&Modelling of Supercritical Carbon Dioxide Extraction of Canola Oilseed in Fixed Beds

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Supercritical carbon dioxide extraction of oil from fixed beds (4.8 mm, 24.5 and 12.7 mm I.D.) of crushed canola seeds is described. Experiments were performed to obtain equilibrium data and extraction rates at 55 C, 36 MPa using solvent velocities ranging from 0.04 to 2.8 mm/s. A one-dimensional, unsteady state mathematical model was used to obtain the oil concentration profiles in both the solvent and solid phases, and to determine the overall volumetric mass transfer coefficients. The calculated concentrations and extraction rates are in good agreement with experimental results. The overall volumetric mass transfer coefficient for the initial, constant rate extraction was correlated with interstitial velocity.

The extraction of vegetable oils using supercritical carbon dioxide has been studied as a potential alternative to the current industrial processes of expeller pressing, prepress solvent extraction and straight liquid solvent extraction (1-3). The fundamental design of supercritical solvent extractors in both fixed-bed and countercurrent flow extractors requires data on the solubility of oil in the solvent phase, the equilibrium distribution of oil between the seed and the solvent phase, the rate of oil transfer from the seeds to the solvent, and the relationship between mass transfer coefficients and operating variables.

In an earlier, preliminary investigation of the CO_2/canola extraction process (3), equipment and procedures were described for obtaining equilibrium data and mass transfer coefficients.

The present paper presents a one-dimensional, unsteady state mathematical model of a fixed bed extractor. The differential equations are solved by using the method of characteristics to provide the concentration history of oil in both the solid and fluid phases. The predicted results are compared with selected experimental data. In addition, overall mass transfer coefficients were obtained by matching the calculated and experimental extraction curves.

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Nomenclature. A_p, specific surface area of seeds, [m^2/m^3 of bed]; A_pK, overall volumetric mass transfer coefficient for initial constant rate period, [kg $CO_2/(m^3s)$]; H, total height of bed, [mm]; h, axial distance along bed, [mm]; M_o, mass of oil extracted, [kg]; R, rate of oil mass transfer, [kg/s]; t, time, [s]; U, superficial velocity of solvent, [mm/s]; v, average interstitial velocity of solvent, u/ε, [mm/s]; x, oil concentration in seeds, [kg oil/kg oil free seeds]; x_o, initial oil content of seeds, [kg oil/kg oil free]; y, oil concentration in the solvent phase, [kg oil/kg CO_2]; y^*, saturation oil concentration in solvent phase, [kg oil/kg CO_2]; $y_o(t)$, oil concentration in solvent phase at extractor outlet at time (t) [kg oil/kg CO_2]; z, $\varepsilon h/U$, [s]; ε, void fraction of the bed of seeds [dimensionless]; ϱ, density of solvent phase, [kg/m^3]; ϱ_s, density of seeds, [kg/m^3].

EQUILIBRIUM DATA

In order to solve the mass balance equations which describe the extraction of oil from a fixed bed of canola seeds (3), the equilibrium relationship must be known:

$$y^* = f\{x\}$$

where y^* denotes the concentration of oil in the solvent phase in equilibrium with seeds having an oil concentration x. The units of y^* and x are [kg oil/kg CO_2] and [kg oil/kg oil free seed], respectively. This relationship was obtained experimentally in the following manner. A portion of the oil in flaked Canola seed was first extracted using either hexane or supercritical CO_2. The resulting oil concentration of the partially extracted flakes ranged from 0.2 to 0.7 g oil/g oil-free seed. Samples of these flakes were then placed in a 12.7 mm ID vessel, and supercritical CO_2 at 36 MPa and 55 C was passed through the bed of flakes at flow rates ranging from 40 to 160 g/hr. The oil concentration in the CO_2 stream leaving the bed was determined as a function of time by passing it through a pressure reducing valve and measuring the quantity of precipitated oil and the corresponding CO_2 volume (3).

For all of the experiments using partially extracted flakes, it was found that the oil concentration in the CO_2 leaving the bed had a constant value of 0.011 ± 0.001 g/g CO_2 at 36 MPa and 55 C. The results indicate that, over the range of seed oil concentrations used, the seed tissue does not have a physical or chemical affinity for the oil and acts merely as an inert substrate. The relationship $y^* = f\{x\}$ can thus be represented by $y^* =$ constant. The constant corresponds to the oil solubility in the CO_2 at a specified pressure and temperature, i.e. for 36 MPa and 55 C, $y^* = 0.011$ g oil/g CO_2.

