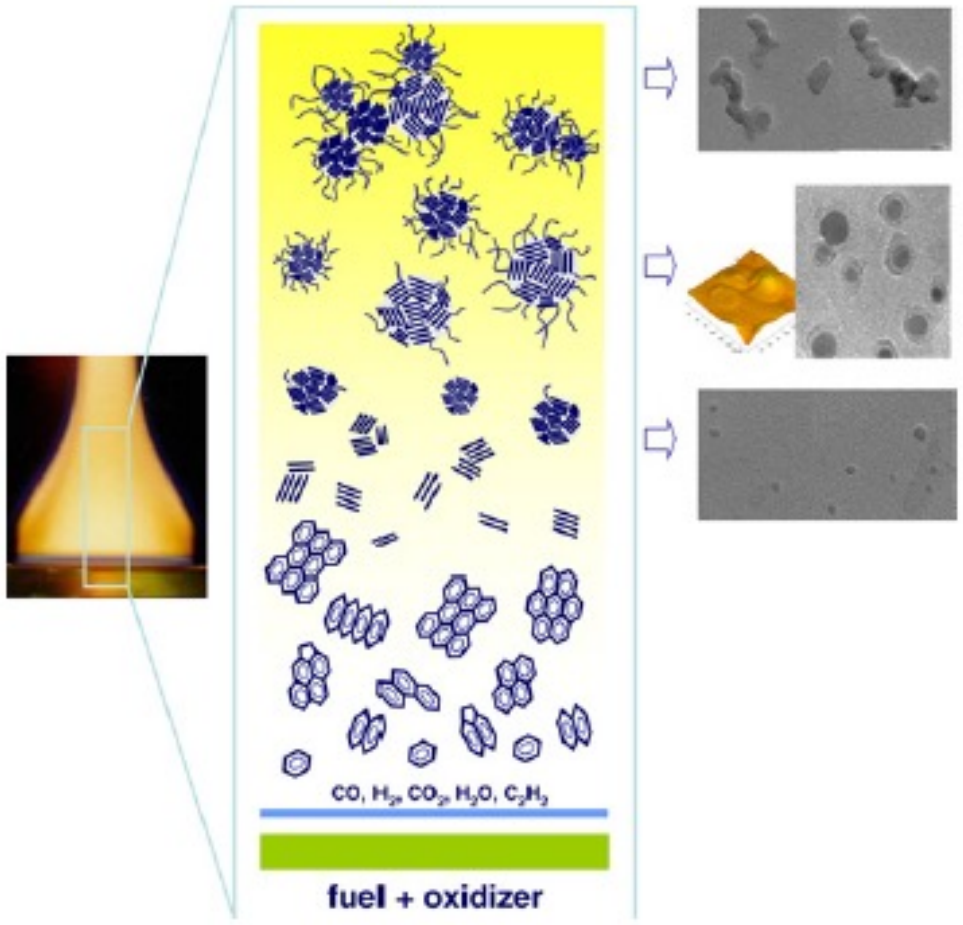
Surrogate Fuel Chemistry from ReaxFF Molecular Dynamics

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Soot precursor chemistry and soot formation



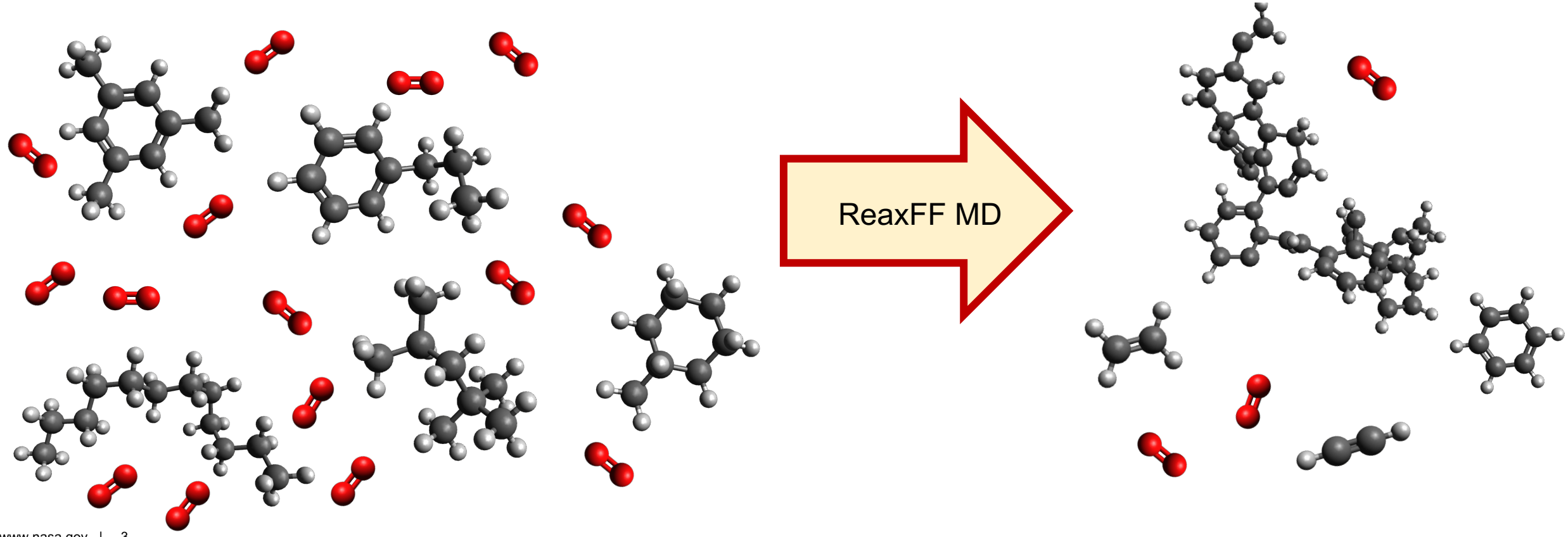
Conceptual model of soot formation[1].
Stacks of lines represent stacked PAH.
Wiggly lines represent aliphatic components.

- "Simplified" soot formation:
  - Precursor chemistry (e.g. form PAH)
  - Nucleation (particle inception)
  - Particle growth
- Some import pathways:
  - Formation of polyaromatic hydrocarbons (PAH)
  - Hydrogen abstraction carbon addition mechanism[1] (HACA)
  - Collisions of resonance stabilized radicals[2]

[1] H. Wang, Proceedings of the Combustion Institute 33 (2011) 41–67
[2] Johansson et al., Science 361, 997–1000 (2018)

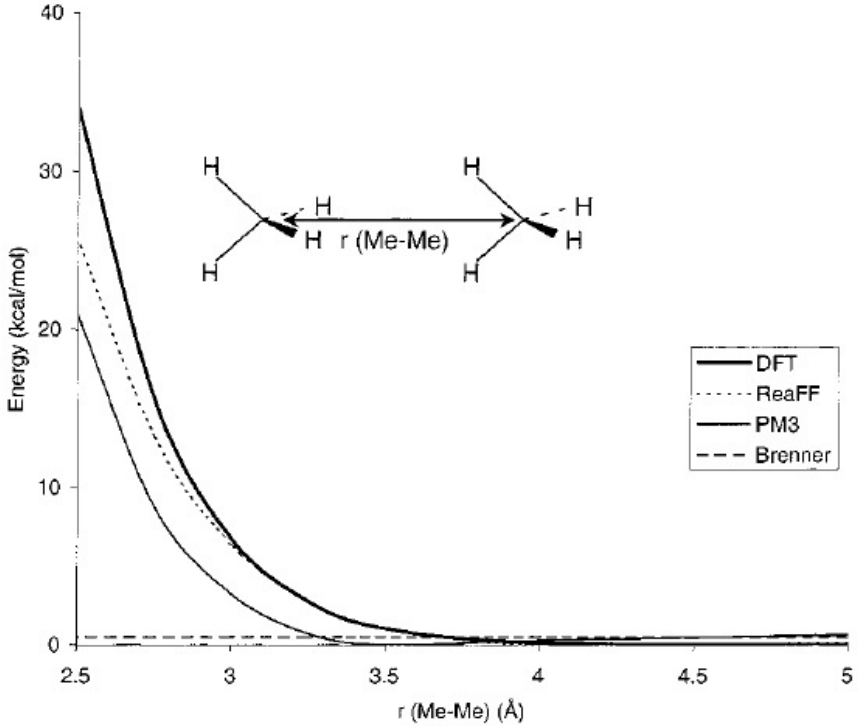
Soot precursor chemistry from reactive molecular dynamics

- Reactive molecular dynamics with Reax FF
- Study effect of fuel components on sooting tendency of a fuel
- Predict threshold sooting index (TSI)

