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Hysteresis and Multiplicity in Wall-Catalyzed Reactors

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A mathematical model of a wall-catalyzed reactor is used to elucidate the effects of inlet velocity and concentration, geometry of the duct, and axial conduction on the hysteresis, multiplicity and parametric sensitivity. The monolith reactor for carbon monoxide oxidation is the prototype considered, with wall catalyst being platinum on alumina on a ceramic substrate. Previous models have dealt with only a single tube of the monolith. Two adjacent ducts are examined to see the effect of heat exchange between them when the velocity in each is different.

1. Hysteresis

The term hysteresis refers to a multiplicity of steady states, and the actual steady state depends on the past history of operation of the reactor. In particular, different outlet conversions are obtained for the same inlet temperature depending on whether the device starts out hot or cold. This effect is illustrated in Figure 1, which was obtained experimentally by Hlaváček and Votruba (1) and Mostercky, et al. (2) in the following manner. Beginning with a cold reactor, desired inlet conditions are maintained at a low temperature until steady state has been reached, giving one data point on the top part of the curve. Then the inlet temperature is raised, and the experiment again proceeds to steady state, giving another data point. This procedure is followed giving the curve denoted by →. At the ignition temperature light off occurs and the concentration of carbon monoxide out of the reactor decreases drastically. Almost complete conversion is obtained for any higher inlet temperature. Then the inlet temperature is lowered, step by step, giving rise to the curve marked ←. At the extinction temperature the exit concentration suddenly increases and little reaction takes place. For a given temperature between the extinction and ignition temperatures it is possible to have two different outlet conditions; thus there is a multiplicity of steady states. When the inlet temperature is near the extinction or ignition temperature, a small change in operating conditions - inlet concentration or temperature or velocity - can cause a large change in the outlet conditions. This phenomena is parametric sensitivity. The hysteresis curve illustrated in Figure 1 thus includes information about the multiplicity of steady state solutions and the regions of parametric sensitivity. What it does not show, however, is whether the two steady states shown are stable, and if there are any other steady states between those shown (probably unstable ones). Judging from studies of packed beds (3) it is probable that both the steady states shown are stable, and any other ones are unstable.

A model developed earlier (4,5) used the collocation method to solve the equations for heat, mass and momentum transfer in a single, adiabatic channel of the monolith. The basic model is the one described as Model II-A(5): a square duct with axial conduction of heat longitudinally in the solid walls, but with infinitely fast conduction peripherally around the square, and including the diffusion of heat and mass in the transfer direction in the fluid (See 5 for a discussion of the importance of including this effec.) Nusselt and Sherwood numbers are not assigned a priori, but are derived from the solution. The reaction rate expression P2 in (5) with a basic form

$$\text{rate} = \frac{D y_{O_2}\, y_{CO}\, e^{-A/T}}{\left[1 + C y_{CO} e^{B/T}\right]^2} = \frac{k_o(E + y)y}{(1 + \alpha y)^2}$$

This is the expression derived by Voltz, et al. to fit their data (6). Here however, we allow diffusion limitations in the very thin catalytic layer. The temperature is assumed constant within the layer since the primary heat transfer resistance occurs in the fluid. The effectiveness factor curve is generated using a one-term collocation method for small Thiele modulus and the asymptotic solution for large Thiele modulus (7). The base case, unless otherwise noted, is for a Reynolds number 160, $y_{CO, inlet}$ = 0.04, P2 kinetics, square geometry, k_f/k_s = 0.04, D_f/D_s = 20. Other parameters are given elsewhere (4,5), and the parameters are characteristic of an Englehard PTX-4 converter.

The theoretical hysteresis curve is shown in Figure 2 for three different inlet CO mole fractions. The correct qualitative trends are exhibted: the hysteresis is wider (greater difference between the ignition and extinction temperatures) for larger concentrations of carbon monoxide. Other calculations (7) indicate the ingnition and extinction temperatures depend on flow rate, too, reflecting the experimental observations: the hysteresis is wider for the lower flow rates.
As in the case of packed beds, the higher velocities tend to blow the reaction zone out the downstream end of the duct, whereas lower velocities lead to ignition that moves upstream towards the inlet. The effect of geometry is examined in Ref. 8, and ducts

