Modeling and simulation of reactive distillation columns using computer algebra

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Abstract

This work presents an extension of a computer algebra (CA) program, Thermath, originally developed for the automatic implementation of physical property calculations, to generate computer codes in Fortran for the simulation of steady-state reactive distillation columns. The adopted procedure requires the simultaneous solution, using the Newton–Raphson method, of mass and energy balances, phase equilibrium equations, chemical equilibrium or rates of reaction equations and an additional equation needed to match the number of degrees of freedom. The Thermath program was used to obtain Fortran subroutines that implement these equations and their derivatives with respect to the process variables and the equation of state and/or excess Gibbs free energy model used in the simulation. The results are in excellent agreement with those available in the literature. By using Thermath, it was possible to reduce the time and effort needed to implement the mathematical models of multistage reaction–separation equipment.

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1. Introduction

Mathematical models used for chemical process simulation and design are increasingly large due to the inclusion of many equipment details and of realistic descriptions of the physico-chemical behavior of the materials processed. Expressions for the physico-chemical properties of materials, such as fugacity or activity coefficients, are often long and intricate, and various tests are needed before assuming that a computational implementation is correct. Moreover, as in the case of steady-state simulations of multistage separators, some applications lead to large systems of nonlinear algebraic equations. If the Newton–Raphson method is used to solve these systems, analytical derivatives of model equations, including those from the physico-chemical model, with respect to the problem unknowns are necessary. Despite the fast convergence of the Newton–Raphson method when a good initial estimate is available, the algebraic effort to obtain the required derivatives manually often prevents its use. In this case, it is common to use numerical approximations or methods that do not need analytical derivatives, like Broyden’s method (1965), even if at the expense of slower numerical convergence.

Computer algebra (CA) can accelerate model development and implementation, because it provides the possibility of manipulating large mathematical expressions and solving problems of great numerical complexity in a single computational environment. CA programs such as Maple and Mathematica are being increasingly used to solve problems in science and engineering (Akers et al., 1998; Braun, 2000; Taylor, 1997; Yildirim & Bayram, 2000). However, numerical calculations in these programs tend to be slow when compared to compiled codes in Fortran or C. In our group, we have used the symbolic capabilities of one of these CA programs, Mathematica, to derive expressions for thermodynamic properties (Castier, 1999). The original features of Mathematica were complemented by developing several computational procedures for the analysis of the derived expressions and their automatic implementation in Fortran.
In this way, it was possible to combine the convenience of using the symbolic capabilities of Mathematica with relatively little effort compared to what a manual implementation would usually require. By developing programs in this way, most of the code is generated automatically, thereby drastically reducing or eliminating the need for debugging.

Thermath was originally developed for the implementation of equations of state and of excess Gibbs free energy models, and expressions derived from them. More recently, we started testing Thermath for the automatic implementation of unit operation calculations. We developed procedures for the steady-state simulation of flashes (Santos, Alfradique, Espósito, & Castier, 1999), distillation columns (Alfradique & Castier, 2001) and extraction columns (Alfradique, Espósito, & Castier, 2002). A procedure for the dynamic simulation of flash drums was also developed (Gonçalves, 2001). Thermath was also extended to allow the implementation of code compatible with the Schepper and Stadtherr (1996) version of the INTBIS/INTLIB package (Kearfott & Novoa, 1990) for solving sets of nonlinear equations using interval arithmetic (Domínguez, Tojo, & Castier, 2002). Continuing this series, this paper addresses the implementation of a procedure for simulating reactive distillation columns using the Thermath package.

Reactive distillation columns may be modeled using various levels of detail, ranging from models that take into account mass transfer and reaction rates in the plates to models that assume chemical and phase equilibria at each stage. Recent reviews of reactive distillation modeling can be found in Taylor and Krishna (2000) and Doherty and Malone (2001). In this work, it is shown how CA, by means of the Thermath program, can aid in the quick development of models for simulating reactive distillation columns. These columns are selected for study because they combine reactions and multi-stage separation in a single piece of equipment, and therefore represent a modeling challenge. We could not identify other contributions in the literature of the systematic development of programs to simulate reactive distillation columns following this approach. By using Thermath, it is possible to generate automatically subroutines for the equipment model and for the evaluation of physical properties, thereby permitting flexibility to rapidly include new thermodynamics models and reducing the time and effort needed to implement this equipment model.

