

An evaluation of detailed reaction mechanisms for hydrogen combustion under gas turbine conditions

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Abstract

Chemical kinetics in hydrogen combustion for elevated pressures have recently become more relevant because of the implementation of hydrogen as a fuel in future gas turbine combustion applications, such as IGCC or IRCC systems. The aim of this study is to identify a reaction mechanism that accurately represents H_2/O_2 kinetics over a large range of conditions, particularly at elevated pressures as present in a gas turbine combustor. Based on a literature review, six mechanisms of different research groups have been selected for further comparisons within this study. Reactor calculations of ignition delay times show that the mechanisms of Li et al. and Ó Conaire et al. yield the best agreement with data from shock tube experiments at pressures up to 33 bar. The investigation of one-dimensional laminar hydrogen flames indicate that these two mechanisms also yield the best agreement with experimental data of laminar flame speed, particularly for elevated pressures. The present study suggests that the Li mechanism is best suited for the prediction of H_2/O_2 chemistry since it includes more up-to-date data for the range of interest.

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1. Introduction

One possibility to reduce CO_2 emissions from power production with fossil fuels is to convert the fuels to gas mixtures consisting mainly of hydrogen and carbon dioxide, and to separate CO_2 from the fuel prior to combustion in a gas turbine process, such as IGCC/IRCC systems. This necessitates the development of a gas turbine combustor for H_2 -rich fuels. Hydrogen has some characteristics that strongly deviate from the main components of conventional fuels, as e.g. methane. The hydrogen molecule is very light and therefore strongly exposed to molecular diffusion processes. Furthermore, hydrogen is a very reactive species with a large flammability range. These characteristics result in a high laminar flame speed of hydrogen/air mixtures. The relatively high adiabatic temperatures of H_2 /air mixtures might cause large amounts of thermal NO_x in the flame. The flame temperature, and therefore NO_x emissions, can be reduced by dilution with nitrogen or steam,

which lowers the efficiency of the process. A more advanced way for NO_x reduction is lean pre-mixing of fuel and air. However, the high reactivity and flame speed of pre-mixed H_2 /air mixtures enhances the danger of auto-ignition and flashback, respectively.

Detailed kinetic mechanisms are necessary to predict auto-ignition, flashback, and NO_x emissions. These mechanisms can also be used within CFD calculations to predict the turbulent reacting flow field inside a combustor. This study is solely dedicated to the reaction kinetics of hydrogen and air. Only pure H_2/O_2 kinetics are considered, i.e. N_2 is treated as inert and reactions for NO_x formation are neglected. Even though evaluation of NO_x was not a part of the present work, the authors emphasize the importance of the H_2/O_2 kinetics for accurate prediction of NO_x chemistry. The small amounts of hydrocarbons prevailing in a real fuel after a reforming process, are not accounted for. This strongly reduces the size of the reaction mechanism. While a typical mechanism for methane consists of around 50 species and 300 reactions, only eight species (without N_2) and about 20 reversible reactions are sufficient to describe pure H_2/O_2 kinetics.

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The aim of this study is to identify a reaction mechanism that accurately represents H_2/O_2 kinetics over a large range of conditions, particularly at elevated pressures between 15 and 35 atm as present in a typical gas turbine combustor. First, a review of reaction mechanisms for hydrogen combustion is given. Then, ignition delay times computed by some selected mechanisms using a closed homogeneous reactor model are compared to experimental data for a large range of pressures. Flame speeds of laminar premixed hydrogen flames are calculated with several mechanisms using a one-dimensional flame code and validated against measurements at atmospheric and elevated pressures. Finally, the results are discussed and concluding remarks are given.

2. Reaction mechanisms for hydrogen combustion

A large number of detailed mechanisms including H_2/O_2 kinetics can be found in the literature. Some of these mechanisms have been optimized for the combustion of pure hydrogen, but most of them are dedicated to the combustion of hydrocarbons including sub-mechanisms for H_2/O_2 chemistry. However, the accuracy of the H_2/O_2 subset is also essential for the overall performance of a hydrocarbon mechanism. In this study, only the mechanisms validated and used for hydrogen combustion are considered.

At the Gas Research Institute (GRI), the well-known GRI mechanism has been developed for C_1/C_2 kinetics [1,2]. The most recent version ‘GRI-Mech 3.0’ [3] contains 26 reversible reactions for H_2/O_2 kinetics. The GRI mechanism is optimized for natural gas combustion, but has also been validated against experimental data for ignition delay of stoichiometric hydrogen/air mixtures at 1 and 2 atm.

The research group around F.L. Dryer at Princeton University has been working on combustion kinetics for more than 20 years. In 1981, Westbrook and Dryer [4] gave a comprehensive review about chemical kinetics of combustion processes stating that the H_2/O_2 mechanism is well validated for a large number of application areas. However, much effort has been invested to optimize this mechanism later on, particularly for non-atmospheric pressures. A detailed hydrocarbon mechanism was published [5] including a H_2/O_2 subset of 21 reversible reactions. Yetter et al. [6] presented a detailed $\text{CO}/\text{H}_2/\text{O}_2$ mechanism containing 19 reversible reactions for the H_2/O_2 system that was validated against experimental data within a temperatures range of 823–2870 K, equivalence ratios between 0.0005 and 6.0, and pressures between 0.3 and 2.2 atm. This mechanism was further improved by Kim et al. [7] using experimental results of a flow reactor for pressures from 1 to 9.6 atm, temperatures from 960 to 1200 K, and equivalence ratios from 0.33 to 2.1. Mueller et al. [8] adjusted the H_2/O_2 system of this mechanism to experimental data over pressures and temperatures of 0.3–15.7 atm and 850–1040 K, respectively. Recently, Li et al. [9] updated the H_2/O_2 mechanism and validated it against a wide range of experimental conditions (298–3000 K, 0.3–87 atm, $\phi = 0.25 - 5.0$) found in laminar premixed flames, shock tubes, and flow reactors. The mechanism is named comprehensive due to excellent agreement of

the model predictions with an extensive set of experimental data.

Based on the mechanism of Mueller et al. [8], another so-called comprehensive H_2/O_2 mechanism with 19 reversible reactions has been developed by Ó Conaire et al. [10] at the National University of Ireland in Galway. The mechanism has been validated against experiments at temperatures ranging from 298 to 2700 K, pressures from 0.05 to 87 atm, and equivalence ratios from 0.2 to 6.

