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Temperature excursions in packed bed reactors with an axial variation of catalyst activity

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Abstract

Research appears to be growing on a type of structured reactor in which catalyst activity varies or in which different catalysts are arranged in the reactant flow direction. These reactors offer improved selectivity for some classes of complex reactions under non-isothermal conditions or when composition modulation is employed. Our examination of the rather extreme case of alternating layers of inert and active catalyst indicate that this reactor structure accentuates wrong-way temperature excursions after a step-change in temperature and amplifies periodic input temperature disturbances. Experiments used a near adiabatic 2.5 cm diameter reactor packed with 3 mm particles of 0.2 wt.% Pt/Al_2O_3. Inert layers were just the 3 mm alumina particles. Step and triangular wave inputs of constant amplitude were used. Temperature response in the bed was measured by an axial array of computer-monitored thermocouples. Measurements were compared to those made on a homogeneous mixture of catalyst and support under identical input conditions. Simulation studies show that accentuation of the temperature excursions depends on layer thickness. Even first-order reaction kinetics show accentuated temperature excursions when layered beds are used. © 2001 Published by Elsevier Science B.V.

Keywords: Temperature excursions; Layered catalyst beds; Wrong-way behavior; Differential flow instability; Temperature perturbations; Packed bed reactor

1. Introduction

This contribution considers a special class of structured beds in which catalyst activity varies in the reactant flow direction or different catalysts are layered in a bed. Layers of different catalysts may improve selectivity for some classes of complex reactions under non-isothermal conditions [3,4]. They can provide higher conversion with reactors exposed to composition modulation [1,2], or with highly exothermic reaction, the region of stability can be extended [5]. Variation of catalyst activity axially can be arranged by temperature control or by changing the loading of active metal on the support. It also arises through on-stream deactivation. Because of concentration change and temperature differences, it is unlikely that packed catalysts will deactivate uniformly. Indeed, we have recently shown that if catalyst deactivation is kinetically controlled and the primary reaction exhibits ignition behavior, a zone of deactivated catalyst will form downstream of the entrance to the packed bed, but well forward of the end of the bed [9]. Thus, a zone of active catalyst followed by a zone of completely deactivated catalyst, followed in turn by active catalyst,

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is formed. Indeed, reactors with axial variation of catalyst activity may be common. We will demonstrate in what follows that abrupt variations in catalyst activity can result in temperature excursions that are much larger than those in beds of uniform activity when temperature disturbances occur upstream of a reactor.

Under appropriate circumstances, disturbances introduced at the inlet of a reactor can be amplified in the region of a reaction front. The physical and chemical interactions that lead to amplification have been referred to as differential flow instability (DFI) by one of us and have been rigorously described in several papers [6–10]. Amplification can be large, reaching 5–10-fold the inlet variation.

Yakhnin and Menzinger [9,10] showed by simulation that a band of completely inactive catalyst in the middle of a catalyst bed accentuates DFI and wrong-way behavior. Our objective in this study was to confirm experimentally greater temperature excursion amplitude for DFI when there is catalyst activity inhomogeneity in a packed bed. Because it is difficult to control catalyst deactivation so as to create zones of low and high activity or to set operating conditions to place a reaction front right after a catalyst layer of lower activity, we assembled the reactor packing into layers of catalyst separated by layers of an inactive solid. This differs, of course, from the simulation study of Yakhnin and Menzinger. The effect of layer depth was investigated by simulation using different kinetic models.

2. Experimental

Oxidation of carbon monoxide (CO) with oxygen in a nitrogen carrier gas over a platinum catalyst was chosen as the test reaction. This reaction is highly exothermic and strongly inhibited by CO. As a consequence, the reaction zone is shallow and exhibits a steep temperature gradient at steady state.

Catalyst was a 3 mm diameter, 0.2 wt.% Pt on a γ-alumina with eggshell impregnation and was obtained from Engelhard. The catalyst was used as received. Inert zones in the bed used the γ-alumina support alone. Layers were created by adding weighed amounts of catalyst and then alumina support to the reactor until the bed was filled. Choice of the amount of catalyst or inert determined the widths of the active and inactive zone layers. Intimate mixing of catalyst and support and then filling the bed reactor created a bed of uniform activity. Total amount of catalyst in the segregated and unsegregated bed was the same.

