National Renewable Energy Laboratory
Innovation for Our Energy Future

Quality, Performance, and Emission Impacts of Biofuels and Biofuel Blends

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Vehicle Technologies Program Merit Review
Fuels Technologies
June 8, 2010
Washington, DC

Project ID: FT003

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Overview

Timeline

Start date: Oct 2009
End date: Sept 2010
Percent complete: 70%
-Program funded one year at a time

Budget

- Total project funding
- FY09: $3.2 M
- FY10: $1.8 M
  - $1.1 diverted to CNG projects
- NBB CRADA provides around $1M per year to cost share biodiesel emission controls testing

Barriers

VTP Draft MYPP NPBFL Goals

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

Partners

- National Biodiesel Board and member companies
- Caterpillar
- Oak Ridge National Laboratory
- Manufacturers of Emission Controls Association
- Engine Manufacturers Association and member companies
- Coordinating Research Council and member companies
- Environmental Protection Agency
- Members of ASTM Biodiesel Task Force
- Colorado School of Mines
- Southwest Research Institute

Relevance

Objective: Resolve technical issues that are preventing expanded markets for biofuels and biofuel blends - Necessary to achieve MYPP petroleum displacement goals

1. Biofuel quality:
   - Need for ASTM standards to help ensure quality in the market place
   - Need for new and improved test methods for biofuels and blends
     - Poorly understood factors affecting biodiesel low-temperature operability
     - Unknown impurities in other new fuels
2. Poor understanding of how biofuels impacts emission control devices:
   - Both short term performance and long-term durability of emission control systems
     - Associated lube oil dilution issues
3. Inadequate information on long-term engine durability impacts:
   - Engine dyno durability tests
   - Quantitative studies comparing petro and biodiesel over multiple years
   - Impacts on lube oil performance are poorly quantified
4. Poor understanding of air quality impacts:
   - No emission data for newer technology engines
   - Limited data on toxic compound and PM number emission effects

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Milestones

Month/Year	Milestone
Mar-09 - Completed	**Long-Chain Alcohols in Gasoline.** Assessment of all available data on utilization of butanol and mixed alcohols as gasoline blending components, including but not limited to fuel property requirements in the ASTM D4814 specification, engine and fuel system durability, catalyst performance, and tailpipe emissions. Submitted as unpublished report to DOE.
Dec-09 - Completed	**Biodiesel in DPF Equipped Production Engines.** Test two 2007-2009 model year medium - or heavy-duty engines using B20 produced from soy-oil and from animal fat. The tests will include tailpipe measurement of regulated pollutant emissions as well as an assessment of the impact of biodiesel on PM reactivity within the diesel particle filter. Unpublished report submitted to DOE.
Jun-10	**Wintertime Biodiesel Blend Quality Survey.** Sample collection completed, analysis ongoing.
Jun-10	**Biodiesel Ash Impacts on DPF Durability.**
Sep-10	**Biodiesel Effects on PM Size/Number Emissions.**
Sep-10	**Biodiesel Impact on Toxic Compound Emissions.**
Dec-10	**Ethanol Blender Pump Fuel Quality Survey.**

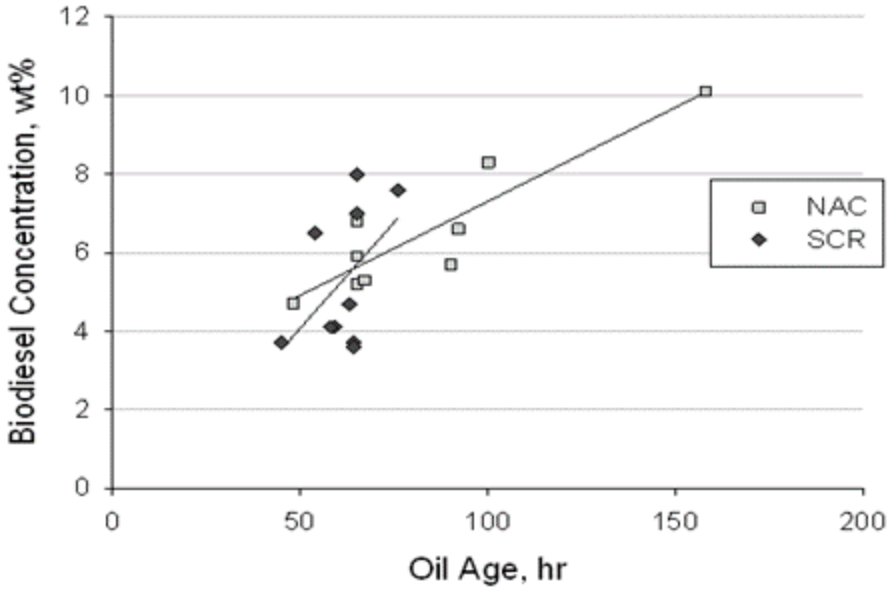
Approach

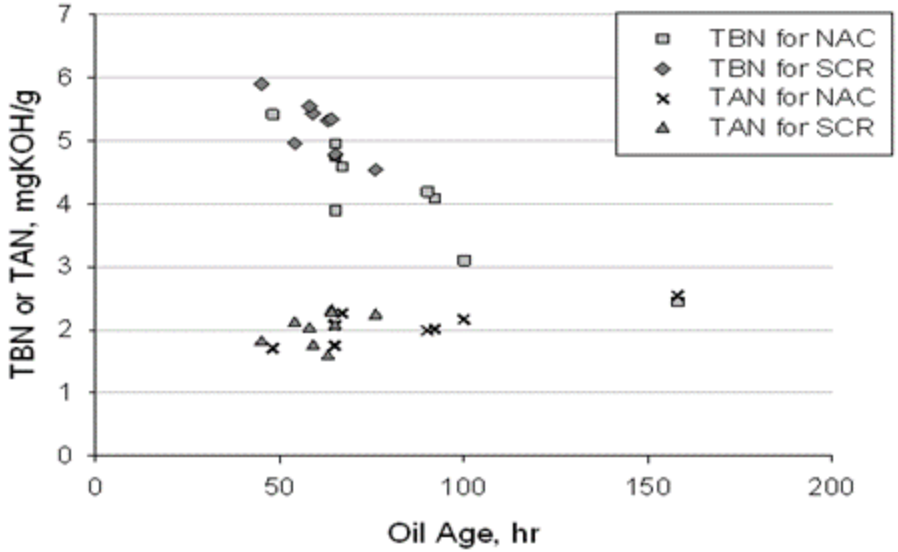
Applied development work focused on underlying fuel chemistry related to empirical studies of full scale systems

