Role of low-temperature chemistry in detonation of n-heptane/oxygen/diluent mixtures

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ABSTRACT

The ZND structure of mixtures of n-heptane, oxygen and diluent has been investigated using a reduced reaction scheme that includes the low-temperature chemistry (LTC) pathways. It is shown that for high CO_2 contents ($X_{CO2} > 0.82$) such that the reaction temperature is relatively low, the structure is affected by LTC and exhibits two distinct stages of energy release caused by low- and high-temperature chemistry, respectively. Based on the ZND structures, the dynamic parameters such as cell size, direct initiation energy and critical tube diameter of detonation within the LTC affected regime have been evaluated using various semi-empirical models. Such detonation structures exhibiting two distinct length scales lead to two distinct values for each of these dynamic parameters. For the evolution of the induction length and cell size, although the total length scales do not show negative response with increasing temperature, the length scale of the first-stage ignition demonstrates negative response when the post-shock temperature decreases within the LTC controlled regime. For the evolution of direct initiation energy, the models based on critical curvature and critical decay rate show negative temperature response, but the model based on cell size predicts continuous increase of critical initiation energy with increasing dilution. For the critical tube diameter, the model based on the critical decay rate approach also exhibits the negative temperature response.

1. Introduction

At low ($T < 650$ K) to intermediate (650 K $< T < 1000$ K) temperatures, the oxidation of large hydrocarbon fuels is dominated by low-temperature chemistry (LTC) [1–3], which is closely related to the cool flame and the negative temperature coefficient (NTC) phenomena, and is considered to be a key factor in engine knock [4]. Consequently, extensive efforts have been made to investigate LTC-affected phenomena in various combustion systems [3–8]. In particular, cool flames with oscillatory volumetric heat release and chemiluminescence have been observed in homogeneous systems such as those in heated closed vessels [5] and jet-stirred reactors [3]. In non-homogeneous systems, the coupling between the LTC and the transport processes involved has been investigated in counterflow flames [6], droplet burning [7] as well as flames in microchannel [8].

However, there have been very limited studies on LTC-affected detonation waves. Romano et al. investigated the effects of partial oxidation on the n-pentane–oxygen detonation cell size [9] and the deflagration-to-detonation transition (DDT) run-up distance [10], showing that when the mixture undergoes LTC reactions, there is a significant reduction of the cell size as well as the DDT run-up distance. Furthermore, while most previous studies on LTC-affected detonations have focused on the global response of detonations to LTC, the detailed detonation structure is not well understood. Specifically, more comprehensive studies of LTC-affected detonation are needed for three aspects. At the fundamental level, the detonation structure is highly sensitive to chemistry and double cellular structure has been correlated with non-monotonous energy release in a number of mixtures including $CH_3NO_2(-O_2)$ [11] and fuel–NO_2/N_2O_4 (fuel: H_2, CH_4, C_2H_6) [12,13]. At the industrial safety level, the dynamic parameters of detonations, namely the detonation cell size, the direct initiation energy and the critical tube diameter [14], which are used for detonation risk assessment through empirical or semi-empirical models, require knowledge of the chemical structure, and hence can be strongly affected by the LTC. Kinetically, while the autoignition delay times of large hydrocarbon fuels demonstrate the relevance of the NTC, it is not clear whether the detonation dynamic parameters would be similarly affected. At the practical level, super-knock [15] in

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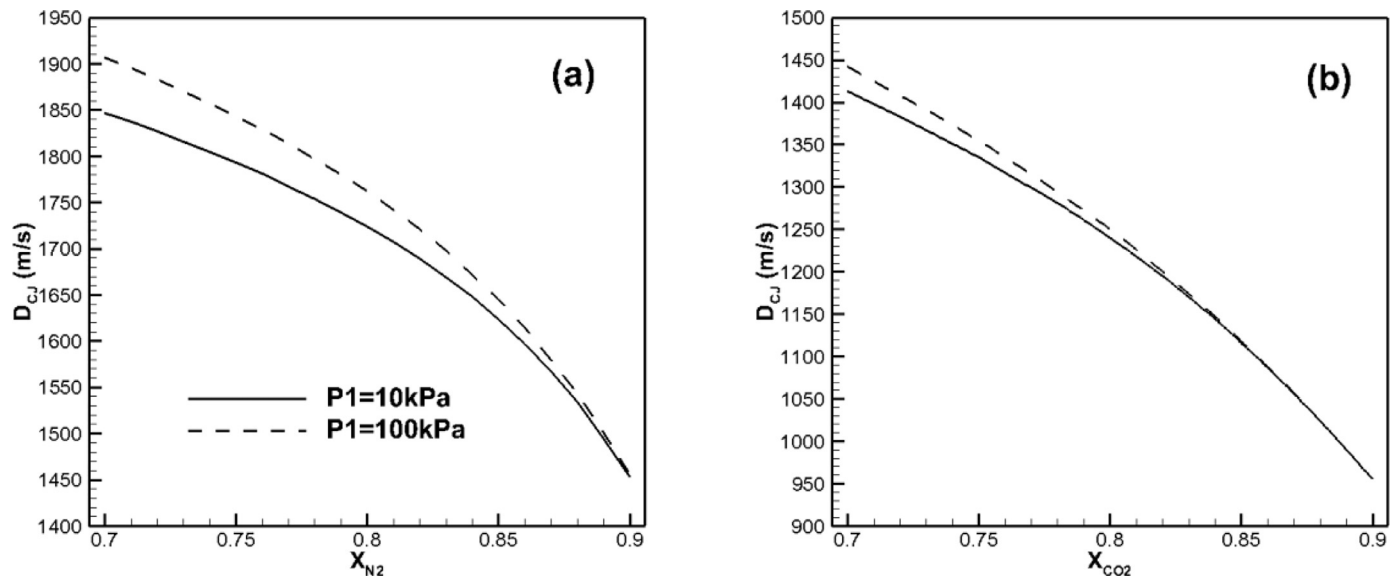*E-mail address:* mevel@mail.tsinghua.edu.cn (R. Mével).

