Quality, Stability, Performance, and Emission Impacts of Biodiesel Blends

Bob McCormick (PI)

with Colleen Alexander, Teresa Alleman, Robb Barnitt, Wendy Clark, John Ireland, Keith Knoll, Mike Lammert, Jon Luecke, Jami Morton, Dan Pedersen, Ami Patel, Ken Proc, Matt Ratcliff, Matt Thornton, Kevin Walkowicz, Aaron Williams, Janet Yanowitz

Vehicle Technologies Program Merit Review
Fuels Technologies
February 27, 2008
Bethesda, MY

This presentation does not contain any proprietary or confidential information

Purpose of the Work

Address, and resolve if possible, technical issues that are preventing expanded markets for biodiesel blends.

- 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

Barriers

1. Biodiesel quality:
   - Some biodiesel producers failing to meet ASTM quality specifications
   - Need for new and improved test methods for B100 and blends
2. ASTM specifications for biodiesel blends:
   - Required by engine OEMs before granting approval
   - Main technical issues have been oxidation stability and low-temperature operability
3. Poor understanding of how biodiesel impacts emission control devices:
   - Both short term performance and long-term durability of DPF, SCR, and LNT systems
4. Inadequate information on long-term engine durability impacts:
   - Not enough operating experience on biodiesel
   - Need for quantitative studies comparing petro and biodiesel over multiple years
5. Conflicting data on air quality impacts:
   - Early studies showed biodiesel blends increasing NO_x emissions – leading EPA and state regulatory agencies to limit biodiesel use
   - More recent work calls this into question

Approach

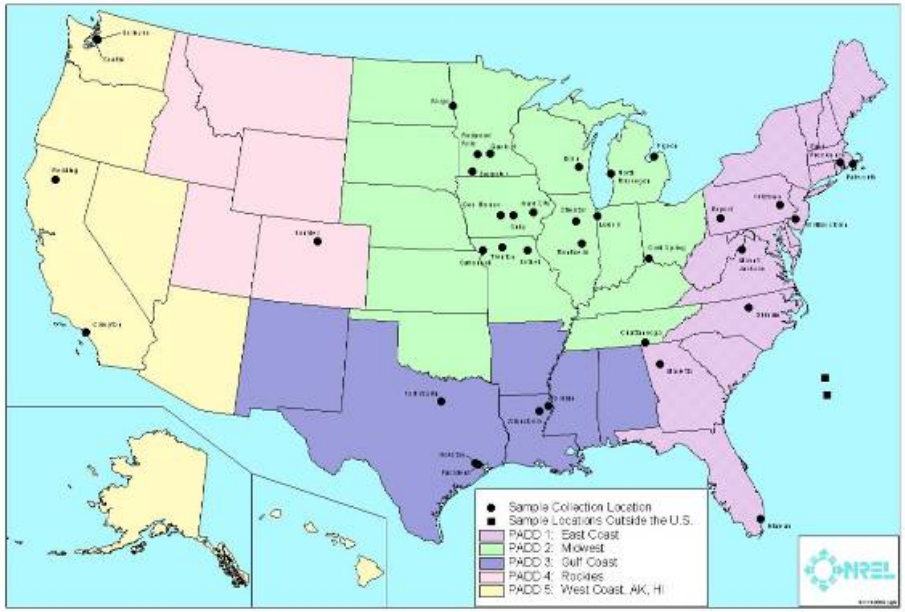
1. Biodiesel quality:
   - Perform surveys of B100 quality
   - Communicate results to industry and regulatory agencies
   - Develop improved quality test methods
2. ASTM specifications for biodiesel blends:
   - Perform study to define how B100 stability impacts blend stability, evaluate stability test methods, and set stability specification limit
   - Determine if conventional predictive tests of low-temperature operability work for biodiesel blends
   - Evaluate issue of precipitates above cloud point
   - Develop test method for determining biodiesel content of fuels
3. Poor understanding of how biodiesel impacts emission control devices:
   - Test biodiesel blend performance with DPF, LNT, and SCR systems
   - Future work: perform laboratory long-term durability tests

Performance Measures and Accomplishments: B100 Quality

- B100 quality surveys should lead to an improving quality trend for biodiesel in the U.S.
  - Quantify the problem
  - Educate the biodiesel producers

- In 2007 we completed a major B100 survey allowing us to estimate that 90% of the volume of biodiesel in the market is meeting critical specifications (results published in 2008)
  - A dramatic improvement over previous surveys in 2004 and 2006
    - >50% failure rate in 2006 survey (2007 Milestone Report)
  - Education of industry and regulatory agencies about the quality issue is being successful

2006 B100 Quality Survey



86 companies in the marketplace (250M gallons)

A subcontractor visited the site of a biodiesel blender, usually a terminal operator or jobber, to collect the B100 sample

