Fuel Research Review

MACCCR Fuels Research Review
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  - Gurpreet Singh
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  and Chitral Naik, Reaction Design
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
  - 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
Many groups are developing mechanisms for small and large molecule fuels

Possible to build a reasonable mechanism for nearly any fuel, using computer-generated or manually-generated techniques

Mechanism reduction is becoming very efficient

New need for “Mechanisms 2.0”
Kinetic mechanisms are usually only as good as they need to be

- Early example from 1976 conference
  - \( \text{CH}_3 + \text{O}_2 = \text{CH}_2\text{O} + \text{OH} \)
  - “This reaction and its rate must be correct because methane won’t ignite without it”
- Eventual solution
  - \( \text{CH}_3 + \text{CH}_3 = \text{C}_2\text{H}_6 \) Warnatz
- There are many ways to get the right answer if the question is a simple one
- Butler ‘Norris’ in “The Big Sleep” –
  - “I make many mistakes”
Early CH$_4$ and CH$_3$OH mechanisms

- Key pairs of reactions had estimated rate expressions
  
  - $\text{HCO} + \text{M} = \text{H} + \text{CO} + \text{M}$
  - $\text{HCO} + \text{O}_2 = \text{HO}_2 + \text{CO}$
  
  - $\text{CH}_2\text{OH} + \text{M} = \text{CH}_2\text{O} + \text{H} + \text{M}$
  - $\text{CH}_2\text{OH} + \text{O}_2 = \text{CH}_2\text{O} + \text{HO}_2$

- Early rates for these reactions were wrong by large margins, but their ratios were correct, and eventually experiments and theory provided better rates.
Very recent paper on methane pyrolysis

- Interested in cracking, H2 production, cooling applications

- Tried existing mechanisms from Dean, GRI-Mech, Leeds, Konnov, Sung, San Diego, Dagaut, Nancy, Sandia, Glarborg, Frenklach, Milano, MIT, LLNL

  - None were satisfactory, according to authors

- Authors were looking for detailed species production, including coke formation, surface effects, small mechanisms
Another example: n-heptane as a Diesel surrogate

- CN = 56 for n-C\textsubscript{7}H\textsubscript{16}
- n-heptane makes soot
- Lots of papers used n-C\textsubscript{7}H\textsubscript{16} mechanism for diesel

- Wait a minute! Diesel fuel has lots of aromatics

- New diesel surrogates have toluene or xylene or some other aromatics

- Another issue: variation in ignition with pressure isn’t quite correct, others?
  - Olefin kinetics are probably not correct
High temperature ignition in shock tubes

Bowman, C&F 1975

methanol ignition
Ignition of many saturated alkane fuels

Burcat et al. 1971, Westbrook et al. 2001
High temperature ignition in shock tubes
Smith et al., IJCK 2005

Figure 5  Heptane experimental (points) and model-predicted (lines) ignition delay times at 1.89% fuel, $P_5 = 2.0 \pm 0.2$ atm, and $\phi = 1.0$ in Ar: —■— n-heptane, —— △ 2,3-dimethylpentane, —— ● 2,2-dimethylpentane, —— ▽ 2,2,3-trimethylbutane.
Shock tube results from Adomeit et al.

Fuel n-heptane  Ciezki et al., 1993
Moving to lower temperatures

Fig. 10. \( n \)-Heptane/air ignition delay times for the low-pressure regime. \( \phi = 1.0 \).

Gautier et al. 2004
Heptane isomers

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.

