Products in Methane Combustion Near Surfaces

D. G. Vlachos, L. D. Schmidt, and R. Aris
Dept. of Chemical Engineering and Materials Science and
Army High Performance Computing Research Center,
University of Minnesota, Minneapolis, MN 55455

Emission of carbon monoxide (CO), formaldehyde (CH_2O), and unburned methane (CH_4) are calculated for premixed methane/air mixtures impinging on a flat surface as functions of surface temperature, equivalence ratio, and strain rate with detailed chemistry involving 46 reversible reactions and 16 species using numerical bifurcation theory. Multiple solutions with different selectivities to stable products are found. On the extinguished branch unburned CH_4, molecular hydrogen (H_2), CO, and CH_2O dominate, whereas on the ignited branch carbon dioxide (CO_2) predominates near the surface. Cold walls can promote the selectivity to CO and CH_2O near extinction, and high flow rates can increase considerably the formation of CO, CH_2O, and unburned CH_4. For example, an ignited stoichiometric methane/air mixture (9.5% CH_4 in air) impinging on a surface of 1,000 K is calculated to produce 2% CO, 150 ppm CH_2O, and 3% unburned CH_4 for a strain rate of 500 s^{-1}. Maximum efficiency of CH_4 and minimum selectivity to CH_2O occur near the stoichiometric ratio, whereas minimum selectivity to CO occurs for fuel lean mixtures. Comparison of combustion near surfaces with freely propagating flames is also shown.

Introduction

As pollution regulations become more stringent, a better understanding of the mechanisms and conditions which lead to formation of pollutants is needed. Unburned hydrocarbons, carbon monoxide (CO), hydrocarbon oxygenates such as formaldehyde (CH_2O), nitrogen oxides (NO_x), sulfur oxides (SO_x), and soot are the most important byproducts encountered in combustion. While CO and oxygenates are products of partial oxidation which are usually precursors for complete oxidation to CO_2 and H_2O, NO_x can be formed in a parallel process (Bowman, 1991) and is frequently not an intermediate byproduct of combustion (thermal NO_x).

For energy generation, complete oxidation of the fuel to CO_2 and H_2O with a minimum amount of any other byproducts is desired. On the other hand, in chemical synthesis like conversion of natural gas to syngas, partial oxidation reactions with a maximum selectivity to specific intermediate products are desired. Partial oxidation paths compete with complete oxidation paths, and these are usually the common routes through which complete homogeneous oxidation is achieved. The distribution of products is determined by the relative time scales of transport to and from a surface compared to the time scales for gas and surface reactions. When products of partial oxidation, such as H_2, CO, and CH_2O, do not have sufficient time to be further oxidized because either of short residence time or of reaction quenching near a cold surface, complete oxidation to CO_2 and H_2O would be retarded. It might then be expected that the operation conditions and spatial heterogeneities, such as surfaces, would strongly affect the distribution and the yield of products.

Surfaces can alter homogeneous combustion through momentum, energy, and mass coupling. Sufficiently hot walls can ignite flames (Bond, 1991) and promote some reactions such as thermal NO_x formation. Quenching by cold walls can freeze reactions near the boundary layer and enhance formation of some pollutants. Thus, the distribution of products under typical operation conditions can be dramatically different from equilibrium compositions, and the role of kinetics and flow/transport conditions on selectivity and pollutant formation can be crucial. This behavior can be further complicated by the existence of multiple solutions caused by the exothermic re-

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Correspondence concerning this article should be addressed to L. D. Schmidt.
Current address of D. G. Vlachos, Dept. of Chemical Engineering, University of Massachusetts, Amherst, MA, 01003.

actions which can exhibit different selectivities towards stable products.

Extensive research has been carried out on homogeneous combustion of CH_4 for both freely propagating flames and opposed jets, either diffusion or premixed gases, for example, Warnatz (1978, 1981), Miller et al. (1983), Rogg (1988), and Giovangigli and Smooke (1987). Kee and coworkers have recently discussed possible practical applications of premixed CH_4/air mixtures impinging on a flat surface (Kee et al., 1993). The role of cold surfaces on emission of unburned hydrocarbons from internal combustion engines has been considered some time ago for one-dimensional geometry when burned mixtures impinge on a surface (Westbrook et al., 1981; Hocks et al., 1981; Sloane and Schoene, 1983). However, the role of surfaces on ignition and extinction and the formation of undesired byproducts such as pollutants CO and CH_2O or other intermediates which diffuse to or from the surface and affect homogeneous reactions are generally poorly understood.

We have recently examined ignition and extinction of lean H_2/air mixtures (Vlachos et al., 1993) and CH_4/air mixtures in the first part of this article for flow impinging on a flat plate. We found unexpected bifurcation behavior with up to five solutions for certain conditions and two ignitions and extinctions. Here, we focus on the role of surfaces on pollutant formation. We examine emission of unburned CH_4, CO, and CH_2O during combustion of premixed, unburned CH_4/air mixtures near isothermal walls as functions of surface temperature, inlet composition, and flow rate for a two-dimensional geometry (stagnation point flow). This behavior is also contrasted to freely propagating CH_4/air flames which have products of equilibrium composition.

