Introducing a work flow for improving kinetic models: a case study using butanol

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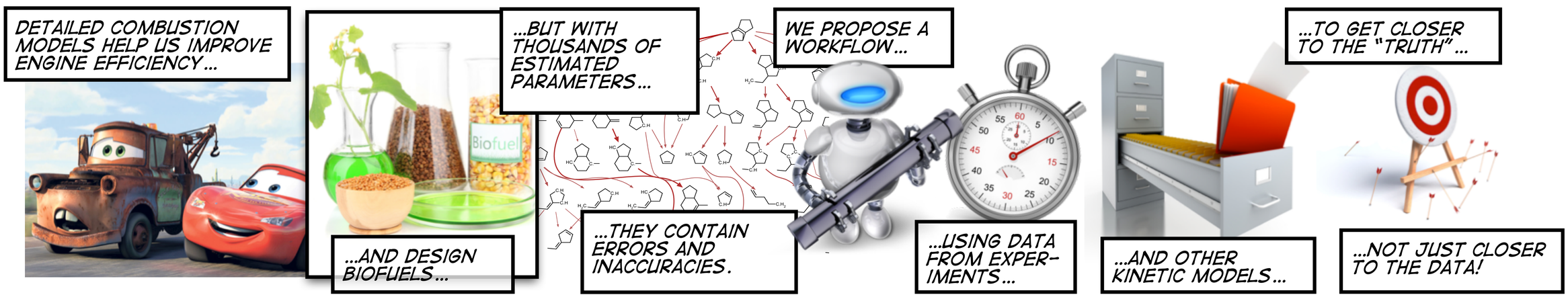
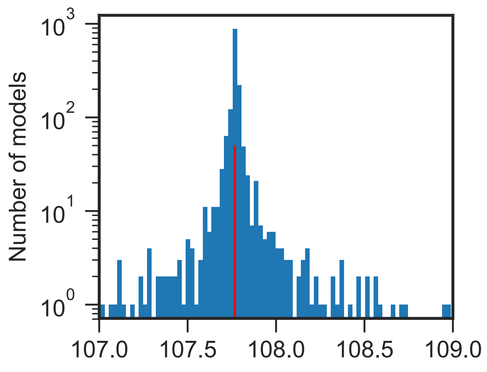


We developed a tool based on the open-source Reaction Mechanism Generator (RMG) to help identify molecular structures of species in detailed kinetic models.



Most parameters have small effect; red line indicates performance of baseline model [3].

$$\mathrm{HCCO} + \mathrm{O_2} \rightleftharpoons \mathrm{CO_2} + \mathrm{CO} + \mathrm{H}$$

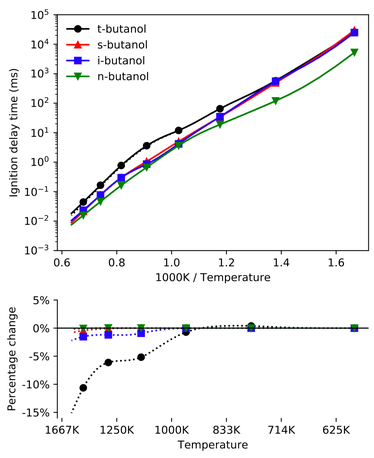
Option 1

- Klippenstein, Miller, and Harding (2002)
- QCISD(T) and MP2 from B3LYP geometries
- Barrier lowered 3.2 kcal/mol to match k_{298K}
- RRKM and dynamics
- Matches experiments

Option 2

- Baulch (1992)
- Only 300-550K
- "Kinetic data on this reaction are very limited, and no products have been suggested"
- Tweaked in a 2003 PhD thesis to match a few flame speeds

In this example we think Option 1 is closer to the truth, which agrees with the model authors, so no substitution is made.



Model performance did not change much in this case.

Collect experimental data from the literature and convert to ChemKED format, including uncertainties when available.

Collate kinetic models from the literature, identifying the molecular structures to allow comparing between models.

Select a base model, and from it generate many alternative models by substituting parameters found in other models, one substitution per model.

Run each of the alternative models against all experimental data, using PyTeCK, to generate overall error metric for each alternative.

Rank parameter substitutions according to highest impact (positive or negative) on the error metric.

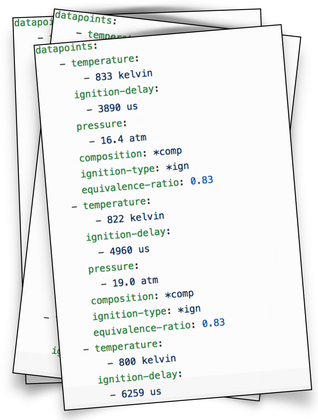
For the N most impactful parameters, follow the paper trail to determine the original source of the values, and decide which are most likely to be more accurate.

Construct a new model using all the selected substitutions.

Evaluate the final model against all available experimental data, using PyTeCK.

