A Simple Application of Murphree Tray Efficiency to Separation Processes

J.J. VASQUEZ-ESPARRAGOZA, J.C. POLASEK, V.N. HERNANDEZ-VALENCIA, M.W. HLAVINKA,
Bryan Research & Engineering, Inc.,
Bryan, Texas

J.A. BULLIN,
Chemical Engineering Department, Texas A&M University,
College Station, Texas

ABSTRACT

Vapor-liquid equilibrium is predicted by using the Soave modification of the Redlich-Kwong equation of state (EOS). The concept of equal fugacities is used to calculate the equilibrium constant, Ki=yi/zi, then, it is shown how the Murphree tray efficiency can be applied on the liquid or the vapor phases to modify that constant. The derivatives needed are calculated numerically, and it is shown that for absorbers and distillation columns, Murphree tray efficiency applied this way can be used to simulate the actual number of stages. Murphree tray efficiency values can be specified for one, several or all of the components on any stages of a column. A dehydration example is shown, the dew point depression values of a mixture of water-gas, using a triethylene glycol solution for dehydration purposes, are calculated by incorporating the method into a process simulator program called PROSIM® and compared with the values reported in the literature.

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INTRODUCTION

For a vapor-liquid separation process, considering that both liquid and vapor phases are mixed perfectly, a measure of the efficiency of distillation for a component i on the stage j, is defined by Murphree [1] as

$$E_V = 1 - e^{-S_j Q} = \frac{y_{i,j} - y_{i,j+1}}{y^*_{i,j} - y_{i,j+1}} \qquad (1a)$$

where, $S_j = \left(\frac{\partial x}{\partial y}\right)_{x=x_j}$ and Q is an average value of the product among the mass transfer coefficient, the area of contact per mole vapor, and the time of liquid-vapor contact. If the definition is upon the liquid composition, this efficiency is given by

(1b)

$$E_L = \frac{x_{i,j} - x_{i,j-1}}{x^*_{i,j} - x_{i,j-1}}$$

The above equations represent the change in composition on a stage with respect to that change when there exists a thermodynamic equilibrium between phases. In the above equations, $y_{i,j}$ and $x_{i,j}$ are the vapor and liquid composition, respectively, and $y^*_{i,j}$, $x^*_{i,j}$ are the composition of the vapor and liquid phases that would be in equilibrium with the other phase that actually leaves the stage (stages are numbered from top to bottom).

In general. these efficiencies are less than unity; however, in a big diameter column, the liquid or vapor leaving a plate has a slightly different composition than the liquid or vapor that reaches the next stage. According to its definition, this results in an efficiency greater than one hundred percent.

By use of an equation of state to estimate the fugacity coefficients of a mixture in equilibrium, the concept of equality of fugacities can be modified to include the Murphree type efficiency. For simulation purposes, this concept is as important as the need of having an actual number of stages in the simulation. A description of how this method can be applied is presented, and an application example to dehydration units is shown.

BACKGROUND

The Murphree tray efficiency has been used for a long time to relate the theoretical number of stages with the actual trays in a distillation column or absorber. This efficiency can be based upon the liquid or the vapor composition on a particular stage at its conditions of temperature and pressure.

Holland and McMahon [2] presented some limitations of the Murphree-type efficiencies. They showed that efficiencies based on the vapor phase could take on values within the whole range of real numbers. This is sometimes due to the performance of the efficiency as a deviation of the stage model rather than the degree of completion of the mass transfer model.

The use of the component Murphree tray efficiency for separation of binary mixtures has been described by several authors [3, 4, 6, 7]. Some of them show how to use it for multicomponent mixtures. However, a simple way to apply Murphree tray efficiency to liquid-vapor separation processes has not been shown.

Edmister [7] presented a description of different types and uses of plate efficiencies. A new efficiency was defined as a multiplier of the absorption or stripping factor on each stage. Takamatsu et al. [8] showed a new solution process for multicomponent distillation columns. They took the liquid mole fractions to be the independent variables and their difference between consecutive iterations to be the functions to be zeroed. Their procedure seems to be stable and fast, and the application of the Murphree efficiency includes a new step in solving the liquid-vapor composition non-equilibrium equations with a successive substitution method.

