

A KINETIC STUDY OF SYNGAS COMBUSTION CHARACTERISTICS FOR GAS TURBINE APPLICATIONS

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Abstract

A comprehensive numerical study has been performed to investigate fundamental characteristics of syngas combustion under gas turbine operating conditions regarding to its compositional variations. Laminar burning velocities and autoignition delay times have been studied using PREMIX and SENKIN codes respectively. Calculations have been performed using four different chemical kinetic mechanisms and a comprehensive parametric study on effects of pressure, temperature, composition, and dilution has been carried out. Results obtained from numerical calculations are compared with experimental data. The predictions indicated that reactants preheating results in considerable deviations between calculated laminar flame speed and experimental data for all reaction mechanisms used which is likely due to assumptions made in optically thin radiation model. In low-temperature and high-pressure conditions, the predicted autoignition delay times using all reaction mechanisms show considerable deviation from the experimental data. The source of this difference is yet uncertain. Some recently proposed engineering approximations are considered to improve the numerical predictions of ignition delay times.

INTRODUCTION

The combustion technology of low calorific heating value gases such as syngas offers considerable opportunity for clean combustion in stationary power generation applications with potential reduction of greenhouse gas emissions.

Synthetic gas is formed through the gasification process and can be produced from virtually any fossil fuel, including coal, biomass, organic waste and refinery residual [1]. Integrated gasification combined cycle (IGCC) systems continue to penetrate the power generation market and there are now a number of IGCC projects in design, construction or operation around the world. The introduction of strategies based upon IGCC plant suggests a need for a more flexible response to fuel mixture variations than has typically been the case in the past [2].

The current generation of premix burners designed for operation with natural gas cannot be reliably operated with syngas. For this reason, syngas in gas turbines is presently combusted in non-premixed flames using special burner designs, which differ substantially from natural gas burners [3]. Development of modern combustors for syngas combustion requires a better understanding of its fundamental combustion characteristics. The fundamental combustor operability criteria must be satisfied regardless of the fuel that is being utilized by the gas turbine are robustness to autoignition, robustness to flashback, emissions compliance (NOX, CO, UHC, and Smoke), acceptable combustion dynamic pressures, and robustness to lean blowout [4]. Therefore, phenomena such as ignition

dynamics, flame propagation, and pollutants level still have to be better understood in order to generalize the use of syngas as an alternative fuel in electricity production industries.

Laminar flame speed is one of the important parameters of a combustible mixture as it contains fundamental information regarding reactivity, diffusivity, and exothermicity. The value of the flame speed has important impacts upon the tendency of a flame to flashback and blowoff, and also controls other key combustion characteristics, such as flame spatial distribution. Autoignition delay time is the most important feature of a reactive system and directly controls the combustion dynamics. Furthermore, the laminar flame structure and pollutants level of syngas must be investigated in detail especially for NO_x emissions to develop reliable reaction mechanisms [5].

Syngas fuels are typically composed primarily of H₂ and CO, and may also contain smaller amounts of CH₄, N₂, CO₂, H₂O, and other higher hydrocarbons. The specific composition depends upon the fuel source and processing technique [6]. Unlike natural gas which has been used over many years and for which much combustion data collected, these gaseous fuel mixtures have not been widely investigated. Understanding the impact of mixture variability on combustor performance or emissions requires an understanding of the combustion kinetics of these mixtures.

In this work, a comprehensive numerical study has been performed to investigate fundamental characteristics of syngas combustion under gas turbine operating conditions regarding to its compositional variations. Laminar burning velocities and autoignition delay times have been studied using PREMIX [7] and SENKIN [8] codes respectively, all developed by Sandia National Laboratory. Calculations have been done using four different chemical kinetic mechanisms and a comprehensive parametric study on effects of pressure, temperature, dilution, and composition has been carried out and results obtained have been compared with experimental data found in literature.

PHYSICAL AND NUMERICAL MODELS

Computations of unstretched laminar burning velocities were performed using the PREMIX code of Kee et al. [7]. This model solves the set of conservation equations that describe the dynamics of the flame. It uses implicit difference methods and a combination of time-dependent and steady-state methods. The algorithm performs coarse-to-fine grid refinement in order to enhance the solution convergence and provide optimal mesh distribution [7]. The employed boundary conditions are the known temperature and fuel/air mixture composition (unburned state) and zero gradient condition of species and temperature profiles for combustion products (burned state) [7]. In freely propagating flames, the mass burning rate must be determined as a part of the solution. Therefore flame location needs to be fixed at a specified temperature to remove one degree of freedom from conservation equations. The conservation equation and boundary conditions are transformed into a system of algebraic equations. The modified damped Newton's method is used to solve non-linear algebraic equations. This method is a combination of two methods: damped Newton's and time-stepping. Initially the damped Newton's method is used and if it fails to converge, time stepping is employed to bring within the Newton's convergence domain. The solver also used grid adaptation by solving the problem on a coarse grid and then mapping the solution onto a refined grid and solving again to achieve desired tolerances [7]. In calculations of laminar flame speed, the multi-component and thermal diffusion (Soret) effects have been considered. Also, the radiation effect has been implemented by optically thin model. The grid independence of the results has been achieved by controlling the values of the GRAD and CURV parameters.

