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Numerical study assessing various ammonia/methane reaction models for use under gas turbine conditions

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HIGHLIGHTS

- Co-firing ammonia/methane blends is a possible choice to reduce carbon emissions.
- Ammonia/methane fuelled gas turbines have been barely studied.
- A comprehensive comparison of different detailed mechanisms was performed.
- Ignition delay and NOx emission analysis show that Tian mechanism performs best.
- Combustion characteristics of NH_3/CH_4 were predicted under gas turbine conditions.

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ABSTRACT

Ammonia as an alternative fuel and hydrogen carrier has received increased attention in recent years. To explore the potential of co-firing ammonia with methane for power generation, studies involving robust mathematical analyses are required to progress towards industrial implementation. To explore a best suited mechanism for ammonia/methane combustion in gas turbines, five different detailed mechanisms were compared to identify their accuracy to represent the reaction kinetics under real gas turbine combustor conditions. Ignition delay time was compared with recent literature showing that the mechanisms of Tian and Teresa exhibit the best accuracy over a large range of conditions. A 1D simulation was also conducted using a Chemical Reactor Network (CRN) model, thus providing a relatively quick estimation of the combustion mechanisms under swirling combustion conditions. The simulation of NOx emissions indicates that Tian mechanism has better performance than the others compared. Hence, the Tian mechanism was selected as the most appropriate for further studies of ammonia/methane combustion through a set of experiments carried out at various equivalence ratios and pressure conditions. Finally, sensitivity and pathway analyses were also performed to identify important reactions and species under high pressurized conditions, areas that need more attention for model development and emission control in future studies.

1. Introduction

Ammonia is a promising energy storage material which could be utilised to replace conventional fossil fuel under the background of ever increasing energy demand and climate change issues. When derived from renewable sources, ammonia can be a long-term sustainable fuel capable of fulfilling some of the energy demand in isolated areas disconnected from main national grids. Compared to other fuels such as hydrogen, biofuels, shale gas and dimethyl ether. Ammonia can also have many advantages for its storage, delivery and distribution. For instance, ammonia contains a large hydrogen component but it does not have the same issues during storage as it can be converted into a liquid at relatively low pressure (~8 bar). Moreover, as ammonia is an important chemical used as a fertilizer, there are already well established infrastructures and experience for its storage, handling, transportation and distribution worldwide.

Abbreviations: CRN, Chemical Reactor Network; STP, standard temperature and pressure; E.R., fuel–air equivalence ratio; T, temperature of unburnt mixture.

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Currently there are several groups trying to utilize ammonia for power systems, mostly in internal combustion engines [1–5]. However, power obtained from such units is relatively modest, typically in the 0.1–1 MW range. Thus similarly responsive but larger power generators will be required to meet the demands of electrical grids. As a result, considering the pressure to reduce carbon dioxide emission and finite resources of fossil fuels, using "green" ammonia in gas turbines for power generation is an interesting proposition. However, there is still a dearth of information relating to the utilization of ammonia in gas turbine combustors.

Although research has been undertaken for operational flame limits, chemical models, flame speed and internal combustion engines, gas turbines have played a minor role using this fuel. Academia has shown some development in the understanding of these systems, but this is limited [6–9]. Results show a series of challenges when utilising this fuel including: (a) lower flame temperatures and slower kinetics; (b) stability and efficiency problem; (c) requirements for pre-vapourising the ammonia; (d) pre-cracking of the molecule to improve ignition reliability and increase burning rate. NASA also identified during their XLR-99 program the need for "combustor enhancers" such as hydrogen, gasoline, kerosene and propane, especially during start-up and idle [9]. Another potential fuel enhancer is methane, as this is the main fuel of gas turbines for power generation. An ammonia/methane blend could be used not only from green ammonia sources, but also from by-product ammonia obtained from industrial processes. Ammonia addition 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 [10,11]. Therefore, this research appraises ammonia/methane as the fuel to be studied for the purpose of application in gas turbine combustion for large scale power generation in these energy intensive industries.

To utilize ammonia/methane effectively in a gas turbine, it is essential to understand better the reaction mechanism using detailed chemical kinetic models. In addition, computational fluid dynamics (CFD) simulations can serve as a powerful tool for analysing and designing ammonia combustion systems. Developing a CFD-based methodology alongside a detailed ammonia mechanism can help to capture more accurate information for the prediction of NO_x emissions, turbulent reacting flows, combustion dynamics, ignition delays, etc. Previous studies [12–15] have concentrated on developing detailed chemical mechanisms of ammonia combustion. However, the challenging conditions in gas turbine combustors such as high inlet temperature, high pressure, recirculation flow fields require a more specific study on the chemical progression of ammonia/methane species, which is still immature in the development of large scale industrial systems.

