

## EFFECTS OF PRESSURE AND PREHEAT ON SUPER-ADIABATIC FLAME TEMPERATURES IN RICH PREMIXED METHANE/AIR FLAMES

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*The structure of freely propagating rich CH<sub>4</sub>/air flames was studied numerically using detailed thermal and transport properties and the GRI-Mech 3.0 mechanism. Different fresh mixture temperatures and ambient pressures were considered in the simulation to investigate the effects of preheat and pressure on the super-adiabatic flame temperature (SAFT) phenomenon. The occurrence of SAFT in rich CH<sub>4</sub>/air flames is chemical kinetics in nature and is associated with the overproduction of CH<sub>2</sub>CO and H<sub>2</sub>O in the reaction zone followed by their endothermic dissociations in the post-flame region. Preheat lowers the degree of H<sub>2</sub>O concentration overshoot and results in faster depletion of CH<sub>2</sub>CO concentration in the post-flame region. Preheat accelerates a rich CH<sub>4</sub>/air flame to approach equilibrium and suppresses the occurrence of SAFT. Increased pressure reduces the H radical concentration in the reaction zone and increases the overshoot of H<sub>2</sub>O concentration and the peak concentration of CH<sub>2</sub>CO. Although pressure also accelerates the approach of a rich CH<sub>4</sub>/air flame to equilibrium, it actually enhances the degree of SAFT.*

**Keywords:** Preheat effect, Pressure effect, Rich premixed freely propagating flames, Super-adiabatic flame temperature

### INTRODUCTION

It has been demonstrated in several studies that the maximum temperature in rich hydrocarbon premixed flames can significantly exceed the adiabatic equilibrium temperature of the mixture (Bertagnolli et al., 1996, 1998; Liu et al., 2002; Meeks et al., 1993; Ruf et al., 2000; Zamashchikov et al., 2004). Understanding of the mechanism responsible for this super-adiabatic flame temperature (SAFT) phenomenon is of fundamental interest and has drawn some attention since the study of Meeks et al. (1993). In their numerical study of diamond chemical vapor deposition (CVD) using a strained rich premixed C<sub>2</sub>H<sub>2</sub>/H<sub>2</sub>/O<sub>2</sub> flame, Meeks et al. (1993) found that the flame temperature exceeds the adiabatic equilibrium temperature.

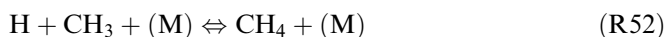
They suggested that the primary reason for the occurrence of SAFT in the rich C<sub>2</sub>H<sub>2</sub>/H<sub>2</sub>/O<sub>2</sub> premixed flame is that unreacted acetylene requires a relatively long

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time to dissociate to its equilibrium concentration. Another explanation of SAFT in this flame was later offered by Bertagnolli et al. (1998), who believed that the presence of super-equilibrium concentrations of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  to be the primary cause of the super-adiabatic flame temperatures. Ruf et al. (2000) noticed the significantly sub-equilibrium concentration of H atom and suggested that the slow and endothermic reaction  $\text{H}_2 + \text{M} \rightleftharpoons \text{H} + \text{H} + \text{M}$  is responsible for the sub-equilibrium concentration of H atom and SAFT.

More recently, the nature of SAFT has been further explored by Liu et al. (2002) and Zamashchikov et al. (2004) in their numerical studies of freely propagating rich hydrocarbon premixed flames. Through a systematic investigation of the structure and maximum flame temperature in  $\text{CH}_4/\text{air}$ ,  $\text{CH}_4/\text{O}_2$ ,  $\text{C}_2\text{H}_2/\text{H}_2/\text{O}_2$ ,  $\text{C}_2\text{H}_4/\text{O}_2$ ,  $\text{C}_3\text{H}_8/\text{O}_2$ , and  $\text{H}_2/\text{O}_2$  flames, Liu et al. (2002) found that SAFT occurs only in rich hydrocarbon flames but not in hydrogen flames and suggested that the nature of SAFT is chemical kinetics. A different view on the nature of SAFT was put forward by Zamashchikov et al. (2004) after a careful examination of the numerically predicted structures of rich  $\text{C}_3\text{H}_8/\text{air}$  and  $\text{CH}_4/\text{air}$  flames.

They believed that the nature of SAFT in rich hydrocarbon flames is the diffusion of molecular hydrogen from the reaction zone to the preheat zone and its preferential oxidation compared to hydrocarbons. To verify the claim of Zamashchikov et al. (2004), Liu and Gülder (2005) conducted a systematic numerical study on the effects of  $\text{H}_2$  and H preferential diffusion on SAFT in rich atmospheric freely propagating  $\text{CH}_4/\text{air}$  and  $\text{CH}_4/\text{O}_2$  flames and once again concluded that the nature of SAFT is chemical kinetics, not the preferential diffusion of  $\text{H}_2$ . More specifically, Liu and Gülder (2005) concluded that the nature of SAFT in rich  $\text{CH}_4/\text{air}$  flames is due to the relative scarcity of H radical in the reaction zone primarily through the following two major reactions for H radical consumption:



It is noted that the numbering of reactions in this study follows that of GRI-Mech 3.0. Although the findings of Liu and Gülder (2005) serve as convincing evidence to dismiss the molecular hydrogen diffusion mechanism suggested by Zamashchikov et al. (2004), their numerical results indicate that the degree of SAFT is significantly enhanced by the preferential diffusion of H atom from the reaction zone to the preheat zone in rich  $\text{CH}_4/\text{O}_2$  flames, but not in rich  $\text{CH}_4/\text{air}$  flames. More recently, Bunev and Babkin (2006) suggested that the chemical kinetics and H atom preferential diffusion mechanisms should be viewed as two aspects of the SAFT phenomenon in rich hydrocarbon premixed flames. This view represents a good summary of the findings of Liu and Gülder (2005).

Although the mechanisms of SAFT have been made relatively clear, there is currently lack of fundamental understanding on how SAFT is affected by different factors. Such understanding is essential to develop effective strategies to control the degree of SAFT in rich premixed flames. Based on the important role of H radical in

the reaction zone to the occurrence and degree of SAFT, it was predicted by Liu and Gülder (2005) that any chemical (such as addition of a chemically active species) or physical factor (such as preheat and pressure) either enhances or suppresses SAFT if it reduces or increases the H radical concentration in the reaction zone, respectively. Their prediction, however, has not been validated against detailed numerical modeling. The object of this study is to numerically investigate the effects of preheat and pressure on SAFT in rich CH<sub>4</sub>/air flames and verify the prediction of Liu and Gülder (2005).

