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COMPARISON OF KINETIC MECHANISM PREDICTIONS OF IGNITION DELAY TIME AT HIGH PRESSURE FOR PARTIALLY-CRACKED AMMONIA

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Abstract

Ammonia, as a fuel, possesses certain combustion properties that are insufficient for efficient burning when used alone. This limitation necessitates methods to enhance its combustion, one of the primary strategies being to blend ammonia with hydrogen. Another approach involves to partially crack ammonia on board, which releases hydrogen and nitrogen. These methods improve the fuel's combustion properties, making it more suitable for practical applications. However, when considering the use of ammonia in internal combustion engines, the challenge becomes more complex due to factors like high temperature and high pressure within the combustion chamber that can lead to knock phenomena, a condition that occurs due to the auto-ignition of end-gases. This knocking can significantly impact engine performance and longevity, making it a critical consideration in the design of future ammonia-powered engines. Therefore, to ensure the successful implementation of ammonia as a fuel, it is crucial to have accurate predictions of its combustion characteristics. Key parameters such as laminar flame speed and auto-ignition delay must be precisely modelled using kinetic mechanisms. Understanding these characteristics is essential for optimizing engine design and ensuring efficient, safe operation. In this context, the present work contributes to the field by measuring ignition delays using a Rapid Compression Machine. This method provides experimental Ignition Delay Times (IDTs) that can be used to evaluate and compare the accuracy of different kinetic mechanisms. The development of a methodology for such comparisons represents a significant step forward in the quest to design effective ammonia-based combustion systems. By refining these predictive models, engineers can better anticipate how ammonia will behave under various conditions, ultimately leading to the development of more efficient and reliable ammonia-powered engines.

Keywords: Ammonia, Ignition Delay Time, Rapid Compression Machine, Partially cracked ammonia, Hydrogen.

Introduction

Today, the need to replace fossil fuels is more urgent than ever. Ammonia is considered more and more as a serious candidate, serving both as a hydrogen carrier and as a carbon-free fuel, due to its extensive synthesis, ease of transport, and storage capabilities. To improve its combustion properties, ammonia can be blended with more reactive fuels as hydrogen (H₂) or partially cracked (NH₃ → 3/2 H₂ + 1/2 N₂) although this tends to promote knock phenomena. To predict this issue, Ignition Delay Times (IDTs) must be accurately simulated at engine relevant conditions, i.e. high pressures (40-70 bars) and moderate temperatures (950 to 1050 K). While the literature provides some IDTs for pressures between 40 and 70 bars [1] for pure ammonia, data for 5 to 10% cracked ammonia is lacking. In this study, a Rapid Compression Machine was employed to expand the existing database within this pressure range at moderate temperatures for ammonia mixed with hydrogen, to identify kinetic mechanisms that align accurately.

Materials and Methods

Experiments were conducted using a Rapid Compression Machine (RCM), which can compress gas in under 33 milliseconds, as detailed in [2]. A significant advancement was made in the crevice volume and shape to better absorb the vortices generated by the piston's movement along the boundary layer of the cylinder liner. This RCM is pneumatically driven, featuring a stroke length of 300 mm and a bore diameter of 50 mm. Dead volumes can be adjusted using additional spacers to achieve the desired compression ratio of 11.75. The piston is decelerated near the top dead center in an oil chamber. The RCM is equipped with a Kistler 6054BRU59-3-1 pressure sensor, which has a range of 0-300 bars and a linearity of 0.2%, to ensure accurate pressure measurements. To provide consistent experimental data and perform simulations, experiments were carried out in two main campaigns. Thermal losses are identified by recording pressure evolution for non-reactive blends, where oxygen (O₂) was replaced by nitrogen (N₂) to prevent oxidation reactions while maintaining equivalent global heat capacity. In the reactive blends, nitrogen content in the air was replaced with argon to achieve higher temperatures, as argon's heat capacity is half that of nitrogen. Details of the different reactive blends used in the experiments are provided in Table 1. As shown in Figure 2, the pressure evolutions for non-reactive and reactive mixtures are depicted in light and dark blue, respectively. In the reactive case, oxidation occurs, resulting in a sharp increase in pressure. From this data, the Ignition Delay Time (IDT) can be measured using the following definition: t_{EOC} represents the time at the End Of Compression (EOC) and $t_{\max(\text{grad}(P))}$ represents the time at which the pressure gradient value is maximum.

