

Effects of Ammonia Substitution on Explosion Limits of Methane

Yanze Guo^{a,b}, Aiguo Chen^a, Xi Deng^c, Jun Li^a, Wenxuan Ying^{a,b}, Xiuhua Ma^{a,b},
Yuhong Nie^a, Guansheng Chen^b, Hua Xiao^{a*}

^a School of Naval Architecture and Ocean Engineering, Guangzhou Maritime University, Guangzhou, China

^b School of Materials and Energy, Guangdong University of Technology Guangzhou, China

^c Department of Architecture, The University of Hong Kong, Hong Kong SAR, China

Abstract

As a hydrogen-rich and carbon-free fuel, ammonia is regarded as a promising carrier and storage medium for clean energy. By mixing methane with ammonia, the emission of carbon dioxide is also significantly reduced, which is of great significance for reducing greenhouse gas emissions and protecting the environment. However, ignition studies of ammonia/methane mixtures are still limited. In this paper, by means of numerical simulation with detailed chemical reaction mechanism, the effect of ammonia replacing methane on combustion was analyzed. Characteristics of explosion limit under different temperature (750-850K), equivalent ratio (0.5, 1.0 and 2.0) and ammonia mixing ratio (0-90%) were studied. The results show that the explosion limit decreases with the increase of temperature and equivalence ratio. When the proportion of NH₃ is around 10%, the explosion limit shows a turning point. When the mole fraction of NH₃ is higher than 50%, the explosion limit shows obvious increasing tendency with ammonia addition. Moreover, sensitivity and rate of production were also analyzed to expand the understanding of explosion limit for premixed ammonia-methane fuel blends.

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Introduction

With the confluence of environmental pollution, greenhouse effect and energy shortage, new alternative energy has attracted more and more attention [1]. As a carbon-free fuel, ammonia is also regarded as a promising carrier and storage medium for clean energy [1]. Compared with hydrogen, ammonia has many advantages [3], for example, the volumetric energy density of ammonia is higher than that of liquid hydrogen (the density of liquid ammonia is 108kg/m³ at 293K and 8.6bar, while the hydrogen density of the most advanced metal hydride is only 25kg/m³ [3,4]). The cost of ammonia is also currently lower than that of liquid hydrogen. The storage pressure of ammonia fuel (8bar) is about 87.5 times lower than that of hydrogen fuel (700bar), and the liquefaction temperature of ammonia fuel (293.8K) is much higher than that of hydrogen fuel (20K) [5]. Therefore, the low storage pressure and volume can save between 10- 47 times the cost, respectively [6]. Production, storage, transportation and utilization of ammonia has a history of more than a century, so the process has been optimized considerably. However, ammonia has a strong irritant smell at 2.0×10⁻⁶~5.3×10⁻⁶ g/m³.

In addition, the auto-ignition point of ammonia is about 800°C. As a fuel, ammonia will burn as it is flammable at a concentration of 13%-34% (vol). Even if leaked accidentally, due to its water-soluble characteristics, it is easy to remediate. The density of liquid ammonia is similar to gasoline, whilst its calorific value is about half that of gasoline. The octane number is much higher than gasoline, so the anti-knock performance is excellent, which can improve the output power of the engine whilst saving fuel [7,8]. Based on these thermofluid and economic characteristics of ammonia fuel, increased research interest has resulted in an increase in the number of studies on ammonia as a fuel for internal combustion and gas turbine engines, and as a hydrogen source for fuel cells [9-4] increasing particularly over the last 10 years. It has been shown that the flame velocity, heat release rate and radiation flux of the hybrid fuel mixtures comprising ammonia with hydrocarbons are all higher than that of pure ammonia fuel. Methane is relatively easy to use as a complementary fuel for combustion of fuel mixtures due to its similar density, viscosity and heat capacity with ammonia [1].

