

Understanding of MILD Combustion Characteristics of NH_3 /Air Flames in N_2 and H_2O (Steam) Diluted Environment at Atmospheric Pressure

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ABSTRACT

Ammonia is becoming increasingly popular as a carbon-neutral fuel with zero carbon dioxide emissions. However, a significant hurdle lies in its combustion, which leads to substantial emissions of NO_x . The current research involves conducting a chemical kinetic investigation to examine the characteristics of Intense Low oxygen Dilution (MILD) or Moderate combustion in ammonia (NH_3)/air flames. This study is carried out under specific conditions, such as oxygen concentrations ranging from 11 % to 23 %, premixed reactant temperatures between 1300 and 1700 K, and a pressure of one atmosphere. The study focuses on investigating the combustion characteristics of MILD using dilution with H_2O and N_2 . With the rise in the inlet temperature of the premixed reactant, the peak temperature of the flame also rises. Moreover, flames diluted with H_2O exhibit lower peak temperatures compared to flames diluted with N_2 . Flames diluted with H_2O result in lower NO_x emissions compared to flames diluted with N_2 . Additionally, for N_2 diluted flames, the exit NO_x emissions rise as the oxygen concentration increases. Despite this, NO_x emissions from H_2O diluted flames demonstrate non-monotonic behaviour. This means that the exit NO_x increases initially as the oxygen concentration reaches 21%, but then begins to decrease. In contrast to N_2 and H_2O diluted flames exhibit a wider regime of no-ignition. Moreover, the rise in peak temperature in H_2O diluted flames is less apparent than in N_2 diluted flames, corresponding to broader ranges MILD combustion ranges. Furthermore, to attain MILD combustion in H_2O diluted flames at a specific O_2 concentration, the temperature of reactant needs to be higher than that required for N_2 diluted flames.

Keywords: MILD combustion, Ammonia, NO_x , Green fuel, N_2 and H_2O dilution

1. INTRODUCTION

The world is under energy transition due to the continuous rise in global energy consumption, fossil fuel depletion, and growing concerns over environmental problems. According to studies, the combustion of fossil fuels supplies more than 80 % of world energy¹. Hence, the existing combustion systems need an extensive transformation imperative for sustainable energy supply and emissions reduction. Recently, green fuels are gaining traction in carbon-free energy supply to fulfill environmental obligations.

Ammonia, with high hydrogen content and entrenched industry, is explored substantially for carbon neutrality. Also, many studies have successfully proven the credibility of ammonia as fuel¹⁻². However, excessive NO_x emissions, slower reaction kinetics, and narrow flammability limit are the primary concern that must be resolved before ammonia combustion systems can be commercialized. The possibility of enhancing NH_3 reaction kinetics is explored using different options, such as adding fuel enhancers (methane, hydrogen, or another higher reactive fuel) to ammonia, oxygen enrichment, and partial dissociating NH_3 before combustion^{1,3-5}. However,

higher NO_x emission in ammonia combustion is still a significant challenge. The reduction of NO_x in ammonia flames has been studied using a variety of options, such as modifying the combustion geometry, porous-assisted combustion, or selective non-catalytic reduction (SNCR)⁶⁻¹¹.

For the combustion of ammonia under conventional conditions, highly swirling burners have already been identified as a means of increasing flame stability. In the swirl combustion of ammonia, flame stability appears more tractable, but NO_x formation remains one of the most significant challenges. Blending of NH_3 with CH_4 can result in higher NO emissions in the exhaust gases compared to pure ammonia flames, even if it is a small percentage (say, 10 % of the total heat input).

The NO concentration can reach up to the order of 10^3 - 10^4 in magnitude, which is much higher than the NO concentration from pure methane combustion. Another viable approach to utilize using NH_3 as an energy source involves employing the well-established principle of MILD combustion. Thus, MILD combustion can be viewed as a promising asymptotic solution. Sorrentino¹², *et al.* experimentally analyzed the trends of NO_x emission for NH_3 /air mixture in a lab-scale cyclonic burner at atmospheric pressure and different preheating temperatures. Sorrentino¹², *et al.* found that the NO_x emissions were

minimized to 100 ppm at stoichiometric conditions. However, unburnt traces of ammonia and hydrogen are observed at the burner exit under fuel-rich conditions. Through a lab-scaled burner, Shi¹³, *et al.* examined the MILD combustion properties of NH_3 /air, CH_4 /air and NH_3/CH_4 /air at various equivalence ratios, NH_3 , and CH_4 concentrations in the mixture. This study shows that the combustion of NH_3 produces much lower levels of NO_x emissions when compared to the emissions generated in NH_3/CH_4 /air combustion. In the context of a controlled MILD combustion environment, the results showed that a crucial NH_3 flow rate exists. As the ammonia mass flow rate reaches the desired value, NO_x production rise because of the increased H radical production resulting from specific reactions $NH_2 + O \rightarrow HNO + H$ and $NH_2 + NH \rightarrow N_2H_2 + H$. The increased formation of H radicals will enhance the production of OH and O radicals via mentioned reaction $H + O_2 \rightarrow OH + O$. The enhancement in oxygen radical production increases the NO_x production through the reaction $NH_2 + O \rightarrow HNO + H$. However, Honzawa¹⁴, *et al.* found that the fuel and oxidizer dilution with exhaust gas reduces the NO emissions regardless of ammonia addition percentages.

