CHEMICAL KINETIC REACTION MECHANISM STUDY FOR AUTOIGNITION OF N-HEPTANE BLEND WITH TOLUENE AND 1,3-CYCLOHEPTADIENE

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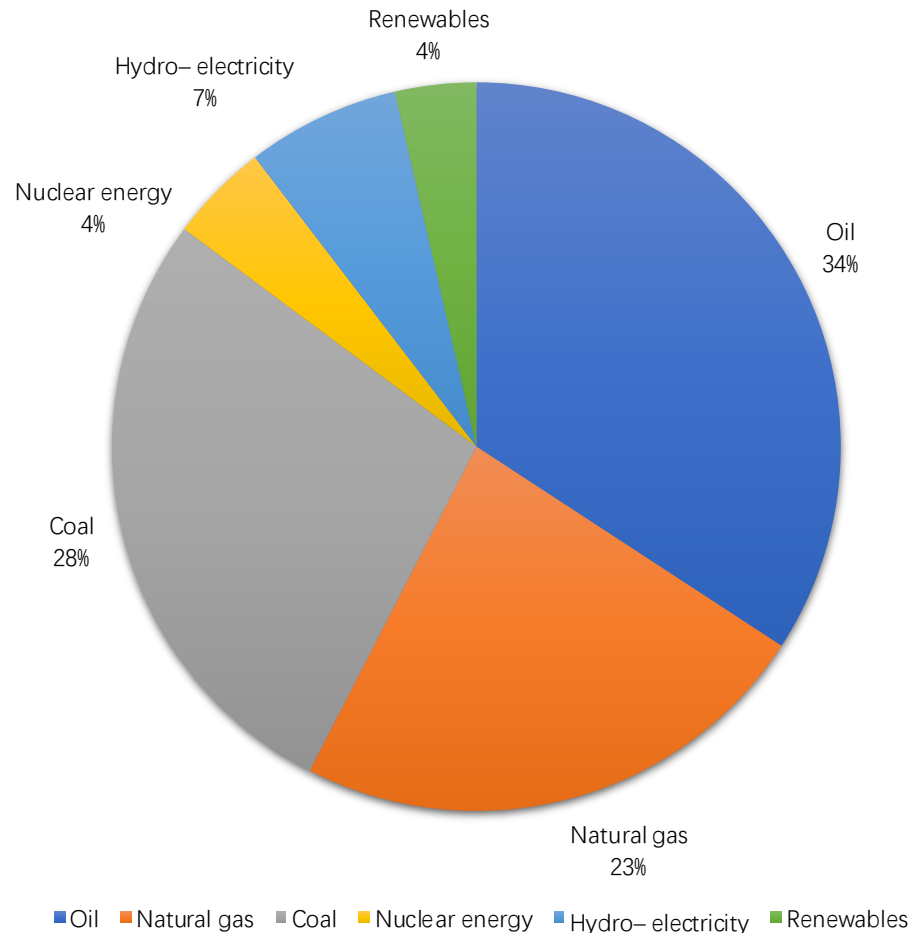# Promoting cleaner fuel combustion requires kinetic mechanisms

Figure 1. 2018 World Energy Consumption[1]

Oil
34%

Natural gas
23%

Coal
28%

Nuclear energy
4%

Hydro– electricity
7%

Renewables
4%

Oil Natural gas Coal Nuclear energy Hydro– electricity Renewables

Energy consumption keeps growing, and fossil fuels will continue to be the primary energy source until 2040[1]

Engine combustion study promotes the design of efficient and clean combustion of hydrocarbons
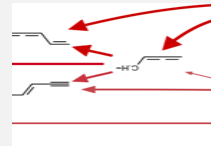
Detailed kinetic reaction mechanism are needed to study combustion chemistry during fuel oxidation.

[1] B Dudley, BP Statistical Review, London, UK, accessed Aug **6**, 2018 (2018).

Brief glance of kinetic reaction mechanisms

1,3-Cycloheptadiene (CHPD)

n-heptane

Toluene

gasoline surrogates
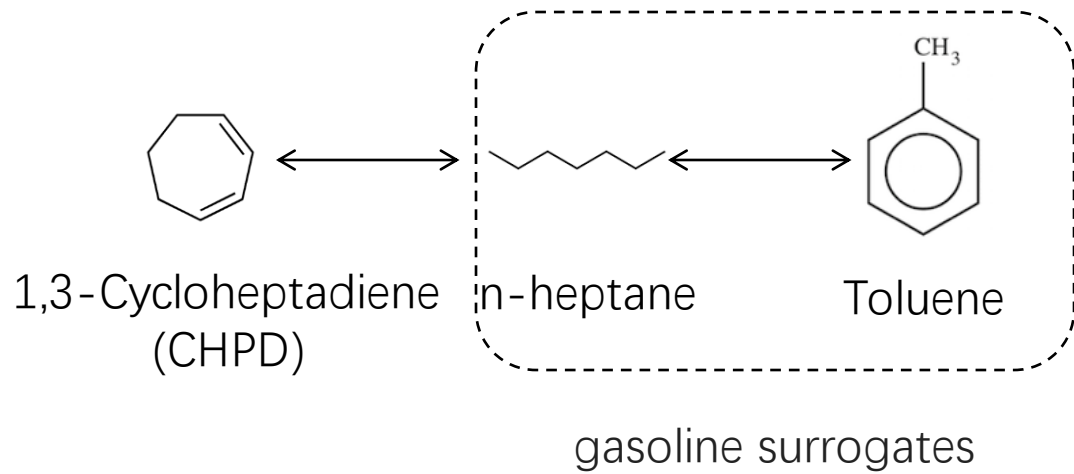
Table 1. RMG kinetic models' information

RMG model	Details
CHPD	870 species and 17120 reactions.
n-Heptane	708 species and 23059 reactions.
Toluene	998 species and 11571 reactions.
Blend of CHPD & n-Heptane	**1734** species and 15096 reactions.
Blend of Toluene & n-Heptane	**1937** species and 33995reactions.

Workflow of proposing a kinetic mechanism
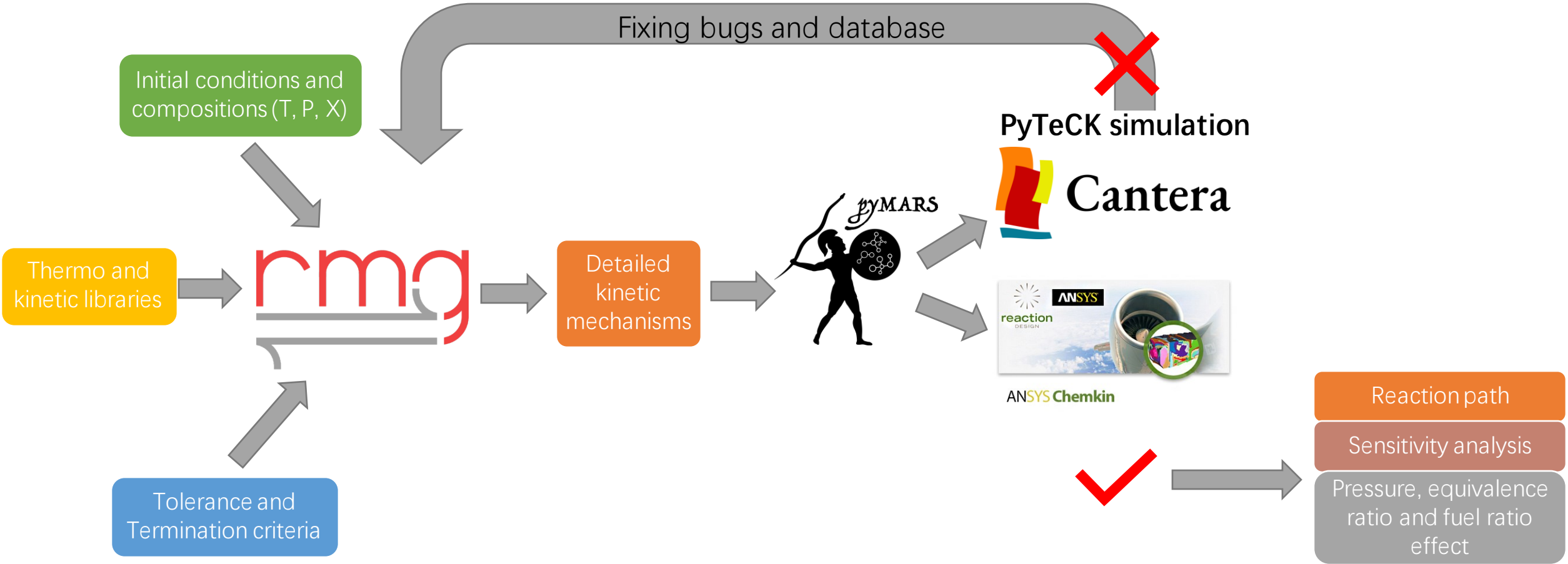
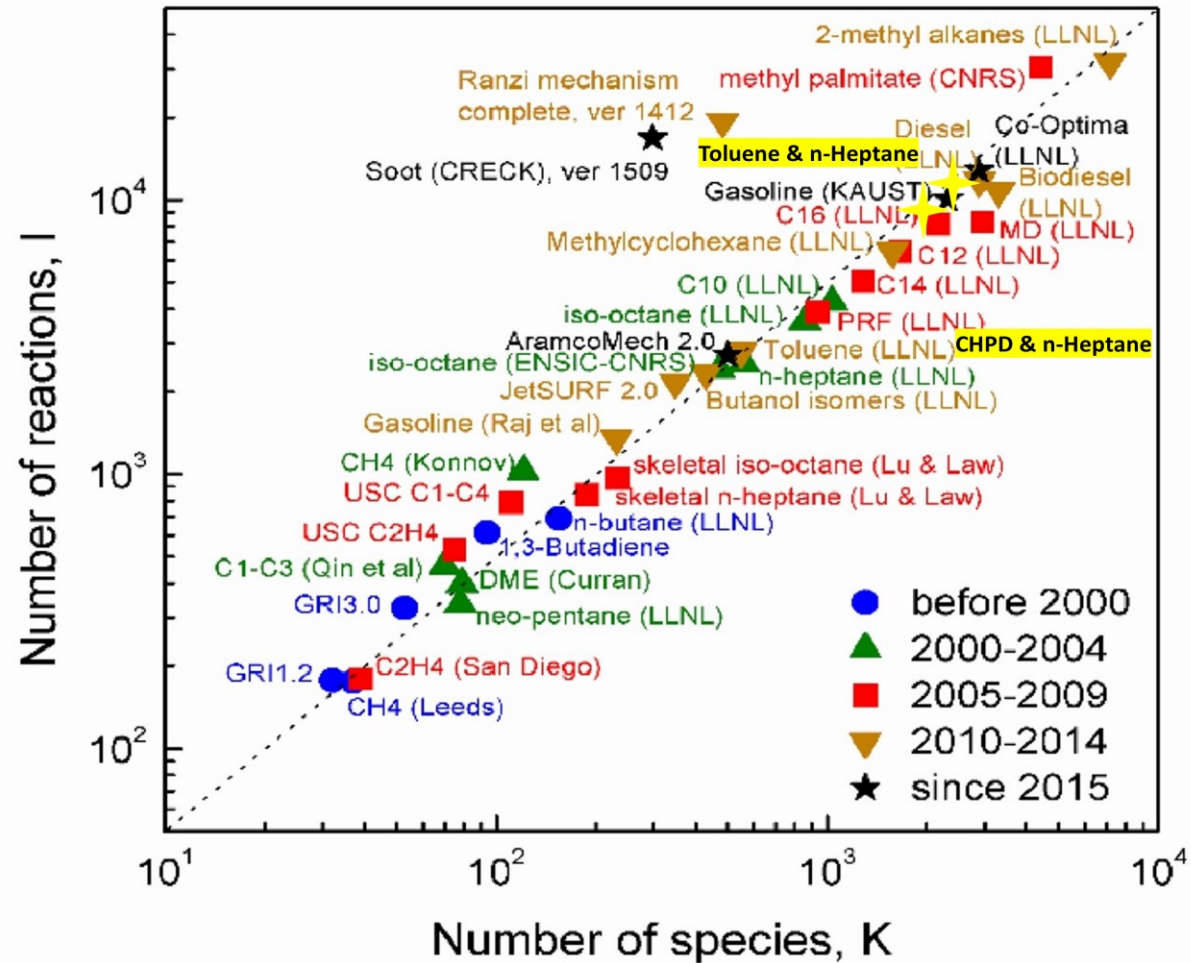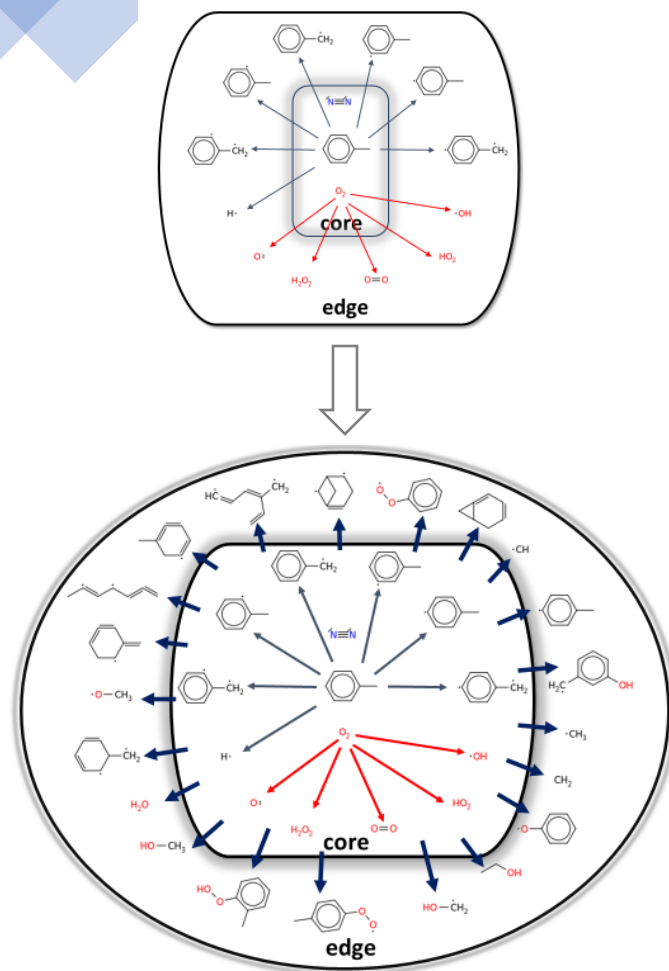# Detailed kinetic mechanisms are bigger over time