MATHEMATICAL MODEL OF FIXED-BED EXTRACTOR

The extraction of oil from a fixed bed of seeds is an unsteady-state process. At any point in the bed, the oil concentrations in the solid and solvent phases vary continuously until equilibrium is reached. Because seeds remain fixed in place, their oil content changes with time and distance along the axis of the bed. A previously developed mathematical model (3) for predicting solvent and seed phase oil concentrations as a function of time and bed position used just two independent variables (time and axial distance). The model is based on the assumptions that plug flow exists in the bed and that axial dispersion in the bed is negligible. If the fluid flow rate, temperature, pressure and bed properties are regarded as constant, the material balances for an element of bed are given by:

Solvent phase: $\varepsilon\varrho \dfrac{\delta y}{\delta t} + \varrho U \dfrac{\delta y}{\delta h} = A_pK(y^*-y)$ [1]

Solid phase: $(1-\varepsilon) \varrho_s \dfrac{\delta x}{\delta t} = -A_p K(y^*\text{-}y)$ [2]

The last terms in Eqs. 1 and 2 represent the rate of interphase transfer of oil. If it is assumed that the solvent is oil-free at the entrance of the extractor and that all the seeds have the same initial oil content (x_o), then the boundary conditions are:

$$y = 0 \text{ at } h = 0 \text{ for } t \geqslant 0$$

$$x = x_o \text{ at } t = 0 \text{ for } 0 \leqslant h \leqslant H$$

Given that the solubility of the oil in CO_2 is known (i.e. y^* = 0.011 g oil/g oil-free seed at 36 MPa, 55 C) Eqs. [1] and [2] can be solved to obtain the concentration profiles of oil in the solvent and solid phases, respectively, as a function of time.

An effective numerical method for solving this system of equations is the method of characteristics (4,5). Equations [1] and [2] are first rearranged as follows:

$$\frac{\delta y}{\delta t} + \frac{\delta y}{\delta z} = \frac{R\{x,y\}}{\varepsilon \varrho} \qquad [3]$$

and

$$\frac{\delta x}{\delta t} = -\frac{R\{x,y\}}{(1-\varepsilon)\varrho_s} \qquad [4]$$

where $z = \varepsilon h/U$ [5]

and $R\{x,y\} = A_p K(y^*\text{-}y)$ [6]

Since y and x are both functions of t and z, their total differentials are given by:

$$\frac{\delta y}{\delta t} dt + \frac{\delta y}{\delta z} dz = dy \qquad [7]$$

$$\frac{\delta x}{\delta t} dt + \frac{\delta x}{\delta z} dz = dx \qquad [8]$$

Equations [3] and [7] are simultaneous equations in the unknown $\delta y/\delta t$ and $\delta y/\delta z$. Setting the determinant of the coefficients of these unknowns equal to zero leads to characteristic curve I(4):

$$(\frac{dt}{dz})_I = 1 \quad \text{or} \quad t = z + \text{constant.} \qquad [9]$$

Similarly, Eqs. [4] and [8] yield the characteristic curve II:

$$(dz)_{II} = 0 \quad \text{or} \quad z = \text{constant.} \qquad [10]$$

Substituting Eq. [9] into Eq. [7] and using Eq. [3] gives:

$$(\frac{dy}{dz})_I = \frac{\delta y}{\delta z} + \frac{\delta y}{\delta t} = \frac{R\{x,y\}}{\varepsilon \varrho} \qquad [11]$$

Similarly, combining Eqs. [10] and [8], and using Eq. [4], gives:

$$(\frac{dx}{dt})_{II} = \frac{\delta x}{\delta t} = \frac{-R\{x,y\}}{(1-\varepsilon)\varrho_s} \qquad [12]$$

Equations [11] and [12] may be integrated numerically. The initial conditions provide the values of x and y along the two characteristic lines z = 0 and t = 0. All other values in the z-t plane may be calculated from a mesh of network characteristic lines having intervals of Δz and Δt. For each Δt interval, x and y are evaluated from the bed entrance to the exit by taking intervals Δz along the bed. Thus, all points of intersection of the characteristic lines $z = n\Delta z$ and $t = z + m\Delta t$ can be computed. Δt and Δz are arbitrary and m and n are integers. Rapid convergence in the integration of Eqs. [11] and [12] is assured by using the modified Euler method and appropriate choices of Δt and Δz (5). In our solution, which was obtained using a computer program designed to solve partial differential equations (6), typical values of Δt and Δz were 60 s and 2 mm, respectively.