Honzawa¹⁴, *et al.* also highlight that the burner diameter and length have an essential role in the burner design, and NO emission gets reduced by increasing the distance between oxidizer & fuel nozzles and reducing the diameters of oxidizer nozzles. Studies conducted on MILD and high-temperature air combustion show that the diluted air decreases NO_x production, while high-temperature air combustion speeds up overall fuel burning rate¹³. The MILD regime consists of

two primary components: dilution and preheating, both of which reduces thermal NO_x and enhance flame stability. The unique properties of this technology enable pollution reduction while increasing combustion performance. Literature reports that MILD combustion holds potential for performance improvements in terms of flexibility and efficiency¹⁵. Numerous kinetic studies at various pressure levels have been undertaken on methane MILD combustion, ranging from atmospheric to higher pressures^{15–18}. However, a rigorous study for ammonia mild combustion has yet to be conducted due to its inherent advantages of producing low emissions. To understand the MILD combustion properties of NH_3 /air flames in a diluted atmosphere with N_2 and H_2O , the current research carries out an extensive chemical kinetic analysis. The temperature and pressure of the premixed mixture are considered as 1300–1700 K and 1 atm. The oxygen concentrations in the mixture varied from 11 to 23 %. Nitrogen and steam dilution in the mixture's ranges from 66 % – 82.4% and 0 % – 48.3%. All the simulations are performed for the combustor capacity of 5 kW.

2. METHODOLOGY

Combustion systems often entail intricate interactions between chemical processes and turbulent flow. The chemical

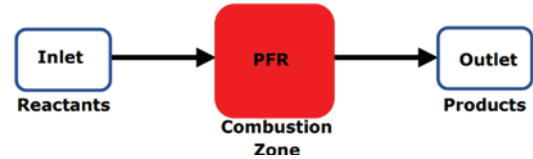


Figure 1. Schematic representation of chemical reactor network.

Table 1. Details of $NH_3/O_2/N_2$ mixtures employed in the numerical simulations

NH_3 (kg/sec)	O_2 (%)	External N_2 Dilution (kg/sec)	Mass fraction (Y)			Total mass flow rate (kg/sec)
			NH_3	O_2	N_2	
2.66E-4	11	1.76×10^{-3}	7.33×10^{-2}	1.02×10^{-1}	8.25×10^{-1}	3.63×10^{-3}
	13	1.24×10^{-3}	8.54×10^{-2}	1.19×10^{-1}	7.96×10^{-1}	3.11×10^{-3}
	15	8.58×10^{-4}	9.73×10^{-2}	1.35×10^{-1}	7.67×10^{-1}	2.73×10^{-3}
	17	5.68×10^{-4}	1.09×10^{-1}	1.51×10^{-1}	7.40×10^{-1}	2.44×10^{-3}
	19	3.39×10^{-4}	1.20×10^{-1}	1.67×10^{-1}	7.13×10^{-1}	2.21×10^{-3}
	21	1.53×10^{-4}	1.31×10^{-1}	1.82×10^{-1}	6.86×10^{-1}	2.03×10^{-3}
	23	0	1.42×10^{-1}	1.97×10^{-1}	6.61×10^{-1}	1.88×10^{-3}

Table 2. Details of $NH_3/O_2/N_2/H_2O$ mixtures employed in the numerical simulations

NH_3 (kg/sec)	O_2 (%)	External H_2O Dilution (kg/sec)	Mass fraction (Y)				Total mass flow rate (kg/sec)
			NH_3	O_2	N_2	H_2O	
2.66E-4	11	1.76×10^{-3}	7.33×10^{-2}	1.02×10^{-1}	3.41×10^{-1}	4.84×10^{-1}	3.63×10^{-3}
	13	1.24×10^{-3}	8.54×10^{-2}	1.19×10^{-1}	3.98×10^{-1}	3.98×10^{-1}	3.11×10^{-3}
	15	8.58×10^{-4}	9.73×10^{-2}	1.35×10^{-1}	4.53×10^{-1}	3.14×10^{-1}	2.73×10^{-3}
	17	5.68×10^{-4}	1.09×10^{-1}	1.51×10^{-1}	5.07×10^{-1}	2.32×10^{-1}	2.44×10^{-3}
	19	3.39×10^{-4}	1.20×10^{-1}	1.67×10^{-1}	5.60×10^{-1}	1.53×10^{-1}	2.21×10^{-3}
	21	1.53×10^{-4}	1.31×10^{-1}	1.82×10^{-1}	6.11×10^{-1}	7.56×10^{-2}	2.03×10^{-3}
	23	0	1.42×10^{-1}	1.97×10^{-1}	6.61×10^{-1}	0	1.88×10^{-3}

reactor network (CRN) is a commonly employed method for examining the combustion chemistry of real-world combustion processes. Various studies have previously considered the CRN approach for chemical kinetic modeling¹⁹⁻²². As shown in Fig.1, the CRN in this work consists of an inlet, a plug flow reactor (PFR), and an outlet. PFR reactors have been widely used to simulate combustion chemistry^{18,21-24}.

