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Transient Response of a Distillation Column Plate. Part I. Theory: Five Models and Their Fourier Transforms

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Transient Response of a Distillation Column Plate. Part I. Theory: Five Models and Their Fourier Transforms

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Abstract

Five models are used to describe the transient behavior of the liquid composition on a distillation column bubble cap tray when the liquid composition entering the tray undergoes a composition transient. The assumptions required for the models are discussed. The equations are transformed by the Laplace operator, and the solutions are left in the frequency response form for comparison with experimental data. The models involving distance, either across a tray or through a downcomer, are solved to relate the composition to the measurable compositions in the downcomers. The five models investigated are models of (1) a perfectly mixed tray; (2) plug flow across a tray; (3) a perfectly mixed plate with a time lag in the downcomer; (4) longitudinal dispersion (Taylor's) across the tray; and (5) longitudinal dispersion with dead zones on a tray.

INTRODUCTION

A mathematical description of the composition changes in a plate distillation column operating at unsteady state is needed for predicting behavior of control systems and, to an extent, for predicting startup behavior of a plant. Various composition models have been previously described, and a satisfactory means of model comparison and evaluation

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is needed. A mathematical description and the Fourier transforms are presented for five models of plate composition behavior. The models are: (1) the perfectly mixed plate; (2) plug flow across a plate; (3) the perfectly mixed plate with time lag for flow between plates in the downcomer; (4) turbulent (Taylor's) dispersion on a plate; and (5) dead zones (with dispersion) on a plate. A subsequent part presents experimental data and statistical comparisons of the five models.

In order to examine the effects of liquid phase mixing, a special case of plate composition changes with no mass transfer with the vapor (no distillation) has been examined in a subsequent part. The input plate concentration changes were assumed to be pulse changes, i.e., a change of concentration and a return to the same base line; this technique affords better model discrimination, is readily performed experimentally, and is adapted to computerized data reduction.

Literature Review

Endtz, Jansen, and Vermeulen (*1*), Rademaker (*2*), and Berg and James (*3*) reported tests of distillation dynamics in terms of generalized observations. They found that temperature, pressure, and flow rate changes were instantaneous compared to composition changes. Rosenbrock (*4*) described three regions in a distillation transient response curve: (1) secondary effects (vapor flow, liquid flow, pressure, and temperature); (2) intermediate region where mass transfer controls; and (3) the final steady state value. He also noted that (*5*) composition changes had 1 hr time constants and were more significant than liquid flow changes with time constants on the order of 1 to 2 min.

Lamb, Pigford, and Rippin (*6*) derived a perfectly mixed distillation plate model for unsteady state composition as a function of liquid flow rate, equilibrium composition, and tray holdup. The model was examined by analog computer simulation and was tested by Gerster et al. (*7*–*9*). Martin (*10*) examined the response of a 12-plate column separating methanol and water with Lamb's model. He found that the model predicted the first portion (6 min) of the response, but it was inadequate for long times. He observed that the model was adequate for control simulation. Since the model predicted the correct magnitude and time lag of the initial output disturbance, the controller-system response could be examined to see if it produced the desired correction action. Also, Martin noted that the transient stripping factor was in error as much as 200%. Huckaba et al. (*11*, *12*) derived a model for perfect mixing of composition and enthalpy on the distillation plate. The model was tested in a tertiary butanol–water system in a 10-in. diameter, 12-plate bubble cap column.

Armstrong et al. (*13–17*) and Brown (*18*) have also examined the perfectly mixed plate model. Voetter (*19*) derived the frequency response form of the perfectly mixed model. His major contribution was an analysis of the error in assuming negligible vapor holdup, an adiabatic column, nonconstant stripping factor, and incomplete tray efficiency. Voetter stated that the maximum error from each assumption could be 20% and that the combined assumptions could result in a maximum error of 40%. However, he observed that this error was not excessive in control theory.

Lewis (*20*) derived an expression for the Murphree efficiency for liquid in plug flow across the plate.

Several authors (*13*, *14*, *20–45*) have realized that the perfectly mixed plate model is an inexact description of mixing on distillation plates. Moczek et al. (*37*) and Armstrong and Wilkinson (*13*) suggested that a plate be modeled by perfectly mixed and plug flow transfer functions. Gatreaux and O'Connell (*31*) and Sakata (*40*) examined Kirshbaum's series of perfectly mixed pools model. With dye testing, Sakata found that plates were described by 1.06 to 1.21 pools. Quentin (*39*) correlated his data as a series of perfectly mixed tanks.

Foss and Gerster (*28*) stated that the liquid on a sieve tray was mixed to some unknown extent between plug flow and perfectly mixed. Oliver and Watson (*38*) said that mixing was between one-quarter and three-quarters complete in an 18-in. diameter tower. Garner and Porter (*30*) noted that mixing in the froth promoted mass transfer and eddy diffusion. They observed that a plate was partially mixed, and that for a bubble cap plate the effective diffusion coefficient was from 1.9 to 70 times greater than molecular diffusion.

Gerster et al. (*32*, *46*) derived the turbulent dispersion model for mass transport across a bubble cap plate. Foss et al. (*29*) and Quentin (*39*) found that the change in variance about the mean of a pulse tracer curve increased linearly with tray length. For a dirac input, the dispersion model predicts this linear increase in the variance. In the American Institute of Chemical Engineers' report (*46*), the eddy diffusion coefficient, D_E, was correlated by the equation

$$(D_E)^{0.5} = 0.0124 + 0.0171u + 0.00250L + 0.0150W$$

Johnson and Marangozis (*36*) derived the splashing model for mixing. This model was mathematically similar to the eddy diffusion model (*21*, *32*, *42*). Barker and Self (*23*), Gilbert (*33*), and Welch, Durbin, and Holland (*44*) analyzed mixing on distillation plates with the dispersion model. Wilkinson and Armstrong (*45*) derived a model equivalent to the dispersion model by a Taylor's series expansion of the change in composition with distance. They found this model favorably described composition–time data from a step change in feed composition.

Holland (*47*) and Tetlow et al. (*48*) considered a distillation plate as composed of parallel segments in which fluid transfer was by bypass, plug flow, and perfect mixing mechanisms. Characteristic curves were presented for each flow pattern.

Rosenbrock (*49*) and Williams (*50*) have compiled literature reviews on distillation models. Williams lists the physical parameters which must be included in a complete mathematical model of distillation. Williams commented that the question that remains unanswered is which model is the most valid, since a complete mathematical description is computationally unmanageable at the present time.

