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MODELLING OF A DYNAMIC MULTIPHASE FLASH: THE POSITIVE FLASH. APPLICATION TO THE CALCULATION OF TERNARY DIAGRAMS.

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ABSTRACT

A general and polyvalent model for the dynamic simulation of a vapor, liquid, liquid-liquid, vapor-liquid or vapor-liquid-liquid stage is proposed. This model is based on the τ -method introduced as a minimization problem by Han & Rangaiah (1998) for steady-state simulation. They suggested modifying the mole fraction summation such that the same set of governing equations becomes valid for all phase regions. Thanks to judicious additional switch equations, the τ -formulation is extended to dynamic simulation and the minimization problem is transformed into a set of differential algebraic equations (DAE). Validation of the model consists in testing its capacity to overcome phase number changes and to be able to solve several problems with the same set of equations: calculation of heterogeneous residue curves, azeotropic points and distillation boundaries in ternary diagrams.

Topical Heading

Process System Engineering

Keywords

Distillation, Dynamic simulation, Phase Equilibrium

INTRODUCTION

In recent years, dynamic simulation has become a valuable and efficient tool for plant design, analysis and operation. Besides, many chemical processes like batch distillation columns or evaporators or continuous distillation column involve phase equilibrium that may lead to the formation of a new phase or to the disappearance of an existing one because of composition, pressure or temperature changes. Such issues are particularly significant for the study of distillation column start up and shut down and of heterogeneous azeotropic distillation column where "... the interface between trays having one and two liquid phase(s) moves in response to disturbances (Widagdo and Seider, 1996)". To detect, handle and manage phase pattern changes in phase equilibrium related dynamic processes, reliable dynamic models are required. As summarized in a review on azeotropic distillation by Widagdo and Seider (1996), "it is important to accurately compute the phase distributions when performing dynamic simulation for heterogeneous azeotropic distillations.". Today, two kinds of approaches are usually proposed, namely the equation solving approach and the global stability analysis (Müller and Marquardt, 1997) which combined search of the number of coexisting phases and solving of the relevant set of equations. But the aim of the paper is to present an alternative approach, furthermore a dynamic one, namely a formulation of a flash able to handle any phase configuration: one (vapor or liquid), two (liquid – liquid or vapor – liquid) or three (vapor – liquid – liquid) with the same single set of equations and without a systematic phase pattern investigation.

First, we review briefly the two existing approaches and also former concepts that led us to the presented formulation. Then, we introduce the "positive flash" modelling which is an adaptation of an equation solving approach to dynamic simulation. Third, we validate the model by evaluating its capacity to handle phase number changes (scenario 1) and by addressing practical problems linked to the assessment of distillation feasibility: the computation of residue curves maps for homogeneous and heterogeneous systems (scenario 2). Further implementation in a heterogeneous dynamic simulator is in progress but out of scope of this contribution.

CALCULATION APPROACHES FOR VAPOR – LIQUID – LIQUID MIXTURE EQUILIBRIUM CALCULATIONS.

Equation solving approaches

The equation solving approach consists in performing a stability test to know the number of phases and in solving a set of non-linear algebraic equations deduced from mass balances and equilibrium relations. This can be done either simultaneously using two imbricated loops or sequentially. As the number of phases changes, so does the set of equations used and such a switching poses serious problems for the integration methods used because the number of equations and of unknown variables change and discontinuities arise (Widagdo and Seider, 1996). More specifically, equation solving approaches use physical insights of the multiphase equilibrium to speed up their calculation. They rely on necessary equilibrium conditions for the different phase combinations. These necessary conditions can be variously formulated as fugacity-equality conditions (Withson and Michelsen, 1989), isoactivity conditions (Cairns and Furzer, 1990b) or as equilibrium conditions in term of K-values (Eckert and Kubicek, 1994). Equation solving methods usually require reasonable computational demand makes them suitable for implementation in a dynamic simulation model of processes based on phase equilibrium (Muller and Marquardt, 1997). Yet, as the number of phase is not known in advance, it is tricky to select the phase number relevant set of equations that is to be solved and numerical problem difficulties may occur due to non-smooth problems or pseudo solutions (Buzzi Ferraris and Morbidelli, 1981, 1982 ; Bullard and Biegler, 1993). To overcome this difficulty, equation-solving method usually involve two sequential or imbricated loops : first the determination of the number and type of coexisting phases relying on a stability test like the tangent plane criterion (Baker et al., 1981, Michelsen, 1982a, 1982b, Cairn and Fürzer, 1990a, 1990b, Gupta et al., 1991, Widagdo et al., 1992, Sun and Seider, 1995 ; Jalali and Seader, 2000) and second, the calculation of phases composition and ratio solving the correct set of governing equations. For more than two coexisting phases like liquid-liquid-vapor equilibria, these two loops may be repeated several times until the correct phase configuration is found. Bullard and Biegler, (1993) considered at that time that the back and forth stability calculation for multiphase equilibria was not very suitable within equation-oriented simulation programs.

Global stability analysis

Approaches based upon a global stability analysis determine the equilibrium solution corresponding to the global minimum of the Gibbs free energy: a non linear optimization method is implemented so as to minimize the Gibbs free energy of an unknown number of phases (Castillo and Grossmann, 1981,

Soares et al., 1982, Mac Donald and Floudas, 1995, 1997, Jalali and Seader, 2000). This approach is known to present the most accurate results but requires a large computational demand.

To perform dynamic simulation, both equation solving and global stability analysis approaches require two calculation loops; phase number calculation one and equation solving one; to be associated to a dynamic set of equations adapted to the appropriate number of phases. Our approach does not necessitate these two loops: the positive flash model is formulated below so as to handle any number of phases during dynamic simulations. With the limitation, and its solution pointed below, of the existence of trivial solution far away from the boundary between one or two liquid phases, at no point during the simulation is the number of coexisting phases calculated independently. Appearance or disappearance of a phase occurs as a discrete event during the solving of the set of equations. Furthermore, as a single set of equations is kept and the same number of unknown variables is used whatever the number of phase (one; Vapor or Liquid, two; VL or LL or three; VLL), the model can be easily integrated as an existing DAE solver is used without any particular modification or tuning. In the literature, papers about models for the dynamic simulation of vapor – liquid – liquid trays have expressed the need to devise an efficient solving strategy and algorithms have been shown (Rovaglio and Doherty, 1990: a sparse Gear method, Wong et al., 1991: a Runge Kutta method, Widagdo et al., 1992, a Gear method and Perregaard et al., 1992: several methods including Backward Differentiation Formula method for stiff problems). Finally initialization and reinitialization of the model; another significant problem of dynamic simulation of heteroazeotropic distillation is discussed in detail in the paper.

