Mathematical modeling of methane oxidation caused by a laser heated inert particle

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The safety of optical fibres in explosive atmospheres, is questioned especially when a high level of optical power is delivered. If energy is focussed onto small particles, ignition of the gas might result from heating of the particles. This would occur, for example, in an underground coal mine where optical fibre sensor and communication systems are used. It is therefore necessary to quantify the power levels at which a combustible gas can be ignited by radiative heating of small particles and investigate the physical and chemical mechanisms involved in the processes. However, the investigations of the ignition caused by laser heating of inert particles or fibres are very limited, [1, 4, 6-7, 9-15, 18, 21].

Modeling of the unsteady process of methane oxidation caused by laser heated inert particles has been investigated in the present work. The model considers the process of heat and mass transfer, which take place in the case of a single particle heated by infrared laser radiation. A stagnant combustible mixture of methane and air surrounds the particle. The following assumptions have been adopted within the mathematical model: the particle was a chemically inert sphere of constant size; the physical properties of the particle (incl. its absorptivity ratio and emissivity) were independent of the temperature; the particle was heated only at its surface; the particle was stagnant; pressure was constant; the gas-phase reaction was represented by a one-step irreversible overall process; the values characteristic of a chemical reaction (activation energy, \(E\), pre-exponential factor, \(A\), heat of reaction, \(H\)) were constant throughout the process; viscous dissipation and natural convection of the gas due to temperature variations were negligible; except for chemical reaction there was no volume heat source; the changes of the critical pressure, \(p_c\) and temperature, \(T_c\), caused by the appearance of the products of the chemical reaction were not examined; the influence of the opposite directed diffusion of the products of combustion was not considered.

The transient energy balance of the system has been used to examine its conductive, connective and radiative components. The dimensional energy balance equation for the particle is given by:

\[
(1.1) \quad r^2 \frac{\partial}{\partial r} \left( r^2 \frac{\partial (k_p \rho_p T_p)}{\partial r} \right) - \frac{\partial (\rho_p c_p T_p)}{\partial t} = 0, \quad \text{where} \quad c_p, \ k_p, \ T_p \ \text{and} \ \rho_p \ \text{are the thermal capacity, conductivity, temperature and density of the particle.} \quad r \ \text{is the radial distance and} \quad t \ \text{- time.} \quad \text{The gas phase}\n\]

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In (1.2) \( Q \) represents the heat generated by the gas chemical reaction, and the heat generation is proportional to the consumption of the fuel - \( Q = H \left( [\text{CH}_4]_0 - [\text{CH}_4] \right) \). For the reaction represented by the stoichiometric equation \( \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \) the over-all methane disappearance rate expression was calculated by using of the experimentally founded by Dryer, F.L., and Glassman, I., [5], for the post induction phase oxidation of methane relation: 
\[
\frac{d[\text{CH}_4]}{dt} = k[\text{CH}_4]^{0.7}[O_2]^{0.8}.
\]

The mass diffusivity, \( D \), for a binary system at low pressures is a function of temperature, pressure and it is almost independent of the composition for the given gas pair. Slattery and Bird, [19], from a combination of kinetic theory and corresponding-states arguments, have developed equation (1.3) for estimation of \( D \) at low pressures:
\[
\frac{d[\text{CH}_4]}{dt} = \frac{D}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial [\text{CH}_4]}{\partial r} \right) - k[\text{CH}_4]^{0.7} \left( [O_2]_0 - 2[\text{CH}_4] \right)^{0.8}.
\]

The mass diffusivity, \( D \), is the gas molecular weight of the components. It was assumed that the process is isobaric (\( p = p_{\text{atm}} \)), and corresponding-states arguments, have developed equation (1.3) for estimation of \( D \) at low pressures:
\[
pD = \left( p_{c, \text{CH}_4}, p_{c, \text{air}} \right)^{0.3} \left( T_{c, \text{CH}_4}, T_{c, \text{air}} \right)^{0.12} \left( \frac{1}{M_{\text{CH}_4}} + \frac{1}{M_{\text{air}}} \right)^{0.12} = a \left( \frac{T}{T_{c, \text{CH}_4}, T_{c, \text{air}}} \right)^b,
\]

where \( M \) is the molecular weight of the components. It was assumed that the process is isobaric (\( p = p_{\text{atm}} \)), and the changes of the critical pressure, \( p_c \), and temperature, \( T_c \), caused by the appearance of the products of the chemical reaction were not examined. The influence of the opposite directed diffusion of the products of combustion was not considered too.

\[
p_{c, \text{CH}_4} = 45.8, \text{ atm}; \quad p_{c, \text{air}} = 36.4, \text{ atm}; \quad T_{c, \text{CH}_4} = 190.7, \quad K; \quad T_{c, \text{air}} = 132.0, \quad K; \quad M_{\text{CH}_4} = 16.04, \text{ mol}; \quad M_{\text{air}} = 28.97, \text{ mol};
\]

and for non-polar gas-pairs, \( a = 2.745 \times 10^{-4}, \quad b = 1.823 \). After the substitution \( D \) becomes, \( D = 6.7 \times 10^{-8} p^1.823, \quad m^2 s^{-1} \).

