

Western States Section of the Combustion Institute - Spring 2016 Meeting  
Hosted by the University of Washington  
March 21–22, 2016.

## An autoignition performance comparison of chemical kinetics models for *n*-heptane

*Kyle E. Niemeyer\**

*School of Mechanical, Industrial, and Manufacturing Engineering,  
Oregon State University, Corvallis OR, USA*

### Abstract

Surrogate models of gasoline typically include the primary reference fuel (PRF) *n*-heptane. The chemical kinetics literature contains many models for *n*-heptane, but no comprehensive survey or performance validation for these models exist. This paper objectively compares the performance of various chemical kinetics models for *n*-heptane for autoignition, using experimental data from a variety of sources. In doing so, recommendations for choosing appropriate models are made and areas of improvement identified. As a secondary goal, this work also collected and standardized a wide range of shock tube and rapid compression machine autoignition data for this neat fuel. This study represents the first step of a comprehensive study of models for *n*-heptane, isooctane, toluene, and ethanol alone and in binary, ternary, and quaternary mixtures.

### 1 Introduction

Surrogate models of gasoline typically include the primary reference fuels (PRFs) *n*-heptane and isooctane. While neither *n*-heptane nor isooctane are present in real gasoline in significant quantities [1], they are the primary reference fuels (PRFs) used to determine the research and motor octane numbers (RON and MON, respectively) and so have long been used as simple surrogates for gasoline [2–4]. These components represent normal and branched alkanes present in gasoline, respectively; however, by definition mixtures of PRFs alone cannot emulate the nonzero sensitivity—the difference between RON and MON—of real gasoline, and so additional components are increasingly being added. Notably, toluene is a popular third component [1, 5] and used to represent aromatics; in addition, toluene is actually present in gasoline in non-negligible quantities [1]. Ethanol is another important surrogate component due to its current and increasing popularity as a blending component with gasoline, particularly in the United States. Common blending levels range from 10 % ethanol (E10) to 85 % ethanol (E85).

Since in reality gasoline contains a spectrum of constituent hydrocarbons, these multicomponent surrogates allow computational studies of engine performance. The chemical kinetics literature contains many models for blends of PRFs, TRFs, and ethanol, but no comprehensive survey or performance validation for these models exist.

The combustion research community has experienced significant growth in the development of chemical kinetic models describing oxidation of fuels ranging from hydrogen to long-chain oxygenated biodiesel surrogates. With multiple models coming from different groups describing the

---

\*Corresponding author email: [kyle.niemeyer@oregonstate.edu](mailto:kyle.niemeyer@oregonstate.edu)

same fuels and the level of maturity of such models continuing to improve, studies comparing the performance of various models have begun to be performed. In particular, Olm et al. [6, 7] compared 19 and 16 models for hydrogen and syngas oxidation, respectively, using hundreds of datasets (and thousands of individual data points) covering a variety of experimental measurement types. However, such rigorous and extensive comparisons have yet to be performed for larger hydrocarbons.

Although some experimental validation accompanied the release of most kinetic models considered here, few comprehensive studies of multiple models have been performed. Khan and Burluka [8] evaluated eight kinetic models for isooctane and mixtures with *n*-heptane, toluene, and ethanol, using shock-tube ignition delays and HCCI engine pressure/temperature profiles for neat isooctane, PRF, and TRF mixtures. However, they did not consider a comprehensive set of validation targets or examine many detailed kinetic models. Sheen and Tsang [9] recently performed a detailed comparison of four kinetic models for *n*-heptane, focusing on the prediction of ignition delay times as well as species concentration histories. They found that all four models predicted ignition delay times in shock tubes within estimated uncertainty limits; of the four models considered, only one (the LLNL *n*-heptane mechanism of Mehl et al. [10]) is a component of the multicomponent models studied in this work.

Thus, this study is motivated by the lack of comprehensive evaluation of models for *n*-heptane in the literature—it represents a first step towards a full evaluation of models for mixtures PRFs, TRFs, and ethanol. First, Section 2 describes the performance evaluation methodology for quantifying the performance of kinetic models. Section 3 summarizes the models considered here, while Section 4 summarizes experimental data for relevant fuels and mixtures. Section 5 describes the simulation methodologies adopted for different experiment types. The performance and qualitative evaluation of kinetics models are presented, compared, and discussed in Section 6. Finally, conclusions and overall outcomes are made in Section 7.

