SUPERCRITICAL MULTISTAGED MULTICOMPONENT SEPARATION: PROCESS SIMULATION

I. E. COLUSI,† M. FERMEGLIA, V. GALLO and I. KIKIC
Istituto di Chimica Applicata e Industriale, University of Trieste, Via Valerio 2, 34127 Trieste, Italy

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Abstract—An efficient program for the simulation of a supercritical multistage multicomponent separation column with ideal stages has been developed.
Models for calculating phase equilibria and densities are briefly described and applied to the simulation of the process. The algorithm used was a simultaneous convergence Newton method combined with Fibonacci search in order to determine the best damping factor. The use of this method is justified by the description of the nature of the problem.
In this work, accurate and rigorous thermodynamic models are combined with robust and reliable simulation algorithms for the description of a supercritical fluid extraction column equipped with a top separator, taking into account enthalpy balances too. In fact, it is important to consider also the occurrence of small temperature changes along the column, because they could give rise to noticeable changes of densities and capacities.
The developed program takes advantage of the form of the model equations, utilizing the band structure of the equations and their Jacobian.
Computing time was saved by attention to the structure of thermodynamic functions and derivatives.

INTRODUCTION

Supercritical and near-critical fluid extraction (SFE and NCE processes are based on some characteristic properties that fluids exhibit in these regions. Generally, the zone which is of interest for this kind of separation process can be specified in the range $0.9 < T_i < 1.4$ and $P_i > 1.0$.

In the supercritical region, quantities such as density, viscosity and vapour-liquid equilibrium ratios become strongly temperature dependent at given pressure.

In order to calculate the real temperature profile for each stage of an adiabatic column, enthalpy balances must be used in the simulation routine.

Fairly limited variations of temperature and pressure produce wide variations of density, in particular in the vicinity of the critical point (Fig. 1). The value of the reduced viscosity is about 1–2 in the region which is of interest for NCE and SFE processes and about 10–20 for a normal liquid–liquid extraction process.

The discussion below will mainly refer to supercritical fluids, but it should be remembered that many of the interesting properties of supercritical fluids are also shown by marginally subcritical liquids.

The solubility of the solute in the supercritical fluid is directly influenced by fluid density; this fact is widely illustrated in the literature.

A supercritical separation process takes advantage of the above-mentioned observations, both for extraction of the solute by means of the supercritical fluid and for recovery of the supercritical fluid itself. Both steps can be effectively carried out only by varying operating temperature and pressure which, by changing fluid density, also change vapour–liquid equilibrium ratios $K_i = y_i / x_i$.

The objective of this study was to develop an efficient and reliable computer program for the simulation of a supercritical fluid extraction column equipped with a top separator, also taking into account enthalpy balances at each stage. In this way, the real temperature profile of the column can be calculated (and hence fluid properties and equilibrium ratios) assuming input data heat duties $Q_j$ for each stage $j$. (The adiabatic column is a particular case of the more general case mentioned above, in which $Q_j = 0$ for each stage.)

The opposite situation is the one in which a temperature value is assigned to each stage. (The isothermal column is a particular case of the more general case mentioned above, in which the same fixed temperature value is assumed at each stage.)

It is very important to consider the occurrence of small temperature changes along the column, because they could give rise to noticeable changes of densities and capacities. In order to demonstrate this assumption, a comparison was made between the results obtained under adiabatic and isothermal conditions.

†To whom all correspondence should be addressed.
supervised models; possible modifications can be summarized as:

—development of new mixing rules in order to take into account polar interactions (density-dependent mixing rules);
—development of new equations of state with mixing rules especially designed for molecules of different sizes and interactions.

Since thermodynamic models are continually being improved and developed, we have set up a calculation procedure in which one of a range of models can be used.

The process condition of supercritical fluid extraction demands an equation of state capable of representing thermodynamic properties at high pressures of multicomponent mixtures whose molecules may be very different in size, shape and intermolecular forces. Consequently simple models such as RK, PR and CS may not always give satisfactory results.

