# Generalized counter-current processes: distillation and beyond

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Abstract

The implementation and exploitation of counter-current movement between different phases is a well-established principle in chemical engineering in order to enhance the performance of separation processes. The improvements are essentially due to the establishment and wide application of more favorable driving forces compared to co-current operation. The success of dedicated multistage counter-current distillation processes has been a key motivator for the development of many other principles of counter-current separation processes. This promoting aspect was strongly stimulated and supported by the availability of elegant and instructive graphical solutions of the underlying mass balance equations, as e.g. the McCabe-Thiele diagram. We will illustrate in this short paper a few applications of counter-current separation processes, which demonstrate extensions exploiting spatial and temporal sub-structures and additional phase changes. The examples selected reveal a large potential for developing new process variants.

## 1) Introduction

Distillation is the workhorse in separation technology [1-4]. Due to its high energy requirements achieving high process efficiency is crucial. Continuously operated distillation processes have been developed and are widely applied, which exploit a counter-current movement between the two phases involved, namely liquid and vapor. The design of rectification columns is typically based on exploiting knowledge regarding the vapor-liquid equilibria of the system of interest within equilibrium stage models [5, 6]. The famous graphical solution developed by McCabe and Thiele has been of tremendous help in understanding and developing distillation technology [7]. Nowadays, the theoretical models have reached a high level of accuracy and are available for designing steady state counter-current multicomponent separation processes based on distillation.

Since many chemical species can not be evaporated without decomposition and due to the high energy amounts needed for distillation, numerous other equilibrium driven separation principles are applied. In order to exploit them efficiently and in an optimal manner, also for these alternative processes, an increase of driving forces in counter-current arrangements is

attractive. Equilibrium stage models, initially developed to quantify distillation processes [5, 6], provide a simple and flexible tool to formulate both the material and energy balances for numerous process variants. This paper will illustrate the exploitation and description for three other separation principles embedded within counter-current arrangements. The configurations considered differ in various features. Nevertheless all examples can be described by applying a unified description of dedicated connections of equilibrium stages. The generalized equations introduced allow for flexible optimization of separation processes within currently increasingly applied superstructure optimization concepts. It is the goal of this short paper in order to demonstrate the elegance, usefulness and wide applicability of equilibrium stage models for quantifying counter-current separation processes exploiting various types of phase constellations and equilibria.

We will introduce first an unified form of an equilibrium stage model capable to describe, among other configurations, transient counter-current separation processes for general phase situations. Hereby, the pioneering work related to designing distillation processes is shortly revised. Subsequently, out of the large spectrum of attractive process options, three more sophisticated counter-current processes will be discussed and compared, namely Solid Liquid Extraction, Simulated Moving Bed Chromatography and Counter-Current Crystallization. These processes are already applied successfully or are currently under development. Finally, a short outlook will be given regarding flexible process variants and the mentioned concept of superstructure optimization.

2) Unified description of stagewise operated equilibrium driven separation processes

If separations can be performed exploiting specific equilibrium distributions of mixture components present in different phases, equilibrium stage models are a well-established and convenient tool to quantify and design the corresponding processes [5, 6]. If the progress of separation achievable in a single stage is insufficient, connections of several stages are the method of choice to increase the degree of separation. As mentioned above, it is a well-known fact, that the implementation of counter-current movements between the phases, instead of using co-current movements, enhances the driving forces for separation and, thus, improves process efficiency [1-4].

The following general mass balance of a stage j in a cascade of $N_S$ stages for a component i present in a mixture of $N_C$ components can be formulated:

$$\frac{dm_{i,j}}{dt} = \sum_{p}^{P} x_{i,p,j} \frac{dm_{tot,p,j}}{dt} = \sum_{p}^{P} \sum_{ji(j)}^{ji,all} x_{i,p,ji}^{in} \dot{m}_{p,ji}^{in} - \sum_{p}^{P} \sum_{jo(j)}^{jo,all} x_{i,p,jo}^{out} \dot{m}_{p,jo}^{out}$$

$$i=1,N_C, \ j=1,N_S \qquad (1)$$

Eq. 1 respects that a component i can be present in several phases indicated by p. The x-values represent mass fractions of a component i in phase p and stage j. The ji(j) designates all the ji,all streams entering stage j from certain other stages and/or from external sources (e.g. feed streams, solvents or recycle streams) and the jo(j) designates all the jo,all streams leaving stage j to other stages or external sinks (e.g. product streams). In this general formulation connections to neighboring stages and also "more remote" stages are included. Thus, simple standard co-current or counter-current operation are included as well as all more complex process schemes connecting each stage with "all" other stages, as assumed in superstructure formulations.

The following dynamic total mass balance results from the sum of the component mass balances (eq.1):

$$\frac{dm_{tot,j}}{dt} = \sum_p^P \sum_{ji(j)}^{ji,all} \dot{m}_{p,ji}^{in} - \sum_p^P \sum_{jo(j)}^{jo,all} \dot{m}_{p,jo}^{out} \qquad\qquad j=1,N_S \qquad\qquad (2)$$

Discretization of eqs. 1 and 2 considering a time interval $\Delta t$ provides (after multiplication with $\Delta t$) the following equations, which quantify changes of mass of a component i or the total mass in stage j in the interval. This interval can be also seen as the time difference between two consecutive discrete temporal steps k and k+1:

$$m_{i,j}^{k+1} - m_{i,j}^{k} = \sum_p^P \sum_{ji(j)}^{ji,all} x_{i,p,ji}^{in,k} m_{p,ji}^{in,k} - \sum_p^P \sum_{jo(j)}^{jo,all} x_{i,p,jo}^{out,k} m_{p,jo}^{out,k} \qquad i=1,N_C, \ j=1,N_S \qquad (3)$$

$$m_{tot,j}^{k+1} - m_{tot,j}^{k} = \sum_p^P \sum_{ji(j)}^{ji,all} m_{p,ji}^{in,k} - \sum_p^P \sum_{jo(j)}^{ji,all} m_{p,jo}^{out,k} \qquad\qquad j=1,N_S \qquad\qquad (4)$$

The adjustment of a discrete real time differences, $\Delta t$, and the duration between two consecutive steps, k and k+1, can be realized via respecting the characteristic residence times of a key phase p , $\tau_{char,p}$, and the total stage number $N_S$ of the unit:

$$\Delta t \ \text{(or duration between steps } k \text{ and } k+1) = \frac{\tau_{char,p}}{N_S} \qquad\qquad (5)$$

In case the processes have reached a steady state, the following conditions holds for all t or all k, respectively:

$$x_{i,j} = \text{const.} \qquad \text{and} \qquad m_{tot,j} = \text{const.} \qquad\qquad i=1,N_C, \ j=1,N_S \qquad\qquad (6)$$

or

3

$$x_{i,j}^{k+1} = x_{i,j}^k \qquad \text{and} \qquad m_{tot,j}^{k+1} = m_{tot,j}^k \qquad\qquad \text{i=1,N}_C, \ \text{j=1,N}_S \qquad\qquad (7)$$

Thus, instead of eqs. 1 and 3, the following continuous or discrete steady state component mass balances hold for all stages:

$$0 = \sum_p^P \sum_{ji(j)}^{ji,all} x_{i,p,ji}^{in} \dot{m}_{p,ji}^{in} - \sum_p^P \sum_{jo(j)}^{jo,all} x_{i,p,jo}^{out} \dot{m}_{p,jo}^{out} \qquad\qquad \text{i=1,N}_C, \ \text{j=1,N}_S \qquad\qquad (8)$$

$$0 = \sum_p^P \sum_{ji(j)}^{ji,all} x_{i,p,ji}^{in} m_{p,ji}^{in} - \sum_p^P \sum_{jo(j)}^{jo,all} x_{i,p,jo}^{out} m_{p,jo}^{out} \qquad\qquad \text{i=1,N}_C, \ \text{j=1,N}_S \qquad\qquad (9)$$

