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Experimental and modeling study of the effect of elevated pressure on lean high-hydrogen syngas flames

M. Goswami\textsuperscript{a,}\textsuperscript{*}, J.G.H. van Griensven\textsuperscript{a}, R.J.M. Bastiaans\textsuperscript{a}, A.A. Konnov\textsuperscript{b}, L.P.H. de Goey\textsuperscript{a}

\textsuperscript{a} Combustion Technology Section, Mechanical Engineering, Eindhoven University of Technology, Eindhoven, The Netherlands
\textsuperscript{b} Division of Combustion Physics, Lund University, Lund, Sweden

Available online 23 June 2014

Abstract

New laminar burning velocity measurements of 85:15\% (by volume) H\textsubscript{2}–CO and H\textsubscript{2}–N\textsubscript{2} mixtures with O\textsubscript{2}–He oxidizer are reported at lean conditions and elevated pressures (1–10 atm). Experiments are conducted using the heat flux method at initial temperature of 298 K. In this technique a near adiabatic flame is stabilized by balancing the heat loss from the flame to the burner with heat gain to the unburnt gas mixture such that no net heat loss to the burner is observed. A new facility was designed for such high pressure burner stabilized flame experiments. The results obtained are compared with five chemical kinetic schemes from literature for syngas mixtures at elevated pressures. Large differences are observed between the kinetic schemes and the experiments which can be attributed to certain key chemical reactions. A study of the kinetics is performed through reaction rate and sensitivity analysis which indicate that a high uncertainty still remains in important reactions that drive the production and consumption of species such as H, HO\textsubscript{2} and OH. For lean mixtures the reaction H + O\textsubscript{2}(+M) = HO\textsubscript{2}(+M) contributes significantly to the deviation of models from the experiments. The present analysis in the lean mixture regime suggests the need for further studies in assessment and modification of rate constants for this reaction.

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Keywords: Syngas; Laminar burning velocity; Heat flux method; Elevated pressure

1. Introduction

Hydrogen remains an important fuel alternative for the present and the future in automotive and power generation sectors. In recent technologies, the Integrated Gasification Combined Cycle (IGCC) using syngas has attracted attention for its efficient and low-emission features. Syngas is a mixture of hydrogen (H\textsubscript{2}), carbon monoxide...
(CO), carbon dioxide (CO₂) and diluents like steam (H₂O) and nitrogen (N₂). In combination with gasification, removal of CO₂ is possible leaving increased levels of H₂. Lean premixed operation of gas turbines then produces more power and lower NOₓ emissions by reducing peak temperature at pressures as high as 30 bar. The laminar burning velocity (SL) of these fuel mixtures is an important requisite in designing combustors in terms of assessing flame quenching, flashback, blow-off and stabilization. It is one of the parameters that validate chemical reaction mechanisms which are used in simulating such high pressure combustion systems.

The laminar burning velocity (SL) defines the rate at which a fuel–oxidizer mixture is consumed in a flame. It is a property of fuel–oxidizer mixtures and is a function of pressure (P), initial temperature (T) and equivalence ratio (ϕ). Experimental techniques like the counterflow flame method, the spherical flame method, the conical flame method and the heat flux method can all be applied in determining this property. To achieve this, a flame which is one-dimensional and adiabatic has to be obtained. In the present study, such a flame is obtained from the heat flux method (HFM). This method stabilizes a stretchless one-dimensional flame and is capable of determining accurate adiabatic laminar burning velocity [1].

A few recent high pressure experimental studies [2–8] for SL have been reported in the literature for syngas (H₂/CO/N₂) mixtures. Most of these studies have not addressed high hydrogen content syngas with a lean mixture at elevated pressure. Much of the focus remains on stoichiometric and rich mixtures of such fuels. Lean mixtures have become important in recent applications such as mentioned above. Table 1 outlines the experimental studies reported in the literature for SL measurement at elevated pressures. It is apparent that high pressure studies of lean mixtures of H₂/CO/N₂ are scarce. In the present study, our focus remains on experimentally determining SL for validation of recent kinetic schemes.

