Co-Optimization of
Fuels & Engines

Predicting Sooting Tendencies from Chemical Structure with Experimental and Theoretical Insight

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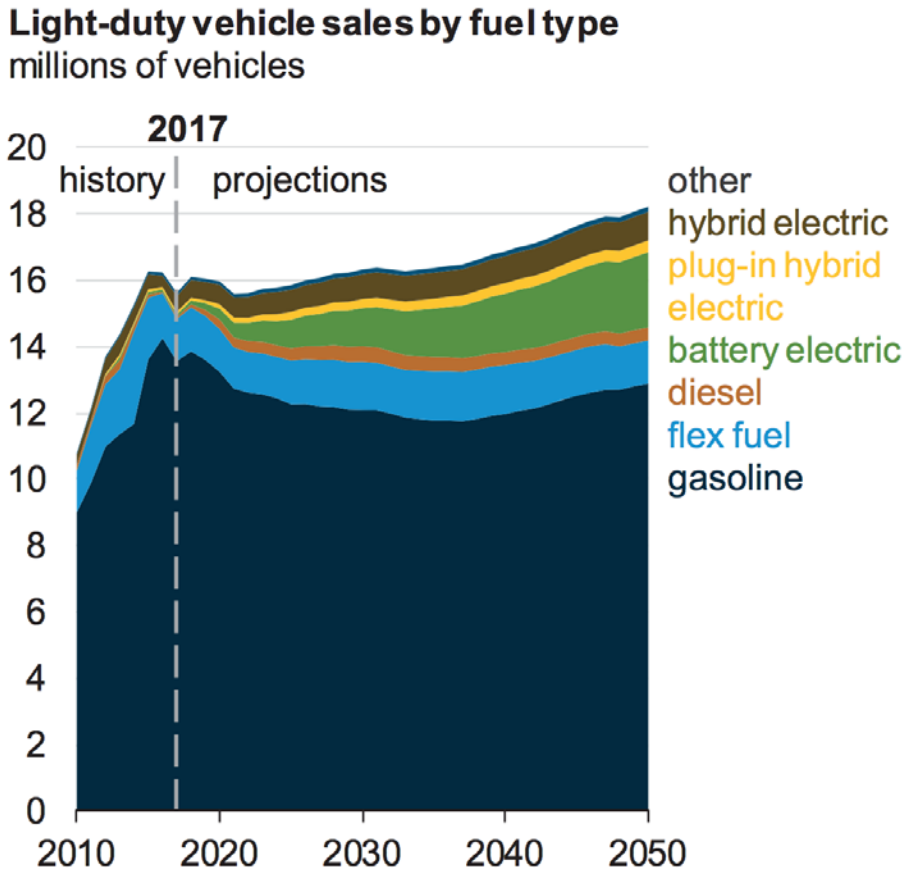
National Renewable Energy Laboratory (NREL)

23rd ANNUAL GREEN CHEMISTRY & ENGINEERING CONFERENCE
– AND –
9th INTERNATIONAL CONFERENCE ON GREEN AND SUSTAINABLE CHEMISTRY

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Global transportation demand by fuel



- Gasoline demand peaks in 2020–2030 and then declines, despite significant growth in vehicle miles traveled.
- Diesel demand grows 30% to meet trucking and marine needs
- Jet fuel, natural gas, biofuels and electricity grow significantly


VANCOUVER
In 1971, Greenpeace was established in Vancouver, and the city has its sights set on becoming the world's greenest city by 2020.

Co-Optima Technical Challenges

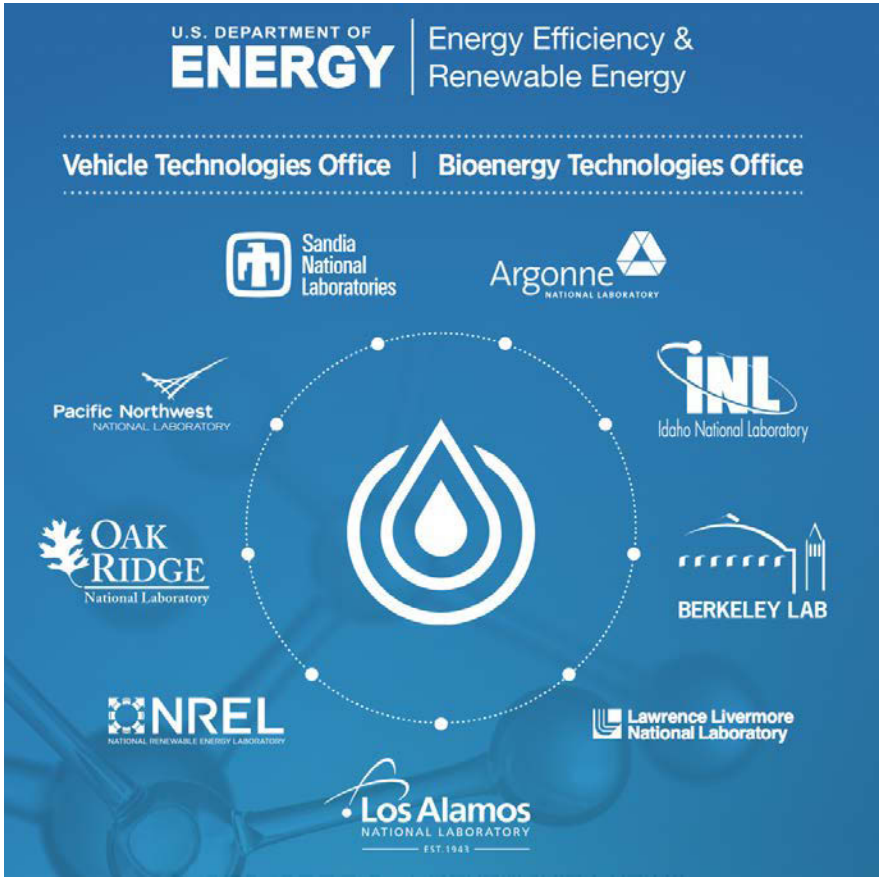
What fuel do engines *really* want?

What fuels can we make?

What will work in the real world?

How do we "co-optimize"?

Project Partners



Leveraging expertise and facilities from
9 National Labs and 13 universities

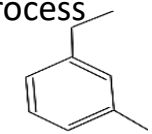
Cornell / UCSD	Identify differences in combustion characteristics of diesel/biofuel blends vs petroleum-based fuels	LSU / TAMU / U Conn.	Develop method to characterize alternative fuel candidates and associated models and metrics for predicted engine performance
Univ. Michigan	Develop engine combustion model to simulate key parameters while reducing computational expense 80%	MIT / Univ. Central Florida	Develop detailed kinetic models for several biofuels using an advanced computational approach
Univ. Michigan - Dearborn	Use a miniature ignition screening RCM to study ignition properties and combustion characteristics of alternative fuels.	Yale	Measure sooting tendencies of various biofuels and develop emission indices relevant to real engines
Univ. Alabama	Examine combustion properties of biofuels and blends using advanced diagnostics under realistic ACI engine conditions.	Univ. Central Florida	Generate fuel characterization data related to fuel spray atomization, flame topology, etc, and compatibility for prioritized fuels

Technical Approach is Fuel Property-Based

Aimed at establishing critical relationships

Establish fuel criteria

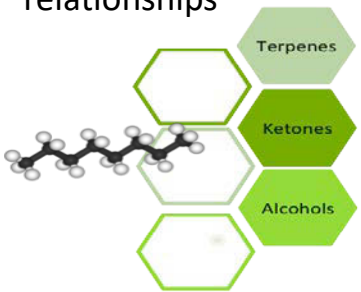
Rigorous candidate screening process



Procure and test blendstocks

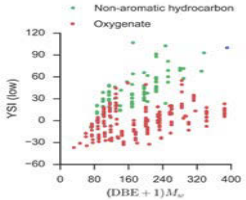
Purchase or produce candidates for evaluation

Create database, generate property relationships



Validate and understand

Determine blend properties, model fuel properties



Establish pathway data

Target fuel properties to generate key data

BC

TC

Retrosynthetic analysis

Feedback to ASSERT & MT*

Compatibility, performance, and production data

* ASSERT (Technoeconomic analysis team) and MT (market transformation team)

Smoke Point as Emissions Quality Index

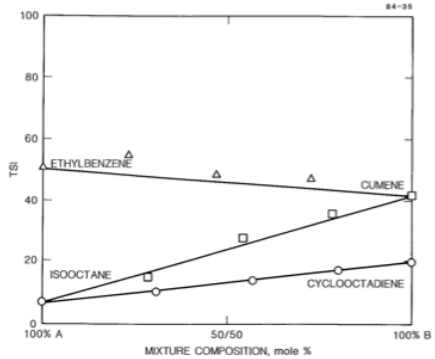
Relation of Smoke Point to Molecular Structure

RUSSELL A. HUNT, JR.
Research Department, Standard Oil Co. (Indiana), Whiting, Ind.