Experiments were carried out in a tubular packed-bed reactor constructed of two concentric stainless steel tubes of different diameters (see Fig. 1). The inner tube with an internal diameter of 25 mm contained the catalyst bed while the outer tube with a diameter of 76 mm formed an empty annulus. Tube lengths were 1020 mm. The annulus was maintained under a vacuum of 10^{-7} Torr to reduce heat loss and minimize radial temperature gradients. Thermal inertia and feedback through the wall of the reactor were controlled by using stainless steel and an internal wall thickness of 0.5 mm. To reduce end effects, the catalyst bed was placed 254 mm away from the top and bottom of the reactor where it rested on 4 mm diameter alumina particles. The section containing the catalyst bed was insulated by a layer of Kaowool$^{\text{TM}}$ covering the outer concentric tube.

Feed to the system was synthesized from cylinders of oxygen, nitrogen, and CO. Each of these gases passed through individual mass flow controllers, mixed in a T-junction and then passed through a bed of Drierite. Thereupon, the gas mixture was heated in a tube wrapped with a heating tape before entering the top of the bed. Voltage imposed on the heating tape was set by a programmable temperature controller.

The measuring system consisted of a set of nine thermocouples placed axially along the center of the reactor tube (Fig. 1b). The first two thermocouples were located in the space above the catalyst bed. One (unlabelled) was the temperature sensor used to control the inlet circuit temperature; beside it, thermocouple TC1 recorded the temperature of the feed gas to the reactor. The next thermocouple (TC2) was located in the first layer of particles in the bed. TC2 was the first of seven (TC2–TC8), located 7.6 cm apart along the bed axis. The final thermocouple was situated 5.1 cm above the bottom of the catalyst bed. Individual thermocouples were bundled together to form an imperfect cone of diameter 0.95 cm at TC2, tapering to 0.08 cm, the diameter of a thermocouple, at TC8 in order to minimize thermal inertia and feedback. The upper portion of the bundle passed through the cap

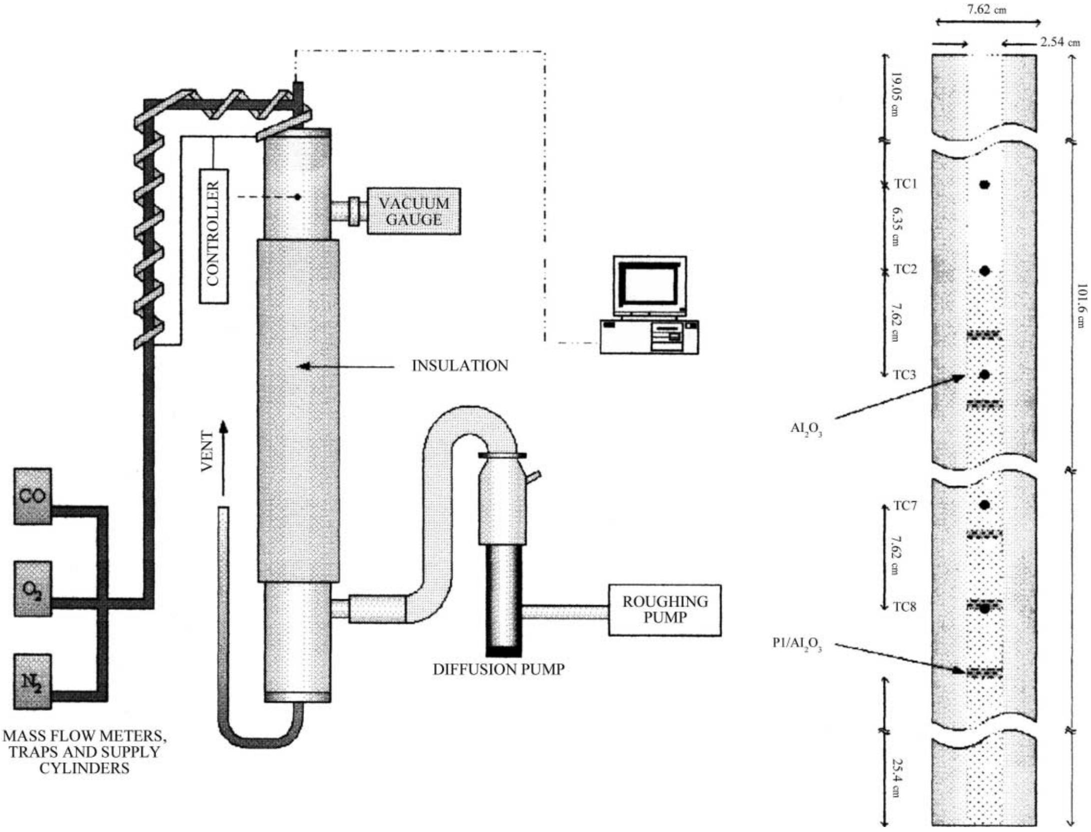

Fig. 1. Overview of the experimental unit showing feed provision, method of inducing the temperature disturbance, the reactor bed with insulation and vacuum system (a); and structure of the segregated bed showing the location of the thermocouples (TC1, TC2, etc.) and Pt catalyst layers separated by inert (alumina) layers (b).

