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GENERATION OF PREMIX LAMINAR FLAME SPEED LIBRARY

By

Sai Prashanth Kumar

A THESIS

Submitted in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

In Mechanical Engineering

MICHIGAN TECHNOLOGICAL UNIVERSITY

2020

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This thesis has been approved in partial fulfillment of the requirements for the Degree of MASTER OF SCIENCE in Mechanical Engineering.

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Abstract

The Laminar flame speed is an essential parameter in measuring turbulent premixed combustion applied in Spark ignition engines. Instead of using power-law correlations, which is valid only for particular ranges, the procedure for generating a premixed laminar flame speed library is defined using MTU – Master mechanism for a wide range of charge mixture conditions inside an engine combustion chamber: Temperature (300 – 700 K), Pressure (1 – 70 bar) and reactant mixture composition of equivalence ratio (0.4 – 2.0). Laminar flame speed library is generated for methane. The mechanism's performance was improved by adjusting the pre-exponential factor of the most sensitive reactions found from the sensitivity analysis to match the simulation results with experimental data in the literature. It is observed that the sensitivity order of reactions changes for different operating conditions, except that $\text{H} + \text{O}_2 = \text{O} + \text{OH}$, is the most sensitive reaction.

1 INTRODUCTION

Combustion of fossil fuels contributes to 80% of primary energy consumption in the US, and this share is expected to increase in the coming years, as per the trends[1]. CO and NO_x emissions that constitute part of combustion products relate to significant problems of global warming. Many combustion developments like fuel economy improvement, development of cleaner combustion methods like flame cooling, air-staging, burning, lean premixed combustion, exhaust gas recirculation, high-temperature air combustion, and flameless combustion have taken place. Complete basic knowledge of these techniques is required to implement these in pragmatic systems. The necessary step towards understanding this is understanding ignition delays and Laminar Flame speed both experimentally and in numerical modeling, which helps us understand its structure and propagation.

Laminar burning velocity is a physicochemical property of fuel-oxidizer mixture resulting from the combined effect of mixture diffusivity, mixture exothermicity, and combination reactivity. It measures the mixture's overall reactivity and helps validate detailed reaction mechanisms and simplified kinetic models. It is also used to study various combustion phenomena like turbulent flame speed calculation, flame stabilization, flame flashback, flame blowout, and flame extinction. Practical applications include the modeling of combustion in Internal Combustion (IC) engines, gas turbine combustors, industrial furnaces, and rocket engines[2].

Laminar flame speed (S_{L0}), by definition, is the velocity of steady one-dimensional adiabatic freely propagating flame in a doubly infinite domain. This definition makes it suitable for calculating 1-D computer codes using well-defined reaction mechanisms, thermodynamic, and transport properties. It is impossible to measure this quantity from a fundamental point of view. Therefore, it is calculated by some assumptions and theories.

1.1 Measurement techniques of Laminar flame speed

The various methods used to study the laminar burning velocity are:

1. Spherical flame method
2. Stagnation flame method
3. Heat flux method
4. Annular stepwise diverging tube
5. Externally heated diverging channel method
6. Burner method

1.1.1 Spherical flame method

In the spherical flame method, a spherical combustion vessel is filled with a premixed mixture of fuel and oxidizer at a known equivalence ratio and ignited at the center, thus propagating the flame. There are stretch effects because of the spherical curvature, corrected to get the exact value of the Laminar burning velocity. There are two methods to measure in spherical flame method:

1. Constant pressure spherical flame method
2. Constant volume spherical flame method

1.1.1.1 Constant pressure flame method

In the constant pressure flame method, flame radius time history is measured, and from that stretched flame speed is calculated by,

$$S_b = \frac{dr_f}{dt}$$

Where

r_f – instantaneous spherical flame radius

t – time

Flame stretch rate,

$$K = \frac{2S_b}{r_f}$$

K needs to be extrapolated to zero to get the unstretched laminar flame speed S_b and burned gas Markstein length, L_b . [3]

1.1.1.2 Constant volume method

In the constant-volume method, a spherical chamber without optical chamber access is used to measure the unsteady pressure-time history, from which laminar flame speed is calculated. [4]

There are many types of stretch correlations that are available in the literature. Non-linear stretch correlation is chosen as it gives the results with little variance.

1.1.2 Stagnation flame method

In the stagnation flame method, two streams of fuel and oxidizer mixture have impinged on each other. So this forms a twin flame configuration, so the only losses which are to be considered are the stretch flame effect due to the hydrodynamics strain effect.[5]

1.1.3 Heat flux method

In the heat flux method, flames are assumed to be planar at the burner exit, and the velocity of the unburned gases is familiar to the flame front, thus defining unburned gas velocity.[6]

1.1.4 Annular Stepwise Diverging Tube

In the annular stepwise diverging method, the concept that flame propagation velocity is comparable to the laminar burning velocity if the flame is not significantly elongated or wrinkled is used. It consists of a quartz tube, and the progress of the development of this setup is defined by the

- Annular diverging tube (ADT) – In this, a tapered core is inside the quartz tube, in which the premixed flames could be stabilized hydrodynamically[7]
- Annular stepwise diverging tube (ASDT) – In this, a stepwise core replaces the tapered core, and the backward steps helps in stabilizing the flames in the azimuthal direction[8]

1.1.5 Externally heated diverging channel method

In the externally heated diverging channel method, a premixed laminar fuel and oxidizer mixture is ignited at the end of a rectangular diverging channel. The flame stabilizes when the mixture's burning velocity and the flow velocity are the same. There are losses in this like heat loss to channel walls and the effect of hydrodynamic strain[9]

1.1.6 Burner method

In the burner method[10], a flame is maintained in the conical form at the exit of a burner, and the velocity at the normal direction to the flame defines the laminar flame speed by

$$S_L = u_g \sin \alpha,$$

u_g – Velocity of unburned gases

α – the semi-cone angle of the conical flame

From the literature, it is found that there is a huge variance in the data of the S_L for any given condition. All this variance is the various measurement techniques, stretch effects,

heat loss effects, data extraction techniques, and methods of application of correction factors. A nonlinear method of stretch correction is used along with heat correction techniques for all the methods involved.

1.2 Numerical analysis of Premixed Laminar Flame Speed

In addition to experimental methods of S_L measurement, there are one-dimensional premixed flame equations of the continuity equation, energy conservation, species conservation, and ideal gas equation, which are solved using detailed reaction mechanisms to calculate the S_L . Transport properties are used in solving these equations, and for calculating these properties, four different methods are used[11], such as TRANLIB, MKC, DRFM and EGLIB

The different codes used for solving these laminar flame equations are:

1. PREMIX/OPPDIFF – It is used to solve Freely propagating flame[12] and counter premixed flame using the Finite Differences Method by the second-order upwind scheme. It is a module of Chemkin – II and was commercially developed by Reaction design and now Ansys.[13]
2. CANTERA – It is used to solve Freely propagating flame and counter premixed flame using the Finite Differences Method by the second-order upwind scheme. It is an open-source code[14].
3. FLAME MASTER – It is used to solve Freely propagating flame and counter premixed flame.[15]
4. COSILAB/RUN1DL – It is used to solve Freely propagating flame, counter premixed flame, and outwardly propagating spherical flames using Finite Differences Method by second-order upwind scheme[16].
5. CHEM1D – It is used to solve Freely propagating flame, counter premixed flame, and outwardly propagating spherical flames using Finite Volume Method by second-order upwind / exponential/central differences scheme in space and first/second order in time.[17]
6. ASURF1D – It is used to solve Freely propagating flame, counter premixed flame, and outwardly propagating spherical flames using the Finite Volume Method by second-order accurate string splitting fractional step scheme[18].
7. OPENSMOKE++ – It is used to solve Freely propagating flame, counter premixed flame, and outwardly propagating spherical flames using the Finite Volume Method by second-order upwind scheme[19].
8. AGNISOFIT – It is used to solve Freely propagating flame, counter premixed flame, and outwardly propagating spherical flames using the Finite Volume Method by second-order upwind scheme[20].

1.3 Literature review

Literature has been organized into the first measurement without considering stretch effects, different measurement methods, development of correlations, chemical kinetic mechanisms, fuels, and engine-controlled measurement.

SPHERICAL FLAMES

In 1980, Ryan et al. determined the effects of fuel composition on the laminar burning velocity of methane, propane, iso-octane, n-heptane, and methanol. They studied the effects of pressure, temperature, charge dilution on the laminar burning velocity. Also, they developed a Nitrous Oxide (NO) model that is to be adopted for use in engines[21]. Faeth et al. studied the laminar burning velocity experimentally using outwardly propagating spherical flames considering methane, ethane, propane, and ethylene/air mixtures. It is observed that the neutral preferential diffusion is shifted towards the fuel-equivalence ratio on the unstable side of unity, which is in agreement with the effects of stretch theories[22].

BUNSEN FLAME

Wu et al. studied the effect of stretch on the measurement of laminar flame speed using lean and rich mixtures of methane, propane, butane, and hydrogen with air whose Lewis number varies widely. The effects due to preferential diffusion and flow divergence are also studied[23].

COUNTERFLOW FLAME

Yu et al. studied the effects of hydrogen addition by linearly extrapolating the stretch flame effects for counterflow arrangement using methane & air and propane & air mixtures. It is observed that the value of S_L increases with the addition of Hydrogen[24].

HEAT FLUX METHOD

De Goey et al. used a unique flames burner method to determine the adiabatic burning velocity and flame temperature. This method was found to be useful in measurement over the entire range of flammability[25]. De Goey et al. also further advanced the technique to reduce errors during measurement. Using this method variety of fuels like methane, ethane, propane, n-butane, and iso-butane were well analyzed[26].

STAGNATION METHOD

Vagelopoulos et al. studied the stability of premixed laminar flames at ultra-low strain rates numerically and experimentally. The stagnation method was introduced to measure the laminar flame speed directly using the Laser Droplet Velocimetry. Experiments were conducted using methane, ethane, and propane mixture[27]. Dahoe et al. developed a new method for measuring laminar burning velocity using a closed vessel gas explosions method. The pressure-time relation is measured based on the calculation of which two

integral models, namely thin-flame and three-zone models, are defined. The model is well validated with the existing experimental data[28].

ANNULAR STEPWISE DIVERGING TUBE METHOD

Kim et al. developed the Assembled – ASDT method for higher dimensional precision and selectively assembled suitable step units so that the Flame propagation velocities measured will match the Laminar burning velocities collected from the literature[8].

STRETCH MEASUREMENT

Halter et al. defined three different methodologies for extracting the laminar flame speed and Markstein length for Laminar flame speed. The other extrapolation methods are linear extrapolation, temporal radius evolution with polynomial function, and analytical resolution[29]. Halter et al. defined a nonlinear approach to measure the laminar flame speed, and Markstein length was measured using methane/air and iso-octane/air mixture. It was observed that in the linear method, errors were starting to follow from the 1.1 equivalence ratio[30].

ERROR IN MEASUREMENT

Chen et al. measured the accuracy of measurement techniques by measuring S_L for methane/air mixtures. Various sources of uncertainty like mixture preparation, ignition, buoyancy, instability, confinement, radiation, nonlinear stretch behavior, and extrapolation were discussed using 1-D simulations.[31]

NUMERICAL METHOD

Hassan et al. studied the effects of stretch using experimental methods of spherical flame methods and numerical methods using PREMIX code. It is found that the numerical value is closer to the observed values so that the mechanism can predict the behavior of methane combustion very closely[32]. Dong et al. used the Particle image velocimetry in stagnation flow conditions to measure the S_L for methane/air and ethane/air mixtures. The results were also validated using GRI mech 3.0 using the PREMIX code of Chemkin and found an underprediction by ethane mixtures' mechanism[33].

Rozenchan et al. used the constant pressure spherical combustion chamber to calculate the laminar burning velocity of methane-air mixture for pressures up to 20 atm, and then compared the results with GRI mech 3.0 using PREMIX code, and found satisfactory agreement with the same[34]. Halter et al. used the spherical combustion chamber coupled to a classical shadowgraph system for equivalence ratio from 0.7 to 1.2 for initial pressure from 0.1 to 0.5 MPa with methane as a fuel. Hydrogen content was increased from 0 to 0.2, and the results were compared with GRI mech 3.0[35].

Numerical comparison of laminar flame speed for methane and wood syngas is made by Ouimette et al. using the PREMIX code. The values are presented using the power law

equation form. The effect of pressure and temperature is found out for the given fuel[36]. Park et al. measured the S_L using both experimental and numerical simulations. Experiments were performed using a counterflow configuration, and simulations were performed using USC Mech II kinetic model[37].

Akram et al. measured and computed S_L for methane/air mixtures at higher mixture temperatures of 370 to 650 K. Results were validated using GRI Mech 3.0, San Diego mechanism, Konnov mechanism, and there was found to be good matching of both the experimental and numerical results[38]. Goswami et al. used the Heat flux method to measure the S_L by varying the pressure from 1 and 5 atm for equivalence ratio from 0.8 to 1.4. Numerical simulations were performed using two mechanisms, and the experimental validation was very close to the actual results[39].

Hu et al. used a constant volume bomb and shock tube to measure the laminar flame speed and ignition delay times. The performance was validated against GRI mech 3.0, USC Mech II, and Aramco 1.3 mechanisms. It was found that USC Mech II was able to predict better for the given conditions. However, at a higher pressure and richer mixtures, the predictions were not perfect, and the mechanism has to be improved[40]. Prathap et al. investigated the effect of dilution of N_2/CO_2 on methane/oxygen mixtures using freely expanding spherical flames and correlations and numerical simulations using GRI Mech 3.0. Also, it was observed that with the addition of CO_2 , the S_L decreased tremendously. Sensitivity analysis was performed to find some elementary reactions, and their reaction rates were modified to match the experimental values[41].

Mitu et al. studied the effect of inert gases on methane-air mixtures with various inlet pressure using a spherical vessel with central ignition. The results were obtained from power-law correlations and numerical simulations of 1-D flame equations[42]. Varghese et al. measured the laminar burning velocities at high temperatures and pressures using the externally heated diverging channel method for a pressure range of 1 – 5 atm, 350 – 650 K. Results of these were validated with GRI Mech 3.0, Aramco 2.0, FFCM-1. Finally, correlations were built to get ready the model to predict any case[43].