In order to compare the experimental and calculated extraction curves, the oil concentration in the solvent phase at the extractor outlet, $y_e\{t\}$, was used to calculate the total mass of oil extracted, (M_e), i.e.:

$$M_e = \dot{m} \int_0^T y_e\{t\} dt \qquad [13]$$

where $\dot{m}$ denotes the solvent mass flow rate. M_e was calculated for various time periods and then plotted for comparison with experimental extraction curves in the determination of the overall mass transfer coefficients.

RESULTS AND DISCUSSION

Typical extraction curves, i.e. plots of total mass of oil extracted vs total CO_2 used, are shown in Figures 1 to 3.
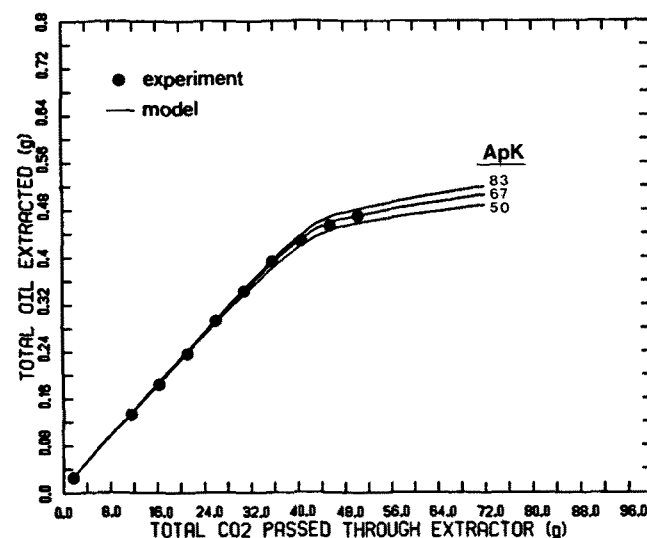

FIG. 1. Extraction results obtained by passing CO_2 at 55 C and 36 MPa through a 4.8 mm ID extractor containing 1.5 g of crushed seed. CO_2 flow-rate: 1.6 g/min, which corresponds to v = 2.8 mm/s. The computed extraction curves were calculated using three different values of $A_p K$.

The experimental data were obtained for different seed pre-treatments, extractors and operating conditions. In all cases, the experimental data fall initially on straight lines, thereby indicating a constant rate of oil extraction. During the initial period, the external surfaces of the seeds probably are completely covered with oil and the effluent solvent is saturated with oil. This is followed by a transition period, during which the rate of extraction drops rapidly. The rapid decrease in the extraction rate may be caused by the depletion of the continuous layer of oil on the seed surfaces, thereby resulting in a reduced effective area available for oil transfer and hence a reduced overall mass transfer coefficient, A_pK. When all of the surface oil has been removed, the rate of extraction depends on the diffusion of oil to the surface from the interior of the solids. This rate is very low compared with the initial rate.

In addition to the experimental data, Figures 1 to 3 also show the corresponding extraction curves predicted by the mathematical model. The good agreement between the experimental and computed values under the different operating conditions indicates that the mathematical model is able to simulate the extraction process quite well.

Further evidence of the validity of the mathematical model is provided by Figure 4, in which the oil concentration is shown as a function of distance from the bed entrance; normalized units are used for the bed height. The experimental results were obtained by passing supercritical CO_2 through the seed bed for 240 min under operating conditions similar to those used in Figure 3. The CO_2 flow was then stopped and the extractor pressure reduced to atmospheric pressure. The extractor was then opened and the seed bed removed in eight separate sections, using a vacuum line connected to a small flask. The oil content of each section was determined by hexane extraction. As seen from Figure 4,

good agreement between the computed and experimental results was obtained. The confidence limits of the experimental results are indicated by the error bars in Figure 4.