March 1953 INDUSTRIAL AND EN

TABLE I. SMOKE POINTS OF ALKANES, ALKENES, ALKYNES, AND CYCLOALKANES

Compound	Refractive Index, n_D^{20} Observed	Lit.	Smoke Point
n-Hexane	1.3750	1.3750	149
2-Methylpentane	1.3717	1.3715	137
3-Methylpentane	1.3763	1.3766	135
2,2-Dimethylbutane	1.3689	1.3688	114
2,3-Dimethylbutane	1.3750	1.3750	120
n-Heptane	1.3877	1.3877	147
2-Methylhexane	1.3850	1.3849	136
3-Methylhexane	1.3885	1.3887	137
2,3-Dimethylpentane	1.3917	1.3920	123
2,4-Dimethylpentane	1.3813	1.3815	117



- Smoke point is a well-known property that describes a compound's tendency to form soot when burned
- Many correlations with molecular structure exist
- Easily extended to mixtures: TSI (Threshold Sooting Index) is linear with mole %
- Difficult to measure for some compounds (low dynamic range)
- Requires a lot (~10 – 50 mL) of sample

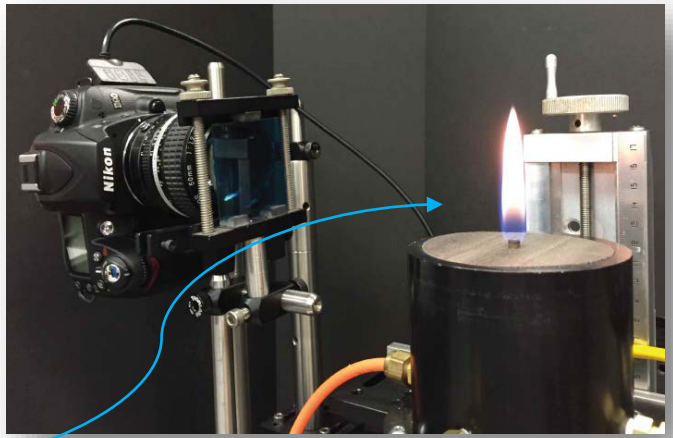
Gill RJ, Olson DB. *Combustion Science and Technology*. 1984;40(5-6):307-315

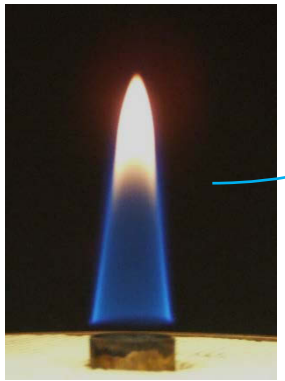
Yield Sooting Index (YSI)

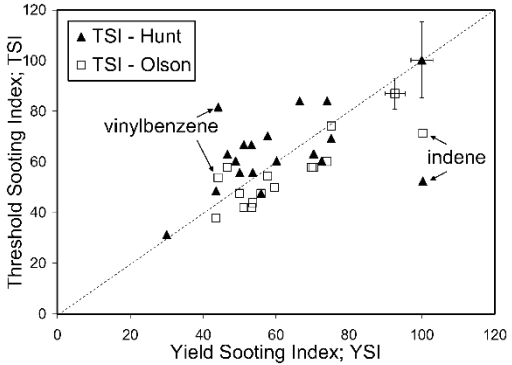
Accurate, modern, low-volume measurement

Flame conditions:
Nonpremixed, doped, methane/N_2 flame

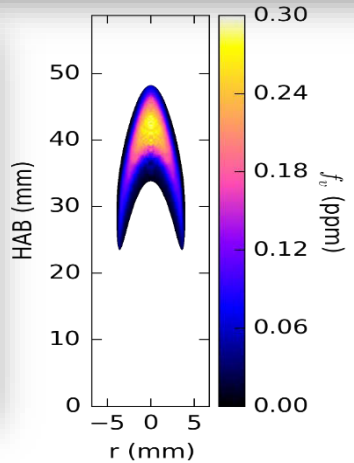
Soot diagnostic:
Color ratio pyrometry







Strongly correlated with TSI



Development of a unified YSI metric

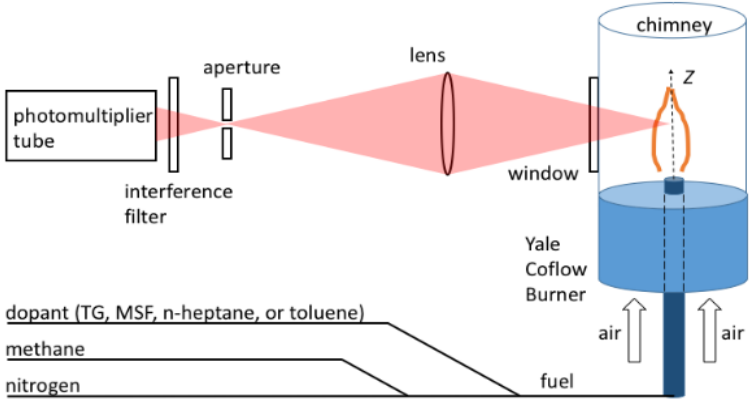


Diagram of the experimental apparatus (Yale University)

$$YSI_{Unified} = 0.64^{[\pm 0.03]} \times YSI_{Low} + 30.4^{[\pm 1.9]}$$

−50 0 50 100 150 Low Scale YSI

0 500 1000 1500 Unified Scale YSI

0 100 200 300 High Scale YSI

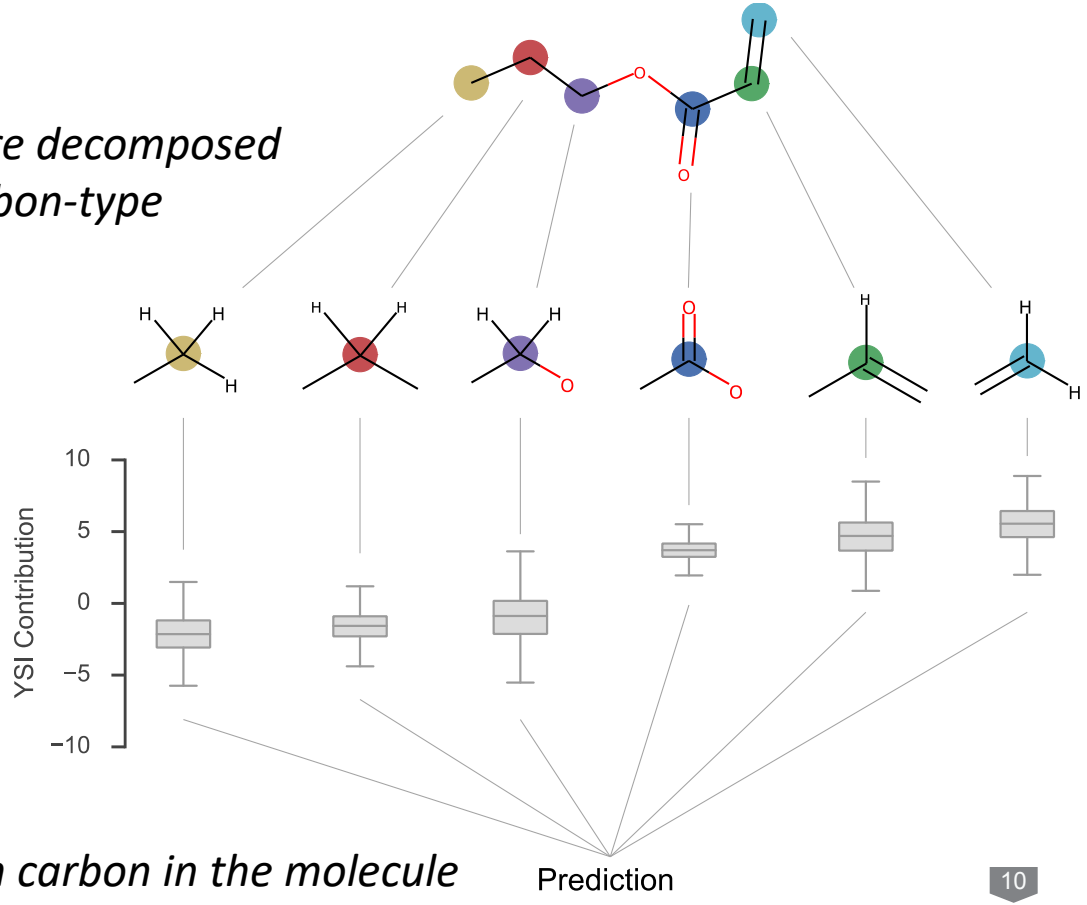
$$YSI_{Unified} = 5.23^{[\pm 0.12]} \times YSI_{High} - 56^{[\pm 5]}$$