of the 25 mm diameter internal tube. Thermocouples were insulated with a fiberglass sheath and connected to a computer. Thermocouples TC1–TC8 were read at a frequency of 0.5 Hz. Experiments done prior to the study indicated complete conversion of CO when the reaction front ended prior to the reactor outlet. Consequently, the outlet composition from the reactor was not monitored.

The temperature controller was programmed to provide a nearly perfect triangular input wave. The period of these waves could be set from between 60 and 12,000 s. Step-changes could also be generated.

Depth of the inert and catalyst layers in the layered bed was set at 4.6 and 0.51 cm, respectively. These depths were selected from considerations apart from this study and were not varied. Choice of depth resulted in 10 active and 10 inert layers in the reactor. To identify accentuation of temperature excursions in the layered bed, experiments were repeated in a homogeneous bed of catalyst and inert support using the same overall ratio of inert to catalyst used in the segregated bed.

Experiments were conducted by passing nitrogen at a constant flow rate and temperature through the reactor bed until the bed reached the operating temperature. Then, CO and O_2 were admitted. The CO concentration was 0.7 vol.% of the feed gas, while the O_2 concentration was 19.3%. Reactant concentrations were not varied within an experiment. Once steady state was attained, a step- or triangular-wave temperature disturbance was imposed upon the feed gas to the reactor.

3. Experimental results

3.1. Wrong-way behavior

In Fig. 2a, we show wrong-way behavior for a reactor bed packed with alternate layers of inert support and catalyst. In the experiments, the feed temperature starts out at about 145°C and drops progressively by 5°C until the feed temperature measured by thermocouples TC1 and TC2 reaches 130°C some 5000 s later. Experiments discussed later on show that for this system, the reaction is extinguished at 130°C.

Wrong-way behavior is not observed as the inlet temperature changes from 145 to 140°C. After a further drop in the feed temperature to 135°C about 2000 s later, temperature falls significantly at TC3 and TC4. There is also a slight disturbance in the temperatures at TC5, TC6, and TC7, probably caused by an undershoot in the feed temperature that can be seen for TC1 and TC2. Changes at TC3 and TC4 are due to the progression of the reaction zone towards the reactor exit. When the feed temperature falls to 130°C, wrong-way behavior is initiated and temperatures at TC5 through TC8 increase before falling below the feed temperature. Reactor temperature increase after a decrease in inlet temperature is a typical wrong-way behavior. What is noteworthy is that it is not seen for the earlier step-wise temperature decreases. It is explained by the extent of the reaction front from about TC3–TC5 prior to the first temperature drop of 5°C. After this drop, the front moves downstream but because the reaction is complete by TC5, the inlet temperature drop does not raise the amount of reactant reaching TC5 and the thermocouples deeper in the bed. Thus, temperatures do not increase. Instead the temperatures detected at TC5–TC8 decrease, reflecting the lower inlet temperature. The absence of wrong-way behavior at thermocouples within the reaction front, namely TC3 and TC4, is surprising but appears to arise from a chance compensation of the wrong-way temperature rise by downstream movement of the reaction front.

A similar scenario occurs for the second temperature drop to 135°C. Wrong-way behavior amounting to 1–2°C can be seen at TC4 and TC5 despite the signal noise and the overshoot in the inlet temperature change. Both thermocouples are still within the reaction front. There is no wrong-way behavior at TC3 because it is now located before the front. However, when the feed temperature drops to 130°C, the reaction is extinguished and thus the reaction front retreats toward the exit of the reactor, progressively raising reactant concentrations at thermocouples TC5, TC6, TC7 and TC8. Thus we see the wrong-way behavior moving down the bed along with the reaction zone. The increasing peak temperature from TC5 to TC8 is accounted for by a decrease in heat loss from the reactor as the reaction zone passes downstream. The region of high temperature following the reaction front continually decreases.

