A COMPUTATIONALLY EFFICIENT ALGORITHM FOR SIMULTANEOUS CHEMICAL AND PHASE EQUILIBRIUM CALCULATIONS

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The paper recommends a particularly effective modification of the *K*-value approach to simultaneous phase and chemical equilibrium. Three examples are presented – the esterification reaction of ethanol with acetic acid, the synthesis of methanol, and the butylation of *m*-xylene. Discussed are the reliability and computational efficiency of the new algorithm.

Key words: Phase and chemical equilibrium.

At the root of most chemical process design problems, such as the distillation column design or alternative separation systems and reactor design, lies the fundamental problem of chemical and phase equilibrium (CPE). Due to its significance in the realm of industrial applications, extensive research has provided a number of proposed methods for its solution.

Smith[1] classifies chemical equilibrium formulations to be either stoichiometric or non-stoichiometric. The stoichiometric formulations require the knowledge of stoichiometric coefficients of linearly independent set of reactions and utilize the extent of the reactions as independent variables. On the other hand, in the non-stoichiometric formulations, elemental abundance constraints are used in the calculations.

Seider *et al.*[2] provide a through review of the literature on solution methods of the simultaneous CPE problem. Applicaiton of optimization methods began with the work of White *et al.*[3] and was further continued by Gautam and Seider[4], George *et. al.*[5], Castillo and Grossmann[6], Lantagne *et al.*[7], Castier *et al.*[8] to name a few.

The CPE problem can also be stated in an alternative formulation. The equilibrium compositions and the number of phases of a system can be obtained by solving a set of mass balance and phase and chemical equilibrium equations for specified components and reactions. This is called the *K*-value method because distribution coefficients K_i (*e.g.*, for vapour/liquid equilibrium systems $K_i \equiv y_i/x_i$) are introduced.

Sanderson and Chien[9] developed a *K*-value method designed for a single-phase or multiphase systems with one or more linearly independent chemical reactions that calculated the equilibrium composition of a mixture at a given temperature, pressure and initial composition. In addition, a prior specification of possible reactions and their equilibrium constants is required.

A new generalized algorithm for solving the simultaneous CPE in two-phase systems, providing considerable improvements in the alternative *K*-value, have been quite recently proposed by Xiao and co-workers[10]. Using effective *K*-values based on single-phase compositions and a rearrangement of the chemical reaction and phase equilibrium calculation loops proposed originally by Sanderson and Chien[8], they reported accelerated convergence of these methods when applied to an esterification reaction and several electrolytic solution equilibria problems.

In general, the problem of chemical equilibrium computation can be posed as: Given the initial composition of a system, calculate the composition, number of phases, and reactions occurring in the final equilibrium state for a specified temperature and pressure. However, this type of calculation is too general and too complex to give much insight into the effect of chemical reaction on phase equilibrium.

In this work an efficient modification of the *K*-value method introduced by Xiao and co-workers[10] is advocated. Firstly, the mathematical background of the simultaneous CPE problem will be given and the algorithm of Xiao *et al.*[10] will be presented briefly. Then the new modification will be introduced and the analysis of its computational efficiency will be carried out. Finally the computational experience of the authors with this new algorithm will be discussed on the basis of three test examples.

THEORETICAL

Formulation of the Problem

The basic thermodynamic relation for a chemical equilibrium at T, P = const, assuming that only one reaction occurs and derived regardless of the phase condition of the reactants, is

$$\Delta G = \Delta[\nu_i \mu_i^*] \equiv \sum_{i=1}^{N} (\nu_i \mu_i^*) = 0 \quad . \qquad (1)$$

Introducing the expression for μ_i^* – the chemical potential of component i at equilibrium, the following is obtained:

$$\sum_{i=1}^{N} \nu_i \ln \frac{f_i}{f_i^0} = -\frac{\sum_{i=1}^{N} \nu_i \mu_i^0}{\boldsymbol{R}T} \equiv \ln Kr \quad , \qquad (1a)$$

where Kr is the chemical equilibrium constant for the only reaction considered.

If a system involving N components and the following M independent chemical reactions is considered:

$$\sum_{i=1}^{N} \nu_{ij} A_i = 0 \ , \qquad i = 1, 2, \ldots; \ j = 1, 2, \ldots, M \ , \tag{2}$$

the material balance constraints for the reactions should be satisfied. However, the moles of component i will not be conserved owing to chemical reactions. The final amount F_i^{out} of each component i is related to its initial amount F_i^{in} through the extent ξ_j of the chemical reaction j taking place.