Autoignition was investigated by using an adiabatic constant-volume closed reactor model, using SENKIN code developed by Lutz et al [8]. SENKIN is a Fortran computer

program that computes the time evolution of a homogeneous reacting gas mixture in a closed system. The model accounts for finite-rate elementary chemical reactions, and performs kinetic sensitivity analysis with respect to the reaction rates. The ideal gas equation of state is used to compute the pressure. The program uses the DASAC software to solve both the nonlinear ordinary differential equations that describe the temperature and species mass fractions and the set of linear differential equations that describe the first-order sensitivity coefficients of temperature and species composition with respect to the individual reaction rates [8], [9]. Selection of suitable kinetic mechanism out of many mechanisms available for fuels is an important task in computational investigations. Although the progress in chemical kinetics mechanism developments is significant, the concerns regarding the mechanism performance beyond their range of validity are growing. The main issue of all mechanisms is the comprehensiveness [10]. The mechanism can be considered as comprehensive if it can predict accurately the chemical responses over the wide range of conditions that are expected to appear. Chemical reaction rates and pathways are coupled and nonlinear in nature with respect to temperature, pressure and species concentrations. In addition, these parameters can vary locally within the flame structure or globally through the operating conditions of the combustion system.

Four reaction mechanisms are considered in this study. The idea behind selection of these mechanisms is to perform a comprehensive evaluation of some of commonly used reaction mechanisms by industrial and academic communities. In addition, these mechanisms are well documented and properly available. The mechanism developed by Ranzi et al. [11] contains 32 elementary reactions. The mechanism is composed by the sub-mechanism H_2/O_2 that consists of 20 reversible reactions, and CO mechanism, that consists of 12 reversible reactions. The GRI 3.0 [12] mechanism which is optimized for methane and natural gas has been also considered. This mechanism is composed by 325 reactions and 53 species. It is also widely used by academia and industries. Moreover, San Diego mechanism [13], developed at the center of energy research of university of California, San Diego, consisting of 235 reactions and 38 species and the mechanism by Davis et al. [14], composed by 30 reactions and 14 species have been chosen. The last reaction mechanism was optimized specially for H_2/CO combustion. It incorporates recent updates for rate parameters and third body efficiencies of a few key reactions. It also includes modifications of thermodynamic and transport properties for species relevant to high temperature H_2 and CO oxidation.

RESULTS AND DISCUSSION

Laminar Flame Speed

Laminar flame speed calculations are performed using freely propagating flame model of PREMIX code. The effects of fuel mixture composition, preheat temperature, working pressure and dilution are investigated. Two fuel mixtures including 50%CO-50% H_2 and 95%CO-5% H_2 (by volume) considered with air (21% O_2 -79% N_2) as oxidizer. For 50%CO-50% H_2 mixture, further parametric studies are done. Several preheat temperatures ranging from 300 to 700K at atmospheric pressure, and high pressure (10 atm) calculations for normal temperature (300K) are also reported. Dilution effects on laminar flame speed of this mixture composition with various amounts of N_2 (0-40%) and CO_2 (0-20%) at normal temperature and pressure (NTP) are performed finally. These conditions seem to properly match the operating envelope of advanced dry low NOX (DLN) gas turbine combustors [15]. Evaluation of numerical predictions is done using experimental data reported in [16-21].

Laminar burning velocity is independent of flame geometry, burner size, and flow rate. It is fundamentally a measure of the overall reaction rate of the flame. The laminar burning velocity is affected by flame radiation and flame temperature, and by local gas properties such as thermal conductivity, viscosity and diffusion coefficient. However, even if its theoretical

definition is straightforward, it is difficult to measure. Therefore, there are considerable differences between the results obtained by the various experimental methods. The main problem of the laminar burning velocity is that it is very difficult practically to obtain a plane flame front. In all practical cases the flame front is curved or it is not normal to the direction of the reactant stream.

McLean et al. [16] measured burning velocity of CO/H₂ mixtures in air of 95%CO-5%H₂ and 50%CO-50%H₂ at temperature of 298K and pressure of 1 atmosphere. Burning velocity was obtained from measurements on constant-pressure expanding flames. Sun et al. [17] used same method and performed experiments for CO/H₂/air mixtures at different equivalence ratios and mixing ratios for pressures up to 40 atmospheres. Bouvet et al. [18] studied the laminar flame speed of undiluted syngas for a wide range of mixture composition at atmospheric conditions. Hassan et al. [19] studied the laminar burning velocities of CO/H₂/air mixtures of 0.6-5.0 equivalence ratio and pressures of 0.5 up to 4 atmospheres for outwardly propagating flame. Natarajan et al. [15,20] measured laminar flame speeds of lean H₂/CO/CO₂ fuel mixtures over a range of fuel compositions (5-95%) for H₂ and CO and up to 40% for CO₂ by volume, reactant preheat temperatures (up to 700K) and pressures (1-15 atm). They used two measurement approaches: one using flame area images of a conical Bunsen burner and the other based on imaging measurements of the reaction zone area. Prathap et al. [21] studied the laminar burning velocity and flame stability of equimolar mixture of CO/H₂ diluted with nitrogen. They used shadowgraphy technique with high-speed imaging camera to record the propagating spherical flames.

Figure (1) plots experimental and computed unstretched laminar flame speeds for a 50%CO-50%H₂ fuel mixture at NTP as a function of equivalence ratio. Predictions of all reaction mechanisms in equivalence ratios of 0.5 up to 1.0 are in good agreement with experimental data except for Sun et al. [17] and Hassan et al [19] results. In rich conditions the discrepancy of various reaction mechanisms is appeared. In this region the Ranzi et al. mechanism [11] is the best one and all other mechanisms overpredict laminar flame speed.

