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Dynamic Modeling of a Packed-Bed Glycerol–Water Distillation Column

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The study of the dynamics of a packed-bed glycerol–water distillation column is valuable for precise control to improve product quality and to conserve material. A differential dynamic model has been established for the continuous distillation of the glycerol–water system at 10 mmHg absolute. In this model, hydraulic and mass transfer models of structured packing were used to estimate the vapor and liquid holdups and the mass transfer coefficients. The model equations were solved numerically using the finite difference method. It was found that numerical solution of the proposed dynamic model with liquid, vapor, and reflux drum holdups took less computation time than the other models even when either liquid or vapor holdup was neglected. This method of solution reduced the size of system of differential equations from $2n + 1$ to $n + 1$, thus improving the numerical accuracy and saving computation time. The effect of liquid, vapor, and reflux drum holdup on the dynamic behavior of the column was studied. It was found that the liquid and vapor holdups have almost no effect on the dynamics of the packed column. The response of the composition along the height of the column showed nonlinear behavior in response to changes in the reflux drum temperature. The results of this work shed some light on the dynamic behavior of packed-bed distillation columns with highly nonlinear equilibrium relationship due to step changes in the reflux drum temperature.

Introduction

The glycerol–water system is an important industrial system having a nonlinear equilibrium relationship. It is obtained either from fat and oil splitting or from the soap industry. Because of its high boiling point (290 °C at 760 mmHg) and heat sensitivity, glycerol is being separated from water by vacuum distillation (5–10 mmHg abs) using packed-bed distillation columns containing structured packings. Such a separation system has a low pressure drop, small liquid holdup, and large surface area per unit volume of packing.^{1,2}

Theories for the design of packed-bed columns based on steady-state conditions are well-developed. However, theories based on dynamics are still behind the demand of precise control for improvement of product quality, conservation of material and energy, and protection of the environment. Most of the existing dynamic theories employ the simplifying assumptions of a linear equilibrium relationship and a total condenser or neglect the reflux drum dynamics and the vapor holdup.^{3,4} Furthermore, the existing dynamic studies concerning packed-bed columns lack the integrity between the hydraulic, mass transfer, and vapor–liquid equilibrium (VLE) models and the dynamic model itself.^{4–6}

One of the most comprehensive studies on the design of packed distillation columns is that of Bolles and Fair⁷

who collected data from the literature. They critically examined the various methods used in packed column design. They reached the conclusion that the available theoretical models are not very good for correlating the results in their data bank. Wagner et al.⁸ developed a model for the prediction and correlation of mass transfer rates in distillation columns containing random packings. The model was found to fit experimental values to within $\pm 25\%$.

A number of hydraulic models for structured packing have been developed.⁹ The prediction capabilities of these models are constrained to the use of either empirical correlations¹⁰ or sophisticated methods such as that proposed by Stichlmair et al.¹¹ Rocha et al.^{12,13} introduced comprehensive hydraulic and mass transfer models describing the performance of the structured packing. Such models made it possible to design packed-bed distillation columns containing structured packing as well as to study their dynamic behavior from a theoretical point of view. Tommasi and Rice³ studied the dynamics of packed distillation column using the ethanol–water system. They neglected the condenser and reflux drum holdups and assumed constant vapor and liquid flow rates, as well as a total condenser. The model was formulated without introducing hydraulic and mass transfer models, which depend on the type of packing used. Hwang^{4,14} provided a mathematical model concerning the dynamics of continuous countercurrent mass transfer process in the most general form using the distributed-parameter model. The model describes the dynamic behavior of packed-bed absorbers with a single component and constant liquid and gas flow rates.

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Afacan and Chaung¹⁵ developed a model for predicting mass transfer in packed columns containing structured packings. Three systems (methanol/2-propanol, water/acetic acid, and methanol/water) were used in testing the model. The average deviation between the measured and model-predicted values was $\pm 10.2\%$.

The assumption of a linear equilibrium relationship made predictions of the transient response of distillation columns inaccurate in many cases because of the nonlinear nature of the equilibrium curve, which must be linearized to be used for the sake of analytical solutions. However, these models with linearized equilibrium relationships are adequate only for small disturbances associated with low-purity columns.⁶ It has been shown,^{5,16} however, that high-purity columns exhibit nonlinear dynamics phenomena such as the strong dependence of the dynamics on the magnitudes and directions of the disturbances and the asymmetric dynamics of the transition between two steady states.

The equilibrium curve of the glycerol–water system is highly nonlinear, and glycerin is commercially required at purities greater than 99.5%.¹⁷ Thus, dynamic models with linearized equilibrium relationship cannot be utilized effectively in predicting the transient response of packed distillation columns used to separate glycerol from water. The equipment used in glycerol–water distillation encountered in industry is of a partial condenser type that avoids condensation of water with glycerol in the final product.¹⁶ Woollat¹ listed the equipment industrially available, along with the equipment previously used in glycerin distillation. The older equipment used in glycerin distillation, such as Van Ruymbeke and Garrigue stills,¹ were made of vaporizer pots with closed and open steam coils connected to a series of partial condensers to separate glycerol from water in a fractional manner. Further developments in still vaporizers used forced circulation heaters to avoid glycerol loss by polymerization resulting from local overheating of the closed coils. One of these stills used a direct-contact main condenser followed by a surface condenser.¹ In 1993, Costruzioni Meccaniche Bernardini (CMB) Company had constructed an efficient vacuum still that operate at pressures of 5–10 mmHg abs connected to a packed rectifying section and two partial condensers. Equilibrium is achieved in this apparatus through control of the reflux drum temperature.¹⁸

The objective of this study is to develop a comprehensive dynamic model for the rectifying section of a packed-bed distillation column containing structured packing taking into account the liquid, vapor, and reflux drum holdups with a nonlinear equilibrium relationship. The dynamic model utilizes steady-state, hydraulic, and mass transfer models of the structured packing. This system is utilized to simulate the separation of glycerol from water at 10 mmHg, with a partial condenser assumed. The dynamic behavior of this packed column is studied by introducing a step change in the reflux drum temperature using the following cases: (1) dynamic model with liquid, vapor, and reflux drum holdups; (2) dynamic model with liquid and reflux drum holdups; and (3) dynamic model with holdup in the reflux drum only.

