

# A Comparison of Steady-State Equilibrium and Rate-Based Models for Packed Reactive Distillation Columns

Jianjun Peng, Sebastien Lextraire, Thomas F. Edgar,\* and R. Bruce Eldridge

Department of Chemical Engineering, The Separations Research Program, The University of Texas at Austin, Austin, TX 78712-1062

A steady-state equilibrium model and a rate-based model were developed and compared for packed reactive distillation columns for the production of *tert*-amyl methyl ether (TAME) and methyl acetate. For the methyl acetate system, both models yield good agreement with experimental data. The results predicted by the equilibrium and rate-based models are similar with very few differences found under all simulation conditions. However, the rate-based model is much more complicated than the equilibrium model and also more difficult to converge. The influence of the reflux ratio, the operating pressure, the catalyst amount, and the heat loss was studied. It was found that reactive distillation behaves very differently from ordinary distillation. The existence of an optimal reflux ratio and an optimal pressure is predicted by both models.

## 1. Introduction

There has been much interest in the modeling of reactive distillation since successful industrial applications were introduced in the 1980s. A reliable model is important for understanding the behavior of reactive distillation. Two different types of models are available in the literature for reactive distillation: the equilibrium model and the rate-based model (or nonequilibrium model). The equilibrium models<sup>1,2</sup> assume vapor–liquid equilibrium at each stage. The departure from equilibrium is accounted for by tray efficiency (tray columns) or the height equivalent of a theoretical plate (HETP, packed columns). The rate-based models<sup>3–8</sup> assume that the vapor–liquid equilibrium occurs only at the interface and use the Maxwell–Stefan equation to describe the mass transfer between the vapor phase and the liquid phase. Lee and Dudukovic<sup>9</sup> compared an equilibrium model with a rate-based model for a tray reactive distillation column for the production of ethyl acetate. They concluded that the rate-based model is preferred because the Murphree tray efficiency is difficult to predict *a priori*. However, no experimental data were available to support their conclusion that rate-based model should be preferred. Baur et al.<sup>8</sup> also compared an equilibrium model with a rate-based model for reactive distillation. The methyl *tert*-butyl ether (MTBE) and ethylene glycol systems were studied for both models. They found that there are multiplicities in both the equilibrium model and the rate-based model but that the “window” within which steady-state multiplicity is observed is much narrower with the rate-based model.

The objective of this paper is to compare the equilibrium model with the rate-based model for packed reactive distillation columns, focusing on temperature and composition profiles. The contrast between reactive distillation and ordinary distillation is also discussed. Both the *tert*-amyl methyl ether (TAME) system and the methyl acetate system were studied with the equilibrium model and the rate-based model. For the methyl acetate system, the simulation results from the equilibrium

model and the rate-based model were compared to the experimental data published by Popken et al.<sup>10</sup> It was found that the results predicted by both the equilibrium model and the rate-based model agree with the experimental data reasonably well.

## 2. Equilibrium Model and Rate-Based Model

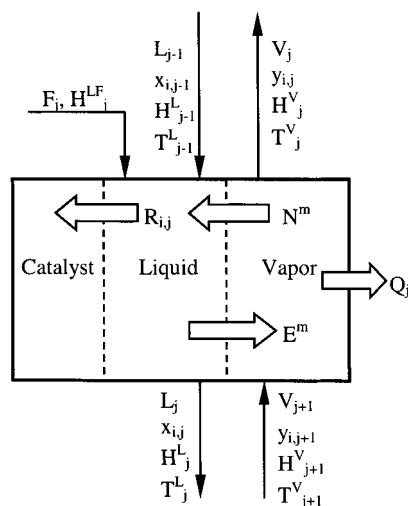
The equilibrium model used in this paper consists of the conventional MESH equations. The reactions are assumed to be pseudohomogeneous. The HETPs of both the reactive packing and the nonreactive packing are chosen empirically, thus determining the number of theoretical stages used in the simulation.

The rate-based model used in this paper follows the approach of Taylor et al.<sup>11</sup> for conventional distillation in combination with the assumptions listed below. The packed reactive distillation column is vertically divided into a number of control volumes. Each control volume contains liquid phase, vapor phase, and catalyst; is homogeneous in temperature and composition; and is referred to as a segment in this paper. The configuration for each segment is shown in Figure 1. The following assumptions were made to simplify the model: (1) Each phase is perfectly mixed in each segment. (2) Vapor–liquid equilibrium is assumed only at the interface. (3) At the liquid–catalyst interface, a pseudohomogeneous reaction is assumed. Thus, reaction and diffusion inside the catalyst are not considered. (4) The finite-flux mass-transfer coefficients are assumed to be the same as the low-flux mass-transfer coefficients. This assumption has been justified by simulation results. (5) The heat-transfer coefficients are assumed to be constant for all segments. This assumption has also been justified by simulation results. (6) The condenser and the reboiler are treated as equilibrium stages.

The equations for the equilibrium model and the rate-based model are given in Tables 1 and 2 for comparison. The equations used to calculate physical and transport properties<sup>12–15</sup> can be found in the Supporting Information.

The overall mass-transfer coefficient approach is a simplified rate-based approach in which the temperature in the liquid phase is assumed to be the same as that in the vapor phase. The mass-transfer coefficients for the liquid phase and the vapor phase are combined

\* Corresponding author. Phone: +1 (512) 471 3080. Fax: +1 (512) 471 7060. E-mail: edgar@mail.utexas.edu.



**Figure 1.** Schematic diagram of a rate-based segment.

to calculate the overall mass-transfer coefficients. The temperature and composition at the interface are not variables in the overall mass-transfer coefficient approach.

Both the equilibrium and rate-based models (including the overall mass-transfer coefficient approach) were implemented in gPROMS, an equation-oriented simulator. Radfrac and Ratefrac in AspenPlus were also used to carry out simulations. The results from AspenPlus were compared with those from the models in this work. The advantage of implementing models in an equation-oriented simulator is that the model is known exactly and can be modified to test the validity of various assumptions. There is also more flexibility when convergence problems are encountered. However, one disadvantage is that solving a model in an equation-oriented simulator is usually slower and convergence is usually poorer than for a sequential simulator with predefined modules, such as AspenPlus.

