

Testing several butanol combustion mechanisms against a large set of experimental data and investigating their thermochemical data inconsistency

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Abstract

The combustion chemistry of butanol, a promising alternative biofuel, is not fully understood yet. A comprehensive set of experimental data for butanol isomers was collected and their simulation was carried out with eighteen butanol mechanisms. The performance of the mechanisms was measured and compared based on a sum-of-square error function that characterized the agreement between the experimental and the simulation data. In general, none of the reaction mechanisms could describe the combustion of all four butanol isomers in all types of experiments consistently well. Mechanism by Sarathy et al. (2014) [29] seemed to be the most predictive.

Introduction

There has been a rising interest in butanol combustion in the last three decades due to the demand for bio-based, renewable liquid fuels. Butanol isomers are well applicable in spark ignition internal combustion engines as their properties are similar to those of petrol. A mixture of solvents containing acetone, n-butanol and ethanol can be produced by bacterial fermentation [1, 2]. Consequently, butanol is considered to be a next-generation biofuel.

The kinetic behaviour of the four butanol constitutional isomers varies and different chemical pathways may be important, while the global combustion properties including heat release and CO₂ emission are very similar. At the conditions of the flame measurements *n*-butanol is the most reactive isomer while *t*-butanol is the least reactive one. The isomers *s*- and *i*-butanol are almost equally reactive in flames. Fundamental differences between the high- and low-temperature pathways are observed [29]. Due to the large diversity of reaction pathways and the large number of species, the simulation of butanol combustion mechanisms are usually computationally expensive.

We have investigated a series of detailed reaction mechanisms for the combustion of hydrogen [3], synthesis gas [4], methanol [5] and ethanol [6]. These studies demonstrated that some of the widely used mechanisms reproduce several experimental data poorly. Also, even the best mechanisms may perform surprisingly badly at some particular conditions. In this work, the same benchmarking methodology is applied on the simulation results of 18 butanol combustion mechanisms published in the last eleven years to gain information on their overall performance so that we can select a good kinetic model with the purpose of isomer-specific optimization.

Methodology of mechanism testing

The method of comparison has been discussed elsewhere in details [3], [4], 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 (RKD) format files [7], [8].

(3) Estimation of the error of the experimental datasets based on the scatter of measured points determined by using code *Minimal Spline Fit* [9] and the reported experimental errors.

(4) Based on a provided list of RKD files, program *Optima++* [10], developed at Eötvös Loránd University (ELTE), reads them and performs all the corresponding simulations for a selected reaction mechanism using the FlameMaster code [11]. Simulations are repeated for each reaction mechanism investigated.

(5) Program *outgen* [12] 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 (defined first in model optimization studies [3]):

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

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}^{exp} and $\sigma(y_{ij}^{\text{exp}})$ are the j -th data point and its standard deviation (called briefly as “scatter”), respectively, in the i -th dataset. The corresponding simulated (modelled) value is Y_{ij}^{sim} obtained from a simulation using the investigated mechanism and an appropriate simulation method. If $\sigma(y_{ij}^{\text{exp}})$ scatters of measured values in a data series are approximately constant, then it can be characterized by an absolute error and the data point is used in the objective function without transformation, that is $Y_{ij} = y_{ij}$. We used this option for laminar burning velocities and measured concentrations. If $\sigma(\ln y_{ij}^{\text{exp}})$ scatters are

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proportional to the measured values in a data series, then it can be characterized by a relative error and the data point is transformed as $Y_{ij} = \ln y_{ij}$, which is characteristic for ignition time measurements. 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 purely statistical and caused by the scatter of the experimental data only. If the deviation of simulated results is on average within 3 standard deviation of the experimental data, then $E \leq 9$.

Experimental data collection

Butanol ignition delay times measured at wide ranges of experimental conditions were collected. In the shock tube experiments, initial temperature and pressure 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 was between 0.56–0.98. In the rapid compression machine 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 was between 0.15–0.78.

Concentration profiles measured at wide ranges of experimental conditions were collected. In the shock tube 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 was between 0.94–0.98. In the perfectly stirred reactor studies, the initial temperatures and pressures covered the 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 was between 0.98–0.99.

Premixed laminar burning 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 ranges 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 was between 0.15–0.77.

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

Butanol combustion simulations

Eighteen detailed reaction mechanisms developed for the combustion of various butanol isomers were investigated. The reaction mechanisms are denoted with the first author's name and the year of publication.

Using code FlameMaster in Optima++ framework the reaction mechanisms have been tested over a wide range of conditions by simulating various types of experiments,

such as shock tube, rapid compression machine, flow reactor and jet-stirred reactor measurements.

