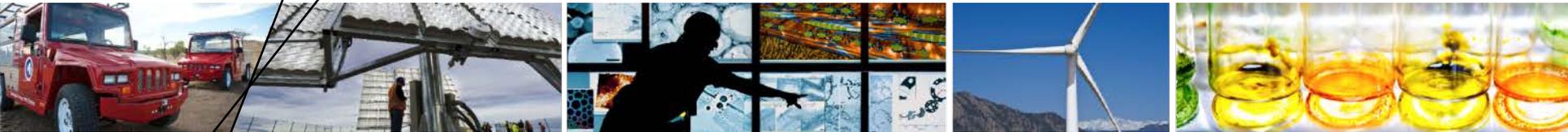


Co-Optimization of Internal Combustion Engines and Biofuels



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

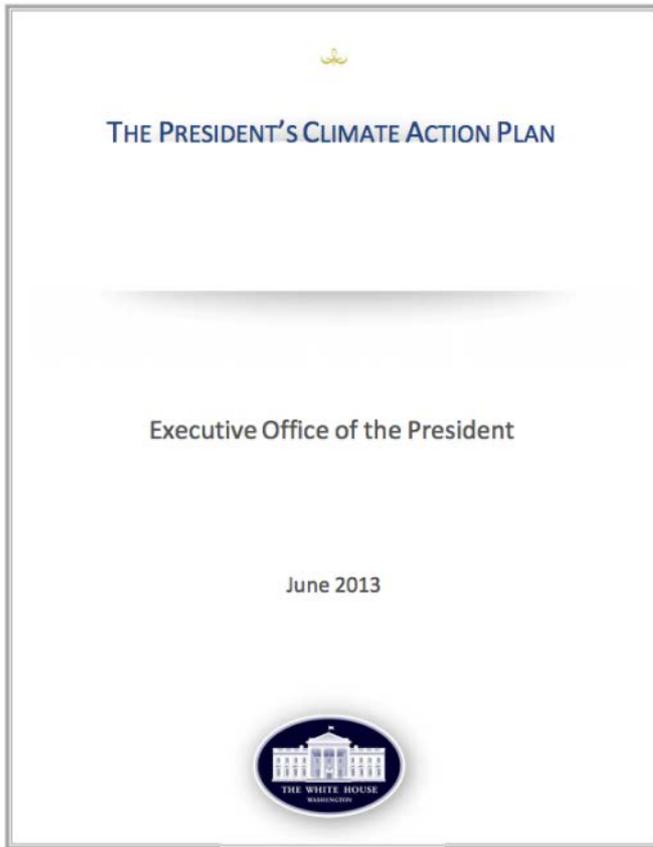
- Grid Integration
- Distributed Energy
- Batteries and Thermal Storage
- Energy Analysis



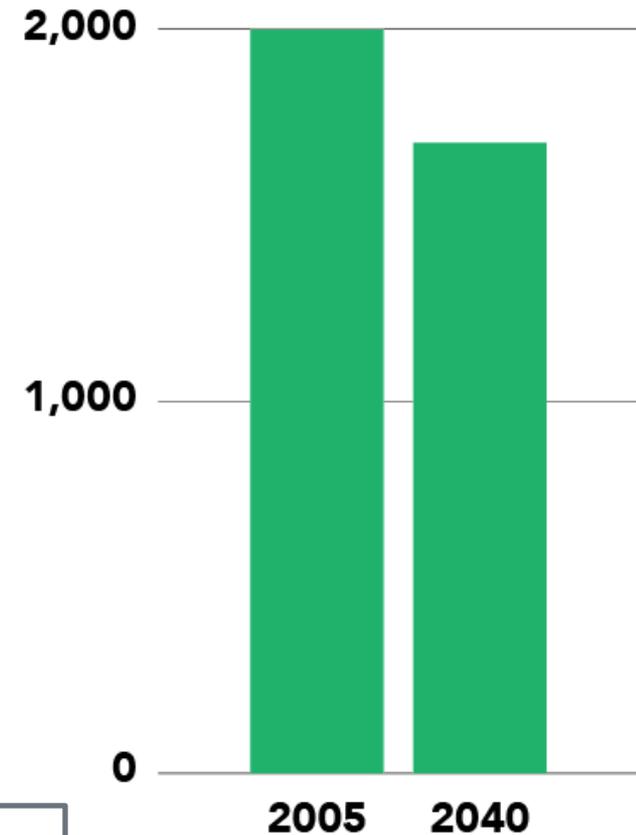
Outline

- **Motivation – GHG Reduction**
- **Optimization Strategy**
- **Biomass Conversion Products**
- **SI Engine Fuels**
 - Screening
 - Knock Resistance
 - 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

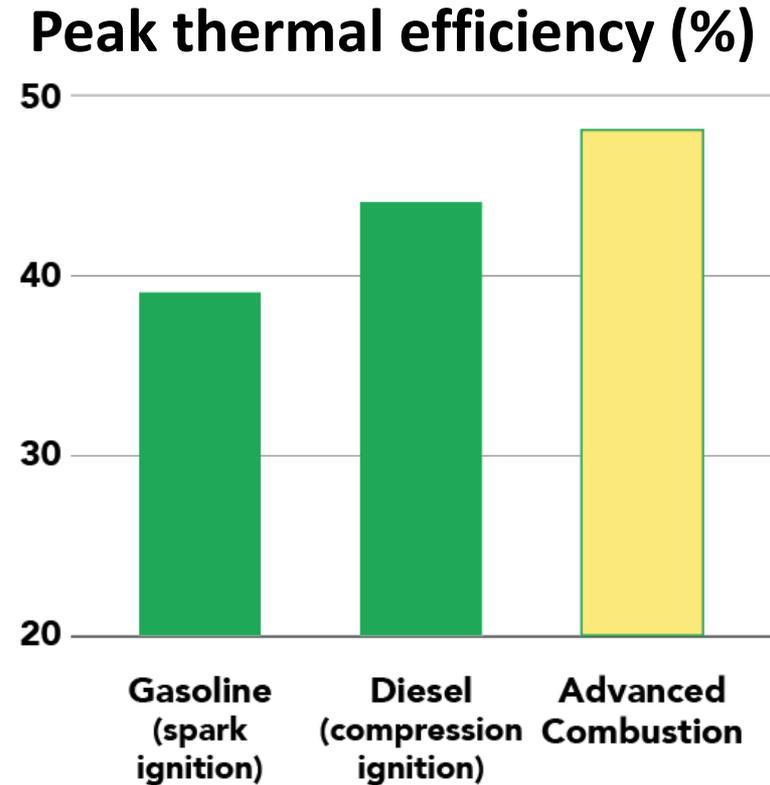
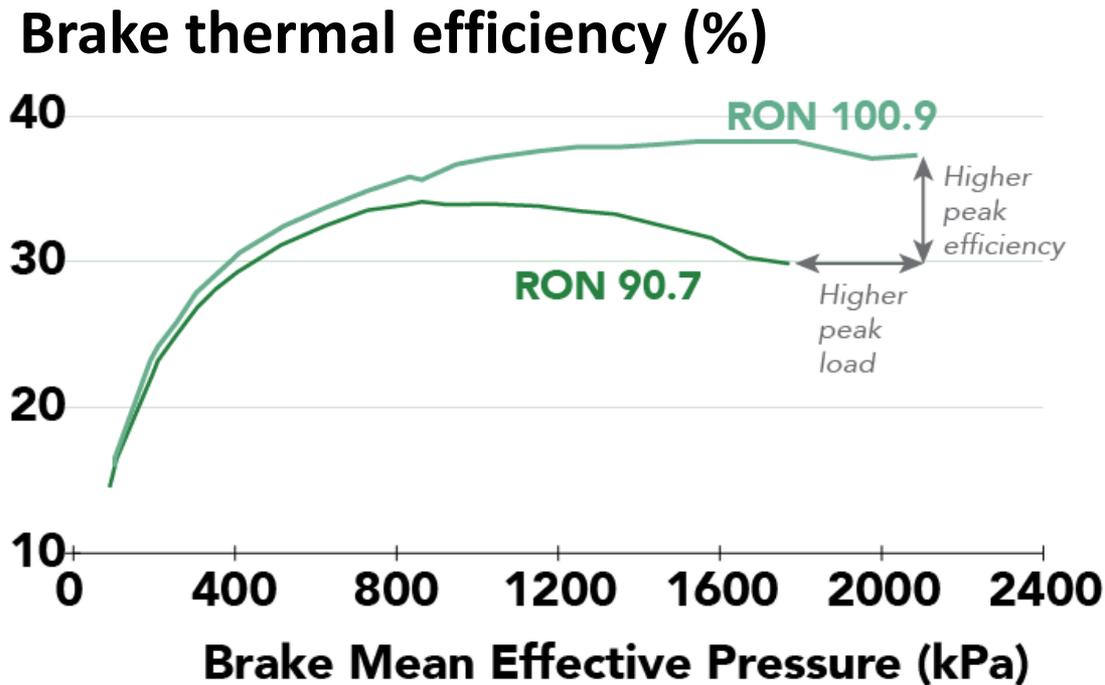


source: EIA 2014
reference case

**fuel and engine developments
not progressing fast enough**

ICEs will dominate the fleet for decades

Yet current fuels constrain engine design

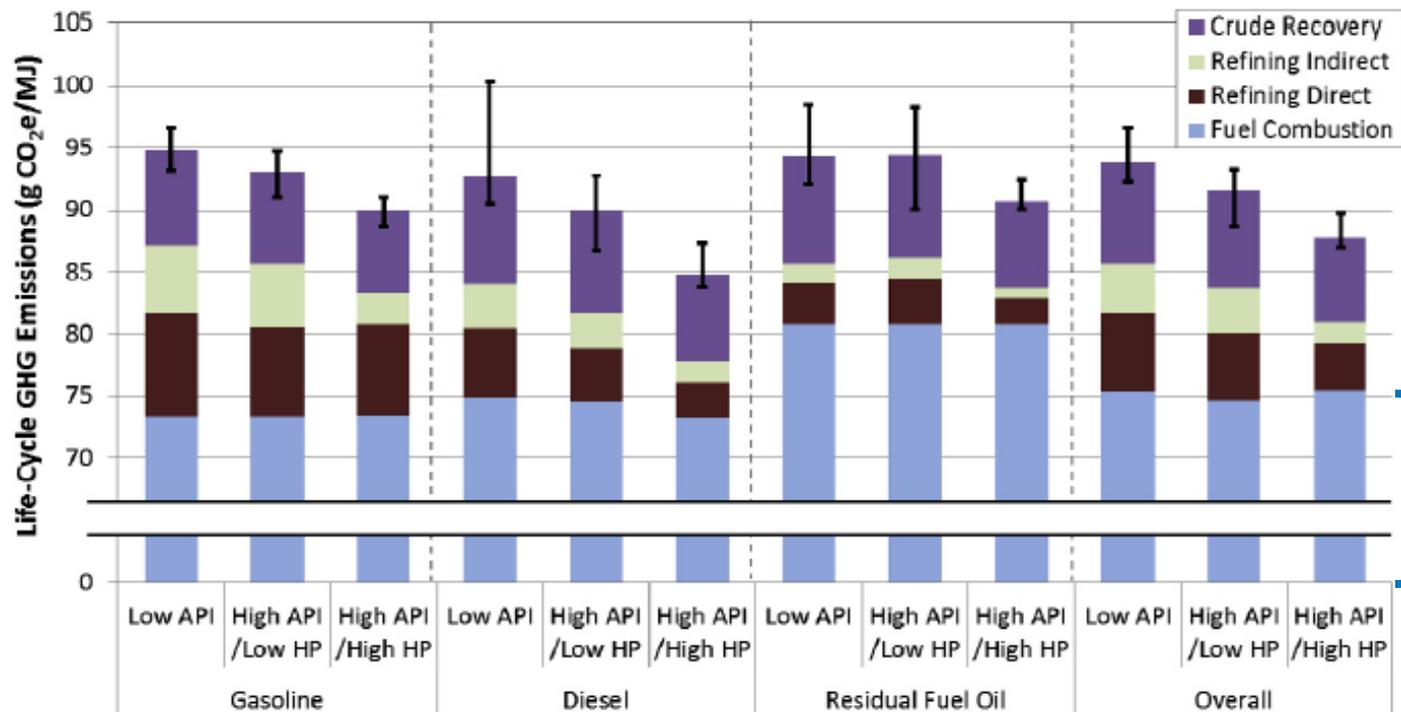


Engine: Ford Ecoboost 1.6L 4-cylinder, turbocharged, direct-injection, 10.1 CR
Source: C.S. Sluder, ORNL

