Recent Research Results from the Sandia Advanced Fuels Laboratory

Charles J. Mueller
Sandia National Laboratories
Livermore, California

Research Supported by
US DOE Office of FreedomCAR and Vehicle Technologies
Program Manager: Kevin Stork

Doshisha University
Kyoto, Japan
July 22, 2007
Presentation Outline

- Overview of Sandia programs and facilities
- Sandia Advanced Fuels Laboratory
- Recent results
  - Dilute clean diesel combustion
  - Biodiesel NO\textsubscript{x} increase
- Conclusions
- Additional recent results and references
What is Sandia?

- A national laboratory funded by the US Dept. of Energy
  - Operated by Lockheed-Martin Corp.

- Technical programs include
  - Engineering Sciences
  - Computational and Information Sciences
  - Materials and Process Science
  - Pulsed Power Sciences
  - Microelectronics and Photonics Sciences

- Sandia has ~ 7500 employees
  - 2100 Masters
  - 1400 Ph.D.
  - Majority are engineers
  - 900 in CA
Sandia Has Facilities in Numerous Locations

- Albuquerque, New Mexico
- Tonopah Test Range, Nevada
- WIPP, New Mexico
- Yucca Mountain, Nevada
- Kauai Test Facility, Hawaii
- Livermore, California

Combustion Research Facility (CRF)
**Engine-Related Research at the CRF**

- **Engine Combustion Department** has 7 laboratories (one principal investigator in each lab, dept. manager is Dennis Siebers)

  - **Constant-Volume Vessel**
    - Lyle Pickett (PI)
    - Tim Williams (PD)

  - **Fuel Effects**
    - Chuck Mueller (PI)
    - Glen Martin (PD)
    - Krishna Lakshminarasimhan (PD)

  - **HCCI Fundamentals**
    - John Dec (PI)
    - Magnus Sjoberg (LTE)
    - Wontae Hwang (PD)

  - **HCCI, Light-Duty**
    - Richard Steeper (PI)
    - Russ Fitzgerald (PD)

  - **HECC, Heavy-Duty Diesel**
    - Mark Musculus (PI)

  - **HECC, Light-Duty Diesel**
    - Paul Miles (PI)
    - Will Colban (PD)
    - Isaac Ekoto (PD)

  - **HECC, Hydrogen**
    - Sebastian Kaiser (PI)
Sandia Fuels Project Vision

High-efficiency, clean combustion (HECC) using advanced and/or non-petroleum fuels:

- Robust operation
- Acceptable heat release
- High power density

HECC = High-Efficiency, Clean Combustion
- Efficiency similar to conventional diesel
- US 2010 heavy-duty regulations achieved with oxidation catalyst

LTC = Low-Temperature Combustion
- No constraints on efficiency
- Peak T low enough to minimize NOx

HCCI = Homogeneous Charge Compression Ignition
New Fuels Can Be Very Different from Conventional Fuels, and Burn Differently

from Farrell et al., SAE 2007-01-0201

from Mueller, CRF News, May/June 2006
Optical Engine Specifications and Schematic

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Research engine</td>
<td>1-cyl. Cat 3176</td>
</tr>
<tr>
<td>Cycle</td>
<td>4-stroke CIDI</td>
</tr>
<tr>
<td>Valves per cylinder</td>
<td>4</td>
</tr>
<tr>
<td>Bore</td>
<td>125 mm</td>
</tr>
<tr>
<td>Stroke</td>
<td>140 mm</td>
</tr>
<tr>
<td>Conn. rod length</td>
<td>225 mm</td>
</tr>
<tr>
<td>Conn. rod offset</td>
<td>None</td>
</tr>
<tr>
<td>Piston bowl diameter</td>
<td>90 mm</td>
</tr>
<tr>
<td>Piston bowl depth</td>
<td>16.4 mm</td>
</tr>
<tr>
<td>Squish height</td>
<td>1.5 mm</td>
</tr>
<tr>
<td>Swirl ratio</td>
<td>0.59</td>
</tr>
<tr>
<td>Displacement per cyl.</td>
<td>1.72 liters</td>
</tr>
<tr>
<td>Compression ratio</td>
<td>11.3:1</td>
</tr>
<tr>
<td>Simulated compr. ratio</td>
<td>16.0:1</td>
</tr>
</tbody>
</table>

Quartz windows in piston and upper periphery of cylinder liner enable optical access
Dilute Clean Diesel Combustion (DCDC) Using Oxygenated and Emerging Fuels
DCDC Simultaneously Achieves Low Emissions and High Efficiency

- **Operating conditions**
  - Diethylene glycol diethyl ether (DGE) fuel
  - 1200 rpm, 7-bar IMEP
  - Steady-state operation
  - -9°C, 1.4 bar intake
  - EGR simulated by N₂ dilution

- **High-load operation also demonstrated in optical engine**
  - 18-bar IMEP (2/3 load)
  - 0.09 g/ihp-hr NOₓ
  - 0.26 FSN smoke
  - Load and efficiency limited by peak cylinder pressure capability of optical engine
Natural Luminosity Imaging of Undiluted and Highly Dilute Combustion (DGE Fuel)