The research group around F.A. Williams at the University of California in San Diego developed a 21-step chemical scheme for hydrogen combustion [11]. This mechanism was recently extended to 22 reactions by Del Álamo et al. [12] and validated against experimental data of ignition delay at pressures up to 33 bar.

The research group around J. Warnatz has also strongly contributed to the development of combustion kinetics. In 1988, Maas and Warnatz [13] presented a detailed $\text{CO}/\text{H}_2/\text{O}_2$ mechanism for modeling of ignition processes. This mechanism was extended for C_1/C_2 species oxidation by Baulch et al. [14]. The H_2/O_2 subset of the mechanism in the latest textbook of Warnatz et al. [15] contains 19 reversible reactions. Through a personal communication, Warnatz [16] provided another H_2/O_2 mechanism that differs slightly from the one in his textbook. Preliminary, computations of ignition delay times have shown that this mechanism performs slightly better than the mechanism in his textbook.

Many other mechanisms have been referred to in the literature. Some of the most recent developments are an optimized kinetic model of H_2/CO combustion by Davis et al. [17] and a refined hydrogen combustion mechanism by Konnov [18]. The latter is based on the methane mechanism of Konnov [19] containing 28 reversible reactions for H_2/O_2 chemistry and has been validated against a large range of experimental data for hydrogen combustion. At Leeds University, a methane mechanism including a H_2/O_2 subset of 46 single reactions has been developed [20]. The H_2/O_2 mechanism of Marinov et al. [21] including 20 reversible reactions was validated against atmospheric laminar flame speed experiments, low-pressure laminar flame compositions, and ignition delay data at 2 atm. Katta and Roquemore [22] used a $\text{H}_2/\text{O}_2/\text{N}_2$ mechanism of Cowart et al. [23] with a H_2/O_2 subset of 17 reversible reactions for the simulation of a premixed H_2 /air Bunsen-type flame. They yielded good agreement of predicted and measured burning velocities at different equivalence ratios at atmospheric pressure. Cain [24] used a mechanism of Jachimowski and McLain [25] containing 17 reversible reactions for the simulation of auto-ignition of hydrogen at pressures between 3.5 and 7 MPa. Miller and Bowman [26] developed a detailed mechanism for nitrogen chemistry including 20 reversible reactions for H_2/O_2 kinetics. Glarborg et al. [27] constructed a mechanism for hydrocarbon/nitric oxide interactions with 22 reversible reactions for H_2/O_2 kinetics. Lindstedt et al. [28] developed a mechanism for ammonia oxidation based on the H_2/O_2 kinetics of Baulch et al. [14].

Furthermore, some comparative studies of various mechanisms have been performed. Qin et al. [29] compared predicted

and measured laminar burning velocities of hydrogen/air mixtures at elevated pressures ranging from 0.1 to 0.5 MPa using three different reaction mechanisms. The mechanisms of Warnatz [30] and Kee et al. [31] revealed large deviations from measurements at high equivalence ratios, while the mechanism of Yetter et al. [6] performed slightly better. The authors suggested some adjustments of the latter to match the experimental data. Schultz and Shepherd [32] performed a comprehensive validation of detailed reaction mechanisms for detonation simulations. They computed ignition delay times of hydrogen, ethylene, and propane using a constant volume explosion model with 19 different mechanisms and compared them to shock tube measurements of 14 different authors, however, without drawing clear conclusions concerning the quality of the individual mechanisms. Ó Conaire et al. [10] compared their mechanism with the GRI-Mech 3.0 [3], the Leeds mechanism [20], and the mechanisms of Konnov [19] and Mueller et al. [8]. Their mechanism showed the best agreement with experimental data of ignition delay times, mass burning velocities, and species profiles over a large range of pressures. Del Álamo et al. [12] computed ignition delay times using several mechanisms and found the mechanisms of Mueller et al. [8], Ranzi et al. [33], and their own mechanism to yield the best agreement with experimental data.

The number of H_2/O_2 mechanisms found in the literature is too long to be applied to a more detailed investigation. Hence, only the most relevant mechanisms are selected based on the degree of validation and on the frequency of being referred to. Within a research group, the latest mechanism is mostly built on the previous ones and is therefore preferred. The mechanisms of Li et al. [9] and Ó Conaire et al. [10], and the San Diego mechanism [12] provide the most comprehensive validation for hydrogen combustion, whereas the GRI-Mech 3.0 [3], the Leeds mechanism [20], and the mechanisms of Warnatz [16] are the most recent versions of the mechanisms with the most references. Hence, these six mechanisms are selected for further comparisons in the following section. These mechanisms and the corresponding thermodynamic and transport data have been either provided by the authors themselves or downloaded from the authors' home pages.

3. Ignition delay calculations

The ignition delay time, τ_{ign} , also called induction time, is the time interval needed by a certain mixture of reactants to ignite without external energy supply. The ignition delay time is a function of the initial composition, temperature and pressure of the mixture. Ignition delay times are usually measured by shock tube experiments, see e.g. [32]. These experiments depart from ideality due to viscous, heat transfer, and non-equilibrium effects. Therefore, mixtures are usually highly diluted, preferably with a monoatomic gas, in order to minimize these effects. Several definitions to determine the moment of ignition are used in the literature, however, the ignition times determined by the different definitions vary only negligibly relative to their absolute values [32].

In this study, the ignition delay time is calculated with a closed homogeneous reactor model at constant pressure and enthalpy using an in-house code similar to the SENKIN code [34]. The assumption of constant pressure is not exact for this configuration. However, corresponding calculations using a constant volume reactor have been performed, and the differences compared to a constant pressure reactor have been found to be negligible. An investigation of species profiles showed that the period of ignition is usually very short compared to the ignition delay time. Hence, the definition of the moment of ignition has only a negligible influence on the results, particularly for long ignition delay times. Even for very short ignition delay times, the differences do not exceed a few percent, so that the ignition criteria does not affect the overall trend of the computed results, especially when plotted in a logarithmical scale. Here, the maximum gradient of H_2 mass fraction is used to define the moment of ignition.

In the following, ignition delay times computed by the GRI-mech 3.0 [3], the Leeds mechanism [20], the San Diego mechanism [12], and the mechanisms of Li et al. [9], Ó Conaire et al. [10], and Warnatz [16] are compared to experimental data for a large range of initial conditions. Although part of the experiments are outside the range of conditions for which some mechanisms are validated for, it might be of interest how these mechanisms behave under such conditions.

