National Renewable Energy Laboratory
Innovation for Our Energy Future

Quality, Performance, and Emission Impacts of Biodiesel Blends

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Vehicle Technologies Program Merit Review
Fuels Technologies
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Overview

Timeline

Start date: FY05
End date: FY12
Percent complete: 60%

Barriers

FCVT 2006-2011 MYPP
- Infrastructure compatibility
- Inadequate data for fuel property effects on combustion and engine optimization
- Inadequate data for fuel effects on emissions and emission control system impacts.
- Long-term impact of fuel and lubricants on engines and emission control systems

Budget

- Total project funding
  - $9.5 M FY05-FY09 DOE
  - $4.8 M FY06-FY09 NBB
    - $3.4 M funds-in CRADA
    - $1.4 M cost share
- FY08: $1.8 M
- FY09: $1 M under CR

Partners

- National Biodiesel Board and NBB member companies
- Cummins
- Caterpillar
- Manufacturers of Emission Controls Association
- Engine Manufacturers Association
- Coordinating Research Council
- Members of ASTM Biodiesel Task Force
- Colorado School of Mines
- Southwest Research Institute®

Objectives

Address and resolve technical issues that are preventing expanded markets for biodiesel blends

1. Biodiesel quality:
   - Need for ASTM standards to help ensure quality in the market place
   - Need for new and improved test methods for B100 and blends
   - Some poorly understood factors affecting low-temperature operability
2. Poor understanding of how biodiesel impacts emission control devices:
   - Both short term performance and long-term durability of DPF, SCR, and LNT 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:
   - Early studies showed biodiesel blends increasing NO_x emissions – leading state regulatory agencies to limit biodiesel use
   - Limited data on toxic compound emission effects

Background

- Multiple, credible life-cycle analyses show that biodiesel displaces imported petroleum
- There is an adequate resource to displace 5% of petroleum diesel, at a minimum
  - R&D to increase oil yield from existing crops, develop new crops, and to develop non-crop feedstock sources (algae, trap grease,…) may dramatically increase this resource
- Installed production capacity for biodiesel already exceeds 5% of the on-highway diesel market
- Biodiesel also reduces greenhouse gas emissions relative to petroleum – even when worst case scenario indirect land-use effects are included (in some analyses)

Milestones

Task 1 FY08 Milestone:

- Revision and update of Biodiesel Handling and Use Guide, postponed from FY07. (September 2008)
  - Biodiesel Handling and Use Guide, 4th Edition. NREL/TP-540-43672, Revised January 2009
  - 3rd edition was downloaded 32,000 times in 2008, 4th edition has been downloaded 2800 times as of March 2009
  - http://www.nrel.gov/vehiclesandfuels/npbf/pdfs/43672.pdf

Task 2 FY08 Milestone:

- Complete a detailed study of the performance and compatibility of biodiesel with urea SCR NOx emission control system. (September 2008)
  - Williams, A., Pedersen, D., Ireland, J., McCormick, R.L., Fang, H.L. "Effect of Biodiesel Blends on Urea Selective Catalytic Reduction Catalyst Performance with a Medium-Duty Engine" Society of Automotive Engineers Technical Paper No. 2008-01-2484 (2008)

Approach

Applied development work focused on fuel chemistry and empirical studies of full scale systems

- Performance testing and chemical analysis of commercial fuels
  - Development of new and improved fuel testing methods
- Engine and vehicle dynamometer testing
  - Emissions, engine and emissions durability
  - Low-temperature operability
- Quantitative, controlled in-use fleet testing
- Meta-analysis of large datasets from published literature
- Industry partners or broad industry participation in work group or steering committee

