Dynamic Rate-Based Model for Multicomponent Batch Distillation

L. U. Kreul and A. Górak
Dept. of Chemical Engineering, University of Dortmund, 44221 Dortmund, Germany

P. I. Barton
Dept. of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139

Dynamic rate-based approach for modeling and simulating batch distillation is presented. To predict separation efficiencies, mass transfer was considered explicitly using the Maxwell-Stefan. Process dynamics were modeled by considering all relevant dynamic changes in the system, including the column periphery. The model, implemented at the large-scale ABACUSS modeling environment, addresses implications of the dynamic and multicomponent nature of the process for its mathematical representation, the use of mass-transfer coefficients, and the need for further experimental correlations. To validate the model, a series of separations of the highly nonideal quaternary system of methyl acetate, methanol, acetic acid, and water in a pilot-plant batch-distillation column with structured packings were conducted. The results show that a rate-based approach can predict the column operation within the experimental error over the entire operation time without fitting of any kind. For the first time the use of a rate-based approach on the ground of the Maxwell-Stefan equations for a multicomponent batch-distillation process was validated experimentally. Comparison of predictions of the rate-based approach with simulations based on an equally tailored equilibrium-stage model shows that the largest differences between the two approaches occur in short periods of very significant changes in the column profile. The additional effort of rate-based modeling can be justified for the design of operating policies of multicomponent batch-distillation processes.

Introduction

Batch distillation is often the process of choice for the separation of multicomponent mixtures containing high-value chemical specialties. Due to their inherent flexibility, batch columns can generally be used for a variety of systems with changing compositions and components. Recognizing these benefits, the engineer must be particularly concerned with some major disadvantages of batch distillation that reduce its competitiveness significantly. In a multipurpose batch plant, distillation is often the bottleneck. Therefore, capacity optimization is of major concern, and the optimal operating policy has to be determined. However, because of constantly changing feedstocks and complex column dynamics, the majority of batch columns are operated far from this optimum. To overcome this weakness, more and more attention is paid to the automation of such processes. Unfortunately, under constantly changing conditions it is very difficult to gather the necessary knowledge about the process from experiments or actual production. Therefore, the simulation, optimization, and model-based control of batch columns is necessary.

Yet all such attempts are restricted by a lack of sufficiently accurate process simulators, since the simplified models found in the literature are not able to cope with complex column dynamics and difficult multicomponent interactions. Moreover, it has never been investigated in detail under which circumstances certain simplifications, such as equilibrium as-

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Correspondence concerning this article should be addressed to A. Górak.

sumptions, are suitable, and almost no experimental validation of batch distillation models of nonideal multicomponent mixtures can be found in the literature.

Batch-distillation modeling

Regarding batch-distillation models, two different classes of assumptions and simplifications can be distinguished. The first class refers to the description of the transfer processes between the phases. Using the equilibrium stage model, vapor and liquid streams leaving specific column segments are considered to reach thermodynamic equilibrium, while the so-called nonequilibrium stage, or rate-based models, calculate the mass and energy transfer between the phases explicitly. The second class deals with the description of process dynamics represented usually as a system of differential-algebraic equations (DAEs). In the majority of all models presented in the literature, *high-index* and other numerical problems have led to the introduction of additional simplifications, such as *static total holdups and static-energy balances*. Therefore, proper model formulation is important to avoid these index problems.

Early dynamic models for distillation, which are restricted to small deviations from the steady-state, have been presented by Mah et al. (1965), Distefano (1968) and Howard (1970). Gani et al. (1986), Gani and Cameron (1989), Cameron et al. (1988), and Ruiz et al. (1988) applied more complex equilibrium-stage models for the simulations of dynamic phenomena in continuously operated columns. In addition, Gani et al. (1987) and Gani and Ruiz (1987) incorporated considerations of dynamic startup/shutdown operations and column hydraulics into an advanced equilibrium-stage model. Perhaps the most accurate rate-based model for the simulation of dynamic deviations from steady state for tray columns was developed by Kooijman (1995) and modified by Pelkonen et al. (1997) for packed columns.

For the simulation of batch distillation, Galindez and Fredenslund (1988) and Diwekar (1994) presented quasi-static models approximating the process as a sequence of continuous operations with changing feed in each time step. This simplification allows for the application of well-known short-cut methods such as Fenske-Underwood and Gilliand correlations, if a constant reflux ratio is assumed. For tray columns, a number of semidynamic models have been published (Albet et al., 1991; Mujtabe and Macchietto, 1991), which consider dynamic changes in component holdups, but contain constant liquid molar holdups and static-energy balances on the tray. Ranzi et al. (1988) discussed the effects of the latter and concluded that the complete consideration of the energy balance is necessary for a correct simulation of the column performance. Jahromi et al. (1982) developed a detailed model on the grounds of a rate-based approach, but simulation results have only been published for a very simplified model with constant vapor fluxes over the height of the column and constant physical properties.

Simulation environment

As far as it is known to the authors, practically all models found in the literature are either restricted to the equilibrium approach, to tray columns, or contain simplifications regarding the description of the process dynamics. Therefore, in this article a completely dynamic rate-based model for batch distillation in packed columns is developed. In addition, the influence of the whole column periphery has been considered in this model. While for the most widely applied models, such as BatchFrac (AspenTech, 1991), BASIS (1989), or BDIST-SimOpt (Diwekar et al., 1991), numerics can be tailored to be more or less efficient for the model implemented, the flexibility of these programs to permit the consideration of the specific column configurations, including condenser and reboiler, liquid distributors, specific packing characteristics, middle vessel, reflux pipeline, control system, and so on, is restricted. To achieve such flexibility, the model equations have been implemented in the discrete/continuous dynamic modeling environment ABACUSS (Allgor et al., 1996).