32 B100s, 6 B99s, and 1 B50

59% of B100 samples tested fail the D6751 specification

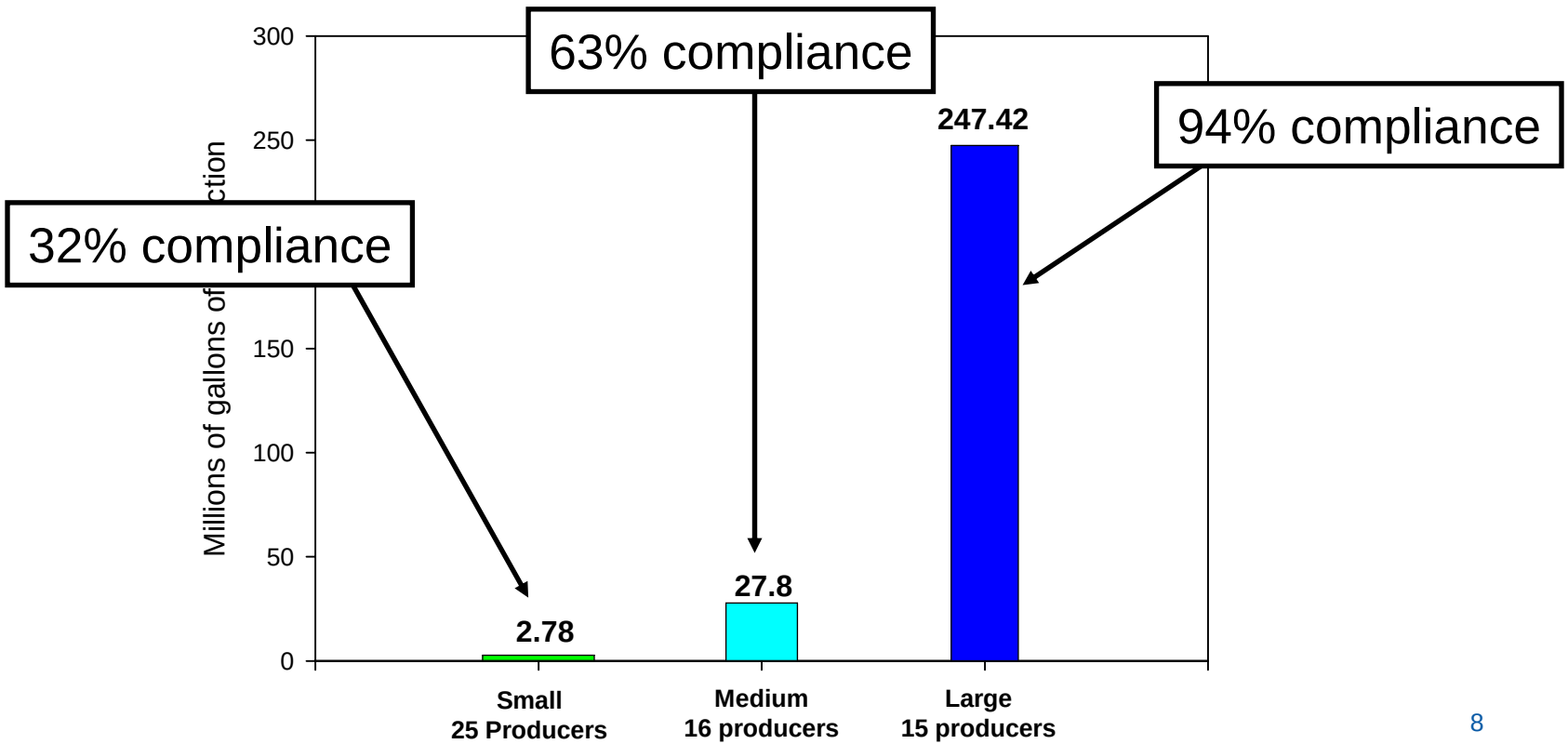
- Importantly, 30% fail total glycerin – immediate operational problems in cold weather and long term injector damage
- Other issue of concern is 20% failure rate for Na+K
  - Significant impact on emissions control systems
- Compares to 15% failure rate in 2004 survey
- Samples were collected randomly, not on production volume basis
  - ***Biodiesel, based on production volume, may have different failure rate***
  - ***Poor quality batch may have contaminated larger aggregated tanks at terminals or jobber locations***

2007 Survey Approach

- Collect B100 sample directly from producers
- Test samples for properties most likely to affect engine performance:
  - Flash point, free and total glycerin, oxidation stability, cloud point, acid value, water and sediment
  - Oxidation stability had only recently passed in D 6751 – samples were tested within 1 week of receipt
- Test samples for minor compounds that could affect new or future diesel after-treatment systems:
  - Phosphorus, Group I and II metals
- Use approximate production volume data from NBB to report results on a production volume basis

2007 B100 Quality Survey

- 56 Samples collected from biodiesel producers, representing 70% of 2007 U.S. production volume
- Tested for critical specification properties
- Results reported on a production volume basis
- ***90% of production volume estimated to meet requirements***



Performance Measures and Accomplishments: ASTM Standards

- Studies should lead to ASTM standards for B100 and blends that are adequate for OEM approval of biodiesel use
- Engine OEMs and petroleum companies at ASTM indicated that adding an oxidation stability requirement to the B100 ASTM spec was critical:
  - For their approval of biodiesel blend use
  - For passage of biodiesel blend ASTM specs
- NREL led a large empirical study of oxidation stability, under the guidance of the ASTM Biodiesel TF
  - Fundamental mechanisms of biodiesel degradation are reasonably well understood (see Fang and McCormick, SAE 2006-01-3300)
- The study results led directly to the passage of a B100 stability requirement at ASTM

Objectives of Empirical Stability Study

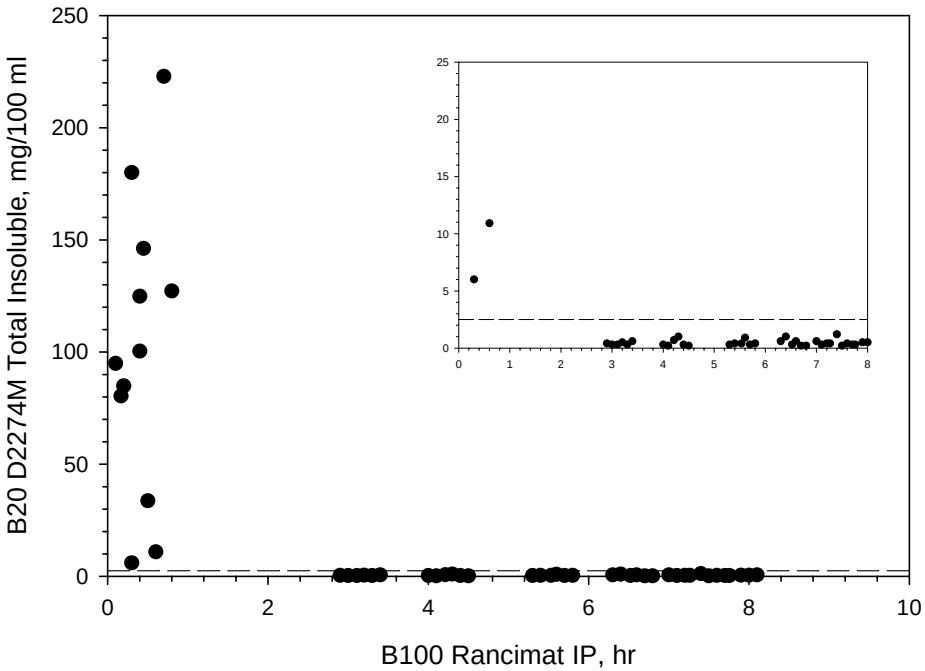
Better define the biodiesel stability “space” through testing of a range of B100 plus B5 and B20 blends using several standard stability tests