2. Modeling

The objective of the work is the modeling and simulation of reactive distillation columns in steady-state operation. The configuration of each stage is shown in Fig. 1. The mass balance of a component in a stage $j$ is given by:

$$
\sum_{k=1}^{n_{\text{E}}} \dot{n}_{i,k} \xi_{k,j} - \left( \dot{n}_{i,j+1} + \dot{n}_{i,j-1} + F_{i,j} + \sum_{k=1}^{n_{\text{E}}} v_{i,k} \right) = 0 \quad (1)
$$

Greek letters

- $\alpha_{i,k}$: kinetic order of component $i$ in reaction $k$
- $\gamma_{i,j}$: activity coefficient of component $i$ in stream II of stage $j$
- $\phi_{i,j}$: fugacity coefficient of component $i$ in stream I of stage $j$
- $\mu_{i,j}$: chemical potential of compound $i$ at stage $j$
- $\mu_{i,j}^{0}$: standard chemical potential of compound $i$
- $v_{i,k}$: stoichiometric coefficient of component $i$ in reaction $k$
- $\xi_{k,j}$: extent of reaction $k$ at stage $j$

Nomenclature

- $C_{i,j}$: molar concentration of component $i$ at stage $j$
- $E_{i,j}$: relation between the liquid and vapor streams
- $F_{i,j}$: equations vector
- $f_{i,j}^{\text{eq}}$: phase equilibrium function of component $i$ in stage $j$
- $f_{i,j}^{\text{p}}$: mass balance function of component $i$ in stage $j$
- $f_{i,j}^{\text{q}}$: energy balance function at each stage
- $f_{i,j}^{\text{f}}$: function relating the liquid and vapor streams
- $f_{i,j}^{\text{aq}}$: binary interaction parameter
- $k_{i,j}$: rate constant of reaction $k$ in each stage
- $n_{i,j}$: molar flow rate of component $i$ in stream I of stage $j$
- $P_{k}$: reference pressure
- $P_{i,j}$: saturation pressure of component $i$ in stage $j$
- $Q_{j}$: heat load to stage $j$
- $R$: universal gas constant
- $R_{i}$: liquid side stream fraction at stage $j$
- $T_{j}$: temperature at stage $j$
- $V_{j}$: liquid holdup of stage $j$
- $v_{i,j}$: liquid molar volume at stage $j$
- $A_{i,j}$: vector of unknowns
- $X_{i,j}$: mole fraction of component $i$ in stream I of stage $j$
- $Z_{j}$: vapor side stream fraction at stage $j$
where $(Z_j + 1)w_{ij}^j$ is the molar flow rate of component $i$ that leaves stage $j$ as vapor, $Z_n0^j$, the flow rate in the vapor side stream and $n_{ij}^j$, is the flow rate to the subsequent stage. $(R_j + 1)w_{ij}^j$ is the molar flow rate of component $i$ that leaves stage $j$ as liquid, $R_n0^j$, the flow rate in the liquid side stream and $n_{ij}^j$, is the flow rate to the subsequent stage. $F_{ij}$ is the molar flow rate of the feed stream to stage $j$. In this equation, $v_{ij}^j$ is the stoichiometric coefficient of component $i$ in reaction $k$. $k_{ij}^j$ is the extent of reaction $k$ in stage $j$ and $nr$ is the number of independent chemical reactions.

Assuming that the streams leaving a stage are in phase equilibrium and that each stream is modeled by an equation of state, we have:

$$f_{ij}^j = \ln(v_{ij}^j) - \ln(K_{ij}^j) = 0$$

(2)

where $v_{ij}^j$ and $K_{ij}^j$ are the mole fraction and fugacity coefficient of component $i$ in stream $j$ of stage $j$, respectively. The energy balance equation is:

$$f_{ij}^j = (R_j + 1)H_{ij}^I + (Z_j + 1)H_{ij}^I - (H_{j+1}^I + H_{j-1}^I + Q_j) = 0$$

(3)

where $H_{ij}^I$ and $H_{ij}^II$ are the total enthalpy flows of streams $I$ and $II$ to the subsequent stage, $Q_j$ is the heat load in each stage and $H_{j}$, is the enthalpy flow of the feed stream to stage $j$. All enthalpy values are referred to the pure elements at 298.15 K, 1 bar.

