Study of Detonation Sensitivity of Hydrogen-Air Mixture Using an Updated Comprehensive Chemical Kinetic Mechanism

Hoi Dick Ng[1], Yiguang Ju[2] and John H. S. Lee[1]

[1]Department of Mechanical Engineering, McGill University, Montreal, Canada
[2]Department of Mechanical and Aerospace Engineering, Princeton University, New Jersey, USA
e-mail: eddie.ng@mail.mcgill.ca

1. Introduction

A hydrogen economy has been recognized for many years as an ideal long-term solution to energy related environmental and supply problems. Because of its high sensitivity to explosion, the widespread use of hydrogen creates great public concern. Although deflagrations are more likely the mode of combustion under practical conditions, detonations cannot be considered highly improbable because of the sensitivity of hydrogen. Perhaps one of the possibilities for the occurrence of detonations is when high-pressure hydrogen storage facilities are contaminated by air entrainment.

For most common hydrocarbon fuels, the detonation sensitivity increases for increasing pressure. In other words, the mixture has a greater likelihood to detonate at higher pressures. However, the detonation sensitivity of hydrogen may not follow a similar trend at elevated pressures because of the chain-termination step that leads to the second explosion limit (Lewis & von Elbe 1951). In this paper, a thorough detonation sensitivity analysis of high-pressure hydrogen-air mixture is carried out in order to provide a more current review of the effect of initial pressure.

The dynamic detonation properties (e.g. cell size, initiation energy, etc.) generally provide a basic indication of detonation sensitivity. Correlations with chemical length scales have been established as an accepted technique for estimating these dynamic detonation parameters (Westbrook & Urtiew 1982; Shepherd 1986; etc.). There are indeed few studies using kinetic computations to quantify the effect of initial pressure on the hydrogen-air detonation sensitivity, notably by Westbrook & Urtiew (1982); Stamps & Tieszen (1991); etc. Nevertheless, it has become clear that their results strongly depend on detailed chemical kinetic mechanisms. In view of the uncertainty in the chemical kinetic models considered in previous studies, particularly the lack of pressure dependence reaction kinetics, there is a need to revisit the problem of detonation sensitivity of high-pressure hydrogen-air mixture using a state-of-the-art reaction mechanism for a more realistic assessment.

In this study, the most recent kinetic data for hydrogen oxidation are considered to accurately compute different chemical kinetics parameters, from which the detonation cell size can be estimated using a semi-empirical correlation. As a result, the detonation sensitivity can be assessed. The present paper thus reports some results obtained using a recently updated H_2/O_2 chemical kinetic mechanism for detonation analysis. The detonation sensitivity of hydrogen-air mixture at elevated pressure is then addressed in detail using the validated reaction mechanism.

