

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



Martin Bolla¹, Carsten Olm¹, Tibor Nagy², István Gy. Zsély¹, Tamás Turányi¹

¹ Institute of Chemistry, ELTE Eötvös Loránd University, Budapest, Hungary

² MTA TTK Research Centre for Natural Sciences, Budapest, Hungary

Introduction

- Butanol is a promising **alternative biofuel** that can be used in gasoline-fueled internal combustion engines at higher mixture fractions than ethanol
- Can be produced via **biotechnological synthesis** and **fermentation** yielding an acetone, *n*-butanol and ethanol mixture
- Subject of **growing research interest**
- Large **diversity of reaction pathways**
- Not all details of butanol combustion chemistry are fully understood
- Measurements and simulations often yield **contradictory results**
- Application of a **quantitative measure to describe the agreement** between the measurements and simulation results
- **Inconsistent thermodynamic data** can lead to numerical problems – leastways, longer simulation times

Highlights

- A comprehensive set of **experimental data** for the four butanol isomers was collected, in total **7103 data points in 253 datasets from 35 publications**
- **Simulations** were carried out with 18 published mechanisms at the conditions of these experiments
- The **performance** of the mechanisms was compared using the a sum-of-square error function to quantify the agreement between the simulations and the collected experiments
- A good butanol combustion mechanism **can be selected** for a given condition
- **Thermodynamic data inconsistency of 82 combustion mechanisms** was investigated (12 hydrogen, 14 syngas, 14 methane, 7 methanol, 14 ethanol, 21 butanol mechanisms)

Error function

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

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

E objective function value
 N number of datasets
 N_i number of data points in the i -th dataset
 Y_{ij}^{mod} j -th modeled value
 Y_{ij}^{exp} j -th experimental value
 σ estimated standard deviation/ scatter

Acknowledgements

The research within project No. VEKOP-2.3.2-16-2017-00013 was supported by the European Union and the State of Hungary, co-financed by the European Regional Development Fund.

This work was facilitated by COST Action CM1404 (SmartCats). The authors thank for the contribution of Mr Hannes Böttler.