Typical computed concentrations of the oil content in the solvent- and seed-phase are shown in Figures 5 and 6, respectively. As anticipated from basic physical considerations, the curves have a sigmoidal shape, with the ascent-portion of the curves advancing through the bed with increasing time. In Figures 7 and 8, the oil concentrations in the seed and solvent phases, respectively, are shown as a function of bed position and time.
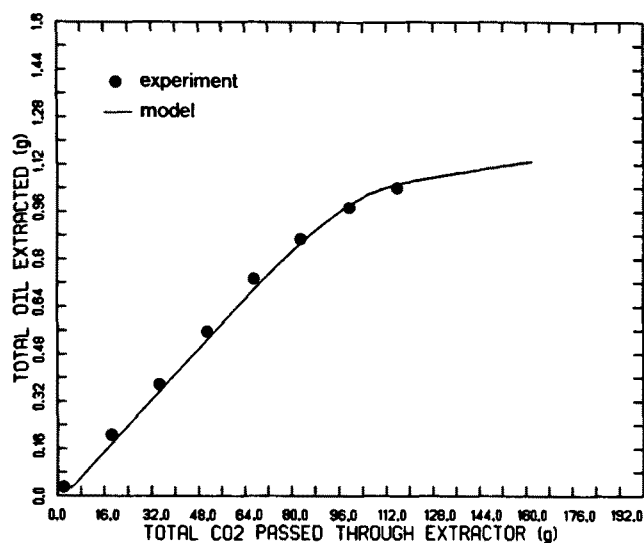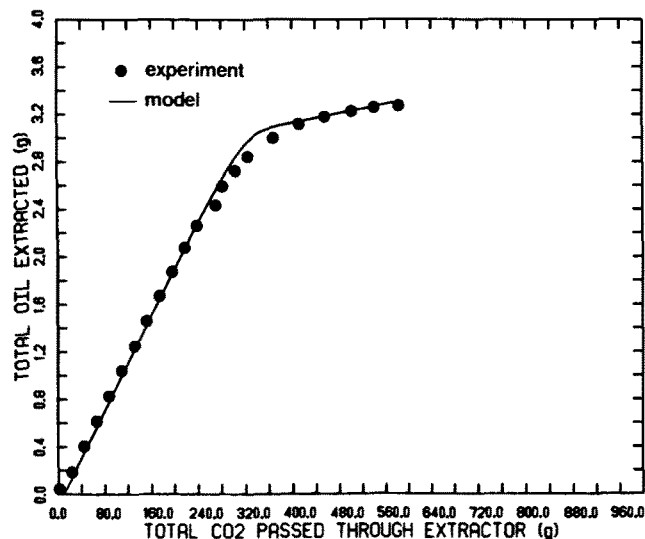

FIG. 3. Extraction results obtained by passing CO_2 at 55 C and 36 MPa through a 25.4 mm ID extractor containing 12.0 g of crushed seed. CO_2 flow-rate: 1.4 g/min, which corresponds to v = 0.08 mm/s. The computed extraction curve was calculated using $A_pK = 10$ kg/m^3s.

FIG. 2. Extraction results obtained by passing CO_2 at 55 C and 36 MPa through a 12.7 mm ID extractor containing 4.0 g of crushed seed. CO_2 flow-rate: 2.7 g/min, which corresponds to v = 0.65 mm/s. The computed extraction curve was calculated using $A_pK = 33.33$ kg/m^3s.
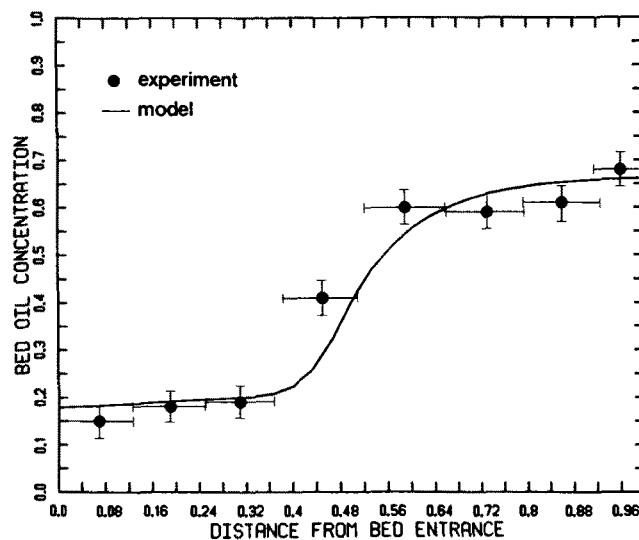

FIG. 4. Oil concentration in the seeds [kg oil/kg oil free seeds] as a function of normalized distance from the bed entrance after 240 min. (185 g CO_2). The conditions correspond to those shown in Fig. 8.

