

Explosion behavior of methane - dimethyl ether /air mixtures

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1. Introduction

Alternative fuels with the properties of high-efficiency and low-emission combustion, have received particular interests because of the rapid increase in energy consumption and increasingly stringent emission regulations. Among them, natural gas (NG) is one of the most widely used alternative fuels for automobiles and has long been considered as a promising alternative fuel due to its favorable chemical characteristics, such as: high H/C ratio, large octane number, and especially its low emissions. Methane CH₄ as an environmental-friendly fuel and the main component of NG produces less carbon dioxide for each unit of heat released, but more heat per mass unit than other complex hydrocarbons. Nonetheless, methane has some drawbacks regarding its combustion properties, e.g., long ignition delay time, low flame speed, low ignitability and narrow flammability limit range. All of these pose great challenges for its wide utilization in combustion engines. However, using more reactive fuel additives, the ignition and combustion performance of methane could be greatly enhanced. From studies conducted by Dagaut [1,2] and Yao et al. [3,4] on the detailed chemical mechanism for low and high temperature DME oxidation and the effect of DME addition to methane for homogeneous charge compression ignition (HCCI) engines, respectively, DME has shown promise as an effective promoter of high temperature methane ignition. Due to an increasing interest in using NG in the automotive industry, a thorough understanding of the fundamental explosion and combustion characteristics of DME-added mixtures is therefore important for developing advanced, NG-based, combustion engines and corresponding operating strategies [5].

While the combustion characteristics of methane mixtures with DME addition have been studied extensively, comparatively little explosion safety data, e.g., maximum explosion pressure, $p_{\max}$, maximum rate of pressure rise $(dp/dt)_{\max}$, and laminar burning velocity S_L , are currently available. In fact, the explosion hazard of CH₄-DME mixtures, within storage infrastructures, is high due to the large destructive energy release associated with the combustion phenomenon. Therefore, in this study, experiments are performed systematically to address the explosion safety problems of CH₄-DME/air mixtures by recording overpressure histories at different composition of CH₄ and DME in a standard 20-L spherical vessel and

analyzing various derived explosion parameters. The data obtained in this study can contribute to a better understanding of the explosion behavior of CH₄-DME/air mixtures.

2. Experimental details

Measurement of the explosion parameters in CH₄-DME/air mixtures were carried out in a standard 20-L explosion spherical vessel according to the international standard ISO6184-1. This facility was used previously for the same type of measurement for other gaseous fuels (e.g., natural gas) and detailed information of the experimental details can be found in [6]. In brief, the 20-L explosion spherical vessel consists of an explosion chamber, an electric ignition system, a control unit, a data acquisition system, a release valve, a vacuum pump and an air pump. A high-voltage electric spark was used to supply the ignition energy. The igniter was mounted at the center of the spherical bomb and a spark energy of 10 J, estimated from $1/2 CV^2$ (“C” and “V” refer the capacitance and voltage, respectively. $C = 0.1102 \times 10^{-3}$ F, $V = 426$ Volts), was delivered by an electric ignition system.

For the explosion experiments, gas concentrations were regulated by the method of partial pressure. The purities of the CH₄ and DME used in this experiment were 99.9% and 99.8%, respectively. During the experiments, the explosion pressure evolutions were measured by a PCB pressure transducer installed in the vessel wall and recorded by a data acquisition system for each shot. These data yielded raw values of the explosion pressure and rate of pressure rise.

