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 immobile in the heating area and no phase transformations or defragmentation occurred; the gas was ideal and 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) $r^{-2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\left(k_pT_p\right)}{\partial r}\right)-\frac{\partial\left(\rho_pc_pT_p\right)}{\partial t}=0$, where c_p, k_p, T_p and ρ_p are the thermal capacity, conductivity, temperature and density of the particle. r is the radial distance and t - time. The gas phase dimensional energy balance equation can be expressed as:

(1.2) $Q+r^{-2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\left(k_gT_g\right)}{\partial r}\right)-\frac{\partial\left(\rho_gc_gT_g\right)}{\partial t}=0$, where c_g, k_g, T_g and ρ_g are the thermal capacity, conductivity, temperature and density of the gas phase. Equations (1.1) and (1.2) are coupled in the following initial and boundary conditions, (T_a is the ambient temperature, r_p - the radius of the particle):

$T_p=T_a$ at $t=0$; $T_g=T_a$ at $t=0$; $\frac{\partial T_p}{\partial r}=0$ on $r=0$; $T_p=T_g$ on $r=r_p$; $T_g=T_a$ as $r\to\infty$;

$\alpha_{p,(\lambda)}q=k_p\frac{\partial T_p}{\partial r}+h\left(T_p-T_a\right)+\bar{\varepsilon}_p\sigma\left(T_p^4-T_a^4\right)$ on $r=r_p$, where h is the heat-transfer coefficient, q - the radiative heat flux, $\alpha_{p,(\lambda)}$ - absorptivity ratio of the particle with respect to wavelength λ, $\bar{\varepsilon}_p$ - the mean emissivity of the particle and σ - the Stefan - Boltzmann constant. I.e. that part of the radiative energy which was absorbed by the particle surface is distributed to the particle inner space by conduction, to the gas phase by convection, and is lost by radiation (the first, second and third term of the RHS of the equation respectively). Note that for the particle the material properties are constant whereas for the gas phase these will depend upon the temperature of the gas.

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 - $Q = H\left([CH_4]_0 - [CH_4]\right)$. For the reaction represented by the stoichiometric equation $\mathrm{CH_4} + 2\mathrm{O_2} \rightarrow \mathrm{CO_2} + 2\mathrm{H_2O}$ 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 $-\dfrac{d[CH_4]}{dt} = k[CH_4]^{0.7}[O_2]^{0.8}$. The temperature dependence of the reaction rate constant k, was expressed in Arrhenius form, $k = A\exp\left(-E/RT_g\right) = 10^{13.2}\exp\left(-48{,}400/RT_g\right)$, [5], where R is the gas constant. This over-all methane disappearance rate expression was studied at atmospheric pressure, over the temperature range of 1100-1400 K and equivalence ratio range of 0.05-0.5. For the above reaction $[O_2] = [O_2]_0 - 2[CH_4]$.

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:

$$\frac{\partial[CH_4]}{\partial t} = \frac{D}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial[CH_4]}{\partial r}\right) - k[CH_4]^{0.7}\left([O_2]_0 - 2[CH_4]\right)^{0.8}.$$

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:

$$(1.3)\qquad \frac{pD}{\left(p_{c,CH_4}p_{c,air}\right)^{1/3}\left(T_{c,CH_4}T_{c,air}\right)^{5/12}\left(\dfrac{1}{M_{CH_4}} + \dfrac{1}{M_{air}}\right)^{1/2}} = a\left(\frac{T}{\sqrt{T_{c,CH_4}T_{c,air}}}\right)^b \text{, where}$$

M is the molecular weight of the components. It was assumed that the process is isobaric (*p*=1 *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.

The following data was used for calculation of *D*, [3,17]:

p_{c,CH_4}=45.8, *atm*; $p_{c,air}$=36.4, *atm*; T_{c,CH_4}=190.7, *K*; $T_{c,air}$=132.0, *K*; M_{CH_4}=16.04, *mol*; M_{air}=28.97, *mol*, and for non-polar gas-pairs, a=2.745x10^{-4}, b=1.823. After the substitution *D* becomes, D=6.7x$10^{-8}T^{1.823}$, $m^2\ s^{-1}$.

The methane concentration must satisfy the conditions

$[CH_4] = [CH_4]_0$ at $t = 0$; $\dfrac{d[CH_4]}{dr} = 0$ on $r = r_p$, and when $r \rightarrow \infty$.

