

EVALUATION OF HYDROGEN, PROPANE AND METHANE-AIR DETONATIONS INSTABILITY AND DETONABILITY

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ABSTRACT

In this paper, the detonation propensity of different compositions of mixtures of hydrogen, propane and methane with air has been evaluated over a wide range of compositions. We supplement the conventional calculations of the induction delay with calculations of the characteristic acceleration parameter recently suggested by *Radulescu, Sharpe and Bradley* (RSB) to characterize the instability of detonations. While it is well established that the ignition delay provides a good measure for detonability, the RSB acceleration, or its non-dimensional form χ , provides a further discriminant between mixtures with similar ignition delays. The present assessment of detonability reveals that while a stoichiometric mixture of hydrogen-air has an ignition delay one and two orders of magnitude shorter than, respectively, propane and methane, hydrogen also has a χ parameter smaller by respectively one and two orders of magnitude. Its smaller propensity for instability is reflected by an RSB acceleration parameter similar to the two hydrocarbons. The predictions however indicate that lean hydrogen mixtures are likely to be much more unstable than stoichiometric ones. The relation between the χ parameter and potential to amplify an unstable transverse wave structure has been further determined through numerical simulation of decaying reactive Taylor-Sedov blast waves. Using a simplified two-step model calibrated for these fuels, we show that methane mixtures develop cellular structures more readily than propane and hydrogen, when observed on similar induction time scales. Future work should be devoted towards a quantitative inclusion of the RSB parameter in assessing the detonability of a given mixture.

Keywords- Detonability, Hydrogen-Air, χ parameter, Two-Step Model.

1.0 INTRODUCTION

Investigation of explosion hazards and detonability has received considerable attention in recent years [1]. Detonability is conventionally assessed by a characteristic time or length scale reflecting the chemical kinetic rates behind the lead shock. The induction time, or alternatively the cell size, has been proposed as indicators of detonability. Consequently, a mixture with faster chemical kinetics rate (shorter induction time scale and smaller detonation cell size) is considered more detonable. On that basis, there have been many experimental measurements of cell size which have been conducted for a wide range of fuels [2]. Empirical correlations now link the cell size to other sensitivity parameters of detonations such as critical initiation energy and critical tube diameter [3].

Nevertheless, taking the ignition delay or cell size alone as the representative of mixture sensitivity does not permit to differentiate between mixtures known to behave differently [4]. For instance, at the same cell size, mixtures with an unstable detonation structure are found more detonable than those with regular detonation structures [5].

Such discrepancies have been attributed to the three-dimensional cellular structure of detonations and potential role of hot spots [6-8]. Recent experimental observations of the reaction zone structure of unstable detonations [9, 10] have revealed the fundamental role of hot spot ignition on the sensitivity of different fuels to detonation. Following the energy addition by shock compression and after the induction process of duration t_i , energy is liberated to fluid element on time scale t_e . Due to energy addition, the fluid element expands which leads to propagation of compression waves. The

compression waves can increase the reactivity of neighboring fluid elements and triggering the exothermicity in phase with pressure wave propagation which would amplify the pressure waves. One-dimensional studies have shown that the propensity for pressure wave amplification requires exothermic times t_e short compared with the ignition delay times t_i [11]. Since t_i is the time scale for the reactivity gradient to be set by the shock, shorter t_e means there is sufficient time to accelerate the pressure wave on the time scale of the gradient. Moreover, a large amount of heat release also contributes to the enhancement of the pressure wave amplification process. Also when the chemical reaction rate sensitivity to reaction is large, i.e., a large activation energy, there would be a strong coupling between the neighboring fluid elements favoring the amplification [11].

Therefore, due to the above mentioned insufficiency of the ignition delay alone to be correlated to detonability, researchers have sought other indicators to characterize the propensity of mixtures to detonation. One-dimensional studies by Radulescu & Tang and Sharpe [11, 12] have identified that the acceleration of reaction wave following shock compression is given non-dimensionally by

$$\chi = \frac{t_i}{t_e} \frac{E_a}{RT} \frac{Q}{RT} \quad (1)$$

In the above equation E_a/RT is the non-dimensional activation energy, T is the local temperature, R is the universal gas constant, Q/RT is the non-dimensional heat release and t_i/t_e the ratio of induction to reaction time scales. Radulescu, Sharpe and Bradley suggested that this parameter controls the acceleration of reaction waves in hot spot ignition. Sharpe [12] and Tang & Radulescu [11] found this parameter by studying the shock induced ignition and acceleration of the reaction zone. Bradley [13] arrived at this parameter by analyzing the propensity of hot spots to amplify pressure waves. Radulescu, Sharpe and Bradley also found the dimensional variant of equation (1) as a characteristic acceleration to indicate the propensity of different reactive mixtures to develop instabilities, strong internal pressure waves and turbulence in the reaction zone [14].

$$a_c = \frac{c\chi}{t_i} = \frac{c}{t_e} \frac{E_a}{RT} \frac{Q}{RT} \quad (2)$$

where c is the local sound speed in the medium.

The precise role of χ on influencing the detonation stability was further investigated numerically in one-dimensional simulations by Ng *et al.* [15] and Leung *et al.* [16]. Both studies, considering the χ parameter without the effect of heat release, showed that the onset of instabilities in many systems correlate with a critical value of $\chi \approx 10$. Taking the heat release normalized by the post shock condition approximately 5-10, yields a critical χ parameter of 50-100 in our scales. Also Borzou *et al.* confirmed these observations in two dimensions [17].

In this paper, we compute both the ignition delay time and the characteristic acceleration χ suggested by Radulescu, Sharpe and Bradley to further discriminate between mixtures of similar ignition delay. Ignition delays and the RSB acceleration parameter are reported for hydrogen-air, methane-air and propane-air using detailed chemical-kinetic models. We also report the results of 2D simulations of decaying reactive blast waves, in which we monitor the instability of the decaying shock wave, and its propensity to develop cellular structures. The simulations are performed using a two-step model, for which the induction and reaction zones can be modeled independently. The results of these numerical simulations are used to determine the relation between the growth of instabilities, regularity of cellular structure and the stability parameter χ .

