Numerical Analysis of Hydrogen Mild Combustion

Pino SABIA
Dipartimento di Ingegneria Chimica, Facoltà di Ingegneria,
Piazzale Tecchio n° 80 80125 Naples-ITALY
e-mail: psabia@unina.it
Eva SCHIEßWOHL
Lehrstuhl für Technische Thermodynamik und Transportprozesse
Universität Bayreuth, GERMANY
Maria Rosaria de JOANNON
Dipartimento di Ingegneria Chimica, Facoltà di Ingegneria
Piazzale Tecchio n° 80 80125 Naples-ITALY
e-mail: dejoannon@irc.cnr.it
Antonio CAVALIERE
Dipartimento di Ingegneria Chimica, Facoltà di Ingegneria
Piazzale Tecchio n° 80 80125 Naples-ITALY
e-mail: antcaval@unina.it

Abstract

Five hydrogen-oxygen combustion mechanisms were analyzed and compared on the basis of experimental ignition delay time data from shock-tube studies available in the literature. Stoichiometric and lean hydrogen/air combustion were considered, as well as Mild Combustion conditions in the presence of different amounts of steam. The temperature varied between 900 and 1300 K, and pressure ranged from 0.1 to 0.9 MPa.

Since deviations in almost all the analyzed conditions occurred, a sensitivity analysis was conducted to characterize the most influential reactions under the various initial conditions.

In order to improve the numerical results, the reaction rate constants of the reaction $HO_2 + H = H_2O_2 + H_2$ were varied, as well as the third body efficiency of water in the breaking reaction $H + O_2 + M = HO_2 + M$. Although these variations did not lead to the identification of new kinetic constants, they clearly showed significant changes in the prediction of the ignition delay time. These results showed that the oxidation process is very sensitive to the reaction $HO_2 + H = H_2O_2 + H_2$ for low temperature values, as well as to the third body efficiency of the steam for higher temperatures.

Key words: Mild combustion, Hydrogen oxidation, Steam dilution.

Introduction

In recent years, new combustion technologies have been developed to produce energy in an efficient and environmentally friendly manner. A very promising process is Mild Combustion (Cavaliere and de Joannon, 2004), characterized by highly diluted and pre-heated reactants. In the framework of hydrogen combustion systems, the use of dilution can lower the high reactivity of hydrogen, facilitating the use of this clean fuel.

Moreover, the use of steam as diluent is relevant since Mild Combustion technology could be applied in steam turbines in which hydrogen and oxygen can be added directly to the steam, resulting in an internal re-heating. Therefore, the behavior of

the hydrogen-oxygen system under Mild Combustion condition and in the presence of steam was preliminarily studied.

Results

The ignition delay time of the system H_2/O_2 has been analyzed with Chemkin 3.7 (Kee et al., 2003) software and its application, Senkin (Kee et al., 2003). Five hydrogen-oxygen reaction schemes were chosen, hereafter referred to as Warnatz (Warnatz, 2005), Westbrook (Marinov et al., 1996; Conaire et al., 2004), Dryer (Allen et al., 1997) (Müller et al., 1999; Li et al., 2004), Oran et al. (1992), and Miller and Bowman (1989) mechanisms. The ignition delay time was defined as the time the system needs to increase the temperature of 10 K in comparison with the inlet temperature (de Joannon et al., 2002). The numerical results were compared with experimental data derived from the shock tube measurements of Slack (1977), Snyder et al. (1965), Craig (1966), Wang et al. (2003), and Blumenthal (1996).

Figure 1 shows the ignition delay times for a stoichiometric hydrogen-air mixture at 0.1 and 0.4 MPa. For high temperatures and 0.1 MPa, a good agreement between experiments and simulations is achieved for each kinetic mechanism. All the mechanisms over-predict the ignition time. Although the general trend is reproduced the Oran mechanism shows the shortest delay time throughout the entire temperature range considered.

It has been underlined that at 0.4 MPa, all the mechanisms over-predict the experimental delay times by about one order of magnitude; whereas the Oran mechanism is the closest to the experimental values. Comparisons carried out for 0.8 MPa have shown an even greater discrepancy between calculations and experiments.

