Chemical Kinetic Modeling of Auto-Ignition Properties of Ammonia at Low-intermediate Temperature and High Pressure using Newly Proposed Reaction Mechanism

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Abstract

Global emissions can be significantly reduced with the use of zero-carbon emission fuels. Ammonia is now at the center of attention because of its promise as a carbon-free energy fuel. So, a detailed study on ammonia’s combustion and emissions characteristics is necessary, especially at low-intermediate temperature and high pressure conditions. Very

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few reaction models are available for low-intermediate temperature ammonia chemistry, and most of them could not show reasonable agreement with experimental conditions. In the present work, new ammonia oxidation reaction model has been proposed by referring to the previous available literature for low-intermediate temperature and high pressure ammonia oxidation chemistry, and also a comprehensive chemical kinetic modeling for autoignition characteristics and NO\textsubscript{x} emissions is performed for ammonia/air mixture using the newly proposed mechanism. The newly proposed ammonia reaction model consists of 32 species and 259 reactions. The proposed mechanism has also been tested by performing the computational fluid dynamics (CFD) modeling for a premixed NH\textsubscript{3}/air mixture in a micro flow reactor with varying wall temperature at an equivalence ratio of 0.8, 1, and 1.2, and the model validation is carried out by comparing the mole fraction profile of species NH\textsubscript{3}, O\textsubscript{2}, and H\textsubscript{2}O with the available experimental results. The proposed reaction model was able to predict the formation of steady weak flames of NH\textsubscript{3}/air premixed mixture within the computational domain. An excellent agreement is observed between computational and experimental results for autoignition properties and CFD model validation using the newly proposed reaction model.

**Keywords:** Ammonia combustion, Chemical kinetics, Energy carrier, Green fuel, Future fuel, Renewable fuel.

## 1 Introduction

World-wide pollution is increasing drastically due to the rapid growth in industrialization and the transportation sector. So, mankind needs to shift its focus from conventional fossil fuel to green fuel such as hydrogen, bio-fuel, bio-diesel, and ammonia [1]. Several other alternatives are also available but having properties like zero-carbon vector, high hydrogen density, and well-developed network for transportation, distribution and storage, ammonia seems to
have great potential as a carbon free or green fuel, which can be employed both in the transportation as well as in energy sector. With the well-developed existing infrastructure, minimum efforts are required in production, storage, and distribution of ammonia. However, the hydrogen-based economy is still not pragmatic due to unique properties of hydrogen; like high diffusivity, extremely low density in both gas and liquid phase, and broad flammability range relative to hydrocarbon fuels. These properties obstacle in the storage, transportation, and distribution of hydrogen. Due to higher hydrogen content, zero carbon-dioxide emissions, and an efficient transportation network, ammonia seems like a perfect alternative to hydrogen fuel. However, ammonia combustion poses specific challenges such as low laminar burning velocity, fuel bound NO\textsubscript{x} emissions, toxicity, higher self - ignition temperature & heat of vapourization, and narrow flammability limit. To overcome these challenges, the ammonia reaction mechanism requires extensive research to determine the optimal operating conditions and minimize NO\textsubscript{x} emissions. Miller et al. [2] computationally studied the different kind of ammonia/oxygen and ammonia/hydrogen/oxygen flames and suggested a detailed reaction model of ammonia oxidation with 22 species & 98 elementary reactions. Miller et al. [2] model shows adequate results for moderately rich conditions, and correctly estimate the flame speed and flame structure. However, in rich flame conditions, the kinetic model does not provide satisfactory results due to incomplete NH\textsubscript{3} pyrolysis mechanism, and it also underestimate the NO mole fraction. In continuation of earlier work, Miller and Bowman [3] studied the nitrogen chemistry in ammonia combustion for different sets of pressure, temperature, and equivalence ratio with special attention on NO\textsubscript{x} chemistry (i.e. NO\textsubscript{x} formation and removal processes). Miller and Bowman [3] also presented a detailed chemical kinetics modeling with 19 species and 73 elementary reactions for ammonia oxidation. The results show that the formation of nitric oxide/nitrogen generally depends on NH\textsubscript{4} radicals’ fate, which forms nitric oxide after the oxidation through
the nitroxyll (HNO) molecule. However, there are still some areas available in the reaction mechanism which fails to explain, such as what will be the lifetime of NNH at high temperature, and the extent up to which N₂O can be produced by the reaction NH + NO → N₂O + H. After Miller and his colleague’s work, the knowledge about the NH₃ oxidation chemistry has enhanced, and several NH₃ oxidation models have been developed. Over the years, the chemical mechanism of Miller et al. [2] has been customized for variety of operating conditions and has been used in various ammonia combustion studies [4–6]. The concentration of O/H radical (where O/H denotes the relative concentration of oxygen and hydrogen radical in the mixture) depends on the quality of flames. The leaner flames will have a high concentration of O/H radical, while for rich flames, O/H concentration will decrease, however in the O/H radical pool, the relative concentration of hydrogen atom in flames will increase. Depending on the O/H radicals concentration, the formation of nitric oxide in lean ammonia flames mainly occurs due to oxidation of NHₓ (x = 0,1, and 2) through an HNO intermediate or depletion of nitric oxide through NHₓ + NO elementary reactions. A high concentration of O/H radicals will favor the transformation of NHₓ to nitric oxide and reduction of NO by NHₓ radicals. In the case of rich flames, the high concentration of hydrogen atom in the O/H radical pool increases the oxidation tendency of NHₓ through reaction with hydrogen atoms, which leads to the production of H₂ commonly from amidogen (NH₂) and finally leads to the creation of nitrogen atoms. The profusion of nitrogen atom in rich flames assists the set of reactions known as the extended Zeldovich mechanism. The thermal or Zeldovich mechanism explains about the oxidation of N₂, and NOₓ production by the reactions N + O₂ → NO + O and N₂ + O → NO + N. In the case of the fuel-rich condition due to unavailability of oxygen atom, the first reaction becomes less sensitive, so a third reaction (N + OH → NO + H) is included in the mechanism, and this is known as the extended Zeldovich mechanism. Although, in ammonia combustion, the
extended Zeldovich mechanism comes in action even if temperature is less, but its contribution towards total NO production can be neglected. Skreiberg et al. [7] suggested a comprehensive reaction mechanism for NH₃ oxidation in the presence of CH₄/CO/H₂ and considered NO + O₂ as oxidant. They observed that the addition of carbon monoxide to lean NH₃/NO/O₂/N₂ flames at 1273 K results in increase in nitric oxide formation via the HNO path due to increase in the O/H radical pool. Presence of low temperature and nitric oxide in this study assists the reaction path NH₃ → NH₂ → N₂ directly or via NNH, preferably over the reaction path NH₃ → NH₂ → NH → N, which plays a vital role at the higher temperature.

While in another study, Mendiara and Glarborg [8] experimentally investigated the effect of high carbon-dioxide concentration on NH₃ oxidation under the oxy-fuel combustion of CH₄ in a flow reactor and observed that the addition of carbon-dioxide under the stoichiometric condition would lower nitric oxide production due to the consumption of hydrogen atom from the O/H radical pool by carbon-dioxide to form carbon monoxide (CO₂ + H → CO + OH).

