A Paper about the Slope of the Equilibrium Line

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There is no simple definition of the slope of the equilibrium line multicomponent systems because vapor liquid equilibrium is represented by a surface. This paper describes a method of approximating the slope in multicomponent systems based on the new concept the *design component*, defined as that compound we seek to eliminate from the mixture in a particular section of the column. Unlike traditional methods, this new approach can also be applied to absorber and stripper columns. Two analytical approximate methods of calculating the design slope are described and shown to be in good agreement with the rigorous design flash calculation even in cases where the relative volatility is far from constant. These simple approximations, which need nothing beyond what is readily available from any column simulation program, appear to be adequate for design and can be easily programmed in any spreadsheet.

1. Background

In the standard model for point, tray, and section efficiencies for distillation in tray columns due to Lewis (1936) the section efficiency is related to the tray efficiency by:

$$\eta_{Section} = \frac{\ln\left(1 + \eta_{Tray} \cdot (\lambda - 1)\right)}{\ln(\lambda)} \tag{1}$$

with the Murphree vapor tray efficiency obtained from:

$$\eta_{Tray} = \frac{e^{\lambda \cdot \eta_{Point}} - 1}{\lambda} \tag{2}$$

The point efficiency is found from

$$\eta_{Point} = 1 - e^{-N_{OG}} \tag{3}$$

where the overall number of transfer units for the gas, N_{OG}, can be expressed as follows:

$$\frac{1}{N_{OG}} = \frac{1}{N_G} + \frac{\lambda}{N_L} \quad \text{with} \quad \lambda = \frac{m}{L/G} \tag{4}$$

where λ is the stripping factor and m is the slope of the equilibrium line.

Inspection of Equations (1-4) shows that the important parameters are the numbers of transfer units for gas and liquid phases and the stripping factor. The way in which the efficiency depends on these parameters is shown in Figure 1a reproduced from Duss and Taylor, 2018.

The performance of packed columns often is be expressed using the *HETP* which is related to the height of packing by

$$HETP = H / N_{EQM} \tag{5}$$

Where N_{EQM} is the number of equilibrium stages needed to accomplish the same separation possible in a real packed column of height H. The equilibrium stage model of distillation and absorption is described in a number of textbooks (see, e.g., Seader and Henley, 2006). If the equilibrium line may be assumed straight, the *HETP* may be related to the height of a transfer unit by

$$HETP = H_{OG} \cdot \ln(\lambda)/(\lambda - 1) \text{ with } H_{OG} = H_G + \lambda \cdot H_L \tag{6}$$

Figure 1b shows how *HETP* varies with the stripping factor. In this figure the values of N_G and H_G are adjusted so that each line has the same maximum value of efficiency and minimum value of *HETP*.
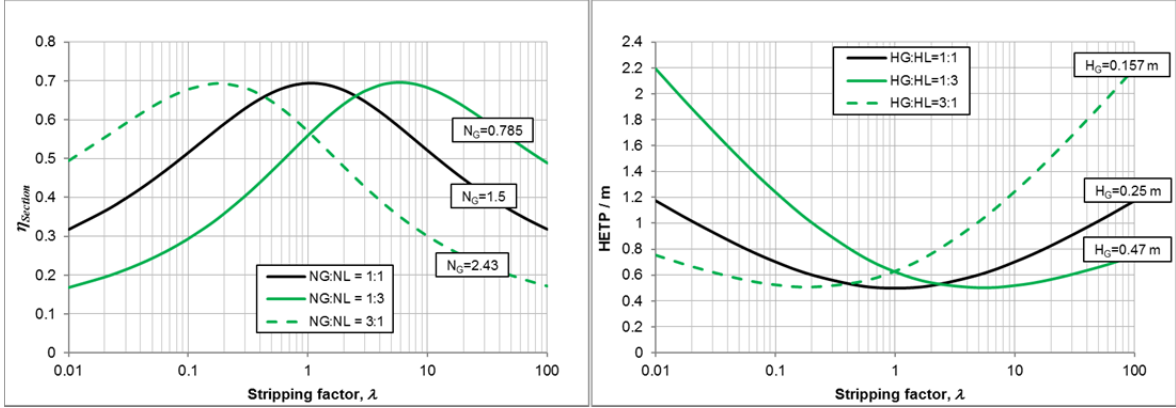

Figure 1: Dependence of (a) section efficiency (left) and (b) HETP (right) on the stripping factor. Numbers and heights of transfer units adjusted so the maximum or minimum is the same for each line in the respective plot.