The values of the calculated overall volumetric mass transfer coefficients (ApK), which gave the best agreement with the experimental results in the constant rate period, are shown in Figure 9. The best fit was obtained by overlaying the computed predictions onto the experimental results. This proved to be fairly simple and accurate, as may be seen from Figure 1, in which the predictions using three different values of A_pK are shown. The vertical bars in Figure 9 indicate the range of A_pK values which gave fairly good agreement between the predicted and measured results. The plotted A_pK values are the arithmetic mean of the extreme values.

Figure 9 shows that the volumetric mass transfer coefficient increases with interstitial velocity and may
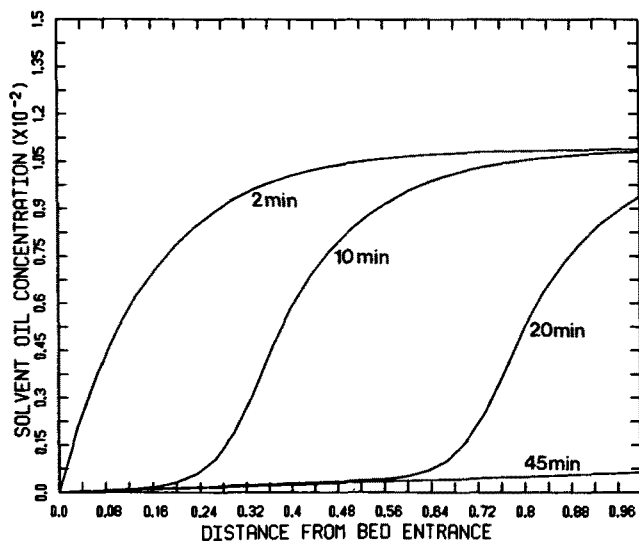

FIG. 7. Predicted oil concentration in the seed-phase [kg oil/kg oil-free seed] as a function of normalized distance from the bed entrance and time. The conditions correspond to those shown in Fig. 1.

FIG. 5. Oil concentration in the solvent-phase (kg oil/kg CO_2) as a function of normalized distance from the bed entrance at four different times. The conditions correspond to those shown in Fig. 1.

FIG. 8. Predicted oil concentration in the solvent phase [kg oil/kg CO_2] as a function of normalized distance from the bed entrance and time. The conditions correspond to those shown in Fig. 1.
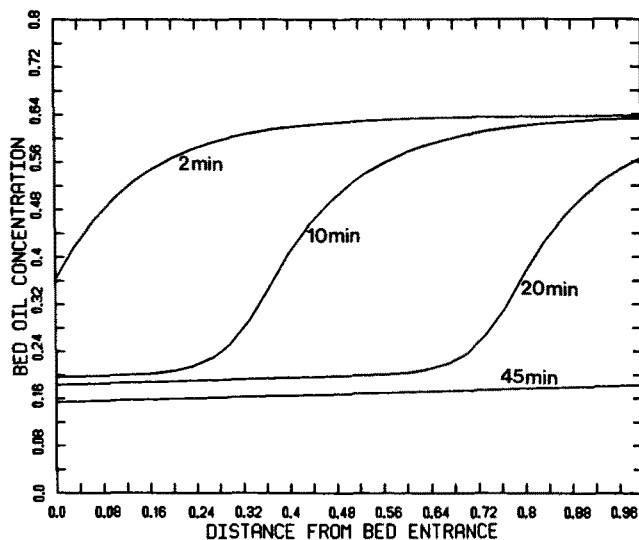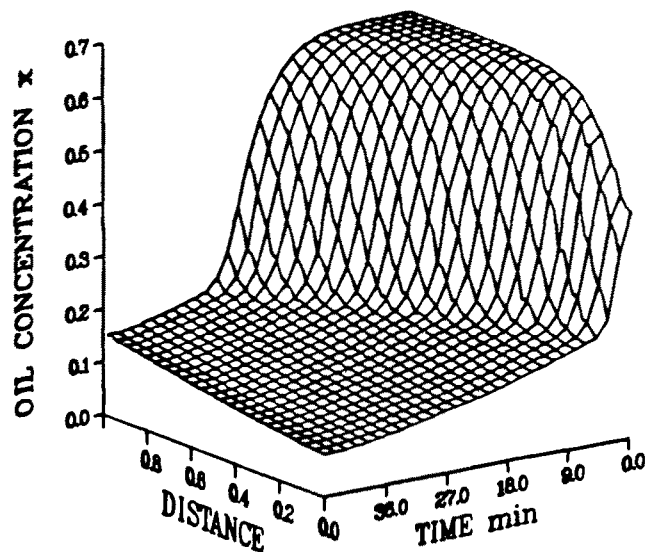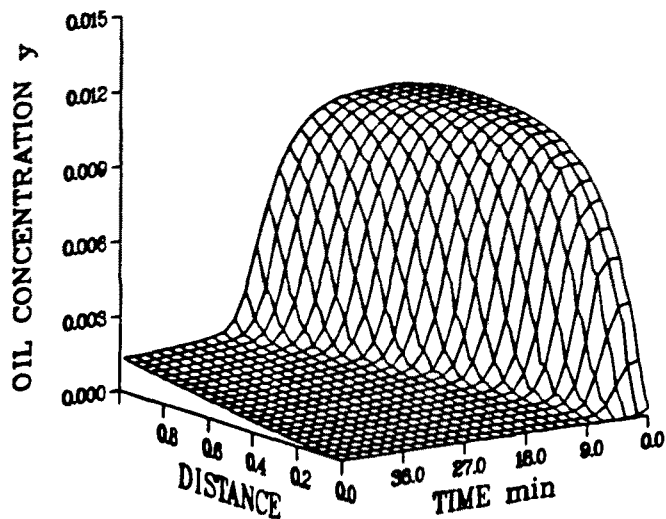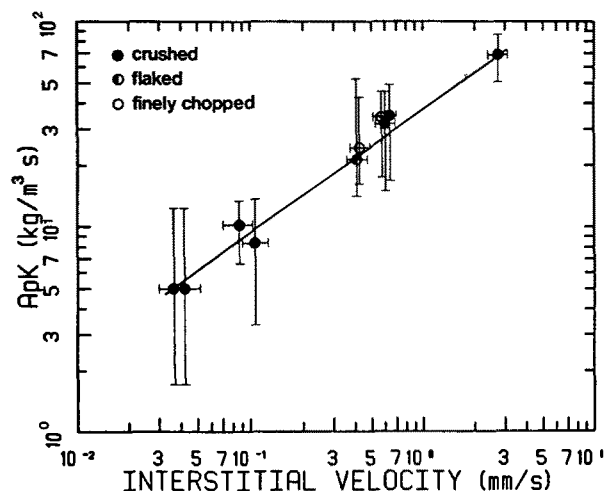