Formulation of the Mathematical Model

Because pure glycerol boils with decomposition at about 290 °C under atmospheric pressure, most industrial glycerin stills are found to operate at 5–10 mmHg abs.^{1,17,18}

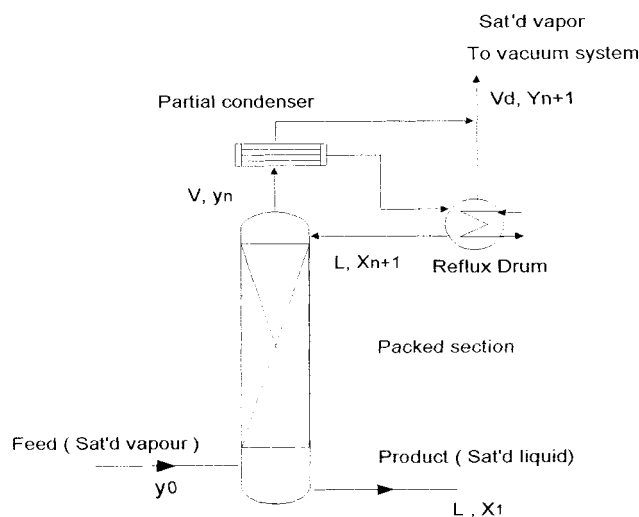


Figure 1. Schematic diagram of the packed distillation column.

Vapor–liquid equilibrium (VLE) data for the glycerol–water system at these lower pressures could not be found in the literature, except for those obtained by CMB¹⁸ for a pressure of 10 mmHg abs. These equilibrium data are predicted well by the UNIFAC model, and so, this model was used to calculate the VLE data for the glycerol–water system. In formulating a distributed model for the rectifying section of the packed-bed distillation column the following assumptions were made: (1) The liquid and vapor streams are assumed to be at bubble and dew points respectively, at any point in the column as well as in the reflux drum or the partial condenser. Thus, no enthalpy balance is required. (2) Because most of the water in the crude glycerine feed is removed in the dryer preceding the distillation still and the vapor stream enters the base of the column at 5% water content; the consumption of either phase is not changed by more than 5%. As a result, one can safely assume that liquid and vapor flow rates are almost constant along the rectifying section.¹

(3) The vapor-phase overall mass transfer coefficient is used to describe the transfer of material between phases. (4) The vapor-phase overall mass transfer coefficient and the liquid and vapor holdups are assumed to be approximately constant because the change in composition along the column is small. This, in turn, results in a small change in the liquid flow rate when a step change in the reflux drum temperature is introduced based on assumptions 1 and 2. (5) The UNIFAC model for the glycerol–water system is used to predict the liquid-phase activity coefficient assuming that the vapor phase is ideal. (6) The temperature of the reflux drum responds instantaneously to any heating disturbance, and the product (glycerin) is removed from the bottom as liquid at its bubble point. (7) Negligible partial condenser holdup occurs, and the vapors leaving the reflux drum are in equilibrium with the liquid leaving it. This condition is met industrially by controlling the temperature of the reflux drum.¹⁸

Realization of assumptions 1 and 2 above requires an energy balance resulting in a rigorous and accurate mathematical model. The development of such a model is in progress. Using the above assumptions and two-film theory, the mathematical model for the enriching section of a packed bed with a partial condenser sketched in Figure 1 is formulated as follows:

Water mass balance for the liquid phase

$$H \frac{\partial x}{\partial t} = L \frac{\partial x}{\partial z} - K_V a_e (y^* - y) \quad (1)$$

Water mass balance for the vapor phase

$$h \frac{\partial y}{\partial t} = -V \frac{\partial y}{\partial z} + K_V a_e (y^* - y) \quad (2)$$

Water mass balance for the reflux drum

$$\frac{dx_{n+1}}{dt} = \frac{V}{M_c} [y_n - Rx_{n+1} + (R-1)y_{n+1}] \quad (3)$$

Bubble-point relationship for the liquid phase

$$\sum_{i=1}^2 \gamma_i x_i P_i^*/P = 1 \quad (4)$$

Equilibrium relationship

$$y^* = \gamma x P^*/P \quad (5)$$

The liquid activity coefficients are estimated using the UNIFAC model and the vapor pressure of the pure components is estimated using the Antoine equations fitted to experimental data.¹⁹ The vapor mass transfer coefficient, k_v , is calculated using a correlation published by Rocha et al.¹³ for structured packing, namely

$$\frac{K_v S}{D_v} = 0.054 Re_v^{0.8} Sc_v^{0.33} \quad (6)$$

The overall vapor mass transfer coefficient K'_V is then given by

$$K'_V = \frac{1}{\frac{1}{K_v} + \frac{m' U_{LS}}{R U_{VS}} \frac{1}{K'_L}} \quad (7)$$

