Articles Chinese Science Bulletin

Engineering Thermophysics

March 2010 Vol.55 No.9: 882–889
doi: 10.1007/s11434-009-0709-y

Numerical study on combustion of diluted methanol-air premixed mixtures

ZHENG JianJun, ZHANG ZhiYuan, HUANG ZuoHua*, HU ErJiang, TANG ChengLong &
WANG JinHua

State Key Laboratory of Multiphase Flow in Power Engineering, Xi'an Jiaotong University, Xi'an 710049, China

Received June 2, 2009; accepted September 30, 2009

The effect of nitrogen dilution on the premixed combustion characteristics and flame structure of laminar premixed methanol-air-nitrogen mixtures are analyzed numerically based on an extended methanol oxidation mechanism. The laminar burning velocities, the mass burning fluxes, the adiabatic flame temperature, the global activation temperature, the Zeldovich number, the effective Lewis number and the laminar flame structure of the methanol-air-nitrogen mixtures are obtained under different nitrogen dilution ratios. Comparison between experiments and numerical simulations show that the extended methanol oxidation mechanism can well reproduce the laminar burning velocities for lean and near stoichiometric methanol-air-nitrogen mixtures. The laminar burning velocities and the mass burning fluxes decrease with the increase of nitrogen dilution ratio and the effect is more obvious for the lean mixture. The effective Lewis number of the mixture increases with the increase of nitrogen dilution ratio, and the diffusive-thermal instability of the flame front is decreased by the nitrogen addition. Nitrogen addition can suppress the hydrodynamic instability of methanol-air-nitrogen flames. The decrease of the mole fraction of OH and H is mainly responsible for the suppressed effect of nitrogen diluent on the chemical reaction in the methanol-air-nitrogen laminar premixed flames, and the NO_x and formaldehyde emissions are decreased by the nitrogen addition.

methanol, dilution, premixed combustion, numerical analysis

Citation: Zheng J J, Zhang Z Y, Huang Z H, et al. Numerical study on combustion of diluted methanol-air premixed mixtures. Chinese Sci Bull, 2010, 55: 882–889, doi: 10.1007/s11434-009-0709-y

With increasing concern about fuel shortage and air pollution control, researches on improving engine fuel economy and reducing exhaust emissions have become the major topics in combustion and engine studies. Because of limited reserves of crude oil, the development of alternative-fuel engines has attracted more attention in the engine community. Alternative fuels usually are clean fuels compared with traditional diesel fuel and gasoline fuel in the engine combustion process. The introduction of these alternative fuels is beneficial to the solution of the fuel shortage and reduction of engine exhaust emissions. Nowadays, clean alternative fuels mainly include hydrogen, compressed natural gas (CNG), liquid petroleum gas (LPG), dimethyl ether (DME), and alcohols in internal combustion engines application [1–4].

Methanol is thought to be one of the most promising alternatives to traditional vehicle fuels for engines since it can be produced from coal, natural gas and biomass with relatively low cost. It has been used as an alternative fuel in automotive engines worldwide [5]. Commonly, methanol is used as the fuel additives and/or the pure fuels in the internal combustion engine. Methanol has high octane number, and the blends of gasoline with methanol can increase the octane number of the fuel blends, thus high compression ratio can be used to increase the engine thermal efficiency and power output [6]. In addition, the latent heat value of methanol is larger than that of gasoline, and this is helpful to increase engine volumetric efficiency. Furthermore, the

---

*Corresponding author(email: zhhuang@mail.xjtu.edu.cn)

presence of oxygen atom in the methanol molecular is beneficial to the reduction of HC, CO and NO_x emissions.

In the utilization of methanol fuel, a lot of work has been conducted, which mainly concentrated on the combustion, performance and emission characteristics of internal combustion engines. Meanwhile, some researches focused on the fundamental combustion theory of the methanol-air flames were also reported, such as the laminar flame speed, the flame instability behavior and the methanol kinetic mechanisms, etc. Metghalchi and Keck [7], Saeed and Stone [8], and Gülder [9] measured the burning velocities of methanol-air mixtures in closed combustion bombs under certain conditions. However, in those previous studies, continuous observations of flame development process were not always implemented, and the laminar burning velocities were generally determined by resolving various combustion models based on combustion pressure traces. In addition, those procedures commonly ignored the influence of the stretch imposed on the flame, and Markstein lengths have not been obtained. Moreover, the discrepancies still exist to some extent within these experimental results. Gibbs and Calcote [10], Muller et al. [11] and Westbrook and Dryer [12] conducted flame chemical kinetics computation to determine the flame speed. However, those computational results still show somewhat obvious discrepancies with the experimental results. Recently, Liao et al. [13] investigated the flame propagation characteristics of laminar premixed methanol-air mixture by using a high-speed schlieren photography system under different initial temperatures and pressures, and it gave a relative accurate experimental result and related empirical correlations of the laminar burning velocities for engine numerical simulations.

Exhaust gas recirculation (EGR) is an effective technique for exhaust emission reduction in automobile engines due to its significant potential for NO_x reduction [14]. Therefore, the dilution effect on the combustion characteristics of premixed methanol-air mixtures is worthy of being investigated. Zhang et al. [15] conducted the research on the laminar premixed combustion characteristics of methanol-air-nitrogen mixtures at elevated initial temperature and pressure. However, the effect of dilution ratio on laminar premixed combustion characteristics of the methanol-air-nitrogen mixtures was just focused on the macroscopical combustion parameters such as laminar burning velocities and Markstein lengths, etc.