FIG. 6. Oil concentration in the seed-phase [kg oil/kg oil-free seed] as a function of normalized distance from the bed entrance at four different times. The conditions correspond to those shown in Fig. 1.

FIG. 9. Volumetric mass transfer coefficients (A_pK) as a function of interstitial velocity (v).

be represented by the equation:

$$A_p K = 32.89 \, v^{0.54} \qquad [14]$$

The units of $A_p K$ and v are kg CO_2/m^3s and mm/s, respectively. The exponent in Eq. [14] lies between the value of 0.33 reported for mass transfer in liquids (7-9) and 0.6 reported for mass transfer in gases (10,11) at comparable Reynolds numbers. Since supercritical fluids have physical and transport properties which fall between those of liquids and gases, the exponent of 0.54 in Eq. [14] is plausible.

ACKNOWLEDGMENT

REFERENCES

1. de Filippi, R.P., *Chem. Ind.* (London) 6:385 (1982).
2. Bott, T.R., *Ibid.* 6:228 (1980).
3. Bulley, N.R., M. Fattori, A. Meisen and L. Moyls, *J. Amer. Oil Chem. Soc.* 61:1362 (1984).
4. Acrivos, A., *Ind. Eng. Chem.* 48:703 (1956).
5. Lapidus, L., in *Digital Computation for Chemical Engineers*, McGraw Hill, New York, NY, 1962.
6. Hyman, J.M., *Manual LA-7595-M(MOL1D)*, Los Alamos Scientific Lab., Los Alamos, NM, (1979).
7. Appel, P.W., and J. Newman, *A. I. Ch. E. J.* 22:979 (1976).
8. Wilson, E.J., and C.J. Geankoplis, *Ind. Eng. Chem. Fund.* 5:9 (1966).
9. Williamson, J.E., K.E. Bazaire and C.J. Geankoplis, *Ind. Eng. Chem. Fund.* 2:126 (1963).
10. Wakao, N., and T. Funazkari, *Chem. Eng. Sci.* 33:1375 (1978).
11. Wakao, N., K. Tanaka and H. Nagai, *Ibid.* 31:1109 (1976).