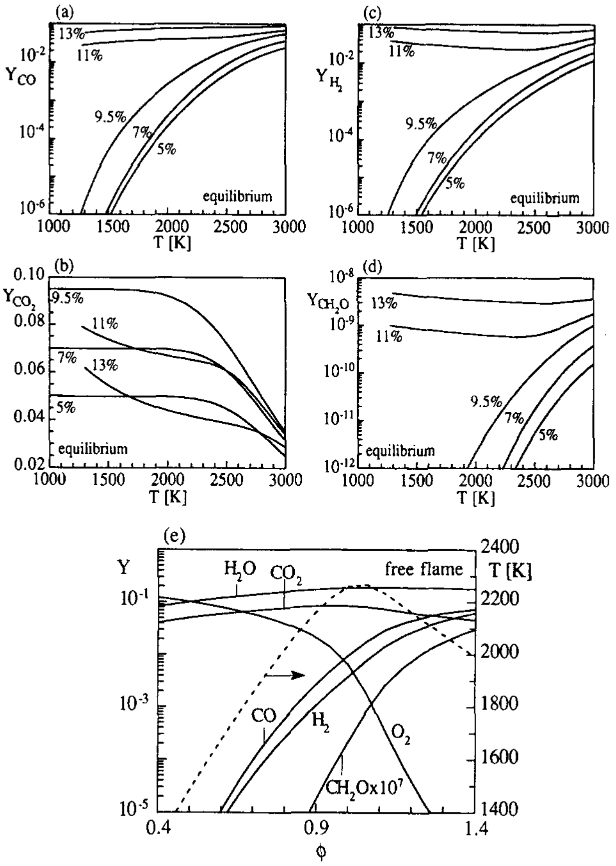

Figure 1. Equilibrium composition of CO (a), CO_2 (b), H_2 (c), and CH_2O (d) vs. temperature for various CH_4/air compositions.

C2 chemistry and formation of carbon are neglected. Adiabatic flame temperature and flame composition in post flame zone of a freely propagating CH_4/air mixture vs. equivalence ratio (e).

Model

The model considered here is the stagnation point flow geometry of laminar, premixed gases impinging on a flat surface. The governing equations and the chemistry for combustion of CH_4 which is taken from Giovangigli and Smooke (1987) are given in the first part of this article. The reaction rate constants of the reverse reactions and the transport properties are calculated using the CHEMKIN thermodynamic and transport database respectively (Kee et al., 1990, 1991). Only C1 reaction path is invoked here since mostly lean mixtures are examined.

Reaction properties are determined by considering a cylindrical control volume of cross-sectional area A which extends from the surface ($z=0$) up to the end of the computational domain ($z=z_o$) as shown in the inset of Figure 2a. The actual value of the radius is not important because of the similarity properties of the stagnation flow. This point is further discussed by Takeno and Nishioka (1993) and Kee and coworkers (1993).

The amount of species j entering the cylinder is:

$$F_{oj}=Av_oY_{oj}P_o/RT_o, \qquad (1)$$

where v_o is the velocity normal to the surface at the entrance of the cylinder, P_o is the pressure (taken to be atmospheric), T_o is the temperature at the entrance (taken to be room temperature), R is the ideal gas constant, Y_{oj} is the mole fraction of species j at the entrance of the cylinder, and the subscript o denotes the end of the computational domain at $z=z_o$.

The amount of species j consumed or produced is:

$$F_{Rj}=\int_{d0}^{z_o} R_jAdz. \qquad (2)$$

The conversion of CH_4 (moles of CH_4 reacted per mole of CH_4 fed at the entrance) or the moles of species j formed per mole of CH_4 fed is:

$$X_j=\frac{\pm F_{Rj}}{F_{oCH_4}}=\frac{\pm\int_0^{z_o} R_jdz}{v_oY_{oCH_4}P_o/RT_o}, \qquad (3)$$

where the positive (negative) sign is used for products (reactants).

The selectivity S_j of CH_4 to species j (number of moles of species j formed per mole of CH_4 consumed) is given by:

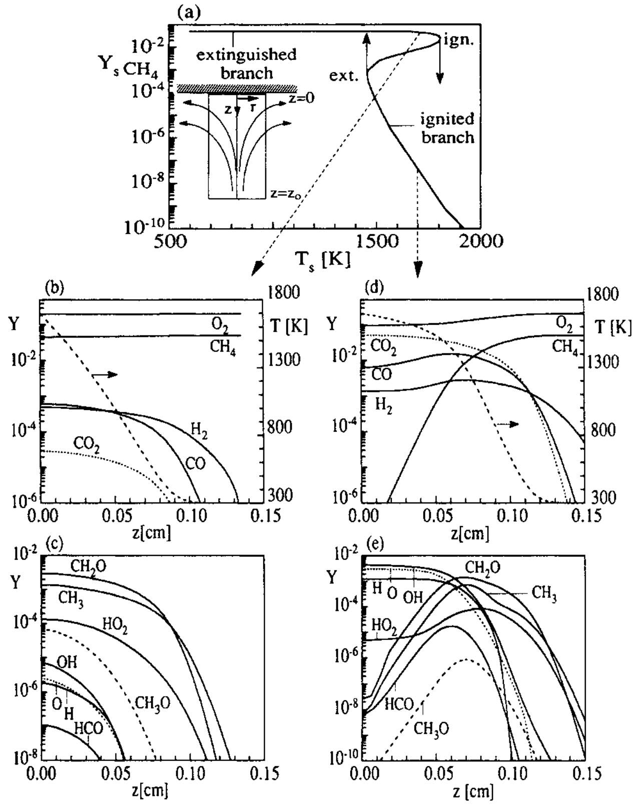

Figure 2. Surface mole fraction of CH_4 (a) in 5% CH_4/ air mixture vs. wall temperature for $\alpha = 500$ s^{-1}.

