

# Auto-ignition kinetics of ammonia/hydrogen mixtures at intermediate temperatures and high pressures

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## Abstract

Autoignition properties of  $\text{NH}_3/\text{H}_2/\text{O}_2$  mixtures have been studied in a rapid compression machine (RCM) at pressures from 20 to 60 bar, temperatures from 950 to 1150 K, and at equivalence ratios ranging from 0.5 to 2. The experiments demonstrate that a higher  $\text{H}_2$  mole fraction in the fuel increases the reactivity of the mixture while the equivalence ratio shows different influence. In addition, numerical simulations were performed based on the literature mechanisms from Glarborg et al. (2018), Mathieu and Petersen (2015), and Klippenstein et al. (2011). None of the models can predict the  $\text{NH}_3/\text{H}_2/\text{O}_2$  mixtures satisfactorily.

## Introduction

The concern of over global greenhouse gas emissions has intensified the demand for the development and use of  $\text{CO}_2$ -neutral energy technologies. Searching for alternative fuels with low or zero  $\text{CO}_2$  emissions after combustion and high fuel efficiency is becoming one of the most important research themes. Besides other candidates like dimethyl ether, biofuels, and hydrogen, ammonia is currently attracting attentions because it has a high energy density of 11.5 MJ/L in liquid form and it can be liquefied and stored more easily at 10 bar and 298 K compared to compressed hydrogen (4.5 MJ/L at 690 bar and 15 °C [1]). Ammonia does not produce any soot or  $\text{CO}_2$  during its chemical conversion in a combustion process due to its carbon-free characteristics and it can be produced from renewable energy sources such as solar, wind, and ocean thermal using concepts of power-to-gas [2].

In the last decade, several studies were also carried out for ammonia/hydrogen combustion and several detailed mechanisms were developed [3–9], however, the reactivity of ammonia at wide range of conditions and the emissions of pollutants such as  $\text{NO}_x$  and unconverted  $\text{NH}_3$  during its chemical conversion are still unclear and further investigations are required. The ignition properties of ammonia/hydrogen blends at pressures higher than 20 bar, temperatures between 800 and 1200 K, and equivalence ratios from 0.5 to 2.0 have not been experimentally investigated. Therefore, the objective of this study was to measure ignition delay times for  $\text{NH}_3/\text{H}_2/\text{O}_2$  mixtures in a rapid compression machine (RCM) under the mentioned conditions. The obtained data were then compared to the literature mechanisms [5,7,9].

## Methods

The rapid compression machine (RCM) experiments were performed at Physikalisch-Technische Bundesanstalt (PTB). A detailed description of the RCM setup can be found in Ref. [10]. In this work, test mixtures were prepared manometrically in a 10 L stainless steel tank at room temperature. Argon and nitrogen were used as bath gas to obtain the appropriate value of the compressed gas temperature. The mixtures were allowed to homogenize overnight before performing the ignition delay experiments. Table 1 summarizes the details of the mixtures studied in this work. The dilution of all mixtures was 70% applying Ar or

Ar/N<sub>2</sub> blend. The ignition during the experiments was monitored via a Kistler pressure transducer installed on the side wall of the reaction chamber. The ignition delay time (IDT) is defined as the interval between the end of compression and the ignition point.

The three mechanisms of Mathieu and Petersen [5], Klippenstein et al. [9], and Glarborg et al. [7] were applied for the kinetic modeling in this study. The simulations in this work were performed using an in-house Cantera code based on a homogeneous reactor at constrained volume taking the non-ideal facility effects in to consideration.

Table 1: Details of the neat ammonia and ammonia/hydrogen blends investigated in this work

No.	H <sub>2</sub> in fuel	Equivalence ratio ( $\phi$ )	Pressure (bar)	Temperature (K)
1	20%	0.5 – 1.5	20	960 – 1050
2	10%	1.0	20	980 – 1060
3	5%	0.5 – 2.0	20	1000 – 1130
4	5%	0.5 – 2.0	40	970 – 1040
5	1%	0.5 – 1.5	40	1030 – 1100
6	0%	1.0	40	1025 – 1130

## Results

Figure 1 presents the comparison between the measured IDTs of NH<sub>3</sub>/H<sub>2</sub> blends with equivalence ratio of 1.0 at 20 and 40 bar. The IDTs of the mixtures containing 0% and 1% H<sub>2</sub> in fuel are only compared at 40 bar because both mixtures showed no ignition at 20 bar up to 1100 K. The IDTs of the mixtures with 10% and 20% H<sub>2</sub> in fuel are only compared at 20 bar because the high content of hydrogen led to much faster ignition at 40 bar and the IDTs (< 5 ms) cannot be reliably determined in the RCM.

