SHORT TERM SCIENTIFIC MISSION (STSM)
SCIENTIFIC REPORT

This report is submitted for approval by the STSM applicant to the STSM coordinator

Action number: CM1404
STSM title: Study on the ignition delay times of diluted mixtures of ammonia at elevated pressures
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PURPOSE OF THE STSM:

Ammonia is currently being investigated as an alternative fuel that does not release carbon-based pollutants. At IST, research has been conducted regarding the combustion of this fuel and its mixtures with methane and hydrogen. Although it was found that combusting ammonia alone presented great flammability challenges, these were overcome by adding other fuel constituents. However, there is still a lack of knowledge regarding the ignition of ammonia and such mixtures. Therefore, the purpose of this STSM was to conduct research on the ignition properties of mixtures of ammonia with methane, by studying their ignition delay times (IDT) at elevated pressures. To achieve this, gas mixtures were compressed to high pressures, and the time interval between the end of compression and the onset of ignition was measured. This allowed to draw conclusions regarding the reactivity of these mixtures and to evaluate the influence of several variables, such as the content of methane in the mixture, pressure, and equivalence ratio. This could help pave the way for practical applications of ammonia in internal combustion engines. Additionally, these results were compared with numerical chemical kinetics simulations, with the future goal of achieving a mechanism that is validated for different types of data.

DESCRIPTION OF WORK CARRIED OUT DURING THE STSMS

The experiments were conducted in a rapid compression machine (RCM) at the Physikalich-Technische Bundesanstalt (PTB). The machine has 3 chambers: the reaction, the hydraulic and the pneumatic chamber. To compress the gases, a single creviced piston is used, which is pneumatically driven and hydraulically braked. A pressure and a temperature sensor are positioned into the ports surrounding the reaction chamber. The sample mixtures were prepared manometrically in 10 L stainless steel tanks at room temperature, with argon and nitrogen being used as diluent gases. The content of ammonia in the fuel mixture represented a molar fraction of 0.8 and 0.9, with a molar fraction of methane in the fuel mixture of 0.2 and 0.1, respectively. The equivalence ratio (ϕ) was varied between 0.5 and 2. For all cases, the dilution applied was of 70% (either Ar only or a Ar/N_2 blend), and all measurements were conducted for pressures of 20 and 40 bar, and temperatures between 920 and 1100 K.
The mixtures were allowed to homogenise overnight before the experiments to guarantee mixing uniformity in the tank. Different ignition temperatures were achieved by either increasing the initial pre-compression temperature (heating the complete setup) or increasing the amount of N_2 present in the dilution of the gas mixtures (which allows reaching lower temperatures). The experiments were compared with previous results for pure ammonia, measured in the same RCM setup.
Throughout the experiments, the ignition was monitored via a pressure transducer placed on the inside wall of the reaction chamber. The pressure history allows for the observation of the mechanical compression and expansion of the gases due to ignition. The ignition delay time (IDT) is defined as the time interval between

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the end of the mechanical compression (EOC) and the ignition point (which is defined as the point for which the derivative of the pressure history is maximum after the EOC). By comparing this time interval across different mixtures and experimental conditions, it was possible to analyse the influence of each of the variables in the reactivity of the gas samples.
These experimental results were used for comparison with numerical predictions. Three chemical kinetics mechanisms, by Glarborg et al., Konnov, and Mendiara et al., were employed together with Cantera (an open-source software for chemical kinetics and thermodynamics calculations) in an internally developed code. The simulations were performed based on a homogeneous reactor at constrained volume. Since the RCM is not an ideal constant volume reactor, a volume profile was generated using the adiabatic core assumption, applying a pressure trace of a non-reactive mixture under similar conditions as in the reactive mixtures.

DESCRIPTION OF THE MAIN RESULTS OBTAINED

The experiments in the RCM allowed for the understanding of the influence of the different variables. It was found that the effect of equivalence ratio on the IDT is consistent for all mixtures, regardless of pressure, with the increase in ϕ leading to a rise in the duration of the ignition delay, for the same temperature. This trend can also be interpreted in a different manner: for fuel-rich mixtures to achieve the same IDT as fuel-lean mixtures, the ignition temperature must be increased. The differences in IDT due to the equivalence ratio were larger for mixtures with higher content of ammonia in the fuel mixture.
It was also found that, for a fixed equivalence ratio, as the quantity of NH_3 in the fuel mixture increases, the ignition onset is progressively delayed. Thus, to achieve equal ignition delay times, higher temperatures are required for higher content of NH_3 in the fuel mixture. Contrastingly, the effect of the addition of CH_4 is visible in the widening of the temperature intervals where ignition occurs and in facilitating its occurrence at lower temperatures, thus increasing the reactivity of the mixture.
In addition, it was observed that an increase in pressure leads to faster ignition, regardless of fuel composition and equivalence ratio.
Regarding the numerical chemical kinetics simulations, the three chosen mechanisms were able to predict successful ignition onset for all conditions, although with different outcomes. The mechanism by Konnov under-predicted the measurements, while the mechanisms by Glarborg et al. and Mendiara et al. were capable of matching more closely the experimental results. Between these two, the values calculated by the Glarborg et al. mechanism are higher for stoichiometry and fuel-rich conditions, although they are lower than the results by the Mendiara et al. mechanism for fuel-lean. Overall, bearing in mind the presented data, the mechanism by Glaborg et al. presents the most potential to be improved in the future.
Nevertheless, research in high pressure, low temperature combustion is still a novelty, and more experimental data is needed to validate chemical kinetics mechanisms and usher in the practical use of ammonia in internal combustion engines.

FUTURE COLLABORATIONS (if applicable)

The work developed in this STSM serves as the basis for a comprehensive study with a goal of developing a chemical kinetics mechanism for ammonia chemistry to be validated with ignition delay, emissions and temperature data. This will allow for a widespread use of such mechanism in practical scenarios. In this sense, work is still needed and future collaborations will be useful in analysing the main reactions that contribute to the reactivity of these fuel mixtures and the main pathways in the formation of reaction products. With this information, it will be possible to collaborate in modifying an underlying mechanism (such as the one by Glarborg et al.), for which solid knowledge in chemical kinetics would be beneficial.
On the other hand, different mixtures of ammonia with other alternative fuels (such as bio-diesel or syngas) could also be studied in the sense of understanding their ignition properties, following the same experimental and numerical campaign as developed in this work. The more diverse the experimental data, the better the validation for chemical kinetics mechanisms, and these mixtures have not yet been studied in this manner.
As such, the possibilities for collaboration are multiple and open to several research partners, since there is still much work to be done in this field, both experimentally and numerically.