Lawrence Livermore National Laboratory

Rate Constant Estimation for Large Chemical Kinetic Models and Application to Biofuels

ICCK 2001, MIT

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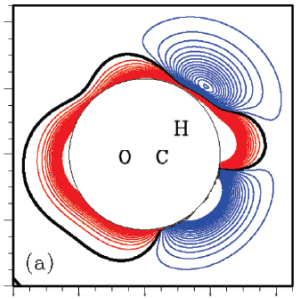
LLNL-PRES-490531

Development of chemical kinetic models for fuels



Fundamental experimental measurements

Ab initio calculations

```
oh         7/13/ 0 rucich    1o   1     0     0g    300.000  5000.000 1710.000     01
 2.85376040e+00 1.02994334e-03-2.32666477e-07 1.93750704e-11-3.15759847e-16     2
 3.69949720e+03 5.78756825e+00 3.41896226e+00 3.19255801e-04-3.08292717e-07     3
 3.64407494e-10-1.00195479e-13 3.45264448e+03 2.54433372e+00                    4
```

c3h8+oh<=>nc3h7+h2o 1.054e+10 0.970 1.586e+03

C1C2 base chemistry

Thermodynamic database

Reaction rate constants

Detailed chemical kinetic model for practical fuels

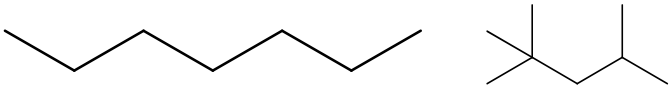
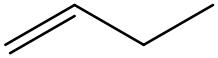
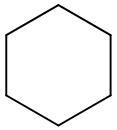
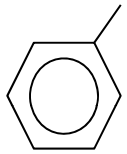
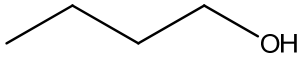
Reaction rate rules

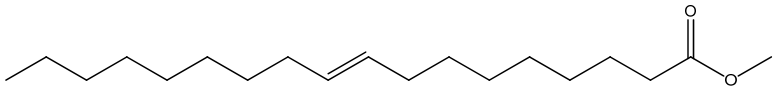
```
reactions
h+o2<=>o+oh 9.65E+14 -0.262 1.62E+04
o+h2<=>h+oh 5.080e+04 2.670 6.292e+03
oh+h2<=>h+h2o 2.160e+08 1.510 3.430e+03
o+h2o<=>oh+oh 2.970e+06 2.020 1.340e+04
h2+m<=>h+h+m 4.577e+19 -1.400 1.044e+05
h2/ 2.5/ h2o/ 12/ co/ 1.9/ co2/ 3.8/
o+o+m<=>o2+m 6.165e+15 -0.500 0.000e+00
h2/ 2.5/ h2o/ 12/ ar/ .83/ co/ 1.9/ co2/ 3.8/ ch4/ 2/ c2h6/ 3/ he/ .83/
o+h+m<=>oh+m 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/
```

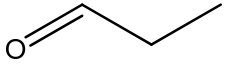
High temperature mechanism

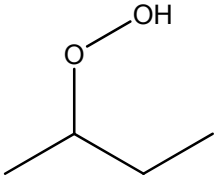
Reaction class 1: Unimolecular fuel decomposition
Reaction class 2: H atom abstractions from fuel
Reaction class 3: Alkyl radical decomposition
Reaction class 4: Alkyl radical + O_2 = olefin + HO_2
Reaction class 5: Alkyl radical isomerization
Reaction class 6: H atom abstraction from olefins
Reaction class 7: Addition of radical species to olefins
Reaction class 8: Alkenyl radical decomposition
Reaction class 9: Olefin decomposition

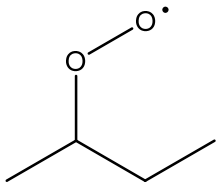
Need reaction rate rules for many chemical classes of fuels

- Alkanes 
- Alkenes 
- Cycloalkanes 
- Aromatics 
- Alcohols 

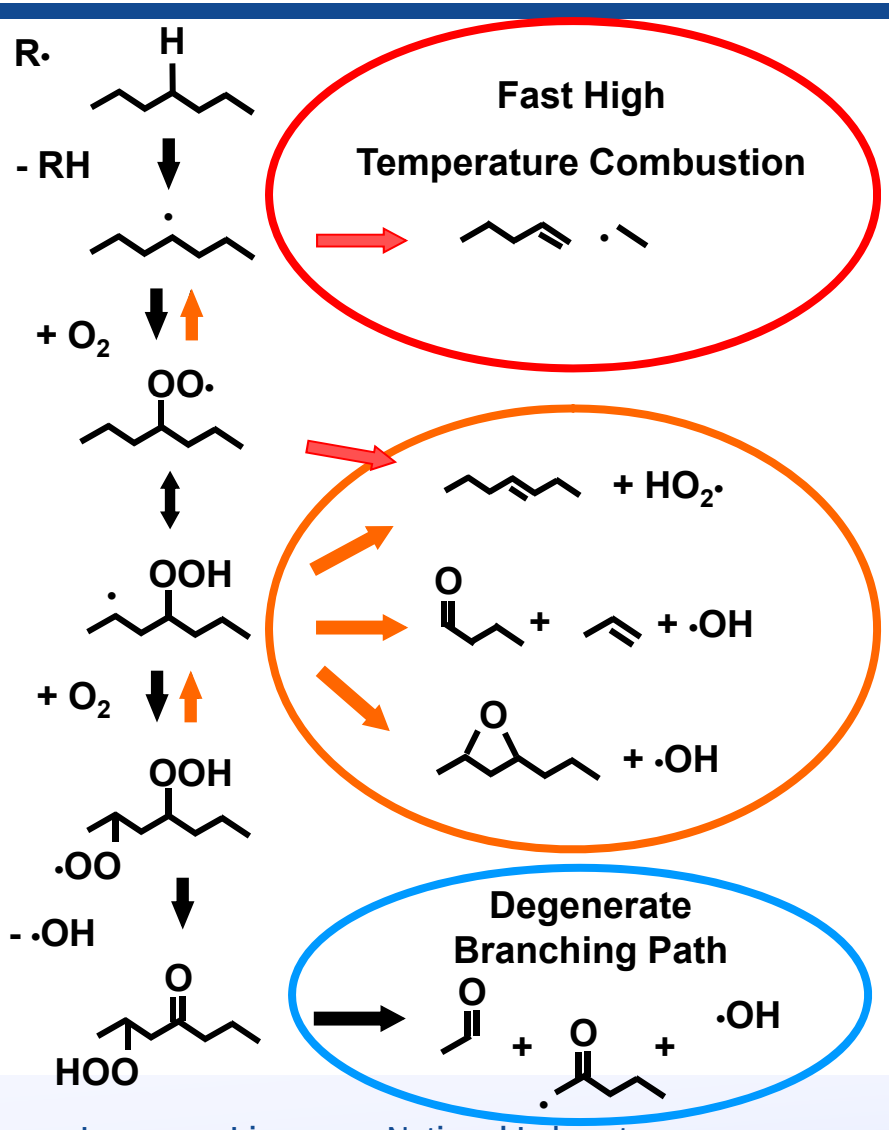


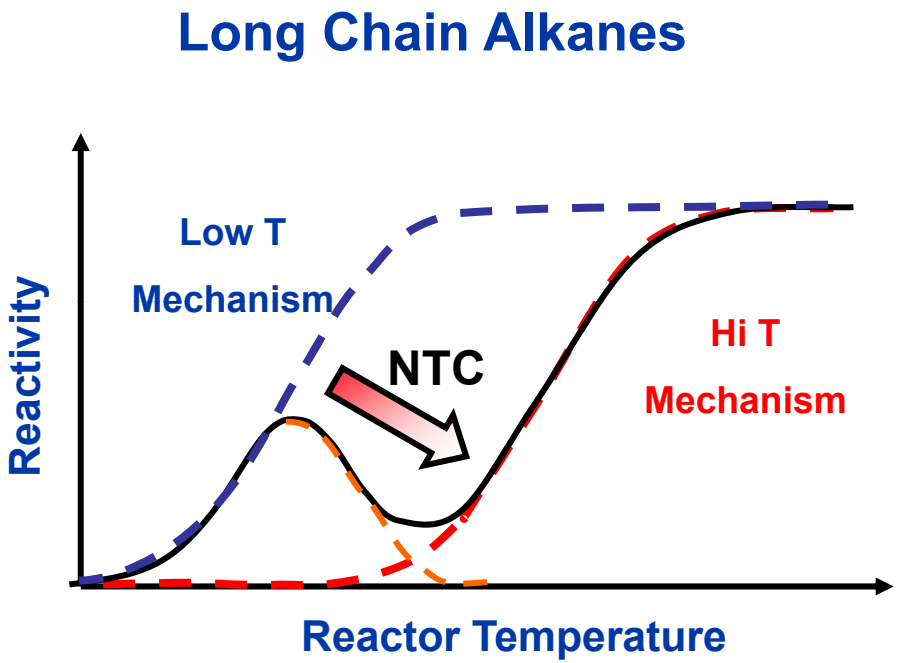
- Methyl esters (biodiesel compounds)
- Carbenes (aldehydes, ketenes) 

- Special structures in intermediate species:
  - Alkylhydroperoxides 

  - Alkylperoxy 

Need reaction rate rules for many types of reaction steps





Assign reaction rate rules by reaction classes

High temperature mechanism

Reaction class 1: Unimolecular fuel decomposition
Reaction class 2: H atom abstractions from fuel
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Reaction class 7: Addition of radical species to olefins
Reaction class 8: Alkenyl radical decomposition
Reaction class 9: Olefin decomposition

Reaction classes for low temperature reactions

Low temperature mechanism

Reaction class 10: Alkyl radical addition to O_2 (R + O_2)
Reaction class 11: R + R'O_2 = RO + R'O
Reaction class 12: Alkylperoxy radical isomerization
Reaction class 13: RO_2 + HO_2 = ROOH + O_2
Reaction class 14: RO_2 + H_2O_2 = ROOH + HO_2
Reaction class 15: RO_2 + CH_3O_2 = RO + CH_3O +O_2
Reaction class 16: RO_2 + R'O_2 = RO + R'O + O_2
Reaction class 17: ROOH = RO + OH
Reaction class 18: RO Decomposition
Reaction class 19: QOOH = Cyclic Ether + OH
Reaction class 20: QOOH = Olefin + HO_2
Reaction class 21: QOOH = Olefin + Aldehyde or Carbonyl + OH
Reaction class 22: Addition of QOOH to molecular oxygen O_2
Reaction class 23: O_2QOOH isomerization to carbonylhydroperoxide + OH
Reaction class 24: Carbonylhydroperoxide decomposition
Reaction class 25: Reactions of cyclic ethers with OH and HO_2

Reaction rate rules make the assignment of reaction rate constants manageable

Class 2

Fuel + (H, OH, CH_3, HO_2) => fuel radical + (H_2, H_2O, CH_4, H_2O_2)

H- atom abstraction rate rules for alkanes

	C-H type	A (cm^3 mol^{-1} s^{-1})	n	E_A (cal)
H	1°	2.22E+05	2.54	6,756
	2°	6.50e+05	2.40	4,471
	3°	6.02E+05	2.40	2,583
OH	1°	1.76E+09	0.97	1,586
	2°	2.34E+07	1.61	-35
	3°	5.73E+10	0.51	63
CH_3	1°	1.51E-01	3.65	7,154
	2°	7.55E-01	3.46	5,481
	3°	6.01E-10	6.36	893
HO_2	1°	6.80E+00	3.59	17,160
	2°	3.16E+01	3.37	13,720
	3°	6.50E+02	3.01	12,090

Class 1

Reaction rate rule issues: fuel decomposition reactions

- Alkanes
  - Set by reverse reaction
    - Exothermic direction
    - C-C bond breaking most important
    - Some variations in forward rate constants, even though you think they should be all the same

C-C-C-C <=> C. + C-C-C.

C-C-C-C <=> C-C. + C-C.

	Fwd				Rate at T 1300 K	rev		
	A fwd	n fwd	AT^n	EA fwd		A rev	n rev	EA rev
	cm3-mol-s units			cal/mole		cm3-mol-s units		cal/mole
C3H8=C2H5+CH3	1.77E+23	-1.889	2.32E+17	9.04E+04	145	1.00E+13	0	0.0
C4H10=CH3+NC3H7	1.59E+23	-1.848	2.80E+17	9.03E+04	184	1.00E+13	0	0.0
c4h10=c2h5+c2h5	6.73E+24	-2.297	4.73E+17	8.93E+04	456	8.00E+12	0	0.0
NC10H22=C7H15-1+NC3H7	4.78E+24	-2.206	6.47E+17	8.89E+04	745	8.00E+12	0	0.0
NC10H22=C6H13-1+PC4H9	7.54E+24	-2.3	5.18E+17	8.88E+04	613	8.00E+12	0	0.0
NC10H22=C5H11-1+C5H11-1	9.81E+23	-2.023	4.92E+17	8.86E+04	622	8.00E+12	0	0.0

Class 2

Reaction rate rules for H-atom abstraction from alkanes

Fuel + (H, OH, CH_3, HO_2) => fuel radical + (H_2, H_2O, CH_4, H_2O_2)

	C-H type	A (cm^3 mol^{-1} s^{-1})	n	E_A (cal)
H	1°	2.22E+05	2.54	6,756
	2°	6.50e+05	2.40	4,471
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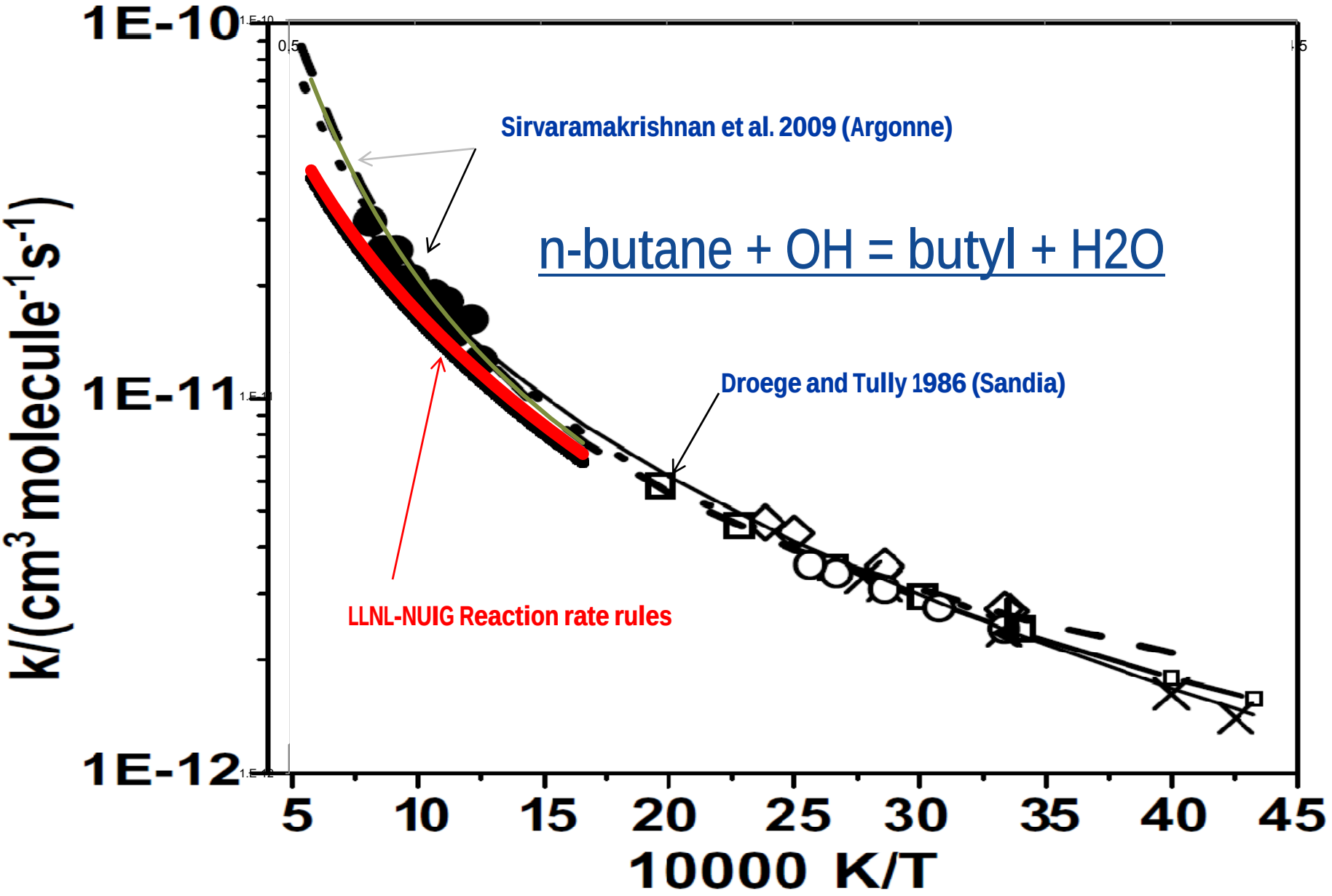
HO_2	1°	6.80E+00	3.59	17,160
	2°	3.16E+01	3.37	13,720
	3°	6.50E+02	3.01	12,090