where K_v is the liquid-phase mass transfer coefficient given by the correlation in Rocha et al.¹³ K'_V can be expressed in kilomoles per meter per second for eqs 1 and 2 to be dimensionally consistent as

$$K_V a_e = K'_V a_e \left(\frac{P}{R_g M T} \right) A_c \quad (8)$$

The fractional liquid holdup is defined in units of cubic meters of liquid in the void space per cubic meter of empty void space.²⁰ For a structured packing where the entire surface is assumed to be covered with liquid,¹² the total fractional liquid holdup is a sum of two components: One is the static holdup, which is defined as the volume of liquid that does not drain (when the flows of liquid and vapor are stopped) per volume of dry packing, which is very small and usually is ignored. The other is the operating liquid holdup, which is the difference between the total and static holdups²⁰ and is given by¹²

$$H_L = \left(4 \frac{F t}{S} \right)^{2/3} \left(\frac{3 \mu_L U_{LS}}{\rho_L \epsilon g_{\text{eff}} \sin(\Phi)} \right)^{1/3} \quad (9)$$

The liquid holdup, H , is related to fractional liquid

holdup through

$$H = \frac{H_L \rho_L A_c}{\bar{M}} \quad (10)$$

The vapor holdup, h , is calculated from the total available void volume (the operating void space)

$$h = \epsilon_0 A_c \left(\frac{P}{R_g \bar{M} T} \right) \quad (11)$$

where the operating void space, ϵ_0 , is given by Tommasi et al.¹³ and Treybal²¹ as

$$\epsilon_0 = \epsilon - H_L \quad (12)$$

The cross-sectional area of the empty column that appears in the above equations is calculated from the pressure drop correlation for a vapor flowing in a wet structured packing published by Rocha and Fair.¹² The estimation of the interfacial area, a_e , has been discussed extensively by Shi and Mersmann,²² where they introduced the following correlation for structured packing

$$\frac{a_e}{a_p} = F_{SE} \frac{29.12 (We_L Fr_L)^{0.15} S^{0.359}}{Re_L^{0.2} \epsilon^{0.6} (1 - 0.93 \cos \alpha) (\sin \Phi)^{0.3}} \quad (13)$$

The dimensionless Reynolds (Re), Schmidt (Sc), and Weber (We) numbers for the liquid phase are defined in the same reference mentioned above.

Equations 1–3 can be written in dimensionless form by the following change of variables

$$N_1 = \frac{Z_1 K_V a_e}{V} \quad (14)$$

$$\zeta = \frac{Z}{Z_1} \quad (15)$$

$$R = \frac{L}{V} \quad (16)$$

$$\theta = \frac{t}{\tau_L} \quad (17)$$

where

$$\tau_L = \frac{Z_1 H}{V} \quad (18)$$

Substituting eqs 14–18 into eqs 1–3, we obtain the following dimensionless equations

$$\frac{\partial x}{\partial \theta} = R \frac{\partial x}{\partial \zeta} - N_1 (y^* - y) \quad (19)$$

$$\omega \frac{\partial y}{\partial \theta} = - \frac{\partial y}{\partial \zeta} + N_1 (y^* - y) \quad (20)$$

$$\frac{dx_{n+1}}{d\theta} = \frac{Z_1 H}{M_c} [y_n - Rx_{n+1} + (R-1)y^*(x_{n+1})] \quad (21)$$

Equations 4–21 complete the unsteady-state model for the rectifying section of a packed-bed distillation column with the following initial and boundary conditions

$$\begin{aligned}
 x(\zeta, 0) &= x(\zeta) \\
 y(\zeta, 0) &= y(\zeta) \\
 y(0, \theta) &= y_0
 \end{aligned}
 \quad (22)$$

The space variable ζ can be discretized to convert the partial differential eqs 19 and 20 to ordinary differential equations (ODEs).²³ To do so, let

$$\frac{\partial x}{\partial \zeta} = \frac{x_{i+1} - x_i}{\Delta \zeta} \quad (23)$$

$$\frac{\partial y}{\partial \zeta} = \frac{y_i - y_{i-1}}{\Delta \zeta} \quad (24)$$

$$y^* = \frac{y^*(x_i) + y^*(x_{i+1})}{2} \quad (25)$$

$$y = \frac{y_{i-1} + y_i}{2} \quad (26)$$

Substituting eqs 23–26 into eqs 19 and 20, we obtain the following two ordinary differential equations for $i = 1, 2, \dots, n$

$$\frac{dx_i}{d\theta} = a_1[x_{i+1} - x_i] - a_2[y^*(x_i) + y^*(x_{i+1})] + a_2[y_{i-1} + y_i] \quad (27)$$

$$\frac{dy_i}{d\theta} = \frac{1}{\omega}[a_4 y_{i-1} - a_3 y_i + a_2(y^*(x_i) + y^*(x_{i+1}))] \quad (28)$$

where

$$a_1 = \frac{R}{\Delta \zeta} \quad (29)$$

$$a_2 = \frac{N_1}{2} \quad (30)$$

$$a_3 = \frac{1}{\Delta \zeta} + a_2 \quad (31)$$

$$a_4 - \frac{1}{\Delta \zeta} - \frac{N_1}{2} = a_3 - 2a_2 \quad (32)$$

$$n = \frac{1}{\Delta \zeta} \quad (33)$$

The height of the packed-bed section is given by^{13,21}

$$N_1 = R \sum_{y_0}^{y_n} \frac{dx}{y^* - y(x)} \quad (34)$$

$$y(x) = y_0 + R(x - x_1) \quad (35)$$

$$H_{OG} = \frac{U_{VS}}{K_V a_e} \quad (36)$$

$$Z_1 = N_1 H_{OG} \quad (37)$$

From the model in eqs 19–21, we can classify three cases of dynamic models as (1) those having liquid, vapor, and reflux drum holdups; dynamic model, (2)

those having liquid holdup and reflux drum holdups, and (3) those having reflux drum holdup only.