Figure 2. Increasing in size of kinetic mechanisms for hydrocarbon fuels [2]

- GRI-Mech 3.0 developed more than two decades ago (1999) and still in use, it contains 53 species and 325 reactions.
- Larger mechanisms construction are plausible as computation ability increases over the years
- Although it is possible to produce large mechanisms of thousands of reactions by hand, automatic generation of kinetic mechanisms can be more efficient, more systematic and less error-prone.

[2] HJ Curran, Proceedings of the Combustion Institute **37** (1), 57 (2019).

Figure 3. RMG iteration of exploring paths with high reaction rates and will move them into the model 'core'.

Reaction Mechanism Generator (RMG) is an open-source software package that automatically generates kinetic mechanisms consisting of elementary reactions based on a general understanding of how molecules react.

RMG uses a rate-based algorithm during model generation to determine model expansion and termination criteria. For all time intervals, if the reaction flux R_i = dC_i/dt of any species is larger than ϵR_{char}, (Epsilon is user-defined error tolerance, R_{char} characteristic flux), which is defined below

$$R_{char} = \sqrt{\sum_j R_j^2} \qquad species\ j\ \in core.$$

Then that species will be moved into the core.

pyMARS reduces detailed kinetic mechanisms for computation concerns

pyMARS (Python-based Model Automatic Reduction) is a Python package for reducing the size of blend mechanism. Directed relation graph with error propagation (DRGEP) method[3] is applied in our application.
In this study, we propose detailed kinetic reaction mechanisms of 1,3-Cycloheptadiene(CHPD), toluene, n-Heptane, and their blends using Reaction Mechanism Generator (RMG).
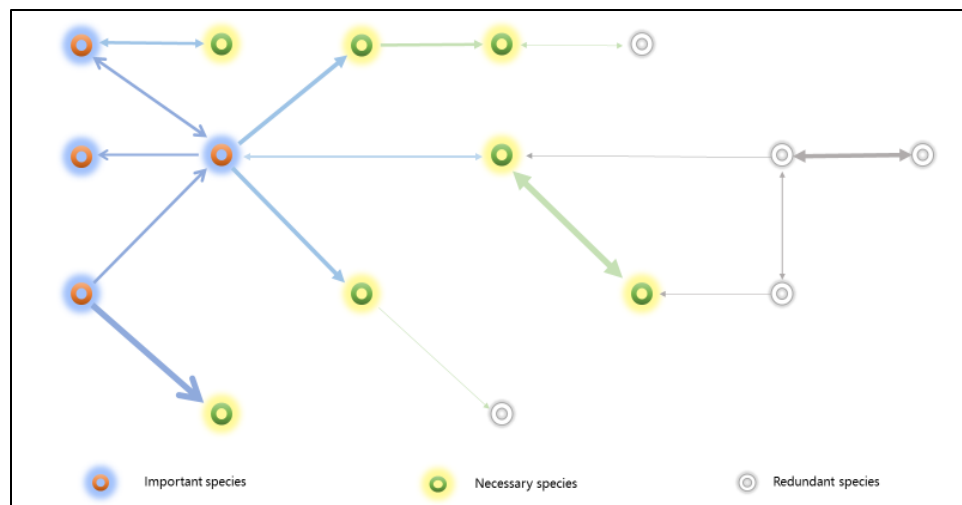
| Blend of CHPD & n-Heptane	Reduced CHPD & n-Heptane
1734 species and 15096 reactions.	**470** species and 8970 reactions.
Blend of Toluene & n-Heptane	Reduced Toluene & n-Heptane
1937 species and 33995 reactions.	**723** species and 20515 reactions.

Figure 4. Relationships between species

[3] P Pepiot-Desjardins and H Pitsch, Combustion and Flame **154** (1-2), 67 (2008).

Workflow of proposing a kinetic mechanism
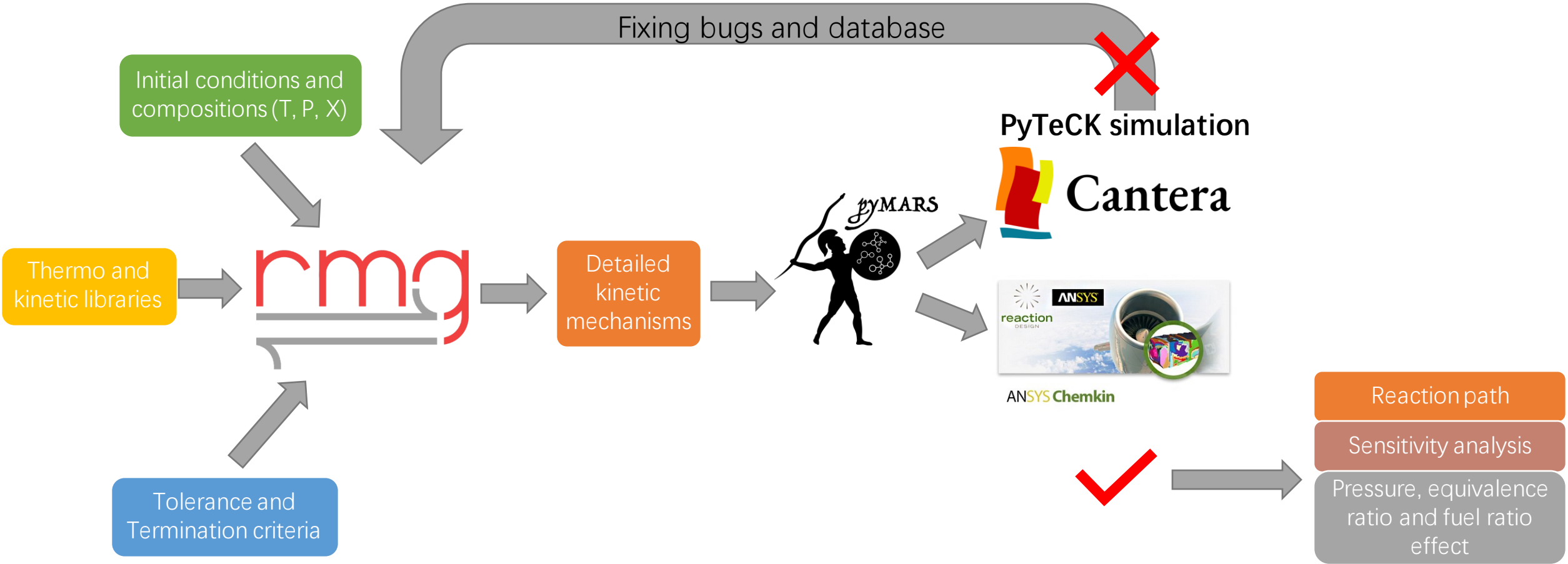
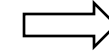# PyTeCK simulation calculates ignition delay time

Ignition Delay Time
(IDT) experimental results at various temperature, pressure and fuel ratio conditions
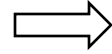
ChemKED
Chemical Kinetics Experiment Data YAML format datasets contains experimental IDT results

