Detailed Chemical Kinetic Models for Large Hydrocarbon and Biodiesel Fuels

Combustion Colloquium in Memory of Ninni D’Alessio

Charles Westbrook
Lawrence Livermore National Laboratory

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The world is looking for new sources of energy

- Wind power
- Solar radiation
- Geothermal power
- Sea waves
- Nuclear power
- Fusion reactors
- Any others? Probably

- But everyone seems to agree that combustion is still a big problem
Today, combustion is responsible for most of the power generation in the world

- 85% of US power production
- 90+% of transportation power
- Perhaps 100 years of fossil fuels remain
- Alternative energy sources are not very mature
  - estimate of 50 – 100 years needed for development
- Combustion is a relatively mature science
- The challenge is to use research to limit the adverse impacts of fossil fuels and buy time for the alternatives to become practical
The pace of combustion research has been accelerating

- Engines are evolving
- Fuels are changing
- New research tools are being used
  - Experimental
  - Modeling
- Many familiar problems still remain, including:
  - Autoignition
  - Soot production
Future hydrocarbon fuels will be from many sources

- Some petroleum will still be available
- Bio-derived fuels
  - ethanol, butanol, algae
  - biodiesel from vegetable and animal oils
- Oil sands
- Oil shale
- Coal-to-liquids
- Fischer – Tropsch
- Natural gas
- Hydrogen

- The fuel world is already becoming more complex
- Each new fuel presents new complications
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
Engines are evolving rapidly

- Spark-ignition and Diesel engine concepts are more than 100 years old
- SI engines operate via premixed flame propagation, combustion is initiated by firing a spark
- Diesel engines have both premixed and diffusion flame regimes, initiated by liquid fuel injection
- Both have been optimized empirically for 100 years, but only recently using modeling and laser diagnostics
- Many fundamentals of both engines were still poorly understood, if at all, limiting progress on them
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)
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.
Predicting the soot precursors is one of the keys to predicting soot emissions from a Diesel engine.

Fuel-rich premixed reaction zone

From:
John Dec,
SAE paper
970873
Products of rich premixed ignition are mostly small unsaturated hydrocarbons, especially acetylene and ethene.
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
Structure of Tripropylene Glycol Monomethyl Ether (TPGME)
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.
How well an oxygenated fuel works depends on its molecular structure.
Engines - II

- Engine efficiency improves with increasing engine compression ratio in SI engines
  - Increasing CR leads to engine knock
- Diesel engine is more efficient and produces more power due to its higher CR
- Both engines are subject to the familiar NOx – UHC trade-off
  - Need higher temperatures completely burn fuel, but higher temperatures make more NOx
- Both engines involve flame propagation, so they are subject to flammability limits
HCCI efficiency similar to diesel engines

\[
\text{engine efficiency} = 1 - \frac{1}{CR^{\gamma-1}}
\]

\(\gamma = 1.4\) for air
\(\gamma = 1.35\) for fuel and air

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HCCI combustion properties

- Very fuel-lean
- Low product temperatures $\rightarrow$ low NOx
- Combustion initiated by thermal autoignition
- Autoignition is sensitive to fuel molecular structure
- HCCI engine still produces UHC, but as long as NOx is near-zero, catalytic after-treatment can address UHC
Alkylperoxy radical isomerization controls the behavior in an HCCI engine.

- 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.
Higher $O_2$ \{ 

Conventional Diesel path

Kitamura, et al. 2002

HCCI

Temperature [K]

Equivalence ratio
HCCI combustion therefore depends more on fuel composition than any earlier engine type

- 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  $13 < C < 22$
- Molecular classes also are different in each application
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 Surrogate Palette for Diesel

- n-alkane
- branched alkane
- cycloalkanes
- aromatics
- others

- n-dodecane
- n-tridecane
- n-tetradecane
- n-pentadecane
- n-hexadecane

- tetralin

- n-decyl-benzene
- alpha-methyl-naphthalene

- butylcyclohexane
- decalin

- hepta-methyl-nonane
n-Hexadecane is a primary reference fuel for diesel and recommended diesel surrogate component

- 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):

- n-hexadecane
- Heptamethylnonane
- N-decyld benzene
- 1-methylnaphthalene
A recent gasoline surrogate fuel mixture contains fuels from each class of molecules

- n-heptane
- iso-octane
- pentene
- cyclohexane, methylcyclohexane
- toluene
- ethanol
Use of surrogate fuels is an important current theme in combustion chemistry

- Same approach has been used by Prof. Sarofim for jet fuel
- 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
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
Good agreement with ignition delay times at “engine-like” conditions over the low to high temperature regime in the shock tube

Shock tube experiments:
Ciezki, Pfahl, Adomeit 1993,1996

13.5 bar stoichiometric fuel/air fuels:
n-heptane n-decane
All large n-alkanes have very similar ignition properties
Ignition Time [µs] vs 1000/T [1/K]

