Conversion and Temperature Profiles for Complex Reactions in Laminar and Plug Flow

LAVAUN S. MERRILL, JR., and CHARLES E. HAMRIN, JR.

University of Denver, Denver, Colorado

An investigation of the mass and heat transfer equations describing radial and axial profiles for tubular reactors in laminar and plug flow is reported. Reactor conditions evaluated were isothermal, constant wall temperature, and adiabatic. Both diffusion and nondiffusion were considered. The reaction investigated was the demethylation of toluene in the presence of hydrogen.

It was found that diffusion plays only a minor role in laminar flow for the conditions investigated. It was also found that isothermal and constant wall temperature reactor operation affected the temperature and concentration profiles very little when *r/R* was less than 0.6.

In recent years, considerable research has been carried out in the analyses of tubular reactors considering both the radial velocity and temperature distributions. Much of this work has been applied to first-order reactions in order to simplify the analysis (*3, 4, 6, 8*); however, the approach has been extended to photochemical reactions by Schecter and Wissler (*10*) and to the treatment of a reversible homogeneous reaction ($A \rightleftharpoons 2B$) by Rothenberg and Smith (9). Few, if any, commercially important reactions have been treated by these techniques. The demethylation of toluene was chosen as an example of a non first-order reaction of considerable industrial significance. It was desired to calculate concentration and temperature profiles rigorously under several methods of reactor operation: isothermal, constant wall temperature, and adiabatic. It was hoped that these results would suggest the optimum method of reactor operation for this reaction.

THEORETICAL DEVELOPMENT

The partial differential equation resulting from an energy balance for tube flow with chemical reaction is as follows:

$$\frac{\partial T}{\partial z} - \frac{k}{MC_P}\left[\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r}\right] + \frac{R^*\Delta H^\circ}{MC_P} = 0 \quad (1)$$

where M is defined by the velocity profile as

$$M = 2VC_0\,[1 - (r/R)^2] \quad (2)$$

In an analogous manner, a mass transfer equation is derived in which diffusion is only considered in the radial direction:

$$\frac{\partial x}{\partial z} - \frac{D}{u}\left[\frac{\partial^2 x}{\partial r^2} + \frac{1}{r}\frac{\partial x}{\partial r}\right] - \frac{R^*}{M} = 0 \quad (3)$$

It is related to the molar flux $M = uC_0$. The following boundary conditions were used in this study:

$$z = 0 \qquad \left.\begin{matrix} T = T_0 \\ x = 0 \end{matrix}\right\}\text{for all } r$$

$$r = 0 \qquad \frac{\partial T}{\partial r} = 0$$

$$\frac{\partial x}{\partial r} = 0$$

$$r = R \qquad \frac{\partial x}{\partial r} = 0$$

In addition, three modes of reactor operation [constant wall temperature (CWT), isothermal, and adiabatic] were considered.

The usual simplifying assumption of plug flow reduces Equations (1) and (3) to

$$\frac{dT}{dz} + \frac{R^*\Delta H^\circ + Q}{MC_P} = 0 \quad (4)$$

and

$$\frac{dx}{dz} - \frac{R^*}{M} = 0 \quad (5)$$

respectively.

Equations (1) and (3) and the simplified Equations (4) and (5) were solved by finite-difference techniques by using a Burroughs B5500 digital computer. Conversion of the partial differential equations to finite-difference equations was carried out by the method outlined by Jensen and Jeffreys (5). Equation (1) for heat transfer becomes

$$T_{m,n+1} = Y\left(1 + \frac{1}{2m}\right)T_{m+1,n} + (1 - 2Y)\,T_{m,n} + Y\left(1 - \frac{1}{2m}\right)T_{m-1,n} - \frac{R^*_{m,n}\Delta H^\circ_{m,n}\Delta z}{MC_P} \quad (6)$$

LaVaun S. Merrill, Jr., is with Marathon Oil Company, Littleton, Colorado. Charles E. Hamrin, Jr., is at the University of Kentucky, Lexington, Kentucky.

