

## MODELING THE REACTIVE PROCESSES WITHIN A CATALYTIC POROUS MEDIUM

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### ABSTRACT

A one-dimensional modelling approach to the reactive processes within a heated homogeneously premixed fuel-air mixture in its passage through a non-adiabatic catalytically reactive porous medium is described. The approach accounts for the three modes of heat transfer between the solid and gas phases, as well as detailed kinetics of both phases. Results presented relate mainly to the fuels methane and hydrogen. It is shown that suitable catalytic beds can oxidize more fully and at lower temperatures very lean mixtures. Some of the results of the simulation using the model developed are shown to validate well against our own experimental results. Comparison of corresponding results obtained while employing overall single step reactions showed significant deviations from those of the more comprehensive approach. The implication of applying the modelling approach to some practical applications is outlined.

### NOMENCLATURE

$a_v$	specific geometric surface
$a_c$	catalytic surface area to volume ratio
$c$	constant pressure specific heat
$D_{i,m}$	diffusivity of species $i$
$h$	convective heat transfer coefficient
$h_i$	overall heat loss coefficient
$H_i$	enthalpy of species $i$
$k$	thermal conductivity
$k_{i,m}$	convective mass transfer coefficient of species $i$
$M_i$	molar mass of species $i$
$\dot{R}$	species production rate in
$T$	temperature
$u$	axial velocity
$Y_i$	mass fraction of species $i$
$s_v$	surface to volume ratio of the reactor wall

### Greek Symbols

$\varepsilon$	porosity
$\eta$	effectiveness factor
$\phi$	equivalence ratio
$\rho$	density

### Subscript

$g$	gas phase
$s$	surface, solid

### INTRODUCTION

It is commonly known that the rates of oxidation reactions of very lean mixtures of common gaseous-fuels in air can be increased significantly through the presence of some catalytic materials. Complete combustion in catalytic devices can be achieved at lower temperatures resulting in very low NO<sub>x</sub> and other pollutants (Everaert et al. 2000, Forzatti 2000). It would be then possible to utilize the energy release from gaseous fuel mixtures of low heating value that are normally considered to be un-exploitable waste. Catalytic reactors that can be used for combustion are of monolith or packed-bed types that operate on essentially the same principles. Numerous experimental and theoretical investigations have been conducted over the years with the aim of improving the understanding of catalytic systems with most focusing on the monolith type. Various methods have been proposed for simulating the combustion process in this type of catalytic reactors (Goralski et al. 1999, Groppi et al. 2001, Maestri et al. 2005, Marin et al. 2005.). However due to the complexity of the physical and chemical phenomena involved, many of these models were developed for specific applications and over a narrow range of operating conditions. Also, most of them neglect some important aspects of the processes involved, such as for example the gas phase reaction activity (Aube et al. 2000) or to assume that the gas and solid phases are throughout in thermal equilibrium (Groppi et al. 1999). Moreover, the majority of models treated the surface and gas reactions as global reactions of the Arrhenius type (Hayes et al. 1992, Groppi et al. 1995, Groppi et al. 1999, Aube et al. 2000) with the needed kinetic data obtained by matching with the relevant experimental data. However, such approaches do not predict the overall reaction rates over a sufficiently wide range of fuel-air mixture concentrations and temperatures. Recently improved models include 2-D and some 3-D treatment of the flow within the monolith and introduce multi-step reaction mechanisms (Quiceno et al. 2000, Manzumder et al. 2002, Deutschmann et al. 2000) which would provide a more realistic simulation of the fuel oxidation rates. The multi-step mechanisms for gas phase reactions are rather well developed and available in the literature for different fuels over a wide range of operational conditions (Deutschmann et al. 2000, Aghalayam et al. 2003). Multi-step mechanisms for catalytic surface reactions depend strongly on the chemical composition of the catalyst employed. Recently, several mechanisms were proposed for Pt catalyst at certain operating conditions (Chou 2000, Quiceno et al. 2000, Reiken et al. 2005). However, the incorporation of multi-step mechanisms in the model resulting in a stiff system of equations of chemical reactions increases the numerical complexity of the model. Another important aspect of modelling combustion processes in a catalytic reactor is the selection of suitable models for all three

major heat transfer modes. Several correlations are available for modelling convection heat transfer, that were shown to yield essentially similar results (Harriot 2003). However, the radiation heat transfer from the solid to gas phases is usually taken into account using an 'effective thermal conductivity' concept. More superior approaches for accounting of radiation heat transfer are available (e.g. method of intensity radiation equation), but tend to contribute towards increased numerical complexity and time.

