

# Testing several butanol combustion mechanisms against a large set of experimental data and investigation of thermochemical data inconsistency

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## Introduction

We have investigated a series of detailed reaction mechanisms for the combustion of hydrogen [1], synthesis gas [2], methanol [3] and ethanol [4]. These works demonstrated that some of the widely used mechanisms reproduce poorly several related experimental data. Also, even the best mechanisms may perform surprisingly badly at some particular conditions. The same methodology has been applied on the combustion of butanol. Also, the consistency of thermochemical data in several combustion mechanisms is also investigated.

## Methodology

The method of comparison has been discussed elsewhere in details [1], [2], and only a brief summary is presented here. The main steps are the following: (1) Collection and processing of all relevant publications dealing with butanol combustion measurements; (2) Encoding the experimental data in ReSpecTh Kinetics Data Format (RKD) files [5], [6]; (3) Estimation of the error of the experimental datasets based on the scatter of measured points determined by using code *Minimal Spline Fit* [7] and the reported experimental errors; (4) Program *Optima++* [8] reads the RKD files and performs the simulations automatically for a selected reaction mechanism using the FlameMaster code [9]. It is repeated for each reaction mechanism investigated. (5) Program *outgen* [10] processes the results and calculates various performance indicators based on all experiments or a selected subset of them for each mechanism.

In this work, the agreement between the experimental and simulation results is characterized using the sum of squares error function  $E$  (used also in model optimization studies [1]) and the average absolute deviation  $D$ :

$$E = \frac{1}{N} \sum_{i=1}^N \frac{1}{N_i} \sum_{j=1}^{N_i} \left( \frac{Y_{ij}^{\text{sim}} - Y_{ij}^{\text{exp}}}{\sigma(Y_{ij}^{\text{exp}})} \right)^2, \quad D = \frac{1}{N} \sum_{i=1}^N \frac{1}{N_i} \sum_{j=1}^{N_i} \frac{D_{ij}}{\sigma(Y_{ij}^{\text{exp}})} = \frac{1}{N} \sum_{i=1}^N \frac{1}{N_i} \sum_{j=1}^{N_i} \frac{(Y_{ij}^{\text{sim}} - Y_{ij}^{\text{exp}})}{\sigma(Y_{ij}^{\text{exp}})}$$

where

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

Here  $N$  is the number of datasets and  $N_i$  is the number of data points in the  $i$ -th dataset. Values  $y_{ij}^{\text{exp}}$  and  $\sigma(y_{ij}^{\text{exp}})$  are the  $j$ -th data point and its standard deviation, respectively, in the  $i$ -th dataset. The corresponding simulated (modelled) value is  $Y_{ij}^{\text{sim}}$  obtained from a simulation using a detailed mechanism and an appropriate simulation method. For ignition delay time measurements the experimental results have relative errors, so we used option  $Y_{ij} = \ln(y_{ij})$ . Error function value  $E$  is expected to be near unity if the chemical kinetic model is accurate, and deviations of the measured and simulated results are caused by the scatter of the experimental data only. The deviation of simulated results is within  $3\sigma$  experimental scatter limits on average if  $E \leq 9$ . The  $D$  values may

show trends like systematic under- or over-prediction. The drawback of the  $D$  values is that positive and negative deviations in different data sets can cancel each other and may result in good average values.

### Experimental data collected

Butanol ignition delay times measured at wide ranges of experimental conditions were collected. In the shock tube (ST) experiments, initial temperatures and pressures varied in the ranges of 716–1886 K and 0.9–90.3 atm, respectively; the equivalence ratios were between  $\Phi = 0.5$ –1.0 and the mole fraction of the diluent between 0.56–0.98. In the rapid compression machine (RCM) measurements, initial temperature and pressure were varied in the ranges of 678–1040 K and 3–30 atm, respectively; the equivalence ratio was changed between  $\Phi = 0.7$ –1.0 and the mole fraction of the diluent between 0.15–0.78.