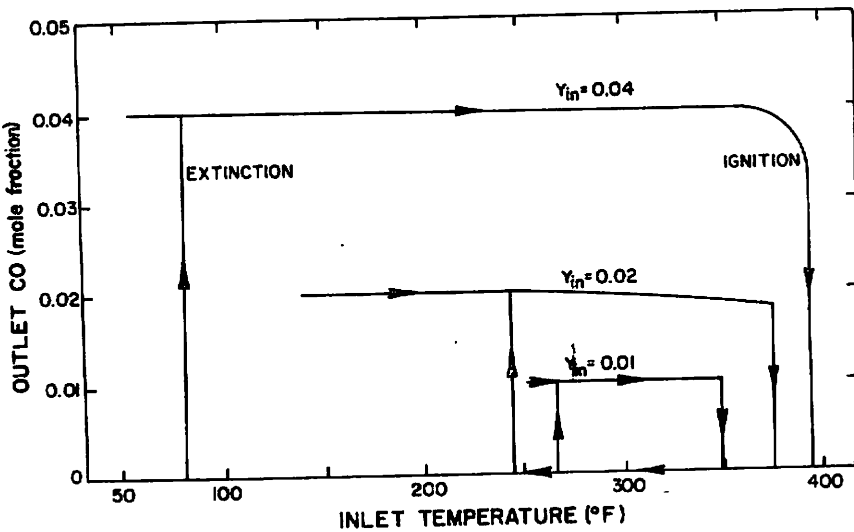

Figure 1. Experimental hysteresis curve, Re = 152, Refs. 1, 2

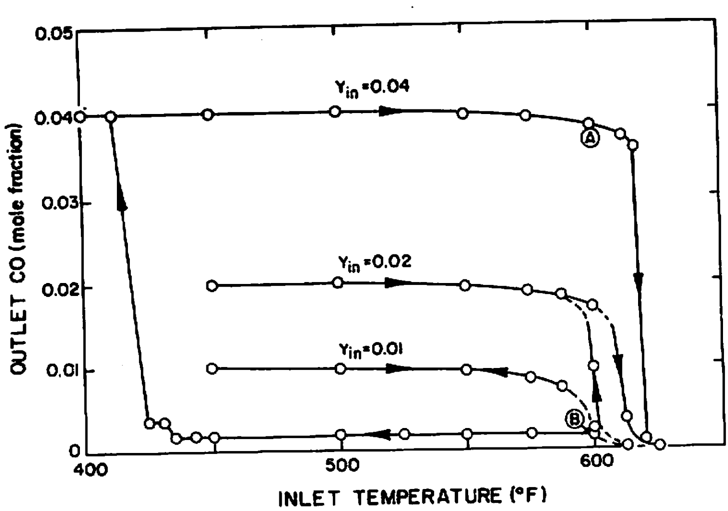

Figure 2. Theoretical hysteresis curves, Re = 160

with four different shapes (square, circle, trapezoid, rectangle) have almost identical hysteresis properties. Consequently it is possible to do calculations with the geometry that leads to the most convenient computations.

The most important effect of the model is the axial conduction of heat in the solid tube wall. Figure 3 shows the temperature and mole fraction profiles for different values of the solid thermal conductivity. The inlet mole fraction of CO is 0.04 and the inlet temperature is 600°F. Figure 2 indicates that for these conditions there are multiple steady state solutions, one with essentially complete reaction, and one with essentially no reaction. The curves marked A and B correspond to the conditions giving the points A and B in the hysteresis curves in Figure 2. The extinguished state has very little reaction and the mole fraction and wall temperature change very little down the length of the duct. This is the same curve obtained if the axial thermal conductivity is set to zero, i.e. the axial conduction of heat is absent, Model II in (5). The ignited state has a sharp rise in temperature inside the duct at $z/L = 0.65$. The oscillations in the solution are due to numerical error caused by using too few elements, 10, rather than the 20 used earlier (5).

The importance of axial conduction of heat is emphasized by the other curves in Figure 3. Shown there are the ignited states for different solid thermal conductivities, and as the solid thermal conductivity decreases the ignition zone moves to the end of the reactor, and for a small enough value only the extinguished state is possible. The hysteresis is thus much enhanced by a large value of k_s, or by thicker walls. This is further demonstrated in Table I.

