Detailed Kinetic Mechanisms for Large Practical Fuel Components

Multi-Agency Coordination Committee
for Combustion Research
Fuels Research Review

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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

Different applications require different fuel mixes

- Most practical 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 $13 < C < 22$
- Molecular classes also are different in each application
- Use of “surrogate” fuels is becoming common

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 (?)

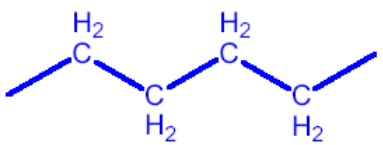
- For the first time, we now have detailed kinetic mechanisms for both diesel and gasoline primary reference fuels

- Surrogate fuels

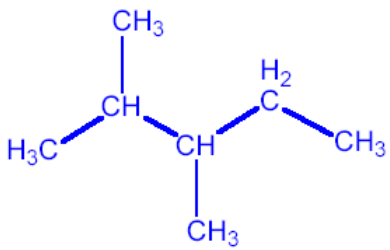
- Gasoline
  - n-heptane
  - iso-octane
- Diesel
  - n-cetane
  - iso-cetane
- Biodiesel

Classes of compounds in practical fuels

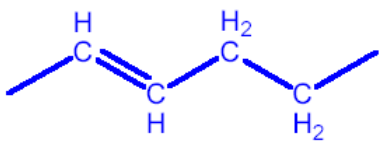
n-paraffin

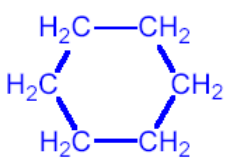


iso-paraffin

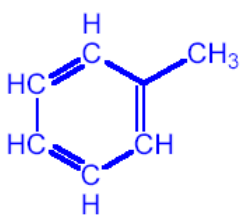


olefin

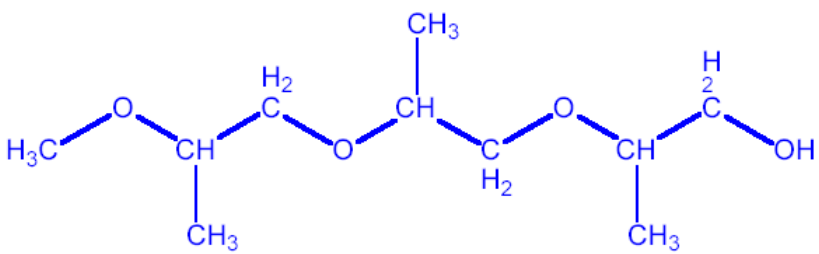




cyclo-alkane



aromatic

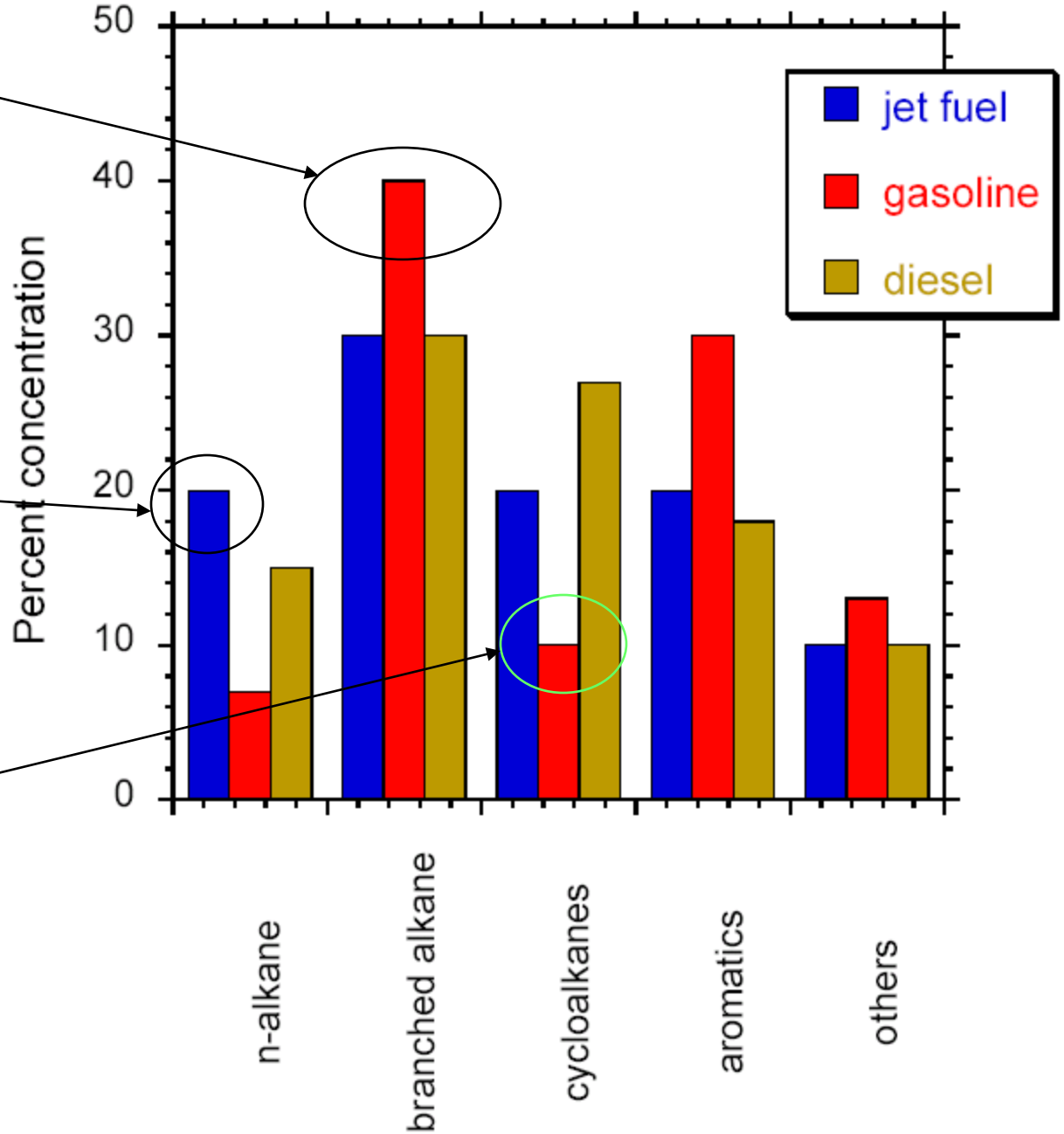


oxygenate

Gasoline has many branched alkanes

Jet fuel has the highest n-alkane

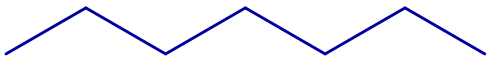
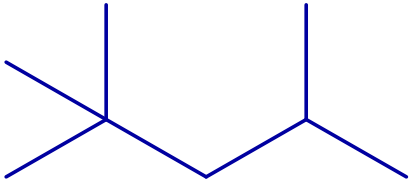
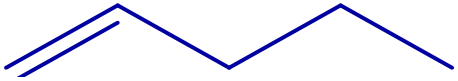
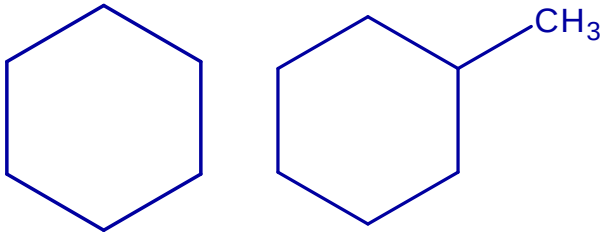
Gasoline is lower in cycloalkanes

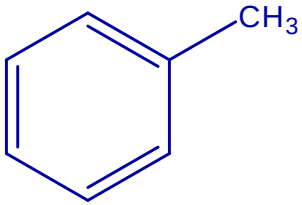


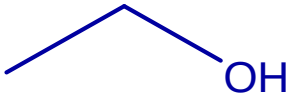
Use of surrogate fuels is an important current theme in combustion chemistry

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

An early gasoline surrogate fuel mixture contained components from each class of molecules

