Combustion characteristics of methanol–air and methanol–air–diluent premixed mixtures at elevated temperatures and pressures

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Abstract

Combustion characteristics of the methanol–air premixed mixtures were studied in a constant volume bomb at different equivalence ratios, initial pressures and temperatures, and dilution ratios. The results show that the combustion pressure, the mass burning rate and the burned gas temperature get the maximum value at the equivalence ratio of 1.1 while the flame development duration and the combustion duration get the minimum value at the equivalence ratio of 1.1. The flame development duration, the combustion duration and the peak combustion pressure decrease with the increase of the initial temperature, while the maximum burned gas temperature increases with the increase of the initial temperature. The peak combustion pressure and temperature increase with the increase of the initial pressure. The flame development duration and combustion duration increase with the increase of the dilution ratio, while the peak combustion pressure and temperature decrease with the increase of the dilution ratio.

Keywords:
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1. Introduction

Alternative fuels for both the spark ignition (SI) and the compression ignition (CI) engines become an important research direction owing to an increased environmental protection concern, and the need to reduce the dependency on petroleum oil promotes the research work [1]. Various types of alternative fuels, including hydrogen, compressed natural gas (CNG), liquid petroleum gas (LPG), alcohols and dimethyl ether (DME), etc, are used to realize the high-efficient low-emissions combustion engines [2–8]. Methanol is the simplest alcohol containing one carbon atom per molecule. Methanol can be produced from the coal with relatively low price. It has high octane number which makes it an ideal fuel for spark-ignition engines. Methanol has high oxygen content and this is favorable to the reduction of CO and HC emissions, and methanol has been using as an alternative fuel in automotive engines worldwide.

In the utilization of methanol fuel, a lot of work was concentrated on the combustion and emission characteristics of the engines fueled with gasoline–methanol or pure methanol [7–8]. There are also some studies in the application of diesel/methanol blend and animal fats/methanol blend in compression ignition engine in the literature. [9–10]. Moreover, some previous researches on the combustion applications and premixed combustion of methanol–air mixtures and gasoline–methanol–air mixtures were also reported [11–17], including the reduced methanol kinetic mechanisms, the flame speed and the flame behavior.

Nevertheless, there are still many aspects for the premixed flames of the methanol–air mixtures needed to be clarified, such as analysis of heat release (or mass burning rate) and burning velocities (flame development duration and combustion duration). The similar parameters in the spark-ignition engines are important for a quantitative analysis of engine behavior. Several key parameters in engine combustion analysis are the maximum cylinder gas pressure, the maximum mean gas temperature, the heat release rate, the flame development duration and the combustion duration etc. These parameters are depended on the equivalence ratio, the dilution ratio, the initial temperature and pressure. It is important to provide some detailed engine-related information for engine MAP optimization fueled with methanol under various equivalence ratios, gas dilution ratios, initial temperatures and pressures etc. However, it is hard to directly know the influence from individual parameters and the initial condition on combustion in engine operation as multi-parameter jointed influence [18]. This individual parameter influence can be indentified by using a constant volume vessel as mixture composition and initial temperature and pressure can be accurately controlled. It is easy to establish quantitatively the individual effect of these initial condition and composition parameters on the combustion characteristics. Moreover, only small quantities of combustible mixture are required for the constant volume vessel, so this method is economic. The data and combustion characteristics obtained from the constant volume vessel experiments not only can be used as reference to engine experiments but also help the understanding of the influence of
individual parameter on premixed methanol–air combustion. The information can also guide the engine experiments. The combustion in spark-ignition engines is carried out on the elevated temperatures and pressures ambient environment. Thus, the combustion characteristics at the elevated temperatures and pressures in the combustion vessel can provide much more data and reference information for engine combustion.

Based on the above considerations, the objective of the study is to clarify the combustion characteristics of the methanol–air premixed mixtures at elevated initial pressures and temperatures based on the analysis of the combustion parameters. The influences of equivalence ratio, gas dilution ratio, initial temperature and pressure on the normalized mass burning rate, the flame development duration, the combustion duration and the maximum burned gas temperature are analyzed.

2. Experimental setup and procedures

Fig. 1 shows the experimental setup in the study. The experimental system is composed of a constant volume vessel, the heating system, the ignition system, the data acquisition system and the high-speed schlieren photography system. The combustion chamber used in this experiment is a hollow cylinder type with inner diameter of 180 mm and volume of 5.5 l as shown in Fig. 2. The top-centrally located electrodes are used to ignite the combustible mixture. The pressure transmitter, thermocouple, pressure transducer, liquid fuel injection valve, the inlet and outlet valve are mounted on the chamber body. Two pieces of quartz windows with the diameter of 80 mm are mounted on the two sides of the vessel, which are transparent to make the inside observable and optical accessible. The partial pressures of each component are regulated by the pressure transmitter at initial pressures and pressures ambient environment. Thus, the initial pressure of methanol–air–diluent mixture is, $p_0 = p_{air} + p_{fuel} + p_{diluent}$ (1)

where $p_{air}, p_{fuel}$ and $p_{diluent}$ are the partial pressures for air, vaporized fuel and diluent, respectively.

