Assessment of detonation hazards in high-pressure hydrogen storage from chemical sensitivity analysis

Hoi Dick Ng[a,*], Yiguang Ju[a], John H.S. Lee[b]

[a]*Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ 08544, USA*
[b]*Department of Mechanical Engineering, McGill University, Montréal, Québec, Canada*

Abstract

In this study, a series of detonation sensitivity analyses have been carried out to assess detonation hazards in hydrogen–air mixture. The present investigation in particular concerns with the effect of elevated initial pressure on the detonation sensitivity, which stems from the renewing interest in preventing possible explosion scenario in hydrogen economy when high-pressure hydrogen storage facilities are contaminated with air. From the steady ZND analyses based on a recently updated comprehensive kinetic mechanism of hydrogen combustion by Li et al. [Int J Chem Kinet 2004;36:566–75] and using improved semi-empirical models, various dynamic parameters, i.e., characteristic cell size and direct initiation energy, for hydrogen–air detonations are estimated and assessed against available experimental data. Results for the hydrogen–air detonation sensitivity indicated that from a purely chemical kinetics consideration, the probability of having a detonation of hydrogen–air mixture at elevated initial pressure is not higher than in other hydrocarbon fuels at elevated initial pressure.
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1. Introduction

A hydrogen economy has been recognized for many years as an ideal long-term solution to energy-related environmental and supply problems. It is perhaps the most ideal fuel that can alleviate the greenhouse gas emissions and a significant fraction of the air pollutant emissions in the world. Particularly in transportation power plants (the automobile engine), hydrogen can replace the diminishing fossil fuel supply.

The simplest and most economical way would be to use hydrogen stored in high-pressure vessel as compressed gas (similar to natural gas). One of the major technical problems associated with the use of hydrogen gas is the safety of storage and handling of the compressed gas in filling stations distributed in a congested populous area. A realistic assessment of explosion hazards in these high-pressure hydrogen storages is thus of practical importance for preventive measures and the

design of effective mitigation scheme in the event of air entrainment into the high-pressure hydrogen storage facilities forming an explosive hydrogen–air mixture. There are many ways in which air could get in the high-pressure hydrogen storage facility. A possible scenario is that when the connection pipe between the multi-stages of the hydrogen compressor cracked and air can then entrain into the system. Moreover, it can also happen that the air in the storage tank may not be purged out completely before hydrogen filling.

Although deflagrations are more likely the mode of combustion under practical conditions, detonations cannot be considered highly improbable because of the high sensitivity of hydrogen. The destructive nature of detonation waves warrants a thorough knowledge of the conditions whereby detonations can be favorably initiated and their propagation can be sustained. This paper critically reviews the effect of elevated initial pressure in hydrogen storage and provides a more current assessment of the detonation sensitivity of high-pressure hydrogen–air mixtures.

The dynamic detonation properties, particularly the characteristic detonation cell size and direct initiation energy,

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* Corresponding author. Tel.: +1 609 258 1411; fax: +1 609 258 6109.
  E-mail address: hoing@princeton.edu (H.D. Ng).

generally provide a basic indication of detonation sensitivity [1]. Correlations with chemical length scales have been established as an accepted technique for estimating these dynamic detonation parameters [2–7]. Advances in the knowledge of the chemical kinetics now permit the idealized reaction zone length of a one-dimensional detonation to be computed (i.e., the so-called ZND reaction zone length) [8]. This represents a characteristic length scale that is based on the chemical kinetics of the reaction, and since the dynamic detonation properties are based on the coupling between the chemistry of the reactions and the gasdynamics of the detonation process, there exists a relationship between the dynamic parameters and the ZND reaction zone length. When experimental data for these detonation parameters of a particular mixture are not available, it is standard practice to compute the ZND reaction zone length and other chemical sensitivity factors and use some semi-empirical correlations to determine the dynamic detonation properties. This procedure has been found to be quite adequate for practical purposes and is used frequently in safety analysis. There are indeed few studies using kinetic computations to quantify the effect of initial pressure on the hydrogen–air detonation sensitivity, notably by Westbrook and Urtiew; Stamps and Tieszen; etc. [3,4]. 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. Therefore, the most recent kinetic data for hydrogen oxidation are considered in this study to accurately compute different chemical kinetics parameters, from which different detonation sensitivity parameters can be estimated using semi-empirical correlations. The detonation sensitivity of hydrogen–air mixture at elevated pressure is then addressed in detail using the validated reaction mechanism.