- Performance testing and chemical analysis of new fuels
  - Development of new and improved fuel analysis and testing methods
  - Surveys of quality and performance properties
  - Examination of chemistry underlying issues
- Engine and vehicle dynamometer testing
  - Regulated and unregulated pollutant emission impacts
  - Engine and emission control system durability
  - Low-temperature operability
- Quantitative, controlled real-world vehicle testing
- Industry partners or broad industry participation in work group or steering committee

Biodiesel Lube Oil Effects Studies

- Car equipped with DPF/SCR and DPF/NAC systems was operated for 700 hr
- Oil changed at intervals of 50 to 150 hr
  - DPF regen 20 – 65 times
  - NAC regen 500 – 2000 times
  - NAC desulf 2 – 7 times
- Up to 10% biodiesel in lube oil
- Oil performance in terms of TBN retention acceptable to 100 hr
- Engine tear down showed no excessive wear
- Detailed studies of medium-duty engine ongoing in 2010

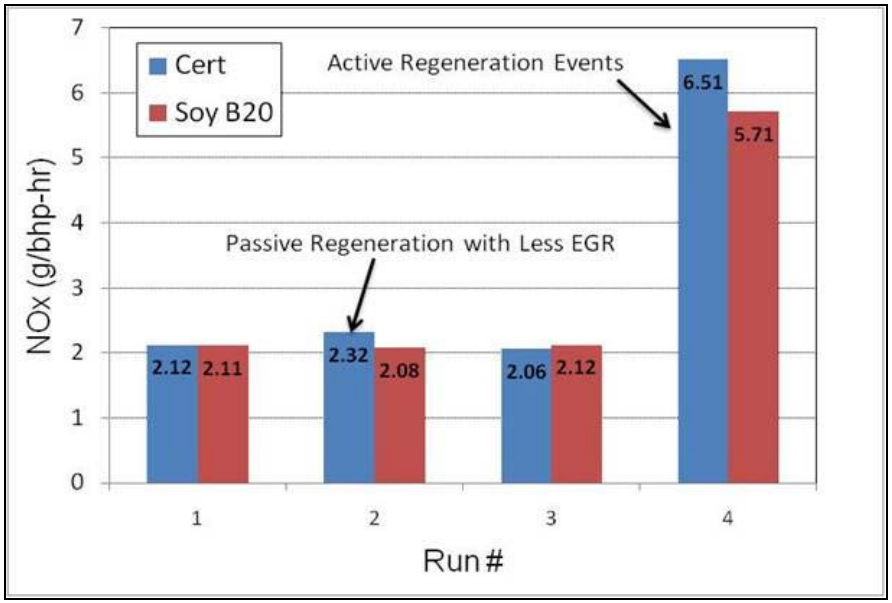




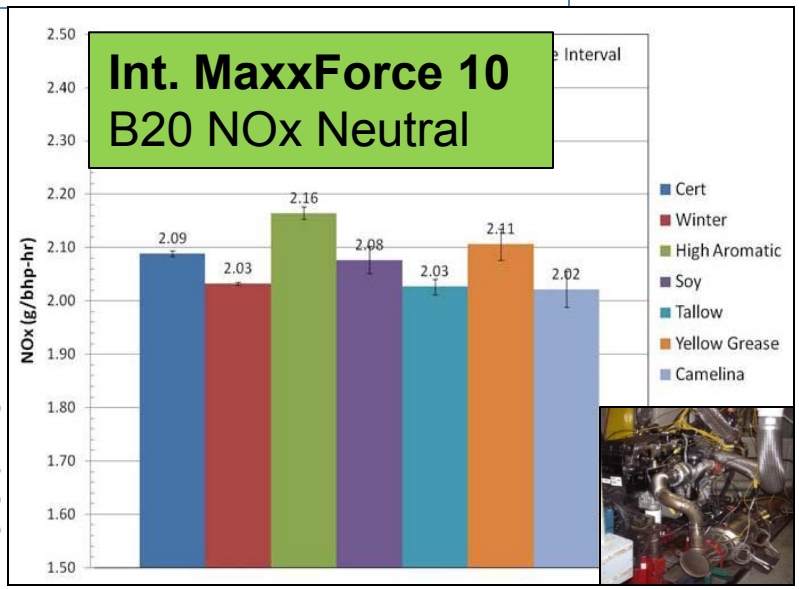
Technical Accomplishments

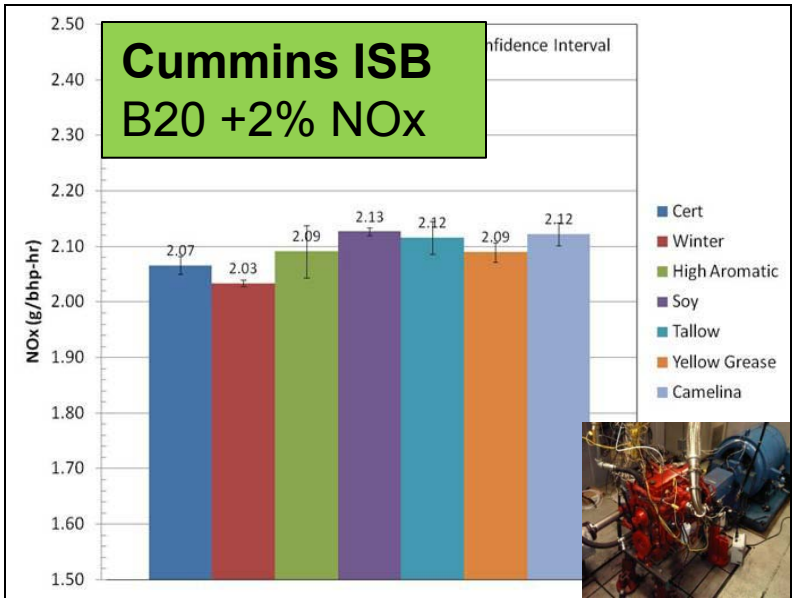
Biodiesel Emission in DPF Equipped Engines

- Tested two MY08 engines (DPF equipped)
  - Some of the first data on biodiesel in DPF engines
- 3 diesel & 4 biodiesel fuels
- International engine was NOx neutral
- Cummins engine ~2% increase in NOx
- DPF regen event ~200% increase in NOx and ~14% increase in fuel consumption
- Does biodiesel reduce regen frequency?