Duva et al. study the effect of CO_2 on laminar burning velocity. In an optically accessible constant volume combustion chamber at elevated temperatures till 473 K by varying the CO_2 dilution from 0 % to 15 %. PREMIX solver is used along with GRI Mech 3.0, and San Diego mechanisms were used to validate the experiments, and it was found that the former was able to predict the results better[44]. Laminar burning velocities of $CH_4/O_2/N_2$ and oxygen-enriched $CH_4/O_2/CO_2$ were measured at high pressures up to 0.5 MPa and equivalence ratio ranging from 0.6 to 1.6 by Wang et al. The results were well validated with GRI-Mech 3.0, and HP-Mech and the sensitivities of the reaction with respect to significant species were analyzed[45].

CORRELATION METHOD

Stone et al. developed a correlation model for a wide range of temperatures (293 to 454 K), pressures (0.5 to 10.4 bar) from experimental values taken from a spherical combustion chamber setup consisting of an equation 12 degrees of freedom[46]. Gu et al. used the spherically expanding flames at constant pressure to determine the laminar burning velocity and effect of stretch by measuring the Markstein length between 300 K to 400 K with pressure varying between 0.1 and 1.0 MPa, and power-law correlations were defined to cover the entire range of predictability[47].

Elia et al. developed the constant volume combustion chamber to measure the laminar burning velocity and the stretch effects using the Markstein length of methane-air combustion. Using these correlations was designed for temperatures from 298 K to 550 K[48]. Amirante et al. analyzed the various single fuel, binary, and ternary fuel combinations of methane, propane, methane/ethane, methane/propane, natural gas, and gasoline combination. They studied their laminar flame speed for temperatures from 298 K – 800 K, pressures from 1 – 50 atm, and equivalence ratio from 0.6 – 1.7 and developed correlation models covering the entire ranges. A comparison with the existing data is also made[49].

Wang et al. used analytical methods to determine the power exponent in the power-law correlations parameter. The value is validated for methane and ethane as a fuel for various input conditions of equivalence ratios varying from 0.6 – 1.6, temperatures up to 500 K, and good agreement of the results is observed. From which it is found that the proposed derivation of power exponent is accurate[50].

DIMETHYL ETHER

Qin et al. derived a method for the measurement of Laminar flame speed using a spherical bomb combustion method, and then the setup was used for the measurement of S_L of Dimethyl ether and air mixture. The experiment results were compared with the mechanisms of both detailed and reduced mechanisms of DME and air[51]. Takizawa et al. established an experimental setup using the spherical combustion method. The methane and propane + air combustion techniques were used to calibrate the setup to the literature values. The setup was then used to measure S_L of 4 Hydrofluorocarbons: difluoromethane, 1,1,2-trifluoroethane, 1,1,1-trifluoroethane and 1,1-difluoroethane[52].

The addition of Dimethyl ether to the methane + air mixture during the S_L shows that DME's addition reduces the ignition delay at high temperatures. It is also found that the most recent mechanism produced by Princeton university can predict the Laminar flame speed of methane and DME air mixture. Laminar burning velocities of DME/methane/air mixtures was measured in constant volume combustion method for initial temperatures (303 – 453 K), initial pressures (0.1 – 0.7 MPa), dilution ratios (0-25 %), equivalence ratios (0.7 – 1.6) and DME blending ratios (0 – 100 %). Zhao DME model and NUIG Aramco Mech 1.3 were validated with the experimental results[53].

Mohammad et al. measured the laminar flame speed using the rectangular diverging channel method of methane/DME/air mixture. Numerical simulations were also performed, and the results were thus validated. After this high-temperature combustion, results are analyzed using the same method, and the addition of DME to the reaction is, therefore, studied[54].

Comparison of alkane + air and alcohol + air was performed by Egolfopoulos et al. containing 1, 2, and 4 carbons. It is found that alkanes have less speed than alcohol, and with Carbons' addition, the speed keeps decreasing[55]. Bai et al. used the net heat flux method to measure the laminar flame speed of biomass-derived gases over a wide range of mixture compositions. The results are verified using the detailed mechanism and GRI mechanism, and the results are found to be in close agreement with the actual values[56].

Ranzi et al. reviewed the laminar flame speed results of small alkanes, alkenes, alkynes, primary reference fuels, cycloalkanes, heavy normal alkanes, aromatics, alcohols, oxygenated species, hydrocarbon mixtures. They provided consolidated results of all the mentioned fuels[57]. Li et al. used a combustion chamber with central ignition to measure the laminar flame speed of methane-n-heptane-air mixture with the concentration of methane varying from 0 to 1 for initial pressure of 0.1 MPa and initial temperatures of 358 K, 393 K, and 428 K and equivalence ratios of 0.7 – 1.5[58].

HYDROGEN ADDITION

Hu et al. measured the S_L of methane-air mixture for the addition of Hydrogen. The effect of change in equivalence ratio with respect to changes in the concentration of Hydrogen is studied. Sensitivity analysis is used to study the impact of the addition of Hydrogen to the mixture[3]. Hermanns et al. analyzed the data of $CH_4+H_2+O_2+N_2$ flames using the heat flux method with the content of Hydrogen varied from 0 to 40 % and oxidizer varied from 20.9 to 16 % while varying the temperature from 298 K to 418 K. A correlation was formed to cover the data in all these ranges[59]. Burning velocities of methane-air and hydrogen-air mixtures were investigated in the spherical combustion bomb by varying the initial input conditions of pressure, temperature, and equivalence ratios using the two-zone combustion model Reyes et. al.[60]

NATURAL GAS

Dirrenberger et al. measured the S_L of natural gas, ethane, propane, and n-butane, in binary and tertiary mixtures, equivalence ratios varying from 0.6 to 2.1 using the heat flux method. The experimental results were compared with correlations and mechanisms to predict the value of S_L [61]. Alkanes such as methane, ethane, and propane in various proportions even in binary blends were tested for their S_L for up to 10 atm pressure using a constant volume combustion vessel by Lowry et. al.[62]

Spherically expanding flames were used by Liao et al. for natural gas-air mixtures for equivalence ratios from 0.6 to 1.4 and temperatures from 300 to 400 K for pressures from

0.05, 0.1, and 0.15 MPa. Correlations of the power-law equation form are used to cover the entire range of data[63]. Laminar burning velocities and Markstein lengths were obtained at various combinations of natural gas. Hydrogen using constant volume bomb for equivalence ratios from 0.6 to 1.4 and a power-law correlation was introduced to calculate the S_L , by Huang et. al.[64] Konnov et al. studied the effect of elevated temperatures and natural gas compositions, containing different proportions of methane, ethane, and propane using the heat flux method at 1 atm and 298 K, 318 K, 338 K. Correlations were developed and working of mechanism of Aramco mech 2.0. An updated version of the mechanism developed by the authors was validated[65].

ETHANE

Experimental data of C2-C3 hydrocarbons, especially alkanes of interest ethane and propane, were studied from outwardly propagating spherical flame in a constant-pressure chamber for extensive ranges of lean-to-rich equivalence ratio and pressures up to 5 atm were studied by Law et. al.[66] Measurement of adiabatic burning velocity in ethane enriched mixtures was analyzed using heat flux method, and the results were well validated using GRI Mech 3.0 mechanism by Ray et. al.[67]

Glaude et al. measured the laminar burning velocity of natural gas components, methane, ethane, propane, and n-butane, including their binary and tertiary mixtures using the heat flux method. Both empirical relations and detailed chemical mechanisms were developed under a wide range of conditions[61]. Alkanes like methane, ethane, and propane under pure composition and binary compositions were measured for their laminar burning velocity using a constant volume vessel under high-pressure conditions using constant volume vessel by Lowry et al. A chemical kinetic mechanism was developed by them to encompass all the tested conditions. The results were verified using the experimental results[62].

C2 hydrocarbons were tested for laminar flame speed, using counterflow configuration. From three different kinetic models, the laminar flame speed was tested to match the experimental results and how each reaction affects the overall sensitivities by Park et. al.[68] Konnov et al. studied the laminar burning velocities of ethane/air and propane/air mixtures from equivalence ratios of 0.8 – 1.3 and pressured up to 4 bar using the heat flux method. The results were compared using existing data and numerical simulations using USC Mech II, San Diego mechanism, and Aramco mech 1.3, and correlations models were also developed to test the results[69].

PROPANE

Dryer et al. studied the laminar flame speed of propane/air mixtures at room temperature, 500 K and 600 K. The measured data was tested using the existing model, and it was found that results were matching well with the experimental results. Laminar flame speed of C3-4 consistent with our interest alkanes of propane and n-butane were measured, and the values were tested for their uncertainties using the USC Mech II[70].

BUTANE

Law et al. studied the various factors affecting the measurement of laminar flame speed using outwardly propagating spherical flames with a nonlinear variation of spherical flames using n-butane/air flames[71].

PENTANE

Using heat flux method, laminar flame speed of methane and n-pentane at 298 K from 1 to 6 atm and at 1 bar from 298 to 398 K and equivalence ratio from 0.6 to 1.9, was measured by Dirrenberger et al. Using these data, empirical correlations were defined for n-pentane[72]. Law et al. measured the C5-C8 n-alkane group's laminar burning velocities at elevated pressures using a high-pressure constant pressure chamber for pressures up to 20 atm. It was also observed that with an increase in pressure, the stretch is lost[73].

HEXANE

Law et al. performed experiments to measure the laminar burning velocities of n-hexane and the cycloalkanes derived from it. Laminar flame speed is measured for pressures up to 10 atm without any stabilization[74].

N-HEPTANE AND ISO-OCTANE

Laminar flame speeds of iso-octane and n-heptane – air mixtures are measured using the counterflow twin flame configuration. The laminar flame speeds of iso-octane were lower than that of n-heptane throughout the range of experimental equivalence ratios. Prediction using detailed kinetic models like those of Held, Curran, Pitz, and Westbrook agreed well with the experimental data by Davis et. al.[75] Laminar flame speeds of n-heptane and iso-octane are measured at atmospheric pressure and a wide range of equivalence ratios using counterflow configuration by Sung et al. both experimental and computational methods verified the results[76].

Chong et al. determine the laminar flame speed of n-heptane/air mixtures using stagnation flame configuration at a high temperature of 470 K and 1 bar under premixed conditions[77]. Counterflow outwardly expanding flames were used to measure the laminar flame speed by Law et al. of iso-octane and n-heptane/air mixture. The experimental measurements were validated with the mechanisms of Curran and Chaos[78].

Liu et al. used the outwardly propagating spherical flame at constant pressure for a wide range of equivalence ratios. Well developed mechanisms were used to validate the experimental results, and sensitivity analysis was performed to find the most reactive reaction[79]. Laminar flame speed calculations were performed using flat flame adiabatic burner using n-heptane, iso-octane of our concerned n-alkanes for equivalence ratios of 0.7 – 1.3 for a range of temperatures of 298 – 358 K. The validation of the data is done with respect to available literature data and kinetic models by Silegham et. al.[80]

The laminar flame speed of a mixture of fuels has been measured at 358 K, and the commercial gasoline has observed 1 bar of n-heptane and iso-octane using the heat flux method by Glaude et al. Very similar values. The results were verified using kinetic mechanisms. Laminar flame speed was measured using constant volume spherical vessel for n-heptane, iso-octane at a temperature of 358 K and pressures varying up to 0.6 MPa for equivalence ratio varying from 0.8 to 1.6, and a correlation model was built to cover the entire range of operating conditions[81].

Spherically expanding flames have been developed for iso-octane/air mixtures. Measurement was done for fuel varying the temperature between 358 K and 450 K at pressures between 1 bar and 10 bar and equivalence ratios ranging between 0.8 and 1.0 by Wooley et. al.[82] A constant volume combustion vessel was used by Marshall et al. to measure the laminar flame speed. A correlation model was built to cover the entire range of pressures of 0.5 – 4 bar, temperatures of 310 – 450 K, and an equivalence ratio of 0.7 – 1.4 for n-heptane and iso-octane[83].

Laminar burning velocities were measured by Konnov et al. using the heat flux method, where the initial conditions were 298 K and 338 K using n-heptane and iso-octane, and the results were compared with existing available literature[84]. Foucher et al. used the combustion chamber at atmospheric pressure and 373 K to study the iso-octane's oxygen-enriched combustion. The detailed chemical kinetic model was used to validate the values. A correlation was proposed to cover the entire range of data[85].

N-DECANE

Laminar flame speeds of n-decane/air and n-dodecane/air are measured by counterflow method combustion method at preheating temperatures varying from 360 to 470 K, atmospheric pressure and equivalence ratio ranging from 0.7 – 1.4 conditions by Sung et al. The results are simulated also using the detailed chemical kinetics mechanisms in the literature. It is found that there is not much matching of the products. Further sensitivity analysis has been done to find the most sensitive reaction, but more research is to be done in matching the prediction[86].

Laminar flame speeds of premixed C5-C12 n-alkanes were determined at atmospheric pressures and elevated temperatures using the counterflow configuration and nonlinear extrapolation. Using the detailed mechanism of chemical kinetics and molecular transport by Egolfopoulos et al., Simulations were performed using Jetsurf 0.2 reaction model containing 194 species and 1459 reactions. It was found that prediction values are lower than experimental at lean and stoichiometric conditions[5].

Laminar flame speeds and Markstein lengths of n-decane/air of particular interest were measured by Singh et al. using spherically expanding premixed flames. Numerical simulations were measured using Jetsurf 0.2 reaction model, which predicted better than

other mechanisms. Hui et al. measured the laminar flame speed in a high-pressure counterflow setup over an equivalence ratio of 0.7 – 1.3, unburnt gas temperatures of 350 – 470 K, and 1 – 3 atm pressures. n-decane, n-dodecane, iso-octane of the interested fuels were tested for the values, and the results were compared with chemical kinetic models[87].

Won et al. studied the critical radius for flame initiation and multiple flame regimes of n-decane/air using experimental and numerical methods using outwardly propagating spherical flames at various equivalence ratios and pressures detailed chemical kinetic mechanisms. Heavier alkanes representing jet fuels are most used for simulating fuels in combustion[88]. Bergthorson et al. used n-decane/air of our interest to measure S_L and validate the JetSurF 2.0 mechanism. It is found that the matching is entirely accurate in both the experimental and numerical simulations[89].