In previous studies, fundamental studies of ammonia combustion have been undertaken. Han et al. [14]

* Corresponding author. Tel.: +86-020-32083083. E-mail address: Xiaohua@gzmtu.edu.cn

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conducted an experimental study on the laminar burning velocity of ammonia/air, ammonia/hydrogen/air, ammonia/carbon-monoxide/air and ammonia/methane/air premixed flame using the heat flux method. Results showed that the laminar combustion velocity of the fuel mixtures has different dependence on the mole fraction of the components in the mixed fuel. The laminar burning velocity of ammonia/methane is quasi-linear, monotonically decreasing with ammonia fraction, while that of ammonia/hydrogen is non-linear. Lavadera et al. [15] used the heat flow method to measure the adiabatic laminar burning rate of methane, n-heptane and isooctane mixed with ammonia at atmospheric pressure and 338K. As the addition of ammonia promoted the increase H concentration, the effect on the laminar rate of methane fuel is more significant. Although ammonia only generates nitrogen and water in the case of complete combustion, it is difficult to avoid the production of nitrogen oxides in the actual combustion process, so how to reduce emissions of NO_x and deal with the exhaust gas has become an important challenge. Liu et al. [16] found that reactions involving H, NH₂ and NH₃ are dominant at low pressures, and with elevated pressures, the effects of oxidation reactions involving NO, NO₂, HNO and H₂NO are enhanced. Luo et al. [17] found that with methane at a fixed concentration, the more ammonia that is added the more effectively explosions are suppressed. When the amount of ammonia was fixed, it had a larger inhibitory effect on samples with high methane concentrations than on samples with lower concentrations.

Most research has focused on flame properties at atmospheric pressure, e.g. flammability, combustion rate, etc. In addition, studies of the ignition characteristics of NH₃/CH₄ mixtures under high pressure, which are particularly relevant to modern combustion systems, are also quite rare. In order to determine the reactivity of NH₃/CH₄ mixtures under a wider range of conditions, further explosion limit studies are needed to provide further understanding of ammonia chemistry. The explosion limits are the boundaries between the explosive and the non-explosive domains in the temperature-pressure diagram. In the present study, the pressure when the fuel-air mixture reaches the explosion criterion is defined as the explosion limit for certain temperature condition. Particularly, the criterion is when the temperature of a mixture rises 50 K within 0.5 s. By utilizing numerical simulations and chemical reaction mechanisms, the effect of ammonia replacing methane on combustion was analyzed, and the characteristics of the explosion limit under different temperature (750-850 K), equivalence ratio (0.5, 1.0 and 2.0) and ammonia mixing ratio (α = 0-90%) were studied. The

sensitivity and rate of production were also analyzed to expand the understanding of premixed ammonia-methane characteristics.

Numerical Modelling

The closed homogeneous reactor model of ANSYS Chemkin-PRO [15] was adopted to calculate the explosion limit of the CH₄/NH₃/air mixtures using the detailed chemical mechanism of Tian et al. [19]. The mechanism enables detailed methane and ammonia oxidation chemistry, consisting of 84 species and 703 elementary reactions based on their experimental and numerical study of the structure of premixed NH₃/CH₄/O₂/Ar stoichiometric flames at 4 kPa, using tunable synchrotron vacuum ultraviolet photoionization and molecular-beam mass spectrometry. The initial pressure and temperature ranges were explored from 10 kPa to 1×10⁵ kPa and 700 to 850 K, respectively. For methane and ammonia fuel mixtures, the equivalence ratios were 0.5, 1.0 and 2.0. α is the proportion of ammonia in the methane/ammonia fuel mixture, and air is taken as the oxidant, represented as 79% N₂ and 21% O₂ mixture. The ignition criterion is defined as temperature increasing by 50 K during 0.5 s [16]. This paper also investigates the explosion limit for different concentrations of CH₄/NH₃ fuel blends. Further analyses were performed by increasing the concentration of ammonia to 100% and using different concentrations of ammonia instead of methane mixtures. Sensitivity analyses of the effect between 1300-1900 K were also carried out.