HDT Results

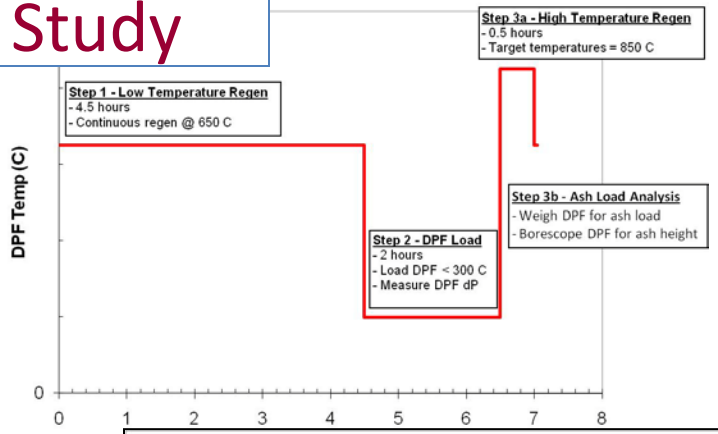


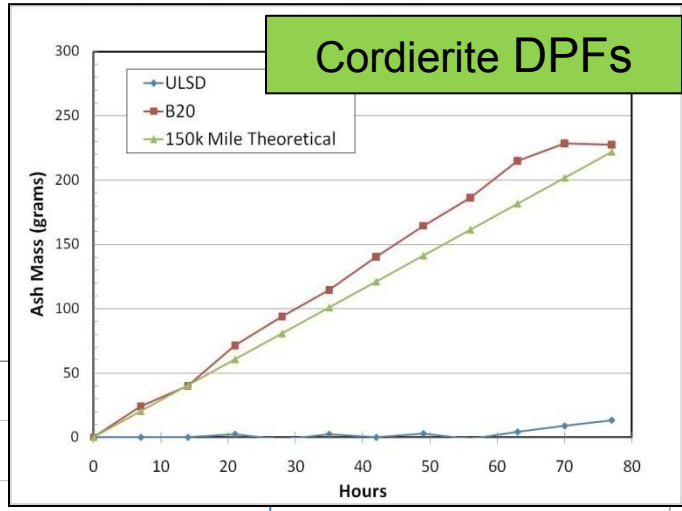


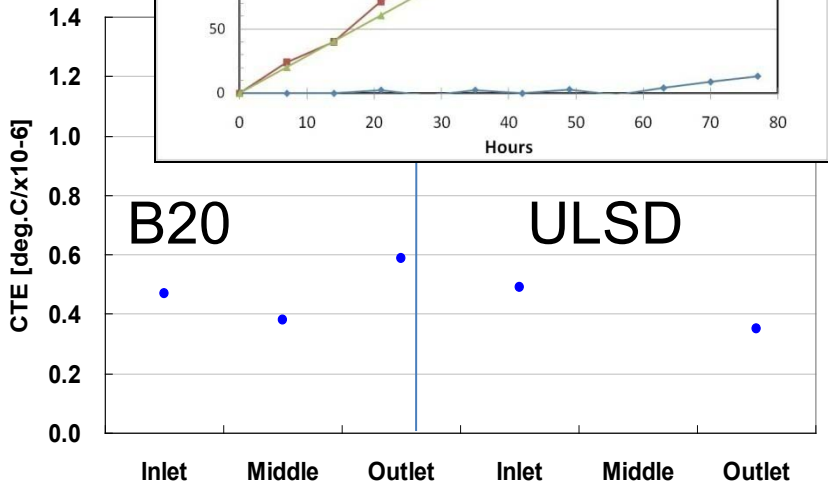
Technical Accomplishments

DPF Ash Loading Study

- Match ash accumulation to 150k mile ash clean interval through accelerated test: 30x alkali levels for 77 hours
  - Doping fuel with Na, K, and Ca
- Match time of exposure to high regen temperatures for 150k miles.
- Completed ash loading on 3 different DPFs
  - Cordierite, Silicon Carbide, Aluminum Titanate
- No impact on pressure drop or PM
- Analysis by MECA partner reveals no change in cordierite thermo-mechanical properties
  - Analysis for other substrates pending
- Study advised by EMA, OEMs, NBB, and MECA
- Currently conducting test to simulated 435k mi ash levels