Simulations are performed using ChemKin Pro ANSYS software. Reactive initial conditions, pressure evolutions from non-reactive compositions, and the tested kinetic mechanism are implemented in the Closed Homogeneous Batch Reactor module to obtain the simulated Ignition Delay Time (IDT), represented by the red curve in Figure 1.

$$IDT = t_{max(grad(P))} - t_{EOC}$$

The closer this simulated IDT is to the experimental IDT, the more accurate the mechanism. To rank kinetic

mechanisms, the quantification method previously described in Hurault & al. [4] was used. This method computes the relative discrepancy between experimental and simulated IDTs for each set, described below:

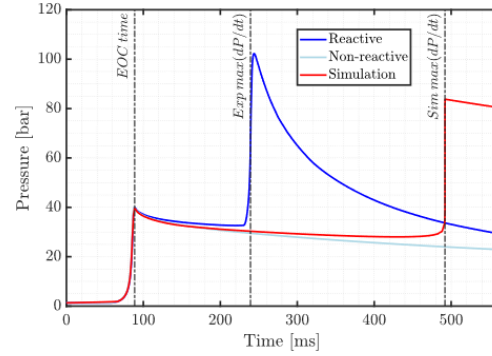


Figure 1 : Example of pressure profile. Measured reactive pressure trace in dark blue, measured non-reactive pressure trace in light blue and simulated reactive pressure in red. End of compression (EOC) is notified with the dotted line crossing the traces at pressure of compression, here 40 bars.

Table 1: Precise table that describes molar fractions of the species, in percentages with their uncertainties, used at different pressure and temperature of compression.

Cracked[%]	Φ	NH ₃ [%]	N ₂ [%]	H ₂ [%]	Ar [%]	O ₂ [%]
0	0.5	12.281(+0.251, -0.124)	0	0	69.298(+0.473, -0.220)	18.421(-0.188, -0.372)
0	1	21.875(+0.378, -0.160)	0	0	61.719(+0.511, -0.132)	16.406(-0.291, -0.493)
0	1.5	29.579(+0.355, -0.059)	0	0	55.633(+0.094, -0.306)	14.788(-0.288, -0.436)
5	1	21.193(+0.105, -0.106)	0.279(+0.001, -0.001)	0.832(+0.003, -0.005)	61.379(+0.306, -0.307)	16.315(+0.060, -0.103)
10	0.5	11.608(+0.057, -0.057)	0.319(+0.002, -0.002)	0.959(+0.004, -0.006)	68.819(+0.345, -0.344)	18.295(+0.070, -0.113)
10	1	20.484(+0.102, -0.103)	0.568(+0.003, -0.003)	1.716(+0.007, -0.010)	61.014(+0.305, -0.305)	16.218(+0.059, -0.103)
10	1.5	27.592(+0.137, -0.138)	0.768(+0.004, -0.004)	2.294(+0.009, -0.014)	54.786(+0.273, -0.274)	14.560(+0.051, -0.094)

$$E_{\Phi,P,T} = 100 \cdot \frac{abs(\tau_{\Phi,P,T,l}^{sim} - \tau_{\Phi,P,T}^{exp})}{\tau_{\Phi,P,T}^{exp}} ; E_{\Phi,P} = \frac{1}{N_T} \sum_{\theta \in T} E_{\Phi,P,\theta} ; E_{\Phi} = \frac{1}{N_P} \sum_{p \in P} E_{\Phi,p}$$

Results and conclusions

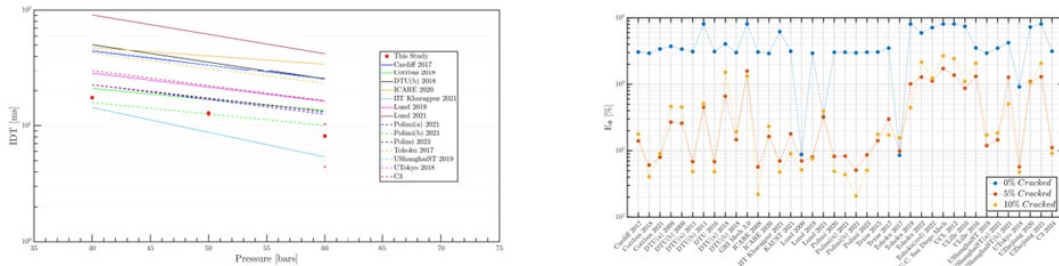


Figure 2: Representation of experimental Ignition delay time (red square) and simulated ones from some kinetic mechanisms (coloured line) for $\Phi = 1$ and $T=950$ K (left) Representation of E_{Φ} for all mechanisms considered for pure ammonia (blue), 2.5% cracked (red) and 5% cracked (orange) (right) at $\Phi = 1$

Figure 2 on the left provides an example of Ignition Delay Times (IDTs) as a function of pressure. Red squares represent the experimental average of an IDT set, while red filled circles indicate the minimum and maximum values of the experimental set. The colored lines represent simulations from various kinetic mechanisms. In this case, the 'Polimi (b) 2021' mechanism predicts IDTs accurately, while most other mechanisms overestimate IDTs at 950 K and $\Phi = 1$. Figure 2 on the right illustrates the accuracy of the mechanisms in predicting experimental results: the lower E_{Φ} , the better the prediction. Almost all mechanisms show improved predictions for cracked ammonia compared to pure ammonia. However, increasing the percentage of cracked ammonia to 10% does not necessarily result in better predictions. For some mechanisms, predictions are more accurate with 5% cracked ammonia than with 10%. Nevertheless, when partially cracked ammonia is included, many mechanisms predict IDTs with less than 100% relative error.

Conflicts of Interest

The authors declare no conflict of interest.

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