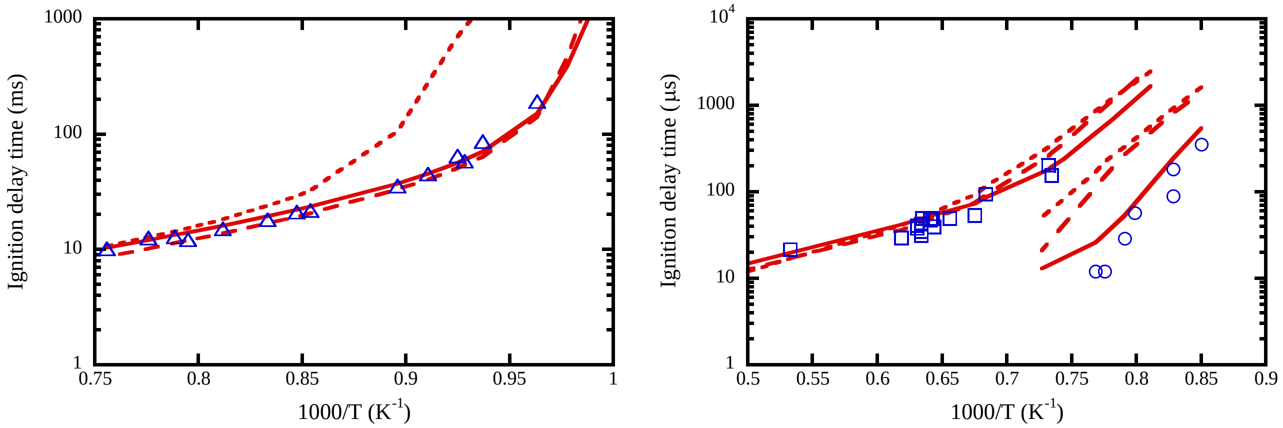

Figure 1. Comparison of ignition delay time obtained by model prediction using the chemical kinetic mechanisms of (—) Li *et al.* (2004), (---) Jachimowski (1988) and (···) Petersen & Hanson (1999) with experimental data by (a) Bhaskaran *et al.* (1973) for stoichiometric hydrogen-air mixture at 2.5atm Δ; (b) Petersen *et al.* (1995) for 2.0%H_2+1.0%O_2+97%Ar at 33atm ○ and 0.1%H_2+0.05%O_2+99.85%Ar at 64atm □

2. An updated comprehensive H_2/O_2 reaction mechanism

A comprehensive chemical kinetic mechanism of H_2 combustion has been recently developed by Li *et al.* (2004). It has been tested against a very wide range of experimental data, including laminar flame speed at normal or elevated temperature and pressure, shock tube ignition delay and other data from static and stirred reactors. The mechanism consists of 19 reversible elementary reactions based on the work of Mueller *et al.* (1999). It has been revised using recently published kinetic and thermodynamic information in literature. Among different updates, the most important revision is the reaction rate constant of the key chain-branching reaction (R1) and the chain termination reaction (R2), which should have significant effects on the prediction of detonation parameters. Some experimental ignition delay data from shock tube experiments along with the prediction using this updated mechanism and two commonly used mechanism for detonation simulations (Shimizu *et al.* 2001) are shown in figure 1.

3. Prediction of detonation cell sizes from chemical kinetics

The characteristic cell size is generally considered as a parameter to characterize the detonation sensitivity of a given mixture. The smaller the cell size, the more sensitive to detonation is the mixture. Knowledge of the cell size also permits the detonation limits as well as the critical energy for direct initiation to be estimated (Lee 1984). It is well established that the cell size can be predicted from some length scale and chemical kinetic properties determined by the reaction zone structure. With the availability of the present detailed reaction mechanism for hydrogen-air, different chemical kinetic parameters can be computed accurately by solving the one-dimensional steady-state ZND structure of a detonation. In the present study, a recently developed correlation is used to predict the characteristic cell size for a given mixture and initial condition (Ng 2005), i.e.:

$$\lambda = A(\chi)\cdot\Delta_I = \sum_{k=0}^{N}\left(a_k\chi^{-k} + b_k\chi^{k}\right)\cdot\Delta_I$$

$$\lambda = A(\chi)\cdot\Delta_I = \left[(a_o + b_o) + \frac{a_N}{\chi^N} + \ldots\frac{a_1}{\chi} + b_1\chi + \ldots b_N\chi^N\right]\cdot\Delta_I$$

$$= \left[A_o + \left(\frac{a_N}{\chi^N} + \ldots\frac{a_1}{\chi} + b_1\chi + \ldots b_N\chi^N\right)\right]\cdot\Delta_I$$

where Δ_I is the induction zone length and χ a non-dimensional stability parameter defined as:

$$\chi = \varepsilon_I\frac{\Delta_I}{\Delta_R} = \varepsilon_I\Delta_I\frac{\dot{\sigma}_{\max}}{u'_{CJ}}$$

ε_I, Δ_R, $\dot{\sigma}_{\max}$ and u'_{CJ} denote the activation energy of the induction process, main heat release zone length, maximum thermicity and CJ particle velocity in shock-attached frame, respectively (Ng *et al.* 2005). The other coefficients, as shown in table 1, are obtained from a multi-variable least square fitting for $N = 3$ with available experimental data using Matlab.

