Co-Optimization of Internal Combustion Engines and Biofuels

Future Fuels Workshop

Presenter: Robert L. McCormick

March 8, 2016

King Abdullah University of Science and Technology, Thuwal, Saudi Arabia
USDOE’s National Renewable Energy Laboratory

NREL develops clean energy and energy efficiency technologies and practices, advances related science and engineering, and provides knowledge and innovations to integrate energy systems at all scales.

- 132 hectare main site, 123 hectare wind technology site
- $350 million annual budget
- 1500 employees plus 800 visiting researchers, interns, and contractors

- **Sustainable Transportation**
  - Vehicles
  - Hydrogen
  - Biofuels

- **Renewable Electricity**
  - Solar
  - Wind
  - Water
  - Geothermal

- **Energy Productivity**
  - Residential Buildings
  - Commercial Buildings

- **Systems Integration**
  - Grid Integration
  - Distributed Energy
  - Batteries and Thermal Storage
  - Energy Analysis
Outline

• Motivation – GHG Reduction
• Optimization Strategy
• Biomass Conversion Products
• SI Engine Fuels
  o Screening
  o Knock Resistance
  o GDI PM Emissions
• Preliminary Thoughts on GCI Fuels
• Conclusions – Acknowledgments – Thanks
80% reduction in transportation GHG by 2050

U.S. transportation emissions
million metric tons CO2

2,000
1,000
0

2005 2040

source: EIA 2014 reference case

fuel and engine developments not progressing fast enough
ICEs will dominate the fleet for decades

Yet current fuels constrain engine design

**Brake thermal efficiency (%)**

- RON 100.9
- RON 90.7

**Peak thermal efficiency (%)**

- Gasoline (spark ignition)
- Diesel (compression ignition)
- Advanced Combustion

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*Engine: Ford EcoBoost 1.6L 4-cylinder, turbocharged, direct-injection, 10.1 CR
Source: C.S. Sluder, ORNL*
Petroleum Fuel Use GHG Emissions

• Predominantly from combustion
• Therefore, low net carbon fuels are essential
  o Blends with petroleum blendstocks displacing fossil carbon
• But advanced biofuels are deploying too slowly

J. Han et al., *Fuel* 157 (2015) 292-298

Reduce by efficiency and low-carbon fuels
Optimization Strategy

• Screening a broad range of pathways and molecules
  o Properties, state of technology, potential scale

• Improved understanding of fuel property – engine performance relationship
  o Wider property range than offered by hydrocarbons and alcohols

• Optimized for life-cycle greenhouse gas emissions and cost
Better Economics for Biomass to Oxygenates

• Biomass has high oxygen content:
  o 40 to 60 wt%
  o Molar O/C about 0.6
• Economically rejecting this oxygen may not be possible
• Example: hydrotreating costs for fast-pyrolysis oils can be very high

Lignin: 15%–25%
Hemicellulose: 23%–32%
Cellulose: 38%–50%

Significant cost reduction in this range

Arbogast, 2009
Extremely broad range of oxygenate and hydrocarbon structures
Biomass Pyrolysis

broader range of molecules

Cellulose

Hemicellulose

Lignin

High T

H₂

Boiling Point, °C

180
200
220
240
260
280
300
320
340

4-Propyl-2,6-Dimethoxyphenol
4-Methyl-2, 6-Dimethoxyphenol
2, 6-Dimethoxyphenol
4-Propylguaiacol
4-Methyldihydroquinone
4-Methylacetophenone
2-Phenylethanol
4-Ethylguaiacol
p-Cresol
Guaiacol
1,2-Dimethoxybenzene
2,4-Xylenol
Phenol
4-Methylanisole
4-Propylanisole
Anisole
2-Hexanol
2,5-Dimethylfuran
Methyltetrahydrofuran
2-Methylfuran

Diesel (160-340)

Gasoline (155-225)
Ethanol Non-ideality

Ethanol is considered “typical” of oxygenates in gasoline, yet:

- Non-linear blending for ON and high bRON
- Highly non-ideal blending for vapor pressure
- Highly non-ideal blending for distillation
- Very high heat of vaporization (920 kJ/kg versus 350-400 kJ/kg)
- Miscible with water
SI and Advanced CI

• Near-term objectives around SI engine fuels/efficiency (~5 yr)
  o Identify one or two bio-blendstocks as good or better than ethanol
  o **Standard properties, octane index, particle formation potential**
  o Auto industry engagement