Petroleum Fuel Use GHG Emissions

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

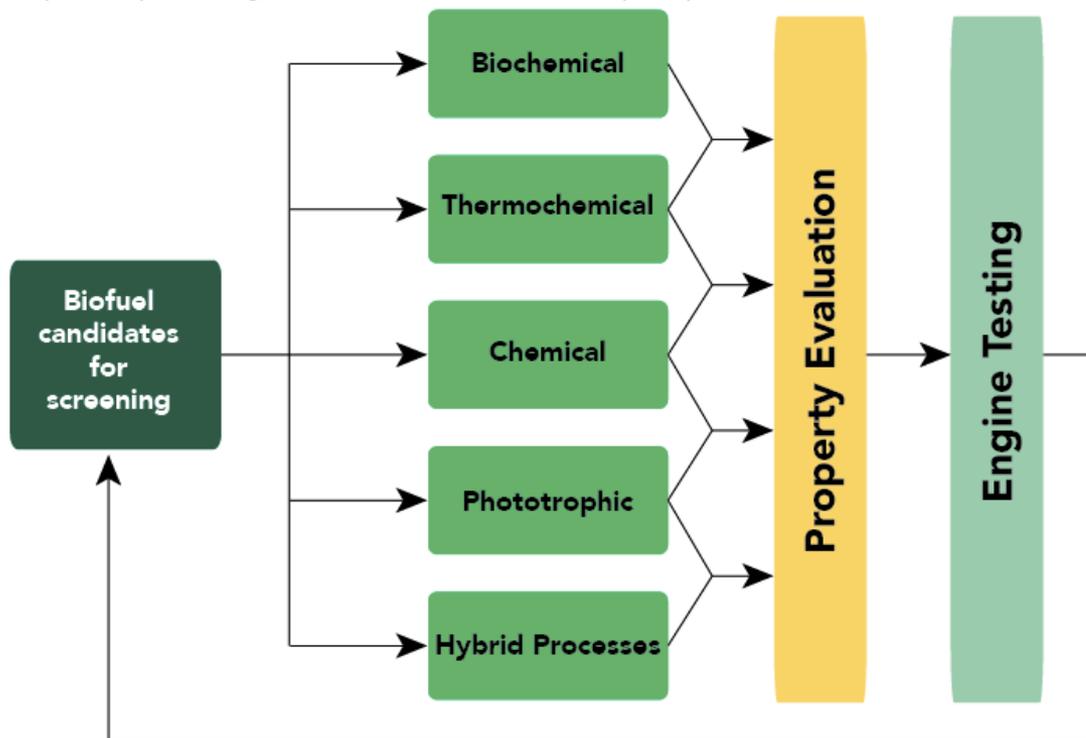
J. Han et al., *Fuel* 157 (2015) 292-298



Reduce by efficiency and low-carbon fuels

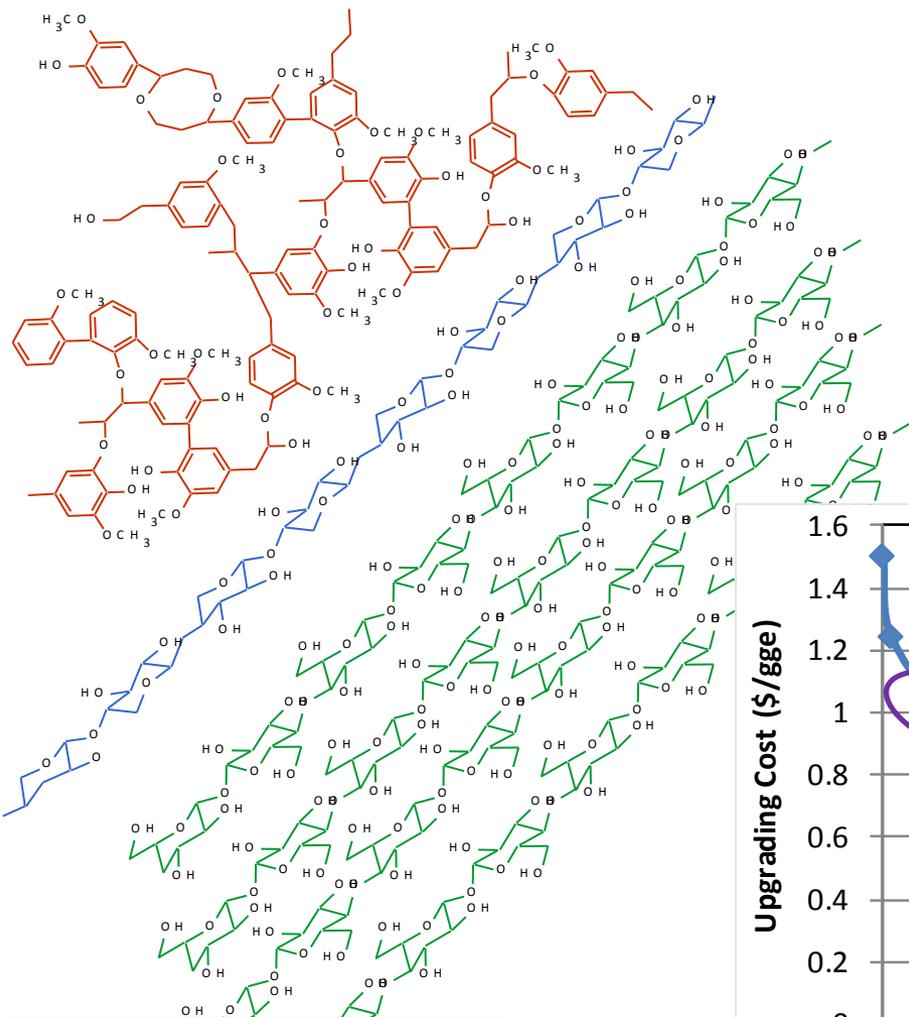
Optimization Strategy

- **Screening a broad range of pathways and molecules**
 - Properties, state of technology, potential scale
- **Improved understanding of fuel property – engine performance relationship**
 - Wider property range than offered by hydrocarbons and alcohols



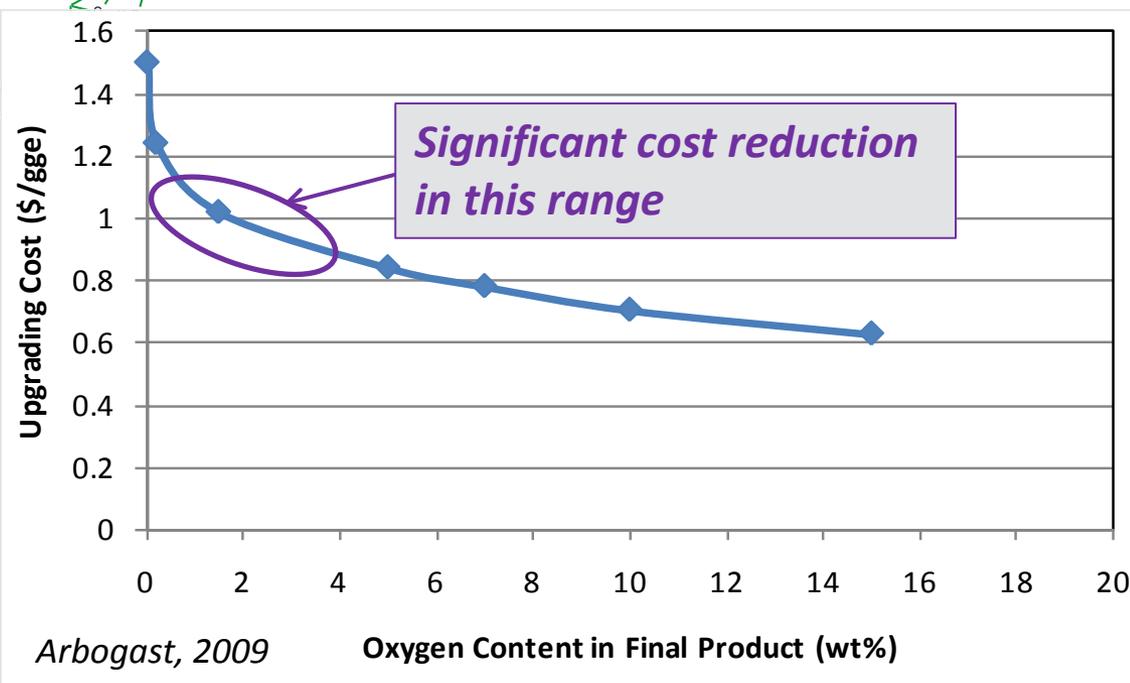
- **Optimized for life-cycle greenhouse gas emissions and cost**

Better Economics for Biomass to Oxygenates



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

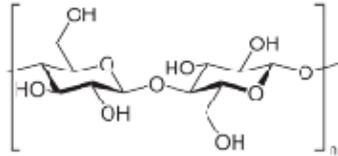
- Biomass has high oxygen content:
 - 40 to 60 wt%
 - Molar O/C about 0.6
- Economically rejecting this oxygen may not be possible
- Example: hydrotreating costs for fast-pyrolysis oils can be very high