In general, the values of the Murphree tray efficiencies are not equal throughout the column. Further, they usually are not equal for the different components in a mixture, even on the same stage.

When describing a mathematical model of a liquid-vapor separation process, the liquid and vapor phases are related by the equilibrium constant $K_{i,j}x_{i,j} = y_{i,j}$, or, in terms of component flow rates

$$K_{i,j}\frac{l_{i,j}}{\sum l_{i,j}} = \frac{v_{i,j}}{\sum v_{i,j}} \qquad (2)$$

where *x* and *y* are component *i* liquid and vapor molar compositions respectively, and *l* and $v_{i,j}$ are component molar flow rates on each stage, *j*.

Using this equation and the vapor Murphree stage efficiency definition in Equation (1a), the resulting equation to add to the model is

$$E_V = \frac{v_{i,j} - v_{i,j+1}\dfrac{\sum v_{i,j}}{\sum v_{i,j+1}}}{\dfrac{K_{i,j}\sum v_{i,j}}{\sum l_{i,j}} l_{i,j} - v_{i,j+1}\dfrac{\sum v_{i,j}}{\sum v_{i,j+1}}} \qquad (3)$$

for each stage *j* and component *i*. The efficiencies introduce another *n* stages by *c* component equations to the model, with the efficiencies as variables. However, in order to satisfy the summation of molar composition to be unity, one of those efficiencies must be dependent. Thus, the problem consists in solving a number of $\left[n \times (c-1)\right]$ more equations added to the model system.

Another approach to incorporate the Murphree efficiency into the model is to work with the vapor component flow rates, $v_{i,j}$, and the molar compositions, and then normalize the results for the new ones, $y_{i,j}$.

$$y_{i,j} = E_V\left(K_{i,j}x_{i,j} - y_{i,j+1}\right) + y_{i,j+1} \qquad (4)$$

where

$$y_{i,j} = \frac{v_{i,j}}{\sum v_{i,j}}\ ;\ x_{i,j} = \frac{l_{i,j}}{\sum l_{i,j}} \qquad (5)$$

The approach presented here consists of adjusting the value of the equilibrium constants and keeping the model equations unmodified. However, some problems can be encountered because of the calculation of a mixture composition which is not in thermodynamic equilibrium with another mixture (phase). For simulation purposes, Murphree tray efficiency modifies the equilibrium constants, and changes the internal flow rate in such a way that the column is always in material balance.

ALGORITHM

A method of predicting liquid-vapor equilibria is to estimate the fugacities of the components in both phases and compare them until their difference is smaller than a predetermined small value. The most common method to estimate the fugacities is by use of an equation of state. The basic condition for thermodynamic equilibrium between two phases states that

$$\hat{f}_i^L = \hat{f}_i^V \qquad (6)$$

where $\hat{f}_i$ represents the fugacity of component *i*, and the superscripts *L* and *V* are used to represent the liquid and vapor phases respectively.

If the fugacity coefficient is defined as $\hat{\Phi}_i = \dfrac{\hat{f}_i}{x_i P}$, and at equilibrium $P^L = P^V$, where *P* is the pressure of the system, and $\hat{\Phi}_i$ is the fugacity coefficient of component *i* with a liquid composition *x* and vapor composition *y*,

$$\hat{\Phi}_i^L x_i = \hat{\Phi}_i^V y_i \qquad (7)$$

Taking logarithms of both sides and rearranging,

$$\frac{y_i}{x_i} = K_i = e^{\left[ln\hat{\Phi}_i^L - ln\hat{\Phi}_i^V\right]} \tag{8}$$

For a Murphree efficiency based in the vapor phase, the composition $y_{i,j}$ can be calculated by rearranging equation (1)

$$y_{i,j} = E_V y_{i,j}^* + (1 - E_V) y_{i,j+1} \tag{9}$$

where $y_{i,j}^*$ is the composition value in equilibrium with the liquid on that stage. Substituting $y_{i,j}^*$ by its value in equilibrium with the liquid phase on stage *j* ($K_{i,j} x_{i,j}$) given by Equation (8) yields

$$y_{i,j} = E_V e^{\left[ln\hat{\Phi}_i^L - ln\hat{\Phi}_i^V\right]} x_{i,j} + (1 - E_V) y_{i,j+1} \tag{10}$$

Equation (10) is used to modify the equilibrium constant of component *i* on stage *j*.