Das and St John *et al. Comb. and Flame* 2018

*Q*uantitative *S*tructure-*P*roperty *R*elationship (QSPR) Models for YSI Prediction

Input molecules are decomposed into individual carbon-type fragments

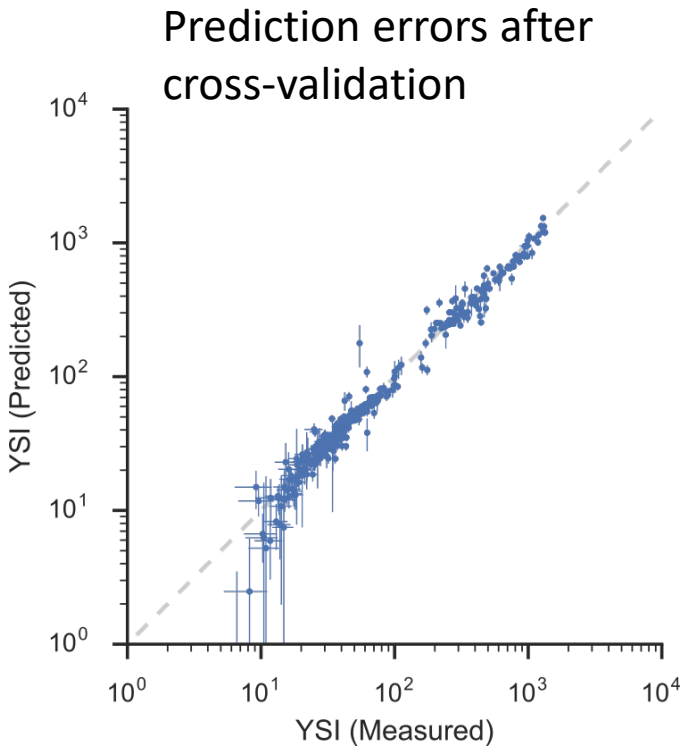
Bayesian linear regression is used to find the YSI contributions from each atom type

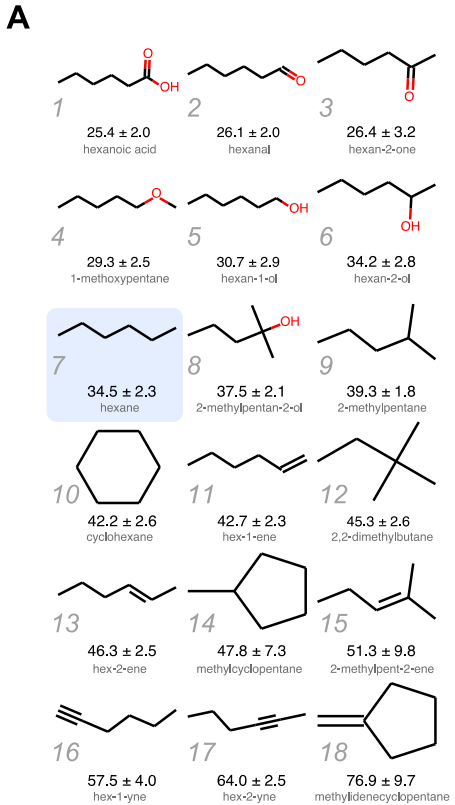


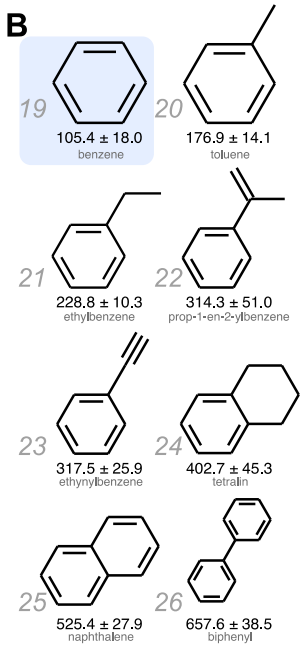
The final YSI prediction is a sum of each carbon in the molecule

Das and St John *et al. Comb. and Flame* 2018

Regressed model is accurate across several orders of magnitude



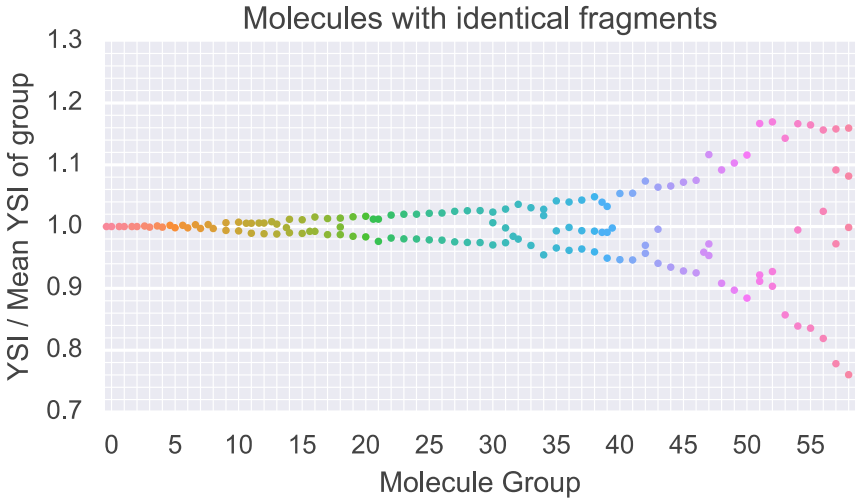




Das and St John *et al. Comb. and Flame* 2018

Model offers insights into the connection between molecular structure and sooting tendency

Molecules with identical carbon types will have the same predicted YSI, but can differ experimentally



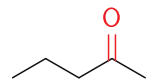
By looking at the functional groups that give rise to these differences, we can infer more detailed kinetics of soot particle formation

Das and St John *et al. Comb. and Flame* 2018

Model offers insights into the connection between molecular structure and sooting tendency

Molecules with identical carbon types will have the same predicted YSI, but can differ experimentally

2-pentanone



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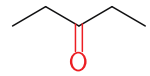
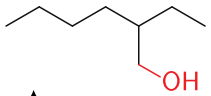


3-pentanone

2-ethylhexan-1-ol



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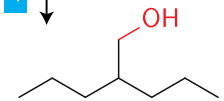
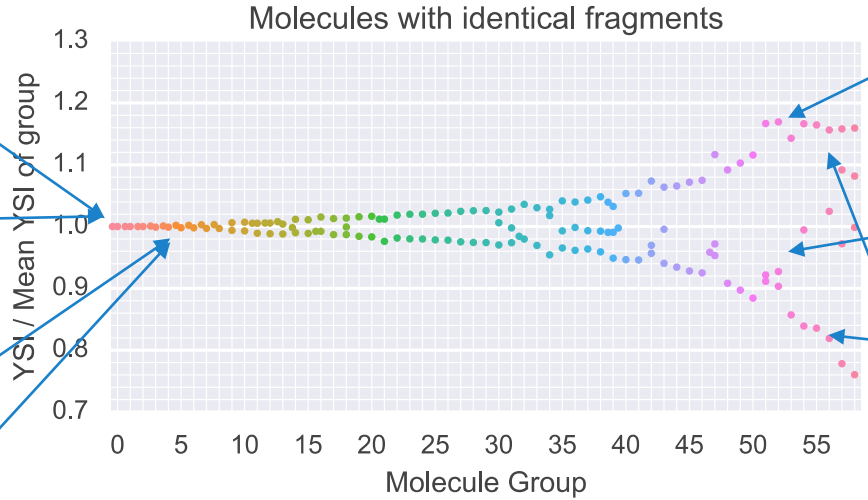
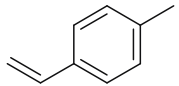


2-propylpentan-1-ol



By looking at the functional groups that give rise to these differences, we can infer more detailed kinetics of soot particle formation

1-methyl-4-vinylbenzene



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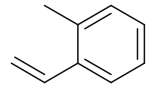
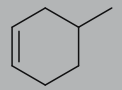


1-methyl-2-vinylbenzene

4-methyl-1-cyclohexene



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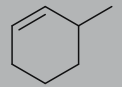
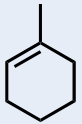
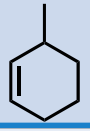
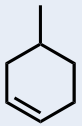


3-methyl-1-cyclohexene

Das and St John *et al. Comb. and Flame* 2018

Measured and predicted YSI of methylcyclohexene isomers and cyclohexene

Compound	YSI (measured)	YSI (predicted)
Cyclohexene 	45.6 ± 2.0	71.1 ± 5.7
1-methyl-1-cyclohexene 	62.0 ± 3.0	90.5 ± 11.0
3-methyl-1-cyclohexene 	85.0 ± 4.0	74.6 ± 9.8
4-methyl-1-cyclohexene 	61.0 ± 3.0	74.6 ± 9.8