2.0 THERMAL AND KINETIC MODELLING

In this paper we have calculated the RSB acceleration for a variety of hydrogen, methane and propane-air mixtures. The calculations have been performed for a range of compositions from the lean to the rich limit in the framework of a two-step model. Evaluation of the RSB acceleration requires

extraction of the characteristic time scales for induction (t_i) and reaction (t_e), the characteristic activation energy of the induction stage, and the heat release. While there are numerous methods that can be used to extract meaningful values for detonation simulations [4, 10, 18], the present study follows the following method.

We choose the Von Neuman (VN) shock state of detonations propagating at CJ velocity as the reference state at which we evaluate the relevant thermal-kinetic parameters. The VN state is found through chemical equilibrium calculations performed with the NASA CEA code [19]. The calculations provide us the shock speed. The post shock conditions are obtained also using the NASA CEA code, by assuming the composition remains frozen across the shock.

The reactivity of the gas at the VN state is then evaluated through constant volume calculations of the reactive mixture. Figure 1, for example, shows the evolution of the temperature for stoichiometric hydrogen-air. We define the induction time as the delay to the point of maximum exothermicity, i.e. maximum dT/dt . The characteristic reaction time t_e is taken as the characteristic time scale for the rise, i.e. $t_e = (d(\ln T)/dt)^{-1}$, evaluated at the point of maximum energy release rate. Figure 1 provides, for example, a graphical representation of this characteristic reaction time.

The activation energy is extracted from the approximate dependence of the ignition delay t_i on initial temperature, which can be approximated by

$$t_i \propto \exp\left(\frac{E_a}{RT}\right) \quad (3)$$

The activation energy can thus be obtained by calculating the ignition delays at two different temperatures bracketing the VN state. We chose the bracketing temperatures as T_{vN} and $T_{vN} + 100K$ to get the corresponding ignition delay times. We obtain

$$\frac{E_a}{RT_{vN}} = \frac{1}{T_{vN}} \left(\frac{\ln(\tau_+) - \ln(\tau)}{1/T_{vN+} - 1/T_{vN}} \right) \quad (4)$$

All the constant volume calculations were performed using the CANTERA package [20]. The hydrogen-air calculations were performed using the Li et al. kinetic mechanism, developed for hydrogen. The propane-air calculations were performed using the Sandiego mechanism [21]. The methane-air calculations were performed using the GRI-3.0 mechanism developed for methane.

The heat release parameter extracted from equilibrium calculations was such that a perfect gas model using this value of energy release and the ratio of specific heats evaluated at the VN point yielded the exact CJ detonation Mach number[1], i.e.,

$$\frac{Q}{RT_o} = \frac{\gamma}{2(\gamma^2 - 1)} \left(M_{CJ} - \frac{1}{M_{CJ}} \right)^2 \quad (5)$$

In order to remain compatible with a perfect gas model, the heat release normalized the VN temperature was obtained by using the perfect gas shock jump relation for the CJ Mach number. This ensures that a perfect gas model using the provided heat release parameter and specific heat ratio will yield the correct Mach number.

The results of ignition delay are shown in figure. 2. The ignition delay time is plotted versus equivalence ratio for the three fuels. As can be seen in figure 2, the shortest ignition delays occur near the stoichiometric composition for all three mixtures. This is due to the fact that the shock temperature is highest at this composition, owing to the largest heat release (see Figure 6). At stoichiometric compositions, hydrogen has an ignition delay shorter than propane by an order of magnitude, which in turn has an order of magnitude lower ignition delay than methane.

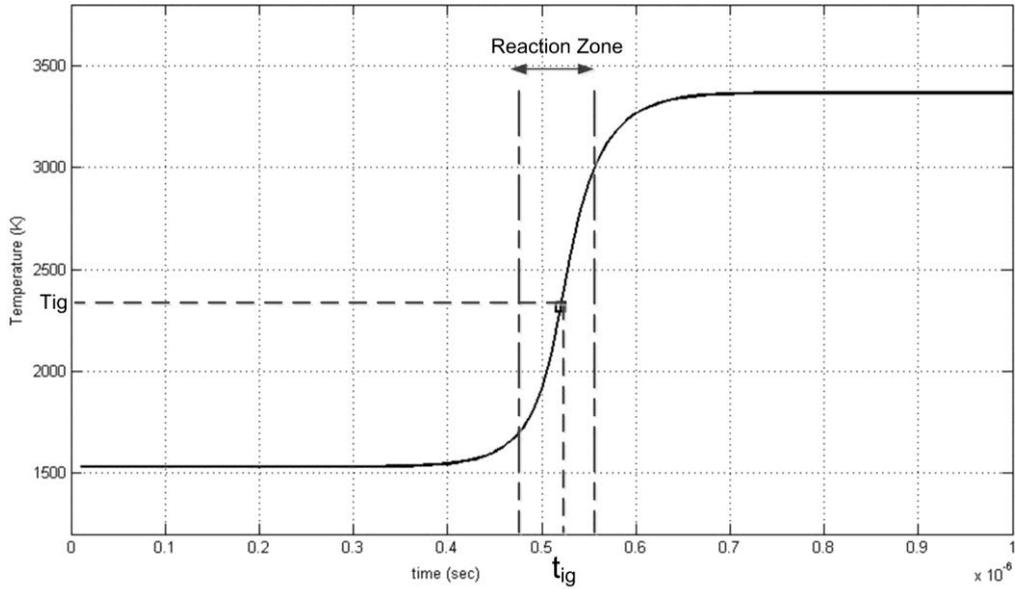


Figure 1. Temperature evolution during the combustion of stoichiometric hydrogen-air mixture

Figure 3 shows the variation of activation energy for the three fuels. While at stoichiometric compositions hydrogen has much lower activation energy than both propane and methane, the activation energy radically grows on both the lean and rich sides. This is due to the fall in the shock temperature. In hydrogen, due to the chain-branching cross-over effect, the activation energy dramatically increases, as already noted elsewhere [22].