A summation of the contributions of all components leads again to the corresponding steady state total mass balances:

$$0 = \sum_p^P \sum_{ji(j)}^{ji,all} \dot{m}_{p,ji}^{in} - \sum_p^P \sum_{jo(j)}^{jo,all} \dot{m}_{p,jo}^{out} \qquad\qquad \text{j=1,N}_S \qquad\qquad (10)$$

$$0 = \sum_p^P \sum_{ji(j)}^{ji,all} m_{p,ji}^{in} - \sum_p^P \sum_{jo(j)}^{jo,all} m_{p,jo}^{out} \qquad\qquad \text{j=1,N}_S \qquad\qquad (11)$$

If there are no external streams entering or leaving intermediate stages, it is often expedient and instructive to lump several stages into a larger zone. This is e.g. characteristic for the rectifying and stripping sections of a distillation column illustrated below. Such spatial lumping can reduce model complexity and provide instructive insight into the process characteristics. Furthermore, it can be efficiently used for process illustration as exemplified in the famous McCabe-Thiele diagram [7]. Based on eq. 1 a dynamic component mass balance for such a spatially lumped zone, designated by jz and consisting of several stages connected externally only via the zone dependent two border stages j1(jz) and j2(jz), can be written as:

$$\frac{dm_{i,jz}}{dt} = \sum_p^P \sum_{j1,j2} x_{i,p,j1/j2}^{in} \dot{m}_{p,j1/j2}^{in} - \sum_p^P \sum_{j1,j2} x_{i,p,j1/j2}^{out} \dot{m}_{p,j1/j2}^{out} \qquad\qquad \text{i=1,N}_C \qquad (12)$$

The corresponding discrete component mass balance equations for a lumped section jz result (after multiplication with $\Delta$t):

$$m_{i,jz}^{k+1} - m_{i,jz}^k = \sum_p^P \sum_{j1,j2} x_{i,p,j1/j2}^{in,k} \Delta m_{p,j1/j2}^{in,k} - \sum_p^P \sum_{j1,j2} x_{i,p,j1/j2}^{out,k} \Delta m_{p,j1/j2}^{out,k}$$

$$\text{i=1,N}_C \qquad (13)$$

Summation of the mass balances of all components (eqs. 12 and 13) provides the corresponding total mass balances considering a continuous time coordinate of discrete time steps (not shown here).

Besides the spatial lumping of several stages j into larger aggregated zones jz (captured by eqs. 12 and 13), another option of structuring the process considered over time exists. It is possible and can be attractive to operate the process only for a certain time (or for a certain number of steps k) with constant operating conditions and to perform, after a certain characteristic "shift time", $t_{shift}$, or after a related number of steps, K, periodically forced modifications in the operating conditions. Such a regime leads, after a sufficient number of shifts, to a cyclic steady state which then satisfies in addition to eqs. 8 to 11 the following conditions:

$$x_{i,j}(t + t_{shift}) = x_{i,j}(t) \quad \text{and} \quad m_{i,j}(t + t_{shift}) = m_{i,j}(t) \quad \text{i=1,N}_C \quad \text{j=1,N}_S \quad (14)$$

or

$$x_{i,j}^{k+K} = x_{i,j}^{k} \quad \text{and} \quad m_{i,j}^{k+K} = m_{i,j}^{k} \quad \text{i=1,N}_C \quad \text{j=1,N}_S \quad (15)$$

For such a periodic "temporal lumping" we will give below two examples.

The core of equilibrium stage models is the provision of functions describing the specific phase equilibria. The precision of equilibrium stage models strongly depends on the quality of this information, i.e. knowledge regarding the following functions:

$$x_{i,p}^{eq} = x_{i,p}^{eq}(x_{1,1}^{eq}, x_{2,1,}^{eq}, \dots, x_{Nc,1}^{eq}, \dots, x_{1,2}^{eq}, \dots, x_{Nc,P}^{eq}) \quad \text{i=1,N}_{C,} \quad \text{p=1,P} \quad (16)$$

Hereby, the well-known basis for quantifying equilibrium compositions in multi-component and multi-phase systems is the identity of the chemical potentials [8-10]:

$$\mu_{i,p=1} = \mu_{i,p=2} = \dots = \mu_{i,p=P} \quad \text{i=1,N}_C \quad (17)$$

The progress achieved in the last decades with respect to predicting vapor-liquid and liquid-liquid equilibria is remarkable. Nevertheless, there are clearly still deficits in the area of predicting equilibria in the presence of solids [9, 10].

The specific type of dependence captured in the equilibrium formulation has an influence on the difficulty of solving the model equations of the stage models. Several simple cases lead to

instructive analytical solutions, as illustrated below. In general, nonlinear coupled functions need to be processed. This leads to the need of applying numerical techniques.

Exploiting the general theoretical framework introduced above (eqs. 1-17) we will illustrate below the broad spectrum of feasible counter-current separation processes considering four process variants illustrated in Fig. 1. Obviously, there are many other variants possible based on exploiting counter-current processes between the specific phases involved, as e.g. Liquid-Liquid-Extraction or Gas-Liquid-Absorption.
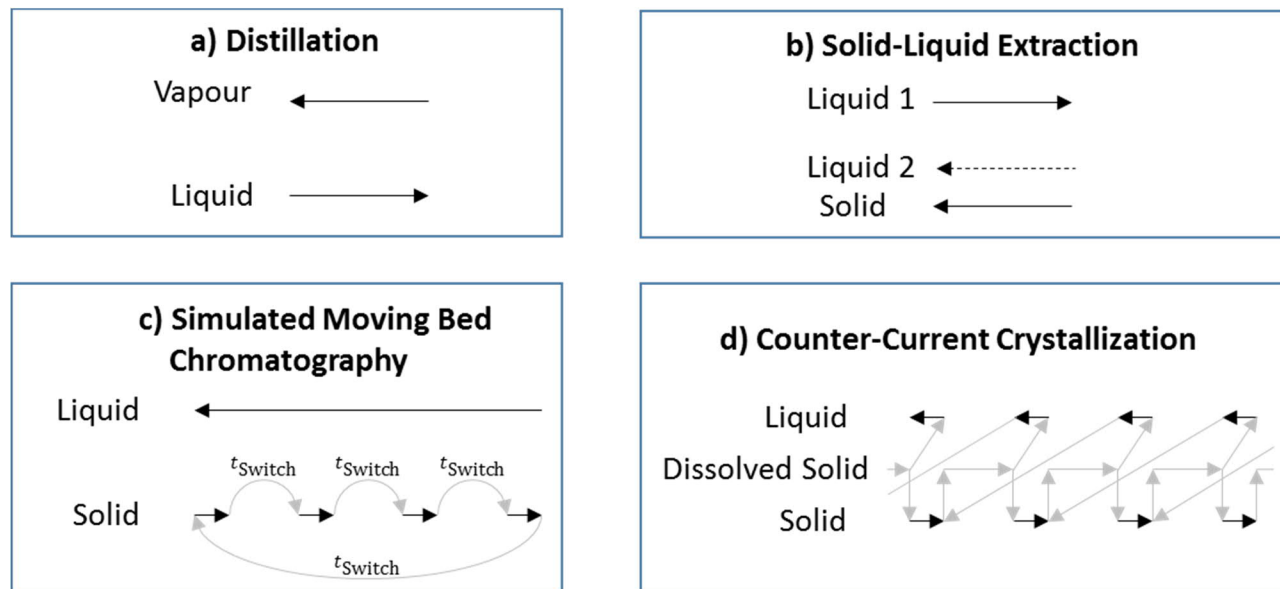


Fig. 1: Illustration of the phases involved and the directions of flows for four different variants of counter-current processes. a) Distillation, b) Solid Liquid Extraction (transport of entrapped fluid in the "wrong" direction), c) Simulated Moving Bed Chromatography (forced dynamic operation), d) Counter-Current Crystallization (exploitation of forced phase transitions).

3) Counter-current distillation

Features of the intensively used counter-current distillation (rectification) [1-4] are the exploitation of the different compositions of the mixture components in equilibrated vapor (p=1) and liquid (p=2) phases. In the standard application two outlet fractions are obtained with compositions, which differ from the feed compositions. Typically, steady state operation is intended. The well-known principle is illustrated in Fig. 2 (left) for a column consisting of $N_S$ stages complemented by a condenser and a reboiler providing the two product streams. To predict the progress of the separation along the stages of the distillation column, instead of solving the equations stage by stage, it is expedient to simulate two lumped zones, namely the

rectifying zone ($jz=1=R$) located between stages $j1_R$ and $j2_R$ and the stripping zone ($jz=2=S$) located between stages $j1_S$ and $j2_S$. These two zones are separated by the feed stage $j_F$.

