

Elevated Temperature effects on Laminar Burning Velocity Temperature Exponent of Liquid Fuels

Amit Katoch, Rohit Kumar, Sudarshan Kumar
Combustion Research Laboratory, Indian Institute of Technology, Bombay
Mumbai, Maharashtra, India

1. Introduction

Increasing greenhouse gas emissions, particulate matter and combustion driven pollutants have prompted the scientific community to look deeply into the combustion research from fundamental and application perspectives. In this context, renewable energy sources have recently become a major part of global and national energy policies and more and more emphasis is being directed towards cutting down the dependency on fossil fuels. Biofuels such as methanol, ethanol, butanol etc. have already been tried and tested in engine design and development is still underway to make their usage more efficient and economical. High octane rating of methanol against ethanol yields better engine performance and reduced emissions. Biofuels can be produced from natural resources such as crops, feedstock and algae.

Towards the end of 2016, researchers at US Department of Energy's Oak Ridge National Laboratory stumbled upon an inexpensive nanostructured catalyst for the direct electrochemical conversion of CO₂ to ethanol at ambient temperature and pressure [1]. In the process of engine design and development, availability of a comprehensive and robust chemical kinetic mechanism is essential for accurate prediction flame response parameters and pollutant formation. Such mechanisms are tested against experimental data of high fidelity such as ignition delay timings, species profile, flame structure and laminar flame velocity measurements. If a proposed model fails to reproduce these important parameters, then its utility requires further scrutiny. Laminar burning velocity is a parameter which embodies fundamental information on diffusivity, reactivity, and exothermicity of a given mixture. Its value depends on equivalence ratio, initial pressure and initial temperature of fuel-air mixture. The dependence of laminar burning velocity on initial mixture temperature is described as:

$$S_u = S_{u,0} \left(\frac{T_u}{T_{u,0}} \right)^\alpha$$

Where α is the temperature exponent and its value depends on pressure and mixture equivalence ratio. For the accurate measurement of burning velocity the flame has to be planar, stretch free and adiabatic. The most popular methods reported in literature for the measurement of this parameter are: Heat flux burner method, Constant Volume Combustion Bomb, Counter flow burner and Bunsen burner. These methods suffer from some limitations and inaccuracies associated to flame stretch, curvature, flame cooling and low temperature operation regimes. In case of stretched spherical flames obtained from constant volume method, extrapolation to zero stretch leads to erroneous predictions at times. A lot of data is available in literature for gaseous fuels unlike liquid fuels for which data is scarce and it shows a huge scatter at higher mixture temperatures. Also, for liquid fuels the temperature measurement range with the aforementioned methods are low. For instance, for methanol-air mixtures at atmospheric pressure, the highest temperature at which burning velocity is reported is 480 K. For ethanol-air mixtures there are very few studies for temperatures

greater than 400 K. The kinetics investigation for temperature exponent at such high temperatures have not been done. Thus, the present work is aimed at high temperature burning velocity measurements from planar, stretch free flames and kinetics analysis of the associated temperature exponent.

2. Experimental set up

The diverging channel technique for measuring laminar-burning velocity was proposed and developed by Akram et al. [2] and used for gaseous fuels like methane, propane and LPG. Later it was modified for liquid fuel measurements [3]. Figure 1 shows the meso-scale channel set-up for measuring the burning velocities of liquid fuel–air mixtures. Quartz channels of varying divergence angles (5° , 10° , 15°) and aspect ratio 12.5 were used. The length of the initial rectangular part was 50 mm and the length of the diverging part was also 50 mm. The channel depth is 2.0 mm, which is of the order of quenching diameter. The flow of gases is regulated using mass flow controllers. The channel is externally heated with an infrared heater. This maintains a steady temperature gradient across the length of the channel and simulates the heat recirculation through the solid walls thus avoiding thermal coupling between the solid and gas phase. A temperature controller driven air preheater heats the incoming air to a temperature above the boiling point of fuel. Since the fuel flow rates used in the current setup are very small, a syringe pump is used to feed liquid fuel to the hot air jet coming from preheater. The mixture is then fed to the diverging channel and ignited using a nichrome ignitor.