Additional calculations have been carried out at a pressure of 0.4 MPa and for a fixed H_2/O_2 lean ratio in the presence of different molar concentrations of steam (15% and 40%). Figure 2a represents the results for a lean mixture of 15% hydrogen and 85% air. In this case, the calculated ignition delay times correspond relatively well to the measured values, even if at low temperatures some deviation occurs. The mechanisms themselves are close together, except the Oran mechanism that predicts the shortest ignition delay time.

For a molar water concentration equal to 15%, the system behaves as shown in Figure 2b. It can be seen that the Oran mechanism is not significantly affected by the presence of water. This kinetic mechanism considers the third body efficiency equal for any species that acts as a third body. This is in contrast with the generally accepted consideration that water efficiency as a third body is very high in comparison with the third body efficiency of other species. Hence, several calculations were run declaring the efficiency of water in the Oran kinetic
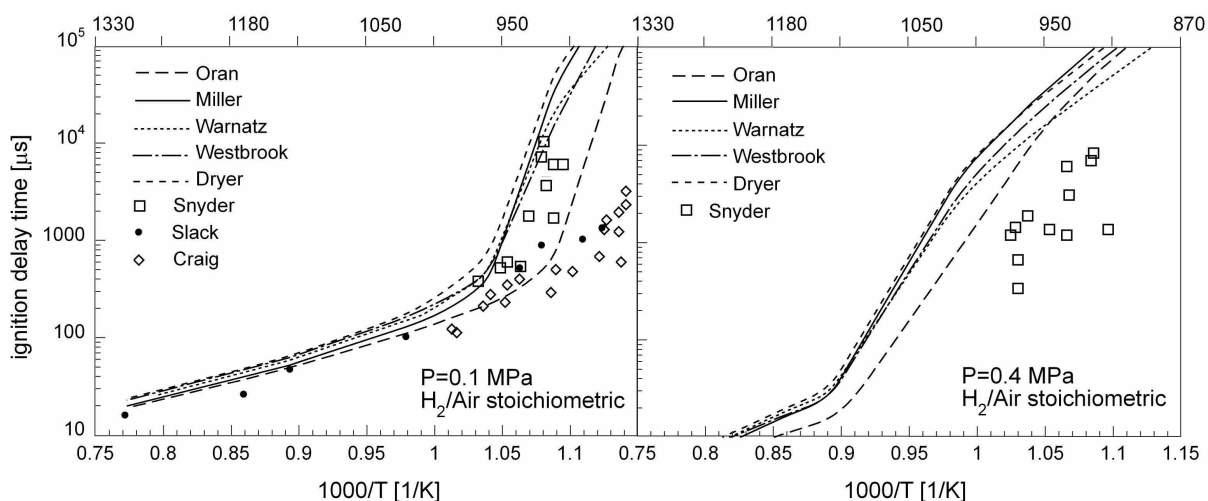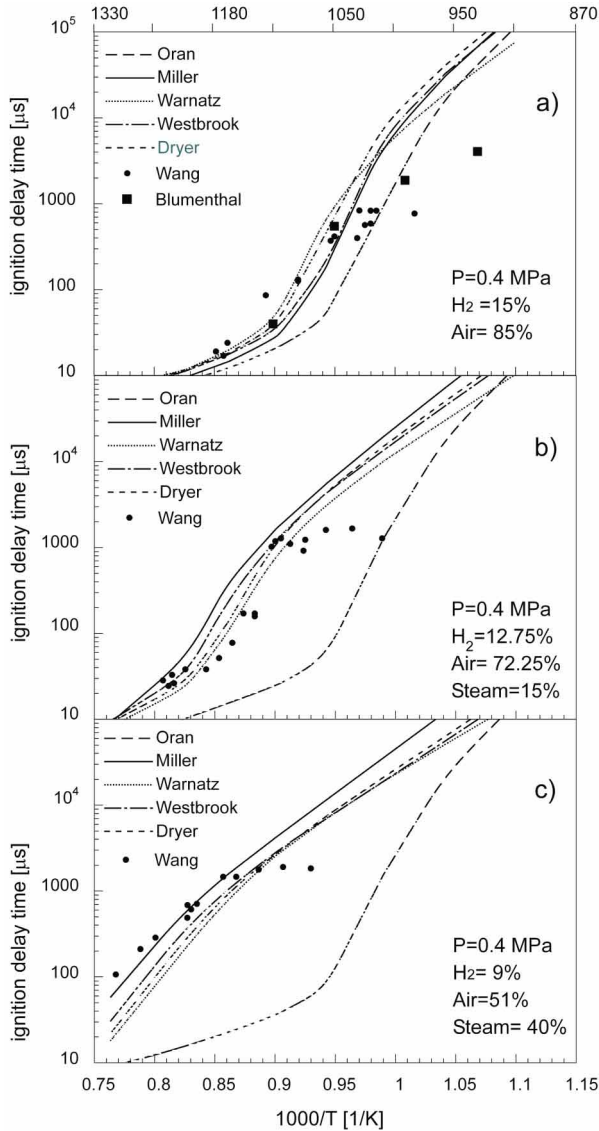