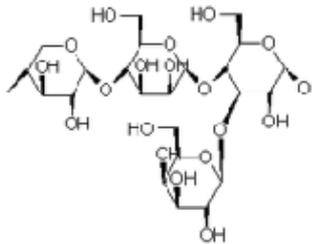
Biomass Pyrolysis

broader range of molecules

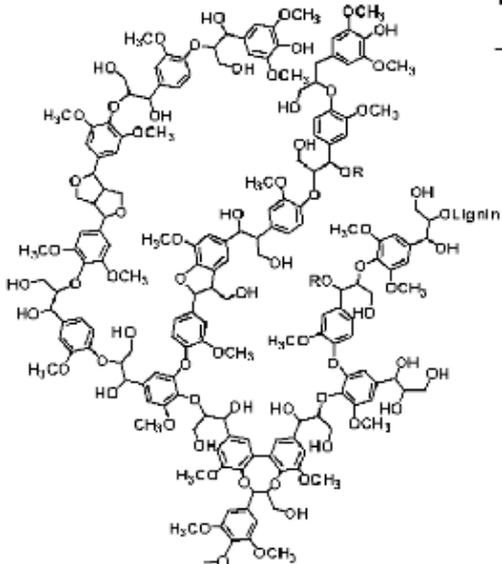
Cellulose



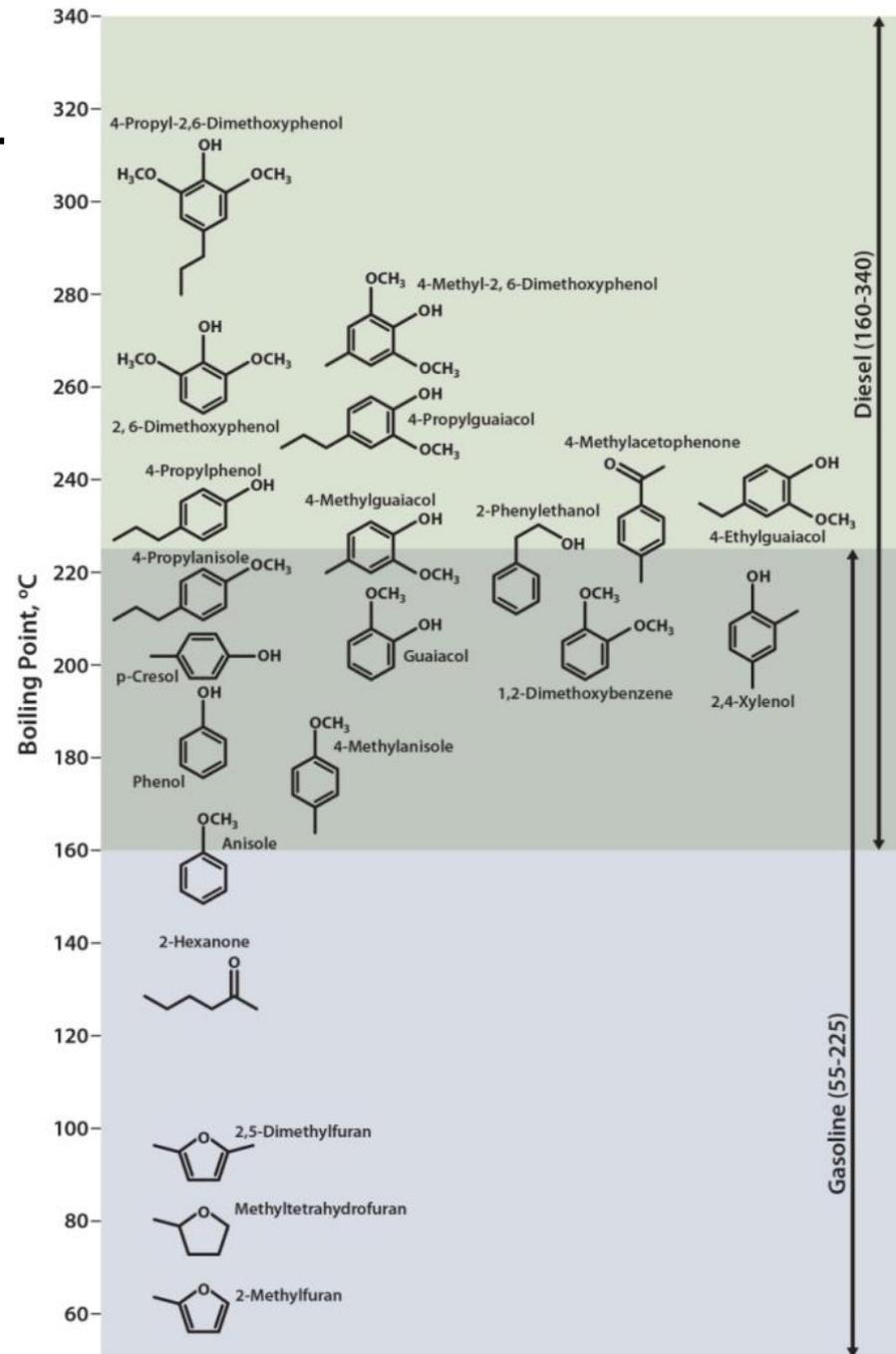
Hemi-cellulose



Lignin



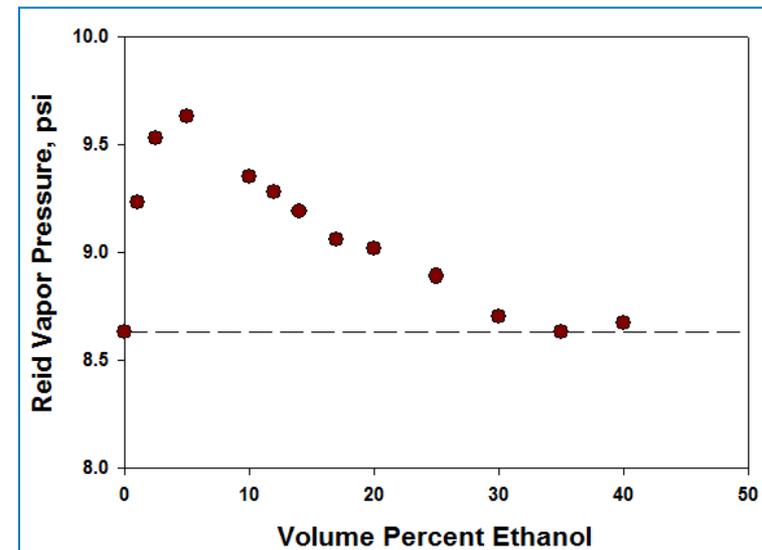
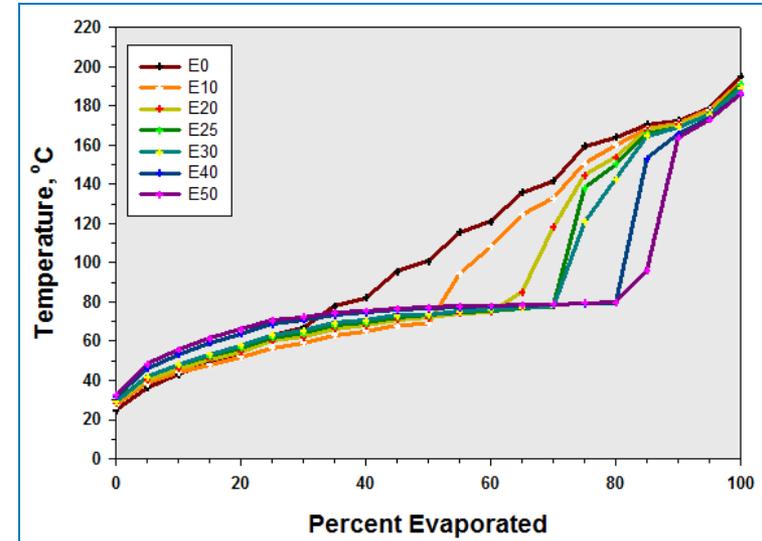
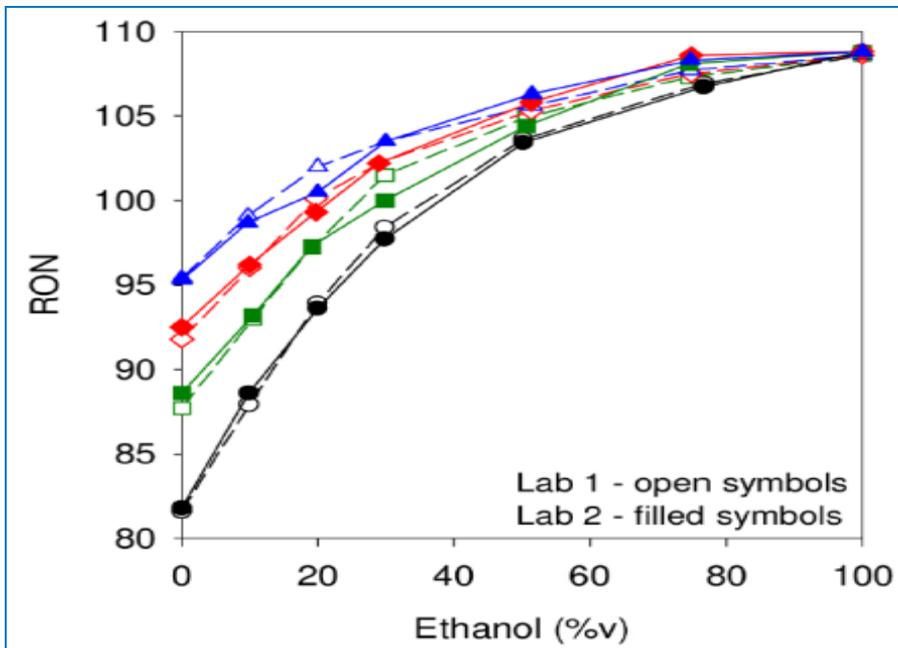
High T
H₂



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**



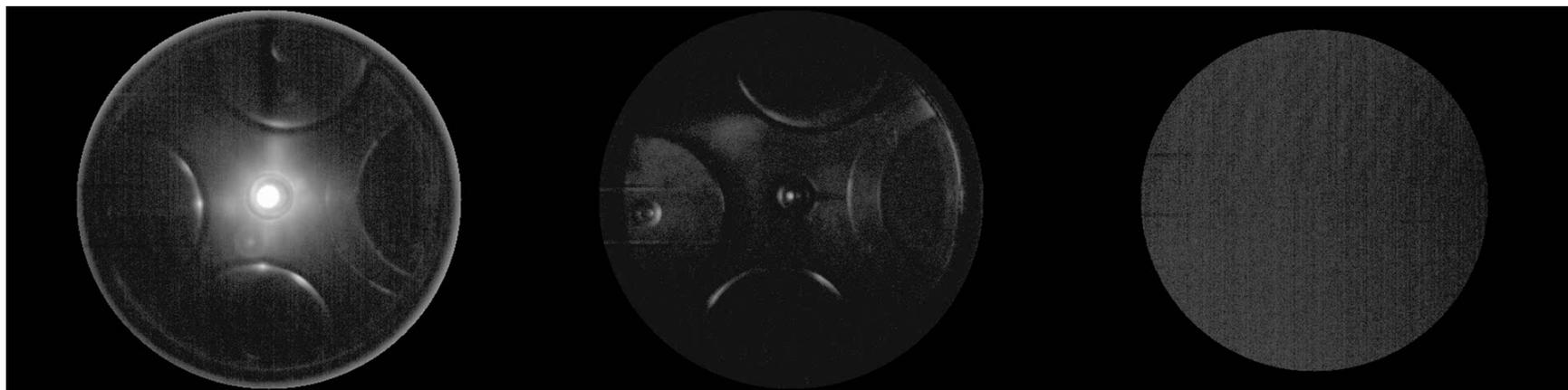
SI and Advanced CI

- **Near-term objectives around SI engine fuels/efficiency (~5 yr)**
 - Identify one or two bio-blendstocks as good or better than ethanol
 - Standard properties, octane index, particle formation potential
 - Auto industry engagement
- **Longer-term focus on advanced compression ignition (10+ yr)**
 - Fundamentally different combustion dynamics require different fuel properties

