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Murphree, Hausen, Vaporization, and Overall Efficiencies in Binary Distillation of Associated Systems

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Abstract

In this paper a comparative study of different plate efficiencies models considering binary systems with association of one component in both phases is presented. The experiments were carried out in a laboratory column with 10 real bubble-cup plates for the benzene–acetic acid and toluene–acetic acid systems. The actual and ideal compositions at each plate are interpreted. The model of associated systems using the concentration-dependent liquid phase association constant was considered.

INTRODUCTION

The design of industrial distillation columns is normally based on estimated values of plate efficiencies. Several different plate efficiencies models have been proposed in the literature (*1–7*).

The relative merits of Murphree, Hausen, and vaporization efficiencies were discussed, among others, by Holland and McMahon, Standart, Ashton, Mediana and McDermott, and Krishna (*5–14*). Severe criticisms of the vaporization and Murphree efficiencies models were produced (*12–14*).

Phase equilibria for systems in which association occurs in one or more phases have been studied over a long period of time. Francesoni, Trevissoi, and Cojutti (*15, 16*) and Tamir and Wisniak (*17–19*) considered the association reaction only in the vapor phase. Marek and Standart developed (*20, 21*) the phase and chemical equilibrium for association reaction which takes place in the vapor and liquid phases.

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Jenkins and Gibson-Robinson developed a new model based on that of Marek and Standart and used it to correlate *P–t–x–y* data (*22–24*). Savković-Stevanović et al. extended the new model with concentration-dependent liquid phase association constant to isobaric and isothermal data of acetic acid–aromatic hydrocarbons systems (*25, 26*).

The aim of this paper is to present a comparative study of the Murphree, Hausen, and vaporization efficiencies models for associated systems with association one component in both phases. The compositions at ideal and actual plate are also determined (*27*).

PLATE EFFICIENCIES

Murphree Efficiencies

Vapor-phase Murphree efficiency for component i and plate j can be defined as

$$E_{\mathrm{MV},i} = \frac{y_{j,i} - y_{j+1,i}}{(y^*_{j,i})_M - y_{j+1,i}} \tag{1}$$

where $(y^*_{j,i})_{\mathrm{M}}$ is the mole fraction of component i in the vapor in equilibrium with the liquid leaving the real plate. This liquid is assumed to be at its boiling point temperature.

$$(y^*_{j,i})_{\mathrm{M}} = (K_{j,i})_{\mathrm{M}}\gamma_i x_{j,i} \tag{2}$$

where

$$\sum_{i=1}^{C} (y^*_{j,i})_{\mathrm{M}} = 1 \tag{3}$$

Thus, $(K_{j,i})_{\mathrm{M}}$ is evaluated at that hypothetical boiling point temperature required to satisfy Eq. (3).

The liquid-phase plate efficiency of component i is

$$E_{\mathrm{ML},i} = \frac{x_{j-1,i} - x_{j,i}}{x_{j-1,i} - (x^*_{j,i})_{\mathrm{M}}} \tag{4}$$

where $(x^*_{j,i})_M$ is the mole fraction of component i in the liquid in equilibrium with the vapor leaving the real plate. This vapor is assumed to be at its dew point temperature.

Both definitions represent a ratio between the separation on a real plate and that on an ideal plate, and Eqs. (1) and (4) lead generally to different numerical values for the same real plate. In fact, if there is a linear equilibrium relationship in the range of compositions of one stage, the two efficiencies are related as follows:

$$\left(\frac{1}{E_{\mathrm{ML},i}} - 1\right) = \left(\frac{1}{E_{\mathrm{MV},i}} - 1\right)\frac{1}{S} \qquad (5)$$

where $S = mG/L$.

Standart (*6*) summarized the most important criticisms of Murphree definitions by emphasizing the fact that they cannot be calculated if unsaturated streams leave the plate.

Modified Murphree Efficiencies

Two modifications of the original Murphree model were proposed by Taylor and Holland (*3, 28*) and by Onda et al. (*29–32*).

In this paper the modification of Taylor and Holland is considered. Taylor and Holland defined a vapor-phase Murphree plate efficiency for component i as

$$E^{\mathrm{M}}_{\mathrm{MV},i} = \frac{y_{j,i} - y_{j+1,i}}{Y_{j,i} - y_{j+1,i}} \qquad (6)$$

where

$$Y_{j,i} = K_{j,i}\gamma_i x_{j,i} \qquad \text{and} \qquad \sum_{i=1}^{C} Y_{j,i} \neq 1 \qquad (7)$$

$K_{j,i}$ is the vapor–liquid equilibrium ratio evaluated at the actual temperature and pressure at which liquid leaves plate j.