This improved correlation takes into account all characteristic features within the ZND reaction zone structure, i.e. both the sensitivity as well as the shape of the reaction structure. It is found to provide a good estimate of cell size within a factor of 2 for a very wide range of mixture and initial conditions. The improved correlation thus involves a minimum number of parameters to represent with a good accuracy a maximum number of experimental data.

Coefficients	**Values**
A_o	30.465860763763
a_1	89.55438805808153
a_2	-130.792822369483
a_3	42.02450507117405
b_1	-0.02929128383850
b_2	1.026325073064710 x 10^{-5}
b_3	-1.031921244571857 x 10^{-9}

Table 1. Values of different coefficients in the cell-size correlation

To illustrate the accuracy of the above correlation, figure 2 shows the predicted cell size using the above correlation and the experimentally measured cell size for hydrogen-air mixture as a function of equivalent ratio ϕ for two different initial temperatures. This comparison shows that the correlation in general gives quantitatively a very good estimate the experimental results.

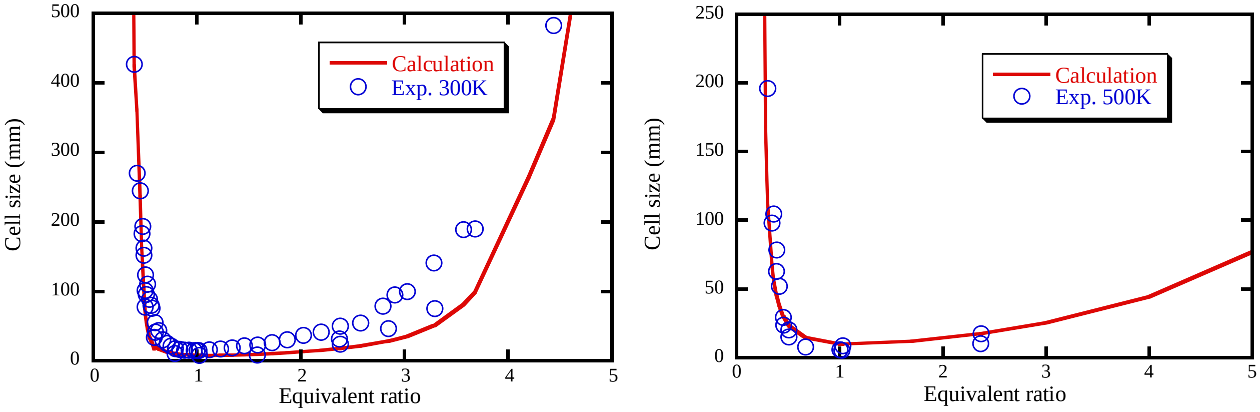

Figure 2. Comparison of cell size between experimental data and calculated values for hydrogen-air mixture as a function of equivalent ratio at different initial temperatures

4. The effect of initial pressure

Using the improved correlation with the updated comprehensive reaction mechanism for hydrogen oxidation, we can predict the cell size with better accuracy and re-examine the detonation sensitivity for hydrogen-air mixtures at elevated initial pressure. Figure 3a shows the predicted cell size and available experimental data as a function of initial pressure for hydrogen-air mixture with different equivalent ratios. For most fuel/air mixtures, it is expected that the cell sizes decrease with increasing initial pressure. However, it can be seen from figure 3a that at a certain range of high initial pressure, there is a gradual increase in the cell size for hydrogen-air mixture. These results agree with calculations from previous studies (e.g. Stamps & Tieszen 1991). It is also shown that this effect is more pronounced for off-stoichiometric conditions (figure 3b).