Figure 1. Ignition delay time for H_2/-air system at different pressures.

mechanism and changing its value. Simulations have evinced an increment of the ignition delay time (not reported here), causing a shift of the ignition delay curve towards the values predicted by the other mechanisms.

Figure 2. Ignition delay time for a lean H₂-air system at P = 0.4 MPa and different steam molar percentages.

The experimental and numerical results reported so far show the strong dependence of the ignition delay time on temperature, pressure, and mixture composition. All the data show that 2 regions can be identified according to the different slopes of the ignition delay time curves. The ignition time increases

with increasing water concentration and pressure. In addition, experimental values in the presence of water reach a plateau, as clearly shown in Figures 2b and 2c. Different behaviors of ignition delay that are dependent on temperature and species concentration underline the presence of different kinetic pathways in the ignition mechanism of the system. Furthermore, it has been shown that the numerical results agree quite well with the experiments at low pressures and high temperature, but they fail for low temperatures and are not able to reproduce the plateau experimentally recognizable in data from the literature.

Effect of pressure and steam on the ignition time

The effect of the working pressure on the ignition delay time has been analyzed by using the Westbrook mechanism was used. In particular, simulations have been realized for a stoichiometric H₂/Air mixture at several pressures: 0.1, 0.4, and 0.8 MPa.

Figure 3 shows the ignition delay time as a function of the parameter 1000/T in parametric curves of the pressure. For temperatures lower than about 1100 K the shortest delay times occur for the system working at atmospheric pressure. An increment of pressure results in a significant increase of the ignition delay time for these temperature values. For 1000/T higher than 1, the system working at 0.4 MPa shows the longest delay ignition time, while for higher inlet temperatures, it presents the shortest one.
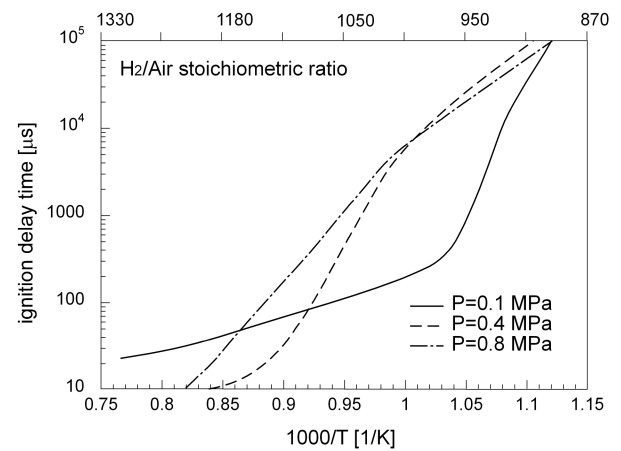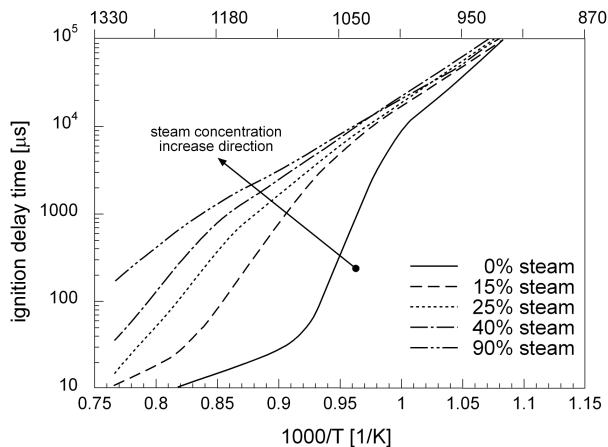