Applying the generalized notation introduced above, the component mass balance equations given in eq. 1 can be formulated for steady state conditions as follows:

$$0 = \sum_p^2 \sum_{ji(j)}^{ji,all} x_{i,p,ji}^{in} \dot{m}_{p,ji}^{in} - \sum_p^2 \sum_{jo(j)}^{jo,all} x_{i,p,jo}^{out} \dot{m}_{p,jo}^{out} \qquad \text{i=1,N}_\text{C}, \text{ j=all} \qquad (18)$$

The corresponding total mass balance equation is:

$$0 = \sum_p^2 \sum_{ji(j)}^{ji,all} \dot{m}_{p,ji}^{in} - \sum_p^2 \sum_{jo(j)}^{jo,all} \dot{m}_{p,jo}^{out} \qquad \text{j=all} \qquad (19)$$

Considering the specific incoming and outgoing streams in eq. 8 holds for a stage j (Fig. 2, right):

$$0 = x_{i,1,j+1} \dot{m}_{1,j+1} + x_{i,2,j-1} \dot{m}_{2,j-1} - x_{i,1,j} \dot{m}_{1,j} - x_{i,2,j} \dot{m}_{2,j}$$

$$\text{i=1,N}_\text{C}; \quad \text{j=2,N}_\text{R}\text{+1 (jz=1)}; \quad \text{j=N}_\text{R}\text{+3, N}_\text{R}\text{+N}_\text{S}\text{+2 (jz=2)} \qquad (20)$$

The corresponding total mass balances are:

$$0 = \dot{m}_{1,j+1} + \dot{m}_{2,j-1} - \dot{m}_{1,j} - \dot{m}_{2,j}$$

$$\text{j=2, N}_\text{R}\text{+1 (jz=1)} \quad \text{or} \quad \text{j=N}_\text{R}\text{+3, N}_\text{R}\text{+N}_\text{S}\text{+2 (jz=2)} \qquad (21)$$

There are three special stages: a total condenser ($j=1$), the feed tray ($j=N_R+2$) and a partial reboiler ($j=N_R+N_S+3$). This requires a modified formulation of the mass balances considering three or five inlet and outlet streams instead of four as used in eqs. 20 and 21.

Combining the condenser and the rectifying section ($jz=1$) the two corresponding mass balances for a stage j* can be written as:

$$0 = x_{i,1,j*+1} \dot{m}_{1,j*+1} - x_{i,2,0} \dot{m}_{2,0} - x_{i,2,j*} \dot{m}_{2,j*} \qquad \text{i=1,N}_\text{C}, \text{ j*=2,N}_\text{R}\text{+1} \qquad (22)$$

The corresponding lumped total mass balance for a stage j* is:

$$0 = \dot{m}_{1,j*+1} - \dot{m}_{2,0} - \dot{m}_{2,j*} \qquad \text{j*=2,N}_\text{R}\text{+1} \qquad (23)$$

Considering a binary separation problem, after substituting of eq. 23 into eq. 22 and isolating $x_{i,1,j*+1}$ the following operating line can be derived for the rectifying section:

$$x_{i,1,j*+1} = \frac{\dot{m}_{2,j*}}{\dot{m}_{1,j*+1}} x_{i,2,j*} + \left(1 - \frac{\dot{m}_{2,j*}}{\dot{m}_{1,j*+1}}\right) x_{i,2,0} \qquad \text{i=1,2, \quad j*=2,$N_R$+1} \qquad (24)$$

The slope of this line corresponds to the reflux ratio of a distillation column, which is typically constant. A similar equation for the operating line with a different (also constant) slope can be derived for the stripping zone (jz=2=S).

Besides the operating lines, as a second important information required to design a rectification column the equilibrium function (eq. 16) needs to be specified. Assuming ideal binary mixtures and a constant volatility $\alpha$ holds:

$$x_{i,1} = x_{i,1}(x_{i,2}) = \frac{\alpha x_{i,2}}{1 + x_{i,2}(\alpha-1)} \qquad \text{i=1,2} \qquad (25)$$

Both operating lines and the equilibrium function can be illustrated as proposed by McCabe and Thiele [1-4, 7]. Stepwise connections between the operating and the equilibrium lines by horizontal and vertical steps illustrate the progress of the separation over the stages. This graphical illustration is very helpful to identify the number of stages required to solve a specific separation problem. Fig. 3 provides an illustration.
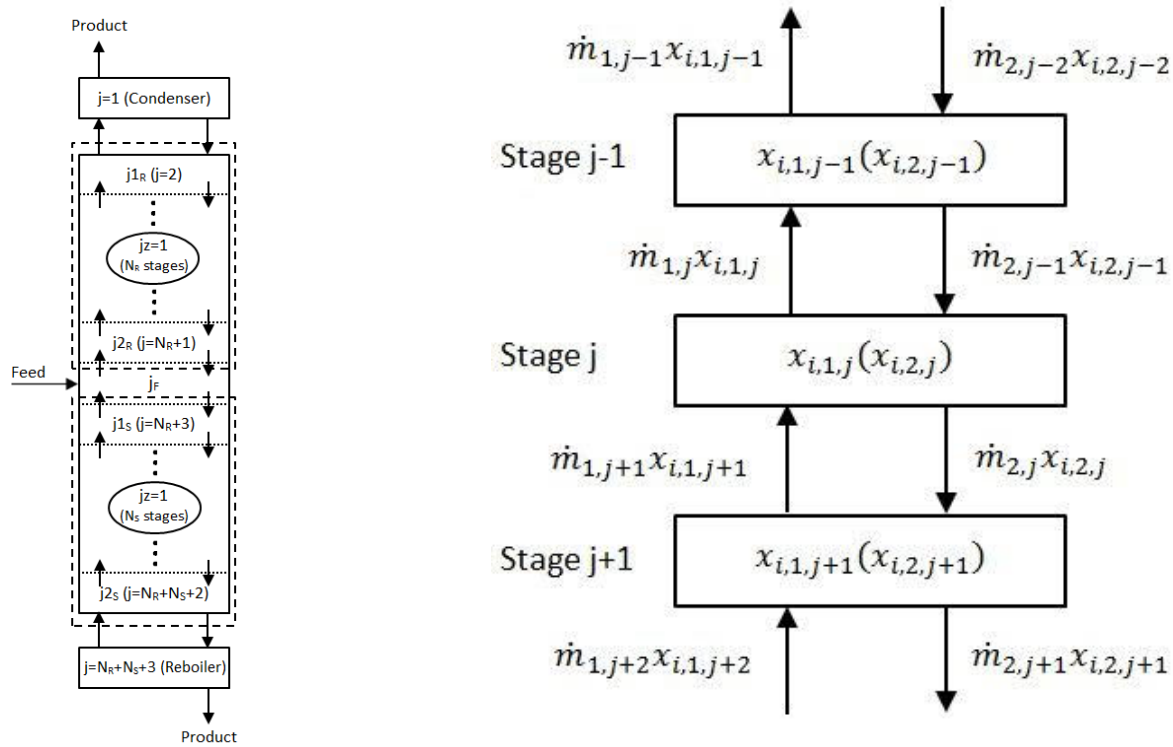