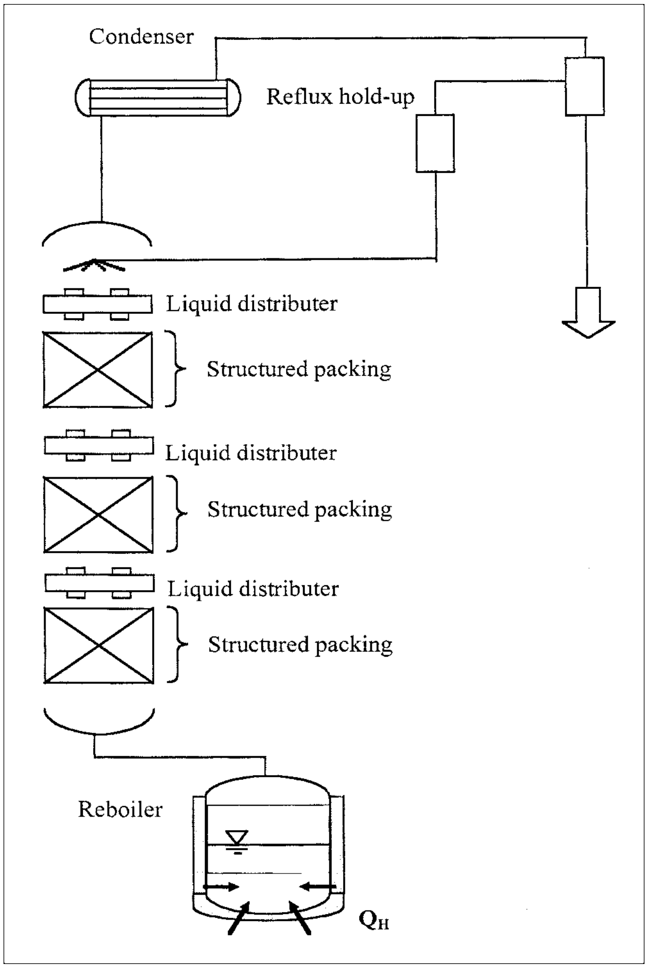

Figure 1. Pilot-plant batch-distillation column and periphery.

Modeling Process Dynamics

In this article, a classic batch-distillation process is considered, as shown in Figure 1. The feedstock is introduced into the bottom. The column is filled with structured packing (RomboPak 6M).

Dynamic model of the column

In the framework of the rate-based approach (see also Koojimann, 1995; Pelkonen et al., 1997), a differential column segment is divided into five regions, namely a liquid and a vapor bulk phase, the interface between the phases, and two stagnant films adjacent to the interface. In the liquid bulk phase, changes of the (volume) specific molar component holdups u_i^{lb}, as well as the changes of the specific total molar holdup, u_t^{lb}, are considered by the dynamic component material balances (CMB)

$$\frac{\partial}{\partial t}\left(u_i^{lb}\right) = -\frac{\partial}{\partial z}\left(lx_i^b\right) + n_i^{lf}a, \quad i = 1, \ldots, m, \tag{1}$$

the definition of the component holdups

$$u_i^{lb} = x_i^b u_t^{lb}, \qquad i = 1, \ldots, m, \tag{2}$$

and the constitutive equation for the liquid mole fractions

$$\sum_{i=1}^{m} x_i^b = 1. \tag{3}$$

As the material balances, the energy balance is dynamic. The dynamic changes in the total molar holdup (short-term dynamics) may be negligible if the column is operated at constant reflux and constant heat input. They gain importance, however, if the reflux ratios and heat duties are varied, as is the case for the optimal operating policy. Since it is difficult to derive fluid dynamic equations from momentum balances for complex packing geometries, hydraulic correlations have to be introduced. In the presented model for structured packings, the liquid flow rate is connected to the total liquid molar holdup, applying a correlation similar to the one of Máckowiak (1991).

The operating pressure in the column is low ($P \leq 1.013$ bar), so that the small vapor holdup is negligible, reducing the CMB for the vapor bulk phase to

$$0 = \frac{\partial}{\partial z}\left(vy_i^b\right) - n_i^{vf}a^i, \quad i = 1, \ldots, m. \tag{4}$$

In addition, in the vapor phase the state variables are related to each other by an equation of state. At the phase interface, thermodynamic equilibrium is assumed. The interface itself is considered to be infinitesimally small, so that continuity of mass and energy fluxes can be assumed. Finally, at the interface the constitutive equations are applied for both phases. The resulting system of PDAE is transformed into a DAE system by approximating the spatial partial derivatives with finite differences.

High-index and pressure drop

In rate-based models a mechanical equilibrium is usually postulated (Taylor and Krishna, 1993; Górak, 1995). Besides the pressure itself, the pressure *drop* in the column is an important hydraulic parameter. In the majority of distillation models, however, it is neglected and only an overall column pressure is defined. In continuous processes, this may be seen as a meaningful simplification, especially if the pressure drop is low. In dynamic systems, on the other hand, the consideration of the pressure drop as a correlation of the vapor (and liquid) fluxes is more vital. A completely dynamic DAE batch distillation model is often of *index two*, if the pressure is not related to the vapor flux, which otherwise enters as a variable in the differential equations only (see Martinson and Barton, 1998), for a discussion of the analogous concept of the index with respect to time of a PDE).