2. H$_2$/O$_2$ reaction mechanism

A comprehensive chemical kinetic mechanism of H$_2$ combustion has been recently developed by Li et al. [9]. 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. [10]. 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 H + O$_2$ → O + OH (R1) and the chain-termination reaction H + O$_2$ + M → HO$_2$ + M (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
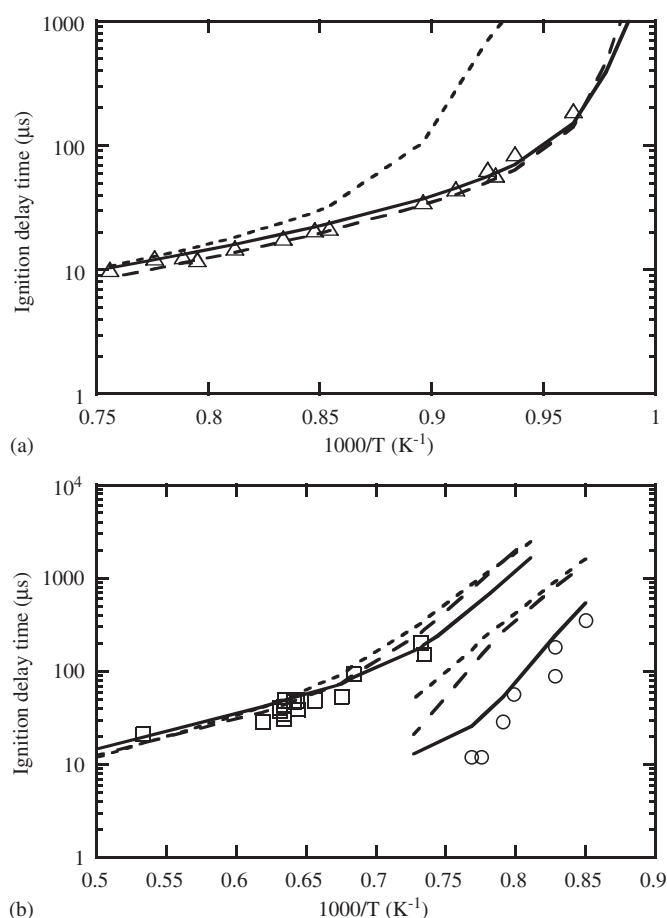

Fig. 1. Comparison of ignition delay time obtained by model prediction using the chemical kinetic mechanisms of (—) Li et al. [9]; (- - -) Jachimowski [25]; and (· · ·) Petersen and Hanson [26] with experimental data by (a) Bhaskaran et al. [27] for stoichiometric hydrogen–air mixture at 2.5 atm △; (b) Petersen et al. [28] for 2.0%H$_2$ + 1.0%O$_2$ + 97%Ar at 33 atm O and 0.1%H$_2$ + 0.05%O$_2$ + 99.85%Ar at 64 atm □.

used mechanisms for detonation simulations [11] are shown in Fig. 1.