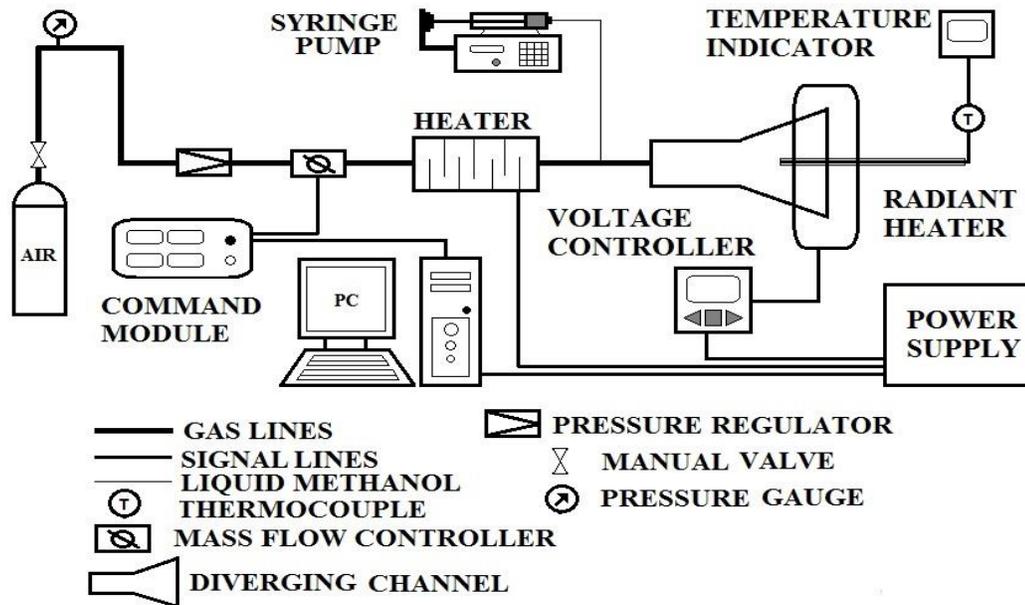


Figure 1. Schematic diagram of experimental setup

All flow paths of vapor-air mixtures are kept heated using tape heated and insulated to avoid vapor condensation. The Peclet number is small since the mixture flow rates inside the channel are low. Therefore, the unburnt mixture is assumed to have attained wall temperature at flame stabilization location. Various

flame dynamics are observed as unburnt mixture flow velocity is varied. Only planar flames are used to extract the burning velocity. The correlation used for the calculation is based on mass balance:

$$S_u = U_{inlet} \left(\frac{A_{inlet}}{A_f} \right) * \left(\frac{T_f}{T_{inlet}} \right)$$

3. Simulations

A Fortran based PREMIX [4] code is used to predict burning velocities computationally at different conditions of temperature and equivalence ratios. It solves the governing equations assuming 1-D flow with uniform inlet conditions. Multicomponent diffusion and thermal diffusion options are used. The laminar burning velocity and sensitivities of methanol-air mixtures are computed using Li et al. mechanism (consists of 21 species and 93 reactions) [5]. For ethanol-air mixtures San Diego mechanism is used (57 species and 256 reactions)[6]. The adaptive mesh parameters were grid independent for GRAD = 0.02 and CURV = 0.1.

4. Results

The burning velocity temperature dependency of two liquid fuels: methanol and ethanol is assessed at ambient pressure. Methanol-air mixtures variations were measured from 350-650 K and equivalence ratio range 0.7-1.3. Ethanol-air mixtures were studied from 350-600 K and equivalence ratios-0.8, 1 and 1.2. The reference temperature $T_{u,0}$ of the unburnt mixture was 300 K. Temperature exponents extracted from burning velocity measurements using power law correlation: $S_u = S_{u,0} \left(\frac{T_u}{T_{u,0}} \right)^\alpha$

4.1 Methanol-Air Mixtures: Kinetics based Analysis

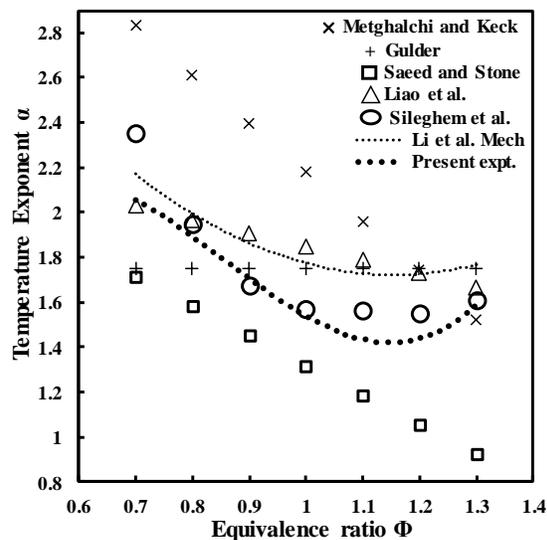


Figure 2. Variation in temperature exponent of methanol-air mixture with equivalence ratio