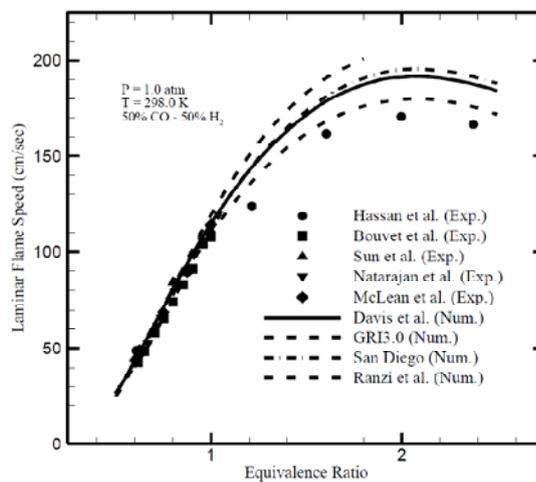


Figure 1. Experimental (symbols) and computed (lines) unstretched laminar flame speed for a 50%CO-50%H₂ fuel mixture at NTP as a function of equivalence ratio.

In figure (2) experimental and predicted laminar flame speed for a 95%CO-5%H₂ fuel mixture at NTP as a function of equivalence ratio is presented. For this fuel mixture composition a similar trend is observed in lean region but Davis et al. mechanism [14] follow the experimental data more closely. In rich conditions, simulation results using all reaction mechanisms overpredict the flame speed and in this case San Diego [13] and Davis et al. [14] mechanisms have more accurate results.

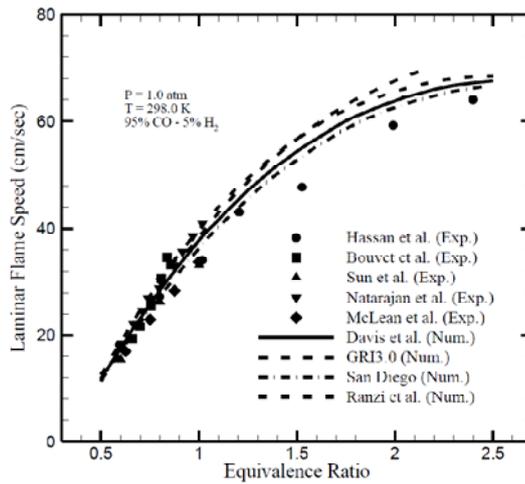


Figure 2. Experimental (symbols) and computed (lines) unstretched laminar flame speed for a 95%CO-5% H_2 fuel mixture at NTP as a function of equivalence ratio.

Effect of reactants preheating is shown in figure (3). In this plot experimental data reported by Natarajan et al. [20] and computed values of flame speed for a 50%CO-50% H_2 fuel mixture at a pressure of 1 atm and preheat temperatures of up to 700K is presented. The measured and predicted flame speeds increase rapidly with the unburned gas temperature for any given equivalence ratio. The predictions from all mechanism are in good agreement with the measured flame speeds up to a preheat temperature of about 500 K throughout the lean equivalence ratios tested. For further increases in preheat temperature, the discrepancy between the measured and predicted flame speeds increases. This difference is likely due to inadequacy of optically thin radiation model precision for laminar flame speed calculations. Figure (4) shows experimental and computed laminar flame for a 50%CO-50% H_2 fuel mixture at a pressure of 10 atm and temperature of 300 K as a function of equivalence ratio. Experimental data are taken from Natarajan et al. [15] and Sun et al. [17].

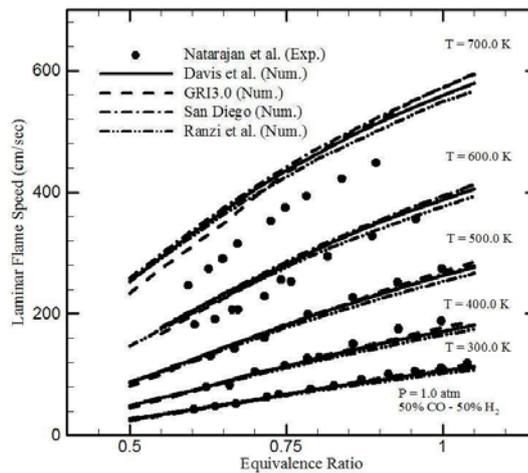


Figure 3. Experimental (symbols) and computed (lines) unstretched laminar flame speed for a 50%CO-50% H_2 fuel mixture at a pressure of 1 atm for various unburned preheat temperatures as a function of equivalence ratio.

Simulations were conducted with a $O_2:He$ mixture (1:7 by volume) as the oxidizer, rather than standard air to match the previous studies results [15,17].

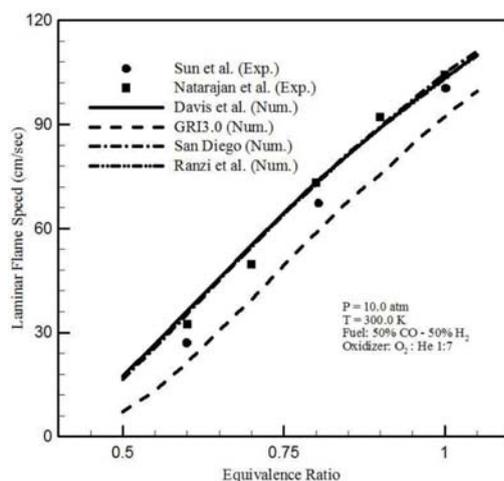


Figure 4. Experimental (symbols) and computed (lines) unstretched laminar flame speed for a 50%CO-50% H_2 fuel mixture at a pressure of 10 atm and temperature of 300 K as a function of equivalence ratio.

As shown in this plot all of mechanisms except GRI3.0 are in good agreement with experimental results and differences between predicted and measured values of flame speeds are less than 10%. GRI3.0 mechanism underpredicts high-pressure laminar flame speed considerably. Effects of dilution on laminar flame speed of syngas are shown in figures (5) and (6). In figure (5) experimental data of Prathap et al. [21] and computed unstretched laminar flame speed for a 50%CO-50% H_2 fuel mixture at NTP for various N_2 dilution levels (0%, 20% and 40%) of fuel as a function of equivalence ratio (0.5-1.05) is presented. Generally, laminar flame speed is decreased with increasing amount of diluents.