Technical Accomplishments

ASTM Approves Specifications for Biodiesel Blends

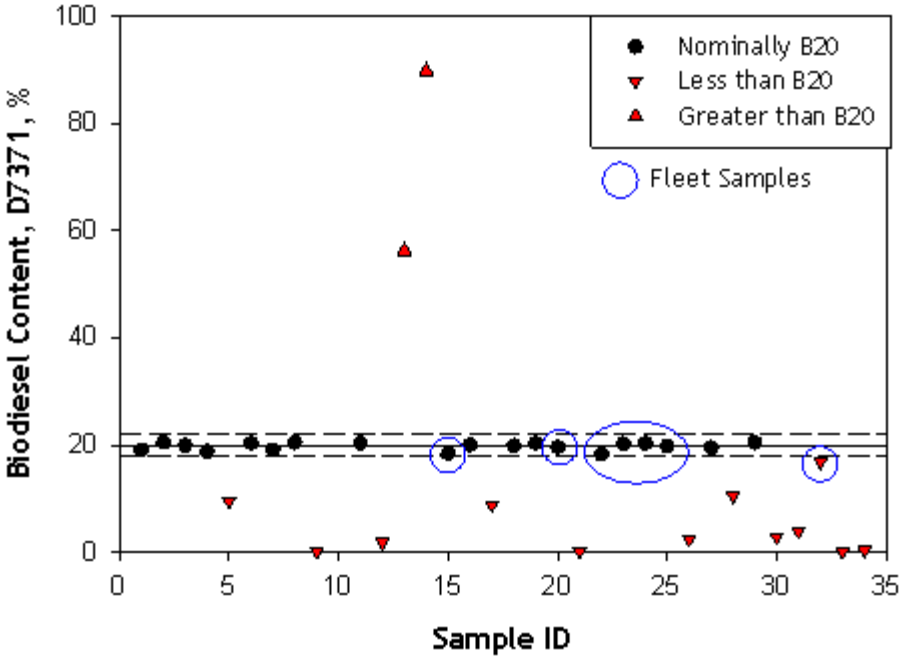
- Allowance of up to 5% biodiesel in D975 diesel fuel and D396 heating oil
- New specification for B6 to B20 blends for diesel engines: D7467
- Data from this program was instrumental in passing these after 10 years of discussion:
  - B100 and B20 quality surveys
  - Oxidation stability study
  - Low-temperature operability study
  - Test method development and improvements

UL Approves Use of B5 In All Equipment Listed for Diesel Fuel

Technical Accomplishments

Completed Nationwide B20 Quality Survey

- 32 samples collected in 25 states from public pumps and fleets
- Samples acquired before D7467 was in effect
- Generally good compliance with D7467 except for oxidation stability (36% of samples failing)

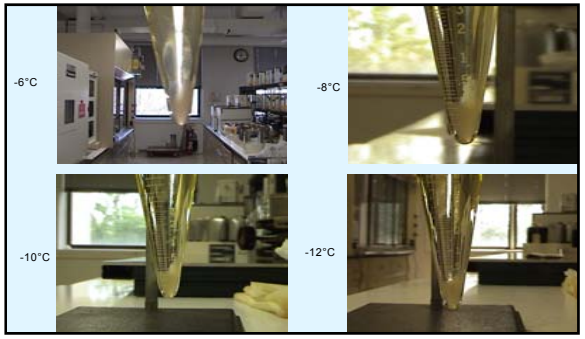


- Average dissolved water content of 130 ppm, water interfacial tension of about 12 mN/m
- All pumps were labeled for B20 but 40% of samples were B11, B5, or B2.

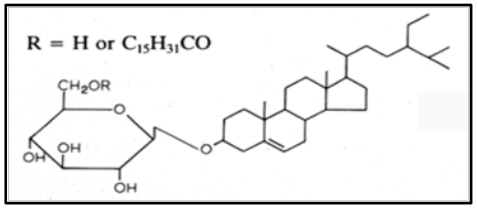
Technical Accomplishments

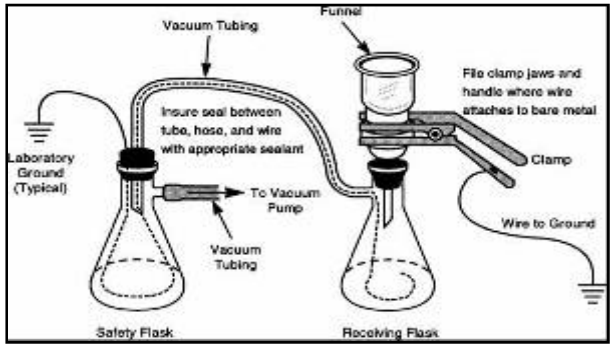
Validated Low-Temperature Operability and Minor Species Tests for Biodiesel Blends