Shock tube experiments for stoichiometric hydrogen/air mixtures at varying pressures have been performed by Snyder et al. [35], Slack [36], Craig [37], and Bhashkaran et al. [38]. Computed ignition delay times as a function of the inverse of the temperature for the various reaction mechanisms are compared with these measurements in Fig. 1. Part of the experimental data [35,37,38] have been taken from Schultz et al. [32]. At 1 and 2 atm (Figs. 1a and b), the experimental data of Craig strongly deviate from the data of Snyder et al. and Slack. The latter two agree well for temperatures around 950–1000 K, so that only these data are considered for validation.

An S-shaped profile of the ignition delay time is predicted for all mechanisms, which is in qualitative agreement with the measurements at 2 atm. The GRI-Mech 3.0, the Leeds mechanism, and the mechanism of Warnatz generally overpredict the ignition delay time. The mechanisms of Li and Ó Conaire are in good agreement with the measurements up to 2.5 atm (Fig. 1c). The performance of the Ó Conaire mechanism performs slightly better for 2 atm, whereas the Li mechanism is slightly more accurate for 2.5 atm. However, these deviations are well within the uncertainty range of the measurements. The performance of the San Diego mechanism lies somewhere between the GRI-Mech 3.0 and the Li mechanism. At high temperatures, the San Diego mechanism predicts a slightly lower ignition delay time than all other mechanisms. For low temperatures at 2 atm, all mechanisms strongly overpredict the experimental data by orders of magnitude. The same behavior can be observed at a pressure of 4 atm (Fig. 1d). Similar results have been obtained for 6 and 8 atm. These discrepancies between calculations and experiments cannot be attributed

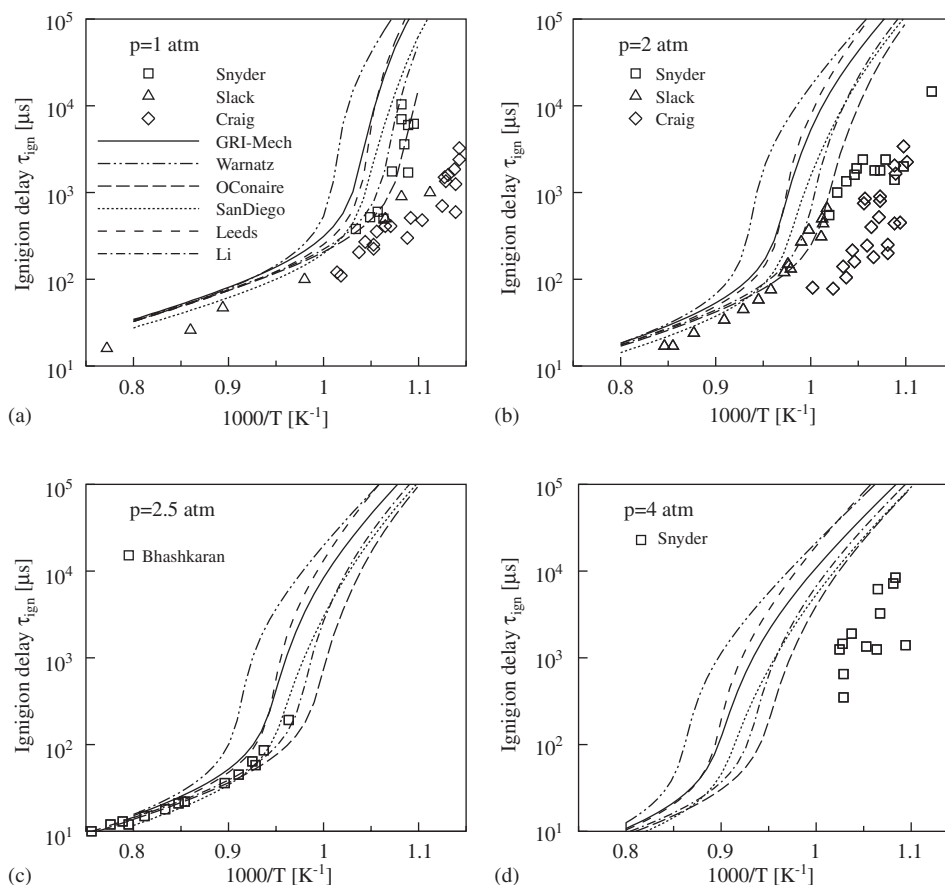


Fig. 1. Ignition delay times of stoichiometric H_2/air mixtures as a function of $1000/T$; shock tube data (symbols) vs. computed results (lines) for various mechanisms.

to the ignition criteria, since its influence becomes negligible for these high-ignition delay times. One reason for these discrepancies might be that for these relatively high-ignition delay times, the experiments might depart so much from ideality that they cannot be represented by a homogeneous reactor model.

More reliable data at elevated pressures have been determined for mixtures strongly diluted with argon. Skinner and Ringrose [39] measured ignition delay times for a H_2/O_2 mixture with an equivalence ratio of $\phi = 2.0$ diluted with 90% argon at 5 atm. Computed ignition delay times as a function of the inverse of the temperature are compared with these measurements in Fig. 2a. The mechanisms of Li and Ó Conaire yield almost identical results that are in good agreement with the measurements, whereas the mechanism of Warnatz overpredicts the experimental data by orders of magnitude. The large deviations of the latter mechanism can be attributed to the fact that it does not include any specific third body efficiencies for argon. The other mechanisms lie somewhere in-between, and out of these, the San Diego mechanism is closest to the measurements.

Recently, Peterson et al. [40] measured ignition delay times for stoichiometric H_2/O_2 mixtures at 33 atm. Re-

sults for 97% dilution with argon at temperatures below 1300 K are presented in Fig. 2b. The mechanisms of Li and Ó Conaire are very close to each other and in good agreement with the experimental data. A slightly better performance is achieved by the Li mechanism. The other mechanisms again overpredict the measurements similarly to the results at 5 atm, however to a larger extent. For 99.25% dilution with argon at temperatures above 1700 K, all mechanisms agreed very well with the experimental data. The argon-rich atmosphere in these experiments has a significant influence on third body reactions, compared to the nitrogen-rich atmosphere in real applications. However, to the knowledge of the authors, these were the only existing experimental data in the pressure range of gas turbines.