Hence, the objectives of this study are to (1) experimentally determine SL of 85% H₂ content in both H₂–CO and H₂–N₂ mixtures at lean conditions (ϕ = 0.5–0.6) up to a pressure of 10 atm using the heat flux method in a new specially designed high pressure facility, (2) comparing recent kinetic models from Li et al. [9], Kéromnès et al. [6], Goswami et al. [8], Burke et al. [10] and GRI Mech 3.0 [11], and (3) analyzing the key reactions and pathways in the kinetics of such lean mixtures at elevated pressure.

2. High pressure experiments

The heat flux method is employed for the determination of laminar burning velocity in the present work. In general, the stabilization of an undisturbed/stable flame in high pressure environment is found to be difficult due to complexities in dynamics of flow and transport. It is known from the literature that to achieve stable flames in high pressure conditions, the outwardly/spherically propagating flame that propagates in time is used more often than stabilized flames. While attempting to extend the heat flux method towards high pressure, our intention is to design a system that stabilizes a flat adiabatic flame and not compromise the stretchless nature even at elevated pressure. Recent high pressure experiments using the heat flux method demonstrated this possibility [8,14].

The heat flux method burner, shown in Fig. 1, consists of two parts; the plenum chamber (bottom) and the burner head (top). Their goal is to create a uniform flow towards the burner plate, which is placed on top of the burner head. The inlet for the premixed fuel–oxidizer mixture is placed on the bottom of the plenum chamber. A perforated plate is placed inside at 1.5 cm from the bottom, which is used as a flow straightener. The holes in this plate have a diameter of 2 mm and a pitch of 4 mm. The plenum chamber is cooled to 25 °C by water flowing through a jacket in the wall. This is done to ensure that the temperature of the

<table>
<thead>
<tr>
<th>Author</th>
<th>Method</th>
<th>Fuel</th>
<th>H₂ fraction</th>
<th>P (atm)</th>
<th>T (K)</th>
<th>ϕ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tse et al. [12]</td>
<td>OPF</td>
<td>H₂</td>
<td></td>
<td>1–20</td>
<td>298</td>
<td>0.5–1.0</td>
</tr>
<tr>
<td>Bradley et al. [13]</td>
<td>OPF</td>
<td>H₂</td>
<td></td>
<td>1–10</td>
<td>365</td>
<td>0.3–1.0</td>
</tr>
<tr>
<td>Sun et al. [3]</td>
<td>OPF</td>
<td>H₂–CO</td>
<td>1–50%</td>
<td>1–40</td>
<td>298</td>
<td>0.6–1.0</td>
</tr>
<tr>
<td>Natarajan et al. [2]</td>
<td>CF</td>
<td>H₂–CO</td>
<td>20–90%</td>
<td>1–15</td>
<td>300–600</td>
<td>0.6–1.0</td>
</tr>
<tr>
<td>Burke et al. [5]</td>
<td>OPF</td>
<td>H₂</td>
<td></td>
<td>1–25</td>
<td>298</td>
<td>0.3–0.7</td>
</tr>
<tr>
<td>Krejci et al. [7]</td>
<td>OPF</td>
<td>H₂/H₂–CO</td>
<td>50, 100</td>
<td>1–10</td>
<td>298–443</td>
<td>0.5–1.0</td>
</tr>
<tr>
<td>Goswami et al. [8]</td>
<td>HFM</td>
<td>H₂–CO</td>
<td>50, 85</td>
<td>1–9</td>
<td>298</td>
<td>0.5–1.0</td>
</tr>
<tr>
<td>Present study</td>
<td>HFM</td>
<td>H₂–CO/H₂–N₂</td>
<td>85</td>
<td>1–10</td>
<td>298</td>
<td>0.5–0.6</td>
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incoming gas mixture stays constant at 25 °C, before it reaches the heated burner head. The inlet and outlet of the water jacket are connected to a water bath which controls the temperature of the water. The burner plate has a diameter of 2 cm and thickness of 1 mm. The plate consists of many holes of diameter 0.3 mm and pitch of 0.4 mm. The unburned gas mixture needs to be heated by the burner plate to compensate for the heat loss of the flame towards the plate. The burner plate is kept at a constant temperature of 85 °C, which is 60 °C higher than the mixture temperature. Six thermocouples of type T (Copper–Constantan) are connected to the burner plate. Data acquisition is done through a NI 9213 16-channel thermocouple input module.

