Development of reduced chemical kinetic mechanism for combustion of ammonia-hydrogen blends

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Abstract
To achieve a reduced kinetic mechanism for comprehensive prediction of ammonia-hydrogen mixture combustion, a detailed kinetic mechanism with 32 species and 213 reactions was used. Directed relation graph with error propagation (DRGEP) as a primary reduction method, reaction path analysis and rate of production analysis were utilized as further refining approaches to simplify the mechanism. The reduction conditions covers; $\varphi = 0.5–2.0$, temperature of 600–1500 K, and pressure 1–10 bar. The final reduced mechanism consisting 18 species and 28 reactions has been used to predict main combustion parameters, such as laminar flame speed (SL), Ignition delay times (IDT) and NOx profiles. The results were compared with available experimental data and simulation results from the detailed mechanism. From the results, it is evident that the reduced mechanism captured the investigated parameters trend fairly well and are in good agreement with the experimental data and simulation results from the detailed mechanism, confirming its accuracy to represent combustion chemistry of the blend under the investigated conditions.

Introduction
Ammonia (NH_3) and hydrogen (H_2), as carbon-free energy sources, hold great promise in addressing concerns related to global warming. However, both have individual drawbacks that present challenges to their sole widespread adoption. Ammonia's low reactivity results in several limitations, including a low laminar flame speed, high auto-ignition temperature, narrow flammability limit and significant toxicity [1], which hinder its practical applications. Similarly, hydrogen's high reactivity lead to flashback, especially in lean premixed combustion scenarios [2]. These challenges underscore the importance of innovative approaches to effectively harness their benefits while addressing their inherent limitations. In this regard, blending NH_3 and H_2, presents a promising solution to address their individual limitations, notably enhancing reactivity while mitigating flashback issues [1]. Yet, understanding their combustion behavior in practical applications requires computationally affordable kinetic models. While utilizing detailed chemistry for high-fidelity simulation offers precision, it comes with significant computational costs and challenges. Thus, there is a critical need to develop reduced and computationally affordable kinetic mechanism. To this aim, Nozari et al.[3] developed reduced mechanism for NH_3-H_2 combustion by modifying the Konnov

mechanism [4], focusing on SL and NOx generation. But, the model overlooked IDT and ignored trace species. Otomo et al. [5] proposed the UT-LCS mechanism offering better predictions for SL, IDT and NOx emissions. Shrestha et al. [6] further improved to better predict SL. Despite significant efforts, most mechanisms remain in the range of 200–300 reactions and 30–50 species, which are still computationally heavy. In this regard, this study is aimed to develop a more simplified and computationally affordable mechanism for NH_3-H_2 blends.

Mechanism Reduction

A graph-based skeletal mechanism approach, employing DRGEP [7] was used to reduce the mechanism. DRGEP builds species dependency paths based on reactants and key products information, removing less critical species and reactions [7]. Mechanism reduction was performed in Cantera with python-based Automatic Mechanism Reduction (pyMARS) program [8]. Cantera, is an open-source software that allows simulations involving chemical kinetics [9] and pyMARS is specific program in Cantera built for mechanism reduction [8]. Detailed mechanism with 32 species and 213 reactions [10] was used as starting mechanism.

DRGEP simulation: The detailed mechanism undergoes a preliminary reduction process using DRGEP method at the following conditions; 600−1500 K, 1–10 bar, φ=0.5−2.0 and cutoff threshold 0.01. Key intermediate species; NH_2, NH, HNO, and NNH were defined as key target components, along with fuels, oxidizer and combustion products. After DRGEP calculations based on the specified conditions, a semi-detailed mechanism with 28 species and 171 reactions was obtained.

Reaction Path Analysis (RPA) and Rate of Production (ROP) Analysis: To further simplify the semi-detailed mechanism, RPA and ROP analysis were performed at; 300–1500 K, 1−10 bar, φ=0.5−2 and 25−75% H_2. Through this, key species from combustion of NH_3-H_2 mixtures were identified and retained in the mechanism, resulting in reduced mechanism consisting 18 species and 28 reactions.