For the nonequidiffusive flames, the instability behavior of the flame front surface mainly depends on the adiabatic flame temperature, global activation energy, Zeldovich number, effective Lewis number, flame thickness and thermal expansion ratio [16]. However, few studies on these important parameters of methanol-air-nitrogen mixtures were reported. In addition, the flame structure obtained by detailed chemical kinetics computation can supply detailed information about the combustion and the chemical reaction process, which is very important to further researches on fundamental combustion and engine application. Therefore, the objective of this study is to numerically analyze the effect of nitrogen dilution on the premixed combustion characteristics and flame structure of the methanol-air-nitrogen flames, which will supply more detailed information of the methanol-air-nitrogen flames under diluted conditions. In addition, it will supply some data and theory support for the decrease of pollutant emission of methanol-air flames under diluted conditions in internal combustion engines.

1 Mechanism validation and computational methods

The methanol-air-nitrogen freely propagated laminar premixed flames were calculated by using the PREMIX code [17] in conjunction with the CHEMKIN package and the TRANSPORT package [18,19].

The PREMIX code adopts a hybrid time-integration/Newton-iteration technique with adaptive meshes to solve the steady-state mass, species and energy conservation equations of the calculated flames. The computations used windward differencing on the convective term and mixture-averaged transport equations. In order to ensure the boundaries sufficiently far from the flame itself, the calculation domain was set 12 cm. The authors made sure that the computational domain was sufficiently long to achieve adiabatic equilibrium downstream. At the upstream boundary, the initial temperature and pressure were set to be 373 K and 1.0 atm, respectively. The adaptive grids were kept between 1500 and 2000 to ensure computation accuracy. Initial guess values of the temperature and species profiles are also assigned to start the calculation.

Li mechanism [20] is an optimized particular chemical reaction mechanism for the calculation of methanol combustion reaction process, including 20 species and 325 elementary chemical reactions. It includes the detailed H_2/O_2, CO, HCO, CH_2O, CH_3, CH_4, CH_2OH, CH_3O and CH_3OH submechanisms and shows well agreement with the experimental results of laminar flame speeds in the methanol-air flames compared with previous methanol oxidation mechanisms [21]. The applicable conditions of Li mechanism are 300–2200 K in temperature, 0.1–2.0 MPa in pressure and 0.05–6.0 in equivalence ratio. Li mechanism can be utilized to calculate the combustion process in methanol-air mixture laminar premixed flames, flow reactors and shock tubes, although it lacks a NO submechanism. Therefore, in order to predict NO_x concentration in the methanol-air-nitrogen flames, an extended methanol oxidation mechanism is proposed by coupling Li mechanism with a new NO mechanism [22] in this paper.

In order to properly simulate and interpret the combustion characteristics of the methanol-air-nitrogen mixtures, the extended methanol oxidation mechanism used in the calculation must be validated. Figure 1 shows the comparison

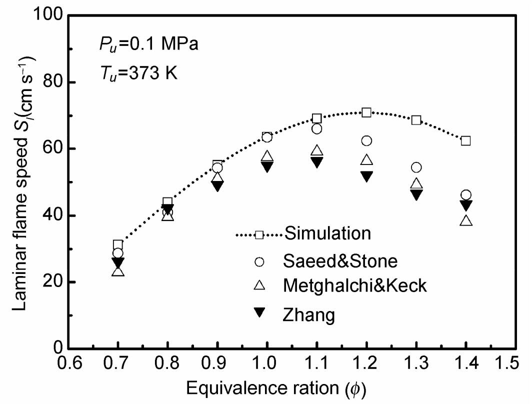

Figure 1 A comparison between the calculated laminar flame speed of methanol-air mixtures and that of the experimental values.

between the calculated laminar flame speed of the methanol-air mixtures by using the extended methanol oxidation mechanism and that of the experimental results by Metghalchi and Keck [7], Saeed and Stone [9], and Zhang et al. [15]. It can be seen that the extended methanol oxidation mechanism can well reproduce the laminar flame speed of the methanol-air mixtures under lean and stoichiometric conditions with a relative error of 8%. However, the calculated value is higher than that of the experimental results at rich conditions, and the relative errors increase with increasing equivalence ratio. This trend is in agreement with the calculated results of Bromberg [23] by using Li mechanism. It suggests that the extended methanol oxidation mechanism can be used to predict the combustion and chemical reaction process in the methanol-air flames under lean and near the stoichiometric mixture conditions. And the high relative error between the calculation and experiment under rich conditions may result from the chemical instabilities in these cases. Therefore, further researches on the methanol oxidation mechanism under rich condition are necessary.

The premixed laminar flame parameters and flame structure of the methanol-air-nitrogen freely propagated laminar premixed flames were calculated in this paper. Three typical equivalence ratios of 0.8, 1.0 and 1.2 were selected for the analysis. The nitrogen dilution ratio was set as 0%, 5%, 10%, 15%, 20%, 25% and 30%. The initial temperature and pressure was 373 K and 0.1 MPa. In this paper, the nitrogen dilution ratio was defined as the ratio of the amount of the additive nitrogen to that of the total mixture.