2001/2002
For a long time I thought we had done a lot of things correctly, but the results for 33c7 mean there are errors that need to be addressed. We now know there are additional errors.
Primary Reference Fuels for Gasoline

n-heptane    Octane Number = 0

iso-octane    Octane Number = 100
We have assembled primary reference fuel mechanism for diesel fuel

- **Diesel PRF:**
  - n-cetane
  - iso-cetane

- **PRF for Diesel mechanism:**
  - 2,837 species
  - 10,719 reactions
Our fuel palettes

### Diesel fuels
- 1-methylnaphthalene
- 1,2,4-trimethylbenzene
- decalin
- n-dodecylcyclohexane
- n-hexadecane
- n-dodecane
- 1,2,4-trimethylbenzene
tetralin
- 2,9-dimethyldecane
- 2-methylpentadecane
- 3-methylundecadecane

### Gasoline fuels
- toluene
- xylene
- 2,2,4-trimethylpentane
- 2,4-dimethylpentane
- methylnexane
- 2-pentene
- ethanol
- n-heptane
- n-pentane

- **n-alkanes**
- **branched alkanes**
- **cycloalkanes**
- **aromatics**
- **olefins**
- **oxygenates**
Key reaction paths for alkanes

- Differences between C – H bond energies for primary sites and secondary sites

- Number of atoms in low temperature transition state rings involved in RO2 isomerizations

- These factors used fundamental chemical principles to explain the sources of octane numbers in SI engines and cetane numbers in Diesel engines. These numbers had been recognized for 75 years but never based on basic chemical principles.
Reactions of alkyl radicals and O$_2$

- Mod 1.0 purely addition reactions with rapid stabilization
- Questions first arose from studies of C$_2$H$_5$ + O$_2$ and C$_2$H$_4$ + HO$_2$ by Dean, Taatjes, Gutman/Slagle, Kaiser, Schaefer, Green, Miller/Klippenstein, etc., led to
- Recent work of Taatjes and Zador on molecular elimination pathways
- Recent work by Dean group on RO$_2$ and QOOH isomerizations
- NTC depends on accurate balance between chain branching and propagation pathways in low T regime – major opportunity?
- Importance of “rule-based” kinetic pathways
- This research system is working the way it is intended
R + O₂ = RO₂ reaction is the gateway to LTO

- Rising temperature leads to dissociation and ends all of the LTO kinetics

- RO₂ can be very unstable if O₂ tries to attach to a weak bonding site

- Weak bonding sites can result from a wide range of structural chemistry reasons
Class 12 – RO₂ isomerization

Transfer H atom within the molecule
Class 12 – RO₂ isomerization

O
H H O H H H
H C – C – C – C – C – C – CH
H H H H H H H
Class 12 – RO₂ isomerization

\[
\begin{align*}
\text{O} & \quad \text{H} \quad \text{H} \quad \text{O} \quad \text{H} \quad \text{H} \\
\text{H} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{O} \quad \text{H} \\
\text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\
\end{align*}
\]
Class 12 – RO₂ isomerization
RO$_2$ isomerization reactions have many uncertainties

- These reactions were initially proposed to explain CN influences of C = C double bonds

- C = C double bonds inside transition state ring could affect rates of isomerization

- cis vs. trans structures can affect rates of these isomerization reactions

- New theory analysis may have resolved these issues, together with better thermochemistry of bis-allylic bonds
These results appear inconsistent with what we know about CN.

- **13.5 bar**
  - Stoichiometric fuel/air

High T chemistry  

- n-C7H16  CN = 56
- n-C16H16  CN = 100

Low T chemistry
Take a closer look at these curves

20 atm, PHI=1

![Graph showing ignition time (s) vs. 1000/T[K] for IC8H18, with different mechanisms and thermodynamic models labeled.]
These ignition curves have lots of structure

$n$-Heptane RCM / ST validation; $\phi = 1.0$

- New ST (13 bar)
- Old ST (10 bar)
- Heufer et al (13 bar)
- Silke Data (10 atm)
- New RCM data (13 bar)
- New RCM data (7 bar)

Mechanism: LLNL $n$-Heptane mechanism
- Solid lines: Adiabatic simulations
- Dashed Lines: Heat loss simulations
- Black line: Simulation at 13 bar
- Orange line: Simulation at 7 bar
Species measurements change the game
More careful analysis showed some errors in n-alkane mechanisms