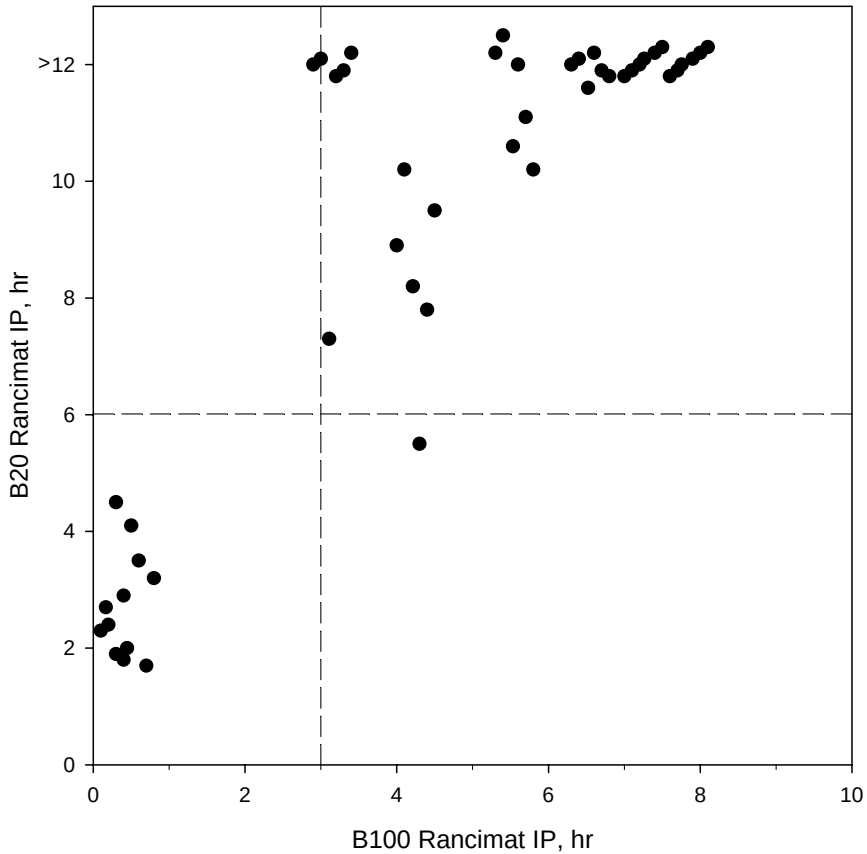
Determine if biodiesel and blend stability on standard tests is predictive of stability on tests simulating real-world situations

Recommend stability test methods and limits for B100, B20, and B5 blends

Impact of B100 Stability on B20 Stability

Note: data points artificially spread out so number of points is more evident

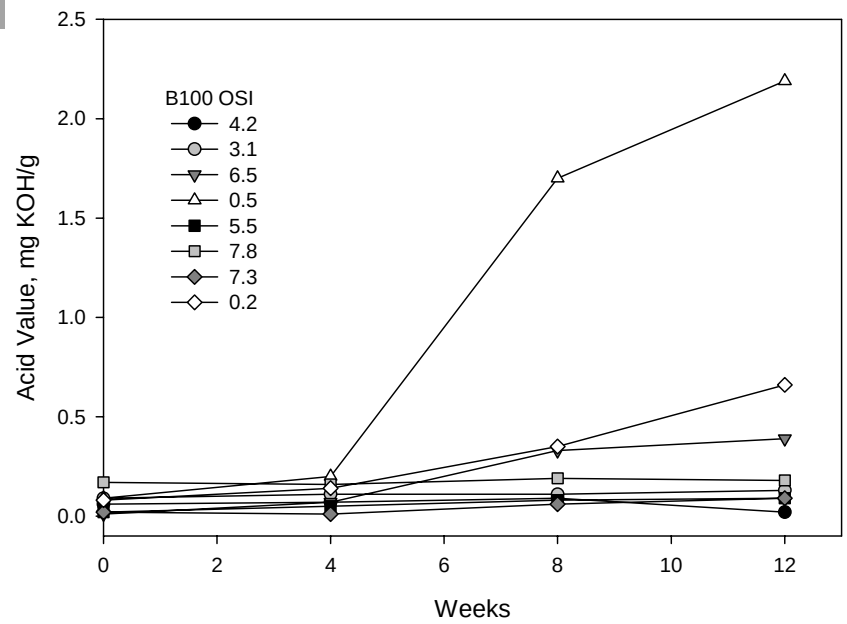


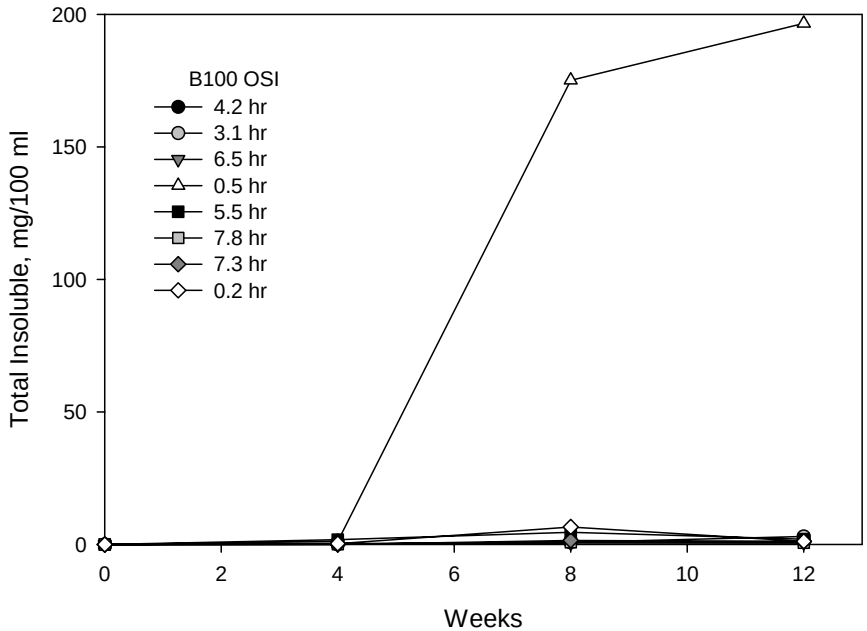


B100 stability appears to be an excellent predictor of blend stability, 3 hour Rancimat ensures low deposits and 6 hr Rancimat in the blend (with one exception out of 48 samples)

