Role of Low-Temperature Chemistry on the Onset of Detonation Behind an Incident Shock Wave

Wenhu Han¹, Du Ning^{2,3}, Rémy Mével^{4,5,*}, Wenkai Liang⁶ and Chung K Law^{4,6}

¹ State Key Laboratory of Explosion Science and Technology,

² Key Laboratory of Light-Duty Gas-Turbine, Institute of Engineering Thermophysics,

Chinese Academy of Sciences, Beijing 100190, China

³ University of Chinese Academy of Sciences, Beijing 100039, China

⁴ Center for Combustion Energy, Tsinghua University, Beijing, China

⁵ School of Vehicle and Mobility, Tsinghua University, Beijing, China

⁶ Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ 08544, USA

1 Introduction

Liquefied petroleum gas (LPG) is widely used as industrial, commercial and civil fuels due to its low pollution, high calorific value, and convenient transportation and storage. Propane (C_3H_8) is the main component of LPG and one of the smallest hydrocarbons which features low-temperature chemistry (LTC) [1]. Studying the basic combustion characteristics of propane is of great significance to industrial safety and power devices.

The impact of LTC on flame acceleration and detonation has been investigated in a number of studies. In 1937, Shchelkin and Sokolik measured the distance required for a deflagration to transit to detonation (DDT run-up distance) in a heated tube containing a pentane-oxygen mixture at low pressure [2]. By varying the delay (τ) between the introduction of the combustible mixture in the tube and the flame initiation by an electrical spark, they observed that the run-up distance curve presented a minimum for a delay corresponding to the time required for a cool flame to be initiated (t_{cf}) . For τ significantly longer than t_{cf} , an increase of the run-up distance was observed. The reduction of the run-up distance by cool flame oxidation may be referred to as the Shchelkin-Sokolik effect. The experimental results of Shchelkin and Sokolik were latter confirmed by Romano et al. [3] who reported a decrease by 50% of the run-up distance. They attributed this reduction to the formation of hydroperoxides and active radicals during the cool flame process. For longer τ , the increase of the run-up distance was attributed to the decrease of total enthalpy. Chaumeix et al. [4] studied the initiation of detonation by incident shock wave in n-heptane-oxygen mixtures at ambiant temperature and low initial pressure, i.e. 2-4 kPa. They showed that for strong incident shocks with shocked temperature (T_2) above 1000 K, the high-temperature chemistry was responsible for the detonation onset, whereas for weaker shocks with T₂ below 950 K, the LTC had a significant impact on the DDT process. Basevich et al. [5] numerically studied the initiation of detonation through shock wave amplification as it propagates in a cool flame. The one-dimensional simulations were performed using a semi-empirical kinetic mechanism consisting of 7 irreversible chemical steps. The evolution of the run-up distance as a function of τ observed experimentally by Shchelkin and Sokolik and by Romano et al. was qualitatively reproduced in Basevich's simulations.

Concerning the impact of LTC on detonation, Romano et al. [6] measured the cell size for detonation propagating in a pre-heated pentane-oxygen mixture. As for their DDT experiments, the delay between the mixture

Beijing Institute of Technology, Beijing 100081, China

Han et al.

introduction in the tube and the detonation initiation was varied. They observed that the evolution of the cell size with τ is similar to that of the DDT run-up distance. More recently, Liang et al. [7] showed, using ZND numerical simulations, that the LTC could be activated at the von Neumann state by applying high dilution of CO₂ to stoichiometric n-heptane-oxygen mixtures at initial temperature and pressure of 300 K and 101 kPa, respectively. Similar results were obtained by Mevel et al. [8] for dimethyl ether-oxygen mixtures.

The goal of the present study was to gain further insights into the impact of LTC on the flame acceleration and detonation onset processes behind an incident shock wave by performing one-dimensional numerical simulations. The simulations were performed with detailed chemistry for a stoichiometric propane-oxygen-carbon dioxide mixture, and the impact of the cool flame on the run-up distance was investigated by activating and deactivating the LTC in the reaction model.

2 Numerical approach

The governing equations were the one-dimensional, reactive, compressible Navier-Stokes equations. The mixture properties were evaluated using the CHEMKIN and TRANSPORT packages. The spatial discretization of the advection term was performed using a 5^{th} -order WENO scheme. To solve the stiff system of equations, an explicit-implicit Additive Runge-Kutta scheme [10] was used for the time discretization. The method based on conservation variables was used to solve the equations, which guarantees mass conservation and ensure an accurate evaluation of the shock speed. Details about the code we employed are given in Han et al. [11].

3 Results and discussion

3.1 Description of the cases studied

The mixture studied was a stoichiometric propane-oxygen mixture diluted with 85% by mole of CO₂. The initial pressure and temperature were 507 kPa and 300 K. Under these conditions, the LTC is active at the von Neumann state behind the shock wave of a planar detonation propagating at the Chapman-Jouguet velocity (D_{CJ}). The chemical model we have employed is the propane model of San Diego [9] which consists in 50 species and 247 reactions. In order to investigate the effect of LTC on flame acceleration and detonation onset, the following four LTC reactions R₁: N-C₃H₇+O₂=C₃H₆OOH; R₂: C₃H₆OOH=C₃H₆+HO₂; R₃: C₃H₆OOH+O₂=OC₃H₅OOH +OH; and R₄: OC₃H₅OOH=CH₂CHO+CH₂O+OH, were kept active (case 1) or deactivated (case 2). Table 1 summarizes the characteristics physical and numerical scales for the two cases.