## 2 Methodology

The approach used here to evaluate the performance of chemical kinetics models for the PRFs, TRFs, and blends with ethanol mostly follows that used by Olm et al. [6, 7] for hydrogen models. The agreement between experimental and simulated ignition delay times is quantified with the average error  $E$  over the  $N$  datasets given by

$$E = \frac{1}{N} \sum_{i=1}^N E_i, \quad (1)$$

where  $E_i$  is the average error for the  $i$ th dataset

$$E_i = \frac{1}{N_i} \sum_{j=1}^{N_i} \left( \frac{\log \tau_{ij}^{\text{exp}} - \log \tau_{ij}^{\text{sim}}}{\sigma(\log \tau_{ij}^{\text{exp}})} \right)^2, \quad (2)$$

$N_i$  is the number of data points in set  $i$ ,  $\tau_{ij}^{\text{exp}}$  and  $\tau_{ij}^{\text{sim}}$  are the experimental and simulated ignition delay times for the  $j$ th data point in set  $i$ , respectively, and  $\sigma$  is the standard deviation. The log function indicates the natural logarithm. Error quantities used the logarithm of ignition delay

rather than the ignition delay itself, following the practice of Olm et al. [6, 7], since the scatter in experimental results is proportional to the ignition delay value.

The standard deviation of an experimental dataset,  $\sigma(\log \tau_{ij}^{\text{exp}})$  is determined by fitting a spline to the experimental ignition delay values with respect to the variable changing in the dataset (typically temperature), following the approach used by Olm et al. [6, 7]. This was implemented via the `interpolation.UnivariateSpline` function [11] of `SciPy` [12]. A minimum value of  $\sigma = 0.10$  was established, used to override any small calculated values. In the future, this approximation will be replaced with actual experimental uncertainty in measured ignition delay, but unfortunately most past studies did not provide such calculations.

### 3 Chemical kinetics models

Table 1 summarizes the chemical kinetics models for *n*-heptane considered in this study, including both semi-detailed and detailed models, ordered by year. This is not an exhaustive list of all available models, but rather representative selections either recently presented or commonly used. All models were converted from their original Chemkin format to Cantera [13] for this study. Minor modifications necessary to enable Cantera interpreting of Chemkin-format files included inserting E between significand and exponent in some thermodynamic entries. Where multiple species thermodynamic entries were present in a thermodynamic database, the first entry was used by default. Reaction counts in Table 1 may differ slightly from published values because Cantera separates reversible reactions with explicit reverse Arrhenius parameters into two irreversible reactions.

Name	Coverage	No. species	No. reactions	Ar/He	Ref.
Tsurushima-2009	PRF	33	48	—/—	14
ERC-2013	PRF	73	454	—/—	15
Ogura-2007	PRF + ethanol	634	3724	×/×*	16
Saisirirat-2011	PRF + ethanol	1046	8576	—/—	17
Dalian-2013	TRF	56	191	—/—	18
Andrae-2013	TRF	138	641	×/—*	19
Princeton-2009	TRF + ethanol	469	1267	×/× <sup>a</sup>	20–23
Tsinghua-2014	TRF + ethanol	91	411	×/—*	24
CRECK-2014	TRF + ethanol	317	12353	×/×	25–29

**Table 1:** Reaction mechanisms for PRFs, TRFs, and their mixtures with ethanol considered in this study. In addition to the other information, the Ar/He column indicates whether the mechanism supports Ar or He bath gases, in addition to the typical N<sub>2</sub>. A \* indicates that the the mechanism contains the species, but no reactions with enhanced third-body efficiencies for them. The <sup>a</sup> indicates that the mechanism as distributed does not contain these species, but contains instructions for necessary modification.

The Tsurushima-2009 PRF model [14] is a manually constructed skeletal model that adopted the low-temperature oxidation pathways from Tanaka et al. [30]; Tsurushima modified some reaction parameters to better fit literature ignition-delay experiments and introduced some artificial global reactions. In contrast, simple high-temperature pathways were added using a combination of el-

elementary and global reactions, consisting primarily of thermal decomposition of alkyl radicals to ethylene and oxidation of ethylene and formaldehyde to products; reaction parameters were modified from values adopted from various literature sources to better agree with experimental species profiles.

Wang et al. [15] developed the ERC-2013 model for PRF mixtures by applying the DRGEP reduction method [31–33], rate of production analysis, sensitivity analysis, and reaction pathway analysis to reduce the LLNL four-component gasoline surrogate model [10]. They produced separate skeletal models for *n*-heptane and isooctane, then combined these with some cross-reactions from the base model to form the final PRF skeletal model. In addition, parameters were updated for the chain-termination reactions  $\text{HO}_2 + \text{OH} \rightleftharpoons \text{H}_2\text{O} + \text{O}_2$  and  $\text{RH} + \{\text{OH}_\text{H}\text{O}_2\} \rightleftharpoons \text{R} + \{\text{H}_2\text{OH}_2\text{O}_2\}$  using newer literature data, and parameters for decomposition reactions of *n*-C<sub>7</sub>ket<sub>24</sub> and C<sub>7</sub>H<sub>15</sub>–2 were optimized using ignition-delay sensitivity analysis.