CONCEPTS LEADING TO THE "POSITIVE FLASH" MODELLING

The “negative flash”

An approach called the “negative flash” in which the vapor – liquid phase split ratio is allowed to take a value outside the physical domain range was introduced (Neoschil and Chambrette, 1978; Withson and Michelsen, 1989). Later, this formulation was extended to liquid – liquid dynamic equilibrium (Heinichen, 1994). The resolution of this model leads to a successful solution whatever the phase region (L or LL) as the set of equation is kept unchanged: If the phase split α takes a value between 0 and 1, two liquid phases exist. Otherwise, if α leaves the physical range, the set of equations remains the same but one of the liquid phases is non existent physically. Although this approach leads to

interesting results, problems may occur due to the absence of solutions or the existence of multiple ones (Müller and Marquardt, 1997).

The Ratchford-Rice equation for multiphase systems

To obtain a model consistent whatever the phase configuration, Michelsen (1994) formulated a general constrained optimization problem. The objective function is deduced from material balances, equilibrium and summation equations and includes variables defining the mole fraction and the molar amount of each phase. The latter are limited to the physical range. Later, Neoschil and Leibovici (1992, 1995) addressed the same concept as an unconstrained problem in which phase amounts may lie outside the physical domain. With this approach, the phase configuration may easily and efficiently be deduced from the solution of a set of non-linear equations solved using a Newton Raphson algorithm. Both approaches are very useful for performing oil or gas reservoir simulations with equation of state thermodynamics where millions of isothermal flash calculations are needed. For such an application, the fugacities and activity coefficients are assumed to be composition independent and the equilibrium constants values are known. Both approaches are non-dynamic formulations that enable the disappearance of any number of phases during the process of finding the solution. So far, these approaches are not extended to dynamic simulation of phase appearance or disappearance and to problems where activity coefficients are used instead of equation of state thermodynamics.

The τ -method

The τ -method proposes an alternative approach. It is a steady state model for the computation of phase equilibrium derived by Han and Rangaiah (1998) that exploits the fact that the mole fraction summation of a non-existent phase is less than unity. Consequently, to deal with all possible regions in multiphase systems, a new variable denoted τ is defined for each phase and is used to modify the mole fraction summation. If the phase exists, the pseudo phase variable τ is equal to 0; on the contrary if the phase is non-existent, τ takes a value between 0 and 1. Consider the n^{th} adiabatic three-phase stage with n_c components as illustrated on figure 1. The relevant equations for modeling the VLL equilibrium in steady state are (Han and Rangaiah, 1998):

Mass Balances ($i=1, \dots, n_c$):

$$F_n + V_{n-1} + L_{n+1}^{\text{II}} + L_{n+1}^{\text{I}} - V_n - L_n^{\text{I}} - L_n^{\text{II}} = 0 \quad (1)$$

$$F_n z_{n,i} + V_{n-1} y_{n-1,i} + L_{n+1}^{\text{II}} x_{n+1,i} + L_{n+1}^{\text{I}} x_{n+1,i}^{\text{I}} - V_n y_{n,i} - L_n^{\text{I}} x_{n,i} - L_n^{\text{II}} x_{n,i}^{\text{II}} = 0 \quad (2)$$

Energy Balance:

$$F_n h_n^{\text{F}} + V_{n-1} H_{n-1} + L_{n+1}^{\text{I}} h_{n+1}^{\text{I}} + L_{n+1}^{\text{II}} h_{n+1}^{\text{II}} - V_n H_n - L_n^{\text{I}} h_n^{\text{I}} - L_n^{\text{II}} h_n^{\text{II}} = 0 \quad (3)$$

Equilibrium relations ($i=1, \dots, nc$):

$$y_{n,i} = K_{n,i}^{\text{I}} x_{n,i}^{\text{I}} \quad (4)$$

$$y_{n,i} = K_{n,i}^{\text{II}} x_{n,i}^{\text{II}} \quad (5)$$

Mole fraction summations:

$$\sum_i^{nc} y_{n,i} + \tau_n^{\text{V}} = 0 \quad (6)$$

$$\sum_i^{nc} x_{n,i}^{\text{I}} + \tau_n^{\text{I}} = 0 \quad (7)$$

$$\sum_i^{nc} x_{n,i}^{\text{II}} + \tau_n^{\text{II}} = 0 \quad (8)$$

Because the resulting model has more unknown variables than equations, it is solved as a minimization problem:

$$\min(\tau_n^{\text{V}} + \tau_n^{\text{I}} + \tau_n^{\text{II}}) \quad (9)$$

subject to the former constraint and to the inequalities:

$$0 \leq x_{i,n}^{\text{I}}, x_{i,n}^{\text{II}}, y_{i,n}, \tau_n^{\text{V}}, \tau_n^{\text{I}}, \tau_n^{\text{II}} \leq 1 \quad (10)$$

$$L_n^{\text{I}}, L_n^{\text{II}}, V_n, T_n \geq 0 \quad (11)$$

The set of equations and the number of unknown variables are kept constant whatever the number of coexisting phases. The efficiency of the τ -method has been illustrated for VL, LL and VLL equilibrium calculations via several examples (Han and Rangaiah, 1998; Shyamsundar and Rangaiah, 2000). Yet, the optimization formulation restricts the model application to steady-state simulations. Nevertheless, a dynamic variant of the τ -method involving a pseudo vapor component has been developed for vapor – liquid dynamic flash calculations (Marci, 2000). It contains an equal number of variables and equations

that can be readily solved using differential algebraic equations (DAE) solvers. In this paper, we extend this dynamic VLE formulation to VLLE systems.

THE POSITIVE FLASH MODELLING

This contribution extends the τ -method to dynamic simulation by adding equations to obtain an equal number of unknown variables and equations. Furthermore, these new equations constrain the pseudo phase variables τ . The resulting model is presented below. It is made of two parts, one that describes the continuous dynamic equations to follow the dynamic evolution of the continuous variables and one that describes the discrete modeling of the phase number switches to cope with changes in the number of coexisting phases.

As suggested in the literature (Rovaglio and Doherty, 1990, Wong et al., 1991, Widagdo et al., 1992), the usual assumptions for dynamic three phases equilibrium modeling have been made:

1. negligible vapor holdup in the mass and energy balance,
2. perfect mixing in the liquid phases,
3. perfect split of the liquid phases,
4. uniform temperature on each tray,
5. negligible heat of mixing,
6. tray outlet vapor and liquid streams are in equilibrium.

