

Super-adiabatic flame temperatures in premixed methane-oxygen flames

Björn Stelzner*, Christof Weis, Peter Habisreuther, Nikolaos Zarzalis, Dimosthenis Trimis

Karlsruhe Institute of Technology, Engler-Bunte-Institute, Combustion Technology, Karlsruhe, Germany

Abstract

Oxy-fuel combustion differs significantly from conventional air combustion. The absence of nitrogen leads to higher flame temperatures and larger concentration of major species as well as intermediate species. In the present work, freely propagating methane-oxygen flames were numerically calculated using a 1D model from lean to rich conditions in order to investigate the appearance of super-adiabatic flame temperatures (SAFT). The calculations were performed for equivalence ratios of $0.5 < \Phi < 3.0$ with an increment of 0.1, different inlet temperatures from 300 K to 700 K and a pressure range of 0.1 MPa to 1 MPa. Additionally, selected results were investigated with different detailed chemical reaction mechanisms.

The results showed that the maximum flame temperature exceeds the equilibrium temperature for equivalence ratios $\Phi > 0.9$. Two different regimes were identified, where SAFT phenomenon appears. The first regime was found in slightly rich conditions ($1.0 < \Phi < 2.1$), whereas the second regime occurred in ultra-rich regime ($\Phi > 2.1$).

A first maximum of temperature difference is observed at an equivalence ratio of $\Phi = 1.5$. Approximately 120 K to 180 K higher temperatures than the equilibrium ones at standard inlet conditions are locally observed, depending on the applied reaction mechanism. The first maximum at $\Phi = 1.5$ correlates with the maximum concentration of the H-radical, which plays a key role in the first SAFT regime. A minimum over-temperature of 50 K was identified at an equivalence ratio of $\Phi = 2.1$. By significantly increasing the equivalence ratio, the maximum flame temperature exceeded the equilibrium up to almost 400 K at $\Phi = 3.0$ in the second SAFT regime.

An increased preheating temperature enhanced the occurrence of SAFT in the first regime and degraded it in the second regime. Elevated pressure leads to the opposite effects with decreased SAFT in the first and increased SAFT in the second regime.

Introduction

As an alternative to usual combustion processes with air as oxidant, oxy-fuel processes are attractive in high temperature thermal or thermochemical processes, novel power plant concepts or in gasification processes. Oxy-fuel processes provide significantly higher flame temperatures and exhibit advantages as increased thermal efficiency, higher processing rates, reduced flue gas volumes and the potential for reduced pollutant emissions at high oxygen concentrations [1]. Especially for production of basic chemicals or synthetic fuels, high-purity synthetic gas without nitrogen dilution is required for further industrial processing.

An interesting phenomenon in oxy-fuel combustion is the local appearance of super-adiabatic flame temperatures (SAFT) which has been identified and investigated in a few studies.

Meeks et al. [2] predicted in numerically calculated $C_2H_2/O_2/H_2$ -flames, that the local flame temperatures exceed significantly the adiabatic equilibrium temperature, even in case of including massive radiative heat losses of the gas phase in the calculations. The occurrence of SAFT in this flame was demonstrated experimentally via CARS spectroscopy by Bertagnolli and Lucht [3] and Bertagnolli et al. [4].

Liu et al. [5] performed a systematic study of SAFT in premixed CH_4 /air-, different hydrocarbons/ O_2 - and H_2/O_2 -flames. They showed that the occurrence of SAFT phenomena comes along with super-equilibrium concentrations of some hydrocarbon species and H_2O in

the flames and results in a local temperature overshoot. It should be noted, that in premixed H_2/O_2 -flames SAFT could not be detected.

Zamashchikov et al. [6] studied numerically super-adiabatic flame temperatures of CH_4 - and C_3H_8 -air in fuel-rich regime. The findings indicate that the degree of SAFT depends on the equivalence ratio, while the phenomenon occurs in rich regime. They proposed, that the diffusion of H_2 from the reaction zone to the preheat zone and its preferential oxidation is responsible for SAFT.

Liu and Gülder [7] analyzed the reaction flux in premixed CH_4 /air and CH_4/O_2 -flames by artificially changing diffusion properties of H_2 and H radicals in their calculations. In contrast to [6], they concluded that the relative scarcity of H-radicals at the end of major heat release reactions and not the preferential diffusion of H_2 causes SAFT phenomenon. The H-radicals at high temperatures enhance the radical chain branching reaction $H + O_2 \rightleftharpoons O + OH$. The reduction of the H-radical in the reaction zone induces a temperature overshoot.