3 Results and discussion

3.1 Maximum explosion pressure and maximum rate of pressure rise

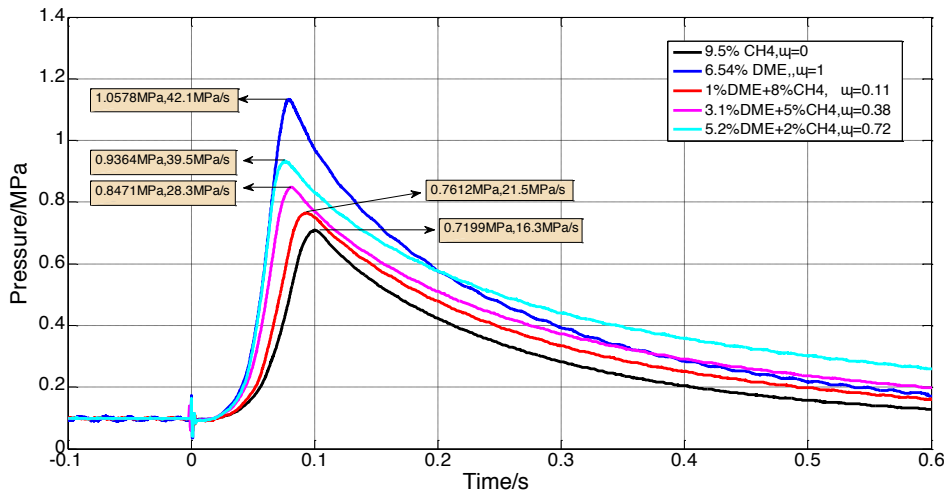


Fig.1 Typical pressure trajectories for different CH₄ and DME compositions

Samples of pressure traces obtained from experiments are shown in Fig. 1. To characterize the mixtures, λ is defined as the ratio of DME over the total fuel (i.e., CH₄ plus DME) as follows:

$$\lambda = \frac{C_{\text{DME}}}{C_{\text{DME}} + C_{\text{CH}_4}} \quad (1)$$

in which C_{CH_4} and C_{DME} denote the CH_4 and DME concentration, respectively. λ varies from 0 (pure CH_4) to 1 (pure DME). Unless specified, the total fuel is at the stoichiometric concentration with air. It can be seen from Fig. 1 that the maximum explosion pressure p_{max} increases with λ . The slope of the pressure history is also observed to become more steep or in other words, the maximum rate of pressure rise $(dp/dt)_{max}$ increases as well with increasing λ . Figure 2 summarizes the p_{max} and $(dp/dt)_{max}$ versus λ at an initial pressure $p_0 = 100$ kPa. It shows clearly that p_{max} and $(dp/dt)_{max}$ increase with increasing DME content in the total fuel.

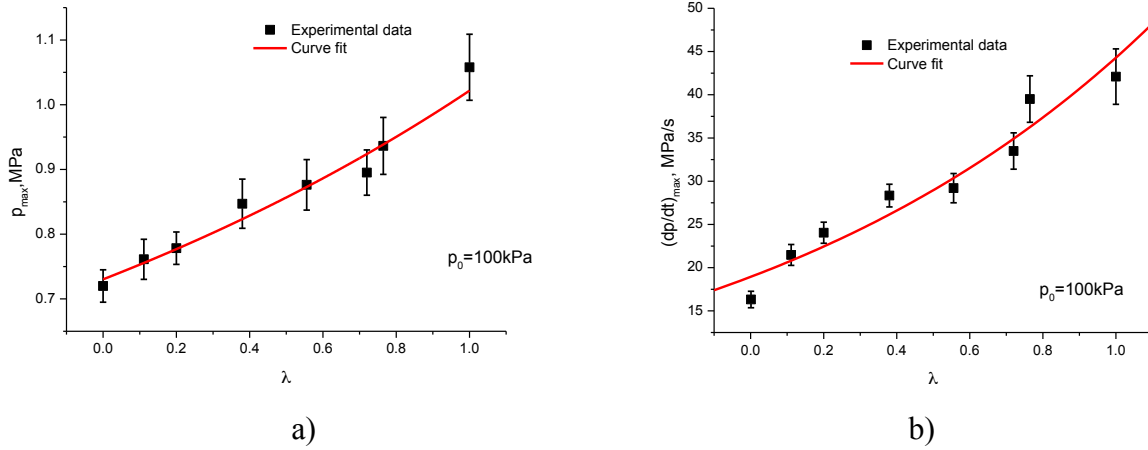


Fig.2 a) p_{max} and b) $(dp/dt)_{max}$ as a function of ratio λ

For pure CH_4 -air and DME-air mixtures, the maximum explosion pressure at different fuel concentrations are shown in Fig.3. The dimensionless pressure p_{max}/p_0 has a maximum value slightly above the stoichiometric concentration ($C_{CH_4} = 9.5\%$ at $\varphi \sim 1.0$). The experimental data and the curve fit of the dimensionless pressure at different CH_4 concentration are shown in Fig. 3a. The dimensionless pressure ($\bar{p}$) at different CH_4 volume fraction is correlated by the following equation:

$$\bar{p} = \frac{1}{2.81839 + 0.22424x_{CH_4} - 2.14347\ln(x_{CH_4})} \quad (2)$$

where, $\bar{p} = p_{max}/p_0$, x_{CH_4} is the volume fraction of CH_4 in air. The coefficient of determination R^2 equals to 0.9026. It should be noted that Eq. (2) is only valid for the initial pressure of 100 kPa and temperature of 298 K.

A similar plot of the dimensionless pressure versus DME concentration at 100 kPa and 298 K is shown in Fig. 3b. The peak of p_{max} appears at the DME concentration C_{DME} of 7%, which is slightly larger than the stoichiometric concentration ($C_{DME} = 6.54\%$ at $\varphi = 1$). This behavior is similar to the CH_4 -air mixture. The dimensionless pressure at different DME volume fraction is given by the following expression:

$$\bar{p} = \frac{1}{1.04153 + 0.12637x_{DME} - 0.94532\ln(x_{DME})} \quad (3)$$

where, x_{DME} is the volume fraction of DME in air, the coefficient of determination R^2 equals to 0.9217.

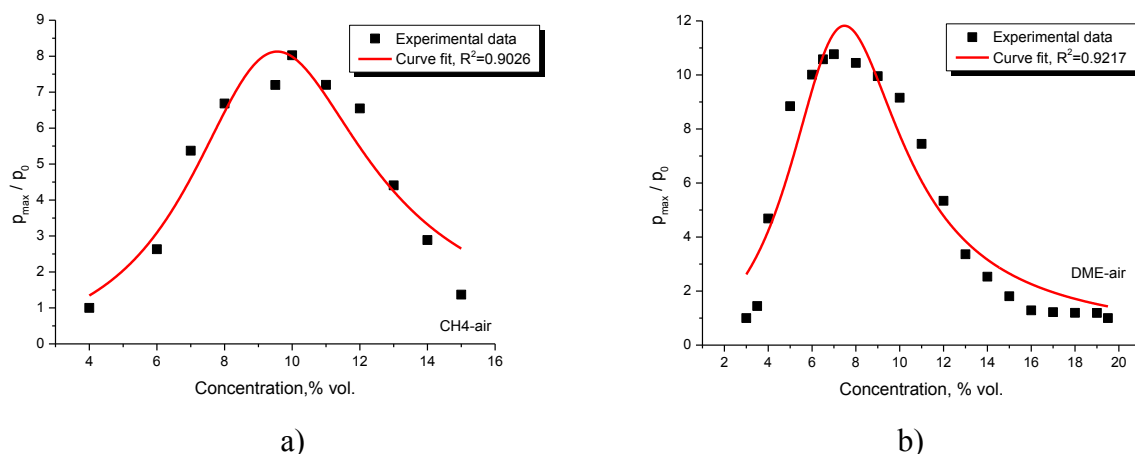


Fig.3 $p_{\max}$ as a function of a)CH₄ and b) DME concentration at 100 kPa

3.2 Laminar burning velocity

The laminar burning velocity, S_L , represents the rate at which the flame front propagates into the unburned gas. It received particular attention not only because it is a basic physico-chemical property (e.g., reactivity, diffusivity, and exothermicity) of the premixed combustible gases, its accurate knowledge is also essential for engine design, modeling of turbulent combustion, and validation of chemical kinetic mechanisms. In addition, the determination of laminar burning velocity is very important for the analysis and calculations used in explosion protection [6].