Results and Discussion

Mechanism Verification

Numerical simulations of ignition delay times were performed for 10% NH₃/90% CH₄ fuel mixtures, as a parallel experimental study was conducted for such mixture at initial pressures of 2 and 5 atm, temperatures of 1300 to 1900K, and equivalence ratios of 0.5 to 2 [20]. As can be seen from Fig. 1, the simulation results from the Tian mechanism are in good agreement with the experimental results, compared with other mechanisms. It is illustrated that generally the numerical model gave good predictive performance in the low temperature region, although in the high temperature region, relatively larger deviations can be observed. The average relative error of Tian mechanism for all the conditions simulated is 20.5%. As can be seen from Fig. 1, increasing the pressure accelerates the ignition process of ammonia substituted methane mixtures at the selected conditions of temperature and equivalence ratio. As shown in the figures, temperature has a significant effect on promoting auto-ignition. Higher initial temperature reduces the auto-ignition delay time. From the experimental results, it is clear that the logarithm of the auto-

ignition delay time of CH₄/NH₃ blends have a similar linear gradient with the inverse of the temperature.

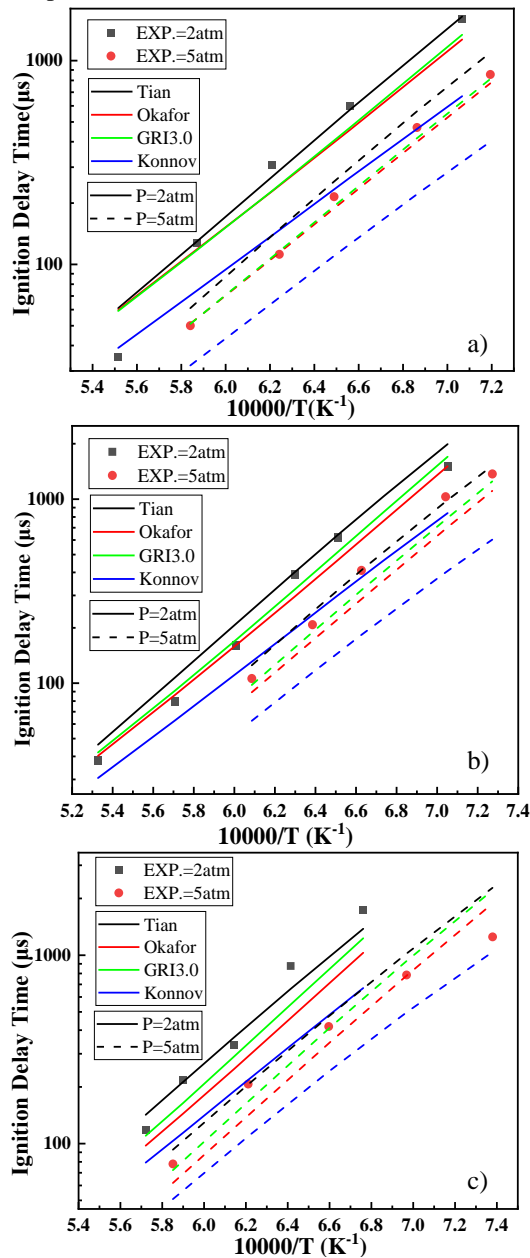


Fig. 1. Auto-ignition Delay Time of $a=10\%$ at Different Equivalence ratio (a) 0.5; (b) 1.0; (c) 2.0.

Explosion Limits

Figure 2 shows the variation of the explosion limit of ammonia/methane mixtures with the change of the mixing ratio for equivalence ratios between 0.5, 1.0 and 2.0 respectively. The criterion for determining the explosion limit is that the temperature of the gas mixture rises 50 K within 0.5 s. Generally, the explosion limit decreases with the increase of equivalence ratio and temperature. When the mole fraction of NH₃ is higher than 50%, the explosion limit increases, while the change is

relatively small at higher temperatures within the specified range.