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:

$t = t^*\tau$, where $t^* = \dfrac{r_p^2\rho_p c_p}{k_p}$; $r = r_p z$, and $x = \begin{cases} z : 0 \le z \le 1 \\ z^{-1} : z \ge 1 \end{cases}$; $T_p = T_a T_1$; $T_g = T_a T_2$; $J_1 = \dfrac{\alpha_{p,(\lambda)} q r_p}{k_p T_a}$;

$J_2 = \dfrac{\bar{\varepsilon}_p \sigma T_a^3 r_p}{k_p}$; $Nu = \dfrac{h r_p}{k_p}$; $F_p = \dfrac{\rho_p c_p}{k_p}$; $F_g = \dfrac{\rho_{g,a} c_{g,a}}{k_{g,a}}$; $J = F_p/F_g$; $\tau = J^{-1}\tilde{t}$;

$\tilde{H} = \dfrac{t^*[CH_4]_0}{\rho_{g,a} c_{g,a} T_a}H$; $y = \dfrac{[CH_4]}{[CH_4]_0}$; $\tilde{Q} = \tilde{H}(1 - y)$; $J_3 = At^*[CH4]_0^{0.5}$; $\tilde{D} = 6.7x10^{-8}T_a^{1.823}F_p$;

$x_I = \dfrac{[O2]_0}{[CH_4]_0}$ and $\tilde{E} = \dfrac{E}{T_a R}$. As noted above the expression for k_g, ρ_g and c_g were taken to be functions of the gas temperature given by $k_g = k_{g,a}\tilde{k}$; $\rho_g = \rho_{g,a}\tilde{\rho}$; $c_g = c_{g,a}\tilde{c}$, and their non-dimensional forms are given by:

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

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

$$\tilde{c} = 1 + \frac{C_1 T_a}{C_0}(T_2 - 1) + \frac{C_2 T_a^2}{C_0}(T_2 - 1)^2 + \frac{C_3 T_a^3}{C_0}(T_2 - 1)^3.,$$

The governing equations than become:

(2.1) $$\frac{\partial T_1}{\partial \tilde{t}} = J^{-1} x^{-2} \frac{\partial}{\partial x}\left(x^2 \frac{\partial T_1}{\partial x} \right),$$ and (2.2) $$\frac{\partial(\tilde{\rho}\tilde{c} T_2)}{\partial \tilde{t}} = x^{-2} \frac{\partial}{\partial x}\left(x^6 \frac{\partial(\tilde{k} T_2)}{\partial x} \right) - 6x^3 \frac{\partial(\tilde{k} T_2)}{\partial x} + \frac{\tilde{Q}}{J}$$

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

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

which must be solved subject to the initial and boundary conditions: $T_1 = T_2 = y = 1$ at $\tilde{t} = 0$; $\frac{\partial T_1}{\partial x} = 0$, $T_2 = 1$, $\frac{\partial y}{\partial x} = 0$ on $x = 0$; $\frac{\partial T_1}{\partial x} = J_1 - Nu(T_1 - 1) - J_2(T_1^4 - 1)$, $T_2 = T_1$, and $\frac{\partial y}{\partial x} = 0$ 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 $x = \sin\left(\frac{\pi(n-1)}{2(N-1)} \right)$, where $n = 1, \ldots, N$. 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 $\tilde{t} \to \infty$, $T_1(z, \tilde{t}) \to T_e$, where T_e 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 $J_1 - Nu(T_e - 1) - J_2(T_e^4 - 1) = 0$ when $T_1 = T_e$ is set. For the test case of $J = J1 = J2 = 1$ and $Nu = 2$ this equation has only one real solution in $Te > 1$ which is given by $Te = 1.14390112$. In the accompanying figures (1. and 2.) presented are plots of T_1 and T_2 versus z for a range of times from $\tilde{t} = 0, 0.2, \ldots, 2.0$. The first plot clearly shows that T_1 is tending to a constant as $\tilde{t}$ increases. In the second figure presented are a plot of the particle temperature at $z = 0$ (the centre of the particle) and $z = 1$ (the surface of the particle), scaled on the equilibrium temperature T_e, versus $\tilde{t}$. From this plot it is clear that the particle rapidly attains its equilibrium temperature.