Fig. 2: Left: Illustration of a distillation column indicating the counter-current movement between vapor (p=1) and liquid (p=2) designating 2 lumped zones (rectifying zone, jz=1, $N_R$ stages, and stripping zone, jz=2, $N_S$ stages), Right: Illustration of three connected stages to illustrate the derivation of the steady mass balances (eqs. 20 and 21).
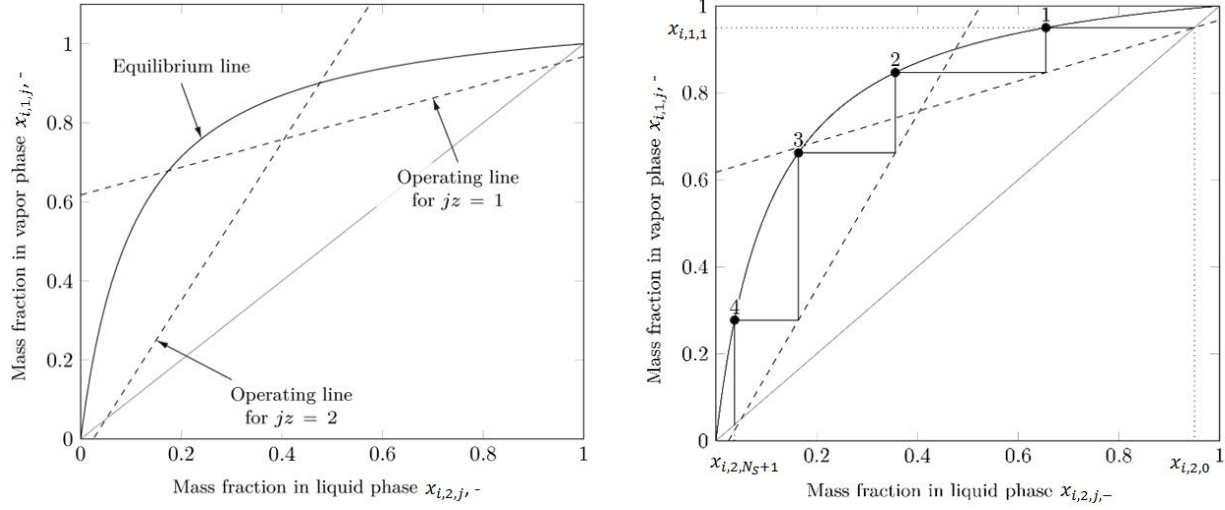
Fig. 3: Left: Illustration of the two operating lines in the phase diagram together with the equilibrium line based on eq. 25 (ideal separation). Right: Illustration of the progress of stagewise separation in the McCabe-Thiele diagram for $\alpha$=10 and slopes of the operating lines of 0.35 (jz=1) and 2 (jz=2), $N_S$=3.

## 4) Multi-stage counter-current solid liquid extraction

In this section a counter-current solid liquid extraction process is described. It is applicable for example to obtain a certain natural product from plants exploiting extraction in a suitable solvent [11-14]. A counter-current movement of the solid plant material and the solvent is capable to efficiently remove a target compound with high yields. The course of the separation process resembles the stagewise progress achieved during rectification described in the previous section. Solid liquid extraction (or "leaching") is preferably performed under steady state conditions with two constant flowrates of the inlet and product streams (designated as raffinate and extract). A difference to distillation is the unwanted fact, that a part of the liquid phase is stored inside the solid phase and travels in the "wrong" direction (Fig. 4). Thus, when studying such processes, in principle, three phases need to be considered, namely external liquid extract (p=1), internal liquid extract (2) and the solid plant matrix (3). It is however helpful to use a simplified phase consideration, which lumps phases 2 and 3 together into a new pseudo-phase (p=2, "phase lumping") as illustrated in Fig. 4.

Also for the extraction process described it is simple to derive the steady state component mass balance for a stage j located within the unit and connected only with stages j-1 and j+1. Exploiting eq. 8 and in analogy to eq. 20 holds:

$$0 = x_{i,1,j+1}\dot{m}_{1,j+1} + x_{i,2,j-1}\dot{m}_{2,j-1} - x_{i,1,j}\dot{m}_{1,j} - x_{i,2,j}\,\dot{m}_{2,j}$$

$$i=1,N_C, \quad j=2,N_S\text{-}1 \qquad (26)$$

The corresponding total mass balance for a stage j is:

$$0 = \dot{m}_{1,j+1} + \dot{m}_{2,j-1} - \dot{m}_{1,j} - \dot{m}_{2,j} \qquad\qquad j=2,N_S\text{-}1 \qquad (27)$$

The two stages at the outlet of the cascade (j=1 and j=N$_S$) have simpler mass balances containing only three instead of four terms (Fig. 4).

Constant mass ratios (phase ratios) between the two phases can be assumed throughout the extraction cascade, i.e.:

$$\tilde{x}_{2/1} = \frac{\dot{m}_2}{\dot{m}_1} \qquad\qquad \text{in all stages} \qquad (28)$$

This phase ratio can be specified knowing the volume fractions and the densities of the phases involved. Its introduction allows eliminating the total mass balance (eq. 27).

Furthermore, in extraction or leaching processes, equilibrium data can be expressed by partition functions, which quantify the ratio of mass fractions of a component i in the liquid phase, $x_{i,1}$ and that in the corresponding solid phase, $x_{i,2}$. In limited concentration ranges linear equilibrium functions can be applied:

$$x_{i,2} = \beta_i x_{i,1} \qquad\qquad i=1,N_C \qquad (29)$$

Since this simple arrangement has no external streams between the inlet and outlet, spatial lumping is very easy and efficient. This can be done by connecting the inlet at j=1, where the plant materials enters, with more stages. The single component mass balance for a first small lumped zone consisting of stage j=1 and stage j*=2 including the equilibrium function is:

$$0 = x_{i,1,3} + \tilde{x}_{2/1} * x_{i,2,0} - x_{i,1,1} - \tilde{x}_{2/1} * \beta_i * x_{i,1,2} \qquad i=1,N_C \qquad (30)$$

or with

$$A_i = \tilde{x}_{2/1} * \beta_i \qquad\qquad (31)$$

$$0 = x_{i,1,3} + \frac{A_i}{\beta_i} * x_{i,2,0} - x_{i,1,1} - A_i x_{i,1,2} \qquad i=1,N_C \qquad (32)$$

Analogously holds for the next larger zone extending up to j*=3:

$$0 = x_{i,1,4} + \frac{A_i}{\beta_i} * x_{i,2,0} - x_{i,1,1} - A_i x_{i,1,3} \qquad \text{i=1,N}_C \qquad (33)$$

Inserting the equations successively into each other provides the following final balance equation lumping over the whole unit, as derived already by Kremser [15] for quantifying counter-current absorption subject to a linear equilbrium function:

$$x_{i,1,N_S+1} = \left(A_i{}^{N_S} + A_i{}^{N_S-1} + \cdots + A_i + 1\right)x_{i,1,1} - \left(A_i{}^{N_S} + A_i{}^{N_S-1} + \cdots + A_i\right)\frac{x_{i,2,0}}{\beta_i}$$

$$\text{i=1,N}_C \qquad (34)$$

or rearranged:

$$x_{i,1,1} = \left(\frac{A_i-1}{A_i{}^{N_S+1}-1}\right)x_{i,1,N_S+1} + \left(\frac{A_i{}^{N_S+1}-A_i}{A_i{}^{N_S+1}-1}\right)\frac{x_{i,2,0}}{\beta_i} \qquad \text{i=1,N}_C \qquad (35)$$

Eq. 35 allows directly calculating the unknown liquid concentration in stage 1 provided the contrations in the entering streams, $N_S$, $\tilde{x}_{2/1}$ and the component specific equilbrium constant $\beta_i$ are known. The corresponding solid phase concentration in this stage follows from eq. 29.

Performing the same successive lumping procedure from the oppsite site, i.e. starting from stage $N_S$ and lumping down to j*=1, provides the following similar equation, which allows calculating the composition of stage $N_S$:

$$x_{i,1,N_S} = \left(\frac{A_i{}^{-1}-1}{A_i{}^{-(N_S+1)}-1}\right)\frac{x_{i,2,0}}{\beta_i} + \left(\frac{A_i{}^{-(N_S+1)}-A_i{}^{-1}}{A_i{}^{-(N_S+1)}-1}\right)x_{i,1,N_S+1} \qquad \text{i=1,N}_C \qquad (36)$$

The procedure described allows also determining all internal concentrations in both phases.

Results of applying eqs. 35 and 36 are illustrated in Fig. 5 for extracting a single component using specific reference values for the key parameters $x_{2,0}$, $N_S$, $\tilde{x}_{2/1}$ and $\beta_i$. In the left part are shown the resulting internal mass fraction profiles over a cascade of 10 stages for both phases. The points marked at stages 1 and 10 show both the provided inlet and the calculated outlet concentrations. In Fig. 5 (right), the different specific impact of the three key parameters is illustrated varying their values around the reference values.

