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Modeling of high-temperature catalytic combustors: Comparison between theory and experimental data

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Abstract

The objective of this work was to model experimental results using the simplest possible mathematical model. Here we report on preliminary results obtained with a one-dimensional model used for parameter-fitting of experimental combustion data with an inlet temperature ramp. It was possible to fit our one-dimensional model with simple power law kinetics to an experimental curve. It was also possible to use a quasi-steady state model with a computing time about a hundred times shorter than for a corresponding transient model. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: One-dimensional model; Parameter fitting; Quasi-steady state model

1. Introduction

A mathematical model may be very sophisticated, with many details and highly rigorous from a mathematical point of view, but it may also include many simplifying assumptions. In mathematical modeling of chemical reactors one usually wants to find the simplest mathematical model describing the reactor and the kinetics of the reaction. This means that one makes a trade-off between the difficulty to solve the model and the accuracy of the modeling results. This is usually necessary since sophisticated models of chemical reactors often are too difficult to solve to be useful. This problem of simplification, that is to what extent mathematical models can be simplified for a given reactor modeling problem, has been studied for monolith reactors in general by Young and Finlayson [1], and Heck et al. [2] and for high-temperature catalytic combustion monolith reactors in particular by Groppi et al. [3] and Hayes et al. [4].

In a previous work [5] we used a one-dimensional transient model for a numerical study of the importance of the porosity and pore surface area in the washcoat for the light-off of a high-temperature monolith combustor. It is worth noting that, as discussed in that paper, for such a study a more rigorous modeling of the diffusion with reaction in the washcoat is required than had been used in some previously published work on modeling of high-temperature catalytic combustion.

High-temperature catalytic combustion constitutes a number of problems for research and development work [6]. The solution to many of those problems may benefit from applying mathematical modeling as a research tool [7,8].

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In attempting to model experimental results from high-temperature catalytic combustion we have chosen to initially use a one-dimensional model for modeling the monolith reactor and to use simple power law kinetics for the chemical reactions. This paper reports our experiences and preliminary results in parameter-fitting such a model to experimental data obtained in this laboratory [9].

2. Model

The one-dimensional model used for parameter evaluation of the heterogeneous rate constants was developed in a previous work [5]. Much of the model formulation follows the earlier work and the details are therefore not provided here. Unlike the previous work, the model was expanded to simulate experiments where the inlet temperature to the monolith was increased linearly with time. This affects the boundary conditions of the model.

Generally, the model considers the transient state adiabatic operation of a well mixed plug flow reactor. The reaction occurs both on the catalyst surface (including pore diffusion) and in the gas phase. Limiting assumptions invoked in the model formulation include:

1. negligible accumulation of mass and energy in the gas phase;
2. negligence of thermal radiation;
3. constant pressure;
4. negligible radial temperature gradients in solid;
5. constant heat and mass transfer coefficients;
6. constant physical properties of monolith and washcoat.

The equations in nondimensional form, with emphasis on the mathematical structure rather than the modeling details, are as follows:

$$\frac{\partial \Theta_g}{\partial \xi} = \alpha_6(r_g \Delta H - \alpha_4 \Theta_g + \alpha_5 \Theta_s), \tag{1}$$

$$\Theta_g \frac{\partial \Psi}{\partial \xi} = \alpha_1 \Psi f(\Theta_s) + (1 + \alpha_2 \Psi)\alpha_3 r_g - \alpha_6 \Psi(\alpha_4 \Theta_g - \alpha_5 \Theta_s), \tag{2}$$

$$\frac{\partial \Theta_s}{\partial \tau} = \alpha_7 \Psi f(\Theta_s) + \alpha_8 \frac{\partial^2 \Theta_s}{\partial \xi^2} + \alpha_9 \Theta_g - \alpha_{10} \Theta_s, \tag{3}$$