At the top and at the bottom, we have the condenser and the reboiler, respectively. We need to add one more equation associated to reflux flow in the column:

$$f_{ij}^j = (Z_j + 1)\sum_{i=1}^{nc} n_{ij}^1 - E_j(R_j + 1)\sum_{i=1}^{nc} n_{ij}^I = 0$$

(4)

Variable $E_j$ is specified for the condenser and reboiler, and is calculated for the inner stages. Equation (4) is used for total or partial condensers and reboilers, depending on the values specified for $R_j$, $Z_j$ and $E_j$, as shown in Table 1.

The chemical equilibrium equation for each reaction $k$ in stage $j$ is:

$$f_{ij}^j = (Z_j + 1)\sum_{i=1}^{nc} n_{ij}^1 - E_j(R_j + 1)\sum_{i=1}^{nc} n_{ij}^I = 0$$

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Table 1 Characterization of condensers and reboilers.

<table>
<thead>
<tr>
<th>Condenser (stage I)</th>
<th>Reboiler (stage I)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Partial</td>
<td>Total</td>
</tr>
<tr>
<td>$Z_n0 = 0$</td>
<td>$Z_n0 = 0$</td>
</tr>
<tr>
<td>$R_n0 = 0$</td>
<td>$R_n0 = 0$</td>
</tr>
<tr>
<td>$E_n0 = 0$</td>
<td>$E_n0 = 0$</td>
</tr>
</tbody>
</table>

At chemical and phase equilibrium, the chemical potential of a component is the same in the liquid and vapor phases. We arbitrarily chose to write the chemical equilibrium equation using the chemical potentials of phase $I$:

$$\mu_{ij} = \mu^0_{ij}(T_j, P_j) + RT_j \ln \frac{n_{ij}^I P_j}{P_0}$$

(6)

We use $P_0 = 1$ bar and $P_j$ in bar. In Equation (6), $\mu^0_{ij}(T_j, P_j)$ is the molar Gibbs free energy of formation of pure component $i$ at temperature $T_j$ and pressure $P_j$, in the ideal gas state. Combining Equations (5) and (6), and the definitions of mole fractions, and dividing by $RT_j$, we obtain the chemical equilibrium equation we used in our formulation:

$$\sum_{i=1}^{nc} v_{ij}^j \mu_{ij} = 0$$

(7)

This form of the chemical equilibrium equation (Equation (7)) is particularly convenient for its easy differentiation. Following Henley and Seader (1981), we defined a vector $\tilde{X}$ that contains the unknowns organized in the following order:

$$\tilde{X} = [x_1^1, x_2^1, \ldots, x_{nc}^1, x_1^I, x_2^I, \ldots, x_{nc}^I]$$

(8)

where $x_i^1$ and $x_i^I$ represent the variables in the reboiler and condenser, respectively. The other $x_i^I$ represents the variables of the inner stages of the column where they are organized in the following way:

$$x_i^j = [n_i^1, n_i^2, \ldots, n_i^{nc} , T_j, H_i^I, H_i^II, \ldots, n_i^{nc} , E_j, Q_j, \ldots, \xi_{ij}^j]$$

(9)

In the condenser and in the reboiler, the vectors of unknowns are organized in the following way:

$$X_1 = [n_1^1, n_1^2, \ldots, n_1^{nc}, T_1, H_1^I, H_1^II, \ldots, n_1^{nc}, Q_1, \xi_{1j}^1, \ldots, \xi_{nj}^1]$$

(10)
\[ X_N = [n_1^H, n_2^H, \ldots, n_{m^H}, T_1^H, n_1^I, n_2^I, \ldots, n_{m^I}, Q, \xi_1, \ldots, \xi_{m^I}]^T \]  

where \(Q_1\) and \(Q_2\) are the heat loads of the condenser and reboiler, respectively. We also defined a vector \(E\) that contains the equations to be solved:

\[ E = [F_T^1, F_T^2, \ldots, F_T^j, \ldots, F_T^{N+1}]^T \]  

where \(F_T^1\) and \(F_T^{N+1}\) represent the reboiler and condenser equations, respectively. The other \(F_T^j\) represents the equations in the inner stages of the column. In any case, these vectors are organized in the following way:

\[ F_j = [F_T^0, F_T^1, F_T^2, \ldots, F_T^j, \ldots, F_T^N]^T \]  

The system of nonlinear algebraic equations resulting from this modeling was solved by the Newton–Raphson method. The analytical derivatives of the equipment model equations and of the physical properties from the equation of state were automatically obtained using the Thermath program. The Thermath input for the generation of the reactive distillation column subroutine is shown in Fig. 2.