The calculation examples reported in the present paper have been obtained by using a somewhat more sophisticated model based on the local composition concept, namely the GCEOS equation of state developed by Skjold-Jørgensen (1984). In addition the GCEOS equation is a group contribution equation of state which allows a confident extrapolation with molecular weight inside its range of applicability. This fact is particularly important in supercritical fluid extraction processes because in most cases we are dealing with ill-defined molecules for which molecular parameters and thermodynamic data may not be available.

The total residual Helmholtz function is defined in the GCEOS model as the sum of an attractive and a repulsive term.

The attractive term is based on the NRTL model and is defined as:

\[
(A^R/RT)_i = -(\varepsilon/2) \sum_{j}^{NC} \sum_{i}^{NG} \frac{n_i n_j \rho_j \rho_i}{RTV} \sum_{k}^{NG} \frac{n_k \rho_k}{RTV} \sum_{l}^{NC} \theta_{ijl},
\]

where

\[
\rho_j = \sum_{i}^{NC} n_i \rho_i,
\]
and

\[
\theta_{ij} = \exp(\alpha_{ij} \Delta g_{ij} / RTV).
\]

The repulsive term is based on the Mansoori mixture hard-sphere model as follows:

\[
(A^H/RT)_i = 3(\beta_1 \beta_2 / \beta_3)(Y - 1)
\]

\[
+ (\beta_1^2 / \beta_3)(- Y + Y^2 - \ln Y)
\]

\[
+ n \ln Y,
\]

\[
\beta_k = \sum_{j}^{NC} n_j d_i^k
\]

and

\[
Y = (1 - n \beta_j / 6V)^{-1}
\]

The hard-sphere diameter is temperature dependent and no interaction parameter is included in the repulsive term.

The attractive energy between segments is expressed by:

\[
\varepsilon_{ij} = k_{ij} (\varepsilon_{ij} \varepsilon_{ij})^{1/2},
\]

with \(k_{ij}\) temperature dependent. The model contains pure group parameters which can be estimated by pure component and/or mixture properties.

Expressions for the fugacity coefficients, residual enthalpy and other thermodynamic properties are
obtained from the expression of Helmholtz free energy by straightforward differentiation.

The GC-EOS equation has been developed giving high priority to the representation of fugacity coefficients and Henry's constant at pressures between 0 and 15 MPa. This priority is not only due to the kind of experimental data used in the parameter estimation, but is also implicit in the model.

As a matter of fact, the GCEOS is an extension of the CS van der Waals' equation of state and it should be expected to yield results of the same quality as obtained by the simple equations of state in common use (e.g. SRK and PR). Therefore the GCEOS is not very accurate in the representation of total as well as partial molar volumes.

**EXTRACTION COLUMN MODELLING**

A generalized SFE equilibrium stage column is represented in Fig. 2, in which a top separator has also been considered.

The extraction column is defined for C components and N stages; for each stage \((j)\), the following quantities are required: rate of feed input \((F_j)\), feed composition \((c_j)\), feed temperature \((T_F)\), pressure \((P_j)\), raffinate flow rate \((R_j)\), extract stream flow rate \((E_j)\), heat duty \((Q_j)\). In addition, values are required for the temperature of the separator \((T_S)\), pressure of the separator \((P_S)\) and top reflux \((R_{N+1})\).

The reflux ratio \((RR)\) is defined as:

\[
RR = \frac{R_S}{SR_S} = \frac{R_{N+1}}{SR_{N+1}}.
\]

Fig. 3. Matrix coefficient structure.
The basic mathematical model equations defining the extraction column are:

(I) Material balances for each component on each stage:

\[ M_{ij} \times \left( E_{j-1} \times y_{j-1,i} \right) - \left[ (S_{E_j} + E_j) \times y_{j,i} \right] \]
\[ - \left[ (SR_j + R_j) \times x_{j,i} \right] + (R_{j+1} \times x_{j+1,i}) \]
\[ + (F_j \times z_{j,i}) = 0, \quad (6) \]

in which

\[ E_0 = 0; \quad R_{N+2} = 0; \quad R_{N+1} = SR_{N+1} \times RR. \]