We would like to emphasize, that it is also possible for this process to use the classical McCabe-Thiele illustration. This is even simpler than for the description of distillation, since only one lumped zone needs to be considered. The application of this concept is in particular useful if nonlinear equilibrium functions need to be respected, which then require the application of numerical methods. A possible application of counter-current extraction devoted to isolate Artemisinin from leaves of Artemisia annua is currently under investigation [16].
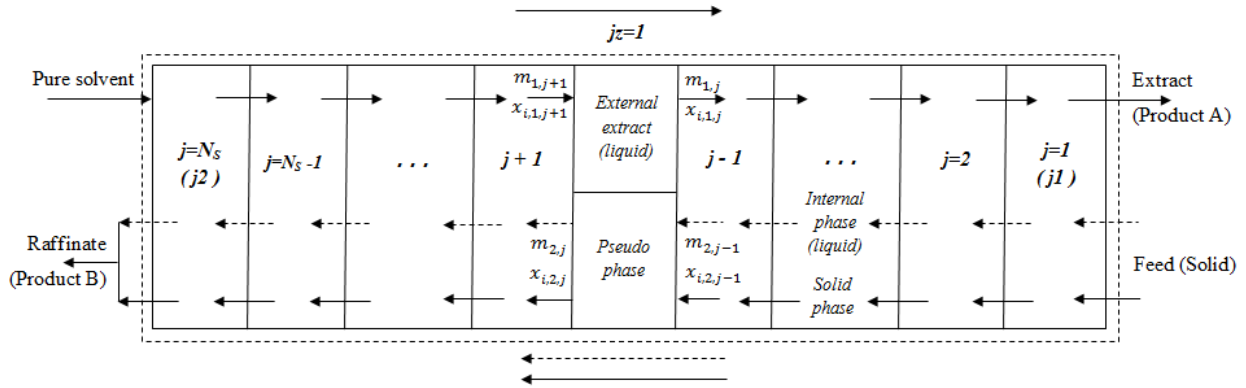


Fig. 4: Illustration of the multi-stage counter-current solid liquid extraction process considering three phases.
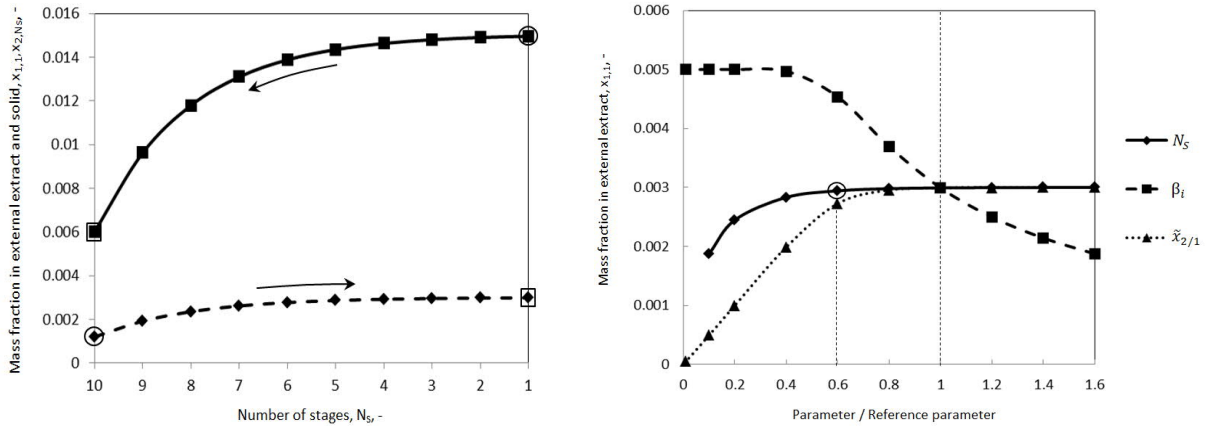


Fig. 5: Left: Illustration of predicted concentration distributions in the external liquid phase and the solid phase (eqs. 29, 35 and 36) with reference parameters $N_S=10$, $x_{2,0}=0.015$, $\tilde{x}_{2/1} = 0.33$ (eq. 28), $\beta_i = 5$ (eq. 29). Right: Influence of important parameters (normalized with respect to the reference parameters) on the mass fraction of the product in the extract (the other parameters are kept at the reference values).

## 5) Column chromatography

Another class of separation processes, which also exploits a relative movement between two phases is chromatography [17]. In the standard form a fluid mobile phase (gas, liquid or supercritical fluid, p=1) moves continuously through a bed packed with particles of a solid phase (p=2), which is fixed in the chromatographic separation column. Thus, traditionally only

one phase is mobile in chromatography. As in the case of solid liquid extraction, also in chromatography a part of the fluid is stored in the solid phase. To simplify the description this additional and not convectively transported third phase might be again conveniently lumped into the solid phase (p=2).

In the classical batch mode of chromatographic operation the mobile phase carries periodically the mixtures to be separated through the column. This transient process can be described by adjusting the dynamic discrete formulation of the general mass balance (eq. 3) to the situation that only the fluid phase (p=1) moves:

$$x_{i,1,j}^{k+1}m_{1,j}^{k+1} + x_{i,2,j}^{k+1}m_{2,j}^{k+1} - x_{i,1,j}^{k}m_{1,j}^{k} - x_{i,2,j}^{k}m_{2,j}^{k} = x_{i,2,j-1}^{k}m_{1,j-1}^{k} - x_{i,1,j}^{k}m_{1,j}^{k}$$

$$i=1,N_C, \ j=1,N_S \qquad (37)$$

Assuming that all information is available for a previous discrete time step k and the equilibria are permanently established the following rearranged set of equations results:

$$x_{i,1,j}^{k+1}m_{1,j}^{k+1} + x_{i,j,2}^{k+1}\left(x_{i,j,1}^{k+1}\right) * m_{j,2}^{k+1} = x_{i,2,j}^{k}m_{2,j}^{k} + x_{i,2,j-1}^{k}m_{1,j-1}^{k}$$

$$i=1,N_C, \ j=1,N_S \qquad (38)$$

This formulation, which corresponds to the classical discrete Craig model of chromatography [18, 19], allows determining the composition in the new step (k+1) provided the so-called phase ratio and the equilibrium functions are known. The phase ratio is the typically well accessible ratio between solid and fluid phase fractions present in the chromatographic columns:

$$\tilde{x}_{2/1} = \frac{m_2}{m_1} = const. \qquad \text{in all stages} \qquad (39)$$

For nonlinear coupled equilibrium functions (adsorption isotherms, eq. 16) numerical methods need to be applied to determine the $x_{i,1,j}^{k+1}$ from eq. 38 For diluted conditions the following linear (and uncoupled) adsorption isotherm model can be applied:

$$\gamma_i = \frac{x_{i,2}}{x_{i,1}} = const. \qquad \text{in all stages} \qquad (40)$$

In order to quantify chromatographic separations typically the capacity factor k' is applied [17]:

$$k_i' = \tilde{x}_{2/1} * \gamma_i \qquad i=1,N_C \qquad (41)$$

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This leads to the following well known analytical solution of eq. 38:

$$x_{i,1,j}^{k+1} = \frac{x_{i,1,j-1}^{k} + k_i' x_{i,1,j}^{k}}{(1+k_i')} \qquad\qquad \text{i=1,N}_\text{C},\ \text{j=1,N}_\text{S} \qquad\qquad (42)$$

To substitute the discontinuous character of batch operation, more productive chromatographic separation processes are based on applying a counter-current between two moving phases. Hereby, a significant problem is the controlled transport of the often fragile and delicate solid phase particles. Thus, this transport is simulated by periodically moving the inlet and outlet ports for the fluid phase as described below. However, to understand and evaluate the process it is instructive to analyze first the hypothetical true moving bed (TMB) process, in which the solid phase really moves continuously counter-currently to the fluid phase and which can be operated under steady state conditions. Fig. 6 illustrates such a TMB process in a ring form. There are four distinct zones (spatially lumped sections) needed in order to realize a continuous separation of a feed mixture constituting of two components A and B and to benefit from efficient regeneration of both phases after the separation. These four spatially separated zones (jz = I, II, III, IV) can have different lengths (stage numbers). They are connected by four additional stages, through which continuously feed and solvent are introduced and the two product fractions are withdrawn.