• **Longer-term focus on advanced compression ignition (10+ yr)**
  o Fundamentally different combustion dynamics require different fuel properties

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*spark ignition (gasoline)*

*kinetically controlled ignition*

*compression ignition (diesel)*

Low Reactivity Fuel  Range of Fuel Properties TBD  High Reactivity Fuel
Strategies to Increase SI Engine Efficiency

(and Lower GHG Emissions):

- Increased compression ratio
  - Greater thermodynamic efficiency

- Engine downsizing/downspeeding
  - Smaller engines operating at low-speed/higher load are more efficient
  - Optimized with 6 to 9 speed transmission

- Turbocharging
  - Recovering energy from the engine exhaust
  - Increase specific power allowing smaller engine

- Direct injection
  - Fuel evaporates in the combustion cylinder, cooling the air-fuel mixture

All of these strategies can take advantage of higher octane (more highly knock resistant) fuels for more aggressive engine design

Target RON of 98-100 min
Target Sensitivity 8 min
Screening Strategy for Bio-Blendstocks

1. Determine Boiling Point and Melting Point
   - Reject if outside of gasoline and diesel boiling ranges (0°C < $T_b$ < 338°C)

2. Apply Solubility Criteria (e.g., solubility parameter)
   - Reject if insoluble in hydrocarbon fuels within required temperature range

3. Apply Corrosion Metric
   - Reject if the material is too corrosive for metals in fueling systems

4. Identify Known Toxicity Issues
   - Reject if significant toxicity hazard beyond conventional fuels

5. Determine Fuel Handling Safety (e.g., rapid peroxide former)
   - Reject if fuel is hazardous or unstable, not addressed with antioxidants

6. Biodegradation
   - Flag for additional examination if less biodegradable than MTBE

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**Autoignition Reactivity Metrics**

- **Gasoline-Like**
  - $T_b$ < 190°C or $T_{90}$ < 190°C
  - SI Engine
    - High RON

- **Diesel-Like**
  - $T_b$ < 338°C or $T_{90}$ < 338°C
  - Diesel Engine
    - CN > 40

- **ACI Engine**
  - Wide range of ON/CN
Database and data development

• Over 400 candidate bio-blendstocks
• Alkanes, alkenes, aromatics, aldehydes, esters, ethers, ketones, and furanics
• Mixtures
• Many only available in small quantity
  - DCN at roughly 30 mL vs RON at >300 mL
  - Approximate with DCN-RON correlation

![Graph showing the relationship between RON and DCN with a quadratic equation: RON = 109.9 - 0.4346 DCN - 0.03 DCN²]
Screening for Gasoline Boiling Range

- About 150 out of roughly 400 proposed bio-blendstocks met gasoline boiling and liquidity requirement
  - RON data available for 95 blendstocks
  - 42 blendstocks >100 RON
    - 8 alcohol
    - 3 alkane
    - 1 alkene
    - 11 aromatic
    - 8 ester
    - 6 ether
    - 3 furan
    - 2 ketone
Additional screening

• 1 known human carcinogen
• 3 suspected human carcinogens
• 1 teratogen
• 2 demonstrated mobility and poor biodegradability in ground water
• 5 suspected ground water issues
Octane Number by Functional Group

- **Ethers**
  - Formula: \(\text{OCH}_3\)
  - Research Octane Number:
    - Count: 0, 1, 2, 3, 4

- **Alcohols**
  - Formula: \(\text{OH} - 	ext{CH}_3\)
  - Research Octane Number:
    - Count: 0, 1, 2, 3

- **Esters**
  - Formula: \(\text{H}_2\text{C} - \text{CO} - \text{O} - \text{CH}_3\)
  - Research Octane Number:
    - Count: 0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5

- **Ketones**
  - Formula: \(\text{O} - \text{CH}_3\)
  - Research Octane Number:
    - Count: 0, 1, 2, 3

- **Alkenes**
  - Formula: \(\text{CH}_3 - \text{C} - \text{CH}_3\)
  - Research Octane Number:
    - Count: 0, 2, 3, 2, 3

- **Alkanes**
  - Formula: \(\text{CH}_3 - \text{C} - \text{CH}_3\)
  - Research Octane Number:
    - Count: 0, 2, 3, 2, 3

- **Aromatics**
  - Formula: \(\text{H}_2\text{C}_6\text{O}\)
  - Research Octane Number:
    - Count: 0, 2, 3, 2, 3
Required Blending RON