## NUMERICAL MODEL

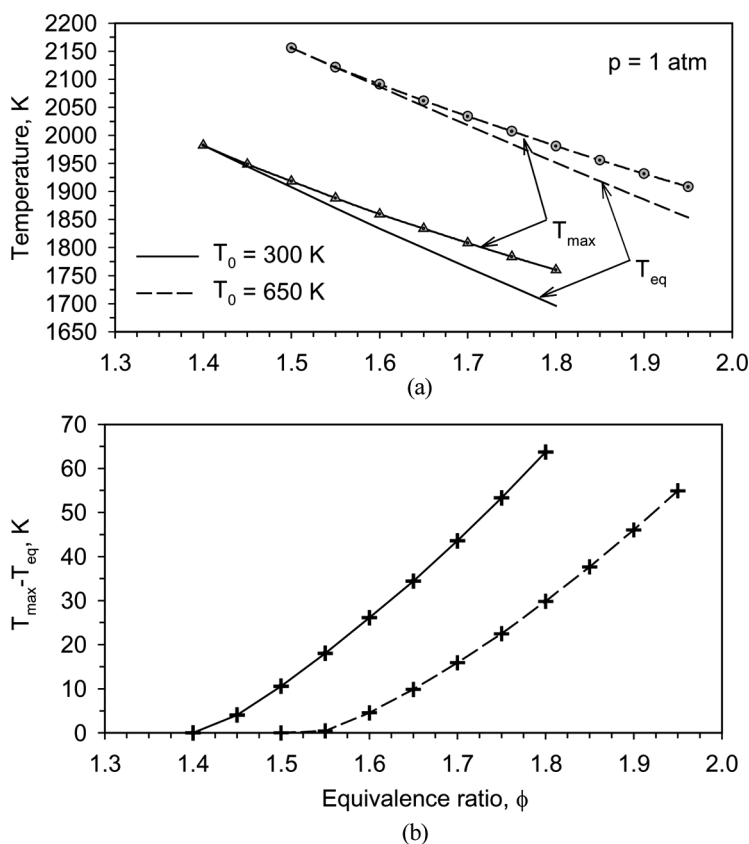
The conservation equations of mass, momentum, energy, and chemical species for steady planar freely propagating premixed flames were solved using a CHEMKIN-based code (Kee et al., 1985). The thermochemical and transport properties of species were obtained from CHEMKIN (Kee et al., 1985) and TPLIB (Kee et al., 1980, 1983) database. Since our previous study found that radiation heat loss has negligible impact on the flame temperature in the reaction zone and the immediate post-flame zone (Liu et al., 2002), all the calculations were conducted without radiation heat loss. At a spatial location of  $x = 0.05$  cm, the mixture temperature is fixed at  $(T_0 + 100)$  K,  $T_0$  is the fresh mixture temperature. In all the calculations, the upstream location (fresh mixture) is always kept at  $x = -2.5$  cm.

The location of downstream (reacted combustion products) specified in the calculations varies with the gas mixture. In all the calculations, however, it was checked that the computational domain was sufficiently long to achieve adiabatic equilibrium. The gas mixture temperature at the upstream boundary was kept at a prescribed value and zero-gradient conditions were specified at the downstream boundary. At the ambient pressure of 1 atm, 2 fresh mixture temperatures were considered: one without preheat at 300 K and one with preheat at 650 K. For the case without preheat, 2 extra ambient pressures of 0.5 atm and 10 atm were considered in the simulation. The GRI Mech 3.0 reaction mechanism (Smith et al.), which was optimized for methane combustion, was used to model the chemical kinetics in this work. The only modification made to this mechanism is the removal of species (except N<sub>2</sub>) and reactions related to NO<sub>x</sub> formation. Detailed thermal and transport properties were employed in the numerical calculations. Species diffusion was treated using the multicomponent formalism.

## RESULTS AND DISCUSSIONS

### Effect of Preheat

For fresh mixture temperature without preheat, i.e.,  $T_0 = 300$  K, CH<sub>4</sub>/air premixed flames were calculated for equivalence ratios ( $\phi$ ) between 1.4 and 1.8. Richer flames with equivalence ratio between 1.5 and 1.95 were calculated with preheat ( $T_0 = 650$  K). Figure 1a shows the variation of the maximum flame temperature and the equilibrium flame temperature with and without preheat at  $p = 1$  atm. Without preheat the adiabatic equilibrium temperature is essentially the same as



**Figure 1** Variation of the maximum and equilibrium flame temperatures with the equivalence ratio at two initial temperatures.

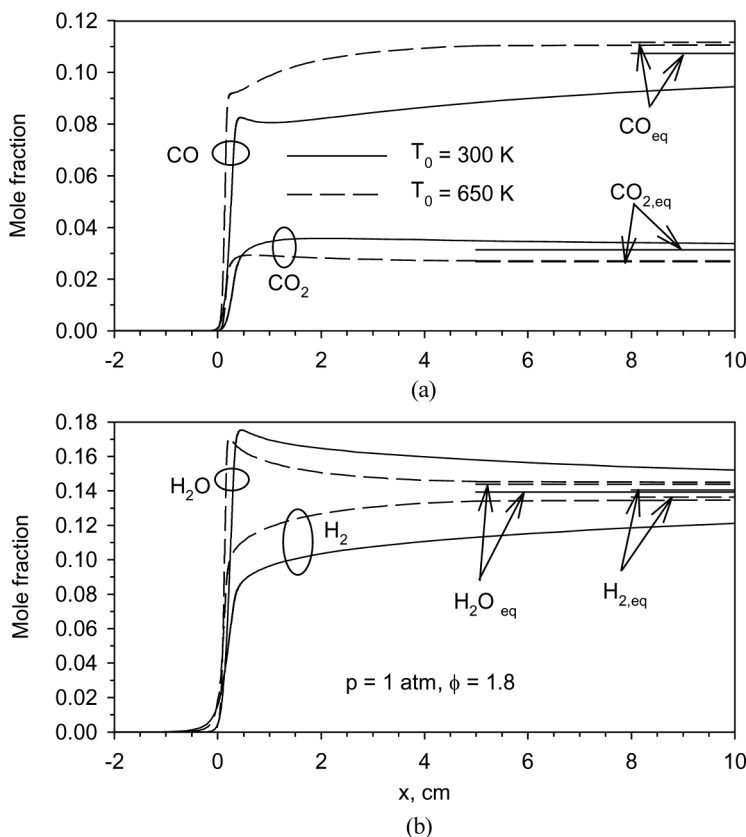
the maximum flame temperature for the mixture of  $\phi = 1.4$ , i.e., SAFT does not occur. As the equivalence ratio increases, the maximum flame temperature starts to exceed the adiabatic flame temperature and the degree of superadiabaticity also increases with  $\phi$ , Figure 1b. At  $\phi = 1.8$ , the maximum flame temperature exceeds the adiabatic equilibrium one by 63.7 K.