The Positive Flash continuous modeling

Considering an n^{th} multiphase tray, equations are:

Mass balance equations ($i=1, nc$):

$$\frac{dU_n^I}{dt} + \frac{dU_n^{II}}{dt} + L_{n+1}^I + L_{n+1}^{II} + V_{n-1} - L_n^I - L_n^{II} - V_n + F_n = 0 \quad (12)$$

$$\frac{dU_n^I x_{n,i}^I}{dt} + \frac{dU_n^{II} x_{n,i}^{II}}{dt} + L_{n+1}^I x_{n+1,i}^I + L_{n+1}^{II} x_{n+1,i}^{II} + V_{n-1} y_{n-1,i} - L_n^I x_{n,i}^I - L_n^{II} x_{n,i}^{II} - V_n y_n + F_n z_{n,i} = 0 \quad (13)$$

Energy balance equation:

$$\begin{aligned} & \frac{dU_n^l h_n^l(T, P, x_n^l)}{dt} + \frac{dU_n^{ll} h_n^{ll}(T, P, x_n^{ll})}{dt} + L_{n+1}^l h_{n+1}^l(T_n, P, x_{n+1}^l) + L_{n+1}^{ll} h_{n+1}^{ll}(T_n, P, x_{n+1}^{ll}) \\ & + V_{n-1} H_{n-1}(T_n, P, y_{n-1}) + F_n H^{Fn} + Q_n - L_n^l h_n^l(T_n, P, x_n^l) - L_n^{ll} h_n^{ll}(T_n, P, x_n^{ll}) - V_n H_n(T_n, P, y_n) = 0 \end{aligned} \quad (14)$$

Equilibrium relations ($i=1, nc$):

$$y_{n,i} = K_{n,i}^l(T_n, P, x_{n,i}^l, y_{n,i}) \cdot x_{n,i}^l \quad (15)$$

$$y_{n,i} = K_{n,i}^{ll}(T_n, P, x_{n,i}^{ll}, y_{n,i}) \cdot x_{n,i}^{ll} \quad (16)$$

Mole fraction summations:

$$\sum_i^{nc} x_{n,i}^l + \tau_n^l - \sum_i^{nc} y_{n,i} - \tau_n^V = 0 \quad (17)$$

$$\sum_i^{nc} x_{n,i}^{ll} + \tau_n^{ll} - \sum_i^{nc} y_{n,i} - \tau_n^V = 0 \quad (18)$$

Model for the liquid Holdups:

$$U_n^l + U_n^{ll} - \text{mod}(U_n) = 0 \quad (19)$$

Relation between the liquid flow rates and the holdups:

$$L_n^l \cdot (U_n^l + U_n^{ll}) - U_n^l \cdot (L_n^l + L_n^{ll}) = 0 \quad (20)$$

Additional equations: Switch equations

$$V_n \cdot \tau_n^V = 0 \quad (21)$$

$$U_n^l \cdot \frac{d(\tau_n^l)}{dt} + \tau_n^l \cdot \frac{d(U_n^l)}{dt} = 0 \quad (22)$$

$$U_n^{ll} \cdot \frac{d(\tau_n^{ll})}{dt} + \tau_n^{ll} \cdot \frac{d(U_n^{ll})}{dt} = 0 \quad (23)$$

Mod U_n means that a model for the total liquid holdup is used (e.g. for tray hydraulic models: Francis weir formula or Mackowiack model (Mackowiack, 1991)). The last three switch equations permit to obtain a system with equal numbers of equations and unknown variables. Furthermore, equation (21) guarantee that either the pseudo-variable τ in the case of an existing phase, or the quantity of the considered phase in the case of a non-existent phase, is equal to 0. Equation (22) and (23) guarantee that either τ_n and its derivative (resp. U_n and its derivative) are equal to zero when the phase exists

(resp. does not exist). Boiling (condensation) phenomena that cause (dis)appearance of the vapor phase is physically well understood: V_n goes rapidly to a large positive value (resp. to zero) when this occurs. But the appearance or disappearance of a liquid phase is less easy to describe physically. In particular, the liquid holdup are likely to display less brutal variations of their magnitude than the vapor does. To us this complies with stricter equations (22) and (23) where the holdup derivative goes smoothly from (or to) zero when a liquid phase (dis)appear.

Both liquid phases are treated symmetrically in the equilibrium and switch equations. The set of $3n_c + 9$ equations and $3n_c + 9$ unknowns ($x_{n,i}^I, x_{n,i}^{II}, y_{n,i}, U_n^I, U_n^{II}, L_n^I, L_n^{II}, V, \tau_n^I, \tau_n^{II}, \tau_n^V, T_n$) can be solved through a DAE solver. H^F, F, z_i, Q_n and P are inputs. Notice that the choice of Q_n and P as inputs is arbitrary. T_n and P can be chosen instead as well. $K_i^I, K_i^{II}, h_i^I, h_i^{II}, H_i$ are non variables provided by appropriate thermodynamic functions. However, an alternative formulation of the model may consider as unknown variables $K_{n,i}^I, K_{n,i}^{II}, h_n^I, h_n^{II}, H_n$. In that case, the following equations are added to keep the system consistent with $5n_c + 12$ equations and unknowns:

$$K_{n,i}^I - \text{mod}(K_{n,i}^I) = 0 \quad (24)$$

$$K_{n,i}^{II} - \text{mod}(K_{n,i}^{II}) = 0 \quad (25)$$

$$h_n^I - \text{mod}(h_n^I) = 0 \quad (26)$$

$$h_n^{II} - \text{mod}(h_n^{II}) = 0 \quad (27)$$

$$H_n - \text{mod}(H_n) = 0 \quad (28)$$

The first modeling requires implementing the thermodynamic functions into the mathematical model subroutine. The second one is more versatile as it enables us to use a thermodynamic interface to a thermodynamic property server. We have used it with the BibPhy thermodynamic library (Prosim, 2000).

The Positive Flash Discrete modeling

The DAE solver DISCO that is used to solve the differential algebraic set of equation is based on a Gear algorithm and is capable of handling index 1 or 2 and sparse sets of equations. It also handles the automatic detection of time or state events and bears an automatic procedure to calculate initial conditions after discontinuities (Sargousse et al., 1999). Indeed, although the model is able to describe all phase configurations, the transition between two configurations leads to discontinuities that

constitute one of the key difficulties of dynamic simulation of heterogeneous azeotropic distillation (Widagdo and Seider, 1996). Consequently, it is necessary to detect the phase transition events and to reinitialize the discontinuous variables accordingly. Figure 2 illustrates through a Finite State Machine, the phase configuration transitions. Each phase configuration of the system (one liquid, one vapor, liquid – vapor, liquid – liquid – vapor) is represented by a state (a circle) and the transitions between these states are triggered by an event. Each event is described by an equation that will take the value zero when the event occurs:

$$G_1 = \text{Flag_vap} \cdot \tau_n^V + (1 - \text{Flag_vap}) \cdot V \quad (29)$$

$$G_2 = \text{Flag_liq1} \cdot \tau_n^I + (1 - \text{Flag_liq1}) \cdot U_n^I \quad (30)$$

$$G_3 = \text{Flag_liq2} \cdot \tau_n^{II} + (1 - \text{Flag_liq2}) \cdot U_n^{II} \quad (31)$$

$$G_4 = U_n^I + U_n^{II} \quad (32)$$

Four kinds of events are related respectively to the four equations above:

- Appearance (Flag_vap=0) or disappearance (Flag_vap=1) of the vapor phase
- Appearance (Flag_liq1=0) or disappearance (Flag_liq1=1) of the liquid I phase
- Appearance (Flag_liq2=0) or disappearance (Flag_liq2=1) of the liquid II phase
- Tray empty or full

Let's take for example, the case of the vapor phase mixture. If we are initially below the mixture boiling temperature, no vapor exists ($V = 0$), $\text{Flag_vap} = 1$ and $\tau^V = 0$. When the liquid boils, vapor rises which triggers $\text{Flag_vap} = 0$, $\tau^V = 0$ and $V \neq 0$.