*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

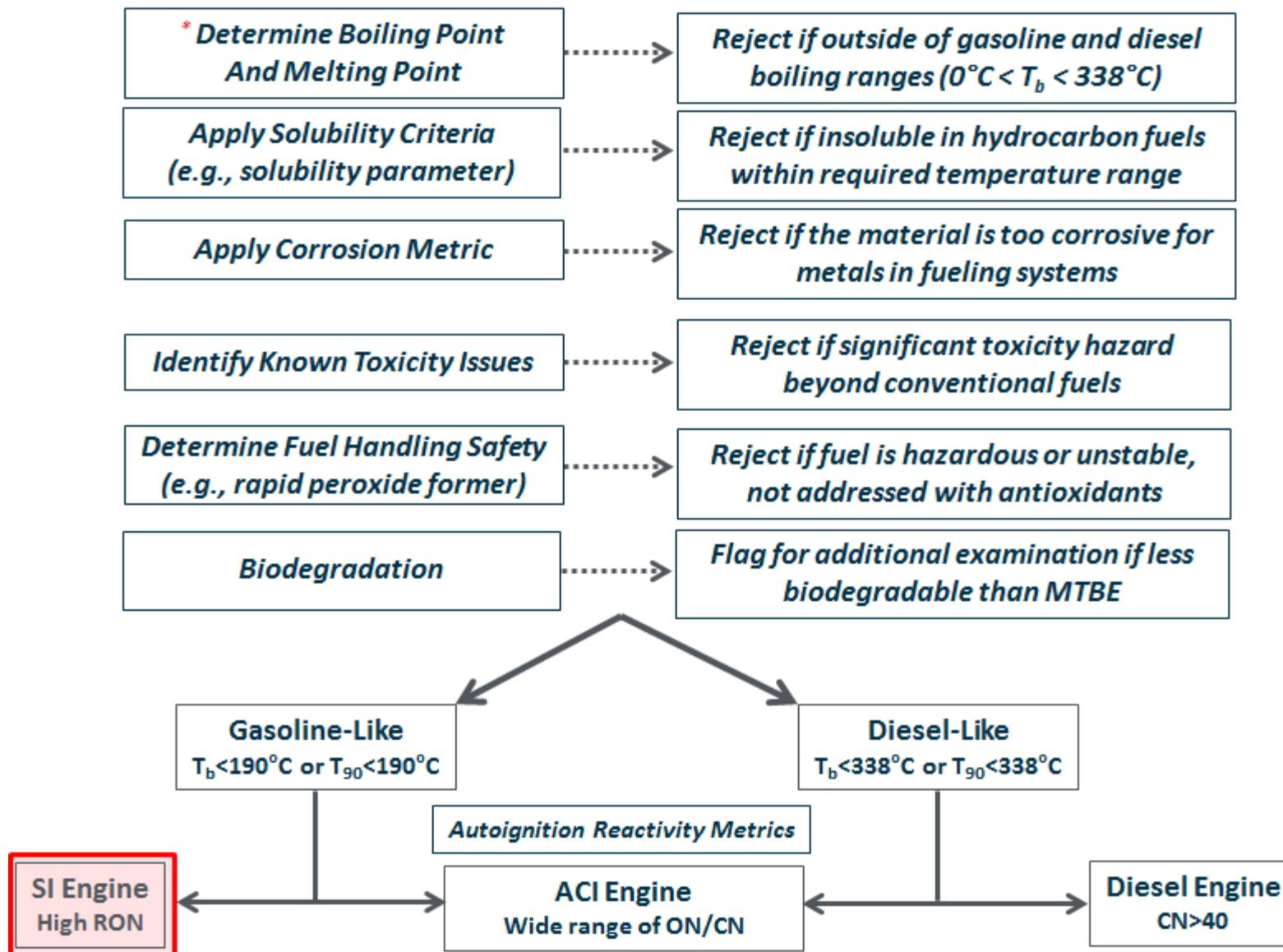
(and Lower GHG Emissions):

- **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

*Target RON of 98-100 min
Target Sensitivity 8 min*

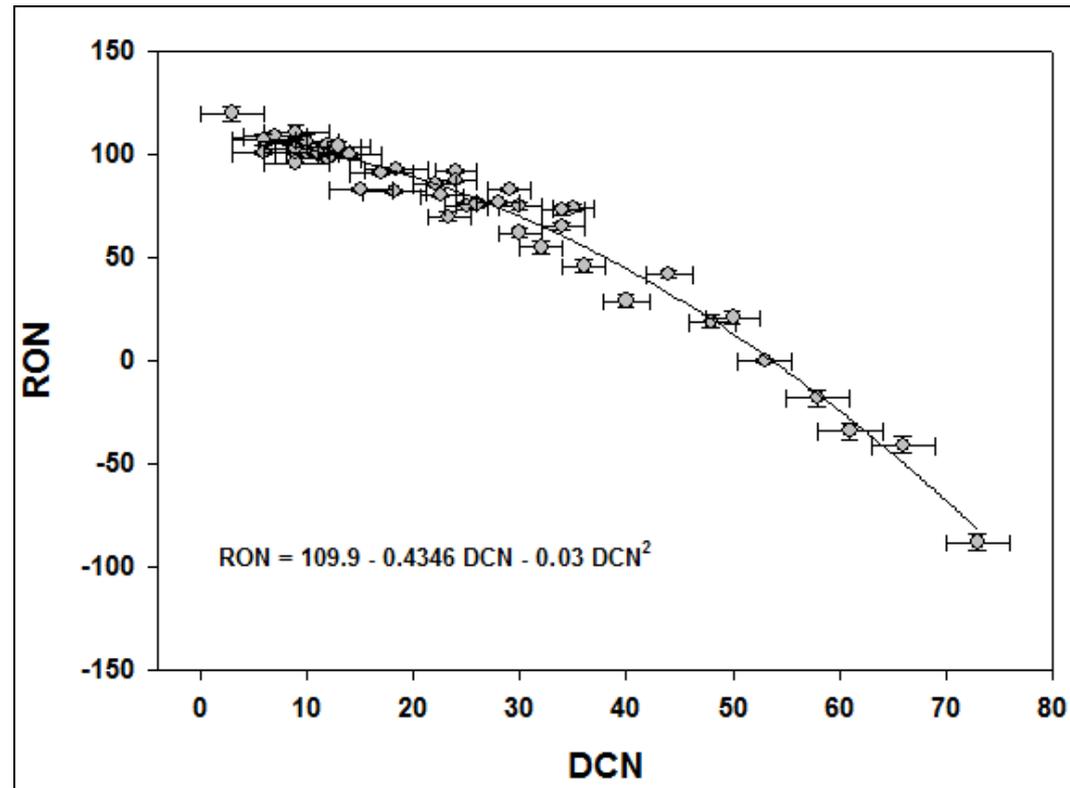
All of these strategies can take advantage of higher octane (more highly knock resistant) fuels for more aggressive engine design