Vaporization Efficiency

Holland (*3*) defined the vaporization efficiency for component i and plate j as

$$E_{V,i} = y_{j,i}/Y_{j,i} \tag{8}$$

where

$$Y_{j,i} = K_{j,i}\gamma_i x_{j,i} \qquad \text{and} \qquad \sum_{i=1}^{C} Y_{j,i} \neq 1 \tag{9}$$

$K_{j,i}$ is evaluated at the actual temperature of the liquid leaving plate j and the pressure of plate j.

Hausen Efficiencies

Hausen (*2*) defined plate efficiencies for component i and plate j as vapor-phase plate efficiency

$$E_{HV,i} = \frac{y_{j,i} - y_{j+1,i}}{(y^*_{j,i})_H - y_{j+1,i}} \tag{10}$$

and as liquid phase plate efficiency

$$E_{HL,i} = \frac{x_{j-1,i} - x_{j,i}}{x_{j-1,i} - (x^*_{j,i})_H} \tag{11}$$

where $(y^*_{j,i})_H$ and $(x^*_{j,i})_H$ are mole fractions of component i in the vapor and liquid which result from a flash calculation with a feed composition equal to the sum of the streams entering the plate.

$$(y^*_{j,i})_H = K_{j,i}\gamma_i(x^*_{j,i})_H \qquad \text{and} \qquad \sum_{i=1}^{C} (y^*_{j,i})_H = 1 \tag{12}$$

The procedure for calculating $(y^*_{j,i})_H$ is given in the literature (*10*). Activity coefficients have been calculated on the basis of the model by using the concentration-dependent liquid phase association constant $k = f(T, x_A)$. A summary of the main relationships of the model used is given in the Appendix (*25*).

MODELING OF MURPHREE, HAUSEN, MODIFIED MURPHREE, VAPORIZATION, AND OVERALL EFFICIENCIES

The distinction between the Murphree and Hausen models has been established for binary systems by Ho and Prince (*33*), and for binary and multicomponent systems by Mediana et al. (*10*).

The equations of the operating lines for real plates and for ideal plates as defined by Murphree and Hausen in terms of the more volatile component are:

Real plate

$$y_j - y_{j+1} = L/V(x_{j-1} - x_j) \tag{13}$$

Ideal plate of Murphree

$$(y_j^*)_M - y_{j+1} = L/V((x_{j-1}^*)_M - x_j) \tag{14}$$

Ideal plate of Hausen

$$(y_j^*)_H - y_{j+1} = L/V(x_{j-1} - (x_j^*)_H) \tag{15}$$

Assuming linearity of the equilibrium and operating lines, the relation between Murphree's and Hausen's efficiencies (*11*) is derived:

$$E_{HV,i} = E_{MV,i}(S + 1)/(1 + SE_{MV,i}) \tag{16}$$

From defining Eqs. (1), (4), (6), and (8), the Murphree, modified Murphree, and vaporization efficiencies are interrelated in the following manner (5):

$$E_{MV,i}^M = E_{MV,i} \frac{(y_{ji}^*)_M - y_{j+1,i}}{Y_{ji} - y_{j+1,i}} \tag{17}$$

$$E_{V,i} = \frac{y_{j+1,i}}{Y_{ji}} + E_{MV,i} \left(\frac{(K_{j,i})_M}{K_{j,i}} - \frac{y_{j+1,i}}{Y_{j,i}} \right) \tag{18}$$

Assuming linearity of the equilibrium and operating lines, one can simply derive the relation between the overall and Murphree efficiencies (*17*) for distillation plates in the form:

$$E_{MV,i} = \frac{e^{E^\circ \ln S} - 1}{S - 1} \tag{19}$$

The theoretical and actual compositions at each plate are

$$(y_j)_{\text{ideal}} = \frac{y_1 + \alpha}{S^{n'}} - \alpha \tag{20}$$

and

$$(y_j)_{\text{actual}} = \frac{y_1 + \alpha}{\tau_{V^n}} - \alpha \tag{21}$$

where

$$\alpha = \frac{y_2 - (1/S)(mx_2 + c)}{(1/S) - 1} \tag{22}$$

and

$$\tau_V = \frac{1}{1 + E_{HV}(S - 1)/(S + 1 - SE_{HV})} \tag{23}$$

The theoretical composition can also be calculated from a McCabe-Thiele diagram.