Undiluted

9% Intake-O₂ Mole Fraction
More-Conventional Fuels and Operating Conditions

- **Fuels**
  - B100 = neat soy biodiesel (Peter Cremer Nexsol BD-0100)
  - CN80 = 80-cetane PRF blend, 76.5 vol% n-hexadecane + balance heptamethylnonane
  - D2 = Phillips #2 diesel reference fuel

- **Operating conditions**
  - 1200 rpm, steady-state
  - 6.7 bar IMEP load
  - Peak injection pressure = 1420 bar, 6 x 0.163 mm x 140° nozzle
  - Start of injection £ 4° BTDC
  - Start of combustion between 0° (TDC) and +0.5° ATDC
  - Simulated intake conditions: 53° C, 1.8 bar (abs.)
  - 960 K, 31 kg/m³ @ TDC (motored)
  - EGR simulated using nitrogen dilution
To What Extent Is DCDC Possible with Conventional and Emerging Fuels? [1,2]

- Answer: With near-term fuels, smoke emissions become ~50X too large at required EGR levels
  - Efficiency drops before compliant smoke emissions obtained
  - Highly oxygenated fuel can remove this barrier

- Very high levels of cooled EGR required for NO\textsubscript{x} compliance
  - Is there a better way to introduce diluent?
Are Fuel-Water Mixtures a Viable Alternative to EGR for NO\textsubscript{x} Control? [3]

Answer: Yes, potentially

- Studied blends of tri-propylene glycol methyl ether with 25 to 50 vol% water
- Stable blends pass corrosivity tests for ferrous metals and copper
- Ignition delay » 40-50 cetane #2 diesel
- Can lower NO\textsubscript{x} by ~10x without using EGR (relative to #2 diesel)
- HC and CO compliance possible with oxidation catalyst
- Exceedingly low in-cyl. soot and engine-out smoke
Are There Limitations to the Benefits of Fuel-Water Mixtures? [3]

Answer: Yes.

- Incomplete combustion when > 40 vol% water
- Even 10x lower NO\textsubscript{x} isn’t enough for 2010 compliance — need EGR or NO\textsubscript{x} aftertreatment
- NO\textsubscript{x} doesn’t decrease as rapidly as expected with simulated EGR

- Equilibrium calc’s corroborate that NO\textsubscript{x} doesn’t decrease quickly with EGR @ high water content
- Even so, fuel-water mixtures could be part of a successful strategy
Biodiesel $\text{NO}_x^{[4]}$

$\text{NO}_x$ emissions increase by $\sim1\%$ for every 10 vol% biodiesel blended into diesel fuel.

Why?
Possible Reasons for Biodiesel NO\textsubscript{x} Increase

- **Increased residence time at higher in-cylinder temperatures** → higher NO\textsubscript{x}
  1. Higher bulk modulus → earlier injection → earlier combustion
  2. Shorter ignition delay → earlier combustion
  3. Larger premixed-burn heat release
  4. Higher adiabatic flame temperature
  5. Less in-cylinder soot → less radiative heat transfer → higher actual flame temperatures
  6. Mixture-stoichiometry effects (thermal, chemical-kinetic)
  7. Others...?
Experiment Design

- Assess mechanisms 1-4 by comparing biodiesel results to those using a hydrocarbon reference fuel with same:
  1. *Injection timing* to remove bulk-modulus effect
  2. *Start of combustion* to remove combustion-phasing effect
  3. *Ignition delay* to remove premixed-burn magnitude effect
  4. *Adiabatic flame temperature*

*If* above matching is accomplished

*and* differences in one (or more) of these is *primary cause of biodiesel NO\textsubscript{x} increase*

*then* biodiesel NO\textsubscript{x} increase should vanish.
Fuels and Operating Conditions

**Fuels**

- **B100** = neat soy biodiesel (Peter Cremer Nexsol BD-0100)
- **CN50** = 50-cetane blend of diesel primary reference fuels (PRFs), 41.2 vol% n-hexadecane + balance 2,2,4,4,6,8,8-heptamethylnonane
- **CN80** = 80-cetane PRF blend, 76.5 vol% n-hexadecane + balance heptamethylnonane
- **CN100** = 100-cetane PRF (i.e., neat n-hexadecane)

**Operating conditions**

- Selected to maximize NO\textsubscript{x} differences between B100 and PRFs
- 800 rpm, steady-state, 0% EGR, conventional injection timing, start of combustion between 0° (TDC) and +0.5° ATDC
- Loads from 10 to 16 bar gross IMEP in 1-bar increments
- Peak injection pressure = 1420 bar, 6 x 0.163 mm x 140 µ nozzle
- Simulated intake conditions 69°C, 1.43 bar for 16:1 CR engine
- 4 repeats at each operating condition
Similar AHRR Curves for B100 and CN80

- Start of injection, start of combustion, and premixed-burn magnitude well matched across load range
- Mixing-controlled heat release also well matched
  - 15% lower LHV of B100 is mostly offset by 12% higher density
  - Injection duration approx. same as for CN80
Adiabatic Flame Temperature ($T_{ad}$) Effects