HNO production typically depends on the reaction of NH₂ with oxygen atoms, and reaction path NH → HNO serves as an additional route for HNO production. Sole oxidation of HNO leads to the production of nitric oxide. Various reaction kinetic studies [2–4] suggest that the reaction of HNO with H, OH, O₂, or through thermal separation leads to nitric oxide production. So at all conditions in ammonia/air flames, nitric oxide production is dominated by HNO intermediate channel. While in another study, based on the work of Miller et al [2], Bian et al. [9] performed an experimental study for the low-pressure NH₃ or NH₃ + NO doped lean stoichiometric H₂/O₂/Ar premixed flat flames using molecular beam mass spectrometry.

Bian et al. [9] suggest that the nitroxyol is not pertinent in fuel NO production, and the formation of nitric oxide is mainly through the oxidation of NHₓ (where x = 1 and 2 ) ( NHₓ + O₂ → Products). Based on Miller and Bowman [3] reaction mechanism, Lindstedt et al. [10]
computationally investigated the variety of laminar premixed \( \text{NH}_3/\text{H}_2/\text{O}_2, \text{NH}_3/\text{NO}/\text{H}_2\text{O}, \) and \( \text{NH}_3/\text{O}_2 \) flames for a wide range of combustion conditions and suggested a comprehensive chemical kinetic model for ammonia oxidation with 21 species and 95 elementary reactions. It was found that the NO production in pure flames is via HNO intermediate and reaction of imidogen ( \( \text{NH} \)) with hydroxyl radical ( \( \text{NH} + \text{OH} \)) plays a vital role in nitric oxide production, while for all conditions \( \text{N}_2\text{O} \) production is primarily due to reaction of NH with nitric oxide (\( \text{NH} + \text{NO} \rightarrow \text{N}_2\text{O} + \text{H} \)). Lindstedt et al. [10] also confirmed the supremacy of nitroxy channel in fuel NO production. Haynes [11] studied the paths leading to generation and depletion of nitric oxide in \( \text{NH}_3 \) flames. Haynes [11] proposed that in rich ammonia flames having lower temperature (where ammonia has high stability), the influence of elementary reaction \( \text{NH}_x + \text{NH}_x \) (where \( x = 1, 2, \) and 3) on \( \text{N}_2 \) formation will be comparatively prominent. Further studies carried by Dean et al. [12] explained the importance of \( \text{NH}_x + \text{NH}_x \) elementary reactions in rich \( \text{NH}_3 \) flames kinetics towards lower NO production. The elementary reaction of the type \( \text{NH}_x + \text{NH}_x \) leads to an alternate nitrogen production route without incorporating the nitric oxide. Conversion of \( \text{NH}_x \) to nitrogen can be explained by the reaction path \( \text{NH}_2 + \text{NH}_x / \text{NH} \rightarrow \text{N}_2\text{H}_2 + \text{H/M} \rightarrow \text{NNH} + \text{M/O/O}_2 \rightarrow \text{N}_2 \). Generation of nitrogen will be primarily through the \( \text{NNH} \) dissociation reaction, while the reaction with \( \text{O} \) and \( \text{O}_2 \) will act as secondary source. While discussing the possible NO production route via the \( \text{NNH} \) mechanism, Dean and Bozzelli [13] proposed that the reaction of \( \text{NNH} \) with oxygen may lead to substantial nitric oxide production via the following reactions; \( \text{NNH} + \text{O} \rightarrow \text{NH} + \text{NO}, \text{NNH} + \text{O} \rightarrow \text{N}_2\text{O} + \text{H}, \) and \( \text{NNH} + \text{O} \rightarrow \text{N}_2 + \text{OH} \). This also suggests that the \( \text{NH}_x \) (where \( x = 1, 2, \) and 3) combination pathway may also lead to substantial nitric oxide production. They also performed the QRRK analysis and suggested that the \( \text{N}_2 + \text{OH} \) has one order larger rate constant value in comparison to \( \text{NH} + \text{NO} \) and \( \text{N}_2\text{O} + \text{H} \). However, the studies of Konnov
& his colleague [14, 15] and Klippenstein et al. [16] show that the NH + NO has a lower rate constant value than estimated by Dean and Bozzelli [13]. Klippenstein et al. [16] theoretically studied NNH’s contribution to nitric oxide production and showed that out of the three above discussed reaction channels by Dean and Bozzelli [13], the N₂ + OH has found to play a significant role. In contrast, N₂O + H has a competitive, and NO + OH has a minor effect on nitric oxide production even at high temperature due to reaction endothermicity. In earlier studies, the formation of N₂H₃ and N₂H₄ from NHₙ (where n = 1 and 2) combination steps were neglected, it was Konnov and De Ruyck [17] who first recognized it, and they included the reactions of these species in their N/H reaction mechanism. Konnov and De Ruyck [17] compared their modeling results with the experimental study performed by the Davidson et al. [18] for ammonia pyrolysis, and suggested that the consideration of N₂Hₙ (where n = 2, 3, 4) reactions in the detailed N/H mechanism gives a more adequate prediction of the peak concentrations and rise-time of NH and NH₂. However, if the temperature is more than 2800 K, the prediction differs significantly. In further successive studies, various forms and upgraded version of Konnov’s mechanism have been reported since then [19–25]. Nakamura et al. [26, 27] studied the suitability of different available mechanisms such as Konnov et al. [23], GRI Mech 3.0 [28], Mathieu and Petersen [29], Tian et al. [30], and Lindstedt et al. [10] for the measurement of combustion and ignition properties of NH₃/air mixture in their micro flow reactor experiment. Nakamura et al. [26, 27] found that for low-temperature oxidation (around 1270 K), only Konnov’s reaction model successfully predicted the formation of weak ammonia/air flames in their micro flow reactor experiment due to better description of N₂Hₙ chemistry. Table 1 shows the details of recently developed or proposed reaction models for NH₃/air mixture. Won et al. [32] found that in the premixed turbulent jet flames, low-intermediate temperature fuel chemistry plays a significant role in ignition characteristics, and stable combustion of ammonia/air mix-
tures can be obtained by introducing a swirler and recirculation near the base of premixed turbulent jet flames [33]. Swirling is used as an effective method to provide clean and efficient combustion in various practical application such as industrial furnaces, utility boilers, and gas turbines systems [34–36]. Despite extensive studies available on ammonia oxidation kinetics, several discrepancies still exist in the available reaction mechanisms to precisely predict the combustion and ignition characteristics of ammonia. There is still limited literature available for low-intermediate temperature ammonia oxidation chemistry. Particularly for ignition data, ignition delay measurements have been studied by mixing ammonia with methane or hydrogen or NH$_3$/O$_2$/Ar for high-temperature conditions (around 2000 K) using shock tube or rapid compression machine. Recent studies of Sabia et al. [37], Rocha et al. [38], and Shu et al. [39] have also highlighted these issues.