(II) Equilibrium assumption for each component and each stage:

\[ E_{ij} \times \left( E_{j-1} \times y_{j-1,i} \right) + \left[ (E_j + SE_j) \times y_{j,i} \right] \]
\[ = \left( E_{j-1} \times y_{j-1,i} \right) - \left( E_{j} \times y_{j,i} \right), \quad (7) \]

(III) Mole fraction summation for the raffinate phase on each stage:

\[ S_{xi} \times \left( E_{j-1} \times y_{j-1,i} \right) + \left[ (E_j + SE_j) \times y_{j,i} \right] \]
\[ = \left( E_{j-1} \times y_{j-1,i} \right) - \left( E_{j} \times y_{j,i} \right), \quad (8) \]

(IV) Mole fraction summation for the extract phase on each stage:

\[ S_{yi} \times \left( E_{j-1} \times y_{j-1,i} \right) + \left[ (E_j + SE_j) \times y_{j,i} \right] \]
\[ = \left( E_{j-1} \times y_{j-1,i} \right) - \left( E_{j} \times y_{j,i} \right), \quad (9) \]

(V) Heat balances for each stage:

\[ H_{j} \times \left( E_{j-1} \times y_{j-1,i} \right) - \left[ (SE_j + E_j) \times H_j \right] \]
\[ - \left[ (SR_j + R_j) \times h_j \right] + (R_{j+1} \times h_{j+1}) \]
\[ + (F_j \times HF_j) - Q_j = 0. \quad (10) \]

The number of equations is \((2C + 3) \times (N + 1)\).

The number of unknowns of the system is also \((2C + 3) \times (N + 1)\):

\[ \delta x_{j,i}, \quad \delta y_{j,i}, \quad \delta R_j, \quad \delta E_j, \quad \delta T_i, \quad \delta SR_{N+1}, \quad Q_{N+1}. \]

**CALCULATION METHOD**

The Newton–Raphson simultaneous convergence method is the most powerful algorithm for solving problems concerning the modelling of multistage, multicomponent separators. This is because of its flexibility in defining the set of independent variables and because of its quadratic convergence which makes it faster than any other method. In the present work, this method, described in detail in the literature (King, 1980), has been used.

To this aim, the system must be linearized and a block-tridiagonal matrix obtained.

Linearized system equations are:

\[ M_{ij}: \]
\[ (-E_{j-1} \times \delta y_{j-1,i}) - (y_{j-1,i} \times \delta E_{j-1}) + [(E_j + SE_j) \times \delta y_{j,i}] \]
\[ + [(R_j + SR_j) \times \delta x_{j,i}] + [x_{j,i} \times \delta (R_j + SR_j)] \]
\[ - (R_{j+1} \times \delta x_{j+1,i}) - (x_{j+1,i} \times \delta R_{j+1}) \]
\[ = (E_{j-1} \times y_{j-1,i}) - [(E_j + SE_j) \times y_{j,i}] \]
\[ - [(R_j + SR_j) \times x_{j,i}] + (R_{j+1} \times x_{j+1,i}) \]
\[ + (F_j \times z_{j,i}), \quad (11) \]

valid with the assumptions:

\[ E_0 = 0, \]
\[ R_{N+2} = 0, \]
\[ \delta (R_{N+1} + SR_{N+1}) = R \times \delta SR_{N+1}, \]
\[ \delta (E_j + SE_j) = \delta E_j, \]
\[ \delta (R_j + SR_j) = \delta R_j; \]

\[ E_{ij}: \]
\[ \delta y_{j,i} \times x_{j,i} \times \left( \frac{\partial K_{ij}}{\partial T} \times \delta T + \sum_k \frac{\partial K_{ij}}{\partial X_k} \times \delta x_{j,k} \right) \]
\[ + \sum_k \frac{\partial K_{ij}}{\partial y_{j,k}} \times y_{j,k} - K_{ij} \times \delta y_{j,i} \]
\[ = K_{ij} \times x_{j,i} \times \delta y_{j,i}; \quad (12) \]

\[ S_{xj}: \]
\[ \sum_i \delta x_{j,i} = 1 - \sum_i x_{j,i}; \quad (13) \]

\[ S_{yj}: \]
\[ \sum_i \delta y_{j,i} = 1 - \sum_i y_{j,i}; \quad (14) \]
\( H_j: \)