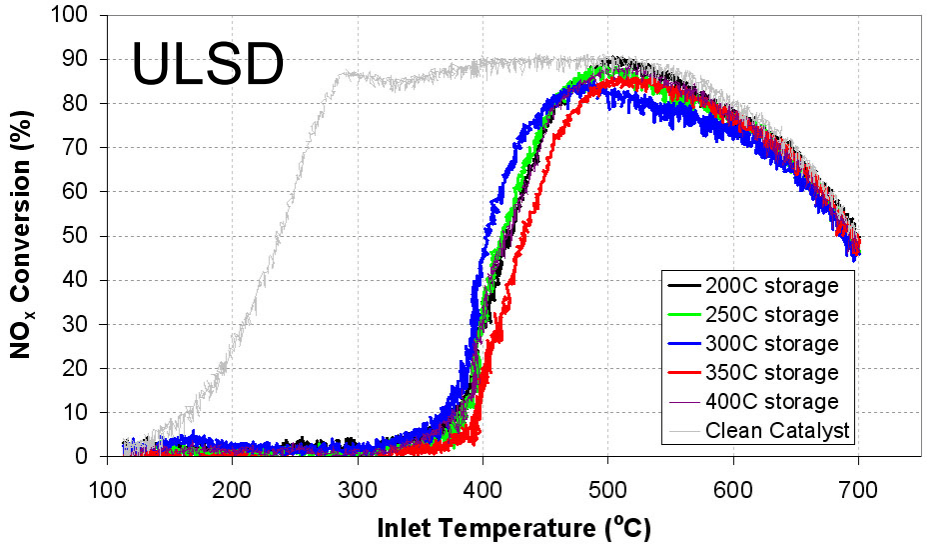


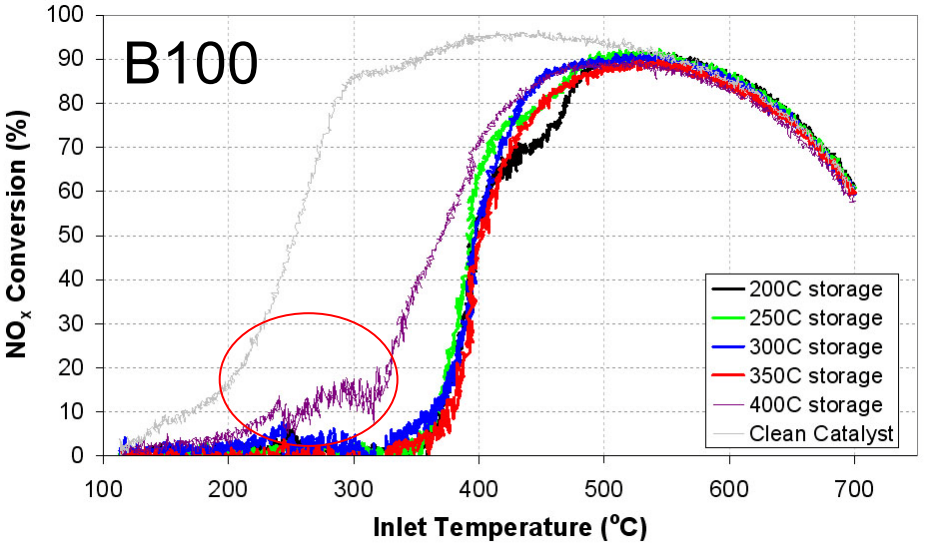


Technical Accomplishments

Biodiesel Effect on Fe-Zeolite SCR HC Storage

- Lab reactor testing with cores from commercial catalyst
- Catalyst fully deactivated with unburned fuel (ULSD or B100)
- Then heated under exhaust gas with urea to observe when NOx activity is recovered
- For B100, we see significant NOx conversion at low temperatures
  - Speculate that B100 saturating the catalyst reacts with NOx
- Follow up with Cu-zeolite in FY10
- Experiments courtesy of Ford in collaboration with NREL

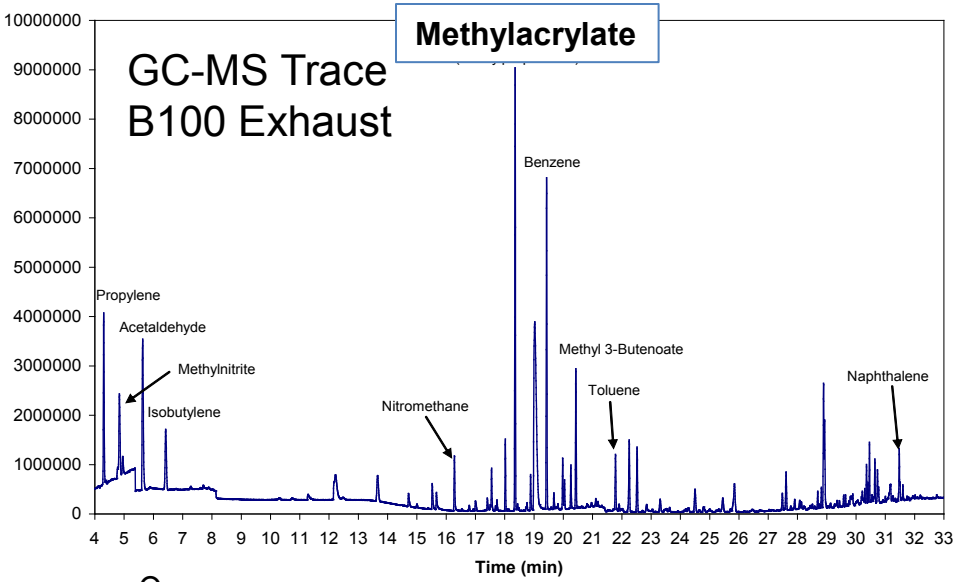


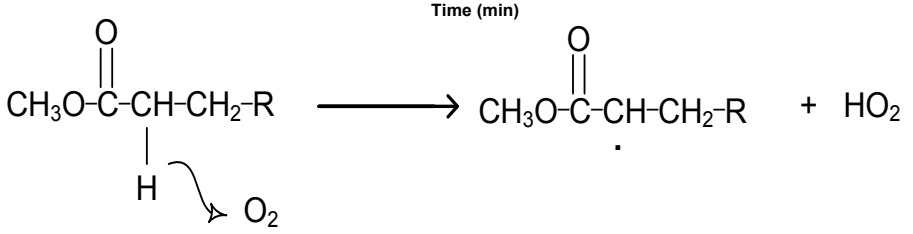


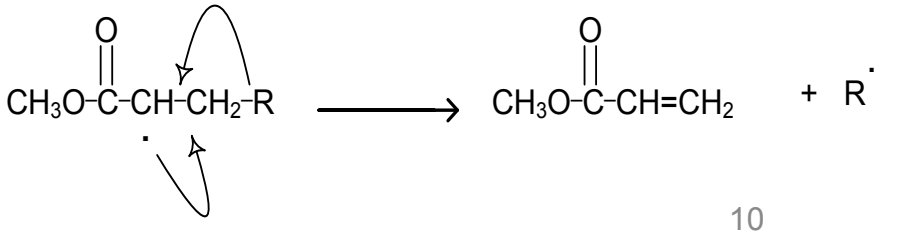
Technical Accomplishments

Biodiesel Exhaust Hydrocarbon Emission Speciation

- Substantial reduction both engine out in total PAH, NPAH, and carbonyls
- DPF effectively reduces PAH, NPAH and carbonyl
  - 1-nitropyrene conversion in DPF much less than anticipated
  - Formaldehyde increased for ULSD and B20
- Methylacrylate (methylpropenoate) observed in exhaust
  - Unique marker for presence of methyl esters in fuel
  - Observed by LLNL as significant intermediate in kinetic models of biodiesel surrogates under high temperature combustion conditions.
  - Collaborating with LLNL to identify the temperature and equivalence ratio zones in that favor production of methylacrylate.