Collection of experimental data

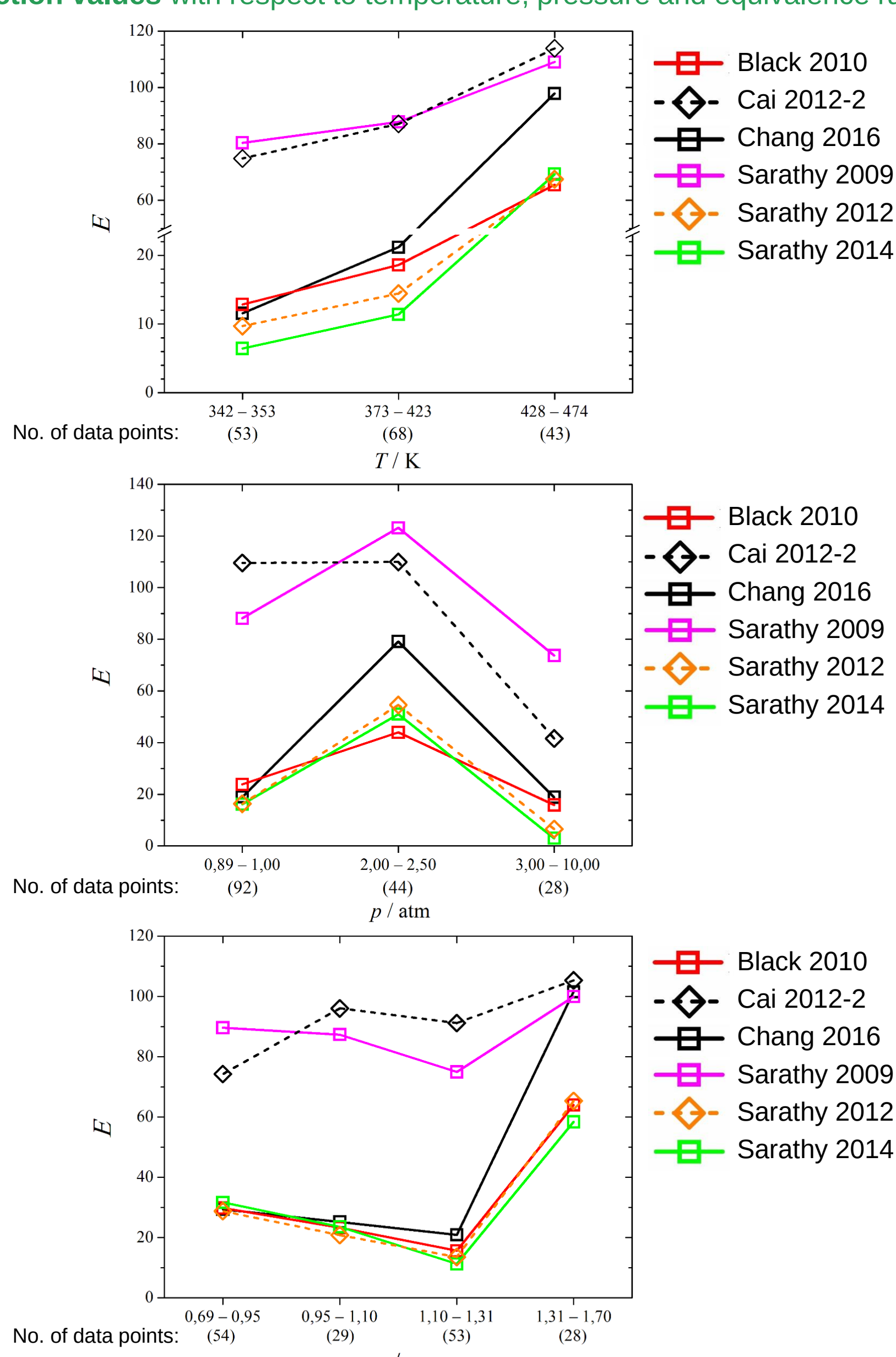
Type of measurement	Data-sets	Data points	p / atm	T / K	ϕ
Shock tube ignition delay times	106	808	0.9–90.3	716–1886	0.25–2
RCM ignition delay times	21	85	3–31.2	714–1034	0.5–2
Laminar burning velocities	43	349	0.89–9.9	343–488	0.7–1.7
Species concentration profiles	79	5832	1–12.5	672–1631	0.25–4
Abbreviations used: IDT Ignition delay time, ST Shock tube, FR Flow reactor, RCM Conc. Rapid compression machine, JSR Species concentration profile, Jet-stirred reactor					

Overview of butanol combustion mechanisms

Mechanism	Ref.	Isomers	Species	Reactions
Moss 2008	[1]	all	234	1399
Dagaut 2009	[2]	<i>n</i>	118	878
Sarathy 2009	[3]	<i>n</i>	117	884
Black 2010	[4]	<i>n</i>	234	1399
Van Geem 2010	[5]	all	281	7205
Veloo 2010	[6]	<i>n</i>	266	1639
Harper 2011	[7]	<i>n, s, t</i>	263	6751
Cai 2012-1	[8]	<i>t</i>	101	511
Cai 2012-2	[9]	<i>n</i>	123	1346
Sarathy 2012	[10]	all	284	3635
Yasunaga 2012	[11]	all	284	3635
Zhang 2012	[12]	<i>n</i>	243	1475
Cai 2013	[13]	<i>n, s</i>	160	2062
Merchant 2013	[14]	all	372	16632
Vasu 2013	[15]	all	283	3635
Cai 2014	[16]	<i>n, i, s</i>	182	2571
Sarathy 2014	[17]	all	687	3435
Chang 2016	[18]	all	66	196

Detailed study of mechanism behaviour

Example: *n*-butanol laminar burning velocities
Error function values with respect to temperature, pressure and equivalence ratio