The high temperature version of mechanism *Sarathy 2014* and *Black 2010* were reduced for the one-dimensional laminar burning velocity calculations. We used these flame data as initial guess for mechanisms *Cai 2012-2*, *Sarathy 2009*, *Sarathy 2012* and *Chang 2016*. The computational grids in the flame calculations contained at least 600 points.

Table 1 Overview of butanol combustion mechanisms

mechanism	ref.	isomers	species	reactions
<i>Moss 2008</i>	[13]	all	234	1399
<i>Dagaut 2009</i>	[14]	<i>n</i>	118	878
<i>Sarathy 2009</i>	[15]	<i>n</i>	117	884
<i>Black 2010</i>	[16]	<i>n</i>	234	1399
<i>Van Geem 2010</i>	[17]	all	281	7205
<i>Veloo 2010</i>	[18]	<i>n</i>	266	1639
<i>Harper 2011</i>	[19]	<i>n, s, t</i>	263	6751
<i>Cai 2012-1</i>	[20]	<i>t</i>	101	511
<i>Cai 2012-2</i>	[21]	<i>n</i>	123	1346
<i>Sarathy 2012</i>	[22]	all	284	3635
<i>Yasunaga 2012</i>	[23]	all	284	3635
<i>Zhang 2012</i>	[24]	<i>n</i>	243	1475
<i>Cai 2013</i>	[25]	<i>n, s</i>	160	2062
<i>Merchant 2013</i>	[26]	all	372	16632
<i>Vasu 2013</i>	[27]	all	283	3635
<i>Cai 2014</i>	[28]	<i>n, i, s</i>	182	2571
<i>Sarathy 2014</i>	[29]	all	687	3435
<i>Chang 2016</i>	[30]	all	66	196

Performance of reaction mechanisms

Due to the high complexity of the investigated butanol reaction mechanisms, not all of the experimental data points could be simulated successfully using code FlameMaster. The flame calculations were especially challenging and only a few mechanisms proved to be applicable in laminar burning velocity calculations.

Tables 2–5 provide the average error of the reaction mechanisms by butanol isomer with respect to type of experiment (ignition delay time measured in shock tubes, concentration profile measurements of shock tubes and flow reactors). Rapid compression machine and jet-stirred reactor simulation results are not shown as only relatively few simulations were successful.

Figure 1 shows the comparison of reaction mechanisms regarding the one-dimensional, premixed flame simulation results. Considering the laminar burning velocities, mechanism *Sarathy 2014* seemed to be the most predictive.

In order for reaction mechanisms to be comparable at a particular type of experiment, we have to select data points that were successfully simulated with a group of reaction mechanisms. First, we selected the largest possible set of data points. However, we had to omit some of the reaction mechanisms accordingly, due to lack of enough successful simulation results. Second, we

selected only those data points that were successfully simulated with all related reaction mechanisms. In most cases, the average error values are therefore based on a larger (left column) and a smaller (right column) set of data points. The colour scale applied in the tables makes it easier to compare average simulation errors where green corresponds to good (3σ), yellow to satisfactory (6σ) and red to poor agreement (9σ).

Table 2 Comparison of the average simulation error of the reaction mechanisms with respect to *n*-butanol.

<i>n</i> -BuOH	ignition delay t.: shock tube		conc.: shock tube, flow reactor	
<i>Moss 2008</i>	92.9	25.3	39.3	20.2
<i>Dagaut 2009</i>	369.7	100.6	24.3	3.6
<i>Sarathy 2009</i>	357.3	106.7	40.1	2.5
<i>Black 2010</i>	79.1	13.9	25.2	3.6
<i>Van Geem 2010</i>	55.2	8.1	312.3	57.0
<i>Veloo 2010</i>	112.0	40.0	68.3	10.4
<i>Harper 2011</i>	97.5	22.8	367.9	56.9
<i>Cai 2012-2</i>	–	16.4	–	92.2
<i>Sarathy 2012</i>	34.7	11.6	241.8	64.8
<i>Yasunaga 2012</i>	69.9	12.4	–	64.8
<i>Zhang 2012</i>	64.2	9.2	15.0	3.8
<i>Cai 2013</i>	–	14.0	254.5	83.3
<i>Merchant 2013</i>	728.0	714.4	253.4	66.6
<i>Vasu 2013</i>	92.1	27.3	–	–
<i>Cai 2014</i>	–	366.4	259.4	81.0
<i>Sarathy 2014</i>	28.3	27.7	15.2	5.1
<i>Chang 2016</i>	63.1	56.5	240.6	41.3
No. of datasets	50	34	14	7
No. of data points	370	142	608	239

Table 3 Comparison of the average simulation error of the reaction mechanisms with respect to *s*-butanol.