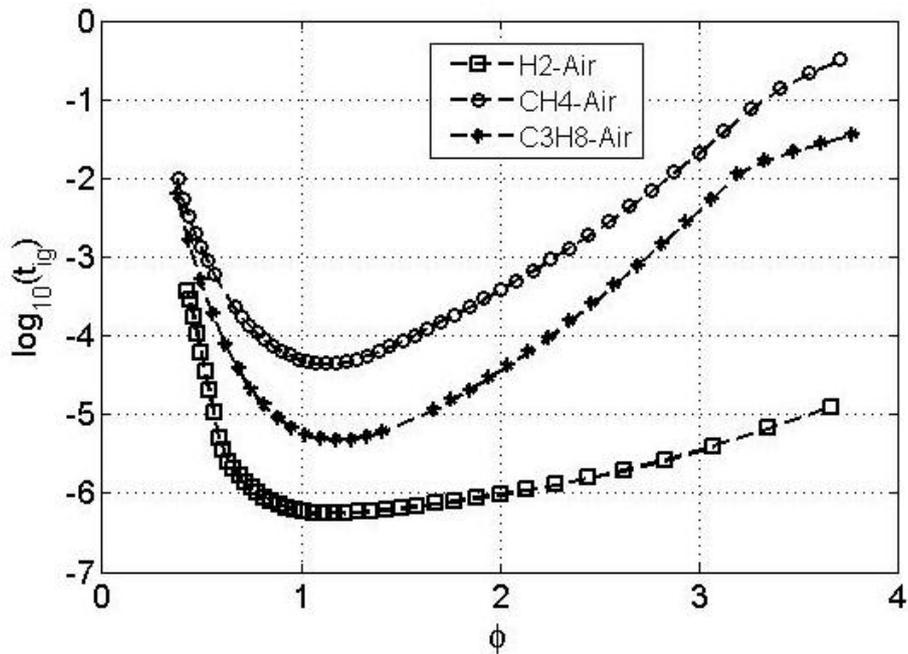


Figure 2. Ignition delay for various compositions of hydrogen, methane and propane

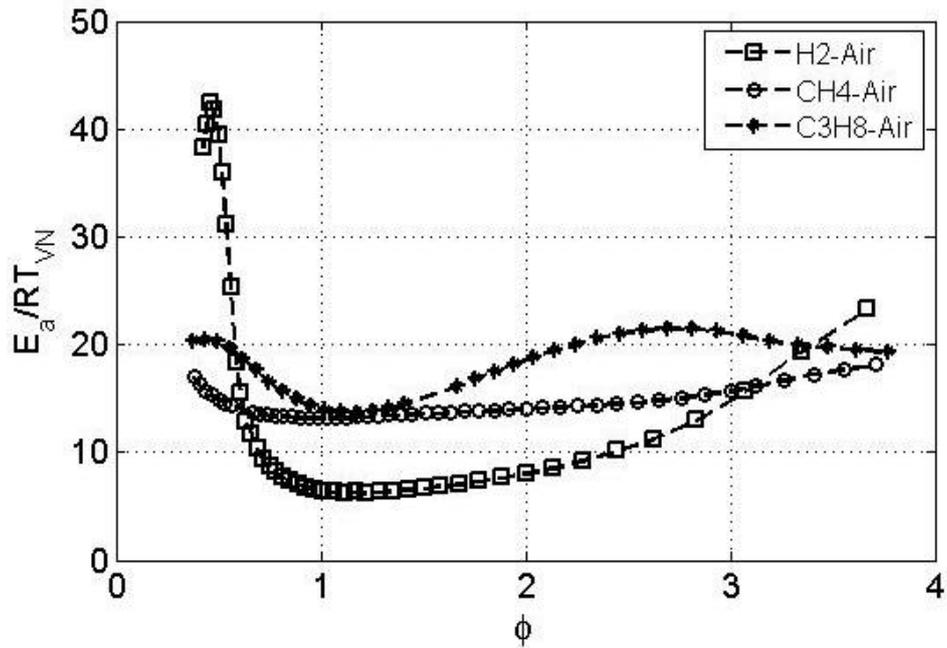


Figure 3. Activation energy measured for hydrogen, methane and propane compositions

Figure 4 shows the variation of the ratio of induction to reaction time in the three fuels. Except near the rich and lean limits, hydrogen has an induction to reaction time ratio significantly lower than the other two fuels. Methane has a reaction time typically 100 times smaller than the induction time.

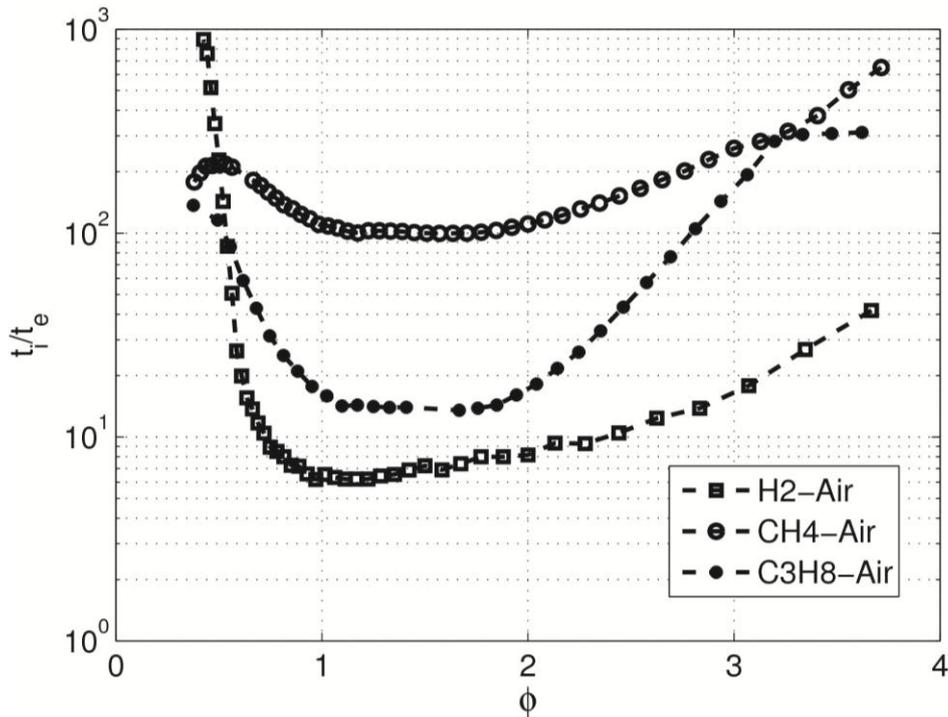


Figure 4. Induction to reaction time ratio for hydrogen, methane and propane compositions

Figure 5 shows the variation of post shock γ for the three fuels. Hydrogen, owing to its diatomic molecular structure, yields the highest values. Figure 6 shows the variation of the heat release parameter. Propane has the highest heat release parameter, while hydrogen-air mixtures have the lowest values.

