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Reduced Chemical Mechanisms for Ammonia/Methane Co-Firing for Gas Turbine Applications

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Abstract

Energy storage is one of the major challenges facing the world towards its challenging 2050 climate-change targets. A potential enabler of a low-carbon economy is the energy vector hydrogen. However, issues associated with hydrogen have led to consider other molecules such as ammonia as a potential candidate for chemical storage. Apart from its relatively high stability under atmospheric temperature, ammonia has the added attraction that it can also be sold on international markets or be used for power generation, making it a very versatile and hence attractive commodity. To explore the feasibility of co-firing ammonia with other fuels, i.e. methane, detailed numerical analyses and flame chemistry are required, usually at very high computational cost. Therefore, this study intends to determine a reduced mechanism for ammonia/methane combustion for practical gas turbine combustor conditions. Five reduced mechanisms of the well-known Konnov's mechanism were compared. Ignition delay time validations (0D) under industrially relevant conditions were used for correlation purposes. Combustion products of ammonia/methane premixed laminar flames (1D) were also validated with results from the full Konnov's mechanism. Finally, CFD simulations of a turbulent flame (2D) including reduced mechanisms were performed at representative industrial conditions. Results showed a reduced reaction mechanism of 48 Species and 500 elementary reactions can provide good results for further analyses.

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Keywords: Reduced mechanism; Gas turbine; Ammonia/methane combustion; CFD

1 Introduction

Energy storage is one of the major challenges facing the UK in developing towards its 2050 zero carbon targets. A potential enabler of a low-carbon economy is the energy vector hydrogen. However, issues associated with hydrogen storage and distribution are currently a barrier to its widespread use.

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Hence, other indirect chemical storage media such as ammonia have been proposed to alleviate such issues. Ammonia has the added attraction that it can also be sold on international markets for use in industrial processes (steelmaking), as an agricultural fertilizer, or for immediate power generation, making it commercially a very versatile and hence attractive commodity. Thus, progress on the use of NH_3 to replace high intensive CO_2 production fuels is a main priority for groups working on the area [1-3]. However, there are several barriers and corresponding research challenges to the adoption and development of ammonia as a viable energy storage medium. For example, today there are no mature products capable of generating significant power (>MW) from ammonia fuel. Gas turbines are potentially versatile candidates for efficient power generation to supply isolated communities, for example, but require considerable research and development to provide optimized, practical designs. Preliminary research has shown that it is likely that novel fuel mixtures and fuel injection strategies will be required.

A series of challenges such as slow ammonia kinetics at low temperatures, stability problems and advanced injection strategies are just some of the disadvantages of using NH_3 as fossil substitute. Thus, fuel enhancers such as hydrogen or methane can be used. Particular to methane, this is a well-known fuel used for long time in gas turbines for power generation. Thus, ammonia/methane blends could be used as a combination of green ammonia, i.e. obtained from renewable sources, and by-product ammonia obtained from industrial processes. This is an idea that has attracted considerable industrial and academic attention, leading to attempts to develop "Power to Ammonia" concepts to turn gas-fired power plants into 'super batteries' [4]. Therefore, this work evaluates NH_3/CH_4 blends for their utilization as fuel in gas turbine combustion systems to support energy intensive industries [5, 6].

Computational fluid dynamics (CFD) in combination with advanced reaction chemistry can help to capture more accurate predictions for NOx emissions, turbulence in reacting flows, combustion dynamics, etc. However, it is recognized that the considerable number of reactions and species in these advanced reaction mechanisms still limits computation performance, thus requiring the usage of reduced models for CFD analyses. For instance, Konnov's mechanism [7], has more than 100 species and ~1,200 reactions. Therefore, a reduced reaction mechanism can considerably cut computational time and memory requirement, thus making practical calculations for gas turbine combustors with complex chemistry under industrially relevant conditions.