The variation in temperature exponent was reported using meso-scale channels and compared with other researchers [7-11], as shown in Figure 2. It is evident that a huge variation (30-50 %) exists amongst reported and computed values. A flow rate based sensitivity analysis was done to identify the key reactions and to understand their effect on the burning velocity of methanol-air mixture.

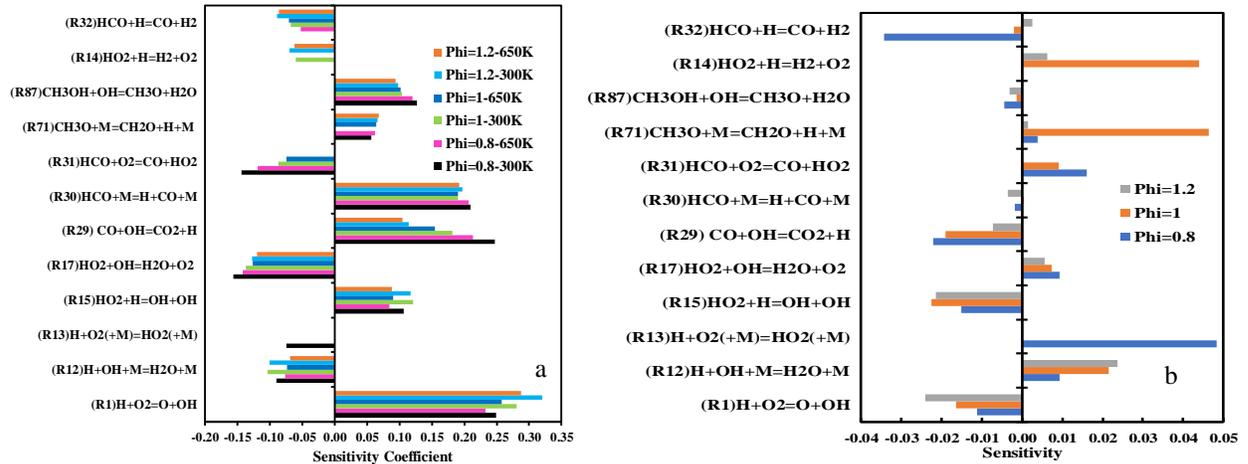


Figure 3. a) Flow rate A-factor sensitivity coefficients for methanol-air mixtures b) Normalized sensitivity coefficients for the power exponent α

The laminar flame speed is directly proportional to the concentrations of H and OH radicals and this is established from the highest sensitivity values for the chain branching reaction (R1): $\text{H} + \text{O}_2 = \text{O} + \text{OH}$. Analysis also shows that the HCO decomposition reaction (R30): $\text{HCO} + \text{M} = \text{H} + \text{CO} + \text{M}$ and CO oxidation reaction (R29): $\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$ are equally important. In a generic sense reactions: R1, R15, R29, R30, R71 and R87 contribute positively towards flame speed. It is worth noticing that reaction R13 shows inhibiting features only for lean condition ($\Phi=0.8$). A sensitivity analysis of power exponent α was carried out to understand the relation between temperature dependence and key reactions. This would also help in assessing how the burning velocity promoting reactions affect the temperature exponent. The normalized sensitivity of the power exponent with respect to flow rate sensitivity can be obtained as:

$$\text{Sens}(\alpha, fl) = \left(\frac{\partial \alpha}{\partial fl} \right) * \left(\frac{fl}{\alpha} \right)$$

$$\text{Sens}(\alpha, fl) = \frac{\text{Sens}(S_w, fl) - \text{Sens}(S_{u,0}, fl)}{\ln\left(\frac{T}{T_0}\right) \alpha}$$

Figure 3b reveals that as the temperature increases from 300 to 650 K (in the present case), several chain promoting reactions (as in figure 3a. R1, R15, R29, R30, R87) become less important and these reactions are now displayed with negative sensitivity. The same is true for several chain inhibiting reactions that

display positive sensitivities. This indicates that kinetic analysis for burning velocity alone is not sufficient for assessing the temperature exponent variations.