2 Results and discussions

2.1 Premixed laminar flame characteristics

Laminar flame speed and mass burning flux are very important physiochemical characteristic parameters, including the reactive, diffusive and heat release abilities of the combustible mixture [24]. Figure 2 gives a comparison between the calculated laminar flame speed and mass burning flux of the methanol-air mixture and that of the experimental results of Zhang et al. [15] versus nitrogen dilution ratio at different equivalence ratios. It can be seen clearly that the calculated laminar flame speed and mass burning flux of the methanol-air mixture are well in agreement with the experimental results of Zhang et al. [15] at ϕ=0.8 and 1.0, although certain errors exist between these two parameters and the experimental results of Zhang et al. [15] at ϕ=1.2 under different nitrogen dilution ratios. However, the calculated results can also show the impact of nitrogen dilution ratio on laminar flame speed and mass burning flux of the methanol-air mixture. The laminar flame speed decreases significantly with the increase of the nitrogen dilution ratio. This is because the specific heat of the non-fuel gases per unit oxygen concentration increased with the addition of the nitrogen dilution. In addition, the amount of the combustible mixture decreased relatively with the addition of the diluent, which will decrease the heat release of the combustible fuels. These factors lead to the decrease of temperature in the reaction region and thus the decrease of the laminar flame speed and mass burning flux [24]. Due to the small difference existing between the molecular weights of methanol and nitrogen, the density of combustible mixtures is insensitive to the variation of nitrogen dilution ratio. Thus, the mass burning flux gives a similar curve pattern to that of the laminar flame speed. As can be seen that, at ϕ=0.8, the laminar flame speed reduces by 70.49% (from 44.43 to 13.11 cm/s) when the nitrogen dilution ratio increases from zero to 30 percent. But the laminar flame speed reduces by 59.22% (from 71.57 cm/s to 29.18 cm/s) when the nitrogen dilution ratio increases from zero to 30 percentage at ϕ=1.2. It indicates that the influence of the nitrogen dilution is relatively stronger at lean mixture than that at rich mixture.

Adiabatic flame temperature is an important parameter which represents the thermodynamic properties of the combustible mixture. Adiabatic flame temperature indicates the heat release capacities of the unburnt mixture and it is related to various chemical phenomena such as flame propagation speed, flame extinction and flammability limits, etc. The adiabatic flame temperature was calculated by using STANJAN [25] in this paper.

Figure 3 gives the adiabatic flame temperature of the methanol-air mixture versus nitrogen dilution ratio. The adiabatic flame temperature decreases with the addition of the nitrogen diluent, which is obviously attributed to the effect of the inert diluent addition. This is because the heat value of the combustible mixture decreased with the addition of the nitrogen diluent. In addition, the addition of the nitrogen diluent adds extra heat capacity to the mixture and the nitrogen diluent absorbs part of the heat released by the combustion of the fuels, which leads to the decrease of the adiabatic flame temperature. The decrease of the adiabatic flame temperature is a reason for the decrease of the laminar flame speed as mentioned above [26].

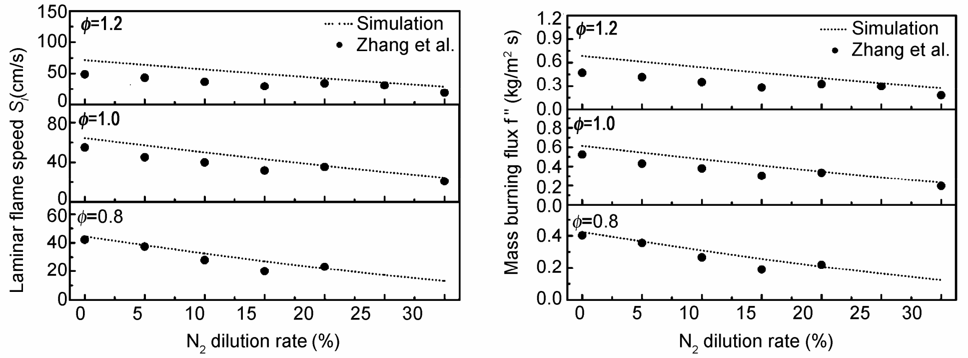

Figure 2 Laminar flame speed and mass burning flux versus nitrogen dilution (T_u=373 K, P_u=0.1 MPa).

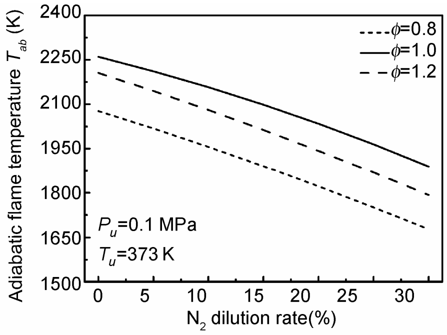

Figure 3 Adiabatic flame temperature versus nitrogen dilution ratio (T_u=373 K, P_u=0.1 MPa).

