Comparison of detailed NO_x reaction mechanisms on syngas combustion systems

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Introduction

The direct combustion of low-quality coal or biomass is not easy to control and may generate much air pollution. An alternative approach is the gasification of these fuels producing syngas. Syngas (or "wet CO") is a fuel mixture consisting of carbon monoxide and hydrogen. However, the combustion of syngas may produce nitrogen oxides (NO_x). Recently Zhang et al. [1] published an article on the elaboration of a new reaction mechanism that describes the generation of NO_x during hydrogen and syngas combustion. This mechanism was tested by Zhang et al. [1] against a large set of experimental data. This collection of experimental data was used here to investigate the performance of not only the Zhang et al. [1] mechanism, but also two other recently published NO_x reaction mechanisms [2], [3].

The experimental data utilized

The experimental data assembled by Zhang et al. [1] included measurements of shock tube ignition delay times, laminar burning velocities and shock tube, flow reactor and jet stirred reactor concentration measurements. These data were collected from 23 publications and included about 88000 data points in 298 datasets. These data covered a wide range of conditions: p = 0.20–98.7 atm, φ = 0–5, cold side temperatures of flames T_c = 294–304 K; initial temperatures of shock tube, flow and jet stirred reactor experiments T_{in} = 702–2712 K. The investigated systems could be classified to the following chemical categories: H_2/N_2O, $H_2/O_2/NO_x$ and NH_3/O_2 systems; investigation of the combustion of $H_2/CO/N_2O/Ar$, $H_2/CO/O_2/NH_3/Ar$, and $H_2/CO/O_2/NO_x$ mixtures.

The mechanisms were tested using the suite of methods and computer codes developed in our group. First, all data were encoded in RKD 2.0 format XML files. The ReSpecTh Kinetics Data (RKD) format [4] is a further developed version of the PrIMe Kinetics Dataformat [5]. The advantage of using XML data files is that these files are both machine and human readable. Technically, the RKD files were created by program Optima++, which is able to read a text file containing the data and print the XML files. The definition of the RKD 2.0 format and program Optima++ (version 1.02) [6] are available from the ReSpecTh Information System [4].

In the next step, program Optima++ was used for the automatic simulation of all data points with any selected reaction mechanism. In this role, Optima++ reads the RKD format experimental datafile, sets up the simulation environment, and calls the FlameMaster [7] simulation code, using a 0D (shock tube, flow reactor or JSR) or 1D (laminar flames) model. All simulations were carried out with the FlameMaster code. The results were the plotted, allowing the comparison of the experimental and simulation results.

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The investigated reaction mechanisms

The investigated reaction mechanisms included the Zhang_2017 mechanism [1], which was recently created to describe the transformation nitrogen compounds during syngas combustion. This mechanism contains 262 reactions of 44 species.

Glarborg et al. recently published a comprehensive review [2] on the transformations of nitrogen species in combustion systems. A new mechanism was published in the Electronic Supplementary of this article. This Glarborg_2018 mechanism describes the combustion of natural gas, the NO production during combustion (in all known ways) and it is able to reproduce the various NO removal methods. The Glarborg_2018 mechanism consists of 1639 reactions of 153 species.

Song et al. [3] investigated the sensitizing effects of NO_2 and NO on methane low temperature oxidation in a jet stirred reactor. As a part of its Electronic Supplementary, this article contains the latest POLIMI mechanism. The previous version of this mechanism (Version 1412, December 2014, high temperature kinetic mechanism with NO_X) was published on the POLIMI web site [8]. The POLIMI_2018 mechanism [3] contains 2361 reactions of 153 species and it is a detailed mechanism for the pyrolysis, partial oxidation and combustion of hydrocarbon fuels up to 24 C-atoms, coupled with the NO_x reactions. The POLIMI_2018 mechanism was slightly modified for the current simulations by removing the reactions that contain C-species except CO, CO_2 and HCO and by adding a mechanism block of excited OH reactions from the optimized syngas mechanism of Varga et al. [9]. The latter allowed the reproduction of shock tube experiments where the ignition delay time was measured via the OH* fluorescence signal.

Results of simulations

The results indicated that most of the experimental data could be well reproduced by the simulations. The three recent NO_x mechanisms provided similar simulation results at most of the experimental conditions, although these mechanisms had different development history and contained different rate parameters for several elementary reactions.

An example of simulation results is given in Figure 1. Mathieu et al. [10] investigated the ignition delay times of $H_2/CO/O_2/NH_3/Ar$ mixtures at three different pressures in the temperature range of 993–1975 K. The mixture contained 200 ppm ammonia. The figure shows that the simulations using any of the three mechanisms could well reproduce the experimental data.

Some of the experimental data were not well reproduced by these three mechanisms. For example, Javoy et al. [11] investigated the decomposition of N_2O in Ar bulk gas in a shock tube in the temperature range of 1500–2500 K by measuring the O-atom concentration profile. The experimental results could be well reproduced at low initial N_2O concentrations, but not at high initial N_2O concentrations.

The POLIMI_2018 mechanism, unlike the other two mechanisms, did not reproduce well the experimental data of Mével et al. [12], [13] (ignition delay in $H_2/N_2O/Ar$ mixtures, measured by shock tube, T_0 = 1300–2000 K) and the data of Kopp et al. [14] (ignition delay in $H_2/CO/N_2O/Ar$ mixtures, measured by shock tube, T_0 = 1654–2221 K). This indicates conditions where this mechanism has to be improved.