Technical Accomplishments

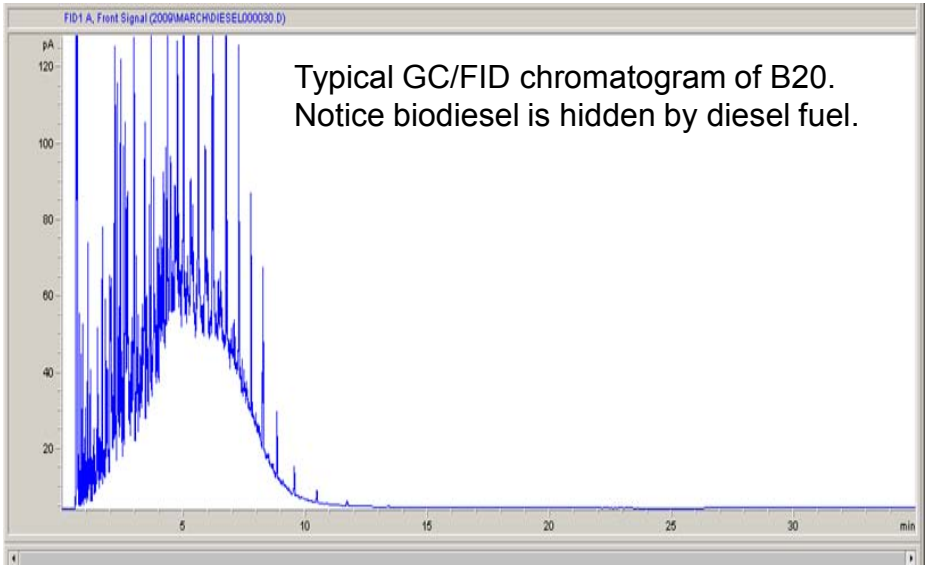
Multidimensional GC Method for Fuels Analysis

Accomplishment

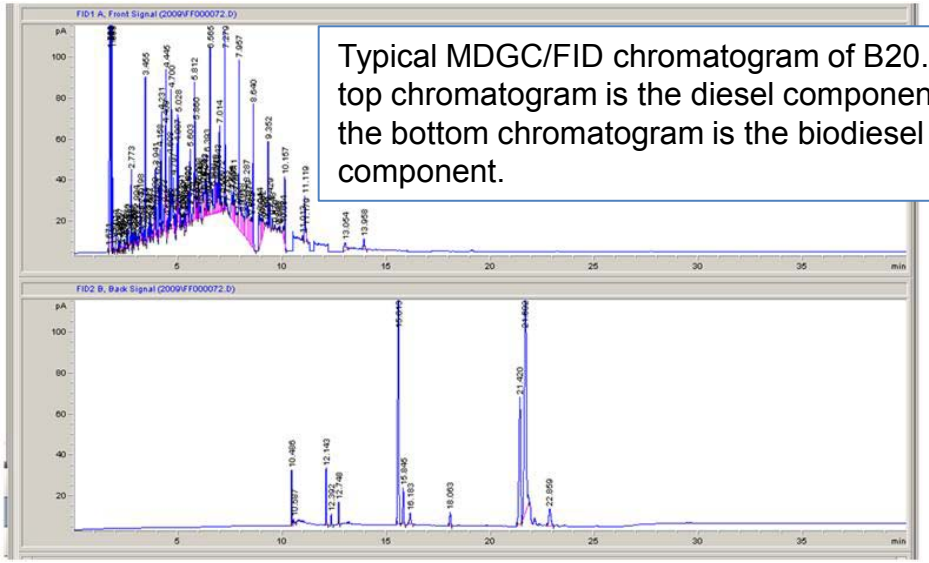
- Developed novel analytical method for measuring biodiesel composition *after* it has been blended into diesel

Significance

- Addresses industry and research need to assess biodiesel source and quality after blending
- Allows fuel users to have B100 quality checked after blending should problems arise
- May prove critical in proving source of biodiesel for RFS compliance



Typical GC/FID chromatogram of B20. Notice biodiesel is hidden by diesel fuel.