Hopefully this work fulfills Rosenbrock's (*49*) wish for an experimental comparison of distillation models. The present study is the first reported work in which the perfectly mixed, plug flow, perfectly mixed plate with time lag, dispersion, and dead zone models for distillation have been examined by frequency response techniques. Also, this is the first work that mathematically considers the variation of the vapor composition for plate n as a function of the model–time–distance–concentration variation on plate $n - 1$.

THEORY

Heat, mass, and momentum transport must be included in a complete mathematical description of distillation. The complete model would be arduous, if not impossible, to solve. In this study, several simplified models are compared using their frequency response forms and data from pulse testing.

Perfectly Mixed Plate Model

The perfectly mixed plate model has been presented in various forms by several authors (*6–8*, *11–18*, *39*, *51–56*). The usual assumptions and those made in this derivation are:

(a) The liquid on each plate unit (bubble cap tray and downcomer) is perfectly mixed.

(b) The time constants for fluid and thermal transfer are negligible compared to mass transfer.

(c) Vapor holdup is negligible compared to liquid holdup.

(d) The column is essentially adiabatic.

(e) The steady state efficiency is not affected by the passage of the pulse across the plate.

(f) Liquid and vapor flows are not affected during the transient periods, so that the liquid holdup on the plate is constant.

(g) A linear equilibrium relationship is valid.

Rosenbrock (*49*) and Quentin (39) stated that thermal and flow quantities reach steady state in one-fifteenth to one-thirtieth the time required for mass transfer. This validated assumption (b).

Huckaba and Danly (*11*) have shown assumption (c) is sound for atmospheric distillation. For the system studied, the liquid residence time was about 30 sec whereas vapor residence time between plates was approximately 1 sec.

Quentin (*39*) found assumption (e) valid for his work.

Assumption (f) is confirmed if the molar latent heats of vaporization are approximately equal and the disturbance is small compared to the average flows. For the benzene–carbon tetrachloride system, the latent heats were 7170 and 7350 cal/g mole, respectively, and the liquid molar densities at 172°F were 0.01035 and 0.00955 g moles/ml, respectively. The average change in mole fraction on the test plate was approximately 0.06. The theoretical equilibrium line slope varied from 1.09 to 1.06. These facts confirm assumption (g).

The calculated heat loss was less than 10% of the heat input, approximating assumption (d).

Assumption (a) distinguishes this model from the other models. The validity of this assumption is the model's ability to best describe the data.

The unsteady state mass balance for the perfectly mixed tray is:

$$\tilde{H}\frac{dx_n{}^T(t)}{dt} = \tilde{V}y_{n-1}{}^T(t) + \tilde{L}x_{n+1}{}^T(t) - \tilde{V}y_n{}^T - \tilde{L}x_n{}^T(t) \qquad (1)$$

If the liquid and vapor mole fractions are redefined as a steady state value $\bar{x}$ and $\bar{y}$ and a transient contribution $x(t)$ and $y(t)$, then Eq. (1) is

$$\begin{aligned}\tilde{H}\frac{dx_n(t)}{dt} = {} & \tilde{V}y_{n-1}(t) + \tilde{L}x_{n+1}(t) - \tilde{V}y_n(t) - \tilde{L}x_n(t) \\ & + \tilde{V}\bar{y}_{n-1} + \tilde{L}\bar{x}_{n+1} - \tilde{V}\bar{y}_n - \tilde{L}\bar{x}_n \qquad (2)\end{aligned}$$

A substitution into Eq. (2) of the steady state mass balance,

$$\tilde{V}\bar{y}_{n-1} + \tilde{L}\bar{x}_{n+1} - \tilde{V}\bar{y}_n - \tilde{L}\bar{x}_n = 0 \tag{3}$$

and the values from assumption (g)

$$y_{n-1}(t) = m'x_{n-1}(t) \tag{4}$$

$$y_n(t) = mx_n(t) \tag{5}$$

and

$$\tilde{H}\frac{dx_n(t)}{dt} = m'\tilde{V}x_{n-1}(t) - (m\tilde{V} + \tilde{L})x_n(t) + \tilde{L}x_{n+1}(t) \tag{6}$$

The input function is the mole fraction entering plate n from plate $n + 1$, $x_{n+1}(t)$, which can be experimentally measured, and the vapor input function is calculated from the model applied to plate $n - 1$. To calculate $x_{n-1}(t)$, the additional assumption that $x_{n-2}^T = \bar{x}_{n-2}$, the total response is the steady state response (i.e., the transient response is insignificant and so much later in time than the response on plate n).

Equation (6) written for plate $n - 1$ is

$$\tilde{H}\frac{dx_{n-1}}{dt} = \tilde{L}x_n(t) - (m'\tilde{V} + \tilde{L})x_{n-1}(t) \tag{7}$$

The Laplace transforms of Eqs. (6) and (7) are

$$\frac{\tilde{H}}{\tilde{L}}sX_n(s) = \frac{m'\tilde{V}}{\tilde{L}}X_{n-1}(s) - \left(\frac{m'\tilde{V}}{\tilde{L}} + 1\right)X_n(s) + X_{n+1}(s) \tag{8}$$

$$\frac{\tilde{H}'}{\tilde{L}}sX_{n-1}(s) = X_n(s) - \left(\frac{m'\tilde{V}}{\tilde{L}} + 1\right)X_{n-1}(s) \tag{9}$$

since the initial conditions were

$$x_n(0) = 0 \tag{10}$$

and

$$x_{n-1}(0) = 0 \tag{11}$$

In terms of the parameter groups

$$\alpha = \tilde{H}/\tilde{L} \tag{12}$$

$$\beta = m\tilde{V}/\tilde{L} \tag{13}$$

$$\beta' = m'\tilde{V}/\tilde{L} \tag{14}$$

$$\alpha' = \tilde{H}'/\tilde{L} \tag{15}$$

Equations (8) and (9), solved for $X_n(s)$, give

$$X_n(s) = X_{n+1}(s)/\left[\alpha s + \beta + 1 - \frac{\beta'}{\alpha' s + \beta' + 1}\right] \tag{16}$$

The model frequency response has both real, $R_p(\omega)$ and imaginary, $I_p(\omega)$, parts.