They were using a spherical combustion bomb method, Comandini et al., at a temperature of 403 K and initial pressure of 1 bar. The experimental results were validated using the JetSurF 2.0 model, and it was found that the results were matching well with the experimental results over a wide range of conditions[90].

DO-DECANE, TETRADECANE, N-HEXANE, ISO-CETANE

A reduced mechanism consists of 11 components consisting of interest n-heptane, iso-octane, n-decane, n-dodecane, n-hexadecane of interest composed of 178 species and 758 reactions for comprehensive distillation fuel covering gasoline, jet, and diesel fuels. The mechanism has been validated for ignition delays, laminar flame speeds, species concentration profiles, and new DICI(Direct Injection Compression Ignition) engine combustion data by Ren et. al.[91] Egolfopoulos et al. measured the laminar flame speed of n-tetradecane, n-hexadecane, and iso-cetane/air mixture of interest in counterflow flame arrangement. They elevated the unburnt gas temperature of 443 K. Data was validated using the newly developed chemical kinetic mechanism of 187 species and 6086 elementary reactions. The computed results were more close to the experimental data. Through sensitivity analysis, it was found that outcomes were more sensitive to the C0-C4 kinetic subset[92]. Laminar flame speeds of n-tetradecane and n-hexadecane were measured by Li et al. using counterflow arrangement at high temperatures and atmospheric pressure, and the chemical kinetic model results were also close to the experimental results. Sensitivity analysis was also performed to find the effects of kinetics and molecular transport[93].

MACHINE LEARNING MODEL

Varghese et al. developed a machine learning model to predict the laminar flame speed of H₂/CO/CH₄/CO₂/N₂/air mixtures using the experimental data measured from the diverging channel method and FFCM-1 mechanism. The model was well studied to predict and to be used in the direct calculation of laminar flame speed at any given temperature, pressure, and equivalence ratio conditions[94].

ENGINE CONDITIONS

Chen et al. analyzed the various power-law correlations and different kinetic mechanisms for the laminar flame speed calculation within engine operating conditions from the temperature of 300 – 1100 K, the pressure of 1 – 120 atm. The newly developed Foundational Fuel Chemistry Model Version 1.0 model closely predicts the data at high pressures and high temperatures. A new correlation model is expected, matching the results well over a wide range of input conditions.[95]

ANSYS – CHEMKIN PRO AND FORTE SIMULATION

Puduppakkam et. al. implemented a methodology to calculate the local turbulent flame speed of spark ignition engines accurately using detailed chemistry calculations of laminar flame speed. Laminar flame speeds of 44 fuels consisting of classes of fuels of n-alkanes, isoalkanes, cyclo-alkanes, alkenes, cyclo-alkene, iso-alkene, aromatics, ethers, cyclo-ethers, alcohols and methyl esters using ANSYS-CHEMKIN 1-dimensional flame speed calculator, and ANSYS FORTE was used to calculate turbulent flame speed. Only 1500 conditions were simulated for pressure, temperature, equivalence ratio and EGR conditions to cover most engine conditions using Model Fuels Library consisting of 9179 species and 38505 reactions representing combustion and pyrolysis of 44 fuel components.[96]

1.4 Background

Along with extensive experimental measurement effort, laminar flame speed has been studied using high-performance computing techniques, with well-developed chemical kinetic mechanisms. In particular, understanding the sensitivity of a specific reaction in the propagation or extinction of a flame is facilitated by numerical simulations. In the present study, focusing on the reactions for methane oxidation, a sensitivity analysis is performed, and the mechanism is improved to match the experimental data better.

1.5 Objectives

The main objectives of the research are to:

1. Use CHEMKIN to calculate the laminar flame speed of methane at various conditions.
2. Perform sensitivity analysis on laminar flame speed to identify important reactions of methane oxidation.
3. Validate the mechanism to match experimental results of laminar flame speed.
4. Perform a parametric study of various inlet conditions of pressure, temperature, and mixture composition.
5. Develop the procedure for generating a Laminar flame speed library for any multi-component fuel.
6. Generate a laminar flame speed library for methane flame

1.6 Thesis formulation

The thesis comprises of the following chapters

Chapter 1 describes the introduction to what is laminar flame speed, its calculation and measurement and the literature review of the things that have taken place in this field, the project's objectives, and a brief review of the project.

Chapter 2 defines the basic approach of the problem, calculation of sensitivities, validation of the mechanism, and generation of laminar flame speed data

Chapter 3 discusses the results of the sensitivity, mechanism validation, and effect of variation of various parameters on the value of laminar flame speed

Chapter 4 concludes the methane laminar flame speed library's different results before discussing future work in Chapter 5.

2 METHODOLOGY – COMPUTATIONAL APPROACH

2.1 Fundamental approach to the problem

The project aims to generate the premix laminar flame speed library for various alkanes component of the multi-component fuels. In this approach, the Premix module of the Ansys Chemkin Pro is used to calculate the Laminar Flame Speed. The Premix module solves the One-dimensional flame equation using the TWOPNT solver, which uses adaptive mesh refinement to solve the transient problem using a steady-state approach.

A parametric study is then performed over a wide range of Temperatures (300 – 1000 K in 50 K increments), Pressures (1 – 70 bar in 5 bar increments), and equivalence ratios (0.4 to 2.0 in 0.1 increments). The input conditions are chosen so that the entire engine combustion chamber's initial state is covered. The non-converged cases are solved by estimating the temperature profile individually. In addition to this, for end cases, an initial change of velocity and number of adaptive grid parameters is performed to get the S_L over the entire input condition range.

First, the mechanism, thermodynamic, and transport data are obtained in the proper ASCII format. Ansys Reaction workbench has a mechanism inspector used to check if the format is consistent. The mechanism used is the MTU - master mechanism. The mechanism is ready to match the high-temperature combustion characteristics, i.e., by matching S_L 's experimental data. The thermodynamic and transport database for several species is obtained from the species' SMILES structure using the Reaction Mechanism Generator (RMG) database[97].

The class of fuels taken into consideration are alkanes of the multi-component fuels. There are 24 fuel components : methane(CH_4), ethane(C_2H_6), propane(C_3H_8), n-butane($n-C_4H_{10}$), n-pentane($n-C_5H_{12}$), iso-pentane (i- C_5H_{12}), n-hexane (n- C_6H_{14}), iso-hexane(i- C_6H_{14}), n-heptane(n- C_7H_{16}), iso-heptane(i- C_7H_{16}), n-octane(n- C_8H_{18}), iso-octane(i- C_8H_{18}), n-nonane(n- C_9H_{20}), iso-nonane(i- C_9H_{20}), n-decane(n- $C_{10}H_{22}$), iso-decane(i- $C_{10}H_{22}$), n-dodecane(n- $C_{12}H_{26}$), n-tridecane(n- $C_{13}H_{28}$), n-tetradecane(n- $C_{14}H_{30}$), n-hexadecane(n- $C_{16}H_{34}$), iso-hexadecane(i- $C_{16}H_{34}$), n-octadecane(n- $C_{18}H_{38}$), Icosane(n- $C_{20}H_{42}$) and Heneicosane(n- $C_{22}H_{46}$), of which only methane matching is done in the current project.

An extensive literature review was done to collect the data for the past 40 years. Considering the various measurements and considering all the effects and losses, consistent data for most alkane fuels is gathered.

First, the mechanism validation is done with the methane fuel component by comparing the data with the experimental data available in the literature. The mechanism was initially altered for 300K & 1 bar and then extended to 443 K & 5 bar. Finally, high temperature and pressure cases are compared. Since only certain single case data is available in the literature, such data are only taken, and validation is performed. The methane data is then

obtained by performing the parametric study for the decided input conditions before proceeding to other fuels.

2.2 ANSYS CHEMKIN – Pro

ANSYS CHEMKIN-Pro is software used to solve complex chemical kinetics problems involving industry-specific reacting-flow conditions in various applications. There are built-in visualization tools and third-party analysis tools like Microsoft Excel. It is an extension of the Chemkin software developed in the Sandia national laboratory to calculate the chemical kinetics problems.

In addition to this, there is also access to a set of core utilities through ANSYS Chemkin-Pro Application Programming Interface (Chemkin-Pro/API), facilitating custom construction Chemkin-Pro applications through C/C++/FORTRAN programming.

The following reactor models are used:

1. Inlet source – External source for inlet gas
2. Flame-speed Table generator – Table creator uses the Flame speed calculator, a 1-dimensional freely propagating flame for determining pre-mixed, laminar flame-speeds, to create a table over a wide range of operating conditions of Unburnt gas temperature, Inlet Pressure, and equivalence ratio. This table can be exported to Computational Fluid Dynamics (CFD) simulation package like KIVA, Star-CD, Ansys Forte, Converge CFD for use in turbulent-flame speed calculations for flame propagation in 3-dimensional engine CFD simulations
3. Outlet source – Outlet flow of reactors, indicating that there is no further processing of the gas

In addition to this, the components of the Chemkin-Pro/API Core Utility models which are used in this process are:

1. Gas-phase kinetics – It is the pre-processor and subroutine library for analyzing gas-phase chemical kinetics
2. Thermodynamic data – It is the thermodynamic property database and the FITDAT data-fitting utility
3. Gas transport is the pre-processor and subroutine library for calculating transport properties for gas-phase species and their multi-component mixtures.

2.3 Modules in a CHEMKIN model

The various modules in a basic CHEMKIN model are :

- 1) Diagram View – The diagram view contains the icons.

- 2) Pre-processing specifies the working directory and the chemistry set, specifying the Gas-Phase Kinetics File, Thermodynamics data file, and the Gas Transport Data File. There are also options to check the mechanism's format and checks whether all the species thermodynamic and transport data are in format. All the species data, along with the distribution charts, can be viewed from the Mechanism viewer. Also, the Gas-phase reactions show each reaction and the parameters associated with it.
- 3) Cluster properties – It consists of:
 - a) Inlet properties – In our problem consists of C1_Flame Speed Library and C1_Inlet1.
 - i) C1_Flame speed Library – It consists of Reactor Physical Properties, Grid properties, and Species-specific Properties, where the later is not used in our simulations
 - (1) Reactor Physical Properties – It is used to specify the inlet conditions like Unburnt gas temperature and pressure. It is also used to determine whether back diffusion is allowed or not. The back diffusion at the inlet boundary is not permitted. Additionally, an automatic estimated temperature profile is used to determine the temperature profile automatically.
 - (2) Grid Properties – It is used to specify the maximum number of grid points allowed, which is set to 2000; Number of adaptive grid points which is used to define as a parameter of adaptive mesh refinement, it is varied between 1 to 10 to get converged solutions; Adaptive Grid Control based on solution gradient which controls the maximum slope between grid points, it is set to 1.0 to find whether there is a solution for the given case; Adaptive Grid control based on solution curvature which controls the maximum curvature between grid points, it is set to 1.0 to find whether there is a solution for the given case; Starting axial Position which specifies the starting position of the shock tube, which is set it 0 cm; Ending axial position which determines the ending part of the shock tube, which is set to 0.3 cm
 - ii) C1_Inlet1 consists of Stream Properties Data and Species-specific Properties
 - (1) Stream properties data – Inlet velocity is set to a default value, and this value is changed to get a converged solution to the failed cases.
 - (2) Species-specific Properties – This is used to set the Equivalence ratio and EGR rate, along with the composition of the fuel mixture, Oxidizer mixture, Complete-combustion Products, and EGR species.
 - b) Solver Parameters – There are default values set for the solver parameters, and it consists of basic and advanced features. These options are only to be used in case of a problematic convergence criterion.
 - c) Output controls – This consists of the Output controls tab as well as the Species sensitivity and Rate of Production tab. The former is used to request additional output, and the latter is used to select specific species for which the sensitivity coefficient and ROP are calculated.
 - d) Continuations – This is used to run the model with the solution of the previous case. Initial grid parameters are changed and run with six continuations with the GRAD and CURV value changing from 1.0 to 0.01 to have a converged solution.

- 4) Run calculations – This is used to run only the model calculation or the parameter study or the uncertainty analysis
- 5) Analyze results – Results are analyzed by getting the flame speed library or post-process the solution to see the variation of individual parameters for a given case.
- 6) Monitor Project Run – This is used to analyze the running of each case

The numerical aspect of the problem is explained in Appendix A

2.4 Mechanisms used in project

The following mechanisms were considered in our analysis:

- 1) GRI Mech 3.0 Mechanism – GRI Mech 3.0 is a mechanism designed to model natural gas combustion, including reburn chemistry and NO formation. It consists of 53 species and 325 reactions, of which three are duplicated (expressing the sum of 2 rate parameters required). It is a well-validated mechanism for the combustion of Methane. So, this mechanism is used to check the working of the Premix code.[98]
- 2) USC MECH II Mechanism – USC Mech II is an H₂/CO/C₁-C₄ kinetic model that is valid for a large variety of practical combustion applications. It consists of 111 species and 784 reactions, and it is an optimized model of H₂-/CO combustion, which is developed from GRI Mech 1.2 and 3.0.[99]
- 3) PRF Mechanism – Primary Reference Fuel (PRF) developed in the lab. is used to validate the master mechanism. Iso-octane and n-heptane are represented as automotive fuels in various blends, hence the name PRF; it consists of 41 species and 130 reactions.[100]
- 4) MTU-Master Mechanism (consisting of only C₃) – The mechanism is generated in the RFFR Lab, consisting of 66 species and 308 reactions. The mechanism was developed, adjusting the reaction rate constants of co + oh reactions. This mechanism was validated to match the experimental values of methane's laminar flame speed by adjusting pre-exponential factors of H+O₂=O+OH reaction.