The methane concentration depends on its diffusivity and reaction rate. The combination of the second Fick’s law of diffusion with the over-all methane disappearance rate expression gives:
\[
\frac{\partial [\text{CH}_4]}{\partial t} = \frac{D}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial [\text{CH}_4]}{\partial r} \right) - k[\text{CH}_4]^{0.7} \left( [O_2]_0 - 2[\text{CH}_4] \right)^{0.8}.
\]

The following data was used for calculation of \( D \), [3, 17]:
\[
p_{c, \text{CH}_4} = 45.8, \text{ atm}; \quad p_{c, \text{air}} = 36.4, \text{ atm}; \quad T_{c, \text{CH}_4} = 190.7, \quad K; \quad T_{c, \text{air}} = 132.0, \quad K; \quad M_{\text{CH}_4} = 16.04, \text{ mol}; \quad M_{\text{air}} = 28.97, \text{ mol};
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The methane concentration must satisfy the conditions:
\[
[\text{CH}_4] = [\text{CH}_4]_0 \quad \text{at} \quad t = 0; \quad \frac{d[\text{CH}_4]}{dr} = 0 \quad \text{on} \quad r = r_p, \quad \text{and} \quad r \to \infty.
\]

In order to place the above system into a non-dimensional form, which is suitable, for computational purposes new independent variables and constants were defined:
\[
t = t^* \tau, \text{ where } t^* = \frac{r_p^2 \rho_p c_p}{k_p}; \quad r = r_p z, \quad \text{and} \quad x = \begin{cases} z: 0 \leq z \leq 1; & T_p = T_a T_1; \quad T_k = T_a T_2; \quad J_1 = \frac{\alpha_{p, A} q r_p}{k_p T_a} \\
z^{-1}: z \geq 1 & J_2 = \frac{\overline{\varepsilon} \sigma T a^3 r_p}{k_p}; \quad N u = \frac{h r_p}{k_p}; \quad F_p = \frac{\rho p c_p}{k_p}; \quad F_g = \frac{\rho g a c_g a}{k_g g}; \quad J = F_p / F_g; \quad \tau = J^{-1} t; \end{cases}
\]

\[
\begin{align*}
\tilde{H} &= \frac{t^* [\text{CH}_4]_0}{[\text{CH}_4]_0}; \quad \tilde{Q} = \tilde{H}(1 - y); \quad J_3 = \alpha_{t^* [\text{CH}_4]_0}^{0.5}; \quad \tilde{D} = 6.7 \times 10^{-8} T a^{1.823} F_p; \quad x_i = \frac{[O_2]}{[\text{CH}_4]_0} \quad \text{and} \quad \tilde{E} = \frac{E}{T_a R}. \quad \text{As noted above the expression for } k_g, \rho_g \text{ and } c_g \text{ were taken to be functions of}
\end{align*}
\]
the gas temperature given by \( k_g = k_{_{g,u}} \tilde{T}_g \); \( \rho_g = \rho_{_{g,u}} \tilde{\rho} \); \( c_g = c_{_{g,u}} \tilde{c} \), and their non-dimensional forms are given by:

\[
\tilde{k} = 1 + \frac{K_1 T_u}{K_0} (T_2 - 1) + \frac{K_2 T_u^2}{K_0} (T_2 - 1)^2 + \frac{K_3 T_u^3}{K_0} (T_2 - 1)^3,
\]

\[
\tilde{\rho} = 1 + \frac{R_1 T_u}{R_0} (T_2 - 1) + \frac{R_2 T_u^2}{R_0} (T_2 - 1)^2 + \frac{R_3 T_u^3}{R_0} (T_2 - 1)^3,
\]

\[
\tilde{c} = 1 + \frac{C_1 T_u}{C_0} (T_2 - 1) + \frac{C_2 T_u^2}{C_0} (T_2 - 1)^2 + \frac{C_3 T_u^3}{C_0} (T_2 - 1)^3.
\]