The gas dilution ratio is defined as the ratio of the dilution gas partial pressure to that of the total mixture,

$$\phi_r = \frac{p_{diluent}}{p_{air} + p_{fuel} + p_{diluent}}$$

Mixture equivalence ratio $\phi$ is defined as,

$$\phi = \frac{(m_{air}/m_{fuel})_{st}}{(m_{air}/m_{fuel})}$$

where $m_{air}$ and $m_{fuel}$ are the amount of air and fuel, respectively, and subscript “st” represents the stoichiometric condition for the complete combustion. $m_{air}$ and $m_{fuel}$ are calculated by,

$$m_{air} = \frac{p_{air} \cdot V}{R_{air} \cdot T_u}$$

$$m_{fuel} = \frac{p_{fuel} \cdot V}{R_{fuel} \cdot T_u}$$

where $R_{air}$ and $R_{fuel}$ are the gas constants of air and fuel, respectively. $V$ is the volume of bomb, and $T_u$ is the initial temperature of mixture.

When initial pressure, $p_u$, initial temperature, $T_u$, dilution ratio, $\phi_r$, and equivalence ratio, $\phi$, are determined, $p_{air}, p_{diluent}$ and $m_{fuel}$ can be calculated from Formulae ((1)–(5)).

2.1. Calculation model

Calculation model is based on the hypothesis of spherical flame. The spherical flame front divides the combustion chamber into the burned zone and the unburned zone as shown in Fig. 3. The symbol $P, T, V,$ and $m$ represent the pressure, the temperature, the volume, and the mass of the chamber gases, respectively, and $Q_r$ is the amount of heat release by fuel combustion. The subscripts u and b represent the unburned and burned states, respectively. Following assumptions are given in the model,
(1) Gases are regarded as the ideal gases,
(2) Complete combustion finishes very rapidly when the unburned charge enters the burned zone,
(3) Pressure reaches its equilibrium value instantaneously, and there is no difference between the burned and unburned zones,
(4) No gas leakage is occurring, and the gas temperature reaches its respective temperature in the burned and unburned zones,
(5) The unburned gases are regarded as the mixture of methanol, air, and nitrogen,
(6) Gas properties of unburned and burned gases are the mixture properties calculated by the fraction of the constituted gases.

According to the mass conservation and energy conservation, the following equations can be established

\[
\frac{dm_u}{dt} = \frac{dm_b}{dt} \quad (6)
\]

\[
\frac{d(m_uu_u)}{dt} = -P \frac{dV_u}{dt} + \frac{dm_u}{dt} h_u + \frac{dQ_u}{dt} \quad (7)
\]

\[
\frac{d(m_bb)}{dt} = -P \frac{dV_b}{dt} + \frac{dm_b}{dt} h_b + \frac{dQ_b}{dt} + \frac{dQ_r}{dt} \quad (8)
\]

Because the same pressure is considered in both the burned and unburned zones, from the ideal gas assumption, we have

\[
P = \frac{m_uR_uT_u}{V_u} = \frac{m_bR_bT_b}{V_b} \quad (9)
\]
From Eqs. ((6)–(8), (9)), the following equations can be derived,

$$\frac{dT_u}{dt} = \frac{1}{\rho_u} \left[ Q_u + \frac{Q_u}{\rho_u} dT_u}{dt} \right] + \frac{1}{\rho_u} \left[ \frac{1}{R_u} \frac{dP}{dt} + \frac{1}{\rho_u} \right] \times \left[ \frac{\partial u_b}{\partial T_b} \right]^{-1}$$

$$dV_b = V_u \left[ -\frac{1}{\rho_u} \frac{dV_b}{dt} - \frac{1}{\rho_u} \frac{dT_b}{dT_u} + \frac{1}{\rho_u} \frac{dP}{dt} \right] + V_u \frac{dV}{dt}$$

2.2. Heat transfer calculation

The model takes into account both convective heat transfer and radiation. The coefficient of convective heat transfer is derived from the plate-plate convective heat transfer correlation as follows:

$$\alpha = \frac{C}{L_c \rho u L_c^2} (13)$$

in which $L_c$ is the characteristic length, and $\rho u L_c$ is the Reynolds number, where $\rho u = \rho u L_c / \mu$.

