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TECHNICAL NOTE

Measurement and chemical kinetic model predictions of detonation cell size in methanol–oxygen mixtures

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Abstract In this study, detonation cell sizes of methanol–oxygen mixtures are experimentally measured at different initial pressures and compositions. Good agreement is found between the experiment data and predictions based on the chemical length scales obtained from a detailed chemical kinetic model. To assess the detonation sensitivity in methanol–oxygen mixtures, the results are compared with those of hydrogen–oxygen and methane–oxygen mixtures. Based on the cell size comparison, it is shown that methanol–oxygen is more detonation sensitive than methane–oxygen but less sensitive than hydrogen–oxygen.

Keywords Methanol · Detonation cell size · Chemical kinetics

1 Introduction

To reduce greenhouse gas emissions produced from gasoline fueled vehicles and to relieve the short supply of fossil fuels, continuous efforts have been made to seek appropriate alternative fuels that could solve the environment problem and petroleum crisis. Methanol (CH_3OH), often considered as one of the candidates for a future alternative fuel, can be produced from natural gas and biomass and, therefore, potentially provides a domestic source of fuel energy. The use of methanol in place of gasoline significantly decreases the related carbon dioxide greenhouse gas emissions [1–5]. Methanol has good chemical and combustion properties which allow it to be efficient as a fuel for combustion engines and fuel cells vehicles. It is thus an excellent choice for a replacement fuel as it could be used with the current refueling infrastructure.

To promote wide use of methanol as an alternative fuel in industrial applications, related safety issues have to be fully addressed. Specifically, fuel–air explosions are a key safety concern for all fuels. Accidental explosions and detonations occur often in industry and can result in casualty and severe loss of property. For the assessment of detonation hazards, measurement of dynamic detonation parameters such as cell sizes provides important information for the characterization of the explosion properties and the detonation sensitivity [6,7]. Despite some previous studies on the combustion characteristics of methanol, few cell size experiment data are reported to date.

In this study, detonation cell sizes of methanol–oxygen mixtures at different initial conditions (i.e., equivalence ratios and initial pressures) are measured from laboratory experiment. A theoretical approach, which is based on the properties obtained from chemical kinetics, is carried out to predict the cell size in methanol–oxygen mixtures and the results are compared with the experimental data. To assess the detonation sensitivity of methanol–oxygen mixtures, the present cell sizes data are then compared with those for some common fuels; namely, hydrogen and methane.

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2 Experimental details

Methanol is in liquid form at room temperature and atmospheric pressure. Hence, a 1 L Lexan container containing the liquid methanol was placed in a hot water bath and evacuated below the 15 kPa vapor pressure in order to vaporize the methanol. A cold trap packed with glass wool acted as a filter to trap moisture droplets between the Lexan container and a high pressure 100 L mixing tank. A schematic diagram of the experimental setup is given in Fig. 1. The mixtures of methanol and oxygen were prepared in the tank by the method of partial pressure and were allowed to mix for at least 20 h to ensure homogeneity. Each detonation experiment was performed in a 4.8 m long steel detonation tube with 65 mm inner diameter. Before every shot, sooted Mylar foils were inserted into the opposite end of the tube from which the detonation was initiated. The detonation tube was initially evacuated to approximately 200 Pa and then filled from both ends with the premixed methanol–oxygen mixture to the desired initial pressure. A 300 mm portion of the tube was used as a driver section. This section was separated from the rest of the tube by a thin Mylar diaphragm and was filled with an acetylene–oxygen mixture. The initiation of the incident Chapman–Jouguet (CJ) detonation in the upstream driver section was achieved via a high energy spark. Ion probes and pressure transducers were used to record the time of arrival of the reaction zone at each location. The experiment was carried out for methanol–oxygen mixtures at different initial conditions, with the equivalence ratios varying from $\phi = 0.5$ to 1.75 and the initial pressures from $p_0 = 2{-}30$ kPa.