• Blending RON can be much higher than pure component
  o But some compounds show no increase or antagonistic effect
  o Methyl acetate pure component RON ~120, blending RON=107

• Currently not well predicted from theory

<table>
<thead>
<tr>
<th>Compound</th>
<th>Pure RON</th>
<th>Blending RON</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,5-Dimethyl-furan</td>
<td>101</td>
<td>150</td>
</tr>
<tr>
<td>4-Methyl-anisole</td>
<td>115</td>
<td>139</td>
</tr>
<tr>
<td>Methyl acetate</td>
<td>~120</td>
<td>107</td>
</tr>
</tbody>
</table>
Blending Octane Index - OI

- More predictive of knock is OI = RON - K\cdot S
- S = RON – MON
- K<0 for advanced SI engines
- E30 in a conventional sub-octane blendstock provides adequate knock resistance for advanced SI
  - RON = 99
  - S = 12
  - OI = 105 at K = -0.5
  - In this case ethanol blending RON is 132 and blending S is 33
Level 2 and Level 3 Evaluation for SI

Tier 1: high-level screening
- boiling point
- melting point
- solubility
- ignition quality
- corrosivity
- toxicity
- biodegradation

Tier 2: candidate selection
- blending ron, mon, S
- blending rvp, distillation
- stability
- life cycle GHG/sustainability
- state of technology
- infrastructure compatibility

Tier 3: candidate evaluation
- evaluation of most promising candidates in engine tests
- Engine combustion efficiency
- PM emission effects

Ongoing
Level 2 Screening – Case Study 2,5 DMF

- Minimal to no vapor pressure increase – or a decrease
- Less boiling point depression in distillation than ethanol
- API Report RON values may significantly underestimate blending RON (bRON 153 and 155)
DMF-Gasoline Blend Oxidative Degradation

- Many published studies on combustion of DMF
  - Promising biomass-derived high octane compound
- DMF blends with gasoline show high levels of insoluble gum formation on D873 test
  - 100°C/100 psi O₂ for 16 hr
  - 600 to 800 mg/100 mL – much higher than base gasoline
  - Also failed gasoline stability test D525
  - No prior reports of this reaction occurring
- \( ^{13} \text{C} \text{ NMR indicates gum is largely 2,5-hexenedione} \) (aka diacetylene or DAE)
  - Melts 5°C, very water soluble
  - Poorly soluble in hydrocarbon
- Evidence of DMF oxidation
  - ASTM method D7525 140°C, 72.5 psi O₂
  - 10% pressure drop defines induction time
  - DMF in isooctane under O₂ and N₂
  - With N₂ no break in 18 hours
  - 1,000ppm BHT increased stability
Direct Injection SI Engine PM Emissions

• Direct injection brings evaporative cooling, improved transient response, and is necessary for engine downsizing

• Yet many studies show increased emissions of particles for DI

• Fuel spray may impinge on cylinder wall or piston top
  - Low vapor pressure/high boiling components burn in diffusion flame

Particulate matter index (PMI)

Based on detailed hydrocarbon analysis of the base fuel

\[
PMI = \sum_{i=1}^{n} \left[ \frac{(DBE_i + 1)}{VP(443K)_i} \times Wt_i \right]
\]

Where-

\[DBE = \frac{(2C + 2 - H)}{2}\] - rough measure of tendency to form particles

\[VP = \text{Vapor pressure at 443K (170}^\circ\text{C)}\] – rough measure of tendency to evaporate

\[Wt_i = \text{Weight fraction of compound}\]


Does PMI breakdown for oxygenates? Studies of oxygenate sooting tendency suggest that it will

### Oxygenates Used in PM/PN Study

<table>
<thead>
<tr>
<th>Oxygenate</th>
<th>Boiling Point (°C)</th>
<th>Vapor Pressure, 443K (kPa)</th>
<th>DBE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>78</td>
<td>1545</td>
<td>0</td>
</tr>
<tr>
<td>Isobutanol</td>
<td>108</td>
<td>596</td>
<td>0</td>
</tr>
<tr>
<td>2,5-Dimethylfuran</td>
<td>94</td>
<td>538</td>
<td>3</td>
</tr>
<tr>
<td>Anisole</td>
<td>154</td>
<td>153</td>
<td>4</td>
</tr>
<tr>
<td>4-Methyl-anisole</td>
<td>174</td>
<td>87.7</td>
<td>4</td>
</tr>
<tr>
<td>2,4-Xylenol</td>
<td>211</td>
<td>30.3</td>
<td>4</td>
</tr>
<tr>
<td>2-Phenyl-ethanol</td>
<td>220</td>
<td>21.5</td>
<td>4</td>
</tr>
</tbody>
</table>