When the unburnt gas velocity is higher than the adiabatic burning velocity (super-adiabatic) the heat gain by the gas is larger than the heat loss from the flame. The situation is opposite in case of a sub-adiabatic flame. The only measurement required in this technique is the temperature profile of the burner plate. The radial profile of temperature on the burner plate close to the adiabatic burning velocity is fitted by the method of least squares to a parabolic profile. The profile accounts for the net heat flux between the unburnt gas, plate and the flame. The coefficients of such polynomials are plotted against gas flow velocities. The adiabatic state is reached for a flat temperature profile. Error components from volume flow rate (uncertainty in flow rate = 0.8 % reading +0.2 % full scale), pressure (uncertainty in P = 0.01 bar), temperature (uncertainty in T = 1 K) of the unburnt gas mixture and scattering in thermocouple measurements amount to the total error in measured $S_L$. The typical error in the present work resulting from the scatter in the thermocouples is 1.5 cm/s. The principle, operation and error analysis of this technique described in details can be found elsewhere [1].

Figure 2 depicts the entire high pressure facility rated up to 30 bar at TU Eindhoven. The gas flow board consist of three gas lines connected to respective cylinders (air/oxidizer, methane and syngas), buffer vessels, valves, filters and mass flow controllers. The appropriate amount of fuel and oxidizer is made to flow to the burner through a high pressure line. The line is long enough to ensure that the gases are premixed well before they are burnt.

The complete assembly of the high pressure cell is shown in Fig. 3. The front cut section of the system including the burner is shown. The burner is connected to the cell from the bottom through a flange which can be bolted. An additional inlet for cold air is provided from the bottom of the cell. The cold pressurized air is first made to pass through layers of glass balls (diameter 5 mm) to prevent heavy pressure drop. Air is then passed through a concentric ring of a nickel–chromium metal foam which is fixed around the burner. This provides conditioned cold air required to cool the hot walls of the high pressure cell.

The high pressure cell includes four high quality quartz windows for optical access. Sensors for pressure and temperature measurement of the cell interior are installed. The pressure sensor is further connected to a pressure regulator that regulates the pressure of the cell as per user command. A pressure gauge (least count = 0.1 bar, range = 30 bar(g)) is also installed for visual information. The high pressure cell can be opened also from the top. The top of the cell is further connected to a heat exchanger. The exhaust gases from the burner are guided through this heat exchanger in order to cool the gases. The water condensed in this process is collected at the bottom of the condenser. The exhaust gases are then guided through the pressure controller and then to the atmosphere. The gases can also be led out through a hand valve (usually closed). A safety valve is installed and configured for pressure release at 30 bar in case of excessive pressure buildup.

Previous studies [2,3,8] have reported unstable flames from combustion of lean syngas mixtures with $O_2$–$N_2$ oxidizers due to lower mixture Lewis numbers. It was observed that syngas mixtures when burnt with $O_2$–$N_2$ oxidizers exhibit unstable cellular flames for pressures higher than 4 atm. This problem was resolved by replacing $N_2$ with Helium (He). Hence, $O_2$–He oxidizers are used in the present experiments. The fundamental chemistry of the combustion process remains
unaffected with such a change. All the experiments were carried out at initial temperature of 298 K.