where Θ_g, Ψ, Θ_s, ξ, τ are scaled variables representing the gas temperature, the gas concentration, the solid temperature, the axial distance and the times, respectively. α_1–α_{10} are constants used in the equations above. With this model, the conversion as a function of inlet gas temperature was calculated. The parameter estimation of the rate constants was approached by minimizing the sum of the squares of the difference between outlet conversion of the model and experimental data. Due to the slowly varying increase in inlet temperature, we made the further assumption in the data fitting calculations that the system was in a quasi-steady state by setting $(\partial \Theta_s/\partial \tau)=0$. This was important for reducing the computer time for solving the model. After the rate constants were evaluated, the transient model was used to simulate the experiments and to see whether the quasi-steady state approximation was reasonable.

3. Numerical solution method

The model equations (1)–(3), with appropriate boundary and initial conditions, were solved numerically by discretization. The space derivative is approximated with the finite difference method thereby transforming the partial differential equations (1) and (2) to nonlinear algebraic equations, while (3) was changed into ordinary differential equations. Hence, after discretization of the space variable ξ we obtained an index-1 differential-algebraic (DAE) system of equations:

$$0 = f_1(\Theta_g, \Psi, \Theta_s), \tag{4}$$

$$0 = f_2(\Theta_g, \Psi, \Theta_s),$$

$$\frac{d\Theta_s}{d\tau} = f_3(\Theta_g, \Psi, \Theta_s), \quad \Theta_s(0) = \Theta_{s0},$$

where Θ_g, Ψ, Θ_s now are τ-dependent vectors. In our application the accuracy obtained by discretizing the ξ-interval (0,1) into N=40 grid points was enough for our purposes.

Since the DAE-system (4) is stiff, it was solved with the Euler backwards method, starting from $\Theta_s(0)=\Theta_{s0}$:

$$0 = f_1\left(\Theta_g^{(n+1)}, \Psi^{(n+1)}, \Theta_s^{(n+1)}\right), \tag{5}$$

$$0 = f_2\left(\Theta_g^{(n+1)}, \Psi^{(n+1)}, \Theta_s^{(n+1)}\right),$$

$$\Theta_s^{(n+1)} - \Theta_s^{(n)} = \Delta\tau f_3\left(\Theta_g^{(n+1)}, \Psi^{(n+1)}, \Theta_s^{(n+1)}\right),$$

$$\tau^{(n+1)} = \tau^{(n)} + \Delta\tau.$$

In (5) the variables at time $\tau^{(n+1)}$ were solved from the nonlinear system of algebraic equations using a modified Newton method. The structure of (5) is sparse; the Jacobian, J, is sparsely banded which is utilized both when calculating a numerical difference approximation of J and when solving the linear system of equations in each iteration. Utilizing the sparsity structure reduces the execution time considerably. A reasonable execution time for solving the model equations (4) on a computer is necessary when performing parameter estimation in which case (1)–(3) are solved several times. By using the quasi-steady state assumption the computer time can be further reduced. Instead of solving the transient case (4), we put $(d\Theta_s/d\tau) = 0$ and solved a number of nonlinear systems of equations corresponding to a sequence of boundary conditions of Θ_g. The parameters were, in this preliminary study, estimated using a nonlinear least squares routine from the Matlab library.

4. Experimental

The experimental combustion data were obtained using a monolithic 10 wt% Cr_2O_3/Al_2O_3 catalyst. The details concerning preparation, aging, and characterization have been reported elsewhere [9]. Combustion of a 1.67 vol% methane in air mixture was studied in a ceramic tubular reactor. The reactor was placed in a furnace, programmed for a linear temperature increase of 2°C/min. The air was preheated before being mixed with the fuel, just upstream of the catalyst. The total flow was 5.7 Nl/min and the data were obtained at atmospheric pressure. The combustion products were analyzed on-line using a Balzers QMG 421C quadrupole mass spectrometer.

5. Results and discussion

The values of the fixed parameters used in the parameter-fitting calculations are given in Table 1.