The Ogura-2007 model [16] couples a model for *n*-heptane and isooctane, generated using Miyoshi's KUCRS automatic kinetic model generation software [34, 35], with the ethanol submechanism of Marinov [36]. This model also includes a submechanism for ethyl tert-butyl ether generated using KUCRS with reaction rate constants determined using density functional theory, Rice–Ramsperger–Kassel–Marcus theory, and master equation analysis [37], although this chemistry was not necessary for the current study.

The Saisirirat-2011 model [17] was developed by merging the 1-butanol and ethanol schemes of Dagaut and Togbé [38, 39] with an LLNL PRF model [40, 41]. Saisirirat et al. [17] validated their model using species profiles from jet-stirred reactor experiments with *n*-heptane/ethanol mixtures, and constant-volume ignition delay times for neat *n*-heptane and mixtures with ethanol taken from HCCI engine experiments.

Liu et al. [18] developed the Dalian-2013 model by combining a previous skeletal PRF model [42] with a new reduced model for toluene. Both the PRF and toluene submodels were generated using a decoupling methodology that separates fuel oxidation into a detailed core C<sub>0</sub>–C<sub>1</sub> model [43] and a skeletal model for fuel-specific large molecules to describe ignition chemistry. Liu et al. [18] took toluene-specific pathways from the models of Andrae et al. [44], Mehl et al. [45], and Sakai et al. [46], and optimized rate parameters based on shock-tube ignition delays and jet-stirred reactor species profiles.

This study considered the Andrae-2013 model [19] instead of an older, larger detailed model from the same author [47] due to updated reaction parameters. Specifically, Andrae updated reactions in the toluene submodel of a previous semi-detailed model [44] based mainly on the quantum chemistry calculations of Murakami et al. [48] and model of Sakai et al. [46] as well as individual rate parameters from the literature [49–51].

The Princeton-2009 model [23] combines the TRF model of Chaos et al. [20, 21] with the ethanol model of Li et al. [22]. Interactions between the TRF components occur in the small radical pool (e.g., OH, O, H, HO<sub>2</sub>, CH<sub>3</sub>) [21] while the alkanes and ethanol are coupled primarily through the HO<sub>2</sub> and OH radical pool [23]. The Princeton-2009 model contains pressure-specific Arrhenius coefficients for reaction  $\text{C}_2\text{H}_5\text{OH} \rightleftharpoons \text{CH}_3 + \text{CH}_2\text{OH}$ , so different versions were created for pressures of 1, 3, 6, 9, 12, 15, 50, and 100 atm; the closest value to the simulation initial pressure (compressed pressure for RCM) was used. In contrast, the Troe fall-off formulation for reaction

$\text{C}_2\text{H}_5\text{OH} \rightleftharpoons \text{C}_2\text{H}_4 + \text{H}_2\text{O}$  was used to account for pressure dependence.

Zhong and Zheng [24] developed the Tsinghua-2014 model by combining their earlier PRF+ethanol model [52], derived from the PRF model of Ra and Reitz [53], with reduced models obtained via sensitivity and/or reaction path analyses from the models for ethanol of Marinov [36], toluene of Andrae [19], and diisobutylene of Metcalfe et al. [54]. No interactions between fuel components were discussed.

Finally, the CRECK-2014 model version 1412 [25–29] combines ethanol pathways [27] with a prior model for hydrocarbon oxidation [25]. Both schemes couple a detailed model for smaller species with lumped descriptions of intermediates of the major species and primary propagation reactions.

## 4 Experimental data

Ignition delay results from various studies were obtained directly from published data where possible, or via communication with the authors. Each dataset was manually encoded in the ReSpecTh XML format [55, 56] to enable automated processing and setup of corresponding simulations. Two extensions were made to the ReSpecTh version 1.0 specification: adding an “InChI” [57–59] attribute to the **speciesLink** element as a unique species identifier, and adding a DOI attribute to the **bibliographyLink** element. In some cases, fuel blends given as volume percentages were converted to mole fractions using the `vol-to-mole` software [60]. Table 2 shows an overview of the experimental data used for *n*-heptane.

Study	Type	$P$ (atm)	$T$ (K)	$\phi$	$\chi_{\text{O}_2}$ (%)
Vermeer et al. [61]	ST	1.4–4.1	1270–1580	1.0	27.5
Burcat et al. [62]	ST	2.0–11.8	1137–1661	0.5–2.0	2.8–33.1
Ciezki & Adomeit [63]	ST	3.16–41.5	660–1350	0.5–3.0	20.5
Fieweger et al. [64]	ST	39.5	700–1200	1.0	20.5
Colket & Spadaccini [65]	ST	4.1–7.8	1229–1427	0.5	2.1, 4.2
Horning et al. [66]	ST	1.15–5.71	1329–1547	0.5–2.0	4.4–19.7
Gauthier et al. [67]	ST	2–60	800–1400	1.0	20.5
Smith et al. [68]	ST	1, 2	1150–1700	0.5–2.0	2.2–16.0
Herzler et al. [69]	ST	49.3	720–1130	0.1–0.4	20.5
Sakai et al. [70]	ST	2	1319–1567	1.0	4.4
Shen et al. [71]	ST	10.5–53.6	786–1396	0.25–1.0	20.6–20.8
Hartmann et al. [72]	ST	39.5	692–1275	0.5, 1.0	20.5
Vandersickel et al. [73]	ST	19.7–64.2	700–1100	0.5–1.0	10.4–20.7
Karwat et al. [74]	RCF	9	660–707	1.0	15