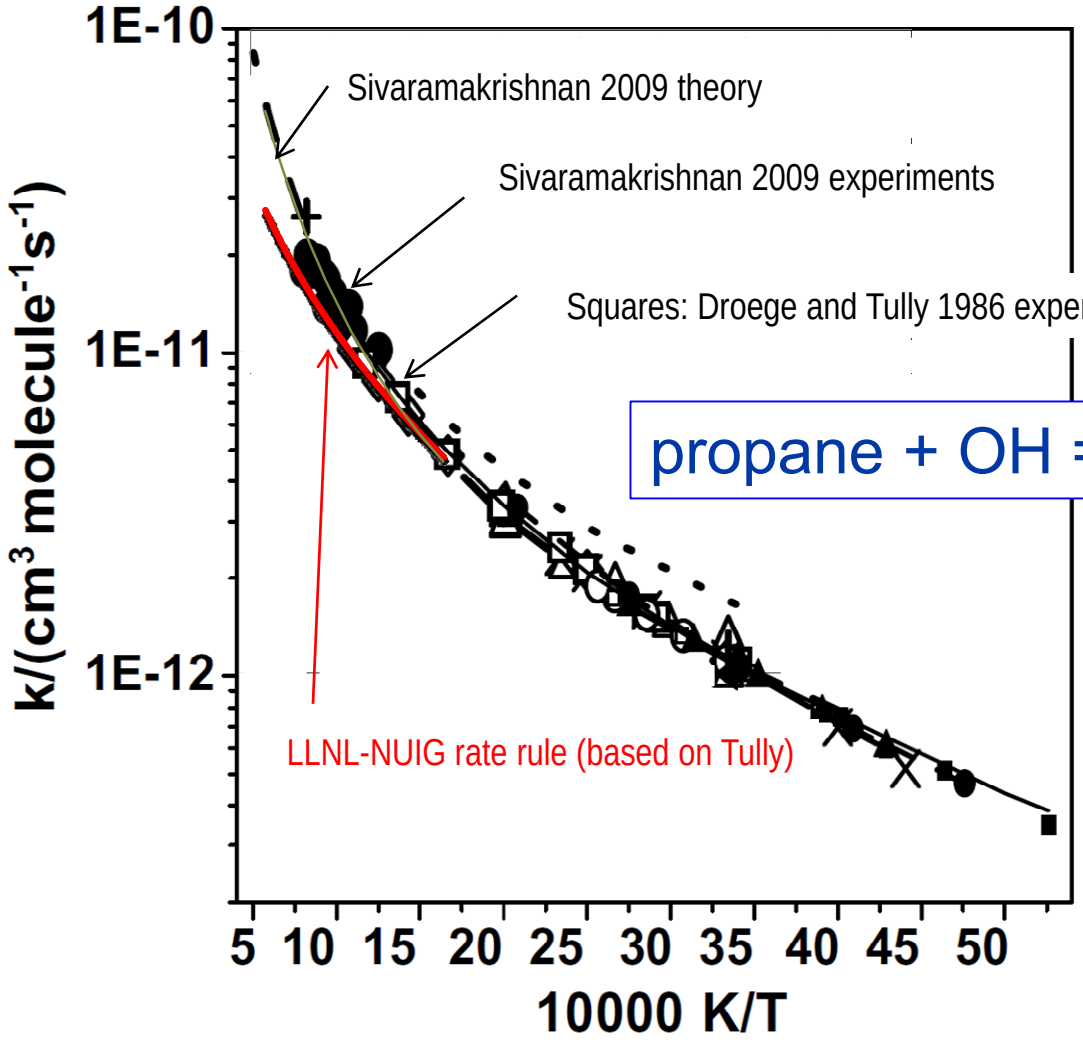
New Argonne data for OH + alkanes

Class 2



New measured and calculated rate constants for OH + alkanes are higher at T > 900K

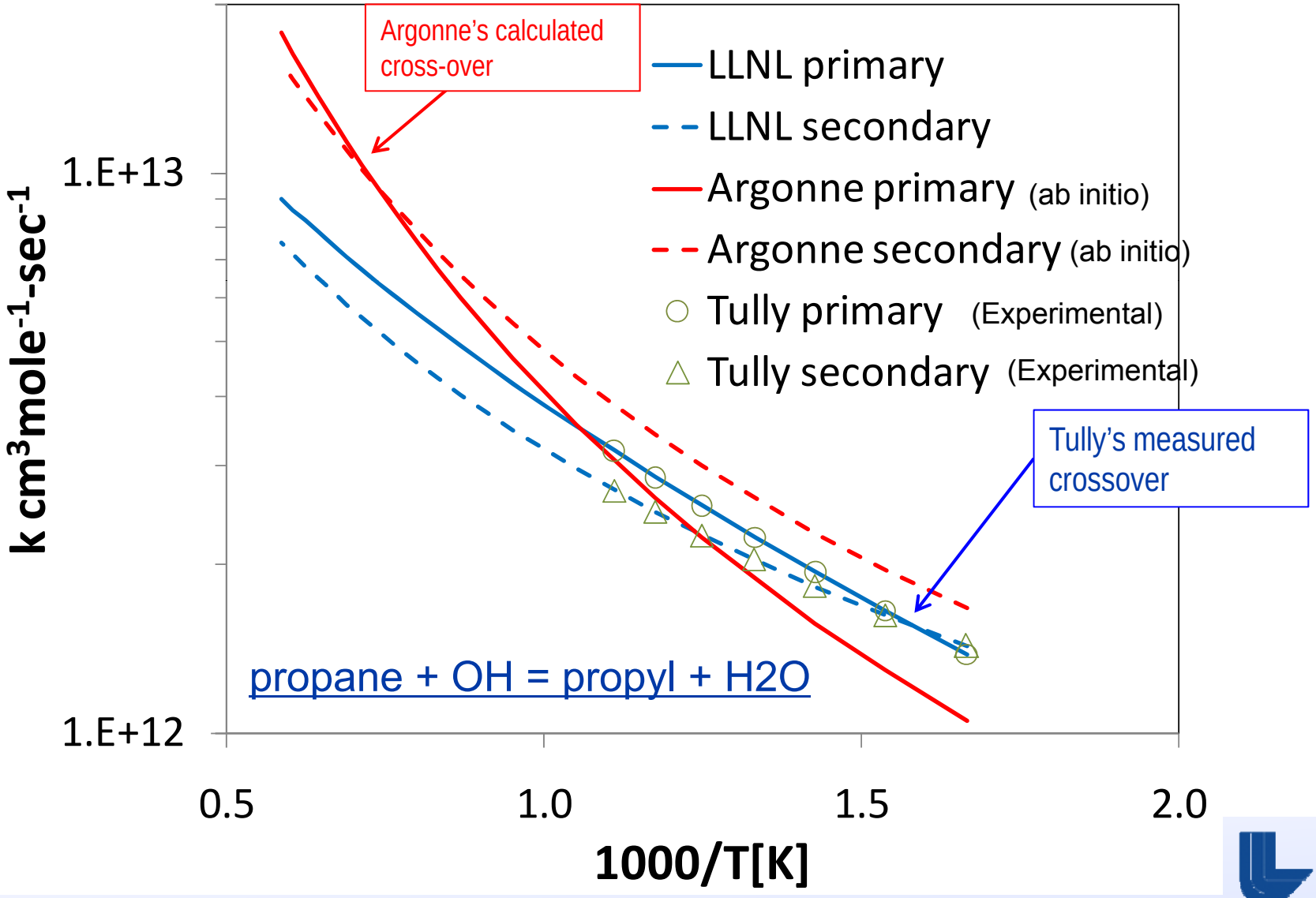
Class 2



propane + OH = propyl + H2O

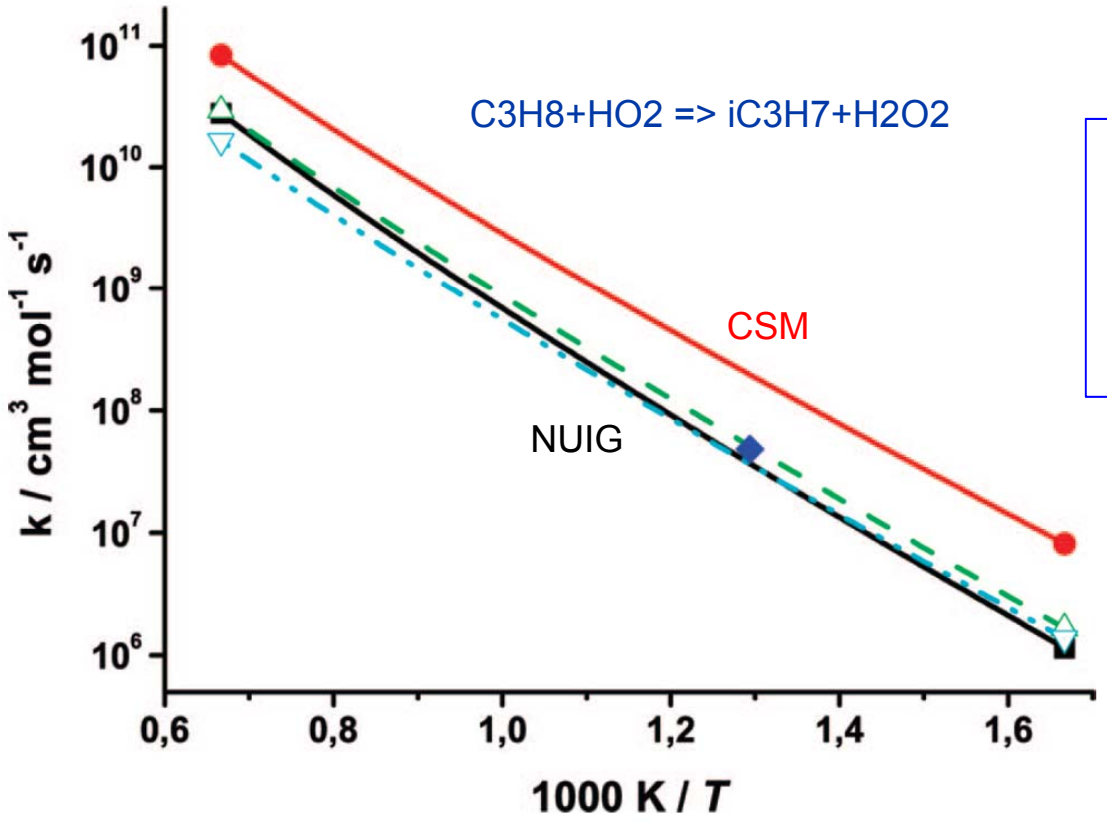
Ab initio calculations show higher rates due to higher primary rate

Class 2



H-atom abstraction from the fuel: HO2 + alkanes
Uncertainty in rate of a factor of 3 - 6

Class 2



Ignition very sensitive to this rate constant under RCM conditions

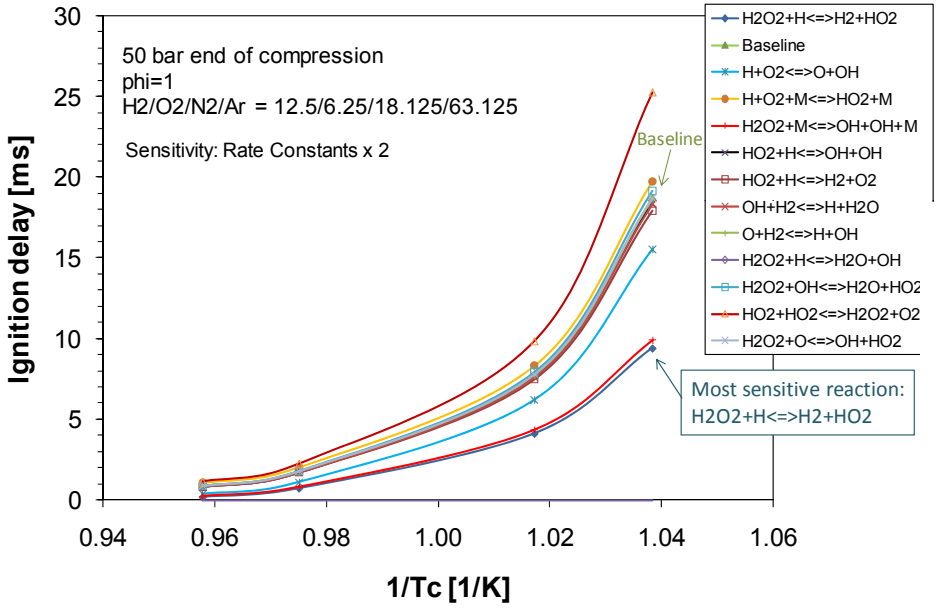
Figure 6. $k(C_3H_8 + HO_2^{\bullet} \rightarrow i\text{-}C_3H_7^{\bullet} + H_2O_2)$. This work (—■—), Carstensen[18] (—●—), Scott[8] (--Δ--), Orme[14] (-••▽-••), Baldwin[11] (◆).

Fuel + HO2 shows high sensitivity when the fuel is hydrogen

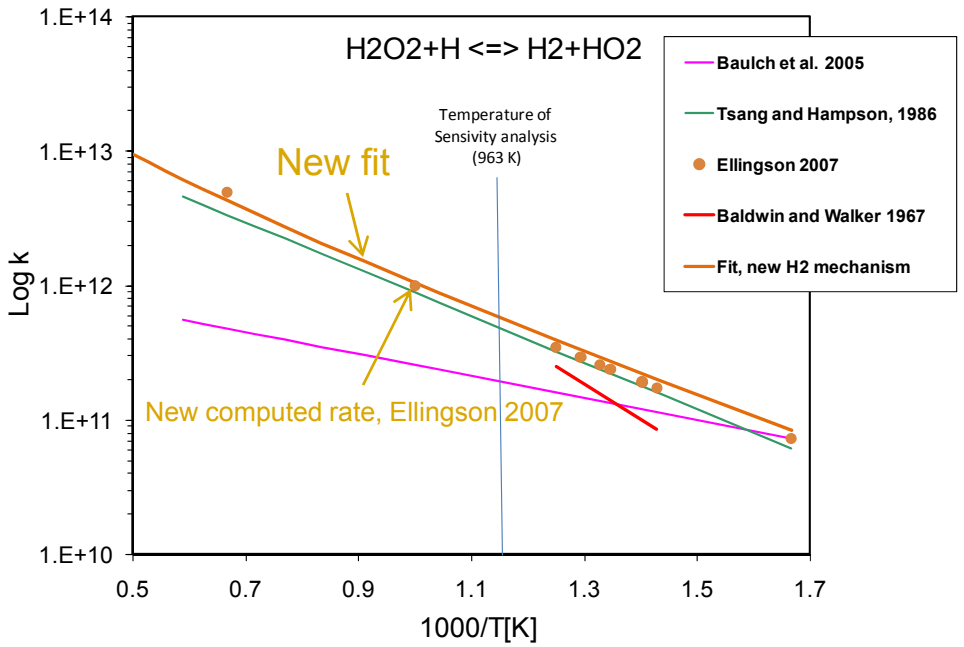
Class 2

Sensitivity results under conditions in rapid compression machine:

H2O2+H⇔H2+HO2



New rate constant fit:



Important branching sequence at high pressure:

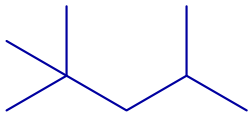
H2+HO2=>H+H2O2

H2O2=>OH+OH

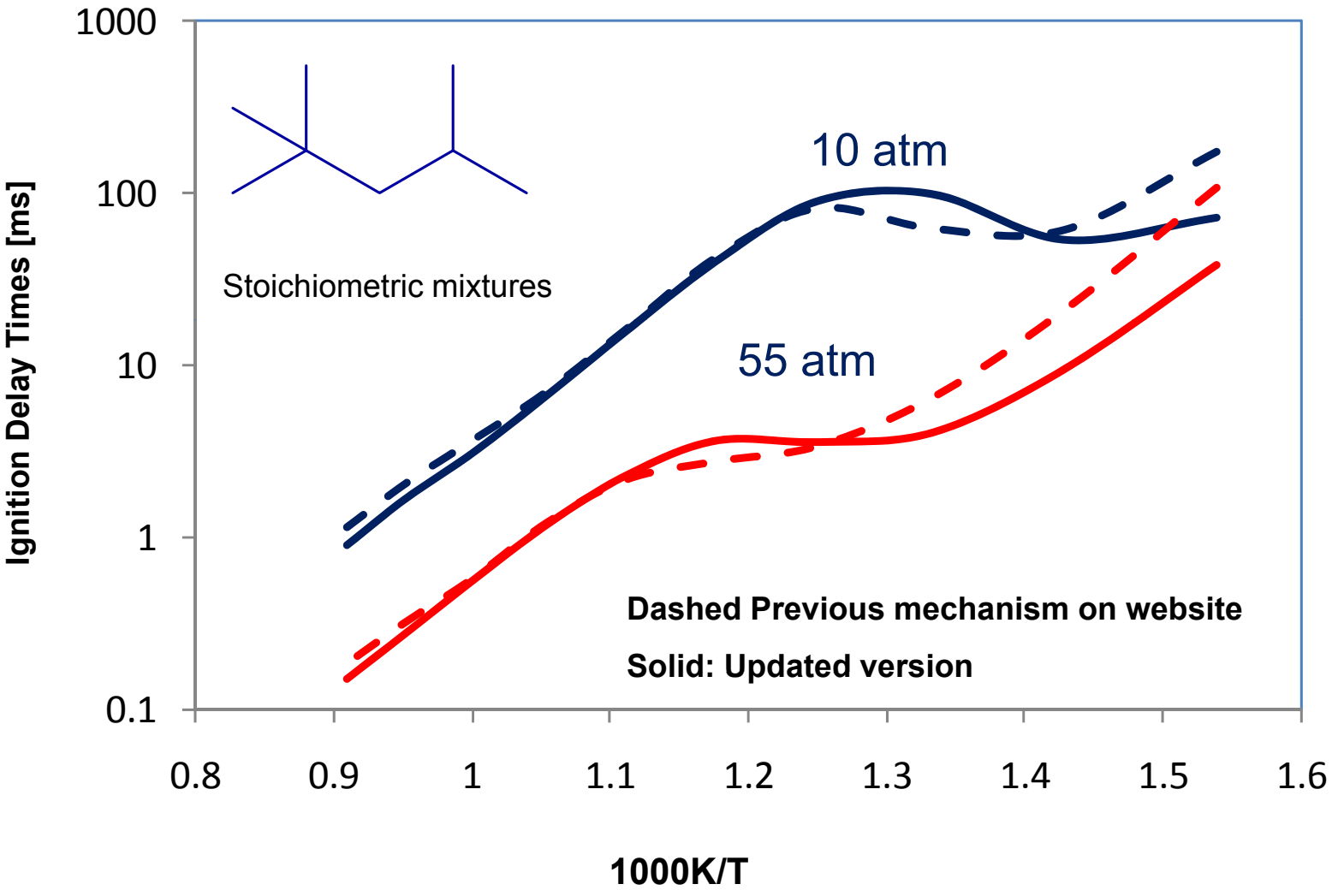
Retarding reaction:

HO2+HO2=>H2O2+O2

Class 3: alkyl radical decomposition. Improvements for iso-octane

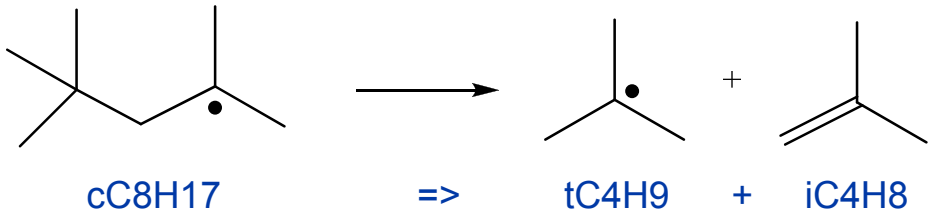


Class 3

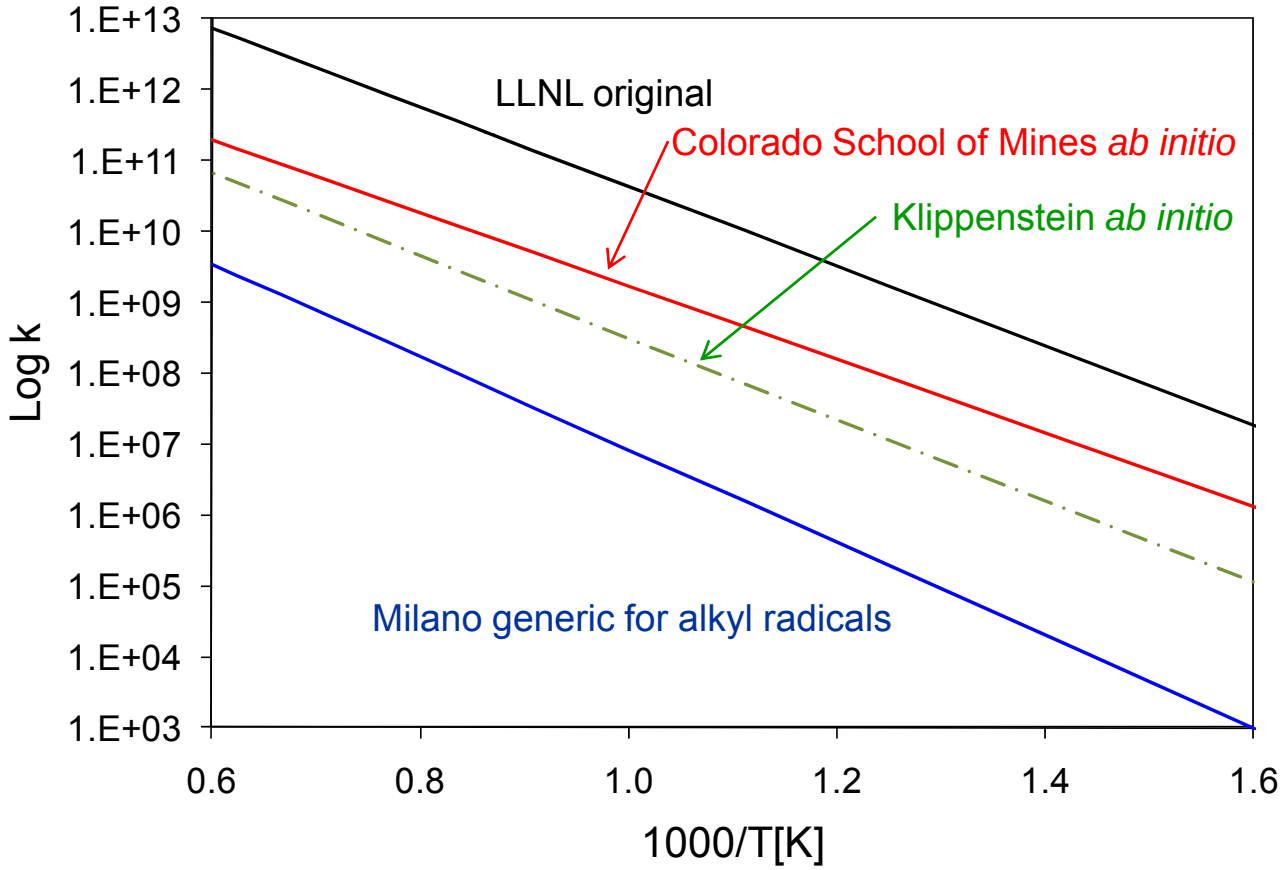


More accurate estimate for iso-octyl radical decomposition rate constant:

Class 3



cC8H17 => tC4H9 + iC4H8

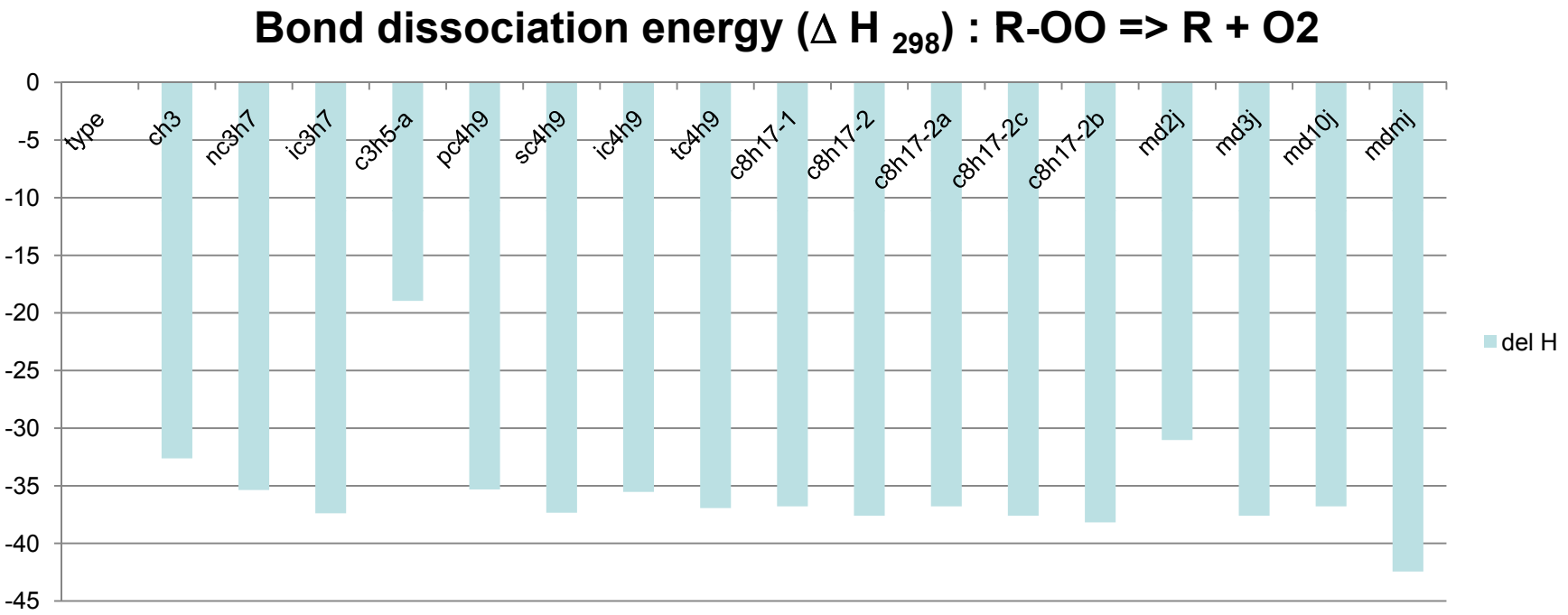


Low temperature reactions:

Effect of R-O2 bond strength varies with bond type and controls amount of low temperature chemistry

Class 10
R+O2 ⇔ RO2

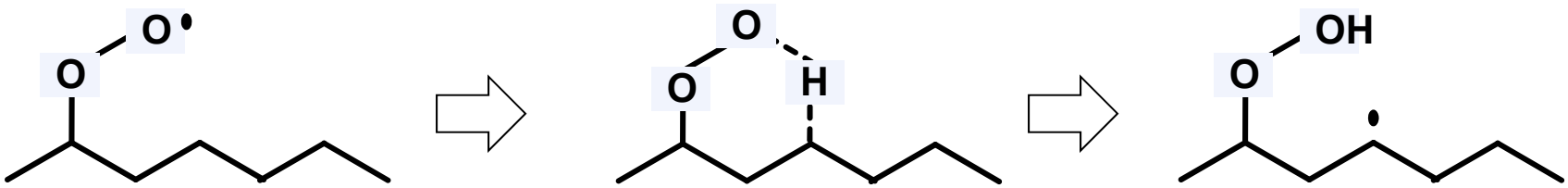
Values used in LLNL models



Low temperature chemistry: ROO → QOOH isomerizations

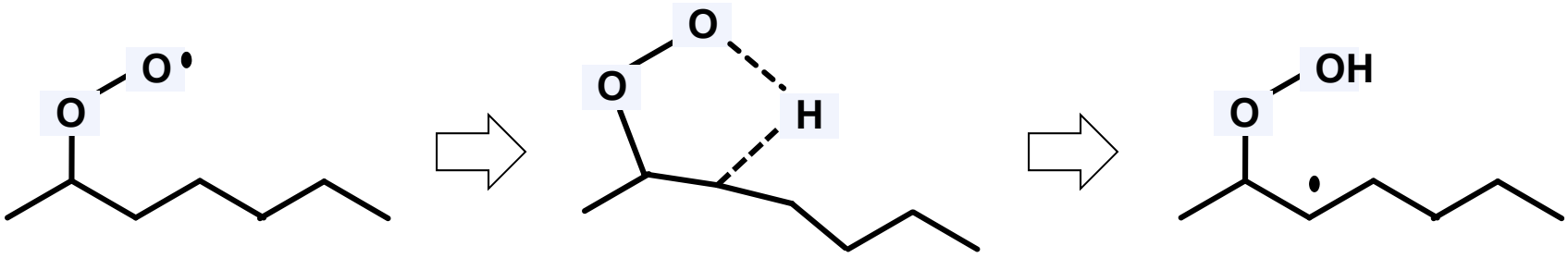
Class 12

6 Member ring isomerization



$K_6 = 2.5E+10 \cdot \exp(-20450/RT)$

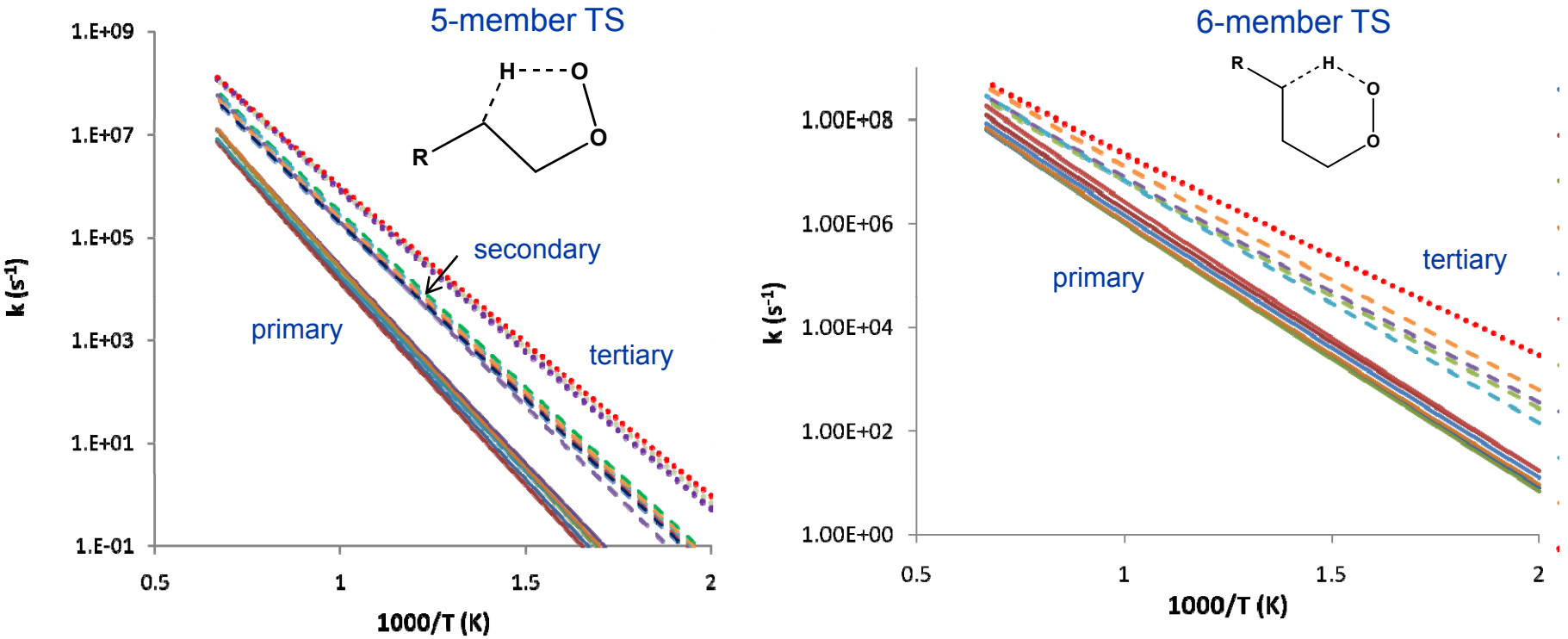
5 Member ring isomerization



$K_5 = 2.0E+11 \cdot \exp(-26450/RT)$

RO_2 isomerizations: Rate constants from computational chemistry (Dean, Carstensen et al. Colorado School of Mines)

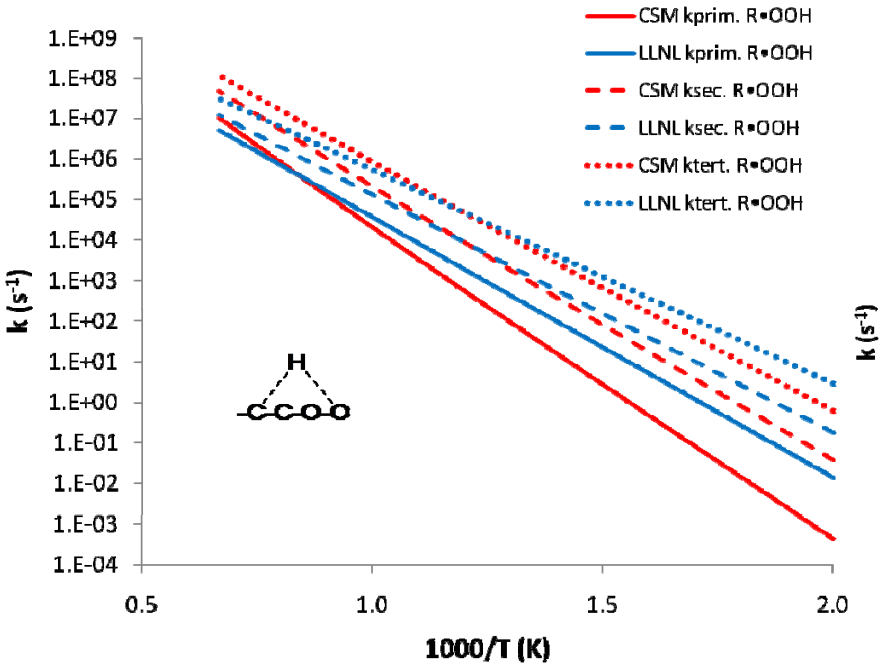
Class 12

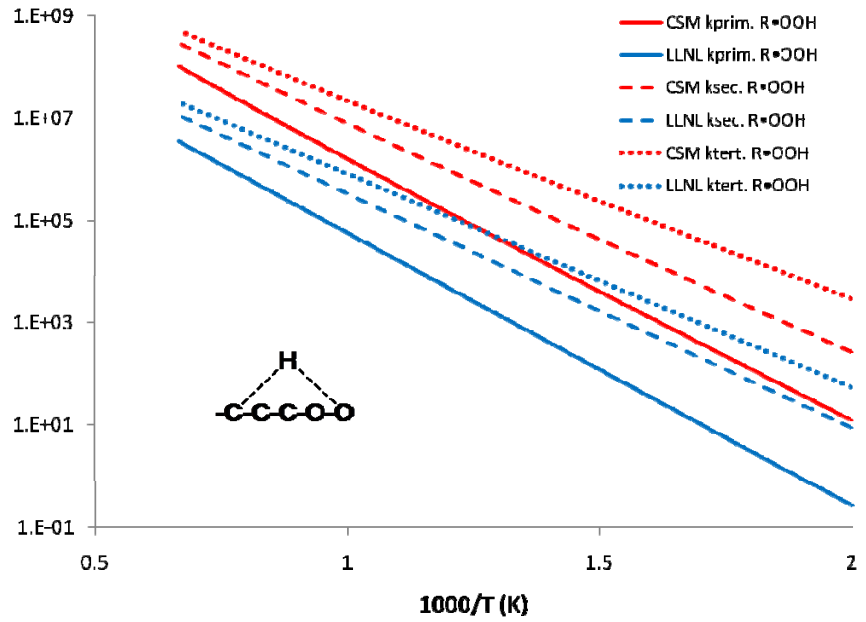


- Activation energy depends on ring size *and* overall thermochemistry
- Amenable to rule generation