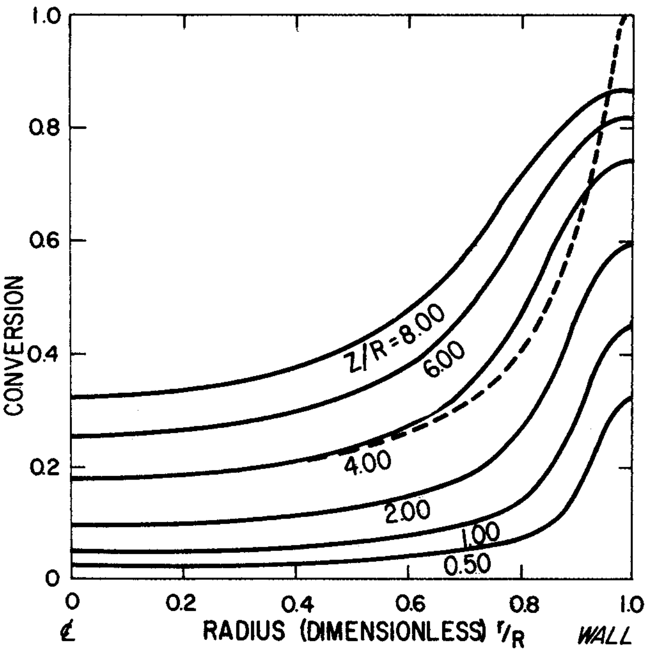


Fig. 1. Radial conversion profiles for an isothermal, laminar flow reactor with diffusion.

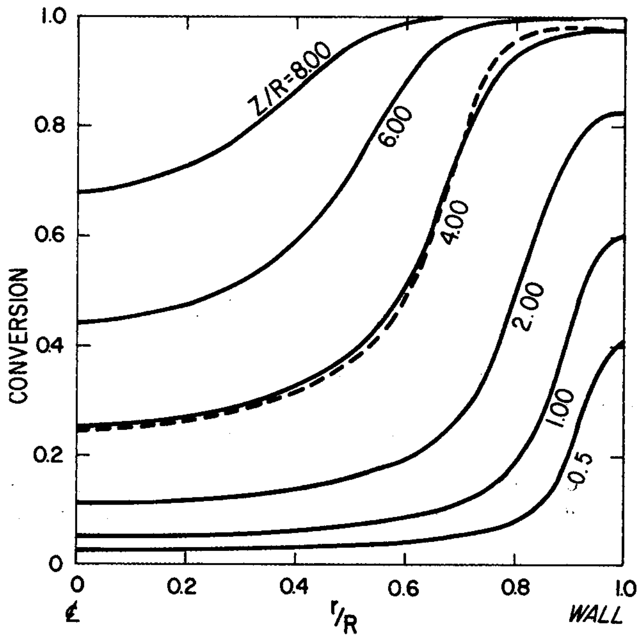


Fig. 2. Radial conversion profiles for a CWT, laminar flow reactor with diffusion.

where

$$Y = \frac{k\ \Delta z}{MC_P(\Delta r)^2} \tag{7}$$

The analogous equation for mass transfer is

$$x_{m,n+1} = W\left(1 + \frac{1}{2m}\right) x_{m+1,n} + (1 - 2W)x_{m,n} + W\left(1 - \frac{1}{2m}\right) x_{m-1,n} + \frac{R^*_{m,n}\Delta z(B+1)}{M} \tag{8}$$

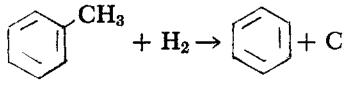
where

$$W = \frac{D\Delta z}{u(\Delta r)^2} \tag{9}$$

The point velocity u was calculated as a function of temperature for each increment in both radial and axial directions. In solving the finite difference equations, the increments Δz and Δr were decreased until no differences were noted in successive temperature and concentration profiles.