- n-heptane 
- iso-octane 
- pentene 
- cyclohexane, methylcyclohexane 

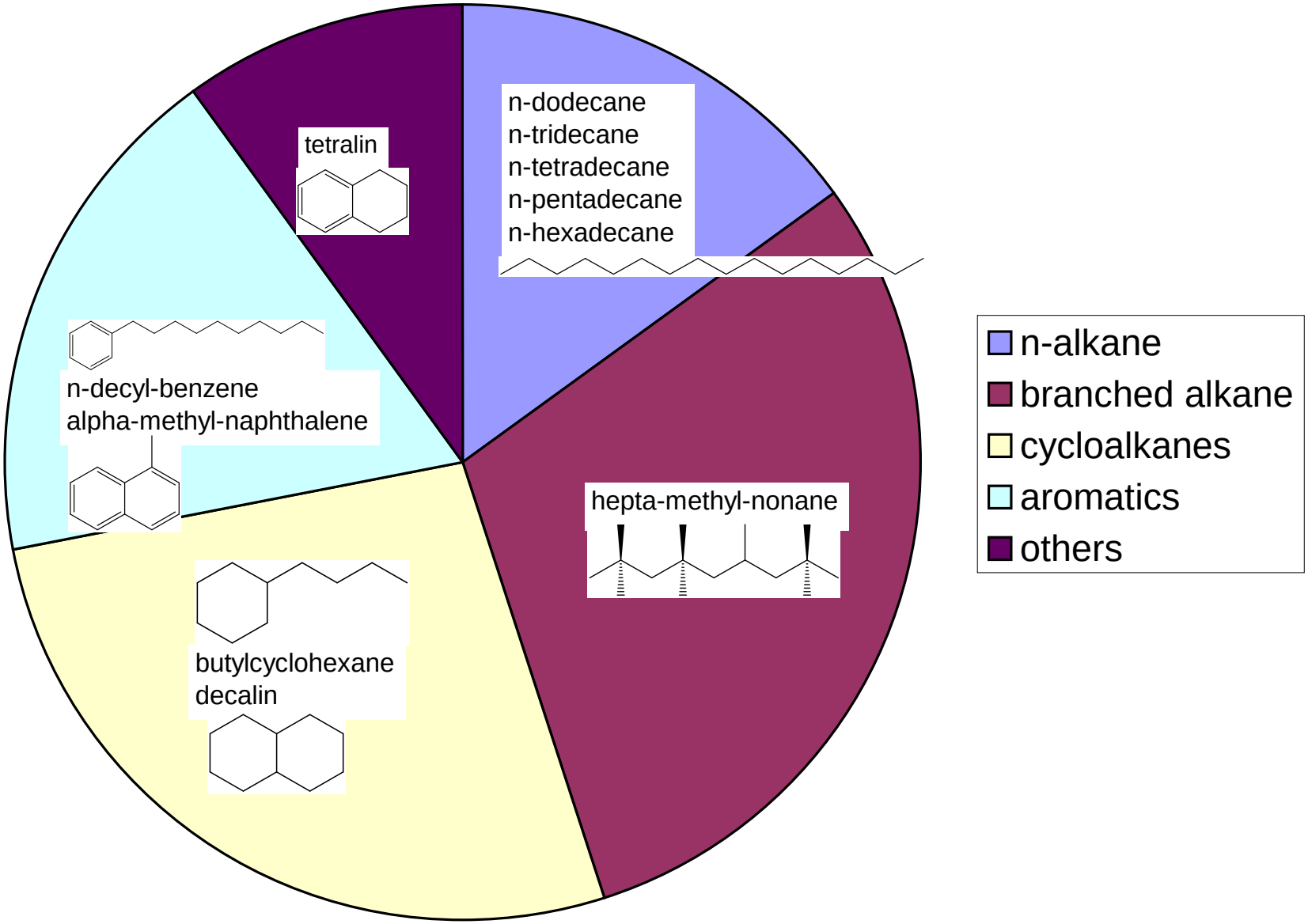
- toluene 

- ethanol 

Further development of surrogate fuels

- 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

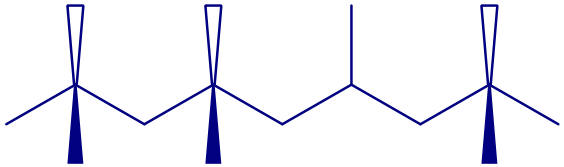
Fuel Surrogate Palette for Diesel



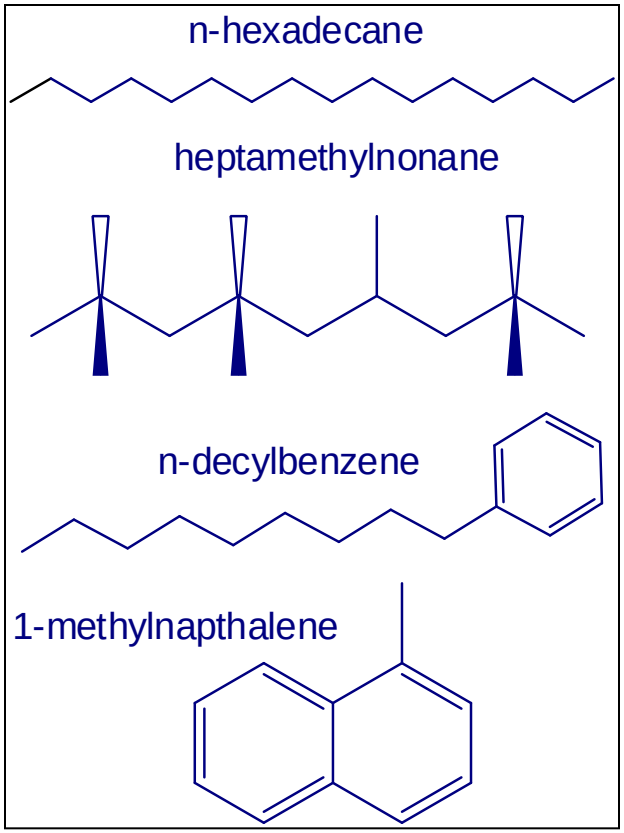
Primary reference fuels for diesel include straight-chain and highly branched components

- Primary reference fuels for diesel ignition properties (cetane number)
  - n-hexadecane

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

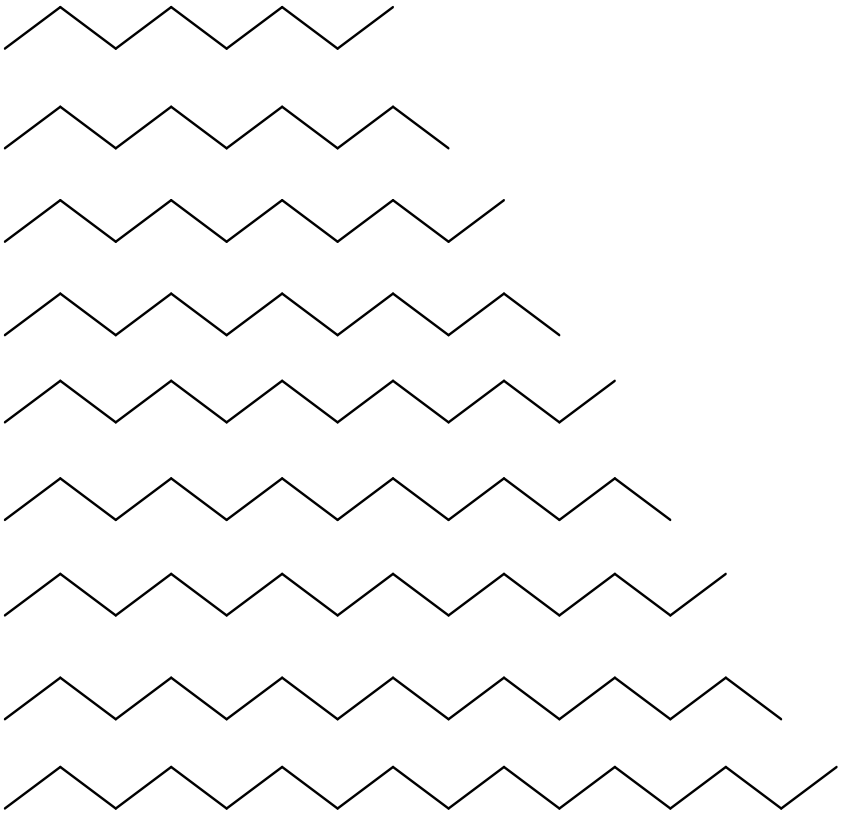


Recommended surrogate for diesel fuel (Farrell et al., 2007):

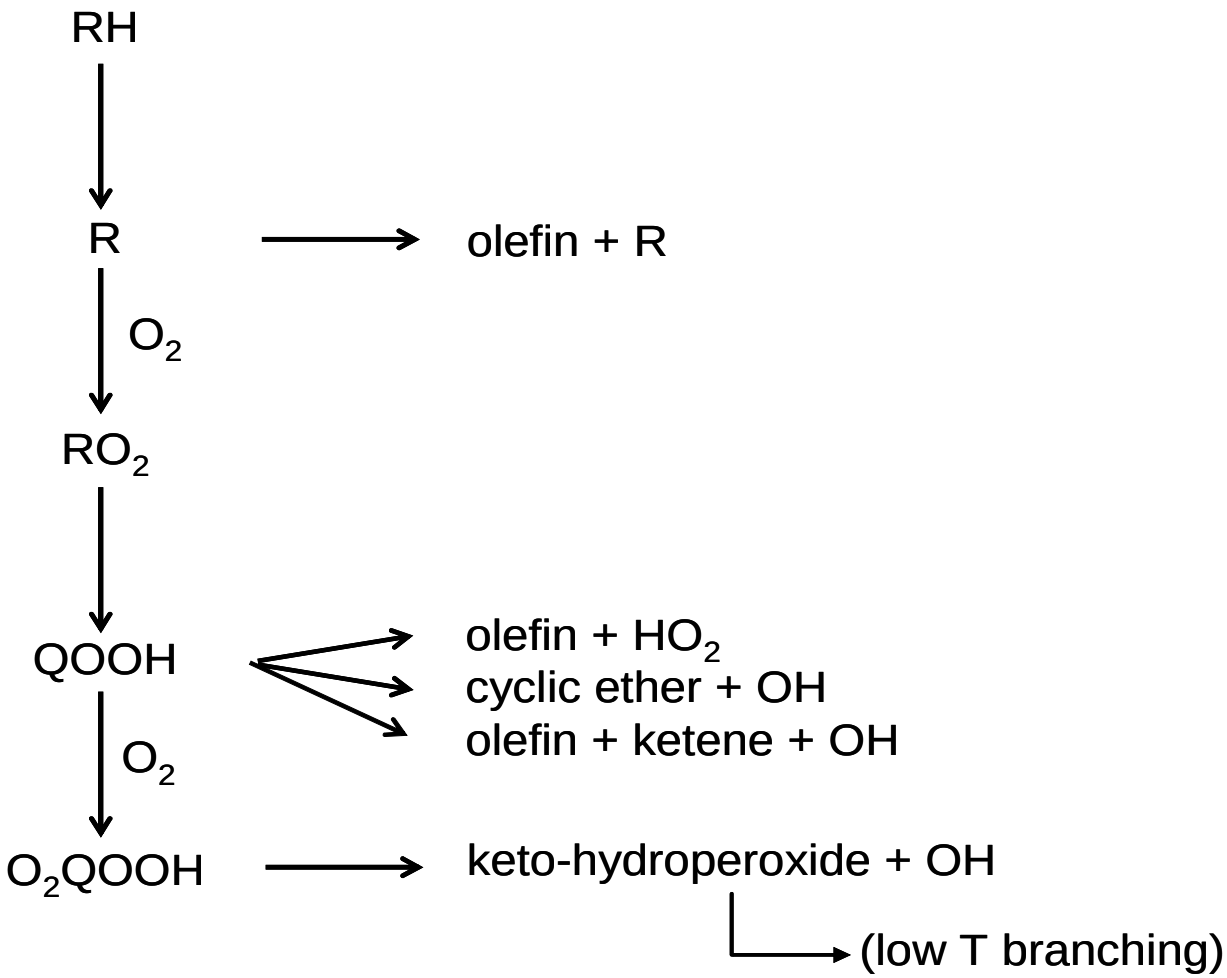


We have greatly extended the components in the palette that can be modeled in the high molecular weight range:

- 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)

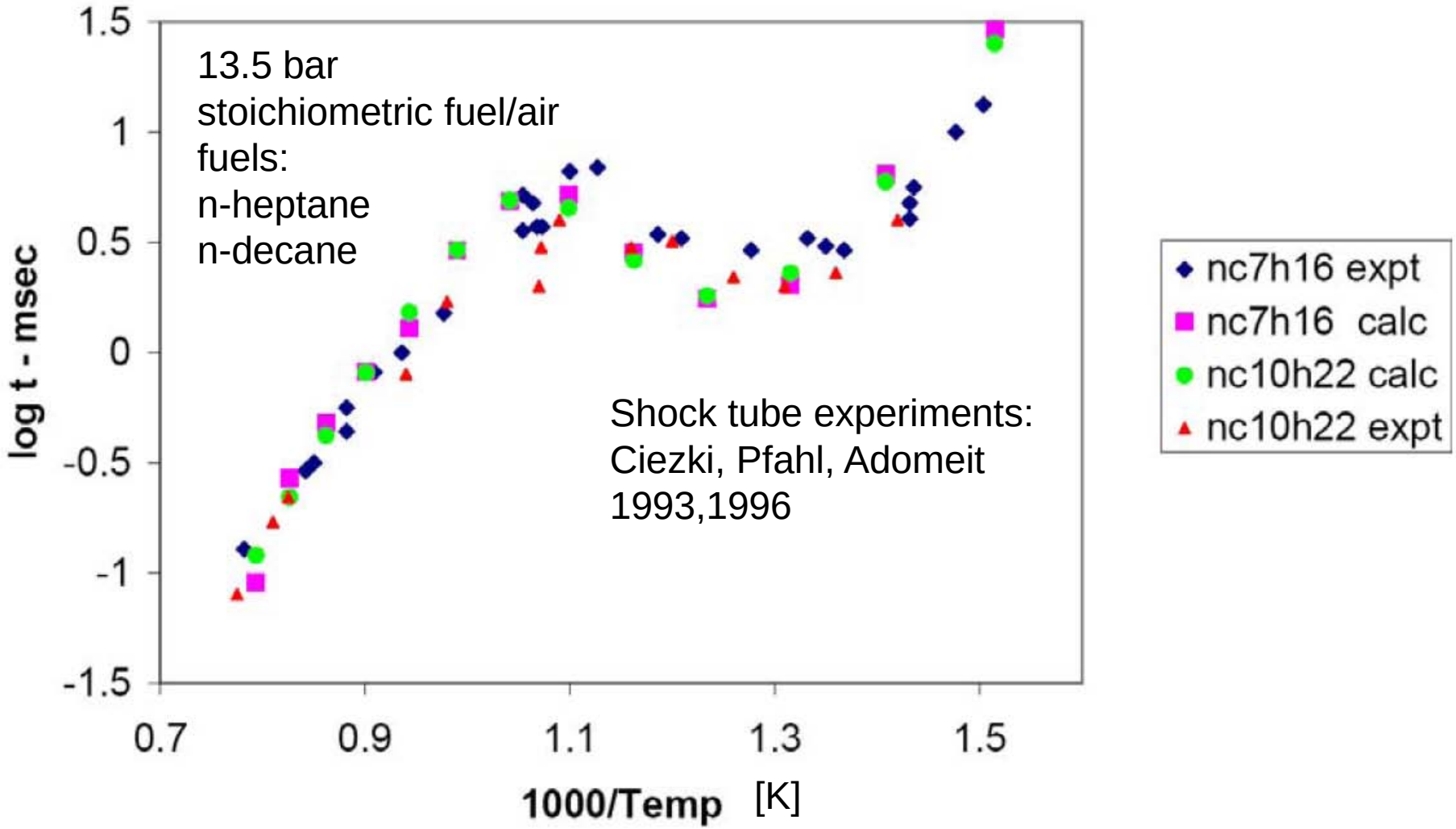


Includes high and low temperature ignition chemistry:
Important for predicting low temperature combustion regimes