$$R_p(\omega) = R_{n+1}(\omega)\left[\frac{ARD}{(ARD)^2 + (AID)^2}\right] + I_{n+1}(\omega)\left[\frac{AID}{(AID)^2 + (ARD)^2}\right] \tag{17}$$

and

$$I_p(\omega) = I_{n+1}(\omega)\left[\frac{ARD}{(ARD)^2 + (AID)^2}\right] - R_{n+1}(\omega)\left[\frac{AID}{(AID)^2 + (ARD)^2}\right] \tag{18}$$

where

$$ARD = \beta + 1 - \frac{\beta'(\beta' + 1)}{(\beta' + 1)^2 + (\alpha\omega)^2} \tag{19}$$

$$AID = \alpha\omega + \frac{\beta'\alpha'\omega}{(\beta' + 1)^2 + (\alpha\omega)^2} \tag{20}$$

One observes that

$$X_{n,p}(\omega) = R_p(\omega) + jI_p(\omega) \tag{21}$$

where $X_{n,p}(\omega)$ is the predicted output of the model.

It may be worthwhile to note that Eq. (8) can be used as the model if $X_{n-1}(s)$ can be measured inside the system.

For testing the mixing assumptions, the model without mass transfer, the terms m and m' are zero.

The flow model corresponding to Eq. (8) is

$$X_n(s) = X_{n+1}(s)/(\alpha s + 1) \tag{22}$$

and the frequency response forms are

$$R_p(\omega) = \frac{1}{(\alpha\omega)^2 + 1}[R_{n+1}(\omega) + \omega\alpha I_{n+1}(\omega)] \tag{23}$$

and

$$I_p(\omega) = \frac{1}{(\alpha\omega)^2 + 1}[I_{n+1}(\omega) - \alpha\omega R_{n+1}(\omega)] \tag{24}$$

Plug Flow Model

The plug flow model uses assumptions (b) through (g). Assumption (a) is replaced by

(a′) The fluid moves across the tray with no horizontal mixing, the effect of a velocity profile is ignored, and the liquid composition is homogeneous in the vertical direction.

The following additional assumption is required:

(h) Flow on a rectangular plate describes the flow geometry of a bubble cap plate,

A differential mass balance applied to a plate segment gives

$$\frac{\partial x_n{}^T(z,t)}{\partial t} = -\frac{\tilde{L}}{\rho_F\rho'_L wh}\frac{\partial x_n{}^T(z,t)}{\partial z} - \frac{\tilde{V}}{\rho_F\rho'_L whz}[y_n{}^T(z,t) - y_{n-1}{}^T(z,t)] \quad (25)$$

Substitution of the sum of the steady state and the transient expressions for x^T and y^T and the mass transfer relations, and subtracting the steady state equation

$$0 = -\frac{\tilde{L}}{\rho_F\rho'_L wh}\frac{d\bar{x}_n(z)}{dz} - \frac{\tilde{V}}{\rho_F\rho'_L whz}[\bar{y}_n(z) - \bar{y}_{n-1}(z)] \quad (26)$$

gives the transient plug flow model

$$\frac{\partial x_n(z,t)}{\partial t} = \frac{\tilde{L}}{\rho_F\rho'_L wh}\frac{\partial x_n(z,t)}{\partial z} - \frac{\tilde{V}}{\rho_F\rho'_L whz}[mx_n(z,t) - m'x_{n-1}(z,t)] \quad (27)$$

If the dimensionless distance

$$\zeta = z/Z \quad (28)$$

and the holdup expression

$$\tilde{H} = \rho_F\rho'_L whz \quad (29)$$

are substituted into Eq. (27) along with the parameters defined previously in Eqs. (12) through (15),

$$\alpha\frac{\partial x_n(\zeta,t)}{\partial t} = -\frac{\partial x_n(\zeta,t)}{\partial \zeta} - \beta x_n(\zeta,t) + \beta' x_n(\zeta,t) \quad (30)$$

for plate n, and

$$\alpha' \frac{\partial x_{n-1}(\zeta,t)}{\partial t} = \frac{\partial x_{n-1}(\zeta,t)}{\partial \zeta} - \beta' x_{n-1}(\zeta,t) \tag{31}$$

for plate $n - 1$.

The boundary conditions for the plug flow model are

$$x_n(\zeta,0) = 0 \tag{32}$$

$$x_n(0,t) = x_{n+1}(t) \qquad \text{for } t \geq 0 \tag{33}$$

$$x_{n-1}(\zeta,0) = 0 \tag{34}$$

$$x_{n-1}(1,t) = x_n(t) \qquad \text{for } t \geq 0 \tag{35}$$

The Laplace transform of Eqs. (30) and (31)

$$L_t[x_n(\zeta,t)] = X_n(\zeta,s) \tag{36}$$

gives

$$\frac{dX_n(\zeta,s)}{d\zeta} = -[X_n(\zeta,s)][\alpha s + \beta] + \beta' X_{n-1}(\zeta,s) \tag{37}$$

and

$$\frac{dX_{n-1}(\zeta,s)}{d\zeta} = (\alpha' s + \beta')X_{n-1}(\zeta,s) \tag{38}$$

The solution of Eq. (38) is

$$X_{n-1}(\zeta,s) = X_n(1,s)\, e^{(\alpha' s+\beta')(\zeta-1)} \tag{39}$$

This equation, substituted into Eq. (37) and solved for $X_n(\zeta,s)$, gives

$$\begin{aligned} X_n(\zeta,s) = {} & X_{n+1}(s)\, e^{-(\alpha s+\beta)\zeta} \\ & - \frac{\beta' X_n(1,s)}{(\alpha + \alpha')s + (\beta + \beta')}[e^{-(\alpha' s+\beta')}\, e^{-(\alpha s+\beta)\zeta} - e^{(\alpha' s+\beta')(\zeta-1)}] \end{aligned} \tag{40}$$

The solution for $X_n(1,s)$, the solution at the point of measurement, is

$$X_n(s) = X_n(1,s) = \frac{X_{n+1}(s)e^{-(\alpha s+\beta)}}{\left\{1 + \frac{\beta'}{(\alpha + \alpha')s + (\beta + \beta')}[e^{-[(\alpha+\alpha')s+(\beta+\beta')]} - 1]\right\}} \tag{41}$$