Therefore, in this work Konnnov's mechanism is compared with 5 reduced mechanisms for wider validation of ammonia combustion analyses [8, 9]. Five reduced mechanisms are compared to existing experimental data and Konnov's mechanism in order to validate their accuracy whilst using ammonia/methane blends under gas turbine combustion conditions. Ignition delay times, laminar flames of NH_3/CH_4 blends and turbulent combustion have been evaluated to validate the performance of the proposed reduced mechanisms. Thus a comprehensive comparison in different dimensional levels (0D, 1D, 2D) allowed the generation and assessment of all reduced kinetic mechanisms to determine the best mechanism for further research in the area.

2 Establishment of Reduced Mechanisms

In this study, Konnov's mechanism was reduced under desired conditions for the study of gas turbine combustors. The reduction was conducted at 1 atm, 5 atm and 15 atm over temperatures ranging from 1000K to 1800K. A constant volume homogeneous model was employed for the same pressures using a Perfectly Stirred Reactor configuration. The mixture fraction of NH_3:CH_4 was set at 61:39, which is the same ratio as that utilized in a generic swirl burner experimental campaign in [5]. Under such conditions, sensitivity analyses and rate of contribution calculations were performed to reduce the number of species and reactions from Konnov's mechanism. It should be mentioned that although the less species and reactions there are in a reduced mechanism, the more computational cost can be saved, the quality of the results gets compromised; hence a balance between the accuracy and efficiency is needed for the use of the reduced mechanisms in simulation studies. Based on the calculated results, five reduced mechanisms were obtained for analysis in this work. These are presented in table 1.

Table 1. Studied reaction mechanism.

Name	No. Species	No. Elementary Reactions
Konnov [7]	129	1231
Mech.1	84	940
Mech.2	77	874
Mech.3	61	687
Mech.4	48	500
Mech.5	31	243

3 Simulation Models

3.1Ignition Delay Times

Ignition delay time calculations are an important validation parameter for detailed chemical mechanisms. Fuel and oxidizer mixtures were highly diluted (98-99%) with argon to minimize viscous effects, heat transfer and non-equilibrium as performed in shock-tube experimental conditions [10]. The simulation was performed with a closed homogeneous reactor using CHEMKIN-PRO [11]. All five reduced mechanisms were tested to validate their accuracy to predict ignition delay times against experimental results of ammonia combustion obtained by Mathieu et al. [12].

3.2 Burner Stabilized Premixed Flame

To validate the emission prediction capability of the reduced mechanisms a burner-stabilized premixed flame model [13] was employed from the Cantera software [14] which is a one-dimensional steady flame simulation. Using this model, simulations with detailed mechanisms can be used to effectively analyse the kinetics of ammonia/methane combustion processes as performed in [13].

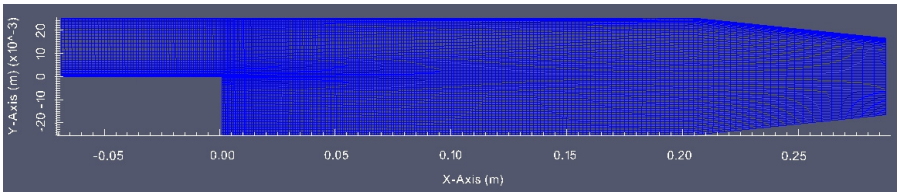

Fig. 1. The geometry of the burner for turbulent combustion

3.3 CFD Turbulent Combustion

The validation of the reduced mechanisms for CFD simulation was conducted using a 2D turbulent flame combustion model, Fig.1. The burner consisting of an inlet tube, a combustion chamber and a transition region [15]. The simulation was conducted with OpenFOAM toolbox [15], using Large Eddy Simulation (LES) for turbulence resolution with a structured mesh that consisted of 13,575 cells. The fuel mixture used consisted of 39%CH_4-61%NH_3 premixed with air at an equivalence ratio of 1.0. The Reynolds number was set ~2.8×10^4. An inlet temperature of 600K and pressure of 17atm was investigated to meet gas turbine combustor conditions.

