NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Performance of Biofuels and Biofuel Blends

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Vehicle Technologies Program Merit Review – Fuels and Lubricants Technologies

May 16, 2013

Project ID: FT003

This presentation does not contain any proprietary, confidential, or otherwise restricted information.

Overview

Timeline

Start date: Oct 2012

End date: Sept 2013

Percent complete: 66%

Program funded one year at a time

Budget

Total project funding

FY12: $1.3 M

FY13: $0.77 M – to date

NBB cooperative research and development agreement provides around $500K to cost-share biodiesel research

Barriers

VTP MYPP Fuels & Lubricants Technologies Goals

- By 2013 identify light-duty (LD) non-petroleum based fuels that can achieve 10% petroleum displacement by 2025
- By 2015 identify heavy-duty (HD) non-petroleum based fuels that can achieve 15% petroleum displacement by 2030

Partners

- National Biodiesel Board (NBB) and member companies
- Manufacturers of Emission Controls Association (MECA) and member companies
- Engine Manufacturers Association (EMA) and member companies
- Coordinating Research Council (CRC) and member companies
- Renewable Fuels Association
- Colorado State University
- Oak Ridge National Laboratory
- State of Colorado
- Underwriters Laboratories
- Many biofuels startups

Milestones

Date	Milestone or Go/No-Go Decision	Status
Nov-12	**Non-methane organic gas emission effects of gasoline oxygenate blends.**	Complete

Relevance

Objective: Solve technical problems that are preventing expanded markets for current and future biofuels and biofuel blends

Necessary to achieve MYPP petroleum displacement goals and renewable fuel standards requirements

Research at the interface of fuel production and engines and infrastructure

PIX 10590

PIX 08432

PIX 07265

PIX 13531

Photo: Aaron Williams, NREL

Photo: Aaron Williams, NREL

Approach/Strategy

- **Performing research on the broad scope of biofuels: ethanol to biodiesel to next-generation oxygenate and hydrocarbons**
- **Quality and performance properties, compatibility with infrastructure, engines, lubricants, and emission controls; and impacts on emissions**

✓Industry collaborations guide our work to be relevant
✓Collaborations with other labs broaden our effective capability (industry, national labs, universities)


PIX 22782

Photo: Mike Lammert, NREL


PIX 17344

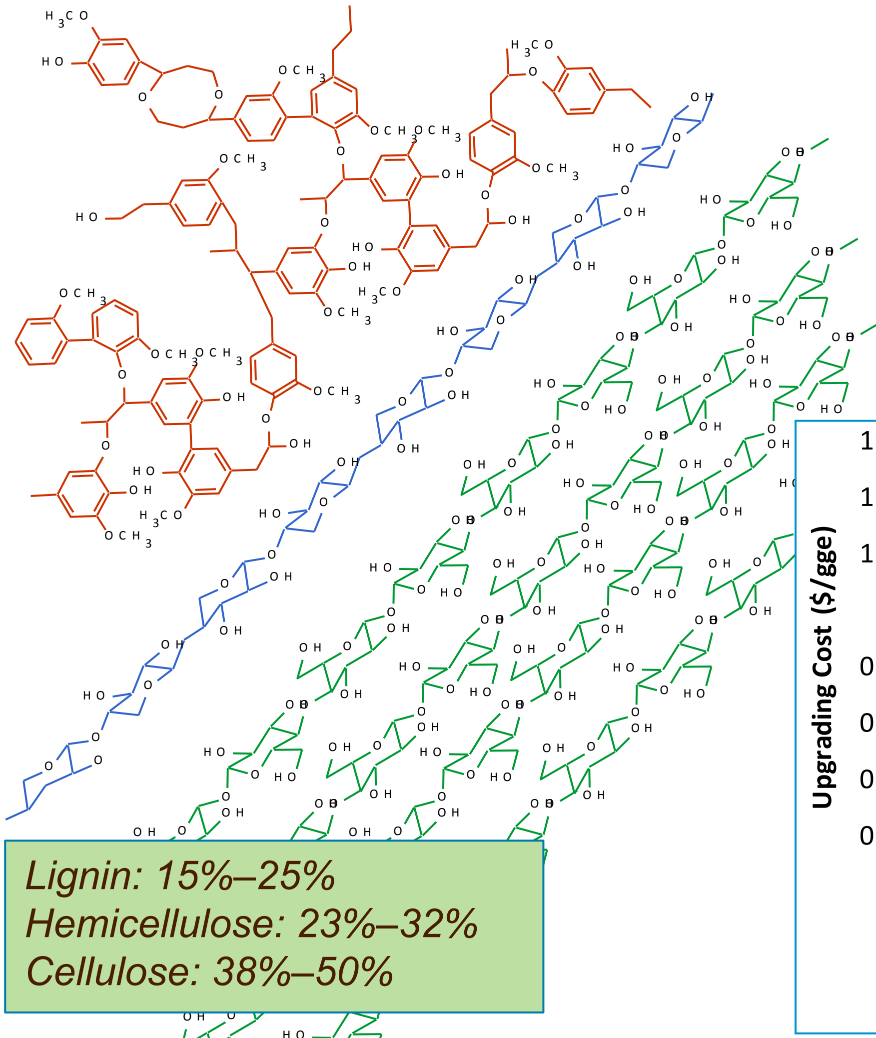
Can Oxygenate Be Tolerated in Drop-in Fuel?

- **Article of faith that "drop-in" fuels are hydrocarbon**
  - Compatible with engines
  - Compatible with fuel distribution (pipeline) and refueling infrastructure
  - Fungible (interchangeable)
- **But biomass has a high oxygen content and many conversion processes produce oxygenates**
- **Can economics be improved if not all of this oxygen is removed?**