The real and imaginary parts of the predicted output of Eq. (41) are

$$R_p(\omega) = QRM \cdot R_{n+1}(\omega) - QIM \cdot I_{n+1}(\omega) \tag{42}$$

$$I_p(\omega) = QRM \cdot I_{n+1}(\omega) + QIM \cdot R_{n+1}(\omega) \tag{43}$$

where

$$QRM = \mathrm{Re}[R_D(\beta + \beta') + (\alpha + \alpha')\omega I_D] - \mathrm{Ie}[(\alpha + \alpha')\omega R_D - (\beta + \beta')I_D] \tag{44}$$

$$QIM = \mathrm{Ie}[R_D(\beta + \beta') + (\alpha + \alpha')\omega I_D] + \mathrm{Re}[(\alpha + \alpha')\omega R_D - (\beta + \beta')I_D] \tag{45}$$

in which

$$R_D = \beta + \beta'\mathrm{Re}' \tag{46}$$

$$I_D = (\alpha + \alpha')\omega + \beta'\mathrm{Ie}' \tag{47}$$

$$\mathrm{Re} = e^{-\beta}\cos(\alpha\omega) \tag{48}$$

$$\mathrm{Ie} = e^{-\beta}\sin(\alpha\omega) \tag{49}$$

and further,

$$\mathrm{Re}' = e^{-(\beta+\beta')}\cos[(\alpha + \alpha')\omega] \tag{50}$$

$$\mathrm{Ie}' = e^{-(\beta+\beta')}\sin[(\alpha + \alpha')\omega] \tag{51}$$

The flow model for testing mixing without mass transfer is

$$\alpha\frac{\partial X_n(\zeta,s)}{\partial t} = -\frac{\partial X_n(\zeta,s)}{\partial\zeta} \tag{52}$$

for which the Laplace transform is

$$X_n(s) = X_{n+1}(s)\, e^{-\alpha s} \tag{53}$$

and the frequency response solution is

$$R_p(\omega) = R_{n+1}(\omega)\cos(\alpha\omega) + I_{n+1}(\omega)\sin(\alpha\omega) \tag{54}$$

$$I_p(\omega) = I_{n+1}(\omega)\cos(\alpha\omega) - R_{n+1}(\omega)\sin(\alpha\omega) \tag{55}$$

Perfectly Mixed Plate with Time Lag

This model considers the concentration on the plate to be uniform, i.e., perfect mixing. The downcomers, which couple the plates, are described by a plug flow model with no interphase mass transfer. Armstrong and Wilkinson (*13*), Rose and Williams (*57*), and Moczek et al. (*37*) have investigated this model.

Assumptions (a) through (g) apply, and an additional assumption (h), that the downcomer exhibits liquid phase plug flow with no interphase mass transfer is required.

Equation (6) modified for this case is

$$\frac{\tilde{H}}{\tilde{L}}\frac{dx'_n(t)}{dt} = \frac{m'\tilde{V}}{\tilde{L}}x'_{n-1}(t) - \frac{m\tilde{V} + \tilde{L}}{\tilde{L}}x'_n(t) + x_{n+1}(t) \tag{56}$$

Downcomer composition is described by

$$\frac{\partial x_n(\zeta,t)}{\partial t} = -\frac{\tilde{L}}{\tilde{H}_D}\frac{\partial x_n(\zeta,t)}{\partial \zeta} \tag{57}$$

where $\tilde{H}_D$ is the molar downcomer holdup (moles).

The Laplace transform solutions of Eqs. (56) and (57) are connected by the boundary condition

$$X'_n(s) = X_n(0,s) \text{ at } \zeta = 0 \tag{58}$$

to give (at the point of measurement $\zeta = 1$)

$$X_n(s) = X_n(1,s) = X_{n+1}(s)\exp(-\tau_d s)\Big/\left[\alpha s + \beta + 1 - \frac{\beta' \exp(-\tau_d s)}{\alpha' s + \beta' + 1}\right] \tag{59}$$

where

$$\tau_d = \tilde{L}/\tilde{H}_D \tag{60}$$

The Laplace solution without mass transfer is

$$X_n(s) = X_{n+1}(s)\exp(-\tau_d s)/[\alpha s + 1] \tag{61}$$

The real and imaginary portions of the predicted response are

$$\begin{aligned} \mathrm{R}_p(\omega) = {} & \mathrm{R}_{n+1}(\omega)[\cos(\tau_d\omega) - \alpha\omega\sin(\tau_d\omega)] \\ & + \mathrm{I}_{n+1}(\omega)[\alpha\omega\cos(\tau_d\omega) + \sin(\tau_d\omega)] \end{aligned} \tag{62}$$

and

$$\begin{aligned} \mathrm{I}_p(\omega) = {} & \mathrm{I}_{n+1}(\omega)[\cos(\tau_d\omega) - \alpha\omega\sin(\tau_d\omega)] \\ & - \mathrm{R}_{n+1}(\omega)[\alpha\omega\cos(\tau_d\omega) + \sin(\tau_d\omega)] \end{aligned} \tag{63}$$

Turbulent Dispersion Model

The eddy dispersion model assumes that the fluid moves across the plate with mixing due to the motion of turbulent eddies. One assumes the mathematical description for diffusion is valid for eddy transport.

The dispersion model has been discussed by several authors (*21*, *23*, *32*, *34*, *41*, *42*, *44*). Johnson and Marangozis (*36*) and Wilkinson and Armstrong (*45*) have derived mathematically similar models. Several authors (*13*, *14*, *20–45*) have noticed concentration gradients on distillation plates, and that plate mixing is due to eddies moving rapidly through the foam on the plate.

For this derivation assumptions (b) through (h) apply, and assumptions (a) and (a′) are replaced by

(a″) The fluid mixing is analogous to diffusion; and the effects of radial dispersion, velocity profile, and molecular diffusion are negligible, and liquid concentration is homogeneous in the vertical direction.