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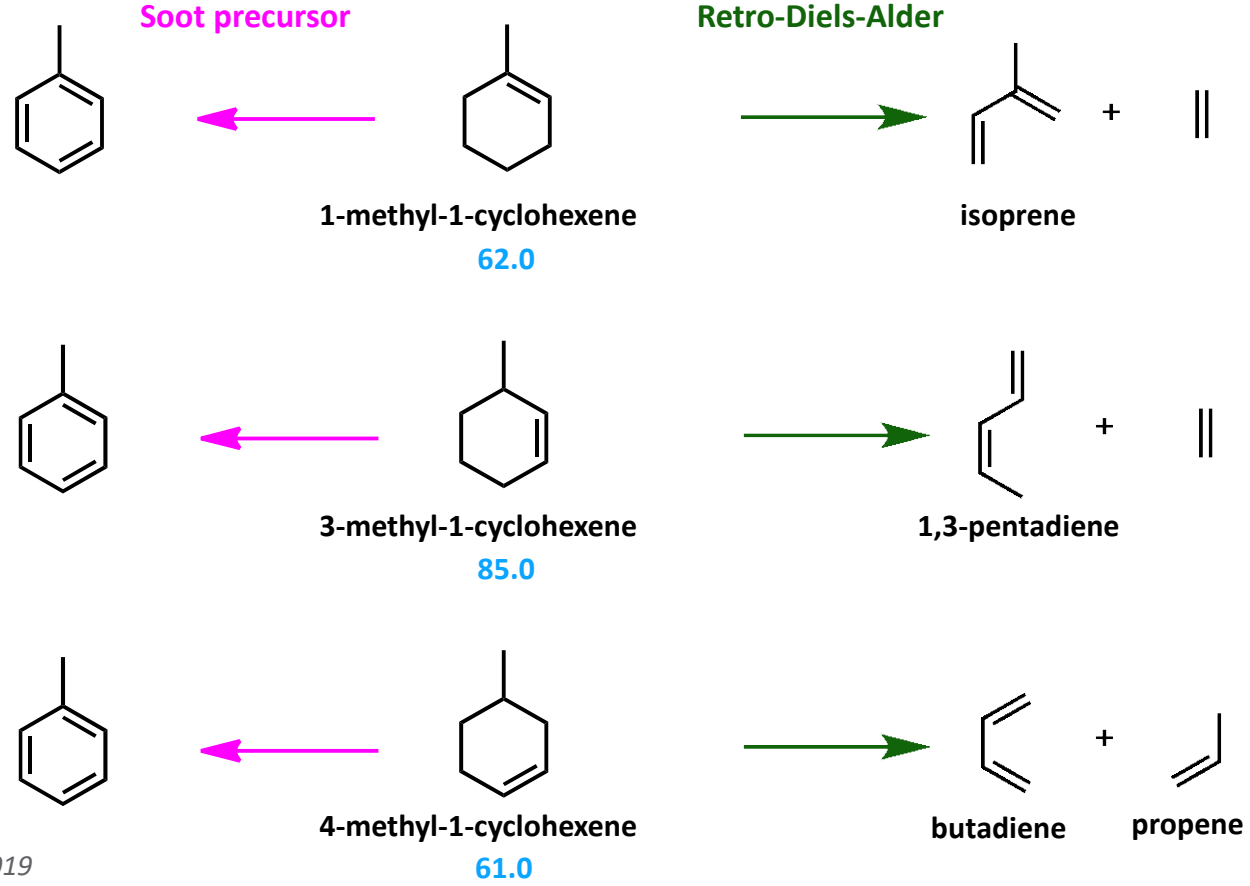
Hypothesis of 3 isomers



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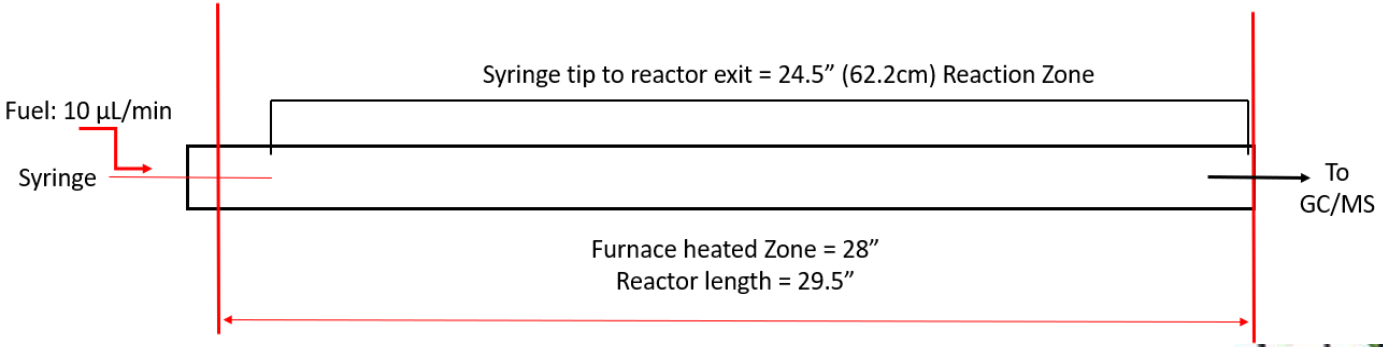
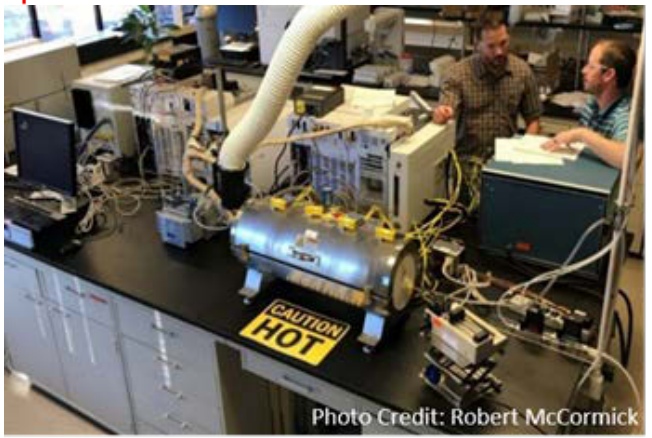
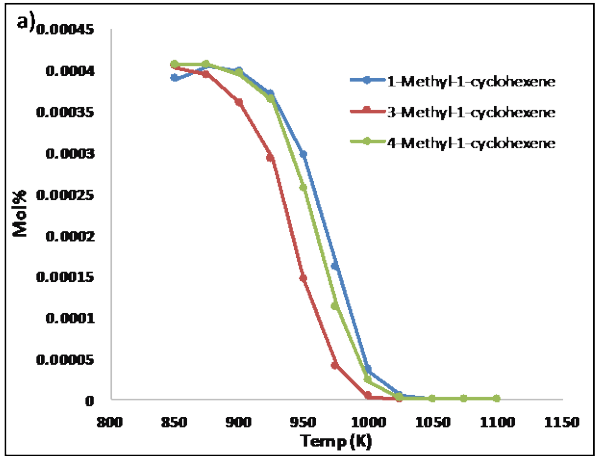
Flow Reactor Setup





Temperature 850 - 1100 K (25 K increments)
Stoichiometric air-to-fuel ϕ=1
Analyzed using two gas chromatographic and mass spectrum (GC/MS) systems

Reactants and product concentrations in Flow Reactor



Retro-DA products

aromatics products

Gina Fioroni and
Bob McCormick (NREL)