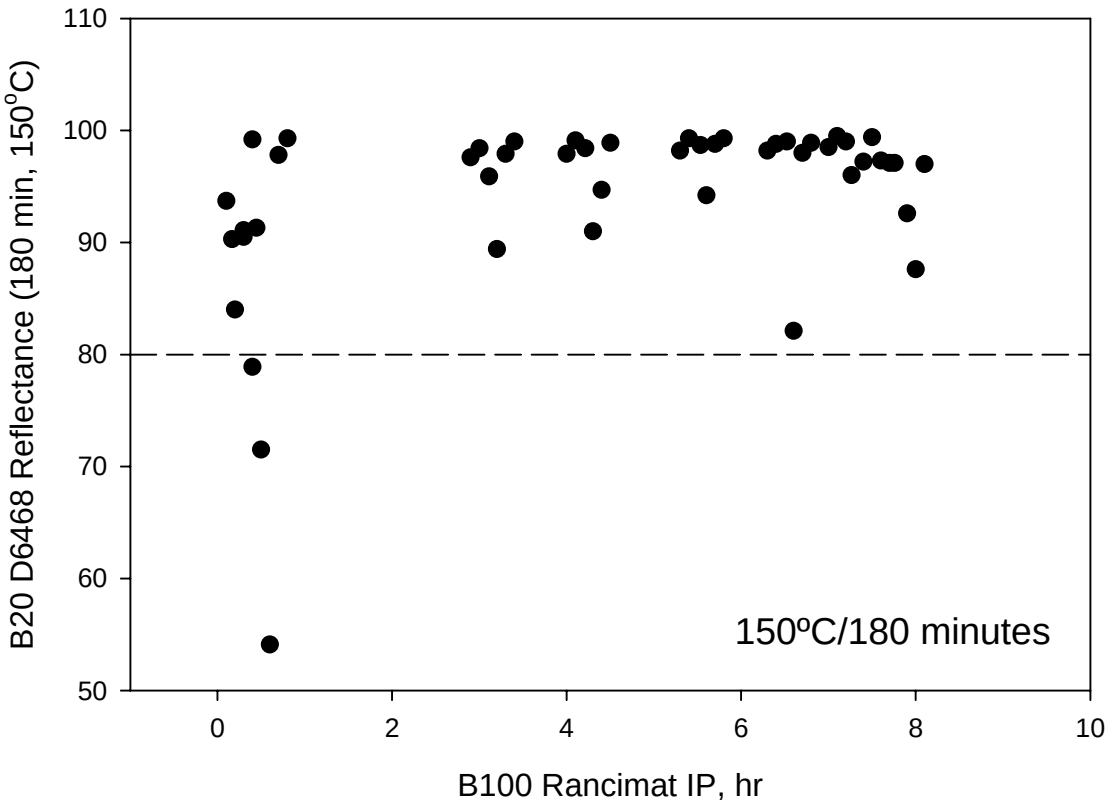
B20 Blends Long Term Storage: D4625

- 12 weeks at 43ºC, vessel open to air
- No oxidation impacts at 4 weeks
- At 8 weeks samples with <3 hr IP are degrading
- Other samples are not degrading – no increase in peroxides for stable B100
- 3 hr IP adequately protects B20 blends under these conditions





B20 High Temperature Stability



B20 blends are thermally stable if produced from oxidatively stable B100 (IP > 3 hr)

Biodiesel Stability

- NREL/NBB stability study shows that blend stability is dominated by B100 stability
- 3 hour induction time was protective of B5 blends, and B20 in most situations (additional stability requirement likely for B6 to B20)
- This work led directly to the adoption of a stability requirement for B100 by ASTM (published in January 2007)
- Publication of study report met milestone for DOE

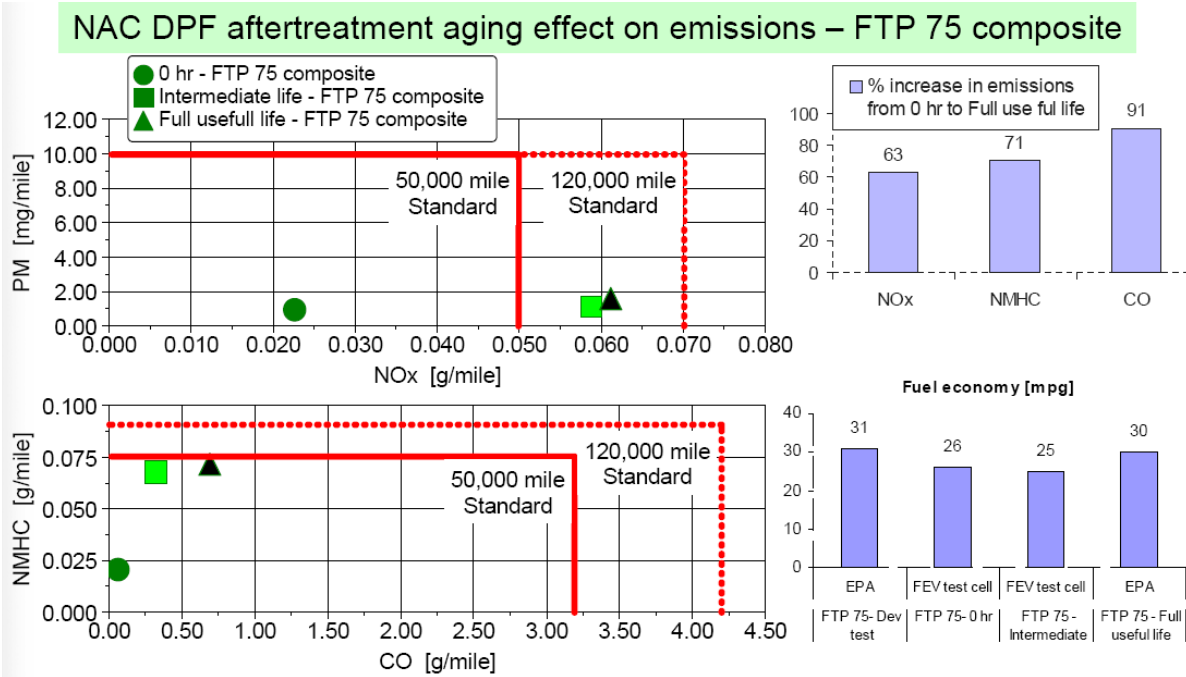
> *"Cummins is able to upgrade its previous position on the use of biodiesel fuel, which limited the use to B5 blends only, up to B20 for three key reasons. First, the American Society of Testing Materials specification ASTM D6751 now includes an important stability specification for B100 biodiesel."*
> *http://www.everytime.cummins.com/every/news/release99.jsp*

Performance Measures and Accomplishments: Emission Control System

- Completed simulated full useful life durability with LD DPF/LNT system
- Short term tests of MD and HD engines with DPF expand knowledge of biodiesel causing enhanced PM reactivity
- Installation of SCR system and initial tests with B20 completed
  - Detailed study to be completed by end of FY08 as DOE Milestone
- Recently convened steering committee to begin planning durability studies