For this composition one ignition and one extinction are found. Inset of Figure 2a is a representation of the stagnation point flow geometry. Profiles of species on extinguished branch and on ignited branch respectively at same wall temperature $T_s = 1{,}700$ K (b, c, d, and e).

$$S_j = \frac{F_{Rj}}{-F_{RCH_4}} = \frac{\int_0^{z_o} R_j dz}{-\int_0^{z_o} R_{CH_4} dz}, \; j \neq CH_4. \tag{4}$$

Equations 3 and 4 are essentially identical to the apparent emission index and to the emission index respectively which have been used before for NO and CO formation (Kee et al., 1993; Takeno and Nishioka, 1993).

The composition of the fluid exiting the cylinder varies with the distance along the cylinder. The mixture composition at the outlet of the cylinder (after quenching and mixing) can be found by a mass balance in each species j. The mass per unit time of species j exiting the cylinder is:

$$\dot{m}_{ej} = \dot{m}_{oj} + \dot{m}_{Rj}, \tag{5}$$

where $\dot{m}_{oj}$ and $\dot{m}_{Rj}$ are the amounts entering and reacting along the cylinder, respectively. The mass fraction W_{ej} of each species j at the outlet is:

$$W_{ej} = \frac{\dot{m}_{ej}}{\sum_{j=1}^{m_g+1} \dot{m}_{ej}} = \frac{\dot{m}_{oj} + \dot{m}_{Rj}}{\sum_{j=1}^{m_g+1} (\dot{m}_{oj} + \dot{m}_{Rj})}$$

$$= W_{oj} + \int_0^{z_o} R_j M_j dz / (v_o \rho_o), \tag{6}$$

where the total mass-flow rate $\dot{m}_o = \sum_{j=1}^{m_g+1} \dot{m}_{oj} = \rho_o v_o A$ has been used in deriving Eq. 6.

Equilibrium Composition and Freely Propagating Flames

The composition of a mixture in equilibrium containing CH_4 (not shown), CO, CO_2, H_2O, H_2, and CH_2O vs. temperature at different compositions of CH_4 in air is shown in Figures 1a-1d. At all temperatures shown CH_4 converts almost completely to products, especially at low temperatures. At each temperature, the fractions of CO and H_2 increase with composition, as shown in Figures 1a and 1c. The composition of H_2 vs. temperature exhibits a minimum for rich mixtures because H_2 converts to H_2O at low temperatures but is reformed at higher temperatures. CO is not thermodynamically favored at low temperatures for fuel lean up to stoichiometric mixtures. For fuel rich mixtures where O_2 is deficient, CO increases with CH_4 composition at the expense of CO_2, and substantial CO can be produced, as shown in Figure 1a.

CO is one of the major pollutants emitted from engines used in transportation (Bowman, 1991). For typical exhaust conditions ($T < 1{,}000$ K), CO composition would be less than 1 ppm (by volume) and not cause a serious pollution problem. However, CO composition in exhaust products typically exceeds the equilibrium values shown in Figure 1a for the exhaust conditions. The amount of CH_2O formed increases with temperature, but up to the high temperatures shown in Figure 1d is extremely small, below 10 ppb (by volume), that is, CH_2O is not thermodynamically favored.

A freely propagating flame is assumed to extend in an infinite one-dimensional domain without energy losses (adiabatic conditions) and to have zero gradients at both ends. In the post flame zone of a freely propagating flame, the reaction products are in equilibrium. The temperature (adiabatic flame temperature T_b) and the composition of the flame are not arbitrary but they are specific points of Figures 1a-1d determined from mass and energy conservation (Bui-Pham et al., 1992):

$$\sum_{j=1}^{m_g+1} N_j \int_{T_o}^{T_b} c_{pj} dT = \sum_{i=1}^{n_g} (-\Delta H_i) \xi_i. \tag{7}$$

Here, ξ_i is the extent of reaction i, $T_o = 300$ K, and c_{pj} and N_j are the constant pressure specific heat and number of moles of species j.

The adiabatic flame temperature and the composition as functions of equivalence ratio ϕ (ratio of CH_4/air over CH_4/air at stoichiometric for complete oxidation of CH_4 to CO_2 and H_2O) are shown in Figure 1e. The adiabatic flame temperature increases with composition up to about the stoichiometric ratio and drops for fuel rich mixtures. The fractions of CO and H_2 are small for sufficiently fuel lean mixtures but become significant for richer mixtures. The fractions of CH_4 and CH_2O in equilibrium are extremely low even for fuel rich mixtures.

Figure 1 indicates that CH_4 converts almost exclusively to CO_2 and H_2O at low temperatures and fuel lean conditions, and the composition to CO increases at high temperatures and fuel rich conditions. However, under typical exhaust conditions neither CO nor CH_2O would create pollution problems.

Combustion Near Surfaces

Role of wall temperature and mixture composition

Figure 2a shows the surface mole fraction of CH_4 vs. the surface temperature T_s for 5% CH_4 in air for a strain rate (velocity gradient) of $\alpha = 500\ s^{-1}$. At low and high temperatures a unique branch of solutions exists which exhibits either very small conversion (hereafter called extinguished branch) or large conversion (hereafter called ignited branch), respectively. At intermediate temperatures, three steady-state solutions can coexist with the middle one being unstable. The two turning points shown in Figure 2a correspond to ignition and extinction of a flame.