The first commands establish the functional dependence of the thermodynamic properties. Afterwards the model equations are entered. The analytical expressions of all the terms of the Jacobian matrix (variable “jacob”) are obtained in a single command. These expressions are analyzed by a procedure called “ordeq” (Castier, 1999) which searches for common subexpressions and symmetries in multi-indexed expressions, aiming at efficient programming. Finally, the procedure “createroutine” writes a complete subroutine in Fortran. In the current version of Thermath, only Fortran subroutines are generated. However, the package can be readily extended to generate code in other programming languages, by only adapting the procedure “createroutine”. Due to its size, the Fortran code obtained as output is not shown but can be obtained from the authors.

In the vicinity of the solution, a full Newton–Raphson step is usually taken, but far from the solution, it may be smaller to prevent the violation of any physical boundary on variables, such as negative mole numbers or temperatures.

Another way of modeling reactive distillation column is by relaxing the assumption of chemical equilibrium and using reaction rates at each stage instead. Following the assumptions of previous authors (Chen, Huss, Malone, & Doherty, 1984),
Assuming that the streams leaving a stage are in phase equilibrium, neglecting the Poynting correction and the fugacity of the pure vapor at saturation pressure, and using an activity coefficient model for the liquid stream, we have:

\[ f_{ij}^k = \ln(a_i^k / x_{i,j} II) - \ln(a_i^0 / x_{i,j} II) = 0 \quad (14) \]

where \( P_j \) is the pressure in each stage, \( P_{ij}^k \) the vapor pressure of component \( i \) in stage \( j \) and \( y_{ii}^k \) is the activity coefficient of component \( i \) in stream \( II \) of stage \( j \). In the agreement with these assumptions, the rate of reaction equation is:

\[ f_{r,j} = \ln V_{ii,j} + \ln \alpha_{ii,j} + \sum_k a_{kk,j} \ln \left( \frac{P_{ij}^k}{T_{ij}^k} \right) - \ln \xi_{kk,j} = 0 \quad (15) \]

where \( V_{ii,j} \) is the liquid holdup of stage \( j \), \( k_{ii,j} \) the rate constant of the reaction \( k \) at stage \( j \), \( a_{ii,j} \) the kinetic order of each component in reaction \( k \) and \( y_{ii}^k \) is the molar volume of stage \( j \). The representation of the rate of reaction equation in the form of Equation (15) is unusual, but is particularly convenient for our purposes because of its explicit dependence with mole fractions, and thereby with mole numbers.

The mass and energy balances and the additional equation are the same as when assuming chemical and phase equilibrium at each stage (Equations (1), (3) and (4)) the model implementation with Thermath used an input analogous to that presented in Fig. 2, properly modified by replacing the chemical equilibrium by the reaction rate equations. The system of nonlinear algebraic equations resulting from this modeling was also solved by the Newton–Raphson method.

3. Results

In this section, some examples of the literature on reactive distillation process are presented. In some cases, it was possible to compare simulation results with experimental data and simulations obtained by other authors, with the objective of verifying the methodology adopted.

In all comparisons with literature information, we adopted the same specifications of the original references for the feed condition and the reflux ratio. However, the molar flow rate of distillate is not directly specified in the modeling adopted in this work, but the reflux ratio. To allow a direct comparison with the results of the selected examples, we specified reboil ratios that result in the same molar flow rates of distillate of the corresponding original references.

