SMARTCATs COST Action

Short Term Scientific Mission Report
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Details of STSM :

STSM title: Low Temperature Auto-Ignition of Ammonia
Period: 2017-10-01 to 2017-12-15

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Host Institution: Physikalisch-Technische Bundesanstalt, Braunschweig, Gernany

Introduction

The STSM program was pursued with Physikalisch-Technische Bundesanstalt to gain expertise in the field of the auto-ignition characteristics of $NH_3/H_2/O_2/N_2$/Ar gas mixtures in low and intermediate temperature range.

The EU regulation 443/2009/EC for reducing greenhouse gas emissions sets the average CO_2 emission for new passenger cars to 130 g/km. From 2020 onwards, this regulation limits the average CO_2 emissions to 95 g/km. In order to achieve this goal, new alternative fuels need to be considered and established in the market. Ammonia is a potential alternative which is carbon free and therefore produces no soot and CO_2 during its chemical conversion process.

Ammonia has higher hydrogen density and thus a promising green energy storage carrier. It also has significant other advantages over hydrogen especially in terms of energy density. Liquid ammonia can be stored in existing infrastructure at ambient conditions of (-33.4 °C and 1 bar) compared to hydrogen (-252 °C) [1]. It is a convenient hydrogen carrier due to the easy storage and transport handling. However, for its potential future use in advanced combustion and energy conversion devices much research is still needed, for example , the knowledge on its auto-ignition properties.

The objective of this program is therefore to investigate the auto-ignition characteristics of $NH_3/H_2/O_2/N_2$/Ar mixtures in a rapid compression machine, develop a reliable kinetic model and validate using an extensive dataset for auto-ignition delays. Therefore, experiments were performed for End of Compression (EOC) pressures around 10, 20 and 40 bar, for temperatures of 950–1100 K, and for equivalence ratios of 0.5. The obtained results were compared to a chemical kinetic mechanism from literature [2-4].

Description of the experiment device

Rapid compression machine (RCM) experiments were performed at Physikalisch-Technische Bundesanstalt (PTB). The design is similar to Mittal et al. [5]. The single piston rapid compression machine is pneumatically driven and hydraulically braked. The RCM consists of three chambers, namely reactor, hydraulic and pneumatic chamber. The reactor chamber has an inside diameter of 50 mm and consists of 6 ports for pressure sensor, gas inlet and exhaust gas outlets. The reactor chamber has a maximum working tolerance of 200 bar and with an operating temperature range of 600 – 1100 K. The design allows creviced piston to compress the gas in reactor chamber, which is driven by an arrangement of pneumatic piston and high-pressure air tank. A solenoid valve connected to the hydraulic chamber and oil reserve chamber was triggered to release the hydraulic pressure to move the piston forward. Towards the end of the compression stroke, the piston is smoothly decelerated and finally stopped by the piston stopping groove. The rapid compression machine was designed with a variable volumetric ratio, through the interchange of the end wall inserts resulting in the change of distance between the piston front and the end wall at the top dead center position.

Heating tape was used to vary the initial temperature of the gas mixtures from 296 K to 363 K. The initial temperatures of the mixture and combustion chamber were measured by a Pt-Rh thermocouples located at the wall of the combustion chamber and the mixing cylinder. This ensures a homogeneous initial temperature and also allows the RCM to study various initial temperatures. The pressure time histories were measured using a Kistler (601H) pressure transducer with charge amplifier (Type 5018) and is recorded using a Spectrum data acquisition card (M2i.3016-Exp).

Test mixtures were first prepared manometrically in a stainless-steel tank at room temperature by using MKS Baratron pressure gauges to measure the partial pressures of the gases. The steel tank was cleaned with bath gases to remove impurities before filling the final mixture. Argon and nitrogen were used as bath gases in the RCM experiments to obtain the appropriate value of the equivalence ratio (ϕ) and the compressed temperature

(T_c). These gaseous mixtures were allowed to homogenize in steel tank for around 12 hours before transferring them to reactor chamber. Fig. 1 represents a typical pressure trace recorded for the probe gas mixture compressed to a peak pressure (P_c) indicates the end of compression (EOC) followed by a slow pressure drop due to heat losses to the reactor walls until a second pressure rise indicating onset of ignition. Ignition delay is defined as the time between the end of compression to start of ignition.

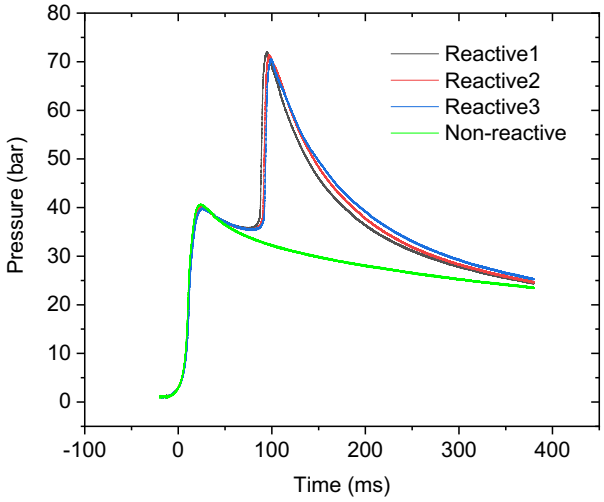

Fig.1 Representative pressure-time profile for RCM investigations
P_0=1.144bar, T_0=306K, P_c=40bar, T_c=975K, ϕ=0.5, H2 in fuel=5%
Reactive mixture was repeated three times and non-reactive mixture once