In comparison with monolith type reactors there is much less information available on catalytic combustion in packed bed reactors, and there are only a few mechanisms proposed for the catalytic oxidation of lean mixtures of methane and air on Pt. Accordingly, the objective of the present contribution is to develop a model of reactive gaseous flow within a catalytic packed bed that would include improved modelling for heat transfer and consider more realistic multi-step reaction mechanisms for both simultaneous gas phase and surface reactions. Such a modelling approach is then applied to investigate the effects of changes in the key operational parameters on the fuel oxidation within the packed bed reactor, including the effects of fuel type and the presence of diluents. The approach can be also employed in combination with experimental data to derive much needed kinetic data for catalytic surface reactions when employing different catalysts and fuels.

## MODEL DESCRIPTION

A schematic diagram of the packed bed being considered is shown in Figure 1

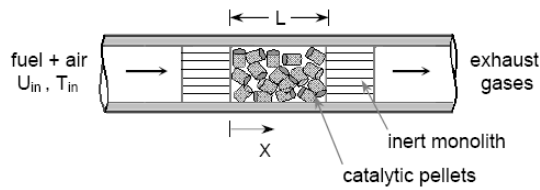


Figure 1. Schematic diagram of the reactor

A premixed, preheated homogeneous fuel-air mixture enters the cylindrical reactor packed with catalytic pellets. The bed is initially at a uniform temperature. The fuel and oxygen diffuse from the bulk fluid to the catalyst surface where they are adsorbed and reacted. The products formed, leave the surface via a desorption process and travel from the surface to the gas mixture via mass diffusion. A portion of the heat released due to the surface reactions increases the solid temperature, while the remainder is transferred to the gas. The heat received by the gas may be high enough to promote gas phase reactions. The three modes of heat transfer (conduction, convection and radiation) contribute jointly to the transport of heat within the reactor. The reactor is assumed to operate non-adiabatically and at atmospheric pressure. The flow within the reactor is assumed to be one-dimensional. The gas and solid are not in local thermal equilibrium. Therefore, separate energy equations are considered for each phase. Radiation heat transfer in the gas phase is considered to be negligible in comparison to the solid pellets radiation. The thermo-physical properties of the gas species are functions of the local temperature and composition. The thermal conductivity of pellets is also considered to be a function of temperature. However,

other properties of the solid phase such as density, specific heat and emissivity are assumed to be uniform and temperature independent since their values were considered to vary insignificantly over the range of temperatures considered (Green et al. 2008). The flow inside the reactor is laminar and the governing equations of continuity, energy balance for solid, energy balance for fluid, mass balance of species in the gas phase and on the catalyst surface are the following:

continuity:

$$\frac{\partial \rho_g}{\partial t} + \frac{\partial (\rho_g u)}{\partial x} = 0 \quad (1)$$

species mass balance in gas phase

$$\rho_g \frac{\partial Y_{g,i}}{\partial t} + \rho_g u \frac{\partial Y_{g,i}}{\partial x} = - \frac{\partial (\rho_g D_{i,m} (\partial Y_{g,i} / \partial x))}{\partial x} + M_i \dot{R}_{g,i} + \frac{k_{i,m}}{\varepsilon} a_v \rho_g (Y_{s,i} - Y_{g,i}), \quad (i=1, \dots, N_g) \quad (2)$$

species mass balance on surface:

$$k_{i,m} a_v \rho_g (Y_{g,i} - Y_{s,i}) = \eta a_c M_i \dot{R}_{s,i}, \quad (i=1, \dots, N_g) \quad (3)$$

energy balance for gas phase:

$$\rho_g c_g \frac{\partial T_g}{\partial t} + \rho_g c_g u \frac{\partial T_g}{\partial x} = - \frac{\partial (k_g (\partial T_g / \partial x))}{\partial x} + \frac{h}{\varepsilon} a_v (T_s - T_g) + \sum_{j=1}^{N_g} M_j \dot{R}_{g,j} H_j \quad (4)$$

energy balance for solid phase:

$$\rho_s c_s \frac{\partial T_s}{\partial t} = - \frac{\partial (k_s (\partial T_s / \partial x))}{\partial x} + \frac{h}{1-\varepsilon} a_v (T_g - T_s) - h_s S_v (T_s - T_{amb}) + \sum_{j=1}^{N_g} \frac{a_c}{1-\varepsilon} M_j \eta \dot{R}_{s,j} H_j \quad (5)$$