3.1. para- and meta-Xylene separation

To verify the program for the simulation of reactive distillation columns, we solved the problem presented by Saito, Michishita, and Maeda (1971) who considered the separation of a meta- and para-xylene mixture by reactive distillation. These isomers are difficult to separate by conventional distillation because of their very close boiling points. Extraction or extractive distillations are not adequate because of the similar molecular structures. The reactions considered are:

\[ \begin{align*}
C_8H_{10} + C_8H_{14} & \iff C_{10}H_{14} + C_6H_6 \\
C_{10}H_{14} + C_8H_{10} & \iff C_8H_{12} + C_6H_6
\end{align*} \]

where the formula \( C_8H_{12} \) represents di-tert-butylbenzene (1), \( C_8H_{10} \) is meta-xylene (2), \( C_{10}H_{14} \) is tert-butyl-meta-xylene (3), \( C_{10}H_{14} \) is tert-butyl-ortho-xylene (4) and \( C_8H_{14} \) is benzene (5). para-Xylene (6) does not appear in these reactions because it is inert at the operation conditions. Using the Joback and Reid (1987) method, Castier (1988) estimated the formation coefficient for component (3), which was estimated equal to 0.2686. Properties for the other components were taken from Reid, Prausnitz, and Poling (1987). Stream specifications are shown in Table 2. The original reference contains experimental data and a model with the following simplifications: (a) the process has reached steady-state, (b) the vapor and liquid phases are ideal mixtures, (c) each stage in the column is an equilibrium stage and (d) chemical equilibrium is reached immediately. Here, we chose the Peng–Robinson equation of state (Peng & Robinson, 1976) with binary interactions \( k_{ii} \) equal to zero to determine the physical properties of the mixture. We adopted a different column model, used the same operating conditions of the original reference, and compared with the experimental data. The reboiler reflux ratio was adjusted to provide a distillate molar flow rate of 1.56 g mol/h. In this example, we use as initial estimates linear temperature and pressure profiles interpolated using the values obtained by Saito et al. (1971) at the top and bottom, and the experimental molar flow rate. Our results are shown in Fig. 3.

<table>
<thead>
<tr>
<th>Variables</th>
<th>Specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (bar)</td>
<td>Condenser: 0.05866</td>
</tr>
<tr>
<td>Reboiler: 0.07199</td>
<td></td>
</tr>
<tr>
<td>Reflux ratio</td>
<td>Condenser: 2</td>
</tr>
<tr>
<td>Reboiler: 0.7918</td>
<td></td>
</tr>
<tr>
<td>Condenser</td>
<td>Total</td>
</tr>
<tr>
<td>Partial</td>
<td></td>
</tr>
<tr>
<td>Stage 21</td>
<td></td>
</tr>
<tr>
<td>Stage 1</td>
<td></td>
</tr>
<tr>
<td>Feed: saturated vapor</td>
<td></td>
</tr>
<tr>
<td>( T = 334.41 ) K</td>
<td></td>
</tr>
<tr>
<td>( P = 0.07199 ) bar</td>
<td></td>
</tr>
<tr>
<td>Saturated liquid</td>
<td></td>
</tr>
<tr>
<td>( T = 375.43 ) K</td>
<td></td>
</tr>
<tr>
<td>( P = 0.09999 ) bar</td>
<td></td>
</tr>
</tbody>
</table>

Table 2: Specified variables for the Saito et al. (1971) problem.
According to the temperature profile shown in Fig. 3, we observe that our simulation is in better agreement with the experimental data than that of Saito et al. (1971). A possible explanation may be the use of a more rigorous method to calculate the thermodynamic properties than in the original reference. The liquid mole fraction profiles calculated using our procedure agree with the experimental data (not shown in Fig. 3), with exception of the meta-xylene profile, whose calculated mole fractions are smaller than the experimental values, indicating a reaction conversion larger than experimentally observed. These differences may be due to the fact that the chemical reactions do not reach equilibrium immediately at each stage, conversely to the modeling assumption. In spite of this fact, our simulation correctly predicted the most important aspects of the column behavior.

It is also interesting to observe in Fig. 3 that the maximum temperature occurs at stage 2 and not at the reboiler. In this column, a mixture of di-tert-butylbenzene and tert-butylbenzene is fed as saturated liquid to the top of the column, at the temperature of 375.43 K (bubble point condition) and a mixture of xylenes (which are more volatile) is fed as saturated vapor at the temperature of 334.41 K (dew point condition) to the bottom of the column. Therefore, there is an unusual aspect in this column, namely a “cold” feed at the bottom and a “hot” feed at the top. We believe that this may originate the maximum in the temperature profile calculated for stage 2 of Fig. 3.