Table 1
Model parameters used in the simulations

Channel length (cm)	2.5
Channel width (cm), square	0.125
Monolith wall thickness (cm)	0.015
Washcoat thickness[a] (μm)	17.3
Washcoat surface area (m^2/g)	112
Washcoat porosity[b] (cm^3/g)	0.45
Washcoat average pore diameter[b] (Å)	162
Effective diffusivity of methane (cm^2/s)	0.011
Gas velocity at STP (cm/s)	34

[a]Average value obtained from washcoat weight and density.
[b]Parameter used in evaluation of effective diffusivity.

The effective diffusivity of the washcoat was estimated from pore size distribution data using the random pore model.

The parameter-fitting calculations for the experiments with a linear inlet temperature ramp were done with the quasi-steady state model. In Fig. 1 the fitted curve according to this model is compared to a transient model simulation without the quasi-steady state assumption. The error introduced by the quasi-steady state assumption is small. Therefore, this assumption is very valuable since the computer time for solving the model with the quasi-steady state assumption is two orders of magnitude less than for the transient model. This gives very significant computer time savings in parameter fitting when the model must be solved hundred or thousand of times.

In Fig. 2 the fitted curve is compared to the experimental results. The fitted parameters were the pre-exponential factor and the activation energy of the catalytic reaction, and the corresponding parameters for the homogeneous reaction. However, at this preliminary stage, it was not possible to get the computer program to converge when fitting all four parameters. Instead, we let only the two catalytic reaction parameters be fitted by the program for some combinations of fixed parameter values for the homogenous reaction. Since the effect of those parameters on the conversion is fairly attenuated it was not difficult to find the values which gave the rather good fitted curve shown in Fig. 2. As a comparison a curve for another combination of the parameter values for the homogenous reaction, which does not fit well with the experimental results, is also shown in Fig. 2. This curve demonstrates the attenuated, but yet significant, effect of those parameters on the simulation results.

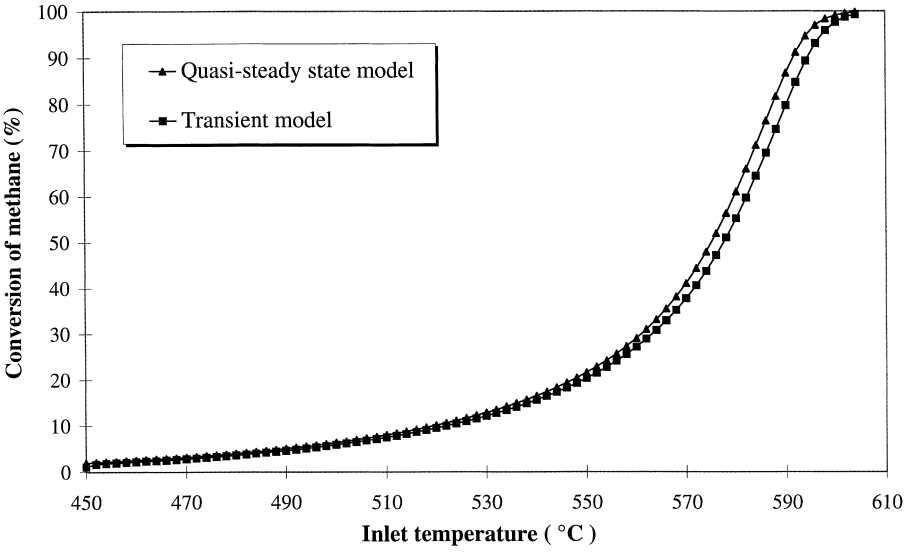

Fig. 1. Comparison between quasi-steady state- and transient model.