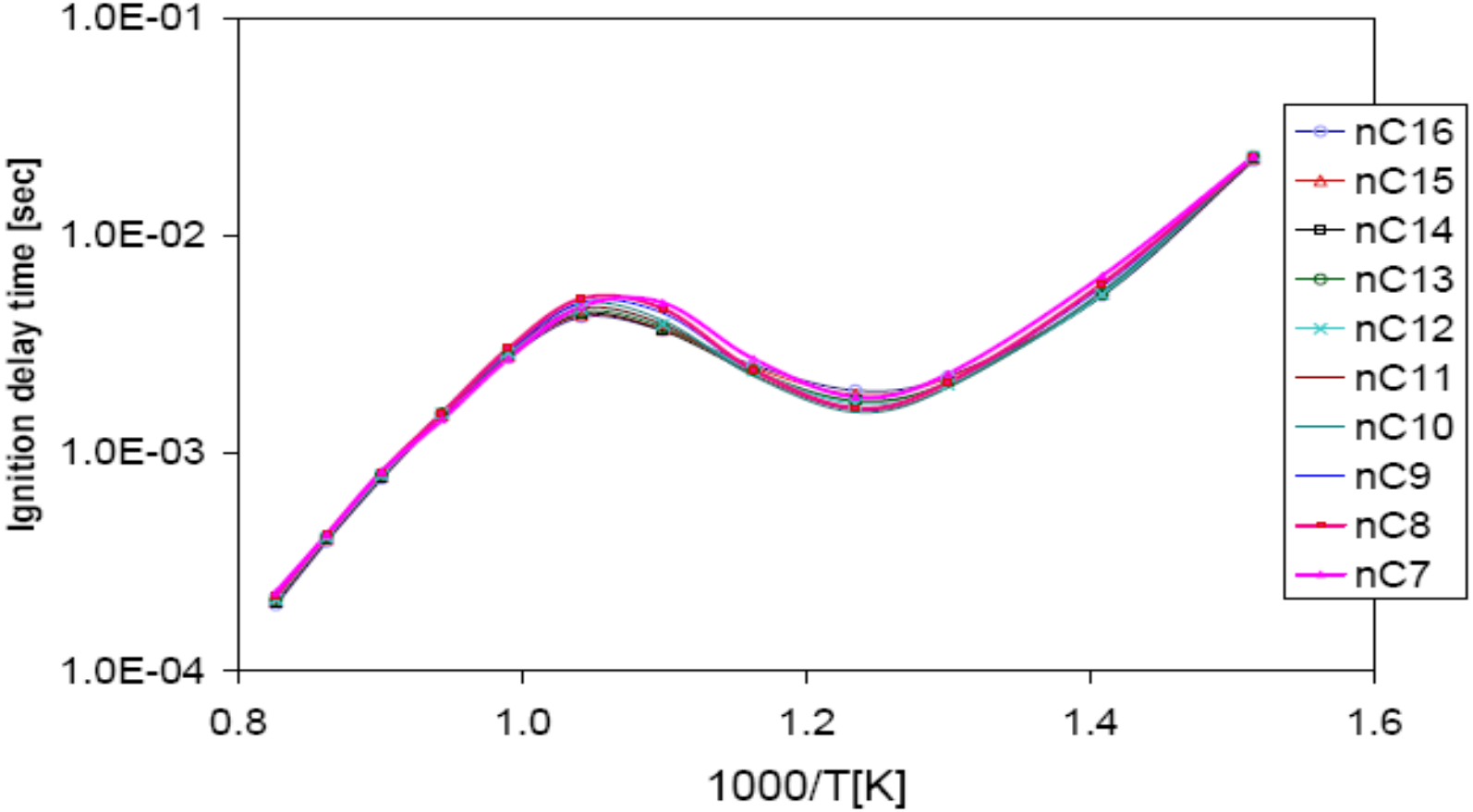


Experimental Validation Data

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

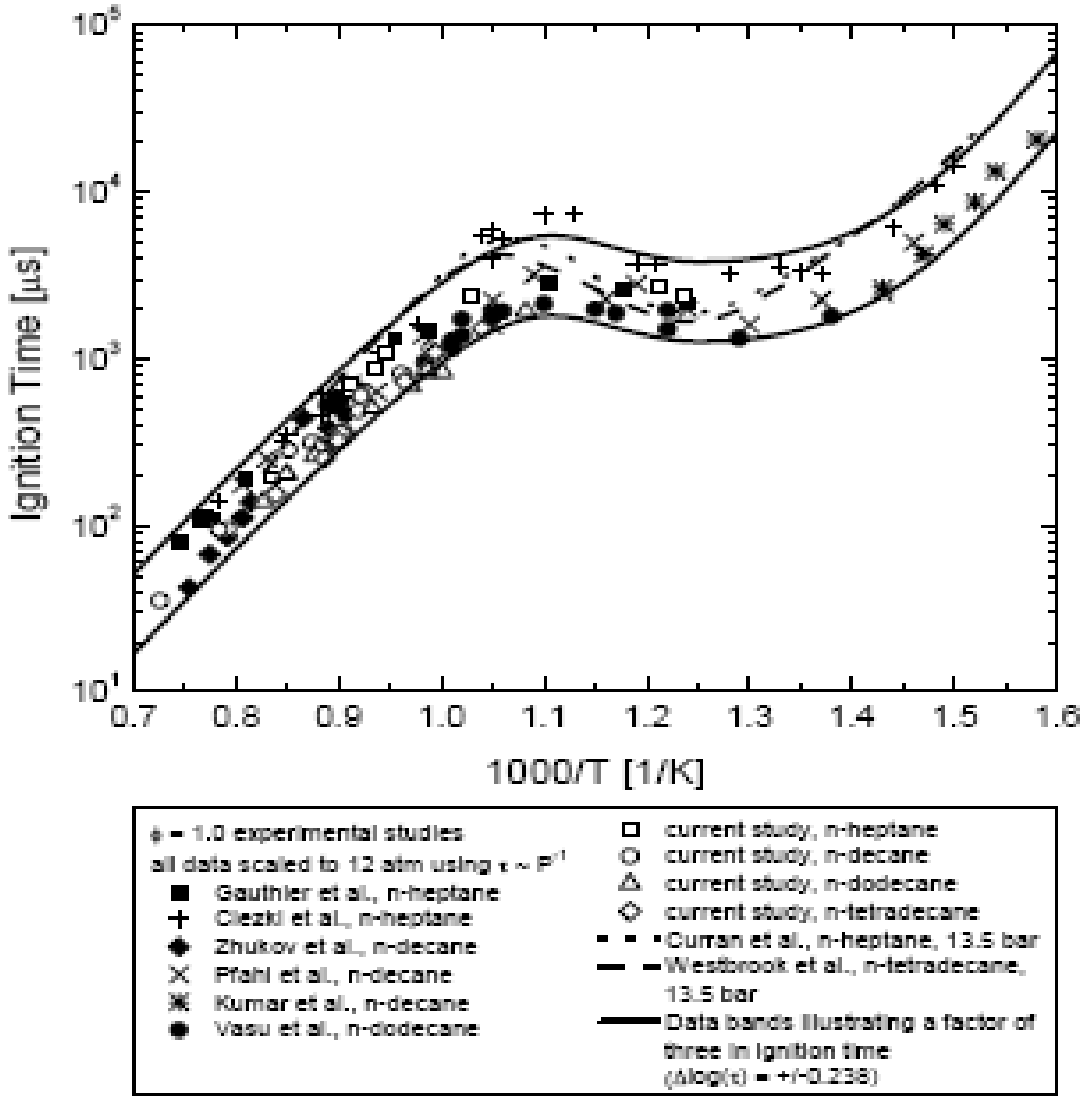


All large n-alkanes have very similar ignition properties



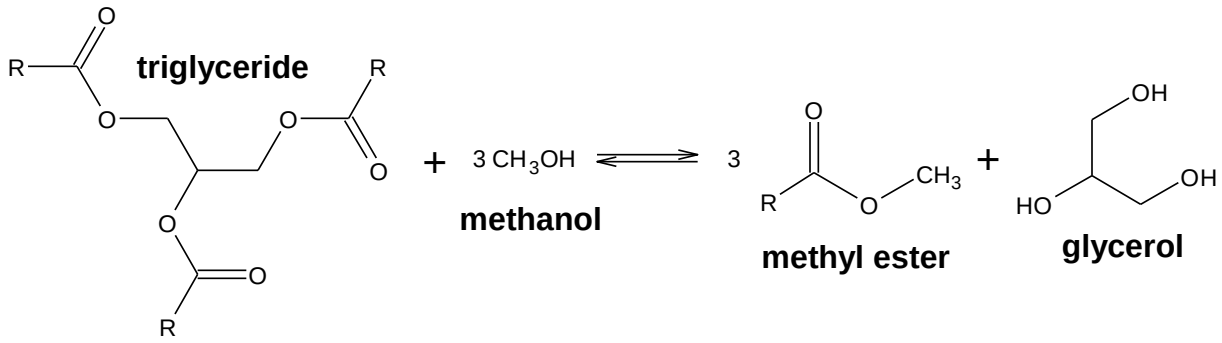
New experiments agree with our computer predictions

Oehlschlager et al., Combustion and Flame



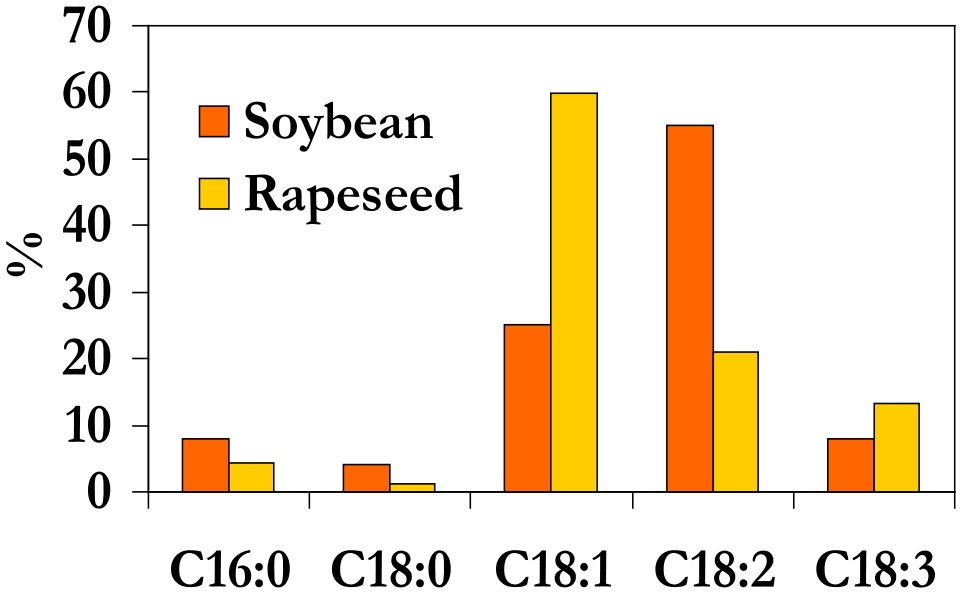
Biodiesel fuels

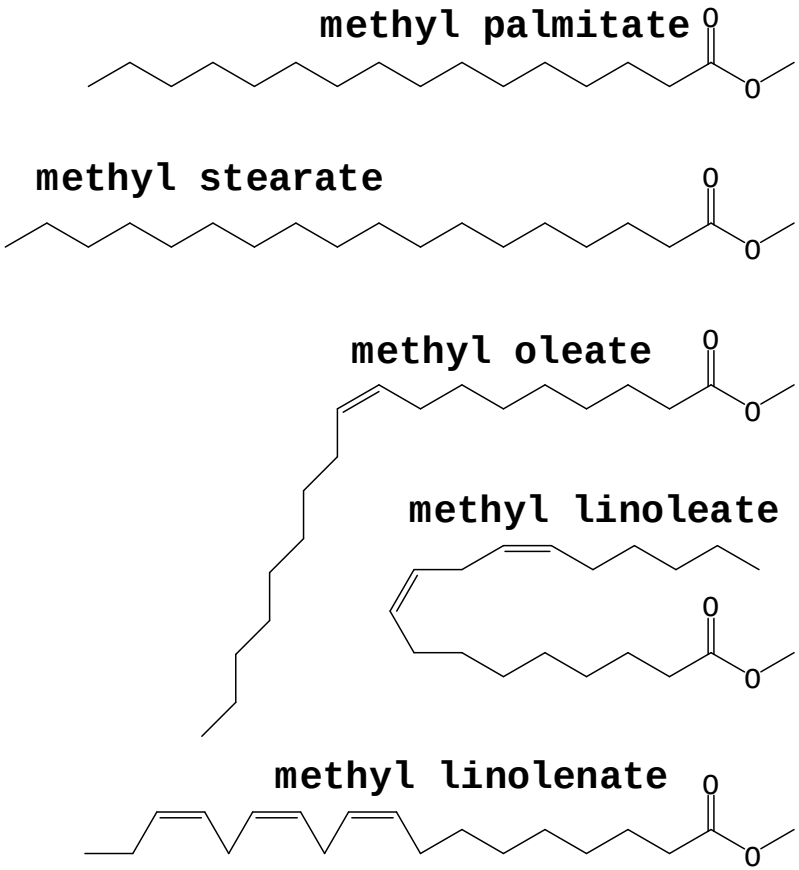
Biodiesel fuels produced from various oleaginous plants
US: soybean / Europe: rapeseed