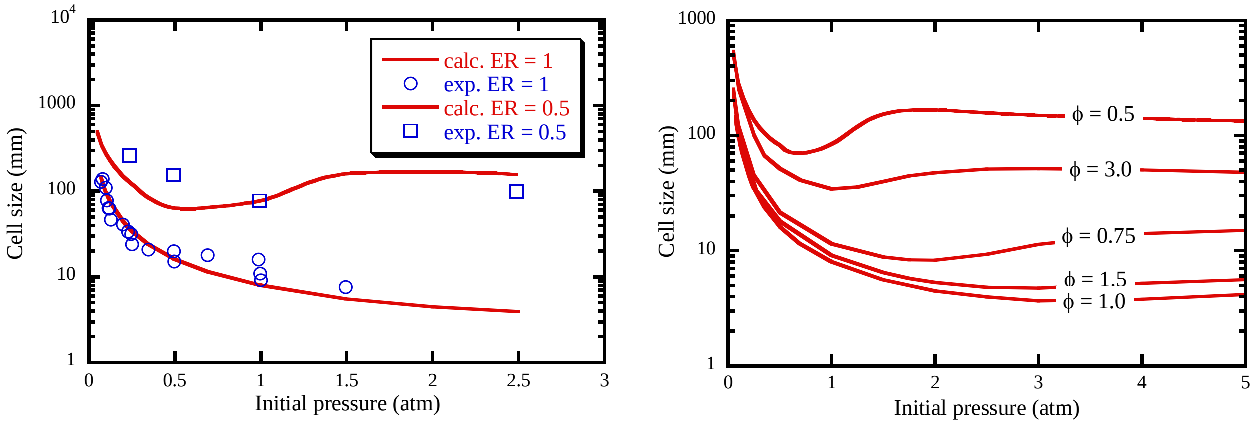

Figure 3. The effect of initial pressure on the detonation cell size of hydrogen-air mixture

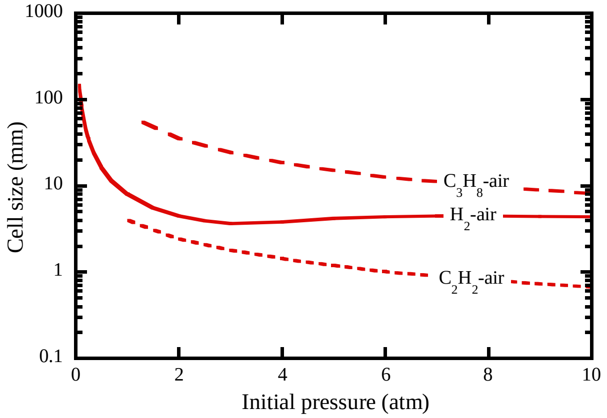

Figure 4. The effect of initial pressure on the detonation cell size of different fuel-air mixtures

Figure 4 compares the influence of initial pressure for some stoichiometric hydrocarbon-air mixture and hydrogen-air mixture. The difference is clear that hydrogen-air does not follow the same trend of a decrease in cell size with increasing initial pressure. One can also note that the magnitude of cell size also becomes comparable with that of hydrocarbon-air mixture at very high initial pressure. Equivalently, hydrogen-air mixture is not more sensitive than any typical hydrocarbon-air mixture at elevated initial pressure.

4.1 Explosion limits

The cause of the gradual increase in cell size at elevated pressure has been understood from the point of view of explosion limits for hydrogen oxidation (Stamps & Tieszen 1991; Lu *et al.* 2003; etc.). The explosion limit refers to the pressure-temperature boundaries that define rapid runaway chemical reactions and the stable conditions in a homogeneous explosive mixture (Lewis & von Elbe 1951). For hydrogen mixture, the three explosion limits are well established, known as the Z-shaped curve on the pressure-temperature diagram. The first and second limits are governed by the generation of radicals H, O and OH via the controlling chain-branching process $H + O_2 \rightarrow O + OH$ (R1). At low pressure, the first limit defines the boundary below which explosion is suppressed, where diffusion losses of free radicals to the wall of the vessel dominate over the production of the radicals via the chain-branching reaction. The second limit results from the quenching of the explosion when the pressure is increased. This is due to the competition between the branching process $H + O_2 \rightarrow O + OH$ (R1) and the three-body chain-termination process $H + O_2 + M \rightarrow HO_2 + M$ (R2). With increasing pressure, the chain-termination effect by the three-body termination reaction (R2) becomes significant and, thus, limits radical explosion by the two-body branching reaction (R1). As pressure further increases, second branching reactions involving the formation and decomposition of H_2O_2 yield the third explosion limit beyond which explosion occurs.