### 3. Simulation Results

Two packed reactive distillation columns for the production of TAME and methyl acetate were used to carry out simulations with the equilibrium and rate-based models developed in this work. The purpose of the simulations is to compare the equilibrium model with the rate-based model under various conditions and to study the behavior of reactive distillation.

There are five components in the TAME system: methanol, 2-methyl-1-butene (2M1B), 2-methyl-2-butene (2M2B), *tert*-amyl methyl ether (TAME), and *n*-pentane. There are three reversible reactions in this system, the etherification reactions of 2M1B and 2M2B and the isomerization reaction between 2M1B and 2M2B. The kinetic model of Rihko et al.<sup>16</sup> was used to calculate the reaction rates. The UNIQUAC equation was used to calculate the liquid activity coefficients with binary interaction parameters from AspenPlus (version 10.2).

The reactive distillation column configuration at the Separations Research Program (SRP) facility in Austin, Texas (UT-SRP), was used as the basis for simulations of the TAME system. The inner diameter of the column is 0.1615 m. The reactive packing is KATAMAX, and the nonreactive packing is FLEXIPAC, both from Koch-Glitsch. The height of the packing for each section is shown in Figure 2.

The methyl acetate system was the first commercial application of reactive distillation. There are four components in this system: methanol, acetic acid, methyl acetate, and water. There is only one reversible reaction in this system, the esterification reaction of acetic acid with methanol. The kinetic model of Popken et al.<sup>17</sup> was used to calculate the reaction rate, and the UNIQUAC equation was used to calculate the liquid activity coefficients with binary interaction parameters from Popken et al.<sup>17</sup>

The vapor–liquid equilibrium (VLE) of the methyl acetate system is much more complicated than that of the TAME system because of the dimerization of acetic acid in the vapor phase. The approach of Marek<sup>18</sup> was followed to calculate the VLE. The VLE experimental data for this system published by Sawistowski et al.<sup>19</sup> were used to check the accuracy of the VLE equations used in this paper. The average error is 0.014 in composition and 1.54 K in temperature.

The one-feed setup and two-feed synthesis setup used by Popken et al.<sup>10</sup> for reactive distillation experiments were used for the simulations of the methyl acetate system. The inner diameter of the column is 0.05 m. The reactive packing is Katapak-S, and the nonreactive packing is Sulzer BX, both from Sulzer Chemtech Ltd.

**3.1. Comparison with Radfrac and Ratefrac.** To check the models developed in this paper, both Radfrac (equilibrium model) and Ratefrac (rate-based model) in AspenPlus were used for simulations of the TAME system and the methyl acetate system. The temperature and composition profiles of the TAME system from the equilibrium model were compared with those from Radfrac under the same conditions, with excellent agreement. Run number 1-12 of the one-feed setup in Popken et al.<sup>10</sup> was used to compare the equilibrium model with Radfrac for the methyl acetate system. The agreement was also excellent.

The temperature and composition profiles of the TAME system predicted by the rate-based model are in excellent agreement with those from Ratefrac under the same conditions, even though different methods were used to calculate the diffusion coefficients. The details of the comparisons can be found in the Supporting Information (Figures 1s, 2s, and 3s).

**3.2. Influence of the Number of Segments.** When the number of segments for the rate-based model is chosen to be the same as the number of theoretical stages for the equilibrium model, there is a significant difference in the temperature and composition profiles predicted by the two models for both the TAME and the methyl acetate systems (see Figures 3 and 4, respectively). However, the difference in the profiles between the two models at the top and the bottom of the column is less than that in the middle of the column. When the number of segments for the rate-based model is increased, both the temperature and composition profiles change significantly (see Figures 5 and 6). The number of segments can be considered as a parameter that accounts for backmixing in the distillation column. When the number of segments is extremely large, essentially no backmixing occurs in the distillation column, and therefore, the separation is the best. Because backmixing and other nonideal conditions do exist in real columns, an appropriate number of segments should be used. However, that number cannot be determined in advance. When experimental data are available, the simulation results can be compared to

**Table 1. Equations for the Condenser and Reboiler**

	total condenser ( $j = 1$ )	total reboiler ( $j = N$ )
material balance	$M_{i1} = V_2 y_{i,2} - (1 + r_1^L) L_1 x_{i,1} = 0 \quad (1)$	$M_{i,N} = L_1 x_{i,N-1} - V_N y_{i,N} - L_N x_{i,N} = 0 \quad (2)$
equilibrium		$Q_{i,N} = y_{i,N} - K_{i,N} x_{i,N} = 0 \quad (3)$
summation	$S_{x1} = \sum_{i=1}^c x_{i,1} - 1 = 0 \quad (4)$	$S_{xN} = \sum_{i=1}^c x_{i,N} - 1 = 0 \quad (5)$
		$S_{yN} = \sum_{i=1}^c y_{i,N} - 1 = 0 \quad (6)$
energy balance	$E_1 = V_2 H_2^N - (1 + r_1^L) L_1 H_1^L - Q_c = 0 \quad (7)$	$E_N = L_{N-1} H_{N-1}^L - V_N H_N^N - L_N H_N^L + Q_r = 0 \quad (8)$
variables	$x_{i1}, Q_c, L_1, x_{i,N}, y_{i,N}, Q_r, V_N, T_N$	
equations	$M_{i1}, E_1, S_{x1}, M_{i,N}, Q_{i,N}, E_N, S_{xN}, S_{yN}$	

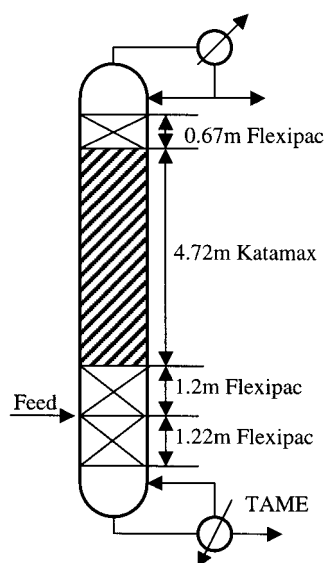
**Table 2. Equations for the  $j$ th Stages (Segments)**

