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Development of a syngas combustion mechanism based on a hierarchical optimization approach

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Abstract

An optimized syngas combustion mechanism has been developed using a large set of indirect experimental data, consisting of ignition measurements in shock tubes and rapid compression machines, and flame velocity measurements covering wide ranges of temperature, pressure, equivalence ratio and H_2/CO ratio. Arrhenius parameters A, n, and E of 16 elementary reaction steps have been optimized. The joint covariance matrix of the optimized parameters has been calculated which characterizes the uncertainty of the optimized reactions rate coefficients and also their correlation. The performance of the optimized mechanism was tested against other previously published syngas combustion mechanisms and, considering all kinds of measurements, was found to be the most accurate one.

Method

A large set of experimental data was collected in which combustion properties of syngas were investigated. The collected data consisted of ignition delay measurements in shock tubes and in rapid compression machines (1041 data points from 10 publications), and laminar flame velocity measurements using outwardly propagating spherical flame, flame cone, counterflow twin-flame and heat flux burner methods (1963 data points from 32 publications). Detailed reaction mechanisms published in the last decade were also collected that described the combustion of syngas. A comprehensive study was carried out to investigate the performance of these mechanisms at the experimental conditions [1].

A sensitivity analysis at the conditions of each experimental data point was performed using the model developed by Kéromnès *et al*. [2] with respect to the Arrhenius parameter A of each elementary reaction of the model, including the A parameters describing the low-pressure limit rate coefficients. Based on the results, the Arrhenius parameters of 16 elementary reactions can be optimized to the available experimental data. Rate coefficient values determined in direct measurements for these sixteen reactions have also been collected and included in the optimization.

10 of the 16 selected rate coefficients also play an important role in the combustion of hydrogen, and have been determined with high accuracy during our recent optimization of the hydrogen combustion sub-mechanism of the Kéromnès *et al*. model [3].

We used the Kéromnès *et al*. model with the previously optimized [3] hydrogen combustion sub-mechanism as the starting point of our optimization. The selected reactions are summarized in Table 1.

Newly optimized reactions	Reactions previously optimized to hydrogen combustion data
$H + H + M = H_2 + M$ (low pressure limit)	$H + O_2 = O + OH$
$CO + O_2 = CO_2 + O$	$O + H_2 = H + OH$
$CO + OH = CO_2 + H$	$OH + H_2 = H + H_2O$
$HCO + M = H + CO + M$ (low pressure limit)	$H + OH + M = H_2O + M$ (low pressure limit)
$HCO + O_2 = HO_2 + CO$	$H + O_2 + M = HO_2 + M$ (low pressure limit)
$HCO + H = CO + H_2$	$HO_2 + H = H_2 + O_2$
	$HO_2 + H = OH + OH$
	$HO_2 + OH = H_2O + O_2$
	$HO_2 + HO_2 = H_2O_2 + O_2$
	$OH + OH + M = H_2O_2 + M$ (low pressure limit)
	$H_2O_2 + H = H_2 + HO_2$

Table 1. Reactions selected for optimization

Response surfaces were calculated for each experiment using the method described in [3]. In each case only those parameters, which the sensitivity analysis indicated as being influential at the experimental conditions, were selected as the independent variables of the response surface.

A global optimization of the selected Arrhenius parameters was performed using the algorithm described in our recent article [4], extended with a hierarchical optimization approach [3]. The following least squares error function was minimized.

$$E = \frac{1}{N}\sum_{i=1}^{N}\frac{1}{N_i}\sum_{j=1}^{N_i}\left(\frac{Y_{ij}^{\mathrm{sim}} - Y_{ij}^{\mathrm{exp}}}{\sigma(Y_{ij}^{\mathrm{exp}})}\right)^2 \qquad (1)$$

Here N is the number of datasets and N_i is the number of data points in the *i*-th dataset. The values Y_{ij}^{exp} and $\sigma(Y_{ij}^{\mathrm{exp}})$ are the *j*-th data point and its standard deviation, respectively, in the *i*-th measurement series and Y_{ij}^{sim} is the corresponding modeled data point. The response surfaces were used during the optimization to decrease the computational cost of evaluating Equation (1). The previously optimized rate coefficients (see the right column of Table 1) were re-optimized using the merged set of hydrogen and syngas combustion data.

Results and discussion

As a result of optimization, a new syngas combustion mechanism was obtained. The joint covariance matrix of the optimized parameters, the temperature dependent uncertainties of the sixteen determined rate coefficients, and the temperature dependent correlation coefficients between the rate coefficient pairs were calculated.

The performance of the optimized mechanism was compared to those of various recently published syngas combustion mechanisms by evaluating the error function defined by Eq. (1) for each mechanism. The overall improvement is demonstrated in Table 2.

Mechanism	Reference	Ignition delay	Flame velocity	Overall
ELTE Syngas Mechanism 2014	this work	6.90	4.76	11.66
NUIG NGM 2010 c5_49	[5]	10.36	6.54	16.90
Kéromnès 2013	[2]	14.95	5.89	20.84
CRECK 2012	[6]	14.29	7.16	21.45
San Diego 2014	[7]	10.58	12.87	23.45
Davis 2005	[8]	19.61	4.43	24.04
Li 2007	[9]	18.88	5.53	24.41
Starik 2009	[10]	13.43	11.17	24.60
Saxena Williams 2006	[11]	29.71	5.04	34.75
Sun 2007	[12]	50.39	6.18	56.57

Table 2. Comparison of the error function values obtained for our optimized mechanism and the previously published combustion mechanisms.

Conclusion

A large amount of experimental data was collected for syngas combustion, including 1041 ignition delay measurements in shock tubes and in rapid compression machines, and 1963 measured flame velocities, covering wide ranges of initial temperature, pressure, equivalence ratio and H_2/CO ratio. The Kéromnès *et al.* mechanism [2] was optimized, and the resultant mechanism gives a better description of the experimental data than any of the published syngas combustion mechanisms published to date.

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