Effect of Elevated Pressures on Laminar Burning Velocity of Methane+Air Mixtures

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1 Introduction

Natural gas (NG) remains one of the major fuels in the production of power. Combustion of methane as the main constituent in NG has been a key field of research for many years. Methane is the simplest of all hydrocarbon fuels and is an easy fuel to handle and employ in experiments. In modeling laminar and diffusion flames for predicting good designs for burners, one of the key inputs is the burning velocity of the fuel. Certain applications like industrial gas turbines require pressures as high as 30 atm. During the modeling process, the chemical reaction mechanism employed plays a very important role and thus the kinetics of the combustion of the fuel, methane in this case, needs to be accurate enough to predict the combustion process. Over the years many methane mechanisms have been developed but an updated mechanism for higher pressures is required. In building up such kinetic mechanisms, available experimental laminar burning velocity results are still scarce for C1-C4 hydrocarbons. The laminar burning velocity ($S_u$) is a key parameter that governs many properties of combustion. Also, in determining turbulent burning velocities, an accurate correlation of the laminar burning velocity is essential [1, 2].

There are a number of methods through which the laminar burning velocity of different mixtures has been measured in the past. For measurements at high pressure, flames employed were counterflow flames, conical burner flames and spherically propagating flames. The counterflow methodology used by Egolfopoulos et al. [3] establishes two symmetrical, planar, nearly adiabatic flames in a nozzle-generated counterflow. The axial velocity profile along the centerline of the flow as determined by Laser Doppler Velocimetry is utilized in extrapolating the flame speed to a zero stretch rate. The most recent work of the same group [4] in this field uses Digital Particle Image Velocimetry for counterflow flames and the USC Mech II kinetic model [4] in simulations. Conical flames were used by Kobayashi et al. [5]. They used a 6 mm diameter slot burner to generate the conical flames and measured the cone angle using a CCD camera. A spherical chamber was utilized by Hassan et al. [6] generating spherically propagating flames of methane-air mixtures at pressures as high as 4 atm. In computing the unstretched burning velocities, these measurements were incorporated into analytical formulations that use density ratios of burnt and unburnt gas mixture. The results obtained were stretched burning...
velocities that were later corrected for stretch. They compared their results with simulations using GRI-mech 2.1 which is the earlier version of GRI-mech 3.0 [7].

In recent years, the heat flux flat flame method, developed at the TU/e, has been used for measuring laminar burning velocity of a number of fuels at atmospheric pressure. This method has been recognized as a potential technique for higher pressures because it primarily does not require stretch corrections or extrapolation of data. The heat flux flame is a flame [8] in a state where heat loss from the flame is compensated by adding heat to the unburnt gas mixture. As the name suggest, the method requires a balance in the heat flux and the only measurement made in this technique is the burner plate temperature. It is a misunderstanding that the heat flux has to be measured. The subsequent section describes this technique in a high pressure environment. The main objective of this work was to demonstrate this technique at elevated pressure (up to 5 atm) and analyze predictions of certain existing mechanisms.

2 High Pressure Experiments using Heat Flux Method

The main principle of the heat flux method is to stabilize a flat flame with unburnt gas velocity such that the heat loss by the flame is compensated by heat gain by the unburnt gases. A more detailed description of the concept and principle is available in the thesis of Bosschaart [8] and Hermanns [9]. A schematic representation of the experimental setup is shown in Fig. 1(a). A perforated plate is fitted on a burner head (Fig. 1(b)). The burner head is maintained at a temperature higher than the unburnt gas temperature. This gives a heat transport from the head to the burner plate and finally to the unburnt gas mixture. An increase in hot water temperature brings the flame closer to the plate.

![Figure 1: (a) Schematic of the present experimental setup and (b) Burner plate (top) and Burner (bottom)](image)

The unburnt gas mixture flows through the plenum chamber of the burner which is maintained at 298 K using a water thermal bath. The burner head is jacketed with a water thermal bath at 383 K. Eight
Copper-Constantan thermocouples are soldered radially on the perforated burner plate with holes of 0.3 mm diameter and 0.4 mm pitch (Fig. 1(b)). The plate has a thickness of 1 mm. The burner is housed in a high pressure vessel made of C45 steel designed for pressures up to 10 bars. A chimney is placed on top through which burnt gases are guided out. A stainless steel connection pipe followed by a needle valve is connected to the exhaust of the chimney. The pressure in the vessel is controlled by this needle valve.

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. Fig. 2(a) illustrates a schematic of heat balance in the system. In practice, it is difficult to attain a strictly adiabatic flame. The only measurement required in this technique is 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 polynomial. The coefficients of such polynomials are plotted against sub and super adiabatic flow velocities. The adiabatic state is reached for zero value of the coefficient. The procedure and model calculation for measuring the temperature and evaluating the burning velocity is described by Hermanns [9]. Fig. 2(b) represents the measured temperatures along the burner plate for lean mixture of CH$_4$ and air at 3 atm and 298 K.

![Figure 2: (a) Heat balance (b) Radial temperature profiles across the burner plate at different gas velocities](image)

### 3 Simulations

The in-house laminar code CHEM1D [10] was used for modeling a 1D combustion process for the determination of the laminar burning velocity. CHEM1D solves a set of equations describing the conservation of mass, momentum, energy and chemical components for chemically reacting flows. It uses an exponential finite volume discretization in space and non linear differential equations are solved with a fully implicit, modified Newton method. An adaptive gridding procedure is also implemented to increase accuracy in the flame front by placing almost 80% of the gridpoints in the area with the largest gradients. The input to this code are the conditions (pressure, temperature, mixture composition), thermodynamic and transport data and the chemical reaction mechanism.