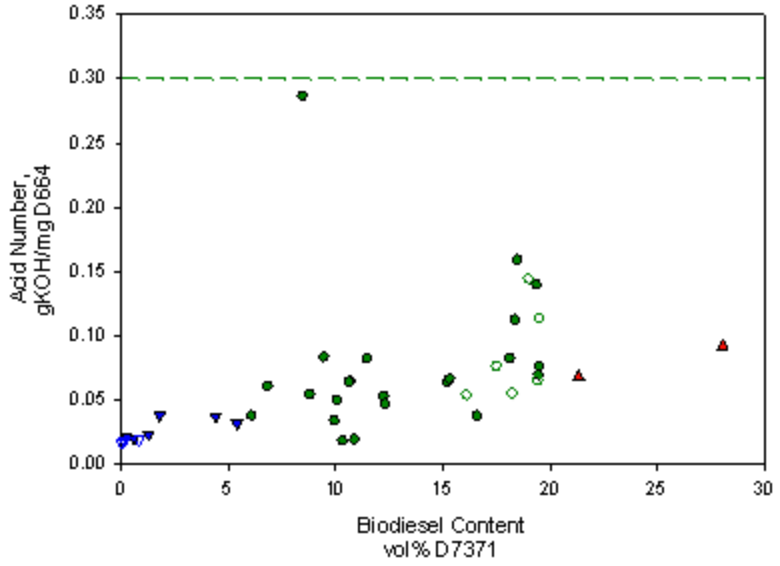


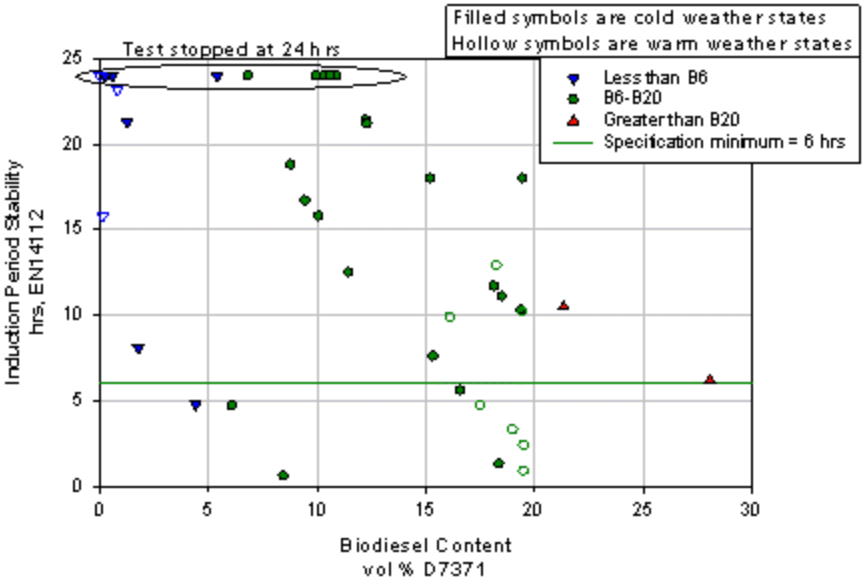
Typical MDGC/FID chromatogram of B20. The top chromatogram is the diesel component and the bottom chromatogram is the biodiesel component.

Technical Accomplishments

2009/2010 Winter Biodiesel Blend Survey - Preliminary

- 40 samples collected across US
  - Compared to D7467 specifications
  - 75% from states with -12°C 10th percentile minimum temperature
- 70% of samples were B6-B20
  - Same for cold or warm weather states
- 2D GC shows primarily soy-derived as expected for winter time
- One sample failing flashpoint
- IC shows no biodiesel failing free and total glycerin
- 20% of samples had less than 6 hr Rancimat induction time





Technical Accomplishments

Low-Temperature Operability Validation for Biodiesel Blends Phase 2

- Follow up study examining additional B100 samples
  - Intermediate levels of cold soak filterability
  - Intended to test idea that ASTM requirements could be relaxed
  - Vehicle testing of B5 and B20 blends
- Identical methodology and base diesel fuels as Phase 1 study (CRC Report No. 650: http://crcao.com/reports/recentstudies2008/DP-2a-07/CRC%20650.pdf)

Conclusions:

- Confirms results of Phase 1 study that B100 with high cold soak filterability times can clog fuel filters above cloud point
- Cold soak limits in ASTM D6751 specification confirmed:
  - 360 second maximum for all B100
  - 200 second maximum if final fuel cloud point at or below -12°C
- Report to be published in FY10

Technical Accomplishments

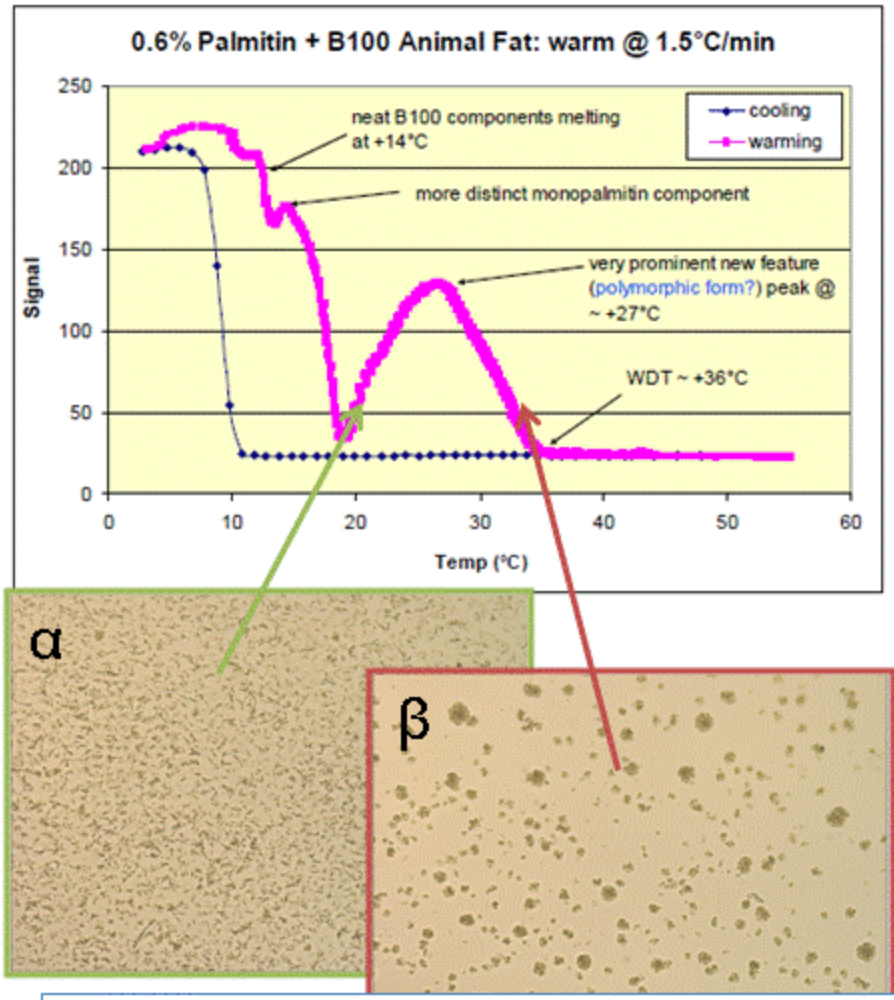
Cause of Biodiesel Low-Temperature Problem Identified