The existence of a critical equivalence ratio for the occurrence of SAFT in rich hydrocarbon flames has been shown previously by Liu et al. (2002) and Liu and Gülder (2005). The chemical kinetics associated with the occurrence of SAFT with increasing equivalence ratio has been discussed recently by Liu and Gülder (2005), who showed that the relative importance of reaction  $\text{OH} + \text{H}_2 \rightleftharpoons \text{H}_2\text{O} + \text{H}$  (R84) increases at the flame front as the equivalence ratio increases and eventually causes the super-equilibrium concentration of  $\text{H}_2\text{O}$  and the occurrence of SAFT when the equivalence ratio reaches the critical value. With preheat, the critical equivalence ratio for the occurrence of SAFT shifts to a higher value of about  $\phi = 1.55$ , i.e., preheat suppresses the occurrence of SAFT. In addition, the degree of temperature overshoot above the adiabatic equilibrium value is also significantly reduced with preheat as shown in Figure 1b. At  $\phi = 1.8$ , the maximum flame temperature exceeds

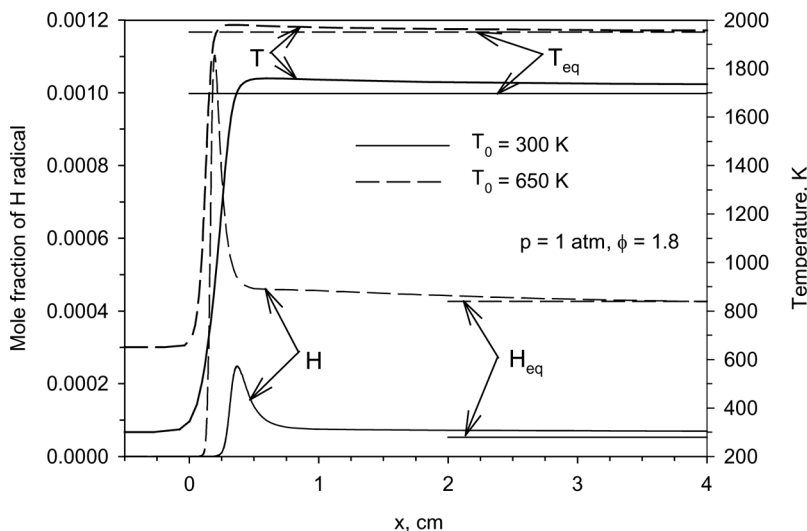
the equilibrium value by only about 30 K, more than half less than that in the case without preheat.

To explore how preheat suppresses the occurrence and the degree of SAFT, the flame structures calculated with and without preheat are examined. Figure 2 compares the spatial distributions of mole fraction of CO, CO<sub>2</sub>, H<sub>2</sub>, and H<sub>2</sub>O for the  $\phi = 1.8$  flame with and without preheat. It is seen that preheat increases the concentrations of the two intermediate species (CO and H<sub>2</sub>) in the reaction zone, but reduces the overshoot of the two major stable species (CO<sub>2</sub> and H<sub>2</sub>O), especially H<sub>2</sub>O. While the equilibrium mole fraction of CO and H<sub>2</sub>O increases slightly with preheat, the equilibrium mole fraction of CO<sub>2</sub> and H<sub>2</sub> decreases slightly. In addition, preheat also significantly accelerates the approach of the flame to equilibrium in the post-flame region.

Figure 3 shows the distributions of H radical mole fraction and temperature in the  $\phi = 1.8$  flame with and without preheat. It is first observed that the equilibrium temperature and radical concentrations of H and OH (not shown) are significantly increased by preheat. The overshoot of radical concentrations (H and OH) in



**Figure 2** Spatial distributions of mole fraction of CO, CO<sub>2</sub>, H<sub>2</sub> and H<sub>2</sub>O in a rich CH<sub>4</sub>/air flame of  $\phi = 1.8$  at  $p = 1$  atm.

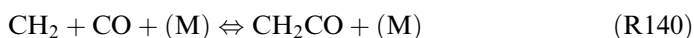


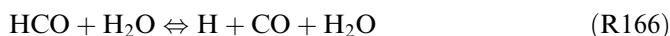
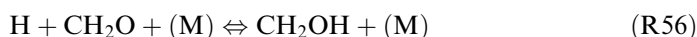
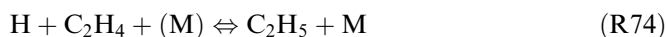
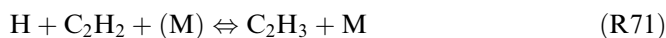
**Figure 3** Spatial distributions of the mole fraction of H radical and temperature in a rich CH<sub>4</sub>/air flame of  $\phi = 1.8$  at  $p = 1$  atm.

premixed hydrocarbon/air flames is well known and is a consequence of fast two-body radical generating reactions in the reaction zone followed by slow three-body recombination reactions as the system proceeds to equilibrium. Preheat leads to much higher H radical concentrations as well as the extent of the H radical concentration overshoot relative to its equilibrium value in the reaction zone.

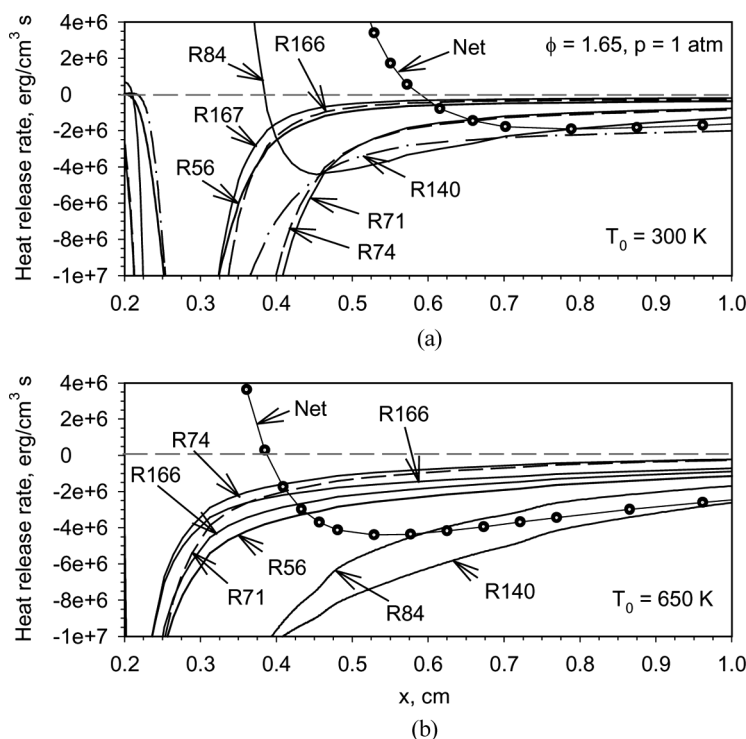
Although not shown, the concentrations of O and OH radicals are also similarly enhanced by preheat. Figures 2 and 3 also illustrate that preheat enhances combustion (sharper temperature rise and narrower reaction zone), which is related to the much higher levels of radical concentrations, and alters the equilibrium species concentrations and temperature. In view of the finding of Liu and Gülder (2005) that the degree of SAFT is directly related to the relative scarcity of H radical in the reaction zone, the suppressed level of SAFT in the preheated CH<sub>4</sub>/air mixtures is believed to be caused by the enhanced concentration of H radical in these flames. On the other hand, the present numerical results also confirm the prediction of Liu and Gülder, (2005).