EXPERIMENTAL MEASUREMENTS

The experiments were carried out by batch distillation at total reflux and atmospheric pressure. Investigation was performed in a laboratory glass column of 50 mm i.d. with 10 real bubble-cup plates using the benzene–acetic acid and toluene–acetic acid systems.

The charge consisted of 90 mol% of acetic acid. The compositions were determined by measurements of the refractive indices by a Zeiss refractometer with an accuracy ±0.01%.

The distillation was made at different flow rates through the column. Previously, hydrodynamic conditions and the optimal flow rate through the column were investigated.

RESULTS AND DISCUSSION

The obtained results are presented in Figs. 1–3. The values of Murphree, Hausen, and overall efficiencies vs flow rate of the vapor and liquid phases are shown in Fig. 1 for the benzene-acetic acid system. A comparison of Murphree, Hausen, and efficiencies of the vapor and liquid phases for the toluene–acetic acid system is shown in Fig. 2.

The values of the efficiencies of all the models examined normally belong to the interval (0,1) for investigated associated systems.

Figure 3 shows the computed actual and ideal compositions of the vapor phase on each plate at the optimal flow rate for the benzene–acetic acid system. The actual composition on each plate is interpreted by the Hausen and Murphree efficiencies. Comparison of calculated with experimental compositions shows that the Hausen's model efficiencies are the best way to reflect the real process on the distillation plates for the investigated associated systems.

CONCLUSIONS

The results obtained of the comparative study of Murphree, vaporization, Hausen, and modified Murphree model efficiencies of binary associated systems show that all models give the plate efficiencies values in the interval (0,1) in agreement with physical reality.

Hausen's model efficiencies are the best for reflecting the transfer processes that occur on distillation plates for the binary systems investigated with association of one component in both phases. The accurate values of plate efficiencies are very important because they have a direct effect on the number of plates required and an indirect effect on the running costs of the equipment.