In Fig. 2b, wrong-way behavior for a homogeneously packed reactor is shown for comparison

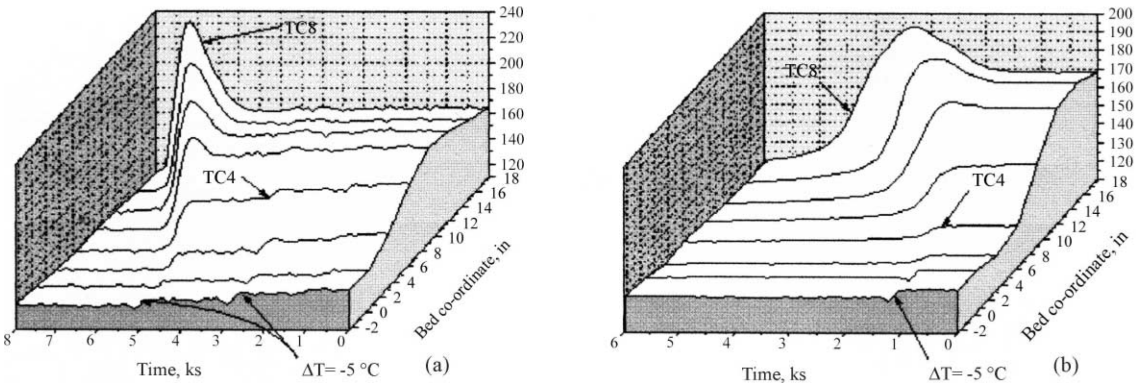

Fig. 2. Wrong-way behavior on successive 5°C step-down changes in feed temperature; (a) segregated bed using 10 layers of 0.2 wt.% Pt on alumina support (average concentration is 0.02 wt.% Pt), (b) homogeneous bed using a mixture of 0.02 wt.% Pt catalyst and alumina support.

purposes. Operating conditions were identical, and the catalyst concentration was equal to the average concentration in the layered bed, i.e., 0.02 wt.%. For both the layered and homogeneous beds, temperature traces following the last drop in temperature show that the reaction zone leaves the reactor after a sufficient length of time. The difference between the peak temperature at TC6 in the layered and homogeneous beds, i.e., the difference in magnitude of the wrong-way behavior, is 30°C. At TC7 it is 28°C and at TC8 it is 40°C. This is a remarkable difference arising only from the arrangement of catalyst in the bed. The explanation for this difference is that in the segregated bed, there is no attenuation of feed concentration in the inert zone, so that the concentration leaving a catalyst-containing zone is transmitted to the next catalyst layer. On the other hand, in the homogeneous reactor, reaction continues between thermocouples, and so the reactant concentration reaching each succeeding thermocouple is reduced.

Numerical studies suggest that if the feed temperature is slowly reduced from one level to another, wrong-way behavior will not be observed. This was tested for the layered bed reactor with a 5°C temperature reduction over 11 h. Experimentally, it is difficult to change temperature at a slower rate than this. Despite the slow change, a wrong-way behavior is observed that is virtually the same as that shown in Fig. 2a. We attribute the presence of wrong-way behavior for very slow temperature change to the ignition–extinction bifurcation that occurs for CO oxidation in the temperature range studied. For the Pt catalyst, the low rate or extinction condition ceases to exist above a specific temperature, whereas the ignited conditions cannot exist below another specific temperature. Consequently, when the reaction is carried out in the bifurcation range, wrong-way behavior is independent of the rate of temperature change.

3.2. Differential flow instability (DFI)

DFI for the layered bed reactor is shown in Fig. 3. The triangular input disturbance is shown by temperature trace for thermocouple TC2 located at the surface of the catalyst bed. Reaction begins after TC3 and the reaction zone extends to between TC5 and TC6 at steady state prior to the inlet disturbance. Once these begin, the zone moves and its range extends from TC3 to TC7. The amplitude near the end of the reaction zone, the largest observed, is given by the temperature trace at TC7. This shows amplitudes of about 35°C compared to an inlet disturbance with an amplitude of