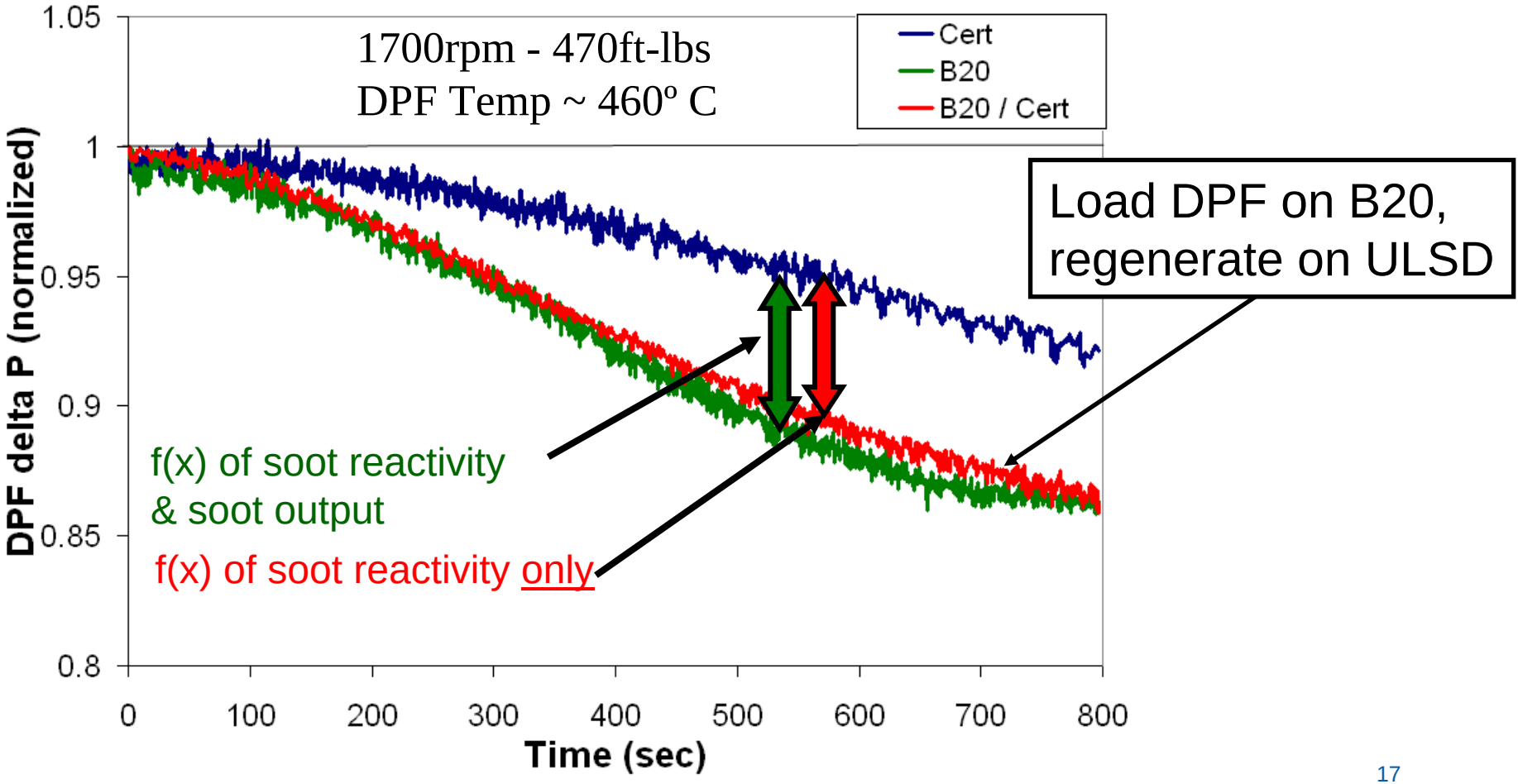
Simulated Full Useful Life Emissions Compliance Demonstrated for B20

- Durability testing of B20 with a NOx adsorber/DPF system was completed
  - 750 hr accelerated durability
  - Consumes the same amount of fuel as 120,000 mile mileage accumulation
- Final emission test performed at EPA
- Results show that the vehicle met EPA requirements