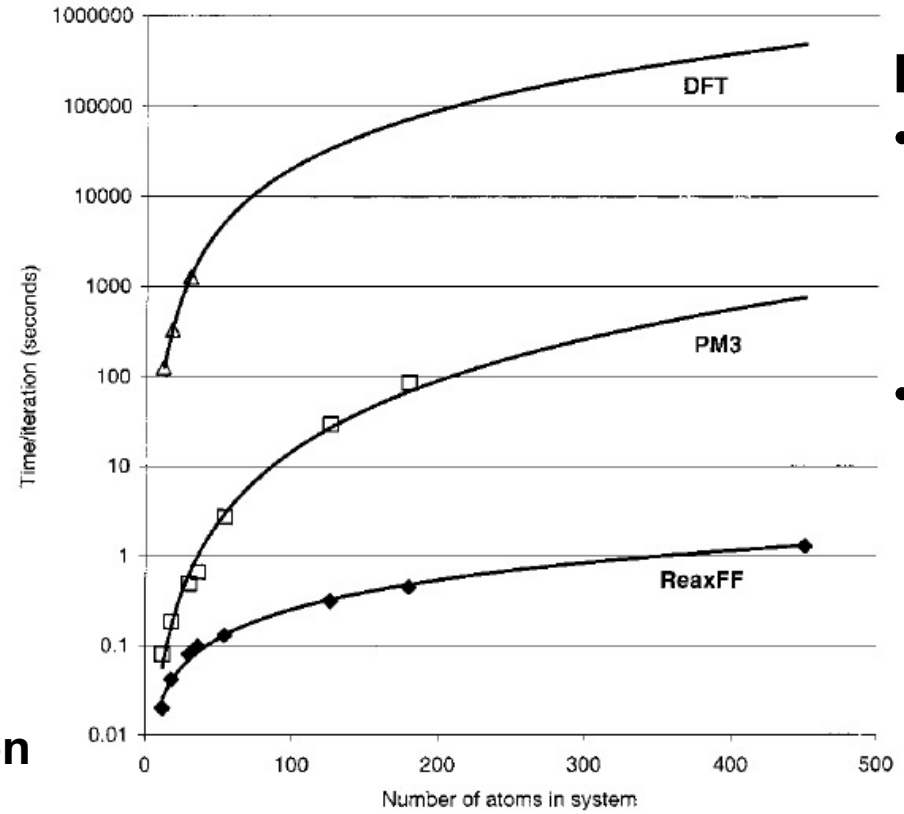


What is ReaxFF Reactive MD?

- ReaxFF is a bond order method: assumes bond order can be determined from the interatomic distance
- Accounts for ‘inter’ and ’intra’ molecular interactions
- Terms of force field include: $E_{system} = E_{bond} + E_{over} + E_{under} + E_{val} + E_{pen} + E_{tors} + E_{conj} + E_{vdWaals} + E_{Coulomb}$
- Includes penalties for non-physical or extreme cases, e.g. Carbon with 5 bonds, H with 2 bonds
- Force field parameters derived to fit dHf within 4.0 kcal/mol, bond lengths to within 0.01 Å, and bond angles to within 2° from quantum chemistry data



Energy curve for van der Waals repulsion between two CH_4 molecules



Computational cost

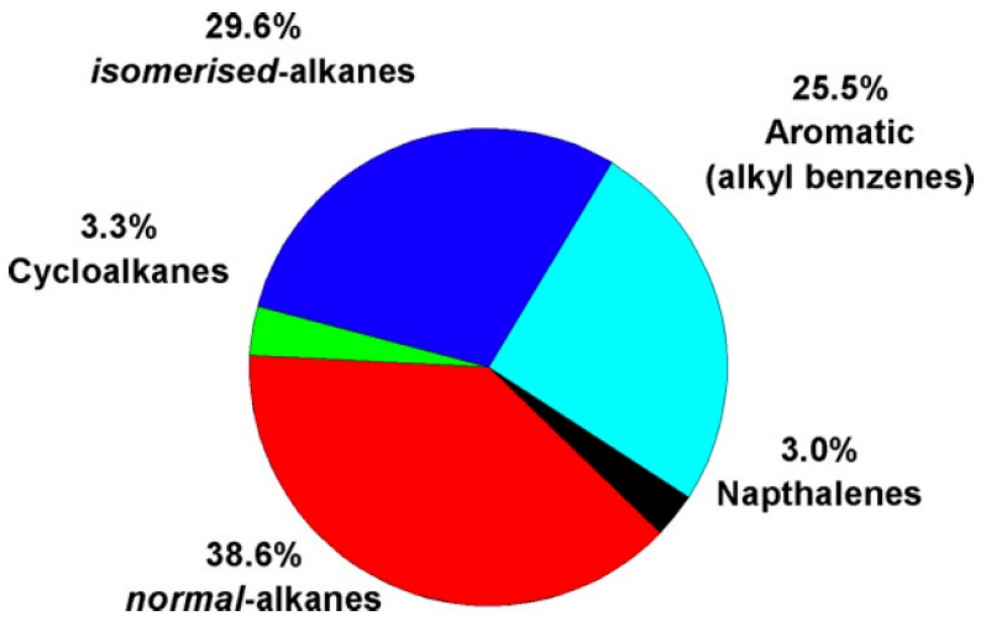
Key points:

- ReaxFF requires no knowledge of the chemistry *a priori*
- Accuracy comparable or better than semi-empirical methods

A.C.T van Duin[4] et al, J. Phys. Chem. A, Vol. 105, No. 41, 2001

Modeling Jet Fuels via Surrogates

- Jet fuels contain several key molecular classes



Molecular classes in Jet A POSF 4568, from GC-MS

- Surrogate fuels are simpler, multi-component formulations, replicating a real fuels properties (density, DCN, etc.)

Proposed Classes for Jet Fuel Surrogates

Component	Formula	Component	Formula
n-decane	$C_{10}H_{22}$	*n*-dodecane	$C_{12}H_{26}$
iso-octane	C_8H_{18}		
Methyl cyclohexane	C_7H_{14}	Butyl cyclohexane	$C_{10}H_{21}$
Toluene	C_7H_8	*n*-propylbenzene	C_9H_{12}
1,3,5-trimethylbenzene	C_9H_{12}	1-methyl naphthalene	$C_{11}H_{10}$

4-Component Mixture

S. Dooley et al. / Combustion and Flame 159 (2012) 1444–1466

Systems studied

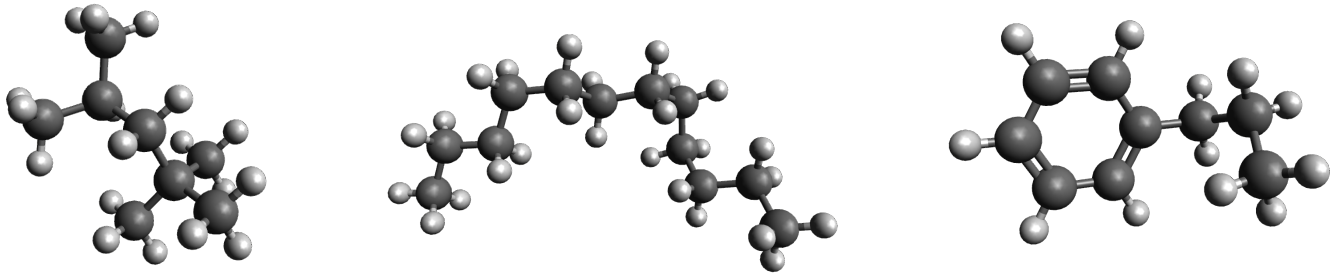
- Surrogate mixtures from Dooley 2012, varying TSI
- TSI scale 0 (least soot) to 100 (most soot)

Mixture 45 (TSI = 21.4)

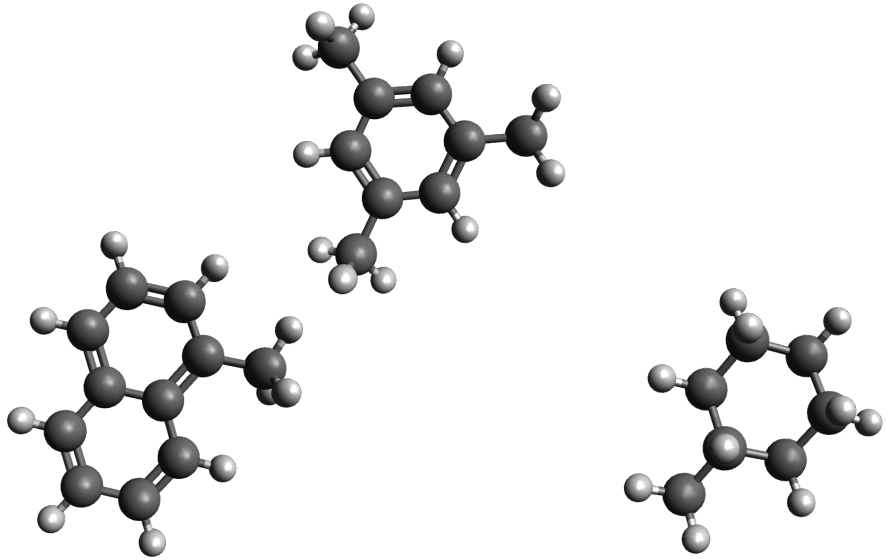
Species	MD Mol. Frac.	Rel. Diff EXP
iso-octane	0.286	-3.1%
n-dodecane	0.405	0.25%
n-propylbenzene	0.238	4.4%
1,3,5-Trimethylbenzene	0.071	-2.7%

Mixture 16 (TSI = 40)

Species	MD Mol. Frac	Rel. Diff EXP
iso-octane	0	0%
n-dodecane	0.4	0%
n-propylbenzene	0	0%
1,3,5-Trimethylbenzene	0.6	0%



