Extending Murphree Tray Efficiency from Mass to Heat Transfer in Distillation

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In this work an extension of the well-known Murphree tray efficiency is proposed. In difference to the original model, vapor and liquid streams leaving the stage have different temperatures. In order to model the vapor temperature, the Murphree efficiency equation is used to calculate the change of vapor temperature between vapor inlet temperature and liquid outlet temperature, which will only be reached at full efficiency. As a result, vapor temperature will be much nearer to its dew point, which better matches reality.

1. Introduction

Equilibrium stage models have a long history in modelling and simulation of distillation processes. Although their limitations are well known and a physically more justified type of model – the mass transfer model – is available, equilibrium stage models are still widely used in process engineering.

When simulating tray columns, the equilibrium stage model is often used in conjunction with the Murphree tray efficiency equation. This equation takes into account the effects of limited mass transfer with the assumption that vapor and liquid will not fully reach the condition of vapor-liquid equilibrium. Instead, the vapor phase is described to cover only a fraction of the composition change between vapor inlet and equilibrium with the liquid phase. However, while characterizing the mass transfer between both phases as limited and not reaching the equilibrium condition, heat transfer is described as achieving equilibrium - liquid and vapor stream leaving the stage have the same temperature. This leads to the fact that the vapor is not at its dew point but subcooled, while the liquid will always be at its boiling point. This artefact often leads to unrealistic top vapor temperatures, especially in the case of stripping columns.

2. Distillation tray efficiency

The first models to describe distillation were equilibrium models. They were based on the assumption that vapor and liquid leaving a tray are in thermodynamic equilibrium. This means, that all components have the same chemical potential μ_i in both phases and that both phases have the same temperature T. However, soon it was clear that on a real distillation tray total equilibrium is never reached and that vapor and liquid streams just approach this state. Therefore, different formulations of tray efficiency have been proposed to describe this behaviour. The most common definition was proposed by Murphree (1925). In his publication Murphree presented a method for "Rectifying Column Calculations" which is based on a mass transfer approach. Although he used a different formulation in his original publication, the so-called Murphree efficiency is usually used in the following form (*IN* denotes the incoming vapor stream, which is usually the vapor stream leaving the lower stage $n+1$ but could also be a vapor feed or a mixture of both):

$$y_{n,i} = y_{IN,i} + \eta\left(y_{n,i}^* - y_{IN,i}\right) \tag{1}$$

The efficiency η can be seen as a mass transfer parameter which describes, how much vapor composition changes from the inlet composition y_{IN} to the outlet composition y_n while approaching the equilibrium composition y^* (which is in thermodynamic equilibrium with the liquid phase on tray n). Therefore, $\eta = 1$ describes negligible mass transfer resistance which results in thermodynamic equilibrium of liquid and vapor

streams leaving a tray. On the other hand, $\eta = 0$ describes no mass transfer at all resulting in an unchanged vapor composition while passing the tray.

The advantage of this formulation is that it can be easily incorporated in the equilibrium tray model. If the efficiency is known, the mathematical column model including the efficiency can be solved with basically the same effort as for the pure equilibrium model.

While at the time of Murphree's publication the detailed modelling of a distillation column using the mass transfer approach was not possible due to its numerical requirements, mass transfer models for distillation processes are available now for some decades. These models allow the detailed description of mass transfer and are therefore well-founded with respect to physics. Many distillation processes can only be described reliable using mass transfer models.

However, despite the advantages of mass transfer models, equilibrium stage models using Murphree efficiency are still widely used as well in industrial practice as in academic research. This is due to the following reasons:

- Equilibrium stage models are computational much less demanding than mass transfer models. This is very important in cases which are already computational demanding (e.g. full plant simulation or flowsheet optimization).
- In many cases the equilibrium stage model with Murphree Efficiency fits reality very well.
- Mass transfer models require a full set of thermodynamic properties including transport properties, while the equilibrium model is based on the thermodynamic description of equilibrium and enthalpies only.
- Many different mass transfer correlations have been proposed in literature. However, the selection of the appropriate model is not straight forward but it will affect the simulation results.

