Modelling Combustion of Ammonia/Hydrogen Fuel Blends under Gas Turbine Conditions

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ABSTRACT: To utilize ammonia as an alternative fuel for future power generation, it is essential to develop combustion chemical kinetic mechanisms which can describe in some detail the reaction characteristics and combustion properties. In present study, a detailed chemical-kinetics mechanism is developed to validate premixed combustion characteristics of ammonia and hydrogen fuel blends comprehensively. In order to obtain a useful model for gas turbine applications, the proposed kinetic mechanism is verified in terms of NO_x emission, laminar burning velocity and ignition delay times, focusing particularly on elevated conditions which are encountered during gas turbine operation. Results have shown that the proposed kinetic model performs with satisfactory accuracy under different practical equivalence ratio conditions. The comparison with other mechanisms from the literature also demonstrates that the model can comprehensively describe the reaction process of ammonia/hydrogen fuels in terms of different combustion properties especially under gas turbine conditions. Finally, to develop the kinetic model for more practical applications, the proposed mechanism is reduced and appraised in a 2D Large-Eddy-Simulation simulation representing turbulent combustion for ammonia/hydrogen fuels under gas turbine conditions. The reduced mechanism shows good agreement with the parent model, whilst offering considerably greater computationally efficiency, hence providing optimism for the application of detailed ammonia chemistry for future CFD analysis under gas turbine combustion conditions.

1. INTRODUCTION

Recently, ammonia (NH_3) has been drawing much attention as a promising alternative under the ever-increasing pressure and demand to mitigate man-made processes giving rise to climate change [1-5]. Ammonia can act as a 'clean' energy carrier and storage medium, for it has a high hydrogen proportion and can in principle be burnt in an environmentally benign way just like hydrogen, yielding only water and nitrogen when completely combusted. But unlike hydrogen, for which storage and transportation problems still are cause for concern, ammonia can be easily stored and there are already well-established infrastructures and experience in producing, distributing and handling the chemical. Moreover, ammonia can be produced from renewable energy resources such as wind power, solar energy, biomass, etc. Hence, ammonia has the potential to play an influential role in future energy systems as an energy storage medium and 'green' fuel.

In the last few decades some studies have already been undertaken leading to significant progress in understanding effective utilisation of ammonia as an alternative fuel. For instance, numerous studies have targeted transportation applications, investigating ammonia combustion in spark ignition engines [6-8], and compression ignition engine [9-11] in particular. In these studies, ammonia is usually mixed with other fuels such as hydrogen [9, 12], diesel[13], gasoline[14], DEM[15], biodiesel[9], etc. to promote combustion performance. These studies have proven the effectiveness of various combustion promoters when using ammonia to overcome problems such as its relatively narrow range of flammability and high ignition energy. Hence, it is attractive to consider combusting ammonia-blended fuels for power generators to enable load matching with typical intermittent renewable resources such as wind or solar resources. Considering the extensive use of gas turbine power plant in recent times for electricity generation, and the pressure to reduce carbon dioxide emission, using ammonia in gas turbines for power generation offers a very interesting proposition. Recently, a new research program 'Power to Ammonia' initiated in the Netherlands is investigating the potential to turn gas-fired power plants into 'super batteries' [16], focusing on co-firing ammonia with methane. However, studies to date have concentrated on utilization of ammonia in reciprocating, rather than gas turbine, engines. The early ammonia combustion research on gas turbines in this century serves to demonstrate some of the low reactivity of ammonia and higher ignition energy compared to fossil fuels [17, 18]. Recently Valera-Medina et al. [19-21] studied ammonia and hydrogen/methane combustion in a laboratory scale generic swirl burner, in which results show that a new injection strategy is required to ensure stable combustion, especially for hydrogen injection with ammonia. Kurata et al. [22, 23] successfully achieved stable combustion using ammonia in a 50-kW class system with diffusion-flame-type combustor, but fuel NO_x emission was still high compared to benchmark natural gas-fuelled gas-turbine combustion. Given the paucity of data from ammonia-blended

power generation, further investigations are required to enhance understanding and control of combustion processes with ammonia-based fuels under gas turbine related conditions.

In the current research programme, ammonia/hydrogen blends are appraised as fuels for application in gas turbine combustion systems for large scale power generation in energy intensive industries [24-28]. Since hydrogen is a carbon neutral fuel, and an excellent combustion promotor for ammonia, whilst ammonia is also a hydrogen carrier and can be cracked to produce hydrogen, ammonia/hydrogen blends can be seen to be a flexible fuel source. To investigate the feasibility and application of ammonia/hydrogen as an alternative fuel for gas turbines, an understanding of combustion kinetics is fundamentally important[20, 29]. A number of previous studies have been undertaken on the chemical kinetic mechanisms of ammonia related combustion. Miller and Bowman [30] developed a detailed kinetic mechanism describing NO_x formation in hydrocarbon/NH_3 and H_2/NH_3 mixtures. Lindstedt's mechanism[31] was developed for predictions of a wide range of flat laminar premixed NH_3/H_2/O_2, NH_3/NO/H_2/O_2 and NH_3/O_2 and it has been employed in several ammonia combustion studies since [32-34]. The Konnov mechanism [35] was developed for the combustion of small hydrocarbon and ammonia fuels. It has been widely used in the ammonia combustion studies, offering better performance on the prediction of NO_x emission and propagation properties compared with previous mechanisms available [27, 28, 33, 36, 37]. Duynslaegher et al. [38] improved the Konnov's ammonia combustion mechanism by modifying the reactions related to nitrous oxide (N_2O) and the amidogen radical (NH_2). The results for NH_3/H_2/O_2/Ar flame show better predictions for NO_x emission. Tian et al. [39] developed a mechanism based on NH_3/CH_4/O_2/Ar flame data under low pressure conditions in order to identify the detailed flame structure. Li et al.[40] used a modified Dagaut-Keromnes[41, 42] mechanism with acceptable calculation results for burning velocity and ignition delay time of ammonia flames with hydrogen addition. Mathieu's mechanism [18] was established for ammonia oxidation and ignition delay time calculations under high pressures up to 30 atm, which is highly relevant to gas turbine operation. These kinetic models have proven reasonable accuracy for ammonia/hydrogen combustion under certain laboratory conditions [43-47]. However, due to the lack of a comprehensive study and experimental verification [29, 48], the applicability of the mechanisms for practical combustion of ammonia-based fuels still needs to be developed and improved, particularly for industrially-relevant conditions.

Hence, it is essential to develop a detailed kinetic mechanism in order to predict phenomena such as auto-ignition, flashback, and emission characteristics under gas turbine operational conditions for future developments. To achieve this goal, the present work develops a kinetic mechanism by improving Mathieu's model to validate comprehensively the combustion properties such as ignition delay times, burning velocity, NO_x emissions, etc. The improved mechanism is prepared for use in CFD calculations for prediction of the turbulent reacting flow field inside a gas turbine combustor for ammonia/hydrogen utilization. Therefore, the developed kinetic mechanism is also appraised in a 2D CFD simulation. Furthermore, the mechanism was reduced to represent the kinetics of ammonia/hydrogen combustion with 'sufficient' accuracy, but including fewer species and reactions. In this way, the reduced mechanism is rendered more suitable for application in 3D CFD simulation studies of practical gas turbines.