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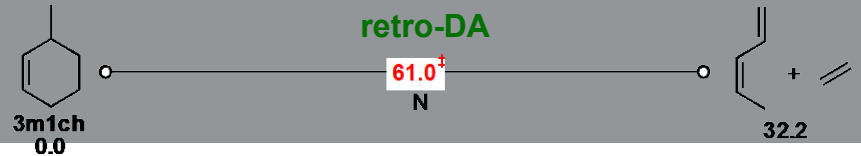
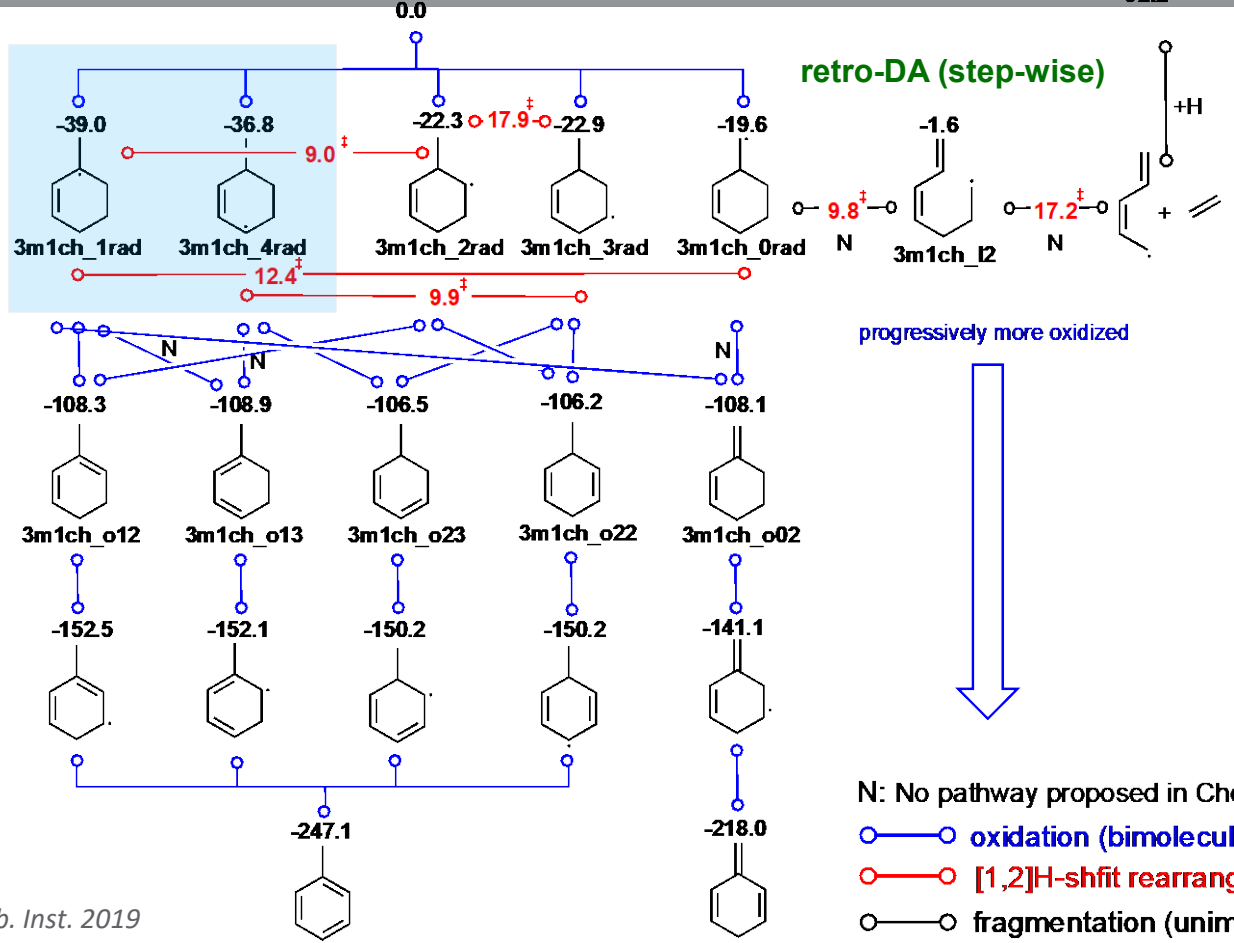
3-methyl-1-cyclohexene





ΔG in G4 (kcal/mol)

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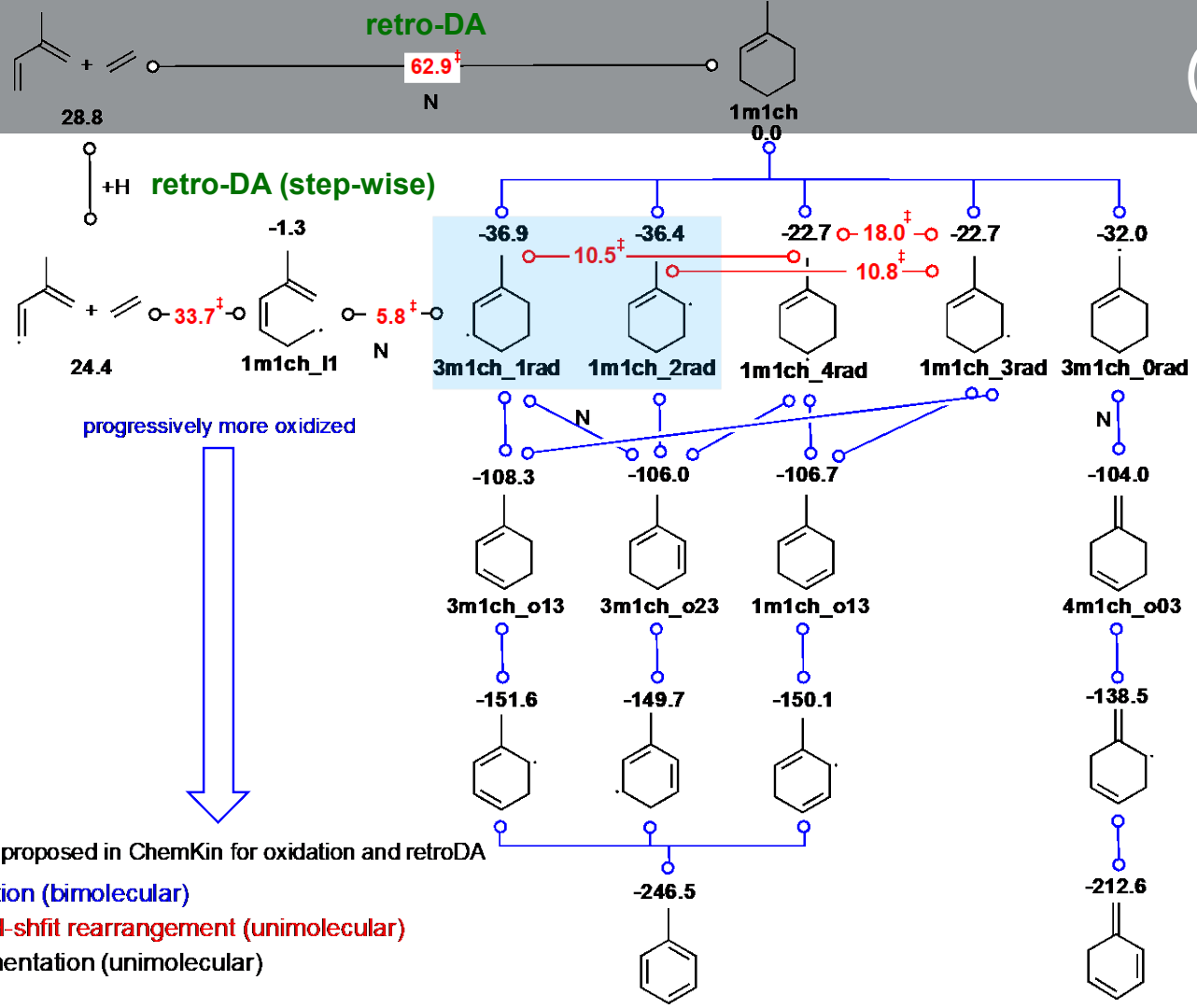
N: No pathway proposed in ChemKin for oxidation and retroDA

oxidation (bimolecular)

[1,2]H-shfit rearrangement (unimolecular)

fragmentation (unimolecular)

1-methyl-1-cyclohexene



ΔG in G4 (kcal/mol)