Laminar burning velocity are computed using the PREMIX module of the CHEMKIN package, and alternatively by a theoretical model developed by Dahoe et al. [7,8]. For the CHEMKIN-PREMIX simulation, the chemical kinetic mechanism involves 46 species and 263 reaction [9]. In the previous work by Chen et al. [10], equivalent PREMIX calculations of the laminar burning velocity for DME/CH₄/air mixtures are performed, and results are in satisfactory agreement with experimental data. As for the theoretical model, the laminar burning velocity depends on $p_{\max}$ and dp/dt . The model was also used in our previous study of natural gas-air mixtures [6] and the mathematical expression is given by:

$$S_L = \frac{1}{(p_{\max} - p_0)} \frac{1}{3} \left(\frac{4\pi}{3V} \right)^{-1/3} \left(\frac{p_0}{p} \right)^{1/\gamma} \left[1 - \left(\frac{p_0}{p} \right)^{1/\gamma} \times \left(\frac{p_{\max} - p}{p_{\max} - p_0} \right) \right]^{-2/3} \frac{dp}{dt} \quad (4)$$

where V is the vessel volume, p and p_0 are the actual pressure and initial pressure, and γ denotes the adiabatic coefficient of the unburned gas. Using Eq. (4) the value of the laminar burning velocity is determined when the pressure reaches to the maximum explosion pressure, i.e., $p = p_{\max}$. In addition, S_L is calculated at a flame radius greater than 6 mm in order to avoid the effects associated with spark ignition so that it can be considered as an ideal spherical flame propagating outward.

The laminar burning velocities computed by the above two methods for CH₄-air and DME-air at 100 kPa are given in Fig. 4. It can be seen from this plot both results agree well with each other. The values of S_L obtained from the theoretical model given by Eq. (4) do not differ significantly from those computed by the CHEMKIN-PREMIX simulation.

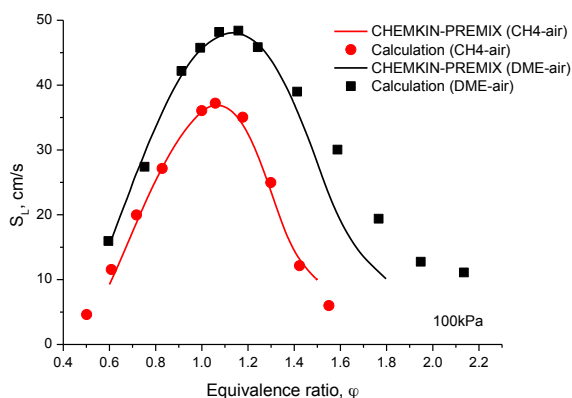


Fig.4 Comparison of the laminar burning velocity from different methods for CH₄-air and DME-air mixtures

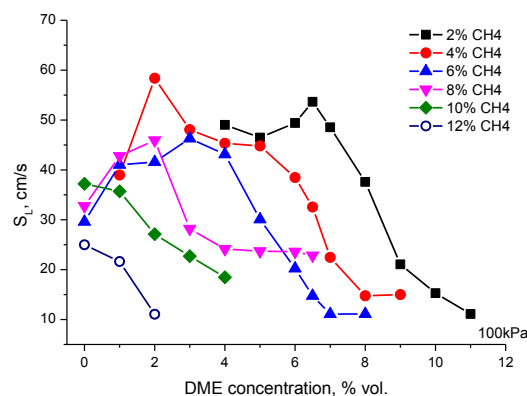


Fig.5 Laminar burning velocity of CH₄-DME/air mixtures

Figure 5 shows the laminar burning velocities of CH₄-DME/air mixtures at 100 kPa. For the mixtures of $\phi < 1$ (with fixed amount of $C_{CH_4} = 2\%, 4\%, 6\%, 8\%$ for each data set), the laminar burning velocity increases to a peak and subsequently decreases as the DME concentration continues to increase. For the mixtures of $\phi > 1$ (i.e., $C_{CH_4} = 10\%$ and 12%), the laminar burning velocity decreases rapidly as more DME is added. This is because for both CH₄-air and DME-air, the values of S_L are usually highest near stoichiometric conditions. Equivalently for CH₄-DME/air mixtures, the value of S_L near $\phi_{total} = 1$ is generally larger than on the fuel lean or rich side as well. As a small amount of DME is initially added into the CH₄ lean mixture, the equivalence ratio of the total fuel-air mixture tends toward stoichiometry, which makes S_L increase. However, if more DME is added into the lean CH₄ mixture (or DME added into the rich CH₄ mixture), S_L decreases.

