

Testing several butanol combustion mechanisms against a large set of experimental data



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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

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 at a given condition **can be selected**

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 error 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

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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 Rapid compression machine
Conc. Species concentration profile
JSR Jet-stirred reactor

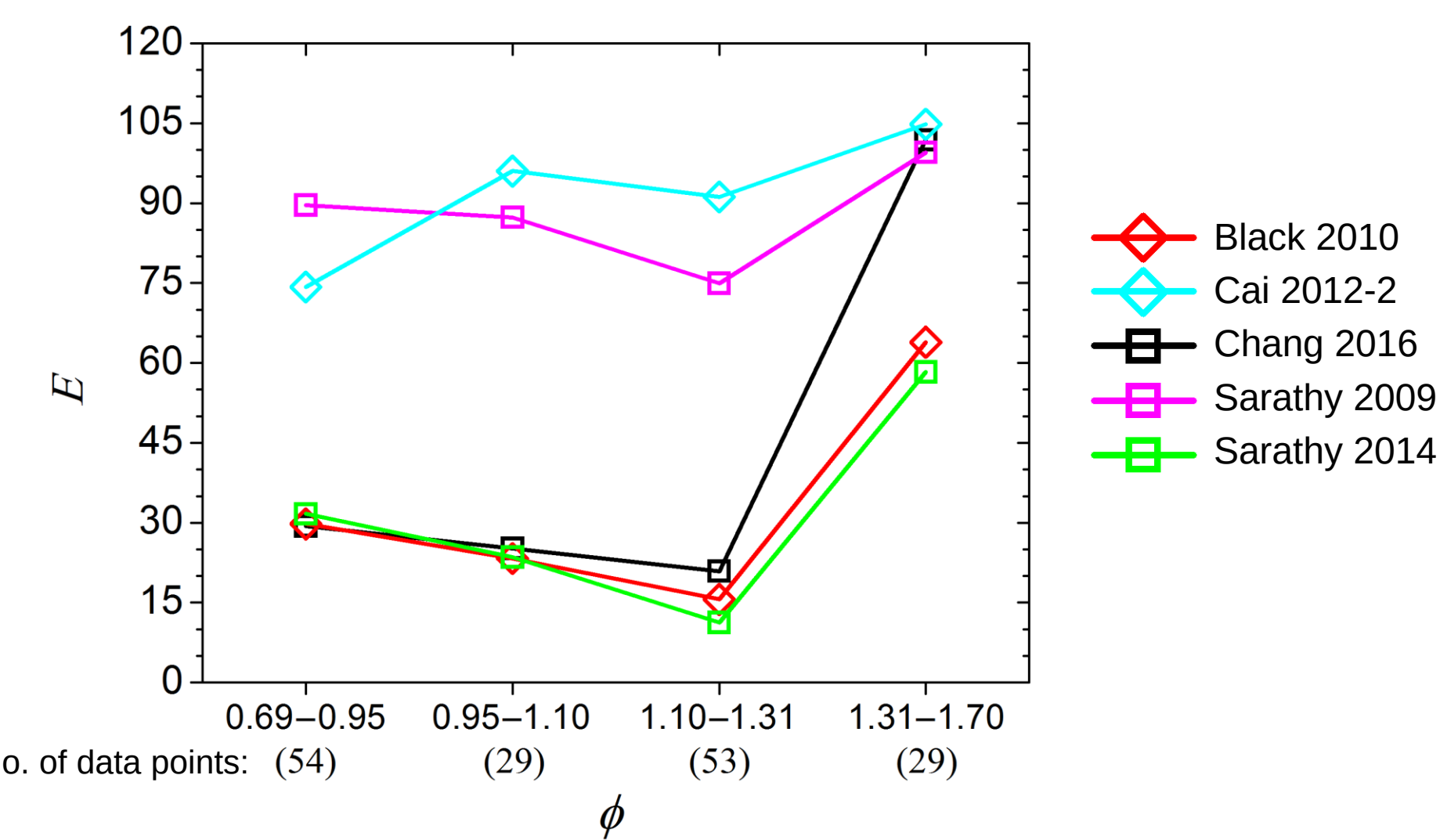
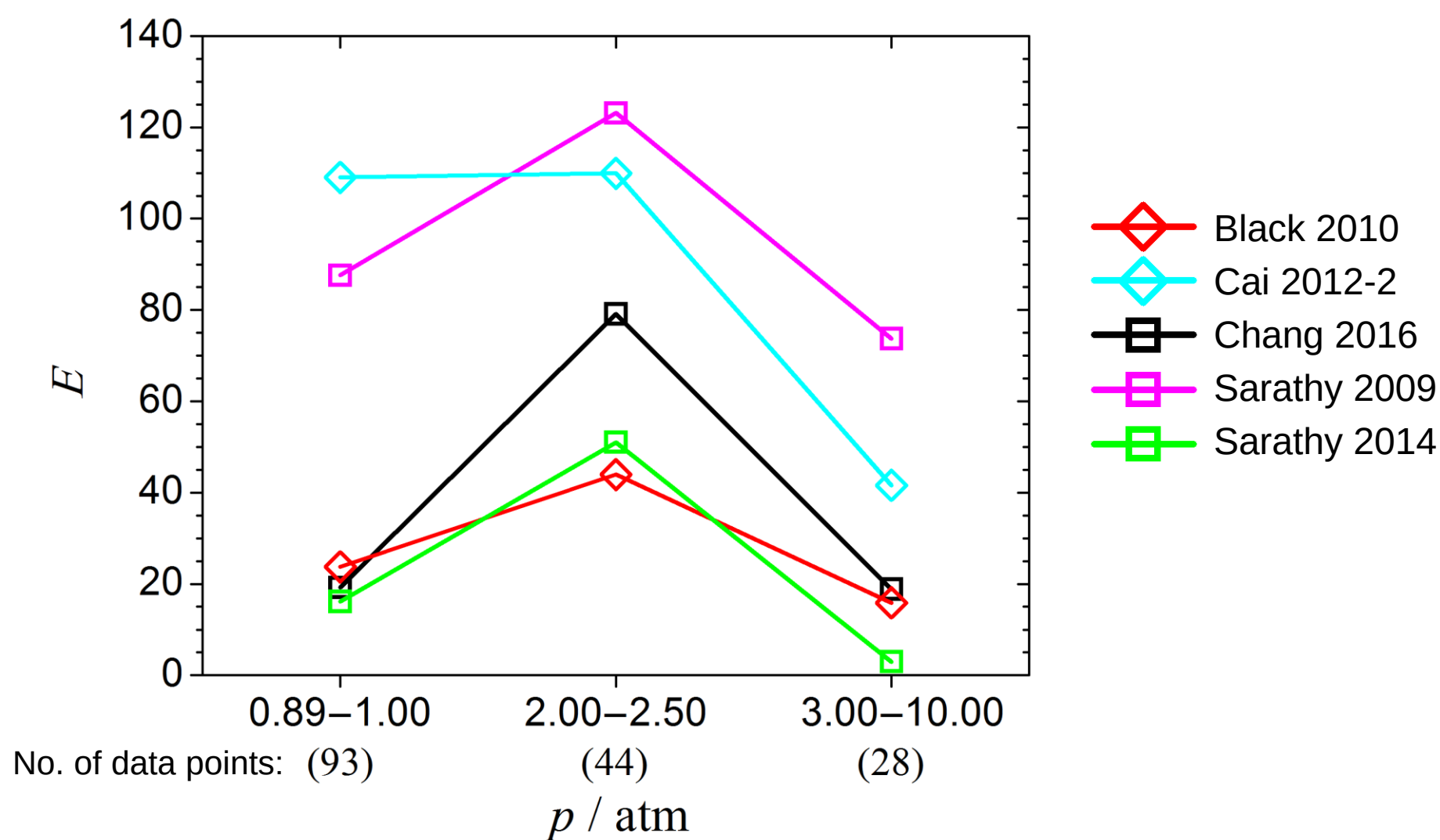
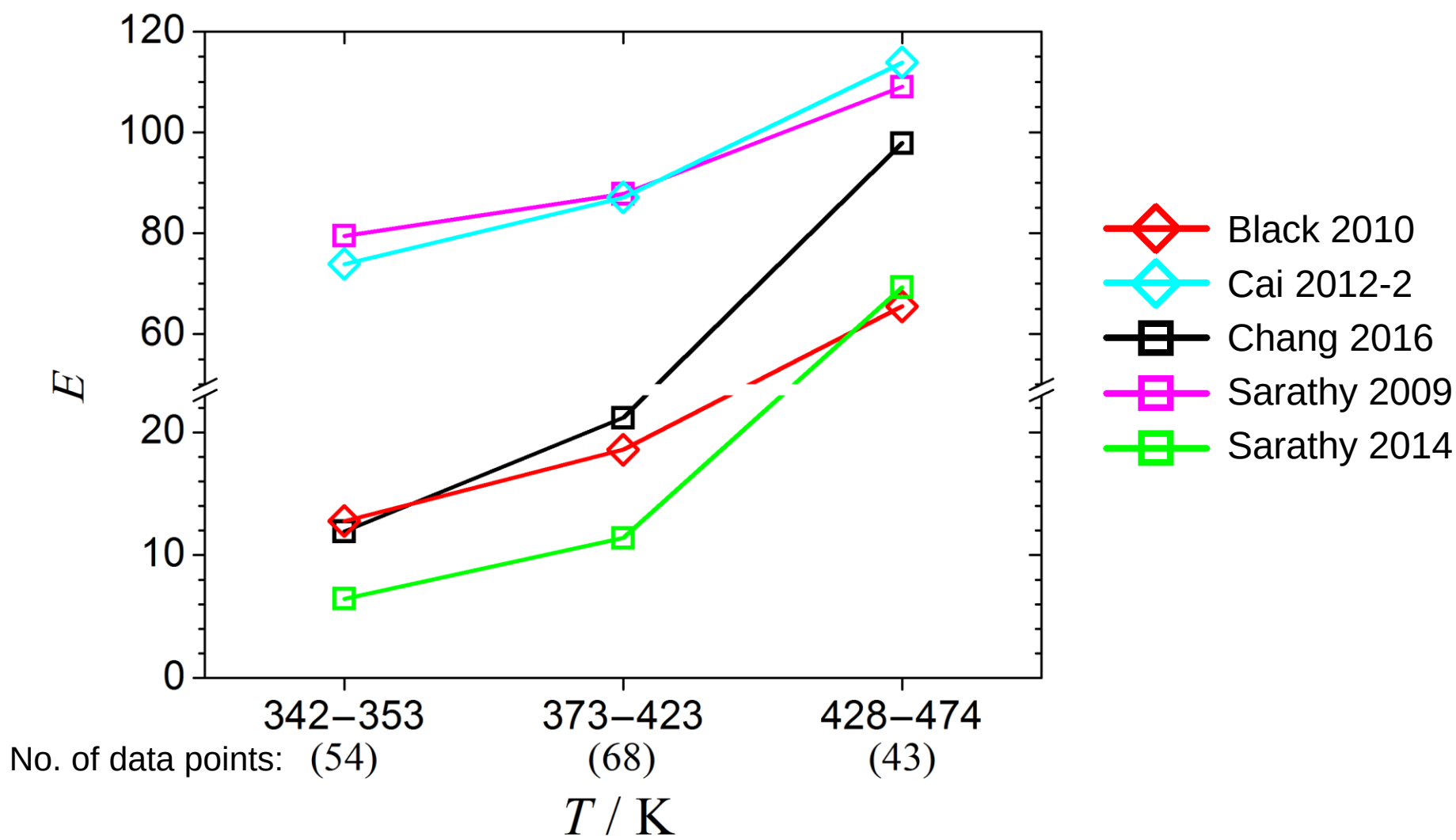
Overview of butanol combustion mechanisms

