Development of a joint hydrogen and syngas combustion mechanism based on an optimization approach

T. Varga[1,2], C. Olm[1,2], I. Gy. Zsély[1], T. Nagy[3], É. Valkó[1,2], R. Pálvölgyi[1], H. J. Curran[4], T. Turányi[1]

1. *Laboratory for Chemical Kinetics, Eötvös University (ELTE) – Budapest, Hungary*
2. *MTA-ELTE Research Group on Complex Chemical Systems – Budapest, Hungary*
3. *Institute of Materials and Environmental Chemistry, RCNS of HAS – Budapest, Hungary*
4. *Combustion Chemistry Centre, National University of Ireland, Galway (NUIG), Ireland*

Introduction

In recent years, there has been an increased interest in studying the combustion of hydrogen, and fuel mixtures consisting of carbon monoxide and hydrogen, referred to as syngas or "wet CO". Both are promising candidates for extensive use as sustainable fuels, as the combustion of hydrogen does not produce carbon-dioxide and syngas can be produced in large quantities in a carbon-neutral way from biomass. The development of clean and efficient combustion technologies for these fuels requires an in-depth and accurate knowledge of the chemical processes that occur during combustion.

The recent studies of Olm *et al.* [1, 2] on the modelling of hydrogen and syngas combustion clearly showed, that while there has been a large improvement in the recent years in the description of syngas combustion, even the most recent models are not able to provide a good reproduction of all types of experimental data from indirect measurements (*e.g.* ignition delays, laminar burning velocities and concentration-time profiles) in the whole range of experimental conditions that has been covered in the literature.

In this work we utilized our recently developed optimization methodology [3] to create an improved syngas and hydrogen combustion mechanism that provides satisfactory reproduction of all available experimental data on both syngas and hydrogen combustion. The optimization was based on the comprehensive collection of experimental data of Olm *et al.* [1, 2], which was extended with several more recent experimental results.

Optimization procedure

We have selected the syngas combustion model of Kéromnès *et al.* [4] as the starting point of our development. The hydrogen combustion sub-mechanism was replaced with our recent optimized hydrogen combustion mechanism [5]. In our initial mechanism, the pressure dependence of the rate coefficient of reaction H + CO + M = HCO + M was based on the study of Yang *et al*. [6]. Local sensitivity analysis was applied to the rate parameters of the initial mechanism at the conditions of all investigated experiments and 18 important reactions were identified. All three Arrhenius parameters (A, n, E) of these reactions (if applicable) and several third-body collision efficiencies were selected for optimization. Direct rate coefficient measurements were collected from the literature for these reactions, and were also used as optimization targets.

corresponding author: Tamás Turányi, turanyi@chem.elte.hu

Global optimization of altogether 48 Arrhenius parameters and 5 third-body collision efficiency parameters was carried out by minimizing a least squares error function. To improve the numerical efficiency of the procedure, a hierarchical optimization strategy, as described in [5], was employed. The optimization was carried out within the uncertainty domains of the rate parameters as published by Nagy *et al.* [7].

Results of optimization

Optimal values were obtained for the 53 rate parameters, and their covariance matrix was estimated using the method described by Turányi *et al.* [3]. From the covariance matrix of the rate parameters, temperature-dependent uncertainty ranges were calculated for the rate coefficients of the optimized reactions. Almost all rate coefficients could be determined with small posterior uncertainty and we consider the optimized values as good recommendations for the physical values of the rate coefficients.

The performance of the optimized mechanism was compared to several hydrogen and syngas combustion mechanisms that have been validated or extensively used for the simulation of hydrogen and syngas combustion. Significant overall improvement was achieved in the description of the syngas combustion data compared to all of the investigated syngas mechanisms, and a similarly good overall performance was achieved for hydrogen combustion as in our previous optimization study [5]. The optimized mechanism provides realistic results in wide ranges of the validation, and it is a good candidate for a base mechanism for the development of larger combustion mechanisms and automatic mechanism generation.

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