Fundamental Concepts in Combustion Kinetics

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Combustion chemistry

- Combustion is the sequential disassembly of a (hydrocarbon) fuel molecule, atom by atom, eventually producing stable products (CO_2 and H_2O)
- All possible chemical species are included with coupled differential equations
- Elementary reactions take place between these species, with assigned reaction rates
- Chain carriers are free radicals H, OH, O, HO_2, CH_3, others

Chain reactions exist in many forms

- Populations of bacteria
- Populations of people
- Nuclear reactors
- Chemical reactions

$$dn/dt = \alpha n$$

$$n(t) = n_o \exp^{\alpha t}$$

$\alpha > 0$ growth

$\alpha < 0$ decay

$\alpha = 0$ stable

Reaction mechanisms

- A reaction mechanism is a collection of the reactions that are “important” and their rate expressions as functions of temperature and pressure

Goals for modeling of large hydrocarbon fuels

- Provide validated chemistry models for combustion in:

  Diesel engines
  Homogeneous Charge Compression Ignition (HCCI) engines
  Spark Ignition (SI) engines
  Turbine engines

- Assist in mechanism reduction for simulations with computational fluid dynamics (CFD)

- Provide combustion insights from kinetic simulations of engine processes

Computational Combustion Chemistry

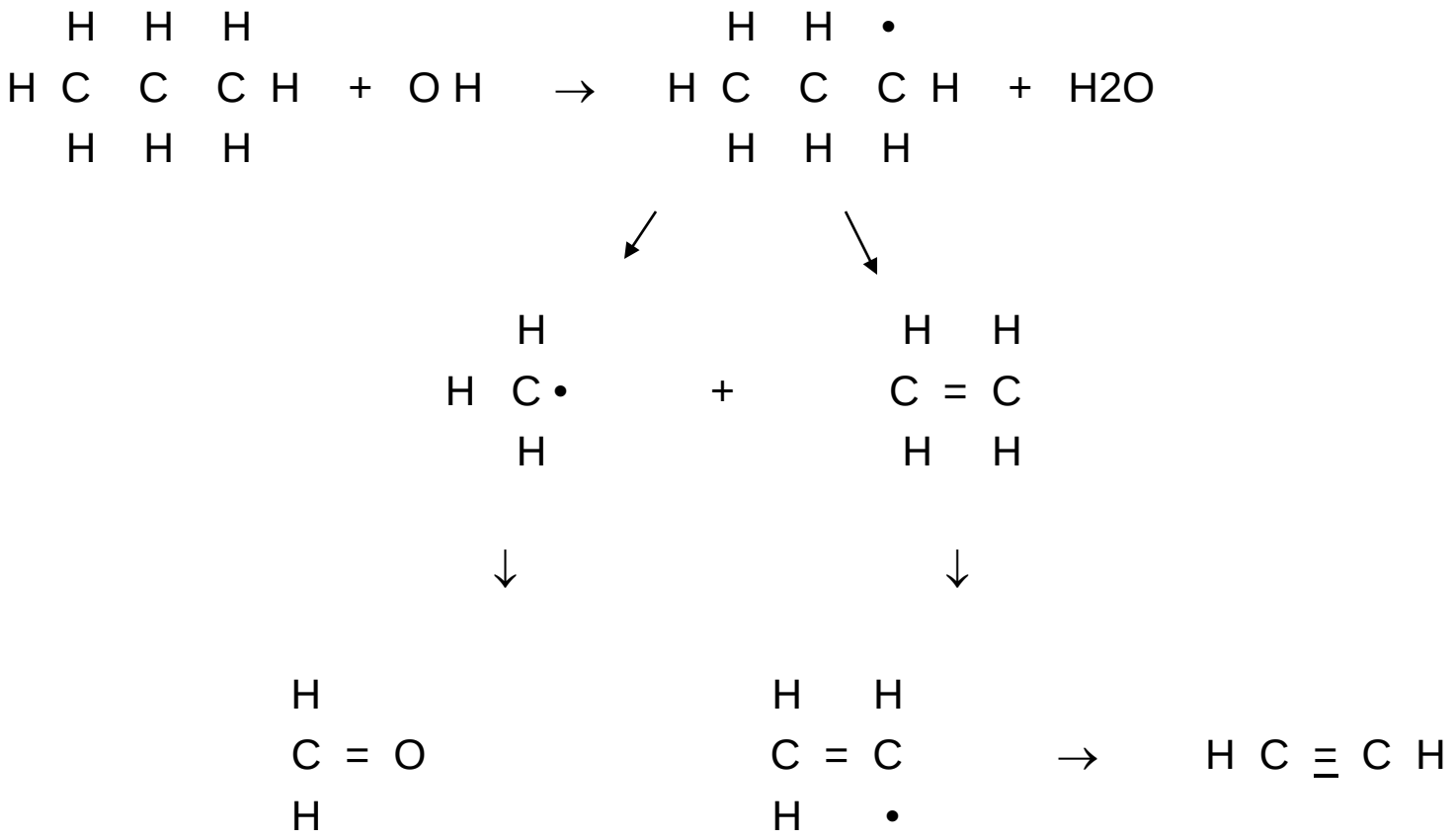
$$\text{Fuel} + (n_1)\, O_2 \longrightarrow (n_2)\, CO_2 + (n_3)\, H_2O$$

$$\text{Rate} = A\, T^{n}\, \exp[-E / R\, T]\, [\text{Fuel}]^{a}\, [O2]^{b}$$

Single reaction step: Useful simplification in 2D or 3D simulations

However, it misrepresents actual reaction paths

An example: propane oxidation



Reaction mechanism construction

Reactions $N_2 + O = NO + N$

$N + O_2 = NO + O$

$$\frac{d[NO]}{dt} = k_{1+}[N_2][O] + k_{2+}[N][O_2] - k_{1-}[NO][N] - k_{2-}[NO][O]$$

$$\frac{d[N]}{dt} = k_{1+}[N_2][O] + k_{2-}[NO][O] - k_{1-}[NO][N] - k_{2+}[N][O_2]$$

$$\frac{d[O_2]}{dt} = k_{2-}[NO][O] - k_{2+}[N][O_2]$$

Chemical Kinetic Model

Contains a large database of:

- Thermodynamic properties of species
- Reaction rate parameters

Size of mechanism grows with molecular size:

Fuel:	H_2	CH_4	C_3H_8 (Propane)	C_6H_{14} (Hexane)	$C_{16}H_{34}$ (Cetane)
Number of species:	7	30	100	450	1200
Number of reactions:	25	200	400	1500	7000

LLNL uses chemical kinetic modeling for a wide range of fuels and problems

Hydrocarbons

Methane, ethane, paraffins through decane

Natural gas

Alcohols (e.g., methanol, ethanol, propanol

Other oxygenates (e.g., dimethyl ether, MTBE, aldehydes)

Automotive primary reference fuels for octane and cetane ratings

Aromatics (e.g., benzene, toluene, xylenes, naphthalene)

Biodiesel fuels (e.g., alkyl monomethyl esters)

Others

Oxides of nitrogen and sulfur (NOx, SOx)

Metals (Aluminum, Sodium, Potassium, Lead)

Chlorinated, brominated, fluorinated species

Silane

Air toxic species

Chemical warfare nerve agents

Kinetic modeling covers a wide range of systems

Types of systems studied

Flames
Shock tubes
Detonations
Pulse combustion
Flow reactors
Stirred reactors
Supercritical water oxidation
Engine knock and octane sensitivity
Flame extinction
Diesel engine combustion
Combustion of metals
CW agent chemistry
Catalytic combustion
Material synthesis
many others . . . .

Waste incineration
Kerogen evolution
Oxidative coupling
Heat transfer to surfaces
Static reactors
Ignition
Soot formation
Pollutant emissions
Cetane number
Liquid fuel sprays
HE & propellant combustion
Gasoline, diesel, aviation fuels
CVD and coatings
Chemical process control
Rapid compression machine

These studies provide extensive model validation

Hydrogen oxidation mechanism

Overall $H_2 + ½\ O_2 \rightarrow H_2O$

Actual $H_2 + OH \rightarrow H_2O + H$

$H + O_2 \rightarrow H + OH$

$H + O_2 \rightarrow HO_2$

$H_2 + O_2 \rightarrow HO_2 + H$

……

Rates of elementary reactions

- Reaction $A + B \rightarrow C + D$

Rate $= k_+ = A\ T^n\ \exp[- E / R\ T]\ [A]\ [B]$

Usually also a reverse reaction $C + D = A + B$

$k_- = k_+ / K_{eq}$ with equilibrium constant from thermochemistry

Of k_+ k_- and K_{eq}, only two are independent

Some authors use k_+ and k_-, but most use k_+ and K_{eq}

Table I
Fuel oxidation mechanism. Reaction rates in cm^3-mole-sec-kcal units, $k=AT^n\exp(-E_a/RT)$

	Reaction	Forward rate			Reverse rate		
		log A	n	E_a	log A	n	E_a
1	$H+O_2 \rightarrow O+OH$	14.27	0	16.79	13.17	0	0.68
2	$H_2+O \rightarrow H+OH$	10.26	1	8.90	9.92	1	6.95
3	$H_2O+O \rightarrow OH+OH$	13.53	0	18.35	12.50	0	1.10
4	$H_2O+H \rightarrow H_2+OH$	13.98	0	20.30	13.34	0	5.15
5	$H_2O_2+OH \rightarrow H_2O+HO_2$	13.00	0	1.80	13.45	0	32.79
6	$H_2O+M \rightarrow H+OH+M$	16.34	0	105.00	23.15	-2	0.00
7	$H+O_2+M \rightarrow HO_2+M$	15.22	0	-1.00	15.36	0	45.90
8	$HO_2+O \rightarrow OH+O_2$	13.70	0	1.00	13.81	0	56.61
9	$HO_2+H \rightarrow OH+OH$	14.40	0	1.90	13.08	0	40.10
10	$HO_2+H \rightarrow H_2+O_2$	13.40	0	0.70	13.74	0	57.80
11	$HO_2+OH \rightarrow H_2O+O_2$	13.70	0	1.00	14.80	0	73.86
12	$H_2O_2+O_2 \rightarrow HO_2+HO_2$	13.60	0	42.64	13.00	0	1.00
13	$H_2O_2+M \rightarrow OH+OH+M$	17.08	0	45.50	14.96	0	-5.07
14	$H_2O_2+H \rightarrow HO_2+H_2$	12.23	0	3.75	11.86	0	18.70
15	$O+H+M \rightarrow OH+M$	16.00	0	0.00	19.90	-1	103.72
16	$O_2+M \rightarrow O+O+M$	15.71	0	115.00	15.67	-0.28	0.00
17	$H_2+M \rightarrow H+H+M$	14.34	0	96.00	15.48	0	0.00

We focus on three distinct chain branching pathways

1) $H + O_2 \rightarrow O + OH$ High T

2) $H + O_2 + M \rightarrow HO_2 + M$ Medium T

$RH + HO_2 \rightarrow R + H_2O_2$

$H_2O_2 + M \rightarrow OH + OH + M$

3) $R + O_2 \rightarrow RO_2$ Low T

$RO_2 \rightarrow QOOH \rightarrow O_2QOOH \rightarrow$ 3+ radicals

Chain branching at high temperatures

$$H + O_2 \rightarrow O + OH$$

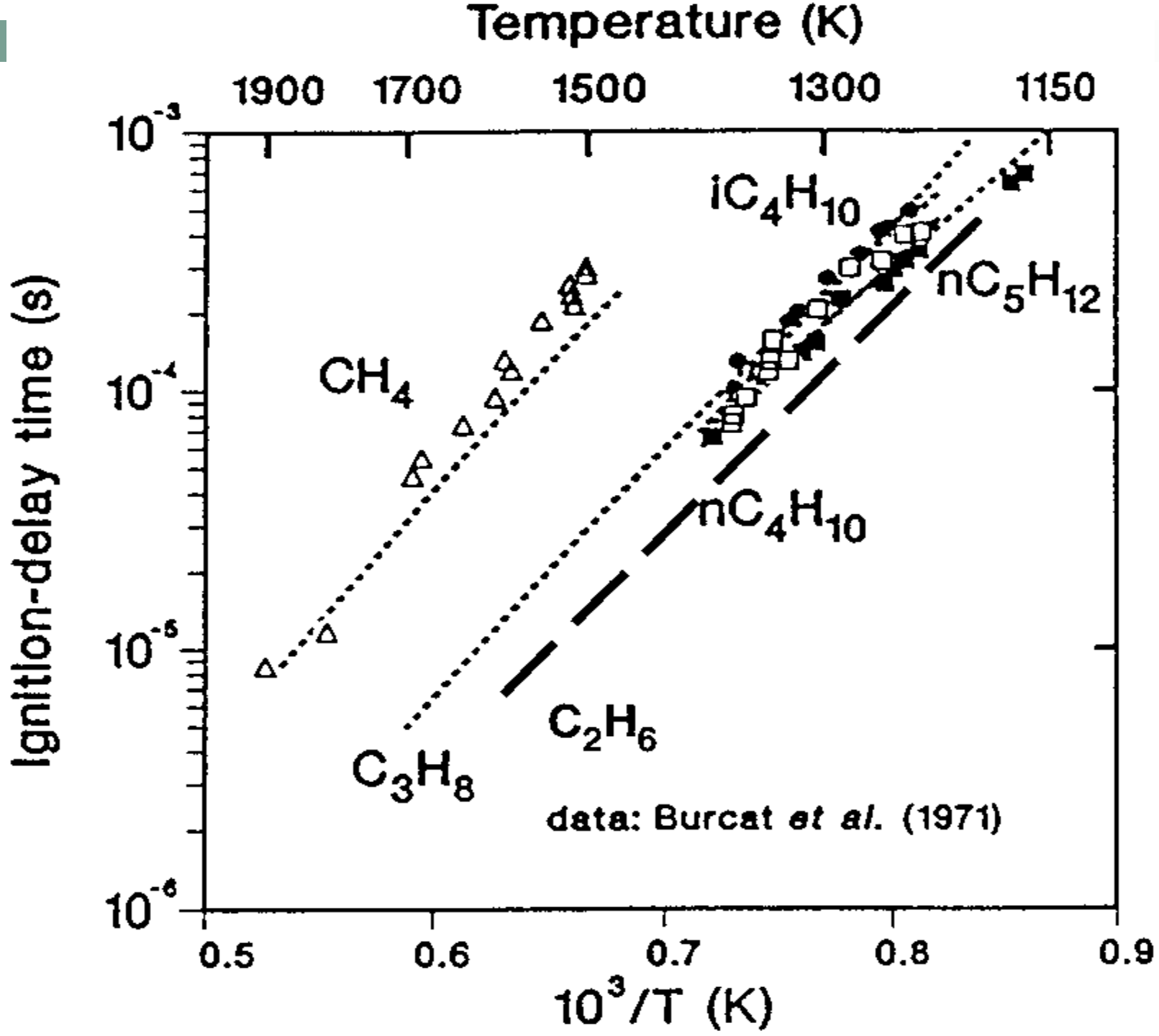
"The most important reaction in combustion"

- Activation energy is relatively high (16.8 kcal/mol)
- H atoms produced by thermal decomposition of radicals
  e.g. C_2H_5 , C_2H_3 , HCO, iC_3H_7 , etc.
  Activation energies relatively high (~ 30 kcal/mol)
- Therefore this sequence requires high temperatures
- Illustrated best by shock tube experiments

Chain branching at high temperatures

$$H + O_2 \rightarrow O + OH$$

- Chain branching for oxidation, not for pyrolysis
- Lean mixtures ignite earlier than rich mixtures
- Different fuels produce H atoms at different rates, and their ignition rates vary correspondingly
- Additives that produce H atoms will accelerate ignition, and additives that remove H atoms slow ignition


Temperature (K)
1900
1700
1500
1300
1150
Ignition-delay time (s)
10^{-3}
10^{-4}
10^{-5}
10^{-6}
iC_4H_{10}
nC_5H_{12}
CH_4
nC_4H_{10}
C_2H_6
C_3H_8
data: Burcat *et al.* (1971)
0.5
0.6
0.7
0.8
0.9
$10^3/T$ (K)

Chain branching often occurs over a series of reactions

Chain branching at intermediate temperatures

$$H + O_2 + M \rightarrow HO_2 + M$$

$$RH + HO_2 \rightarrow R + H_2O_2$$

$$H_2O_2 + M \rightarrow OH + OH + M$$

- At temperatures below about 900K, H_2O_2 decomposition is inhibited, leading to degenerate chain branching (see below)
- At higher temperatures, H_2O_2 decomposes as quickly as it is formed, leading to conventional chain branching
- Other low temperature chain branching paths can be much longer than this sequence (see below)

H_2O_2 decomposes at a fairly distinct temperature

- Reaction consuming H_2O_2 is:

$$H_2O_2 + M \rightarrow OH + OH + M$$

$$k_+ = 1.2 \times 10^{17} \times \exp(-45500/RT)$$

- Resulting differential equation is:

$$\frac{d[H_2O_2]}{dt} = -[H_2O_2][M]\,k_+$$

Characteristic time for H_2O_2 decomposition

$$\frac{d[H_2O_2]}{dt} = -[H_2O_2][M]k_+$$

define $\tau = [H_2O_2] / (d[H_2O_2]/dt)$

$\tau = 1 / (k_+ [M])$

$\tau = 8.3 \times 10^{-18} \times \exp(22750/T) \times [M]^{-1}$

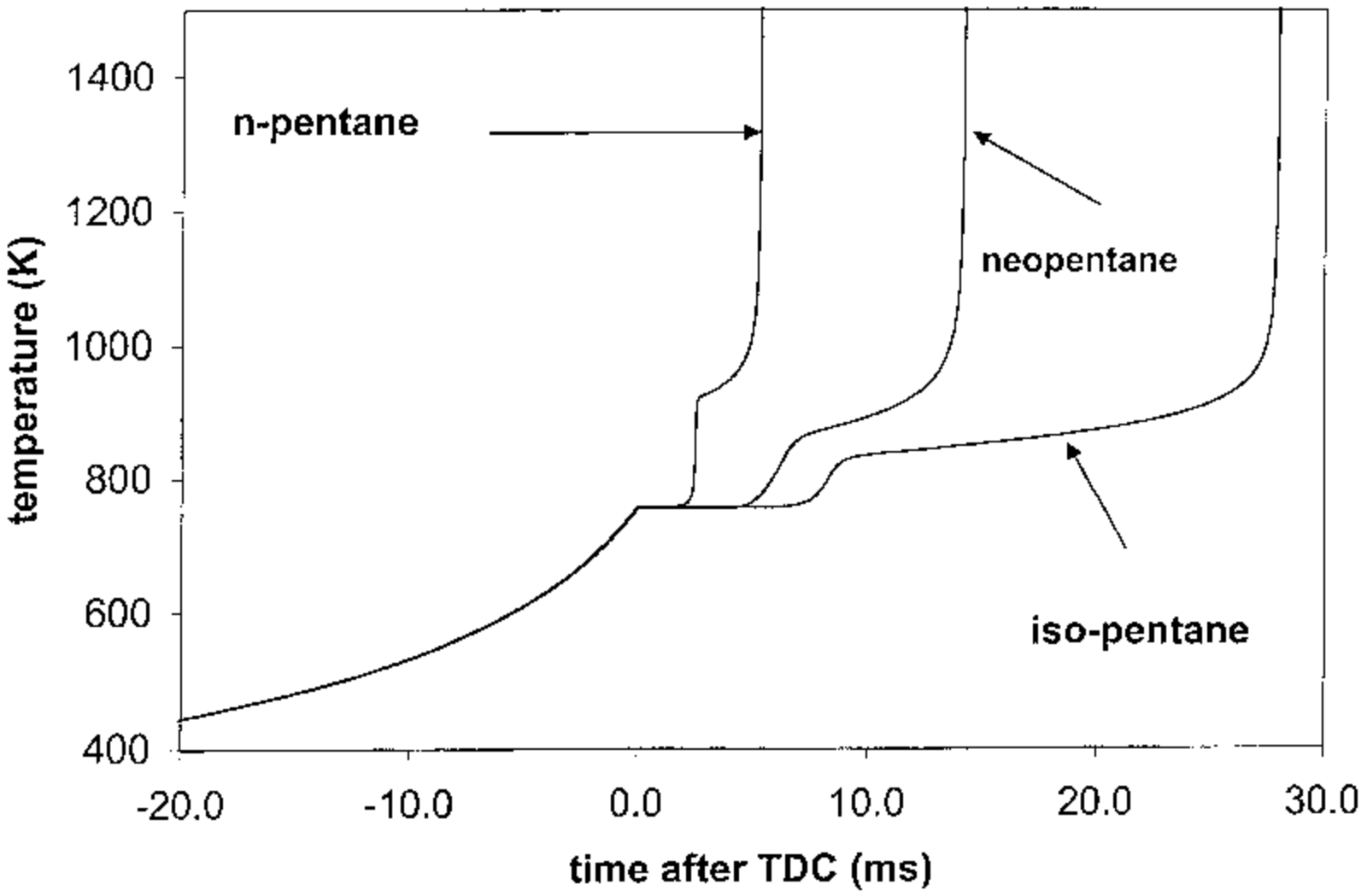
At RCM conditions, with [M] ≈ 1 x 10-4 mol/cc, values of τ are approximately:

7.8 ms at 900K 640 μs at 1000K 80 μs at 1100K

At higher compressions (pressures), values of τ are smaller at comparable temperatures

Rapid compression machine and some turbulent flow reactor experiments are controlled by H_2O_2 decomposition

- Rapid compression machine (RCM) usually operates in a degenerate branching mode
  - H_2O_2 produced at temperatures lower than 900K
  - When system reaches H_2O_2 decomposition temperature, ignition is observed
- Many turbulent flow reactor experiments operate at temperatures between 900 - 1100K where H_2O_2 decomposes as quickly as it is produced


n-pentane
neopentane
iso-pentane
temperature (K)
1400
1200
1000
800
600
400
-20.0
-10.0
0.0
10.0
20.0
30.0
time after TDC (ms)

The central role of the high temperature chain branching reaction

$$H + O_2 = O + OH$$

Ignition

Flame propagation

Flame inhibition

Sensitization of methane for natural gas

Effects of pressure on oxidation rates from competing $H + O_2 + M$ reaction

Laminar flames in quenching problems

- Mid-volume quenching in direct injection stratified charge (DISC) engine
- Bulk quenching due to volume expansion in lean-burn engine mixtures
- Flame quenching at lean and rich flammability limits
- Flame quenching on cold walls and unburned hydrocarbon emissions from internal combustion engines

Causes and implication of flammability limits

$$H + O_2 = O + OH$$

$$H + O_2 + M = HO_2 + M$$

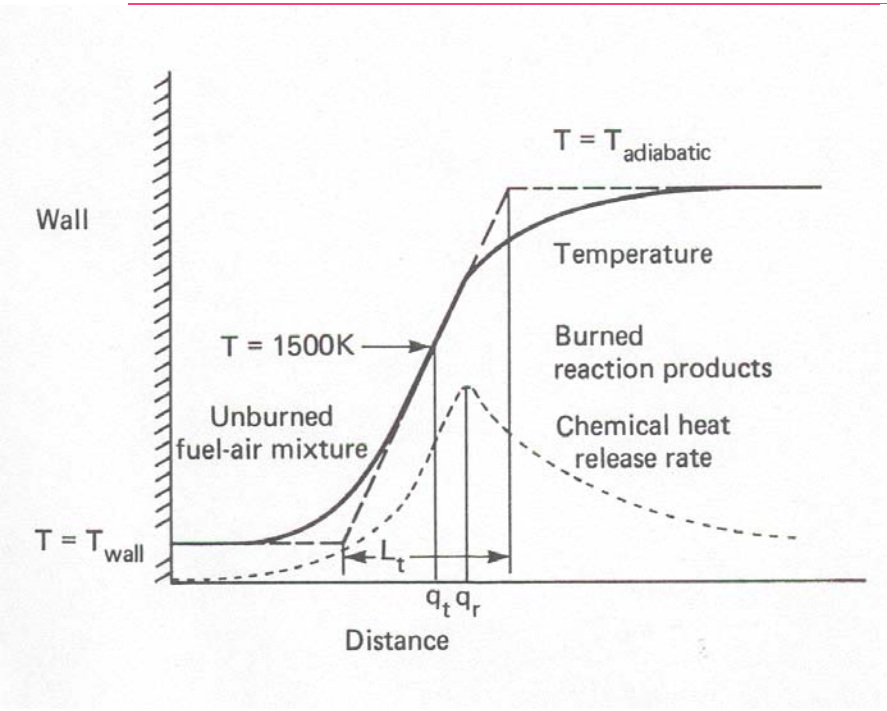
- Law and Egolfopoulos for atmospheric pressure flames
- Flynn et al. extensions to engine pressures

Lean limit moves to richer compositions as pressure increases, and at engine pressures, lean-limit mixtures still produce significant amounts of NO_x

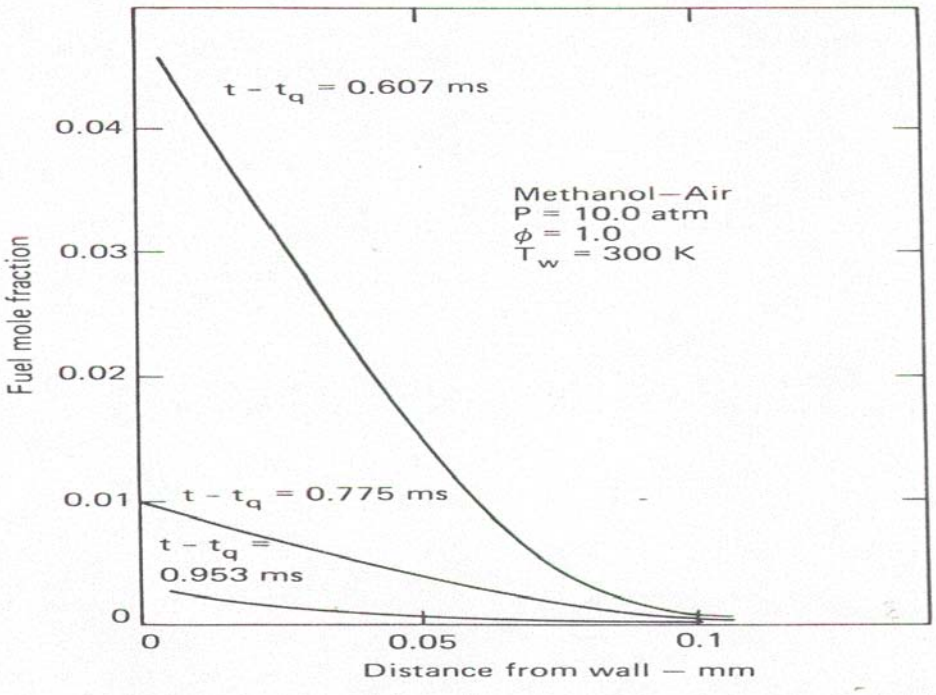
Flame quenching on engine walls

- Previous concept of UHC emissions
- Idea of making wall layers thinner
- Simple flame model results at Ford weren't believed
- Detailed modeling results
- Evidence had been there, Wentworth

Pictures of wall quenching



Flame approaching wall



Fuel diffuses away from wall and is rapidly consumed

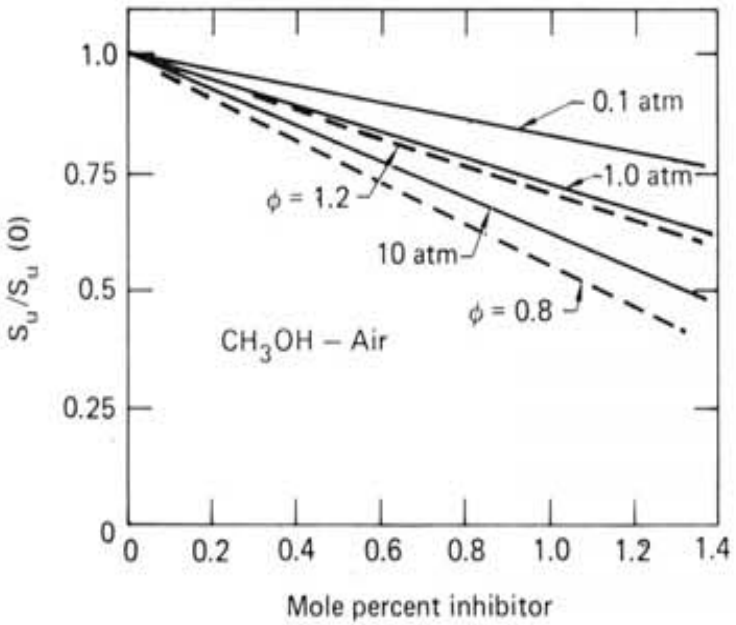
Flame inhibition

- **Halogens**
  - **HBr Dixon-Lewis, Lovachev 1970's**
  - **CF_3Br Biordi et al., Westbrook 1980's**
- **Organophosphorous compounds (OPC's)**
  - **Twarowski early studies**
  - **NIST studies, Linteris, Babushok, Gann, etc.**
  - **Korobeinichev, Melius, Jayaweera et al.**
- **Net removal of H atoms from radical pool reduces chain branching from reaction of $H + O_2 = O + OH$**

Flame inhibition by halogens

$$H + HBr = H_2 + Br$$
$$H + Br_2 = HBr + Br$$
$$Br + Br = Br_2$$
$$\overline{H + H = H_2}$$

$$CH_3Br + H = HBr + CH_3$$
$$CH_3 + Br_2 = CH_3Br + Br$$
$$H + HBr = H_2 + Br$$
$$Br + Br = Br_2$$
$$\overline{H + H = H_2}$$



Other inhibitors

- Organophosphorus compounds
- Iron and other metal compounds

$$H + H = H_2$$

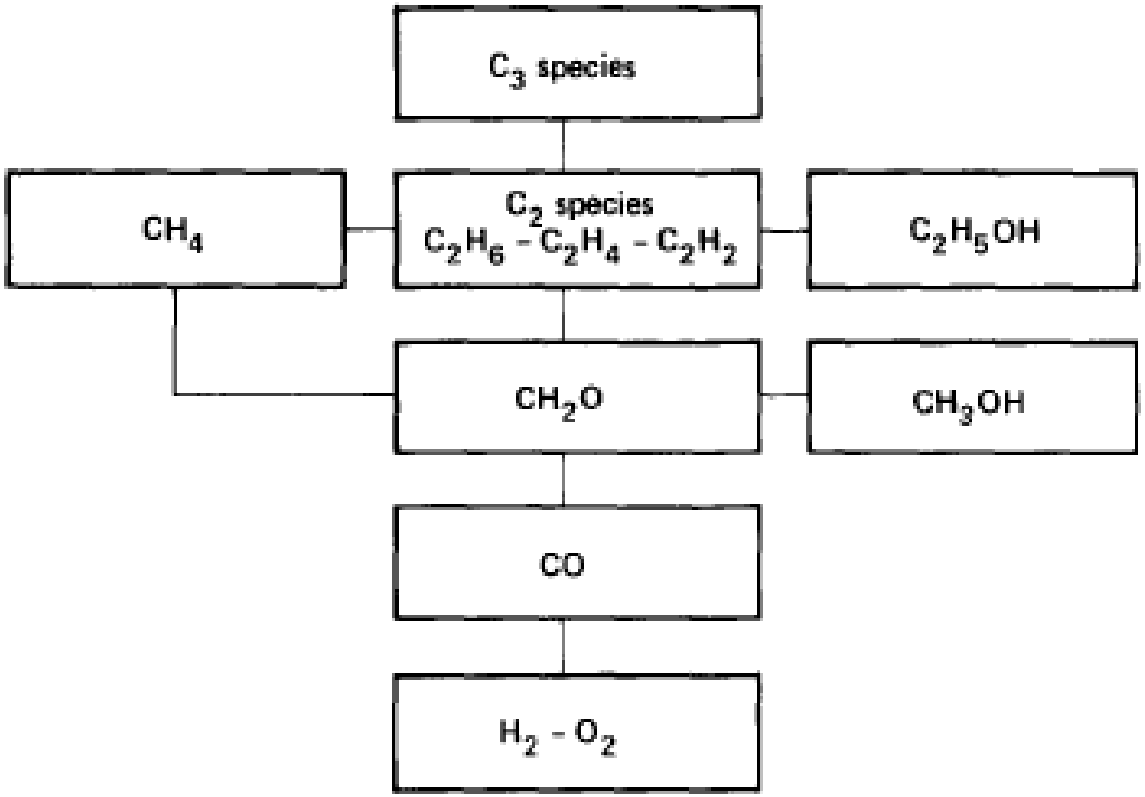
$$H + OH = H_2O$$

others

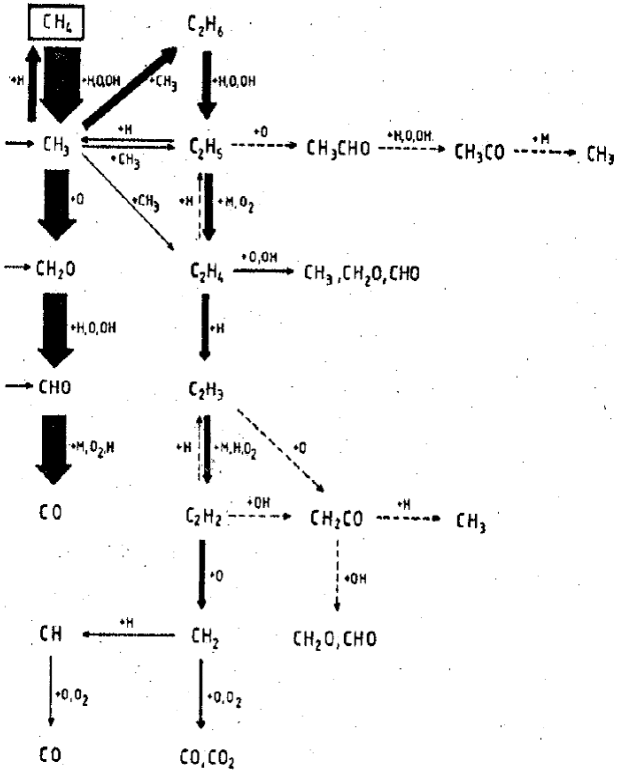
- All remove radicals and reduce the overall chain branching rates

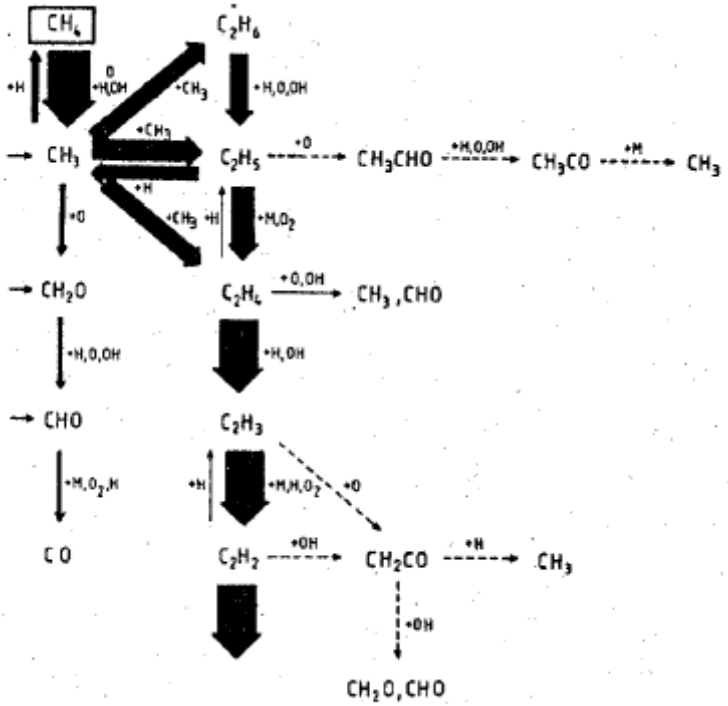
Hierarchical mechanisms

- H_2/O_2 is the foundation
- CO/CO_2 is the next level
- $CH_4/CH_2O/CH_3OH$ is the next level
- $C_2H_6/C_2H_4/C_2H_2$ is next
- This pattern continues to C10 and C20
- There are many side branches to this tree

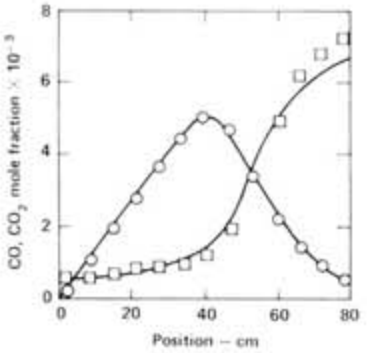

C_3 species
CH_4
C_2 species
$C_2H_6 - C_2H_4 - C_2H_2$
C_2H_5OH
CH_2O
CH_3OH
CO
$H_2 - O_2$

One of the most significant reaction flux diagrams in all of combustion chemistry





Delay of final oxidation by fuel



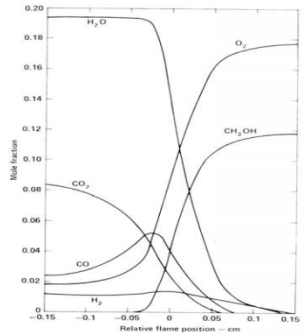
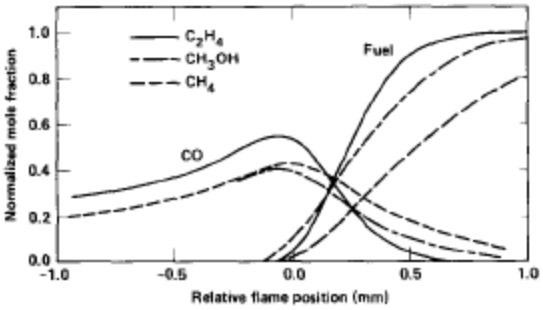
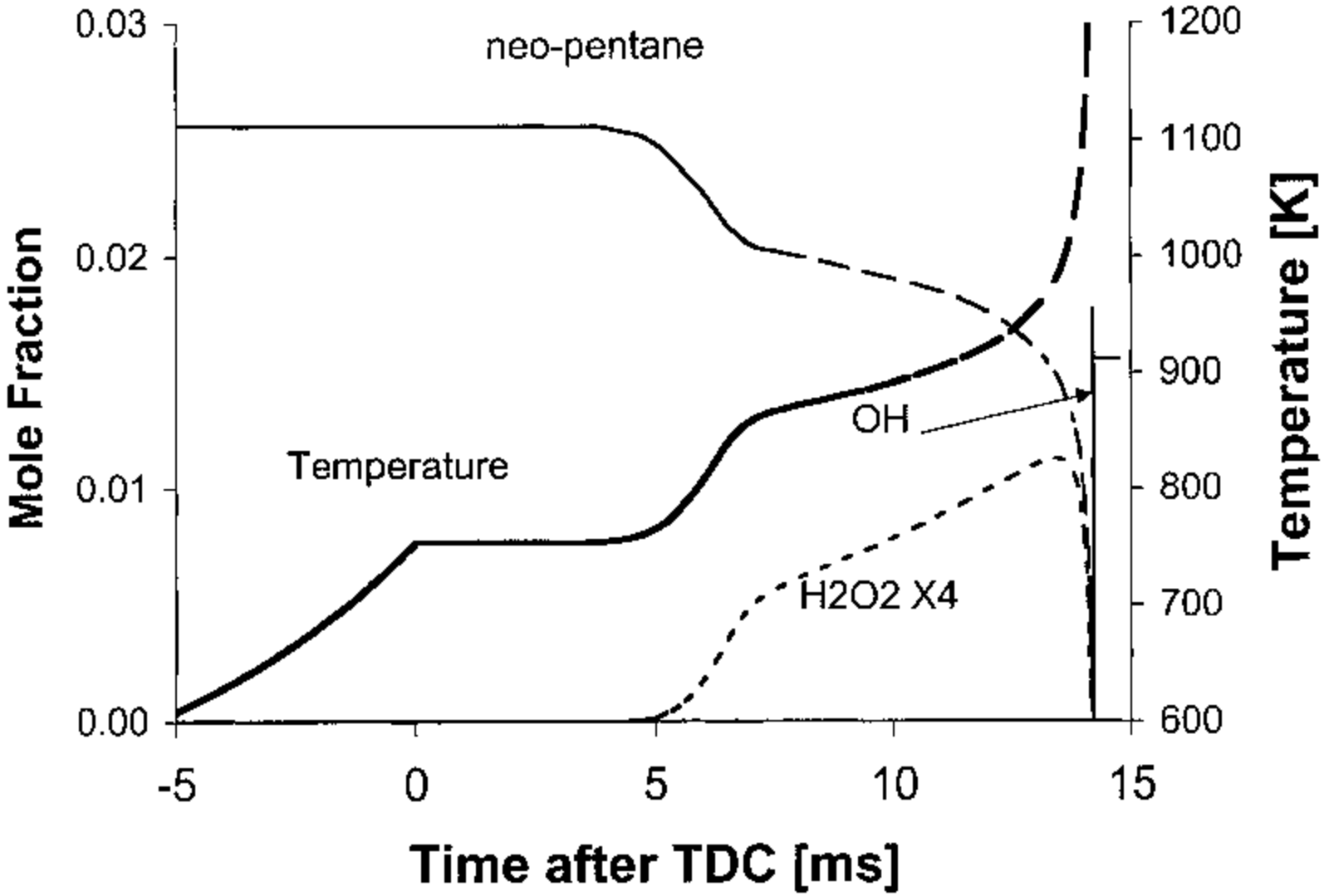
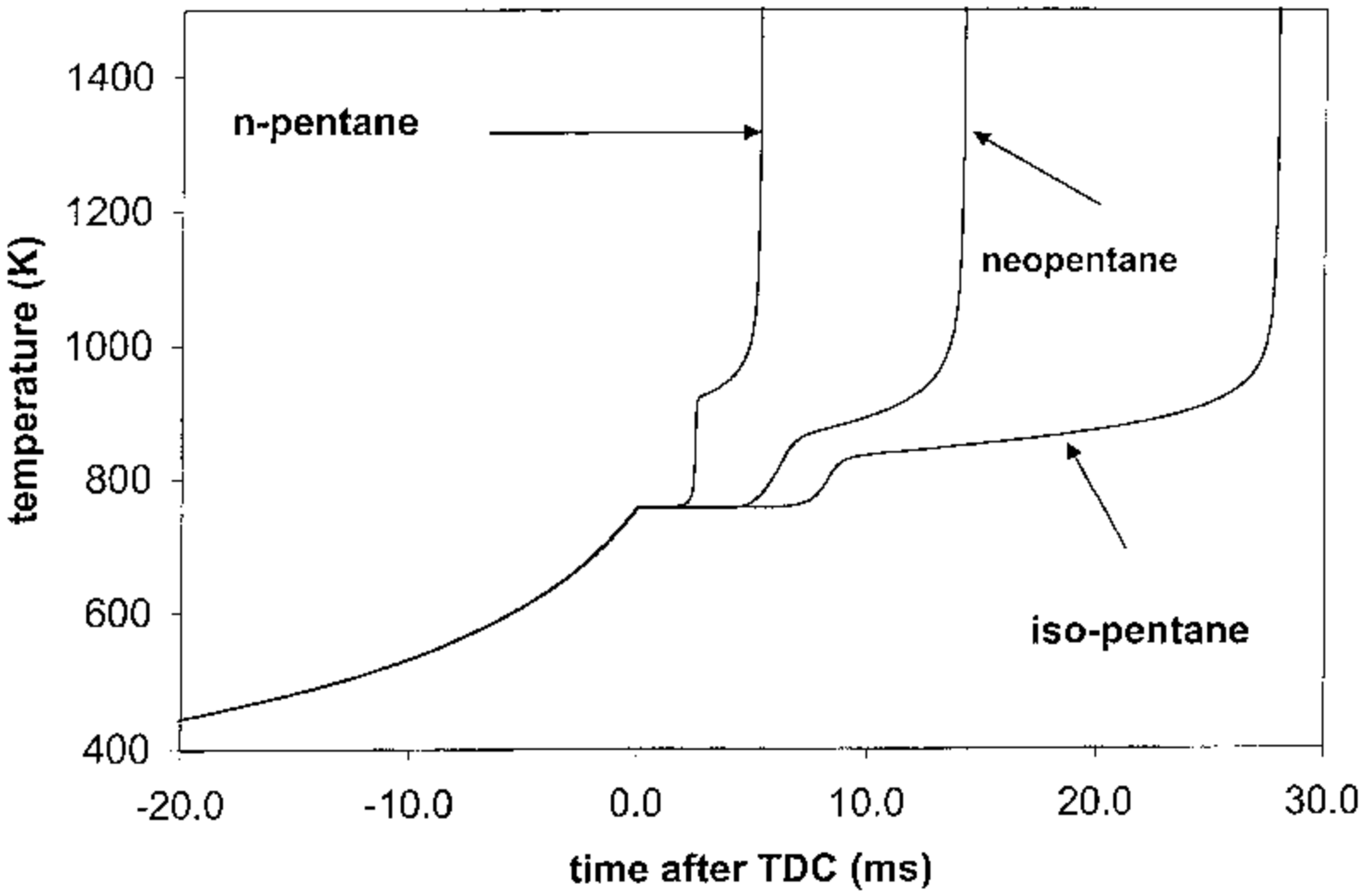
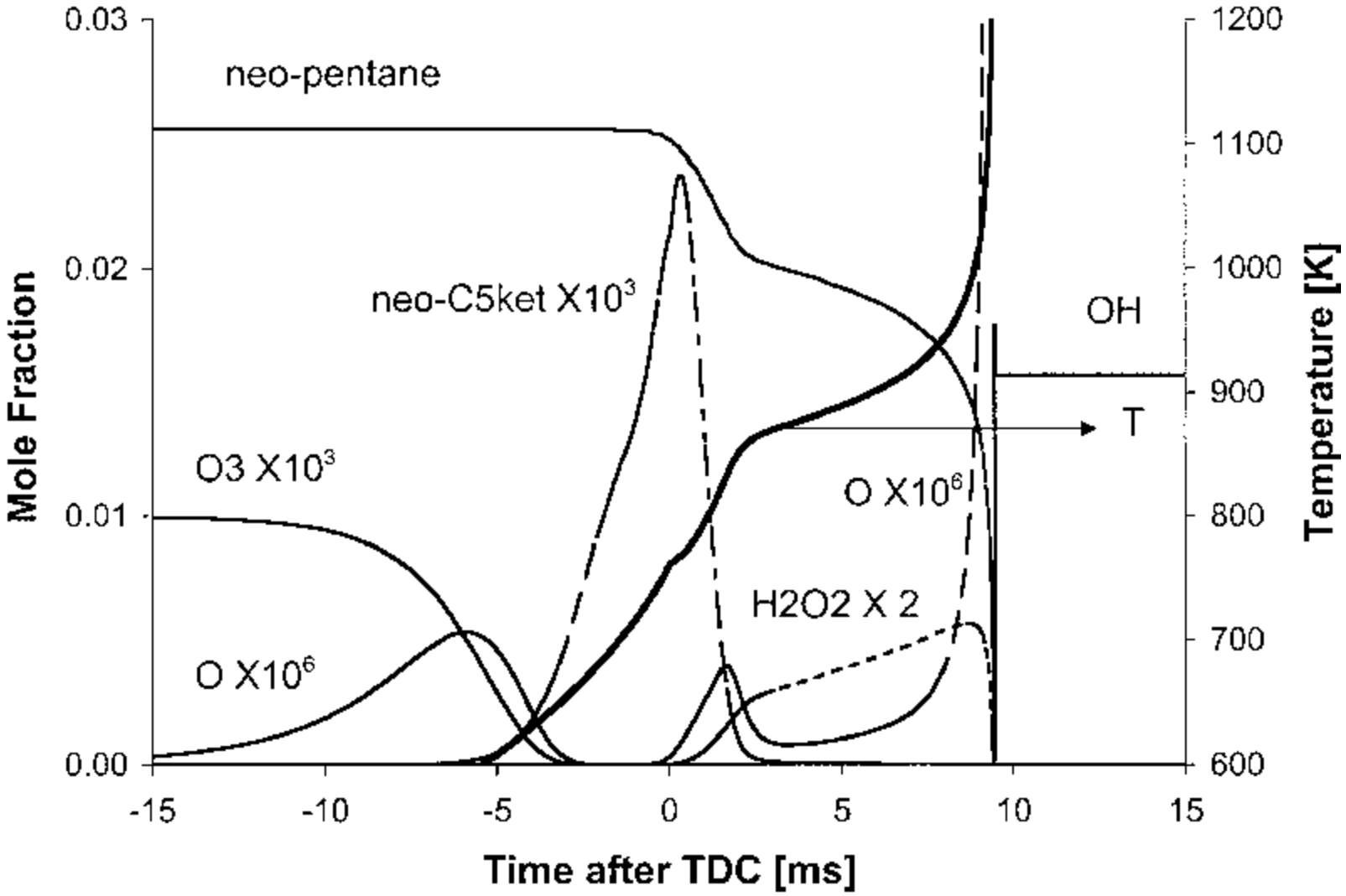


FIGURE 9b Flame profiles of major species in the methanol flame.




neo-pentane
Temperature
OH
H2O2 X4
Mole Fraction
Temperature [K]
Time after TDC [ms]
0.03
0.02
0.01
0.00
1200
1100
1000
900
800
700
600
-5
0
5
10
15


n-pentane
neopentane
iso-pentane
temperature (K)
1400
1200
1000
800
600
400
-20.0
-10.0
0.0
10.0
20.0
30.0
time after TDC (ms)


neo-pentane
neo-C5ket X10^3
OH
T
O3 X10^3
O X10^6
H2O2 X 2
O X10^6
Mole Fraction
Temperature [K]
Time after TDC [ms]
0.03
0.02
0.01
0.00
1200
1100
1000
900
800
700
600
-15
-10
-5
0
5
10
15

Calculations of H2/Air Laminar Flame Speeds

A Comprehensive Modeling Study of Hydrogen Oxidation

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ABSTRACT: A detailed kinetic mechanism has been developed to simulate the combustion of H_2/O_2 mixtures, over a wide range of temperatures, pressures, and equivalence ratios. Over the series of experiments numerically investigated, the temperature ranged from 298 to 2700 K, the pressure from 0.05 to 87 atm, and the equivalence ratios from 0.2 to 6.

Ignition delay times, flame speeds, and species composition data provide for a stringent test of the chemical kinetic mechanism, all of which are simulated in the current study with varying success. A sensitivity analysis was carried out to determine which reactions were dominating the H_2/O_2 system at particular conditions of pressure, temperature, and fuel/oxygen/diluent ratios. Overall, good agreement was observed between the model and the wide range of experiments simulated. © 2004 Wiley Periodicals, Inc. Int J Chem Kinet 36: 603–622, 2004

Table I Revised H_2/O_2 Reaction Mechanism (units: cm^3, mol, s, kcal, K)

	Reaction	A	n	E_a	Ref.
		H_2/O_2 chain reactions			
1	$\dot{H} + O_2 = \dot{O} + \dot{O}H$	1.91×10^{14}	0.00	16.44	[39]
2	$\dot{O} + H_2 = \dot{H} + \dot{O}H$	5.08×10^{4}	2.67	6.292	[40]
3	$\dot{O}H + H_2 = \dot{H} + H_2O$	2.16×10^{8}	1.51	3.43	[41]
4	$\dot{O} + H_2O = \dot{O}H + \dot{O}H$	2.97×10^{6}	2.02	13.4	[42]
		H_2/O_2 dissociation/recombination reactions			
5[a]	$H_2 + M = \dot{H} + \dot{H} + M$	4.57×10^{19}	−1.40	105.1	[43]
6[b]	$\dot{O} + \dot{O} + M = O_2 + M$	6.17×10^{15}	−0.50	0.00	[43]
7[c]	$\dot{O} + \dot{H} + M = O\dot{H} + M$	4.72×10^{18}	−1.00	0.00	[43]
8[d,e]	$\dot{H} + \dot{O}H + M = H_2O + M$	4.50×10^{22}	−2.00	0.00	[43] ×2.0
		Formation and consumption of $H\dot{O}_2$			
9[f,g]	$\dot{H} + O_2 + M = H\dot{O}_2 + M$	3.48×10^{16}	−0.41	−1.12	[44]
	$\dot{H} + O_2 = H\dot{O}_2$	1.48×10^{12}	0.60	0.00	[45]
10	$H\dot{O}_2 + \dot{H} = H_2 + O_2$	1.66×10^{13}	0.00	0.82	[6]
11	$H\dot{O}_2 + \dot{H} = \dot{O}H + \dot{O}H$	7.08×10^{13}	0.00	0.30	[6]
12	$H\dot{O}_2 + \dot{O} = \dot{O}H + O_2$	3.25×10^{13}	0.00	0.00	[46]
13	$H\dot{O}_2 + \dot{O}H = H_2O + O_2$	2.89×10^{13}	0.00	−0.50	[46]
		Formation and consumption of H_2O_2			
14[h]	$H\dot{O}_2 + H\dot{O}_2 = H_2O_2 + O_2$	4.2×10^{14}	0.00	11.98	[47]
	$H\dot{O}_2 + H\dot{O}_2 = H_2O_2 + O_2$	1.3×10^{11}	0.00	−1.629	[47]
15[i,f]	$H_2O_2 + M = \dot{O}H + O\dot{H} + M$	1.27×10^{17}	0.00	45.5	[48]
	$H_2O_2 = \dot{O}H + O\dot{H}$	2.95×10^{14}	0.00	48.4	[49]
16	$H_2O_2 + \dot{H} = H_2O + \dot{O}H$	2.41×10^{13}	0.00	3.97	[43]
17	$H_2O_2 + \dot{H} = H_2 + H\dot{O}_2$	6.03×10^{13}	0.00	7.95	[43] × 1.25
18	$H_2O_2 + \dot{O} = \dot{O}H + H\dot{O}_2$	9.55×10^{06}	2.00	3.97	[43]
19[h]	$H_2O_2 + \dot{O}H = H_2O + H\dot{O}_2$	1.0×10^{12}	0.00	0.00	[50]
	$H_2O_2 + \dot{O}H = H_2O + H\dot{O}_2$	5.8×10^{14}	0.00	9.56	[50]

[a] Efficiency factors are $H_2O = 12.0$; $H_2 = 2.5$.
[b] Efficiency factors are $H_2O = 12$; $H_2 = 2.5$; Ar = 0.83; He = 0.83.
[c] Efficiency factors are $H_2O = 12$; $H_2 = 2.5$; Ar = 0.75; He = 0.75.
[d] Original pre-exponential A factor is multiplied by 2 here.
[e] Efficiency factors are $H_2O = 12$; $H_2 = 0.73$; Ar = 0.38; He = 0.38.
[f] Troe parameters: reaction 9, $a = 0.5$, $T^{***} = 1.0 \times {}^{-30}$, $T^{*} = 1.0 \times 10^{+30}$, $T^{**} = 1.0 \times 10^{+100}$; reaction 15, $a = 0.5$, $T^{***} = 1.0\times{}^{-30}$, $T^{*} = 1.0 \times 10^{+30}$.
[g] Efficiency factors are $H_2 = 1.3$; $H_2O = 14$; Ar = 0.67; He = 0.67.
[h] Reactions 14 and 19 are expressed as the sum of the two rate expressions.
[i] Efficiency factors are $H_2O = 12$; $H_2 = 2.5$; Ar = 0.45; He = 0.45;

Table II ΔH_f (298.15 K) kcal mol^{-1}, S(300 K) and C_p(T) in cal mol^{-1} K^{-1}

Species	$\Delta H_f^{298\,K}$	$S^{300\,K}$	Specific heat capacity, C_p					
			300 K	400 K	500 K	800 K	1000 K	1500 K
$\dot{H}$	52.098	27.422	4.968	4.968	4.968	4.968	4.968	4.968
$\dot{O}$	59.56	38.500	5.232	5.139	5.080	5.016	4.999	4.982
$\dot{O}H$	8.91	43.933	6.947	6.992	7.036	7.199	7.341	7.827
H_2	0.00	31.256	6.902	6.960	6.997	7.070	7.209	7.733
O_2	0.00	49.050	7.010	7.220	7.437	8.068	8.350	8.721
H_2O	−57.77	45.154	8.000	8.231	8.446	9.223	9.875	11.258
$H\dot{O}_2$	3.00	54.809	8.349	8.886	9.465	10.772	11.380	12.484
H_2O_2	−32.53	55.724	10.416	11.446	12.346	14.294	15.213	16.851
N_2	0.00	45.900	6.820	7.110	7.520	7.770	8.280	8.620
Ar	0.00	37.000	4.900	4.900	4.900	4.900	4.900	4.900
He	0.00	30.120	4.970	4.970	4.970	4.970	4.970	4.970

```
 elements
c h n o ar he
end

 species
 h          h2          o          o2          oh
 h2o          n2          ho2          h2o2          ar
 co          co2          ch4          c2h6          he
 !
 end
```

39. Pirraglia, A. N.; Michael, J. V.; Sutherland, J. W.; Klemm, R. B. J Phys Chem 1989, 93, 282–291.
40. Sutherland, J. W.; Michael, J. V.; Pirraglia, A. N.; Nesbitt, F. L.; Klemm, R. B. Proc Combust Inst 1986, 21, 929–941.
41. Michael, J. V.; Sutherland, J. W. J Phys Chem 1988, 92, 2853–3857.
42. Sutherland, J. W.; Patterson, P. M.; Klemm, R. B. Proc Combust Inst 1990 23, 51–57.

Table I Revised H_2/O_2 Reaction Mechanism (units: cm^3, mol, s, kcal, K)

	Reaction	A	n	E_a	Ref.
		H_2/O_2 chain reactions			
1	$\dot{H} + O_2 = \dot{O} + \dot{O}H$	1.91×10^{14}	0.00	16.44	[39]
2	$\dot{O} + H_2 = \dot{H} + \dot{O}H$	5.08×10^{4}	2.67	6.292	[40]
3	$\dot{O}H + H_2 = \dot{H} + H_2O$	2.16×10^{8}	1.51	3.43	[41]
4	$\dot{O} + H_2O = \dot{O}H + \dot{O}H$	2.97×10^{6}	2.02	13.4	[42]

h+o2<=>o+oh 3.547e+15 -0.406 1.660e+04
!rev/ 1.027e+13 -0.015 -1.330e+02 /
o+h2<=>h+oh 5.080e+04 2.670 6.292e+03
!rev/ 2.637e+04 2.651 4.880e+03 /
oh+h2<=>h+h2o 2.160e+08 1.510 3.430e+03
!rev/ 2.290e+09 1.404 1.832e+04 /
o+h2o<=>oh+oh 2.970e+06 2.020 1.340e+04
!rev/ 1.454e+05 2.107 -2.904e+03 /

An Updated Comprehensive Kinetic Model of Hydrogen Combustion

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ABSTRACT: A comprehensively tested H_2/O_2 chemical kinetic mechanism based on the work of Mueller et al. [1] and recently published kinetic and thermodynamic information is presented. The revised mechanism is validated against a wide range of experimental conditions, including those found in shock tubes, flow reactors, and laminar premixed flame. Excellent agreement of the model predictions with the experimental observations demonstrates that the mechanism is comprehensive and has good predictive capabilities for different experimental systems, including new results published subsequent to the work of Mueller et al. [1], particularly high-pressure laminar flame speed and shock tube ignition results. The reaction $H + OH + M$ is found to be primarily significant only to laminar flame speed propagation predictions at high pressure. All experimental hydrogen flame speed observations can be adequately fit using any of the several transport coefficient estimates presently available in the literature for the hydrogen/oxygen system simply by adjusting the rate parameters for this reaction within their present uncertainties.
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Table I Detailed H_2/O_2 Reaction Mechanism

		A	n	E	Reference
H_2/O_2 chain reactions					
1. $H + O_2 = O + OH$		3.55×10^{15}	−0.41	16.6	[16]
2. $O + H_2 = H + OH$		5.08×10^{4}	2.67	6.29	[44]
3. $H_2 + OH = H_2O + H$		2.16×10^{8}	1.51	3.43	[45]
4. $O + H_2O = OH + OH$		2.97×10^{6}	2.02	13.4	[46]
H_2/O_2 dissociation/recombination reactions					
5. $H_2 + M = H + H + M^a$		4.58×10^{19}	−1.40	104.38	[47]
$H_2 + Ar = H + H + Ar$		5.84×10^{18}	−1.10	104.38	[47]
$H_2 + He = H + H + He$		5.84×10^{18}	−1.10	104.38	See text
6. $O + O + M = O_2 + M^a$		6.16×10^{15}	−0.50	0.00	[47]
$O + O + Ar = O_2 + Ar$		1.89×10^{13}	0.00	−1.79	[47]
$O + O + He = O_2 + He$		1.89×10^{13}	0.00	−1.79	See text
7. $O + H + M = OH + M^a$		4.71×10^{18}	−1.0	0.00	[47]
8. $H + OH + M = H_2O + M^b$		3.8×10^{22}	−2.00	0.00	See text
Formation and consumption of HO_2					
9. $H + O_2 + M = HO_2 + M^c$	k_0	6.37×10^{20}	−1.72	0.52	[19]
$H + O_2 + M = HO_2 + M^d$	k_0	9.04×10^{19}	−1.50	0.49	[19]
	k_∞	1.48×10^{12}	0.60	0.00	[48]
10. $HO_2 + H = H_2 + O_2$		1.66×10^{13}	0.00	0.82	[1]
11. $HO_2 + H = OH + OH$		7.08×10^{13}	0.00	0.30	[1]
12. $HO_2 + O = OH + O_2$		3.25×10^{13}	0.00	0.00	[34]
13. $HO_2 + OH = H_2O + O_2$		2.89×10^{13}	0.00	−0.50	[34]
Formation and consumption of H_2O_2					
14. $HO_2 + HO_2 = H_2O_2 + O_2^e$		4.20×10^{14}	0.00	11.98	[49]
$HO_2 + HO_2 = H_2O_2 + O_2$		1.30×10^{11}	0.00	−1.63	
15. $H_2O_2 + M = OH + OH + M^f$	k_0	1.20×10^{17}	0.00	45.5	[50]
	k_∞	2.95×10^{14}	0.00	48.4	[51]
16. $H_2O_2 + H = H_2O + OH$		2.41×10^{13}	0.00	3.97	[47]
17. $H_2O_2 + H = H_2 + HO_2$		4.82×10^{13}	0.00	7.95	[47]
18. $H_2O_2 + O = OH + HO_2$		9.55×10^{6}	2.00	3.97	[47]
19. $H_2O_2 + OH = H_2O + HO_2^e$		1.00×10^{12}	0.00	0.00	[52]
$H_2O_2 + OH = H_2O + HO_2$		5.8×10^{14}	0.00	9.56	

16. Hessler, J. P. J Phys Chem A 1998, 102, 4517.
17. Troe, J. In Proceedings of the Combustion Institute, The Combustion Institute, Pittsburgh, PA, 2000; pp. 28, 1463.
18. Bates, R. W.; Golden, D. M.; Hanson, R. K.; Bowman, C. T. Phys Chem Chem Phys 2001, 3, 2337.
19. Michael, J. V.; Su, M. C.; Sutherland, J. W.; Carroll, J. J.; Wagner, A. F. J Phys Chem A 2002, 106, 5297.

44. Sutherland, J. W.; Michael, J. V.; Pirraglia, A. N.; Nesbitt, F. L.; Klemm R. B. In 21st Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA, 1986; p. 929.
45. Michael, J. V.; Sutherland, J. W. J Phys Chem 1988, 92, 3853.
46. Sutherland, J. W.; Patterson, P. M.; Klemm, R. B. In 23rd Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA, 1990; p. 51.
47. Tsang, W.; Hampson, R. F. J Phys Chem Ref Data 1986, 15, 1087.
48. Cobos, C. J.; Hippler, H.; Troe, J. J Phys Chem 1985, 89, 342.
49. Hippler, H.; Troe, J.; Willner, J. J Chem Phys 1990, 93, 1755.
50. Warnatz, J. In Combustion Chemistry; Gardiner, W. C. (Ed.); Springer-Verlag: New York, 1985.
51. Brouwer, L.; Cobos, C. J.; Troe, J.; Dubal, H. R.; Crim, F. F. J Chem Phys 1985, 86, 6171.
52. Hippler, H.; Troe, J. Chem Phys Lett 1992, 192, 333.
53. Vandooren, J.; Van Tiggelen, P. J. Combust Flame 1997, 109, 647.
54. Ruscic, B. In 25th Annual Combustion Research Conference, Arlie Conference Center, Warrenton, VA, June 2004; p. 253; http://cmcs.org.

H_2/O_2 dissociation/recombination reactions

5[a]	$H_2 + M = \dot{H} + \dot{H} + M$	4.57×10^{19}	−1.40	105.1	[43]
6[b]	$\dot{O} + \dot{O} + M = O_2 + M$	6.17×10^{15}	−0.50	0.00	[43]
7[c]	$\dot{O} + \dot{H} + M = O\dot{H} + M$	4.72×10^{18}	−1.00	0.00	[43]
8[d,e]	$\dot{H} + \dot{O}H + M = H_2O + M$	4.50×10^{22}	−2.00	0.00	[43] ×2.0

h2+m<=>h+h+m 4.577e+19 -1.400 1.044e+05
!rev/ 1.145e+20 -1.676 8.200e+02 /
h2/2.5/ h2o/12/ co/1.9/ co2/3.8/

43. Tsang, W.; Hampson, R. F. J Phys Chem Ref Data 1986, 15, 1087–1279.

o2+m<=>o+o+m 4.420e+17 -0.634 1.189e+05
!rev/ 6.165e+15 -0.500 0.000e+00 /
h2/2.5/ h2o/12/ ar/.83/ co/1.9/ co2/3.8/
ch4/2/ c2h6/3/ he/.83/

oh+m<=>o+h+m 9.780e+17 -0.743 1.021e+05
!rev/ 4.714e+18 -1.000 0.000e+00 /
h2/2.5/ h2o/12/ ar/.75/ co/1.5/ co2/2/ ch4/2/
c2h6/3/ he/.75/

h2o+m<=>h+oh+m 1.907e+23 -1.830
1.185e+05
!rev/ 4.500e+22 -2.000 0.000e+00 /
h2/.73/ h2o/12/ ar/.38/ ch4/2/ c2h6/3/ he/.38/

Formation and consumption of HO_2

9[f,g]	$\dot{H} + O_2 + M = H\dot{O}_2 + M$	3.48×10^{16}	−0.41	−1.12	[44]
	$\dot{H} + O_2 = H\dot{O}_2$	1.48×10^{12}	0.60	0.00	[45]
10	$H\dot{O}_2 + \dot{H} = H_2 + O_2$	1.66×10^{13}	0.00	0.82	[6]
11	$H\dot{O}_2 + \dot{H} = \dot{O}H + \dot{O}H$	7.08×10^{13}	0.00	0.30	[6]
12	$H\dot{O}_2 + \dot{O} = \dot{O}H + O_2$	3.25×10^{13}	0.00	0.00	[46]
13	$H\dot{O}_2 + \dot{O}H = H_2O + O_2$	2.89×10^{13}	0.00	−0.50	[46]

h+o2(+m)<=>ho2(+m) 1.475e+12 0.600 0.000e+00
!!rev/ 3.091e+12 0.528 4.887e+04 /
low / 3.4820e+16 -4.1100e-01 -1.1150e+03 /
troe / 5.0000e-01 1.0000e-30 1.0000e+30 1.0000e+10 / !troe fall-off reaction
h2/1.3/ h2o/14/ ar/.67/ co/1.9/ co2/3.8/ ch4/2/ c2h6/3/ he/.67/

ho2+h<=>h2+o2 1.660e+13 0.000 8.230e+02
!rev/ 3.166e+12 0.348 5.551e+04 /

ho2+h<=>oh+oh 7.079e+13 0.000 2.950e+02
!rev/ 2.028e+10 0.720 3.684e+04 /

ho2+o<=>oh+o2 3.250e+13 0.000 0.000e+00
!rev/ 3.217e+12 0.329 5.328e+04 /

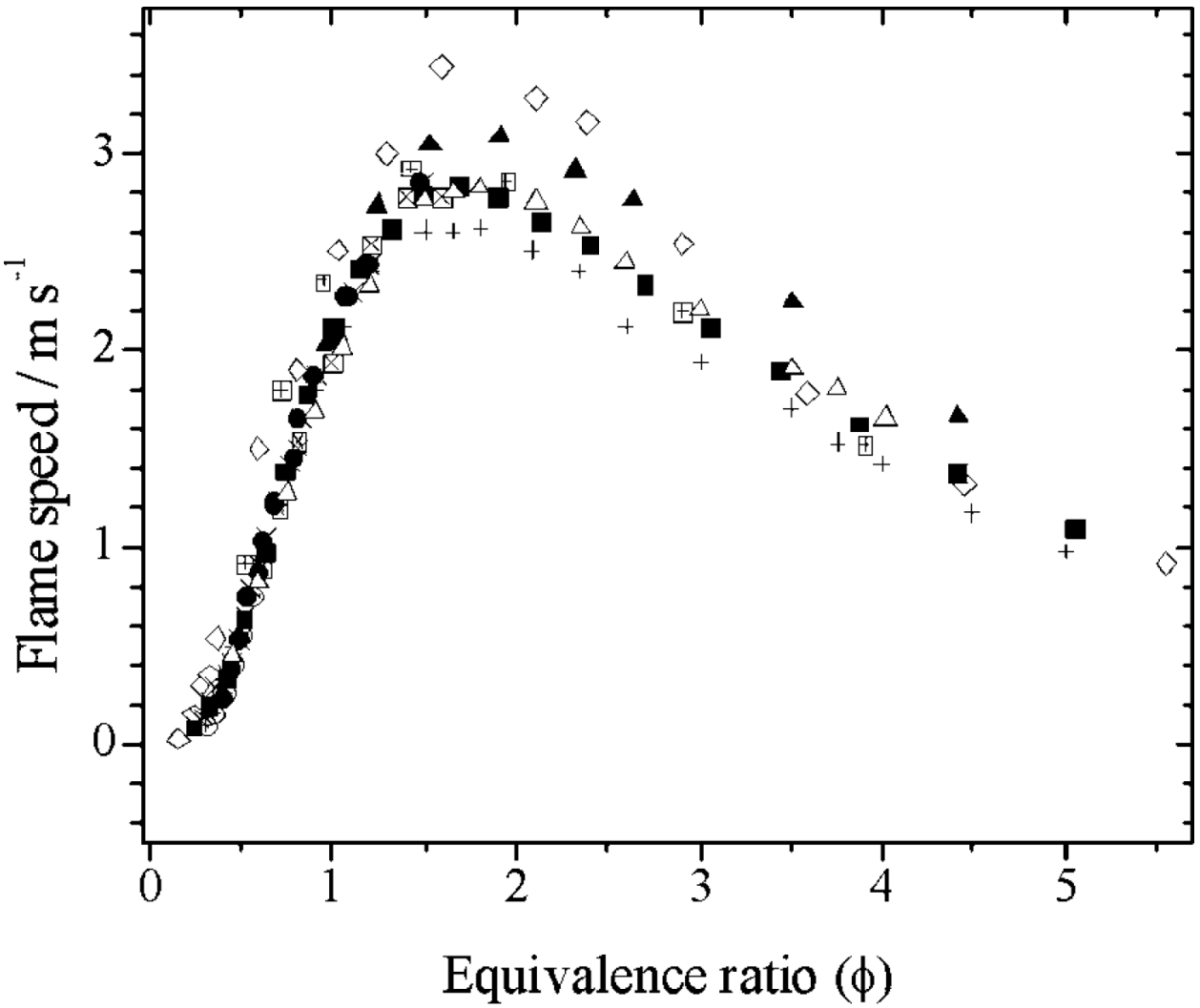
ho2+oh<=>h2o+o2 1.973e+10 0.962 -3.284e+02
!rev/ 3.989e+10 1.204 6.925e+04 /

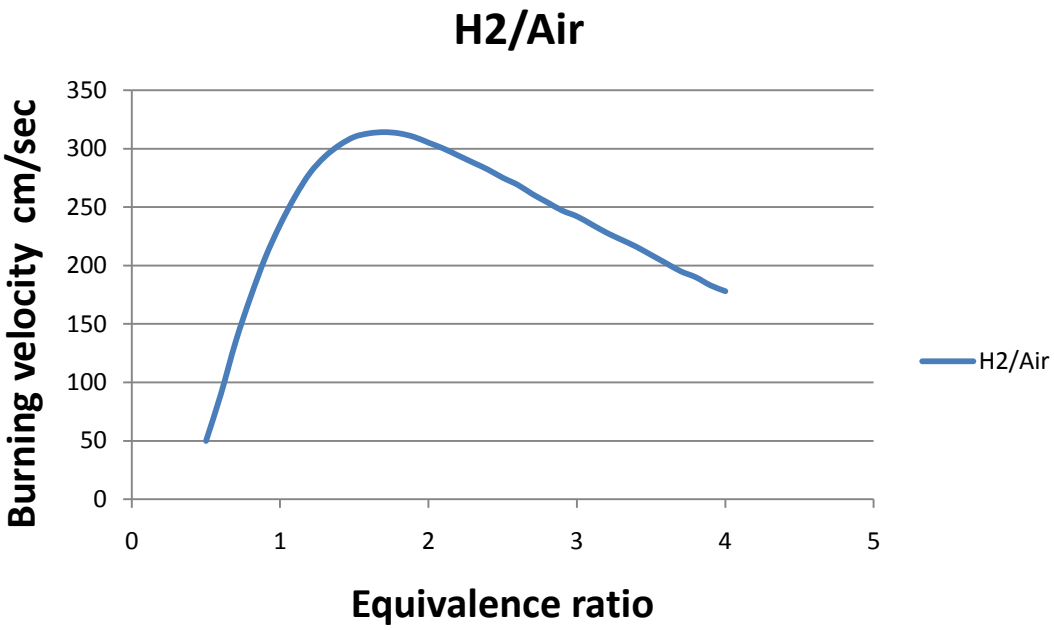
	Formation and consumption of H_2O_2				
14[h]	$H\dot{O}_2 + H\dot{O}_2 = H_2O_2 + O_2$	4.2×10^{14}	0.00	11.98	[47]
	$H\dot{O}_2 + H\dot{O}_2 = H_2O_2 + O_2$	1.3×10^{11}	0.00	−1.629	[47]
15[i.f]	$H_2O_2 + M = \dot{O}H + O\dot{H} + M$	1.27×10^{17}	0.00	45.5	[48]
	$H_2O_2 = \dot{O}H + O\dot{H}$	2.95×10^{14}	0.00	48.4	[49]
16	$H_2O_2 + \dot{H} = H_2O + \dot{O}H$	2.41×10^{13}	0.00	3.97	[43]
17	$H_2O_2 + \dot{H} = H_2 + H\dot{O}_2$	6.03×10^{13}	0.00	7.95	[43] × 1.25
18	$H_2O_2 + \dot{O} = \dot{O}H + H\dot{O}_2$	9.55×10^{06}	2.00	3.97	[43]
19[h]	$H_2O_2 + \dot{O}H = H_2O + H\dot{O}_2$	1.0×10^{12}	0.00	0.00	[50]
	$H_2O_2 + \dot{O}H = H_2O + H\dot{O}_2$	5.8×10^{14}	0.00	9.56	[50]

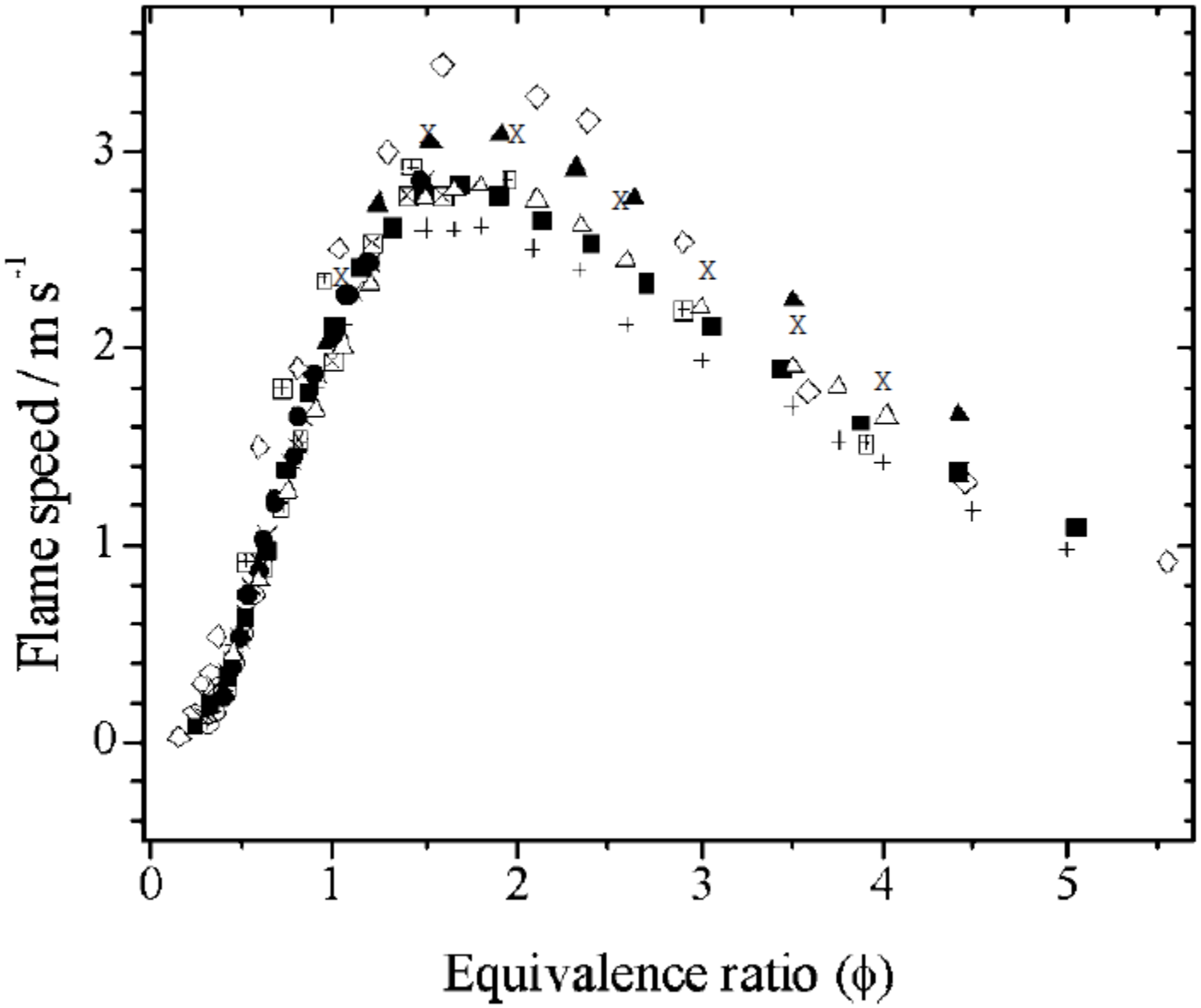
```
h2o2+o2<=>ho2+ho2 1.136e+16 -0.347 4.973e+04
!rev/ 1.030e+14 0.000 1.104e+04 /
dup
h2o2+o2<=>ho2+ho2 2.141e+13 -0.347 3.728e+04
!rev/ 1.940e+11 0.000 -1.409e+03 /
dup
h2o2(+m)<=>oh+oh(+m) 2.951e+14 0.000 4.843e+04
!!rev/ 3.656e+08 1.140 -2.584e+03 /
low / 1.2020e+17 0.0000e+00 4.5500e+04 /
troe / 5.0000e-01 1.0000e-30 1.0000e+30 1.0000e+10 / !troe fall-off reaction
h2/2.5/ h2o/12/ ar/.64/ co/1.9/ co2/3.8/ ch4/2/ c2h6/3/ he/.64/
h2o2+h<=>h2o+oh 2.410e+13 0.000 3.970e+03
!rev/ 1.265e+08 1.310 7.141e+04 /
h2o2+h<=>h2+ho2 2.150e+10 1.000 6.000e+03
!rev/ 3.716e+07 1.695 2.200e+04 /
h2o2+o<=>oh+ho2 9.550e+06 2.000 3.970e+03
!rev/ 8.568e+03 2.676 1.856e+04 /
h2o2+oh<=>h2o+ho2 2.000e+12 0.000 4.272e+02
!rev/ 3.665e+10 0.589 3.132e+04 /
dup
h2o2+oh<=>h2o+ho2 1.700e+18 0.000 2.941e+04
!rev/ 3.115e+16 0.589 6.030e+04 /
dup
!
```

Transport coefficients for species in flames

```
!
ar              0   136.500     3.330     0.000     0.000     0.000
c2h6            2   247.500     4.350     0.000     0.000     1.500 ! nmm
ch4             2   141.400     3.746     0.000     2.600    13.000
co              1    98.100     3.650     0.000     1.950     1.800
co2             1   244.000     3.763     0.000     2.650     2.100
h2o             2   572.400     2.605     1.844     0.000     4.000
h2o2            2   107.400     3.458     0.000     0.000     3.800
he              0    10.200     2.576     0.000     0.000     0.000 ! *
n2              1    97.530     3.621     0.000     1.760     4.000
o               0    80.000     2.750     0.000     0.000     0.000
o2              1   107.400     3.458     0.000     1.600     3.800
oh              1    80.000     2.750     0.000     0.000     0.000
h2              1    38.000     2.920     0.000     0.790   280.000
h               0   145.000     2.050     0.000     0.000     0.000
ho2             2   107.400     3.458     0.000     0.000     1.000 ! *
```


Flame speed / m s-1
0
1
2
3
0
1
2
3
4
5
Equivalence ratio (ϕ)


H2/Air
Burning velocity cm/sec
350
300
250
200
150
100
50
0
0
1
2
3
4
5
Equivalence ratio
H2/Air


Flame speed / m s-1
0
1
2
3
0
1
2
3
4
5
Equivalence ratio (ϕ)

Kinetic Modeling of Autoignition: Engine Knock, HCCI and fuel economy

Charles K. Westbrook
Lawrence Livermore National Laboratory

CEFRC

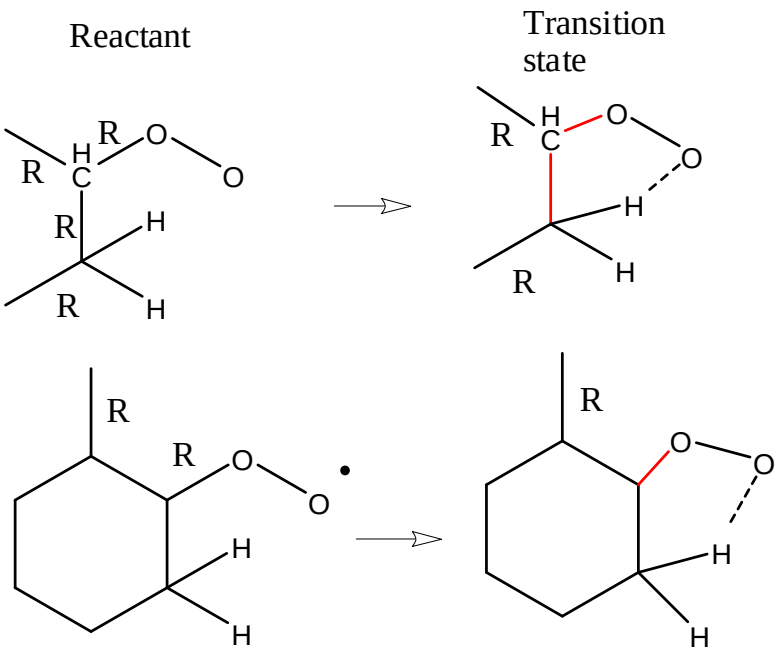
June 2010

The fuel situation in 1922 looks pretty familiar

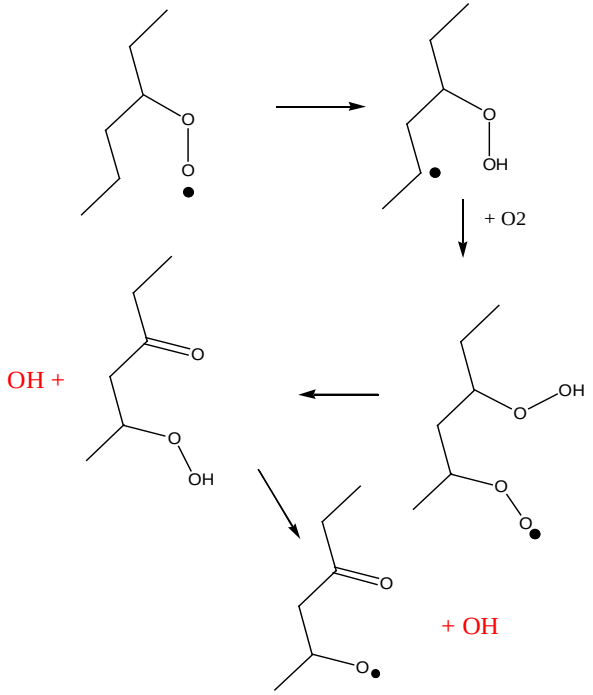
- Thomas Midgley, Chief of Fuels Section for General Motors, 1922
  - US Geological Survey -- 20 years left of petroleum reserves
  - Production of 5 billion gallons of fuel in 1921

- Potential new sources of petroleum
  - Oil shale
  - Oils from coal
  - Alcohol fuels from biomass
- Higher efficiency a high priority for conservation reasons
  - People will not buy a car “lacking in acceleration and hill climbing”
  - Solution is higher compression ratio, then at about 4.25 : 1
  - Obstacle is engine knock, whose origin is unknown
  - Result was development of TEL as antiknock
  - Phenomenological picture with no fundamental understanding

Explanation of engine knock, ON, antiknocks, diesel ignition, and HCCI ignition came in the 1990's from DOE/BES theoretical chemistry and supercomputing and EERE knock working group



Alkylperoxy radical isomerization rates are different in paraffin and cyclic paraffin hydrocarbons



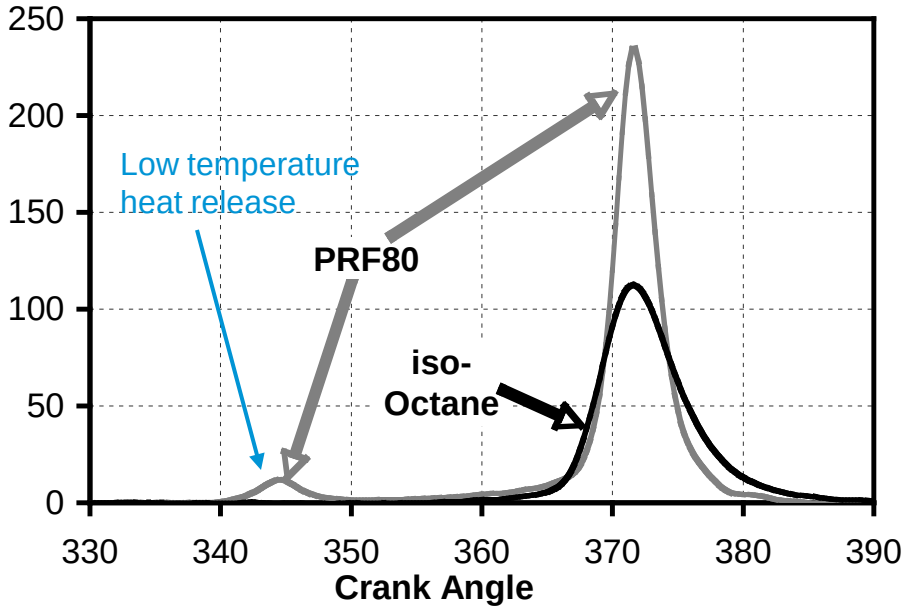
Low temperature chain branching paths

Most work has been done for alkane fuels, and many questions remain for aromatics, cyclic paraffins, large olefins

Chemistry of alkylperoxy radical isomerization has reached street-level awareness

- Heat release rates in HCCI combustion of two fuels, iso-octane with no low T heat release, and PRF-80 with two stage heat release

- We are seeing researchers debating which makes the better HCCI fuel. Both debaters have completely accepted the existence and source of the low T reactivity.



This is serious, black-belt fuel chemistry and computational chemistry

Results from experiments of Sjöberg and Dec, SNL 2006

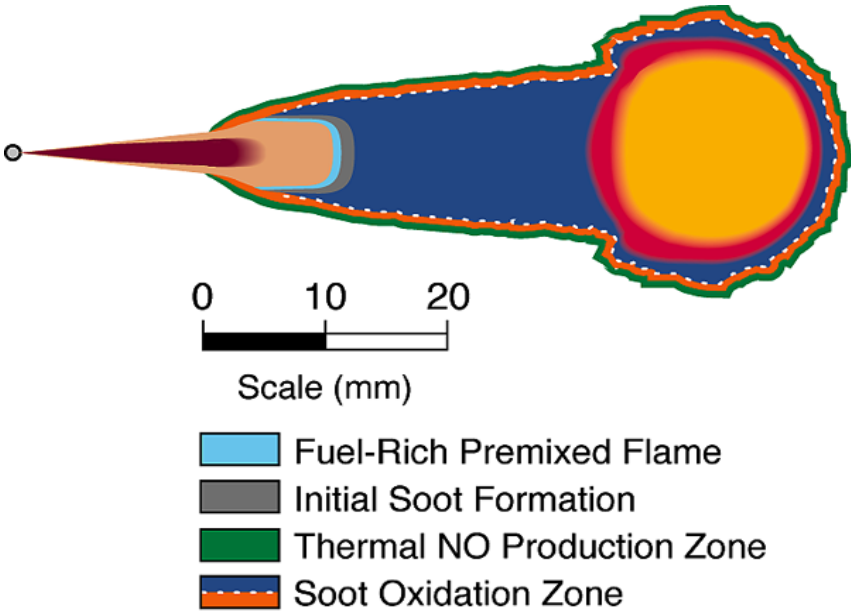
New conceptual picture developed 1990 - 1997

- Extended role of multiple advanced laser diagnostic techniques
- Team led by John Dec, SNL
- Explains
  - 2 stages in diesel burning
  - ignition and cetane
  - sooting logic
- This is serious, black-belt optical physics science

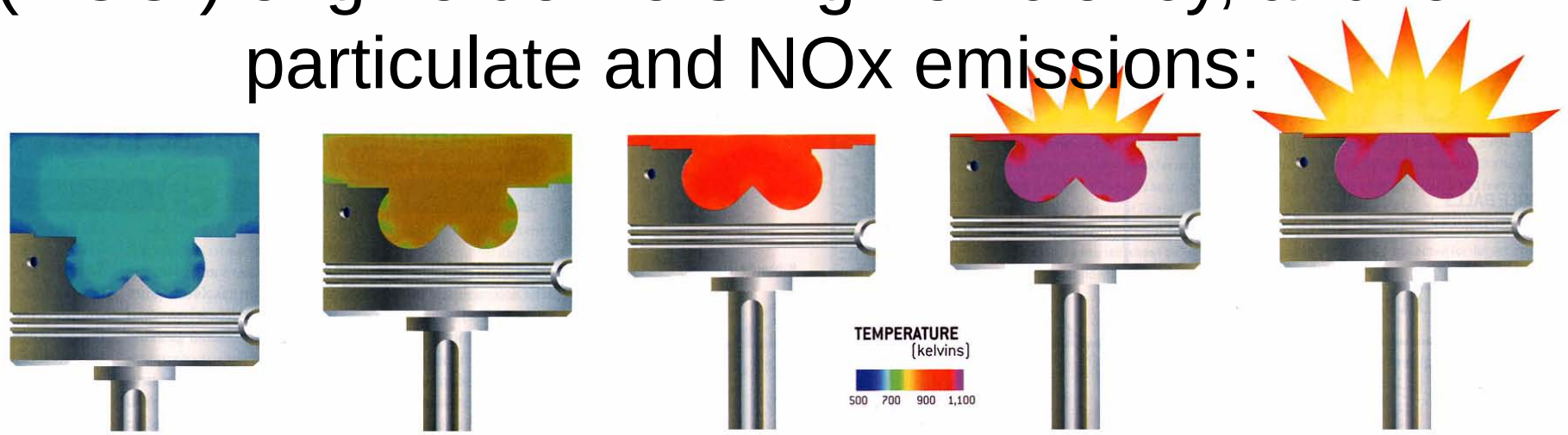
Lots still unknown,

soot chemistry, spray dynamics

fuel effects, etc.