The reinitialization procedure is adapted to the number of phases existing after the phase transition detected. In particular, derivatives of the molar fractions are reinitialized to non zero values, preferably to unity. Liquid holdup derivatives are set to zero to comply with switch equations (22) and (23). If the enthalpies are considered as unknowns as well, their derivatives are also reinitialized. The integration step is also reduced at each reinitialization.

ILLUSTRATIVE EXAMPLES

The use of a dynamic multiphase flash formulation is particularly interesting in the study of distillation processes. During conception and design steps, residue curve maps are thoroughly analyzed to assess distillation feasibility and distillation column sequences; at the simulation level, the dynamic behavior of a distillation column offers insights to its practical operation, startup and shutdown and may exhibit changes in the number of phases in equilibrium on the column trays. In this paper, we validate the model by evaluating its capacity to handle phase pattern changes and by computing residue curves to draw maps for homogeneous and heterogeneous ternary systems as well as to predict azeotropes.

Scenario 1. Detection of phase configuration transitions

In this example, the positive flash model is applied to the dynamic simulation of a vapor – liquid – liquid equilibrium Rayleigh distillation of the water – ethanol – cyclohexane mixture (figure 3). The NRTL thermodynamic model is used with vapor – liquid – liquid binary parameters taken from the DECHEMA (see Table 1) (Gmehling and Onken., 1982). For this system, the model is similar to the former one without equations (19) and (20) related to the holdups. A scenario is described on figure 4. Two key parameters of the process, the heat duty Q and the pure ethanol feed flow rate F_{ethanol} , are sequentially modified to trigger off the apparition or the disappearance of one of the phases:

- First, the mixture is heated at a constant rate from its initial liquid – liquid state until it boils and enters the vapor – liquid – liquid region.
- Further heating removes a vapor rich in ethanol that moves the mixture composition across the vapor – liquid – liquid boiling envelope and settles it in the vapor – liquid region.
- Then, the heat duty is reduced until vapor condenses once the mixture temperature reaches the boiling temperature. Further cooling causes the apparition of a second liquid phase.
- Finally, pure ethanol is added to the mixture to make disappear the aqueous liquid phase.

As illustrated in figure 5, this scenario permits to test the LL/VLL, VLL/VL, VL/L, L/LL and LL/L transitions. At the transitions, the unknown variables which present discontinuities are reinitialized (e.g. the vapor flow rate V for the LL / VLL transition). As can be seen on figure 5, whenever a phase disappears, its corresponding τ value becomes strictly positive: At the beginning, the vapor phase does not exist then its corresponding τ^V value is positive. τ^V becomes zero when the two liquid phases

mixture boils up while V becomes positive. This event is triggered by equation (29) meanwhile the switch equation (21) is always valid. The vapor flow rate V and its derivatives show discontinuities and are reinitialized accordingly. While heating is continued, the mixture composition moves away and exits the VLL region as the phase II disappear: U^{II} becomes zero and τ^{II} becomes positive. Then the mixture is cooled down until the vapor is totally condensed to leave a single liquid phase I: V becomes zero and τ^V becomes positive. Cooling proceeds, forcing the composition to enter again the two liquid phase region: U^{II} becomes positive and τ^{II} equals zero. Finally, ethanol is added to exit the LLE region and end with a single liquid mixture. Liquid phase numbering is not known in advance. It is a result of the calculation.

Two comments are worthy: first, any phase pattern change is readily assessed without any need to implement a phase stability test; second, the number of unknown variables and equations of the models remains the same whatever the phase number configuration.

Scenario 2. Solving the initialization problem.

In scenario 1, the initial mixture composition is in the liquid – liquid equilibrium region. The positive flash model readily finds correctly that two phases coexists and that the pseudo phase variable τ^I and τ^{II} equals zero. However, further tests showed that in most of the vapor – liquid region, the most attractive solution is not a solution where one of the liquid phases has disappeared and the corresponding pseudo phase variable τ has some positive value. It is rather the so-called 'trivial solution': both liquid phases have equal compositions and both τ^I and τ^{II} equals zero. This readily makes the two equilibrium (equations (15) and (16)) and the two liquid switch (equations (22) and (23)) equations identical two by two and the set of equations looks like a usual VLE dynamic model.. This is annoying because once it is found by the DAE solver, the trivial solution is always found even if the composition may move into the vapor – liquid – liquid region. In that case, the mixture behaves in the whole composition simplex as a one vapor – one liquid system: residue curves, azeotropic points and distillation boundaries are not computed accurately which may lead to an erroneous assessment of the distillation process conception and design.

Such a problem was already been pointed out by Han and Rangaiah (1998). It has also been known to occur in equilibrium calculation problems where phases are treated symmetrically, for example using identical equation of states for both phases (Ferraris and Morbidelli, 1981, 1982). The general

formulation of the positive flash model falls into this category: the model is perfectly symmetrical concerning the two liquid phases and the trivial solution seems to be the most attractive one. Another possible explanation for this problem could also reside in the absence of physical meaning we attribute to the liquid τ values. Indeed, a positive τ^V value can always be assimilated to an incondensable (e.g. air) composition that resides above any liquid or liquid – liquid state mixture in consideration. On the other hand, a positive τ^I or τ^{II} value could be assimilated to a non volatile component (e.g. coke) unable to be involved in a liquid – liquid equilibrium. Yet, although the presence of a pseudo-vapor phase above a liquid phase is conceivable, the continuous existence of a second pseudo liquid phase remains difficult to imagine if coke is not present initially.

To overcome the problem a method that is able to provide the system with initial values of the liquid τ variables when one comes close to a VLLE region is needed. An adaptation of the τ method is the ideal initialization method candidate as it does consider liquid τ variables. As we do not know beforehand whether there is a VLLE region and where it is eventually located, we have to solve with each step of integration a modified τ method to make sure that one is not near or in a VLLE region until a positive pseudo phase τ variable value is found. As in Han and Rangaiah (1998). an Iterative Linear Programming method to solve the τ method. The ILP method can handle inequality constraints and uses Newton Raphson method concepts as it is quadratically convergent towards the solution (Llovel 2002).

