LETTER

Self-promoted fuel pyrolysis under oxygen enrichment enables clean and efficient ammonia combustion

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Dear Editor,

Ammonia (NH_3) is one of the world's most important chemical products and had a global industrial production of 238 million tons in 2022.[1] It is extensively used in the production of fertilizers [2] and the synthesis of various pharmaceutical products and commercial cleaning products.[3] In recent years, ammonia has garnered significant attentions in energy sectors due to its carbon-free nature, which aligns with the growing needs for a carbon-neutral world.[4] Additionally, ammonia serves as an efficient hydrogen (H_2) carrier, boasting a 17.8% hydrogen capacity by mass, and benefits from a well-established infrastructure for its transportation and storage.[3]

Combustion is a robust energy conversion approach for chemical energy storage agents such as ammonia and hydrogen, and will play a significant role in future carbon-free energy systems, helping to balance the fluctuations of solar and wind energies.[5] However, implementing ammonia in practical combustion devices faces tremendous challenges due to its low reactivity and high pollutant emissions.[6] To enhance ammonia combustion, several fuel-modification strategies have been successfully proposed, including reactive fuel co-firing and ammonia pre-cracking.[6] Nonetheless, there is an urgent need for efforts in simultaneous pollutant control during ammonia combustion enhancement. Ammonia can easily oxidize into NOx at thousand-ppmv-level emissions, which are 1-2 orders of magnitude higher than current emission regulations. A more serious issue is the trade-off between combustion enhancement and pollutant control for conventional fuel-modification strategies.[7] Fortunately, there exists a natural NOx reduction mechanism, known as the thermal deNOx mechanism. As the equivalence ratio (ϕ) shifts from fuel-lean to fuel-rich conditions, NOx formation can be rapidly suppressed by excess ammonia, eventually removing the majority of NOx emissions under slightly fuel-rich conditions. However, under these conditions, excess ammonia may not be fully oxidized, resulting in rapidly growing NH_3 emissions as the equivalence ratio rises. Consequently, a low NOx/NH_3 emission window of equivalence ratio (Φ_{LE}) emerges, which is crucial for simultaneous pollutant control during ammonia combustion enhancement.[6]

It is important to note that previous studies on ammonia combustion have demonstrated only narrow Φ_{LE} widths at the primary combustion stage,[6] specifically 0.01-0.06 at a NOx/NH_3 emission level of 200 ppmv which is compliant with regulatory requirements considering staged combustion and post-treatment scenarios. To ensure stable gas turbine operation amidst flow rate fluctuations, reliable power plant frequency adjustments, and flexible grid-supported peak regulation,[8] it is imperative to expand this low NOx/NH_3 emission window as much as possible at the primary combustion stage. Consequently, achieving simultaneous combustion enhancement and pollutant control at this stage remains a long-standing and elusive "Holy Grail" challenge in ammonia energy conversion.

In 2019, we reported a significant enhancement in the laminar flame propagation of ammonia due to markedly elevated flame temperatures achieved through oxygen (O_2) enrichment.[9] Specifically, only doubling the oxygen content in the oxidizer (from 21%O_2 to 40%O_2) increased the laminar burning velocity of ammonia fivefold, reaching levels comparable to those of natural gas/air. This provided an alternative strategy for enhancing ammonia combustion, distinct from fuel-modification strategies. However, previous experiences in hydrocarbon combustion suggested that increased flame temperatures could significantly intensify NOx emissions, predominantly due to thermal NOx formation. This raised concerns about potential NOx emission deterioration in oxygen-enriched ammonia combustion, despite a shift in the dominant NOx formation mechanism to fuel NOx. In this work, our findings indicate that oxygen enrichment can, surprisingly, promote the overall fuel pyrolysis and facilitate the simultaneous expansion of both stable combustion and low NOx/NH_3 emission windows for ammonia in single swirl premixed flames, a common combustion regime used in the primary stage of practical combustion devices, such as gas turbines, furnaces, and boilers.

