

# Kinetic Modeling for NO<sub>x</sub> prediction with improved base Chemistry

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## Introduction

There has been several NO<sub>x</sub> mechanism developed in recent years often dedicated to particular condition of interest. Unlike hydrocarbons, there has not been enough studies for nitrogen related chemistry on experimental and numerical side. Still today we lack reliable rate parameter values, thermochemistry and experimental data base for validating the NO<sub>x</sub> model. Our main objective is to develop kinetic model which covers a wide range of experiments (laminar flame speed, oxidation in jet stirred reactor (JSR), oxidation in plug flow reactor (PFR), shock tube ignition delay time and speciation in burner stabilized flame) for different fuels. An updated kinetic mechanism of H<sub>2</sub> and C<sub>1</sub> system along with NO<sub>x</sub> prediction mechanism has been developed on the basis of an extensive literature review and including wide set of experimental data. The kinetic model has been developed on a hierarchical basis.

## H/N/O KINETIC MODEL AND VALIDATION

A H<sub>2</sub>/O<sub>2</sub> model was developed and validated extensively and alongside N/H/O mechanism was developed. Ammonia (NH<sub>3</sub>) as a carbon-free alternative fuel is taken as the reference fuel in internal combustion devices and developing N/H/O model. Most recently there has been various experimental studies on the NH<sub>3</sub> and H<sub>2</sub>-NH<sub>3</sub> due to which the development and validation of the NO<sub>x</sub> model will be accurate. The two key parameter for fuel combustion laminar flame speed (see Fig 1 (a)) and ignition delay time (see Fig 1 (b)) are numerically investigated for NH<sub>3</sub> in this study. All the simulation were performed using LOGEsoft 1.08.00 [1].

To develop the N/H/O model various fuel mixtures at different conditions have been studied and validated against the wide set of experimental data available from literature. Speciation of the NH<sub>3</sub>-H<sub>2</sub>, NH<sub>3</sub>-H<sub>2</sub>-NO and NH<sub>3</sub>-NO system was studied in burner stabilized flame set-up. Oxidation of H<sub>2</sub>-NO system was studied in the JSR. In flames of NH<sub>3</sub> and NH<sub>3</sub>-H<sub>2</sub> system NO formation is mainly controlled by  $N+O_2 \rightleftharpoons NO + O$  and  $N+OH \rightleftharpoons NO + H$  reactions. NH<sub>3</sub> subsequently decomposes to Amidogen radical (NH<sub>2</sub>) and this radical further decomposes to Imidogen radical (NH) both of which are very reactive species and their reactions with H, O, OH, NO control the overall reactivity of the system. Overall good agreement between the model prediction and experimental data is observed. With the available published experimental data for H<sub>2</sub>-N<sub>2</sub>O system in shock tube and PFR model was validated. H<sub>2</sub> oxidation in JSR in presence of NO was also investigated (see Fig 1 (c, d)). In the NO<sub>x</sub> model reactions of N<sub>2</sub>O and NO<sub>2</sub> with H and O were found to be important for these systems.

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The flame speed of  $\text{NH}_3$  is very low compared to hydrocarbons and may not be well suited for internal combustion engines. However, the laminar flame speed of  $\text{NH}_3$  can be increased by the addition of  $\text{H}_2$  as it is done for hydrocarbons which will promote formation of  $\text{H}$ ,  $\text{O}$  and  $\text{OH}$  radicals. The model shows good agreement with published data (not shown here).

