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: Consultation on the further developments of methane combustion mechanisms and learning the experimental details of the applications of flow reactors
STSM start and end date: 12/03/2019 to 26/03/2019
Grantee name: Peng Zhang

PURPOSE OF THE STSM:

The topic of my research team at the ELTE Eötvös Loránd University is "experimental data collection and detailed kinetics mechanisms comparison and optimization toward a virtual chemistry of Smart Energy Carriers". Currently, I am participating in the development of a methane combustion mechanism based on a large amount of experimental data. We have collected more than 5000 shock tube experimental data points and about 400 data points from rapid compression machine measurements. The comparison results show that the mechanisms from Professor Glarborg at the Technical University of Denmark (DTU), are the most accurate in general among the investigated 13 mechanisms. Therefore, we planned to carry out detailed consultations on the development of more accurate methane combustion mechanisms.
In addition, a great part of the experimental data used in the comparison of methane combustion mechanisms is based on flow reactor measurements. The CHEC Research Centre at DTU has a high pressure (up to 100 bar) flow reactor for the studies of homogenous reaction kinetics processes. An aim of the mission is to visit the flow reactor and study its principles and details, and also to get more knowledge on the reliability of the related experimental data. This information is helpful for the future data collection works and further improvements of the ReSpecTh database.

DESCRIPTION OF WORK CARRIED OUT DURING THE STSMS

(max.500 words)
During the 2 weeks of the scientific mission, under the guidance of Professor Peter Glarborg, I learned about the methods for the development of combustion mechanisms. In addition, I presented the main features and progress of my work, and the Professor made comments and helpful suggestions concerning it. Furthermore, we discussed the comparison of methane combustion mechanism based on shock tube experimental data. Prof. Glarborg shared his opinion on my finished work, and gave suggestions for my future studies.The PhD student of Professor Glarborg, Mr. Hamid Hashemi guided my visit to the high pressure flow reactor and introduced me to the main principles of the facility. Based on his demonstration, I did flow reactor simulations with different settings of the boundary conditions and compared the results. This significantly helped me at the understanding of the operation of high pressure flow reactors.

DESCRIPTION OF THE MAIN RESULTS OBTAINED

After consulting with Professor Glarborg and his coworkers, it is clear for me that they develop kinetic mechanisms based on reviewing of the individual elementary reactions reported in the literature with

particular emphasis on the conditions relevant to the investigated work. The reactions and their rate constant with lower uncertainty are inserted into the new models [1][2][3][4]. Quantum chemistry calculations are also applied for determining unknown rate constants [1]. Unlike some other research groups, Professor Glarborg and his coworkers do few modifications in rate constants if they are available. Furthermore, own measurement data and published experimental data are collected for validating the obtained models. Usually Professor Glarborg and his coworkers carry out flow reactor experiments at high pressure (20 - 100 bar) and low / medium temperature (600 – 900 K). Therefore, the experimental data used cover a wide range of pressure. Moreover, their collaborators provide large amount of data from rapid compression machine measurements [4], which is implemented at relatively low pressure (15 – 50 bar) and high temperature (higher than 900 K) conditions. Thereby, the available data cover a large domain of experimental conditions. Considering also the experimental data collected from published articles, it is clear that the validation of the mechanisms of Professor Glarborg and his coworkers have been carried out at a very comprehensive range of pressure and temperature. Collecting high quality rate constants and mechanism validation at a wide range of conditions are the two main reasons of their success in mechanism development. However, based on my work of comparing several methane mechanisms, I found that the model of Professor Glarborg and his coworkers has a slightly higher error function value at low diluent ratio (less than 0.45). This range of conditions could be a possible field of improvement for their methane combustion mechanism.

Under the guidance of Mr. Hashemi, I visited the High Pressure Flow Reactor Laboratory of the CHEC Research Center of DTU, and carried out simulations of flow reactor experiments. The flow reactor system consists of five sections. These are the gas supply, gas distribution, reaction, pressure adjustment, and product analysis sections. As shown in Fig. 1, all gas supplying facilities in the CHEC Research Center are located out of the building for safety reasons. In Fig. 2, the four digital mass flow controllers (MFC) transfer the reactant gas mixtures to the reactor inlet. The tubular quartz reactor is covered by a steel shell. These are placed in an electrically heated oven with three heating units, and the apparatus is placed into a closed box as seen in Fig. 3. There are two pressure adjustment systems. The first one consists of two thermal mass flow pressure controllers, transferring N_2 into the void between quartz reactor and the steel shell with pressure similar to the one inside the quartz reactor, therefore the pressure difference inside and outside of the reactor is small to protect the fragile glass tube reactor. The second pressure adjustment system, as shown in Fig.4, has the function to decrease the pressure of product mixture into suitable level for the measurement by gas chromatograph (Fig. 5).