Method of Solution

Typical design and operating conditions encountered in industry are listed in Table 1.²⁴ The physical properties of the glycerol–water system were estimated from correlations found in the literature.²⁵ The type of structured packing used in the design is Gempak2A, whose characteristics are given in Rocha et al.¹³ The cross-sectional area of the column, A_c , was calculated using the pressure drop model that was developed by Rocha et al.,¹² and it was found to be 0.181 m² ($D_c = 0.48$ m). Similarly, the height of the packed section was calculated by eq 37 and found to be $Z_1 = 1.1$ m, where the slope of the equilibrium line is evaluated at ($x_1 = 0.0001$) and N_1 is found to be 0.051 from eq 34. These design values were used in conjunction with the steady-state versions of eqs 21, 27, and 28 to find the steady-state conditions in the column before the introduction of a step change in the reflux drum temperature (step in R). These equations were solved iteratively as a linear system by first guessing an initial profile of the liquid composition as being linear between $x_1 = 0.0001$ and x_{n+1} found from bubble-point calculations, where the nonlinear terms are made constant using this guess at each iteration. Note that the system of equations represented by eq 28 could be solved iteratively either at steady state or with neglect of the vapor holdup. The general solution of this system of equations is

$$y_i = \left(\frac{a_4}{a_3}\right)^i y_0 + \frac{a_2}{a_3} \sum_j \left(\frac{a_4}{a_3}\right)^{i-j} (y_j^* + y_{j+1}^*) \quad (38)$$

The size of the system of equations given by eqs 21, 27, and 28 is reduced from $2n + 1$ to $n + 1$ using eq 38. The remaining system of equations could be written in matrix form as

$$\mathbf{A}(X^{(m+1)})X = \mathbf{B}(X^{(m)}), \quad m = 0, 1, 2, \dots \quad (39)$$

where \mathbf{A} is an $n \times n$ matrix with nonzero elements given by

$$A_{i,i} = \frac{N_1 \Delta \xi}{2R} k(x_1) + 1 \quad (40)$$

$$A_{i,i+1} = \frac{N_1 \Delta \xi}{2R} k(x_{i+1}) - 1, \quad i = 1, 2, \dots, n \quad (41)$$

$$B(x_i) = \frac{N_1 \Delta \xi}{2R} (y_{i-1} + y_i), \quad i = 1, 2, \dots, n-1 \quad (42)$$

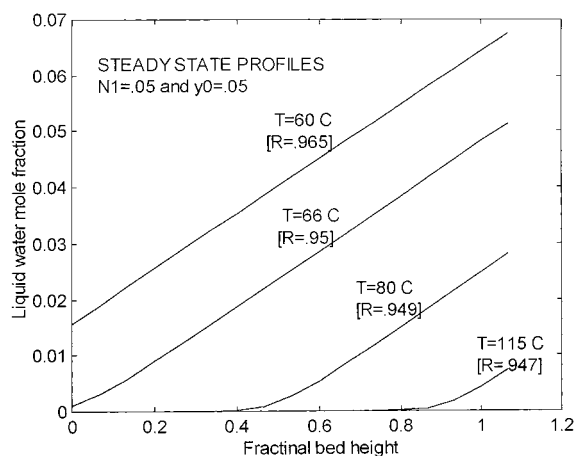
$$B(x_n) = \frac{N_1 \Delta \xi}{2R} [y_{n-1} + y_n] - \left[\frac{N_1 \Delta \xi}{2R} k(x_{n+1}) - 1 \right] x_{n+1} \quad (43)$$

$$k(x) = \gamma P_w^* / P \quad (44)$$

where the composition of the liquid leaving the reflux drum, x_{n+1} , is found from eq 4 at a given reflux drum temperature. Equation 44 is evaluated using the bubble-point calculations at each level of discretization (i). The steady-state solution is determined by first guessing the

Table 1. Typical Operating and Design Conditions of a Glycerol–Water Distillation Column

parameter	value
operating temperature (°C)	166
operating pressure (mmHg abs)	10
vapor flow rate V (kg/s)	0.06
internal reflux ratio $R = L/V$	0.95
mole fraction of water in liquid leaving bottom of column x_1	0001
mole fraction of water in liquid entering top of packed section x_{n+1}	051
mole fraction of water in vapor leaving top of packed section y_n	098
mole fraction of water in vapor entering bottom of packed section y_0	05
allowable pressure drop along packed section (mmHg/m)	1.0
average liquid density at $x = 0.025\rho_L$ (kg/m ³)	1200
average vapor density at $y = 0.074\rho_V$ (kg/m ³)	0.032
average liquid viscosity at $x = 0.025\mu_L$ (kg/(m s))	3.32×10^{-4}
average vapor viscosity at $y = 0.074\mu_V$ (kg/(m s))	1.1×10^{-5}
surface tension of liquid at $x = 0.025\sigma$ (N/m)	0.052
reflux drum holdup M_c (kmol)	1.0

