

# Transient Modeling of a Catalytic Converter to Reduce Nitric Oxide in Automobile Exhaust

Mathematical models are developed to study the catalytic reduction of nitric oxide contained in automobile exhaust in which the temperature, flow rate, and concentrations of various species vary widely with time. The quasi-static approximation is compared to the fully dynamic model. In the quasi-static model all processes are steady state except for the solid temperature and inlet conditions. Suggestions are given for deciding a priori if the quasi-static model is appropriate. Suggestions are also given for integrating the quasi-static equations in order to minimize errors compared to the dynamic model. The performance of three different catalysts is examined with the mathematical model, when the inlet conditions correspond to typical values of temperature, flow rate, and concentration when the automobile is operated according to the Federal Test Procedure.

**NOBLE B. FERGUSON**  
and  
**BRUCE A. FINLAYSON**

Department of Chemical Engineering  
University of Washington  
Seattle, Washington 98195

## SCOPE

The exhaust gas from an automobile contains nitric oxide which must be reduced to nitrogen in order to meet Federal pollution standards. The problem is complicated because the temperature, flow rate, and concentrations of different species vary in time over wide ranges. We develop transient mathematical models for a catalytic muffler applicable to this situation. The mathematical model is then used to examine the performance of three different catalysts.

The inlet conditions correspond to those encountered when an automobile is operated in the Federal Test Procedure. The automobile begins cold, and as it operates the catalyst bed gradually warms up. The one feature of interest is to compare catalysts having different properties so that they warm up at different rates. Furthermore, as the automobile changes driving modes the exhaust properties (or their time rates of change) may change discontinuously.

The mathematical models employ a mixing-cell model for the packed bed and consider the reduction of nitric oxide with two catalytic reactions. The reaction rate of nitric oxide with carbon monoxide is closely coupled with the reaction rate of nitric oxide with hydrogen because nitric oxide is reacted essentially completely inside the catalyst. Thus one new feature of this model is the inability to construct plots of effectiveness factor vs. Thiele modulus a priori, due to the coupling of the two reaction

rates. Rather, the problem of diffusion and reaction inside the catalyst pellet must be solved at each time for each mixing cell, and the orthogonal collocation method is used to do this efficiently.

Three models are developed. The main model employs the quasi-static approximation which recognizes that the time response of the system is governed by the thermal response of the packing. All other processes are assumed to occur so fast that they are essentially steady state. A dynamic model is also used to test the conditions under which the quasi-static model is inappropriate. In the dynamic model all processes are allowed to be transient. Due to the wide difference in time constants for the system, the dynamic model leads to stiff ordinary differential equations, which necessitate small integration time steps. The comparison of the two models is interesting because the quasi-static model is frequently used but seldom tested. An even simpler model results when, in the quasi-static model, the reaction rate expression is assumed with a pseudo first order reaction rate constant.

The question of when it is possible to use the quasi-static model is an important one. Guidelines to help answer this question are obtained by summarizing available literature. The guidelines are based on ratios of time constants for various heat and mass transfer phenomena, such as residence time in the reactor, transfer between the fluid and catalyst, and diffusion within the catalyst.

## CONCLUSION AND SIGNIFICANCE

A quasi-static model was developed for the reduction of nitric oxide by carbon monoxide and hydrogen in

automobile exhaust. For this situation the relevant transport processes are found to be the transient heat transfer across the film between the fluid and catalyst particle and internal diffusion inside the catalyst. Less important factors are axial and radial dispersion, external diffusion, and the remaining transient effects. A quasi-static model was

Correspondence concerning this paper should be addressed to B. A. Finlayson. N. B. Ferguson is with Getty Oil Company, Bakersfield, California.

found to be appropriate when the conditions listed in Table 1 apply.

Calculations were made using the quasi-static model for three catalysts having different properties. The catalyst chosen for fastest warm-up achieves significantly better conversion of nitric oxide when the catalyst bed is warming up, but a smaller conversion results when the catalyst bed is already hot. Due to the lower inlet nitric oxide concentrations during the early times, the two catalysts perform about equally over the entire time period. A catalyst having more internal diffusion resistance proved to be less suitable.

Results of calculations made with the quasi-static model are comparable to the results obtained with the more complex dynamic model provided the following guidelines are used for the time step in the numerical integration:

1. It should be small enough that there are several time steps between discontinuities in the inlet conditions;
2. It should be small enough that there are several time steps between a discontinuity in the inlet conditions and the time the solution is examined;
3. The time period between successive discontinuities

in the inlet conditions should be divided into an integral number of time steps.

The simplest model gave results within 5% of those of the quasi-static model. For preliminary design the simple model is adequate and it is the fastest model.

The dynamic model is very time-consuming due to the very different time constants of the transient processes. To solve the transient problem the improved Euler method was used and the resulting calculations took 40 times real time on a CDC 6400 computer. Although the dynamic model would seldom be used, if it were necessary the orthogonal collocation method is an efficient method to use.

The orthogonal collocation method proved useful for the quasi-static model where two coupled effectiveness factor problems are solved for each mixing cell and at each time. Computation time was 1/7 of real time.

These conclusions can be used in other situations with similar characteristics. The most important characteristic of this system is that there are only small temperature effects due to chemical reaction and the reaction rate is pseudo first order, with a time varying reaction rate constant.

## REVIEW OF LITERATURE

Automobile exhaust contains various oxides of nitrogen which must be eliminated to meet future Federal pollution standards. Here we lump all oxides of nitrogen as nitric oxide since that is the predominant component. The nitric oxide would be reduced to nitrogen by reaction with either carbon monoxide or hydrogen. Since the automobile operates at various speeds, the temperature and concentration of pollutants vary in time. Thus a catalytic converter to react the nitric oxides operates in a transient mode. A transient mode of particular interest is the Federal Test Procedure\* [U.S. Federal Register, 1970], since pollution standards are based on it. We present a mathematical model for a nitric oxide catalytic converter when the exhaust gases have time-varying properties typical of the Federal Test Procedure. The objective is to show which phenomena must be included in the mathematical model, with particular attention focused on the quasi static approximation. Under this simplification all processes are steady state except for the solid temperature and inlet conditions. Suggestions are given for integrating the quasi-static equation in order to minimize errors compared to the dynamic model.

Previous mathematical models for catalytic mufflers have concentrated on the oxidation of carbon monoxide and various hydrocarbons since the earliest pollution standards applied to those species. Kuo et al. (1971) developed a cell model for the oxidation of these species and applied it to transient exhaust which would be typical of an automobile operating in the Federal Test Procedure mode. Harned (1972) developed a plug flow model for the same situation and also illustrated how the steady state results depended on various parameters. In each of these models the reactions were coupled as follows. In Kuo et al. (1971) the hydrocarbons were divided into two groups—

faster and slower reacting groups. Combined with carbon monoxide there were thus three independent species. The rate of reaction of each of these was determined using an effectiveness factor plot for each reaction. Since the reactions are coupled by means of the concentration of oxygen, but oxygen is in great excess, it was possible to separate the reactions and assume that the effectiveness factor plot for one reaction was not influenced by the extent of the other reactions. Harned (1972) considered carbon monoxide and propylene only and assumed that the conversion of propylene was the same as the conversion of carbon monoxide since both reactions light off at about the same temperature. Thus again the two reactions can be separated. In the application to nitric oxide reduction we use a cell model, following Kuo et al. (1971), due to the very short reactor length. Nitric oxide is reduced with both carbon monoxide and hydrogen, all of which are present in the exhaust. However, the species appearing in both reaction rates is now nitric oxide, which is reacted essentially to completion inside the catalyst. The effectiveness factor for the nitric oxide-hydrogen reaction depends on the extent of the nitric oxide-carbon monoxide reaction and vice versa. Thus the two effectiveness factor plots cannot be prepared a priori, and the actual rate of reaction must be computed in the model by solving for the diffusion and reaction in the catalyst. This greatly increases the computation time because two two-point boundary value problems must be solved for each mixing cell and at each time rather than two simple algebraic calculations. The orthogonal collocation method is shown to be an efficient means for tackling such problems.

An important simplification results if one makes the quasi-static approximation. The usual approximation is to neglect the accumulation or hold up of mass in the catalyst particle and the accumulation or hold up of mass and energy in the voids of the beds. This is done by setting to zero the appropriate time derivatives in the mass and energy balances. This was done by Kuo et al. (1971) and Harned (1972) in their models for oxidation of carbon

\* Here we use an older testing mode because of the availability of data for it. See Huls (1973) for a summary of the changing testing methods.

monoxide in catalytic mufflers. The justification for this is the same as discussed below for the nitric oxide reactor.

Consider first the accumulation term in the energy balance. The volumetric ratio of heat capacities

$$C_r = \frac{\epsilon(\rho C_p)_f}{(1 - \epsilon)(\rho C_p)_s} \quad (1)$$

is the parameter determining if the accumulation term can be neglected in the energy balance. It is also the ratio of the velocity of thermal wave to fluid velocity (Crider and Foss, 1966). Tinkler and Lamb (1965) and Crider and Foss (1966) did not make this quasi-static approximation for homogeneous reactions in a liquid flowing past inert packings. Both papers compared the dynamic calculations to experiments and found that the thermal capacity of both the solid and liquid were important parameters in the calculations.  $C_r$  was 0.73 and 1.32, respectively. Vardi and Biller (1968) studied the transient thermal response of a packed bed simulating a catalytic muffler. They found calculations using the quasi-static approximations agreed with experiment for a case with  $C_r = 0.004$ . Hoiberg et al. (1971) studied the dynamic behavior of a hydrogen-oxygen reactor and the experiments agreed with calculations made using a quasi-static model. Here the thermal time constant was 1 s, and the residence time was 0.6 s, so that the time constants are too close to say one process is fast compared to the other. However,  $C_r = 0.0013$ , so that they proved with a  $C_r$  this small the quasi-static assumptions are valid. Waede Hansen et al. (1971) present results of calculations using two models. One model is a fully dynamic model and the other neglects the accumulation terms in the particle mass balance and assumes that there is no temperature drop across the particle. In the second model the method of characteristics is used, moving with the velocity of the thermal wave, rather than the fluid velocity, and one effect of this approximation is essentially to neglect the accumulation of mass in the fluid. The agreement between the two models depended on  $C_r$ : for  $C_r = 0.002$  the two models agreed, so that the quasi-static model was appropriate, whereas when  $C_r = 0.02$  the two models did not agree so that the dynamic model was needed. The dynamic model required 60 times as much computation time. Thus we conclude that if  $C_r$  is less than 0.002 the quasi-static model is appropriate, whereas if  $C_r \geq 0.02$  the quasi-static model is definitely not appropriate. This result is summarized in Table 1.