\[
\left( -E_{j-1} \times \frac{\partial H_{j-1}}{\partial T} \times \delta T_{j-1} \right) - (H_{j-1} \times \delta E_{j-1}) \\
- \left( E_{j-1} \times \sum_i \frac{\partial H_{j-1}}{\partial y_i} \times \delta y_{j-1,i} \right) \\
+ \left[ (E_j + SE_j) \times \frac{\partial H_j}{\partial T} \times \delta T_j \right] + \left[ H_j \times \delta (E_j + SE_j) \right] \\
+ \left[ (E_j + SE_j) \times \sum_i \frac{\partial H_j}{\partial y_i} \times \delta y_{j,i} \right] \\
+ \left[ (R_j + SR_j) \times \frac{\partial H_j}{\partial T} \times \delta T_j \right] + \left[ h_j \times \delta (R_j + SR_j) \right] \\
+ \left[ (R_j + SR_j) \times \sum_i \frac{\partial H_j}{\partial x_i} \times \delta x_{j,i} \right] \\
- \left( R_{j+1} \times \frac{\partial H_{j+1}}{\partial T} \times \delta T_{j+1} \right) - \left[ h_{j+1} \times \delta (R_{j+1}) \right] \\
+ \left[ R_{j+1} \times \sum_i \frac{\partial h_{j+1}}{\partial x_i} \times \delta x_{j+1,i} \right]
\]

\[
= (F_j \times H_j) + (E_{j-1} \times H_{j-1}) - [(E_j + SE_j) \times H_j] \\
- [(R_j + SR_j) \times h_j] + (R_{j+1} \times h_{j+1}) - Q_j. \quad (15)
\]

The coefficient matrix associated with the linear system defined by equation (11) to (15) is illustrated in Fig. 3.

At the \( i \)th iteration, the system can be represented in vectorial form as follows:

\[
-J'(\mathbf{x}^i) \times \delta \mathbf{x}^i = \mathbf{G}'(\mathbf{x}^i), \quad (16)
\]

in which the vector \( \delta \mathbf{x}^i \) is defined by:

\[
\mathbf{x}^{i+1} = \mathbf{x}^i + t \times \delta \mathbf{x}^i \quad (17)
\]

Computation can be advantageously performed by applying the Fibonacci method for evaluation of the damping factor \( t \).

In particular, in the present work we resorted to the Fibonacci method until the norm \( \| \Theta \| > 10^{-2} \); on the contrary, when the norm was \( < 10^{-2} \), the calculated values of \( t \) resulted to about 1, so that the assumption \( t = 1 \) was made and the Fibonacci method automatically removed from the algorithm. It is evident that each iteration in which the calculation of the damping factor is carried out requires greater computer time as compared to the simple N–R method, but in this way the number of iterations which are necessary to reach convergence of the system is notably lowered.

A guess of initial values is needed for application of the N–R method, possibly close to the solution in order to ensure rapid convergence.

In the present calculation program, a good initial guess for the solution vector is generated automatically by the algorithm.

**INITIAL GUESS OF VARIABLES**

The procedure adopted in order to determine a good initial guess of the values of the variables is such that, starting from a limited set of values assigned to some of the elements of the solution vector, a reasonable initial guess can be obtained which assures rapid convergence of the system.

The data which are necessary in order to define an initial guess of values are: \( T_1 \) and \( T_N \); (temperature profile is considered linear along the column, as a beginning); \( R_i \) and \( x_{1,i}; SR_{N+1} \) and \( x_{N+1,i}; K_{x+1,i} \).

In addition, it is necessary to specify for each feed stream, a value which indicates the fraction of feed that is supposed to remain in the reafinate phase, \( SR_j \).