The effects of pressure and preheating on SAFT in rich premixed CH_4 /air flames were studied for equivalence ratios of $\phi = 1.4$ to $\phi = 1.8$ by Liu and Gülder [8]. Preheating leads to elevated combustion temperatures, which finally suppress a H_2O overshoot in the flame and hence, the SAFT phenomena. In pressurized systems, the degree of SAFT is enhanced.

* Corresponding author: bjoern.stelzner@kit.edu

Kumagami et al. [9] calculated laminar premixed $\text{CH}_4/\text{O}_2/\text{H}_2\text{O}$ -flames for fuel rich conditions under elevated pressures up to 3 MPa. They identified two different SAFT regimes: the first regime occurs for equivalence ratios of 1.0 to 2.0 and low water dilutions. The SAFT phenomenon gets less pronounced with increased pressure in the first regime, whereas it occurs in the second regime under all pressure conditions. Furthermore, it was shown, that the laminar burning velocity decreases with increased pressure for the first regime, whereas a slight increase with pressure was found under more fuel-rich conditions.

The present study focuses on the SAFT phenomenon in gasification and oxy-fuel processes. Therefore, CH_4/O_2 flames are systematically investigated with established kinetics sets. Since industrial processes are operated with preheat and elevated pressure, their influence on SAFT is additionally analyzed.

Numerical Approach

In the present study, the numerical calculations were carried out with the reactor for freely propagating premixed flames of the software package CHEMKIN 4.1. The PREMIX code was originally developed by Kee et al. [10,11].

The GRI 3.0 was used as a reference kinetic mechanism in the calculations [12], consisting of 53 species and 325 reactions. Additionally, the mechanism of Appel et al. [13] (99 species and 544 reactions) with detailed C_2 -pathway chemistry was used for selected cases. Unless otherwise stated, all presented results were carried out with the GRI 3.0 mechanism.

An initial grid of 24 points was used, which was adaptively refined to approximately 250 grid points. Grid independency was ensured in preliminary investigations. Full multicomponent and thermal diffusion were considered. A total reactor length of 10 cm was chosen for all calculations. The feed consists of a pure methane-oxygen mixture.

The oxy-fuel flames were studied for a range of equivalence ratios of $0.5 < \phi < 3.0$ with an increment of 0.1 with three different inlet temperatures of 300 K, 500 K and 700 K, respectively. In addition, the pressure was varied from 0.1 MPa to 1 MPa for $\phi = 1.0$ to $\phi = 3.0$ with an increment of 0.5.

Results and Discussion

Since oxy-fuel combustion leads to significant higher flame temperatures and species concentrations than in air combustion, substantial dissociation and hence amount of radicals may be expected. Selected species of the H-O-system and the temperature in equilibrium state for methane-oxygen are presented in Fig. 1 for various equivalence ratios at standard inlet conditions.

The maximum equilibrium temperature is found at slightly rich conditions at equivalence ratios of $\phi = 1.0$ to $\phi = 1.2$. Here, the temperature varies in a range of approximately 3050 K only a few Kelvins. Those high temperatures lead to notable dissociation products. An

amount of 8% molecular oxygen is found at stoichiometry and drops at an equivalence ratio of $\phi = 1.5$ below 1%. The peak of the O-radical (5%) and OH radical (10%) are located on the lean side, whereas the H-radical finds its maximum of 6.5% in rich conditions at an equivalence ratio of $\phi = 1.4$. Here, still an extremely high equilibrium temperature of 2973 K is present and hence, a large diffusion flux of the H-radical may be expected under those conditions.

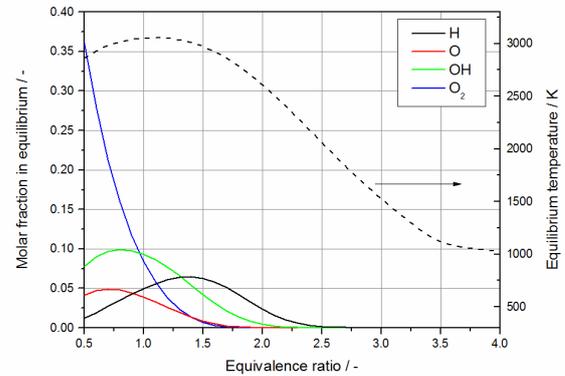


Figure 1. Equilibrium temperatures and selected species at standard inlet conditions depending on equivalence ratio

The local maximum flame temperature, the equilibrium temperature and their difference is shown in Fig. 2 for standard inlet conditions.