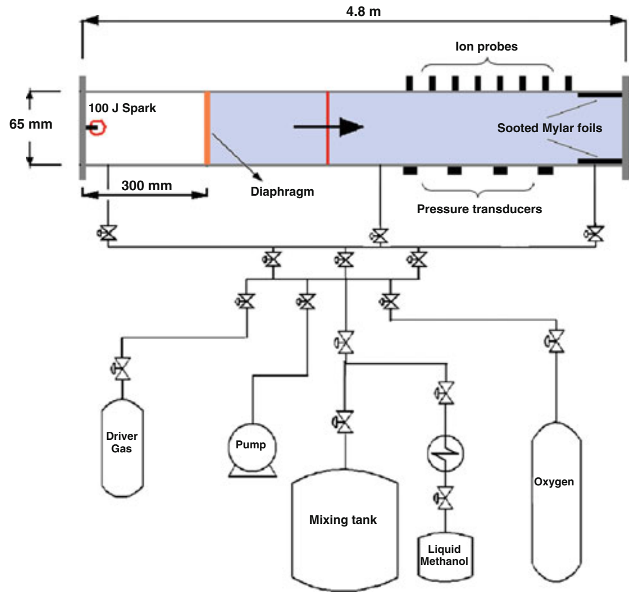


Fig. 1 Schematic diagram of the experimental setup

3 Results and discussion

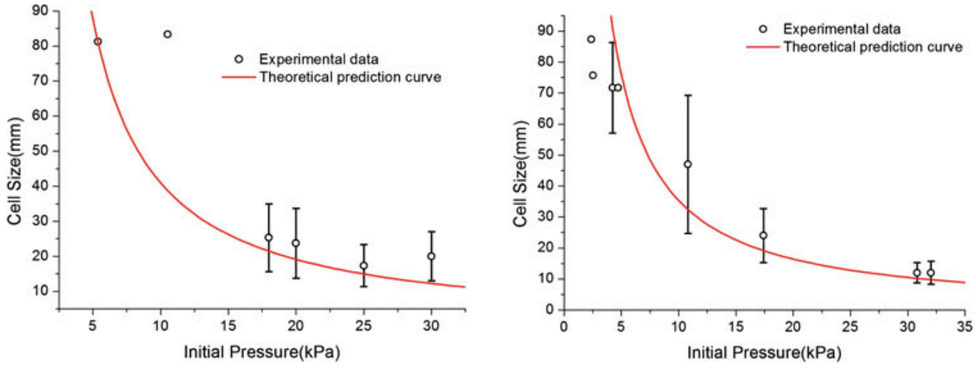
3.1 Experimental measurement

For each experiment, the wave velocity was obtained from the ion probes and pressure transducers and compared with the theoretical CJ velocity calculated using the chemical equilibrium code (Cantera) [8]. The detonation cell sizes are measured only for experimental shots where the detonation velocity measurement is within 5% of the theoretical CJ velocity. Figure 2 shows the cell size as a function of initial pressure for lean, stoichiometric and rich methanol–oxygen mixtures. Owing to the detonation instability of the methanol–oxygen mixture, the smoked foil sample for each detonation has a degree of irregularity (see Fig. 3), and thus there is an associated uncertainty with the corresponding cell size measurement. To gain a perspective of the size of this error, error bars for the 95% confidence interval [9] were calculated and plotted in Fig. 2. Noted that error bars are not graphed for data points derived from a sample size of less than five cells. With such a small sample size, not enough data are available to calculate accurate error bars. Thus, for the points that do not have error bars plotted with them, the error bars can be assumed to be on the same order as the rest of the data. It is observed from the graphs that the error bars appear to be increasing as pressure decreases. For low initial pressures, the detonation cell sizes are larger and therefore, there are fewer cells available to be measured per foil.