- Lumping of alkenyl radicals done incorrectly

  in n-C\textsubscript{8}H\textsubscript{18} mechanism
  \[ C - C = C - C - C - C - C - C - C \]

  in n-C\textsubscript{12}H\textsubscript{26} mechanism
  \[ C - C = C - C - C - C - C - C - C - C - C - C \]

  Rate of \( 2\text{C}_{8}\text{H}_{16} + R = \text{RH} + 2\text{C}_{8}\text{H}_{15} \) equal to
  Rate of \( 2\text{C}_{12}\text{H}_{24} + R = \text{RH} + 2\text{C}_{12}\text{H}_{23} \)
Details of alkene reactions relatively unimportant if the only question is to predict the ignition delay or laminar burning velocity.

For me, the issue didn’t arise until we became interested in biodiesel fuels, but it also affects kinetics of any hydrocarbon fuel with C=C double bonds, where the fuel itself is an olefin.

Species-specific experiments are essential, recently there have been many more such experiments.
Similar calculations at higher equivalence ratio give different results

Ignition Delay Time (s)

n-alkanes, 20 atm, phi=3, in air

1000/T (1/K)

- nC8H18
- nC10H22
- nC12H26
- nC14H30
- nC16H34
This led us to use our kinetic models to look in depth at kinetics of CN

- Some reaction conditions and results don’t depend on the size and structural features that influence CN
  - e.g. $\phi = 1$, 13 bar shock tube ignitions
- Try to find conditions where CN makes a difference but can be examined in idealized laboratory experiments
  - e.g. PSR, RCM and pressures and equivalence ratios
- Diesel ignition occurs for high pressure, fuel-rich conditions, so 13.5 bar and $\phi = 1$ may be unrealistic
- At the same time, we want to understand what kinetic factors affect CN
- We now have more classes of mechanisms to use in these kinetic studies
HMN ignition results at 13 bar:

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

Iso-octane

fuel/air stoichiometric 13 bar

n-alkanes

1000/T [K]

log τ [ms]

nc7h16 expt
nc7h16 calc
nc10h22 calc
nc10h22 expt
iso-c8h18 calc
ic8h18 expt
hmn calc
Chemical Kinetic Mechanism for 2-methyl alkanes

Includes all 2-methyl alkanes up to C20 which covers the entire distillation range for gasoline, jet 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

Key fuel species to study Fischer-Tropsch fuels
2-methyl alkanes ignite slower than n-alkanes

n-alkanes and 2-methylalkanes, 20 atm, phi=3, in air
PSR separates the n-alkanes by CN value

Fuel – rich (\(\phi = 3.0\)) and high pressures (50 bar) conditions
We use the PSR to spread out the reaction zone

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

- **Methyl Palmitate (C16:0)**
- **Methyl Stearate (C18:0)**
- **Methyl Oleate (C18:1)**
- **Methyl Linoleate (C18:2)**
- **Methyl Linolenate (C18:3)**

![Chemical structures of various biodiesel components](image)

**Graph showing composition of biodiesels for Soybean and Rapeseed**

<table>
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<tr>
<th>Component</th>
<th>Soybean (%)</th>
<th>Rapeseed (%)</th>
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<tr>
<td>C18:3</td>
<td>10</td>
<td>5</td>
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</table>
Assembled chemical kinetic model for all of the remaining 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:
Cetane numbers of biodiesel components

- Methyl stearate  C18:0   CN = 101
- Methyl oleate    C18:1   CN = 59
- Methyl linoleate C18:2   CN = 38
- Methyl linolenate C18:3   CN = 23
- Methyl palmitate C16:0   CN = 86

Number of C = C double bonds strongly affects CN
Chain length strongly affects CN
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, $\Phi=2$ (Fuel: 200 ppm, residence time = 0.05 s)

