  Pa; mole ratio of benzene to olefin in feed: 1.0)

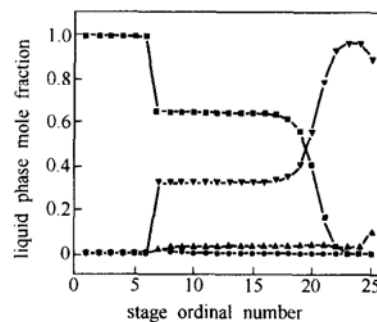
—□— EQ model prediction; —×— experimental data



**Figure 4** Flow rates of vapor and liquid calculated by EQ model (operation pressure:  $1.621 \times 10^5$  Pa; mole ratio of benzene to olefin in feed: 1.0)

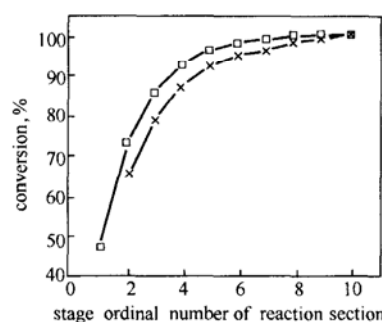
—×— liquid phase; —▽— vapor phase

Comparisons of the computed temperatures with experimental data of Wen<sup>[14]</sup> at the operation pressure of  $1.013 \times 10^5$ ,  $1.317 \times 10^5$  and  $1.621 \times 10^5$  Pa are shown in Figs. 2, 3 respectively. Fig. 4 indicates the computed profiles of flow rates of two phases. Fig. 5 shows the computed concentration profiles of liquid while Fig. 6 is a comparison between simulated and experimental conversions. As shown, for every stage in reaction and rectifying sections, the computed temperatures and conversions agree well with the experimental data. However, there are some deviations from



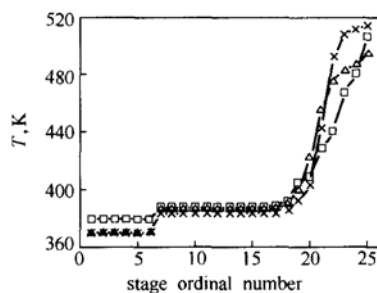
**Figure 5** Mole fraction of liquid phase calculated by EQ model

(operation pressure:  $1.621 \times 10^5$  Pa; mole ratio of benzene to olefin in feed: 1.0)  
 —■— benzene; —●— 1-dodecene; —▲— LAB;  
 —▽— n-dodecane



**Figure 6** Comparison of conversions predicted by EQ model and experimental data (operation pressure:  $1.621 \times 10^5$  Pa; mole ratio of benzene to olefin in feed: 1.0)

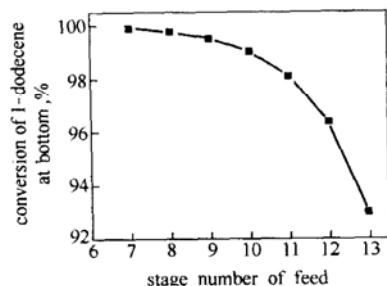
—□— EQ model prediction; —×— experimental data



**Figure 7** Comparison of temperature predicted by EQ model and experimental data (operation pressure:  $1.621 \times 10^5$  Pa; mole ratio of benzene to olefin in feed: 1.0)

—□— experimental value;  
 —×— EQ model (4 components);  
 —△— EQ model (7 components)

experimental values on several stages near the reboiler. These deviations are probably caused by the simplifications adopted. Obviously, lumping all paraffins to *n*-dodecane and neglecting other heavy components strongly influence the simulation results of stripping section. As seen from Fig. 5, the concentrations of the heavy components are very low. The concentration of benzene in reaction and rectifying section is much higher than that of other three components.



**Figure 8** Comparison of conversions corresponding to different stage numbers of feed (operation pressure:  $1.621 \times 10^5$  Pa; mole ratio of benzene to olefin in feed: 1.0)

Especially when the pure benzene is obtained in the condenser, the temperature profiles in these two sections are close to the boiling point of benzene at corresponding pressure. While stripping section removes all unreacted benzene to the reaction section and the concentration of benzene is very low especially on stages near the reboiler. Thus the temperature of this section is controlled by the concentration of other heavy components. Other heavy components in addition to the four used in model simulation also existed at the bottom of the column in Wen's experiment [14]. It makes the composition distribution slightly different from the results calculated by EQ model and causes the temperature deviation between experimental values and computed profiles.

Figures 2 and 3 show the comparisons of temperature profiles predicted by EQ model with the experimental data at different pressures. At  $1.013 \times 10^5$  Pa, the temperatures in the reaction zone are about 82–86°C, but when operation pressure is regulated to  $1.317 \times 10^5$  Pa or  $1.621 \times 10^5$  Pa the temperatures increase to catalyst activation temperature, 90–120°C.

It can be seen that SCD process inherently maintains a high concentration of benzene in the reaction section even though the mole ratio of benzene to olefin is very low. Thus it has several advantages when used to the synthesis of LAB: (1) The temperature profiles in the reaction section fluctuate slightly over the range suitable for reaction; (2) High local benzene/olefin ratio in reaction zone minimizes undesirable side reactions such as further alkylation reaction of LAB with olefin or dimerization of olefins, resulting in LAB with extremely high purity; (3) High purity benzene flowing from the condenser could continuously wash catalyst particles suspended in liquid phase, prolonging catalyst life remarkably.

