Comparison of the performance of several recent wet CO combustion mechanisms

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Abstract

A large set of experimental data was collected for wet CO combustion: ignition measurements in shock tubes (532 data points in 50 datasets) and rapid compression machines (444 data points in 46 datasets), flame velocity measurements (1711 data points in 175 datasets) and concentration–time profiles in jet-stirred reactors (54 data points in 9 datasets), covering wide ranges of temperature, pressure, CO/H_2 ratio and equivalence ratio. The performance of 15 recently published wet CO combustion mechanisms was tested against these experimental data. The dependence of simulation accuracy on the type of experiment and the error of reproduction of flame velocity measurements at the various experimental conditions was investigated.

Introduction

In the recent years, there has been an increased interest in studying the combustion of fuel mixtures consisting of carbon monoxide and hydrogen, referred to as "wet CO" or syngas. These fuels can be produced from coal and biomass via gasification, and are considered to be a promising option towards cleaner combustion technologies for power generation. The combustion chemistry of wet CO, which also forms the basis of the combustion of hydrocarbons and oxygenates, has been the subject of many experimental and modelling studies over decades. In accordance with its high significance, several new wet CO combustion mechanisms were published even in the last decade. In these publications, the agreement between the measurements and the simulations is usually characterized by plots, in which the experimental data and the simulation results are depicted together. However, quantitative agreement of the simulation results with the experimental data has not been investigated.

Experimental data

A large set of experimental data was collected on the investigation of wet CO combustion. This type of measurements, called indirect measurements or bulk measurements, is used for testing detailed reaction mechanisms. We utilized all measurements that were used for testing the recent mechanisms of Davis *et al.* [1], Li *et al.* [2] , Sun *et al.* [3] and Kéromnès *et al.* [4]. The references for the measurements were collected from these recent review articles, but the experimental data were digitalized from the original experimental publications. Also, a comprehensive literature review was carried out to find all other measurements that can be used for testing wet CO combustion mechanisms. Our data collection is much wider-ranging than any other set of data that has ever been used for testing wet CO combustion mechanisms.

The data include ignition measurements in shock tubes (532 data points in 50 datasets from 6 original publications) and rapid compression machines (444 data points in 46 datasets from 3 publication), flame velocity measurements (1711 data points in 175 datasets from 24 publications) and concentration–time profiles in jet-stirred reactors (54 data points in 9 datasets from one publication). A dataset contains those data points that were measured on the same apparatus at the same time at similar conditions except for one factor that was systematically changed. One experimental publication usually contains one or a few datasets.

All experimental data were encoded in PrIMe file format [5], which is an XML scheme used for the systematic storage of various kinds of combustion experiments. Encoding the experimental conditions and results in PrIMe format allows an automatic simulation of all experiments. A MATLAB code was written that reads the PrIMe datafile and prepares CHEMKIN-II [6] input files. The MATLAB code then calls the corresponding CHEMKIN simulation code (SENKIN, PREMIX or PSR), collects the simulation results, and evaluates the agreement between the experimental and simulation results. In principle, the complete investigation of a mechanism against several thousand of very different experimental data can be carried out in a single run. The chemical mechanism was then replaced and the same investigation was performed with another mechanism. The MATLAB code saved the simulation results in Excel tables.

Methodology

In this work the agreement of experimental and simulation results is investigated using the following objective function:

$$E_i = \frac{1}{N_i}\sum_{j=1}^{N_i}\left(\frac{Y_{ij}^{sim} - Y_{ij}^{exp}}{\sigma(Y_{ij}^{exp})}\right)^2$$

$$E = \frac{1}{N}\sum_{i=1}^{N} E_i$$

where

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$$Y_{\mathrm{ij}} = \begin{cases} y_{ij} & \text{if } \sigma(y_{ij}^{\mathrm{exp}}) \approx \text{constant} \\ \ln y_{ij} & \text{if } \sigma(\ln y_{\mathrm{ij}}^{\mathrm{exp}}) \approx \text{constant} \end{cases}$$