Next consider the accumulation of mass in the fluid. If we let  $\tau_4$  be the time constant for heat transfer between the fluid and catalyst (it is defined precisely below) and  $\tau_3$  the residence time, then we propose that  $\tau_4/\tau_3$  be used to decide if the accumulation of mass can be neglected in the fluid mass balance. Large values of this quantity indicate the flow through the reactor is fast compared to the time for temperature change of the catalyst bed.

Sinai and Foss (1970) found good agreement between their calculations and experiments for the dynamic behavior of a homogeneous reaction in a liquid flowing around an inert packing. Since  $C_r$  was 1.17 the accumulation terms were retained in the energy balances. The ratio  $\tau_4/\tau_3$  was 0.09 and the accumulation terms were retained in the mass balances, too. Waede Hansen et al. (1971) compared results from quasi-static and dynamic models and found the accumulation terms needed to be retained when  $\tau_4/\tau_3$  was 0.7, whereas for a ratio of 7 the quasi-static model was appropriate. Thus we take  $\tau_4/\tau_3 > 7$  as sufficient justification to neglect the accumulation of mass in the fluid.

If  $\tau_1$  is the time constant for mass diffusion inside the catalyst particle, then we use the ratio  $\tau_4/\tau_1$  to determine

TABLE 1. JUSTIFICATION FOR ASSUMPTIONS IN QUASI-STATIC MODEL

Criterion	Assumption	Typical values
$\frac{\tau_4}{\tau_1} > 1$	Neglect accumulation term in particle mass balance	50
$\frac{\tau_4}{\tau_3} > 7$	Neglect accumulation term in fluid mass balance	500-5000
$C_r < 0.002$	Neglect accumulation term in fluid energy balance	0.0002
$Bi < 3.5$	Lump particle energy balance	0.8

if the accumulation terms can be neglected in the particle mass balance. McGreavy and Thornton (1970) have compared calculations which retained and neglected this term. They concluded that the mass hold-up in the catalyst particle was negligible since in transients the concentration profile changes very rapidly to a pseudo steady state profile, which depends only on the instantaneous temperature profile. Waede Hansen et al. (1971) found that when this parameter was 1.3 the dynamic model agreed with the quasi-static model for predicting the transient temperature profile in the bed, but with a value of 0.13 the peak temperature predicted by the quasi-static model was considerably in error. McGreavy and Thornton (1971) found that the quasi-static model was appropriate when  $\tau_4/\tau_1 = 20$ , while Waede Hansen (1973) used the fast model calculation scheme (implying the quasi-static model was not correct) when this parameter was 0.8. Thus, from the evidence to date, it appears that if  $\tau_4/\tau_1$  is greater than one the quasi-static model is appropriate.

The consensus of the results is summarized in Table 1. They suggest that the quasi-static model is appropriate when the time constants are widely different, and  $C_r$  is small, and this conclusion is supported by the results given below. It is also clear that there may be bizarre behavior [such as the transient particle calculations by Lee and Luss (1970) which gave rise to a limit cycle] which would make a quasi-static model inappropriate even though the time constants are widely different.

A number of other publications have used the quasi-static approximation as an eminently reasonable assumption, but without testing it. Liu and Amundson (1962) made such assumptions in their transient model for a reactor with a steep thermal gradient. In their case the various time constants gave  $\tau_4/\tau_1 = 1100$ ,  $\tau_4/\tau_3 = 140$  and  $C_r = 0.0008$ , which suggest that the quasi-static approximation is valid. Many extensions of this work have made the same assumptions for the same reason: Liu et al. (1963) (nonadiabatic reactor), Vanderveen et al. (1968) (coupling of heat and mass transfer between adjacent cells), Ervin and Luss (1970) (effect of fouling), and Eigenberger (1972) (axial conduction in the solid, catalyst phase). Kardos and Stevens (1971) also made these assumptions for a system with  $\tau_4/\tau_1 = 600$ ,  $\tau_4/\tau_3 = 1000$ .

There have been a few dynamic model calculations leaving in all the accumulation time-derivative terms: cell models—Batke et al. [1957], Deans and Lapidus (1960),  $C_r = 0.7$ , McGuire and Lapidus (1965),  $C_r = 0.5$ ; plug flow models—Feick and Quon (1970),  $C_r = 0.5$ , Waede Hansen et al. (1971),  $C_r = 0.02$ , and Stewart and Sørensen (1972),  $C_r = 0.0002$ . Liu and Amundson (1963) neglected the accumulation terms for the fluid mass balance and fluid and particle energy balance. They included axial dispersion in the model, and when this is included the method of characteristics does not lead to a

simplification of the equations when the fluid accumulation terms are ignored. In order to get around the problem of stiff equations resulting from the very different time constants, an implicit finite difference method was used. Thus, when axial dispersion is included, one might as well leave in the fluid accumulation terms and use an implicit method. Brian et al. (1965) kept the accumulation terms in the energy balances only in their simulation of an ammonia synthesis reactor, but they did not permit a heat transfer resistance between the fluid and particle—that is, the fluid and particle were at the same temperature. Turner (1967) devised a method of measuring the heat transfer coefficient and thermal conductivity of particles. In the computed test cases all accumulation terms were retained even though the time constants gave  $\tau_4/\tau_3 = 1800$ ,  $C_r = 0.0006$ , and the time constant for heat transfer inside the particle was 3 times  $\tau_4$ . These dynamic model calculations were done without comparison to experimental results or other calculations so that the effect of possible simplifying assumptions cannot be assessed. Waede Hansen (1973) also made computational comparisons of a quasi-static and fully dynamic model. His simulation employed a fast mode calculation (dynamic model) for short periods of time, while the rest of the calculation was done with a slow mode calculation (quasi-static model). For a reactor with  $\tau_4/\tau_1 = 6.4$ ,  $\tau_4/\tau_3 = 0.8$ , and  $C_r = 0.0005$  the fast mode calculation was needed only a very small portion of the time. He did not compare to results neglecting the fast mode altogether.

Several authors have obtained good comparison between experimental results and transient calculations which retained all accumulation terms even though the time constants might suggest simpler models. Goss and Turner (1971) had  $C_r = 0.0006$  and the time constant for heat transfer to the particle was 700 times the residence time in their dynamic method of measuring the particle thermal conductivity. Vortmeyer and Jahnle (1972) modeled a reactor with no separate particle problem and retained the accumulation of mass in the fluid even though the time constant for heat transfer was 500 times that for mass transfer. Good agreement was obtained with experiment. Benham and Denny (1972) studied a single catalyst pellet and retained all the time derivatives when the Lewis number was about 500. These three studies, of course, do not indicate that the quasi-static model is inappropriate—just that the fully dynamic model compares well with experiment.

Another simplification that is often made in transient studies is to lump all the heat transfer resistance between the particle and fluid at the boundary between the catalyst and fluid. Steady state, plug flow reactor studies give guidance to the reasonableness of such a procedure since the only difference in the equations is a diffusion operator for a cylindrical domain (reactor) in place of a diffusion operator for a spherical domain (particle). Those studies, summarized by Finlayson (1971), show that a lumped parameter model is appropriate if the Biot number  $h_w R/k_{e,bed}$  is small (say less than 3) and a one-term orthogonal collocation solution gives a means for evaluating an overall heat transfer coefficient.

$$\frac{1}{U} = \frac{1}{h_w} + \frac{R}{3 k_{e,bed}}$$

For the transient particle problem, Vardi and Biller (1968) and Sinai and Foss (1970) give experimental evidence that such a lumping procedure is valid, appropriately extended to the proper geometry, for cases when  $Bi = h R_p/k_e = 3$  and 1.3, respectively. McCreavy and

Thornton (1971) report calculations with and without the lumping for a case when  $Bi = 2.0$ . They find that the lumping is acceptable in that the model with the lumping predicts the same transient reactor performance as the model without the lumping. Waede Hansen (1971) reports computations for the particle problem only, using several models. The distributed parameter model used a Biot number = 12.5 and the results do not agree with those for the model which lumps the thermal resistance. In the lumped parameter model he used the heat transfer coefficient  $h$  rather than the combined, overall coefficient  $U$ , which for a spherical catalyst and a one-term collocation solution is given by

$$\frac{1}{U} = \frac{1}{h} + \frac{R}{3.5 k_e} \quad (2)$$

If these calculations are repeated using  $U$  in place of  $h$  in the lumped parameter model [M3 of Waede Hansen (1971)] the effective Biot number is  $3.5 Bi/(3.5 + Bi)$ , and here is 2.734. The lumped parameter transient calculations do not agree with the distributed model (M6 of Waede Hansen) so that lumping is not appropriate here. This may be due to the large Biot number (suggesting the primary thermal resistance is in the pellet) or due to the fact that with an effective Biot number of 2.734 the solution exhibits a run-away condition that is not exhibited in the distributed parameter problem. Fortunately, neither condition applies to the nitric oxide converter below. McGuire and Lapidus (1965) compared two models, one lumping both concentration and temperature and the other neither. The two models gave very different transient behavior of the reactor for a case with  $Bi = 27$ , showing that the lumping is not feasible for such large values of  $Bi$ . Rearrangement of Equation (2) gives

$$\frac{h}{U} = 1 + \frac{Bi}{3.5}$$

which gives a rough idea of how important the heat transfer processes inside the catalyst are.