Values of  $K$  for each component at each stage are summarized in Table 5. It is observed that the values of  $K$  for 1-dodecene and  $n$ -dodecane are close, making separation of these two components very difficult if no reactions happen. However, separation of these closely boiling mixtures becomes feasible because one of the components, 1-dodecene, can be removed away by alkylation of benzene.

**Table 5** Vapor-liquid equilibrium constant of LAB system

Stage No.	$K_{i,j}$			
	benzene ( $\times 10^0$ )	1-dodecene ( $\times 10^{-2}$ )	LAB ( $\times 10^{-5}$ )	$n$ -dodecane ( $\times 10^{-2}$ )
1	1.000	1.447	4.533	1.458
2	1.000	1.447	4.533	1.458
3	1.000	1.447	4.535	1.458
4	1.001	1.447	4.538	1.457
5	1.002	1.445	4.551	1.455
6	1.007	1.442	4.594	1.447
7	1.528	2.283	15.55	2.104
8	1.534	2.325	16.00	2.143
9	1.538	2.348	16.23	2.164
10	1.540	2.360	16.36	2.175
11	1.541	2.366	16.43	2.180
12	1.541	2.369	16.46	2.183
13	1.542	2.371	16.49	2.185
14	1.542	2.373	16.51	2.187
15	1.544	2.378	16.56	2.191
16	1.549	2.389	16.72	2.201
17	1.563	2.427	17.20	2.234
18	1.610	2.549	18.83	2.341
19	1.770	3.000	25.17	2.738
20	2.399	5.155	62.22	4.657
21	5.130	19.87	506.2	17.97
22	10.859	71.96	3462	65.93
23	13.545	104.4	6002	96.09
24	14.023	110.9	6556	102.2
25	14.238	119.0	7201	110.3

To verify that the temperature deviation between the simulation profiles and experimental values may be caused by the simplification of components in the reaction system, a seven-component system is adopted, which has three more components,  $n$ -decane,  $n$ -undecane and  $n$ -tridecane. Its simulation results compared with the four-component system are summarized in Fig. 7. It can be seen that the former system agrees better with the experimental value than the latter, which indicates that it is necessary to include more components to improve the simulation. At last, effect of different location of feed on the reaction conversion at the bottom of distillation column is probed, which is shown in Fig. 8.

Present work focuses mainly on simulation of the SCD technology from an academic viewpoint through EQ model, and there are several problems from an industrial perspective. For example, liquid hold up at top or bottom of the column or each stage in the middle of the column is very important parameter in industrial plant, but EQ stationary model can not describe them adequately, and specifying the same value of  $E_{mv,ij}$  for each component on each stage is also a disadvantage for EQ model. In addition, the liquid recycling from the catalyst sedimentation facility to the mixing vessel before pumped to feed stage should be considered adequately when applying SCD technology to industrial practice.

#### 4 CONCLUSIONS

SCD process using tungstophosphoric acid supported catalyst, as an advanced technology for the production of LAB, is worthwhile for further research and development. Based on some reasonable simplification, an equilibrium stage model is developed to simulate this new process for LAB synthesis. Simulation results not only agree well with experimental data but also explain some advantageous characteristics of SCD process which are suitable for LAB synthesis. Due to not strong non-ideality of LAB synthesis system, EQ model could be applied to its simulation and conceptual design.

#### NOMENCLATURE

$A_{m,q}$	the Arrhenius pre-exponent factor for $m$ th reaction
$C$	total number of components
$c_{i,j}$	concentration of component $i$ on stage $j$ , mol·m <sup>-3</sup>
$E_{mv,i,j}$	Murphree vapor efficiency of component $i$ on stage $j$
$E_{m,q}$	activation energy for $m$ th reaction, J·mol <sup>-1</sup>
$F$	vector of independent functions
$F_j$	feed flow rate to stage $j$ (zero for non-feed stages), mol·h <sup>-1</sup>
$H$	enthalpy, J·mol <sup>-1</sup>
$K$	vapor-liquid equilibrium constant
$k_{m,q}$	reaction coefficient for the $m$ th reaction
$k_s$	reaction rate constant, min <sup>-1</sup>
$L_j$	flow rate of liquid leaving stage $j$ , mol·h <sup>-1</sup>
$p$	pressure, Pa
$p^{\text{sat}}$	vapor pressure of pure liquid, Pa
$Q$	heat duty, J·h <sup>-1</sup>
$R$	universal gas constant, J·mol <sup>-1</sup> ·K <sup>-1</sup>
$R_{m,j}$	reaction rate of $m$ th reaction on stage $j$ , mol·m <sup>-3</sup> ·h <sup>-1</sup>
$r$	number of chemical reaction
$T$	temperature, K
$U$	side stream flow rate, mol·h <sup>-1</sup>
$V_j$	vapor flow rate leaving stage $j$ , mol·h <sup>-1</sup>
$X$	vector of independent variables
$x_{i,j}$	liquid mole fraction of component $i$ on stage $j$
$y_{i,j}$	vapor mole fraction of component $i$ on stage $j$
$z_{i,j}$	feed mole fraction of component $i$ on stage $j$
$\gamma_i$	liquid phase activity coefficient of component $i$
$\varepsilon_j$	reactive volume on stage $j$ , m <sup>3</sup>
$\nu_{i,m}$	stoichiometric coefficient of component $i$ in reaction $m$

#### Superscripts

F	feed stream
L	liquid-phase
$m_i$	exponent of component $i$ in $m$ th chemical kinetics rate expression
T	transpose representation
V	vapor-phase

#### Subscripts

$i$	component index
$j$	stage index
$m$	reaction index
$q$	$q = 1$ indicates the forward reaction, $q = 2$ is the reverse reaction
$t$	total

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