Thermochemical data inconsistency

- The **NASA polynomials** describe the temperature dependence of C_p , S° and H° with polynomials defined in two adjacent temperature ranges. At the mid-temperature, the two polynomials have to connect smoothly so that these thermodynamic functions will be **continuous** and **continuously differentiable**.
- **Considerable discontinuities** were found at the **mid-temperature** (T_{mid}) in butanol mechanisms. The absolute deviations at the connecting point of the polynomials were investigated with code ThermCheck [21] listing the species where C_p/R , S°/R and H°/RT functions have larger discontinuity than 10^{-3} .
- Mechanism by Sarathy et al. (2014) [17] contains 22 inconsistent connections at the NASA polynomials and 95 inconsistent connections at their first derivative functions. **Correction** is needed by refitting the polynomials.

References

- [1] J.T. Moss, A.M. Berkowitz, M. A. Oehlschlaeger, J. Biet, V. Warth, P.A. Glaude, F. Battin-Leclerc, *J. Phys. Chem. A* 112 (2008) 10843–10855.
- [2] P. Dagaut, S.M. Sarathy, M.J. Thomson, *Proc. Combust. Inst.* 32 (2009) 229–234.
- [3] S.M. Sarathy, M.J. Thomson, C. Togbé, P. Dagaut, F. Halter, C. Mounaim-Rousselle, *Combust. Flame* 156 (2009) 852–864.
- [4] G. Black, H.J. Curran, S. Pichon, J.M. Simmie, V. Zhukov, *Combust. Flame* 157 (2010) 363–373.
- [5] K.M. Van Geem, S.P. Pyl, G.B. Marin, M.R. Harper and W.H. Green. *Ind Eng Chem Res*, 49 (2010) 10399–10420.
- [6] P.S. Veloo, Y.L. Wang, F.N. Egolfopoulos, C.K. Westbrook, *Combust. Flame* 157 (2010) 1989–2004.
- [7] M.R. Harper, K.M. Van Geem, S.P. Pyl, G.B. Marin and W.H. Green. *Combust Flame*, 158 (2011) 16–41.
- [8] J. Cai, L. Zhang, J. Yang, Y. Li, L. Zhao, F. Qi, *Energy* 43 (2012) 94–102.
- [9] J. Cai, L. Zhang, F. Zhang, Z. Wang, Z. Cheng, W. Yuan and F. Qi. *Energy Fuels*, 26 (2012) 5550–5568.
- [10] S.M. Sarathy, S. Vranckx, K. Yasunaga, M. Mehl, P. Oßwald, W.K. Metcalfe, C.K. Westbrook, W.J. Pitz, K. Kohse-Höinghaus, R.X. Fernandes and H.J. Curran. *Combust Flame*, 159 (2012) 2028–2055.
- [11] K. Yasunaga, T. Mikajiri, S.M. Sarathy, T. Koike, F. Gillespie, T. Nagy, J.M. Simmie, and H.J. Curran. *Combust Flame*, 159 (2012) 2009–2027.
- [12] J. Zhang, L. Wei, X. Man, X. Jiang, Y. Zhang, E. Hu, Z. Huang, *Energy & Fuels* 26 (2012) 3368–3380.
- [13] J. Cai, W. Yuan, L. Ye, Z. Cheng, Y. Wang, L. Zhang, F. Zhang, Y. Li and F. Qi. *Combust Flame*, 160 (2013) 1939–1957.
- [14] S.S. Merchant, E.F. Zanoelo, R.L. Speth, M.R. Harper, K.M. Van Geem and W.H. Green. *Combust Flame*, 160 (2013) 1907–1929.
- [15] S.S. Vasu and S.M. Sarathy. *Energy Fuels*, 27 (2013) 7072–7080.
- [16] J. Cai, W. Yuan, L. Ye, Z. Cheng, Y. Wang, W. Dong, L. Zhang, Y. Li, F. Zhang and F. Qi. *Combust Flame*, 161 (2014) 1955–1971.
- [17] S.M. Sarathy, P. Oßwald, N. Hansen, K. Kohse-Höinghaus, *Prog. Energy Combust. Sci.* 44 (2014) 40–102.
- [18] Y. Chang, M. Jia, J. Xiao, Y. Li, W. Fan, M. Xie, *Energy. Conv. Manage.* 128 (2016) 250–260.
- [19] T. Varga, Á. Busai, Optima++ v1.0: A general C++ framework for performing combustion simulations and mechanism optimization. <http://respecth.hu>.
- [20] H. Pitsch, FlameMaster v3.3.11 (<http://www.itv.rwth-aachen.de/en/downloads/flamemaster/>).
- [21] T. Nagy and T. Turányi, SEM: mechanism reduction based on simulation error minimization, 2009. <http://respecth.hu>.
- [22] A. Cuoci, A. Frassoldati, T. Faravelli, and E. Ranzi, *Comput. Phys. Commun.*, 192 (2015) 237–264.