In the presented work the *high-index* problem has *not* been avoided by the introduction of such simplifications as constant vapor fluxes, static total holdups, and static energy balances, but by the experimental study of the pressure drop in the column. In the laboratory, a pressure drop over one meter of packing was measured for different liquid and vapor loads and a mathematical correlation for the pressure drop per meter of the form

$$\Delta P = f(v, l) \tag{5}$$

was determined and integrated into the model.

Modeling the column periphery

For accurate modeling of column dynamics, the influence of the periphery has to be considered in detail. The flexibility of the modeling platform (ABACUSS) allows for the simultaneous solution of the complete system model, including reboiler, condenser, reflux pipeline, and liquid distributors. In the reboiler thermodynamic equilibrium and perfect mixing were assumed because of large residence time and high turbulence in the boiling. The volume of the vapor phase in the reboiler is by a factor 10^3 bigger than the neglected vapor volume of the column segments. Contrary to the reboiler, in the (total) condenser both vapor and liquid holdups are sufficiently small, so dynamic changes are neglected. As in the reboiler, a thermodynamic equilibrium between the phases is assumed. The influence of the liquid holdup in the reflux pipeline on the column dynamics was considered. Backmixing and dead time in the reflux is modeled by a cascade of stirred tanks. Finally, the liquid distributors have been considered as ideal stirred tanks with constant total, but variable liquid-component holdups.

Mass-Transfer Modeling

Using the film model (Whitman, 1923; Bird et al., 1960; Sherwood et al., 1975), the thickness of the imaginary stagnant films has to be derived from binary. A traditional way to describe ordinary diffusion through the film is based on the simple generalized Fickian law, for which the diffusion coefficients unfortunately depend in a complex way on the composition of the mixture, and no theoretical way exists to predict them for multicomponent systems.

In distillation the mass transfer is assumed to be located in the gas phase only (Ronge, 1995; Pelkonen et al., 1998). Its modeling is possible for a multicomponent system, including diffusional interactions using binary diffusion coefficients on the grounds of generalized Maxwell-Stefan equations (Bird et al., 1960; Taylor and Krishna, 1993; Górak, 1995). Empirical mass-transfer coefficients have to be determined as correlations of the hydraulic conditions in the column, namely packing geometry and diameter, liquid and vapor load, maldistribution, and so on. While the calculation of multicomponent diffusion is based on the knowledge of binary Maxwell-Stefan diffusion coefficients, the calculation of the real mass-transfer fluxes using binary mass-transfer coefficients is not without some logical problems, even if this concept is applied in the most widespread approach (Taylor and Krishna, 1993). Therefore, its validity must repeatedly be assured by experimental validation.

For *batch* distillation, an additional problem has to be considered in this regard: almost all useful mass-transfer correlations found in the literature are derived from experiments in steady-state processes. Unfortunately, the validity of these correlations has hardly ever been tested for dynamic operations, where the variety of changes in hydraulic conditions is significantly larger than in stationary processes. Consequently, it has been one of the main purposes of this work to investigate if the traditional approach of using binary mass-transfer correlations for the description of multicomponent separation is meaningful for batch distillation. In addition, we were particularly interested in whether the application of "steady state" mass-transfer correlations leads to sufficiently correct results or if completely new correlations must be determined. For RomboPak 6 M (a metal lamella sheet packing), Ronge (1995) has derived a binary mass-transfer correlation for the gas phase. It has been modified by Pelkonen (1998) to consider the influence of column diameters in the range of 100 to 600 mm. The authors showed that mass-transfer resistance in the liquid phase could be neglected.

Modeling of Thermodynamics

As a test system, the quaternary mixture of methanol, acetic acid, methyl acetate, and water was chosen. That system was used for experimental investigation of the batch reactive distillation, as reported elsewhere (Kreul et al., 1998). In the absence of strong inorganic acids or ion exchangers, it shows a negligible disposition to chemical reactions, and a homogeneous liquid phase could be assured under process conditions. On the other hand, the overall behavior of the mixture is highly nonideal, making it a significant example of a complicated industrial multicomponent system. In our model, the influence of these nonidealities on the diffusion coefficients and the phase equilibrium was considered.

In the vapor phase, the dimerization of acetic acid was taken into account. The formation of cross-, tri- and polymers, which especially may be found under high pressure, was neglected. Our approach is based on the work of Marek and Standart (Marek and Standart, 1954; Marek, 1955) and the chemical theory (Prausnitz, 1980). It is assumed that the association of acetic-acid molecules is strong enough to be considered as a chemical equilibrium reaction. According to Prigogine and Defay (1954), the macroscopic chemical potential of the associated component equals the chemical potential of the monomer and the fugacity coefficient φ_i of a component i is determined by the ratio between the real and the virtual molar fraction of the component. If the nonideality of the vapor phase cannot be attributed mainly to dimerization, additional molecular interactions have to be considered. The rule of Lewis should be applied, for the calculation of fugacity coefficients (Nothnagel et al., 1973). The second virial coefficient should be either taken from the literature (Dymond and Smith, 1969) or calculated using the method of Hayden and O'Connell (1975). If besides the dimerization of acetic acid, cross-dimers should be considered, an analytical solution is not possible (Prausnitz, 1980). In addition, knowledge of all binary equilibrium constants K_{ij} is necessary, either from the literature or according to Hayden and O'Connell (1975), who refer K_{ij} to one part of the second virial coefficient B. For the presented system the dimerization of acetic acid is by far the most important influence, and other nonidealities are negligible (Sawistowski and Pilavakis, 1982). Finally, the influence of the dimerization on diffusion was considered by the use of diffusion coefficients of the monomer/dimer pseudocomponents, according to Cussler (1984).