Equilibrium Model	Rate-Based Model
$M_{i,j} = V_{j+1} y_{i,j+1} + L_{j-1} x_{i,j-1} + F_j x_{i,j}^F -$ $V_j y_{i,j} - L_j x_{i,j} - W_{ej} R_{i,j} = 0 \quad (9)$	<b>Material Balance</b> $M_{i,j}^N = V_{j+1} y_{i,j+1} - V_j y_{i,j} - \frac{\pi}{4} D_T^2 I_{sj} a_{ej} N_{i,j}^m = 0 \quad (10)$ $M_{i,j}^L = L_{j-1} x_{i,j-1} + F_j x_{i,j}^F - L_j x_{i,j} + \frac{\pi}{4} D_T^2 I_{sj} a_{ej} N_{i,j}^m - W_{ej} R_{i,j} = 0 \quad (11)$
<b>Equilibrium</b> $Q_{i,j} = K_{i,j} x_{i,j} - y_{i,j} = 0 \quad (12)$	<b>Equilibrium at the Interface</b> $Q_{i,j}^I = y_{i,j}^I - K_{i,j} x_{i,j}^I = 0 \quad (13)$
$S_{xj} = \sum_{i=1}^c x_{i,j} - 1 = 0 \quad (14)$ $S_{yj} = \sum_{i=1}^c y_{i,j} - 1 = 0 \quad (15)$	<b>Summation</b> $S_{xj} = \sum_{i=1}^c x_{i,j} - 1 = 0 \quad S_{yj} = \sum_{i=1}^c y_{i,j} - 1 = 0 \quad (16)$ $S_{xj}^I = \sum_{i=1}^c x_{i,j}^I - 1 = 0 \quad S_{yj}^I = \sum_{i=1}^c y_{i,j}^I - 1 = 0 \quad (17)$
$E_j = V_{j+1} H_{j+1}^N + L_{j-1} H_{j-1}^L + F_j H_j^F -$ $V_j H_j^N - L_j H_j^L - Q_j = 0 \quad (18)$	<b>Energy Balance</b> $E_j^N = V_{j+1} H_{j+1}^N - V_j H_j^N - \frac{\pi}{4} D_T^2 I_{sj} a_{ej} [h_j^N (T_j^N - T_j^I) +$ $\sum_{i=1}^c N_{i,j}^m \bar{H}_{i,j}^N] = 0 \quad (19)$ $E_j^L = L_{j-1} H_{j-1}^L + F_j H_j^F - L_j H_j^L - Q_j + \frac{\pi}{4} D_T^2 I_{sj} a_{ej} [h_j^L (T_j^I - T_j^L) +$ $\sum_{i=1}^c N_{i,j}^m \bar{H}_{i,j}^L] = 0 \quad (20)$ $E_j^I = h_j^N (T_j^N - T_j^I) + \sum_{i=1}^c N_{i,j}^m \bar{H}_{i,j}^N - h_j^L (T_j^I - T_j^L) -$ $\sum_{i=1}^c N_{i,j}^m \bar{H}_{i,j}^L = 0 \quad (21)$
	<b>Mass-Transfer Rates</b> $R_j^V = N_j^m - C_{vj}^V (y_j - y_j^I) - y_j \sum_{i=1}^c N_{i,j}^m = 0 \quad (i = 1, \dots, c-1) \quad (22)$ $R_j^L = N_j^m - C_{vj}^L (x_j^I - x_j) - x_j \sum_{i=1}^{nc} N_{i,j}^m = 0 \quad (i = 1, \dots, c-1) \quad (23)$
	The approach of Taylor et al. <sup>11</sup> is followed to calculate $k^L$ and $k^V$ . <b>Variables</b> $x_{i,j}, y_{i,j}, x_{i,j}^I, y_{i,j}^I, T_j^L, T_j^V, L_j, V_j, N_{i,j}^m$ <b>Equations</b> $M_{i,j}, Q_{i,j}, S_{xj}, S_{yj}, E_j, M_{i,j}^N, M_{i,j}^L, Q_{i,j}, R_{i,j}^L, E_j^L, E_j^V, E_j^I, S_{xj}, S_{yj}, S_{xj}^I, S_{yj}^I, R_{i,j}^V$

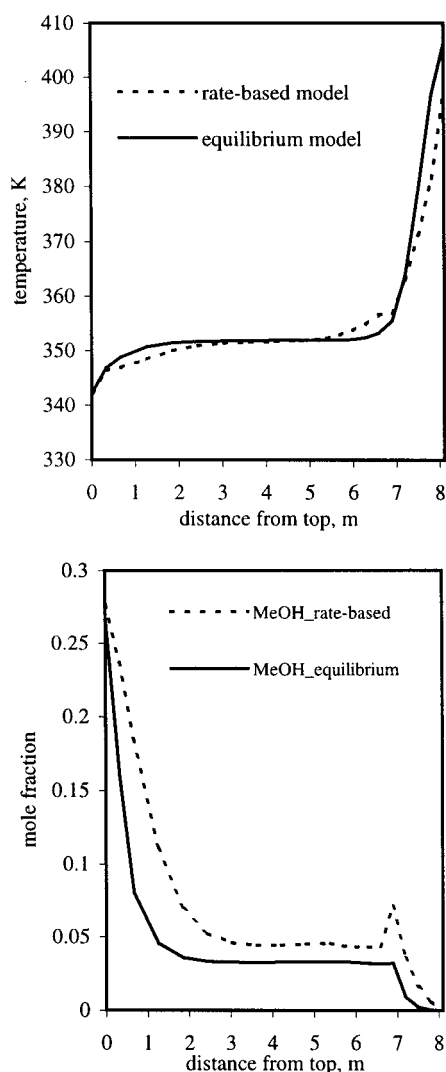
experimental data, and the optimal number of segments can be determined. The influence of the number of segments for ordinary distillation without reaction was also studied and was found to be much weaker.