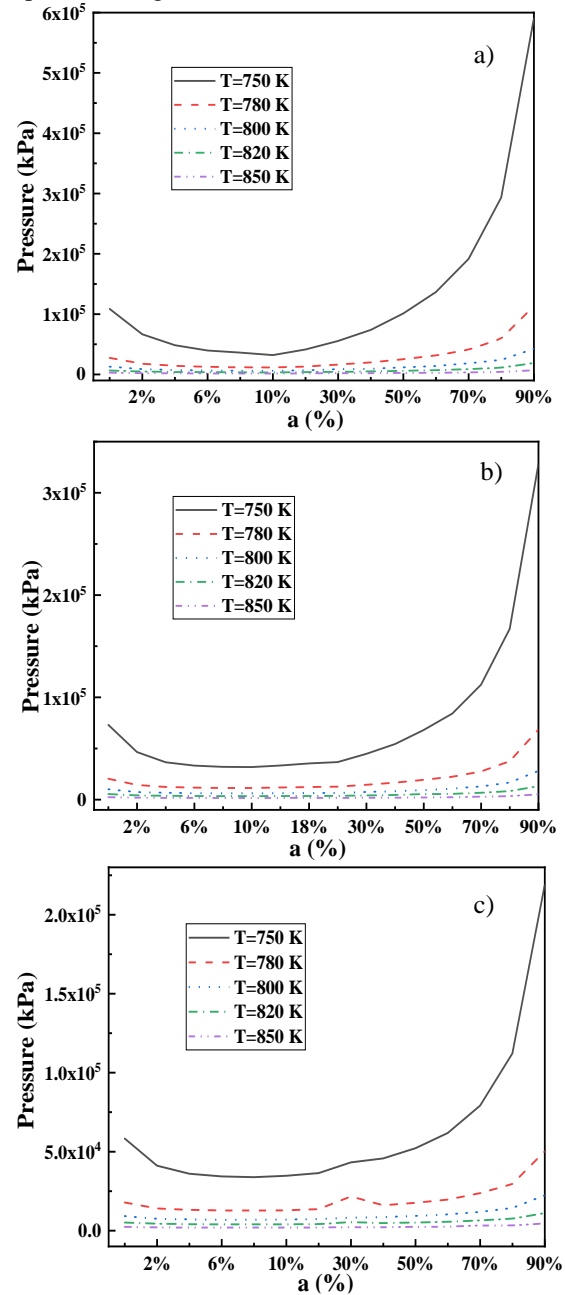


Fig. 2. Explosion Limits at Different Temperature and Equivalence ratios (a) 0.5; (b) 1.0; (c) 2.0.

As it can be seen from the figures, from fuel lean to rich conditions, turning points appear around $a=10\%$ when the temperature is 750 K. To illustrate the influence of different gas mixture proportions, the explosion limit was further analyzed for an equivalence ratio of 1.0 and an ammonia mole fraction (a) from 0 to 40%, as shown in Fig. 3. As can be seen from the figures, when $a<6\%$, the explosion limit decreases with ammonia substitution, whilst when $a>10\%$ there is clearly an upward trend.

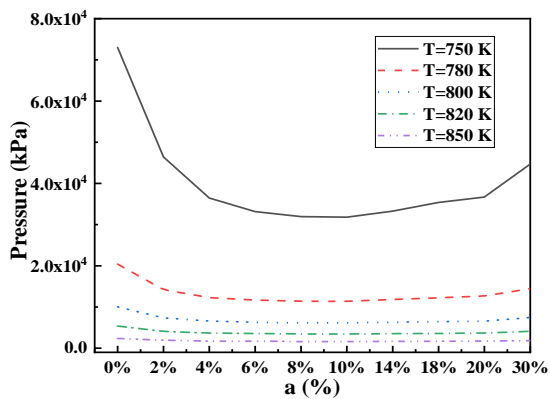


Fig. 3. Explosion Limits at $a=0-40\%$, temperature= $750-850$ K and equivalence ratio= 1.0

