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Numerical study of combustion characteristics of ammonia as a renewable fuel and establishment of reduced reaction mechanisms

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HIGHLIGHTS

- Ammonia is a promising fuel with available production and distribution infrastructure.
- A numerical study of combustion characteristics of ammonia as a renewable fuel.
- Two reduced mechanisms are proposed for ammonia combustion.
- The mechanisms are able to predict laminar flame speed and NO_x emission level.
- High prediction accuracy and performance efficiency is achieved.

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ABSTRACT

With its high hydrogen density and already existing infrastructure, ammonia (NH_3) is believed to be an excellent green fuel that can be used in energy generation and transportation systems. Combustion of ammonia has certain challenges (associated with its low flame speed and fuel bond NO_x emissions) that need to be addressed before its widespread use in practical systems. The primary objective of this study is to develop a reduced reaction mechanism for the combustion of ammonia which can be used to expedite the design of effective ammonia combustors through numerical simulations of realistic combustor geometries with accurate kinetics models. First we have investigated the combustion characteristics of NH_3/H_2/air mixtures at elevated pressure and lean conditions which are encountered in practical systems such as gas turbine combustors. Laminar premixed freely propagating flame model is used to calculate the combustion properties. The results of sensitivity study of total NO_x formation with respect to the equivalence ratio indicates the possibility of localized rich combustion as an effective way to reduce the NO_x concentration down to levels that are the same order as the modern gas turbine engines. In the second part of the study, by considering a wide range of conditions in terms of pressure, fuel mixture, and equivalence ratio we have developed two reduced mechanisms based on the Konnov mechanism. The reduced mechanisms are capable of predicting the total NO_x emission level and the laminar flame speed at an acceptable accuracy over a wide range of conditions. Evaluating the performance of the reduced mechanisms with respect to the full mechanism and experimental data shows that the mechanisms are able to predict the combustion properties almost at the same accuracy level as the Konnov mechanism, but at a nearly five times less CPU time expense.

1. Introduction

The extensive use of fossil fuels and resulting CO_2 emissions has caused harmful problems to the environment and human welfare. As the problems has become noticeably upsetting, the search for alternative fuels has gained critical global concern. To reduce the environmental impact of industrial activities, some sustainable and renewable fuels have been proposed by scientists. Some of the major parameters noted in studies are economic viability, energy efficiency, and the environmental impact of alternatives. Liquefied petroleum gas, natural compressed gas, oxygenated fuels, biodiesel, and hydrogen are some of the fuels that have been studied extensively. Even though hydrogen has been recognized as a promising fuel, the realization of a global hydrogen-based

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Nomenclature

a_{stoi}	moles of air for stoichiometry
ICE	internal combustion engine
CR	compression ratio
b, c	coefficients of products in NH_3/H_2/Air chemical reaction
x, y	coefficient of reactants in NH_3/H_2/Air chemical reaction
k	rate constant of chemical reaction
E_a	activation energy (cal/mole)
LHV_{fuel}	lower heating value of fuel (kJ/kg)
NH_i	nitrogenous radicals, mainly NH and NH_2
OX	oxygenated species
X_i	mole fraction of ith species in the fuel mixture
dn/dt	mole conversion rate (mole/s)
SI	spark ignition
STP	standard temperature and pressure
T	flame temperature (K)
ϕ	fuel–air equivalence ratio

economy is a not a feasible approach until a safe and practical storage method could be found [1].

Carbon free ammonia (NH_3) is a promising green energy carrier/storage medium due to its high hydrogen density, which is better than liquid hydrogen. As a matter of fact, 108 kg H_2 is stored in 1 m^3 of liquid ammonia at 20 °C and 8.6 bars. The hydrogen density of NH_3 is 4 times higher than the demonstrated density in the most advanced methods involving metal hydrides [2]. Furthermore ammonia's cost per volume of stored energy is about three times less expensive than that of hydrogen. Ammonia is easier to produce, handle, store, and distribute with the existent infrastructure and is believed to have a promising commercial viability. Presently, ammonia is a strategically important chemical, which is widely used as a fertilizer or as a feedstock for most other synthetic fertilizers. Despite its toxicity, ammonia presents a significantly lower fire hazard compared to hydrogen and gasoline. High ignition temperature of ammonia makes it a relatively safe chemical in transportation and distribution, while hydrogen systems are prone to explosions due to its wide explosion limits and very low minimum ignition energy [3].

