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Study on Premixed Combustion Characteristics of Co-firing Ammonia/Methane Fuels

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Abstract

Ammonia is believed eventually play an important role in substituting conventional fossil fuels for future energy systems. In this study, to gain a deep insight into the combustion properties of co-firing ammonia/methane fuel blends for the power and steel industry, a detailed chemical-kinetics mechanism model was developed for comprehensively modelling ammonia/methane fuels combustion. Characteristics of ignition delay time, unstretched laminar burning velocity and NO, CO_2 and CO emissions in the exhaust gas were obtained over a wide range of equivalence ratios and ammonia fractions. High NO emissions will be a main problem as CO and CO_2 emissions tend to drop when adding ammonia into methane. To gain a further understanding of the effect of ammonia substituting methane for combustion use, analyses of laminar premixed flame structures were performed. The impact of ammonia substitution was illustrated by analysing relevant specific radicals. Furthermore, to study the combustion characteristics of ammonia/methane under more practical conditions, effects of engine relevant conditions (elevated pressure and initial temperature) were also studied. Results indicate that pressure has a more prominent effect than initial temperature and there is a good potential that unwanted emissions can be reduced significantly under industrial conditions.

Keywords: Emissions, ammonia/methane, chemical-kinetics mechanism, co-firing

1 Introduction

To deal with the contradiction between environment detrimental and human development, a low-carbon economy concept is regarded as the future choice of economic development via moderate and sustainable energy consumption, low greenhouse gas emissions and low pollution [1]. Recently, ammonia, which is a carbon free chemical, is receiving attention as an alternative fuel in the context of an ever increasing energy demand and concerns about global warming [2, 3]. Just like hydrogen, ammonia can act as a potential enabler of a low-carbon economy, but without issues associated with hydrogen storage and distribution which are currently still tough barriers to the widespread use of hydrogen [4, 5]. Since ammonia is widely used as an agricultural fertilizer, refrigeration liquid, and in industrial processes (e.g. steelmaking), knowledge on its production, delivery, storage, handling and distribution through existing infrastructures reaches more than a century of expertise. Moreover, ammonia has the added attraction that it can also be sold on international markets making it a very versatile and hence attractive commodity. Also, ammonia can be produced from different energy sources such as wind power, biomass, nuclear energy, etc., which means it is a promising green future fuel potentially yielding no carbon dioxide.

Thus, due to the potentially beneficial aspects of utilizing ammonia as a fuel, progress on the use of NH_3 to replace high intensive CO_2 production fuels is a main priority for groups working on this area [6-8]. However, previous studies also show that to achieve satisfying performance in combustion facilities, there are still considerable challenges for ammonia to be solved, e.g. toxicity, corrosion to container materials, narrow flammability range, high resistance to ignition, low burning velocity, etc. In order to improve ammonia combustion rate for successful applications combustion promoters have been proposed to be co-fired with ammonia. Some fundamental flame studies investigated the effect of burning ammonia/hydrogen fuel mixtures with deep insight into combustion chemical kinetics [4, 9-11]. Some internal combustion engine studies tested different fuels for ammonia combustion implementation into practical transportation applications, such as hydrogen [2, 8], gasoline [6, 12], diesel [13, 14], DME [15], etc. Some favourable results in IC engines studies indicate a good potential to use ammonia mixtures for practical power systems.

Furthermore, to apply ammonia into similarly responsive but larger power generators to meet local demands, the use of “green” ammonia in gas turbines for power generation is another promising proposition. Valera-Medina et. al.[16-18] experimentally tested and numerically analysed ammonia/methane blends in a laboratory scale swirl combustor and suggested low swirl and different injection strategies to optimise gas turbine power generation. Kurata et. al.[19] studied NH_3–CH_4–air combustion gas turbine power generation systems at various power outputs and suggested that mixed CH_4 improves the low-combustion intensity of NH_3 and effectively enhances the flame stability in the gas-turbine combustors. As a potential “substitute of natural gas”, ammonia is more easily transportable than LNG. Furthermore, ammonia/methane blends could be used not only from green ammonia sources, but also from by-product ammonia obtained from industrial processes. Thus, ammonia substitution could support peak-hour energy consumption requirements with fuel cost reduction. For instance, an immediate beneficiary of this blend could be steelworks companies that produce ammonia as a by-product of coke oven gas cleaning [20, 21]. More recently, a new research program “Power to Ammonia” has initiated in the Netherlands looking into potentially turning gas-fired power plants into ‘super batteries’ [22]. Initial tests will focus on co-firing ammonia with methane in order to determine fuel blends that cause the lowest impact on gas turbine systems in order to reduce retrofitting costs in currently running facilities. Actually, with ammonia co-firing, reduced CO_2 emissions in these projects can be achieved due to lower carbon content of the fuels. Base on the situations above, in this research ammonia/methane blends are appraised to be used to improve the performance of ammonia combustion and at the same time to use ammonia to substitute some conventional fossil fuels - natural gas as well, of which methane is the main ingredient.

To successfully utilize ammonia/methane combustion for practical application, it is essential to have a deep understanding on the characteristics of fundamental combustion properties of methane/ammonia fuel mixtures. There is a considerable amount of studies investigating ammonia-based flames experimentally and numerically [23-28]. For instance, Lindstedt et. al.[26] conducted detailed chemistry modelling for ammonia oxidation and verified the mechanism in flat laminar premixed flames. Skreiberg et. al.[27] studied the oxidation of ammonia in the presence of H_2, CO, and CH_4 below 1400 K under fuel-rich conditions. A detailed chemical kinetic model was established and validated against flow reactor measurements. Tian et. al.[23] studied a series of premixed $NH_3/CH_4/O_2/Ar$ flames at low pressure to identify the effect of different mole ratio of NH_3/CH_4 and also proposed a chemical mechanism based on the Skreiberg mechanism for premixed combustion of ammonia/methane. In this study only the stoichiometric conditions were investigated and the ammonia was still added in the fuel mixtures as the minor ingredient. Recently, the Tian mechanism was tested in several ammonia combustion studies [29-31] showing good performance. Mathieu and Petersen [28] investigated the ammonia oxidation in shock-tube experiments over a wide range of temperatures, pressures (up to 30 atm) and equivalence ratios. Specifically, in this study new ignition delay time measurements were used to provide data for ammonia oxidation under engine relevant conditions (e.g. pressure above 10atm) which before then remained fairly unexplored. However, previously most of the relevant studies only have investigated small amounts of ammonia addition into methane and rarely comprehensively analysed the different combustion properties under a wide range of conditions regarding ammonia as main fuel.

Therefore, the objective of this study is to analyse the effects of ammonia substitution on ammonia/methane flames through numerical simulations with a proper detailed chemical reaction mechanism in order to help finding the way and feasibility of implementing ammonia as a primary fuel. In the present study, properties such as autoignition, flame propagation, flame temperature and emissions concentration have been analysed to extend the knowledge of premixed ammonia/methane flame characteristics.