Screening Strategy for Bio-Blendstocks



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



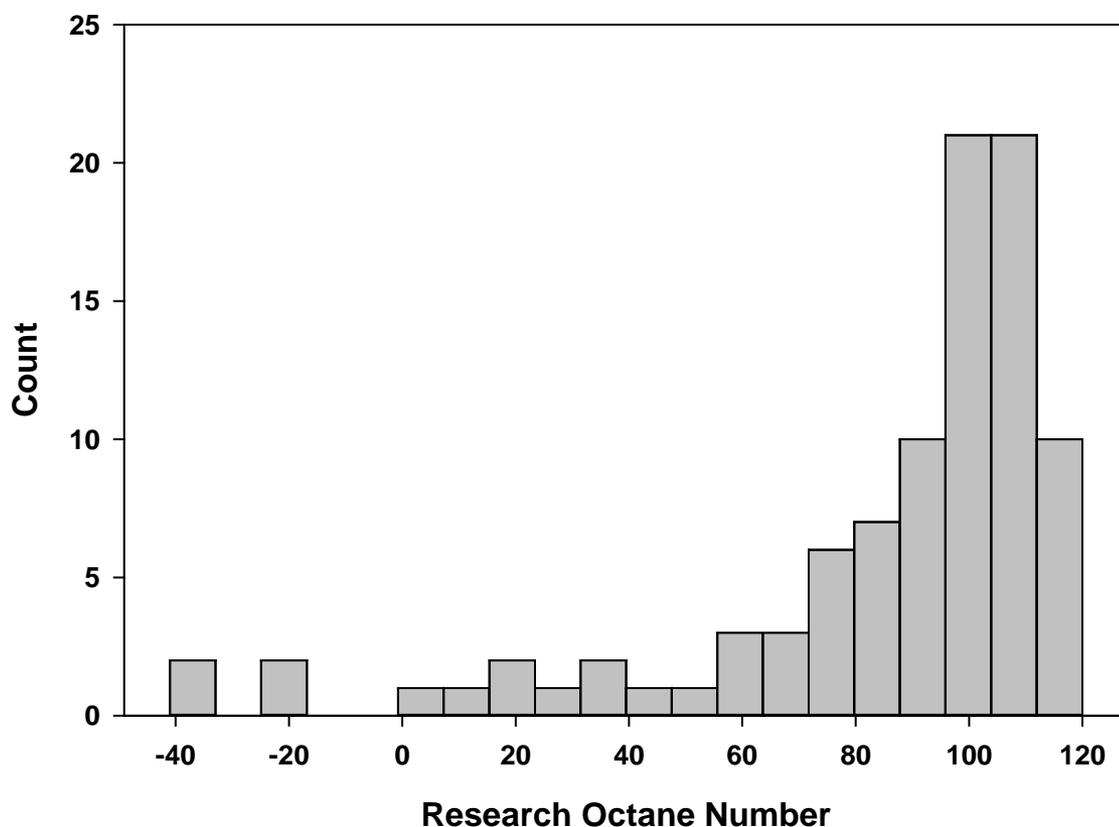
Screening for Gasoline Boiling Range

- **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

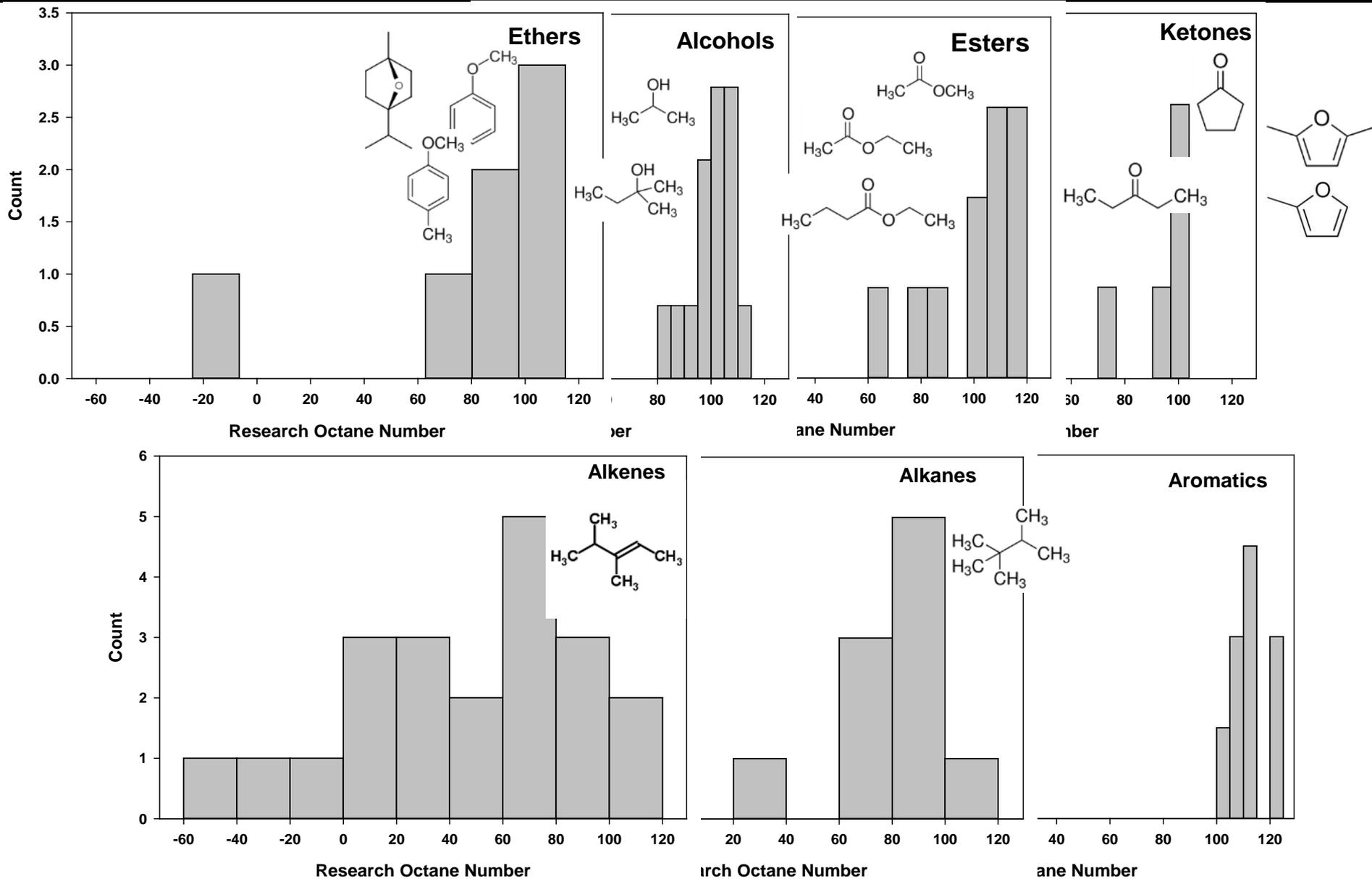
- 8 alcohol
- 3 alkane
- 1 alkene
- 11 aromatic
- 8 ester
- 6 ether
- 3 furan
- 2 ketone



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

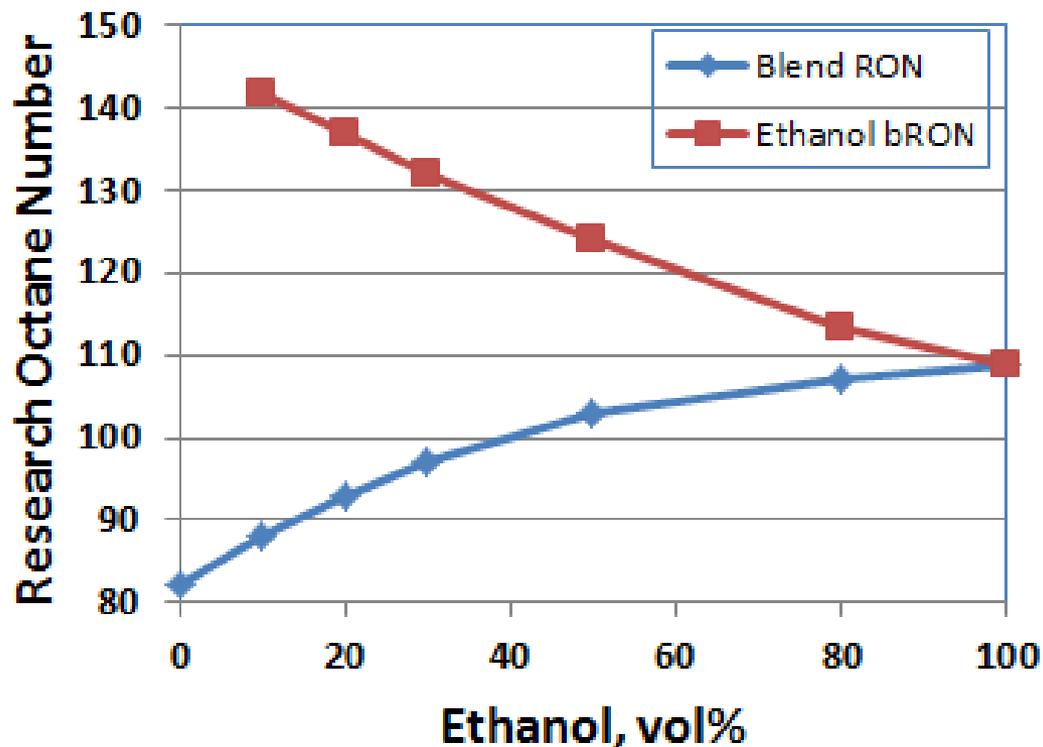


Required Blending RON

- **Blending RON can be much higher than pure component**

- But some compounds show no increase or antagonistic effect
- Methyl acetate pure component RON ~120, blending RON=107

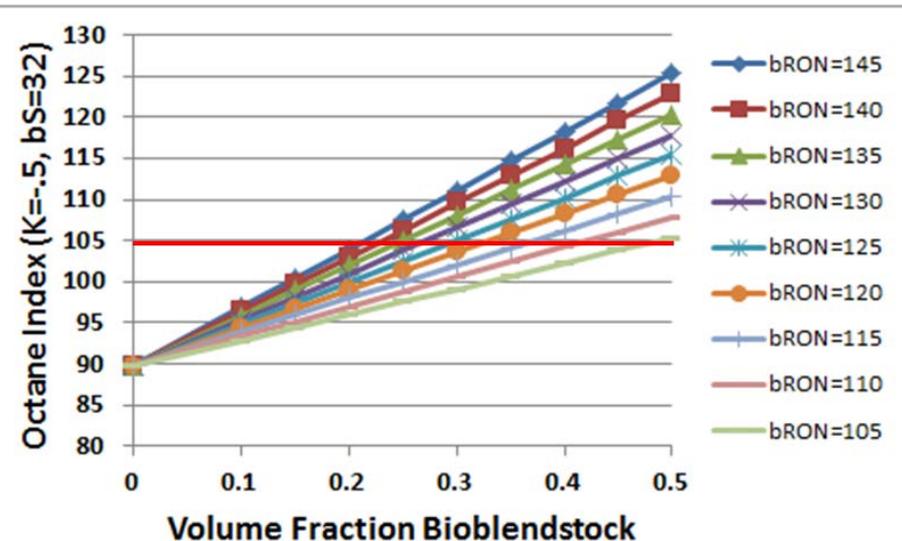
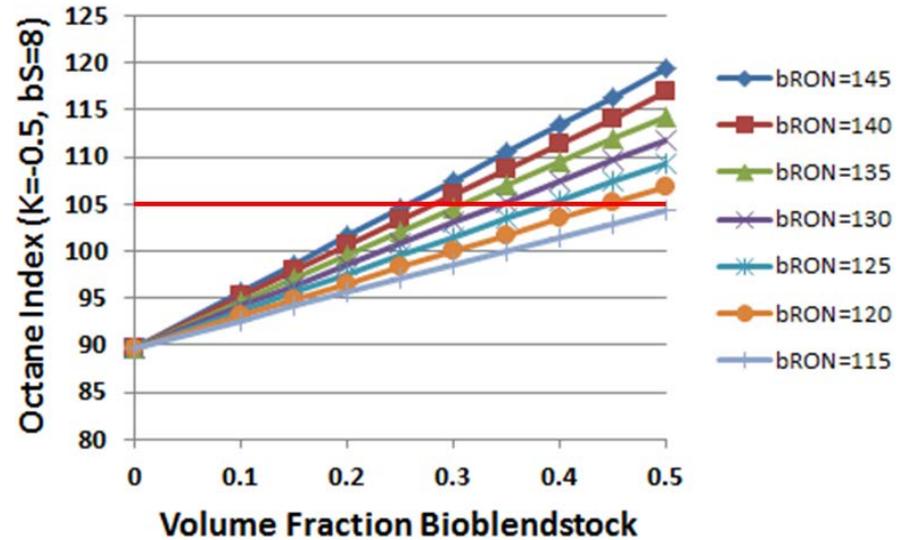
- **Currently not well predicted from theory**