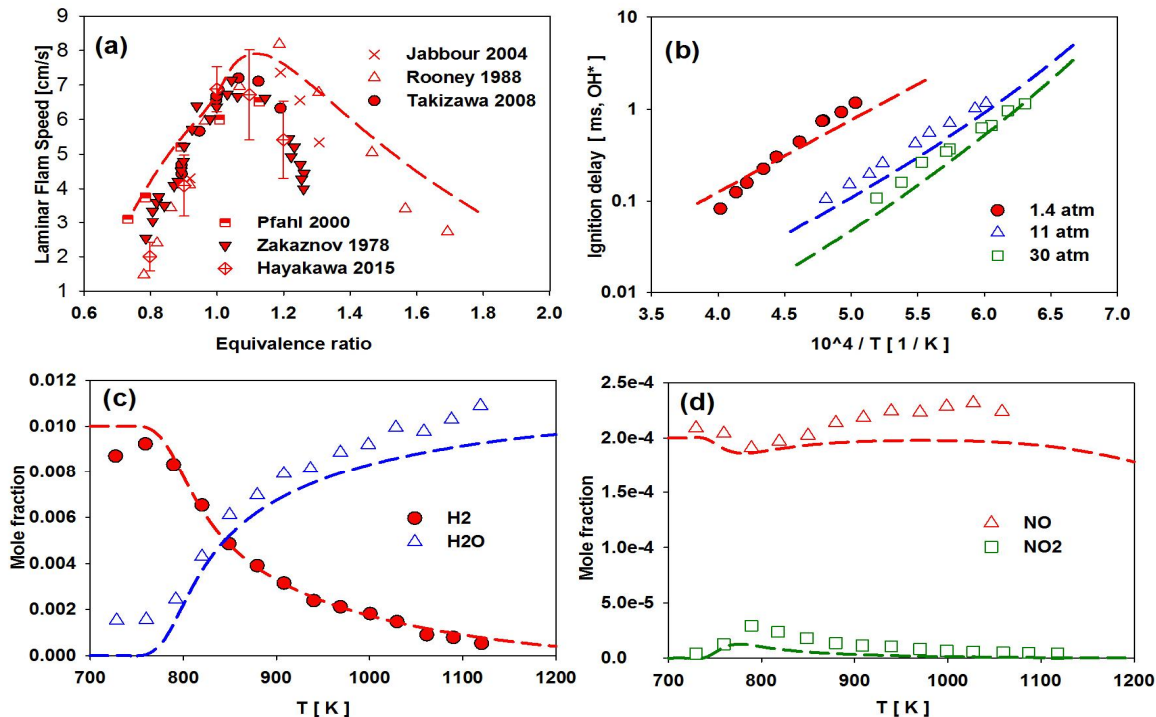


Fig 1: Comparison between model prediction and measurements. Symbols: Experimental data. Lines: model prediction. (a) laminar flame speed of  $\text{NH}_3/\text{air}$  at 298 K, 1 atm [2–6]; (b) ignition delay time of  $\text{NH}_3/\text{O}_2/\text{Ar}(99\%)$ ,  $\Phi=1.0$  [7]; (c), (d)  $\text{H}_2/\text{NO}/\text{O}_2/\text{N}_2$  oxidation in JSR at  $\Phi=1.0$ ,  $p = 10$  atm,  $\tau=1.0$  s [8].

## $\text{C}_1 - \text{NO}_x$ KINETIC MODEL AND VALIDATION

In next phase of our study, N/H/O model was extended to include the  $\text{C}_1$  chemistry and hence new N/H/ $\text{C}_1$ /O model was developed. The model includes carbon monoxide, methane, methanol and formaldehyde as fuels and validated against a wide set of experimental data available from literature.

Special attention was given to the formation and consumption of NO. In flames prompt-NO formation results from the reaction between CH and  $\text{N}_2$  yielding Cyanonitrene (NCN) and H. This NCN radicals reacts with H and O atoms yielding  $\text{HCN}+\text{N}$  and  $\text{CN}+\text{NO}$ , respectively. Sensitivity of thermochemistry on  $\text{NO}_x$  prediction was investigated, especially for NCN radical for which the enthalpy values reported in the literature varies by more than 10 kJ/mol (see Fig 2(b) and Fig 3(a)). Finally based on our study we choose the NCN thermochemistry from the theoretical study of Goos et.al. 2013 [9]. The rate parameter for the two main reactions ( $\text{CH} + \text{N}_2 \rightleftharpoons \text{NCN} + \text{H}$  and  $\text{NCN} + \text{H} \rightleftharpoons \text{HCN} + \text{N}$ ) which are important for the  $\text{NO}_x$  prediction in flames was reviewed based on the experimental and theoretical study from literature (see Fig 2(a)). The product branching ratio of the reactions  $\text{NCN} + \text{H}$  are also of importance which subsequently effects the  $\text{NO}_x$  prediction. In burner stabilized low pressure flames vali-

dation focuses mainly on prompt-NO formation with CH<sub>4</sub> as fuel using data from the literature.