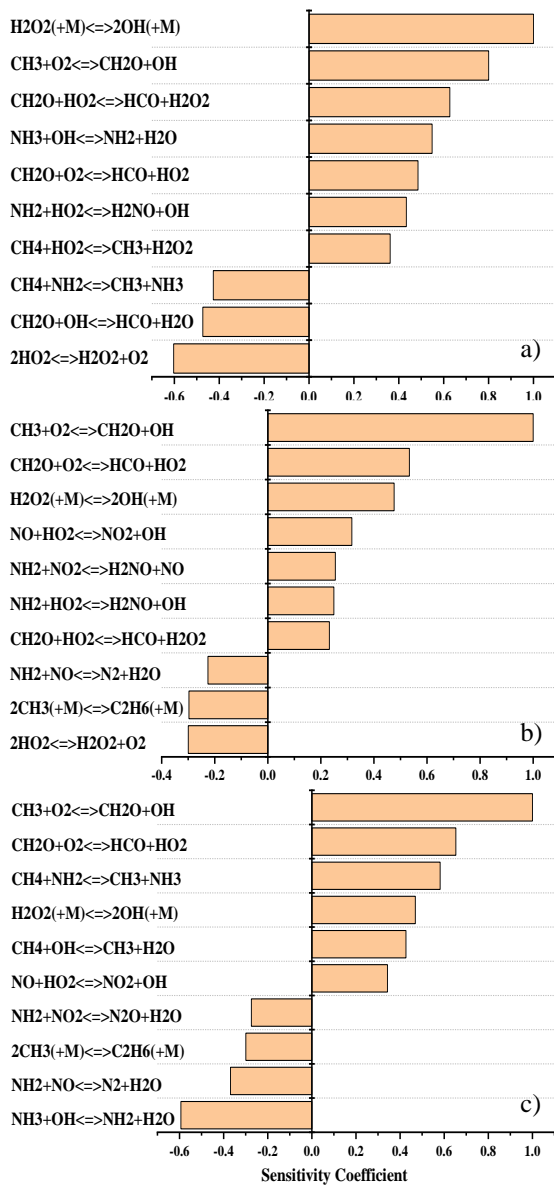


Fig. 4. Sensitivity Analysis at Different Mixing Ratios (a) 2% ; (b) 10% ; (c) 20% . $T=750$ K and Equivalence ratio= 1.0

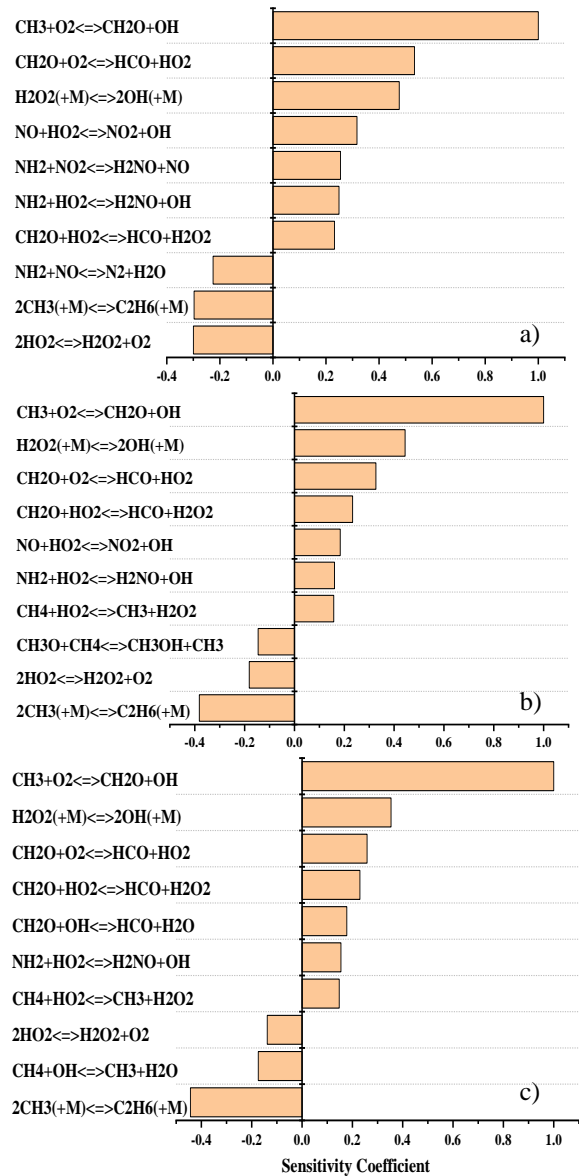


Fig. 5. Sensitivity Analysis at Different Temperatures (a) 750 K; (b) 800 K; (c) 850 K. $a=10\%$ and Equivalence ratio= 1.0 .

Sensitivity Analyses

Sensitivity analyses of OH radicals are conducted to gain a deep understanding of the simulation results of NH_3/CH_4 mixtures. Normalized sensitivity of OH is obtained by dividing the explosion sensitivity of an individual reaction by the largest absolute value among all the reactions for a given fuel [16]. Figures 4-6 compare the top 10 major reactions in the ignition process of the OH radical. The positive sensitivity coefficient indicates that the reaction in the forward direction will generate more OH with a pre-exponent factor increase, while the negative sensitivity coefficient indicates that the reaction will lead to the reduction of OH.