Homogeneous Charge Compression Ignition (HCCI) engine delivers high efficiency, and low particulate and NOx emissions:



Advantages:

- low NO_x
- low particulate matter
- high efficiency

Technical challenges:

- engine control
- multi-cylinder balancing
- startability
- low power output
- high HC and CO emissions

Have we have come a long way since 1922?

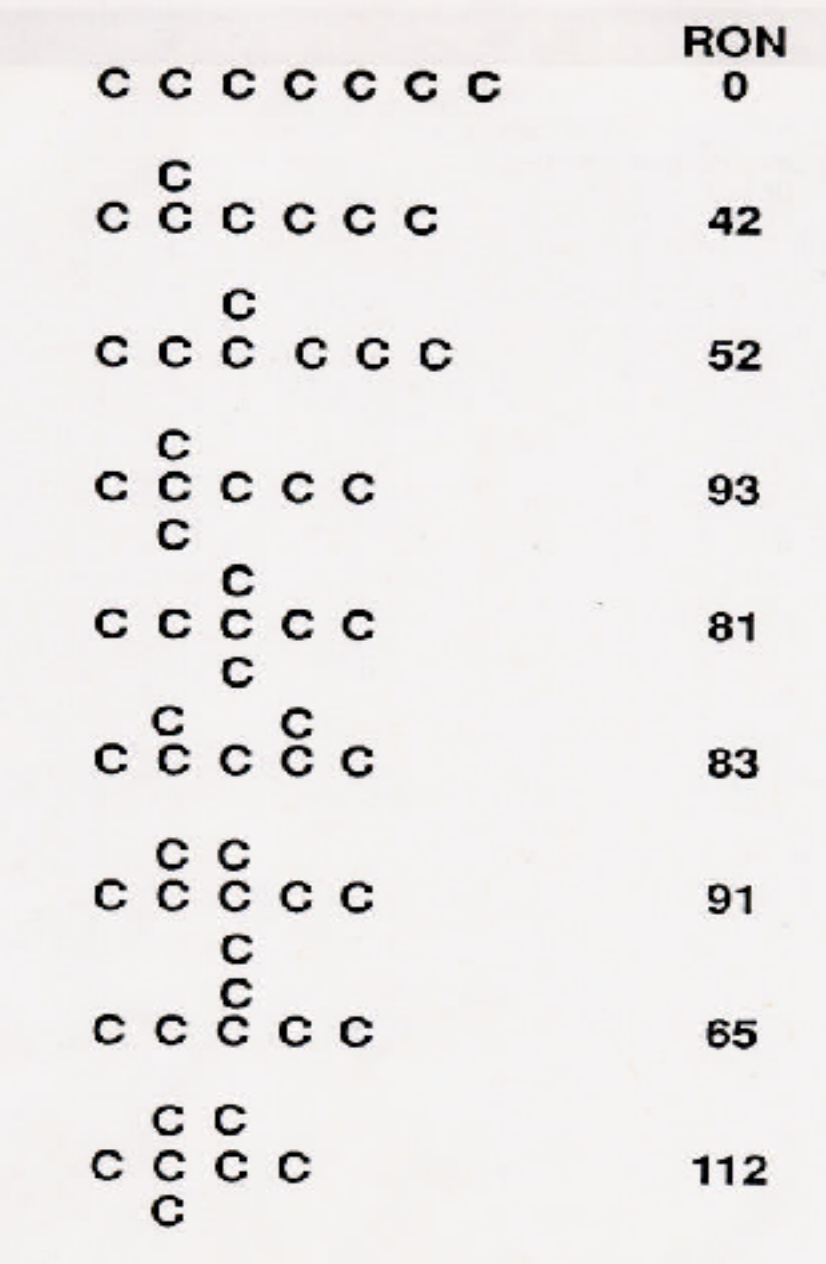
- We still are looking to oil shale, oil sands and biomass for the future
- However, our understanding of knocking, antiknocks and low T chemistry has grown enormously
  - e.g., Current engine designers debate how much low T heat release is best, and take its sources for granted
- Conceptual model for diesel combustion has led to breakthroughs
  - e.g., Understanding of anti-sooting action of oxygenates
- Entirely new concept engine (HCCI) is being developed

Great majority of this progress is due to basic science understanding, e.g., optical diagnostics, quantum chemistry and electronic structure theory, high performance computing, etc.

We have used basic science advances to make big jumps in understanding, but we are back to trial and error in many cases

Octane numbers of heptanes are due exclusively to their different molecular structures

This was recognized in 1920's but no explanation in fundamental terms had been provided prior to our work



Engine knock is an undesirable thermal ignition

We focus on three distinct chain branching pathways

1) $H + O_2 \rightarrow O + OH$ High T

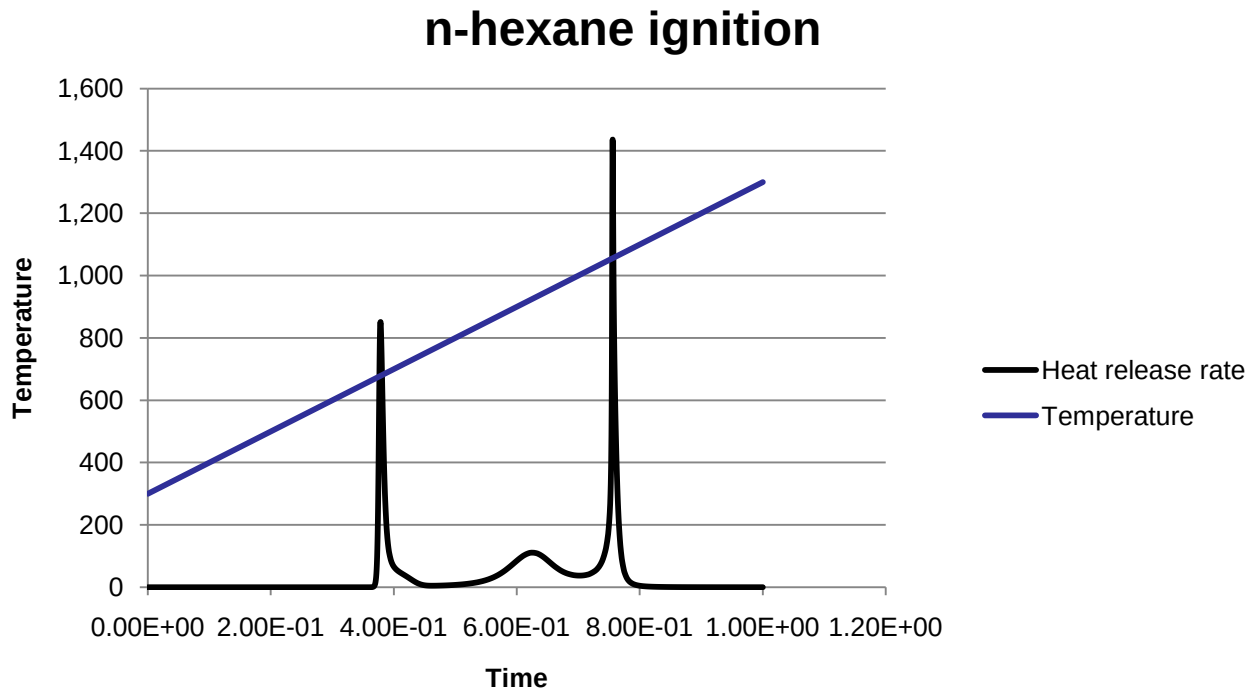
2) $H + O_2 + M \rightarrow HO_2 + M$ Medium T

$RH + HO_2 \rightarrow R + H_2O_2$

$H_2O_2 + M \rightarrow OH + OH + M$

3) $R + O_2 \rightarrow RO_2$ Low T

$RO_2 \rightarrow QOOH \rightarrow O_2QOOH \rightarrow$ 3+ radicals


n-hexane ignition
1,600
1,400
1,200
1,000
800
600
400
200
0
Temperature
0.00E+00
2.00E-01
4.00E-01
6.00E-01
8.00E-01
1.00E+00
1.20E+00
Time
Heat release rate
Temperature

Chain branching at high temperatures

$$H + O_2 \rightarrow O + OH$$

- Activation energy is relatively high (16.8 kcal/mol)
- H atoms produced by thermal decomposition of radicals
  e.g. C_2H_5 , C_2H_3 , HCO, iC_3H_7 , etc.
  Activation energies relatively high (~ 30 kcal/mol)
- Therefore this sequence requires high temperatures
- Illustrated best by shock tube experiments

Chain branching often occurs over a series of reactions

$$H + O_2 + M \rightarrow HO_2 + M$$

$$RH + HO_2 \rightarrow R + H_2O_2$$

$$H_2O_2 + M \rightarrow OH + OH + M$$

- At temperatures below about 900K, H_2O_2 decomposition is inhibited, leading to degenerate chain branching
- At higher temperatures, H_2O_2 decomposes as quickly as it is formed, leading to conventional chain branching
- Other low temperature chain branching paths can be much longer than this sequence (see below)

H_2O_2 decomposes at a fairly distinct temperature

- Reaction consuming H_2O_2 is:

$$H_2O_2 + M \rightarrow OH + OH + M$$

$$k_+ = 1.2 \times 10^{17} \times \exp(-45500/RT)$$

- Resulting differential equation is:

$$\frac{d[H_2O_2]}{dt} = -[H_2O_2][M]\,k_+$$

Characteristic time for H_2O_2 decomposition

$$\frac{d[H_2O_2]}{dt} = -[H_2O_2][M]k_+$$

define $\tau = [H_2O_2] / (d[H_2O_2]/dt)$

$\tau = 1 / (k_+ [M])$

$\tau = 8.3 \times 10^{-18} \times \exp(22750/T) \times [M]^{-1}$

At RCM conditions, with [M] ~ 1×10^{-4} mol-cm^{-3}, values of τ are approximately:

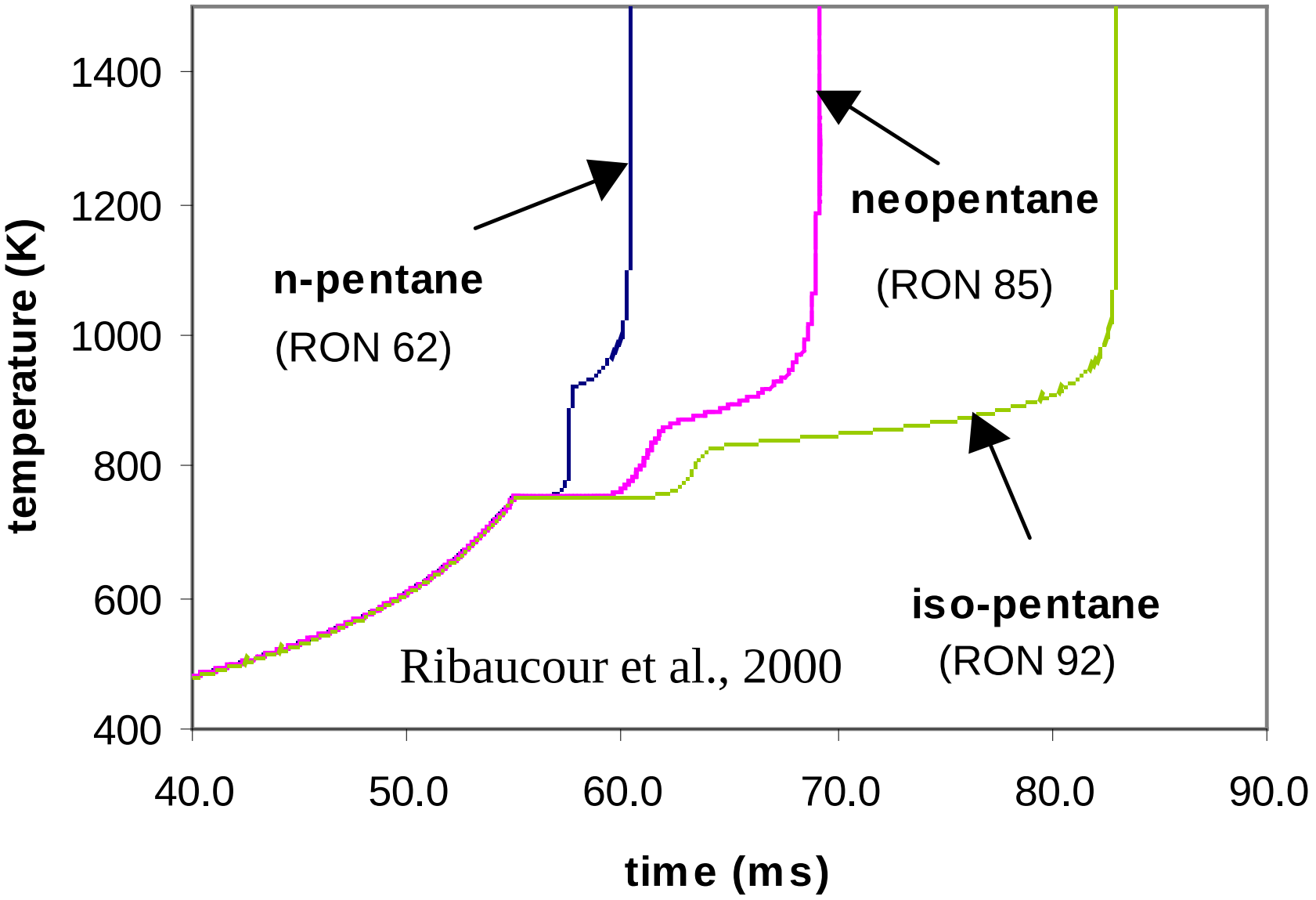
7.8 ms at 900K 640 μs at 1000K 80 μs at 1100K

At higher compressions (pressures), values of τ are smaller at comparable temperatures

Rapid compression machine and some turbulent flow reactor experiments are controlled by H_2O_2 decomposition

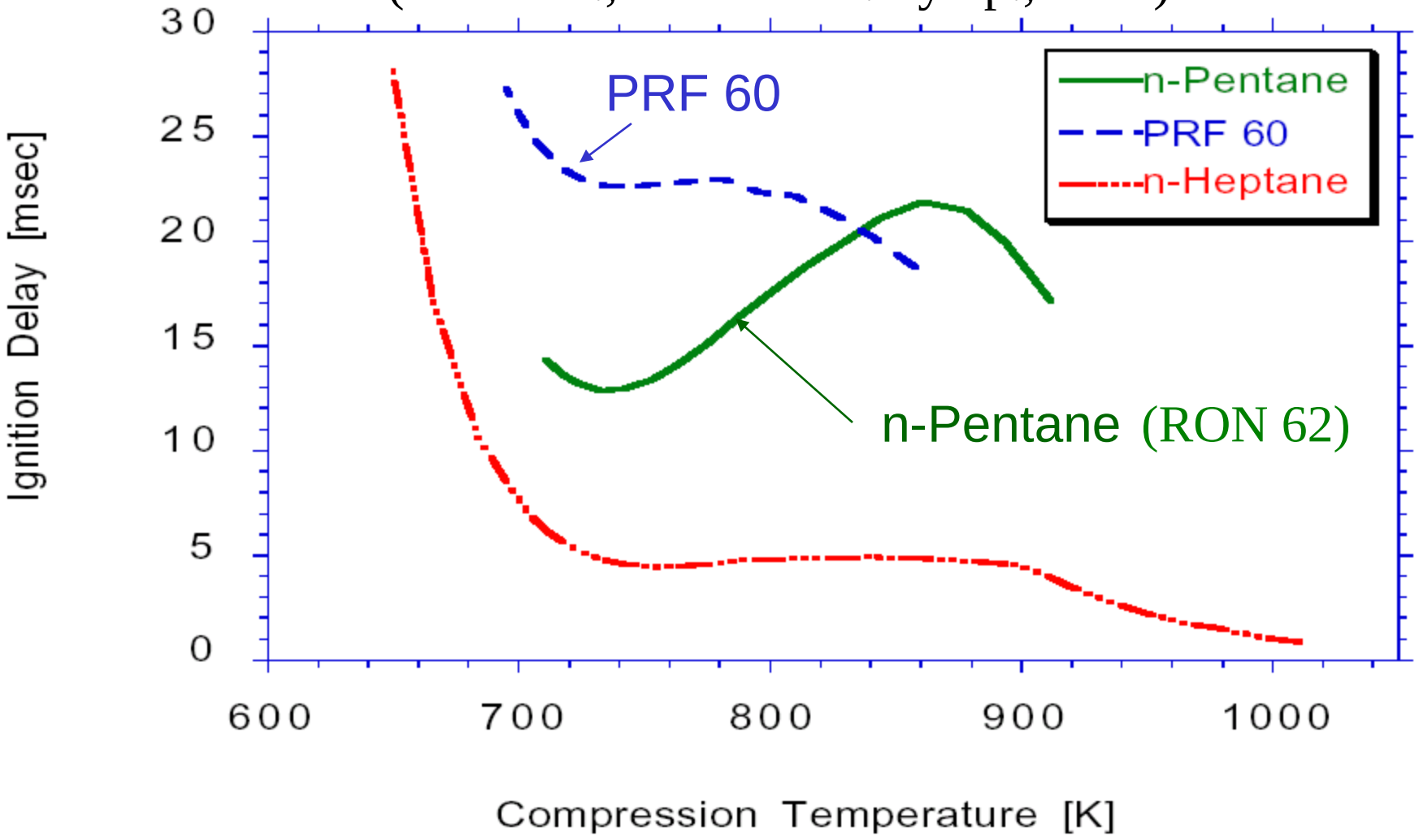
- Rapid compression machine (RCM) usually operates in a degenerate branching mode
  - H_2O_2 produced at temperatures lower than 900K
  - When system reaches H_2O_2 decomposition temperature, ignition is observed
- Many turbulent flow reactor experiments operate at temperatures between 900 - 1100K where H_2O_2 decomposes as quickly as it is produced

Pentane isomers ignite in order of their octane numbers



n-Pentane (RON 62) and PRF 60 show different behavior in rapid compression machine

(Cox et al., 26th Comb. Symp., 1996)



Role of H_2O_2 decomposition is very general

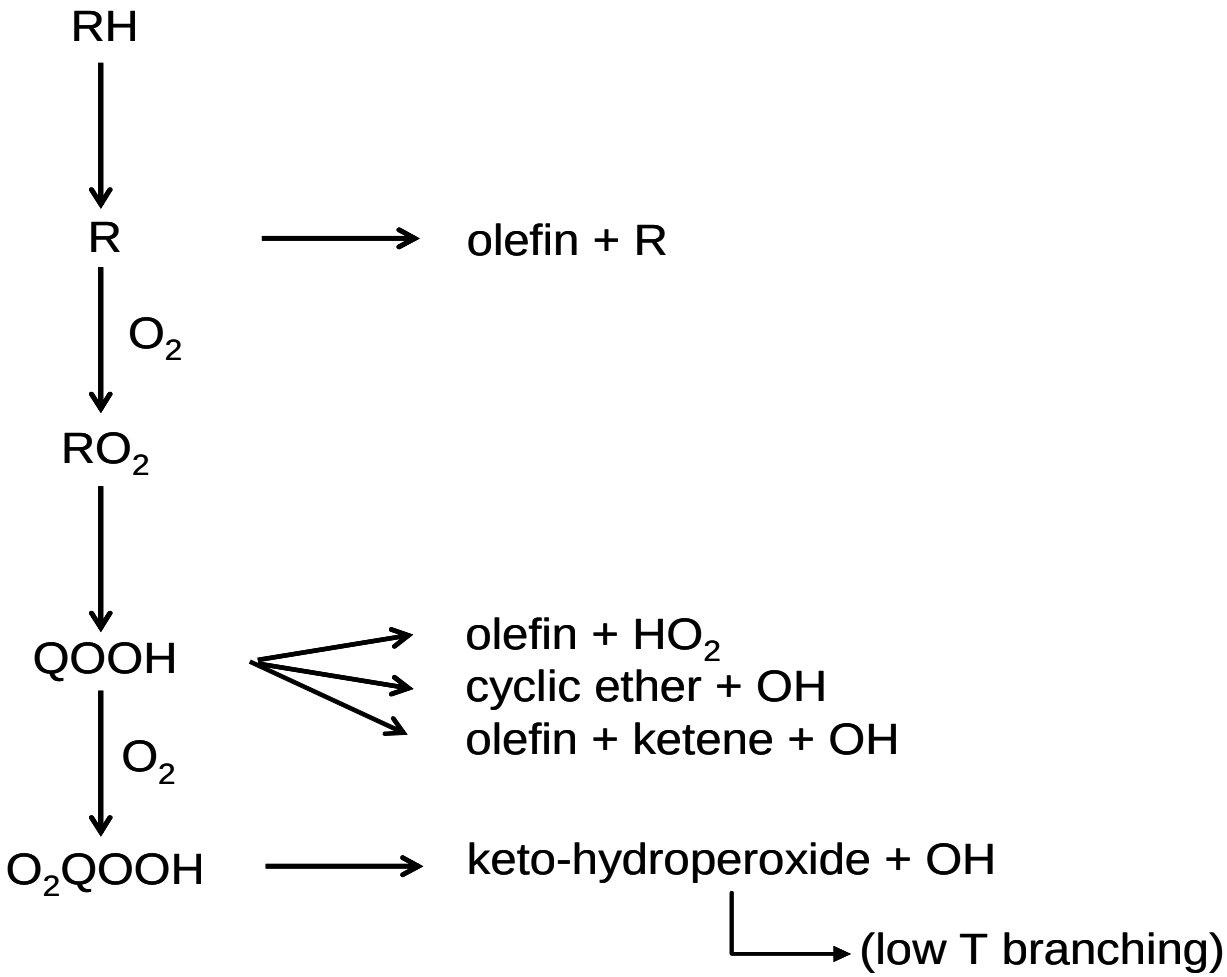
- RCM ignition
- Engine knock
- HCCI ignition
- Diesel ignition
- Each system follows a unique pathway in the relevant phase space to arrive at this ignition temperature where H_2O_2 decomposes

Kinetic features of engine knock

- History of octane numbers and empirical observations
- End gas self-ignition prior to flame arrival
- Actual ignition driven by H_2O_2 decomposition at ~ 900K
- Kinetic influence of molecular size and structure
- Effects of additives, both promoters and inhibitors
- Reduced models must retain H_2O_2 decomposition reaction to describe ignition
- Issue of real SI engine fuel being complex mixture of components
- Lots of kinetics research still needed (aromatics, cyclics, etc.)

Detailed Chemical Kinetics for Components

Includes high and low temperature ignition chemistry: Important for predicting low temperature combustion regimes



High Temperature Mechanism

Reaction Class 1: Unimolecular fuel decomposition

Reaction Class 2: H-atom abstractions

Reaction Class 3: Alkyl radical decomposition

Reaction Class 4: Alkyl radical + O2 = olefin + HO2

Reaction Class 5: Alkyl radical isomerization

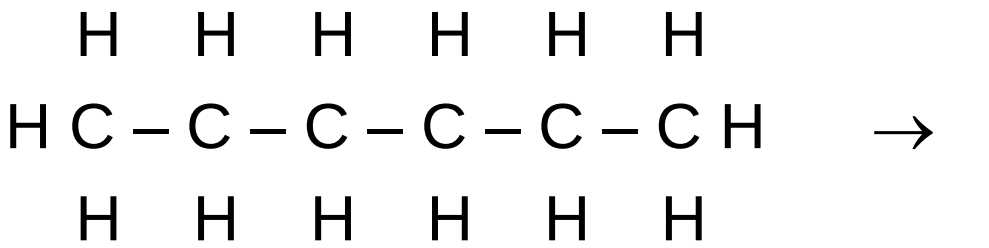
Reaction Class 6: H atom abstraction from olefins

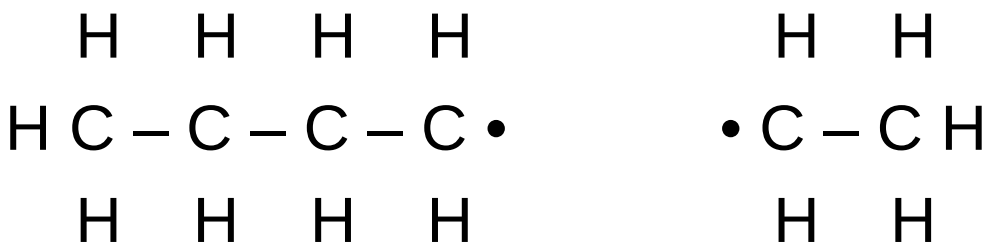
Reaction Class 7: Addition of radical species to olefins

Reaction Class 8: Alkenyl radical decomposition

Reaction Class 9: Olefin decomposition

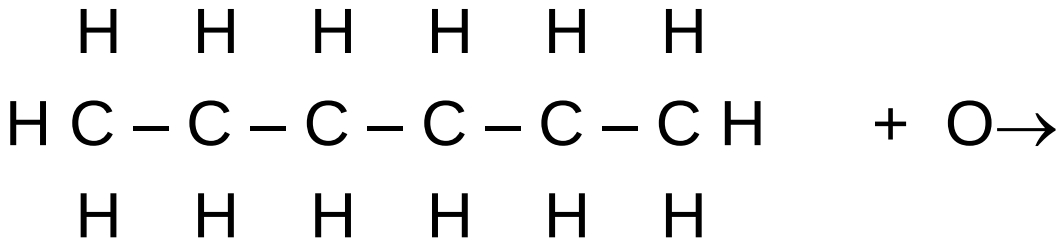
Class 1 – Unimolecular fuel decomposition

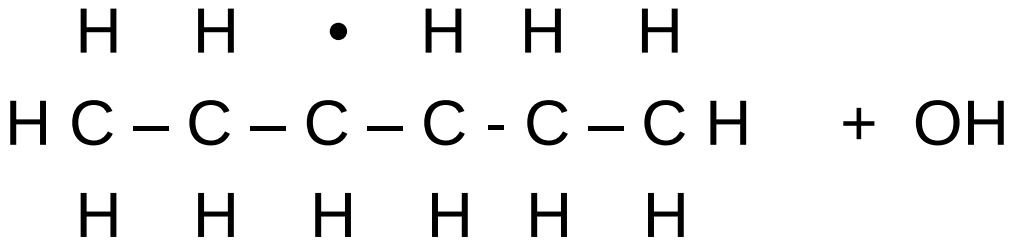




Products are two alkyl radicals pC_4H_9 and C_2H_5

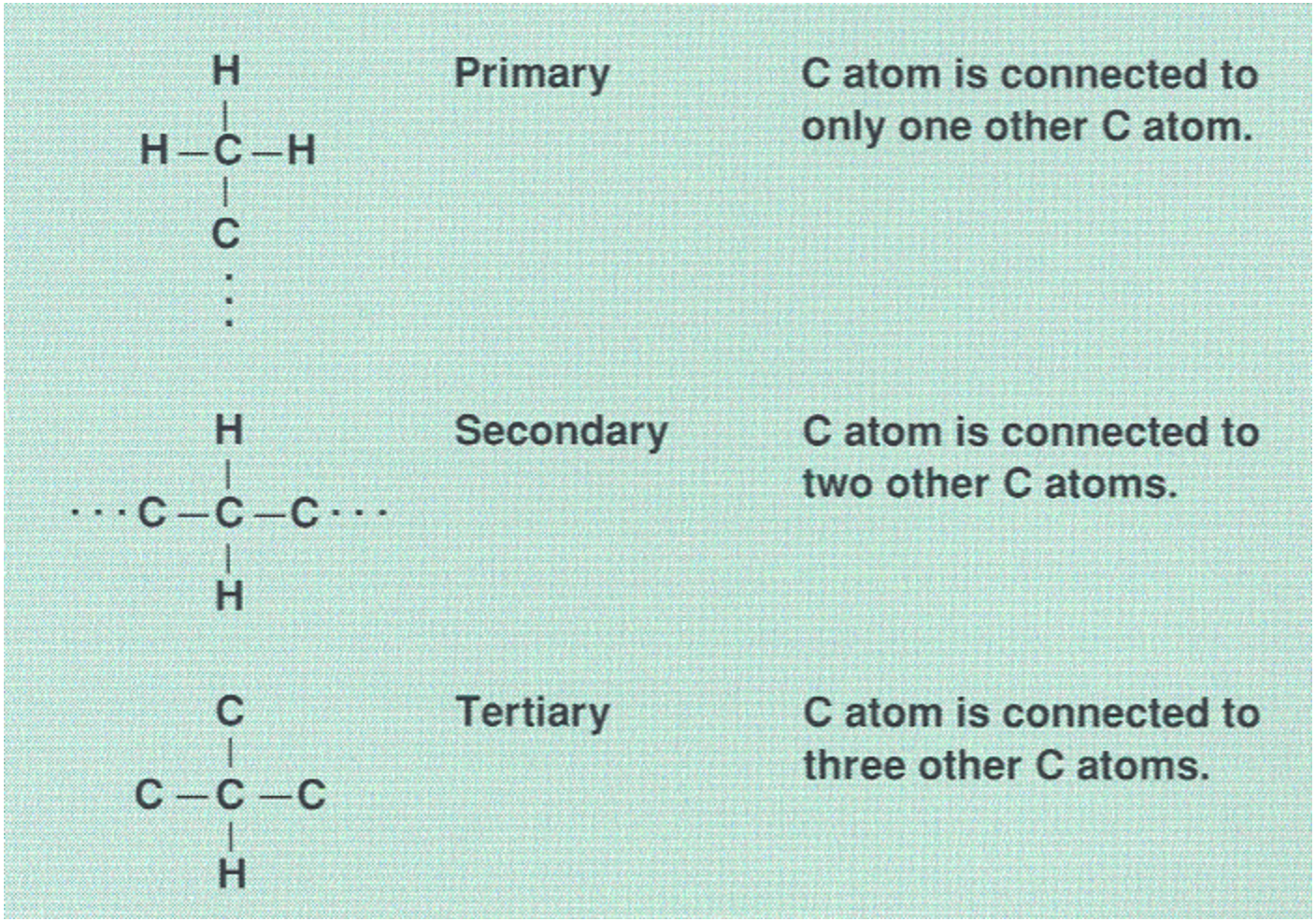
Class 2 – H atom abstractions





Rate depends on the abstracting radical and on the site where the H is located (more later)

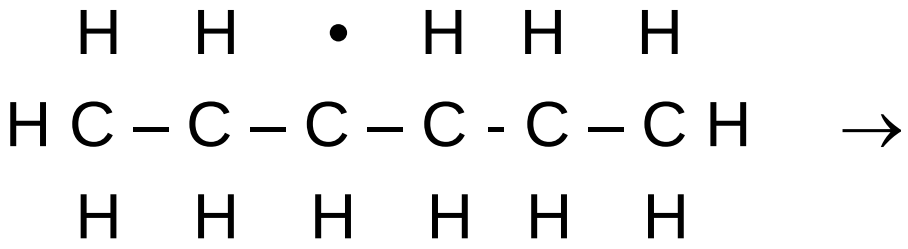
Two major keys to low temperature reactions



BE (primary) > BE (secondary) > BE (tertiary)

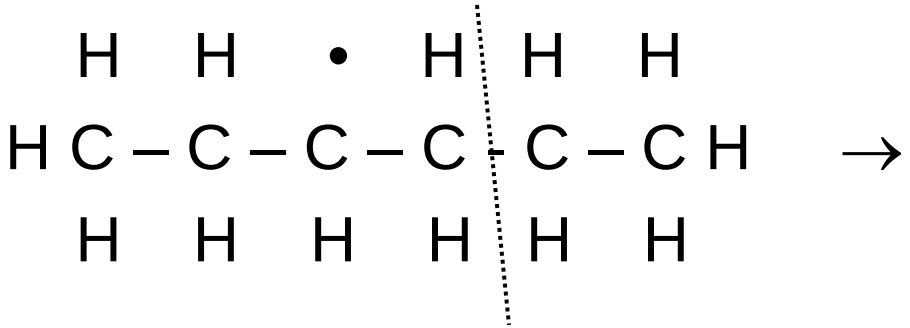
25

Class 3 – radical decomposition



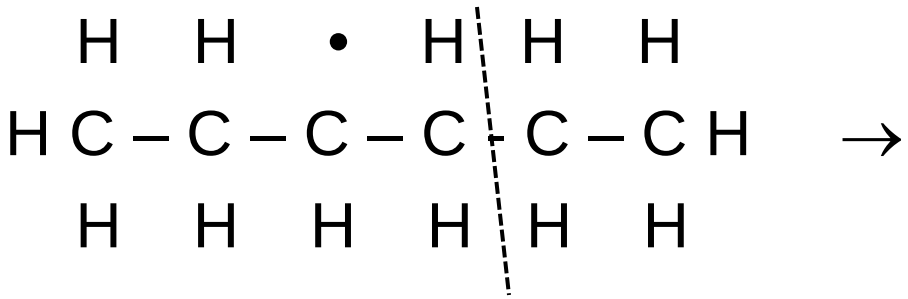
Decomposition reaction based on beta-scission or “one bond away”

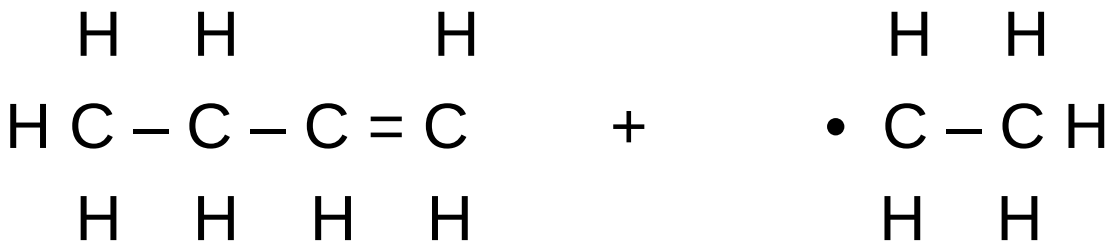
Class 3 – radical decomposition



Decomposition reaction based on beta-scission or “one bond away”

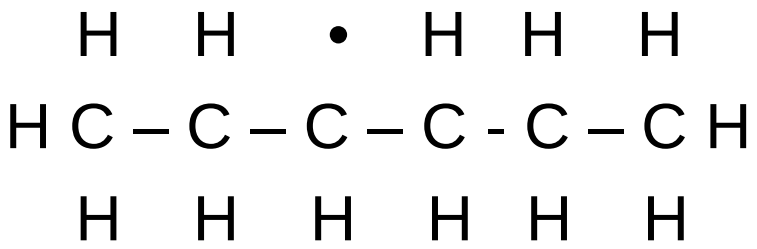
Class 3 – radical decomposition



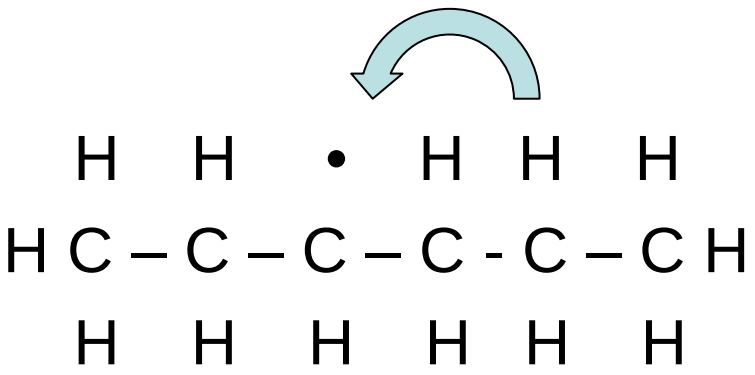


$_1C_4H_8$ + C_2H_5 one stable olefin and one radical

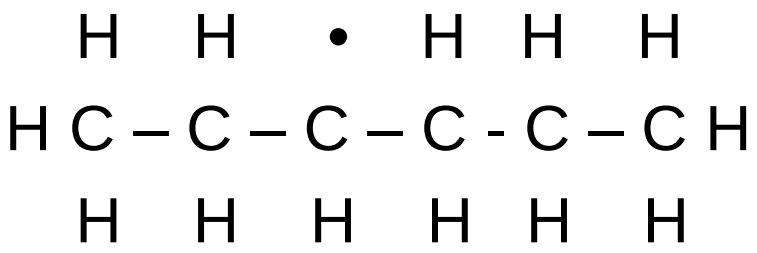
Class 5: Alkyl radical isomerization

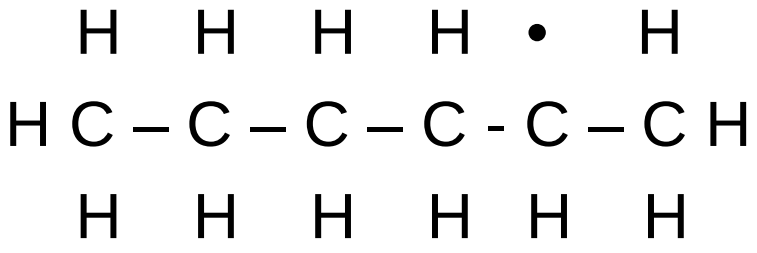


Class 5: Alkyl radical isomerization

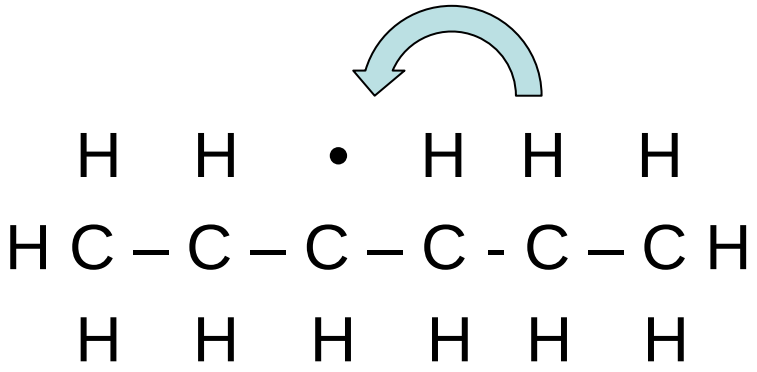


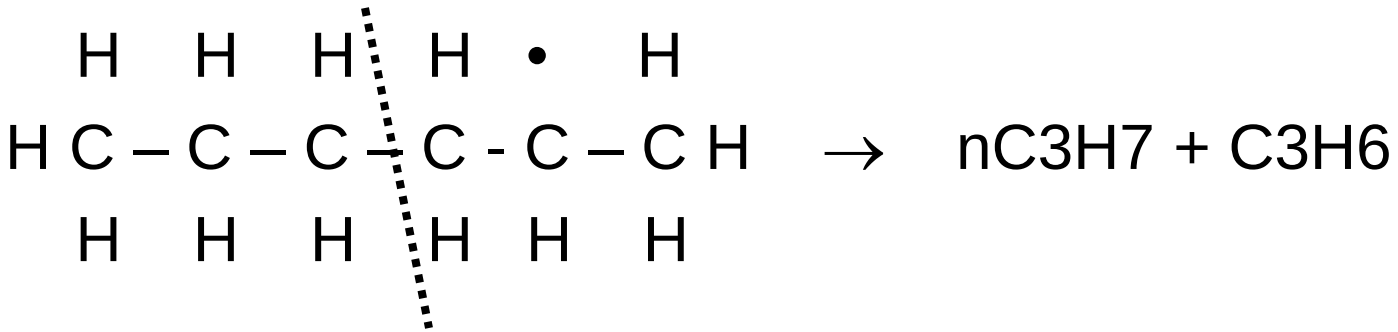
Class 5: Alkyl radical isomerization





Class 5: Alkyl radical isomerization

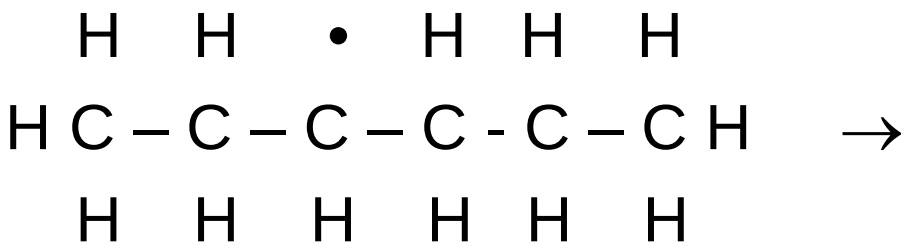


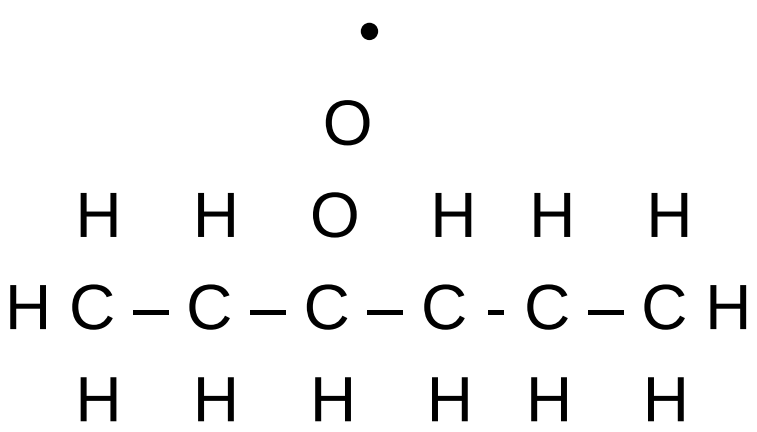


Low Temperature (High Pressure) Mechanism

Reaction Class 10: Alkyl radical addition to O2
Reaction Class 11: R + R'O2 = RO + R'O
Reaction Class 12: Alkylperoxy radical isomerization
Reaction Class 13: RO2 + HO2 = ROOH + O2
Reaction Class 14: RO2 + H2O2 = ROOH + HO2
Reaction Class 15: RO2 + CH3O2 = RO + CH3O + O2
Reaction Class 16: RO2 + R'O2 = RO + R'O + O2
Reaction Class 17: RO2H = RO + OH
Reaction Class 18: Alkoxy radical decomposition
Reaction Class 19: QOOH decomposition and production of cyclic ethers
Reaction Class 20: QOOH beta decomposition to produce olefin + HO2
Reaction Class 21: QOOH decomposition to small olefin, aldehyde and OH
Reaction Class 22: Addition of QOOH to molecular oxygen O2
Reaction Class 23: O2QOOH isomerization to carbonylhydroperoxide + OH
Reaction Class 24: Carbonylhydroperoxide decomposition
Reaction Class 25: Reactions of cyclic ethers with OH and HO2

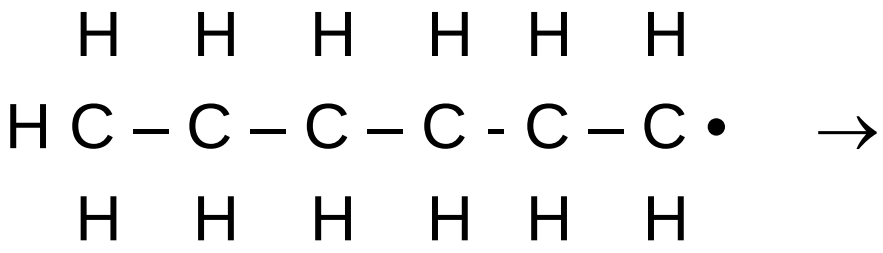
Class 10 – addition of O_2 to alkyl radical

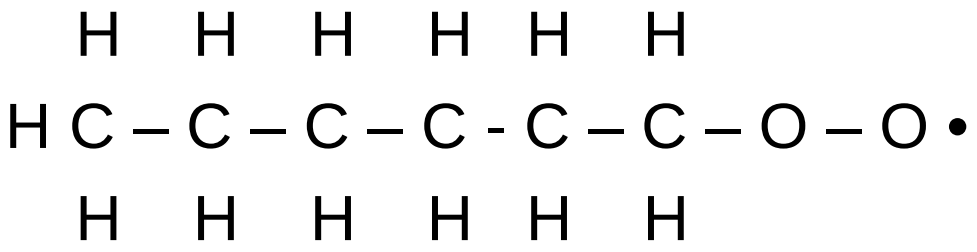




Rate depends on the type of site where the O_2 attaches

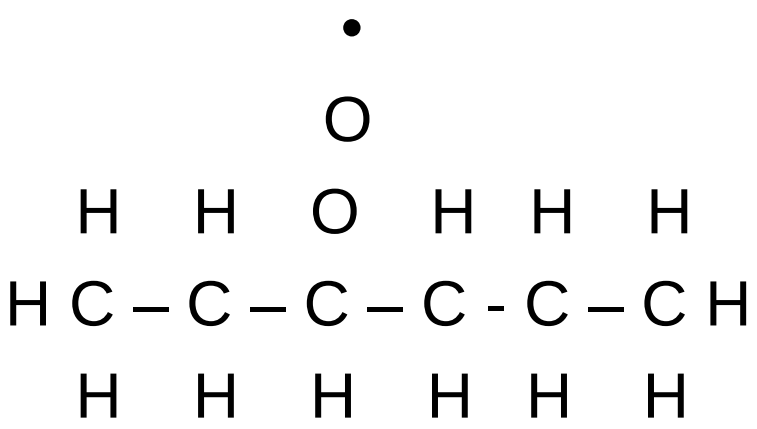
Class 10 – addition of O_2 to alkyl radical





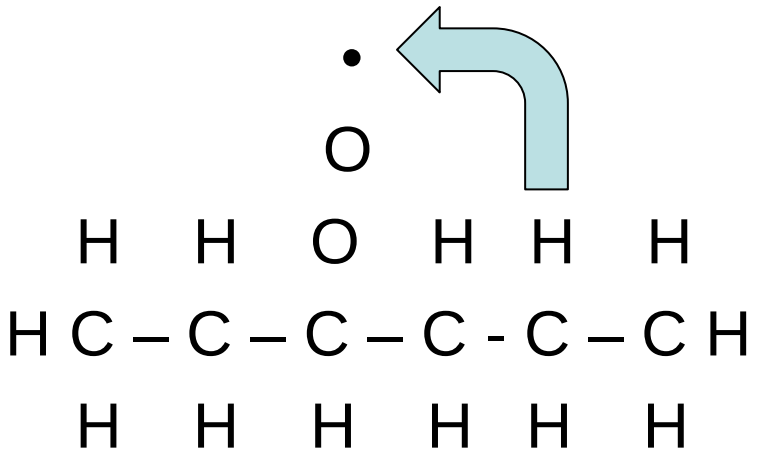
Rate depends on the type of site where the O_2 attaches

Class 12 – RO_2 isomerization

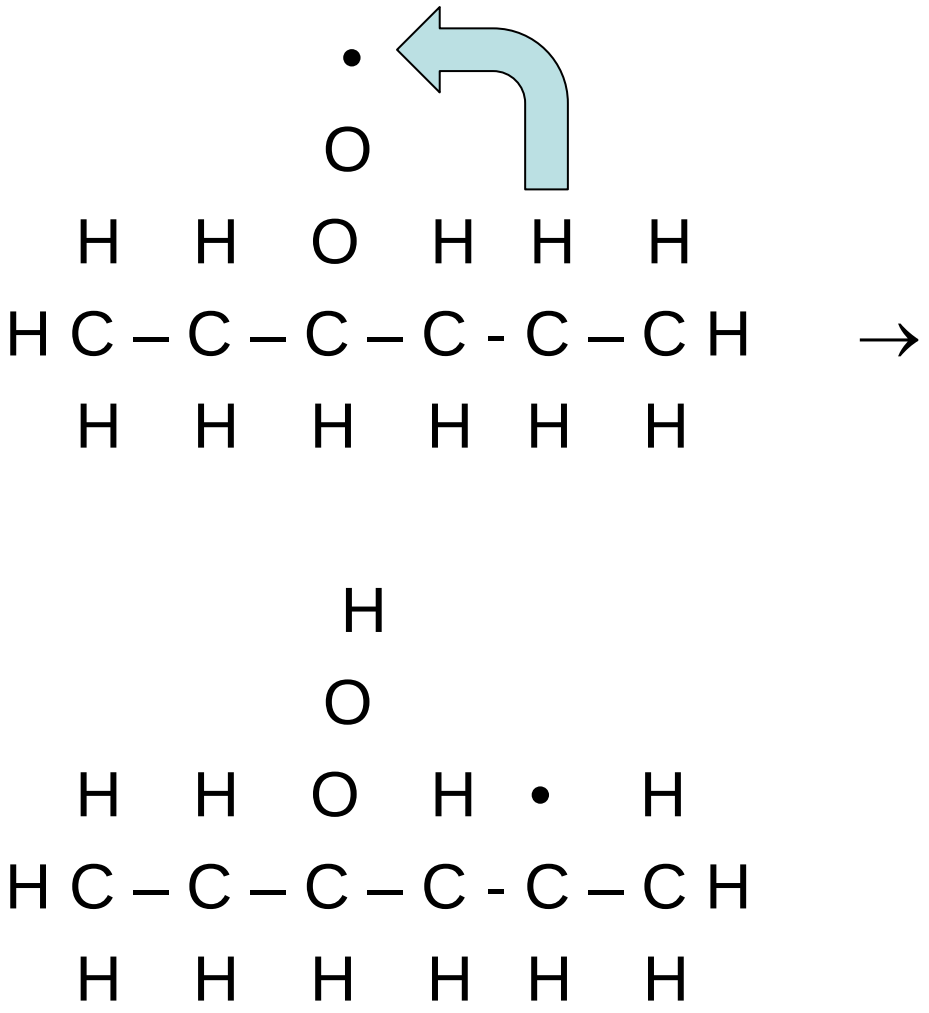


Transfer H atom within the molecule

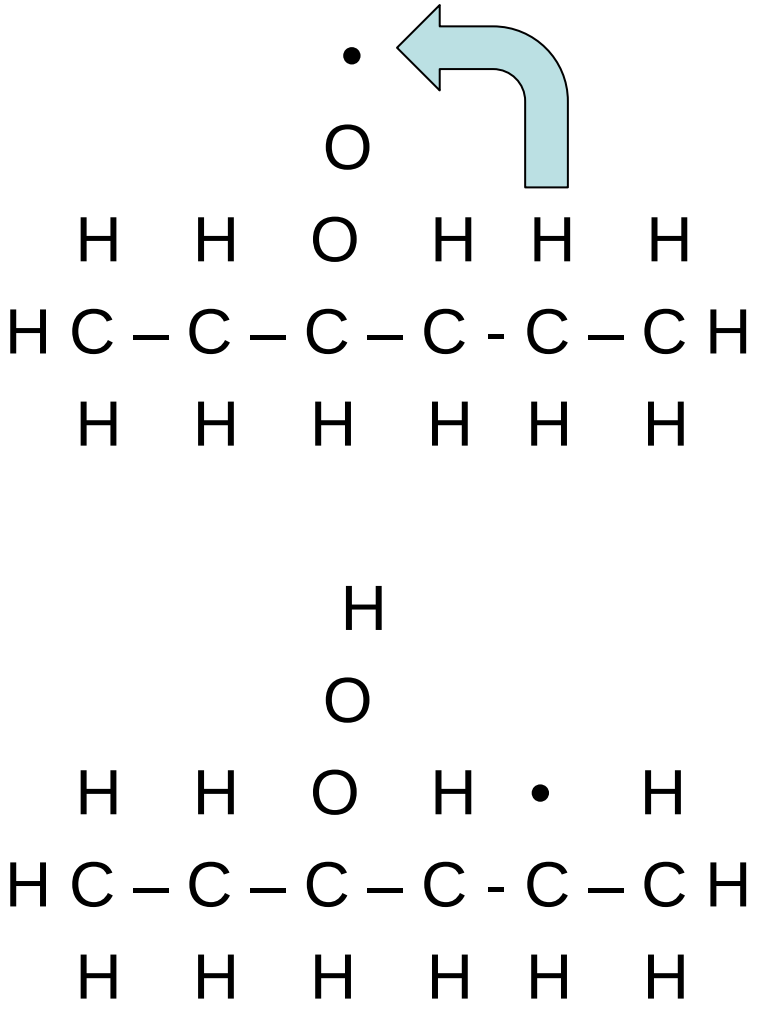
Class 12 – RO_2 isomerization



Class 12 – RO_2 isomerization



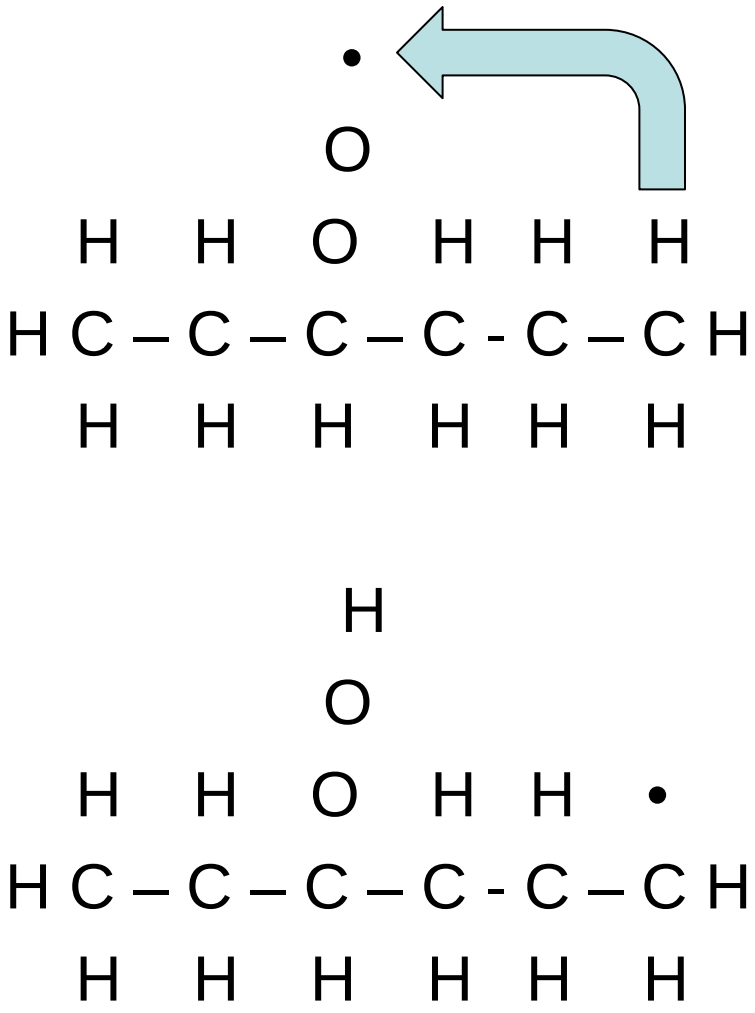
Class 12 – RO_2 isomerization



6-membered transition state ring, secondary → C – H bonds

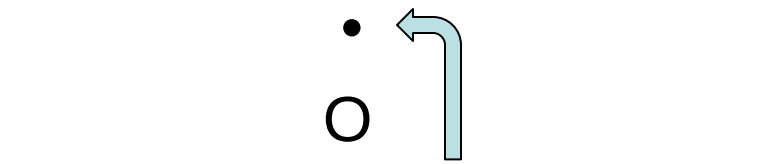
2 H atoms available

Class 12 – RO_2 isomerization

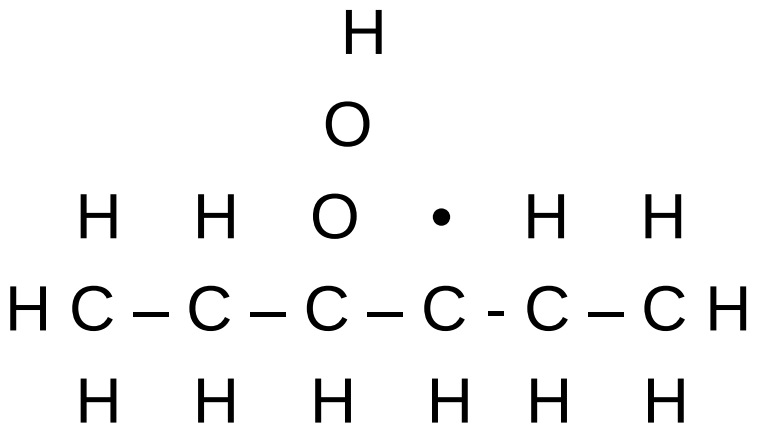


7-membered transition state ring, tertiary C – H bonds → 3 H atoms available

Class 12 – RO_2 isomerization



5-membered transition state ring, secondary C – H bonds 2 atoms available



Rates of Class 12 reactions

- Size of the transition state ring, “transition state ring strain energy barrier”
  - 5 membered ring has highest energy barrier
  - 7 membered ring has lowest energy barrier
- Type of C – H bond that is broken to remove the H atom
  - Primary bond strongest, tertiary bond is weakest
- Number of equivalent H atoms

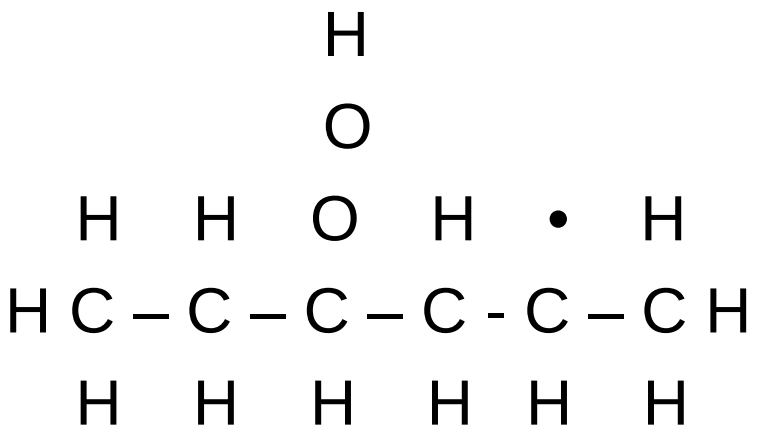
We have rules for each class of reactions: Reaction rates for RO_2 isomerization rate constants

$$k = A\,T^{n} \exp(-E_a/RT)$$

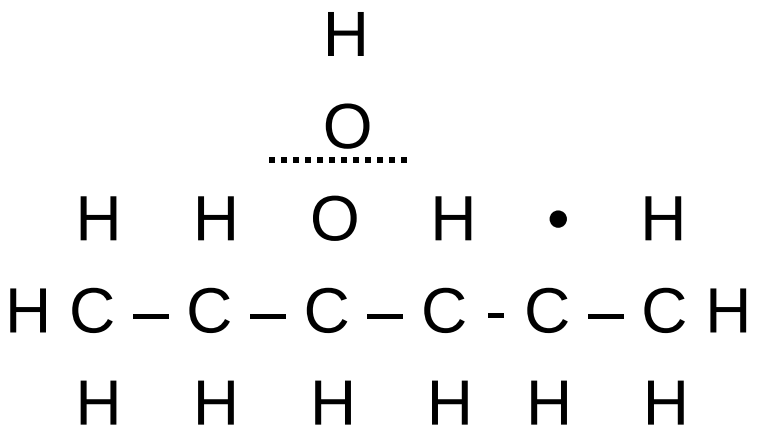
Rate constant expressions for $R\dot{O}_2$ isomerization reactions (cm^3–mol–sec–cal units)

Ring size	Site	Rate expression (per H atom)		
		A	n	ϵ_a
5	Primary	1.00×10^{11}	0.0	29400.
	Secondary	1.00×10^{11}	0.0	26850.
	tertiary	1.00×10^{11}	0.0	24100.
6	Primary	1.25×10^{10}	0.0	24400.
	Secondary	1.25×10^{10}	0.0	20850.
	tertiary	1.25×10^{10}	0.0	19100.
7	Primary	1.56×10^{9}	0.0	22350.
	Secondary	1.56×10^{9}	0.0	19050.
	tertiary	1.56×10^{9}	0.0	17050.
8	Primary	1.95×10^{8}	0.0	25550.
	Secondary	1.95×10^{8}	0.0	22050.
	tertiary	1.95×10^{8}	0.0	20050.

Class 19 – QOOH decomposition into cyclic ether



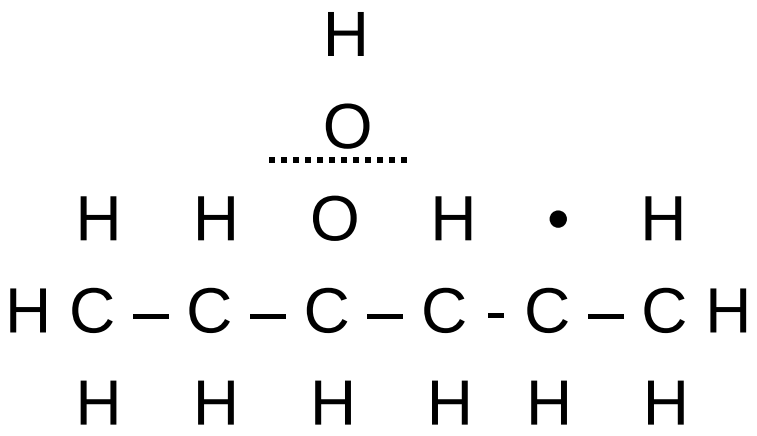
Class 19 – QOOH decomposition into cyclic ether

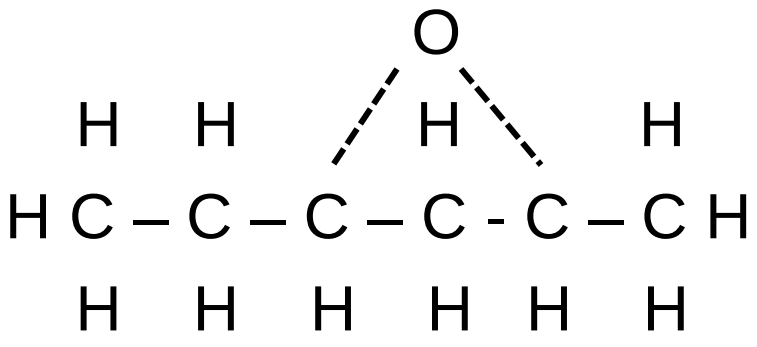


Reaction begins by breaking O – O bond,

which produces OH radical

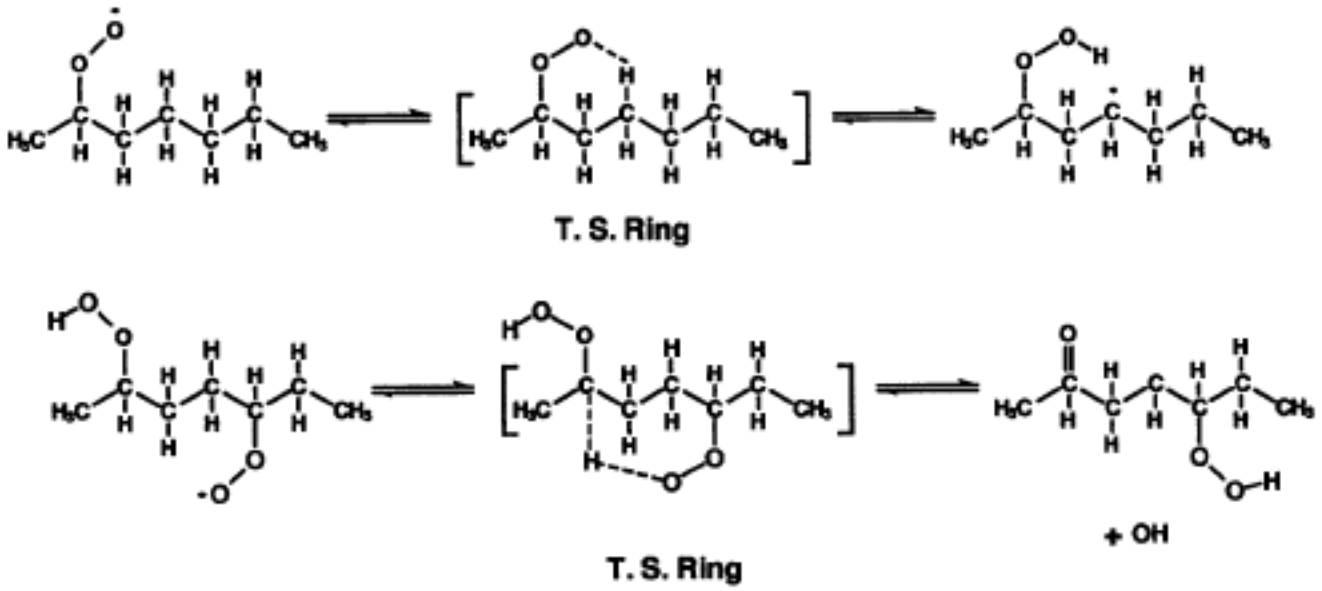
Class 19 – QOOH decomposition into cyclic ether





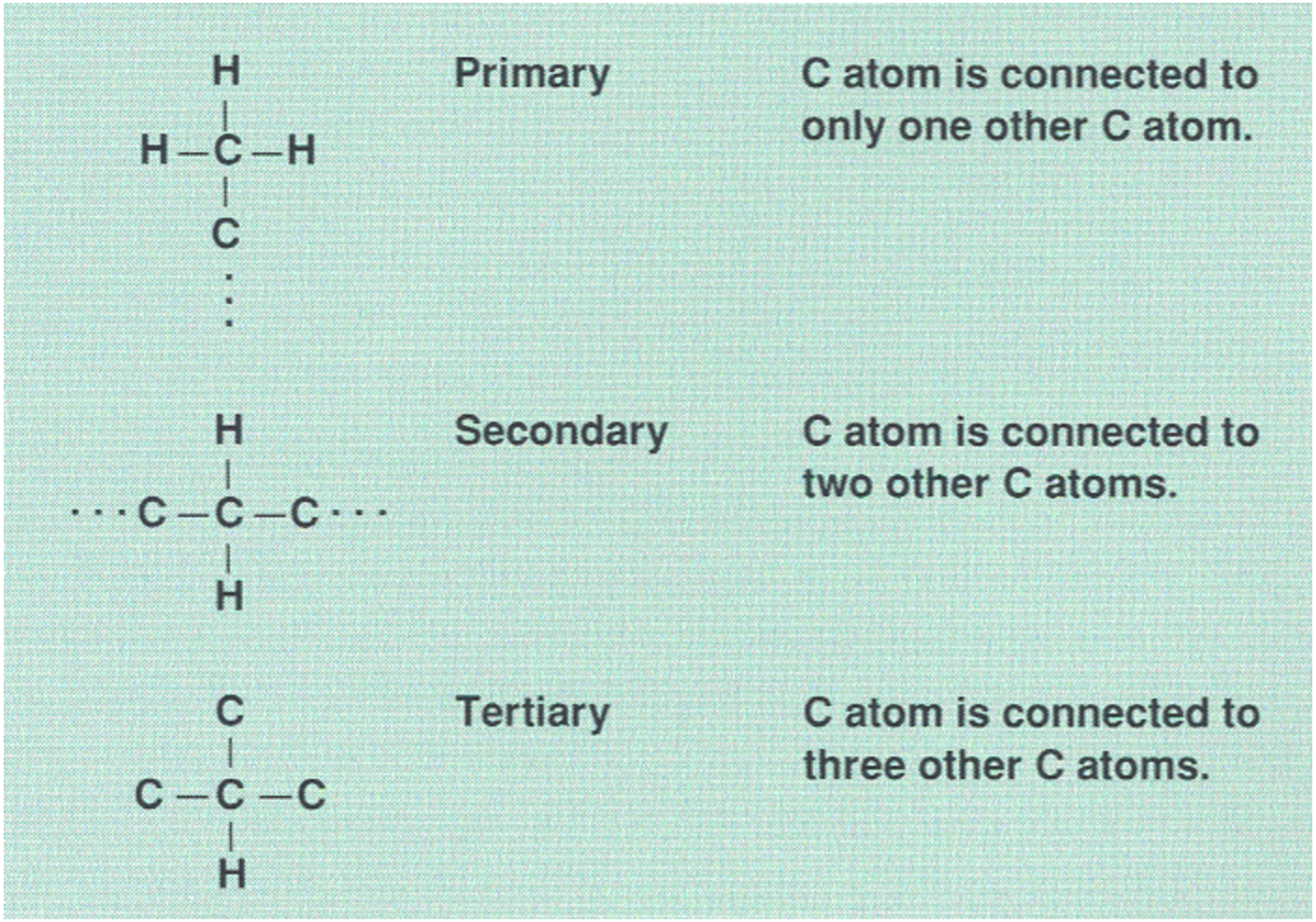
4-membered ring cyclic ether

Low temperature kinetics involve intra-molecular H atom transfers



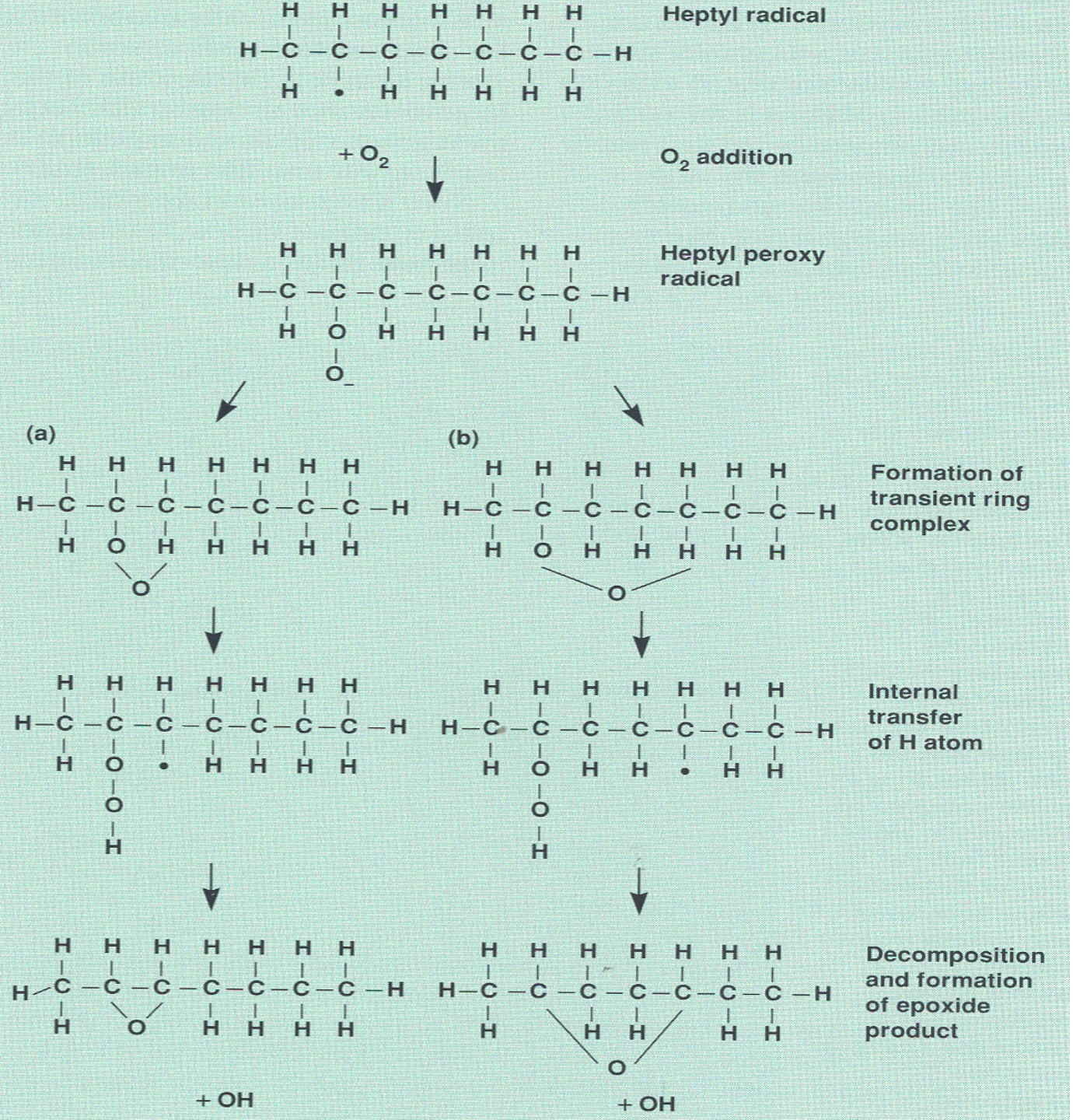
These reactions lead to OH radical production at low temperatures, which then produce water and heat
This heating reduces the time delay for the fuel to reach the H_2O_2 decomposition temperature

Two major keys to low temperature reactions



BE (primary) > BE (secondary) > BE (tertiary)

48



RSE (5-ring) >

RSE (6-ring) >

RSE (7-ring) <

RSE (8-ring)

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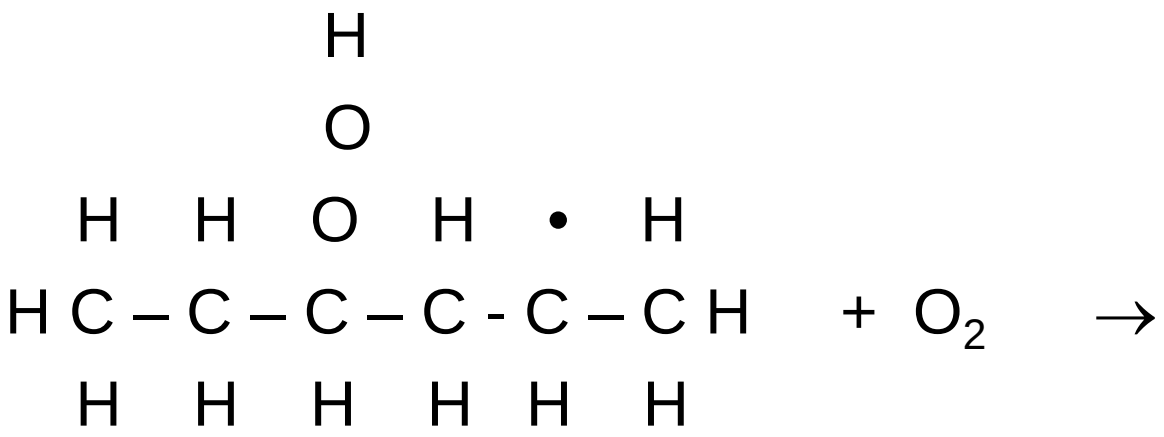
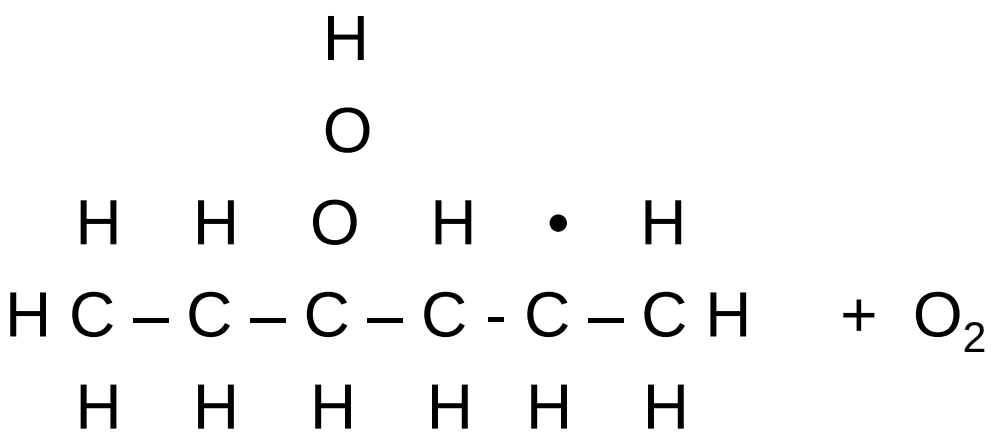
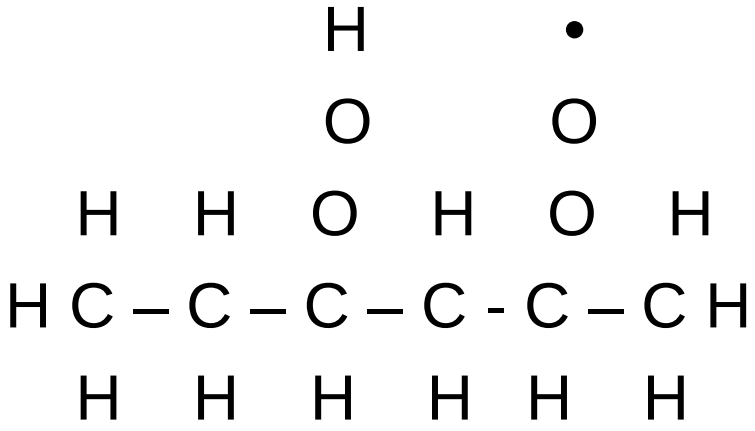
Class 22 – addition of O_2 to QOOH

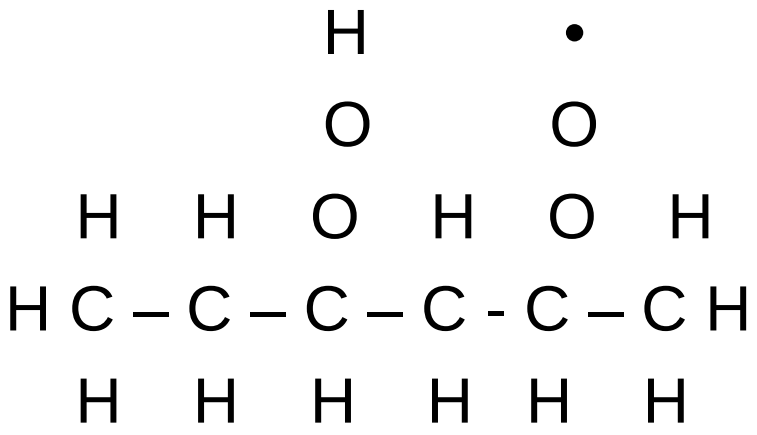


Class 22 – addition of O_2 to QOOH

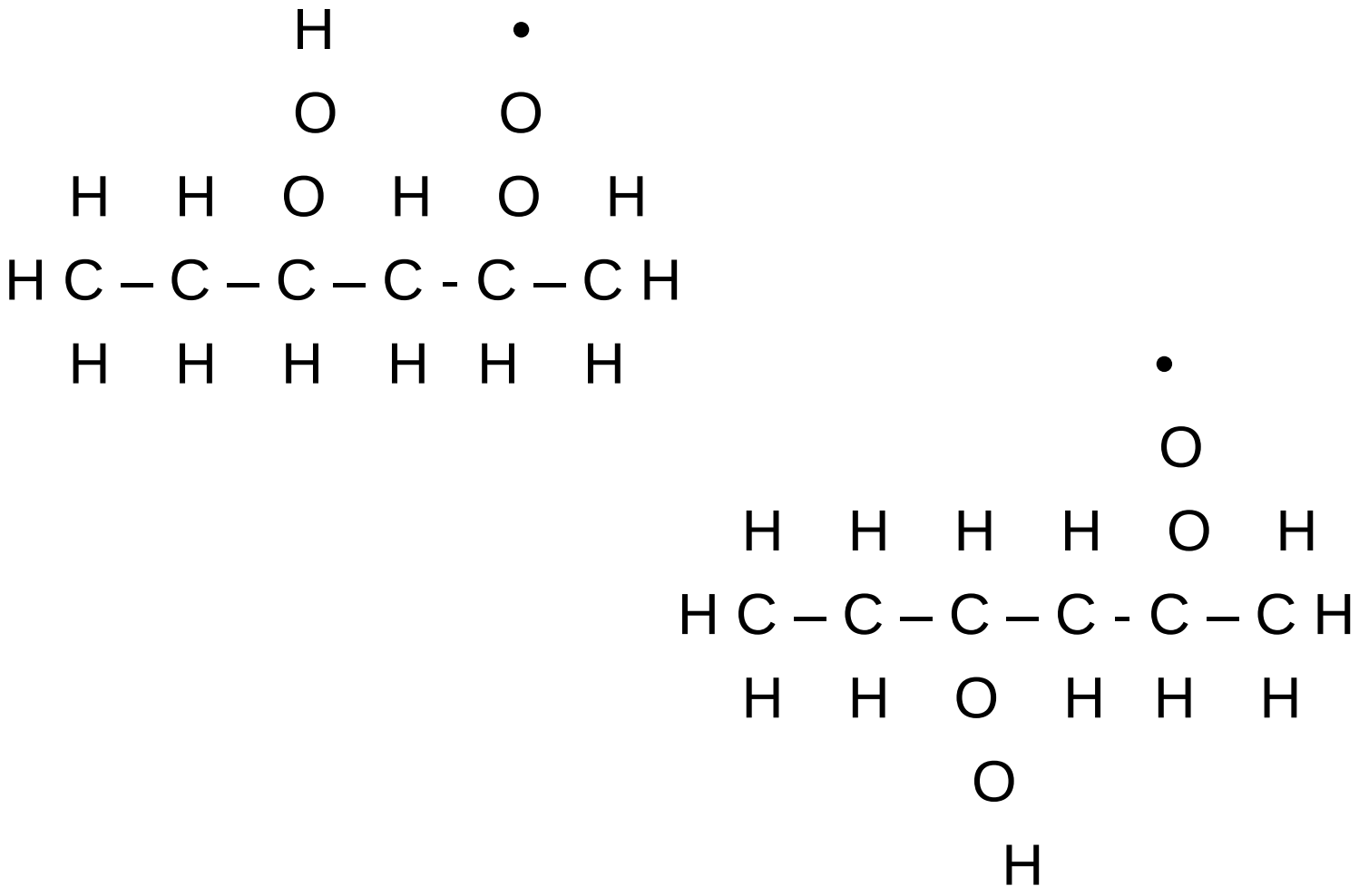




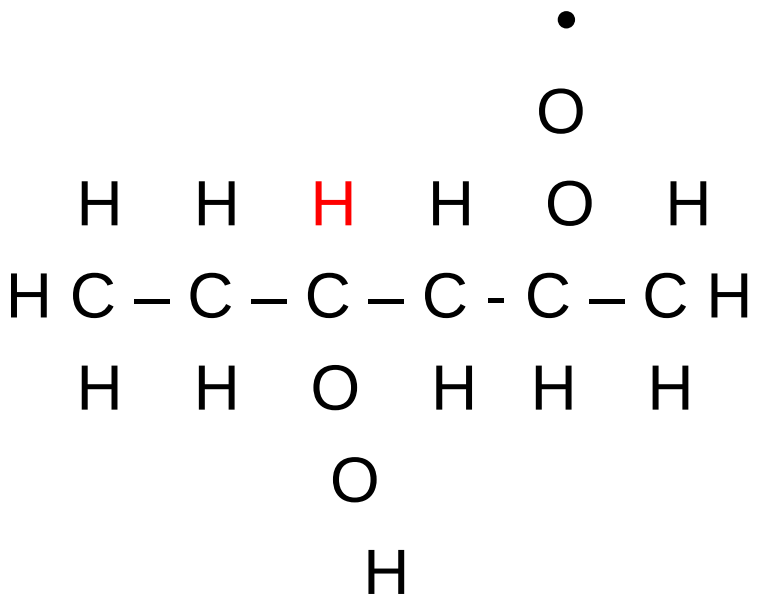
Class 23 – isomerization of O_2QOOH



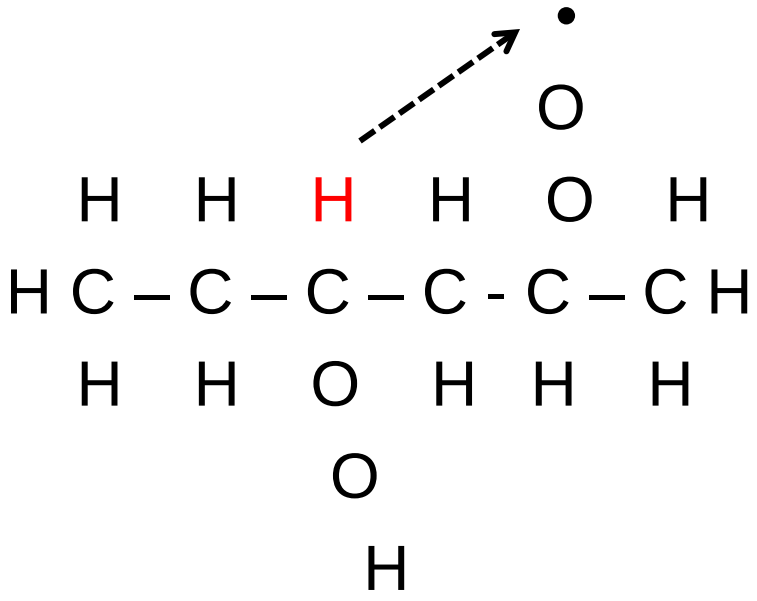
Class 23 – isomerization of O_2QOOH



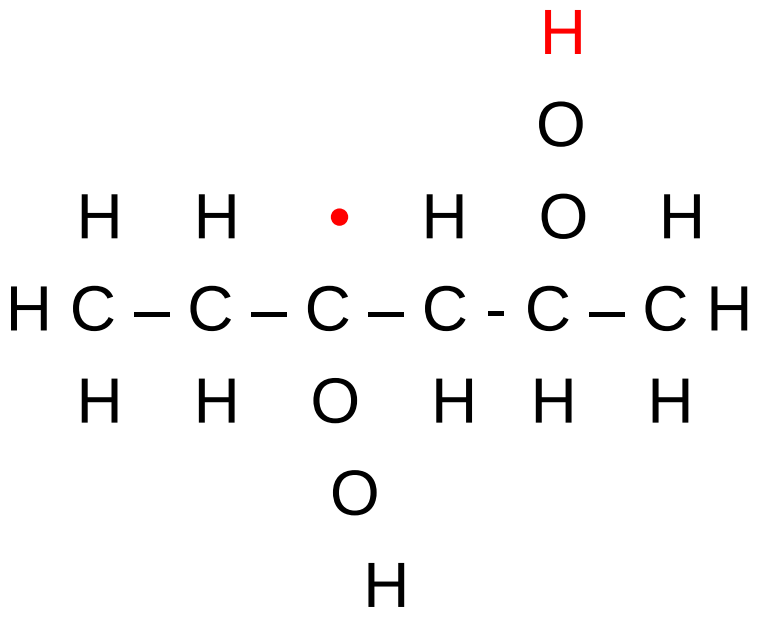
Class 23 – isomerization of O_2QOOH



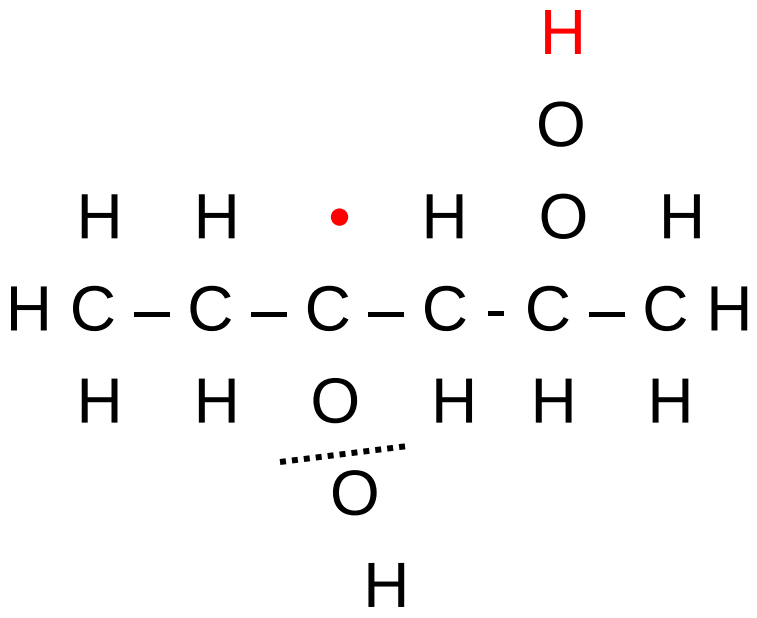
Class 23 – isomerization of O_2QOOH



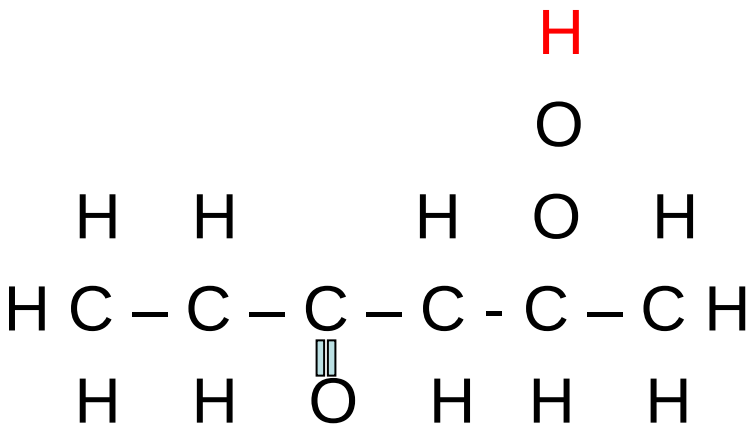
Class 23 – isomerization of O_2QOOH



Class 23 – isomerization of O_2QOOH



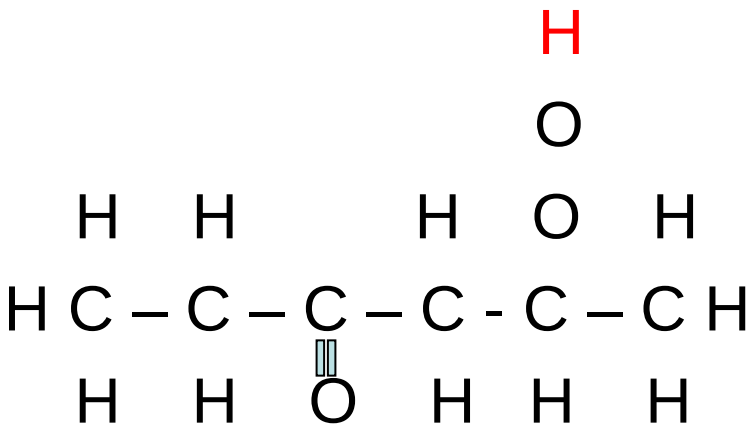
Class 23 – isomerization of O_2QOOH



to produce a ketohydroperoxide species

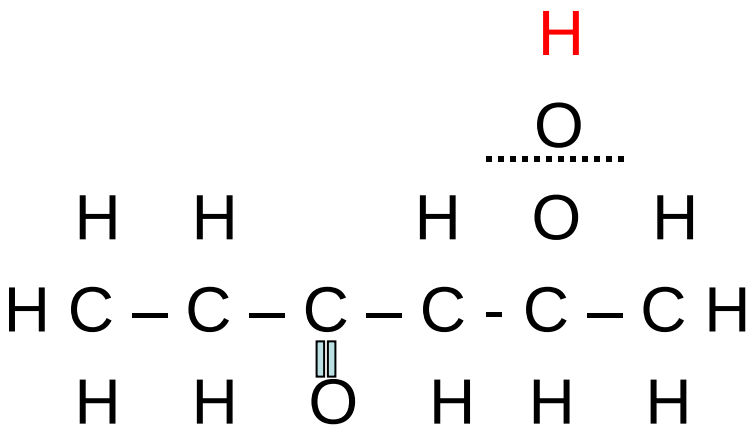
+ OH (#1)