The modified τ method set of equations that we solve to check any occurrence of a non trivial solution bears some modifications compared to the τ method equations written in the first section: for the purpose of residue curve calculations, the vapor phase is supposed to always exist. The initial mixture temperature is then set at its boiling point. The equations become:

$$\min(\tau_n^I + \tau_n^{II}) \quad (33)$$

$$U_n^{\text{Total}} = U_n^I + U_n^{II} \quad (34)$$

$$U_n^{\text{Total}} \cdot x_i^{\text{Total}} = U_n^I \cdot x_{n,i}^I + U_n^{II} \cdot x_{n,i}^{II} \quad i = 1, \dots, nc \quad (35)$$

$$y_{n,i} = K_{n,i}^I(P, T_n, x_{n,i}^I, y_{n,i}) \cdot x_{n,i}^I \quad i = 1, \dots, nc \quad (36)$$

$$y_{n,i} = K_{n,i}^{II}(P, T_n, x_{n,i}^{II}, y_{n,i}) \cdot x_{n,i}^{II} \quad i = 1, \dots, nc \quad (37)$$

$$\sum_{i=1}^{nc} x_{n,i}^I + \tau_n^I = 1 \quad (38)$$

$$\sum_{i=1}^{nc} x_{n,i}^II + \tau_n^{II} = 1 \quad (39)$$

$$\sum_{i=1}^{nc} y_{n,i} = 1 \quad (40)$$

with the constraints:

$$0 \leq U_n^I, U_n^{II} \quad (41)$$

$$0 \leq x_{n,i}^I, x_{n,i}^{II}, y_{n,i}, \tau_n^I, \tau_n^{II} \leq 1 \quad (42)$$

The combination of the modified τ method VLL flash calculation and of the dynamic positive flash formulation tempers our initial ambition of developing a single model suitable for any phase regions. But it performs quite well and consists of an efficient alternative to phase stability VLL equilibrium models usually implemented in distillation column dynamic simulators: the positive flash model handles any phase pattern change as long as it is correctly initialized by the modified τ method.

To illustrate these concepts, scenario 2 is devised for a cyclohexane – water – ethanol mixture. Figure 6 depicts its composition movements on the ternary diagram and Figure 7 shows the evolution of key variables during the scenario. At first, the initial ternary mixture is located in the liquid –vapor region of the cyclohexane – water – ethanol diagram. Then the mixture is cooled and its composition follows a residue curve in the opposite direction towards an unstable node. At some arbitrary point in the vapor – liquid – liquid region, cooling is stopped and water is added to shift the composition. Then the mixture is heated and its composition follows a residue curve ending at the pure water stable node.

At each integration step of the positive flash model until a VLLE region is encountered, the modified τ method is solved to check whether any pseudo phase τ variable has a positive value. From the initial mixture composition of scenario 2, both modified τ method and positive flash converge at the trivial solution until the limit of trivial solution attractiveness region depicted in figure 6 is reached. At this point, the modified τ method finds one positive τ variable (figure 7). This value is then used to initialize the positive flash model solving and convergence is obtained at a non trivial solution. Once a positive τ value is found, the modified τ method is no longer solved and integration of the positive flash model

proceeds normally: at the vapor – liquid – liquid boiling envelope, a VL – VLL transition is triggered like in scenario 1. Integration proceeds into the VLLE region until it is arbitrarily stopped to add water. The resulting mixture is then heated and integration resumes normally: the composition follows a residue curve towards and across the VLLE envelope boundary and the VLL – VL transition is triggered at the VLLE envelope. Again, at some point located on the approximate dotted line (the limit of the trivial solution attractiveness region) on figure 6, the number of iterations required to solve the positive flash model increases exponentially (up to 1000 iterations) until it converges at the trivial solution thanks to the internal reinitialization procedure of the DAE solver DISCo (figure 7). Finally, integration proceeds correctly along the residue curve in the VL region until the mixture composition reaches the water vertex.

Scenario 2 has illustrated the initialization procedure when residue curves are integrated in the reverse way (cooling of the Rayleigh kettle). In the direct integration procedure, the same initialization procedure is implemented as it may happen that a residue curve starting in a VLE region enters a VLLE region for ternary diagrams where a binary heteroazeotrope is a saddle point (e.g. the water – acetonitrile – acrylonitrile diagram shown in figure 8).

Residue curve maps

A residue curve is a trajectory of the liquid composition versus time left in a heated kettle. This is equivalent to a simple distillation process (Rayleigh distillation – figure 3). Residue curves maps are very useful for the feasibility analysis of distillation processes: they enable in particular to display azeotropes and distillation boundaries that make some separations impossible and to hint at column liquid composition profiles in continuous packed distillation towers (Widagdo and Seider, 1996, Kiva et al., 2003). Homogeneous residue curve maps are easy to compute, but residue curve maps for heterogeneous systems that exhibit a vapor – liquid – liquid region are more complicated because the dynamic set of equation must handle phase number changes along the calculation of some residue curves and distillation boundaries are not trivial to compute. A usual solution is to solve a VL flash and run a liquid – liquid stability check at every integration step. When a liquid – liquid split is detected, one shifts to a VLL set of equations. Instead, the “positive flash model” presented here enables to keep a single set of equations along the calculation of a residue curve. For both homogeneous and heterogeneous residue curve maps, starting from an initial mixture composition at boiling temperature, the dynamic set of equations of the positive flash model is integrated in two opposite directions to

calculate a whole residue curve. Direct (resp. inverse) integration corresponds to heating (resp. cooling) the Rayleigh kettle and removes the light (resp. heavy) component and the trajectory moves towards the stable (resp. unstable) node of the basic distillation region. Unlike the heating of the Rayleigh kettle, which corresponds to evaporation, cooling has no physical meaning as it condensates some vapor overhead.

The “positive flash model” set of equations is kept all along the calculation. As stated previously, unless a VLLE region has been encountered, the modified τ method is also solved to detect any non trivial solution. As this happens, the liquid τ values then found are used to reinitialize the positive flash model. Then the τ method is no longer used and the integration resumes. For the purpose of residue curve calculation, the vapor phase existence is assumed beforehand. Then $\tau^V = 0$ and the first call to the modified τ method finds a temperature value equal to the boiling temperature.

For practical purposes, the residue curve computation is stopped when the equality of vapor and liquid compositions in equilibrium is obtained with a given tolerance. In a composition diagram, this condition is satisfied for all singular points (vertexes and azeotropes), and in particular for the unstable and stable nodes that are respectively the starting point and the ending point of residue curves. But it also applies to saddle points to which residue curve may come very close. In order to avoid an unexpected stop at these points, the convergence tolerance is lowered whenever a unary or a binary saddle point is neared during integration.

In addition to residue curves, residue curve maps may display other key features that are the knowledge of all singular points (pure components and azeotropes), their stability within a distillation region (stable – highest boiling point of the region ; unstable – lowest boiling point; saddle – intermediate boiling point) and distillation boundaries existence and curvature (Kiva et al. 2003).

Including all singular points, the topology equation (Zharov and Serafimov 1975, Matsuyama 1977, Doherty and Perkins, 1979, Widagdo and Seider 1996, Kiva et al., 2003) must be verified. The topology equation for ternary mixtures is:

$$2 \cdot N_3 - 2 \cdot S_3 + N_2 - S_2 + N_1 = 2 \quad (38)$$

Where N_3 is the number of ternary node, S_3 the number of ternary saddle points, N_2 the number of binary nodes, S_2 the number of binary saddle points and N_1 the number of pure components nodes.