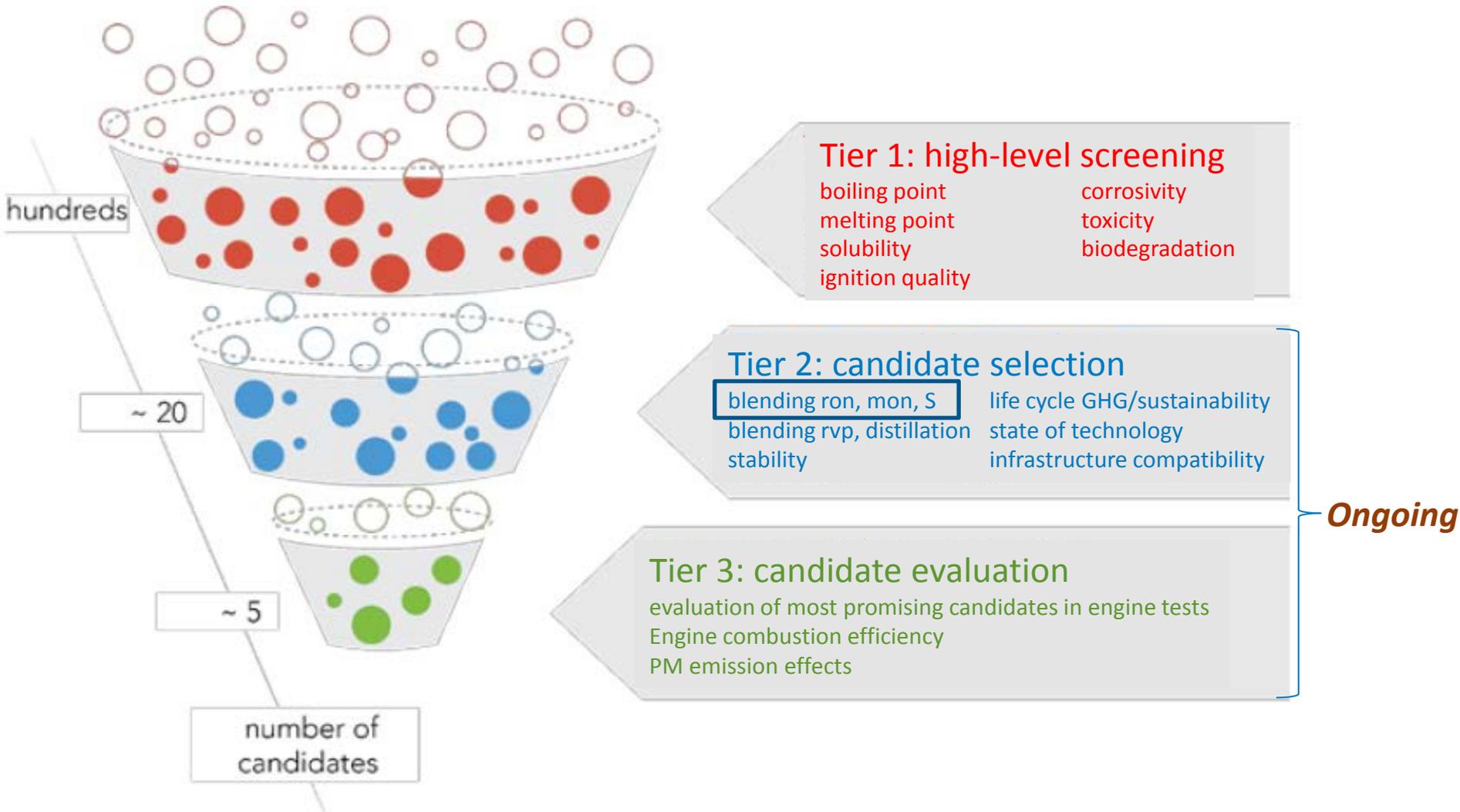
Compound (10 - 20 vol%)	Pure RON	Blending RON
2,5-Dimethyl-furan	101	150
4-Methyl-anisole	115	139
Methyl acetate	~120	107

Blending Octane Index - OI

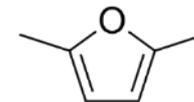
- More predictive of knock is $OI = RON - K \cdot S$
- $S = RON - MON$
- $K < 0$ for advanced SI engines
- E30 in a conventional sub-octane blendstock provides adequate knock resistance for advanced SI
 - $RON = 99$
 - $S = 12$
 - $OI = 105$ at $K = -0.5$
 - In this case ethanol blending RON is 132 and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



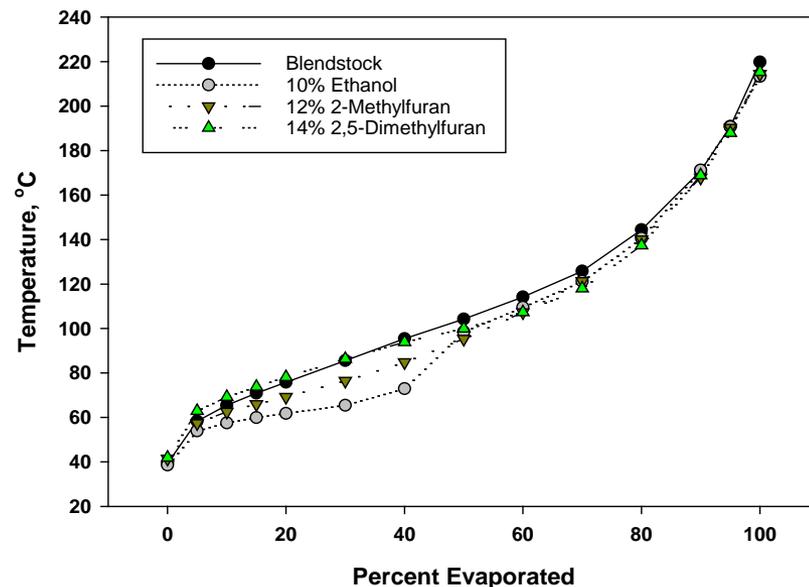
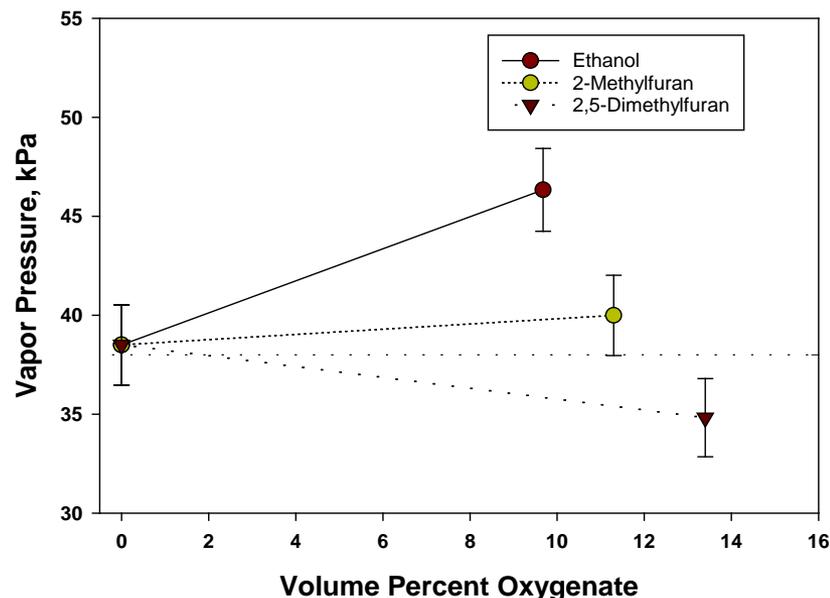
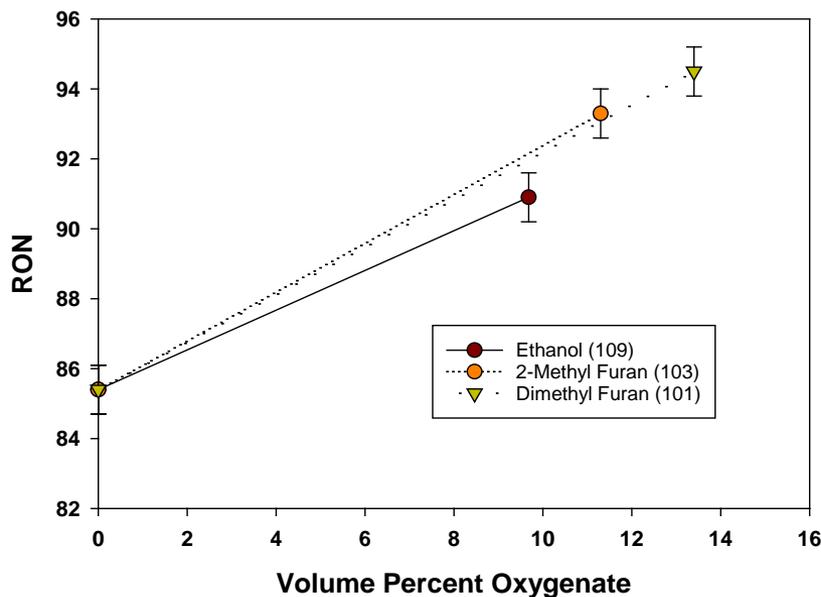
Level 2 and Level 3 Evaluation for SI



Level 2 Screening – Case Study 2,5 DMF

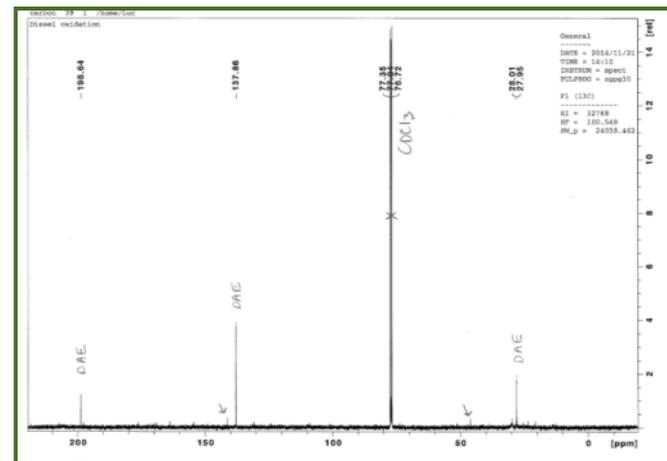


- Minimal to no vapor pressure increase – or a decrease
- Less boiling point depression in distillation than ethanol
- API Report RON values may significantly underestimate blending RON (bRON 153 and 155)



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

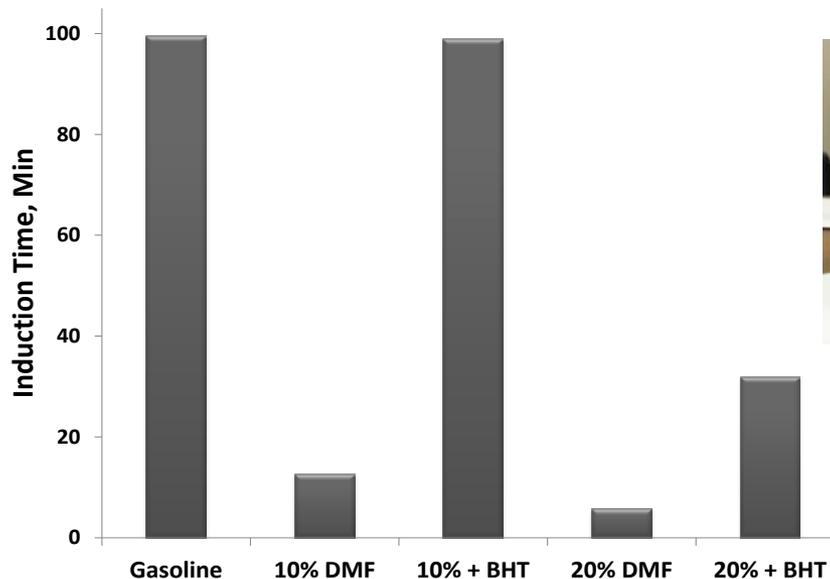
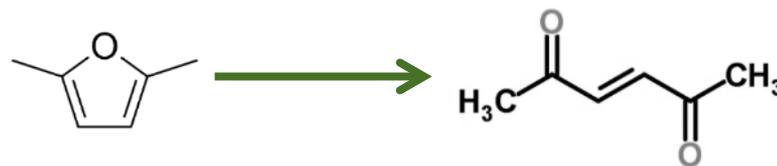