3. Kinetic modeling

The in-house laminar flame code CHEM1D [15] was used for modeling one-dimensional free flames for the determination of laminar burning velocity. A set of equations describing the conservation of mass, momentum, energy and species for chemically reacting flows are solved using an exponential finite-volume discretization in space. Non-linear differential equations are solved with a fully implicit, modified Newton method along with a complex transport model. An adaptive gridding procedure is also implemented to increase accuracy in the flame front by placing almost 80% of the grid points in the area with the largest gradients. Thermodynamic data used are from the database of Burcat and Ruscic [16]. Recent mechanisms of Li et al. [9], Burke et al. [10], Kéromnès et al. [6], Goswami et al. [8] and GRI Mech 3.0 [11] are used in the present simulations for comparison. Mechanism of Burke et al. [10] was published only for H₂/O₂ system. The CO sub-mechanism is borrowed from its predecessor [9]. Therefore, the H₂/O₂ branch of the mechanism by Li et al. [9] is replaced with the more
recent, high-pressure kinetic scheme by Burke et al. [10]. Along with lean mixtures the mechanism of Goswami et al. [8] was validated for stoichiometric and rich mixtures and is originally based on the mechanism of Konnov [17]. GRI Mech 3.0 is a mechanism for natural gas combustion including NO formation and reburn chemistry. It is used extensively in research community and industrial environments for the past many years even for fuels like hydrogen and syngas. The models are listed with the corresponding number of species and reactions in Table 2.

4. Results and discussion

Stable flat flames were obtained using the heat flux method. Experiments were focussed at lean mixtures (\(\phi = 0.5–0.6\)) of 85:15% H\(_2\)-CO and 85:15% H\(_2\)-N\(_2\) with O\(_2\)-He oxidizer since these mixtures have not been tested in earlier studies (Table 1). Flames were first obtained at atmospheric pressure and then gradually increased to 10 atm in steps of 0.1 atm. Since flames are sensitive to change in pressure, sufficient time was allowed between successive measurements (steps of 0.5 atm) in obtaining stable flames. Figure 4 depicts variation of \(S_L\) of 85:15% H\(_2\)-CO (burnt with 11:89% O\(_2\)-He) with pressure obtained experimentally up to 5 atm and equivalence ratio (\(\phi\)) 0.6. The decrease in burning velocity is observed due to higher burning rate at high pressure. This measurement set was compared with results obtained from another high pressure experimental setup [8]. \(S_L\) of methane-air mixtures were also measured in the present setup up to 5 atm and validated with literature.

The comparison with the mechanisms reveal that the models over-predict the experiments except GRI Mech 3.0 which under-predicts all the experiments. Similar trend of under-prediction by GRI Mech 3.0 was also observed recently by Burke et al. [4]. The reason for the disparity of GRI Mech 3.0 in this case is obvious since the optimization of this mechanism was specifically done for natural gas mixtures and not syngas mixtures. A kinetic study by Burke et al. [5] also demonstrated the substantial impact of H\(_2\)/O\(_2\) subset of GRI Mech 3.0 when compared to the subset provided by Davis et al. [18] for predictions at elevated pressures.

Qualitatively, all the mechanisms used in the present comparison exhibit similar trend. However, the predictions of Goswami et al. [8] and