**Table 2:** Summary of experimental conditions for *n*-heptane autoignition, where  $\chi_{\text{O}_2}$  indicates the molar percentage of  $\text{O}_2$  in the reactants. “ST” stands for shock tube experiments, while “RCF” refers to rapid compression facility.

## 5 Simulations of experiments

Experiments were modeled differently depending on both the apparatus used (i.e., shock tube or RCM). All simulations were performed using Cantera [13], with each experiment modeled using a `ReactorNet` that contains `IdealGasReactor` and `Wall` objects.

### 5.1 Simulations of shock tubes

Typically, validation of chemical kinetic models using shock tube experiments use adiabatic constant-volume conditions based on the reflected shock temperature and pressure, and initial reactant composition [75–77]. Thus, most shock tube experiments considered here were modeled using this assumption. However, this approach does not account for the polytropic pressure increase observed at longer ignition delay times (e.g.,  $\geq 1$  ms) [75–77] due to a lack of pressure history information. In general, neglecting this effect results in longer modeled ignition delays compared to experiment [23].

For shock tube studies that provided information about preignition pressure rise, typically given as a constant pressure-rise rate  $\frac{dP}{dt}$ , an approach modified from that suggested by Chaos et al. [76] was used here. First, the preignition pressure history  $P(t)$  was determined, and then converted to a volume history  $v(t)$  by assuming isentropic compression/expansion:

$$P(t) = P_0 + \int_0^{t_{\text{end}}} \left( \frac{dP}{dt} \right) dt, \quad (3)$$

$$v(t) = v_0 \frac{\rho_0}{\rho(t)} \Big|_{s_0}, \quad (4)$$

where  $s_0$ ,  $P_0$ ,  $v_0$ , and  $\rho_0$  indicate the entropy, pressure, volume, and density of the initial mixture;  $t_{\text{end}}$  is the time interval of interest; and  $\rho(t)$  is the time-varying density. Finally, the volume history was in turn numerically differentiated for a wall velocity used in the `Wall` object, similar to the approach used to model RCMs discussed next.

### 5.2 Simulations of RCMs

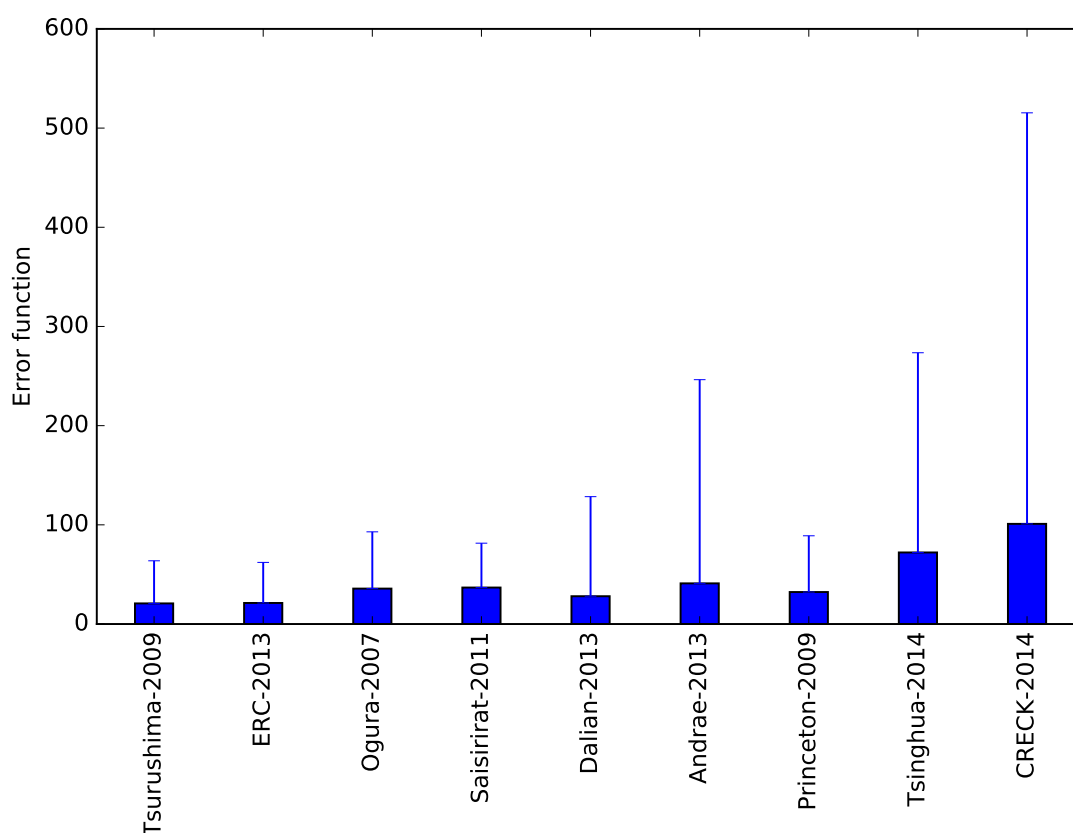
RCM experiments measuring ignition delay were modeled following the approach discussed by Sung and Curran [78]. Heat loss in the RCM is typically determined using a nonreactive pressure trace, and then converted to an effective volume history using the mixture time-varying specific heat ratio and relations based on the assumption an adiabatic core. Provided effective volume histories were used in the same manner as those generated for shock tubes above: differentiated with respect to time to obtain a wall velocity for the `Wall` object.