The basic steady state continuous mass balance for each stage of a TMB process originates from eq. 8:

$$0 = x_{i,1,j+1}\dot{m}_{1,j+1} + x_{i,2,j-1}\dot{m}_{2,j-1} - x_{i,1,j}\dot{m}_{1,j} - x_{i,2,j}\dot{m}_{2,j}$$

$$\text{i=1,N}_\text{C}\ ,\quad \text{in all "internal" stages} \qquad (43)$$

For each of the mentioned four TMB zones the spatial lumping, explained already in the distillation and extraction examples, is applicable as well. Furthermore, in case of linear equilibria, the described Kremser approach [15] (see extraction example) can be efficiently applied providing instructive analytical solutions [20].

Due to the fact, that a solid phase transport is usually connected with too much back-mixing the TMB process can not be used for difficult separations. For this reason the Simulated Moving Bed (SMB) process was suggested [21] and is now frequently applied, in particular in petrochemistry but also in the pharmaceutical industry. Due to the fixation of the solid phase and the periodic movement of the inlet and outlet ports, several columns are needed, which are connected in series. The SMB process increasingly mimics the more the hypothetical real counter-current TMB process the larger the number of columns. Due to forced periodic operation a dynamic model is needed to describe its essential features. The general model

structure was already illustrated above for a single batch column (eq. 38). To describe the SMB process just the connection of all columns needs to be implemented in the process model respecting a discrete periodically applied switching time, $t_{shift}$, at which all ports are synchronously shifted by one column position in the direction of the fluid flow. Here we do not provide the detailed model equations capturing all process features. Instead we just point out the fact that the SMB process reaches after a certain number of switches a cyclic steady state. In this state the patterns of the internal concentration profiles as well as the transients of the two component profiles in the two product streams (raffinate and extract) repeat after each shift. This can be implemented in a discrete model by expressing the shift time , $t_{shift}$, via multiplying the intrinsic process time step $\Delta t$ by a factor K, which takes the periodicity into account:

$$t_{shift} = K * \Delta t \tag{44}$$

The following condition defines cyclic steady state operation:

$$x_{i,j}(k + K) = x_{i,j}(k) \quad \text{and} \quad m_{tot,j}(k + K) = m_{tot,j}(k) \qquad \text{i=1,N}_C, \ \text{j=1,N}_S +4, \ \text{all k} \tag{45}$$

To illustrate the SMB operation Fig. 7 shows predicted outlet and internal concentration profiles. A configuration with 8 columns with 50 stages each is considered. Two columns are placed in each of the four zones. Linear equilibria are assumed. Building block for the simulations are eqs. 38-42. Main challenge for a successful separation is the identification of suitable values for the internal flowrates and the switching time to allow the desired binary split. Exploiting the so-called equilibrium theory of chromatography reliable tools for solving this task are available [22].

In the left part of Fig. 7 are given the internal concentration profiles over the 8 columns in the beginning and at the end of the shift time. The feed is introduced continuously between columns 4 and 5. The two product streams leave the unit between columns 2 and 3 and columns 6 and 7, respectively. As also reflected in the right part of Fig. 7, where the outlet concentrations are depicted over a few cycles, the second outlet contains over the whole shift time only the desired component, whereas between columns 2 and 3 in the extract outlet for the parameters studied a contamination can be noticed at the beginning of each tact, which then gradually vanishes.
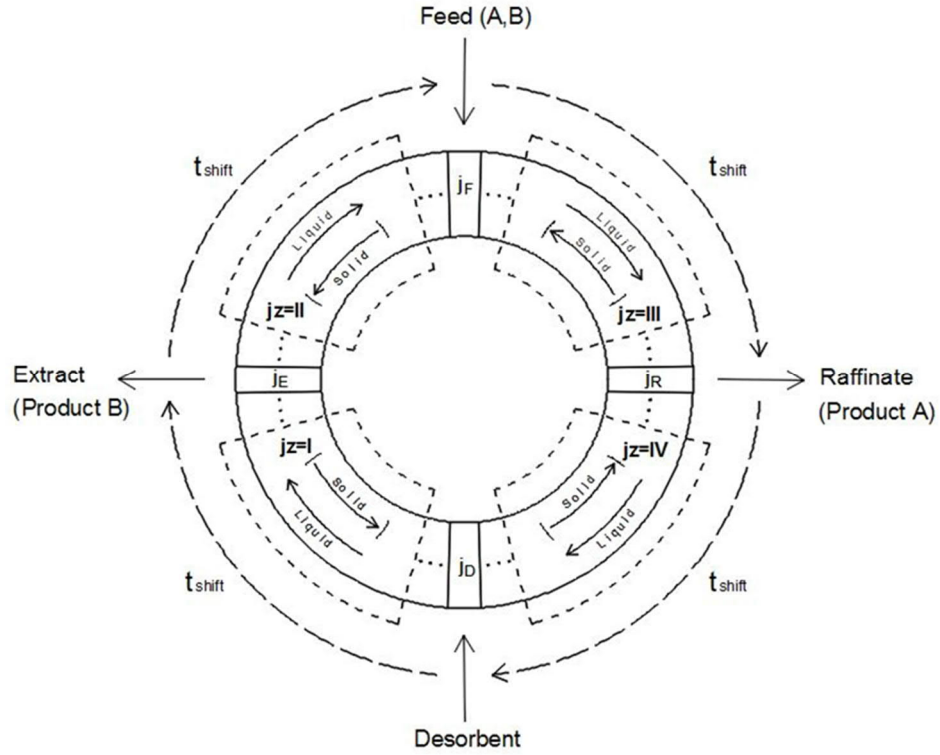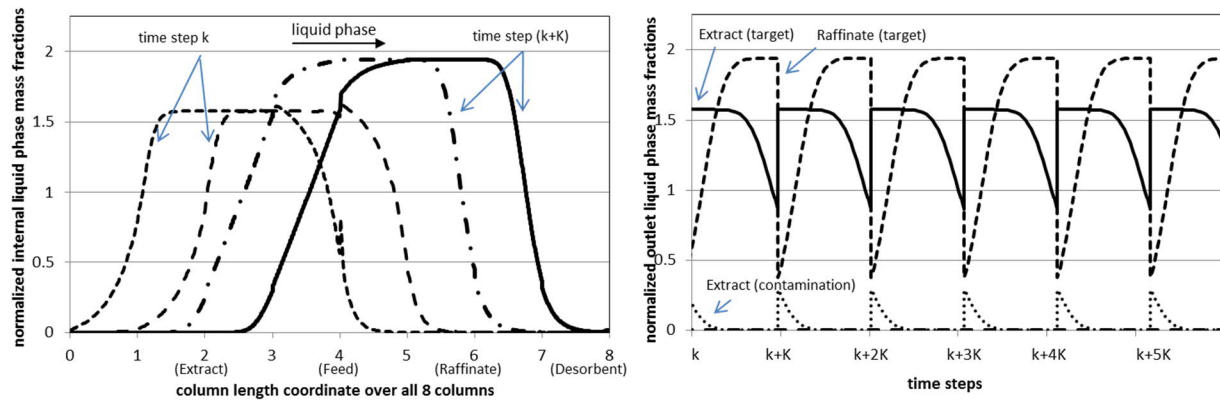
Fig. 6: Illustrating chromatographic counter-current separation exploiting the hypothetical True Moving Bed (TMB) principle. Four distinct zones (jz = I, II, II ,IV) are exploited, which can continuously split a feed into two outlets streams using a desorbent as additional second inlet stream.



Figs. 7: Left: Illustration of the internal cyclic steady state composition profiles of a periodically operated SMB process over the 8 columns (50 stages each). Right: Corresponding outlet concentration profiles. Configuration and parameters: $N_S=8*50+4=404$, $k_1'=0.667$, $k_2'= 1.333$, the four internal flowrates and the shift were selected based on equilibrium theory [12].