- Collaboration with CRC, EMA, and NBB – in support of ASTM and setting of blend specifications
- Precipitates in biodiesel blends have been observed above the cloud point
  - Requires long cooling time (8-16 hr)
  - Can occur for on-specification fuel
- Exact chemical character poorly defined
- Low Temperature Operability Study
  - CRC Study DP-2a-07
  - Validate low-temperature tests for biodiesel blends (cloud point, CFPP, CSF)
  - Validate cold soak filtration test to eliminate minor components
  - Actual testing of vehicles (HD trucks) at low temperature to determine operability limits



Courtesy of John Chandler





Technical Accomplishments

Low-Temperature Operability Validation for Biodiesel Blends -II

- Tests performed at Imperial Oil, Sarnia, ON: 4 B5 and 4 B20
- Class 8 trucks with roughly 25% to 30% market share for each engine manufacturer (Caterpillar, Cummins, DDC)
- Vehicle inertia of 80,000 lb

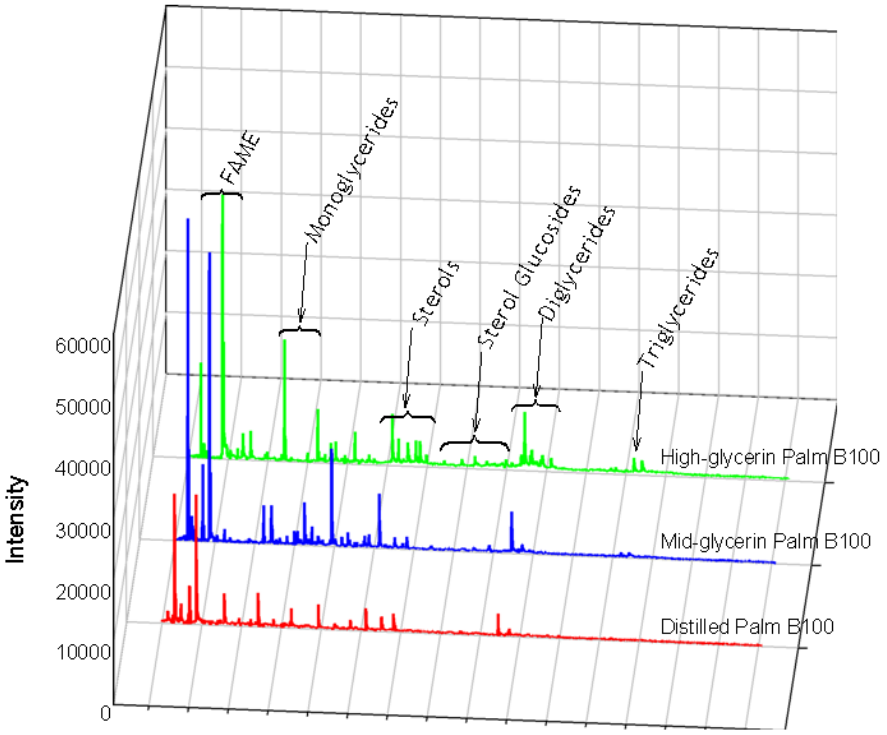
Conclusions:

- Cloud point is a good estimate of minimum operability temperature for blends up to B20 from B100 with CSFT<200 sec
- For the single B100 tested with CSFT >720 sec:
  - For B5 blend operability limit was at or below cloud point
  - For B20 blend failure to operate at and above cloud point was observed for one vehicle design
- Final report (CRC Report No. 650): *http://crcao.com/reports/recentstudies2008/DP-2a-07/CRC%20650.pdf*

Technical Accomplishments

Working to identify minor species causing cold weather issues

- No fundamental understanding of the cause of precipitates above the cloud point in biodiesel blends
- No fundamental understanding of what causes B100 to have high cold soak filtration time
- Goal is to be able to quantify all minor species that might precipitate or form emulsions above cloud point
- Laboratory cold soaking and centrifugation produces complex mixtures
- Developing advanced analytical tools to use in concert with cold soak tests and other sample treatments (MS/MS, MALDI-TOF, others)