- 1.0 experimental studies
- All data scaled to 12 atm using ε ~ P^1
- Gauthier et al., n-heptane
- Cleek 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
- Currin 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(t) = ±0.238)
Chemical kinetic mechanism for nC8-nC16 surrogate components:

- 2116 species
- 8130 reactions
- Low and high temperature chemistry => can use to investigate low temperature combustion strategies
- Same reaction rate rules as highly validated n-heptane mechanism
- Tailor the mechanism to fit specific fuels for computational efficiency

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<th>C_{16}H_{34}</th>
<th>C_{14}H_{30}</th>
<th>C_{12}H_{26}</th>
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<td>Reactions</td>
<td>8130</td>
<td>6449</td>
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<td>2116</td>
<td>1668</td>
<td>1282</td>
<td>940</td>
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Biodiesel fuels

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

\[ \text{triglyceride} + 3 \text{CH}_3\text{OH} \rightleftharpoons 3 \text{CH}_3\text{O} \text{C} \text{H}_3 + \text{glycerol} \]

(R = hydrocarbon chain)
Composition of Biodiesels

![Bar chart showing the composition of biodiesels from soybean and rapeseed.](chart)

- **Soybean**
  - C16:0: 5%
  - C18:0: 10%
  - C18:1: 40%
  - C18:2: 20%
  - C18:3: 15%

- **Rapeseed**
  - C16:0: 10%
  - C18:0: 5%
  - C18:1: 50%
  - C18:2: 20%
  - C18:3: 15%

**Chemical structures**

- **Methyl palmitate**
- **Methyl stearate**
- **Methyl oleate**
- **Methyl linoleate**

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The early formation of CO$_2$ is better reproduced by the MD mechanism.

Early CO$_2$ formation reduces effectiveness of oxygenated fuels for reducing soot formation.
Methyl stearate (n-C$_{18}$ methyl ester) has the same ignition properties as large alkanes.
Comparison with n-Decane Ignition Delay Times

Equivalence ratio: 1, in air

n-Alkanes:
cannot reproduce the early formation of CO$_2$

but
reproduce the reactivity of methyl esters very well

Symbols: n-decane experiments (Pfahl et al.)
Line: methyl decanoate mechanism

Ignition delay times very close
Mechanism Structure

- Written in a systematic way (reaction rate rules)

- High and low T chemistry

→ 8580 reactions
→ 3034 species
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
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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
HMN and iso-octane ignition is slower than n-alkanes only in the Low Temperature regime.

13.5 bar pressure
Recent experimental results show excellent agreement with modeling.
Basic science research is solving the long-standing puzzle of engine knock and autoignition

- Structural chemistry
- Site-specific reaction rates from bond energies
- Ability to compute reaction histories was a crucial feature
- Same chemistry is involved in Diesel and HCCI engines
- Autoignition and soot production are closely tied together in the Diesel engine
Pentane isomers ignite in order of their octane numbers.

Ribaucour et al., 2000
Interesting note

Experience with biodiesel and methyl esters suggests strategies for kinetic modeling of n-alkyl benzenes and n-alkyl cyclohexanes.
Cycloalkanes: methyl cyclohexane

- Cycloalkanes are interesting due to oil sands
Oil-sand derived fuels have focused attention on cyclo-alkanes
• 1.7-2.5 trillion barrels of bitumen in place in the oil sands of Alberta, Canada
• More oil than the known reserves of the Middle East

Composition of Oil Sands

http://www.oilsandsdiscovery.com/oil_sands_story/pdfs/vastresour...ce.pdf
Graphic: pp. 194, Athabasca Oil Sands - The Karl A. Clark Volume
Asphaltene molecule typical of oil sands

\[ \text{C}_{419}\text{H}_{498}\text{N}_6\text{O}_4\text{S}_8\text{V} \]

Mol. Wt.: 5989.94
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.
Closing comments

- Capability has followed the computer industry
- Early applications models grew slowly along with early computers. Later applications have emerged very rapidly when computing was already available.
- Overall system models have developed to the point that they can be used for practical problems
- Capabilities are growing so rapidly that many real problems are no longer out of reach, and we expect computer capabilities to continue to grow
- Fuels are evolving, and new fuel chemistry models have become robust and general enough to cope
Closing comments - 2

- More than 100 years from now, we will still need liquid hydrocarbon fuels, because of their power density.
- Methods to convert CO$_2$ to hydrocarbons will be available and worth the expense for some applications.
- Alternative energy sources will dominate the energy picture, but some combustion will still be very important.
- It will always be important to do that combustion in a responsible and efficient manner.
- We should understand and appreciate the pioneering work of pioneers including Ninni D’Alessio who have made these advances possible.