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Effect of Feed Concentration in Equilibrium Parametric Pumps

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Abstract

The effect of high initial feed concentration in batch equilibrium parametric pumping was experimentally investigated at different bed temperatures and cycle times. The system studied was benzene-*n*-hexane over a silica gel bed. It was observed that the initial feed concentration which leads to the best separation is dictated by the shape of the equilibrium isotherms of the system. An increase in the temperature difference between hot and cold cycles was shown to improve the separation because it led to a more favorable equilibrium relationship. Experiments also indicated that a long enough cycle time must be selected for true equilibrium to be established within the system, otherwise maximum separation cannot be obtained. In mathematical modeling studies the effect of nonlinearity of equilibrium isotherms at high feed concentrations was shown to be very effective for predictions of the model.

INTRODUCTION

Parametric pumping is a separation technique which utilizes the coupling of periodic changes in equilibrium conditions caused by periodic changes in an intensive variable, such as temperature, with the flow direction of a fluid mixture flowing past a solid adsorbent bed.

The method, first described by Wilhelm et al. (*1*, *2*), was later modeled by several researchers (*3-6*). Different versions of the process were described (*7-14*).

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In this study the effect of high initial feed concentrations on batch parametric pumping under various operating conditions was investigated for the system benzene-*n*-hexane over a silica gel bed. The effect of nonlinearity of equilibrium isotherm at high feed concentrations was mathematically studied.

EXPERIMENTAL

The schematic diagram of the experimental unit is shown in Fig. 1. The main unit was a jacketed glass column with reservoirs in each end. The column was made of Pyrex glass. It was 50 cm in length and 0.55 cm in inside diameter. It was packed with 35 to 70 mesh chromatographic-grade silica gel. The reservoirs were 50 mL plastic syringes driven by a Harward infusion-withdrawal pump. It was possible to manipulate the volumetric flow rate of the fluid in the 0.02 to 100 mL/min range with this pump. The

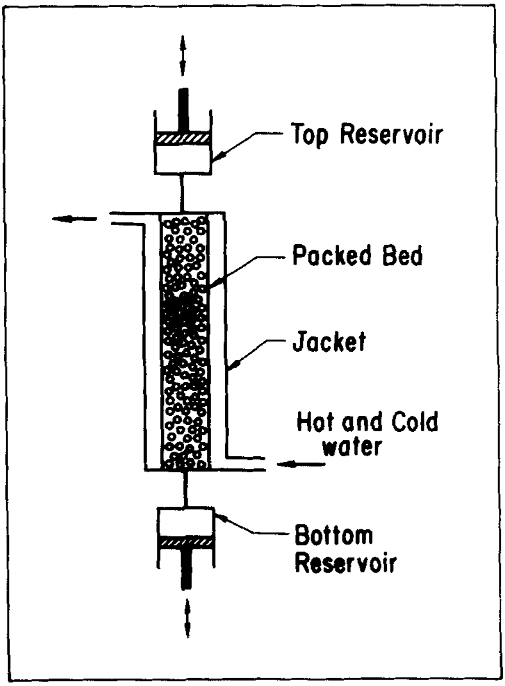

FIG. 1. Schematic diagram of the experimental unit.

bed temperature was changed by passing hot water through the jacket during upflow and cold water during downflow.

In a typical run the bottom reservoir and interstitial column volume were filled with the liquid mixture to be studied. The column was maintained at high temperature, T_H, and the reservoir pump was operated at a selected flow rate. When 50 mL of fluid was fed to the system, one half cycle was completed. At that point the pump operation was interrupted and the column was maintained at low temperature, T_L, by switching from hot water to cold water in the jacket. The pump was then operated in the reverse direction to complete the cycle. At the end of selected cycles, samples were collected from both reservoirs and analyzed with an Abbe refractometer. A summary of the experimental conditions is presented in Table 1.

The equilibrium isotherms for a benzene-*n*-hexane binary system over a silica gel bed were experimentally determined at 14 and 57°C (Fig. 2) by the method described by Rieke (*15*). The equilibrium isotherm data were fitted to a two-constant curve of the following form:

$$x_s = \frac{ax_l}{1 + bx_l} \tag{1}$$

A least-squares optimization of the data gave the constants of Eq. (1) as $a = 5.06$ and $b = 4.14$ at 14°C, and $a = 2.61$ and $b = 1.60$ at 57°C.