3. Detonation cell size

3.1. Prediction 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 [12]. 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 model is used to predict the

Table 1
Coefficients of the improved detonation cell size correlation with $N = 3$

Coefficients	Values
A_0	30.465860763763
a_1	89.55438805808153
a_2	-130.792822369483
a_3	42.02450507117405
b_1	-0.02929128383850
b_2	$1.026325073064710 \times 10^{-5}$
b_3	$-1.031921244571857 \times 10^{-9}$

characteristic cell size for a given mixture and initial condition [13,14], i.e.,

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

$$\lambda = A(\chi) \cdot \Delta_I = \left[(a_0 + b_0) + \frac{a_N}{\chi^N} + \cdots + \frac{a_1}{\chi} \right.$$
$$\left. + b_1 \chi + \cdots + b_N \chi^N \right] \cdot \Delta_I$$
$$= \left[A_0 + \left(\frac{a_N}{\chi^N} + \cdots + \frac{a_1}{\chi} + b_1 \chi + \cdots + b_N \chi^N \right) \right] \cdot \Delta_I,$$
(1)

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

$$\chi = \varepsilon_I \frac{\Delta_I}{\Delta_R} = \varepsilon_I \Delta_I \frac{\dot{\sigma}_{\max}}{u'_{CJ}}.$$
(2)

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 [15]. 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 temperature 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 correlation thus involves a minimum number of parameters to represent with a good accuracy a maximum number of experimental data.

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

3.2. The effect of initial pressure

Using the improved correlation with the updated comprehensive reaction mechanism for hydrogen oxidation, we can predict
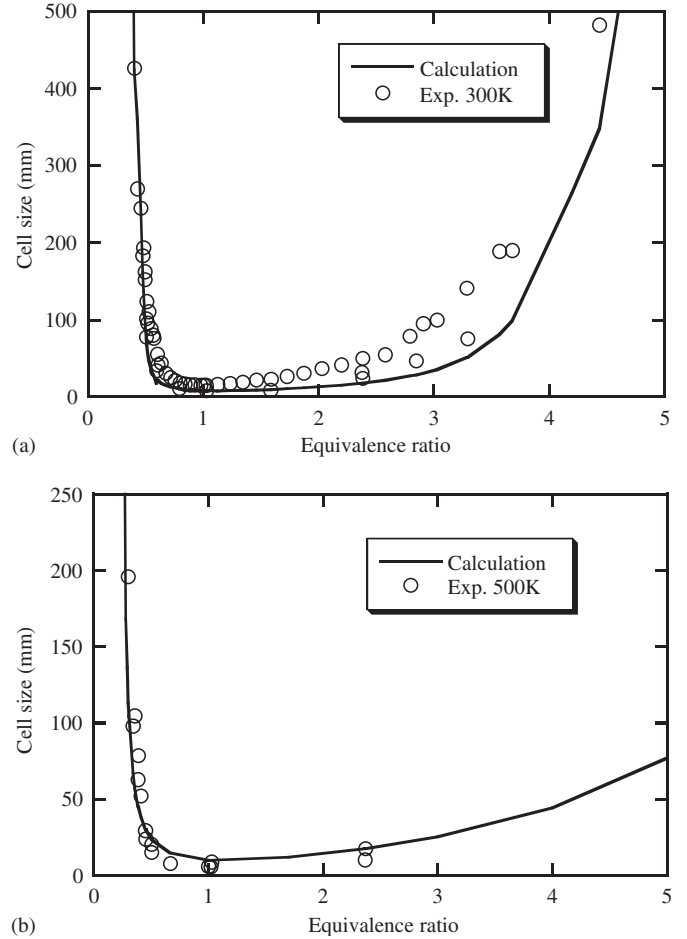

Fig. 2. Comparison of cell size between experimental data [6,29–31] and calculated values for hydrogen–air mixture as a function of equivalence ratio at different initial temperatures.

the cell size with better accuracy and re-examine the detonation sensitivity for hydrogen–air mixtures at elevated initial pressure. Fig. 3a shows the predicted cell size and available experimental data as a function of initial pressure for hydrogen–air mixture with different equivalence ratios.

For most fuel/air mixtures, it is expected that the cell sizes decrease with increasing initial pressure. In other words, the mixture has a greater likelihood to detonate at higher pressures. However, it can be seen from Fig. 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 [4]. It is also shown that this distinct effect is more pronounced for off-stoichiometric conditions (Fig. 3b).