Here N is the number of datasets and N_i is the number of data points in the i-th dataset. The different experiment types were weighted according to their respective number of datasets for the calculation of final performance. However, weighting according to the number of datapoints leads to similar results. Values y_{ij}^{exp} and $\sigma\left(y_{ij}^{\mathrm{exp}}\right)$ are the j-th data point and its standard deviation, respectively, in the i-th dataset. The corresponding simulated value is Y_{ij}^{exp} obtained from a simulation using an appropriate detailed mechanism. We used $Y_{ij} = y_{ij}$, if the measured values have an absolute error (independent of the value of y_{ij}). This option was chosen for laminar flame velocities and measured concentrations. We used option $Y_{ij} = \ln(y_{ij})$, if the experiments have relative error (proportional to the value of y_{ij}), which is characteristic for ignition time measurements. Error function values E_i and E would be equal to one if the chemical kinetic model were accurate, and the deviations of the measured and simulated results were caused by the scatter of the experimental data only. This objective function is very similar to those that has been used at the estimation of rate parameters from experimental data [7], [8].

Mechanisms

Our aim was to test all wet CO combustion mechanisms that were published in the last decade. Table 1 contains the list of the investigated mechanisms.

Table 1. The investigated reaction mechanisms

No.	Mechanism	Ref.	Species	Reactions
1	NUIG NGM c5_49 2010	[9]	15	41
2	Starik 2009	[10]	16	44
3	Kéromnès 2012	[4]	15	49
4	Li 2007	[2]	15	45
5	Davis 2005	[1]	14	38
6	CRECK 2012	[11]	14	34
7	USC II 2007	[12]	14	48
8	San Diego 2011	[13]	15	37
9	Sun 2007	[3]	15	48
10	Rasmussen 2008	[14]	15	59
11	Ahmed 2007	[15]	14	37
12	Saxena Williams 2006	[16]	14	30
13	GRI 3.0 1999	[17]	15	48
14	Zsély 2005	[18]	13	44
15	Dagaut 2003	[19]	13	34

Several of these mechanisms were originally developed for wet CO combustion ([1], [3], [4], [11], [16], [18]), while other mechanisms were elaborated for the combustion of hydrocarbons or oxygenates ([2], [9], [12], [13], [15], [17], [19]). For the latter, Table 1 refers to the number of species and reactions of the wet CO combustion part of these mechanisms.

Reproduction of the various types of measurements

The results of the testing are sorted according to the types of experiments. First, the performance of the mechanisms is investigated according to type of measured values (ignition delays, outlet concentrations in jet stirred reactors and flame velocities).

1) Ignition delays in RCMs and shock tubes

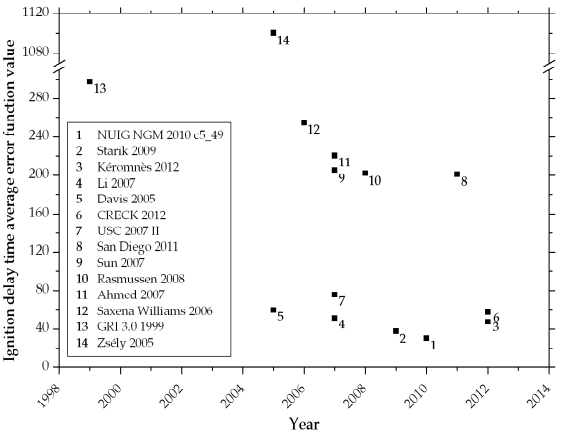

Fig. 1. Performance of the mechanisms on ignition delay measurements *vs.* year of publication.

2) Outlet concentrations in jet stirred reactors

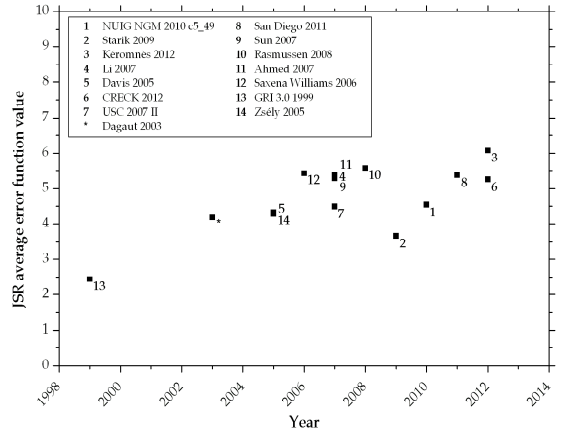

Fig. 2. Performance of the mechanisms on JSR measurements *vs.* year of publication.