**3.3. Relationship between the Equilibrium and Rate-Based Models.** There is a relationship between the equilibrium and rate-based models. When the number of segments in the rate-based model is chosen

to be the same as the number of theoretical stages in the equilibrium model and the vapor–liquid interfacial area is increased, the profiles from the rate-based model become closer to those from the equilibrium model. When the vapor–liquid interfacial area is about 100 times as large as the actual area, the profiles from the rate-based model are almost identical to those from the equilibrium model (see Figure 7). This is reasonable

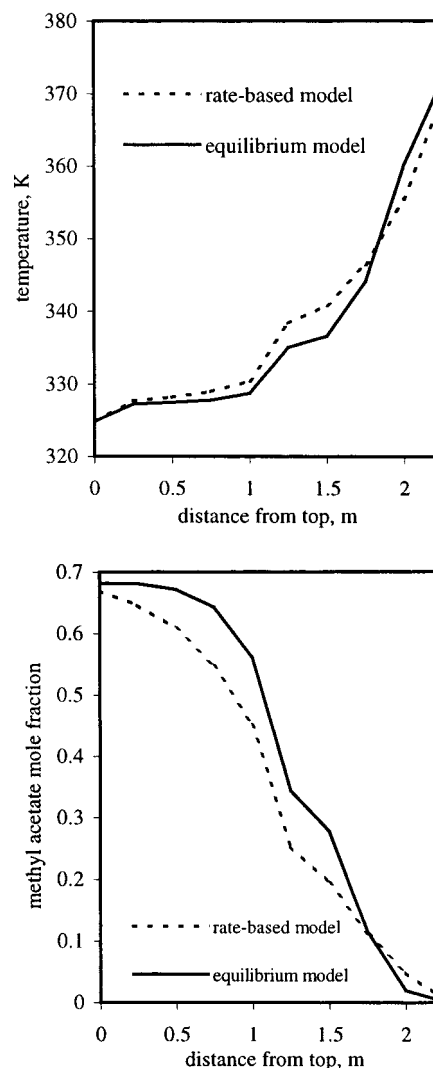


**Figure 2.** Pilot-plant reactive distillation column at UT-SRP.



**Figure 3.** Comparison of temperature and composition profiles between the equilibrium model and the rate-based model for the TAME system.

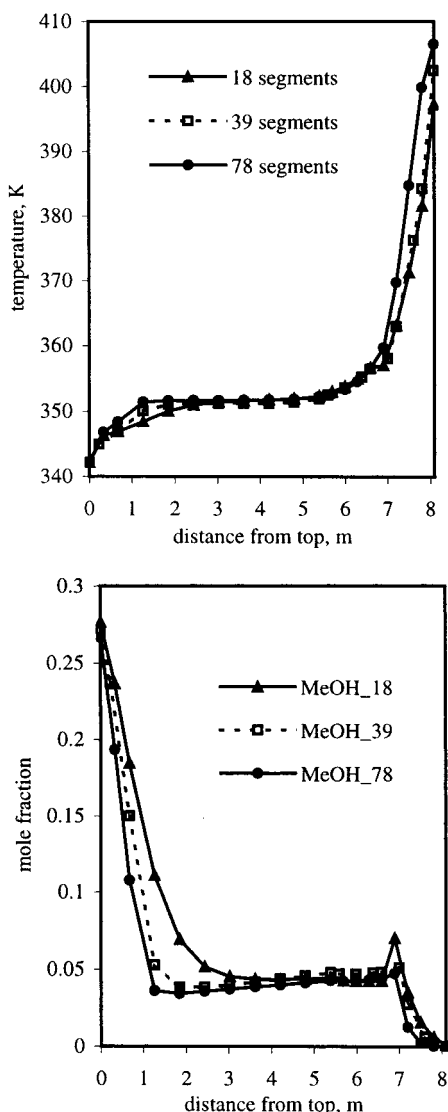
because, when the interfacial area is very large, the vapor and liquid phases should contact each other very



**Figure 4.** Comparison of temperature and composition profiles between the equilibrium model and the rate-based model for the methyl acetate system.

well and be in equilibrium. This relationship is important for improving the convergence of the rate-based model. Solving the rate-based model was always much more difficult than solving the equilibrium model for all of the simulations carried out in this work. The equilibrium model can be solved first, and the results can be used as the initial guess for the rate-based model. Then, a large value can be used for the interfacial area, and the solution of the rate-based model can be reached easily, because the initial guess is close to the solution. After that, the interfacial area can be decreased gradually to the actual value to yield the solution for the real configuration.

**3.4. Comparison with Experimental Data.** For the methyl acetate system, experimental reactive distillation data are available.<sup>10</sup> Therefore, a comparison between the experimental data and model predictions is summarized in Table 3 (one-feed setup) and Table 4 (the two-feed setup). No parameters in the models developed in this paper were fitted from experimental data. For the one-feed setup, the accuracies of the equilibrium model and the rate-based model are almost the same. Increasing the number of segments for the rate-based model can slightly reduce the error in the predicted compositions. For the two-feed setup, the accuracies of the equilibrium and rate-based models are

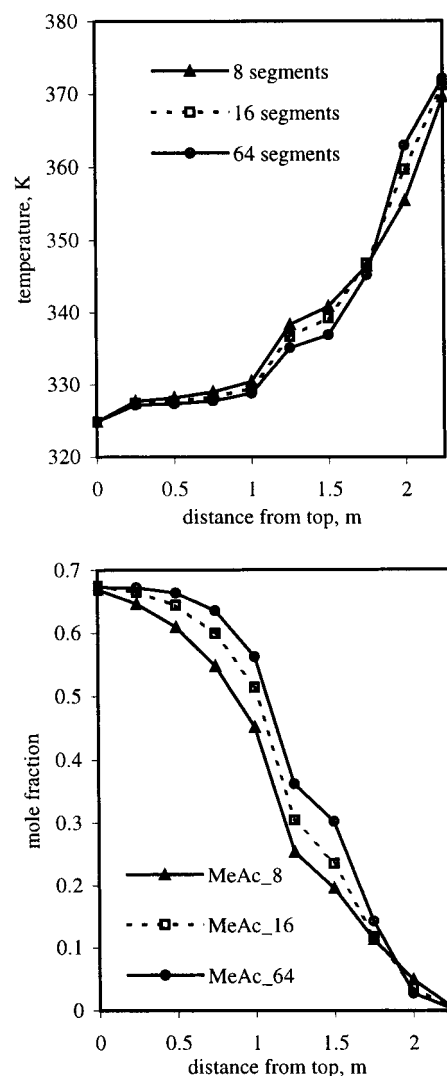


**Figure 5.** Influence of the number of segments on temperature and composition profiles for the rate-based model for the TAME system.

