Effect of CO_2 Dilution on the Burning Velocity of Equimolar Syngas Mixtures at Elevated Temperatures

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1 Introduction

Gasification converts organic or fossil fuel based carbonaceous materials into a mixture of CO and H_2, which serves as a fuel. Synthetic gas (syngas) is the product of gasification of carbon-containing fuel comprising mainly of H_2 and CO. The composition of syngas can vary depending upon the type of carbon-containing fuel used and gasification methodology. Integrated Gasification and Combined Cycle (IGCC) power plants have been proved a better power generation technology than conventional coal combustion-based technology. They offer better energy efficiency and environmental performance [1]. IGCC power plants can use syngas as an alternative fuel if the fundamental combustion characteristics of the gasification output are known. Laminar burning velocity is one such parameter that governs the combustion process and which contains information regarding the mixture reactivity, diffusivity, and exothermicity. The importance of this parameter has led to the development of different measurement techniques with both steady and dynamic flames. The various methods in practice are constant-volume combustion bomb (expanding spherical flame) [2–4], heat flux method [1, 5], counter-flow stagnation, Bunsen burner.

Cheng Dong et al. [6] determined burning velocities of H_2/CO/air mixtures using Bunsen flame method at ambient temperature and pressure. The results show, an increase in hydrogen fraction increases the burning velocity due to higher hydrogen reactivity. Burbano et al. [7] using Bunsen flame method determined burning velocities for syngas at different dilutions of N_2 and CO_2. There was a significant reduction in burning velocities using CO_2 dilution as compared to N_2. Kishore et al. [1] studied the effect of different (40-60% by volume) CO_2 dilution on equi-molar syngas mixtures at ambient conditions using Heat Flux method. Cellular structures were observed for lean mixtures of these dilutions which may have obscured the reported results.

The different methods discussed above invariably extrapolate the measured data of burning velocities to that of adiabatic flame(zero heat loss) to obtain the laminar burning velocity of a given fuel-air mixture. The preheated diverging channel technique used in this study do not use any such extrapolation. Properties of the

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planar flames stabilized in the channel are used to determine the burning velocities for a range of elevated temperatures (350-650 K).

Typical syngas compositions obtained from biomass gasifiers contain 60-80 % diluents (CO_2 and N_2) [4]. Effective use of these mixtures in IGCC engines requires accurate knowledge of laminar burning velocities at elevated temperatures and pressures. The study focuses on the experimental determination of burning velocities of equi-molar syngas with two (60, 70 %) different CO_2 dilutions at elevated temperatures. The flame structure of the mixtures are then analyzed, and most sensitive reactions that influence the flame propagation are presented.

2 Methodology

The present work uses a high aspect ratio diverging channel for stabilizing the planar flames and uses a similar scheme of the experimental segment as [8]. Akram et al. [9] adequately explain dynamics of stabilization of planar flames in these diverging. Figure 1: Left shows the schematic of the experimental setup. High aspect ratio channel as shown in the Fig. 1 provides a uniform velocity field and the divergence aids in preventing flashback. The inlet of the diverging duct is the premixed H_2-CO-CO_2-air mixture at ambient conditions at various equivalence ratios and inlet flow velocities. The mixture equivalence ratio and flow velocity were precisely controlled and monitored using the coupled system of Mass Flow Controllers, a command module, and a personal computer. The preheating of the incoming mixture is done with an (SHTS) super high-temperature heater (Max. 1200 W). This will provide a positive temperature gradient along the axial direction, which helps in the stabilization of the planar flames, balance the heat loss from the flame to the channel walls and thereby attain near adiabatic conditions [8].