A differential mass balance applied to the plate gives

$$\frac{\partial x_n{}^T(z,t)}{\partial t} = D_L \frac{\partial^2 x_n{}^T(z,t)}{\partial z^2} - \frac{\tilde{L}}{wh\rho_F\rho_L'}\frac{\partial x_n{}^T(z,t)}{\partial z} - \frac{\tilde{V}}{whZ\rho_F\rho_L'}[y_n{}^T(z,t) - y_{n-1}{}^T(z,t)] \tag{64}$$

where D_L is the eddy diffusion or turbulent dispersion coefficient. The transient equation for plate n is

$$\alpha\frac{\partial x_n(\zeta,t)}{\partial t} = \frac{\alpha}{\eta}\frac{\partial^2 x_n(\zeta,t)}{\partial \zeta^2} - \frac{\partial x_n(\zeta,t)}{\partial \zeta} - \beta x_n(\zeta,t) + \beta' x_{n-1}(\zeta,t) \tag{65}$$

where

$$\eta = Z^2/D_L \tag{66}$$

The boundary conditions for Eq. (65) and for this equation written for plate $n - 1$ are:

$$x_n(\zeta,0) = 0 \tag{67}$$

$$x_n(0,t) = x_n(t) \qquad \text{for } t \geq 0 \tag{68}$$

$$\lim_{\zeta\to\infty} x_n(\zeta,t) = 0 \tag{69}$$

$$x_{n-1}(\zeta,0) = 0 \tag{70}$$

$$x_{n-1}(1,t) = x_n(1,t) \qquad \text{for } t \geq 0 \tag{71}$$

$$\lim_{\zeta\to-\infty} x_{n-1}(\zeta,t) = 0 \tag{72}$$

It should be noted that for $\zeta > 1$, $x_{n-1}(\zeta,t)$ is zero and similarly $x_n(\zeta,t) = 0$ for $\zeta < 0$.

The solution for $X_{n-1}(\zeta,s)$ is

$$X_{n-1}(\zeta,s) = X_n(1,s)\exp\left[-\frac{\eta'}{2\alpha'} + \frac{\eta'}{2\alpha'}\sqrt{1 + \frac{4\alpha'}{\eta'}(\alpha's + \beta')}\right][\zeta - 1] \tag{73}$$

where

$$\eta' = Z^2/D'_L \tag{74}$$

The solution for Eq. (65) for X_n at the point of measurement is

$$X_n(s) = X_n(1,s) = X_{n+1}(s)e^{\psi}/\{1 + G[1 - e^{(\psi-\psi')}]\} \tag{75}$$

where

$$G = \beta'/\left[\psi'^2\left(\frac{\alpha}{\eta}\right) - \psi' - (\alpha's + \beta)\right] \tag{76}$$

$$\psi = \frac{\eta}{2\alpha} - \frac{\eta}{2\alpha}\sqrt{1 + \frac{4\alpha}{\eta}(\alpha s + \beta)} \tag{77}$$

$$\psi' = -\frac{\eta'}{2\alpha'} + \frac{\eta'}{2\alpha'}\sqrt{1 + \frac{4\alpha'}{\eta'}(\alpha's + \beta')} \tag{78}$$

The Laplace transform solution of the model without mass transfer is

$$X_n(s) = X_{n+1}(s)\exp\frac{1 - \sqrt{1 + \dfrac{4\alpha^2 s}{\eta}}}{\dfrac{2\alpha}{\eta}} \tag{79}$$

The frequency response solution for the predicted output of the model is

$$\mathrm{R}_p(\omega) = (\overline{\mathrm{M.R.}})[\cos(\overline{\mathrm{P.A.}})\,\mathrm{R}_{n+1}(\omega) - \sin(\overline{\mathrm{P.A.}})\,\mathrm{I}_{n+1}(\omega)] \tag{80}$$

$$\mathrm{I}_p(\omega) = (\overline{\mathrm{M.R.}})[\cos(\overline{\mathrm{P.A.}})\,\mathrm{I}_{n+1}(\omega) + \sin(\overline{\mathrm{P.A.}})\,\mathrm{R}_{n+1}(\omega)] \tag{81}$$

where

$$(\overline{\mathrm{M.R.}}) = \exp\left\{\frac{\eta}{2\alpha} - \frac{\eta}{2\alpha}\left[1 + \left(\frac{4\alpha^2\omega}{\eta}\right)^2\right]\cos\bar{b}\right\} \tag{82}$$

$$(\overline{\mathrm{P.A.}}) = -\frac{\eta}{2\alpha}\left\{\left[1 + \left(\frac{4\alpha^2\omega}{\eta}\right)^2\right]^{1/4}\sin\bar{b}\right\} \tag{83}$$

and

$$\bar{b} = 1/2 \tan^{-1}\left(\frac{4\alpha^2\omega}{\eta}\right) \tag{84}$$

The Perfectly Mixed Dead Zone Model

A dead zone model was first proposed by Turner (*58*). Hays (*59*) investigated a modification of this model for tracer mixing in river channels.

Assumptions (a″) through (h) are applicable. In addition the following assumption must be made:

(i) In contact with the main stream, the active zone, there exists a perfectly mixed dead zone; mass can be transferred from the stream to the dead zone and vice versa; and all the dispersive flow is in the active zone.

A mass balance applied to the active zone gives, for plate n

$$\begin{aligned}\frac{\partial x_n{}^T(z,t)}{\partial t} &= D_L\frac{\partial^2 x_n{}^T(z,t)}{\partial z^2} - \frac{\tilde{L}}{\rho_F\rho_L' hw}\frac{\partial x_n{}^T(z,t)}{\partial z}\\ &\quad - \frac{\tilde{V}}{\rho_F\rho_L' hwZ}[y_n{}^T(z,t) - y_{n-1}{}^T(z,t)] + \frac{P}{\rho_F\rho_L' wh}N_d\end{aligned} \tag{85}$$

and for the perfectly mixed dead zone, according to Hays (*59*, *60*),

$$\frac{dx_{n,D}{}^T(t)}{dt} = \frac{PK'}{\rho_F\rho_L' A_d}[x_n{}^T(x,t) - x_{n,D}{}^T(t)] \tag{86}$$

The steady state equations for plate n are

$$0 = D_L\frac{d^2\bar{x}_n(z)}{dz^2} - \frac{\tilde{L}}{\rho_F\rho_L' wh}\frac{d\bar{x}_n(z)}{dz} - \frac{\tilde{V}}{\rho_F\rho_L' hwZ}[\bar{y}_n(z) - \bar{y}_{n-1}(z)] \tag{87}$$

for the active zone; and for the dead zone

$$0 = [\bar{x}_n(z) - \bar{x}_{n,D}]\frac{PK'}{\rho_F\rho_L' A_d} = N_d \tag{88}$$

Usually mass transfer coefficients are written as "Ka" where a is the ratio of the contact area to the main stream volume

$$a = PZ/whZ = P/wh \tag{89}$$

and for the dead zone

$$d = PZ/A_dZ = P/A_d \tag{90}$$

and K_d is the mass transfer coefficient based on the dead zone volume.