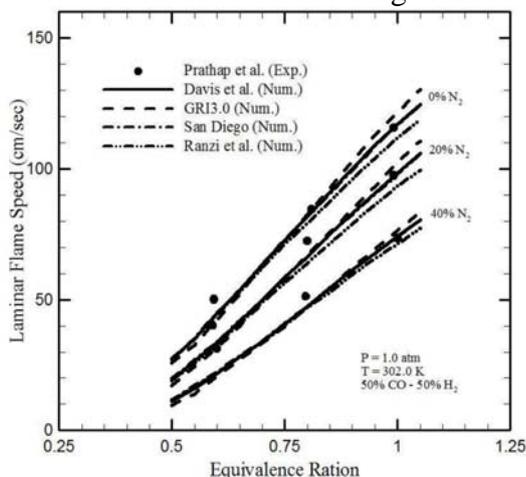


Figure 5. Experimental (symbols) and computed (lines) unstretched laminar flame speed for a 50%CO-50% H_2 fuel mixture at NTP for various N_2 dilution levels of fuel as a function of equivalence ratio.

In the range of equivalence ratios between 0.5 and 0.8 all mechanisms have similar behavior. Beyond this range, with increasing the equivalence ratio the discrepancies between predicted results of various mechanisms are appeared. In this range the mechanisms of Davis et al. [14] and San Diego [13] have similar results and both of them have more accurate predictions of experimental data. Ranzi et al. [11] underpredicts and GRI3.0 [12] overpredicts flame speed. Figure (6) shows the influence of CO_2 dilution (0% and 20%) on syngas flame speed. In this figure experimental data of Natarajan et al. [20] and computed value of flame speed for a 50%CO-50% H_2 fuel mixture at NTP as a function of equivalence ratio is

presented. Results are generally similar to N₂ dilution case. The major difference is that the discrepancies between various reaction mechanisms are considerable beyond the equivalence ratio of 0.95. To identify the relevant reactions, sensitivity analysis has been performed for a 50%CO-50%H₂ fuel mixture at atmospheric pressure for two conditions: (i) unburned pre-heat temperature of 300K and equivalence ratio of 0.8, and (ii) unburned pre-heat temperature of 700K and equivalence ratio of 0.6. According to figure (3) these cases are in best and worst agreement with experimental data and results are shown in figures (7) and (8) respectively. The two equivalence ratios have been chosen to keep the flame temperature nearly constant at 2200K. All of reaction mechanisms are considered for these analysis and the normalized sensitivity of mass burning rate to pre-exponential factor in the rate constant for all the important reactions are calculated. To perform a logical comparison between various mechanisms, only the reactions which are present in all mechanisms have been considered in this analysis. As can be seen in figures (7) and (8), the magnitude of the sensitivity coefficient for most of the H₂ oxidation reactions increases as the pre-heat temperature increases. Reaction CO+OH=CO₂+H is very sensitive for flame speed predictions. As stated by Chaos and Dryer [22], this reaction is of critical importance in the oxidation of H₂/CO/O₂ as well as moist CO mixtures. Moreover, under these conditions reactions that involve H atom and OH radical are the most sensitive reactions and need further investigation. It can be concluded that at NTP conditions the GRI3.0 results are worse for both 50%CO-50%H₂ and 95%CO-5%H₂ fuel mixture compositions. In these cases, laminar flame speed predictions for lean mixtures are more accurate for all mechanisms compared to rich conditions. Preheating above 500K results in discrepancy of flame speed prediction of all mechanisms with compared to experimental data.

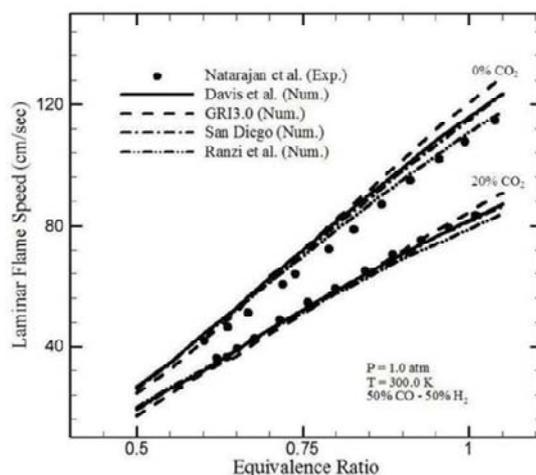


Figure 6. Experimental (symbols) and computed (lines) unstretched laminar flame speed for a 50%CO-50%H₂ fuel mixture at NTP for various CO₂ dilution levels of fuel as a function of equivalence ratio.

At high pressure conditions the GRI3.0 mechanism again fails to reproduce the experimental data and all other mechanisms behave similarly. With fuel mixture dilution both with N₂ and CO₂, differences between results of four reaction mechanisms is more obvious as equivalence ratio approaches unity. For diluted mixtures the Davis et al. [14] and San Diego [15] mechanisms show better results. The numerical results usually lie within the experimental error range which is generally below 10%, except for high pre-heat conditions of figure (3).