In the absence of body forces, laminar premixed flames are subjected to two modes of cellular instability, the diffusive-thermal instability and the hydrodynamic instability [27]. The diffusive-thermal instability results from the non-equidiffusive properties of the reactive mixture and an appropriate parameter indicating the extent and influence of non-equidiffusion is the Lewis number (*Le*), which can be estimated through the ratio of the mixture thermal diffusivity to the mass diffusivity of the limiting reactant relative to the inert usually presented in abundance [16]. Generally, when *Le* is larger than unit, it indicates that the influence of thermal diffusivity is more important than that of the mass diffusivity. In this case, the combustion is weakened at the convex segment and is intensified at the concave segment (relative to the unburned mixture side), leading to the suppression of the wrinkles and cellular structure on the flame front. This will gradually reduce the flame front fluctuation and makes the flame front be stable. On the contrary, when *Le* is less than unit, the influence of thermal diffusivity is less important than that of the mass diffusivity on the flame front, and the combustion is intensified at the convex segment while it is weakened at the concave segment, leading to the flame front into diffusively unstable. Furthermore, positive flame curvature tends to stabilize the hydrodynamic instability, while its influence on the diffusive-thermal instability depends on the nature of the mixture non-equidiffusivity.

For a global reaction scheme in which fuel and oxidizer react to products, the mixture is characterized by two distinct Lewis numbers, Le_E and Le_D, corresponding to relatively excess or deficient reactants, respectively.

The analysis of the flame zone then shows that these two combine into a single effective Lewis number [28] ,

$$Le_{\mathrm{eff}} = 1 + \frac{(Le_E - 1) + (Le_D - 1)\bar{\lambda}}{1 + \bar{\lambda}}, \tag{1}$$

where $\bar{\lambda} = 1 + Ze(\Phi - 1)$ is a measure of the mixture's strength. Here, Φ is defined as the ratio of the mass of excess-to-deficient reactants in the fresh mixture relative to their stoichiometric ratio and *Ze* is the Zeldovich number.

Figure 4(a) gives the effective Lewis number of the methanol-air-nitrogen laminar premixed flames versus nitrogen dilution ratio. The effective Lewis number increases with the increase of nitrogen dilution ratio, and the dilution effect is becoming larger when the mixture becomes leaner (ϕ=0.8). The addition of nitrogen as diluent will lead to the increase of thermal diffusive coefficient and thus the increase of effective Lewis number [29]. The study suggests that the flame front trends to be more stable at lean mixture and high dilution ratio for the methanol-air-nitrogen laminar premixed flames.

Since the development of the diffusive-thermal instability involves the change of the flame structure, the global activation temperature (or the Zeldovich number) should also affect the cell development [30]. In particular, it is reasonable to expect that a large global activation temperature will facilitate (suppress) the cell development of a diffusionally unstable (stable) flame. Based on the mass burning flux and adiabatic flame temperature, the activation temperature and Zeldovich number can be calculated as follows:

$$T_a = -2\frac{\mathrm{d}\ln(f^0)}{\mathrm{d}(1/T_{ad})_{p,\phi}}, \tag{2}$$

$$Ze = \frac{T_a(T_{ad} - T_u)}{T_{ad}^2}, \tag{3}$$

where, T_u is the temperature of the unburnt mixture. The differential in eq. (1) can be evaluated by calculating mass burning flux and adiabatic flame temperature for the given *p*

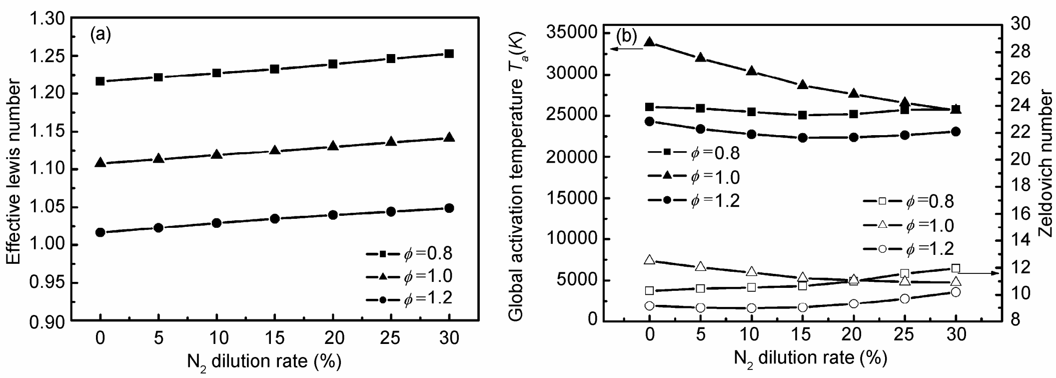

Figure 4 Effective Lewis number, global activation temperature and Zeldovich number versus nitrogen dilution ratio (T_u=373 K, P_u=0.1 MPa).

and ϕ, and by slightly varying its value through, say, the substitution of a small quantity of the nitrogen by inert argon [16].

Figure 4(b) shows the global activation temperature and Zeldovich number of methanol-air-nitrogen laminar premixed flames versus nitrogen dilution ratio. It can be seen that the global activation temperature and Zeldovich number decrease with the increase of nitrogen dilution ratio at stoichometric condition, which may suppress the cell development of a diffusionally unstable. However, the global activation temperature varies very little with the increasing nitrogen dilution ratio when the equivalence ratio departs from the stoichometric condition, but the Zeldovich number shows a slightly increasing trend with the addition of nitrogen diluent, which indicates the dominant influence of adiabatic flame temperature on Zeldovich number and the cell development of a diffusionally unstable may be facilitated in these cases.