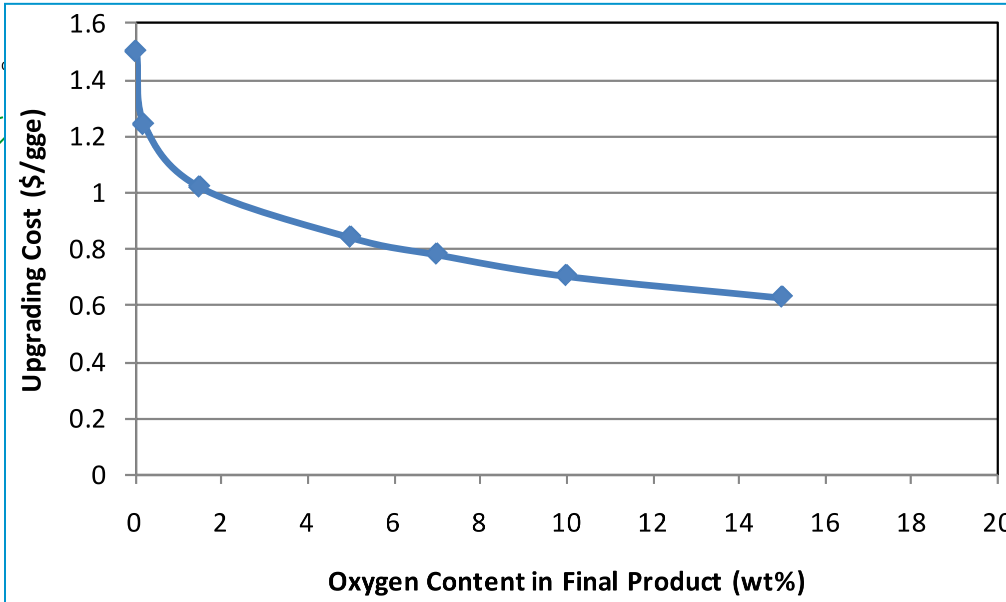
Determine if and at what levels biomass-derived oxygenates are scientifically and commercially feasible in drop-in fuels

Ligno-Cellulosic Biomass

- Biomass has high oxygen content:
  - 40 to 60 wt%
  - Molar O/C about 0.6
- Economically rejecting this oxygen may not be possible



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

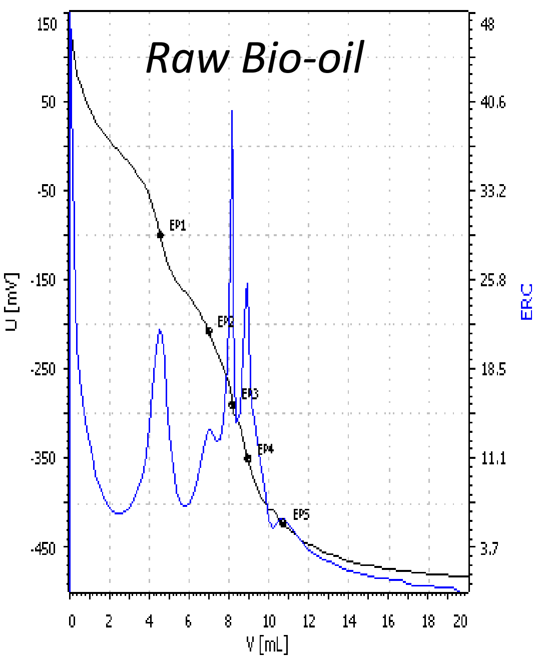


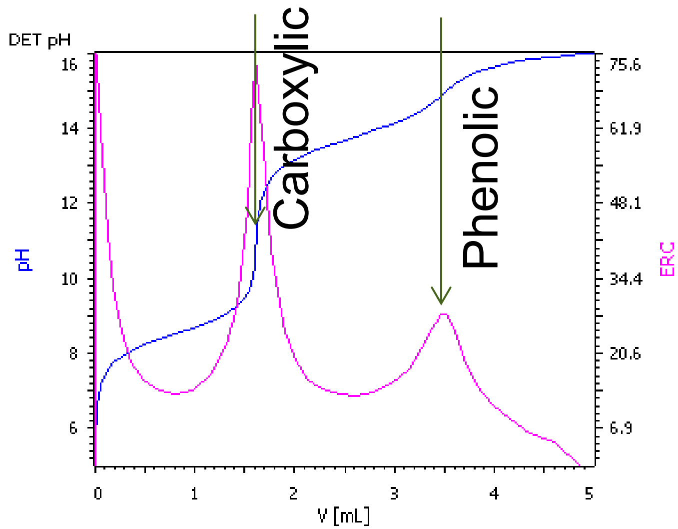
Economic evaluation of biomass pyrolysis oil upgrading costs as a function of final product oxygen content

Arbogast, S.V. *Upgrading Requirements for the Transport and Processing of Pyrolysis Oil in Conventional Petroleum Refineries*, Houston, TX: Global Energy Management Institute, 2009.

Technical Accomplishment: Characterization of Acids in Hydrotreated Pyrolysis Products

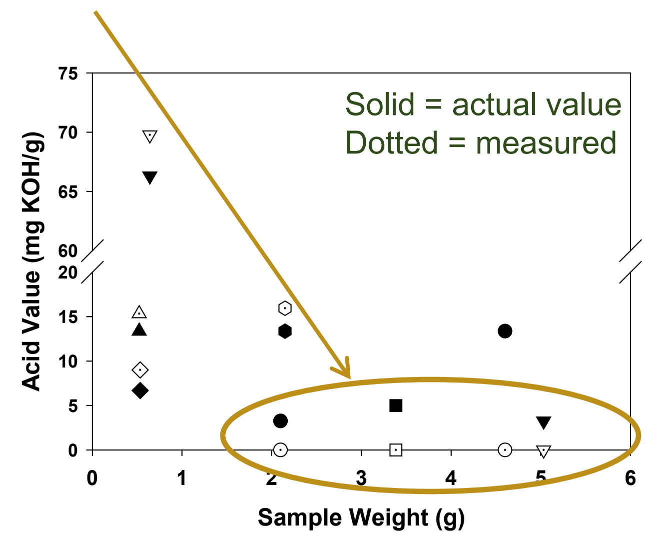
- Developed improved approach to acid characterization - multiple endpoints not detected by standard Total Acid Number measurement (ASTM D664)
- Differentiate weak (phenolic) and strong (carboxylic) acids based on pH buffer calibration
- Low detection limits observed for model compounds in heptane and diesel fuels
- In a bio-oil matrix titration of phenol showed poor detection limit, indicating interference in titration. Further refinement underway





Standards in Heptane

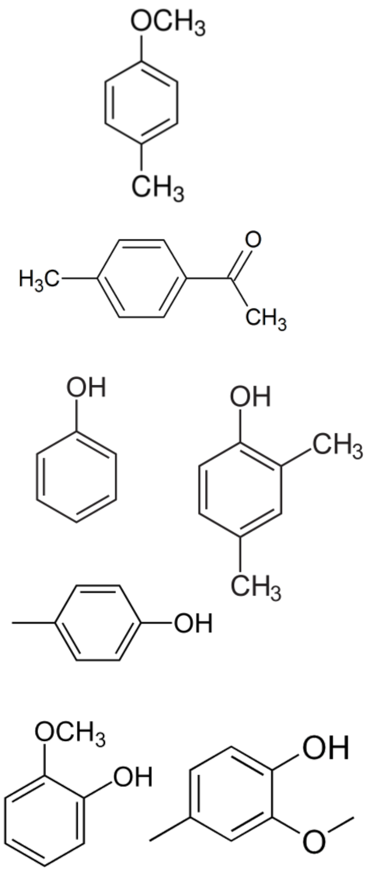
Phenol not detected by titration at TAN<6