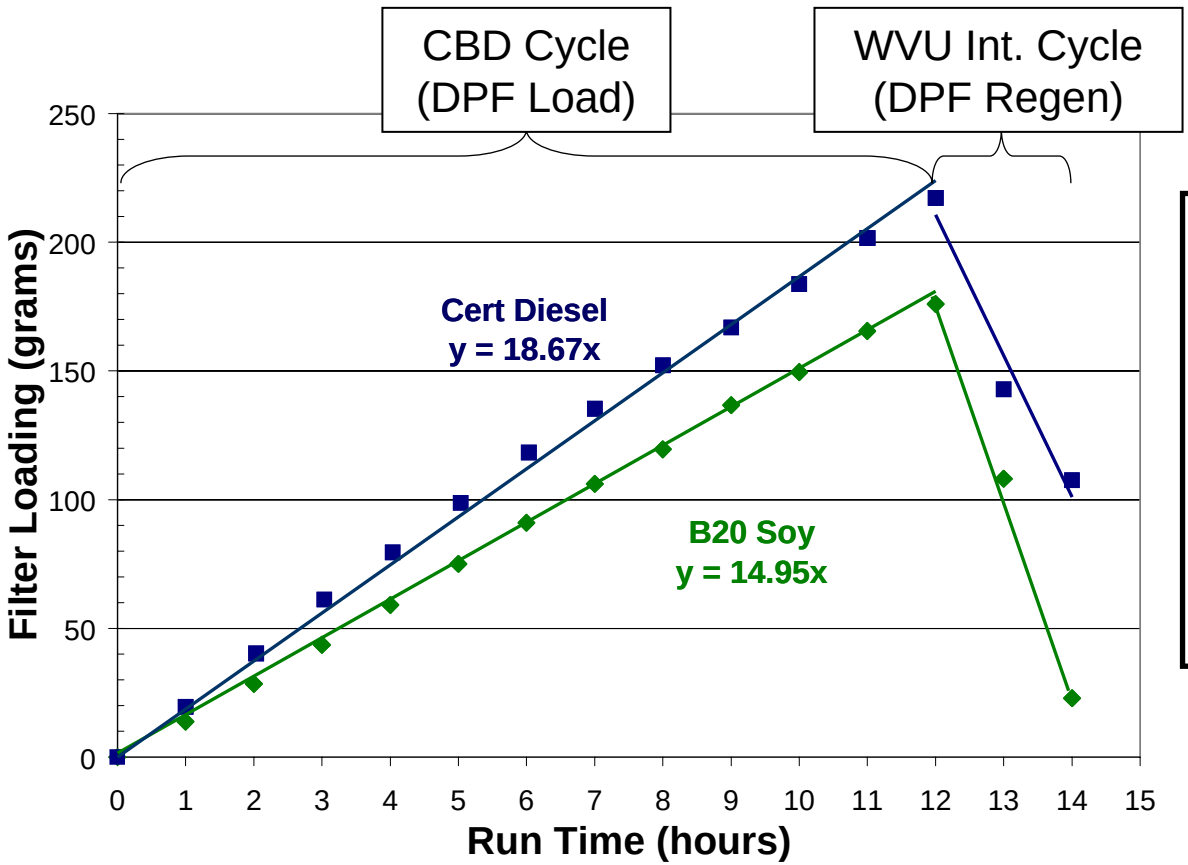


DPF Regeneration Rate Test Results

- Increased regeneration rate is a function of increased soot reactivity and lower soot output with biodiesel
- Further testing decouples the dependence on soot reactivity vs soot output



Soot Load & Regeneration Rate for Cert Fuel & B20



Future work: Can lower soot loading rate and faster, lower temperature regeneration translate into reducing the fuel economy penalty for DPF operation?

How are SCRs impacted by blending with biodiesel?

Compare SCR catalyst performance with different fuels

- Measure NOx conversion efficiency, exhaust temp and space velocity impacts
- Steady-state modal tests and Transient tests

Test hypothesis of HC mask effect on SCR catalyst performance

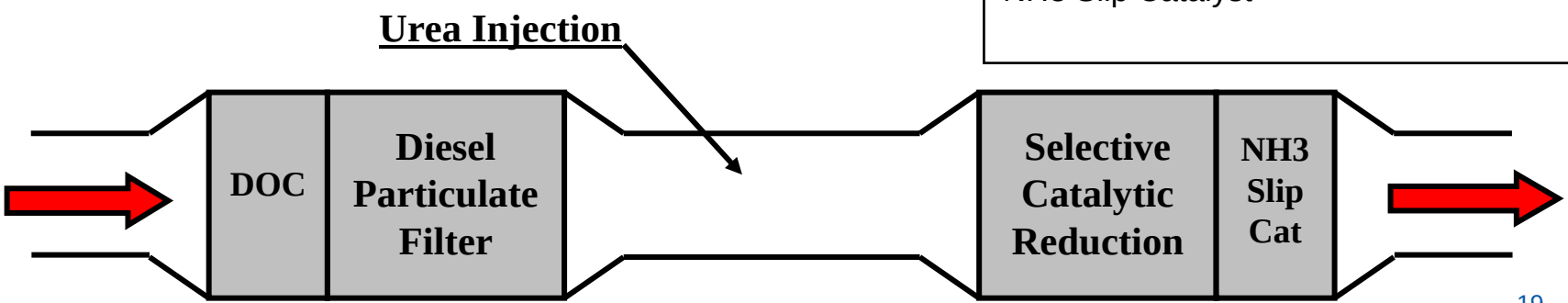
- Does fuel significantly impact exhaust HC composition entering SCR
- Measure NOx conversion efficiency after 50 hours of low temp operation

de-NOx Aftertreatment

JM Zeolite SCR (15.5 Liters)

Urea Injection (air assisted)