Methods for estimating the slope of the equilibrium line in multicomponent systems are based on adaptations of methods proposed for binary systems, which use the two key components in a pseudo-binary mixture (see, for example, Lockett, 1986). These methods suffer from one or more drawbacks:
1. They ignore the impact of other compounds on the thermodynamic behaviour of the mixture,
2. They can lead to improper estimates of the slope (e.g. negative values),
3. They apply only to distillation, and cannot be used for absorption or stripping operations.

The method we propose now avoids all of these drawbacks.

2. The Design Component

2.1 Definition and Slope Calculation

The design component is defined to be that component which we seek to eliminate from the column section for which it is defined. The concept of the "design component" can be interpreted as an extension of the HK/LK methodology to multicomponent systems with multiple product streams. The slope of the design component is obtained as follows, where y_D^* is the equilibrium concentration:

$$m_D = \frac{y_D^*(x_D + \Delta x_D) - y_D^*(x_D)}{\Delta x_D} \tag{7}$$

A rigorous procedure to estimate the slope is as follows:
1. Carry out a bubble point calculation using, as a basis, the temperature and the composition of the liquid on the tray in question. This will provide the equilibrium vapor composition $y_D^*(x)$
2. Add a small amount Δx_D to the mole fraction of the design component $x_D + \Delta x_D$
3. Normalize the liquid fractions
4. Carry out a second bubble point calculation to get $y_D^*(x_D + \Delta x_D)$
5. Compute the slope from Equation (7)

It should be noted that the second flash calculation in step 4 of the above procedure is to be carried out at the same temperature used for the flash calculation in step 1. This method is easily applied to absorption and stripping where two key components can be difficult or impossible to identify.

2.2 Analytical Approximations to Design Component Flash

In this section we present two analytical approximations that are easily programmed in a spreadsheet, that are capable of good to excellent estimations of the design component slope and that require no more information than is routinely available from a flowsheet simulation package.

The vapor liquid equilibrium surface for a multicomponent system can be represented by

$$y_i^* = \alpha_i \cdot x_i / S \quad \text{with} \quad S = \sum_{j=1}^{c} \alpha_j \cdot x_j \quad \text{and} \quad \alpha_i = K_i / K_D \tag{8}$$

It is important to recognize that this equation is valid at all points on the equilibrium surface regardless of the constancy of the relative volatilities.

The slope of the VLE surface in the primary direction taken by the design component, m_D, is given approximately by:

$$m_D = m_{\alpha,D} - \Delta m_D \tag{9}$$

where $m_{\alpha,D}$ is the slope for systems where the relative volatilities are assumed constant, and where Δm_D is a correction for composition dependent relative volatilities. These two terms are defined by:

$$m_{\alpha,D} = \frac{1}{S} - \frac{x_D}{S^2} \cdot \frac{1-S}{1-x_D} \tag{10}$$

$$\Delta m_D = \frac{x_D}{S^2} \cdot \left(\sum_{k=1}^{c} \left(\frac{\partial \alpha_k}{\partial x_k} \right) \cdot x_k \right) \tag{11}$$

A complete derivation of these results is provided by Taylor and Duss (2018).
From the definition of the relative volatilities we find:

$$\left(\frac{\partial \alpha_i}{\partial x_D} \right) = \frac{1}{K_D} \cdot \left(\left(\frac{\partial K_i}{\partial x_D} \right) - \alpha_i \cdot \left(\frac{\partial K_D}{\partial x_D} \right) \right) \tag{12}$$

To make use the approximation derived above we need the mole fraction derivatives of the K-values. Our proposal is to approximate the mole fraction derivatives using mole fraction and K-value differences. For example:

$$\left(\frac{\partial K_i}{\partial x_D} \right) \approx \frac{(K_{i,s} - K_{i,s+1})}{(x_{D,s} - x_{D,s+1})} \approx \frac{(K_{i,s} - K_{i,s-1})}{(x_{D,s} - x_{D,s-1})} \approx \frac{(K_{i,s-1} - K_{i,s+1})}{(x_{D,s-1} - x_{D,s+1})} \tag{13}$$

where s is the stage index. In other words, we use the differences between the K-values and mole fractions on two adjacent stages or, in the third approximation, the two stages either side of the one of immediate interest denoted by s. For the topmost stage it is necessary to use the downwards differences. Conversely, for the bottom stage it is necessary to use the upwards difference. The identity of the design component may change at feed stages and at intermediate product take-off points. It is, however, essential not to change the identity of the component designated by the subscript D when using Eq(8) for such a stage. Other circumstances that require some care in taking the derivatives will be discussed in Taylor and Duss (2018).