In plug flow reactors, the fluid is assumed to be perfectly mixed radially while not being mixed axially. An analysis of the laminar premixed $NH_3/O_2/N_2$ combustion under diluted and atmospheric-pressure conditions is carried out in the domain of length (L) and diameter (D) of 1.4 and 0.01 m, respectively. The dimensions of the reactor are based on the experimental study of Sabia²⁵, *et al.* Similar dimensions for plug flow domain are also considered in the work of Garnayak¹⁸, *et al.* for analyzing the MILD combustion characteristics of $CH_4/O_2/N_2$ mixture at atmospheric and higher pressures of 1 and 10 atm. In this present work, a stoichiometric ($\phi = 1$) premixed mixture of NH_3 and oxidizer (O_2 , N_2 , and H_2O) is considered, at different N_2 and H_2O addition percentages. Tables 1 and 2 show the details of mixture composition considered in the numerical simulations. The premixed temperature mixture is varied from 1100 to 1700 K. To validate the model, numerical simulations of LBV have been done using the 1-D freely propagating flame speed model included in ANSYS CHEMKIN PRO. The value for parameters such as CURV, GRAD, and the number of grids is considered as 0.03, 0.02, and 1000. In regions of high gradients, the GRAD parameter controls how many grids and points are inserted. A smaller GRAD and CURV value use more grid points. CURV specifies the number of grid points to insert in areas with high curvatures as part of the adaptive mesh. The simulations also consider the multi component transport and thermal diffusion (Soret) effect. The reaction model proposed by Singh¹, *et al.* is used in all computational simulations in this investigation and consists of 32 species and 259 reactions.

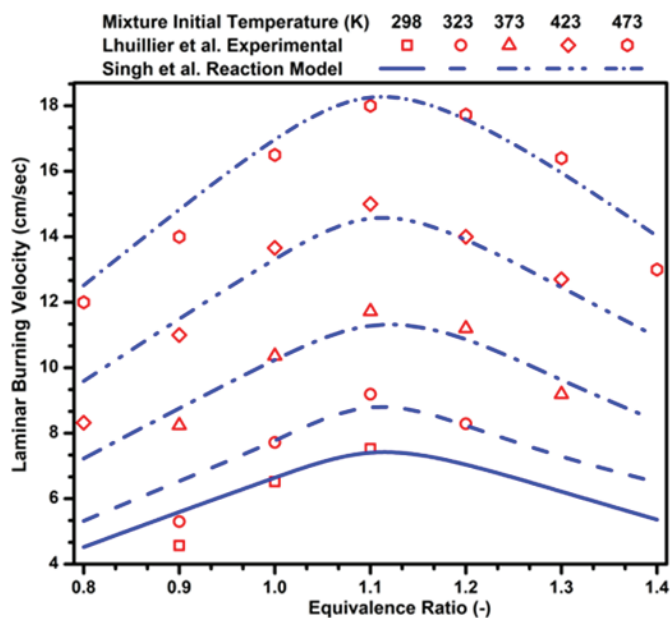


Figure 2. LBV variation of premixed NH_3/H_2 /air mixture at respective premix temperatures and pressures of 298 - 473 and 1 bar.

3. REACTION MODEL VALIDATION

The laminar burning velocity (LBV) plays a crucial role in fundamental flame characteristics, making it essential for validating chemical reaction model. To evaluate the accuracy of the ammonia reaction model used in this investigation, the LBV of a premixed NH_3 /air mixture is computed and the outcomes are compared to those obtained experimentally by Lhuillier²⁶, *et al.* Figure 2 illustrates how the LBV changes with different equivalence ratios at a pressure and mixture temperature of 1 bar and 298-473K, respectively. The findings demonstrate that rising the initial temperature of the premixed mixture enhances LBV of the NH_3 /air mixture. Furthermore, the computed results utilizing Singh¹, *et al.* reaction model closely align with the experimental trends seen by Lhuillier²⁶, *et al.*

4. RESULTS AND DISCUSSION

4.1 Variation of Axial Temperature Along the Reactor Length

Figure 3 (a-f) shows the variation in axial temperature along the reactor length of premixed $NH_3/O_2/N_2$ and $NH_3/O_2/N_2/H_2O$ mixture at different oxygen concentrations (11-23%), reactant temperatures (1300-1700 K), and reactant pressure of 1 atm. It is analyzed from Fig. 3. that the higher premixed temperature will be required to stabilize the flame inside the combustor for lower oxygen or higher nitrogen or steam concentration in the mixture. As the reactant temperature increases at a specific oxygen concentration, the mixture's peak temperature also rises. Nitrogen-diluted flames lead to higher flame temperature than steam-diluted flames. Also, the flame location in nitrogen diluted flames is observed more upstream side of the combustor than the steam diluted flames.