3.2. Ethyl acetate production

The esterification of acetic acid with ethanol towards ethyl acetate and water occurs according to the reaction:

\[
\text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O}
\]

(1) (2) (3) (4)

The model of reaction rate used in this work is (Alejski, Szymanowski, & Bogacki, 1988):

\[
r = k_1 C_1 C_2 - k_2 C_3 C_4
\]

(16)

The rate constants \( k_1 \) and \( k_2 \) are (Alejski et al., 1988):

\[
k_1 = 4.76 \times 10^{-4} \exp \left( \frac{-59774 \text{ (J/g mol)}}{RT} \right) \text{ in (L/g mol min)}, \ T(\text{K})
\]

(17)

\[
k_2 = 1.63 \times 10^{-4} \exp \left( \frac{-59774 \text{ (J/g mol)}}{RT} \right) \text{ in (L/g mol min)}, \ T(\text{K})
\]

(18)

In this example, the column has eight stages (reboiler, six adiabatic plates and condenser). The stream specifications are presented in Table 3. In the modeling presented in the original reference, the \( K_v \) vapor–liquid equilibrium coefficients were calculated according to a method proposed by Komatsu (1977) based on empirical correlations. Here, we considered ideal behavior in the vapor phase that the liquid phase was described by the Wilson model (1964), and neglected the heat of reaction. The Antoine equation with constants taken from Hála, Boublík, and Vojtech (1984) was used for vapor pressure calculations and the vaporization enthalpies were calculated using the Clausius–Clayperon equation.

Table 3

<table>
<thead>
<tr>
<th>Variables</th>
<th>Specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (atm)</td>
<td>All stages 1</td>
</tr>
<tr>
<td>Reflux ratio</td>
<td>Condenser 2.1</td>
</tr>
<tr>
<td></td>
<td>Reboiler 0.5945</td>
</tr>
<tr>
<td>Holdup (L)</td>
<td>Reboiler 0.6</td>
</tr>
<tr>
<td></td>
<td>Inner stages 0.4</td>
</tr>
<tr>
<td>Condenser</td>
<td>Total Stage 8</td>
</tr>
<tr>
<td></td>
<td>Reboiler Partial Stage 1</td>
</tr>
<tr>
<td>Feed (saturated liquid)</td>
<td>0.2584 g mol/min, 0.2559 ( T = 355.815 \text{ K} )</td>
</tr>
<tr>
<td></td>
<td>0.6159 ( (1) )</td>
</tr>
<tr>
<td></td>
<td>Stage 6 0.6159 ( (2) )</td>
</tr>
<tr>
<td>( P = 1 \text{ atm} )</td>
<td>0.0539 ( (3) )</td>
</tr>
<tr>
<td></td>
<td>0.0743 ( (4) )</td>
</tr>
</tbody>
</table>
equation. The parameters of the Wilson model were obtained from Barbosa and Doherty (1988) who studied this reactive system at atmospheric pressure. The Wilson model was also used by Simandl and Svrcek (1991) in simulations of the esterification of acetic acid with ethanol in reactive distillation columns. We neglected the possibility of forming heterogeneous azeotropes following the work of Alejski et al. (1988), Barbosa and Doherty (1988), Komatsu (1977) and Simandl and Svrcek (1991).

In this example, we adopt as initial estimates a linear temperature profile between the column top and bottom, and the liquid and vapor molar flow rates based on calculations by Komatsu (1977). In our simulation, we adopt the same values of Alejski et al. (1988) for the feed condition and of the condenser reflux ratio. The initial estimates of the extents of reaction are in the order of $10^{-12}$ g mol/min. The distillate molar flow rate is equal to $0.0425$ g mol/min, according to the original reference. In the close vicinity of the solution, a quadratic convergence rate was obtained (Fig. 4), as should be expected from correct implementations of the Newton–Raphson procedure. The numerical results are shown in Figs. 5 and 6.

Fig. 5 shows the calculations of the liquid mole fractions of each component and compares them to the numerical results of Alejski et al. (1988) and experimental data of Komatsu (1977). The calculations show qualitative agreement with experimental data and better agreement with them than those of Alejski et al. (1988). An interesting observation regarding the temperature profile (Fig. 6) is that the experimental data presents an unusual behavior because of the existence of a minimum in temperature inside the column (stage 7) and not in the condenser (stage 8).
Fig. 6. Temperature profile in the ethyl acetate production.