Fig. 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. Another important fact to be observed is 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.
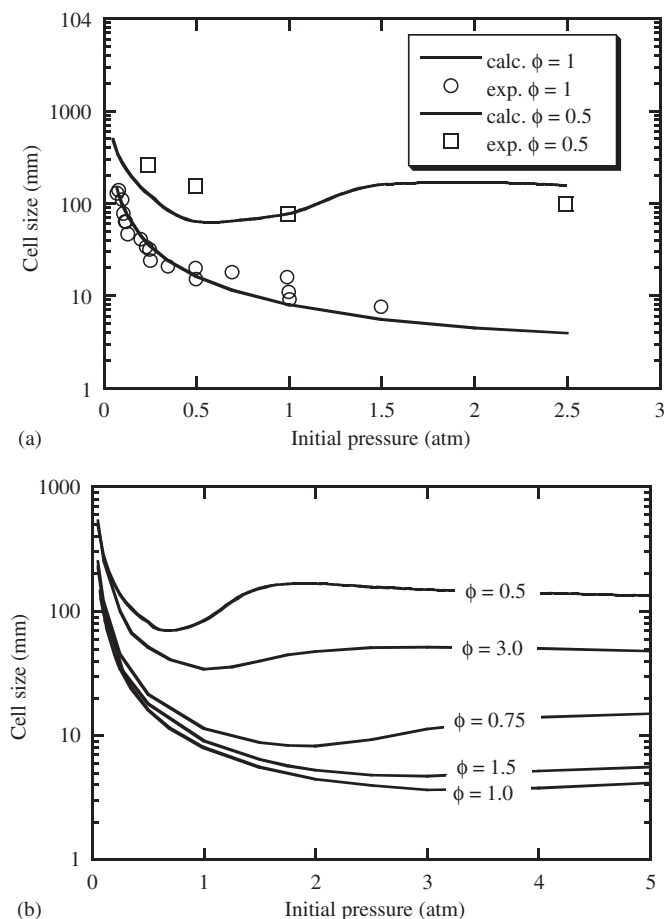
Fig. 3. The effect of initial pressure on the detonation cell size of hydrogen–air mixture. The experimental data are measured by Bull et al. [32] and Stamps and Tieszen [4].
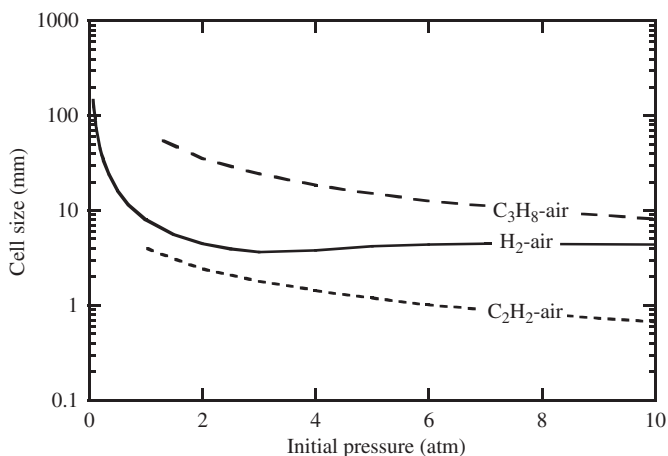

Fig. 4. The effect of initial pressure on the detonation cell size of different fuel–air mixtures. Konnov mechanism [33] is used for the computations of C_2H_2 and C_3H_8.

3.3. 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 [4,16]. Recently, an interesting study has also been carried out by Liang and Bauwens [17] to analyze the reaction zone structure for developing a simplified chemical kinetic model and to investigate the increase of cellular detonation instability near these explosion limits. The explosion limit refers to the pressure–temperature boundaries that define rapid runaway chemical reactions and the stable conditions in a homogeneous explosive mixture [18]. 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 [19], 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.