Profiles of temperature and of major and minor species on the extinguished and on the ignited branch when $T_s = 1{,}700$ K are shown in Figures 2b, 2c, 2d, and 2e respectively. On the extinguished branch CH_4 and O_2 remain almost unreactive and the temperature decreases sharply near the surface to ambient temperature, as shown in Figure 2b. At low temperatures and before ignition CO dominates over CO_2 along the stream line from ambient to the surface and considerable H_2 is formed. CH_2O is the dominant stable product near the surface. The fractions of H, O, and OH are lower than those of carbon species CH_3, CH_3O, and CH_2O, and considerable HO_2 is observed.

On the ignited branch, CH_4 reacts strongly before it reaches the surface and no CH_4 is left near the wall. Even though our calculations are different than those carried out before (Westbrook et al., 1981; Hocks et al., 1981; Sloane and Schoene, 1983), both calculations are in qualitative agreement concerning the fractions of CH_4 near the surface. The temperature changes slowly up to ~0.5 mm and then drops sharply to room temperature. CO_2 dominates over CO near the surface but CO dominates far away from the surface. That is, CO is formed when CH_4 starts reacting close to the edge of the boundary layer where the temperature is relatively low but it converts to CO_2 in the reaction zone near the surface. The carbon species peak off the surface where high reactivity of CH_4 occurs. Even though the surface temperature in Figure 2d is the same as in Figure 2b, on the ignited branch high temperatures are observed even far from the surface, and the fractions of H, O, and OH are considerably higher than those on the extinguished branch.

The conversion of CH_4 as a function of wall temperature is shown in Figure 3a at different percentages of CH_4 in air. For mixtures where hysteresis is found, the conversion increases sharply on the extinguished branch up to the ignition point, indicating a kinetic limiting regime, where a discontinuous increase would be observed. The conversion decreases slowly with decreasing surface temperature on the ignited branch until the extinction point, indicating a mass-transfer limited regime, where a discontinuous drop in the conversion would be observed. For mixtures without hysteresis, the conversion increases sharply at low temperatures and more gradually at higher temperatures but without discontinuity. As the equivalence ratio increases, the conversion increases up to the stoichiometric ratio ($\phi = 1$) and then decreases for richer mixtures, that is, the maximum efficiency of CH_4 combustion occurs for $\phi \sim 1$. However, the maximum conversion obtained for this strain rate ($\alpha = 500\ s^{-1}$) is only ~70%, as indicated in Figure 3a. Thus, more than 30% CH_4 does not react, an undesirable situation from energy production and pollution perspectives.

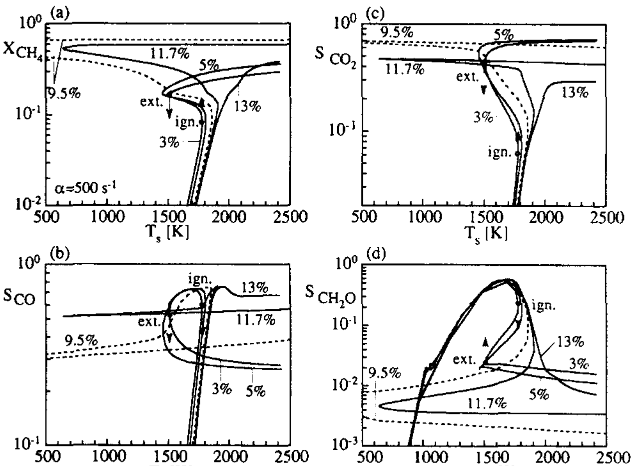

Figure 3. Conversion of CH_4 (a) selectivity of CH_4 to CO (b), CO_2 (c), and CH_2O (d) respectively vs. surface temperature for various compositions with strain rate of $\alpha = 500\ s^{-1}$.

For illustration, ignition and extinction points for 3% CH_4 in air are indicated. Selectivities to CO and CH_2O show a maximum near ignition and before ignition, respectively.

Figure 3b shows that the selectivity of CH_4 to CO S_{CO} increases sharply with surface temperature on the extinguished branch, reaches a maximum near ignition, and then decreases upon transition to the ignited branch. S_{CO} does not change strongly along the ignited branch but increases close to extinction for fuel lean mixtures. Figure 3b indicates a very nonlinear dependence of selectivity on the mixture composition; S_{CO} is a minimum for fuel lean mixtures. The selectivity of CH_4 to H_2 on the ignited branch (not shown) increases with equivalence ratio. The ratio of H_2/CO is important for the natural gas to syngas transformation. We find that H_2 is selectively produced over CO at low temperatures (the H_2/CO ratio can be much larger than one), but the fractions produced are low.

Figure 3c shows the selectivity of CH_4 to CO_2. Comparison of Figures 3b and 3c indicates that at low temperatures and up to the ignition temperature, CO is favored over CO_2, resulting in a low selectivity of CH_4 to CO_2. After ignition CO converts substantially to CO_2 near the wall. However, even at high temperatures only ~75% CO_2 is formed and ~25% of partial oxidation products (CO and CH_2O) are produced.