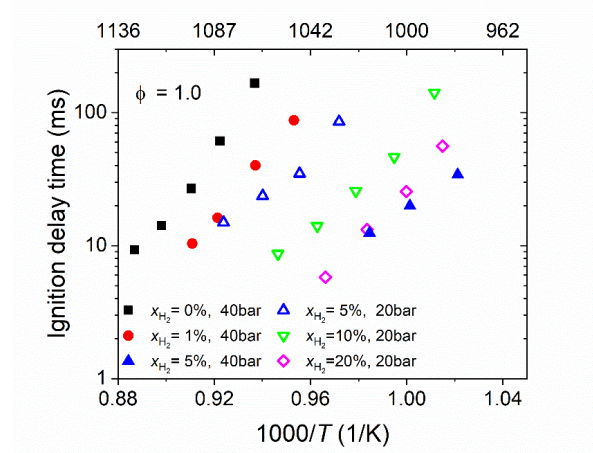


Figure 1: Effect of the NH<sub>3</sub>-H<sub>2</sub>-ratio on the ignition delay time,  $\phi=1$ .

The addition of H<sub>2</sub> shows strong promotion on the reactivity of NH<sub>3</sub>. At 40 bar, the measured IDTs of the mixture containing 1% H<sub>2</sub> in fuel are shorter than that of pure NH<sub>3</sub> with a factor of 3 and ignition starts at lower temperature. The ignition onset of the blend with 5% H<sub>2</sub> in fuel is further shifted to lower temperature, *i.e.*, 970 K, that is nearly 100 K below that of the pure ammonia mixture which begins to ignite at 1064 K. A similar behavior can be observed for the ignition delay times measured at 20 bar. Note that the measured IDTs of the mixture having 20% H<sub>2</sub> in fuel at 20 bar are almost the same as that of the blend containing 5% H<sub>2</sub> in fuel at 40 bar. Moreover, by comparing the ignition delay of mixture with 5% H<sub>2</sub> in fuel at

both 20 and 40 bar directly, one can see that the increased pressure leads to a higher reactivity and reduces the ignition delay times of the mixture by a factor of 10.

Simulations were performed based on the mechanisms from Klippenstein et al. [9], Mathieu et al. [5], and Glarborg et al. [7] and shown in Figure 2. In general, the IDTs decrease with decreasing equivalence ratio for the 1% H<sub>2</sub> in fuel mixture while for the 20% H<sub>2</sub> in fuel blend case an opposite trend is observable, *i.e.*, the IDTs increase with decreasing  $\phi$ . All three models can capture well this different tendency on ignition for both NH<sub>3</sub>/H<sub>2</sub> blends. The simulations based on the Klippenstein et al. mechanism shows better agreement to the experimental data especially for the 1% H<sub>2</sub> blend. For the 5% H<sub>2</sub> cases, equivalence ratio shows interesting effect on the IDT, *i.e.*, the stoichiometric mixtures have the shortest IDTs. None of the three mechanisms are capable to predict the experimental data satisfactory. Although the measurements show large difference between each condition, the simulated IDTs from all three mechanisms are very close to each other without a clear equivalence ratio dependency.