2.5 Sensitivity analysis

Sensitivity analysis is performed to find the most sensitive reaction, which can be altered to match the numerical simulations with the experimental data. The Pre-exponential factor of a reaction is changed by a factor of 5, and then the sensitivity coefficient is calculated by

$$\text{Sensitivity coefficient, } Si = \frac{k_i}{m^0} \frac{\partial m^0}{\partial k_i}$$

where,

k_i – Rate of a reaction

$$m^0 - \text{Mass flux} = \rho_u S_u$$

Rearranging,

$$Si = \frac{\frac{1}{m^0} \partial m^0}{\frac{1}{k_i} \partial k_i}$$

Reducing it to,

$$Si = \frac{\partial(\ln m^0)}{\partial(\ln k_i)}$$

Approximating it to

$$Si \approx \frac{\Delta(\ln m^0)}{\Delta(\ln k_i)}$$

Considering numerator,

$$\begin{aligned} \Delta(\ln m^0) &= \ln m^{0'} - \ln m^0 = \ln \left(\frac{m^{0'}}{m^0} \right) \\ &= \ln \left(\frac{\rho_u S_u'}{\rho_u S_u} \right) \\ &= \ln \left(\frac{S_u'}{S_u} \right) \end{aligned}$$

Considering denominator,

$$\Delta(\ln k_i) = \ln k_i' - \ln k_i = \ln \left(\frac{k_i'}{k_i} \right) = \ln(5)$$

(Since pre-exponential factor is increased by a factor of 5)

Therefore,

Sensitivity coefficient,

$$S_i = \frac{\ln \left(\frac{S_u'}{S_u} \right)}{\ln 5}$$

2.6 Matching of S_L of Experimental and Mechanism

The sensitivity coefficient is calculated for all significant reactions using this equation, and the most sensitive reaction with respect to change in pressure and equivalence ratio is found out. That reaction pre-exponential is changed by 2 for matching the numerical simulation results with experimental results.

The average percentage error is changed by giving preference to the values near the stoichiometric ratio and slightly rich mixture and less importance to extreme cases using a weightage factor. For the minimum value of percentage error, mechanism is matched with the experimental results.

2.7 Procedure for problem setup

The steps for setting up a problem are:

- 1) Launch ANSYS Chemkin-Pro
- 2) Click the new project file and give the name to the project.
- 3) In the diagram view, create the general approach of the problem of setting up the inlet, premixed laminar flame speed library, and exhaust, and then update the project
- 4) In the pre-processing panel setup, the working directory, and the chemistry set
- 5) In the new chemistry set, give the mechanism file, thermodynamic file, and the transport file, and then save the entire chemistry set for easy access.
- 6) The chemistry set is applied by Running pre-processor, which creates the gas-phase kinetics output filename_gas and transport output filename_gtran. These files contain all the reactions data, thermodynamic data, and the transport data of all the species involved in the mechanism.
- 7) The C1_flame speed library, C1_inlet1, solver, output control, and continuations are set inside the model.
- 8) Parametric cases are setup
- 9) Run calculations are run for both individual and parametric studies.
- 10) Results are post-processed using excel to study the variation of the composition of the species, temperature, pressure, and the velocity, i.e., Laminar flame speed (S_L). Variation of S_L with respect to various parameters is also studied.

2.8 Solving failed cases

The problem is analyzed from the solution file of the failed cases. It is examined whether there is a problem in the mechanism file or thermal file, or transport file. Usually, if the format is followed, then there are mostly no errors. However, exceptional errors were found in

- 1) Thermodynamic data when there were continuity errors for the temperature ranges
- 2) Transport data error when there was a mistake in the transport data
- 3) Diverging error

2.8.1 Thermodynamic data error

For certain species, when expanding the equation at the common temperature, there was a variance of the order of $1e-5$. This error was corrected for the species, and the simulation was running fine.

2.8.2 Transport data error

For certain species, the Lennard-Jones collision diameter, σ is 0, and this parameter caused the temperature to escalate to 6000 K. It was found that the RMG database was not founding the alkyl extension to the benzyl component. This error was rectified by informing the team.

2.8.3 Diverging error

This type of error is due to numerical error and can be corrected by:

- 1) Giving an exact temperature profile to the problem
- 2) Changing the boundary values and grid parameters

CHANGING INPUT CONDITIONS

Additionally, if the errors were bound to surpass this, then the output file will be analyzed. If there is diverging in the first step itself, then it is concluded that there is some mechanism fault since the solution is not converging. If the answer is crossing the first step into the first continuation, then it can be concluded that a solution to the problem exists. If there are failures in any of the continuations, it can be supposed that the solution is not formed since the solution is diverging. The input velocity or the number of adaptive grid points is changed to get the converged solution. It is also observed that the solution is within the range of 2 decimal points for any given problem with the given conditions.

TEMPERATURE PROFILE

A code was written to interpolate the temperature profile between 2 success cases. The code consists of a hyperbolic equation for which the minimum, maximum, and mid-point temperature points are taken as the geometric mean between the two success cases. This interpolation was highly successful if the interpolation was done based on temperature rather than pressure and equivalence ratio. The simple reason that the variation of the profile is not consistent in them.

3 RESULTS AND DISCUSSION

First, grid selection and then mechanism validation is taken. Then the case of a single case analysis is taken, followed by a parametric study and concluding with methane results.

3.1 Grid selection

As explained in Section 2.3, it is already understood that number of continuations is needed to get converged solutions. So, the parameters involved in getting a successful solution are GRAD & CURV and the number of continuations.

3.1.1 GRAD and CURV

The master mechanism at 300K temperature, 1 bar pressure, and stoichiometric mixture conditions, with methane as a fuel, is taken. With no continuations and varying the GRAD & CURV from 1.0 to 0.005, it is observed that the number of grid points increases with a steady decrease in GRAD & CURV. Also, it is found that the CPU time is steadily increasing, as shown in Table 1

Table 1 GRAD and CURV analysis

GRAD & CURV	NO OF GRID POINTS	S_L (cm/s)	CPU TIME
1	12	41.105	2s
0.9	24	39.652	2s
0.8	31	39.005	2s
0.7	33	38.170	2s
0.6	38	38.400	2s
0.5	52	37.799	2s
0.4	60	37.609	2s
0.3	74	37.505	3s
0.2	105	37.019	3s
0.1	188	36.089	5s
0.09	207	35.856	6s
0.08	228	35.872	7s
0.07	264	35.720	7s
0.06	301	35.571	8s
0.05	356	35.514	11s
0.04	438	35.413	13s
0.03	593	35.257	22s
0.02	851	35.155	40s
0.01	1677	35.037	2 min 16s
0.005	3357	34.969	6 min 20s

Figure 1 Grid parameter analysis

It is found that initially, there is a slight variation in the value of S_L . Still, with further increase in no of grid points, S_L value is almost becoming constant, i.e., with a further decrease in GRAD and CURV, there is no significant change in the value of S_L , as seen in Figure 1. From the literature[43], it is known that 500 – 2000 points is required to get a converged solution. Considering the time and computational cost, GRAD & CURV is kept at 0.02.

3.1.2 No. of continuations

To determine the effect of no continuations, the same Master mechanism with Methane (CH_4) as a fuel, at 300 K temperature, 1 bar pressure, and stoichiometric mixture conditions, GRAD = CURV = 0.01, is taken. The effect of the number of continuation is studied by varying it consistently so that no grid points are continuously changing.

In Table 2, it is observed that Horizontally the continuation number is varying, and vertically the number of continuations is varying. It is observed that since the GRAD and CURV are the same, the number of grid points is almost constant, implying that S_L 's value is also consistent. It is also found that with the increase in the number of continuations, solution time is not varying consistently. However, it is deduced that increasing the number of continuations increases the memory of the generated solutions; this is because of the increase in no of continuations prints more data to the output file.

Table 2 No of continuations analysis

CONT.	0	1	2	3	4	5	6	7	NO. OF GRID POINTS	SL (cm/s)	CPU TIME	MEMORY (Mb)
0	0.01								1690	35.037	2m 16s	4.59
1	1.00	0.01							1678	35.037	2m 38s	4.71
2	1.00	0.02	0.01						1654	35.038	2m 47s	9.56
3	1.00	0.04	0.02	0.01					1653	35.038	2m 48s	12
4	1.00	0.08	0.04	0.02	0.01				1643	35.039	2m 39s	13.2
5	1.00	0.20	0.08	0.04	0.02	0.01			1650	35.039	2m 49s	13.7
6	1.00	0.40	0.20	0.08	0.04	0.02	0.01		1653	35.037	2m 50s	14
7	1.00	0.80	0.40	0.20	0.08	0.04	0.02	0.01	1654	35.037	2m 55s	14.2

So, an optimum of 6 no of continuations is chosen with each continuation's value, as shown in Table 3. Also, the tube's length is increased for each continuation so that there is no backflow problem and there is no numerical discontinuity. The final values of the continuations are shown in Table 3.

Table 3 Final input parameters

CONTINUATION	GRAD & CURV	STARTING AXIAL POSITON (cm)	ENDING AXIAL POSITION (cm)
0	1	0	0.3
1	0.9	-0.1	1
2	0.5	-0.2	2
3	0.2	-0.5	5
4	0.08	-1	7
5	0.04	-1.5	8.5
6	0.02	-2	10

3.2 Mechanism validation

The SL's numerical simulation is matched with experimental values to generate a more accurate laminar flame speed library. The data is taken from the literature survey of the past 40 years of data after applying corrections for all the factors considered. 300 K, 1 bar, and 443 K, 5 bar is chosen as the input conditions at which the validations will match the experimental results. Sensitivity analysis is to be done to determine the given condition's most sensitive reaction to perform the mechanism validation. In addition to these conditions, sensitivity analysis in 700 K, 40 bar is also performed for understanding the behavior of reactions at high temperature and pressure conditions.

3.3 Sensitivity analysis with respect to Laminar flame speed for methane

The most sensitive reactions for methane are:

$\text{H}+\text{OH}+\text{M}=\text{H}_2\text{O}+\text{M}$	(M 9)
$\text{H}+\text{O}_2(+\text{M})=\text{HO}_2(+\text{M})$	(M 10)
$\text{CH}_3+\text{H}(+\text{M})=\text{CH}_4(+\text{M})$	(M 11)
$\text{OH}+\text{HO}_2=\text{H}_2\text{O}+\text{O}_2$	(M 12)
$\text{CH}_3+\text{OH}(+\text{M})=\text{CH}_3\text{OH}(+\text{M})$	(M 13)
$\text{CH}_3+\text{CH}_3(+\text{M})=\text{C}_2\text{H}_6(+\text{M})$	(M 14)
$\text{HCO}+\text{H}=\text{CO}+\text{H}_2$	(M 15)
$\text{HCO}+\text{O}_2=\text{CO}+\text{HO}_2$	(M 16)

The pre-exponential factor is changed by the multiplication factor (Δ) of 5 for the most sensitive reaction found using the sensitivity coefficient value for any reactions. For a change in input conditions, the order of the sensitivity of the reactions is studied.

3.3.1 Sensitivity Analysis of USC Mechanism

Sensitivity analysis is performed using USC Mech II, as shown from the work of Hu et. al.[40] The results are as shown in Figure 2.

Figure 2 Sensitivity analysis of USC Mechanism at 300 K

For case by case analysis, M1 reaction is taken and compared with both the paper values and the calculated values, as shown in Figure 3. Also, the Δ is changed to 2 to find the effect of the change of Δ . It is found that for both cases of Δ , the paper's trend is replicated by our simulation, but the values are not matching. This error may be because they have been using the FORTRAN PREMIX code, where it can be programmed to calculate this value to a minimal value to find its effect.

Figure 3 Behavior of delta change with change in pressure for M1 reaction

3.3.2 Sensitivity analysis of Master Mechanism at 300 K

Table 4 Top 5 ranked reactions at 300 K for pressure

RANK	1 bar	5 bar	7 bar	10 bar
1	M1	M1	M1	M1
2	M2	M2	M2	M2
3	M6	M11 - TROE	M11 - TROE	M3
4	M11 - TROE	M10 - TROE	M10 - TROE	M10 - TROE
5	M10 - TROE	M3	M3	M11 - TROE
RANK	40 bar	60 bar	100 bar	
1	M1	M1	M1	
2	M3	M3	M3	
3	M12	M12	M12	
4	M2	M2	M2	
5	M10 - TROE	M10 - TROE	M10 - TROE	

This condition is chosen as it is the most tested condition in the literature, as it is the primary room temperature and pressure, and much of the setup testing and methodology testing has been done in this condition. First, pressure variation and then mixture composition variation sensitivity is done to find the most sensitive reactions to match the experimental results with numerical results.

Figure 4 Sensitivity analysis of Master mechanism at 300 K with pressure

Figure 5 Sensitivity analysis of Master mechanism at 300 K with equivalence ratio

The sensitivity of various reactions for pressure for methane at 300 K is shown in Figure 4. The top 5 reactions at each pressure are given in Table 4. It is observed that the M1 reaction is the most sensitive, regardless of the direction of sensitivity. Also, it is observed that M2, M10-TROE & M3 are most sensitive in all pressure ranges. It is also found that

M11-TROE reaction is the most sensitive reaction in low-pressure ranges, i.e., 1 bar – 10 bar pressure. Similarly, M12 is most sensitive only in high-pressure ranges.

Table 5 Top 5 ranked reactions at 300 K for equivalence ratios

RANK	0.5	0.6	0.7	0.8	0.9
1	M1	M10 - TROE	M1	M1	M1
2	M2	M1	M10 - TROE	M2	M2
3	M6	M2	M2	M10 - TROE	M6
4	M3	M16	M6	M6	M10 - TROE
5	M12	M6	M16	M11 - TROE	M11 - TROE
RANK	1	1.1	1.2	1.3	1.4
1	M1	M1	M1	M1	M1
2	M2	M2	M11 - TROE	M11 - TROE	M11 - TROE
3	M6	M11 - TROE	M6	M6	M2
4	M11 - TROE	M6	M2	M15	M3
5	M10 - TROE	M15	M15	M2	M6
RANK	1.5	1.6	1.7		
1	M1	M1	M1		
2	M2	M2	M2		
3	M3	M3	M3		
4	M6	M6	M6		
5	M15	M12	M12		

The sensitivity of various reactions for change in equivalence ratio for methane at 300 K is shown in Figure 5. The top 5 reactions for each equivalence ratio is shown in Table 5. Here it is observed that M1; M2; M6; is the most sensitive reaction in all mixture compositions. M10-TROE is most sensitive in lean mixture conditions, whereas M11 – TROE is reactive in mixture conditions from 0.8 to 1.4. While M3, M12 is sensitive in lean and rich mixture conditions, M16 is only reactive in lean mixture conditions, and M15 is only reactive in rich mixture conditions.