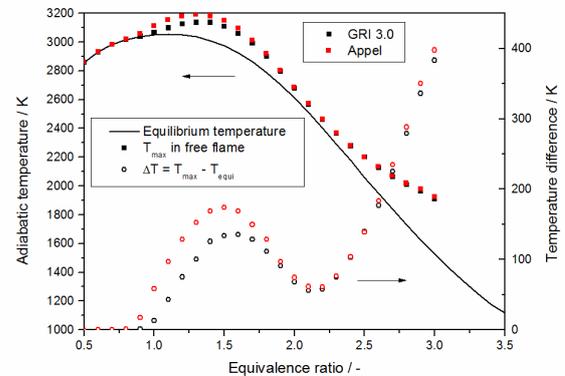


Figure 2. Maximum flame temperature, equilibrium temperature and their difference depending on the equivalence ratio at standard inlet conditions

Slightly depending on the applied reaction mechanism, SAFT is observed under fuel rich conditions for $\phi > 1$. The first peak of the difference of maximum flame temperature and equilibrium temperature is found with approximately 150 K at an equivalence ratio of $\phi = 1.5$. Similar values were found in [7]. At equivalence ratios of $\phi > 1.5$, no significant molecular oxygen exists at equilibrium, thus most of the oxygen will be consumed in the oxidation process (compare Fig. 1). At an equivalence ratio of $\phi = 2.1$ the still evident over-temperature decreases to a minimum of 50 K. An increase of the temperature difference, up to 400 K at $\phi = 3.0$, follows in the ultra-rich regime.

It should be noted that the first SAFT regime is more affected by the applied reaction mechanism, whereas the minimum $\phi = 2.1$ as well as the second SAFT regime shows no significant influence by the used kinetic set.

a.) Identification of SAFT regimes

The H-radical plays a key role in the SAFT phenomenon [7]. The profiles of the H-radical are presented in Fig. 3 for selected cases under standard inlet conditions.

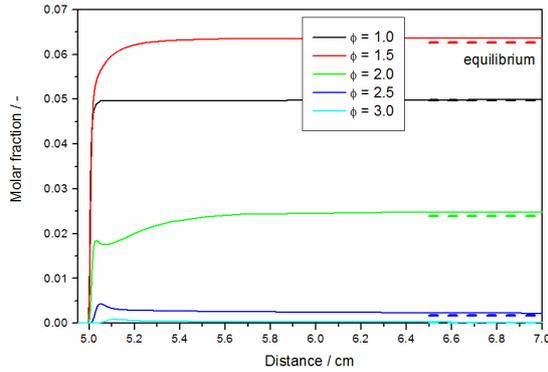


Figure 3. Profiles of the H-radical for selected flames at standard inlet conditions

The results confirm the conclusion of Fig. 1 that the highest H-concentration is present in slightly rich flames. For equivalence ratios of $\phi = 1.0$ and $\phi = 1.5$, the H-radical reaches equilibrium in the flame front without trough. A small peak is recognized at $\phi = 2.0$, where the H-radical is consumed shortly after till it finally reaches equilibrium state. In ultra-rich cases of equivalence ratios of $\phi = 2.5$ and $\phi = 3.0$, the H-radical reaches super-equilibrium and drops in the post flame zone to equilibrium. It can be concluded from the results that the peak H-concentration in rich flames seems to be indicator of the degree of the second SAFT regime.

A comparison of the H-concentration for equilibrium state and peak in the flame is presented in Fig. 4. In a range of the equivalence ratio of $\phi = 0.9$ to approximately $\phi = 2.2$, the maximal H-concentration is found in the equilibrium state, i.e. no local concentration higher than in equilibrium state is found in those flames, which can be classified to the first SAFT regime. Although the absolute value of the local maximum H-fraction rapidly decreases in ultra-rich regime, a significant super-equilibrium H-concentration is locally found at equivalence ratios of $\phi > 2.2$. The same trend is seen alleviated in lean flames. However, SAFT in flames with an equivalence ratio $\phi > 2.2$ can be associated with the main mechanism of the second SAFT regime.