Thus, the material balance equations for the reactions are:

$$F_i^{\text{out}} = F_i^{\text{in}} + \sum_{j=1}^{M} \nu_{ij} \xi_j \ , \quad i = 1, 2, \ldots, N \ ; \ j = 1, 2, \ldots, M \ . \tag{3}$$

It should be noted that the stoichiometric coefficient ν_{ij} is positive if the component i is a product of reaction j and negative if the component i is a reactant of reaction j.

In case of a simultaneous CPE for a two-phase vapour–liquid system involving N components and M reactions, the equilibrium constant Kr_j for reaction j is defined by:

$$\prod_{i=1}^{N} (x_i P \varphi_i^{\text{L}})^{\nu_{ij}} = \prod_{i=1}^{N} (y_i P \varphi_i^{\text{V}})^{\nu_{ij}} = Kr_j \ , \quad j = 1, 2 \ldots, M \ . \tag{4}$$

The constant Kr_i may be determined experimentally or calculated by:

$$Kr_j = \exp\left(\frac{-\Delta G_j^0}{\boldsymbol{R}T}\right) , \tag{5}$$

where

$$\Delta G_j^0 = \sum_{i=1}^{N} \nu_{ij} G_i^0 \ . \tag{5a}$$

The phase equilibrium and the flash equations for a two-phase liquid–vapour (LV) system are:

$$z_i = \frac{F_i^{\text{out}}}{\sum_{k=1}^{N} F_i^{\text{out}}} \ , \quad i = 1, 2, \ldots, N; \quad k = 1, 2, \ldots, N \tag{6}$$

$$z_i = \alpha y_i + (1 - \alpha)x_i \ , \quad i = 1, 2, \ldots, N \tag{7}$$

$$y_i = K_i x_i \ , \quad i = 1, 2, \ldots, N \tag{8}$$

$$S(\alpha) \equiv \sum_i^N \frac{(K_i - 1)z_i}{1 + \alpha(K_i - 1)} = 0 \ . \tag{9}$$

The KZ Algorithm of Xiao et al.[10]

For a system with fixed T, P and initial feed composition, Eqs (*3*), (*4*), (*6*)–(*9*) constitute the mathematical model of CPE. They are solved iteratively for the $4N + M + 1$ unknowns:

$$F_i^{\text{out}} \quad i = 1, 2, \ldots, N$$

$$x_i, y_i, z_i \quad i = 1, 2, \ldots, N$$

$$\xi_j \quad j = 1, 2, \ldots, N$$

and α.

Sanderson and Chien[9] suggest an algorithm to solve the above non-linear equation problem that searches for the extents ξ_j and F_i^{out}'s to satisfy Eqs (*3*) and (*4*) in an outer loop, and for x_i, y_i, z_i and α to satisfy Eqs (*7*)–(*9*) in an inner loop of the calculations.

Xiao *et al.*[10] introduce a modification of the above algorithm. They argue that it is efficient for an algorithm to reduce the number of K-value evaluations as much as possible and suggest to move the entire flash loop to the outside and keep the inner loop for the chemical equilibrium computations. They rearrange Eqs (*3*), (*4*), (*7*)–(*9*) and substitute the expression for the equilibrium liquid mole fraction x_i

$$x_i = \frac{z_i}{1 + \alpha(K_i - 1)} \ , \quad i = 1, 2, \ldots, N \tag{10}$$

into Eq. (*4*):

$$\prod_{i=1}^{N} (z_i)^{\nu_{ij}} = Kz_j \ , \quad i = 1, 2, \ldots, M \ , \tag{11}$$

where

$$Kz_j = Kr_j \prod_{i=1}^{N} \left(\frac{P\varphi_i}{1 + \alpha(K_i - 1)} \right)^{-\nu_{ij}} . \qquad (12)$$