Thus, there is a need to compare the performance of different detailed ammonia combustion mechanisms in order to define the most suitable at present, simultaneously identifying its weaknesses for further research. This can be resolved using numerical models to distinguish which one is capable of providing a better correlation to ammonia combustion kinetics under conditions of a typical gas turbine combustor. Without any previous study on the field, it is clear that there is a great opportunity in the area to develop new mechanisms, CFD simulations, experimental setups and industrial designs.

The aim of this study is mainly to compare the performance of different detailed ammonia (NH_3) combustion mechanisms and distinguish which is most capable of representing ammonia/methane combustion kinetics under conditions of a typical gas turbine combustor. As a convenient way of evaluating the accuracy of detailed kinetic mechanisms, the ignition delay time of ammonia diluted with argon was calculated firstly for a wide range of temperatures and pressures. NO_x emissions were also predicted for validation against experiment data obtained through experiments using a gas turbine swirl burner. A 1D simulation was conducted for NO_x emissions calculation using a Chemical Reactor Network (CRN) model. Thus, influence of the boundary conditions towards NO_x formation were also analysed using the most suitable mechanism.

1.1. Reaction mechanisms for ammonia combustion

A considerable number of studies on detailed mechanisms for ammonia oxidation have been conducted previously. Tian et al. [16] developed a 703 steps mechanism for CH_4/NH_3 premixed combustion at low pressure. The influence of NH_3/CH_4 mole ratio on flame structure was identified by using molecular-beam mass spectrometry (MBMS) and tunable synchrotron VUV photoionization. The model was validated recently against the experimental data of laminar burning velocity at various pressures [17]. Teresa et al. [18] studied the oxidation of NH_3 during oxy-fuel combustion of methane. A detailed chemical kinetic model is developed based on experimental data covering equivalence ratios ranging from fuel-rich to fuel-lean conditions at temperature ranges of 973–1773 K, involving 97species and 779 reactions.

Another mechanism – which has over 85 species and 1200 reactions – was developed for small hydrocarbons flames by Konnov [19]. This mechanism provides full implementation of kinetic data for NO formation. This mechanism has been validated by many combustion studies including flame speed [13] and NO formation [20]. The Åbo Akademi (ÅA) scheme [21] is a gas-phase detailed chemical kinetic model that involves 60 species in 371 elementary gas-phase reactions. This mechanism was created for the simulation of biomass derivative gases combustion at moderate temperature. Since it takes into account the oxidation of light hydrocarbons, ammonia as well as the interactions between hydrocarbon and nitrogen-containing species, this mechanism is suitable for this study. The mechanism has been validated against various studies on flame speed, NO_x concentration, etc. over a wide range of temperatures and equivalence ratio [22]. The Gas Research Institution released its most updated version of the GRI 3.0 mechanism for methane combustion in 2005 [23], which contains 53 species and 325 chemical reactions. This mechanism has already been validated for ammonia-doped methane combustion [22]. GRI 3.0 has also been widely used for predicting nitrogen-oxide pollutants since it includes detailed kinetic mechanisms for NO_x formation through CH_4 combustion [24,25].

In addition, there are a large number of studies concerning mechanisms for ammonia combustion. Skreiberg [26] established a detailed mechanism for ammonia oxidation in flames under fuel-rich conditions and moderate temperatures. Since ammonia chemical reactions are studied in the presence of CH_4, H_2 and CO, it is recommended for modelling NO_x emissions of biomass combustion. Olivier [14] studied ammonia combustion kinetic mechanisms under high temperatures (1560–2455 K) and high pressure conditions for comparison with ignition delay time data. Glarborg et al. [24] created a detailed chemical kinetic model in which interactions between hydrocarbons and nitrogenous species are well established. A modified model of the Dagaut mechanism has also been proposed in which significant improvements are achieved in modelling NO_x/N_2O data [14]. Li et al. [27] studied methane and air flames doped with ammonia to analyse the formation of NO_x from fuel-N. This study also validated the capability of Konnov and Skreiberg mechanisms in predicting ammonia conversion. Kumar et al. [13] studied ammonia/hydrogen combustion and laminar flame speed by comparing the performance of GRI-Mech3.0, Tian and Konnov detailed mechanisms. The study shows Tian and Konnov mechanisms are perform best inpredicting