It has been shown in our previous studies (Liu et al., 2002; Liu and Gülder, 2005) that the occurrence of SAFT in rich hydrocarbon flames is characterized by over-reaction of some exothermic reactions leading to super-equilibrium concentration of H<sub>2</sub>O in the reaction zone followed by endothermic dissociation reactions in the post-flame region. In rich CH<sub>4</sub>/air flames, the major endothermic reactions in the post-flame region have been identified to be





Effects of preheat on the heat release rate of these endothermic reactions in the post-flame region are compared in Figure 4 in the  $\phi = 1.65$  mixture. The first two reactions (dissociation of  $\text{CH}_2\text{CO}$  and  $\text{H}_2\text{O}$  via R140 and R84) contribute more to the endothermicity in the post-flame region than the others. It is noticed that, except the first reaction, H radical is involved in all other reactions. It is interesting to observe that the degree of temperature overshoot actually reduces by preheat, Figure 1, albeit preheat leads to larger negative heat release rate, Figure 4.



**Figure 4** Spatial distributions of the heat release rate of endothermic reactions in the post-flame region in a rich  $\text{CH}_4/\text{air}$  flame of  $\phi = 1.65$  at  $p = 1 \text{ atm}$ .

This can be explained in terms of the energy balance relationship:

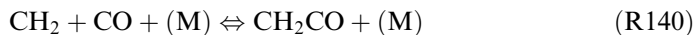
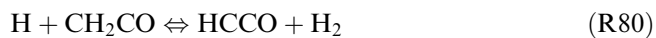
$$-\dot{m}c_p(T_{\max} - T_{\text{eq}}) = \int_{x_c}^{\infty} Q_r dx \quad (1)$$

where  $\dot{m}$  is the mass flux,  $c_p$  is the specific heat of the mixture (weakly dependent on temperature),  $x_c$  is the location where the heat release rate  $Q_r$  starts to become negative. Due to the much faster approach to equilibrium with preheat, Figures 2 and 3, the total energy flux, the right hand side of Eq. (1), required by the dissociation reactions in the post-flame region with or without preheat differs only slightly (with that in the preheated flame higher by about 4%). However, the mass flux in the preheated flame is about 2.8 times the value in the non-preheated flame.

As a result, the temperature overshoot,  $(T_{\max} - T_{\text{eq}})$ , in the preheated flame is much smaller than that in the non-preheated flame (9.86 K vs. 34.43 K at  $\phi = 1.65$ ). The larger endothermic heat release rates caused by preheat, Figure 4b, are not necessarily directly related to the degree of temperature overshoot, but an indication of faster approach to equilibrium. For example, the endothermic reaction  $\text{OH} + \text{H}_2 \rightleftharpoons \text{H}_2\text{O} + \text{H}$  (R84) (dissociation of  $\text{H}_2\text{O}$ ) absorbs energy at a much higher rate in the preheated flame than that in the non-preheated flame. Correspondingly, the peak  $\text{H}_2\text{O}$  concentration in the preheated flame is reduced to its equilibrium value much faster than in the non-preheated flame, Figure 2.

The delayed occurrence of SAFT at a higher equivalence ratio due to preheat can be attributed to the enhanced levels of important radicals such as H and OH. As shown in Figure 4, the occurrence of SAFT in rich  $\text{CH}_4/\text{air}$  flames is clearly linked to the overproduction of  $\text{H}_2\text{O}$  and  $\text{CH}_2\text{CO}$  (and to a lesser extent  $\text{C}_2\text{H}_3$ ,  $\text{C}_2\text{H}_5$ , and  $\text{HCO}$ ). A detailed examination of the numerical results indicates that  $\text{H}_2\text{O}$  is primarily formed from  $\text{H}_2$  through  $\text{OH} + \text{H}_2 \rightleftharpoons \text{H} + \text{H}_2\text{O}$  (R84). The second important pathway of  $\text{H}_2\text{O}$  formation in  $\text{CH}_4/\text{air}$  flames is from  $\text{CH}_4$  through  $\text{OH} + \text{CH}_4 \rightleftharpoons \text{CH}_3 + \text{H}_2\text{O}$  (R98).

On the other hand,  $\text{CH}_2\text{CO}$  is formed predominantly by the decomposition of  $\text{CH}_2\text{CHO}$  via  $\text{H} + \text{CH}_2\text{CHO} + (\text{M}) \rightleftharpoons \text{CH}_2\text{CO} + (\text{M})$  (R198). The major path for the destruction of  $\text{CH}_2\text{CO}$  is by H radical attack through  $\text{H} + \text{CH}_2\text{CO} \rightleftharpoons \text{CH}_3 + \text{CO}$  (R81). Other less important reactions for the production and destruction of  $\text{CH}_2\text{CO}$  are:



Reaction R80 first proceeds forward to destroy  $\text{CH}_2\text{CO}$  and then proceeds in the reverse direction to produce  $\text{CH}_2\text{CO}$ . Reaction R140 is a major endothermic decomposition reaction in the post-flame region. Reaction R107 proceeds very slowly in the forward direction towards equilibrium. Vinyoxy radical  $\text{CH}_2\text{CHO}$



is very unstable. Once formed, it dissociates rapidly to  $\text{CH}_2\text{CO}$  via R198.  $\text{CH}_2\text{CHO}$  is formed almost exclusively from the following two reactions:



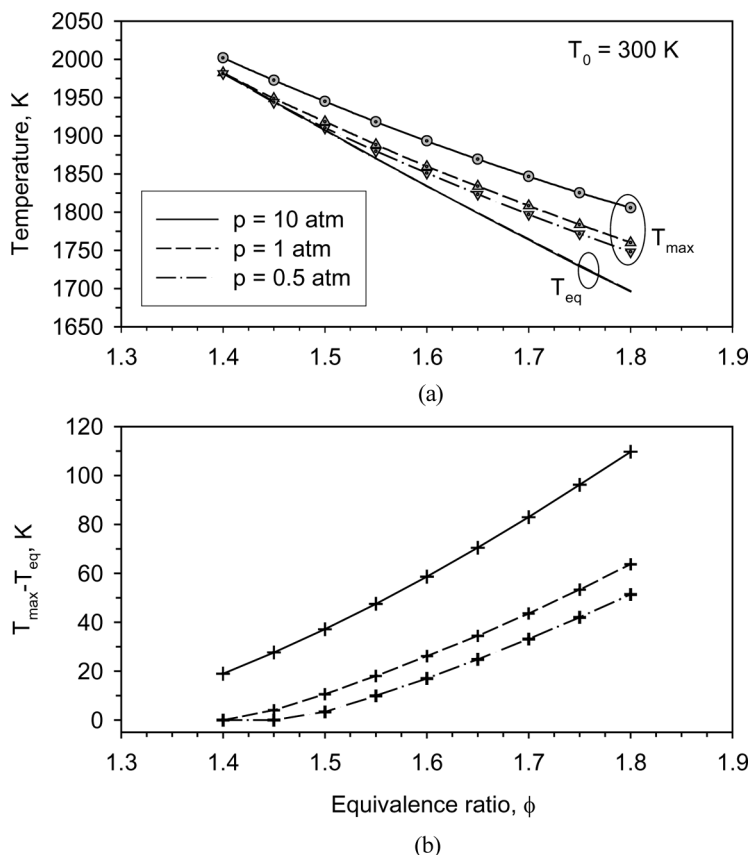
Based on the pathways for the formation of  $\text{H}_2\text{O}$  and the formation and destruction of  $\text{CH}_2\text{CO}$  outlined above, together with the increased temperature and radical (H and OH) concentrations as a result of preheat, we can gain some insights into the suppression effect of preheat on SAFT. For a mixture of given equivalence ratio, preheat increases the flame temperature, which significantly enhances the production of radicals such as H and OH through two-body reactions, Figure 3.

As shown in a recent study by Liu and Gülder (2005), the relative scarcity of H radical in rich  $\text{CH}_4$  flames is the fundamental cause of SAFT. Therefore, increased H radical concentration and temperature in the preheated flame not only enhances the overall combustion (sharper temperature rise, thinner reaction zone, and higher mass flux), but also enhances the relative importance of the reverse reaction of R84 directly, leading to reduced peak  $\text{H}_2\text{O}$  mole fraction (reduced degree of SAFT) and much higher  $\text{H}_2$  mole fraction in the reaction zone, Figure 2b. In addition, increased H radical concentration in the reaction zone and the post-flame region by preheat, Figure 3, significantly enhances the destruction rate of  $\text{CH}_2\text{CO}$  by H radical attack through R81. The reduced level of  $\text{H}_2\text{O}$  overshoot and the enhanced destruction of  $\text{CH}_2\text{CO}$  are 2 important indications of the suppression of SAFT by preheat. The fundamental chemical cause of the preheat effect on SAFT is the increased H radical concentration in the preheated flame.

### Effect of Pressure

The effect of pressure on SAFT was investigated for a fresh mixture temperature of  $T_0 = 300$  K and ambient pressures of 0.5, 1, and 10 atm for equivalence ratios between 1.4 and 1.8. The effect of pressure on the degree of temperature overshoot is summarized in Figure 5. First it is noticed that pressure has negligible impact on the adiabatic equilibrium temperature  $T_{\text{eq}}$ , Figure 5a. Secondly, pressure significantly enhances SAFT. At  $p = 0.5$  and 1 atm, SAFT does not occur in the  $\phi = 1.4$  mixture. However, at  $p = 10$  atm the maximum temperature exceeds the equilibrium value by about 20 K in this mixture, Figure 5b.

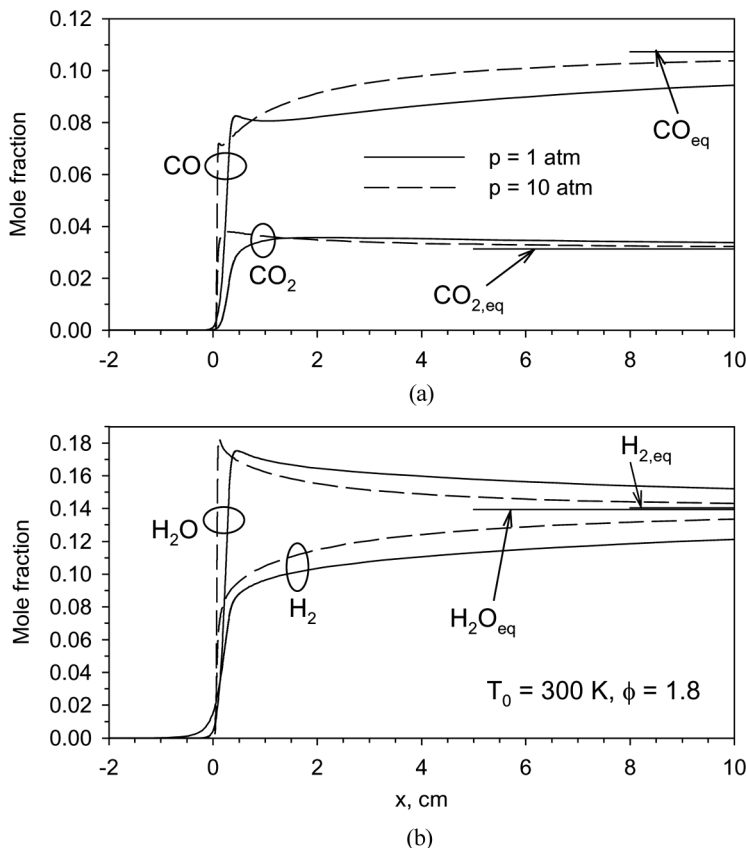
The effect of pressure on the flame structure can be revealed by comparing the spatial distributions of species and temperature calculated at different pressures. Figure 6 displays the spatial distributions of mole fraction of CO,  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{H}_2\text{O}$  for the flame of  $\phi = 1.8$  and under  $p = 1$  and 10 atm. Figure 7 shows the spatial distributions of H radical mole fraction and temperature under the same conditions as those of Figure 6. Pressure has negligible effect on the equilibrium mole fractions of CO,  $\text{CO}_2$ ,  $\text{H}_2$ , and  $\text{H}_2\text{O}$  as well as temperature. It does, however, lower the equilibrium mole fraction of H radical, Figure 7. Unlike preheat, pressure reduces the mole fraction of CO, but significantly increases that of  $\text{CO}_2$  at the flame front, Figure 6a. On the other hand, increased pressure leads to higher  $\text{H}_2\text{O}$  and  $\text{H}_2$  mole fraction at the flame front, Figure 6b.