<i>s</i> -BuOH	ignition delay t.: shock tube		conc.: shock tube, flow reactor	
<i>Moss 2008</i>	62.6	53.7	160.4	
<i>Van Geem 2010</i>	44.0	26.2	190.1	
<i>Harper 2011</i>	–	181.8	242.6	
<i>Sarathy 2012</i>	41.8	21.0	97.6	
<i>Yasunaga 2012</i>	41.8	21.0	–	
<i>Cai 2013</i>	–	192.2	63.7	
<i>Merchant 2013</i>	1146.5	1196.0	139.0	
<i>Vasu 2013</i>	40.6	19.9	–	
<i>Cai 2014</i>	–	99.7	56.1	
<i>Sarathy 2014</i>	68.7	38.0	5.6	
<i>Chang 2016</i>	26.3	26.2	101.9	
No. of datasets	17	16	23	
No. of data points	129	72	1273	

Table 4 Comparison of the average simulation error of the reaction mechanisms with respect to *i*-butanol.

<i>i</i> -BuOH	ignition delay t.: shock tube		conc.: shock tube, flow reactor
<i>Moss 2008</i>	33.4	31.4	16.5
<i>Van Geem 2010</i>	80.2	80.1	29.9
<i>Sarathy 2012</i>	12.8	13.1	9.3
<i>Yasunaga 2012</i>	12.8	13.1	–
<i>Merchant 2013</i>	193.6	181.8	40.2
<i>Vasu 2013</i>	12.6	12.9	–
<i>Cai 2014</i>	–	60.5	1.1
<i>Sarathy 2014</i>	58.4	61.8	9.1
<i>Chang 2016</i>	32.6	34.6	70.4
No. of datasets	16	15	15
No. of data points	101	85	1192

Table 5 Comparison of the average simulation error of the reaction mechanisms with respect to *t*-butanol.

<i>t</i> -BuOH	ignition delay t.: shock tube		conc.: shock tube, flow reactor
<i>Moss 2008</i>	91.8		136.8
<i>Van Geem 2010</i>	19.4		–
<i>Harper 2011</i>	40.6		–
<i>Cai 2012-1</i>	379.0		115.9
<i>Sarathy 2012</i>	140.0		84.7
<i>Yasunaga 2012</i>	139.5		–
<i>Merchant 2013</i>	2183.4		–
<i>Vasu 2013</i>	139.4		63.9
<i>Sarathy 2014</i>	26.0		99.8
<i>Chang 2016</i>	72.5		205.2
No. of datasets	13		1
No. of data points	99		104

Mechanism *Sarathy 2014* describes the combustion of *n*-butanol consistently well or satisfactorily at both types of experiments (Table 2). The agreement is very good in concentration measurements for *s*-butanol (Table 3) and *i*-butanol (Table 4). The performance of mechanism *Sarathy 2012* proved to be consistently good for *i*-butanol. (Table 4). Experimental data of *i*-butanol have been relatively satisfactorily reproduced with the reaction mechanisms. For *i*-butanol concentration experiments, mechanism *Cai 2014* attained the lowest average simulation error among all results presented in the tables (Table 4).

In general, none of the reaction mechanisms could 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 (Figure 2). Some mechanisms were accurate for one isomer at a narrow range of conditions, but completely failed in other cases. Overall, the *Sarathy 2012* [22] and *Sarathy 2014* [29] mechanisms performed the best.