2. COMPUTATIONAL SETUP

2.1 Establishment of Chemical Mechanism

To study ammonia/hydrogen combustion in gas turbines, it is necessary to develop a detailed chemical-kinetics mechanism which can validate comprehensively the combustion properties under high pressure conditions. Mathieu's mechanism was built for shock-tube experiments of ammonia ignition delay time measurements under pressure conditions of up to 30 atm. Therefore, the chemical kinetic model proposed in the present work was mostly based on recent work performed by Mathieu under high-pressure conditions [18]. To improve the performance of the mechanism concerning NO_x emissions and burning velocity prediction, several reactions are modified according to the kinetic analysis of the main reactions as shown in Table 1. The mechanism developed involves 55 species and 276 elementary reactions, and is available in the *Supporting Information*.

Table 1. Modified reactions compared with the Mathieu mechanism

Reactions	A	n	Ea	Ref.
$N+NO=N_2+O$	2.10E+13	0	0	[49]
$NO+H+M=HNO+M$	1.50E+15	-0.4	0	[39]
$HNO+H=NO+H_2$	4.40E+11	0.7	650	[39]
$N_2O+H=NH+NO$	6.70E+22	-2.16	37155	[35]
$N_2O+H=N_2+OH$	5.00E+13	0	15200	[38]

The modifications of rate constants were performed based on contribution rate calculations and sensitivity analysis. To develop a kinetic mechanism which can comprehensively validate different combustion properties of NH_3/H_2 fuel blends, NO_x emission, laminar burning velocity and ignition delay times are all taken into consideration in the present study. Therefore, the sensitive reactions were firstly extracted for modification. Then, through modifications of rate constants of the most sensitive reaction for a particular combustion property, the performance of such properties can be systematically improved. After simulation predictions, various choices can be made to effect a balance between the accuracy of different combustion properties. According to this procedure, five reactions were modified. Taking the

reaction NO+H+M=HNO+M for instance, the modification of the kinetic data set in the present work slowed down this reaction, which gives rise to higher NO_x emission predictions to overcome the problem of underestimating NO_x associated with Mathieu's mechanism.

In order to use the detailed chemical kinetics mechanism for future practical application and design of gas turbine combustor research, it is necessary to reduce the scale of the ammonia/hydrogen mechanism. Actually it was found in this study that the CFD calculation takes a long time for NH_3/H_2 combustion in a simple burner, which is mainly due to the fact that the mechanism developed in the present study is still too large. Hence it is desirable to reduce the improved chemical-kinetical mechanism so it can be implemented in full scale 3D CFD numerical simulations. Therefore, a preliminary mechanism reduction was performed for the improved mechanism using the Directed Relation Graph (DRG) method, which has been described in detail by Bendtsen et al [50], and implemented in the Chemked II software program [51]. In the present study the detailed chemical-kinetic mechanism was evaluated with homogeneous (ignition delay) simulations generated by perfectly stirred reactor (PSR) simulations at constant pressure. The computation was conducted for initial temperatures at 2000K and a constant pressure of 17atm. The mixture with mole fractions of $NH_3/H_2/O_2/N_2$ 0.088/0.0565/0.1795/0.675 was chosen, corresponding to stoichiometric fuel-in-air conditions for a NH_3/H_2 molar ratio of 60/40, which is the same ratio as that utilized in a recent experimental study within a generic swirl burner [24]. After this case of reaction chemistry is calculated under such particular initial conditions, the results were prepared for the reduction of the mechanism model. The formation process using the DRG method starts with specifying several important species. Then, with all these initial targeted species the generation of a reactions graph is undertaken. A subset of reactions that are important for the targeted species is selected to be included in the list of important reactions. Simultaneously, new species appearing in these reactions are added into the important species list. The next step selects reactions that are important for the new species. The procedure is repeated until no new species appear. Finally, a reactions graph is produced with the important species to be considered in the reduced model. Thus, the final list forms a particular reduced reaction mechanism for the specific initial conditions. In the reduction procedure, three reduced kinetic models were generated by exercising different control indexes, which are related to the accuracy of the reactions selected. In the following study, the three reduced mechanisms with 108 reactions, 91 reactions and 74 reactions are specified by 'Mech. 1', 'Mech. 2' and 'Mech. 3' as shown in Table 3, and which are available in *Supporting Information*.

Table 2. Full mechanism of present study and reduced mechanisms

Name	No. Species	No. Elementary Reactions
The full mechanism	55	276
Mech. 1	22	108
Mech. 2	22	91
Mech. 3	21	74

2.2 Numerical Simulations

A 2D model for turbulent combustion was developed for further corroboration against data from practical systems. The same geometry of the burner in a previous study [48] was used in this study, which consists of an inlet tube and a combustion chamber. The flame is stabilized down the dump in a recirculation zone resulting from the sudden expansion. The burner is meshed with a structured grid of 13,575 cells. The modelling work is performed with Large Eddy Simulation (LES) coupled with detailed combustion chemistry. The CFD calculation was performed with the OpenFOAM toolbox [52, 53]. The case studied has a fuel mixture of 60%NH_3 and 40%H_2 premixed with air at an equivalence ratio of 1.0. The Reynolds number is ~2.8×10^4. To explore the performance of CFD simulations under gas turbine conditions, an inlet temperature of 600K and pressure of 17atm was specified. 2D CFD turbulent combustion simulation studies were performed with parallel computing to assess the applicability and performance for the reduced mechanisms, in which 64 cores were used during the calculation process with different reduced mechanisms. More detailed descriptions of the method, burner and numerical setup can be found elsewhere in [48].

3. RESULTS AND DISCUSSION

3.1 NO_x Emission Analysis

To develop ammonia as an alternative fuel, NO_x emission is a primary concern. A burner-stabilized premixed flame model was employed to validate the performance of the NH_3/H_2 combustion mechanism developed for NO_x emission predictions. In the model, simulation of this kind of flame can effectively provide data of the chemical kinetics of the NH_3/H_2 combustion process and help to interpret flame experiments. The simulation was carried out under low pressure conditions with various ammonia/hydrogen ratios and equivalence ratios to simulate the experimental results of premixed ammonia/hydrogen combustion provided by Duynslaegher et al [47].