Mechanism Validation

Laminar Flame Speed and Ignition Delay Times

In this section, the reduced mechanism is validated by computing SL and IDT. All simulations were performed using the open-source Cantera suite [9], with appropriate reactor modules to mimic real-world combustion conditions. An adaptive grid was determined based on criteria such as the maximum acceptable ratio among adjacent solutions (ratio=3), maximum first derivative for adjacent solutions (slope=0.06), and maximum acceptable second derivative for adjacent solutions (curve=0.12) [11]. SL was estimated assuming a 1D laminar flame model whereas IDT was simulated assuming 0D reactor model. The validation covers; 298–1500 K, 1–10 bar, φ=0.4–2 and H_2 fraction of 40–75%. Results were validated against experimental data from relevant literatures where available and simulation results from the detailed mechanism.

NOx emission profile

In this section, the reduced mechanism has been used to investigate the NOx emission trend from the combustion of a perfectly premixed mixture of 25% NH_3 – 75% vol. H_2 at constant equivalence ratio (φ) of 0.29, temperature of 498 K and pressures of 1.1, 1.5 and 2 bar. A chemical reactor network (CRN) comprising perfectly stirred reactor (PSR) and plug flow reactor (PFR) models were used for the investigation. Simulations were conducted in Cantera software.

Results and discussion

Laminar flame speed: Figures 1–3, depicted the SL results from both mechanisms compared with experimental data from the literatures. From the results, it is evident that the reduced mechanism effectively captured the SL trend under the specified conditions. The close agreement between the two mechanisms and the experimental data demonstrates the capability of the reduced chemistry to represent the combustion behavior of the NH_3-H_2 mixtures.

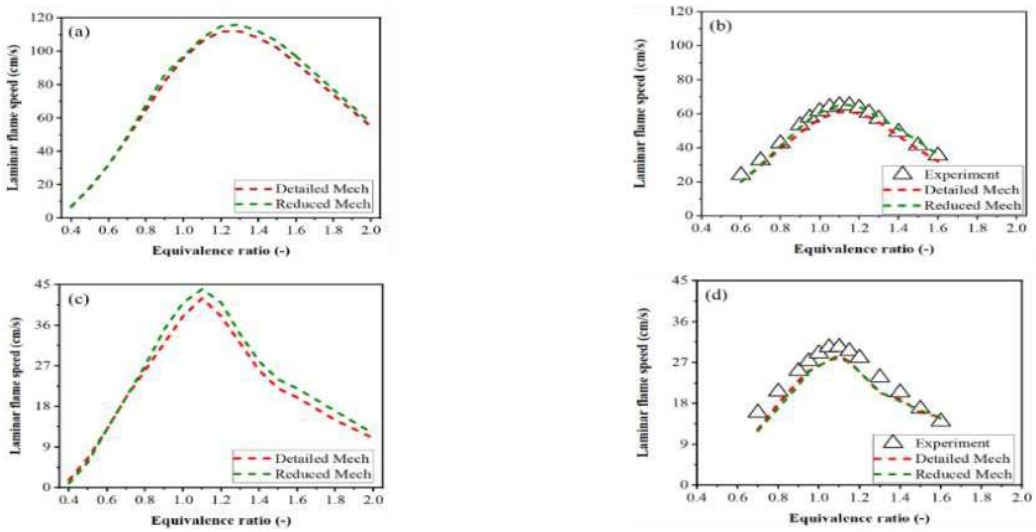

Figure 1. SL for NH_3–H_2 blends at 298 K and 1 bar; a) 25/75%, b) 40/60%, c) 50/50%, d) 60/40%. Symbols; experimental data [12, 13], lines; simulation results.