**Figure 2.** Experimental and predicted vapor liquid equilibria of the glycerol–water system at 10 mmHg absolute.¹⁶

value of R and assuming a linear liquid composition profile along the packed section, given y_0 and the reflux drum temperature. New values of composition and the internal reflux ratio are then calculated by solving the linear system given by eqs 39 and 21, and the procedure is repeated until convergence is achieved. The required level of space discretization ($n = 20$) is found by trial and error. The variations of the overall mass transfer coefficient, the liquid holdup, and the vapor holdup as functions of the internal reflux ratio, R , are found to have the following empirical linear relationships with correlation coefficients of no less than 99.4%

$$K_v a_e = (1.256 + 2.217R) \times 10^{-5} \quad (45)$$

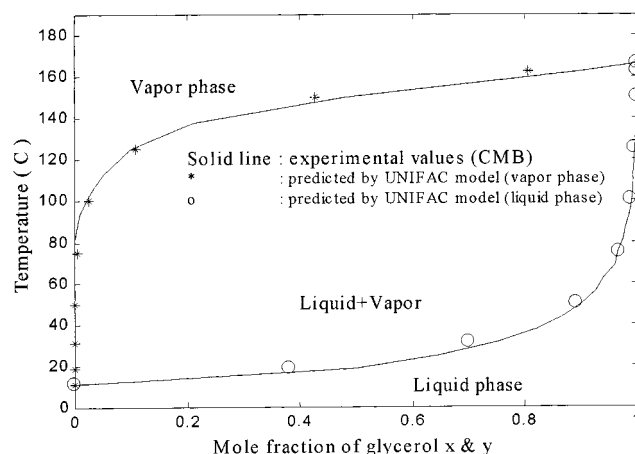
$$H = 0.008115 + 0.013837R \quad (46)$$

$$h = 6.254 \times 10^{-5} - 4 \times 10^{-7}R \quad (47)$$

The system of differential equations given by eqs 21, 27, and 28 was found to be very stiff, and so, it was solved using an implicit numerical algorithm with the MATLAB subroutine ode15s.

Results and Discussion

The variations of the composition profiles along the column height at different reflux drum temperatures, and hence different internal reflux ratios (R), are shown in Figure 2. It is obvious that the composition profiles become linear at low values of the reflux drum temperature, that is, at increasing values of the internal reflux

**Figure 3.** Steady-state composition profiles at different reflux drum temperatures ($n = 20$, $N_1 = 0.051$, $y_0 = 0.05$).

ratio R . This behavior is evident when eqs 19 and 20 are written at steady-state conditions. Because of the form of the vapor–liquid equilibrium curve (Figure 3), the water mole fraction in the vapor phase (y) becomes almost independent of the water mole fraction in liquid phase (x). If the equilibrium relationship is written as: $y^* = c$ (where c is constant) for $T \in [11.5, 70^\circ\text{C}]$, then the steady-state versions of eqs 19 and 20 can be integrated to produce

$$\frac{dx}{d\zeta} = \frac{N_1}{R}(c - y_0)e^{-N_1\zeta} \approx \frac{N_1}{R}(c - y_0) \quad (48)$$

for small values of $N_1\zeta$. The internal reflux ratio is almost constant over the temperature range concerned in this work, as illustrated in Figure 4. This clearly supports assumption number 2 used in the formulation of our model and also justifies assumption 4 of constant H , h , and $k_v a_e$. This result is expected as the change in composition of the liquid is not more than 5%.

The results for the response of liquid composition based on models 1–3 are shown in Figure 5. As can be seen, the response of the three models to a step change in the reflux drum temperature (from 115 to 64 °C) is almost the same. This means that the liquid and vapor holdups have almost no effect on the dynamics of a packed bed containing structured packings when used to separate glycerol from water. This result is anticipated because the liquid and vapor holdups, as given by eqs 46 and 47 respectively, are small when compared to reflux drum holdup M_c ($M_c = 1$ kmol, $h + H = 0.022$ kmol), and this is inconsistent with the behavior of

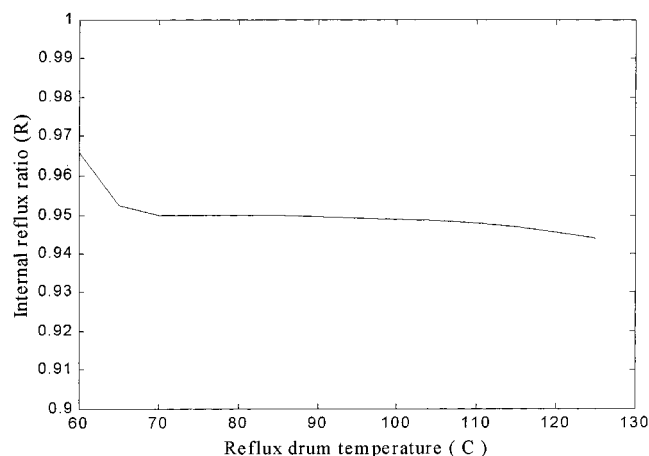


Figure 4. Variation of the internal reflux ratio with the reflux drum temperature.

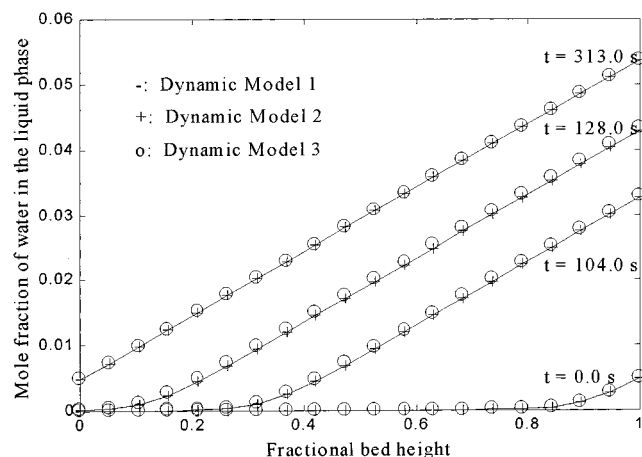


Figure 5. Composition profiles of water in the liquid phase along the height of the packed section as a function of time in response to a step change in the reflux drum temperature from 115 to 64 °C for dynamic models 1–3 ($n = 20$, $N_1 = 0.051$, $y_0 = 0.05$).

industrial distillation columns operating at low pressure.²⁶ The figure also shows that the composition profiles along the fractional height of the packed bed from the initial to the final steady state progress in time from highly nonlinear to linear profiles.