**Figure 5** Variation of the maximum and equilibrium flame temperatures with the equivalence ratio in rich  $\text{CH}_4/\text{air}$  mixtures under different pressures.

It is interesting to observe that increased pressure results in a much sharper rise in the temperature, even though the mole fraction of H radical is drastically reduced, Figure 7. Results shown in Figures 6 and 7 imply that the atmospheric pressure flame has a very different kinetic path to equilibrium from that of the high pressure flame ( $p = 10$  atm), though they have almost identical equilibrium temperature and major species concentrations (but not radicals). Results shown in Figure 7 demonstrates that the enhanced relative scarcity of H radical in the reaction zone with increasing pressure is responsible for the greater degree of SAFT, consistent with the conclusion made by Liu and Gülder (2005). The present numerical results of the pressure effects on SAFT once again support of the prediction of Liu and Gülder (2005) about the relationship between a chemical or physical factor on the degree of SAFT.

Although both preheat and increased pressure enhances the overall combustion intensity of a mixture, they play a very different role in achieving this. Preheat enhances combustion through elevated initial temperature (the mixture density actually decreases), which leads to higher reaction rates for reactions having larger activation energy. On the other hand, increased pressure improves the combustion

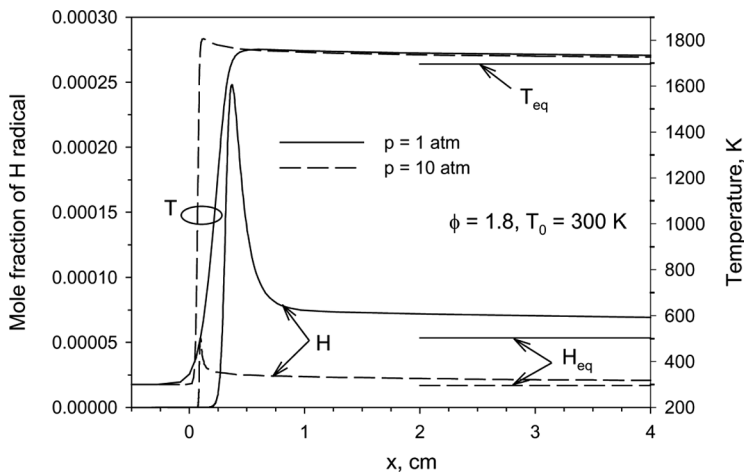


**Figure 6** Spatial distributions of mole fraction of CO, CO<sub>2</sub>, H<sub>2</sub> and H<sub>2</sub>O in a rich CH<sub>4</sub>/air flame of  $\phi = 1.8$  at  $T_0 = 300$  K.

intensity primarily by increasing the mixture density, though pressure also affects species diffusion and chemical kinetics through pressure dependent third-body reactions. As such, it enhances the reaction rates of reactions that are weakly dependent on or even independent of temperature.

To illustrate further the effect of pressure on the structure of the  $\phi = 1.8$  flame, Figure 8 shows the spatial distributions of mole fraction of O<sub>2</sub>, CH<sub>4</sub>, and CH<sub>3</sub>. Consistent with the enhanced combustion by increasing pressure seen in Figures 6 and 7, O<sub>2</sub> and CH<sub>4</sub> are consumed much more rapidly at  $p = 10$  atm. It is interesting to observe, however, that the mole fraction of CH<sub>3</sub> decreases significantly with the increase of pressure, suggesting a very different pathway for fuel consumption when pressure is increased from 1 atm to 10 atm. The major pathways for CH<sub>4</sub> consumption and generation and for O<sub>2</sub> consumption in the  $\phi = 1.8$  flame are shown in Figure 9. At  $p = 1$  atm CH<sub>4</sub> is mainly consumed by the following reactions, in order of decreasing importance, Figure 9a,

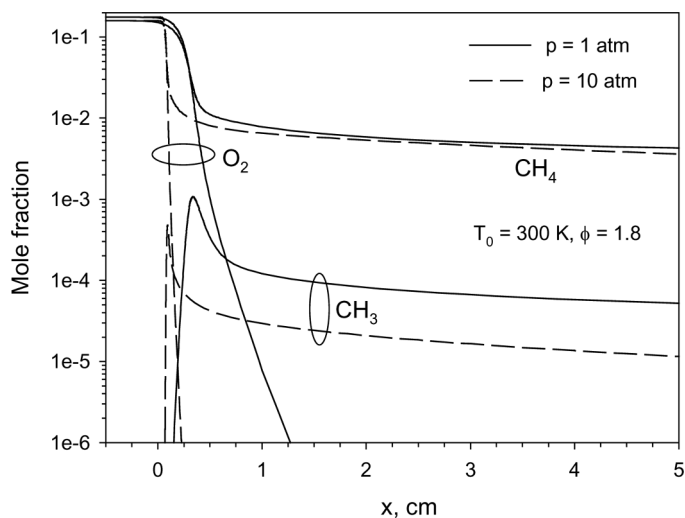
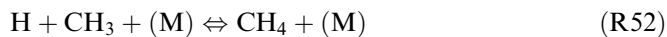




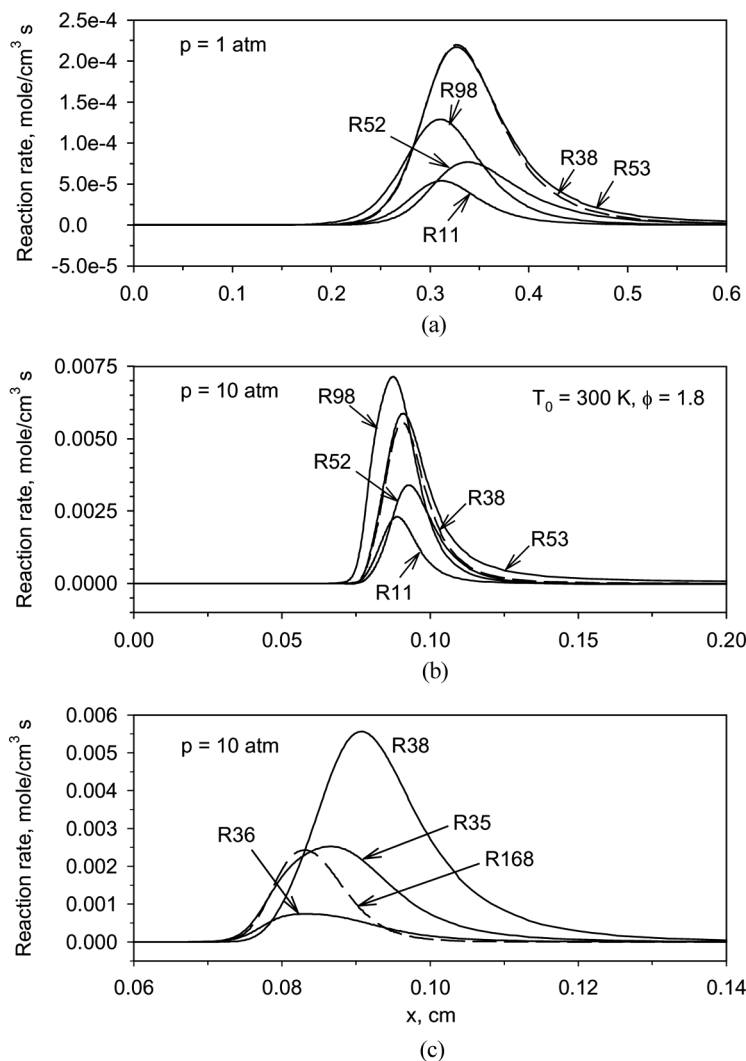
**Figure 7** Spatial distributions of the mole fraction of H radical and temperature in a rich  $\text{CH}_4/\text{air}$  flame of  $\phi = 1.8$  at  $T_0 = 300$  K.