Fig. 1: Warehouse of gas supply facilities (within the dashed line)

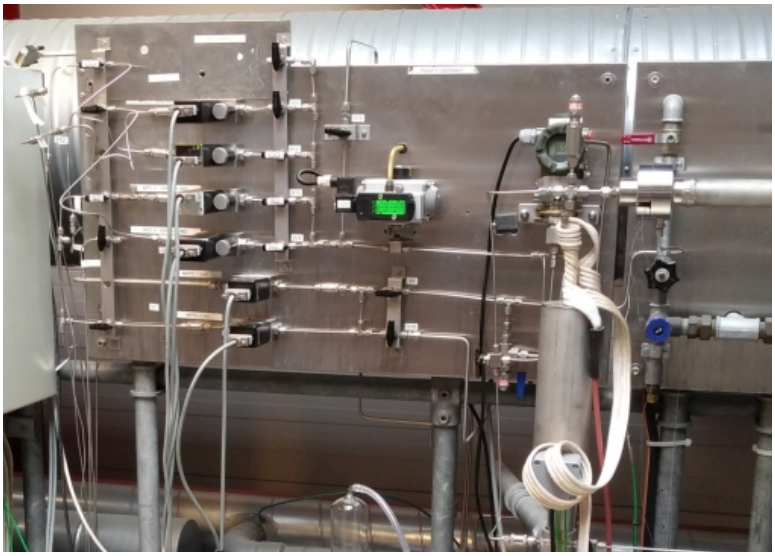


Fig. 2: Gas distribution section

Fig. 3: Reaction section

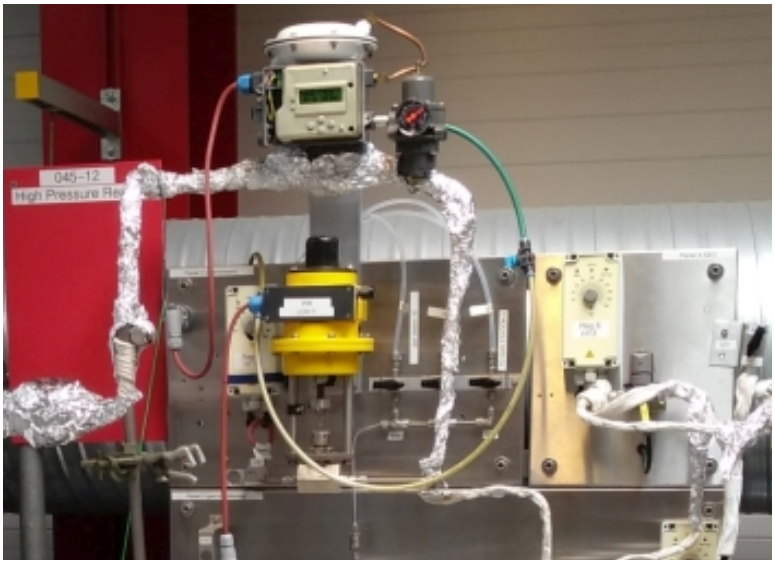


Fig. 4: Pressure adjustment section

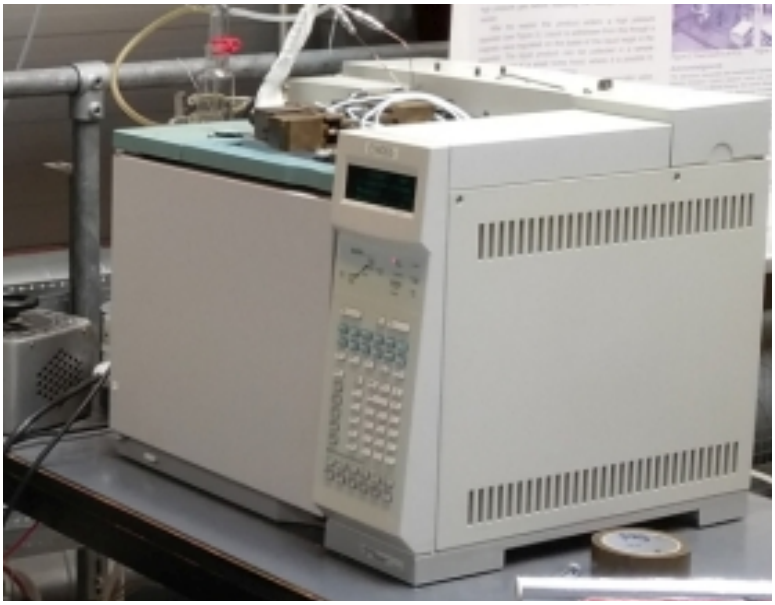
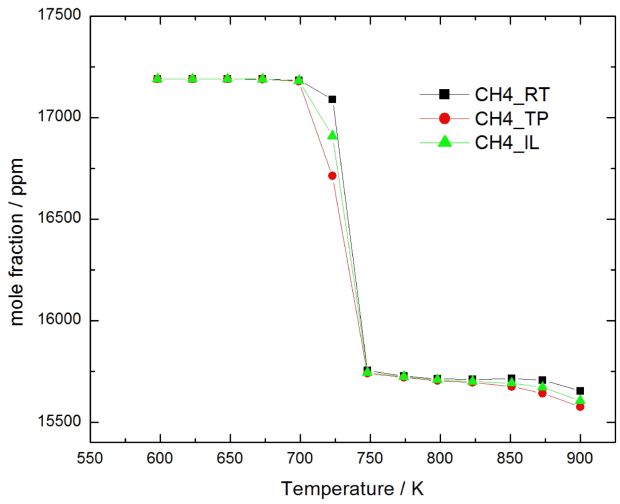
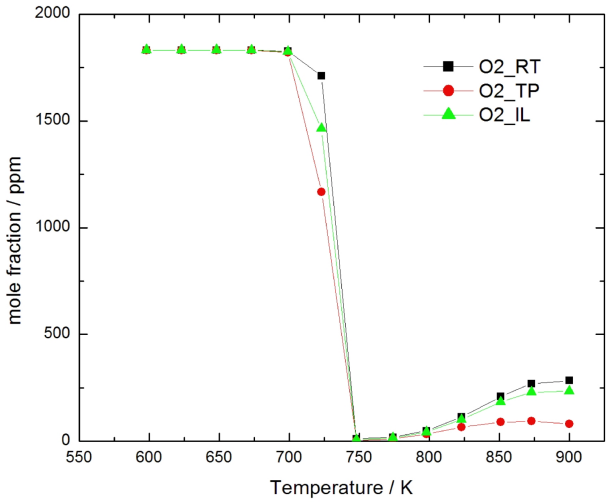


Fig. 5: Gas analysis by a gas chromatograph

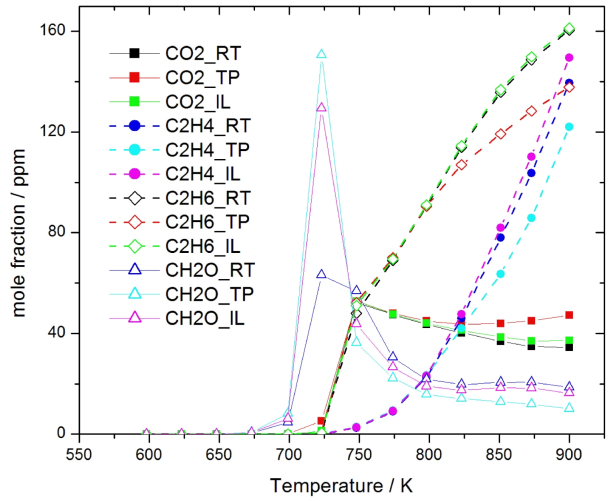
In simulations of the flow reactor, we compared the calculated species mole fractions with three different experimental assumptions, which are fixed residence time ($\tau = 9586/T$, unit: s) (**RT**), fixed isothermal section length of the reactor ($L_{iso} = 43\ cm$) (**IL**), and measured temperature profiles (this is the closest to the reality) (**TP**). The simulations were carried out with the following three equivalence ratios: 0.06, 1.0, and 19.45. The comparisons of the calculated species mole fractions from various experimental assumptions are shown in Figs. 6 to 8.