Concentration profiles measured at wide ranges of experimental conditions were collected. In the ST experiments, the initial temperature and pressure were varied in the ranges of 1276–1631 K and 1.4–1.9 atm, respectively; the initial mole fraction of butanol was 0.99. In the flow reactor measurements, initial temperatures and pressures were in the ranges of 672–1475 K and 1–12.5 atm, respectively; the equivalence ratios were between  $\Phi = 0$ –1.54 and the mole fraction of the diluent between 0.94–0.98. In the perfectly stirred reactor studies, the initial temperatures and pressures covered ranges of 770–1250 K and 1–10 atm, respectively; the equivalence ratio were changed between  $\Phi = 0.38$ –2.67 and the mole fraction of the diluent between 0.98–0.99.

Laminar flame velocities measured with the outwardly propagating flame, counterflow twin-flame and heat flux methods were collected. The initial temperature and pressure were varied in the range of 343–488 K and 0.89–9.9 atm, respectively; the equivalence ratio was changed between  $\Phi = 0.72$ –1.64 and the mole fraction of the diluent between 0.15–0.77.

Altogether 7074 data points in more than 248 datasets were encoded in RKD Format XML files based on 35 publications.

### Mechanisms investigated

Eighteen detailed reaction mechanisms recently developed for the combustion of various butanol isomers were investigated. Some mechanisms contain the chemistry of all isomers ([11]–[18]), others just some of them ([19]–[21]), or only one isomer (n-butanol: [22]–[27], t-butanol: [28]).

### Performance of the mechanisms

The simulations were performed with each reaction mechanism, but were not successful for all experimental points. Especially the flame calculations were challenging and only a few mechanisms could be used in the flame calculations. In general, none of the mechanisms can describe the combustion of all four butanol isomers accurately at all types of conditions. The average description of the experimental data by the simulation results showed hectic variation depending on the isomer, the type of experiment and the initial conditions. Some mechanisms are accurate for one isomer at a narrow range of conditions, but completely fail in other cases. Overall, the Sarathy 2012 [12] and Sarathy 2014 [14] mechanisms performed the best.

### Investigation of the consistency of thermochemical data in combustion mechanisms

Thermochemical data in the reaction mechanisms are used for the calculation of the temperature change due to heat release and for the calculation of the backward rate coefficients

of reversible reactions whose rate coefficient given in only one direction. The NASA polynomial format used in CHEMKIN-II describes the temperature dependency of the standard molar heat capacity, enthalpy and entropy with NASA polynomials defined in two temperature ranges. At the common mid-temperature, the two polynomials have to connect smoothly so that these thermodynamic functions will be continuous and continuously differentiable. Any violation of these requirements can lead numerical problems or at least slower integration during the simulations. One can expect that these fundamental requirements are fulfilled in recent reaction mechanisms, but according to our analysis this is not the case.

The numerical problems at the connecting point of the polynomials were investigated by code ThermCheck [29]. Not only the butanol mechanisms cited above were investigated, but also further 61 detailed reaction mechanisms developed for the description of hydrogen, syngas, methane, methanol, ethanol combustion. All examined hydrogen and syngas combustion mechanisms are free of discontinuity, and so are most of the methanol combustion mechanisms. However, more than half of the methane and ethanol mechanisms contain problematic polynomials and only a few butanol mechanism (Grana 2014, Harper 2011 and Van Geem 2010) are error-free in this respect. The best performing Sarathy 2014 mechanism contains 42 inconsistent connections and much more problems with the first derivative functions. Simulation package OpenSMOKE++ [30] was used to correct these discontinuity errors and a series of simulations were carried out with the original and the refitted thermodynamic data to test whether the inconsistencies might affect the average run time. Due to the correction of the thermodynamic data, the average simulation time of the rapid compression machine simulations decreased by a few percent, while the ignition delay times changed to a negligible extent.

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