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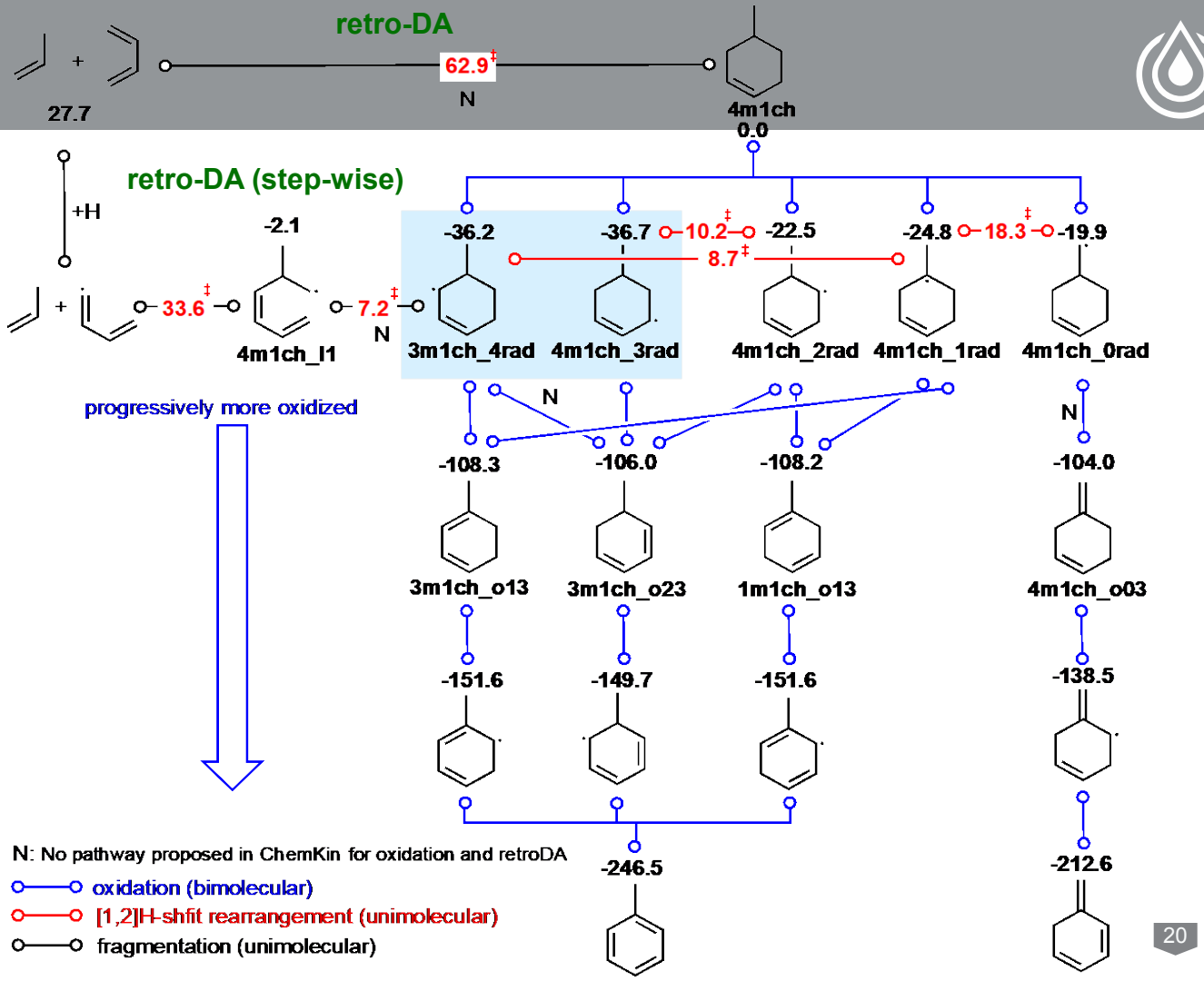
4-methyl-1-cyclohexene



ΔG in G4 (kcal/mol)

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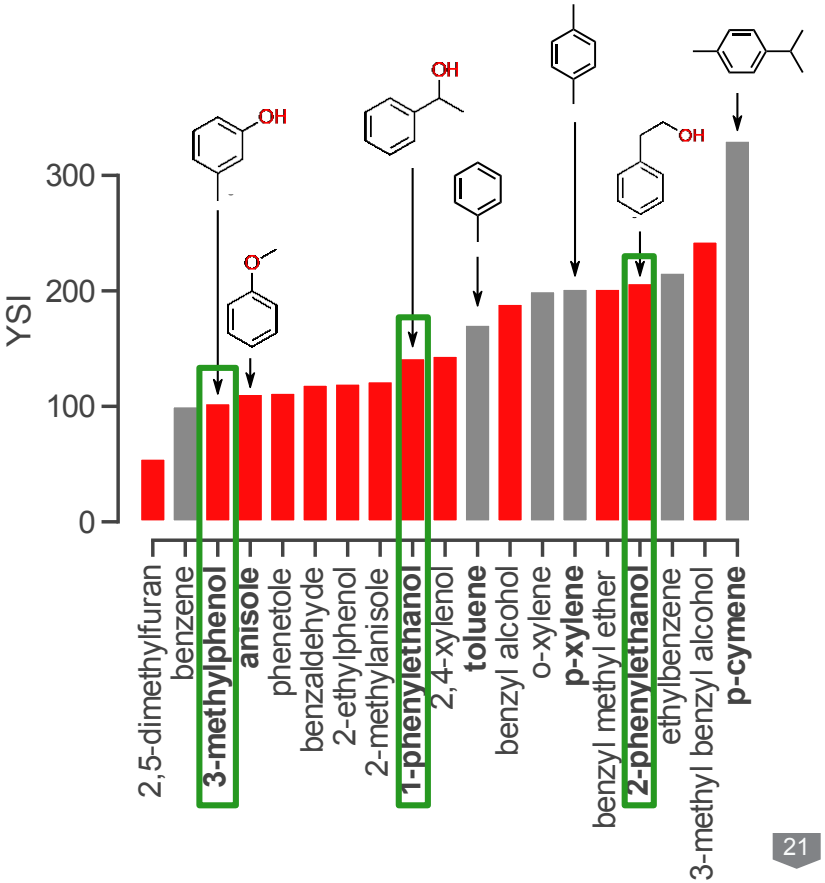
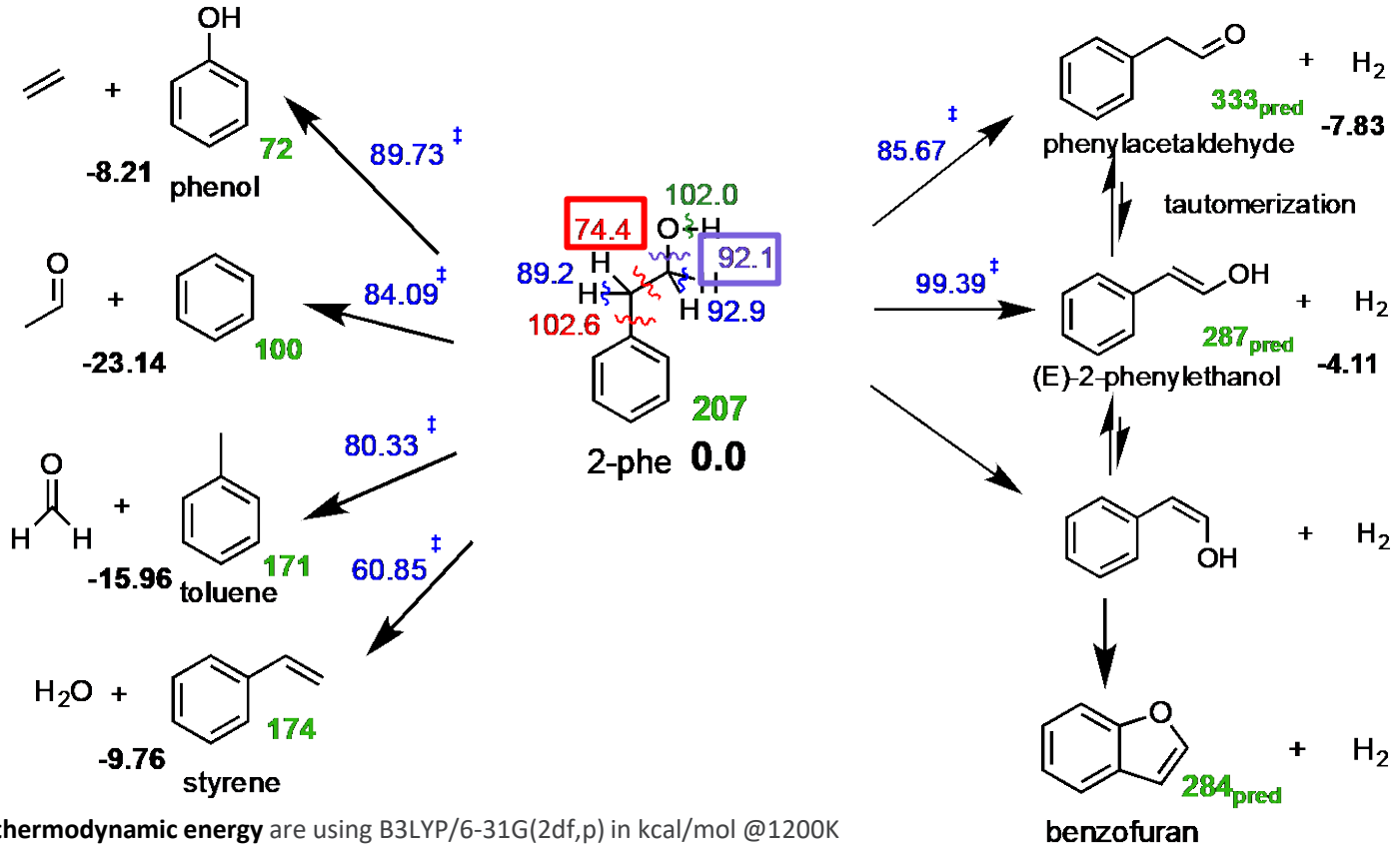
Potential performance advantage for oxygenates

- Oxygenated aromatics can be produced readily from biomass, and may reduce PM formation (relative to non-oxygenates) ***in some cases***
- Characterizing these advantages will be required to drive conversion and separations processes
- Slight differences in aromatic side-chains lead to drastic differences in soot formation
- Understanding the mechanism of these differences will help tune conversion pathways for beneficial oxygenates



Bond dissociation energies determine combustion pathways

Bond-Dissociation-Energy (BDE)