Fig. 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 equivalence ratio, as shown in Fig. 6. From Fig. 6, it can be seen that above the initial
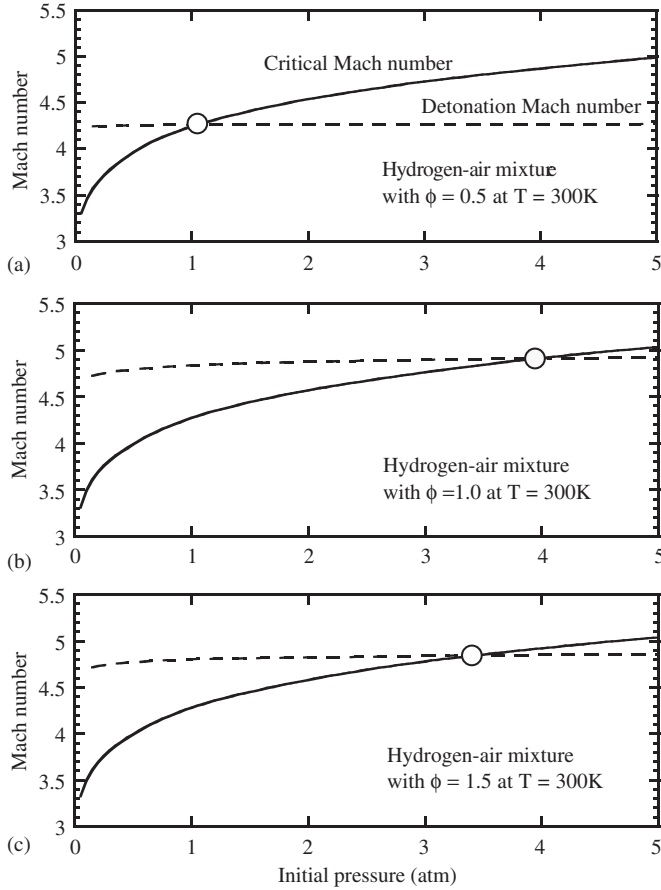
Fig. 5. The critical Mach number corresponding to the second explosion limit criterion and detonation Mach number as a function of initial pressure for hydrogen–air mixture. The circle indicates the crossover point between these two Mach numbers.
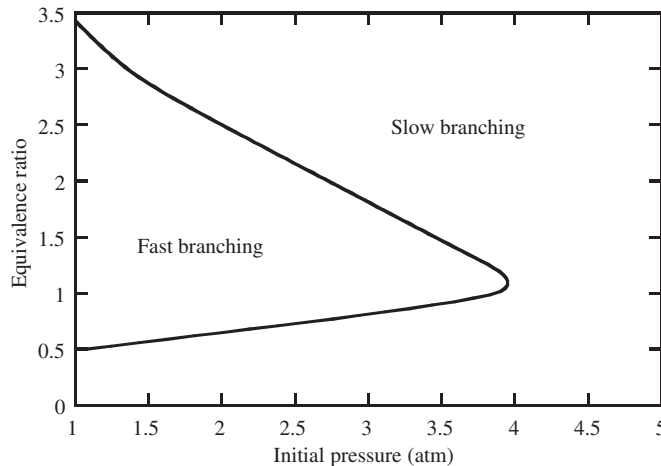

Fig. 6. Boundary between fast and slow branching regimes for hydrogen–air mixture at $T_0 = 300$ K.

pressure $p_0 \sim 4$ atm, the chemical kinetics is characterized by slow branching reaction and the global energy release rate is thus generally small. This again implies that at elevated initial pressure, the mixture becomes chemically less sensitive, in which a detonation also becomes less sensitive to occur. The slow-branching reaction characteristics may not be favorable for the detonation to maintain its high burning rate necessary for the self-propagation.