In order to evaluate the origin of the H-radical in the flames, its rate of production was examined. The rate of production of the H-radical is presented for the two selected cases for equivalence ratios of $\phi = 1.0$ and $\phi = 3.0$ and are presented in Fig. 5 and Fig. 6, respectively.

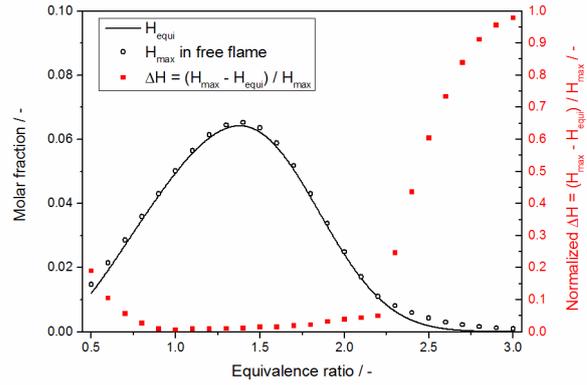


Figure 4. Comparison of the H-concentration for equilibrium and peak in the flame at standard inlet conditions

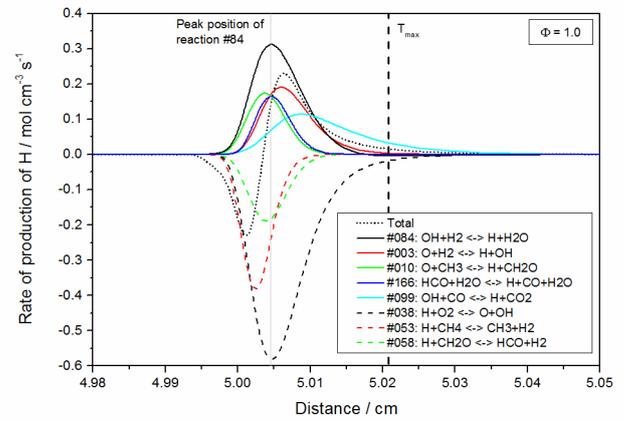


Figure 5. Rate of production of the H-radical for an equivalence ratio of $\phi = 1.0$ at standard inlet conditions

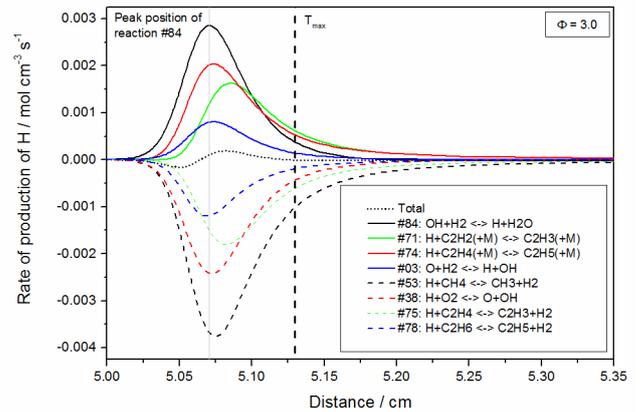


Figure 6. Rate of production of the H-radical for an equivalence ratio of $\phi = 3.0$ at standard inlet conditions

The analysis of the production rates of the H-radical revealed that in all cases substantial amount of the H is formed by reaction #84 ($\text{OH} + \text{H}_2 \rightleftharpoons \text{H} + \text{H}_2\text{O}$). The main consumption of the H-radical is required in all cases for both oxygen destruction reactions #38 ($\text{H} + \text{O}_2 \rightleftharpoons \text{O} + \text{OH}$) and the fuel destruction reaction #53 ($\text{H} + \text{CH}_4 \rightleftharpoons \text{CH}_3 + \text{H}_2$), respectively, where the consumption

is shifted to reaction #53 with increased equivalence ratio.

Since substantial amount of oxygen is still present under low rich conditions (compare Fig. 1), high temperature oxidation reactions (formyl \rightarrow formaldehyde \rightarrow carbon monoxide) produce and consume the H-radical in the first SAFT regime. In ultra-rich flames, the production and consumption shifts to the C₂-pathway in absence of oxygen. A balance of high temperature oxidation reactions and C₂-pathway-reactions were found at an equivalence ratio of approximately $\phi = 2.0$. The turn over point of the reaction path way correlates with the minimum of SAFT phenomenon (see Fig. 2).