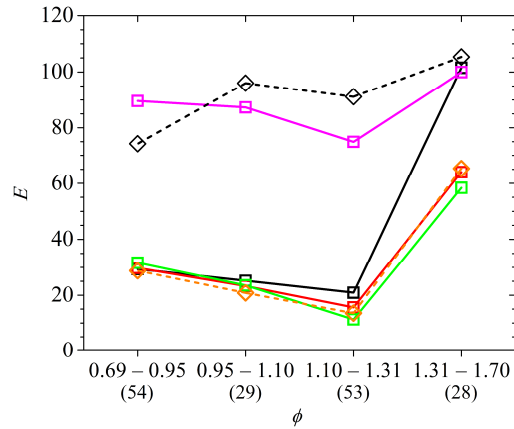
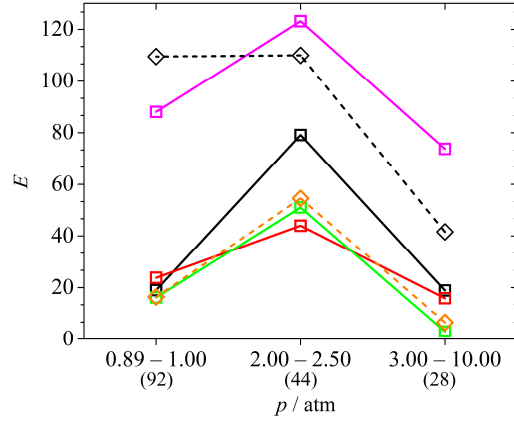
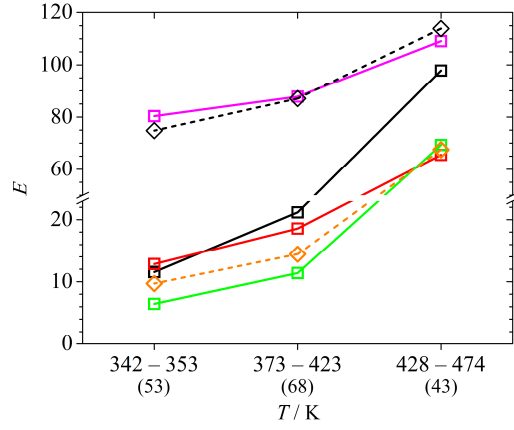


Figure 1 Average simulation error of reaction mechanisms depending on initial temperature, pressure and equivalence ratio based on premixed *n*-butanol laminar burning velocity experiments. Numbers in parentheses below correspond to the number of data points taken into account.

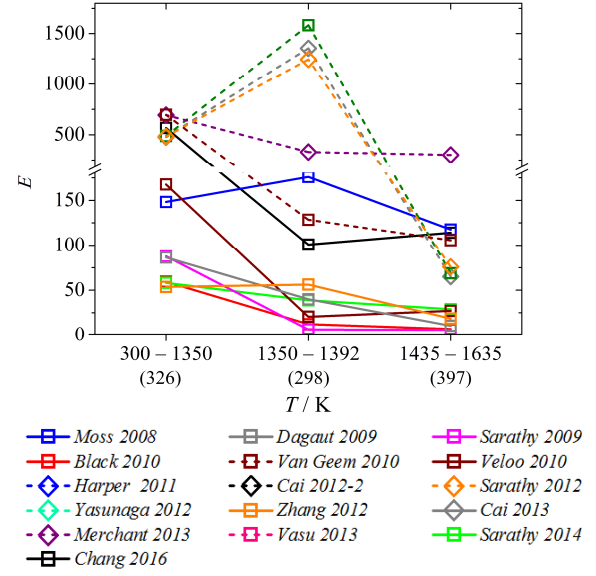


Figure 2 Average simulation error of reaction mechanisms depending on initial temperature based on concentration profiles of *n*-butanol experiments measured in shock tube and flow reactor. Numbers in parentheses below correspond to the number of data points taken into account.

Investigation of consistency of thermochemical data in combustion mechanisms

Thermochemical data in kinetic 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 polynomials used in CHEMKIN-II describes the temperature dependence of the standard molar heat capacity, enthalpy and entropy with polynomials defined in two adjacent 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 here, too. Any violation of these requirements can lead to numerical problems – leastways, slower integration during the simulations. One may expect that these fundamental requirements are fulfilled in recent reaction mechanisms, but according to our analysis this is not the case.

The absolute deviations at the connecting point of the polynomials were investigated with code ThermCheck [31] listing the species where C_p/R , S°/R , H°/RT functions have larger discontinuity than 10^{-3} (Table 6). 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, and ethanol combustion.

Table 6 Discontinuity of C_p/R polynomials at mid-temperature in butanol mechanisms. N is the number of species with significant discontinuity error ($\text{abs}(\Delta C_p/R) > 10^{-3}$), max. is the maximal absolute discontinuity error occurred in the mechanism.

mechanism	N	max.
<i>Black 2010, Zhang 2012</i>	4	$3 \cdot 10^{-3}$
<i>Cai 2012-1, Cai 2012-2</i>	9	$8 \cdot 10^{-1}$
<i>Cai 2013</i>	9	$8 \cdot 10^{-1}$
<i>Cai 2014</i>	10	$8 \cdot 10^{-1}$
<i>Chang 2016</i>	2	$1 \cdot 10^{-2}$
<i>Dagaut 2009, Sarathy 2009</i>	22	$3 \cdot 10^{-2}$
<i>Harper 2011, Van Geem 2010</i>	0	$6 \cdot 10^{-4}$
<i>Merchant 2013</i>	1	$1 \cdot 10^{-2}$
<i>Moss 2008</i>	141	1.9
<i>Sarathy, Yasunaga 2012, Vasu 2013</i>	14	$9 \cdot 10^{-2}$
<i>Sarathy 2014</i>	22	$9 \cdot 10^{-2}$
<i>Veloo 2010</i>	1	$3 \cdot 10^{-3}$

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. The most considerable discontinuities are found in the butanol mechanisms.