Hydrotreated Bio-oil Matrix

Technical Accomplishment: Biomass Residual Oxygenate Effects on Diesel Performance Properties

Residual Oxygenates
<u>Tested in Diesel</u>

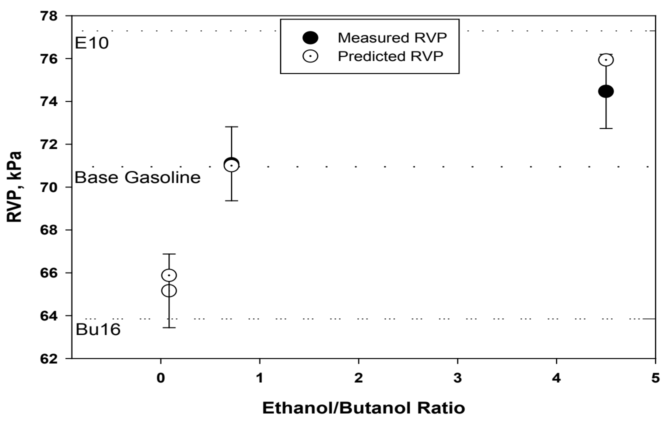


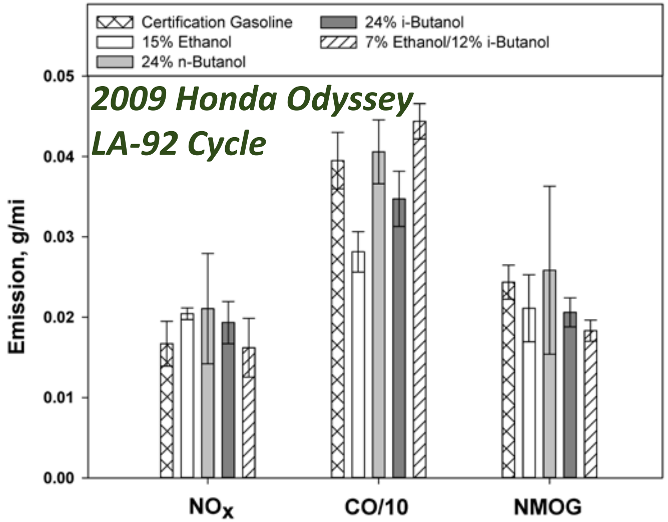
- Oxygenates selected from those observed in: Christensen, E., et al., "Analysis of Oxygenated Compounds in Hydrotreated Biomass Fast Pyrolysis Oil Distillate Fractions" <u>Energy Fuels</u> <u>25</u> (11) 5462–5471 (2011).
- Blended into certification diesel at 2 vol%
- Assessed by ASTM D975 standard plus oxidative (D2274) and thermal (D6468) stability
- Results:
  - Carbon residue – *no change*
  - Cloud point – *no change*
  - Copper corrosion – *no change*
  - Conductivity – *no change*
  - Lubricity – *improved (548 µm wear scar base fuel)*
  - Oxidation stability – *improved (7.9 mg/100 ml base fuel)*
  - Thermal stability – *no change*
- Water solubility of phenols may limit their concentrations in a drop-in fuel:
  - *Phenol – about 8 wt%*
  - *Cresols – about 3 wt%*
  - *Xylenols – about 0.5 wt%*

Materials compatibility and engine tests ongoing

Technical Accomplishment: Properties and Emissions of Gasoline/Ethanol/Butanol Blends

- Properties and emissions for gasoline blended with ethanol, 1-, 2-, and iso-butanol, and mixtures of ethanol and butanol were measured
- At constant 5.5 wt% oxygen, blends of 12% i-butanol/7% ethanol showed no increase in vapor pressure
- Ethanol was more effective than the other alcohols at reducing CO emissions (for this vehicle)
- Ethanol produced much higher unburned alcohol emissions, but much lower carbonyl emissions, than the butanols – such that NMOG was largely unaffected
- 12% i-butanol/7% ethanol blend significantly reduced NMOG relative to cert gasoline because both carbonyl and unburned alcohol emissions were lower.





<u>Major carbonyl emissions:</u>

Ethanol: *formaldehyde, acetaldehyde*

1-butanol: *formaldehyde, acetaldehyde, butyraldehyde*

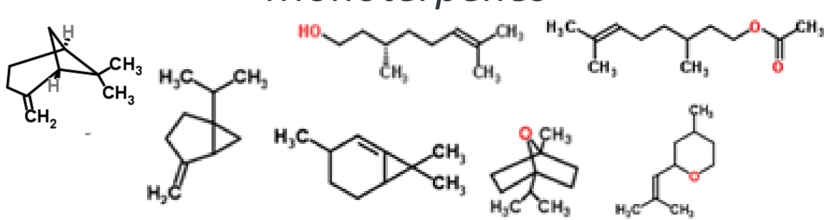
i-butanol: *formaldehyde, acetone, methacrolein*

Lipid Biomass

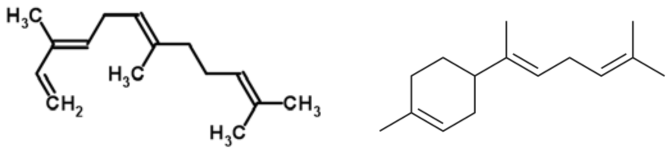
- **Natural fats and oils (including algal oil)**
- **Terpenoid natural products (aka Isoprenoid)**
  - Pine turpentine
  - Fermentation
- **Less than 10% oxygen content**
  - Removed by hydroisomerization (fats and oils) or hydrogenation (terpenoid)

Terpenoids:

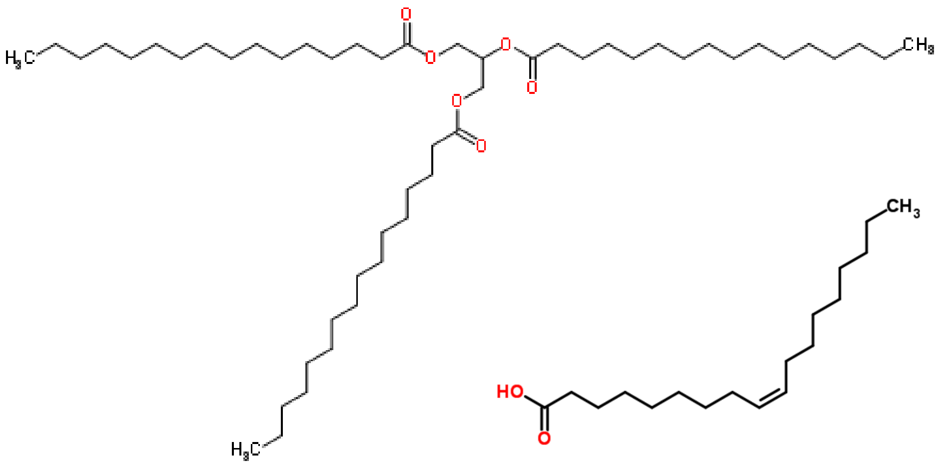
Monoterpenes



Sesquiterpenes

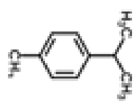
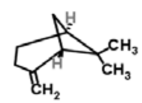
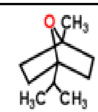
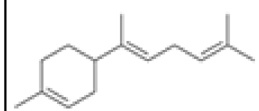


Fats and Oils:



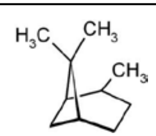
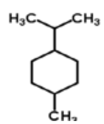
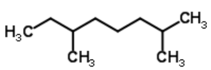
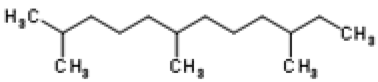
Technical Accomplishment: Properties of Terpene Biofuels

- **A range of terpene compounds characterized**
- **All unsaturated or oxygenated**

Property	Method	P-cymene	β-pinene	1,4-cineole	Bisabolene	Jet Spec	Diesel Spec
							
Freeze point, °C	D5972	-63	-61	-46	<-80	-40, max	No spec
Boiling point, °C	Literature	158	166	174	277	300, max	338, max
Flash point, °C	D93	32	36	51	110	38, min	52, min
Cetane No.	D6890	23	23	--	30	NA	40, min
RON	D2699	110	80	98	--	NA	NA
Smoke point, mm	D1322	10.5	12.3	--	9.8	25, min	NA

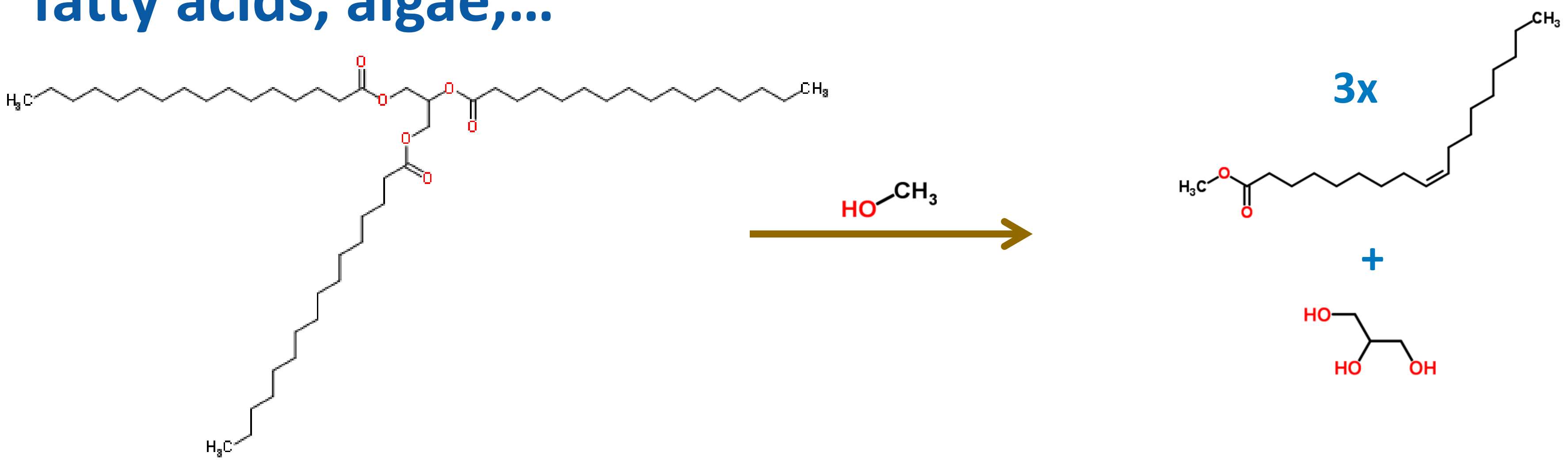
Technical Accomplishment: Properties of Terpene Biofuels

- **Hydrogenation may improve properties**
- **Ring opening hydrogenation collapses all monoterpenes to 2,6 dimethyl octane or similar compounds**
- **Bicyclic alkanes are dense and may have high smoke point**

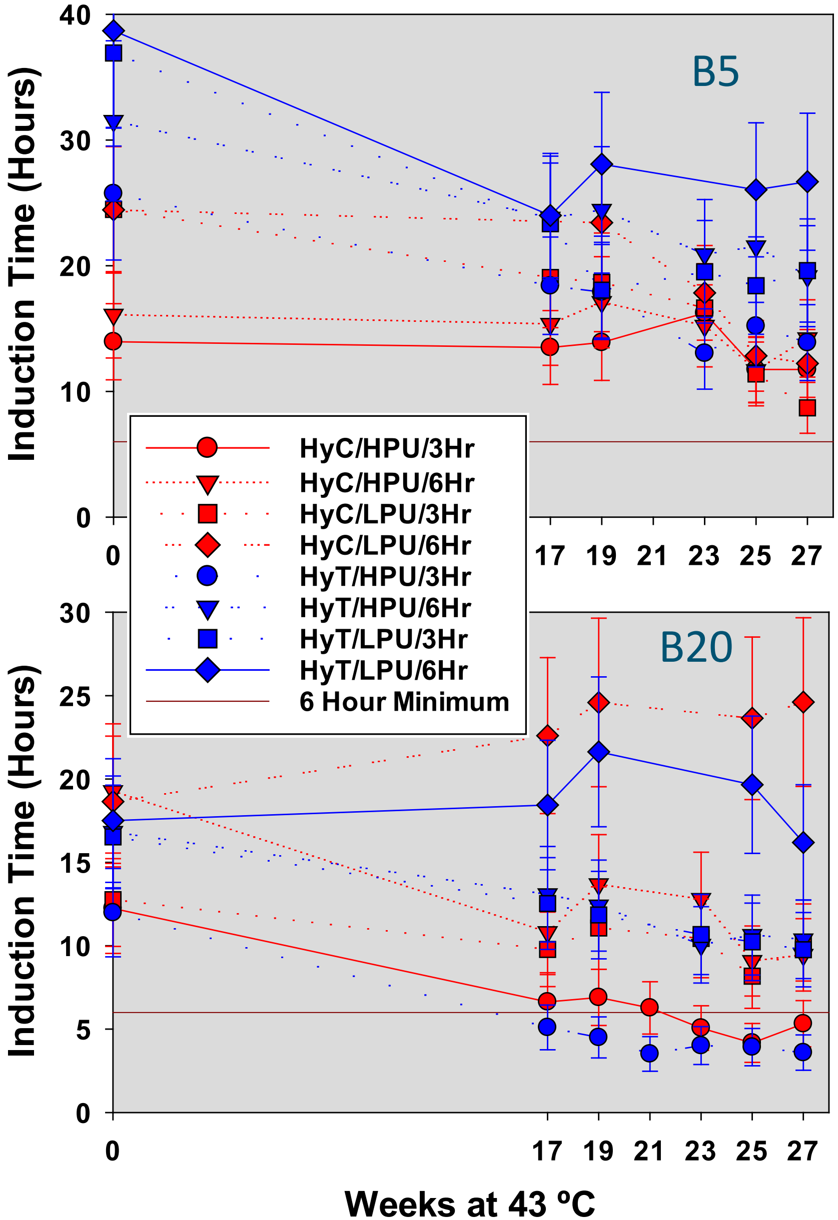
Property	**Method**	**pinane**	**methane**	**2,6 dimethyl octane**	**farnesane**	**Jet Spec**	**Diesel Spec**
							