Simulated conversions of biodiesel components

Jet stirred reactor

Derived cetane numbers from Knothe (2010)
Effects of $\text{C} = \text{C}$ double bonds in long chain molecules

$s\quad s\quad s\quad s\quad s\quad s\quad s\quad s\quad s\quad s$

- $\text{C} – \text{C} – \text{C} – \text{C} – \text{C} – \text{C} – \text{C} – \text{C} – \text{C} – \text{C} – \text{C} – \text{C} – \text{C}$

$s\quad s\quad s\quad s\quad s\quad s\quad s\quad s\quad s\quad s\quad s\quad s$

With no $\text{C} = \text{C}$ double bonds, all $\text{CH}_2$ groups in the chain have the same $\text{C} – \text{H}$ (and $\text{C} – \text{O}$) bond strengths
C = C double bonds reduce low T reactivity

- C – C – C – C = C – C – C – C

- Inserting one C=C double bond changes the C-H bond strength for 6 H atoms in the C chain
- Allylic C – H bond sites are weaker than most others
- Therefore they are preferentially abstracted by radicals
- O₂ is also very weakly bound at allylic sites and falls off rapidly, inhibiting low T reactivity
Two double bonds make a huge difference

\[ \text{s s a v v a s s s s} \]
\[ - \text{C - C - C - C = C - C - C - C - C - C -} \]
\[ \text{s s a a s s s s} \]
Two double bonds make a huge difference

\[
s \quad s \quad a \quad v \quad v \quad a \quad s \quad s \quad s \quad s \\
- \quad C \quad - \quad C \quad - \quad C \quad - \quad C \quad = \quad C \quad - \quad C \quad - \quad C \quad - \quad C \quad - \\
s \quad s \quad s \quad a \quad a \quad s \quad s \quad s \quad s \quad s
\]

\[
s \quad s \quad s \quad a \quad v \quad v \quad a' \quad v \quad v \quad a \\
- \quad C \quad - \quad C \quad - \quad C \quad - \quad C \quad = \quad C \quad - \quad C \quad - \quad C \quad = \quad C \quad - \quad C \quad - \\
s \quad s \quad s \quad a \quad a' \quad a \quad a
\]
Two double bonds make a huge difference

C – H \textit{s} bond > C – H \textit{a} bond > C – H \textit{a' bond}

Same trend with C – OO bonds
Kinetic factors involved

- Equilibrium of \( R + O_2 + M = RO_2 + M \) additions
  Particularly weak bond at allylic sites

- Some authors have reported that transition state rings for \( RO_2 \) isomerizations at low temperatures are strongly inhibited if there is a double bond in the transition state ring.

- We need theory analysis to examine these and other related factors
C = C double bonds reduce low T reactivity

Does the C=C double bond change the rate of isomerization?

\[ \text{O} \]
\[ s \quad s \quad O \quad v \quad v \quad a \quad s \quad s \]
\[ - \text{C – C – C – C = C – C – C – C} \]
\[ s \quad s \quad a \quad a \quad s \quad s \quad s \]
Does the C=C double bond change the rate of isomerization?

Probably not very much
Methyl linoleate has three C=C double bonds, one pair of allylic, weak C-H bonds and two very weak, bis-allylic CH$_2$ locations

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The low bis-allylic bond strengths are also responsible for poor fuel stability of many of these fuels with 2 or 3 C=C double bonds.

Some cell biology research is trying to increase oleate and decrease stearate, linoleate and linolenate in soy biodiesel fuel.
Biodiesel components reactivities in JSR

Stoichiometric
Single-component fuels
Atmospheric pressure
Very dilute in He

Temperature - K

Conversion

- stearate
- palmitate
- oleate
- linoleate
- linolenate
Soy and rapeseed biodiesel fuels in JSR
Differences between soy and rapeseed fuels

C18:1
Rapeseed diesel major component

C18:2
Soy diesel major component

Rapeseed  CN = 54  Soy  CN = 47

Double bonds in the carbon chain inhibit low T chemistry
Plant and animal fat oils have different fatty acid profiles that affect reactivity in a diesel engine.