For the thermodynamic description of the liquid phase, a four-parameter Wilson activity coefficient model was used, which showed good performance in the description of the quaternary mixture. The parameters were calculated from phase-equilibrium experiments considering the nonideality in the vapor phase, as discussed. Calculations were carried out at the BASF AG using the Dechema-Chemistry Data Series (Gmehling and Onken, 1977).

Validation and Comparison of Models

To validate the model posed in this article, a series of seven experiments of batch distillation in a pilot plant (Figure 1) has been carried out.

At the beginning, the reboiler is charged with the quaternary mixture in equimolar concentration. The column is run at total reflux. Once a constant temperature profile is reached, the reflux ratio is changed to $r = 1$ and product is withdrawn to investigate dynamic changes in the system. The variable heat policy during the operation is shown in Figure 2. Temperatures were measured continuously in the reboiler and the reflux pipeline, and samples for the determination of liquid-phase compositions were taken regularly over the

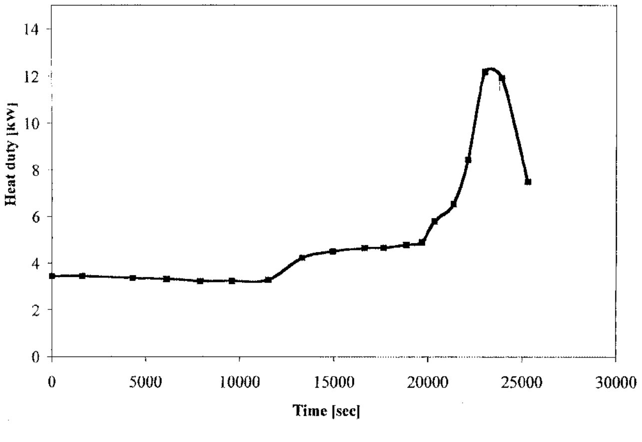

Figure 2. Heating policy.

whole process time of almost 8 h. The liquid-sample compositions were determined using gas chromatography. In addition, concentrations where measured continuously with near infrared (NIR) spectroscopy using a flow cell in the reflux pipeline and a single-sided transmission probe in the reboiler. The NIR system allows for the concentration measuring over the whole process time in intervals of 15 s with the same accuracy as the GC standard.

Figure 3 shows the measured concentrations in the reflux after the start of product withdrawal, including error margins. A systematic error of the gas chromatograph (FID and WLD) was quantified as a function of the water concentration and considered by calibration; a small random error of about 1 mole percent could, however, not be further diminished, even if all GC measurements were repeated three times and averaged. In addition, all repetitions of the experiment vary slightly in their results, though not more than about 3–4 mole percent, however. The compositions shown later in Figures 4 and 5 are taken from the fourth run, while all others show no qualitative differences.

The presented completely dynamic rate-based model was implemented into the ABACUSS large-scale equation-based modeling environment (Allgor et al., 1996). The method of lines was applied to discretize the spatial dimensions using finite differences. Besides its flexibility, ABACUSS allows for a sequence of time and state events with automated consistent reinitialization of the system of equations, so that it is able to solve discrete/continuous dynamic problems efficiently, and the complete operating policy for the batch distillation could be specified as task schedule. For the solution of the DAE system, the large-scale sparse BDF integrator DSL48S (Feehery et al., 1997) is used in ABACUSS.

Figure 4 shows the comparison of experimental and simulation results based on the rate-based model. Applying this model approach, *no fitting* was performed: all model parameters used in the simulation were either taken from the literature or have been determined independently in laboratory experiments. It is evident that the simulation based on the rate-based model is able to predict the batch operation within the error margins of the experiment over the whole process time for the highly nonideal quaternary mixture.

Obviously, for the first time the application of the rate-based approach on the grounds of the Maxwell-Stefan equations for a multicomponent batch-distillation process could be validated experimentally. The use of binary mass-transfer coefficients for the prediction of mass transfer in nonideal multicomponent systems seems to be meaningful. Finally, the extrapolation of transfer correlations derived from steady-state experiments to describe the dynamic operation of a batch-distillation column is, at least in the investigated case, possible without introducing any significant error.

Besides its accuracy and much higher physical significance, the rate-based approach has the major advantage of being more predictive than its main rival, the equilibrium-stage model, for which important parameters as *stage efficiency* or *height equivalent to a theoretical stage* (*HETS*) have to be fitted for each separated multicomponent system. On the other hand, the proper formulation and use of a dynamic rate-based model is complicated, so that it should be tested under which circumstances such an effort is justified. Therefore, the experimental data shown earlier have been compared with the predictions of a detailed equilibrium-stage model, which has been tailored to the pilot-plant distillation column and its periphery. Figure 5 shows the comparison of the simulation results with the experimental data. The general behavior of the process is predicted with sufficient accuracy. However, difficulties arise in periods of significant change in the column, as demonstrated in the following figures. It took between 12,000