4 Results and Discussion

4.1 Ignition Delay Times under High Pressure Conditions

Figure 2 presents validation results using Konnov's mechanism and the five different reduced mechanisms. Composition of the blend used for calibration contained a mixture of 0.02%NH_3 /0.089%CH_4/ 0.297%H_2/ 0.297%CO/ 0.21%H_2O/ 0.157%CO_2/ 0.950%O_2/ 97.98%Ar. Compared to

experimental data, the results suggest good performance in predicting ignition delay times with full and all the reduced mechanisms under high pressure conditions.

Figure 3 shows ignition delay time predictions of ammonia/methane mixtures under gas turbine conditions at 17 atm. Ammonia/methane mixtures were diluted in 99%Ar under an equivalence ratio of 1.0. The mole ratio of ammonia to methane was set at 61% to 39% according to a generic swirl burner experimental campaign previously performed [5]. High consistency of the reduced mechanisms with full Konnov's mechanism is observed in most cases, Fig. 3.

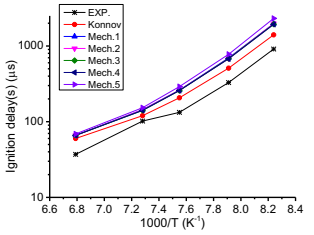

Fig. 2. Ignition delay times of NH_3/CH_4 contained mixtures 12.0 atm. Experiments as in [12].

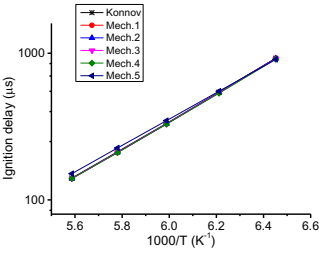

Fig. 3. Ignition delay times prediction of NH_3/CH_4 mixtures under gas turbine conditions (17atm)

4.2 Emissions of Laminar Flames

Validation for major emission products of the burner-stabilized premixed flames is shown in Figs 4-5. The experimental data of NH_3/CH_4 combustion used for validation were investigated by Tian[13].

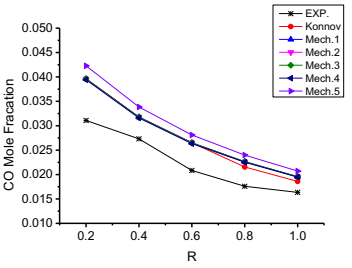

Fig. 4. Final mole fraction of CO with different R

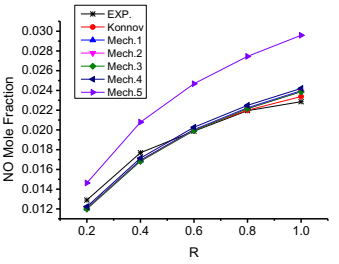

Fig. 5. Final mole fraction of NO with different R??

All mechanisms have a satisfying performance when it comes to predict major emission species, showing clear patterns for the decrease of CO and increase of NO when augmenting R(mole ratio of NH_3/CH_4) as expected. It is evident that development of these blends will require substantial efforts to bring down these two emissions before industrial implementation, the gas blend being one of the important parameters to study. Thus, to find out proper fuel mixture ratios of NH_3/CH_4 for the development of gas turbine, Konnov's mechanism and the reduced mechanisms can help to analyse the combustion kinetics effectively.

4.3 2D Turbulent Combustion under Gas Turbine Conditions

The CFD simulation of turbulent combustion was performed to test the feasibility of the reduced mechanisms. As a result, the shortest computational time was achieved with Mech. 5 taking 6.05h whilst Konnov's mechanism and Mech. 1-4 took 56.32h, 46.94h, 37.75h, 30.28h and 19.79h respectively. Fig. 6 shows simulation results of the temperature field in the burner using full Konnov's mechanism. To illustrate the performance of the reduced mechanisms, different parameters along the dashed line were compared, Figs. 7-9.