<table>
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<tr>
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<th>Sunflower</th>
<th>Safflower</th>
<th>Linseed</th>
<th>Jatropha</th>
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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!
Plant and animal fat oils have different fatty acid profiles that affect reactivity in a diesel engine

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Biodiesel fuels from different oils

- Methyl ester fuels from different plant and animal fats and oils have different CN values.

- Detailed composition of these biodiesel fuels determine their CN values.

- Biggest factor for CN 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.
Additives are used to increase CN

- Blending higher CN components
- We developed kinetic reaction mechanisms recently for ethyl hexyl nitrate and di-tertiary butyl peroxide
- For both additives, there is one very weak bond that is broken at quite low temperatures, producing very early heat release and promoting ignition
Additives are used to increase CN

- Add additives to biodiesels with low CN (e.g. linseed derived biodiesel)

- We developed kinetic reaction mechanisms recently for ethyl hexyl nitrate (ENH) and di-tertiary butyl peroxide (DTBP)

- For both additives, there is one very weak bond that is broken at quite low temperatures, producing very early heat release and promoting ignition
Biodiesel fuel with lowest CN is linseed biodiesel

Linseed oil methyl ester fuel has CN = 39
Ethyl Hexyl Nitrate increases CN

Linseed oil

Conversion

Temperature - K

500 600 700 800 900 1000 1100

0.1% of the fuel is Ethyl Hexyl Nitrate
More EHN has only a small incremental effect

More Ethyl Hexyl Nitrate has smaller proportional effect
Shock tube simulations illustrate enhanced ignition from EHN and DTBP

nc7h16 - 13.5bar - phi=1.0

Ignition delay - ms

100.0
10.0
1.0
0.1

0.8 1 1.2 1.4 1.6

1000/T

nc7h16
5% EHN
0.1% EHN
5% DTBP
We can explain and model major factors that affect CN

- Most of the effects occur at low temperatures
  - \(550K \leq T \leq 750K\)
- Molecular structure has a big effect
  - \(CN(n\text{-cetane}) = 100\)
  - \(CN(iso\text{-cetane}) = 15\)
- Molecule chain length has a big effect
  - \(CN(n\text{-heptane}) = 56\)
  - \(CN(n\text{-cetane}) = 100\)
  - \(CN(methyl\text{ decanoate}) = 47\)
  - \(CN(methyl\text{ stearate}) = 101\)
- \(C=C\) double bonds have a big effect
  - Methyl stearate \(\rightarrow\) methyl linolenate \(CN: 101 \rightarrow 23\)
- Effects of diesel ignition enhancers such as EHN and DTBP
Still many reaction pathways are uncertain

- Nobody has studied kinetics in large species with multiple C=C bonds
- Rates and products highly uncertain but important in biodiesel fuels
- Tough to do kinetics experiments (low vapor pressures)
- Many groups are doing experiments with smaller alkyl ester fuels, saturated and unsaturated.
- Little of this body of new experiments includes smaller alkyl esters with multiple C=C bonds
- Uncertainties in thermochemistry, known to have significant influences
- cis/trans issues with multiple double bonds
Next steps

- We need to extend this analysis to aromatics, cyclo-paraffins, olefins and other fuel types

- We need mechanism validation experiments for all of these fuel types

- We need theory support for the types of reactions that we have found to be important in these systems

- In the past several years, the numbers and structures of fuels with kinetic mechanisms have grown rapidly
Conclusions

Validated chemistry models can eventually be used in practical applications

New Chemical kinetic model have been developed for:
- Branched alkanes
- 2-methylheptane, 3-methylheptane, and 2,5-dimethylhexane
  - C8 Aromatics
  - Xylenes and Ethylbenzene
- Gasoline Surrogates
  - Alcohols
  - Butanol isomers and iso-pentanol