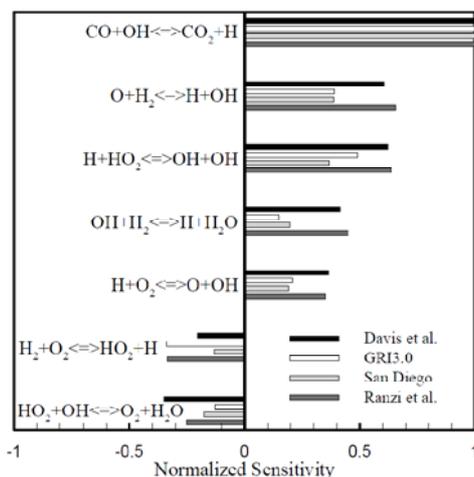


Figure 7. Normalized sensitivity of mass burning rate to pre-exponential rate constants for most important reactions calculated for a 50% CO-50% H₂ fuel and air mixture of equivalence ratio 0.8 at a pressure of 1 atm and unburned preheat temperature of 300 K.

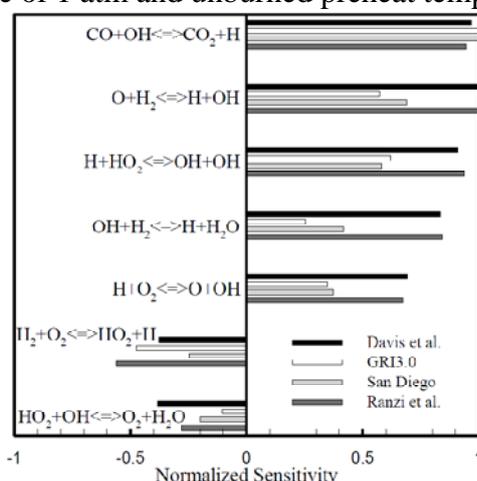


Figure 8. Normalized sensitivity of mass burning rate to pre-exponential rate constants for most important reactions calculated for a 50% CO-50% H₂ fuel and air mixture of equivalence ratio 0.6 at a pressure of 1 atm and unburned preheat temperature of 700 K.

Autoignition Delay Time

Autoignition delay time calculations are performed using constant volume model of SENKIN code. Like for the experimental approaches, a definition of ignition delay needs to be applied in the interpretation of the results obtained from SENKIN code. For the present study, the maximum rate of production of OH radical is selected for ignition delay time calculation. The effects of fuel mixture composition, pressure, and temperature are investigated. Three fuel mixtures including 20%CO-80%H₂, 40%CO-60%H₂, and 60%CO-40%H₂ (by volume) considered with air (21%O₂-79%N₂) as oxidizer. Also, for 80%CO-20%H₂ and 90%CO-10%H₂ mixtures the effect of pressure is investigated. Finally, the autoignition delay time for 51.1%CO-38.6%H₂-10.3%CO₂ fuel mixture at low temperature and high pressure conditions is studied in more detail. Evaluation of numerical predictions is done using experimental data reported in [22-25]. Kalitan et al. [22] studied the ignition and oxidation characteristics of CO/H₂ fuel blends. Shock-tube experiments were conducted behind reflected shock waves at intermediate temperatures (890-1300K) for three pressure regimes of approximately 1, 2.5, and 15 atm. Petersen et al. [23] improved the results of Kalitan et al. [22] to include low temperature region down to approximately 760K using flow reactor facility. Poschke and Spadaccini [24] studied the autoignition delay time of 51.1%CO-

38.6% H_2 -10.3% CO_2 fuel mixture in a continuous flow reactor at pressures up to 26 atm and temperature range of 633K to 781K. Walton et al. [25] studied autoignition of syngas mixtures of hydrogen, carbon monoxide, oxygen, nitrogen, and carbon dioxide using a rapid compression facility over a broad range of conditions relevant to current and proposed gas-turbine technologies (pressures from 7.1 to 26.4 atm, temperatures from 855K to 1051K, equivalence ratios from 0.1 to 1.0, oxygen mole fractions from 15% to 20%, and $H_2:CO$ ratios from 0.25 to 4.0). Figure (9) presents experimental and computed ignition delay time for a 20% CO -80% H_2 fuel mixture at a pressure of 1.1 atm. The experimental data was reported by Kalitan et al. [22].

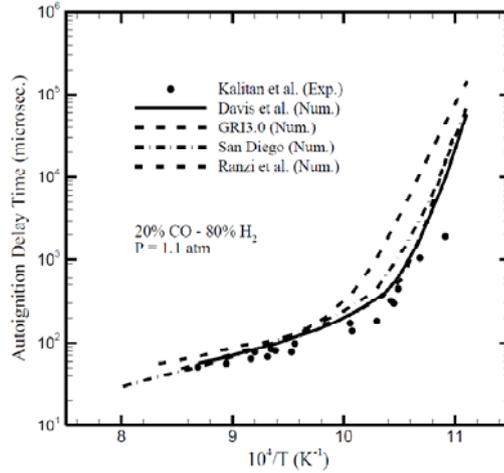


Figure 9. Experimental (symbols) and computed (lines) ignition delay time for a 20% CO -80% H_2 fuel mixture at a pressure of 1.1 atm.

In high temperature region ($>1300K$) all reaction mechanisms except Ranzi et al. [11] show similar results. With decreasing the temperature the GRI3.0 mechanism [12] overpredicts the ignition delay time compared to other mechanisms. Similar behavior is observed in figures (10) and (11) where experimental and computed ignition delay time is presented for 40% CO -60% H_2 and 60% CO -40% H_2 fuel mixture respectively at a pressure of 1.1 atm. Ranzi et al. [11] mechanism shows the worst results at high temperature region while GRI3.0 [12] shows the worst results at low temperature conditions. Davis et al. [14] and San Diego [13] mechanisms have similar results under these conditions and both of them show good agreement with experimental data except at high temperature region. The aforementioned results show that at near atmospheric conditions fuel mixture composition has not profound impact on autoignition delay time responses.