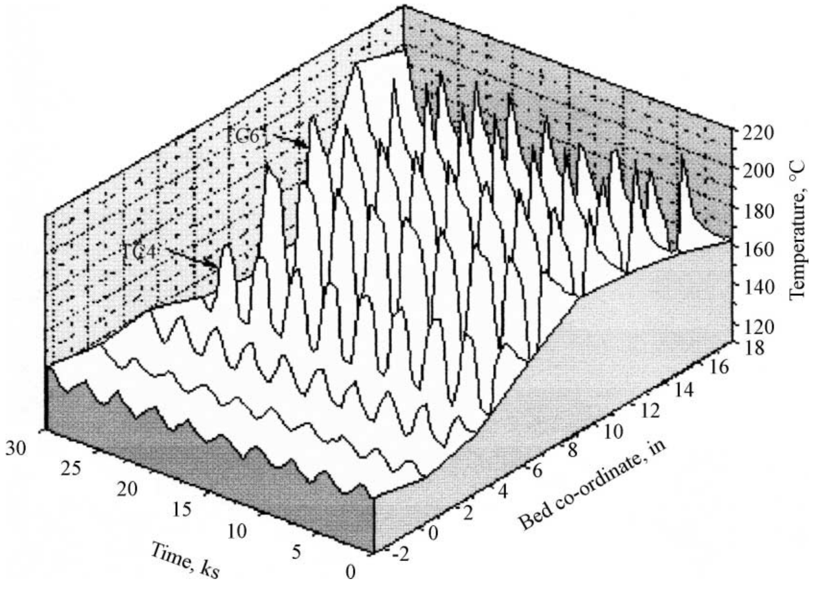

Fig. 3. DFI for the layered bed reactor at a cycle period of 3120 s (52 min). Feed rate and composition as in Fig. 2.

5°C. These large oscillations are attributable to operation around the limit of extinction, that is between ignited and extinguished steady states. Although not illustrated in this figure, the amplitudes at TC7 significantly exceed the maximum temperature variation that would be observed if the reactor were operated at steady temperatures of about 145 and 135°C. The amplitude of excursions at TC4–TC6 are smaller as these thermocouples are located within the reaction zone. The system can sustain oscillations up to a certain inlet temperature perturbation period. If this period is very large, the system will shift to an extinguished state and cannot be re-ignited.

Variations greater than those for the corresponding steady states provide one indication of DFI. Another is a resonance in the response amplitude as frequency changes. A dependence of amplitude on the frequency of the inlet temperature disturbance was observed, but resonance was not found. Fig. 4 illustrates the effect of cycle period or frequency on the variation at thermocouples located in the reaction zone. Once again, the reaction zone extends from TC3 to TC6. It is evident that at TC6, the amplitude of the variations is small for a 20 min cycle period (near time 0) and increases as the period is raised to 40 min. Amplitude increases further when the period goes to 52 min as shown in Fig. 3. Thus, for these operating conditions, close to extinction, we do not observe a classic resonance. As period increases, amplitudes rise to where the period is large enough for extinction to set in so that the system cycles at or below the input amplitude.

Short intervals of steady operation establish the range of variations in steady-state temperatures that can then be compared with variations in cycling temperatures. In Fig. 4, for the layered bed, variation of temperature in excess of maximum steady-state temperatures for thermocouples in the reaction zone is 0°C at TC4, 5 or 6°C at TC5, 9–13°C at TC6 and 9–12°C at TC7 for a cycle period of 2400 s (40 min). If the period drops to 1200 s (20 min), the variation of the temperature in excess of the maximum steady-state temperature drops to 2–4°C at TC5 and 3–6°C at TC6.

Fig. 5 shows the results of cycling and steady-state experiments performed in a homogeneous packed bed of catalyst formed from a mixture of 10% of 0.2 wt.% Pt with 90% of inert giving an overall Pt/inert support ratio of 0.02 wt.%, exactly the same as the layered reactor. Thus, Figs. 4 and 5 compare the effect of bed inhomogeneity on the magnitude of DFI. For the homogeneous bed, the reaction zone begins at TC3 and ends close to TC6. The maximum variations in the temperature at TC5 and TC6 for a cycle period of 2400 s are both about 10°C; temperature variations at TC6 exceed by 8° the steady-state temperature span. The variation, furthermore, increases with the cycle

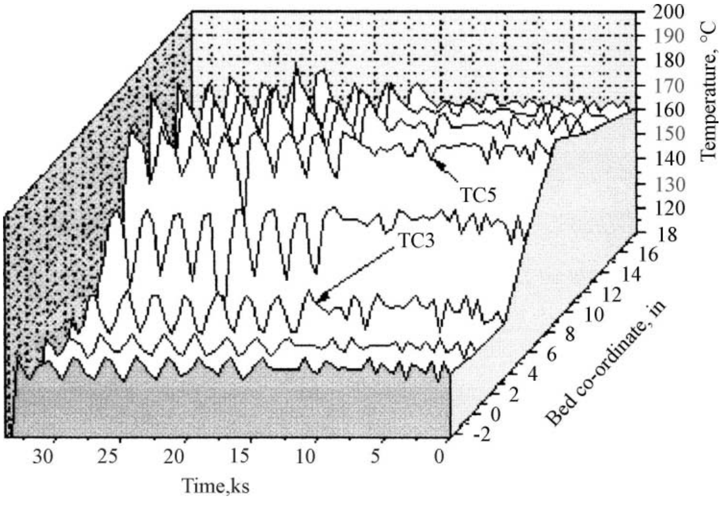

Fig. 4. Effect of cycle period on DFI for cycle periods of 1200, 1600 and 2400 s (20, 28 and 40 min) in the layered bed reactor. Feed rate and composition as in Fig. 3.