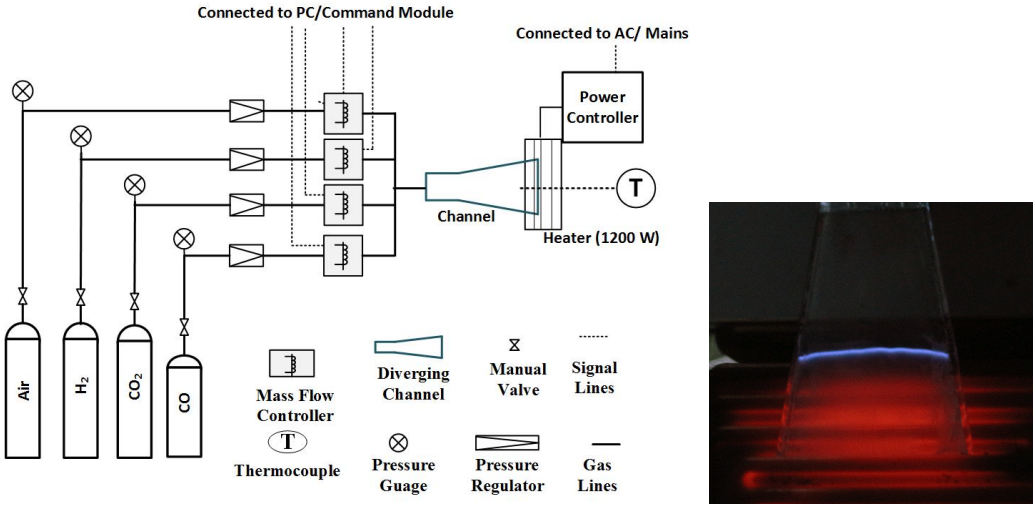

Figure 1: Left: Experimental setup Right: Stabilized Planar flame at $\phi = 1$ inlet velocity of 1 m/s

Paidi et al. [8] discuss in detail the Laminar Burning Velocity (LBV) calculation employed in this work. Experiments are carried out for various equivalence ratios ($\phi = 0.7 - 1.3$) and different inlet velocities. Planar flames stabilize inside the diverging duct at the position where the flame propagation velocity matches the inlet velocity. Temperature is measured at the position where the flame stabilizes, assuming the unburnt

gas temperature being same to the temperature of the wall just before the flame position. The flame position is recorded using a camera, and the flame area is extracted. Figure 1: Right shows the stabilized planar flame for $\phi = 1$ inlet velocity of 1 m/s.

3 Results and Discussion

This section discusses the determination of laminar burning velocities of syngas-CO_2-air mixtures at various equivalence ratios ($\phi = 0.7 - 1.3$), unburnt mixture temperatures of (400-650 K). The diverging channel (Quartz material) stabilizes thin planar flames; the heat loss to the duct walls is compensated by external heating. The reduction in burning velocity owing to this heat loss is less than 5 % [9]. The burning velocity is found to increase with an increase in unburnt mixture temperature ($T_{u,o}$) (Figure 2: Left). The reasons for this increase are product dissociation, preheating and change in thermodynamic and transport properties due to increase in mixture temperature. Authors have chosen GRI 3.0 chemical kinetic mechanism for numerical predictions. GRI 3.0 mechanism is widely used in multi-component mixtures similar to the present work for numerical modeling. The optimization of GRI 2.11 to GRI 3.0 has provided with basic kinetics for predictability of basic combustion properties. The optimization target of the GRI 3.0 also included experimental LBV for similar mixture composition of syngas with different dilutions. The comparison with the numerical predictions using GRI 3.0 [10] kinetic mechanism shows that the experimental results agree well with the predictions. The power law correlation obtained from the experimental data gives the temperature exponent and the laminar burning velocity (Su, o) which can be employed to determine burning velocities for higher mixture temperatures. The uncertainty of the measured results are $\pm$ 5%. [11]

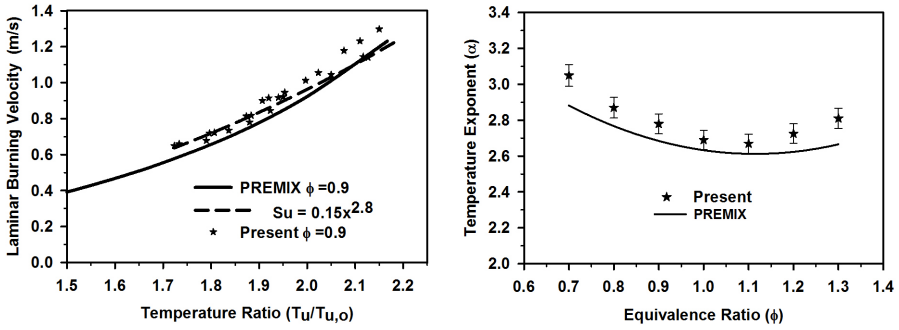

Figure 2: Left: Variation of laminar burning velocities at elevated temperatures at $\phi = 0.9$. Right: Comparison of experimental results at 300K for 60 % CO_2 dilution.