KINETICS OF TOLUENE DEMETHYLATION

In addition to the previously mentioned criteria, a reaction was desired for which the kinetics were well established and which showed a minimum amount of side reaction. The reaction chosen on this basis was the demethylation of toluene as represented by the equation



(10)

The kinetics of this vapor-phase reaction have been studied by several investigators (*1, 7, 11, 12, 13, 16*) over the temperature range of 580° to 920°C. The rate equation originally proposed by Silsby and Sawyer (*11*) and verified by subsequent investigators is of the form

$$R^* = Ae^{-\Delta E/RT}C_T C^{1/2}_{H_2} \tag{10a}$$

Table 1. Reactor Parameters Selected for Study

Toluene flow rate	0.1 g.-mole/sec.
Hydrogen/toluene molar ratio	5
Reactor pressure	10 atm.
Reactor diameter	
laminar flow	30 cm.
plug flow	3 cm.

A least-squares fit of the rate constant data was made, and the values obtained were

$$\Delta E = 52.8 \text{ kcal./g.-mole}$$

and

$$A = 9.12 \times 10^{10} \text{ (liters/mole)}^{1/2} \text{ (sec.)}^{-1}$$

EVALUATION OF THERMODYNAMIC AND TRANSPORT PROPERTIES

Evaluation of the thermodynamics of Equation (10) was made by using values in the API Project 44 tabulation. The equilibrium constant varied from 280 at 580°C. to 40 at 920°C., indicating that Equation (10) may be considered irreversible as written. The standard heat of reaction was calculated to be −10,019 cal./g.-mole at 298°K. The variation of the heat of reaction with temperature was calculated from the equation

$$\Delta H^\circ = \Delta H^\circ_{298} + \int_{298}^{T} \Delta C_P dT \tag{11}$$

Over the temperature range of interest, the heat of reaction increased approximately 25%.

The temperature variation of the viscosity of the reactants and products was calculated from

$$\frac{\mu}{\mu_{\text{ref}}} = \sqrt{\frac{T}{T_{\text{ref}}}}\left[\frac{1 + C/T_{\text{ref}}}{1 + C/T}\right] \tag{12}$$

Table 2. Values of Dimensionless Numbers at Inlet Conditions

	Laminar flow	Plug flow
Reynolds number	1,700	17,000
z/R	8.0	8,000
$R^*\ L/M$	526†	115,000
Prandtl number	0.7	
Lewis number	1.8	

† At center line.

To calculate the viscosity of gaseous mixtures, the equation proposed by Wilke (*15*) was used:

$$\mu_{\text{mix}} = \sum_{i=1}^{\gamma} \mu_i \left[1 + \sum_{\substack{k=1\\k\neq i}}^{\gamma} G_{ik} \frac{y_k}{y_i} \right]^{-1} \tag{13}$$

in which

$$G_{ik} = \frac{1}{2^{3/2}} \left[1 + \frac{MW_i}{MW_k} \right]^{1/2}$$

$$\left[1 + \left\{ \frac{\mu_i}{\mu_k} \right\}^{1/2} \left\{ \frac{MW_k}{MW_i} \right\}^{1/4} \right]^2 \tag{14}$$

Thermal conductivities for the mixture were calculated from the Eucken relationship by using the mixture viscosity [Equation (13)] and a mixture specific heat.

Temperature variation of binary diffusivities were accounted for by the Gilliland equation. The diffusivity of toluene in the multicomponent mixture was evaluated from the Wilke (*14*) correlation

$$D = \frac{1 - y_T}{\frac{y_B}{D_{TB}} + \frac{y_C}{D_{TC}} + \frac{y_D}{D_{TD}}} \tag{15}$$

In the computer program, the thermal conductivity was held constant at the inlet conditions, but the diffusivity of toluene was calculated at centerline conditions for each axial increment.

RESULTS AND DISCUSSION

The solutions of Equations (6) and (8) for the demethylation of toluene require that a system of reactor parameters be selected. These values are shown in Table 1. A hydrogen/toluene ratio of 5 was used to minimize side reactions and to force the equilibrium in favor of the products. Based on the diameters chosen, the Reynolds numbers (at inlet conditions) for the laminar and plug flow reactors were 1,700 and 17,000, respectively.

For this study, the technique used was to solve Equations (6) and (8) for the physical system given in Table 1. Conversion and temperature profiles, however, are plotted as functions of reactor radius, length, and volume in dimensionless forms. In making the equations dimensionless, the groups whose values are shown in Table 2 were obtained.