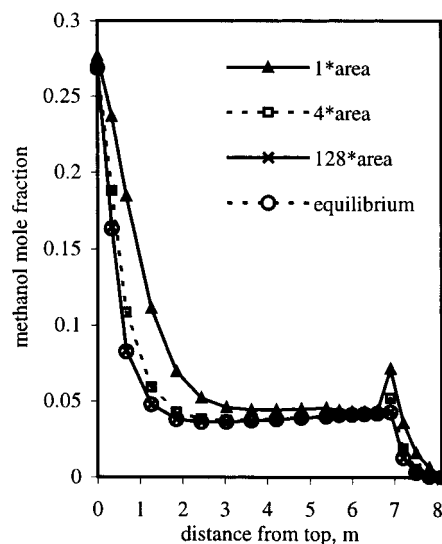
close in general. However, increasing the number of segments for the rate-based model increases the error in the predicted compositions for run number S-1 significantly. Therefore, a larger number of segments does not always yield better results. It is interesting to note that, when a larger number of segments is used in the rate-based model, the results are very close to those obtained from the equilibrium model. For all of the runs, only minor differences could be observed between the results from the equilibrium model and the rate-based model.

For the TAME system, no experimental data have been published in the open literature. Pilot-plant reactive distillation experiments will be carried out at the Separations Research Program (SRP) facility in Austin, Texas (UT-SRP). The experimental data will be compared with the predictions from the models developed in this work.

**3.5. Comparison of Computational Effort.** The rate-based model is much more complicated than the equilibrium model. The number of equations in the rate-based model is 5–7 times the number of equations in the equilibrium model if the number of segments in the rate-based model is the same as the number of theoretical stages in the equilibrium model. However, the



**Figure 6.** Influence of the number of segments on temperature and composition profiles for the rate-based model for the methyl acetate system.



**Figure 7.** Relationship between the equilibrium model and the rate-based model for the TAME system.

number of segments in the rate-based model required to obtain an accurate solution is usually several times the required number of theoretical stages in the equi-



**Table 3. Comparison of Experimental Data with Model Predictions for the Methyl Acetate System (One-Feed Setup)**

stages (segments)	EXP <sup>a</sup>	EQ <sup>b</sup>	RB <sup>c</sup>				EXP <sup>a</sup>	EQ <sup>b</sup>	RB <sup>c</sup>			
		8	16	32	64			8	16	32	64	
run number	1-11						1-12					
$x_{D\_MeOH}$	0.410	0.342	0.342	0.354	0.361	0.347	0.311	0.314	0.320	0.324		
$x_{D\_MeAc}$	0.584	0.638	0.628	0.625	0.623	0.647	0.681	0.674	0.674	0.673		
$x_{D\_H_2O}$	0.006	0.020	0.028	0.019	0.015	0.006	0.008	0.012	0.006	0.003		
$x_{B\_MeOH}$	0.127	0.163	0.157	0.154	0.151	0.003	0.029	0.031	0.026	0.024		
$x_{B\_HAC}$	0.322	0.294	0.288	0.292	0.293	0.244	0.256	0.261	0.262	0.263		
$x_{B\_MeAc}$	0.049	0.051	0.062	0.060	0.061	0.000	0.002	0.004	0.003	0.003		
$x_{B\_H_2O}$	0.502	0.492	0.493	0.494	0.496	0.753	0.713	0.704	0.709	0.710		
MeOH conversion	0.523	0.524	0.532	0.527	0.526	0.645	0.653	0.648	0.647	0.645		
$T_{bottom}$ , °C	83.1	84.2	82.7	82.0	82.0	95.1	98.7	99.1	98.6	98.9		
$x_{error}^d$		0.026	0.028	0.023	0.021		0.016	0.017	0.015	0.015		

<sup>a</sup> Experimental data.<sup>10</sup> <sup>b</sup> Equilibrium model predictions. <sup>c</sup> Rate-based model predictions. <sup>d</sup>  $x_{error}$  is the average error of the mole fractions at the top and the bottom.

**Table 4. Comparison of Experimental Data with Model Predictions for the Methyl Acetate System (Two-Feed Setup)**

stages (segments)	EXP <sup>a</sup>	EQ <sup>b</sup>	RB <sup>c</sup>				EXP <sup>a</sup>	EQ <sup>b</sup>	RB <sup>c</sup>			
		23	25	50	100			23	25	50	100	
run number	S-1						S-2					
$x_{D\_MeOH}$	0.107	0.041	0.086	0.059	0.044	0.028	0.010	0.031	0.017	0.011		
$x_{D\_HAC}$	0.000	0.000	0.003	0.001	0.001	0.000	0.000	0.005	0.003	0.002		
$x_{D\_MeAc}$	0.877	0.932	0.876	0.912	0.932	0.966	0.968	0.929	0.955	0.966		
$x_{D\_H_2O}$	0.016	0.027	0.035	0.028	0.023	0.006	0.022	0.034	0.025	0.020		
$x_{B\_MeOH}$	0.070	0.069	0.079	0.071	0.066	0.013	0.052	0.067	0.057	0.052		
$x_{B\_HAC}$	0.104	0.065	0.113	0.082	0.064	0.175	0.136	0.163	0.144	0.135		
$x_{B\_MeAc}$	0.002	0.000	0.000	0.000	0.000	0.013	0.000	0.000	0.000	0.000		
$x_{B\_H_2O}$	0.824	0.866	0.808	0.847	0.870	0.812	0.812	0.771	0.799	0.813		
MeOH conversion	0.876	0.889	0.836	0.909	0.889	0.924	0.929	0.892	0.917	0.928		
$T_{bottom}$ , °C	91.7	92.4	92.8	92.7	92.7	99.6	95.6	94.9	95.3	95.5		
$x_{error}^d$		0.027	0.010	0.018	0.027		0.016	0.024	0.018	0.016		

<sup>a</sup> Experimental data.<sup>10</sup> <sup>b</sup> Equilibrium model predictions. <sup>c</sup> Rate-based model predictions. <sup>d</sup>  $x_{error}$  is the average error of the mole fractions at the top and the bottom.

librium model. Therefore, the total number of equations in the rate-based model is at least an order of magnitude higher than that in the equilibrium model.