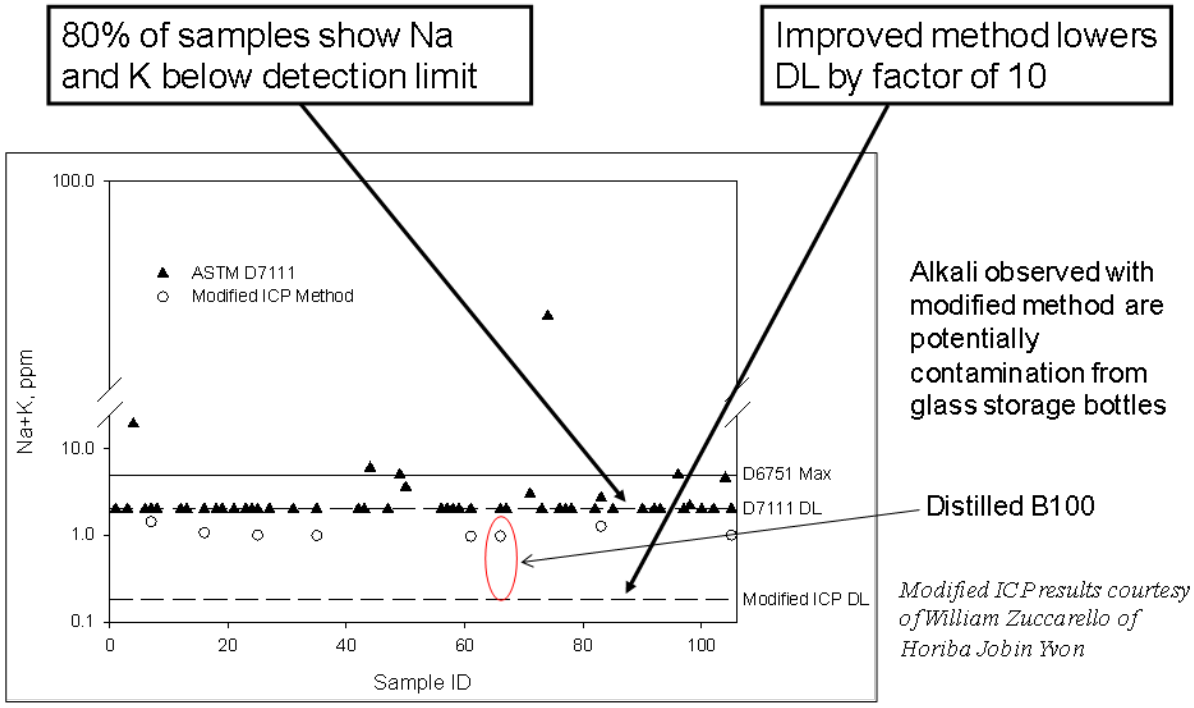


- Matrix-Assisted Laser Desorption Ionization-Time of Flight mass spectrometry
- Produces primarily molecular ions and enhances separation of minor species

Technical Accomplishments

Lower Detection Limits for Metals and Phosphorus in B100

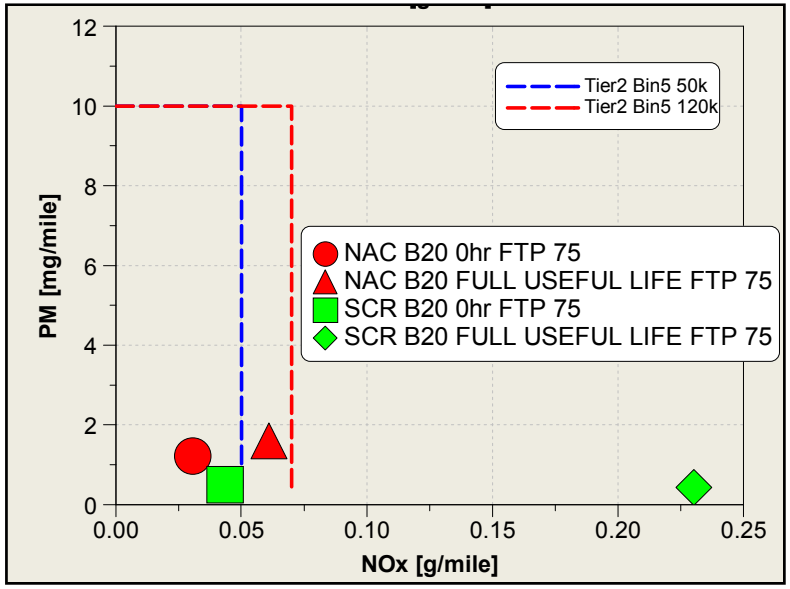
- Metals in B100 derive from the manufacturing process (Na, K, Ca, and Mg), phosphorus can be present in vegetable oil feedstocks.
- They are a major concern for DPF durability and meeting the EPA required useful life requirements
- May also be of concern for SCR systems
- Metals at detection limit of current methods are high enough to be of concern
- Modified ICP-AES instrument leads to much lower detection limits than available in current ASTM methods
- New method DL:
  - Na&K: 100 ppb
  - Ca&Mg: 10 ppb
  - P: 500 ppb