4 Concluding remarks

A detailed investigation on the explosion behavior of methane - dimethyl ether /air mixture is performed in this study. Some conclusions are made as follows:

1. p_{max} and $(dp/dt)_{max}$ increase with increasing DME content λ in the total fuel. For both CH₄-air and DME-air mixtures, the dimensionless pressure at the equilibrium state has a maximum value at slightly above the stoichiometric concentration, and dimensionless pressure $\bar{p}$ can be approximated by the correlations: $\bar{p} = 1/[2.81839 + 0.22424\chi_{CH_4} - 2.14347\ln(\chi_{CH_4})]$ and $\bar{p} = 1/[1.04153 + 0.12637\chi_{DME} - 0.94532\ln(\chi_{DME})]$ at 100kPa, respectively.

2. The relation between p_{max} and DME concentration exhibits an inversely “U-shaped” curve for CH₄ lean mixture, and an exponential decay curve for CH₄ rich mixture.

3. The comparison of laminar burning velocity results between the CHEMKIN-PREMIX simulations and a theoretical model shows a satisfactory agreement for both CH₄-air and DME-air mixtures at 100 kPa. For CH₄-DME/air mixtures, S_L near $\phi_{total} = 1$ is larger than fuel lean or rich mixtures. As initially a small amount of DME is added into the lean CH₄ mixture, the mixture ϕ_{total} moves closer to 1 causing S_L to increase. Further additions of DME into the lean CH₄ mixture, or any DME added into the rich CH₄ mixture, only result in a decrease of S_L .

References

- [1] Dagaut P, Boettner J, Cathonnet M. (1996). Chemical kinetic study of dimethylether oxidation in a jet stirred reactor from 1 to 10 atm: Experiments and kinetic modeling. *Proc. Combust. Inst.* 26: 627-632.
- [2] Dagaut P, Daly C, Simmie JM, Cathonnet M. (1998). The oxidation and ignition of dimethylether from low to high temperature (500 – 1600 K): Experiments and kinetic modeling. *Proc. Combust. Inst.* 27: 361-369.
- [3] Yao MF, Zheng ZQ, Qin J. (2005). Experimental Study on Homogeneous Charge Compression Ignition Combustion With Fuel of Dimethyl Ether and Natural Gas. *J Eng Gas Turb Powe.* 128: 414-420.
- [4] Yao MF, Zheng ZL, Liu HF. (2009). Progress and recent trends in homogeneous charge compression ignition (HCCI) engines. *Prog Energ Combust.* 35: 398-437.
- [5] Dai P, Chen Z, Chen SY. (2014). Ignition of methane with hydrogen and dimethyl ether addition. *Fuel.* 118: 1-8.
- [6] Zhang B, Xiu GL, Bai CH. (2014). Explosion characteristics of argon/nitrogen diluted natural gas-air mixtures. *Fuel.* 124: 125-132.
- [7] Dahoe AE. (2005). Laminar burning velocities of hydrogen-air mixtures from closed vessel gas explosions. *J Loss Prevent Proc.* 18: 152-166.
- [8] Dahoe AE, Zevenbergen JF, Lemkowitz SM, Scarlett B. (1996). Dust explosions in spherical vessels: the role of flame thickness in the validity of the 'cube-root law '. *J Loss Prevent Proc.* 9: 33-44.
- [9] Zhao ZW, Chaos M, Kazakov A, Dryer FL. (2008). Thermal decomposition reaction and a comprehensive kinetic model of dimethyl ether. *Int J Chem Kinet.* 40: 1-18.
- [10] Chen Z, Qin X, Ju Y, Zhao Z, Chaos M, Dryer FL. (2007). High temperature ignition and combustion enhancement by dimethyl ether addition to methane-air mixtures. *Proc. Combust. Inst.* 31: 1215-1222.