2 Methodology

2.1 Ignition Delay Times Modelling

Autoignition is a fundamental phenomenon of premixed combustion studies, which is the spontaneous and homogeneous ignition of the fuel-air mixture. Therefore the ignition delay time, representing the time for a mixture to reach autoignition, is an essential property for premixed combustion, which is highly dependent on the reactivity of a mixture. Numerical prediction of ignition delay times is helpful in understanding autoignition parameters, detailed kinetics and reduction of detailed mechanisms. In practice, as an important well-known validation technology, computational prediction of ignition delay times is usually compared with shock-tube experiments [32, 33]. In the present study, ignition delay times were modelled with a closed homogeneous reactor in Cantera[34]. The ignition delay times are extracted as the time corresponding to the steepest rate of OH generation[28]. The model is calculated at constant volume and adiabatic conditions. In the simulation, the ammonia and oxidiser mixtures are highly diluted to minimize effects of viscosity, heat transfer and non-equilibrium as performed in shock-tube experimental conditions[35]. The numerical work was carried out under the same conditions as in the experimental work performed by Mathieu et al [28].

2.2 Freely Propagating Laminar Flame Modelling

In this study, a one dimensional premixed freely propagating flame model has been employed to study the premixed combustion of NH_3/CH_4 fuel blends. Numerical simulations were performed using the computational code of premixed flame from Cantera [34] for the modelling of laminar flames. The steady state mass, energy and species equations were solved with adaptive meshes and mixture-averaged transport parameters to get quick convergence to an accurate solution. This freely propagating flame model can provide analysis of unstretched flame speed, reaction rates, radical concentrations, sensitivity analyses, etc., as used in previous studies [31, 36]. In the model, flame speed of the freely propagating flame is calculated based on a point of reference which is a fixed position on the flame. The laminar flame speed is defined as the inlet velocity that keeps the flame to stay in a fixed position. Then an eigenvalue can be obtained as flame speed from the solution method. More details of the well-established conservation equations for the one-dimensional laminar flame and the solution strategy can be referred to the Cantera's theory. In the present study, numerical simulations were conducted similarly to the experimental conditions in [25] firstly to verify the model in terms of laminar flame speed of NH_3/CH_4 mixtures. The validated model can be used to study other different parameters, e.g. the maximum temperature in the flames was extracted as the adiabatic flame temperature. Then the validated model was used to study the characteristics of NH_3/CH_4 mixtures under different conditions.

2.3 Establishment of a Chemical Kinetic Mechanism

To study premixed combustion of ammonia/methane, it is desirable to have a well-validated detailed chemical-kinetics mechanism model which can comprehensively describe the combustion properties under a wide range of conditions. Although there are a number of kinetic mechanisms for ammonia combustion in literature, mechanisms suitable for NH_3/CH_4 fuel mixtures are quite limited. The Konnov mechanism [37] was developed for the combustion of small hydrocarbon fuels with ammonia. It has been widely used in the ammonia combustion studies, offering satisfying performance especially on the prediction of NO_x emission and propagation compared with most of the mechanisms available [29, 31, 38-40]. However, it was found that the Konnov mechanism shows a relatively poor performance in ignition delay chemistry studies [16, 28]. Due to still lack of information about NH_3/CH_4 fuel mixtures with high ammonia concentration, difference in composition can introduce numerous control problems for premixed combustion and therefore complicate practical applications such as gas turbine or engine design and operation. In this situation, a new chemical kinetic model has been employed in this study, which was proposed in a parallel kinetic modelling study work. The model is mostly based on the chemical mechanism model by Konnov et. al. [37]. To improve the performance of the mechanism concerning ignition delay time calculations, several reactions were modified according to the kinetic analysis of the main reactions as shown in Table 1. The modified mechanism involves 55 species and 276 elementary reactions, and is available in Appendix A. Using the modified mechanism, ignition delay time calculations were performed as shown in figure 1. Another mechanism, which Tian et al. [23] developed for CH_4/NH_3 premixed combustion at low pressure, also has a potential for use in the present study. Since this mechanism was also validated recently against the experimental data [31] and showed satisfying performance as Konnov mechanism, the Tian mechanism was also employed for reference. The comparison of ignition delay time calculation with different mechanisms verifies the accuracy and feasibility of the mechanism used in the present study. As illustrated in figure. 1, the average relative errors for ammonia ignition delay time calculation are 6.25%, 31.03% and 17.12% respectively with the mechanism of the present study, the Konnov mechanism and the Tian mechanism. Thus, it can be determined that the present chemical mechanism model shows a satisfying performance in ammonia ignition studies.

Table 1 Modified reactions in the mechanism of present study

Reactions	A	n	Ea	Ref.
$NH_2+NH_2=NH_3+NH$	5.0E13	0	10000	[23]
$NO+H(+M) = HNO(+M)$	3.000E+20	-1.75	0	[28]

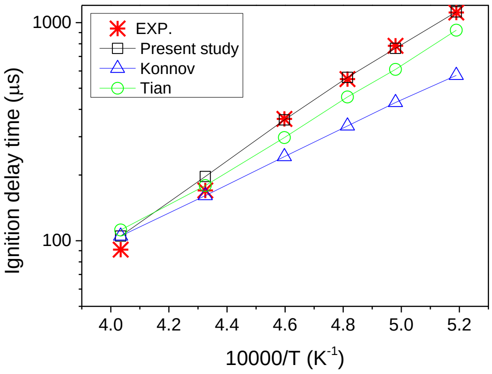


Figure 1. Performance of the modified Konnov mechanisms with respect to ignition delay times of NH_3 mixtures (0.4%NH_3/0.6%O_2/99%Ar) 1.4 atm. Experiments as in [28].

2.4 Laminar Flame Model Validation with the New Chemical Mechanism

To study premixed combustion of NH_3/CH_4 flames, the one-dimensional laminar flame model was used to simulate NH_3/CH_4 flames characteristics. Laminar flame speed is one of the critical factors that influence the propagation of premixed combustion flames. It is the flame front velocity relative to the flow into the unburnt mixture [41], which is widely used as an essential parameter for detailed chemical mechanisms' verification. Thus, in this study simulation of the freely propagating laminar flames were performed using NH_3/CH_4 fuel blends similarly to the experimental conditions in [25], in which laminar flame speed of NH_3/CH_4 mixtures were studied. The new chemical kinetics mechanism was implemented in the laminar flame model. As shown in Figure 2, comparison of unstretched laminar flame speed values with experimental data has demonstrated quite good accuracy in fuel lean regions while under fuel rich conditions the calculation results were lower than experimental data. However, the comparison is still of acceptably accurate with an average relative error around 10.46%.