Figure 3. Ignition delay times for a stoichiometric H₂-air system as a function of pressure.

In all these cases, the curves present 3 different slopes that suggest the establishment of 3 different oxidation pathways. For a pressure of 0.8 Mpa the curve does not show 3 different slopes because the third one occurs for lower values of the parameter 1000/T with respect to the ones reported in the figure.

The effect of steam concentration has been valued for an H_2/O_2 stoichiometric mixture diluted to 90% with nitrogen and steam by means of numerical simulations. Steam and nitrogen concentration have been contemporaneously changed keeping the dilution degree constant. The steam concentration has been changed from 0% to 90%.

Figure 4 shows the ignition delay time as a function of the parameter 1000/T for different steam concentrations for a stoichiometric mixture at 0.4 MPa. For 1000/T higher than 1 curves relative to mixtures with a steam molar percentage different than zero are very close to each other, while the shortest delay times occur for the system diluted with nitrogen.

For 1000/T lower than 1, as the steam concentration increases the difference among the ignition delay times relative to the several considered systems increases. Therefore, the presence of water affects the evolution of the oxidation process, mainly for high temperatures. This is essentially due to the higher heat capacity of steam in comparison with nitrogen, as well as to the high efficiency of water as a third body.

Figure 4. Ignition delay times for a stoichiometric H_2-air system at 0.4 MPa as function of the steam molar percentage.

Sensitivity analyses

A sensitivity analysis of the respective elemental reactions was carried out for each selected mechanism. Specifically, sensitivity analyses were conducted for different inlet temperatures and for different diluents in order to assess the most influential reactions as a function of these 2 variables. Although the absolute sensitivity values among the mechanisms differ, the main reactions are always identical. The results obtained using the Westbrook mechanism are reported in Figure 5. The bar diagrams show the maximum values of the sensitivity coefficient with respect to the temperature for the main reactions of the system H_2/O_2.

A system composed by H_2 and O_2 with a molar concentration equal to 15% and 18%, respectively, and diluted with nitrogen (67%) is considered in case 5a. The inlet temperature is 900 K and the pressure is 0.4 MPa. The final temperature for the adiabatic closed reactor is 1990 K. The maximum sensitivity values occur for a working temperature equal to 1450 K ($T_{sens.max}$) during the transitory period. The time for reaching the $T_{sens.max}$ is 0.20 s, while the ignition delay time (τ_{ign}.) is 0.15 s.

Case 5b is relative to a system in which the H_2/O_2 ratio is the same, but the dilution level is 80%. Steam and nitrogen in equimolar fractions are used as diluents. The inlet temperature is 900 K and the pressure is 0.4 MPa. The adiabatic temperature in this case is 1500 K and the $T_{sens.max}$ is 1400 K. This value is reached 0.27 s after the beginning of the simulation, while the system ignites after 0.19 s.

In Figure 6, this analysis is reported for the same mixtures, but for an inlet temperature equal to 1300 K. In case 6a, the adiabatic temperature is 2300 K and the temperature for which the system shows the maximum sensitivity coefficients ($T_{sens.max}$) is 1600 K; this temperature is reached 8 μs after the beginning of the simulation, while the ignition delay time is equal to about 6.3 μs; in case 6b, the final temperature is 1860 K and $T_{sens.max}$ is 1600 K. The time that passes from the beginning of the process to $T_{sens.max}$ is 37 μs, while τ_{ign}. is about 34 μs.