3) Flame velocity measurements

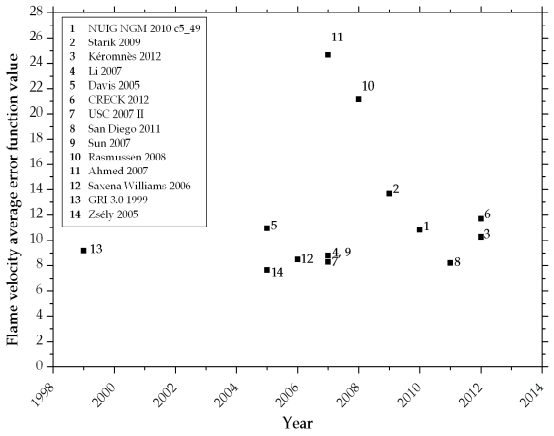

Fig. 3. Performance of the mechanisms on flame velocity measurements *vs.* year of publication.

Figure 1 shows that the best mechanisms for the description of ignition delay times are the NUIG NGM, Starik *et al.* and Kéromnès *et al.* mechanisms. The worst mechanisms in this respect are the Zsély *et al.* and the GRI 3.0 mechanisms. Note, that the Zsély *et al.* mechanism [18] contains the rate parameters recommended by Baulch *et al.* [20] without modification. This shows that although the Baulch *et al.* evaluated rate parameter values are widely used at the creation of combustion mechanisms, further tuning or optimisation is needed for a good description of ignition delay times in the wet CO combustion system.

Figure 2 demonstrates the performance of the mechanisms on the simulation of the exit concentrations of jet stirred reactor experiments. Here GRI 3.0 is the best. The general trend is that the newer mechanisms describe these experimental data worse. The mechanism of Dagaut *et al.* differs from all others, as it includes neither Ar nor He as possible bath gases. This affects the comparison with respect to ignition delay times and flame velocities, since argon or helium was used as a bath gas in many experiments. However, in the JSR measurements always N_2 was used as the bath gas and therefore the performance of the Dagaut *et al.* mechanism was visualized only for this type of experiments. The performance of this mechanism was tested also on the measured ignition delay times and flame velocities where N_2 bath gas was used and typically it was in the middle range among all mechanisms.

For the reproduction of all flame velocity measurements (Figure 3), the Zsély *et al.* mechanism is the best, however, all mechanisms have a similar performance, except for that of the Ahmed *et al.* and Rasmussen *et al.* mechanisms.

Dependence of the error of simulated flame velocity on the experimental conditions

Exemplary for flame velocity data, the performance of the mechanisms in different ranges of equivalence ratio, cold side temperature, pressure, the types of diluent and experimental facility is shown in Figures 4 to 8.

Figure 4 demonstrates the error of the simulated flame velocities with increasing cold side temperature. While below 400 K most mechanisms predict similar flame velocities, between 400 K and 600 K the agreement is slightly worse, and above 600 K cold side temperature all mechanisms predict very different flame velocities. The single exception is the CRECK mechanism that has a similar good performance at all temperatures, while the error of the Starik *et al.*, Kéromnès *et al.* and NUIG NGM 2010 mechanisms becomes very large above 600 K.

Figure 5 shows that the mechanisms tend to be more accurate at lean conditions and the performance of all mechanisms is getting worse moving towards the simulation of rich mixtures. However, the deterioration of the accuracy is not dramatic, except for the Ahmed *et al.* and Rasmussen *et al.* mechanisms.

According to Figure 6, the performance of the mechanisms on flame velocity measurements improve with increasing pressure. The only exception is the mechanism of Starik *et al.*, which produces increasing error at higher pressures. On the contrary, the Ahmed *et al.* and Rasmussen *et al.* mechanisms are inaccurate near atmospheric pressure, but become very accurate above 15 atm.