Without nitrogen diluent addition, the global activation temperature and Zeldovich number get their maximum values under stoichometric condition, which is in agreement with the results of Liao et al. [13]. Meanwhile, when the nitrogen dilution ratio exceeds 20 percents, the Zeldovich number get its maximum value at the equivalence ratio apart from stoichometric condition. This may be due to the fact that the effect of nitrogen addition on the global activation temperature is more significant than that on adiabatic flame temperature under stoichometric condition and thus the Zeldovich number shows a decreasing trend with the increasing nitrogen dilution. However, the effect of nitrogen addition on the global activation temperature is less significant than that on adiabatic flame temperature apart from stoichometric condition, which leads to an increasing trend of the Zeldovich number with the increasing nitrogen dilution ratio. Therefore, the Zeldovich number gets its maximum value apart from the stoichometric condition when the nitrogen dilution exceeds a certain number.

Hydrodynamic instability is generated by the thermal expansion through the flame front surface [24], which can be qualitatively estimated by thermal expansion ratio and flame thickness. A high value of thermal expansion ratio tends to promote the hydrodynamic instability while a large thickness of flame tends to inhibit the hydrodynamic instability.

Thermal expansion ratio can be defined by the density ratio of unburned gas to burned gas at two sides of the flame front, and it is calculated from the STANJAN [24].

Based on Thierry and Denis' [31] recommendation, an accurate flame thickness δ_L can be defined as follows,

$$\delta_L = (T_{ad} - T_u)/\max\left(\left|\frac{\mathrm{d}T}{\mathrm{d}x}\right|\right). \tag{4}$$

Figure 5 gives the thermal expansion ratio and the flame thicknesses versus nitrogen dilution ratio. The results show that the thermal expansion ratio decreases with the increase of nitrogen dilution ratio, and the flame thickness increases with the increase of dilution ratio, because laminar flame speed and chemical reaction rate decreases with the addition of nitrogen diluent. Therefore, the addition of nitrogen as the diluent can suppress the occurrence of hydrodynamic cells and maintain a stabilized flame surface. Figure 5 also shows that thermal expansion ratio varies very little with the equivalence ratio, but flame thickness gets its minimum value near the stoichometric condition. It suggests that the hydrodynamic instability is stronger and the hydrodynamic

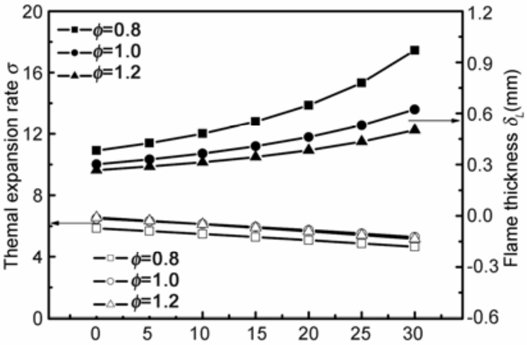

Figure 5 Thermal expansion ratio and flame thickness versus nitrogen dilution ratio (T_u=373 K, P_u=0.1 MPa).

cellular structure is easy to form near the stoichometric condition for methanol-air-nitrogen premixed flames. This is because the laminar flame speed and chemical reaction rate is commonly stronger near the stoichometric condition.

2.2 Premixed laminar flame structure

The representative flame structure in methanol-air-nitrogen laminar premixed flames is shown in Figure 6($\phi = 1.0$). This figure displays the mole fraction profiles of the reactants (CH_3OH and O_2), the products (CO, CO_2 and H_2O), the free radicals (H, OH, O, HO_2 and H_2O_2) and the carbon based intermediate species (CH_2OH, CH_3O, CH_2O,CH_3 and HCO), which are all the functions varying with the distance between the calculation point and the flame surface. It can be seen that the orders of magnitude of the mole fractions of the reactants and the products are between 10^{-2} and 10^{-1}. Meanwhile, the orders of magnitude of the mole fractions of the free radicals are between 10^{-4} and 10^{-3} and the orders of magnitude of the mole fractions of the carbon based intermediate species are between 10^{-5} and 10^{-3}. Therefore, the mole fractions of the major species in the laminar premixed flames are mainly determined by the composition of the reactants and the related chemical reaction processes. It can be seen that the mole fractions of the reactants and products decrease with the increase of nitrogen dilution ratio. This may be due to the dilution effect and the nonlinear chemical effect of nitrogen diluent addition. The decrease of mole fraction of the reactants will give large impact on the laminar flame structure in methanol-air-nitrogen laminar premixed flames.

The free radicals such as H, O and OH are extremely active due to the presence of unpaired electrons and are short-lived during combustion. The chain branching and chain propagating reactions initiated by free radicals play the most important role in chemical reaction [32]. The mole fractions of the free radicals are illustrated in Figure 6. It can be seen that the concentration of OH gets the largest value in free radicals of the methanol-air-nitrogen laminar premixed flames. Meanwhile, the concentration of H radical takes the second place (about 87% of the OH radical) and the total concentrations of HO_2 and H_2O_2 radicals are fewer than 35% of the OH radical. Therefore, the OH and H radicals will play an important role in chemical reaction processes. Also it can be seen that the mole fractions of OH and H decrease as nitrogen dilutent is added. Meanwhile the mole fractions of O, HO_2 and H_2O_2 vary very little with the increase of nitrogen dilution ratio. Therefore, the decrease of the mole fractions of OH and H is mainly responsible for the suppressed effect of nitrogen dilutent on the chemical reaction in the methanol-air-nitrogen laminar premixed flames. Also the change in the mole fraction of these free radicals can explain the decrease of the laminar flame speed partially.