3.3.3 Sensitivity analysis of Master Mechanism at 443 K

Table 6 Top 5 ranked reactions at 443 K for pressure

RANK	1 bar	5 bar	7 bar	10 bar
1	M1	M1	M1	M1
2	M2	M2	M2	M2
3	M6	M11 - TROE	M11 - TROE	M3
4	M11 - TROE	M10 - TROE	M10 - TROE	M11 - TROE
5	M10 - TROE	M6	M3	M10 - TROE
RANK	40 bar	60 bar	100 bar	
1	M1	M1	M1	
2	M3	M3	M3	
3	M2	M12	M12	
4	M12	M2	M2	
5	M10 - TROE	M10 - TROE	M10 - TROE

Figure 6 Sensitivity analysis of Master mechanism at 443 K with pressure

Table 7 Top 5 ranked reactions at 443 K for equivalence ratios

RANK	0.5	0.6	0.7	0.8	0.9
1	M1	M10 - TROE	M1	M1	M1
2	M10 - TROE	M1	M10 - TROE	M10 - TROE	M2
3	M3	M2	M2	M2	M10 - TROE
4	M2	M16	M6	M6	M11 - TROE
5	M12	M3	M3	M3	M6
RANK	1	1.1	1.2	1.3	1.4
1	M1	M1	M1	M1	M1
2	M2	M11 - TROE	M11 - TROE	M11 - TROE	M11 - TROE
3	M11 - TROE	M2	M2	M3	M2
4	M10 - TROE	M3	M3	M2	M3
5	M6	M6	M6	M12	M11
RANK	1.5	1.6	1.7	1.8	1.9
1	M1	M1	M1	M1	M1
2	M11 - TROE	M11 - TROE	M2	M11 - TROE	M2
3	M2	M2	M11 - TROE	M3	M11 - TROE
4	M3	M3	M3	M2	M3
5	M11	M11	M11	M11	M11
RANK	2				
1	M1				
2	M3				
3	M2				
4	M11 - TROE				
5	M11				

Unburned mixtures at 443 K were simulated, aiming at a combination of medium pressure and medium temperature. Again, in this case, pressure and mixture composition variation sensitive analysis is performed to find the most sensitive reaction, and then the reactions' pre-exponential factors are tuned to match the experimental results at this condition.

The sensitivity of various reactions for change in pressure at 443 K for methane is shown in Figure 6. The top 5 reaction sensitivity for change in pressure is given in Table 6. It is observed that at a higher temperature of 443 K, in all pressure conditions M1; M2; M10 - TROE dominate the top 3 reactions sensitivity. M6 and M11 – TROE are sensitive only in low-pressure conditions up to 5 bar and 10 bar, respectively. At the same time, M3 and M12 are sensitive only from 7 bar and 40 bar, respectively.

Figure 7 Sensitivity analysis of Master mechanism at 443 K with equivalence ratio

Similarly, the sensitivity of various reactions for change in equivalence ratios for methane at 443 K is shown in Figure 7. From Table 7, it is observed that M1; M3; M2 is sensitive in all equivalence ratios. While M10 – TROE is sensitive only in the lean mixture, whereas M11 – TROE is in a rich mixture. However, it is also found that M6 is sensitive from 0.7 to 1.2.

3.3.4 Sensitivity analysis of Master Mechanism at 700 K

For understanding the behavior of the reactions at higher temperature conditions, sensitivity analysis is performed at 700 K. Again, pressure and temperature sensitivity is performed to find the most sensitive reactions and behavior for change in pressure and mixture composition.

Table 8 Top 5 ranked reactions at 700 K for pressure

RANK	1 bar	5 bar	7 bar	10 bar
1	M1	M1	M1	M1
2	M2	M2	M2	M2
3	M6	M6	M6	M3
4	M15	M10 - TROE	M3	M10 - TROE
5	M10 - TROE	M3	M10 - TROE	M11 - TROE
RANK	40 bar	60 bar	100 bar	
1	M1	M1	M1	
2	M2	M3	M3	
3	M3	M2	M2	
4	M12	M12	M12	
5	M11 - TROE	M11 - TROE	M11 - TROE

Figure 8 Sensitivity analysis of Master mechanism at 700 K with pressure

The sensitivities of various reactions for change in pressure for methane at 700 K is shown in Figure 8. At the highest temperature conditions from Table 8, M1 and M2 are the most sensitive reaction at all pressure conditions. It is also observed that these reactions are sensitive only at low-pressure ranges: M15 (atmospheric pressure); M6 (up to 7 bar) and M10 – TROE (up to 10 bar). Some reactions are sensitive only at higher pressure, like M3 (from 5 bar) M11 – (from 10 bar), M12 (from 40 bar).

Table 9 Top 5 ranked reactions at 700 K for equivalence ratios

RANK	0.4	0.5	0.6	0.7	0.8
1	M1	M1	M1	M1	M1
2	M12	M3	M3	M3	M3
3	M3	M12	M12	M12	M2
4	M10 - TROE	M10 - TROE	M2	M2	M12

5	M2	M2	M10 - TROE	M10 - TROE	M10 - TROE
RANK	0.9	1	1.1	1.2	1.3
1	M1	M1	M1	M1	M1
2	M2	M2	M3	M12	M3
3	M3	M3	M2	M11 - TROE	M2
4	M12	M12	M12	M11	M12
5	M10 - TROE	M10 - TROE	M11 - TROE	M5	M11
RANK	1.4	1.5	1.6	1.7	1.8
1	M1	M1	M1	M1	M1
2	M3	M3	M3	M3	M3
3	M2	M11	M2	M2	M2
4	M11	M12	M11	M11	M11
5	M12	M11 - TROE	M11 - TROE	M12	M11 - TROE
RANK	1.9	2			
1	M1	M1			
2	M3	M3			
3	M2	M2			
4	M11	M11			
5	M11 - TROE	M11 - TROE

Figure 9 Sensitivity analysis of Master mechanism at 700 K with equivalence ratio

The sensitivities of various reactions for change in equivalence ratios are shown in Figure 9. It is observed that at the highest temperature from Table 9: the most sensitive reactions at all mixture compositions are: M1, M12, M3, M2. However, M10 – TROE is sensitive only in lean mixtures, whereas M11 – TROE is sensitive only in rich mixtures.

3.3.5 Overall observations

Table 10 Pressure condition analysis

PRESSURE	300 K	443 K	700 K
All pressure conditions	M1; M2; M10-TROE;	M1; M2; M10 – TROE	M1; M2
Low pressure conditions	M6; M11-TROE	M6; M11-TROE	M6; M15;M10 – TROE
High pressure conditions	M12; M3	M12; M3	M12; M3; M11

From the pressure condition analysis (Table 10), it is observed that at all pressure conditions, M1 ($H + O_2 = O + OH$) and M2 ($CO + OH = CO_2 + H$) are the most sensitive reactions in all pressure conditions. At the same time, M6 ($HCO + M = CO + H + M$) is the most sensitive reaction in low-pressure conditions, whereas M12 ($OH + HO_2 = H_2O + O_2$) and M3 ($CH_3 + HO_2 = CH_3O + OH$) are the most sensitive reactions in high-pressure conditions.

Table 11 Mixture composition analysis

MIXTURE CONDITION	300 K	443 K	700 K
All mixture conditions	M1; M2; M6	M1; M2; M3;	M1; M2; M3; M12;
Lean mixture conditions	M10-TROE, M16	M10 – TROE	M10 – TROE
Rich mixture conditions	M15	M11 – TROE	M11

From the mixture composition analysis (Table 11), it is observed that while , M1 ($H + O_2 = O + OH$) and M2 ($CO + OH = CO_2 + H$) are the most sensitive in all mixture compositions, whereas M10-TROE ($H + O_2 (+M) = HO_2 (+M) - TROE$) is most sensitive only in lean mixture conditions.

Finally, it is computed that the reaction M1 is the most sensitive in all temperature, pressure, and mixture composition conditions. It is also observed that specific reactions are more sensitive in equivalence ratio conditions, like M10-TROE is more sensitive in lean mixture conditions. Such reactions will be used to match the numerical simulation of the experimental data.

3.4 Mechanism Adjustment

The leading factor of multiplication/division by which a particular reaction can be changed is 2. A parametric analysis by changing a particular reaction with a sweep of multiplication factor from 2 times more and less is done, and for each of the values, the average error in each case is calculated.

Figure 10 Comparison of experimental (2010_Halter et. al. [29]; 2011_Park et. al. [37]; 2013_Akram et. al. [38]; 2014_Lui et. al. [8]; 2015_Dirrenberger et. al. [72] and 2015_Hu et. al. [40]) and mechanism values for methane at (a) 300 K & 1 bar; and (b) 443 K & 5 bar

Figure 11 Comparison of average error and error of each case at 1st stage adjustment

The initial comparison of the mechanism is shown in Figure 10. In the first part, the comparison of the experimental results with the numerical data at 300 K, 1 bar is shown, and in the second part, the comparison at 443 K, 5 bar is shown. It is observed that the

numerical value predicts more than the experimental range, and the average percentage of error is 12.27 %. So, the adjustment of the mechanism is performed.

Figure 12 Comparison of mechanism after 1st stage adjustment at (a) 300 K, 1 bar; (b) 443 K, 5 bar

Figure 13 Comparison of average error and error of each case at 2nd stage adjustment

The sensitivity analysis found that the M1 reaction is the most sensitive reaction at all temperatures and pressures. A parametric analysis is done by changing the division factor

from 1.0 to 2.0 for both testing conditions. Average values of errors for both conditions are then plotted, as shown in Figure 11.

It is found that at 1.07 minimum value of error (7.91%) is achieved, giving equal weightage to both the input conditions. After the first stage adjustment, the behavior of the mechanism is as shown in Figure 12. It is observed that the performance of the mechanism is better than the original mechanism.

Furthermore, it is observed that M10-TROE reaction is most positively sensitive in lean mixture conditions from the sensitivity analysis. Hence, a multiplication factor is used. After doing a parametric analysis, it is found that for a multiplication factor of 2.0 least minimum average percentage error of 5.2% is achieved, as shown in Figure 13.

Figure 14 Comparison of mechanism after 2nd stage adjustment at (a) 300 K, 1 bar & (b) 443 K, 5 bar

Applying both the factors for the reaction and comparison of the mechanism is shown in Figure 14. It is observed that the new prediction is better than the old prediction taking into account all the available existing data, as shown in Figure 15.

The adjusted mechanism is used to compare the mechanism with experimental values at, say, a higher temperature of which experimental data is available, say, 573 K and 1 bar pressure. It is observed that there is a 10.98% error in that given condition. So, it is concluded that the predicted values are well close within range at any given temperature and pressure condition, as shown in Figure 16.

Figure 15 Comparison of experimental (2010_Halter et. al. [29]; 2011_Park et. al. [37]; 2013_Akram et. al. [38]; 2014_Lui et. al. [8]; 2015_Dirrenberger et. al. [72] and 2015_Hu et. al. [40]) and mechanism values for methane at (a) 300 K & 1 bar; and (b) 443 K & 5 bar

Figure 16 Comparison of experimental (Mohammad et al. [54]) and numerical simulation values for methane at 573 K and 1 bar

3.5 Analysis of Methane simulation

Figure 17 Distribution of (a) Temperature; (b) Axial velocity and Density near the flame location.

Figure 18 Mole fraction profiles of (a) reactants and products; (b) major intermediate species and radicals

Effects of different simulation parameters on the solution of premix laminar flame speed are done. At 300 K, 1 bar, the various solution parameters are as plotted below:

Figure 17 (a) depicts the temperature profile, one of the solutions to the problems. Location at the axial distance of zero is the upstream, i.e., the unburnt gas entering the domain, and increasing axial distance indicates farther downstream. It is observed in the figure that temperatures rapidly rise to the burnt gas temperatures as the mixture passes through the flame ($x \approx 1.5$ cm).

In Figure 17, (b) distribution of axial velocity and density along with the axial distance. It is observed that as density decreases, axial velocity increases; this is logical as both of them are inversely related. However, it is also notable that the velocity at the far-left end of the corner is the velocity of the flow or the laminar flame speed (S_L), which for the given conditions is approximately 35.13 cm/s.

Profiles of reactants, significant products, and radicals are shown in Figure 18. In (a), it is observed that the concentration of reactants decreases during the process of combustion, and the concentration of products is increasing.

Figure 19 Distribution of minor species near the flame location.

Intermediate species are formed during combustion but are consumed during the process. The primary species formed and consumed during the reaction are CO, H_2 , OH, H, O, and CH_2O , and their profiles are shown in Figure 18 (b). Notably, these species are involved in the most sensitive reactions M1 and M2.

The formation of minor species is also shown in Figure 19. The different species which are formed are H_2O_2 , HO_2 , CH_3O , HCO, CH_2 , C_2H_2 , C_2H_3 , CH_2 , C_2H_4 , C_2H_5 , C_2H_6 , CH_3O_2 , CH_3O_2H , CH_2CO , CH_2CHO , CH_3CO , CH_3CHO , C_3H_5 , C_3H_6 , HCCO, CH_3OH , CH_2OH ,

$\text{C}_2\text{H}_5\text{OH}$, CH_3CHOH , $\text{CH}_3\text{CH}_2\text{O}$, CH_3OCH_3 , $\text{CH}_3\text{OCH}_2\text{O}_2$, HCO_2H , and $\text{C}_2\text{H}_5\text{CHO}$. The maximum mole fraction of these species is only 2.25×10^{-5} .

Figure 20 Distribution of nitrogen oxides and nitrous oxide along the flow direction.

The formation of nitrogen oxides (NO_x) and nitrous oxide (N_2O) is shown in Figure 20. It is found that even though the concentration is significantly less, yet NO and NO_2 increases even after the combustion reaction is complete, whereas N_2O is stagnant; this is because of the high temperature after combustion, which makes the excess N_2 to react and form the species. It is observed that the concentration of NO is around 3.5×10^{-4} , whereas the concentration of species like N_2O is only around 7×10^{-8} .