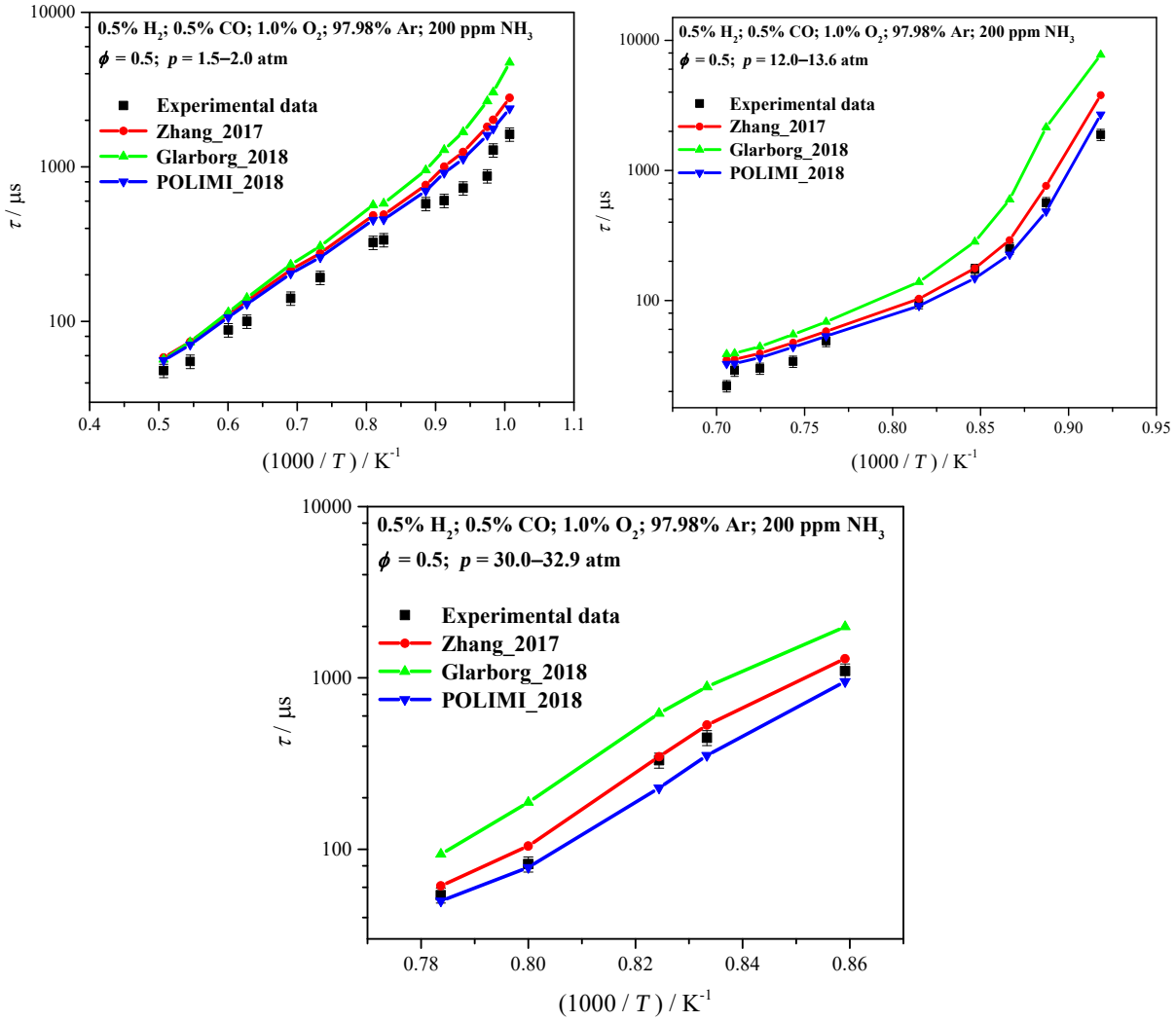

Figure 1 Ignition delay times measured by Mathieu et al. [10] in shock tube and the related simulation results.

Investigation of some mechanistic details

Until now, most published syngas combustion mechanisms (see [15] and [16]) did not contain the reactions of species HOCO. However, all the three investigated mechanisms contain these reactions (Zhang_2017: 9 HOCO reactions, Glarborg_2018: 15 HOCO reactions, POLIMI_2018: 2 HOCO reactions). Elimination of the HOCO reactions from the mechanisms did not change the POLIMI_2018 results, but significantly changed the Zhang_2017 and especially the Glarborg_2018 results in the high-pressure experiments (p > 20 bar). This indicates that considering the HOCO reactions is really important for the reproduction of high pressure syngas combustion experiments.

The Zhang_2017 mechanism contains reaction $N_2O + H_2 = N_2 + H_2O$, while this reaction is missing from the Glarborg_2018 and POLIMI_2018 mechanisms. Zhang et al. used the rate coefficient measured by Kosarev et al. [17] and using these rate parameters the reaction has significance in several experiments. Recently Mulvihill et al. [18] determined this rate coefficient with higher accuracy and found it to be 30 times smaller. Using the updated rate parameters for this reaction modified the simulation results obtained with the Zhang_2017 mechanism in several experiments. It was shown that this reaction is not important at any of the experimental conditions when the rate parameters of Mulvihill et al. [18] are used.

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