As shown in Figure 6, the maximum values of the mole fractions of the carbon based intermediate species move towards the downstream of the flame region with the increase of nitrogen dilution ratio. Because temperature in the flame region decreases with the addition of nitrogen diluent, the production and consumption reactions of carbon based intermediate species will move to the higher temperature region near the hot boundary. Also it can be seen that the concentration of CH_2O is dominant in the carbon based intermediate species of the methanol-air-nitrogen laminar premixed flames while the orders of magnitude of the concentration of CH_2OH, CH_3O, CH_3 and HCO is less than that of CH_2O. In addition, the mole fractions of CH_2O, CH_2OH, CH_3O, CH_3 and HCO decrease with the increase of nitrogen addition because the mole fraction of methanol in the reactants decrease owing to the dilution effect of nitrogen. Furthermore, the decrease of the mole fractions of CH_2O and HCO indicates that the addition of nitrogen diluent is good for the decrease of formaldehyde emission in the methanol-air-nitrogen laminar premixed flames.

Since the temperature has great influence on chemical reaction process, the temperature profiles and the rate of production of methanol in laminar premixed methanol-air-nitrogen flames were calculated as given in Figure 7. This figure shows that the effect of nitrogen dilution on flame temperature on the reaction region begins from 0.5 mm apart from the cold boundary. In addition, the temperature in the flame region decreases as nitrogen dilutent is added, as it can be seen clearly that the maximum temperature in the flame region reduces by 16.53% (from 2262 K to 1888 K) when the nitrogen dilution ratio increases from zero to 30 percents. This is because the addition of the nitrogen diluent increases the heat capacity of the mixture, which leads to the decrease of the flame temperature. The decrease of the flame temperature leads to the decrease of rate of consumption of methanol. In addition, the decrease of the mole fraction of methanol in the reactant will also lead to the decrease of rate of consumption of methanol.

The extended methanol oxidation mechanism used in this paper includes the submechanisms of NO, NO_2 and N_2O. Figure 8 gives the mole fraction profiles of nitrogen oxides in the methanol-air-nitrogen flames based on the extended methanol oxidation mechanism. It can be seen that the concentration of NO is dominant in the nitrogen oxides of the methanol-air-nitrogen flames and the orders of magnitude of the concentration of NO_2 and N_2O is less than that of NO. The concentration of NO increases with the increase of the temperature in the flame region, and it gets its maximum value at the hot boundary. Meanwhile, N_2O gets its maximum concentration in the flame region and the concentration of NO_2 is insensitive to the variation of the temperature in the flame region. Also it can be seen that the mole fraction of NO decreases significantly with the increase of nitrogen addition, but the mole fraction of NO_2 and N_2O varies very little with the addition of nitrogen diluent. Nevertheless, the total amount of nitrogen oxides in the metha-