Ammonia has found some limited use in the past as fuel for internal combustion engines, rocket engines and fuel cells [4]. Due to its noticeably low flame speed, ammonia cannot be used directly in regular ICEs [5]. A way to make ammonia a practical fuel in regular ICEs is to partially decompose it to hydrogen and nitrogen. The improvement in combustibility of partially cracked ammonia is directly related to the presence of hydrogen in the fuel mixture, which boosts the combustion process. Westlye et al. [6] conducted experiments on NH_3/H_2 mixtures in SI engines in order to quantify the emissions. Another practical way to make ammonia operable in ICEs is to mix it with a vigorous fuel which acts as combustion promoter. Gross and Kong [7] combusted ammonia-dimethyl ether mixtures in a compression-ignition engine and Reiter and Kong [8] studied the combustion and emission characteristics of ammonia-diesel mixtures in the same type of engine. Additionally, ammonia has proven to be a satisfactory substitute for hydrocarbon fuels in gas turbine engines. Past experience with ammonia fueled gas turbines by Solar Company [9] and UC Berkeley [10] in the 60's showed that efficiencies were high with the ammonia combustors.

As a clean fuel that can be used in various power generating systems, ammonia combustion has attracted many experimental studies especially in the last decade. Parallel to experimental investigations, a number of numerical studies have been dedicated to predict the ammonia combustion process. The structure of ammonia–air flames and partially cracked ammonia-air flames has also been the subject of several studies in the past [11–13].

Due to the lack of carbon in the chemistry, nitrogen oxides are the only pollutants of ammonia combustion. Therefore, one of the main goals in most of the past studies has been to minimize the concentration of nitrogen oxides in ammonia combustion. Generally the main contributor of NO_x formation in ammonia flames is fuel-bound nitrogen rather than the thermal NO_x production by atmospheric nitrogen [14]. Therefore, a comprehensive understanding of NH_3 combustion chemistry and detailed analysis of NO_x formation pathways is required for accurate prediction of emissions due to fuel-bound nitrogen.

Several chemical kinetics models have been developed and implemented to analyze the ammonia oxidation and NO_x formation reactions. The Bian et al. [11] model is specific to ammonia oxidation and has been tested on H_2/O_2/Ar flames seeded with ammonia and nitrogen monoxide (NO) and for ammonia flames burning in oxygen or in nitrogen monoxide. The Lindstedt et al. [17] model is also specific to ammonia combustion and has been tested for the oxidation of ammonia in flat laminar premixed flames of $H_2/NH_3/O_2$, $NH_3/NO/H_2/O_2$ and NH_3/O_2. Konnov [19] has developed mechanisms for simulating hydrocarbon/NH_3 and H_2/NH_3 oxidation reactions. The well-known Gas Research Institute (GRI) [18] model is used to simulate natural gas flames burning in oxygen or air but it also takes into account nitrogenous species like ammonia, radical amidogen, and nitrogen monoxide. There are many other mechanisms in the literature which are not discussed here for the sake of brevity.

In certain studies, comparison of results obtained by the reaction mechanisms and experimental data was performed to establish the accuracy of the mechanisms [12,13]. The ability of each mechanism to predict the combustion process varied as function of fuel mixture, stoichiometry, and combustion conditions. Obtaining a reaction mechanism valid over a wide range of conditions is an important factor in obtaining reliable numerical simulation results.

In order to simulate a practical combustion system in reasonable CPU time, reduced reaction mechanisms need to be used. In other words, reduced mechanisms are significant, since they make it possible to apply accurate chemical kinetics to commercial or research computational fluid dynamics (CFD) codes for combustion modeling within a reasonable simulation time for solving real life engineering problems. The main concern is to maintain the accuracy of reaction mechanism in an acceptable range to avoid inaccurate and possibly misleading results. In the open literature, there exists one reduced mechanism proposed for ammonia combustion which was established by Duynslaegher et al. [12]. The reduced mechanism which was established by Duynslaegher et al. is unable to produce reliable predictions for flame speed and NO_x emission especially for cases of very lean or very rich conditions.

In the first part of this study, we aim to theoretically investigate the combustion characteristics of NH_3/H_2/air mixtures at elevated pressures and under lean premixed conditions, which are commonly encountered in gas turbine combustors. The conditions are similar to the study by Strohle et al. [21], which focused on hydrogen combustion under gas turbine combustor conditions. For simulating the combustion characteristics, we use a recently