Nonuniform Residence Times and the Production of Intermediates in Tubular Reactors

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H. E. Hoelscher, in his work published in the *A.I.Ch.E. Journal*, [9, 569 (July, 1963)], deals with nonuniform residence times and the production of intermediates in tubular reactors. In a tubular reactor, the author determines the intermediate R yield of two consecutive reactions of the first order, with no assumption of plug flow, by reckoning a comparative index of such yield with the yield obtainable with an ideal, uniform flow. This index, which practically consists of the ratio between the mean concentration of the intermediate R in both the above mentioned cases in a tubular element about the axis having diameter $2\,\overline{R}\,\sigma_c$ $\left(\sigma = \dfrac{r}{R}\right)$, has been reckoned by means of the following Equation (6), where

$$K_1 = k_1 \frac{L}{B}; \quad K_2 = k_2 \frac{L}{B}$$

$$\frac{Y_m(\sigma_c)}{Y_{pf}(\sigma_c)} = \frac{2\int_0^{\sigma_c} \sigma \left[e^{-\frac{K_1}{1-\sigma^n}} - e^{-\frac{K_2}{1-\sigma^n}} \right] d\sigma}{\sigma_c^2 \left[e^{-K_1\frac{B}{V_m}} - e^{-K_2\frac{B}{V_m}} \right]}$$

To draw Equation (6) the velocity profile has been reckoned according to Equation (4), $V = B(1 - \sigma^n)$. Equation (6) could be extended for the whole flow writing $\sigma_c = 1$.

The author integrated the local concentration referring to the corresponding infinitesimal area, and then divided the integral value by the area of the section. The value resulting from this calculation may be considered as a mean value, according to a geometrical concept. However, it is of no importance with regard to practical use. In our opinion such an integration should be better exploited by referring it to the flow rate in the section taken into consideration. This is the only possible way to reckon the mean concentration value in the fluid coming out the reactor. Thus it can be written

$$\frac{Y_m(\sigma_c)}{Y_{pf}(\sigma_c)} = \frac{2\pi B \int_0^{\sigma_c} \sigma(1 - \sigma^n) \left[e^{-\frac{K_1}{1-\sigma^n}} - e^{-\frac{K_2}{1-\sigma^n}} \right] d\sigma}{\left[e^{-K_1\frac{B}{V_m}} - e^{-K_2\frac{B}{V_m}} \right] 2\pi B \int_0^{\sigma_c} \sigma(1 - \sigma^n) d\sigma}$$

For the whole duct it can be written

$$\frac{Y_m(\sigma_c = 1)}{Y_{pf}(\sigma_c = 1)} = \frac{2B \int_0^1 \sigma(1 - \sigma^n) \left[e^{-\frac{K_1}{1-\sigma^n}} - e^{-\frac{K_2}{1-\sigma^n}} \right] d\sigma}{V_m \left[e^{-K_1\frac{B}{V_m}} - e^{-K_2\frac{B}{V_m}} \right]}$$

and in laminar flow

$$\alpha) \quad \left[\frac{Y_m(\sigma_c = 1)}{Y_{pf}(\sigma_c = 1)} \right]_{n=2} = \frac{4 \int_0^1 \sigma(1 - \sigma^2) \left[e^{-\frac{K_1}{1-\sigma^2}} - e^{-\frac{K_2}{1-\sigma^2}} \right] d\sigma}{e^{-2K_1} - e^{-2K_2}}$$

The results shown in Hoelscher's Figure 2 can be explained by his calculations; from these results it appears that $\dfrac{Y_m(\sigma_c = 1)}{Y_{pf}(\sigma_c = 1)}$ is greater than 1, and the more the velocity profile differs from plug flow the more it increases. This is in contrast with the conclusions one comes to, even through physical reasoning, when in the proximity of the mean residence time in the reactor one has $\dfrac{d^2 C_R}{dt^2} < 0$. In fact, in such a case, it is found that the increase of yield R in the fluid delayed in respect to the mean residence time in the reactor, does not compensate the decrease of yield in the fluid, the velocity of which is superior to the mean velocity. $\dfrac{d^2 C_R}{dt^2} < 0$ always occurs when $k_2 = 0$ and also occurs when $k_2 \neq 0$ for residence times of practical interest when R is the useful product. On the contrary, Hoelscher's results show values of $\dfrac{Y_m(\sigma_c = 1)}{Y_{pf}(\sigma_c = 1)} > 1$, because the integration referring to the area of the section gives a fictitious increase of the influence of the slower liquid nearer the wall.

As a demonstration, in Figure 1 we show in function of K_2 the values of the ratio $\dfrac{Y_m(\sigma_c = 1)}{Y_{pf}(\sigma_c = 1)}$, which we have reckoned through Equation (6) for $K_1 = 10^{-4}$ and $n = 2$ (laminar flow) and the corresponding values reckoned according to equation α.