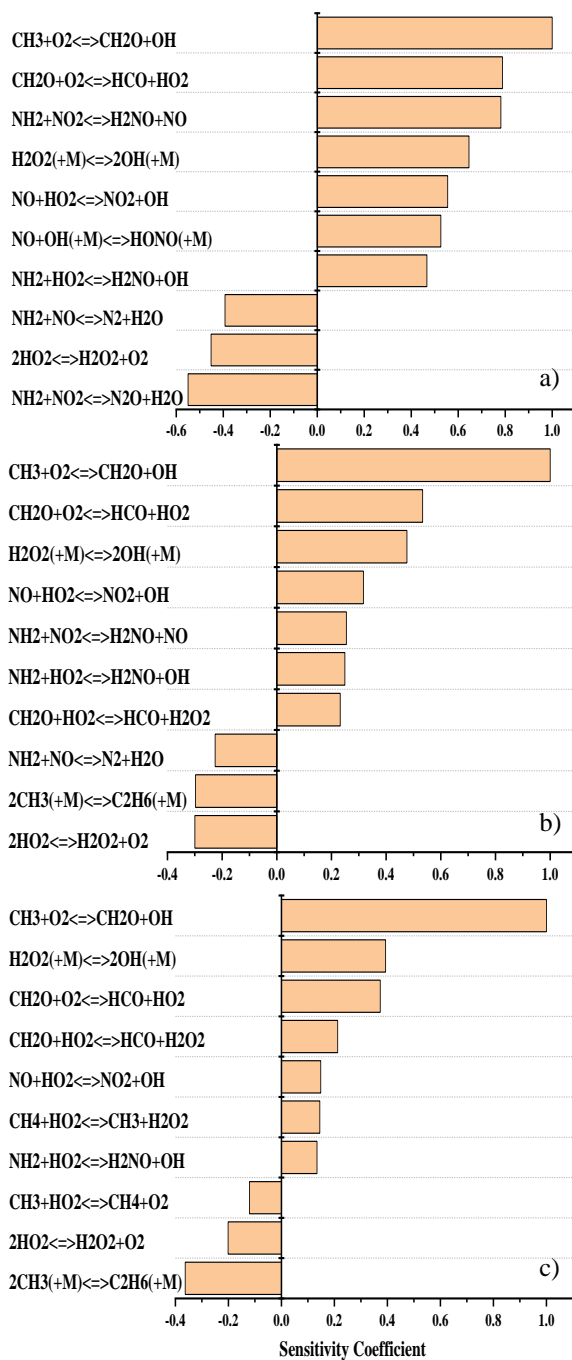


Fig. 6. Sensitivity Analysis at Different Equivalence ratios (a) 0.5; (b) 1.0; (c) 2.0. $\alpha=10\%$ and $T=750\text{ K}$

From the perspective of the overall sensitivity analysis, when α increases from 2% to 20%, the normalized sensitivity coefficient decreases by promoting reactions $\text{H}_2\text{O}_2(+\text{M})\leftrightarrow 2\text{OH}(+\text{M})$ and $\text{NH}_2+\text{HO}_2\leftrightarrow\text{H}_2\text{NO}+\text{OH}$, while the normalized sensitivity coefficient of the inhibiting reaction $2\text{HO}_2\leftrightarrow\text{H}_2\text{O}_2+\text{O}_2$ increases. The same phenomena can be observed for temperatures from 750-850K and equivalence ratios from 0.5 to 2.0. The sensitivity coefficient of the dominant reaction $\text{CH}_3+\text{O}_2\leftrightarrow\text{CH}_2\text{O}+\text{O}$ also shows an increasing