Accomplishment

- Biodiesel can show unusual cold weather behavior:
  - Filter clogging above cloud point
  - Fuel/vehicle must be warmed to well above cloud point to alleviate problem
- Caused by crystallized saturated monoglycerides undergoing a phase transition
  - α-phase forms from solution on cooling
  - Some α is converted to β-phase on standing or heating, seeding the formation of more β
  - Final melting point 15° to 20°C higher than expected for B100

Significance

- May solve long-standing and poorly understood problem
- Potential basis for a performance specification (final melting point)



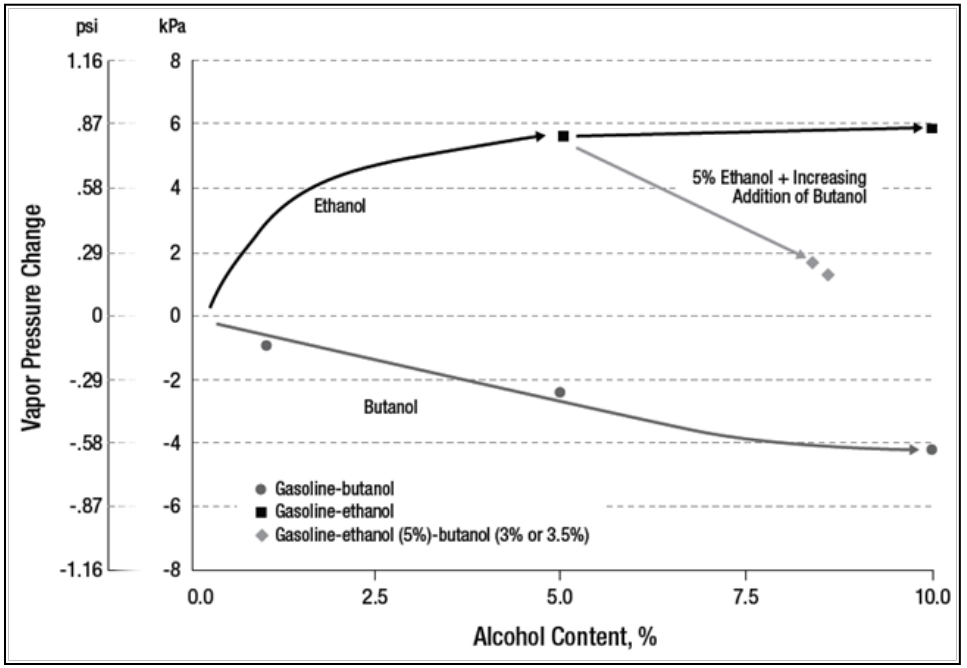
Data for B100 shown, effect is even larger for blends with hydrocarbon

Technical Accomplishments

Use of Higher Alcohols as Gasoline Blending Components

Review of all published data

- Physical properties and performance of butanol and other alcohols
  - Neat and blended with gasoline
  - Single as well as blended alcohols
- Study finds potential advantages:
  - Vapor pressure impact
  - Water tolerance
- But also large data gaps:
  - Physical and performance property data in a range of gasolines and BOBs
  - Essentially no test data in modern vehicles
    - Evaporative/permeation emission effects
    - Aldehyde emissions
- FY10 project is filling property datagaps
  - Pure alcohol properties
  - Properties in a range of gasolines
- Future year emission testing planned



Technical Accomplishments

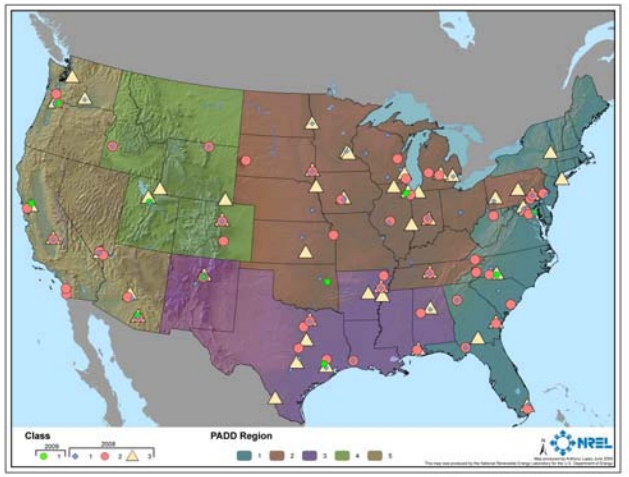
NREL/CRC Report on FFV Fuel (E85) Quality Published

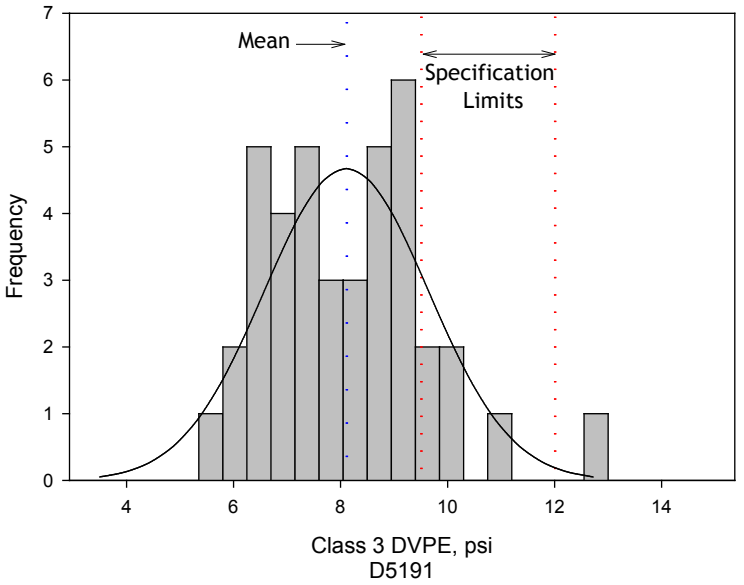
Accomplishment

- NREL/CRC published report on nationwide FFV fuel quality survey (Project E-85 at www.crcao.com)

Significance

- The quality of E85 has not been surveyed nationwide to assess compliance with specification (ASTM D5798-09).
- Results show most samples had low volatility and excess ethanol content.
  - Failure to meet volatility requirement associated with difficulty in cold starting and poor driveability
  - Low volatility has recently been cited by Marathon as key reason to cease E85 sales
  - Difficult to blend adequately volatile FFV fuel using conventional gasoline, which has low vapor pressure
- NREL/CRC will embark on second E85 survey in FY10.