3. Vapor temperature using Murphree tray efficiency

In modern simulators an equilibrium tray n using Murphree efficiency may be implemented as follows:

$$0 = L_{n-1}x_{n-1,i} + V_{n+1}y_{n+1,i} - L_n x_{n,i} - V_n y_{n,i} \tag{2}$$

$$0 = L_{n-1}h^L(\boldsymbol{x}_{n-1}, T_{n-1}, p_{n-1}) + V_{n+1}h^V(\boldsymbol{y}_{n+1}, T_{n+1}, p_{n+1}) - L_n h^L(\boldsymbol{x}_n, T_n, p_n) - V_n h^V(\boldsymbol{y}_n, T_n, p_n) \tag{3}$$

$$y_{n,i}^* = k_i(\boldsymbol{x}_n, \boldsymbol{y}_n^*, T_n, p_n)x_{n,i} \tag{4}$$

$$y_{n,i} = y_{IN,i} + \eta\left(y_{n,i}^* - y_{IN,i}\right) \tag{5}$$

$$1 = \sum_{i=1}^{C} y_{n,i}^* \tag{6}$$

$$1 = \sum_{i=1}^{C} x_{n,i} \tag{7}$$

For sake of simplicity equations are stated for a stage without feed.

The Murphree tray efficiency is based on a mass transfer approach for the change of vapor composition during tray transition. While this approach is reasonable, Murphree does not consider heat transfer between phases: "The sensible heat of the gases is neglected in the heat balance." (Murphree, 1925) Therefore, only one temperature T_n is considered per tray which applies to both liquid and vapor phase. However, the dew/boiling condition is stated only for the liquid phase $\boldsymbol{x}$ and the corresponding vapor phase in equilibrium $\boldsymbol{y}^*$, but not for the vapor stream composition $\boldsymbol{y}$. Thus, while the liquid is always at its boiling point, the vapor may not. The vapor stream has the same temperature as the liquid stream, which is only in the case of $\eta = 1$ the dew temperature (as in this case vapor composition $\boldsymbol{y}$ is equal to equilibrium composition $\boldsymbol{y}^*$). In all other cases, the vapor stream is subcooled.

This is illustrated by the example in Figure 1 on the left for the system benzene/o-xylene at 1 bar. Composition of inlet streams (y_{IN} and x_{n-1}) and total reflux ($L = V$) were chosen in favour of a simple and clear illustration. In this case the Murphree efficiency is set to 0.7. Therefore, the outlet vapor composition does not reach the equilibrium composition y^*, but changes only 70 % of the range from y_{IN} to y^*. However, the temperature of the outlet vapor is set to the temperature of liquid phase x and equilibrium phase y*. Therefore, the outlet vapor is strongly subcooled, as can be seen in Figure 1 on the left.
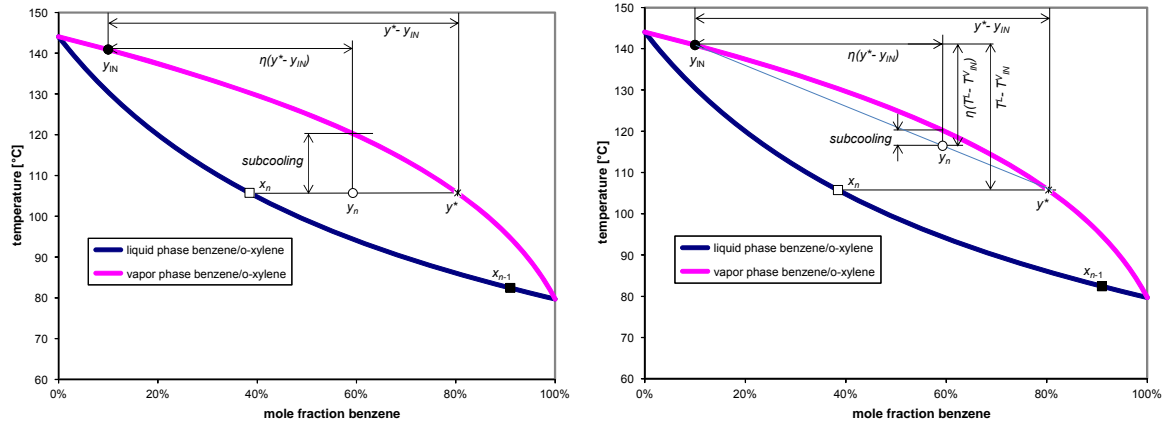
Figure 1: Effect of Murphree Efficiency (η = 0.7) on vapor temperature for the system benzene/o-xylene at 1 bar and total reflux ($L = V$): standard (left) and extended Murphree (right).

Conditions for the example in Figure 1 were chosen in a way to achieve a strong effect. Therefore, in real world distillation models it will not be that strong. However, in many cases it is considerable. These are for example systems with high separations factors (wide difference in vapor pressures/boiling points of substances) and big changes in composition over the top trays. In these cases especially the top vapor temperature is calculated wrong. The calculated vapor temperature also affects the energy balance and thus vapor and liquid streams.