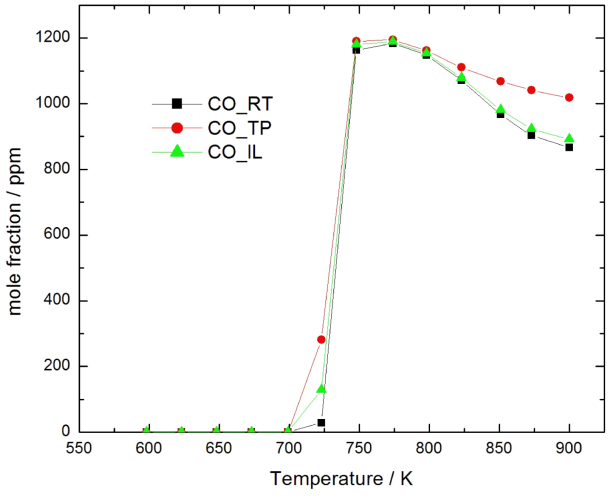
(a)


O2_RT
O2_TP
O2_IL
mole fraction / ppm
Temperature / K
0
500
1000
1500
2000
550
600
650
700
750
800
850
900

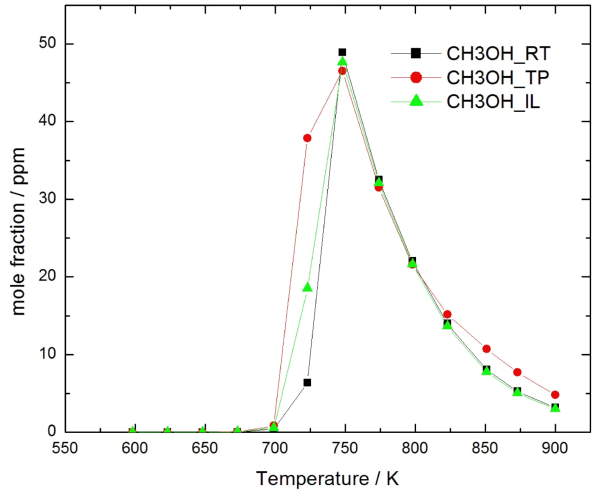
(b)


CO2_RT
CO2_TP
CO2_IL
C2H4_RT
C2H4_TP
C2H4_IL
C2H6_RT
C2H6_TP
C2H6_IL
CH2O_RT
CH2O_TP
CH2O_IL
mole fraction / ppm
Temperature / K
0
40
80
120
160
550
600
650
700
750
800
850
900

(c)

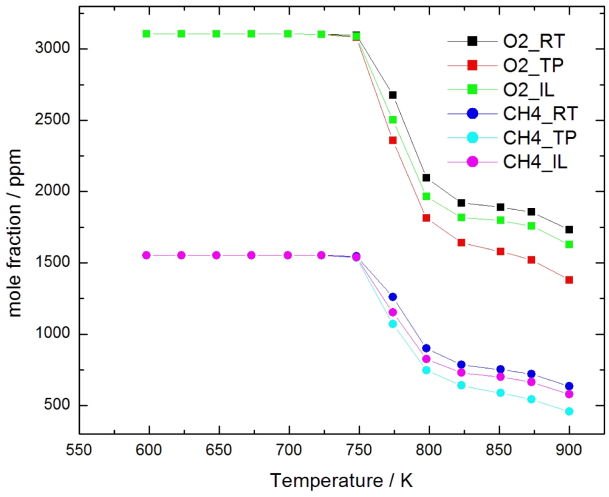

CO_RT
CO_TP
CO_IL
mole fraction / ppm
Temperature / K
0
200
400
600
800
1000
1200
550
600
650
700
750
800
850
900

(d)

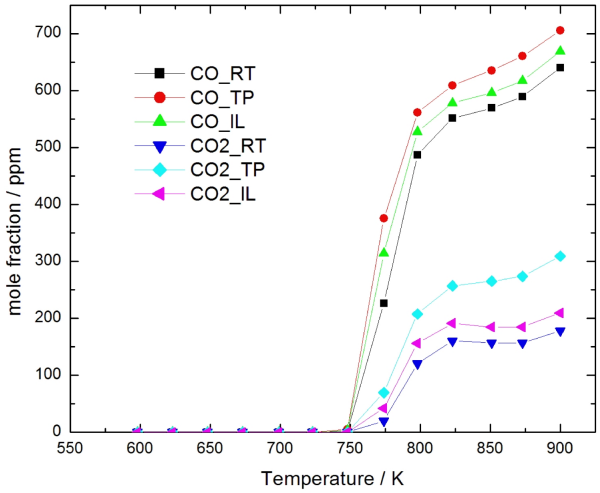


(e)