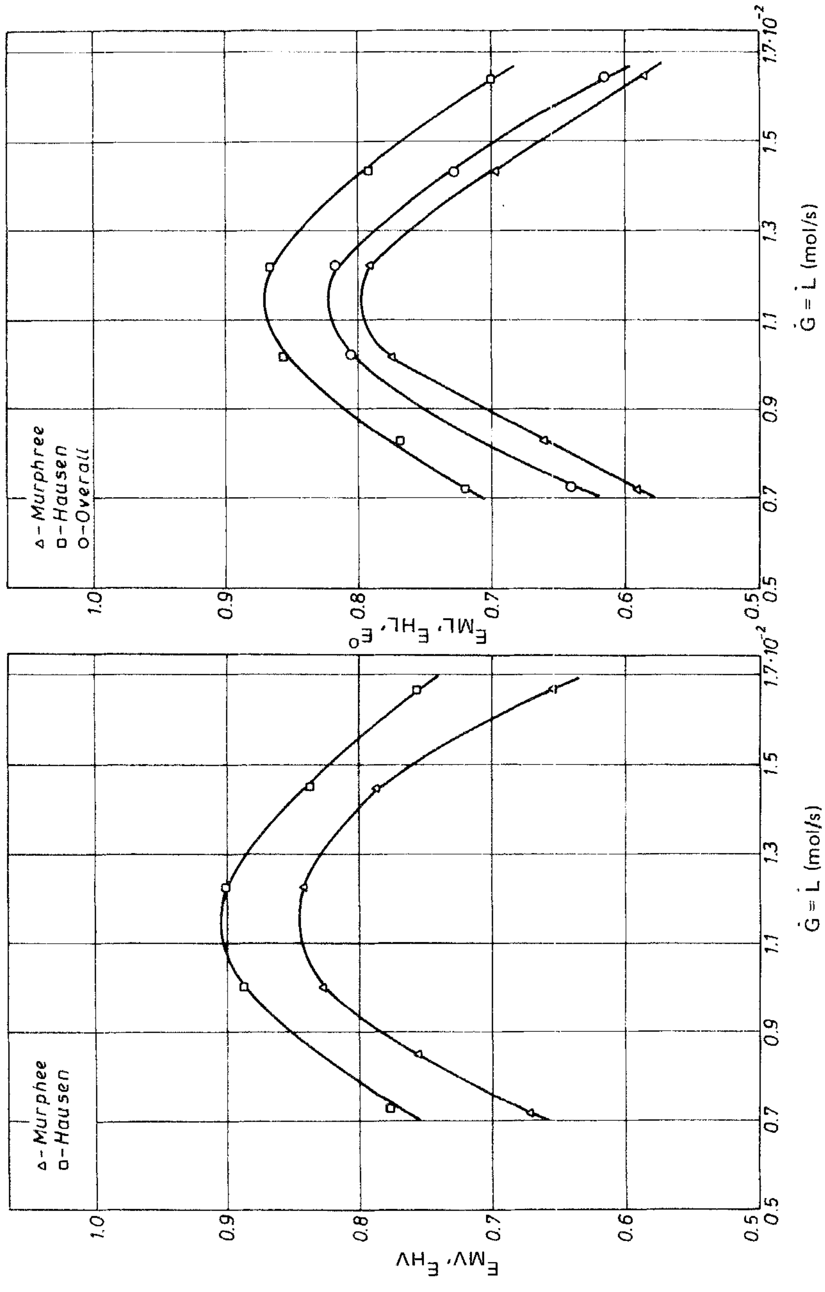

FIG. 1. Comparison between Murphree, Hausen, and overall efficiencies of the vapor and liquid phases for the benzene–acetic acid system.

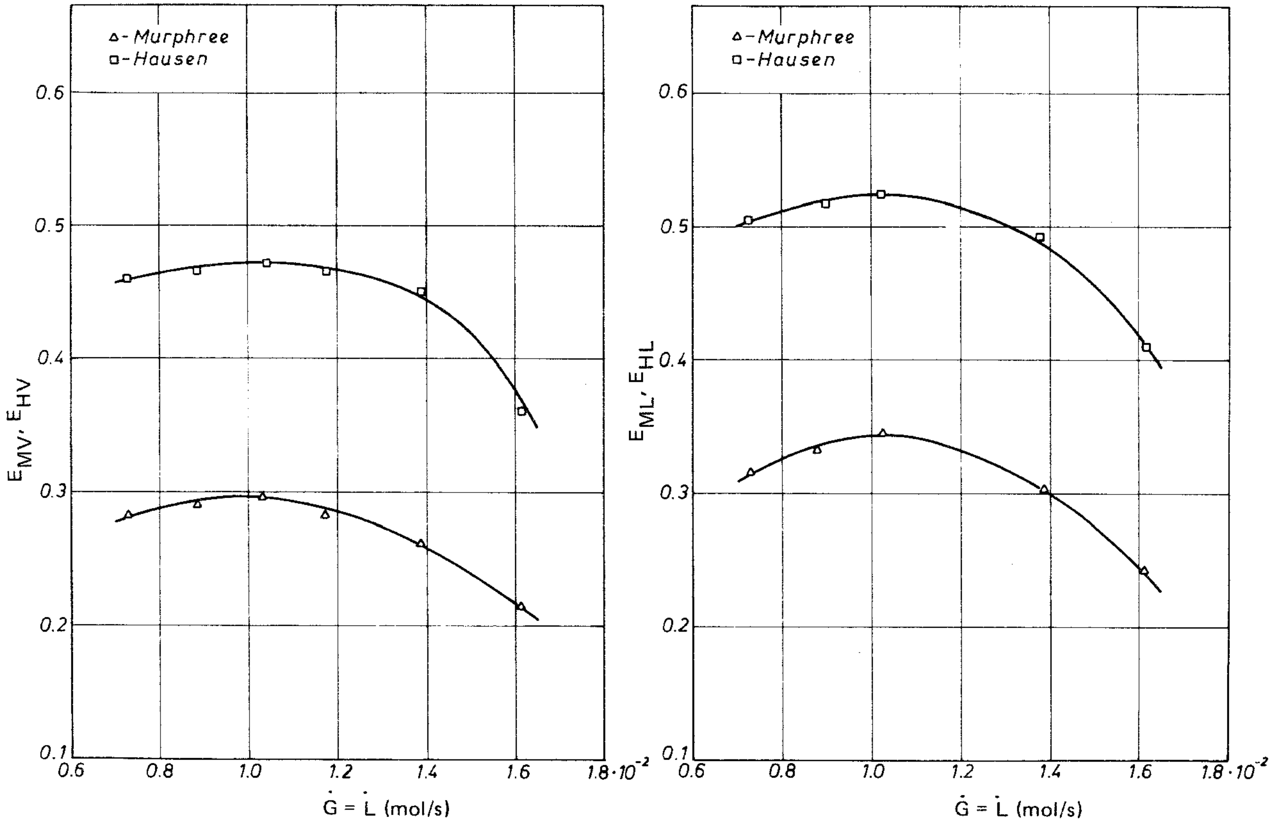

FIG. 2. Comparison between Murphree and Hausen efficiencies of the vapor and liquid phases for the toluene–acetic acid system.