Furthermore, the competition of H-production by reaction #84 and H-consumption by reaction #38 and #53 is indicated by the peak position of #84 in Fig. 5 and Fig. 6. The first SAFT regime is dominated by rapid H-consumption, where reactions with high activation energies like #38 take place earlier. The total reaction rate shows a distinct negative production rate in the preheat zone and has to be fed by diffusive H-transport. In the second regime at higher equivalence ratios (and hence lower flame temperatures) the degree of H-consumption is reduced in the preheat zone. The preferential diffusion of the H-radical prompts an overshoot in the H₂O-production [7].

The profiles of the H₂O are presented in Fig. 7 for selected cases at standard inlet conditions.

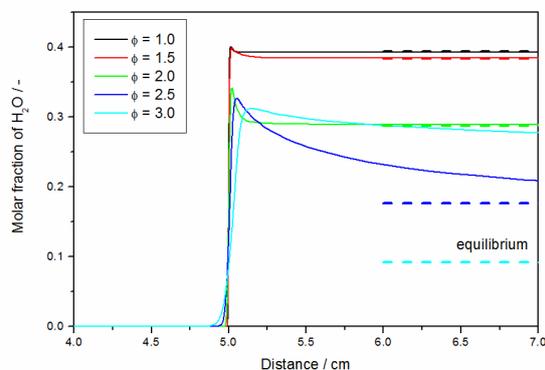


Figure 7. Profiles of H₂O for selected flames at standard inlet conditions

An overshoot of the H₂O-production is noticed in all selected cases, where it becomes more pronounced, compared to equilibrium state, with increased equivalence ratio. The local super-equilibrium production of H₂O is closely related to the degree of SAFT [7]. Further downstream in the flames, the consumption of H₂O takes place by endothermic reactions, which lowers subsequently the flame temperature in the post flame zone.

The rate of production of H₂O is shown in Fig. 8 for $\phi = 1.5$ (first SAFT regime) and Fig. 9 for $\phi = 3.0$ (second SAFT regime) at standard inlet conditions.

The results show that the reactions #84 and #98 are noteworthy and responsible for the main water production, especially in ultra-rich conditions. In the

first SAFT regime (Fig. 8), the oxidation pathway of CH₄ (reactions #96, #97, #98) produces an additional amount of water. Furthermore, H₂O-dissociation to OH is observed. In the post flame zone, the H₂O-consumption occurs due to third body reaction #43 and #84. Additionally, the HO₂- and H₂O₂-radical are involved in the H₂O-degradation (#89 and #287). Equilibrium state is reached relatively fast due to high temperatures.

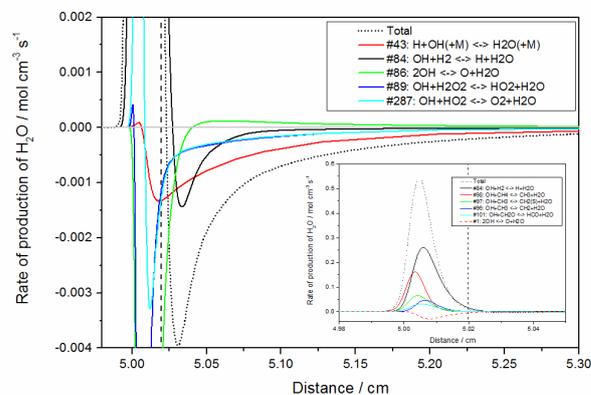


Figure 8. Rate of production of H₂O for an equivalence ratio of $\phi = 1.5$ at standard inlet conditions

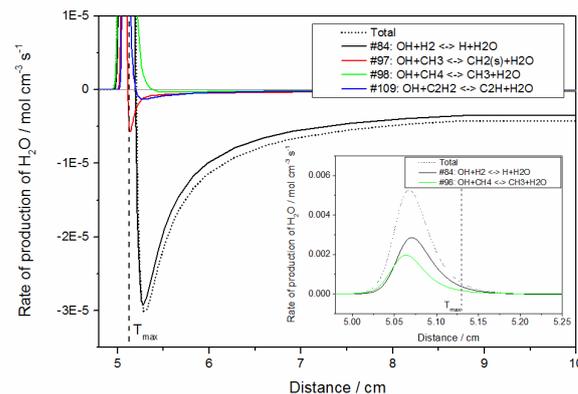


Figure 9. Rate of production of H₂O for an equivalence ratio of $\phi = 3.0$ at standard inlet conditions

