Detonation Properties in Dimethyl Ether-Oxygen Mixtures

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1 Introduction

To reduce environmental problems caused by the direct combustion of fossil fuels and to solve the diminishing energy supply, there is an urgent need to investigate alternative fuels and energy systems. Dimethyl ether (DME: CH₃OCH₃), which can be synthesized from natural gas, coal or biomass, has been traditionally used as a diesel substitute or additive. It does not attack stratospheric ozone and allows better emission controls of NOx, CO, SOx, non-methane hydrocarbon and particulates such as soot [1]. Since DME burns neatly, it has attracted great attention as a fuel for household heating and cooking. DME represents a potential alternative to liquified petroleum gas, liquified natural gas and diesel. Many Asian countries such as Japan and China are anticipating a DME infrastructure in the near future [2]. DME can also be an ideal fuel as a hydrogen carrier due to its high H/C ratio, high energy density, ease of storage, and ease of transportation. Due to its potential as a future energy alternative, the combustion characteristics of DME have attracted significant attention in recent years. Most fundamental studies have been focused on the deflagration (flame) mode of combustion. Basic combustion characteristics of DME flames (i.e., chemical mechanism and laminar flame speed) have been wellestablished [3-8]. However, comparatively little information exists on the explosion characteristics of DME. Although deflagrations are most common in practical conditions, detonations cannot be considered highly improbable. The destructive nature of detonation waves warrants a thorough knowledge of the conditions whereby detonations can be initiated, their propagation can be sustained, and turbulent flame acceleration can lead to the onset of detonation.

For detonation hazard assessment, measurement and prediction of different detonation properties (in particular, the detonation cell size) of the mixture of interest provide important data for the characterization of the explosion properties. Despite some preliminary studies [9], there is a lack of experimental data on the detonation properties of DME-based mixtures. Therefore, in this work, a series of experiments is carried out to measure detonation velocities and to analyze detonation cell sizes in DME-oxygen mixtures. These experimental results are compared to the predictions obtained using ZND chemical kinetics analyses with a recently developed cell size correlation model [10].

2 Experimental apparatus and procedure

Experiments were performed in a 4.5 m long steel detonation tube with an inner diameter of 65 mm. The mixtures were prepared beforehand in a separate vessel by the method of partial pressures. The gases were allowed to mix in the vessel for at least 24 hours in order to ensure homogeneity. For any given experiment, the detonation tube was initially evacuated to approximately 100 Pa. It was then filled from both ends to the desired

initial pressure, and a high energy spark (~100 J) was used to directly initiate a CJ detonation. Smoked Mylar foils were inserted into the detonation tube in order to record the characteristic detonation cell patterns. Pressure transducers were also used to monitor the detonation velocity.

3 Results and analysis

A stoichiometric dimethyl ether-oxygen mixture CH₃OCH₃ + 3O₂ was first tested in the present investigation. The sensitivity of the mixture was varied by the initial pressure Po. The measured detonation velocities are shown in figure 1. The STANJAN equilibrium program (with species and thermodynamic data given in [8]) is used to calculate the Chapman-Jouguet (CJ) properties. The wave speed obtained from the experiments is checked against the computed value and they are within few percent to each other. Hence, in all cases, the length of the tube is sufficient for cell measurements to be unaffected by the initiation transient. Typical smoked foils showing the cellular detonation structure in stoichiometric DME-oxygen mixtures for three different Po are given in figure 2. Cell width data of stoichiometric DME-oxygen mixture for a range of initial pressure are plotted in figure 3.

It is shown that for P_o greater than ~15 kPa, the cell pattern is regular and a single representative cell size can be determined without any peculiarity. For lower initial pressure, the range of cell size value increases (as indicated by the error bar in figure 3). At $P_o = 5$ kPa, it is shown that there appears a double cellular structure in stoichiometric dimethyl ether-oxygen mixture and two distinct cell size values have been recorded. This type of cellular structure is very similar to the case of nitromethane or H₂-NO₂/N₂O₄ detonations as observed by Desbordes and co-workers [11,12].



