NUMERICAL INVESTIGATION OF MILD COMBUSTION IN NH_3/H_2 MIXTURES USING A PERFECTLY STIRRED REACTOR

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Abstract

This numerical study examines the potential of Moderate or Intense Low Oxygen Dilution (MILD) combustion for ammonia (NH_3) and ammonia/hydrogen (NH_3/H_2) blends, utilizing the Perfectly Stirred Reactor (PSR) model implemented in CHEMKIN-Pro. The investigation aims to facilitate the transition to the MILD combustion regime by attaining the critical oxygen concentration (X^*_{O2}) at the minimum achievable inlet temperature. Results show that adding moderate H_2 significantly reduces self-ignition (T_{si}) and extinction (T_{ex}) temperatures, highlighting hydrogen's role in enabling ignition and stable combustion. The result also shows that as a concentration of H_2 increases, MILD combustion occurs at low inlet temperatures and reduced NR and USC, promoting earlier ignition, and stable combustion, while the decrease in X^*_{O2} indicates that more dilution is required to achieve the MILD regime.

Introduction

Ammonia has emerged as a promising zero-carbon fuel and hydrogen carrier, offering a viable route to global carbon neutrality by replacing fossil fuels. Its complete combustion emits only nitrogen and water vapor, resulting in zero carbon emissions, and its safe and cost-effective storage capabilities make it an appealing energy source [1]. However, some challenges prevent widespread adoption, including poor ignition, low burning velocity, limited flammability, unstable flame propagation, and excessive NOx emissions. To address these challenges, researchers have investigated mixing NH_3 with H_2 or hydrocarbons to improve combustion performance and reduce NO_x emissions. Although these techniques might significantly improve NH_3 combustion stability, they will raise the combustion temperature and worsen the NOx-related issue. Therefore, more work is needed to get over these challenges in order to burn NH_3 effectively. Conventional flame stabilization methods struggle to achieve both high combustion stability and low NO_x emissions, prompting the exploration of advanced combustion techniques such as MILD. MILD combustion is ideally suited for NH_3 and its mixes because it naturally promotes fuel flexibility, sustainability, and low emissions. To this end, NH_3 and NH_3/H_2/air mixture were numerically examined under highly diluted and preheated conditions utilizing the PSR model to thoroughly explore their potential for MILD combustion characteristics.

Numerical Methodology

This study presents a numerical investigation of NH_3/H_2/air combustion using a Perfectly Stirred Reactor (PSR) model in CHEMKIN-Pro. The simulations were at a pressure of 1 atm, an equivalence ratio (Φ) of 1, and a residence time (τ) of 1 s to ensure complete fuel oxidation. Szanthoffer et al. [2] compared NH_3/H_2 mechanisms and found that the Zhang 2021 [3] mechanism performed well with flow reactor data, which closely matches our PSR approach. Thus, the Zhang 2021 mechanism was chosen for the present simulations.

Result and discussion

To characterize combustion regimes for NH_3/H_2 mixtures across a wide range of H_2 from 0 to 100% and X_{O2} from 1 to 35%, PSR simulations were conducted, generating maps in T_{in} - X_{O2} plots. This analysis involved examining S-curves in a T_{in} - T_{PSR} plot, as demonstrated in Fig. 1, for various hydrogen blends at constant X_{O2}. The results demonstrate that the addition of H_2, ranging from 0 to 100%, to the NH_3/air mixture has a significant effect on both the T_{si} and T_{ex}. As the hydrogen concentration increases, both T_{si} and T_{ex} decrease, emphasizing the crucial role hydrogen plays in lowering the temperatures needed for ignition and maintaining stable combustion. Furthermore, ΔT increases with the addition of H_2, primarily due to the elevated combustion temperatures associated with hydrogen-enriched conditions. These findings indicate that hydrogen affects not only T_{si}, T_{ex}, and ΔT, but also modifies boundary conditions, such as X_{O2} and T_{in}, which are essential for achieving MILD combustion.