In the second SAFT regime, H₂O is mainly produced by both reactions # 84 and #96 due to the consumption of OH-radical upstream the position of the maximum flame temperature. Afterwards downstream the location of the maximal temperature, the H₂O is mainly consumed and H₂ is produced due to the reaction #84 in reversed direction. Here, a concentration of almost 8% methane is still present in the flame and is slowly consumed by reaction #53, which provides the required H-radical in order to feed the H₂O-consumption in the post flame zone. The released OH-radical of reaction #84 is partly consumed in reaction #99 (OH + CO₂ \leftrightarrow H + CO) for CO-production.

b.) Influence of preheating temperature

Increased preheat alters the radical compositions of the H-O-system to higher concentrations. The maximum H-concentration changes from 6.5% to 7.5% in

equilibrium state when the preheat temperature is increased from 300 K to 700 K at an equivalence ratio of $\phi = 1.4$. In contrast to the radicals, there is no clear effect to the main species; the H_2O concentration for example is increased for equivalence ratios $\phi < 2.3$ and slightly decreased for $\phi > 2.3$, both with increasing preheating temperature.

The local maximum flame temperature, the equilibrium temperature and their difference is shown in Fig. 10 for different inlet temperatures at atmospheric pressure.

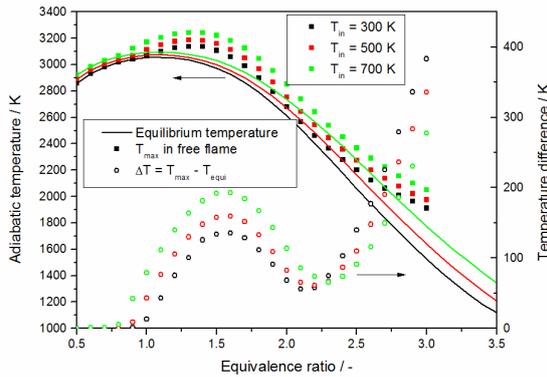


Figure 10. Maximum flame temperature, equilibrium temperature and their difference depending on the equivalence ratio for different inlet temperatures at a pressure of 0.1 MPa

Figure 10 shows that the first SAFT peak at an equivalence ratio of $\phi = 1.5$ increases with increased preheat. The minimum SAFT shifts slightly from $\phi = 2.1$ at 300 K to richer conditions of $\phi = 2.3$ at 700 K. In the second SAFT regime, an increase of the inlet temperature leads to a smaller temperature difference and reduces the SAFT phenomenon.

c.) Influence of pressure

With increasing the pressure, the main species composition alters in equilibrium near stoichiometric conditions. The concentration of H_2O and CO_2 increases and hence the equilibrium temperature elevates. In rich mixtures, no significant change of the equilibrium gas composition and temperature are observed. The temperature difference of the equilibrium temperature at given and atmospheric pressure are presented for selected equivalence ratios in Fig. 11.

The increase of the temperature is most pronounced at stoichiometric conditions. A pressure increase to 1 MPa elevates the temperature by approximately 300 K. In ultra-rich flames ($\phi = 2.5$ and $\phi = 3.0$) the effect becomes negligible. Furthermore, it should be noted, that the pressure elevation also leads to a substantial reduced H-radical pool in equilibrium for all cases.

The difference of maximum flame temperature and equilibrium temperature is presented in Fig. 12 for selected equivalence ratios in a pressure range of 0.1 MPa to 1 MPa.