<table>
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<th>Test No.</th>
<th>No. of stages</th>
<th>No. of iterations</th>
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<th>Flashes routine</th>
<th>Thermodynamic routine</th>
<th>Simultaneous convergence routine</th>
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<td>4</td>
<td>32</td>
<td>17.96</td>
<td>19.98</td>
<td>5.26</td>
<td>43.20</td>
</tr>
<tr>
<td>1B</td>
<td>7 + 1</td>
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<td>30</td>
<td>15.76</td>
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<td>39.32</td>
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<td>18.45</td>
<td>19.49</td>
<td>5.71</td>
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*Computer used—IBM PC AT: main processor Intel 80386, coprocessor Intel 80387.*

System 1: \( \text{H}_2\text{O} - \text{EtOH} - \text{ethane} \)
System 2: \( \text{H}_2\text{O} - \text{EtOH} - \text{propane} \)
System 3: \( \text{H}_2\text{O} - \text{EtOH} - \text{CO}_2 \)
System 4: \( \text{H}_2\text{O} - \text{acetone} - \text{propane} \)
System 5: \( \text{H}_2\text{O} - \text{acetone} - \text{CO}_2 \)
FINAL RESULTS

K(A) = 0.2323e-02
K(B) = 0.2904e-02
K(C) = 4.511

SEPARATOR 6

RF = 0.0000
EX = 1.550

SR = 0.5005e-01

1.000 moles - 305.0 K

A = 0.9583
B = 0.1467e-01
C = 0.0000

STAGE 5

K(A) = 0.3130e-02
K(B) = 0.8188
K(C) = 43.98

RF = 1.0100
EX = 1.530

A = 0.9478
B = 0.3006e-01
C = 0.2211e-01

STAGE 4

K(A) = 0.2426e-02
K(B) = 0.7610
K(C) = 43.93

RF = 1.0020
EX = 1.522

A = 0.9552
B = 0.2255e-02
C = 0.2232e-01

STAGE 3

K(A) = 0.2364e-02
K(B) = 0.7523
K(C) = 43.53

RF = 0.9962
EX = 1.516

A = 0.9614
B = 0.1590e-01
C = 0.2265e-01

STAGE 2

K(A) = 0.2673e-02
K(B) = 0.7934
K(C) = 43.52

RF = 0.9907
EX = 1.511

A = 0.9675
B = 0.3091e-02
C = 0.2274e-01

STAGE 1

K(A) = 0.3175e-02
K(B) = 0.8350
K(C) = 44.27

RF = 0.9800

A = 0.9733
B = 0.4302e-02
C = 0.2244e-01

EXTRACT PHYSICAL PROPERTIES

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<th>TEMP.</th>
<th>PRESS.</th>
<th>DENSITY</th>
<th>Z</th>
<th>MOL. ENTH.</th>
<th>SPEC. HEAT</th>
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<td>MPa</td>
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<td>J/mol</td>
<td>J/mol/K</td>
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<td>275.00</td>
<td>1.976</td>
<td>44.98</td>
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<td>.8665</td>
<td>-438.65</td>
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1.500 moles - 305.5 K

A = 0.0000
B = 1.000

Fig. 4. Adiabatic column. Calculation results for the carbon dioxide-ethanol-water system. GCEO thermodynamic subroutine with original parameters determined by Skjold-Jorgensen (1988).
FINAL RESULTS

A = H2O
B = CH3CH2OH
C = CO2

EX 1.471

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<th>.2443E-03</th>
<th>B</th>
<th>.1776E-02</th>
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<td>K(B)</td>
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<td>K(C)</td>
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<td>Q</td>
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RF 0.0000 EX 1.523

SR .5222E-01

1.000 moles - 305.0 K
A .9583
B .4167E-01
C .0000

K(A) | .4407E-02  | T  | 305.0      | K   |
| K(B) | .8291      | P  | 9.049      | MPa |
| K(C) | 44.01      | Q  | -.832.2    | J   |

STAGE 5

RF 1.011 EX 1.534

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STAGE 4

RF 1.01 EX 1.524

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<td></td>
</tr>
<tr>
<td>K(B)</td>
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<td>9.059</td>
<td>MPa</td>
<td></td>
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<tr>
<td>K(C)</td>
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<td>Q</td>
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STAGE 3

RF 0.9330 EX 1.516

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<tr>
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STAGE 2