A number of RCM studies were not considered here due to lack of volume history data necessary for simulations [79–84]. One exception was the study of Karwat et al. [74], where the authors found that neither reactions during the compression stroke nor post-compression heat losses contributed significantly to computed results. Therefore, modeling comparisons for this study used constant-volume adiabatic simulations.

## 6 Results and discussion

The results will compare and show the performance of the nine kinetic models listed in Table 1 using the experimental data described in Table 2. The full sample of ignition delay data consists of 662 points spread across 64 datasets. Models without Ar and/or N<sub>2</sub> skipped experimental cases with those species as reactants; such cases made up 359 points in 28 datasets. In addition, various experimental cases specified ignition based on the maximum or maximum derivative of excited radicals such as OH\* or CH\*. Models with these species used them to determine the autoignition delay, while models without them fell back on their unexcited equivalent (i.e., OH or CH); in certain cases where the model contained neither species, the maximum gradient of pressure was used instead.

All calculations were performed using Python [85], and figures generated using Matplotlib [86].



**Figure 1:** Mean error function for various chemical kinetic models in reproducing *n*-heptane ignition delay times, with error bars indicating the standard deviation among the datasets. Errors were sampled using 662 data points grouped into 64 datasets. Lower values indicate better agreement between a model and the experimental data.

Figure 1 summarizes the predictive capabilities of the kinetic models considered in this study for predicting ignition delay times of *n*-heptane. Out of the studies considered, the Tsurushima-2009 model demonstrated the lowest error function at 20.8, while the CRECK-2014 model performed the worst with a mean error function of 101.0. Furthermore, with a standard deviation of 414.4 in the error function among the datasets, the CRECK-2014 model exhibited wide variation in



performance. However, the apparent lower error function for the Tsurushima-2009 model, as well as those for the ERC-2013, Saisirirat-2011, and Dalian-2013 models, may be influenced by the smaller possible sample sizes, due to the lack of Ar and He in these models; such cases comprised approximately 54 % of the sample. That said, the strong performance of these fairly compact models—especially compared to the larger detailed models—is surprising, and may be attributed to calibrating of models to better fit experimental data.

## 7 Conclusions

This study compared the performance of kinetic models in predicting autoignition delay for *n*-heptane. The nine models considered exhibited wide ranges of performance, with the compact Tsurushima-2009 model performing the best and the CRECK-2014 model performing the worse for the experimental data considered. In addition to rigorously quantifying the ability of the models considered to predict ignition delay, a large set of data from shock tube and RCM experiments was collected and standardized for such mixtures; these data—in addition to the supporting software—will be made openly available to support future model investigation.

The immediate next steps for this project include extending the study to additional models for *n*-heptane from Anderlohr et al. [87], Sakai et al. [46], Mehl et al. [10, 88], and Cancino et al. [89]. Following that, models and experimental data for mixtures of PRFs, TRFs, and ethanol will be considered.

## Acknowledgments

The author thanks the School of Mechanical, Industrial, and Manufacturing Engineering at Oregon State University for partially funding this work. In addition, he thanks Dr. Bryan Weber for helpful discussions on RCM modeling and experimental uncertainty, as well as numerous colleagues for sharing their kinetic models and experimental data.

## References

### References

- [1] William J Pitz, Nicholas P Cernansky, Frederick L Dryer, Fokion N Egolfopoulos, John T Farrell, Daniel Friend, and Heinz Pitsch. Development of an experimental database and chemical kinetic models for surrogate gasoline fuels. SAE Technical Paper 2007-01-0175, 2007. doi:[10.4271/2007-01-0175](https://doi.org/10.4271/2007-01-0175).
- [2] Graham Edgar. *Ind. Eng. Chem.*, 19 (1927) 145–146.
- [3] B M Sturgis, E N Cantwell, W E Morris, and D L Schultz. *Proc. API*, 34 (1954) 256–269.
- [4] A J Pahnke, P M Cohen, and B M Sturgis. *Ind. Eng. Chem.*, 46 (1954) 1024–1029.
- [5] K Anand, Youngchul Ra, Rolf D Reitz, and B Bunting. *Energy Fuels*, 25 (2011) 1474–1484.