Table I. Ignition and Extinction Temperatures for Different Wall Thermal Conductivities (from 7)

k_f/k_s	T_{ex}(°F)	T_{ig}(°F)	ΔT(°F)
0.04	418	618	200
1.0	560	619	59
100.	615	615	0

Since the mechanism for hysteresis is due to the axial conduction of heat in the wall, the hysteresis should decrease as k_s or the wall thickness decrease, as illustrated by the parameter affecting the rate of axial conduction

$$\frac{k_s}{k_f} \; \frac{2r_h^2}{L^2} \; \frac{1-\varepsilon}{\varepsilon} .$$

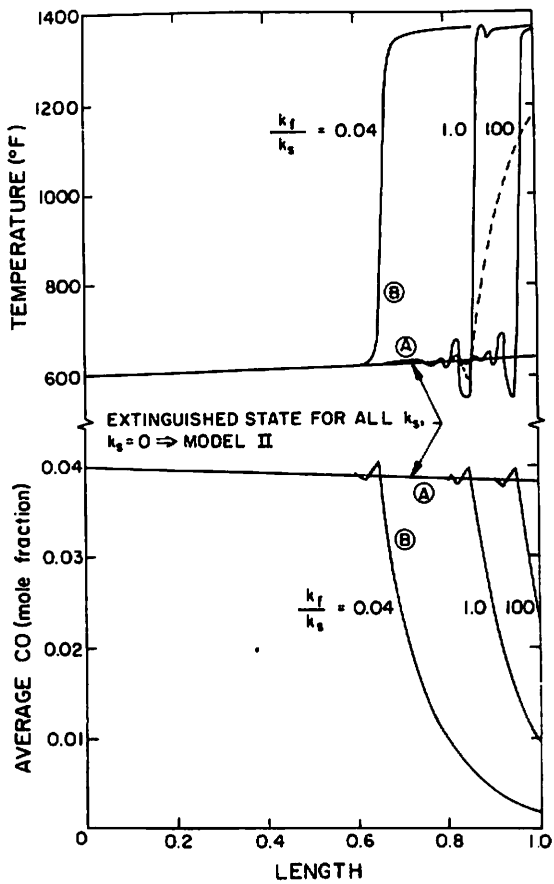

Figure 3. Axial temperature and mole fraction profiles for different thermal conductivities

2. Effect of Multiple Channels

The calculations reported above were for a single, adiabatic channel of a duct in a multi-channel monolith. If each channel is not the same it is possible that further complications can arise. We investigate this possibility in a preliminary way. Since the material entering all the channels is the same (coming from the same larger channel originally), it is likely that the inlet concentration and temperature are identical in the adjacent channels. We thus focus on the effect of velocity differences in adjacent channels. To simplify the computational task we consider only two channels which share the same solid wall. We saw above that the behavior of the hysteresis curve was not influenced by the shape of duct, and here we use a circular duct for computational convenience. The combined geometry is then a checkerboard effect, with every other cell being the same. We still assume that there is infinitely fast peripheral conduction of heat, so that at any axial position the wall temperature is everywhere the same. For this preliminary situation we also assume that the axial conduction of heat is negligible, even though we know this is not the case. However, since the wall temperature is everywhere the same at a given axial location, it should be possible to study the effect of velocity variations in adjacent channels and axial conduction of heat separately, and the results add credence to this supposition. Such a drastic, but plausible, assumption was made for computational convenience.

The computations for multiple channels were made with a revised version of the program REACOLL. This program converts a set of parabolic partial differential equations into a larger set of ordinary differential equations by using the orthogonal collocation method (9,10). Previous versions of REACOLL have used a fifth order Runge-Kutta variable step size integration routine to integrate in the axial direction. We modified the program to use Gear's algorithm (11,12). Gear's algorithm is a collection of multi-step methods, with the step and order of the method automatically controlled to achieve a user-specified accuracy within a minimum computation time. We chose the option of an implicit method with the nonlinear algebraic equations solved with the Newton-Raphson method, with a numerical generation of the Jacobian at each Δz step. The Jacobian is not reevaluated at each Δz step, but is evaluated if the iteration cannot converge in three iterations. If the iteration still does not converge, a smaller Δz is chosen and the calculation is repeated. The advantageous feature of the method is that it will always work for a small enough Δz, but the computational cost may be high. For these problems comparisons were made with a fifth-order Runge-Kutta integration in Δz, too, and Gear's algorithm was about twice as fast for the same user-specified accuracy.