- Two pure component cases, min/max TSI:
  - 1-methylnapthalene (TSI = 100)
  - Methylcyclohexane (TSI = 5.0)



S. Dooley et al. / Combustion and Flame 159 (2012) 1444–1466

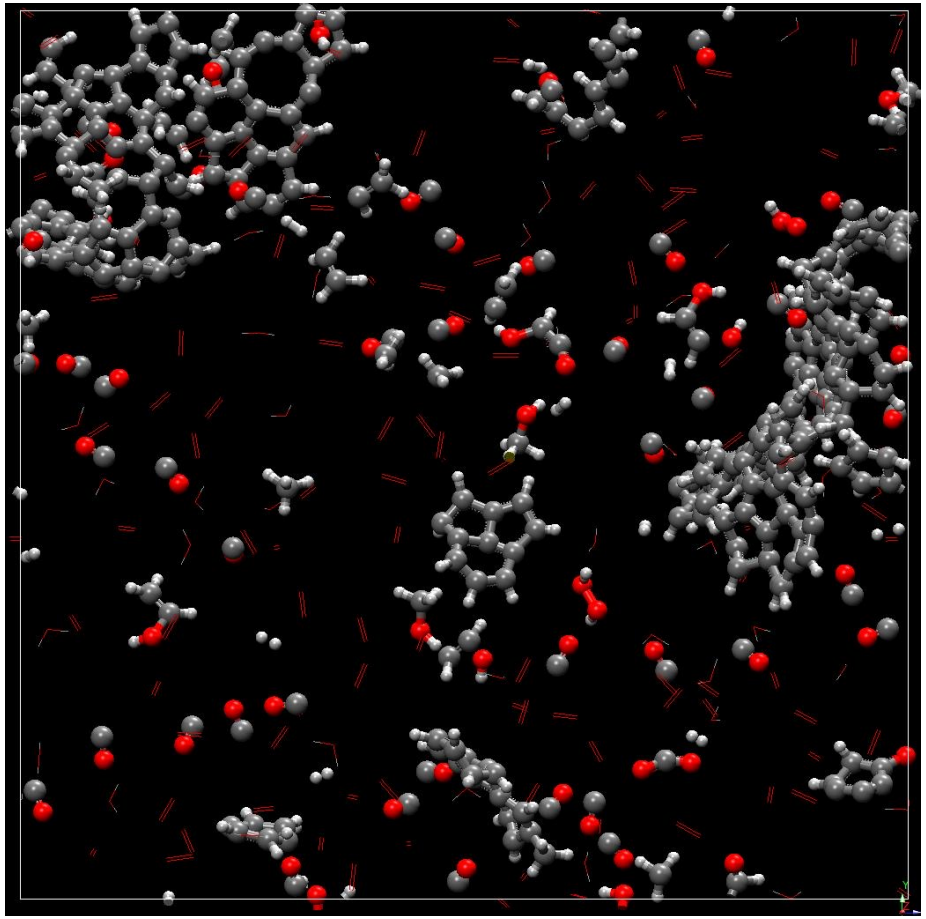
Modeling Approach

- Equilibrate at low temperature (300 to 1500 K) where reactions don't occur
- Ramp temperature to desired production run (2200K) at a rate of 20K/ps
- Size of cubic C/H/O system
  - About 30-40 molecules of fuel
  - Phi = 2.5
  - Total atoms: 600 to 1500
- Force field: Reax FF CHO 2016 (better for C1 chemistry, than CHO 2008)
- Simulation type: NVT -- fix moles, volume (density) and temperature
  - Berendsen thermostat with damping factor of 100 fs
  - Fix density to 0.20 g/cm^3
  - At 2200K, 0.20 g/cm3 → P is ~ 1000 atm (supercritical fluid)
- Production run at 2200K for 10 ns
- Software used: MAPS 4.4, LAMMPS (30Jun2020), **lots of python** (ChemTraYzer, RDKit)

Pure component: system snapshots

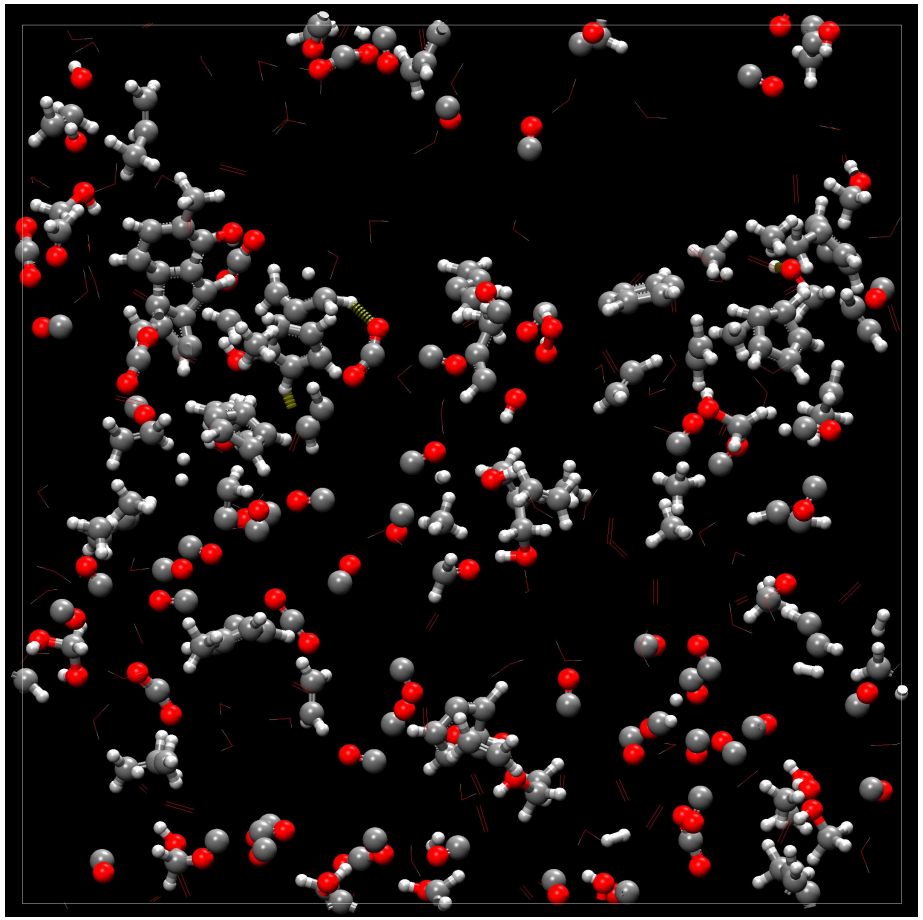
- 1-Methylnapthalene (TSI = 100)

Legend:
Carbon
Hydrogen
Oxygen



C11H10 system snapshot at 9.9 ns

- Methylcyclohexane (TSI = 5.0)