Table 3. Flame inlet composition and initial conditions (from [47])

No.	NH_3	H_2	O_2	Ar	ER	p(mbar)

1	0.25	0.05	0.21	0.48	1	60
2	0.24	0.07	0.21	0.47	1	50
3	0.22	0.1	0.21	0.46	1	50
4	0.21	0.13	0.21	0.45	1	50
5	0.22	0.1	0.24	0.43	0.9	50
6	0.22	0.1	0.2	0.48	1.1	50
7	0.25	0.05	0.21	0.48	1	90
8	0.25	0.05	0.21	0.48	1	120
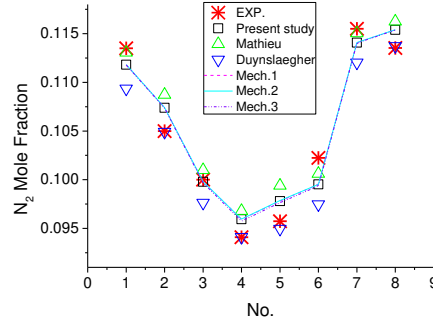
Figure 1. Mole fraction of N_2 in burnt gas. Experiments corresponding to [47]
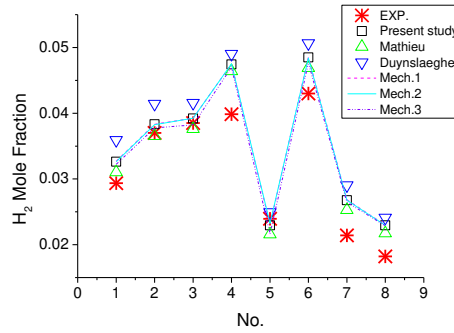
Figure 2. Mole fraction of H_2 in burnt gas. Experiments corresponding to [47]
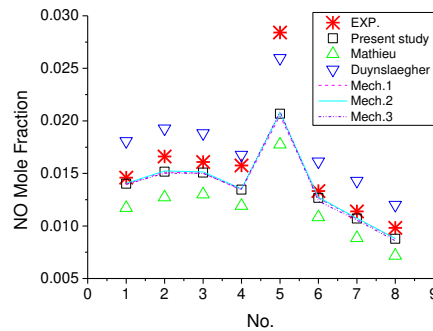
Figure 3. Mole fraction of NO in burnt gas. Experiments corresponding to [47]

As shown in Figure 1, NO_x emissions and some major species of $NH_3/H_2/O_2/Ar$ combustion were properly predicted with the reaction kinetics model developed in the present study against experimental data from burner-stabilized premixed flames investigated by Duynslaegher et al. [47]. To provide a comprehensive evaluation of the chemical-kinetics mechanism model of present study, the up-to-date ammonia mechanisms Mathieu [18] and Duynslaegher [47] mechanisms were also used in the calculation for reference. The experimental conditions were replicated in the simulation, which represent different conditions, such as different initial NH_3 concentrations (flame2-4), different equivalence ratios (flames 3,5,6), different pressures (flames 1,7,8), etc. As shown in Figure 1, prediction of N2 using different mechanisms varies with the initial conditions. The Mathieu mechanism and the present mechanism

show better performance for test No. 1,3,6,7 while the Duynslaegher mechanism shows better prediction of N_2 for other test points. Generally, all the mechanisms tested have shown acceptable performance with average relative errors of 17.04%, 20.03%, 18.49%, 17.09%, 16.91% and 16.68% respectively using the present mechanism, the Mathieu mechanism, the Duynslaegher mechanism, Mech. 1, Mech. 2 and Mech.3. Figure 2 shows the calculation results of H_2, in which the predictions by most mechanisms are quite near to each other. At some test points such as No.4 the deviation from the experiment is higher, which indicates the prediction of H_2 needs to be improved when using high hydrogen concentration in NH_3/H_2 mixtures. The average relative errors of the present mechanism, the Mathieu mechanism and the reduced mechanisms are around 10% while the average relative error for the Duynslaegher mechanism is higher than others with 19.37%. From the predictions in Figure 3, it can seen that the Mathieu mechanism under-predicts NO_x emissions, whilst the Duynslaegher mechanism over-predicts them in most cases. Generally, the chemical-kinetics mechanism model developed in the present study shows the best performance among the three mechanisms used for comparison with the average relative error of 10.26%. The largest discrepancy occurred during test No.5, which is the only condition using fuel lean mixtures. This indicates that further development of reaction mechanism is needed for fuel lean combustion conditions. Moreover, the reduced mechanisms also shows good agreement with the full mechanism of the present study with relative errors of around 10% against experimental data.

The simulation results show that all the mechanisms correctly capture the trend of NO_x emission under different experimental conditions. Comparing flame 2, 3 and 4, it can be seen that increase of NH_3 concentration in the fuel leads to higher NO concentration in the burnt gas, which is mainly due to the increase of 'fuel-bond' NO_x emissions. Flames 3, 5 and 6 demonstrate a strong dependence of equivalence ratio on NO yield. From fuel lean condition to fuel rich condition, a large drop in the NO concentration is observed from ER=0.9 to ER=1.1. This indicates the fuel rich combustion is preferential for practical, industrial use of ammonia/hydrogen fuel. A comparison of flame 1, 7 and 8 reveals the effect of pressure on the formation of NO emissions. From 60-120mbar, an obvious decrease of NO concentration can be observed.

To illustrate NO formation processes in the NH_3/H_2 flame, the main reaction pathways of NO formation were analysed (Figure 4), using the chemical-kinetic mechanism developed in the present study. It shows that the major source of the NO formation comes from oxidation of HNO, N and NH. When ammonia is consumed initially with O/OH, NH_2 is produced. NH_2 is then converted mainly into HNO and NH. Through production rate analyses, it was found the reaction $HNO+H \Leftrightarrow NO+H_2$ gives rise to the biggest contribution in the NO formation process. The conversion from N and NH to NO is mainly through the reactions $N+O_2 \Leftrightarrow NO+O$ and $NH+O \Leftrightarrow NO+H$, but with smaller net contribution to NO formation in comparison with HNO.
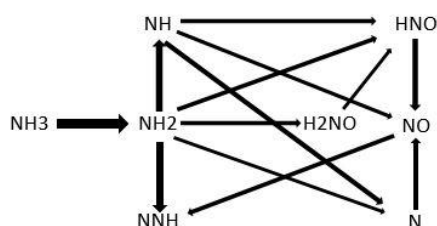

Figure 4. Pathway analysis of the NO formation

To investigate the potential of utilizing NH_3/H_2 fuels in gas turbine power generation sets, the effects of elevated pressure conditions were appraised with the improved chemical-kinetic mechanism. Take the fuel mixture of flame No. 1 as example, as shown in Figure 5, NO_x emissions decrease with the increase of pressure with considerable decreases observed from 'medium' pressure to 'high' pressure. Quantitatively, the results show that NO_x emission levels can be less than 5ppm when the pressure condition is more than 10atm, and less than 1ppm when pressure is higher than 20atm. This significant result indicates that the deployment of NH_3/H_2 blends in gas turbines is very promising as NO_x emissions are likely to be reduced under real operating conditions.
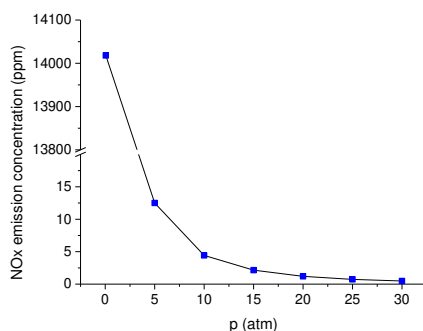