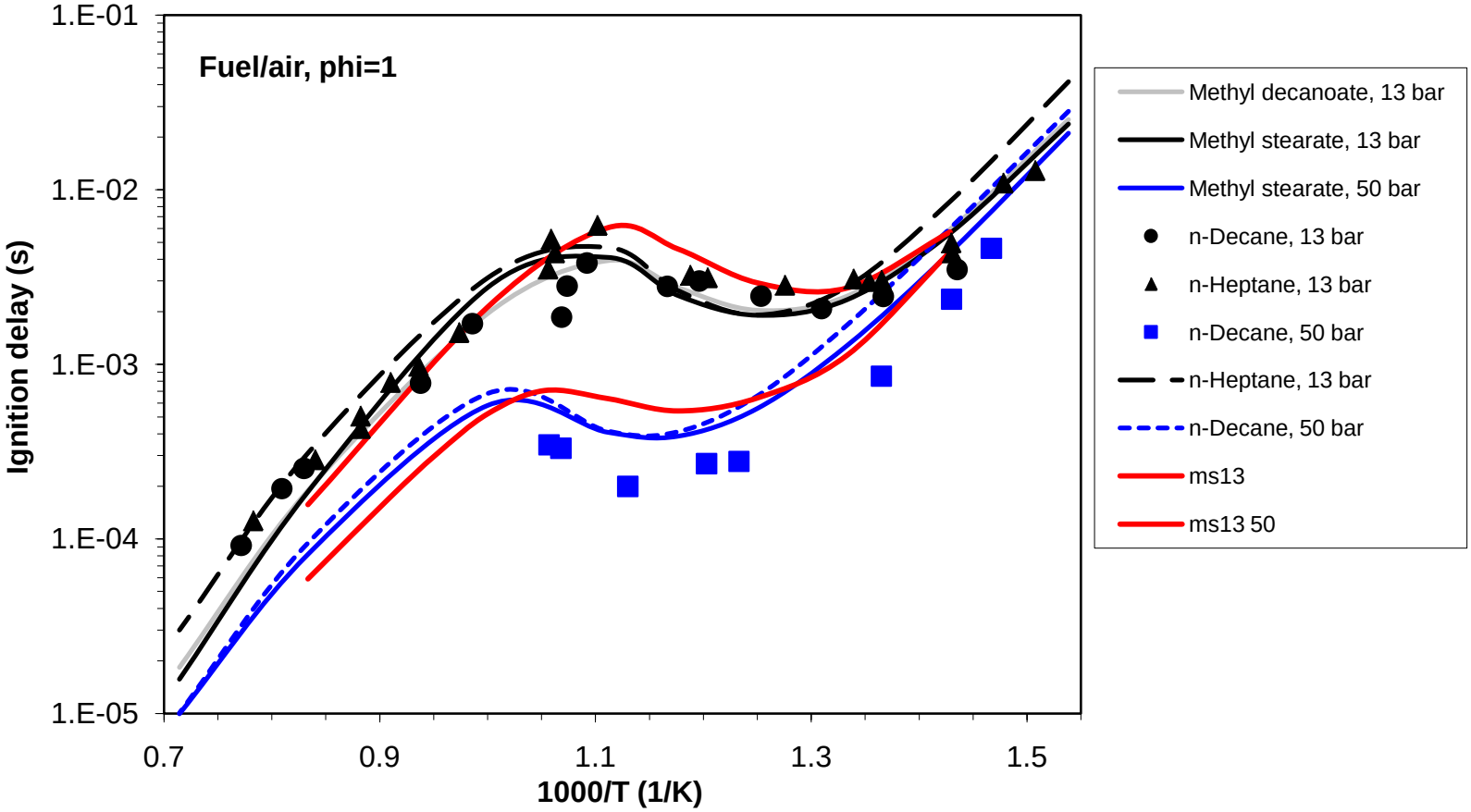
(R = hydrocarbon chain)

Composition of Biodiesels





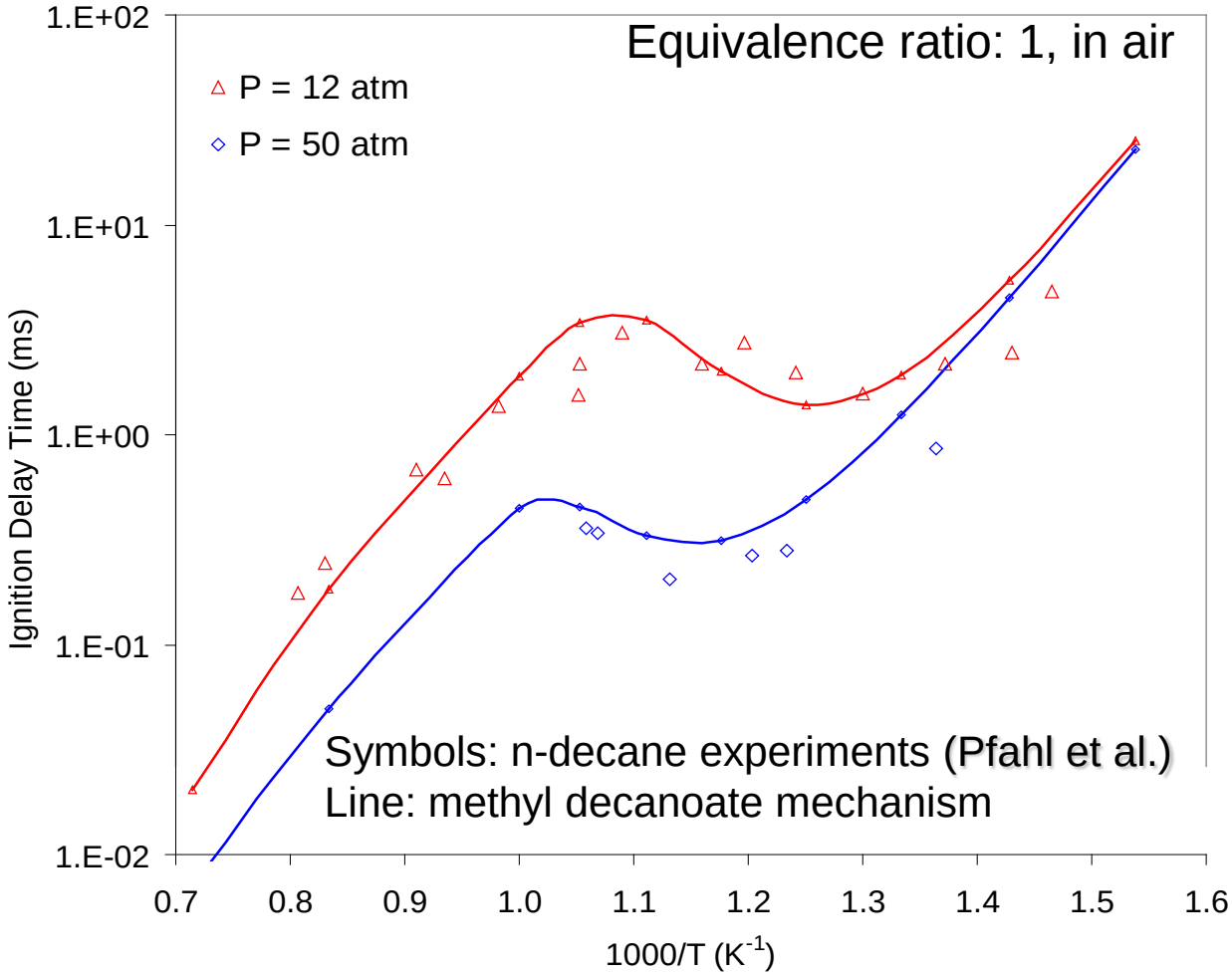
Methyl stearate (n-C_{18} methyl ester) has the same ignition properties as large alkanes



Biodiesel fuel mechanisms

- Together with Reaction Design, we are completing a detailed, full temperature range mechanism for all of the 5 components of soy biodiesel
- Unique case where a practical fuel can be represented by all its components

Comparison with n-Decane Ignition Delay Times



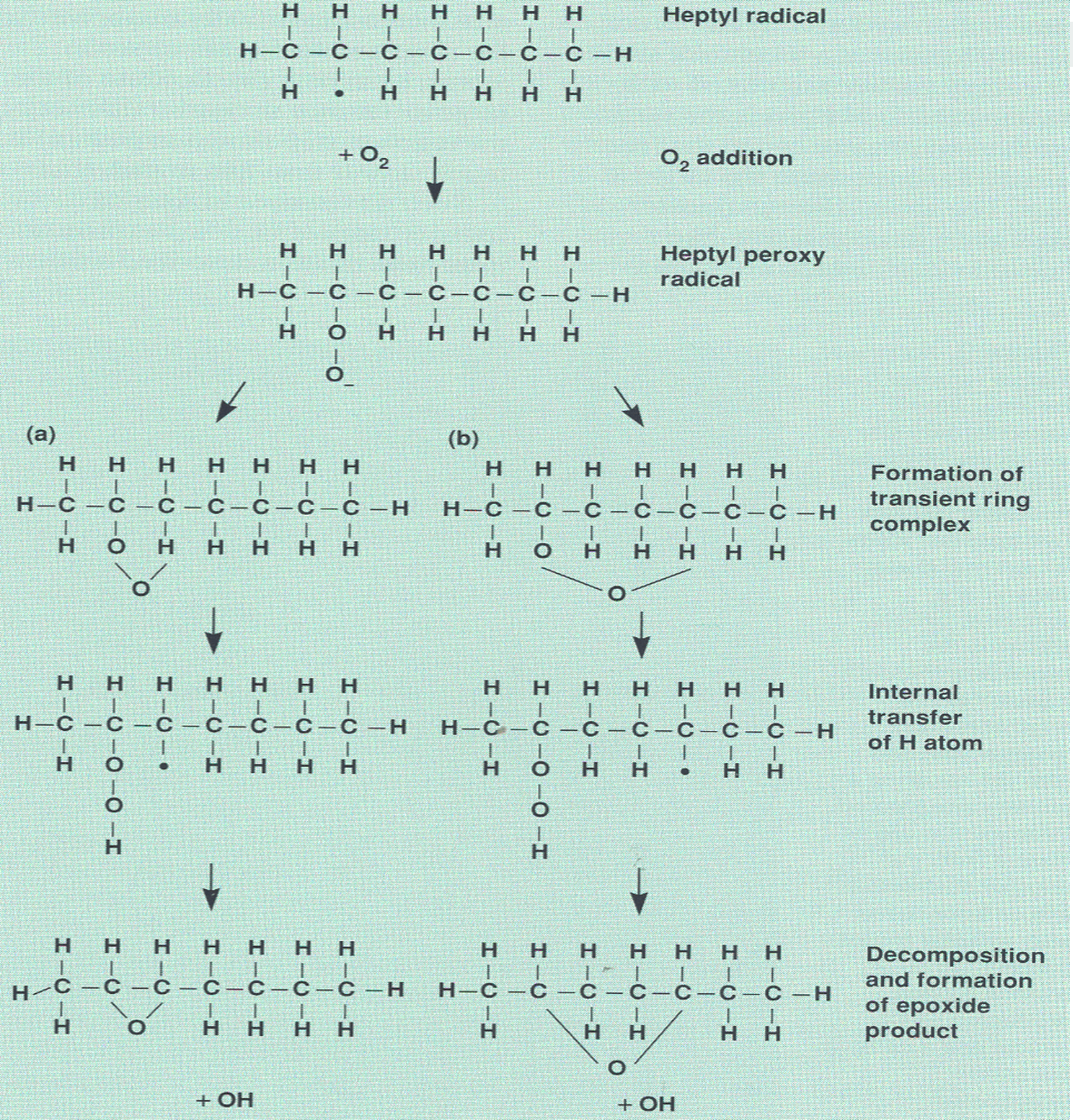
Ignition delay times very close

n-Alkanes:

cannot reproduce the early formation of CO_2

but

reproduce the reactivity of methyl esters very well



RSE (5-ring) >

RSE (6-ring) >

RSE (7-ring) >

RSE (8-ring)