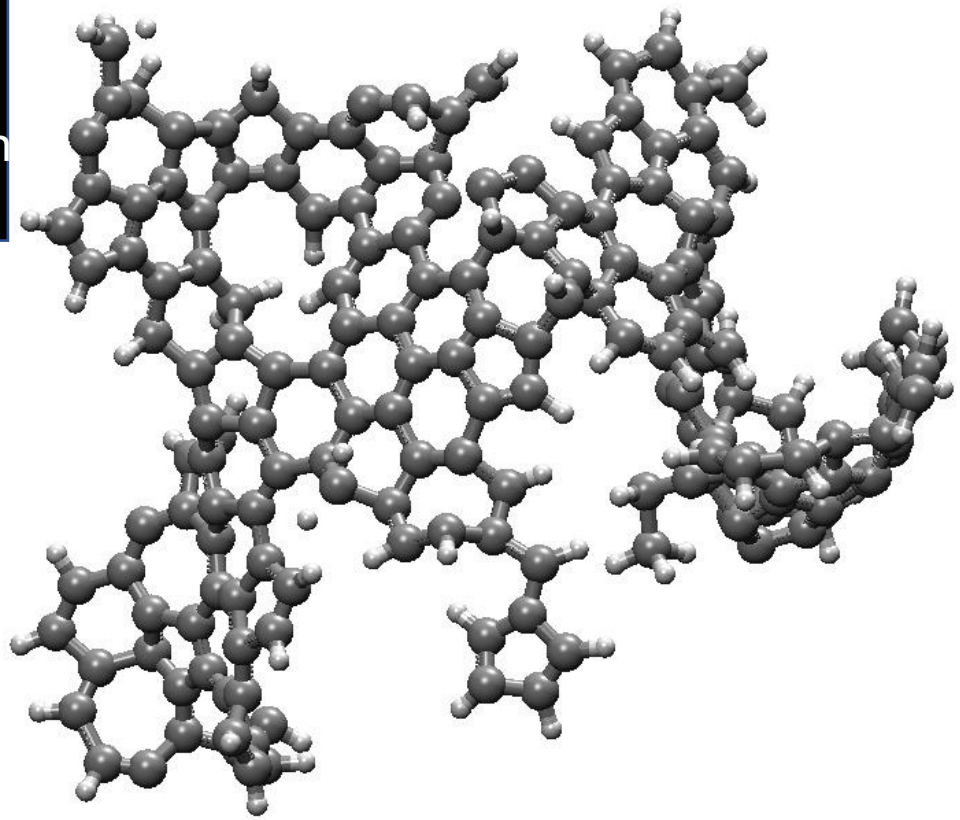


C7H14 system snapshot at 9.9 ns

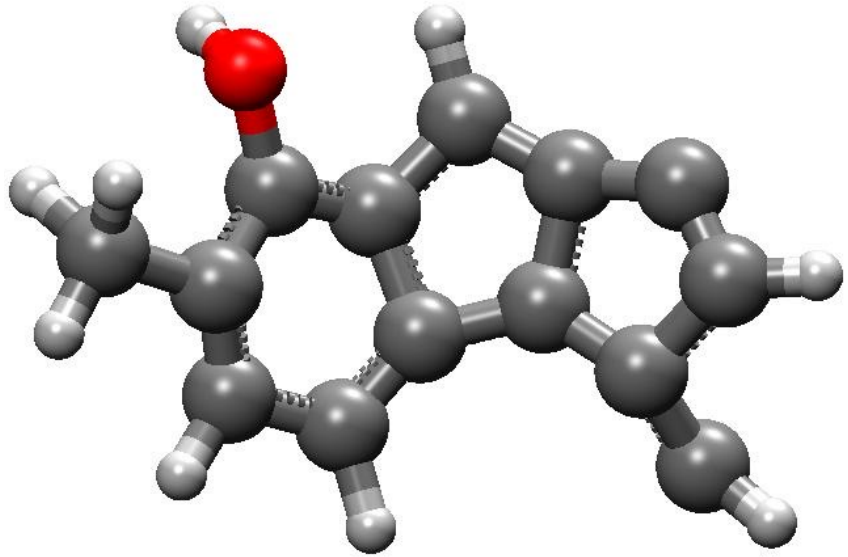
Pure component: largest observed species

- Largest species observed in final snapshot
  - 1-Methylnapthalene (TSI = 100)
  - Methylcyclohexane (TSI = 5.0)

Legend:
Carbon
Hydrogen
Oxygen



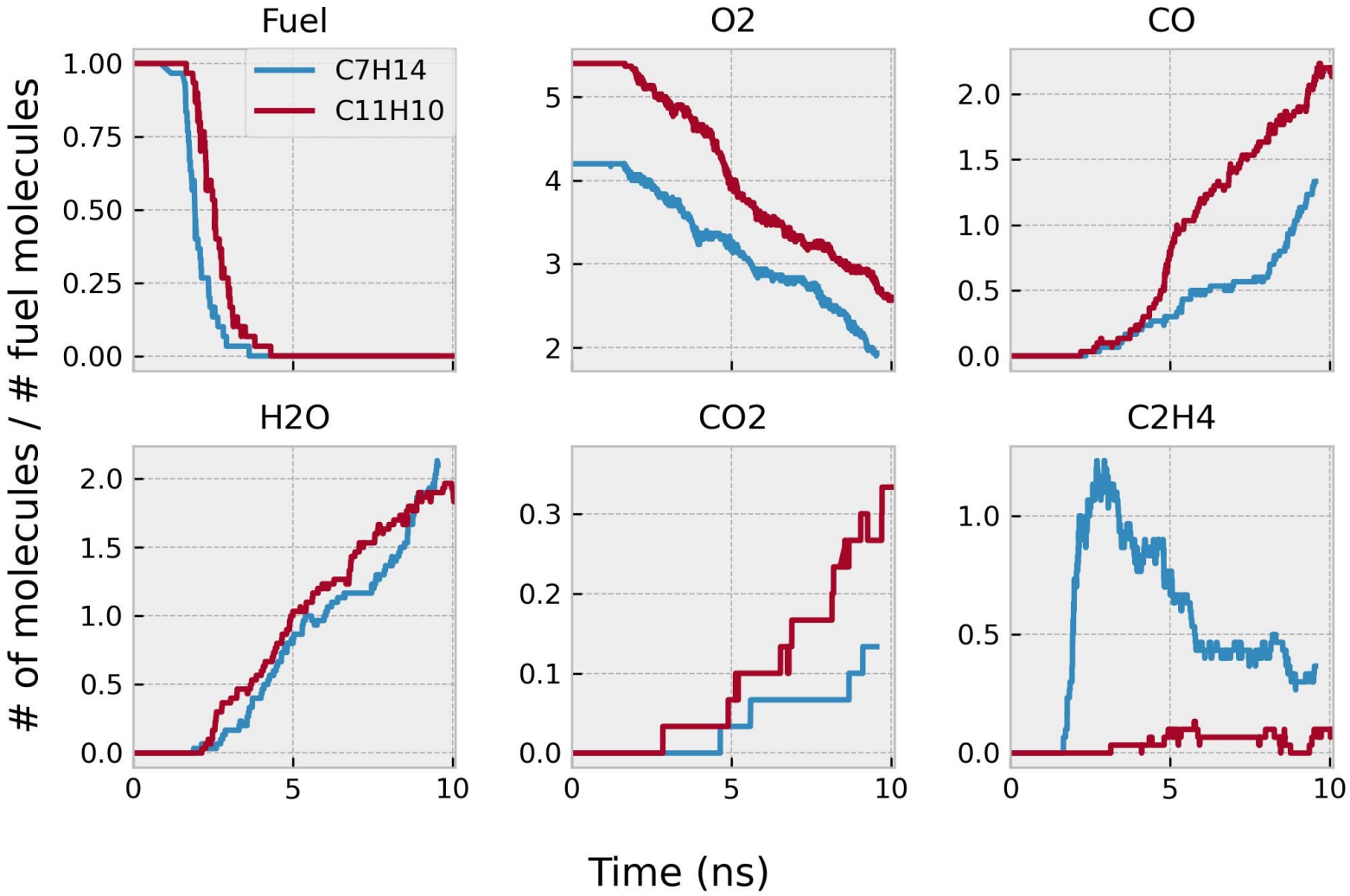
C182H73



C14H11O

Pure component: key species

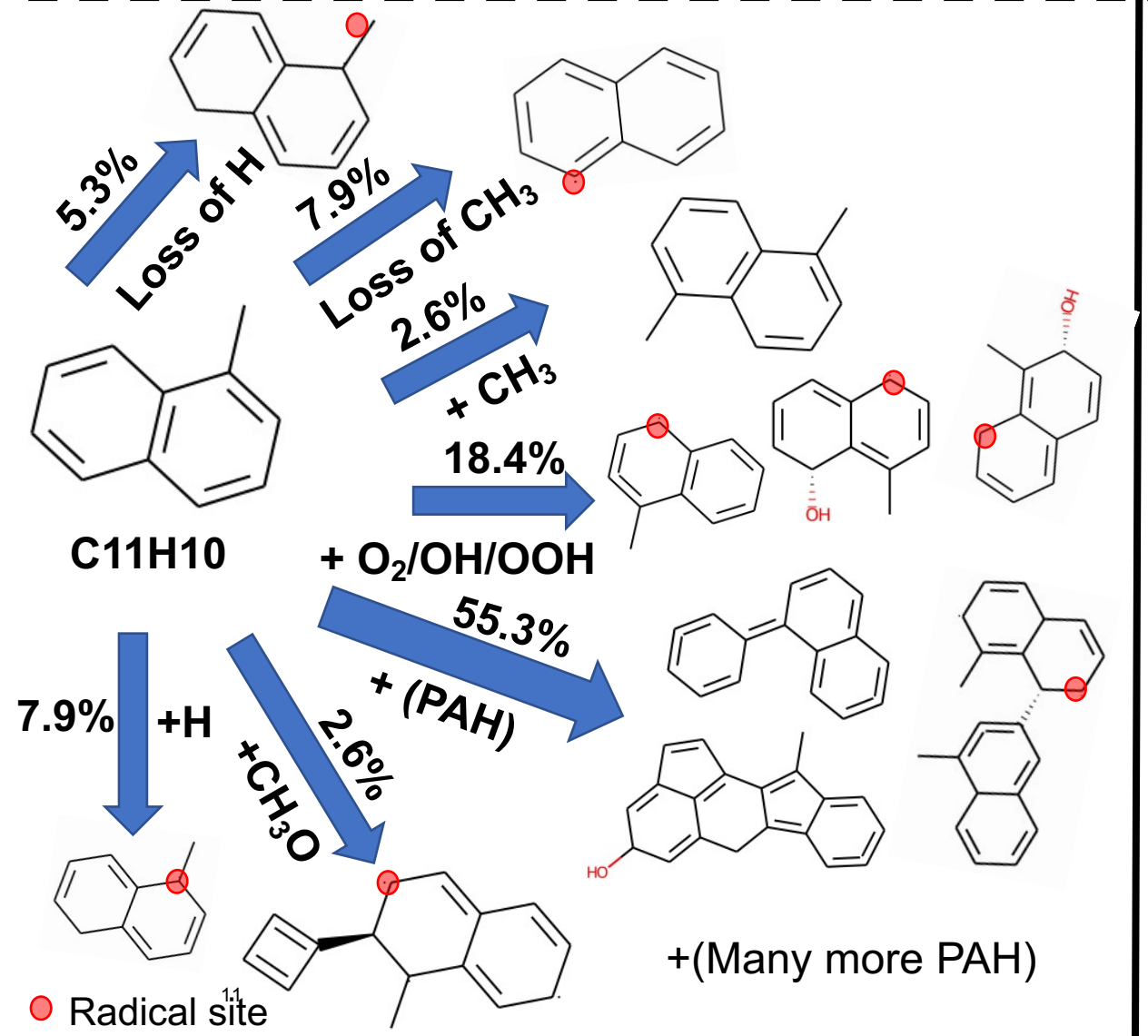
- Time history of key species: Fuel, O_2, CO, CO_2, H2O, C_2H_4