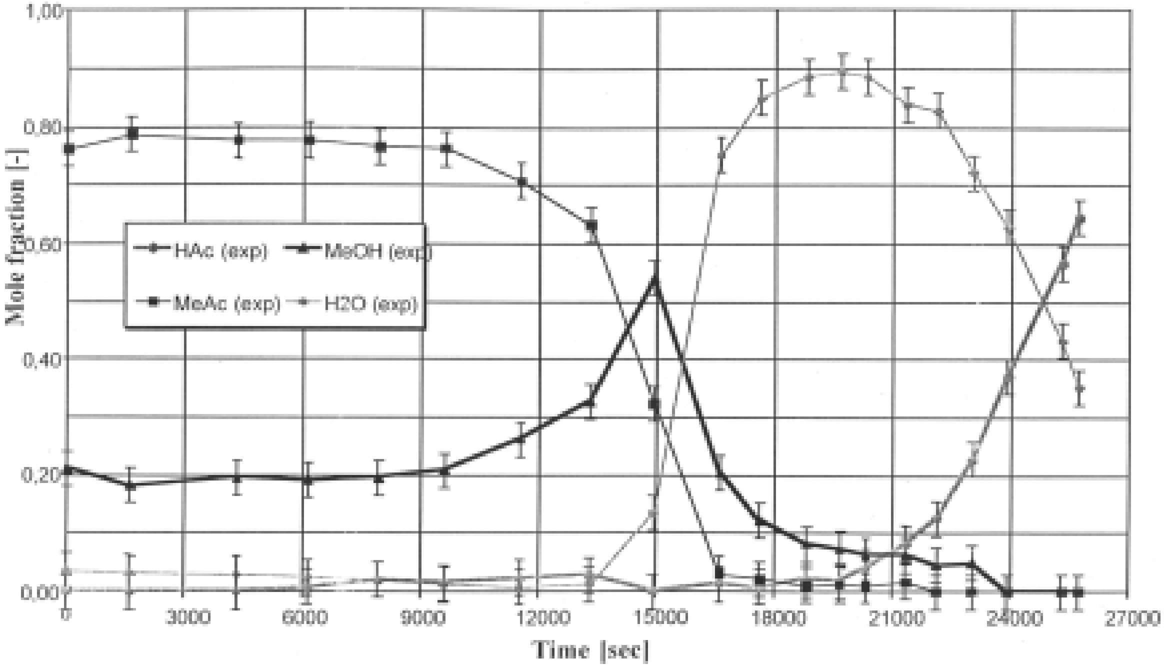

Figure 3. Experimental liquid compositions in the reflux.

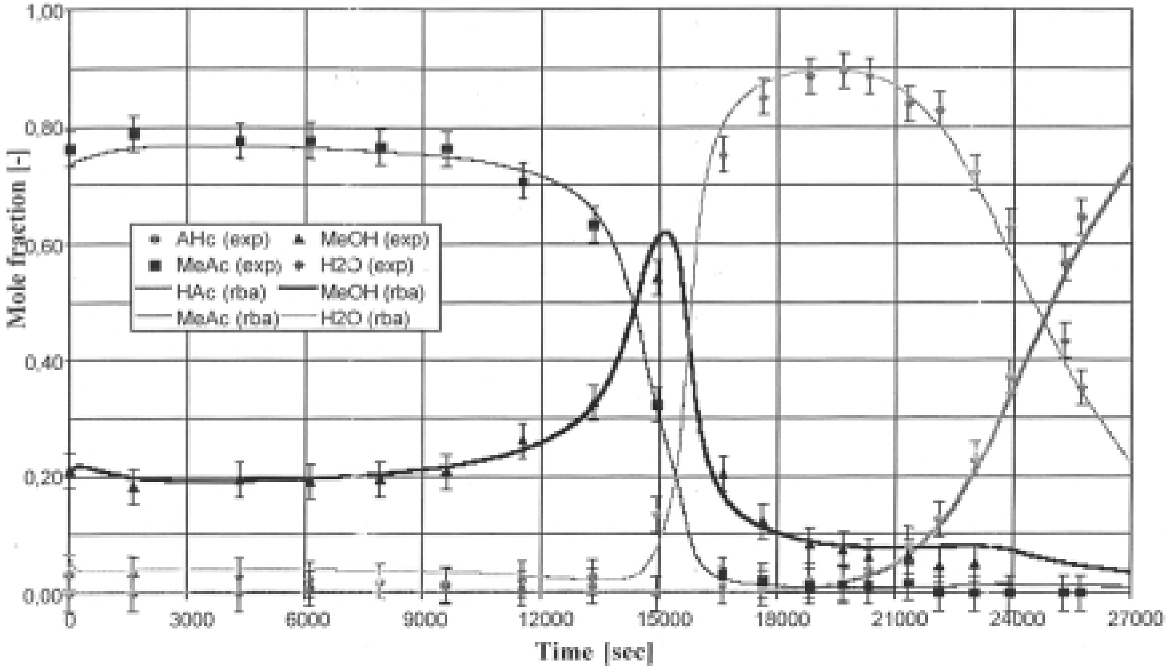

Figure 4. Experiment vs. simulation: rate-based model.

and 15,000 s to withdraw all of the methyl acetate from the column (Figure 6), and its concentration in the distillate is diminished dramatically. In the same period methanol was increasingly found in the distillate, until (between 15,000 and 18,000 s) its concentration decreased again (Figure 7), while water started to move up through the column. Both figures concentrate on the model comparison in this critical period.