In the case of data reported in Figure 6, the reactions that affect the evolution of the oxidation process are the same, but the reaction, $H_2O_2 + H = HO_2 + H_2$, does not have the same importance. Furthermore, the presence of water enhances the sensitivity coefficients of reactions that involve a third body species.
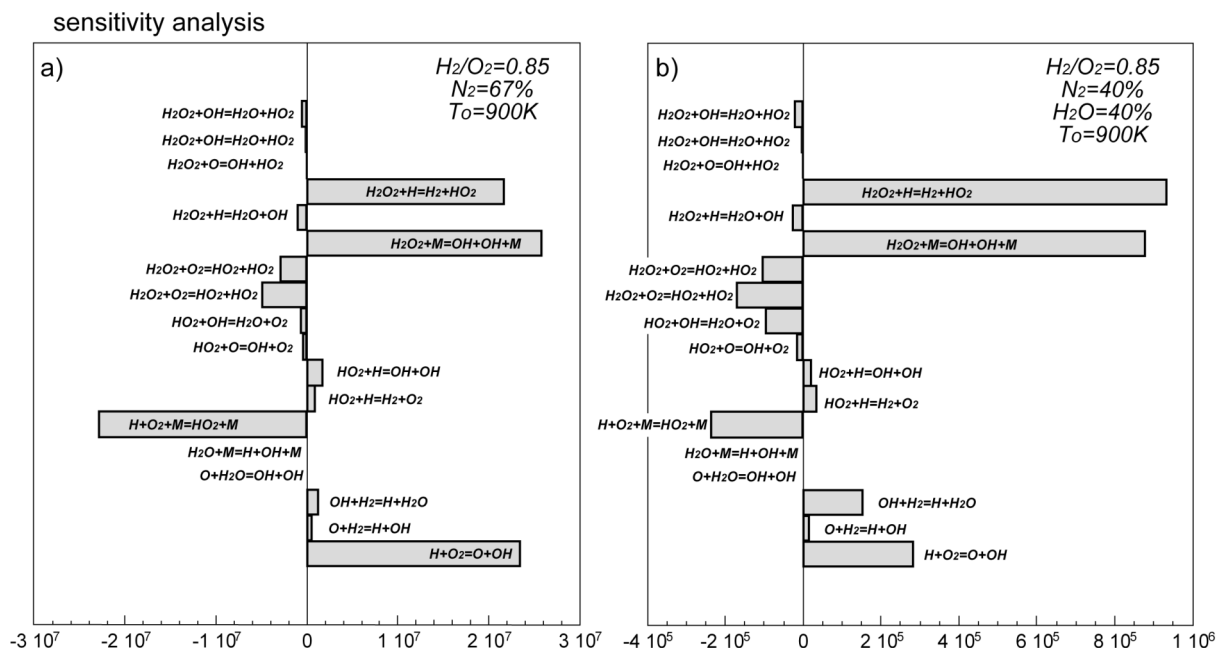
sensitivity analysis

Figure 5. Sensitivity analyses for H_2/O_2 mixture diluted with nitrogen and/or steam for T inlet equal to 900 K.
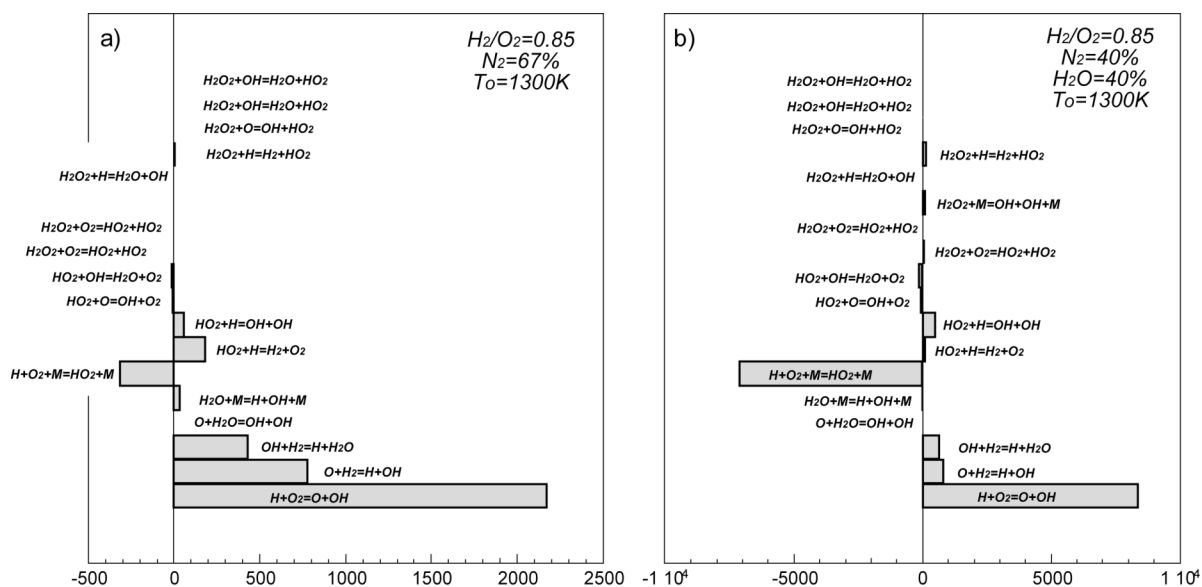