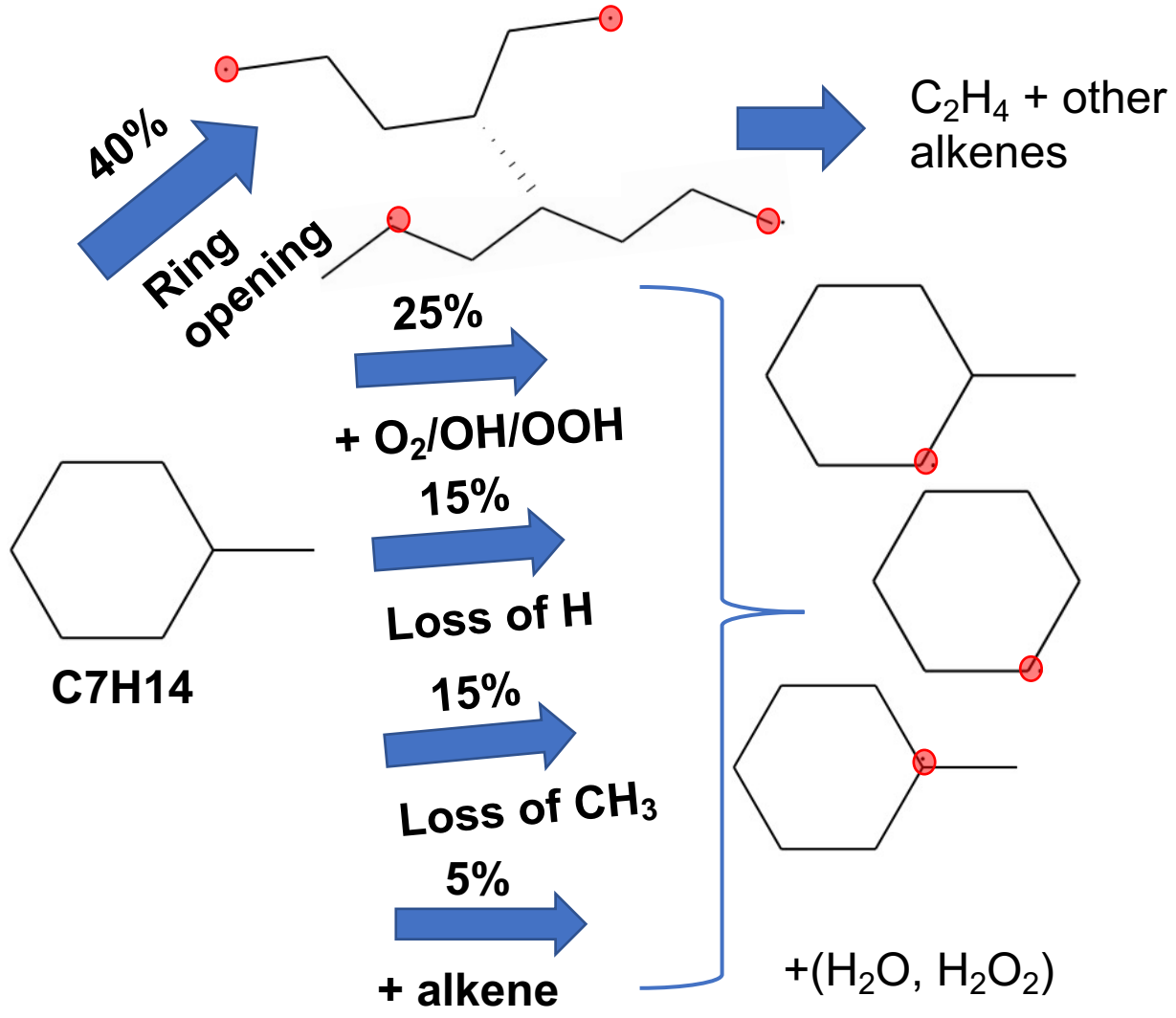
C11H10, 1-Methylnapthalene (TSI = 100)
C7H14, Methylcyclohexane (TSI = 5.0)

Pure component : Initial Fuel chemistry

- 1-Methylnapthalene (TSI = 100)



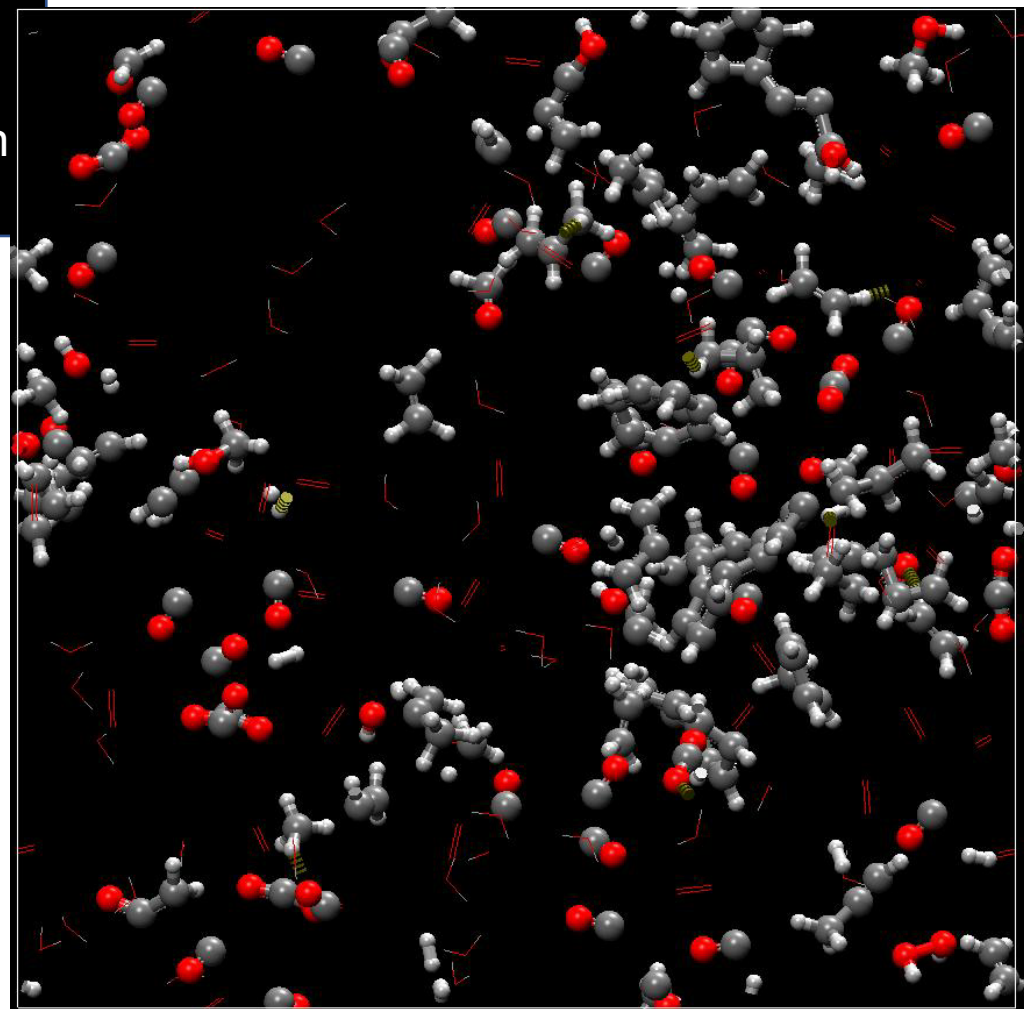
- Methylcyclohexane (TSI = 5.0)