<table>
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<th>No.</th>
<th>Author</th>
<th>Species</th>
<th>Reactions</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Li et al. (2007)</td>
<td>20</td>
<td>91</td>
<td>[9]</td>
</tr>
<tr>
<td>2</td>
<td>Burke et al. (2012)</td>
<td>21</td>
<td>95</td>
<td>[10]</td>
</tr>
<tr>
<td>3</td>
<td>Kéromnès et al. (2013)</td>
<td>17</td>
<td>48</td>
<td>[6]</td>
</tr>
<tr>
<td>4</td>
<td>Goswami et al. (2014)</td>
<td>16</td>
<td>52</td>
<td>[8]</td>
</tr>
</tbody>
</table>
Burke et al. [10] are closer to the experimental results by almost 10 cm/s when compared to the other mechanisms. Similar predictions are observed in Figs. 5 and 6 where $\text{H}_2$–$\text{CO}$ and $\text{H}_2$–$\text{N}_2$ mixtures are burnt in $\text{O}_2$–He (12.5% $\text{O}_2$) at $\phi = 0.5$ and initial temperature of 298 K up to a pressure of 10 atm. The adiabatic flame temperature calculated using CHEM1D is around 1500 K for the former mixture. The burning velocities obtained for $\text{N}_2$ diluted mixture are lower than the $\text{CO}$ added mixture as expected. It is noteworthy, at this point, that the chemical reaction mechanisms used in the present work and available in the most recent literature are not sufficient in predicting such lean high-$\text{H}_2$ syngas mixtures burning velocities. This suggests a further analysis of the reactions involved in such combustion processes.

An assessment of the kinetic pathways involved at elevated pressures is performed using the mechanism by Goswami et al. [8] for lean mixture. Figure 7 presents the sensitivity of laminar burning velocity to the rate of reactions for 85:15% $\text{H}_2$–$\text{CO}$ mixture with $\text{O}_2$–He oxidizer (12.5% $\text{O}_2$) for pressure 1, 5 and 10 atm and $\phi = 0.5$. Among the most important reactions is $\text{H} + \text{O}_2 = \text{OH} + \text{O}$ (R3) which shows high sensitivity to changes in pressure. Reaction $\text{O} + \text{H}_2 = \text{OH} + \text{H}$ (R2) shows significant sensitivity but remains unaffected by increase in pressure. $\text{CO}$ oxidation reaction $\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$ (R8) also exhibits sensitivity of the order of other important reactions. The present and earlier studies [4,8] suggest, through flux analysis of species, that reaction $\text{H} + \text{O}_2(+\text{M}) = \text{HO}_2(+\text{M})$ (R1) contributes significantly in the lean mixture regime. The production and consumption of important intermediate species such as $\text{H}$, $\text{OH}$ and $\text{HO}_2$ depend on this reaction. The sensitivity increases by 11.5 times from 1 atm to 10 atm which is highest among all the reactions presented in Fig. 7. This reaction is also one of the major heat release reactions in the early part of a $\text{H}_2$ flame [2]. Since, the sensitivity coefficient of reaction R1 is small compared to the one derived in the work of Burke et al. [4], a reaction flux analysis was further performed to judge the importance of reaction R1. This facilitates a model analysis which is not entirely based on sensitivity. The consumption of $\text{H}$ becomes competitive between reactions R1 and R3 as observed [8] when initially R3 is slightly ahead of R1, but eventually, with increase in pressure R1 dominates every reaction that consumes $\text{H}$. This observation is supported by Goswami et al. [8] (for 85:15% $\text{H}_2$–$\text{CO}$ mixture) and Fig. 8 in the present work that shows the rate of reactions R1, R3, R5 and R6 for the 85:15% $\text{H}_2$–$\text{N}_2$ mixture with $\text{O}_2$–He oxidizer (12.5% $\text{O}_2$) at 1, 5 and 10 atm, $\phi = 0.5$ and initial temperature of 298 K. The increase in pressure brings along higher densities and collision rates (stronger kinetics) thereby reducing the thickness of the reaction layer. Subsequent production of $\text{HO}_2$ and $\text{OH}$ completes the pathway in assisting oxidation processes. Excess of $\text{O}_2$ in a lean mixture makes it also a major contributor in reactions R1 and R3 which suggests more competition. The dependences of reactions R1, R3, R5 and R6 on temperature are also observed in Fig. 8. At lower pressures reaction R1 exhibits activity from 600 K when compared to reaction R3 which is active only after 900 K. The figure also indicates the importance of the pressure dependent reaction R1 that dominates at higher pressures at both lower and higher temperature. In fuel mixtures where CO is 15% (present and earlier study [8]), the chemistry is primarily dominated by $\text{H}_2$. Among CO reactions,
R8 which shows high sensitivity (Fig. 7), contributes to the radical pool at a later stage (around 1200 K). The production of CO$_2$ which has larger collision efficiency, therefore, further helps R1 at this stage.