The above guidelines on the Biot number refer to chemical reactors. Elrod (1960) and Butterfield et al. (1967) have developed lumping techniques for heat transfer problems with small Biot numbers. However, Turner (1967) reports on a method to measure both  $h$  and  $k_e$  by using a transient heat transfer experiment. He is able to deduce the value of  $k_e$  for a case with  $Bi$  as small as 1, and a distributed parameter analysis is necessary to deduce  $k_e$ . Handley and Heggs (1969) studied computationally a thermal regeneration problem when the bed is at a constant temperature and the inlet gas temperature is suddenly increased to a new value. The breakthrough curve was calculated with two models—one neglecting particle effects and the other solving for the transient heat transfer in the particle as well as in the fluid. They find the two models agree within 1% over most of the breakthrough curve provided

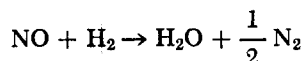
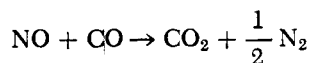
$$A = \frac{3(1 - \epsilon)L k_e}{G_0 C_p R_p^2} > 60 \quad (3)$$

This parameter is the ratio of residence time to the time constant for heat transfer within the particle and does not even contain the heat transfer coefficient. Most of the chemical reactors discussed above have this parameter less than 60, in the range 2 to 10, suggesting the lumping procedure is not valid. However, the correct model may be very problem dependent. When there is chemical reaction the temperature increase in the particle is more affected by the chemical reaction, and if most of the temperature increase occurs across the film surrounding

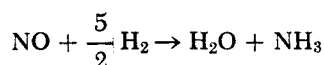
the particle (as happens for small  $Bi$ ) then the lumped parameter model is appropriate.

## DEVELOPMENT OF MATHEMATICAL MODELS

The most important part of the mathematical model is the reaction rate expression. Here we consider the two reactions



and ignore the formation of ammonia by the reaction



The last reaction is important in applications since any ammonia formed would be oxidized back to nitric oxide in the carbon monoxide converter downstream. We have left it out because of the lack of reaction rate data. We used reaction rate expressions of the form

$$r_1 = \frac{k K_{\text{CO}} K_{\text{NO}} p_{\text{CO}} p_{\text{NO}}}{[1 + K_{\text{CO}} p_{\text{CO}} + K_{\text{NO}} p_{\text{NO}}]^2} \quad (4)$$

for the first reaction, with a similar form for the second reaction with  $K_{\text{CO}} \rightarrow K_{\text{H}_2}$ ,  $p_{\text{CO}} \rightarrow p_{\text{H}_2}$ . Parameters were taken from data by Ayen and Ng (1966) for the carbon monoxide reaction on a catalyst of  $\text{BaO}$ ,  $\text{Cr}_2\text{O}_3$ , and  $\text{CuO}$  and by Ayen and Peters (1962) for the hydrogen reaction on a catalyst of  $\text{ZnO}$ ,  $\text{Cr}_2\text{O}_3$ , and  $\text{CuO}$ . These catalysts are different and neither is expected to be finally chosen by automobile manufacturers, but the rate expressions were used as typical examples and because data was available. See Shelef and Kummer (1971) for a summary of available information. Most other data in the literature is in the form of results of tests used to screen different catalysts. The data is thus often incomplete, covers a narrow range of parameters, or results from ill-defined conditions so that extracting reaction rate expressions is difficult at best. The rate data were obtained under conditions without diffusional limitation, but they are used here under other conditions involving a diffusional limitation. The effective diffusivity had to be estimated since the authors were unable to find experimental values for this reaction. The results given below should thus be viewed as representative or typical results rather than as predictions of specific behavior.

The reactor studied below has a volume of 2800  $\text{cm}^3$ , and is packed with 0.32-cm diam. spherical catalyst pellets. In order to maintain a low pressure drop, the cylindrical reactor is made with a large diameter and small length; the  $L/D$  used here is 1/6. The importance of axial dispersion was investigated. Steady state calculations (Ferguson, 1971) indicated that the inclusion of axial dispersion affected the concentration profile slightly near the inlet but very little near the outlet. In addition the criterion developed by Young and Finlayson (1973) predicted an error in reaction rate at the inlet of 0.2% if axial dispersion were left out of the steady state model. For the transient case, the moving reaction zone caused by axial conduction of heat through the particle is expected to be unimportant due to the small changes in temperature in the nitric oxide reactor compared to those found by Vortmeyer and Jahnel (1972). Consequently axial dispersion is relatively unimportant here. The reactor is 14 particle diameters long and is modeled by four mixing cells,

following Wei (1969). We found that the transient results do not depend on the number of mixing cells, presumably because axial dispersion is unimportant. The mixing cell model was used rather than a plug flow model in order to minimize the computation time. For each mixing cell and each time it was necessary to solve a problem of reaction and diffusion of several species in a catalyst particle. Since this calculation is done thousands of times the cumulative effect is time-consuming. If a plug flow model had been used, each mixing cell would have been replaced by several axial positions, thus increasing the computation time.

## Dynamic Model

The reactor is then modeled as a series of mixing cells. When comparing the dynamic model with the quasi-static model we considered the first of these mixing cells. The mass and energy balances on a catalyst particle and the mixing cell give the following dimensionless equations.

$$\tau_1 \frac{\partial \text{NOP}}{\partial t} = \nabla^2 (\text{NOP}) - C_1 (r_1 + r_2) \quad (5)$$

$$\frac{\partial \text{NOP}}{\partial r} = 0 \quad \text{at } r = 0 \quad (6)$$

$$\frac{\partial \text{NOP}}{\partial r} = C_2 [\text{NO} - \text{NOP}] \quad \text{at } r = 1 \quad (7)$$

$$\tau_2 \frac{\partial \text{TP}}{\partial t} = \nabla^2 \text{TP} + C_4 [-\Delta H_1 r_1 - \Delta H_2 r_2] \quad (8)$$

$$\frac{\partial \text{TP}}{\partial r} = 0 \quad \text{at } r = 0 \quad (9)$$

$$\frac{\partial \text{TP}}{\partial r} = Bi [T - \text{TP}] \quad \text{at } r = 1 \quad (10)$$

$$\tau_3 \frac{d\text{NO}}{dt} = \text{NO}_{\text{in}}(t) - \text{NO} + C_5 [\text{NOP}(1, t) - \text{NO}] \quad (11)$$

$$\tau_3 \frac{dT}{dt} = T_{\text{in}}(t) - T + C_6 [\text{TP}(1, t) - T] \quad (12)$$

The terms  $r_1$  and  $r_2$  are the reaction rates for the CO and  $\text{H}_2$  reaction, respectively, and are evaluated using the local concentrations and temperatures,  $\text{NOP}(r, t)$ ,  $\text{TP}(r, t)$ . The time constants for diffusion within the particle, heat transfer within the particle, and the bed residence time are

$$\tau_1 = \epsilon_s R_p^2 / (D_{e, \text{NO}}), \quad \tau_2 = (\rho C_p)_s R_p^2 / k_e \quad (13)$$

$$\tau_3 = \epsilon V / F \quad (14)$$

Equation (5) is a mass balance of NO within the catalyst. Equation (7) is the boundary condition relating the flux within the catalyst to the rate of transfer of NO through the film resistance at the boundary of the catalyst. The parameter  $C_2$  is then a Biot number for mass transfer and depends on the mass transfer coefficient (see Notation). Similar equations are written for carbon monoxide and hydrogen concentrations; the effective diffusivities of carbon monoxide and nitric oxide are assumed to be the same since predictions gave a very small difference; the effective diffusivity of hydrogen is different, however, and that equation has the diffusion operator multiplied by  $C_9 = D_{e, \text{H}_2} / D_{e, \text{NO}}$ , and the boundary conditions used  $C_{10}$  instead of  $C_2$ , which is a Biot number for mass transfer based on coefficients for hydrogen. Equation (8) represents the energy balance within the particle with a bound-

any condition involving the heat transfer coefficient contained in  $Bi$ , the Biot number. Equations (11) and (12) are the nitric oxide and energy balance in the mixing cell, with the first terms on the right-hand sides representing the difference between the inlet and outlet values, and the last term representing the removal of nitric oxide, or energy transfer, by transfer to the catalyst particles. The parameters  $C_5$  and  $C_6$  then include the effects of flow rate and the amount of catalyst in one mixing cell. Similar equations can be written for carbon monoxide and hydrogen with the parameter  $C_5$  changed to  $C_{11}$  to allow for different properties of hydrogen.

In all three models physical properties were permitted to vary with the inlet conditions. Thus as the inlet temperature changed, the viscosity and diffusivities of the gas changed. This changes the effective diffusivities in the catalyst as well as other properties. As the flow rate changed, so did the Reynold's number, and hence the heat and mass transfer coefficients, which were calculated using the correlations of Thoenes and Kramers (1958). It was necessary to take these variations into account since the inlet temperature varied from 220°F during the cold start to almost 1000°F during the final cycles of the Federal Test Procedure.