3.6 Parametric analysis of Laminar Flame Speed

It is known that laminar flame speed is dependent on unburnt gas temperature, pressure, and mixture composition. Only the equivalence ratio is considered for the mixture composition, and it is varied from 0.4 to 2.0. So, the variation of each of the parameters is studied.

3.6.1 Variation of Equivalence Ratio

Five different cases of pressure and temperature combination are studied:

- 1) Low temperature and low pressure
- 2) High temperature and low pressure
- 3) Low temperature and high pressure
- 4) High temperature and high pressure

3.6.1.1 Low temperature and low pressure

Normal room conditions of low temperature and low pressure is considered, say 300 K & 1 bar. This condition is the widely tested condition, so one of the most critical and well-validated conditions.

Figure 21 Comparison of (a) S_L ; and (b) temperature profiles along the flow direction for various equivalence ratios at low temperature and low pressure

Figure 21 maximum S_L is observed at a slightly rich mixture ($\phi \approx 1.1$) typical of the laminar flame speed of hydrocarbons reported in the literature. For the inlet conditions, the trends of flame speed variation are the same on both sides. From the temperature profile on the right, it is observed that the temperature rise is minimum for the leanest ($\phi = 0.6$) and richest ($\phi = 1.6$) mixture conditions. It is also interesting to note that for maximum S_L value at an equivalence ratio of 1.1 ($S_L = 36.93\text{ cm/s}$), the temperature rise is maximum. It is also observed that the slope of the temperature profile at the flame location is reduced as flame speed decreases.

Laminar flame speed increases with the increase in the concentration of fuel in the mixture. In addition to this, we can also say that leaner mixture, there is less fuel to produce the energy, and the energy produced is not enough to heat the entire fuel-air mixture, so the laminar flame speed is low. Similarly, in a richer mixture, there is not enough oxidizer for the combustion to take place, and the energy produced from the combustion is not enough to make the other fuel atoms to achieve their activation energy in order for the reaction to take place, so the laminar flame speed is low. So, theoretically speaking, it should have the maximum laminar flame speed at a 1.0 equivalence ratio. However, due to the chemical kinetics, like the dissociation of Carbon dioxide at a higher temperature, and other reaction

pathways playing dominating behavior, the highest laminar flame speed is achieved at a slightly richer mixture.

3.6.1.2 High temperature and low pressure

The effect of an increase in temperature is studied by considering the higher temperature. So, at 700 K and 1 bar conditions, the SL and temperature profile variation is shown in Figure 22.

Figure 22 Comparison of (a) S_L ; and (b) temperature profile with a change in equivalence ratio at high temperature and low pressure

Figure 22 shows that maximum S_L is observed at a slightly rich mixture ($\phi \approx 1.1$), a typical characteristic of the laminar flame speed of hydrocarbons reported in the literature. For the inlet conditions, flame speed variation trends are found to be slightly different on both sides. From the temperature profile on the right, it is observed that the temperature rise is minimum for the leanest ($\phi = 0.5$) and richest ($\phi = 2.0$) mixture conditions. It is also interesting to note that the value of S_L increases with the increase in unburnt gas temperature, for maximum S_L value is observed at an equivalence ratio of 1.1 ($S_L = 170.89 \text{ cm/s}$). It is worthwhile to note that the maximum temperature rise is at $\phi = 1.2$, even though the maximum S_L is at $\phi = 1.1$; this is because the rate of rising will be more in the case of $\phi = 1.1$

3.6.1.3 Low temperature and high pressure

A temperature of 300 K and 70 bar is studied to study the effect of pressure, as shown in Figure 23.

Figure 23 Comparison of (a) S_L ; and (b) temperature profile with a change in equivalence ratio at low temperature and high pressure

Figure 23 maximum S_L is observed at a richer mixture ($\phi \approx 1.1$) typical of the laminar flame speed of hydrocarbons reported in the literature. For the inlet conditions, flame speed variation trends are found to be slightly different on both sides. From the temperature profile on the right, it is observed that the temperature rise is minimum for the leanest ($\phi = 0.4$) and richest ($\phi = 2.0$) mixture conditions. It is also interesting to note that for maximum S_L value at an equivalence ratio of 1.2 ($S_L = 6.6$ cm/s). It is observed that the rise in flame speed is not achieved for the most rise in temperature.

It is observed that with an increase in pressure, S_L decreases, but due to the increased reactivity at higher pressure, the richer mixtures, having more fuel, still produce more laminar flame speed, unlike the leaner mixtures. Hence the non-symmetric behavior of the laminar flame speed profile is observed.

3.6.1.4 High temperature and high pressure

To study the effect of both the temperature and pressure, high temperature and high-pressure conditions of 700 K and 70 bar are depicted in Figure 24.

Figure 24 maximum S_L is observed at a richer mixture ($\phi \approx 1.1$) typical of the laminar flame speed of hydrocarbons reported in the literature. For the inlet conditions, flame speed variation trends are found to be slightly different on both sides. From the temperature profile on the right, it is observed that the temperature rise is minimum for the leanest ($\phi = 0.4$) and richest ($\phi = 2.0$) mixture conditions. It is also interesting to note that for maximum S_L value at an equivalence ratio of 1.2 ($S_L = 37.34$ cm/s). It is observed that the rise in flame speed is not achieved for the most rise in temperature, but for the rate of rising.

The combined effect of pressure and temperature is observed; with an increase in temperature, laminar flame speed should be increased, but due to the increased pressure, the laminar flame speed again decreases. Due to pressure, shifting of the maximum S_L to a richer mixture is also observed.

Figure 24 Comparison of (a) S_L ; and (b) temperature profile with a change in equivalence ratio at high temperature and high pressure

3.6.2 Variation of Temperature

Variation of S_L for temperature is studied at stoichiometric, lean, and rich mixture conditions at 1 bar pressure with temperature varying from 300 to 700 K.

3.6.2.1 Stoichiometric mixture conditions

From Figure 25, for stoichiometric conditions ($\phi \approx 1.0$) it is observed that with an increase in unburnt gas temperature, the value of S_L increases from 35.13 cm/s to 166.54 cm/s. The maximum value of S_L is achieved at an unburned gas temperature of 700 K. From the

temperature profile on the right, it is observed that with the increase in unburnt gas temperature, the burned gas temperature also increases. However, the temperature profile's slope remains almost constant, thus maintaining the parallel nature between the temperature profiles.

Figure 25 Comparison of (a) S_L ; and (b) temperature profile with a change in the unburned temperature of stoichiometric mixtures

3.6.2.2 Lean mixture conditions

From Figure 26, it is observed that even with lean mixtures ($\phi \approx 0.4$) with an increase in unburned gas temperature, the laminar flame speed increases from 6.44 cm/s at 500 K to 21.73 cm/s at 700 K. However, from the temperature profile, it is observed that they are not parallel, especially in the slope profile, and they have a common point of interference. This point of interference is one reason why low-temperature cases could not achieve converged solutions. Also, it is observed that the axial distance is completely changed for the change in input conditions.

Figure 26 Comparison of (a) S_L ; and (b) temperature profile with a change in the unburned temperature of lean mixtures

3.6.2.3 Rich mixture conditions

Figure 27 Comparison of (a) S_L ; and (b) temperature profile with a change in the unburned temperature of rich mixtures

Figure 27 shows that even with rich mixtures ($\phi \approx 2.0$) with an increase in unburned gas temperature, the laminar flame speed increases from 20.16 cm/s at 500 K to 48.41 cm/s at 700 K. Also, from the temperature profile, it is observed that with the increase in unburned gas temperature, the slope of the curve almost remains the same, maintaining the parallel nature of the curve.

3.6.3 Variation of Pressure

Variation concerning the rise in pressure is also studied for stoichiometric, lean, and rich mixture conditions at 300 K and with pressure varying from 1 to 70 bar.

3.6.3.1 Stoichiometric mixture conditions

Figure 28 Comparison of (a) S_L ; and (b) temperature profile with a change in the pressure of stoichiometric mixtures

Figure 28 observed that for stoichiometric mixture conditions ($\phi \approx 1.0$) with an increase in pressure, the value of S_L decreases; this is in agreement with the literature's observation. The value of S_L decreases from 35.13 cm/s to 5.44 cm/s. Also, from the temperature profile, it is observed that with an increase in pressure, the slope of the curve increases, but the burned gas temperature and the unburned gas temperature almost remain the same.

3.6.3.2 Lean mixture conditions

Figure 29 shows that for lean mixtures ($\phi \approx 0.4$) with an increase in pressure, the value of S_L decreases; this agrees with the literature's observation. The value of S_L decreases from

0.096 cm/s to 0.09 cm/s. Also, from the temperature profile, it is observed that with an increase in pressure, the slope of the curve increases, but the burned gas temperature and the unburned gas temperature almost remain the same. There is a common point of intersection, and this logic can be used to generate the temperature profile. However, it is calculated that leaner mixtures at lower temperatures have temperature profiles have fewer slopes, and hence the axial distance is completely changed

Figure 29 Comparison of (a) S_L ; and (b) temperature profile with a change in the pressure of lean mixtures

3.6.3.3 Rich mixture conditions

Figure 30 shows that for rich mixtures ($\phi \approx 2.0$) with an increase in pressure, the value of S_L decreases from $S_L = 5.154\text{ cm/s}$ to 4.689 cm/s till pressure range of 25 bar, after which the value of S_L increases again to $S_L = 4.723\text{ cm/s}$. From the temperature profile, it is observed that with an increase in pressure, the slope of the curve increases, but the burned gas temperature and the unburned gas temperature almost remain the same. There is a common point of intersection, and this logic can be used to generate the temperature profile. However, it is also observed that the burned gas temperature is less than the peak temperature of combustion. It is also to be noted that with an increase in pressure, the laminar flame speed decreases, but after some time, it is observed to decrease; this is due to the dominant nature of the reactivity of the molecules at higher pressure, which tends to increase the laminar flame speed at higher pressure. This increase implies that if we increase the pressure for lean and rich mixture conditions, the S_L will again increase.

Figure 30 Comparison of (a) S_L ; and (b) temperature profile with a change in the pressure of rich mixtures

3.6.4 Variation of S_L with Temperatures at different Pressures

Figure 31 shows that laminar flame speed distribution has a maximum value at a slightly rich mixture, and on both sides of the maximum, the value of S_L decreases with an increase in leanness or richness of the mixture. This observation is in agreement with the review from the literature. Also, it is inferred that with the increase in temperature, the value of S_L increases for any mixture composition. However, it is also observed that with the increase in initial pressure ($P = 1\text{ bar}$ to 70 bar), the maximum point shifts from 1.1 to 1.2 equivalence ratio of the mixture composition. As already explained, this increase is due to the effect of the higher reactivity of richer mixtures at higher equivalence ratios.

Figure 31 Comparison of S_L with change in equivalence ratio & temperature at (a) 1 bar; (b) 70 bar

3.6.5 Variation of S_L with Pressures at different Temperatures

Figure 32 Comparison of S_L with change in equivalence ratio & pressure at (a) 300 K; & (b) 700 K

Figure 32 shows that S_L always has the maximum value at a slightly rich mixture at lower pressure. However, the richness of the mixture increases with the increase in pressure. Also, it is observed that with an increase in pressure, the value of S_L decreases, as observed

from the previous observations. It is also noteworthy that the observation is repeated for both the low temperature ($T = 300$ K) and high temperature ($T = T00$ K) observations.

3.7 Sensitivity of Ethane

The reactions involved in the initiation of ethane (C_2H_6) oxidation are:

Figure 33 Sensitivity analysis of ethane at 300 K and 1 bar

By doing sensitivity analysis, as shown in Figure 33 for change in pressure, it is computed that E1 is having the most sensitivity at 5 bar pressure. While, E5 is the most sensitive reaction, which is having all pressures in the same direction sensitivity, whereas E2 and E4 have sensitivity in the same directions and follow numerically the values of the second-most sensitive reaction.

Further analysis needs to be done using this sensitivity data to match the higher alkanes' results with their respective experimental results.

3.8 Behavior of mechanism with higher alkanes

Predicted laminar flame speeds of other higher alkanes are compared and shown below. The following plots show that there is not much proper matching between the experimental and numerical simulation values. To match both the values, sensitivity analysis must be done for each component's reactions for oxidation and alter the reactions, ensuring that the ignition delay calculations are not affected by the change in the pre-exponential factor's values. The behavior of the mechanism for other higher alkanes is compared and shown below.

3.8.1 Ethane

Figure 34 Comparison of experimental (2008_Kishore et. al. [67]; 2011_Dirrenberger et. al. [61]; 2013_Park et. al. [68]; 2016_Goswami et. al. [69]; 2005_Jomaas et. al. [66] and 2011_Lowry et. al. [62]) and numerical simulation values of ethane at (a) 300 K & 1 bar and (b) 300 K & 5 bar

A comparison of data of ethane experimental results with numerical simulation is shown in Figure 34. It is observed that there is slight over-prediction in both the cases of 300 K & 1 bar as shown in Figure 34 (a) and 300 K & 5 bar as shown in Figure 34 (b)

3.8.2 Propane

Figure 35 Comparison of experimental (2011_Dirrenberger et. al.; 2012_Akram et. al. [101]; 2016_Goswami et. al. [69]; 2016_Park et. al. [102]; 2005_Jomaas et. al. [66]; 2011_Lowry et. al. [62]; 2004_Zhao et. al. [70] and 2012_Akram et. al. [101]) and numerical simulation values of propane at (a) 300 K & 1 bar ; (b) 300 K & 5 bar and (c) 650 K & 5 bar

A comparison of propane's behavior with experimental results is shown in Figure 35 at 300 K & 1 bar in (a), 300 K & 5 bar in (b), and 650 K & 5 bar in Figure 36. The effect of temperature and pressure is to be dealt with separately; that is why separate cases are taken. It is observed that there is a slight overprediction in each case.

3.8.3 Butane

Figure 36 Comparison of experimental (2009_Kelly et. al. [71]; 2011_Dirrenberger et. al. [61]; 2016_Park et. al. [102]; 2004_Farrell et. al. [103] and 2010_Marshall et. al. [104]) and numerical simulation values of butane at (a) 300 K & 1 bar and (b) 450 K & 3 bar

A comparison of the mechanism with butane behavior is shown in Figure 37. at 300 K & 1 bar in Figure 37 (a) and 450 K & 3 bar in Figure 37 (b). It is found that there is slight over-prediction at 300 K and 1 bar, but at 450 K & 3 bar, it is found that there is a slight mismatch of the mechanism, as an equivalence ratio of 1.0 there is correct prediction, whereas at lean mixtures there is slight over prediction and at rich mixtures, there is slight under prediction.