Class 24 – decomposition of ketohydroperoxide

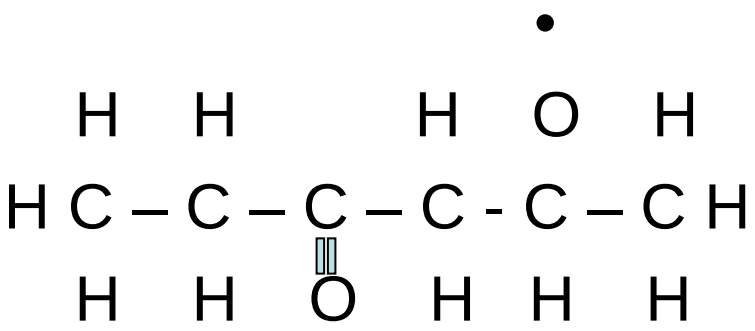


Because this is a stable species, it requires a temperature increase to break the O – O bond

Class 24 – decomposition of ketohydroperoxide

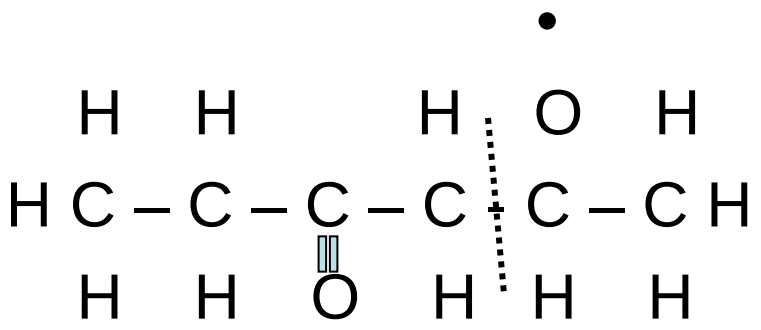


Class 24 – decomposition of ketohydroperoxide

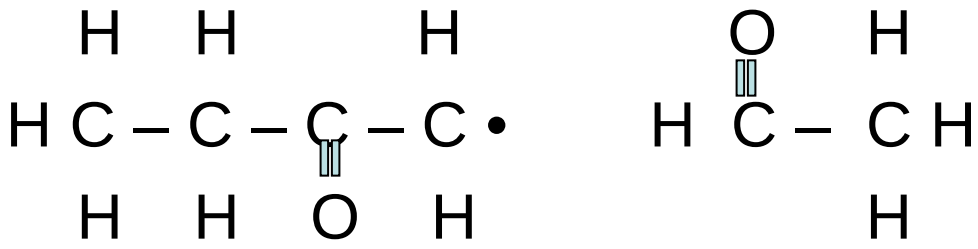


+ OH (#2)

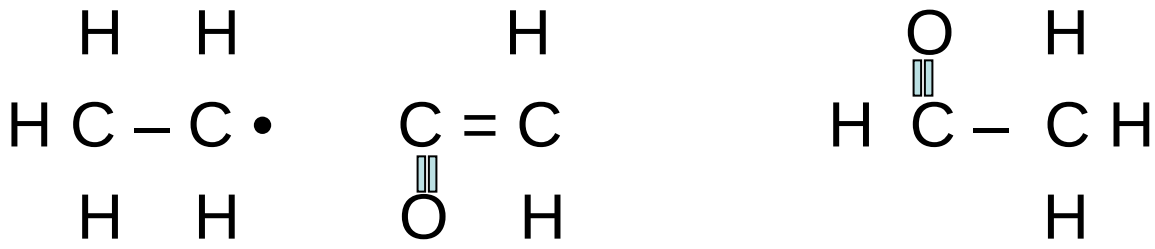
Class 24 – decomposition of ketohydroperoxide



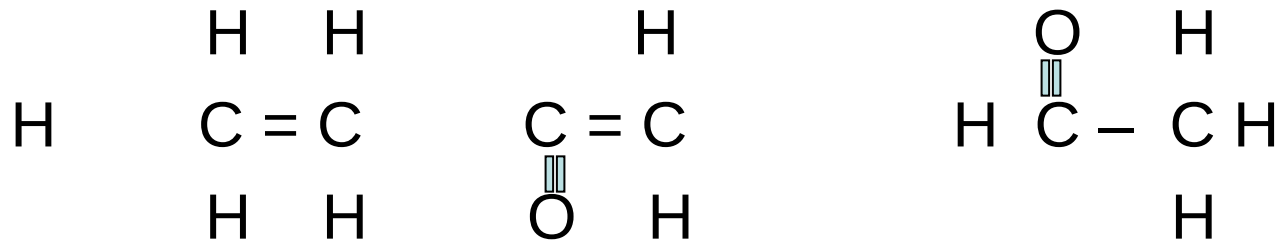
Class 24 – decomposition of ketohydroperoxide



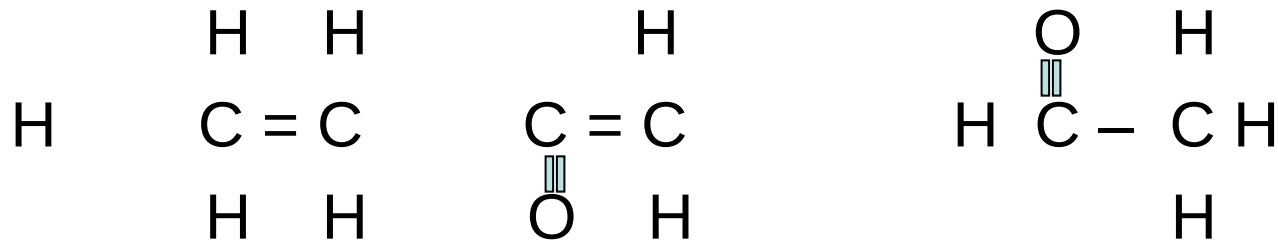
Class 24 – decomposition of ketohydroperoxide



Class 24 – decomposition of ketohydroperoxide

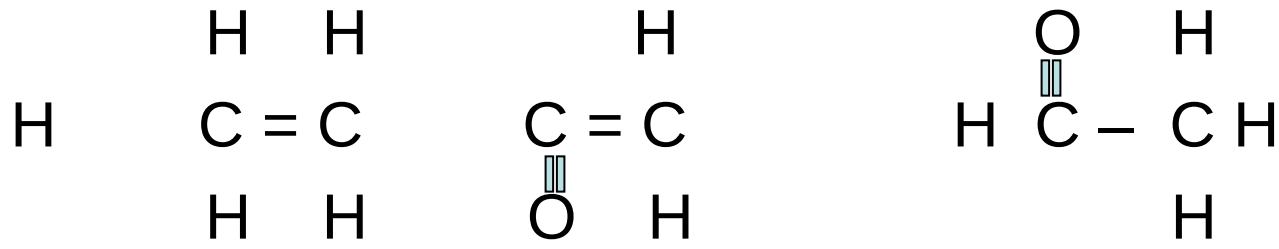


Class 24 – decomposition of ketohydroperoxide



H (radical) + ethene + ketene + acetaldehyde

Class 24 – decomposition of ketohydroperoxide



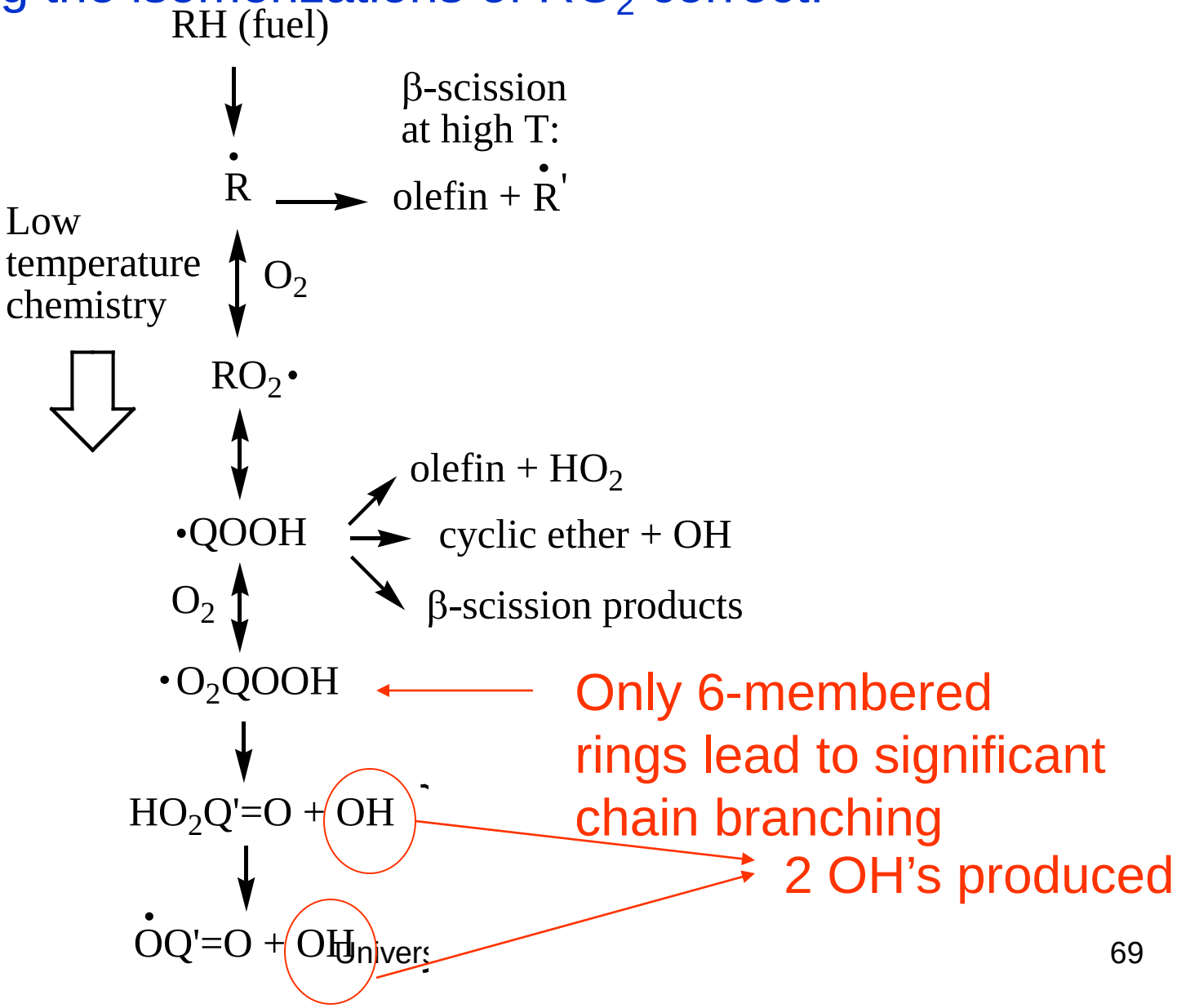
H (radical) + ethene + ketene + acetaldehyde

and don’t forget OH (#1) and OH (#2)

Alkylperoxy radical isomerization, followed by the dihydroperoxide pathway

- At least 3 small radical species
  - OH + OH + H (or another OH or HO_2)
- Several small stable species, many of them highly reactive aldehydes and olefins
- These reaction pathways provide intense chain branching
- This pathway quits when increasing temperature shuts down the R + O_2 and O_2 + QOOH equilibria

Key to understanding the low temperature chemistry of MCH was getting the isomerizations of RO_2 correct:

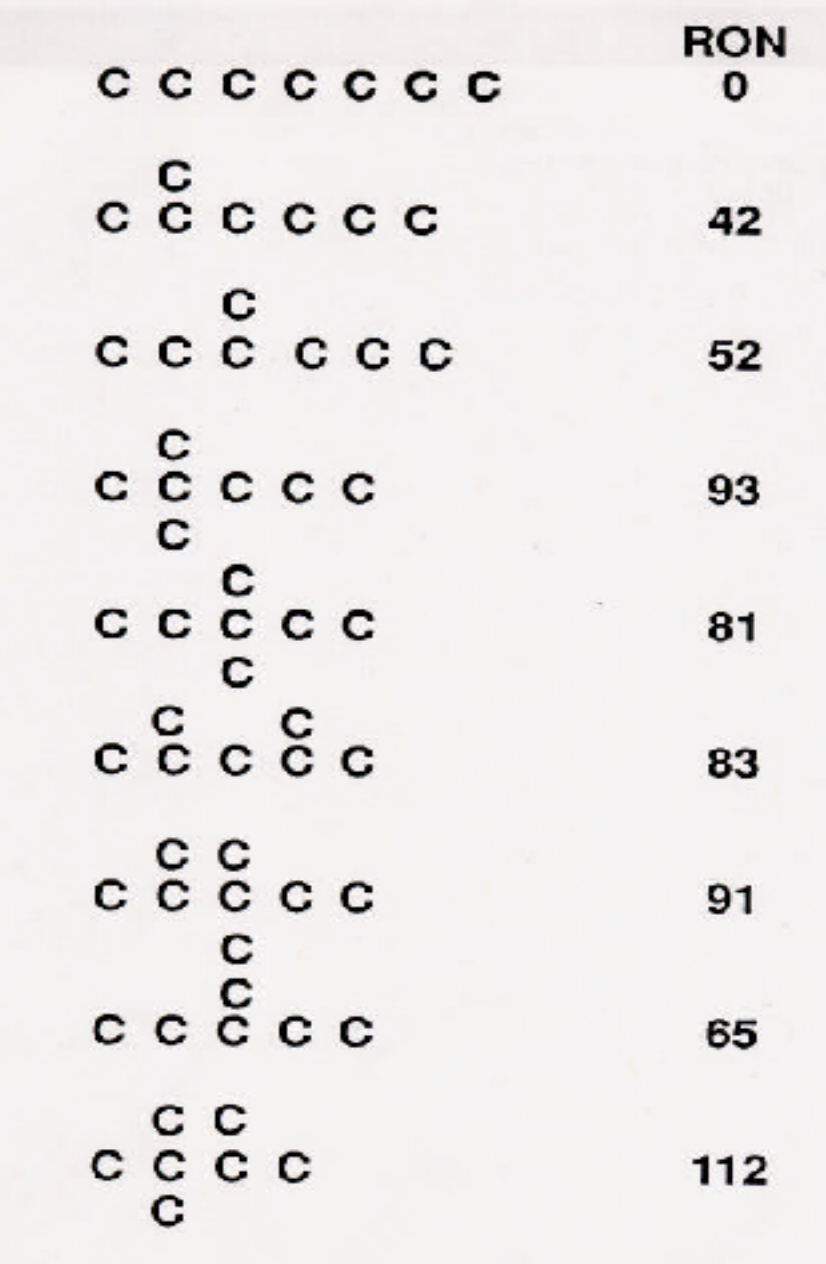


Alkyl radical isomerization possible for most fuels

- Remember the key kinetic factors
- Primary, secondary and tertiary C – H bonds
- Ring strain energy variations with ring size, especially for nearest-neighbor abstractions
- Other molecular structure effects

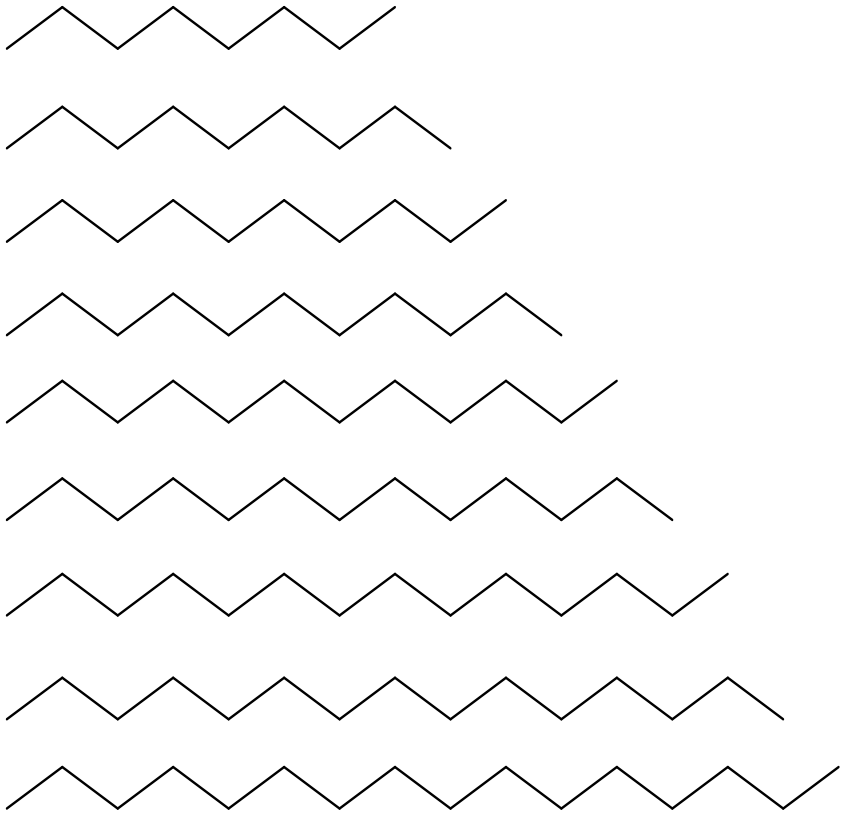
Octane numbers of heptanes are due exclusively to their different molecular structures

Low octane fuels have lots of secondary C-H bonds and high octane fuels have lots of primary C-H bonds and lots of tight, 5-membered TS rings



N-alkanes all have straight C chains with lots of secondary C – H bonds and low ring strain energy barriers

- n-octane (n-C8H18)
- n-nonane (n-C9H20)
- n-decane (n-C10H22)
- n-undecane (n-C11H24)
- n-dodecane (n-C12H26)
- n-tridecane (n-C13H28)
- n-tetradecane (n-C14H30)
- n-pentadecane (n-C15H32)
- n-hexadecane (n-C16H34)



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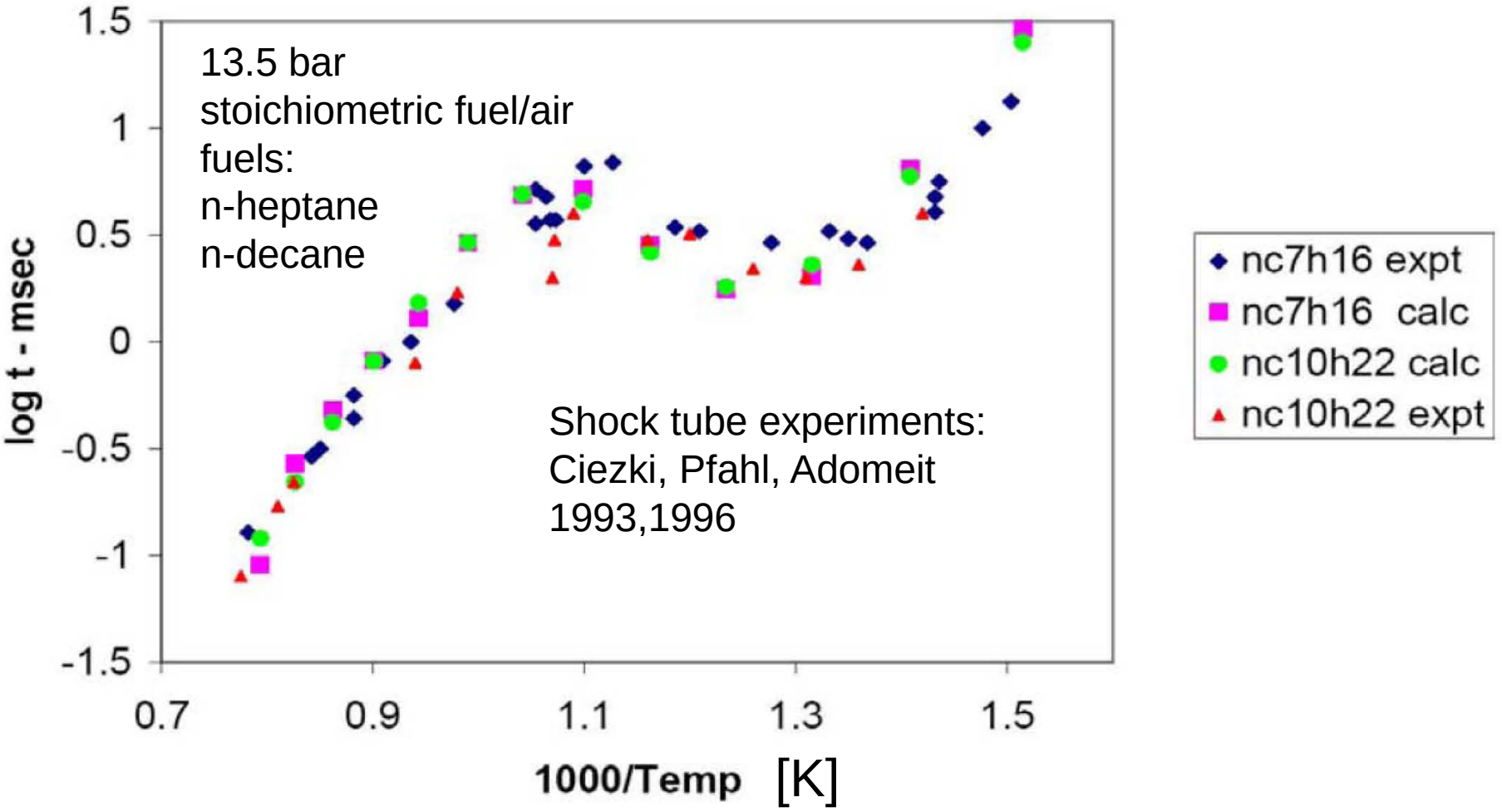
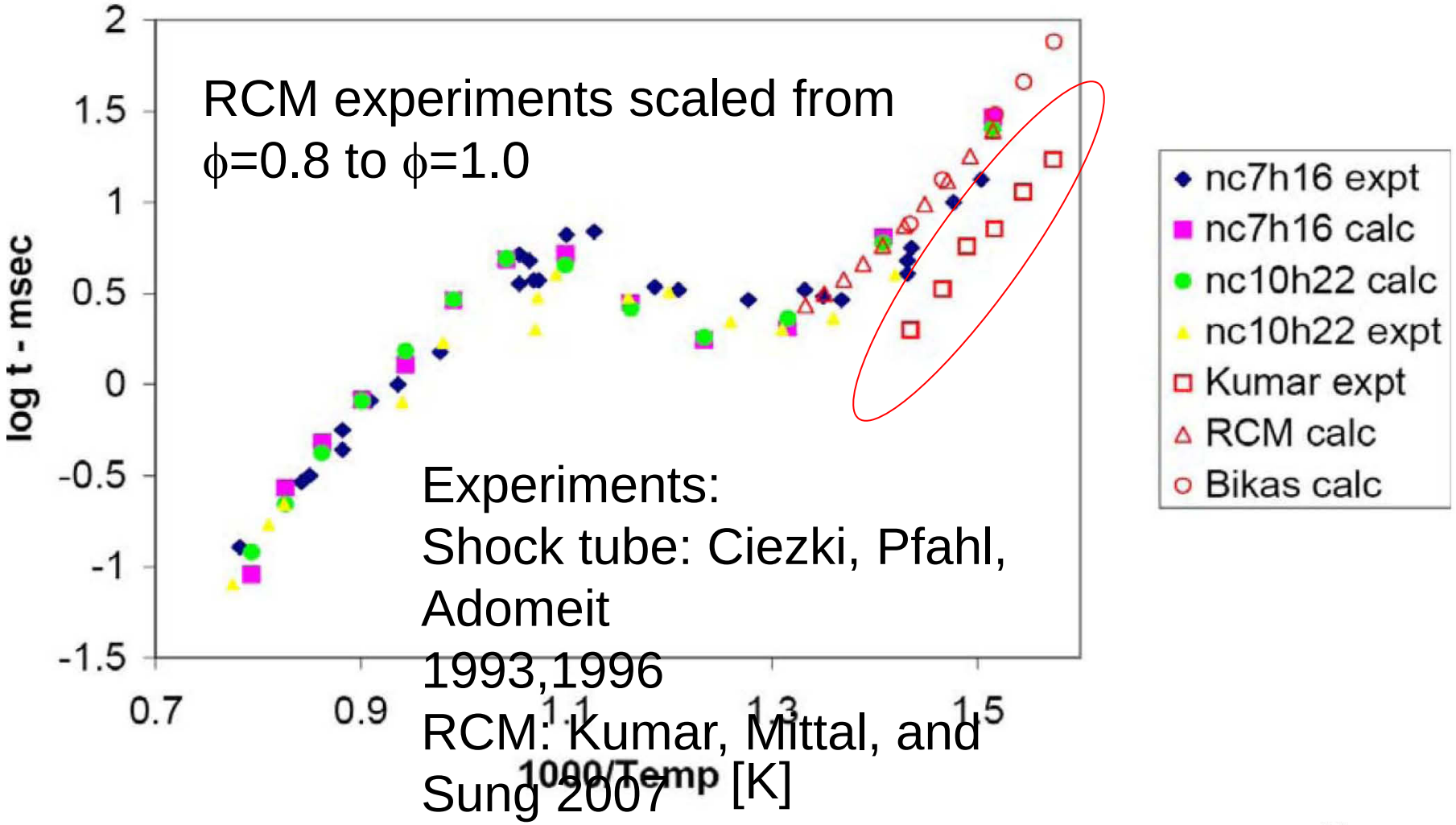
Experimental Validation Data

Good agreement with ignition delay times at “engine-like” conditions over the low to high temperature regime in the shock tube



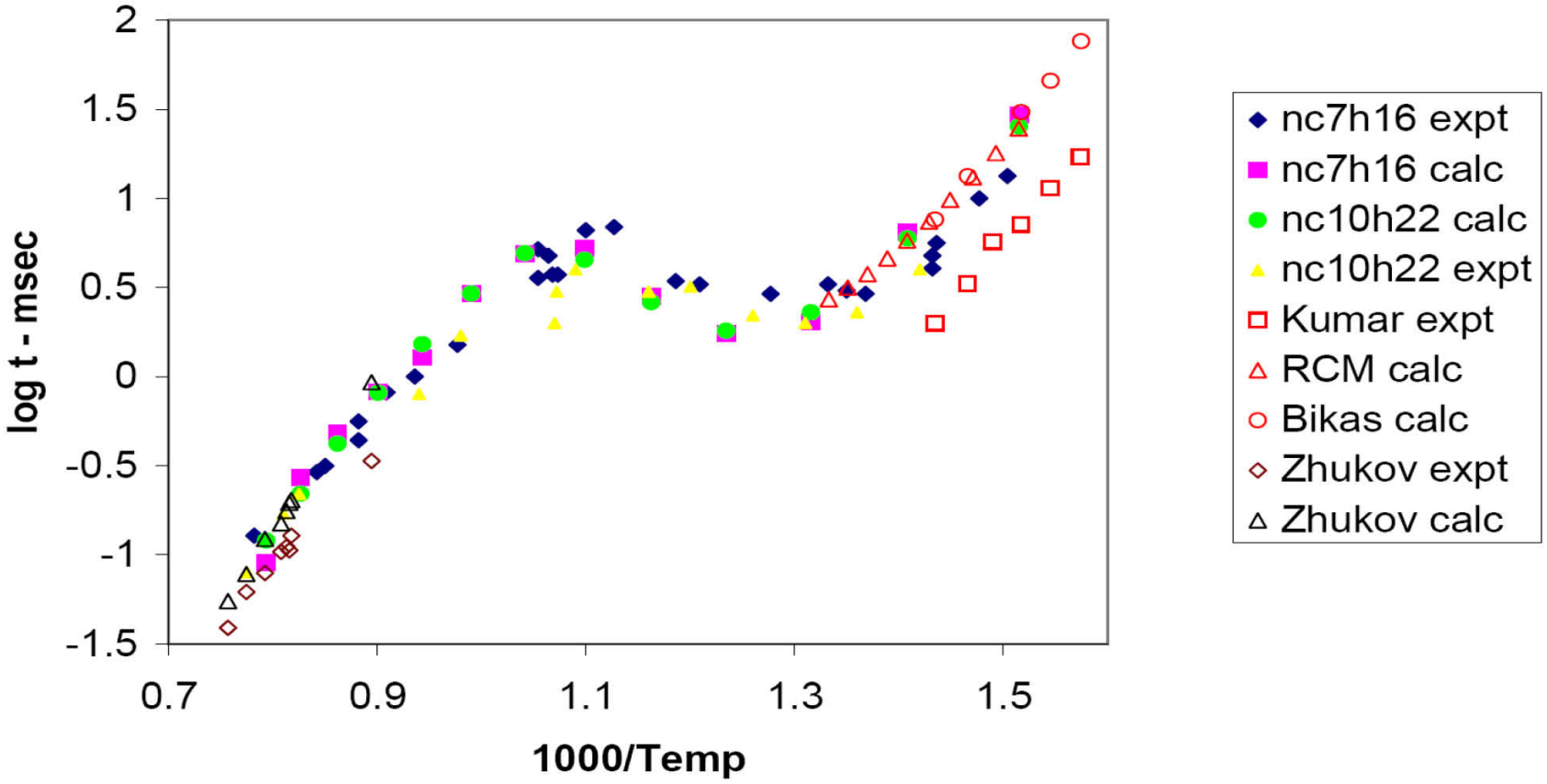
Comparison to rapid compression machine data which is at "engine-like" conditions (14.3 bar, n-decane)

Experimental Validation Data



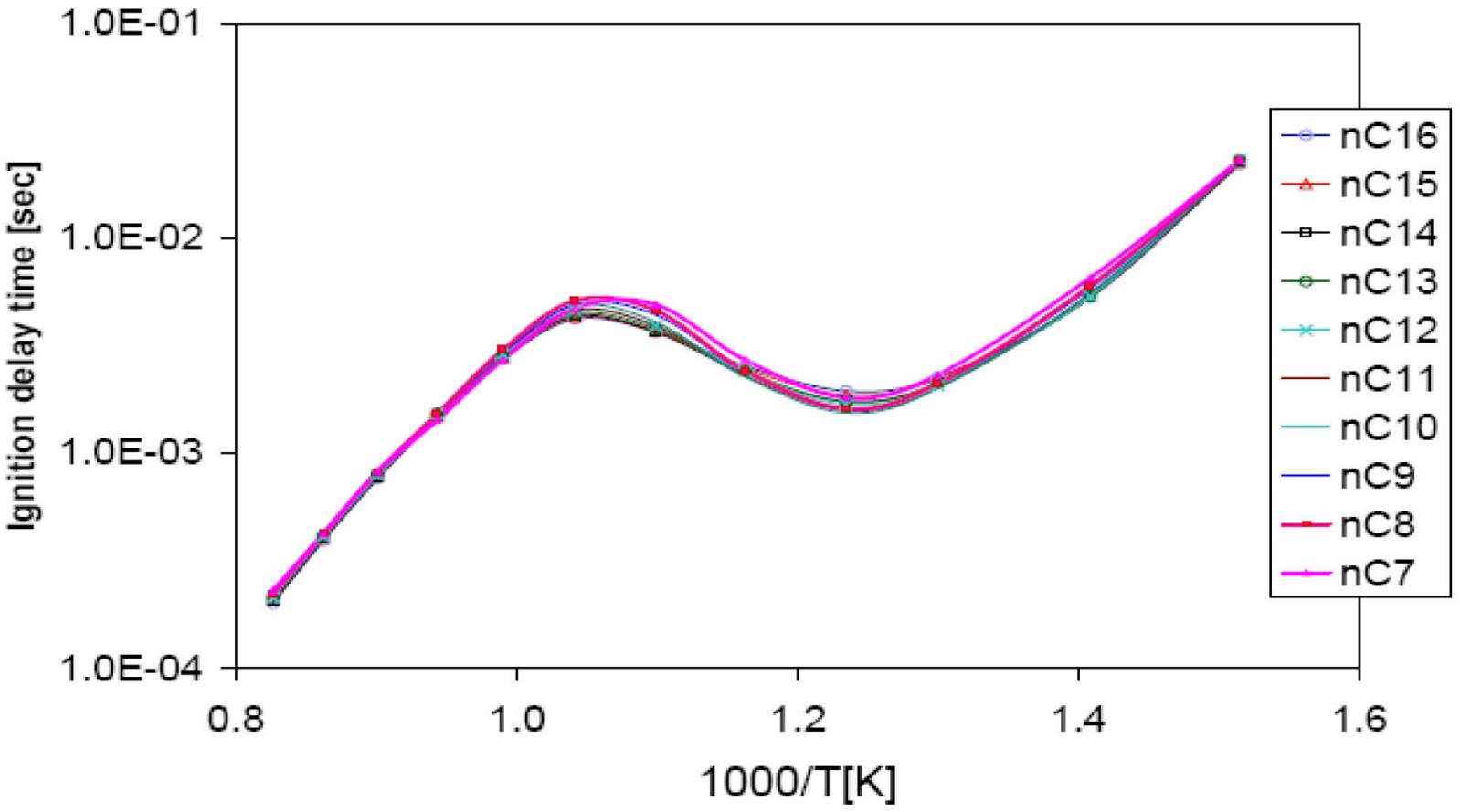
Family of ignition simulations – a valuable analysis tool

n-decane, ϕ = 1.0, 13 bar pressure

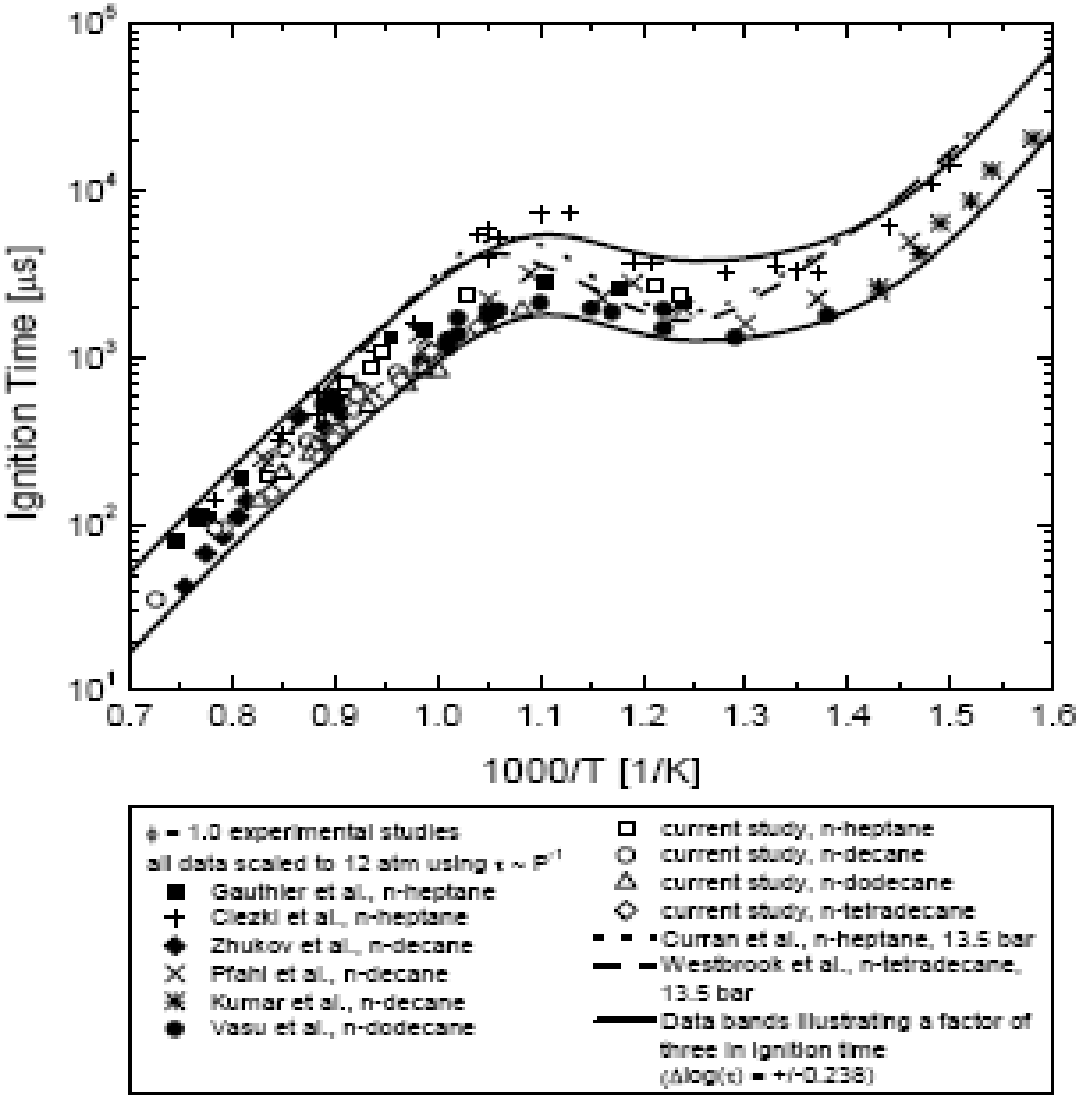


Same approach used by Petersen et al. for propane ignition analyses

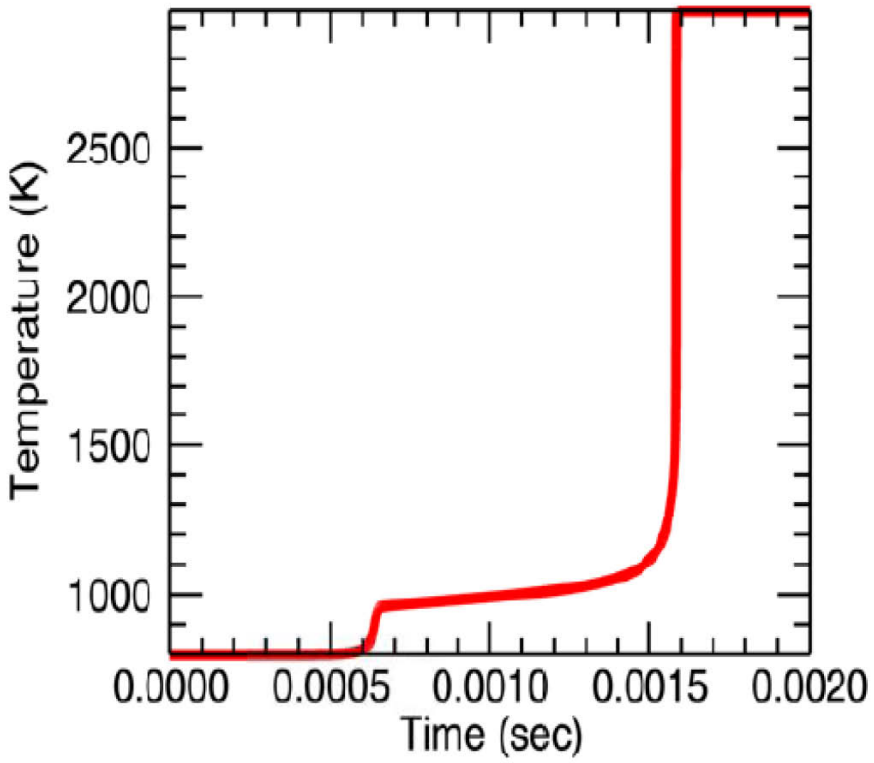
All large n-alkanes have very similar ignition properties

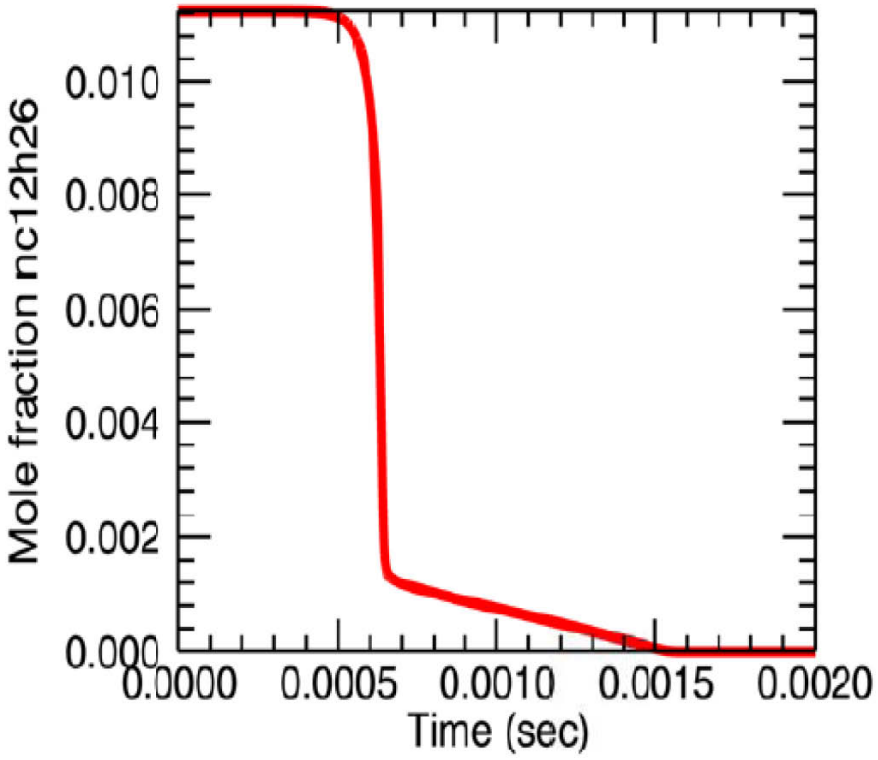


New experiments agree with our computer predictions



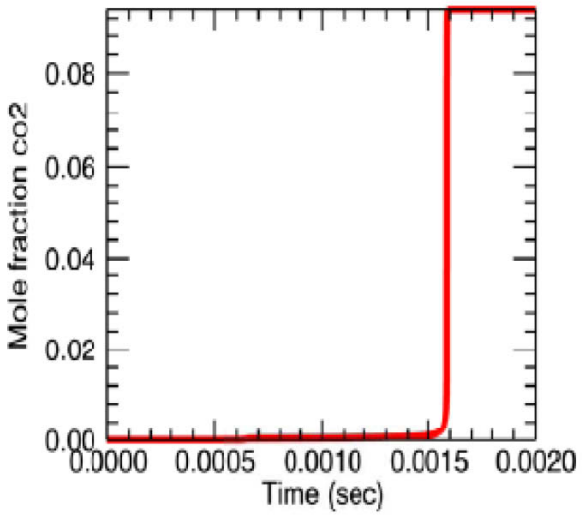
Ignition of n-dodecane at 800K, 13 bar pressure is a familiar 2-stage ignition

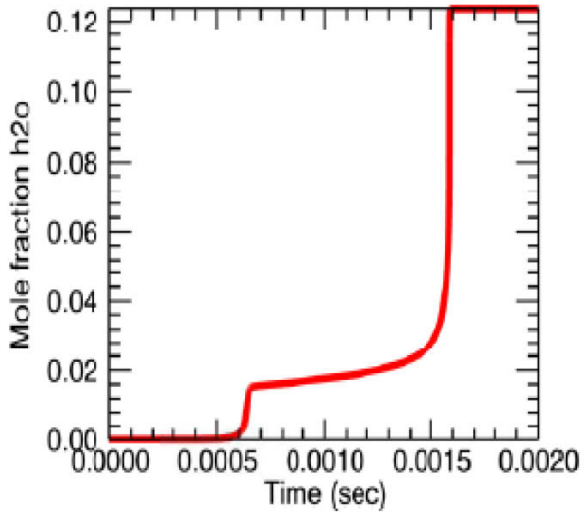




Note that 80% of the fuel is consumed in the first stage ignit

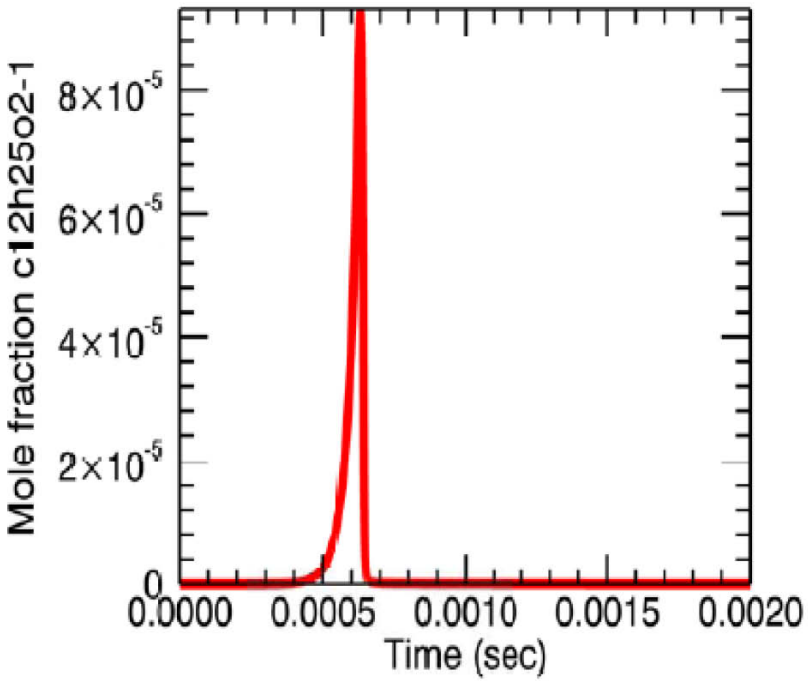
Examples of use of Chemkin Reaction Path Analysis Tools

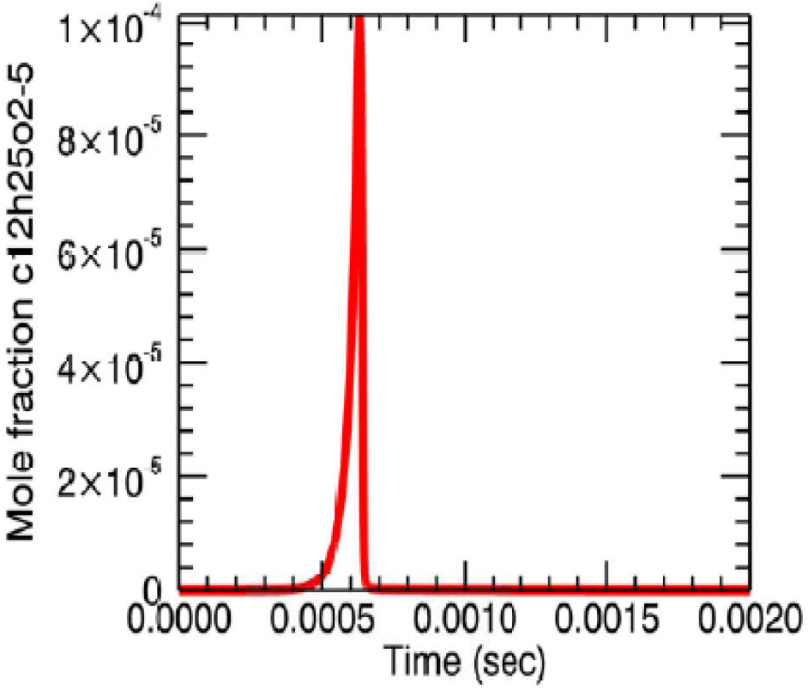




First stage produces H2O but very little CO2

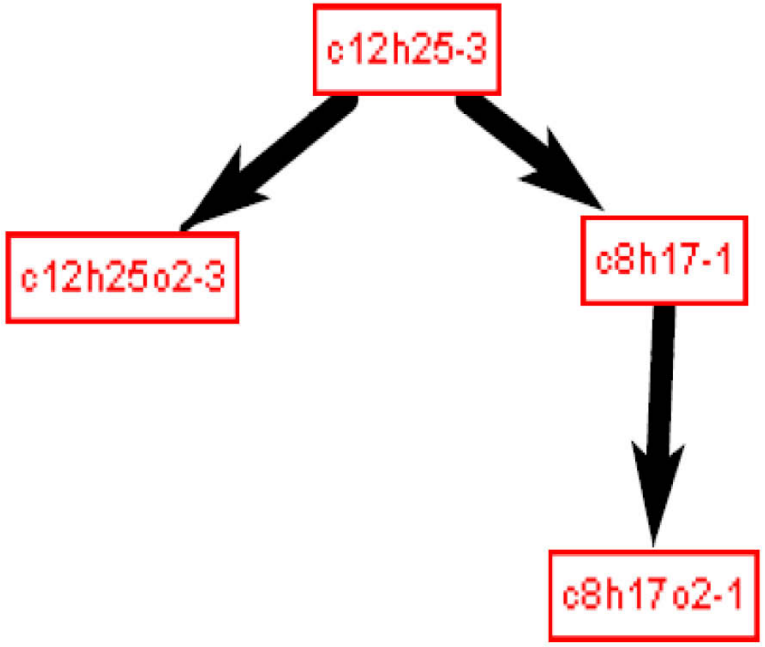
A lot of the “action” occurs at the time of the first ignition stage

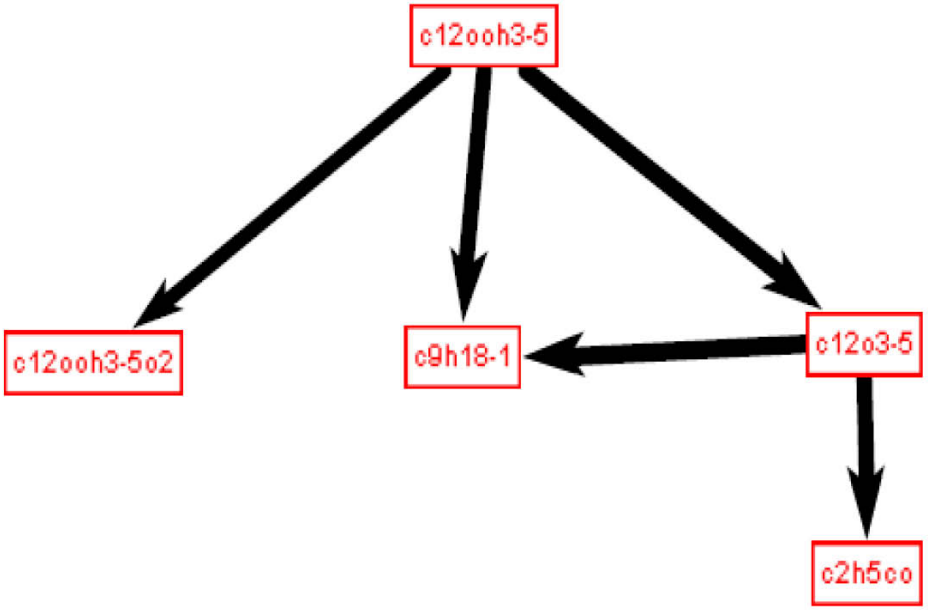




During the low temperature ignition, alkyl radicals add to mo

oxygen and also decompose directly to smaller alkyl radical



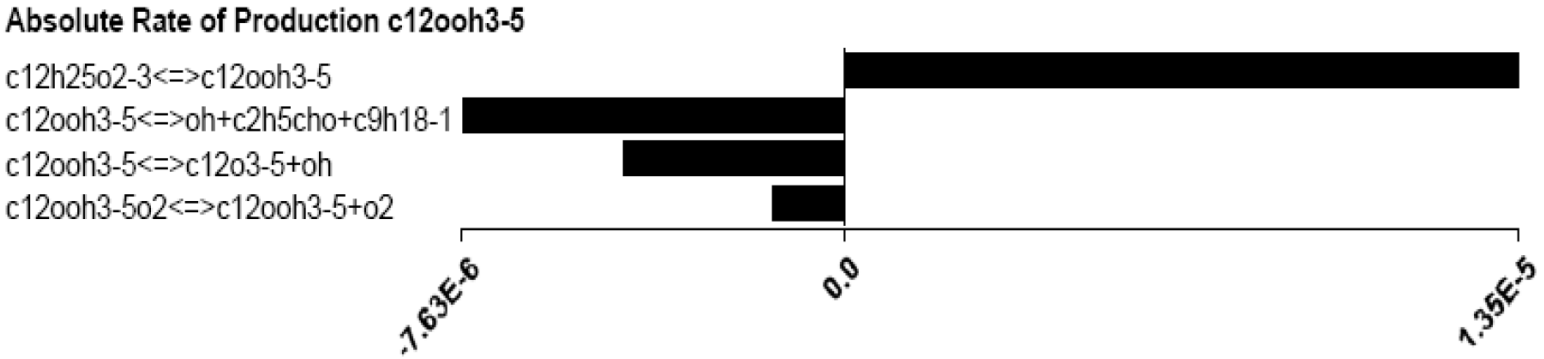


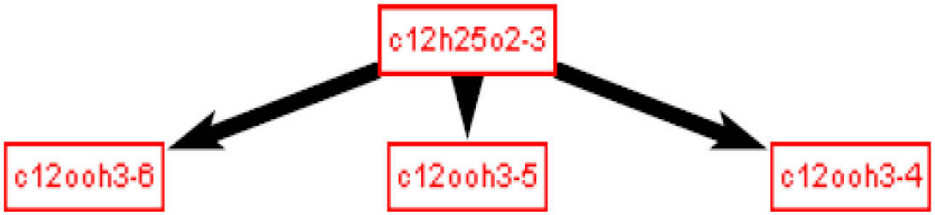
QOOH species can react by 3 pathways

QOOH + O2 → O2QOOH

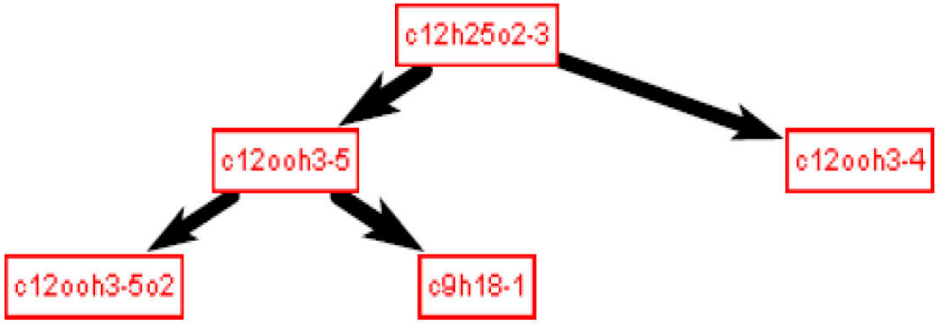
QOOH → β-scission

QOOH → cyclic ether

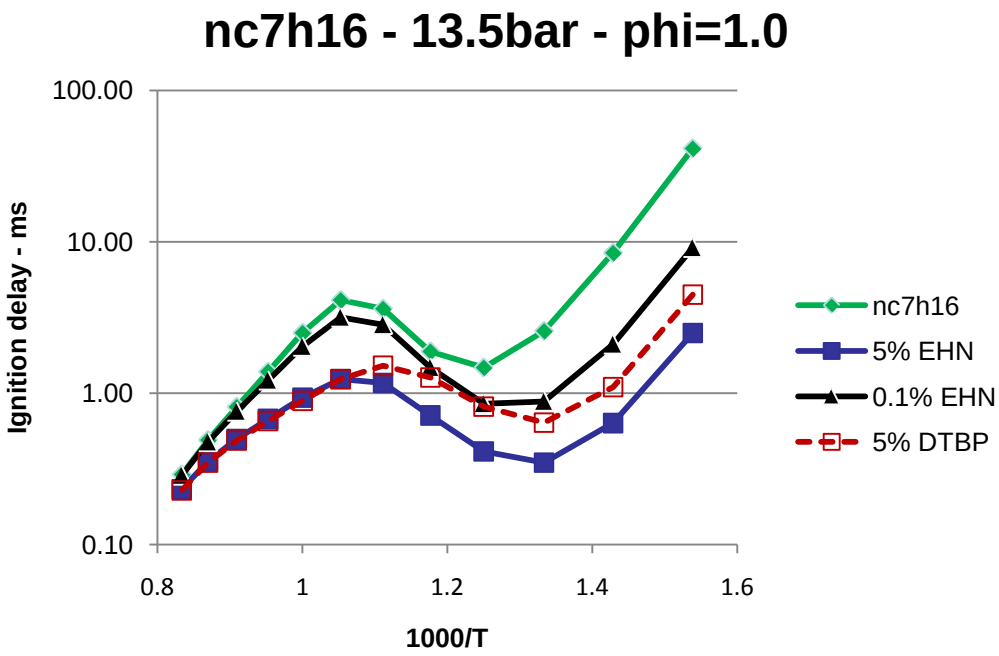


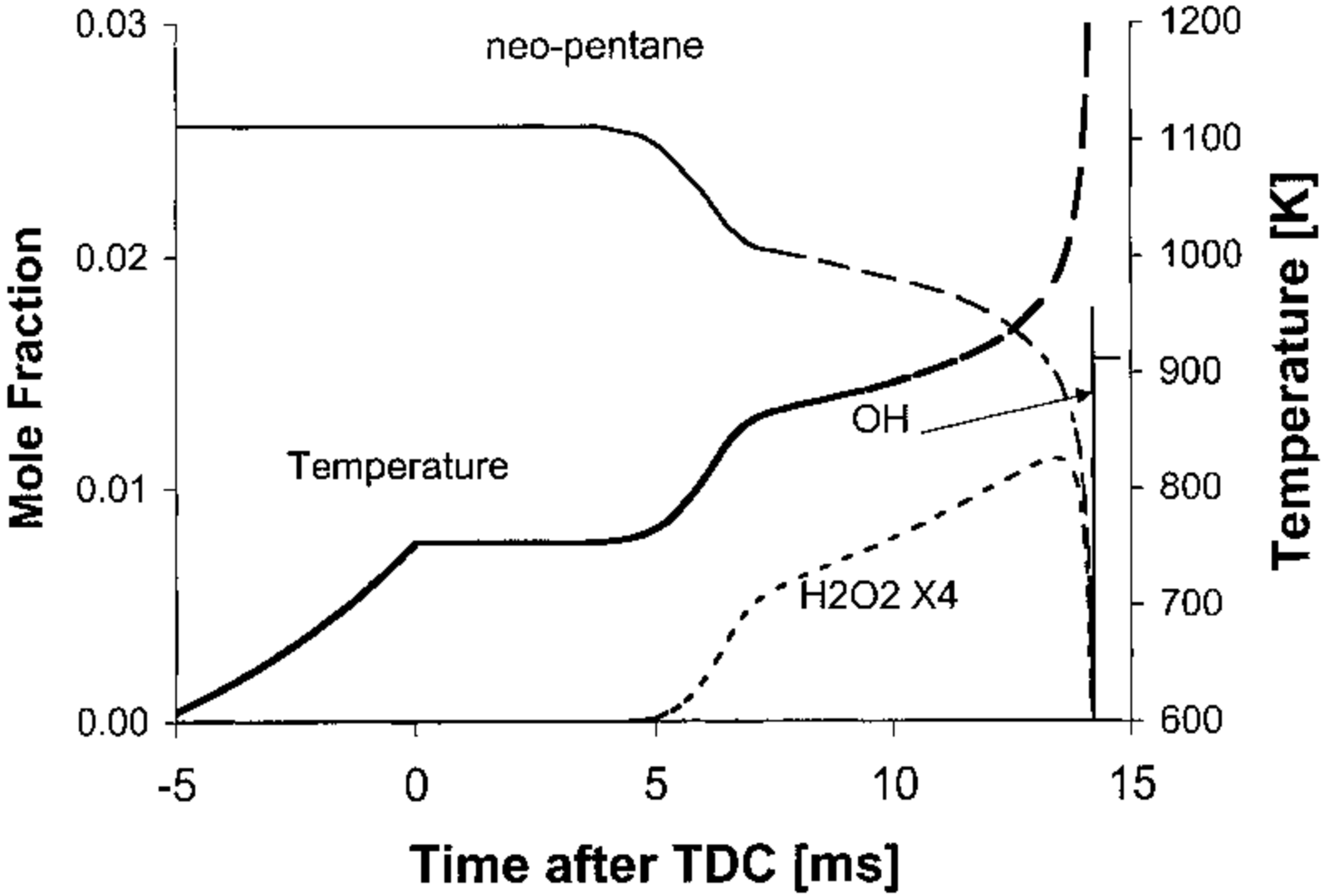


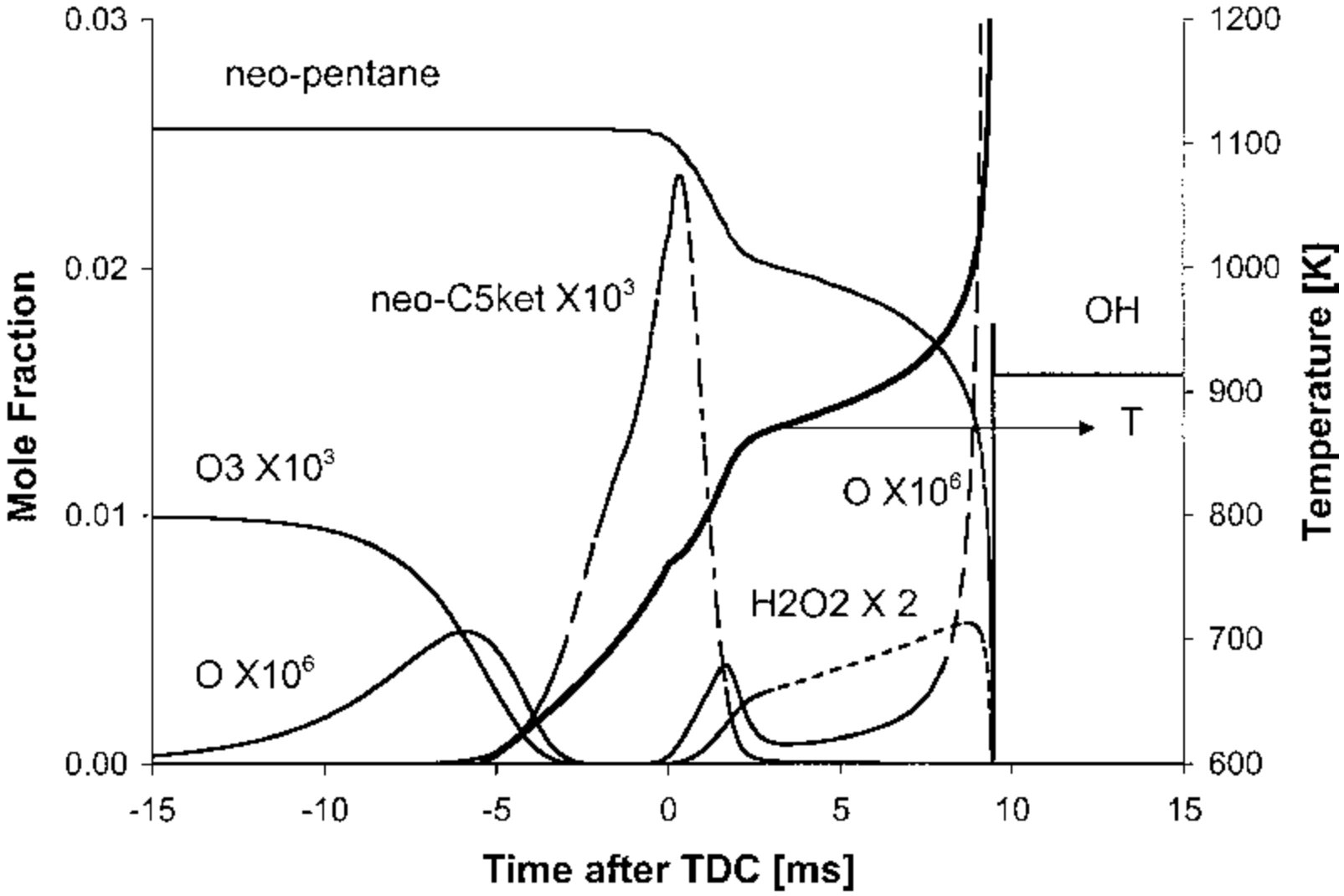
Each QOOH species has multiple possible reaction pathways available



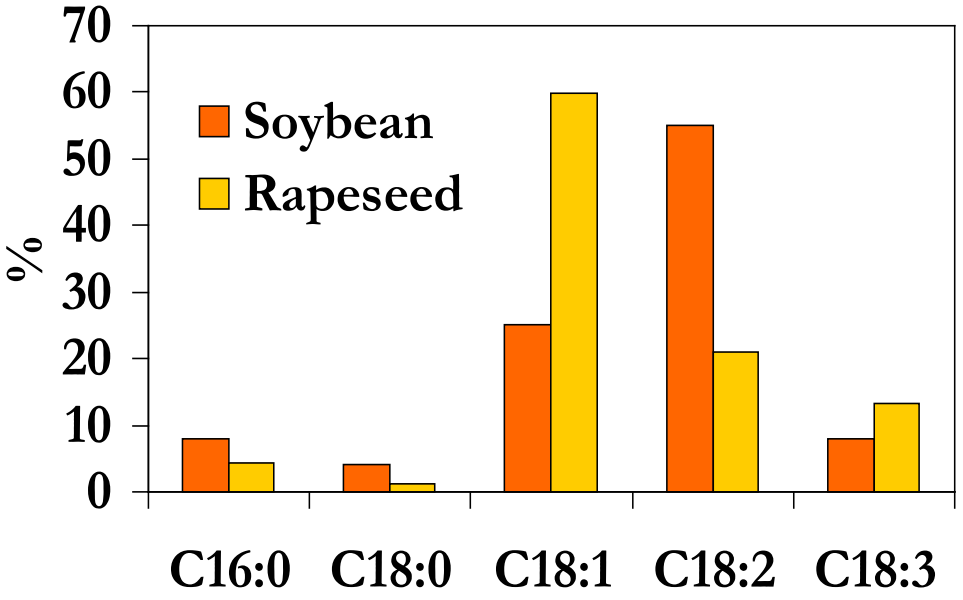
The rates of those possible reaction pathways depends on the exact structure of the QOOH species

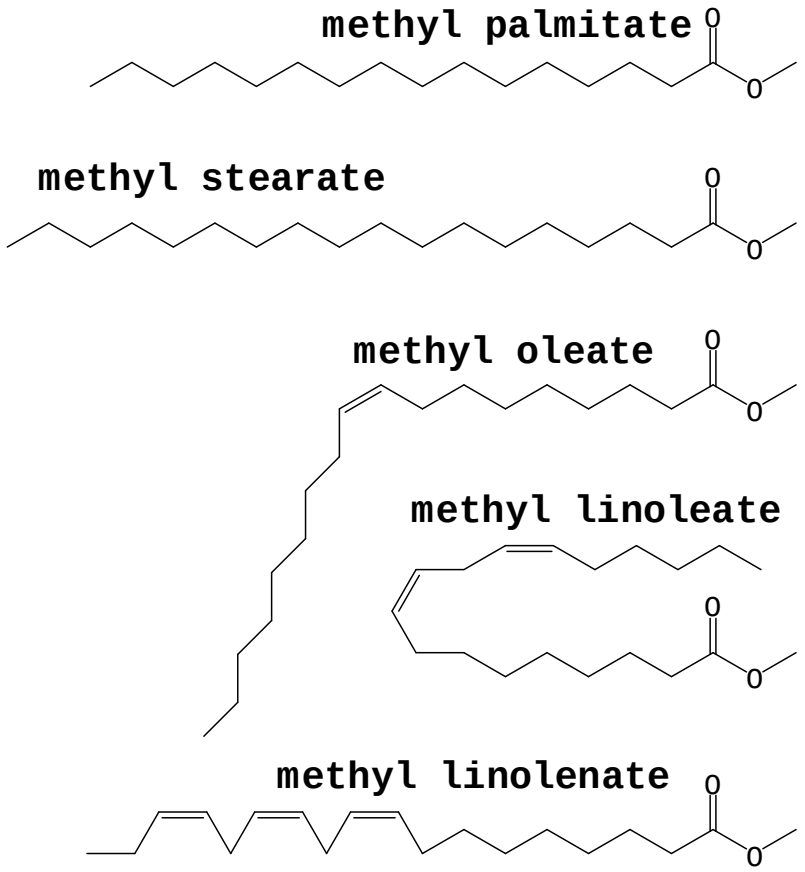

nc7h16 - 13.5bar - phi=1.0
100.00
10.00
1.00
0.10
Ignition delay - ms
0.8
1
1.2
1.4
1.6
1000/T
nc7h16
5% EHN
0.1% EHN
5% DTBP


0.03
0.02
0.01
0.00
Mole Fraction
neo-pentane
Temperature
OH
H2O2 X4
1200
1100
1000
900
800
700
600
Temperature [K]
-5
0
5
10
15
Time after TDC [ms]


neo-pentane
neo-C5ket X10^3
OH
T
O3 X10^3
O X10^6
H2O2 X 2
O X10^6
Mole Fraction
Temperature [K]
Time after TDC [ms]
0.03
0.02
0.01
0.00
1200
1100
1000
900
800
700
600
-15
-10
-5
0
5
10
15

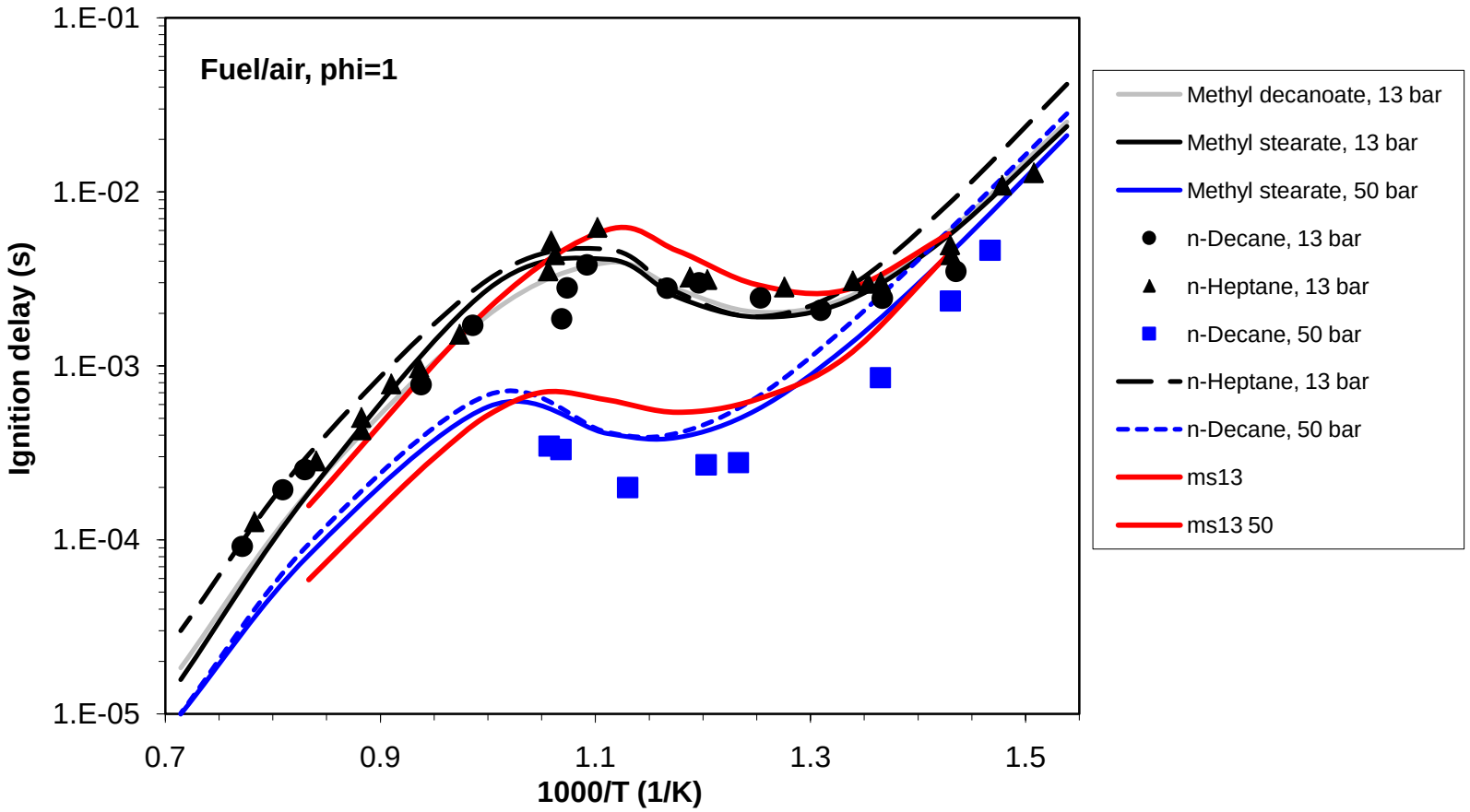
Composition of Biodiesels



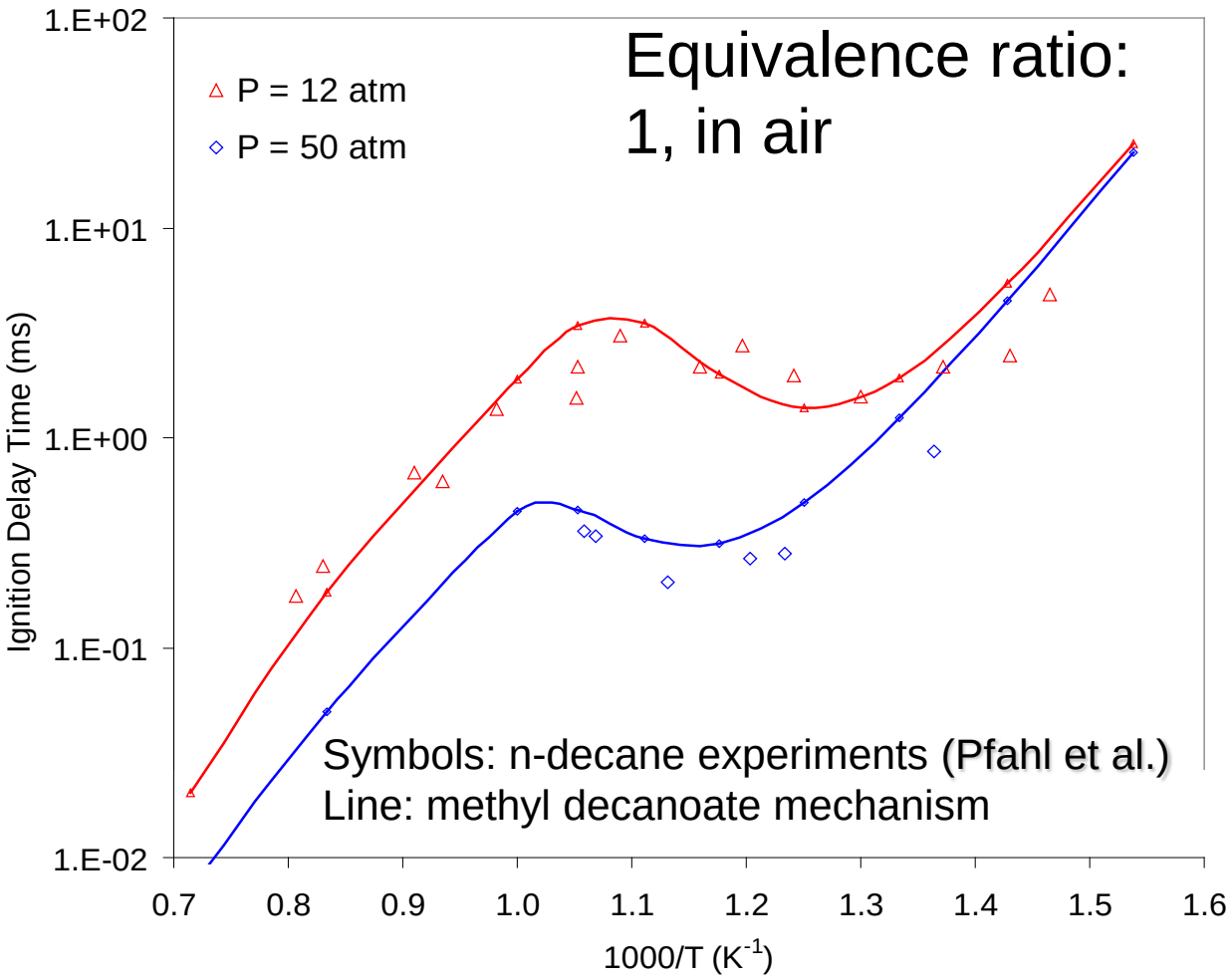


Biodiesel fuels can be made from vegetable oils such as soy, palm, flaxseed, canola, and olive oil and animal fats

Methyl stearate (n-C_{18} methyl ester) has the same ignition properties as large alkanes



Comparison with n-Decane Ignition Delay Times



Ignition delay times very close

n-Alkanes:

cannot reproduce the early formation of CO_2

but

reproduce the reactivity of methyl esters very well

Interesting note

Experience with biodiesel

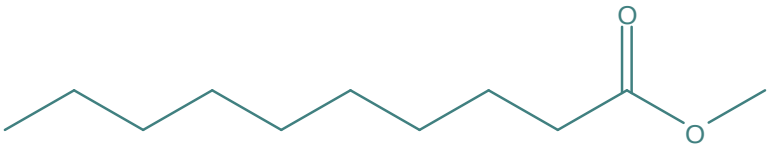
and methyl esters

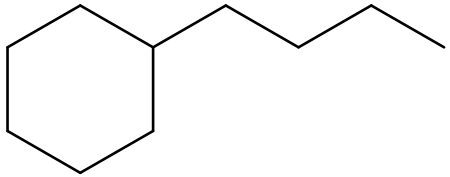
suggests strategies for

kinetic modeling of n-alkyl

benzenes and n-alkyl

cyclohexanes

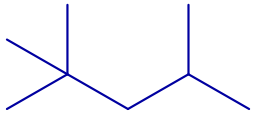




Branched hydrocarbons are different

- Both octane and cetane rating systems have a straight-chain reference fuel that is easy to ignite and a branched reference fuel that is hard to ignite
- iso-octane and 2,2,4,4,6,8,8-heptamethyl nonane
- n-heptane and n-hexadecane
- Are all branched hydrocarbons as similar to each other as the straight-chain hydrocarbons?
- Very few laboratory experiments available for mechanism validation of HMN
- Base a reaction mechanism on previous sets of reaction classes

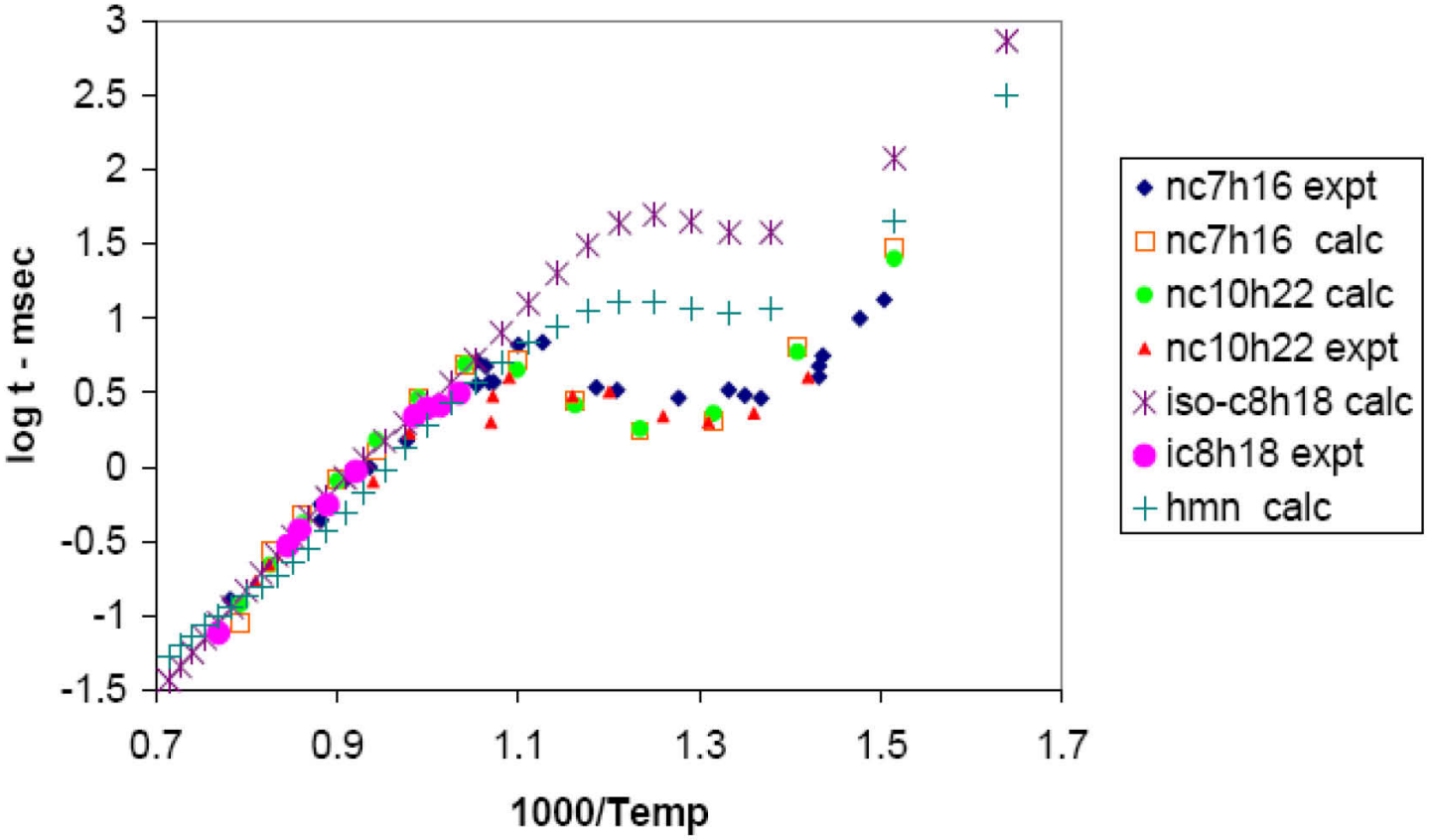
- Iso-octane



- 2,2,4,4,6,8,8 heptamethylnonane (iso

HMN and iso-octane ignition is slower than n-alkanes only in the Low Temperature regime

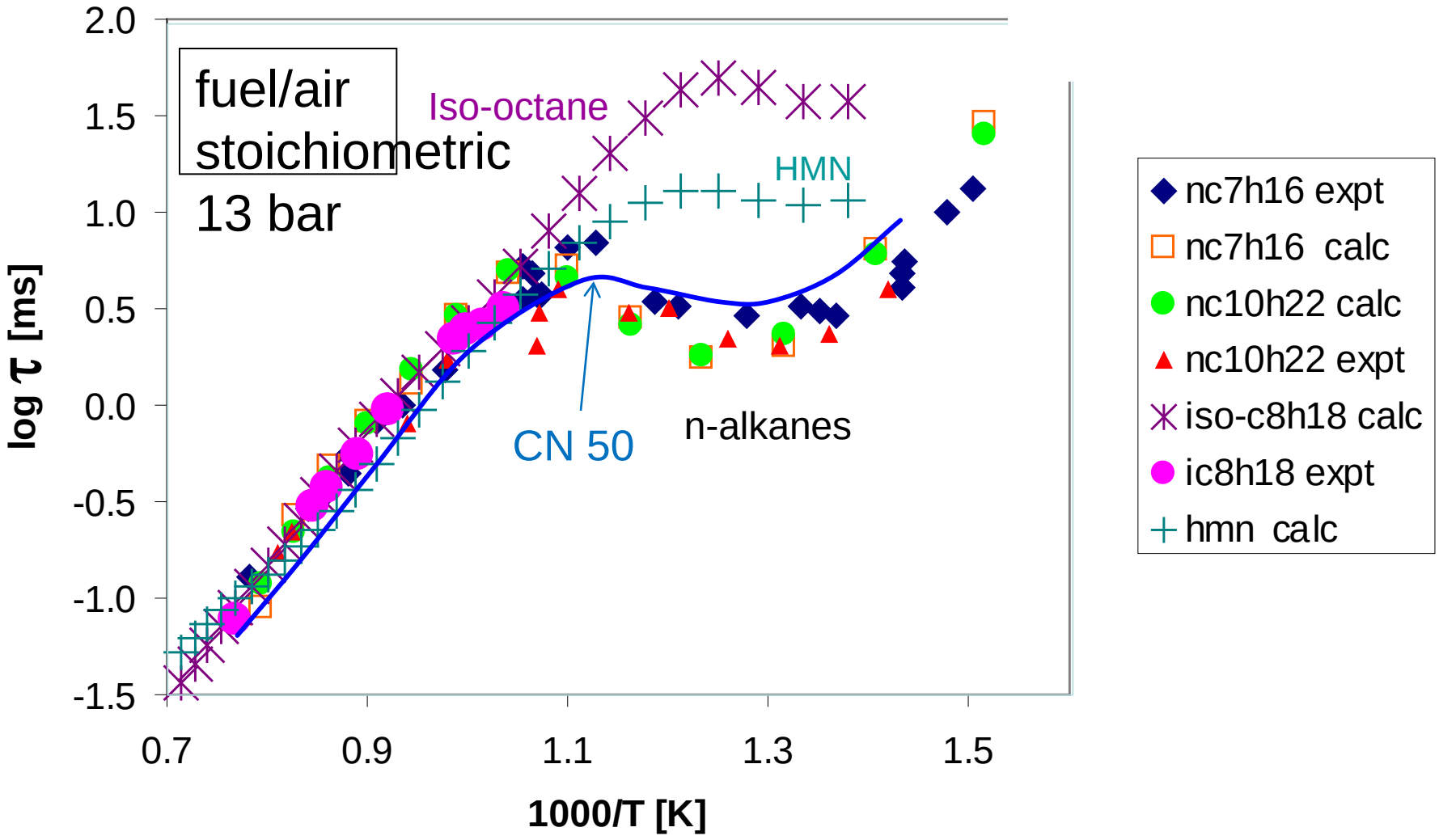
13.5 bar pressure



PFR Ignition results at 13 bar:

n-hexadecane

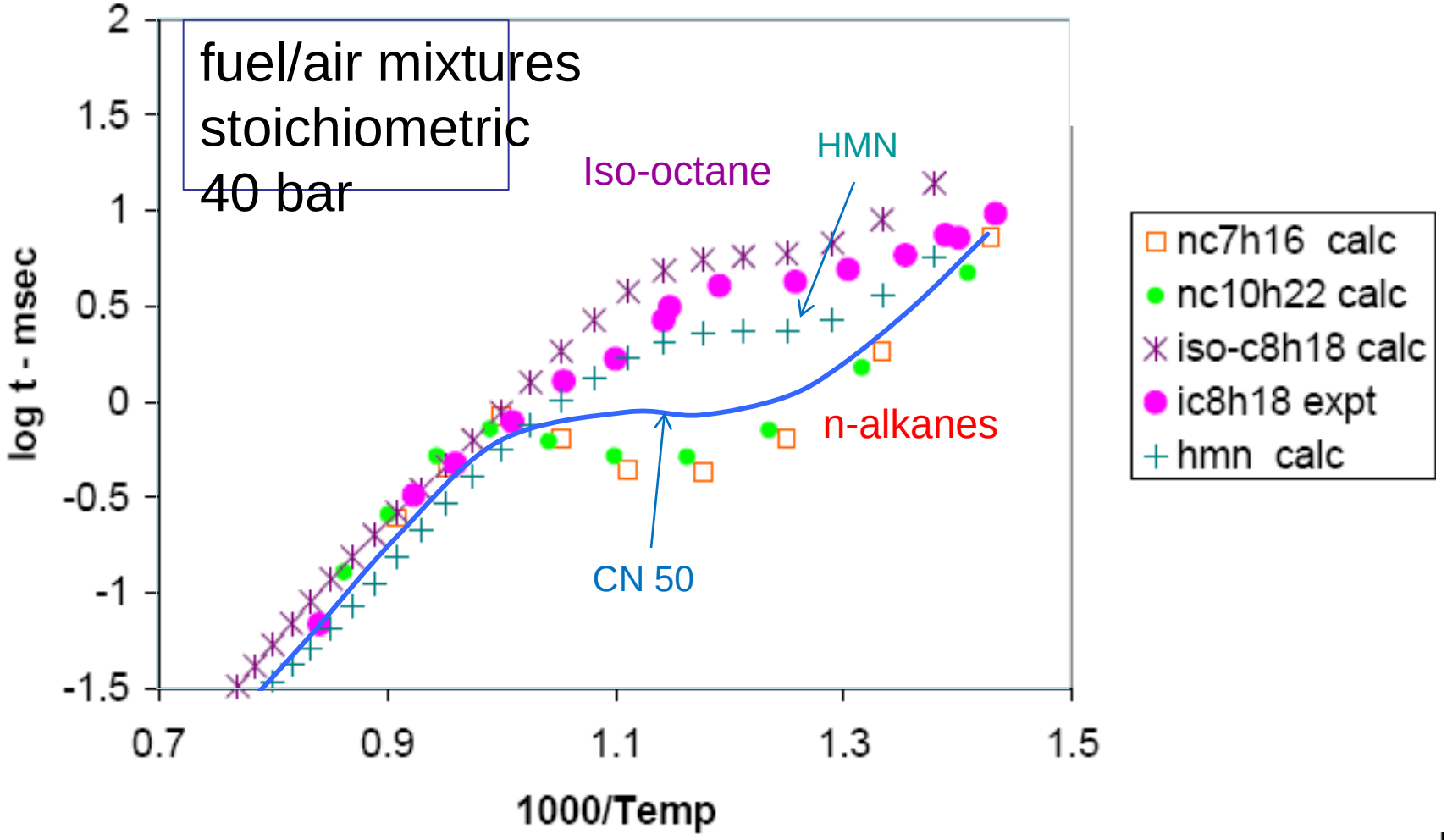
2,2,4,4,6,8,8, heptamethylnonane



PFR Ignition results at 40 bar:

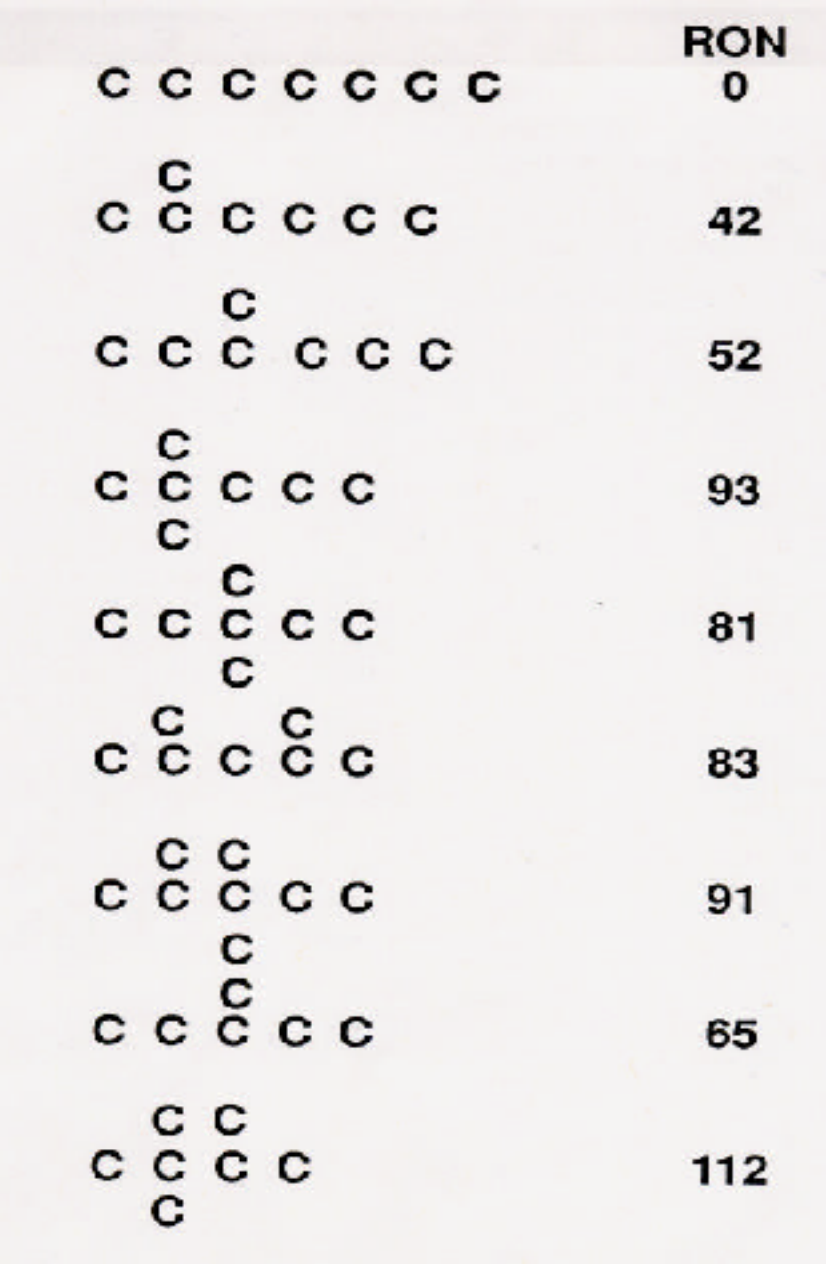
n-hexadecane

2,2,4,4,6,8,8, heptamethylnonane

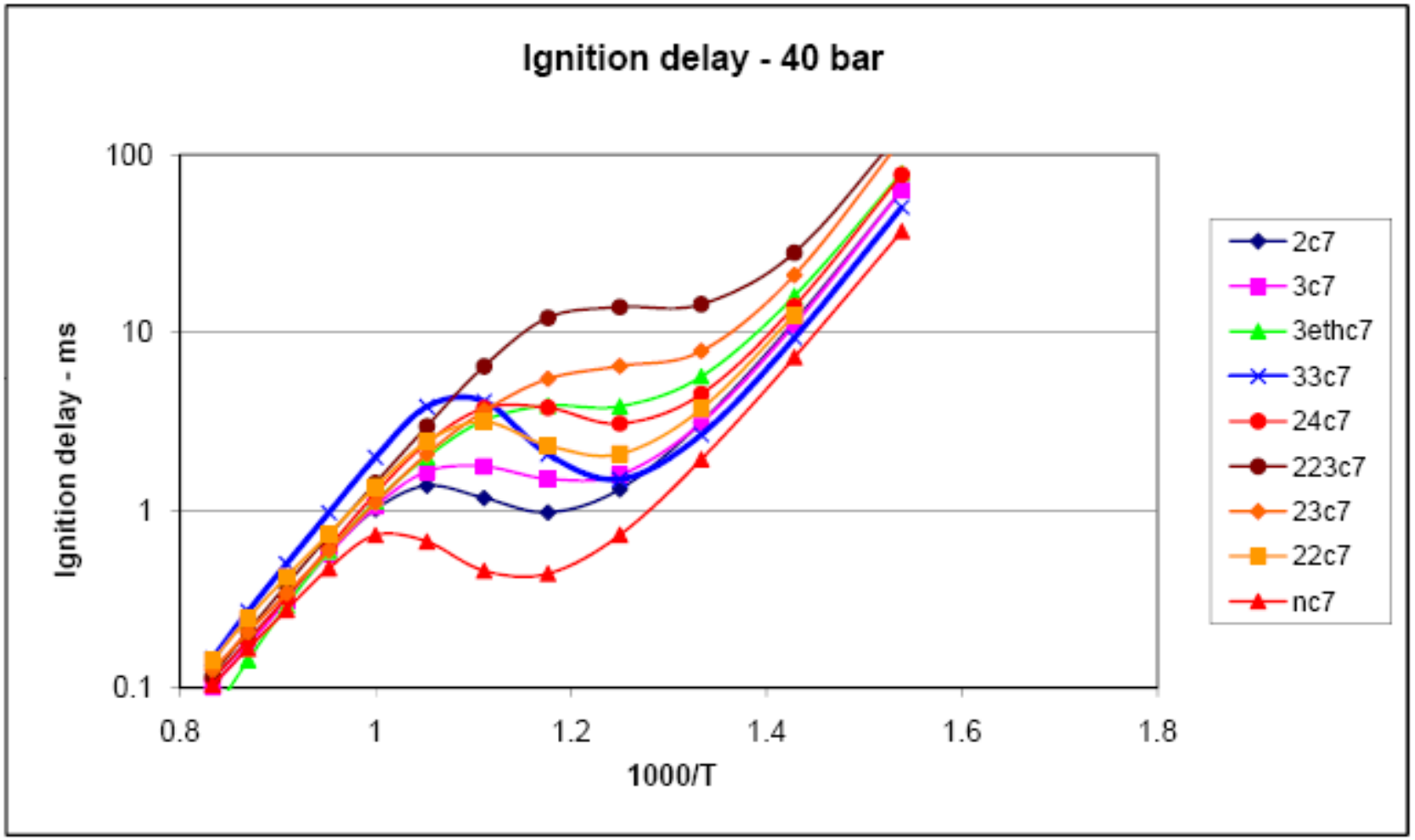


Octane numbers of heptanes are due exclusively to their different molecular structures

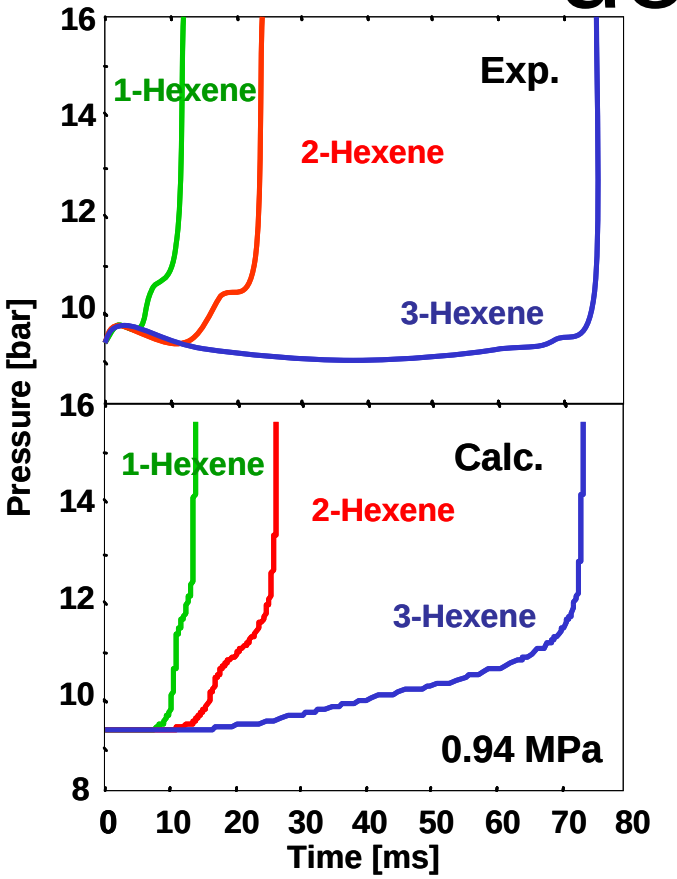
Low octane fuels have lots of secondary C-H bonds and high octane fuels have lots of primary C-H bonds and lots of tight, 5-membered TS rings

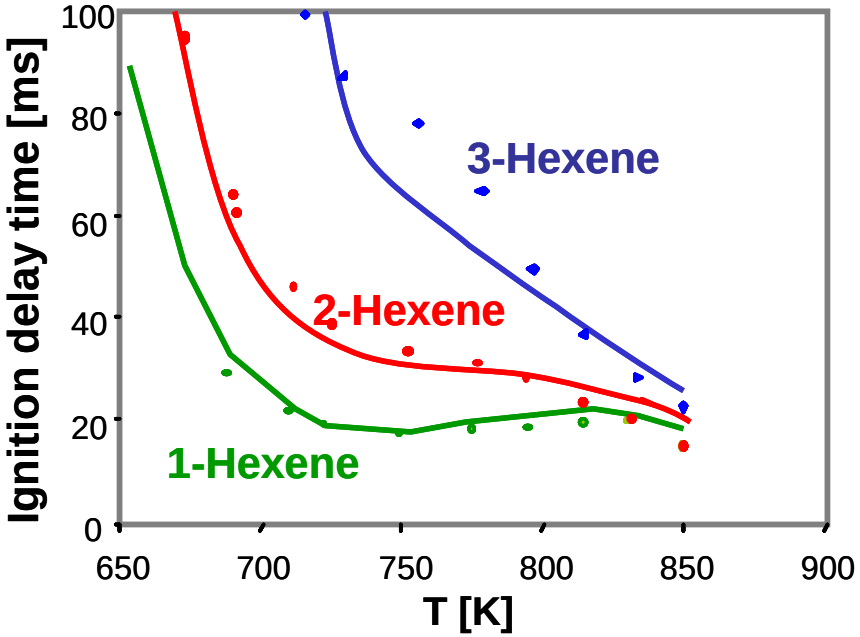


Heptane isomers provide an interesting family of fuels
RON varies from 0 to 112



Effect of the position of the double bond



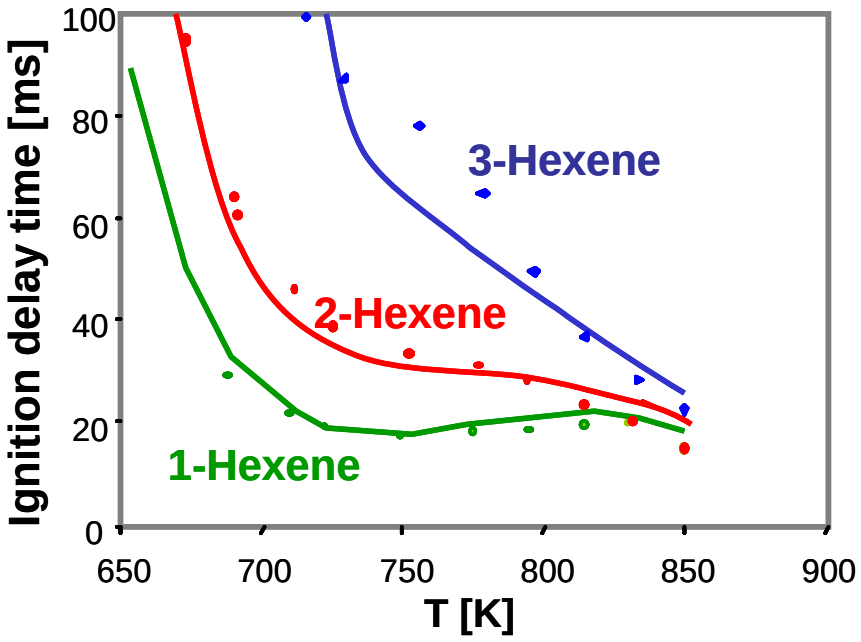


The length of the free saturated carbon chain determines the reactivity

C = C - C - C - C - C 1-hexene

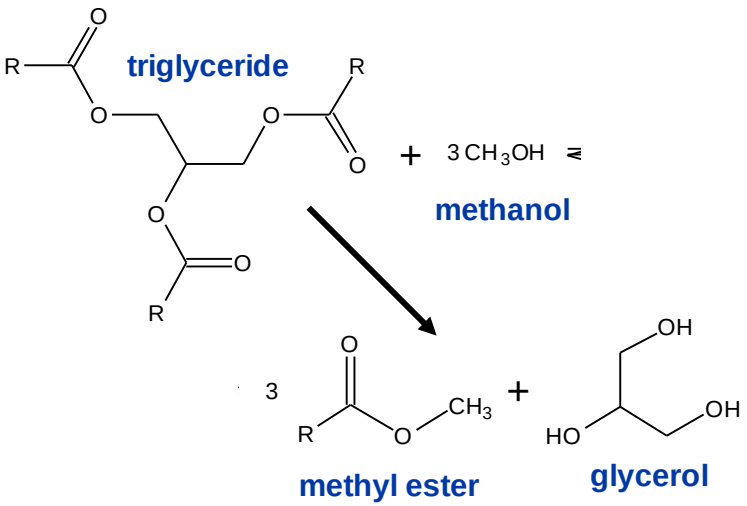
C - C = C - C - C - C 2 – hexene

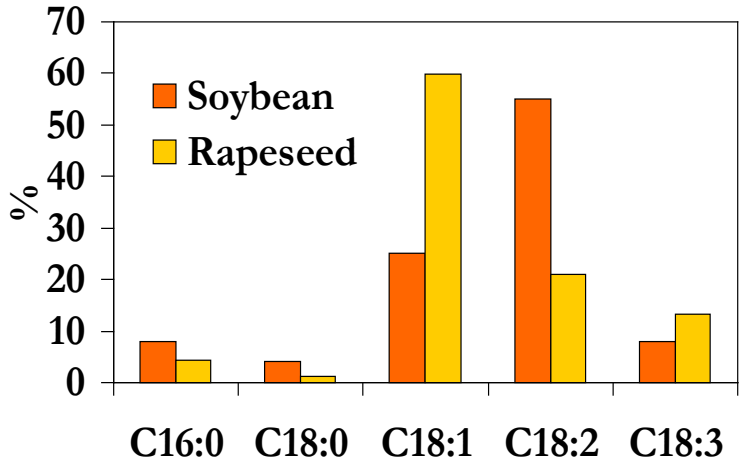
C - C - C = C - C - C 3 – hexene



RCM Ignition delay times of hexene isomers (0.86-1.09 MPa, Φ=1):

Composition of Biodiesels





Methyl Palmitate (C16:0)

Methyl Stearate (C18:0)

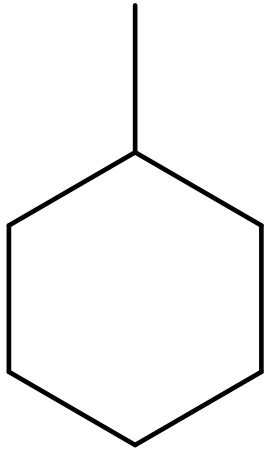
Methyl Oleate (C18:1)

Methyl Linoleate (C18:2)

Methyl Linoleanate (C18:3)

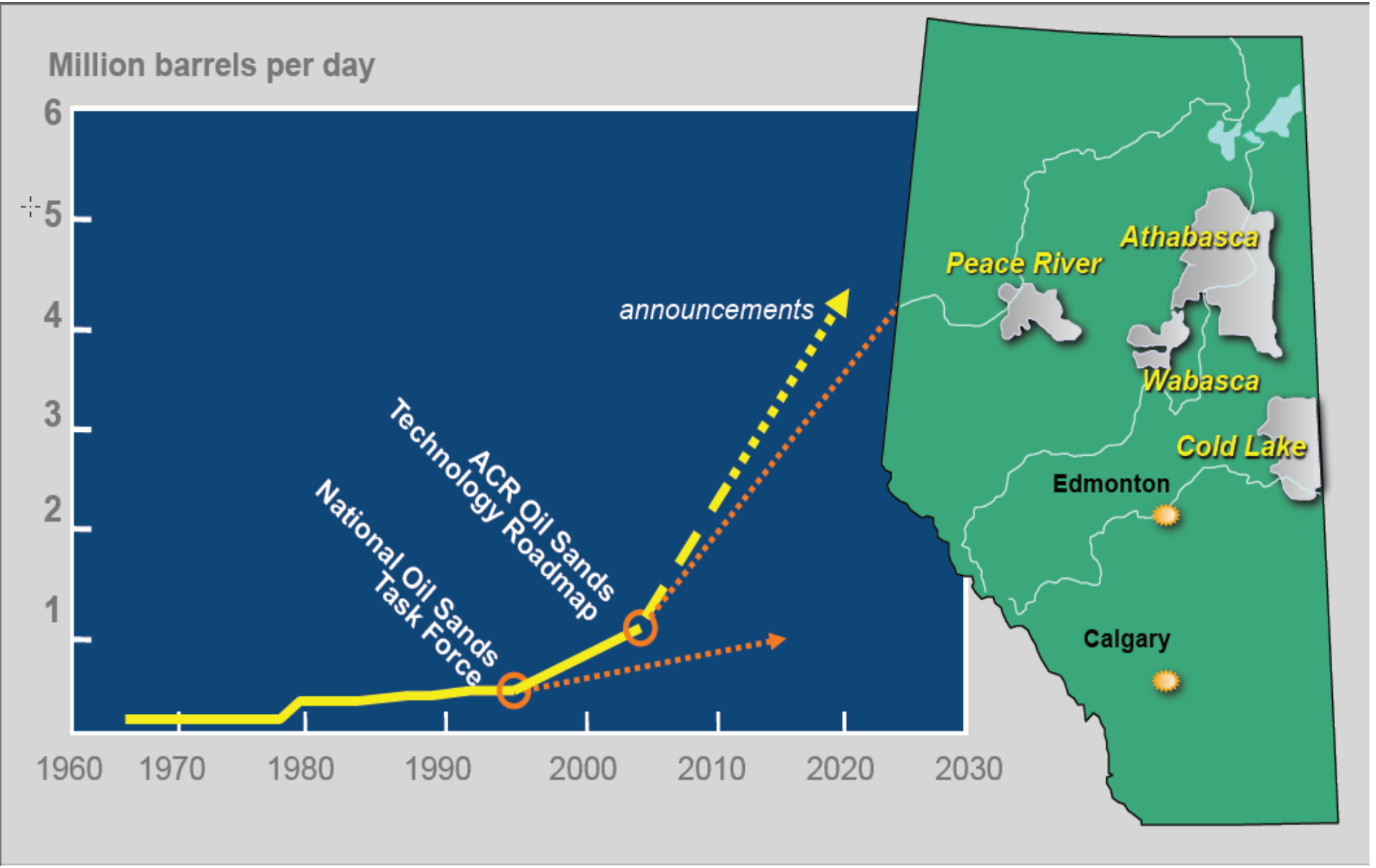
Cycloalkanes: methyl cyclohexane

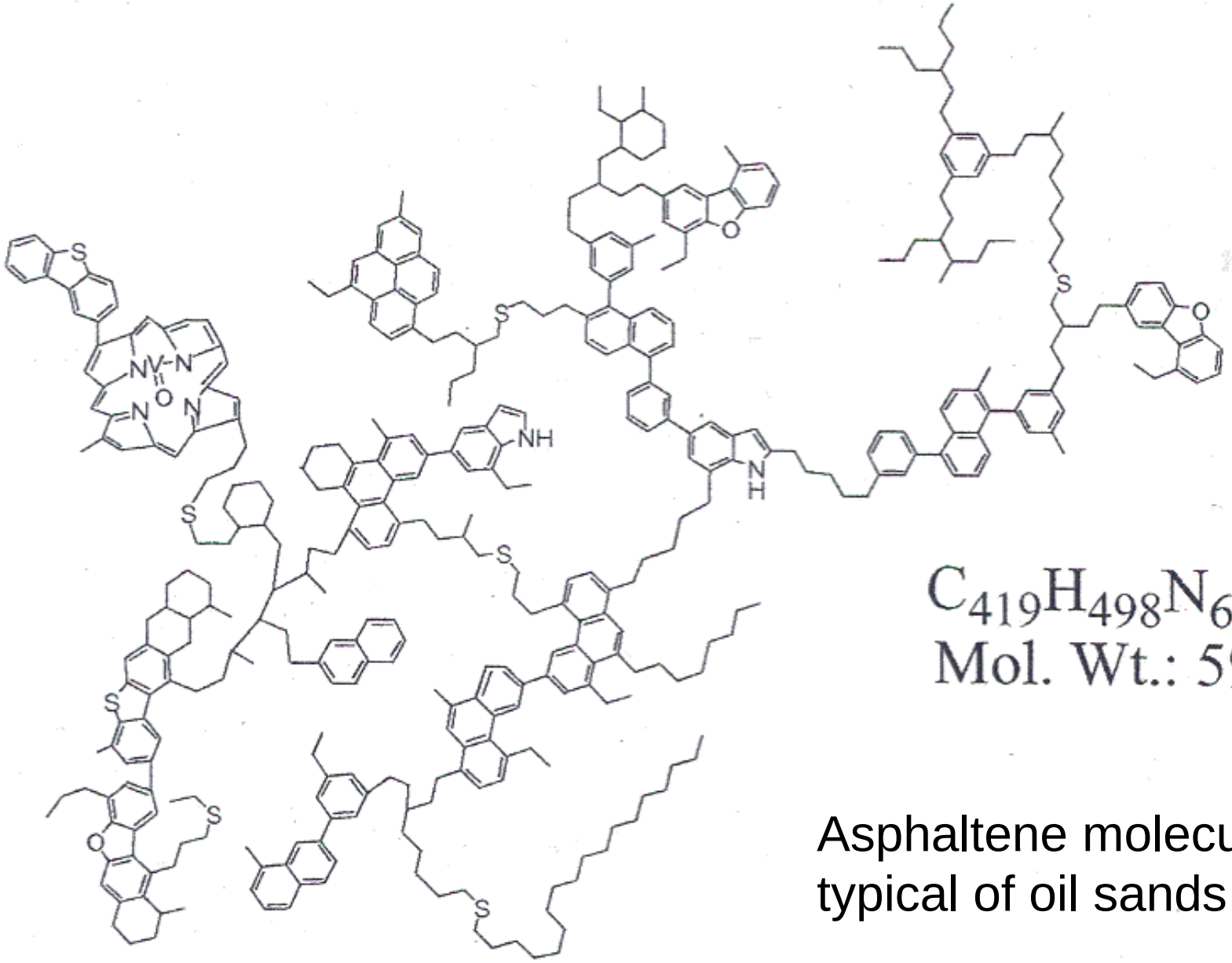
- Cycloalkanes are interesting due to oil sands
- Cycloalkanes are present in most practical fuels and surrogate fuels



methylcyclohexane

Oil-sand derived fuels have focused attention on cyclo-alkanes

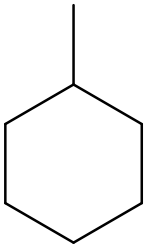




$C_{419}H_{498}N_6O_4S_8V$
Mol. Wt.: 5989.94

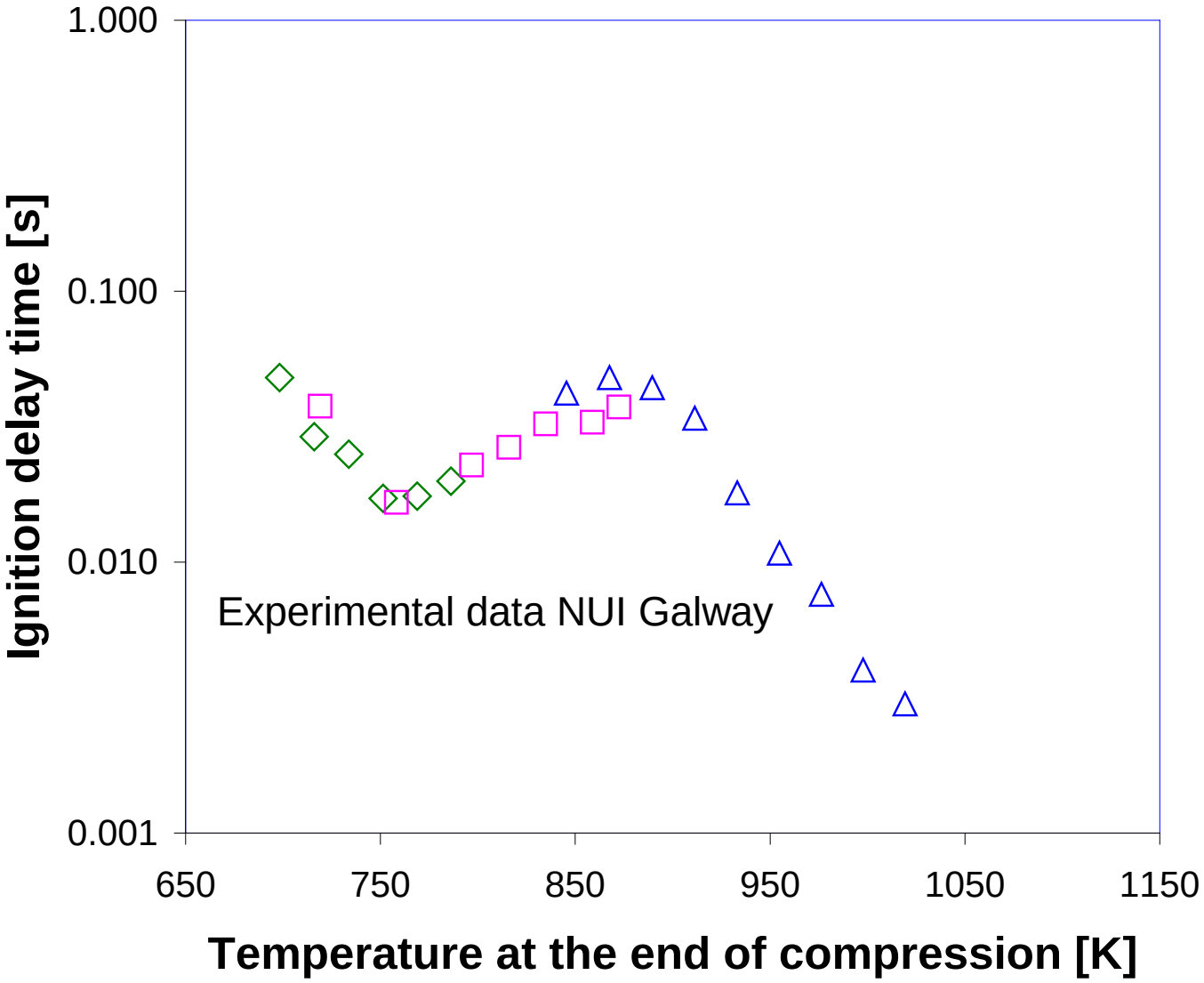
Asphaltene molecule typical of oil sands

Experiments: Rapid compression machine (RCM) at NUI Galway

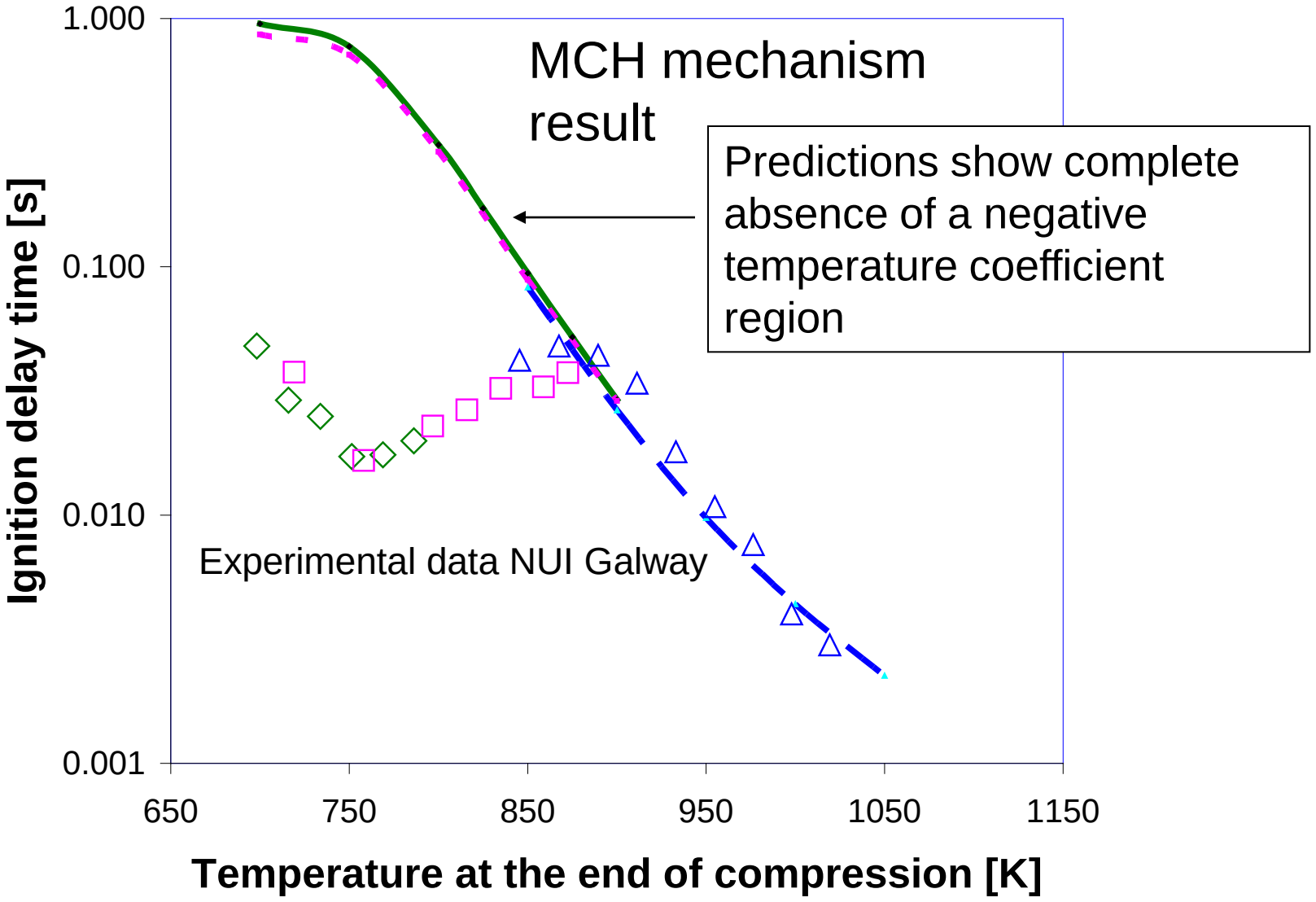


- Opposed piston RCM originally used by Shell
  - => fast compression times of about 16 ms
- Large crevice on perimeter of piston to contain wall boundary layer
  - =>uniform temperatures across combustion chamber
- Use N_2 and Ar as diluents to attain range of compressed gas temperatures
- Stoichiometric mixtures of MCH/O_2/Ar/N_2
- 10,15 and 20 atm pressure at the end of compression.

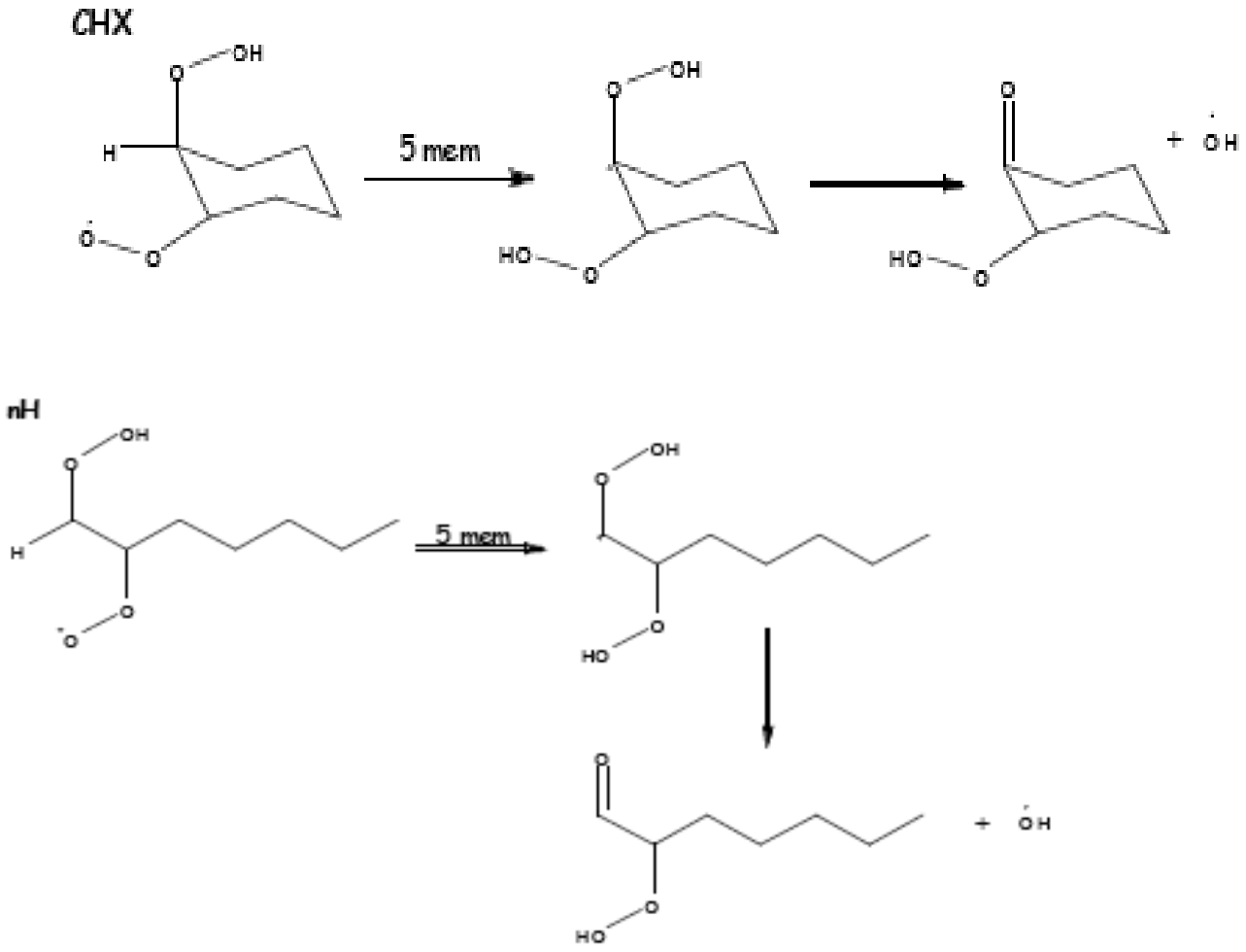
Experimental data at 10 atm shows distinct NTC region:



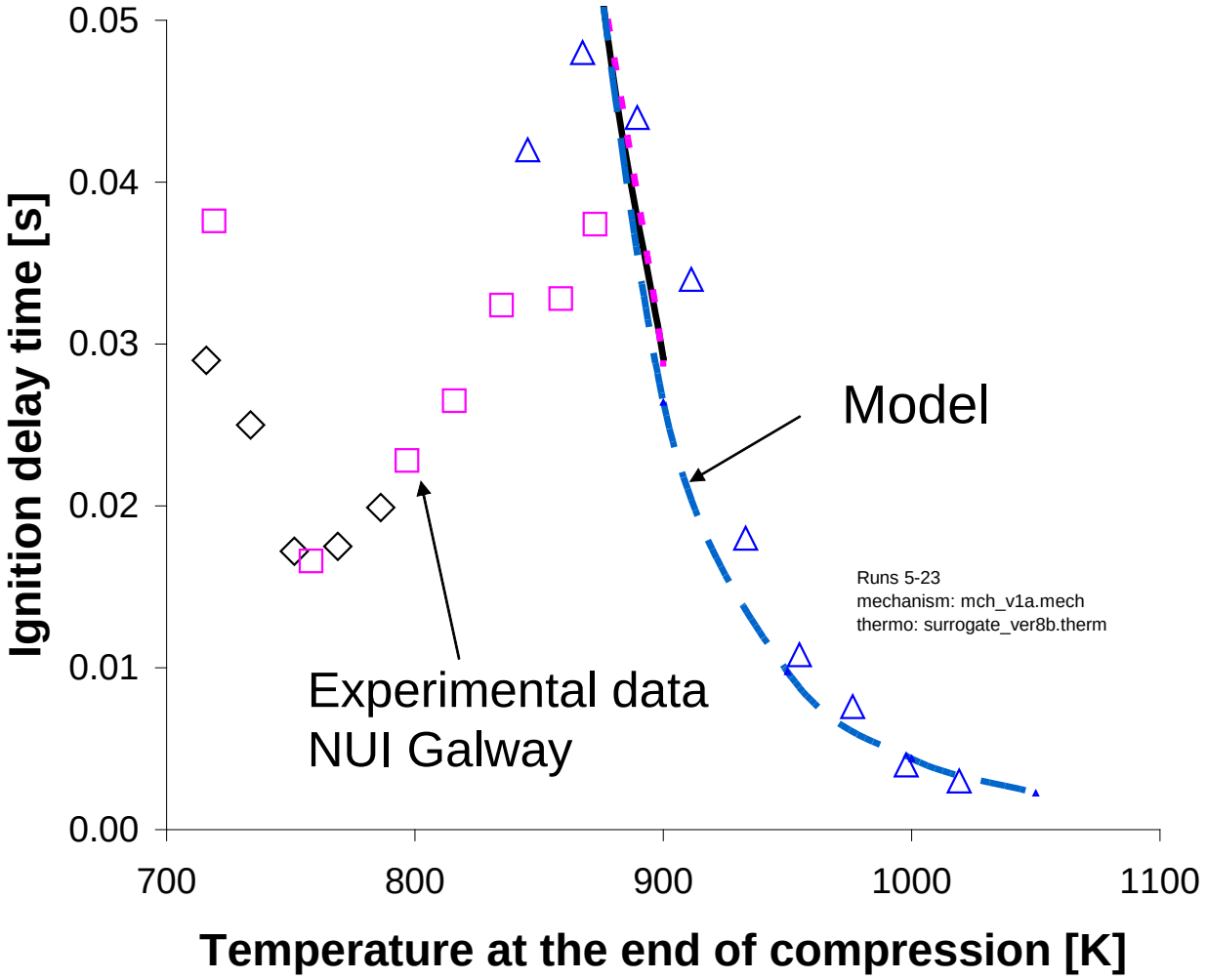
N-alkane based RO2 isomerization rates gave too slow ignition delay times in rapid compression machine at low temperatures:



Rates of important isomerization reactions were estimated by comparison with known reactions for alkanes



Comparisons with rapid compression machine results shows predicted low temperature chemistry for MCH is too slow



Examine RO2 isomerization rate constants based on n-alkane rates:

Ring size in transition state	A	n	Ea	Rate at 750K	Branching fraction
Alkylperoxy-corrected estimate:					
5	5.0e12	0	26850	8.0e4	0.4%
6	5.0e12	0	20850	4.5e6	23%
7	5.0e12	0	19050	1.5e7	77%

Small fraction going to six membered ring that leads to chain branching

Walker et al. has carried out low temperature kinetic experiments on simple cycloalkanes.

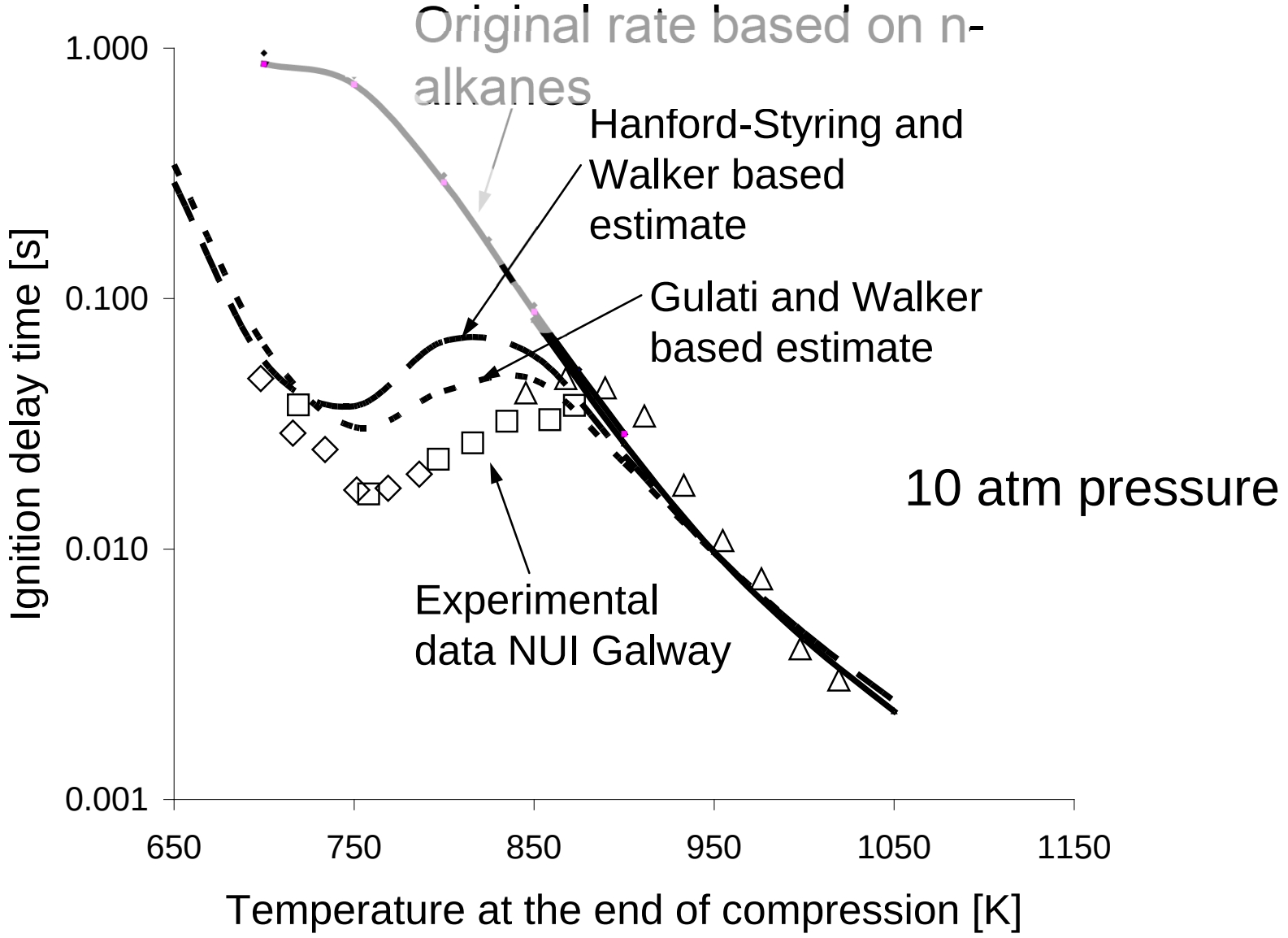
- Small amounts of cyclohexane added to H2/O2
- Derived cyclohexylperoxy (RO2) isomerization rates from initial products observed

Experimentally-based RO2 isomerization rate constants give lots of 6 membered rings and chain branching:

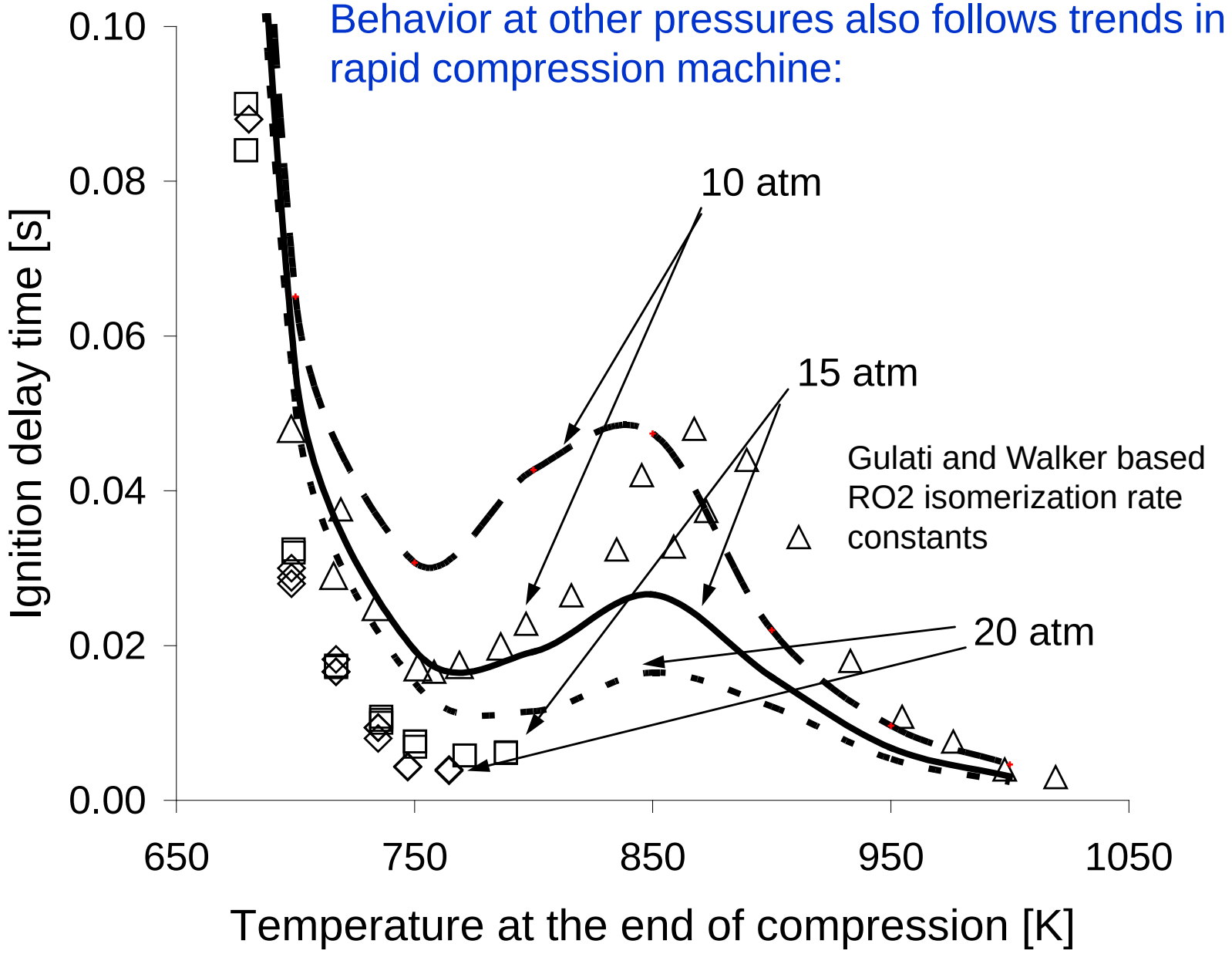
Ring size in transition state	A	n	Ea	Rate at 750K	Branching fraction
Alkylperoxy-corrected estimate:					
5	5.0e12	0	26850	8.0e4	0.4%
6	5.0e12	0	20850	4.5e6	23%
7	5.0e12	0	19050	1.5e7	77%
Gulati and Walker based estimate:					
5	1.00e11	0	29350	3.0e2	12%
6	1.25e10	0	23350	2.1e3	82%
7	1.50e9	0	24050	1.6e2	6%
Hanford-Styring and Walker based estimate:					
5	6.20e10	0	27495	6.0e2	11%
6	1.25e10	0	24076	4.5e3	81%
7	1.50e9	0	24355	4.3e2	8%

Rate constants emphasize 6-membered rings

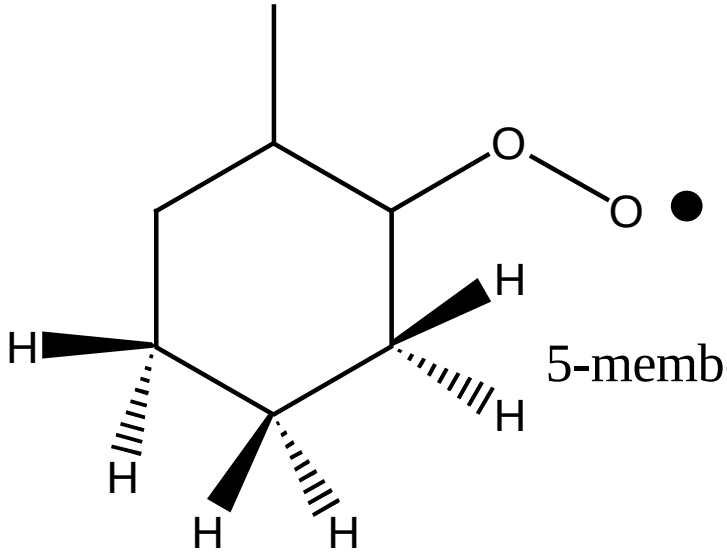
New MCH isomerization rates give good behavior for low temperature chemistry in rapid compression machine:



Behavior at other pressures also follows trends in rapid compression machine:

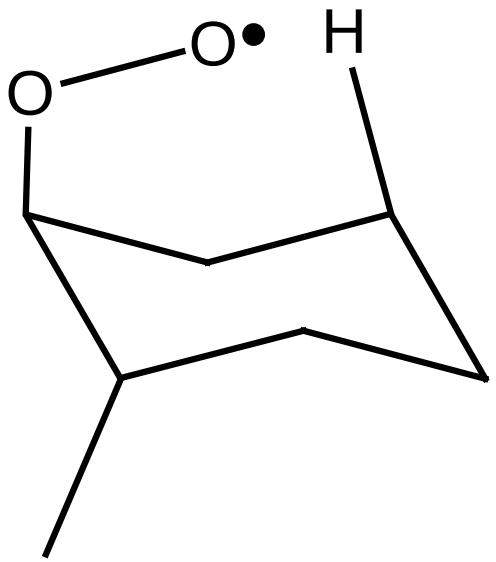


6-member ring RO_2 isomerization:



7-membered

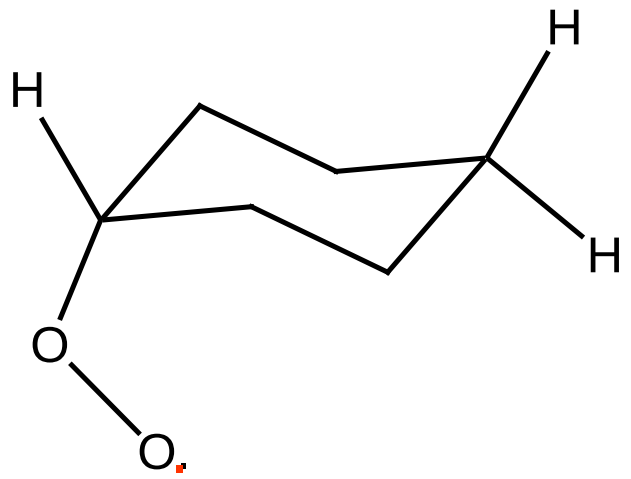
6-membered



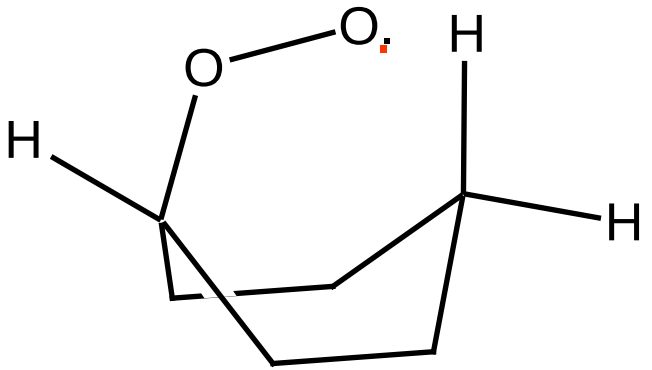
5-membered

Low temperature RO_2 isomerizations are a key

Trans (chair) ring form of cyclohexylperoxy does not readily isomerize



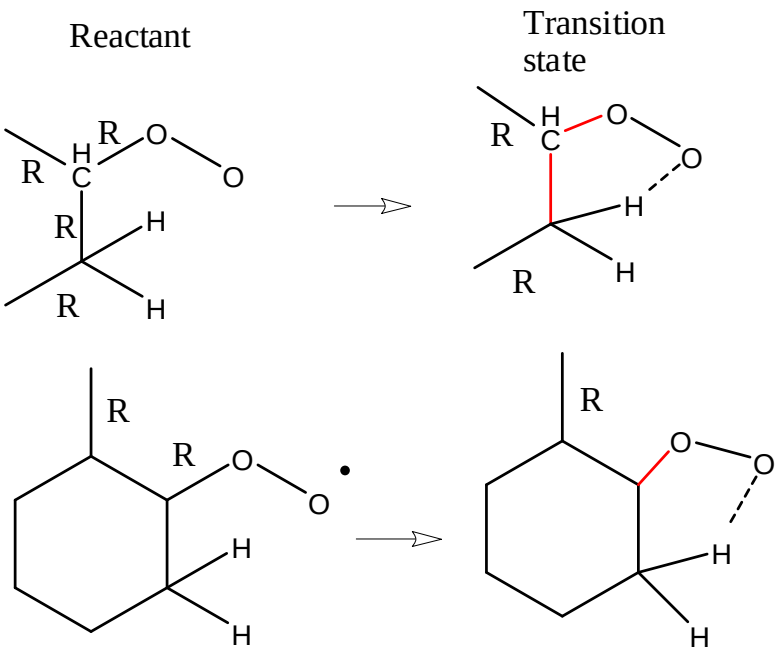
Cis (boat) ring form of cyclohexylperoxy does isomerize



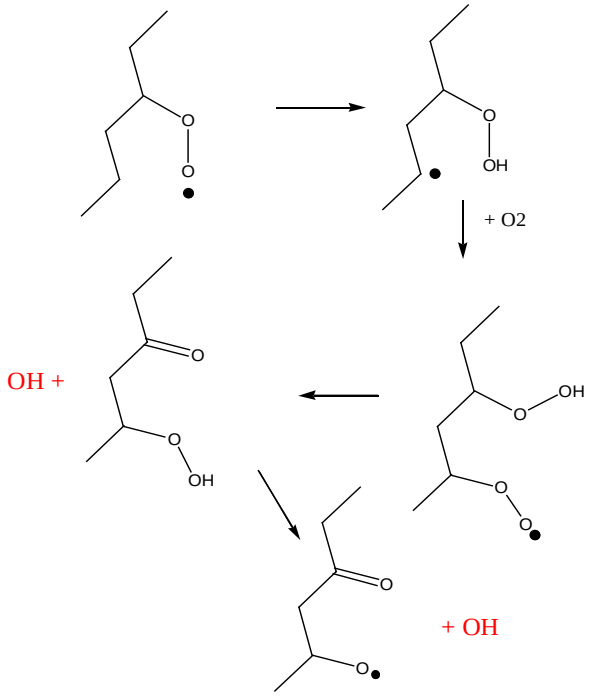
Compare Handford-Styring rates to n/iso-alkane rates and see diff in A-factor and Ea

Ring size in transition state	A	n	Ea [cal]	Rate at 750K	Branching fraction
Hanford-Styring and Walker based estimate:					
5	6.20e10	0	27495	6.0e2	11%
6	4.63e10	0	24076	4.5e3	81%
7	5.50e9	0	24355	4.3e2	8%
Non-cyclic alkylperoxy rates [7]					
5	1.00e11	0	26850	1.5e3	9%
6	1.25e10	0	20850	1.0e4	64%
7	1.50e9	0	19050	4.4e3	27%

Explanation of engine knock, ON, antiknocks, diesel ignition, and HCCI ignition came in the 1990's from DOE/BES theoretical chemistry and supercomputing and EERE knock working group



Alkylperoxy radical isomerization rates are different in paraffin and cyclic paraffin hydrocarbons



Low temperature chain branching paths

Most work has been done for alkane fuels, and many questions remain for aromatics, cyclic paraffins, large olefins

There are many poorly understood phenomena

- All of our intuition, experience and theory of flame properties is based on flames at atmospheric and lower pressures
- In engines, at high pressures due to compression, unburned gas temperatures are also quite high
- Characteristic times to autoignition can be much shorter than characteristic times for flame propagation
- Assumptions built into our picture of flame propagation break down at high pressures, and it is not clear how to define limiting conditions
- Extrapolation of flame data to 100 bar not appropriate; great need for high pressure “flame” data of all kinds
- We don’t know very much about combustion at high pressures
- We simply extrapolate phenomena from atmospheric pressure to high pressure, but they probably are no longer valid
- We don’t even know if “flames” still exist

Reference Fuels and Surrogate Fuels

C.K. Westbrook, W.J. Pitz, H.J. Curran and M. Mehl
Lawrence Livermore National Laboratory

June 2010

Practical hydrocarbon fuels present new challenges for kinetic modeling

- For many years, methane and propane were “large” fuel molecules, and they still can be challenging
- Most common transportation fuels produced from petroleum or other common sources contain molecules much larger than C1 to C4
- Hydrogen and C1 – C4 species will continue to be an essential part of fuel models and still need lots of work
- Large fuel species modeling requires significant computing resources
- Mechanism reduction will be necessary for applications with realistic geometry

All petroleum-derived fuels contain a complex mixture of HC molecules

- Refining produces a still-complex mixture that is “targeted” towards its application type
- Gasoline $6 < C < 10$
- Jet fuel $9 < C < 13$
- Diesel $13 < C < 22$

- HCCl $1 < C < 22$

Variability of real transportation fuels

- Composition of gasolines at different gas stations on a single day is often quite different
- Composition of same gas station will vary every day
- Same is true of diesel and other fuels
- Quantity used to test fuels is often not very demanding or specific (e.g., ON, CN)

There are two important pathways for practical fuel mixture mechanisms

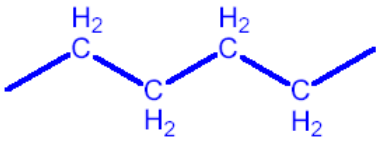
- Reference fuels
  - Gasoline - n-heptane and iso-octane
  - Diesel - heptamethyl nonane and n-hexadecane
  - Jet fuel – n-dodecane (?) and iso-dodecane (?)
- For the first time, we now have detailed kinetic mechanisms for both diesel and gasoline primary reference fuels
- Surrogate fuels

Use of surrogate fuels is an important current theme in combustion chemistry

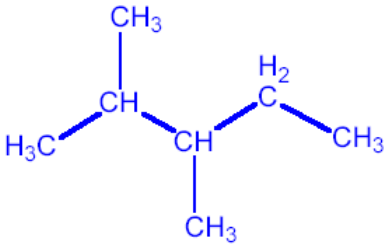
- First surrogate for diesel fuel was n-heptane
- Early surrogates included one representative from each fuel molecule class

Classes of compounds in practical fuels

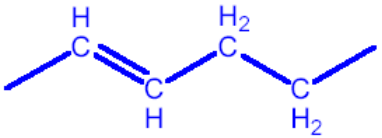
n-paraffin

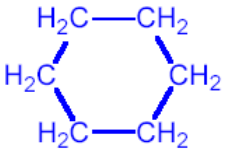


iso-paraffin

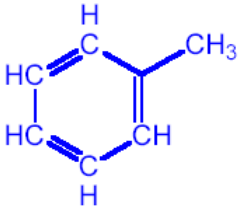


olefin

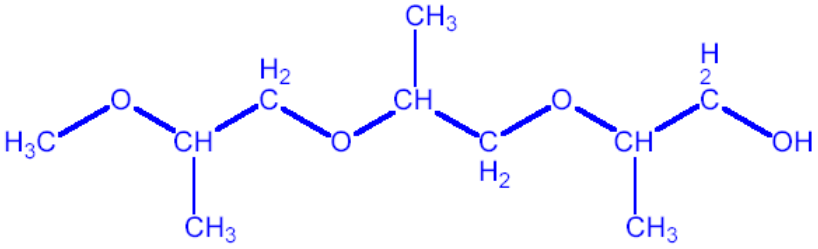




cyclo-alkane

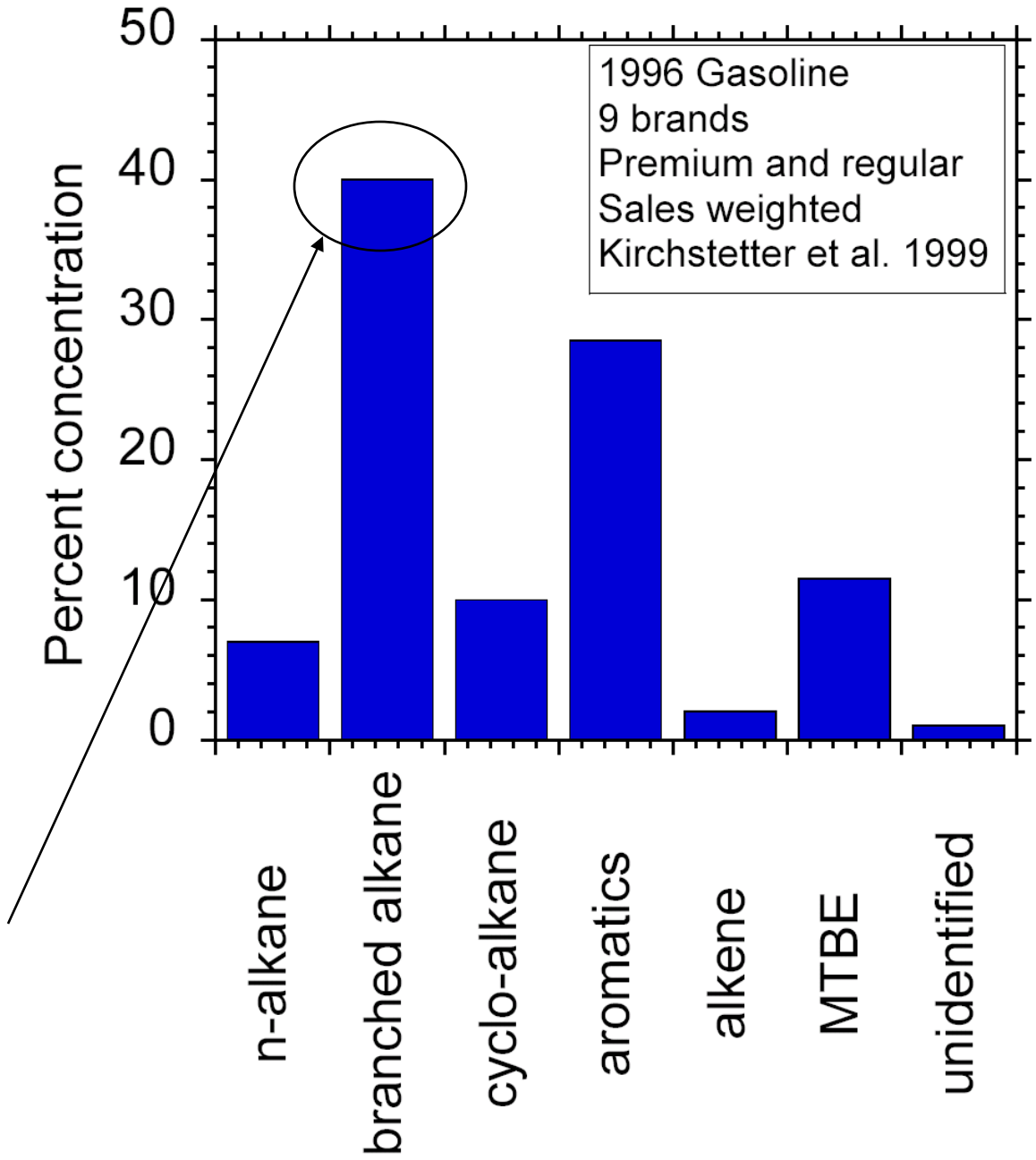


aromatic



oxygenate

Gasoline composition

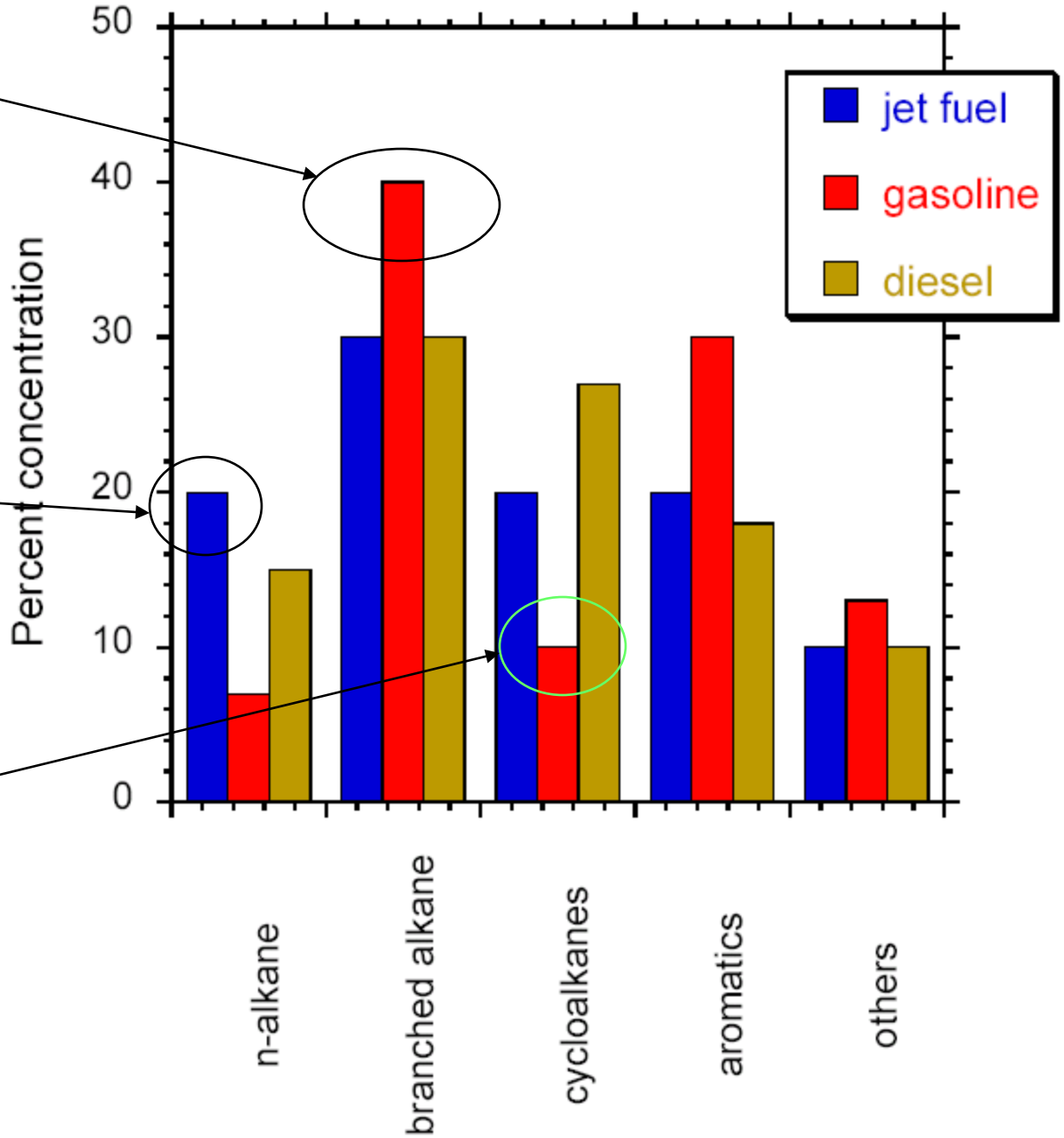


Many branched paraffins

Gasoline has many branched alkanes

Jet fuel has the highest n-alkane

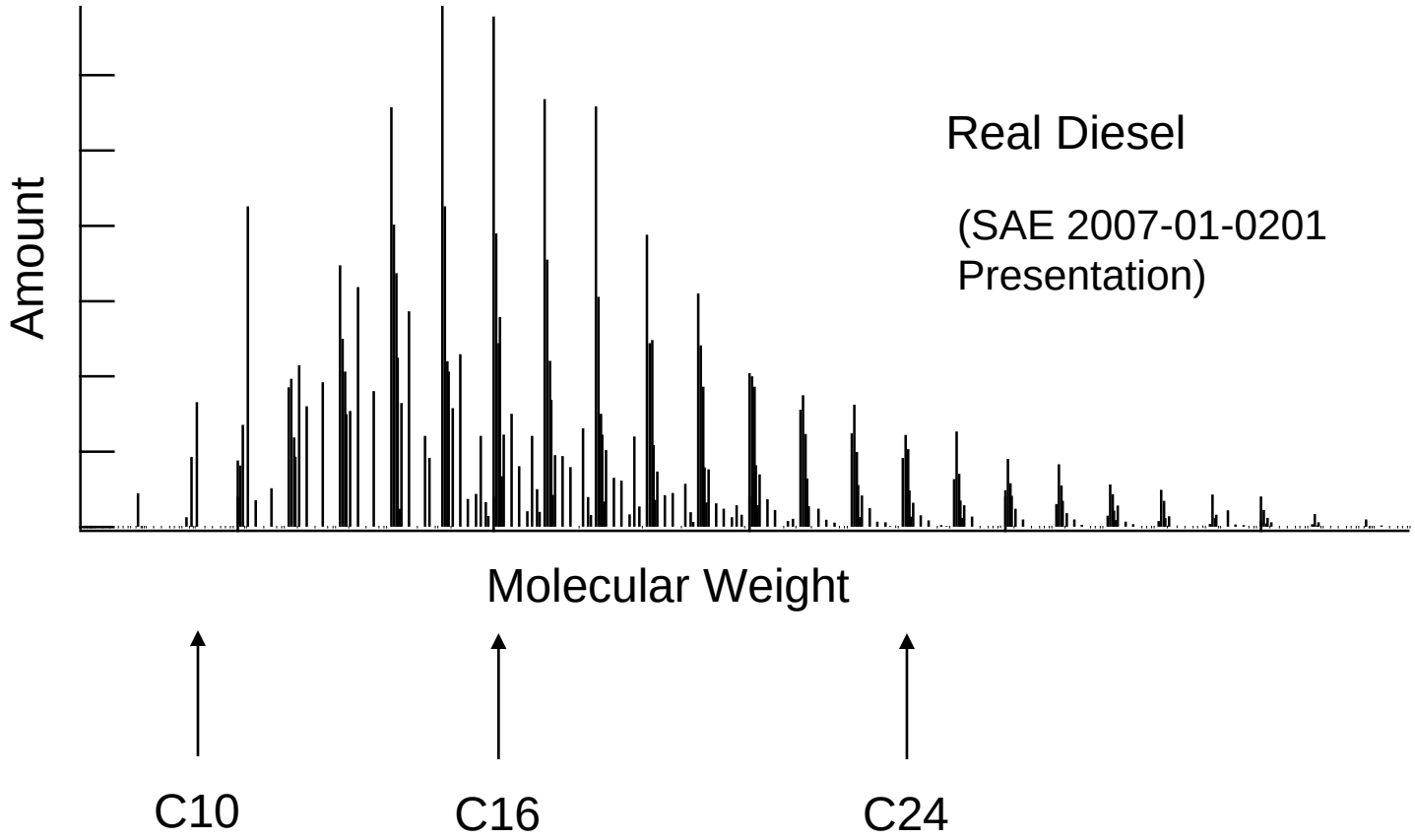
Gasoline is lower in cycloalkanes



Fuel components that have higher molecular weights are needed

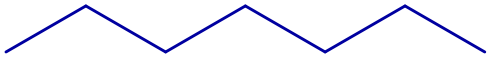
Surrogate Fuel Component Selection

- Diesel fuel has mostly C14 to C24 components centered around C16

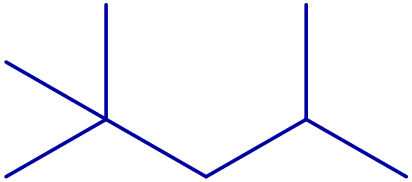


Recommended components by the surrogate fuel working group, gasoline team

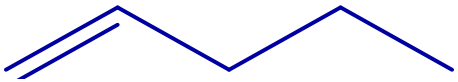
- n-heptane



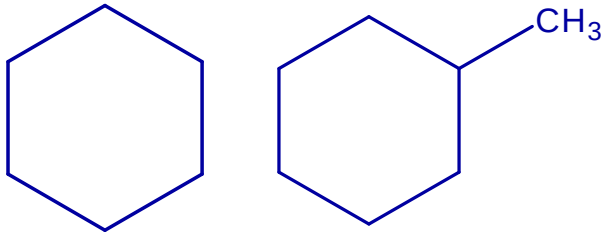
- iso-octane



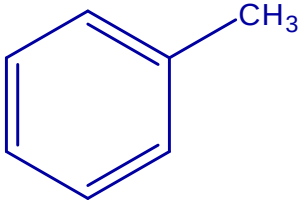
- pentene



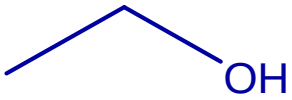
- cyclohexane, methylcyclohexane



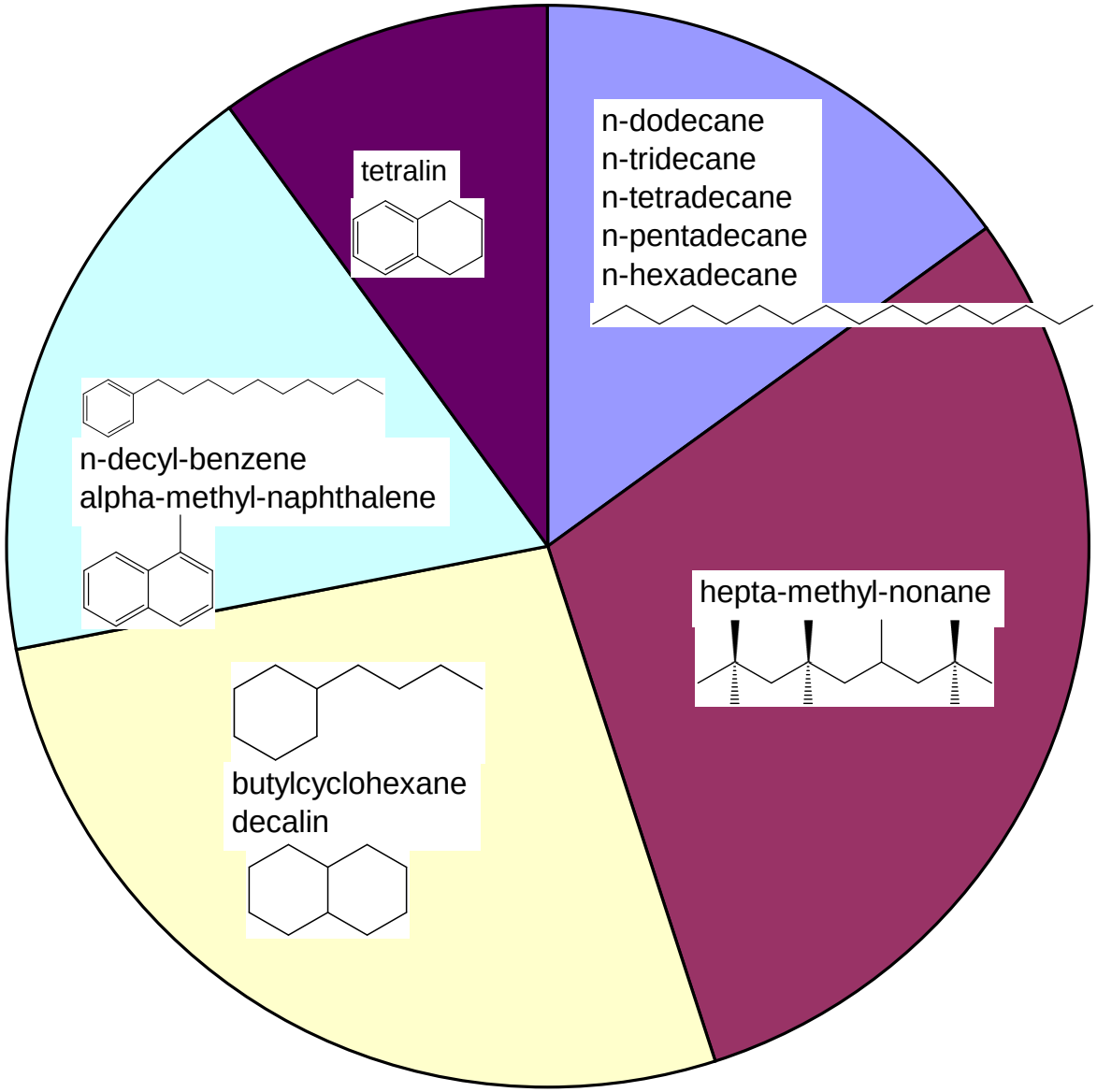
- toluene



- ethanol



Fuel Surrogate Palette for Diesel



Use of surrogate fuels is an important current theme in combustion chemistry

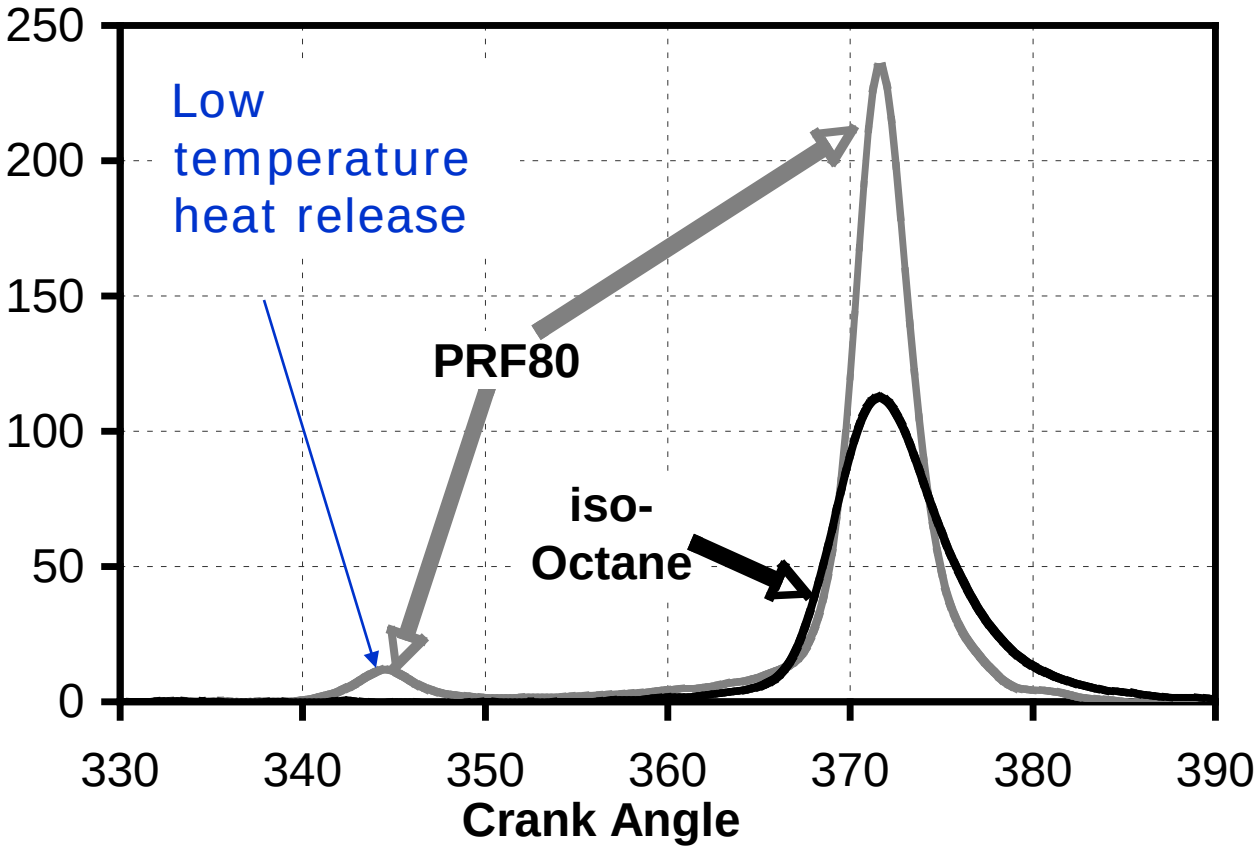
- Advantages of having multiple samples from each class of molecules
- Our research has been focused on developing kinetic models for many examples in each class
- Mechanism reduction can then be applied to those fuel components to be used

In some classes, we have many examples of fuels with reaction mechanisms

- n-paraffins
  - CH_4 (methane) through $nC_{16}H_{34}$ (n-hexadecane)
- iso-paraffins
  - all isomers through octanes, selected larger iso-paraffins
- Large variety of olefins through C8 and selected larger species

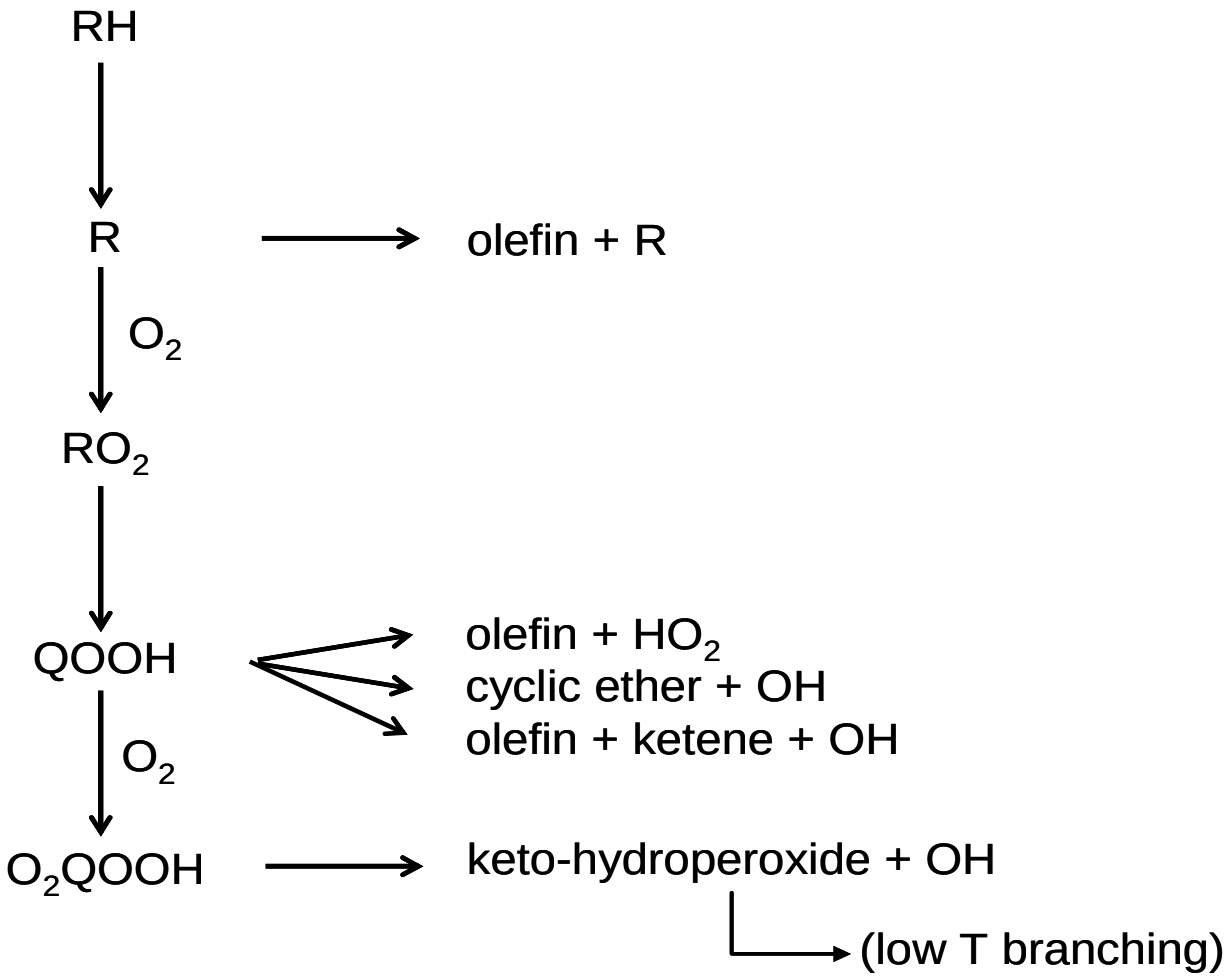
Alkylperoxy radical isomerization and low temperature are important in all types of engines

- Heat release rates in HCCI combustion of two fuels, iso-octane with no low T heat release, and PRF-90 with two stage heat release



Results from experiments of Sjöberg and Dec, SNL 2006

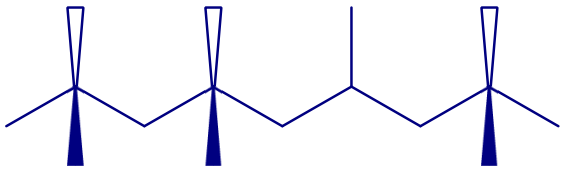
Includes high and low temperature ignition chemistry: Important for predicting low temperature combustion regimes



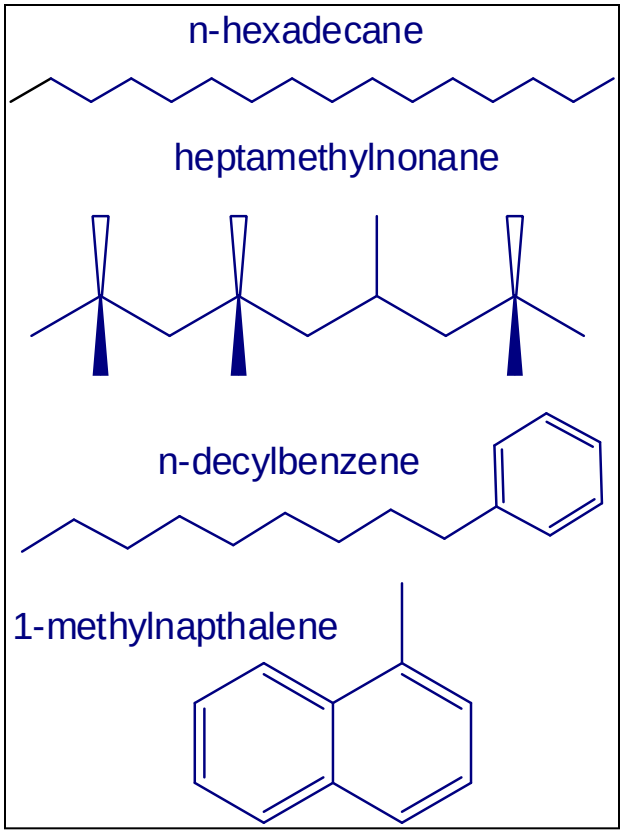
n-Hexadecane and heptamethyl nonane are primary reference fuels for diesel and recommended diesel surrogate components

- The two primary reference fuels for diesel ignition properties (cetane number)
  - n-hexadecane

  - 2,2,4,4,6,8,8 heptamethylnonane

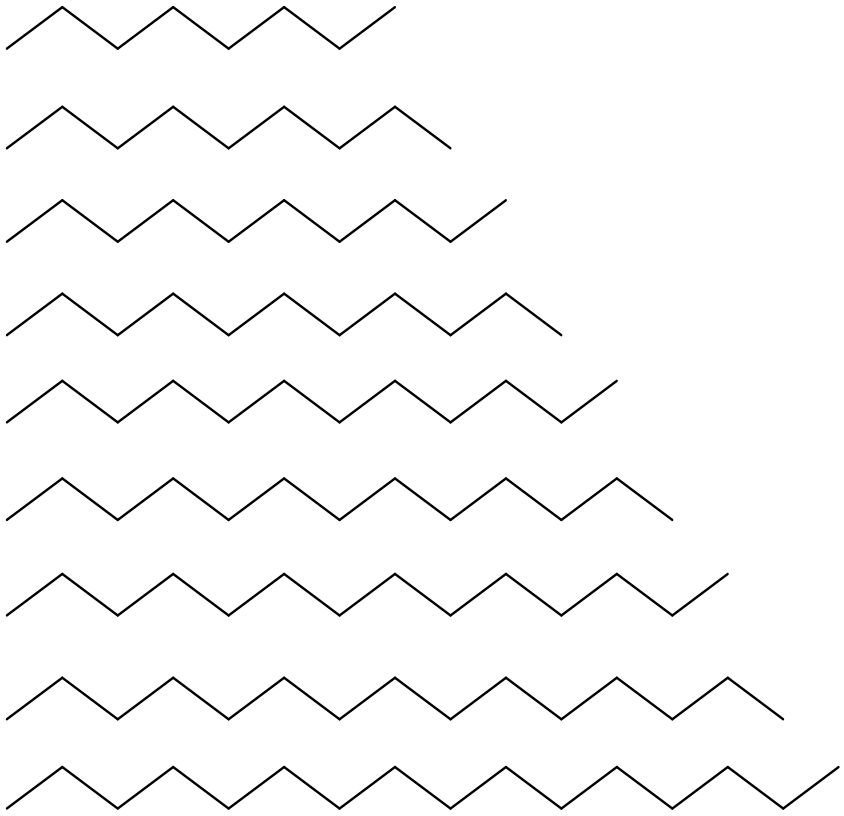


Recommended surrogate for diesel fuel (Farrell et al., 2007):



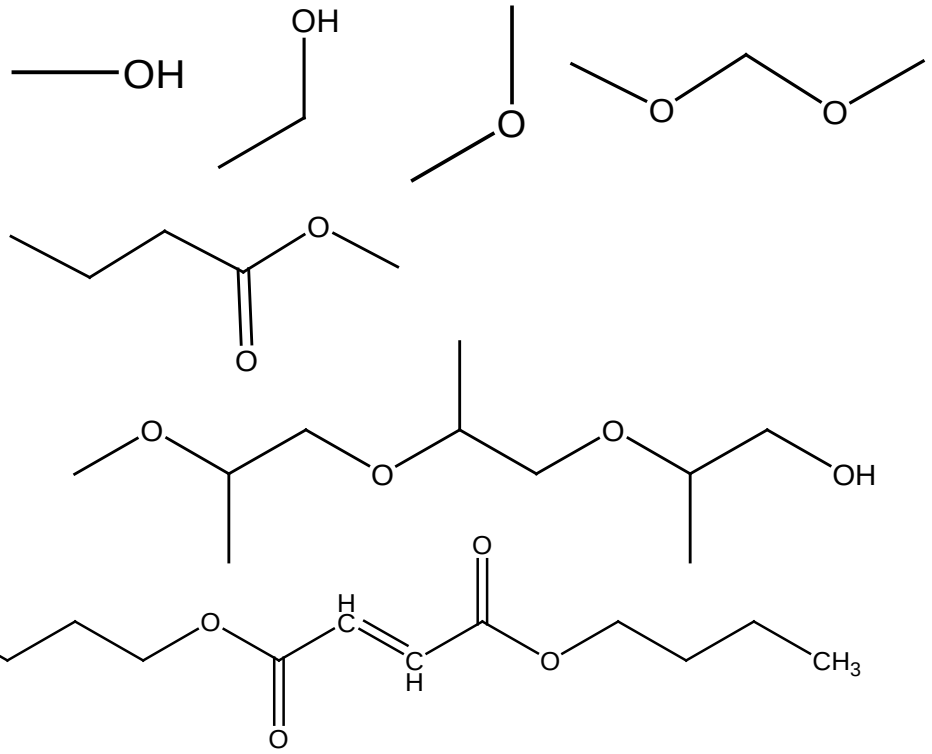
We have greatly extended the components in the palette that can be modeled into the high molecular weight range:

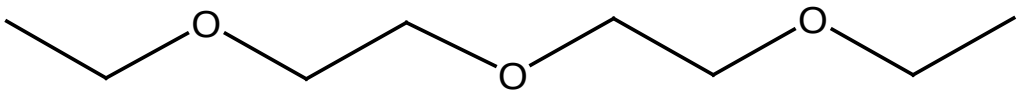
- n-octane (n-C8H18)
- n-nonane (n-C9H20)
- n-decane (n-C10H22)
- n-undecane (n-C11H24)
- n-dodecane (n-C12H26)
- n-tridecane (n-C13H28)
- n-tetradecane (n-C14H30)
- n-pentadecane (n-C15H32)
- n-hexadecane (n-C16H34)



We have mechanisms for many oxygenated components

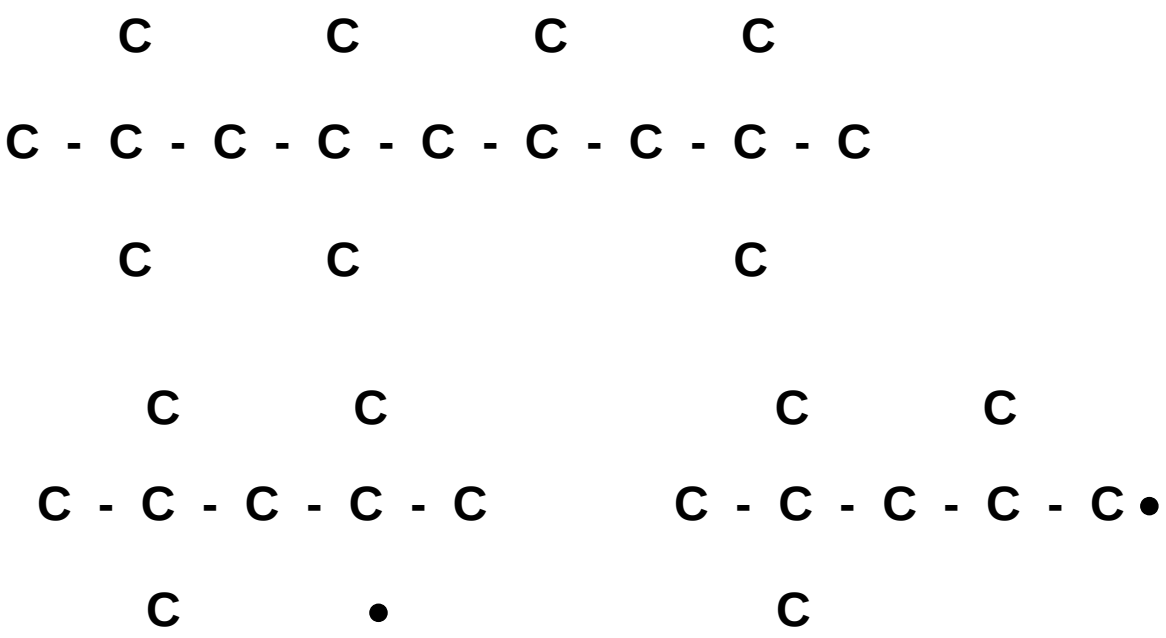
- Methanol, ethanol
- dimethyl ether, dimethoxymethane
- Methyl butanoate (surrogate for biodiesel)
- TPGME (tripropylene glycol monomethyl ether)
- DBM (di-butyl maleate)
- DGE (diethylene glycol diethyl ether)





We have developed a detailed kinetic reaction mechanism for the other diesel PRF, heptamethyl nonane

2,2,4,4,6,8,8-heptamethyl nonane is 2 iso-octyl radicals



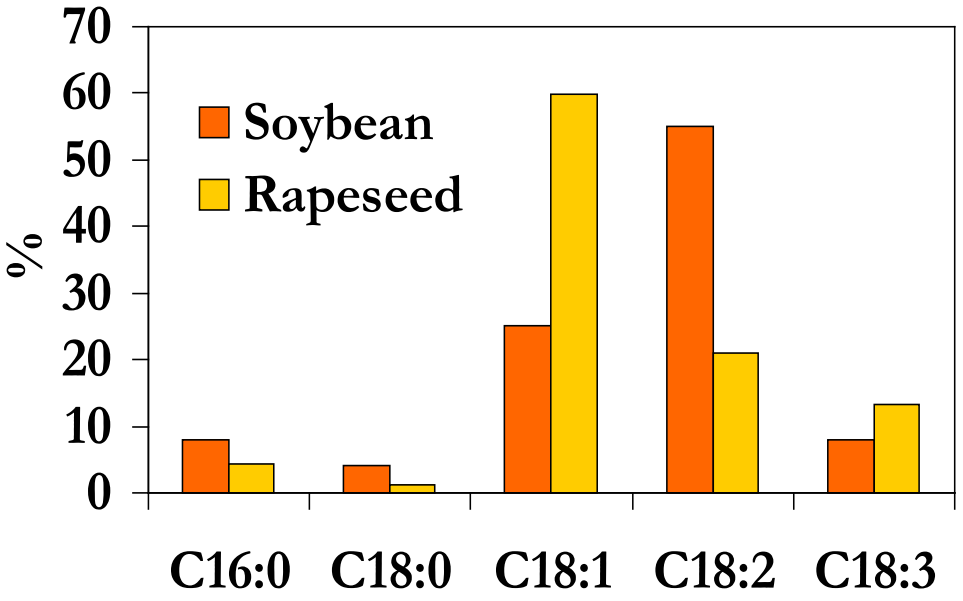
We should expect HMN kinetics to be quite similar to iso-octane

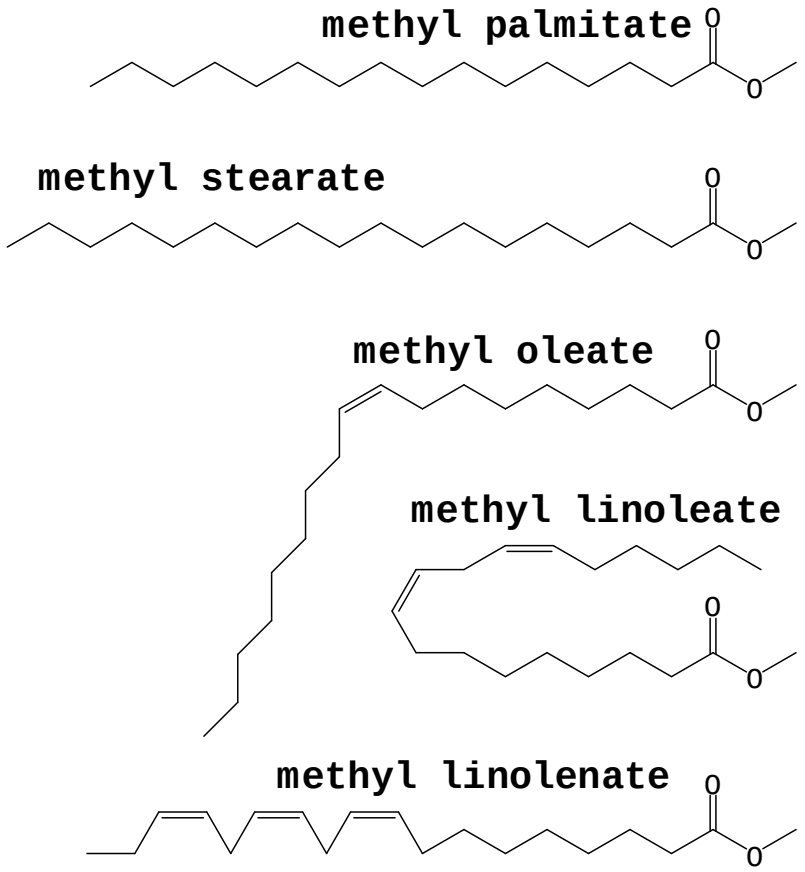
We have been modeling the effect of the position of the double bond

on ignition of olefins

		Amount of low T reactivity
C = C - C - C - C - C	1-hexene	high
C - C = C - C - C - C	2 – hexene	medium
C - C - C = C - C - C	3 – hexene	low

Composition of Biodiesels



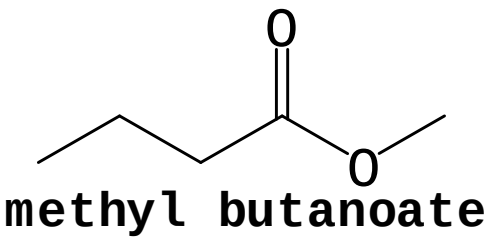


see paper Tuesday afternoon by Naik for more complete description of biodiesel fuel kinetics

Choice of Surrogates

- Methyl butanoate :

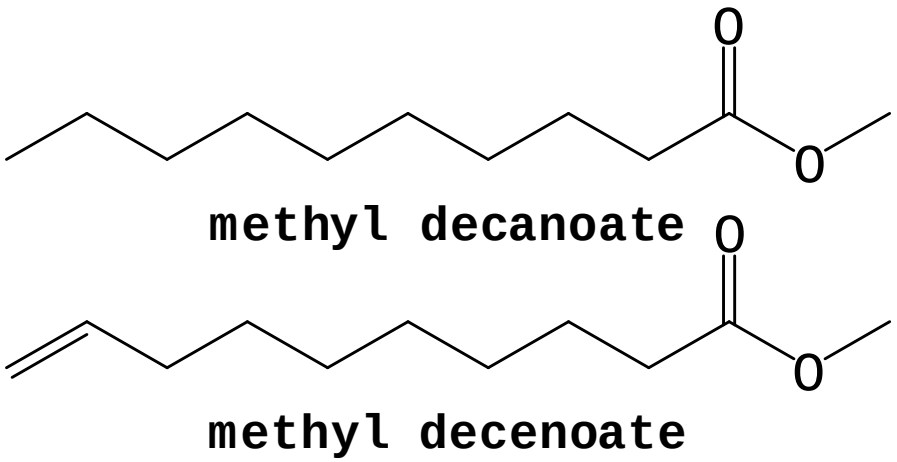
Molecular size too small compared to biodiesel



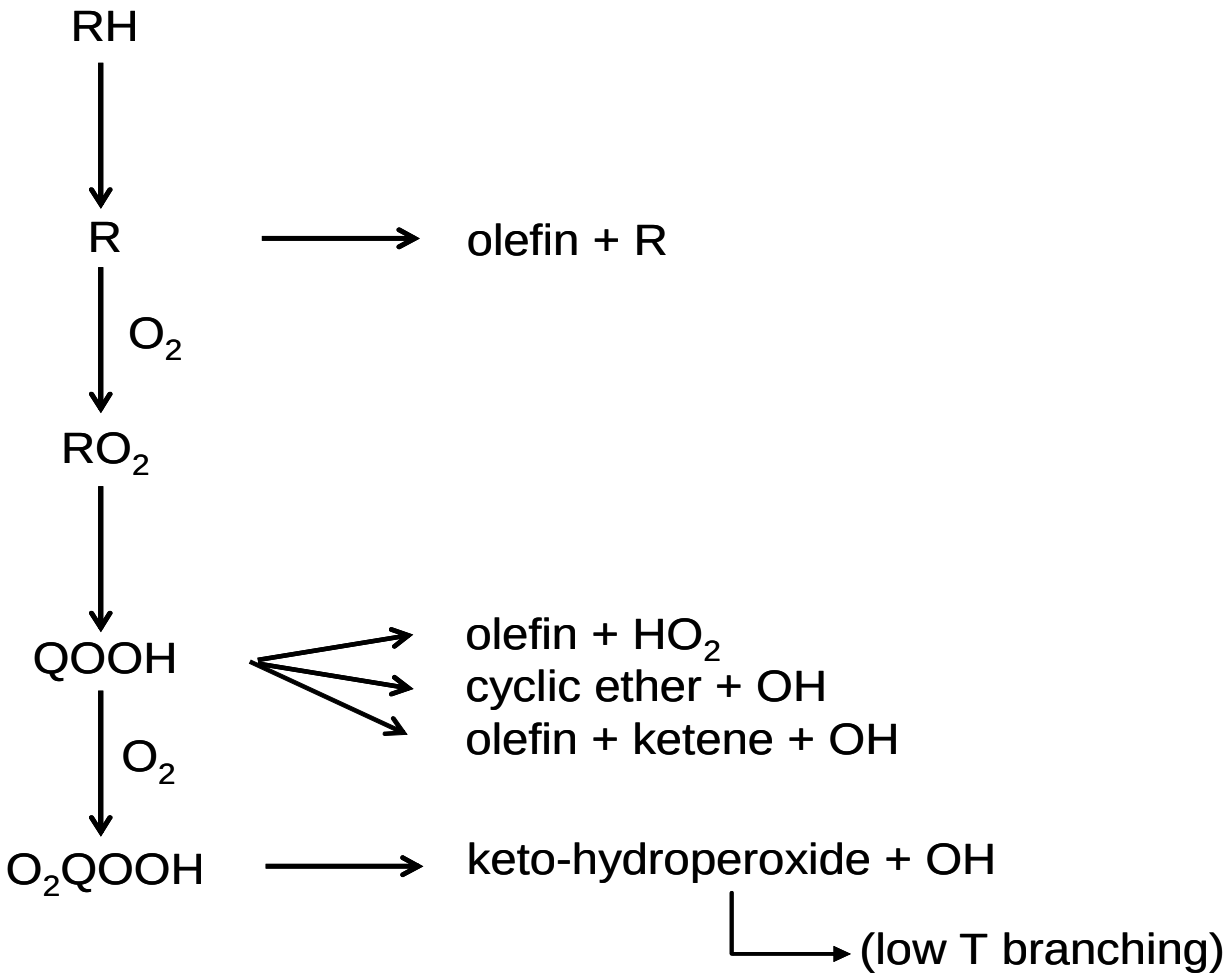
More realistic:

→ methyl decanoate

→ methyl decenoate

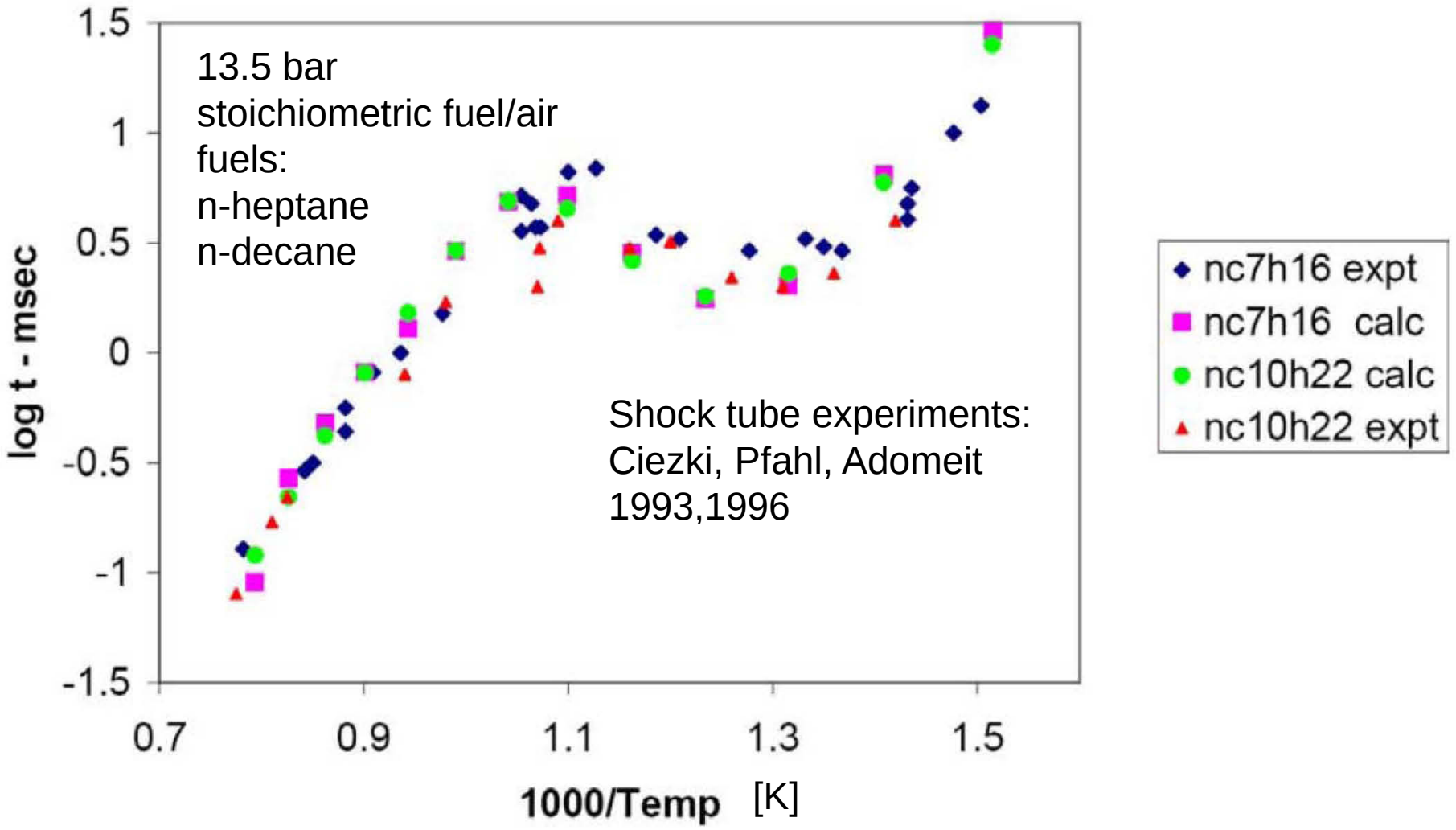


Includes high and low temperature ignition chemistry: Important for predicting low temperature combustion regimes

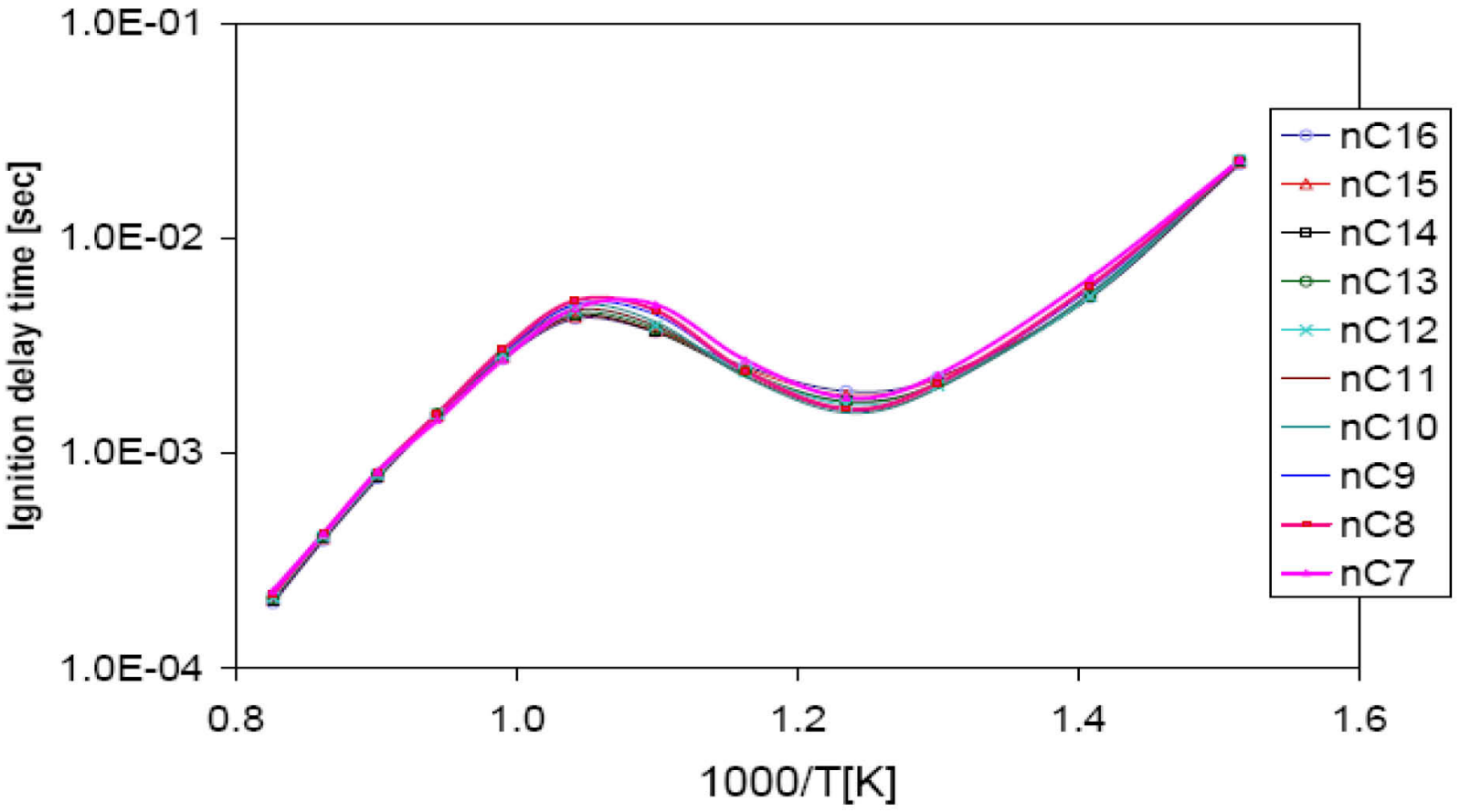


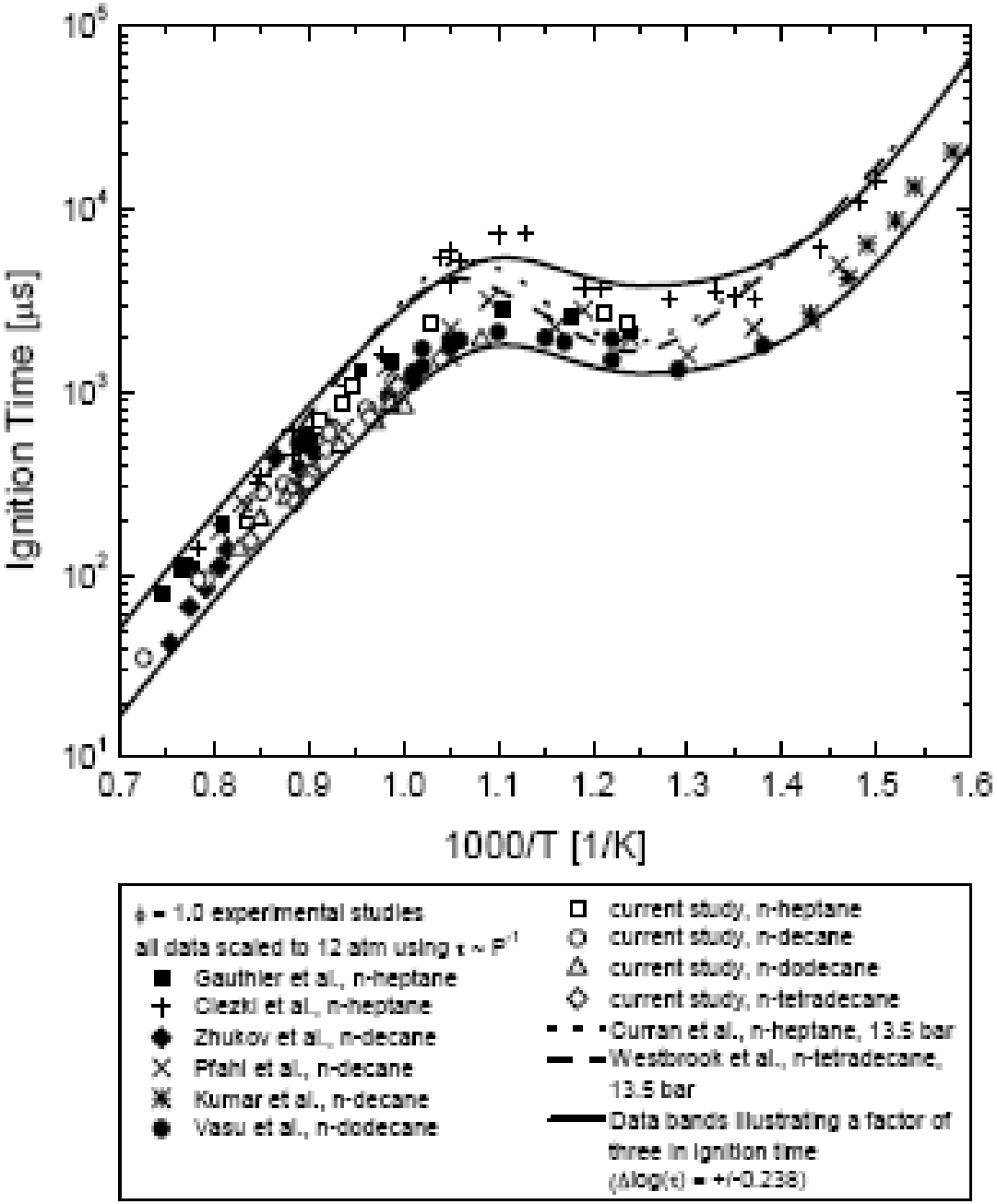
Experimental Validation Data

Good agreement with ignition delay times at “engine-like” conditions over the low to high temperature regime in the shock tube

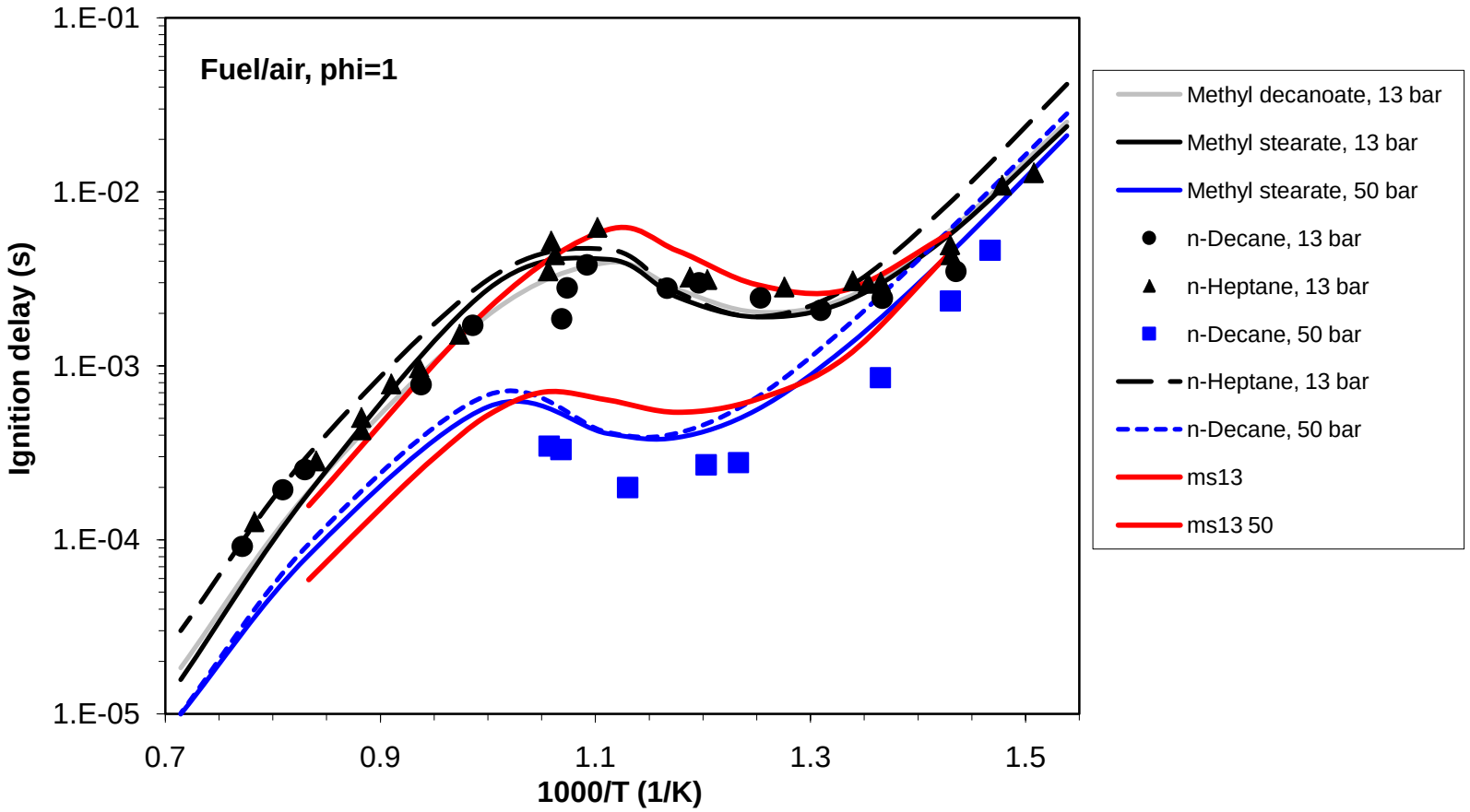


All large n-alkanes have very similar ignition properties

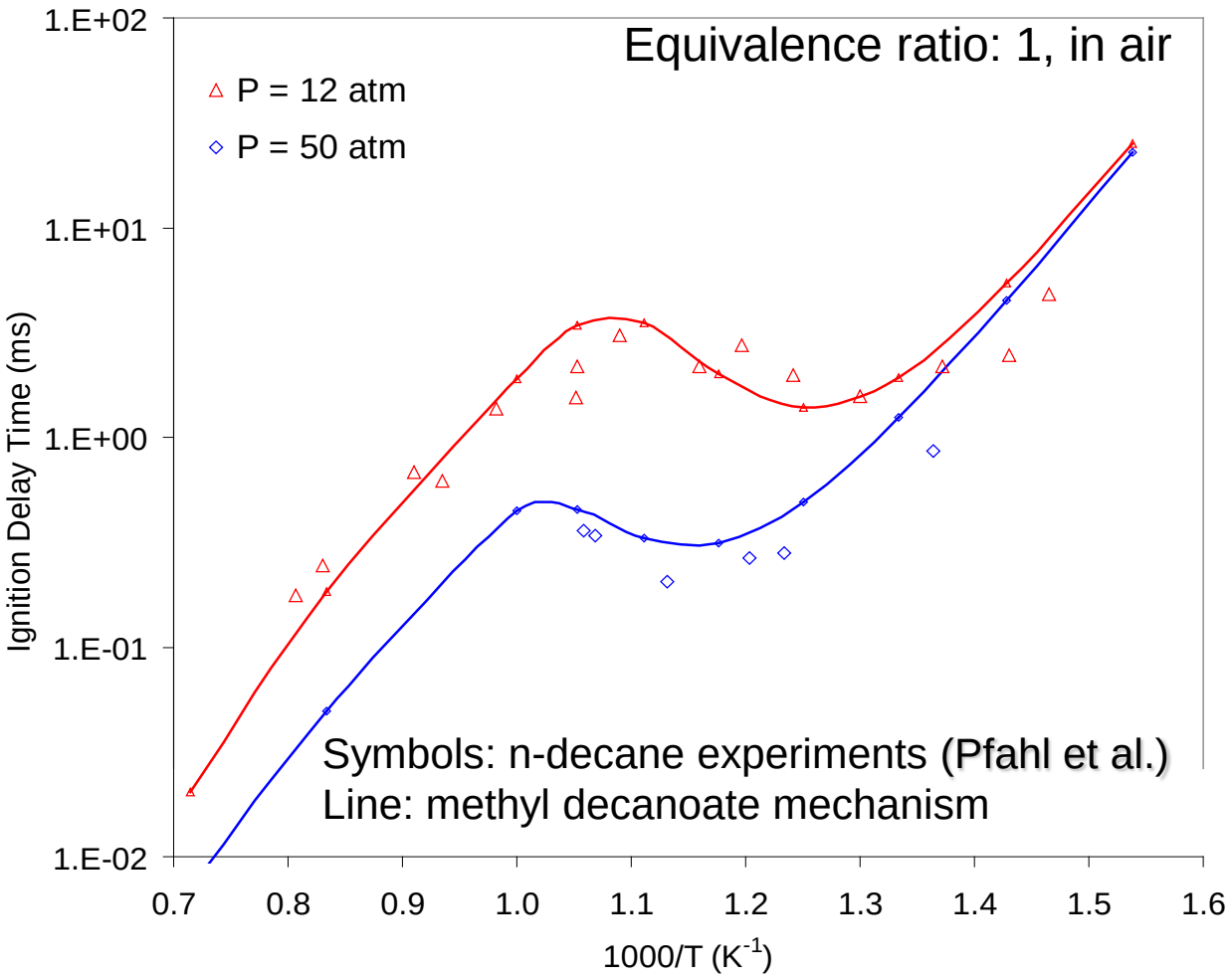



Ignition Time [µs]
1000/T [1/K]
ϕ = 1.0 experimental studies
all data scaled to 12 atm using τ ~ P^-1
Gauthier et al., n-heptane
Ciezki et al., n-heptane
Zhukov et al., n-decane
Pfahl et al., n-decane
Kumar et al., n-decane
Vasu et al., n-dodecane
current study, n-heptane
current study, n-decane
current study, n-dodecane
current study, n-tetradecane
Curran et al., n-heptane, 13.5 bar
Westbrook et al., n-tetradecane, 13.5 bar
Data bands illustrating a factor of three in ignition time
(Δlog(τ) = +/-0.238)

Methyl stearate (n-C_{18} methyl ester) has the same ignition properties as large alkanes



Comparison with n-Decane Ignition Delay Times



Ignition delay times very close

n-Alkanes:

cannot reproduce the early formation of CO_2

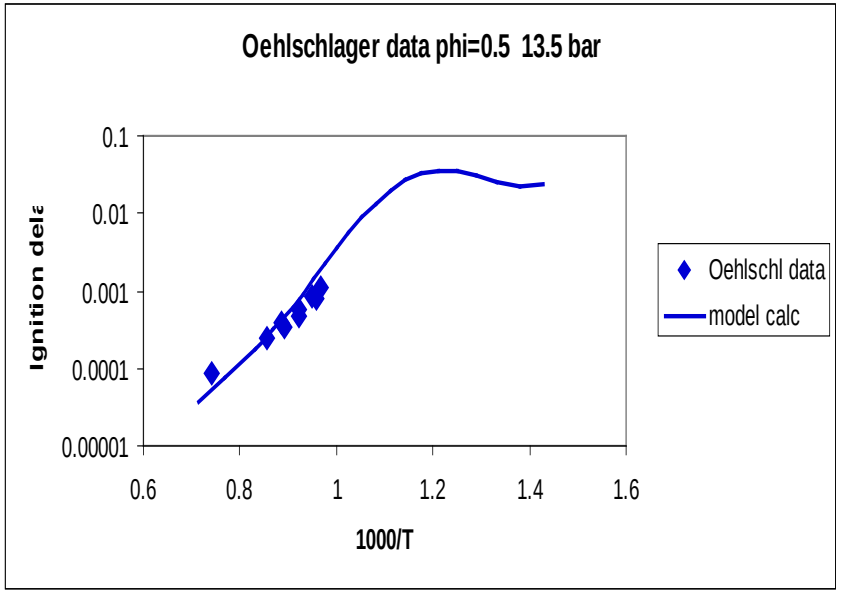
but

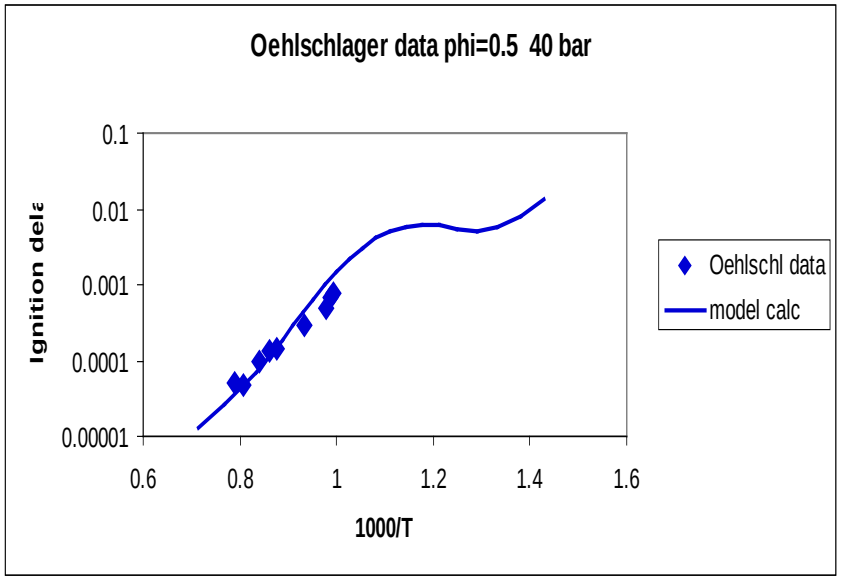
reproduce the reactivity of methyl esters very well

Branched hydrocarbons are different

- Both octane and cetane rating systems have a straight-chain reference fuel that is easy to ignite and a branched reference fuel that is hard to ignite
- iso-octane and 2,2,4,4,6,8,8-heptamethyl nonane
- n-heptane and n-hexadecane
- Are all branched hydrocarbons as similar to each other as the straight-chain hydrocarbons?
- Very few laboratory experiments available for mechanism validation of HMN
- Base a reaction mechanism on previous sets of reaction classes

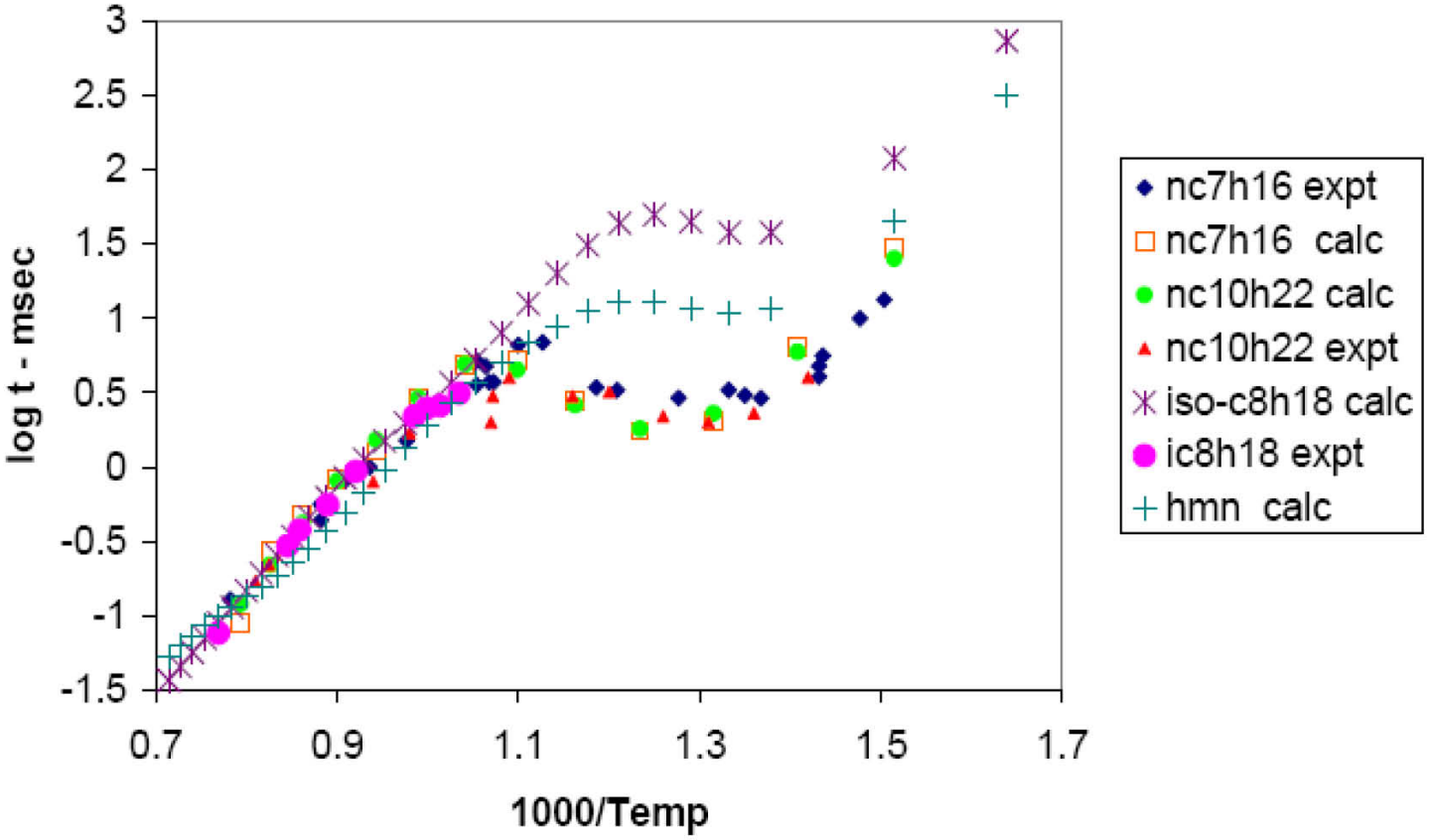
Recent experimental results show excellent agreement with modeling





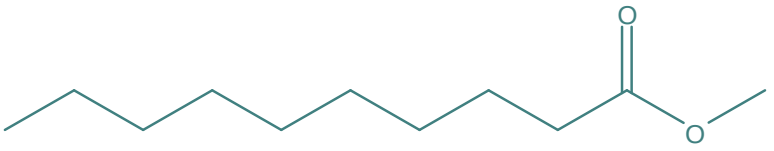
HMN and iso-octane ignition is slower than n-alkanes only in the Low Temperature regime

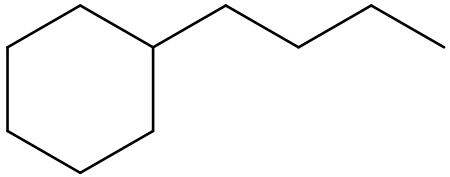
13.5 bar pressure



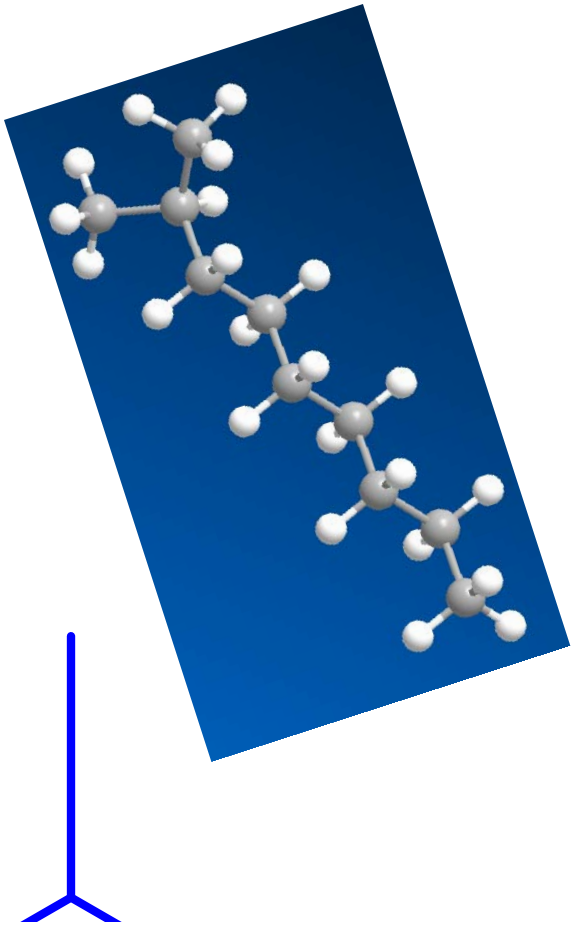
Interesting note

Experience with straight chain, biodiesel and methyl esters suggests strategies for kinetic modeling of n-alkyl benzenes and n-alkyl cyclohexanes





Assembled chemical kinetic model for a whole series of iso-alkanes to represent this chemical class in gasoline and diesel fuels

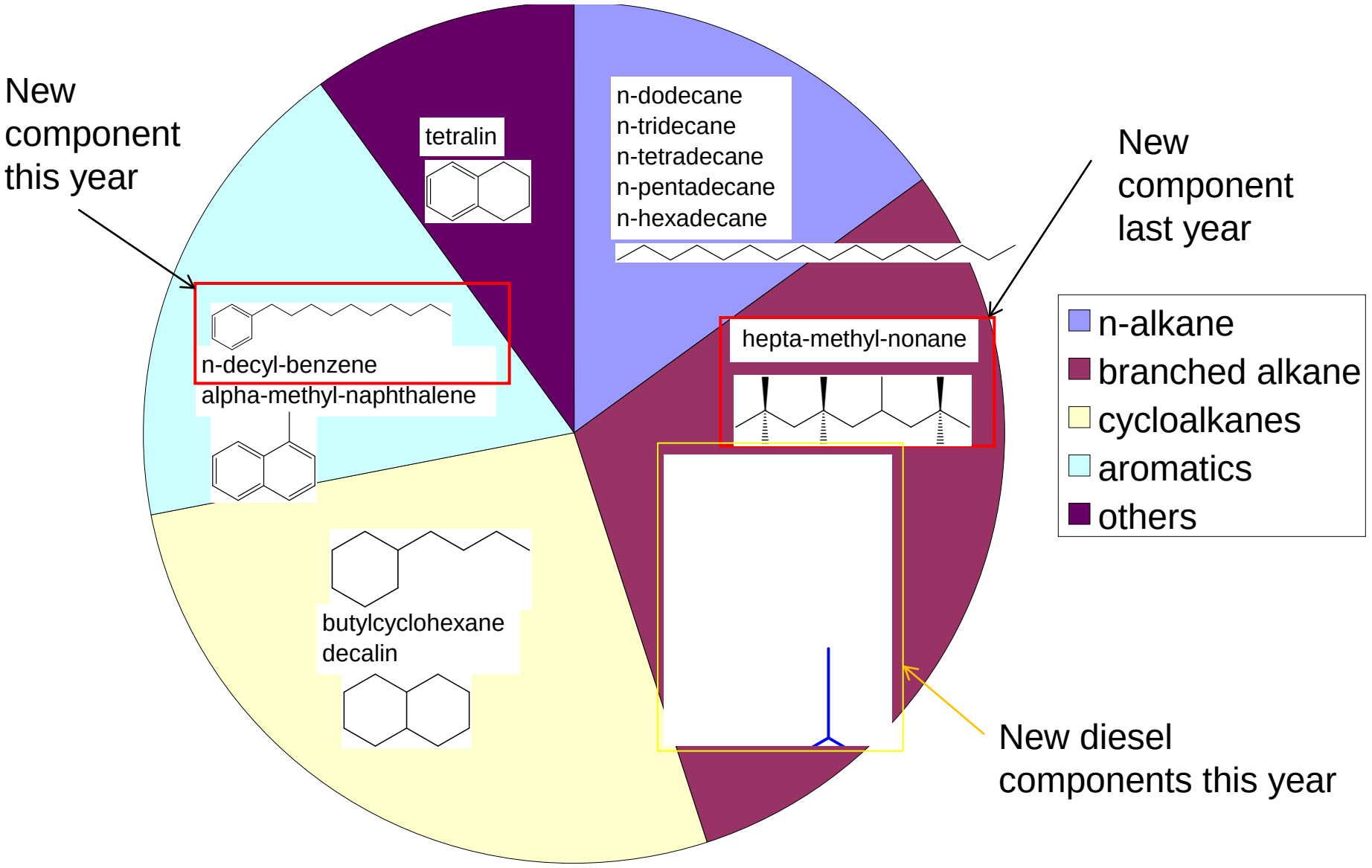


Includes all 2-methyl alkanes up to C20 which covers the entire distillation range for gasoline and diesel fuels

Built with the same reaction rate rules as our successful iso-octane and iso-cetane mechanisms.

7,900 species
27,000 reactions

Diesel Fuel Surrogate palette:



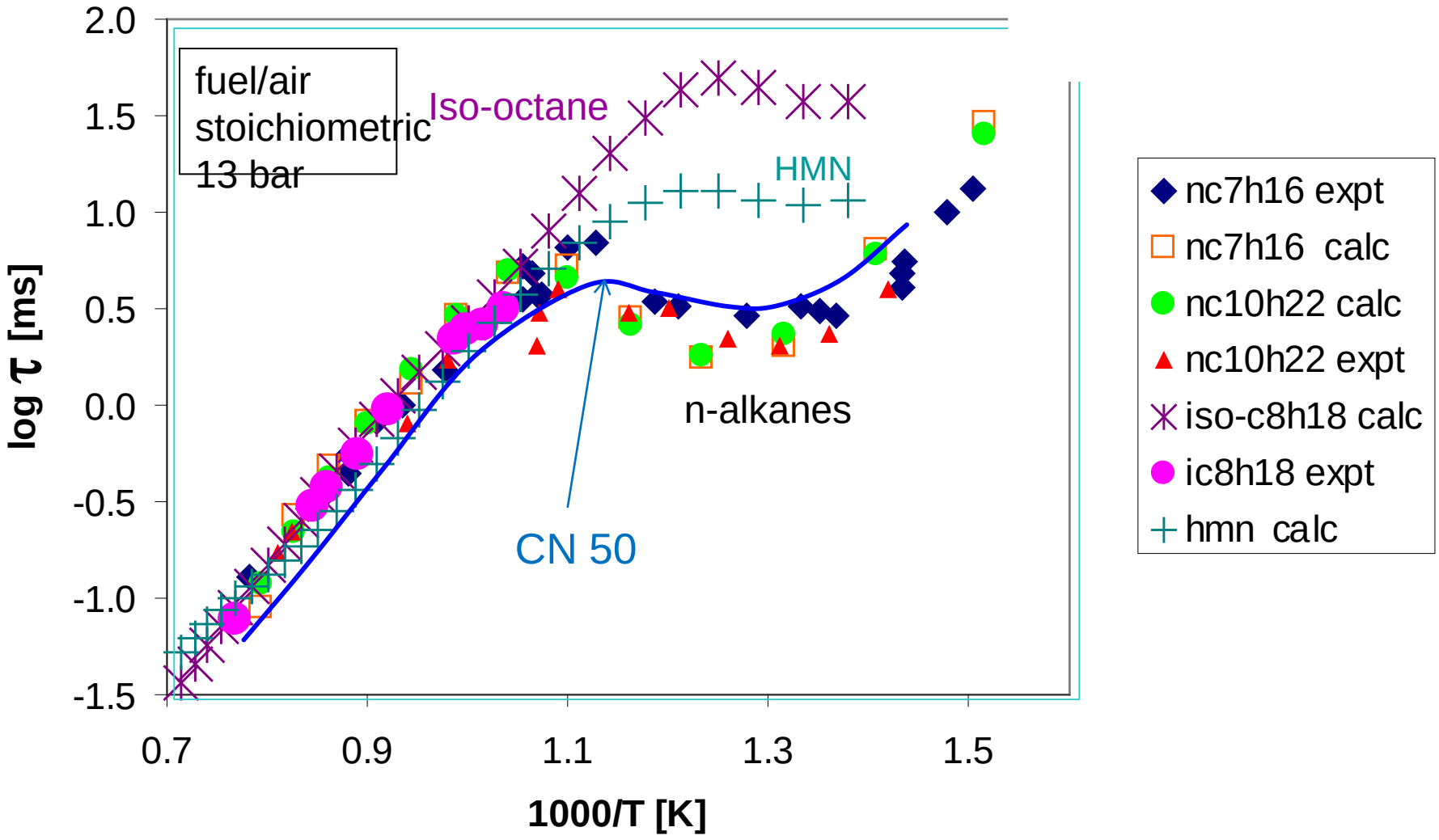
Have assembled primary reference fuel mechanism for diesel fuel

- Diesel PRF: (n-hexadecane)
  - n-cetane
  - iso-cetane (2,2,4,4,6,8,8-heptamethylnonane
- PRF for Diesel mechanism:
  - 2,837 species
  - 10,719 reactions

PFR Ignition results at 13 bar:

n-hexadecane

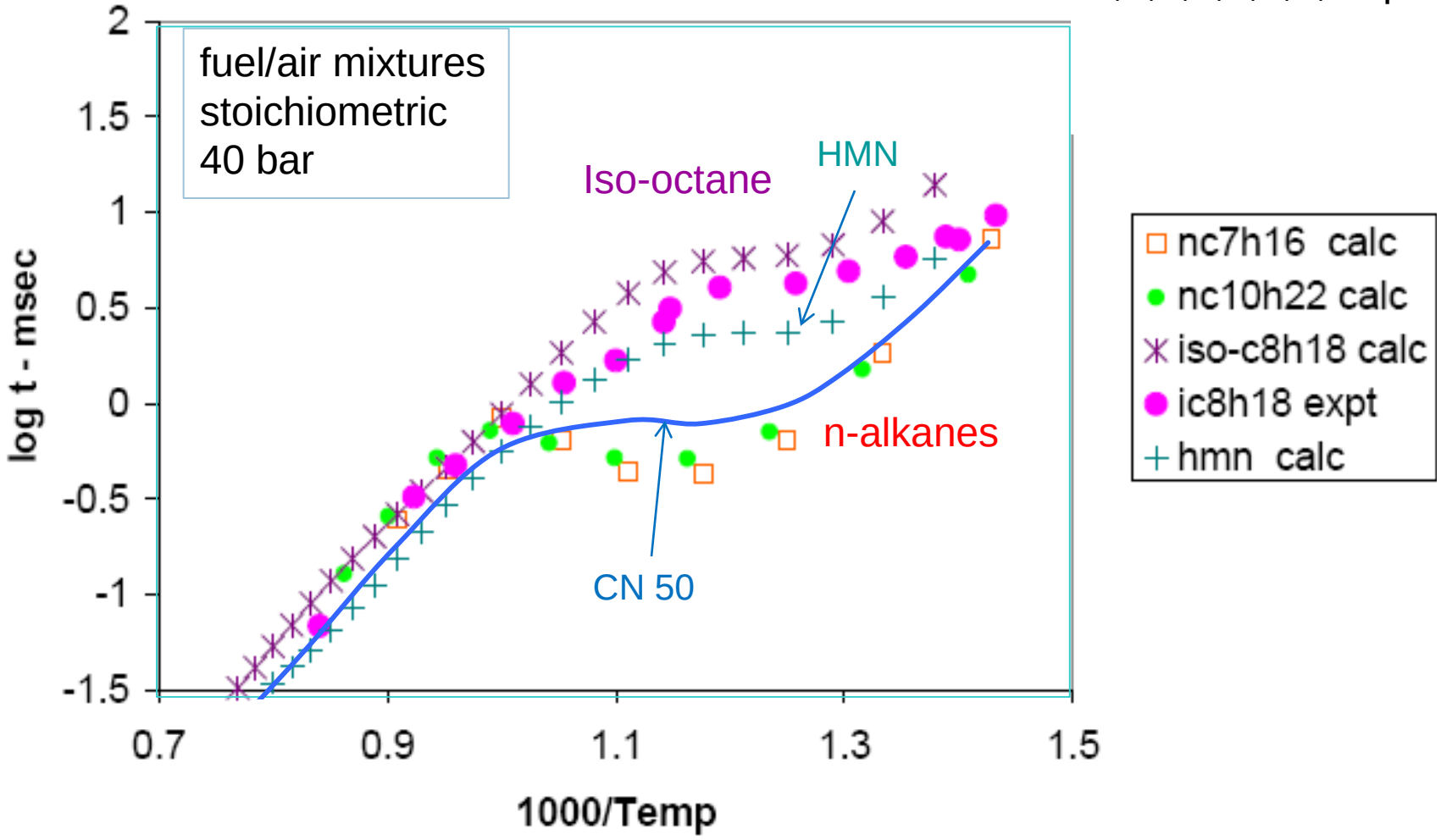
2,2,4,4,6,8,8, heptamethylnor



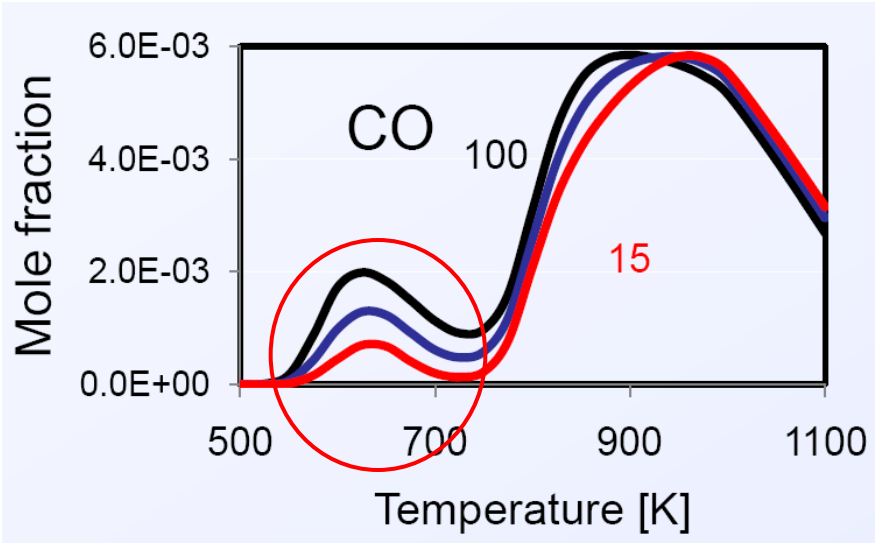
PFR Ignition results at 40 bar:

n-hexadecane

2,2,4,4,6,8,8, heptamethylnor

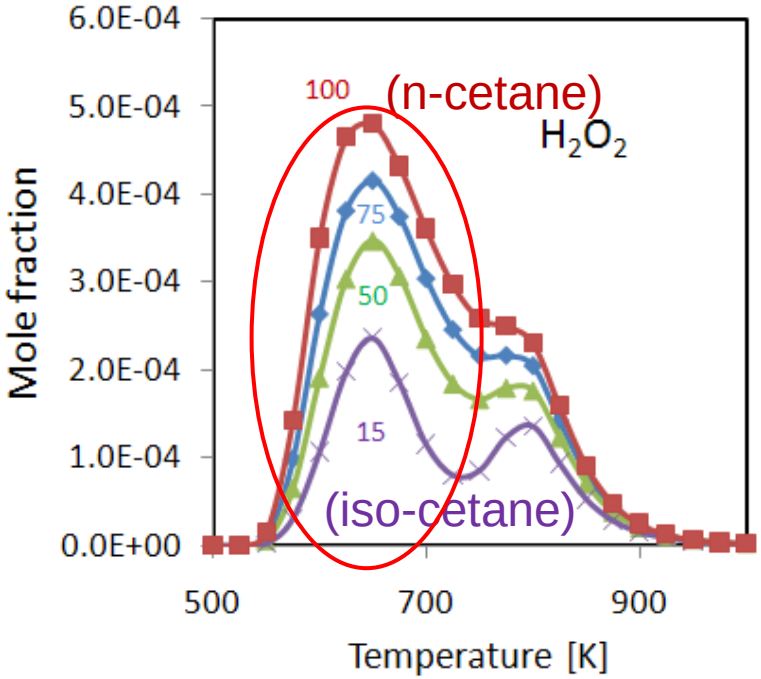


Diesel PRFs: Cetane number has a big effect at low temperatures



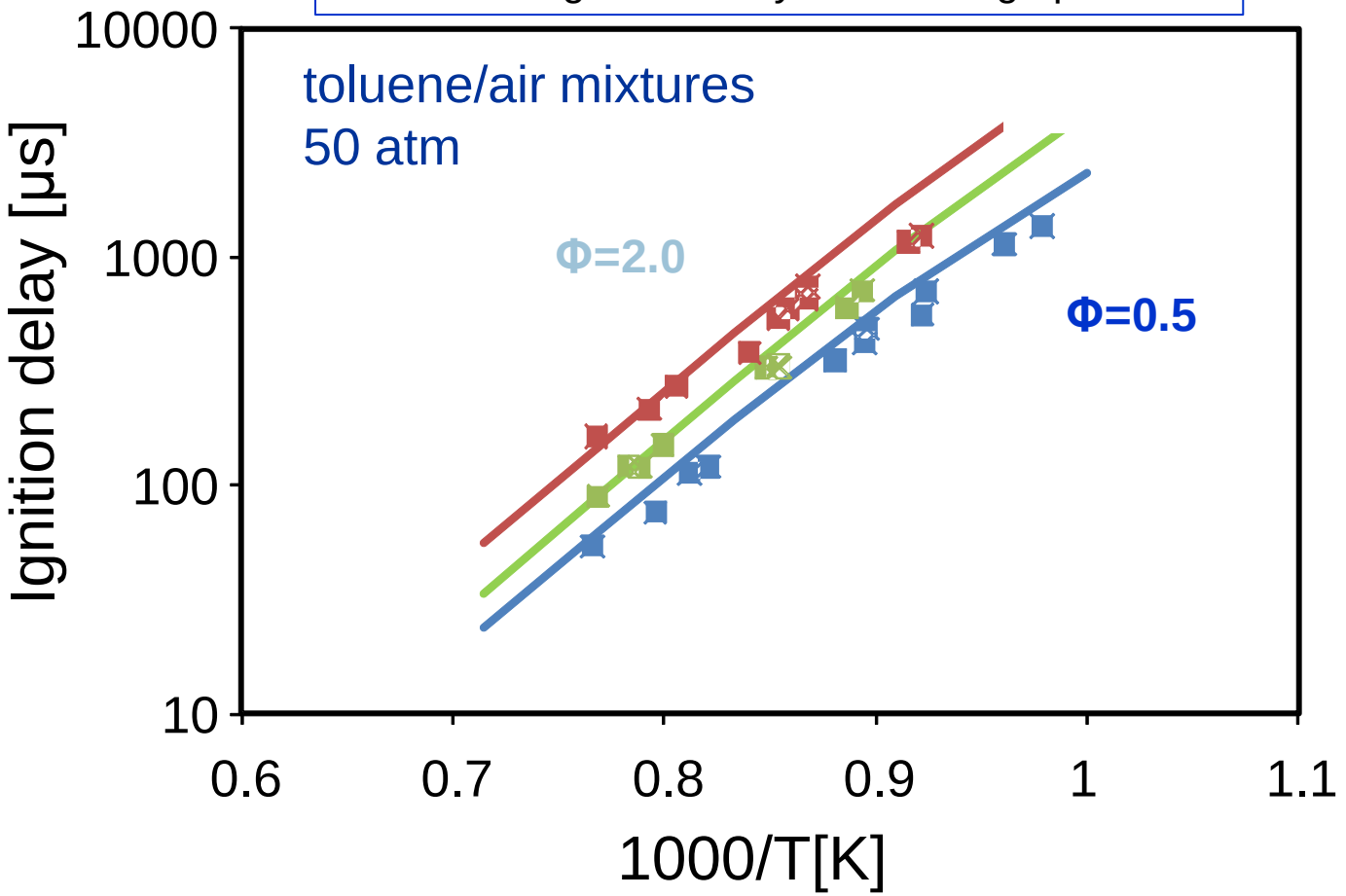
Perfectly stirred reactor
stoichiometric mixtures
10 atm

High cetane PRFs lead to more H2O2 which decomposes to reactive OH radicals



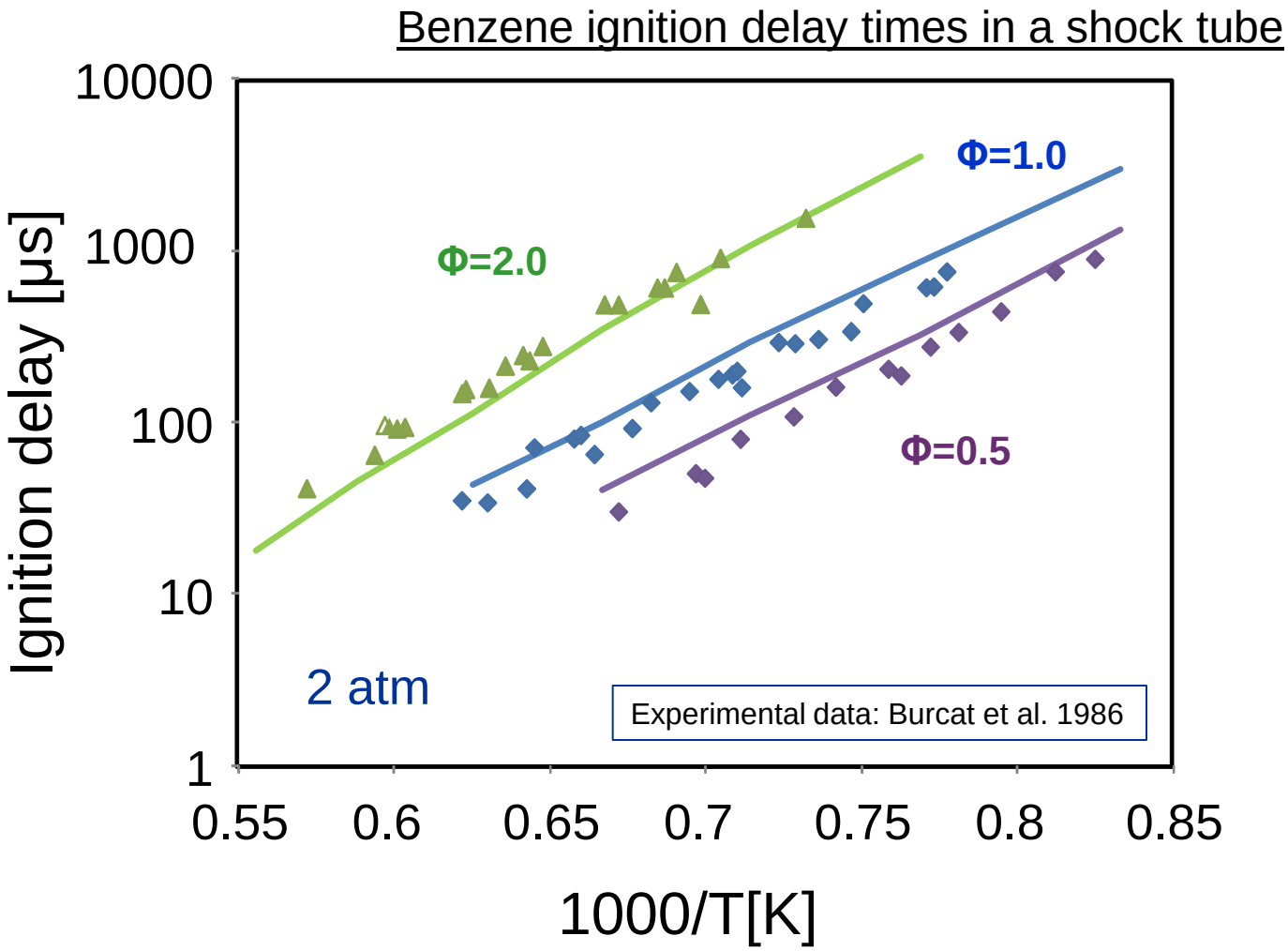
Improved toluene model well predicts ignition at high pressure

Shock tube ignition delay times at high pressure

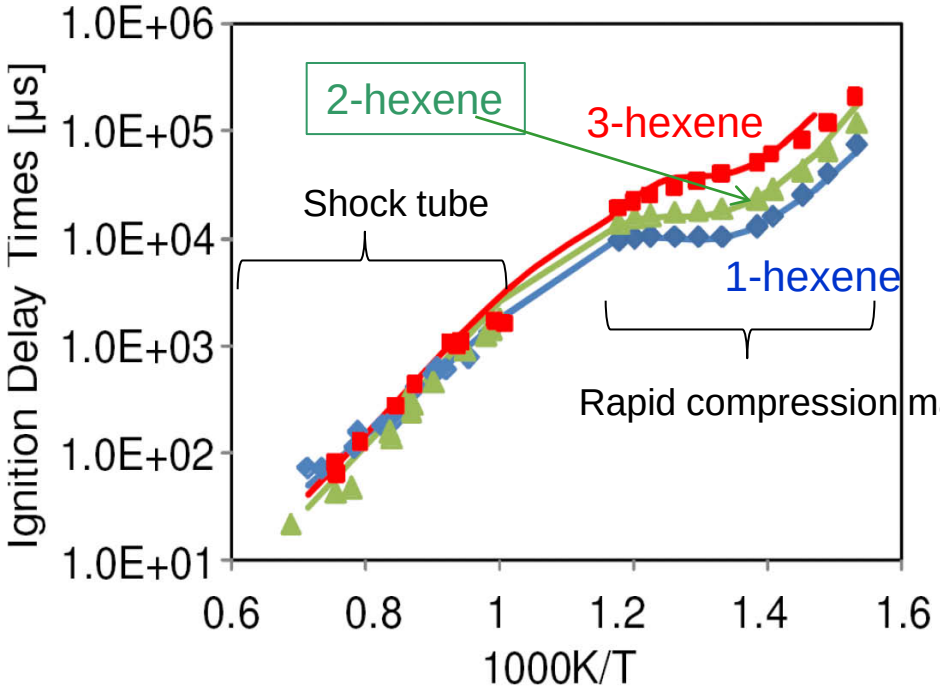


Experimental data: Shen, Vanderover and Oehlschlaeger (2009)

Improving building blocks for toluene: benzene



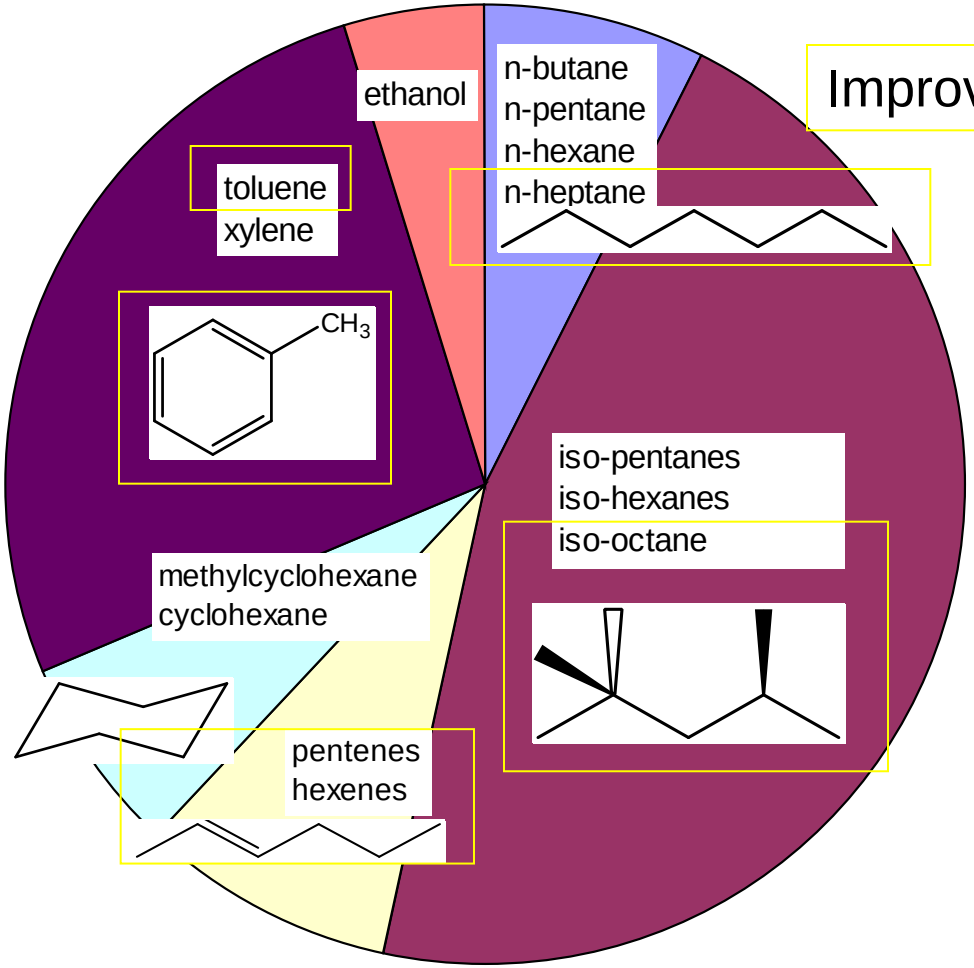
Improved the predictive behavior of hexenes and pentenes mechanisms over the entire temperature range



Mehl, Pitz, Westbrook, Yasunaga and Curran, The 33rd International Symposium on Combustion, 2010.

RCM experiments: Vanhove et al. 2007
Shock tube experiments: Yasunaga and Curran, 2010

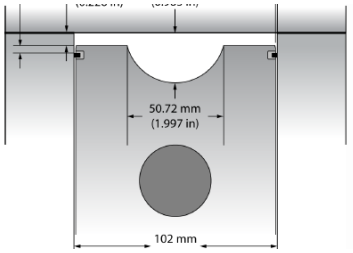
Recent improvements to fuel surrogate models: Gasoline



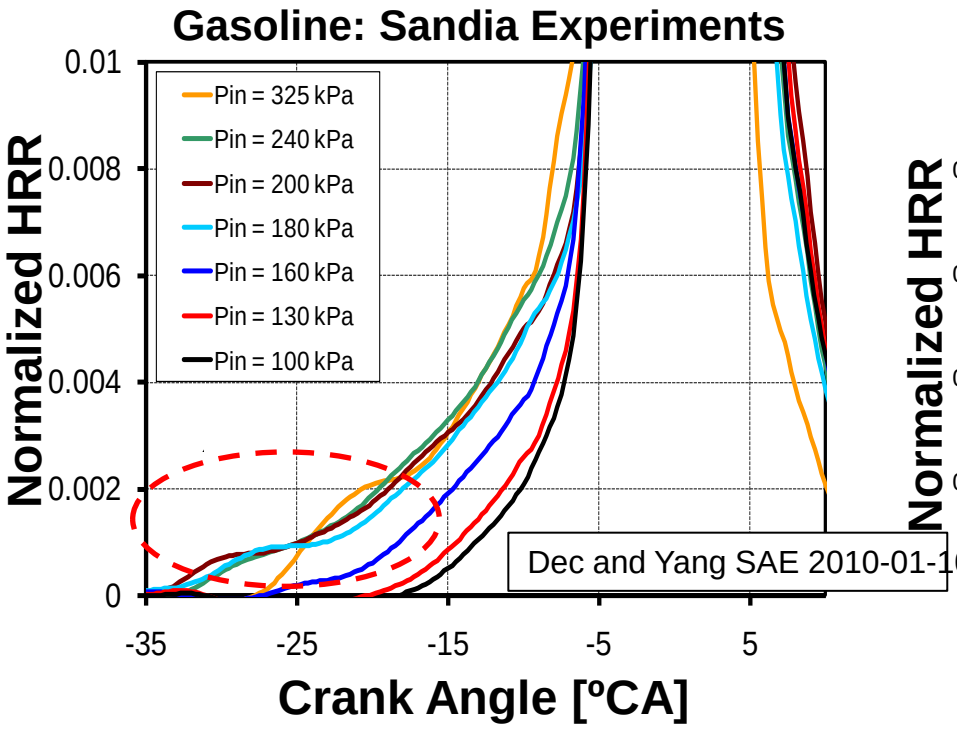
Improved component models

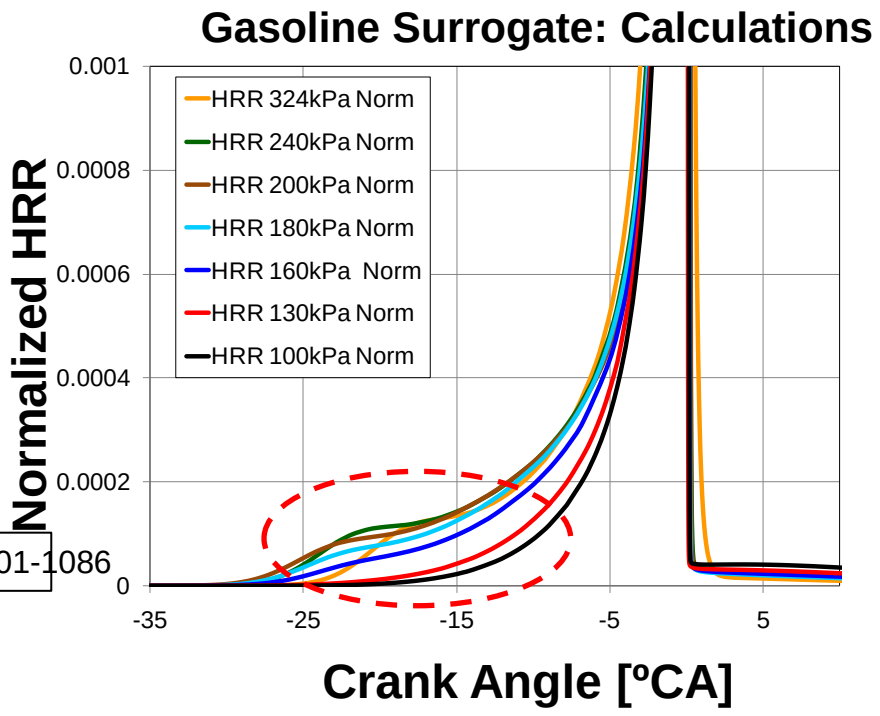
- n-alkane
- branched alkane
- olefins
- cycloalkanes
- aromatics
- oxygenates

Successful simulation of intermediate heat release in HCCI engine using gasoline surrogate blends

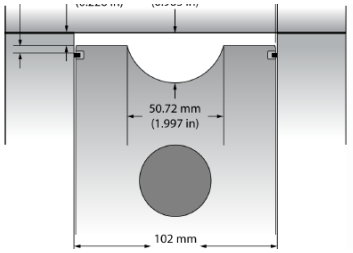


Dec and Yang, 2010: Intermediate heat release allows highly retarded combustion phasing and high load operation with gasoline





(Curves are aligned by time of peak heat release and normalized by tota



4-component gasoline surrogate: Matched gasoline composition targets and reactivity

Gasoline surrogate:

n-heptane (n-alkanes)

iso-octane (iso-alkanes)

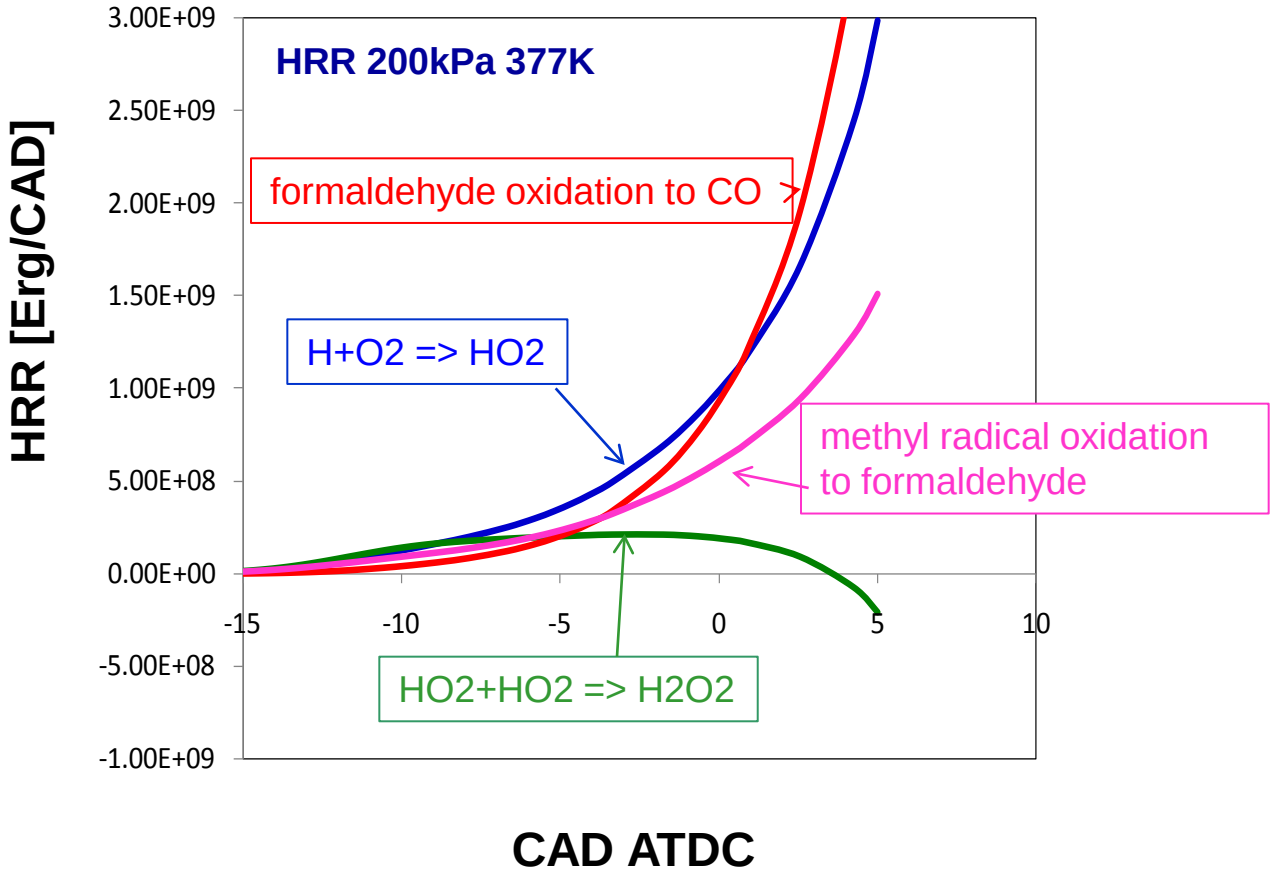
2-hexene (olefins)

toluene (aromatics)

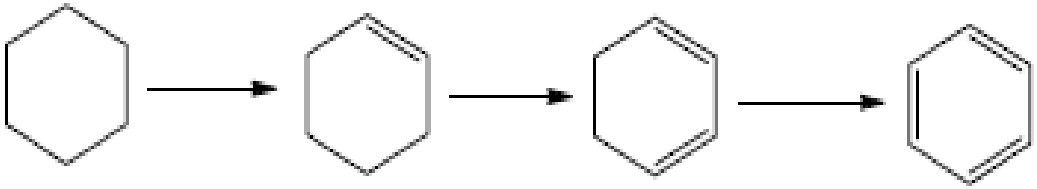
	Surrogate (%Vol)	Gasoline (%Vol)
n-alkanes	0.16	0.731
iso- alkanes	0.57	
olefins	0.04	0.04
aromatics	0.23	0.23
A/F Ratio	14.60	14.79
H/C	1.92	1.95

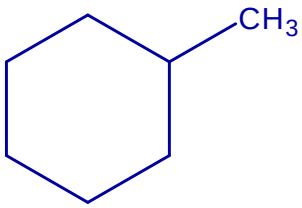
Matched the reactivity of a mixture having the same RON and MON as the gasoline

Reaction contributions to intermediate heat release rate



Cyclic paraffins are a fuel type that is poorly represented





Next steps

- We are continuing to add new species to each fuel class in the surrogate palette
- We have added 2-methyl and are adding 3-methyl alkanes to simulate F-T fuels
- We are adding component models for biodiesel species with double bonds

Next Activities

- Develop detailed chemical kinetic models for another series iso-alkanes:
  3-methyl alkanes

- Validation of 2-methyl alkanes mechanism with new data from shock tubes, jet-stirred reactors, and counterflow flames
- Develop detailed chemical kinetic models for alkyl aromatics:

- More accurate surrogates for gasoline and diesel
- Further develop mechanism reduction using functional group method

n-decylbenzene - Diesel Fuels

Surrogate fuels

- past use of n-heptane surrogate for diesel
- many similarities between all large n-alkanes
- n-decane surrogate for kerosene (Dagaut)
- n-hexadecane surrogate for biodiesel
- n-decane and methyl decanoate similarities
- role of methyl ester group
- potential of n-cetane + methyl decanoate or smaller methyl ester for biodiesel surrogate

Lawrence Livermore National Laboratory

Detailed kinetic modeling of transportation fuels

EFRC

June 2010

Charles K. Westbrook, Marco Mehl

Lawrence Livermore National Laboratory

Lawrence Livermore National Laboratory, P. O. Box 808, Livermore, CA 94551

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344

Combustion in human history: from the early steps…

- **500,000 – 100,000 BP**
  First use of controlled fire

- **100,000 – 50,000 BP**
  Routine use of fire

Prometheus Brings Fire to Mankind, 1817
Heinrich Friedrich Füger

- **500 BC**
  Heraclitus - Fire as fundamental substance

- **500 – 430 BC**
  Empedocles – Fire as one of the four elements

…to today

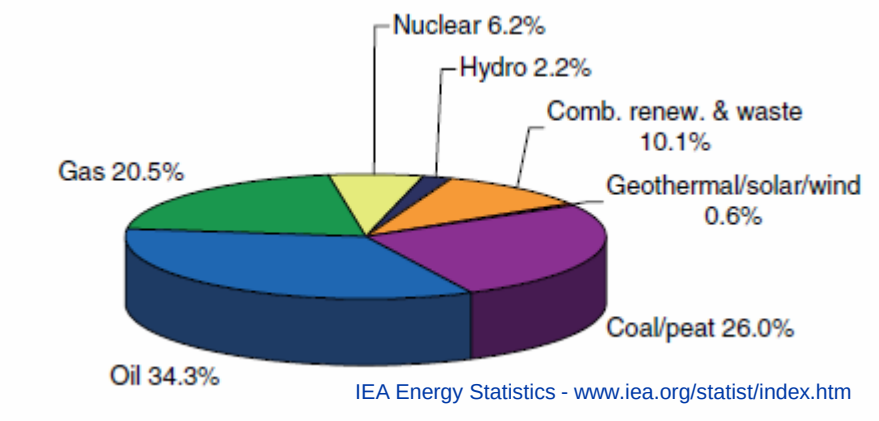
"Stripped to its bare bones, the industrial revolution consisted of the application of new sources of power to the production process, achieved with transmission equipment necessary to apply this power to manufacturing.

[…]

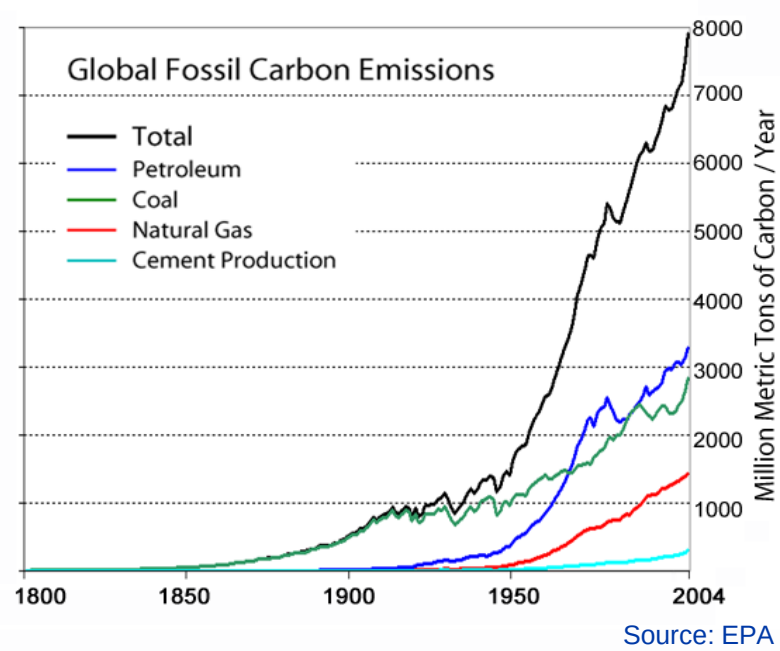
The industrial revolution progressively replaced humans and animals as the power sources of production with motors powered by fossil fuels […]."

The industrial revolution in world history
By Peter N. Stearns

Share of total primary energy supply in 2006 (World)



Combustion and Emissions

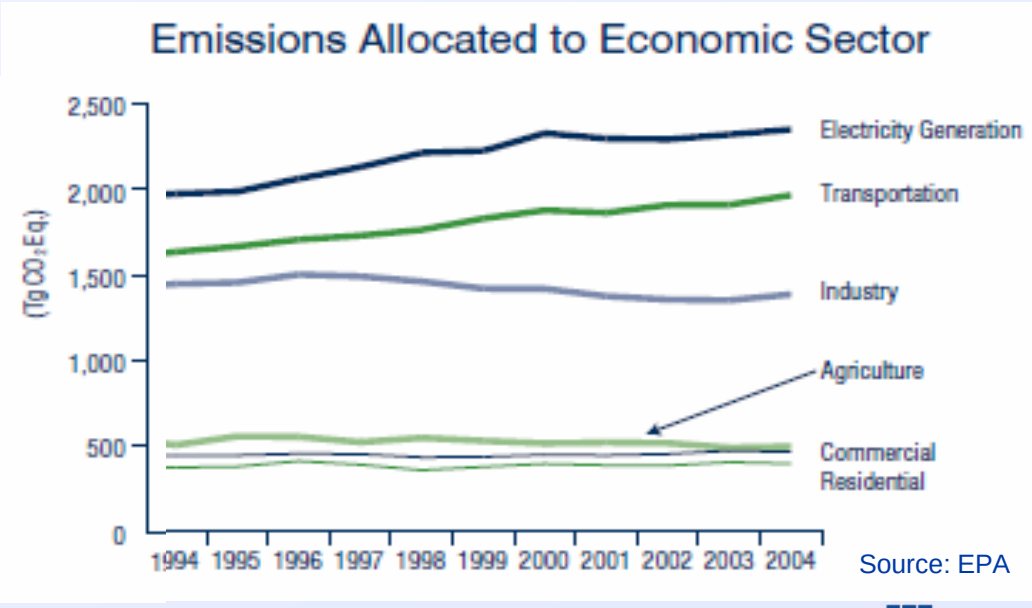


Source: EPA

There are drawbacks to large scale use of combustion:

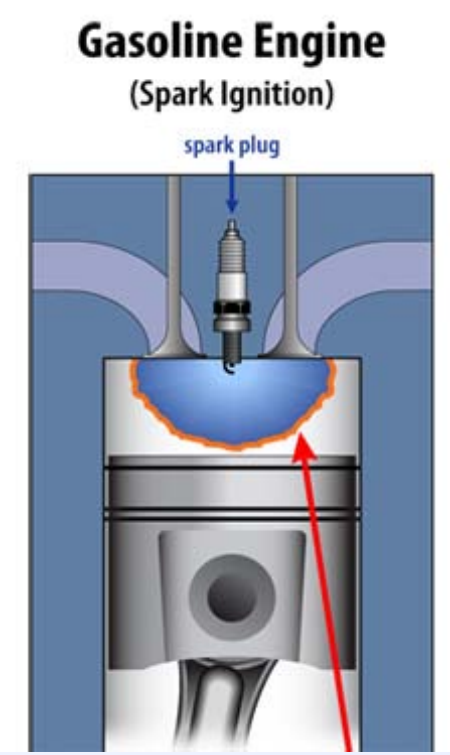
- **GHG emissions → Global warming**
- **Micropollutant emissions (NO_x, soot, SO_x, water pollution, …)**
- **Fossil fuels are a limited resource**

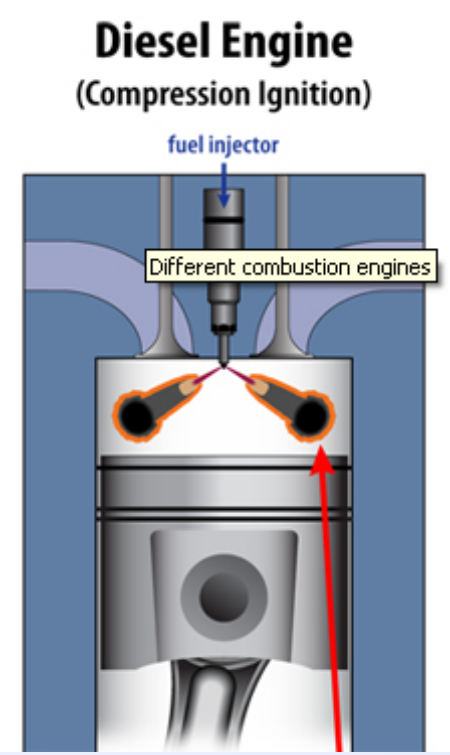
Transportation accounts for the 30% of the emissions of GHG, the trend is growing.