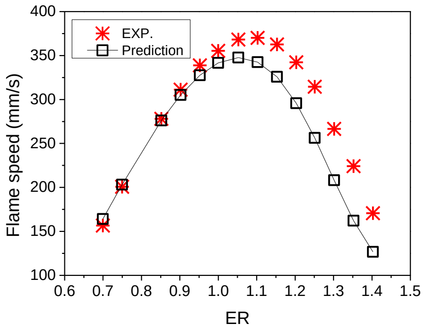


Figure 2. Burning velocity calculation of NH_3/CH_4 flame with dilution ratios of oxygen D = $O_2/(O_2 + N_2) = 0.209$. Experiments as in [25]

Thus, in the following study different ammonia/methane flames are modelled to comprehensively investigate the characteristics of co-firing ammonia/methane fuels. To study the effect of ammonia substitution on methane, ammonia mole fraction in ammonia/methane mixtures was varied from 0 to 100%. Initially simulations were performed under normal pressure and temperature conditions (initial pressure of 0.1 MPa and initial temperature of 300 K). Equivalence ratio conditions from 0.6 to 1.4 were also considered in the calculation. Finally the model was also used to study elevated temperature and pressure conditions related to more practical industrial uses. For different ammonia mole fractions (X_{NH3}) in fuel blends, the overall fuel-air mixture required can be expressed as,

$$\left(1 - X_{NH_3}\right)CH_4 + X_{NH_3} \cdot NH_3 + \left(\frac{2}{\varphi}\left(1 - X_{NH_3}\right) + \frac{3}{4\varphi}X_{NH_3}\right)\left(O_2 + 3.762N_2\right) \quad (1)$$

where φ is equivalence ratio.

3 Results and Discussion

3.1 Ignition Delay Times Prediction

Auto-ignition is one of common problems that occur in real industrial facilities e.g. gas turbine engines. It can happen in the premixer which leads to overheating and subsequent damage to the fuel injector [42] . It is therefore essential to understand the influence of NH_3 on the ignition characteristics of the NH_3/CH_4 fuel blends system. Figure 3 shows ignition delay time calculation results with a variation of NH_3 mole fraction in NH_3/CH_4 fuel blends at temperatures ~2000K. A clear increase of ignition delay times can be found with more NH_3. It is generally the same trend as shown in the work of Mathieu [28] for ammonia ignition under different equivalence ratios. It can be seen that same as Mathieu's work, equivalence ratio seems to have a moderate effect compared with the effect of ammonia content. It is shown that the values of ignition delay times are below the averaged values estimated by mole proportions of NH_3 to CH_4, which indicates a strong non-linear influence of ammonia substitution effect of CH_4 on chemical kinetics. When the NH_3 mole fraction is more than 50% in the fuel blend, the increased rate of ignition delay time augments, meaning that ammonia dominates the process of ignition delay. For instance, for stoichiometric mixtures a factor ~3.4 can be found between ignition delay times obtained at a NH_3 mole fraction of 100% and 50%, whist a smaller factor of 1.6 is found between NH_3 mole fractions of 50% and 0%.

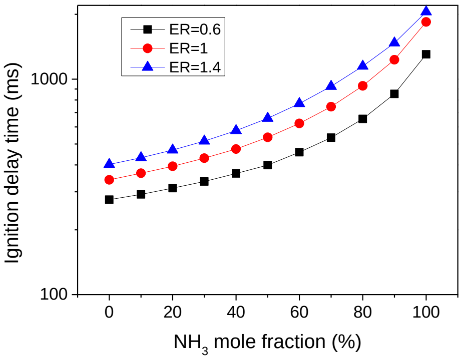


Figure 3. Ignition delay times as a function of ammonia fraction in the fuel blend.

The ignition delay time prediction was also performed under different equivalence ratio conditions as shown in Figure 3. It can be observed that for a certain NH_3/CH_4 fuel mixture the increase of equivalence ratio ignition delay times will also increase. Actually, in practical applications auto-ignition becomes a more common issue especially when using conventional fuels at higher pressure ratios as those used in modern gas turbines. From the results above, it can be identified that since ammonia substituting methane will lead to an obvious increase in the ignition delay times, using NH_3/CH_4 as fuel can help reduce the risk of auto-ignition in premixed gas turbine chambers.

3.2 Laminar Flame Speed

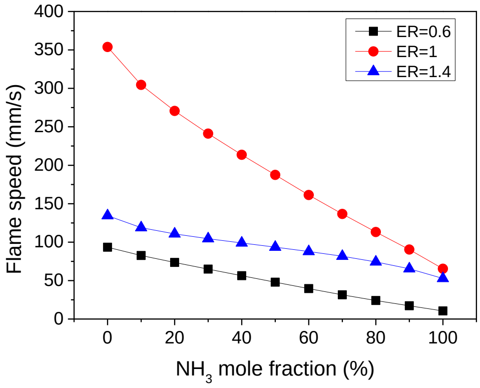


Figure 4. Flame speed as a function of ammonia fraction in the fuel.

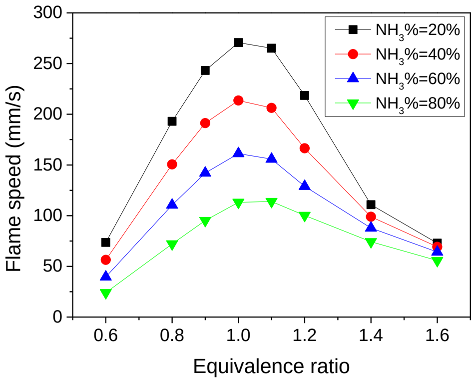


Figure 5. Laminar flame speed as a function of ER

Numerical simulation results of characteristics for NH_3/CH_4 flame propagation are illustrated in Figure 4 and Figure 5. In Figure 4, unstretched laminar flame speed is plotted as a function of NH_3 fraction at three different equivalence ratios (ER=0.6, 1.0, 1.4). It can be seen that from pure methane (NH_3%=0) to pure ammonia (NH_3%=100%) laminar flame speed decreases almost linearly with the increase of NH_3 fraction in the fuel blend. These results have shown the same tendency of flame speed with ammonia addition with the work of Nozari and Karabeyoglu[36] in which ammonia is combusted with hydrogen. For different equivalence ratios, the flame speed exhibits a significant sensitivity to ammonia substitution, in which near stoichiometric conditions a more significant change in gradient can be observed. Under stoichiometric conditions, the flame speed decreases about 30mm/s with each 10 percentage increase of NH_3 fraction whilst the decrease rate drops to about 8mm/s for equivalence ratios of 0.6 and 1.4. The reason of this phenomenon is mainly due to the relatively lower reactivity and flame speed of ammonia than that of methane. As flame speed is a key parameter for a fuel in real combustion development, this suggests that the low flame speed of high NH_3 mixture can limit its application in practical energy devices.

Figure 5 shows the unstretched laminar flame speed against equivalence ratios ranging from 0.6 to 1.6 at different ammonia fractions. For all the cases of NH_3/CH_4 combustion studied, laminar flame speed of fuel-lean mixtures increases with the equivalence ratio up to those to stoichiometric conditions and then decreases under fuel-rich regimes. The maximum value of the flame speed is presented at the equivalence ratio of 1.0. For a certain equivalence ratio the flame speed increases with the decrease of ammonia fraction with the increase becoming more remarkable for NH_3/CH_4 flames near stoichiometric conditions. Passing stoichiometry, hot, unreacted ammonia in the fuel-air mixture will start recombining with NO present in the flue gases, thus promoting two effects, e.g. reduction of NOx [5] and increase of flame speed compared to lean fuel conditions. Similar results have also been reported in previous ammonia combustion related research where the flame speed and NOx emission of ammonia combustion were studied in relation to the effect of equivalence ratio [44]. This indicates that in practical application to utilise ammonia to substitute methane, equivalence ratios near stoichiometric condition are more favourable for better flame propagation properties, with rich fuel conditions more favourable than lean environments.