There are two independent reactions but three chemical species. For the dynamic model when the accumulation terms are retained in the mass balances and the effective diffusivities of the different species are different it is not possible to relate the hydrogen concentration to the carbon monoxide and nitric oxide concentrations. This results from the fact that mass of any species may accumulate in the reactor voids and in the particles themselves, and where it actually accumulates depends on the parameters, such as effective diffusivity, which are different for different species. In the quasi-static model such a combination is possible.

The Equations (5) to (12) were solved using the orthogonal collocation method to reduce them to a set of ordinary differential equations (see Ferguson and Finlayson, 1970). A typical result is

$$\tau_1 \frac{dNOP_j}{dt} = \sum_{i=1}^{N+1} B_{ji}NOP_i - C_1(r_{1j} + r_{2j}) \quad j = 1, \dots, N \quad (15)$$

$$\sum_{i=1}^{N+1} A_{N+1,i}NOP_i = C_2(NO - NOP_{N+1}) \quad (16)$$

$$\tau_3 \frac{dNO}{dt} = NO_{in}(t) - NO + C_5(NOP_{N+1} - NO) \quad (17)$$

$r_{1j}$  = reaction rate  $r_1$  evaluated using  $NOP_j$ ,  $TP_j$ , etc.  
Equations (15) and (16) are combined to give

$$\tau_1 \frac{dNOP_j}{dt} = \sum_{i=1}^N \left( B_{ji} - B_{j,N+1} \frac{A_{N+1,i}}{A_{N+1,N+1} + C_2} \right) NOP_i + B_{j,N+1} \frac{C_2 NO}{A_{N+1,N+1} + C_2} - C_1(r_{1j} + r_{2j}) \quad (18)$$

Equations (17) and (18), together with similar equations for temperature and the other species, are then integrated numerically using the improved Euler method. In other computations, this scheme was found to be faster than the Runge-Kutta method. Due to the different time constants the equations are stiff, and a fully implicit method might give even better results. Due to the computer time limitations the dynamic calculations were carried out for only a small time interval ( $\frac{1}{2}$  to 1 sec. real time) during

times in the Federal Test Procedure when the most rapid changes occur.

#### Quasi-Static Model

The time response of Equations (5) to (12) is governed by the relative magnitude of  $\tau_1$ ,  $\tau_2$ , and  $\tau_3$ . Typical values are  $\tau_1 = 0.27$  s,  $\tau_2 = 21$  s,  $\tau_3 = 2.7 \times 10^{-3}$  s. Since  $F/V$  is the space velocity,  $\epsilon/\tau_3$  is also the space velocity, which here is  $130 \text{ s}^{-1}$  ( $470,000 \text{ hr}^{-1}$ ) for the first cell, or  $39,000 \text{ hr}^{-1}$  for the reactor. Of course  $F$  varies by an order of magnitude during the simulation.

From the review of previous work we know that the slowest time response is the heat transfer to the catalyst, with a time constant

$$\tau_4 = \frac{(\rho C_p)_s R_p}{3h} \quad (19)$$

A typical value of this quantity is 12 sec.

For the nitric oxide reactor, then  $\tau_4/\tau_1 = 50$ ,  $\tau_4/\tau_3 = 500$ -5000, and  $C_r = 0.0002$ . Thus the conditions listed in Table 1 for the quasi-static model are satisfied.

The Biot number for the catalyst particle in the NO reactor is typically 0.8, and this is small enough that the lumping procedure is valid provided an overall heat transfer coefficient is used as in Equation (2).

We obtain the quasi-static model by setting  $\tau_1 = \tau_3 = 0$  in Equations (5), (11), and (12), integrating Equation (8) from  $r = 0$  to  $r = 1$ , applying the boundary condition (10), and using the fact that the temperature profile inside the catalyst is uniform.

$$0 = \nabla^2 (NOP') - C_1(r_1' + r_2') \quad (20)$$

$$\frac{\partial NOP'}{\partial r} = C_2(NO' - NOP') \quad \text{at } r = 1 \quad (21)$$

$$\tau_4 \frac{dTP'}{dt} = T' - TP' + \frac{R_p \rho_s}{h} [-\Delta H_1 \langle r' \rangle - \Delta H \langle r_2' \rangle] \quad (22)$$

$$0 = NO_{in}(t) - NO' + C_5[NOP'(1, t) - NO'] \quad (23)$$

$$0 = T_{in}(t) - T' + C_6[TP' - T'] \quad (24)$$

The primed variables refer to the quasi-static model and the brackets  $\langle \rangle$  mean that the term is averaged over the spherical catalyst particle, that is,

$$\langle r_1 \rangle = \int_0^1 r_1 r^2 dr$$

where the reaction rate varies with radius and time because of its dependence on concentration and temperature.

Similar particle mass balances are written for carbon monoxide and hydrogen. There are two independent reactions, and one might solve Equation (20) and (21) by constructing effectiveness factor plots to be used in the transient calculations. However, the two reactions are strongly coupled through the NO concentration. Thus the  $H_2$  reaction with NO depends not just on the parameters for that reaction, but also on the CO reaction. Thus it would not be possible to construct one effectiveness factor plot for the  $H_2$  reaction and one for the CO reaction since the reactions interact in the catalyst pellet through the concentration profile of NO. This means the particle problem, Equations (20) to (21), must be solved at each  $t$  along with Equation (22) and hence solved thousands of times. The efficiency of the orthogonal collocation method is especially welcome. The equations are solved after some rearrangement. Equation (24) can be solved for  $T'$  to give

$$T' = \frac{T_{in}(t) + C_8 TP'}{1 + C_8} \quad (25)$$

and this put into Equation (22) gives

$$\tau_4 \frac{dTP'}{dt} = \frac{1}{1 + C_8} [T_{in}(t) - TP'] + \frac{R_p \rho_s}{h} [-\Delta H_1 \langle r_1' \rangle - \Delta H_2 \langle r_2' \rangle] \quad (26)$$

A similar manipulation of the nitric oxide balances gives

$$NO' = \frac{NO_{in}(t) + C_5 NOP'(1, t)}{1 + C_5} \quad (27)$$

and

$$\frac{\partial NOP'}{\partial r} = \frac{C_2}{1 + C_5} [NO_{in}(t) - NOP'(1, t)] \quad \text{at } r = 1 \quad (28)$$

We have found in other calculations, however, (Ferguson, 1971), that the best approximation of the flux comes not from the boundary condition (28) but from integrating Equation (20) to get

$$\left. \frac{\partial NOP'}{\partial r} \right|_{r=1} = C_1 (\langle r_1' \rangle + \langle r_2' \rangle)$$

Thus the boundary condition becomes

$$C_2 [NO' - NOP'(1, t)] = C_1 (\langle r_1' \rangle + \langle r_2' \rangle)$$

and the cell mass balance becomes

$$NO' = NO_{in}(t) - 3C_8 (\langle r_1' \rangle + \langle r_2' \rangle) \quad (29)$$

The orthogonal collocation formulation of the Equations (20) and (21) is

$$0 = \sum_{i=1}^{N+1} B_{ji} NOP'_i - C_1 (r_{1j}' + r_{2j}') \quad j = 1, \dots, N \quad (30)$$

$$\sum_{i=1}^{N+1} A_{N+1,i} NOP'_i = C_2 (NO' - NOP'_{N+1}) \quad (31)$$

$$\langle r_1 \rangle = \sum_{i=1}^{N+1} W_i r_{1i}', \quad W_{N+1} = 0 \quad (32)$$

Equation (31) can be solved for  $NOP'_{N+1}$ , this is substituted into Equation (30) and Equation (29) is used to give

$$\sum_{i=1}^N \left( B_{ji} - \frac{B_{j,N+1} A_{N+1,i}}{A_{N+1,N+1} + C_2} \right) NOP'_i = C_1 (r_{1j}' + r_{2j}') - \frac{B_{j,N+1} C_2}{A_{N+1,N+1} + C_2} \left[ NO_{in}(t) - 3C_8 \sum_{i=1}^N W_i (r_{1i}' + r_{2i}') \right] \quad (33)$$

The equations to solve in the quasi-static model are then (26) and (33), with equations similar to (33) for both carbon monoxide and hydrogen. These are solved as follows. A temperature at a given time is known. This temperature is used in Equation (33) to find the concentration profile in the catalyst. The average reaction rates corresponding to that profile are used in Equation (26) to find the temperature at the next time step. The improved Euler method was used so that this procedure

was followed twice for each time step. The cell concentrations and temperatures were calculated using Equations (29) and (25). The method used to solve Equation (33) was a Newton-Raphson method with the reaction rate expression assumed (for purposes of iteration only) to be first order in  $NOP'_i$ . The corresponding equations for CO and  $H_2$  were solved using a successive substitution method: the nonlinear reaction rate is evaluated with the previous iteration, linear equations are solved to get the new guess, and the process is repeated until successive iterations agree to within some prescribed tolerance.

For the quasi-static model the hydrogen concentration can be eliminated from the equations by stoichiometry. When the hydrogen properties differ from those of the other species, however, it is simpler to just retain the separate hydrogen balance. This was done for the comparison of dynamic and quasi-static models. When the quasi-static model was employed with the Federal Test Procedure the diffusivities of all components were taken as the same\* and the hydrogen concentration was derived from

$$H_2' = H_{2in} - (NO_{in} - NO') + (CO_{in} - CO')$$

$$H_2 P'(r) = H_2' + (NOP'(r) - NO') - (COP'(r) - CO')$$

### Simple Model

A third model is obtained by simplification of the quasi-static model. Under typical automobile operating conditions the CO concentration is much larger than the NO concentration. In the reaction rate expression, Equation (4), the term  $K_{NO} p_{NO}$  in the denominator is negligible compared to the other terms. Thus Equation (4) can be modeled as a first-order reaction. In the quasi-static model the temperature is constant throughout the catalyst, with a temperature change at the boundary. Thus the problem of diffusion and reaction in the catalyst reduces to a first-order, isothermal reaction. The effectiveness factor is known, and concentrations out of the mixing cell can be calculated analytically. Using these simplifications we obtain what we call the simple model.