Figure 7 shows the reproduction of the experimental flame velocity according to the type of diluent. Most mechanisms perform better when CO_2/H_2O and N_2/H_2O mixtures were used as diluents. However, the reproduction of experiments with He, N_2/CO_2 and pure N_2 is only slightly worse. Experimental data using other diluents were also collected (pure Ar, CO_2, H_2O, He/CO_2, He/H_2O), but these data are fewer in comparison to the ones with diluents presented in Figure 7, and therefore do not allow for the investigation of general trends.

In Figure 8, the performance of the mechanisms with respect to the reproduction of the flame velocity measurements using different experimental techniques is presented. The flame velocities are measured by using four different types of methods. These are the flame cone method (for a discussion of this method see *e.g.* [21]), the outwardly propagating spherical flame method [22], the counterflow twin-flame method [23], and the heat flux burner method [24]. Generally, traditional approaches (flame cone method, outwardly propagating spherical flame) seem to be less accurate in comparison to newer techniques (counterflow twin-flame, heat flux method). Note that the ranges of covered operating conditions may differ largely between the different techniques, which also influence the comparison of the experimental methods. In contrast to the results of the hydrogen mechanism comparisons [25], here the prediction of measurements using the outwardly propagating flame approach is much less accurate, while the reproduction of flame cone method data is better.

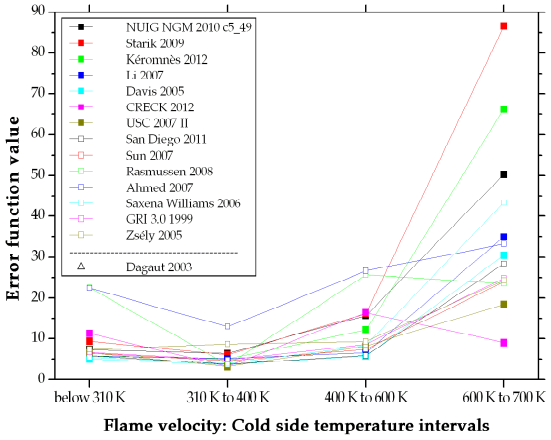

Fig. 4. Performance of the mechanisms on flame velocity measurements for various ranges of cold side temperature.

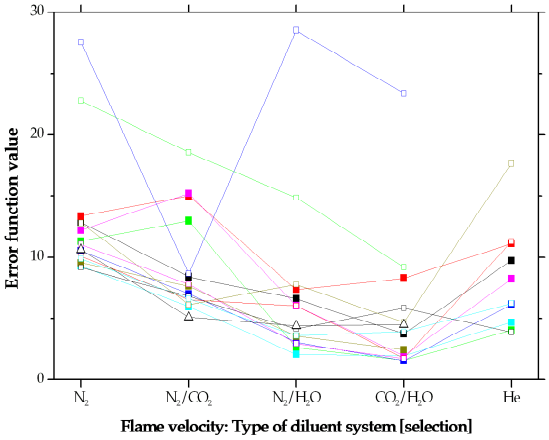

Fig. 7. Performance of the mechanisms on flame velocity measurements according to the type of the bath gas.

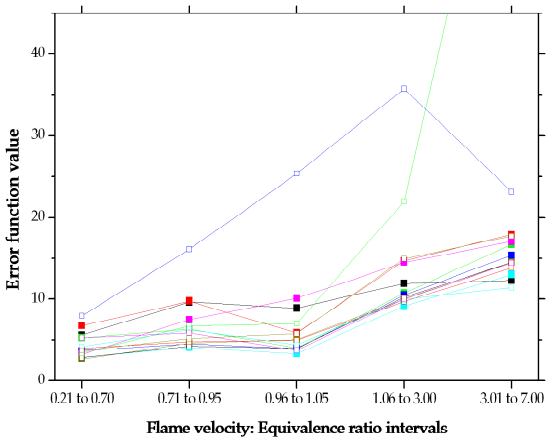

Fig. 5. Performance of the mechanisms on flame velocity measurements for various ranges of equivalence ratio.