The boundary conditions for plate n are

$$x_n(0,t) = x_{n+1}(t) \qquad \text{for } t \geq 0 \tag{91}$$

$$\lim_{\zeta \to 0} x_n(\zeta,t) = 0 \tag{92}$$

$$x_n(\zeta,0) = 0 \tag{93}$$

$$x_{n,D}(0) = 0 \tag{94}$$

and for plate $n - 1$,

$$x_{n-1}(1,t) = x_n(1,t) \qquad \text{for } t \geq 0 \tag{95}$$

$$\lim_{\zeta \to -\infty} x_{n-1}(\zeta,t) = 0 \tag{96}$$

$$x_{n-1}(\zeta,0) = 0 \tag{97}$$

and

$$x_{n-1,D}(0) = 0 \tag{98}$$

with the restrictions that

$$x_n(\zeta,t) = 0 \qquad \text{for } \zeta < 0 \tag{99}$$

$$x_{n-1}(\zeta,t) = 0 \qquad \text{for } \zeta > 1 \tag{100}$$

The solution for the dead zone model at the point of measurement is

$$X_n(s) = X_n(1,s) = X_{n+1}(s)\exp(\psi_d)/\{1 + G_d[1 - \exp(\psi_d - \psi_d')]\} \tag{101}$$

where

$$\psi_d = \frac{\eta}{2\alpha} - \frac{\eta}{2\alpha}\sqrt{1 + \frac{4\alpha}{\eta}\left[\beta + \alpha s\left(1 + \frac{\theta}{\tau s + 1}\right)\right]} \tag{102}$$

$$G_d = \beta'/\left\{\frac{\alpha}{\eta}\psi_d'^2 - \psi_d' - \left[\alpha s\left(1 + \frac{\theta}{\tau s + 1}\right) + \beta\right]\right\} \tag{103}$$

$$\psi_d' = -\frac{\eta'}{2\alpha'} + \frac{\eta'}{2\alpha'}\sqrt{1 + \frac{4\alpha'}{\eta'}\left[\beta' + \alpha' s\left(1 + \frac{\theta'}{\tau' s}\right)\right]} \tag{104}$$

and where

$$\tau = 1/Kd \quad \text{and} \quad \tau' = 1/K'd \tag{105}$$

$$\theta = Ka/Kd = a/d = A_d/A_a \tag{106}$$

$$\theta' = K'a/K'd \tag{107}$$

Similarly, the mixing model is

$$X_n(s) = X_n(1,s) = X_{n+1}(s) \exp\left[\frac{\eta}{2\alpha} - \frac{\eta}{2\alpha}\sqrt{1 + \frac{4\alpha}{\eta}\left(1 + \frac{\theta}{\tau s + 1}\right)}\right] \tag{108}$$

The frequency response solution for this model is

$$R_p(\omega) = R_{n+1}(\omega)\mathrm{Re} - \mathrm{I}_{n+1}(\omega)\mathrm{Ie} \tag{109}$$

$$\mathrm{I}_p(\omega) = R_{n+1}(\omega)\mathrm{Ie} + \mathrm{I}_{n+1}(\omega)\mathrm{Re} \tag{110}$$

where

$$\mathrm{Re} = (\mathrm{M.R.})\cos(\mathrm{P.A.}) \tag{111}$$

$$\mathrm{Ie} = (\mathrm{M.R.})\sin(\mathrm{P.A.}) \tag{112}$$

and where

$$(\mathrm{M.R.}) = \frac{\eta}{2\alpha} - \frac{\eta}{2\alpha}\sqrt{1 + \frac{4\alpha^2\omega^2\tau\theta}{\eta[(\tau\omega)^2 + 1]}}[1 + (\bar{a})^2]^{\frac{1}{4}}\cos\bar{b} \tag{113}$$

$$(\mathrm{P.A.}) = -\frac{\eta}{2\alpha}\sqrt{1 + \frac{4\alpha^2\omega\tau\theta}{\eta[(\tau\omega)^2 + 1]}}[1 + (\bar{a})^2]^{\frac{1}{4}}\sin\bar{b} \tag{114}$$

$$\bar{b} = 1/2\tan^{-1}(\bar{a}) \tag{115}$$

$$\bar{a} = \frac{4\alpha^2\omega}{\eta}\left[1 + \frac{\theta}{[(\tau\omega)^2 + 1]}\right] \bigg/ \left\{1 + \frac{4\alpha^2\omega^2\tau\theta}{\eta[(\tau\omega)^2 + 1]}\right\} \tag{116}$$

The complete derivations of these equations along with expanded frequency response forms are available elsewhere (*41*).

The Advantage of Pulse Testing and Fourier Analysis

A principal advantage of pulse testing is that a smaller amount of tracer is needed than in step or sinusoidal testing; therefore, liquid and vapor flow rate changes are less drastic.

A closed form of the time domain solution is possible for the flow models of the perfectly mixed plate, plug flow, perfectly mixed plate with downcomer time lag, and dispersion model for step and dirac inputs. No simple closed solution is available for the dead zone flow model. The mass transfer models have not been solved in a closed time domain form. All these models can be analyzed with frequency response techniques, making a closed time solution form unnecessary.

When the input and output pulses are measured inside the system, parameter fitting can be accomplished with frequency response techniques, and no assumptions are required about the form of the input. In time domain solutions the input usually must be mathematically described, such as a step, sinusoid, or impulse input. Physically producing such an input can be extremely difficult.

Finite difference solutions either in analog or digital simulations require more computer time than a frequency response solution.

For testing the linear models of this work, the easiest and most direct method of investigation was pulse testing and Fourier transform analysis.

Fourier Transform of the Pulses

The predicted output is calculated from the frequency response of the model multiplied by the frequency description of the input pulse. The predicted output is compared to the output pulse Fourier transform by regression techniques. Hays (*59*) and others (*35*, *61*, *62*) have described the method of calculating the pulse Fourier transforms. The Fourier transform is restricted to a special case of the Laplace transform with the Laplace transform variable s having no real part (i.e., $s = j\omega$), and the input function having a zero value for times less than $t = 0$.