The radiant heat transfer flux, $q_r$, is calculated by

$$q_r = K\sigma(T^4 - T_w^4)$$

in which $\sigma$ is the Boltzmann constant, $\sigma = 5.67 \times 10^{-11}$ kW m$^{-2}$ K$^{-4}$. Thus, the transient heat transfer to the wall, $dQ_w/dt$, and the transient heat transfer from burned gas to unburned gas, $dQ_b/dt$, are determined by

$$\frac{dQ_w}{dt} = A_\alpha \left[ \alpha(T_w - T_u) + K\sigma(T^4 - T_w^4) \right]$$

$$\frac{dQ_b}{dt} = A_\alpha \left[ \alpha(T_b - T_u) + K\sigma(T_b^4 - T_w^4) \right]$$

This is the typical Annand’s heat transfer formula. Here, the constant $K$ uses the value of 1.5; $A_\alpha$ is the wall surface area; and $A_f$ is the spherical flame front area, which can be calculated by $A_f = (4\pi/3)(3V_b)^{1/3}$. $T_w$ and $T_u$ are the gas temperature for unburned and burned zones, while $T_w$ is the wall temperature.

In the Eqs. ((10)–(12)), $dp/dt$ is obtained from the pressure data in the experiments and $dV/\rho u$ takes the value zero for the constant volume bomb. The initial unburned gas temperature $T_u$ uses the adiabatic flame temperature $T_{ad}$, using the fourth-order Runge-Kutta scheme, and the $m_b$, $T_b$, $T_u$, and burning rate, $dmb/\rho u$, can be obtained. During the combustion process, gas compositions and properties are calculated through chemical equilibrium with 11 species and 7 equations [19].

Fig. 4. Combustion pressure and normalized mass burning rate versus the time at different equivalence ratios.

Fig. 5. Combustion pressure and normalized mass burning rate versus the time at three initial temperatures.
The normalized mass burning rate (NMBR) is defined as \( \frac{1}{C_1} \frac{dm}{dt} \), where \( m \) is the total mass of combustible mixture and \( m_b \) refers to the mass of burned gas. The NMBR rate is calculated from the two-zone model described above. This parameter reflects the burning velocity of the mixture during the combustion process.

The flame development duration is defined as the time interval from the spark ignition to the timing of 10% accumulated mass burned [20]. This parameter can be used to reflect the flame early development. The combustion duration is defined as the time interval from the spark ignition to the timing of 90% accumulated mass burned.

The study covers the equivalence ratios ranging from 0.7 to 1.8, nitrogen dilution ratios of 0.05, 0.1 and 0.15, initial temperatures of 373, 423 and 473 K, and initial pressures of 0.1, 0.25, 0.5 and 0.75 MPa.

3. Results and discussions

Fig. 4 gives the combustion pressure and the normalized mass burning rate versus the time for the methanol-air mixtures at different equivalence ratios. At the initial temperature of 423 K and the initial pressure of 0.1 MPa, the fastest normalized mass burning rate is presented at the equivalence ratio between 1.0 and 1.2 along with the shortest time interval from the ignition start to the peak pressure or peak mass burning rate. This reveals the fact that the fastest flame speed is presented at this equivalence ratio. In the case of rich mixture combustion, the flame propagation speed decreases and the combustion duration increases due to insufficiency of oxygen. For lean mixture combustion, the decrease in flame propagation speed and amount of fuel result in the decrease of peak pressure and the slowing of normalized mass burning rate. The phenomenon becomes more obviously for further richer or leaner mixtures.

Fig. 5 shows the combustion pressure and normalized mass burning rate at three initial temperatures for the stoichiometric methanol-air mixtures. The results show that the normalized mass burning rate increases with the increase of the initial temperature. The time interval from the start of ignition to peak pressure decreases with the increase of the initial temperature. The increase of the flame propagation speed with the increase of the initial temperature is responsible for this. The peak pressure decreases with the increase of the initial temperature, and this is resulted from the decrease of fuel density and the amount of heat released with the increase of the initial temperature when the initial pressure is fixed.

Fig. 6 illustrates the combustion pressure and the normalized mass burning rate for the stoichiometric methanol-air mixture at four initial pressures. The peak combustion pressure and the time interval from the start of ignition to peak pressure increase with the increase of the initial pressure, while the normalized mass burning rate decreases with the increase of the initial pressure. This reveals the fact that the amount of fuel will be increased with the increase of the initial pressure.

Fig. 7 shows the combustion pressure and normalized mass burning rate versus the time at different dilution ratios.
increasing the initial pressure decreases the flame propagation speed, thus the normalized mass burning rate is decreased and the time interval from the start of ignition to peak pressure is increased.