3.3 Emission Characteristics

NO_x emissions are an essential concern when using ammonia as a fuel [13, 18, 43]. In this study, NO concentrations in the final flame exhaust gas were investigated to gain a deep insight into characteristics of the main NO_x product with a wide range of NH_3 fractions and equivalence ratios as shown in Figure 6 and Figure 7. It must be remembered that ammonia based flames not only produce high temperature, Zeldovich NOx, but also fuel bound emissions due to the intrinsic characteristics of ammonia. Figure 6 shows the NO emission fractions in the burnt gas as a function of NH_3 fraction under different equivalence ratios. It can be observed that the NO emission curves show the same pattern, increasing first and then dropping with the increase of NH_3 fraction. However, the peaks of NO emission are quite different for different equivalence ratios. For instance, for equivalence ratio at 1.4, the maximum value is presented at NH_3 fractions of ~20% whilst it is at about NH_3 fraction of 60% for an equivalence ratio of 1.0. This indicates the influence of equivalence ratio on NO_x emissions production is critical as illustrated in figure 7. From figure 6 it can also be observed that ammonia substituting methane in a large proportion can have the same level of NO_x emissions as high-methane proportion fuel blends (low content ammonia cases), which suggests the feasibility of using ammonia as primary fuel.

Furthermore, the characteristics of NO_x emission in figure 6 indicate the variation of NO_x formation in NH_3/CH_4 combustion with different fuel blends. To understand the phenomenon, the adiabatic flame temperature was plotted against NH_3 fraction in figure 8, in which flame temperature is decreased with the increase of NH_3 fraction in fuel blends as NH_3 has a lower adiabatic temperature than CH_4. Comparing figure 6 with Figure 8, it can be noticed that NO_x emissions vary with the same trend as the adiabatic flame temperature only at high NH_3 fraction regions. For instance, under stoichiometric condition when NH_3 mole fraction is more than 60%, the adiabatic flame temperature and NO_x emission decrease with the increase of NH_3 mole fraction, whilst NO_x emissions increase with more CH_4 being substituted by NH_3 within the region where NH_3 is less than 60%. Actually, the trend of temperature and NO emission within the range of ammonia mole fraction less than 50% is the same as in Tian's work [23], which can be a good demonstration for the results of present study. Moreover, reference [36] also shows some NO_x emission results with the effect of ammonia added in hydrogen: The NO_x formation level increases with ammonia content in the fuel mixture decreasing when energy fraction of ammonia in the fuel mixture is less than 20%, and then NO_x emission drops with the ammonia percentage increasing after ammonia fraction is more than 20%.

In low NH_3 content regions where thermal NO_x have more contribution to the total NO_x production, the result seems contradictory to the general understanding of thermal NO_x and fuel bond NO_x, as a first glance would expect a decrease in total NO_x production with increasing NH_3 fraction in fuel blends. A detailed sensitivity analysis in the present study shows that reactions $NH+H_2=NH_2+H$, $NH_2+O=HNO+H$ and $NH+H_2O=HNO+H_2$ play as the most promoting reactions in NO_x formation in a wide range of fuel blends and equivalence ratios. Thus when ammonia begins to be added to the methane, more NH and NH_2 are available to promote fuel bound NO formation. It can be determined that the fuel-bond NO_x is more sensitive than thermal NO_x to the increase of total NO_x emission in low NH_3 content blends regions, although in such regions thermal NO_x is the dominating mechanism in the total NO_x emission. Therefore the NO_x emission trend is still a result of fuel bond versus thermal NO_x production: when NH_3 mole fraction is low in the fuel blends, the increase of fuel bond NO_x formation is more sensitive and plays a more prominent role in NO_x emission increase. Consequently, with more ammonia and oxygen, e.g. lean conditions, in the fuel mixtures NO_x emissions increase due to abundant fuel-bound nitrogen in ammonia. In high NH_3 mole fraction regions, the recombination of ammonia with NOx produces a decay of the pollutant, thus consuming not only thermal NOx but also those produced during fuel-bonding reactions.

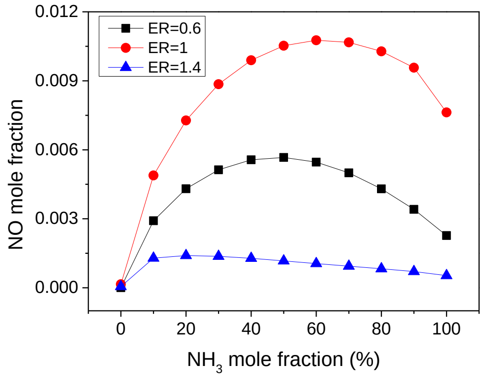


Figure 6. NO mole fraction in burnt gas as a function of ammonia fraction in fuel blends

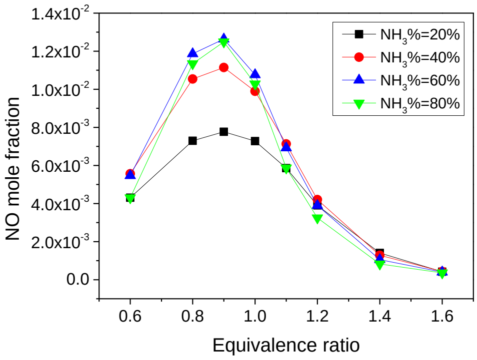


Figure 7. NO mole fraction in burnt gas as a function of ER

Figure 7 shows the effect of equivalence ratio ranging from 0.6 to 1.6 on NO formation for different NH_3/CH_4 mixture compositions. It is obvious that equivalence ratio conditions have significant impact on NO emission level in exhaust. Also, there is no variation with NH_3/CH_4 fuel blends composition observed on the position of NO peak emissions: under fuel lean conditions (ER<1.0), NO emissions increase with the increase of equivalence ratio and reaches the maximum point at equivalence ratio of around 0.9 for all curves. After the peak value, NO emissions drop with increase of equivalence ratio.

When comparing figure 7 with figure 5, one interesting phenomenon can be observed is that the flame speed is higher with ER=1.4 than ER=0.6, which indicates the rapid combustion with ER=1.4 resulting in higher combustion temperatures (figure 8b) and therefore one will expect a higher NO emission formation. However the simulation results presented in Fig. 7 shows NO emissions with ER=1.4 are lower than ER=0.6. Taking a detailed look into the NO_x calculation results in Figure 7, it can be seen that the NO_x emission drops quickly in the fuel rich region with the increase of equivalence ratio. Actually, the reason why NO emission at ER of 1.4 is lower than ER of 0.6 is mainly due to the excess unreacted ammonia for high equivalence ratio conditions, as previously stated. Under the ER of 1.4 there are much more unreacted ammonia in the fuel-air mixture, thus the ammonia can play an important role in the deNO_x process as NO is removed by further reactions with NH_2 generated from ammonia [9]. Similar phenomena as the ammonia/methane flames in this study have already been reported in previous ammonia combustion study [44], in which the flame speed and NO_x emission of ammonia combustion were studied in relation to the effect of equivalence ratio. Also, similar conclusions can also be found in [4, 36] for ammonia/hydrogen mixtures combustion, which demonstrates the consistent characters of ammonia-based fuel combustion. Moreover, as tested in real engine applications of ammonia/hydrocarbon studies in [18, 45], relatively much lower NO$_x$ emissions are observed under fuel rich conditions for ammonia-based fuels.