Pulse segments, composed of equally spaced time points, are approximated with a second degree polynomial

$$y_{i+1} = a_{i+1}t^2 + b_{i+1}t + c_{i+1} \qquad \text{for } T_{i+1} \le t \le T_i \tag{117}$$

The frequency response forms for the $i + 1$th approximating segment is

$$\mathrm{R}_{i+1} = \frac{1}{\omega^2}\left\{\frac{2}{\omega}[a_{i+1} - a_i] \sin(T_i\omega) - [b_{i+1} - (2a_iT_i + b_i)] \cos(t_i\omega)\right\} \tag{118}$$

$$\mathrm{I}_{i+1} = \frac{1}{\omega^2}\left\{\frac{2}{\omega}[a_{i+1} - a_i] \cos(T_i\omega) - [b_{i+1} - (2a_iT_i + b_i)] \sin(t_i\omega)\right\} \tag{119}$$

The real and imaginary parts for the entire pulse are calculated by summing over all approximating sections for each desired frequency.

Regression

The minimum integral of the squared error is a convenient basis for a fitting procedure. This quantity is defined as

$$\Phi = \int_0^\infty [y_o(t) - y_p(t)]^2 \, dt = \int_0^\infty [e(t)]^2 \, dt \tag{120}$$

Parseval's theorem applied to Eq. (20) gives

$$\Phi = \int_0^\infty [e(t)]^2 \, dt = \frac{1}{\pi} \int_0^\infty |E(j\omega)|^2 \, d\omega \tag{121}$$

where $E(j\omega)$ is the Fourier transform of $e(t)$. Equation (121) shows that there is a direct correlation between minimization of the squared error in the time domain and a minimization of the absolute squared error of the frequency response.

$E(j\omega)$ is defined as

$$E(j\omega) = Y_o(j\omega) - Y_p(j\omega) \tag{122}$$

where $Y_o(j\omega)$ and $Y_p(j\omega)$ are the transforms of $y_o(t)$ and $y_p(t)$, respectively, or in terms of real and imaginary quantities

$$\Phi = \frac{1}{\pi} \int_0^\infty \{[\mathrm{R}_o(\omega) - \mathrm{R}_p(\omega)]^2 + [\mathrm{I}_o(\omega) - \mathrm{I}_p(\omega)]^2\} \, d\omega \tag{123}$$

In data processing the Φ function must be made discrete. Allowing $Z(\omega_n)$ to be the integrand in Eq. (123), the Φ relation is

$$\Phi = \frac{1}{\pi} \sum^{\infty} Z(\omega_n) \tag{124}$$

Summation over an infinite range of frequencies is physically impractical, so the summation is truncated at some finite frequency limit, ω_c. Sokolnikoff and Redheffer (*63*) state that the partial sums of a Fourier series give a smaller mean square error than any other linear combination, and successive terms in the Fourier series tend to zero as the number of terms increases. These statements imply that the function has been approximated by the best least squares method available, and that if ω_c has been chosen sufficiently large, the loss in accuracy is small. Truncation of the frequency spectrum is beneficial in that it discards erroneous data fluctuations which occur at high frequencies. These fluctuations are caused by inaccuracies in the data and the use of parabolic segments to represent continuous tracer curves.

Data Reduction

Linear relationships existed between concentration and conductivity, and between refractive index and mole fraction of the form

$$v = qg + p \tag{125}$$

In pulse testing the function of interest is the deviation term; the base or steady state value must be subtracted from the measured value; thus

$$v - v_0 = q(g - g_0) \tag{126}$$

or

$$V_e = qG_e \tag{127}$$

These constants were determined in the calibration of the conductivity cells and the recording refractometers.

In the distillation column the sample time lag had to be corrected, so that the concentration was a function of time at the downcomer base, not at the refractometers. The correction was made by adding sampling time back to the transformed data with the terms

$$\mathrm{R}_c(\omega) = \mathrm{R}_{me}(\omega)\cos(T_s\omega) - \sin[T_s\omega \mathrm{I}_{me}(\omega)] \tag{128}$$

and

$$\mathrm{I}_c(\omega) = \mathrm{R}_{me}(\omega)\sin(T_s\omega) + \cos[T_s\omega \mathrm{I}_{me}(\omega)] \tag{129}$$

where these terms are defined as

$\mathrm{R}_c(\omega), \mathrm{I}_c(\omega)$ = corrected real and imaginary data parts

$\mathrm{R}_{me}(\omega), \mathrm{I}_{me}(\omega)$ = measured transform data

T_s = sample time lag

The sample time lag was calculated from the sample lines flow rate taken at the end of each run.

SYMBOLS

A_a	area of active zone (ft^2)
A_d	area of dead zone (ft^2)
a	ratio of contact area to volume of the main stream ($\mathrm{ft}^2/\mathrm{ft}^3$)
$a_1, a_2, a_3, a_4, a_i, a_{i+1}$	polynomial coefficients

b_1, b_2, b_i, b_{i+1}	polynomial coefficients
D_L, D_E	longitudinal or eddy dispersion coefficient ($\mathrm{ft}^2/\mathrm{sec}$)
d	ratio of contact area to volume of the dead zone ($\mathrm{ft}^2/\mathrm{ft}^3$)
d_i	difference between pairs of data when subjected to two effects
$E(j\omega)$	frequency domain error
$e(t)$	time domain error
F	F factor, $u\sqrt{\rho_V}$, [ft^3 square root of gas density in $\mathrm{lbm}/\mathrm{ft}^3/\mathrm{sec}$ (square feet of bubbling area)]
G	repetitive frequency domain grouping in dispersion model, $\beta'/\left[\left(\frac{\alpha}{\eta}\right)\psi'^2 - \psi' - (\alpha s + \beta)\right]$
G_d	repetitive frequency domain grouping in dead zone model, $\beta'/\left\{\psi_d'^2\left(\frac{\alpha}{\eta}\right) - \psi_d' - \left[\alpha s\left(1 + \frac{\theta}{\tau s + 1}\right)\right]\right\}$
G_e	effective deviation in measured quantity, $g - g_0$
G_n, G_{n+1}, G_{n-1}	effective deviation quantity for plates n, $n + 1$, and $n - 1$, respectively
$\bar{G}$	normalized variable
g	measured variable, either conductivity or refractive index
g_0	base conductance or steady state refractive index
$\tilde{H}$	molar holdup (lb moles)
$\tilde{H}_D$	molar holdup in the downcomer (lb moles)
h	total liquid height on a plate (ft)
I	imaginary part of the $i + 1$th approximating segment
$\mathrm{I}_c(\omega)$	corrected imaginary part of the data
$\mathrm{I}_m(\omega)$	imaginary part of the model function
$\mathrm{I}_{me}(\omega)$	imaginary part of the measured transform data