Figure 6. Sensitivity analyses for H_2/O_2 mixture diluted with nitrogen and/or steam T inlet equal to 1300 K.

By analysing the diagrams of Figure 5 and 6 it is clear that the most influential reactions of the system H_2/O_2 are the ones summarized in the Table.

The reaction R1 is important in the initiation phase of the oxidation process. Hence although, it does not have a high sensitivity coefficient, it is reported in the table.

Figure 7 shows the typical hydrogen explosion ignition diagram and the darker band represents conditions in which simulations have been run. This area goes through the extended second explosion limit (Meyer and Oppenheim, 1971; Lee and Hochgreb, 1998) that divides the ignition zone into a "weak" and "strong" regime.

Table. Main reactions of the system H_2/O_2.

$H_2 + O_2 = OH + OH$	R1
$OH + H_2 = H + H_2O$	R2
$H + O_2 = O + OH$	R3
$O + H_2 = H + OH$	R4
$H + O_2 + M = HO_2 + M$	R5
$H_2O_2 + O_2 = HO_2 + HO_2$	R6
$H_2O_2 + H = HO_2 + H_2$	R7
$H_2O_2 + M = OH + OH + M$	R8

In the "strong" regime, the branching reaction, R3, leads to a rapid increase in the amount of radicals through the exothermic reaction R2 and R4, and enhances the reactivity of the system. In the "weak" region reaction, R5 subtracts radicals H from the system H_2/O_2, leading to HO_2. These radicals form H_2O_2 via reactions R6 and R7, which decomposes into 2 radicals OH via the endothermic reaction R8. The reactivity of the system is thus lowered.

Therefore, the second explosion limit is controlled by the competition between the "branching" reaction R3 and the "termination" reaction R5. Numerical calculations with water addition and experimental data showed that steam increases ignition delay time and leads to a shift of the second and extended second explosion limit towards higher temperatures, leading to an increase in the "no ignition" and in the "weak ignition" region, and hence to an enhancement of the ignition delay time for mixtures characterized by the same hydrogen/oxidant ratio and same inlet pressure.

This is due to the high third body efficiency of water. In fact, the breaking reaction R5, in the presence of water and at high pressure, becomes faster than the branching reaction R3.

Discussion

The most significant difference between experimental and numerical ignition delay times occurs in the "weak" ignition zone, expecially for low temperatures. The experimental data of Wang show nearly constant ignition delay times between 1050 and 1150 K. In the literature this behavior has been identified also for several hydrocarbons, for instance, decane (http://www.itm.rwth.de). In order to reproduce this trend, the mechanism of Westbrook has been selected and the kinetics constants of the most influential reactions in this area have been modified. These modifications have been carried out for several