At a lower oxygen concentration of 11 %, a higher distance is observed between the peak temperature of nitrogen and steam diluted flames. However, once the oxygen concentrations increased from 11 to 23 %, the distance between the temperature peaks started decreasing, and flame locations started moving on the upstream side of the combustor. At 21-23 % oxygen concentration, almost similar location of temperature peaks is observed for the nitrogen and steam diluted flames. In all the cases of oxygen concentrations, no ignition is observed at the 1100 and 1300 K reactant temperatures. At a temperature of 1500 K for the reactant, no ignition is observed at a lower oxygen concentration of 11 % and 13 % for steam diluted flames. However, nitrogen diluted flames exhibit only a minor rise in temperature. The temperature of the combustion flame tends to be lowered by N_2 and steam dilution overall. Steam dilution creates a cooling effect because heat is absorbed during phase changes. Dilution of N_2 affects the flame temperature by increasing the mixture's heat capacity without contributing to combustion due to the inert nature of nitrogen.

4.2 NO_x Emissions

Figure 4 demonstrates the difference of NO , N_2O , and NO_2 mole fraction along the reactor axial length for the oxygen concentration in the mixture ranges from 11-23 %. The value of NO , N_2O , and NO_2 mole fractions are higher in N_2 diluted

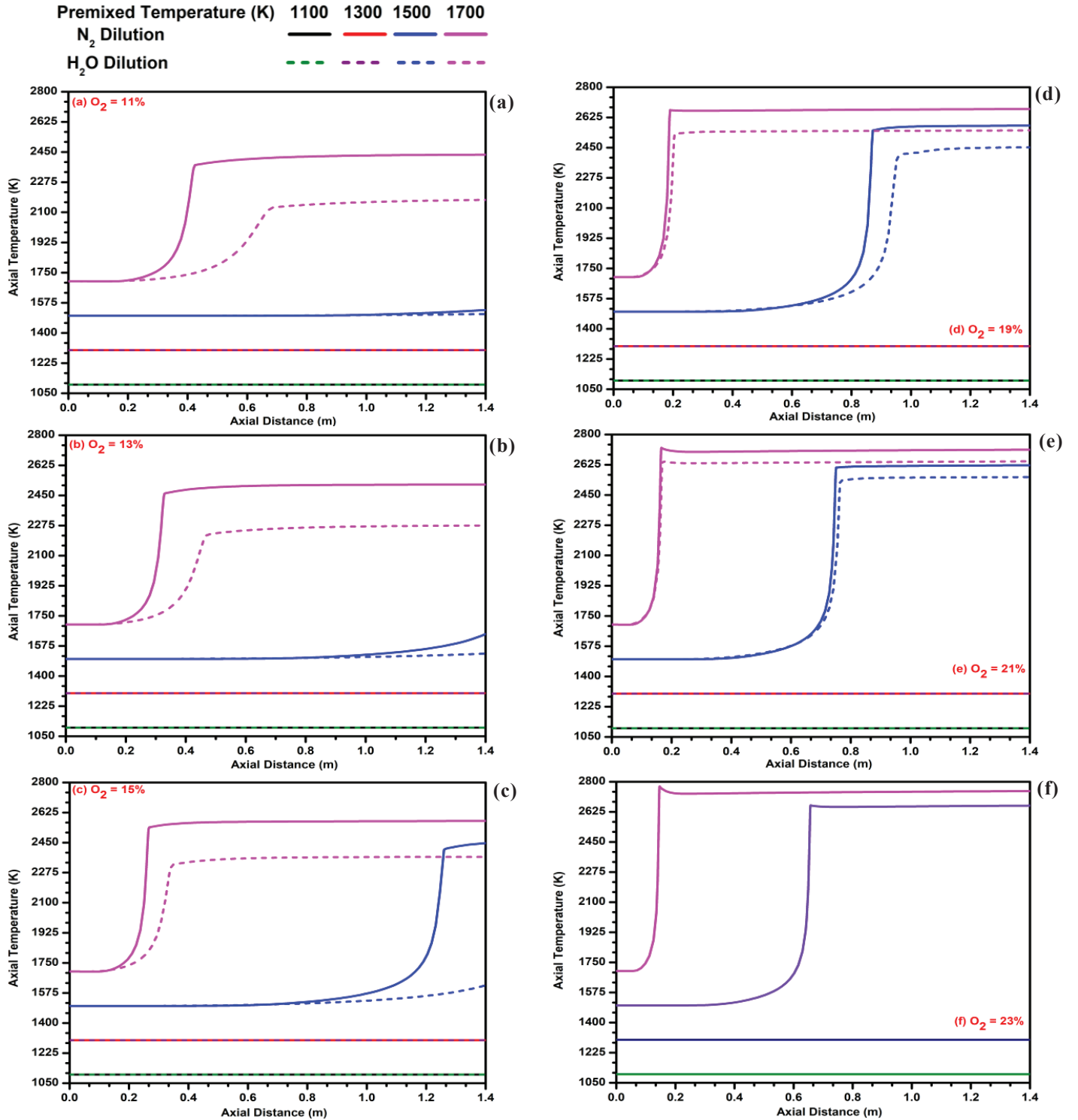


Figure 3. (a-f) Variation of axial temperature profile for N_2 and H_2O dilution at oxygen concentrations of 11-23 % and reactant temperature of 1100-1700 K.