In order to account heat losses in the RCM, a number of non-reactive experiments were conducted by replacing O_2 content of reactive mixture with N_2. Heat capacity values of O_2 and N_2 are quite similar, which doesn't change the heat capacity of the reacting and non-reactive mixtures. Nonreactive pressure traces are used in 0-D simulations. The direct measurement of the temperature inside the RCM is not possible due to the short ignition delay process. Therefore, an indirect method is used to determine the compressed temperature (T_c) by using the experimental pressure trace. T_c was determined by considering adiabatic core hypothesis.

Results and Discussion

Five different mixtures were chosen to investigate the ignition characteristics of pure Ammonia or NH3/H2 blend gas. The compositions of the mixtures are listed in the following table.

Table 1 Compositions of gas mixtures investigated

	H2 in fuel	Equivalence ratio	Dilution	Ar in dilution	N2 in dilution	comment
MIX1	20%	1	95%	60%	40%	no ignition
MIX2	20%	0.5	70%	100%	0%	
MIX3	10%	0.5	70%	100%	0%	
MIX4	0%	0.5	70%	100%	0%	no ignition
MIX5	5%	0.5	70%	100%	0%	

Although the initial condition already reached high EOC pressure (40bar) and temperature (1050K), mixture 1 and 5 were not able to ignite because of high dilution and no hydrogen in the mixtures, respectively. According to the experimental results of the other three mixtures, the influence of pressure and H_2 concentration on the ignition delay of NH3/H2/O2/Ar gas mixtures can be found. In the following figures (Fig.2-4) the experiments results will be presented in comparison with the simulation results using the mechanisms of Mathieu and Petersen [2], Dagaut et al. [3] and Klippenstein et al. [4]. Numerical calculations are performed using an inhouse Cantera code by giving a wall velocity profile into the constant volume reactor to compensate the heat loss during and after compression in RCM.

For MIX2 (H2 in fuel: 20%), the experiments were conducted under P_c=10bar and 20bar. With higher pressure the mixture shows higher reactivity. Furthermore, the repeatability in lower pressure condition is not as good as in higher pressure condition. The simulation results using different mechanisms deviate clearly, but the trends of each mechanism are similar. Comparing the magnitude shows that klippenstein's mechanism is close to the experiment results.

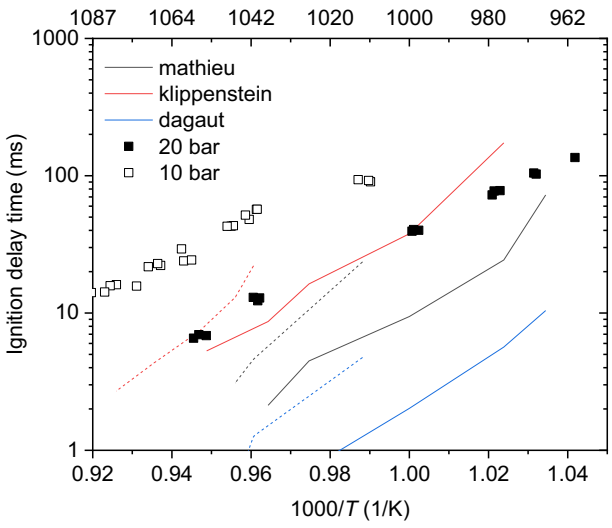

Fig.2 Effects of the pressure on the ignition delay time of MIX2

(Symbols refer to experimental data in this work. Lines correspond to modeling, solid line: Pc=20 bar, dash line: Pc=10 bar)

For MIX 3 (H2 in fuel: 10%) the experiment was only conducted at Pc=20bar. The experimental points show very good linearity in the observed temperature range. The simulation results are similar to that of MIX2.

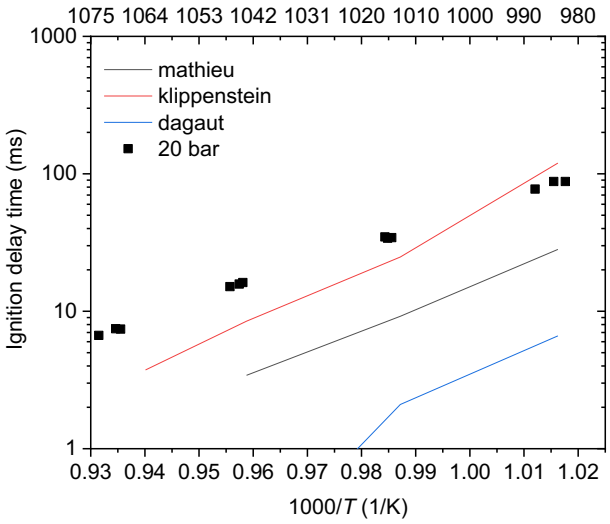

Fig.3 Ignition delay time of MIX3
(Symbols refer to experimental data in this work. Lines correspond to modeling)

For MIX5 (H2 in fuel: 5%) the experiments were performed under Pc=20bar and 40bar. The pressure in this case plays an more important role on the ignition delay time than in MIX2. Higher pressure reduces the ignition delay significantly. Different from last two mixtures, the simulation results of each mechanism present similar slopes to the experiments, but even klippenstein's mechanism obviously under-predicts the magnitude.