Freeze point, °C	D5972	-53	-53	-100	-70	-40, max	No spec
Boiling point, °C	Literature	168	169	160	240	300, max	338, max
Flash point, °C	D93	36	--	82	101	38, min	52, min
Cetane No.	D6890	--	--	51	58	NA	40, min
RON	D2699	77	60	--	--	NA	NA
Smoke point, mm	D1322	?	?	--		25, min	NA

Biodiesel

- Fatty acid methyl esters – a low cost approach to fuels from fats and oils
- 1.1 billion gallon in United States (in both 2011 and 2012)
- Produced from soy oil, animal fats, waste cooking oil, corn oil from corn ethanol plants,…
- Many new feedstocks emerging: canola, camelina, tall oil fatty acids, algae,…



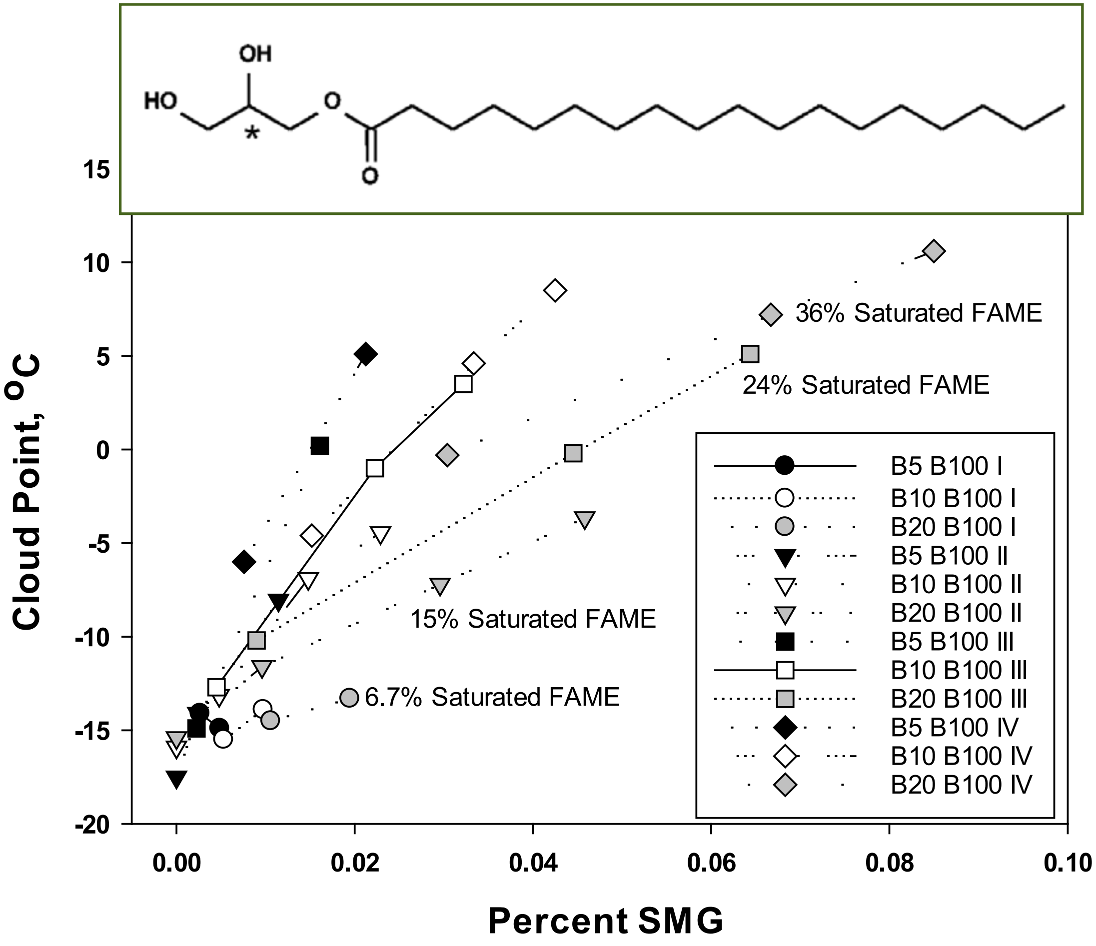
Technical Accomplishment: Long-Term Storage of Biodiesel Blends



- **Simulating 3 years storage of B5 and B20 blends (D4625 accelerated storage)**
  - 2 year simulation completed (26 weeks storage)
  - Measuring Rancimat induction time (6 hr minimum)
- **Saturated vs unsaturated biodiesel, different antioxidant levels, hydrocracked and hydrotreated diesel fuels**
- **B5 blends all meet 6 hr requirement (at 2 years)**
  - Higher oxidation rate for more unsaturated biodiesel, lower antioxidant (lower initial B100 Rancimat)
  - Blends with hydrocracked diesel showed significantly lower stability
- **B20 blends meet 6 hr minimum if initial B100 Rancimat is 6 hr**
  - Blends with low polyunsaturate B100 also met requirement for 3 hr initial B100 Rancimat
  - Effect of diesel fuel chemistry not evident in B20 data

Technical Accomplishment: Saturated Monoglyceride (SMG) Effects on Biodiesel Blend Low-Temperature Performance