TABLE 1
Conditions for Experimental Runs

Experiment	Initial feed concentration (vol % benzene)	T_{hot} (°C)	T_{cold} (°C)	Flow rate (mL/min)
1	25	57	14	4.77
2	10	57	14	4.77
3	5	57	14	4.77
4	50	57	14	4.77
5	50	57	17	4.77
6	50	57	20	4.77
7	50	45	14	4.77
8	50	61	14	4.77
9	50	58	13	4.77
10	50	58	13	1.91
11	50	58	13	0.96

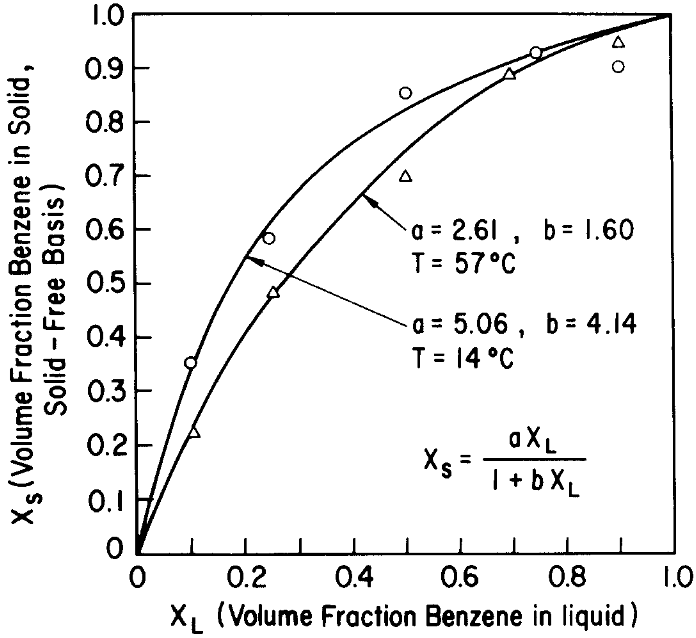

FIG. 2. Equilibrium isotherms for benzene-*n*-hexane on silica gel.

THEORY

In the present model, axial dispersion and the general nonlinear form of the equilibrium isotherm were taken into account. The process was considered to be isothermal per half cycle. Neglecting the radial diffusion term and following the terminology of Rieke (*13*), the solute mass balance in the bed may be written

$$\alpha \frac{\partial x_l}{\partial t} + (1 - \alpha)\varepsilon \frac{\partial x_s}{\partial t} + \alpha V \frac{\partial x_l}{\partial z} = \alpha D \frac{\partial^2 x_l}{\partial z^2} \tag{2}$$

with boundary conditions:

$$x_{lf} = x_l(0,t) \tag{3}$$

$$x_{lf} = x_l(z,0) \tag{4}$$

$$0 = \partial x_l/\partial z \qquad (z = L,t) \tag{5}$$

In general, the equilibrium relation between the phases can be written

$$x_s = F(x_l, T) \tag{6}$$

In the present work, the functional form given by Eq. (1) was adopted. Differentiation of Eq. (6) gives

$$\frac{\partial x_s}{\partial t} = \left(\frac{\partial x_s}{\partial x_l}\right)_T \left(\frac{\partial x_l}{\partial t}\right) + \left(\frac{\partial x_s}{\partial T}\right)_{x_l} \left(\frac{\partial T}{\partial t}\right) \tag{7}$$

since in each cycle the temperature remained constant, Eq. (7) is reduced to

$$\frac{\partial x_s}{\partial t} = \left(\frac{\partial x_s}{\partial x_l}\right)_T \left(\frac{\partial x_l}{\partial t}\right) \tag{8}$$

where $(\partial x_s/\partial x_l)_T$ is the slope of the equilibrium isotherm at a given concentration x_l. Combining Eq. (8) with Eq. (2):

$$\frac{\partial x_l}{\partial t} + V_c \frac{\partial x_l}{\partial z} = D_c \frac{\partial^2 x_l}{\partial z^2} \tag{9}$$

where $V_c = V/(1 + m)$ and $D_c = D/(1 + m)$ with $m = (1 - \alpha)\varepsilon/\alpha(\partial x_s/\partial x_l)_T$.