Figure 2: Right shows the comparison of present results with the computational results using GRI 3.0 mechanism [10] and Kishore et al. [1]. The difference between the experimental measurements and PREMIX predictions with GRI Mech 3.0 is relatively negligible for lean mixtures and increases to $\approx$ 2 cm/s for the rich mixtures ($\phi = 1.3$). The predictions of laminar burning velocity of rich mixtures with high CO_2 content differs significantly when compared with the data reported by other researchers [1]. Further investigation to understand the effect of chemical and thermal behavior of CO_2 addition, is important to explain the underlying physics adequately. Figure 2: Right shows that the burning velocity is maximum for slightly rich mixtures $\phi = 1.1$, where the adiabatic flame temperature is maximum.

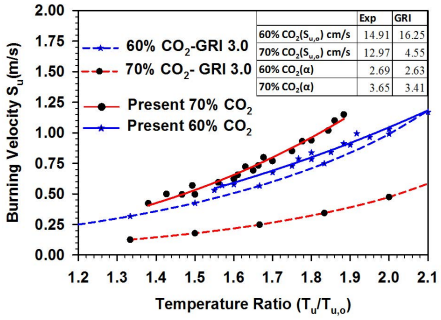

Figure 3: Burning velocities at different dilutions of CO_2 for stoichiometric mixture at elevated temperatures. Solid lines - Present, dotted - GRI 3.0. $S_{u,o}$: laminar burning velocity at 300 K and atmospheric pressure; α : Temperature exponent.

The laminar burning velocities of 60, 70 % dilution cases of equi-molar syngas mixtures with that of CO_2 are investigated and discussed here. Figure 3 shows the variation of laminar burning velocities of stoichiometric mixtures at elevated temperatures. The decrease in laminar burning velocity with the further addition of CO_2 is evident. The decrease in burning velocity is due to an increase in heat capacity and a decrease in thermal diffusivity of the mixture with the addition of CO_2. The predictions at 70 % dilution vary with the PREMIX computations as compared to the lower dilution case. Numerical calculations using PREMIX fail to predict low burning velocities ($<$ 5 cm/s) because numerically the burning rates are not sufficient to stabilize a freely propagating adiabatic flame. Predictions at 300-400 K using GRI Mech 3.0 does not converge to a solution for the 70 % case and hence the $S_{u,o}$ is extrapolated from predictions at high temperatures (400 - 650 K). The laminar burning velocities obtained from experiments and computations for 60 % case compare well. However, the predictions do not match well with the experiments for 70 % dilution of CO_2. These discrepancies of 70 % CO_2 may be due to the low H_2 (15 %) content of the fuel as reported by Natarajan et al. [12] and also, the high (70 %) dilution of CO_2.

4 Flame Structure

The flame structure of these mixtures was studied in detail to understand the fundamental chemical kinetics involved. H, OH and O radicals are mainly used for analyzing the effect of dilution. The rate of production (ROP) analysis aids in determining the contribution of each reaction to the production or destruction of species. ROP of H and OH radicals were analyzed to isolate the most sensitive reactions that contribute to the oxidation of the mixture.