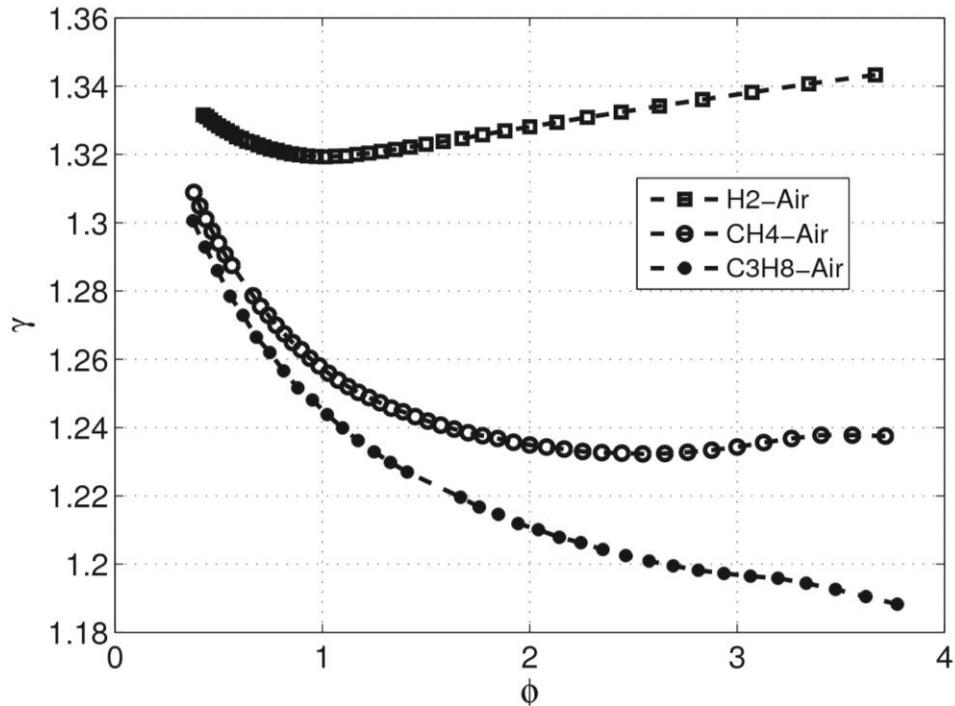


Figure 5. Isentropic exponent evaluated behind the lead shock for hydrogen, methane and propane-air mixtures

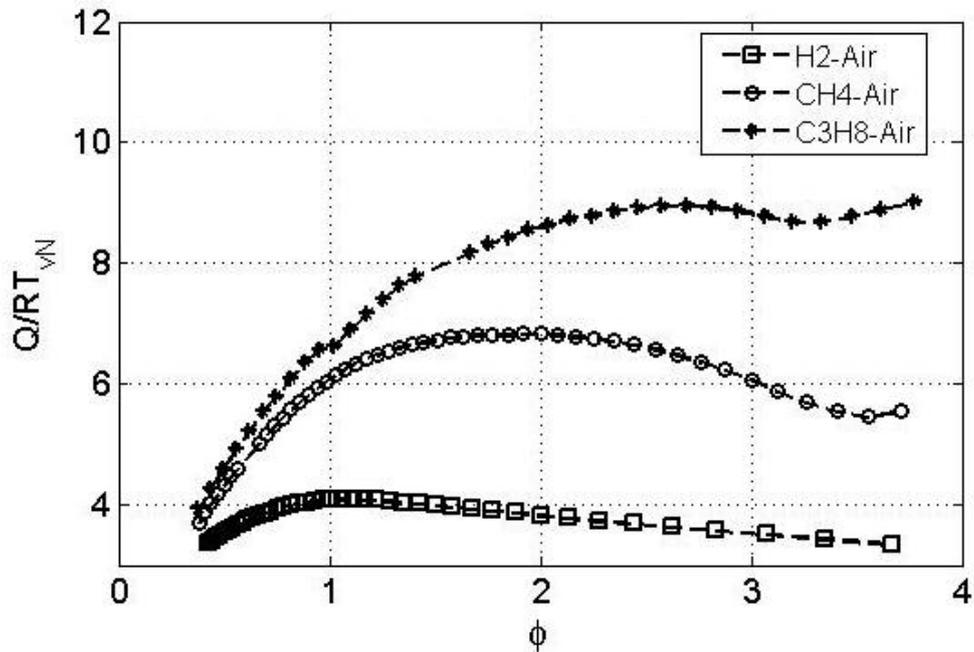


Figure 6. Non-dimensional heat release measured for hydrogen, methane and propane compositions

Figure 7 shows the variation of the characteristic acceleration suggested by *Radulescu, Sharpe and Bradley* as an indicator for hotspot formation, instability and turbulence in the reaction zone of detonations. On the basis of the dimensional RSB prediction, hydrogen remains the most prone to instability. However, the characteristic RSB acceleration has values comparable to both methane and propane at stoichiometric compositions. In lean mixtures, however, hydrogen retains its propensity for instability, while the other two hydrocarbons do not. This is again due to the large values of activation energy in lean hydrogen mixtures.

Figure 8 shows the variation of the stability parameter χ defined in (1). At stoichiometric compositions, hydrogen has the lowest value of approximately 200, while propane and methane have values higher by respectively one and two orders of magnitude. This parameter reflects the stability of the detonation, where it was determined that a value of approximately ~ 50 -100 is the threshold for instability and turbulence in the reaction zone. The high values of χ for methane are consistent with the very irregular cellular structures observed in methane detonations. Of noteworthy mention is that in lean mixtures, hydrogen becomes comparable and exceeds the value for the other two fuels. This is due to the large activation energies caused by the favoring of the recombination steps occurring at low temperatures, as described above. The large values of χ for lean hydrogen mixtures are compatible with the very turbulent detonation structures observed by Eder in lean hydrogen-air mixtures [23].