If methyl acetate is the (first) desired product, the reflux ratio has to be increased and the product withdrawal shut down or switched to an alternative vessel to collect the methanol fraction. For a switching criteria, as, for example, $x_{\mathrm{MeAc}} \leq 0.7$ or $x_{\mathrm{MeOH}} \geq 0.2$, both modeling approaches predict the crucial points in time similarly. If this varies slightly, however, and switching criteria like $x_{\mathrm{MeAc}} \leq 0.6$ or $x_{\mathrm{MeOH}} \geq$

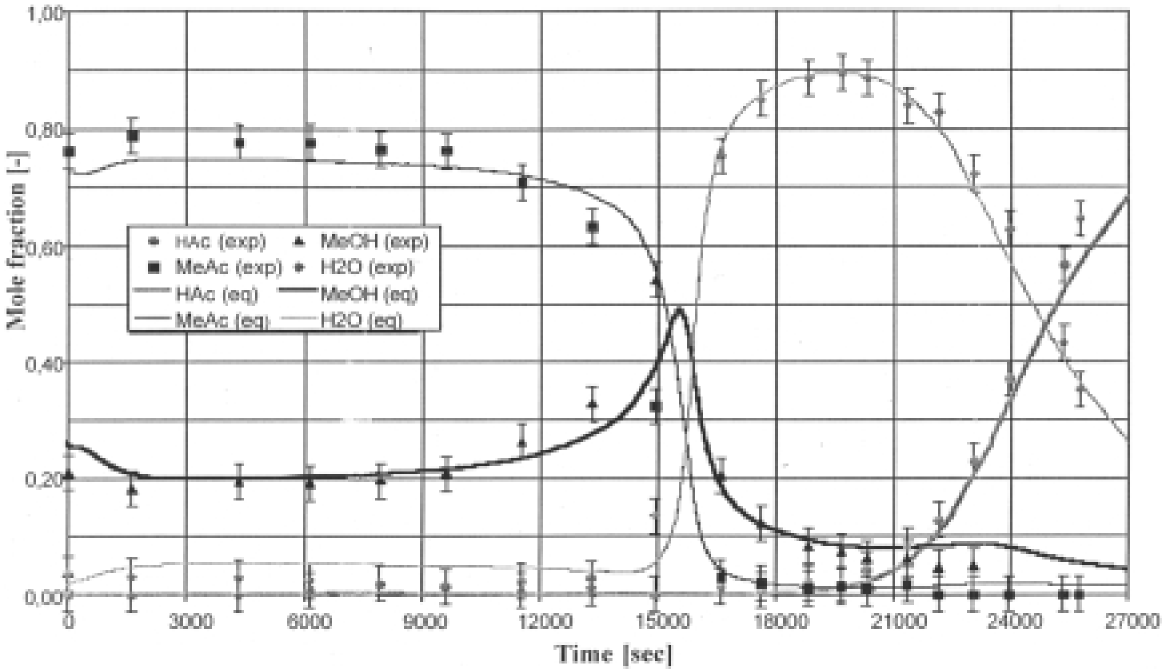

Figure 5. Experiment and simulation, equilibrium stage model.

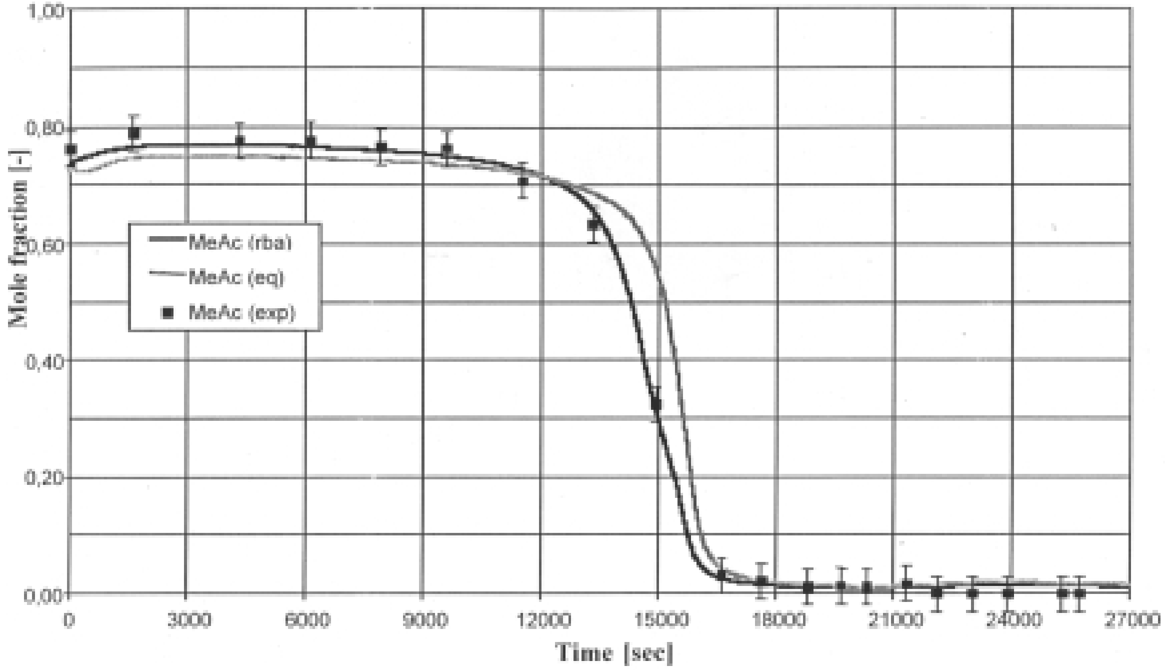

Figure 6. Comparison of general modeling approaches: MeAc profile.