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</i> , <i>s</i> , <i>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</i> , <i>s</i>	160	2062
Merchant 2013	[14]	all	372	16632
Vasu 2013	[15]	all	283	3635
Cai 2014	[16]	<i>n</i> , <i>i</i> , <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



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

The simulation framework is freely **available for download**:
<http://respecth.hu> (See poster 4P030 on Thursday)

Comparison of combustion mechanisms

Error function values

(lower value = better agreement between simulations and measurements)

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

<i>n</i> -BuOH 	Ignition delay time				Flame velocity	Concentration		
	ST		RCM			ST, FR	JSR	
Moss 2008	92.9	25.3				39.3	20.2	-
Dagaut 2009	369.7	100.6	292.4	330.5		24.3	3.6	-
Sarathy 2009	357.3	106.7	294.2	332.6	88.0	40.1	2.5	169.6
Black 2010	79.1	13.9	127.5	143.2	16.7	25.2	3.6	111.6
Van Geem 2010	55.2	8.1	-	9.6		312.3	57.0	-
Veloo 2010	112.0	40.0	37.3	33.7		68.3	10.4	-
Harper 2011	97.5	22.8				367.9	56.9	88.7
Cai 2012-2	-	16.4			86.3	-	92.2	-
Sarathy 2012	34.7	11.6	23.6	24.0		241.8	64.8	-
Yasunaga 2012	69.9	12.4	65.9	72.5		-	64.8	53.8
Zhang 2012	64.2	9.2	77.2	85.1		15.0	3.8	104.9
Cai 2013	-	14.0				254.5	83.3	-
Merchant 2013	728.0	714.4	-	338.1		253.4	66.6	676.5
Vasu 2013	92.1	27.3	66.3	72.9		-	-	-
Cai 2014	-	366.4				259.4	81.0	-
Sarathy 2014	28.3	27.7	22.7	23.3	5.9	15.2	5.1	136.9
Chang 2016	63.1	56.5	30.3	27.0	13.3	240.6	41.3	334.1
No. of datasets	50	34	40	24	16	14	7	2
No. of data points	370	142	40	24	128	608	239	166

s-BuOH 	Ignition delay time				Flame velocity	Concentration	
	ST		RCM			ST, FR	JSR
Moss 2008	62.6	53.7				160.4	
Van Geem 2010	44.0	26.2	128.7	90.2		190.1	
Harper 2011	–	181.8	43.5	46.0		242.6	
Sarathy 2012	41.8	21.0	11.4	12.9		97.6	
Yasunaga 2012	41.8	21.0				–	
Cai 2013	–	192.2				63.7	
Merchant 2013	1146.5	1196.0	–	224.0		139.0	
Vasu 2013	40.6	19.9	80.9	51.2		–	
Cai 2014	–	99.7				56.1	
Sarathy 2014	68.7	38.0	11.9	13.4	20.9	5.6	140.0
Chang 2016	26.3	26.2	20.1	17.8	50.6	101.9	365.3
No. of datasets	17	16	14	12	5	23	4
No. of data points	129	72	14	12	42	1273	525

<i>i</i> -BuOH 	Ignition delay time				Flame velocity	Concentration	
	ST		RCM			ST, FR	JSR
Moss 2008	33.4	31.4				16.5	
Van Geem 2010	80.2	80.1	5.9	4.1		29.9	
Sarathy 2012	12.8	13.1	30.1	18.6		9.3	
Yasunaga 2012	12.8	13.1				–	
Merchant 2013	193.6	181.8	–	10.0		40.2	
Vasu 2013	12.6	12.9	20.3	20.2		–	
Cai 2014	–	60.5				1.1	
Sarathy 2014	58.4	61.8	29.9	17.2	16.3	9.1	51.7
Chang 2016	32.6	34.6	37.4	25.1	12.5	70.4	131.6
No. of datasets	16	15	10	8	12	15	4
No. of data points	101	85	10	8	102	1192	512

<i>t</i> -BuOH 	Ignition delay time			Flame velocity	Conc. ST, FR
	ST	RCM			
Moss 2008	91.8				136.8
Van Geem 2010	19.4	21.2	1.8		-
Harper 2011	40.6	71.2	37.1		-
Cai 2012-1	379.0				115.9
Sarathy 2012	140.0	89.6	45.1	198.8	84.7
Yasunaga 2012	139.5				-
Merchant 2013	2183.4	-	724.0		-
Vasu 2013	139.4	30.3	36.0		63.9
Sarathy 2014	26.0	90.5	45.0	20.5	99.8
Chang 2016	72.5	20.8	3.4	40.6	205.2
No. of datasets	13	21	4	10	1
No. of data points	99	21	4	77	104

- **Reproduction of the experimental data:** few mechanisms describe the combustion of the butanol isomers correctly over wide ranges of experimental conditions and initial compositions. Accurate simulation results were obtained only in certain ranges of conditions and at some types of experiment.
- **Mechanism Sarathy 2014** seems to have the best performance:
 - e.g. laminar flame velocities, concentration profiles measured in shock tube
 - relatively low E values: ignition delay time of *n*- and *t*-butanol in shock tube

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