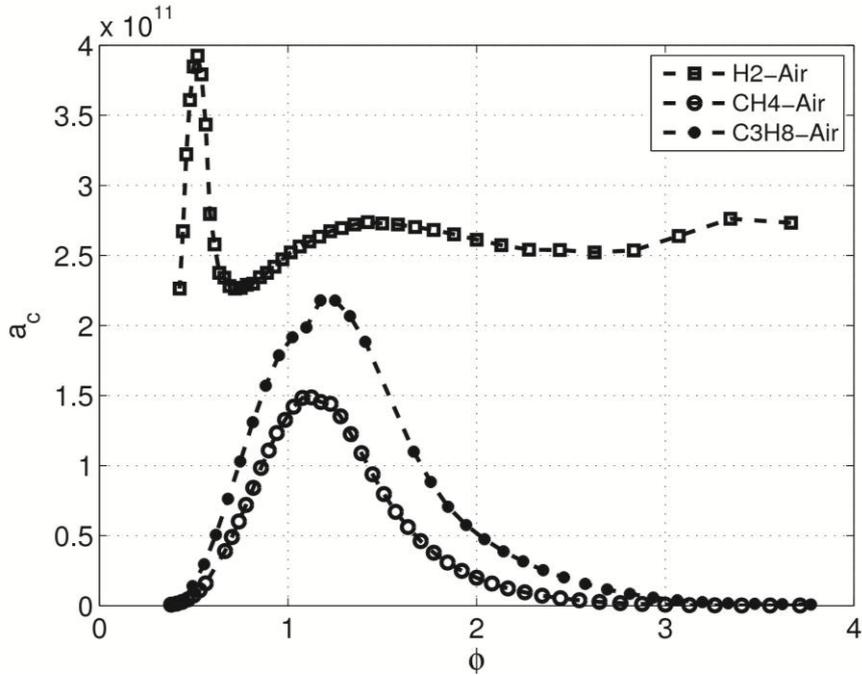


Figure7. Characteristic a_c for hydrogen, methane and propane compositions

3.0 INFLUENCE OF χ ON CELLULAR DYNAMICS

The link between large values of χ and detonation instability has been well established for 1D detonations, as reviewed in the Introduction. Borzou and Radulescu have also shown that detonations with larger values of χ are more unstable [17]. They have performed 2D simulations using a 2 step model, where they monitored the onset of cellular instabilities developing on the ZND structure for moderately unstable detonations. They initialized the simulations, with forming a detonation at the beginning of a fixed domain and imposed the ZND profile onto the domain. Initially perturbing the wave, they have triggered the instabilities and investigated the formation of detonation. Some of their results are reproduced in Figures 9 and 10 for two χ parameters of 24 and 95. As seen in these figures, they found that the case with $\chi=95$ is more unstable and builds the instabilities earlier.

Unfortunately, this technique cannot be applied to highly unstable detonations because of presence of non-oscillatory 1D modes, which quench the detonation before any growth of instability [24]. For this reason, the present study further studied the link between cellular instability and the χ parameter given by (1) in simulations where this artifact is absent. The numerical simulations thus focus on the stability of decaying Taylor-Sedov blast waves in a reactive gas. For simplicity, we focus on planar blast waves originating from a plane source of energy, which decay towards self-sustained detonations. During this shock decay, we monitor the onset of instabilities on the structure of the reactive blast wave.

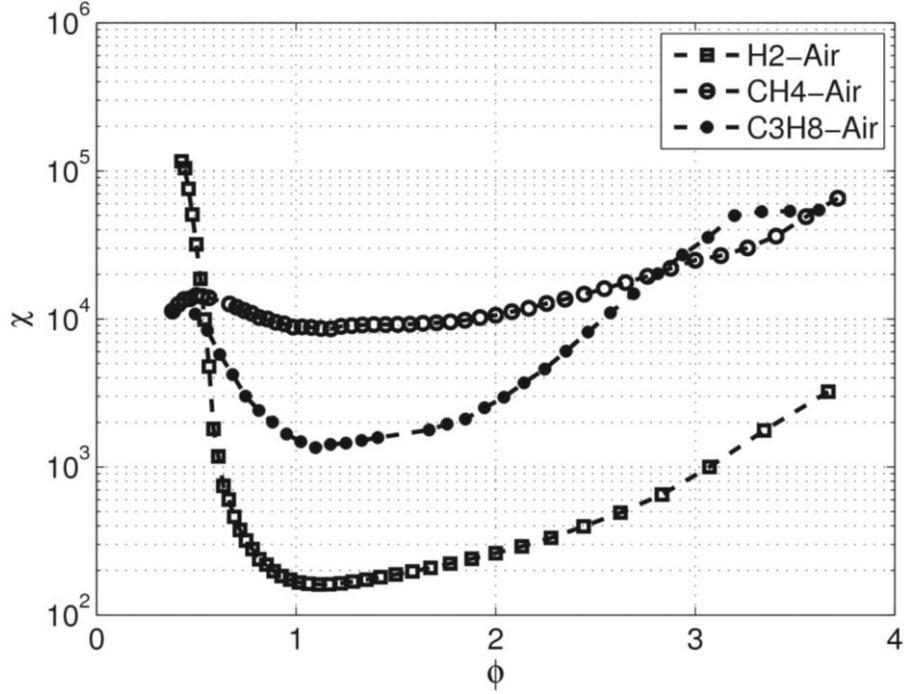


Figure8. Characteristic χ parameter for hydrogen, methane and propane compositions