In this formulation, effects of multiple phases and their non-ideality on the reaction equilibria have been merged into a set of new parameters Kz_j, $j = 1, 2, \ldots, M$ which represent “effective” chemical equilibrium constants. Given these parameters, solving Eqs (*3*), (*6*) and (*11*) is equivalent to the chemical equilibrium calculation of a single-phase ideal mixture. Xiao *et al.*[10] call their new algorithm the KZ algorithm, and, in order to avoid division by zero and the non-linearity of division, they rewrite Eqs (*11*) into the kinetic form:

$$S_j \equiv Kz_j \left(\prod_{i=1}^{N} (z_i)^{-\nu_{ij}} \right)_{\nu_{ij}<0} - \left(\prod_{i=1}^{N} (z_i)^{\nu_{ij}} \right)_{\nu_{ij}>0} , \quad j = 1, 2, \ldots, M \qquad (13a)$$

for $Kz_j \geq 1$ and

$$S_j \equiv \left(\prod_{i=1}^{N} (z_i)^{-\nu_{ij}} \right)_{\nu_{ij}<0} - \frac{1}{Kz_j} \left(\prod_{i=1}^{N} (z_i)^{\nu_{ij}} \right)_{\nu_{ij}>0} , \quad j = 1, 2, \ldots, M \qquad (13b)$$

for $Kz_j < 1$.

The material balance equations (Eqs (*3*)) are redefined to be:

$$S_{M+i} \equiv F_i^{\text{out}} = F_i^{\text{in}} + \sum_{j=1}^{M} \nu_{ij} \xi_j , \quad i = 1, 2, \ldots, N . \qquad (14)$$

Equations (*6*), (*13*) and (*14*) are placed in the inner loop of the KZ algorithm. The system of Eqs (*13*) and (*14*) is solved for the extents ξ_{ij} and F_i^{out}’s (total number of the iterative variables equals $M + N$) by a modified Marquardt method[10].

The New Modification of the Chemical Equilibrium Computations

The present paper introduces a modification of the KZ algorithm in its part concerning the chemical equilibrium calculations. As a result of this modification, the initial system, Eqs (*13*) and (*14*) with $M + N$ non-linear equations, is partitioned into two independent parts, namely a system of M non-linear equations and N linear expressions.

They are solved subsequently. The partitioning is realized introducing the following transformations:

1. After taking the logarithm, Eq. (*11*) can be rewritten in the different form:

$$\ln Kz_j - \sum_{i=1}^{N} \nu_{ij} \ln z_i = 0 \quad , \quad j = 1, 2, \ldots, M \quad . \tag{15}$$

2. Substituting Eq. (*6*) into Eq. (*15*) yields:

$$\ln Kz_j - \sum_{i=1}^{N} \nu_{ij} \left(\ln F_i^{\text{out}} - \ln \left(\sum_{k=1}^{N} F_i^{\text{out}} \right) \right) = 0 \quad , \quad j = 1, 2, \ldots, M \quad . \tag{16}$$

3. Introducing Eq. (*3*) into Eq. (*16*), the following system of *M* non-linear equations is obtained:

$$\Phi_j (\xi_1, \xi_2, \ldots, \xi_M) \equiv \sum_{i=1}^{N} \nu_{ij} \left(\ln F_i^{\text{out}}(\xi_1, \xi_2, \ldots, \xi_M) - \ln \left(\sum_{k=1}^{N} F_i^{\text{out}}(\xi_1, \xi_2, \ldots, \xi_M) \right) \right) -$$

$$- \ln Kz_j = 0 \quad , \quad j = 1, 2, \ldots, M \quad . \tag{17}$$

The unknown variables of the system are ξ_j, $j = 1, 2, \ldots, M$, while the parameters Kz_j can be calculated directly from Eq. (*12*).

4. The linear functions (Eqs (3)) constitute the second independent part. F_i^{out}, $i = 1, 2, \ldots, N$ can be calculated directly when ξ_j, $j = 1, 2, \ldots, M$ are known.

The Algorithm

The new modification of the chemical equilibrium computations, as given by Eqs (*3*) and (*17*), is introduced in an algorithm for simultaneous CPE calculations. It follows the organization, advocated by Xiao *et al.*[10] – namely the phase equilibrium calculations with constant *K*-values are performed in the outer loop and the inner loop is for chemical equilibrium computations. The algorithm is a part of the strategy for solving the simultaneous CPE problem in its generalized form, *i.e*. the strategy for determining the composition and number of phases occurring in the final equilibrium state of a multicomponent reacting system for a specified temperature and pressure. The strategy is under development at present and will be advocated in a future communication. However, to ensure the objectivity of comparison of the effectiveness and efficiency of the two methods, all further developments and discussions will be kept into the framework of the Xiao *et al.* paper[10].