The reaction rate term, Equation (4), is written as  $r_1 = R_1 NO'$  and a similar expression is used for the  $H_2$  reaction,  $r_2 = R_2 NO'$ . The effectiveness factor for a first-order isothermal reaction is given by

$$\eta = \frac{3}{\phi^2} \frac{\phi \coth \phi - 1}{\frac{\phi \coth \phi - 1}{C_2} + 1} \quad (34)$$

where  $\phi^2 = C_1(R_1 + R_2) R_p \rho_s / D_{e,NO}$ . The equations to solve are then (25), (26), (29) with

$$\langle r_1' \rangle = \eta R_1 NO, \quad \langle r_2' \rangle = \eta R_2 NO$$

and Equation (34) for  $\eta$ . This model differs from the quasi-static model in having a direct calculation for  $\eta$ , as opposed to solving two boundary value problems as in Equation (33). Thus it is expected to be much faster since the reduction in computer time applies at each time step. The improved Euler method was used here, too.

## RESULTS

### Comparison of Dynamic and Quasi-Static Models

To compare the dynamic model with the quasi-static model we picked a portion of the Federal Test Procedure

\* This is not a good assumption ( $D_{e,H_2}/D_{e,NO} = 3.5$ ) but has only a small effect on the results since the hydrogen reaction is only of importance at the highest temperatures encountered.

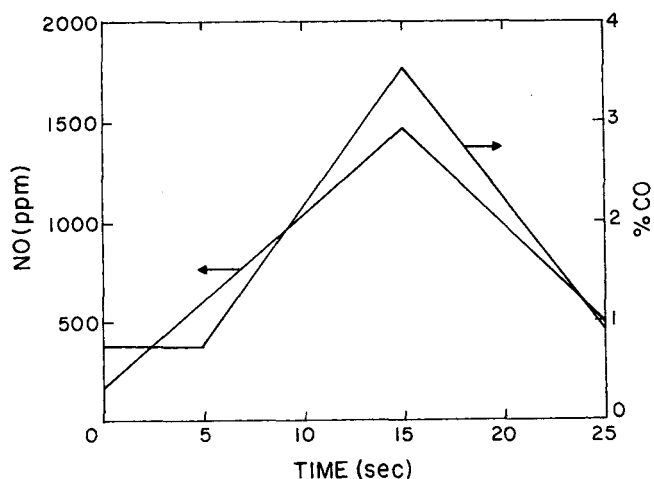


Fig. 1. Inlet conditions for nitric oxide and carbon monoxide.

during which the NO and CO concentrations were changing rapidly. The portion chosen roughly simulates the time beginning at 20 sec. and continuing for 20 sec. more in the third cycle. The NO and CO inlet concentrations are shown in Figure 1. The flow rate was constant at 130 m<sup>3</sup>/hr. (76.8 std.cu.ft./min.) until  $t = 15$  sec., when it was reduced to 83.6 m<sup>3</sup>/hr. (49.2 std.cu.ft./min.). The temperature was 479°C from  $t = 0$  to  $t = 10$ , changed to 521°C until  $t = 15$ , when it dropped to 491°C. The sharp changes at  $t = 15$  provide a rigorous test of the quasi-static model. The integration was begun at  $t = 14.7$  and continued until about  $t = 15.5$ . The initial conditions corresponded to the catalyst being at the inlet temperature and concentrations for  $t = 0$ . Thus the first transient is basically the response to a step change, while the transient at  $t = 15$  arises from rapid changes in inlet conditions.\*

The concentrations of NO in each catalyst particle in the first mixing cell are shown in Figure 2 for  $t = 14.71$ . The dynamic and static particle concentration profiles are almost identical. The profiles are almost the same for  $N = 3$  as for  $N = 6$  although the error in the flux (the slope of the curve at  $r = 1$ ) gives rise to a 4% error in the NO concentration coming out of the mixing cell. This error persists as time proceeds but is not serious so that  $N = 3$  is adequate.

The effect of the step change is more dramatic in the CO particle concentration as shown in Figure 3. The initial CO concentration is very low compared to the steady state value, and the transient is important during this first 0.01 sec. The quasi-static model overestimates the CO particle concentration by 500%. However, the error in CO concentration out of the mixing cell is only 8% and this decreases rapidly to ½% by  $t = 14.77$  as shown in Figure 4. This result suggests that if one is interested in the solution at one time, say  $t = 14.77$  sec., it is feasible to use the quasi-static model with a time step small enough (0.01) so that several quasi-static calculations are made between the time of the discontinuity (14.70) and the time of interest (14.77). However, the quasi-static model cannot be used if one is interested in the solution too close to the discontinuity. For example, the quasi-static model with  $\Delta t = 0.0004$  gives essentially the same results

(CO particle concentration off by 500%) at  $t = 14.71$  as does the quasi-static model with  $\Delta t = 0.01$ . This is reasonable when one recalls the time constants for the phenomena neglected in the quasi-static model: mass diffusion in catalyst— $\tau_1 = 0.27$  sec., heat transfer within the catalyst— $\tau_2 = 21$  sec.

The particle NO concentrations are shown in Figure 5 for  $t = 15.01$ , just after the large change in flow rate and the change from increasing to decreasing concentrations of CO and NO. Here the quasi-static and dynamic cell concentrations differ by 17%, but this difference is reduced to 0.02% by the next time step and for subsequent times. If the quasi-static model uses a larger  $\Delta t$  (0.4 instead of 0.01), with the time steps being at 14.7 and 15.1 (that is, crossing over the rapid changes) then the error at 15.1 is 16%, and this is reduced to essentially 0% at 15.5. This suggests that as the discontinuities and changes

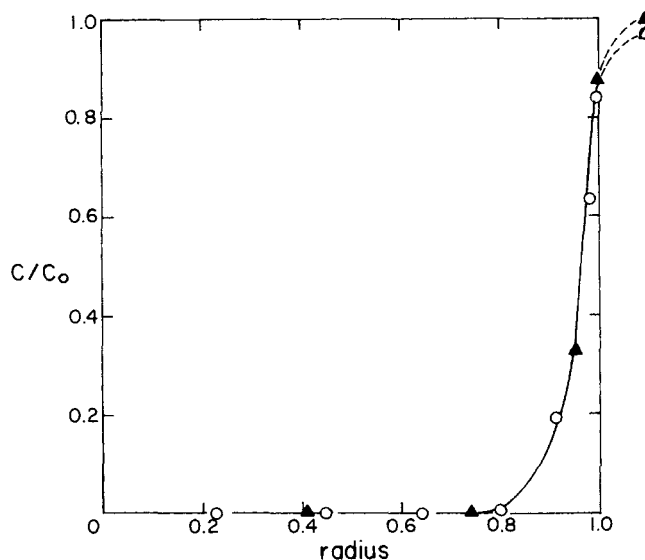


Fig. 2. Nitric oxide concentrations in catalyst pellet at  $t = 14.71$ : Quasi-static model— $\blacktriangle$   $N = 3$ ,  $\triangle$   $N = 6$ ,  $\Delta t = 0.01$ . Dynamic model:  $\bullet$   $N = 3$ ,  $\circ$   $N = 6$ ,  $\Delta t = 4 \times 10^{-4}$  and  $5 \times 10^{-5}$ ;  $c_0 = 1.6061 \times 10^{-5}$  kg.moles/m<sup>3</sup>.

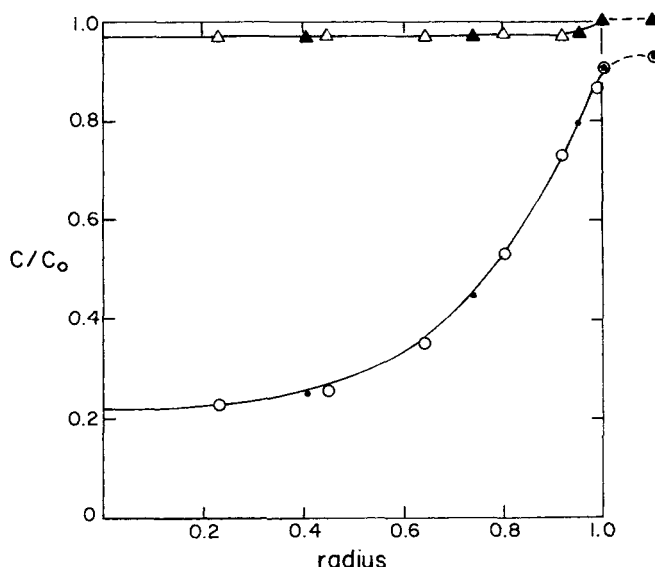


Fig. 3. Carbon monoxide concentrations in catalyst pellet at  $t = 14.71$ .  $c_0 = 5.2352 \times 10^{-4}$  kg.moles/m<sup>3</sup>, other values same as for Figure 2.

\* When comparing the dynamic and quasi-static models, the size of the mixing cell was inadvertently taken as 1/12 the volume of the whole reactor. For the calculations corresponding to the Federal Test Procedure, the mixing-cell volume was ¼ the volume of the whole reactor.