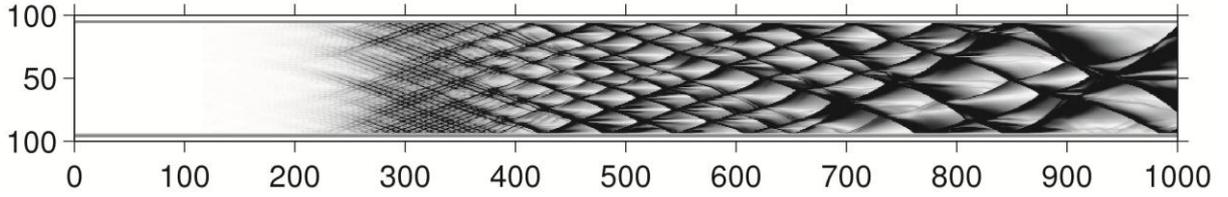


Figure9. Numerical soot foil for a mixture with $\chi=24$

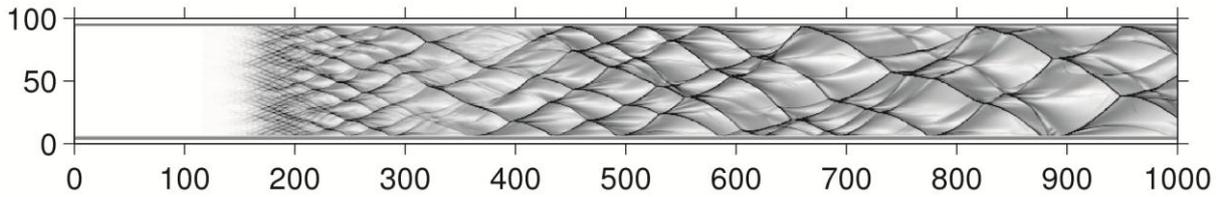


Figure10. Numerical soot foil for a mixture with $\chi=95$

The simulations were performed in the frame work of the two-step reaction model used by Short and Sharpe [25] and Leung et al. [16] in 1D simulations and Borzou & Radulescu in 2D [17]. Similar to the profile shown in Figure 1, the model admits a thermally neutral induction zone followed by a temperature independent reaction zone. The duration of induction zone is controlled by an Arrhenius expression. Consequently, the two-step model offers independent control of the induction and reaction zones. If λ_i denotes a progress variable for the induction zone, with a value of 1 in reactants and 0 at the end of the induction zone, the evolution of this progress variable is given by

$$\frac{D\lambda_i}{Dt} = -K_i H(\lambda_i) \exp\left(-\frac{E_a}{RT}\right) \quad (6)$$

where K_i is a rate constant and $H(\alpha)$ is a Heaviside function which turns off the progress variable, λ_i , at the end of the induction zone. Immediately following the induction zone is the exothermic reaction zone, which proceeds independently of temperature. The evolution of the progress variable is λ_r , which is 0 in the induction zone and 1 in the burned products, is assumed to take the form

$$\frac{D\lambda_r}{Dt} = (1 - H(\lambda_i))K_r(1 - \lambda_r)^\nu \quad (7)$$

where ν denotes the reaction order. In the simulations, a blast wave with the pressure of 1000 ambient pressure was sent through the stoichiometric compositions of hydrogen, propane and methane air mixtures with the corresponding χ parameter values of 132, 1920 and 7260 respectively and the initiation of the blast wave into a detonation was examined. The dynamics were computed numerically by solving the reactive Euler equations using the AMRITA computational facility developed by J.J. Quirk [26]. A Roe solver was used to evaluate the fluxes in the Euler equations. The width of the computational area has been taken as 1 induction length. Using such a thin domain is justifiable in this case because when the blast wave is overdriven at the onset of instability, the induction length is orders of magnitude smaller than what ZND model predicts at CJ conditions. Also the resolution covering the reaction zone structure was 128 grid points per induction length. In the simulations, the path of triple points have been tracked on the detonation front propagating from left to right in order to obtain the time history of the detonation cellular structure. These trajectories of the triple points were obtained by recording the maximum vorticity. As results, figures 11, 12 and 13 are showing the cellular structure for the initiated detonation in stoichiometric hydrogen, propane and methane respectively.



Figure11. Cellular structure for detonation of stoichiometric hydrogen-air mixture



Figure12. Cellular structure for detonation of stoichiometric propane-air mixture

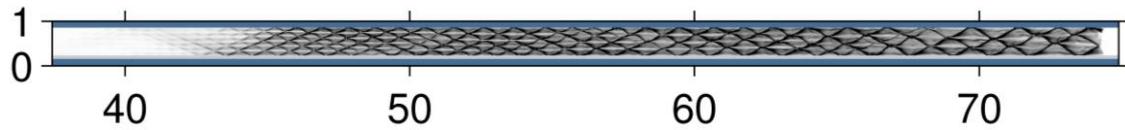


Figure13. Cellular structure for detonation of stoichiometric methane-air mixture

As can be seen in these figures, the growth of instabilities in the methane case (having the highest χ parameter) and hydrogen case (having the lowest χ parameter) happens the earliest and the latest respectively.

Also qualitatively, the shock pressure tracks shown in figure 14, 15 and 16 respectively corresponding to hydrogen, propane and methane, show the sequence of instability growth for the mixtures. These pressures have been recorded on the wall of the domain. It can be seen that the pressure signal starts to get unstable relatively earlier in methane compared to propane and hydrogen. Also propane pressure signal becomes unstable earlier than hydrogen. Remembering the results of figure 8 in which methane and hydrogen had the highest and lowest χ parameters respectively, the order of instability growth verifies the χ parameter being a measure of instability and turbulence in the reaction zone structure.