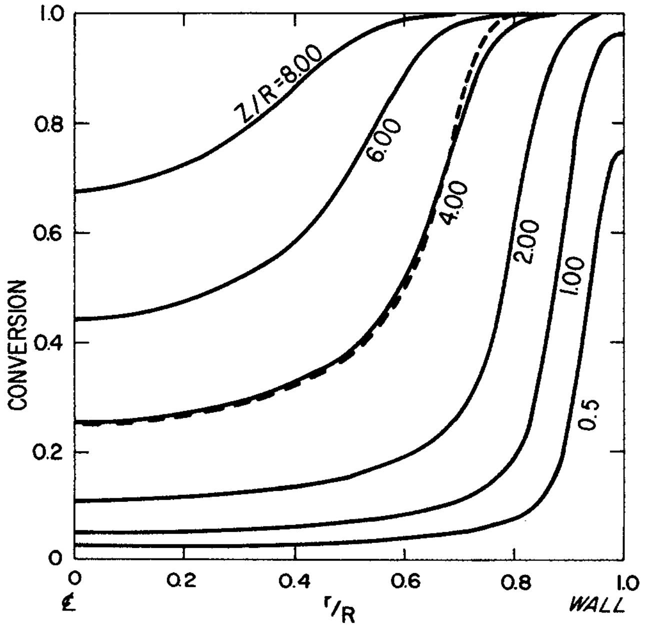


Fig. 3. Radial conversion profiles for an adiabatic, laminar flow reactor with diffusion.

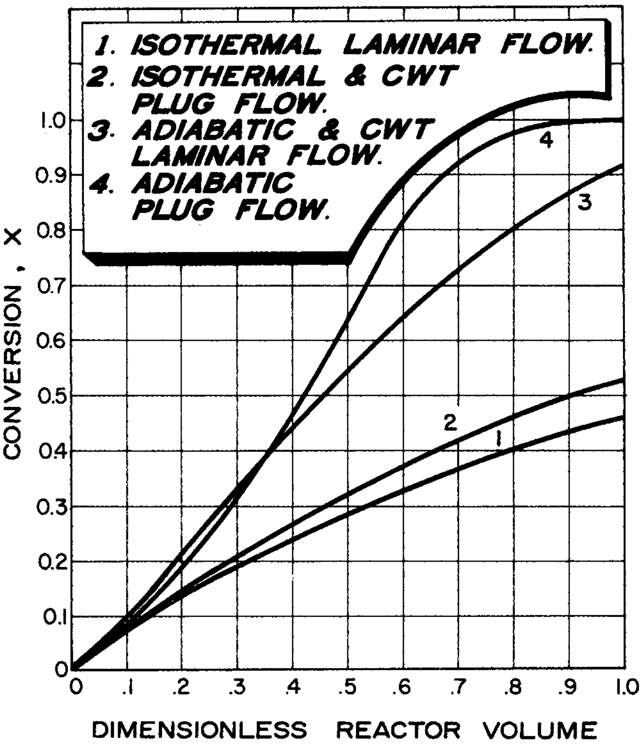


Fig. 4. Comparison of conversions obtained in plug flow and laminar flow reactors of equal volumes.

Conversion in Laminar Flow

The solutions of Equations (6) and (8) are presented as temperature and conversion profiles for tubular flow. In Figures 1, 2, and 3, the conversion of toluene is plotted against a dimensionless radius r/R which varies from zero at the center line to 1.0 at the wall. The dimensionless length z/R is a parameter which is plotted over the range of 0.50 to 8.0. Three laminar flow cases including radial diffusion are illustrated; isothermal (Figure 1), CWT (Figure 2), and adiabatic (Figure 3). An inlet temperature of 975°K. was used for each case.