Significant differences in CSM vs. LLNL rate constants: RO2 isomerization

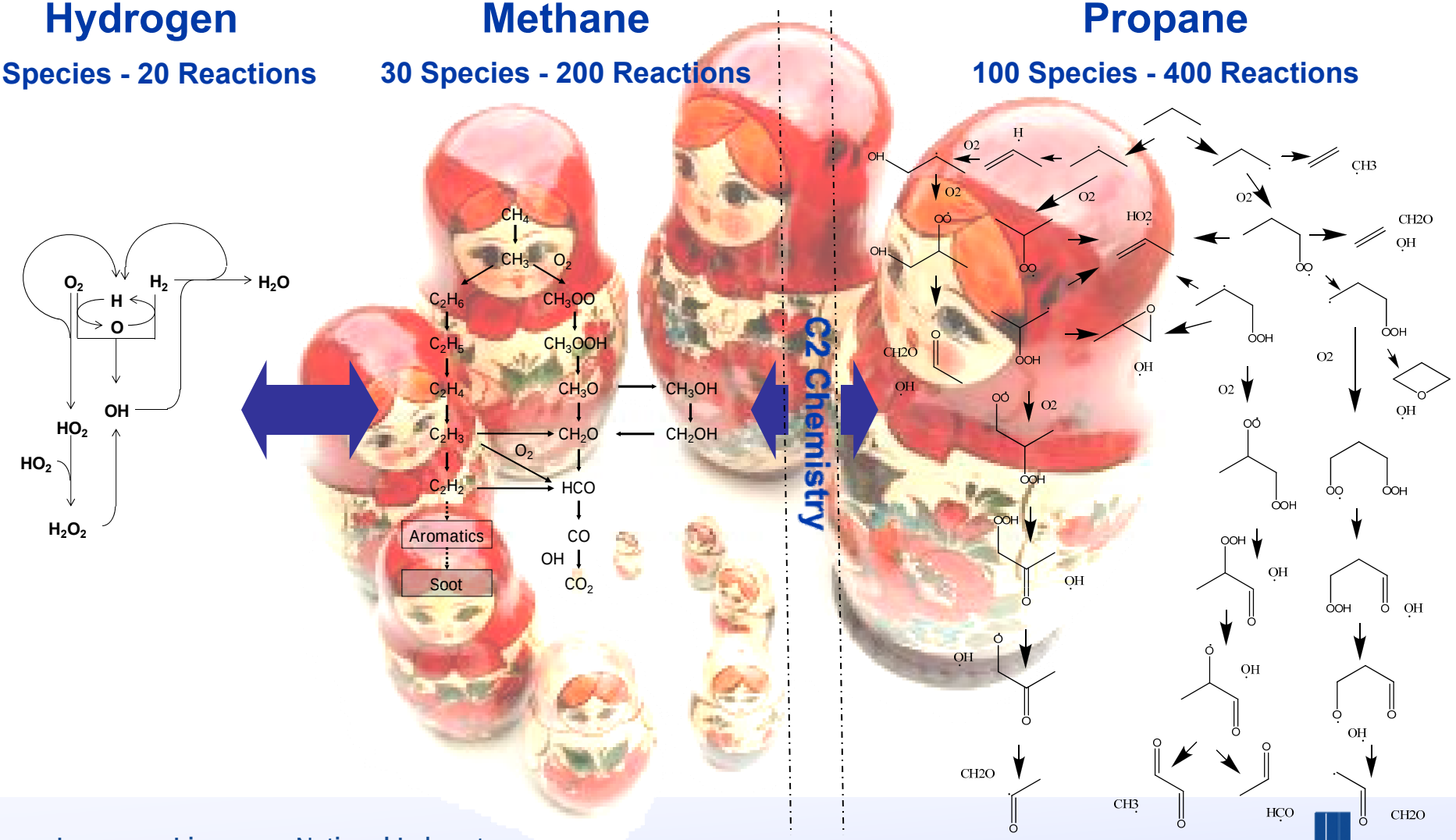
Class 12



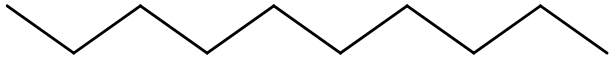
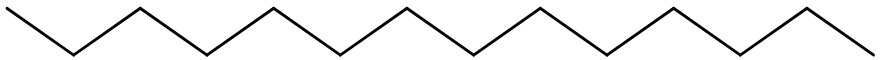


- CBS-QB3 results generally lower than LLNL values for 5-member TS
- CBS-QB3 results much higher than LLNL values for 6-member TS
  - Mainly due to higher A-factors (much higher than alkyl isomerizations)
- Differences lead to significantly different reaction pathways

Mechanisms for fuels are built in a hierarchical manner and increase rapidly in size with fuel size

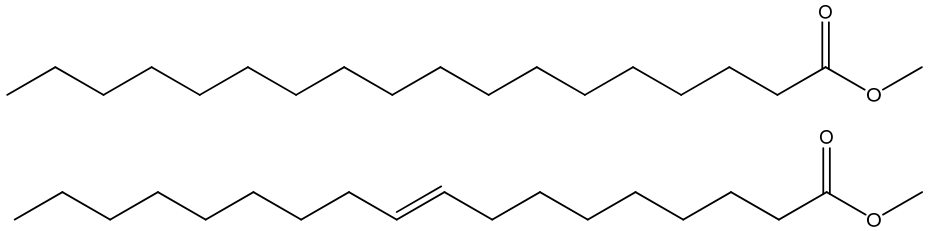


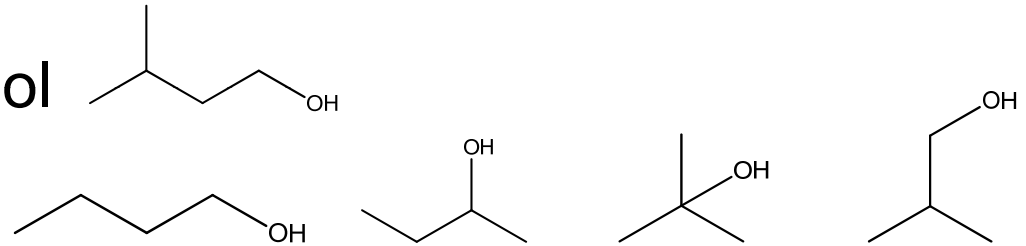
Fuels Size and Mechanism Size

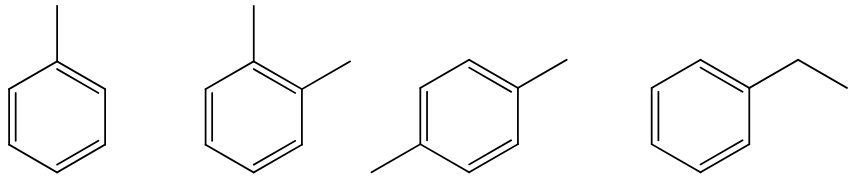
n-Alkane	Mechanism Size (Detailed Mechanism)
C_8H_{18} 	700 Species 3150 Reactions
$C_{10}H_{22}$ 	950 Species 4050 Reactions
$C_{12}H_{26}$ 	1250 Species 5150 Reactions
$C_{14}H_{30}$ 	1650 Species 5150 Reactions
$C_{16}H_{34}$ 	2100 Species 8150 Reactions

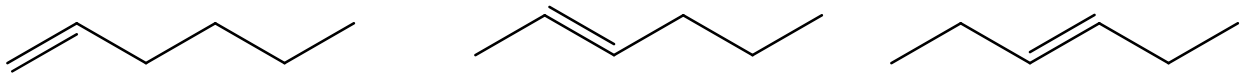
Application of rules to biofuels

- Biodiesel
  - Large methyl esters
- Alcohols
  - Iso-pentanol
  - Butanol
- Aromatics
- Olefins









Biofuels

- Biodiesel
- New types of biofuels
  - Biomass
  - derived from algae and other single cell organisms

rapeseed

Algal pilot scale bioreactor in Lawrence, Kansas

From: Smith, Sturm, deNoyelles and Billings, Trends Ecol. Evol. (2010)

Algal oil-derived fuels contain additional esters

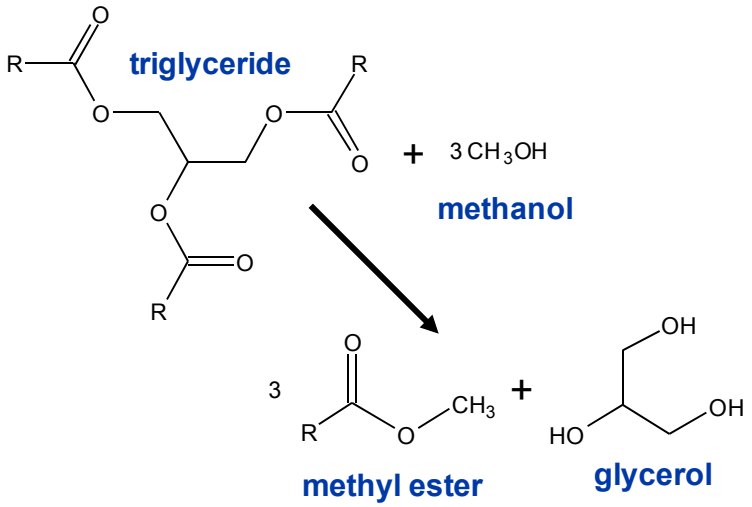
Approximate weight percent of fatty acids in various vegetable and algal oil feedstocks [15,19, present work]. The nomenclature Cx:y denotes the length of the hydrocarbon chain (x) and the number of double bonds in the hydrocarbon chain (y) of the fatty acid.

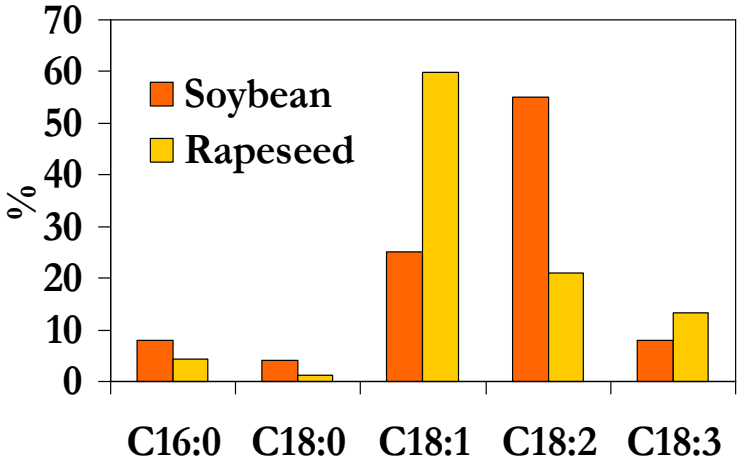
Feedstock	C8:0	C10:0	C12:0	C14:0	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3	C20:0	C20:4	C20:5	C22:6
Soy					10		4	24	54	8				
Canola					5		2	64	20	8				
Coconut	9	6	49	17	8		2	5	2					
Palm				1	42		5	41	10					
Jatropha					11		17	13	47		5			
Nannoch. Oculata				4	29	24	9	4	1	1		5	22	
Iso. Galbana				13	36	32	1	4	4				7	3

Table 1 also includes the fatty acid composition for two algal oils: *Nannochloropsis Oculata* and *Isochrysis Galbana 3*. The former algae species is currently under consideration for wide scale production and its fatty acid composition was measured from algal oil samples provided by Solix Biofuels [18].

From: Marchese and B. Fisher, "Measurement of Gaseous and Particulate Emissions from Algae-Based Fatty Acid Methyl Esters," SAE 2010-01-1523.

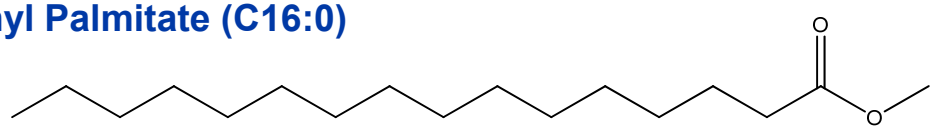
Soybean and rapeseed derived biodiesels have only 5 principal components



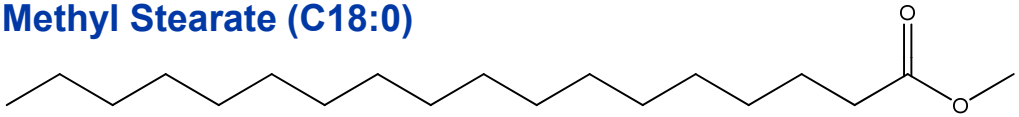


Fatty acid methyl esters (FAMEs):

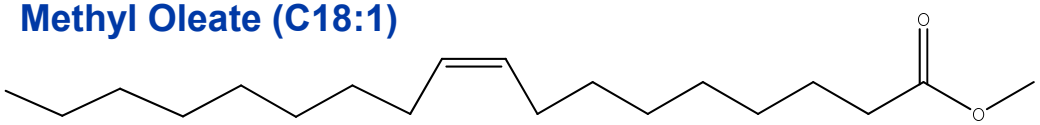
Methyl Palmitate (C16:0)



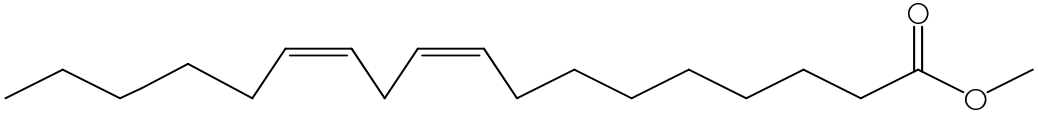
Methyl Stearate (C18:0)



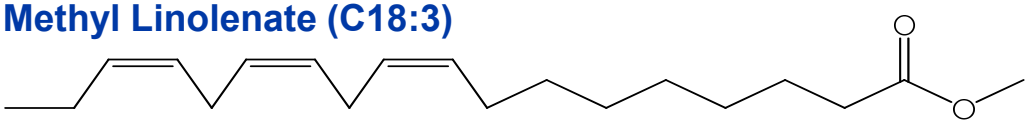
Methyl Oleate (C18:1)



Methyl Linoleate (C18:2)

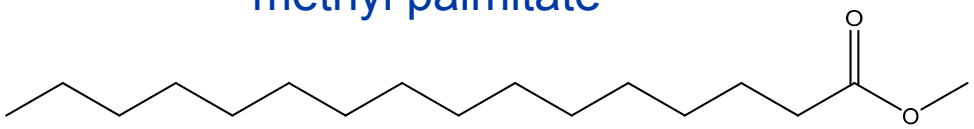


Methyl Linolenate (C18:3)

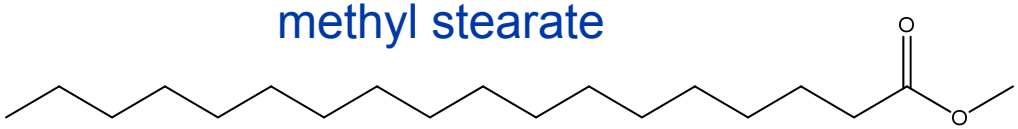


Assembled chemical kinetic model for all of the five main components in biodiesel derived from soybeans or rapeseed oil

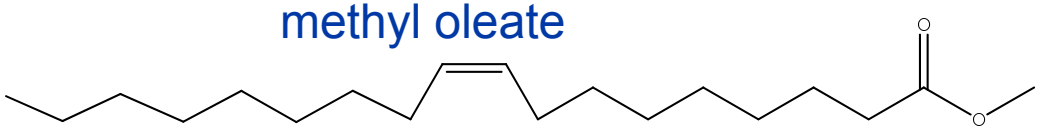
methyl palmitate



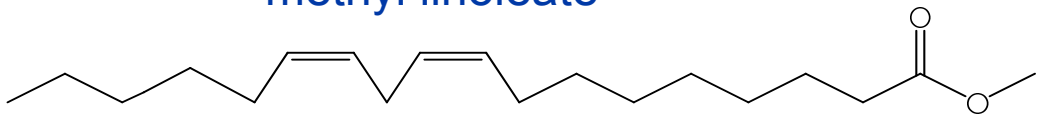
methyl stearate



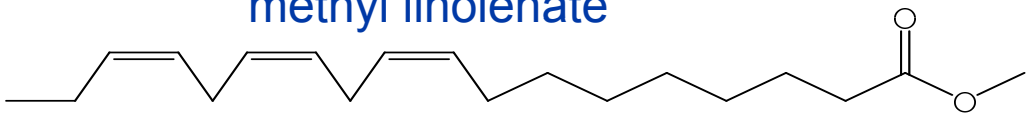
methyl oleate



methyl linoleate



methyl linolenate



Built with the same reaction rate rules as our successful methyl decanoate and methyl decenoate mechanism

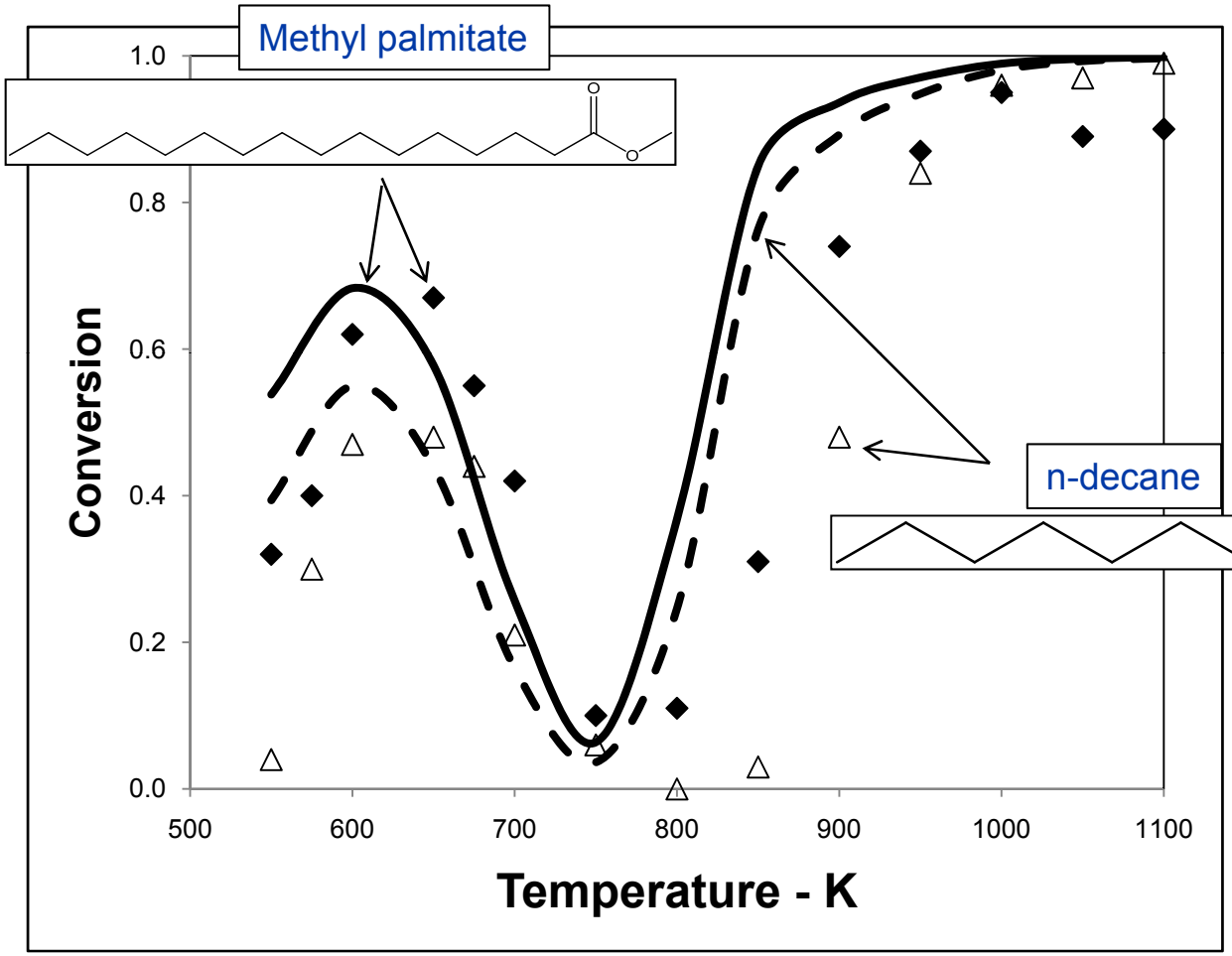
5 component mechanism, approximately

5,000 species
20,000 reactions

Model with all 5 components now published and available:

Westbrook, Naik, Herbinet, Pitz, Mehl, Sarathy and Curran, "Detailed chemical kinetic reaction mechanisms for soy and rapeseed biodiesel fuels," Combustion and Flame, 2011.