- **Common impurity in biodiesel, present at up to about 0.5 wt%**
- **Likely responsible for most incidents of "unexplained" cold weather filter clogging**
- **Completed a factorial designed study (over 140 samples) to examine effects of several variables on Cloud Point (CP):**
  - SMG
  - Saturated FAME
  - Diesel CP
  - Diesel aromatic content
- **SMG had the largest effect on CP**
- **Increasing biodiesel blend level at constant SMG content reduced CP**
  - Solubility effect
- **Increasing saturated FAME content had no effect at B5 or B10, but increased CP at B20**
- **Higher diesel aromatics reduced the CP effect of both SMG and saturated FAME**
  - Solubility effect



Collaboration and Coordination with Other Institutions

- **Assessment of Acidic Components in Hydrotreated Biomass Pyrolysis Oil**
  - National Bioenergy Center (NREL)
  - National Advanced Biofuels Consortium (NREL)
  - Pacific Northwest National Laboratory
- **Biomass Residual Oxygenate Effects on Diesel Performance**
  - Colorado State University
  - Underwriters Laboratories
- **B20 DPF/DOC/SCR Durability Research**
  - MECA and member companies, including
    - Umicore
    - BASF Catalysts, LLC
  - Caterpillar
  - Ford Motor Company
  - National Biodiesel Board
  - EMA and member companies
  - Cummins
  - Oak Ridge National Laboratory
- **Ethanol/Butanol Blend Performance**
  - SGS-Environmental Testing Corporation
- **FFV Emissions/Adaption on E40**
  Colorado Department of Public Health and Environment
- **Terpene Biofuels Characterization**
  - J Craig Venter Institute
- **Biodiesel Transit Bus Emissions**
  - Transit agencies in Denver, Ft. Collins, Aspen, and Colorado Springs, CO
  - DOE Clean Cities Program (cofunding)
- **Long-Term Stability of Biodiesel Blends**
  - Renewable Energy Group
  - ADM
  - Griffin Industries
  - Flint Hills Resources
  - National Biodiesel Board
- **Saturated Monoglyceride Effects on Biodiesel Low-Temperature Performance**
  - Phase Technology, Inc.
  - Innospec Fuel Specialties
  - Flint Hills Resources
- **Others**
  - Renewable Fuels Association
  - USDA: Agricultural Research Service

Proposed Future Work

- **Definition of Drop-In Fuels**
  - Effect of specific oxygenates on gas/diesel properties, storage and handling
  - Compatibility with materials
  - Engine operation and emissions
  - Expansion to employ actual biomass products rather than model compounds
- **Acid in upgraded pyrolysis oils and distillate fractions**
  - UPLC for detailed speciation of acids present
  - Improved titration for pKa measurement
  - Measurement of corrosion
- **ASTM specifications**
  - Specification development for butanol blendstock
  - Inclusion of E15 in gasoline standard
  - Variables affecting ethanol conductivity and correlation to corrosivity
- **Impact of High Octane Biofuels on DI Engine Efficiency**
  - Effects of RON, MON, heat of vaporization, and compression ratio
  - Distillation curve and heat of vaporization as a function of fraction evaporated
- **IQT Study ofLubricant Effects on Low-Speed Pre-Ignition in Highly Boosted Engines**
- **Completion of 3 year Biodiesel Blend Storage Study**