Considerable CH_2O is formed at low temperatures, as shown in Figure 3d. The surface mole fraction and selectivity of CH_2O vs. surface temperature exhibit a maximum before ignition, and decrease close to ignition and upon transition to the ignited

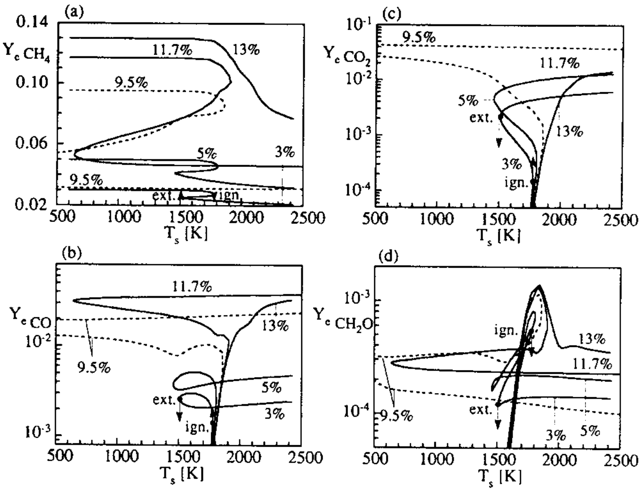

Figure 4. Outlet compositions (see text) of CH_4 (a), CO (b), CO_2 (c), and CH_2O (d) respectively vs. surface temperature for various CH_4/air compositions with strain rate of $\alpha = 500\ s^{-1}$.

For illustration, ignition and extinction points for 3% CH_4 in air are indicated. Considerable fractions of unburned CH_4, CO, and CH_2O are observed even at elevated temperatures.

branch. As the surface temperature decreases along the ignited branch the surface mole fraction of CH_2O can increase by several orders of magnitude. Thus, cold walls favor the formation of CH_2O in flames near them but the selectivity (an average quantity along the reactor) is only slightly increased. The selectivity to CH_2O exhibits a minimum for mixtures near the stoichiometric ratio, as shown in Figure 3d. At low temperatures, CH_3 radicals convert to CH_2O which is not oxidized to CO. At slightly higher temperatures but before ignition, the selectivity to CH_2O decreases at the expense of the selectivity to CO, that is CH_2O converts to CO.

The mole fractions of selected stable species vs. surface temperature at various ambient compositions for $\alpha = 500\ s^{-1}$ are shown in Figure 4. Figure 4a indicates that unburned hydrocarbon is emitted from the cylinder shown in Figure 2a even on the ignited branch. The mole fractions of CO (Figure 4b) and H_2 (not shown) increase with equivalence ratio whereas that of CO_2 (Figure 4c) has a maximum near the stoichiometric ratio. The amount of CH_2O (Figure 4d) exhibits a local maximum and a local minimum as the composition increases from fuel lean to fuel rich conditions.

Comparison with free flames (Figures 1-4) indicates that combustion near surfaces exhibits strikingly different behavior from mixtures in equilibrium. CH_4 remains almost unreactive and CH_2O, H_2, and CO are the preferred products (besides H_2O) near surfaces at low temperatures. In contrast, CH_4 converts completely to CO_2 and H_2O under equilibrium conditions. Approximately an order of magnitude more of CO can be formed near surfaces compared to that under equilibrium conditions for fuel lean mixtures, even at high temperatures ($\sim$2,000 K) on the ignited branch. The most remarkable deviation from equilibrium behavior is observed for CH_2O, where the predictions of the two calculations can differ by a factor of up to 10^7 for 9.5% CH_4 in air and even more for leaner mixtures.

Profiles of temperature and selected stable species for different CH_4/air compositions for $\alpha = 500\ s^{-1}$ and $T_s = 2{,}400$ K are shown in Figure 5. As the equivalence ratio increases, the flame moves off the surface, reaches a maximum distance at $\sim$3.5 mm away from the surface (for mixtures near the stoichiometric ratio) and then is pushed back toward the wall for fuel rich mixtures. Comparison of 8% ($\phi = 0.83$) with 11.7% ($\phi = 1.26$) CH_4 in air indicates the absence of symmetry around the stoichiometric point ($\phi = 1$).

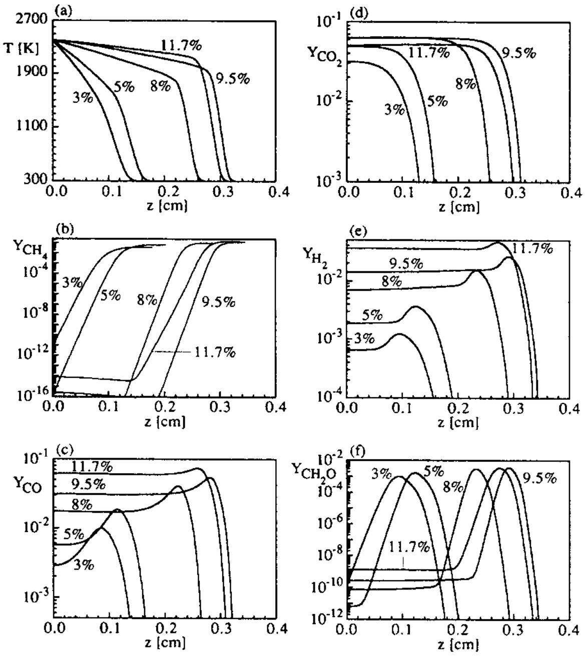

Figure 5. Temperature profiles (a) and species profiles for flames of various compositions (on ignited branch) with $T_s = 2{,}400$ K and $\alpha = 500\ s^{-1}$ (b-f).

Flame location (distance from wall where sharp change in T or peak of carbon intermediate species occur) is maximum for mixtures around stoichiometric ratio. Compositions of CO, H_2, and CH_2O in post flame zone increase with equivalence ratio for sufficiently fuel rich mixtures.