Table 1: Composition and characteristics physical and numerical scales for the two cases studied at T₁=300 K and P₁=507 kPa. δ_x : resolution used for the simulation. t_i : time to $(dT/dt)_{max}$). l_i : distance to $(dT/dt)_{max}$.

Case	C ₃ H ₈ :O ₂ :CO ₂	D_{CJ} (m/s)	δ_x (m)	t_i (ms)	l_i (m)
1(w LTC)	1:5:34	1083.52	0.001	6.855	1.2685
2 (wo LTC)	1:5:34	1083.52	0.005	87.708	15.018

3.2 Steady ZND structures

In a first step, we have calculated the steady ZND structure for both cases. Figure 1 a) compares the temperature and thermicity profiles obtained with and without LTC in the physical space. As reported in Table 1, the induction induction distance for case 1 is more than an order of magnitude shorter than for case 2. To facilitate the comparison between the two cases, we have also plotted the temperature and thermicity profiles in a normalized space in Figure 1 b). The normalization was performed by dividing the distance by the total induction length for each case. For case 1, the temperature profile demonstrates two main steps of temperature increase whereas the

thermicity profile exhibits four peaks. One of the thermicity peak is due to the LTC and is clearly separated from the three other peaks which are due to intermediate- and high-temperature chemistry (ITC and HTC) and form a quasi-continuous, long step of energy release. For case 2, the temperature profiles demonstrate a monotonous increase and the thermicity profiles demonstrate a single peak. It is noted that the temperature increase during the main step of energy release is much sharper for case 2 than for case 1.



Figure 1: Steady ZND structure of detonation propagating in a $1C_3H_8$ - $5O_2$ - $34CO_2$ mixture with and without LTC. Black lines: case 1. Red lines: case 2. Solid lines: temperature. Dashed lines: thermicity.

3.3 Flame acceleration and detonation onset

To study the effect of LTC on flame acceleration and detonation onset, unsteady 1-D simulation were performed for both cases. The simulations were initiated by imposing an inflow condition on the left boundary of the domain. The inflow temperature, pressure, and velocity correspond to T_{vN} , P_{vN} , and D_{CJ} for a $1C_3H_8$ -5O₂-34CO₂ mixture initially at 300 K and 507 kPa. The mixture composition at the left boundary corresponds to the fresh mixture. Considering a detonation propagating in the fresh mixture initially at 300 K and 507 kPa, the grid resolution was 634pts/ $I_{1/2}$ for case 1 and 1502pts/ $I_{1/2}$ for case 2, where $I_{1/2}$ is the half-reaction length.

Results obtained for case 1 are shown in Figure 2. At early time, a cool flame is initiated at a distance around $x/l_i=0.25$ whereas, by definition, hot flame is ignited at $x/l_i=1$. The velocity of the cool flame is much lower than that of the hot flame and is rather constant whereas hot flame is accelerating. Around the main ignition time, the temperature increase within the hot flame is relatively smooth and extend over a normalized distance of 0.3. After about 2 ms, the temperature increase in the hot flame becomes sharper and non-monotonous with a distinct peak of energy release appearing behind the main hot flame front. The two hot flame combustion fronts progressively merge and accelerate. A simultaneous amplification of the lead pressure wave is observed and after about 3.5 ms at a distance of $x/l_i=0.6$, a typical detonation pressure trace is seen. This sequence is characteristic of a SWACER mechanism during which the coupling of the energy release and of the acoustic waves induces the formation of an overdriven detonation wave. The detonation exits the cool flame region, a higher velocity and a higher pressure peak are generated which is due to the higher total enthalpy in the fresh mixture as compared to that of the partially oxidized mixture in the cool flame region. The propane and formaldehyde profiles demonstrate a two-stage evolution with a period of low chemical activity between the two phases of fast consumption/production. This is a typical feature of LTC-affected hydrocarbon combustion.

Results obtained for case 2 are shown in Figure 3. Without LTC, the induction length becomes much longer and is characterized by an increase of about 100 K with respect to the von Neumann state and a continuous consumption and production of propane and formaldehyde, respectively. A similar acceleration of the hot flame and amplification of the pressure wave as for case 1 is observed for case 2. After approximately 3.6 ms following the hot flame initiation, a detonation is formed and demonstrates slight oscillation in velocity and pressure peak height at latter stage as it propagates into the partially reacted gas within the induction zone.