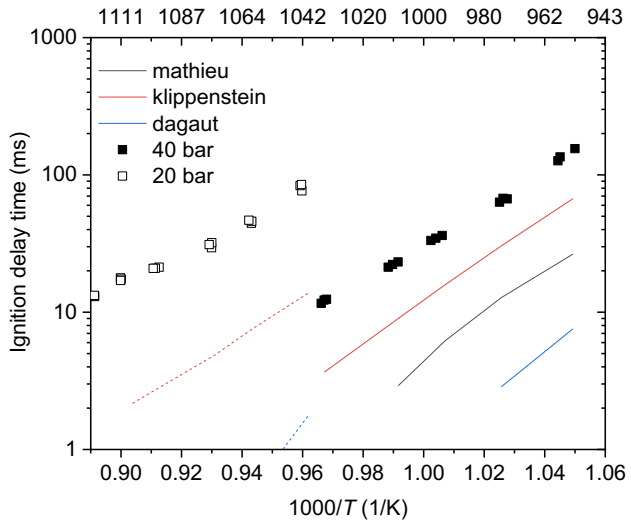

Fig.4 Effects of the pressure on the ignition delay time of MIX5

(Symbols refer to experimental data in this work. Lines correspond to modeling, solid line: Pc=40 bar, dash line: Pc=20 bar)

Comparing these three mixtures (Fig.5) under a same pressure shows the influence of hydrogen concentration. The interval between the ignition delay of 5% and 10% hydrogen concentration is much larger than the one between 10% and 20% hydrogen concentration. Hydrogen in fuel improves the reactivity of the mixture very significantly, but this effect is weaker when the hydrogen concentration is higher than 10%.

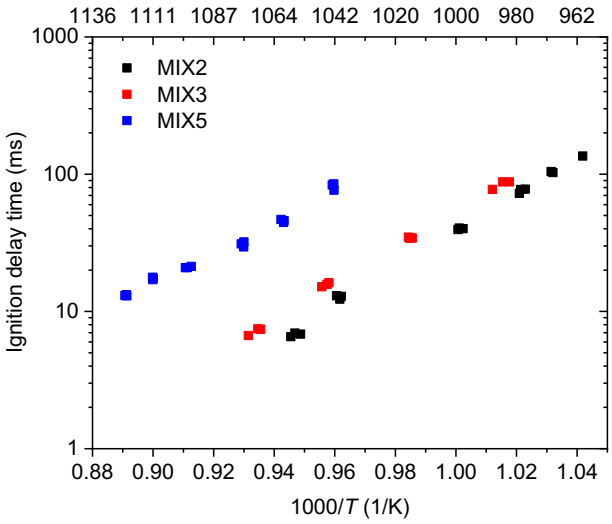

Fig.5 The influence of Hydrogen concentration on the ignition delay time of blend gas

Future collaboration with host institution

The host institution (PTB) will continue to collaborate with IST on Ammonia combustion in the future. Both institutions have agreed to perform further experiments with ammonia and ammonia enriched with hydrogen using RCM (PTB) and a two-stage burner (IST). Furthermore, detailed chemical kinetic models will be developed and validated for diverse experimental targets. This work will both enhance the ongoing cooperation with both institutions as well as unravel chemical mechanisms underlying the combustion of ammonia at wide operation conditions, for device scale applications. The results of this work will be presented in future symposiums and published in peer-reviewed journals. Both institutions also envisage to submit joint research proposals.

References

[1] Tamour Javed, Combustion Kinetic Studies of Gasolines and Surrogates, Ph.D. Dissertation, King Abdullah University of Science and Technology, Thuwal, Kingdom of Saudi Arabia, 2016.

[2].D. Lee, S. Hochgreb. Combust. Flame, 114 (1998), pp. 531–545

[2] O. Mathieu, A. Levacque, E. L. Petersen, Effects of N2O addition on the ignition of H2-O2 mixtures: experimental and detailed kinetic modeling study, International Journal of Hydrogen Energy 37(20) (2012) 15393-15405.

[3] P. Dagaut, P. Glarborg, M. U. Alzueta, The oxidation of hydrogen cyanide and related chemistry, Progress in Energy and Combustion Science 34(3) (2008) 1-46.

[4] S.J. Klippenstein, L.B. Harding, P. Glarborg, J.A. Miller, The role of NNH in NO formation and control, Combustion and Flame 158(4) (2011) 774-789.

[5] Mittal G, SungCJ. A rapid compression machine for chemical kinetic studies at elevated pressure and temperatures. Combustion Sci. Technol 2007;179:497-530.