Equation (9) can be solved numerically using the finite difference approximation method in which

$$\left(\frac{\partial^2 x}{\partial z^2}\right)_i = \frac{x_{i-1} - 2x_i + x_{i+1}}{\Delta z^2} \tag{10}$$

$$\left(\frac{\partial x}{\partial z}\right)_i = \frac{x_i - x_{i-1}}{\Delta z} \tag{11}$$

$$\left(\frac{\partial x}{\partial t}\right)_i = \frac{x_i(t) - x_i(t-1)}{\Delta t} \tag{12}$$

Implicit differencing is used by working with averages between current and previous cycles in distance, i.e.,

$$x_i = \frac{[x_i(t) + x_i(t-1)]}{2} \tag{13}$$

from which the following relation may be written:

$$-(\lambda + R)x_{i-1}(t) + (2 + 2\lambda + R)x_i(t) - \lambda x_{i+1}(t) = (\lambda + R)x_{i-1}(t - 1)$$
$$+ (2 - 2\lambda - R)x_i(t - 1) + \lambda x_{i+1}(t - 1) \qquad (14)$$

where $\lambda = (\Delta t D_c)/\Delta z^2$ and $R = (\Delta t V_c)/\Delta z$.

By applying Eq. (14) to grid points for $i = 1$ to $i = n - 1$, and employing Taylor's expansion at the boundary condition $(\partial x_i/\partial z)_{z=L} = 0$, it is reduced to

$$-2\lambda x_{i-1}(t) + (2 + 2\lambda)x_i(t) = (2 - 2\lambda)x_i(t - 1) + 2\lambda x_{i-1}(t - 1) \qquad (15)$$

Equations (14) and (15) may be solved simultaneously by computer.

RESULTS AND DISCUSSION

Eleven experimental runs were carried out with experimental conditions outlined in Table 1. The results are illustrated in Figs. 3 to 6.

The effect of initial feed concentration on solute distribution profile was investigated by changing the initial benzene concentration from 5 to 50% by volume (Experiments 1 to 4). Figure 3 depicts concentration profiles as a function of the number of cycles. The results indicate that concentration profiles were shifted downward at higher initial feed concentrations, particularly in the bottom reservoir. This meant that the bottom reservoir was depleted of benzene more quickly at higher initial feed concentrations. This may be explained by considering the equilibrium relationship of the present system (Fig. 2). As the initial feed concentration was changed from 5 to 50% by volume benzene, the gap between the hot and cold equilibrium isotherms widened. This was an indication of an increase in the tendency of more adsorption per pass during the early cold cycles. This led to a quicker reduction of benzene concentration in the bottom reservoir. This result indicates the importance of the shape of the equilibrium isotherm of a system under consideration for parapump operation. A starting concentration in the favorable concentration range of the equilibrium isotherm plot should be selected for successful separations.

To observe the effect of temperature of the bed at high feed concentrations, bed temperatures were manipulated in Experiments 4 to 8. The results are depicted in Figs. 4 and 5. The change in the cold cycle temperature, T_L, did not indicate a particular trend, probably because the change was not large enough to affect the shape of the cold equilibrium isotherm. In the case of a change of the hot cycle temperature, T_H (Fig. 5),

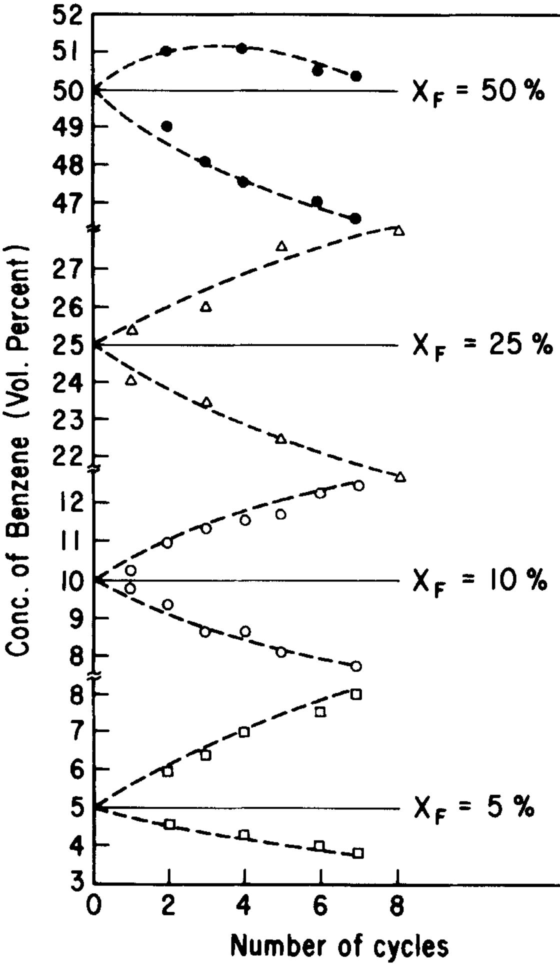

FIG. 3. Effect of initial feed concentration. Dashed lines are by regression.