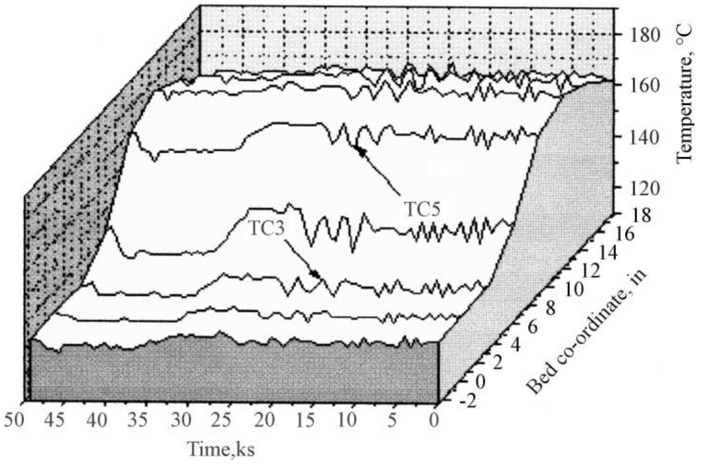

Fig. 5. DFI for homogeneous catalyst bed with mixed catalyst and alumina support at cycle periods of 960, 1440 and 2400 s (16, 24 and 40 min). Feed rate and composition as in Fig. 3.

period, just as in Fig. 4. At a cycle period of 1200 s, the variation at TC5 and TC6 are 9 and 12°C, respectively. The variation is largest at a period of 2400 s, being 25°C at TC6 in Fig. 4, while it is 10°C at TC6 in Fig. 5. Input variations were the same. The layered bed results in larger temperature variation absolutely as well as larger excesses over the steady-state temperature differences.

Careful inspection of both Figs. 4 and 5 indicates that large variations in temperature occurred at TC4. At this position, the reaction zone actually moves back and forth across TC4 as the feed temperature changes. This is quite evident in Fig. 5 from a steady-state temperature difference that exceeds the amplitude at TC4 under cycling.

Experimental reproducibility was examined for the homogeneous bed by replicating the experiment shown in Fig. 5 twice more 5 days apart. Replicates were virtually identical except that the temperature trace for TC4 was shifted lower by about 10–15°C. However, measurements for TC4 showed that the amplitude under cycling was still less than the difference in the temperatures corresponding to the two steady states at the extremes of the feed temperature. Consequently, the downward shift was caused by a slight displacement of the reaction front. As observed in many experiments, the location of this front is extremely sensitive to operating conditions; a minute change in a variable can shift the zone position by several centimeters.

A question of generality of these experimental observations arises because of the well-documented complex kinetics of CO oxidation. Adsorbed CO inhibits the dissociation of O_2 on Pt. This influences kinetics when the CO/O_2 mole ratio is greater than about 0.5. Inhibition leads to ignition and extinction behavior that may change the magnitude of temperature excursions for both layered and homogeneously mixed beds. Rather than repeating the experiments for an exothermic system without reactant inhibition, we examined the generality question using simulation.

4. Modeling and simulation

Our objective in modeling was to explore the effect of the kinetic model on the accentuation of temperature excursions in layered beds and how accentuation changes with the depth of the inert and catalyst layers.

A one-dimensional, pseudo-homogeneous, adiabatic packed-bed reactor was assumed with an exothermic, catalytic reaction, A → B, that is described by a first-order kinetic expression. The resulting set of two partial differential equations has been given many times in the literature (see, e.g., [7]). When the heat and mass balances are made dimensionless by introducing reactor length and space–time, the model has six parameters. The Dankwerts boundary conditions were used with constant O_2 and CO concentration but with time-varying inlet temperature. Both empty-bed and steady-state initial conditions were employed.

The model was applied to each layer using the output of the previous layer as input. FlexPDE was employed for integration. Model parameters were: Peclet No. for mass = 300, for heat = 50, Damköhler No. = 0.4, Lewis No. = 2000, Arrhenius function = 16 and the thermicity = 0.5. This set gave a response that resembled the experimental results with CO oxidation over the 0.2 wt.% Pt/Al_2O_3 catalyst.