The (extended) second explosion limit effects can be used to address the detonation sensitivity behavior of hydrogen-air mixture at elevated initial pressure. It can be shown using steady-state approximation that the second explosion limit condition can be obtained from the kinetic rate relation $2k_1 = k_2 \cdot [M]$, where $[M]$ is the third body concentration. This expression relates the chemical-kinetic condition for branched-chain explosion in terms of temperature, pressure and mixture composition and yields the crossover temperature T_B. As shown by Belles (1959), it is convenient to express the branched-chain explosion condition in terms of shock strength by using the standard normal shock wave relationship. This gives a critical Mach number satisfying the kinetic requirement for explosion.

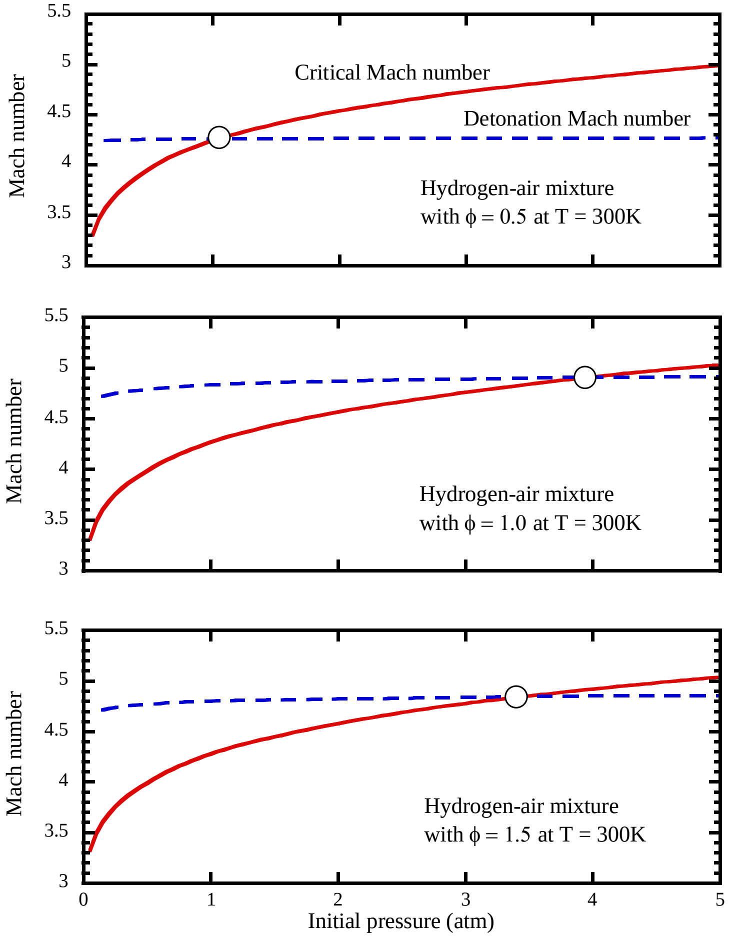

Figure 5. The critical Mach number corresponding to the second explosion limit criterion and detonation Mach number as a function of initial pressure for hydrogen-air mixture. The circle indicates the crossover point between these two Mach numbers.