Fig. 1.: T vs. z for a range of times, (Code validation test)

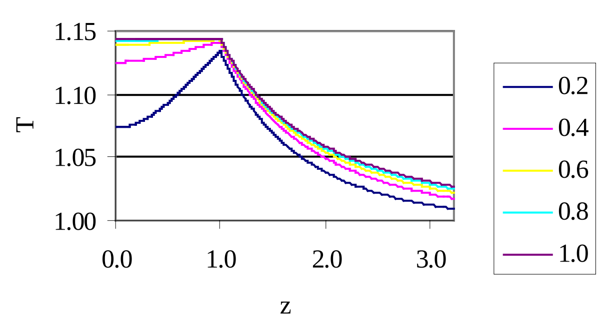
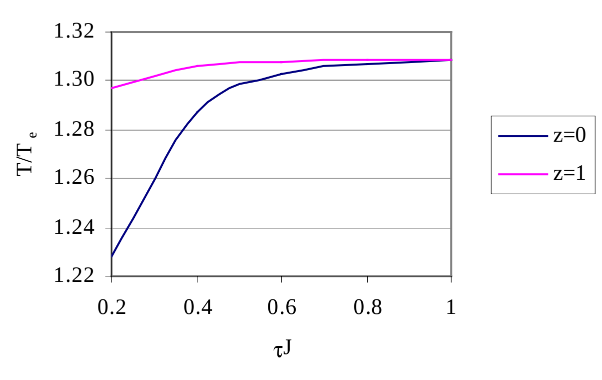


Fig. 2. T/Te vs. τJ, (Code validation test)



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 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:

1. Adler, J., Carleton, F.B., and Weinberg, F.J., „Ignition of flammable atmospheres by radiation-heated fibrous agglomerates“, Proc. Roy. Soc. A., (1993).
2. Berzins, M., Dew, P.M., and Furzeland, R.M., „Developing software for time-dependent problems using the method of lines and differential-algebraic integrations“, Appl. sum. Math. 5, 375-397, (1989).
3. Bird, R.B., Steward, W.E., Lightfoot, E.N., Transport phenomena, J. Wiley & Sons, (1960).
4. Carleton, F. B., and Weinberg, F. J., Fibre Optics ‘90, London, SPIED Vol. 1314, (1990).
5. Dryer, F.L., and Glassman, I., 14th Symp. (Int.) on Combust., 987, (1973).
6. Hildyard, C. J., Ph.D. thesis, University of Leeds, (1993).
7. Hills, P.C., Zhang, D.K., Samson, P.J. and Wall, T.F., Combust. Flame 91: 399., (1992).
8. Ihsan Barin, Thermochemical Data of Pure Substances, VCH, (1995).
9. Kumar, R. K., Combust. Flame 75, 197 215, (1989).
10. McGeehin, P., In SPIE Meeting Fibers-92 USA. 8-11.,Sept., (1992).
11. McGeehin, P., EEC/BCR Final Report. Contract no. 3365/1/0/165/90/8-BCR-UK(30), (1994).
12. McGeehin, P., Proc. SPIE 1715, 1504-1507, (1991).
13. Moore, S. R., and Weinberg, F. J., Nature 240:39-40, (1981).
14. Moore, S. R., and Weinberg, F. J., Proc. R. Soc. Lond. A 385:373-387, (1983).
15. Moore, S. R., and Weinberg, F. J., Proc. R. Soc. Lond. A 409:1-20, (1987).
16. Perry, R. H., Editor, Perry’s Chemical Engineers’ Handbook, 7th Edition, McGraw-Hill, (1997).
17. Reid, R.C., Praunsnitz, J.M., Poling, B.E., The Properties of Gases and Liquids, McGraw-Hill, (1987).
18. Scott, S. K., and Smith, J. D. B., Proc. R. Soc. Lond. A 450, 199-217, (1995).
19. Slattery, J.C., Bird, R.B., A.I.Ch.E. Journal, 4, 137-142, (1958).
20. The NAG suite of subroutines.
21. Tortoishell, G., Process Optical Measurements and Industrial Methods, The Hague, Netherlands, SPIE Vol. 1266, Paper 14, (1990).
22. Touloukian, Y.S., Editor, Thermophysical Properties of High Temperature Solid Materials, The Macmillan Company, (1967).