The present algorithm requires input information which includes the following parameters: temperature, pressure, initial mixture composition, number of components, number of independent chemical reactions and their chemical equilibrium constants, stoichiometric coefficients. The algorithm presents the case of a two-phase vapour–liquid equilibrium in order to be in accordance with the original KZ algorithm. Its main steps can be briefly summarized as follows:

1. Input $T, P, z_i, N, M, Kr_j, \nu_{ij}, \quad i = 1, 2,\ldots, N; j = 1, 2,\ldots, M$.

2. The phase equilibrium calculations. They constitute the outer loop.

2a. Estimate K_i, $i = 1, 2,\ldots, N$. The acceptable first estimate can be determined from Wilson's low pressure equation:

$$K_i = \frac{P_{c_i}}{P}\left(5.42\left(1 - \frac{T_{c_i}}{T}\right)\right) , \quad i = 1, 2,\ldots, N \ .$$

2b. Estimate α. The phase fraction is estimated automatically by the secant method within the following boundaries:

$$\alpha_{\min} = \frac{1}{1 - K_{\max}} \le \alpha \le \alpha_{\max} = \frac{1}{1 - K_{\min}}$$

as suggested by Whitson and Michelsen[11].

2c. Find x_i from Eq. (*10*) and y_i from Eq. (*8*).

2d. Calculate the fugacity coefficients φ_i for the components in the liquid and vapour phases applying the corresponding thermodynamic models (in our case Eq. (*21*)).

3. The chemical equilibrium calculations. They constitute the inner loop.

3a. Find Kz_j, $j = 1, 2,\ldots, M$ from Eq. (*12*).

3b. Solve Eq. (*17*) for ξ_j, $j = 1, 2,\ldots, M$. The system is solved by Newton's method. The Jacobian of system (*17*) is known analytically:

$$\frac{\partial \Phi_j}{\partial \xi_l} = \sum_{i=1}^{N} \nu_{ij}\left(\frac{\nu_{il}}{F_i^{\text{out}}} - \frac{\sum_{k=1}^{N} \nu_{kl}}{\sum_{k=1}^{N} F_k^{\text{out}}}\right) , \quad l = 1, 2,\ldots, M \ . \qquad (18)$$

Upon convergence, new values for $\xi_1, \xi_2, \ldots, \xi_M$ are obtained.

4. Calculate F_i^{out} from Eq. (*3*).

5. Calculate new values for z_i^{new} from Eq. (*6*).

6. Check whether Eq. (*9*) is satisfied.

If satisfied, continue with step *7*, otherwise return to step *2b*.

7. Calculate new values for K_i from the current values of fugacity coefficients according to:

$$K_i^{\text{new}} = \frac{\varphi_i^{\text{L}}}{\varphi_i^{\text{V}}} \ , \quad i = 1, 2, \ldots, N \ .$$

8. Check the following criterion:

$$\sum_i^N \left(\frac{K_i^{\text{new}} - K_i^{\text{old}}}{K_i^{\text{new}}} \right)^2 \leq 10^{-12} \ , \quad i = 1, 2, \ldots, N \ .$$

If the criterion is satisfied, end the program, otherwise return to step *2a*.

The algorithm has analogous structure in case of different types of phase equilibrium.

Comparison of the Present Algorithm with the KZ Algorithm

The system Φ (Eq. (*17*)) solved in the chemical equilibrium calculations of our algorithm consists of M non-linear equations as compared to the system of Eqs (*13*) and (*14*), solved by Xiao *et al.*[10], which contains $M + N$ non-linear equations. The corresponding Jacobian in the former case is of dimension ($\boldsymbol{M} \times \boldsymbol{M}$) while in the latter case – ($\boldsymbol{M} + \boldsymbol{N}$) × ($\boldsymbol{M} + \boldsymbol{N}$).