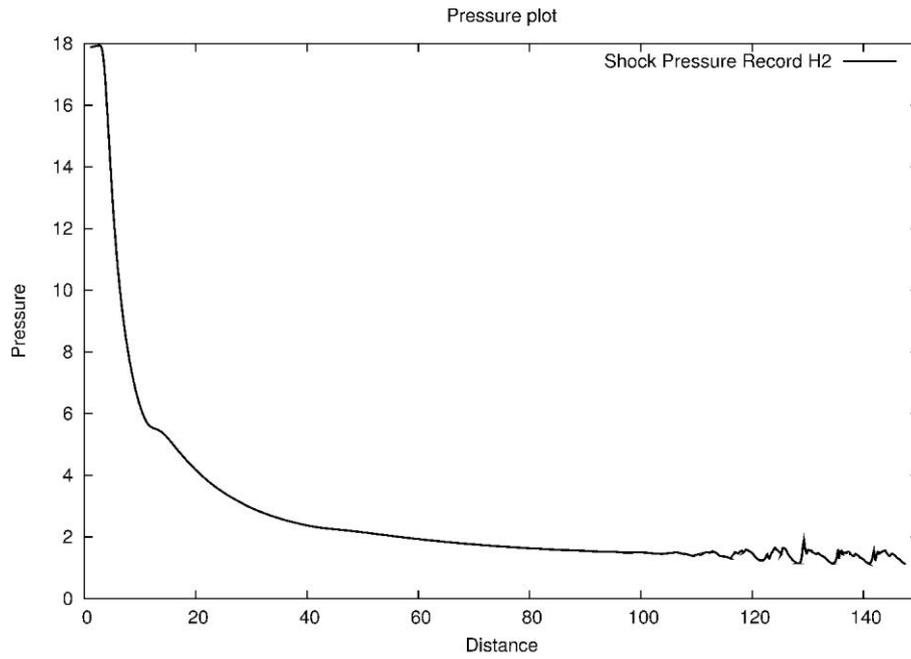


Figure14. Shock pressure record for the stoichiometric hydrogen-air mixture

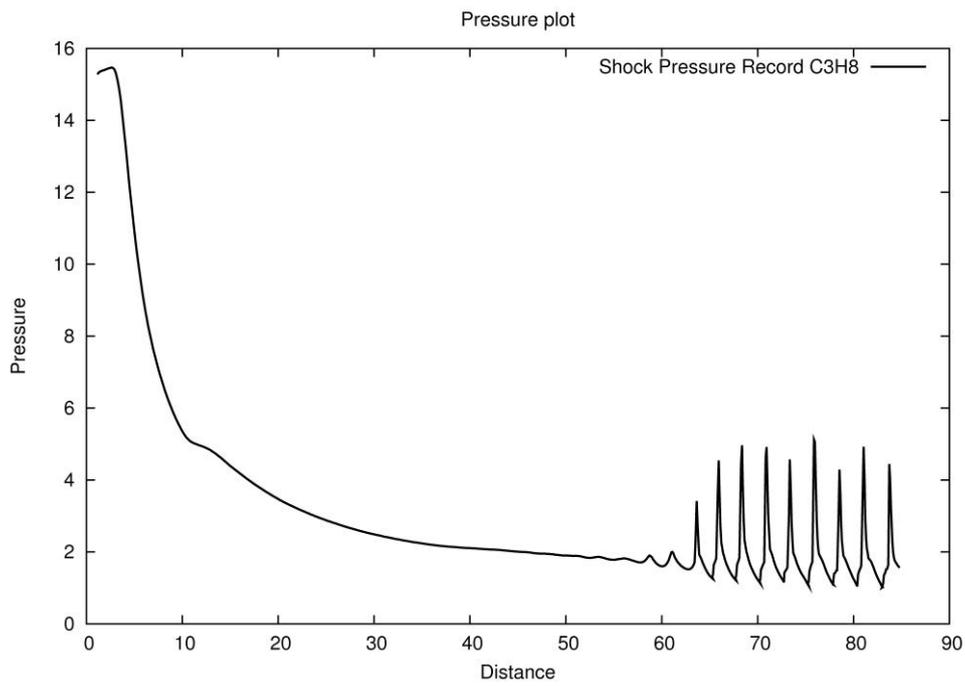


Figure15. Shock pressure record for the stoichiometric propane-air mixture

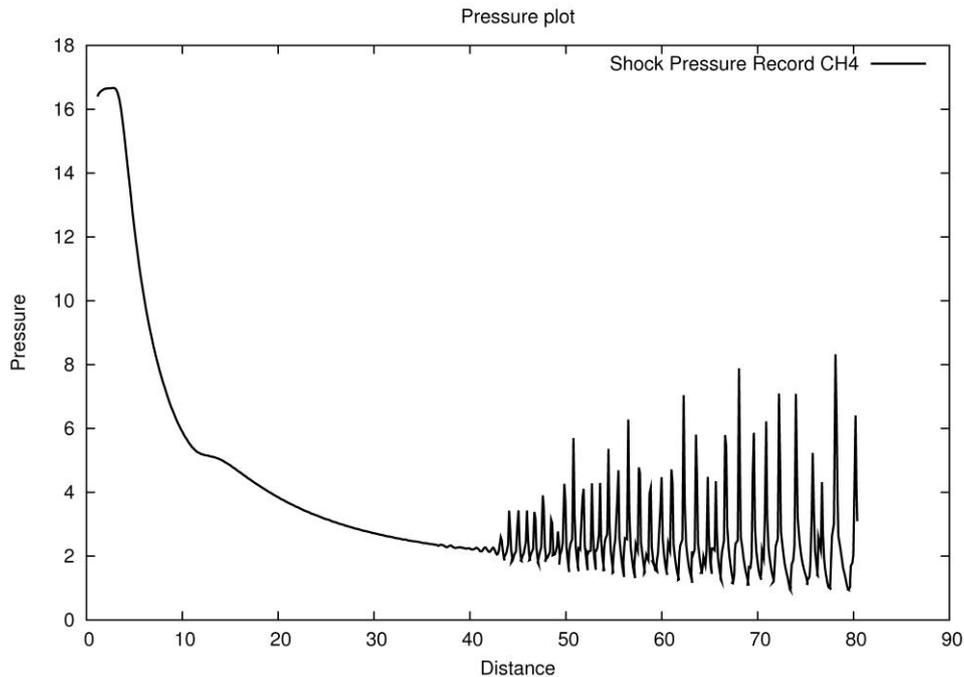


Figure 16. Shock pressure record for the stoichiometric methane-air mixture

4.0 CONCLUSIONS

In this paper, the detonation propensity of different compositions of mixtures of hydrogen, propane and methane with air has been evaluated over a wide range of compositions. Induction delay times evaluated at the Von Neumann state of the detonations and the characteristic acceleration parameter recently suggested by *Radulescu, Sharpe and Bradley* (RSB) were used to characterize the detonability of a given mixture. While it is well established that the ignition delay provides a good measure for detonability, the RSB acceleration, or its non-dimensional form χ , provides a further discriminant between different mixtures with similar ignition delays. The present assessment of detonability reveals that while a stoichiometric mixture of hydrogen-air has an ignition delay one and two orders of magnitude shorter than, respectively, propane and methane, hydrogen also has a χ parameter smaller by respectively one and two orders of magnitude. Its smaller propensity for instability is reflected by an RSB acceleration parameter similar to the two hydrocarbons. The predictions however indicate that lean hydrogen mixtures are likely to be much more unstable than stoichiometric ones. The relation between the RSB parameter and potential to amplify an unstable transverse wave structure has been further determined through numerical simulation of decaying reactive Taylor-Sedov blast waves. Using a simplified two-step model calibrated for these fuels, we show that a methane-air mixture develops cellular structures more readily than propane and hydrogen, when observed on similar induction time scales. Future work should be devoted towards a quantitative inclusion of the RSB parameter in assessing the detonability of a given mixture.