PyTeCK
Python tool for Testing Chemical Kinetics
Need: proposed kinetic mechanism
Output: all simulation results from ChemKED datasets
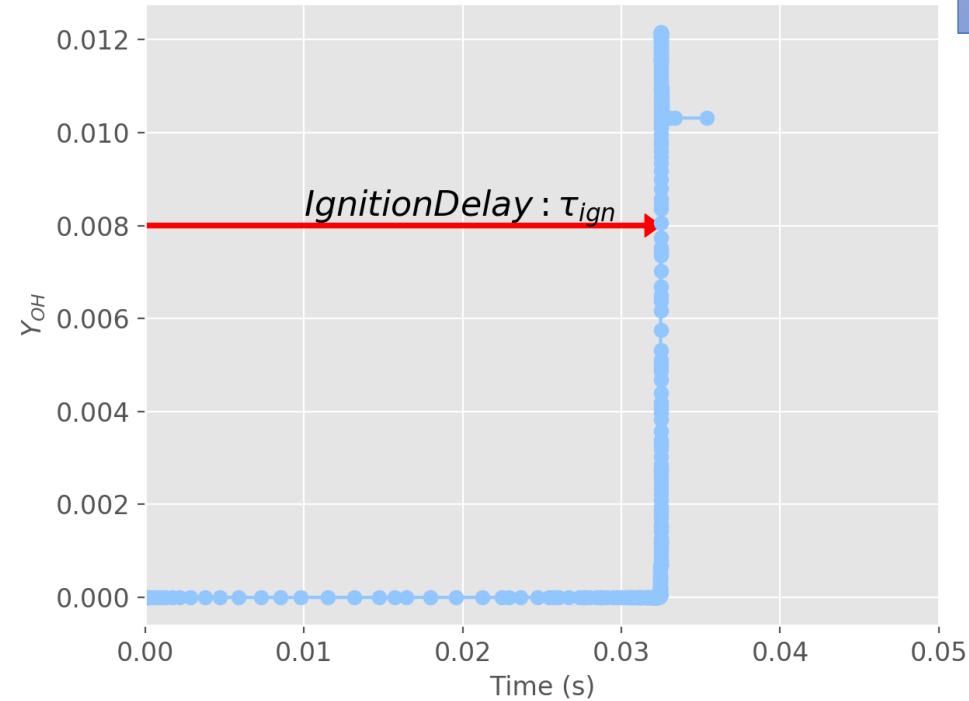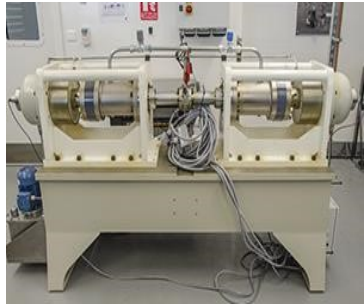
Rapid Compression Machine   Shock Tube

Figure 5.Illustration of ignition delay using OH radical

How ChemKED datasets are created

Table2. References with detailed experimental conditions[4-15]

Literature	Experimental conditions
Darshan M.A.Karwat **RCM**	Pressure: 9 atm Temperatures: 660–710 K Phi: 1
Alexander Burcat **ST**	Pressure: 2 to 12 atm Temperatures: 1100-1700 K Phi: 0.5-2
H.K.Ciezki **ST**	Pressure: 3.2 to 42 bar Temperatures: 660–1350 K Phi: 0.5-3

······ (12 references in total)

Listed left are 3 references with detailed experimental conditions when testing n-Heptane IDTs. These data were recompiled into 56 ChemKED datasets, and ready for PyTeCK comparison

NO.	Pressure(bar)	phi
1	3.2	1
2	6.5	1
3	13.5	1
4	13.5	0.5
5	13.5	2
6	13.5	3
7	19.3	1
8	30	1
9	42	1

[4] DM Karwat et al., Combustion and flame **160** (12), 2693 (2013).
[5] A Burcat et al., 1971.
[6] H Ciezki and G Adomeit, Combustion and flame **93** (4), 421 (1993).
[7] MB Colket III and LJ Spadaccini, Journal of propulsion and power **17** (2), 315 (2001).
[8] K Fieweger et al., Combustion and Flame **109** (4), 599 (1997).
[9] M Hartmann et al., Combustion and Flame **158** (1), 172 (2011).
[10] J Herzler et al., Proceedings of the Combustion Institute **30** (1), 1147 (2005).
[11] DC Horning et al., Journal of Propulsion and Power **18** (2), 363 (2002).
[12] JM Smith et al., International journal of chemical kinetics **37** (12), 728 (2005).
[13] A Vandersickel et al., Fuel **93**, 492 (2012).
[14] D Vermeer et al., Combustion and Flame **18** (3), 327 (1972).
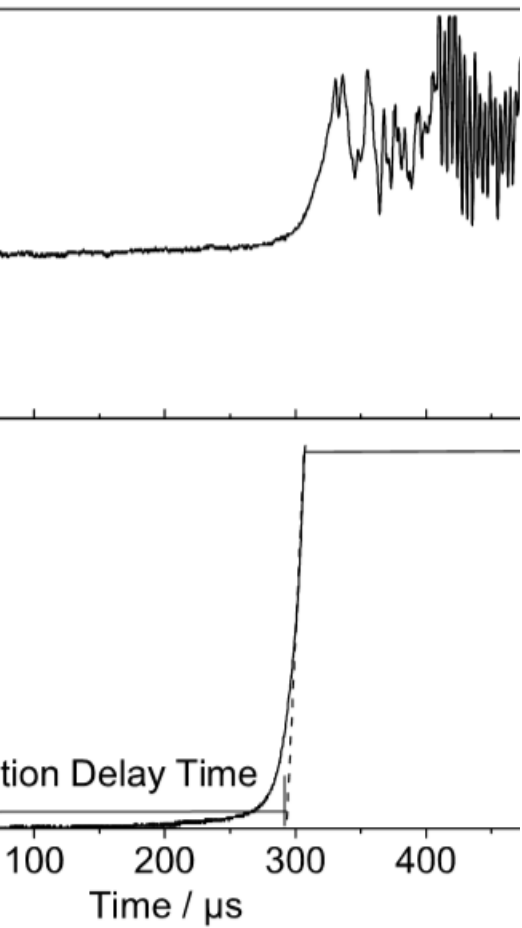[15] K Zhang et al., Combustion and Flame **172**, 116 (2016).

n-Heptane experiments and simulation IDT comparison over a wide range conditions

Phi=1
Pressure: 4 bar
692–1264 K

Phi=1
Pressure: 15 bar
1058-1297.5 K
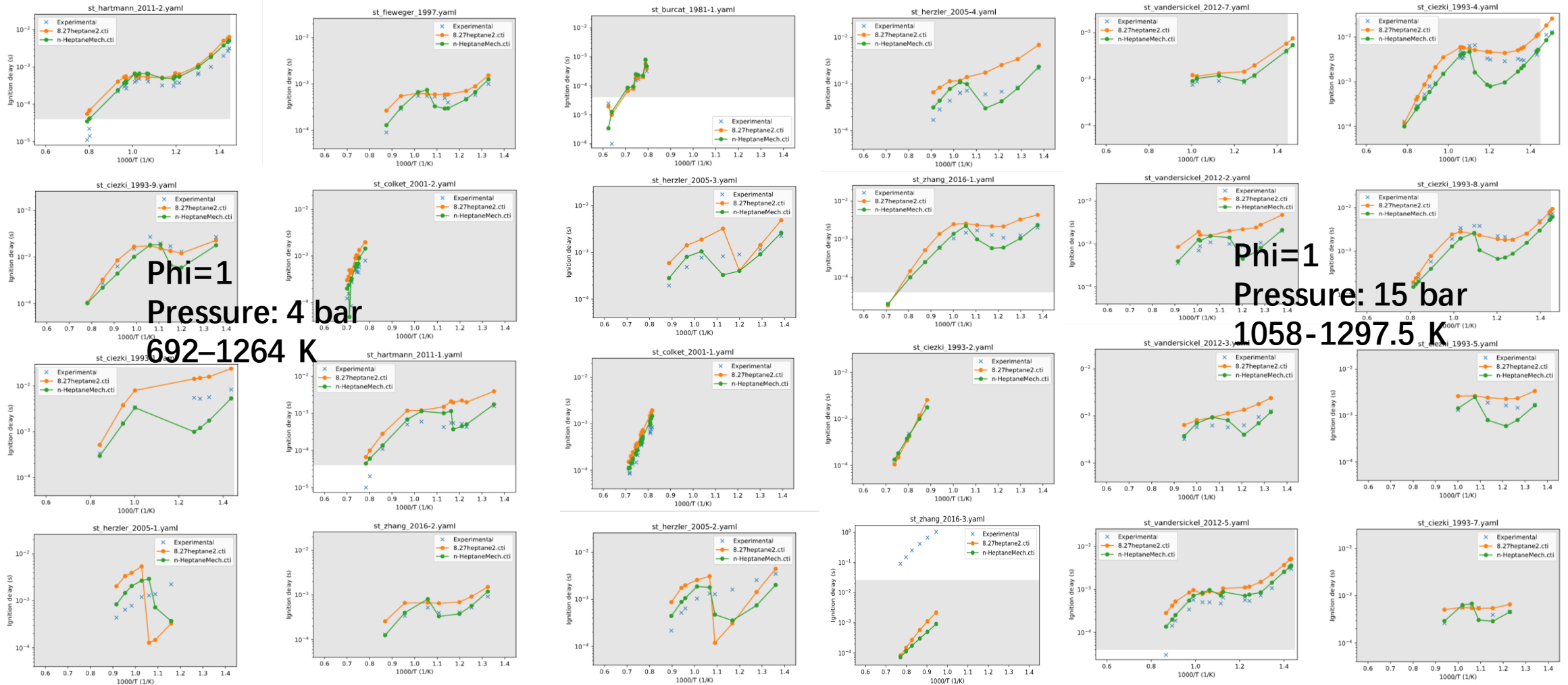
(56 subfigures in total)

Figure 6. PyTeCK results of n-Heptane

re (upper part) and CH* emis
ndicating ignition delay in a lea
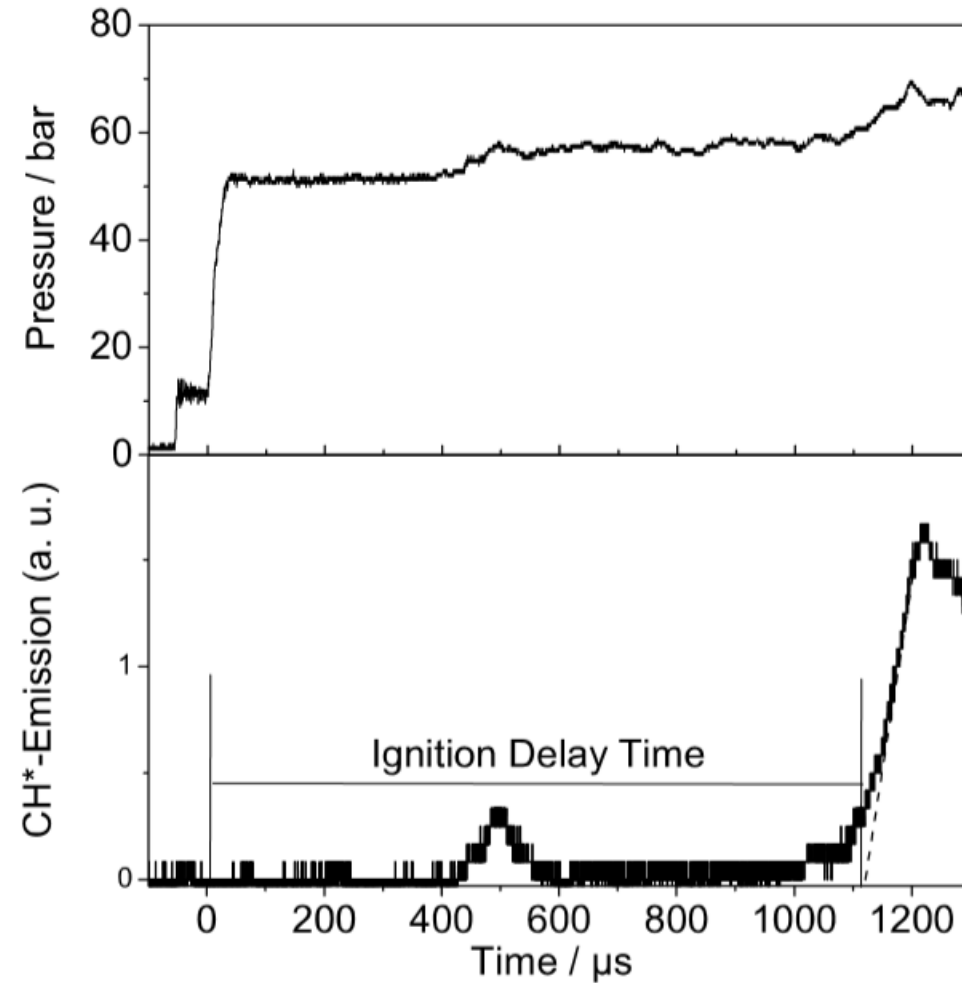Reaction conditions: Φ =
= 51.5 bar.