It is a well-recognized fact that the CPU time required to solve any system of non-linear equations increases exponentially with increasing number of its variables[12]. The present algorithm, in addition to the system Φ, calculates only N linear expressions which practically do not consume any CPU time. Our algorithm thus leads to a considerable decrease in the problem dimension and has a substantial impact on the CPU time consumed by the program in the chemical equilibrium calculations. This positive effect is especially pronounced in case of reacting systems with many components and not too many reactions. For example, if there are two reactions ($M = 2$) and seven components ($N = 7$), a “simplified” rough comparison of the CPU time required by the KZ algorithm and that required by ours (TS) can be presented introducing an “efficiency ratio” ER:

$$\text{ER} = \frac{(\text{CPU})_{\text{KZ}}}{(\text{CPU})_{\text{TS}}} = \frac{\exp(M + N)}{\exp(M)} = \exp(N) = \exp(7) \approx 1\,000 \ . \qquad (19)$$

Thus, in the part where the chemical equilibrium calculations are carried out, the present algorithm is about 1 000 times more efficient than that of Xiao *et al.*[10] provided any preliminary information is not available. However, if there is some information, for example a good starting point for the corresponding algorithm, then the ER will be reduced as shown in the test examples.

In our case an additional advantage arises from the possibility of using the Newton method to solve system Φ (Eq. (*17*)). Xiao *et al.*[10] use a modified Marquardt method to solve Eqs (*13*) and (*14*) without giving any particular reasons why they have decided to do that. Two things have to be taken into consideration: Firstly that any method from the Levenberg–Marquardt class is used exclusively in the cases when the condition for the positive definiteness of the Jacobian of the system to be solved is not satisfied, and secondly that in such cases the Newton method does not converge. Therefore it might be accepted with a high degree of certainty that Xiao *et al.* are forced to use that method because the Jacobian of their system (Eqs (*13*) and (*14*)) demonstrates the above characteristics.

If a more refined analysis of the efficiency of the two algorithms is carried out, then the following should be considered as well: It is obvious that the set of non-linear equations solved in the present case (Eqs (*17*)) differs in form from the set of non-linear equations solved by Xiao *et al.* The structure of Eqs (*17*) could eventually result in:

a) exhibiting more complex solution space than the original set (*e.g.* changing the number of its solutions) and

b) increasing the computational efforts and respectively the computational time to find the true solution.

The first effect will not be observed since the transformation of Eq. (*11*) to Eq. (*17*), namely taking the logarithm and then introducing on two subsequent steps two linear functions (firstly Eq. (*6*) into Eq. (*15*) and secondly Eq. (*3*) into Eq. (*16*)), will not lead to a change in the number of its solutions since the logarithm and the linear functions are monotonous.

With regard to the numerical efforts and the computational time required to find the true solution of Eqs (*17*) and Eqs (*13*) and (*14*), respectively, we present a detailed comparison of the two algorithms on the basis of the number of multiplication operations required and carried out by a computer on a single iteration step from only one known set of initial estimates. This approach is recommended in a number of books on numerical methods as being better and more reliable than CPU time comparison (see for example Fletcher[12]). The following must be taken into account: one division operation is equal approximately to 24 and one logarithm – to 52 multiplications.

The total number of multiplication operations on one iteration step consists of three components:

a) Operations required to calculate the expressions constituting the corresponding non-linear system,

b) operations required to calculate the Jacobian, corresponding to each of the systems and,

c) operations required by the numerical method applied to find the true solution.

Ad *a*) To calculate the corresponding expressions, constituting Eqs (*13*) and (*14*), the KZ algorithm requires approximately: $M + 2MN + M \sum_{i=1}^{N} \sum_{j=1}^{M} |\nu_{ij}|$ multiplications and M divisions or approximately $M + 2MN + M \sum_{i=1}^{N} \sum_{j=1}^{M} |\nu_{ij}| + 24M$ multiplications.

The TS algorithm requires approximately $2MN$ multiplications plus (N + 2) logarithms or approximately 52(N + 2) + 2MN multiplications for calculating the expressions constituting Eq. (*17*).

Ad *b*) To calculate the Jacobian in the KZ algorithm approximately $MN^3 + 2MN^2 + \sum_{i=1}^{N} \sum_{j=1}^{M} |\nu_{ij}|$ multiplications plus (M + N) divisions are required or approximately $MN^3 + 2MN^2 + \sum_{i=1}^{N} \sum_{j=1}^{M} |\nu_{ij}| + 24(M + N)$ multiplications.

To calculate the Jacobian in the TS algorithm, approximately M^2N multiplications and N divisions are required or approximately $M^2N + 24N$ multiplications.