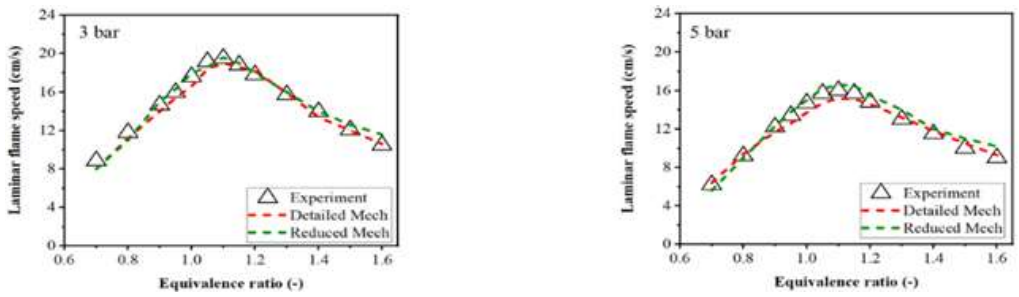

Figure 2. SL for 60%NH_3 + 40%H_2 at 298 K, 3–5 bar; a) 3 bar, b) 5 bar. Symbols; experimental data [12, 13], lines; simulation results.

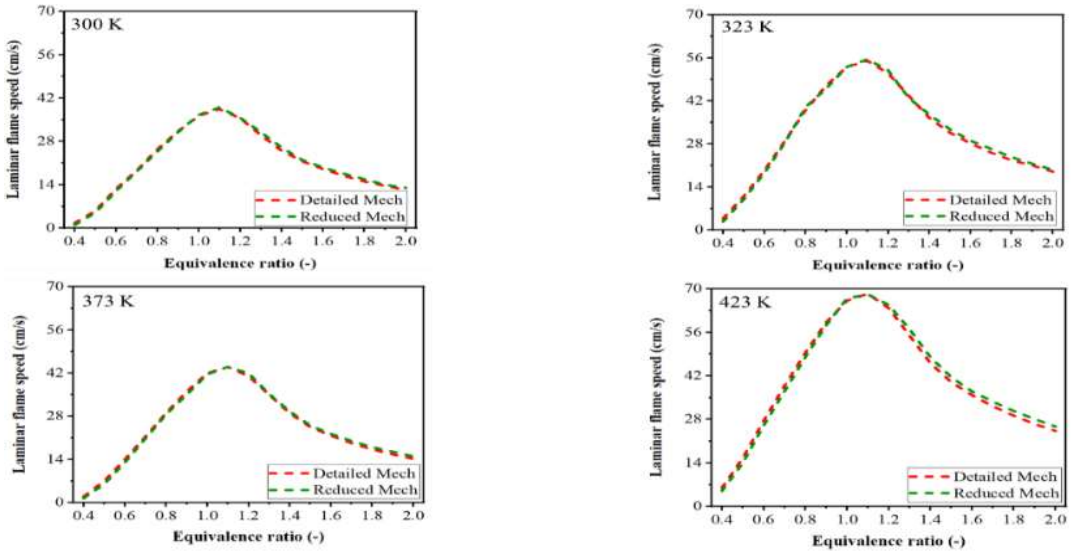

Figure 3. SL for 50%NH_3+50%H_2, 1bar, 300–423 K. Lines; simulation results.

Ignition Delay Times: Figure 4, depicted the IDT results obtained using the reduced and detailed mechanisms. The results reveal good agreement between the two mechanisms, confirming the capability of the reduced mechanism to capture the IDT trend under the studied conditions.