Another phenomenon that can be observed is that for a certain equivalence ratio NO emissions increase with the increase of ammonia fraction but the variation becomes slight for fuel rich conditions. On the other hand from the stoichiometric region to fuel rich conditions, the increase of NO emissions as a result of more CH$_4$ being replaced by NH$_3$ becomes much smaller in comparison to the fuel lean region, e.g. NO emissions with 40%NH$_3$ and 80%NH$_3$ are quite close. The results also show that for all the flames with different NH$_3$/CH$_4$ mixture composition, the NO emissions in the fuel-rich region are relatively lower than under fuel-lean conditions. These results imply the necessity and importance of optimal control of the stoichiometry using ammonia-based fuels. Specifically, operating NH$_3$/CH$_4$ in fuel rich conditions can be a choice to reduce NO emissions in practical combustion applications.

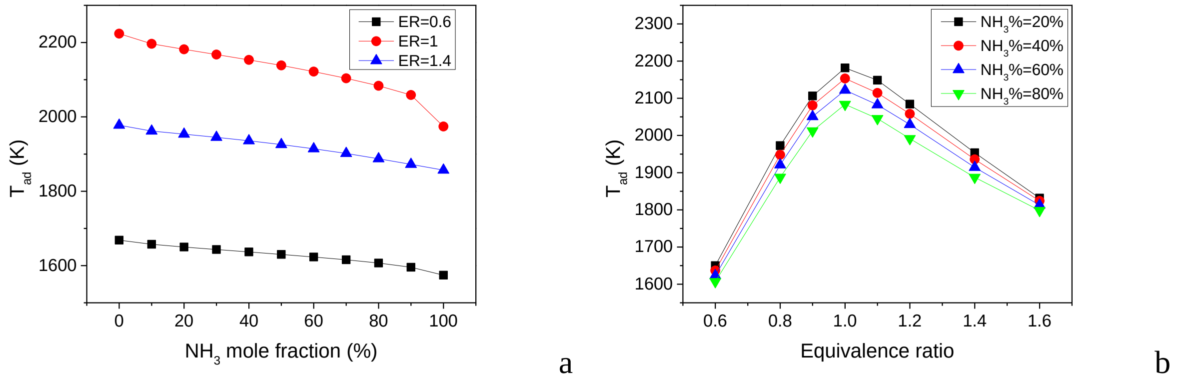


Figure 8. Adiabatic flame temperature as a function of ammonia fraction in fuel blends (a) and equivalence ratio (b)

As an essential parameter influencing the NO$_x$ emissions, the effect of equivalence ratio were studied on adiabatic flame temperature at different NH$_3$ fractions as illustrated in figure 8b. The curves show a peak value at about equivalence ratio of 1.0 as the same phenomena observed in laminar flame speed calculation shown in Figure 5, which represents the maximum net heat release considering the endothermic procedure of NH$_3$ decomposition. Comparing with Figure 7, it can be observed that the peak of adiabatic flame temperature is at the higher equivalence ratio than NO$_x$ emission at equivalence ratio of ~0.9. When ER<0.9, the adiabatic temperature increases with the increase of equivalence ratio. As expected, the increasing trend of adiabatic temperature leads to higher NO$_x$ emission production due to more thermal NO$_x$ formation. However, in the region of 0.9<ER<1.0, although the adiabatic temperature increases with the increase of equivalence ratio, NO$_x$ emission begins to decline, which indicates thermal NO$_x$ formation is less dominant in relation to fuel bond NO$_x$ formation under such conditions. When ER>1.0, NO$_x$ emission levels drop quickly due to both surplus NH$_3$ functioning on NO$_x$ reduction and decrease of the adiabatic temperature leading to less thermal NO$_x$ emissions.

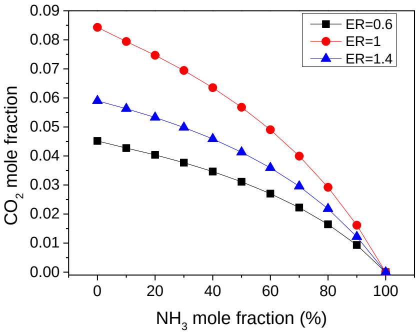


Figure 9. CO_2 mole fraction in burnt gas as a function of ammonia fraction in fuel blends

Figures 10-12 show the main carbonous products concentration in burnt gas at different NH_3 mole fractions and equivalence ratios. In Figure 10, as expected with more fraction of CH_4 substituted by NH_3 the CO_2 emission drops accordingly as less carbon is available in the fuel blends. It also can be seen that stoichiometric conditions have more CO_2 products than fuel lean and fuel rich conditions. This is mainly due to the better combustion efficiency. As expected, blends with >60% NH_3 produce half CO_2 than pure methane. Figure 11 and Figure 12 give the CO emission characteristics at different NH_3 mole fractions and equivalence ratios. In Figure 11, CO emission levels drop as the NH_3 mole fraction increases. Specifically, CO emissions drop faster as the NH_3 fraction increases under high equivalence ration conditions, e.g. ER=1.4. The trend of two major carbonous products CO and CO_2 with different NH_3 fractions in the fuel blends agrees with the conclusions of NH_3/CH_4 combustion in the work of Tian et. al. [23]. These decreasing trends result primarily from the reduced methane component in the NH_3/CH_4 mixture. The results of the present work not only give satisfactory agreement with the experimental data in [23], but also expand the knowledge on high ammonia content fuels and different equivalence ration conditions which have not been studied before. Figure 12 shows CO fraction in burnt gas as a function of equivalence ratio ranging from 0.6 to 1.6. The results clearly show an increasing trend of CO emission with the increase of equivalence ratio. As shown in the figure it is possible to identify three regimes in the NH_3/CH_4 flames depending on the equivalence ratio. In the cases of equivalence ratio less than 0.9, CO emission production grows slightly with equivalence ratio. In the cases of 0.9<ER<1.1, CO emission increases almost exponentially with the increase of equivalence ratio. Finally when equivalence ratio is larger than 1.1 the increase of CO emissions become relatively slow as the equivalence ratio increases. Thus in this situation, to control the CO emission level in the exhaust for practical use, it is better to conduct the combustion of NH_3/CH_4 mixture in the fuel lean regime. However, from previous analyses it has been shown that NO_x emissions are noticeably high under fuel lean conditions. Thus the contradictory between NO_x and CO emissions reduction suggests an optimisation that needs to be carefully settled in terms of stoichiometry design. To meet the stringent emission standard of industrial application nowadays, other possible solutions can also be considered including selective catalytic reduction (SCR) of NO_x, reburning techniques, oxygen-enhanced combustion etc., which are out of the scope of this study.