Technical Accomplishments

Full Useful Life Aging of LD NAC/DPF and SCR/DPF Systems Completed

- Parameters:
  - 113 kW, 4 cylinder, common rail, late in-cylinder injection
  - B20
  - Vehicle emission tests, ECS mounted on engine dyno for 120,000 mi simulated aging
- NAC system achieved Tier 2 Bin 5 emission levels at full useful life (120K)
  - 20% degradation of NO_x conversion efficiency at full useful life
- SCR System did not achieved Tier 2 Bin 5 emission levels at full useful life (120K)
  - 30% degradation of NO_x conversion efficiency at full useful life
  - SCR manufacturer found that performance degradation caused by thermal runaway, not a fuel issue
- Engine measurement show no degradation of engine parts – after 2x useful life aging
- Lubricant testing shows biodiesel content up to 10% for NAC system – analysis ongoing



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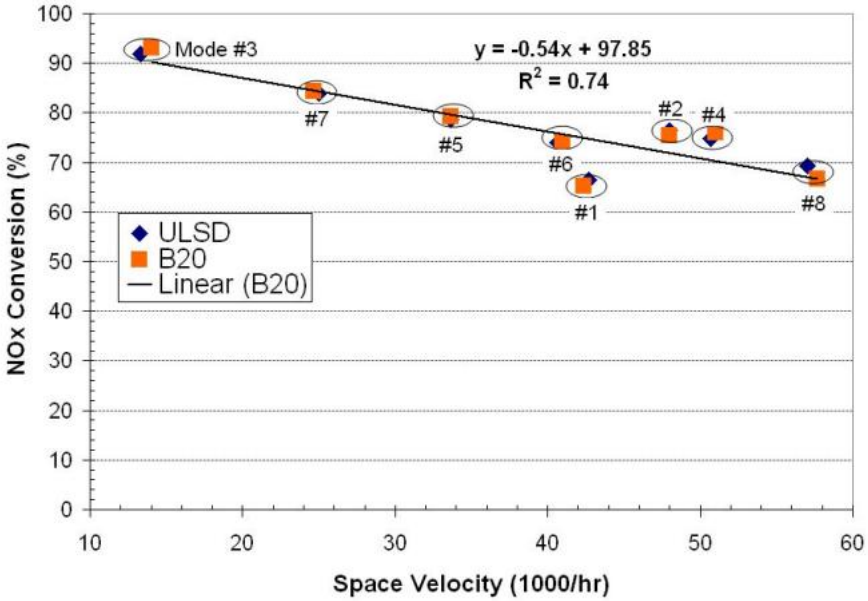
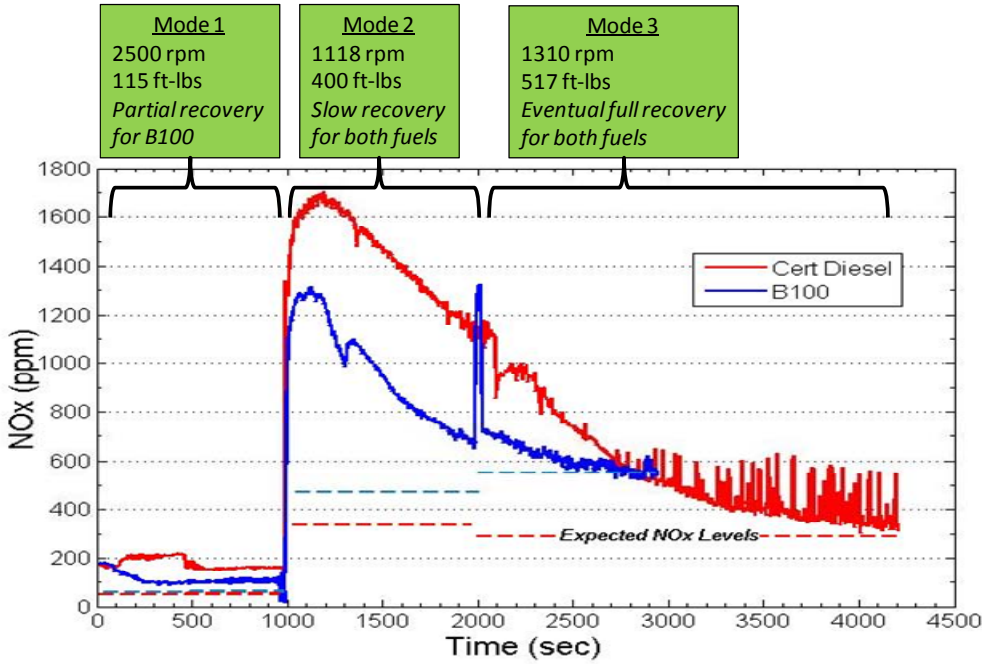
Technical Accomplishments