Oxygenates blended with 88 RON summertime BOB at 10 to 20 vol%

- Wall-guided 0.5L DISI SCE
- TSI Fast Mobility Particle Sizer (FMPS) w/ Dekati diluter & thermodenuder for PN
- AVL Micro-soot sensor and dilution system for PM
Oxygenate Effect on GDI Engine PM Emissions

- PM vs PMI trends for Hydrocarbon + Linear Alcohol (ethanol) versus other oxygenates are different
- High boiling/low vapor pressure oxygenates produce less PM than expected – likely not evaporating and burning – swept into lube oil
Routes from Oxygenates to Soot Formers


SI Fuel-Engine Optimization

• Target low life-cycle GHG emissions at moderately high blend levels
• Meeting OI requirement to enable engine design
• Particle emission requirement to be defined
• Currently working to understand tradeoffs to set up optimization
Next Phase Optimization: Gasoline Compression Ignition

Diesel-like efficiency without the complex emission controls

- Compression ignition and lean engine operation for efficiency
- LTC to improve to achieve low NOx and PM
- Highly reactive fuels (diesel) undesirable (ignite before adequate mixing)
- Straight-run gasoline RON~70 (OI 66 to 68) acceptable
  - Reduced GHG emissions and refining cost

http://www.princeton.edu/puceg/perspective/combustion.html
GCI Fuel Screening

- Likely similar boiling point range, vapor pressure, stability, cleanliness, etc. as SI engines
- Range of bio-blendstocks available in naphtha range

<table>
<thead>
<tr>
<th>Compound</th>
<th>RON</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Methyltetrahydrofuran</td>
<td>86</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>83</td>
</tr>
<tr>
<td>Pentan-1-ol</td>
<td>82</td>
</tr>
<tr>
<td>1,1,3-Trimethylcyclohexane</td>
<td>81</td>
</tr>
<tr>
<td>Alpha-Pinene</td>
<td>80</td>
</tr>
<tr>
<td>Beta-pinene</td>
<td>80</td>
</tr>
<tr>
<td>Pinane</td>
<td>77</td>
</tr>
<tr>
<td>Hexanoic acid, ethyl ester</td>
<td>77</td>
</tr>
<tr>
<td>1-Hexene</td>
<td>76</td>
</tr>
<tr>
<td>Methylcyclohexane</td>
<td>75</td>
</tr>
<tr>
<td>4E-octene (trans)</td>
<td>73</td>
</tr>
<tr>
<td>2-Heptene (trans)</td>
<td>73</td>
</tr>
<tr>
<td>2-Heptanone</td>
<td>70</td>
</tr>
<tr>
<td>Rose oxide</td>
<td>70</td>
</tr>
<tr>
<td>Ethylcyclopentane</td>
<td>67</td>
</tr>
<tr>
<td>Pentane</td>
<td>62</td>
</tr>
<tr>
<td>Menthan</td>
<td>60</td>
</tr>
<tr>
<td>Hexyl acetate</td>
<td>60</td>
</tr>
<tr>
<td>3-methylhexane</td>
<td>52</td>
</tr>
</tbody>
</table>
OI for Blending GCI Fuel with Biobblendstock

• OI = RON - K*S
• For GCI K may be -2
  o Versus -0.5 or so for boosted GDI
• SRG primary blendstock
• High and low limits on OI constrain suitable biobblendstock
ICEs will dominate ground transportation for decades

Achieving GHG emission goals will require:

- Fuels that enable more efficient engine design
- Low-carbon biofuels and lower carbon petroleum fuels

Developing new fuels and new engines together – co-optimization
Acknowledgements

• United States Department of Energy
  o Vehicle Technologies Office
  o Bioenergy Technologies Office

• NREL Researchers:
  Gina Fioroni, Matt Ratcliff, Gregg Beckham, Tom Foust, Lisa Fouts, Seonah Kim, Jon Luecke, Mark Nimlos, Petr Sindler, Miao Tian, Brad Zigler, Jon Burton, Earl Christensen
Thank you to KAUST for this Invitation

robert.mccormick@nrel.gov