$\text{CH}_4$  is also formed by recombination of  $\text{CH}_3$  and H



**Figure 8** Spatial distributions of the mole fraction of  $\text{O}_2$ ,  $\text{CH}_4$ , and  $\text{CH}_3$  in a rich  $\text{CH}_4/\text{air}$  flame of  $\phi = 1.8$  at  $T_0 = 300$  K.



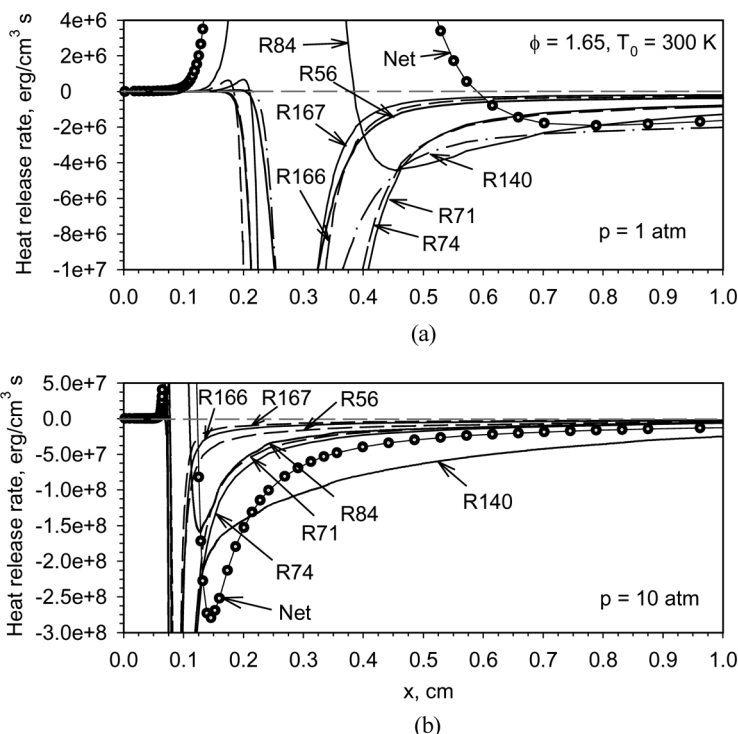
**Figure 9** Spatial distributions of reaction rates in the flame of  $\phi = 1.8$  at  $T_0 = 300$  K. (a) major pathways for CH<sub>4</sub> consumption at  $p = 1$  atm. (b) major pathways for CH<sub>4</sub> consumption at  $p = 10$  atm. (c) major pathways for O<sub>2</sub> consumption at  $p = 10$  atm.

At  $p = 10$  atm, however, reaction R98 becomes the dominant route for CH<sub>4</sub> consumption over reaction R53, Figure 9b, which is likely due to the fact that R98 has a lower activation temperature. The O<sub>2</sub> consumption paths also exhibit significant difference at  $p = 1$  and 10 atm. At  $p = 1$  atm (not shown), R38 ( $\text{H} + \text{O}_2 \rightleftharpoons \text{O} + \text{OH}$ ) is the dominant O<sub>2</sub> depletion reaction, with R168 ( $\text{HCO} + \text{O}_2 \rightleftharpoons \text{HO}_2 + \text{CO}$ ) being the second important reaction, but at a much lower rate. At  $p = 10$  atm, however, reaction R38 is no longer the most important pathway for O<sub>2</sub> consumption in the preheat zone, where O<sub>2</sub> is now depleted by R35 ( $\text{H} + \text{O}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HO}_2 + \text{H}_2\text{O}$ ), R168, and R36 ( $\text{H} + \text{O}_2 + \text{N}_2 \rightleftharpoons \text{HO}_2 + \text{N}_2$ ) to a lesser extent,

Figure 9c. R38( $\text{H} + \text{O}_2 \rightleftharpoons \text{O} + \text{OH}$ ) becomes increasingly important as the temperature increases. Therefore, the role of chain-propagation reaction R38 in high pressure flames is weakened. This is perhaps why the concentrations of radicals (O, OH, and H) become much lower with increasing pressure. While preheat leads to an increase in  $\text{CH}_3$  mole fraction (not shown), pressure actually suppresses its formation.

In view of the increased importance of R98( $\text{OH} + \text{CH}_4 \rightleftharpoons \text{CH}_3 + \text{H}_2\text{O}$ ) in  $\text{CH}_4$  conversion to  $\text{H}_2\text{O}$  with increasing pressure, it is not surprising to see the increased concentration overshoot of  $\text{H}_2\text{O}$ , Figure 6. The significant reduction in the mole fraction of  $\text{CH}_3$  in the high pressure flame, Figure 8, is the result of the drastic increase in the rate of temperature independent reaction R119 ( $\text{HO}_2 + \text{CH}_3 \rightleftharpoons \text{OH} + \text{CH}_3\text{O}$ ) leading to rapid depletion of  $\text{CH}_3$  to form  $\text{CH}_3\text{O}$ .  $\text{CH}_3\text{O}$  formed from reaction R119 is then converted to  $\text{CH}_2\text{O}$  by rapid thermal decomposition through reaction R57( $\text{H} + \text{CH}_2\text{O} + (\text{M}) \rightleftharpoons \text{CH}_3\text{O} + (\text{M})$ ).  $\text{CH}_2\text{O}$  is further converted to  $\text{HCO}$  via reaction R58( $\text{H} + \text{CH}_2\text{O} \rightleftharpoons \text{HCO} + \text{H}_2$ ).  $\text{HCO}$  further reacts with  $\text{O}_2$  in the preheat zone to form  $\text{HO}_2$  and  $\text{CO}$  via reaction R168 ( $\text{HCO} + \text{O}_2 \rightleftharpoons \text{HO}_2 + \text{CO}$ ).