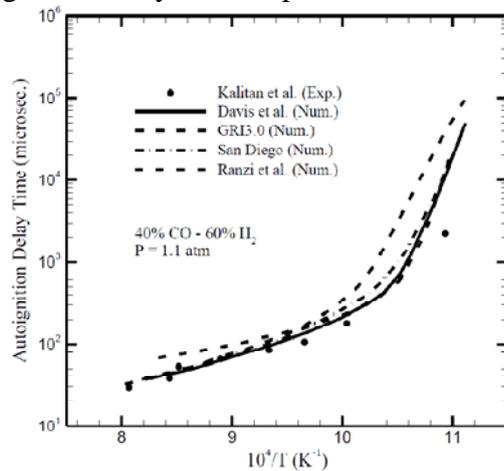


Figure 10. Experimental (symbols) and computed (lines) ignition delay time for a 40% CO -60% H_2 fuel mixture at a pressure of 1.1 atm.

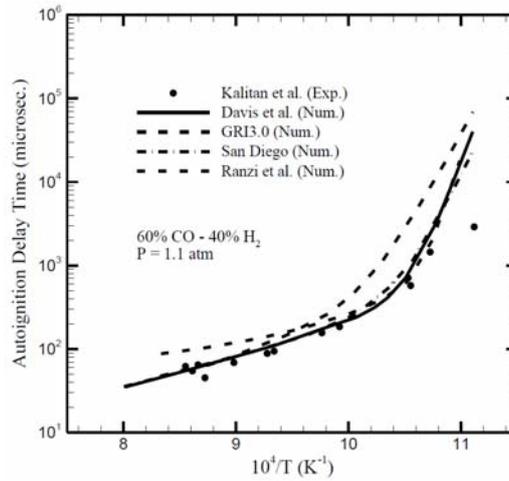


Figure 11. Experimental (symbols) and computed (lines) ignition delay time for a 60%CO-40% H_2 fuel mixture at a pressure of 1.1 atm.

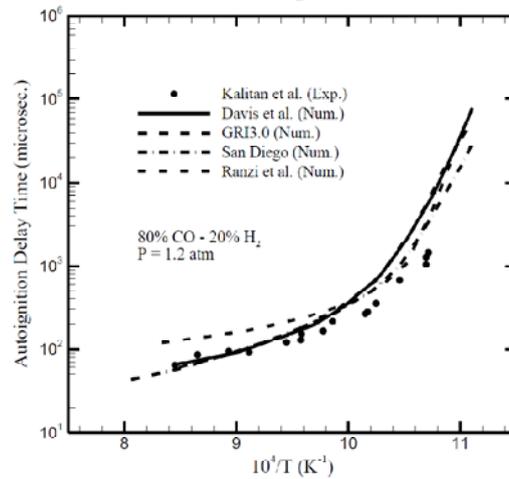


Figure 12. Experimental (symbols) and computed (lines) ignition delay time for a 80%CO-20% H_2 fuel mixture at a pressure of 1.2 atm.

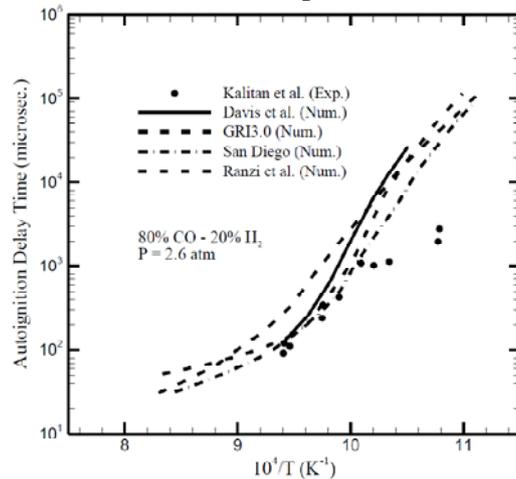


Figure 13. Experimental (symbols) and computed (lines) ignition delay time for a 80%CO-20% H_2 fuel mixture at a pressure of 2.6 atm.

In figures (12) to (14) experimental data of Kalitan et al. [22] and computed autoignition delay times for 80%CO- 20% H_2 fuel mixture composition at pressures of 1.2, 2.6, and 15.4 atm are presented respectively. Results of figure (12) are similar to previous near atmospheric results but for this low H_2 content fuel mixture the San Diego [13] mechanism have the most accurate results. Again the Ranzi et al. [11] mechanism show poor agreement with the

experimental data at high temperature conditions. By increasing the pressure to 2.6 atm in figure (14) and at temperatures below 1000K none of reaction mechanism reproduced experimental data accurately.

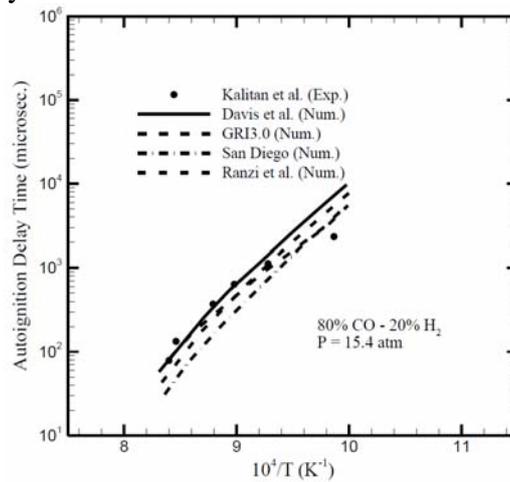


Figure 14. Experimental (symbols) and computed (lines) ignition delay time for a 80%CO-20% H_2 fuel mixture at a pressure of 15.4 atm.