RF 0.9869 EX 1.510

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STAGE 1

EXTRACT PHYSICAL PROPERTIES

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<th>STAGE</th>
<th>TEMP.</th>
<th>PRESS.</th>
<th>DENSITY</th>
<th>Z</th>
<th>MOLE. ENTH.</th>
<th>SPEC. HEAT</th>
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<tr>
<td>No.</td>
<td>K</td>
<td>MPa</td>
<td>kg/m3</td>
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<td>J/mol</td>
<td>J/mol/K</td>
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<td>571.11</td>
<td>.3071</td>
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<td>44.98</td>
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<td>9.0210</td>
</tr>
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</table>

ITERATIONS 2 - THERMODYNAMIC SUBROUTINE CALLS 12 - CALCULATION TIME = 26.97 SECONDS

Fig. 5. Isothermal column. Calculation results for the carbon dioxide-ethanol-water system. GCEOS thermodynamic routine with original parameters determined by Skjold-Jorgensen (1988).
Input data are:

Feeds \( F_{j,i}, T_{F_{j,i}}, (j, i = 1, N) \),
Heat duties \( Q_{j,i}, (j, i = 1, N) \),
Side streams \( S_{R_{j,i}}, S_{E_{j,i}}, (j, i = 1, N) \),
Reflux ratio \( R_R \),
Temperature \( T_{N+1} \),
Pressures \( P_1, P_N, P_{N+1} \) (pressure profile is assumed to be linear).

**Computational procedure**

Step 1. Assume linear temperature (initial) and pressure profiles.

Step 2. Calculate the following quantities:

\[
R_{N+1} = RR \times S_{R_{N+1}},
\]

\[
E_{N+1} = \sum_{j} F_{j} - \sum_{i} S_{E_{j,i}} - \sum_{j} S_{R_{j}} - R_{N+1} \times S_{R_{N+1}},
\]

\[
E_N = E_{N+1} + S_{R_{N+1}} \times (R_R + 1),
\]

\[
\frac{\{E_{N+1} \times K_{N+1}\}}{[S{R_{N+1}} \times (R_R + 1)]]} \times x_{N+1, i},
\]

\[
K_i = \left(\frac{Y_{N+1, i}}{x_{N+1, i}}\right)^{1/N},
\]

(mean value of \( K_i \) along the column).

Step 3. Compute flash calculations for the first stage in which \( F_i \) and \( R_i \) are considered to be entering streams, by using the \( K_i \) values determined in Step 2. Consequently, the values \( K_{i,j}, x_{i,j} \), and \( R_i \) can be calculated. The new values of \( E_{N+1} \) and \( E_N \) are obtained by considering the overall material balance.

Step 4. Compute flash calculations for the \( N \)th stage in which \( F_N \), \( E_N \) and \( R_{N+1} \) are supposed as entering flows; then the values of \( K_{N,j} \) and \( y_{N,i} \) can be calculated.

Step 5. Compute flash calculations for the separator, considering the system formed by the flow \( E_N \); in this way, good values of \( K_{N+1,j} \) can be determined.

Step 6. Assume a linear profile for the values of \( K_{j,i} \) according to the equation:

\[
K_{j,i} = K_{j,1} + K_{N-1,j} \times (j-1).
\]

This assumption roughly represents the real situation, but is very useful for determination of a good initial guess for the solution vector.

Step 7. Calculate all lacking streams \( E_i \) and \( R_i \), supposing that there is no mass transfer between flows on each stage, according to the equations:

\[
R_i = R_{i+1} + F_i \times SRF_i - S_{R_{i+1}}
\]

\[
E_i = E_{i+1} + F_i \times (1 - SRF_i) - S_{E_{i+1}}
\]

Step 8. Calculate lacking compositions \( x_{i,j} \) and \( y_{i,j} \) by applying the tridiagonal matrix method (Wang and Henke, 1966).

Step 9. Normalize all molar fractions, giving very small values to the ones having a negative sign.

Step 10. Use the values calculated by Steps 1–9 as initial guesses for the solution vector.

---

**Fig. 6.** Comparison of temperature and extract density between tests 1A (●) and 1B (○).
TEST OF THE PROGRAM AND RESULTS

Different chemical systems were used to test the proposed calculation program (named GLOBUS: GLObal Balance Unit Simulation) with the aim of verifying the validity of the algorithm.