All in all, the mechanisms of Li and Ó Conaire show the best agreement with experimental data of ignition delay, and the San Diego mechanism yields quite satisfactory results. This is not surprising since these three mechanisms have been partly developed based on the same experimental data shown before, whereas some other mechanisms have not been validated against high-pressure data at all. Hence, these three mechanisms are selected for further investigation. In addition, the

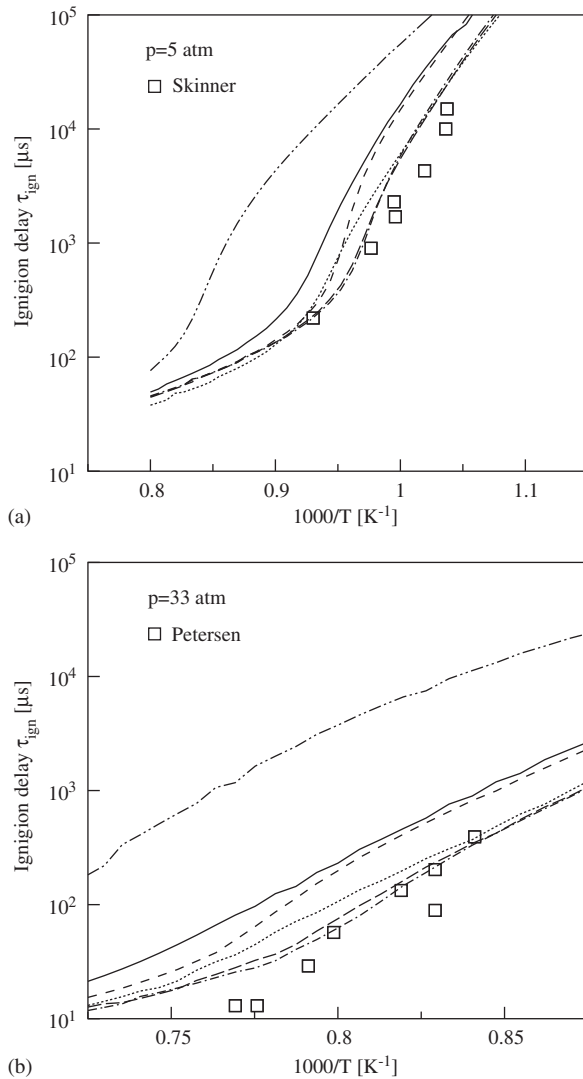


Fig. 2. Ignition delay times of $\text{H}_2/\text{O}_2/\text{Ar}$ mixtures as a function of $1000/T$; shock tube data (symbols) vs. computed results (lines, legend see Fig. 1a) for various mechanisms.

GRI-Mech 3.0 is also included since it is used as a reference by many researchers.

4. Laminar flame speed analysis

One of the important issues in a comprehensive validation of a detailed reaction mechanism is the comparison of calculated flame speeds with corresponding flame speed measurements. The laminar flame speed, or the laminar burning velocity, is defined as the velocity at which the flame front propagates normal to itself and relative to the flow into the unburned mixture. It depends primarily on the composition, temperature, and pressure of the unburned mixture temperature, and it is often used to characterize the combustion of various fuel-oxidizer combinations over a certain range of pressure. The laminar flame speed at high pressures is of practical importance in the design and analysis of combustors as well as for evaluating theoretical models.

4.1. Previous flame speed measurements

Numerous flame speed studies have been performed for hydrogen/air flames at atmospheric pressures. Only a few, that are believed to be some of the most representative, are mentioned here. Dowdy et al. [41] reported on laminar burning velocities in expanding spherical laminar flames. They studied hydrogen/air mixtures for equivalence ratios varying from 0.3 to 5. Aung et al. [42] also studied burning velocities of hydrogen/air flames for the same equivalence ratio range. They measured laminar burning velocities in freely propagating spherical laminar premixed flames. Tse et al. [43] determined flame speeds of expanding spherical flames in $\text{H}_2/\text{O}_2/\text{inert}$ mixtures for equivalence ratios varying from 0.4 to 4. Kwon and Faeth [44] reported on experimentally determined laminar flame speeds for H_2/O_2 flames using $\text{N}_2/\text{He}/\text{Ar}$ as diluents in freely propagating spherical laminar premixed flames. Ó Conaire et al. [10] gave a review of several of the data reported of laminar flame speeds at atmospheric pressure. Among the existing data sets, they characterized the data of Dowdy et al. [41] and Tse et al. [43] as intermediate (maximum flame speed of 285 cm/s at $\phi = 1.75$), whereas the data set of Aung et al. [42] was characterized as slow (maximum flame speed of 260 cm/s at $\phi = 1.65$). They considered the flame speed measurements of Dowdy et al. [41] and Tse et al. [43] to be the most representative of the entire datasets available.

Flame speed measurements of hydrogen/air flames at high pressures are, for obvious reasons, harder to find than for atmospheric pressures. The limiting complication of performing flame speed measurements at high pressures is the facilitated onset of flame front instability due to decreased flame thickness [43]. As mentioned by several authors [10,43], the importance of stretch on laminar flame speed was first identified by Wu and Law [45] in 1984. Stretch-free data have only recently become available, and such data have only been determined up to a few atmospheres. Apparently, there is a need for more high pressure flame speed data. In addition to their atmospheric pressure measurements, Tse et al. [43] reported on measurements of flame speed at higher pressures. They measured mass burning velocities for $\text{H}_2/\text{O}_2/\text{He}$ mixtures for pressures between 1 and 20 atm at an initial temperature of 298 K. They used helium as a diluent to minimize flame instability at higher pressures. Aung et al. [46] studied the effects of positive flame stretch on the laminar burning velocities of $\text{H}_2/\text{O}_2/\text{N}_2$ flames at elevated pressures. They reported on stretch-corrected flame speeds for pressures in the range of 0.35–4 atm. Kwon and Faeth [44] experimentally determined un-stretched laminar flame speeds for H_2/O_2 flames using $\text{N}_2/\text{He}/\text{Ar}$ as diluents for elevated pressures, however only up to 3 atm. Qin et al. [29] have performed laminar burning velocity measurements for H_2/air mixtures at pressures up to 0.5 MPa.

4.2. Present flame speed calculations

Calculations of laminar flame speeds in freely propagating one-dimensional laminar flames have been performed using the

well-known CHEMKIN PREMIX code [31]. This code can be used to calculate species, temperature profiles, and to study laminar flame speeds of combustible gases in steady-state burner stabilized and freely propagating premixed laminar flames. The PREMIX code includes effects important in hydrogen combustion, such as thermal diffusion (the Soret effect) and multicomponent diffusion. Since the inclusion of such effects is necessary for interpreting data from flame speed experiments, all calculations in the present work were performed including thermal diffusion and multicomponent diffusion effects.