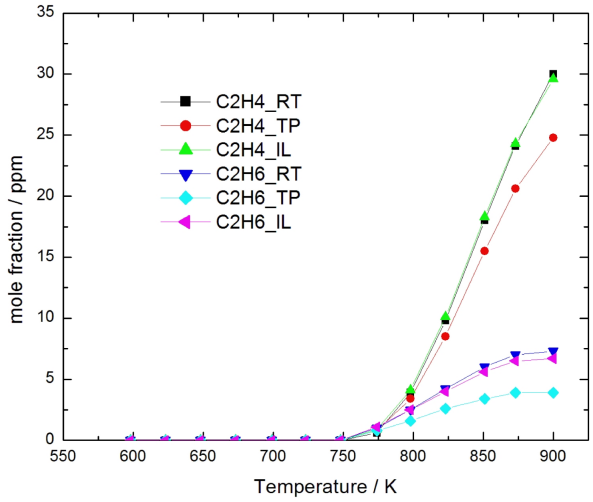
Fig. 6 Results of simulations under fuel-rich conditions
(0.18% O_2 / 1.75% CH_4 in N_2, φ = 19.7, pressure 100 bar)



(a)



(b)



(c)

Fig. 7 Results of simulations under stoichiometric conditions
(0.31% O_2 / 0.16% CH_4 in N_2, φ = 1.0, pressure 100 bar)

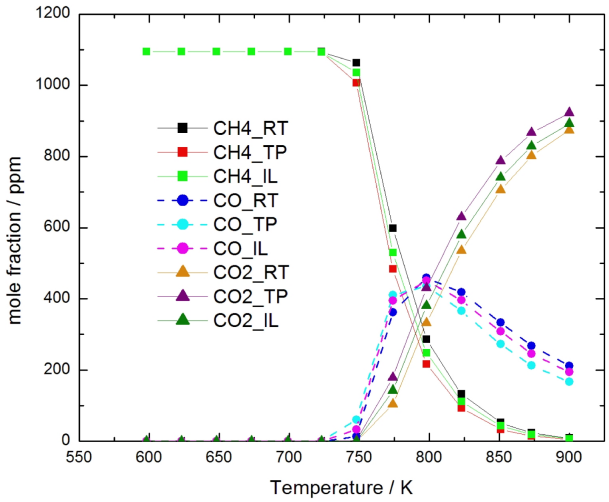


Fig. 8 Results of simulations under fuel-lean conditions
(3.96% O_2 / 0.11% CH_4 in N_2, φ = 0.06, pressure 100 bar)

As seen from Figs. 6, 7, and 8, although the different experimental assumptions do not influence much the calculated species concentration curves as a function of temperature, but there are still obvious deviations between the results simulated with different calculating criteria. Based on experimental experience, if the mixture includes some particular larger molecules, such as C_4H_{10} or CH_3OCH_3, this kind of deviation would be more serious. Therefore, this result indicates that we have to to collect the flow reactor experimental data together with measured temperature - distance profiles in the reactor for more accurate simulations. During the STSM, I received several hundreds of raw RCM experimental datasets which are being encoded into ReSpecTh database.

References:
[1]. Rasmussen C L , Hansen, Jørn, Marshall P , et al. Experimental Measurements and Kinetic Modeling of $CO/H_2/O_2/NO_x$ Conversion at High Pressure. *International Journal of Chemical Kinetics*, 2008, 40(8):454-480.
[2]. Rasmussen C L , Rasmussen A E , Glarborg P . Sensitizing effects of NOx on CH4 oxidation at high pressure. *Combustion and Flame*, 2008, 154(3):529-545.
[3]. Rasmussen C L , Jakobsen J G , Glarborg P . Experimental measurements and kinetic modeling of CH4/O2 and CH4/C2H6/O2 conversion at high pressure. *International Journal of Chemical Kinetics,* 2008, 40(12):778-807.
[4]. Hashemi H , Christensen J M , Gersen S , et al. High-pressure oxidation of methane. *Combustion and Flame*, 2016, 172:349-364.

FUTURE COLLABORATIONS (if applicable)

Prof. Peter Glarborg interested in the error evaluation methods and a series of programs for the interpretation of experimental data that were developed in the Chemical Kinetics Laboratory of ELTE. On the other hand, large amount of experimental data from the group of Professor Glarborg are important for the extension of the ReSpecTh reaction kinetics database. These fields look promising for future cooperations between the two groups.