Fig. 7 gives the combustion pressure and normalized mass burning rate for the stoichiometric methanol–air mixture under different dilution ratios at the initial temperature of 373 K and the initial pressure of 0.1 MPa. The results show that the peak combustion pressure and the normalized mass burning rate decrease with the increase of dilution ratio whereas the time interval from the ignition start to peak pressure increases with the increase of the dilution ratio. Increase in dilution ratio will decrease the amount of fuel and flame propagation speed, leading to the decrease of normalized mass burning rate and the increase of time interval from ignition start to peak pressure.

Fig. 8 illustrates the effects of initial temperature on the flame development duration, the combustion duration, the maximum combustion pressure and temperature for the methanol–air mixtures at the initial pressure of 0.1 MPa. The shortest flame development duration and combustion duration are presented at the same equivalence ratio of 1.1. For lean mixture combustion, both the flame development duration and the combustion duration increase with the decrease of the equivalence ratio, and for rich mixture combustion, the flame development duration and the combustion duration increase with the increase of the equivalence ratio. The increase of flame development duration and combustion duration at both lean mixtures and rich mixtures are due to the decreased flame speed for a given equivalence ratio, the flame development duration and the combustion duration decrease with the increase of initial temperature. This reflects the fact that high initial temperature will increase the flame propagation speed, leading to short flame development duration and combustion duration. For the fixed initial pressure, increasing the initial temperature will decrease the peak combustion pressure, and this is due to the decrease of fuel density and amount of heat released. The study also reveals that maximum combustion temperature shows slightly increase with the increase of the initial temperature, and this suggests that maximum combustion temperature is insensitive to the variation of initial temperature. The increase of flame propagation speed and decrease of temperature are contributed to this behavior. The results show that the shortest flame development duration and combustion duration are decreased by 32% and 30%, respectively, as the initial temperature increases from 373 to 473 K. The maximum value of peak combustion pressure is decreased by 15%, while the maximum value of peak combustion temperature is increased by 0.7% as the initial temperature increases from 373 to 473 K.

Fig. 9 shows the flame development duration, the combustion duration, the peak combustion pressure and temperature of the methanol–air mixtures at three initial pressures. The results show
that the flame development duration and the combustion duration give the shorter period at low initial pressure. In the case of lean mixture combustion, the flame propagation speed decreases with the increase of initial pressure, thus, the flame development duration and combustion duration show an increase with the increase of initial pressure. For rich mixture combustion, the flame tends to the diffusional-thermal instability, and the hydrodynamic instability is enhanced with the increase of initial pressure due to the decrease of flame thickness. Cellular flame structure is easy to occur at the elevated initial pressure and rich mixture, leading to the increase of flame speed as increasing the flame front area between the unburned and the burned gases. Thus, the flame development duration and combustion duration increase with the increase of initial pressure (from 0.1 to 0.25 MPa) and they decrease with further increasing the initial pressure (from 0.25 to 0.5 MPa).

The peak combustion pressure remarkably and the peak temperature increase slightly, this is due to the increase in amount of fuel as initial pressure increases. The peak combustion pressure and temperature are presented at the equivalence ratio of 1.1 regardless of the initial pressures. Increasing the initial pressure directly increases the peak pressure, but increasing the initial pressure leads to equivalent increase in the amount of fuel and the amount of air, resulting in the small influence on peak temperature.

4. Conclusions

Combustion characteristics of methanol–air and methanol–air–diluent mixtures at different equivalence ratios, initial pressures
and temperatures, and dilution ratios are studied. The main conclusions are summarized as follows:

1. The methanol–air mixtures slightly richer than stoichiometric equivalence ratio give the peak combustion pressure, peak mass burning rate and burned gas temperature give their maximum values at the equivalence ratio of 1.1, while the shortest flame development duration and combustion duration are presented at the equivalence ratio of 1.1.
2. Flame development duration and combustion duration decrease with the increase of initial temperature. The shortest flame development duration and combustion duration are decreased by 32% and 30%, respectively, as the initial temperature increases from 373 to 473 K. Peak combustion pressure decreases with the increase of initial temperature, while the maximum burned gas temperature increases with increasing the initial temperature. The maximum value of peak combustion pressure is decreased by 15%, while the maximum value of peak combustion temperature is increased by 0.7% as the initial temperature increases from 373 to 473 K.
3. Flame development duration and combustion duration are increased with the increase of dilution ratio. At $\phi_r = 15\%$, the shortest flame development duration is double to that of the mixture without the diluent gas. Peak combustion pressure and temperature are decreased with the increase of dilution ratio, and the maximum values of peak combustion pressure and temperature at $\phi_r = 15\%$ are decreased by 14% and 0.6%, respectively, comparing with those without diluent gas addition.

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**References**


**Fig. 10.** Combustion parameters versus the equivalence ratios at different dilution ratios.