Figure 1A shows images of stable ammonia swirl flames, illustrating that both the flame shape and size undergo dramatic changes under oxygen enrichment. As the oxygen content increases, the flame retracts back toward the base plate, due to an increase in laminar burning velocity, resulting in a more compact size. At 21%O_2, both fuel-lean and fuel-rich flames experience local extinction at the flame root, a consequence of weak combustion intensity. This phenomenon is not observed in flames at 40%O_2. An increasing number of stable flame images are observed on both fuel-lean and fuel-rich sides as the oxygen content increases. Therefore, oxygen enrichment can enhance the combustion intensity and flame stability, allowing flames to stabilize at the burner exit.

The enhancement of ammonia combustion through oxygen enrichment is also evident in the recorded chemiluminescence results. Figure 1B displays the normalized integrated intensities of OH* chemiluminescence at ϕ = 1.0 and various oxygen contents, indicating the increased combustion intensity in oxygen-enriched ammonia combustion. Moreover, the particle imaging velocimetry (PIV) results (Figure 1C) reveal that the ammonia swirl flames maintain similar flow regimes while displaying increasing mean axial velocities as the oxygen content increases.

Figure 1D shows the measured lean blowout (LBO) and rich blowout (RBO) limits of ammonia swirl flames at various oxygen contents. As the oxygen content increases, the LBO limit progressively decreases, while the RBO limit significantly rises. This suggests that oxygen enrichment can substantially expand the stable combustion window of equivalence ratio (Φ_{SC}) for ammonia. The Φ_{SC} widths are 0.66 at 21%O_2 and 1.86 at 40%O_2, exhibiting nearly a threefold expansion. The findings (Figure 1A-D) can be predominantly attributed to the increased adiabatic flame temperature (T_{ad}), which shows a rise of nearly 500 K from 21%O_2 to 40%O_2 (Figure 1B).

Figure 1E shows the measured NOx and NH_3 emissions at 21%O_2 and 40%O_2. At 21%O_2, the Φ_{LE} width is approximately 0.05. The abnormally high NH_3 emissions at ϕ = 0.7 are primarily due to local extinction at the flame root, as the flame approaches the LBO limit at ϕ = 0.61. At 40%O_2, although the NOx emissions under fuel-lean conditions increase several-fold, the Φ_{LE} width is remarkably expanded to about 0.31, which is more than six times that at 21%O_2. Consequently, oxygen enrichment effectively expands both the stable combustion and low NOx/NH_3 emission windows for ammonia.

Kinetic analysis is a widely used approach for obtaining thermochemical information in swirl combustion, characterized by similar flow regimes and distinct chemistry variations.[10] Figure 1E also illustrates the simulated NOx and NH_3 emissions at 21%O_2 and 40%O_2. Similar to the measured results, a substantial expansion of Φ_{LE} under oxygen enrichment is evident, suggesting a common mechanism underlying these phenomena. Figure 1F shows the main reaction network in fuel-rich (ϕ = 1.5) ammonia flames at both 21%O_2 and 40%O_2, derived from rate of production (ROP) analysis. Consistent with our previous findings,[9] oxygen enrichment does not alter the main reaction pathways in ammonia combustion, but it does change the contribution of each pathway.

According to the ROP analysis, ammonia is primarily consumed through the H-abstraction reactions by H, OH, and O, forming the NH_2 radical. NH_2