4. Extended Murphree tray efficiency

To tackle the problem described above, an extension of the Murphree efficiency is proposed. This extension is based on the same considerations as the original mass transfer efficiency. The tray is considered as an ideal mixed liquid phase, which is in contact with the passing vapor phase. Mass transfer resistance is assumed to be totally in the vapor phase. In this case mass transport will take place between the boundary layer of the liquid phase (y^*) and the bulk vapor (y). Thus, the driving force is (y^* - y). Due to the finite mass transfer coefficient and area mass transfer will not be complete and equilibrium is never reached. The Murphree efficiency is a measure for the incompleteness of this mass transfer.

On the other hand, in the Murphree/equilibrium model it is believed, that the vapor temperature instantaneously reaches the liquid temperature. The analogy between mass and heat transfer is well known (e.g. Chilton and Colburn, 1932 or Martin, 2005) and therefore it seems questionable, that thermal equilibrium is reached, while with identical flow pattern mass transfer equilibrium is not.

Instead, heat transfer between the hot vapor stream (coming from the tray below with a higher temperature) and the liquid phase may also be modelled as non-complete. Based on the analogy between mass and heat transfer it can be shown, that the relation between the corresponding dimensionless numbers (Nusselt for heat and Sherwood for mass transfer) is given by the Lewis number (which is the ratio of Schmidt and Prandtl numbers, both based on physical properties only) with the exponent m (typically about 1/3). As the Lewis number has the order of magnitude of one for many systems, it can be concluded that heat transfer resistance is similar to mass transfer resistance. Therefore, the Murphree equation (1) is used to model the new variable vapor stream temperature T^V also (12): it is assumed, that heat transfer between the phases is as effective as mass transfer. The tray model then becomes:

$$0 = L_{n-1}x_{n-1,i} + V_{n+1}y_{n+1,i} - L_n x_{n,i} - V_n y_{n,i} \tag{8}$$

$$0 = L_{n-1}h^L(\boldsymbol{x}_{n-1}, T_{n-1}^L, p_{n-1}) + V_{n+1}h^V(\boldsymbol{y}_{n+1}, T_{n+1}^V, p_{n+1}) - L_n h^L(\boldsymbol{x}_n, T_n^L, p_n) - V_n h^V(\boldsymbol{y}_n, T_n^V, p_n) \tag{9}$$

$$y_{n,i}^* = k_i(\boldsymbol{x}_n, \boldsymbol{y}_n^*, T_n^L, p_n)x_{n,i} \tag{10}$$

$$y_{n,i} = y_{IN,i} + \eta\left(y_{n,i}^* - y_{IN,i}\right) \tag{11}$$

$$T_n^V = T_{IN}^V + \eta(T_n^L - T_{IN}^V) \tag{12}$$

$$1 = \sum_{i=1}^{C} y_{n,i}^* \tag{13}$$

$$1 = \sum_{i=1}^{C} x_{n,i} \tag{14}$$

The advantage of this approach is that by adding just one new variable (T^V) and one equation (12) per tray, the subcooling described above can be strongly decreased. As the efficiency is already known from the standard Murphree/equilibrium model, no additional parameters need to be determined. Due to the addition of just one linear equation, computational demand does not increase considerably compared with the standard Murphree/equilibrium model. Note, that the extended Murphree model is equivalent to the standard Murphree model, if the efficiency η in equation (12) is set to 1. In this case vapor and liquid temperatures are identical (no heat transfer resistance).

Figure 1 shows the extended Murphree model on the right for the same conditions as in the previous example. Using the extended Murphree model, the vapor temperature is calculated using the same linear equation as for the vapor composition, the point y_n lies on a straight line between y_{IN} and y^*. As a result, the vapor temperature is calculated nearer to the equilibrium curve and thus less subcooled (subcooling is decreased by 70 %). Again it must be stated that the example was selected to clearly show the differences. In typical distillation systems the vapor temperature will be much nearer to the dew point.

In principle, efficiencies for mass and heat transfer may be different. For example, heat transfer efficiency could be calculated based on the Chilton and Colburn analogy. However, as Murphree efficiency is already a rough model of mass transfer, the differentiation between both efficiencies seems questionable in practice.