Methods for the computation of all azeotropes are out of scope of this paper (Widagdo and Seider, 1996; Kiva et al. 2003). In our cases, existing binary azeotropes are first computed, from residue curve calculation on binary mixtures. Their existence is evaluated from the simple following algorithm:

```

For each binary mixture A-B do {
  Evaluate quickly possible azeotropy {
    - Component A being the most volatile, compute  $K_A = \frac{x_A}{y_A}$  at  $x_A \approx 0$ 
    and at  $x_A \approx 1$ 
    - if  $K_A^{x_A \approx 0} > 1$  and  $K_A^{x_A \approx 1} < 1$  then there exists a minimum boiling
    temperature azeotrope
    - if  $K_A^{x_A \approx 0} < 1$  and  $K_A^{x_A \approx 1} > 1$  then there exists a maximum boiling
    temperature azeotrope
    - else no binary azeotrope exists
  }
  Calculate accurately azeotrope composition, type and stability {
    - compute a residue curve (direct integration for maximum boiling
    temperature azeotrope and inverse integration for minimum boiling
    temperature azeotrope). The final point is the binary azeotrope.
  }
}

```

Then unary and binary stability is obtained from an eigenvalue analysis related to the jacobian associated to the dynamic model (Doherty and Perkins, 1978, 1979). Knowing them, the topology equation tells us whether there exists any ternary saddle azeotrope or any ternary unstable azeotrope. If so, the saddle composition and temperature is found from a procedure devised by Doherty and Perkins (1978, 1979) any consisting in successive maximization and minimization along the boiling temperature surface to follow crests and valley towards the saddle points. To find an eventual unstable azeotrope, a residue curve is computed using an inverse integration scheme from an initial composition involving all three components.

Finally, as distillation boundaries have the property of being residue curves, they are computed using information provided by the ternary diagram classification of serafimov (Kiva et al. 2003) as this classification readily indicates from which singular point should a residue curve calculation be started to give a distillation boundary.

This methodology is applied to the automatic computation of several residue curve maps shown on figure 8 with thermodynamic parameters displayed in tables 1 to 3. VLLE envelope is computed

externally through VLLE flash calculation using BibPhyAddIn in an Excel spreadsheet (Prosim, 2000) using the same thermodynamic model and set of binary parameters. VLLE envelope results fully agree with the information on the VLLE envelope found during the integration: compositions at the phase pattern change events and compositions of the two coexisting liquid phases in the VLLE region.

In figure 8a, the well known cyclohexane – water – ethanol diagram is displayed with an unstable ternary heteroazeotrope. Figure 8b shows the chloroform – acetone – methanol diagram which saddle ternary homogeneous azeotrope is found solving the topology equation. Its composition and temperature is the mean of the distillation boundaries end composition computed with the dichotomy procedure explained above. The saddle point temperature and composition maximum deviation is less than 0.1 °C and 0.03 in molar fraction. Such accuracy is far better than for values obtained from flash calculations and boiling temperature maps.

CONCLUSION

A general and polyvalent model for the dynamic simulation of a vapor, liquid, liquid-liquid, vapor-liquid or vapor-liquid-liquid tray is proposed: the positive flash model. It handles any phase pattern changes that may occur in the dynamic simulation of equilibrium distillation columns or during the computation of heterogeneous residue curve maps. Whatever the number of phases, the set of equation and the number of variables is kept unchanged, thanks to pseudo phase variables τ that take a positive value when a phase is not physically existent. Phase number changes are considered as events described by switch equations involving the variables τ . Nevertheless, practical implementation requires using a modification of the τ -method introduced as a minimization problem by Han & Rangaiah (2000) for steady-state simulation. It enables to find initial values of the pseudo phase variables τ suitable for the positive flash model. Validation of the model is showed through testing of its capacity to overcome phase number changes and to compute heterogeneous ternary residue curves maps. Further application will concern the building of a multipurpose distillation column dynamic simulator.

NOMENCLATURE

F	feed flow rate	1	[mol.s ⁻¹]
Flag_liq1	liquid I appearance/disappearance index	1	[-]
Flag_liq2	liquid II appearance/disappearance index	1	[-]

Flag_vap	vapor appearance/disappearance index	1	[-]
H	vapor enthalpy	1	[J.mol ⁻¹]
h ^I	liquid phase I enthalpy	1	[J.mol ⁻¹]
h ^{II}	liquid phase II enthalpy	1	[J.mol ⁻¹]
K _i ^I	vapor – liquid I equilibrium constant vector	nc	[-]
K _i ^{II}	vapor – liquid II equilibrium constant vector	nc	[-]
L ^I	liquid phase I flow rate	1	[mol.s ⁻¹]
L ^{II}	liquid phase I flow rate	1	[mol.s ⁻¹]
LL	liquid – liquid coexisting phases	-	[-]
VLL	vapor – liquid – liquid coexisting phases	-	[-]
VL	vapor – liquid coexisting phases	-	[-]
nc	number of components	1	[-]
P	pressure	1	[Pa]
Q	molar heat	1	[J.mol ⁻¹]
T	temperature	1	[K]
t	time	1	[s]
U ^I	liquid phase I holdup	1	[mol]
U ^{II}	liquid phase II holdup	1	[mol]
V	vapor flow rate	1	[mol.s ⁻¹]
x _i ^I	liquid phase I molar fraction vector	nc	[%]
x _i ^{II}	liquid phase I molar fraction vector	nc	[%]
y _i	vapor molar fraction vector	nc	[%]
z _i	feed molar fraction vector	nc	[%]
Greeks:			
α	phase split	1	[%]
τ ^I	liquid phase I pseudo molar fraction	1	[%]
τ ^{II}	liquid phase II pseudo molar fraction	1	[%]
τ ^V	vapor phase pseudo molar fraction	1	[%]

Subscript:

i component i

n, n-1, n+1 stage n, n-1 or n+1 respectively

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TABLE CAPTION

- Table 1. Thermodynamic model, binary parameters and calculated azeotropic data for the cyclohexane – water – ethanol system.
- Table 2. Thermodynamic model, binary parameters and calculated azeotropic data for the chloroform – acetone – methanol system.
- Table 3. Thermodynamic model, binary parameters and calculated azeotropic data for the acrylonitrile – acetonitrile – water system.