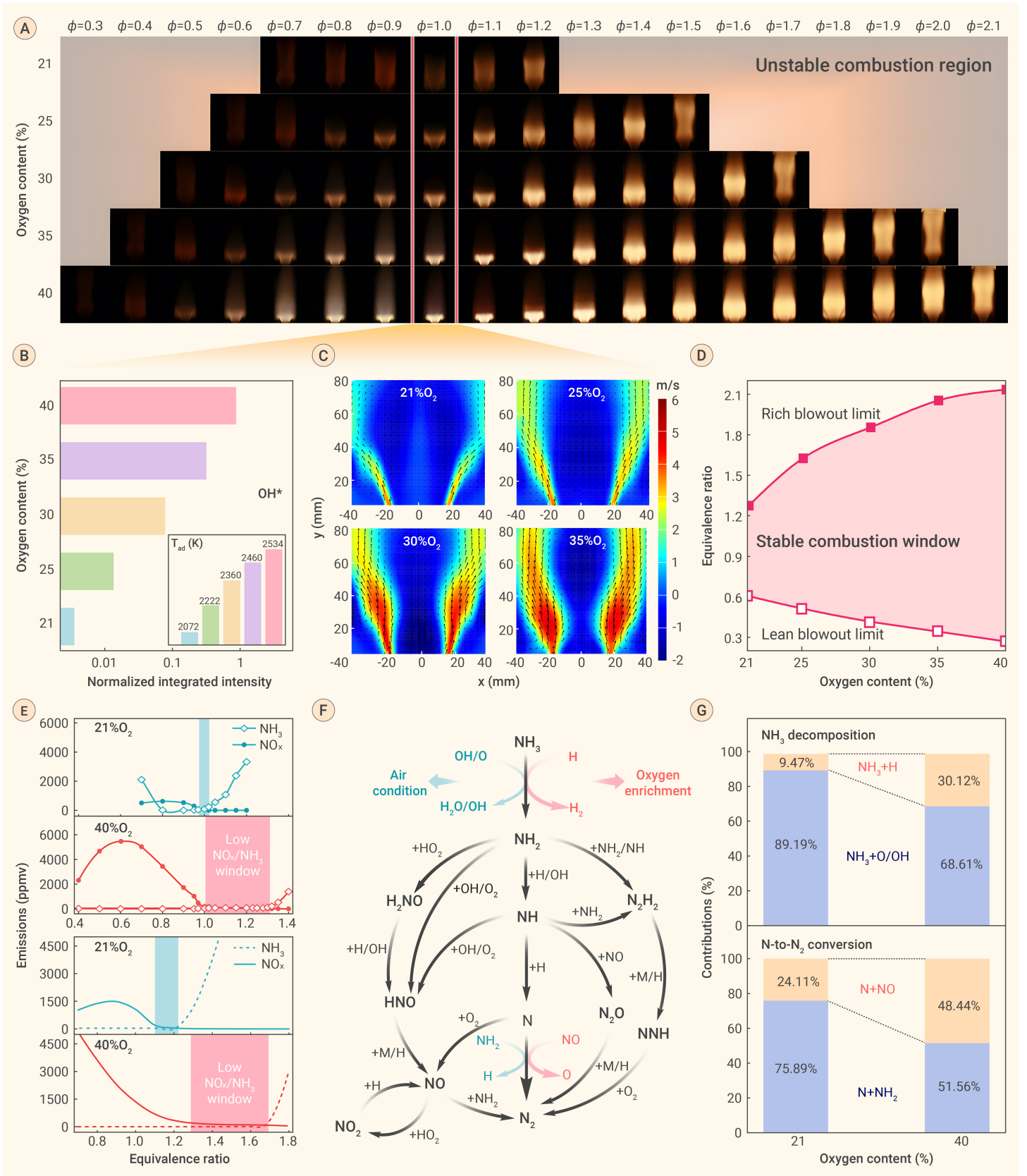

Figure 1. Experimental results and kinetic analysis of ammonia/oxygen/nitrogen flames (A) Images of stable swirl flames at various equivalence ratios and oxygen contents. (B) Normalized integrated intensities of OH* chemiluminescence and simulated T_{ad} values and (C) mean axial velocity distributions at ϕ = 1.0 and various oxygen contents. (D) Lean and rich blowout limits at various oxygen contents. (E) NOx and NH_3 emissions at 21%O_2 and 40%O_2 measured in swirl flames (top) and simulated in freely propagating flames (bottom). (F) Main reaction network in fuel-rich (ϕ = 1.5) ammonia flames at both 21%O_2 and 40%O_2. (G) Contributions of key reactions to ammonia decomposition (top) and N-to-N_2 conversion (bottom).