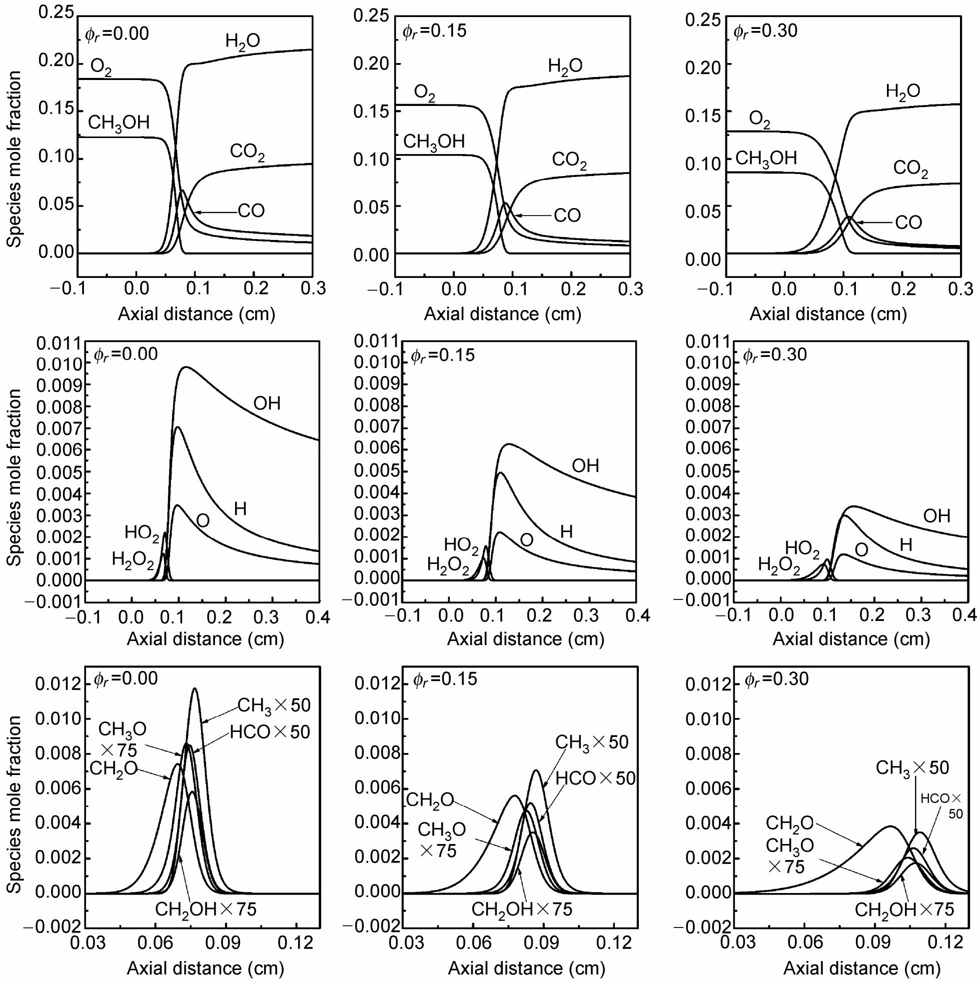

Figure 6 Representative laminar flame structure in methanol-air-diluent mixture(T_u=373 K, P_u= 0.1 MPa, ϕ =1.0) .

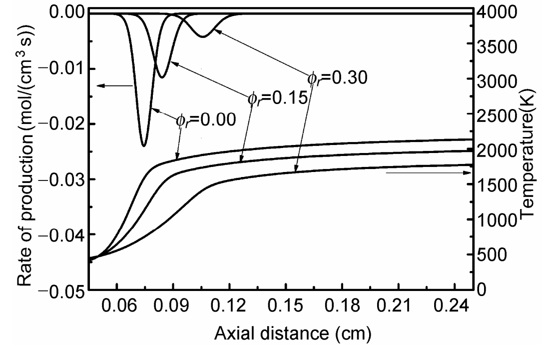

Figure 7 Flame temperature and rate of production of methanol in the laminar premixed methanol-air-diluent flames (T_u=373 K, P_u= 0.1 MPa).

nol-air-nitrogen flames will decrease with the addition of nitrogen diluent. The species of N_2, O_2, H, O, OH and N are very important species for the generation of NO_x, and they are generated in the higher temperature region. The flame temperature in the reaction zone decreases significantly with nitrogen diluent addition as illustrated in Figure 7. Therefore, the total amount of nitrogen oxides in the methanol-air-nitrogen flames will decrease with the addition of nitrogen diluent.

3 Conclusions

The effect of nitrogen dilution on the premixed combustion characteristics and flame structure were analyzed numerically based on an extended methanol oxidation mechanism. The results are summarized as follows:

(1) The extended methanol oxidation mechanism can well reproduce the laminar premixed burning characteristics and the combustion chemical reaction process for lean and near stoichiometric methanol-air-nitrogen flames.

(2) The adiabatic flame temperature decreases with the addition of the nitrogen diluent, which is obviously contributed to the effect of the inert diluent addition. The laminar burning velocities and the mass burning fluxes decrease with the increase of nitrogen dilution ratio and the effect is more obvious for the lean mixture.

(3) Without nitrogen diluent addition, the global activetion temperature and Zeldovich number get their maximum value at stoichometric condition while when the nitrogen dilution

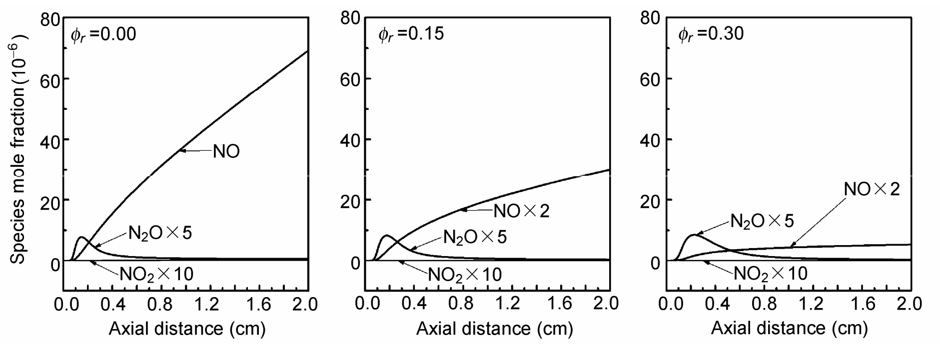

Figure 8 Nitrogen oxides mole fraction profiles of the methanol-air-diluent flames(T_u=373 K, P_u= 0.1 MPa, ϕ = 1.0).

ratio exceeds 20 percents, the Zeldovich number gets its maximum value apart from stoichometric condition.

(4) The effective Lewis number of the mixture increases with the increase of nitrogen dilution ratio, and the diffusive-thermal instability of the flame front is decreased by the nitrogen addition. Nitrogen addition can suppress the hydrodynamic instability of the methanol-air-nitrogen flames.

(5) The temperature in the reaction region decreases as nitrogen dilutent is added. The decrease of the mole fraction of OH and H is mainly responsible for the suppressed effect of nitrogen diluent on the chemical reaction in the methanol-air-nitrogen laminar premixed flames, and the NO_x and formaldehyde emissions are decreased by the nitrogen addition.