3. Case Studies

As part of this investigation we have looked at a wide range of column designs: a 74 valve-tray C4 splitter, a 54 valve-tray BTX column, a C4-C5 splitter, multiple columns from a light ends sequence (Luyben 2013), a sidestream column, a simple absorber, a more complicated absorber with multiple feeds, a reboiled absorber, and a reboiled stripper. In the latter we have non-ideal distillation, extractive distillation (Holland, 1981), and azeotropic distillation processes (Seader and Henley, 2006).
The models considered are identified in the discussion and on the figures by the following acronyms:
      Design Flash: Rigorous method. Eq(7).
      CRV: Constant relative volatility model, Eq(10).
      XVRV: ApproXimate Variable Relative Volatility model, Eq(9-13).
      AVRV: Accurate Variable Relative Volatility model, Eq(9-11,12).

Here "accurate" refers to the computation of the K-value derivatives, not to the model itself (which may not always be better than the other methods listed).

We illustrate the implications for design by looking at the impact of the slope on section efficiency using Eq(1-4). The numbers of transfer units were obtained using the Chan and Fair correlation and typical values are 2 for the gas phase and 3-6 for the liquid. The section efficiency has been estimated assuming the numbers of transfer units to remain constant in each column section (but are not necessarily the same in all sections of a column). The efficiency difference plots (Figures 2 to 4), show the deviations of the outcome of analytical approximations relative to the design flash slope.

3.1 Depropanizer

Our first example is the depropanizer from the distillation train described by Luyben (2013). The specifications were selected to obtain a bottoms product that contains no more than 0.1% propane and an overhead that has no more than 0.02% n-butane. The design component in the rectifying section is n-butane and for the stripping section, the design component is propane.

The slopes of the equilibrium line computed from the methods we are considering is shown in Figure 2. The CRV model is, in fact, closer to the design flash method than either of the approximations that consider K-value derivatives. Efficiency discrepancies also are shown in Figure 2 (right). For this column the differences do not exceed 3.5% (and often are much less). Thus, any of the approximate methods is adequate for design purposes; the CRV model being simplest is suggested here.
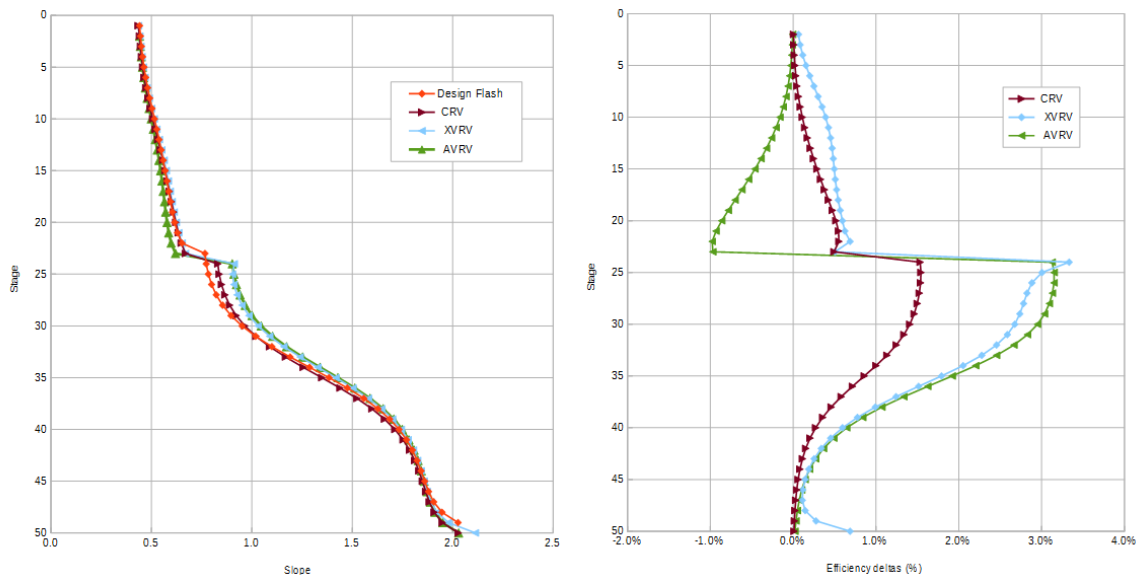

Figure 2: (a) Slope profiles (left), and (b) efficiency differences (right) for depropanizer from Luyben (2013). Design components are n-butane in the rectifying section and propane in the stripping section.