Fig. 3. Typical pressure (upper part) and CH* emission (lower part) profiles indicating two-stage ignition delay
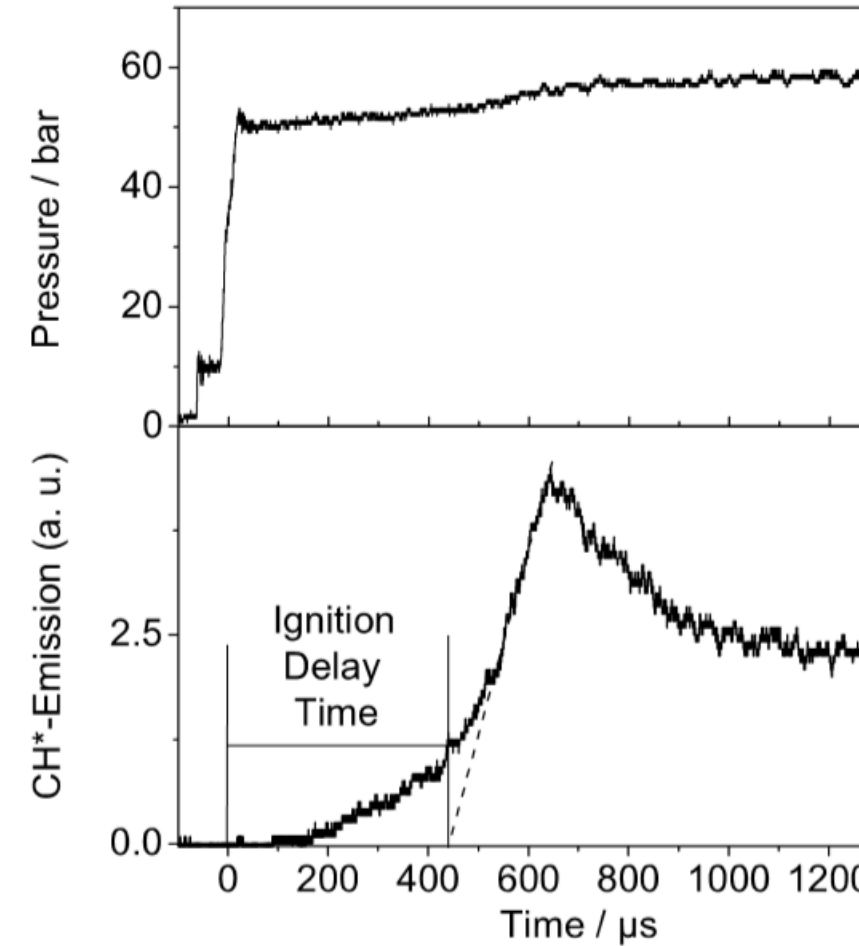in a lean n-heptane/air mixture. Reaction conditions:

Fig. 5. Typical pressure (upper part) and CH* e
(lower part) profiles indicating ignition delay in a
heptane/air mixture. Reaction conditions:

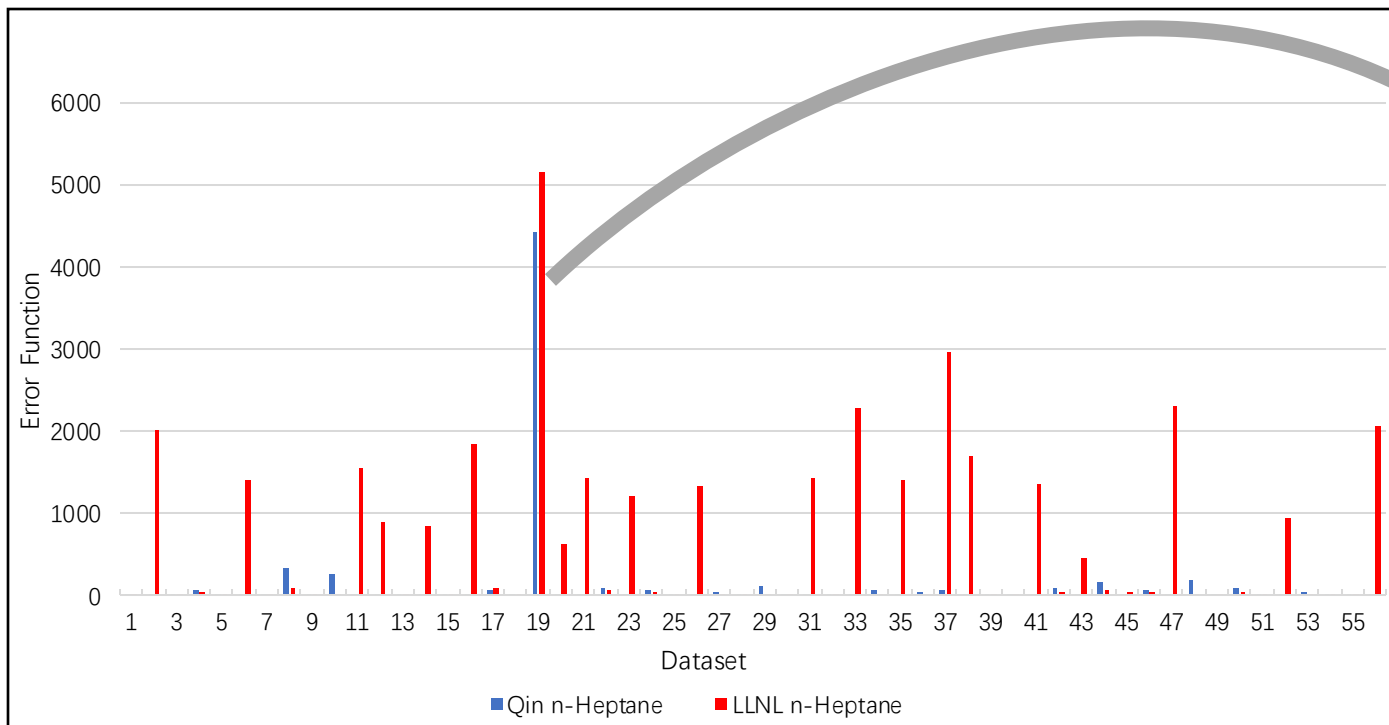# n-Heptane IDT simulation show large errors due to wrong stage of IDTs

Figure 7. Error function of two tested models for n-Heptane IDT simulation

$$\text{Error function} = \left(\frac{\log(\text{ignition\_delays\_sim})}{\log(\text{ignition\_delays\_exp})}\Big/\text{standard\_deviation}\right)^2$$

Where $\text{standard\_deviation}$ is defined as the standard deviation of the difference between data and best-fit line, and it is explained in the "eval_model" file in the PyTeCK website.
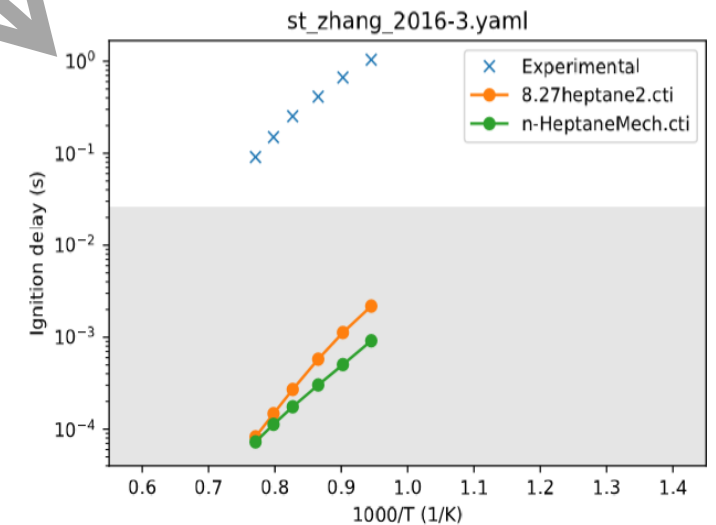

Figure 8. experimental and situational IDTs over 1000/K Phi=1 15 bar

In dataset 19, there is a 3-magnitude error between experimental and simulation IDTs. Two model did not correctly predict IDT and we attribute this to wrong IDT selection.

Ignition delay time selection is tricky

st_herzler_2005-3.yaml

Phi=0.3
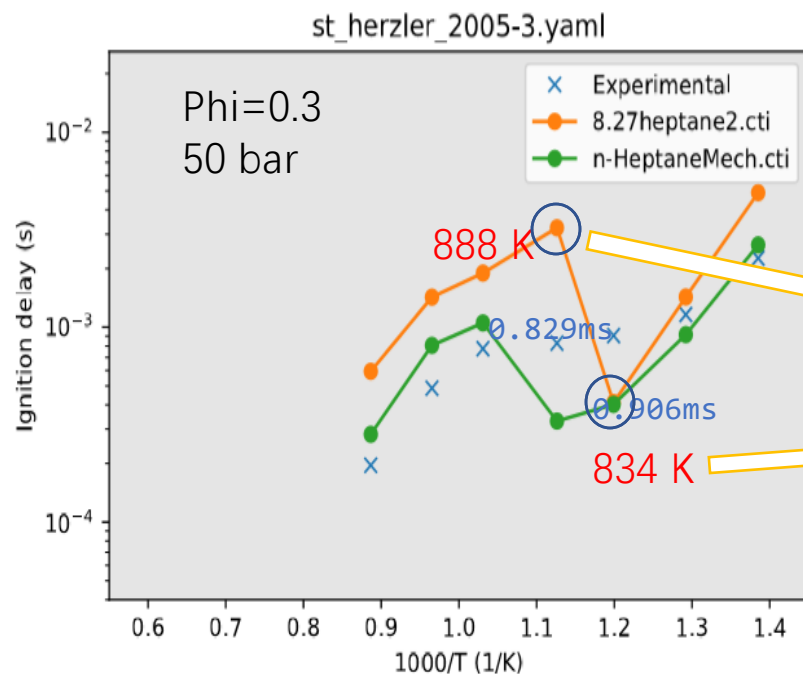50 bar

888 K

0.829ms

834 K

0.906ms

Figure 9. experimental and situational IDTs over 1000/K

Some experiments measure pressure rise; some monitor the concentration of an intermediate like OH via laser absorption; but other studies monitor the luminescence of excited OH∗ decaying to ground state OH (which it does by emitting a photon).