0.2 are chosen, the differences are striking. According to the equilibrium-stage model, changes had to be introduced only in the moment when the methyl acetate concentration had already dropped to less than 40 mole percent, or the methanol concentration had increased to more than 40 mole percent. In this particular case, it would not be recommended to use the equilibrium-stage simulation for the design of the operating policy of the column.

The significant differences between both modeling approaches are further illustrated by Figures 8 and 9, where the movement of the methanol front through the column is shown. At each point the position of the front, as well as its maxi-

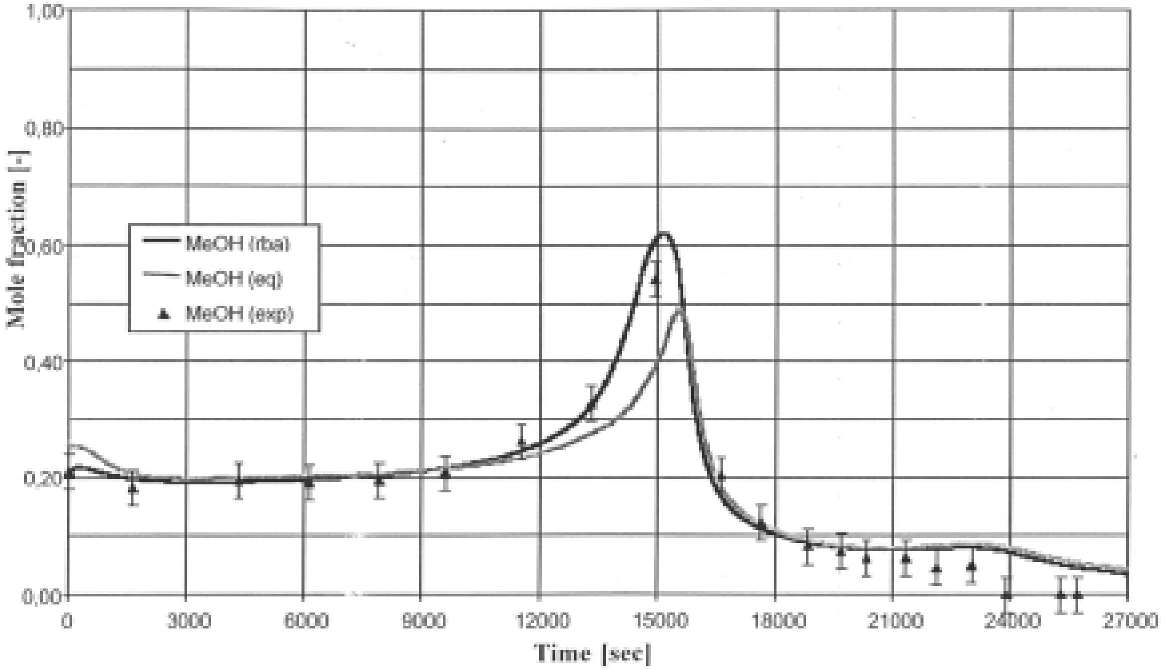

Figure 7. Comparison of general modeling approaches: MeOH profile.

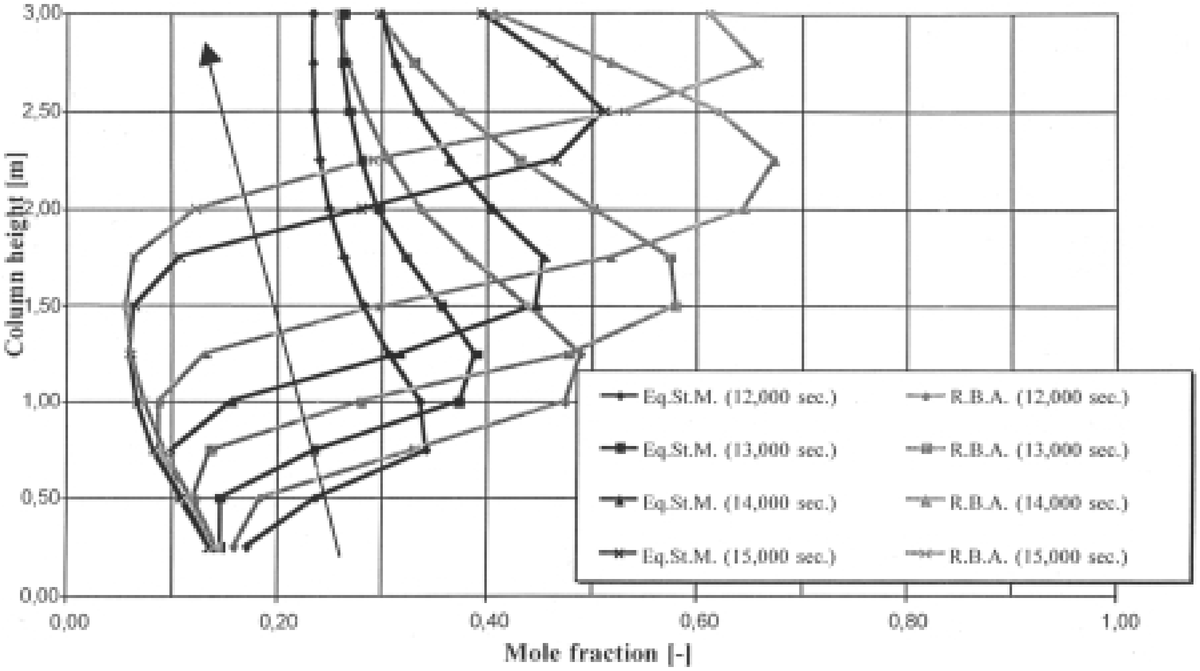

Figure 8. Comparison of models: MeOH front.

mum, is predicted quite differently based on different models, with differences increasing with time.