Thus, a detailed study is required for autoignition characteristics of ammonia/air mixture at low-intermediate temperature and high pressure to develop future ammonia based combustors. Therefore, this study’s main objective is to propose a detailed reaction model for NH$_3$ combustion, which can capture low-intermediate temperature and high pressure chemistry of ammonia oxidation. In this work, an extensive chemical kinetic modeling has been performed to analyze the ammonia/air mixture ignition delay time, laminar flame speed, and nitric oxide concentration in combustion products for low-intermediate temperature and high pressure conditions using this newly proposed reaction model (details of newly proposed reaction model can be seen in the table 3). In this study, an extensive chemical kinetic modeling has been also performed for the reaction pathway analysis, OH radical and laminar flame sensitivity analysis, and highlighted the important chemical reactions which play a crucial role in autoignition and emissions characteristics of NH$_3$/air mixture. Further, a detailed CFD study has also been carried out using the newly proposed reaction mechanism, and model validation is carried out by
comparing the computational results of mole fraction profile of species NH$_3$, O$_2$, and H$_2$O with the available experimental results.

Table 1: Details of recently developed or proposed reaction model for NH$_3$/air mixture

<table>
<thead>
<tr>
<th>Author</th>
<th>Fuel mixture</th>
<th>No. of species</th>
<th>No. of reactions</th>
<th>Working condition</th>
<th>Important conclusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tian et al. [30] (2009)</td>
<td>NH$_3$/O$_2$/Ar</td>
<td>31</td>
<td>191</td>
<td>P = 0.04 bar, T = 1200 - 2000 K, and $\phi$ = 1</td>
<td>Reactions: NH + NO $\rightarrow$ N$_2$O + H, NH$_2$ + O $\rightarrow$ HNO + H, NH$_4$ + NO $\rightarrow$ N$_2$ + H$_2$O, and H + O$_2$ $\rightarrow$ O + OH plays crucial role in NO and N$_2$ conversion.</td>
</tr>
<tr>
<td>Duyunslaegher et al. [25] (2012)</td>
<td>NH$_3$/H$_2$/O$_2$/Ar</td>
<td>19</td>
<td>80</td>
<td>P = 60-120 mbart, $\phi$ = 0.9 - 1.1, and $X_{H_2} = 5$ - 12.5%</td>
<td>Modified the rate constant of the reactions; N$_2$O + H, N$_2$O + H $\rightarrow$ N$_2$ + OH, NH$_2$ + H $\rightarrow$ NH$_2$ + H, and NH$_2$ + NH$_2$ $\rightarrow$ N$_2$H$_2$ + H</td>
</tr>
<tr>
<td>Mathieu and Peterson [29] (2015)</td>
<td>NH$_3$/O$_2$/Ar</td>
<td>35</td>
<td>159</td>
<td>P = 1.1, 11, and 30 bar, T = 1560 - 2455 K, and $\phi$ = 0.5, 1.0, and 2</td>
<td>Reaction; N$_2$O + H $\rightarrow$ N$_2$ + OH* enhances the OH* mechanism for simulating the ammonia oxidation.</td>
</tr>
<tr>
<td>Song et al. [40] (2016)</td>
<td>NH$_3$/O$_2$</td>
<td>32</td>
<td>204</td>
<td>P = 30 &amp; 100 bar, T = 450 - 925 K, and $\phi$ = 0.22, 0.23, 0.24, 1.03, and 1.04</td>
<td>Modified the rate constant of the reaction; H$_2$NO + O$_2$ $\rightarrow$ HNO + HO$_2$, and updated the rate constant of NH$_2$ subset reactions.</td>
</tr>
<tr>
<td>Nakamura et al. [27] (2017)</td>
<td>NH$_3$/air</td>
<td>38</td>
<td>232</td>
<td>P =1 atm, $\phi$ = 0.8 - 1.2, and maximum wall temperature = 1400K</td>
<td>Included the N$_2$H$_x$ (where $x = 2, 3,$ and 4) subset reactions and H$_2$NN chemistry.</td>
</tr>
<tr>
<td>Shrestha et al. [41] (2018)</td>
<td>NH$_3$/air</td>
<td>34</td>
<td>264</td>
<td>P = 1.4, 11, and 30 atm, T= 1428-2587 K, and $\phi$ = 0.5-2</td>
<td>Consideration of additional reaction of species; NH$_2$H$_x$, H$_2$NN, HNOH, NH$_2$OH, HONO, NO$_2$, and HNO$_3$.</td>
</tr>
<tr>
<td>Otomo et al. [43] (2018)</td>
<td>NH$_3$/air</td>
<td>32</td>
<td>213</td>
<td>P = 1.4, 11, and 30 atm, T = 1538-2350 K, and $\phi$ = 0.5-2</td>
<td>Modified the rate constant of NH$_2$H$_x$, and HNO subset reactions.</td>
</tr>
<tr>
<td>Li et al. [31] (2019)</td>
<td>NH$_3$/H$_2$O</td>
<td>34</td>
<td>252</td>
<td>P = 0.1 - 5 MPa, T = 1000-2000 K, and $\phi$ = 0.5-2</td>
<td>NO concentration will be higher in high temperature zone, and near stoichiometric mixture fraction while, N$_2$O concentration will higher in fuel-lean case, and lower near the stoichiometric mixture fraction.</td>
</tr>
</tbody>
</table>