For the isothermal reactor, the conversion is shown to remain relatively constant over half of the tube radius and then to increase sharply to the wall conversion. The boundary condition $(\partial x/\partial r)_{r=R} = 0$ accounts for the horizontal nature of the curves near the wall. The CWT reactor shows the same constant conversion behavior for $z/R < 2$. As z/R increases, the effect of the exothermic nature of the reaction on conversion becomes readily apparent. For the maximum reactor length ($z/R = 8.0$) the center-line conversion for this reactor is 0.68, whereas for the isothermal reactor it is only 0.32. The adiabatic and CWT profiles are superimposable at $r/R < 0.6$. Beyond this radius, the adiabatic conversion is higher at any r/R as the wall is approached.

The effect of neglecting radial diffusion is shown for each reactor at $z/R = 0.4$ by a dashed line. The major difference occurs for the isothermal case at $r/R > 0.6$ (Figure 1). Conversion at the wall with diffusion is 0.74; neglecting diffusion gives a value of 1.0. Similar behavior for the other z/R values was found.

Similar comparisons between reactors with and without diffusion for the CWT and adiabatic cases also show slight differences over the entire reactor radius as shown by the

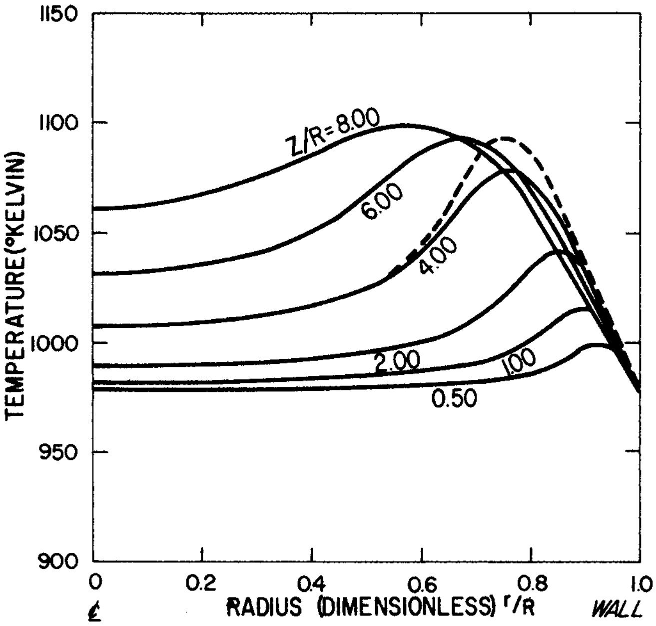


Fig. 5. Radial temperature profiles for a CWT, laminar flow reactor with diffusion.

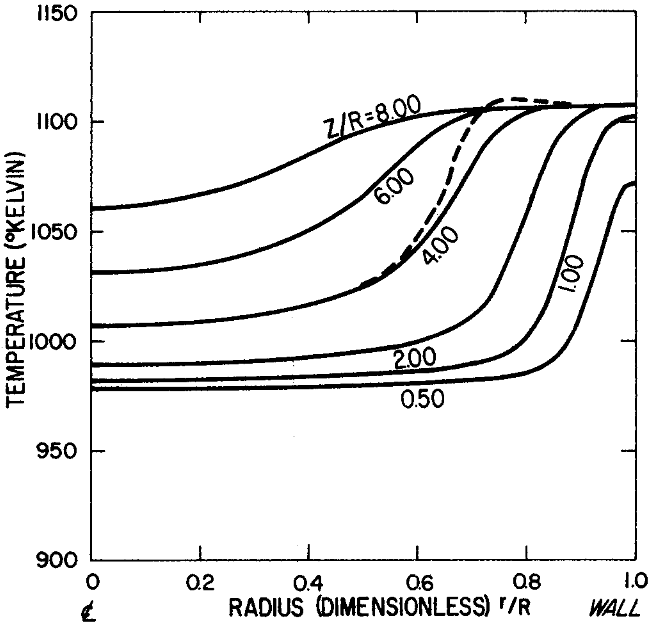


Fig. 6. Radial temperature profiles for an adiabatic, laminar flow reactor with diffusion.

dashed curves in Figures 2 and 3.

To show the effect of diffusion, the flow average conversion was calculated for the profiles of $z/R = 8.0$. Results for the three cases are shown below:

Flow average conversion for $z/R = 8.0$

Reactor	With diffusion	Without diffusion
Isothermal	0.489	0.466
CWT and adiabatic	0.913	0.915

These values show that even for the isothermal case where the profiles differed appreciably near the wall, the effect of neglecting diffusion amounts to less than 5% difference on the overall conversion.