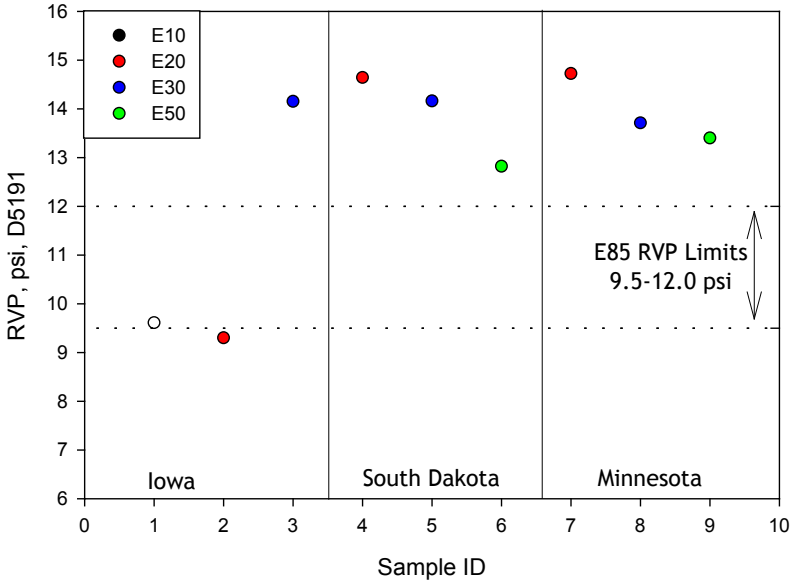


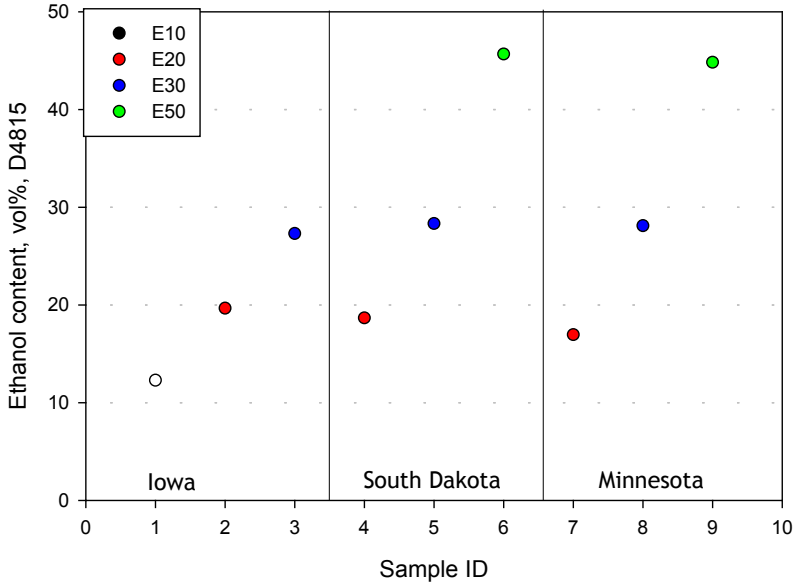


Technical Accomplishments

Pilot Blender Pump Survey

- ***Ethanol Content***
- Samples show expected ethanol values, indicating good mixing practices
- All other oxygenates were below detection limits





Vapor Pressure

- Off-specification for E85 limits (Class 3)
- All samples would meet gasoline specification for volatility (Class E, 15 psi max)

New survey in collaboration with CRC in FY10

Future Work

- Fuel Quality Focus Area:
  - Continued surveys of biofuel quality (B100 survey, E85 and blender pump surveys)
  - Biodiesel stability study focused on possible need for additional stability parameter
  - Determine how new understanding of impurity effects on biodiesel low-temperature performance can be used to improve ASTM spec
- Engine and Emission Control Focus Area:
  - Biodiesel ash effects on DPF and SCR durability
  - Biodiesel impact on DPF performance: regen frequency, regen emissions, …
  - Lube oil performance impacts, especially in systems with late in-cylinder injection for emission control system regeneration
- Next Generation Biofuels
  - Initiating studies with other diesel range oxygenates as well as hydrocarbon renewable diesel from two different processes
  - Long-chain alcohol performance in gasoline
  - Fuel performance property effects and engine emissions
- Air Quality Impacts Focus Area:
  - Have implemented systems for PM number emission studies and will begin to apply these to testing of various biofuels

Summary

- Fuels Technologies biofuels effort listens to industry stakeholders and supplies unbiased data to address concerns relevant to displacing more petroleum
- Important accomplishments in FY09/FY10 include:
  - Publication of initial biodiesel lube oil study with ongoing followup
  - Emission testing of biodiesel in 2008 MY production engines
  - Significant results from biodiesel DPF ash loading study
  - Observation of unusual low-temperature SCR conversion for biodiesel
  - Detailed hydrocarbon, PAH, and NPAH speciation for biodiesel
  - Wintertime biodiesel blend quality survey
  - Development of multi-dimensional GC method for biodiesel composition in blends
  - Identification of fundamental cause of biodiesel low-temperature operability issues
  - Review of performance of higher alcohols in gasoline
  - E85 and blender pump fuel quality surveys
  - Completion of Phase 2 of CRC biodiesel low-temperature operability study
- Ongoing and planned projects expand our work into new biofuels and PM number emission measurement