The response of the liquid composition at the bottom, middle, and top of the packed column, as well as in the reflux drum, to a step change in the reflux drum temperature is shown in Figure 6. It is clear that there is a time lag in the response of the liquid composition that increases descending the packed section. These results are in agreement with the physical situation of the system as the reflux drum is expected to be the first to feel the change in the reflux temperature. The results in Figure 6 also show the nonlinear behavior of the liquid composition response along the height of the packed-bed section. This nonlinearity is obviously reflected in the variation of the steady-state gain values of the response with the position along the column as given in Table 2. The nonlinearity of the liquid composition response was cross-checked by introducing positive and negative step changes of equal magnitude (15 °C) in the temperature of the reflux drum around a steady-state temperature of 90 °C as illustrated in Figure 7. A comparison of the speed of the responses to positive and negative steps at the corresponding positions of the packed bed clearly shows the nonlinear behavior in the

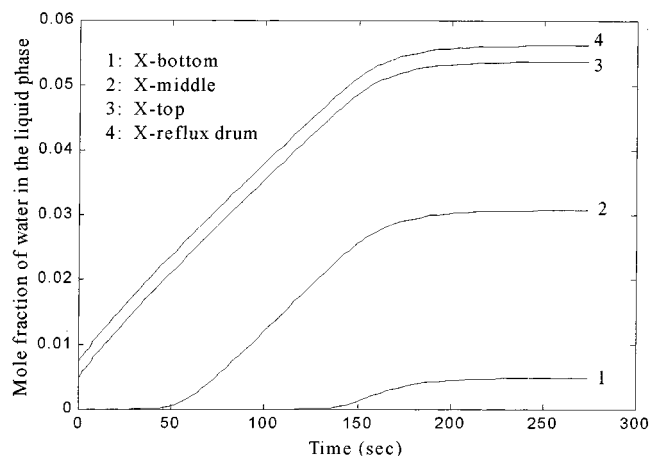


Figure 6. Response of the liquid composition at the bottom, middle, and top of the packed column, as well as in the reflux drum, to a step change in the reflux drum temperature from 115 to 64 °C ($n = 20$, $N_1 = 0.051$, $y_0 = 0.05$).

Table 2. Steady-State Gain of the Response of the Liquid Composition at Different Positions in the Column to a Step Change in the Reflux Drum Temperature

position of the response	steady-state gain of the liquid composition response (mol/(L °C))
bottom of the column	0.95×10^{-4}
middle of the column	5.99×10^{-4}
top of the column	9.55×10^{-4}
reflux drum	9.557×10^{-4}

response. The figure also shows that the nonlinearity of the response increases from the top to the bottom of the packed column.

The most difficult parameter to estimate in the developed model is the overall vapor-phase mass transfer coefficient (K_V). This might introduce some uncertainty in the model predictions. To investigate the degree of uncertainty, a sensitivity analysis for the overall vapor-phase mass transfer coefficient was performed. Figure 8 shows the model predictions for a relative error of magnitude $\pm 5\%$ in K_V . It is clear that the model accuracy is quite good in the reflux drum and at the top of the packed column. However, the uncertainty in the model predictions increases descending toward the bottom of the column. This behavior is attributed to the nonlinearity of the model, as discussed above. The magnitude of the uncertainty in the model predictions is measured here using the mean integral of the percent relative error, which is defined as

$$I_m = \left[\left(\int_0^{t_{ss}} \frac{|x_e(t) - x_o(t)|}{x_o(t)} dt \right) / t_{ss} \right] \times 100 \quad (49)$$

The dependence of I_m on the position along the packed column is shown in Figure 9. It is evident that I_m is large at the bottom of the column and becomes almost negligible (2%) at the top of the column and in the reflux drum. Also, it is clear that the magnitude of I_m is dependent on the sign of the relative error in the overall vapor-phase mass transfer coefficient. Again, this is a reflection of the model nonlinearity.

The stiffness ratio²⁷ is traced at each integration step to view how the stiffness of the Jacobian of the differential equations changes with time. It was found that the stiffness ratio starts on the order of 10^4 , increases rapidly as the slope of the liquid profiles is sharply increased, and then diminishes slowly as the steady-