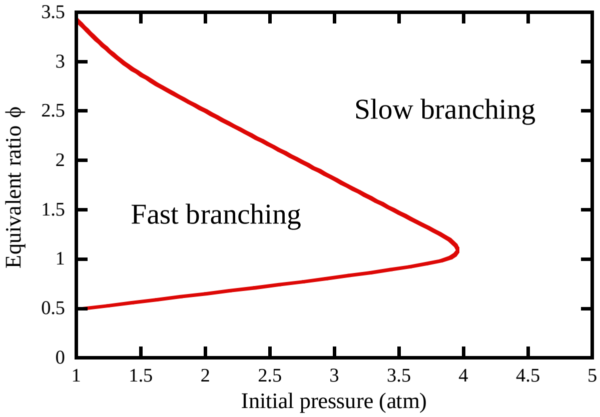

Figure 6. Boundary between fast and slow branching regimes for hydrogen-air mixture at $T_o = 300K$

Figure 5 shows the variation of the critical Mach number associated with the extended second explosion limit and the detonation Mach number as a function of initial pressure for some given mixture compositions. It is observed from the figure that in general the detonation Mach number does not change significantly with initial pressure. On the contrary, the critical Mach number increases with increasing initial pressure. At some critical initial pressure, there is a crossover point between these two Mach numbers. Above this critical point, the temperature behind the leading front of the ZND detonation structure is below the crossover temperature T_B, at which the chain-termination reaction dominates over the chain-branching reaction, as predicted by the extended second-limit criterion.

It is possible to generalize the above results to identify the regime between slow and fast branching by plotting the critical initial pressure versus equivalent ratio, as shown in figure 6. From figure 6, it can be seen that above the initial pressure $p_o \sim 4$ atm, the chemical kinetics is characterized by slow branching reaction and the global energy release rate is thus generally small. This implies that detonation is unlikely to occur or even if a detonation is directly initiated in an un-congested environment at which turbulence generation by external mean such as obstacles is minimal, it may not be able to maintain its high burning rate necessary for the self-propagation.

5. Critical energy for direct initiation

With the knowledge of characteristic cell sizes, different dynamic detonation parameters can be determined by semi-empirical correlations. For instance, the critical direct initiation energy for hydrogen-air detonation can be estimated using the detonation kernel theory of Lee & Ramamurthi (1977). This phenomenological model states that there exists a critical size of detonation kernel for direct initiation. The size of the detonation kernel corresponds to the shock radius R_s* at which the shock wave has decayed to some critical Mach number M_s* before it re-accelerates back to a Chapman-Jouguet detonation. The appropriate choice of M_s* should reflect the critical shock strength below which any detonation would fail. In many initiation models, the half-CJ value is generally used for the critical Mach number. However, as shown recently by Ng & Lee (2003), the critical Mach number should take into account the chemistry and M_s* corresponds to the value of chain-branching cross-over temperature T_B may appear to be a better choice. For direct initiation of spherical detonations, experimental observations also conclude that the critical radius at which the first explosion bubbles are observed is approximately 10λ (Radulescu *et al.* 2003). For the blast trajectory in a reacting gas, Korobeinikov (1991) derives the solution by treating the contribution from the chemical reactions as a second-order perturbation to the self-similar classical solution of Taylor & Sedov, yielding for the spherical case:

$$R = \left(\frac{E_{source}}{\alpha_2 \rho_o}\right)^{\frac{1}{3}} \left(\frac{2}{5}\frac{1}{U}\right)^{\frac{2}{3}} \exp\left(\frac{\beta_2 Q}{3U^2}\right)$$

where Q is the heat of reaction, α_2 and β_2 are dimensionless constants estimated by Korobeinikov using the following fit:

$$\alpha_2 = 0.31246(\gamma - 1)^{-1.1409 - 0.11735 \log_{10}(\gamma - 1)}$$
$$\beta_2 = 4.1263(\gamma - 1)^{1.2530 + 0.14936 \log_{10}(\gamma - 1)}$$

Together with the value of critical Mach number M_s* obtained from the second-limit criterion and the cell size correlation discussed earlier in the paper, the critical direct initiation energy for a given hydrogen-air mixture can be obtained.

Figure 7 compares the results from theoretical prediction with available experimental data for hydrogen-air mixture with different equivalent ratios at T_o = 300 K and p_o = 1 atm. It can been seen that both results are in very good agreement (within an order of magnitude for a wide range of equivalent ratio ϕ). Figure 7b shows the effect of initial pressure on the critical initiation energy. Similar to the cell size variation, the critical energy for direct initiation also increases gradually with increasing initial pressure, which equivalently implies that the mixture is actually less sensitive at elevated pressure.