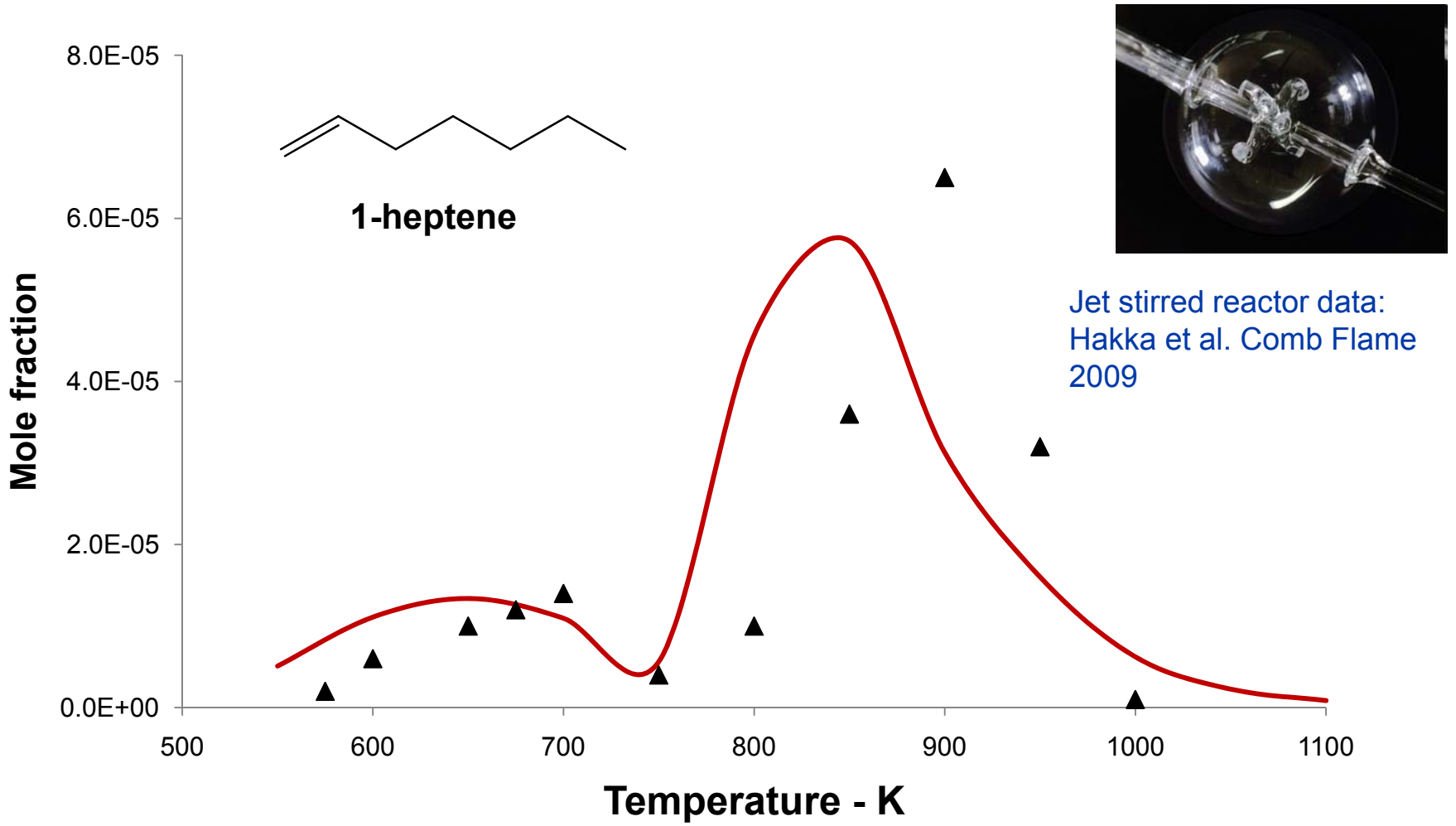
Experimental validation: New biodiesel model reproduces oxidation of n-decane/methyl palmitate mixture in jet stirred reactor



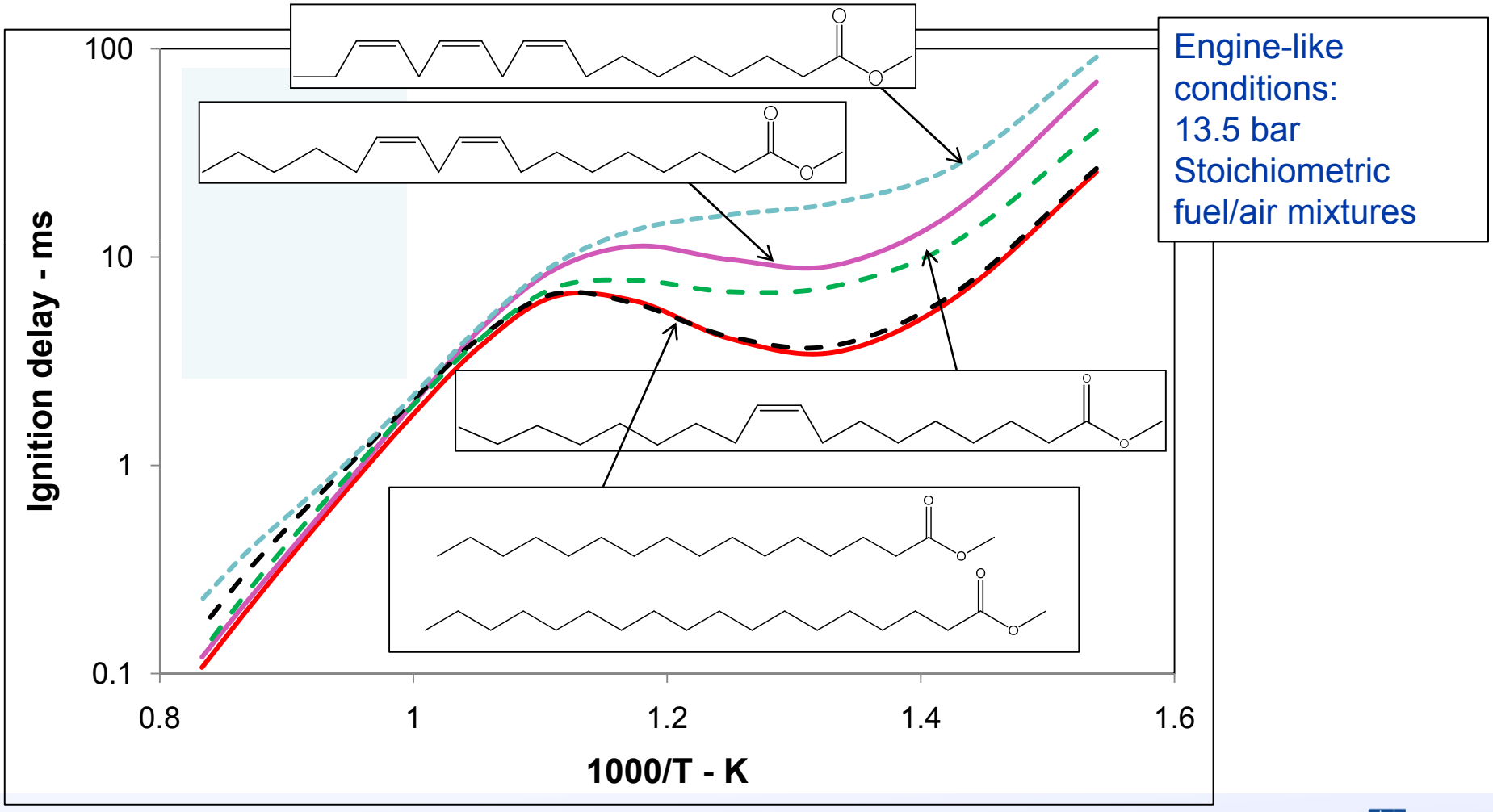
Stoichiometric fuel/O_2/He mixtures
1 atm
1.5 s residence time

Jet stirred reactor data: Hakka et al. Comb Flame 2009

Many of the predicted species profiles compare well with experiments: e.g. 1-heptene



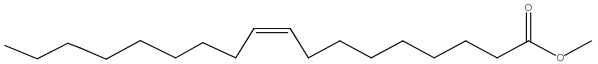
Biodiesel components ignite in order of number of double bonds



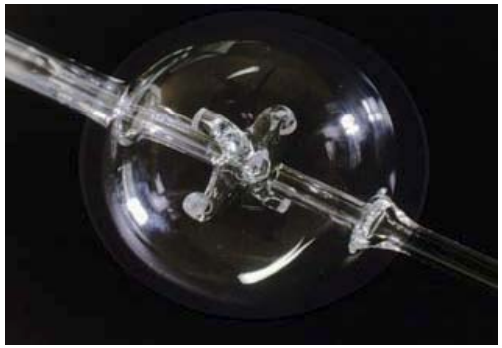
Increased number of double bonds reduces low T reactivity of individual components in stirred reactor at diesel conditions

Diesel engine conditions of high pressure and fuel-rich mixtures:
50 bar, Φ=2 (Fuel: 200 ppm, residence time = 0.05 s)

methyl stearate CN101

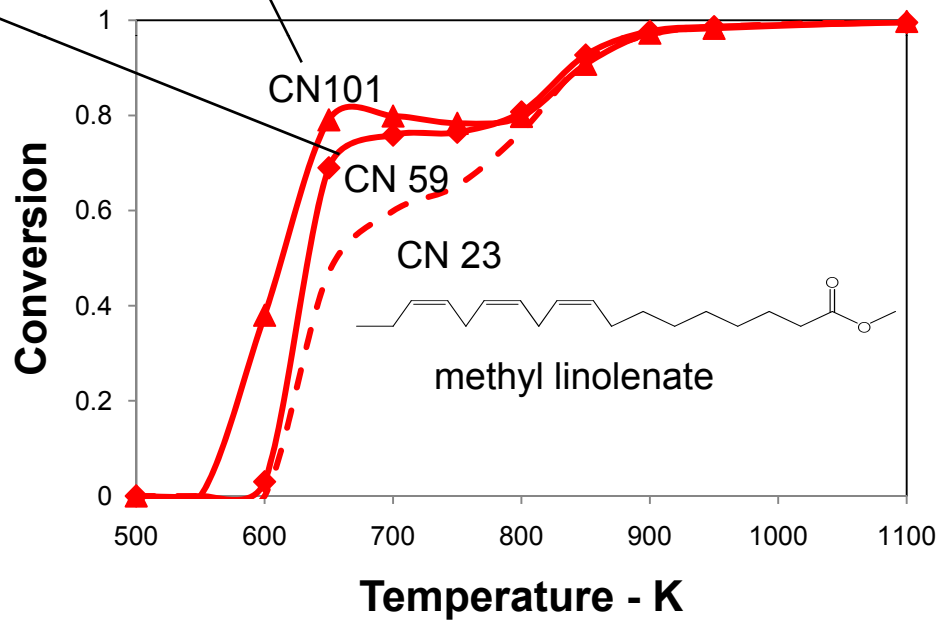


methyl oleate CN 59



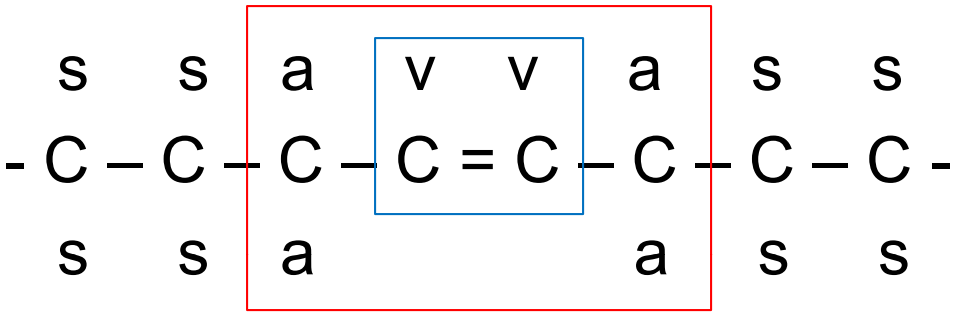
Jet stirred reactor

Simulated conversions of biodiesel components



Derived cetane numbers from Knothe (2010)

C = C double bonds reduce low T reactivity



- Inserting one C=C double bonds changes the reactivity of 4 carbons atoms in the C chain
- Allylic C – H bond sites are weaker than most others
- Therefore they are preferentially abstracted by radicals
- O_2 is also very weakly bound at allylic sites and falls off rapidly, inhibiting low T reactivity

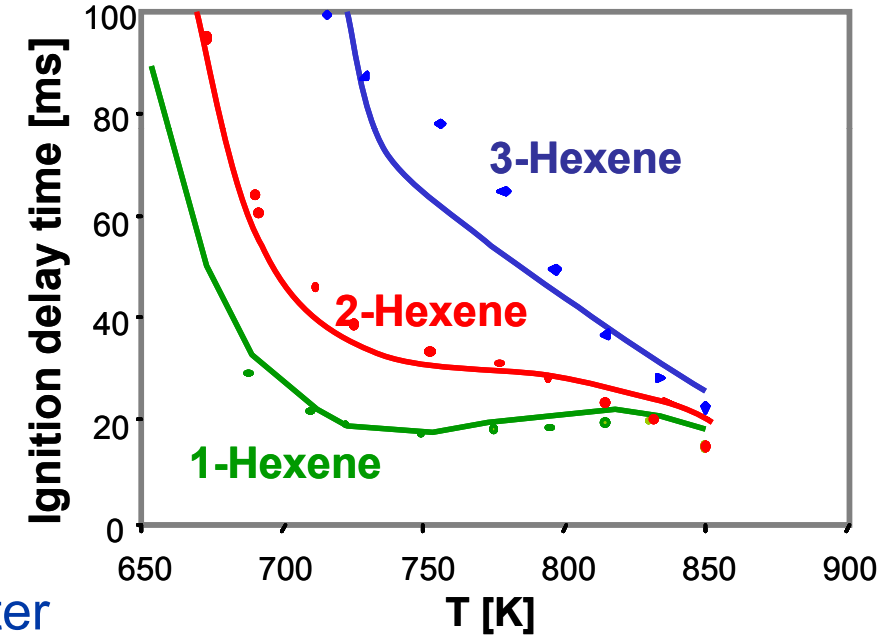
We have seen the same effect in hydrocarbon fuels: hexenes

C = C - C - C - C - C	1-hexene
C - C = C - C - C - C	2-hexene
C - C - C = C - C - C	3-hexene

RO2 isomerization initiates low temperature reactivity

Moving the double bond towards the center of the molecule "blocks" more RO2 kinetics

Ignition delay times in a rapid compression machine of hexene isomers (0.86-1.09 MPa, Φ=1):



Experimental data: Vanhove et al. PCI2005
Simulations: Mehl, Vanhove, Pitz, Ranzi Combustion and Flame 2008

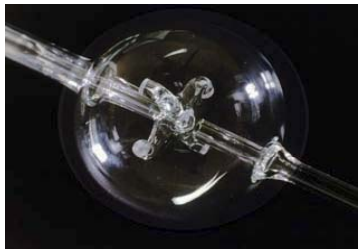
Plant and animal fat oils have different fatty acid profiles that affect reactivity in a diesel engine

	Sunflower	Safflower	Linseed	Jatropha	Cottonseed	Corn	Olive	beef tallow	Palm	Peanut	Soy	rapeseed
palmitate	7	7	7	4	23	10	13	28	46	11	8	4
stearate	5	2	1	8	3	4	4	21	4	8	4	1
oleate	19	13	19	49	20	38	72	47	40	49	25	60
linoleate	68	78	19	38	53	48	10	3	10	32	55	21
linolenate	1	0	54	1	1	0	1	1	0	0	8	14
CN	49	50	39	58	51	49	55	58	62	54	47	54

With models for all 5 major components, we can now model all these types of biodiesel:

- Not a surrogate model, but a real biodiesel (B100) model !