Figure 6 is a flowchart of carbon species reactions which indicates the most important reactions for fuel lean mixtures on the ignited branch. The major path for CH_4 decomposition in descending order is the attack by OH radicals, H atoms, and O atoms, respectively. Thermal decomposition of CH_4 (reaction R1) is a very endothermic process because of the high strength of the C-H bond and thus is not favored at low temperatures. In contrast, CH_3 radicals recombine with H atoms to produce CH_4. We find that the major path for CH_3 consumption is the direct conversion to CH_2O. Before ignition, both reaction paths $CH_3 \rightarrow CH_2O$ and $CH_3O \rightarrow CH_2O$ contribute significantly to CH_2O formation, leading to a large fraction of CH_2O near the wall as shown in Figure 2c, but after ignition, only the former path is significant.

The major path for formation of HCO is the attack of CH_2O by OH radicals, H atoms, and O atoms. The reactions of thermal decomposition of HCO and of attack of HCO by O_2 are mainly responsible for CO production before ignition. Attack of HCO by H, O, and OH becomes important after ignition. Before ignition, conversion of CO to CO_2 occurs mainly through attack by OH, O_2, and HO_2, but the rates of these reactions are slower than those of CO formation resulting

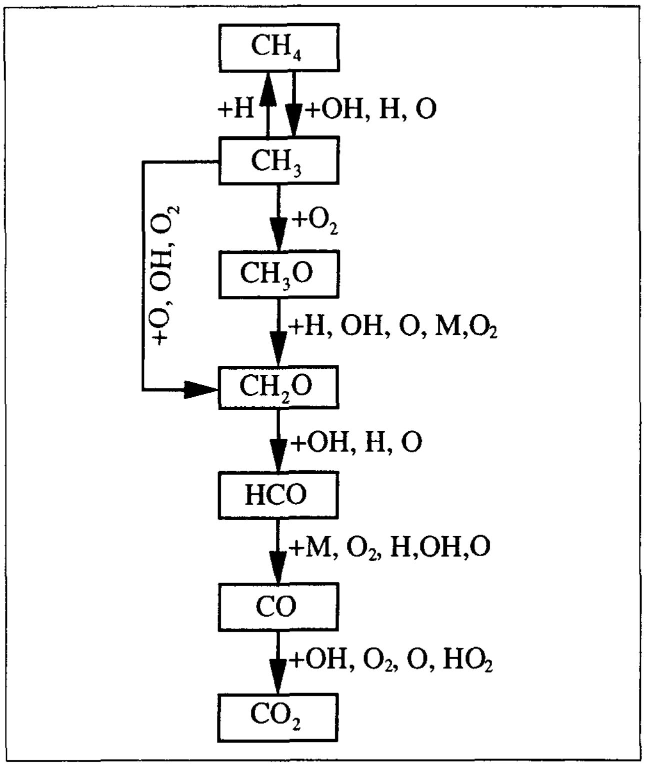

Figure 6. Flowchart of reaction paths for conversion of CH_4 to CO_2.

Species next to each arrow are listed in descending order of importance (on ignited branch) for each reaction path.

in high selectivity of CH_4 to CO. After ignition, the attack of CO by OH is the dominant reaction for oxidation of CO to CO_2.

The high selectivity of CH_4 to CH_2O and CO at low temperatures is in striking contrast from the composition of equilibrium mixtures or free propagating flames shown in Figure 1 and indicates that combined effects of short residence time and kinetic limitations affect strongly combustion products. The reaction of CO with O_2 has a large activation energy and is negligibly small at low temperatures (reaction R17). Even though significant fractions of HO_2 exist before ignition, the attack of CO by HO_2 is an activated process and is not favored at low temperatures. The most important path for the oxidation of CO to CO_2 is the attack of CO by OH (reaction R16) which before ignition is limited by the low availability of OH radicals. Hence, the rate of R16 is low and conversion of CO to CO_2 is not favored at low temperatures. Similar behavior also holds for the attack of CO by O atoms (reaction R15).

Role of strain rate

Transport limitations become important for low residence times. The residence time is related to the strain rate α (velocity gradient) which is an increasing function of the inlet velocity, that is, of the flow rate. As the strain rate increases, the residence time of the fluid in a cylinder shown in the inset of Figure 2a decreases, and this can strongly affect the conversion of CH_4 and the selectivity to stable products.

Figure 7a shows the conversion of 5% CH_4 in air vs. surface temperature for different strain rates. As the flow rate increases, the ignition and extinction temperatures increase as expected and the conversion of CH_4 decreases because combustion becomes more incomplete as a result of reduced residence time. CH_4 escapes out of the cylinder due to the divergent nature of the stagnation flow.

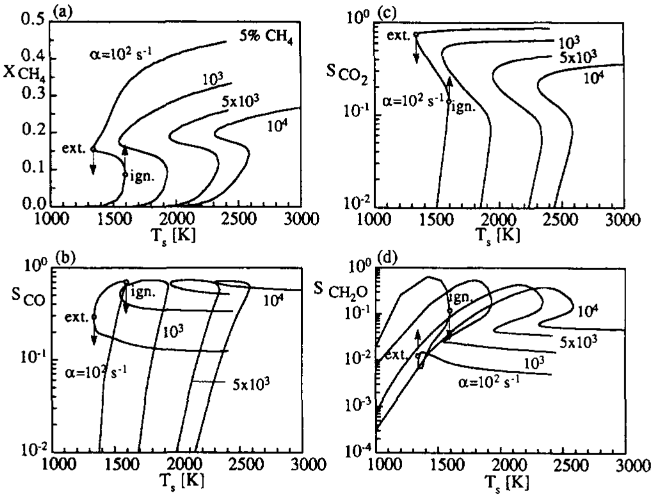

Figure 7. Conversion of 5% CH_4 (a) in air and selectivity of CH_4 to CO (b), CO_2 (c), and CH_2O (d) respectively vs. surface temperature at different strain rates.