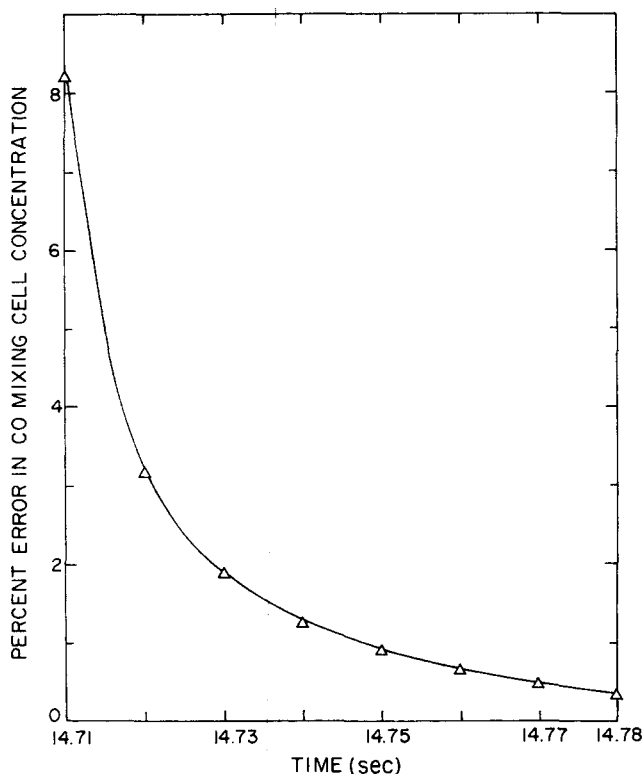


Fig. 4. Percent error in CO mixing-cell concentration as a function of time.

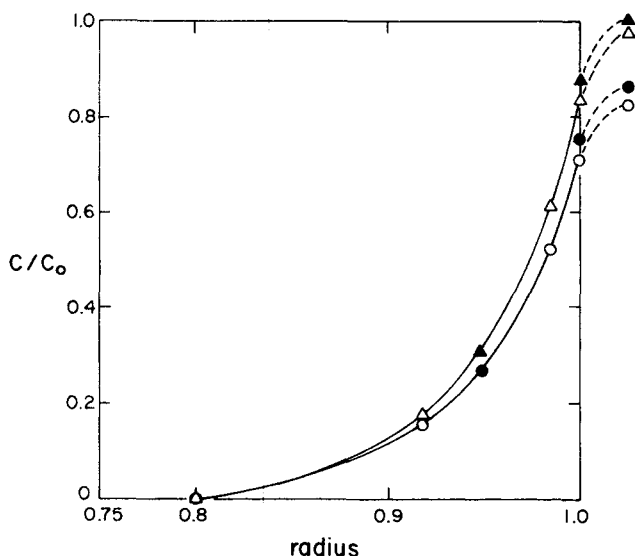


Fig. 5. Nitric oxide concentrations in catalyst at  $t = 15.01$ .  $c_0 = 1.6917 \times 10^{-5}$  kgmoles/m<sup>3</sup>; other values same as for Figure 2.

are encountered in the variables dictated by the Federal Test Procedure, the  $\Delta t$  used in the integration must be small enough to permit several steps past the point of discontinuity before the results are accurate compared to the dynamic model.

We conclude that the quasi-static model is a valid representation of the dynamic model provided the fast transients are not investigated. It is therefore possible to set  $\tau_1 = \tau_3 = 0$  in Equations (5), (11), and (12). The orthogonal collocation method with  $N = 3$  is an adequate approximation. This is fortunate because the  $\Delta t$  step size for  $N = 6$  was considerably smaller than for  $N = 3$ ,

resulting in computation times 15 times as long. Even for  $N = 3$ , the dynamic calculations took 40 times real time (on a CDC 6400 computer), which is too slow to permit the use of the dynamic model over the entire test procedure of 979 sec. Use of an implicit integration scheme might reduce this computation time considerably since the limitation arises from stability of the calculations.

For the quasi-static model to be valid, the time steps must be taken small enough that several time steps are permitted between points of discontinuity in the inlet conditions. In addition several time steps must be allowed between the time of discontinuity and the time one is interested in the solution, since the quasi-static model gives poor results the first few time steps after a discontinuity. Thus the time step in the quasi-static model is limited by the accuracy desired, whereas the time step in the dynamic model was limited by stability, when using an explicit, predictor-corrector method of integration.

#### Comparison of Quasi-Static and Simple Model

The simple model is compared to the quasi-static model in Figure 6. The difference in the models is that the quasi-static model solves a set of three coupled boundary value problems twice for each time step, and in the simple model we simply calculate the effectiveness factor twice for each time step. Figure 6 shows that the two models compare favorably (within 5%) for a single cell. Each mixing cell in the reactor is expected to add an additional error so that the total error could be as high as 10%. This comparison must be qualified by the realization that the conditions used to compute Figure 6 resulted in very little reaction between  $H_2$  and  $NO$ . Thus the coupled nature of the reaction rates has not been tested.

Which model to use—dynamic, quasi-static or simple—depends on a trade-off between accuracy and computation time. The computer times are listed in Table 2. Clearly the dynamic model is too lengthy to use for the full Federal Test Cycle of 979 sec. The quasi-static model can be used with a large step size. The simple model is the fastest with only a small error. For most purposes the simple model would be the best choice. For the Federal Test Procedure calculations reported below we used the quasi-static model rather than the simple model for three reasons: (1) to examine the nonlinearity of the model, (2) the computation times were reasonable, and (3) to illustrate the application of the orthogonal collocation method in this situation.

#### Calculations for the Federal Test Procedure

The quasi-static model was used for the full seven cycles simulating the Federal Test Procedure. Four mixing cells

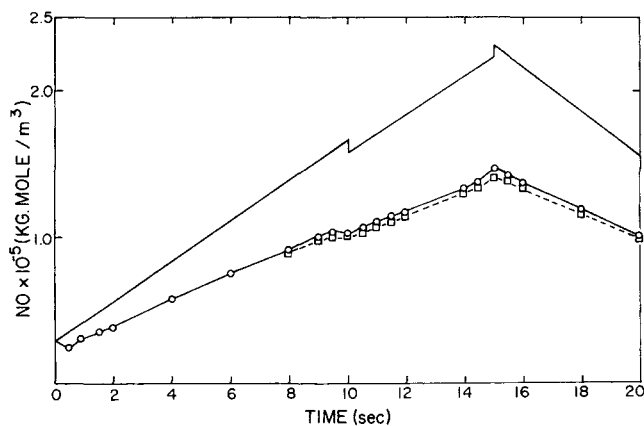


Fig. 6. Comparison of quasi-static and simple model,  $\Delta t = 0.5$  sec.

were used and typical inlet gas temperatures and inlet NO concentrations are shown in Figures 7 and 8. The inlet temperature and volumetric flow rate are from Kuo et al. (1971), and the concentration of NO and CO are from Bernstein et al. (1971). Complete data on inlet conditions are available elsewhere (Ferguson, 1971). The time step in the integration varied from 1 to 4 sec. The flow rate is a discontinuous function of time and the time rates of change of temperature and concentration are discontinuous functions of time, too. We found it important to divide the time interval between successive discontinuities into an integral number of time steps if accuracy was to be preserved in the integration. Thus a variable time step was essential.

We consider three sets of parameter values, corresponding to different catalyst properties, as listed in Table 3. The thermal inertia of Case A is about one third that of Case B. In Case A the solid heats up more rapidly and hence the reaction rate is faster in the first cycle. When

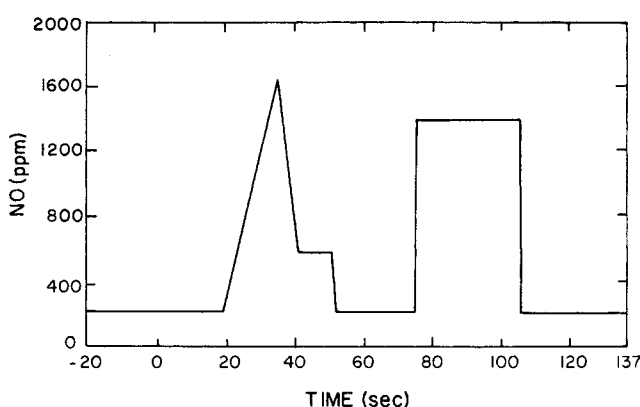


Fig. 7. Inlet nitric oxide concentration during one cycle of Federal Test Procedure.

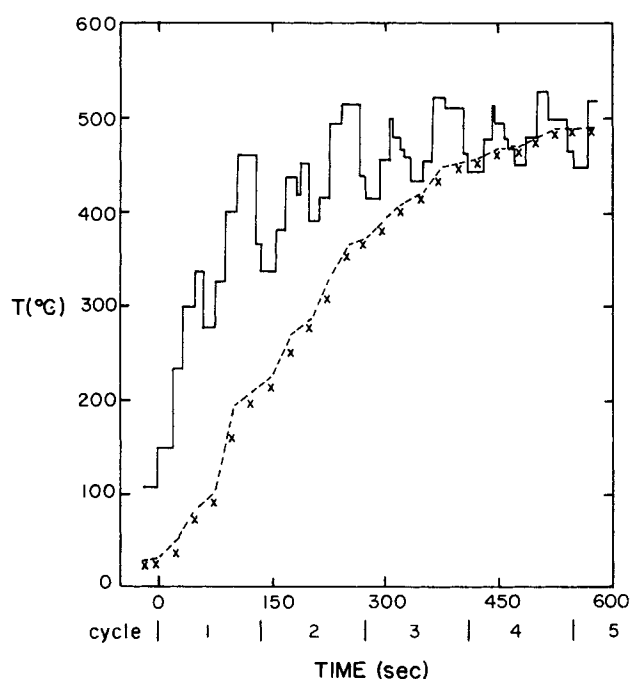


Fig. 8. Gas and solid temperatures vs. time (— inlet to first mixing cell, — exit from second mixing cell, x solid temperature in second mixing cell).