2 Chemical Kinetic Modeling

The present work aims to propose a reaction mechanism that can explain NH$_3$ combustion chemistry for low-medium temperature range. Subsequently, different mechanisms are taken into consideration [25,29,40–43] for improvement of the existing mechanisms for better prediction. It was observed that majority of the mechanisms under-predict the ignition delay time as compared to the experiment results of He et al. [44], whereas, the Klipenstein et al. [16] model over-predicts the same. Subsequently, sensitivity analysis of these mechanisms was carried out for different ignition properties like laminar flame speed and ignition delay time to understand
the important reactions and species in the oxidation and pyrolysis pathway of ammonia. It was observed that NH$_2$ species has a profound effect on the overall pathway and responsible for the phenomenon of chain branching and propagation. This was also observed in the analysis of our proposed mechanism, which is discussed in the further sections. After adopting a different set of reactions and rate parameters involving NH$_2$ from various mechanisms, it was found that the inclusion of NH$_2$ subset of reactions from Song et al. [40] was able to better predict the ignition delay time and laminar flame speed. The work of Shrestha et al. [41] encompasses the recent development in mechanisms, including the different rate parameters from the literature. Therefore, this has been adopted as the base file upon which modifications have been carried out using the updated NH$_2$ set of reactions from Song et al. [40]. However, Shrestha et al. [41] performance was also not in considerable agreement with experimental results for more than 30 bar pressure. The Song et al. [40] model (32 species, 204 reactions) was mainly based on the model of Klipenstein et al. [14], and the Shrestha et al. [41] model (34 species, 264 reactions) was mainly based on the reaction model of Skreiberg et al. [7], Klipenstein et al. [14, 45], Miller and Glaborg [46], Glaborg et al. [47, 48], Mathieu et al. [29], Klaus [49], Allen et al. [50], Coppens et al. [51], Mendiara and Glaborg [8], Powell et al. [52], Rasmussen et al. [53], and Duynslaegher et al. [25]. Table 2 shows details of rate coefficients of NH$_2$ subset reactions considered from Song et al. [40] work, and added to baseline mechanism of Shrestha et al. [41]. Where the terms A, n, and $E_{activation}$ represent the pre-exponential factor, temperature exponent, and activation energy, respectively. Table 3 shows the details of the newly proposed detailed reaction model (32 species, 259 reactions), and it is tested using CHEMKIN PRO [54]. The proposed reaction model is attached in the supplementary material. For gas phase kinetics, the normalized net rate of formation or production and consumption can be described using the equation 1 and 2.
Table 2: Details of rate coefficients of NH$_2$ subset reactions considered from Song et al. [40] work, and updated to baseline mechanism of Shrestha et al. [41].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>A</th>
<th>n</th>
<th>E$_{activation}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_2$ + H = NH + H$_2$</td>
<td>7.2E+05</td>
<td>2.320</td>
<td>799</td>
</tr>
<tr>
<td>NH$_2$ + O = HNO + H</td>
<td>6.6E+13</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>NH$_2$ + OH = NH + H$_2$O</td>
<td>3.3E+06</td>
<td>1.949</td>
<td>-217</td>
</tr>
<tr>
<td>NH$_2$ + HO$_2$ = NH$_3$ + O$_2$</td>
<td>1.7E+04</td>
<td>1.550</td>
<td>2027</td>
</tr>
<tr>
<td>NH$_2$ + HO$_2$ = H$_2$NO + OH</td>
<td>5.0E+13</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>DUPLICATE</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH$_2$ + HO$_2$ = H$_2$NO + OH</td>
<td>2.5E+17</td>
<td>-1.280</td>
<td>1166</td>
</tr>
<tr>
<td>DUPLICATE</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH$_2$ + HO$_2$ = HNO + H$_2$O</td>
<td>1.6E+07</td>
<td>0.550</td>
<td>525</td>
</tr>
<tr>
<td>DUPLICATE</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH$_2$ + HO$_2$ = HNO + H$_2$O</td>
<td>5.7E+15</td>
<td>-1.120</td>
<td>707</td>
</tr>
<tr>
<td>DUPLICATE</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH$_2$ + HO$_2$ = HON + H$_2$O</td>
<td>2.1E+07</td>
<td>0.640</td>
<td>811</td>
</tr>
<tr>
<td>NH$_2$ + O$_2$ = HNO + OH</td>
<td>2.9E-02</td>
<td>3.764</td>
<td>18185</td>
</tr>
<tr>
<td>NH$_2$ + N = N$_2$ + 2 H</td>
<td>7.0E+13</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>NH$_2$ + NO = N$_2$ + H$_2$O</td>
<td>1.3E+16</td>
<td>-1.25</td>
<td>0.000</td>
</tr>
<tr>
<td>DUPLICATE</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH$_2$ + NO = N$_2$ + H$_2$O</td>
<td>-3.1E+13</td>
<td>-0.48</td>
<td>1180</td>
</tr>
<tr>
<td>DUPLICATE</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH$_2$ + NO = NNH + OH</td>
<td>3.1E+13</td>
<td>-0.48</td>
<td>1180</td>
</tr>
<tr>
<td>NH$_2$ + NO$_2$ = N$_2$O + H$_2$O</td>
<td>2.6E+18</td>
<td>-2.191</td>
<td>455</td>
</tr>
<tr>
<td>NH$_2$ + NO$_2$ = H$_2$NO + NO</td>
<td>9.1E+11</td>
<td>0.0321</td>
<td>-1512</td>
</tr>
</tbody>
</table>
Where, the term $v_{mn}$ represents the stoichiometric coefficient of $m^{th}$ species and $n^{th}$ elementary reaction, $q_n$ represents the rate of reaction of $n^{th}$ elementary reaction, $R$ represents the total number of elementary reactions, and $r^p_{mn}$ & $r^c_{mn}$ represents the coefficient of production and contribution [55]. Generally, sensitivity analysis is performed to identify the crucial reactions whose contribution plays a crucial role in the analysis, and it is calculated using the Jacobi matrix method.

\[ r^p_{mn} = \frac{\max\left(v_{mn}, 0\right) q_n}{\sum_{r=1}^{R} \max\left(v_{mn}, 0\right) q_n} \quad (1) \]

\[ r^c_{mn} = \frac{\min\left(v_{mn}, 0\right) q_n}{\sum_{r=1}^{R} \min\left(v_{mn}, 0\right) q_n} \quad (2) \]

\[ s^t = \left( k_n \frac{\partial c_m}{\partial k_n} \right) = \left( \frac{\partial ln c_m}{\partial ln k_n} \right) \quad (3) \]

The equation 3 represents the normalized matrix of local sensitivity coefficient ($s^t$). Where, the term $\frac{\partial c_m}{\partial k_n}$ represents the sensitivity coefficient for $m^{th}$ species and $n^{th}$ reaction rate, $k_n$ & $c_m$ represents the reaction rate constant and concentration of $n^{th}$ reaction and $m^{th}$ species, respectively [56, 57]. Premixed flame speed model is adopted to estimate laminar flame speed using the adaptive grid meshing method. The number of grid points adopted to obtain a mesh independent solution was found to be 900. The grid parameters like GRAD and CURL are varied from 0.01 to 0.9 in a series of continuation runs. The converged solution obtained for GRAD and CURL values is found to be 0.03, and 0.1 respectively. The deviation of velocity between the measured mesh independent grid size and the further refined mesh was less than 0.1 cm / sec. Numerical prediction of ignition delay time plays a important role in the analysis of autoignition parameters. In combustion applications, there are several ways to define the ignition delay time both experimentally and computationally. Experimentally, it is mainly measured
by using a rapid compression machine (RCM) or shock tube (ST). In CHEMKIN [54], the ignition delay time is mainly defined either by the maximum value of hydroxyl radical (OH) concentration or temperature inflection point criteria.

Table 3: Details of newly proposed mechanism in present work

<table>
<thead>
<tr>
<th>Species</th>
<th>No. of Species</th>
<th>No. of Reactions</th>
</tr>
</thead>
<tbody>
<tr>
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</table>

3 Reaction Model Validation

3.1 Ignition Delay Time Validation

In this work, ignition delay time (IDT) simulations were executed using a 0-D closed homogeneous reactor model with constant volume and adiabatic conditions. Ignition delay simulation conditions are considered from the experimental work of by He et al. [44] for IDT in rapid compression machine for NH₃/O₂ at pressure 40 and 60 bar, temperature ranges from 950 to 1150 K, and equivalence ratio of 0.5, 1, and 1.5. IDT validation has been compared with the experimental result of He et al. [44], and other kinetic models of Mathieu and Petersen [29], Klippenstein et al. [16], Glaborg et al. [42], Song et al. [40], Shrestha et al. [41], and Otomo et al. [43]. Figure 1 and 2 shows the variation of ammonia ignition delay as a function of the inverse temperature at an equivalence ratio of 0.5, 1, and 1.5 and pressure of 40 and 60 bar. As shown at a particular pressure, the ignition delay time increases with decreasing temperature at all equivalence ratios. The reaction model proposed in this work predicts ignition delay time well compared to experimental results for most of the conditions, but for few conditions, it
deviates from the experimental conditions with a maximum deviation factor of 1.5. Klippenstein et al. [16] over-predict the IDT by more than a factor of 4 at both 40 and 60 bar pressure. While, the other models of Shrestha et al. [41], Otomo et al. [43], Mathieu and Petersen [29], and Glaborg et al. [42] under-predict the ignition delay time at 40 bar for all three equivalence ratio conditions. While in case of the fuel-rich and stoichiometric mixture at 60 bar, the model of Galborg et al. [42] and Mathieu and Petersen [29] shows considerably good agreement with the experimental results, but the model of Galborg et al. [42] and Mathieu and Petersen [29] under-predict the IDT for fuel lean condition, while the model of Otomo et al. [43], Song et al. [40], and Shrestha et al. [41] under-predict the ignition delay time at 60 bar for all three conditions. At high pressure, generally, the pre-ignition pressure rise commonly occurs, which increases the uncertainty of measured ignition delay time, which could be the possible disagreement between the experimental and computational results [44].