- [6] Carsten Olm, István Gyula Zsély, Róbert Pálvölgyi, Tamás Varga, Tibor Nagy, Henry J Curran, and Tamás Turányi. *Combust. Flame*, 161 (2014) 2219–2234.
- [7] Carsten Olm, István Gyula Zsély, Tamás Varga, Henry J Curran, and Tamás Turányi. *Combust. Flame*, 162 (2015) 1793–1812.
- [8] A F Khan and A A Burluka. An investigation of various chemical kinetic models for the prediction of autoignition in HCCI engine. In *ASME 2012 Internal Combustion Engine Division Fall Technical Conference*, number ICEF2012-92057, pages 737–745, Vancouver, BC, Canada, September 2012.
- [9] David A Sheen and Wing Tsang. *Combust. Flame*, 161 (2014) 1984–1992.
- [10] Marco Mehl, William J Pitz, Charles K Westbrook, and Henry J Curran. *Proc. Combust. Inst.*, 33 (2011) 193–200.
- [11] Stéfan van der Walt, S. Chris Colbert, and Gaël Varoquaux. *Comput. Sci. Eng.*, 13 (2011) 22–30.
- [12] Eric Jones, Travis Oliphant, Pearu Peterson, and et al. SciPy: Open source scientific tools for Python. <http://www.scipy.org/>, 2001–. [Online; accessed 2016-03-04].
- [13] David G. Goodwin, Harry K. Moffat, and Raymond L. Speth. Cantera: An object-oriented software toolkit for chemical kinetics, thermodynamics, and transport processes. <http://www.cantera.org>, 2015. Version 2.2.0.
- [14] T Tsurushima. *Proc. Combust. Inst.*, 32 (2009) 2835–2841.
- [15] Hu Wang, Mingfa Yao, and Rolf D Reitz. *Energy Fuels*, 27 (2013) 7843–7853.
- [16] Teppei Ogura, Yasuyuki Sakai, Akira Miyoshi, Mitsuo Koshi, and Philippe Dagaut. *Energy Fuels*, 21 (2007) 3233–3239.
- [17] P Saisirirat, C Togbe, S Chanchaona, F Foucher, C Mounaim-Rousselle, and P Dagaut. *Proc. Combust. Inst.*, 33 (2011) 3007–3014.
- [18] Yao-Dong Liu, Ming Jia, Mao-Zhao Xie, and Bin Pang. *Energy Fuels*, 27 (2013) 4899–4909.
- [19] J C G Andrae. *Fuel*, 107 (2013) 740–748.
- [20] Marcos Chaos, Andrei Kazakov, Zhenwei Zhao, and Frederick L Dryer. *Int. J. Chem. Kinet.*, 39 (2007) 399–414.
- [21] Marcos Chaos, Z Zhao, Andrei Kazakov, P Gokulakrishnan, M Angioletti, and Frederick L Dryer. A PRF+toluene surrogate fuel model for simulating gasoline kinetics. In *5th National Combustion Meeting*, number Paper #E26, March 2007.
- [22] J Li, Andrei Kazakov, Marcos Chaos, and Frederick L Dryer. Chemical kinetics of ethanol oxidation. In *5th National Combustion Meeting*, number Paper #C28, San Diego, CA, March 2007.