3.2 Ternary Nonideal Distillation

This significantly more challenging example is taken from Doherty and Malone (2001) who refer to it as the De Rosier problem. The task is to design a distillation column to separate a feed of 20 mol/s methanol, 10 mol/s isopropanol, and 20 mol/s water. The bottom product is to contain no more than 0.5 mol% methanol and the distillate is to contain at least 99 mol% methanol but no more than 50 ppm water.

Following Doherty and Malone, the NRTL model was used for the activity coefficients. They estimate the minimum reflux as 5; we used a value of 8 in this example and specified the bottoms product rate at 30 mol/s. We found that 99 equilibrium stages with the feed to stage 20 were needed to get the distillate product below 50 ppm water. Since this is the key specification, the design component in the top section of the column must be water (and isopropanol in the bottom section).

Slope profiles and efficiency differences relative to the design flash method are shown in Figure 3. The difference between efficiencies estimated with the XVRV model is less than 1.5%. The AVRV model is barely distinguishable from the XVRV model (which is why it cannot be seen in the figure). The efficiency discrepancy for the CRV model is less than 2% except for a few stages near the feed where it is between 4 and 5.5%.
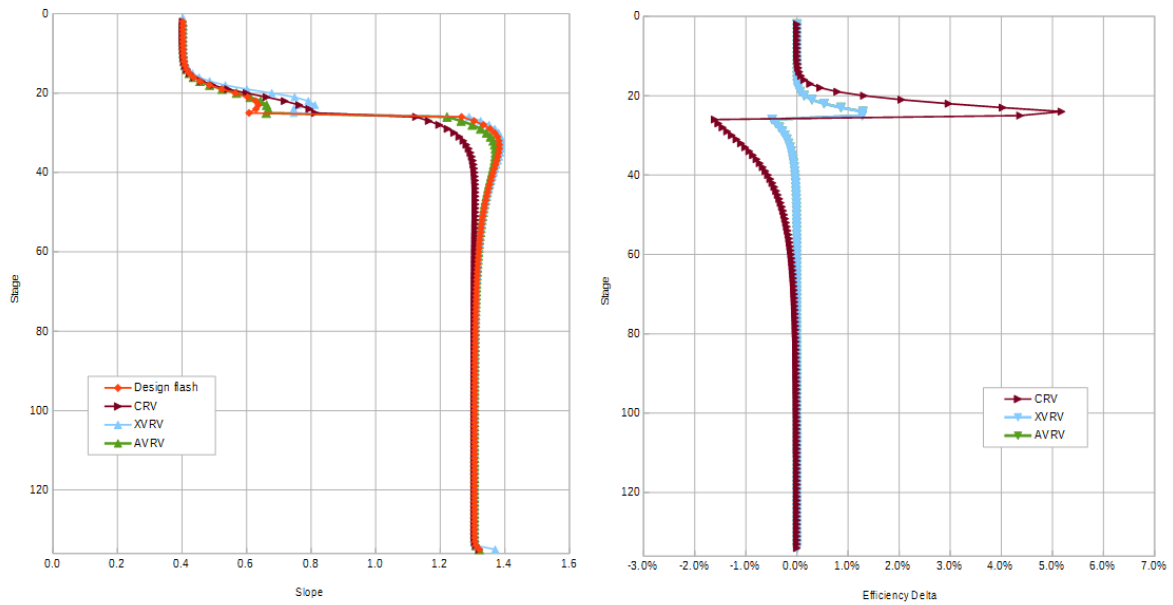
Figure 3: (a) Equilibrium slope profiles (left), and (b) efficiency differences relative to design flash in nonideal distillation process. Design components are water in the top section, and methanol below the feed.

3.3 Extractive Distillation

Extractive distillation columns are more difficult to analyse because they are likely have multiple sections with corresponding changes in design components. The purpose of this example, from Holland (1981) is to separate the azeotropic mixture acetone – methanol using water as an entrainer. The design components are water in the top section, methanol in the section between the feeds and acetone in the bottom section.