NH3 Slip Catalyst

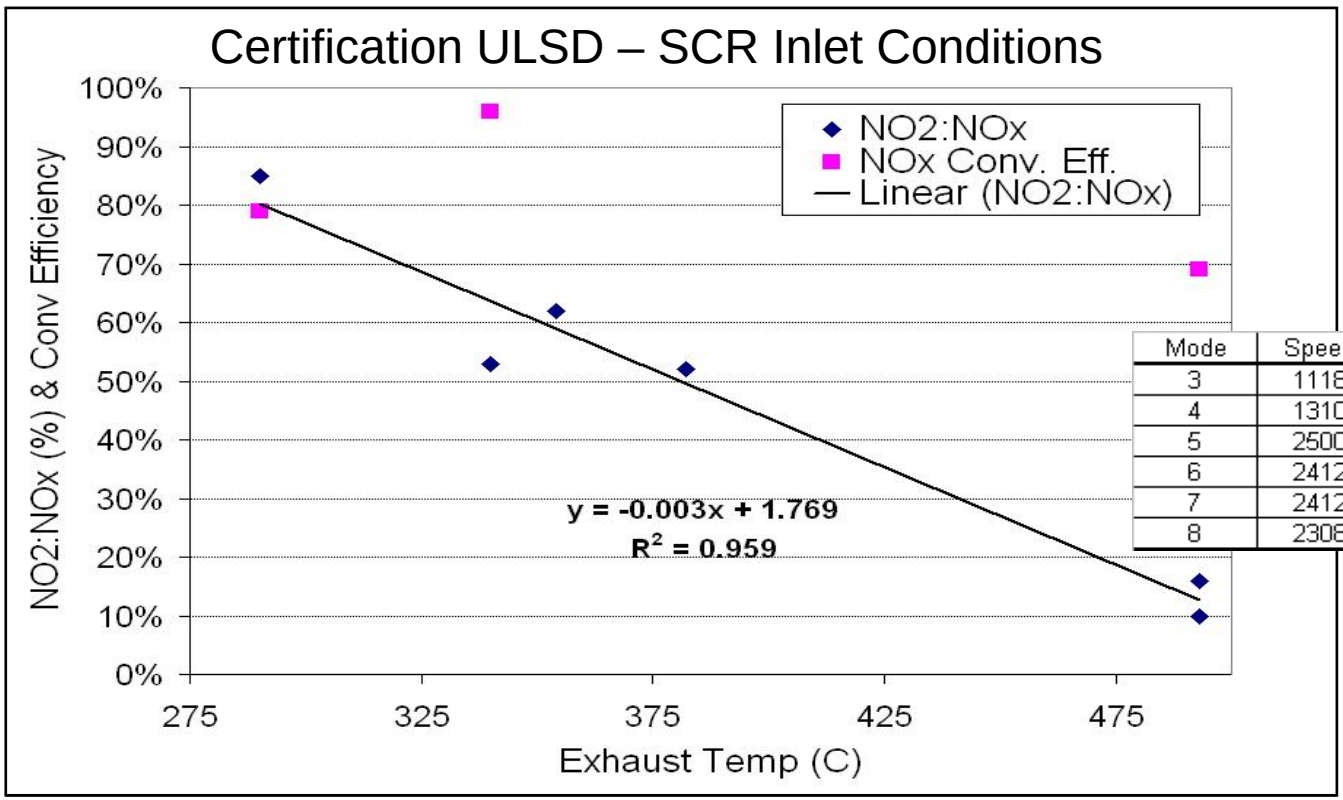


SCR Dependence on NO_2:NOx and Temperature

Data thus far shows that NO_2:NOx dominates

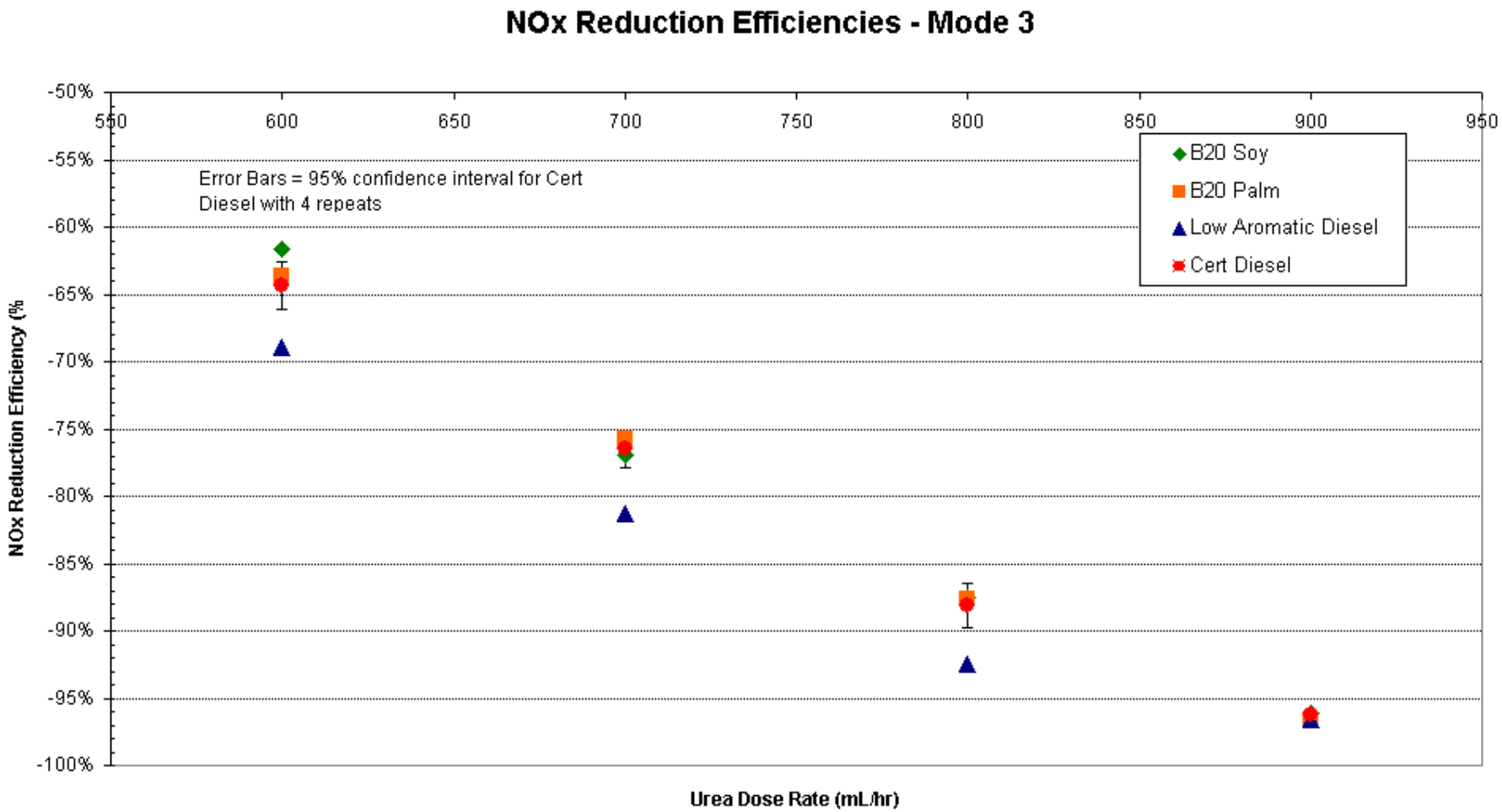
- (96% reduction with NO_2:NOx=53%)

Data shows strong correlation between NO_2:NOx and DPF temperature



8-mode Test Points

Mode	Speed	Torque	NO2:Nox	Temp	SCR Conv
3	1118	306	53%	340	96%
4	1310	502	10%	493	
5	2500	115	85%	290	79%
6	2412	261	62%	354	
7	2412	330	52%	382	
8	2308	592	16%	493	69%