flames than in the steam diluted flames. Total NO_x production consists of NO , N_2O , and NO_2 . The contribution of NO to NO_x production is more significant than the N_2O and NO_2 (mentioned in Fig. 4 (a), (b), and (c)). Therefore, the reduction of NO in ammonia-seeded flames is of uttermost importance. In the reaction zone, mole fractions of NO sharply increased, and at higher oxygen concentrations, the peak of the curve began to shift upstream of the reactor.

Similarly, the reaction zone began to shift upstream of the combustor for N_2O and NO_2 as the oxygen concentration increased. Also, the reaction zone for N_2O and NO_2 starts growing narrower with an increase in the O_2 concentration. Significant differences in the peak NO fraction are observed between the nitrogen and steam-diluted flames at the lower oxygen concentrations of 11-17 %. However, these differences are much small in higher oxygen concentrations of 21 and 23 %.

Outside the reaction zone, a gradual reduction in the NO mole fraction is observed. For the cases of oxygen concentration of 11-17 %, the equilibrium is observed within the reactor length of 1.4 m. However, a higher residence time and longer reactor length are required to reach its equilibrium value for the cases of oxygen concentrations of 21 and 23 %.

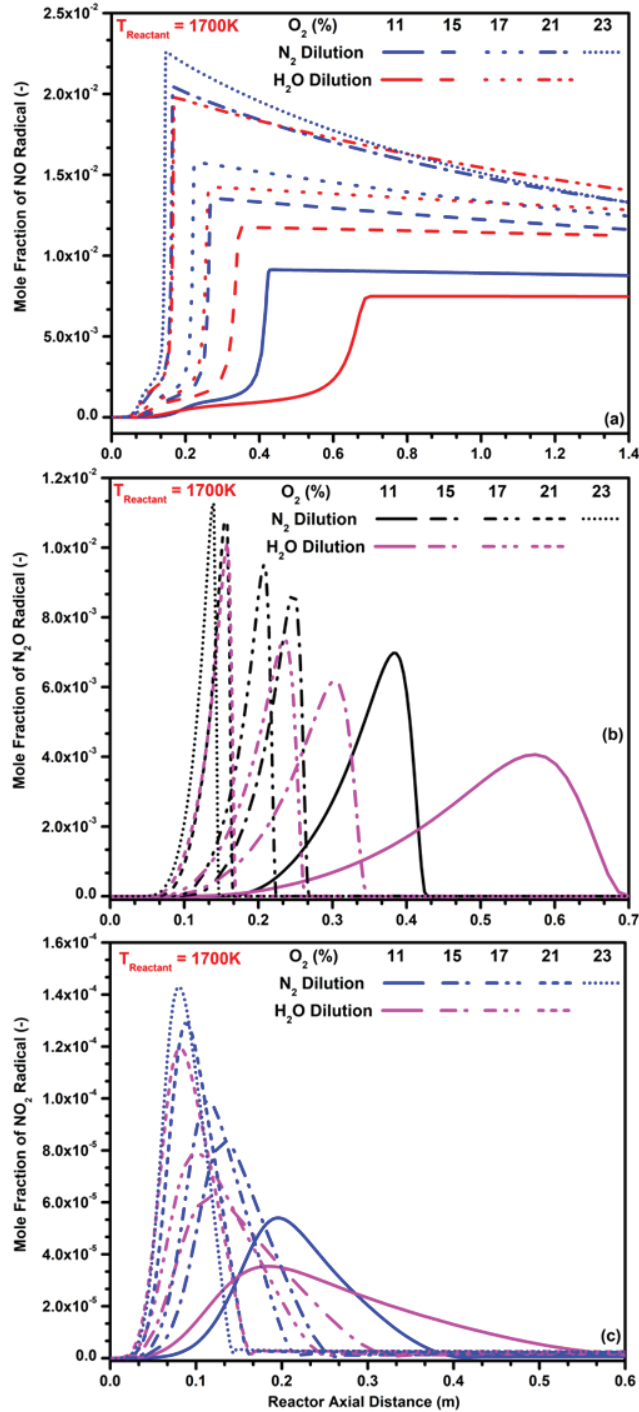


Figure 4. Axial variation of NO , N_2O , and NO_2 mole fraction at reactant preheat temperature of 1700 K and oxygen concentration of 11-23 %.