5.0 REFERENCES

- [1] Lee, J.H.S., *The Detonation Phenomenon*, 2008, Cambridge University Press, New York.
- [2] Kaneshige, M., Shepherd, J.E., *Detonation Database*, Technical Report FM97-8, GALCIT, July 1997.
- [3] Lee, J.H.S., *Dynamic Parameters of Gaseous Detonations*, *Annual Review of Fluid Mechanics*, 16, 1984, pp. 311-336.
- [4] Radulescu, M.I., *The Propagation and Failure Mechanism of Gaseous Detonations: Experiments in Porous-walled tubes*, PhD Thesis, McGill University, 2003.

- [5] Radulescu, M.I., Lee, J.H.S., The Failure Mechanism of Gaseous Detonations: Experiments in Porous Wall Tubes, *Combustion and Flame*, 16, No. 1-2, 2002, pp. 29-46.
- [6] Lee, J.H.S., Soloukhin, R.I., Oppenheim, A.K., Current Views on Gaseous Detonations, *Astronautica Acta*, 14, No. 5, 1969, pp. 565.
- [7] Moen, I.O., Sulmistras, A., Thomas, G.O., Bjerketvedt, D., Thibault, P.A., The Influence of Cellular Regularity on The Behaviour of Gaseous Detonations, 10th International Colloquium on Dynamics of Explosion and Reactive Systems, Berkeley, CA., USA, August 1985.
- [8] Shepherd, J.E., Moen, I.O., Murray, S.B., Thibault, P.A., Analyses of The Cellular Structure of Detonations, *International Symposium on Combustion*, 21, 1988, pp. 1649-1658.
- [9] Radulescu, M.I., Sharpe, G.J., Law, C.K., Lee, J.H.S., The Hydrodynamic Structure of Unstable Detonations, *Journal of Fluid Mechanics*, 421, 2000, pp. 147-183.
- [10] Liang, Z., Browne, S., Deiterding, R., Shepherd, J.E., Detonation Front Structure and The Competition for Radicals, *Proceeding of the Combustion Institute*, 31, 2007, pp. 2445-2453.
- [11] Tang, J., Radulescu, M.I., Dynamics of Shock-Induced Ignition in Fickett's Model: Influence of χ , *Proceedings of Combustion Institute*, 34, No. 2, 2013, pp. 2035-2041.
- [12] Sharpe, G.J., Shock-Induced Ignition for a Two-Step Chain-Branching Kinetics Model, *Physics of Fluids*, 14, No. 12, 2002, pp. 4372-4388.
- [13] Bradley, D., Autoignitions and Detonations in Engines and Ducts, *Philosophical Transactions of the Royal Society A-Mathematical Physical and Engineering Sciences*, 370, No. 1960, 2012, pp. 689-714.
- [14] Radulescu, M.I., Sharpe, G.J., Bradley, D., Detonability and Hotspot Formation: The Chi Number, 7th International Seminar on Fire and Explosion Hazards, Providence, R.I., USA, May 2013.
- [15] Ng, H.D., Radulescu, M.I., Higgins, A.J., Nikiforakis, N., Lee, J.H.S., Numerical Investigation of the Instability for One-Dimensional Chapman-Jouguet Detonations with Chain-Branching Kinetics, *Combustion Theory and Modeling*, 9, 2005, pp. 385-401.
- [16] Leung, C., Radulescu, M.I., Sharpe, G.J., Characteristic Analysis of The One-Dimensional Pulsating Dynamics of Chain-Branching Detonations, *Physics of Fluids*, 22, 2010, 126101.
- [17] Borzou, B., Maxwell, B., Radulescu, M.I., Influence of the Induction to Reaction Length Ratio on the Stability of Cellular Detonations, 23rd International Colloquium on the Dynamics of Explosions and Reactive Systems, Irvine, USA, 2011.
- [18] Browne, S., Zeigler, J., Shepherd, J.E., Numerical Solution Methods for Shock and Detonation Jump Conditions, Technical Report FM2006.006, GALCIT, 2004.
- [19] McBride, B.J., Gordon, S., Computer Program for Calculation of Complex Chemical Equilibrium Compositions, Technical Report E-8017-1, National Aeronautics and Space Administration, Washington D.C., June 1996.
- [20] Goodwin, D., An object-oriented software toolkit for chemical kinetics, thermodynamics, and transport processes, Caltech, Pasadena, 2009.
- [21] Chemical Kinetic Mechanisms for Combustion Applications, San Diego Mechanism, Mechanical and Aerospace Engineering, <http://combustion.ucsd.edu>, University of California at San Diego.
- [22] Shepherd, J.E., Chemical Kinetics of Hydrogen-Air Diluent Mixtures, *Progress in Astronautics and Aeronautics*, 106, 1986, pp. 263-293.
- [23] Eder, A., Brennerverhalten schnellnaher und Überschall-schneller Wasserstoff-Luft Flammen, PhD Thesis, Technische Universität München, Munich, 2001.
- [24] He, L., Lee, J.H.S., the Dynamic Limit of One-Dimensional Detonations, *Phys. Fluids*, 7, No. 5, 1960, 1995, pp. 1151-1158.
- [25] Short, M., Sharpe, G.J., Pulsating Instability of Detonations with A Two-Step Chain-Branching Reaction Model: Theory and Numerics, *Combustion Theory and Modeling*, 7, 2003, pp. 401-416.
- [26] Quirk, J.J., A Computational Facility for CFD Modeling, 29th Computational Fluid Dynamics VKI Lecture Series, von Karman Institute, H. Deckoninck Ed., 1998.