TABLE 2. COMPUTER TIMES FOR DIFFERENT MODELS

	Ratio of computer time* to real time
Dynamic model	
$N = 6, \Delta t = 5 \times 10^{-5}$	700
$N = 3, \Delta t = 4 \times 10^{-4}$	41
Quasi-static model, $N = 3$	
$\Delta t = 4 \times 10^{-4}$	100
$\Delta t = 0.01$	6
$\Delta t = 0.5$	0.14
Simple model	
$\Delta t = 0.5$	0.02

\* CPU time on CDC 6400.

TABLE 3. CATALYST PROPERTIES

	Case A (fast thermal response)	Case B (base case)	Case C (diffusion limited)
$D_{e,NO}(m^2/s)$	$6 \times 10^{-6}$	$1.7 \times 10^{-6}$	$0.1 \times 10^{-6}$
$C_{ps}(J/kg^\circ K)$	750	1100	1100
$\rho_s(kg/m^3)$	680	1300	1300

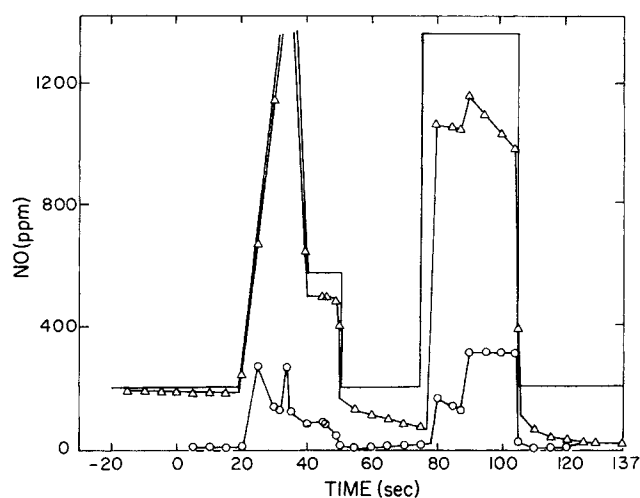


Fig. 9. Nitric oxide concentration vs. time (— inlet to reactor,  $\Delta$  outlet from fourth mixing cell, Cycle 1,  $\circ$  outlet from fourth mixing cell, Cycle 7).

reactor is heated up, Case B would produce better conversion because of the greater amount of catalyst. Case C, in which the diffusivity approximates that of a micro-porous catalyst (rather than a macro-porous catalyst) should take as long to heat up as Case B but have lower conversions due to the increased mass transfer resistance.

For Case B the concentration of NO in the inlet and outlet of the reactor is shown in Figure 9. The conversion during the first cycle is quite poor because the bed is not yet hot enough but during the seventh cycle the conversion is very good. During the first cycle the engine is often choked and the NO concentrations are low. We used the same NO concentrations for all cycles due to the lack of data as a function of time during the first cycle. Thus the problem of warm-up would not be as severe as indicated in Figure 9.

The three different catalysts are compared in Table 4. As expected the conversion is best during the first cycle

TABLE 4. CONVERSION WHEN USING DIFFERENT CATALYSTS

	Case A	Conversion, % Case B	Case C
First cycle	46	26	16
Seventh cycle	82	85	73

TABLE 5. INLET GAS PROPERTIES

	Case D	Case B	Case E
NO, ppm	450	850	2900
NO, approx. g/mile	1.6	3.0	10
CO, %	4.3	1.5	1.3

TABLE 6. CONVERSIONS FOR DIFFERENT INLET CONDITIONS

	Case D	Conversion, % Case B	Case E
Cycle 1	12	26	22
Cycle 7	89	85	82

for Case A, whereas the conversion is best during the seventh cycle for Case B. The decreased conversion of Case C is also apparent. From the data in Table 4 it is not clear which catalyst is best overall, Case A or B. Case A has a much higher conversion during the first cycle, but as noted above the NO concentration is usually decreased when the automobile is choked at the beginning of the first cycle. The reduced conversion of Case A during the seventh cycle is expected to be similar to the performance during the third through seventh cycle, so that even though the conversion difference between Cases A and B is very small in the seventh cycle, the difference applies over a much longer time period than the results for the first cycle. To further differentiate between Cases A and B more detailed data would have to be available concerning the NO concentration in different cycles. In any case the difference is slight, despite the large change in properties of the catalyst.

We next examine the effect of different levels of NO and CO concentrations. The cases studies are listed in Table 5. The shape of the NO and CO inlet concentration curve vs. time was shifted up or down to achieve the averaged concentrations shown.\* The conversions obtained are listed in Table 6. The fact that the conversions change with concentration is an indication of the importance of the nonlinearity of the problem.

## ACKNOWLEDGMENT

The research was supported in part by NSF Grant GK-12517, and in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society under Grant PRF #5965-AC7.

## NOTATION

$A = 3\tau_3/(\tau_2 C_r)$ , Equation (3), dimensionless  
 $A_{ji}$  = matrix arising in collocation method, representing the first derivative

\* Note that the average is not just the integral under the curve, Figure 9, since the volumetric flow rate also varies in time.

$Bi$  =  $hR_p/k_e$ , dimensionless Biot number  
 $B_{ji}$  = matrix arising in collocation method, representing the Laplacian operator  
 $CO$  = carbon monoxide concentration in mixing cell, kg moles/m<sup>3</sup>  
 $COP$  = carbon monoxide concentration in catalyst, kg mole/m<sup>3</sup>  
 $C_p$  = heat capacity, J/(kg °C)  
 $C_r$  = heat capacity ratio, Equation (1), dimensionless also  $C_r = \tau_4 C_6 / \tau_3$   
 $C_1$  =  $\rho_s R_p^2 / D_{e,NO}$ , kg cat s/m<sup>3</sup>  
 $C_2$  =  $k_{m,NO} R_p / D_{e,NO}$ , dimensionless  
 $C_4$  =  $R_p^2 \rho_s / k_e$ , kg s °C/J  
 $C_5$  =  $6 k_{m,NO} (1 - \epsilon) V / (F d_p)$ , dimensionless  
 $C_6$  =  $6 h (1 - \epsilon) V / (F d_p \rho_f C_{pf})$ , dimensionless  
 $C_8$  =  $C_1 C_5 / (3 C_2) = \rho_s (1 - \epsilon) V / F$ , kg s/m<sup>3</sup>  
 $C_9$  =  $D_{e,H_2} / D_{e,NO}$ , dimensionless  
 $C_{10}$  =  $k_{m,H_2} R_p / D_{e,H_2}$ , dimensionless  
 $C_{11}$  =  $C_5 k_{m,H_2} / k_{m,NO}$ , dimensionless  
 $C_{12}$  =  $\rho_s d_p / (6h)$ , kg s °C/J  
 $D$  = diameter of cylindrical catalyst bed, m  
 $D_{e,i}$  = effective diffusivity of  $i$ th species inside catalyst  
 $d_p$  = diameter of catalyst, m  
 $F$  = gas flow rate, m<sup>3</sup>/s  
 $G_0$  = mass flux based on cross sectional area of empty tube, kg/m<sup>2</sup> s  
 $h$  = heat transfer coefficient to sphere, J/s m<sup>3</sup> °C  
 $h_w$  = heat transfer coefficient to reactor wall, J/s m<sup>2</sup> °C  
 $-\Delta H_i$  = heat of reaction  $i$ , J/kg mole  
 $H_2$  = hydrogen concentration in mixing cell, kg mole/m<sup>3</sup>  
 $H_2P$  = hydrogen concentration in catalyst, kg moles/m<sup>3</sup>  
 $k$  = reaction rate constant, kg mole/(s kg catalyst)  
 $K_i$  = reaction rate constant, atm<sup>-1</sup>  
 $k_e$  = effective thermal conductivity in catalyst, J/s m °C  
 $k_{e,bed}$  = effective thermal conductivity in packed bed, J/s m °C  
 $k_{m,i}$  = mass transfer coefficient for  $i$ th species, m/s  
 $L$  = length of cylindrical catalyst bed, m  
 $Le$  =  $D_{e,NO}(\rho C_p)_s / k_e$ , Lewis number  
 $N$  = number of interior collocation points  
 $NO$  = nitric oxide concentration in mixing cell, kg moles/m<sup>3</sup>  
 $NOP$  = nitric oxide concentration in catalyst, kg mole/m<sup>3</sup>  
 $p_i$  = partial pressure of  $i$ th species, atm  
 $r$  = radial position in catalyst, dimensionless  
 $\tau_1$  = rate of reaction with CO, kg moles/(s kg catalyst)  
 $\tau_2$  = rate of reaction with H<sub>2</sub>, kg moles/(s kg catalyst)  
 $R$  = reactor radius, m  
 $R_p$  = catalyst particle radius, cm  
 $R_1$  = pseudo first order reaction rate constant for CO reaction, s<sup>-1</sup>  
 $R_2$  = pseudo first order reaction rate constant for H<sub>2</sub> reaction, s<sup>-1</sup>  
 $t$  = time, s  
 $TP$  = temperature in catalyst pellet, °C  
 $T$  = temperature in mixing cell, °C  
 $y$  = dummy variable in Equation (18)  
 $U$  = overall heat transfer coefficient, Equation (2), J/m<sup>2</sup> s °C  
 $V$  = volume of mixing cell, 236 cm<sup>3</sup>  
 $W_i$  = vector arising in collocation method, quadrature weighting function