- Methyl oleate (C18:1) used as surrogate for B100
- EQUIL module of CHEMKIN software used to compute $T_{ad}$
  - Initial conditions: 950 K, 23 kg/m$^3$
- No differences in $T_{ad}$ observed at $f_W = 1.0$
  - B100 LHV is lower but $(F/O)_{st}$ is larger - effects exactly compensate for one another

$T_{ad}$ differences do not appear to be cause of increased biodiesel NO$_x$
$\text{NO}_x$ is 10.5% Higher for B100 Than CN80

Factors other than ignition delay, start of combustion and premixed-burn magnitude contribute to increased biodiesel $\text{NO}_x$. 
Conclusions

- **Dramatic fuel changes can enable mixing-controlled HECC, avoiding common problems of more-premixed LTC strategies**
  - No problems with ignition-timing control, light-load misfire, or high-load knock and NO\(_x\)

- **Nevertheless, significant technical advancements are required to enable practical mixing-controlled HECC**
  - Mixture preparation and fuel must be optimized together to avoid:
    - Excessive EGR requirements for NO\(_x\) control
    - High smoke emissions with current and emerging fuels

- **Current hypotheses are inadequate to explain the NO\(_x\) increase when fueling with biodiesel (relative to a diesel PRF blend)**
  - Changes in start of injection, start of combustion, premixed-burn magnitude, and adiabatic flame temperature are not con rolling factors over a range of load conditions
  - Differences in radiant heat transfer and/or mixture stoichiometry could play roles (investigation underway)
Acknowledgments

Dr. Glen C. Martin - post-doc
Caterpillar Inc. - hdwe. support, guidance
Dr. Ansis Upatnieks - former post-doc
Prof. A.S. (Ed) Cheng - collaborator
Dr. Randy L. Vander Wal - collaborator
Advanced Engine Combustion, Diesel Surrogates - working groups
Questions
**What Compounds Should Be Used to Create a Diesel Surrogate for Kinetics Studies?** [5]

- **Answer:** Diesel Surrogates Working Group has selected...

<table>
<thead>
<tr>
<th>Near-Term</th>
<th>Longer-Term</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>(n-decane)</em> ((C_{10}H_{22}))</td>
<td><em>(n-hexadecane)</em> ((C_{16}H_{34}))</td>
</tr>
<tr>
<td><em>(iso-octane)</em> ((C_{8}H_{18}))</td>
<td><em>(heptamethylnonane)</em> ((C_{16}H_{34}))</td>
</tr>
<tr>
<td><em>(methyl cyclohexane)</em> ((C_{7}H_{14}))</td>
<td><em>(n-decylbenzene)</em> ((C_{16}H_{26}))</td>
</tr>
<tr>
<td><em>(toluene)</em> ((C_{7}H_{8}))</td>
<td><em>(1-methylnaphthalene)</em> ((C_{11}H_{10}))</td>
</tr>
</tbody>
</table>

- Compounds can be blended to match characteristics of real diesel: ignition delay, molecular structures, C/H ratio, volatility, ...
- Compounds readily obtainable for experimental research efforts
- Detailed kinetic mechanisms already exist or can be developed
How to Quantify Mixture Stoichiometry Once Reactions Have Begun? [6]

- **Answer:** The oxygen equivalence ratio, $f_w$

  \[ f_\Omega \equiv \frac{2n_C + \frac{1}{2}n_H}{n_O} \], neglecting atoms bound in CO$_2$ and H$_2$O

- **Important for tracking reaction progress in ($f$,T) space**

- **Important when oxygenated fuels are used (e.g., biodiesel, ethanol, DME, ...)**

- **Same as traditional $f$ definition before reactions have begun**
  - As long as fuel not oxygenated
  - General relationship between $f$ and $f_w$ provided
How to Quantify Degree of Achievement of Many Simultaneous Operational Targets? [2]

Answer: Overlimit function succinct evaluation of constrained systems

\[ F \equiv \sum \max \left( 0, \frac{x_i^* - 1}{x_i} \right) \]

where

- \( x_i \) \( \equiv \) \( i^{th} \) constrained output parameter
- \( x_i^* \) \( \equiv \) constraint on \( i^{th} \) parameter
- \( i \) \( \equiv \) index over constrained parameters

Answer: Yes.

- Soot with less-ordered nanostructure oxidizes up to 5X faster
- Soot produced by different fuels has different nanostructure (similar operating conditions)
  - Hydrocarbon ref. fuel — highly ordered soot
  - Neat biodiesel — less order in nanostructure
  - DGE — greatest disorder in nanostructure
- DGE soot has shortest fringe lengths and largest tortuosity — enhanced oxidation rate

![Graph showing PEAK SINL (mW) vs IMEP (bar) for different fuels: CN50, B100, DGE.]

![Graph showing SMOKE (FSNI) vs IMEP (bar) for different fuels: CN50, B100, DGE.]

![Images comparing CN45, B100, and DGE soot layers: Roughly concentric soot layers, Highly curved soot layers, Greatest disorder in nanostructure.]
References