tendency with ammonia addition. As can be seen from Fig. 4, with the increase of ammonia mole fraction, the normalized sensitivity coefficient of reactions $\text{CH}_2\text{O}+\text{HO}_2\leftrightarrow\text{HCO}+\text{H}_2\text{O}_2$ and $\text{NH}_3+\text{OH}\leftrightarrow\text{NH}_2+\text{H}_2\text{O}$ decrease, whilst the reaction coefficient of $\text{NH}_3+\text{OH}\leftrightarrow\text{NH}_2+\text{H}_2\text{O}$ changes from positive to negative. With ammonia added, the sensitivity coefficient of the reactions $\text{CH}_2\text{O}+\text{O}_2\leftrightarrow\text{HCO}+\text{HO}_2$ and $\text{CH}_4+\text{NH}_2\leftrightarrow\text{CH}_3+\text{NH}_3$ increases. The increasing proportion of NH_3 in the fuel mixture promotes the reaction with CH_3 , whilst weakening the reaction with OH .

It can be observed in Fig. 5 and Fig. 6 that temperature and equivalence ratio have only a small influence on the reactions with OH . With the increase of temperature or equivalence ratio, the reaction $\text{CH}_3+\text{O}_2\leftrightarrow\text{CH}_2\text{O}+\text{OH}$ consistently plays a leading role. The sensitivity decreases with temperature increase for the reactions $\text{H}_2\text{O}_2(+\text{M})\leftrightarrow 2\text{OH}(+\text{M})$, $\text{CH}_2\text{O}+\text{O}_2\leftrightarrow\text{HCO}+\text{HO}_2$ and $\text{NH}_2+\text{HO}_2\leftrightarrow\text{H}_2\text{NO}+\text{OH}$, while the sensitivity increases for $2\text{HO}_2\leftrightarrow\text{H}_2\text{O}_2+\text{O}_2$.

Rate of Production

In order to further understand the phenomenon of explosion limit variation with turning point, analyses of the constant volume adiabatic reaction path were performed by tracing the nitrogen elements of ammonia/methane mixtures at different mixing ratios, a temperature of 750 K and an equivalence ratio of 1.0. As observed by others [21-24] and as in Fig. 7, the first step of NH_3 oxidation is to generate NH_2 . After NH_2 reacts with HO_2 , etc., HNO is further oxidized through H_2NO , whilst HNO reacts with H and O_2 to form NO . It can be seen that with the increase of NH_3 content in the mixed gas, the role of HNOH element gradually increases, and the conversion of $\text{HNO}\rightarrow\text{NO}$ and $\text{H}_2\text{NO}\rightarrow\text{HNO}$ is accelerated.

As can be seen from Fig. 7, when the ammonia mole fraction increases from 2% to 4%, the radicals in the reaction do not change, however the conversion rate of NH_2 and NO is enhanced, due to the increase of N elements. As HCNO reacts mainly with OH radical to produce NCO , the process leads to a greater production of NO by the reactions with O_2 . This is consistent with the study of Schoor et al. [25], where the addition of ammonia promotes the formation of NO , making the reaction path in the methane oxidation scheme faster. When α continues to increase (Fig. 7c-d), the role of NCO decreases and new radicals such as HNOH appear.