Interesting note

Experience with biodiesel

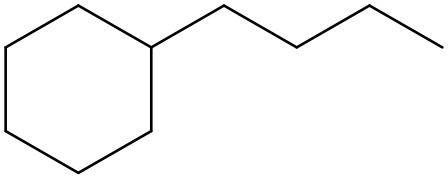
and methyl esters

suggests strategies for

kinetic modeling of n-alkyl

benzenes and n-alkyl

cyclohexanes



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

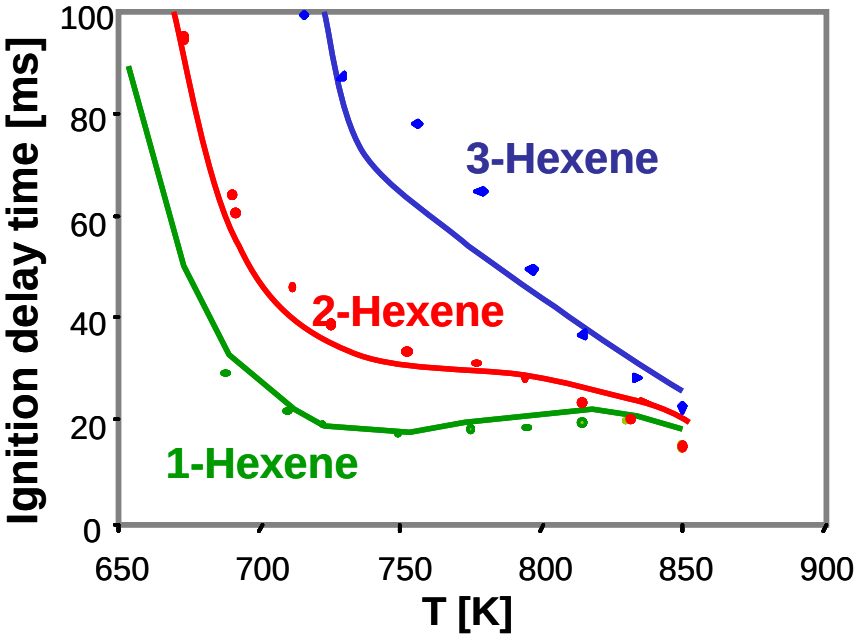
C - C = C - C - C - C 2 – hexene

C - C - C = C - C - C 3 – hexene

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

C - C = C - C - C - C 2 – hexene

C - C - C = C - C - C 3 – hexene



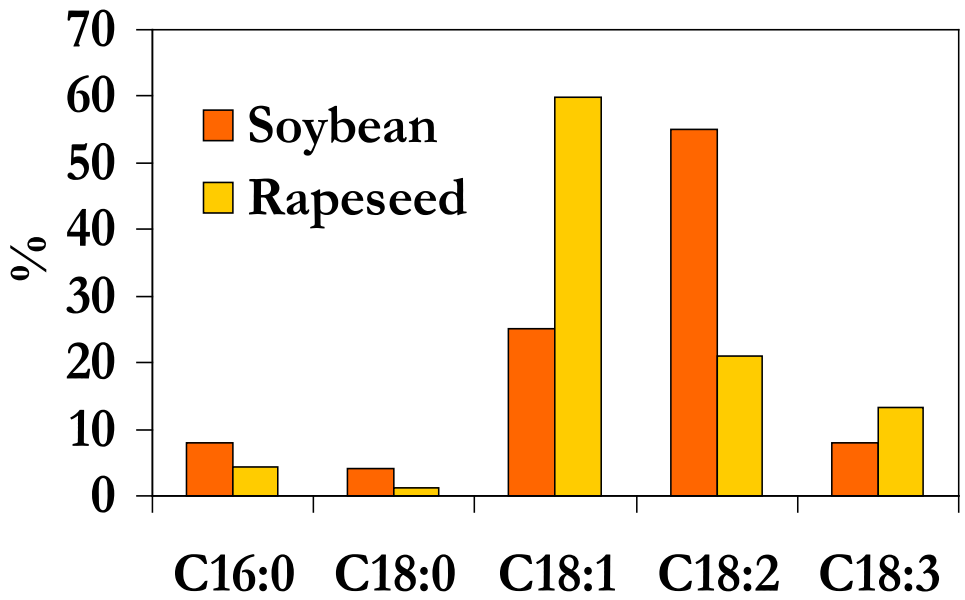
RCM Ignition delay times of hexene isomers (0.86-1.09 MPa, Φ=1):

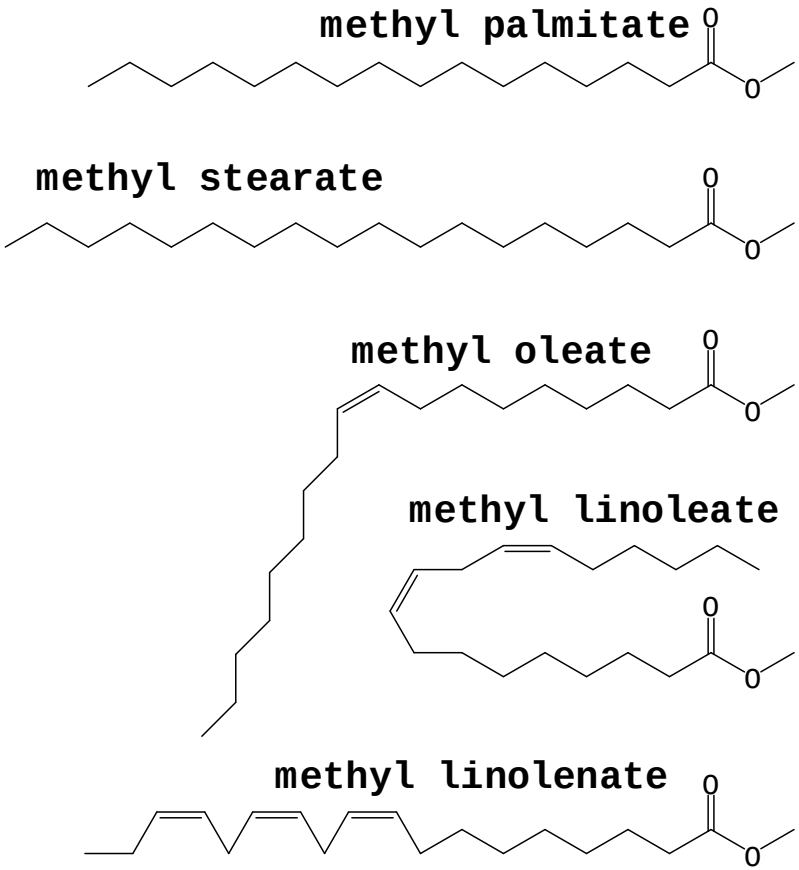
Rates of low temperature reactions producing chain branching depend on energy barriers

Energy barrier = BE (C-H bond) + RSE (ring strain) + ΔH (reaction)

Double bonds in bio-diesel long chain molecules provide another interesting “wrinkle”. Ring strain energies across one of these double bonds are dramatically larger than those across normal, saturated bonds, so double bonds strongly inhibit low temperature reactivity

Composition of Biodiesels





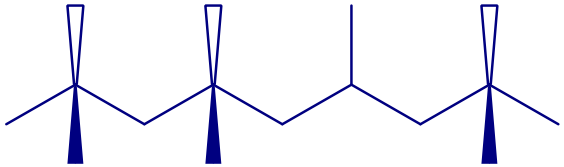
Branched hydrocarbons are different

- 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

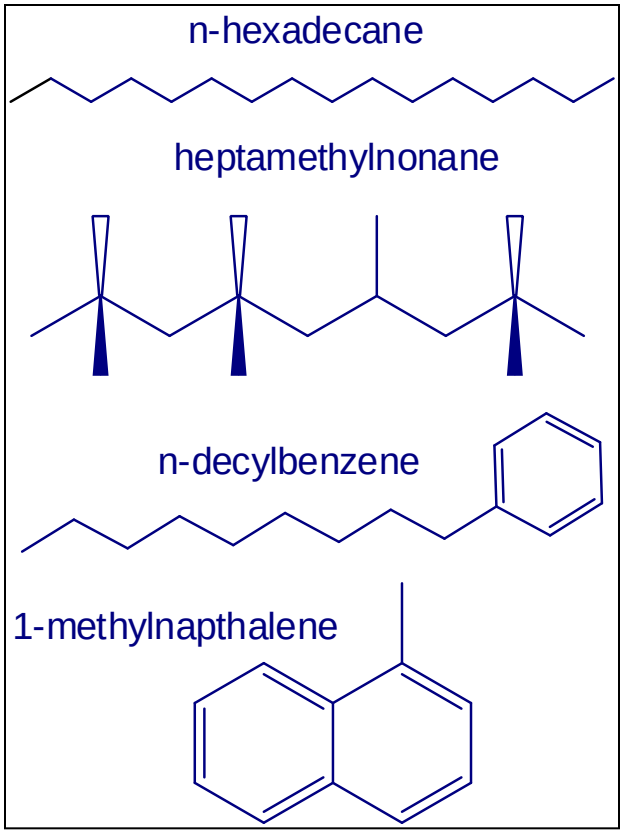
Heptamethyl nonane is a primary reference fuel for diesel