Short-Term Testing of HD Urea SCR System Completed

- Parameters:
  - 2002 Cummins ISB retrofitted with DOC/DPF – SCR (Fe-Zeolite)/NH_3 Slip
  - Air assisted urea injection
  - 8-mode steady-state test
  - HC inhibition after 35 hr exposure
- Short term test shows no difference in NO_x reduction performance of B20 and ULSD
- Significantly less HC inhibition for B100
  - Lower engine out HC emissions
  - Quicker recovery to steady-state NO_x conversion after increasing temperature
  - Sample collected for HC speciation – analysis ongoing
- Initiating collaboration with LD OEM to improve understanding of these effects



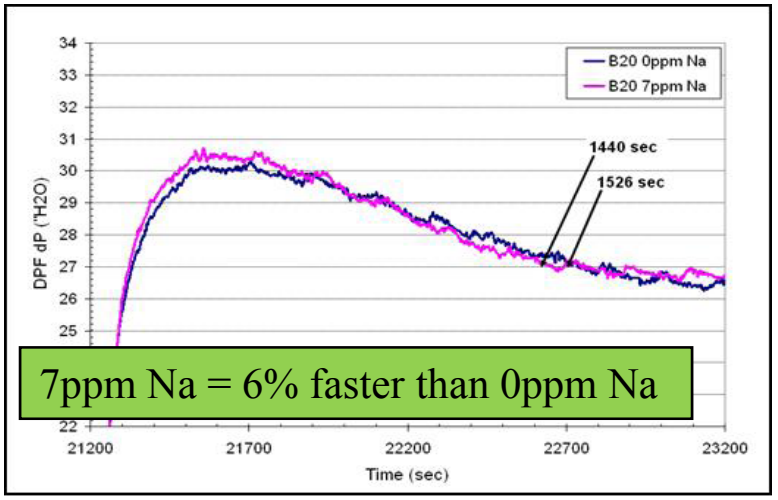


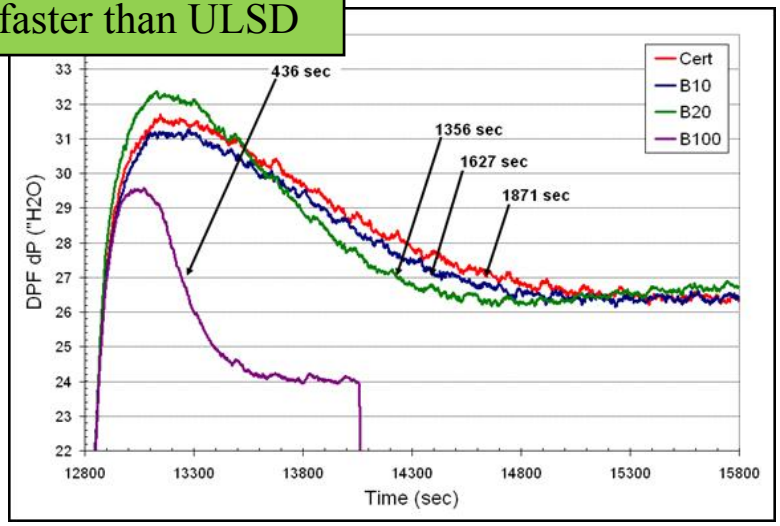
Technical Accomplishments

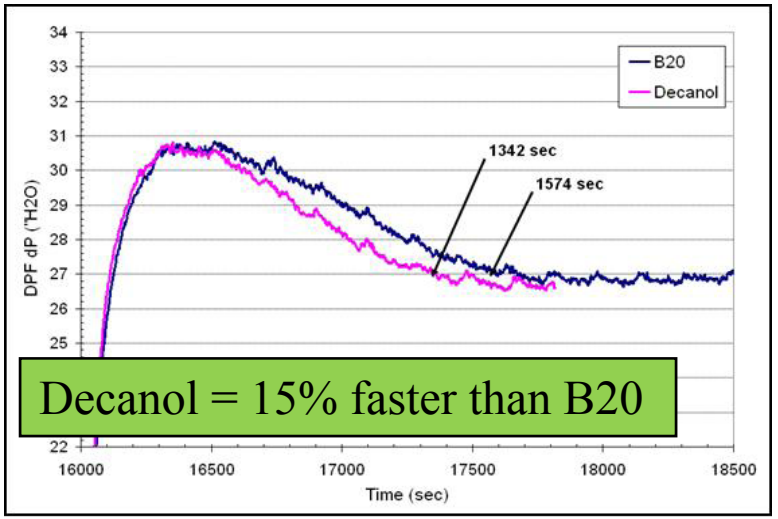
Completed Additional Study of Biodiesel Affect on PM Reactivity

- Previous studies showed that biodiesel soot is more reactive and has higher oxygen content & more amorphous soot structure
- Engine test results show clear dependence on biodiesel blend level & oxygenate structure
- Impact of Na may be within measurement error
- Collaboration with ORNL will provide detailed characterization and reactivity of soot samples

B10 = 13% faster than ULSD
B20 = 28% faster than ULSD
B100 = 77% faster than ULSD