Figure 5. NO_x emission as a function of pressure

To evaluate the performance of the kinetic model for gas turbines further, pressurised conditions need to be investigated. However, there are still scarce experimental data of NO_x emission available in the literature for validation of ammonia combustion simulation. Figures 6-8 show the NO sub-mechanism validation under 10 atm conditions using the experimental data by Dayma and Dagaut, where $H_2/O_2/NO$ mixtures in N_2 [54] were measured in a jet stirred reactor . Under fuel-lean conditions, the mechanism advocated in the present study and the Mathieu mechanism show good agreement with the NO profile under 10 atm, especially for temperatures higher than 900K, whilst the Duynslaegher mechanism largely under-predicts NO emissions. Below 900K, the improved mechanism and the Mathieu mechanism slightly over-predicts NO emissions, but the transition point around 790 K is successfully captured, whereas the Duynslaegher mechanism shows temperatures 60K higher than experimental results. For stoichiometric conditions, the improved mechanism and the Mathieu mechanism successfully capture the trend for NO emission predictions, whilst considerable discrepancies can be observed between the results of the Duynslaegher mechanism and the experiments. For fuel rich conditions, the improved mechanism and Mathieu's mechanism slightly over-predicted NO emissions at high temperature ranges but still with acceptable values, whilst the Duynslaegher mechanism fails to capture the profile of NO emission. In all the equivalence ratio conditions, the reduced mechanisms have shown good agreement with the full mechanism as shown in the figures. Generally, the improved mechanism and Mathieu's mechanism perform very similarly under elevated conditions. This indicates that the new mechanism proposed has good potential for NO_x emission predictions for gas turbine operational conditions.
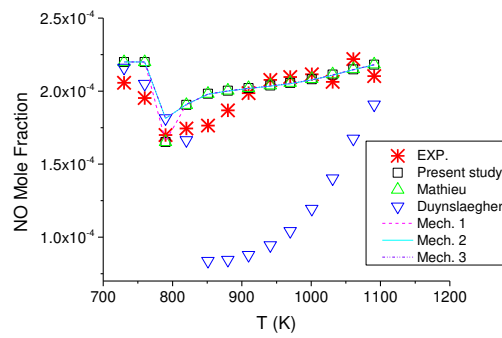

Figure 6. NO prediction of hydrogen-oxygen-nitrogen and 220ppm NO mixtures in a jet stirred reactor at 10 atm, ER=0.5. Experiments as in [54]
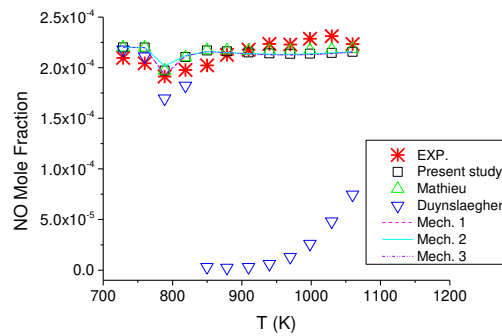

Figure 7. NO prediction of hydrogen-oxygen-nitrogen and 220ppm NO mixtures in a jet stirred reactor at 10 atm, ER=1. Experiments as in [54]
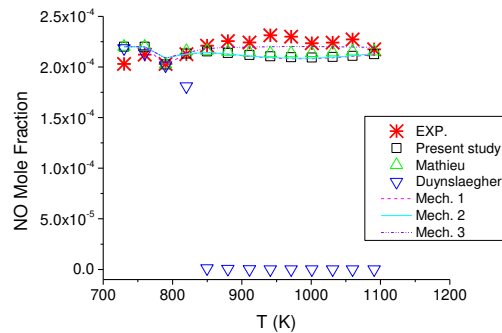

Figure. 8. NO prediction of hydrogen-oxygen-nitrogen and 220ppm NO mixtures in a jet stirred reactor at 10 atm, ER=1.5. Experiments as in [54]

3.2 Laminar Burning Velocity

Laminar burning velocity is one of the most important properties of premixed combustion flames. It is also used as an essential parameter for verification of detailed chemical mechanisms. Therefore, numerical simulations were performed by modelling one dimensional premixed freely propagating laminar flames of ammonia/hydrogen mixtures. The computational code of a premixed flame from Cantera [55] is employed in the present study. This modelling approach [33, 46] can in principle provide analysis of unstretched burning velocity, reaction rates, radical concentrations, sensitivity analyses, etc. In the model, burning velocity is defined as the flame front velocity relative to the flow into the unburnt mixture. The burning velocity calculation model is used to determine the characteristic flame speed of the gas mixture at specified pressure and inlet temperature. The flame speed prediction model in Cantera is stabilized in an axisymmetric stagnation flow, and computed along the stagnation streamline using a similarity solution to reduce the three-dimensional governing equations to a single dimension. The flame speed is calculated based on details of the well-established governing equations for the burning velocity, calculations that can be referred to Cantera's theory of one-dimensional reacting flows[55]. To validate the performance of the improved mechanism comprehensively, numerical simulations were undertaken under conditions corresponding to the experiments of Li [43] and Hayakawa [33] to enable the comparison of unstretched laminar burning velocity values, in which different ammonia/hydrogen ratios, equivalence ratios and pressure conditions were studied.
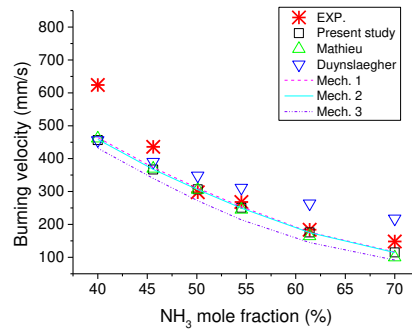

Figure 9. Burning velocity calculation of different NH_3 fractions in NH_3/H_2 fuel blends under fuel lean condition (ER=0.8). Experiments as in [43]
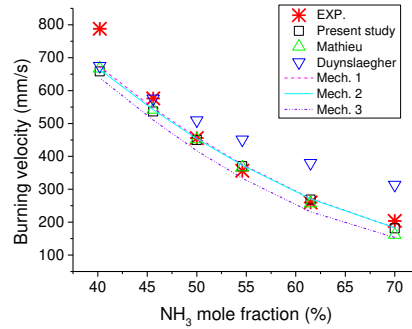

Figure 10. Burning velocity calculation of different NH_3 fractions in NH_3/H_2 fuel blends under stoichiometric condition (ER=1). Experiments as in [43]
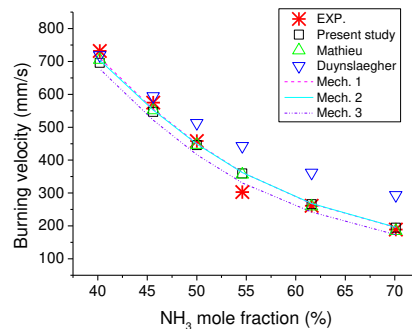
Figure 11. Burning velocity calculation of different NH_3 fractions in NH_3/H_2 fuel blends under fuel rich condition (ER=1.25). Experiments as in [43]

In Figures 9-11 the simulation results show a decrease in burning velocity of the NH_3/H_2 mixtures with the increase of NH_3 concentration due to less amount of free hydrogen atoms in the flame as the H_2 addition decreases.