These results are in agreement with the criterion suggested by Bosworth (2) for determining the importance of diffusion. He defined a dimensionless number $D\theta/R^2$ and stated that when this number is less than 3.1×10^{-3}, diffusion is negligible. Cleland and Wilhelm (4), using a different approach, determined that diffusion is negligible when $D\theta/R^2 < 1.95 \times 10^{-3}$. This number averaged about 3.5×10^{-3} in this study.

Figure 4 is a plot comparing overall conversions for similar conditions in laminar and plug flow reactors of the same volume. It is interesting to note that an isothermal, laminar flow reactor of a given volume gives about the same conversion as an isothermal, plug flow reactor of the same volume. This is also true for the adiabatic reactors up to a conversion of 0.4, after which the conversion in the plug flow case increases faster than for the laminar. For CWT reactors, the conversions vary considerably, approaching adiabatic conversion for laminar flow and isothermal conversion for plug flow.

Temperature Profiles for Laminar Flow

Solutions of Equation (6) for a CWT reactor are shown in Figure 5. Inlet temperature was assumed constant at 975°K. It is apparent that a maximum in temperature occurs for each z/R and moves from the region near the wall at low z/R to an area of approximately $r/R = 0.55$. This behavior is due to the higher conversion of the slower moving fluid in the vicinity of the wall and the exothermic nature of the reaction. Eventually, this maximum would occur at the center line as complete conversion is achieved.

When radial diffusion was neglected, the temperature profiles for the CWT reactor showed a maximum at the same radius as shown in Figure 5; however, the maximum temperature is approximately 10°K. higher for the curves in which $2 < z/R < 8$. The dashed line shown for $z/R = 4.0$ was calculated neglecting diffusion and illustrates this behavior.

Temperature profiles for the adiabatic reactor are shown in Figure 6. A sharp temperature rise is observed near the wall at low z/R ratios. This temperature increase becomes less pronounced for the higher z/R ratios. This trend shows that the reactor temperature is approaching the upper limit for total conversion. A slight temperature maximum was found when radial diffusion was neglected. This is shown as the dashed line on Figure 6 for $z/R = 4.0$.

Comparison of Results

The results of this investigation can be compared qualitatively with the conversion and temperature profiles published by Rothenberg and Smith (8) for a first-order reaction. These authors present curves for a relative concentration equivalent to $1 - x$ in this paper. Their concentration profiles for a high reaction rate are similar in shape to those of Figure 2, except at high values of z/R. They also present temperature profiles which for high reaction rates are similar to those shown in Figure 5. This favorable comparison must not be assumed to hold for all cases, since the effect of several parameters, including the order of reaction, must be evaluated.

CONCLUSIONS

Concentration and temperature profiles were calculated for a non first-order reaction from the basic energy and mass transfer equations. Radial diffusion was found to affect concentration profiles most markedly near the wall but did not have a significant effect on the overall conversion. This indicates that diffusion can be safely neglected when parameters are chosen so that $D\theta/R^2 < 3 \times 10^{-3}$.

For the demethylation of toluene, adiabatic reactor operation with plug flow appears most desirable. Second choice would be adiabatic or constant wall temperature in laminar flow. This is followed by isothermal or constant wall temperature in plug flow. Least desirable is an isothermal laminar flow reactor.

ACKNOWLEDGMENT

The authors wish to express their appreciation to the Marathon Oil Company for assistance in this work.