Surrogate mixtures: snapshots

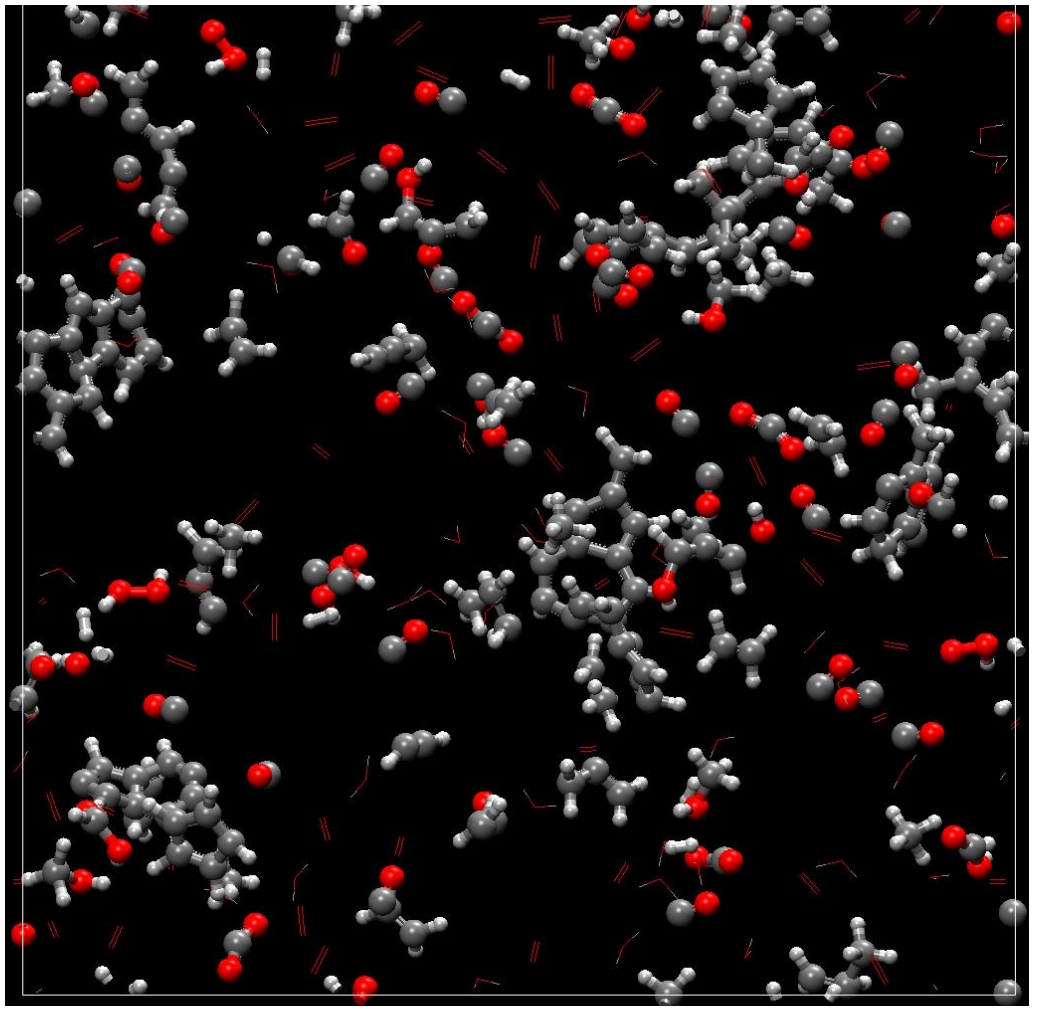
- Mixture 45 (TSI = 21.4)

Legend:
Carbon
Hydrogen
Oxygen



Mix 45 system snapshot at 9.9 ns

- Mixture 16 (TSI = 40.0)

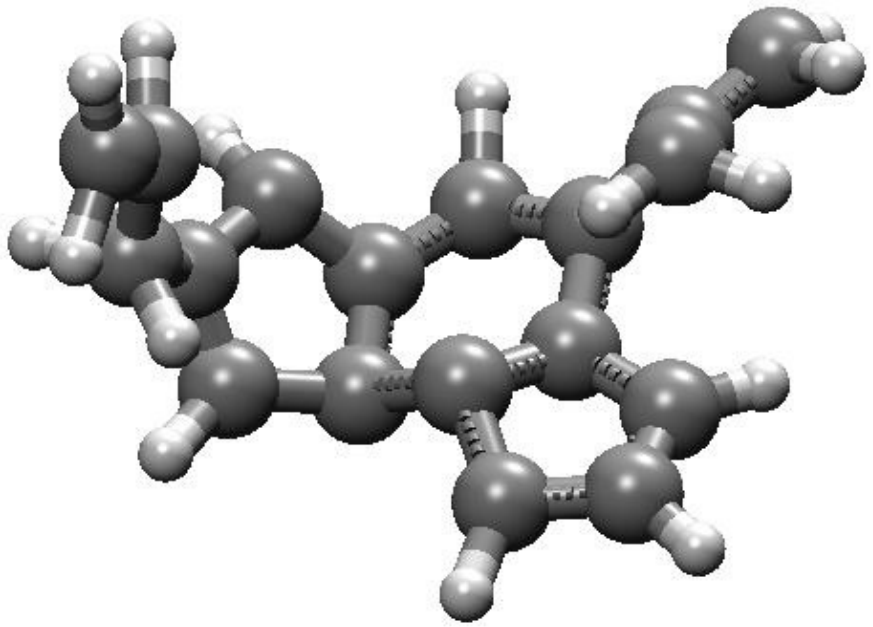


Mix 16 system snapshot at 9.9 ns

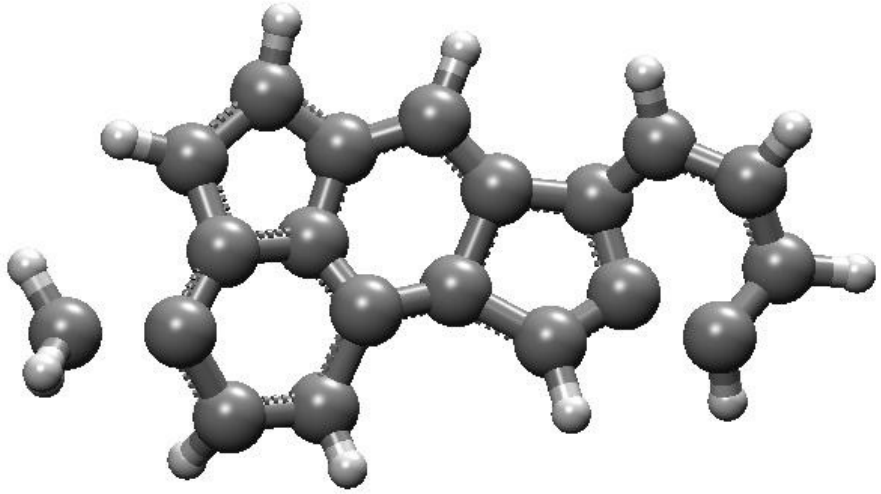
Surrogate mixtures: largest species

- Largest species observed in final snapshot
- Mixture 45 (TSI = 21.4)
- Mixture 16 (TSI = 40.0)