## Greek Letters

$\epsilon$  = void fraction in reactor  
 $\epsilon_s$  = void fraction inside catalyst  
 $\eta$  = effectiveness factor, defined by Equation (34)

- $\phi$  = Thiele modulus,  $[C_1(R_1 + R_2)]^{1/2}$   
 $\rho$  = density, g/cm<sup>3</sup>  
 $\rho_s$  = density of catalyst, kg cat/m<sup>3</sup> vol. (including voids in catalyst)  
 $\tau_1$  = time constant for mass transfer inside catalyst, Equation (13), s  
 $\tau_2$  = time constant for heat transfer inside catalyst, Equation (13), s  
 $\tau_3$  = residence time in mixing cell, Equation (14), s  
 $\tau_4$  = time constant for heat transfer to catalyst, Equation (19), s

#### Superscripts

- ' = quasi-static model

#### Subscripts

- in = inlet value to mixing cell  
 i = value at *i*th collocation point  
 j = value at *j*th collocation point  
 s = solid  
 f = fluid

#### LITERATURE CITED

- Ayen, R. J. and Y. S. Ng, "Catalytic Reduction of Nitric Oxide by Carbon Monoxide," *Air-Water Pollution*, **10**, 1 (1966).  
 Ayen, R. J., and M. S. Peters, "Catalytic Reduction of Nitric Oxide," *Ind. Eng. Chem. Process Design Develop.*, **1**, 204 (1962).  
 Batke, T. L., R. G. Franks, and E. W. James, "Analog Simulation of a Chemical Reactor," *Inst. Soc. Am. J.*, **4**, 14 (1957).  
 Benham, C. B. and V. E. Denny, "Transient diffusion of heat, mass species and momentum in cylindrical pellets during catalytic oxidation of CO," *Chem. Eng. Sci.*, **27**, 2163 (1972).  
 Bernstein, L. S., K. K. Kearby, A. K. S. Raman, J. Vardi, and E. E. Wigg, "Application of Catalysts to Automotive NO<sub>x</sub> Emissions Control," paper presented at Soc. Auto. Eng. meeting, Detroit (1971).  
 Brian, P. L. T., R. F. Baddour, and J. P. Eymery, "Transient Behavior of an Ammonia Synthesis Reactor," *Chem. Eng. Sci.*, **20**, 297 (1965).  
 Butterfield, P., J. Schofield, and P. A. Young, "Hot Blast Stoves," *J. Iron Steel Inst.*, **21**, 497 (1967).  
 Crider, J. E., and A. S. Foss, "Computational Studies of Transients in Packed Tubular Chemical Reactors," *AIChE J.*, **12**, 514 (1966).  
 Deans, H. A., and L. L. Lapidus, "A Computational Model for Predicting and Correlating the Behavior of Fixed-Bed Reactors I. Derivation of Model for Nonreactive Systems, II. Extension to Chemical Reactive Systems," *ibid.*, **6**, 656, 663 (1960).  
 Eigenberger, G., "On the dynamic behavior of the catalytic fixed-bed reactor in the region of multiple steady states I. The influence of heat conduction in two phase models," *Chem. Eng. Sci.*, **27**, 1909 (1972).  
 Elrod, H. G., Jr., "Improved Lumped Parameter Method for Transient Heat Conduction Calculations," *J. Heat Transfer, Trans. Am. Soc. Mech. Eng., Sec. C*, **82**, 181 (1960).  
 Ervin, M. A., and D. Luss, "Effect of Fouling on Stability of Adiabatic Packed Bed Reactors," *AIChE J.*, **16**, 979 (1970).  
 Feick, J., and D. Quon, "Mathematical Models for the Transient Behavior of a Packed Bed Reactor," *Can. J. Chem. Eng.*, **48**, 205 (1970).  
 Ferguson, N. B., "Orthogonal Collocation as a Method of Analysis in Chemical Reaction Engineering," Ph.D. thesis, Univ. of Washington (1971).  
 Ferguson, N. B. and B. A. Finlayson, "Transient Chemical Reaction Analysis by Orthogonal Collocation," *Chem. Eng. J.*, **1**, 327 (1970).  
 Finlayson, B. A., "Packed Bed Reactor Analysis by Orthogonal Collocation," *Chem. Eng. Sci.*, **26**, 1081 (1971).  
 Goss, M. J., and G. A. Turner, "Simultaneous Computation of Heat Transfer and Dispersion Coefficients and Thermal Conductivity Value in a Packed Bed of Spheres II, III," *AIChE J.*, **17**, 590, 592 (1971).  
 Handley, D., and P. J. Heggs, "The Effect of Thermal Conductivity of the Packing Material on Transient Heat Transfer in a Fixed Bed," *Intern. J. Heat Mass Transfer*, **12**, 549 (1969).  
 Harned, J. L., "Analytical Evaluation of a Catalytic Converter System," paper presented at Soc. Auto. Eng. meeting, Detroit (1971).  
 Hoiberg, J. A., B. C. Lyche, and A. S. Foss, "Experimental Evaluation of Dynamic Models for a Fixed-Bed Catalytic Reactor," *AIChE J.*, **17**, 1434 (1971).  
 Huls, T. A., "Evaluation of Federal Light-Duty Mass Emission Regulations," paper presented at Soc. Auto. Eng. meeting, Detroit (1973).  
 Kardos, P. W., and W. F. Stevens, "Transient State Simulation of a Distributed Parameter System: Control of Hot Spot in a Packed-Bed Tubular Reactor," *AIChE J.*, **17**, 1090 (1971).  
 Kuo, J. C. W., C. R. Morgan, and H. G. Lassen, "Mathematical Modeling of CO and HC Catalytic Converter Systems," paper presented at Soc. Auto Eng. meeting, (1971).  
 Lee, J. C. M., and D. Luss, "The Effect of Lewis Number on the Stability of a Catalytic Reaction," *AIChE J.*, **16**, 620 (1970).  
 Liu, S. L., and N. R. Amundson, "Stability of Adiabatic Packed Bed Reactors. An Elementary Treatment," *Ind. Eng. Chem. Fundamentals*, **1**, 200 (1962).  
 ———, "Stability of Adiabatic Packed-Bed Reactors," *ibid.*, **2**, 183 (1963).  
 Liu, S. L., R. Aris, and N. R. Amundson, "Stability of Non-adiabatic Packed-Bed Reactors," *ibid.*, **2**, 12 (1963).  
 McGreavy, C., and J. M. Thornton, "Stability Studies of Single Catalyst Particles," *Chem. Eng. J.*, **1**, 296 (1970).  
 ———, "A Dynamic Model of a Fixed Bed Catalytic Reactor," paper presented at IFAC Symp. on Control of Distributed Parameter Systems, Banff, Canada (1971).  
 McGuire, M. L., and L. Lapidus, "On the Stability of a Detailed Packed-Bed Reactor," *AIChE J.*, **11**, 85 (1965).  
 Shelef, M., and J. T. Kummer, "The Behavior of Nitric Oxide in Heterogeneous Catalytic Reactions," *Chem. Eng. Progr. Symp. Ser. No. 115*, **67**, 74 (1971).  
 Sinai, J., and A. S. Foss, "Experimental and Computational Studies of the Dynamics of a Fixed Bed Chemical Reactor," *AIChE J.*, **16**, 658 (1970).  
 Stewart, W. E., and J. P. Sørensen, "Transient Reactor Analysis by Orthogonal Collocation," 2nd Intern. Symp. Chemical Reaction Eng. (1972).  
 Thoennes, D., Jr., and H. Kramers, "Mass Transfer from spheres in various regular packing to a flowing fluid," *Chem. Eng. Sci.*, **8**, 271 (1958).  
 Tinkler, J. C., and D. E. Lamb, "Dynamics and Feed forward Control of a Fixed-Bed Chemical Reactor," *Chem. Eng. Progr. Symp. Ser. No. 55*, **61**, 155 (1965).  
 Turner, G. A., "A Method of Finding Simultaneously the Values of the Heat Transfer Coefficient, the Dispersion Coefficient, and the Thermal Conductivity of the Packing in a Packed Bed of Spheres: Part I," *AIChE J.*, **13**, 678 (1971).  
 U.S. Federal Register, **35**, 219 (Nov. 10, 1970).  
 Vanderveen, J. W., D. Luss, and Amundson, N. R., "Stability of Adiabatic Packed Bed Reactors: Effect of flow variations and coupling between the particles," *AIChE J.*, **14**, 636 (1968).  
 Vardi, J., and W. F. Biller, "Thermal behavior of an exhaust gas catalytic converter," *Ind. Eng. Chem. Process Design Develop.*, **7**, 83 (1968).  
 Vortmeyer, D., and W. Jahnelt, "Moving reaction zones in fixed bed reactors under the influence of various parameters," *Chem. Eng. Sci.*, **27**, 1485 (1972).  
 Waede Hansen, K., "Analysis of transient models for tubular reactors by orthogonal collocation," *ibid.*, **26**, 1555 (1971).  
 ———, "Simulation of the transient behavior of a pilot plant fixed-bed reactor," *ibid.*, **28**, 723 (1973).  
 ———, H. Livbjerg, and J. Villadsen, "Dynamic Modeling of Catalytic Fixed-Bed Reactors," IFAC Symp. on Digital Simulation of Continuous Processes, Győr, Hungary (1971).  
 Wei, J., "Catalysis and Reactors," *Chem. Eng. Progr. Monograph Ser. No. 6*, **65**, (1969).  
 Young, L. C., and B. A. Finlayson, "Axial Dispersion in Nonisothermal Packed Bed Chemical Reactors," *Ind. Eng. Chem. Fundamentals*, **12**, 412 (1973).

Manuscript received November 13, 1973; revision received and accepted March 1, 1974.