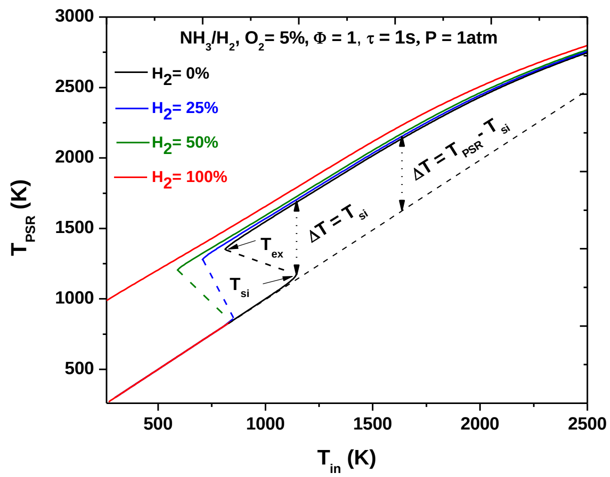

Figure 1. S-curve for a mixture of NH_3/H_2 and diluted air (5% O_2 + 95% N_2).

To identify the MILD combustion regime specifically, the characteristic temperatures T_{in}, T_{si}, and ΔT were evaluated based on the criteria [4] outlined below:

• Unconditional MILD combustion	UMC	$T_{in}>T_{si}$ and $\Delta T<T_{si}$ and $X_{O2}<X^*_{O2}$
• Conditional MILD combustion	CMC	$T_{in}>T_{si}$ and $\Delta T<T_{si}$ and $X_{O2}> X^*_{O2}$
• High-temperature combustion	HTC	$T_{in}>T_{si}$ and $\Delta T>T_{si}$
• Feedback combustion	FC	$T_{in}<T_{si}$ and $\Delta T>T_{si}$
• Unsteady combustion	USC	$T_{ex}<T_{in}<T_{si}$ and $\Delta T<T_{si}$
• No reaction	NR	$T_{in}<T_{ex}$

Each combustion regime is distinctly mapped in Figure 2 through T_{in} - X_{O2} plots for varying hydrogen concentrations. For pure NH_3, the self-ignition occurs at 1088 K with X^*_{O2}= 12.32%, resulting in a MILD regime bounded by extensive NR and USC regimes. The addition of H_2 leads to a significant reduction in both the T_{si} and the X^*_{O2}, lowering them to 855 K and 7.89% for 25% of H_2, 822 K and 7.16% for 50% of H_2. This reduction in T_{si} and the X^*_{O2} demonstrates that the addition of moderate H_2 significantly suppresses NR and USC regions and shifts both UMC and CMC MILD combustion regimes toward lower temperatures and oxygen levels. Conversely, the increase in H_2 content increases the HTC regime because the temperature rise (ΔT) surpasses the MILD threshold. A further increase in H_2 content up to 100% continues to reduce the X^*_{O2} from 7.16% at 50% H_2 content to 6.45% at 100% hydrogen content, while having a relatively minor effect on the T_{si}. As a result, achieving and maintaining MILD combustion at higher H_2 levels requires greater oxygen dilution.