The results obtained in five chemical systems are summarized in Table 1, in which a comparison is made between case A: calculation carried out without enthalpy balances; and case B: calculation carried out with enthalpy balances. The number of stages was the number of equilibrium stages + 1 (the top separator).

Flash calculations were computed by using the Michelsen algorithm (Michelsen, 1982a,b).

Analytical results are reported in Figs 4 and 5 for the H₂O–EtOH–CO₂ system, in cases with and without enthalpy balances calculations, respectively, together with the calculated physical properties of the extract stream at each stage. It can be seen that the results are quite different; in particular, the temperature profile has a great influence on the physical properties of the streams. This fact is clearly shown...
Fig. 11. Adiabatic column. Calculation results for the carbon dioxide-ethanol-water system. GCEOS thermodynamic routine with optimized group-group parameters determined by Inomata et al. (1990).
**FINAL RESULTS**

\[
\begin{align*}
A &= H_2O \\
B &= CH_3CH_2OH \\
C &= CO_2
\end{align*}
\]

- **Separator 6**
  \[
  \begin{align*}
  K(A) &= 0.832E-03 \\
  K(B) &= 0.229E-02 \\
  K(C) &= 9.910 \\
  T &= 275.0 \text{ K} \\
  P &= 1.974 \text{ MPa} \\
  Q &= -1.116E+05 \text{ J}
  \end{align*}
  \]

- **Stage 5**
  \[
  \begin{align*}
  A &= 0.9583 \\
  B &= 0.5167E-01 \\
  C &= 0.0000
  \end{align*}
  \]

- **Stage 4**
  \[
  \begin{align*}
  A &= 0.9307 \\
  B &= 0.4060E-01 \\
  C &= 0.2875E-01
  \end{align*}
  \]

- **Stage 3**
  \[
  \begin{align*}
  A &= 0.9306 \\
  B &= 0.4060E-01 \\
  C &= 0.2876E-01
  \end{align*}
  \]

- **Stage 2**
  \[
  \begin{align*}
  A &= 0.9306 \\
  B &= 0.4060E-01 \\
  C &= 0.2876E-01
  \end{align*}
  \]

- **Stage 1**
  \[
  \begin{align*}
  A &= 0.9306 \\
  B &= 0.3300E-02 \\
  C &= 0.2685E-01
  \end{align*}
  \]

---

### Extract Physical Properties

<table>
<thead>
<tr>
<th>Stage</th>
<th>Temp.</th>
<th>Press.</th>
<th>Density</th>
<th>Z</th>
<th>MOL. ENTH.</th>
<th>SPEC. HEAT</th>
</tr>
</thead>
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<td>566.74</td>
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**ITERATIONS 4**  -  **THERMODYNAMIC SUBROUTINE CALLS 24**  -  **CALCULATION TIME = 35.95 SECONDS**

Fig. 12. Isothermal column. Calculation results for the carbon dioxide-ethanol-water system. GCEOS thermodynamic routine with optimized group-group parameters determined by Inomata et al. (1990).
in Fig. 8, in which the data reported in Figs 4 and 5 are graphically compared.

The calculated profiles of temperature and extract density for: water–ethanol–ethane, water–ethanol–propane, water–ethanol–carbon dioxide, water–acetone–propane, water–acetone–carbon dioxide are reported in Figs 6–10, respectively. In some cases (see Figs 8–10), these results indicate a noticeable difference between top and bottom temperatures, which means a wide range of values for important properties (\(k_{ij}\), density, viscosity, etc.).

In all the above-mentioned VLE calculations, we used the group contribution equation of state (GCEOS) proposed by Skjold-Jørgensen (1984) and the revised parameter tables published by the same author (Skjold-Jørgensen, 1988).

In order to emphasize that the validity of the predictions is strongly dependent on the thermodynamics used, we report in Figs 11 and 12 the results obtained by using the GCEOS in which Skjold-Jørgensen’s original parameters for the \(\text{H}_2\text{O–EtOH–CO}_2\) system have been substituted by the optimized group–group parameters determined by Inomata et al. (1990), in cases with and without enthalpy balances calculations, respectively. It can be seen that the results are quite different from those of Figs 4 and 5, though the same thermodynamic model is used.