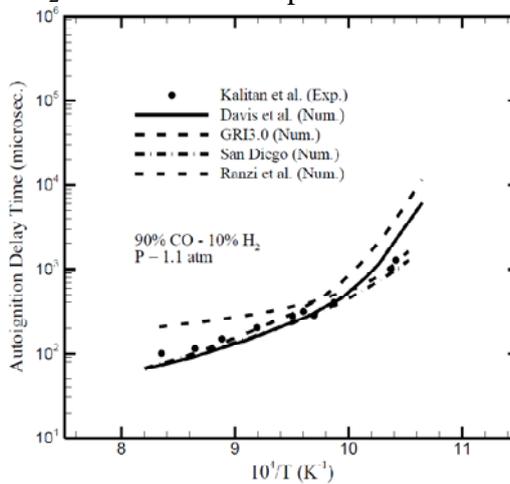


Figure 15. Experimental (symbols) and computed (lines) ignition delay time for a 90%CO-10% H_2 fuel mixture at a pressure of 1.1 atm.

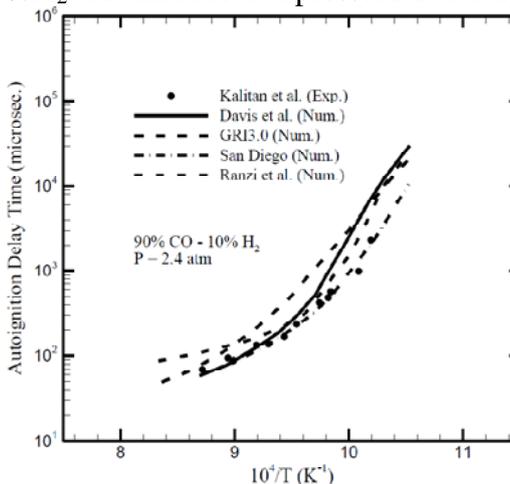


Figure 16. Experimental (symbols) and computed (lines) ignition delay time for a 90%CO-10% H_2 fuel mixture at a pressure of 2.4 atm.

Furthermore, the San Diego [13] mechanism shows the closest predictions of experimental data. For this fuel mixture composition and at high pressure of 15.4 atm all mechanisms show

good agreement with experimental data as presented in figure (15). In this case, San Diego [13] and Davis et al. [14] mechanisms have the best results at low and high temperatures respectively. The influence of pressure on ignition delay time is further studied for very low H_2 content mixture of 90%CO-10% H_2 at pressures of 1.1, 2.4, and 14.3 atm in figures (15) to (17). For this fuel mixture composition and near atmospheric pressures the results of figure (15) shows that San Diego [13] mechanism results are in close agreement with experimental data. Ranzi et al. [11] mechanism again fails to follow the experimental data at high temperature conditions and GRI3.0 [12] and Davis et al. [14] mechanisms fail to predict low temperature autoignition delay time. By increasing the pressure up to 2.4 atm in figure (14) and especially at low temperature conditions the San Diego [13] mechanism shows the best performance. In figure (15) results are shown at pressure of 14.3 atm and under this conditions San Diego [13] mechanism results underpredicts autoignition delay time. The results presented in the figure show that at high pressure and high temperature conditions the best results are obtained using Davis et al. [14] mechanism.

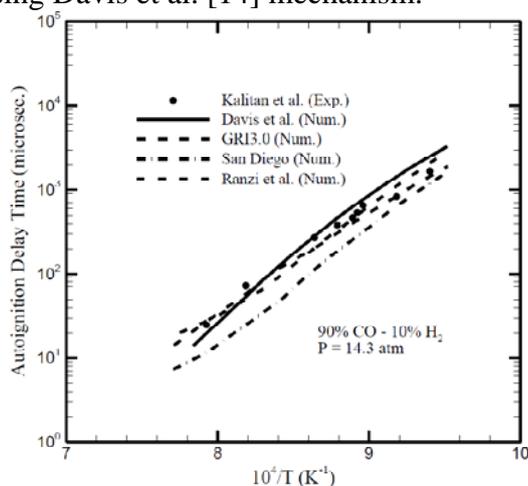


Figure 17. Experimental (symbols) and computed (lines) ignition delay time for a 90%CO-10% H_2 fuel mixture at a pressure of 14.3 atm.

According to the results of figures (9) to (17) it is obvious that at low temperature region the difference between calculated autoignition delay times with experimental data significantly increases. On the other hand for gas turbine applications the most important characteristics of reactive mixture that directly affects the combustion dynamics is ignition delay time at low temperature ($<1000K$) and high pressure ($10 < P < 30$ atm) conditions. Therefore, a more detailed investigation of autoignition has been performed under these conditions and results are presented in figure (18). Firstly, similar to previous figures the numerical values of autoignition delay time are calculated with all of reaction mechanisms and results are compared to experimental data. In this figure experimental data are taken from Petersen et al. [23], Peschke and Spadacni [24], Walton et al. [25] and Blumenthal et al. [26] and a wide range of temperature values especially at low temperature region down to 633K is covered. It is clear from figure (18) that by decreasing the temperature the difference between calculated and measured values of ignition delay time shows a difference of more than four orders of magnitude. To deal with this problem Cavaliere et al. [28] have recently proposed that a modification is needed in reaction rate of $OH+OH(+M)=H_2O_2(+M)$. In reference [28] two modifications has been proposed for San Diego [13] mechanism. First, the reaction rates proposed by Baulch et al. [29] are used. The results obtained with this new mechanism show better agreement with experimental data as shown in figure (18). Cavaliere et al. [28] has further modified the rate of this reaction and the resulting mechanism show acceptable agreement with experimental data of figure (18) at entire temperature range. In their study,

Cavaliere et al. never discuss whether these changes maintain the thermochemical reversibility of the reactions or how they affect the pressure dependence of this reaction which is likely the case. Furthermore, these changes are never evaluated against other target data such as flame speed, product speciation, etc. In another study, Dryer and Chaos [30] have stated that the most important reactions that control autoignition delay time under these conditions are those that lead to generation of reactive radical species from hydroperoxyl radicals, namely $\text{H}_2 + \text{HO}_2 = \text{H}_2\text{O}_2 + \text{H}$ and $\text{H}_2\text{O}_2 + \text{M} = \text{OH} + \text{OH} + \text{M}$. Surface catalysis effects on shortening chemical induction times and, therefore, ignition delays have been approximated as homogenous gas phase processes with modified rate constants using the mechanism of Li et al. [31]. These results are also presented in figure (18). More details could be found in [22] and [30].