Ad *c*) The modified Levenberg–Marquardt method[10] requires on one iteration approximately: $(M + N)^4 + 2(M + N)^2$ multiplications plus (M + N) divisions or approximately $(M + N)^4 + 2(M + N)^2 + 24(M + N)$ multiplications.

The Newton method requires approximately: M^3 multiplications plus M divisions or approximately $M^3 + 24M$ multiplications.

Two additional advantages of the present TS method, not reflected in the above comparison, have to be taken into account as well. The first arises from the fact that the number of iterations required by the Levenberg–Marquardt method are always more than or equal to that required by the Newton method to find the correct solution of a given system of non-linear equations. The second is connected with the assumption of using a good of set of starting points for an alogorithm to find the solution of a systems of non-linear non-convex functions in the radius of convergence for the corresponding numerical method (see Results and Discussion).

Thermodynamic Model

Different strategies can be utilized in the flash calculations depending on the thermodynamic model. In the present paper, the Redlich–Kwong–Soave (RKS) cubic equation of state (EOS) is used as the thermodynamic model of all phases. However, the mixing rule is given by:

$$q_1(\beta_{\text{mix}} - \sum_{i=1}^{N} z_i\, \beta_{ij}) + q_2(\beta_{\text{mix}}^2 - \sum_{i=1}^{N} z_i\, \beta_{ij}^2) = \frac{g^{\mathrm{E}^*}}{\boldsymbol{R}T} + \sum_{i=1}^{N} z_i \ln\left(\frac{b}{b_{ij}}\right) \qquad (20)$$

which is the modified Huron–Vidal second-order (MHV2) mixing rule. The recommended values of q_1 and q_2 are –0.478 and –0.0047, as recommended by Dahl and Michelsen[13].

The expression for the fugacity coefficient derived from the MHV2 mixing rule is:

$$\ln \varphi_i = \ln \left[\frac{\boldsymbol{R}T}{P(v-b)} \right] + \left[\frac{1}{v-b} - \frac{\beta}{v+b} \right] b_{ii} - \ln \left(\frac{v+b}{v} \right) \left[\frac{\partial (n\beta)}{\partial n_i} \right]_{T,n_j} \quad . \qquad (21)$$

Any appropriate model for the excess Gibbs energy g^{E^*} can be used in connection with the mixing rule. The present study implements the modified UNIFAC (ref.[14]).

RESULTS AND DISCUSSION

In this section, the proposed new algorithm is applied to three CPE problems, the first two of which have been extensively discussed in the literature. The purpose is to test the performance of the TS algorithm and compare its efficiency to that of the KZ algorithm. The results will not be compared with published data of other authors since this information concerns the reliability of the thermodynamic model rather than the efficiency of the algorithm applied.

Example 1: Ethanol–Acetic Acid Reaction LV Equilibria

An equimolar mixture of ethanol and acetic acid reacts reversibly according to the following esterification reaction[10]

$$\mathrm{EtOH + HAc \leftrightarrow EtAc + H_2O} \quad . \qquad (A)$$

This simultaneous CPE problem is studied at T = 355 K and P = 0.1013 MPa. The MHV2 is used as the thermodynamic model of the liquid and vapour phases. The reaction equilibrium constant is calculated as suggested by Stull *et al.*[15].

The results obtained in this study are presented in Table I. Table II lists the number of multiplication operations required by the KZ and TS algorithms on one iteration step and from a known starting point. The TS algorithm requires approximately 3 times less multiplication operations than the KZ algorithm when there is one reaction (M = 1) and four components (N = 4).

Example 2: Methanol Synthesis

$$\mathrm{CO + 2\,H_2 \leftrightarrow CH_3OH} \ , \qquad (B)$$

$$\mathrm{CO_2 + H_2 \leftrightarrow CO + H_2O} \ . \qquad (C)$$

The methanol synthesis reaction is studied at $T = 473.15$ K and $P = 10.13$ MPa. In order to illustrate the performance of the new algorithm in CPE three-phase LLV calculations, the synthesis reaction takes place in the presence of a large amount of an inert heavy oil which, as suggested in refs[9,16], is modelled as n-octadecane $C_{18}H_{38}$. The values for the equilibrium constants of reaction (*B*) and (*C*) are calculated from the expressions suggested by Bissett[17] and Cherednichenko[18] which determine Kr_i to be a function of temperature as follows:

$$Kr_B = 9.740 \,.\, 10^{-5} \exp\left[21.225 + \frac{9\,143.6}{T} - 7.492 \ln T + 4.076 \,.\, 10^{-3} T - 7.161 \,.\, 10^{-8} T^2\right] , \qquad (22)$$