3.2 OH Sensitivity Analysis

To get a deeper insight into the numerical simulation result and crucial reaction influencing the ignition delay time, a sensitivity analysis has been performed for hydroxyl radical (OH) at the time of ignition (≈1% ammonia conversion [58]). Figure 3 shows the 10 most sensitive elementary reaction at T = 1060 & 1100 K, P = 40 & 60 bar, and \( \phi = 0.5, 1.0, \) and 1.5. Sensitivity analysis shows that at 40 and 60 bar pressure, the most sensitive reactions are the same, and these reactions are; \( \text{NH}_2 + \text{NO} \rightarrow \text{N}_2 + \text{H}_2\text{O}, \text{NH}_2 + \text{NO} \rightarrow \text{NNH} + \text{OH}, \) and \( \text{H}_2\text{NO} + \text{O}_2 \rightarrow \text{HNO} + \text{HO}_2. \) Where the ignition inhibiting or hindering reactions are the terminating steps \( \text{NH}_2 + \text{NO} \rightarrow \text{N}_2 + \text{H}_2\text{O} \text{ and } \text{NH}_2 + \text{NO}_2 \rightarrow \text{H}_2\text{O} + \text{N}_2\text{O}, \) which compete with the ignition enhancing reactions; \( \text{NH}_2 + \text{NO} \rightarrow \text{NNH} + \text{OH}, \) and \( \text{H}_2\text{NO} + \text{O}_2 \rightarrow \text{HNO} + \text{HO}_2. \) So the reaction of \( \text{NH}_2 + \text{NO} \) is the most significant reaction for autoignition of \( \text{NH}_3. \) The
Figure 1: Variation of ignition delay time of NH$_3$/air mixture at equivalence ratio (\(\phi\)) of 0.5, 1.0, and 1.5, and pressure (P) of 40 bar.

Product channel of NH$_2$ + OH to NNH + OH and N$_2$ + H$_2$O under wide range of pressure and temperature conditions are either enhancing or inhibiting the autoignition characteristics. The additional sensitive reactions are those producing HNO by the reaction of H$_2$NO with O$_2$ or HO$_2$ or reaction of NH$_2$ with O$_2$. H$_2$NO formed due to the bimolecular reaction of NH$_2$ with molecular oxygen. OH sensitivity analysis for ignition delay time at the same operating conditions using the reaction model of Song et al. [40] and Shrestha et al. [41] have been attached in supplementary material.
Figure 2: Variation of ignition delay time of NH$_3$/air mixture at an equivalence ratio (\(\phi\)) of 0.5, 1.0, and 1.5, and pressure (P) of 60 bar.

3.3 Laminar Flame Speed Validation

Laminar flame speed is a crucial combustion parameter, and it plays a key role in flame stability and in reaction model validation. Flame speed is generally a combination of density ratio and burning rate, and it also plays a significant role in the analysis of flame’s fundamental characteristics. Since ammonia flames possess a lower flame speed than conventional hydrocarbon flames like methane (35 cm/sec) or propane flames (43 cm/sec), so it is critical to evaluate the laminar flame speed of ammonia. Due to low flame speed, i.e. low flow rate, experimental analysis of ammonia flames is highly challenging because, with low flow rates, the relative weight
Figure 3: OH radical sensitivity analysis at the time of ignition for NH$_3$/air mixture at temperature (T) = 1060 K & 1100 K, pressure (P) = 40 & 60 bar, and equivalence ratio (\(\phi\)) of 0.5, 1, and 1.5.

of buoyancy force will come into the picture. In this work, the newly developed mechanism is tested with the experimental result of Hayakawa et al. [59], Takizawa et al. [60], Ronney et al. [61], Pfahl et al. [62], and Han et al. [63] and with the mechanisms of Song et al. [40], Lindstedt et al. [10], Shrestha et al. [41], Tian et al. [30], Miller et al. [2], and Konnov et al. [23].

Figure 4 shows the laminar flame speed variation with equivalence ratio at unburnt mixture pressure of 1, 3, and 5 atm and mixture temperature of 298 K. The mechanism developed in the present work predicts laminar flame speed well for all three operating pressures compared to experimental results for most of the conditions. However, for a few conditions, it deviates from the experimental conditions with a maximum deviation factor of 15%. It can be seen from figure 4 for ambient condition that the several experimental results show the different value of flame speed at same conditions. This difference in values may be due to the different measurement techniques used for flame speed measurement and uncertainty associated within it. In general, at unburnt mixture pressure of 1 atm, the mechanism of Song et al. [40], Tian et
Figure 4: Laminar flame speed variation of NH$_3$/air mixture at unburnt mixture initial temperature (T$_u$) = 298 K, and pressure (P$_u$) of 1, 3, and 5 atm.

al. [30], and Shrestha et al. [41] over-estimates the flame speed for both fuel-rich and fuel-lean equivalence ratio conditions. At unburnt mixture pressure of 3 atm and 5 atm, the mechanism of Song et al. [40] highly over-predicts the laminar flame speed for the whole range of mentioned equivalence ratios. While the mechanism of Shrestha et al. [41] also overestimates the laminar flame speed for both fuel-rich and fuel-lean conditions at unburnt mixture pressure of 3 and 5 atm, but deviation is less compared to Song et al. [40]. The laminar flame speed reaches its maximum value around the equivalence ratio of 1.1. The experimental results of Hayakawa et al. [59] show that the maximum flame speed of premixed NH$_3$/air is around 7 cm/sec, which is around 1/5$^{th}$ of methane/air flame. Figure 5 shows laminar flame speed variation with an initial pressure of the unburnt mixture (P$_u$) at an equivalence ratio of 0.8, 1.0, and 1.2. As can be seen from the figure 5, increase in the unburnt mixture’s initial pressure decreases the laminar flame speed. The numerical simulation result of the proposed reaction model closely follows the experimental results of Hayakawa et al. [59]. However, the models of Miller et
al. [2], Lindstedt et al. [10], Shrestha et al. [41], Song et al. [40], Tian et al. [30], and Konnov et al. [23] model strongly overpredicts the laminar flame speed. Figure 6 shows the laminar flame speed variation with the equivalence ratios at a different initial temperature ($T_u$) of the unburnt mixture. The temperature ranges from 298 K to 448 K with a step of 25 K. The mechanism proposed in this work closely follows the experimental trends of Han et al. [63], however, at all temperatures, it under-estimates the laminar flame speed with a maximum deviation of 16%, while the reaction model of Song et al. [40] overestimate the laminar flame speed at all stated conditions, and Shrestha et al. [41] model follows the experimental trend in fuel-lean
conditions, but it strongly deviates from the experimental trend in fuel-rich conditions.