Conclusions

Batch distillation is an important, yet difficult unit operation. For the improvement of its application, computer simulation, optimization, and model-based control are necessary, which depend on accurate methanol models able to cope with complex column dynamics and system nonidealities. In this article, a completely dynamic rate-based model for the simulation of batch columns was presented. Laboratory experiments were carried out to derive certain model parameters, such as pressure-drop correlations, which are applied to avoid

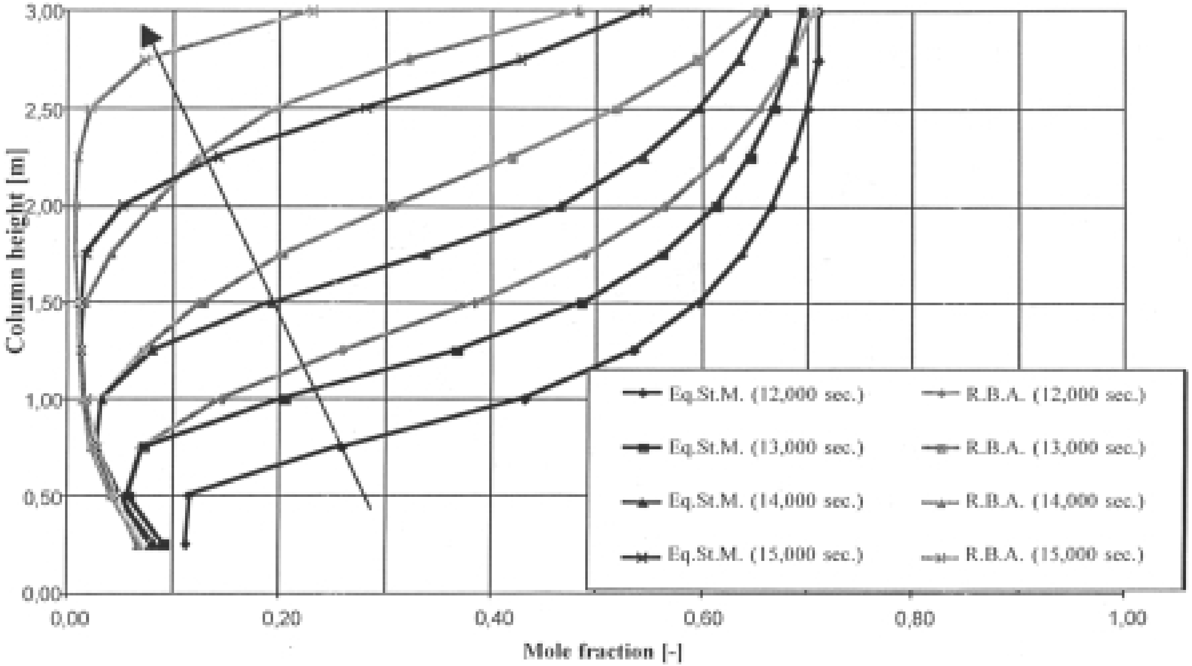

Figure 9. Comparison of models: MeAc front.

high-index problems. The model equations were implemented into the ABACUSS large-scale modeling environment, including all important parts of the column periphery and the operating policy. To validate the model, a pilot-plant batch-distillation column with structured packings was used for experiments. The simulation results predict the experiments without any fitting of parameters. It could be shown that the highly complex model is able to describe the process accurately, so that for the first time the application of a rate-based model on the grounds of the Maxwell-Stefan equations could be approved for multicomponent batch distillation. The use of binary mass-transfer coefficients for the prediction of mass transfer in a nonideal quaternary system was validated. It was shown that the extrapolation of ''steady state'' mass-transfer correlations to a batch-distillation process is possible, and that no additional correlations must be derived.

The rate-based approach has the major advantage of being more predictive than the equilibrium-stage model. Nevertheless, the formulation of a dynamic rate-based model is complicated, so it was tested under which circumstances such an effort is justified. The experimental results were compared with the predictions of a detailed equilibrium-stage model. It was shown that the two models differ significantly in the prediction of moving fronts in the column. If a simulator should be used for the design of operating policies of multicomponent batch distillation, the additional effort of rate-based modeling seems to be justified.

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Notation

a = specific interfacial area, $m^2 \cdot m^{-3}$
H = column height, m
K_D = equilibrium constant dimerization, bar^{-1}
l = liquid molar fluxes, $kmol \cdot s^{-1} \cdot m^{-2}$
m = number of components
n = molar flux, $kmol \cdot s^{-1} \cdot m^{-2}$
Q_H = heat stream, $kJ \cdot s^{-1}$
r = reflux ratio
t = time, s
U = molar holdup, kmol
V = vapor load, $kmol \cdot s^{-1}$
v = vapor molar flux, $kmol \cdot m^{-2} \cdot s^{-1}$
x = liquid mole fractions
y = vapor mole fractions
z = spatial coordinate
z_B = correction factor
δ = film thickness, m
γ = activity coefficient

Superscripts and subscripts

g = vapor phase
i = interface
D = dimers

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