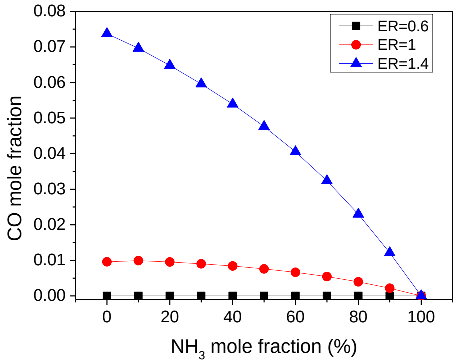


Figure 10. CO mole fraction in burnt gas as a function of ammonia fraction in fuel blends

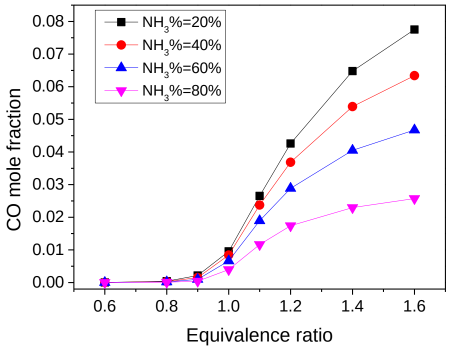


Figure 11. CO mole fraction in burnt gas as a function of ER

3.4 Flame Structure Analysis

To gain a deep insight into the flames NH_3 to substituting CH_4 for premixed combustion application, studies of detailed flame structure were also performed for NH_3/CH_4 flames. As shown in figure 12, some major radicals in flame structures of freely propagating NH_3/CH_4 flames are illustrated for different NH_3 fractions in fuel blends under stoichiometric conditions. Figure 12a-c shows the concentration of OH, H and O radicals as a function of distance through the flames. The peaks of these radicals are all presented at the position of about 11 mm above the burner. Comparison of the figures shows that in stoichiometric NH_3/CH_4 flames OH radical has the largest maximum concentrations among these radicals while the peak concentrations of O radical is much lower compared to OH and H. For all the three radicals, it is obviously observed that with more mole fraction of NH_3 in fuel blends, peak concentrations of the radicals are decreased indicating decreasing reaction rates and thus laminar flame speed. This is due to the relatively less reactivity of ammonia compared to methane leading to weaker flames. On the contrary, as shown in figure 12d NH_2 originated from ammonia shows a different trend in the flames' reaction zone as more NH_3 substituting CH_4: the peak value of NH_2 keeps increasing with the increase of NH_3 in the fuel blends. The trend observed has been demonstrated to be consistent with the unstretched laminar flame speed calculation results in Figure 4, which shows that an increase of NH_3 fraction in the fuel blends the laminar flame speed tends to decrease. Quantitatively, as demonstrated in previous studies [4, 46, 47], certain key radicals concentration has a strong correlation with laminar flame speed for premixed flames. In the present study, calculations of NH_3/CH_4 flame speed show that the peak value of OH, H, O and NH_2 are of the highest relevance. In figure 13, laminar flame speed of NH_3/CH_4

fuel blends under stoichiometric conditions are plotted as the function of $(OH+H+O+NH_2)_{max}$. It suggests a quasi-linear relation between the NH_3/CH_4 flame speed and the maximum mole fraction of $OH+H+O+NH_2$ in the flames.

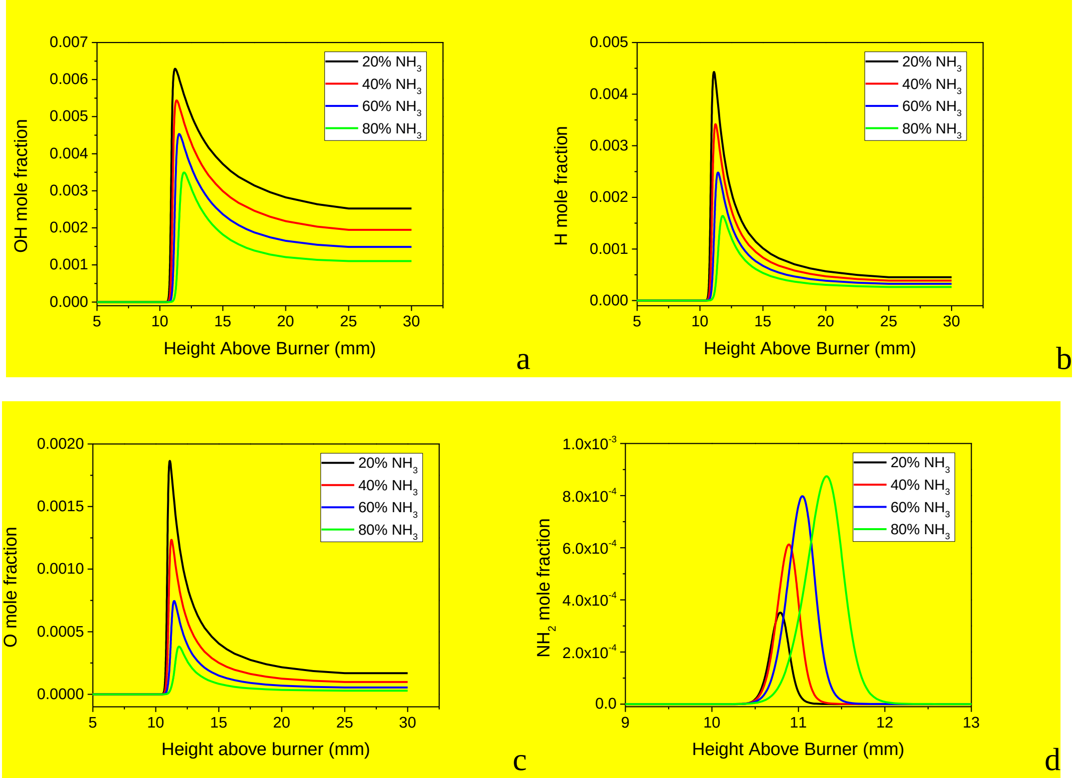


Figure 12 Predicted OH, H, O and NH_2 radicals in premixed ammonia/methane flames (ER=1)

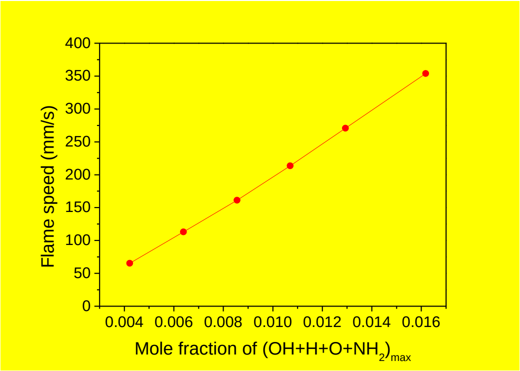


Figure 13. Laminar flame speed as a function of maximum mole fraction of $OH+H+O+NH_2$ radicals

Figure 14 shows the concentration of NO and CO as a function of distance through the flames. For CO profiles, it is shown that the peak value of CO concentration declines when increasing ammonia fraction in fuel blends, which is the same decreasing trend as CO concentration in the exhaust. The maximum value of NO concentration in the flame shows the same trend of NO concentration in the burnt gas as shown in Figure 6, that NO emission of 60%NH_3 fuel mixture is higher than other fuel blends, e.g. 40%NH_3 and 80%NH_3 cases. Comparing with figure 12, it can be observed that the maximum concentration of CO and NO is presented at the same position of the OH, H, O radical peaks in the reaction zone. This indicates emissions are mainly generated in the flame front as these extremely active radicals play essential roles in branching chain reactions. Furthermore, the formation of the CO and NO emission can be characterised by some important precursors. Through production rate and sensitivity analysis, HNO and HCO are the predominate promotors for NO and CO formation, respectively. For instance, most of the NO is formed from the reactions HNO + H = NO + H_2 and HNO + OH = NO + H_2O in NH_3/CH_4 combustion. Therefore, the profiles of HNO and HCO radicals in stoichiometric premixed flames are described as shown in Figures 15. As expected, the trends of maximum HNO and HCO radical concentration with different NH_3 concentration in fuel blends are the same as NO and CO.