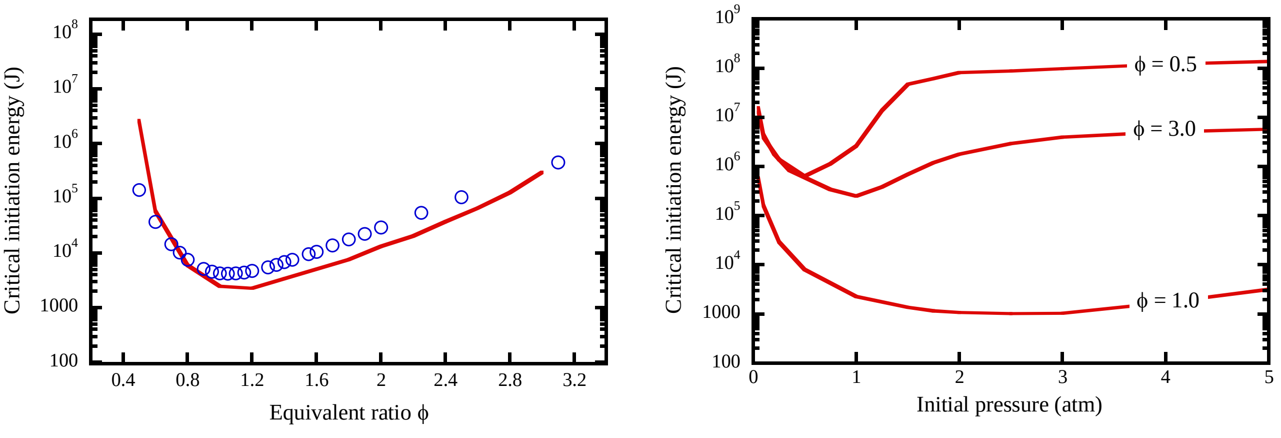

Figure 7. Critical initiation energy for direct initiation of a spherical detonation obtained from the prediction (solid line) and experimental data (o Benedick *et al.* 1986) in hydrogen-air mixture as a function of (a) equivalent ratio; and (b) initial pressure

6. Concluding remarks

This paper presented results of a detonation sensitivity analysis using a recently updated kinetic mechanism of H_2 combustion. Using simple semi-empirical models, the chemical kinetic analysis based on the updated mechanism provides good estimation of various dynamic parameters for hydrogen-air detonations.

The objective of this study is to use an accurate detailed chemical kinetics model to minimize the uncertainty in determining and studying the detonation sensitivity at some extreme conditions where experimental data are lacking. In particular, the effect of elevated initial pressure on the detonation sensitivity of hydrogen-air mixture is examined. It is found that after a critical initial pressure around 4 atm, the hydrogen-air mixture becomes less sensitive with further increase in initial pressure. It is shown that the second explosion limit effect plays a significant role leading to slow branching reactions above this critical pressure.

In conclusion, in spite of the fact that hydrogen as a fuel is the most sensitive one compared to the other common gaseous fuels at standard conditions, it appears from the present study that the probability of having a detonation of hydrogen-air mixture in elevated initial pressure is not higher than in the other hydrocarbon fuels.

Acknowledgement

The authors would like to thank Juan Li for providing the chemical reaction mechanism.