Figure 5 shows the exit NO_x variation at a reactant temperature of 1700 K and oxygen concentrations in the mixture ranging from 11-23 % for the H_2O and N_2 diluted flames. The

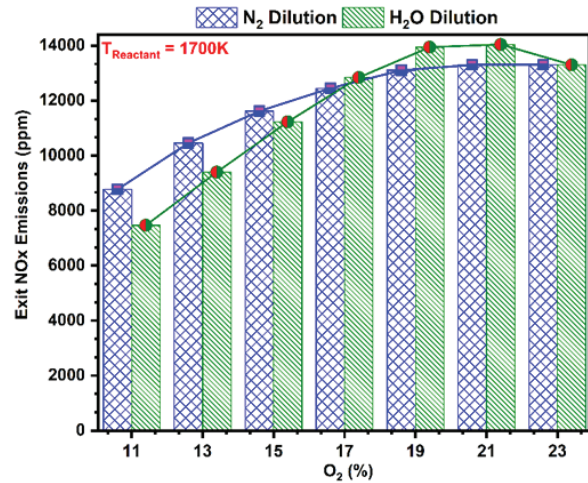


Figure 5. Exit NO_x emissions at different oxygen concentrations and reactant temperature of 1700 K for N_2 and H_2O dilution.

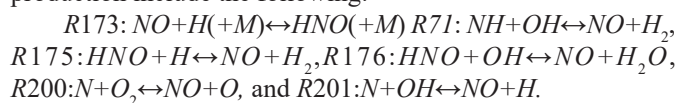
oxygen concentration of 23 % corresponds to without dilution. Exit NO_x emissions begin to rise as oxygen concentration rises (i.e., reduction in nitrogen concentration). Nevertheless, the NO_x emissions at the exit for H_2O diluted flames exhibit non-monotonic behavior. The exit NO_x magnitude is higher for the nitrogen diluted flame up to the oxygen concentration of 15%, and after that steam diluted mixture have higher NO_x emissions.

For H_2O diluted flames, the NO_x emissions increase up to the oxygen concentration of 21 % (compared to 11 % oxygen concentration), and after that, it starts decreasing (when oxygen concentration starts increasing from 21 %). At higher oxygen concentrations (greater than 15%), the steam-diluted flames show higher NO_x emissions due to the abundance of O/H . The oxygen produced from the steam decomposition and oxygen available in the oxidizer increases the relative oxygen-radical concentration in the mixture, further increasing the NO_x emissions. The oxygen coming through the oxidizer (air) has a more pronounced effect on NO_x emission.

Therefore, conclusion can be made that steam dilution is more preferable for lower or higher oxygen enriched flames, while nitrogen dilution is more suitable for lower oxygen concentration flames. Also, an optimization would be required to find the trade-off between the NO_x emissions and different dilution levels without sacrificing the flame stability.

4.3 NO Rate of Production or Consumption

Figure 6 (a-d) demonstrate the NO rate of production (ROP) and consumption (ROC) analysis along the reactor axial length of nitrogen diluted $NH_3/O_2/N_2$ mixture. The peak of total ROP rises with an increase in the oxygen concentration in the mixture, and it also starts shifting upstream of the reactor. As seen in Fig. 6 (a-d), the reactions participating in NO consumption and production can be categorized into three major pathways: NHi (where $i=1$ and 2), HNO , and extended Zeldovich mechanism. The main reactions that govern NO production include the following:



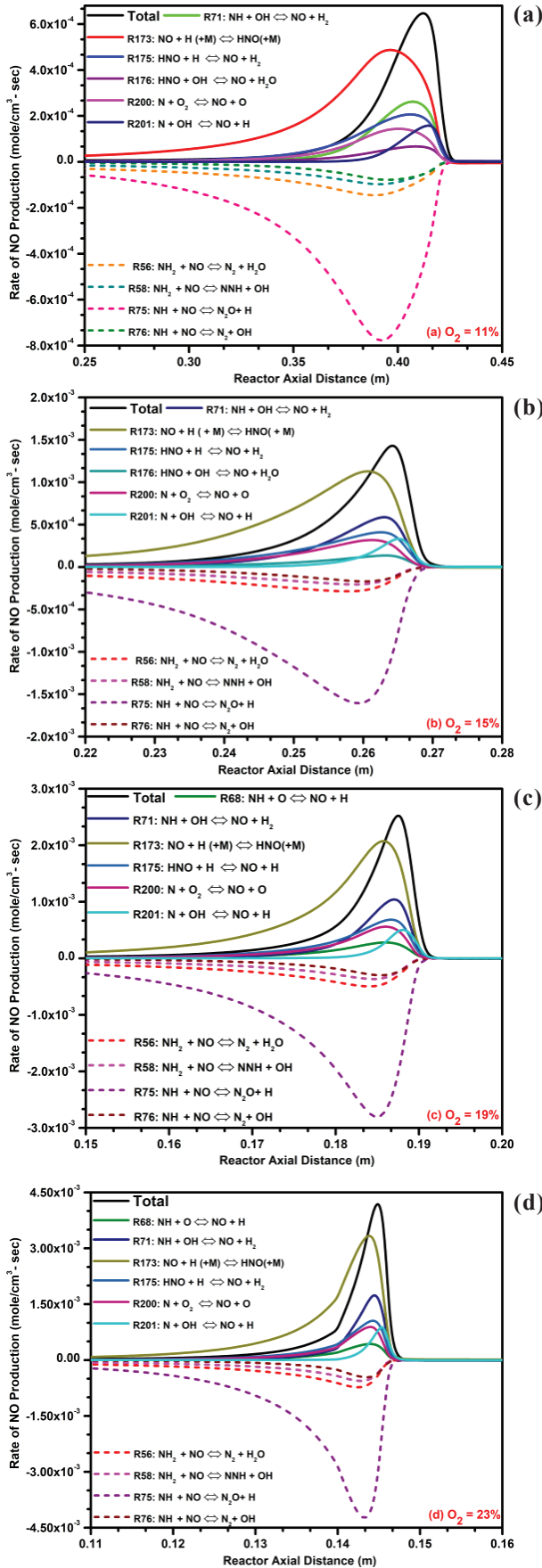


Figure 6. (a-d) NO ROP and ROC analysis of $NH_3/O_2/N_2$ mixture at reactant temperature of 1700 K and oxygen concentration of 11-23 %.

Similar reaction sets have also been significant for NO consumption and production in the cases of steam diluted flames and only the difference in the magnitude is observed. NO production in ammonia/air flames is primarily determined by the availability of O/H radicals. As oxygen concentration increases in the $NH_3/O_2/N_2$ mixture, it increases the availability of O/H radicals in the mixture, led to increasing NO production. A rise in oxygen concentration also accelerates NO production and consumption reactions.

In Fig.6, the third bodies species reaction $R173:NO+H(+M)\leftrightarrow HNO(+M)$ has major role in NO production compared to reaction $R71:NH+OH\leftrightarrow NO+H_2$ and extended Zeldovich mechanism reactions $R200:N+O_2\leftrightarrow NO+O$ and $R201:N+OH\leftrightarrow NO+H$. However, reaction between the NH and OH radical ($R71:NH+OH\leftrightarrow NO+H_2$) is also acting as O production source, but the contribution of reaction $R71:NH+OH\leftrightarrow NO+H_2$ in total NO production is less significant. Furthermore, reactions between the NO and NHi radicals are acting as a NO consumption source, and reaction $R175:NH+NO\leftrightarrow N_2O+H$ acts as a major source of NO consumption.

4.4 Identification of MILD Combustion Regime

Figure 7 (a) & (b) show the description of the MILD combustion regime for N_2 and H_2O dilution flames, respectively. The oxygen concentration and reactant temperature varied from 11-23 % and 1100-1700 K, respectively. We observed three distinct modes of combustion (i) No ignition, (ii) MILD, and (iii) High-temperature air combustion (HiTAC). In Fig. 7(a) and (b), The identification of MILD combustion regimes is based on the conditions proposed by Cavaliere and Joannon²⁷. Cavaliere and Joannon²⁷ suggested that the MILD is a subset of HITAC combustion. Furthermore, in order to accomplish

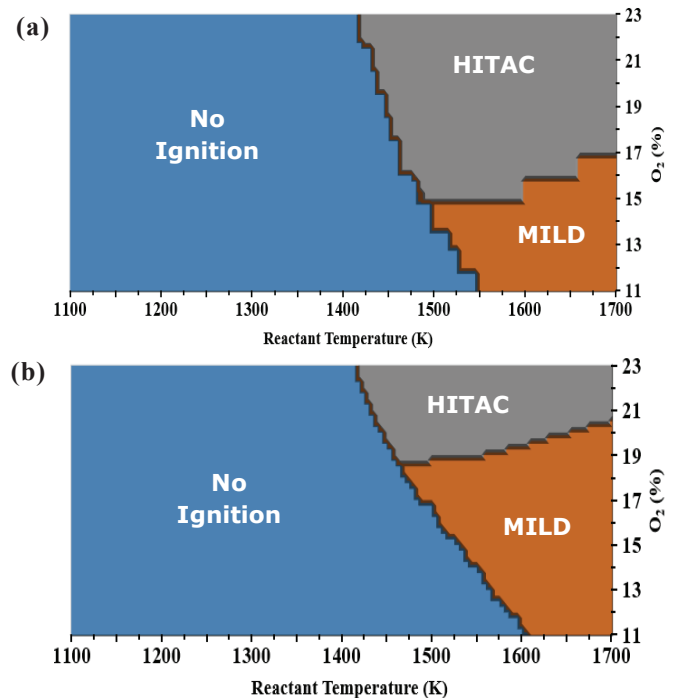


Figure 7. Regime showing different combustion modes for (a) N_2 (b) H_2O dilution.