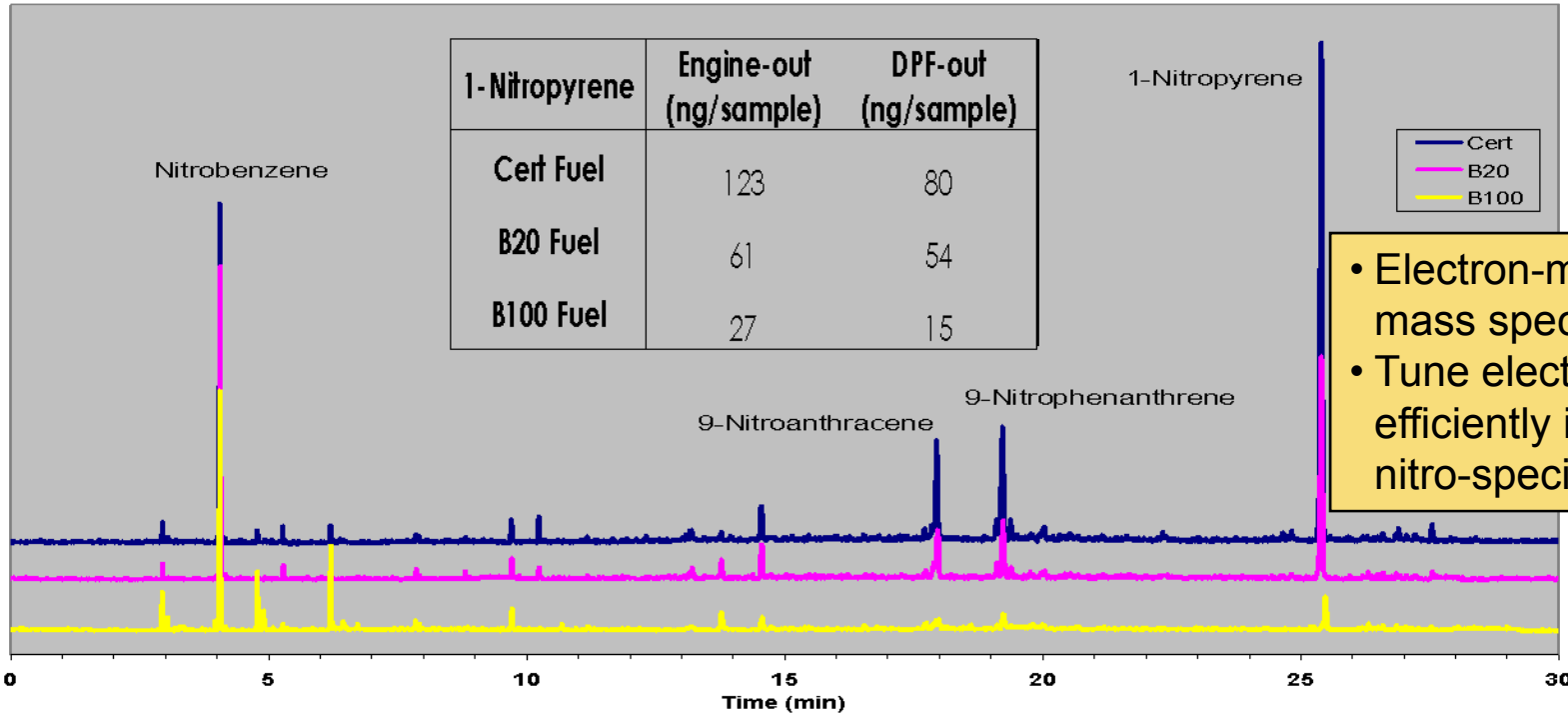




Technical Accomplishments

Emission Speciation Using GC/EM-MS Reveals Effects on NPAH

1-Nitropyrene	Engine-out (ng/sample)	DPF-out (ng/sample)
Cert Fuel	123	80
B20 Fuel	61	54
B100 Fuel	27	15



- Electron-monochromator mass spectrometry
- Tune electron energy to efficiently ionize only nitro-species

- Chart shows engine-out NPAH for SS test of 2004 diesel engine retrofitted with DOC/DPF, DCM extracts of PM from dilute exhaust
- DOC/DPF effectively oxidized most NPAH, except 1-Nitropyrene
- Biodiesel blending reduced engine-out and DPF-out NPAH
- B100 increased semi-volatile nitro-compounds emissions (not shown)
- More volatile nitro-compounds exiting DPF may not be fully accounted

Future Work

- Fuel Quality Focus Area:
  - Chemical analysis and performance testing to show conclusively what minor species cause low-temperature operability issues
  - Oxidation stability study focused on fuel injection equipment compatibility
  - Support ASTM method development and improvement as needed
    - Lower detection limits for metals, improved glyceride method, methods for minor species
- Engine and Emission Control Focus Area:
  - Biodiesel ash effects on DPF and SCR durability
  - Biodiesel emission and performance in DPF equipped engines
  - Lube oil performance impacts, especially in systems with late in-cylinder injection for emission control system regeneration
  - Long-term fleet evaluation with DPF equipped engines
    - Major new study in collaboration with NYC Sanitation Department (Mack/Volvo engines)
  - Testing of biodiesel from new and sustainable sources
- Air Quality Impacts Focus Area:
  - Additional analysis to identify semivolatile NPAH and other compounds observed in speciation study

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Future Work: DPF Durability