conditions. In the following, the most interesting results are reported for the system with 0.4 MPa and 40% water dilution.
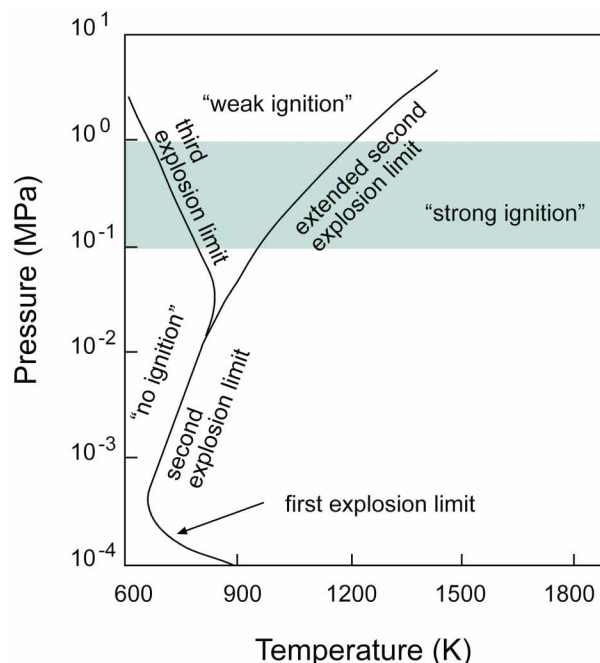
Figure 7. Explosion Hydrogen/Air diagram with the second extended limit.

Furthermore, the rate constants of the reactions $HO_2 + H = H_2O_2 + H_2$ and $HO_2 + HO_2 = H_2O_2 + O_2$ have been modified in several ways. The most interesting result was achieved with a multiplication of the pre-exponential factors of $HO_2 + H = H_2O_2 + H_2$ by 10, as is shown in Figures 8a and 8b. The ignition delay times are decreased at about one order of magnitude. Since this reaction is influential only at low temperatures, it is suitable for modifications. Moreover, the ignition delay times for low temperatures seem to match the experimental values very well. In the zone of the "weak" region, the reaction $H + O_2 + M = HO_2 + M$ has been recognized as the most important. Its kinetic constants have been very well studied, but the influence of water dilution in combustion systems is, in general, less known. Therefore, a variation of the third body efficiency for water has been carried out. In Figure 8c, it is illustrated that an increase of the efficiency (default 14) to 20, 25, and 30 leads to longer delay times at high temperatures, whereas the influence at low temperatures is negligible.
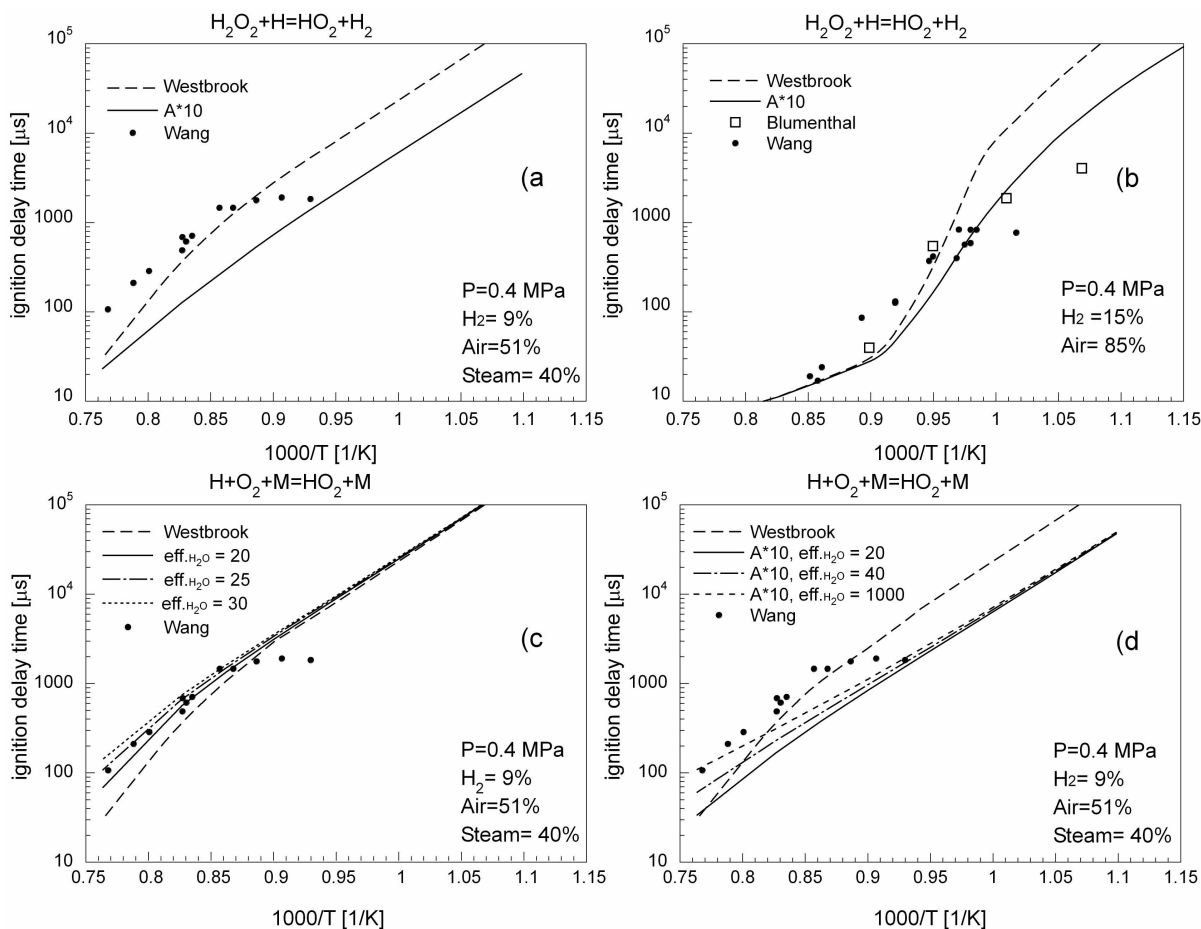
Figure 8. Variation of kinetic constant values in the Westbrook kinetic mechanism.