To examine the effect of layer depth, five configurations were considered with the same amount of catalyst and inert in each configuration. Each configuration began with a layer of catalyst at the reactor entrance, followed by a layer of identical depth but consisting of inert of the same bulk density and particle size. The two layers constituted a pair. In our study, reactors of identical length were subdivided into different numbers of identical layer pairs, i.e., 1, 2, 4, 8 and ∞ (the last indicating intimately mixed catalyst and inert particles in a 50:50 mass ratio to form a homogeneous bed).

Axial temperature profiles at steady-state were determined for each configuration. The reaction zone is the steepest and the front is located at $\xi = 0.3$ for the single pair 1: complete separation between catalyst and inert where the first half of the reactor is packed with catalyst and the rest with alumina support. Increasing the number of layers (reducing segregation) spreads out the reaction zone because of reduced thermal feedback from the separation provided by the inert layer. Consequently, the reaction front moves further down the bed as the number of pairs increases. The shallowest temperature profile occurs when the bed is homogeneously mixed. Complete conversion was obtained in all cases as indicated by a temperature plateau at the reactor exit.

4.1. Wrong-way behavior

Simulation of a step-decrease of inlet temperature for a packed-bed reactor initially at steady state caused a wrong-way response, the magnitude of which depended on bed structure. Fig. 6 shows the temperature overshoot as gain, namely dimensionless overshoot measured from the initial steady state divided by dimensionless step-decrease of temperature. Concentration waves were also simulated, but space

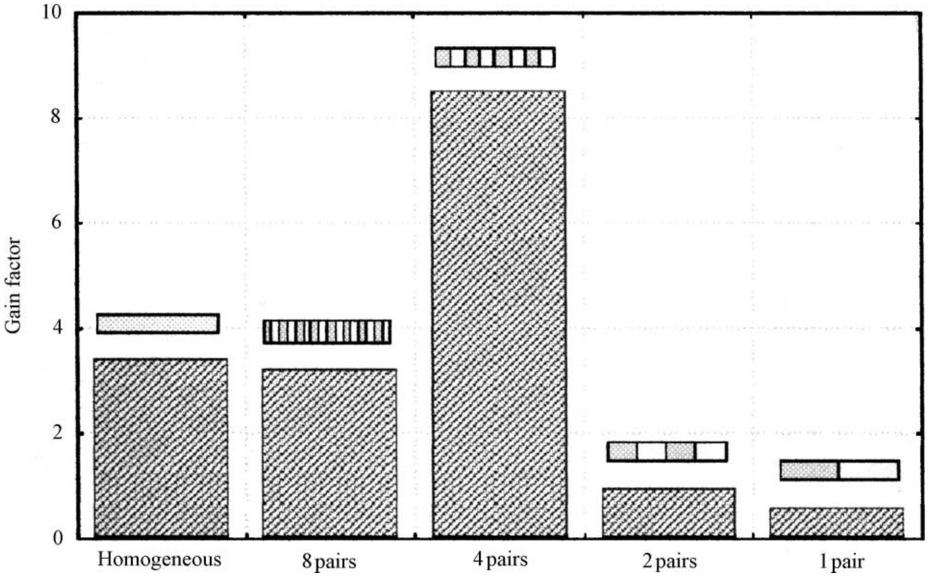

Fig. 6. Wrong-way temperature responses for different bed structures for an input temperature step change with dimensionless amplitude: $a_0 = 0.005$.

restrictions prohibits showing them. For complete segregation, temperature rise during the transient is relatively small, because the steep temperature gradient at the front or the narrow reaction zone results in high heat dispersion that dissipates energy from the reaction zone to neighboring regions during the transient. An increase in the gain factor was observed for two pairs of layers, because the reaction zone begins in the first catalyst layer and extends over an inert layer, increasing its breath. This allows build-up of a larger concentration wave than when the front is entirely in the first layer. The gain factor is the largest for four layer pairs. In this case, the steady-state reaction zone spreads over the first three catalyst layers. This permits the build-up of an even larger concentration wave after a step disturbance. The gain drops for eight pairs because the bed approaches the homogeneously mixed case. Formation of a concentration wave is limited in the initial bed layers because of the low temperatures. It fails to grow substantially in succeeding catalyst layers because of reactant consumption.

4.2. *Resonance behavior*

Simulation of a sinusoidal inlet temperature fluctuation on reactors resulted in amplitude gains. These gains were largest in the region of the reaction front and all exceeded 1 except at the highest frequencies used. Fig. 7 plots the maximum gain observed for two dimensionless amplitudes of the fluctuation versus dimensionless frequency. Resonance with input frequency is seen clearly. This combined with gains greater than 1 indicate DFI.