NOTATION

A = frequency factor, (liter/mole)$^{1/2}$/sec.
B = molar ratio of hydrogen to toluene
C = constant in Equation (12)
C_0, C_{H_2}, C_T = concentrations: initial, hydrogen, and toluene, respectively, g.-mole/cc.
C_P = specific heat of reaction mixture, cal./(g.-mole) (°K.)
D = diffusivity of toluene in reaction mixture, sq.cm./sec.
D_{TB}, D_{TC}, D_{TD} = binary diffusion coefficients with toluene as one of the components, sq.cm./sec.
E = activation energy, cal./g.-mole
$\Delta H°$ = heat of reaction, cal./g.-mole
k = thermal conductivity of reaction mixture, cal./(sec.) (cm.) (°K.)
L = reactor length, cm.
m = radial increment index
M = molar flux, g.-moles/(sec.) (sq.cm.)
MW = molecular weight, g./g.-mole
Q = rate of heat transfer, cal./(cc.) (sec.)
r = radial distance from center line, cm.
R = reactor radius, cm.
R^* = reaction rate, g.-mole/(cc.) (sec.)
T = temperature, °K.
T_0 = inlet temperature, °K.
u = point velocity, cm./sec.
V = center-line velocity, cm./sec.
x = conversion of toluene
y_T, y_B ... = mole fraction of toluene, component B, etc.
z = axial distance from reactor inlet, cm.
μ = viscosity, poise
θ = time, sec.

Subscripts

m = radial increment index
mix = mixture
n = axial increment index
ref = reference conditions

LITERATURE CITED

1. Bethea, S. R., R. L. Heinrich, A. M. Souby, and L. T. Yule, *Ind. Eng. Chem.*, **50**, 1245 (1958).
2. Bosworth, R. E. L., *Phil Mag.*, **39**, 847 (1948).
3. Chambre, P. L., *Appl. Sci. Res.*, **A9**, 157 (1960).
4. Cleland, F. A., and R. H. Wilhelm, *AIChE J.*, **2**, 489 (1956).
5. Jensen, V. G., and G. V. Jeffreys, "Mathematical Methods in Chemical Engineering," Academic Press, New York (1963).
6. Lauwerier, H. A., *Appl. Sci. Res.*, **A8**, 366 (1959).
7. Matsui, H., A. Amano, and H. Tokuhisa, *Bull. Japan Petrol. Inst.*, **1**, 67 (1959).
8. Rothenberg, R. I., and J. M. Smith, *AIChE J.*, **12**, 213 (1966).
9. ————, *Can. J. Chem. Eng.*, **44**, 67 (1966).
10. Schecter, R. S., and E. H. Wissler, *Appl. Sci. Res.*, **A9**, 334 (1960).
11. Silsby, R. I., and E. W. Sawyer, *J. Appl. Chem.*, **6**, 347 (1956).
12. Stijntjes, G. J. F., H. Voetter, E. F. Roelofsen, and J. J. Verstappen, *Erdol und Kohle*, **14**, 1011 (1961).
13. Tsuchiya, A., A. Hashimoto, H. Tominaga, and S. Masamune, *Bull. Japan Petrol. Inst.*, **1**, 73 (1959).
14. Wilke, C. R., *Chem. Eng. Progr.*, **46**, 95 (1950).
15. ————, *J. Chem. Phys.*, **18**, 517 (1950).
16. Zimmerman, C. C., and R. York, *Ind. Eng. Chem.*, **3**, 254 (1964).

Manuscript received September 29; 1967; revision received July 8, 1968; paper accepted July 31, 1968.

Distillation Decoupling

WILLIAM L. LUYBEN
Lehigh University, Bethlehem, Pennsylvania

This paper presents a quantitative study of two types of decoupling elements to achieve noninteracting feedback control of overhead and bottoms compositions in binary distillation. Ideal decoupling, where the closed loop response of each loop is the same as it would be if the other loop were on manual control, and simplified decoupling, where two interaction compensators are used to isolate each loop, are investigated.

The decoupling elements themselves are physically realizable in both cases, but unstable loops develop with ideal decoupling in higher purity columns because of increased positive feedback. Simplified decoupling gave effective, stable, noninteracting loops for all the cases studied.

The decoupling elements are designed in the frequency domain from a linear model of the column, and their effectiveness is tested by digital simulation of the nonlinear column model.

Distillation columns continue to represent major control problems in many industries. The complex, multistage nature of distillation columns requires proficiency in the fundamentals of operation, both steady state and dynamic, plus experience to successfully analyze and diagnose their operation.

Of all the distillation column control problems, one of the most important and controversial, and still unresolved,