The convective heat transfer and mass transfer coefficients were determined using Chilton Colburn approach. The diffusion of species from the fluid bulk to the surface of the pellets and from there into the pores has been taken into account via a convective mass transfer coefficient (Yoshida et al. 1962) and an effectiveness factor, respectively. The effectiveness factor, which is a function of porosity, gas species concentration at the pellet surface, surface reaction rates and the diffusion coefficients of the gas species, was estimated using Thiele's approach (Harriot 2003) and was computed for every computational cell and every time step during the simulations. Heat loss to the surroundings was also included in the model. The overall heat transfer coefficient includes the thermal resistances of the boundary layer near the wall, conduction through the reactor wall and natural convection outside of the reactor (Harriot 2003). The effective thermal conductivity of the pellets, accounts for both conduction and radiation heat transfers. The multi-step mechanisms for the gas phase and surface reactions have been described and listed by authors elsewhere. They are based on mechanisms proposed in (Zerkel et al. 2000, Quiceno et al. 2000, Deutschmann et al. 2000, Chou 2000, Aghalayam et al. 2003, Reiken et al. 2005) with some relatively small modifications (Shahmiri et al. 2009).

## NUMERICAL APPROACH

The governing equations for a packed bed reactor were solved using the commercial software, 'Fluent' along with a number of modifying subroutines (UDF). These

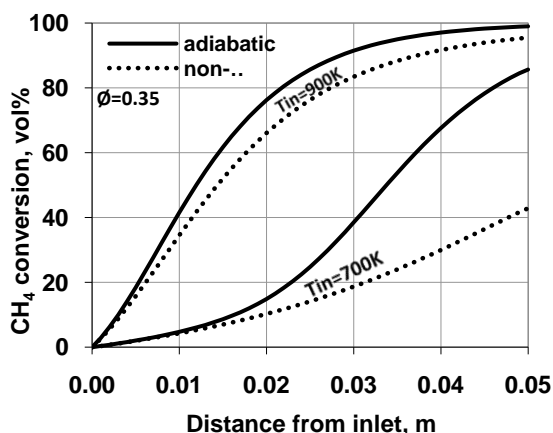
subroutines were developed to compute the thermo-physical properties, heat and mass transfer coefficients, species concentrations in the gas and on the surface, and the amount of heat release. The integrator CVODE (Hindmarsh et al. 2003) was also implemented into the subroutines for solving the system of equations of chemical reactions and obtaining the corresponding temporal concentrations of species at each numerical time step.

The steady state solution for each condition was obtained by performing a sufficient number of iterations. Eight hundred computational cells for spatial discretization of the domain and a time step of 10  $\mu$ s were used in the simulation. To validate the developed model, simulations were conducted for hydrogen and methane for the same operational conditions of the reactor that we experimentally employed previously (Depiak et al. 2003). The reactor bed has inside diameter of 28 mm and length of 50 mm. The bed porosity is 0.4. The catalyst used is polycrystalline Pt deposited on a substrate in the form of cylindrical pellets 3.2 mm long and 3.2 mm diameter made of  $\text{Al}_2\text{O}_3$ . The pressure along the reactor was assumed to be 89 kPa, the same as in the experiments and the ambient temperature was 293 K. For all the cases presented the mixture approach space velocity was  $7.2 \times 10^4 \text{ m}^3/\text{m}^3\text{h}$ . The estimated value of overall heat transfer coefficient was  $280 \text{ W}/\text{m}^2 \text{ K}$ . This value is in agreement with the experimental value obtained for the same reactor (Depiak et al. 2003). To validate the gas phase reaction mechanism employed, the simulations were also conducted for comparative purposes for an inert bed reactor.