- [23] Francis M Haas, Marcos Chaos, and Frederick L Dryer. *Combust. Flame*, 156 (2009) 2346–2350.
- [24] Bei-Jing Zhong and Dong Zheng. *Fuel*, 128 (2014) 458–466.
- [25] Eliseo Ranzi, Alessio Frassoldati, Silvia Granata, and Tiziano Faravelli. *Ind. Eng. Chem. Res.*, 44 (2005) 5170–5183.
- [26] Tom Bieleveld, Alessio Frassoldati, Alberto Cuoci, Tiziano Faravelli, Eliseo Ranzi, Ulrich Niemann, and Kalyanasundaram Seshadri. *Proc. Combust. Inst.*, 32 (2009) 493–500.
- [27] Alessio Frassoldati, A Cuoci, Tiziano Faravelli, and E Ranzi. *Combust. Sci. Technol.*, 182 (2010) 653–667.
- [28] Chiara Saggese, Alessio Frassoldati, Alberto Cuoci, Tiziano Faravelli, and Eliseo Ranzi. *Combust. Flame*, 160 (2013) 1168–1190.
- [29] CRECK Modeling Group. Primary Reference Fuels (PRF) + PAH + alcohols + ethers (version 1412). <http://www.chem.polimi.it/CRECKModeling>, December 2014. Accessed: 2016-01-11.
- [30] Shigeyuki Tanaka, Ferran Ayala, and James C Keck. *Combust. Flame*, 133 (2003) 467–481.
- [31] Perrine Pepiot-Desjardins and Heinz Pitsch. *Combust. Flame*, 154 (2008) 67–81.
- [32] Yu Shi, Hai-Wen Ge, Jessica L Brakora, and Rolf D Reitz. *Energy Fuels*, 24 (2010) 1646–1654.
- [33] Kyle E Niemeyer and Chih Jen Sung. *Combust. Flame*, 158 (2011) 1439–1443.
- [34] Akira Miyoshi. *Trans. Soc. Automot. Eng. Jpn.*, 36 (2005) 35–40.
- [35] Neal Morgan, Andrew J Smallbone, Amit Bhawe, Markus Kraft, Roger Cracknell, and Gautam T Kalghatgi. *Combust. Flame*, 157 (2010) 1122–1131.
- [36] Nick M Marinov. *Int. J. Chem. Kinet.*, 31 (1999) 183–220.
- [37] Teppei Ogura, Akira Miyoshi, and Mitsuo Koshi. *Phys. Chem. Chem. Phys.*, 9 (2007) 5133–5142.
- [38] Philippe Dagaut and Casimir Togbé. *Energy Fuels*, 23 (2009) 3527–3535.
- [39] Philippe Dagaut and Casimir Togbé. *Fuel*, 89 (2010) 280–286.
- [40] Henry J Curran, William J Pitz, Charles K Westbrook, G V Callahan, and Frederick L Dryer. *Symp. (Int.) Combust.*, 27 (1998) 379–387.
- [41] Henry J Curran, Paolo Gaffuri, William J Pitz, and Charles K Westbrook. *Combust. Flame*, 129 (2002) 253–280.
- [42] Yao-Dong Liu, Ming Jia, Mao-Zhao Xie, and Bin Pang. *Energy Fuels*, 26 (2012) 7069–7083.

- [43] Stephen J Klippenstein, Lawrence B Harding, Michael J Davis, Alison S Tomlin, and Rex T Skodje. *Proc. Combust. Inst.*, 33 (2011) 351–357.
- [44] J C G Andrae, T Brinck, and Gautam T Kalghatgi. *Combust. Flame*, 155 (2008) 696–712.
- [45] Marco Mehl, Tiziano Faravelli, Eliseo Ranzi, David Miller, and Nicholas Cernansky. *Proc. Combust. Inst.*, 32 (2009) 2843–2850.
- [46] Yasuyuki Sakai, Akira Miyoshi, Mitsuo Koshi, and William J Pitz. *Proc. Combust. Inst.*, 32 (2009) 411–418.
- [47] J C G Andrae, P Björnbohm, Roger Cracknell, and Gautam T Kalghatgi. *Combust. Flame*, 149 (2007) 2–24.
- [48] Yoshinori Murakami, Tatsuo Oguchi, Kohtaro Hashimoto, and Yoshio Nosaka. *J. Phys. Chem. A*, 111 (2007) 13200–13208.
- [49] Gabriel da Silva and Joseph W Bozzelli. *Proc. Combust. Inst.*, 32 (2009) 287–294.
- [50] Matthew A Oehlschlaeger, David F Davidson, and Ronald K Hanson. *Combust. Flame*, 147 (2006) 195–208.
- [51] W K Metcalfe, S Dooley, and F L Dryer. *Energy Fuels*, 25 (2011) 4915–4936.
- [52] Bei-Jing Zhong and Dong Zheng. *Combust. Sci. Technol.*, 185 (2013) 627–644.
- [53] Youngchul Ra and Rolf D Reitz. *Combust. Flame*, 155 (2008) 713–738.
- [54] Wayne K Metcalfe, William J Pitz, Henry J Curran, John M Simmie, and Charles K Westbrook. *Proc. Combust. Inst.*, 31 (2007) 377–384.
- [55] Tamás Varga, T Turányi, E Czinki, T Furtenbacher, and A G Császár. ReSpecTh: a joint reaction kinetics, spectroscopy, and thermochemistry information system. In *7th European Combustion Meeting*, pages P1–04, Budapest, Hungary, March 2015.
- [56] Tamás Varga. ReSpecTh kinetics data format specification. Documentation version v1.0, <http://respecth.hu/>, March 2015.
- [57] InChI Trust. The IUPAC International Chemical Identifier (InChI). <http://www.iupac.org/home/publications/e-resources/inchi.html>, Accessed: 2016-01-10, sep 2011.
- [58] Stephen E. Stein, Stephen R. Heller, and Dmitrii Tchekhovskoi. An open standard for chemical structure representation: The IUPAC chemical identifier. In *2003 International Chemical Information Conference (Nîmes)*, pages 131–143, Tetbury, 2003. Infonortics.
- [59] Stephen Heller, Alan McNaught, Stephen Stein, Dmitrii Tchekhovskoi, and Igor Pletnev. *J. Cheminform*, 5 (2013) 7.
- [60] Kyle E Niemeyer. *vol-to-mole* v1.0. Zenodo, doi:[10.5281/zenodo.44328](https://doi.org/10.5281/zenodo.44328), January 2016.