TABLE I
Equilibrium phase compositions (in mole fractions) for the esterification reaction (Eq. (*A*)) at $T = 355$ K and $P = 0.1013$ MPa

Component	Feed	Liquid phase	Vapour phase
EtOH	0.5	0.1472	0.1910
HAc	0.5	0.2673	0.0593
EtAc	–	0.2192	0.4555
H_2O	–	0.3663	0.2941

Phase split and extent of reaction calculated by the TS algorithm: $\alpha = 0.477$; $\xi = 0.3318$.

TABLE II
Number of multiplication operations required to find the true solution of the esterification problem by the KZ and TS algorithms

Step	Algorithm	
	KZ	TS
a	39	268
b	240	100
c	995	25
Total	1 274	393

$$Kr_C = \exp\left[13.148 - \frac{5\,639.5}{T} - 1.077 \ln T + 5.44\,.\,10^{-4}T + 1.125\,.\,10^{-7}T^2 + \frac{49\,170}{T^2}\right]\,. \qquad (22a)$$

The thermodynamic model applied is the MHV2 model. The parameters between the modified UNIFAC groups and the corresponding gases are those given by Dahl *et al.*[19].

The obtained results are presented in Table III while the comparison of the number of multiplication operations required by the KZ and TS algorithms on one iteration step is given in Table IV. For one iteration step and from a known starting point, the TS algorithm requires approximately 13 times less multiplication operations than the KZ algorithm when there are two reactions (M = 2) and seven components (N = 7).

TABLE III
Equilibrium phase compositions (in mole fractions) for the methanol synthesis (Eqs (*B*), (*C*)) in the presence of a heavy hydrocarbon $C_{18}H_{38}$ at T = 473.15 K and P = 10.13 MPa

Component	Feed	Water-rich phase (L_1)	$C_{18}H_{38}$-rich phase (L_2)	Vapour phase
CO	0.1071	traces	$3\,.\,10^{-6}$	$3\,.\,10^{-5}$
H_2	0.5286	0.0071	0.06	0.5328
CO_2	0.0571	traces	traces	traces
CH_3OH	–	0.2871	0.1418	0.2275
H_2O	0.2143	0.7046	0.0070	0.1635
CH_4	0.0214	0.0011	0.0210	0.0752
$C_{18}H_{38}$	0.0715	traces	0.7702	0.0010

Phase splits and extents of the reactions calculated by the TS algorithm: α_1 = 0.4843; α_2 = 0.3780; ξ_1 = 0.1642; ξ_2 = 0.057.

TABLE IV
Number of multiplication operations required to find the correct solution for the methanol synthesis problem by the KZ and TS algorithms

Step	Algorithm	
	KZ	TS
a	98	496
b	1 108	196
c	8 235	56
Total	9 441	748

Example 3: m-Xylene Butylation

m-Xylene (MX) reacts preferentially with di-*tert*-butylbenzene (DTBB) or *tert*-butylbenzene (TBB) to produce *tert*-butyl-*m*-xylene (TBMX) and benzene (BZ), according to the following reactions:

$$\text{DTBB} + \text{MX} \leftrightarrow \text{TBMX} + \text{TBB} \tag{D}$$

$$\text{TBB} + \text{MX} \leftrightarrow \text{TBMX} + \text{BZ} \quad . \tag{E}$$

These reactions are used to separate the close boiling *m*- and *p*-xylenes, because the resulting butylated product can be easily removed due to its heavy molecular weight. The values for the equilibrium constants of reactions (*D*) and (*E*) are assumed to be $Kr_D = 0.6$ and $Kr_E = 0.16$, as suggested by Venkataraman *et al.*[20].

The results of the CPE calculations for $T = 346$ K and $P = 6.87$ kPa are presented in Table V. The TS algorithm requires approximately 6.7 times less multiplication operations than the KZ algorithm in case of two reactions ($M = 2$) and six components ($N = 6$).