A combination of theses variations is shown in Figure 8d. In this case, advantage has been taken of the influence of the 2 reactions in the respective temperature regions. First, the velocity of $HO_2 + H = H_2O_2 + H_2$ was increased by a factor of 10, and then the third body efficiency for water in reaction $H + O_2 + M = HO_2 + M$ was raised up to 1000. Although this value might not be very realistic, these simulations clearly show a net increase in the ignition delay time for 1000/T smaller than 1.

Several modifications of the kinetic parameters of the decomposition reaction R8 ($H_2O_2 + M = OH + OH + M$) were realized as well, since it appears to play a very important role in the evolution of the oxidation process, but very significant improvements were not achieved; furthermore, this reaction is very well studied in the literature, and hence it was not considered very suitable for further investigations.

Conclusion

The comparison between experimental and calculated ignition delay times has led to the conclusion that at low temperatures, as well as at high pressures, all investigated hydrogen-oxygen reaction mechanisms are not able to properly reproduce the experimental behavior of H_2/O_2 ignition. Therefore, it is necessary to improve the mechanisms in these ranges of parameters. The aim of this work was the identification of the most influential reactions under the considered conditions. The predicted ignition delay times as a function of the different investigated parameters are correlated to the "weak" and "strong" ignition regimes in which the former is controlled by the pathway responsible for the formation and consumption of H_2O_2, and the latter by radical branching reactions. Since the differences between experimental and calculated ignition delay times occur particularly in the weak ignition zone,

the reactions occurring in this regime were modified. For this investigation, the mechanisms of Westbrook have been selected. An increase of the reaction rate of $HO_2 + H = H_2O_2 + H_2$ by a factor of 10 leads to an elevated H_2O_2 production, and thus to a faster ignition and better agreement with the experiments. The reaction $H + O_2 + M = HO_2 + M$, instead, has been influenced positively by an increased third body efficiency for water.

Although the hydrogen-oxygen mechanism is one of the most investigated chemical systems, the present study has shown that there are still many unanswered questions. Therefore, it is necessary to continue and extend the research in this area, especially concerning experiments under non-standard conditions, such as they are required in new combustion systems like Mild Combustion.

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