3.8.4 Pentane

The behavior of Pentane's mechanism is shown in Figure 38 for 300 K & 1 bar, as shown in Figure 38 (a) and 353 K & 2 bar, as shown in Figure 38 (b). It is observed that there is a slight prediction.

Figure 37 Comparison of experimental (1998_Davis et. al. [105]; 2015_Dirrenberger et. al. [72] and 2011_Kelley et. al. [73]) and numerical simulation values of pentane at (a) 300 K & 1 bar and (b) 353 K & 2 bar

3.8.5 Hexane

Figure 38 Comparison of experimental (2012_Wu et. al. [74]) and numerical simulation values of hexane at (a) 353 K & 1 bar and (b) 353 K & 5 bar

The mechanism for hexane is shown in Figure 39 at 353 K & 1 bar, as shown in Figure 39 (a) and 353 K & 5 bar, as shown in Figure 39 (b). It is observed that in (a) at lean mixture, there is an accurate prediction, whereas, in rich and stoichiometric conditions, there is over prediction. Also, it is observed that in Figure 39 (b), the prediction is somewhat accurate with a small offset at stoichiometric conditions.

3.8.6 Heptane

Figure 39 Comparison of experimental (1998_Davis et. al. [75]; 2004_Huang et. al. [76]; 2007_Kumar et. al. [106]; 2011_Chong et. al. [77]; 2013_Silegham et. al. [80]; 2014_Dirrenberger et. al.[81]; 2015_Mannaa et. al. [107] and 2007_Kumar et. al. [106]) and numerical simulation values of heptane at (a) 300 K,1 bar; (b) 358 K,2 bar; & (c) 470 K,1 bar

Comparing the experimental value of n-heptane with numerical simulation is as shown in Figure 40. It is observed that Figure 40 (a) is at 300 K & 1 bar and (b) is at 358 K & 2 bar, and (c) is at 470 K & 1 bar. Comparison is made thus, to study the effects of both the change in temperature and pressure. It is found that the prediction is almost the same, with the least error in all the cases.

3.8.7 Iso-octane

Figure 40 Comparison of experimental (1998_Davis et. al.[75]; 2004_Huang et. al. [76]; 2007_Kumar et. al. [106], 2011_Vanlipzig et. al. [84], 2011_Zhou et. al. [85]; 2013_Silegham et. al. [80]; 2014_Dirrenberger et. al. [81], 1998_Bradley et. al. [82] and 2004_Farrell et. al. [108]) and numerical simulation values of iso-octane at (a) 300 K & 1 bar and (b) 450 K & 3 bar

It is observed that in Figure 41 (a) at 300 K & 1 bar, the prediction is slightly over prediction. At 450 K & 3 bar, as shown in (b), it is observed that the prediction is highly over predicted in all the cases.

3.8.8 n-decane

At 400 K & 1 bar, as shown in Figure 42 (a), the prediction is slightly overpredicted near the stoichiometric mixture condition, whereas in lean and rich mixtures, the prediction matches. Similarly, at a higher temperature of 473 K & 1 bar as shown in (b), the prediction matches experimental in lean mixtures, whereas there is slight over-prediction in rich mixtures.

Figure 41 Comparison of experimental (2007_Kumar et. al. [86], 2010_Ji et. al. [5], 2011_Singh et. al. [87]; 2013_Hui et. al. [109]; 2013_Kim et. al. [88]; 2013_Munzar et. al. [89]; 2015_Comandini et. al. [90] and 2003_Rasumennen et. al. [110]) and numerical simulation values of n-decane at (a) 400 K & 1 bar and (b) 473 K & 1 bar

3.8.9 n-dodecane

Figure 44 shows that at 400 K & 1 bar, as shown in Figure 43 (a), the prediction matches in leaner and richer mixtures, whereas there is a slight over-prediction near stoichiometric conditions. Similarly, it is observed that at higher temperature conditions of 470 K & 1 bar (c), the prediction is not matching only at near stoichiometric conditions. Nevertheless, at a higher pressure condition of 400 K & 3 bar, as shown in (b), the prediction only matches the leaner mixture but not at other conditions.

Figure 42 Comparison of experimental (2007_Kumar et. al. [86]; 2010_Ji et. al. [5]; 2013_Hui et. al. [109] and 2017_Ren et. al. [91]) and numerical simulation values of n-dodecane at (a) 400 K & 1 bar; (b) 470 K & 1 bar; and (c) 400 K & 3 bar

3.8.10 n-tetradecane

Figure 44 shows that at standard conditions of 443 K and 1 bar Figure 45, the prediction is slightly overpredicted.

Figure 43 Comparison of experimental (2014_Li et al. [92]) and numerical simulation values of n-tetradecane at 443 K & 1 bar

3.8.11 Hexadecane

Figure 45 (a) shows slight over-prediction in all mixture conditions at 443 K & 1 bar inlet conditions, but the prediction is way off in more prosperous mixture conditions than other conditions.

3.8.12 Iso-cetane

Figure 45 (b) observed that for iso-cetane at 473 K and 1 bar, the prediction is off at all mixture conditions.

So, all alkanes' behavior to the mechanism is thus shown; further analysis needs to be done to match the experimental ones' results.

Figure 44 Comparison of experimental (2014_Li et. al. [92] and 2017_Ren et. al.[91]) and numerical simulation values of (a) hexadecane at 443 K & 1 bar; and (b) iso-cetane at 473 K & 1 bar

4 CONCLUSIONS

From the study, it can be summarized that Premix laminar flame speed for any given component at any given input condition is computed, and the appropriate parameters for analysis for getting converged solutions are calculated. In addition to that, sensitivity analysis is performed for the methane oxidation reactions, and the most sensitive reactions are adjusted for matching the numerical simulation with the experimental values of S_L . Finally, the laminar flame speed of methane of the alkane component of multi-component fuel is calculated at engine relevant conditions of a temperature of 300 K to 700 K (room temperature to auto-ignition temperature) pressure from 1 bar to 70 bar, equivalence ratio of 0.4 to 2.0.

Sensitivity analysis on the MTU master mechanism's alkane sub-mechanisms for important methane combustion reactions yielded some critical findings. The sensitivities of any reaction are dependent on input conditions, and the order of sensitivity is also somewhat reliant on it. M1 ($H + O_2 = O + OH$) was the most sensitive reaction in almost all pressures, temperatures, and equivalence ratios. M10-TROE ($H + O_2 (+M) = HO_2 (+M) - TROE$) is most sensitive in lean mixture conditions

This work's significant contributions are that, based on the sensitivity analysis, the mechanism was improved to capture the measured data with an average error of 10 % in a wide range of pressure and temperature conditions. The library for methane fuel for the given conditions is generated, and this library is to be implemented to CFD code. Further investigation and improvement of reaction mechanisms for alkanes heavier than methane through detailed sensitivity analysis are warranted to reduce the discrepancy between model predictions and measured data.

5 FUTURE WORK

The laminar flame speed library developed in the study is to be converted to a format that can be implemented into CFD codes. After improving the prediction performance of heavy alkanes, the library is to be extended to other classes of the multi-component fuel. Proper scrutiny of the reactions must be performed with detailed sensitivity analysis to improve the laminar flame speed prediction while maintaining auto-ignition processes' prediction performance, including ignition delay prediction.

6 References

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A BASICS OF CHEMKIN

A.1 Setting up a problem with CHEMKIN-Pro

The necessary steps to be followed for setting up the problem of Flame speed calculator, with Chemkin pro is discussed below in the six steps:

- Deciding on modeling approach – It is decided to take the Flame-speed table generator, as it can generate the table, which can be post-processed to do a detailed analysis of the results. Simultaneously, the results can be post-processed using generated data using MS Excel to study the variation of all characteristics of the problem, species, and input conditions.
- Create a diagram of the reactor network that represents the modeling approach, including inlets and outlets.
- Pre-process the chemistry set, which includes:
 - Gas-phase Kinetics input
 - Species thermodynamic data
 - Gas-phase species transport data
- Set up the reactor inlet conditions, like
 - Process conditions
 - Solution method options
 - Parameter study options
- Solving problem
- Analyze results using:
 - ANSYS Chemkin-Pro Visualizer
 - Reaction path analyzer
 - Export to Excel (only on Windows OS)
 - Exporting to other software using a text file

A.2 Arrhenius Rate equation

The forward rate constants for the reactions are represented by:

$$k_{fi} = A_i T^{\beta_i} \exp(-E_i/R_C T)$$

Where,

A_i - pre-exponential factor

T – a temperature of consideration

β_i – temperature exponent

E_i - Activation energy

R_c – Gas constant for the reaction

A.3 CHEMKIN – Pro input manual

The Chemkin Pro-Input manual consists of Gas-phase kinetics input, Thermodynamic data, and Transport database.

A.3.1 Gas-phase kinetics input

It provides a symbolic representation of the elementary reactions and their related rate constants. This input consists of Elements that specify the elements used in species, Species that are formed in reactions, and Reactions involved in the mechanism. Also, Thermodynamic data, Real gas data, and transport data can be specified. The summary of the rules for each case is specified as follows:

Elements Data

- The beginning must be with the word ELEMENT (or ELEM).
- Element or isotopes are represented as 1/2 character symbols.
- An isotope name (not from the periodic table) must be followed by atomic weight (in g/mol) delimited by slashes.
- Each element or isotope should be specified only once.
- They can appear anywhere on the line.
- No matter may be present in a line, and more than one line can also be used.
- If there are more than two elements, they should be separated by a space.
- A name that begins on one line may not continue to the next line.
- No blank spaces between elements and their atomic weights, but spaces can be allowed between slashes.
- There may be more than one ELEMENT statement.
- Anything following an exclamation mark is a comment.
- It is recommended to use END after the elements are specified.
- Elements required in Surface Kinetics must be specified in the Gas-phase Kinetics input file.

Species Data

- Species must begin with SPECIES (or SPEC).
- It can contain a string of 16 characters in upper- or lower-case alphabets. Ionic species may be represented as '+' or '-' at the end of the species, not at the beginning. No other characters are allowed.
- Each species should be declared only once, as duplicate ones will be ignored.
- Each species that are going to appear in the reaction must be declared here.
- The species can be written anywhere in the line.

- Lots of several species can come in a line, and any number of lines of species can be used.
- Space must separate species on the same line.
- Species must end in the same line.
- There can be one or more SPECIES statement.
- Anything following an exclamation mark is a comment.
- It is recommended to use END after the species are specified.

Reaction Data

- First-line must begin with REACTIONS (or REAC) and can include units.
- Reactions can be specified anywhere in the line along with Arrhenius coefficients, and all spaces except the ones between the Arrhenius parameters are ignored.
- Each reaction must contain '=' / '<=>' / '=>' between reactants and products.
- Any reaction must be written in a single line.
- The Arrhenius parameters must appear in the order A_i , β_i , and E_i on the same reaction line. They must be separated by at least a single space but no space within the numbers.
- No more than six reactants or six products are allowed.
- Anything following an exclamation mark is a comment.
- It is recommended to use END after the species are specified.

In addition to the basic rate equation, particular additional reaction representation is also possible for which the keywords are specified

- Species name - Neutral third body efficiency
- CHEB - Chebyshev Polynomial Rate expressions
- COLLEFF - Efficiency of collision frequency expression
- DUP - Duplicate reactions
- EXCI - Energy loss parameter
- FIT1 - Supersedes the default reaction rate expressions by an expression which introduces power series within the exponential of a modified Arrhenius expression
- FORD - Forward reaction order parameter
- HIGH - High-pressure limit reactions
- JAN - Optional Rate Fit Expressions – Janev-Langer reaction rate
- LOW - Low-pressure limit reactions
- LT - Landau-Teller Reactions
- MOME - Plasma Momentum-Transfer Collision Frequency Options
- PCHEB - Supersedes the default pressure limits for a Chebyshev polynomial rate expression
- PLOG - Pressure dependence through logarithmic interpolation
- REV - Reverse rate parameters

- RLT - Supersedes default reverse reaction rate expression by Landau-Teller Reaction rate
- RORD - Reverse reaction order parameter, supersedes for any species in the mechanism reverse reaction order
- SRI - SRI Pressure-dependent reaction rate
- TCHEB – Supersedes default temperature limits for a Chebyshev polynomial rate expression
- TDEP - Species temperature dependence
- TROE - Troe Pressure dependent reaction rate
- UNITS - Reaction units
- USRPROG - Optional user rate subroutine CKUPROG
- XSMI – In a plasma simulation, the ion's momentum transfer collision frequency calculation signifies collision cross-section information to determine ion momentum transfer collision frequencies.

These keywords are applied to the following rules.