This work was supported by the National Natural Science Foundation of China (Grant Nos. 50521604 and 50876086).

1 Demirbas A. Fuel properties of hydrogen, liquefied petroleum gas (LPG), and compressed natural gas (CNG) for transportation. Energ Source, 2002, 24: 601–610

2 Teng H, McCandless J C, Schneyer J B. Thermodynamic properties of dimethyl ether-an alternative fuel for compression-ignition engines. SAE Paper, 2004–01–0093

3 Liao S Y, Jiang D M, Cheng Q, et al. Effect of methanol addition into gasoline on the combustion characteristics at relatively low temperatures. Energ Fuel, 2006, 20: 84–90

4 Yuksel F, Yuksel B. The use of ethanol-gasoline blend as a fuel in an SI engine. Renew Energ, 2004, 29: 1181–1191

5 Moreira J R, Goldemberg J. The alcohol program. Energ Policy, 1999, 27: 229–245

6 Bromberg L, Cohn D R. Effective Octane and Efficiency Advantages of Direct Injection Alcohol Engines. MIT Plasma Science and Fusion Center Report PSFC JA–08–02

7 Metghalchi M, Keck J C. Burning velocities of mixtures of air with methanol, isooctane, and indolene at high pressure and temperature. Combust Flame, 1982, 48: 191–210

8 Gülder Ö L. Laminar burning velocities of methanol, isooctane and isooctane/methanol blends. Combust Sci Technol, 1983, 33: 179–192

9 Saeed K, Stone C R. Measurements of the laminar burning velocity for mixtures of methanol and air from a constant-volume vessel using a multizone model. Combust Flame, 2004, 139: 152–166

10 Gibbs G J, Calcote H F. Effect of molecular structure on burning velocity. J Chem Eng Data, 1959, 4: 226–237

11 Muller U C, Bollig M, Peters N. Approximation for burning velocities and Markstein numbers for lean hydrocarbon and methanol flames. Combust Flame, 1997, 108: 349–356

12 Westbrook C K, Dryer F L. A comprehensive mechanism for methanol oxidation. Combust Sci Technol, 1979, 20: 125–140

13 Liao S Y, Jiang D M, Huang Z H, et al. Characterization of laminar premixed methanol-air flames. Fuel, 2006, 85: 1346–1353

14 Zhang Z Y, Huang Z H, Wang X G, et al. Measurements of laminar burning velocities and Markstein lengths for methanol-air-nitrogen mixtures at elevated pressures and temperatures. Combust Flame, 2008, 155: 358–368

15 Jomaas G, Law C K, Bechtold J K. On transition to cellularity in expanding spherical flames. J Fluid Mech, 2007, 583: 1–26

16 Kee R J, Grcar J F, Smooke M D, et al. A FORTRAN Program for Modeling Steady Laminar One-Dimensional Premixed Flames, Report SAND85-8240, Sandia National Laboratories, Albuquerque, NM, 1985

17 Kee R J, Rupley F M, Miller J A. CHEMKIN II: A FORTRAN Chemical Kinetics Package for the Analysis of Gas Phase Chemical Kinetics, Report SAND89-8009B, Sandia National Laboratories, Albuquerque, NM, 1993

18 Kee R J, Dixon-Lewis G, Warnatz J, et al. A FORTRAN Computer Code Package for the Evaluation of Gas-Phase, Multicomponent Transport Properties, Report SAND86-8246, Sandia National Laboratories, Albuquerque, NM, 1992

19 Li J, Zhao Z, Kazakov A, et al. A comprehensive kinetic mechanism for CO, CH_2O, and CH_3OH combustion. Int J Chem Kinet, 2007, 39: 109–136

20 Egolfopoulos, F N, Du D X, Law C K. A Comprehensive Study of Methanol Kinetics in Freely-Propagating and Burner-Stabilized Flames, Flow and Static Reactors, and Shock Tubes. Combust Sci Technol, 1992, 83: 33–75

21 Kong S C, Sun Y, Reitz R D. Modeling diesel spray flame lift-off, sooting tendency and NOx emissions using detailed chemistry with phenomenological soot models. J Eng Gas Turb Power, 2007, 129: 245–251

22 Bromberg L. Benchmarking of Alcohol Chemical Kinetic Mechanism for Laminar Flame Speed Calculations. MIT Plasma Science and Fusion Center Report PSFC JA–08–10

23 Law C K, Sung C J. Structure, aerodynamics, and geometry of premixed flamelets. Progr Energ Combust Sci, 2000, 26: 459–505

24 Reynolds W C. The Element Potential Method for Chemical Equilibrium Analysis: Implementation in the Interactive Program STANJAN, Department of Mechanical Engineering, Stanford University

25 Kuo K K. Principles of Combustion. New York: Wiley, 1986

26 Kadowaki S, Hasegawa T. Numerical simulation of dynamics of premixed flames: Flame instability and vortex-flame interaction. Progr Energ Combust Sci, 2005, 31: 93–241

27 Bechtold J K, Matalon M. The dependence of the Markstein length on stoichiometry. Combust Flame, 2001, 127: 1906–1913

28 Thierry P, Denis V. Theoretical and Numerical Combustion. Philadelphia: R.T. Edwards, Inc, 2005