6) Counter-current crystallization

As the last and most complex example we consider a counter-current crystallization process devoted to resolve solid solutions as described in [23]. These are solids consisting out of two components, which are totally miscible in the solid phase. In contrast to eutectic systems, resolution of solid solutions forming systems cannot be achieved by a single crystallization, but always need a multistage operation [24-26]. Here we assume that these solids solutions ("mixed crystals") are free of solvent.

The periodically operated process described below is characterized by various features. There is one inlet for the solid (p=2) feed at a certain stage within a cascade of $N_S$ crystallizer stages and two product outlets (as in distillation and extraction) intended to provide the two purified ingredients of the solid solution. The counter-current movement of the equilibrated solid phases is realized periodically (as in SMB chromatography). For this, mother liquor (p=1) present in stage j+1 is added to the previously filtrated solid phase in stage j-1. Further solvent addition ensures the full dissolution of the solid phase, such that pumping into stage j is possible. Finally, solvent is removed periodically by evaporation causing precipitation. Altogether the process sequence is characterized by five sequentially and periodically carried out unit operations.

In Fig. 8 we can see a simplified scheme of the counter-current crystallization cascade using a column analogy just considering the inlets and outlets of a separation stage. The figure does not illustrate the also required dissolution and transport steps. Solid feed is added to stage $j_F$, while products leave the cascade at the top and the bottom via stages 1 and $N_S$. More details about the process can be found in [27]. The process design is difficult, due to the complex ternary phase equilibria and the challenging solid phase transport.

Fig. 9 (left) illustrates the sequence of the five periodically repeated sub-steps performed in a crystallizer stage j required to realize one complete crystallization cycle. For this, corresponding pathways are additionally given in this ternary phase diagram. The sequence of these five steps (kz = i, ii, iii, iv, v) corresponds to operating only one sub-step and switching off periodically the four other sub-steps. After completing this temporal sequence, a new identical cycle starts, which leads under cyclic steady state conditions to the same pattern of concentration profiles. The corresponding in- and outputs of a single separation stage j are illustrated in Fig. 9 (right).
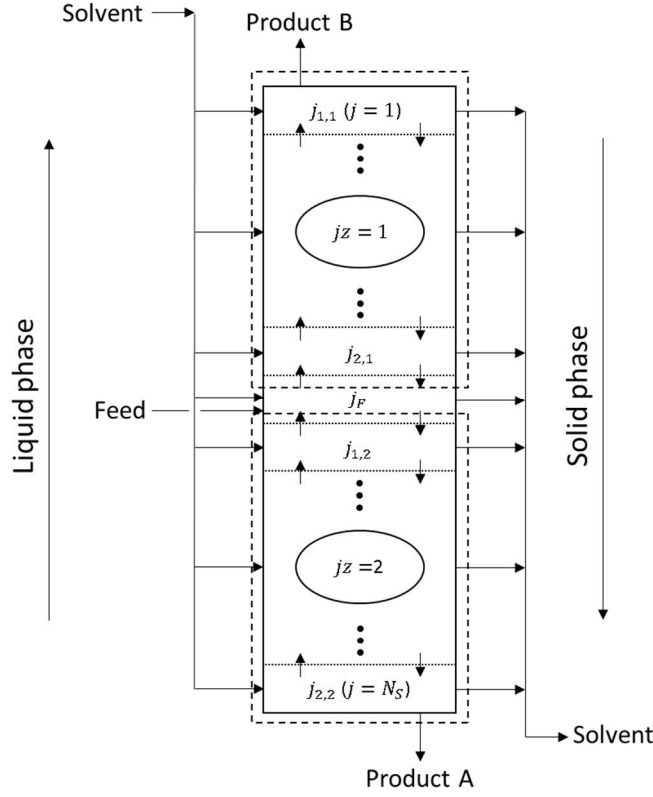
Fig. 8: Illustration of the counter-current crystallization cascade devoted to resolve continuously a solid solution consisting of two components A (i=1) and B (i=2).



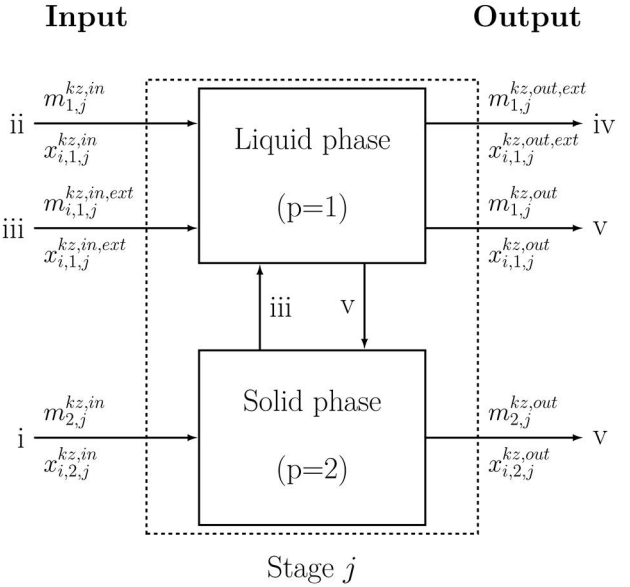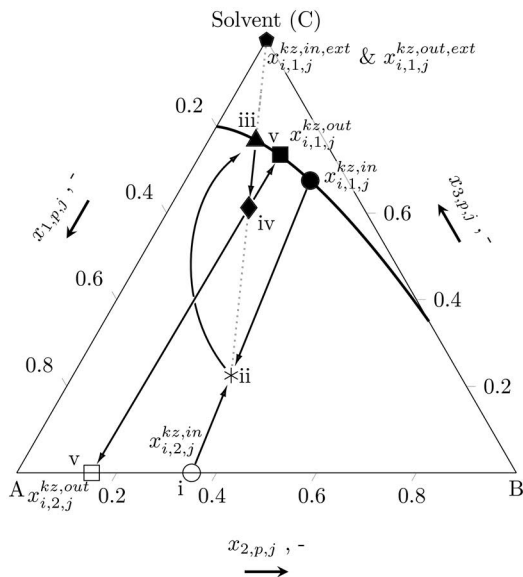Fig. 9: Left: Illustration of the sequence of the five sub-steps (kz = i , ii, iii, iv and v) for a stage j in the ternary phase diagram of a solid solution forming system. Right: Designation of masses entering (in; in,ext) and leaving (out,ext; out) the two phases present in the stage.

As other counter-current process variants discussed above, also this process can be described starting from the discretized steady state component mass balances given above (eq. 9). Most of the stages can be described by the following discrete component mass balances respecting the temporal changes in using the stages:

$$0 = m_{1,j}^{kz,in} x_{i,1,j}^{kz,in} + m_{2,j}^{kz,in} x_{i,2,j}^{kz,in} + m_{1,j}^{kz,in,ext} x_{i,1,j}^{kz,in,ext} - x_{i,2,j}^{kz,out} m_{2,j}^{kz,out} - m_{2,j}^{kz,out} x_{i,2,j}^{kz,out}$$
$$- m_{1,j}^{kz,out,ext} x_{i,1,j}^{kz,out,ext}$$

$$\text{i=1,N}_C, \quad \text{j=1,N}_S \quad \text{kz= i, ii, iii, iv, v} \qquad (46)$$

A similar total mass balance equation can be derived from eq. 11, which is not given here.

As in distillation there are three specific stages for which the balance equations differ slightly from eq. 46, namely the feed stage as well as stages 1 and $N_S$.