The ratio of catalytic surface area to the geometric surface area used in simulations was 2.31 and the catalyst site density was assumed to be  $2.72 \times 10^{-9} \text{ mol}/\text{cm}^2$  (Deutschmann et al. 2000).

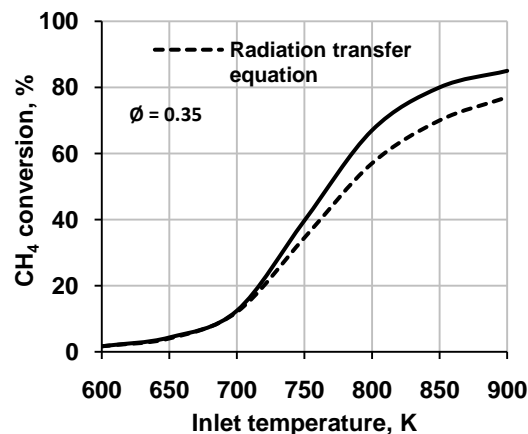
## RESULTS

The results of application of the model showed the importance of proper accounting for external heat loss off the reactor, as shown in Figure 2. At a relatively low inlet mixture temperature of 700 K the methane conversion at the exit from the reactor when operated non-adiabatically is 42%, while it is 85% in the adiabatic reactor.



**Figure 2.**  $\text{CH}_4$  conversion along the reactor for adiabatic and non-adiabatic reactors; Pt catalyst; multi-step reaction model.

The effect of the radiation model employed on methane conversion within the bed is shown in Figure 3. The ‘effective thermal conductivity’ and ‘radiation transfer equation’ models were used for the simulation of methane-air mixture reactions for an equivalence ratio of 0.35, in the reactor with  $\text{Cr}_2\text{O}_3/\text{Co}_3\text{O}_4$  catalyst while using a single-step (global) chemical reaction (a multi-step reaction mechanism is not available at present for such catalyst).



**Figure 3.**  $\text{CH}_4$  conversion at the exit from the reactor as a function of inlet temperature;  $\text{Cr}_2\text{O}_3/\text{Co}_3\text{O}_4$  catalyst; single-step reaction model.

It can be seen that the effect of the radiation model applied tends to be relatively small at relatively low mixture intake temperatures but becomes more noticeable at higher intake temperatures. The calculation time for this case when applying the ‘Radiation Transfer Equation’ model was eight times larger than when employing the ‘effective thermal conductivity model’. Accordingly, the results presented for other simulations were obtained with the ‘effective thermal conductivity’ model accounted for radiation heat transfer.

It was found that the single-step (global) reaction approach can predict the conversion of the fuel in the reactor reasonably well provided that the corresponding experimental data obtained for the same reactor and the same operational conditions were available beforehand to derive the proper kinetic data for the global reaction. It can be seen (Figs. 4 & 5) that the simulation results for  $\text{H}_2$  and  $\text{CH}_4$  conversion over Pt and  $\text{Cr}_2\text{O}_3/\text{Co}_3\text{O}_4$  catalysts are in very good agreement with the corresponding experimental data employed in the kinetic derivation (Depiak et al. 2003).

If such experimental data were not available then resorting to the very time consuming calculations of employing multi-step reaction mechanisms for both the gas and solid phases is justified. This is especially valid, for example, when investigating the effect of changes in equivalence ratio of the feed mixture. It can be seen in Figure 6 that employing a single-step reaction based on kinetic data obtained for a certain equivalence ratio (0.35 in this case) to simulate the behaviour of hydrogen-air mixtures of different equivalence ratios gives very poor agreement with our corresponding experimental data.

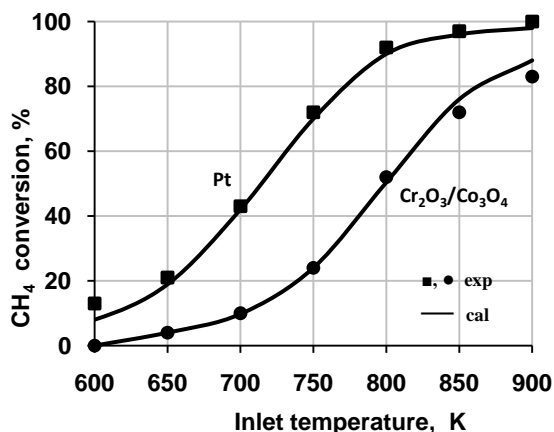


Figure 4. CH<sub>4</sub> conversion as a function of inlet temperature for two different catalysts;  $\Phi = 0.35$ ; single-step reaction model.