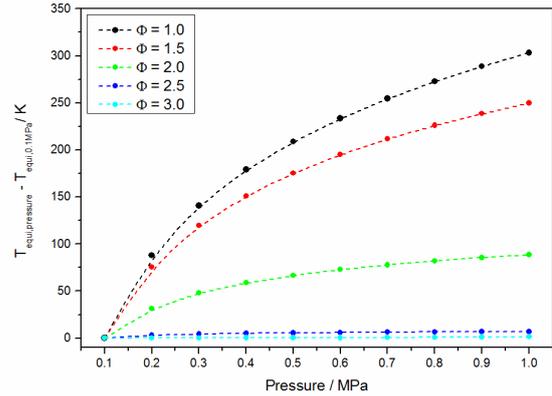


Figure 11. Difference of the equilibrium temperature at given and atmospheric pressure for selected equivalence ratios at an inlet temperature of 300 K

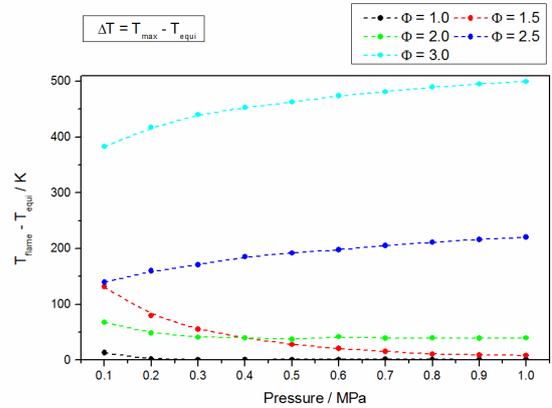


Figure 12. Difference of maximum flame temperature and equilibrium temperature depending on the pressure for different equivalence ratios at an inlet temperature of 300 K

In the first regime ($1.0 < \phi < 2.0$), the temperature difference decreases with increased pressure. At $\phi = 2.0$ an almost constant temperature difference independent of pressure is observed. A balance of the SAFT decrease of the first and the SAFT increase of the second regime may be assumed. An increase of the temperature difference is found under ultra-rich conditions.

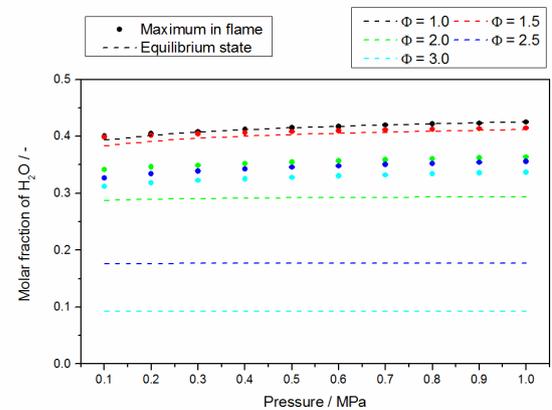


Figure 13. Comparison of maximum H_2O -concentration in the flames with equilibrium state

The tendency of temperature overshoot in the flames is also visible in the overshoot of the H₂O-production. A comparison of the maximum H₂O-concentration in the flame and in equilibrium state is illustrated in Fig. 13.

Similar to the temperature dependency on pressure, the H₂O-concentration is increased near stoichiometry in equilibrium state and is unaffected in ultra-rich mixtures with increased pressure. In the flame, the maximum H₂O-concentration increases constantly with elevated pressure so that the relative H₂O-overshoot increases. Approaching stoichiometry ($\phi = 1.0$ and $\phi = 1.5$) the H₂O-overshoot vanishes and therewith the SAFT phenomenon. In ultra-rich regime with slower kinetics, the tendency is contrary and SAFT is enhanced.

Conclusions

The SAFT phenomenon was parametrically investigated for premixed CH₄-O₂-flames for different equivalence ratios, preheat temperatures and pressures. The results revealed that SAFT occurs for all fuel rich conditions in premixed CH₄-O₂-flames. In the slightly rich regime, a local maximum of the flame temperature occurs at an equivalence ratio of $\phi = 1.5$ and exceeds by about 150 K the equilibrium state temperature. A minimum of 50 K over-temperature was found at an equivalence ratio of $\phi = 2.1$, while at higher stoichiometries the SAFT effect increases again. A turn-over point in the kinetics from the oxidation- to the C₂-pathway at this equivalence ratio is supported by the presented results.

In the present study, the rate of production of the H-radical and H₂O-molecule were analyzed in order to identify the mechanisms of the two different SAFT regimes. The SAFT phenomenon occurs in both regimes due to overshoot of H₂O-production.

In the first regime, the H-radical is rapidly consumed by both reactions #53 and #84 faster than produced by reaction #38 and hence, the maximum level of H-concentration does not exceed equilibrium state. The sufficient level of oxygen leads to relative high participation of reactions in the high temperature fuel oxidation pathways.