Use Diesel PRF as a scale to compare reactivity of biodiesel compounds

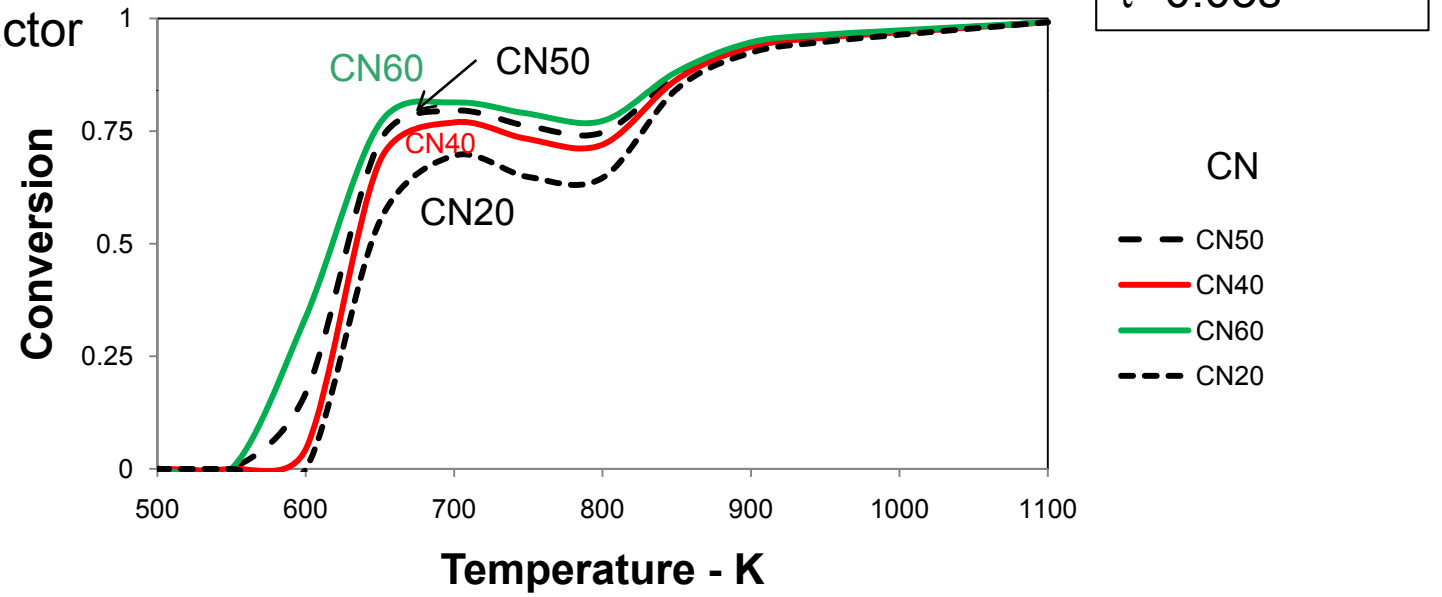


Jet stirred reactor

Simulated Diesel PRF scale in a PSR

(n-hexadecane and 2,2,4,4,6,8,8-heptamethylnonane)

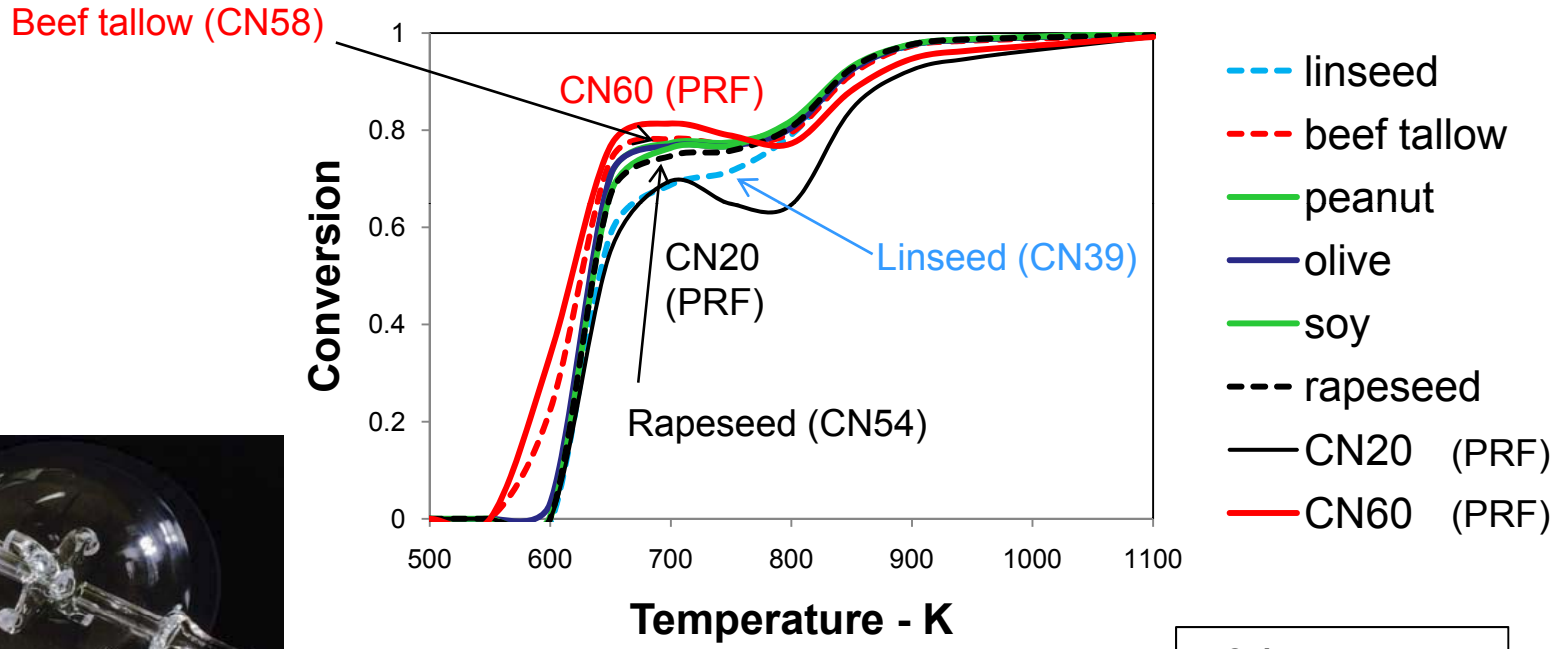
50 bar
Φ=2
fuel: 200 ppm
τ=0.05s

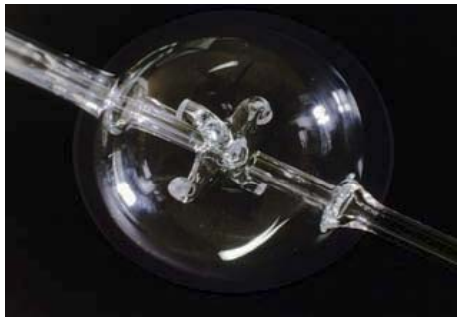


As CN increases, reaction in PSR starts at lower temperatures and has a greater extent of low T combustion

Diesel PRF scale allows assessment of the reactivity of biodiesel from different sources

Simulated reactivity profiles for biodiesel fuels





Jet stirred reactor

50 bar
Φ=2
fuel: 200 ppm
τ=0.05s

Observations on reactivity of biodiesel fuels from different oils

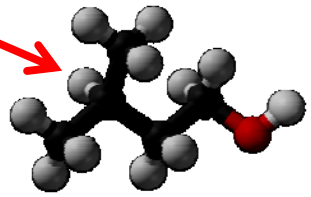
- Methyl ester fuels from different plant and animal fats and oils have different reactivity
- Detailed composition of these biodiesel fuels determine their reactivity
- Biggest factor for reactivity variability of biodiesel, large methyl ester fuels is the number of C=C double bonds
- We can model kinetics of most of these biodiesel fuels using the new biodiesel kinetic mechanism
- The mechanisms still need refinements and testing, and careful laboratory experiments would be very valuable

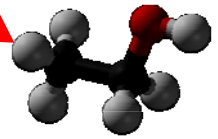
What & Why Isopentanol ?

A Next Generation BioFuel:

- Isopentanol (3-Methyl-1-Butanol or 3 Methylbutane-1-ol) is one of biomass derived alcoholic fuel, like Ethanol

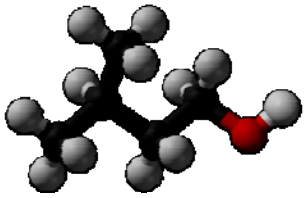
jbei Joint BioEnergy Institute http://www.jbei.org/



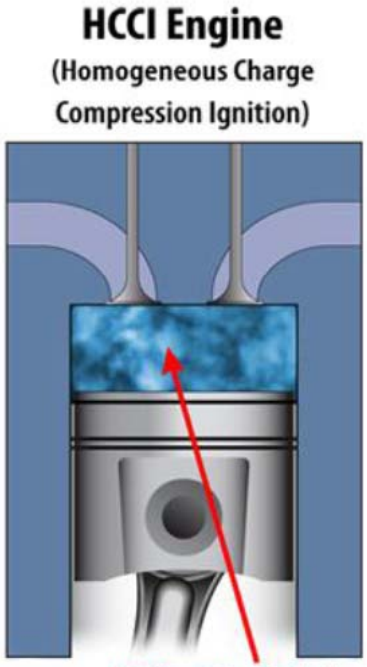


- The challenge of **JBEI**: To convert all monomer sugars (hexoses and pentoses) released from depolymerization of lignocellulosic biomass into transportation fuels and other chemicals. And the **initial targets of JBEI** is ethanol, butanol, **isopentanol**, hexadecane, and geranyl decanoate ester.
- Higher alcohols such as isopentanol has **higher energy density** and **lower hygroscopicity** compared to ethanol.
- Volatility is **moderate** like gasoline, "Not" too high

Approach

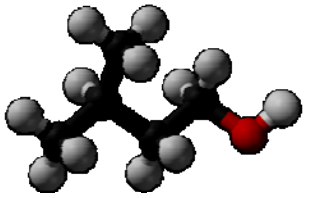


- **Development of Isopentanol reaction mechanism**
- **Single-zone Simulations → Validation**
- **Study of the kinetics involved in the auto-ignition process**
- **Simulate an HCCI Engine Combustion**
- **Compare with representative experimental results**



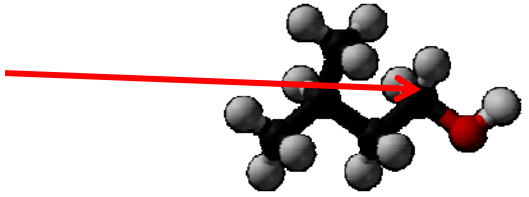
Source: https://www-pls.llnl.gov/?url=science_and_technology-chemistry-combustion

Development of Reaction Mechanism



High temperature chemistry:

- Unimolecular decomposition and H atom abstraction from fuel by activated radicals mainly occur
- Alcohols have weak C-H bonds at α site



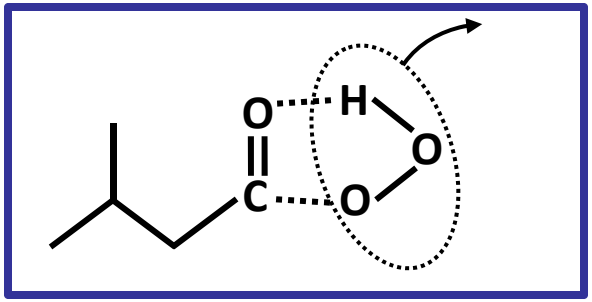
Low temperature chemistry:

- Based on low temp. chemistry of isooctane because isooctane has some similar structures to isopentanol

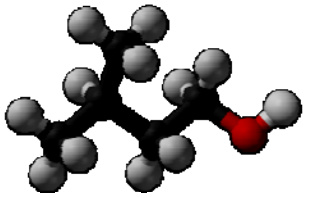
➔ Results showed "Too Short Ignition Delay & Too Strong NTC"

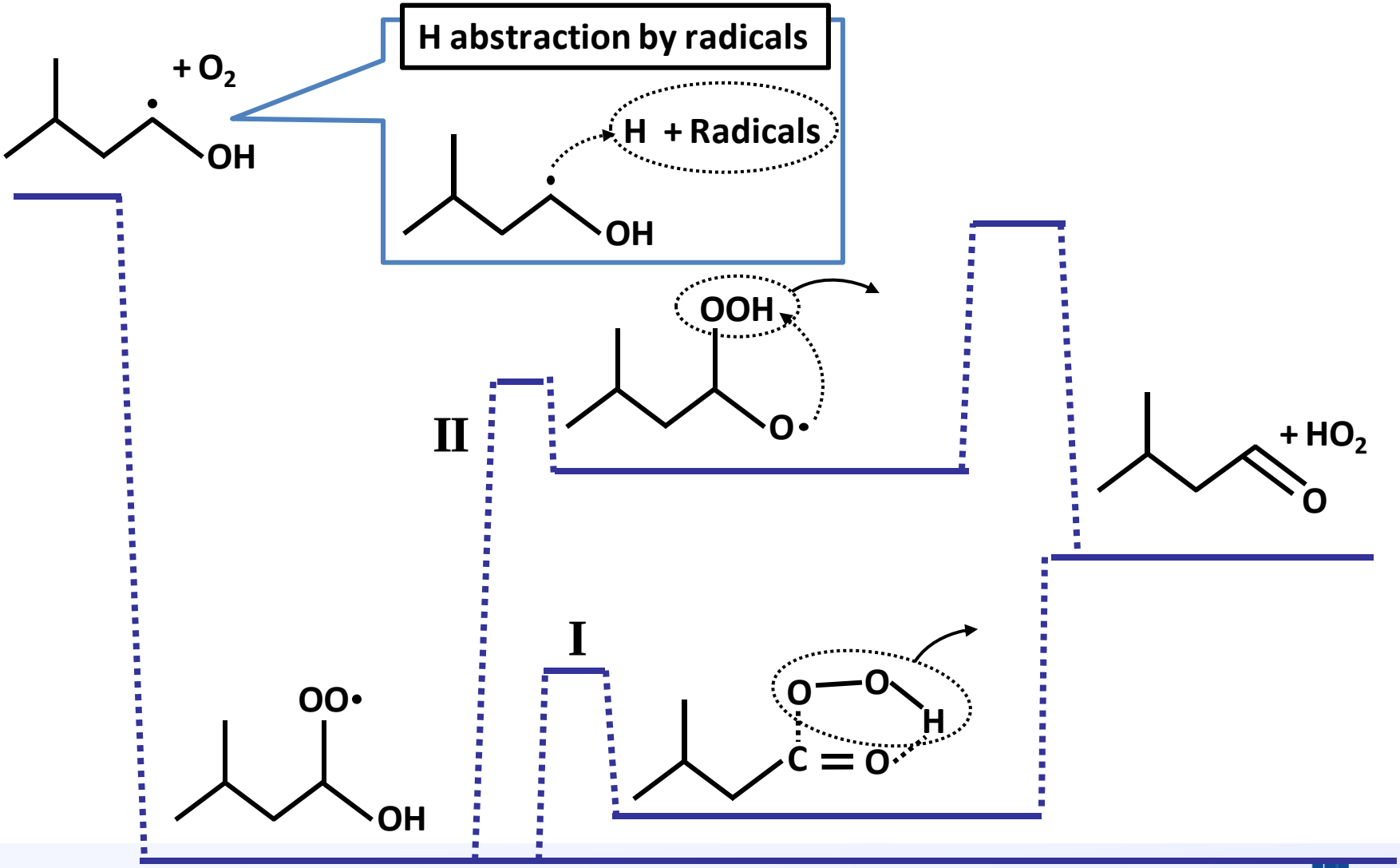
Concerted elimination of HO_2:

- Concerted elimination forming aldehyde and HO_2 from RO_2 is so fast that low temperature reactions would be slowed down

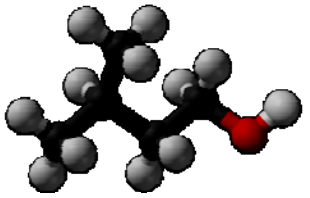


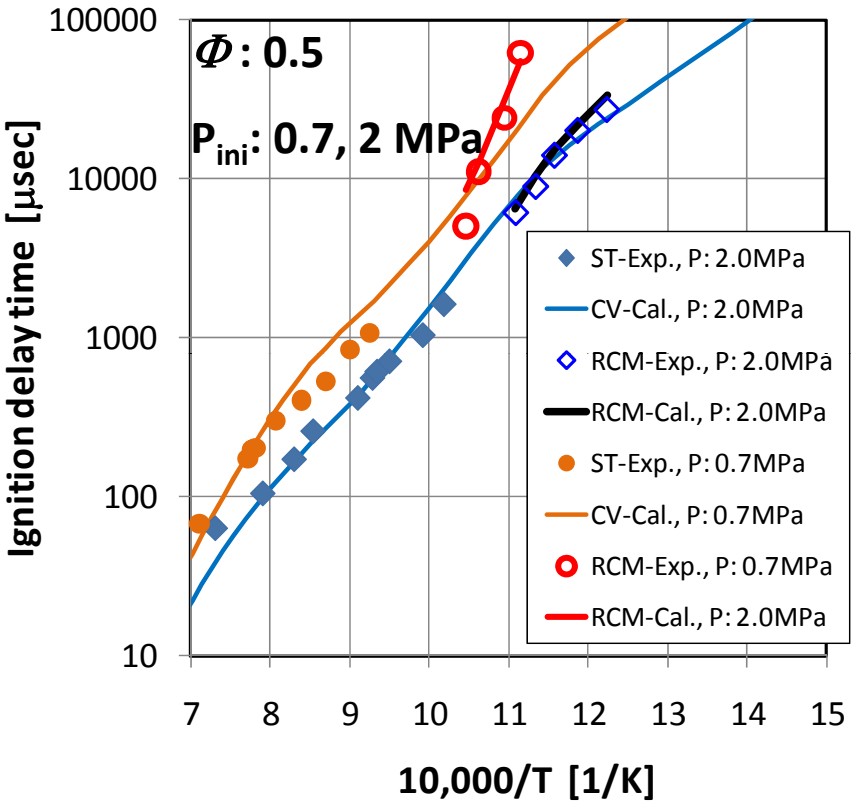
Schematic Energy Diagram for the Concerted Elimination of HO_2

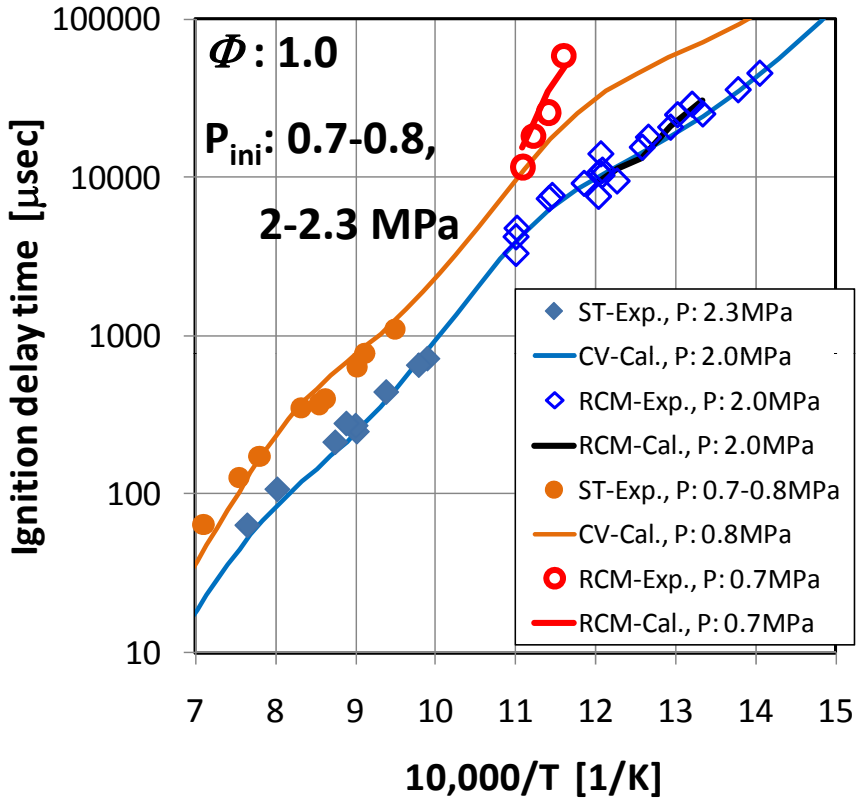




Validations of Reaction Mechanism





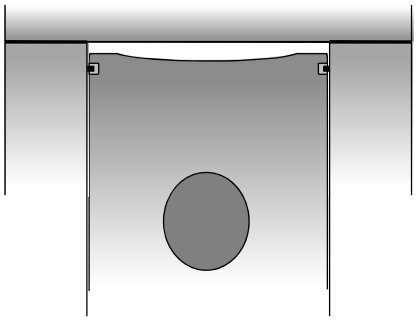


- Isopentanol model developed in this study can reproduce the experimental data which were acquired under various Φ, T, and P conditions with a shock tube and an RCM

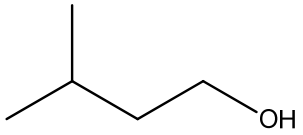
Shock tube experiments: Kenji Yasunaga, Fiona Gillespie, and Henry Curran (NUI Galway - Ireland)
Rapid compression machine (RCM) experiments: Bryan Weber, Yu Zhang and Chih-Jen Sung (UConn.)