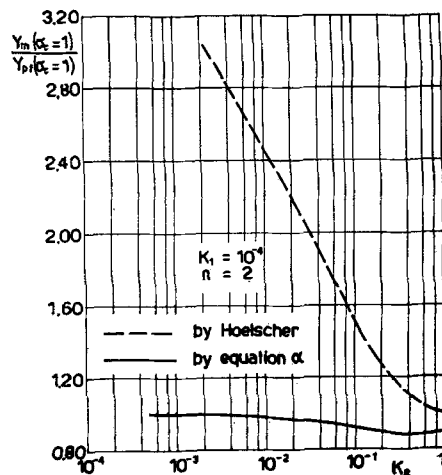In Figure 1, K_1 and K_2 have been used as parameters because in our diagram one value of n only has been

Fig. 1.

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taken into consideration, in contrast with Hoelscher's Figure 2. In fact, if n also varies, the shape of the velocity profile varies and consequently, if the volumetric flow rate is constant, B also varies.

Therefore, K_1 and K_2 are not only functions of the volumetric flow rate and of the kinetic constants, but also depend upon n. Thus it is not advisable to use them to make a comparison when variations of n occur.

Equations (4), (5), and (6), and Figure 2, as well as the notation, are quoted from Hoelscher's work.

NOTATION

A = reagent
B see the equation of the veloc-
ity profile $V = B(1 - \sigma^n)$, cm./s
C = concentration, moles/cc.
k_1 = rate constant of step 1, s^{-1}
k_2 = rate constant of step 2, s^{-1}
K_1 = $k_1 \dfrac{L}{B}$, adim
K_2 = $k_2 \dfrac{L}{B}$, adim
L = reactor length, cm.
n = constant in the equation of the velocity profile $V = B (1 - \sigma^n)$, adim
r = radial distance measured from axis of tube, cm.
R = intermediate product
$\overline{R}$ = radius of the tube, cm.

t = reaction time, s
Y = $\dfrac{C_R}{C_{A_0}\left(\dfrac{k_1}{k_2 - k_1}\right)} = e^{-k_1 t} - e^{-k_2 t}$
modified concentration ratio, adim
V = local velocity, cm./s
σ = dimensionless position variable = $\dfrac{r}{\overline{R}}$, adim

Subscripts

m = mean value
o = initial value
pf = plug flow value
c = particular radial position ≤ 1

On the Minimum Time Operation of a Batch Reactor

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In a recent paper Cotter (1) treats the control problem of the minimum time operation of a batch reactor with a single exothermic reaction controlled by a cooling coil. The control variable is a function of the cooling water rate, and it is proved that the optimal control is bang-bang. The main purpose of this present paper is to establish that for the time-optimal problem considered by Cotter the optimal control is bang-bang with, at most, one discontinuity point. Furthermore, the same result is established for various systems more general than the system considered by Cotter (1). The control theory terminology of Pontryagin et al. (2) is used throughout the paper. An assumption for the analysis is that an optimal control exists for the time-optimal problems under consideration. Some aspects of the present paper have also been discussed from a more general point of view by Hermes and Haynes (3).

MINIMUM TIME OPERATION OF A BATCH REACTOR

Cotter (1) treats the problem of the minimum time operation of a batch reactor with a single exothermic reaction controlled by a cooling coil. The reaction is pseudo first order. Cotter considers an irreversible reaction with

$$\text{rate} = -xk_1(T) \qquad (1)$$

The system equations are given by

$$\frac{dx}{dt} = \frac{-xVk_1(T)}{W_x} \qquad (2)$$

$$\frac{dT}{dt} = \frac{VH_r k_1(T)}{W_T} - \frac{(T - T_o)\,\varphi}{W_T} \qquad (3)$$

For Equations (2) and (3) Cotter chooses the function φ as the control variable and assumes the state variables are given initially by $x(t_o)$, $T(t_o)$ and at the final time by $x(t_1)$, $T(t_1)$.

In the terminology of Pontryagin (2), the time-optimal problem consists of determining an admissible control $\varphi(t)$ that transfers the phase point $x(t_o)$, $T(t_o)$ to the phase point $x(t_1)$, $T(t_1)$ in least time. In reference 1, admissible controls are piecewise continuous functions in $t_o \leq t \leq t_1$. Cotter establishes that the optimal control is bang-bang (1).

PROBLEM FORMULATION

We shall analyze the problem treated by Cotter by considering a more general system of first-order differential equations.

$$\frac{dz_1}{dt} = A_1(z_1, z_2) \qquad (4)$$

$$\frac{dz_2}{dt} = B_1(z_1, z_2) + B_2(z_1, z_2)y \qquad (5)$$