There are further algebraic equations required to connect the five temporal sub-steps. Considering the also needed thermodynamic equilibrium in the three component system a simplification can be used. In case of solid solutions each tie line defines a unique liquid and solid phase composition. Hence, if the mass fraction in equilibrium of one single component is known for a given temperature and using the closure conditions for solid and liquid phases, all other mass fractions are fixed. Therefore, eq. 16 can be expressed as:

$$x_{i,p}^{eq} = x_{i,p}^{eq}(x_{2,2}^{eq}, T), \qquad \text{i=1,2,3} \quad \text{p=1,2} \qquad (47)$$

To describe such ternary equilibria for isothermal conditions polynomials of order M can be used introducing 2M parameters:

$$\begin{pmatrix} x_{1,1}^{eq} \\ x_{2,1}^{eq} \end{pmatrix} = \begin{pmatrix} \sum_{m=1}^{M} a_{1,m}(1 - x_{2,2}^{eq})^m \\ \sum_{m=1}^{M} a_{2,m} x_{2,2}^{eq} \end{pmatrix} \qquad (48)$$

Moreover, the mass balance equations need to be complemented by the conditions required for guaranteeing the periodicity and the achievement of a cyclic steady state (eq. 15):

$$x_{i,p,j}^{kz+5} = x_{i,p,j}^{kz} \qquad \text{p=1,2 i=1,N}_C, \text{ j=1,N}_S \text{ kz=I,ii,iii,iv,v(5)} \qquad (49)$$
$$m_{tot,j}^{kz+5} = m_{tot,j}^{kz} \qquad \text{j=1,N}_S \text{ kz=I,ii,iii,iv,v(5)} \qquad (50)$$

Also in this more complicated process the application of an additional spatial lumping of several stages into two zones providing A and B, respectively (Fig. 8), and the exploitation of graphical

methods (as provided by the McCabe-Thiele theory), can be a powerful tool to analyze the process and to estimate stage numbers required to reach a specific process goals. A difficulty of using the latter for the described counter-current crystallization processes is due to the presence of the third component, namely the solvent. To analyze the overall process it is expedient to eliminate the solvent from the balances using modified total masses and fractions for the liquid phase:

$$\bar{m}_{1,j} = m_{1,j}(1 - x_{3,1,j}) \qquad\qquad \text{j=1,N}_S \qquad\qquad\qquad (51)$$

$$\bar{x}_{i,1,j}^{out} = \frac{x_{i,1,j}^{out}}{x_{1,1,j}^{out} + x_{2,1,j}^{out}}, \qquad\qquad \text{i=1,2 j=1,N}_S \qquad\qquad (52)$$

A special case of eq. 48, based on first order polynomials, provides the equilibrium for ideal phase equilibria introducing a separation factor $\alpha^{Cr}$ (similar to the one already used in the distillation section, eq. 25).

$$\bar{x}_{2,1,j}^{out} = \frac{\alpha^{Cr} \cdot x_{2,2,j}^{out}}{1 + x_{2,2,j}^{out}(\alpha^{Cr} - 1)} \qquad\qquad \text{i=2 j=1,N}_S \qquad\qquad (53)$$

With the solvent-reduced liquid phase mass fractions, a modified McCabe-Thiele theory can be applied, exploiting two lumped zones between stages $j_{1,1}$ (liquid product outlet) and $j_{2,1}$ (Fig. 8). A mass balance can be formulated for a specific stage j* located in these zones (as in the above given distillation example). This leads to the following operating line for stage j* in the first zone between stages $j_{1,1}$ and $j_{2,1}$:

$$\bar{x}_{2,1,j^*+1}^{out} = \left(1 - \frac{m_{2,j^*}^{out}}{\bar{m}_{1,j^*+1}^{out}}\right) \bar{x}_{2,1,1}^{out} - \frac{m_{2,j^*}^{out}}{\bar{m}_{1,j^*+1}^{out}} \cdot x_{2,2,j^*}^{out} \qquad\qquad \text{j*=j}_{1,1}\text{=1, j}_{2,1} \qquad (54)$$

In contrast to distillation, the slopes of the operating lines are not constant and change from stage to stage due to the dedicated solvent removals and additions (Fig. 9, left).

Analogously, the operating line for the second lumped zone (Fig. 8) is described by the following equation:

$$\bar{x}_{2,1,j^*}^{out} = \left(\frac{m_{2,j^*-1}^{out}}{\bar{m}_{1,j^*}^{out}} - 1\right) \cdot x_{2,2,N_S}^{out} - \frac{m_{2,j^*-1}^{out}}{\bar{m}_{1,j^*}^{out}} \cdot x_{2,2,j^*-1}^{out} \qquad\qquad \text{j*=j}_{1,2}\text{, j}_{2,2}\text{,=N}_S \qquad (55)$$

Fig. 10 (left) shows predicted steady state mass fractions in the phase distribution plot for component B (i=2). It can be seen that a feed mixture of a 1:1 mixture of A and B, introduced periodically to stage 5, can be resolved in a cascade of 9 stages. Component A is collected as

solid product in stage 9 and component B is collected in the liquid phase in stage 1. In Fig. 10 (left) are given additionally the McCabe-Thiele operating lines with their varying slopes calculated with eqs. 54 and 55. The plot given in Fig. 10 (right) provides the corresponding composition changes over the stage numbers.
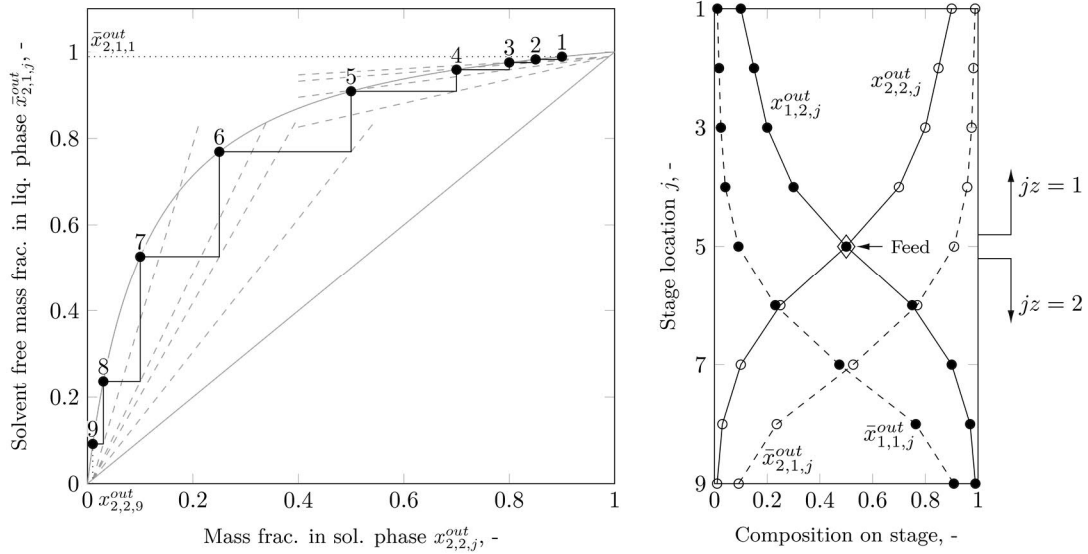


Figure 10: Left: Predicted steady state mass fractions and operating lines calculated (eqs. 54 and 55) and corresponding McCabe-Thiele representation (step v). Parameters: $\alpha$=10 ($a_1$=0.08, $a_2$=0.8), $N_S$=9, $j_F$=5. Right: Stage vs. composition plot illustrating the continuous purity increase of A (i=1) and B (i=2) towards the outlets of the cascade (in zones jz=1 and jz=2).

## 7) Summary and outlook

The above described different configurations of counter-current separation processes as well as numerous other concepts are characterized by a large number of degrees of freedom. Important questions to be solved are related to identify for example the best specific positions of crucial stages (e.g. for the feed inlet) and the identification of optimal spatial or temporal sub-structures. Answering these questions using equilibrium stage models and nonlinear equilibrium functions requires solving challenging mixed integer nonlinear programing problems. In the last years remarkable progress has been achieved in this area and the mathematical tools required have been developed [28-30]. These theoretical concepts will be increasingly applied in the future to wider apply the powerful counter-current principle in separation science, as for example in the case studies discussed above. However, also the suggestion of completely new and probably partly unexpected non-trivial configurations can be expected. Promising applications of superstructure analysis are already used to evaluate and optimize the already large spectrum of modified more flexible new SMB process configurations [31] as shown in [32].

Notation of indices used

i          components, $[1, N_C]$

j          stages, $[1, N_S]$

jz        spatially lumped zones, [I,II, ...]

j*        running index in spatially lumped zone

j1        inlet into a spatially lumped zone

j2        outlet from spatially lumped zone

k          time steps

kz        lumped time steps, [i, ii, ...]

K         special number of multiple time steps k related to process periodicity (cycles)

p          phases, $[1, P]$

$x_{i,p,j}^{k}$     mass fraction of component i in phase p and stage j at time step k

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