Legend:
Carbon
Hydrogen
Oxygen



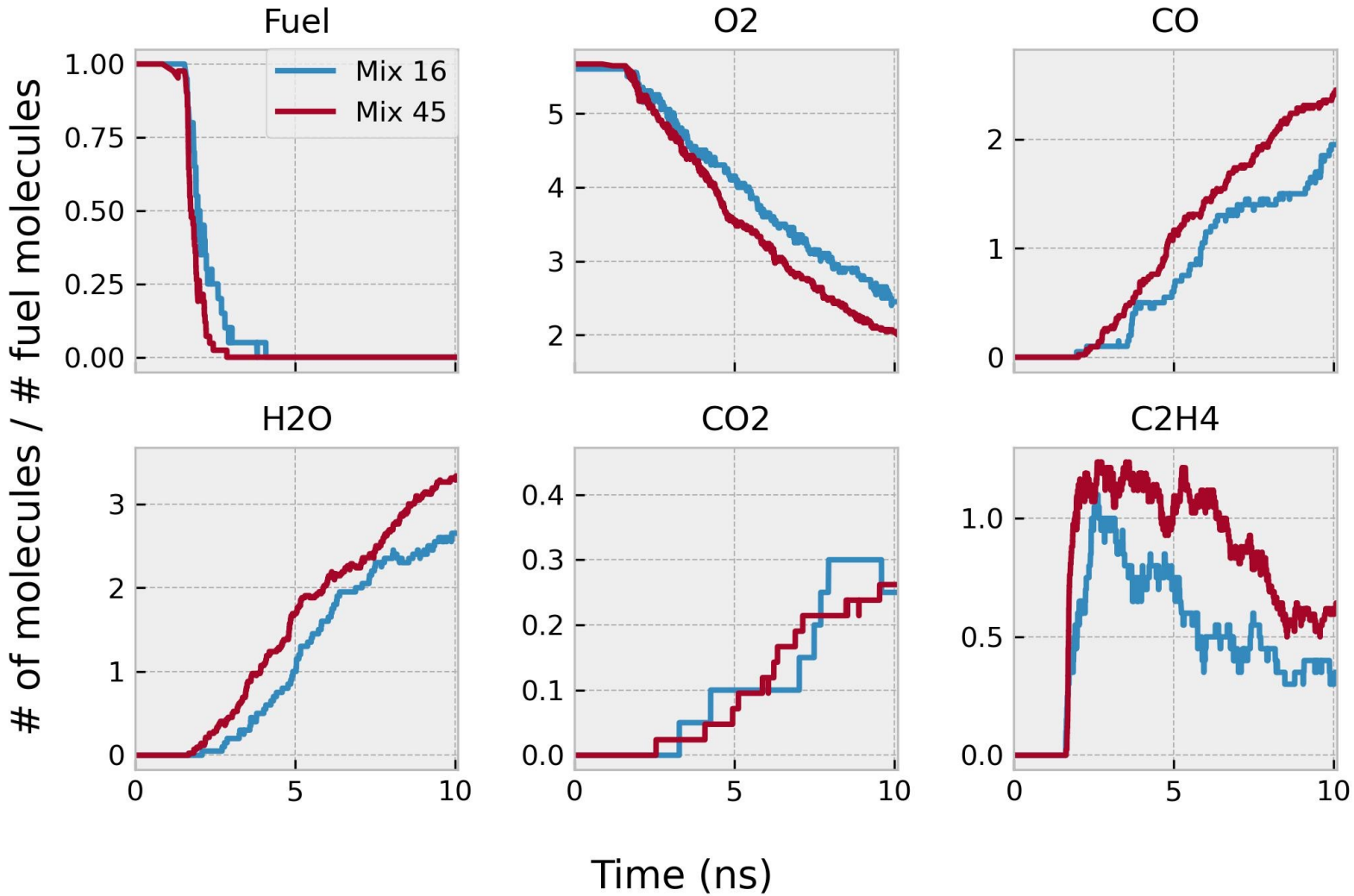
C18H15



C20H13

Surrogate mixtures: key species

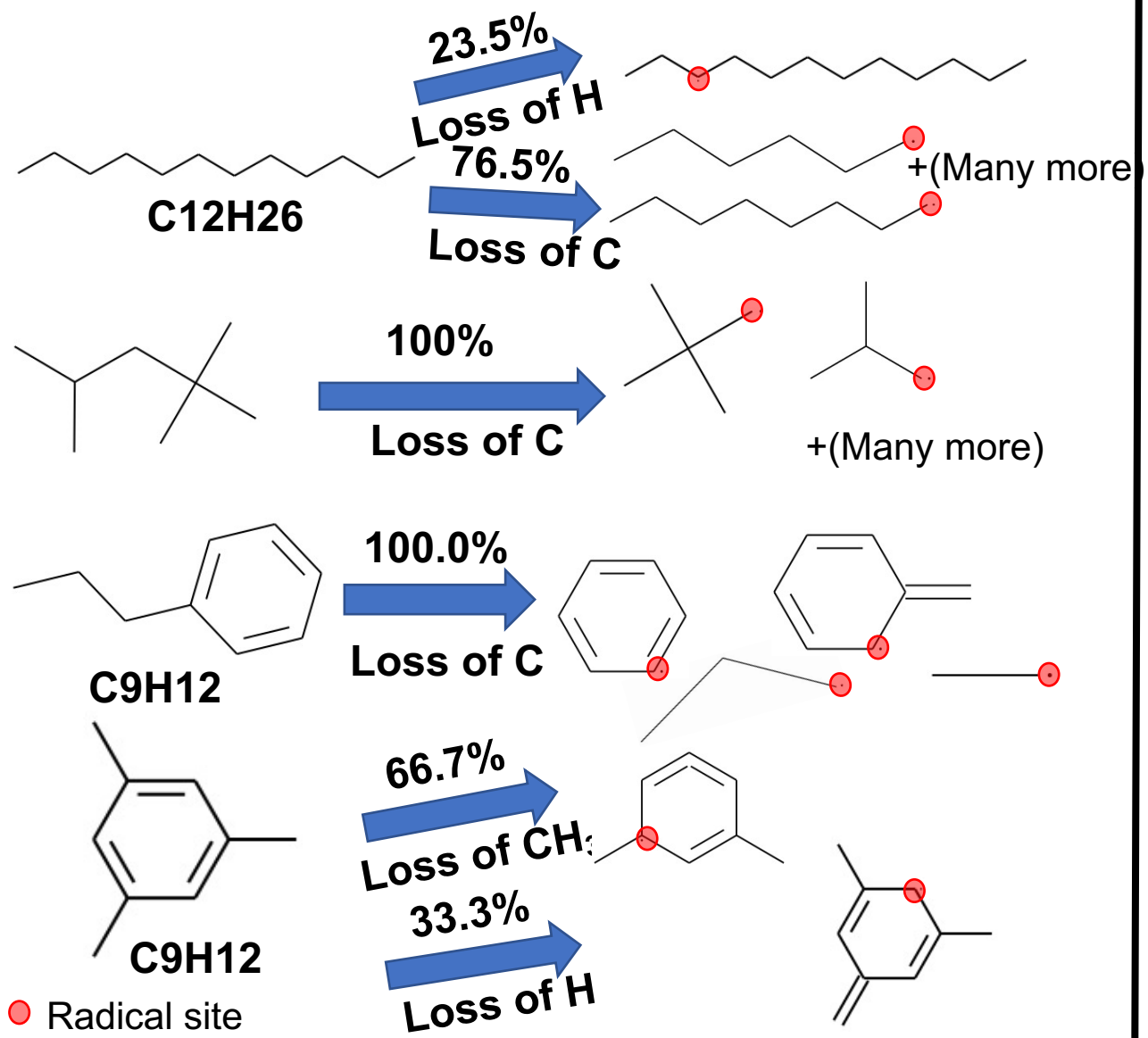
- Time history of key species: Fuel, O_2, CO, CO_2, H2O, C_2H_4



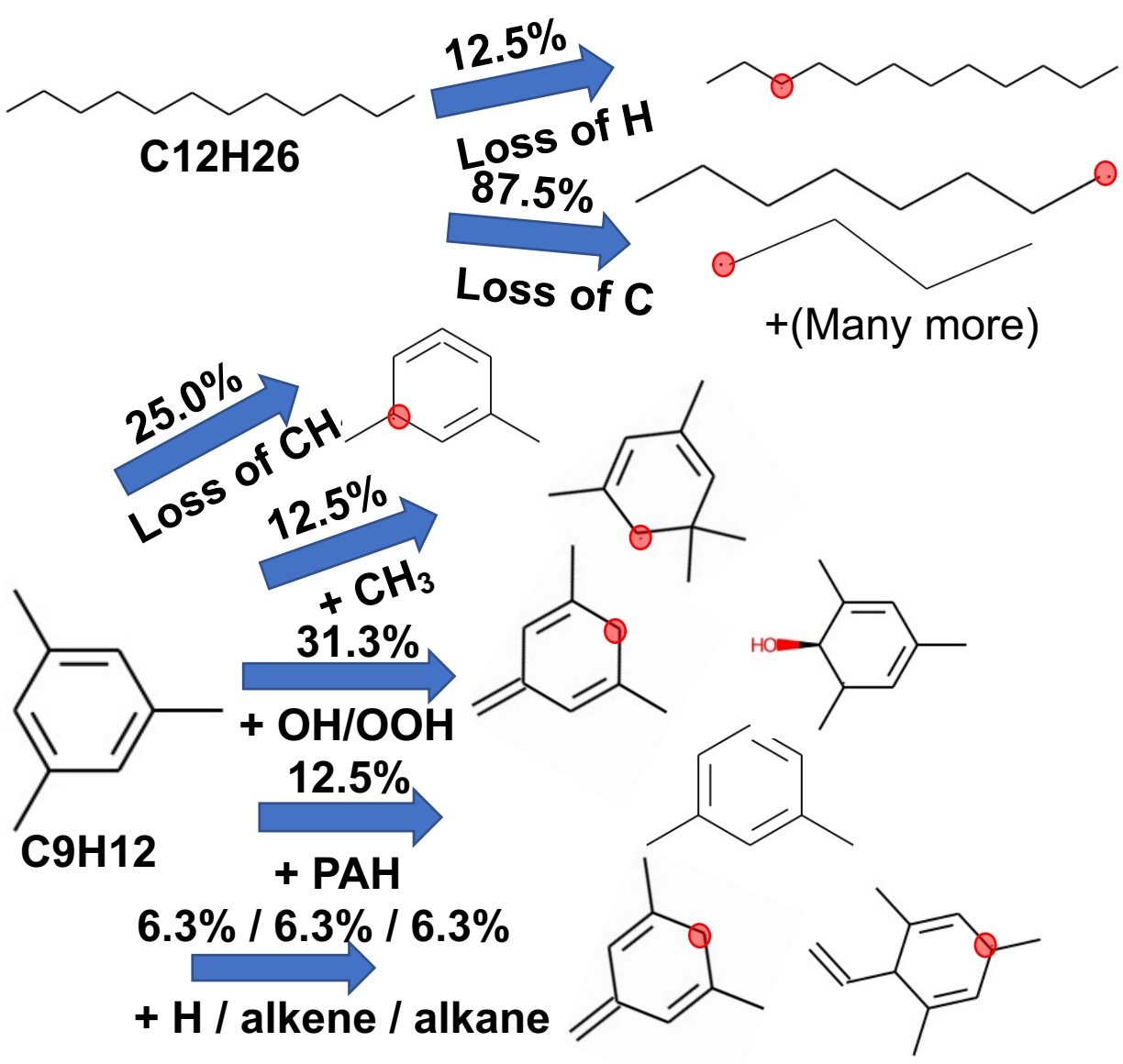
Mix 45, n-dodecane/iso-octane /n-propylbenzene/Mesitylene (TSI = 21.4)
Mix 16, n-dodecane/Mesitylene (TSI = 40.0)

Surrogate mixtures: initial fuel chemistry

- Mix 45 (TSI = 21.4)