One of the most extreme examples of jump is the C_p/R function of acetaldehyde in mechanism *Moss 2008*. Mechanism *Sarathy 2014* is a good example for this species (Figure 3). The C_p/R function of buta-1,2-diene in mechanism *Sarathy 2014* is not continuously differentiable as opposed to the same function in methane reaction mechanism *Aramco II* (Figure 4).

The best performing *Sarathy 2014* mechanism contains 22 inconsistent connections at the NASA polynomials and 95 inconsistent connections at their first derivative functions. Simulation package OpenSMOKE++ [32] was used to correct these discontinuity errors and 22 rapid compression machine (RCM) simulations were carried out with the original and the refitted thermochemical data 4 times to test whether the inconsistencies might affect the average run time (Table 7). Due to the correction of the thermochemical data, the average simulation time did not decrease drastically, only by a few percent. According to the two-sample t -test, however, there was a significant difference between the average run times while the ignition delay times changed only to a negligible extent.

Table 7 Average run time of a series of RCM simulations using the original and the corrected thermochemical data.

<i>Sarathy 2014</i>	original	corrected
average run time	2073 s	1999 s
change		-73 s
standard deviation	18 s	25 s
t -value for t -test		0.0043
average error (E)	73.31	73.32

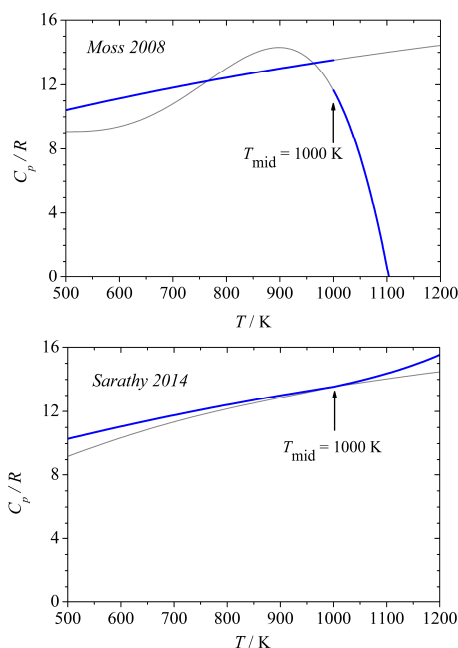


Figure 3 Jump discontinuity at C_p/R function of acetaldehyde (CH_3CHO).

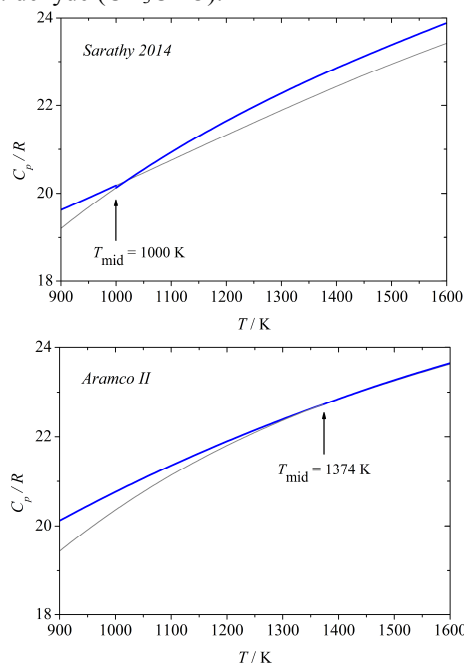


Figure 4 Not continuously differentiable C_p/R function of buta-1,2-diene (C_4H_6).

Conclusions

The purpose of the presented study was to provide a comparison of performance of the butanol combustion mechanisms published in the last eleven years. A good reaction mechanism can be selected for a given type of experiment and initial experimental conditions. Considering the laminar burning velocities, mechanism *Sarathy 2014* seemed to be the most predictive.

Significant discontinuities of the thermochemical functions of butanol reaction mechanisms have been demonstrated. Optimization of a selected butanol reaction mechanism is advisable with the usage of refitted, consistent thermochemical data.

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