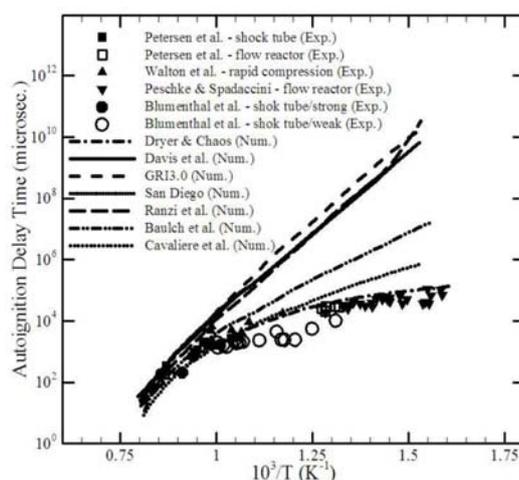


Figure 18. Experimental (symbols) and computed (lines) ignition delay time for a 51.1%CO-38.6% H_2 -10.3% CO_2 fuel mixture at an equivalence ratio of 0.5 and pressure of 20.0 atm.

Syngas autoignition delay and the large discrepancies observed at high pressures and low temperatures have been a topic of several recent publications, e.g. [22] and [32-34]. It can be concluded from these studies that the large differences observed between experimental data and chemical kinetic models are due to a combination of compressible flow effects, inhomogeneities, and perturbation of the gas phase chemistry by multi-dimensional surface effects at high pressure and low temperatures. Under these conditions the assumption of ideal closed adiabatic system do not suffices the modeling requirements. Another interesting nature of experimental data shown in figure (18) is that whatever the perturbation maybe, the resulting reductions in chemical induction times are of the same order of magnitude in all of the experimental devices considered. Additional efforts are needed to experimentally confirm the relevance of various process as a perturbing factor in each of these devices. It can be concluded that modification proposed by Dryer and Chaos [30] has an acceptable engineering accuracy for syngas autoignition under gas turbine conditions. However, these modifications need further study for laminar flame speed and other relevant combustion calculations. It can be concluded that at atmospheric pressures the accuracy of results obtained for autoignition delay time by various mechanisms depends on amount of hydrogen content of fuel mixture and reactants temperature. At high temperature conditions and for all values of hydrogen content in fuel mixture, Ranzi et al. [11] mechanism shows worst agreement with experimental results. At low temperature conditions there is two considerable situations regarding to hydrogen content of fuel mixture. For high hydrogen content the Ranzi et al. [11] mechanism show best results. With decreasing the amount of hydrogen San Diego [13] mechanisms show best results. Furthermore, the behavior of San Diego [13] mechanism at atmospheric pressure and for low hydrogen content fuel is superior at entire range of

temperature. At high pressure conditions the results of all reaction mechanisms are similar and there is no significant difference between them. However, in low temperature region all of reaction mechanisms fail to capture the experimental results and there is a considerable difference between computed and measured ignition times. In high temperature region all mechanisms results are in good agreement with experimental data. In low temperature region all of reaction mechanisms show considerable difference with the experimental results. Although the source of this difference is not yet certain, but approximations proposed by Cavaliere et al. [28] and Dryer and Chaos [30] improved the numerical predictions of ignition delay times.

CONCLUSIONS

The main conclusions of this study are as follow:

1. For laminar flame speed velocity at NTP conditions the GRI3.0 results are worse for both 50%CO-50%H₂ and 95%CO-5%H₂ fuel mixture compositions. In these cases, laminar flame speed predictions for lean mixtures are more accurate for all mechanisms compared to rich conditions. Preheating above 500K results in discrepancy of flame speed prediction of all mechanisms with compared to experimental data which is likely due to assumptions made in optically thin radiation model. At high pressure conditions the GRI3.0 mechanism again fails to reproduce the experimental data and all other mechanisms behave similarly. With fuel mixture dilution both with N₂ and CO₂, differences between results of four reaction mechanisms is more obvious as equivalence ratio approaches unity. For diluted mixtures the Davis et al. and San Diego mechanisms show better results.

2. For autoignition delay time at atmospheric pressures the accuracy of results obtained by various mechanisms depends on amount of hydrogen content of fuel mixture and reactants temperature. At high temperature conditions and for all values of hydrogen content in fuel mixture, Ranzi et al. mechanism shows worst agreement with experimental results. At low temperature conditions there is two considerable situations regarding to hydrogen content of fuel mixture. For high hydrogen content the Ranzi et al. mechanism show best results. With decreasing the amount of hydrogen San Diego mechanism shows best results. The behavior of San Diego mechanism at atmospheric pressure and for low hydrogen content fuel is superior at entire range of temperature. At high pressure conditions the results of all reaction mechanisms are similar and there is no significant difference between them. In high temperature region all mechanisms results are in good agreement with experimental data. However, in low temperature region all of reaction mechanisms show considerable difference with the experimental results. The source of this difference is yet uncertain. Recently proposed engineering approximations by Cavaliere et al. and Dryer and Chaos are considered to improve the numerical predictions of ignition delay times for gas turbine applications.

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