The numerical method in the PREMIX code is based on a hybrid time-integration/Newton-iteration technique to solve the equations for energy and mass fractions. The largest source of errors in relation to the numerical method is the spatial discretization. In the present work, a sufficiently fine grid was used to minimize such errors. Li et al. [9] reported that they used up to 1000 grid points to give an accurate prediction of the laminar flame speed. The effect of grid resolution was extensively tested in the present work with simulations up to 1400 grid points. However, the simulations presented here were performed with a grid resolution of about 700 to about 800 points. These grid resolutions were sufficient to produce grid independent solutions. The mechanisms of Li et al. [9], Ó Conaire et al. [10], the San Diego mechanism [12] and GRI-Mech 3.0 [3] were compared for hydrogen-air flames at both atmospheric and elevated pressures. All of the calculations were run with an initial unburned mixture temperature of 298 K.

The calculated laminar flame speed of hydrogen/air mixtures at atmospheric pressure as a function of equivalence ratio is compared to measurements of Dowdy et al. [41] and Tse et al. [43] in Fig. 3a. The Li mechanism and the Ó Conaire mechanism predict almost identical results that are generally in good agreement with the measurements. The GRI mechanism predicts a slightly faster maximum flame speed at $\phi \approx 1.75$ and a slower flame speed for very rich and very lean mixtures. For the GRI mechanism, the agreement with the measurements is not as good as for the other two mechanisms. The San Diego mechanism generally overpredicts the flame speed data, particularly at its maximum around $\phi = 1.75$. In a personal communication, F.A. Williams commented that replacing rate parameters for the two steps ($\text{HO}_2 + \text{H} = 2\text{OH}$ and $\text{H} + \text{OH} + \text{M} = \text{H}_2\text{O} + \text{M}$) by the rate parameters of Li et al. [9] brings the curve close to the other curves in the vicinity of the maximum while not affecting auto-ignition significantly.

The calculated laminar flame speed of hydrogen/air mixtures at 4 atm as a function of equivalence ratio is compared to measurements of Aung et al. [46] in Fig 3b. The Ó Conaire mechanism predicts slightly higher values than the Li mechanism. As for atmospheric pressure, the GRI mechanism predicts a slightly faster maximum flame speed and a slower flame speed for very rich and very lean mixtures. Looking at the experimental data, there might be a reason for arguing about the accuracy. Aung et al. [46] reports a maximum of 12% inaccuracy for their laminar flame speed measurements, which means that the predictions from all three mechanisms shown in Fig. 3b lie within this margin for most of the equivalence ratio range. The GRI-Mech 3.0 shows the largest deviations from the experimental

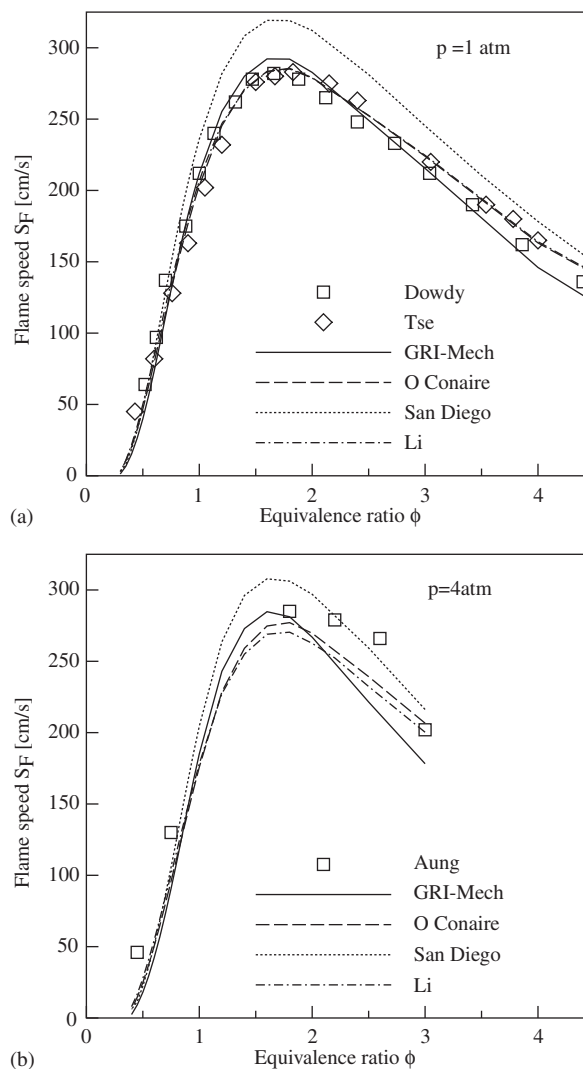


Fig. 3. Laminar flame speed of H_2/air mixtures as a function of equivalence ratio. Experimental data (symbols) vs. computed results (lines) for various mechanisms.

data for very rich conditions, whereas the San Diego mechanism strongly overpredicts the maximum at $\phi \approx 1.75$. To verify the present predictions obtained with the PREMIX code, the present results with the Li mechanism were thoroughly compared with similar predictions performed by Li et al. [9] with the same PREMIX code. The present predictions are identical with the predictions from Li et al.

The effect of pressure on the flame speed was investigated by running several calculations at pressures in the range of 1–5 atm for hydrogen/air flames at $\phi = 0.75$. The results are compared to measurements of Aung et al. [46] in Fig. 4. The calculated flame speed of the Li mechanism is faster and closer to the experimental data than the Ó Conaire mechanism and GRI-Mech 3.0. At increasing pressure the difference between the Li mechanism and the Ó Conaire seem to remain constant, whereas the difference between the GRI mechanism and the other two continues to increase. The San Diego mechanism shows a similar qualitative behavior as the GRI-Mech 3.0, however, at higher

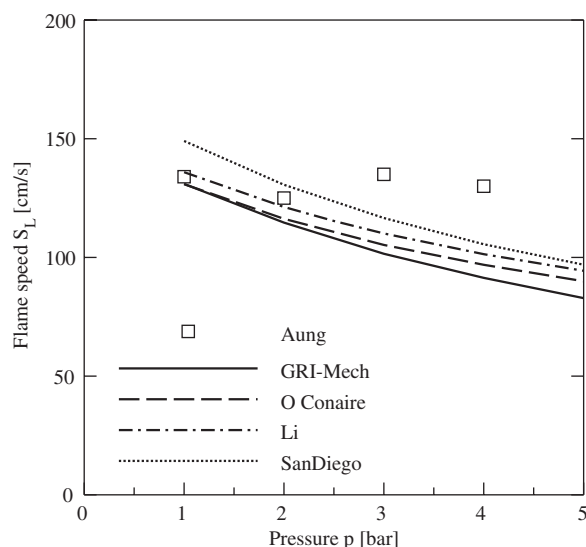


Fig. 4. Laminar flame speed of H₂/air mixtures at $\phi = 0.75$ as a function of pressure. Experimental data (symbols) vs. computed results (lines) for various mechanisms.