- ¹³C NMR indicates gum is largely 2,5-hexenedione (aka diacetylene or DAE)

- 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

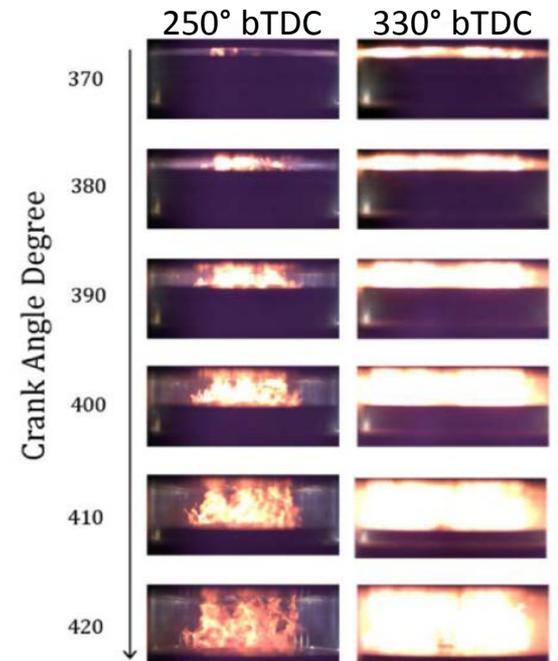
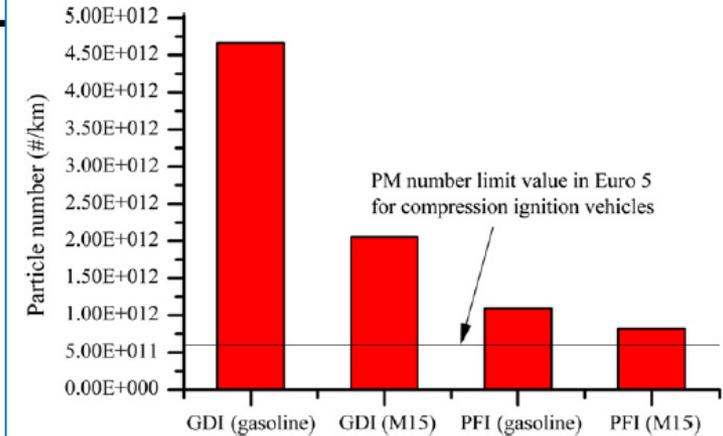


NREL 32488

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

B. Liang et al. / Journal of Aerosol Science 57 (2013) 22–31



Fatouraie, M., Wooldridge, M. and Wooldridge, S., *SAE Int. J. Fuels Lubr.* 6(1):2013, doi: 10.4271/2013-01-0259

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-

$DBE = (2C + 2 - H)/2$ -rough measure of tendency to form particles

$VP =$ Vapor pressure at 443K (170°C) –rough measure of tendency to evaporate

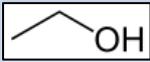
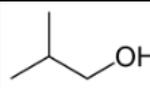
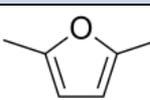
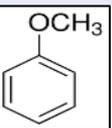
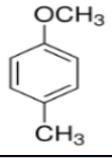
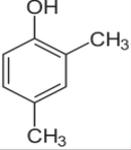
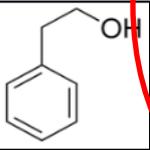
$Wt_i =$ Weight fraction of compound

Aikawa, K., Sakurai, T. and Jetter, J. J. Development of a Predictive Model for Gasoline Vehicle Particulate Matter Emissions. SAE International 2010-01-2115.

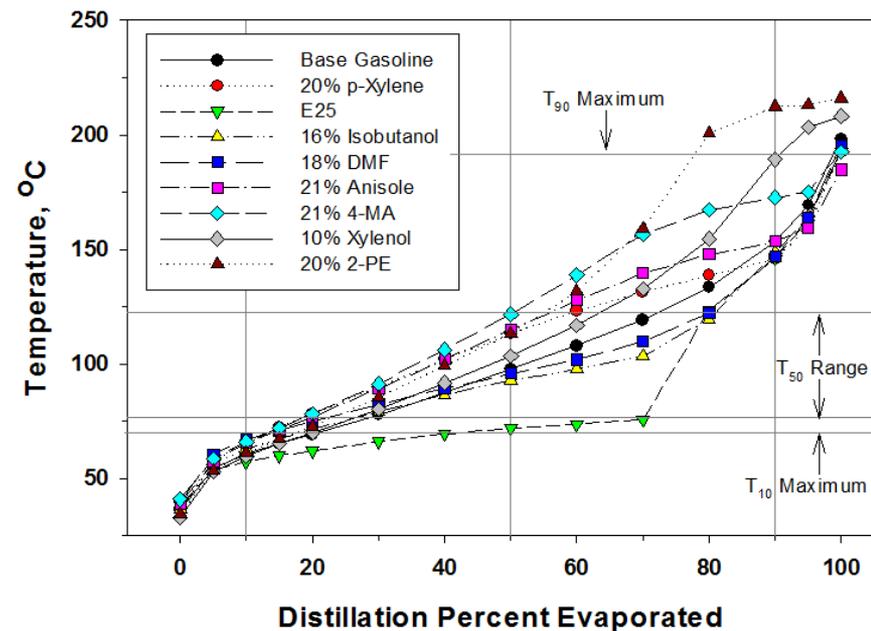
Does PMI breakdown for oxygenates? Studies of oxygenate sooting tendency suggest that it will

McEnally, C.S., Pfefferle, L.D. Sooting Tendencies of Oxygenated Hydrocarbons in Laboratory Scale Flames. *Environ. Sci. Technol.*, 2011, 45 (6), pp 2498–2503.

Oxygenates Used in PM/PN Study

		Boiling Point (°C)	Vapor Pressure, 443K (kPa)	DBE
Ethanol		78	1545	0
Isobutanol		108	596	0
2,5-Dimethyl-furan		94	538	3
Anisole		154	153	4
4-Methyl-anisole		174	87.7	4
2,4-Xylenol		211	30.3	4
2-Phenyl-ethanol		220	21.5	4

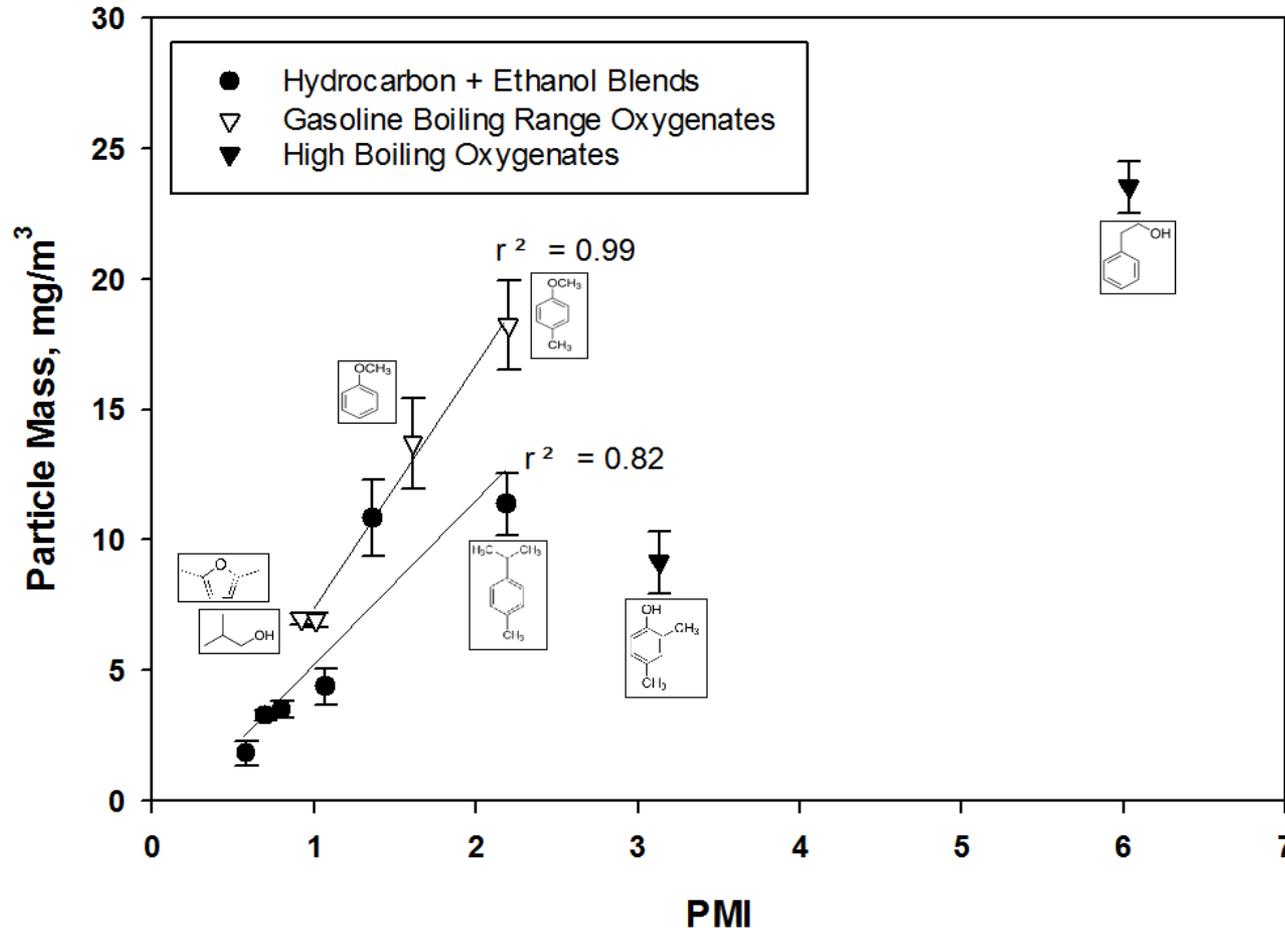
Oxygenates blended with 88 RON summertime BOB at 10 to 20 vol%



- 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

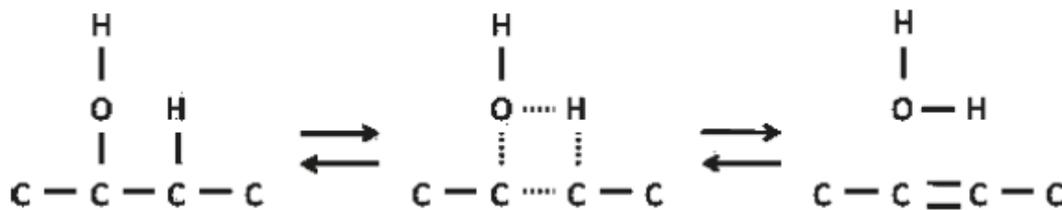
Oxygenate Effect on GDI Engine PM Emissions