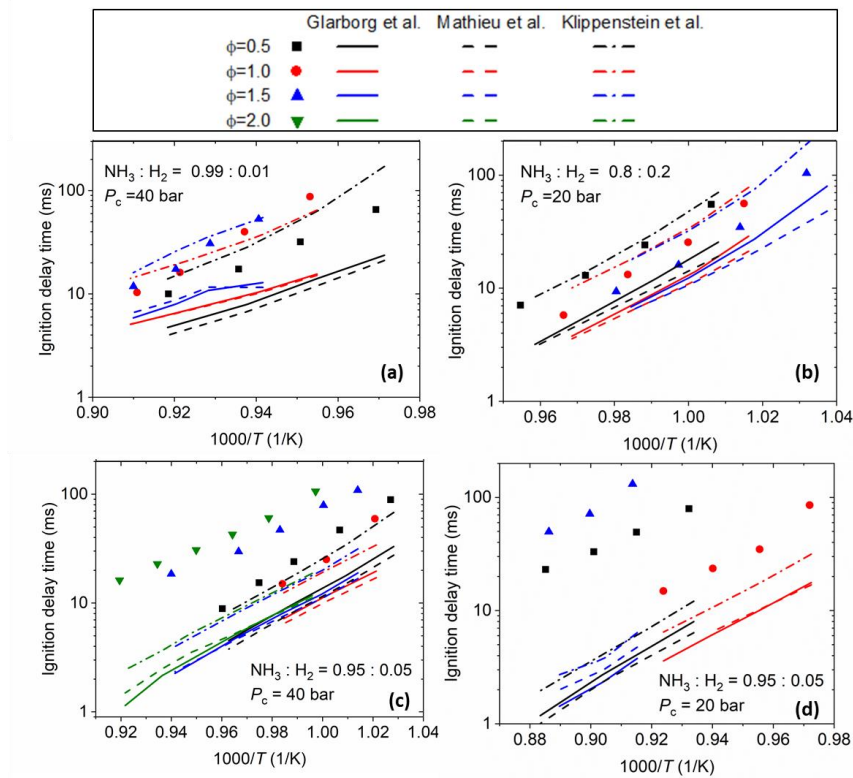


Figure 2: Comparison between the simulated and measured IDTs of the NH<sub>3</sub>/H<sub>2</sub> mixtures.

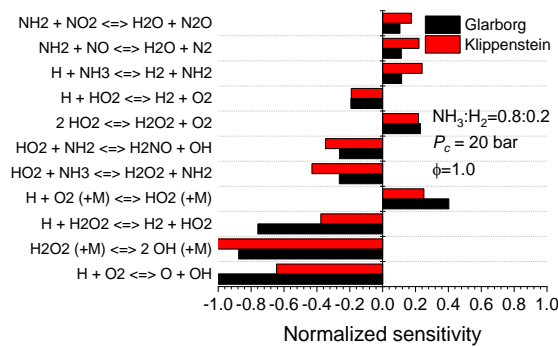


Figure 3: Sensitivity analysis for ignition delay time of NH<sub>3</sub>/H<sub>2</sub> mixture at 998 K.

A sensitivity analysis (SA) on the ignition delay was performed based on the mechanisms of Klippenstein et al. [9] and Glarborg et al. [7] as shown in Figure 3. The negative value indicates the promoting effect on the ignition while the positive value indicates an inhibiting effect. The most important reactions that are sensitive to IDT from both mechanisms are similar. However, the  $\text{H}_2\text{O}_2$  related reactions show more significance in promoting the ignition in the Glarborg et al. mechanism than in the Klippenstein et al. and make the Glarborg et al. mechanism overreactive comparing to the measurements.

## Conclusion

The auto-ignition kinetics of ammonia/hydrogen blends were investigated in a RCM at elevated pressures (20, 40, and 60 bar), within a temperature range varying from 950 to 1150 K, and equivalence ratios from 0.5 to 2.0. The experimental results demonstrate that a higher  $\text{H}_2$  mole fraction in fuel improves the reactivity of the mixture effectively. When the mixtures contain 20%  $\text{H}_2$  in fuel, fuel-richer mixtures have shorter ignition delay times, while for the mixtures with 1%  $\text{H}_2$  the equivalence ratio dependence is reverse. Simulations were performed based on the mechanism of Glarborg et al. [7], Mathieu et al. [5], and Klippenstein et al. [9]. In the investigated temperature range mechanism from Klippenstein et al. works better than the other both but none of the models can capture the measured IDTs satisfactorily.

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