absolute values. Even though the Li mechanism is closest to the experimental data for this single comparison, it is difficult to say if one performs better than the other, since only one set of experimental data is used in the comparison here. An inaccuracy of about 12% for the laminar flame speed was reported by Aung et al. [46]. All mechanisms are within the range of accuracy of 12% up to 2 atm, and all are outside for higher pressures. The effect of pressure on the laminar burning velocity has been discussed by several authors [5,47,48]. According to flame speed theory, the laminar flame speed of H₂/O₂ is expected to decrease with increasing pressure due to the increasing importance of the third order reaction $\text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M}$ [5]. This is also the most common tendency shown in experimental results [29,43,44,47]. Hence, the qualitative behavior of the computational results seems to be more accurate than that of the measurements in Fig. 4.

Finally, high-pressure laminar flame speed calculations for H₂/O₂/He mixtures with $\text{O}_2/(\text{O}_2 + \text{He}) = 0.08$ at 10, 15, and 20 atm are compared to experimental data of Tse et al. [43] in Fig. 5. The measured and predicted flame speed decreases with increasing pressure, which supports the discussion in the previous paragraph. As might be expected, the differences between the results of the different mechanisms become larger with increasing pressure. The GRI-Mech generally strongly underpredicts the experiments. The San Diego mechanism yields good agreement with the measurements at 10 atm, but underpredicts them at higher pressures for fuel-rich conditions. The mechanism of Ó Conaire generally yields good results for fuel lean conditions, but slightly underpredicts the maximum around $\phi = 1.5$. In contrast, the mechanism of Li et al. catches this maximum well, but slightly overpredicts the flame speed at stoichiometric and fuel lean conditions. Although the pressure range of these experiments covers that of gas turbine conditions, the diluent helium might have a large effect on the

chemical kinetics due to its Chaperon efficiencies, compared to N₂-rich conditions when air is used as an oxidizer. However, to the knowledge of the authors, no flame speed experiments for H₂/air mixtures exist in that pressure range.

5. Discussion

The comparisons in the previous sections show that the mechanisms of Li et al. [9], and Ó Conaire [10] are best suited for the prediction of hydrogen combustion. However, a clear preference for one of them cannot be found from these results. Here, some fundamental differences between the Li and the Ó Conaire mechanisms and some applications to hydrogen combustion in IGCC/IRCC systems are discussed.

As mentioned before, both mechanisms are based on the mechanism of Mueller et al. [8]. As an example, the Li mechanism for H₂-air combustion is listed in Table 1. A sensitivity study of the Li mechanism was performed here to show the importance of each reaction under gas turbine conditions. The PREMIX code was used to calculate the sensitivity of the pre-exponential factor, A_j , of each reaction, j , in Table 1 on the laminar flame speed, S_L . The sensitivity coefficients, s_j , for the lean H₂/air mixture at $\phi = 0.5$, 17 bar and 609 K are shown in Fig. 6.

The reactions R1 and R9 have the largest impact on the laminar flame speed. An increase of the reaction rate of R1 will enhance flame speed to the same degree as an increase of the reaction rate of R9 will lower the flame speed. Hence, the propagation of the flame is to a large degree controlled by the competition of these two reactions corresponding to the second ignition limit. In addition to R1, reaction R3 also strongly enhances the flame speed. Furthermore, reactions R2, R8, R11, and R13 have significant sensitivity on flame speed. Except for a small negative contribution of R19, the sensitivity of all reactions including H₂O₂ is very small. Hence, H₂O₂ seems to play a negligible role under these conditions.

The differences between the Li mechanism and the Ó Conaire mechanism are expressed through four reactions R1, R8, R9, and R17. The sensitivity study shows that the reactions recently updated by Li et al. and Ó Conaire et al. are very important ones under gas turbine conditions. The competition between reaction R1 and R9 is probably the most important issue for high-pressure hydrogen combustion. Li and co-workers have updated their rate constant for R1 to that of Hessler [49], whereas Ó Conaire et al. kept the original rate constant from the Mueller mechanism. Mueller et al. [8] used the rate constant expression by Pirraglia et al. [50] for R1. Mueller et al. reported that using the data set by Pirraglia et al. led to over-predictions at high temperatures (above 1700 K), which is an important temperature range in gas turbine combustion. Hessler [49] excluded the consideration of certain sets of available elementary rate data based upon a defined uncertainty envelope. The resulting rate constant from Hessler better predicts several high-temperature data and more closely predicts rates at low temperatures within close proximity to those predicted by the expression by Pirraglia et al.