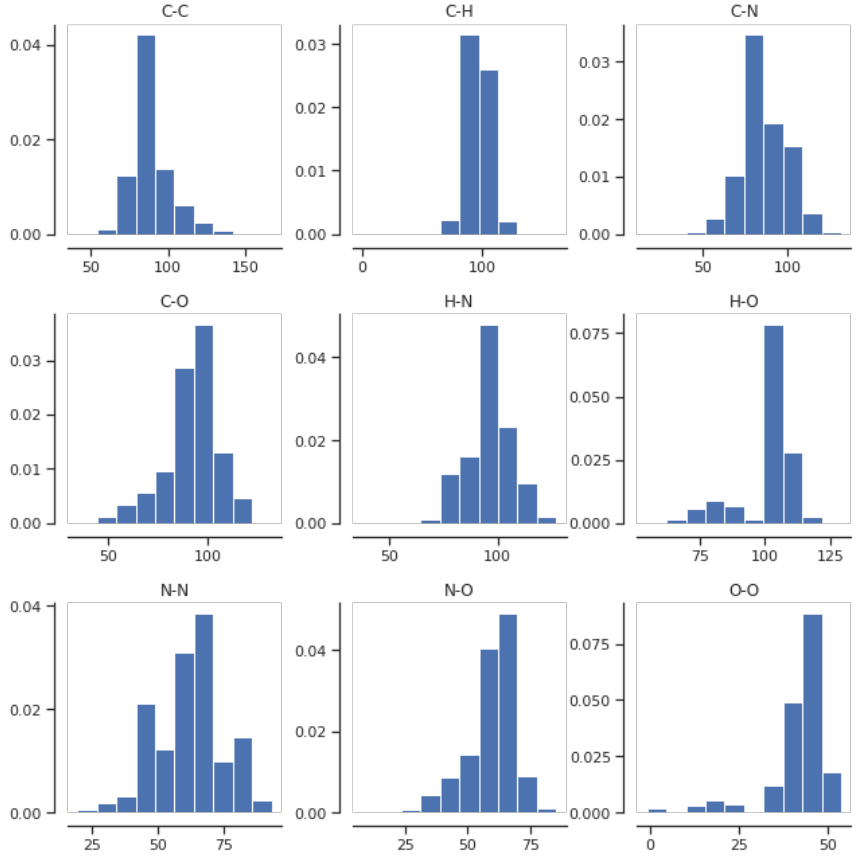
YSI values

BDE are G4, barriers and **thermodynamic energy** are using B3LYP/6-31G(2df,p) in kcal/mol @1200K

Developing a BDE database

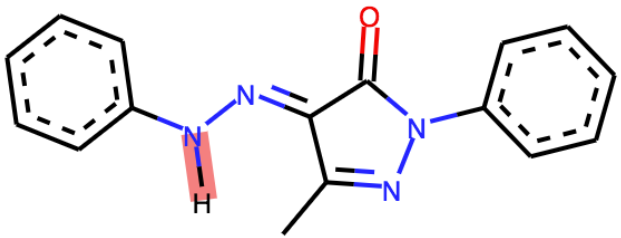
- 504,529 BDEs,
  - 320,376 unique BDEs
- 39,163 parent molecules
  - 249,685 gaussian calculations
- 1000 molecules reserved for validation and test sets
- Some quality checks on data:
  - Bond lengths must be less than 0.4Å + Σ(covalent radius)
  - Checks for gaussian convergence

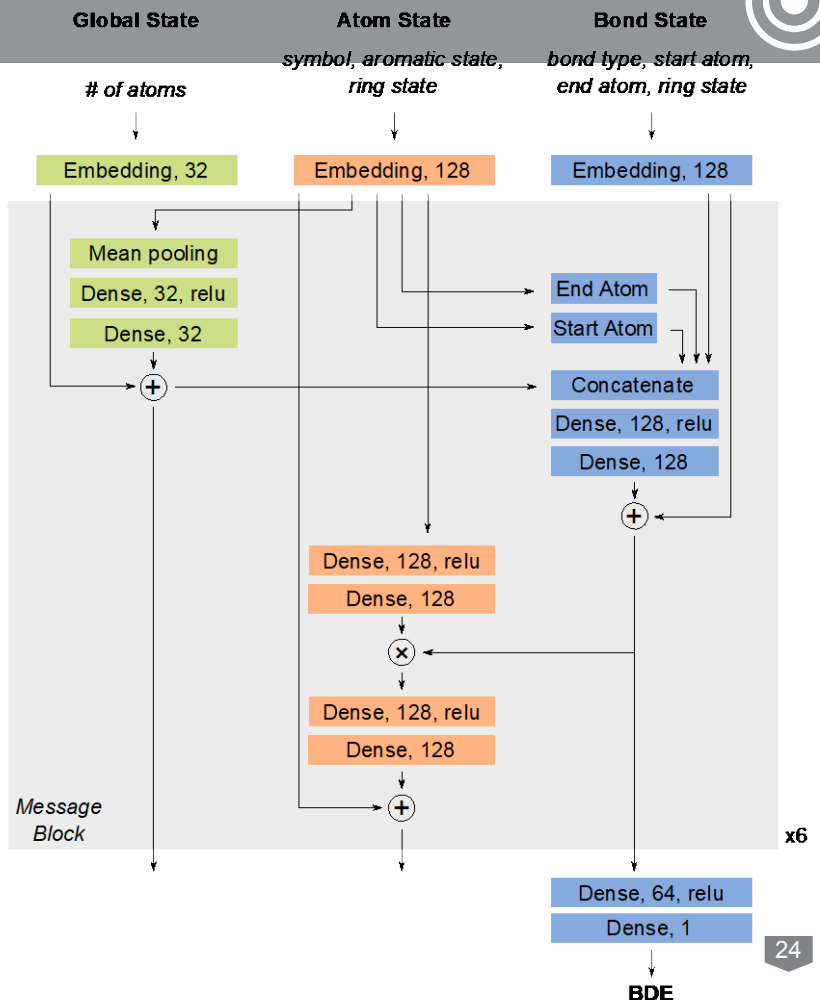
Type	Count
C-H	312,771
C-C	93,636
C-O	29,706
C-N	27,072
H-N	26,151
H-O	11,726
N-O	1,620
N-N	1,542
O-O	305



Model Structure

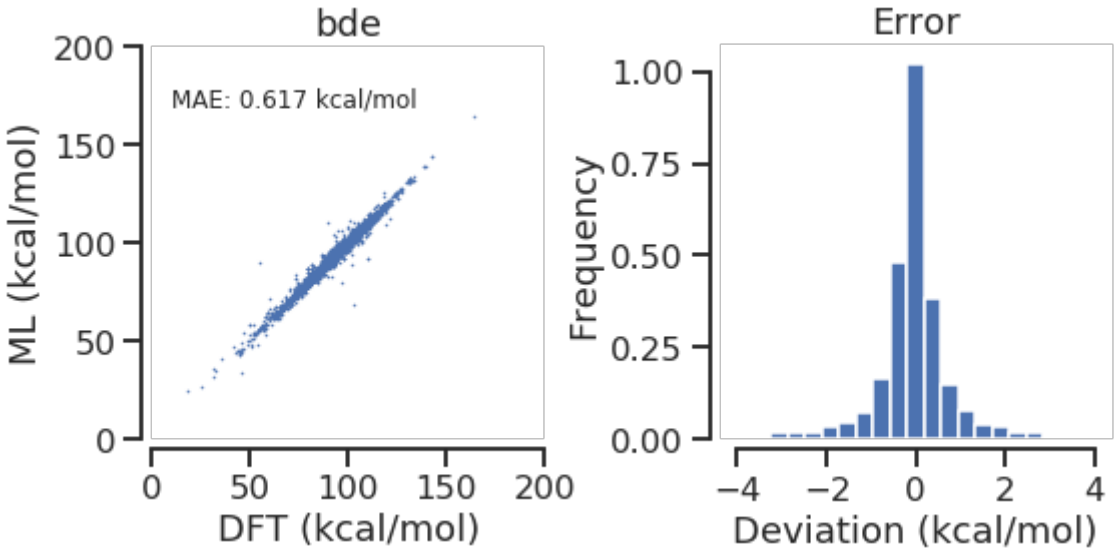
- BDE is a property of each bond
  - Model learns numerical representation for bond environment, uses this to predict bond strength
- Based only on 2D inputs (connectivity)