It is not easy to compare the computational efforts required by the two models because convergence is not guaranteed for either model. If an arbitrary initial guess is used for both models, both models will fail to converge in most cases. One comparison method is to use the previously converged solution as the initial guess and, therefore, to obtain the CPU time needed to perform one iteration. Another comparison is to use the previous solution as the initial guess and increase the feed flow rate by a certain percentage. The convergence of the methyl acetate system is poorer than that of the TAME system because of the complicated VLE equations. If the feed flow rate is increased by more than 20%, both the equilibrium model and the rate-based model frequently fail to converge.

A comparison of the computational efforts of the two models is given in Tables 5 and 6. It is obvious that the rate-based model requires much more computation time than the equilibrium model and that the convergence of the rate-based model is also poorer than that of the equilibrium model. For the TAME system, when the feed flow rate was doubled, the rate-based model failed to converge for any number of segments, whereas the equilibrium model converged quickly. It was observed that, if the number of segments is increased, the CPU time increases almost quadratically.

**3.6. Influence of Heat-Transfer Coefficients.** There is no good way to calculate the heat-transfer coefficients in a multicomponent distillation column. The Chilton–Colburn analogy is most commonly used to calculate the heat-transfer coefficients from the mass-

**Table 5. Comparison of the Computational Efforts<sup>a</sup> of the Two Models for the TAME System**

model	equilibrium		rate-based		
stages (segments)	14	14	33	66	132
number of equations	600	4430	10 225	20 650	41 212
CPU time, s (one iteration)	0.16	1.3	7.4	27	129
CPU time, s ( $\Delta F = 20\%$ )	0.41	3.1	15.9	65	306
CPU time, s ( $\Delta F = 50\%$ )	0.55	3.2	16.7	71	failed
CPU time, s ( $\Delta F = 100\%$ )	2.51	failed	failed	failed	failed

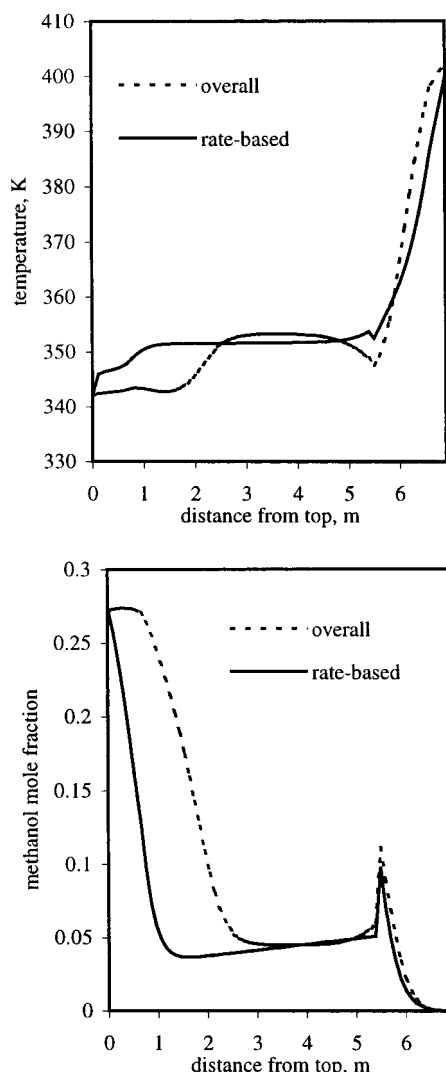
<sup>a</sup> PIII 550 PC with 512-M memory.

**Table 6. Comparison of the Computational Efforts<sup>a</sup> of the Two Models for One-Feed Setup of the Methyl Acetate System**

model	equilibrium		rate-based		
stages (segments)	8	8	16	32	64
number of equations	407	1899	3707	7323	14 555
CPU time, s (one iteration)	0.1	0.4	0.7	2.2	8.9
CPU time, s ( $\Delta F = 10\%$ )	0.4	0.9	2.5	7.7	28.3

<sup>a</sup> PIII 550 PC with 512-M memory.

transfer coefficients. However, for multicomponent distillation, the  $j$ -factor for mass transfer is a matrix, but the  $j$ -factor for heat transfer is a scalar. An average diffusion coefficient could be used to calculate the  $j$ -factor for mass transfer. However, the method used to

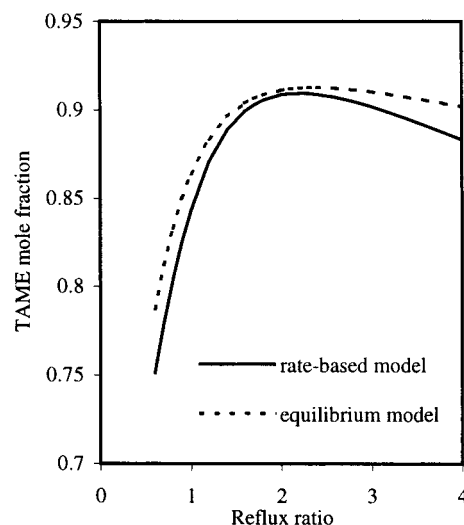


**Figure 8.** Profiles predicted by the overall mass-transfer coefficient approach for reactive distillation of the TAME system.