5. Applications

5.1 Modelling a stripper column

The effect of the extended Murphree efficiency is strongest, when temperature differs considerably between stages. This is very often the case for stripper columns. Figure 2 shows calculation results (VLE modelled using NRTL) as well as plant measurements for a stripper column with trays. Based on process knowledge, the column is modelled with a Murphree efficiency of $\eta = 0.4$. As the liquid feed is heated up on the upper stages by the internal vapor stream, the column exhibits a strong temperature gradient. The measured top vapor temperature is higher than the feed temperature. Using the standard Murphree model (left diagram), the top vapor temperature equals the top tray temperature which is very near to the feed temperature. Using the extended Murphree model (right diagram) liquid and vapor temperatures are distinct and the top vapor temperature much better fits the measured process value.
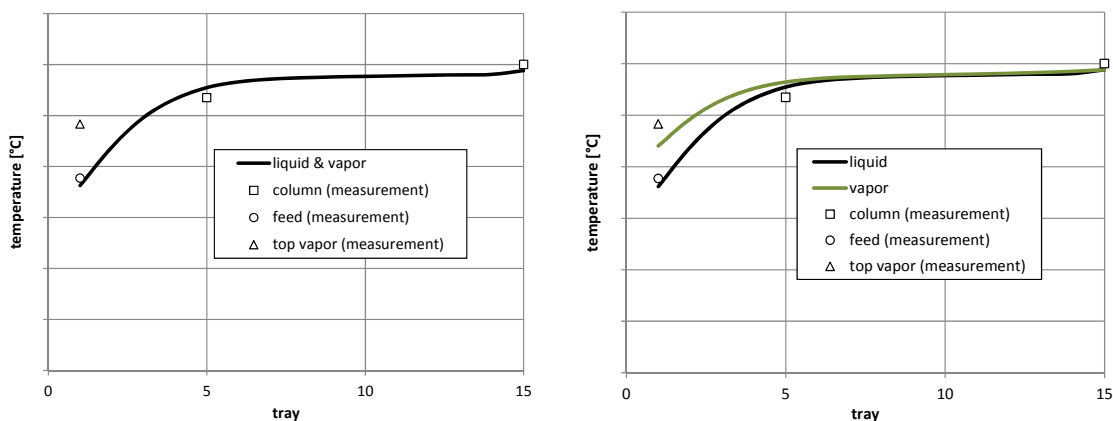

Figure 2: Temperature profiles for a stripper column. Standard (left) and extended Murphree (right).

5.2 Superheated vapor feed

For this (academic) example a distillation column with 28 stages ($\eta = 0.5$) is run with an equimolar feed of benzene/toluene/o-xylene at 1 bar. The mole fraction of o-xylene is specified to be 0.1 at the top and 0.9 at the bottom. The vapor feed is superheated by 40 K.
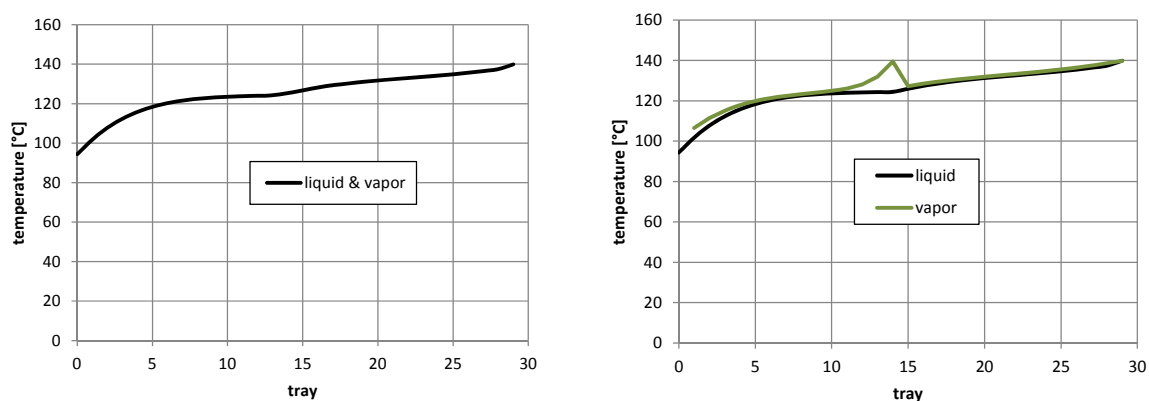
Figure 3: Temperature profile for an example separation with superheated (40 K) vapor feed. Standard Murphree model on the left and extended Murphree model on the right.

The results for the two models are depicted in Figure 3: On the left side, vapor and liquid temperature can be seen for the standard Murphree model. Due to the forced thermal phase equilibrium both temperatures are identical. The extra enthalpy of the feed stream is taken into account for the energy balance, but it has no effect on the vapor temperature profile. On the right hand side the result for the extended Murphree model can be seen. Here, vapor and liquid temperature are distinct and the influence of the superheated feed can be seen over several stages. This seems much more plausible, although this is not supported by process data.