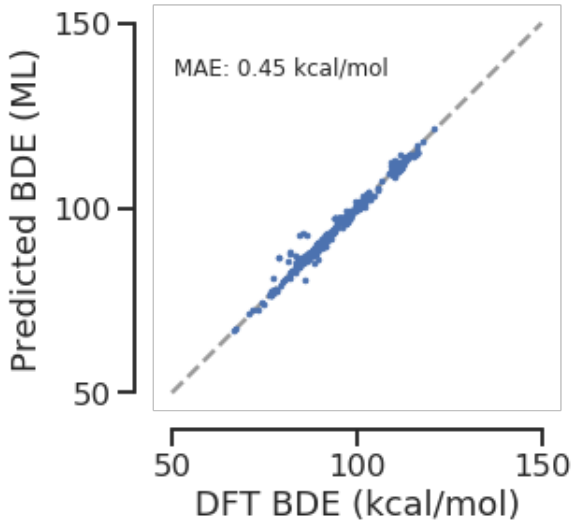


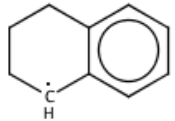
Prediction Results

- Vast majority of new molecules have BDEs predicted within 2 kcal/mol



Performance on larger molecules





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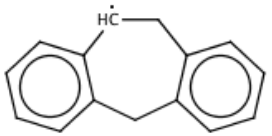
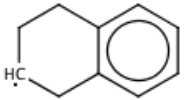


DFT: 86, ML: 93



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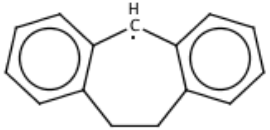
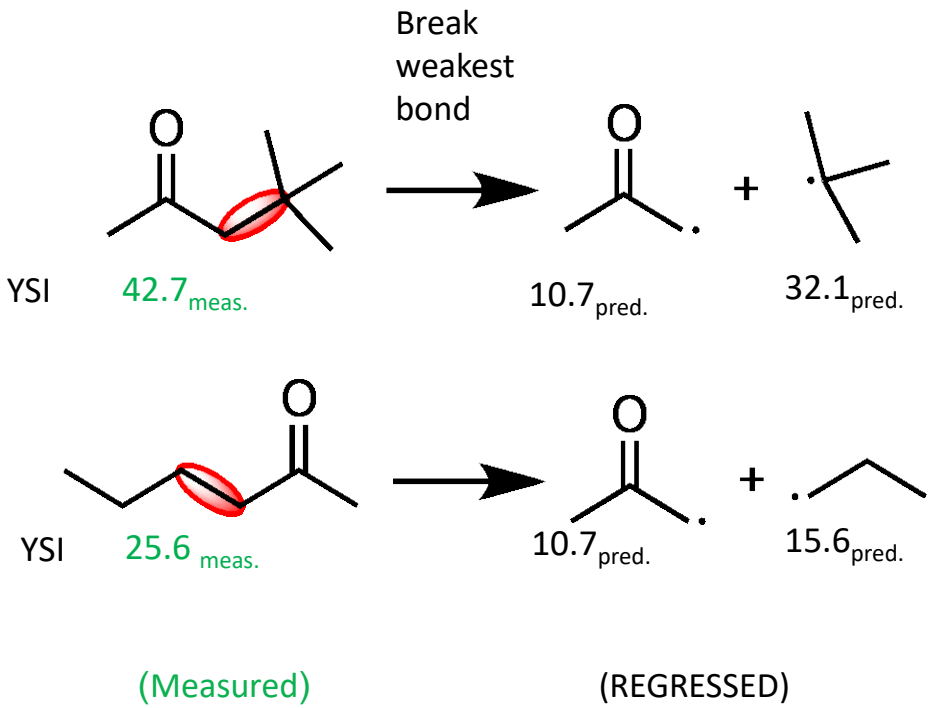
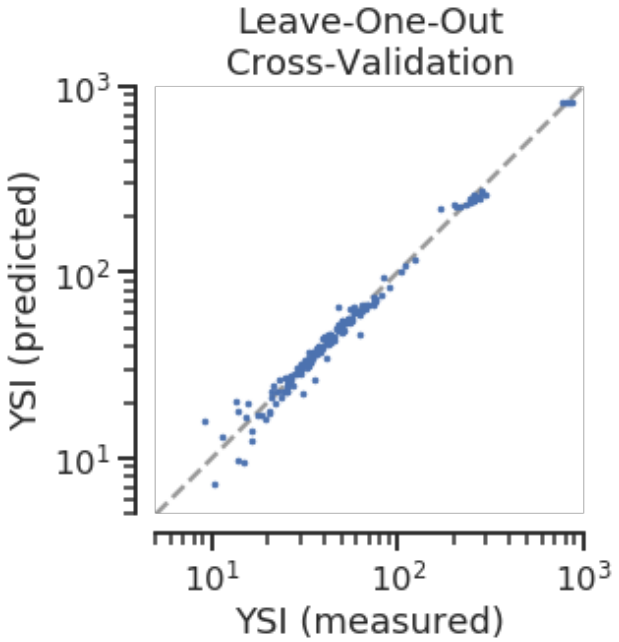


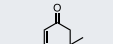
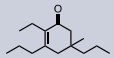
DFT: 79, ML: 86

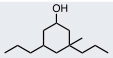
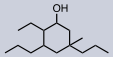
Predicting YSI through decomposition products

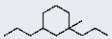
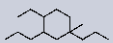


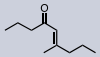
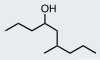


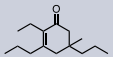
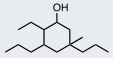
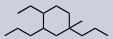
YSI Fuel Property Prediction Tool

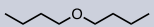
No.	Trimer Enone Compound	Structure	CN	YSI	Melting Boiling (°C)	Water Solubility (g/L)
5	3,5,5-trimethylcyclohex-2-en-1-one		12	109	30 224	P
89	5-methyl-3,5-dipropylcyclohex-2-en-1-one		22	133	76 316	P
19	2-ethyl-5-methyl-3,5-dipropylcyclohex-2-en-1-one		16	165	111 367	P

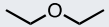
No.	Trimer R-OH Compound	Structure	CN	YSI	Melting Boiling (°C)	Water Solubility (g/L)
6	3,3,5-trimethylcyclohexan-1-ol		10	91	1 235	HC
90	3-methyl-3,5-dipropylcyclohexan-1-ol		23	114	46 327	HC
20	2-ethyl-5-methyl-3,5-dipropylcyclohexan-1-ol		15	134	65 368	HC

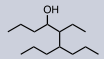
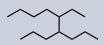
No.	Trimer HC Compound	Structure	CN	YSI	Melting Boiling (°C)	Water Solubility (g/L)
7	1,1,3-trimethyl cyclohexane		31	81	-55 148	HC
91	1-methyl-1,3-dipropylcyclohexane		39	125	8 280	HC
21	4-ethyl-1-methyl-1,3-dipropylcyclohexane		39	105	-10 239	HC

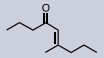
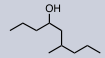
No.	Dimer HC Compound	Structure	CN	YSI	Melting Boiling (°C)	Water Solubility (g/L)
16	6-Methylnon-5-en-4-one		38	67	-40 213	P
17	6-Methylnonan-4-ol		31	62	-40 247	P
18	4-Methyl-nonane					

No.	Trimer HC Compound	Structure	CN	YSI	Melting Boiling (°C)	Water Solubility (g/L)
19	2-ethyl-5-methyl-3,5-dipropylcyclohex-2-en-1-one		16	165	111 367	HC
20	2-ethyl-5-methyl-3,5-dipropylcyclohexan-1-ol		15	134	65 368	HC
21	4-ethyl-1-methyl-1,3-dipropylcyclohexane		39	105	-10 239	HC

No.	Ether Compound	Structure	CN	YSI	Melting Boiling (°C)	Water Solubility (g/L)
41	Diethyl ether		160	18	-116 41	60.5
46	1-Ethoxy butane		116	30	-94 86	Pending
43	Dibutyl ether		115	42	-71 132	0.6

Ether Compound	Structure	CN	YSI	Melting Boiling (°C)	Flash Point (°C)
Diethyl ether		160	17 4.5	-116 41	-45

No.	Central Ketone Dimers	Structure	CN	YSI	Melting Boiling (°C)	Water Solubility (g/L)
39	5-Ethyl-6-propylnonan-4-ol		40	90	-10 338	P
40	5-Ethyl-4-propyl nonane		49	91	-56 246	HC

No.	Terminal Ketone Dimers	Structure	CN	YSI	Melting Boiling (°C)	Water Solubility (g/L)
16	6-Methylnon-5-en-4-one		38	67	-40 213	P
17	6-Methylnonan-4-ol		31	62	-40 247	P

Collaboration with Derek Vardon (HPF)

Conclusions and Future Works

- Develop YSI prediction tool and provide screening tool with Web app (https://ysipred.herokuapp.com)
- Small structural features can impact combustion processes and importance of relative stability of the first radical intermediates via retro-DA
- Expand skeletal soot precursor mechanisms with Flow reactor, PIMS
- Deployment of graph neural-network based predictions to online tool
  - Cetane Number, YSI, other properties
- Development of suitable outlier detection method

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