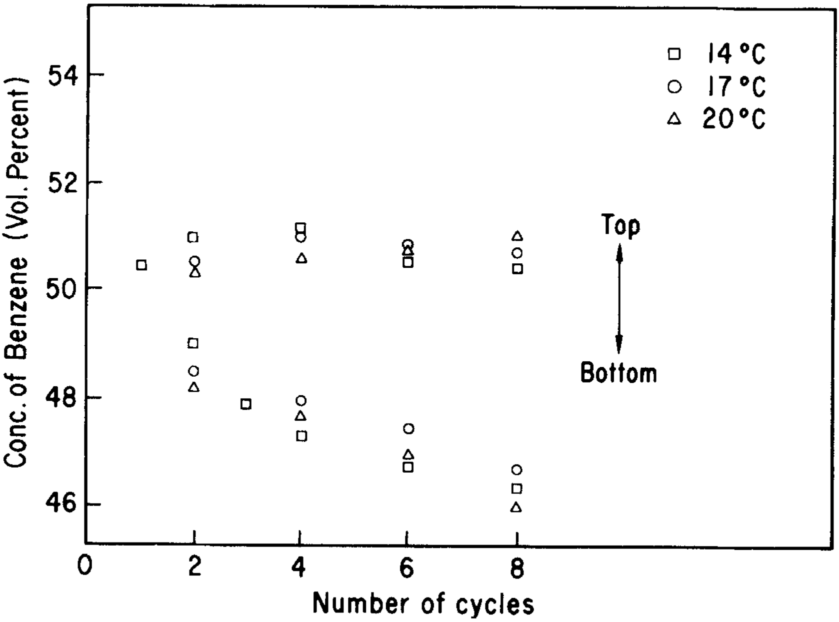

FIG. 4. Effect of change of cold cycle bed temperature, T_L.

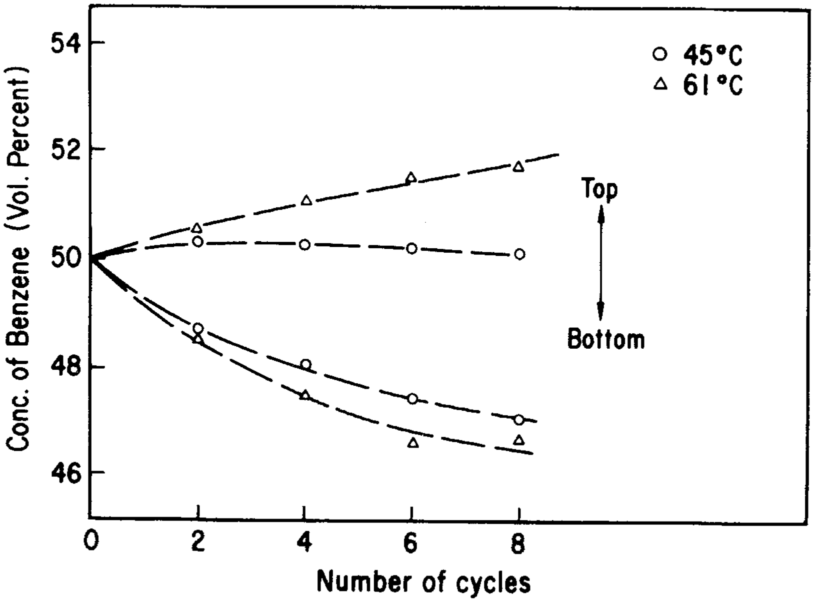

FIG. 5. Effect of change of hot cycle bed temperature, T_H. Dashed lines are by regression.

a more effective separation was observed as T_H increased from 45 to 61°C while keeping other experimental conditions the same. This is in agreement with the equilibrium model, since an increase in T_H shifts the high temperature equilibrium isotherm downward and the net effect is a widening of the gap between the equilibrium isotherms of cold and hot cycles. This leads to more effective separation as discussed before.