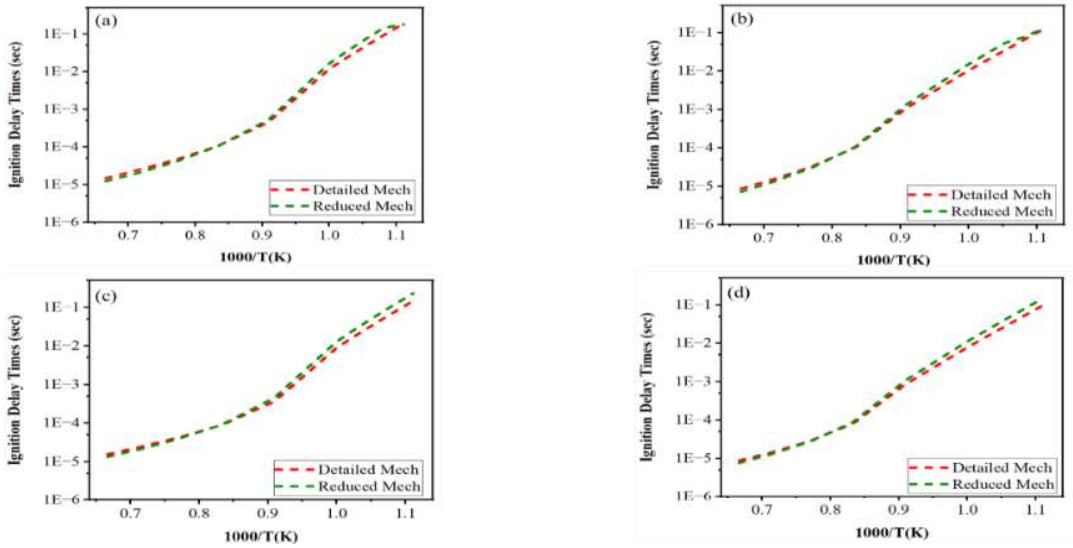

Figure 4. IDT data for 50%NH_3+50%H_2 at 850–1500 K, 5– 10 bar, φ=0.5–1.0; a) φ = 0.5, 5 bar, b) φ = 0.5, 10 bar, c) φ = 1.0, 5 bar, d) φ = 1.0, 10 bar

NOx Emissions: Figure 5 shows the fraction of NOx emission results obtained from the reduced mechanism compared against experimental campaign from Mozzatta et al. [14]. Despite few discrepancies, the reduced mechanism fairly captured the experimental trend. Increasing pressure led to decreased NOx due to improved combustion conditions (i.e., complete combustion) inhibiting NOx formation.

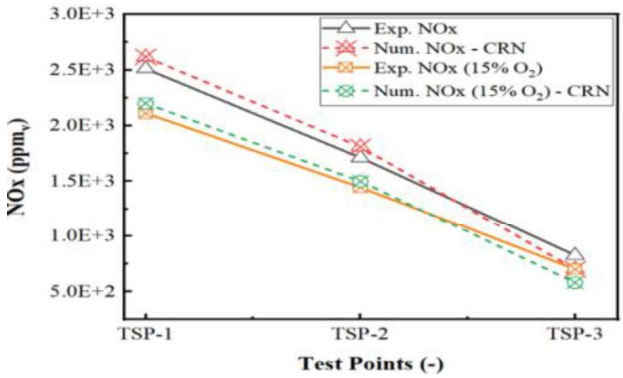

Figure 5. NOx emission results. Solid lines; experimental data [14], broken lines; simulation results for TSP-1 (1.1 bar), TSP-2 (1.5 bar), and TSP-3 (2 bar).

The pressure dependency of the NOx fraction can be attributed to the varying consumption pathways of NO over the different pressures, as illustrated in Figure 6. From the pathways, it is evident that R_1 and R_2 reactions are the primary contributors to NO consumption, with their impact becoming more pronounced at 2 bar. In the same way, R_3–R_5 have slight or no effect across the different pressures.

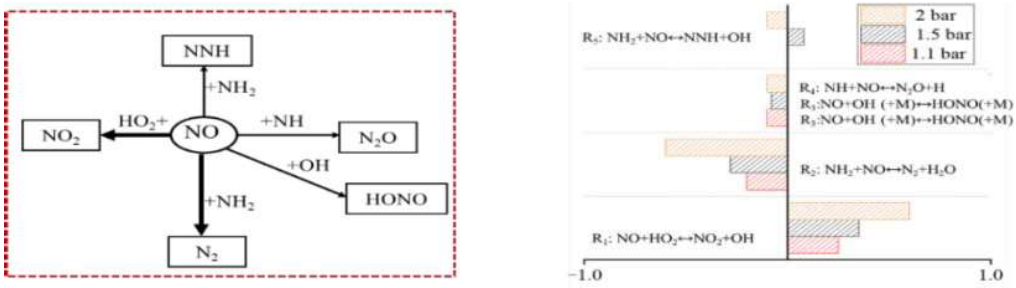

Figure 6. Main NOx consumption pathways at 498 K, φ=0.29, 1.1–2 bar

Conclusion

The detailed mechanism with 32 species and 213 reactions was simplified to 18 species and 28 reactions using the DRGEP method. The reduced mechanism was validated for key combustion parameters over ranges of reaction conditions, showing reliability and accuracy for studying NH_3-H_2 combustion properties.

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