- 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

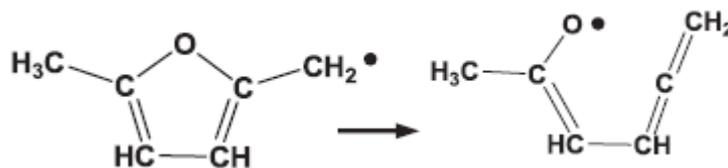


Routes from Oxygenates to Soot Formers

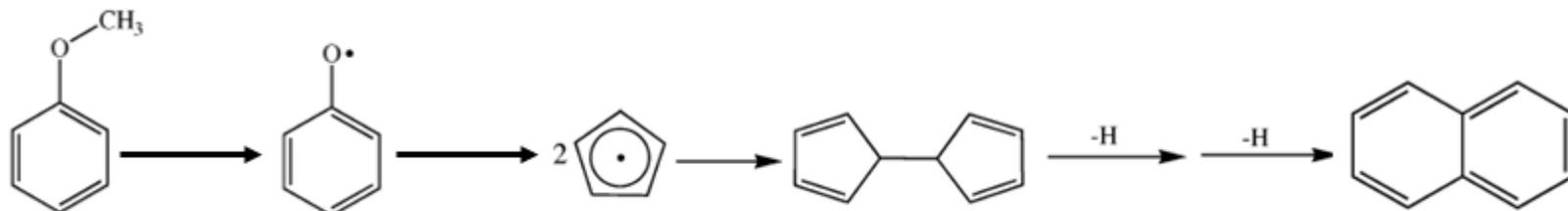
- Alcohol dehydration to alkene (McEnally and Pfefferle, *Environ Sci Technol*, 2011, 45 (6), pp 2498–2503):



- 2,5-DMF decomposition to olefinic carbonyls and radicals (Djokic, M., et al, *Proc Comb Inst*, 2013, 34 251–258):



- Anisole forms cyclopentadienyl radical which couples to naphthalene (Scheer, A., et al., *J. Phys. Chem. A* 2010, 114, 9043–9056):



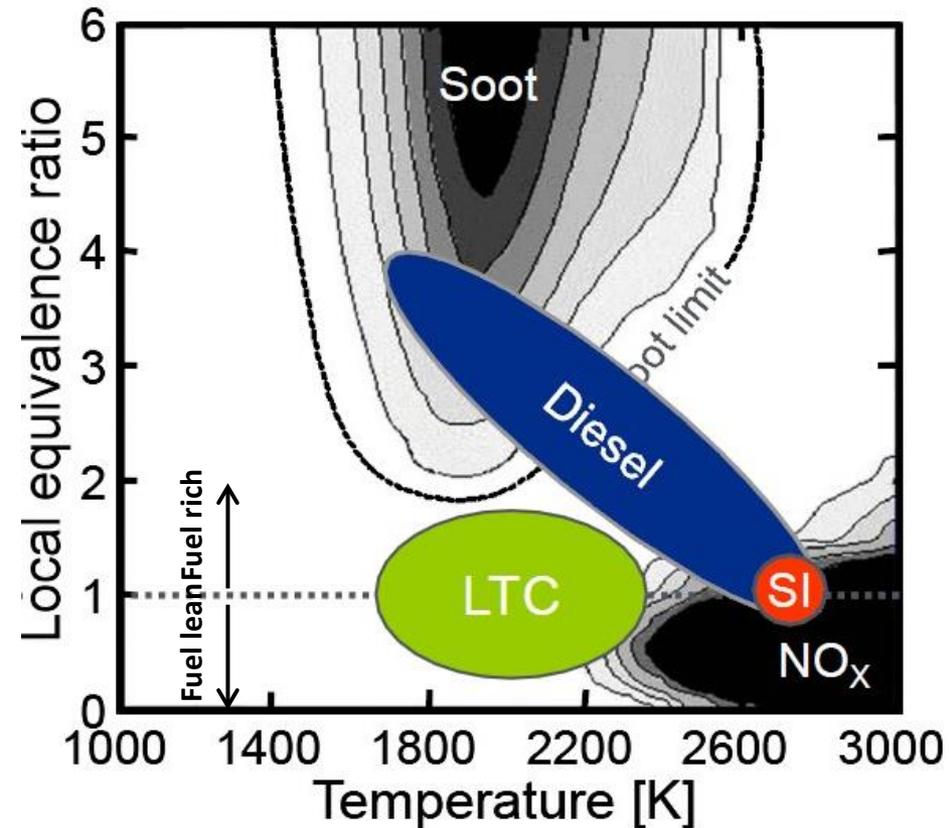
SI Fuel-Engine Optimization

- **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

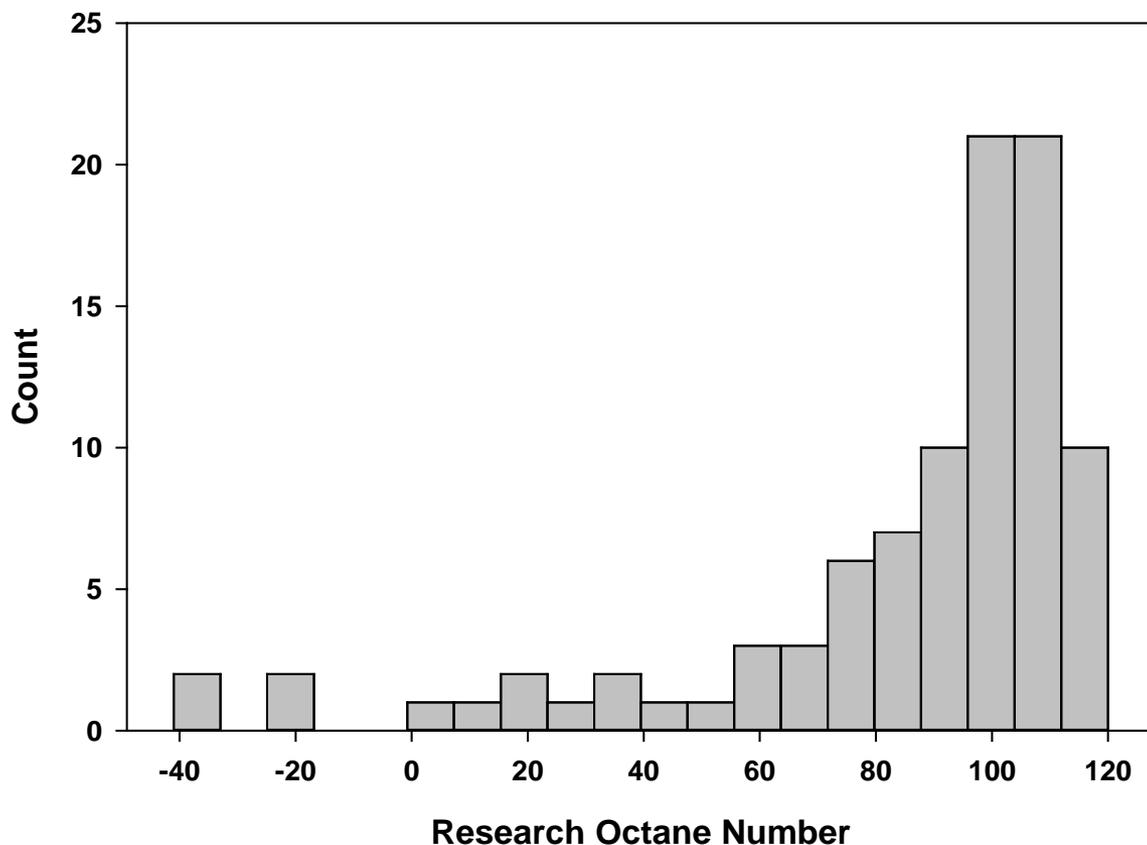
- Compression ignition and lean engine operation for efficiency
- LTC to improve to achieve low NO_x and PM
- Highly reactive fuels (diesel) undesirable (ignite before adequate mixing)
- Straight-run gasoline RON~70 (OI 66 to 68) acceptable
 - Reduced GHG emissions and refining cost



<http://www.princeton.edu/puceg/perspective/combustion.html>

GCI Fuel Screening

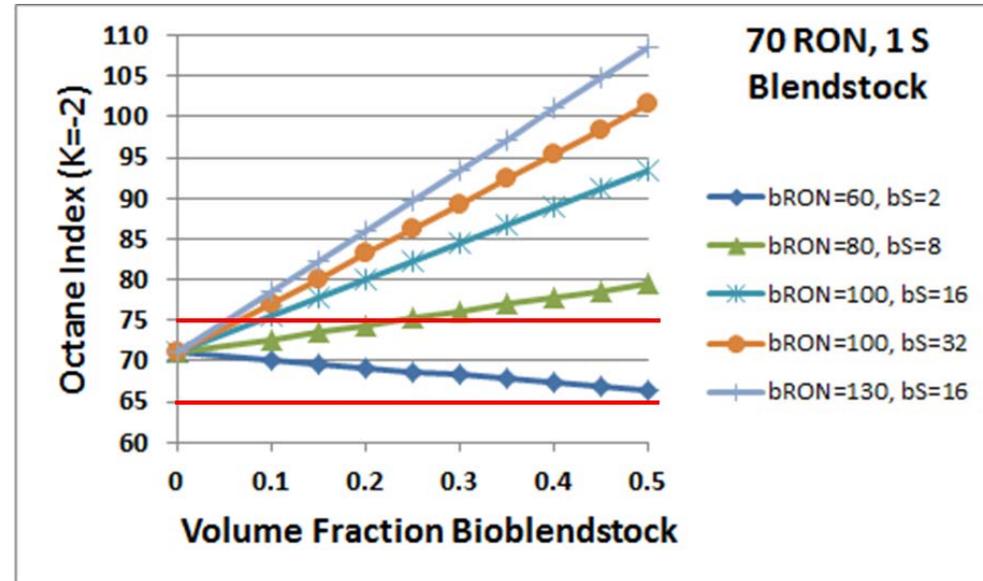
- Likely similar boiling point range, vapor pressure, stability, cleanliness, etc. as SI engines
- Range of bio-blendstocks available in naphtha range



	RON
2-Methyltetrahydrofuran	86
Cyclohexane	83
Pentan-1-ol	82
1,1,3- Trimethylcyclohexane	81
Alpha-Pinene	80
Beta-pinene	80
Pinane	77
Hexanoic acid, ethyl ester	77
1-Hexene	76
Methylcyclohexane	75
4E-octene (trans)	73
2-Heptene (trans)	73
2-Heptanone	70
Rose oxide	70
Ethylcyclopentane	67
Pentane	62
Menthane	60
Hexyl acetate	60
3-methylhexane	52

OI for Blending GCI Fuel with Bioblendstock

- $OI = RON - K \cdot S$
- For GCI K may be -2
 - Versus -0.5 or so for boosted GDI
- SRG primary blendstock
- High and low limits on OI constrain suitable bioblendstock





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**

- Vehicle Technologies Office
- Bioenergy Technologies Office

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Thank you to KAUST for this Invitation

robert.mccormick@nrel.gov