The governing equations than become:

\[
\frac{\partial T_1}{\partial t} = J^{-1} x^{-2} \frac{\partial}{\partial x} \left( x^3 \frac{\partial T_1}{\partial x} \right), \quad \text{and} \quad \frac{\partial (\tilde{\rho} \tilde{c} T_2)}{\partial t} = x^{-2} \frac{\partial}{\partial x} \left( x^6 \frac{\partial (\tilde{k} T_2)}{\partial x} \right) - 6x^3 \frac{\partial (\tilde{k} T_2)}{\partial x} + \frac{\tilde{Q}}{J}
\]

together with the equation for the methane concentration, (2.3):

\[
\frac{\partial y}{\partial t} = \frac{D}{J x^2} \frac{\partial}{\partial x} \left( x^6 T_2^{1.823} \frac{\partial y}{\partial x} \right) - \frac{D}{J} x^3 T_2^{0.823} \left[ 6T_2 + 1.823x \frac{\partial T_2}{\partial x} \right] \frac{\partial y}{\partial x} - \frac{J_3}{J} y^{0.7} (x - 2y)^{0.8} \exp \left( - \frac{E}{T_2} \right)
\]

which must be solved subject to the initial and boundary conditions:

\[
T_1 = T_2 = y = 1 \text{ at } \tilde{t} = 0; \quad \frac{\partial T_1}{\partial x} = 0, \quad T_2 = 1, \quad \frac{\partial y}{\partial x} = 0 \text{ on } x = 0; \quad \frac{\partial T_1}{\partial x} = J_1 - Nu(T_1 - 1) - J_2 (T_1^4 - 1), \quad T_2 = T_1, \quad \text{and} \quad \frac{\partial y}{\partial x} = 0 \text{ on } x = 1.
\]

The systems of partial differential equation was solved using the routine D03PCF from the NAG suite of subroutines, [20]. This routine employs a finite difference discretization in the spatial direction and the method of lines was used to reduce the partial differential equations to a system of ordinary differential equations. The resulting system of time dependent ordinary differential equations was solved using a backward differentiation formula method. Full details of this method can be found in [2] and [20]. The system was solved on a staggered grid chosen to ensure good resolution in the vicinity of the particle surface (i.e. \( x = 1 \)). After some experimentation the following distribution of grid points was chosen:

\[
x = \sin \left( \frac{\pi (n-1)}{2(N-1)} \right), \quad \text{where} \quad n = 1,K,N.
\]

In order to check the accuracy of the numerical scheme the usual tests on grid dependency were undertaken. It was found that a thousand grid points in the range of integration more than adequately resolved the structure with both the particle and the gas phase. As a further check on the code it was noted that there is an "exact" solution available for the particle temperature (exact in the sense that it is asymptotically valid in the limit \( \tilde{t} \to \infty \)). It was supposed therefore that in the limit \( \tilde{t} \to \infty \), \( T_1(\tilde{z},\tilde{t}) \to T_\epsilon \), where \( T_\epsilon \) is a constant to be determined. In this case the differential equation (2.1) is automatically satisfied. All that remains is to satisfy the flux boundary condition at the particle surface, and

\[
J_1 - Nu(T_1 - 1) - J_2 (T_1^4 - 1) = 0 \quad \text{when} \quad T_1 = T_\epsilon \quad \text{is set. For the test case of} \quad J = J_1 = J_2 = 1 \text{ and} \quad Nu = 2 \text{ this equation has only one real solution in} \quad Te > 1 \text{ which is given by} \quad Te = 1.14390112. \quad \text{In the accompanying figures (1. and 2.) presented are plots of} \quad T_1 \text{ and} \quad T_2 \text{ versus} \quad \tilde{z} \text{ for a range of times from} \quad \tilde{t} = 0,0.2,K,2.0. \quad \text{The first plot clearly shows that} \quad T_1 \text{ is tending to a constant as} \quad \tilde{t} \text{ increases. In the second figure presented are a plot of the particle temperature at} \quad \tilde{z} = 0 \text{ (the centre of the particle) and} \quad \tilde{z} = 1 \text{ (the surface of the particle), scaled on the equilibrium temperature} \quad T_\epsilon, \text{ versus} \quad \tilde{t}. \text{ From this plot it is clear that the particle rapidly attains its equilibrium temperature.}
Discussion: The using of the over-all methane disappearance rate expression is limited by the temperature range (1100-1400 K) and equivalence ratio range (0.05-0.5) for which it is valid. Thus, further investigations, which consider more detailed mechanism of the initial stages of the methane-air reaction, are necessary. It is essential to estimate the importance of the methane diffusion over the complex mass and energy balance of the system. The numerical experiments with the program clearly showed that at large values the parameter $J_3$ in the equation (2.3) can be solved numerically only if advection terms are introduced. This will be done in the future study of the problem.

References:
20. The NAG suite of subroutines.