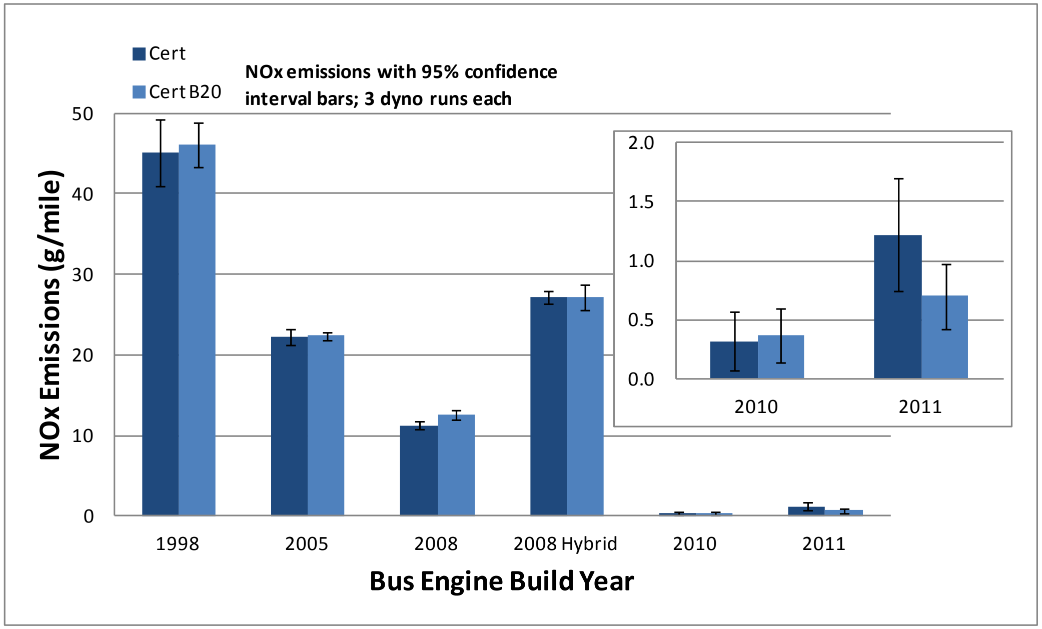
Summary

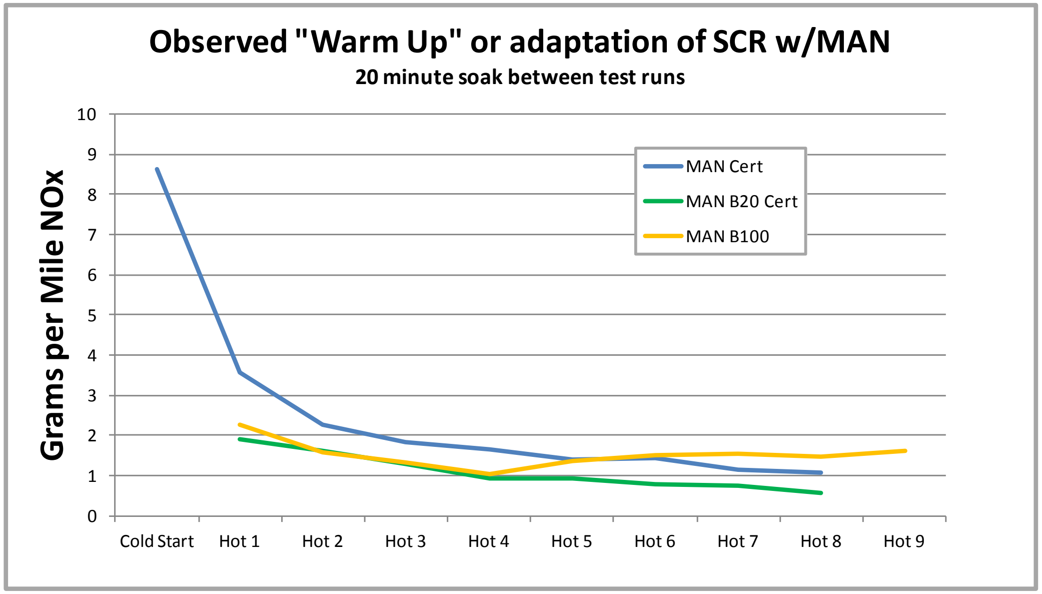
- **Guidance from last year's AMR has improved the quality of this activity**
- **In particular, the emphasis is shifting to a focus on defining what is a drop-in fuel**
- **Studies focused on impurities in biofuels and how these are measured and affect performance:**
  - Acids in hydrotreated biomass pyrolysis oils
  - Monoglycerides and metals in biodiesel
- **Studies also examined the performance of new fuels in storage and handling, as well as engine operation**
- **Fuel quality surveys led to improved ASTM specifications**

Technical Back-Up Slides

Technical Accomplishment: B20 Bus NOx Comparison

- 6 buses tested on NREL's Renewable Fuels and Lubricants (ReFUEL) laboratory HD Chassis Dynamometer
- B20 effect on NOx statistically significant in fewer than half of comparisons
- Note near-zero NOx for 2010-2011 buses with SCR
  - *Eliminates B20 and B100 effect on NOx emissions*
- ***Potential for very high NOx emissions on cold start and for low-speed/low-load operation***



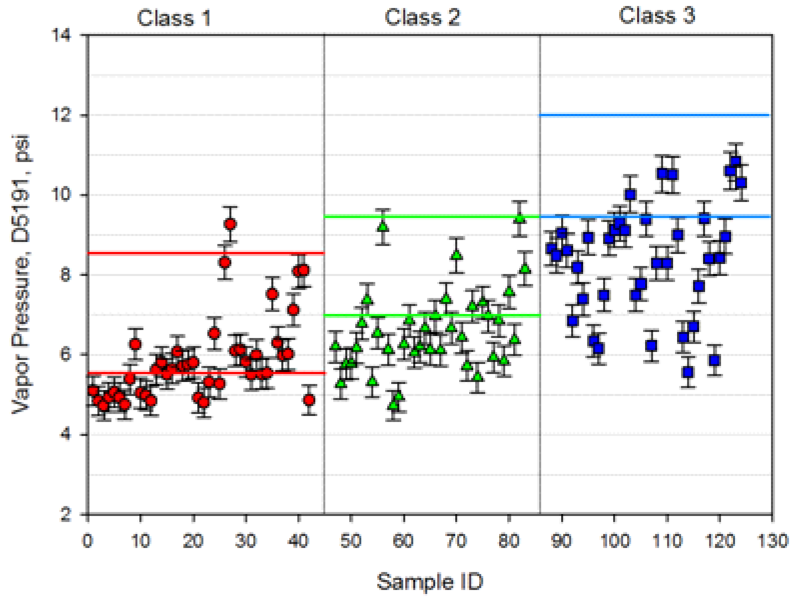


Technical Accomplishment: Fuel Surveys and Their Influence on ASTM Specifications

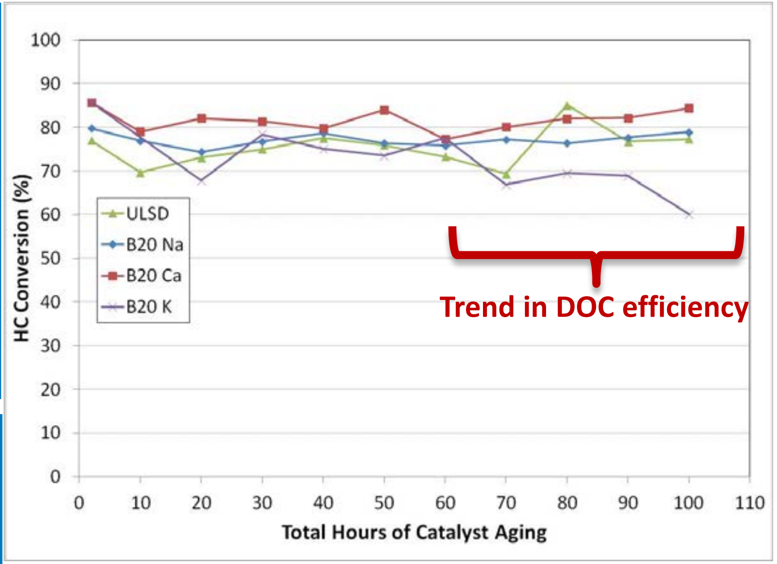
- **Vapor pressure requirements for gasoline and E85 are critical for cold starting and driveability**
  - Many anecdotal reports of difficulty starting and poor performance
- **Survey conducted in 2009 showed as many as 90% of samples failing minimum RVP**
- **Changes were made to the D5798 ASTM specification to allow higher levels of ethanol to increase vapor pressure**
- **NREL worked with CRC to assess the quality of E85 nationwide in and published report**
  - Conducted in late 2010 and early 2011
- **New survey shows large increase in compliance**

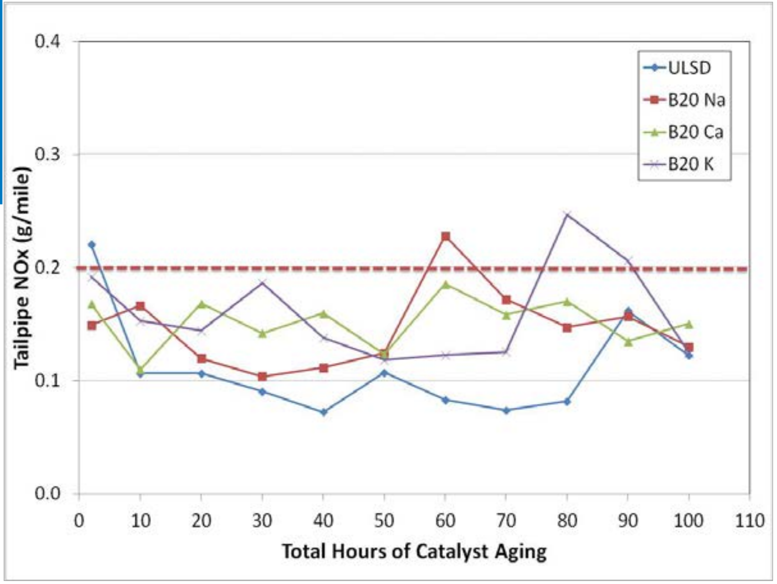
- **Survey of 106 samples from around U.S.**
- **All three volatility classes**
- **Nearly 50% of samples met vapor pressure requirements**
- **A marked improvement over previous surveys**