Source: EPA

Engine typologies and Combustion Processes





Hi T burnt gases → NOx
CR limited by Knock (Lower Eff)

Hi T Flame Front→ NOx
Rich Combustion → Soot
Higher CR (Higher Eff)

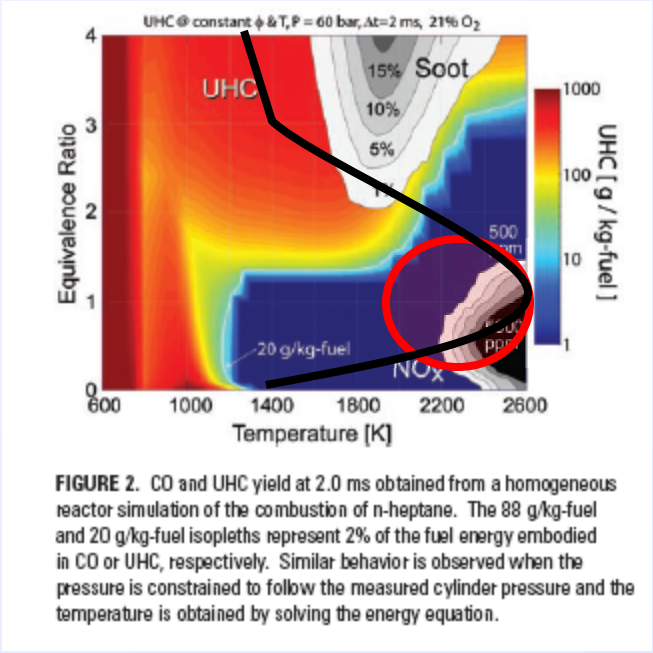


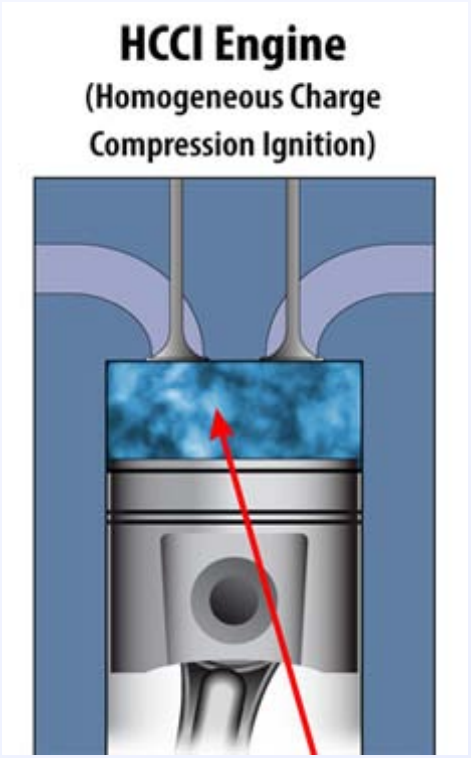
FIGURE 2. CO and UHC yield at 2.0 ms obtained from a homogeneous reactor simulation of the combustion of n-heptane. The 88 g/kg-fuel and 20 g/kg-fuel isopleths represent 2% of the fuel energy embodied in CO or UHC, respectively. Similar behavior is observed when the pressure is constrained to follow the measured cylinder pressure and the temperature is obtained by solving the energy equation.

2008 annual report
ADVANCED COMBUSTION ENGINE TECHNOLOGIES,
VehicleTechnologiesProgram
Paul Miles - Low-Temperature Automotive Diesel Combustion

The heat release timing is determined by the spark (premixed flame)

The heat release timing is controlled through the injection strategy

The HCCI Concept



Very lean conditions (no Soot)
Low T (no NOx, some UHC)
High CR (Hi Eff)

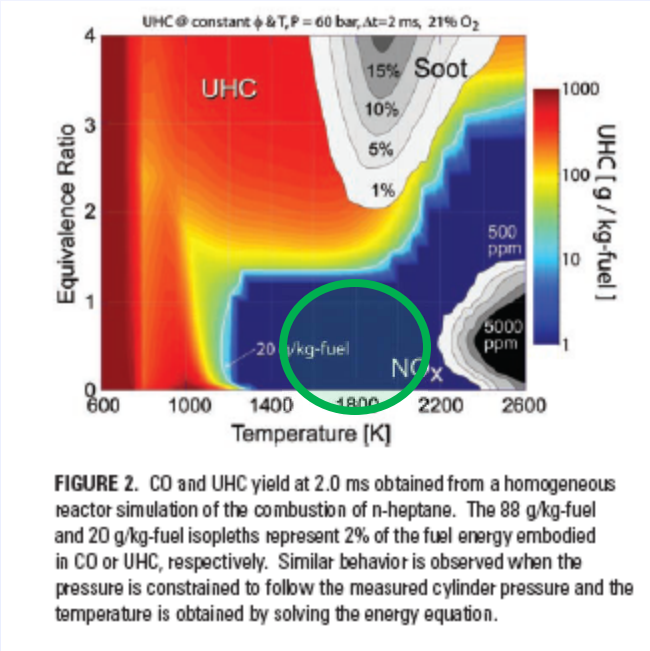


FIGURE 2. CO and UHC yield at 2.0 ms obtained from a homogeneous reactor simulation of the combustion of n-heptane. The 88 g/kg-fuel and 20 g/kg-fuel isopleths represent 2% of the fuel energy embodied in CO or UHC, respectively. Similar behavior is observed when the pressure is constrained to follow the measured cylinder pressure and the temperature is obtained by solving the energy equation.

The heat release timing is determined by autoignition (Chemical Kinetics)

Fuels and energy carriers

Traditional Fossil fuels:

NG: CH4
LPG: C3-C4
Gasoline: C6-C10, reforming
Kerosene: C9-C13
Diesel: C13-C22
….

Fuels from gasification:

FT fuels
Hydrogen

Biofuels:

Ethanol
Biodiesel

Real Fuels and Surrogates

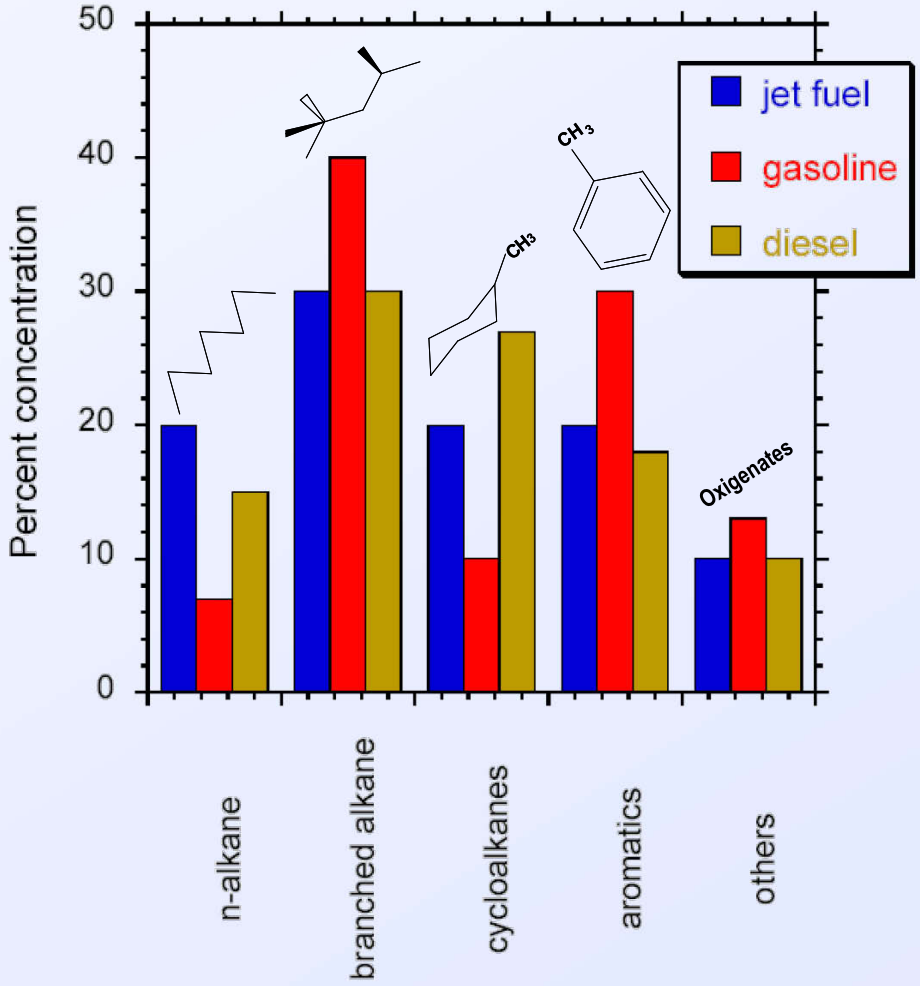
Real fuels are complex mixtures of hundreds of components

Qualitative composition is known

Their composition is intrinsically variable (seasonally, depending on the feedstock, ….)

The introduction of alternative fuels is making things even more complicated

Simpler surrogates have to be defined for modeling and more reproducible experiments



Gasoline $6 < C < 10$ **Jet fuel** $9 < C < 13$ **Diesel** $13 < C < 22$

The development of Surrogate Fuels

- **First surrogate for diesel fuel was n-heptane (iso-octane and then Primary Reference Fuels for gasoline fuel)**
- **Early surrogates included one representative from each fuel molecule class**
- **Advantages of having multiple samples from each class of molecules**
- **Our research has been focused on developing kinetic models for many examples in each class**
- **Mechanism reduction can then be applied to those fuel components to be used**

Kinetic Mechanisms

Modified Arrhenius Law: $A \cdot T^{n} \cdot exp(-Ea/RT)$

Reaction

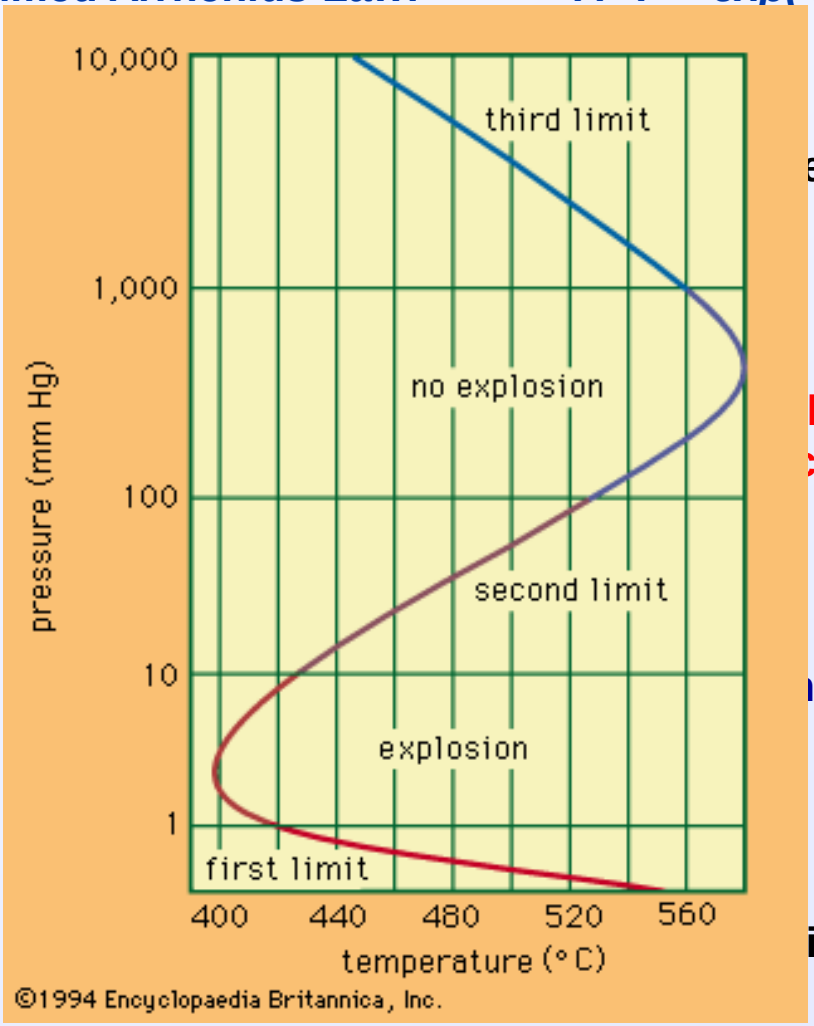
H2+M<=>H+H+M
O2+M<=>O+O+M
H2O2(+M)<=>OH+OH(+M)

H+O2<=>O+OH
O+H2<=>H+OH

OH+H2<=>H+H2O
HO2+H<=>OH+OH
H2O2+H<=>H2+HO2

H+O2(+M)<=>HO2(+M)

HO2+OH<=>H2O+O2
H2O+M<=>H+OH+M
H2O2+O2<=>HO2+HO2



Initiation

e molecules decompose to unstable radicals)

H+O2+H2⇔H+2OH
Chain Branching
he number of radical is creased through a chain reaction)

Propagation

he number of radicals is conserved)

Termination

icals recombine to stable products)

From “the Simple”… to the Complex!

Hydrogen

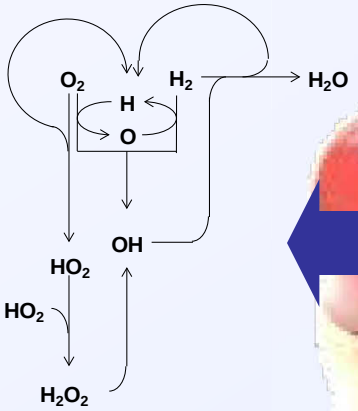
7 Species - 20 Reactions

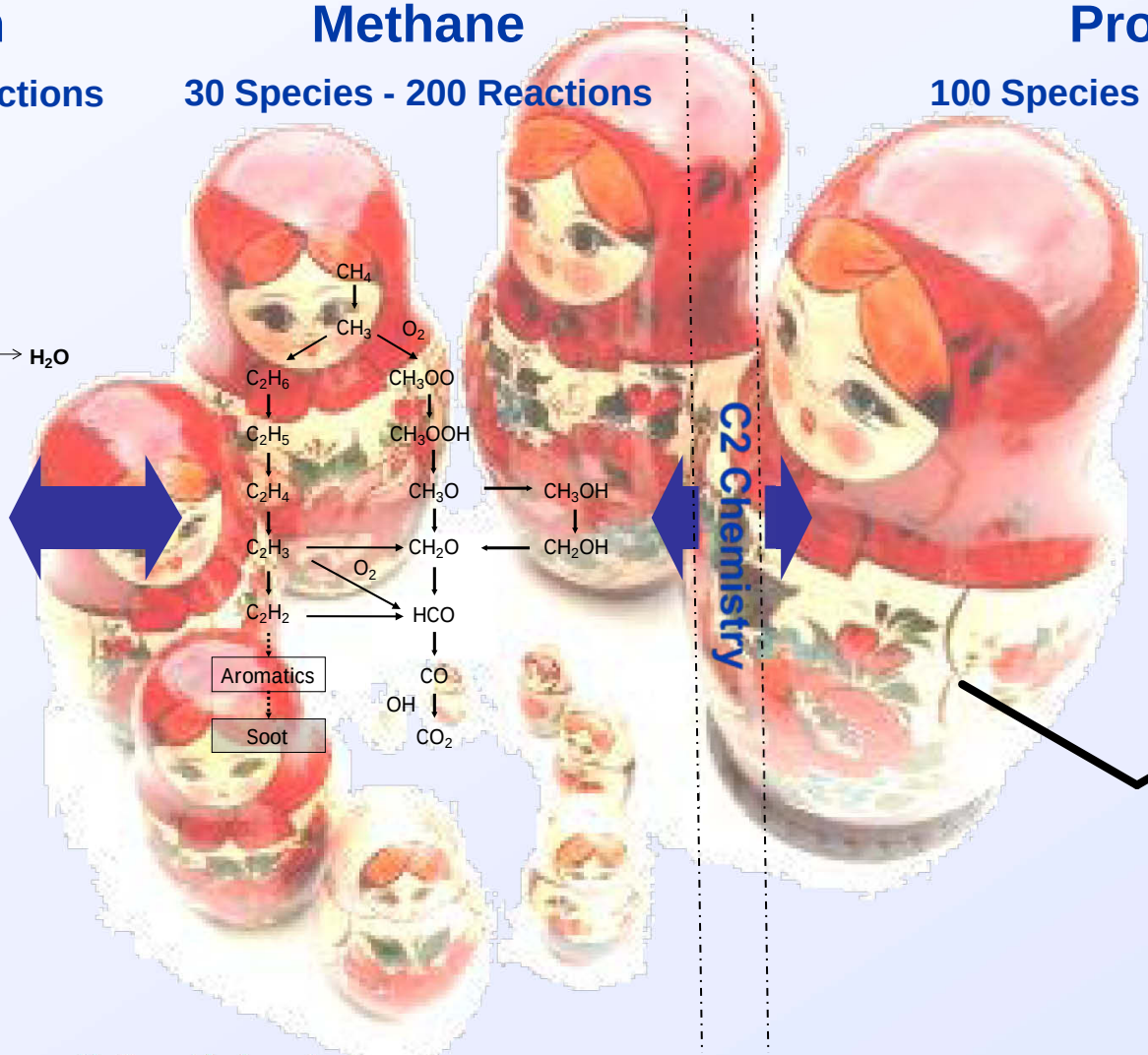
Methane

30 Species - 200 Reactions

Propane

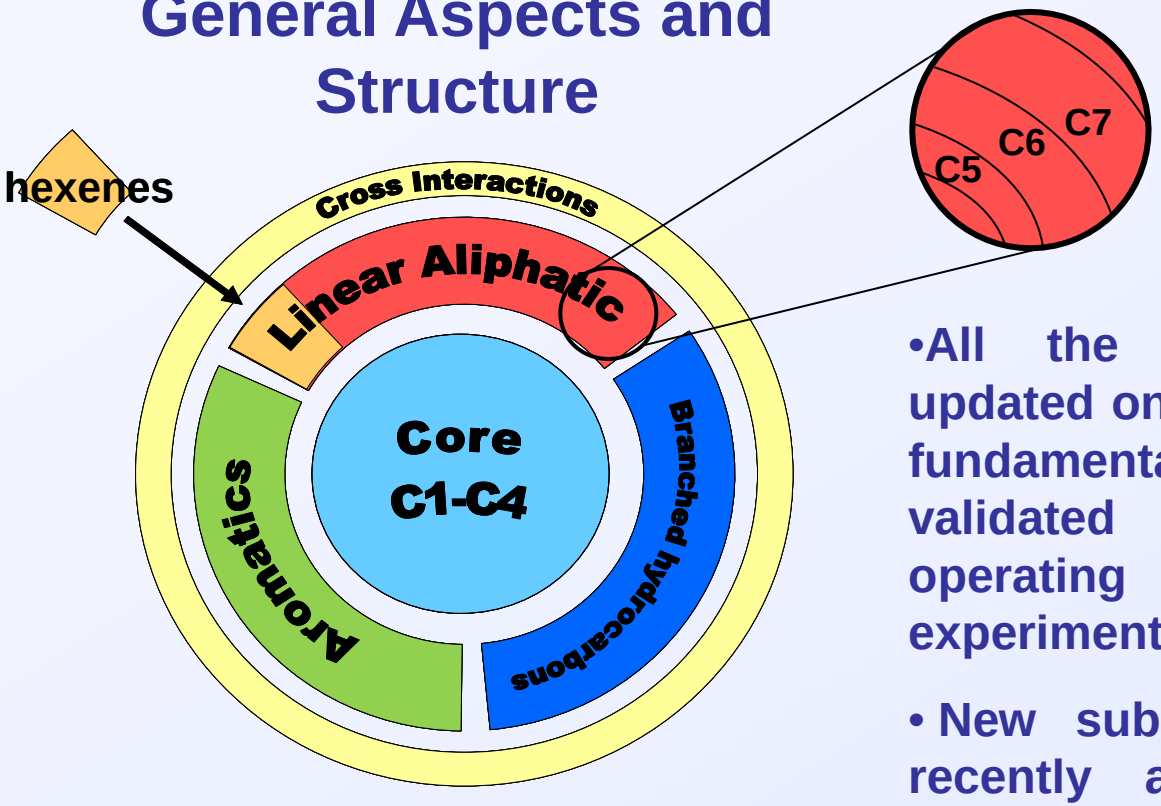
100 Species - 400 Reactions





The LLNL Kinetic Mechanism

General Aspects and Structure

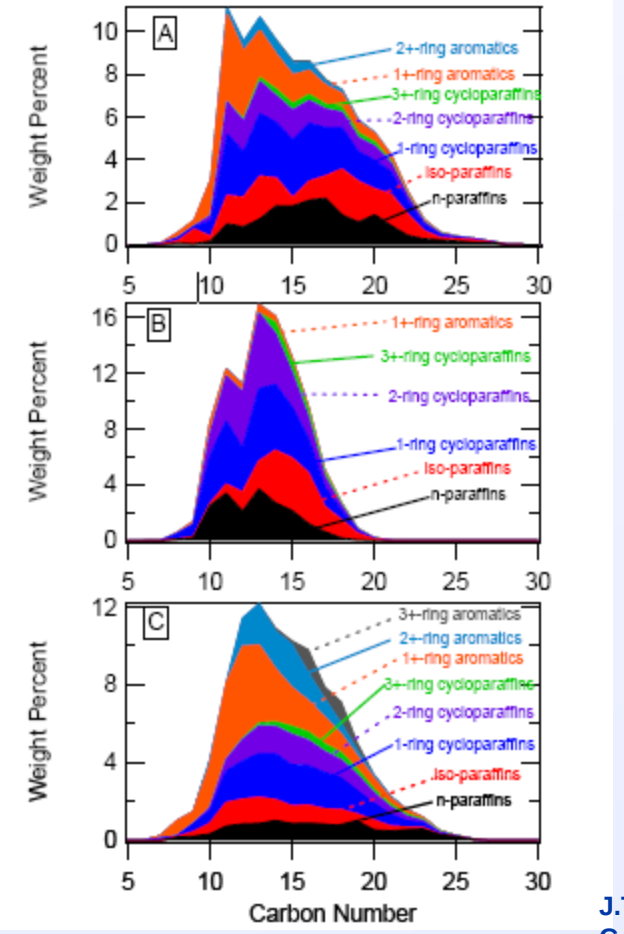


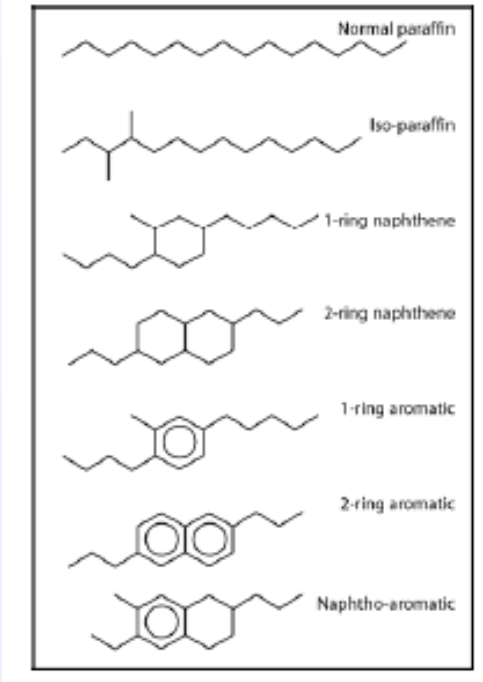
- All the blocks are constantly updated on the basis of the available fundamental information and validated on a wide range of operating conditions when new experimental data are published.
- New sub-mechanisms have been recently added (low temperature reactivity of some large alkenes.

- The oxidation of the reference components is interconnected by the mechanism core and by the direct cross reactions among the different fuels

Diesel fuel composition

Detailed hydrocarbon analysis of commercial diesel fuels

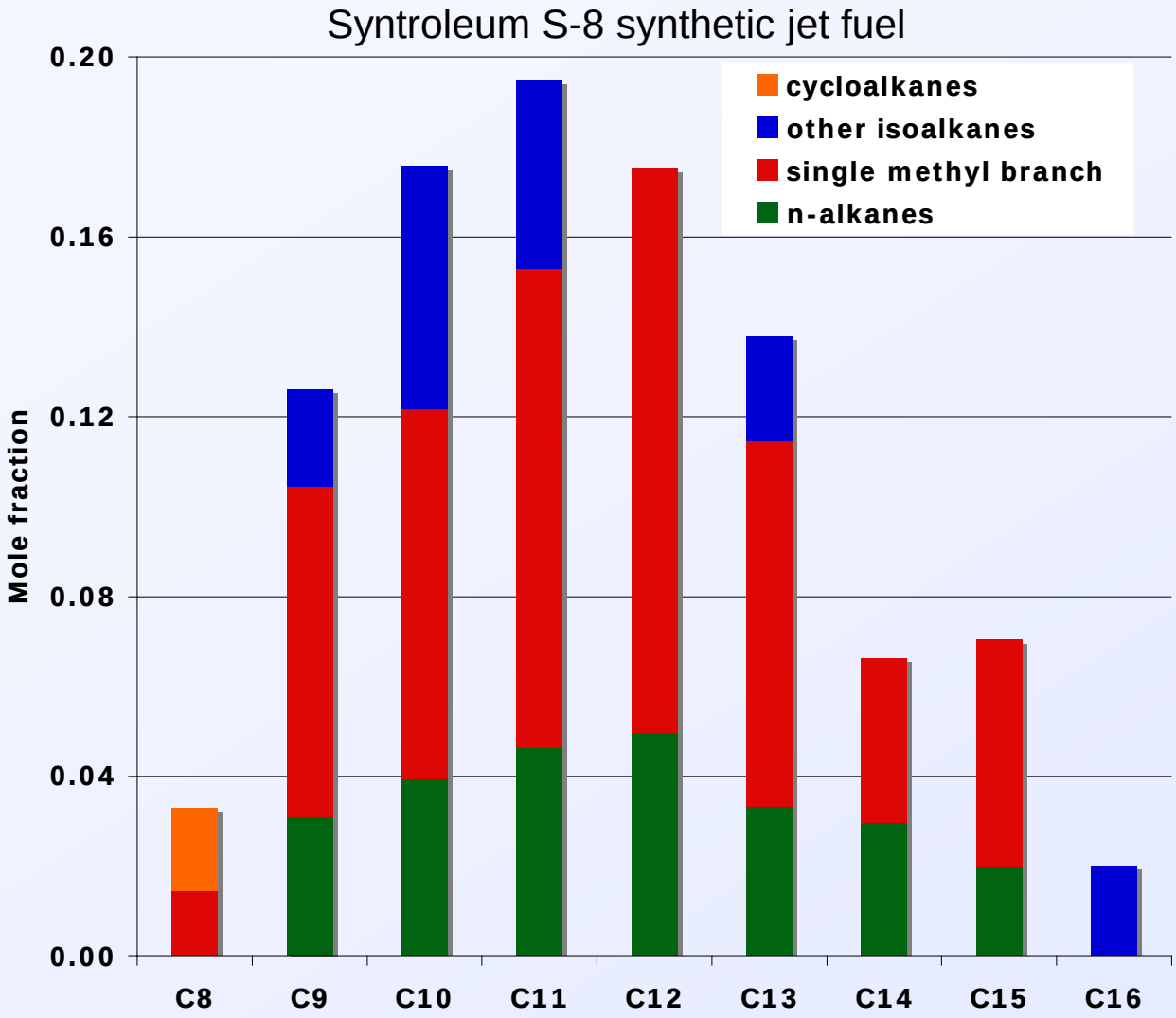




- **Compositional variability**
- **Broad range of molecular weight**
- **The straight chain structures are dominant**
- **Aromatics are important as well**
- **n-heptane is traditionally used to approximate their autoignition behavior**

J.T. Farrell, N.P. Cernansky, F.L. Dryer, D.G. Friend, C.A. Hergart, C. K. Law, R.M. McDavid, C.J. Mueller, A.K. Patel, and H. Pitsch, SAE 2007-01-0201

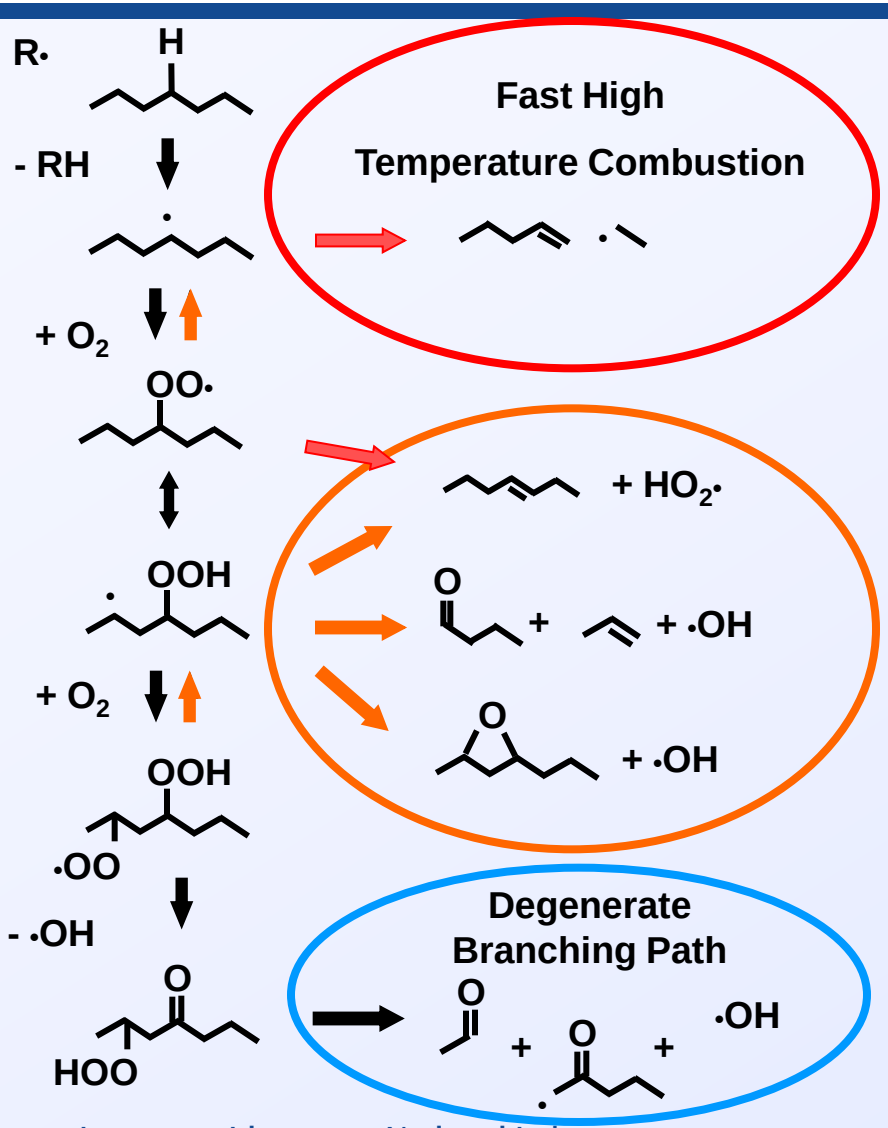
Fischer-Tropsch fuel composition

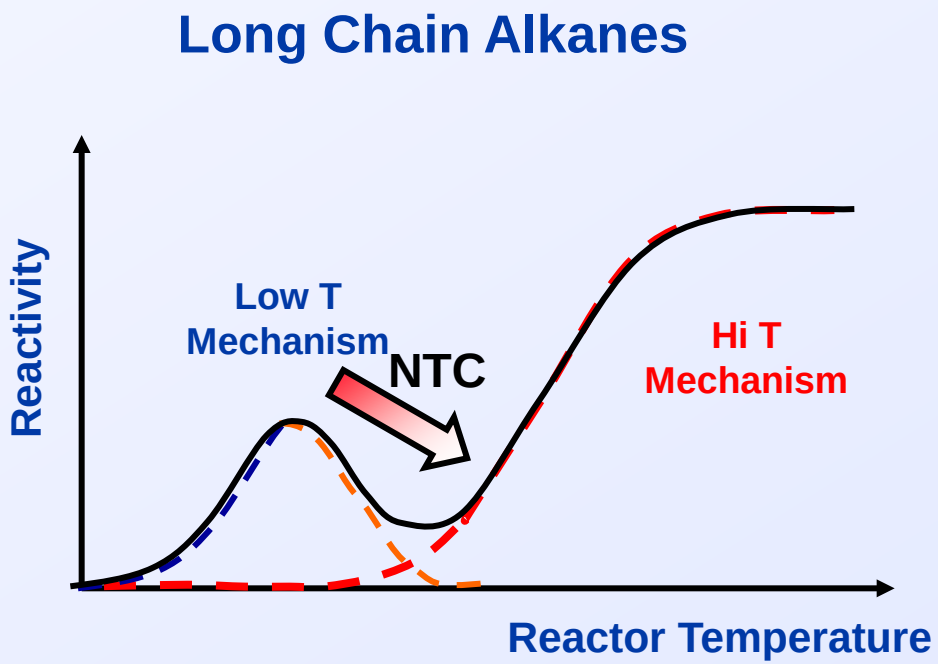


- FT analysis (NIST*)
  - 57% single methyl branch alkanes
  - 25% n-alkanes
  - 16% multiple branched alkanes
  - 2% cycloalkanes

* Smith, B. L.; Bruno, T. J. *J. Propulsion* 2008, *24*, 618.

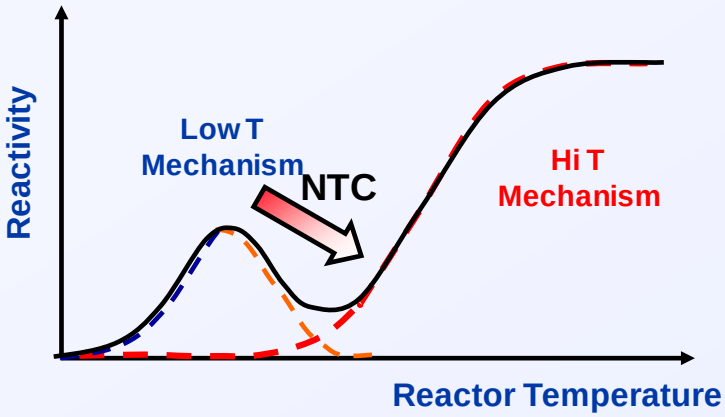
Cool flames

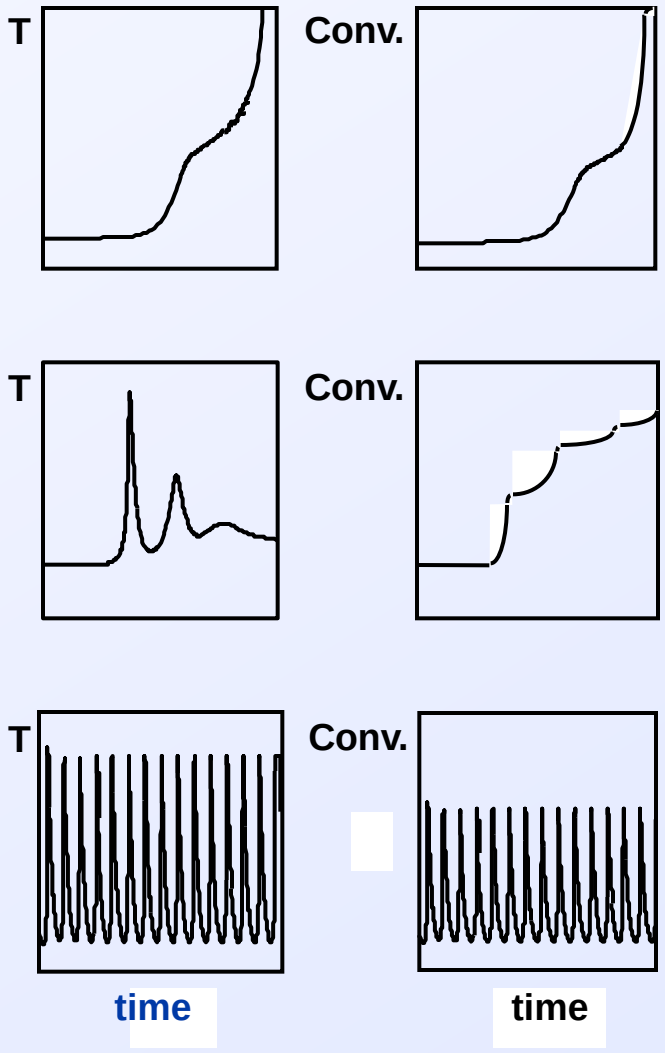

R·
H
- RH
+ O_2
OO·
OOH
+ O_2
OOH
·OO
- ·OH
O
HOO
Fast High
Temperature Combustion
+ HO_2·
O
+
+ ·OH
O
+ ·OH
Degenerate
Branching Path
O
+
O
+
·OH


Long Chain Alkanes
Reactivity
Low T
Mechanism
NTC
Hi T
Mechanism
Reactor Temperature

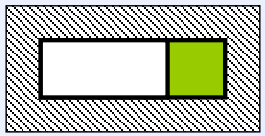
Alkanes oxidation in different reacting systems

Long Chain Alkanes

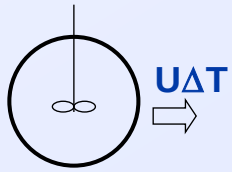




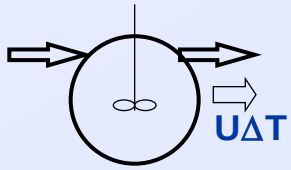
Closed Adiabatic



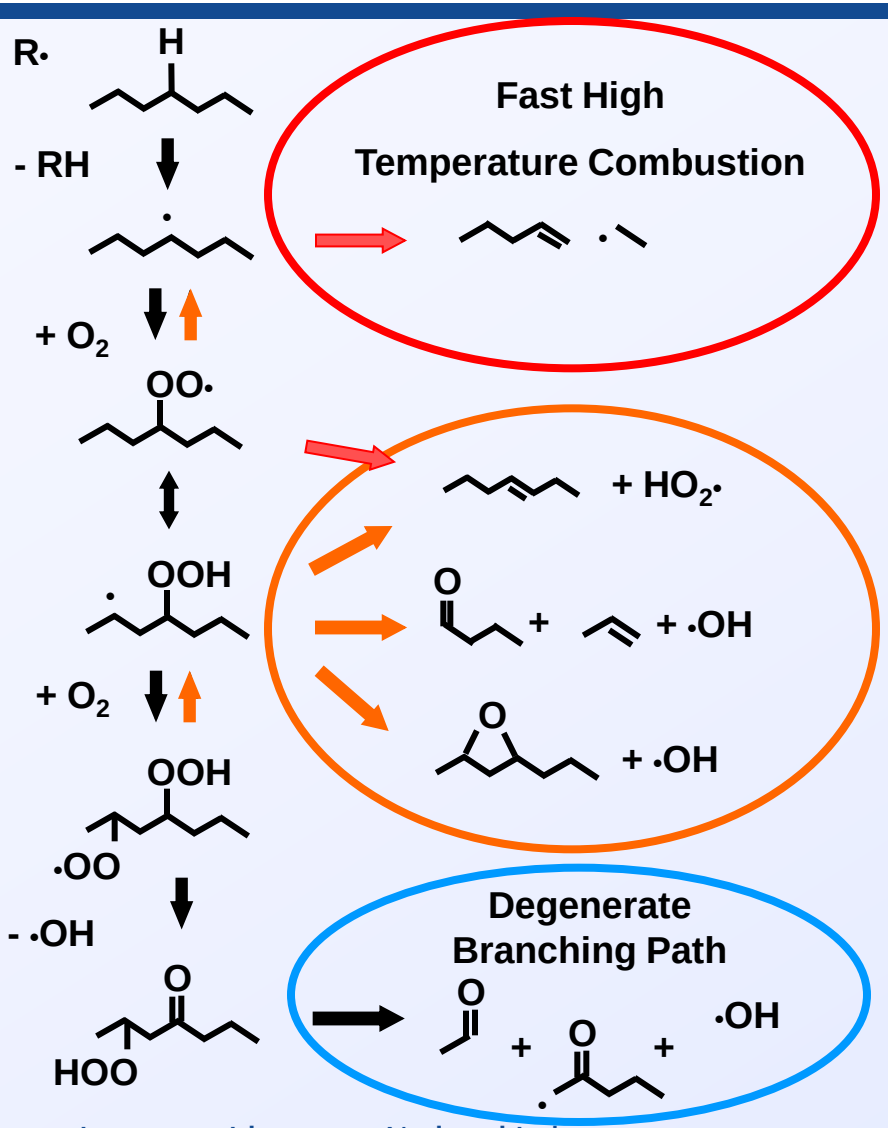
Closed
Non-Adiabatic



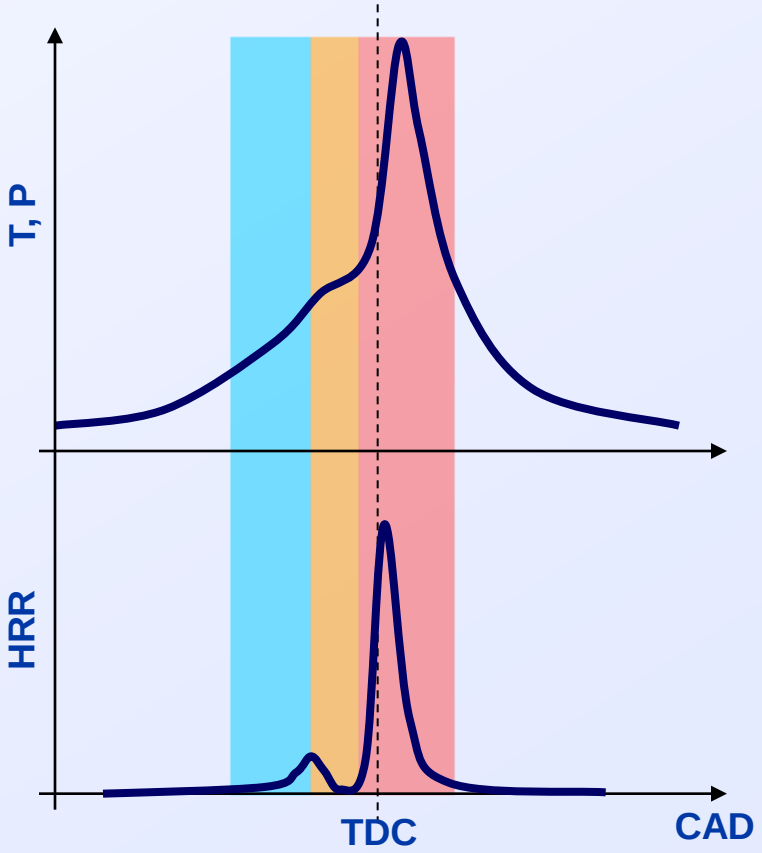
Open
Non-Adiabatic



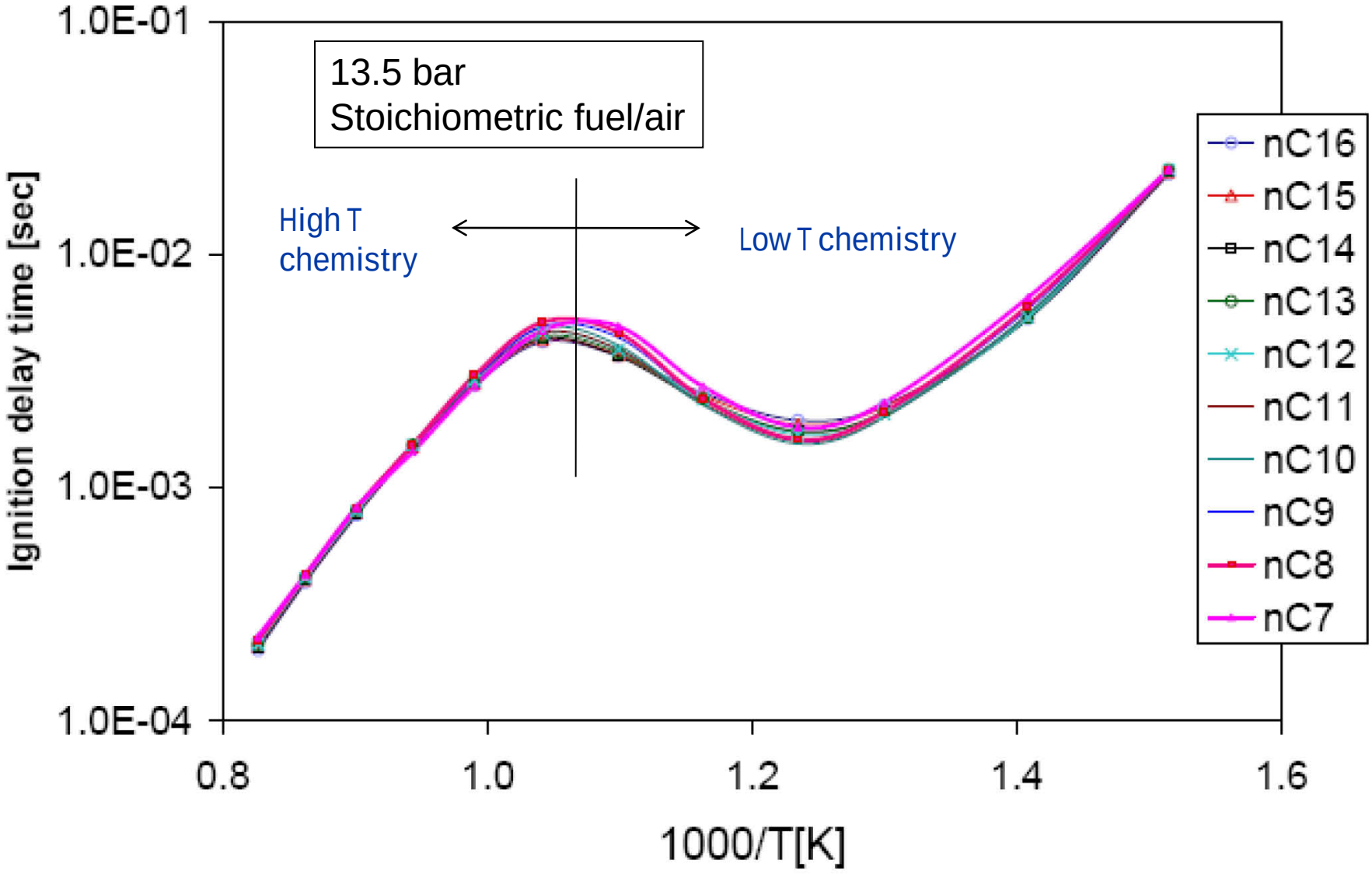
HCCI combustion kinetics: two Stage Fuels



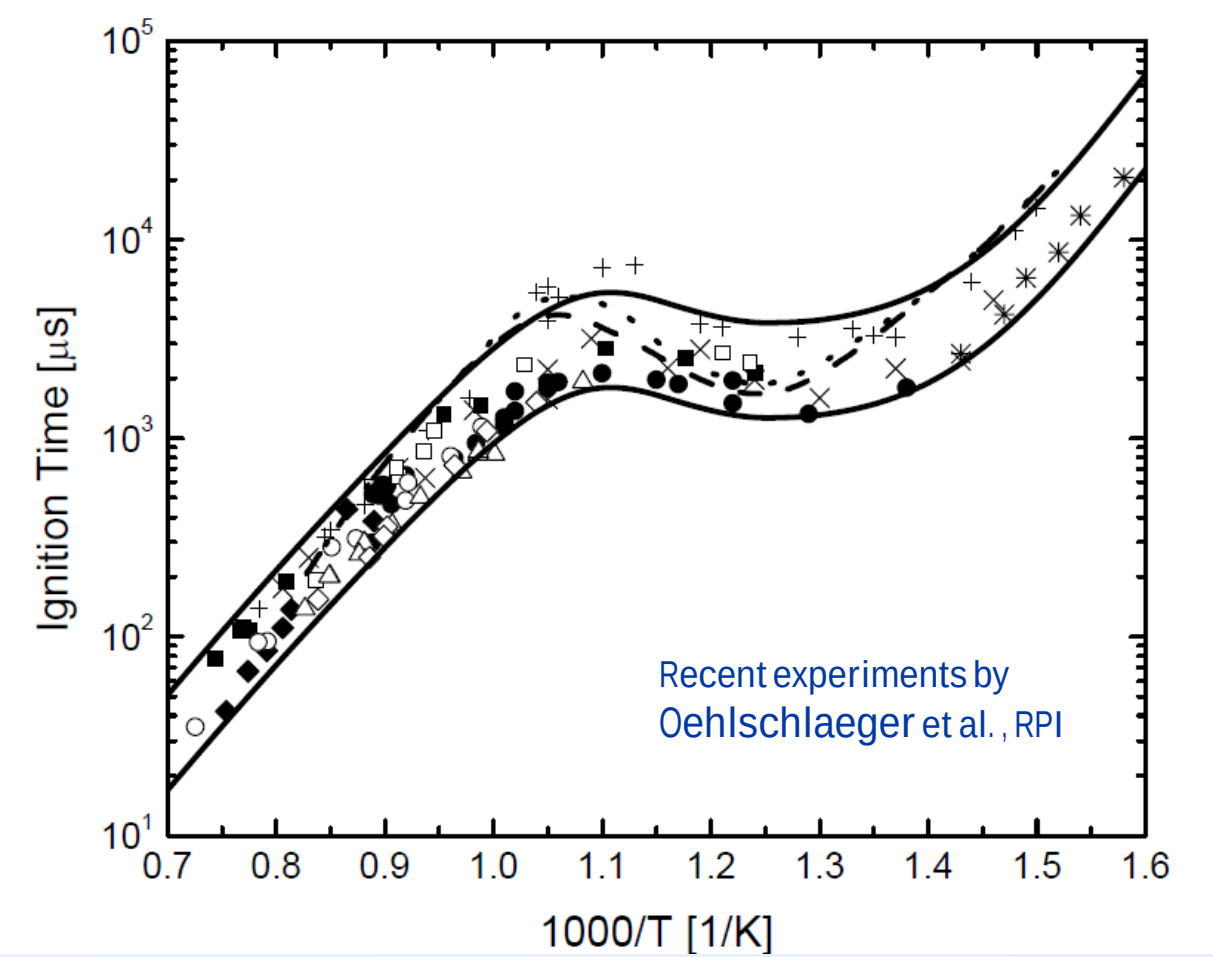
Typical HCCI Combustion Temperature and Heat Release Rate profiles

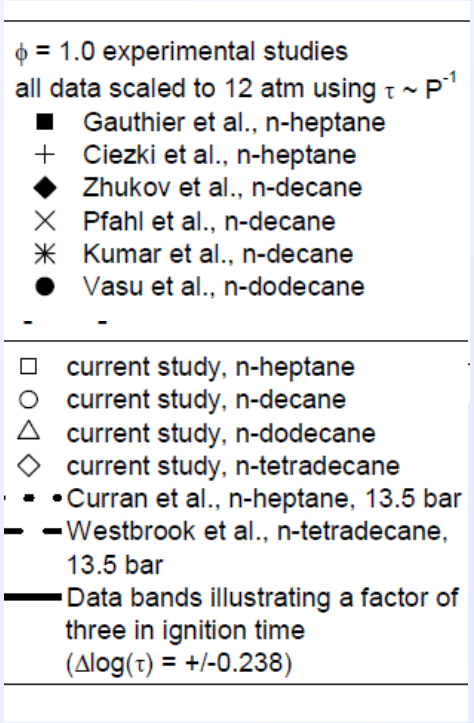


Predicted ignition behavior similar for C7-C16 n-alkanes



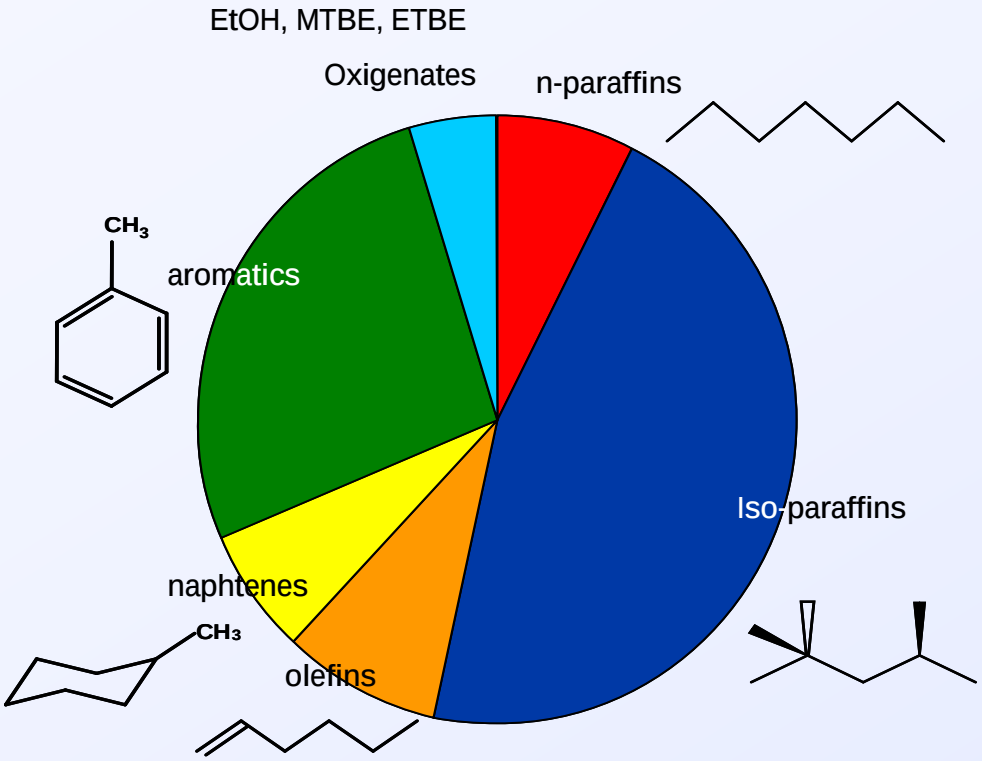
Experimental ignition behavior similar for C7-C14 n-alkanes





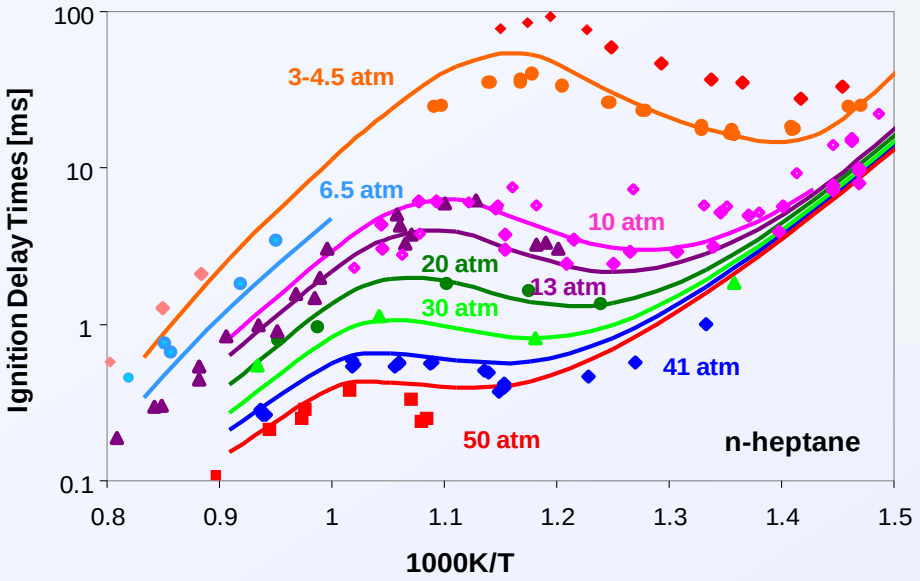
Recent shock tube experiments show all large n-alkanes ignite within a factor of 3

Gasoline and gasoline surrogates



- **Compositional variability**
- **The branched chain structures are dominant**
- **Aromatics, oxygenates and olefins are desirable octane enhancer**
- **iso-octane is traditionally used to approximate their autoignition behavior**

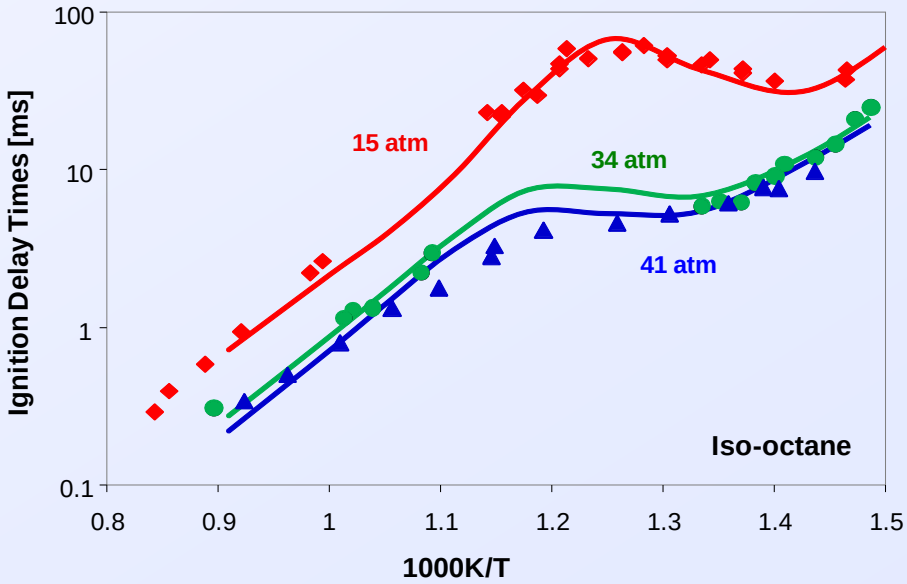
PRFs: Validation



iso-octane:
P = 15 - 45 atm T = 650K - 1150K
Fi = 1

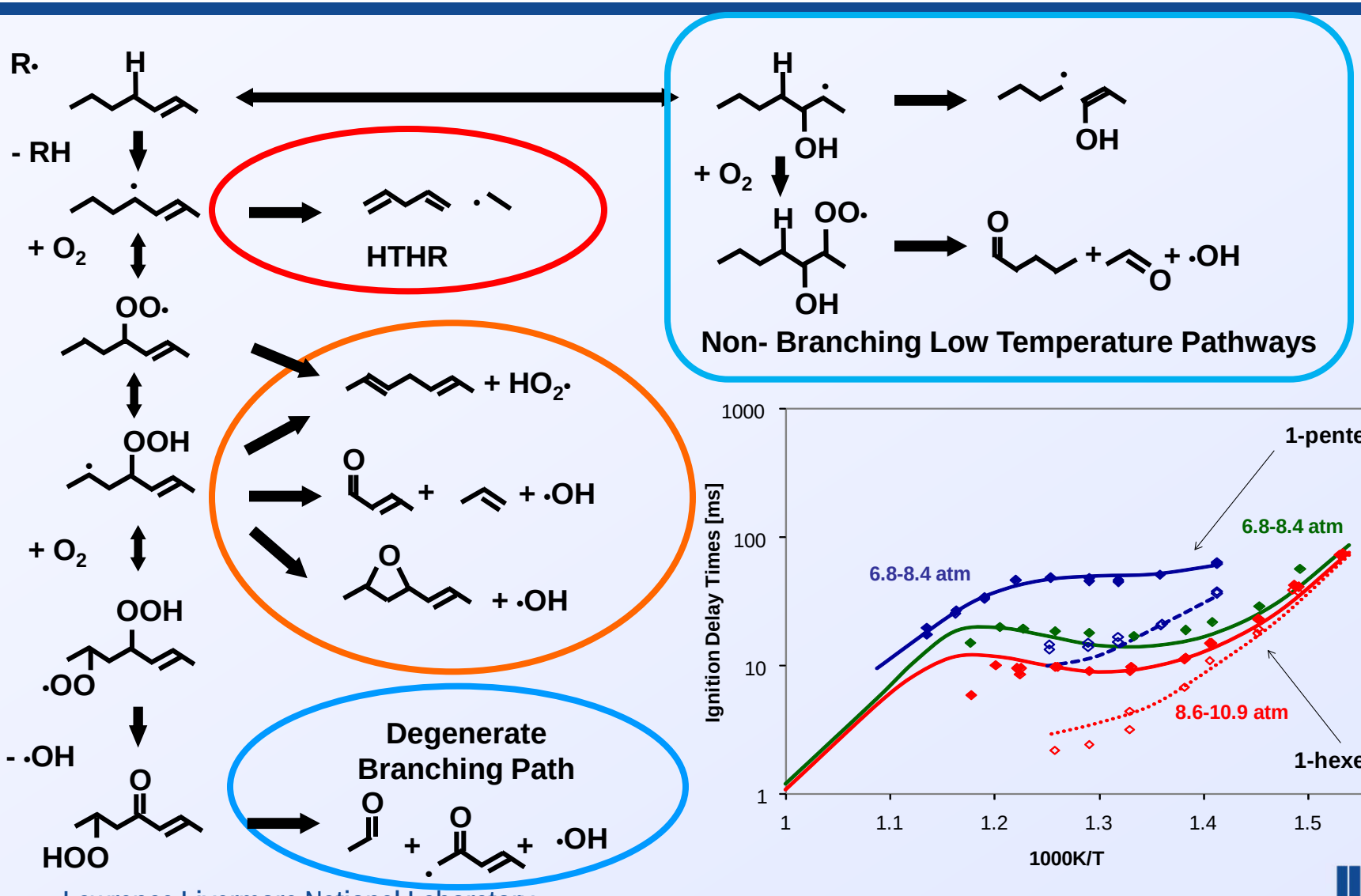
Shock tube and rapid compression machine validation of n-heptane & iso-octane mechanisms:

n-heptane:
P = 3 - 50 atm T = 650K - 1200K
Fi = 1

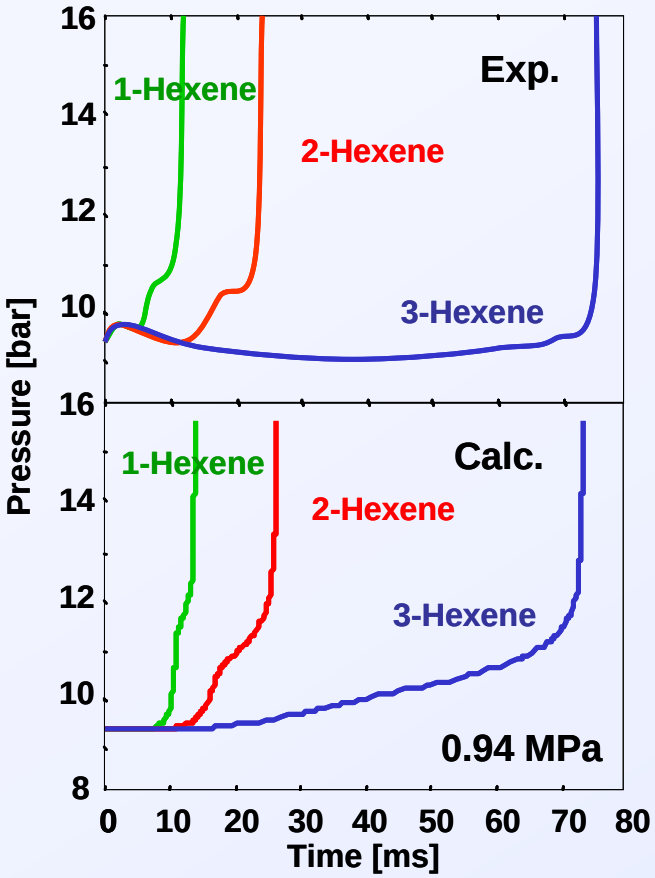


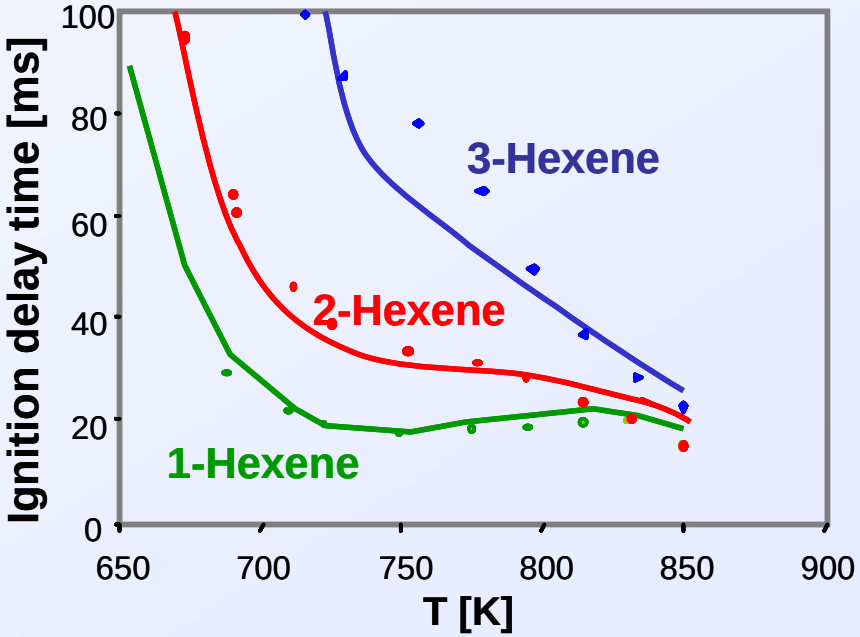
Minetti R., M. Carlier, M. Ribaucour, E. Therssen, L. R. Sochet (1995); H.K.Ciezki, G. Adomeit (1993); Gauthier B.M., D.F. Davidson, R.K. Hanson (2004); Mittal G. and C. J. Sung,(2007); Minetti R., M. Carlier, M. Ribaucour, E. Therssen, L.R. Sochet (1996); K. Fieweger, R. Blumenthal, G. Adomeit (1997).

Alkenes reactivity & Mechanism Validation



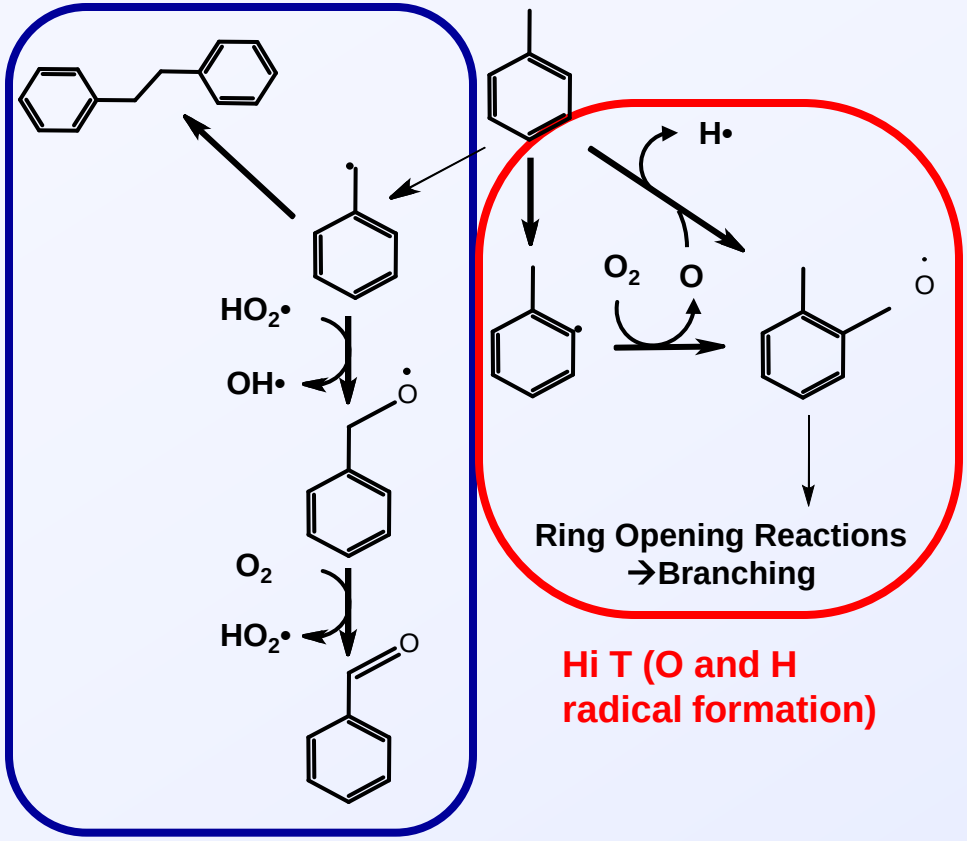
Effect of the position of the double bond





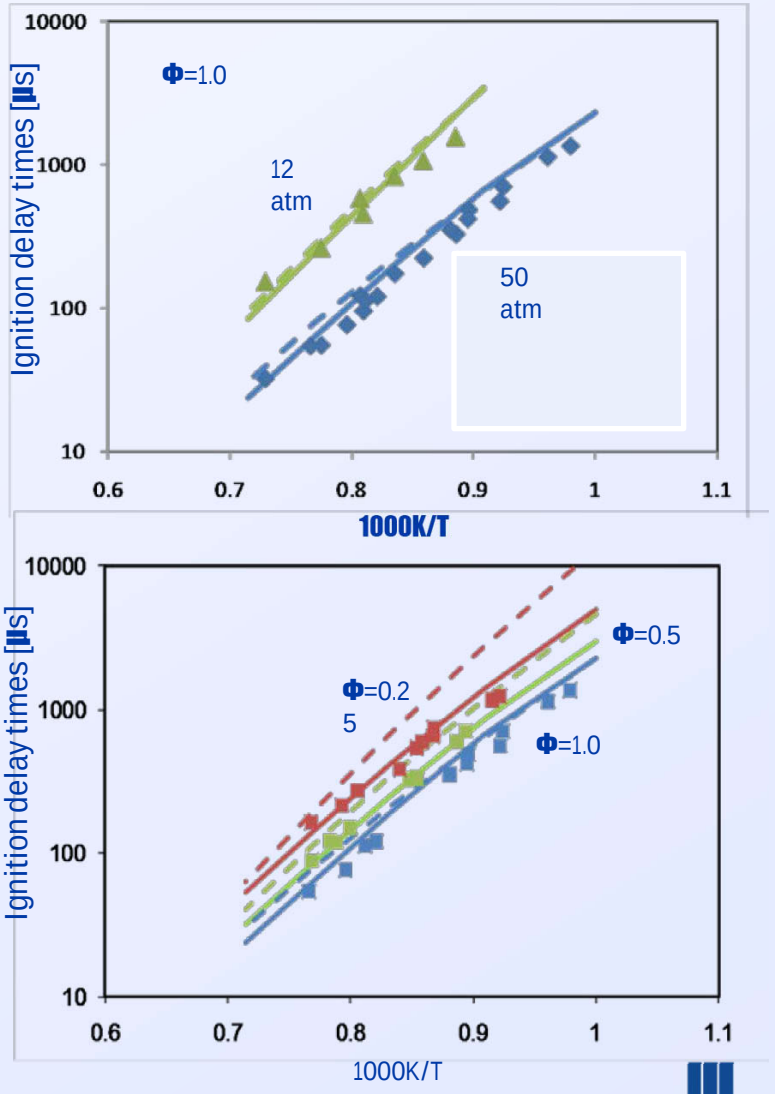
The length of the free saturated carbon chain determines the reactivity

Toluene: a Single Stage Fuel

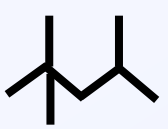


Hi T (O and H radical formation)

Low T (HO_2 radicals, resonantly stabilized radicals and termination reactions



Iso-octane/Toluene Mixtures



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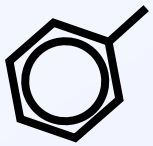

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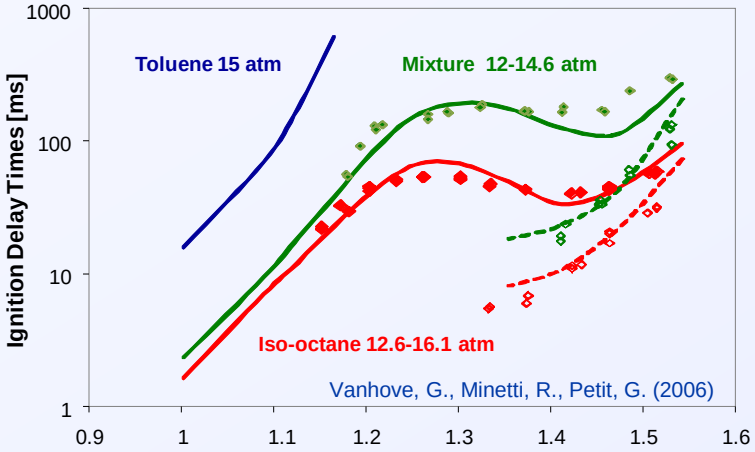
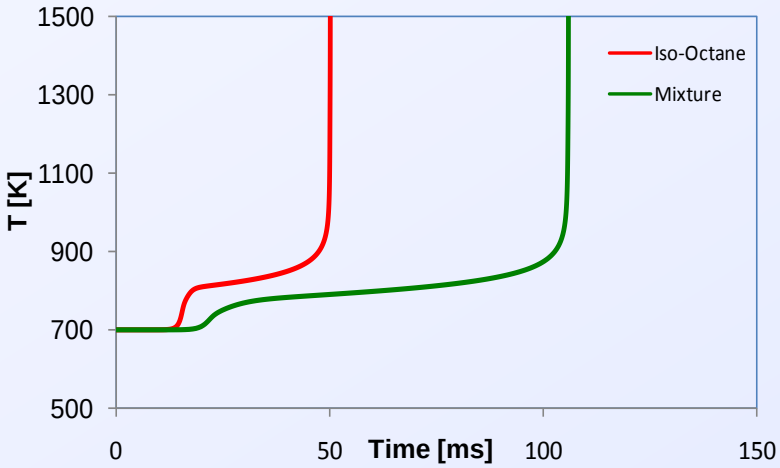
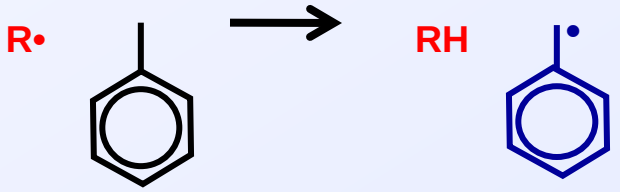
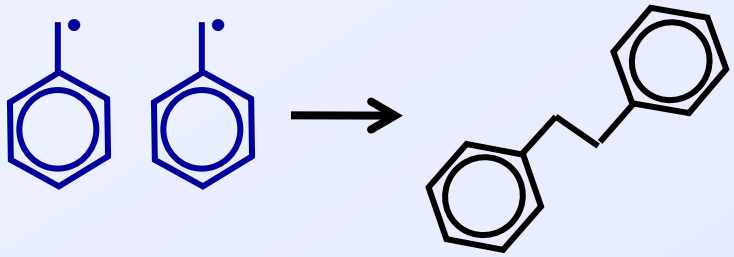




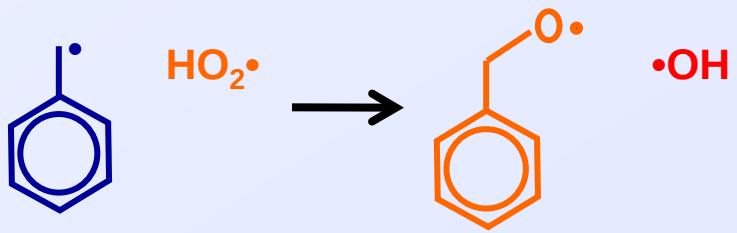
Extremely long delays between cool flame and thermal ignition:



Active radicals abstract the benzylic hydrogen

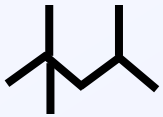


Termination of the benzyl radicals



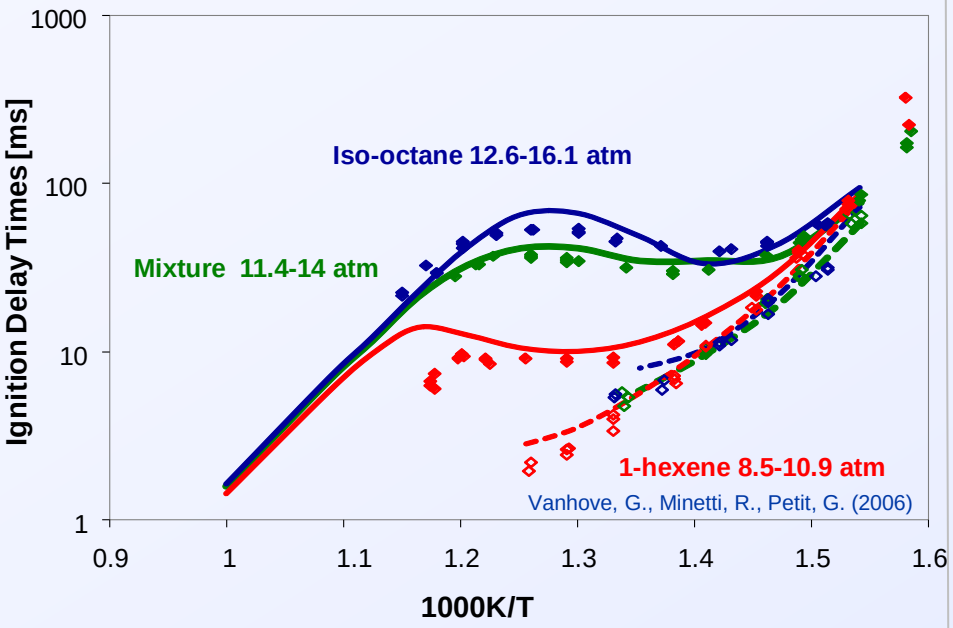
Activation of peroxy radicals

Iso-octane/1-hexene Mixtures

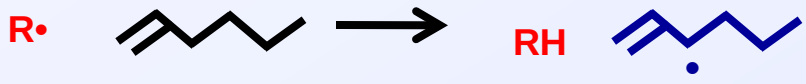


82%

18%



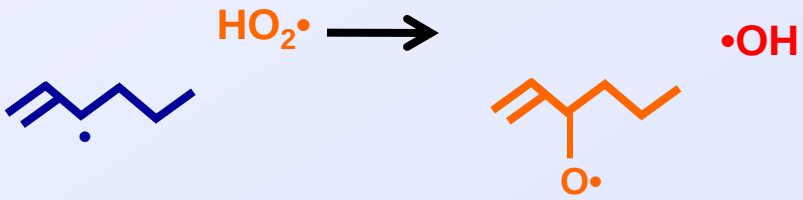
Limited effect on the Ignition from the mixing (LT reactivity too close) but complex chemistry behind it



Active radicals abstract the allylic hydrogen

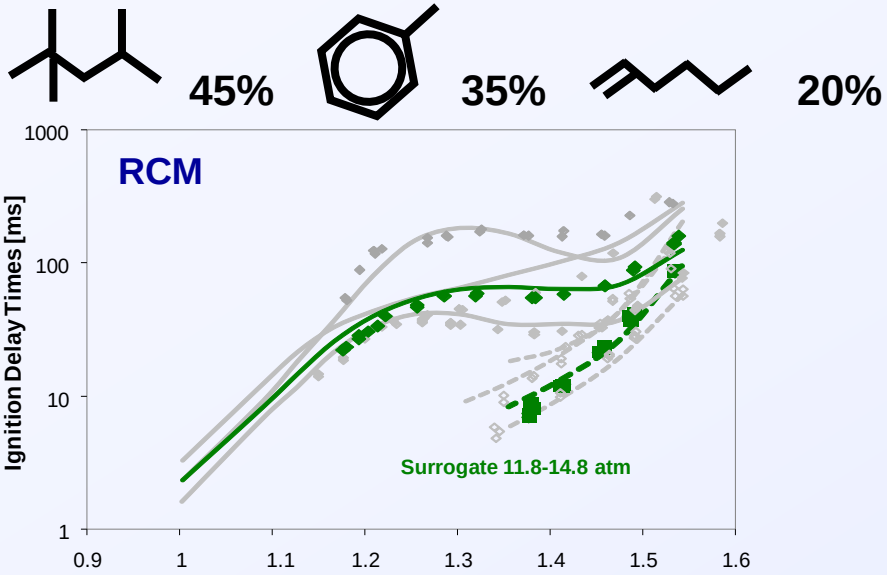
Some LT reactivity from 1-hexene

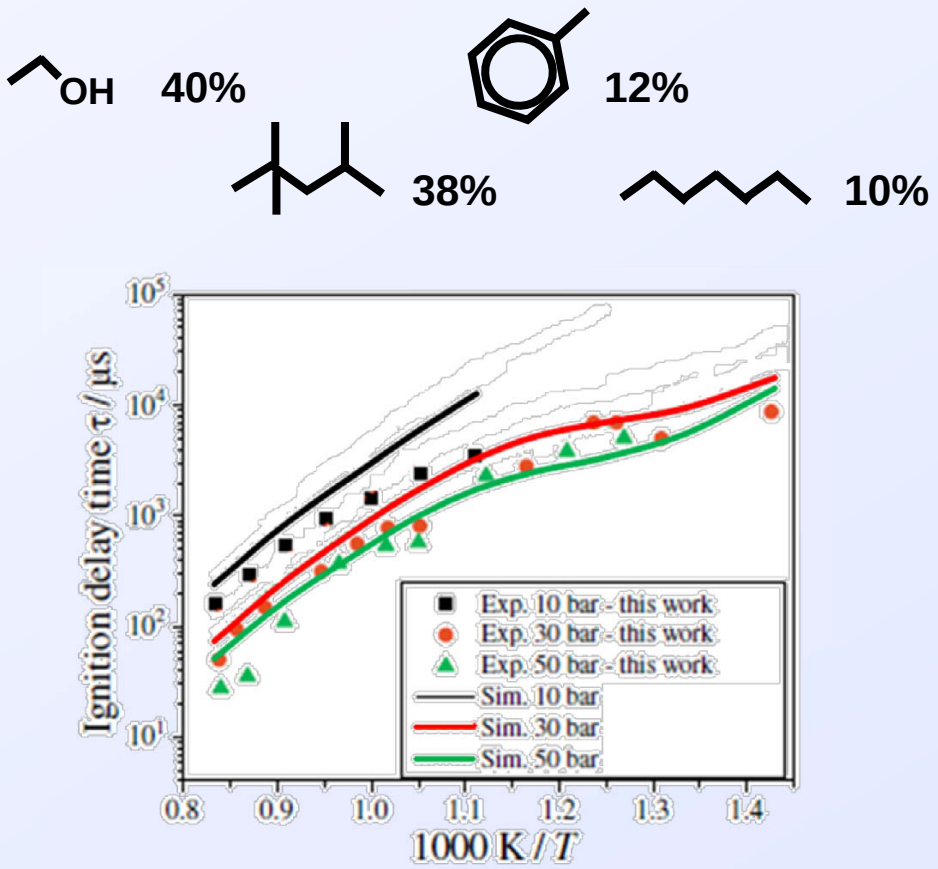
Radical Scavenging from the double bond



Activation of peroxy radicals

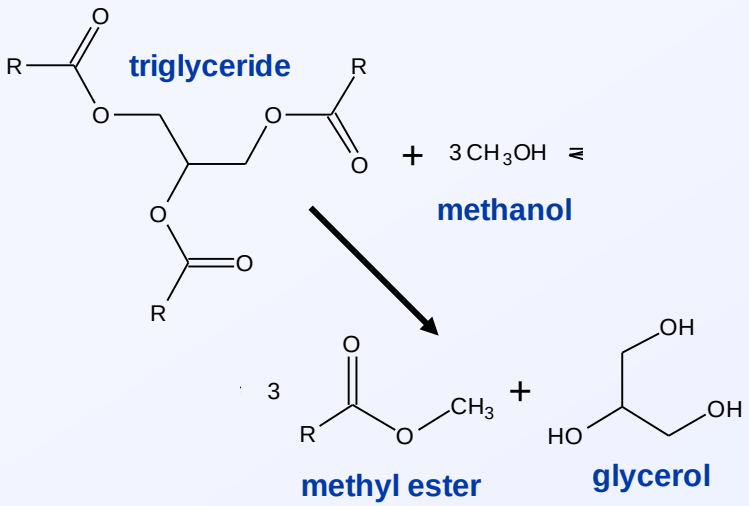
Gasoline Surrogates

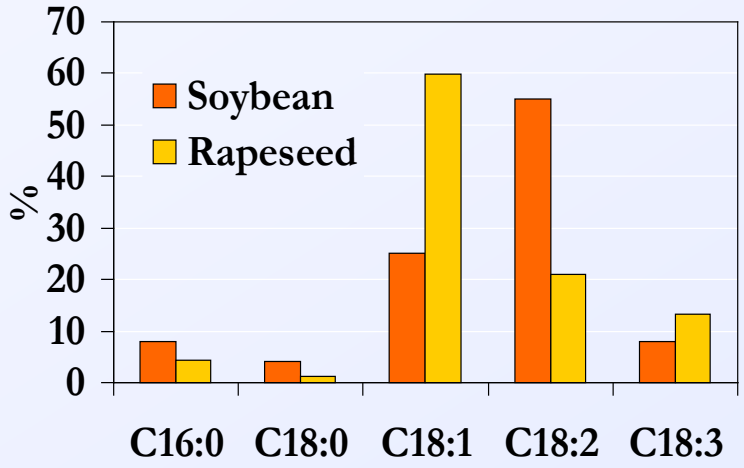




Vanhove, G., Minetti, R., Petit, G. (2006), M. Yahyaoui, N. Djebaïli-Chaumeix, P. Dagaut, C.-E. Paillard, S. Gail (2007) , Cancino L.R., Fikri M., Oliveira A.A.M., Schulz C. (2009)

Composition of Biodiesels





Methyl Palmitate (C16:0)

Methyl Stearate (C18:0)

Methyl Oleate (C18:1)

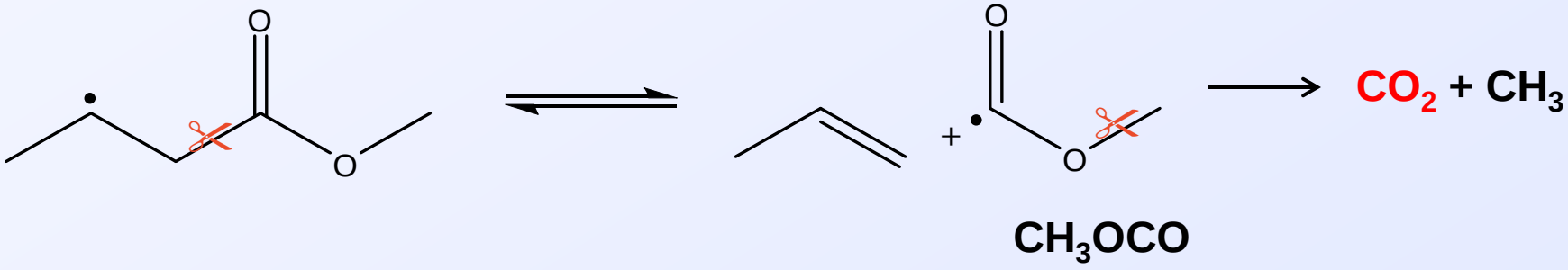
Methyl Linoleate (C18:2)

Methyl Linoleanate (C18:3)

CO_2 Formation Routes Involving the Ester Group

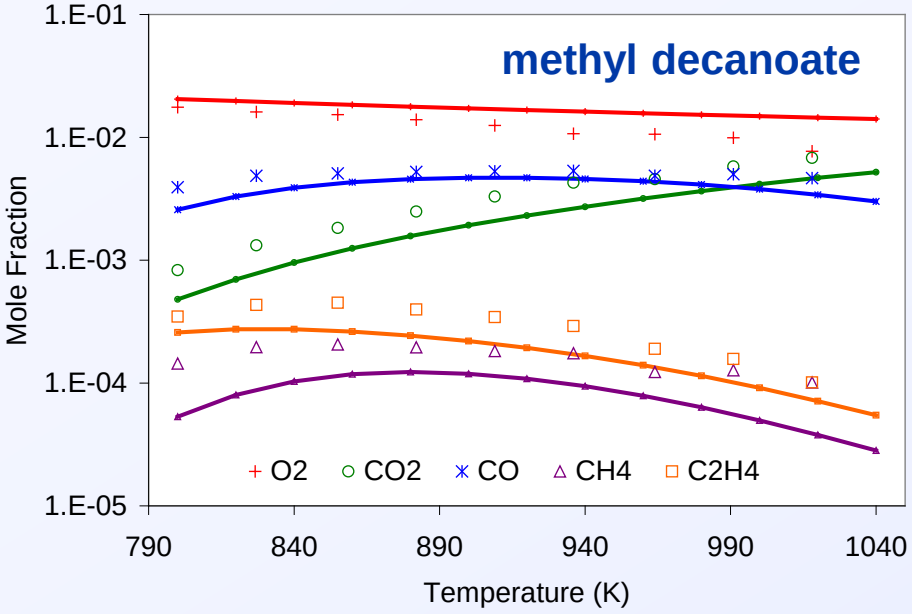
Methyl Stearate (C18:0)

Decomposition of 3-alkyl-ester radicals



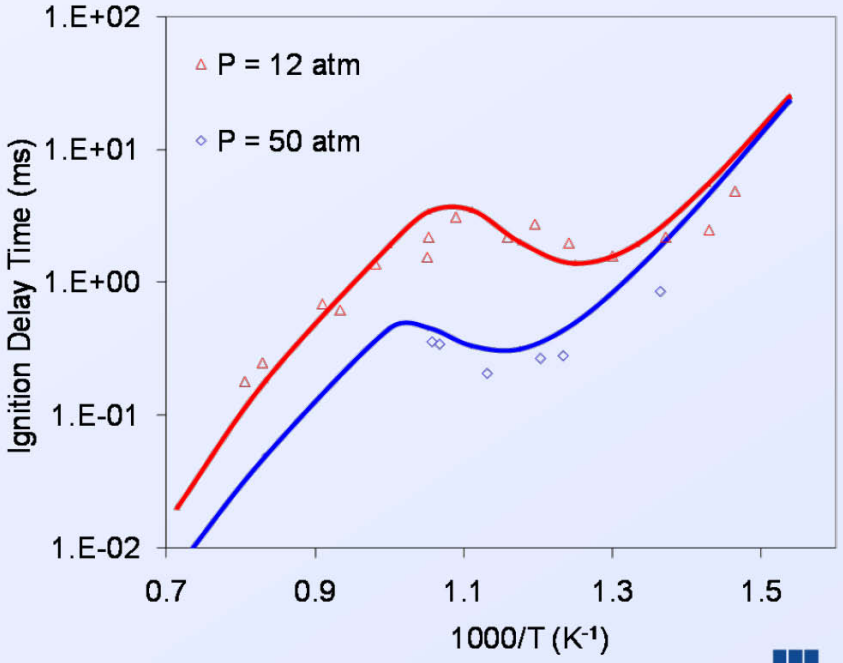
….but we still have a long residual chain

Long Chain Methyl Esters



Early CO_2 formation due to the ester function… (Experiments refer to Rapeseed oil)