From the above analysis it is apparent that further discussion is required in assessing the rate constant for reaction R1 (H + O$_2$ (+M) = HO$_2$ (+M)). In addition to this, the third body efficiencies also play a major role in this reaction. When compared to gases like N$_2$, Ar and He, the larger molecules such as H$_2$O and CO$_2$ are more efficient.

Therefore, being one of the most important reactions in H$_2$/O$_2$/CO chemistry, a few research studies have been reported in the recent literature. The experimental and modeling studies by Troe [19], Michael et al. [20], Fernandes et al. [21] and Bates et al. [22] have reported rate constants of reaction R1 over a range of 300–2000 K. Their recommendations are used in the most recent kinetic models [6,8,10] used in the present work. In the work of Burke et al. [4], the authors discuss the range of efficiencies and their uncertainties suggested in the literature. In their subsequent work [10], the rate constant of reaction R1 among others was analyzed and modified according to the recommendations mentioned above. The lean mixtures of pure H$_2$ (H$_2$/O$_2$/He) (0.3 < φ < 0.85) were predicted well. However, the mechanism [10] still shows discrepancies in predicting the experiments reported in the present work. The other important reaction R3 (H + O$_2$ = OH + O) was recently studied by Hong et al. [23] and recommended a rate constant derived from absorption measurements over a range of 1100–3370 K. This recommendation is used in all the recent kinetic schemes [6,8,10]. This modification improved the capability of these mechanisms which is reported in their respective work. In general, the most recent mechanisms for syngas (H$_2$–CO) combustion cited in the present work show similar trends in predicting laminar burning velocity since the pathways remain the same. However, the predictions are different on account of different sources of the rate constants in literature, validated from certain sets of experiments and their conditions. In some mechanisms [6], the reaction parameters are adjusted to fit prediction curves. Thus, for such mechanisms the above analysis might not be completely representative.

5. Conclusions

Stretchless adiabatic laminar burning velocities are determined for lean 85:15% (by volume) H$_2$–CO and H$_2$–N$_2$ mixtures in combination with O$_2$–He oxidizer using the heat flux method. A new facility was designed for such high pressure burner stabilized flame experiments. The one-dimensional flames are stabilized in a high pressure environment with zero net heat loss which was reflected in the temperature profile of the burner plate. Experimental results are obtained for pressures up to 10 atm, for equivalence ratio of 0.5 and 0.6 at 298 K. Predictions using five kinetic schemes from recent literature are performed using an in-house laminar flame code CHEM1D [15]. A comparison with the experimental results show differences which can be attributed to key reactions H + O$_2$ (+M) = HO$_2$ (+M) and H + O$_2$ = OH + O for such lean fuel-oxidizer mixtures. A study of the kinetics is performed through
reaction rate and sensitivity analysis which indicates that these reactions along with the pair of \( \text{H} + \text{HO}_2 \) reactions drive the production and consumption of species such as \( \text{H} \), \( \text{HO}_2 \) and \( \text{OH} \). Flux pool coordinated by reaction \( \text{H} + \text{O}_2 \text{(+M)} = \text{HO}_2 \text{(+M)} \) dominates all the other reactions with increase in pressure. A further need for assessment of this reaction is suggested as this pressure dependent reaction exercises collisions of various important molecules.

Acknowledgment

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.proci.2014.05.057.

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