For illustration, ignition and extinction points for $\alpha = 10^2\ s^{-1}$ are indicated. Maximum selectivity to CO is nearly independent of strain rate and that to CH_2O decreases slightly with strain rate.

Figures 7b-7e show the selectivities of CH_4 to CO, CO_2, and CH_2O respectively at different strain rates. CH_4 converts selectively to CO, H_2, and CH_2O on the extinguished branch. The maximum selectivity to CO (near ignition) is nearly independent of the strain rate whereas that to H_2 (near ignition) increases and that to CH_2O (before ignition) decreases with increasing strain rate. On the ignited branch, a high strain rate favors the products of partial oxidation (CO, H_2, CH_2O) at the expense of products of complete oxidation (CO_2 and H_2O).

The mole fractions of selected stable species at the exit of the cylinder are shown as functions of surface temperature for various strain rates in Figure 8. Increase of the flow rate results in an increase of hydrocarbon, CO, H_2, and CH_2O emission and in a decrease of CO_2 emission. When α increases by two orders of magnitude, CO and CH_2O increase by factors of ~ 3 and ~ 4 respectively and CO_2 decreases by a factor ~ 5. Even at high surface temperatures, high emissions of CO ($\sim$7,000 ppm), CH_2O ($\sim$600 ppm), and unburned CH_4 can occur at high strain rates (below the critical extinction value).

Figure 9 shows profiles of temperature and of selected stable species for 5% CH_4 in air at different strain rates when the surface temperature is $T_s = 2{,}400$ K. At low strain rates, CH_4 reacts before it reaches the wall and its surface mole fraction is essentially zero. As the strain rate increases, the flame is pushed toward the wall and combustion becomes more incomplete. The mole fraction of H atoms near the wall is higher at high strain rates and the surface mole fractions of OH radicals and O atoms are comparable with those at low strain rates. Despite the high surface mole fractions of chain carriers, incomplete combustion occurs because the chain carriers have not sufficient time to oxidize products of partial oxidation.

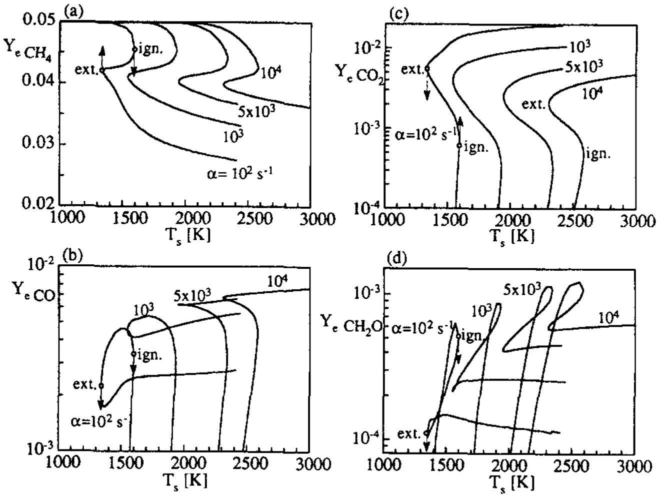

Figure 8. Outlet compositions (see text) of CH_4 (a), CO (b), CO_2 (c), and CH_2O (d) respectively at outlet of cylinder vs. surface temperature at different strain rates for 5% CH_4 in air.

For illustration, ignition and extinction points for $\alpha = 10^2\ s^{-1}$ are indicated. As strain rate increases, unburned CH_4 and partial oxidation products are favored.

Thus, as the strain rate increases, the surface mole fraction of CH_4 increases by many orders of magnitude, and incomplete reaction occurs due to low residence time.

Figures 7-9 indicate that when the residence is low (high strain rate), the intermediate stable products do not have sufficient time to be oxidized and thus, as the strain rate increases, the compositions of partial oxidation products and of unburned CH_4 increase. Our data indicate that the wall temperature and flow rate, which are extra degrees of freedom (besides composition and ambient temperature) in combustion near surfaces, can have a profound effect on combustion and pollutant emission.

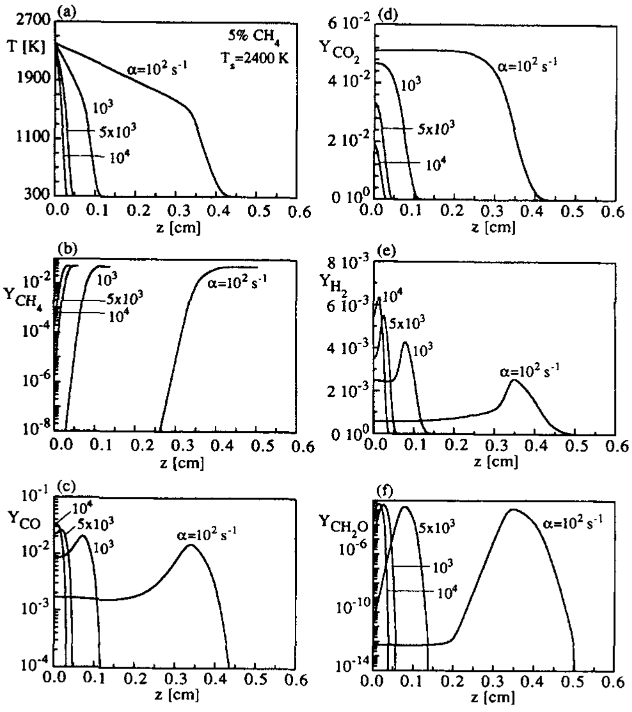

Figure 9. Temperature profiles (a) and selected species profiles for various strain rates (ignited branch) for 5% CH_4 in air flames at $T_s = 2{,}400$ K (b-f).