The effect of cycle time was observed in Experiments 8 to 11 (Fig. 6). The results indicate that separations achieved at 50- and 104-min cycles were close to each other while separation achieved by 20-min cycles was significantly less. This may be an indication of the fact that the shorter time of 20-minute cycles was not enough to permit the establishment of a true equilibrium distribution of compounds between the phases. A similar result was reported by Chen et al. (*16*).

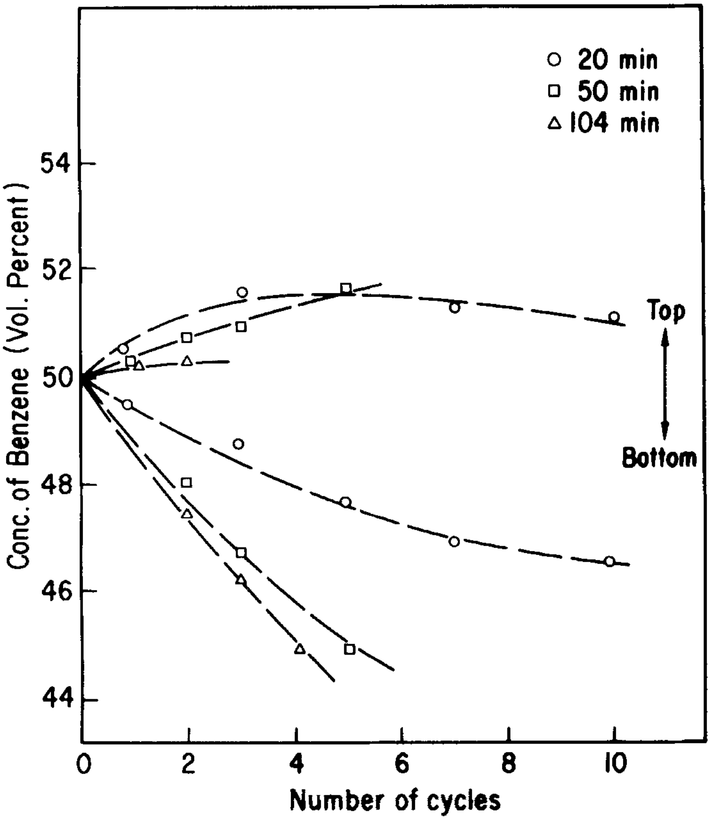

FIG. 6. Effect of cycle time. Dashed lines are by regression.

MODELING STUDIES

In the application of the mathematical model presented in the Theory section to the experimental results, two versions of the model were investigated. In Version 1, the equilibrium isotherms were assumed to be "linear per pass," that is, for each half cycle the equilibrium relation was assumed to be linear with a slope read from a tangent line at x_l at the beginning of that particular half cycle. In contrast, in Version 2 the nonlinearity of the isotherms was considered within the half-cycles, that is, equilibrium values were reevaluated from gridpoint to gridpoint within one half cycle by a computer using Eq. (1). The comparative results are illustrated in Fig. 7 for a low initial feed concentration of 10% by volume benzene (Experiment 2) and in Fig. 8 for a higher initial feed concentration of 25% by volume benzene (Experiment 1). Agreement among the two versions of the model and the data at lower feed concentrations are satisfactory. The two versions predict close values because both isotherms are almost linear up to 10% benzene. At higher feed concentrations up of 25%, due to the nonlinearity of the isotherms in