The model equations can be written as

$$v(r) \frac{\partial c_i}{\partial z} = \alpha_i \frac{1}{r} \frac{\partial}{\partial r} (r \frac{\partial c_i}{\partial r})$$

with the first two variables as the mole fraction and temperature in the first channel, and the third and fourth variable being the mole fraction and temperature in the second channel. The conditions at the wall require that the diffusion of mass towards the wall equal the generation of mass by the wall-catalyzed reaction, and the same is true for heat. We thus have the boundary conditions

$$- \frac{\partial c_1}{\partial r}\bigg|_{r=1} = \beta_1 R(c_1, T), \quad - \frac{\partial c_3}{\partial r}\bigg|_{r=1} = \beta_3 R(c_3, T)$$

$$- \frac{\partial c_3}{\partial r}\bigg|_{r=1} \quad - \frac{\partial c_4}{\partial r}\bigg|_{r=1} = \beta_2 R(c_1, T) + \beta_4 R(c_3, T)$$

$$c_2 = c_4 = T \text{ at } r=1$$

The mathematical structure of the problem is thus a set of partial differential equations which are coupled with a set of nonlinear algebraic equations at each axial position. The algebraic equations are solved using a Newton-Raphson iteration with the derivatives calculated numerically. The same reaction rate expression (P2)was used.

The first case corresponds to a case which has not "lit off." We note first that without axial conduction of heat in the wall the solution has to be unique (5), and there is no hysteresis curve. For an inlet temperature of 600°F the wall temperature profile is shown in Figure 4 for different average velocities. The three solid curves are for cases in which the velocity in each channels is the same, but the magnitude of the average velocity is different. In all cases a parabolic velocity distribution is taken as a function of radius of the duct, since the flow is laminar and only the average velocity is changed. The solid curves then represent three separate unrelated cases, in which the average velocity is increased. The calculation for multiple channels is made with the velocity in one channel being 0.8 the normal velocity (giving Re = 128) and the velocity in the other channel being 1.2 times the normal velocity (giving Re = 192). The multiple channel results are denoted by the ■ in the Figure 4, and it is seen that they are very close to the results expected from two channels with the same average velocity in each