Developed chemical kinetic model for new biofuel iso-pentanol and compared it to experiments in Sandia HCCI engine

HCCI engine experiments:
Yang and Dec, Sandia, SAE 2010



Iso-pentanol mechanism

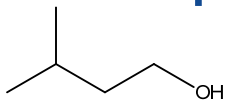


New generation biofuel proposed by DOE Joint BioEnergy Institute (JBEI)

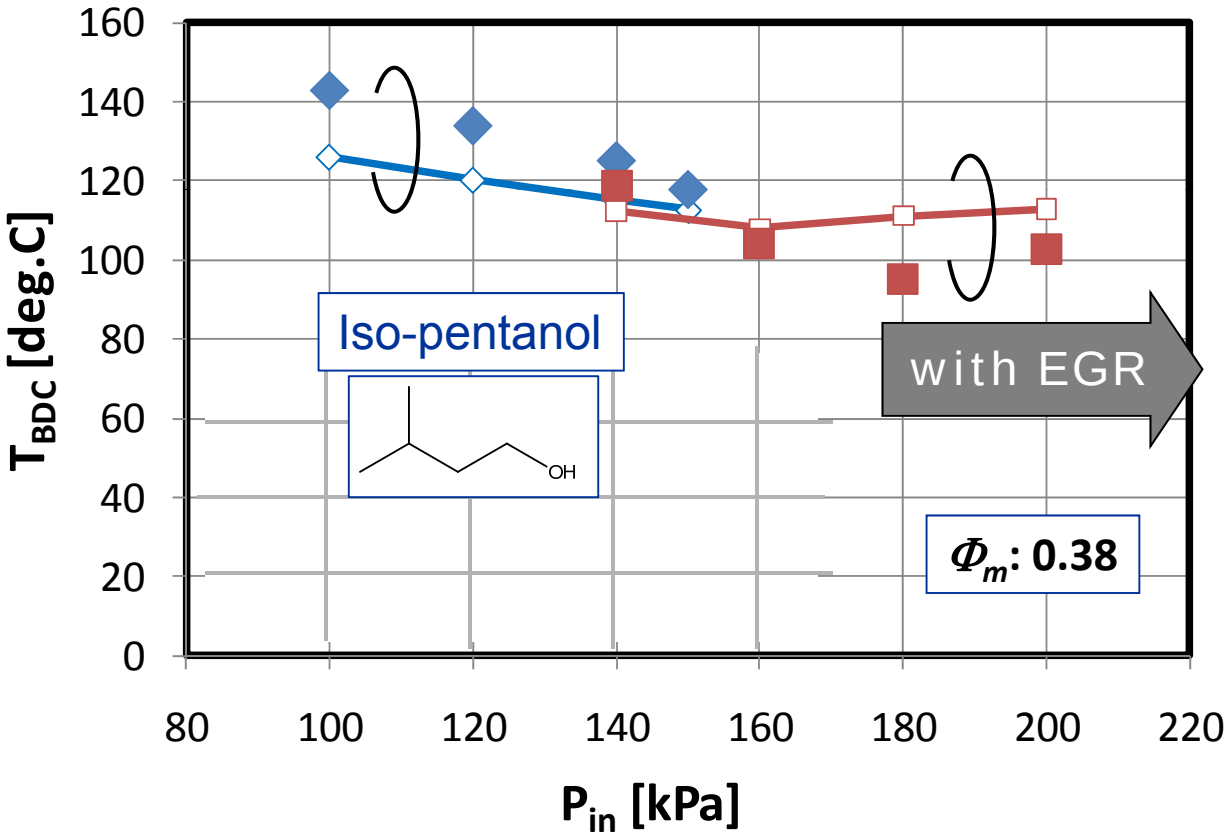
Reaction rate rules on successful iso-octane because it has some similar structures

Model development and application:
LLNL visiting scientist
Dr. Taku Tsujimura
National Institute of Advanced Industrial Science and Technology, Japan

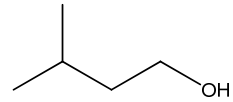
Iso-pentanol model predicts correct combustion phasing as load is increased in Sandia HCCI engine



Experiments and Calculations:
Required T_{BDC} for constant combustion phasing

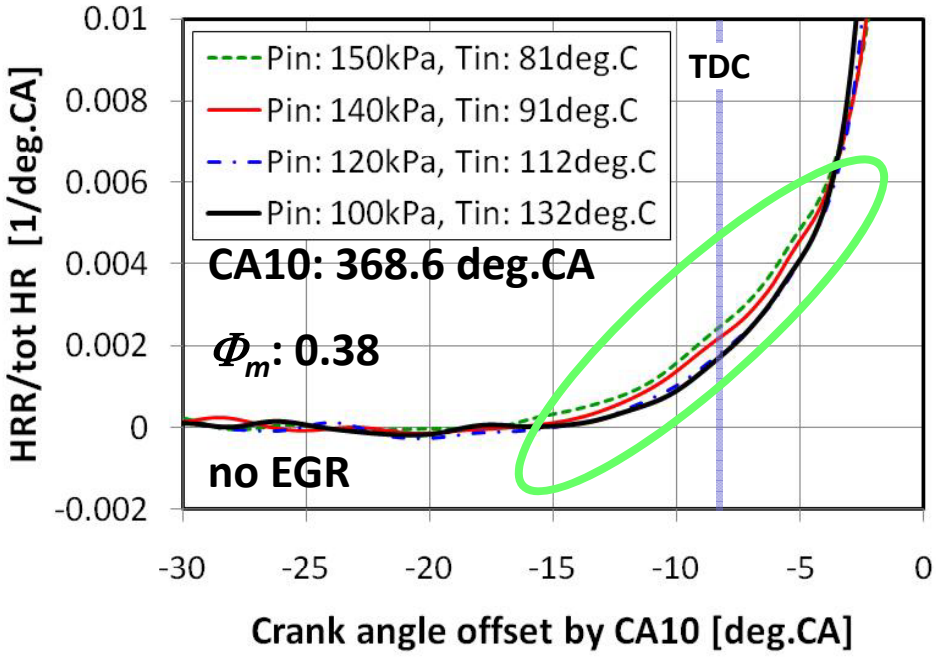


Iso-pentanol model predicts intermediate heat release that allows high load operation for HCCI

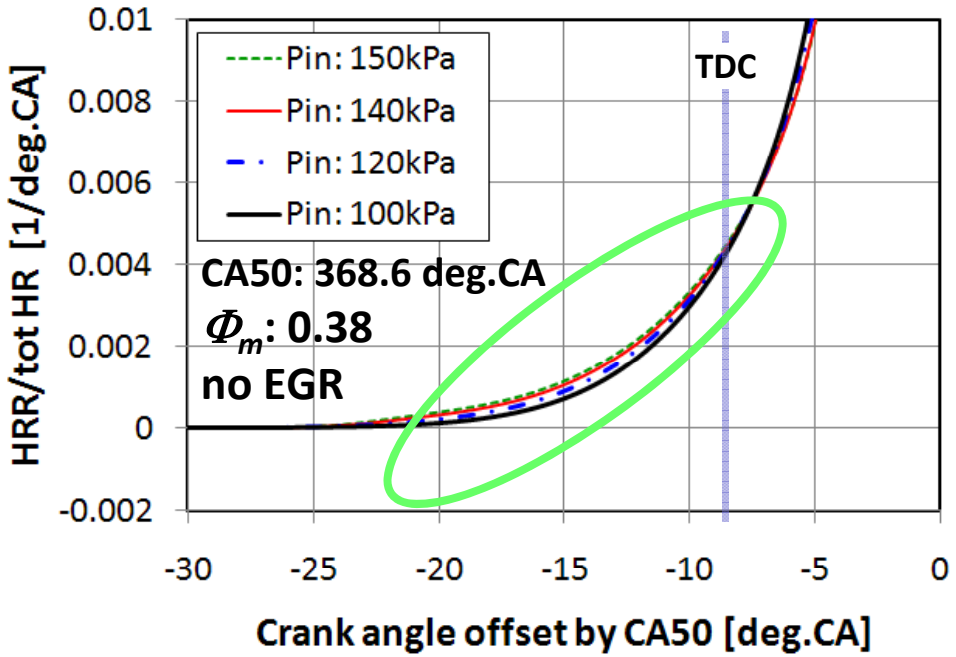


Iso-pentanol

Experiments



Calculations



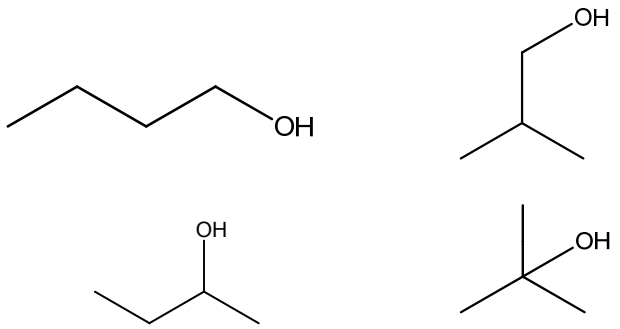
HCCI engine experiments:
Yang and Dec, Sandia, SAE 2010

Developed model for 4 isomers of butanol and compared model predictions to flame experiments at USC

Flame speed measurements: Egolfopoulos et al. USC

Twin premixed counterflow flames

butanol mechanism: 4 isomers

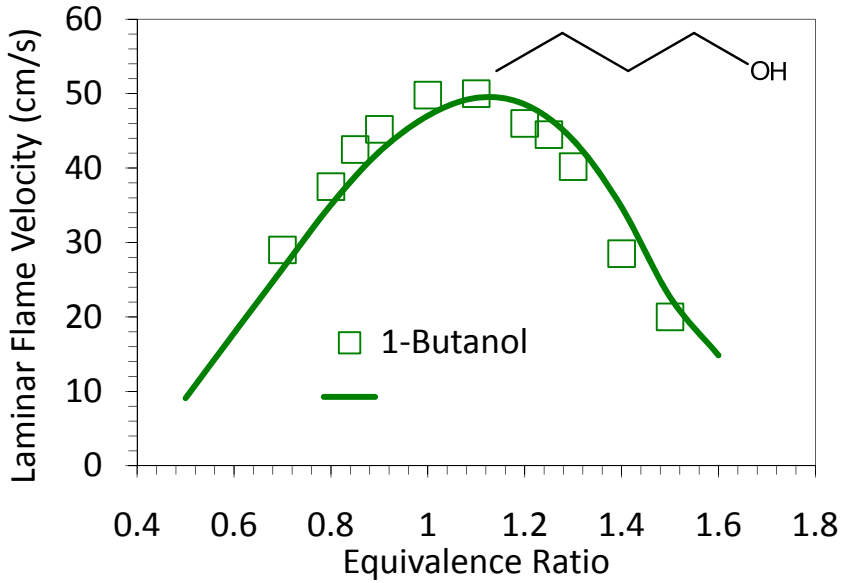


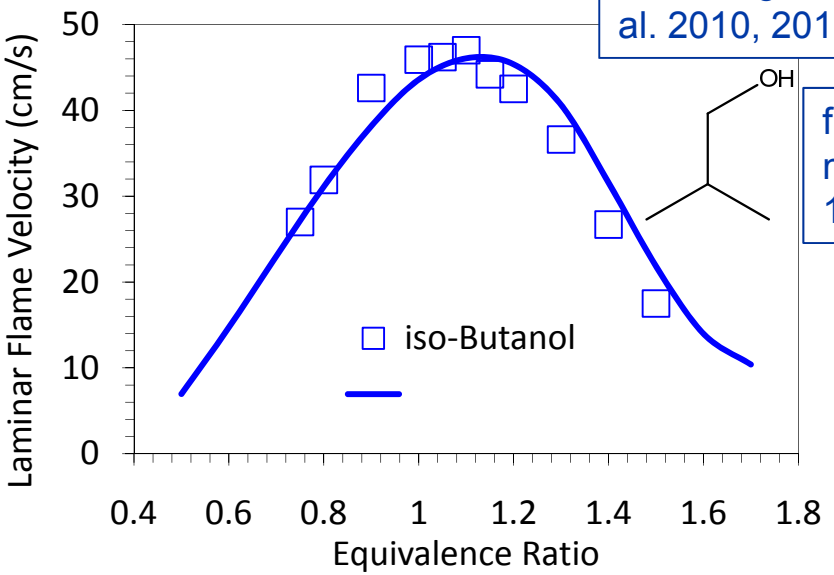
Iso-butanol is a new type of biofuel that can be made directly from cellulose using bacteria

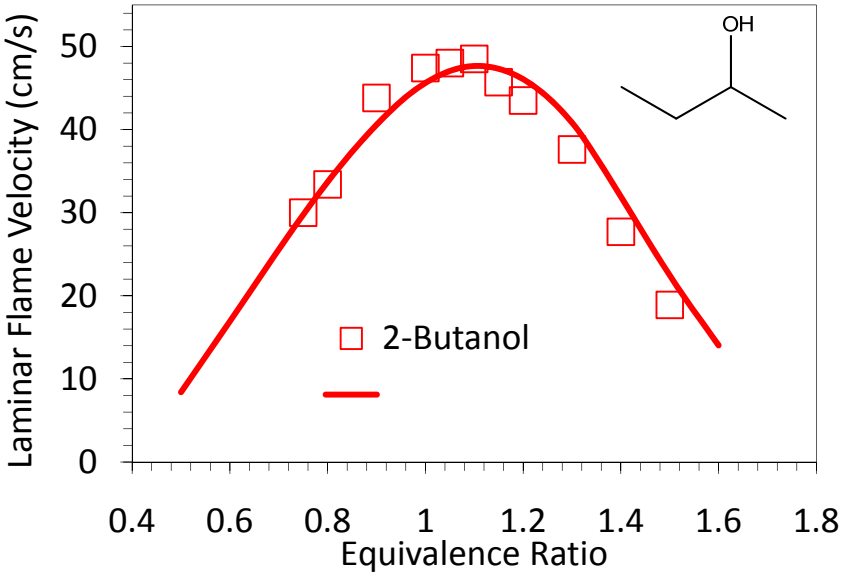
Butanol mechanism accurately simulates flame speeds important for predicting spark ignition engine combustion