$I_n(\omega)$, $I_{n+1}(\omega)$, $I_{n-1}(\omega)$	imaginary parts of the data for plates n, $n + 1$, and $n - 1$, respectively
$I_p(\omega)$	predicted imaginary part of the model
j	imaginary number, $\sqrt{-1}$
K	mass transfer coefficient (lb moles/sec ft^2)
K'	mass transfer coefficient, $K' = K\rho'_L\rho_F$ (ft/sec)
L	L factor, liquid flow rate [gal/min (average feet tray width)]
L_t	Laplace transform operator $L_t(g(t)) = \int_0^\infty g(t)e^{-st}\,dt$
$\tilde{L}$	molar liquid flow rate (lb moles/sec)
m	constant in equilibrium relationship $y = mx + b$
m'	equilibrium relationship on plate $n - 1$
N_d	mass flux from dead zone (lb moles/ft^2 sec)
P	contact length between zones (ft)
p	a constant
q	a constant
R	real part of the $i + 1$th approximating segment
$R_c(\omega)$	corrected real part of the data
$R_m(\omega)$	real part of the model function
$R_{me}(\omega)$	real measured part of the transformed data
$R_n(\omega)$, $R_{n+1}(\omega)$, $R_{n-1}(\omega)$	real parts of the data for plates n, $n + 1$, and $n - 1$, respectively
$R_p(\omega)$	real predicted part of the model
s	Laplace transform variable
T_s	sample time lag (sec)
T_1, T_2, T_i	time at the end of the 1st, 2nd, and ith approximating segments, respectively
t	time (sec)
t_d	Student's statistic calculated for the difference variable
$t_{0.95}$	value for the two sided t statistic for the 95% confidence limit
u	u factor, linear gas velocity [ft^3/sec (square feet of tray bubbling area)]

V_e	effective deviation in measured quantity
$\tilde{V}$	molar gas flow rate (lb moles/sec)
v	mass variable either concentration or mole fraction
V_0	base concentration or steady state mole fraction
W	outlet weir height (in.)
w	width of distillation tray (ft)
X	total length of travel on a distillation plate (ft)
$X_n(s)$, $X_{n+1}(s)$, $X_{n-1}(s)$	Laplace transform of mole fraction function on plates n, $n + 1$, and $n - 1$, respectively
$X_n(\omega)$, $X_{n+1}(\omega)$, $X_{n-1}(\omega)$	Fourier transform of mole fraction function on plates n, $n + 1$, and $n - 1$, respectively
$X_{n,p}(\omega)$	predicted output of model for plate n
$X_n'(\omega)$	composition on a perfectly mixed plate in the perfectly mixed plate with time lag model
x	liquid mole fraction
x_d	liquid mole fraction in dead zone
x^T	total liquid mole fraction, $x^T = x(t) + \bar{x}$
$x(t)$	transient liquid mole fraction
$\bar{x}$	steady state liquid mole fraction
$Y_o(j\omega)$	Fourier transform of observed output
$Y_p(j\omega)$	Fourier transform of predicted output
y	vapor phase mole fraction
$y(t)$	transient vapor mole fraction
$y_o(t)$	observed output
$y_p(t)$	predicted output
$y_1(t)$, $y_2(t)$	first and second approximating polynomials
y^T	total vapor mole fraction $y^T = y(t) + \bar{y}$
$\bar{y}$	steady state vapor mole fraction
Z	total tray length (ft)
$Z(\omega)$	integrand of Eq. (124)
z	length on a tray (ft)
α, α'	residence time on tray n and $n - 1$, respectively (sec)
β, β', β''	mass transfer terms on trays n, $n - 1$,

	$n - 2$, respectively, either $m\tilde{V}/\bar{L}$ or $\tilde{H}K_y am/\bar{L}\rho_F\rho'$
Δz	incremental distance (ft)
ζ	reduced length, $\zeta = z/Z$
η, η'	dispersion coefficient function, D_L/X^2, on plates n and $n - 1$, respectively (sec)
θ, θ'	ratio of dead zone cross sectional area to active zone area for plates n and $n - 1$, respectively
ρ_F	froth density cubic feet of liquid per cubic foot of froth
ρ_L	liquid density (lbm/ft^3)
ρ'_L	clear liquid density (lb moles/ft^3)
$\sum$	indicates summation
τ, τ'	inverse of dead zone mass transfer coefficient times the ratio of dead zone cross sectional area to volume on plates n and $n - 1$, respectively (sec)
τ_d, τ'_d	residence time in downcomers on plates n and $n - 1$, respectively (sec)
Φ	sum or integral of the squared error
ψ	repetitive frequency domain grouping in dispersion model, $\frac{\eta}{2\alpha} - \frac{\eta}{2\alpha}\sqrt{1 + \frac{4\alpha}{\eta}(\alpha s + \beta)}$
ψ_d	repetitive frequency domain grouping in dead zone model, $\frac{\eta}{2\alpha} - \frac{\eta}{2\alpha}\sqrt{1 + \frac{4\alpha}{\eta}\left[\alpha s\left(1 + \frac{\theta}{\tau s + 1}\right) + \beta\right]}$
ψ'	repetitive frequency domain grouping in dispersion model, $\frac{\eta'}{2\alpha'} + \frac{\eta'}{2\alpha'}\sqrt{1 + \frac{4\alpha'}{\eta'}(\alpha' s + \beta')}$
ψ'_d	repetitive frequency domain grouping in dead zone model, $\frac{\eta'}{2\alpha'} + \frac{\eta'}{2\alpha'}\sqrt{1 + \frac{4\alpha'}{\eta'}\left[\alpha' s\left(1 + \frac{\theta'}{\tau' s + 1}\right) + \beta'\right]}$

ψ_+ repetitive frequency domain grouping in dispersion model,

$$\frac{\eta}{2\alpha} + \frac{\eta}{2\alpha}\sqrt{1 + \frac{4\alpha}{\eta}(\alpha s + \beta)}$$

ω frequency (sec^{-1})
ω_c cutoff frequency (sec^{-1})
$*$ denotes convolution

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