Figure 1. Measured and computed detonation velocity in stoichiometric dimethyl ether-oxygen mixtures with varying initial pressures



Figure 2. Experimental smoked foils showing the cellular detonation structure in stoichiometric dimethyl ether-oxygen mixtures with initial pressures: top) $P_o = 30$ kPa; middle) $P_o = 10$ kPa; and bottom) $P_o = 5$ kPa.

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Chemical kinetic analysis has been carried out to analyze the experimental observations. Different chemical kinetic parameters are computed by solving the one-dimensional steady-state ZND detonation structure using a DME detailed reaction mechanism [8]. All chemical kinetic computations have been done using Shepherd's ZND codes within the framework of CHEMKIN [13]. Figure 4 shows the temperature and thermicity profiles behind the ZND detonation for stoichiometric DME-oxygen mixture with two initial pressures $P_0 = 5$ kPa and 30 kPa. It is observed that the heat release rate of DME oxidation (characterized by the thermicity) exhibits some non-monotonic behavior. DME reaction inside the ZND structure behaves as a two-stage-like process, as indicated by the two local maxima in the thermicity profile. This is again similar to the case of nitromethane or H₂-NO₂/N₂O₄ reactions, where the two-stage reaction process is found to be related to the appearance of double cellular structures.



Figure 3. Experimental and predicted cell sizes for different initial pressures in stoichiometric DME-oxygen mixtures



Figure 5. Induction lengths of each reaction stage and their related ratios



Figure 4. Steady ZND detonation profiles (temperature and thermicity profiles) for initial pressures: top) $P_o = 30$ kPa; and bottom) $P_o = 5$ kPa

However, at high initial pressure P_0 , this feature has only minimal effect on the monotonicity of the temperature profile. Both stages occur very fast relatively to each other and the difference between the two corresponding scales as defined in the figure is not significant i.e. $L_1 \sim L_2$. In such cases, as discussed in [11], the characteristic cell size is still uniquely controlled by one scale and results should be comparable to those obtained for the case where the heat release occurs monotonically. When the initial pressure further decreases, L_2 increases relative to L_1 as shown in figure 4. Simultaneously, the heat release rate (characterized by the thermicity σ) of the first stage also increases rapidly relative to that of the second stage below $P_0 = 20$ kPa. The result is thus also suggested that below a certain critical value of L_1/L_2 , this reaction zone profile may result in the appearance of double cellular structure.

To compare with experimental measurement, the cell width is estimated from chemical kinetics using the linear proportionality relationship $\lambda = A(\chi) \cdot \Delta$ where Δ is the characteristic induction zone length (either L_1 or L_2)

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for each reaction stage). $A(\chi)$ represents a proportionality factor, which can be estimated using a recently developed correlation model [10] and is a function of a stability parameter χ [14]. It is important to point out that, due to the existence of the two-stage reaction, the stability parameter χ for a given mixture is always determined based the maximum value in the thermicity profile in this investigation. The predicted values of cell size of stoichiometric DME mixtures are shown by the dashed curve for $\Delta = L_1$ and by solid line for $\Delta = L_2$ in figure 3. At higher initial pressure P_0 , the experimentally measured cell sizes are always bounded by the predicted values associated with the two length scales and their values are very close. It is interesting to note that the kinetic prediction also gives a very good estimate for the two cell widths corresponding to the possible double cellular structure at $P_0 = 5$ kPa.

4 Concluding remarks

Works reported here has followed the conventional approaches to assess the detonation hazards of DMEbased mixtures. Detonation velocities and cell widths have been measured. Chemical kinetic analysis is carried out to explore the detonation characteristics of DME. It is shown that DME reaction behind the ZND wave can exhibit a weak two-stage-like process. In all cases, characteristic cell sizes are estimated using a recent correlation model based on each reaction length scale and it is shown to provide good estimation of the cell size for DME mixtures. This work is ongoing and further experimental data and kinetic analysis will be obtained to understand the effect of multiple reaction stages and for other different mixture conditions.

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