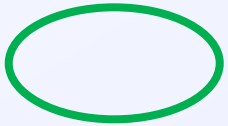
… but the autoignition behavior is similar to the one of n-alkanes (long alkyl chain) (Experiments refer to n-decane)



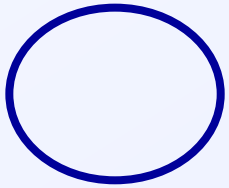
Kinetic Mechanisms for New Fuels

n-heptane

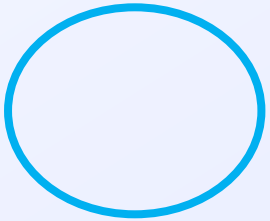
3-hexene



Methyl Butanoate



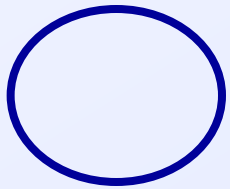
iso-octane



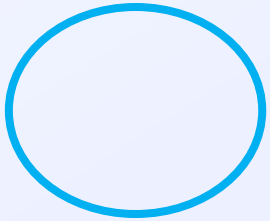
Toluene

Ethanol

Methyl Oleate (C18:1)

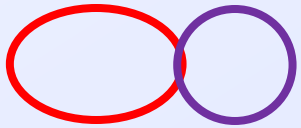


Iso-cetane (2,2,4,4,6,8,8-heptamethylnonane)



n-decylbenzene

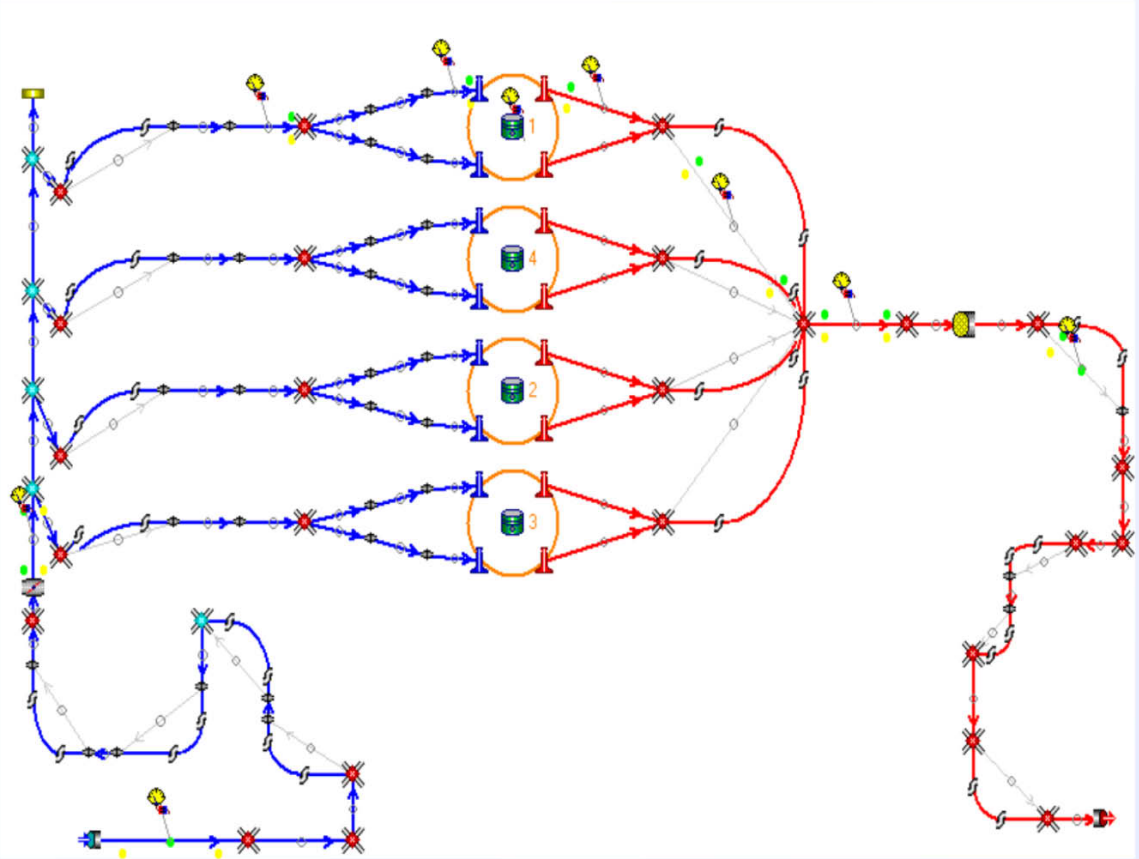
Butanol



Alkene effect in gasoline surrogate

		Surrogate 1	Surrogate 2
Density (15° C)	Kg/m^3	.7572	.7504
Reid Vapour Pressure	kPa	21.0	19.5
RON	-	97.3	97.3
MON	-	89.2	86.6
IBP	° C	66	76
10%	° C	89	89
50%	° C	99	99
90%	° C	102	102
FBP	° C	108	109
n-heptane	vol %	13	19
iso-octane	vol %	42	24
Toluene	vol %	32	26
MTBE	vol %	13	13
di-isobutylene	vol %	-	18

Applications: Engine simulations



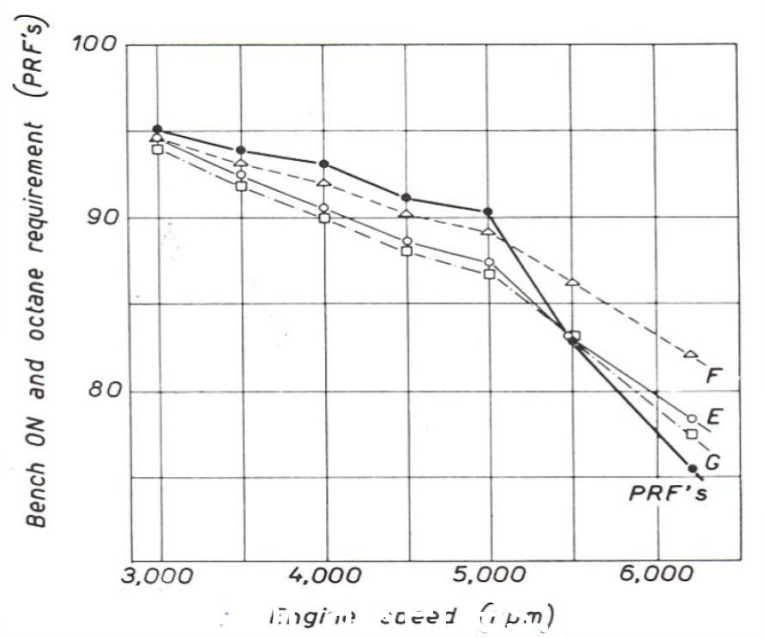
FIAT-Lancia Engine schematization:

Intake/exhaust: 1D Model

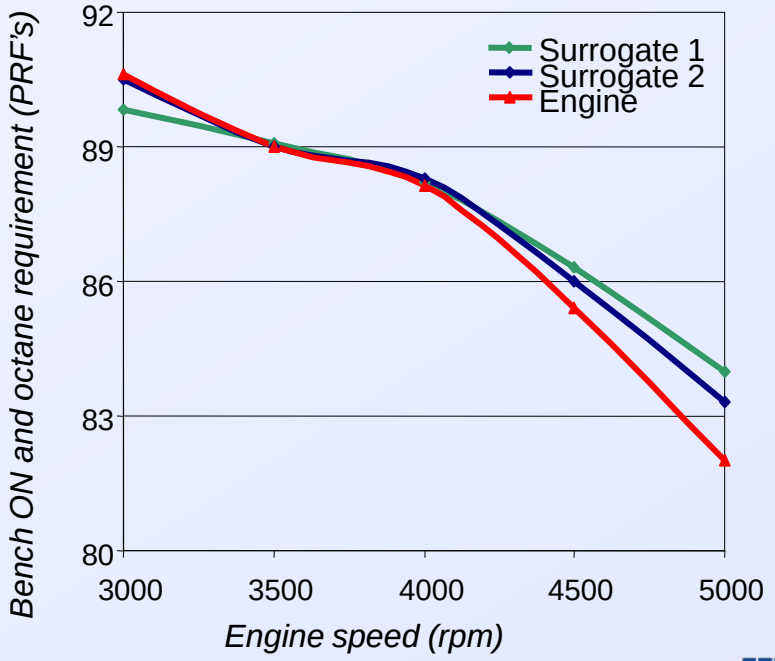
Cylinder: 0D – 2 zone model

Full Chemistry, Simplified fluid dynamics

Octane performances



Experimental and Calculated Octane Performances of different fuels in on-road conditions…

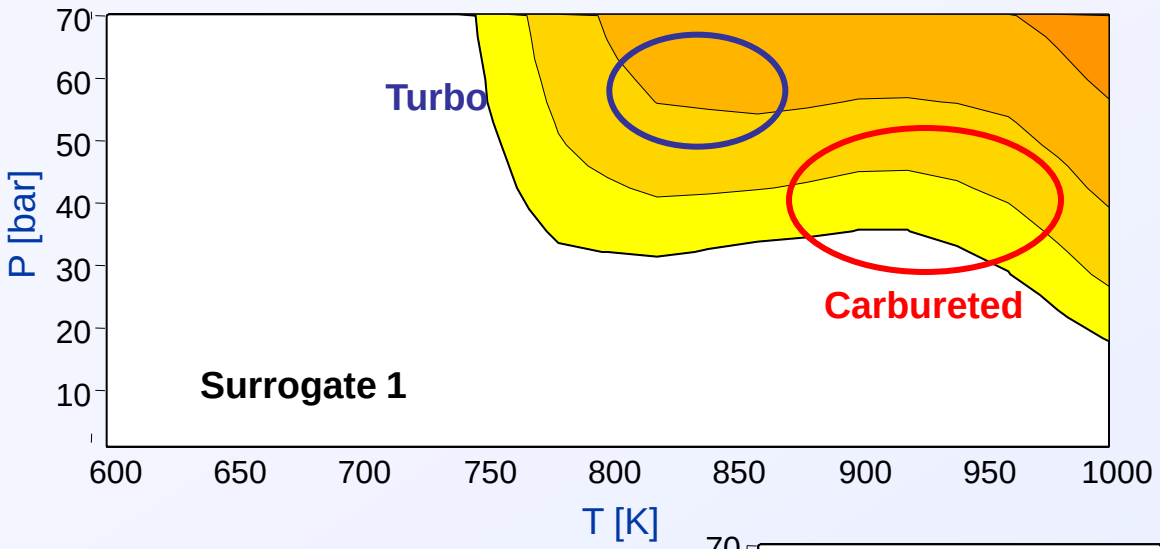


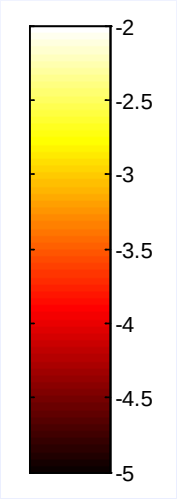
Engine Octane Requirement

Gasoline without Alkenes

Gasoline containing Alkenes

Applications: Reactivity maps

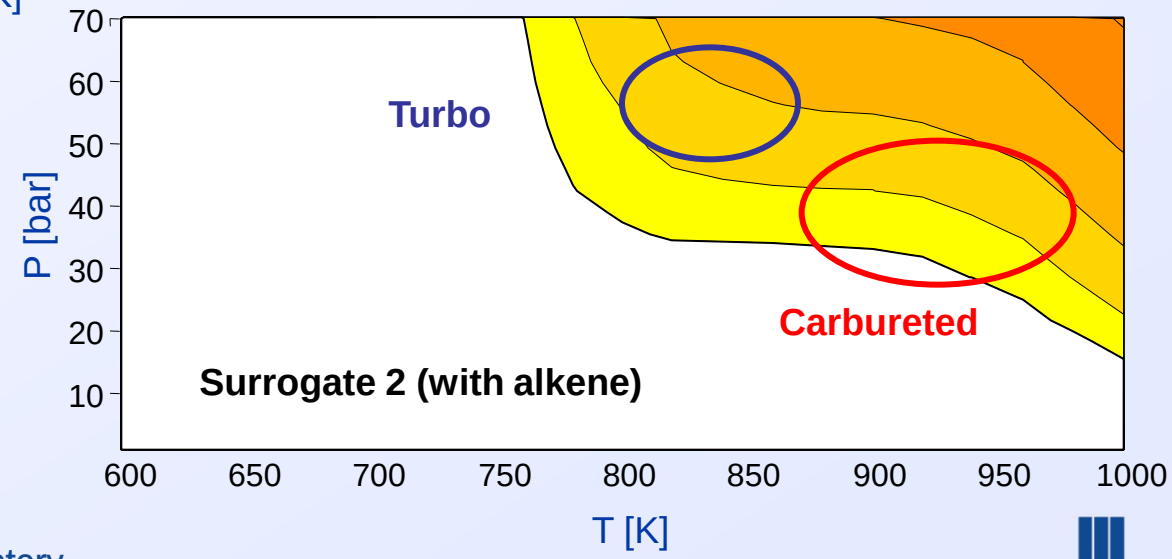




Time Scale: 10^X

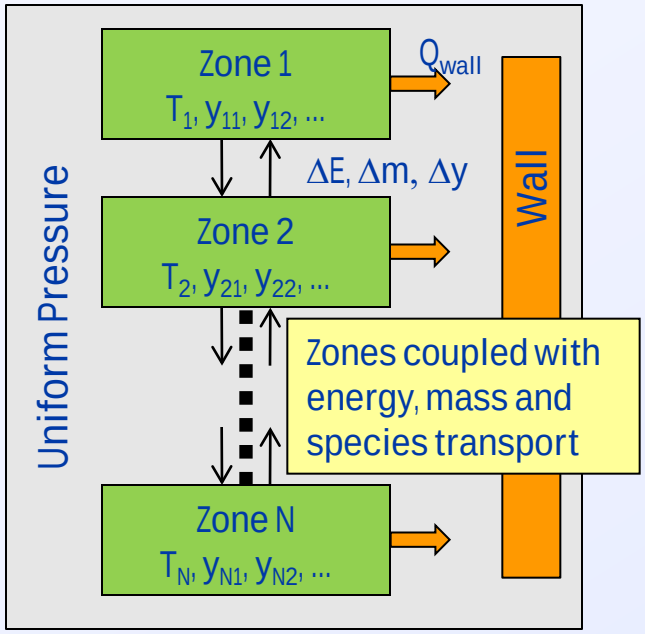
Mehl M., T. Faravelli, F. Giavazzi, E. Ranzi, P. Scorletti, A. Tardani, D. Terna, Energy & Fuels. 20, 2391–2398 (2006)

Andy D. B. Yates, André Swarts and Carl L. Viljoen, SAE 2005-01-2083



Engine combustion simulation (HCCI)

CFD



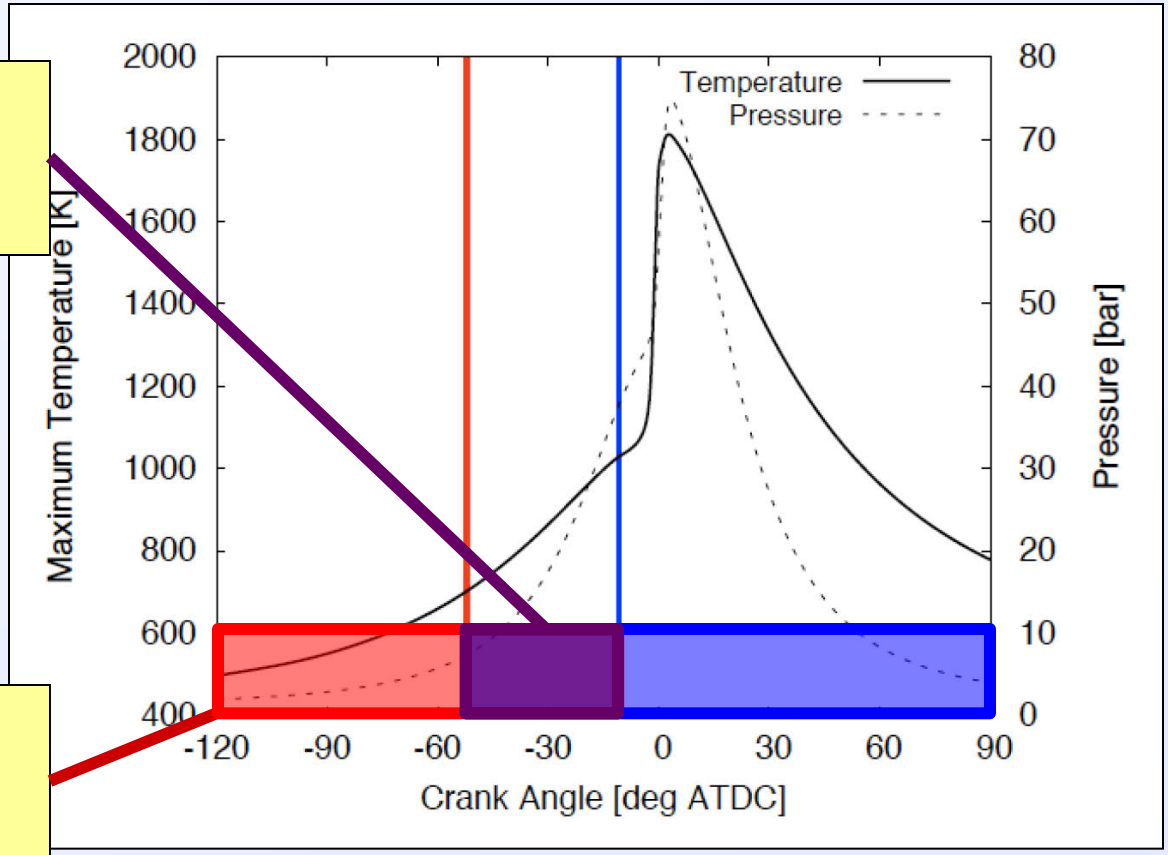
- Coupled well-mixed reactors represent different T (and f) regions of the cylinder.
- Typical number of zones N = 10's to 100's.
- Allows large kinetic mechanisms to be simulated for the cycle at a relatively low cost.
- Savings comes at the cost of low resolution of the fluid dynamics.
- Transport between zones not captured in detail (unlike CFD) – only phenomenological.
- Most accurate when chemical kinetic effects dominate behavior (HCCI).

Multizone example: 1-way coupling with KIVA

Step 2: track the temperature from the partitioned KIVA zones in the multi-zone (with CHEMKIN) model until main heat release begins

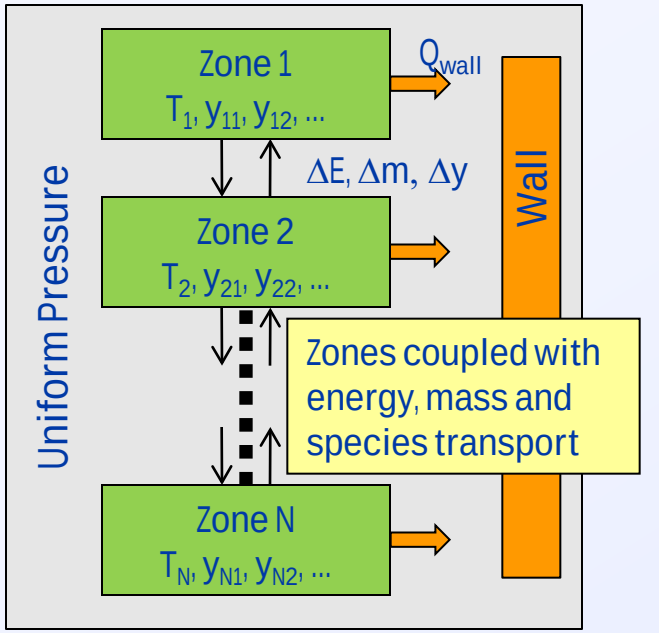
Multizone (overlap): accurate species production, energy corrected to match KIVA

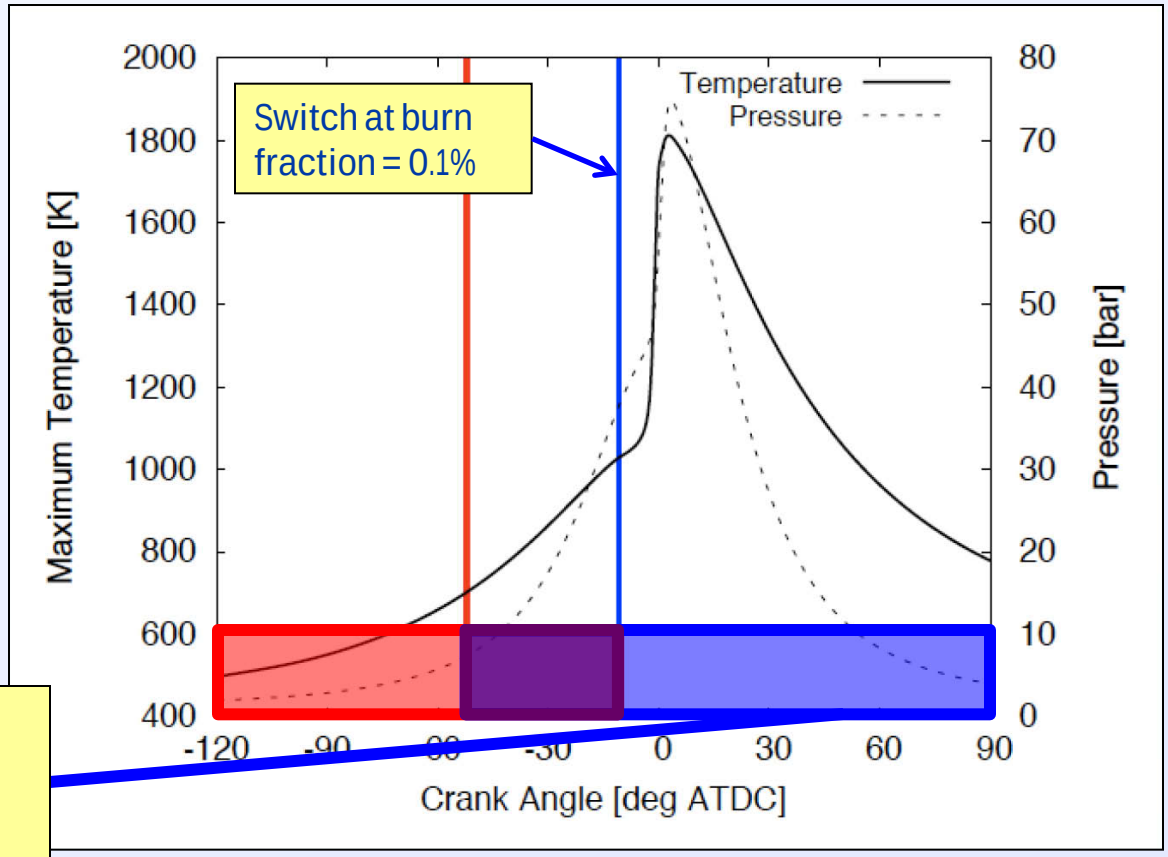
KIVA: accurate pressure and temperature for detailed cylinder geometry



Multizone example: 1-way coupling with KIVA

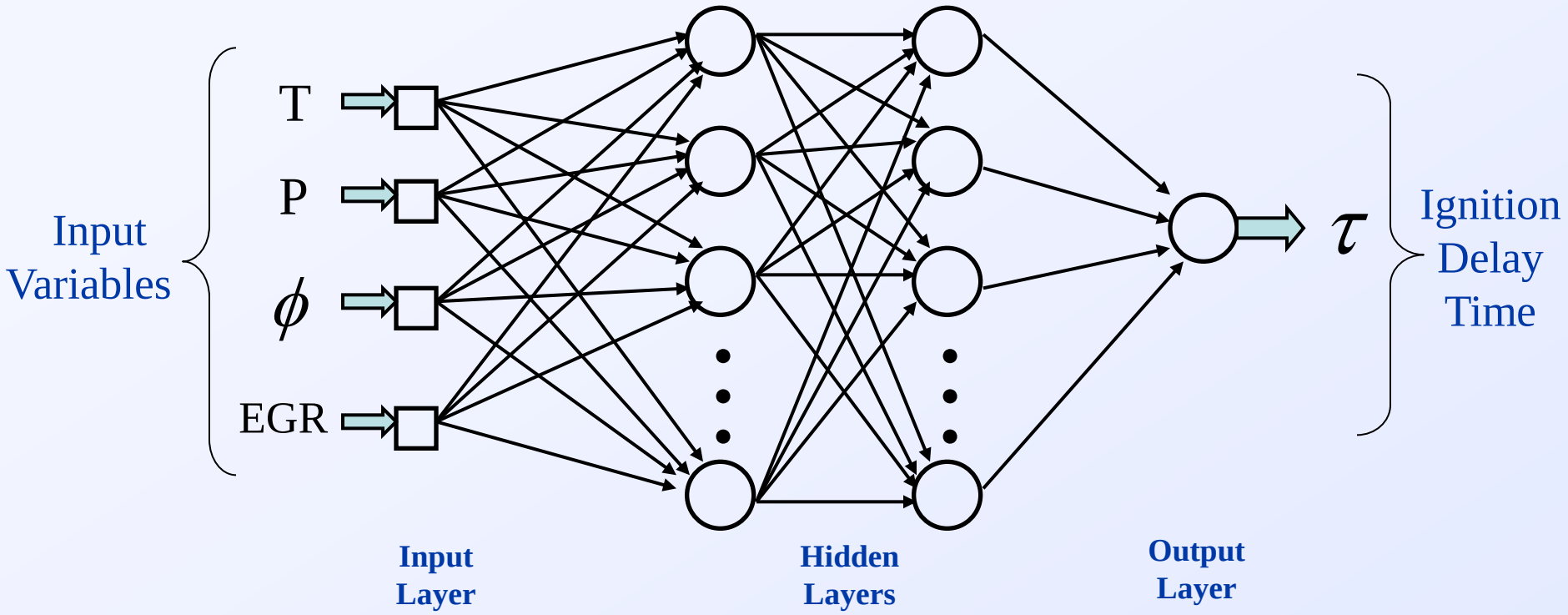
Step 3: complete the remainder of the cycle containing the main heat release using the multizone model alone





Multizone (solo): accurate species production, chemical energy released

KIVA3V coupled with an ANN combustion model for fast analysis of HCCI combustion and emissions



Ignition Condition: $$I(t) = \int_{t(0)}^{t_k} \frac{1}{\tau} dt = 1$$

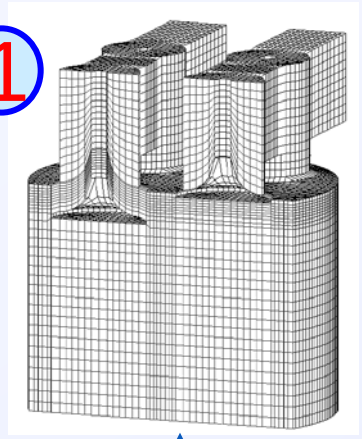
The ignition integral criterion determines ignition a two step global mechanism analyzes combustion

Calculate Ignition Integral in Each Cell

2

$$I(t) = \int_{t(0)}^{t_k} \frac{1}{\tau} dt$$

1



3

Is Ignition Criterion met?

Yes

No

Turn on global fuel conversion mechanism

$C_8H_{18} + 8.5O_2 \rightarrow 8CO + 9H_2O$

$CO + ½O_2 \rightarrow CO_2$

4

Future activities

- **Development of detailed kinetic models for new fuels of interests (alkyl aromatics, more details in PAH formation, unsaturated bio- esters, …)**

- **Interactions among fossil and bio-fuels (ethanol, butanol, bio esters, etc…)**

- **Validation of the surrogate model in engine conditions (Sandia)**

- **Development of effective strategies for the reduction of mechanism for complex surrogates**

Closing Comments

- **In the years to come we will still need combustion for many applications (liquid hydrocarbons have a very high energy density)**
- **Fuels are evolving, and new fuel chemistry models have become more powerful**
- **Capability has followed the computer industry and the laser**
- **Overall system models have developed to the point that they can be used for practical problems**
- **The fundamental knowledge we are building up is opening the way to a more energy efficient design of engine and to a better insight in fuel effect compositions**

Acknowledgments

LLNL Combustion modeling group : Charles Westbrook, William Pitz, Marco Mehl…. But many researchers and post docs have contributed during the years to the development of these mechanisms and models:

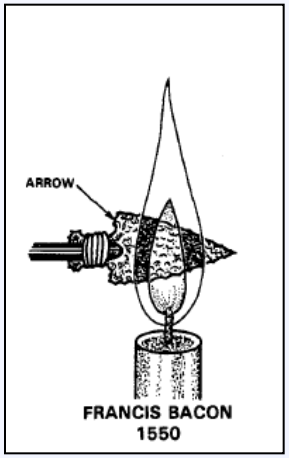
- **Henry Curran and coworkers, NUI Galway (C1-C5)**
- **Olivier Herbinet, Nancy (Methyldecanoate)**
- **Salvador Aceves Group (Slides are courtesy of Matt McNenly)**

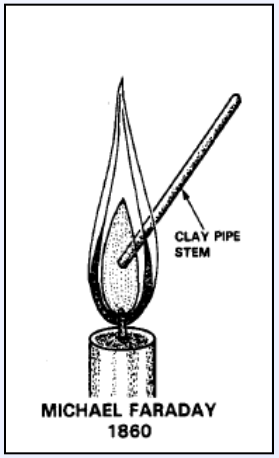
Some of the activity presented was carried out in Milano:

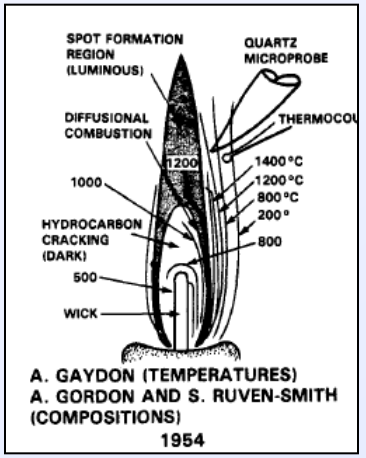
- **Ranzi's kinetic modeling group**
- **Onorati's engine group**

Thanks for your attention!

We came a long way…







1550 1600 1650 1700 1750 1800 1850 1900 1950

Phlogiston Theory
J.B. van Helmont, J. Becher

"The Chemical History of a Candle"
M. Faraday

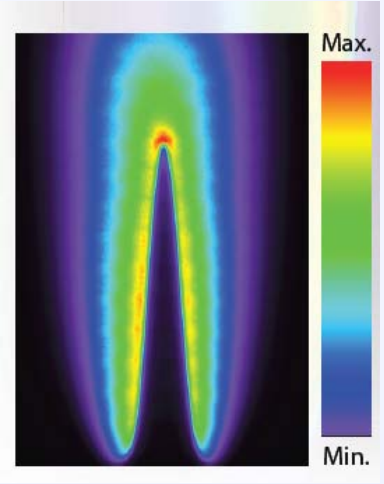
Combustion as Oxidation
A. Lavoisier , P. S. Laplace

Chain reaction and thermal ignition (Nobel 1956)
Semenov, Hinshelwood

→Theory of gas kinetics, free radicals, elementary reactions and reaction mechanisms for combustion applications

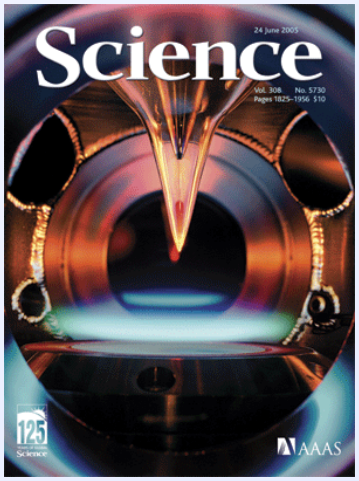
Fristrom R. M. (1990)

Combustion Science Today



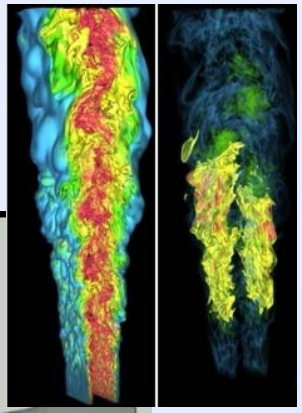
Interference-free composite H-atom LIF image produced with ps excitation in a Φ=1.2 premixed CH4/O2/ N2 flame.

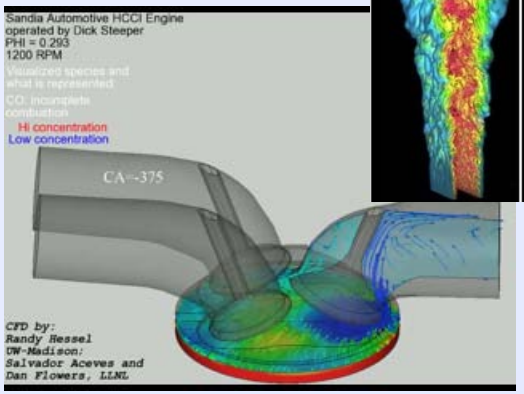
CRF - Sandia



Molecular-beam flame sampling and synchrotron-photoionization mass spectrometry analysis
[Science - 24 June 2005]

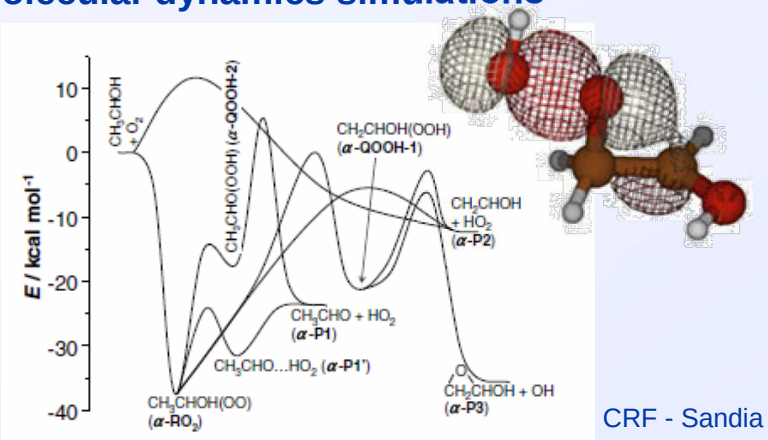
CFD calculations: RANS, LES, DNS. Coupling of numerical chemistry and fluid dynamics





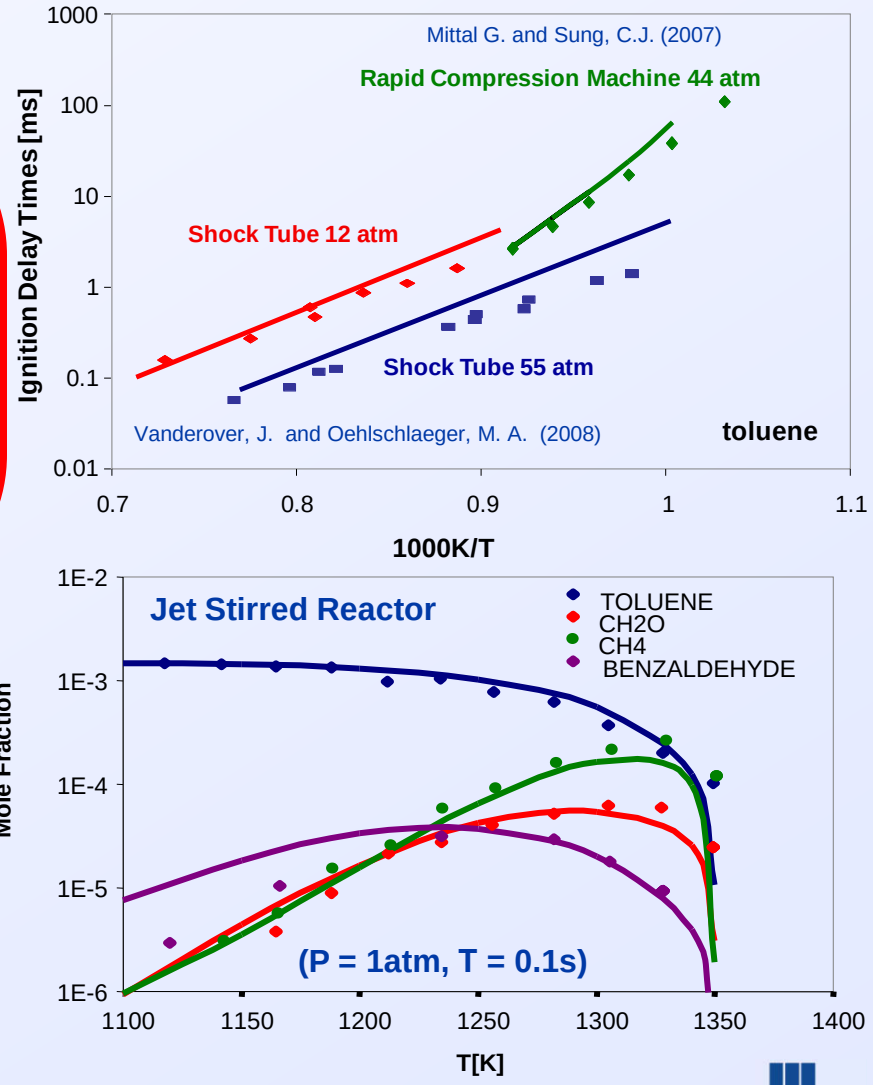
CRF - Sandia

***Ab initio* electronic-structure calculations and molecular dynamics simulations**



CRF - Sandia

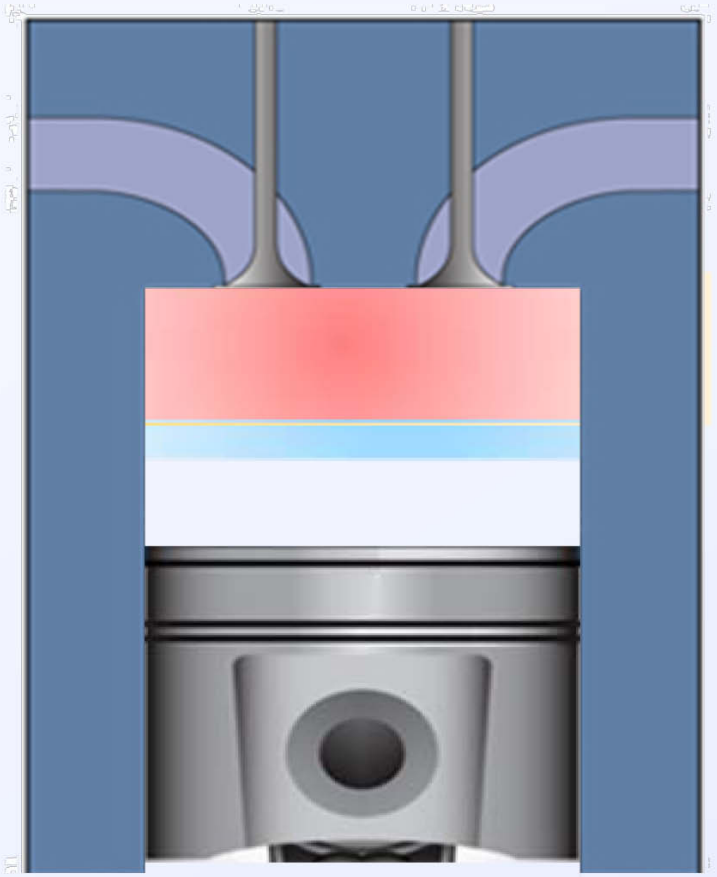
Toluene



Hi T (O and H radical formation)

Low T (HO_2 radicals, resonantly stabilized radicals and termination reactions

Engine Combustion: Homogeneous Charge Compression Ignition (HCCI)

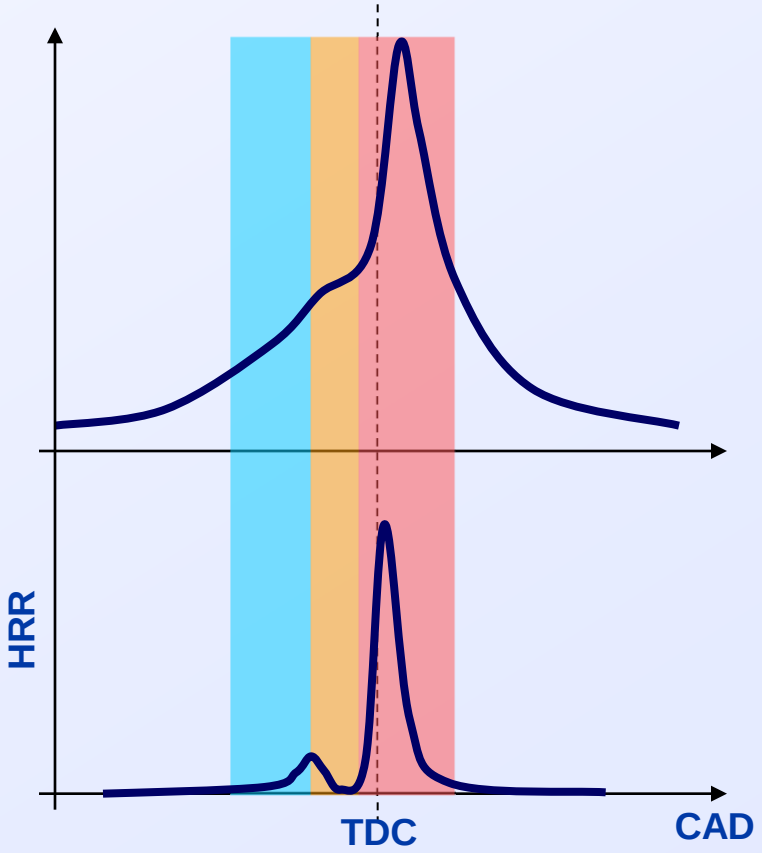


Typical HCCI Combustion Temperature and Heat Release Rate profiles

1st Heat release stage

The HRR slows down (NTC)

Main Heat Release



Kinetic Modeling

Reaction	A	n	Ea
H2+M<=>H+H+M	4.577E+19	-1.40	1.044E+05
O2+M<=>O+O+M	4.420E+17	-0.63	1.189E+05
H2O+M<=>H+OH+M	1.907E+23	-1.83	1.185E+05
H2O2+O2<=>HO2+HO2	1.136E+16	-0.34	4.973E+04
H2O2(+M)<=>OH+OH(+M)	2.951E+14	0.00	4.843E+04
H+O2<=>O+OH	3.547E+15	-0.40	1.660E+04
O+H2<=>H+OH	5.080E+04	2.67	6.292E+03
OH+H2<=>H+H2O	2.160E+08	1.51	3.430E+03
O+H2O<=>OH+OH	2.970E+06	2.02	1.340E+04
OH+M<=>O+H+M	9.780E+17	-0.74	1.021E+05
H+O2(+M)<=>HO2(+M)	1.475E+12	0.60	0.000E+00
HO2+H<=>OH+OH	7.079E+13	0.00	2.950E+02
HO2+O<=>OH+O2	3.250E+13	0.00	0.000E+00
H2O2+H<=>H2O+OH	2.410E+13	0.00	3.970E+03
H2O2+H<=>H2+HO2	2.150E+10	1.00	6.000E+03
H2O2+O<=>OH+HO2	9.550E+06	2.00	3.970E+03
H2O2+OH<=>H2O+HO2	2.000E+12	0.00	4.272E+02
HO2+H<=>H2+O2	1.660E+13	0.00	8.230E+02
HO2+OH<=>H2O+O2	1.973E+10	0.96	-3.284E+02

Modified Arrhenius Law:

$$A \cdot T^{n} \cdot \exp(-Ea/RT)$$

Initiation

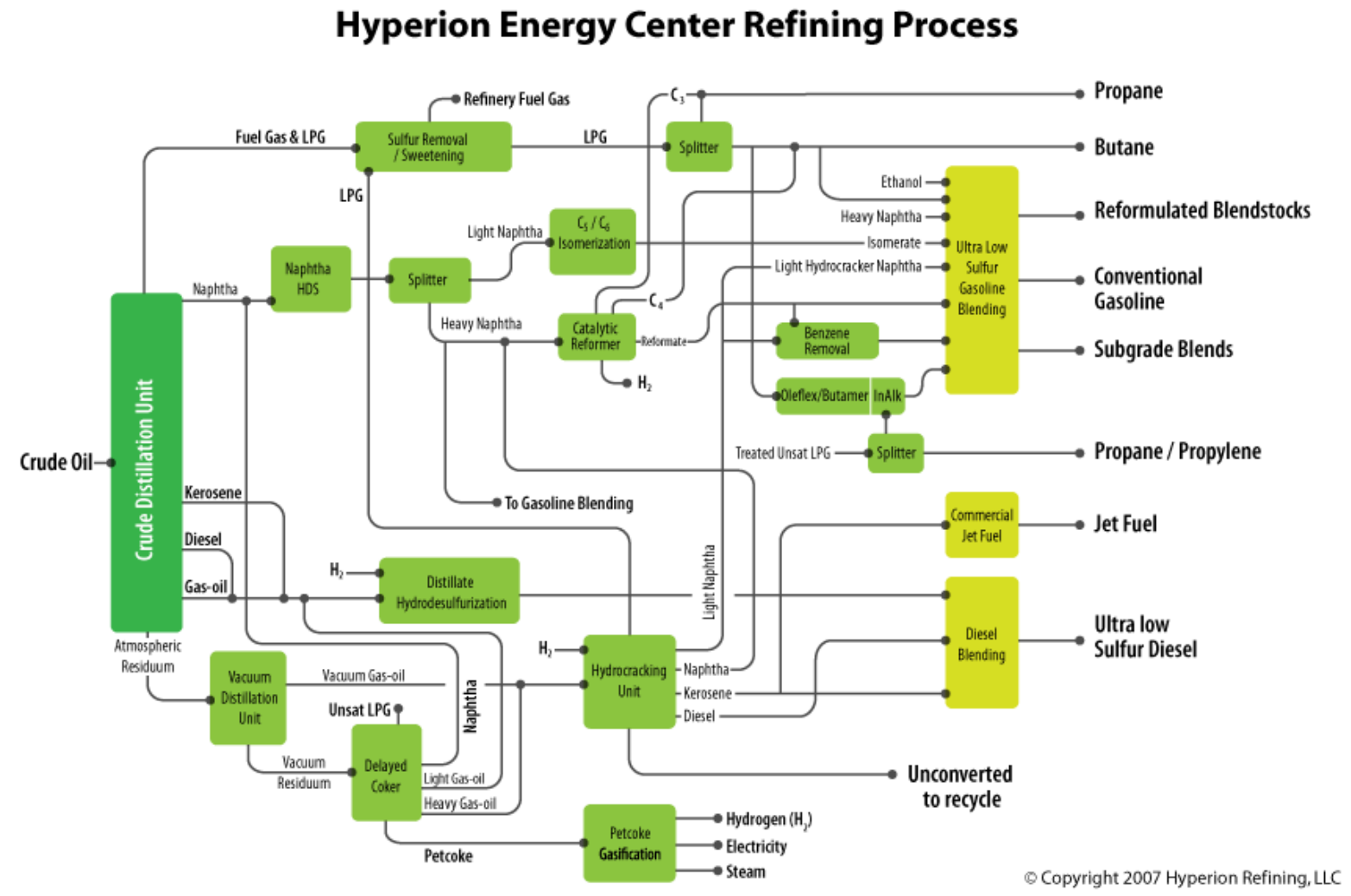
H+O2+H2⇔H+2OH
Chain Branching

Propagation

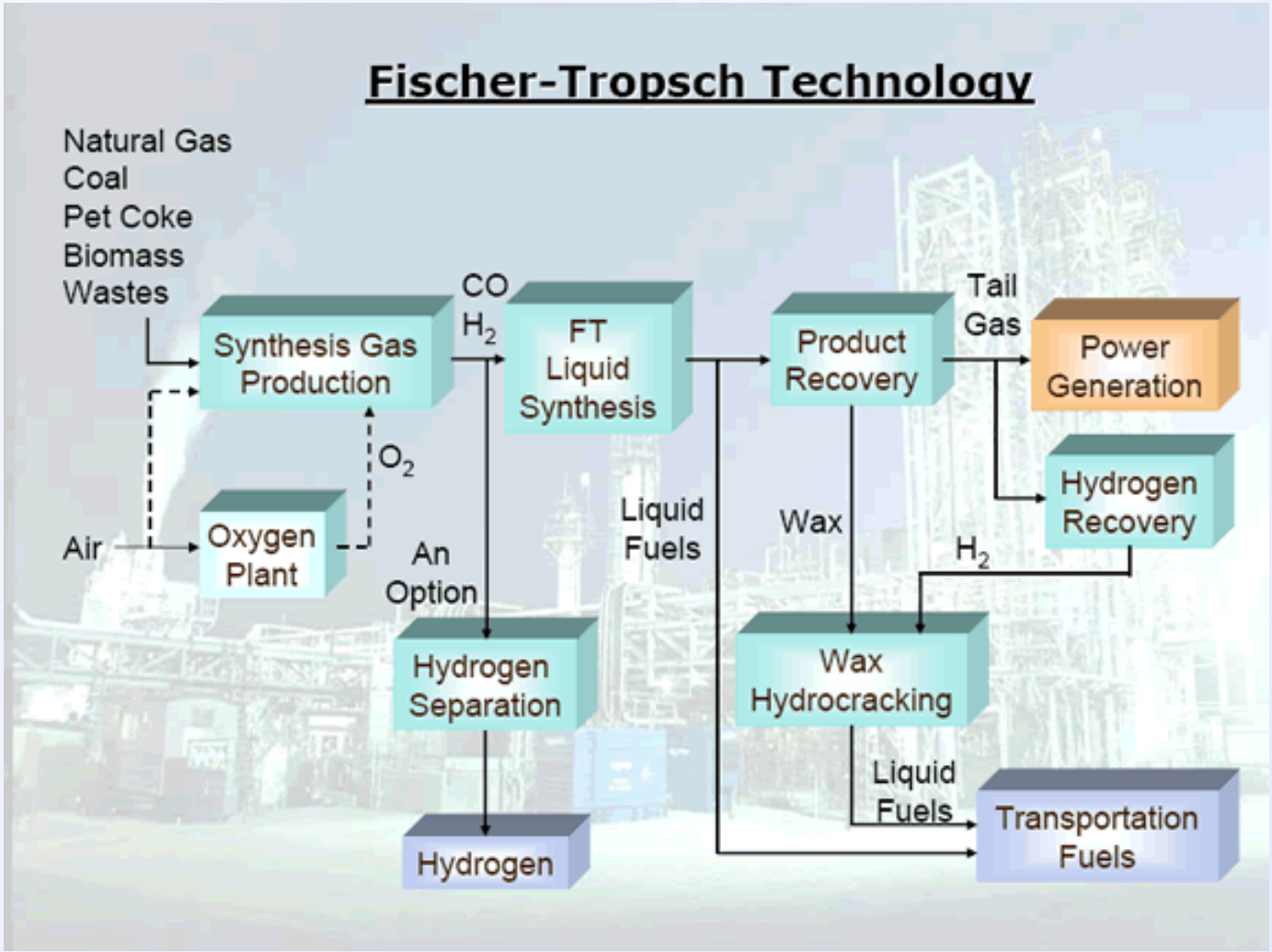
Termination

This mechanism provide a quantitative explanation of ignition timing, explosion limits, flame speed, …

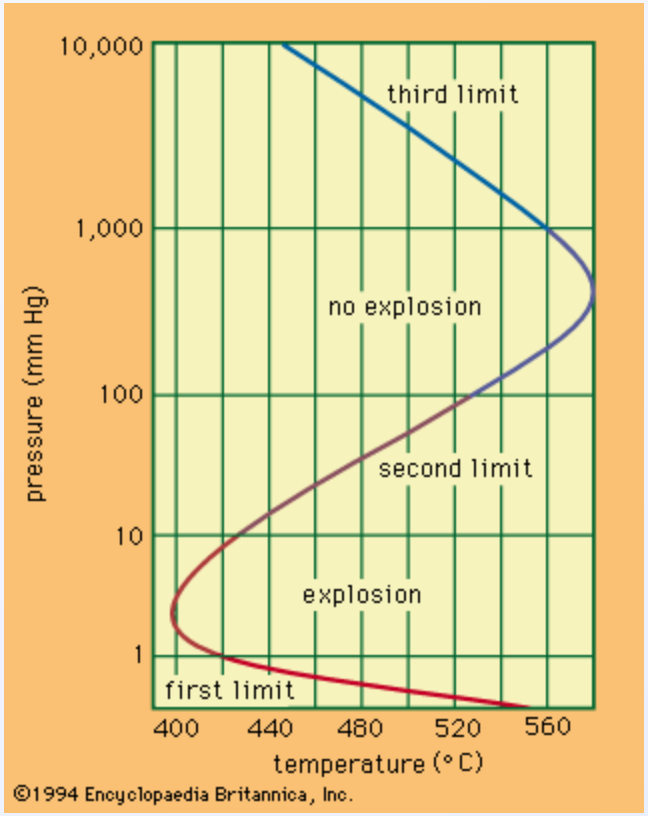
Fossil Fuels

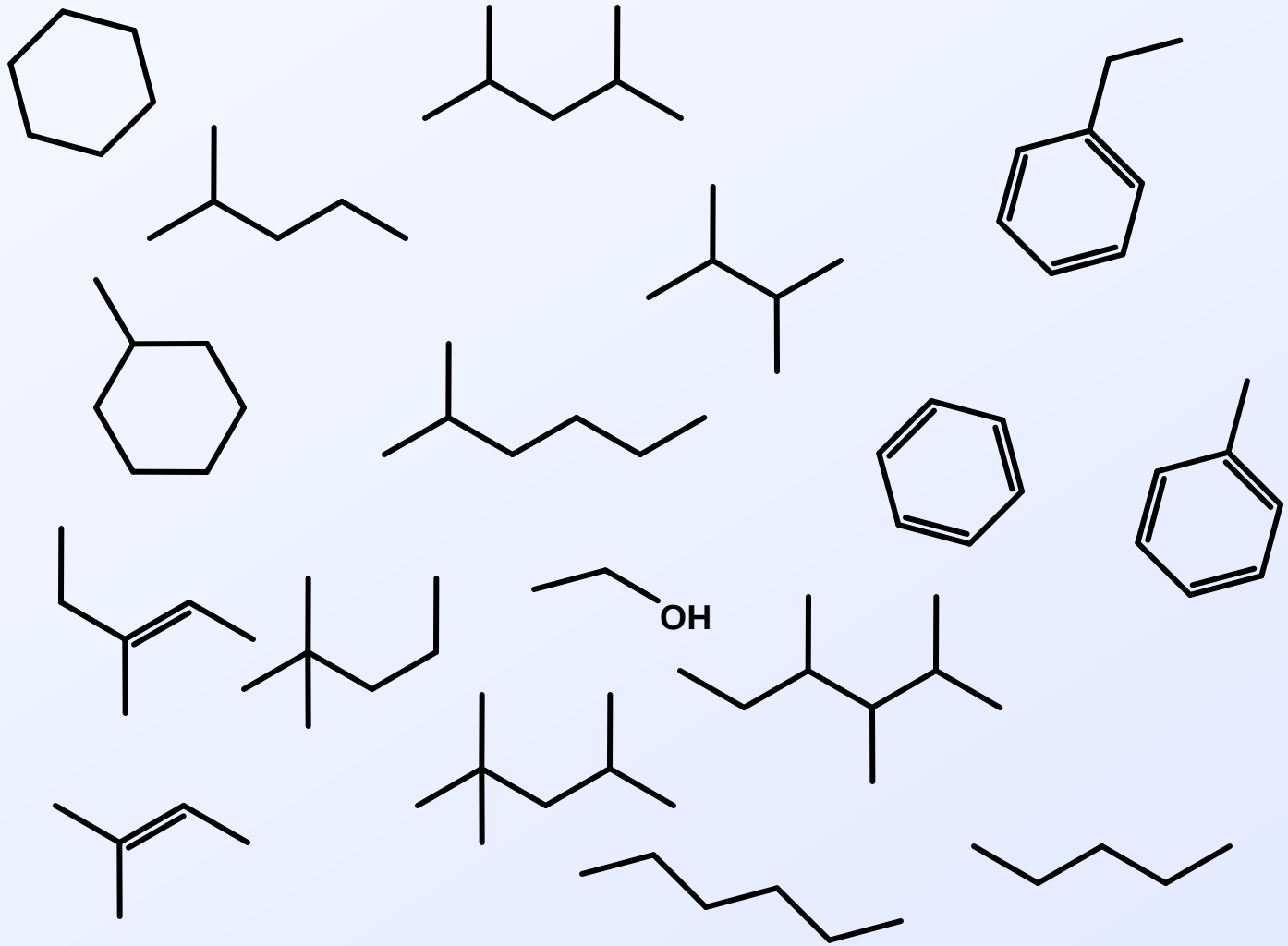


Fuel from gasification



Autoignition: Hydrogen



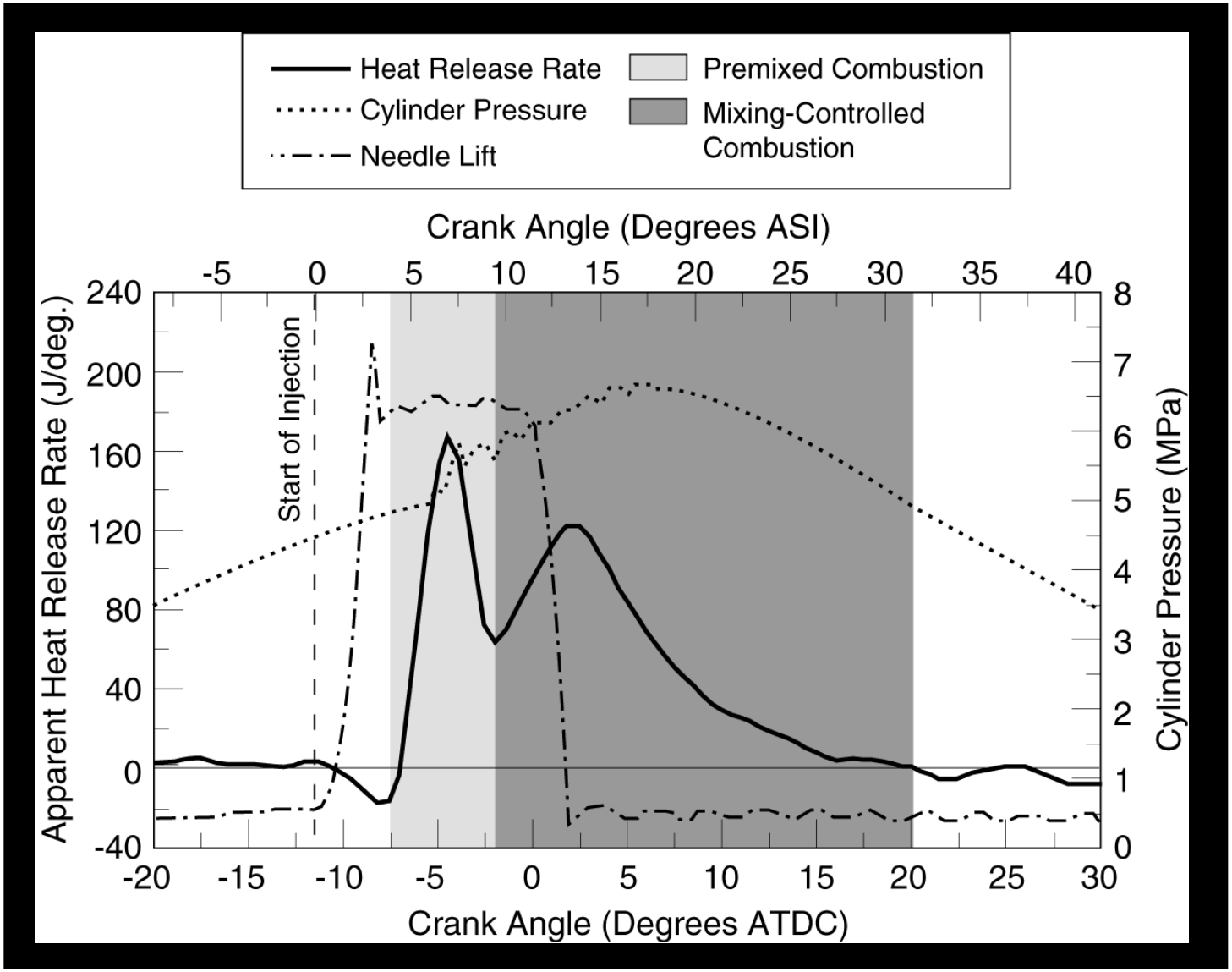

OH

Chemical Kinetics and Soot Production

Charles Westbrook
Lawrence Livermore National Laboratory

CEFRC
June 2010

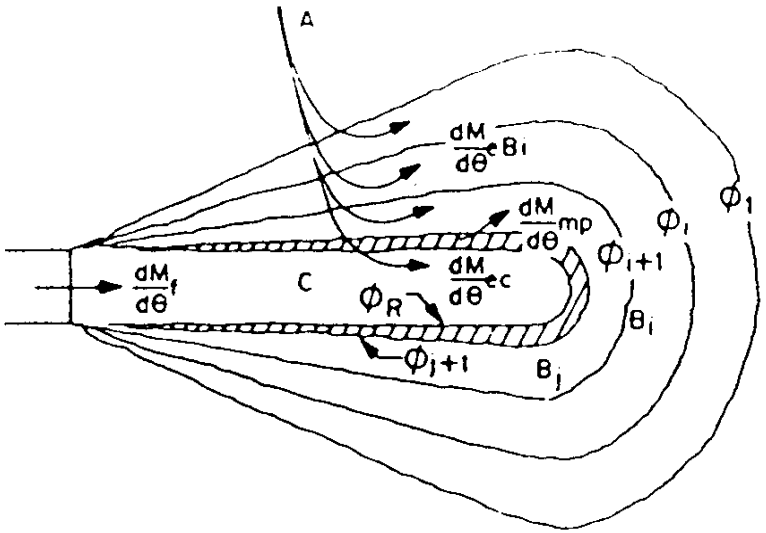
Diesel engine combustion: A revolution



Early models of Diesel combustion

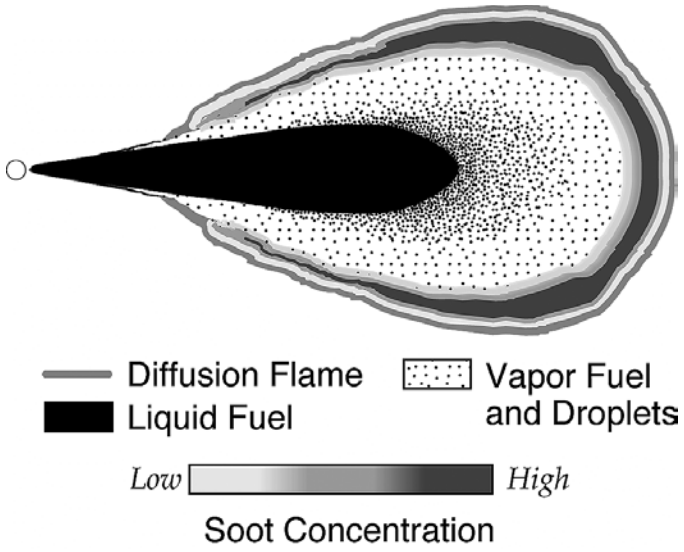
Liquid core with continuous evaporation

(1976)



Early models of Diesel combustion

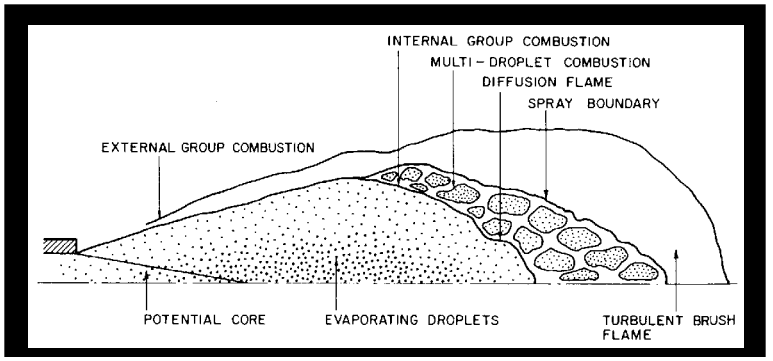
Liquid fuel jet shedding droplets, with combustion at the edge of a stoichiometric shell (diffusion flame)



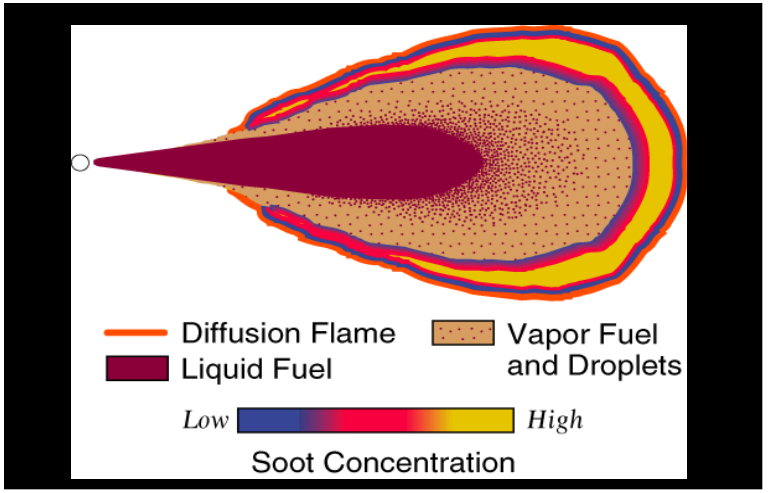
Prior to Laser-Sheet Imaging

- Autoignition and premixed burn were thought to occur in near-stoichiometric regions.
- The "quasi-steady" portion of Diesel combustion was thought to be adequately described by steady spray combustion theory.
- Appeared to fit most available data.
- This "old" description was never fully developed into a conceptual model.

  A "representative" schematic is given.



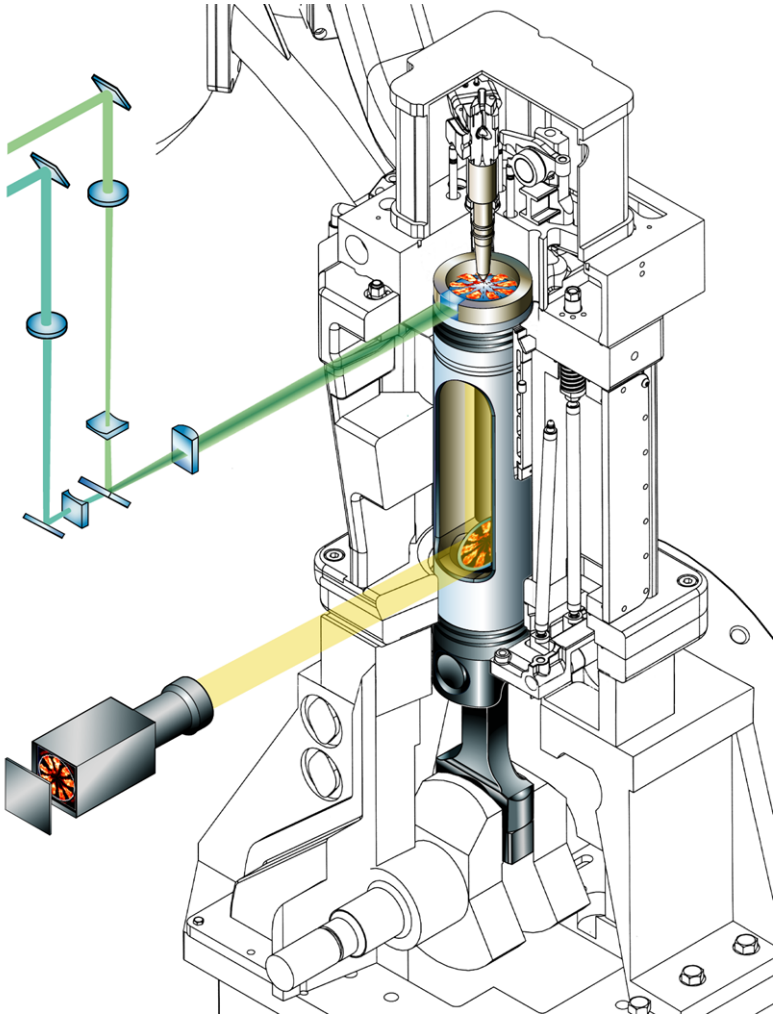
Schematic of group combustion for a fuel spray.
From Kuo, as adapted from H. Chiu and Croke



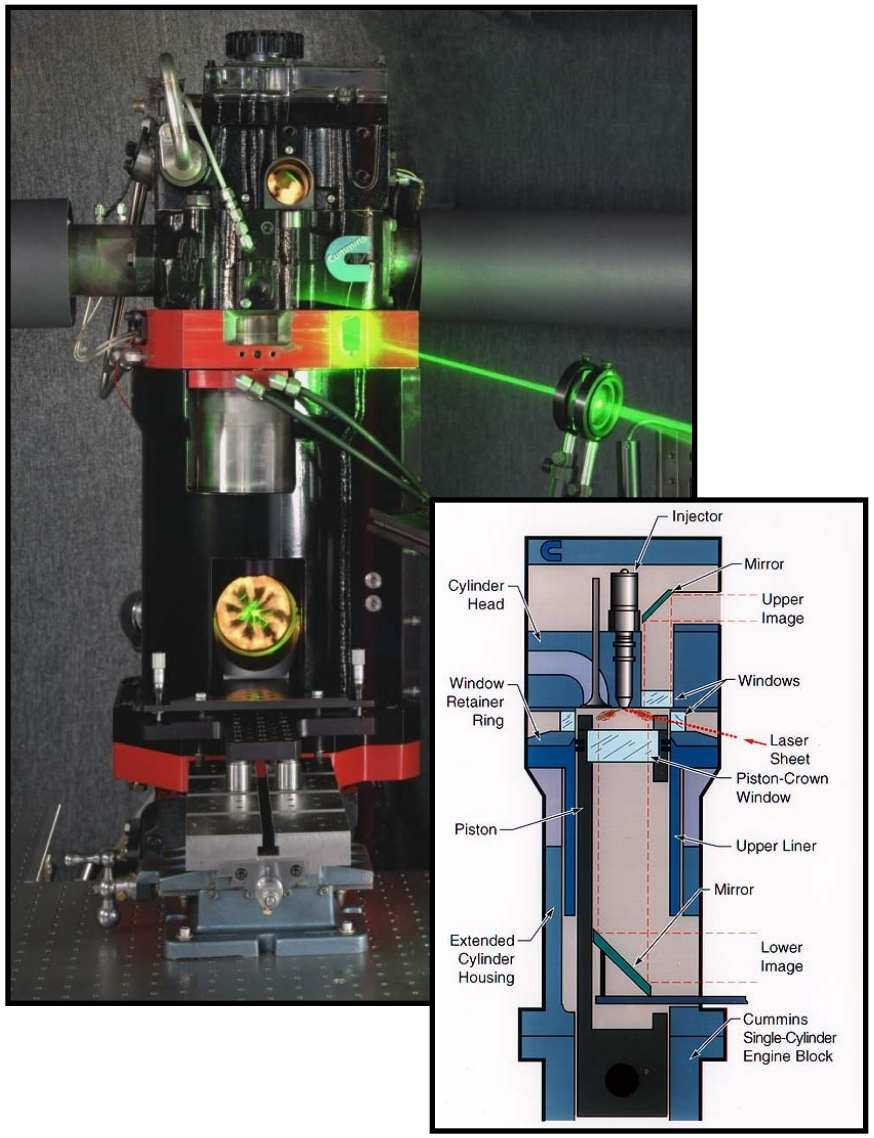
Old description of DI Diesel combustion.

The DOE Engine Combustion Research Program at Sandia's CRF played a major role in solving the diesel "mystery".

- ***Mission*** - Develop the science-base for in-cylinder combustion and emissions processes.
  - Help U.S. manufacturers reduce emissions & improve performance.
- ***Approach*** –
  - Strong interaction and collaboration with industry.
  - Optical diagnostics.
  - Realistic engine geometries with optical access through:
    - *pistons*
    - *cylinder liner*
    - *spacer plates*
    - *exhaust ports*



Heavy-Duty Diesel Engine Research

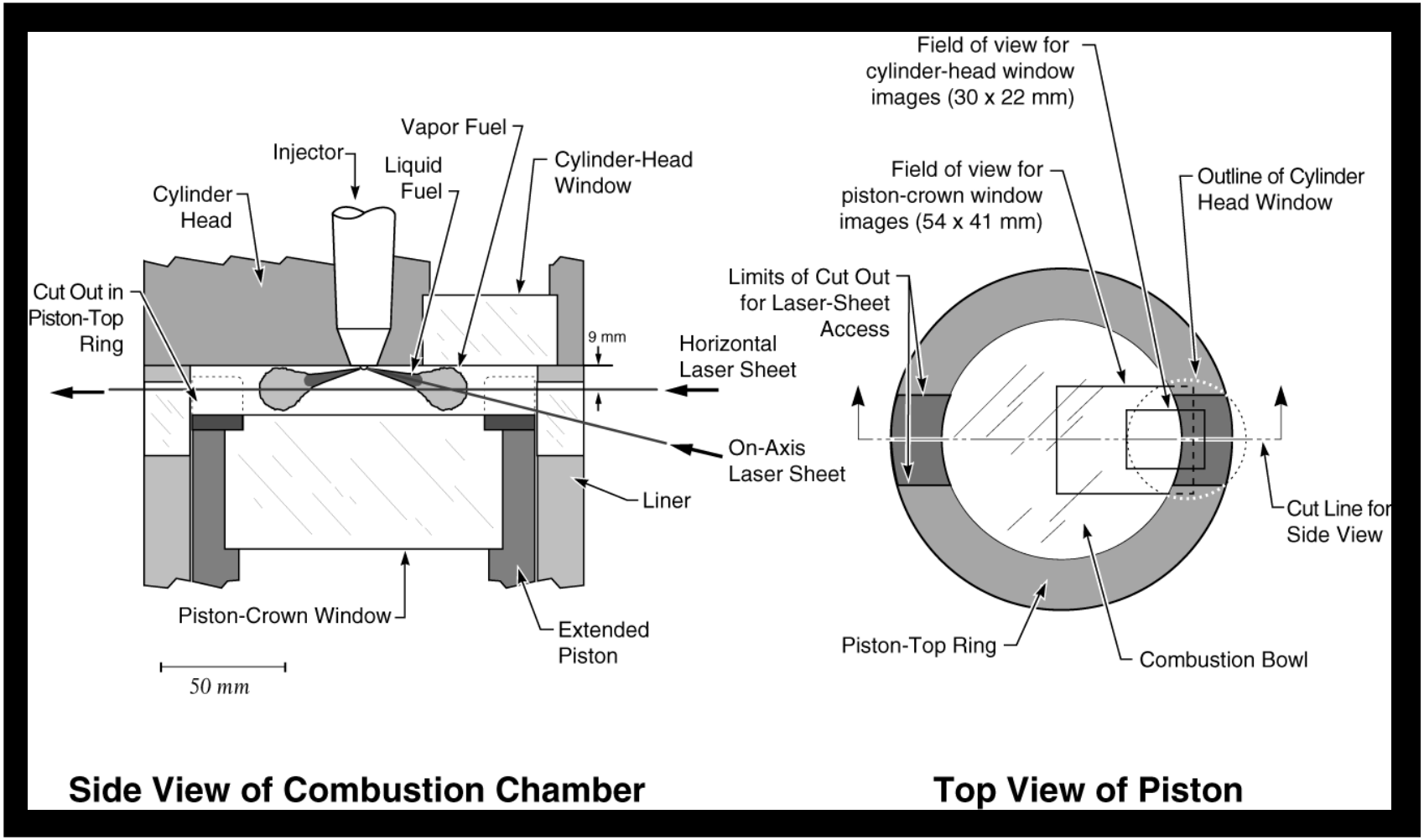


Approach: Investigate the processes in the cylinder of an operating diesel engine using advanced optical diagnostics

Modified heavy-duty truck engine provides good optical access while maintaining the basic combustion characteristics of a production engine.

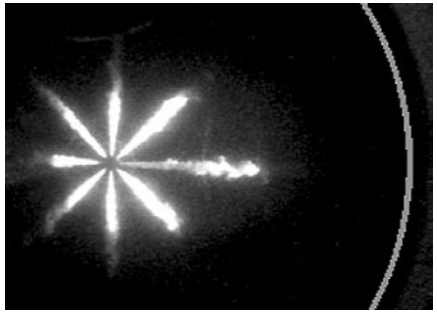
Data from multiple advanced laser diagnostics have substantially improved our understanding of diesel combustion and emissions formation.

Optical Setup



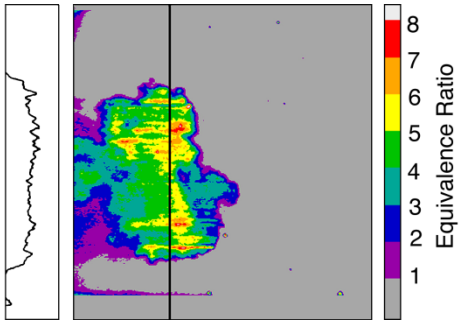
Laser-Sheet Imaging Data - 1

Liquid-phase Fuel



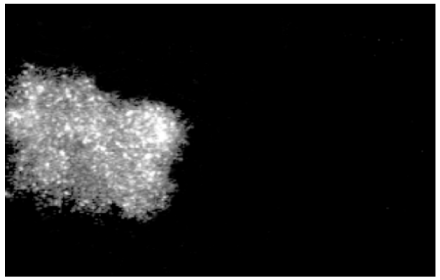
- Liquid fuel images show that all the fuel vaporizes within a characteristic length (~1 inch) from the injector.

Vapor-phase Fuel



- Vapor fuel images show that downstream of the liquid region, the fuel and air are uniformly mixed to an equivalence ratio of 3-4.

Chemiluminescence

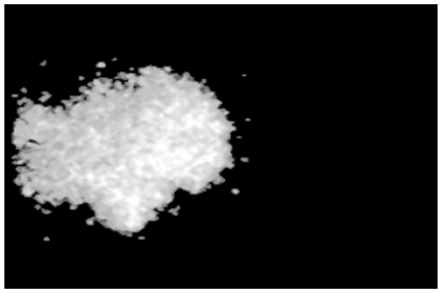


- Chemiluminescence images show autoignition occurring across the downstream portion of the fuel jet.

Quiescent Chamber, 1200 rpm, T_{TDC} = 1000 K, ρ_{TDC} = 16.6 kg/m^3

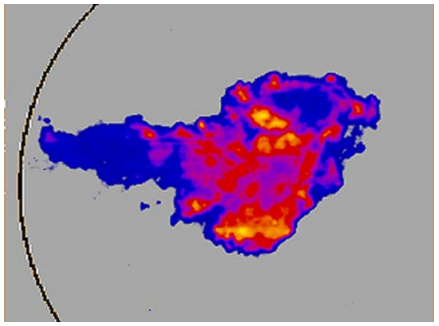
Laser-Sheet Imaging Data - 2

PAH Distribution



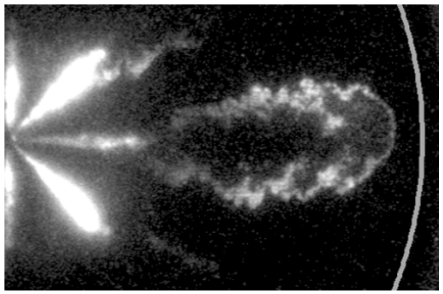
- PAHs form throughout the cross-section of the fuel jet immediately following fuel breakdown at the start of the apparent heat release.

Soot Distribution



- LII soot images show that soot forms throughout the cross-section of the fuel jet beginning just downstream of the liquid-fuel region.

OH PLIF Image



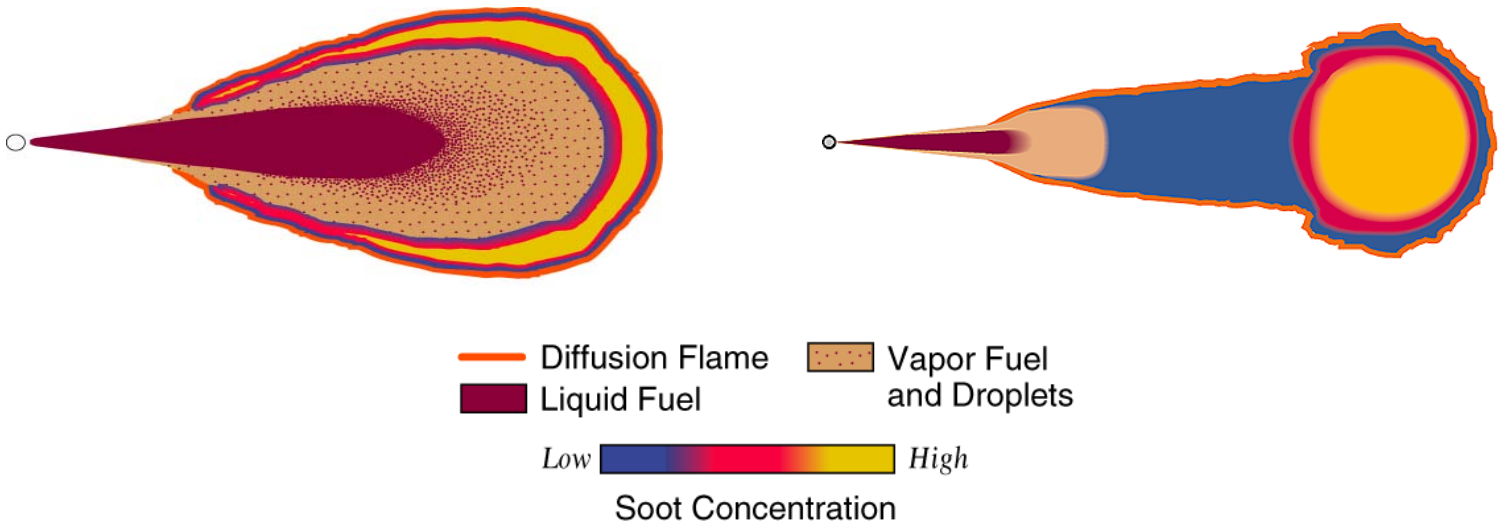
- OH radical images show that the diffusion flame forms at the jet periphery subsequent to an initial fuel-rich premixed combustion phase.

Quiescent Chamber, 1200 rpm, T_{TDC} = 1000 K, ρ_{TDC} = 16.6 kg/m^3

Laser Sheet Imaging is Providing a New Understanding of DI Diesel Combustion

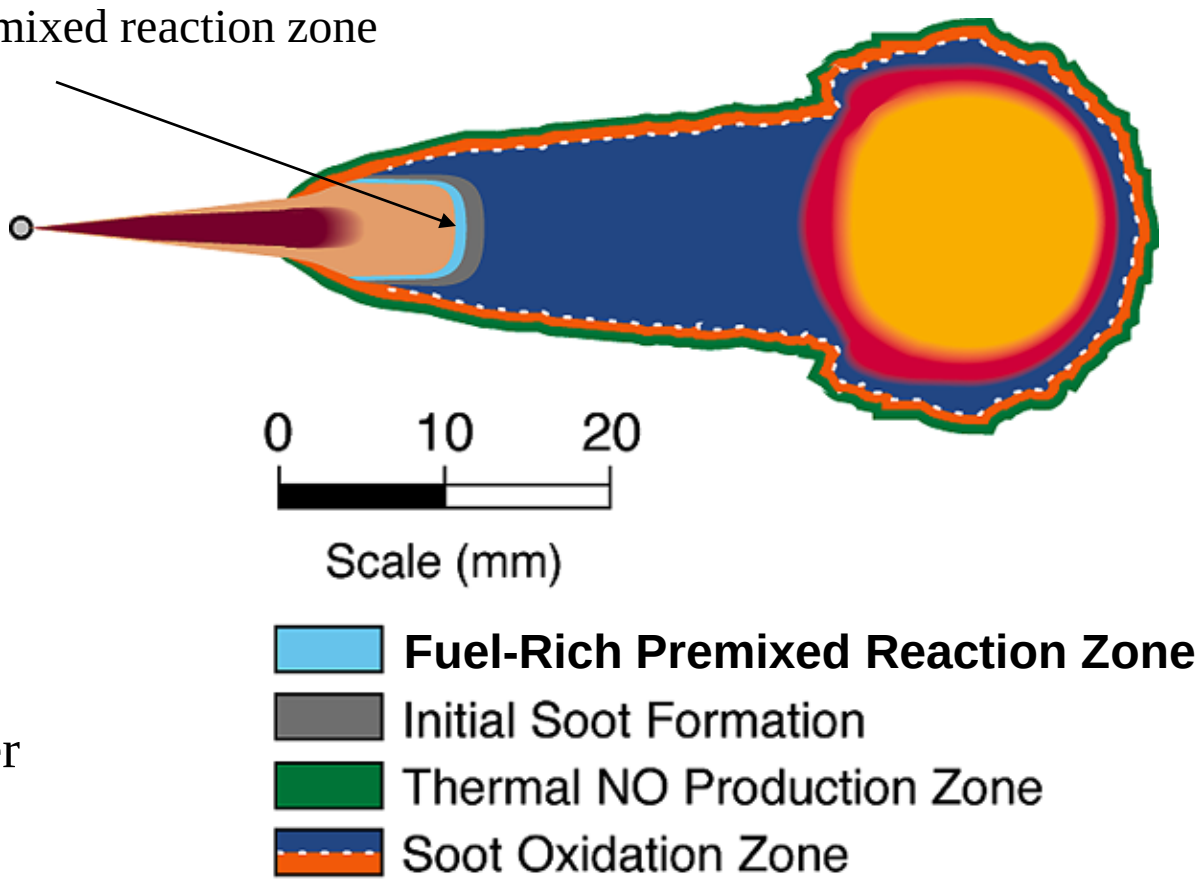
Old Description

New Conceptual Model



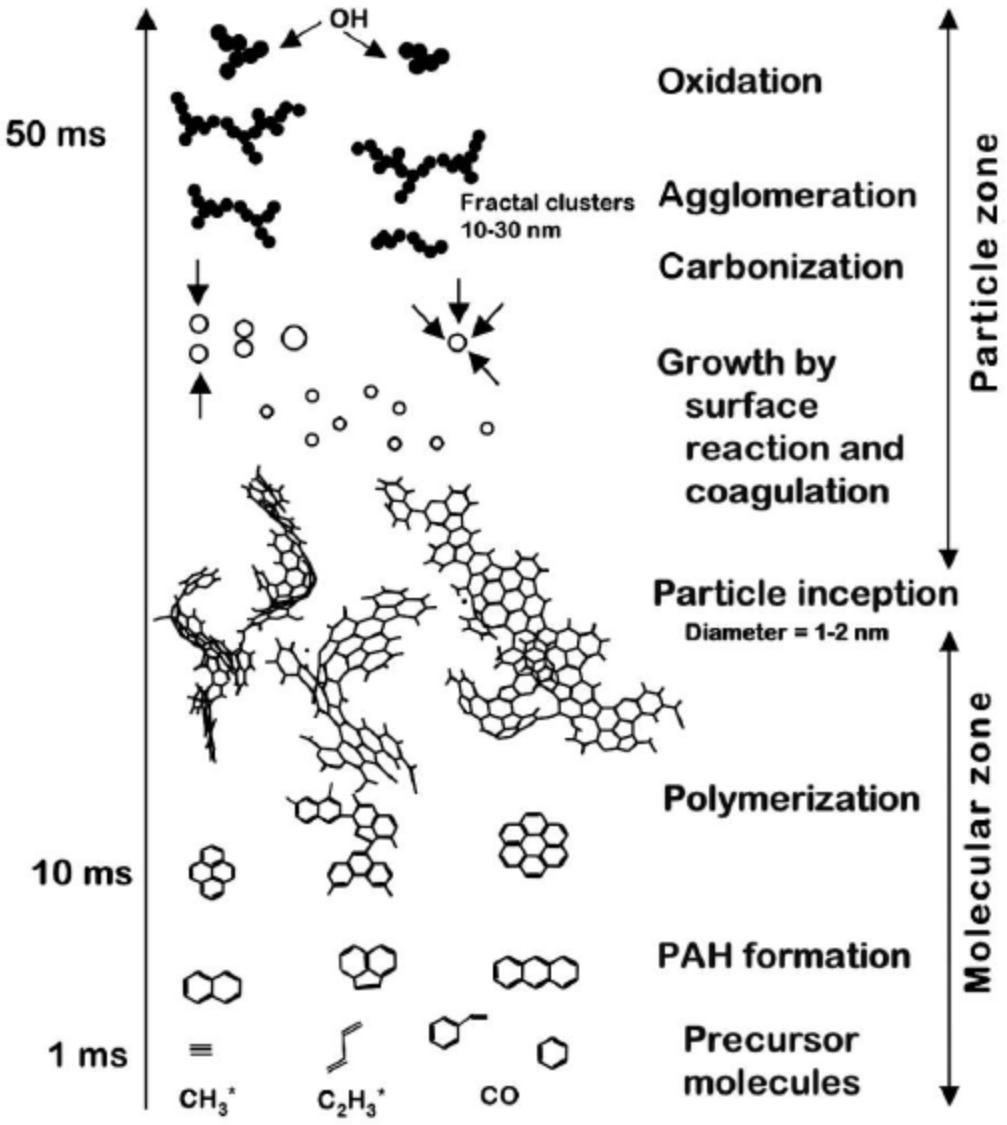
- The appearance is significantly different.
  - Regimes of Diesel combustion are different than thought. (flame standoff, upstream mixing, instantaneous vs. averaged).

Predicting the soot precursors is one of the keys to predicting soot emissions from a Diesel engine



From:
John Dec,
SAE paper
970873

Steady growth in molecular size leads to visible soot



Correlations between Fuel Structural Features and Benzene Formation

Hongzhi R. Zhang, Eric G. Eddings, Adel F. Sarofim
The University of Utah

and Charles K. Westbrook
Lawrence Livermore National Lab

presented at
2008 International Combustion Institute Meeting
Montreal, Canada, August 8th, 2008

Outline

- Introduction
- Chemistry of Benzene Precursors and Comparison of Measured and Predicted Benzene Concentrations
- Benzene Formation Potential
- Benzene Formation Pathways

Introduction

- Combustion generated benzene is a health concern
  - Benzene is a major precursor for particulate pollution
  - Benzene is a known carcinogen
  - Benzene is a major precursor of PAH, also carcinogens

- We want to identify fuel properties that are critical to major benzene formation pathways and benzene formation potentials for individual fuel components
  - Fuel structure: between normal, iso-, and cyclo paraffins
  - Fuel structure: C_3, C_4 vs. C_{12}, C_{16} fuels
  - Other properties: Equivalence ratio, Hydrogen deficiency, Combustion temperature

- 22 premixed flames; C_1-C_{12} fuels; Φ = 1.0-3.06; P = 20-760 torr; T_{max} = 1600-2370 K

- Benzene concentrations were predicted within 30% of the experimental data for 15 flames (total of 22 flames)

Major Benzene Formation Pathways Revisited

- Class 1: Acetylene addition (Westmoreland et al., 1989; Frenklach et al., 1985)
  - R1: $C_2H_2 + CH_2CHCHCH = C_6H_6 + H$
  - R2: $C_2H_2 + HCCHCCH = C_6H_5$
- Class 2: C_3 combination (Hopf, 1971; Miller-Melius, 1992)
  - R3: $H_2CCCH + H_2CCCH = C_6H_6$
  - R4: $H_2CCCH + CH_2CCH_2 = C_6H_6 + H$
  - R5: $H_2CCCH + H_2CCCH = C_6H_5 + H$
  - R6: $H_2CCCH + CH_2CHCH_2 =$ FULVENE + 2H
- Class 3: Combination of CH_3 and C_5H_5
  - R7: $C_5H_5 + CH_3 = C\text{-}C_6H_8 = C_6H_6 + 2H$
- Class 4: Cascading dehydrogenation (Zhang et al., 2007)
  - R8: cycloC_6-R $\leftrightarrow$ C-C_6H_{10}(–R) $\leftrightarrow$ C-C_6H_8(–R) $\leftrightarrow$ C_6H_6(–R)
- Class 5: De-alkylation
  - R9: C_6H_5-R + H $= C_6H_6 + R$

Natural Gas, Synfuel, Indicator Fuels, Biofuels

Liquid Fuels from Oil and Coal

Experimental: Benzene from Cyclo-Paraffins

Author	Fuel	Φ	P torr	T(Max) in K	$[C_6H_6]_{Max}$
V	C_7H_{16}	1.0	760	1843	12 PPM
HSP	gasoline	1.0	760	1990	344
LWC	C-C_6H_{12}	1.0	30	1960	473

Questions:

1. Why gasoline produces more benzene than n-heptane, the indicator fuel for octane rating?
2. What are the benzene sources in gasoline?
3. How is benzene formed from various chemical classes?