CONCLUSIONS

The presented algorithm for simultaneous CPE calculations is general by nature and can be used with any of the available and appropriate thermodynamic models. It is robust and demonstrates good convergence qualities even if the initial estimates of the required variables are not in a close proximity of the solution. In addition, it is ex-

TABLE V
Equilibrium phase compositions (in mole fractions) for the *m*-xylene butylation reactions (Eqs (*D*), (*E*)) in the presence of *p*-xylene at $T = 346$ K and $P = 6.87$ kPa

Component	Feed	Liquid phase	Vapour phase
MX	0.3405	0.0008	0.0012
PX	0.3839	0.3045	0.4890
TBB	0.0586	0.0061	0.0044
DTBB	0.2170	0.1252	0.0059
TBMX	–	0.5282	0.0899
BZ	–	0.0352	0.4096

Phase split and extents of the reactions calculated by the TS algorithm: $\alpha = 0.4305$; $\xi_1 = 0.1431$; $\xi_2 = 0.1964$.

tremely efficient from a computational point of view, especially in its chemical equilibrium calculation part. The algorithm is completely reliable and can be successfully implemented in a process simulator for modelling and design of processes characterized with simultaneous chemical and phase equilibria of reacting strongly non-ideal systems.

SYMBOLS

a	cubic EOS mixture parameter, kPa m^6 mol^{-2}
A_i	chemical species *i*
b	van der Waals volume, m^3 mol^{-1}
f_i^0	fugacity of component *i* in reference state, kPa
f_i	fugacity of component *i* in mixture, kPa
F_i^{in}	initial amount of species *i*, mol
F_i^{out}	final amount of species *i*, mol
G	Gibbs free energy, J
G_i^0	standard Gibbs free energy of formation of species *i*, J
ΔG_j^0	standard Gibbs free energy change of reaction *j*, J
g^{E^*}	excess Gibbs energy, J mol^{-1}
Kr_j	chemical equilibrium constant for reaction *j*, Eq. (*4*)
Kz_j	constant for reaction *j* defined by Eqs (*11*), (*12*)
K_i	*K*-value for component *i*
$K_{\max}$	the maximum *K*-value (among all) at equilibrium
$K_{\min}$	the minimum *K*-value (among all) at equilibrium
M	number of independent chemical reactions
n	number of moles
N	number of components in reacting system
P	pressure, kPa
q_1, q_2	constants, Eq. (*20*)
$\boldsymbol{R}$	gas constant, kPa m^3 mol^{-1} K^{-1}
$S(\alpha)$	error function, Eq. (*9*)
T	temperature, K
v	mixture molar volume, m^3 mol^{-1}
x_i	mole fraction of species *i* in liquid phase
y_i	mole fraction of species *i* in vapour phase
z_i	mole fraction of species *i* in entire system
α	phase split, Eqs (*7*), (*9*)
$\beta = a/b\boldsymbol{R}T$	equation of state mixture parameter, Eqs (*20*), (*21*)
φ_i	fugacity coefficient, component *i*
Φ	system of *M* equations, Eq. (*17*)
μ_i^*	chemical potential of component *i* at equilibrium, J
μ_i^0	chemical potential of component *i* in reference state
ν_i	stoichiometric coefficient of component *i* in single reaction
ν_{ij}	stoichiometric coefficient of component *i* in reaction *j*
ξ_j	extent of reaction *j*, mol
Abbreviations	
BZ	benzene

DTBB	di-*tert*-butylbenzene
ER	efficiency ratio, Eq. (*19*)
EtAc	ethyl acetate
EtOH	ethanol
HAc	acetic acid
L	liquid phase
LV	liquid–vapour system
LLV	liquid–liquid–vapour system
MX	*m*-xylene
PX	*p*-xylene
TBB	*tert*-butylbenzene
TBMX	*tert*-butyl-*m*-xylene
Superscripts	
E	excess
in	initial
L	liquid phase
new	value of variable obtained at current iteration
old	value of variable obtained at previous iteration
out	final
V	vapour phase
Subscripts	
c	critical value
i	component index, $i = 1, 2, \dots$
j	reaction index, $j = 1, 2, \dots$
ii	corresponding to pure component
KZ	corresponding to KZ algorithm, ref.[10]
max	corresponding to maximum value
min	corresponding to minimum value
mix	corresponding to mixture
TS	corresponding to present algorithm
1	corresponding to first liquid phase in LLV system
2	corresponding to second phase in LLV system

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