Generally, under all the equivalence ratio conditions the improved mechanism and Mathieu's mechanism perform almost similarly with reasonable accuracy in predicting burning velocities of NH_3/H_2 blends, while the performance of the Duynslaegher mechanism is consistently relatively poorer. For fuel lean conditions, the deviation between simulation results and experimental results is greater when the ammonia fraction is low (<50%). For stoichiometric and fuel rich conditions, reasonable agreement with experimental data was obtained by using the improved mechanism and Mathieu's mechanism. Therefore, the improved chemical-kinetics mechanism performs well for burning velocity predictions under lean, stoichiometric and fuel rich cases with average relative errors of 13.21%, 7.18% and 6.01% respectively. The reduced mechanisms have given almost the same accuracy as the full mechanism. However, the results can also indicate that fuel lean combustion chemistry for NH_3/H_2 still needs more optimization especially for low NH_3 fraction fuel blends.
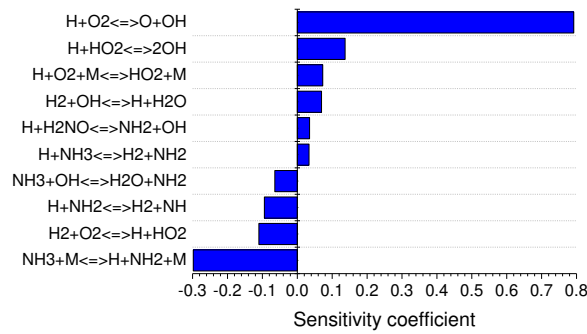

Figure 12. Sensitivity analysis of burning velocity by the mechanism developed in the current study
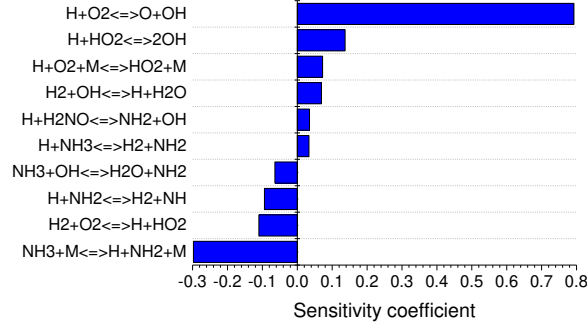

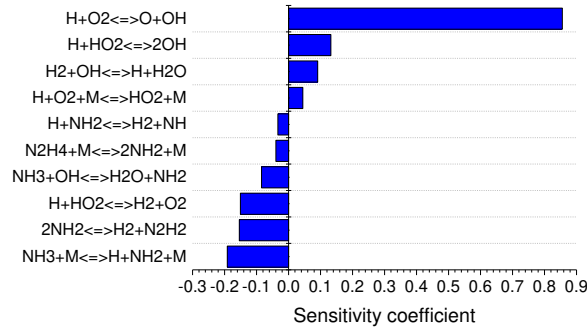**Figure 13.** Sensitivity analysis of burning velocity by the mechanism of the Mathieu mechanism

Figure 14. Sensitivity analysis of burning velocity by the mechanism of the Duynslaegher mechanism
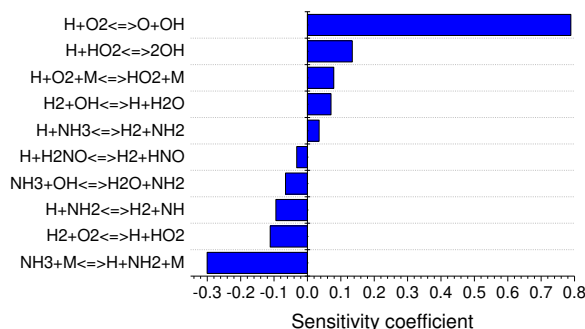
Figure 15. Sensitivity analysis of burning velocity by the reduced mechanism Mech. 1
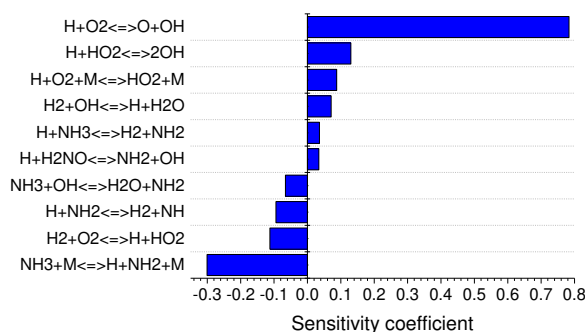

Figure 16. Sensitivity analysis of burning velocity by the reduced mechanism Mech. 2
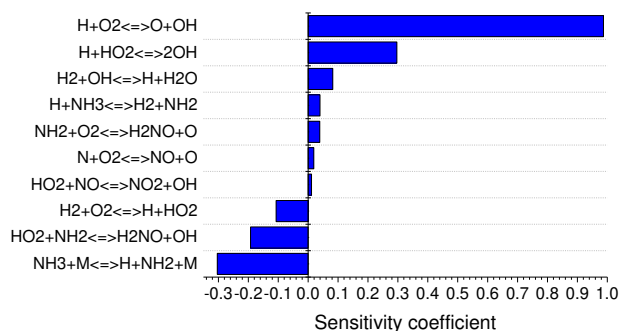

Figure 17. Sensitivity analysis of burning velocity by the reduced mechanism Mech. 3

To illustrate the difference between different mechanisms, sensitivity analyses were performed. Taking stoichiometric conditions for instance, sensitivity analyses are illustrated in Figure s 12-17 for the combustion of a blend with 61.5% NH_3 concentration. As shown in Figures 12 and 13, the most-sensitive reactions for the burning velocity calculation are almost the same for the improved mechanism and Mathieu's mechanism, which have produced the most accurate predictions as in Figures 9-11. It can be seen that that the most influential promoting reactions $H+O_2 \Leftrightarrow O+OH$ and $H+HO_2 \Leftrightarrow 2OH$ and the most inhibiting reaction $NH_3+M \Leftrightarrow H+NH_2+M$ has the largest impacts on the predictions of burning velocity in all the six mechanisms. The difference between them is that reaction $H+O_2 \Leftrightarrow O+OH$ plays a more prominent role whereas the reaction $NH_3+M \Leftrightarrow H+NH_2+M$ is less prominent in the Duynslaegher mechanism than in the improved mechanism and Mathieu's mechanism. This illustrates the reason why Duynslaegher's mechanism predicts a faster burning velocity than the mechanism of present study. As for the reduced mechanisms, most of the main sensible elementary reactions are the same with the full mechanism. For instance, the sentitivity analysis of Mech. 1 and Mech. 2 are almost the same with the full mechanism as shown in the comparision of figures 12, 15 and 16. In Mech. 3 the reaction $HO2+NH2 \Leftrightarrow H2NO+OH$ plays a more prominent inhibiting reaction compared to the other two reduced mechanism, which accounts for relatively lower burning flame speed calculations than the full mechanism and the reduced mechanisms Mech. 1 and Mech. 2. In fact, differences between rate constants of some key reactions produce an important impact on burning velocity calculation. For instance, concerning the most-sensitive reaction $H+O_2 \Leftrightarrow O+OH$, the rate constant is $k=1.04 \times 10^{14} exp(15286/RT)$ in the mechanism of present study and the Mathieu mechanism while in Duynslaegher mechanism the value is $k= 9.750 \times 10^{13} exp(14850/RT)$. This case shows how these differences can alter the performance when predicting laminar burning velocity.