References

1. Belles, F. E. (1959) Detonability and chemical kinetics: prediction of limits of detonability of hydrogen. *Proc. Comb. Inst.* **7**, 745-751
2. Benedick, W. B., Guirao, C. M., Knystautas, R. & Lee, J. H. S. (1986) Critical charge for the direct initiation of detonation in gaseous fuel-air mixtures. *Prog. Astronaut. Aeronaut.* **106**, 181-202
3. Bhaskaran, K. A., Gupta, M. C. & Just, T. (1973) Shock tube study of the effect of unsymmetric dimethyl hydrazine on the ignition characteristics of hydrogen-air mixtures. *Combust. Flame* **21**, 45-48
4. Eckett, C. A., Quirk, J. J. & Shepherd, J. E. (2000) The role of unsteadiness in direct initiation of gaseous detonation. *J. Fluid Mech.* **421**, 147-183
5. Jachimowski, C. J. (1988) An analytical study of the. hydrogen-air reaction mechanism with application to scramjet combustion. *NASA TP*- 2791
6. Kaneshige, M. & Shepherd, J. E. (1997) Detonation database. *GALCIT Technical Report FM97-8* (http://www.galcit.caltech.edu/detn_db/html/)
7. Korobeinikov, V. P. (1991) *Problems of Point-Blast Theory*. American Institute of Physics, New York
8. Lee, J. H. S. (1977) Initiation of gaseous detonation. *Ann. Rev. Phys. Chem.* **28**, 75-104

9. Lee, J. H. S. (1984) Dynamic parameters of gaseous detonations. *Ann. Rev. Fluids Mech.* **16**, 311-336
10. Lewis, B. & von Elbe, G. (1951) *Combustion, Flames, and Explosions of Gases*. New York, Academic Press
11. Li, J., Zhao, Z. W., Kazakov, A. & Dryer, F. L. (2004) An updated comprehensive kinetic model of hydrogen combustion. *Int. J. Chem. Kinet.* **36**, 566-575
12. Lu, T., Law, C. K. & Ju, Y. (2003) Some aspects of chemical kinetics in Chapman-Jouguet detonation- Induction length analysis. *J. Prop. Power* **19**(5), 901-907
13. Mueller, M. A., Kim, T. J., Yetter, R. A. & Dryer, F. L. (1999) Flow reactor studies and kinetic modeling of the H_2/O_2 reaction. *Int. J. Chem. Kinet.* **31**, 113-125
14. Ng, H. D. (2005) *The Effect of Chemical Reaction Kinetics on the Structure of Gaseous Detonations*. Ph.D. Thesis, McGill University, Montreal, Canada
15. Ng, H. D. & Lee, J. H. S. (2003) Direct initiation of detonation with a multi-step reaction scheme. *J. Fluid Mech.* **476**, 179-211
16. Ng, H. D., Radulescu, M. I., Higgins, A. J., Nikiforakis, N. & Lee, J. H. S. (2005) Numerical investigation of the instability for one-dimensional Chapman-Jouguet detonations with chain-branching kinetics. *Combust. Theory Modelling.* (In press)
17. Petersen, E. L. & Hanson, R. K. (1999) Reduced kinetics mechanisms for ram accelerator combustion. *J. Prop. Power* **15**, 591-600
18. Petersen, E. L., Davidson, D. F., Roehrig, M. & Hanson, R. K. (1995) Shock-induced ignition of high-pressure H2O-O2-Ar and CH4-O2-Ar mixtures. *AIAA/ASME/SAE/ASEE Joint Propulsion Conference and Exhibit, 31st, San Diego, USA. AIAA paper* 95-3113
19. Radulescu, M. I., Higgins, A. J., Murray, S. B. & Lee, J. H. S. (2003) An experimental investigation of the direct initiation of cylindrical detonations. *J. Fluid Mech.* **480**, 1-24
20. Shepherd, J. E. (1986) Chemical kinetics of hydrogen-air-diluent detonations. *Prog. Astronaut. Aeronaut.* **106**, 263-293
21. Shimizu, H., Tsuboi, N. & Hayashi, A. K. (2001) Study of detailed chemical reaction model on hydrogen-air detonation. *40th AIAA Aerospace Sciences Meeting and Exhibit, Reno, AIAA paper* 2001-0478
22. Stamps, D. W. & Tieszen, S. R. (1991) The influence of initial pressure and temperature on hydrogen-air-diluent detonations. *Combust. Flames* **83**, 353-364
23. Westbrook, C. K. & Urtiew, P. (1982) Chemical kinetic prediction of critical parameters in gaseous detonation. *Proc. Comb. Inst.* **19**, 615-623