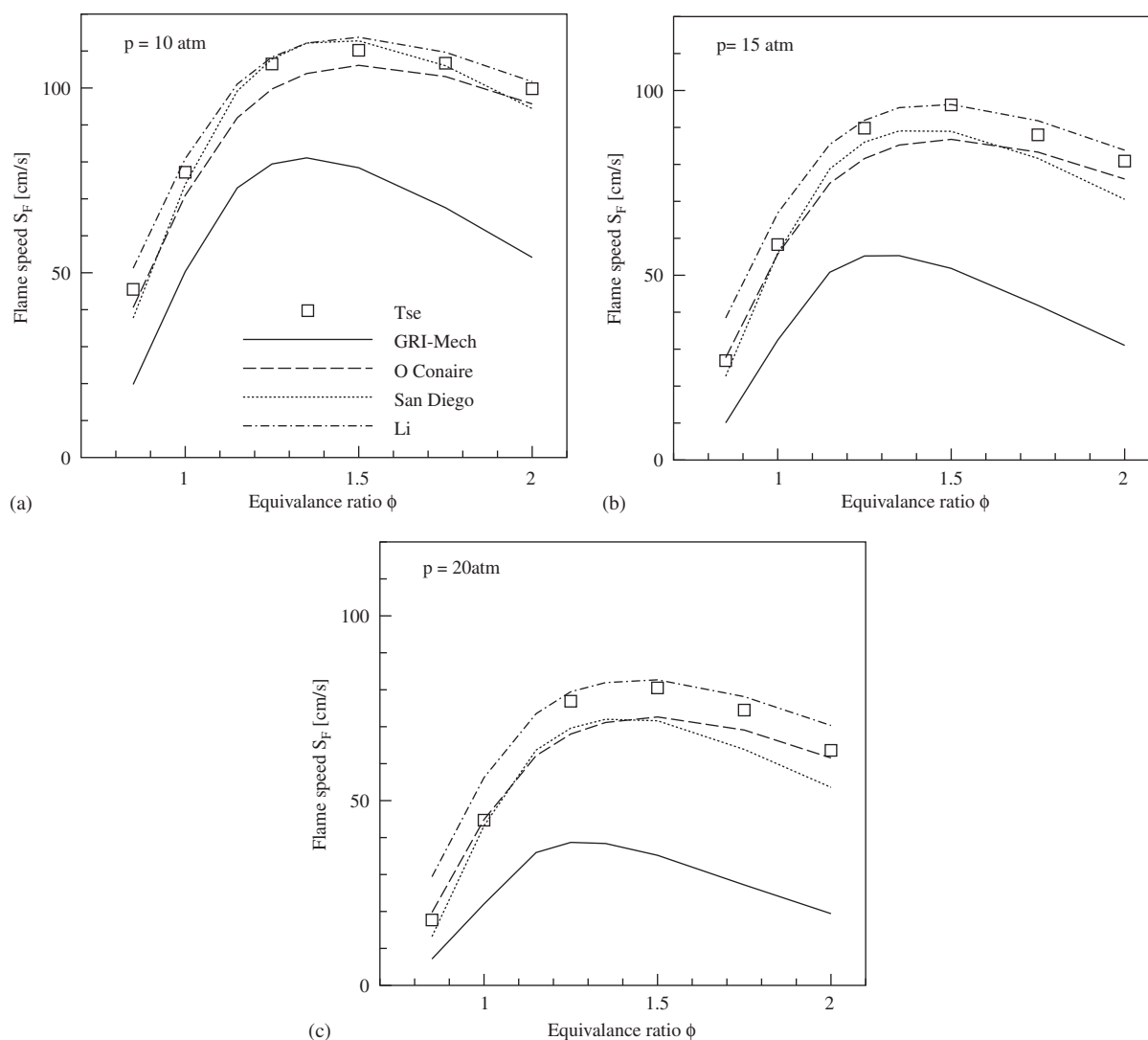


Fig. 5. Laminar flame speed of $\text{H}_2/\text{O}_2/\text{He}$ mixtures as a function of equivalence ratio. Experimental data (symbols) vs. computed results (lines) for various mechanisms.

Li et al. found that reaction R9 was very sensitive to the consumption of species in a flow reactor, some sensitive to laminar flame speed, and that it was almost insensitive to ignition delay. However, Ó Conaire altered the efficiency factors of H_2 to improve ignition delay calculations. As mentioned before, reaction R8 has some effect on laminar flame speed, whereas R17 is solely relevant for ignition delay.

To discuss the effect of detailed chemistry on more relevant practical flames, the authors studied the effect of differences between the two mechanisms on the predictions of a turbulent lifted H_2/N_2 jet flame, where the lift-off height of the flame is controlled by the chemical kinetics [51]. A comparison was performed by successively changing the elementary rates for the four reactions R1, R8, R9, and R17 in the Li and the Ó Conaire mechanism mentioned above. The results from those simulations showed that the differences between the mechanisms expressed through changes in R9 had much larger effect on the predicted lift-off height than any of the other reactions.

Here, the Li mechanism predicted a lift-off height much closer to the measured flame than predictions with the Ó Conaire mechanism. The results further showed that the differences in R1 had some effect on the predicted lift-off height and the updates used by Li et al. gave predictions closer to the measured flame. The same tendency was shown for changes in reaction R8. The predicted lift-off height was insensitive to the changes made in R17 by Ó Conaire et al.

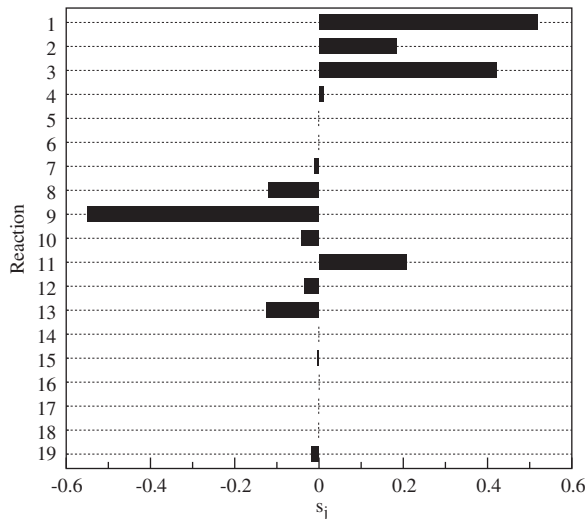
This discussion suggests that the Li mechanism theoretically is best suited for the prediction of H_2/O_2 chemistry. In addition, the turbulent flame calculations performed showed better performance with the Li mechanism. The results show that the recent updates made by Li et al. in those reactions important under relevant gas turbine conditions (R1 and R9) was the reason for the better predictions here. For laminar flame speed calculations of lean mixtures, however, the Ó Conaire mechanism performed best in our calculations of the $\text{H}_2/\text{O}_2/\text{He}$ mixtures at high pressures measured by Tse et al. The effect of pressure on

Table 1

Hydrogen mechanism of Li et al. [9] in the form $k = A T^n \exp(-E/RT)$ for N_2 as the main bath gas