National 2010-2011 Survey of E85: CRC Project E-85-2
http://www.nrel.gov/docs/fy12osti/52905.pdf



Technical Accomplishment: Biodiesel Catalyst Durability Study

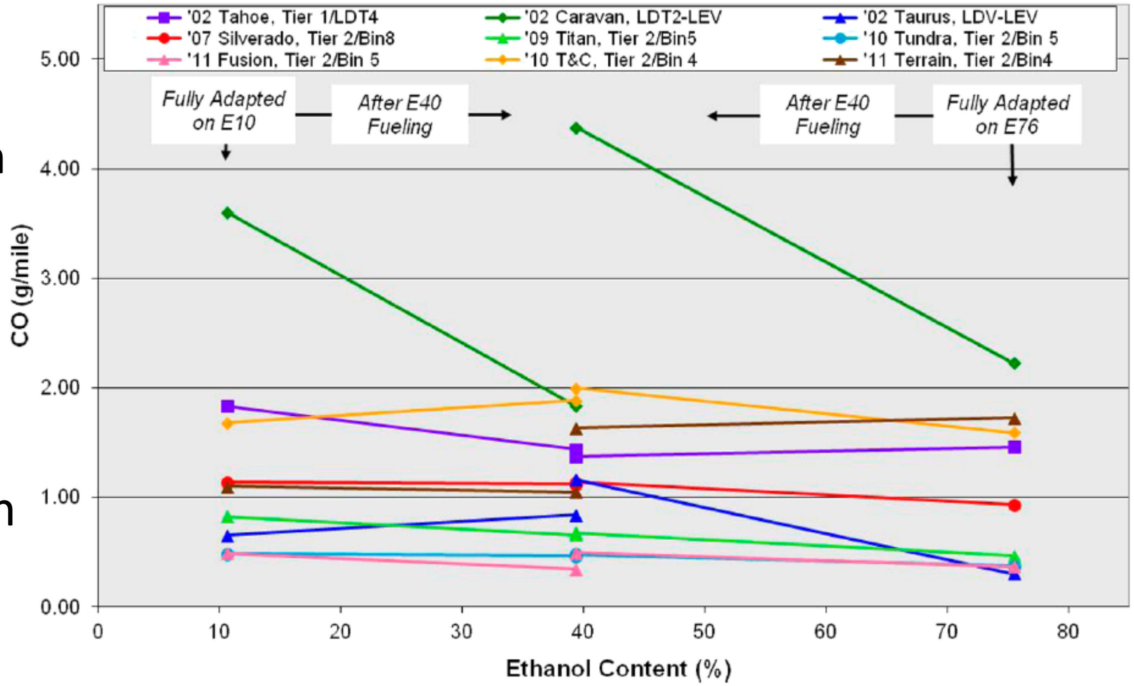




- *Major collaboration with ORNL and Ford*
- *Accelerated aging of LD diesel catalysts*
- *2011 Ford F250 with DOC+SCR+DPF*
- *Ultralow sulfur diesel, B20+Na, B20+K and B20+Ca*
- *After 150,000 miles equivalent exposure, no significant emission degradation observed for NOx*
- *Alkali metals may be affecting DOC performance*

Technical Accomplishment: FFV Adaption to E40

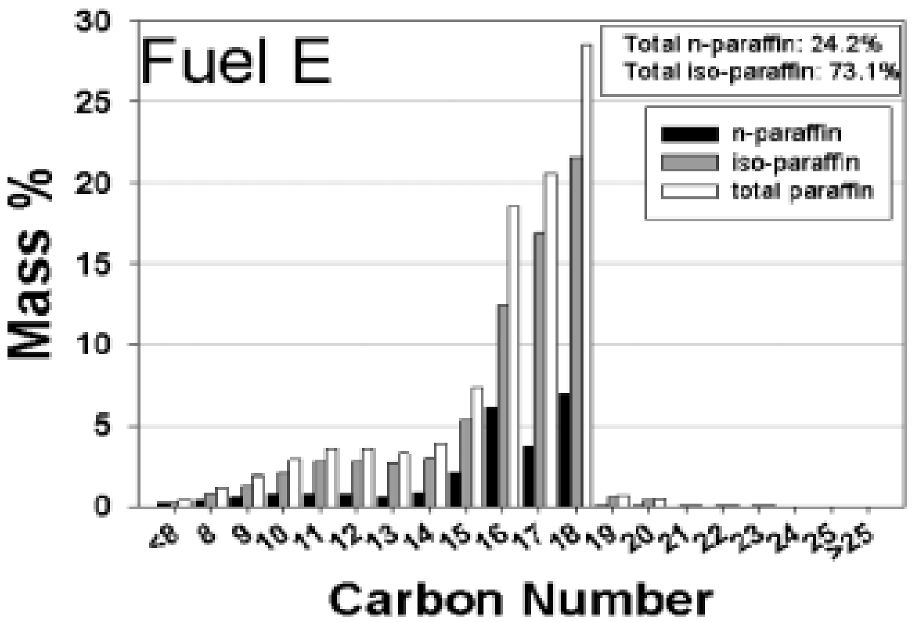
- Modern cars use adaptive learning to optimize engine control for different fuels (oxygen and energy content)
- Adaption affects emissions and fuel economy
- Mid-level ethanol blends (E20-E50) are becoming more common
- Nine cars (2002-2011) tested on E40 – after adaption on either E10 or E76
- Older FFVs may not readily adapt to E40 – they are set up to adapt to E10 or E70-E85
- More modern FFVs adapted rapidly – with the time of a 3 phase LA92 emission test



Yanowitz, J., Knoll, K., Kemper, J., Luecke, J., McCormick, R.L. "Impact of Adaptation on Flex-Fuel Vehicle Emissions When Fueled with E40" Environ. Sci. Technol. February 11, 2013, DOI: 10.1021/es304552b.

Technical Accomplishment: Performance of Hydrocarbon Renewable Diesel Fuels

- Commercial and prototype fuels
  - 10 samples from industry partners
  - Produced by hydroisomerization and fermentation
- High quality, high cetane number materials
  - Low level of residual oxygen in some samples
- Fat/veg oil derived fuels are highly isomerized (85%+)



Terpenoid-Derived