Fig. 1. CJ detonation velocity of stoichiometric *n*-heptane/oxygen mixtures (T1 = 298 K) with dilutions of (a) N_2 and (b) CO_2.

spark-ignition (SI) engines is a challenge for the development of low-speed and high-load operating conditions, and with the cause attributed to the occurrence of strong detonation resulting from pressure waves induced by end-gas autoignition. The LTC effect on the oxidation of large hydrocarbon fuels will fundamentally affect the autoignition kinetics and the subsequent detonation development. Hence, it is important to understand the LTC-affected detonation to help overcome the obstacle of super-knock.

Motivated by the above considerations, the present study aims at investigating the effects of LTC on detonation structures and dynamic parameters. Specifically, the conditions at which LTC would strongly influence the detonation structure are identified and the ZND structures of detonation in *n*-heptane/oxygen/diluent mixtures are simulated with detailed kinetics. Further, based on the ZND structure we analyze the chemical kinetic effects on the temperature profiles and the energy release dynamics. Following the analysis of the ZND structures, several important dynamic parameters within the LTC-affected regime, namely the detonation cell size, critical direct initiation energy and critical tube diameter will be evaluated by various empirical and semi-empirical models.

2. Identification of LTC-affected conditions

As a typical primary reference fuel (PRF) and a well-studied large hydrocarbon fuel with LTC, *n*-heptane is selected as the fuel and a skeletal mechanism consisting of 88 species and 387 reactions [16], which has been applied in several previous studies on LTC affected phenomena [6,8], is used for the simulation. To identify the conditions at which LTC would be activated behind the leading shock, we first conducted a parametric investigation of the CJ detonation velocities and von Neumann conditions of detonation in *n*-heptane/oxygen mixtures, with different dilutions of N_2 and CO_2 and at various initial pressures. Figure 1 shows the change of the CJ detonation velocity with the dilution mole fraction for both N_2 and CO_2, demonstrating lower detonation velocity for the CO_2 diluted cases as compared with the N_2 diluted cases, while there is no strong pressure dependence for the CJ velocity.

Then, Fig. 2 shows the pressure and temperature at the von Neumann state as a function of the dilution mole fraction, noting that as the dilution increases, both pressure and temperature decrease such that the mixture at the von Neumann state could
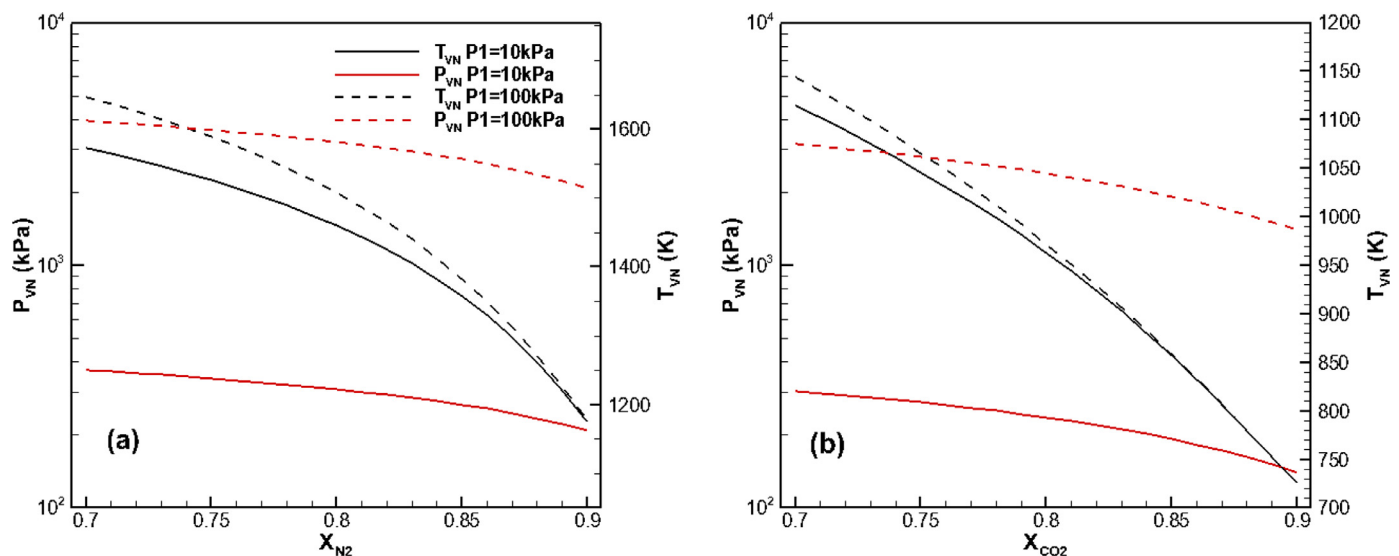

Fig. 2. Pressure and temperature of stoichiometric *n*-heptane/oxygen mixtures (T1 = 298 K) with dilutions of (a) N_2 and (b) CO_2 at the von Neumann state.