The application is simple. Whenever the *K* value is needed, instead of using the equilibrium constant $K_{i,j} = \frac{y_{i,j}}{x_{i,j}}$, the $K_{i,j}$ used is the one that has been modified by the Murphree tray efficiency. For example, using the composition in the vapor phase, one obtains a value of $K_{i,j}$ by an equation of state or some other means. The value of $y_{i,j}$ in equilibrium with $x_{i,j}$ by use of the equilibrium equation $y_{i,j}^* = K_{i,j} x_{i,j}$ is then calculated, and modifies the value of $y_{i,j}$ by

$$y_{mod\,i,j} = E_V y_{i,j}^* + (1 - E_V) y_{i,j+1} \tag{11}$$

Then, the modified equilibrium constant

$$K_{mod\,i,j} = \frac{y_{mod\,i,j}}{x_{i,j}} \tag{12}$$

can be used in the model equations. For the liquid composition, the procedure is similar. Calculate the $K_{i,j}$ with a thermodynamical model, then calculate $x_{i,j} = \frac{K_{i,j}}{y_{i,j}}$ to obtain the modified equilibrium constant value by

$$K_{mod\,i,j} = \frac{y_{i,j}}{x_{mod\,i,j}} \tag{13}$$

where

$$x_{mod\,i,j} = E_L x_{i,j}^* + (1 - E_L) x_{i,j-1} \tag{14}$$

If needed, the derivatives can be calculated numerically by use of the modified $K_{i,j}$ value.

APPLICATIONS

The techniques described in this paper are applied to the definition of the independent parameters and volatilities described in the "inside-out" methods [9, 10]. These values are functions of the equilibrium constants. The component molar flow rates are related by

$$v_{i,j} = K_{i,j}\left(\frac{V_j}{L_j}\right) l_{i,j} \qquad (15)$$

and the volatility parameters $\alpha_{i,j}$,

$$K_{b,j}\sum_{i=1}^{c}\alpha_{i,j}x_{i,j} = 1 \qquad (16)$$

In other methods, the application would be in the same way. For example, in the 2N Newton-Raphson method [3], the *F* functions are defined in terms of the equilibrium constants as

$$F_j = \frac{1}{V_j}\sum_{i=1}^{c}\left[\frac{1}{K_{i,j}} - 1\right] v_{i,j} \qquad (17)$$

In using the above model equations, whenever the equilibrium constant, $K_{i,j}$, is needed, instead of using

$$K_i = e^{\left[\ln\hat{\Phi}_i^L - \ln\hat{\Phi}_i^V\right]} \qquad (18)$$

the K_i used is the one that has been modified by the Murphree tray efficiency as described earlier (equations 12 and 13). However, the model equations are not changed.

This method has been implemented in a simulation package called PROSIM® [12], which is a general processes computer simulator. Table I shows the results of the application of this method to a stand alone absorber (Figure 1) in the service of dehydrating a water saturated gas stream. Stream 1 contains a mixture of methane, 100 lb-mol/h (45.4 kg-mol/h) and water, 0.215 lb-mol/h (0.00976 kg-mol/h), at 100°F and 500 psia (37.7°C, 34.5 bar), or 0.0646 lb of water/min (0.0293 kg/min). To obtain a TEG circulation rate of 3 gal/lbH_2O (25 l/kgH_2O), the number of gallons per minute needed are (3)(0.0646) = 0.19 SGPM (0.74 SLPM).

Table I. Dew Point Depression values*

Number of Actual Trays	TEG Rate gal/lbH_2O in gas (l/kgH_2O)	Composition Weight % TEG	Figures 20[39-41]** °F (°C)	Murphree Efficiency ***E_V	Efficiency E_{V,H_2O} = 0.60 °F (°C)	Ideal Stages**** °F (°C)
4	3 (25.0)	98.5	57 (31.6)	0.54	61 (33.8)	70 (38.8)
4	4 (33.3)	99.0	66 (36.6)	0.57	68 (37.7)	79 (43.8)
4	5 (41.7)	99.5	77 (42.7)	0.63	74 (41.1	95 (50.5)
4	6 (50.0)	99.9	88 (48.8)	0.63	84 (46.6)	129 (71.6)
6	3 (25.0)	99.9	94 (52.2)	0.55	102 (56.6)	129 (71.6)
6	4 (33.3)	99.5	88 (48.8)	0.60	88 (44.8)	95 (52.7)
8	2 (16.6)	98.5	66 (36.6)	0.43	69 (38.3)	71 (39.4)