Outline

- Introduction
- Chemistry of Benzene Precursors and Comparison of Measured and Predicted Benzene Concentrations
- Benzene Formation Potential
- Benzene Formation Pathways

Sub-Models Compiled from Literatures

We took

- Marinov-Westbrook-Pitz's hydrogen model
- Hwang, Miller et al.'s, and Westbrook's acetylene oxid. models
- Wang and Frenklach's acetylene reaction set with vinylic and aromatic radicals
- Marinov and Malte's ethylene oxidation sub-model
- Tsang's propane and propene chemical kinetics
- Pitz and Westbrook's n-butane sub-model
- Miller and Melius benzene formation sub-model
- Emdee-Brezinsky-Glassman's toluene and benzene oxidation sub-model

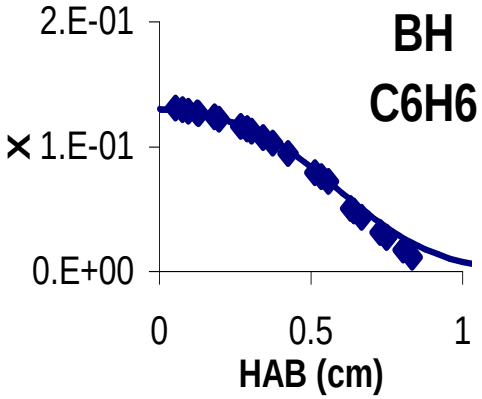
We have added

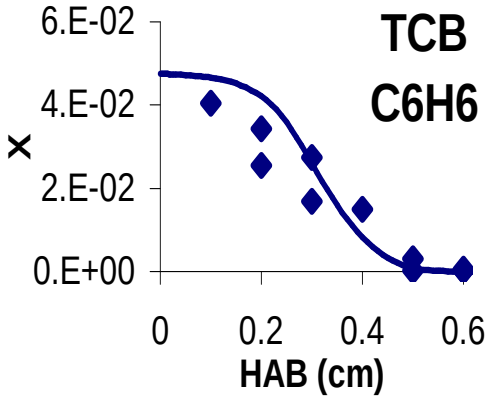
- 100 modification steps to the base gas core concerning benzene chemistry
- Fuel Component Sub-Mechanisms

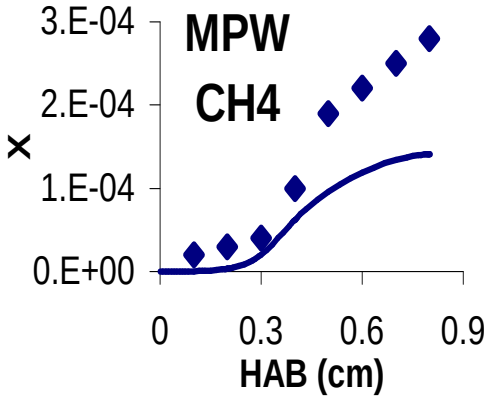
Precursor Chemistry

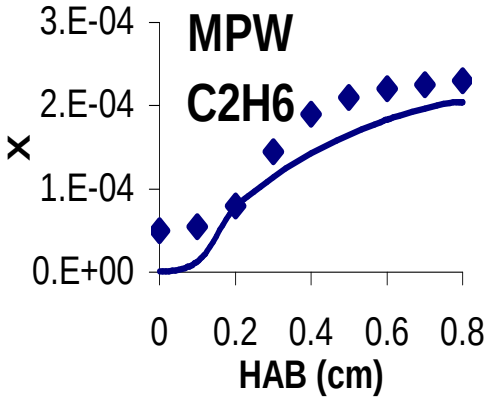
- A list of benzene precursors includes
  - Major precursors: C_3H_3, C_2H_2, n-C_4H_3, n-C_4H_5
  - Minor precursors: C-C_5H_5, C-C_6H_x, Ph-R
  - Bridging Species: a-C_3H_5, C_2H_3
  - Other Related Species: a-C_3H_4, p-C_3H_4, C_4H_6 isomers, C_3H_5 isomers, C-C_5H_6, C_4H_4, C_4H_2, C_2-C_4 olefins
- New Reactions in the mechanism
  - Large olefin decomposition: 1-C_7H_{14} = a-C_3H_5 + C_4H_9-1
  - New addition of chemistry of p-C_3H_4
    - p-C_3H_4 has comparable, if not higher, concentrations in flames, in comparison with those of a-C_3H_4
    - It is easier to form C_3H_3 radicals from p-C_3H_4 than from a-C_3H_4
  - Reactions involving C_4 species
- Reaction of C_2H_3=C_2H_2+H critically examined

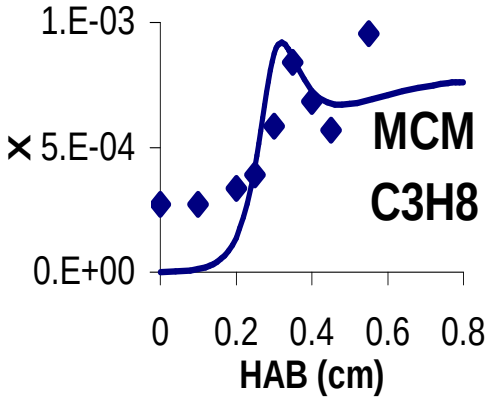
Modeled Benzene Concentrations

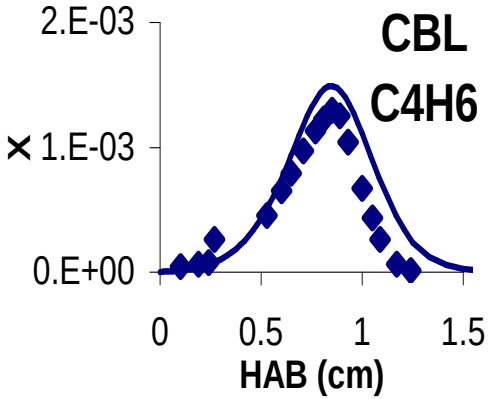




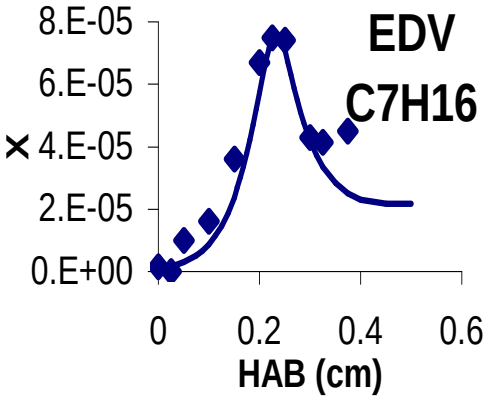


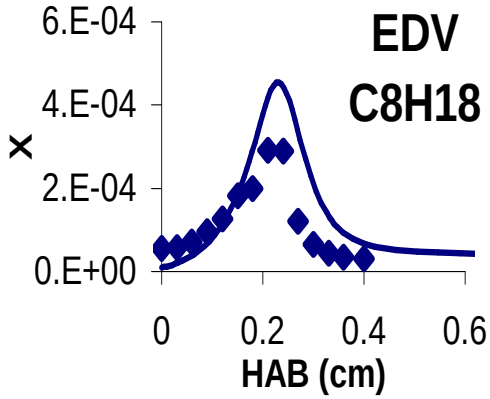


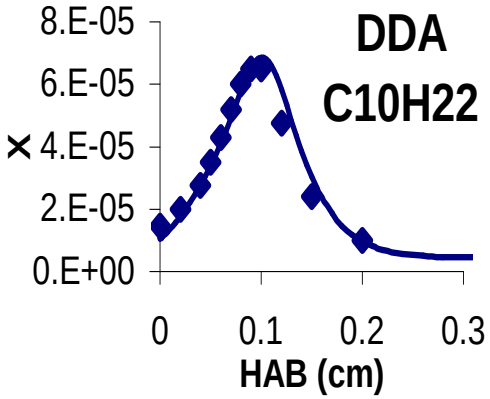


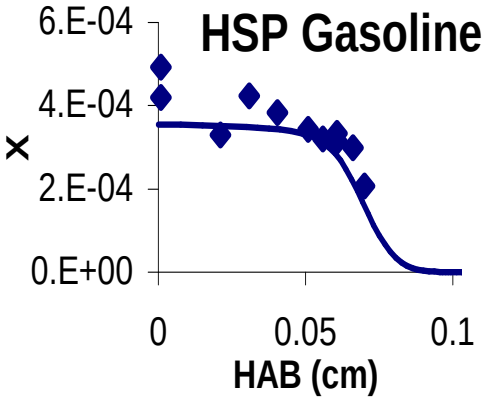


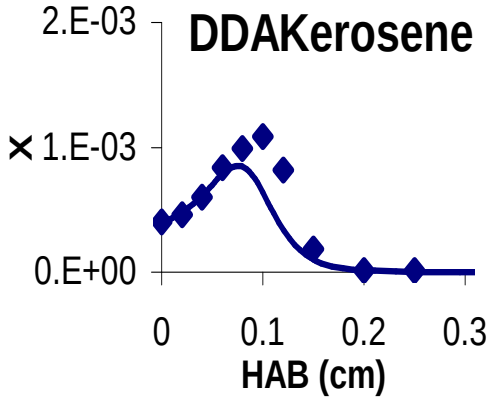
Modeled Benzene Concentrations

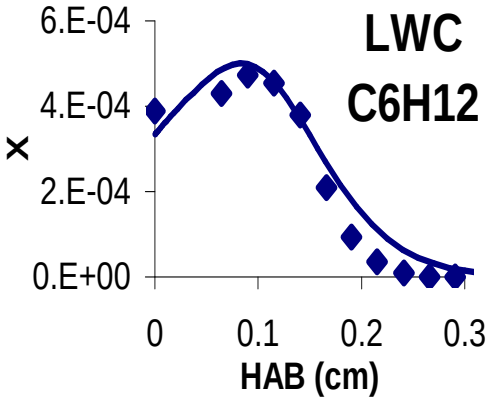












Outline

- Introduction
- Chemistry of Benzene Precursors and Comparison of Measured and Predicted Benzene Concentrations
- Benzene Formation Potential
- Benzene Formation Pathways

Benzene Formation Potential

#	Fuel	Inert Ar, %	C/O	Eq. Ratio	P torr	T(Max) K at cm	Exp. Max. $[C_6H_6]^b$ at cm	Cal. Max. $[C_6H_6]^b$ at cm	Deviation
F1	CH_4	0.453	0.626	2.50	760	1605 at 0.4	280 at 0.8	141 at 0.8	-49.6
F2	C_2H_6	0.453	0.715	2.50	760	1600 at 0.24	230 at 0.8	205 at 0.8	-10.9
F3	C_3H_8	0.44	0.833	2.78	760	1640 at 0.4	840 at 0.35	922 at 0.32	+9.8
F4	C_3H_8	0.424	0.54	1.80	30	2190 at 0.95	17.5 at 0.75	72.9 at 0.77	+×4.2[e]
F5	C_2H_2	0.05	0.959	2.40	20	1901 at 1.0	40 at 0.37	82.7 at 0.37	+×2.1[e]
F6	C_2H_2	0.45	1.00	2.50	19.5	1850 at 1.0	58.9 at 0.6	39.1 at 0.64	-33.6
F7	C_2H_2	0.55	1.103	2.76	90	1988 at 0.73	140 at 0.6	96.7 at 0.55	-30.9
F8	C_2H_4	0.5	0.634	1.90	20	2192 at 1.7	33.1 at 0.9	11.4 at 0.77	-×2.9[e]
F9	C_2H_4	0	0.80	2.40	760	1815 at 0.1	936 at 0.15	136 at 0.14	-×6.9[e]
F10	C_2H_4	0.656	0.92	2.76	760	1600 at 0.3	250 at 0.35	212 at 0.35	-15.2
F11	C_2H_4	0.578	1.02	3.06	760	1420 at 0.3	575 at 1.0	553 at 1.0	-3.8
F12	C_3H_6	0.25	0.773	2.32	37.5	2371 at 0.71	1220 at 0.39	927 at 0.39	-24.0
F13	C_4H_6	0.03	0.874	2.40	20	2310 at 1.65	1300 at 0.85	1490 at 0.85	+14.6
F14	C_6H_6	0.3	0.717	1.79	20	1905 at 0.2	N/A	N/A	Good
F15	C_6H_6	0.752[c]	0.72	1.80	760	1850 at 0.45	N/A	N/A	Good
F16	C_7H_{16}	0.841[c]	0.318	1.00	760	1843 at 0.25	12 at 0.08	1.77 at 0.09	-×6.8[e]
F17	C_7H_{16}	0.73[c]	0.605	1.90	760	1640 at 0.30	75 at 0.225	75.8 at 0.23	+1.1
F18	i-C_8H_{18}	0.682[c]	0.608	1.90	760	1670 at 0.30	292 at 0.21	455 at 0.23	+55.8
F19	$C_{10}H_{22}$	0.682[c]	0.558	1.73	760	1688 at 0.20	65 at 0.10	68.5 at 0.10	+5.4
F20	gasoline	0.768[c], 0.01[d]		0.9-1	760	1990 at 0.046	344 at 0.05	330 at 0.05	-4.1
F21	kerosene	0.684[c]		≈1.7	760	1775 at 0.20	1090 at 0.1	850 at 0.75	-22.0
F22	C-C_6H_{12}	0.325	0.333	1.00	30	1960 at 0.6	473 at 0.09	498 at 0.09	+5.3

X means “a Factor of X”

Benzene Formation Potential

The Highest and Lowest Benzene Producer

Fuel	Inert Ar, %	C/O	P torr	Exp. Max. $Y(C_6H_6)^b$	Cal. Max. $Y(C_6H_6)^b$	Deviation, %
C_4H_6	0.03	0.874	20	1300 at 0.85	1490 at 0.85	+14.6
C_3H_6	0.25	0.773	37.5	1220 at 0.39	927 at 0.39	-24.0
kerosene	0.684[c]	ϕ=1.7	760	1090 at 0.1	850 at 0.75	-22.0
C_2H_4	0	0.80	760	936 at 0.15	136 at 0.14	-X6.9[e]
C_3H_8	0.44	0.833	760	840 at 0.35	922 at 0.32	+9.8
C_7H_{16}	0.73[c]	0.605	760	75 at 0.225	75.8 at 0.23	+1.1
$C_{10}H_{22}$	0.682[c]	0.558	760	65 at 0.10	68.5 at 0.10	+5.4
C_2H_2	0.45	1.00	19.5	58.9 at 0.6	39.1 at 0.64	-33.6
C_2H_2	0.05	0.959	20	40 at 0.37	82.7 at 0.37	+X2.1[e]
C_2H_4	0.5	0.634	20	33.1 at 0.9	11.4 at 0.77	-X2.9[e]
C_3H_8	0.424	0.54	30	17.5 at 0.75	72.9 at 0.77	+X4.2[e]
C_7H_{16}	0.841[c]	0.318	760	12 at 0.08	1.77 at 0.09	-X6.8[e]

Benzene Formation Potential

Effects of Carbon Backbone: C_3 Species

Fuel	C/O	P torr	T(Max) K at cm	T(Max), K at cm, Fitted	Exp. Max. $Y(C_6H_6)^b$	Cal. Max. $Y(C_6H_6)^b$	Deviation, %
C_3H_6	0.773	37.5	2371 at 0.71		1220 at 0.39	927 at 0.39	-24.0
C_2H_4	0.92	760	1600 at 0.3		250 at 0.35	212 at 0.35	-15.2
C_2H_4	1.02	760	1420 at 0.3		575 at 1.0	553 at 1.0	-3.8
C_3H_8	0.833	760	1640 at 0.4		840 at 0.35	922 at 0.32	+9.8
CH_4	0.626	760	1605 at 0.4		280 at 0.8	141 at 0.8	-49.6
C_2H_6	0.715	760	1600 at 0.24		230 at 0.8	205 at 0.8	-10.9

- Fuel decomposition
  - $C_3H_8 \rightarrow C_3H_6 \rightarrow a\text{-}C_3H_5 \rightarrow C_3H_4 \rightarrow C_3H_3$
  - $C_3H_8 \rightarrow C_2H_4 \rightarrow C_2H_2 \rightarrow C_3H_3$
- Benzene formation
  - $C_3H_3 + C_3H_3 = bC_6H_6$
  - $C_3H_3 + C_3H_3 = C_6H_5 + H$
  - $C_3H_3 + a\text{-}C_3H_4 = bC_6H_6 + H$
  - $C_3H_3 + a\text{-}C_3H_5 = fC_6H_6 + 2H$

Benzene Formation Potential

Effects of Carbon Backbone: C_4 Species

Fuel	C/O	P torr	T(Max) K at cm	T(Max), K at cm, Fitted	Exp. Max. $Y(C_6H_6)^b$	Cal. Max. $Y(C_6H_6)^b$	Deviation, %
C_4H_6	0.874	20	2310 at 1.65	2050 at 1.75	1300 at 0.85	1490 at 0.85	+14.6
C_2H_2	0.959	20	1901 at 1.0		40 at 0.37	82.7 at 0.37	+X2.1[e]
C_2H_2	1.00	19.5	1850 at 1.0		58.9 at 0.6	39.1 at 0.64	-33.6

- Fuel decomposition
  - C_4H_6 → C_4H_5 → C_4H_4 → C_4H_3
  - C_4H_6 → C_2H_3
  - C_4H_5 → C_2H_3 & C_2H_2
  - $C_4H_5 + H$ → C_3H_3
- Benzene formation
  - $C_2H_2 + C_4H_3 = C_6H_5$
  - $C_2H_2 + C_4H_5 = bC_6H_6 + H$
  - $C_3H_3 + C_3H_3 = bC_6H_6$

Benzene Formation Potential

Effects of Carbon Backbone: Cyclohexanes

Fuel	C/O	P torr	T(Max) K at cm	T(Max), K at cm, Fitted	Exp. Max. $Y(C_6H_6)^b$	Cal. Max. $Y(C_6H_6)^b$	Deviation, %
kerosene	ϕ=1.7	760	1775 at 0.20	1775 at 0.25	1090 at 0.1	850 at 0.75	-22.0
$C_{10}H_{22}$	0.558	760	1688 at 0.20	1688 at 0.22	65 at 0.10	68.5 at 0.10	+5.4
C-C_6H_{12}	0.333	30	1960 at 0.6	1960 at 0.55	473 at 0.09	498 at 0.09	+5.3
C_7H_{16}	0.318	760	1843 at 0.25		12 at 0.08	1.77 at 0.09	-X6.8[e]
gasoline	ϕ=1	760	1990 at 0.046	1990 at 0.106	344 at 0.05	330 at 0.05	-4.1

- Benzene formation
  - Cascading dehydrogenation & Interweaving dehydrogenation

- C-C_6H_{12} → C-C_6H_{10} → C-C_6H_8 → bC_6H_6
- R-C-C_6H_{11} → C-C_6H_{10} → C-C_6H_8 → bC_6H_6
- R-C-C_6H_{11} → R-C-C_6H_9 → C-C_6H_8 → bC_6H_6
- R-C-C_6H_{11} → R-C-C_6H_9 → R-C-C_6H_7 → bC_6H_6
- R-C-C_6H_{11} → R-C-C_6H_9 → R-C-C_6H_7 → R-C_6H_5

Benzene Formation Potential

Effects of Branching: cyclo > iso > normal paraffins

Fuel	C/O	P torr	T(Max) K at cm	T(Max), K at cm, Fitted	Exp. Max. $Y(C_6H_6)^b$	Cal. Max. $Y(C_6H_6)^b$	Devi on, %
i-C_8H_{18}	0.608	760	1670 at 0.30	1670 at 0.36	292 at 0.21	455 at 0.23	+55.8
C_7H_{16}	0.605	760	1640 at 0.30	1640 at 0.40	75 at 0.225	75.8 at 0.23	+1.1
$C_{10}H_{22}$	0.558	760	1688 at 0.20	1688 at 0.22	65 at 0.10	68.5 at 0.10	+5.4
C-C_6H_{12}	0.333	30	1960 at 0.6	1960 at 0.55	473 at 0.09	498 at 0.09	+5.3
C_7H_{16}	0.318	760	1843 at 0.25		12 at 0.08	1.77 at 0.09	-X6.8

- Fuel decomposition
  - i-C_8H_{18} → i-C_4H_8 → i-C_4H_7
  - i-C_4H_7 → a-C_3H_4 → C_3H_3
  - i-C_4H_8 → s-C_3H_5 → p-C_3H_4 → C_3H_3
- Benzene formation
  - $C_3H_3 + C_3H_3 = bC_6H_6$
  - $C_3H_3 + C_3H_3 = C_6H_5 + H$
  - $C_3H_3 + a\text{-}C_3H_4 = bC_6H_6 + H$

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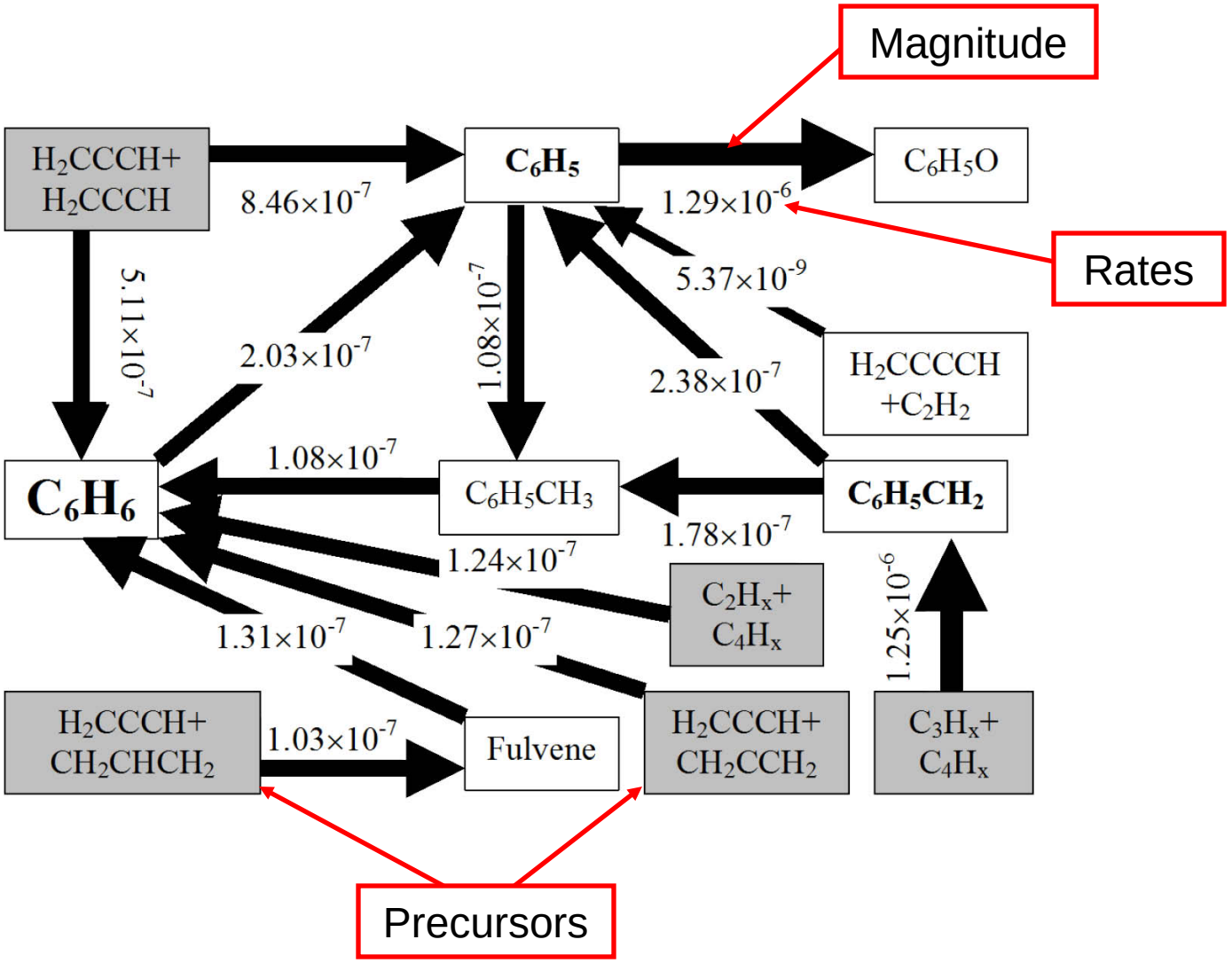
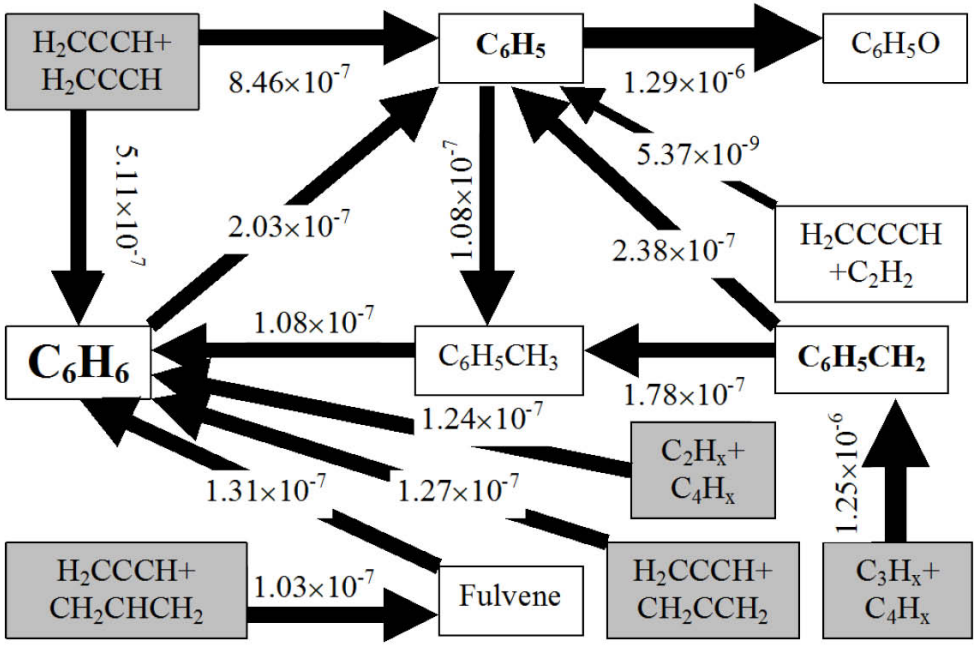
Benzene Formation Pathways

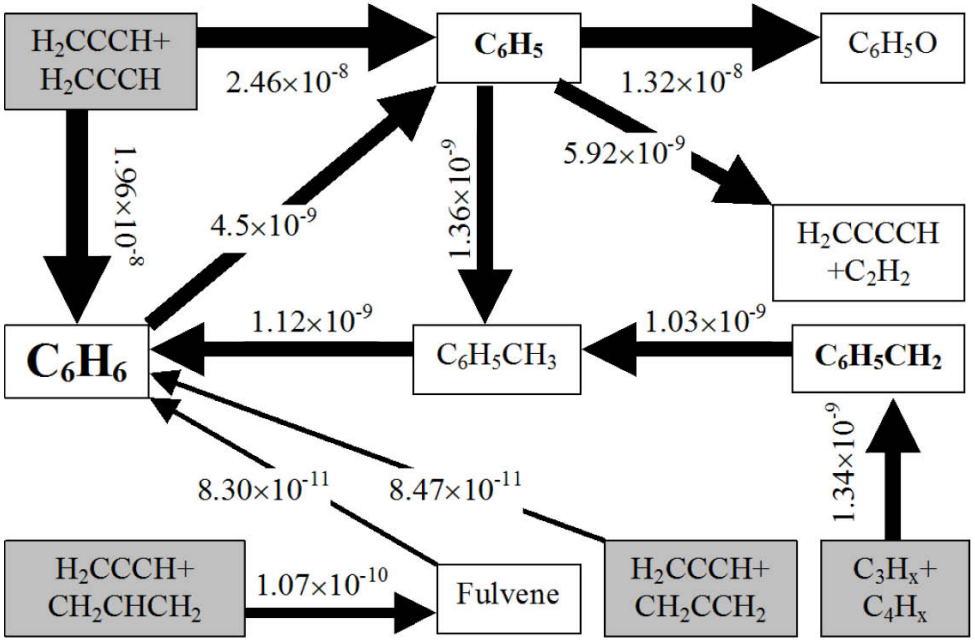


In a Normal Decane Flame



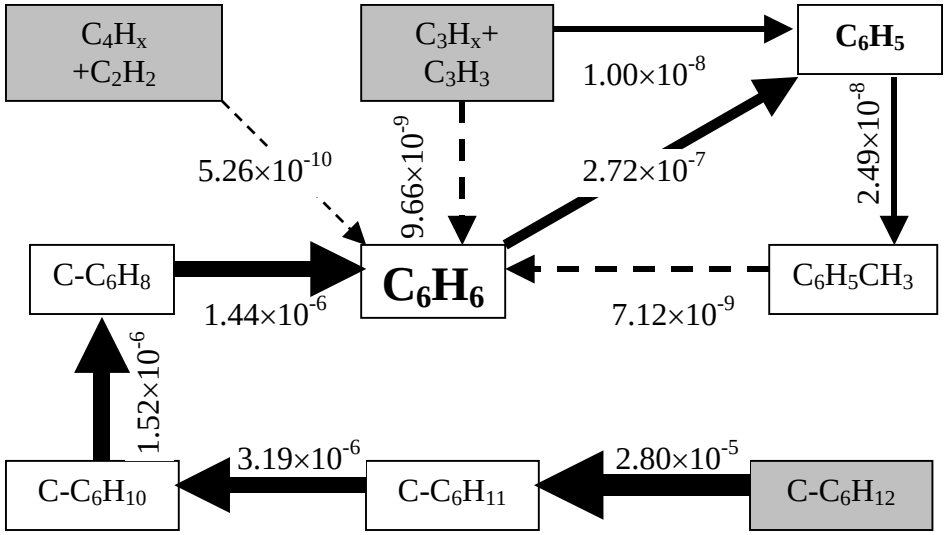
- Contribution of Major Benzene Formation Pathways
  - 51% from $C_3H_3 + C_3H_3$ = bC_6H_6
  - 13% from $C_3H_3 + a\text{-}C_3H_5$ = $fC_6H_6 + 2H$
  - 13% from $C_3H_3 + a\text{-}C_3H_4$ = $bC_6H_6 + H$
  - 12% from $C_2H_3 + C_4H_3\,(C_4H_5)$ = C_6H_5 ($bC_6H_6 + H$)
  - 11% from $C_6H_5\text{-}CH_3 + H$ = $C_6H_6 + CH_3$

In an Acetylene Flame



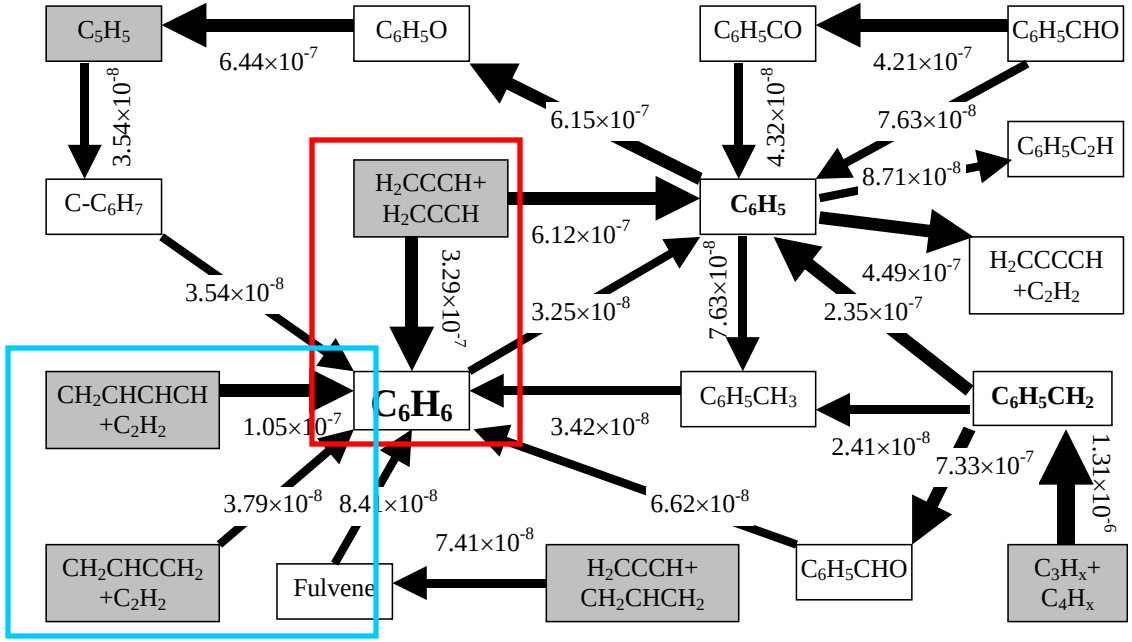
- Contribution of Major Benzene Formation Pathways
  - 94% from $C_3H_3 + C_3H_3$ = bC_6H_6
  - 5% from $C_6H_5\text{-}CH_3 + H$ = $C_6H_6 + CH_3$
- Propargyl Radical Formation Pathways
  - 87% $^1CH_2 + C_2H_2$ = $H_2CCCH + H$
  - 11% $^3CH_2 + C_2H_2$ = $H_2CCCH + H$

In a Cyclohexane Flame



- Contribution of Major Benzene Formation Pathways
  - 100% from cycloC_6-R ➔ C-C_6H_{10} ➔ C-C_6H_8 ➔ bC_6H_6

Benzene Formation Pathways: in Butadiene Flames

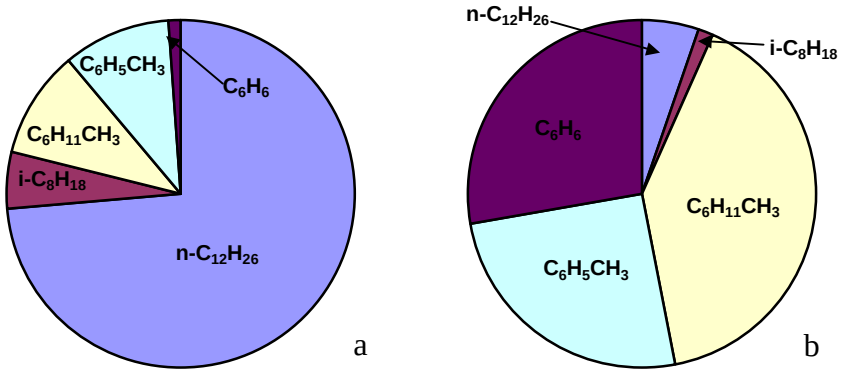


- Contribution of Major Benzene Formation Pathways
  - 48% from $C_3H_3 + C_3H_3$ = bC_6H_6
  - 20% from $C_2H_2 + C_4H_3$ (C_4H_5) = C_6H_5 (bC_6H_6 + H)
  - 12% from $C_3H_3 + a\text{-}C_3H_5$ = fC_6H_6 + 2H
  - 10% from $C_6H_5\text{-}CHO$ + H = C_6H_6 + CHO
  - 5% from $C_6H_5\text{-}CH_3$ + H = C_6H_6 + CH_3
  - 5% from $C_5H_5 + CH_3$ = $C\text{-}C_6H_8$ = C_6H_6 + 2H

Soot Precursor Production Potential

Contribution from Individual Surrogate Components to the Formation of Benzene (a kerosene fuel)

- Benzene Contributors: Benzene (28%), Toluene (26%) and Methyl Cyclohexane (40%)
- Component Fractions: Benzene (1%), Toluene (10%), Methyl Cyclohexane (10%), and paraffins (79%)



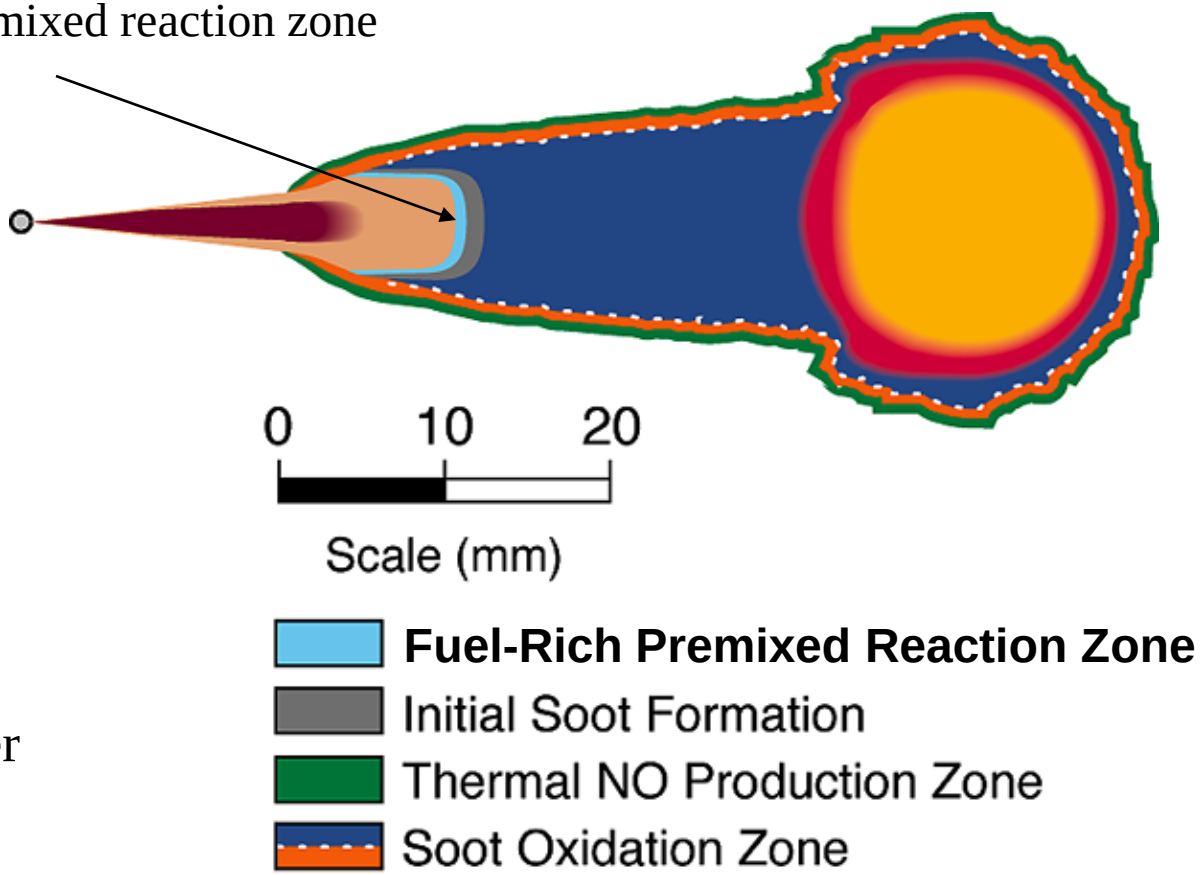
Surrogate Distribution Benzene Formation

* Experimental: Doute et al., *Combustion Science Technology*, 106 (4-6) (1995) 327–344.
* Modeling: Zhang et al., *Proceedings of Combustion Institute*, (2007) 31, 401-409.

Concluding Comments

- The Utah Surrogate Model Was Validated for 22 Premixed Flames of Various Fuels (C_1-C_{12} fuels; Φ = 1.0-3.06; P = 20-760 torr; T = 1600-2370 K).
- Benzene Concentrations Were Predicted within 30% of the Experimental Data for 15 (out of 22) Flames.
- Both Formation Pathways and Formation Potential of Benzene Were Found to Be Dependent on the Fuel Structure, and C_3, C_4 and C-C_6 Were among the Most Productive Fuels.
- C_3 Combination Was Identified to be the Major Benzene Formation Pathway for Most Fuels; That Is Replaced with Dehydrogenation Only for Cyclohexanes.
- Acetylene Addition Was Found to Be Important in C_4 Flames and Those with Large Paraffinic Fuels.

Predicting the soot precursors is one of the keys to predicting soot emissions from a Diesel engine

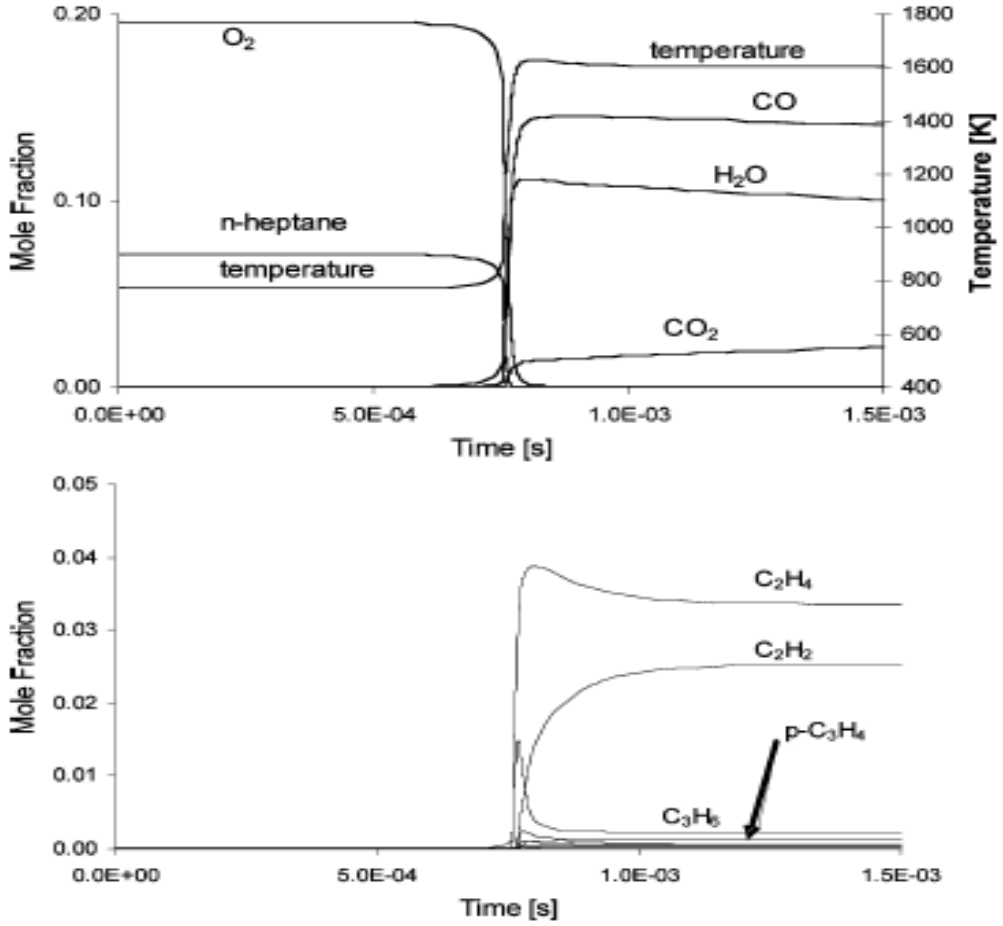


From:
John Dec,
SAE paper
970873

Premixed ignition in Diesel combustion

- Fuel-rich conditions ($\Phi \approx 4$)
- Relatively low temperature ($T \approx 850$ K)
  - Source of cetane ratings in Diesel engines
  - Very similar to conditions of engine knock
  - Very complex chemical kinetic pathways
- Products are good producers of soot precursor species
- Ignition kinetics are the same as in engine knock in SI engines, driven by H_2O_2 decomposition

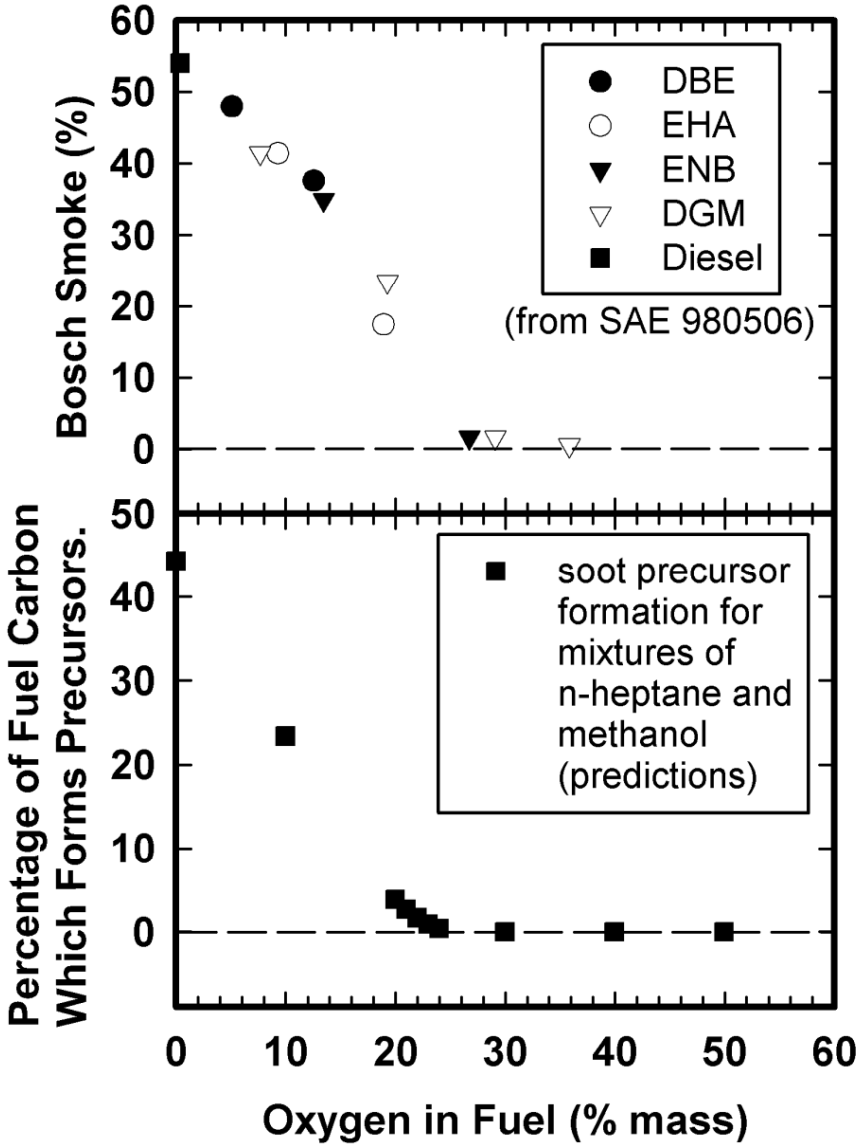
Products of rich premixed ignition are mostly
small unsaturated hydrocarbons, especially acetylene and ethene, which are known precursors to soot



Experimental background

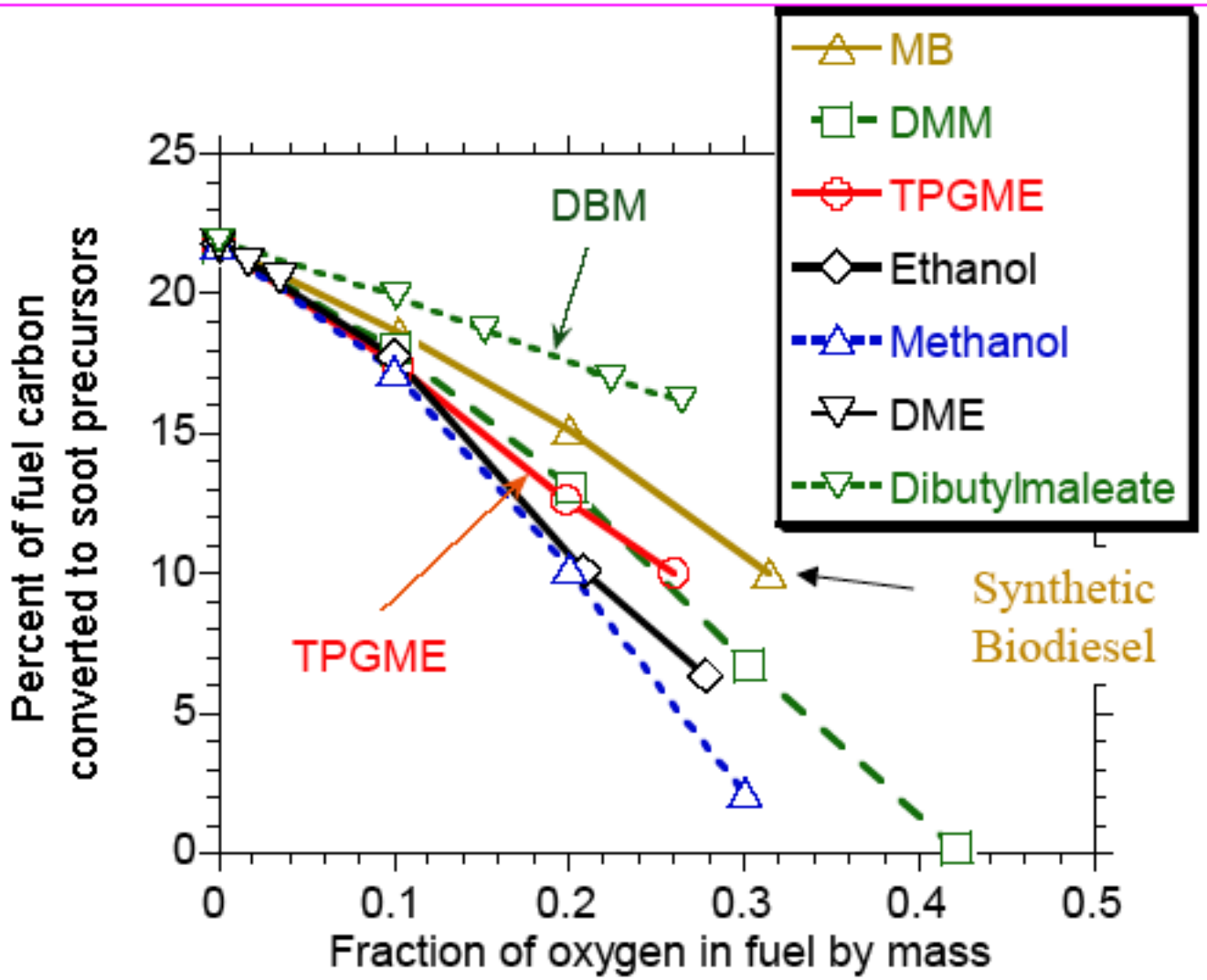
- Addition of oxygenated species reduces soot
  - Important possible oxygenates include biodiesel fuels
- Soot production correlates with post-ignition levels of selected chemical species
- Suggestions that this is due to presence of C - C bonds or total O concentrations
- Use kinetic model to examine these possibilities

Predicted level of soot precursors correlates well with soot emissions from a Diesel engine

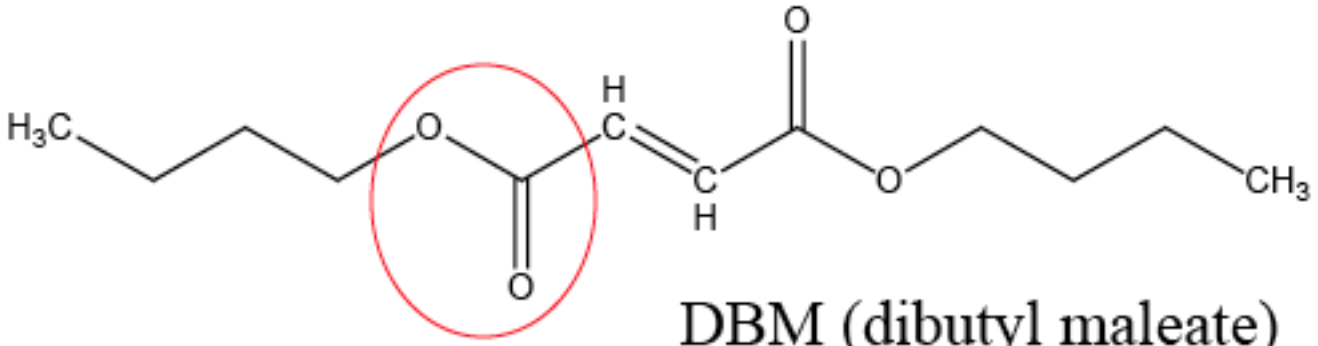


From:
Flynn, Durrett, Dec, Westbrook, et al., SAE paper 1999-01-0509

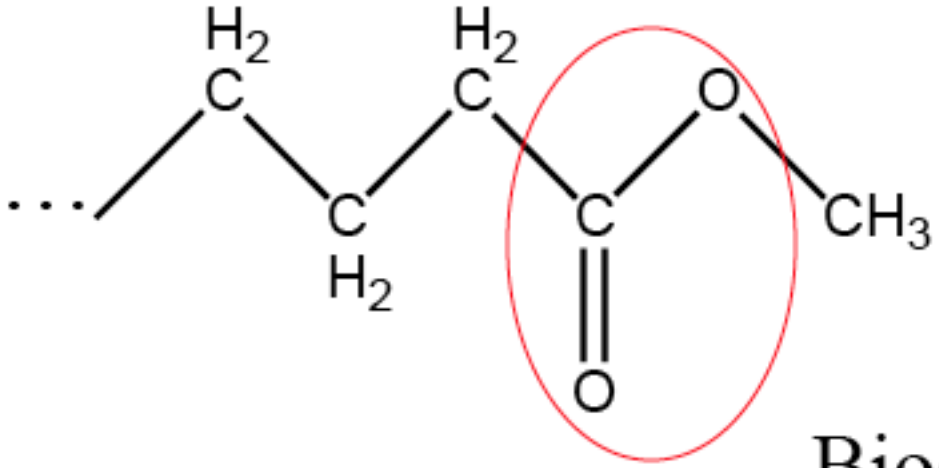
How well an oxygenated fuel works depends on its molecular structure



One large group of oxygenates have ester structures where one carbon atom is attached to two oxygen atoms



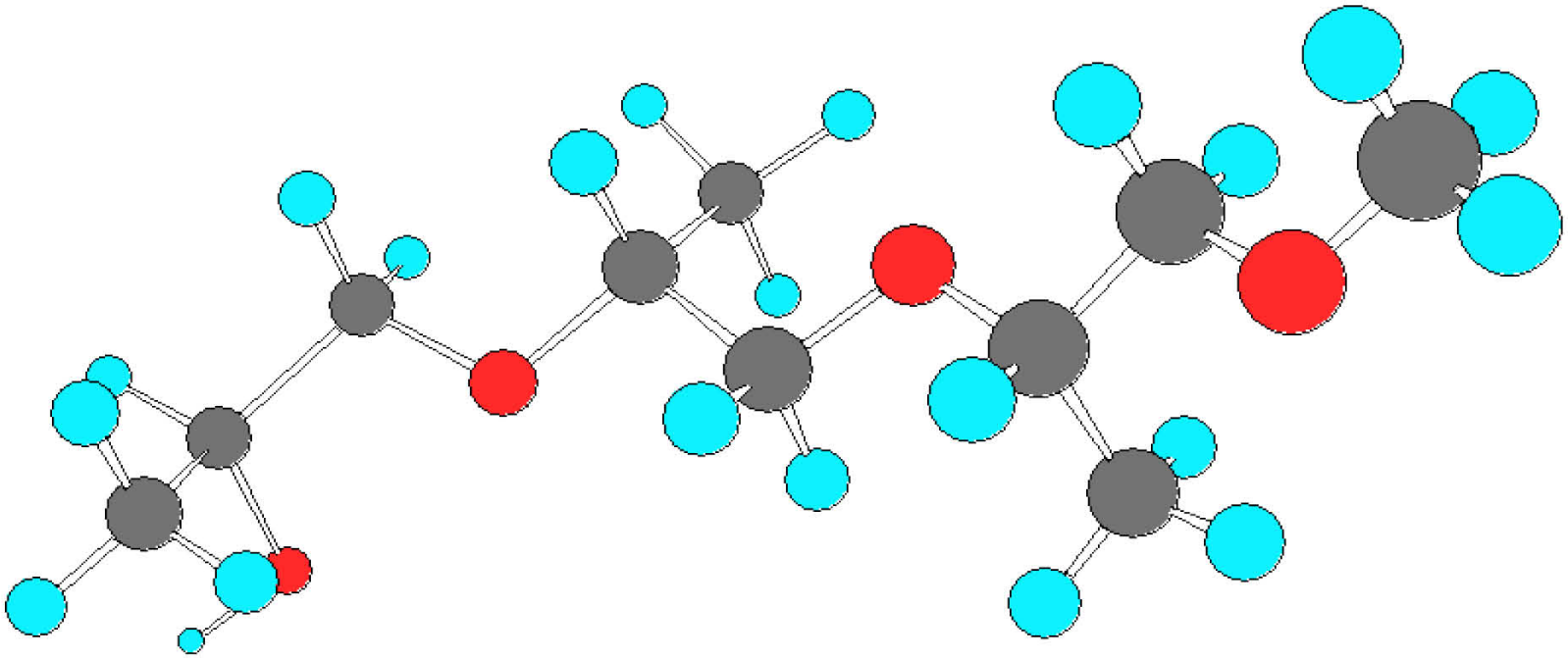
DBM (dibutyl maleate)



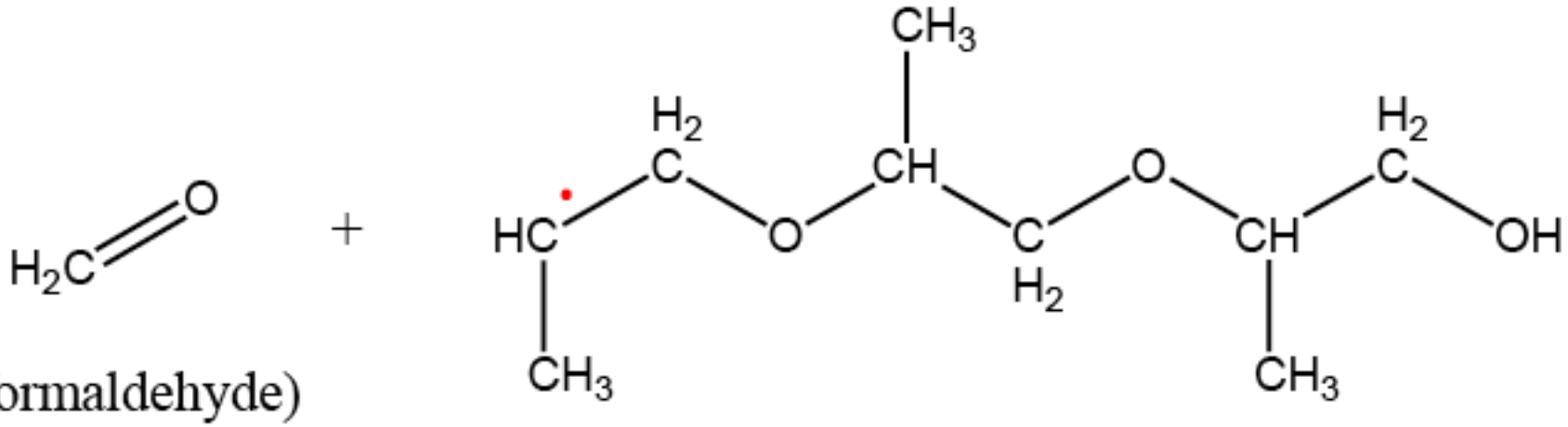
Biodiesel

One oxygen atom could be wasted

Structure of
Tripropylene Glycol Monomethyl Ether (TPGME)



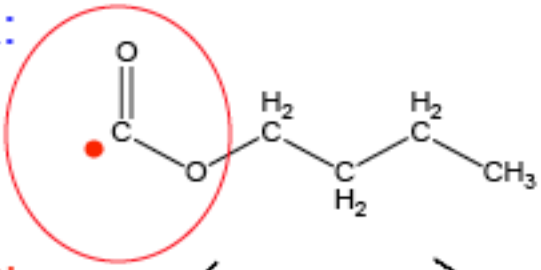
As the oxygenate is consumed, ideally each O atom should stay attached to one C atom to make CO



(formaldehyde)

Goes to CO

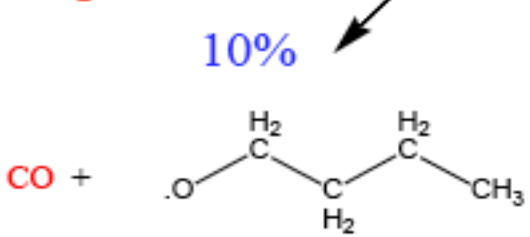
Based on new rates, 90% of key ester structure in DBM goes to CO_2 at 1000K:

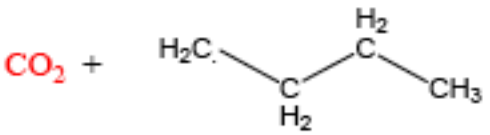


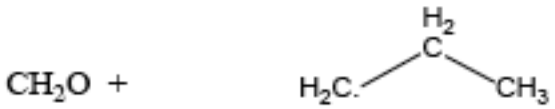
Key branching ratio:

10%

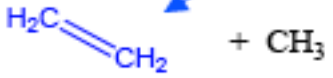
90%

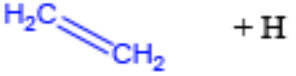




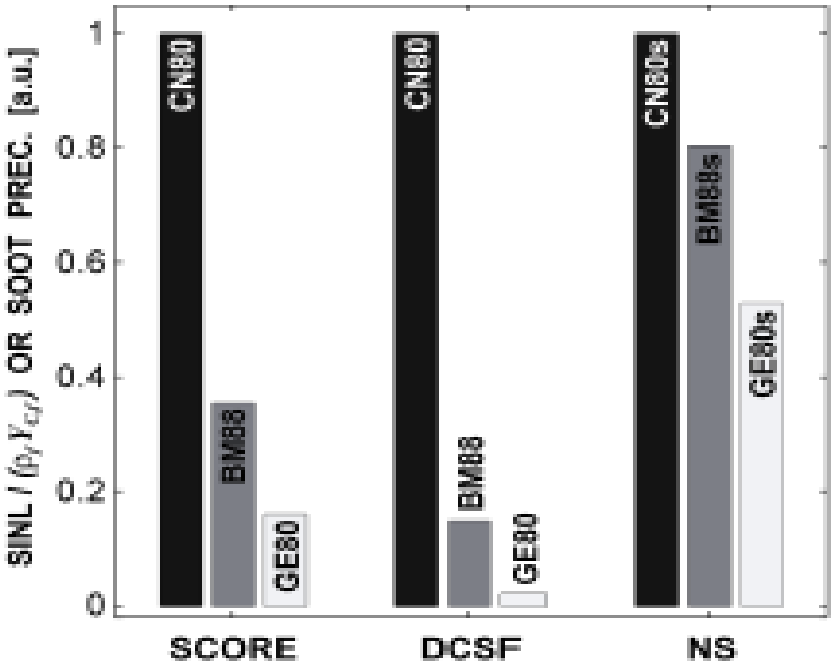


soot precursors



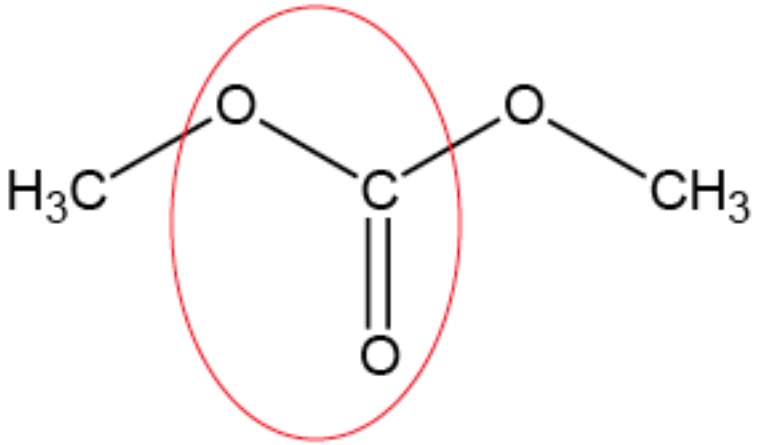


Experiments at Sandia show same trends as LLNL kinetic models



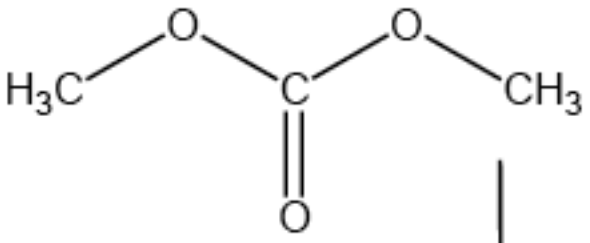
DBM and TPGME reduce sooting, but DBM is less effective than TPGME

DMC (dimethylcarbonate) has ester structure



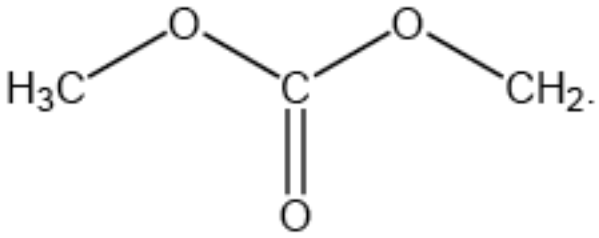
⇒study it, because it is a small, simpler molecule than the large DBM or biodiesel fuels and some experimental data was available

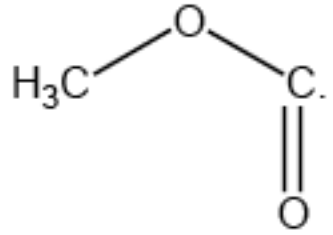
DMC leads to choice of CO or CO_2 too



+ H, OH, etc

(mainly H)



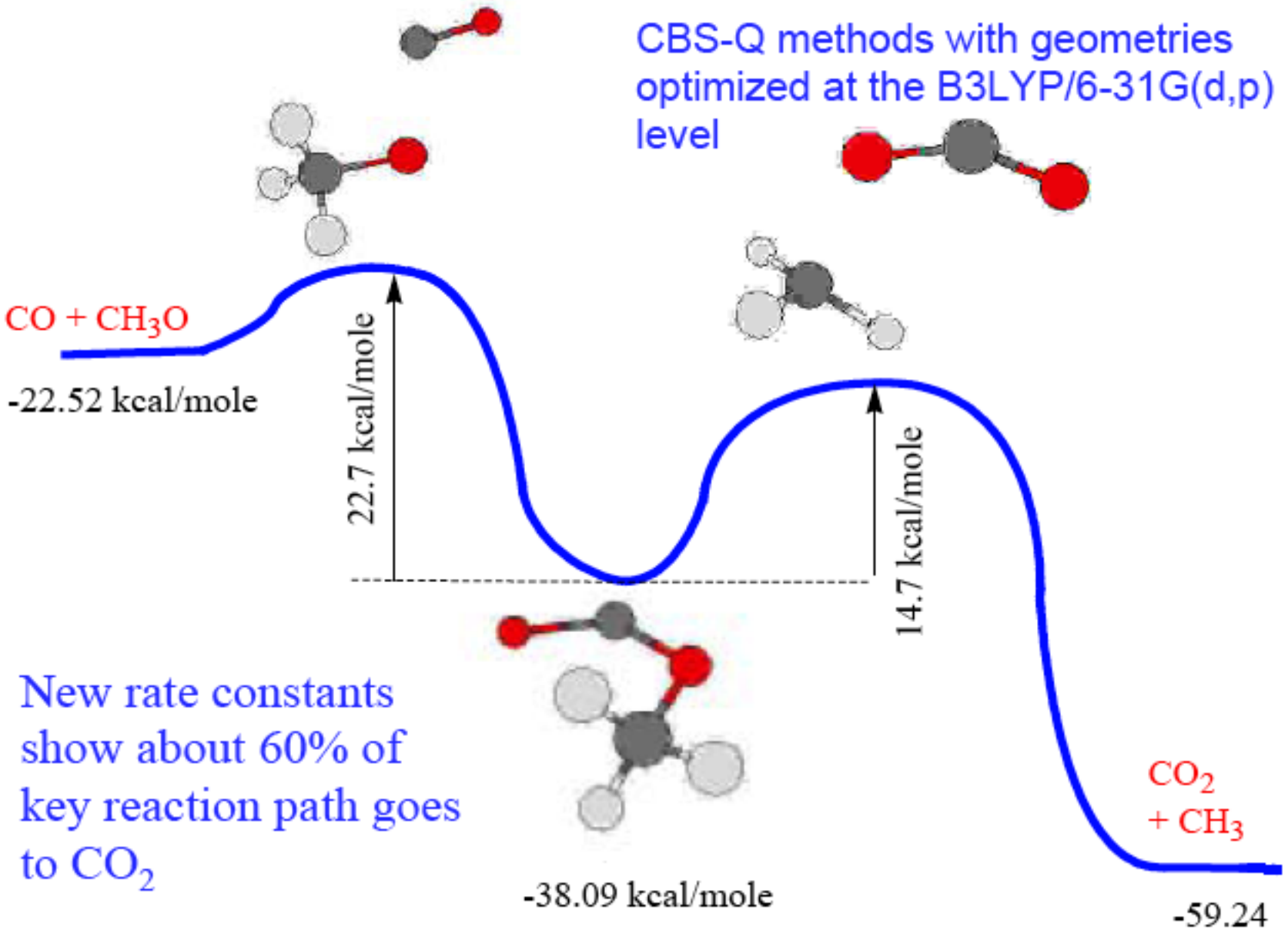


+ CH_2O

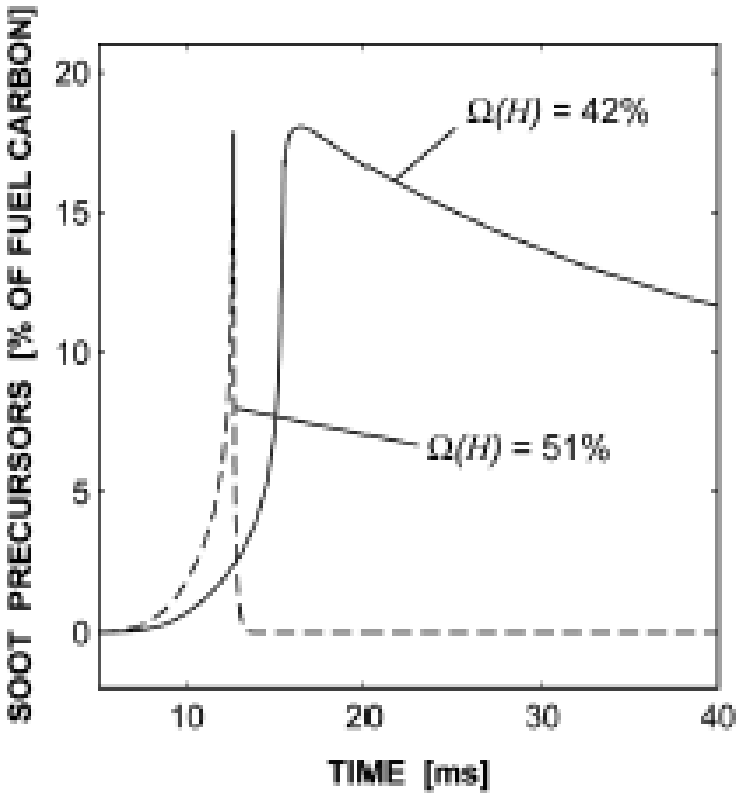
What is the branching ratio?

CO + CH_3O

CO_2 + CH_3


CBS-Q methods with geometries optimized at the B3LYP/6-31G(d,p) level
CO + CH3O
-22.52 kcal/mole
22.7 kcal/mole
14.7 kcal/mole
New rate constants show about 60% of key reaction path goes to CO2
-38.09 kcal/mole
CO2 + CH3
-59.24

Models show same soot precursor formation, but oxygen enhances precursor consumption



Example of $C_2H_3 + O_2$ breaking C - C bond

Understand and predict emissions from open burning or detonation of explosives

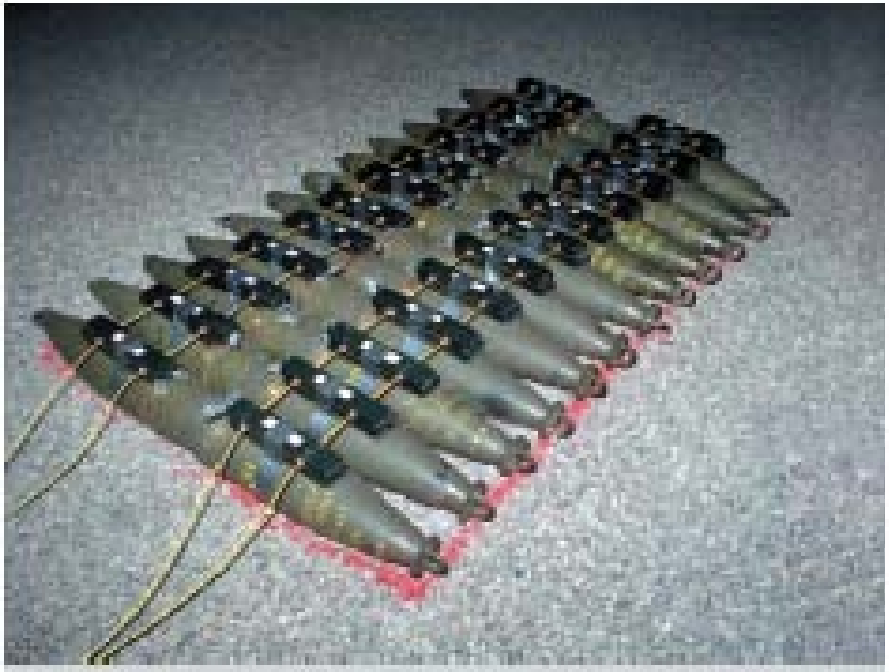
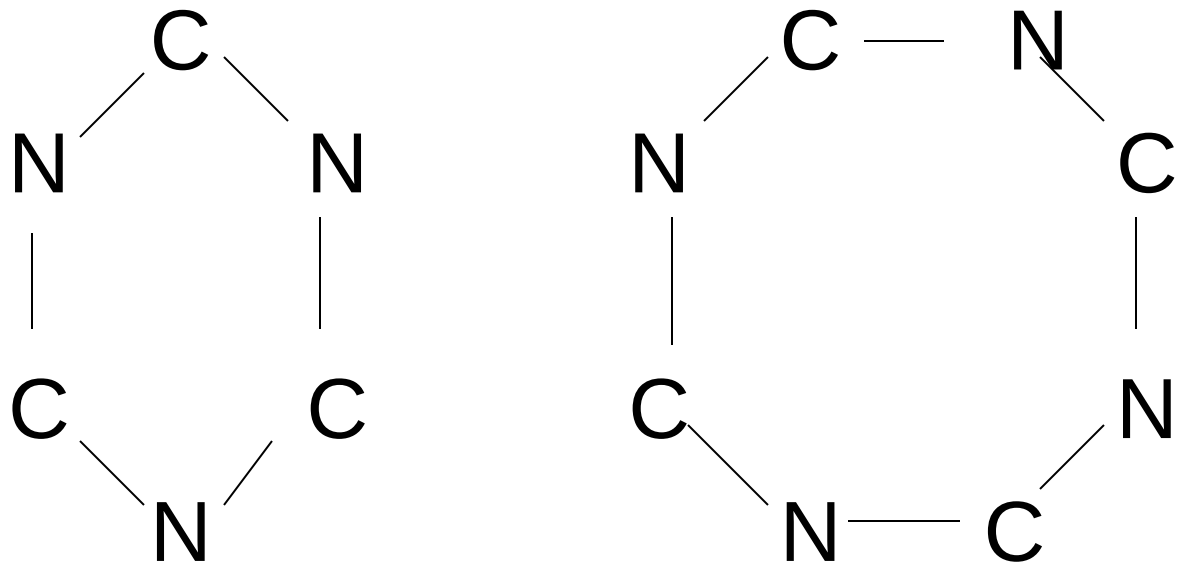


Figure 5. Projectile placement for FY99 Tests 1 and 2.

Figure 6. Projectile placement for FY99 Test 3.

Fig. 3. Open detonation of TNT. Upper figure shows ignition and early burn, lower figure shows entrained cloud of dirt and soot.

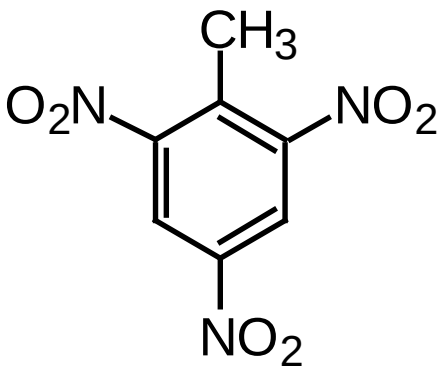
RDX and HMX are based on non-aromatic rings



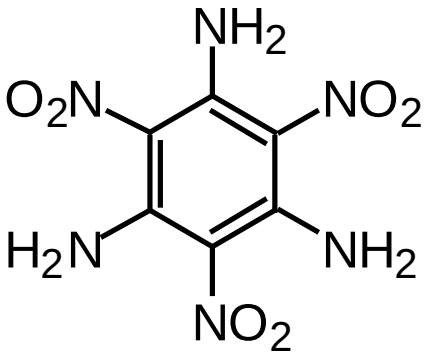
Note the absence of C - C bonds or aromatic rings

Presence of aromatic rings indicates explosive will lead to soot.

TNT

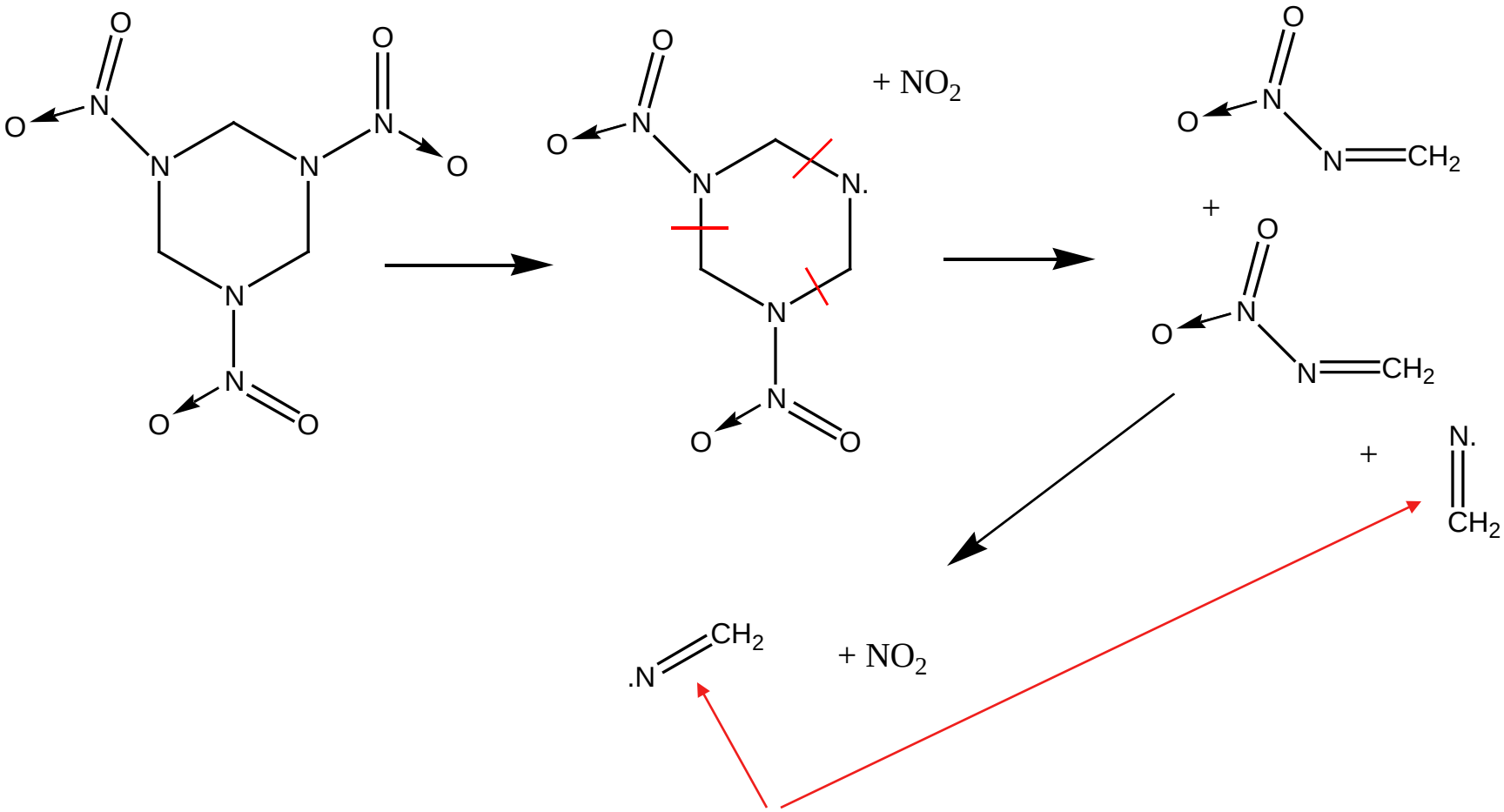


TATB



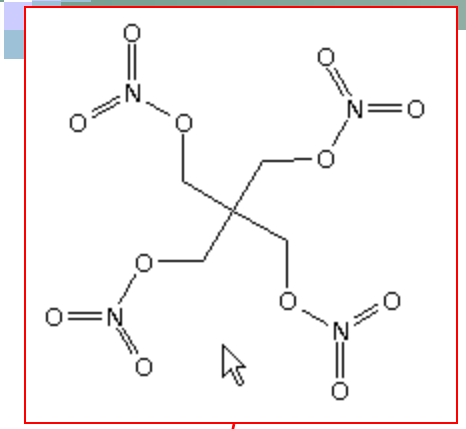
Aromatic rings and lots of C - C bonds

RDX does not produce soot precursors



No carbon – carbon bonds!

Soot tendencies depend on molecular structure



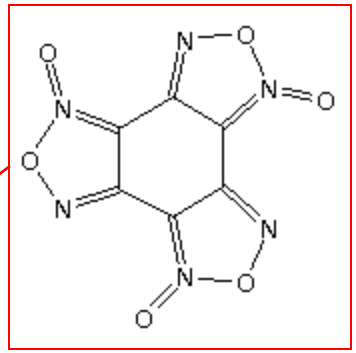
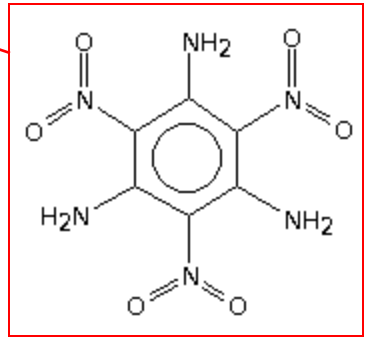


TABLE 1: Detonation Products (in mol) of PETN, BTF, and TATB from Calorimetry Data vs Two Equilibrium Predictions Taken along the CJ Adiabat[a]

	condition		CO	CO_2	graphite	CH_4	H_2O	N_2
PETN 1.74 g/cm^3	confined	experiment	1.6	3.4	0.0	0.0	3.5	2.0
	frozen 1800 K	CHEQ	1.6	3.4	0.0	0.0	3.6	2.0
	equilibrium	CHEQ	0.0	3.8	0.0	0.2	3.1	2.0
BTF 1.86 g/cm^3	confined	experiment	2.9	1.6	1.6	0.0	0.1	2.9
	frozen 1800 K	CHEQ	3.9	1.1	1.1	0.0	0.0	3.0
	equilibrium	CHEQ	0.6	1.7	2.7	0.0	0.0	3.0
TATB 1.87 g/cm^3	confined	experiment	0.4	2.0	3.6	0.0	2.1	2.3
	frozen 1800 K	CHEQ	0.8	1.5	3.6	0.2	2.3	2.9
	equilibrium	CHEQ	0.0	1.7	4.1	0.2	2.6	3.0

[a] "Frozen" data are taken at 1800 K, and "equilibrium" data at 1 atm. These data are computed by the CHEQ code. Results are based on 1 mol of explosives.



From Ree et al, J. Phys. Chem. A, 1996

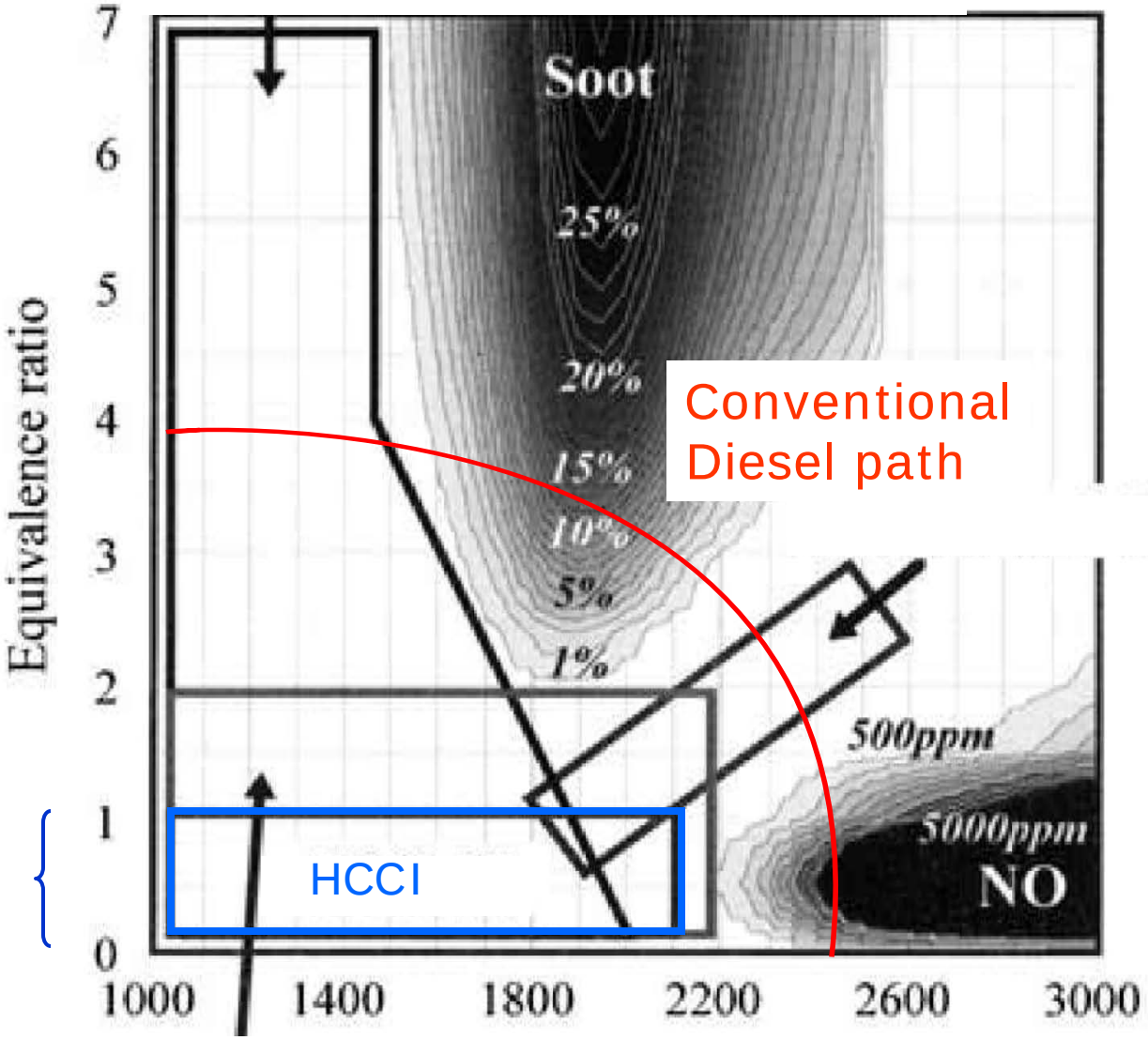
Oxygen is the main obstacle to soot production

- Goal is to produce C - O bonds
- There are many possible sources of oxygen
  - Simplest alternative is air
  - Oxygenated hydrocarbon or other molecules
- This is the principle used in diesel engines to reduce soot production
- This is the explanation for some munitions combustion observations

Molecular structure of oxygenated fuel additive determines its soot reduction properties

- Variability in soot precursor production observed computationally
- Before modeling approach was used, all oxygenates were believed to be equally effective at soot reduction
- Subsequent engine experiments consistent with model results
- Reaction pathways that lead to early CO_2 production “waste” available oxygen atoms in the oxygenate
- Same approach provided sooting estimates for oil sands fuel
- All analysis based on single-component “diesel fuel” surrogate
- Need for more thorough, multicomponent diesel simulations
- Opportunities for designing optimal oxygenated additives

Kitamura, et al. 2002



Higher O_2

Multiscale modeling

- Growth of computing capabilities makes it possible to address a newer class of demanding computational problems
- Multiscales can refer to wide ranges in spatial length scales or, more commonly, time scales
- These problems occur in virtually every discipline
- This offers the potential for including fine scale, short time constant phenomena in practical, engineering simulations
- Example taken from Violi, Kubota et al., 29th Symposium

Nanoparticle Evolution

Young soot growth in flame conditions with assumed constant temperature (1700K) and gas-phase species profile (H, H_2, C_8H_{10}, C_8H_9, $C_{12}H_8$, $C_{12}H_7$) for 10 msec using Violi-Sarofim kinetics.

Violi-Sarofim Mechanism 0x Cyclo-Elimination Rates	Violi-Sarofim Mechanism 1x Cyclo-Elimination Rates	Violi-Sarofim Mechanism 100x Cyclo-Elimination Rates

QuickTime™ and a Cinepak decompressor are needed to see this picture.

QuickTime™ and a Cinepak decompressor are needed to see this picture.

2 nm

Nanoparticles follow different evolutionary paths dependent on the mechanism and kinetic rates defined by the user.