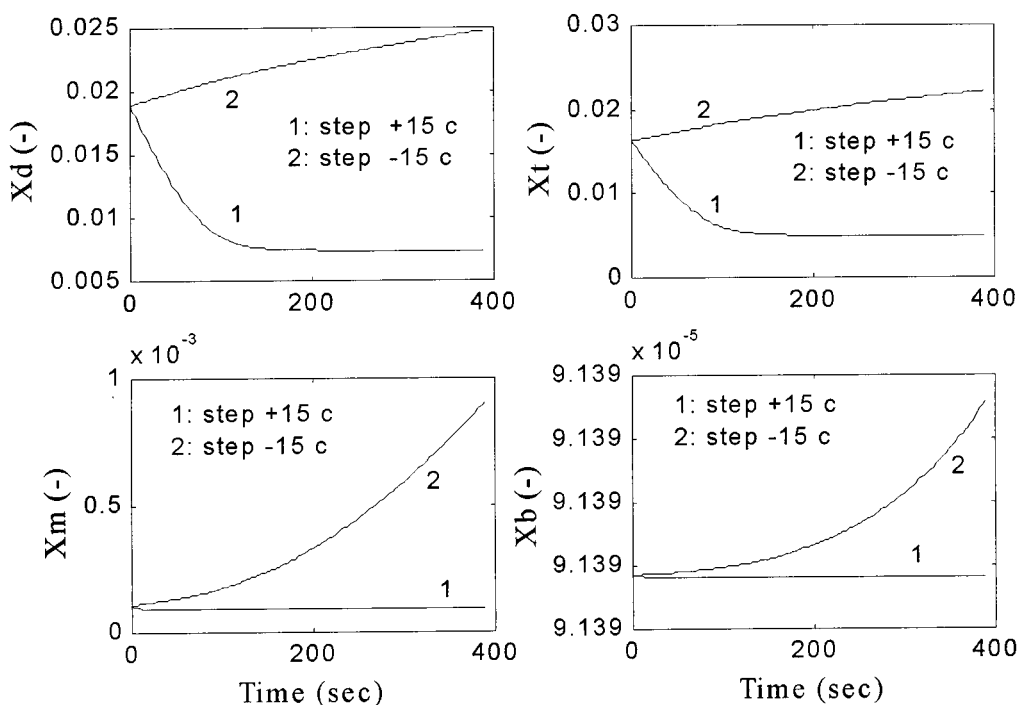


Figure 7. Response of the water mole fraction in the liquid phase in the reflux drum (X_d) and at the top (X_t), middle (X_m), and bottom (X_b) of the packed-bed column to negative and positive step changes in the reflux drum temperature of magnitude 15°C around a steady-state temperature of 90°C ($n = 20$, $N_1 = 0.051$, $y_0 = 0.05$).

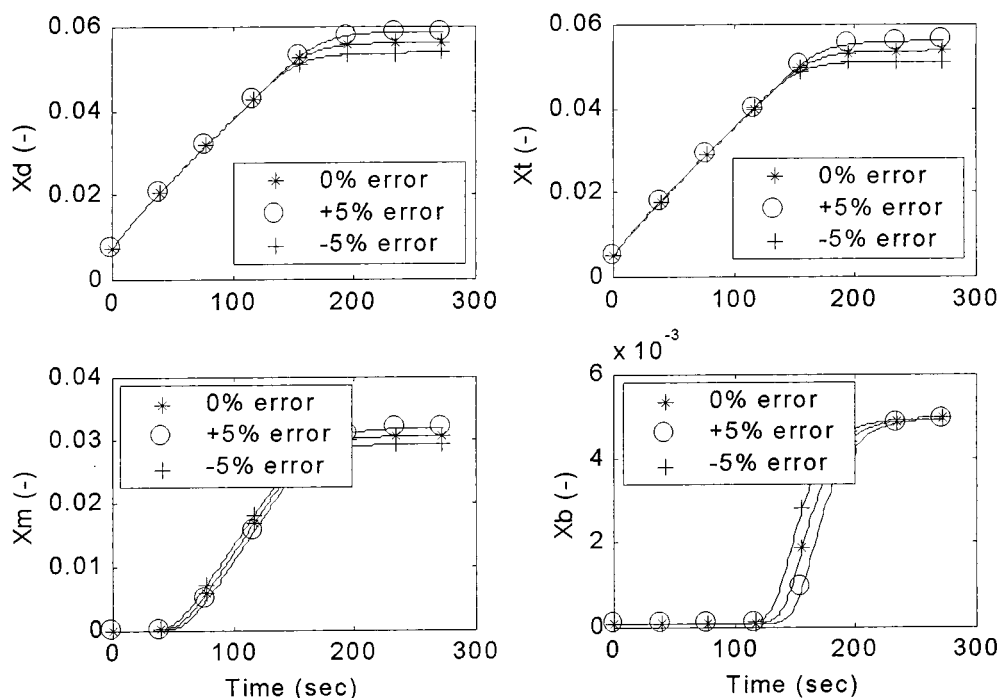


Figure 8. Model predictions for $\pm 5\%$ relative error in the overall vapor-phase mass transfer coefficient ($K_{v,a}$).

state solution is approached. It is noticed that the stiffness ratio increases as the level of discretization n increases, being on the order of 10^3 for $n = 10$ and 10^6 for $n = 16$. This behavior is predicted by the model differential eqs 21, 27, and 28, where the elements a_1 , a_3 , and a_4 are functions of n . The Jacobian of the system of differential equations comprising model 2 is more complex than that in dynamic model 1. However, the number of differential equations is reduced from $2n + 1$ to $n + 1$, and the stiffness ratio is reduced from the order of 10^5 to 10^3 , which permits the step size used in integration to be larger than in former case. Thus, the

computational time was reduced while the same level of accuracy was maintained.²⁷ Unfortunately, the Jacobian of this model comprise an $(n + 1) \times (n + 1)$ matrix that is full of elements below the diagonal plus one row element above the diagonal, and so, a long time is required to evaluate this matrix during integration steps. On the other hand, the Jacobian matrix of dynamic model 1 has only $8n$ nonzero elements. Hence, the ratio of the number of nonzero elements to the total number of elements approaches $2/n$ as n increases for model 1, whereas for dynamic model 2, this ratio approaches $1/2$ as n increases. In dynamic model 3, both