- One of 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):



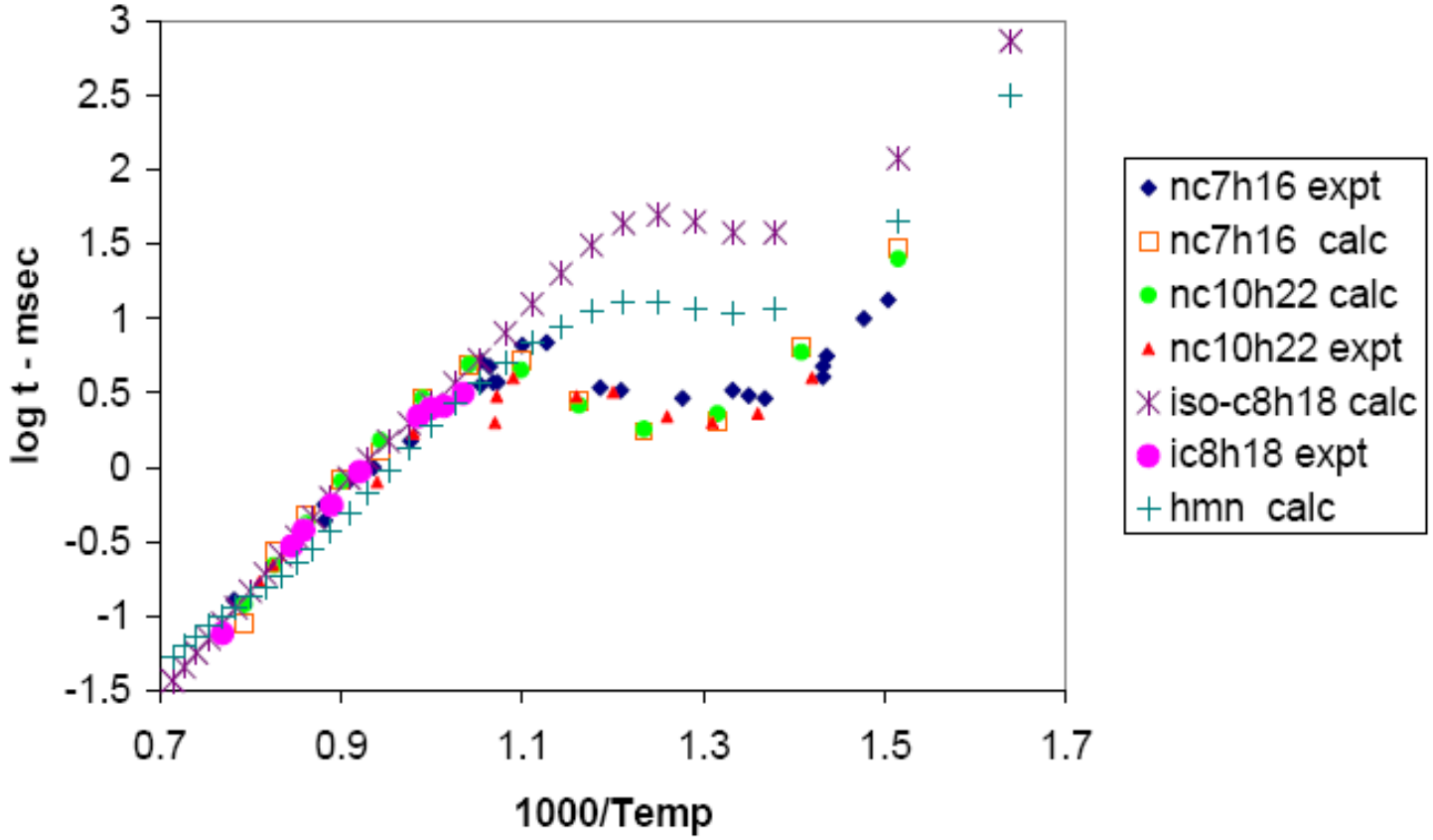
2,2,4,4,6,8,8-heptamethyl nonane is 2 iso-octane radicals

```
    C       C       C       C
C - C - C - C - C - C - C - C - C
    C       C               C

   C       C           C       C
C - C - C - C•      •C - C - C - C - C
   C       C                   C

    C       C           C       C
C - C - C - C - C     C - C - C - C - C•
    C       •           C
```

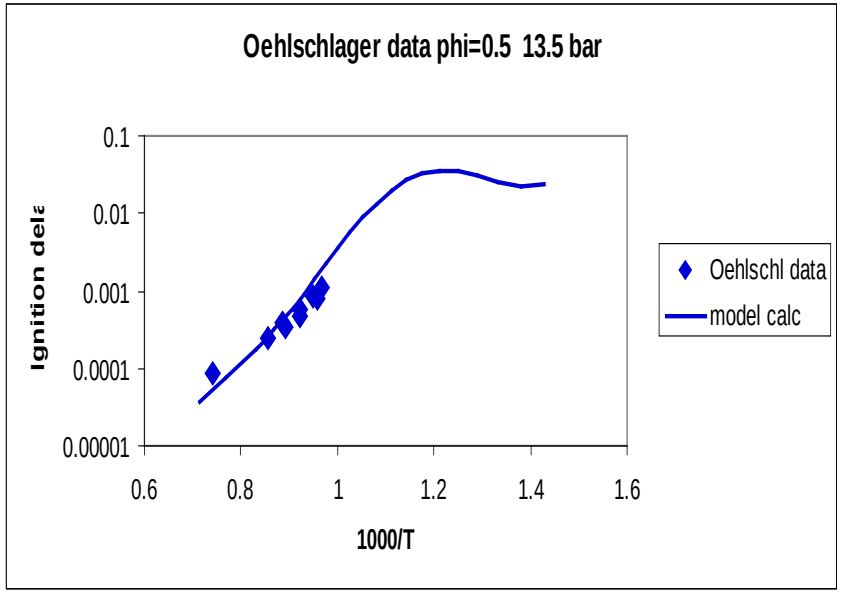
We should expect HMN kinetics to be quite similar to iso-octane

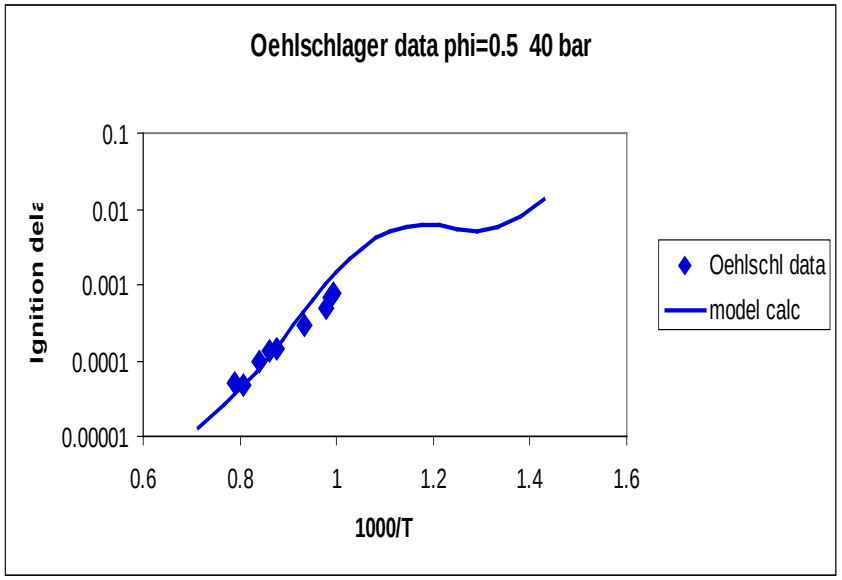
HMN and iso-octane ignitions are slower than n-alkanes only in the Low Temperature regime

