SMARTCATs COST Action

Short Term Scientific Mission Report

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Details of STSM

STSM title: Experimental investigation of autoignition delay times in a wide range of operating conditions

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Introduction

The STMS was conceived under the idea of discussing the possibility of a collaboration between the Physikalisch -Technische Bundesanstalt (PTB), Braunschweig, Germany, and the Institute for Research on Combustion (IRC), Naples, Italy.

Among the common scientific interests on combustion processes, the attention was mainly devoted to the opportunity to characterize the ignition delay times of standard and alternative fuels coupling the potentialities of different experimental facilities present at the two reference institutes.

The activity was carried out by a visit to the laboratories at the PTB with an illustration of the experimental facilities and a presentation on the scientific activities carried out by Dr. Pino Sabia at Institute for Research on Combustion, Naples. The experimental conditions that can be exploited at the PTB by the Rapid Compression Machine (RCM) and the Shock Tube (ST) reactors, and at the IRC (Tubular Flow and Jet Stirred Flow Reactor) were clarified. Thus, within the STMS period, the complementarity of the experimental

facilities, as well as of the different diagnostics to resolve the ignition delay time process, were examined.

Main Activities

In particular way, the attention was focused on the possibility to characterize the ignition in combustion processes assisted by steam and/or carbon dioxide, thus considering conditions relevant for EGR engines or MILD/Oxy-fuel systems.

Such species can modify the chemical routes involved during the fuel ignition and oxidation processes. In fact, they participate as third body species in third molecular reactions with collisional Chaperon efficiencies relatively higher with respect to nitrogen (air), or as active species in elementary bimolecular reactions.Their chemical effects on the ignition process should be clarified.

Experimental tests realized at the IRC revealed that the interaction of such species with the fuel oxidation chemistry may change in dependence of temperature, pressure and mixture dilution and composition. The results showed that at low temperatures the reference species lead to shorter ignition delay time with respect to systems diluted in nitrogen, while at high temperatures they delay the ignition process.

Such experimental data were simulated by means of commercial software and detailed chemical kinetic mechanisms. The numerical analyses suggested that steam and carbon dioxide accelerate the ignition process by enhancing the reaction rates of third-molecular reactions at low temperatures, while delay it throughout the promotion of recombination/ pyrolytic reactions (third-molecular reactions), to the detriment of the oxidation reactions, and throughout decompositions reactions. Such reactions decelerate the reaction rate of the typical high temperature branching reactions of the system H_2/O_2, delaying the ignition process of fuels.

The analysis of several kinetic detailed schemes have showed that there are huge uncertainties in the third body Chaperon collisional efficiencies of carbon dioxide and steam.

Fig. 1 reports the collisional efficiencies of the reference species normalized with respect to the nitrogen one for the elementary reaction “$H + O_2 + M = HO_2 + M$”, considering several detailed kinetic mechanisms available in literature.

It is possible to note that for CO_2 the collisional efficiency may vary from 1.50 up to 3.80.

In case of H_2O, the third body efficiency changes from 6.50 up to 16.25.

Within the discussion of such data, it has come out that the problems related to the performance of kinetic models in predicting experimental results for combustion systems assisted by steam and carbon dioxide arise from the uncertainty of the third body

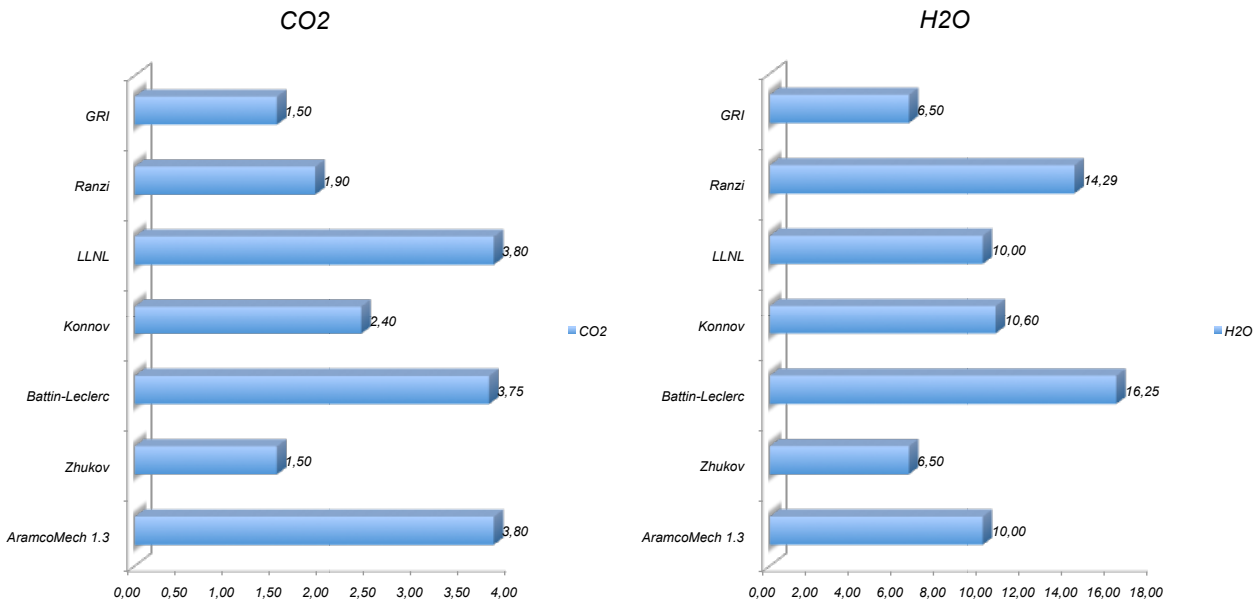

Fig. 1 Third body collisional efficiencies for CO_2 and H_2O. Reference reaction: H + O_2 + M = HO_2 + M.

efficiency values. The lack of information about the species collisional efficiencies is correlated to the lack of experiments and to the absence of reliable theoretical models able to describe the physical-chemical interaction between third body species within combustion systems especially for CO_2 and H_2O. As matter of fact, the most of experiments devoted to the assessment of kinetic parameters are realized with fuel/ oxygen mixtures diluted in Ar, He and N_2. Furthermore, the collisional efficiencies are declared in detailed kinetic mechanisms by means of a deductive and indirect methodology, based on a fitting procedure with experimental data and/or on the basis of theoretical suggestions.