Cyclohexane (Cy) – Water (W) – Ethanol (E) at 1 atm.

temperature dependent NRTL thermodynamic model: $A_{ij,0} + A_{ij,T} \cdot T$; $A_{ji,0} + A_{ji,T} \cdot T$; $\alpha_{ij,0} + \alpha_{ij,T} \cdot T$

Binary interaction parameters	$A_{ij,0}$	$A_{ji,0}$	$\alpha_{ij,0}$	$A_{ij,T}$	$A_{ji,T}$	$\alpha_{ij,T}$
Cy-W	2835	3125	0.274	0	0	0
Cy-E	1390.42	876.793	0.4485	0	0	0
W-E	1616.8	635.56	0.1448	2.0177	0.9907	0

azeotrope	node type	molar fraction		T (°C)		Relative error vs. exp
		calculated	experimental *	calc.	exp.*	
Cy-W	saddle heterogeneous	0.701 / 0.299 / 0.000	0.700 / 0.300 / 0.000	69.4	69.5	0.1%
Cy-E	saddle homogeneous	0.548 / 0.000 / 0.452	0.545 / 0.000 / 0.455	64.7	64.8	0.4%
W-E	saddle homogeneous	0.000 / 0.116 / 0.884	0.000 / 0.107 / 0.893	78.1	78.2	1.2%
Cy-W-E	unstable heterogeneous	0.158 / 0.536 / 0.306	0.167 / 0.527 / 0.306	62.9	62.6	1.3%

* (Gmehling et al., 1994)

Table 1. Thermodynamic model, binary parameters and calculated azeotropic data for the cyclohexane – water – ethanol system.

Chloroform (C) – Acetone (A) – Methanol (M) at 1 atm.

NRTL thermodynamic model: A_{ij} ; A_{ji} ; α_{ij}

Binary interaction parameters		$A_{ij,0}$	$A_{ji,0}$	$\alpha_{ij,0}$	
C-A		228.457	643.277	0.3043	
C-M		2736.860	-1244.030	0.0950	
A-M		184.701	222.645	0.3084	

azeotrope	node type	molar fraction		T (°C)		Relative error vs. exp
		calculated	experimental *	calc.	exp.*	
C-A	stable homogeneous	0.646 / 0.354 / 0.000	0.659 / 0.341 / 0.000	65.1	64.4	1.8%
C-M	unstable homogeneous	0.654 / 0.000 / 0.346	0.650 / 0.000 / 0.350	53.3	53.4	0.6%
A-M	unstable homogeneous	0.000 / 0.787 / 0.213	0.000 / 0.794 / 0.206	55.4	55.5	1.0%
C-A-M	saddle homogeneous	0.207 / 0.373 / 0.420	0.215 / 0.356 / 0.429	57.0	57.5	2.1%

* (Gmehling et al., 1994)

Table 2. Thermodynamic model, binary parameters and calculated azeotropic data for the chloroform – acetone – methanol system.

Acrylonitrile (Acr) – Acetonitrile (Ace) – Water (W) at 1 atm.

NRTL thermodynamic model: A_{ij} ; A_{ji} ; α_{ij}

Binary interaction parameters		$A_{ij,0}$	$A_{ji,0}$	$\alpha_{ij,0}$	
Acr-Ace		-336.251	475.621	0.3042	
Acr-W		584.640	2122.310	0.2960	
Ace-W		364.836	1321.730	0.2858	

azeotrope	node type	molar fraction		T (°C)		Relative error vs. exp
		calculated	experimental *	calc.	exp.*	
Acr-W	unstable heterogeneous	0.684 / 0.000 / 0.316	0.698 / 0.000 / 0.302	71.2	71.0	2.0%
Ace-W	saddle homogeneous	0.000 / 0.675 / 0.325	0.000 / 0.690 / 0.310	76.8	76.5	2.1%

* (Gmehling et al., 1994)

Table 3. Thermodynamic model, binary parameters and calculated azeotropic data for the acrylonitrile – acetonitrile – water system.

FIGURE CAPTION

- Figure 1. Adiabatic vapor – liquid – liquid equilibrium stage for the τ -method
- Figure 2. discrete part of the positive flash model : finite State machine for the phase transitions
- Figure 3. Rayleigh VLLE distillation
- Figure 4. Scenario 1 for the detection of phase transitions
- Figure 5. Evolution of t variables (\blacksquare U^I \blacktriangle U^{II} \diamond U^V) and holdup, vapor flow rate and temperature during simulation of scenario 1 (\square U^I , \circ U^{II} , $*$ U^V)
- Figure 6. Composition path during scenario 2 in the composition ternary diagram
- Figure 7. Evolution of composition and liquid τ variables during scenario 2
- Figure 8. Residue Curve maps