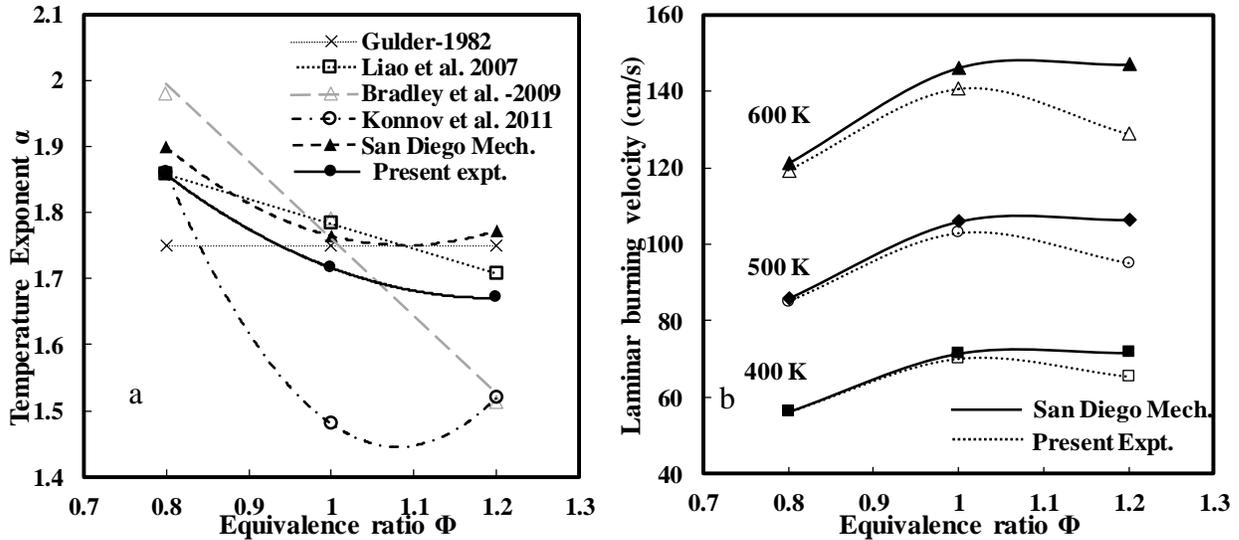


Figure 4: a) Variation in temperature exponent of Ethanol-air mixtures with equivalence ratio b) Variation of laminar burning velocity with temperature

4.2. Ethanol-Air Mixtures: Laminar burning velocity and Temperature exponent variation

Figure 4a shows the variation of temperature exponent, α with the mixture equivalence ratio and its comparison with results from other values reported in literature. The unburnt mixture temperature range for deducing temperature exponents was 350-600 K. Variations in temperature exponent values reported in literature range from 12% to 18%. A linear decrement in the values of temperature exponent was reported by Bradley et al. [12] and Liao et al. [10] whereas Gulder [14] reported a constant value of 1.75. Konnov et al. [13] reported an inverted parabolic profile with a minimum at $\Phi \approx 1.1$. San Diego Mech also predicts a similar profile with a minimum at $\Phi \approx 1.1$. The present experimental results were fitted to a second order polynomial which yielded a minimum value of temperature exponent at $\Phi \approx 1.2$. The variation of temperature exponent α with equivalence ratio, Φ can be correlated using a second -order polynomial as:

$$\alpha = 5.25\Phi^2 - 11.35\Phi + 7.58.$$

The burning velocity values from experiment were compared with San Diego Mech results at high temperatures as shown in Figure 4b. A good agreement was observed for lean and stoichiometric conditions. On the rich side the predictions were higher than experimental values. This difference increases with increasing temperature. Therefore, the fuel kinetics in the rich mixture domain needs further investigation.

5. Conclusions

The temperature dependency of laminar burning velocity was used to extract the temperature exponent variation using preheated meso-scale channels. The effect of reaction kinetics on burning velocity and temperature exponents for methanol-air mixtures was assessed. The reactions which contribute positively towards burning velocity were found to have a suppressing effect for exponent. For ethanol-air mixtures

the exponent was found to decrease from lean to rich mixtures with a minima at $\Phi=1.2$. A good agreement between experimental and mechanism predictions was observed for burning velocities.

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