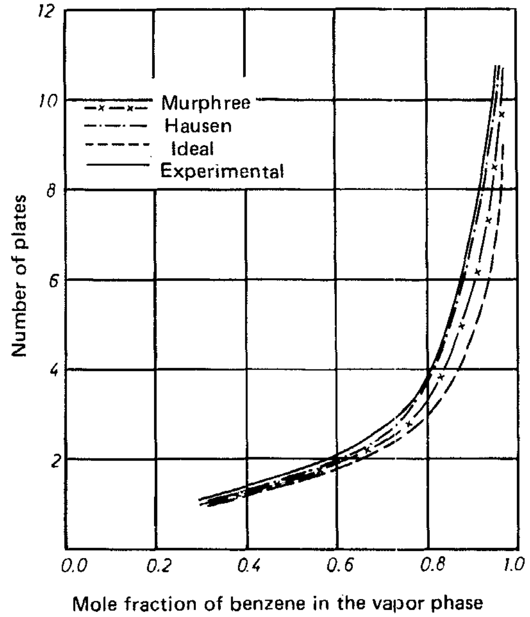

FIG. 3. The compositions of the vapor phase on each plate for the optimal flow rate through a column for the benzene–acetic acid system.

APPENDIX

For associated systems $2A_1 + B \rightleftharpoons A_2 + B$ the phase equilibrium for associating component A

$$Py_A Z_A \Phi_A = p_{A_0} x_A \delta_A \gamma_A \tag{A1}$$

and for the nonassociating component B

$$Py_B Z_B \Phi_B = p_{B_0} x_B \delta_B \gamma_B \tag{A2}$$

The model with the concentration-dependent liquid phase association constant states that

$$K' = K'_A = f(T) \tag{A3}$$

for the vapor phase, and

$$k' = f(T, x_A) = k'_A \beta \gamma_A \tag{A4}$$

for the liquid phase where β is a ratio of correction factors given by

$$\beta = Z_A \Phi_A \delta'_A / Z'_A \Phi'_A \delta_A \tag{A5}$$

SYMBOLS

A	associating component (acetic acid)
B	nonassociating component
C	number of component
c	y intercept
E°	overall efficiency
E_{MV}	Murphree vapor-phase plate efficiency
E_{HV}	Hausen vapor-phase plate efficiency
E_{HL}	Hausen liquid-phase plate efficiency
$E_{\mathrm{MV}}^{\mathrm{M}}$	modified Murphree efficiency
E_{V}	vaporization efficiency
G	vapor flow rate
K	vapor–liquid equilibrium ratio
K'	vapor-phase association constant at total pressure of mixture (Pa^{-1})
K'_A	vapor-phase association constant at saturated vapor pressure of pure associating component (Pa)
k'	liquid-phase association constant for the mixture
k_A	liquid-phase association constant for the pure associating component
L	liquid flow rate
m	slope of the equilibrium line
n	number of real plate
n'	number of theoretical (ideal) plate
P	total pressure of system (Pa)
P_{A_0}, P_{B_0}	saturated vapor pressure of the pure associating component and nonassociating component, respectively (Pa)
S	ratio between the slopes of equilibrium and operating line
T	temperature (°K)
Z_A, Z'_A	vapor-phase correction factor of the associating component for monomer and dimer, respectively
Z_B	vapor-phase correction factor for the nonassociating component

Greek Letters

α	correction factor as defined by Eq. (22)
β	ratio of correction factors as defined by Eq. (A5)
γ	activity coefficient
δ_A, δ'_A	liquid-phase correction factor of the associating component for the monomer and dimer, respectively
δ_B	liquid-phase correction factor for the nonassociating component
Φ_A, Φ'_A	ratio of fugacity coefficient for the monomer and dimer, respectively
τ	correction factor as defined by Eq. (23)

Subscripts

A	associating component
B	nonassociating component
i	component number
j	plate number
V	vapor phase
1, 2	monomer, dimer

Superscript

*	equilibrium

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