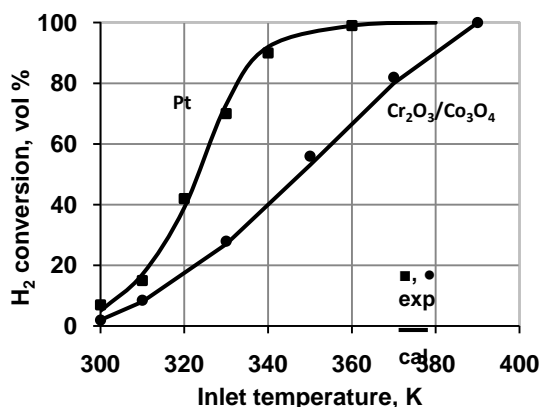


Figure 5. H<sub>2</sub> conversion as a function of inlet temperature for two different catalysts;  $\Phi = 0.35$ ; single-step model.

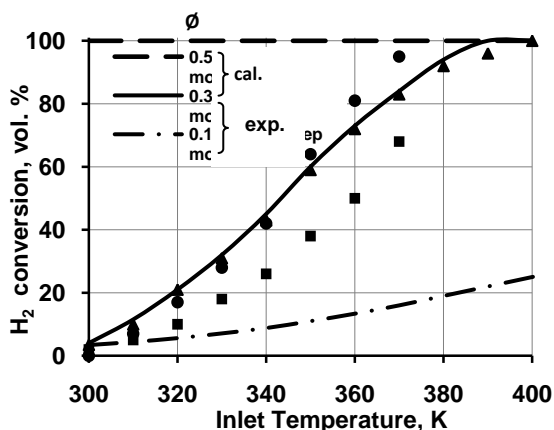


Figure 6. H<sub>2</sub> conversion as a function of inlet temperature for different equivalence ratios; Cr<sub>2</sub>O<sub>3</sub>/Co<sub>3</sub>O<sub>4</sub> catalyst; single-step reaction model.

Although this comparison was conducted for Cr<sub>2</sub>O<sub>3</sub>/Co<sub>3</sub>O<sub>4</sub> catalyst the same trends can be expected for a Pt catalyst. The single-step model overestimates hydrogen conversion rates for richer mixtures and underestimates those for leaner mixtures especially for higher intake temperatures. For example, for a mixture of " $\Phi = 0.5$ " the results of the simulation shows 100% conversion of hydrogen for the intake temperature of 300 K while the corresponding experimental value is only about 2%. Similarly, for a very

lean mixture of  $\Phi = 0.15$  at the inlet temperature of 370 K, the predicted value is 16 % yet the experimental value is 67%.

The need for experimental data beforehand is unnecessary when employing multi-step reaction mechanisms for catalytic surface and gas-phase reactions. Figure 7 shows a comparison between the calculated and experimental values of CH<sub>4</sub> conversion within catalytic (Pt) and non-catalytic (inert) beds for a CH<sub>4</sub>-air mixture with an equivalence ratio of 0.35, while Figure 8 shows a similar comparison for H<sub>2</sub>-air mixture. The agreement appears to be very good, validating the surface and gas-phase reaction mechanisms employed. It can be seen also the enormous effectiveness of the employment of the catalytic bed in comparison with the corresponding case of a non-catalytic bed for both fuels.