Auxiliary Reaction Data

- These lines may contain an M to symbolize third-body efficiencies, reverse reaction rate factors, Landau-Teller parameters. They must follow duplicate reactions and reactions, signifying pressure-dependent behavior.
- Species in any reaction can have only one enhanced third body efficiency regarding it.
- In a reaction, only one radiation wavelength can be declared.
- Enhanced third body information is referenced in the subroutine package in the same order as they are declared in the text.
- The maximum no of enhanced third bodies is ten.
- The declarations of the keyword can appear in any order anywhere on the line.
- A keyword and its factors must appear in a line, and more than one line can be used to represent all the keywords, and in a single line, more than one set of keywords and its parameters can be set up.
- Space must separate keyword declarations on the same line.
- No blank spaces are allowed within a keyword or a parameter, but there can space between a keyword, slash, and a parameter.
- Anything following an exclamation mark is a comment.
- There must be precisely two species which are reactant, one of which must be an ion in an ion momentum-transfer collision
- There must be precisely two species which are reactant, one of which must be an electron in an electron momentum-transfer collision

A.3.2 Thermodynamic data

Thermodynamic data are defined for calculating the thermodynamic properties. The raw format of the file is:

- The first line is THERMO/THERMO ALL
- The second line contains two temperature ranges for corresponding coefficients: the lowest T, medium T, and highest T. The numbers can be three floating-point values; each is allocated ten columns, i.e., a total of 30 columns
- The third line must contain
 - Species name from 1st column which is in 16 alpha-numeric characters, contained in first 16 columns
 - The date, which is six alpha-numeric characters, contained in 19 to 24 columns
 - Atomic symbols and formula which is four sets of data each having two alpha-numeric representing elements followed by three integer value representing the number of elements, contained in columns 25 to 44
 - A phase of species (S/L/G for solid-liquid or gas) contained in column 45
 - The low temperature, which is ten columns for a real value contained in columns 46 to 55
 - High temperature, which is ten columns for a real value contained in columns 56 to 65
 - Common temperature if needed, which is eight columns for a real value contained in columns 66 to 73
 - Atomic symbols and formula If needed, which is two alphanumeric columns followed by three integer value contained in columns 74 to 78
 - Integer 1, contained in column 80
 - Atomic symbols and formula if needed which is four sets of data each having two alpha-numeric representing elements followed by three integer value representing the number of elements, contained in columns 81 to 100
- The fourth line must contain:
 - Coefficients a_1 through a_5 representing the equations for an upper-temperature interval, which is five sets of real values, each having 15 columns representing scientific notations having eight values after the decimal point, contained in columns 1 to 75
 - Integer 2, contained in column 80
- The fifth line must contain:
 - Coefficients a_6 and a_7 representing the equations for upper-temperature interval and a_1 , a_2 , and a_3 for lower temperature interval, which is five sets of real values each having 15 columns representing scientific notations having eight values after the decimal point, contained in columns 1 to 75
 - Integer 3, contained in column 80
- The sixth line must contain:

- Coefficients a_4 through a_7 representing the equations for lower temperature interval, which is four sets of real values, each having 15 columns representing scientific notations having eight values after the decimal point, contained in columns 1 to 60
- Integer 4, contained in column 80
- The rest of the lines must repeat lines 3 – 6 for each species
- The last line can contain the optional END representing the end of thermodynamic data.

EQUATIONS REPRESENTED BY THERMODYNAMIC DATA

The seven coefficients for the thermodynamic data are used to calculate the Specific heat capacity at constant pressure (C_p), Species Molar Enthalpy (H_k), and Species Molar Entropy (S_k). Other thermodynamic properties are calculated from these seven coefficients. The equations are :

$$C_{pk}^0 = a_{1k} + a_{2k}T_k + a_{3k}T_k^2 + a_{4k}T_k^3 + a_{5k}T_k^4$$

$$\frac{H_k^0}{RT_k} = a_{1k} + \frac{a_{2k}}{2}T_k + \frac{a_{3k}}{3}T_k^2 + \frac{a_{4k}}{4}T_k^3 + \frac{a_{5k}}{5}T_k^4 + \frac{a_{6k}}{T_k}$$

$$\frac{S_k^0}{R} = a_{1k}\ln T_k + a_{2k}T_k + \frac{a_{3k}}{2}T_k^2 + \frac{a_{4k}}{3}T_k^3 + \frac{a_{5k}}{4}T_k^4 + a_{7k}$$

A.3.3 Transport data

Transport data is unique data of the species, which is required for premix laminar flame speed calculations. There are six parameters which are defined for specifying the transport properties, and they are defined as follows:

- The first number indicates the geometrical configuration, like whether it is monoatomic, linear, or non-linear.
- Lennard-Jones potential well depth ϵ/k_B in Kelvins
- Lennard-Jones collision diameter, σ in angstroms
- Dipole moment μ in Debye
- Polarizability, α in cubic angstroms
- Rotational relaxation collision number, Z_{rot} at 298 K

There are additional rules like the first 16 columns representing the species' name, and the rest columns through 80 are free-format and contain the above six parameters. Also, any line which follows an exclamation mark (!), period(.), or slash(/) is taken as a comment line, and anything following an exclamation mark is a comment.

A.4 Premixed Laminar Flame Speed solver

The premixed flame models solve a set of governing partial differential equations using implicit finite difference methods and a combination of steady-state and time-dependent methods. The solver algorithm automates coarse to fine grid refinement to enhance the steady-state approach's convergence properties and provide optimal mesh placement. By definition, a freely propagating flame is used to calculate the Laminar flame speed (SL) for a given temperature, pressure, and mixture composition. There are no heat losses by description. Therefore all the temperatures are obtained through solving the energy equation. Also, it is imminent that S_L depends on heat transport, and therefore it becomes logical that predicting the temperature distribution is an integral part of determining it.

A.4.1 1-D flame equations

For the flame speed calculation, 1-dimensional flow is adopted with uniform inlet conditions. Therefore, the governing equations reduce to:

Continuity equation

$$\dot{M} = \rho u A$$

Energy conservation Equation

$$\dot{M} \frac{dT}{dx} - \frac{1}{C_p} \frac{d}{dx} \left(\lambda A \frac{dT}{dx} \right) + \frac{A}{C_p} \sum_{k=1}^K \rho Y_k V_k c_{pk} \frac{dT}{dx} + \frac{A}{C_p} \sum_{k=1}^K \dot{\omega}_k h_k W_k + \frac{A}{C_p} \dot{Q}_{rad=0}$$

Species conservation Equation

$$\dot{M} \frac{dY_k}{dx} + \frac{d}{dx} (\rho A Y_k V_k) - A \dot{\omega}_k W_k = 0 \quad (k = 1, \dots, K_g)$$

Ideal gas equation

$$\rho = \frac{P \bar{W}}{R T}$$

where,

x – spatial coordinate

$\dot{M}$ – mass flow rate

T – temperature

Y_k – a mass fraction of the k^{th} species

$\bar{W}$ – mean molecular weight of the mixture

R – universal gas constant

λ – thermal conductivity of the mixture

c_p – specific heat at a constant pressure of the mixture

c_{pk} – constant pressure heat capacity of k^{th} species

$\dot{\omega}_k$ – the molar rate of production by chemical reaction of k^{th} species per unit volume, which follows a modified Arrhenius form

h_k – specific enthalpy of k^{th} species

V_k – diffusion velocity of k^{th} species

$\dot{Q}_{\text{rad}}$ – heat loss due to gas and particle radiation

A – cross-sectional area of tube encompassing flame, assumed to be constant and equal to unity

The mixture averaged method is used to calculate the transport properties.

Diffusion velocity

$$V_k = V_k + W_k + V_c$$

where,

V_k – Ordinary diffusion velocity

W_k – Non-zero thermal diffusion velocity for low molecular weight species (H, H₂, and He)

V_c – Correction velocity

Ordinary diffusion velocity (V_k)

According to Curtiss-Hirschfelder approximation,

$$V_k = - D_{km} \frac{1}{X_k} \frac{dX_k}{dx}$$

where,

X_k - mole fraction

D_{km} – mixture-averaged diffusion coefficient

Mixture-averaged diffusion coefficient (D_{km})

$$D_{km} = \frac{1 - Y_k}{\sum_{j \neq k}^K \frac{X_j}{D_{kj}}}$$

where,

D_{kj} – Binary diffusion coefficients

Thermal diffusion velocity (W_k)

$$W_k = \frac{D_{km} \Theta_k}{X_k} \frac{1}{T} \frac{dT}{dx}$$

where,

Θ_k – thermal diffusion ratio

Correction Velocity (V_c)

It is included to make mass fractions sums to unity.

A.4.2 Boundary Conditions

For freely propagating flames, the boundary conditions are deduced. The location of the flame is constrained by fixing temperature at one point so that temperature and species gradients vanish at the cold boundary, so that solution of the flame speed eigenvalue $\dot{M}$ is achieved.

At the cold boundary,

$$\varepsilon_{k,1} - Y_{k,1} - \left(\frac{\rho A Y_k V_k}{\dot{M}} \right)_{j=1} \frac{1}{2} = 0 \text{ and } T_1 - T_b = 0$$

where

$\varepsilon_{k,1}$ – inlet reactant fraction of the k^{th} species

T_b – Specified burner temperature

At the hot boundary,

$$\frac{Y_{k,J} - Y_{k,J-1}}{X_J - X_{J-1}} = 0 \text{ and } \frac{T_J - T_{J-1}}{X_J - X_{J-1}} = 0$$

A.4.3 Finite Difference approximations

First, the governing equations are discretized. They are then applying finite-difference approximations on the non-uniform grid with J grid points, i.e., one at the cold boundary and J at the hot boundary.

Energy conservation equation

$$\dot{M} \frac{dT}{dx} - \frac{1}{C_p} \frac{d}{dx} \left(\lambda A \frac{dT}{dx} \right) + \frac{A}{C_p} \sum_{k=1}^K \rho Y_k V_k c_{pk} \frac{dT}{dx} + \frac{A}{C_p} \sum_{k=1}^K \dot{\omega}_k h_k W_k + \frac{A}{C_p} Q_{rad=0}$$

On the convective terms, there is an option of using central differences or windward differences formula.

Considering j to be the mesh point, applying windward differences to the convective term

$$\left(\dot{M} \frac{dT}{dx} \right)_j \approx \dot{M}_j \frac{T_j - T_{j-1}}{X_j - X_{j-1}}$$

where,

$$h_j = X_{j+1} - X_j$$

Windwards differences scheme introduces the artificial diffusion in the coarse mesh. Therefore, the central differences scheme gives more accurate results. Nevertheless, the windward differences scheme is used to get the solution to the problem, as GRAD = CURV = 0.02 is used in our simulations, which leads to a great grid, and in fine grid resolution, the artificial diffusion becomes relatively unimportant.

On the first derivative in the summation term, evaluating the coefficients at j and applying the central differences formula,

$$\left(\frac{dT}{dx} \right)_j \approx \left(\frac{h_{f-1}}{h_j(h_j + h_{j-1})} T_{j+1} + \frac{h_j - h_{j-1}}{h_j h_{j-1}} T_j - \frac{h_j}{h_{j-1}(h_j - h_{f-1})} T_{j-1} \right)$$

On the second derivative term, evaluating the coefficients (at j + 1/2) using the dependent variable's average between mesh points and approximating by the second-order central differencing scheme,

$$\begin{aligned} \frac{d}{dx} \left((\lambda A) \frac{dT}{dx} \right)_j & \approx \left(\frac{2}{X_{j+1} - X_{j-1}} \right) \left[(\lambda A)_{j+\frac{1}{2}} \left(\frac{T_{j+1} - T_j}{X_{j+1} - X_j} \right) + \left(-(\lambda A)_{j+\frac{1}{2}} \right) \left(\frac{T_j - T_{j-1}}{X_j - X_{j-1}} \right) \right] \end{aligned}$$

Species conservation equation

$$\dot{M} \frac{dY_k}{dx} + \frac{d}{dx} (\rho A Y_k V_k) - A \dot{\omega}_k W_k = 0 \quad (k = 1, \dots, K_g)$$

The diffusion term is considered in the species conservation equation. Approximating thermal and diffusion velocities at $j + 1/2$

$$(Y_k V_k)_{j+1/2} \approx \left(\frac{W_k D_{km}}{\bar{W}} \right)_{j+1/2} \left(\frac{X_{k,j+1} - X_{k,j}}{X_{j+1} - X_j} \right)$$

$$(Y_k W)_{j+1/2} \approx - \left(\frac{W_k D_{km} \Theta_k}{\bar{W} T} \right)_{j+1/2} \left(\frac{T_{j+1} - T_j}{X_{j+1} - X_j} \right)$$

$Y_k V_k$ is formed since that is the term required in the equation.

Correction velocity is computed from

$$V_c = \sum_{k=1}^K (V_k + W_k)$$

Therefore, the diffusion velocity is calculated.

The diffusion term is approximated by:

$$\frac{d}{dx} (\rho A Y_k V_k)_j \approx \frac{(\rho A Y_k V_k)_{j+1/2} - (\rho A Y_k V_k)_{j-1/2}}{X_{j+1/2} - X_{j-1/2}}$$

All the other non-differentiated terms and coefficients are evaluated at mesh points j

A.4.4 Transient forms of the equations

The problem is solved by the steady-state method; sometimes, it requires pseudo-time-stepping to condition the solution iterate. For this reason, the transience forms of the equation are considered by adding the time derivatives to the equation. Therefore the equations become:

$$\begin{aligned} \rho A \frac{\partial T}{\partial t} + \dot{M} \frac{\partial T}{\partial x} - \frac{1}{C_p} \frac{\partial}{\partial x} \left(\lambda A \frac{\partial T}{\partial x} \right) + \frac{A}{C_p} \sum_{k=1}^K \rho Y_k V_k c_{pk} \frac{\partial T}{\partial x} + \frac{A}{C_p} \sum_{k=1}^K \dot{\omega}_k h_k W_k \\ + \frac{A}{C_p} \dot{Q}_{rad=0} \end{aligned}$$

$$\rho A \frac{\partial Y_k}{\partial t} + \dot{M} \frac{\partial Y_k}{\partial x} + \frac{\partial}{\partial x}(\rho A Y_k V_k) - A \omega_k W_k = 0 \quad (k = 1, \dots, K)$$

Therefore, the full system of equations becomes a system of parabolic partial differential equations, and the solution to this problem is obtained through the backward Euler method, where the time derivatives are calculated by

$$\rho A \frac{\partial T}{\partial t} \approx \rho_j^{n+1} A_j \left(\frac{T_j^{n+1} - T_j^n}{h} \right)$$

where,

h – the size of time step

n – time level

All other terms are approximated at time level n+1, where the problem is just a system of nonlinear algebraic equations for dependent variable vector ϕ .

The problem is considered a two-point boundary value problem, where the TWOPNT solver solves the equations. Here the solution is obtained by steady-state 1-D solution methods

A.4.5 Steady-state 1-D solution methods

The numerical solution procedure is started by reducing the boundary value problem to algebraic equations using finite difference approximations. The initial approximations are on a very coarse mesh. After obtaining the coarse mesh solution, new mesh points are added to the places where the gradient change is sharp. An initial guess for the solution is obtained by interpolating the coarse mesh solution. This step is continued until the refinement is required obtained. A damped modified Newton algorithm solves the system of equations in TWOPNT solver. However, if the Newton algorithm fails to converge, the solution estimate is conditioned by integrating in time, which provides a new starting closer to the solution.