This is essentially due to the fact that a simple equation of state cannot represent volumetric properties of pure components, specially in the vicinity of the critical point. Cubic EOS are constrained to pass through the critical point, but this fact produces distortion of the isotherms in the vicinity of it. To solve the problem, a much more complicated model should be considered, such as a noncubic EOS based on the Perturbed Hard Chain Theory (Gregorowicz et al., 1991), and their implementation in the program is considered for future development of the program itself.

Since the present paper is primarily concerned with the computing procedure, no detailed attention was given to the comparison of the results obtained by different models or correlations. It is beyond the scope of this paper to analyze which are the “best” models or the “best” parameters of a model. For this reason, starting from the fact that thermodynamic models are continually being improved and developed, the proposed computing procedure is such that one of a range of models can be used.

CONCLUSIONS

The proposed program GLOBUS combines a rigorous method for column solving (simultaneous convergence method) to a rigorous thermodynamic routine (GCEOS), taking into account enthalpy balance too.

The program takes advantage of the form of the model equations, utilizing the band structure of the equations and their Jacobians.

Computing time was saved by attention to the structure of the thermodynamic functions and derivatives.

In the present calculation program, a good initial guess for the solution vector was generated automatically by the algorithm.

The program GLOBUS showed its reliability for simulation of supercritical and near-critical multi-stage multicomponent extraction columns, provided that the given chemical system is well-described by the thermodynamic model used.

Acknowledgement—The authors thank Ministero della Pubblica Istruzione (MPI) for financial support.

NOMENCLATURE

\[
\begin{align*}
C &= \text{Number of components} \\
E &= \text{Extract flowrate in column} \\
F &= \text{Feed stream flowrate to stage} \\
H &= \text{Extract phase enthalpy} \\
h &= \text{Raffinate phase enthalpy} \\
HF &= \text{Feed enthalpy} \\
K &= \text{Vapour–liquid equilibrium ratio} \\
N &= \text{Number of stages} \\
P &= \text{Pressure} \\
PS &= \text{Pressure at the separator} \\
Q &= \text{Heat duty to/from stage} \\
R &= \text{Raffinate flowrate in column} \\
RR &= \text{Reflux ratio} \\
SE &= \text{Extract stream flowrate from stage} \\
SR &= \text{Raffinate stream flowrate from stage} \\
SRF &= \text{Fraction of feed in raffinate phase} \\
t &= \text{Damping factor} \\
T &= \text{temperature} \\
TF &= \text{Feed temperature} \\
TS &= \text{Separator temperature} \\
x &= \text{Mole fraction in raffinate phase} \\
y &= \text{Mole fraction in extract phase} \\
z &= \text{Compressibility factor} \\
q &= \text{Density} \\
\text{Subscripts} & \\
i &= \text{Component} \\
j &= \text{Stage number} \\
t &= \text{Reduced variable} \\
\text{Superscripts} & \\
i &= \text{Number of iteration}
\end{align*}
\]

Thermodynamic section

\[
\begin{align*}
\Delta^e &= \text{Residual Helmholtz function} \\
d &= \text{Hard-sphere diameter} \\
\varepsilon_j &= \text{Attractive energy parameter for group j} \\
k_{ij} &= \text{Binary interaction parameter} \\
n &= \text{Number of moles} \\
NC &= \text{Number of components} \\
NG &= \text{Number of different groups} \\
q &= \text{Group surface area fraction} \\
R &= \text{Gas-law constant}
\end{align*}
\]
\[ V = \text{Total volume} \]
\[ Y = \text{Hard sphere equation parameter} \]
\[ z = \text{Coordination number} \]
\[ \eta_j = \text{Nonrandomness parameter} \]
\[ y_j = \text{Number of groups of type } j \text{ in molecule } i \]
\[ \delta_j = \text{Surface fraction of group } j \]
\[ \tau_j = \text{Exponential weighting factor} \]

**Subscripts**

\[ a = \text{Attractive} \]
\[ f = \text{Free volume} \]
\[ i = \text{Molecule} \]
\[ j = \text{Type of group} \]

**REFERENCES**