- [61] D J Vermeer, J W Meyer, and A K Oppenheim. *Combust. Flame*, 18 (1972) 327–336.
- [62] A Burcat, R F Farmer, and A Matula. Shock initiated ignition in heptane-oxygen-argon mixtures. In *Proc 13th Int Symp Shock Tubes Waves*, pages 826–833, 1981.
- [63] H K Ciezki and G Adomeit. *Combust. Flame*, 93 (1993) 421–433.
- [64] K Fieweger, R Blumenthal, and G Adomeit. *Combust. Flame*, 109 (1997) 599–619.
- [65] Meredith B Colket III and Loius J Spadaccini. *J. Propul. Power*, 17 (2001) 315–323.
- [66] D C Horning, D F Davidson, and R K Hanson. *J. Propul. Power*, 18 (2002) 363–371.
- [67] B M Gauthier, David F Davidson, and Ronald K Hanson. *Combust. Flame*, 139 (2004) 300–311.
- [68] John M Smith, John M Simmie, and Henry J Curran. *Int. J. Chem. Kinet.*, 37 (2005) 728–736.
- [69] J Herzler, L Jerig, and P Roth. *Proc. Combust. Inst.*, 30 (2005) 1147–1153.
- [70] Yasuyuki Sakai, Hiroaki Ozawa, Teppei Ogura, Akira Miyoshi, Mitsuo Koshi, and William J Pitz. Effects of toluene addition to primary reference fuel at high temperature. SAE Technical Paper 2007-01-4104, 2007. doi:[10.4271/2007-01-4104](https://doi.org/10.4271/2007-01-4104).
- [71] Hsi-Ping S Shen, Justin Steinberg, Jeremy Vanderover, and Matthew A Oehlschlaeger. *Energy Fuels*, 23 (2009) 2482–2489.
- [72] M Hartmann, I Gushterova, M Fikri, C Schulz, R Schießl, and U Maas. *Combust. Flame*, 158 (2011) 172–178.
- [73] A Vandersickel, M Hartmann, K Vogel, Y M Wright, M Fikri, R Starke, C Schulz, and K Boulouchos. *Fuel*, 93 (2012) 492–501.
- [74] Darshan M A Karwat, Scott W Wagnon, Margaret S Wooldridge, and Charles K Westbrook. *Combust. Flame*, 160 (2013) 2693–2706.
- [75] David F Davidson and Ronald K Hanson. *Int. J. Chem. Kinet.*, 36 (2004) 510–523.
- [76] Marcos Chaos and Frederick L Dryer. *Int. J. Chem. Kinet.*, 42 (2010) 143–150.
- [77] Ronald K Hanson and David F Davidson. *Prog. Energy Comb. Sci.*, 44 (2014) 103–114.
- [78] Chih-Jen Sung and Henry J Curran. *Prog. Energy Comb. Sci.*, 44 (2014) 1–18.
- [79] C M Coats and Alan Williams. *Symp. (Int.) Combust.*, 17 (1979) 611–621.
- [80] J F Griffiths, P A Halford-Maw, and D J Rose. *Combust. Flame*, 95 (1993) 291–306.
- [81] R Minetti, M Carlier, M Ribaucour, E Therssen, and L R Sochet. *Combust. Flame*, 102 (1995) 298–309.
- [82] J F Griffiths, P A Halford-Maw, and C Mohamed. *Combust. Flame*, 111 (1997) 327–337.

- [83] Shigeyuki Tanaka, Ferran Ayala, James C Keck, and John B Heywood. *Combust. Flame*, 132 (2003) 219–239.
- [84] Emma J Silke, Henry J Curran, and John M Simmie. *Proc. Combust. Inst.*, 30 (2005) 2639–2647.
- [85] Python Software Foundation. Python language reference, version 2.7.10. Available at <http://www.python.org>, 2015.
- [86] John D. Hunter. *Comput. Sci. Eng.*, 9 (2007) 90–95.
- [87] J M Anderlohr, R Bounaceur, A Pires Da Cruz, and Frédérique Battin-Leclerc. *Combust. Flame*, 156 (2009) 505–521.
- [88] Marco Mehl, William J Pitz, Charles K Westbrook, and Henry J Curran. Llnl gasoline surrogate v1.0. <https://combustion.llnl.gov/mechanisms/surrogates/gasoline-surrogate>, Accessed: 2016-01-13, March 2012.
- [89] L R Cancino, M Fikri, A A M Oliveira, and C Schulz. *Fuel*, 90 (2011) 1238–1244.