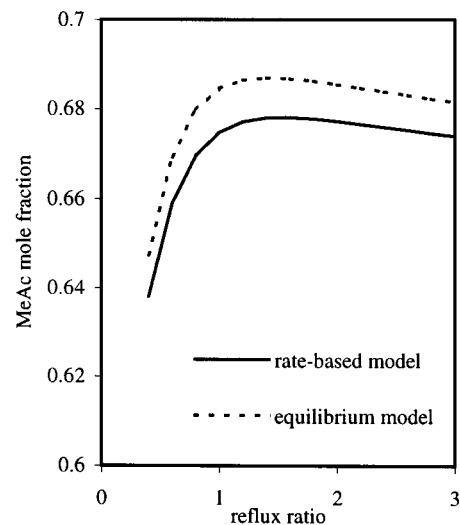
average the diffusion coefficients is arbitrary, and the calculated values of diffusion coefficients from different methods can differ widely. It was observed from the simulation results that heat-transfer coefficients do not change very much over the column length. Therefore, constant values based on the overall column averages were assumed in the rate-based model. It was found that the influence of the heat-transfer coefficients on the temperature and composition profiles is negligible. Even if the values of the heat-transfer coefficients are changed by an order of magnitude, the largest difference in composition profiles is only 0.0056. Therefore, assuming constant heat-transfer coefficients appears justifiable.

### 3.7. Overall Mass-Transfer Coefficient Approach.

The overall mass-transfer coefficient approach was used for simulating the TAME system. The configuration used for this simulation is slightly different from that in Figure 2, as the 1.2 m of Flexipac packing above the feed is removed from the column. It was found that the results are very different from those of the rigorous rate-based model and the equilibrium model (Figure 8). Although no experimental data are available for this system, the methanol composition profile predicted by the overall mass-transfer coefficient approach is clearly not correct. The overall mass-transfer coefficient ap-



**Figure 9.** Influence of the reflux ratio on product purity for the TAME system.

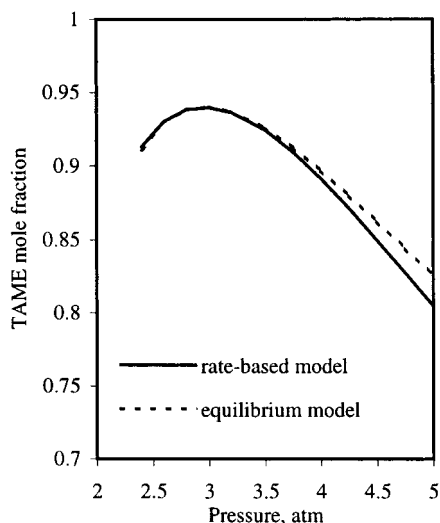


**Figure 10.** Influence of the reflux ratio on product purity for the methyl acetate system.

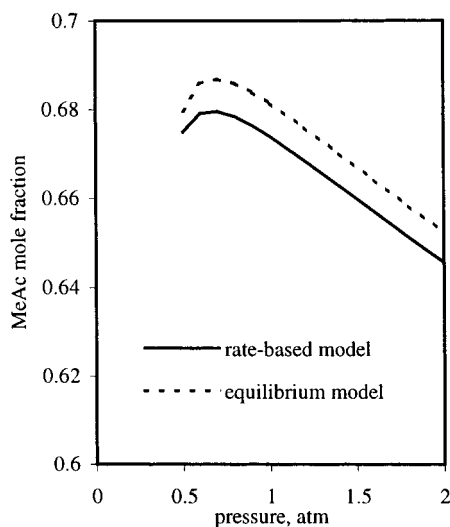
proach is even worse for ordinary distillation (see Supporting Information). Therefore, this approach should be discarded. A similar conclusion was reported by Alopaeus and Aittamaa<sup>20</sup> for conventional tray distillation columns.

**3.8. Parametric Behavior.** The two reactive distillation models were used to study the influence of several parameters, including the reflux ratio, pressure, catalyst amount, and heat loss. The configuration used for these simulations is the same as that in Figure 2 except that the 1.2 m of Flexipac packing above the feed is removed from the column. It was found that the parametric behavior of reactive distillation is very different from that of ordinary distillation.

The influence of the reflux ratio on product purity is shown in Figures 9 and 10. Both the equilibrium model and the rate-based model predict an optimal reflux ratio of around 2.2 for the TAME system and around 1.5 for the methyl acetate system. This behavior was validated experimentally for the methyl acetate system.<sup>10,21</sup> The product purity initially increased with the reflux ratio, reached a maximum, and then decreased if the reflux ratio was increased further. However, for ordinary distillation, the product purity should always increase



**Figure 11.** Influence of the operating pressure on product purity for the TAME system.

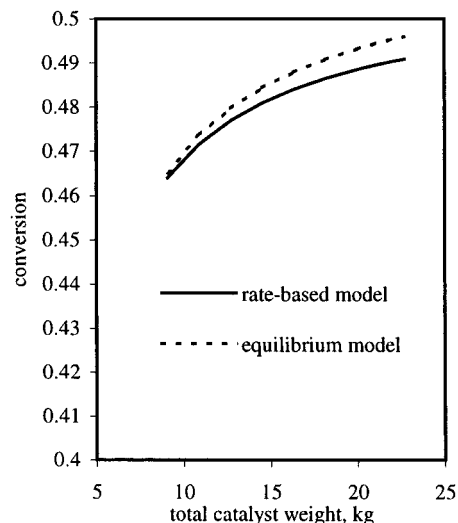


**Figure 12.** Influence of the operating pressure on product purity for the methyl acetate system.

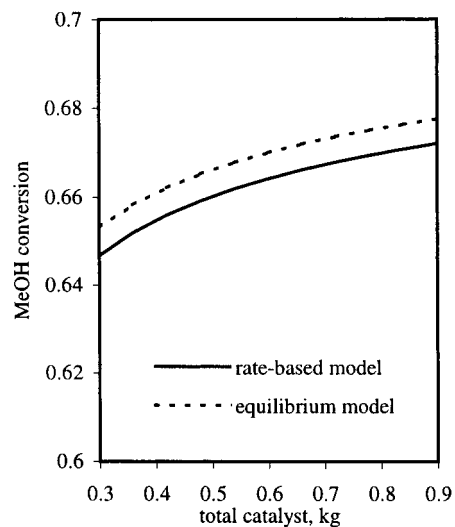
with increasing reflux ratio as long as the column is operating normally. The counterintuitive behavior of reactive distillation is caused by the complex interaction between reaction and distillation. When the reflux ratio is small, the separation is not good and the product purity is low. When the reflux ratio is too large, the residence time in the reactive zone is not long enough to allow sufficient product to be generated. Therefore, the product purity decreases.