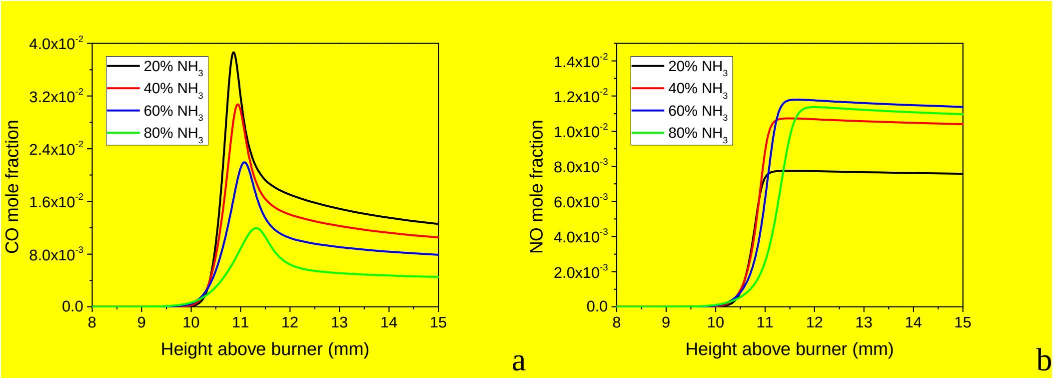


Figure 14 Predicted CO (a) and NO (b) species in premixed ammonia/methane flames (ER=1)

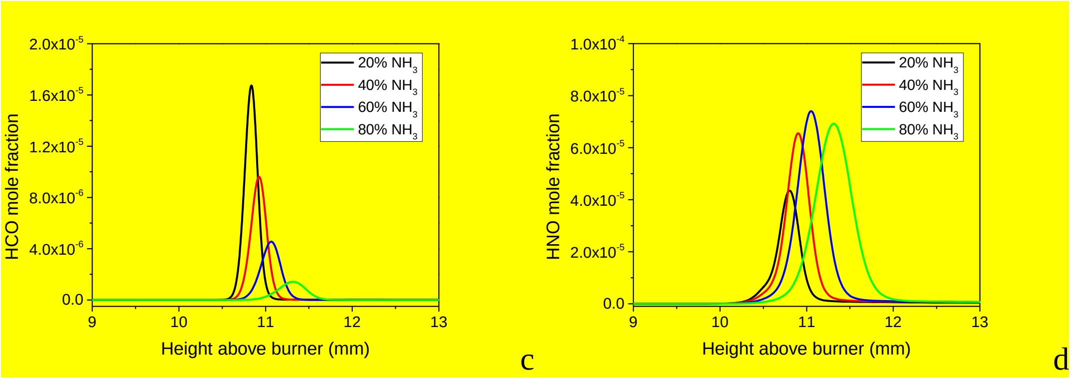


Figure 15 Predicted HCO (a) and HNO (b) radicals in premixed ammonia/methane flames (ER=1)

3.5 Effect of Pressure and Temperature

To explore the feasibility of utilizing ammonia/methane blend as fuel for practical application, it is essential to investigate the combustion characteristics under elevated pressure and temperature conditions, which is usually encountered in industrial power facilities such as internal combustion engines or gas turbine engines. For instance, for a typical heavy-duty industrial gas turbine with compression ratio of 17, an isentropic compression process in the compressor will lead to an initial temperature of unburnt ammonia/methane mixture rising to about 680K and a pressure of 17atm before it is ignited in the combustor. Unfortunately, up to now there is no data on realistic industrial operational conditions for NH_3/CH_4 combustion which can be used to help analyse or optimize gas turbine applications. Therefore, it is necessary to investigate the effects of pressure and temperature for NH_3/CH_4 combustion. In Figure 16-21, premixed flames of 60%NH_3/40%CH_4 fuel blends, which were proved to be a potential composition choice for practical gas turbine engine use[18], were numerically studied under stoichiometric conditions to obtain typical combustion properties such as laminar flame speed and emissions concentration.

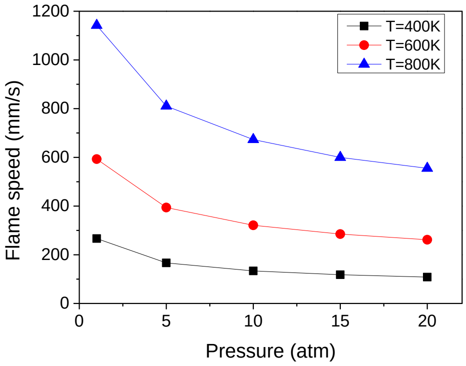


Figure 16. Flame speed as a function of pressure

Figure 16 shows the effect of pressure on laminar flame speed at different initial temperature conditions. It can be observed that the increase of pressure has a negative effect on the flame propagation. However with the increase of pressure, the negative effect on laminar flame speed tends to be much smaller when it comes to high pressure conditions. The results also indicate that under relative high temperature conditions, the effect of pressure tends to have more impact on the laminar flame speed. For instance, under the initial temperature of 800K the laminar flame speed of NH_3/CH_4 shows an obvious decrease with the increase of pressure whilst quite slight decrease of laminar flame speed can be observed when the initial temperature is 400K. This suggests that under practical industrial conditions (e.g. gas turbine), pressure conditions will be an essential factor for the design and optimisation of performance of NH_3/CH_4 combustion applications.