To validate the NH_3/H_2 combustion chemistry further for practical gas turbine application, elevated pressure conditions were also investigated. Recently, Hayakawa et al.[33] derived the unstretched laminar burning velocity of premixed ammonia flames experimentally at various pressures up to 0.5 MPa. Therefore, the chemical-kinetics mechanism developed in the present study was appraised against this experimental dataset, as shown in Figure 18 and 19. The results show that the burning velocity decreases with the increase of pressure, which is consistent with the conclusions in previous studies[32, 33]. The main reason for this effect is that under different pressure conditions, the sensitive elementary reaction will vary. As a result, the decrease in burning velocity can be attributed to higher burning rates at high pressure conditions as observed in experiments[33, 56]. It can be observed that the improved mechanism, the reduced mechanisms and Mathieu's mechanism show good agreement with the data under elevated conditions (all the average relative errors less than 15%), while the Duynslaegher mechanism shows a significant deviation from experimental data as shown in the figures.
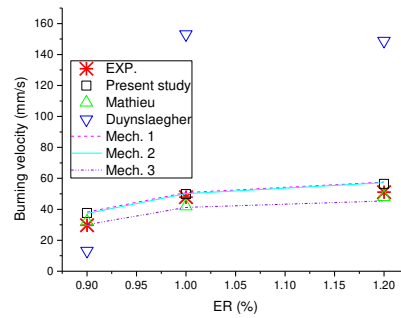

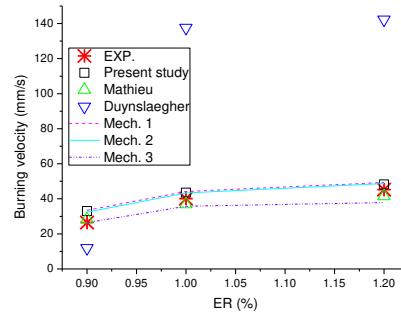**Figure 18.** Burning velocity calculation of ammonia (p=0.3MPa). Experiments as in [33]

Figure 19. Burning velocity calculation of ammonia (p=0.5MPa). Experiments as in [33]

3.3 Ignition Delay Times

The ignition delay time is another important parameter which describes autoignition properties of the combustion phenomenon. For operational aspects of gas turbine, it is crucial to avoid pre-ignition phenomena due to the variation of the fuel auto-ignition delay time. Therefore, the ignition delay time is one of the fundamental parameters that helps validate chemical kinetic models and aids the design of combustors utilizing NH_3/H_2 in gas turbines. Thus, computational predictions of ignition delay times are usually compared with shock-tube experiments [57-59]. In this study, ignition delay times were modelled with a closed homogeneous reactor in CHEMKIN PRO. In this model, the ignition delay time can be defined based on different criteria such as the time at which a certain species reaches the maximum concentration or the time at which an inflection point appears in pressure or temperature profiles [18, 57, 59]. In the present work, ignition delay times were extracted as the time corresponding to the steepest rate of the OH* generation [18]. The model was calculated at constant volume and adiabatic conditions. In the simulation, the ammonia and oxidiser mixtures are highly diluted (98.0-99.0%) to minimize effects of viscosity, heat transfer and non-equilibrium corresponding to the shock-tube experimental conditions [60]. The numerical work was carried out under high pressure conditions with different temperatures and equivalence ratios to simulate the experimental results provided by Mathieu et al, [18]. The mechanism developed in the present study was tested to validate its accuracy in predicting the ignition delay times.
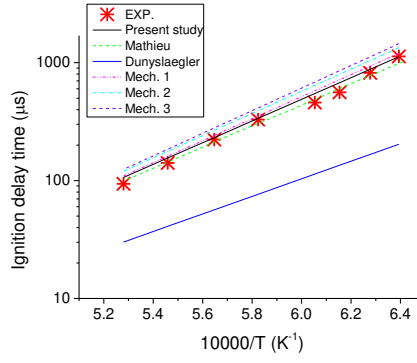
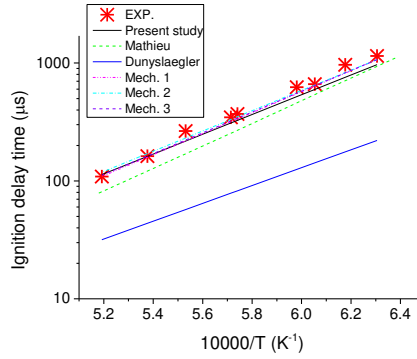**Figure 20.** Ignition delay times of NH$_3$ mixtures diluted in 99% Ar at around 30atm, ER=0.5. Experiments from [18]

Figure 21. Ignition delay times of NH$_3$ mixtures diluted in 99% Ar at around 30atm, ER=1. Experiments from [18]
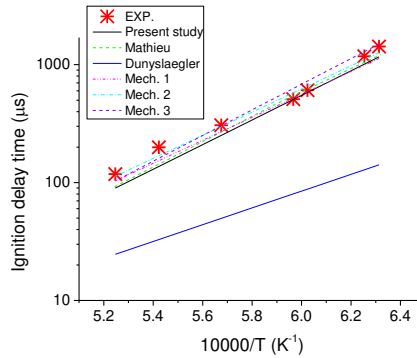

Figure 22. Ignition delay times of NH$_3$ mixtures diluted in 99% Ar at around 30atm, ER=2. Experiments from [18]

Figures 20-22 show the ignition delay time calculations using the improved chemical-kinetics mechanism together with Mathieu's, the Duynslaegher's mechanisms under high pressure conditions and the reduced mechanisms relevant to gas turbine operation. Generally, under all equivalence ratios studied both the improved mechanism and Mathieu's mechanism show excellent agreement with the ignition delay time data. Specifically, the improved mechanism prediction in this study shows a good accuracy with an average relative error of 10% in fuel lean conditions. The reduced mechanisms predicts a bit higher data than experiments. For stoichiometric conditions the improved mechanism slightly under-predicted the ignition delay times with an average relative error of 10% whilst Mathieu's mechanism predicts smaller ignition delay times than those obtained during the experiments. For fuel rich conditions both mechanisms show equal accuracy under high pressure conditions. On the other hand, the Duynslaegher mechanism shows poorer performance throughout.

To illustrate the difference between the chemical mechanisms for ignition chemistry further, sensitivity analysis was also undertaken. Taking the equivalence ratio of 1.00 for example, as shown in Figures 23-28, under 30atm it can be seen that the reaction H+O$_2\Leftrightarrow$O+OH plays the most prominent role in all the three mechanisms. The second most sensitive reaction is the same in both the improved and Mathieu's mechanisms. A noticeable difference amongst the three mechanisms is that NH$_3$+OH$\Leftrightarrow$NH$_2$+H$_2$O is the most inhibiting reaction, whilst NH$_3$+M$\Leftrightarrow$ NH$_2$+H+M is the most inhibiting reaction in the Duynslaegher mechanism. Another difference is that the N$_2$H$_2$ species plays a more important role in the Duynslaegher mechanism than in the other two. These differences account for the deviation from

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experimental data for the prediction results of Duynslaegher mechanism. As for the reduced mechanisms, most of the sensitive reactions are the same as for the full mechanism. For example, the three most promoting reactions and the three most inhibiting reactions are the same with the full mechanism, which leads to close ignition delay time results compared to the full mechanism as in figures 20-22.
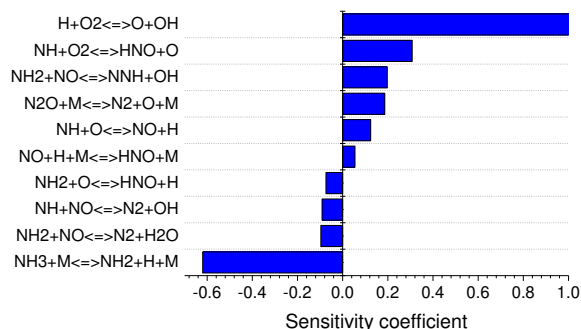