- Determine if there is a need to lower current ASTM standard for alkali metals in biodiesel. *Does current standard affect ash clean interval or durability of DPF?*
- Approach
  - Match total ash accumulation to 150k mile ash clean interval through accelerated test: 30x alkali levels for 110 hours
  - Match total time of exposure to high regeneration temperatures for 150k miles. *Achieve 50 hours regen time by operating at >650 C for 45 hours and >850 C for 5 hours*
- Test plan developed with input from NREL, MECA, EMA, NBB and other Industry Stakeholders
- Testing to commence in March 2009

Engine : – 2006 C9 ACERT™ loaned by Caterpillar, Tier 3 off-road, 8.8L 300hp

DPFs: – 10.5” x 12” (17L) cylinders donated through MECA
– Cordierite , SiC & AlTi substrates supplied by different mfg.
– All samples coated to agreed upon loading to ensure consistency

Fuel:
– Doped with Na-soap or Na-naphthenate (and other metals)
– 30x spec limits for B100
– B20/ULSD

Summary

- Fuels Technologies biodiesel effort listens to industry stakeholders and supplies unbiased data to address concerns relevant to displacing more petroleum with this biofuel
- Important accomplishments in FY08/FY09 include:
  - Major contributions to passage of biodiesel blend specifications at ASTM
  - Completion of nationwide B20 quality survey
  - Validation of low-temperature operability tests
  - Developing new analytical methods for minor species in biodiesel
  - Lowering detection limits for metals in biodiesel
  - Demonstrating FUL effects of B20 on LD NAC/DPF and SCR/DPF systems
  - Evaluating performance effects of B20 on HD DPF and SCR systems
  - Applying powerful new methods to speciation of compounds in exhaust
- Ongoing and planned projects will reveal HD long-term durability impacts on emission controls and lubricant