MILD combustion, the reactant mixture inlet temperature must be greater than the mixture auto-ignition temperature, and the temperature rise with respect to the reactant mixture inlet temperature must be lower than the mixture auto-ignition temperature. The minimum temperature at which a mixture self-ignites at a given pressure is referred to as auto-ignition temperature. Ammonia is deemed to have an auto-ignition temperature of 923 K at atmospheric pressure⁶. The regime diagram shown in Fig. 7 (a) & (b) is developed by studying the maximum temperature of a stable temperature profile for N_2 and H_2O diluted combustion.

In Fig. 7(a) & (b), a no-ignition region is observed where the premixed mixture does not ignite. Towards the no-ignition region (separating no-ignition), The line thickness in this region is around 15-20 K, making it a narrow zone (in the inlet temperature of the reactant (x-axis-scale)) where the reaction is still in progress (i.e., the reactions have just started at the near the outlet of the combustor with a slight increase in temperature).

If the length of the combustor had been more than 1.4 m, there would have been a perfectly steady flame temperature profile. In order to simplify the analysis, we include these small regions within the no-ignition zone. H_2O diluted flames exhibit a broader no-ignition regime than N_2 diluted flames.

This is due to the higher ignition delay time required for steam-diluted flames than for nitrogen-diluted flames. In the case of MILD combustion, the broader regime is observed for the H_2O diluted than the N_2 diluted flames due to the lesser increment in the peak temperature of the mixture. For steam diluted flames, MILD combustion regime is found for O_2 concentrations ranging from 11 to 20 %, while for nitrogen diluted flames, it is observed for 11-17 %. This means that a higher amount of dilution is required for the nitrogen diluted than the steam diluted flames. Furthermore, at a particular oxygen concentration, a higher reactant temperature is required for H_2O diluted flames compared to N_2 diluted flames to achieve mild combustion.

5. CONCLUSIONS

Growing costs of energy, the limited availability of fossil fuels, and more stringent restrictions of carbon-dioxide and other pollutants emissions are the primary concern in today's world. The development of highly efficient and cleaner combustion systems and the search for alternative zero-carbon vector fuels are of prime importance. Recent studies on ammonia have demonstrated its potential as a future green fuel. However, the main issues with its application in gas turbine engines or industrial burners are slow reaction kinetics and significant NO_x emissions. Therefore, the NO_x reduction from the pure ammonia or ammonia blended with other higher reactive fuels is still a significant drawback for its wide-scale adoption. The flame anchoring and NO_x formation depend on the operating conditions, mixture composition, diluent, and combustor geometry. The following observation are made in the present study:

- No ignition occurs at the reactant temperatures of 1100 and 1300 K in all cases of oxygen concentration. Furthermore, higher reactant temperatures are necessary for stabilizing

the flame inside the combustor for mixtures containing less oxygen concentration (i.e., more N_2 or H_2O dilution).

- The peak temperature of flame enhances with an increase in the reactant inlet temperature, and steam diluted flames have a lesser temperature than the nitrogen diluted flames.
- At a reactant temperature of 1500 K and oxygen concentrations of 11 & 13 % for steam diluted flames, no ignition is detected. However, a modest increase in temperature is observed for nitrogen diluted flames.
- The magnitude of NO_x emissions are higher in N_2 diluted flames than the H_2O diluted flames.
- The equilibrium is observed within the reactor length of 1.4 m for oxygen concentrations ranging from 11 to 17%. However, with oxygen concentrations of 21 and 23%, a longer residence time and a longer reactor length are necessary to achieve its equilibrium value.
- (f) The exit NO_x magnitude from N_2 diluted flames start increasing as the oxygen concentration increases from 11-23 % (i.e., reduction in N_2 concentration). Nonetheless, in the case of H_2O diluted flames, at lower O_2 concentrations, the exit NO_x starts to drop and continues to rise until the O_2 concentration reaches 21 %.
- The third bodies species reaction $R173: NO+H(+M) \leftrightarrow HNO(+M)$ has major role in NO production compared to reaction $R71: NH+OH \leftrightarrow NO+H_2$ and extended Zeldovich mechanism reactions $R200: N+O_2 \leftrightarrow NO+O$ and $R201: N+OH \leftrightarrow NO+H$. Reactions of NO with NH & NH_2 radicals are acting as a NO consumption source, and reaction $R75: NH+NO \leftrightarrow N_2O+H$ acts as a major source of NO consumption
- When compared to N_2 diluted flames, H_2O flames have a more extensive no-ignition regime. H_2O diluted flames, with their lower peak temperature increase, display a more extensive range of MILD combustion than N_2 diluted flames. Furthermore, H_2O diluted flames require a higher reaction temperature than N_2 diluted flames for MILD combustion to occur.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the support received for this work from ISIRD, IIT Kharagpur, under seed grant.

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