The slopes of the equilibrium line and efficiency differences (relative to the design flash value) are shown in Figure 4. With the exception of the CRV model around the feed stages, none of the slope models has an efficiency delta of more than 5%. The methods that take relative volatility derivatives into account (XVRV and AVRV) rarely differ by more than 2% from the design flash method.
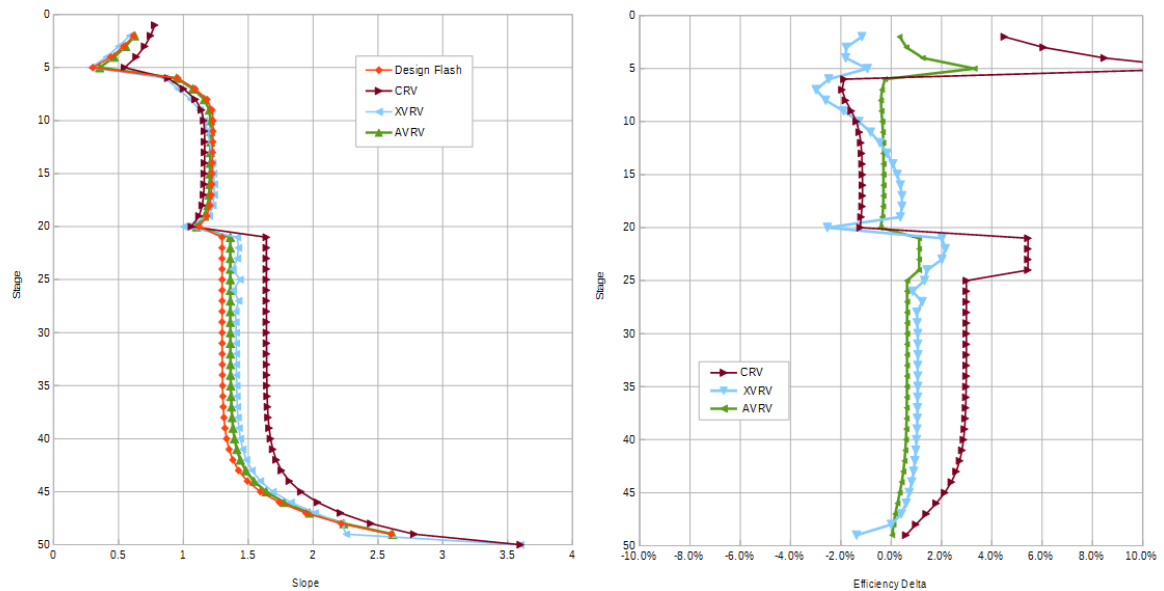

Figure 4: (a) Equilibrium slope profiles (left), and (b) efficiency differences relative to design flash in extractive distillation process. Design components are water in the top section, methanol between the feeds, and acetone in the bottom section.

4. Conclusions and Recommendations

In this paper we have proposed a new method for estimating the slope of the equilibrium line for multicomponent systems based on differentiation of the phase equilibrium surface with respect to the mole fraction of the *design component*. That component is defined as that which we seek to eliminate from the mixture in a particular section of the column. There is only one design compound per column section. The concept can be easily applied to absorber and stripper columns.

We have provided two simple approximate analytical formulae that will allow the easy calculation of the design slope from the results provided by any column simulation program. The CRV (Locally Constant Relative Volatility) model works reasonably well for hydrocarbon systems (with or without light gases). More interestingly, it also seems to work well for *some* non-ideal systems where the relative volatility is definitely not independent of composition. For such cases the XVRV method generally is superior as long as we pay attention to the approximation of the K-value derivatives. Differences between efficiencies estimated using the simplest analytical approximation and the rigorous design flash method are rarely more than 5%, and often are less than 2%. We therefore appear to have a straightforward method for estimating the slope that requires no specially programmed flash calculations and which is easily implemented in any spreadsheet using only information available from a standard flowsheet simulation, i.e. equilibrium liquid and vapor compositions of each stage.

The design flash concept has been used for the design of packed columns by Sulzer for many years and has proven to be successful. The simplified method presented here allows others easily to use the method.

Symbols

c	(-)	Total number of components
H_G, H_L	(m)	Heights of transfer unit in gas and liquid phases
H_{OG}	(m)	Overall height of transfer unit
$HETP$	(m)	Height equivalent to a theoretical plate
m	(-)	Slope of the equilibrium line
N_G, N_L	(-)	Number of transfer units in gas and liquid phases
N_{OG}	(-)	Number of transfer units overall gas
x_i, y_i	(-)	Mole fraction in the liquid, vapour
α	(-)	Relative volatility
$\Delta m_{\alpha D}$	(-)	Slope correction for composition dependency
η	(-)	Efficiency
λ	(-)	Stripping factor = $m / (L/G)$

Subscripts/Superscripts

D	Pertaining to design component
i,j,k,A,B	Compound indices
Point, Tray, Section	Denoting type of efficiency
$*$	Denoting equilibrium

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