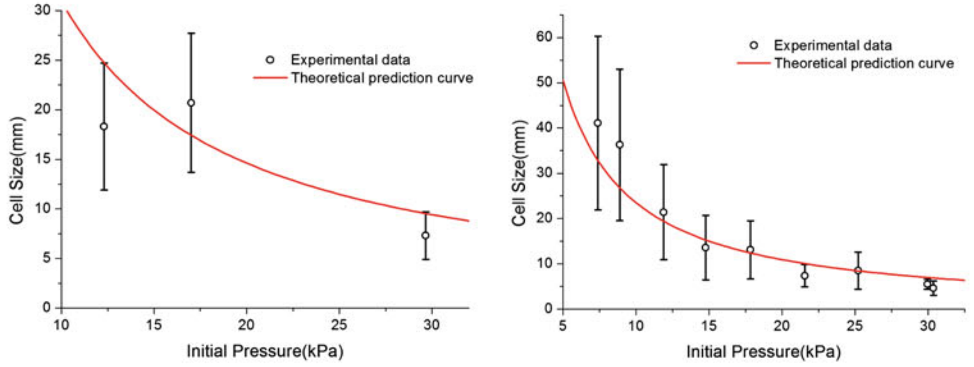
3.2 Theoretical prediction

Theoretical prediction of cell size can also be obtained from the chemical kinetic approach using the Zel'dovich–von Neumann-Döring (ZND) model [10]. The ZND detonation properties and different chemical length scales in methanol–oxygen mixtures were calculated using the Chemkin software package [11] and Konnov chemical kinetic mechanism [12]. The Konnov mechanism has been assessed and proved to be suitable for detonation simulation of a number of hydrocarbon systems [13]. Furthermore, this mechanism was previously extended and validated for high-temperature methanol ignition and oxidation [14]. As reported in [15], the Konnov mechanism is also found to provide better estimation of detonation cell size in methanol–oxygen mixtures than the GRI 3.0 mechanism [16]. With computed chemical kinetic information, Ng et al. [17–20] proposed a model to predict the characteristic cell size for a given mixture and initial condition. This model has been validated primarily for a number of different hydrocarbon and hydrogen fuels–oxygen–diluent mixtures. It has also been assessed by Mével et al. [21] for estimating the detonation cell size of hydrogen–nitrous oxide–diluent mixtures. In this model, the cell size is estimated from chemical kinetics

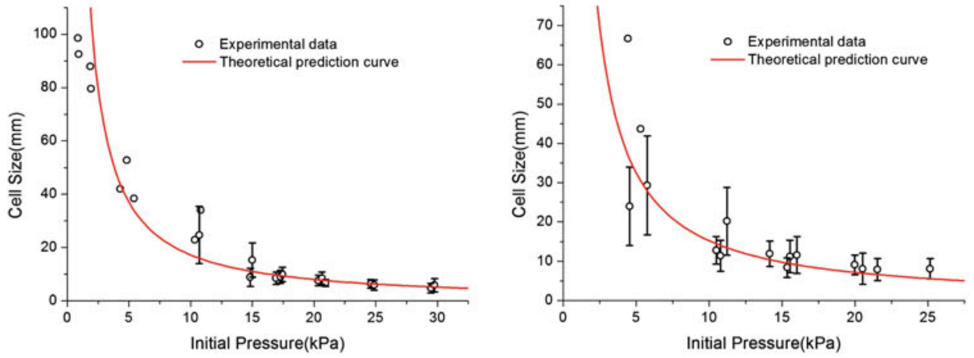
Fig. 2 Cell size variation with initial pressure for different methanol–oxygen mixtures at the equivalence ratios $\phi = 0.5, 0.55, 0.6, 0.75, 1.0, 1.25, 1.5$ and 1.75



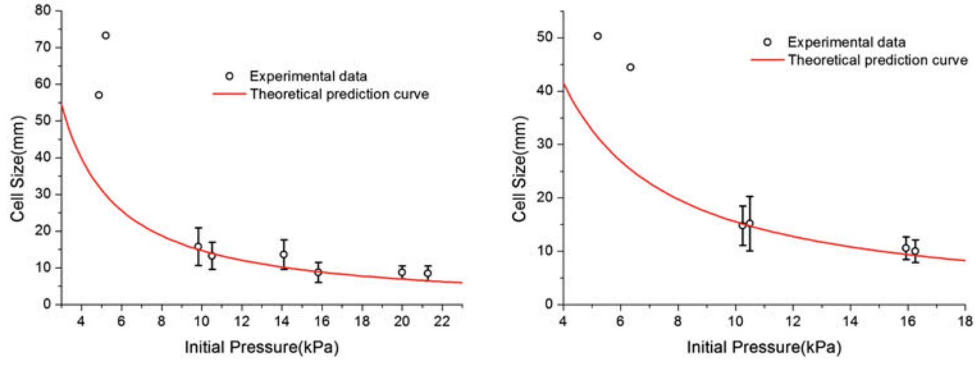
(a) $\phi = 0.5$ **(b)** $\phi = 0.55$



(c) $\phi = 0.60$ **(d)** $\phi = 0.75$



(e) $\phi = 1.0$ **(f)** $\phi = 1.25$



(g) $\phi = 1.5$ **(h)** $\phi = 1.75$

Fig. 3 Typical cell size sample from smoke foil for methanol–oxygen mixture ($p_0 = 10.7\,\text{kPa}$, $\phi = 1.0$)