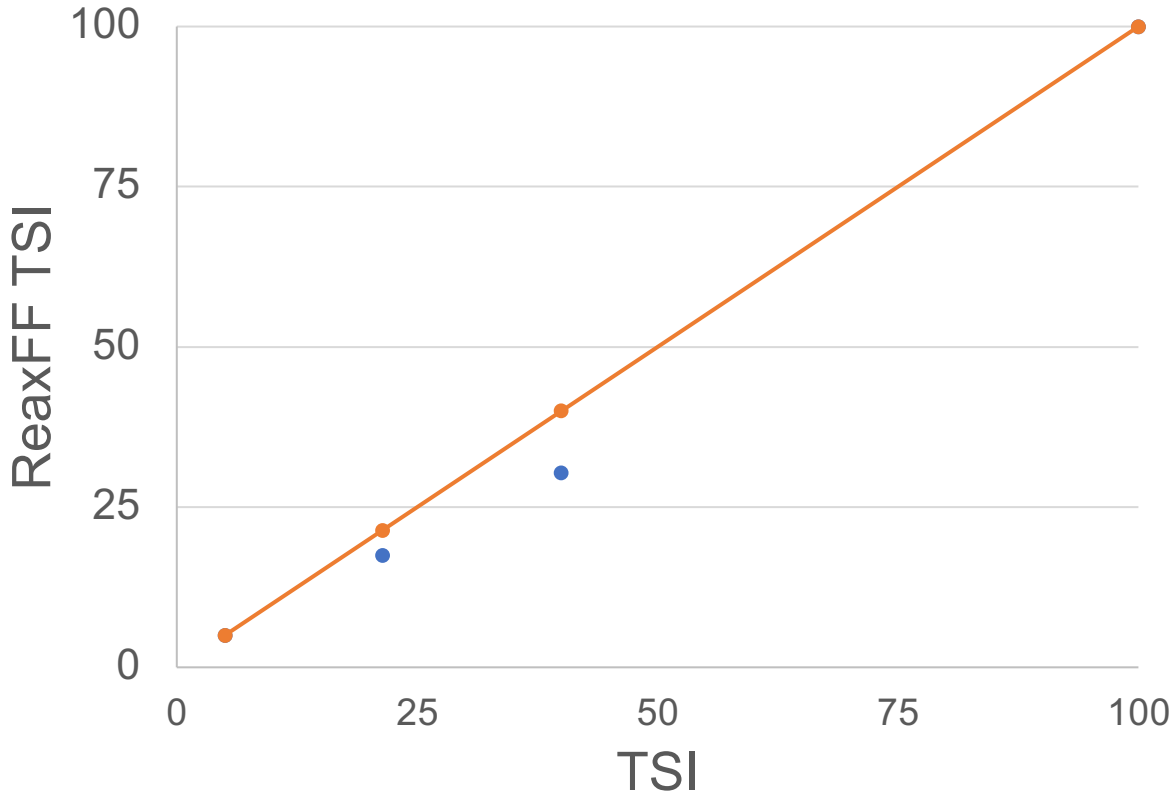


- Mix 16 (TSI = 40)



Prediction of Threshold Sooting Index (TSI)

- Empirical definition: TSI = a(MW/SmokePoint) + b
- Define ReaxFF TSI as: ReaxFF TSI = a *(mass C > C7) + b
- Compute a & b from C7H14 and C11H10 using known values of TSI



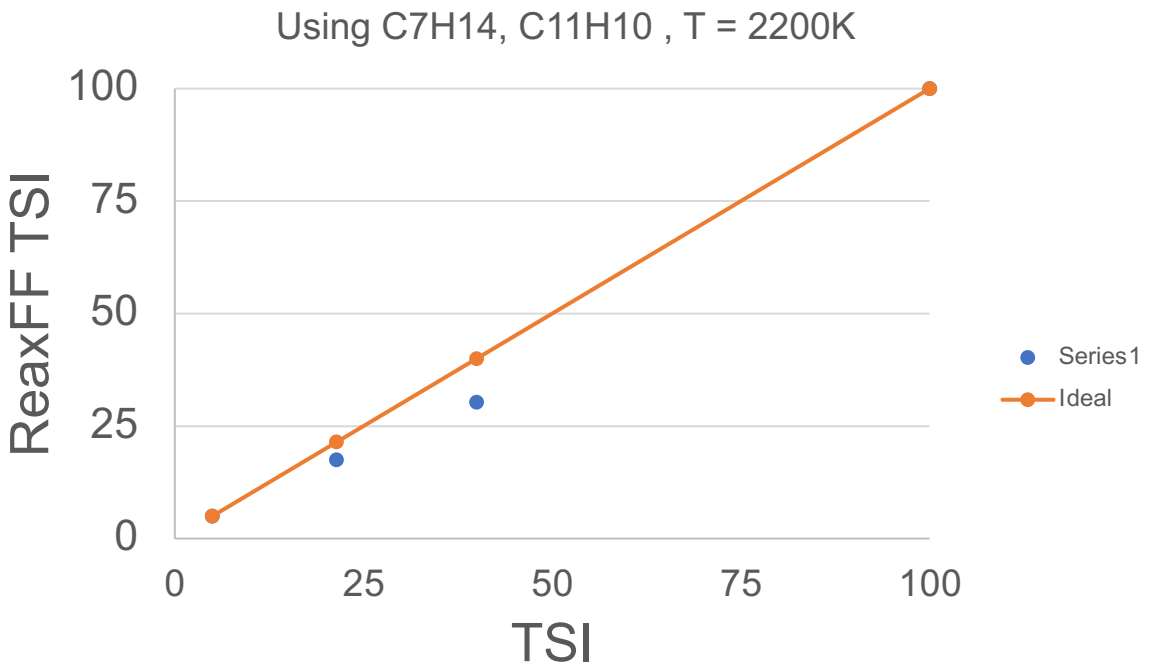
C7H14 (TSI = 5.0) **Mixture 45** (TSI = 21.4) **Mixture 16** (TSI = 40.1) **C11H10** (TSI = 100)

TSI and Computed ReaxFF TSI

- Relative difference ~ 20%
- Correct trend across fuels

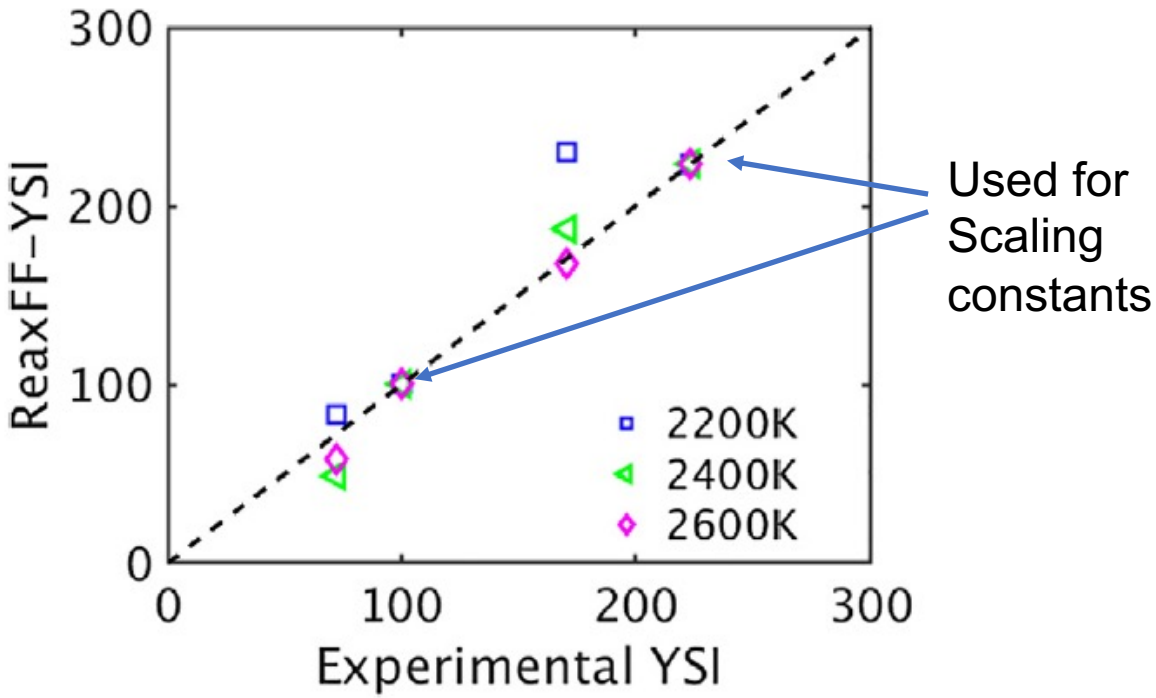
Comparison of TSI and YSI

- Comparison with A.C.T. van Duin[a], YSI (Yield Sooting Index)
- Reax FF YSI = a *(mass C > C10) + b



C7H14 (TSI = 5.0) Mixture 45 (TSI = 21.4) Mixture 16 (TSI = 40.1) C11H10 (TSI = 100)

TSI and Computed ReaxFF TSI



YSI and Computed ReaxFF YSI[a]

[a] Kwon, et.[17]al., Fuel, Vol 262 (2020)

Conclusions and on-going work

- Reactive MD with ReaxFF sensitive to fuel chemistry
- TSI prediction shows correct trend across fuel mixtures
- ReaxFF framework has potential as a quantitative soot prediction tool
- On-going work includes pure component studies, trying other surrogate mixtures (vary TSI), and expand to derived cetane number predictions

- Work is supported by the NASA ARMD Transformational Tools and Technology Program

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