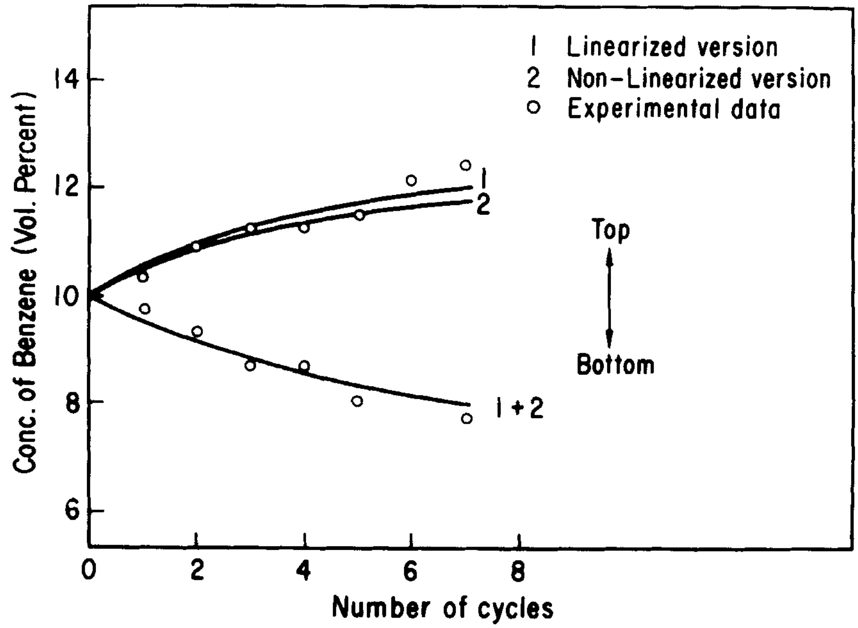

FIG. 7. Model predictions versus experimental results at 10% initial feed concentration.

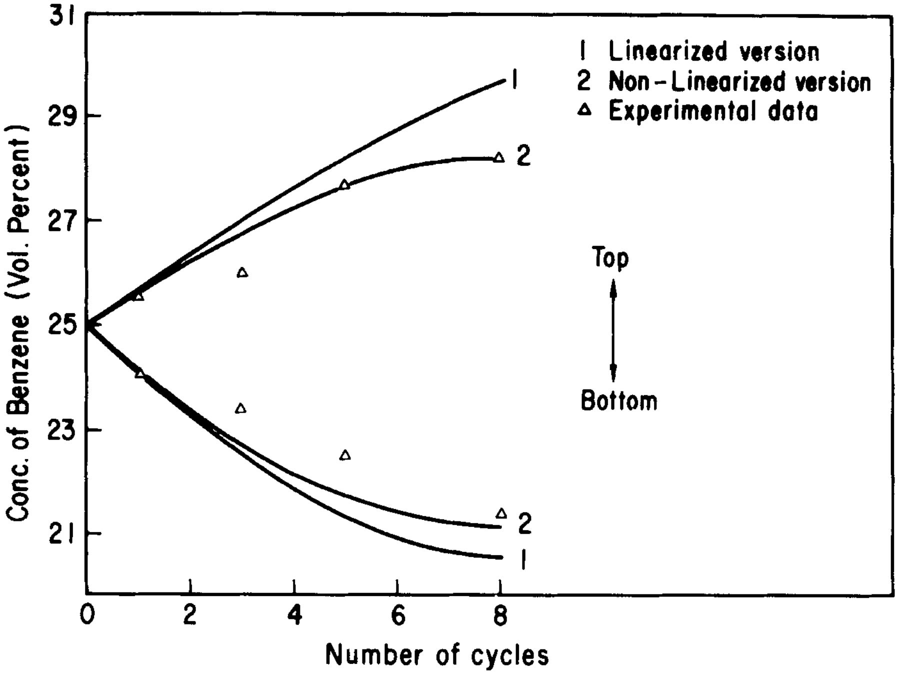

FIG. 8. Model predictions versus experimental results at 25% initial feed concentration.

this concentration range, Version 2 shows a better performance in comparison to Version 1. None of the models gives satisfactory results at concentrations higher than 25%. In modeling studies the coefficient D was used as a parameter which gives the best fit to available data at low benzene concentrations. The values of the parameters used in the computations are given in Table 2.

TABLE 2
Parameters Used in the Computations

Δt = 750 s
$t_{\max}$ = 10,500 s
D = 4.8×10^{-3} cm^2/s (calculated)
V = 0.5 cm/s
L = 50 cm
n = 10 (number of grids)

SYMBOLS

D	diffusion coefficient
D_c	$D/(1+m)$
L	bed length
R	$V_c(\Delta t/\Delta z)$
T	temperature
V	interstitial velocity
V_c	$V/(1+m)$

Lowercase

m	$\frac{(1-\alpha)\varepsilon}{\alpha}\left(\frac{\partial x_s}{\partial x_l}\right)_T$
t	time
x	volume fraction or volume percent in benzene
z	distance along the axial direction

Greek Letters

α	interparticle void fraction
ε	intraparticle void fraction
λ	$D_c(\Delta t/\Delta z^2)$

Subscripts

H	high temperature
L	low temperature
l	liquid composition
lf	feed concentration
s	solid composition

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