13.5 bar pressure

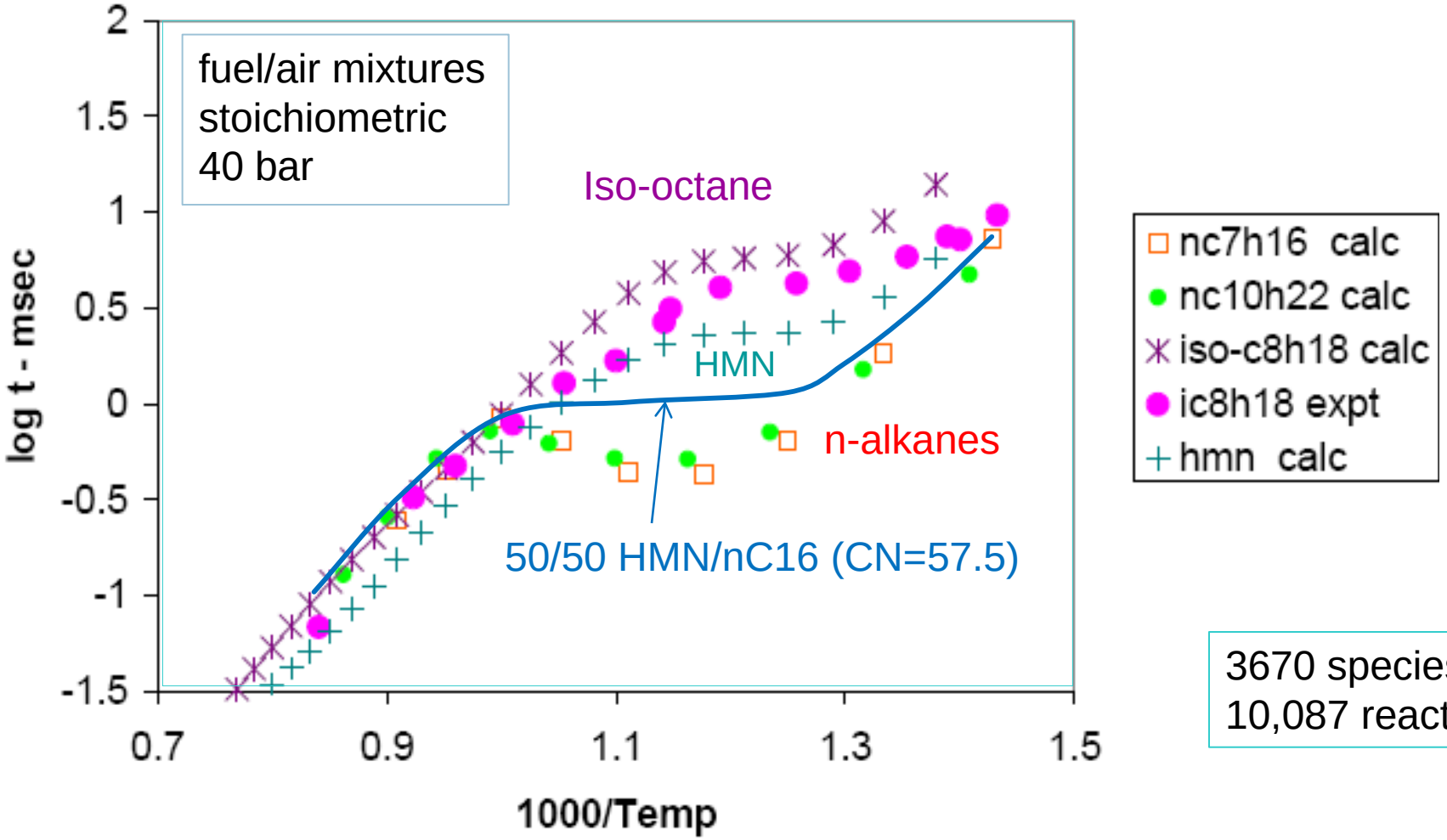


Recent experimental results show excellent agreement with modeling



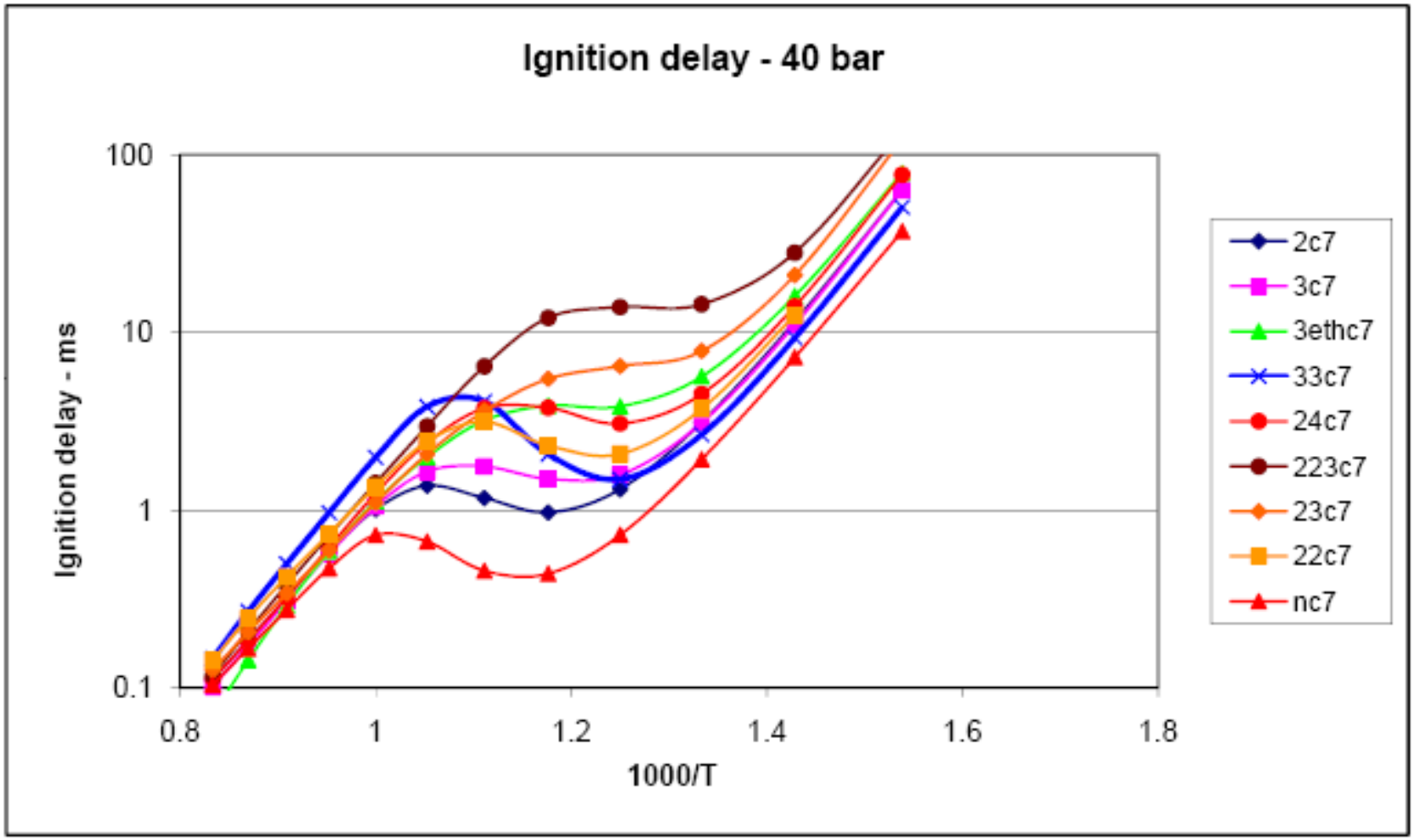


Computed PRF Mixtures for Diesel



3670 species
10,087 reactions

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



Current development of iso-dodecane mechanisms

```
     C   C   C   C   C
     |   |   |   |   |
C - C - C - C - C - C - C
```

```
     C       C       C
     |       |       |
C - C - C - C - C - C - C
     |               |
     C               C
```

Both isomers

suggested by Sandia

as surrogates for jet fuel

All of these large molecule reaction mechanisms need many improvements

- RO_2
- QOOH
- O_2QOOH
- Major needs for collection, curation and evaluation of reactions, rates, thermochemisty, etc.
- Olefin site-specific reactions
- Continued refinement of C_1 – C_5 core mechanism

Proposed new project

- Team approach to develop a commonly accepted C1 – C4 core mechanism
- Incremental funding for participation
- Parallels with atmospheric chemistry programs at NASA, NIST and DOE

High value of making mechanisms widely available

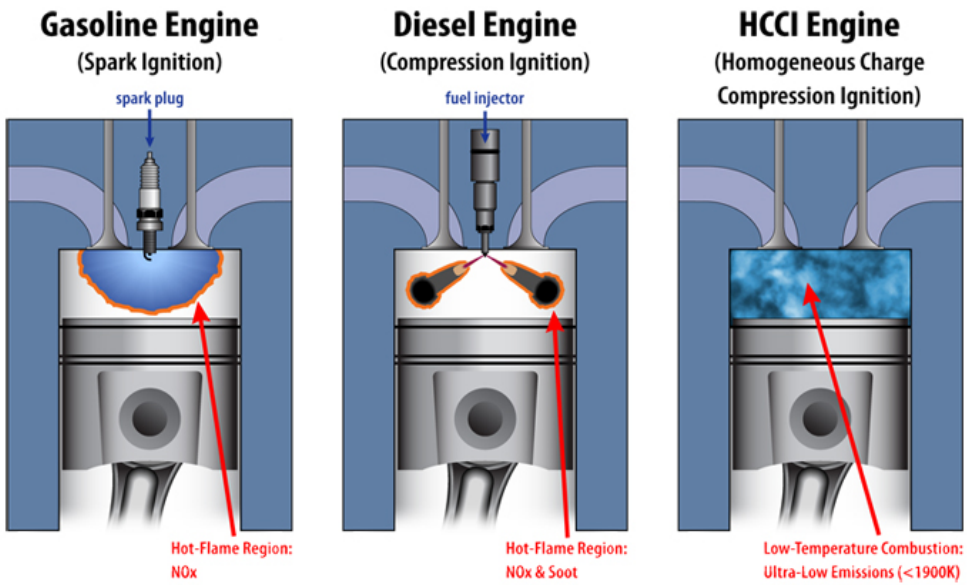
http://www-pls.llnl.gov/?url=science_and_technology-chemistry-combustion

- Hydrogen
- 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
- Dimethyl Carbonate
- Heptane, Detailed Mechanism
- Heptane, Reduced Mechanism
- iso-Octane
- Primary Reference Fuels: iso-Octane / n-Heptane Mixtures
- Organophosphorus Compounds under Incineration Conditions
- Organophosphorus Compounds in Propane Flames
- Organophosphorus Compounds Effect on Flame Speeds

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 for fuels from hydrogen and methane through much larger fuels including heptanes and octanes. Other classes of fuels for which models have been developed include flame suppressants such as halons and 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.

C8-C16 n-Alkanes