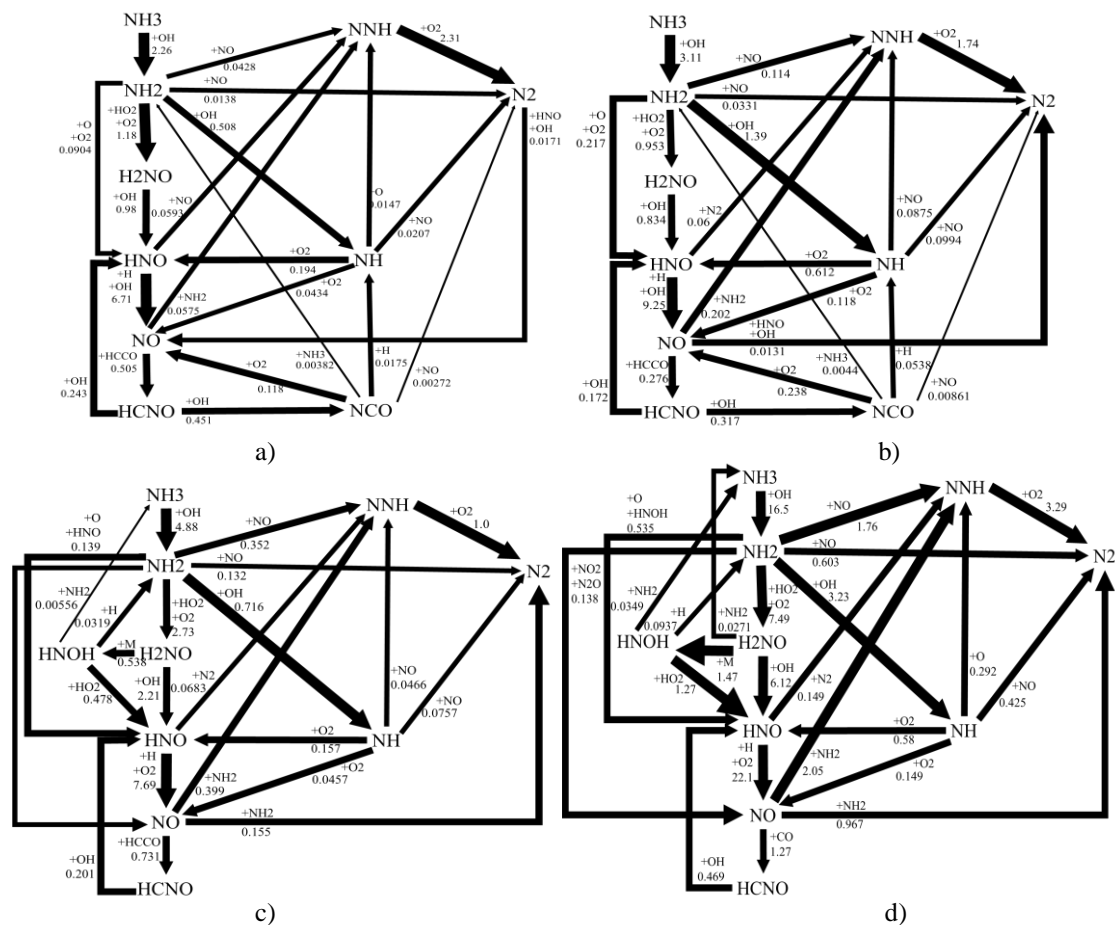


Fig. 7. Rate of Production at Different Mixing Ratios (a) 2%; (b) 4%; (c) 10%; (d) 20%. $T=750$ K and Equivalence ratio=1.0. Thickness is indicative of the rate of production.

It is worth noting that when the ammonia content increases from 10% to 20%, the reaction path of $\text{NO} \rightarrow \text{HCNO}$ is weakened, while the reaction paths of $\text{NO} \rightarrow \text{N}_2$ and $\text{NO} \rightarrow \text{NNH}$ are strengthened. As more ammonia is added in the fuel blends, fewer reactions of the small hydrocarbon radicals play important roles in the reaction path of ammonia oxidation. Meanwhile, the role of HNOH gradually increases. The transformation of $\text{HNOH} \rightarrow \text{NO}$ are enhanced. It is also indicated that the selectivity for forming NO or N_2 is mainly determined by the fate of small amine radicals, since few interactions between hydrocarbon and nitrogen species are depicted in the pathway analyses.

Conclusions

In this paper, effects of ammonia replacing methane on explosion limits have been analyzed using a detailed chemical reaction mechanism. Characteristics of explosion limits under different temperatures (750-850 K), equivalence ratios (0.5, 1.0 and 2.0) and ammonia mixing ratio ($a = 0$ -90%) were investigated.

In general, it is found that the explosion limit decreases with the increase of temperature and equivalence ratio. When the proportion of NH_3 is around 10%, the explosion limit shows a turning point, first decreasing and then increasing. When the mole fraction of NH_3 is higher than 50%, the explosion limit increases more acutely.

Sensitivity analyses show that when the mole fraction of NH_3 in fuel blend is between 2%-20%, the increasing proportion of NH_3 in the mixed gas leads to greater influence of CH_3 groups. Analyses of rates of production show that with the increase of NH_3 content, the role of the HNOH radical gradually increases and the conversion of $\text{HNO} \rightarrow \text{NO}$ and $\text{H}_2\text{NO} \rightarrow \text{HNO}$ are accelerated.

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Conflicts of Interest

The authors declare no conflict of interest.

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