and its subsequent H-loss product, the NH radical, have two primary fates. First, their oxidation pathways, involving HNO which is a characteristic intermediate in fuel-NOx formation, predominantly contribute to the formation of NOx (mainly NO and NO_2). Secondly, the NH radical can further loss the rest

H atom to produce an N atom, which primarily reacts with NH_2 or NO to form nitrogen (N_2), the final product of the nitrogen element. Therefore, an overall fuel pyrolysis mechanism leading to hydrogen and nitrogen can be identified, with greater significance under fuel-rich conditions.

Figure 1G demonstrates that under oxygen enrichment, the roles of the H-abstraction by H in ammonia decomposition and the N+NO reaction in nitrogen formation become much more significant than under air condition. It is concluded that the significantly increased flame temperature promotes the overall fuel pyrolysis process, enhancing the conversion of excess ammonia to hydrogen and nitrogen under fuel-rich conditions. This self-promoted ammonia pyrolysis is further evidenced by the observed increase in hydrogen production, leading to the shift of the fuel-pyrolysis ratio in the middle of Φ_{LE} from 0.029 at 21%O_2 to 0.146 at 40%O_2. For practical staged combustion in gas turbines, boilers, and furnaces, integrating this oxygen-enriched primary combustion stage can effectively mitigate the significant NH_3-to-NO conversion penalty at the extremely fuel-lean secondary combustion stage. Moreover, the secondary stage can eliminate the residual hydrogen generated from the self-promoted ammonia pyrolysis, thereby offering a promising clean and efficient combustion technology applicable to ammonia energy conversion in practical scenarios.

In summary, we find that the self-promoted ammonia pyrolysis under oxygen enrichment enables the simultaneous pollutant control during ammonia combustion enhancement. This is evidenced by the simultaneous expansion of both the stable combustion and low NOx/NH_3 emission windows in ammonia swirl flames. As the oxygen content increases, the flames exhibit enhanced combustion intensity and flame stability, with the Φ_{SC} width dramatically expanding from 0.66 at 21%O_2 to 1.86 at 40%O_2. Oxygen enrichment also promotes the overall fuel pyrolysis into hydrogen and nitrogen, significantly expanding the Φ_{LE} width from 0.05 at 21%O_2 to 0.31 at 40%O_2. This intriguing finding highlights the potential for transitioning ammonia energy from laboratory research to practical applications. Kinetic insights into the competing chemistry and advanced computational fluid dynamics simulations will play pivotal roles in achieving a more comprehensive and thorough understanding of these processes.

In this work, experiments were conducted in a single swirl gas turbine model combustor. Ammonia, oxygen, and air were thoroughly mixed before entering the plenum. Flame images were captured using a digital camera. Emission measurements were conducted by utilizing a FT-IR gas analyzer, an oxygen analyzer, and a hydrogen analyzer. All emission results were converted to values at 15%O_2. All experiments were performed at a constant bulk velocity of 2.25 m/s, with the oxygen contents ranging from 21% to 40%, using nitrogen as the diluent gas. Stoichiometric flames were characterized using a photomultiplier tube for spatially-integrated OH* chemiluminescence. The mean axial velocity distributions were measured using a PIV system, which consists of a Nd:YAG laser generating the 532 nm laser pulses at 10 Hz with a pulse separation of 60 μs and a double-shutter CCD camera recording Mie scattering signals from the seeding particles illuminated in the flow. Kinetic analysis was carried out with the Premixed Laminar Flame Speed Calculation module of the Chemkin-Pro software. Our ammonia combustion mechanism which was validated against both ammonia/air combustion and oxygen-enriched ammonia combustion data was used in the simulation.[9]

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DECLARATION OF INTERESTS

The authors declare no competing interests.