| No. | Reaction | A | n | E |
|-----|------------------------------|------------------------|--------|---------|
| 1 | $H + O_2 = O + OH$ | 3.547×10^{15} | -0.406 | 16599 |
| 2 | $O + H_2 = H + OH$ | 0.508×10^5 | 2.67 | 6290 |
| 3 | $H_2 + OH = H_2O + H$ | 0.216×10^9 | 1.51 | 3430 |
| 4 | $O + H_2O = OH + OH$ | 2.970×10^6 | 2.02 | 13400 |
| 5 | $H_2 + M = H + H + M^a$ | 4.577×10^{19} | -1.40 | 104380 |
| 6 | $O + O + M = O_2 + M^a$ | 6.165×10^{15} | -0.50 | 0 |
| 7 | $O + H + M = OH + M^a$ | 4.714×10^{18} | -1.00 | 0 |
| 8 | $H + OH + M = H_2O + M^a$ | 3.800×10^{22} | -2.00 | 0 |
| 9 | $H + O_2 + M = HO_2 + M^b$ | 1.475×10^{12} | 0.60 | 0 |
| | | k_0 | | |
| | | 6.366×10^{20} | -1.72 | 524.8 |
| 10 | $HO_2 + H = H_2 + O_2$ | 1.660×10^{13} | 0.0 | 823 |
| 11 | $HO_2 + H = OH + OH$ | 7.079×10^{13} | 0.0 | 295 |
| 12 | $HO_2 + O = O_2 + OH$ | 0.325×10^{14} | 0.0 | 0 |
| 13 | $HO_2 + OH = H_2O + O_2$ | 2.890×10^{13} | 0.0 | -497 |
| 14 | $HO_2 + HO_2 = H_2O_2 + O_2$ | 4.200×10^{14} | 0.0 | 11982 |
| | | | | |
| | | 1.300×10^{11} | 0.0 | -1629.3 |
| 15 | $H_2O_2 + M = OH + OH + M^c$ | 2.951×10^{14} | 0.0 | 48430 |
| | | k_0 | | |
| | | 1.202×10^{17} | 0.0 | 45500 |
| 16 | $H_2O_2 + H = H_2O + OH$ | 0.241×10^{14} | 0.0 | 3970 |
| 17 | $H_2O_2 + H = HO_2 + H_2$ | 0.482×10^{14} | 0.0 | 7950 |
| 18 | $H_2O_2 + O = OH + HO_2$ | 9.550×10^6 | 2.0 | 3970 |
| 19 | $H_2O_2 + OH = HO_2 + H_2O$ | 1.000×10^{12} | 0.0 | 0 |
| | | | | |
| | | 5.800×10^{14} | 0.0 | 9557 |

Units are cm, mol, s, cal, K.

^aThird body enhancement factors: $H_2 = 2.5$, $H_2O = 12$.^bThird body enhancement factors: $H_2 = 2$, $H_2O = 11$, $O_2 = 0.78$; Troe parameter: 0.8.^cThird body enhancement factors: $H_2 = 2.5$, $H_2O = 11$; Troe parameter: 0.5.Fig. 6. Sensitivity coefficients, s_j , of the reactions in Table 1 on the laminar flame speed, S_L , of a lean H_2 /air mixture at $\phi = 0.5$, 17 bar, and 609 K.

the flame speed of fuel lean $H_2/O_2/He$ mixtures is $\phi = 0.85$ is shown in Fig. 7a. The Ó Conaire mechanism generally yields very good agreement with the measurements, particularly at 15 and 20 atm.

In IGCC/IRCC pre-combustion, however, hydrogen is combusted with air so that N_2 is the main diluent. The computed laminar flame speed of H_2 /air mixtures with the same equivalence ratio of 0.85 is shown in Fig. 7b. Under these conditions with N_2 as the main diluent, the small difference between the mechanisms of Li and Ó Conaire remains approximately constant for varying pressure. Hence, these two mechanisms are expected to yield very similar results for lean H_2 /air mixtures within the pressure range of interest. The large discrepancies in Fig. 7a between these mechanisms are most probably caused by the different third body efficiencies of the main diluent helium for the reaction R9. The importance of this reaction increases with increasing pressure.

6. Conclusions

Many different detailed mechanisms including kinetics for hydrogen combustion can be found in the literature. However, only few of them have been validated against experimental data of hydrogen combustion at elevated pressures. The mechanisms of the group around Dryer [8,9] and the mechanism of Ó Conaire et al. [10] provide the most comprehensive validation at pressures up to 87 atm. The San Diego mechanism [12] has also been extensively validated for ignition delay times up to 33 atm. The GRI-mechanism [1–3], the Leeds mechanism [20],

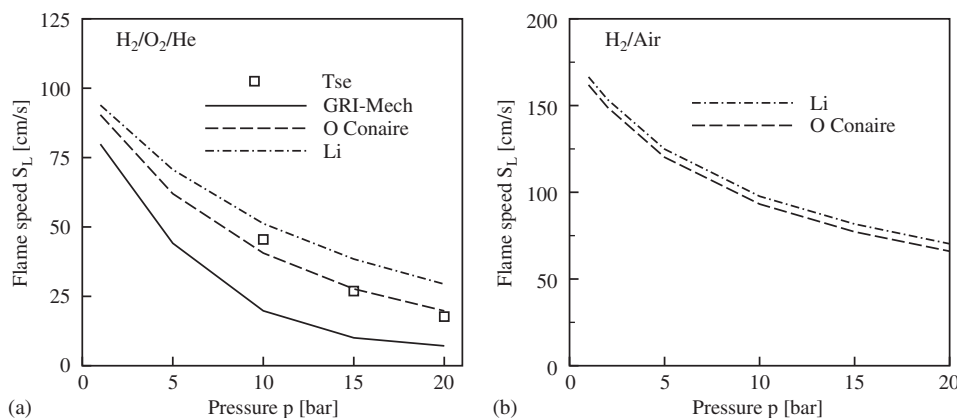


Fig. 7. Laminar flame speed, S_L , of: (a) $H_2/O_2/He$ and (b) H_2/air mixtures with $\phi = 0.85$ at 298 K as a function of pressure, p ; experimental data (symbols) vs. computed results (lines) for different mechanisms.

and the mechanisms of the group around J. Warnatz [13–16] are the ones most frequently referred to.

Reactor calculations of ignition delay times show that the mechanisms of Li et al. [9] and Ó Conaire et al. [10] yield the best agreement with data from shock tube experiments at pressures up to 33 bar. The largest deviations from the experimental data are observed for the mechanism of Warnatz [16]. The results of the San Diego mechanism, the GRI-mech 3.0, and the Leeds mechanism generally lie somewhere in-between.

The investigation of laminar flame speed indicates that the mechanisms of Li or Ó Conaire show very good agreement with experimental data for H_2/air mixtures at atmospheric pressure, and for $H_2/O_2/He$ mixtures at elevated pressures. The San Diego mechanism yields reasonable results for the helium diluted high-pressure flames, but overpredicts the flame speed of the atmospheric H_2/air flames. The GRI-Mech 3.0 generally shows poor performance for the laminar flame speed of $H_2/O_2/He$ mixtures at high pressures.

This study shows that the mechanisms of Li or Ó Conaire accurately represent H_2/O_2 kinetics under gas turbine conditions. The almost equally good performance of these two mechanisms at elevated pressures is not surprising since they used the same experimental data for model development. The present study suggests that the Li mechanism is best suited for the prediction of H_2/O_2 chemistry since it includes more up-to-date data for the range of interest. Additional experimental data are needed for a more comprehensive evaluation of the mechanisms, particularly under a nitrogen-rich atmosphere.

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