Simulations were carried out within the **Optima++ simulation framework** [19], used in conjunction with the **FlameMaster** [20] solver.

The Optima++ simulation framework is freely available for download: <http://respecth.hu>

The numerical problems at the connecting point of the NASA polynomials were investigated by code **ThermCheck** [21]. Some related simulations were performed with **OpenSmoke++** [22].

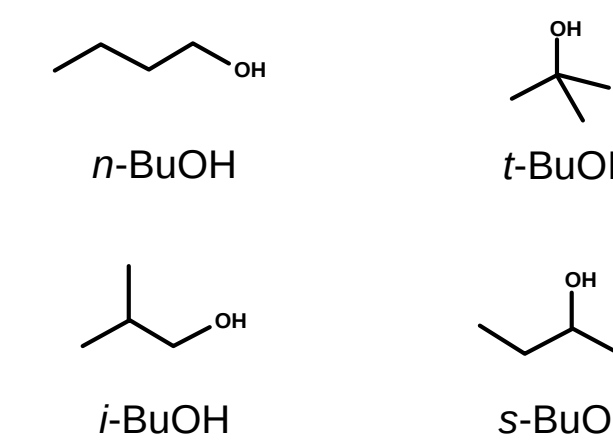
Comparison of combustion mechanisms

Error function values
(lower value = better agreement between simulations and measurements)

IDT: ignition delay time in shock tube
conc.: concentration profiles in shock tube and flow reactor

In several cases, error function values are based on a larger and a smaller set of data points since some average values could not be obtained due to lack of enough successful simulation results (“–”)

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



<i>i</i> -BuOH	IDT	conc.		<i>s</i> -BuOH	IDT	conc.	
Moss 2008	33.4	31.4	16.5	Moss 2008	62.6	53.7	160.4
Van Geem 2010	80.2	80.1	29.9	Van Geem 2010	44.0	26.2	190.1
Sarathy 2012	12.8	13.1	9.3	Harper 2011	–	181.8	242.6
Yasunaga 2012	12.8	13.1	–	Sarathy 2012	41.8	21.0	97.6
Merchant 2013	193.6	181.8	40.2	Yasunaga 2012	41.8	21.0	–
Vasu 2013	12.6	12.9	–	Cai 2013	–	192.2	63.7
Cai 2014	–	60.5	1.1	Merchant 2013	1146.5	1196.0	139.0
Sarathy 2014	58.4	61.8	9.1	Vasu 2013	40.6	19.9	–
Chang 2016	32.6	34.6	70.4	Cai 2014	–	99.7	56.1
No. of datasets	16	15	15	Sarathy 2014	68.7	38.0	5.6
No. of data points	101	85	1192	Chang 2016	26.3	26.2	101.9
				No. of datasets	17	16	23
				No. of data points	129	72	1273

laminar burning velocity *n*-BuOH *s*-BuOH *i*-BuOH *t*-BuOH

Black 2010	16.7			
Cai 2012-2	86.3			
Chang 2016	13.3	50.6	12.5	40.6
Sarathy 2009	88.0			
Sarathy 2012	9.0	26.0	39.5	198.8
Sarathy 2014	5.9	20.9	16.3	20.5
No. of datasets	16	5	12	10
No. of data points	128	42	102	77

- **Reproduction of the experimental 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)** [17] seemed to be the most predictive considering the laminar burning velocities.