Figure 23. Sensitivity analysis of OH with the mechanism of present study (ER=1, 30 atm, 1700K)
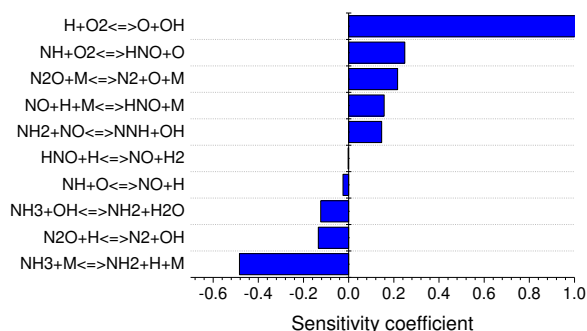

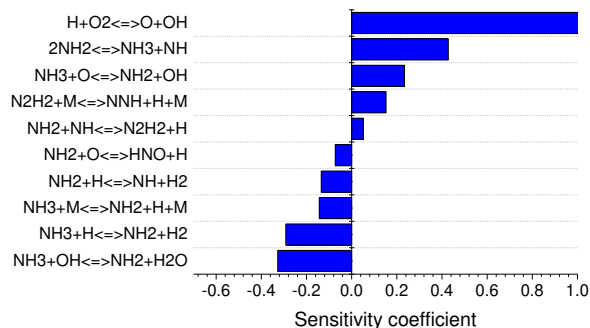**Figure 24.** Sensitivity analysis of OH with the Mathieu mechanism (ER=1, 30 atm, 1700K)

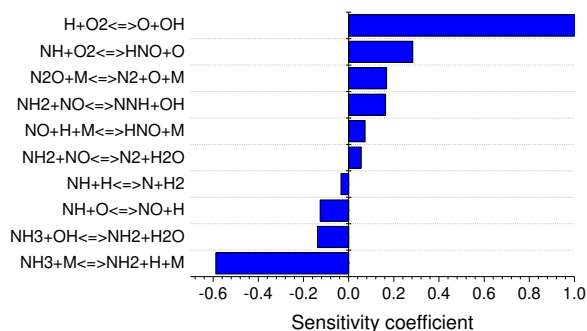**Figure 25.** Sensitivity analysis of OH with the Duynslaegher mechanism (ER=1, 30 atm, 1700K)

Figure 26. Sensitivity analysis of OH with the reduced mechanism Mech. 1 (ER=1, 30 atm, 1700K)
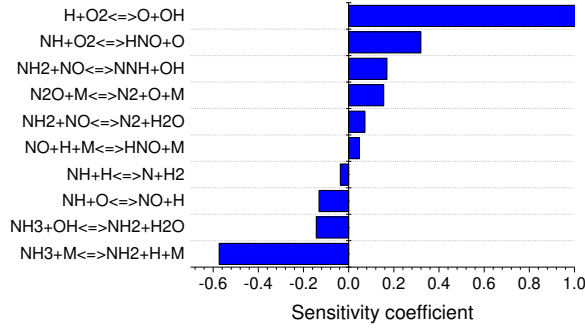
Figure 27. Sensitivity analysis of OH with the reduced mechanism Mech. 2 (ER=1, 30 atm, 1700K)
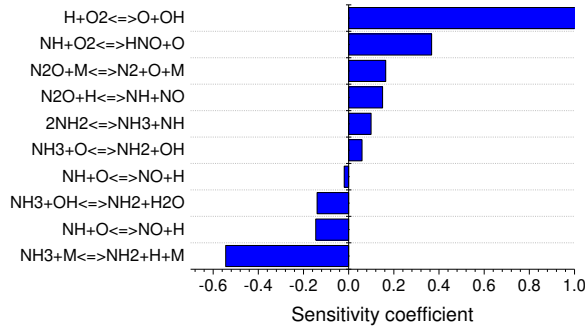

Figure 28. Sensitivity analysis of OH with the reduced mechanism Mech. 3 (ER=1, 30 atm, 1700K)
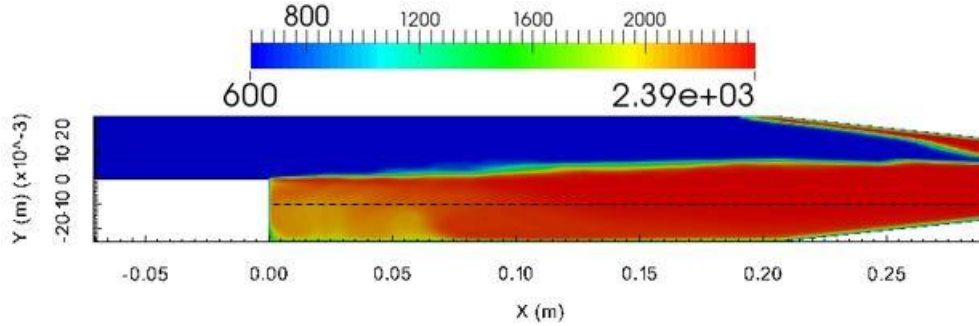
3.4 Turbulent Combustion CFD Modelling

Figure 29. Temperature distribution with the full mechanism of present study

Since this kinetic mechanism study lies on a fundamental position of the gas turbine combustor research, the aim of this development is to use a reduced model for practical 3D simulation studies. Thus, the 2D CFD study was used to verify the reduced mechanisms by comparing them with the full mechanism, thus establishing the path to the 3D simulation in the near future. The simulation results presented were obtained after running the model for 40000 time steps (0.2 s), when the flame fully propagates the burner after ignition. Comparing the processing time of the turbulent combustion generation procedure with the full kinetic mechanism and reduced ones, the shortest computational time was achieved with Mech. 3 taking 37.2 core-hrs whilst the full mechanism and Mech. 1 and 2 took 91.8 core-hrs, 68.5 core-hrs, and 47.8 2 core-hrs respectively. As shown in Figure 21, the temperature field for the turbulent flame simulation using full mechanism was obtained.

The results provided an overview of the entire field, in which a recirculation zone has been formed down the dump plane resulting from the sudden expansion. This recirculation brings back hot combustion products and reactive radicals, igniting the fresh fuel mixture and stabilising the flame under the conditions analysed. Temperature was observed in the range of 300 to 2400K. Similar calculations were also obtained using the reduced mechanisms. To quantitatively validate the reduced mechanisms, results of different parameters along the dashed line ($y=-10^{-2}$ m) are extracted and compared against the full mechanism developed in the present study, Figures 30-33. Temperature profiles using the reduced mechanisms agree with the full mechanism achieving ~2400 K in the post flame zone, Figure 30. As expected,

the radicals keep changing their concentration as they move downstream, which is associated with various reactions that contribute to increasing temperature.
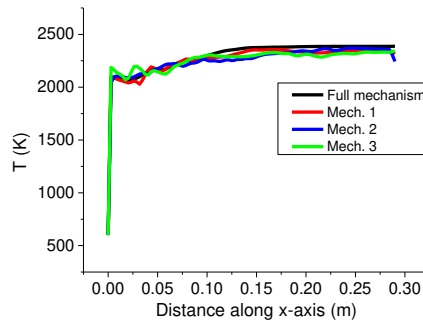

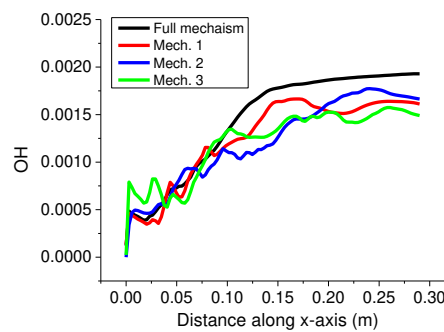**Figure 30.** Temperature profiles along the burner

Figure 31. OH mass fraction profiles along the burner

For OH species (Figure 31), the reduced mechanisms predict slightly lower values than the full mechanism, but at smaller distances (x<0.05m), Mech. 3 predicts a higher OH concentration than others. The difference of OH profiles account for differences in temperatures between simulations. Since the OH radical is a significant molecule through the combustion process of ammonia/hydrogen fuels, these mechanisms should be capable to carry out preliminary analyses towards combustion characterisation of such blends.