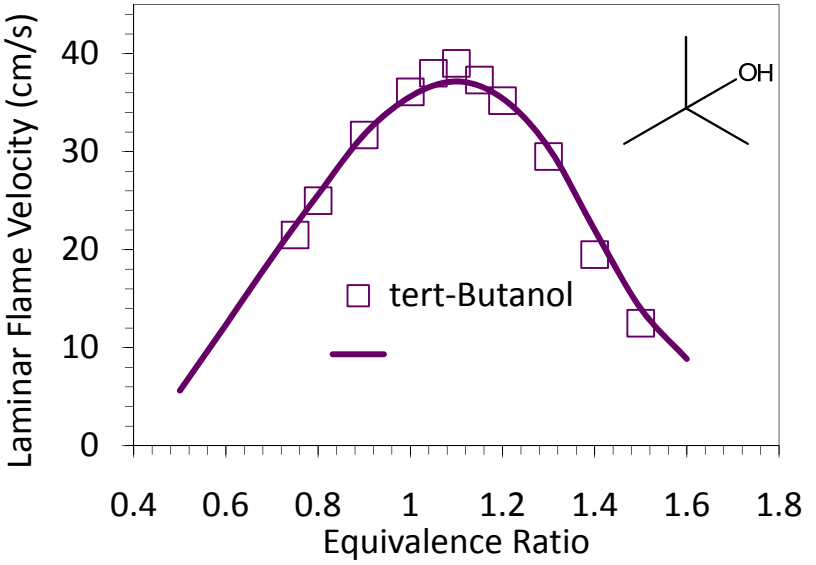
Experimental data: Veloo, Egolfopoulos et al. 2010, 2011

fuel/air mixtures 1 atm

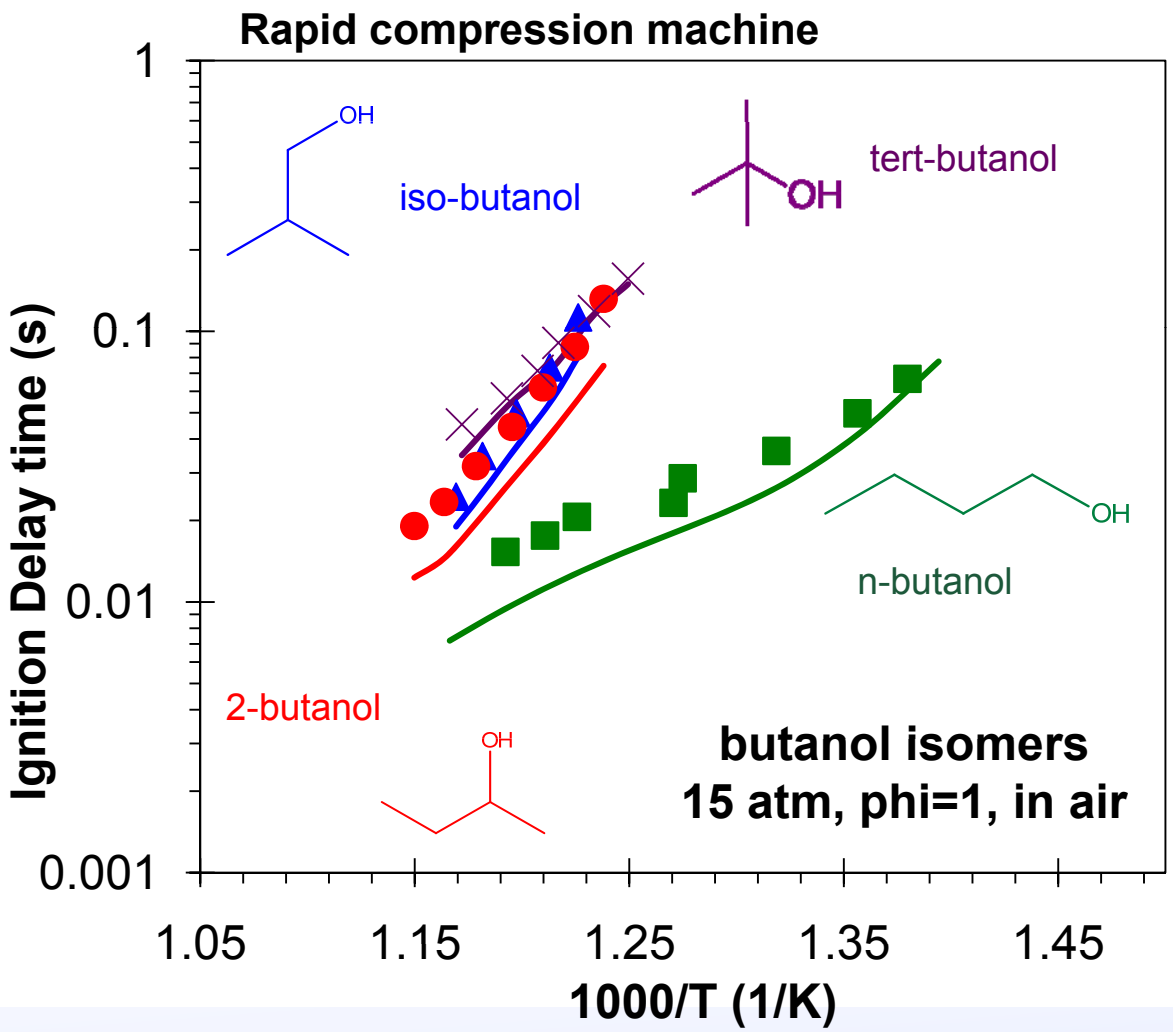




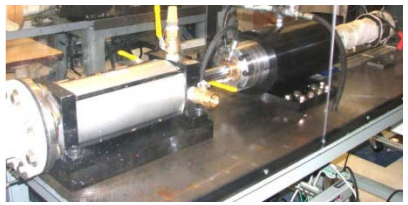




Butanol model well predicts ignition delay times at pressures and temperatures found in IC engines

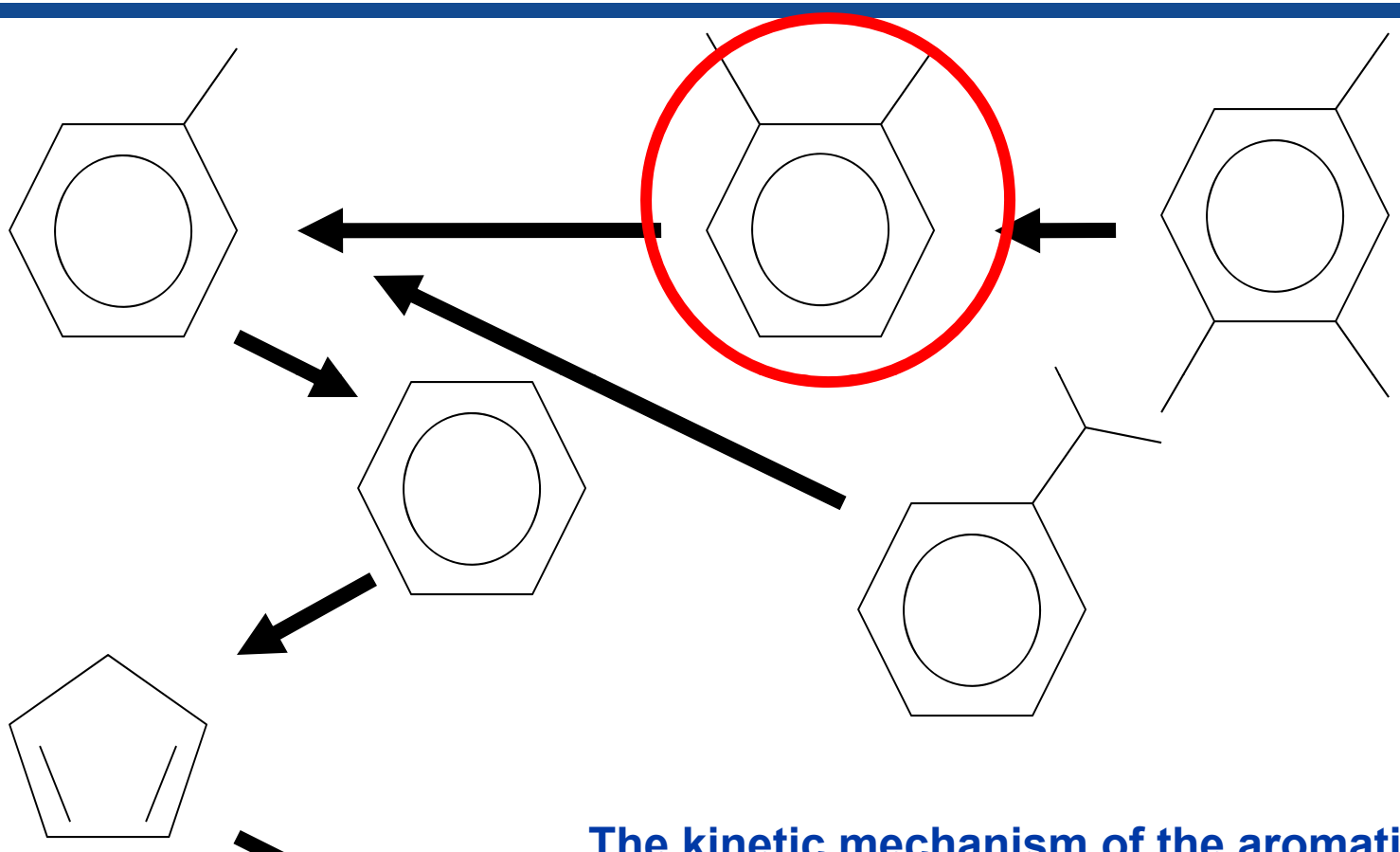


Symbols:
experimental data
Sung et al.,
AIAA paper, 2011



Rapid compression machine
University of Connecticut

Chemical kinetic mechanism for larger aromatics



CO

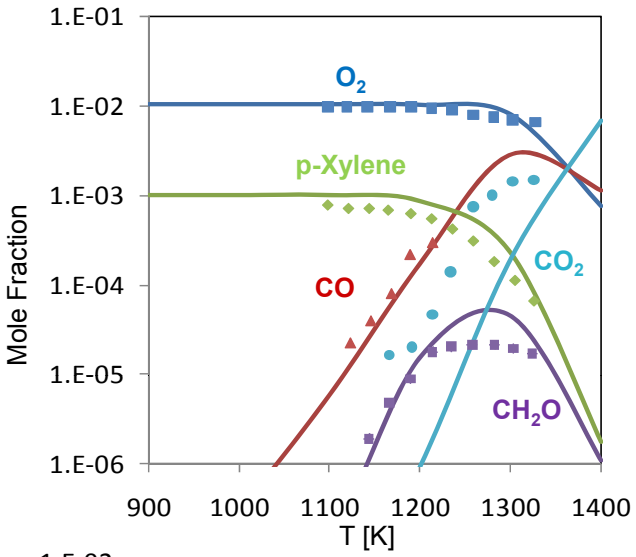
CO_2

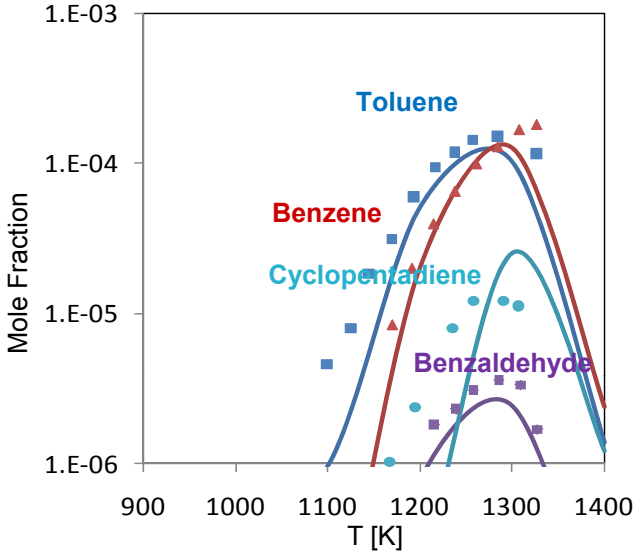
H_2O

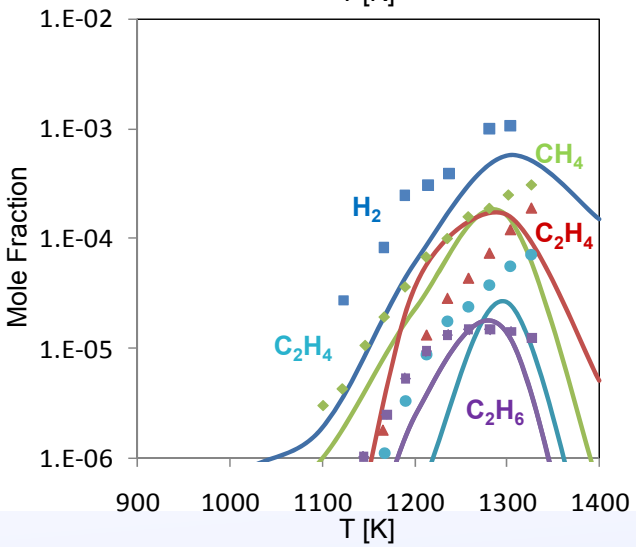
The kinetic mechanism of the aromatics has an intrinsic hierarchical structure

A new module specific to C8 alkyl aromatics is now under development

p-Xylene mechanism well reproduces species profiles in jet stirred reactor







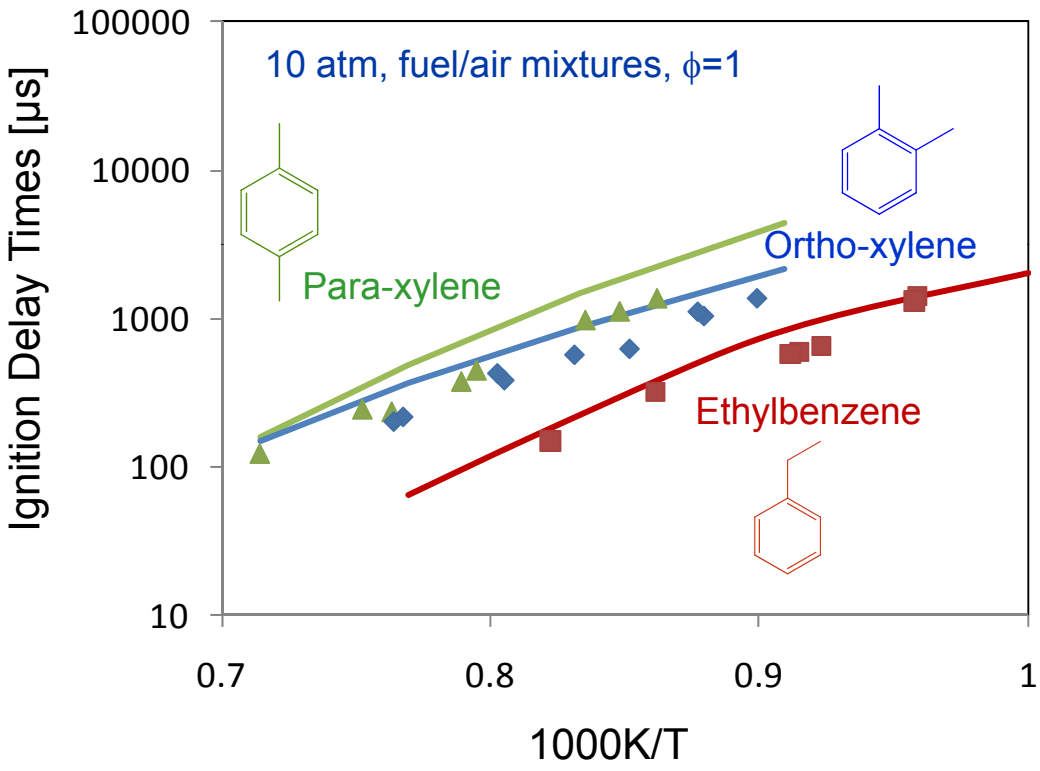
Jet stirred reactor

P = 1 atm, Φ = 1, τ = 0.1s

Experiments: Gail and Dagaut Combustion and Flame 2005

Ortho-, para- and ethyl-benzene models compare well to ignition delay times measured at pressure and temperatures relevant to engines

Ignition delay times in a shock tube for aromatics



Shock tube experimental data: Shen and Oehlschlaeger, Combustion and Flame 2009

Mechanisms are available on LLNL website and by email

http://www-pls.llnl.gov/?url=science_and_technology-chemistry-combustion

- Ethanol
- Dimethyl Ether
- CH4, C2H4, C2H6, C3H8, and nC4H10
- CH4, C2H4, C2H6, C3H6, C3H8, and NOx
- C8-C16 n-Alkanes
- Cyclohexane
- Methylcyclohexane
- Methyl Butanoate and Methyl Formate
- Methyl Decanoate
- Methyl Decenoates
- Biodiesel Surrogates
- Dimethyl Carbonate
- Heptane, Detailed Mechanism
- Heptane, Reduced Mechanism
- iso-Octane
- Primary Reference Fuels: iso-Octane / n-Heptane Mixtures
- 2,2,4,4,6,8,8-Heptamethylnonane
- Organophosphorus Compounds under Incineration Conditions
- Organophosphorus Compounds in Propane Flames
- Organophosphorus

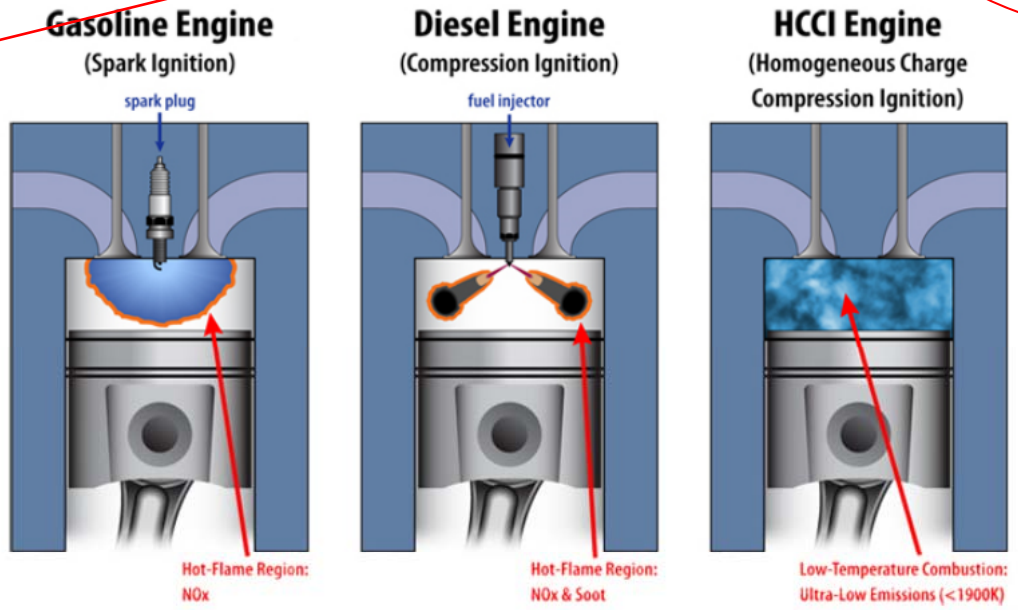
Combustion Chemistry

Go Directly to Mechanisms...

The central feature of the Combustion Chemistry project at LLNL is our development, validation, and application of detailed chemical kinetic reaction mechanisms for the combustion of hydrocarbon and other types of chemical fuels. For the past 30 years, our group has built hydrocarbon mechanisms fuels from hydrogen and methane through much larger fuels including heptanes and octanes. Othe classes of fuels for which models have been developed include flame suppressants such as halons organophosphates, and air pollutants such as soot and oxides of nitrogen and sulfur.

Reaction mechanisms have been tested and validated extensively through comparisons between computed results and measured data from laboratory experiments (e.g., shock tubes, laminar flames, rapid compression machines, flow reactors, stirred reactors) and from practical systems (e.g., diesel engines, spark-ignition engines, homogeneous charge, compression ignition (HCCI) engines). We have used these kinetic models to examine a wide range of combustion systems.

Biodiesel Surrogates



Summary

- Reaction classes and reaction rate rules greatly simplify the task of developing chemical kinetic models and assigning rate constants
- Continually updating reaction rate rules and adding new rules for new moieties such as those from new biofuels
- Made a lot of progress in chemical kinetic modeling new classes of compounds like esters and alcohols and difficult compounds to model like aromatics

Acknowledgements

- Fokion Egolfopoulos, butanol
- Jackie Sung, iso-pentanol
- John Dec and Yi Yang, iso-pentanol

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- DOE Office of Basic Energy Sciences
  - Wade Sisk
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