Amplification is very small for complete segregation for both input amplitudes. When the catalyst is divided into two layer pairs, the maximum gain at the resonant frequency increases from 2.1 to 2.75 for $a_0 = 0.01$. Changing the bed structure to four paired layers of catalyst and inert boosts the maximum to 9.2 and skews the resonance curve significantly towards low frequencies. Resonance frequency thus correlates with bed structure. This was expected because temperature and concentration waves travel at different velocities between catalyst layers. Highest gains arise when the waves reach the catalyst layer π radians out of phase. Phase lags for layer depth depends on frequency. The resonance frequency for 4 layer pairs is about 0.0005, while with eight pairs it is somewhat greater than 0.001. Noting that characteristic times associated with resonance are related to the reciprocal of the resonance frequency, the dimensionless characteristic time for four layer pairs is 2000 while that for eight is 1000. Layer depth for the two cases also differ by a factor of 2. Fig. 7a and b shows that the amplitude of the inlet perturbation changes the dimensionless resonance frequency for 4 layer pairs slightly from 0.0004 to 0.0006. Amplitude also seems to affect the layer depth giving the largest gain. At $a_0 = 0.01$, 4 layer pairs shows the highest gain, whereas at $a_0 = 0.005$, it is eight pairs with a shallower layer depth. The maximum gain observed was 9.2.

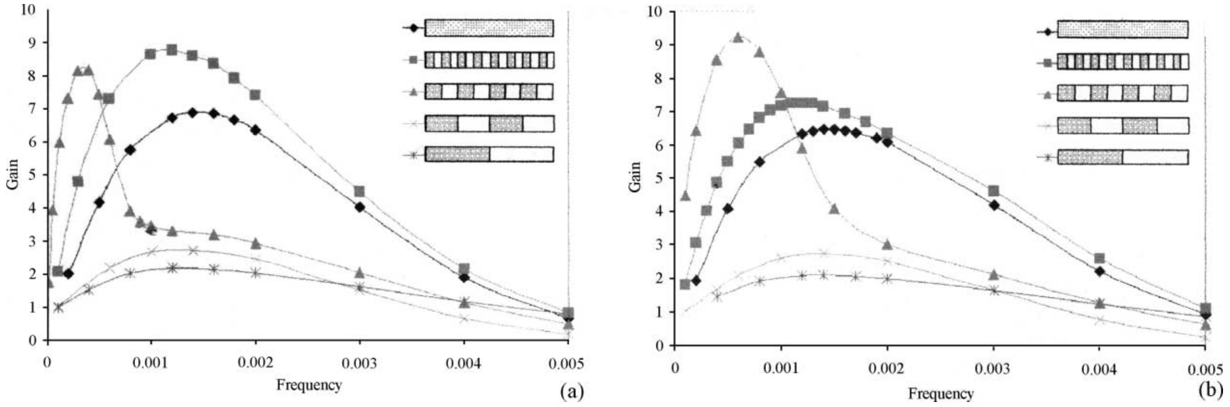

Fig. 7. Resonance temperature responses for different bed structures for dimensionless amplitudes: (a) $a_0 = 0.005$; (b) $a_0 = 0.01$.

Fig. 7 confirms that by eight pairs of layers, the segregated bed approaches the limit of a homogeneously mixed bed. Once the overall segregation is reduced from the extreme of a two-part bed, resonance shifts to lower frequencies and a much greater gain factor, reflecting the complex interaction of the concentration wave amplitude and the phase lag, both of which change with bed structure.

When a model with inhibition kinetics was employed for the bed structure studied experimentally assuming just a single layer of catalyst particle, larger temperature excursions were not observed; so there does appear to be a dependence of excursions on the kinetic model. Presumably, gains and resonance frequencies are also affected by the model used.

5. Discussion

Our experimental observations demonstrate that segregating catalyst into alternate layers of active and inactive material accentuates wrong-way behavior and DFI. It is reasonable, therefore, to conclude that inhomogeneity in a catalyst bed caused by catalyst distribution or by catalyst deactivation can lead to much larger disturbance amplifications or temperature excursions following step-changes in the feed condition than would be encountered for beds with homogeneous catalyst activity. Accentuation of temperature excursion was found in simulations for a system that does not exhibit reactant inhibition and rate bifurcation. Thus, the phenomenon investigated is a general one. Simulations demonstrate that bed structure has an important effect on temperature excursions which are smaller with maximum bed segregation and for the homogeneous bed. An intermediate degree of segregation can result in remarkably large excursions.

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