This approach is not very injurious for models performance in predicting the oxidation features of traditional flame combustion systems, where carbon dioxide and steam appear as combustion products and for the most in the post-flame region. In case of novel combustion systems where the exhaust gas recirculation strategy is implemented, steam and carbon dioxide are present ab-initio with fresh reactants. Thus they strongly interact

with the fuel oxidation mechanism. Hence, for such novel technologies a lot of attention should be devoted to develop and/or update reliable kinetic schemes.

The complexity of the topic is enhanced by the temperature dependence of collisional efficiencies. For instance, for the reaction H + O_2 + M = HO_2 + M, Baulch et al. (2005) report a k(M = H_2O)/k(M = N_2) = 1.36 $T^{0.4}$. For instance, Fig. 2 reports the collisional efficiency of steam with the temperature for the reaction H + O_2 + M = HO_2 + M. It is possible to note that the collisional steam Chaperon efficiency changes from 13 at T = 300 K up to 27 at 2000 K.

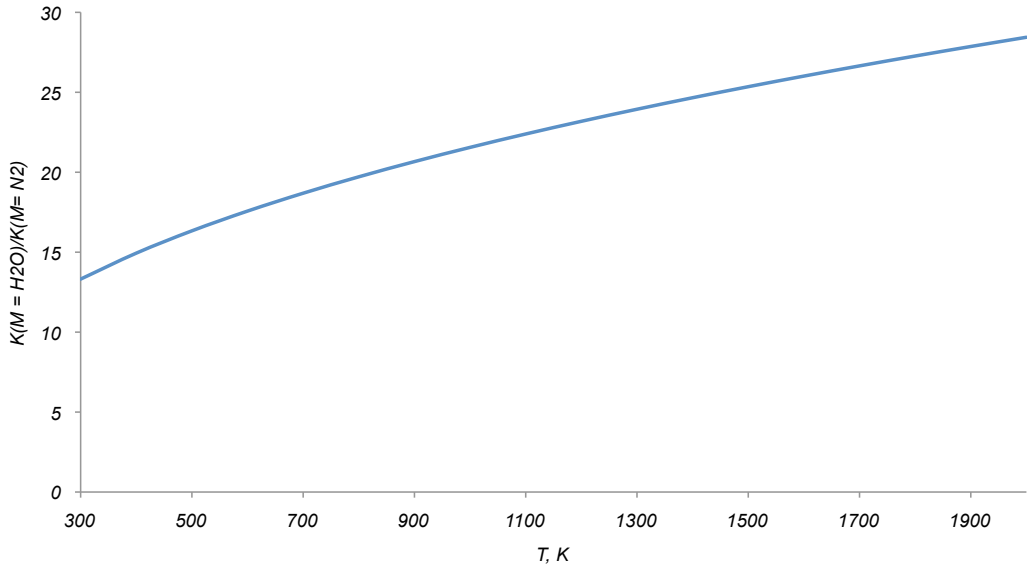

Fig. 2 Third body collisional efficiencies for H_2O, reference reaction: H + O_2 + M = HO_2 + M.

Recently Jasper et al. (2013) studied the collision efficiency of water in the unimolecular reaction $CH_4(+H_2O) \leftrightarrows CH_3+H(+H_2O)$ by means of the MASTER equation theory. The collision efficiency for M = H_2O relative to the other bath gases (defined as the ratio of low-pressure limit rate coefficients) was found to depend on temperature, with, e .g.,$k_0(H_2O)$/ k_0(Ar) = 3 at 300 K, and 7 at 2000 K.

Such an aspect covers a crucial importance in the modeling activity of combustion systems assisted by CO_2 and/or H_2O. As matter of fact, detailed kinetic models do not involve the temperature dependence of species collision efficiency.

Conclusion

Several meetings and discussions were then organized to define a common work-plan. In such a sense, there are plenty of opportunities of collaborations between the two institutes.

First, the experimental facilities located at the two institutions can be synergistically used to characterize the fuels ignition delay process in a wide range of temperatures and pressures, i.e. from low to very high pressures as well as for low to high temperatures, relevant from furnaces to engines and turbines. Several experiments have to be planned also to collect experimental data for combustion systems in presence of steam and carbon dioxide.

Second, the collaboration between the institutes can be based on the development and validation of kinetic models for combustion systems. As matter of fact, at the PTB parts of the scientific activities are devoted to the implementation of procedures to standardize thermo and kinetic data for fuel oxidation processes. This represents the starting point to develop reliable and robust tools to use in the predictive activities of combustion features. In this sense, the success of a modeling activity could rely on the expertise of Prof. Fernandes on chemical kinetics, and on the expertise of Dr. Pino Sabia in modeling non-conventional combustion systems.

The future collaboration will be realized by the submission of proposals within the European H2020 CALLS and further strategies to promote and define the synergistic coupling of the institutes activities will be discussed in next meetings.

Reference

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