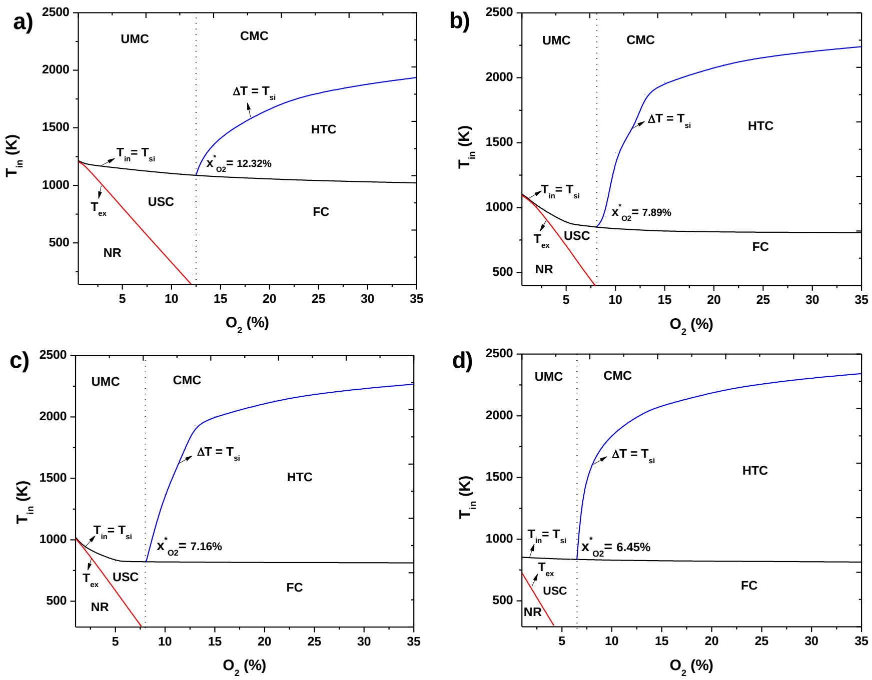

Figure 2. T_{in} - X_{O2} regime maps for an NH_3/H_2/air mixture at $\Phi = 1$, $\tau = 1$ s, and a pressure of 1 atm. (a) $H_2 = 0\%$, (b) $H_2 = 25\%$, (c) $H_2 = 50\%$, and (d) $H_2 = 100\%$.

Conclusion

This numerical study examines the potential of MILD combustion for NH_3 and NH_3/H_2 blends, utilizing the PSR model implemented in CHEMKIN-Pro. The results demonstrate that moderate hydrogen enrichment significantly influences the combustion regime, reducing both the T_{si} and T_{ex} required for MILD combustion. For pure NH_3, MILD combustion is achieved at T_{si} = 1088 K with X^*_{O2} = 12.32%. However, the addition of H_2 substantially lowers these thresholds with 25% H_2, T_{si} decreases to 855 K and X^*_{O2} drops to 7.89%, while at 50% H_2, they further reduce to 822 K and 7.16%, respectively. As H_2 content increases, MILD combustion occurs at low inlet temperatures and reduced NR and USC, promoting earlier ignition, and stable combustion, while the decrease in X^*_{O2} indicates that more dilution is required to achieve the MILD regime.

Acknowledgment

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References

[1] Shah Z.A., Mehdi G., Congedo P.M., Mazzeo D., De Giorgi M.G, "A review of recent studies and emerging trends in plasma-assisted combustion of ammonia as an effective hydrogen carrier", *Int J Hydrogen Energy*,51: 354-374 (2024).

[2] Jakub Tumidajski, Wojciech Adamczyk, Agnieszka Ciesielska, Sławomir Sładek, Andrzej Szlęk, Adam Klimanek, "Recognition of MILD combustion regimes of hydrogen oxy-combustion diluted with steam", *Fuel* 394: 135050 (2025).

[3] Zhang Xiaoyuan, Shamjad P. Moosakutty, Rajitha P. Rajan, Mourad Younes, S. Mani Sarathy. "Combustion chemistry of ammonia/hydrogen mixtures: Jet-stirred reactor measurements and comprehensive kinetic modeling", *Combustion and* Flame 234:111653 (2021).

[4] Luan C., Xu S., Shi B., Tu Y., Liu H., Li P., Liu, Z., "Re-Recognition of the MILD Combustion Regime by Initial Conditions of Tin and XO2 for Methane in a Nonadiabatic Well-Stirred Reactor", *Energy & Fuels*, 34: 2391–2404 (2020).