5.3 Using the extended Murphree tray efficiency as a modelling tool

The extended Murphree efficiency has properties beneficial for numerical simulation and optimization inside process simulators. It allows for modelling of totally inactive stages, in which neither the vapor temperature nor the vapor composition is affected. This is in contrast to the standard Murphree model, where vapor temperature and thus the flowrates changes even at $\eta = 0$.

In this example a distillation column with 10 (effective) equilibrium trays is run with a mixture of 100 kmol/h benzene/toluene/p-xylene and feed composition 30/30/40 mol-% at 1 bar. VLE is modelled by NRTL. The reboiler is modelled as a single flash stage (kettle-type) and a total condenser is used. The bottom product is specified at 98 mol-% and the top product at 1 mol-% p-xylene. In this case study three variants are examined. In case A the column is modelled with 10 equilibrium stages at full efficiency. In case B the column is modelled with 11 stages of which stage 3 has an efficiency of 0, while the others are operating at $\eta = 1$. In case C the column is modelled with 11 stages and stage 2 and 3 both have an efficiency of $\eta = 0.5$. Case B is thermodynamically identical to case A, as the inactive stage 3 has no impact on the mass or energy balance. However, in case C the column has to be operated at a higher reflux ratio r in order to meet the specifications (c.f. Table 1). Therefore, two stages with $\eta = 0.5$ are less efficient than one stage with full efficiency.

Table 1: Energy requirements, reflux ratio r and boilup ratio b (molar vapor fraction of reboiler) of the three cases.

Case	$\dot{Q}_{Reboiler}$	$\dot{Q}_{Condenser}$	r	b
	kW	kW	[-]	[mol/mol]
A	1672	-1654	1.96	0.80
B	1672	-1654	1.96	0.80
C	1772	-1755	2.14	0.81

A geometric explanation for this phenomenon is given in Figure 4. The summed composition change contributions of stages 2 and 3 for $\eta = 0.5$ (black step lines) are less than the change occurring in one stage at full efficiency (blue step lines). This causes a higher reflux ratio and thus higher energy consumption in the reboiler as well as in the condenser, when the specifications have to be met. For illustrative purposes the reflux ratio is kept constant in Figure 4.

When this model is used in an optimization context and the stage efficiencies are treated as free variables, the optimal values tend to be 0 or 1, when the total energy is part of the cost function to be minimized. The optimization problem can be formulated without binary variables for the efficiencies (i.e. stage existence), turning the mixed integer nonlinear program (MINLP) into a simpler nonlinear program (NLP). A similar

observation was made by Dowling (2015) for their formulation of bypass efficiency. Compared to their proposed bypass formulation, the extended Murphree efficiency has a simpler equation form as the virtual mixing and splitting nodes can be omitted.
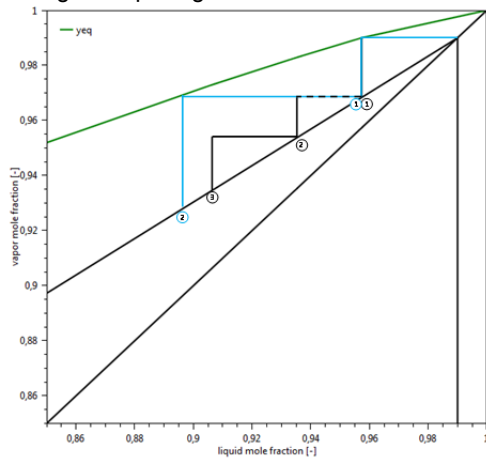

Figure 4: McCabe-Thiele-like plot of the concentration profile of the example separation process for cases A and C. This diagram shows the composition of the light-boiling pseudo component (sum of benzene and toluene). The solid green line represents the equilibrium vapor composition y^*.

6. Conclusions

In this work, an extension of the well-known Murphree stage efficiency is proposed. In contrast to the standard Murphree model, not only mass but also heat transfer resistance is considered. Therefore, results for vapor temperature are much more plausible for columns with a high temperature gradient. As only one additional equation and variable per tray is added to the set of equations to solve, it is simple to implement and does not increase computational demand considerably. Besides its benefits in acurately modelling the physical system, it can be also used as a tool for model specification, as it allows the user to turn stages on and off by changing the efficiency, without the need to modify the model structure. Therefore it may also be used in process optimization.

Nomenclature

$*$	equilibrium state
C	number of components
i	component index
IN	incoming stream
k_i	VLE equilibrium coefficient of component i
L	molar liquid flowrate
n	tray number, counting top-down
η	Murphree efficiency
T	temperature
p	pressure
V	molar vapor flowrate
x_i	mole fraction of component i in the liquid phase
y_i	mole fraction of component i in the vapor phase

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