In herzler's experiments, all ignition delay time values were determined by extrapolating the highest increase of the emission signal to its zero level at the time axis. In short, **d(CH∗)/dt max** as IDT signal.

834 K

888 K

(a)

(b)

0.385ms

0.147ms

4.041ms
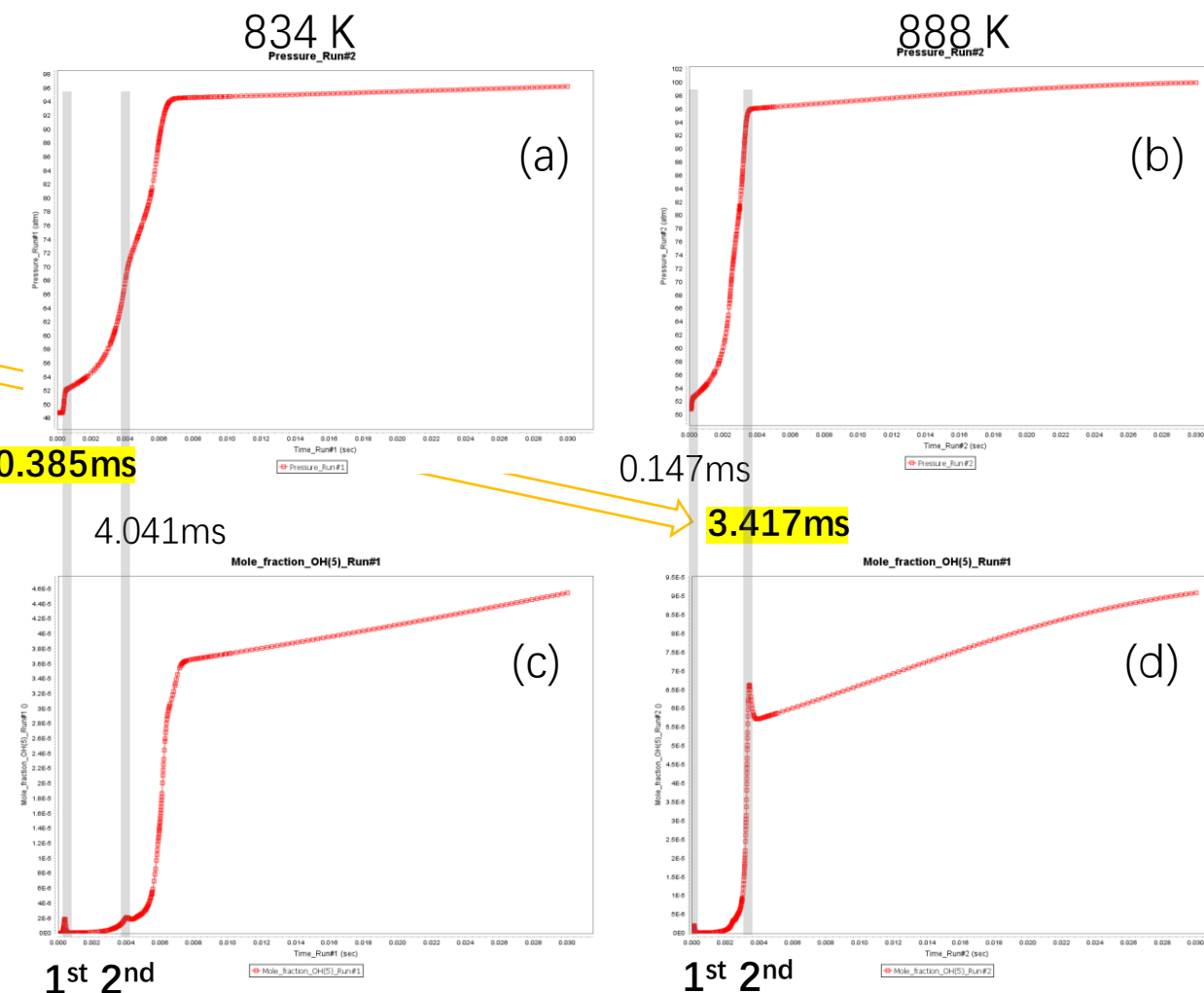
3.417ms

(c)

(d)

1st 2nd

1st 2nd

Figure 10. Pressure and OH mole fraction variation over time

In simulation, we use dP/dt max as the IDT signal. At 834 K, the simulation use 0.385 ms as IDT, while at 888 K, it consider 3.417 ms as IDT.

Blend model of n-Heptane&Toluene validation using same process above

Table2. References with detailed experimental conditions[16-20]

Literature	Experimental conditions
R Di Sante **RCM**	Pressure: 11 bar Temperatures: 710–790 K Phi: 1 Toluene ratio: 25-60 %vol
M Hartmann **ST**	Pressure: 40 bar Temperatures: 710-1184 K Phi: 0.5-1 Toluene/n-Heptane: 10/90 %vol
J Herzler **ST**	Pressure: 10-50 bar Temperatures: 640–1180 K Phi: 0.3-1 Toluene/n-Heptane: 65/35 %vol
Z Malliotakis **ST RCM**	Pressure: 10-30 bar Temperatures: 690–1480 K Phi: 0.5-2 Toluene ratio: 50-90 %vol
S Goldsborough **RCM**	Pressure: 20-40 bar Temperatures: 715-870 K Phi: 0.5-2 Toluene ratio: 25-50 %vol

Pressure ranging from 10-50 bar

Temperature ranging from 640-1480 K

Equivalence ration ranging from 0.3-2

Toluene volume fraction in fuels from 25-90 %

[16] R Di Sante, Combustion and flame **159** (1), 55 (2012).
[17] M Hartmann et al., Combustion and Flame **158** (1), 172 (2011).
[18] J Herzler et al., Combustion and flame **149** (1-2), 25 (2007).
[19] Z Malliotakis et al., Combustion and Flame **199**, 241 (2019).
[20] S Goldsborough, unpublished.

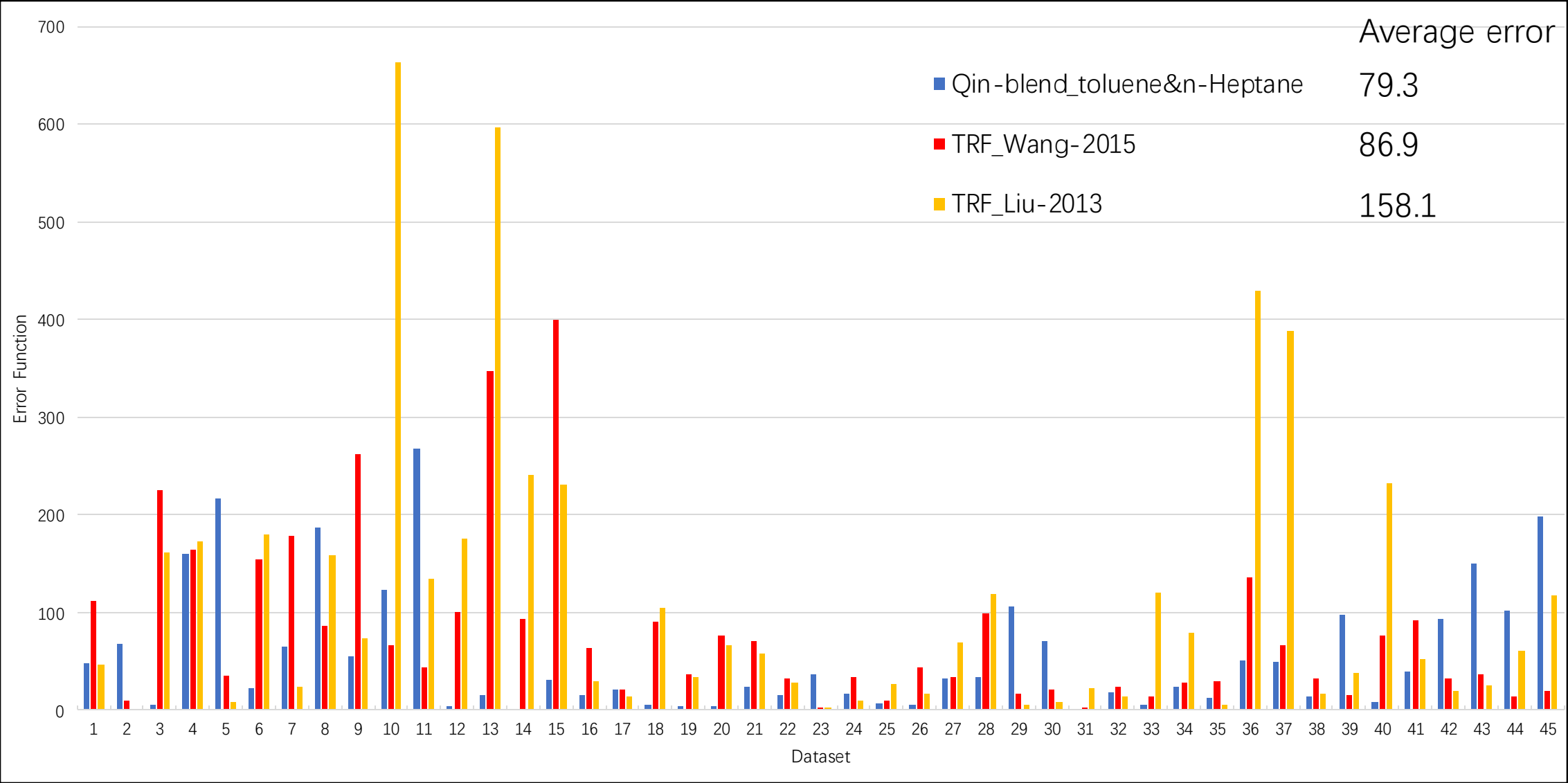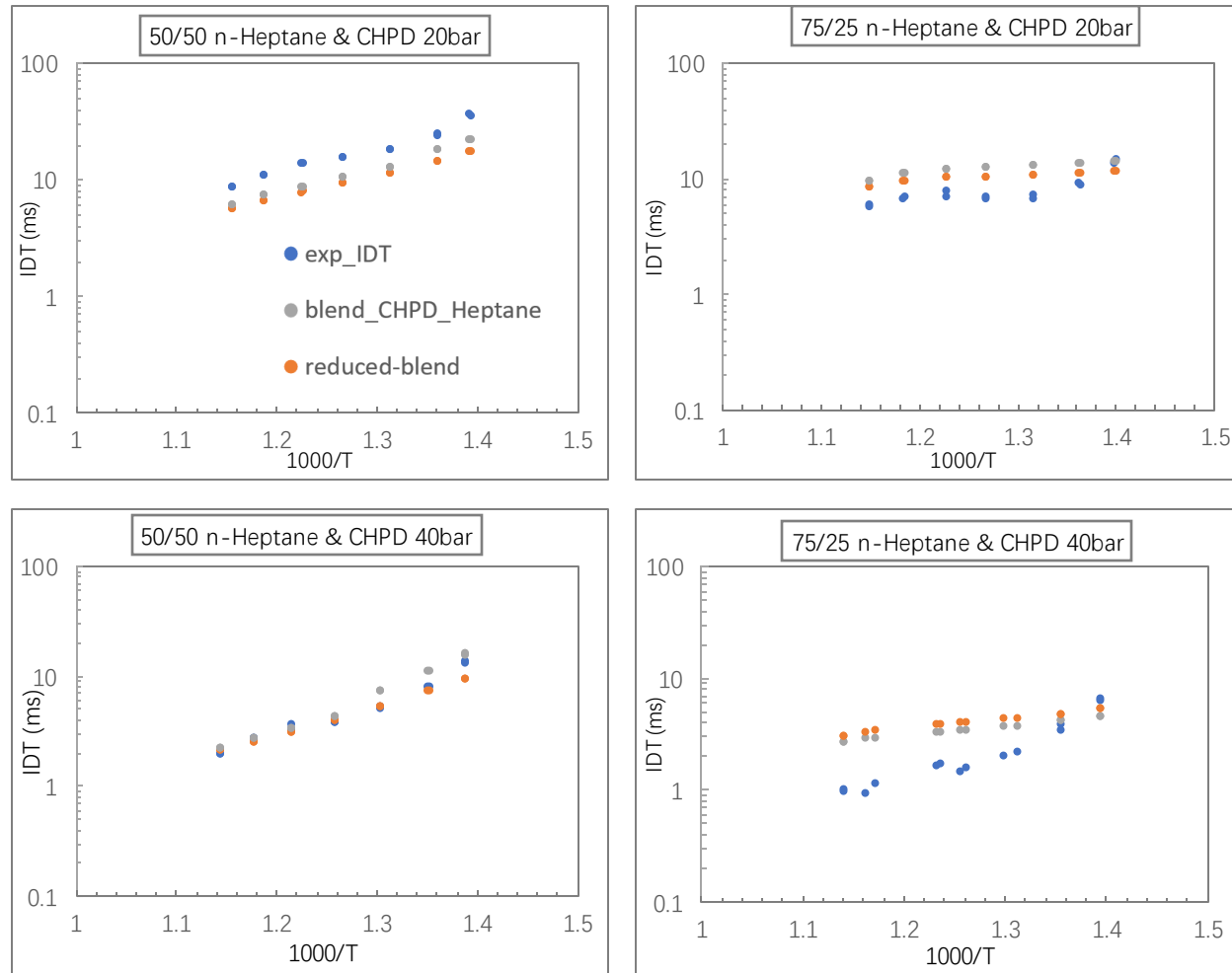# Three blended models' performance expressed using error function