4. 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 and Ramamurthi [20]. 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 and Lee [21], the critical Mach number should take into account the chemistry and M_s^* that 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 [22]. For the blast trajectory in a reacting gas, Korobeinikov [23] derives the solution by treating the contribution from the chemical reactions as a second-order perturbation to the self-similar classical solution of Taylor and Sedov, yielding for the spherical case [24]:

$$R = \left(\frac{E_{\text{source}}}{\alpha_2 \rho_0} \right)^{1/3} \left(\frac{2}{5} \frac{1}{U} \right)^{2/3} \exp\left(\frac{\beta_2 Q}{3U^2} \right), \qquad (3)$$

where Q denotes the heat of reaction, U the shock velocity and ρ_0 the initial density. α_2 and β_2 are dimensionless constants estimated by Korobeinikov using the following fit:

$$
\begin{aligned}
\alpha_2 &= 0.31246(\gamma - 1)^{-1.1409 - 0.11735 \log_{10}(\gamma - 1)}, \\
\beta_2 &= 4.1263(\gamma - 1)^{1.2530 + 0.14936 \log_{10}(\gamma - 1)},
\end{aligned} \qquad (4)
$$

where γ is the specific heat ratio of the mixture. 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.

Fig. 7 compares the results from theoretical prediction with available experimental data for hydrogen–air mixture with different equivalence ratios at $T_0 = 300$ K and $p_0 = 1$ atm. It can been seen that both results are in very good agreement (within an order of magnitude for a wide range of equivalence ratio ϕ). Fig. 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.
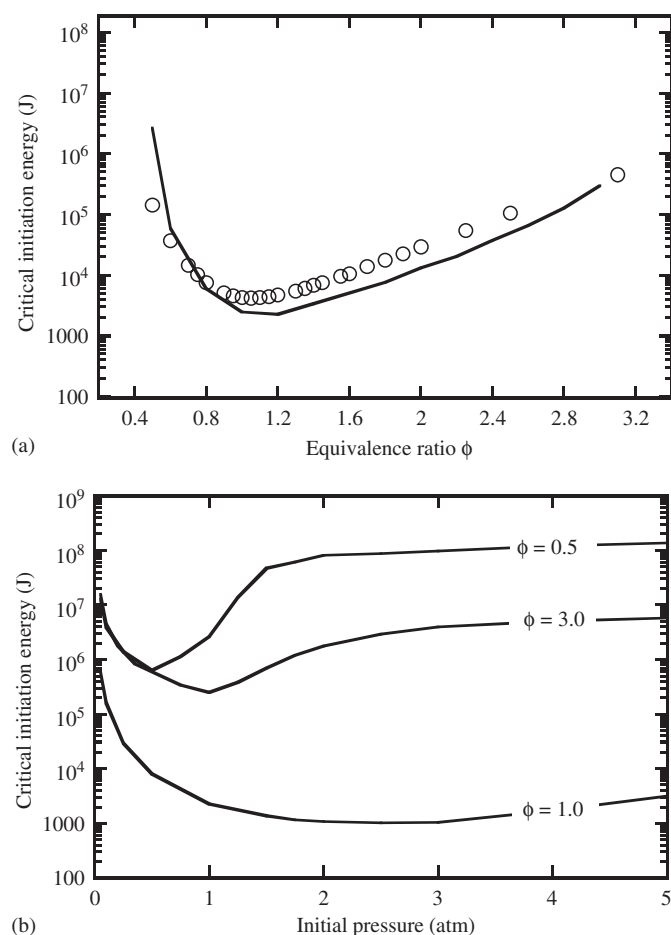
(a)

(b)

Fig. 7. Critical initiation energy for direct initiation of a spherical detonation obtained from the prediction (solid line) and experimental data [34] in hydrogen–air mixture as a function of (a) equivalence ratio and (b) initial pressure.

5. 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 demonstrated 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 at elevated initial pressure is not higher than in other hydrocarbon fuels at elevated initial pressure.

Acknowledgments

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