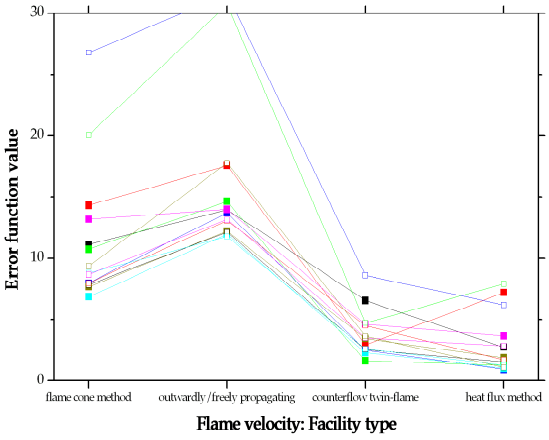

Fig. 8. Error of the reproduction of the flame velocity according to the type of measurement.

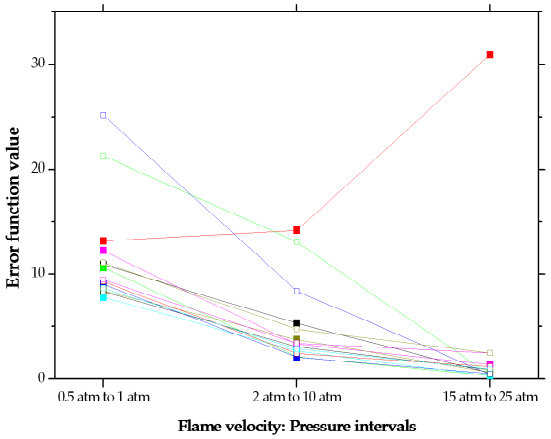

Fig. 6. Performance of the mechanisms on flame velocity measurements according to ranges of flame pressure.

Conclusions

The accurate description of the combustion of wet CO is important from both scientific and industrial points of view. An excellent review [4] was elaborated recently in which new developments in this field are discussed. However, a comprehensive investigation and comparison of all recent wet CO combustion mechanisms has not been published.

The best mechanisms for the reproduction of ignition delay times, JSR experiments and flame velocity measurements are the NUIG NGM 2010 , GRI 3.0, and Zsély *et al.*, respectively. Several mechanisms do not work properly at high/low equivalence ratio, temperature, and pressure and particularly for RCM simulations (for example, the Zsély *et al.* and GRI 3.0 mechanisms). Investigations of the performance of the mechanisms at various experimental conditions, such as those presented in Figures 4 to 7, may help the selection of a

mechanism for simulations to be carried out at given industrial conditions.

Figure 9 shows the performance of each mechanism, tested against all collected experimental data. There is a very slow improvement of the accuracy of the published reaction mechanisms over the years. Currently, the most accurate mechanism for modelling the wet CO combustion is the NUIG NGM c5_49 (published in 2010), but the Starik *et al.* mechanism (2009), the Kéromnès *et al.* mechanism (2012), the Li *et al.* mechanism (2007) and the Davis *et al.* mechanism (2005) have a similarly good performance, considering all types of experimental data.

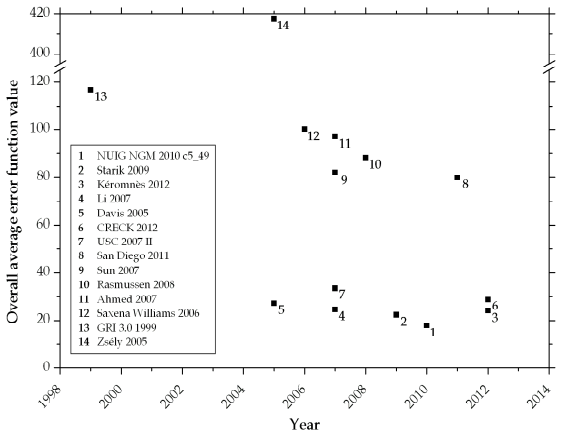

Fig. 9. Performance of the mechanisms considering all experimental data *vs.* year of publication.

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