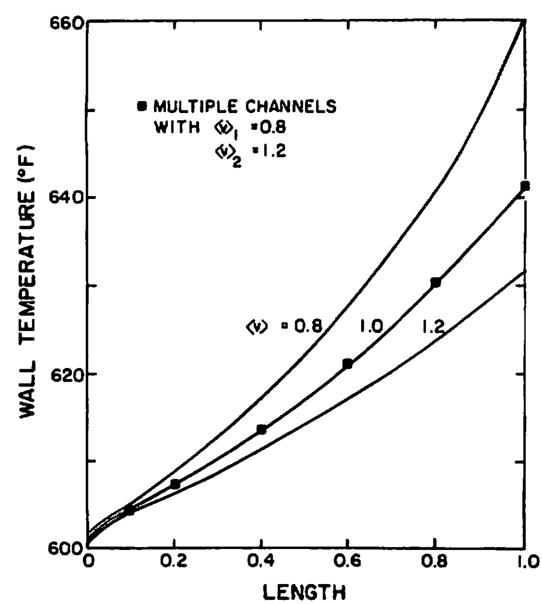

Figure 4. Wall temperature in multiple channels, $T_{inlet} = 600°F$

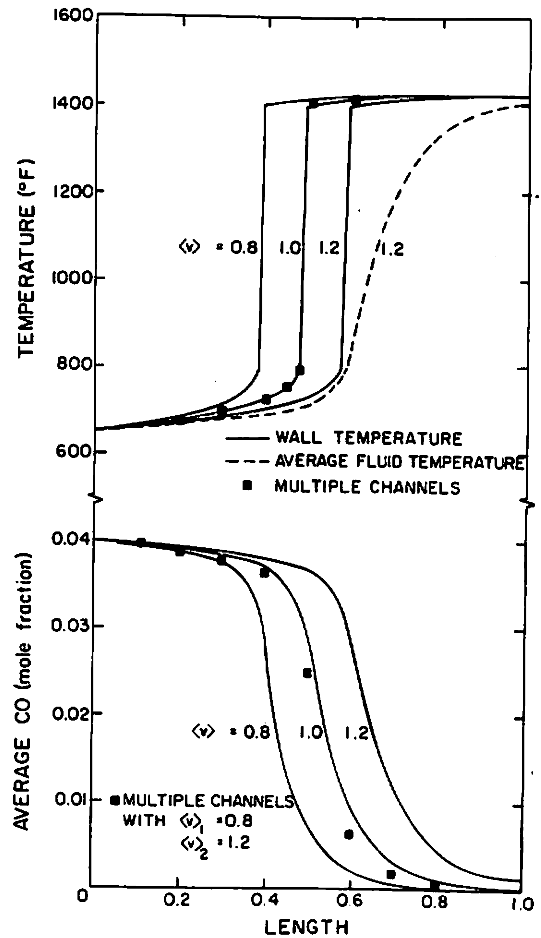

Figure 5. Wall temperature in multiple channels, T_{inlet} *= 650°F*

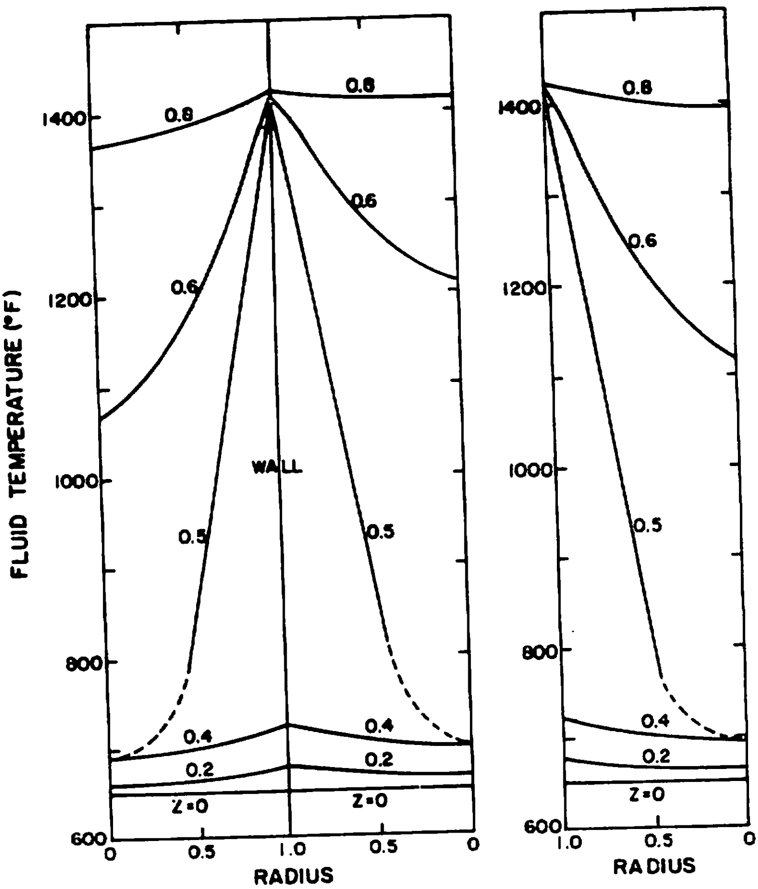

Figure 6. Radial temperature profiles in multiple channels, T_{inlet} = *650°F*

channel. Here the effect of different velocities in different channels is minimal.

The effect of different velocities may be more pronounced for a case which has "lit off", and this is examined in Figure 5. The nomenclature is the same as in Figure 4 and we see that even at light off the multiple channel with different velocities gives results which are almost identical to the two channels with the same average velocity. The temperature profiles in the radial direction are shown in Figure 6. For the multiple channel case, with different velocities, the fluid temperature profiles are different but with the same wall temperature (since that is shared); despite that discrepancy the overall effects are very similar to the average case shown at the right.

We thus conclude that the effect of different velocities in adjacent channels is not great. This conclusion was reached, however, for a model which excludes axial conduction of heat. However, we have made calculations for three different types of transverse conduction: different geometries of the duct (7), peripheral conduction around the duct (5), and now different velocities in adjacent ducts. In the first two cases the inclusion or exclusion of axial conduction had little effect on the qualitative conclusion as to the importance of the effect, and there is no reason to assume that the multiple channel analysis will be any different. The inclusion of axial conduction will have a dramatic effect on the hysteresis but that hysteresis should not be greatly affected by any of the three transverse phenomena: different geometries, peripherical conduction, or multiple channels with different velocities. We thus conclude that analyzing a single channel suffices.

3. Conclusions

The hysteresis of a wall-catalyzed reactor for oxidizing carbon monoxide, as illustrated in Figures 1 and 2, is greatly affected by axial conduction of heat in the solid. This can be influenced by changing either the wall material or the wall thickness. Having different velocities in adjacent channels does not change the results: they are very similar to those for a single channel under the average conditions. The theoretical model displays hysteresis of the same qualitative features as experiments: the hysteresis is enhanced by higher CO concentrations, lower velocities, and higher solid thermal conductivity. The geometry of the duct has minimal impact.

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