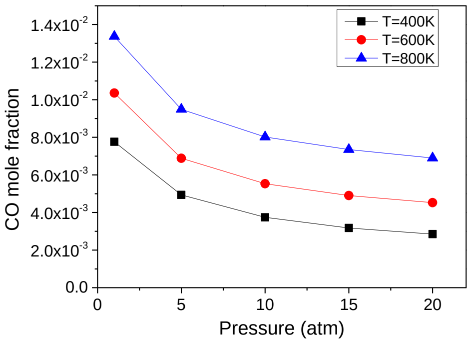


Figure 17. CO mole fraction in burnt gas as a function of pressure

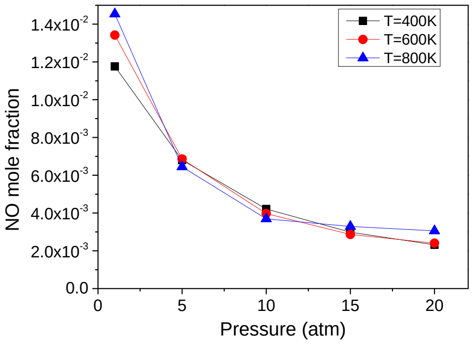


Figure 18. NO mole fraction in burnt gas as a function of pressure

Figures 17 and 18 illustrate the CO and NO emission concentrations in the burnt gas as a function of pressure at different initial temperature conditions. With the increase of pressure, reduction of both CO and NO emissions is obtained. For instance, a significant reduction in NO is observed with the increase of pressure: the NO concentration in the burnt gas under 20atm is only about 20% of that under atmospheric conditions. From the figures, NO emissions are more sensitive to pressure than CO as a greater NO reduction is obtained from 1atm to 20atm. Furthermore, a difference on the profiles of CO emissions can also be observed at different inlet temperature. As the pressure increases, the adiabatic temperature tends to increase slightly as shown in Figure 19, which will lead to a little more thermal NO_x formation in the flame. Therefore, the decrease of total NO emission with the increase of pressure suggests that pressure is a more important factor which affects the kinetics of fuel-bond NO formation more significantly than for thermal NO. These results agree with similar emission trends of the pressure effect on ammonia-based fuel reported in previous experimental and numerical work [18, 36, 44]. Especially as an important concern in ammonia combustion, the significant NO reduction effect shown in the simulation can suggest a quite good potential using ammonia-based fuel under elevated conditions in practice.

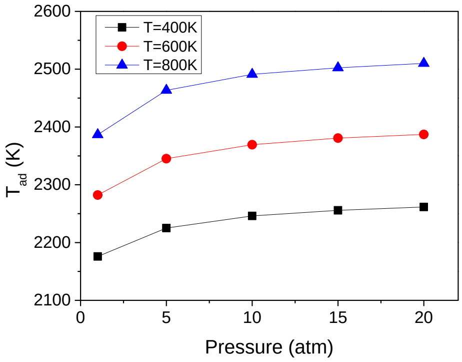


Figure 19. Adiabatic flame temperature as a function of pressure

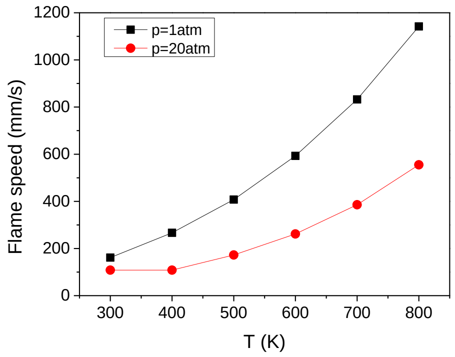
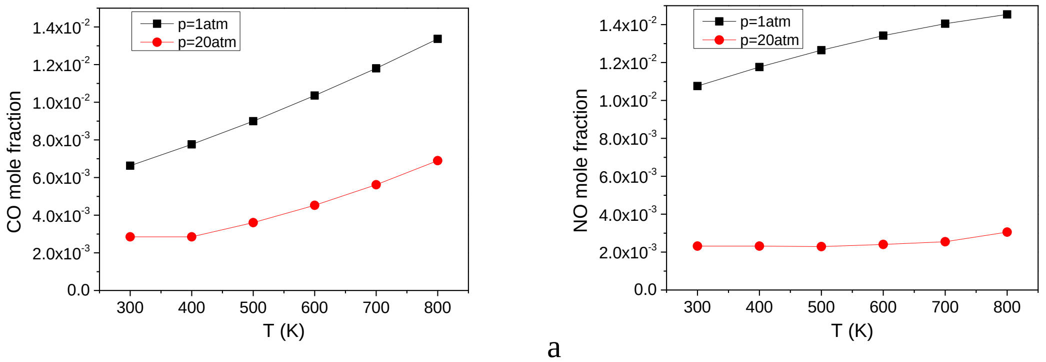


Figure 20. Effect of unburnt gas temperature on flame speed

Figure 20-21 show the effect of initial temperature on different properties of NH_3/CH_4 premixed combustion under stoichiometric condition. In Figure 20, laminar flame speed increases with the increase of initial temperature due to augmentation of flame temperature and therefore higher reaction rates. The promoting effect of initial temperature on flame propagation is smaller under high pressure conditions than low pressure conditions, which indicates that the augmentation of pressure has an inhibiting effect on the flame speed enhancement. In Figure 20a, CO emissions increase with the increase of initial temperature at both atmospheric and high pressure conditions, while in Figure 20b NO emissions also increase with initial temperature but much slower than the CO profile. The results suggest that the combined effect of elevated pressure and initial temperature can eventually lead to a decrease in NO_x and CO emissions. Specifically, under high pressure conditions (20atm), it can be observed the effect of initial temperature condition on NO emission is extremely small, which means pressure is the main factor influencing the NO formation in practical engine operational conditions.



a

b

Figure 21. Effect of unburnt gas temperature on CO and NO emission in exhaust

4 Conclusions

In this study, to explore the potential of utilising ammonia as a fuel for low carbon future energy systems, numerical simulation of co-firing ammonia with methane were performed. A detailed chemical-kinetics mechanism model was firstly developed in which ignition chemistry was improved for ammonia/methane combustion especially for high ammonia content or pure ammonia based on an existing chemical mechanism model.

The ignition delay time calculations show that both the ammonia fraction in fuel blends and equivalence ratio have important impact on the ignition delay time of ammonia/methane fuel blends. Significant higher ignition delay time using NH_3/CH_4 fuel blends were observed to those using pure methane..

Laminar flame speed calculation results show that NH_3 fraction in the fuel blends has a significant negative effect on flame speed. As with the increase of ammonia fraction, ammonia/methane flame propagation is weakened, suggesting the need of developing new techniques to promote stable operational conditions using these blends. However, fuel-rich conditions show greater values to lean conditions as a consequence of further ammonia reaction.

Emission characteristic results show that when using ammonia as primary fuel in the blends, CO emission will be lower. Ammonia substituting methane in a large proportion can have the same level of NO_x emissions as low content ammonia cases, which suggests the feasibility of using ammonia as primary fuel, with the advantage of going richer in equivalence ratio to ensure recombination of unburned ammonia with NOx, thus lowering the latter.

Flame structure analyses show that decrease in chemical reactivity with more ammonia fraction leading to the reduction of flame speed, phenomenon illustrated by the decrease of H, O and OH radical mole fractions in the flame. Also, NO and CO emissions have strong correlations with maximum radical concentrations like HNO and HCO in the reaction zone at different NH_3 fractions.

The study on the effects of engine-relevant conditions show that the elevated pressure will decrease the NO and CO emissions whilst increased initial temperature will lead to the augmentation of emissions. However, simulation results show that pressure is a more prominent factor which affects the kinetics in practical engine operational conditions than temperature, which indicates a good potential of using ammonia-based fuels under engine relevant conditions.

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