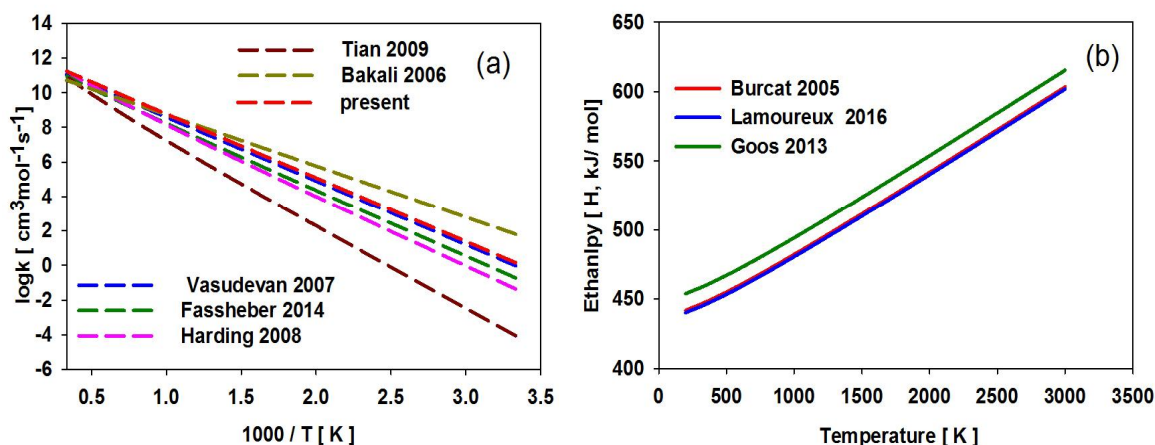


Fig 2: (a)  $CH+N_2 = NCN+H$  rate constant comparison from different authors. Blue [10], Green [11], pink [12], dark red [13], dark yellow [14], red: present rate in this work. (b) NCN Enthalpy comparison between different authors; red [15]: $HF_{298}=445.7$  kJ/mol, blue [16]: $HF_{298}=444.1$  kJ/mol, green [9]: $HF_{298}=457.8$  kJ/mol.

Species profiles of main radicals other than NO (CH, NCN, CN, HCN and NCO) in nitrogen chemistry (see Fig 3(b)) are also taken into consideration for model development and validation. Experiments dedicated to HCN oxidation in a JSR are considered. Ignition delay time of CH<sub>4</sub>/NO<sub>2</sub> and CH<sub>4</sub>/N<sub>2</sub>O mixture in shock tube was also taken into account as development target. Methanol oxidation in presence of NO in JSR [17,18] was also investigated and model performs well at those condition, too.

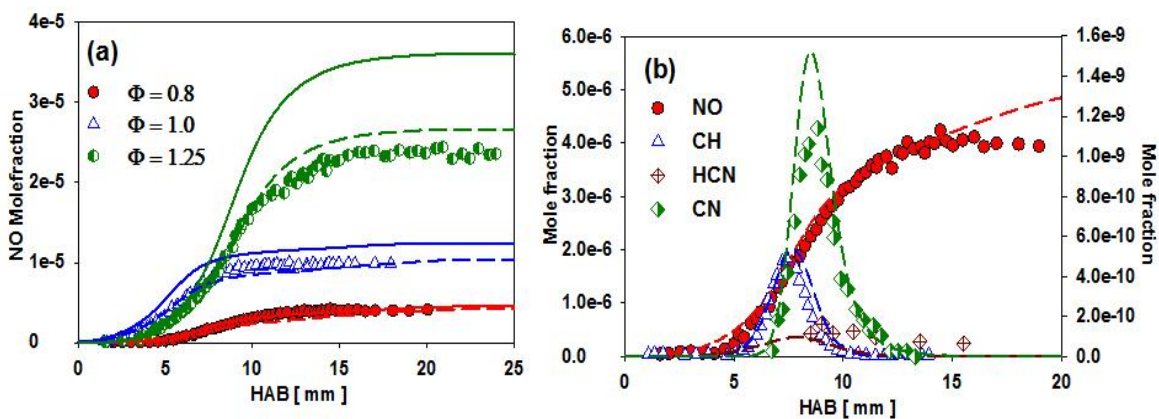


Fig 3: (a) Effect of NCN thermochemistry on NO prediction in CH<sub>4</sub>/O<sub>2</sub>/N<sub>2</sub> low pressure burner stabilized flame. Symbols: Experimental data from [16]. Lines: model prediction; continuous lines: prediction using the NCN thermochemistry of Lamoureux et.al. 2016 ( $HF_{298}=444.1$  kJ/mol) [16]; dash lines: prediction using NCN thermochemistry of Goos et.al. 2013 ( $HF_{298}=457.8$  kJ/mol) [9]. Colour of symbols corresponds to colour of lines. (b) Lines: model prediction using this work; symbols: experimental data from [16] at  $\phi: 0.8$ ,  $p: 5.3$  kPa,  $T: 273$  K, for CN mole fraction right axis.

## Conclusion

An improved N/H/C<sub>1</sub>/O kinetic model was developed and overall there is good agreement between the model prediction and measurements for wider range of experimental conditions. Effect of NCN thermochemistry on prompt NO formation was found to be significant. More accurate and reliable thermochemistry of NCN and other nitrogen related species are of importance to enhance the understanding of NO<sub>x</sub> chemistry and improve kinetic models. The knowledge about rate parameters of reactions related to nitrogen chemistry are limited, so future work should be dedicated for more reliable rate constant values at combustion condition.

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