In the second regime, the degree of rapid H-consumption is reduced due to lower flame temperatures, so that an adequate H-pool higher than at equilibrium state is established. Next to the main reactions #38, #53 and #84, the H-pool is strongly influenced by pyrolysis reaction of the C₂-pathway. The H₂O is mainly formed by reaction #53 and #84, where the H₂O-consumption in the post flame zone takes place only by reaction #84 in reversed direction.

Preheat increases SAFT in the first regime and decreases in the second regime, where the turnover point of both regimes is shifted to higher equivalence ratios.

The equilibrium temperature and concentrations are affected by elevated pressure most in the near stoichiometry equivalence ratios, while the pressure influence on equilibrium temperature and

concentrations is negligible in ultra-rich flames. Pressure increase leads to a decrease of SAFT in an equivalence ratio of $\phi = 1.0$ to $\phi = 2.0$ and to an increase for $\phi > 2.0$.

Acknowledgments

The present research work contributes to the Research Field Energy of Helmholtz Association (HGF).

References

- [1] C.E. Baukal, Oxygen-Enhanced Combustion, CRC Press LLC, Boca Florida (1998).
- [2] E. Meeks, R.J. Kee, D.S. Dandy, M.E. Coltrin, Computational simulation of diamond chemical vapor deposition in premixed C₂H₂/O₂/H₂ and CH₄/O₂-strained flames, *Comb. Flame* 92 (1993) 144.
- [3] K.E. Bertagnolli, R.P. Lucht, Temperature profile measurements in stagnation-flow diamond-forming flames using hydrogen CARS spectroscopy, *Proc. Combust. Inst.* 26 (1996) 1825-1833.
- [4] K.E. Bertagnolli, R.P. Lucht, M.N. Bui-Pham, Atomic hydrogen concentration profile measurements in stagnation-flow diamond-forming flames using three-photon excitation laser-induced fluorescence, *J. Appl. Phys.* 83 (1998) 2315-2326.
- [5] F. Liu, H. Guo, G.J. Smallwood, Ö.L. Gülder, Numerical study of the superadiabatic flame temperature phenomenon in hydrocarbon premixed flames, *Proc. Combust. Inst.* 29 (2002) 1543-1550.
- [6] V.V. Zamashchikov, I.G. Namyatov, V.A. Bunev, V.S. Babkin, On the nature of superadiabatic temperatures in premixed rich hydrocarbon flames, *Combust. Explosion Shock Waves* 40 (2004) 32-35.
- [7] F. Liu, Ö.L. Gülder, Effects of H₂ and H preferential diffusion and unity Lewis number on superadiabatic flame temperatures in rich premixed methane flames, *Comb. Flame* 143 (2005) 264-281.
- [8] F. Liu, Ö.L. Gülder, Effects of pressure and preheat on super-adiabatic flame temperatures in rich premixed methane/air flames, *Combust. Sci. and Techn.* 180 (2008) 437-452.
- [9] M. Kumagami, Y. Ogami, Y. Tamaki, H. Kobayashi, Numerical analysis of extremely-rich CH₄/O₂/H₂O premixed flames at high pressure and high temperature considering production of higher hydrocarbons, *J. Therm. Sci. Techn.* 5 (2010) 109-123.
- [10] R.J. Kee, J.F. Grcar, M.D. Smooke, J.A. Miller, PREMIX, Report No. SAND85-8240, Sandia National Laboratories.
- [11] R.J. Kee, F.M. Rupley, J.A. Miller, CHEMKIN-II: A Fortran chemical kinetics package for the analysis of gas phase chemical kinetics, Report No. SAND 89-8009B, Sandia National Laboratories.
- [12] G.P. Smith, D.M. Golden, M. Frenklach, N.W. Moriarty, B. Eiteneer, M. Goldenberg, C.T. Bowman, R.K. Hanson, S. Song, W.C. Gardiner, V.V. Lissianski, Z. Qin http://www.me.berkeley.edu/gri_mech/
- [13] J. Appel, H. Bockhorn, M. Frenklach, Kinetic modeling of soot formation with detailed chemistry and physics: Laminar premixed flames of C₂ hydrocarbons, *Comb. Flame* 121 (2000) 122-136.