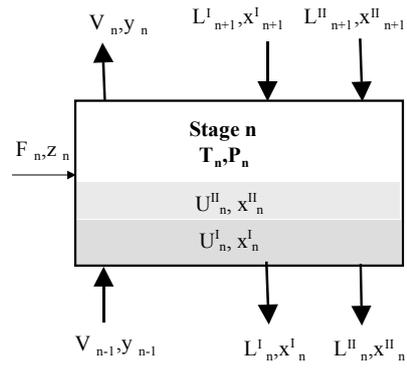


Figure 1. Adiabatic vapor – liquid – liquid equilibrium stage for the τ -method

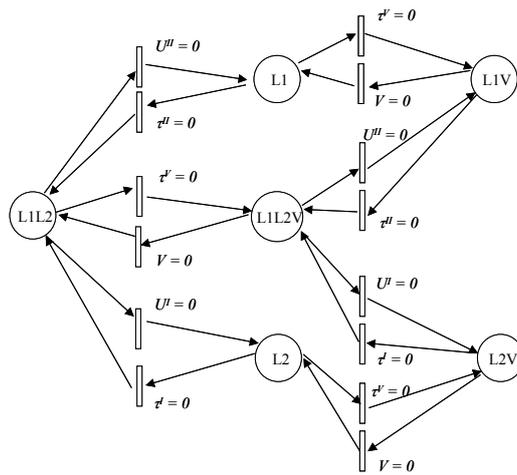


Figure 2. Finite State machine for the phase transitions

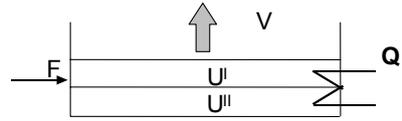


Figure 3. Rayleigh VLE distillation

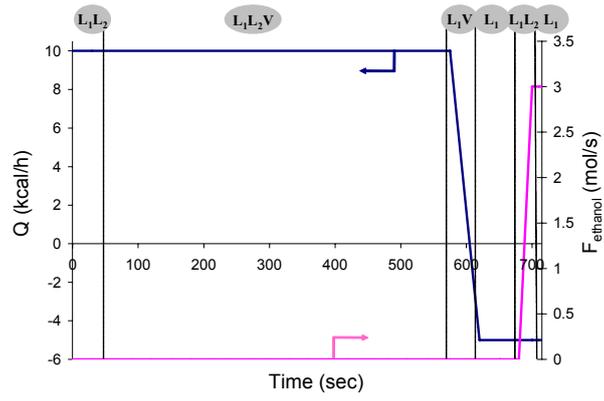


Figure 4. Scenario 1 for the detection of phase transitions

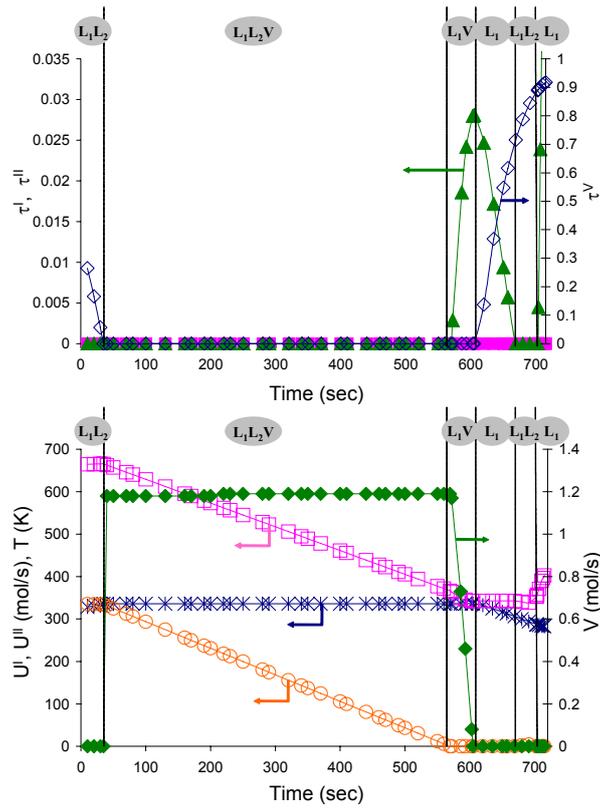


Figure 5. Evolution of τ variables (\blacksquare τ^I \blacktriangle τ^{II} \diamond τ^V) and holdup, vapor flow rate and temperature during simulation of scenario 1 (\square U^I , \circ U^{II} , $*$ T , \blacklozenge V)

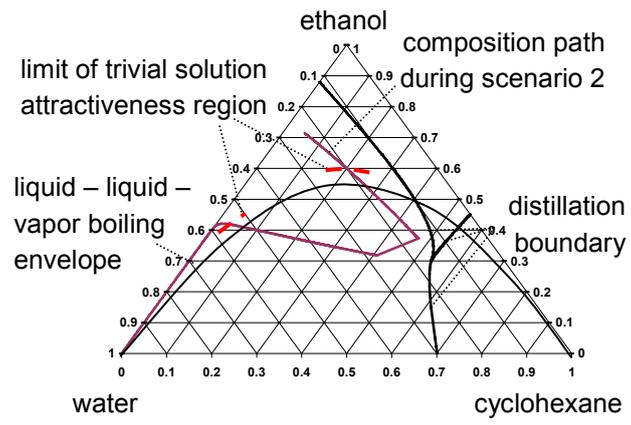


Figure 6. Composition path during scenario 2 in the composition ternary diagram

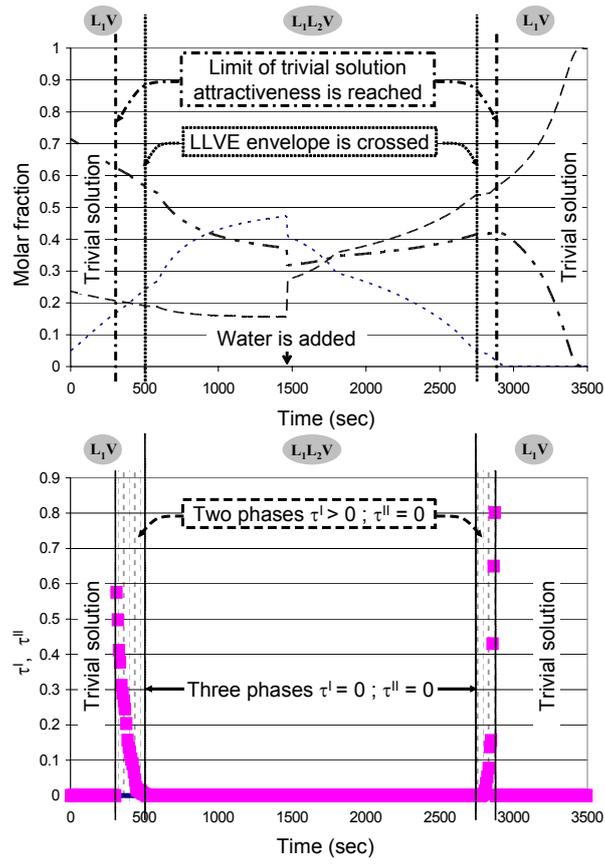


Figure 7. Evolution of composition and liquid τ variables during scenario 2

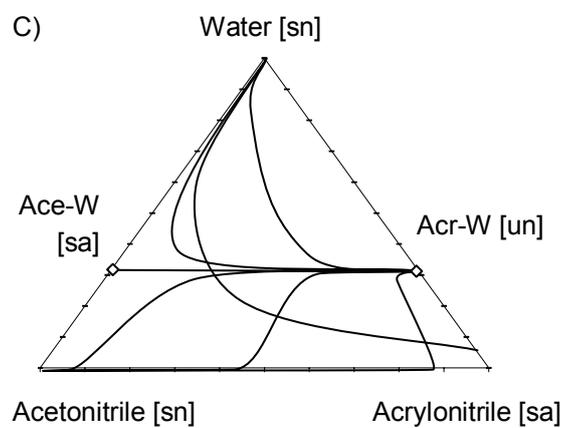
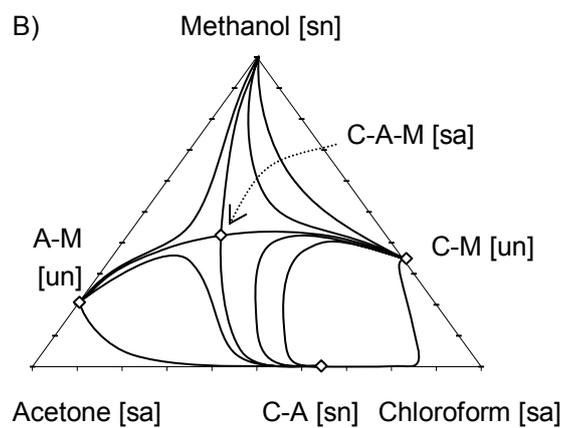
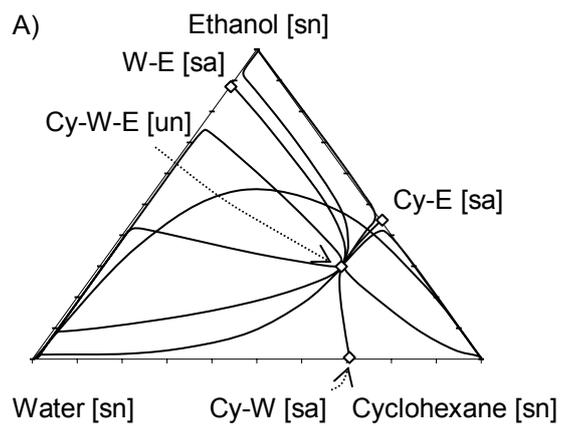


Figure 8. Residue Curve maps