The peak mole fraction of  $\text{CH}_2\text{CO}$  in the reaction zone is found to increase with increasing pressure. This is primarily attributed to the enhanced reverse reaction rate of R198 ( $\text{H} + \text{CH}_2\text{CO} + (\text{M}) \rightleftharpoons \text{CH}_2\text{CHO} + (\text{M})$ ). Reaction R140 ( $\text{CH}_2 + \text{CO} + (\text{M}) \rightleftharpoons \text{CH}_2\text{CO} + (\text{M})$ ) is once again an important endothermic pathway to lower



**Figure 10** Spatial distributions of the heat release rate of endothermic reactions in the post-flame region in a rich  $\text{CH}_4/\text{air}$  flame of  $\phi = 1.65$  at  $T_0 = 300 \text{ K}$ .

the super-adiabatic temperature to its equilibrium value at high pressure. To illustrate this point, the major endothermic reactions in the post-flame region of the mixture of  $\phi = 1.65$  at  $p = 1$  and 10 atm are compared in Figure 10. It is evident that as the pressure increases the decomposition of  $\text{CH}_2\text{CO}$  (R140) plays an increased role to the endothermicity of the mixture in the post-flame region than the dissociation of  $\text{H}_2\text{O}$  via R84 ( $\text{OH} + \text{H}_2 \rightleftharpoons \text{H}_2\text{O} + \text{H}$ ). Although the mass flux of the flame also increases with pressure ( $8.0804 \times 10^{-3} \text{ g cm}^{-2} \text{ s}$  at  $p = 1$  atm vs.  $4.9969 \times 10^{-2} \text{ g cm}^{-2} \text{ s}$  at  $p = 10$  atm), the increase in the magnitude of endothermic heat release rate is much larger than that in mass flux. Therefore, the degree of temperature overshoot increases with pressure, Eq. (1) and Figure 7.

## CONCLUSIONS

A numerical study was conducted in freely propagating planar rich  $\text{CH}_4/\text{air}$  premixed flames to investigate the effects of preheat and pressure on the occurrence and degree of super-adiabatic flame temperature. Although both preheat and pressure enhances the overall combustion intensity, they play a very different role in the chemical kinetics in these flames. Preheat prompts combustion through elevated temperature, which benefits reactions of larger activation energies. Consequently, concentrations of O, OH, and H radicals are greatly enhanced. These conditions are in favor of  $\text{H}_2$  formation, but suppressive to  $\text{H}_2\text{O}$  formation. The reduced degree of  $\text{H}_2\text{O}$  overshoot, faster depletion of  $\text{CH}_2\text{CO}$  by H radical in the post-flame region, and enhanced mass flux of the flame all contribute to the delayed occurrence or the reduced degree of super-adiabatic flame temperature.

Preheat also significantly alters the temperature and species concentrations of the equilibrium mixture. On the other hand, pressure enhances combustion through increased mixture density and prompts reactions that are weakly dependent on temperature or temperature independent. Although concentrations of radicals (O, OH, H, and  $\text{CH}_3$ ) are much lowered, pressure leads to enhanced overshoot of  $\text{H}_2\text{O}$  concentration and increased peak  $\text{CH}_2\text{CO}$  concentration. Pressure enhances the occurrence and the degree of super-adiabatic flame temperature, even though the temperature and species concentrations (except radicals) in the equilibrium mixture are almost unchanged.

## REFERENCES

- Bertagnolli, K.E. and Lucht, R.P. (1996) Temperature profile measurements in stagnation-flow, diamond-forming flames using hydrogen CARS spectroscopy. *Proc. Combust. Instit.*, **26**, 1825–1833.
- Bertagnolli, K.E., Lucht, R.P., and Bui-Pham, M.N. (1998) Atomic hydrogen concentration profile measurements in stagnation-flow diamond-forming flames using three-photon excitation laser-induced fluorescence. *J. Appl. Phys.*, **83**, 2315–2326.
- Bunev, V.A. and Babkin, V.S. (2006) Chemical reactions in the low-temperature zone of a laminar rich propane-air flame. *Combust. Explosion Shock Waves*, **42**, 503–508.
- Kee, R.J., Grcar, J.F., Smooke, M.D., and Miller, J.A. (1985) A FORTRAN program for modeling steady laminar one-dimensional premixed flames. Sandia National Laboratories Report SAND 85-8240.

- Kee, R.J., Miller, J.A., and Jefferson, T.H. (1980) CHEMKIN: A general-purpose, problem-independent, transportable, FORTRAN chemical kinetics package. Sandia National Laboratories Report SAND 80-8003.
- Kee, R.J., Warnatz, J., and Miller, J.A. (1983) A FORTRAN computer code package for the evaluation of gas-phase viscosities, conductivities, and diffusion coefficients. Sandia National Laboratories Report SAND 83-8209.
- Liu, F. and Gülder, Ö.L. (2005) Effects of H<sub>2</sub> and H preferential diffusion and unity Lewis number on superadiabatic flame temperatures in rich premixed methane flames. *Combust. Flame*, **143**, 264–281.
- Liu, F., Guo, H., Smallwood, G.J., and Gülder, Ö.L. (2002) Numerical study of the superadiabatic flame temperature phenomenon in hydrocarbon premixed flames. *Proc. Combust. Instit.*, **29**, 1543–1550.
- Meeks, E., Kee, R.J., Dandy, D.S., and Coltrin, M.E. (1993) Computational simulation of diamond chemical vapor deposition in premixed C<sub>2</sub>H<sub>2</sub>/O<sub>2</sub>/H<sub>2</sub> and CH<sub>4</sub>/O<sub>2</sub>-strained flames. *Combust. Flame*, **92**, 144–160.
- Ruf, B., Behrendt, F., Deutschmann, O., Kleditzsch, S., and Warnatz, J. (2000) Modeling of chemical vapor deposition of diamond films from acetylene-oxygen flames. *Proc. Combust. Instit.*, **28**, 1455–1461.
- Smith, G.P., Golden, D.M., Frenklach, M., Moriarty, N.W., Eiteneer, B., Goldenberg, M., Bowman, C.T., Hanson, R.K., Song, S., Gardiner, Jr. W.C., Lissianski, V.V., and Qin, Z., [http://www.me.berkeley.edu/gri\\_mech/](http://www.me.berkeley.edu/gri_mech/).
- Zamashchikov, V.V., Namyatov, I.G., Bunev, V.A., and Babkin, V.S. (2004) On the nature of superadiabatic temperatures in premixed rich hydrocarbon flames. *Combustion, Explosion, and Shock Waves*, **40**, 32–35.