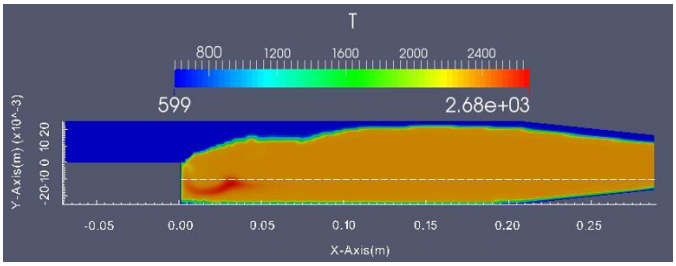

Fig. 6. Temperature distribution calculation with Konnov mechanism

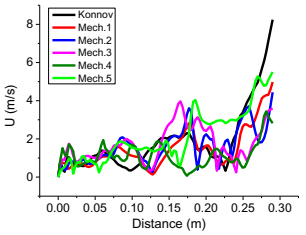

Fig. 7. Computed profiles of velocity

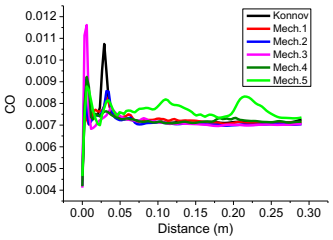

Fig. 8. Computed profiles of CO mass fraction

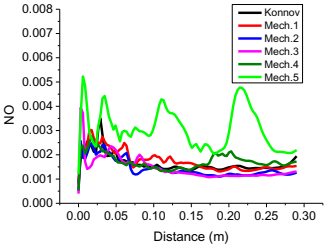

Fig. 9. Computed profiles of NO mass fraction

Figure 7 shows how velocity magnitudes fluctuate along the burner. All reduced mechanisms have given acceptable predictions if compared to the full mechanism. NO and CO emission prediction profiles were also compared against Konnnov's mechanism using all reduced mechanisms, Figs. 8 and 9. Good consistency is found with the full Konnov's mechanism for CO emission predictions. However, it is evident that Mech.5 over-predicts the results. Similarly, Mech.1-4 have predicted concentration profiles close to the Konnov's mechanism for NO emissions. Therefore, it can be concluded that all reduced mechanisms apart from Mech.5 have given acceptable predictions as compared to Konnov's mechanism. Thus, the reduced mechanisms show good potential for use of the complex chemistry coupled with turbulence fluctuation, making Mech.4 the best candidate for its high accuracy and low computation cost to move forward into 3D analyses and further improvement.

5 Conclusions

This study has presented five reduced chemical kinetic mechanisms based on Konnov's mechanism. The reduced mechanisms were assessed under gas turbine conditions with different levels of modelling simulation work. Ignition delay time calculations for ammonia/methane blends at high pressure conditions provided good correlations to Konnov's reduced mechanisms, thus showing good agreement with experimental data. Under gas turbine conditions, ignition delay time predictions for ammonia/methane using Mech.1-4 demonstrated good performance against the full Mechanism. In terms of CO and NO emission concentrations, calculations using a 1D burner-stabilized flame model with NH_3/CH_4 combustion showed good accuracy when using all reduced mechanisms included the full Konnov mechanism. Finally, parameters such as velocity profiles, CO and NO emissions were examined under gas turbine conditions using CFD analyses through the five reduced mechanisms. All but Mech.5 showed good, general agreement with the full Konnov's mechanism. As Mech.4 contains only 48 species and 500 elementary reactions, and the mechanism provides good accuracy with the full model. Mech.4 has been recommended as the model for future ammonia/methane combustion research on this and other gas turbine combustors.

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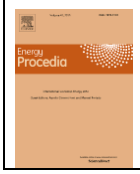

Biography

Mr. Xiao is a Ph.D. candidate at Cardiff University. He works on topics about green fuel for power generation in gas turbine.