Figure 11. Error function of three tested models for toluene & n-heptane blend IDT simulation
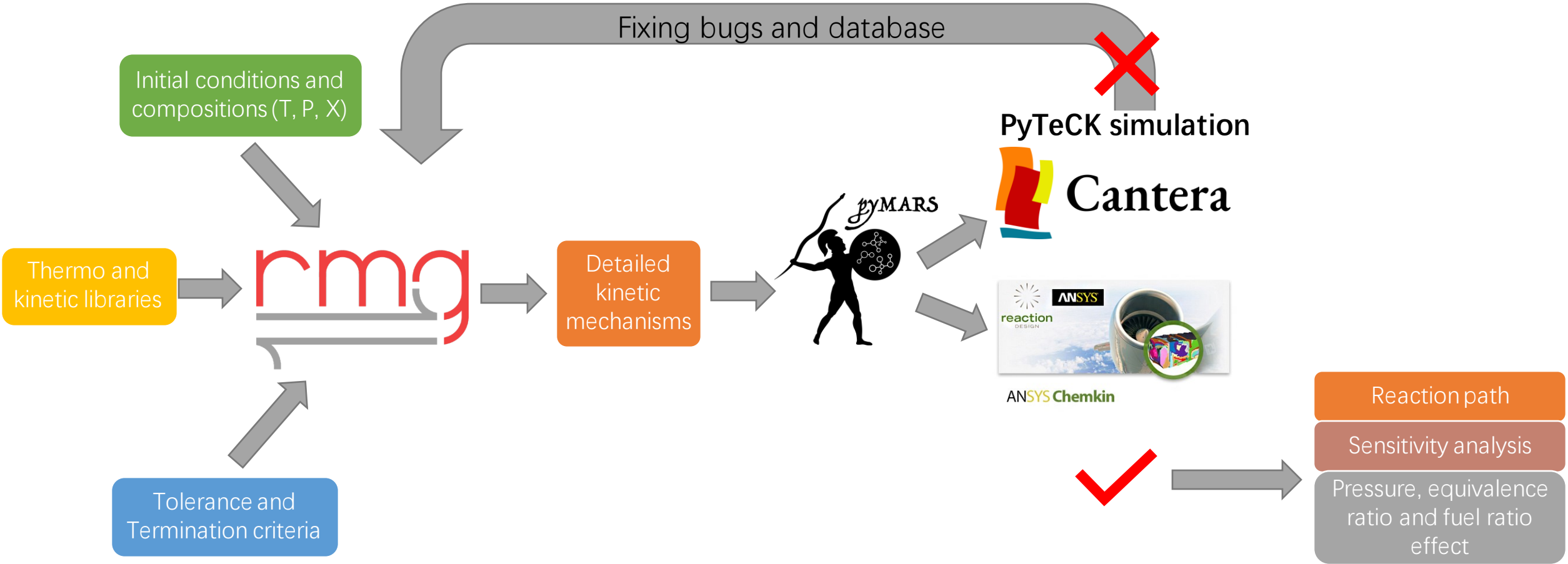
Blend model IDT simulations show acceptable discrepancy with exp data

Figure 12. Comparison between experimental data and simulation results of CHPD & n-Heptane blend models

- The experimental data are from Scott's RCM experimentation, and as far as we know, these are the only IDT experimentation about CHPD and n-Heptane blends.

- The simulation IDT results of the blend model and reduced blend model shows good uniformity, and this can help prove our reduced model does capture the core pathways of a detailed kinetic reaction model.

- Similarly, original model VS reduced model of toluene & n-Heptane blend is attached in Appendix B.

Workflow of proposing a kinetic mechanism

Fixing bugs and database

Initial conditions and compositions (T, P, X)

PyTeCK simulation

Thermo and kinetic libraries

rmg

Detailed kinetic mechanisms

pyMARS

Cantera

ANSYS Chemkin

Tolerance and Termination criteria

Reaction path

Sensitivity analysis

Pressure, equivalence ratio and fuel ratio effect

Model generation	Model reduction	Model validation	**Model analysis**

Reaction pathway for n-Heptane
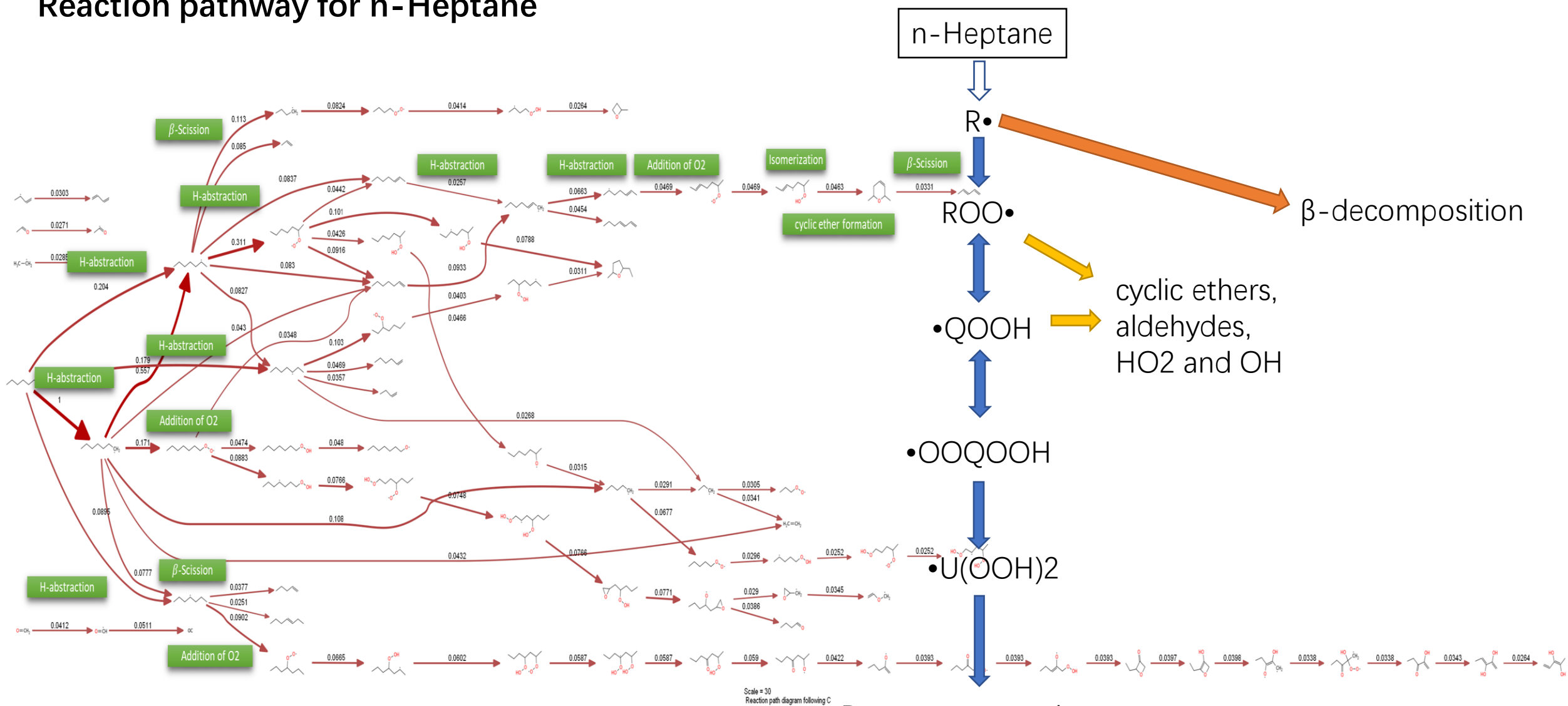
Figure 13. Reaction path for n-Heptane at 950 K