Chemical **K**inetics **E**xperimental **D**ata (ChemKED) [1]

- Human and machine readable
- Written in YAML
- For now, only shock tube data were included. More types are coming soon.



```
datapoints:
  - temperature:
      - 833 kelvin
    ignition-delay:
      - 3890 us
    pressure:
      - 16.4 atm
    composition: *comp
    ignition-type: *ign
    equivalence-ratio: 0.83
  - temperature:
      - 822 kelvin
    ignition-delay:
      - 4960 us
    pressure:
      - 19.0 atm
    composition: *comp
    ignition-type: *ign
    equivalence-ratio: 0.83
  - temperature:
      - 800 kelvin
    ignition-delay:
      - 6259 us
```

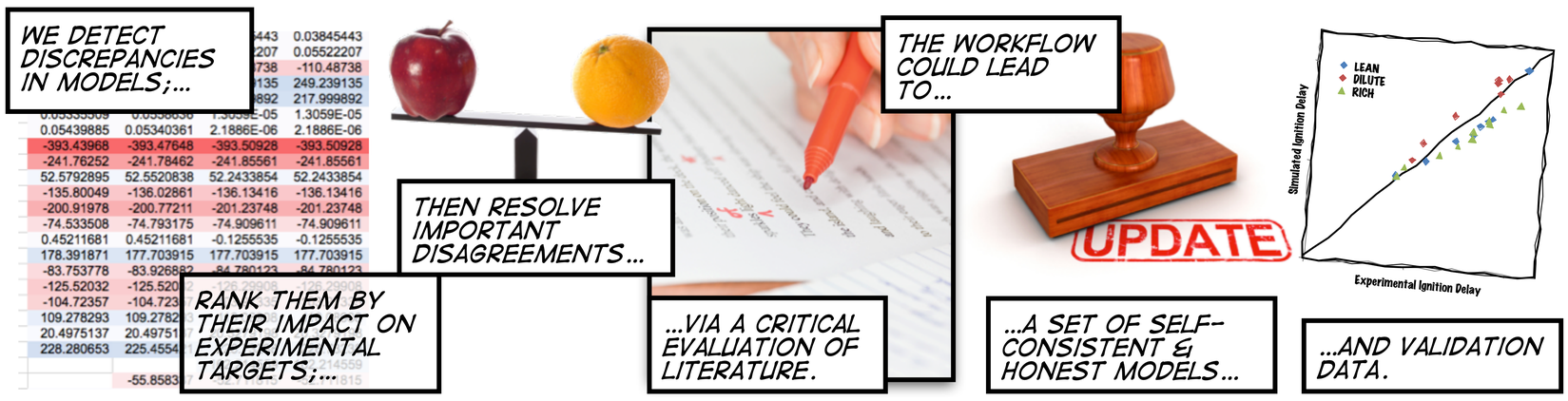
For this case study the base model was for butanol from LLNL [2]. We found 1600 possible substitutions:

- 300 reactions with one alternative rate
- 471 reactions with two alternative rates
- 65 species with one alternative thermo set
- 127 species with two alternative thermo sets

Type	Reaction or species no.	Variant no.	E	ΔE
Thermochemistry	190	1	122.514	14.747
Kinetics	293	2	98.359	−9.408
Kinetics	187	2	98.420	−9.347
Kinetics	59	1	98.422	−9.344
Thermochemistry	224	1	98.430	−9.337
Thermochemistry	190	2	116.494	8.728
Kinetics	187	1	102.222	−5.545
Kinetics	1440	1	102.276	−5.490
Kinetics	61	1	102.319	−5.447
Kinetics	291	1	113.119	5.353
Kinetics	180	1	102.707	−5.059
Kinetics	272	1	112.315	4.548
Kinetics	272	2	112.085	4.318
Kinetics	391	2	104.632	−3.134
Thermochemistry	90	1	104.744	−3.023
Kinetics	1441	1	105.343	−2.424
Kinetics	535	1	110.085	2.318
Kinetics	391	1	105.461	−2.305
Kinetics	535	2	110.008	2.241
Kinetics	189	2	105.700	−2.067
Kinetics	1267	1	105.714	−2.053
Kinetics	1441	2	105.767	−1.999
Thermochemistry	107	1	109.659	1.892
Kinetics	168	2	105.950	−1.817
Kinetics	321	2	109.583	1.816

The 25 most influential parameters on overall error metric E [3].

In this case, we most often agreed with the model authors, and made only a few substitutions.



References

[1] ChemKED: a human- and machine- readable data standard for chemical kinetics experiments. B.W. Weber, K.E. Niemeyer; *International Journal of Chemical Kinetics* 50 (2018):135–148.

[2] A comprehensive chemical kinetic combustion model for the four butanol isomers. S.W. Sarathy, S. Vranckx, K. Yasunaga, M. Mehl, P Oßwald, W.K. Metcalfe, C.K. Westbrook, W.J. Pitz, K. Kohse-Höinghaus, R.X. Fernandes, H.J. Curran; *Combustion and Flame* 159 (2012) 2028–2055

[3] Assessing impacts of discrepancies in model parameters on autoignition model performance: A case study using butanol. S.K. Sirumalla, M.A. Mayer, K.E. Niemeyer, R.H. West; *Combustion and Flame* 190 (2018) 284-292.

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