by correlating the ZND induction length scale Δ_I using the following relationship:

$$\lambda = A(\chi) \cdot \Delta_\text{I} = \sum_{k=0}^{N} \left(a_k \chi^{-k} + b_k \chi^k \right) \cdot \Delta_\text{I}$$

$$\lambda = \left[(a_0 + b_0) + \frac{a_N}{\chi^N} + \ldots \frac{a_1}{\chi} + b_1 \chi + \ldots b_N \chi^N \right] \cdot \Delta_\text{I}$$

$$= \left[A_0 + \left(\frac{a_N}{\chi^N} + \ldots \frac{a_1}{\chi} + b_1 \chi + \ldots b_N \chi^N \right) \right] \cdot \Delta_\text{I} \quad (1)$$

where χ is a non-dimensional stability parameter given by the degree of temperature sensitivity in the induction zone ε_I multiplied by the ratio of induction length Δ_I to the reaction length Δ_R, which is approximated by the inverse of the maximum thermicity ($1/\dot{\sigma}_\text{max}$) multiplied by the CJ particle velocity u'_CJ.

$$\chi = \varepsilon_\text{I} \frac{\Delta_\text{I}}{\Delta_\text{R}} = \varepsilon_\text{I} \Delta_\text{I} \frac{\dot{\sigma}_\text{max}}{u'_\text{CJ}} \quad (2)$$

and the thermicity is given by:

$$\dot{\sigma} = \sum_{i=1}^{N_\text{s}} \left(\frac{W}{W_\text{i}} - \frac{h_\text{i}}{C_\text{p} T} \right) \frac{\text{d}Y_\text{i}}{\text{d}t} \quad (3)$$

where W is the mean molar mass of the mixture, C_p is the mixture specific heat at constant pressure, and h_i is the specific enthalpy of specie i [22]. The global activation energy in the induction process ε_I can be obtained by constant–volume explosion calculations. Assuming that the induction time τ_i has an Arrhenius form:

$$\tau_\text{i} \sim A \exp\left(\frac{E_\text{a}}{RT} \right) \quad (4)$$

Table 1 Coefficients in the detonation cell size correlation model by Ng et al. [17,18] with $N = 3$

Coefficients	Values
A_0	30.466
a_1	89.554
a_2	−130.793
a_3	42.025
b_1	−0.02929
b_2	1.02633×10^{-5}
b_3	-1.0319×10^{-9}

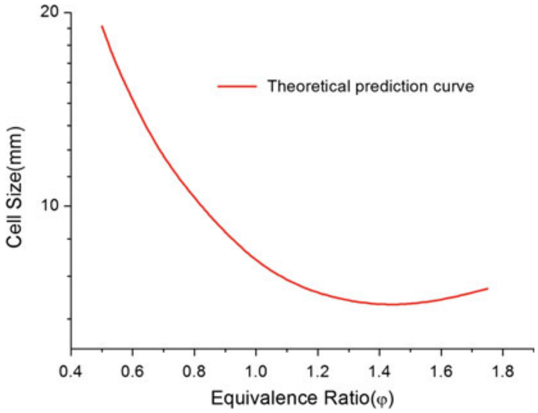


Fig. 4 Cell size variation with equivalence ratio for methanol–oxygen mixture ($p_0 = 20\,\text{kPa}$)

The activation temperature E_a/RT_s can be determined by

$$\varepsilon_\text{I} = \frac{E_\text{a}}{RT_\text{s}} = \frac{1}{T_\text{s}} \frac{\ln \tau_2 - \ln \tau_1}{\frac{1}{T_2} - \frac{1}{T_1}} \quad (5)$$

where two constant–volume explosion simulations are run with initial conditions (T_1, τ_1) and (T_2, τ_2). Conditions for states one and two are obtained by considering the effect of a change in the shock velocity by $\pm 1\% D_\text{CJ}$ [23]. Other parameters are fit coefficients obtained from previous correlation studies and are given in Table 1.

Also shown in Fig. 2 are the theoretical curves predicted using the above model. Overall, it is indicated that the chemical kinetic prediction gives a good estimate for the cell size of methanol–oxygen at the compositions considered in this experiment. The average deviation between the predicted values and the experimental data is 27.08%, which is within, and dominated by, the uncertainty in the low-pressure data.