Scale = 30
Reaction path diagram following C

n-Heptane

R•

ROO•

•QOOH

•OOQOOH

•U(OOH)2

Degenerate products

β-decomposition

cyclic ethers, aldehydes, HO2 and OH

β-Scission

H-abstraction

H-abstraction

H-abstraction

H-abstraction

H-abstraction

H-abstraction

Addition of O2

β-Scission

H-abstraction

Addition of O2

H-abstraction

Addition of O2

Isomerization

β-Scission

cyclic ether formation

Low temperature

Intermediate

High temperature

Reaction pathway for toluene in blend of toluene & n-Heptane

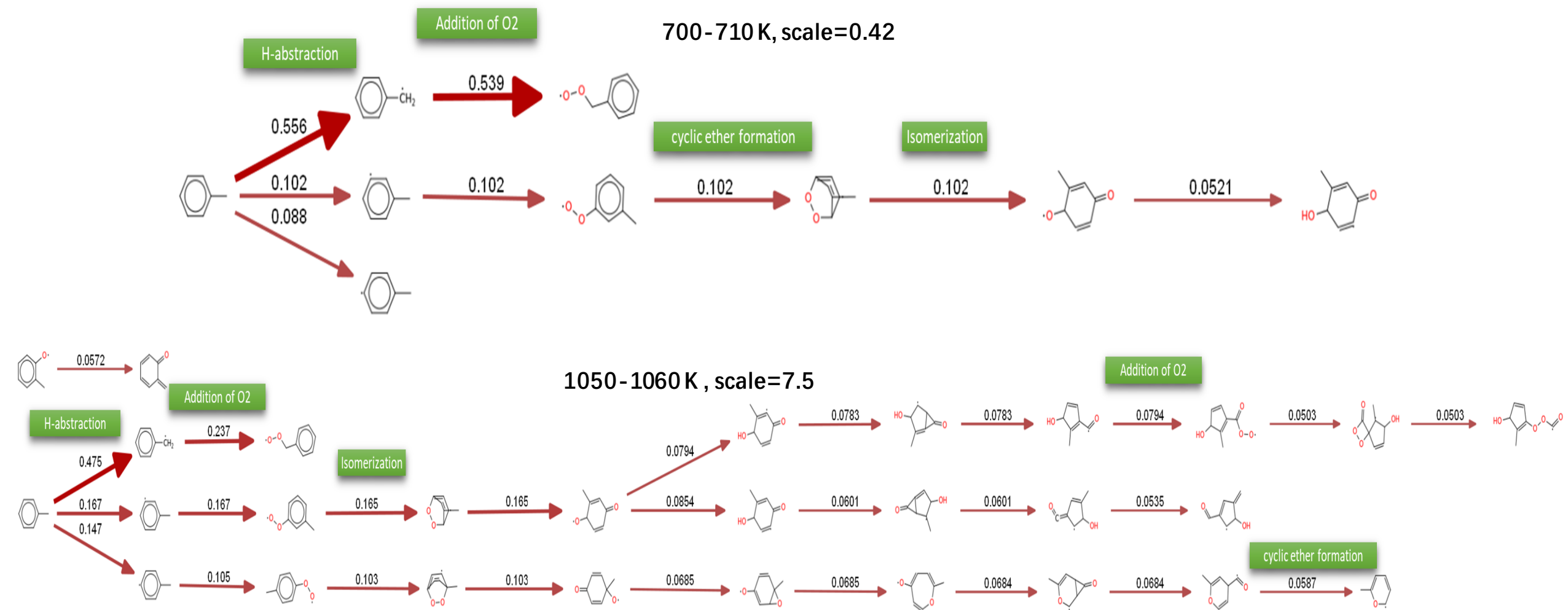700-710 K, scale=0.42

1050-1060 K, scale=7.5

Figure 14. Reaction path for toluene at different initial temperatures

OH sensitivity for toluene & n-Heptane blend over NTC region

This paper we compute normalized OH radical concentration sensitivity against rate constant for reaction i below:

$$\frac{\partial \ln[OH]}{\partial \ln k_i} = \frac{\partial[OH]}{[OH]} \cdot \frac{k_i}{\partial k_i}$$
$$= \frac{k_i}{[OH]} \cdot \frac{\partial[OH]}{\partial k_i}$$

A positive sensitivity result means the increase in the reaction rate will favor the production of OH radicals and speed up the reaction chain and vice versa.
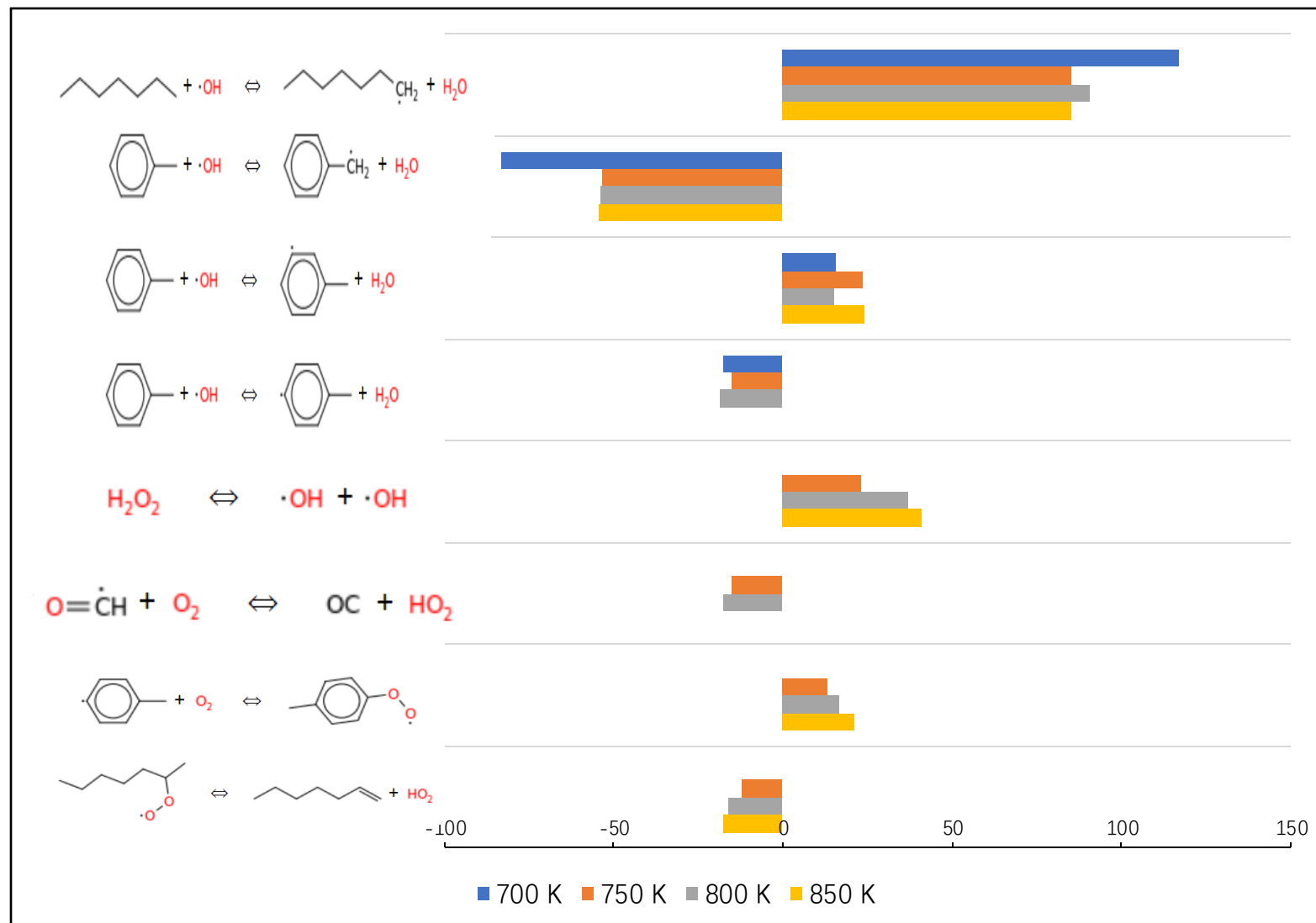

Figure 15. OH sensitivity for Toluene & n-Heptane blend at 700-850 K and 40 atm

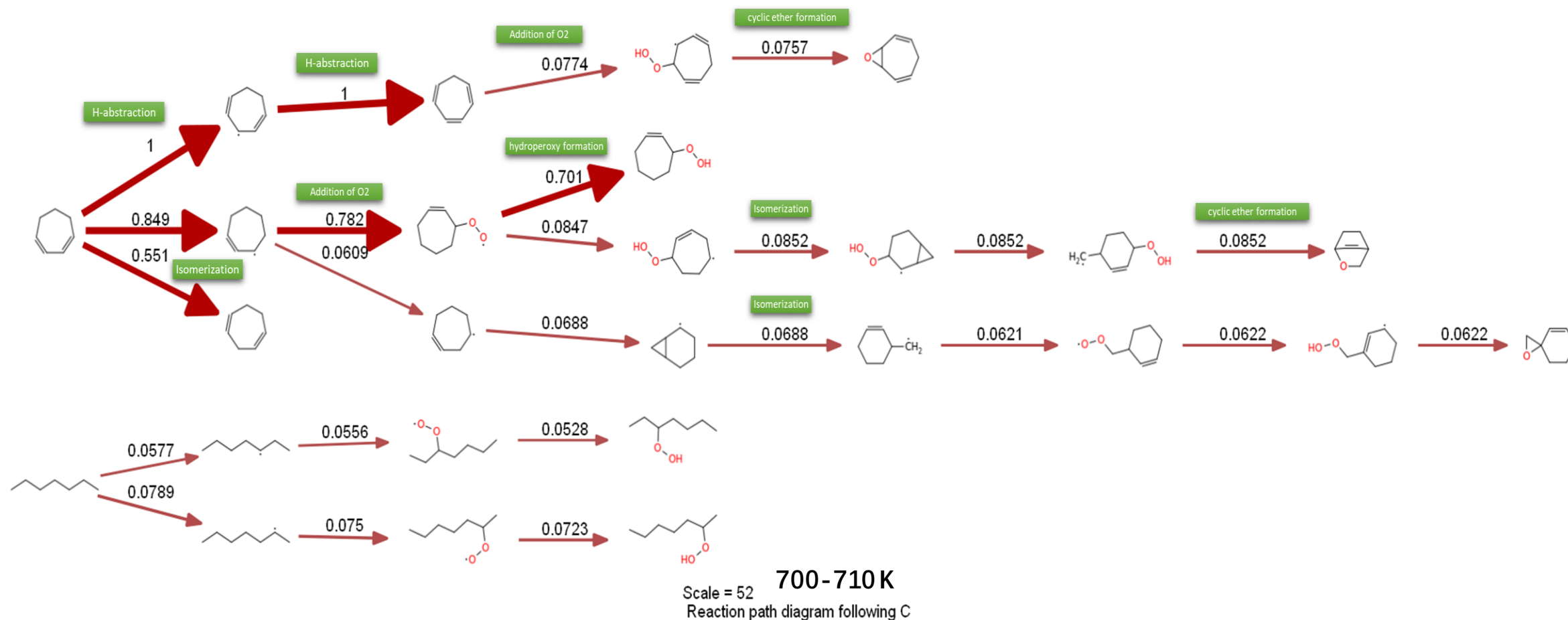# Reaction pathway for CHPD & n-Heptane blend

Figure 16. Reaction path for the blend fuel of CHPD and n-Heptane at different initial temperatures