The two reaction mechanisms used in this work are GRImech 3.0 [7], USC Mech II [11]. The former was optimized to model natural gas combustion, including NO formation and reburn chemistry. It has been used over the years for modeling and has been successful in delivering good results for natural gas and methane. USC Mech II kinetic model is a comprehensive reaction mechanism relevant mainly for high-temperature oxidation of hydrogen, carbon monoxide and C1-C4 hydrocarbons.
4 Results and Discussion

For stoichiometric CH₄/Air mixtures at atmospheric conditions (P = 1 atm, T = 298 K), Sₓ is ≈ 36cm/s. Therefore, at conditions P > 1 atm, Sₓ must be lower than this value. Methane is used in these experiments as this value of unburnt gas velocity and lower are well below the safe limit for these experiments that uses burner plate hole diameter of 0.3 mm. Often the notation Sₓ° is used in describing unstretched Sₓ. In the present work, the flames are unstretched and it is referred as Sₓ.

Results of the heat flux method in determining laminar burning velocity for gases like CH₄, C₂H₆, C₃H₈, C₄H₁₀, CH₄/H₂, Ethanol, H₂/N₂/O₂ etc. have been consistent with literature at atmospheric pressures [8,9]. This is the motivation for applying this technique to elevated pressure. Heat flux flames are maintained flat for velocities close to the adiabatic range. At elevated pressures the flames are strained as the flow rates are higher. At too sub-adiabatic conditions the flows are low enough to pull the flame close to the burner plate and cause sudden increase in plate temperature. Hence, the range of velocity must lie within this region which is close to the adiabatic region. A prediction of the possible range of velocity is done using CHEM1D.

Experiments were performed from P=1.5 to 5 atm for 0.8 < ϕ < 1.4 where ϕ is the equivalence ratio. This range of equivalence ratio was chosen to cover both lean and rich behavior of the flame at high pressure. The maximum error estimate for laminar burning velocity associated with this technique was 0.6 cm/s. Errors associated with equivalence ratio were less than 0.025 for all experiments. Fig. 3 and 4 show the dependence of Sₓ for 0.6 < ϕ < 1.4 for pressures up to 5 atm. Experimental results for P=1 atm have been taken from Hermanns [9] as they are the most recent results using heat flux method. For comparison, experimental data from literature [4-6,12,13] have also been included. GRImech 3.0 has been efficient in capturing the behavior of Sₓ at lower pressure (Fig. 3) but not at higher pressure (Fig. 4). USC Mech II uses certain reaction rate constants from GRImech 3.0 and still showcases a significant difference. The fact that this mechanism is tuned for high temperature applications makes it behave a little differently. To view the trend of the mechanisms more closely Fig. 5(a) shows a comparison for ϕ = 0.8 and 1.2. In general, GRImech 3.0 shows better agreement than USC Mech II.

The kinetic reaction scheme primarily consists of many sub-mechanisms. H₂/O₂ reactions are a very important part of the CH₄ kinetic scheme. This can be easily seen from the sensitivity analysis (figure 4 (b)) for reactions like

\[ H + O₂ = O + OH \]  
\[ H + O₂ + H₂O = HO₂ + H₂O \]

Rate of reaction (1) shows the highest effect on laminar burning velocity at all pressures. This reaction leads to chain branching production of OH radicals that play a major role in oxidizing species like CH₄.
and CO. Frenklach et al. [14] in a study on optimization and analysis of large mechanisms defined a rate constant for reaction (2) which shows a negative sensitivity. GRI mech 3.0 uses a modified rate based on this study and shows high influence on burning velocity especially for lean flames.

One of the most important species in methane chemistry is CH$_3$. Peterson et al. [15] have highlighted that at high pressure and low temperature species like HO$_2$, CH$_3$O$_2$ and H$_2$O$_2$ find increased importance. GRI mech 3.0 does not include CH$_3$O$_2$ radical which is a product of one of the oxidation reactions of CH$_3$. Although CH$_3$O$_2$ radical does not show influence on burning velocity, it affects the behavior of ignition delay time predictions. CH$_3$ also oxidizes and opens channels to the formation of HCO that subsequently converts to CO and CO$_2$. Also, from Fig. 5(b) it is evident that HCO has an effect on burning velocity. Reaction

$$OH + CO = H + CO_2$$

has therefore a lot of influence in the overall chemistry. This reaction also plays a similar role in H$_2$/CO mixtures. Production of H$_2$ [16] is mostly attributed to reactions

$$CH_4 + H = CH_3 + H_2$$
$$H + CH_2O = H_2 + HCO$$
5 Conclusions

The heat flux method is being demonstrated in burning velocity measurements for elevated pressures up to 5 atm. Comparisons with several literature sources (experiments) show good agreement. Numerical simulations have been performed using two reaction mechanisms [7,11] for comparison. Through sensitivity analysis at higher pressures, relevant chemical reactions that influence burning velocity predictions have been discussed and the need to improve such mechanisms have been proposed.

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References