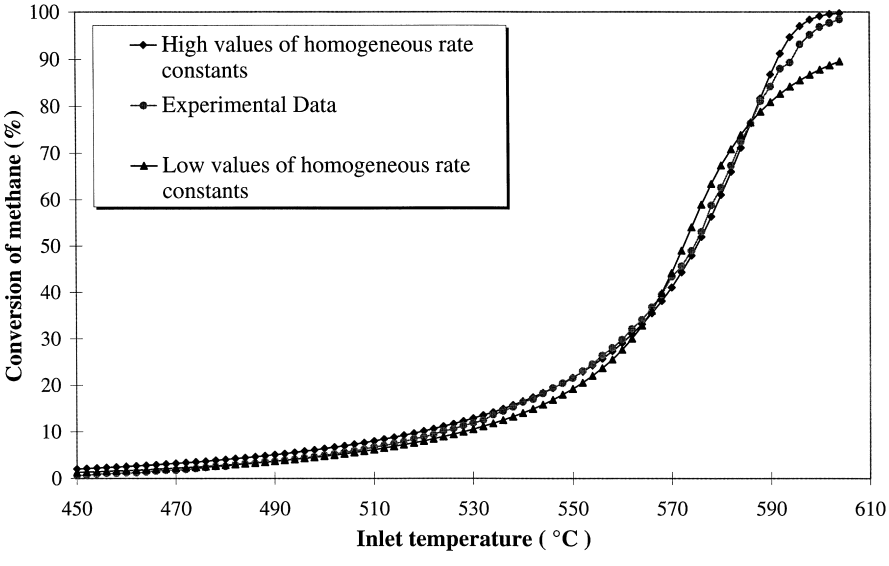

Fig. 2. Data fitting of experimental results with linearly increased inlet temperature.

The fitted parameter values for the two different homogeneous rate cases are given in Table 2.

Due to the preliminary state of our investigation as well as the well-known general aspects on interpretation of parameter fitting results one should be careful to draw definite conclusions from the results in Fig. 2. However, as a hypothesis which merits further investigation, we suggest that this result gives some hints about the importance of the homogeneous combustion compared to the catalytic process in a catalytic combustor.

We have further studied the properties of the simulation case corresponding to the fitted curve in Fig. 2 by calculating the Thiele modulus and the F-ratio

Table 2
Fitted parameter values for two different homogeneous rate cases

	Case of high homogeneous rate constants	Case of low homogeneous rate constants
E_g (fixed)[a]	167.32×10^3 (J/mol)	197.44×10^3 (J/mol)
K_g (fixed)[a]	2.51×10^{15} (cm^3/mol s)	2.51×10^{13} (cm^3/mol s)
E_s (fitted)[b]	104.87×10^3 (J/mol)	121.30×10^3 (J/mol)
K_s (fitted)[b]	244 (cm/s)	2330 (cm/s)

[a]Homogeneous activation energy (E_g) and preexponential factor (K_g).
[b]Catalytic activation energy (E_s) and preexponential factor (K_s).

defined in [5], the latter characterizing external mass transfer. Again the results should be taken as a hypothesis for further investigation. These results are remarkable since they unexpectedly show that the mass transfer resistance effects, both pore diffusion resistance and external resistance, are small all over the reactor, which means that the chemical reaction is rate determining, for most of the inlet temperatures. Even for the highest inlet temperatures at the end of the temperature ramp those mass transfer effects are small except at the end of the reactor where they increase.

Finally, it is worth mentioning that the simulation results depend on the boundary conditions especially at the inlet. Some possible options are to consider the inlet of the monolith adiabatic or to assume temperature equilibrium between the inlet of the monolith and the inlet gas stream, resulting from the effect of radiation. In the present investigation we used the latter option.

6. Conclusions

In a first attempt it was possible to fit our one-dimensional model with simple power law kinetics to an experimental curve.

It was possible to use a quasi-steady state model for simulation of the experiments with a linear inlet temperature ramp. The computer execution time was two orders of magnitude less than that for using a transient model.

As a hypothesis which merits further investigation the fitted simulation case gives hints about the importance of homogeneous combustion. Another hypothesis suggests that the chemical reaction to a large extent is rate determining for the catalytic reaction.

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