As strain rate increases flame is pushed toward wall and surface mole fractions of partial oxidation products and of CH_4 increase.

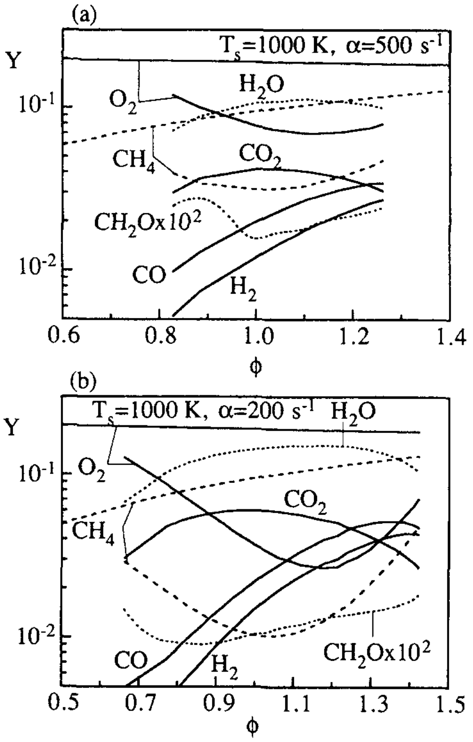

Figure 10. Outlet compositions of selected stable species as functions of equivalence ratio at $T_s = 1{,}000$ K and $\alpha = 500\ s^{-1}$ (a).

Corresponding data for $\alpha = 200\ s^{-1}$ (b). Bistability is found for $\phi \geq 0.7$ (compositions of products on extinguished branch are not shown). Under typical exhaust conditions high fractions of CO and CH_2O can be formed.

Figure 10 summarizes the effect of equivalence ratio and strain rate on pollutant formation at $T_s = 1{,}000$ K. For each strain rate, sufficiently fuel lean or rich mixtures are extinguished by the relatively cold wall, and essentially all CH_4 is emitted. For intermediate equivalence ratios, mixtures can be either extinguished or ignited (bistability). For the ignited mixtures substantial fractions (much higher than those for freely propagating flames shown in Figure 1e) of CO, CH_2O, and CH_4 are emitted. As the strain rate increases, combustion becomes more incomplete, H_2O and CO_2 decrease, whereas CH_2O increases.

Conclusions

The composition and selectivity in homogeneous combustion of premixed CH_4/air mixtures impinging on a flat surface have been simulated as functions of surface temperature, equivalence ratio, and strain rate with detailed chemistry and compared with those in free flames.

We find multiple steady-state solutions with different selectivities to stable species as the wall temperature varies. High selectivity to products of partial oxidation is favored on the extinguished branch, whereas high selectivity to products of complete oxidation is favored on the ignited branch. Instabilities in a reactor which can drive the system to the extinguished branch would result in emission of unburned hydrocarbons and considerable emissions of CO and CH_2O.

The composition of species in combustion near surfaces can deviate significantly from that of freely propagating flames and is determined by a combination of kinetic and transport effects. On the ignited branch, the selectivity (average along the reactor) to pollutants CO and CH_2O is not a strong function of surface temperature (mass-transfer limited), but in most cases the selectivity can increase near cold walls just before extinction. Implications in multiple ignitions and extinctions for turbulent flames near surfaces are obvious.

The equivalence ratio affects the selectivity in a highly nonlinear way. The selectivity of CH_4 to CH_2O exhibits a minimum around the stoichiometric ratio, whereas the selectivity to CO exhibits a minimum for fuel lean mixtures. High strain rates favor unburned CH_4, CO, and CH_2O and disfavor the complete oxidation product CO_2.

In this article the C1 reaction path was considered. In future publications we shall consider the C2 reaction path and NO_x formation by including nitrogen chemistry.

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Notation

A = cross-sectional area, cm^2
c_{p_j} = specific heat of species j at constant pressure, cal/g·K
F_j = mol/s of species j
F_{R_j} = mol/s of species j produced or consumed
m = mass per time, g/s
m_g = number of gas-phase species (not counting N_2)
M_j = molecular weight of species j
n_g = number of gas-phase reactions
N_j = moles of species j
P = pressure, atm
R = ideal gas constant, cal/mol·K
R_j = consumption or production rate of species j, mol/cm^3·s
S_j = selectivity of methane to species j (mol j produced/mol of CH_4 consumed)
T = absolute temperature, K
T_b = adiabatic flame temperature, K
v = axial velocity, cm/s
W_j = mass fraction of species j
X = conversion
Y_j = mole fraction of species j
Y_{e_j} = average mole fraction of species j
z = axial distance from the wall, cm

Greek letters

α = strain rate
$-\Delta H_i$ = enthalpy of reaction i, cal/mol·K
ξ_i = extent of reaction i
ρ = gas density, g/cm^3

Subscripts

o = ambient
s = surface

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