8	3 (25.0)	99.5	90 (50.0)	0.55	92 (51.1)	95 (52.7)
8	6 (50.0)	99.9	124 (68.8)	0.61	123 (68.3)	129 (71.6)

* as calculated using PROSIM
** from reference 11

*** value of E_V (for all components) used to match the values of previous column

**** depression value obtained when $E_V = 1.00$

FIGURE 1

The conditions are taken from Figures 20[39-41] in the *Engineering Data Book* [11]. The table shows the actual number of stages and the values of the dew point depressions given by an absorber with ideal stages. Also shown are the values of the Murphree tray efficiencies used to match those points. Additionally, Table I shows the values of the dew point depression obtained when a value for the Murphree tray efficiency of 60% was applied only to water. In both cases, the inside-out algorithm was used to model the absorbers. As can be seen, the values shown agree with the values from the chart.

Figure 2 shows the liquid-vapor equilibrium composition for a mixture of benzene-toluene at 1 atm of pressure. It also shows the operating lines and the number of ideal stages (10 total, including total condenser and reboiler) needed to separate a mixture of 50 mole % benzene, to a top product specification of 95 mole % benzene. By applying the efficiency to the well known graphical McCabe-Thiele technique, one can conclude that for a 50% stage efficiency, approximately 15 real stages are needed to complete the separation. Figure 3 shows the results of simulating the same column using PROSIM with 15 stages and 50% efficiency. A good agreement with the graphical procedure was found. For simulation purposes, condensers, reboilers and plates considered as equilibrium flash stages always have efficiencies of 100%.

FIGURE 2

CONCLUSIONS

A simple method for applying the Murphree stage efficiency is presented. This method can be used with any thermodynamic model. In some cases, the method presented slight stability problems, particularly in finding a good initial guess to start the solution procedure when applying a stage efficiency (same efficiency for all components). This problem was solved by using the 100% efficiency of the same case, as the initial guess for a different efficiency value, or by running 2 or 3 iterations with an efficiency value of 100% before applying the specified value. In general, the stability problem was not encountered when using component efficiencies.

It was noted a component that might give some stability problems is the one whose composition does not change, or has a minimum variation through the column. If, for example, the composition $y_{i,j}$ is equal to $y_{i,j+1}$, the Murphree efficiency approaches zero. On the other hand, if the equilibrium value $y^*_{i,j}$ is equal to $y_{i,j+1}$, the efficiency becomes undefined ($\frac{0}{0}$). A solution of this is to set the efficiency to be 100% for that particular component.

For simulation purposes, this technique shows a good way to deal with the problem of real or actual stages in a distillation column. For glycol dehydration units, it was found that a Murphree tray efficiency value within the range of 45-65% can be used to simulate the actual number of stages (where the overall efficiency is within 30-40%).

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NOMENCLATURE

c	number of components
E_L	Murphree stage efficiency based upon liquid composition
E_V	Murphree stage efficiency based upon vapor composition
EOS	equation of state
F	set of functions defined by Equation (17)
$\hat{f}_i$	fugacity of component *i*
K	equilibrium constant = $\frac{x}{y}$
$l_{i,j}$	liquid flow rate of component *i* on stage *j*
n	number of stages
P	pressure
Q	average product of mass transfer coefficient, area of contact per mol vapor and time of contact
$S_j = \left(\frac{\partial x}{\partial y}\right)$	derivative of the equilibrium curve at $x = x_j$
SGPM	standard gallons per minute
TEG	triethylene glycol
$v_{i,j}$	vapor flow rate of component *i* on stage *j*
x	liquid composition
y	vapor composition

Greek Letters:

$\alpha_{i,j}$	volatility parameter defined in Equation (16)
$\hat{\Phi}_i = \frac{\hat{f}_i}{x_i P}$	fugacity coefficient of component *i*

Subscripts:

i	component *i*
j	stage *j*
mod	modified equilibrium value
L	liquid
V	vapor

Superscripts:

L	liquid
V	vapor
*	equilibrium value

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