![Figure 6: Variation of laminar flame speed of NH₃/air mixture at unburnt mixture initial temperature (T_u) = 323, 398, and 448 K.](image)

### 3.4 Flame Speed Sensitivity

Figure 7 shows the 10 most sensitive elementary reaction of ammonia/air for flame speed at T_u = 298 K, P_u = 1 bar, and φ = 0.8, 1.0, and 1.2. It can be seen that the important sensitive reactions are same for all three conditions of equivalence ratios and these are; O₂ + H → OH + O, NH₂ + NO → NNH + OH, N₂O ( + M) → N₂ + O ( + M), N₂O + H → N₂ + OH, and NO + H ( + M) → HNO ( + M). Amongst the highly sensitive reactions, the reaction
Figure 7: Flame speed sensitivity of NH$_3$/air mixture at unburnt mixture initial temperature ($T_u$) = 298 K, pressure ($P_u$) = 1 bar, and equivalence ratio ($\phi$) of 0.8, 1.0, and 1.2.

O$_2$ + H $\rightarrow$ OH + O has highest sensitivity value of around 0.5. Studies of Mathieu and Petersen [29] and Otomo et al. [43] shows that the reaction NO + H (+ M) $\rightarrow$ HNO (+ M) also plays a vital role in flame speed analysis. The model which over-predicts the flame speed has either not included these reactions like in the case of Konnov et al [23], or it has smaller sensitivity value as in the case of Song et al. [40] and Shrestha et al. [41] work. While studies of Konnov et al. [23], Klippenstein et al. [16], and Glaborg et al. [42] highlights that the reaction NH$_2$ + NO $\rightarrow$ NNH + OH as the most important reaction for flame speed analysis with sensitivity value higher than 0.1. Discrepancy seen in flame speed results among the several available mechanisms is due to the relative significance of the HNO and NNH sub-mechanisms reactions. Laminar flame speed sensitivity analysis at the same conditions using the model of Song et al. [40] and Shrestha et al. [41] have been attached in supplementary material.
3.5 Reaction Pathway Analysis

In figure 8, the reaction pathway analysis of NH$_3$/air mixture is presented using the newly proposed mechanism in the present work. Backward reaction paths have not been shown here to prevent the cluttering in the reaction pathway diagram. The red lines in the reaction pathway diagram indicate that the reaction contribution is equal to 100%. It can be seen that the amine radical (NH$_2$) is the central species, and it is mainly formed from the reaction of NH$_3$ with radical OH, O, and NO$_2$ through the reaction NH$_3$ + OH $\rightarrow$ NH$_2$ + H$_2$O, NH$_3$ + O $\rightarrow$ NH$_2$ + OH, and NH$_3$ + NO$_2$ $\rightarrow$ NH$_2$ + HONO. The conversion of ammonia to NH$_2$ is mainly due to the reaction with hydroxyl radical (OH), while the contribution of O and NO$_2$ in NH$_2$ formation is very less. NH$_2$ radical is responsible for the phenomenon of chain propagation and branching, and it is converted into nitric oxide and nitrogen dioxide via the path NH$_2$ $\xrightarrow{\text{NO}_2,\text{NH}_3,\text{O}_2,\text{OH}}$ H$_2$NO $\xrightarrow{\text{O}_2,\text{HONO}}$ NO $\xrightarrow{\text{HO}_2}$ NO$_2$. The chain branching reaction of NH$_2$ will lead to formation of NNH and NH via the reactions NH$_2$ + NO $\rightarrow$ NNH + OH, and 2 NH$_2$ $\rightarrow$ NH$_3$ + NH, NH$_2$ + NO$_2$ $\rightarrow$ NH + HONO. The equilibrium product N$_2$ will be formed by the NNH oxidation reactions NNH + O$_2$ $\rightarrow$ N$_2$ + HO$_2$, NNH + O$_2$ $\rightarrow$ N$_2$ + H + O$_2$, and thermal decomposition reaction NNH + M $\rightarrow$ N$_2$ + H + M. Reaction of NH radical with nitrogen dioxide and nitric oxide will also lead to the formation of N$_2$ via following reactions: NH + N$_2$O $\rightarrow$ N$_2$ + HNO and NH + NO $\rightarrow$ N$_2$ + OH. The equilibrium product N$_2$ can be recycled back to nitric oxide and NH$_2$ via the reactions; N$_2$ + OH $\rightarrow$ NH + NO and N$_2$ + H$_2$O $\rightarrow$ NH$_2$ + NO. So the final conclusion can be made that the NH$_3$ oxidation and NO$_x$ emissions significantly depends on NH$_2$ radical consumption reactions, and reaction pathway for present analysis can be described as NH$_3$ $\rightarrow$ NH$_2$ $\rightarrow$ H$_2$NO $\rightarrow$ HNO $\rightarrow$ NO.
Figure 8: Reaction pathway analysis of NH₃/air mixture at temperature \(T = 1060\) K, pressure \(P = 40\) bar, and equivalence ratio \(\phi = 1.0\).
3.6 NO\textsubscript{x} Analysis

3.6.1 NO and N\textsubscript{2}O Mole Fraction Validation

Figure 9: Comparison of experimental (Vandooren et al. [64]) and numerical simulation results (using proposed mechanism) of mole fraction variation of species NO and N\textsubscript{2}O at an equivalence ratio ($\phi$) of 1.4 for NH\textsubscript{3}/NO/Ar mixture.

Figure 9 shows the numerical simulation results of variation of mole fraction of species NO, and N\textsubscript{2}O (at equivalence ratio of 1.46) along the axial length of burner calculated using proposed reaction model, and its comparison with experimental results of Vandooren et al. [64]. Vandooren et al. [64] experimentally studied the flame structure of NH\textsubscript{3}-NO flames and mole fraction profile of NO, N\textsubscript{2}O, NH\textsubscript{3}, H\textsubscript{2}O, Ar, NH\textsubscript{2}, H\textsubscript{2}, N\textsubscript{2}, and H species at a pressure and equivalence ratio of 7.2 kPa and 1.46. The test mixture initial composition for NH\textsubscript{3}/NO/Ar flames was 46.1, 47.2, and 6.7\%, respectively. Figure 9 shows the sharp decrease in mole fraction of species NO around the axial length of 0.5 cm, while the peak in N\textsubscript{2}O mole fraction has been observed at the axial length of 0.8 cm. The computational results using the proposed reaction model shows considerably good agreement with the experimental results of Vandooren.
3.6.2 NO Rate of Production Analysis