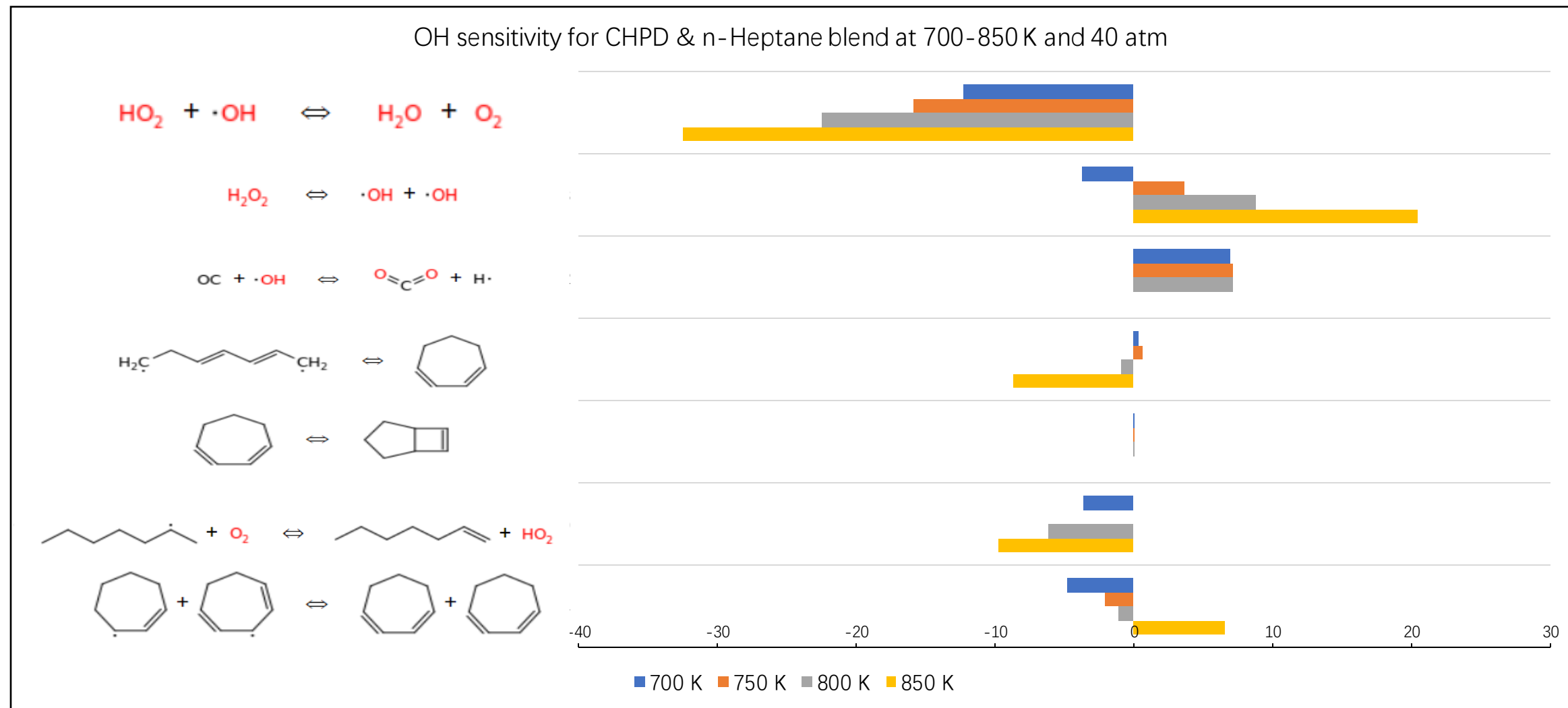# OH sensitivity for CHPD & n-Heptane blend

Figure 17. OH sensitivity for CHPD & n-Heptane blend at 700-850 K and 40 atm

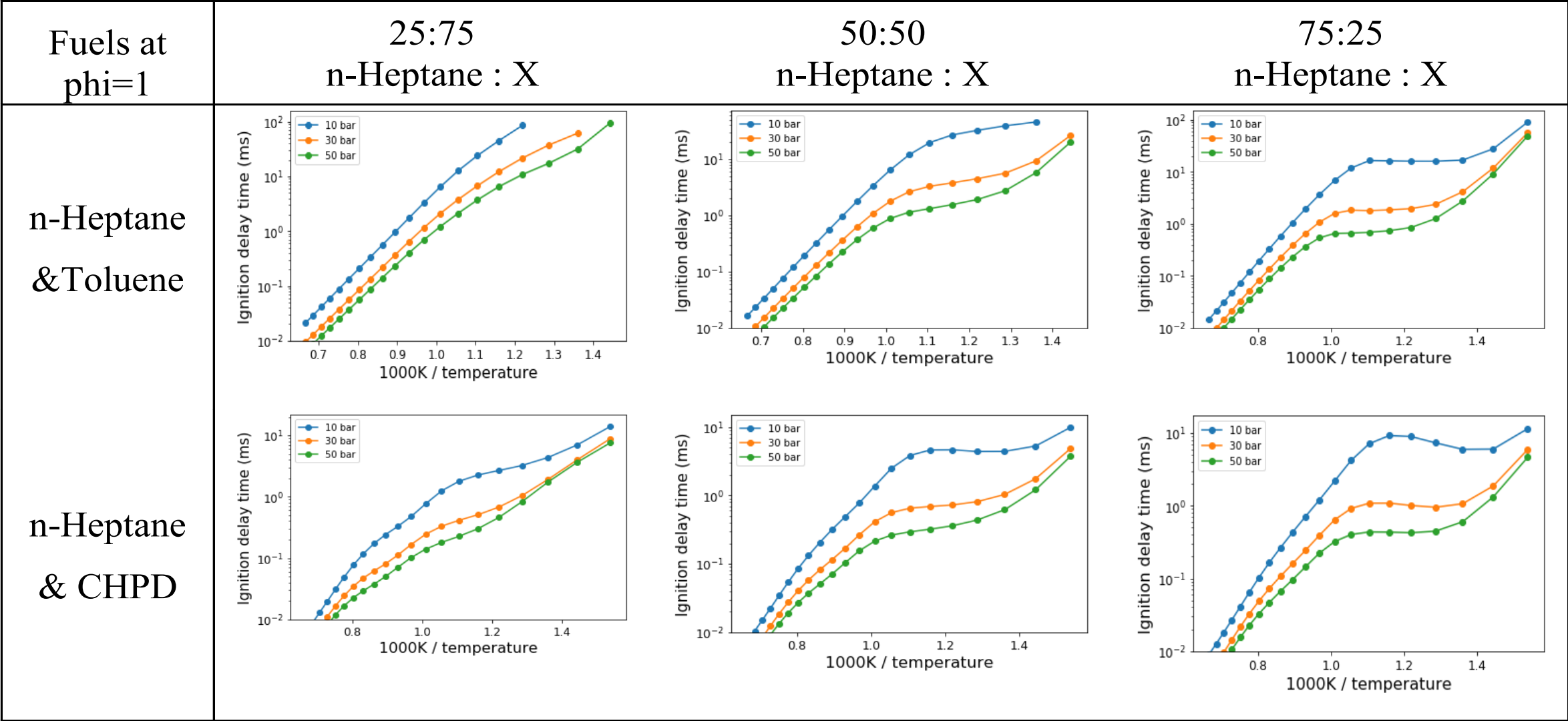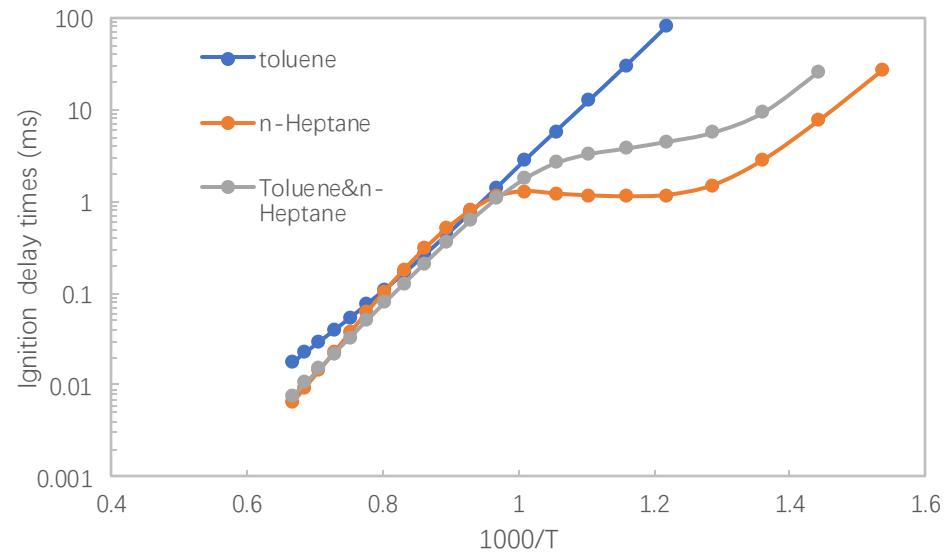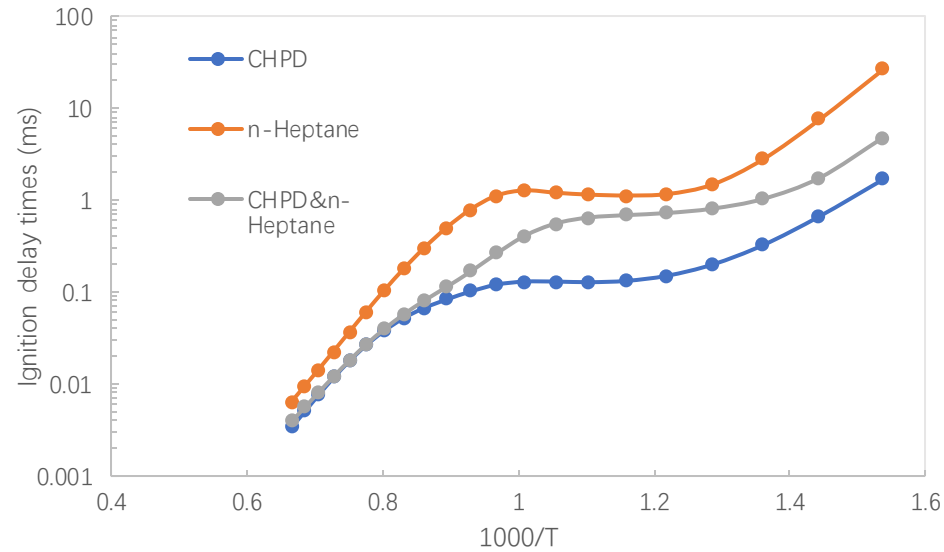# Model performance of fuel X from lean to rich in volume ratio

Fuels at phi=1	25:75 n-Heptane : X	50:50 n-Heptane : X	75:25 n-Heptane : X
n-Heptane &Toluene			
n-Heptane & CHPD			

Figure 18. Simulated IDT of fuels at various equivalence ratio and pressures

CHPD and toluene performance when blended with n-Heptane

Figure 19. Simulated IDT of fuel blends at 30 bar and phi=1

- The blend of CHPD & n-Heptane shows a similar ignition curve to n-Heptane and CHPD, but the blend NTC region moves to lower temperature than the two fuels alone.
- Toluene oxidation is a line, while blended with n-Heptane, a relatively slightly NTC region shows.
- Toluene delays blend of toluene & n-Heptane IDT. E.g., at 30 bar, and phi equals 1, the blend is about 3 ms higher than n-Heptane for temperature range from 730 to 900 K.

Thank you!

Richard and all the members in Computational Modeling in Chemical Engineering(CoMoChEng) Group,

Committee members: Scott Goldsborough and Benjamin Woolston.

Department of Chemical Engineering at Northeastern University

And all my family members