Using the results from the theoretical prediction, it is interesting to look at the methanol–oxygen cell size variation with the compositions at the same initial pressure. Figure 4 shows the cell size as a function of equivalence ratio for methanol–oxygen mixture at initial pressure of 20 kPa. The typical 'U' shaped relationship between cell size and equivalence ratio is observed, where the cell size increases more abruptly at

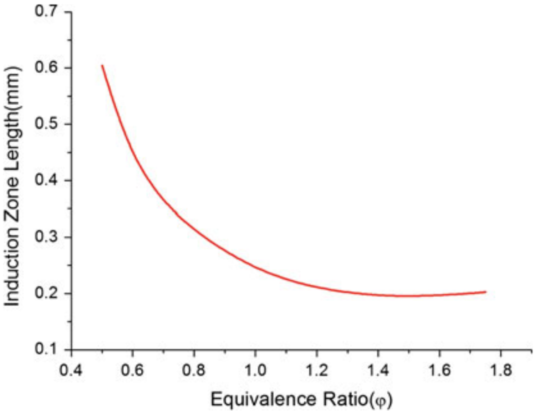


Fig. 5 Induction length variation with equivalence ratios for methanol–oxygen mixture ($p_0 = 20\,\text{kPa}$)

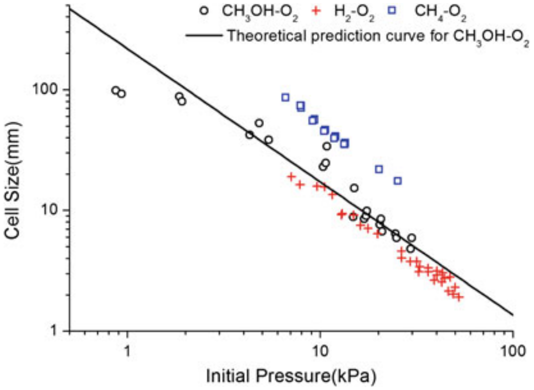


Fig. 6 Comparison of detonation cell sizes

the fuel lean side. The minimum cell size value arrives at $\phi = 1.4$, which means the mixture at $\phi = 1.4$ is the most detonation sensitive and is easiest to form a detonation when the other initial conditions are the same. This can be elaborated by calculating the induction zone length scale, which is shown in Fig. 5. It also shows that the minimum induction length occurs at the composition where the cell size has the minimum value, and the behavior between induction zone length and equivalence ratio is very similar to the variation of cell sizes with equivalence ratio.

3.3 Comparison of detonation sensitivity

Methane and hydrogen are two widely used fuels in the industry and their combustion or detonation characteristics have been well studied. By comparing the cell size of methanol with that of hydrogen and methane, it can provide some ideas on the detonation sensitivity of methanol mixtures. Figure 6 shows the cell size variation with the initial pressure for three stoichiometric fuel–oxygen mixtures, the cell size data for hydrogen–oxygen is from the study of Barthel [24], cell size for methane–oxygen are from Laberge et al. [25], Abid et al. [26] and Knystautas et al. [27]. By comparing the cell size of CH_3OH-O_2 mixture from this study with the H_2-O_2 and CH_4-O_2 mixtures from previous studies, it is indicated that the cell sizes of CH_3OH-O_2 are bigger than H_2-O_2 but smaller than CH_4-O_2 when at the same initial pressure. Equivalently, it means that CH_3OH-O_2 mixtures are more detonation sensitive than CH_4-O_2 but less sensitive than H_2-O_2.

4 Concluding remarks

In this study, the detonation cell sizes of methanol–oxygen mixtures are experimentally measured at different initial pressures and compositions. A theoretical approach, based on chemical kinetic calculations developed by Ng et al. is used for cell size prediction. By comparing the experimental data with the theoretical prediction curves, the agreement is within reasonable accuracy. By looking at the cell sizes of methanol–oxygen mixtures from chemical kinetic prediction at the same initial pressure but different compositions, it is found that the cell size of the mixture has a minimum value at the equivalence ratio $\phi = 1.4$, which also agrees with the ZND induction length variation. Cell sizes of methanol–oxygen from this study are compared with hydrogen–oxygen and methane–oxygen mixtures from previous studies, the results shows that the cell sizes of methanol–oxygen are bigger than hydrogen–oxygen but smaller than methane–oxygen when at the same initial condition, which means methanol–oxygen is more sensitive than methane–oxygen, but less sensitive than hydrogen–oxygen.

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