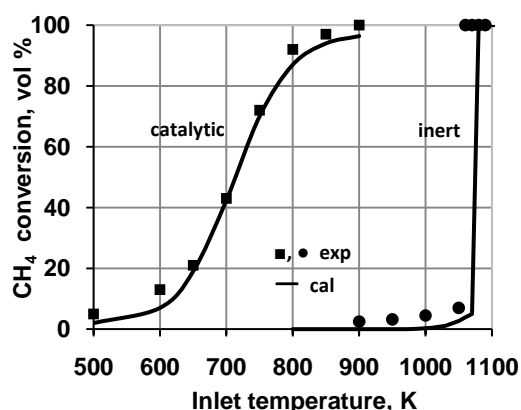


Figure 7. CH<sub>4</sub> conversion as a function of inlet temperature within inert and catalytic reactors;  $\Phi = 0.35$ ; Pt catalyst; multi-step reaction model.

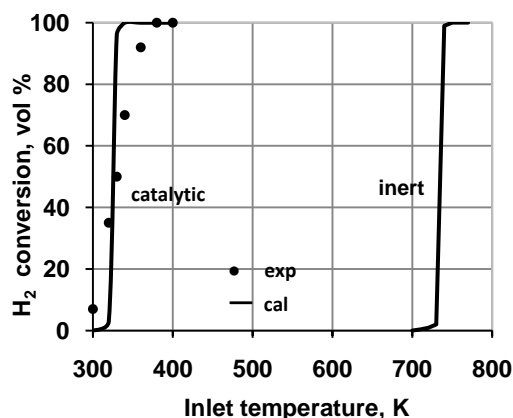
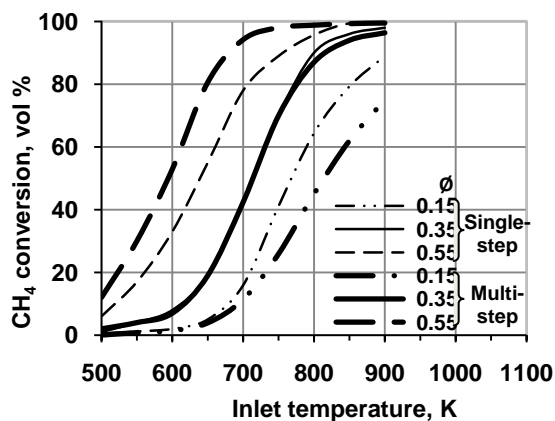


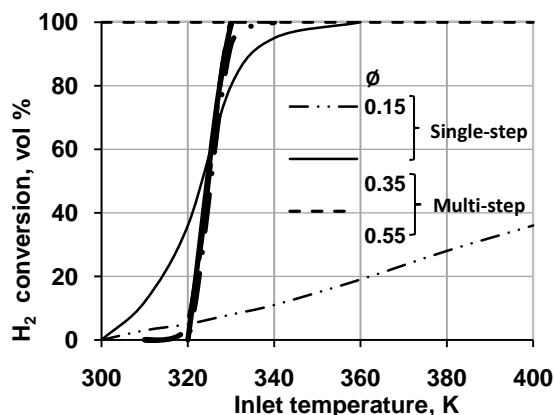
Figure 8. H<sub>2</sub> conversion as a function of inlet temperature within inert and catalytic reactors;  $\Phi = 0.35$ ; Pt catalyst; multi-step reaction model.

The comparison of the results of the simulations obtained with these two types of reaction models for both CH<sub>4</sub>-air and H<sub>2</sub>-air mixtures of different equivalence ratios and inlet temperatures is shown in Figs. 9 and 10, respectively. It can be seen, that the results deviate greatly, especially for hydrogen-air mixtures. Predicted results when based

on using the detailed kinetic scheme produce much more realistic results.



**Figure 9.** CH<sub>4</sub> conversion as a function of inlet temperature for different equivalence ratios using different reaction models; Pt catalyst.



**Figure 10.** H<sub>2</sub> conversion as a function of inlet temperature for different equivalence ratios using different reaction models; Pt catalyst.

## CONCLUSION

The model developed was shown to allow the prediction of the oxidation of lean methane-air and hydrogen-air mixtures in catalytic and non-catalytic packed bed reactors. It is shown that the employment of an 'effective thermal conductivity' to account for radiation heat transfer is adequate for producing satisfactory predictions. A single-step approach for surface and gas-phase reactions can be used only when derived from sufficient experimental data that need to be available for the same reactor and operational conditions. The use of such data for different operating conditions can lead to significantly erroneous results. However, the use of multi-step reaction mechanisms produces results that are in good agreement with a much wider range of experimental data.

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