It is observed that the concentration of OH radicals remains at a high level even until the end of the burner. For example, using the full mechanism the concentration of OH radicals at the outlet is about 0.002 [mole fraction]? while $4.4*10^{-5}$ [mole fraction]? of OH concentration is obtained for equilibrium level calculations under the same conditions. This indicates that combustion reactions are still progressing. Thus, it should be made clear that the 2D CFD simulation cannot totally provide the representative geometry of a real gas turbine combustor, which results in the fuel being not combusted completely in such configuration. However the 2D configuration can generate recirculation zones to stabilize the flame, which provides representative information related to the turbulent combustion of practical cases. The results also indicate the importance of good injection strategies for practical designs of the NH_3/H_2 turbulent combustion. Thus, the 2D simulation in the present study was mainly performed to determine if the reduced mechanisms have good correlation with the full mechanism under gas turbine representative conditions.

Figure 32 shows velocity magnitude profiles along the dashed line. As chemical reactions interact with turbulence in the flame, the flow field will also be an essential indication for the performance of the mechanisms and the overall simulation. Comparing the reduced mechanisms with the full mechanism, it can be seen that before the distance of 0.1 m, the predicted velocity magnitude fluctuates a lot along the burner. The different trend of velocity calculation at the distance around 0.1m indicates the deviation in prediction of the recirculation zone using reduced mechanism Mech. 3. The reason can be that the effect of relatively strong turbulence existing in the recirculation zone will interact with chemical reactions leading to the different results of flow field calculation when using reduced mechanisms. However, in terms of the whole flow field results from the CFD simulation, generally the reduced mechanisms still provide acceptable predictions relative to the full mechanism.
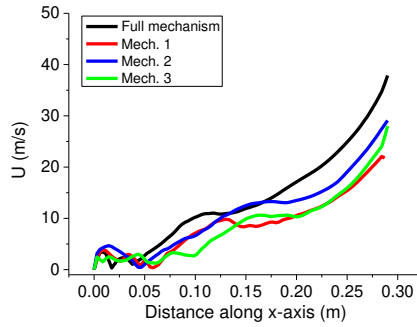
Figure 32. Velocity magnitude profiles along the burner

Figure 25 shows NO_x emission prediction profiles using the different mechanisms. In terms of exhaust NO emission concentration Mech. 1 produces the best agreement with the full mechanism. With less reactions in Mech. 2 and Mech. 3, the deviation of exhaust NO emission becomes greater. At middle distances (around 0.13m), the reduced mechanism Mech. 2 and Mech. 3 give considerably lower predictions. Comparing with Figure 32, the difference in the flow field also has an effect on the distribution of species concentrations in the turbulent flame. This indicates that to capture NO formation within the flame structure, the reduced mechanisms can cause some deviation from the full mechanism but are still capable of providing reasonable approximations of exhaust NO. Moreover, the general satisfying performance of the reduced mechanisms can be illustrated with the average relative errors of 10.58%, 14.52% and 11.72% for Mech. 1-3 respectively. As a highly temperature sensitive radical, NO profiles give good reference for future simulation studies using complex chemistry coupled with advanced turbulence models.
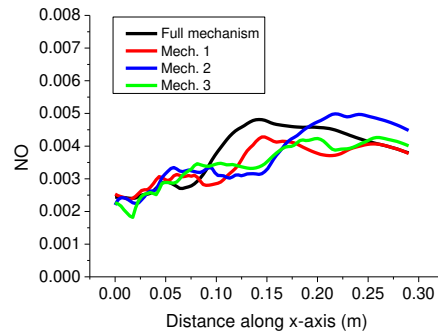

Figure 33. NO mass fraction profiles along the burner [UNITS?)]

In general, with more species and reactions in the mechanisms, the closer the results are to those corresponding to the full mechanism. The results indicate that the reduced mechanisms Mech. 1-3 are qualified for the study of temperature fields, exhaust emissions and flow field of NH_3/H_2 flames in CFD simulations. From the present study, overall Mech. 1 is recommended best for future use in 3D CFD simulations due to its relatively reasonable accuracy and short computational time compared to the full kinetics mechanism model.

However, it must be emphasized that when conducting LES simulations using the detailed chemical mechanism, it was found that even the 2D CFD calculation takes quite a long time for NH_3/H_2 blends combustion in the burner, which suggests that the computational cost is an essential barrier for the implementation of the present mechanism in practical 3D gas turbine simulations.

4. CONCLUSION

This study has proposed an improved chemical-kinetics mechanism model for ammonia/hydrogen premixed combustion. The mechanism was developed mainly by improving the Mathieu mechanism in terms of NO_x emission calculations. The chemical-kinetic model was then tested to simulate ammonia/hydrogen flames against experimental data in Duynslaegher's study for various equivalence ratios, pressures and initial ammonia contents. Results show that the general performance of the improved kinetic model is better than the Mathieu mechanism and significantly better than the Duynslaegher mechanism. Then the proposed mechanism was validated for laminar burning velocity calculations under different ammonia concentrations in NH_3/H_2 fuel blends and equivalence ratios ranging from fuel lean to fuel rich conditions. Laminar burning velocities of ammonia combustion under high pressure conditions were also used to provide further validation of the proposed mechanism. Results demonstrate that the mechanism developed in the present study provides the best performance in terms of predicting burning velocities under gas turbine conditions. For ignition delay time calculation, the improved kinetic model has also shown good results for highly diluted ammonia mixtures under high pressure conditions. Thus, the improved chemical-kinetics mechanism model has been shown to

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be capable of predicting different essential properties of ammonia/hydrogen combustion under gas turbine related conditions. Finally, reduction analyses were undertaken to enable reduced mechanisms to be developed for utilisation in more practical CFD simulations. Three reduced combustion mechanisms were derived using the DRG method. Utilisation of the reduced mechanisms under realistic gas turbine conditions in 2D simulations has justified the implementation of the optimised reduced mechanism in future 3D CFD simulations of ammonia/hydrogen combustion systems, with the benefit of significantly reduced computational cost.

SUPPORTING INFORMATION

The chemical-kinetics mechanism of present study and reduced mechanisms in CHEMKIN format. This material is available free of charge via the Internet at http://pubs.acs.org.

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