As shown in Figures 11 and 12, both the equilibrium model and the rate-based model predict an optimal product purity near 3 atm for the TAME system and near 0.7 atm for the methyl acetate system. A low pressure yields a reduced temperature in the reactive zone and a low reaction rate. Therefore, little product is generated by reaction. When the pressure is too high, the temperature is high enough that the reaction rate is high. However, a higher temperature will favor the reverse reaction and result in lower conversion because the forward reaction is exothermic. The product purity decreases because less product is generated in the reactive zone.

The effect of the amount of catalyst on the reactant conversion is shown in Figures 13 and 14. If more



**Figure 13.** Influence of the catalyst amount on conversion for the TAME system.



**Figure 14.** Influence of the catalyst amount on conversion for the methyl acetate system.

catalyst is put into the packing while the height of packing is kept the same, the conversion is higher. However, the increase in conversion is not significant even if the amount of catalyst is doubled. This is caused by the interaction between reaction and distillation. When more catalyst is used, more product will be generated. However, if the product generated by the reaction is too great to be separated from the system, chemical equilibrium will force the reaction in the wrong direction. Therefore, it is not helpful to put too much catalyst into the packing. A better way to increase conversion is to increase the height of the column.

It was observed that heat loss along the column does not influence the product purity significantly for a heat loss of up to 60% of the reboiler duty (see Supporting Information for details). However, the liquid and vapor flow rate profiles change significantly. When heat loss increases, both the liquid and vapor flow rates increase to offset the heat loss.

#### 4. Conclusions

A steady-state equilibrium model and a rate-based model were developed for a packed reactive distillation



column. The two models were compared for both the TAME system and the methyl acetate system. In general, the predictions from the equilibrium and rate-based models are similar, with no major differences being found for a range of simulation conditions. However, the rate-based model is much more complicated than the equilibrium model and is also more difficult to converge.

It was found that there is a relationship between the equilibrium model and the rate-based model. When the number of segments in the rate-based model is chosen to be the same as the number of theoretical stages in the equilibrium model and the vapor–liquid interfacial area is increased, the profiles from the rate-based model approach those from the equilibrium model. When the vapor–liquid interfacial area is about 100 times as large as the real area, the profiles from the rate-based model are almost identical to those from the equilibrium model.

The heat-transfer coefficients in the rate-based model can be assumed to be constant for both the TAME system and the methyl acetate system. Even if the values of the heat-transfer coefficients are changed by an order of magnitude, there is little change in the temperature and composition profiles.

The two models were used to study the influence of several parameters, including the reflux ratio, pressure, catalyst amount, and heat loss. It was found that the behavior of reactive distillation is very different from that of ordinary distillation. However, the two chemical systems behave quite similarly. An optimal reflux ratio and an optimal operating pressure were found for both the TAME system and the methyl acetate system. The optimal values predicted by the equilibrium model and the rate-based model were very close. The influence of the amount of catalyst in the reactive section is not strong. Increasing the amount of catalyst will increase the conversion only slightly. It was found that heat loss affects only the liquid and vapor flow rates inside the column. It does not affect the temperature and composition profiles significantly for a heat loss of up to 60% of the reboiler duty.

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**Supporting Information Available:** More figures of the simulation results and a table describing the equations used to calculate physical and transport properties. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## Nomenclature

$a_e$  = specific effective interfacial area between the vapor and liquid phases ( $\text{m}^2/\text{m}^3$ )  
 $c$  = number of components  
 $C_t$  = total molar concentration ( $\text{mol}/\text{m}^3$ )  
 $D_r$  = diameter of the column (m)  
 $F$  = feed flow rate ( $\text{mol}/\text{s}$ )  
 $H^L$  = liquid enthalpy ( $\text{J}/\text{mol}$ )  
 $H^V$  = vapor enthalpy ( $\text{J}/\text{mol}$ )  
 $h^L$  = liquid heat-transfer coefficients [ $\text{W}/(\text{m}^2 \text{ K})$ ]

$h^V$  = vapor heat-transfer coefficients [ $\text{W}/(\text{m}^2 \text{ K})$ ]  
 $i$  = component index  
 $j$  = section index  
 $\mathbf{k}^L$  = liquid mass-transfer coefficient matrix ( $\text{m}/\text{s}$ )  
 $\mathbf{k}^V$  = vapor mass-transfer coefficient matrix ( $\text{m}/\text{s}$ )  
 $K$  = vapor–liquid equilibrium constant  
 $l_{sj}$  = height of section  $j$  (m)  
 $L_j$  = liquid flow rate in section  $j$  ( $\text{mol}/\text{s}$ )  
 $N$  = number of stages (segments) in the column, including condenser and reboiler  
 $N^m$  = mass flux [ $\text{mol}/(\text{m}^2 \text{ s})$ ]  
 $Q_j$  = heat loss in section  $j$  ( $\text{J}/\text{s}$ )  
 $R_{i,j}$  = reaction rate of component  $i$  in section  $j$  [ $\text{mol}/(\text{kg s})$ ]  
 $T^I$  = interface temperature of section  $j$  (K)  
 $T^L$  = liquid temperature of section  $j$  (K)  
 $T^V$  = vapor temperature of section  $j$  (K)  
 $V_j$  = vapor flow rate in section  $j$  ( $\text{mol}/\text{s}$ )  
 $W_{cj}$  = weight of dry catalyst in section  $j$  (kg)  
 $x_{i,j}$  = liquid molar fraction of component  $i$  in section  $j$   
 $x_{i,j}^I$  = liquid molar fraction of component  $i$  at the interface of section  $j$   
 $y_{i,j}$  = vapor molar fraction of component  $i$  in section  $j$   
 $y_{i,j}^I$  = vapor molar fraction of component  $i$  at the interface of section  $j$

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