No significant difference between B20 and certification diesel at any mode

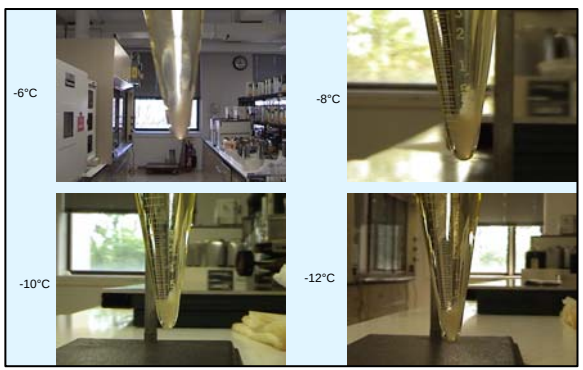
Future Plans: Biodiesel

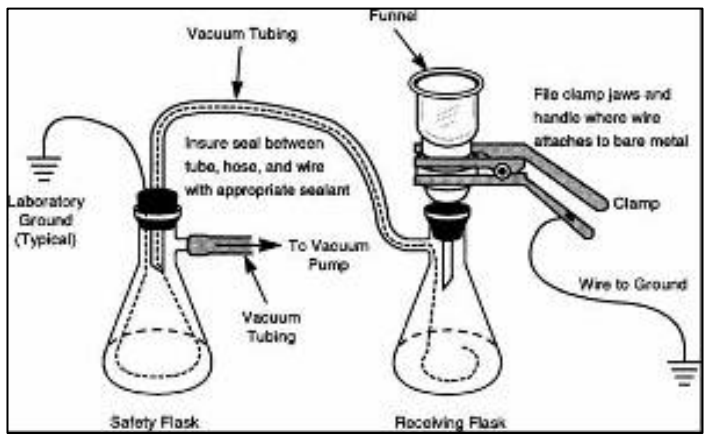
- Analytical chemistry
  - Improved methods for biodiesel
  - Identification of the cause of cold temperature filter plugging
- Passage of biodiesel blend specs at ASTM
  - Complete low temperature operability study
- B20 and B100 Quality Surveys
- B20/B5 Water Separator Performance Study
- Complete emissions meta-analysis
- Speciation of oxygenates, nitrocompounds in exhaust
- Study potential fuel economy benefit of B20 with DPF
- Initiate fleet evaluation with 2007 engines
- Complete B20 SCR study
- Testing to determine impact of Na, K on DPF, SCR, and LNT systems

Future Work: Biodiesel Blend ASTM Standards

- Addition of oxidation stability requirement to D6751 opened the door for passage of blend specifications
- Blend specifications passed the first stage (subcommittee E) in December 2007 – a major accomplishment for the Biodiesel TF at ASTM
- The final step is passage at Committee D02
  - Contingent upon resolution of low-temperature operability issues
    - Understanding precipitation above cloud point
    - Validation of cold soak filtration
- NREL leading cold temperature vehicle testing study for CRC

CP~-13ºC

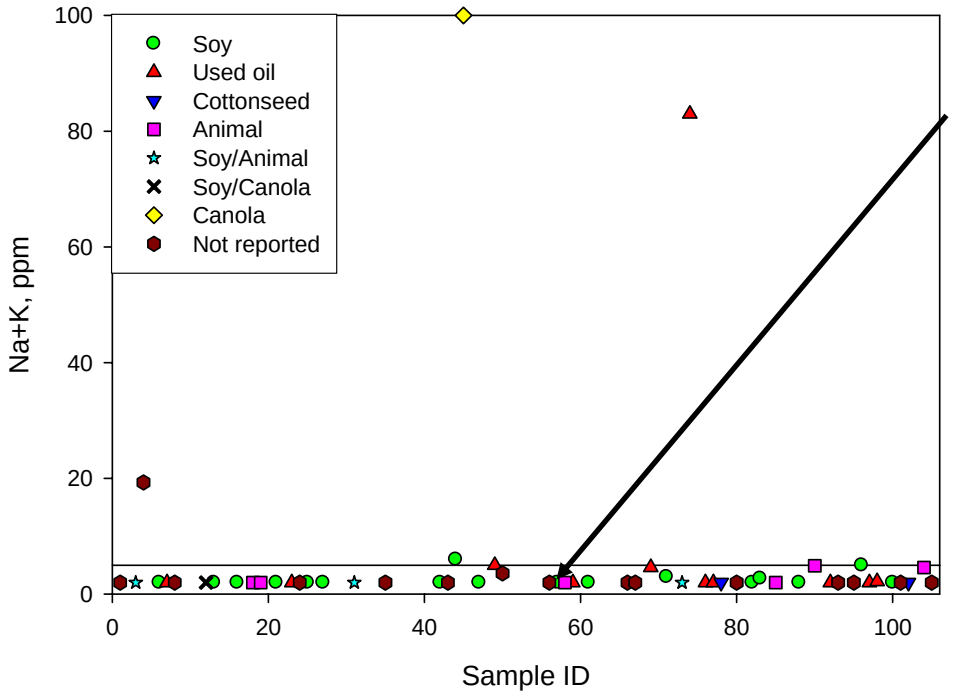




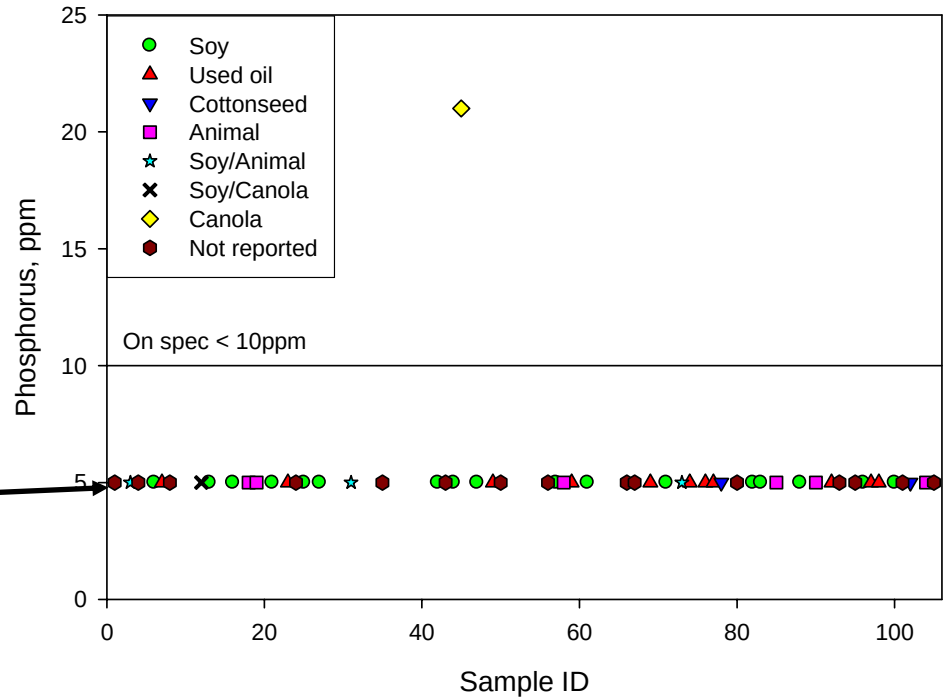
Future Work: Emission Control System Durability

- Industry steering committee discussing best path forward
- Anticipate combination of short term lab tests, 1000 hour dyno durability tests, and field testing
- Primary concerns are impact of impurities that can be present in biodiesel: Na, K, and P

Potential Catalyst Poisons in Biodiesel



80% of samples show Na and K below detection limit



Essentially all B100 shows P below detection limit

Summary

Testing of biodiesel for DOE under NPBF has been highly focused on important market barriers and is having significant success at eliminating these.

Future work will expand this effort to ethanol and potentially to second generation biofuels (butanol, mixed alcohols, other forms of renewable diesel).