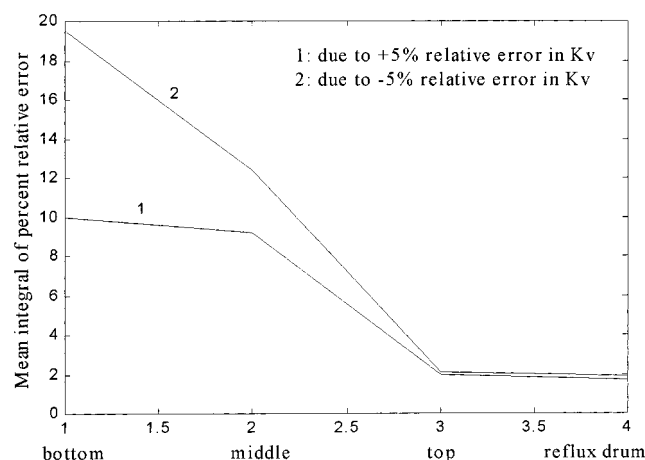


Figure 9. Variation of the mean integral of the percent relative error as a function of the position along the packed column.

the vapor and liquid holdups are neglected, and hence, the model equations are all algebraic, except for the reflux drum equation, which was solved using a fourth-order Runge–Kutta–Merson method of variable step size.²⁸ This model requires more computation time than the previous ones because it involves the solution of a system of nonlinear equations at each integration step. However, model 3, as mentioned above, involves the solution of n nonlinear equations simultaneously at each integration step, which means that it is less accurate than the aforementioned models from a numerical point of view, because, as the number of computational steps increases, the round off and truncation errors grow.^{27,28}

Conclusions

The activity coefficients of glycerol and water in the liquid phase are found to be close to unity over the whole composition range at 10 mmHg abs. This was in agreement with the predictions obtained using UNIFAC. Thus, it was concluded that the glycerol–water system can be considered ideal at 10 mmHg abs without the introduction of considerable errors.

The steady-state composition profiles are found to depend on the reflux drum temperature and, hence, on the internal reflux ratio R . These profiles shift from nonlinear to almost linear as the reflux drum temperature is lowered from 115 to 64 °C or, equivalently, as the internal reflux ratio approaches unity.

The dynamics of the system was modeled by a set of nonlinear partial differential equations that is not amenable to analytical solution. The model was solved numerically to investigate the response of the liquid composition to a step change in the reflux drum temperature. It was found that the vapor and liquid holdups have almost no effect on the dynamics of the column. The response of the system to a step change in the reflux drum temperature is highly nonlinear. There is a time lag in the liquid composition response as it descends the packed section.

From a numerical point of view, dynamic model 2 is found to require less computational effort than the other models because of the sequential solution of the vapor-phase equations given by eq 38. Thus, dynamic model 2 is recommended when numerical solution is attempted using the finite difference method, even though the liquid phase holdup is negligible. The technique employed to convert the nonlinear system of algebraic

equations to linear ones in the solution of the steady-state model was found to be stable and to always converge to the solution, provided that a linear composition profile is used as first guess.

Nomenclature

- A_c = cross-sectional area of the column (m^2)
- a_e = effective interfacial area of the packing (m^{-1})
- a_p = interfacial area of the packing (m^{-1})
- D_v = vapor-phase diffusion coefficient (m^2/s)
- Ft = correction factor for the total liquid holdup
- F_{SE} = correction factor in the equation for surface enhancement
- Fr_L = Froude number of the liquid phase
- g_{eff} = effective gravity (m/s^2)
- H = liquid holdup ($kmol/m$)
- H_L = fractional liquid holdup
- H_{OG} = overall height of the gas transfer unit (m)
- h = vapor holdup ($kmol/m$)
- K_L = liquid-phase mass transfer coefficient (m/s)
- K_v = vapor-phase mass transfer coefficient (m/s)
- K'_v = overall vapor-phase mass transfer coefficient ($1/s$)
- K_v = overall vapor-phase mass transfer coefficient ($kmol/s$)
- L = liquid molar flow rate ($kmol/s$)
- \bar{M} = average molecular weight of glycerol–water mix ($kg/kmol$)
- M_c = reflux drum holdup ($kmol$)
- m' = slope of the equilibrium curve
- N_1 = number of gas transfer units
- n = discretization level
- P = total pressure ($mmHg$)
- R = internal reflux ratio
- Re_L = Reynolds number of the liquid phase
- Re_v = Reynolds number of the vapor phase
- R_g = ideal gas constant
- S = side dimension of the corrugated packing (m)
- Sc_v = Schmidt number of the vapor phase
- T = temperature ($^{\circ}C$)
- t = time (s)
- U_{LS} = liquid-phase superficial velocity (m/s)
- U_{Vs} = vapor-phase superficial velocity (m/s)
- V = vapor flow rate ($kmol/s$)
- We_L = Weber number for the liquid phase
- x = mole fraction of water in the liquid phase
- y = mole fraction of water in the vapor phase
- y^* = equilibrium mole fraction of water at the vapor interface
- Z_i = height of the packed section (m)
- ρ_L = density of the liquid phase (kg/m^3)
- μ_L = viscosity of the liquid phase ($kg/(m\ s)$)
- ω = ratio of vapor to liquid holdup, h/H
- ϵ = void space of the packing
- ϵ_o = operating void space
- ζ = dimensionless space variable
- θ = dimensionless time
- ΔP = pressure drop through the packing ($mmHg/m$)
- $\Delta \zeta$ = dimensionless space increment
- ΔZ = space increment (m)

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