Figure 2: Temperature, pressure, X_{C3H8} , and X_{CH2O} profiles in x/l_i space for case 1 at times: t=0.00535 (red line on the left), 0.4360, 0.8598, 1.29, 1.72, 2.20, 2.52, 2.84, 2.94, 3.05, 3.16, 3.26, 3.37, 3.42, 3.48, 3.53, 3.58, 3.64, 3.69, 3.74, 3.80, 3.85, 3.90, 3.95, 4.01, 4.06, 4.12, 4.17, 4.22, 4.28 (black line) ms. t_i is the reference time.

Figure 4 a) shows the velocity of the hot combustion front for both cases. It was defined as $U = -(x_t - x_0)/\Delta t$, where x_t and x_0 are respectively the location of the maximum temperature gradient at t and t_0 in the shockattached frame of reference. If a normalized time is considered, the delay required for the hot flame to accelerate and detonation to occur is more than 10 times shorter for case 2 than for case 1. Note that in Figure 4 a), $t=t_o-t_i$ where t_o is the time to detonation onset. The propagation velocity of the detonation is higher for case 1 than for case 2, ~2020 against ~1850 m/s. This is due to the higher fraction of propane consumed within the induction zone of the hot combustion front for case 2 than in the cool flame region for case 1.

To explain this feature, we have examined the temperature gradient ahead of the hot combustion front at the time of ignition as shown in Figure 4 b). For case 1, at $x/l_i=0.3$, a small hump in the temperature gradient curve is observed and is attributed to the cool flame event. Following this, the temperature gradient is essentially

Han et al.

Role of LTC on Detonation Initiation

zero until $x/l_i=0.9$. In the range $x/l_i=0.9-1$, the temperature gradient increases smoothly up to approximately 0.25-0.3 K/m. For case 2, the temperature gradient first increases from 0 to 1 K/m in the range $x/l_i=0.3-0.7$, and then from 1 to 4.6 K/m in the range $x/l_i=0.7-0.95$. Finally, the temperature gradient decreases sharply to reach 1.6 K/m at $x/l_i=1$. The difference in the evolution of the temperature gradients between case 1 and 2 can be explained as follows: (i) for case 1, the cool flame and the hot flame regions are largely separated; (ii) following the cool flame region, a quasi-equilibrium is reached with weak chemical activity, which results in a weak temperature gradient; (iii) for case 2, the induction zone is long and characterized by a continuous chemical activity which results in a stronger temperature gradient; (iv) the energy release rate in the high-temperature regime is higher for case 2 than for case 1.



Figure 3: Temperature, pressure, X_{C3H8} , and X_{CH2O} profiles in x/l_i space for case 2 at times: t=0.028 (red line on the left), 2.03, 2.70, 3.21, 3.35, 3.48, 3.55, 3.65, 3.78, 3.91, 4.05, 4.18, 4.33, 5.21 (black line) ms. t_i is the reference time.

4 Conclusion

In the present study, the effect of LTC on the flame acceleration and detonation onset behind an incident shock wave has been studied using unsteady 1-D numerical simulations performed with detailed chemistry. The simulations employed a stoichiometric propane-oxygen-carbon dioxide mixture and the LTC was either held active or deactivated by removing four reactions from the reaction model. It was found that, in a space normalized by the induction distance of the main ignition event, detonation was initiated faster when LTC was deactivated. This feature was attributed to the weaker temperature gradient formed behind the cool flame region where chemical



Figure 4: a) Velocity of the hot combustion front. b) Temperature gradient ahead of the hot combustion front at the time of ignition. A $1C_3H_8-5O_2-34CO_2$ with and without LTC was considered. Black lines: case 1. Red lines: case 2.

activity is weak. Under the specific conditions we have investigated, although the LTC enables a much faster ignition of the reactive mixture, it does not generate conditions particularly favorable to flame acceleration and detonation onset. To confirm if this observation is a general behavior of the LTC-affected shock ignition phenomenon, further investigation with different fuels, such as large alkanes and dimethyl ether, which demonstrate stronger LTC than propane, are needed.

References

- [1] Griffiths and Scott (1987). Progress in Energy and Combustion Science 13:161.
- [2] Shchelkin and Sololik (1937). Zhurnal Fizicheskoi Khimii 10:484.
- [3] Romano et al. (2003). Combustion and Flame 132:387.
- [4] Chaumeix et al. (2014). Combustion Science and Technology 186:607.
- [5] Basevich et al. (2010). Russian Journal of Physical Chemistry B 4:101.
- [6] Romano et al. (2002). Proceedings of the Combustion Institute 29:2833.
- [7] Liang et al. (2018). Combustion and Flame 193:463.
- [8] Mevel et al. (2017). Proceedings of the Asia-Pacific Conference on Combustion 11.
- [9] Chemical-Kinetic Mechanisms for Combustion Applications, San Diego Mechanism web page, Mechanical and Aerospace Engineering (Combustion Research), University of California at San Diego (http://combustion.ucsd.edu)
- [10] Kennedy and Carpenter (2003). Applied Numerical Mathematics 44:139.
- [11] Han et al. (2019). Journal of Fluid Mechanics 865:602.

 $27^{\rm th}$ ICDERS – July $28^{\rm th}\text{-August}~2^{\rm nd},$ 2019 – Beijing, China