NO formation in ammonia flames primarily occurs due to the oxidation NH$_x$ (where $x = 0, 1,$ and 2 ) of via HNO intermediate (which can also be seen in figure 8), and the reaction NH$_x$ + NO (where $x = 0, 1,$ and 2 ) leads to the reduction of NO based on the available concentration of O/H radical. The O/H radical concentration will be abundant in lean flames, so lean ammonia flames will lead to higher nitric oxide formation. However, in the rich flames, the O/H concentration will be lower, so it will lead to lower NO production from NH$_x$ (where $x = 0, 1,$ and 2 ) oxidation. In rich flames, the relative concentration of H will increase in the O/H radical pool. So, oxidation of NH$_x$ (where $x = 1, 2,$ and 3 ) will occur by reacting with H atoms and which will produce H$_2$ mainly from NH$_2$, and will finally lead to the formation of nitrogen. Figure 10 shows the nitric oxide rate of production and consumption for ammonia/air flame using the mechanism proposed in this work. Present study observed that the most important reactions for NO formation for stoichiometric and fuel-lean conditions are; HNO + OH $\rightarrow$ NO + H$_2$O, HNO ($+ M$) $\rightarrow$ NO + H ($+ M$), NH + OH $\rightarrow$ NO + H$_2$, HNO + O$_2$ $\rightarrow$ NO + HO$_2$, and for NO consumption are; NH$_2$ + NO $\rightarrow$ N$_2$O + H, NH$_2$ + NO $\rightarrow$ N + H$_2$O, NH$_2$ + NO $\rightarrow$ NNH + OH. However, for the fuel-rich condition the scenario is slightly different from the fuel-lean and stoichiometric. In fuel-rich condition, the reaction HNO ($+ M$) $\rightarrow$ NO + H ($+ M$) is acting as DeNO$_x$ reaction, while, NH$_2$ + NO $\rightarrow$ N$_2$O + H behave as NO formation reaction. The magnitude of thermal NO formation via the reaction N + O$_2$ $\rightarrow$ NO + O is comparatively less for all three examined conditions. The magnitude of total NO production is highest for fuel-lean condition ($\phi = 0.8$), and it start decreasing as condition shifted towards fuel-rich ($\phi = 1.2$). So the conclusion can be made that the amine radical NH$_2$
is a crucial species (it can also be shown from the reaction pathway diagram that the NH$_2$ act as central species and ammonia oxidation chemistry and NO$_x$ emissions significantly depends on it) which can consume nitric oxide and act like a DeNO$_x$ agent and produce nitrogen and water.

Figure 10: Rate of nitric oxide (NO) production of NH$_3$/air mixture at an equivalence ratio ($\phi$) of 0.8, 1.0, and 1.2, $P = 1$ bar, and $T = 298$ K.

This mechanism of NO consumption by NH$_2$ radical is same as the selective catalytic reduction processes. In the case of NH$_3$/air combustion, the fuel-lean condition is not a sensible choice in practical situations due to the higher concentration of NO in combustion products. However, in fuel-rich conditions, the NO formation is significantly less, but the ammonia con-
centres increases in exhaust gas due to its incomplete decomposition.

4 CFD Validation

4.1 Computational Approach

ANSYS FLUENT 2019 R3 [65] is utilized for numerical simulations of premixed combustion process under various operating conditions. Ansys fluent [65] uses the finite volume method (FVM) to discretize the governing partial differential equations into algebraic equations, and an implicit numerical solution scheme is used to solve these equations. The governing partial differential equations for continuity, momentum, energy, and species are shown in equations (4) to (7). Table 4 gives the details of various models and boundary conditions considered in the numerical simulations. The term $\rho$, $u_i$, $\tau_{ij}$, $E_{h,j}$, $m_k$, $D_{k,j}$, $R_k$, $p$, and $h$ represents the density, velocity in the $i^{th}$ direction, stress tensor, energy flux of $x_j$ direction, mass fraction, diffusion flux, and rate of production of species $k$, pressure, and total enthalpy respectively.

Continuity equation:

$$\frac{\partial}{\partial x_i}(\rho u_i) = 0$$

(4)

Momentum equation:

$$\frac{\partial}{\partial x_j}(\rho u_i u_j) + \frac{\partial p}{\partial x_i} = \frac{\partial}{\partial x_j}(\tau_{ij})$$

(5)

Figure 11: Schematic representation of computational domain.
Energy equation:

\[
\frac{\partial}{\partial x_j} (\rho u_i h) + \frac{\partial}{\partial x_j} (E_{h,j}) - (\tau_{ij}) \frac{\partial u_i}{\partial x_j} = (u_j) \frac{\partial p}{\partial x_j}
\]  \hspace{1cm} (6)

Species equation:

\[
\frac{\partial}{\partial x_j} (\rho u_i m_k) + \frac{\partial}{\partial x_j} (D_{k,j}) = R_k
\]  \hspace{1cm} (7)

In the present study, the geometry and other operating parameters for numerical simulations have been considered from the experimental studies of Nakamura et al. [26, 27]. Nakamura et al. [26, 27] studied the combustion and ignition characteristics of weak NH\textsubscript{3}/air flames in a micro flow reactor with varying wall temperature. The wall temperatures for zone 1 and zone 3 have been considered around 300 and 1400 K, while the wall temperature for zone 2 has been considered a function of the axial distance of the micro flow reactor. In numerical simulations, the variation in wall temperature has been considered by writing a user-defined function (UDF) and incorporating it within the solver. The schematic representation of computational domain and employed wall temperature profile considered in the present work can be seen in figure 11 and 12. Table 5 shows the details of the mixture considered in the present study from the experimental study of Nakamura et al. [26, 27] for CFD simulation.
### Table 4: Models / Parameters used in the numerical simulation

<table>
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<th>Item</th>
<th>Model / Parameter</th>
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<td>Elements</td>
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<td>Viscous model</td>
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<tr>
<td>Solver</td>
<td>Pressure based</td>
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<td>Pressure velocity coupling scheme</td>
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<td>Radiation</td>
<td>DO</td>
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<tr>
<td>Spatial discretization</td>
<td>Second order upwind</td>
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<tr>
<td>Absorption coefficient of gas mixture</td>
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<tr>
<td>Convergence absolute criteria for energy and DO equations</td>
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**Boundary conditions**

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<tr>
<td>Premixed mixture inlet pressure &amp; temperature</td>
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<tr>
<td>Micro flow reactor outlet</td>
<td>Pressure outlet</td>
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<td>Wall</td>
<td>Stationary and no slip</td>
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</table>

### Table 5: Details of mixture considered for CFD simulation

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<th>SL.No</th>
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<th>$X(N_2)$</th>
<th>$X(O_2)$</th>
<th>Inlet velocity (cm/sec)</th>
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<td>0.645</td>
<td>0.172</td>
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<td>1.2</td>
<td>0.251</td>
<td>0.592</td>
<td>0.157</td>
<td>10</td>
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</table>
4.2 Grid Independence Test

The accuracy of the numerical solution significantly depends on the accuracy of the mesh. So mesh independence study, or grid independence test, is performed to check the output result’s novelty. A grid independence test is performed by varying the mesh size from coarse to fine and examining each mesh’s output result. The process continues until the test finds the optimum point where output solutions do not change by varying the mesh size at the expense of the least computational cost. This study has considered the grid size of 4000, 10000, and 18000 elements for inlet flow velocity of 0.1 m/sec and $\phi = 1.0$.