The differences between the values of the calculation and those of the experiment may be due to some aspects of the thermodynamic modeling. In this system, ideal vapor phase behavior may be a strong simplifying assumption because acetic acid molecules are known to dimerize in the vapor phase, causing considerable deviations from ideal gas behavior.

3.3. Diethyl carbonate (DEC) production

The transesterification of dimethyl carbonate (DMC) and ethanol consists of two reversible reactions with intermediate methyl ethyl carbonate (MEC) (Luo & Xiao, 2001):

\[
\begin{align*}
\text{H}_3\text{COOCOC}_2\text{H}_5 & \rightleftharpoons \text{H}_3\text{COOCOCH}_3 + \text{CH}_3\text{OH} \\
\text{H}_3\text{COOCOC}_2\text{H}_5 + \text{C}_2\text{H}_5\text{OH} & \rightleftharpoons 2\text{C}_2\text{H}_5\text{OCOOC}_2\text{H}_5 + \text{CH}_3\text{OH}
\end{align*}
\]

The reaction rate model used in this work is (Luo & Xiao, 2001):

\[
\begin{align*}
 r_1 &= k_{11}C_1C_2 - k_{12}C_3C_4 \\
 r_2 &= k_{21}C_3C_2 - k_{22}C_5C_4
\end{align*}
\]

The rate constants \(k_{11}, k_{12}, k_{21}, k_{22}\) are (Luo & Xiao, 2001):

\[
\begin{align*}
 k_{11} &= 2.148 \times 10^4 \exp\left(-\frac{12454.9}{RT}\right) \text{ in } (\text{L/(g mol h)}), T(\text{K}) \\
 k_{12} &= 147.174 \exp\left(-\frac{13083.3}{RT}\right) \text{ in } (\text{L/(g mol h)}), T(\text{K}) \\
 k_{21} &= 3.076 \times 10^3 \exp\left(-\frac{12210.2}{RT}\right) \text{ in } (\text{L/(g mol h)}), T(\text{K}) \\
 k_{22} &= 92.5892 \exp\left(-\frac{12804.1}{RT}\right) \text{ in } (\text{L/(g mol h)}), T(\text{K})
\end{align*}
\]

In this example, the column has 50 stages (reboiler, 48 adiabatic plates and condenser). The stream specifications are presented in Table 4. The model considerations are the same as those of the previous example. The Wilson parameters were obtained from Luo and Xiao (2000) and the Antoine constants from Luo, Xiao, and Zhu (2000). We adopt as initial estimates the calculations by Luo and Xiao (2001) of pressure and temperature profiles and of vapor molar flow rates. The initial estimates of the extents of reaction are in the order of \(10^{-12}\) g mol/min. The distillate molar flow rate is equal to 33 g mol/min, according to the original reference. Fig. 7 shows the calculations of the temperature and liquid mole fraction profiles. The calculations show excellent agreement with the simulation by Luo and Xiao (2001).
In this paper, models for steady-state reactive distillation columns were developed and implemented with the aid of computer algebra. This type of equipment was selected for study because it represents a complex unit operation, due to the simultaneity of reaction and separation. In some cases, our simulations are in better agreement with experimental data than other simulations available in the literature for the same systems, because of the adoption of more rigorous thermodynamic modeling, what could be done with relative ease using computer algebra. This type of equipment was selected for the simultaneity of reaction and separation. In some cases, our simulations are in better agreement with experimental data than other simulations available in the literature for the same systems, because of the adoption of more rigorous thermodynamic modeling, what could be done with relative ease because of the use of computer algebra. However, more than the numerical results themselves, what should be stressed as innovative here is the way the equipment simulation software was developed, i.e., by extending a computer algebra package, Thermath, to generate code for the simulation of complex processing equipment. Because of the full use of analytical derivatives of both equipment and thermodynamic models, the Newton–Raphson method could be used to promote numerical convergence for both process simulation and optimization, also requires analytical derivatives for its proper implementation. Therefore, the implications of our modeling success extend beyond the implementations presented in this paper, opening the possibility of the quick development of codes for use with interval analysis software.

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References