Figure 4 shows the ROP of H and OH radicals with the different dilutions for stoichiometric mixture at T_u = 400 K. Dimensionless temperature ($\tau = \frac{T-T_u}{T_{ad}-T_u}$) is used as the axial direction. Unburnt gas temperature $T_u = 400$ K, T_{ad} is adiabatic flame temperature. Two Y axes are depicted for 60 % (Left) and 70 % (Right) CO_2 dilutions. The dominant reactions remain unchanged for 70 % CO_2 dilution with decreased peak ROP and a slight shift to the downstream. The comparison of numerical results for 50, 60 % dilutions reveals that the flame speeds variations are consistently smaller than the change between 60 and 70 %. The change in ROPs' of 50 % and 60 % dilutions compared to the difference between 60 and 70 % case is much larger. The reduction in peak ROP is expected with the further addition of CO_2 [4] however, detailed analysis and

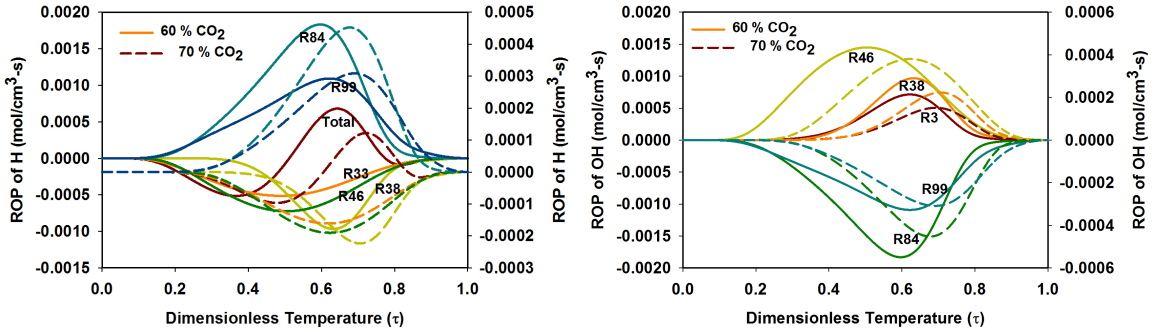

Figure 4: ROP of H and OH radicals for CO/H_2/air mixtures with CO_2 dilution; solid lines-60 % CO_2, dotted lines-70 % CO_2

modification is required for better prediction of flame speeds at these dilutions because of the consistent 80 % decrease in ROPs' of H and OH for the 70 % dilution case.

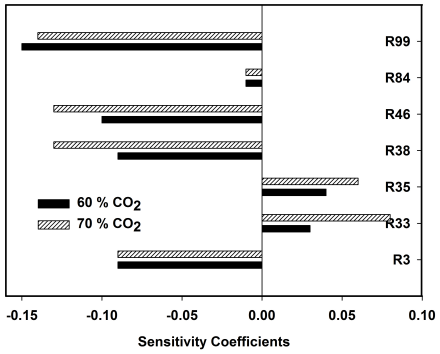

Figure 5: Sensitivity Coefficients

The sensitivity analysis shows how the predicted flame speed depends on the important reactions quantitatively. The temperature sensitivity coefficients were determined for the inlet flow rate with respect to the reaction pre-exponential (A) factors. The maximum sensitivity coefficients for the different dominant reactions are depicted in Fig. 5. The important reactions remains the same for both dilutions however, the most positive sensitivity reaction shifts from R35 ($H + O_2 + H_2O = HO_2 + H_2O$) to third body reaction R33 ($H + O_2 = HO_2 + M$). The negative sensitive coefficients are consistent for both dilutions with R99 ($OH + CO = H + CO_2$) showing the highest magnitude.

5 Conclusions

The laminar burning velocities of equi-molar syngas mixtures at elevated temperatures were determined both experimentally and numerical predictions using GRI Mech 3.0. The burning velocities increase with an increase in mixture temperature since; the inlet mixture enthalpy is higher and hence the adiabatic flame temperature. The dilutions of the mixture with CO_2 decreases the burning velocity because of the reduction

in reactive species, the higher specific heat capacity of CO_2, and the impeding effect of CO_2 on the CO oxidation. The predictions using GRI 3.0 mechanism compare well with the experimental results at 60 % dilution. However, the 70 % dilution varies with the predictions considerably. Flame structure studies show the need for the modification of the mechanism for accurate predictions at high dilution rates.

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