![Comparison of mole fraction variation of O$_2$ along the axial length of micro flow reactor for 4000, 10000, and 18000 elements.](image)

Figure 13: Comparison of mole fraction variation of O$_2$ along the axial length of micro flow reactor for 4000, 10000, and 18000 elements.

Figure 13 shows the mole fraction variation of O$_2$ along the axial length of micro flow reactor for 4000, 10000, and 18000 elements, and it has been found that the deviations are minute between 10000 and 18000 elements. Thus, this indicates that the grid of 10000 elements is optimum for computational modeling, and it has been considered for the present computational studies.
4.3 Model Validation

Figure 14 shows the numerical simulation results of variation of mole fraction of species NH$_3$, O$_2$, H$_2$O (at equivalence ratio of 0.8, 1.0, and 1.2) along the axial length of micro flow reactor calculated using proposed reaction model, and its comparison with experimental results of Nakamura et al. [27].

![Figure 14: Comparison of experimental (Nakamura et al. [27]) and numerical simulation results (using proposed mechanism) of mole fraction variation of species NH$_3$, O$_2$, and H$_2$O at an equivalence ratio ($\phi$) of 0.8, 1.0, and 1.2 for NH$_3$/air.](image)

The studies of Nakamura et al. [26, 27] described three types of flame based on the inlet mean flow velocity; weak flames, flame with repetitive ignition and extinction, and steady
flame for low velocity, intermediate velocity, and high-velocity regime, respectively, and spe-
cial attention was paid on the study of steady weak flames. Nakamura et al. [26, 27] observed
the existence of NH₃/air weak flame at a temperature of 1270 K. In our work also, the gas phase
temperature was almost equal to the employed wall temperature even for the reaction zone
(which was observed near the axial distance of 6 cm and temperature of 1270 K in Nakamura
et al. [26, 27] studies) lying in the weak flame regime similar to the observation of [66]. Figure
15 and 16 shows the mole fraction variation contours of species NH₃, O₂, H₂O, and OH along
the axial length of micro flow reactor at equivalence ratio of 0.8, 1.0, and 1.2. Figure 14 shows
the sharp decrease in mole fraction of species NH₃ and O₂ around the axial length of 6 cm and
temperature of 1280 K, while the increase in H₂O mole fraction has been observed for the same
conditions for all three equivalence ratios. In this study, the proposed reaction model was also
able to predict the formation of steady weak flames of NH₃/air premixed mixture within the
computational domain (which can be seen from the OH mole fraction variation contours in fig-
ure 16). The computational results using the proposed reaction model shows considerably good
agreement with the experimental results. The variation of intermediate species like OH, CH₂O,
HCO is a local phenomenon and are subjected to some aberrations. The instabilities in the OH
contours are also inflated at lean conditions where a part of the excess oxygen concentration, as
observed in Figure 15 (a), converts to OH radicals. In the lean premixed combustion systems,
controlling combustion instabilities is a significant challenge. The combustion instabilities in
lean premixed combustion lead to increase in the heat release rates and pressure fluctuations
inside the combustor [67]. The concentration of OH radicals in the mixture is dependent on the
exothermic reactions which are a function of the heat release rate. These fluctuations in the net
heat release rate could lead to the small peaks forming past the single large peak as observed
in Figure 16 (a) for the lean condition as compared to the richer mixture condition. The macro
parameters along-with the emissions are however predicted satisfactorily.

Figure 15: Mole fraction variation contours of species NH$_3$, O$_2$, H$_2$O along the axial length of micro flow reactor at (a) $\phi = 0.8$, (b) $\phi = 1.0$, and (c) $\phi = 1.2$.

Figure 16: Mole fraction variation contours of hydroxyl radical (OH) along the axial length of micro flow reactor at (a) $\phi = 0.8$, (b) $\phi = 1.0$, and (c) $\phi = 1.2$. 
5 Conclusion

In this work, chemical kinetic modeling is presented using a newly proposed reaction model for low-intermediate temperature and high pressure chemistry of ammonia oxidation. The newly proposed ammonia oxidation reaction model is based on the previous available literature for low-intermediate temperature and high pressure ammonia oxidation chemistry. In the literature, several reaction models are available, but they are not able to correctly predict the low-intermediate temperature ammonia chemistry. So in this study, efforts have been made to overcome the above problem, and also a comprehensive validation for autoignition properties have been performed with the reaction mechanism proposed in the present work. The present reaction model consists of 32 species and 259 reactions. The results show that the proposed reaction model closely follows the experimental trends, and lesser inconsistency is observed than other available reaction models. Sensitivity analysis for hydroxyl radical (OH) shows that the reactions \( \text{NH}_2 + \text{NO} \longrightarrow \text{N}_2 + \text{H}_2\text{O}, \text{NH}_2 + \text{NO} \longrightarrow \text{NNH} + \text{O}_2, \) and \( \text{H}_2\text{NO} + \text{O}_2 \longrightarrow \text{HNO} + \text{O}_2 \) plays a crucial role in ignition delay time computation. While, the Sensitity analysis of laminar flame speed shows that the reactions \( \text{O}_2 + \text{H} \longrightarrow \text{OH} + \text{O}, \text{NO} + \text{H} + \text{M} \longrightarrow \text{HNO} + \text{M}, \) and \( \text{NH}_2 + \text{NO} \longrightarrow \text{NNH} + \text{OH} \) are of high importance. However, still there is a difference in opinion are available between the reaction models over the importance of reactions \( \text{NO} + \text{H} + \text{M} \longrightarrow \text{HNO} + \text{M} \) and \( \text{NH}_2 + \text{NO} \longrightarrow \text{NNH} + \text{OH} \).

Ammonia flames possess lower flame speed than conventional hydrocarbon fuels, and the combustion performance of ammonia can be enhanced by blending with the fuel like hydrogen and methane. Computational results show that the NO production was substantially higher in fuel-lean than the stoichiometric and fuel-rich condition, which shows that the equivalence ratio has a crucial impact on NO production. So in practical applications, it is not a sensible choice to use fuel-lean conditions. In the proposed reaction model, the species \( \text{NH}_2, \text{HNO}, \) and \( \text{NNH} \).
plays a significant role in low-intermediate temperature and high pressure ammonia oxidation chemistry and NO\textsubscript{x} emission. The reaction pathway for present analysis can be described as 

\[ \text{NH}_3 \rightarrow \text{NH}_2 \rightarrow \text{H}_2\text{NO} \rightarrow \text{HNO} \rightarrow \text{NO} \].

In this study, the suitability of the proposed mechanism has been evaluated by performing the CFD analysis. Computational analysis has been performed for a premixed NH\textsubscript{3}/air mixture in a micro flow reactor with varying wall temperature at an equivalence ratio of 0.8, 1, and 1.2. In numerical simulations, the variation in wall temperature has been considered by writing a user-defined function (UDF) and incorporating it within the solver. The model validation is carried out by comparing the mole fraction profile of species NH\textsubscript{3}, O\textsubscript{2}, and H\textsubscript{2}O with the available experimental results. The numerical simulation results using the proposed reaction model exhibits considerably good agreement with the experimental results.

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**References**


