Biodiesel Research Update

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Acknowledgment

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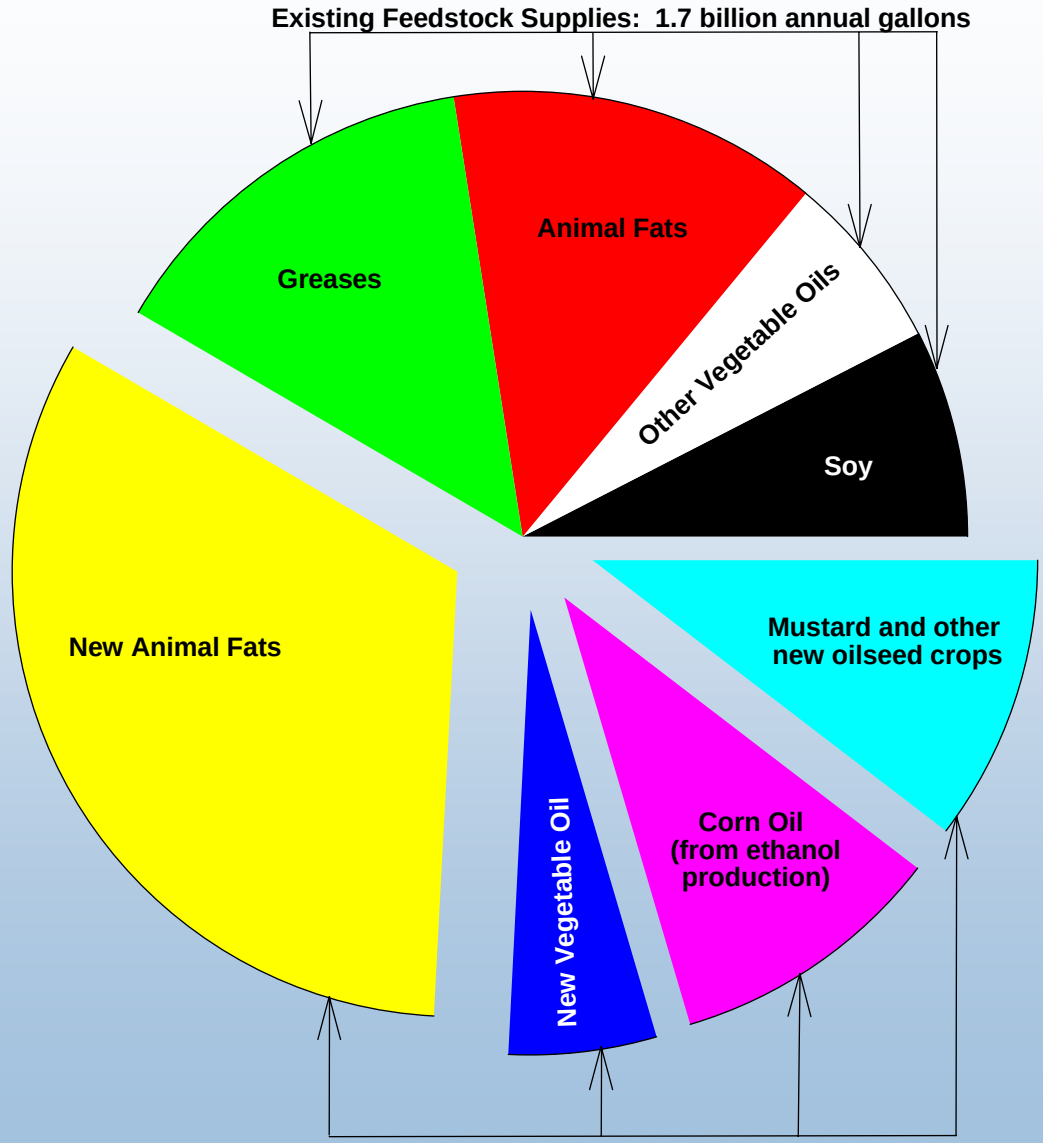
Office of FreedomCAR and Vehicle Technologies
Fuels Technology Subprogram

U.S. Biodiesel Feedstock Supply Analysis

- 1.7 billion annual gallon existing resource
- Additional 3.5 billion annual gallons by 2015
- Perhaps 10 billion annual gallons by 2030
- Technical barriers:
  - Glycerin
  - Cloud point for animal fat-based fuels
  - Plant breeding and production methods for new crops
- US on-road market: ~40 billion annual gallons



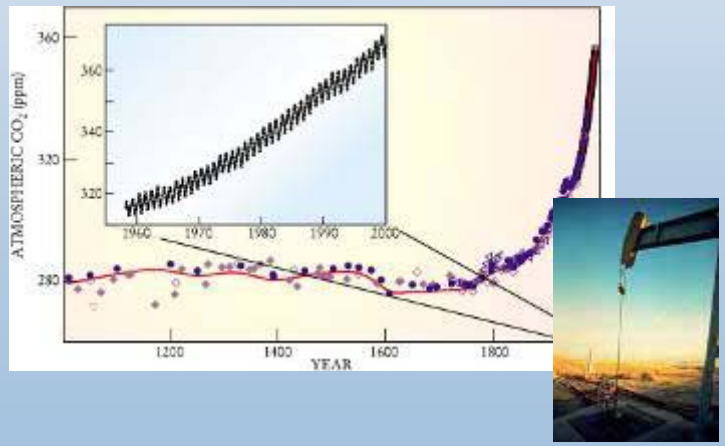
Feedstock analysis from NREL/TP-510-34796, June 2004

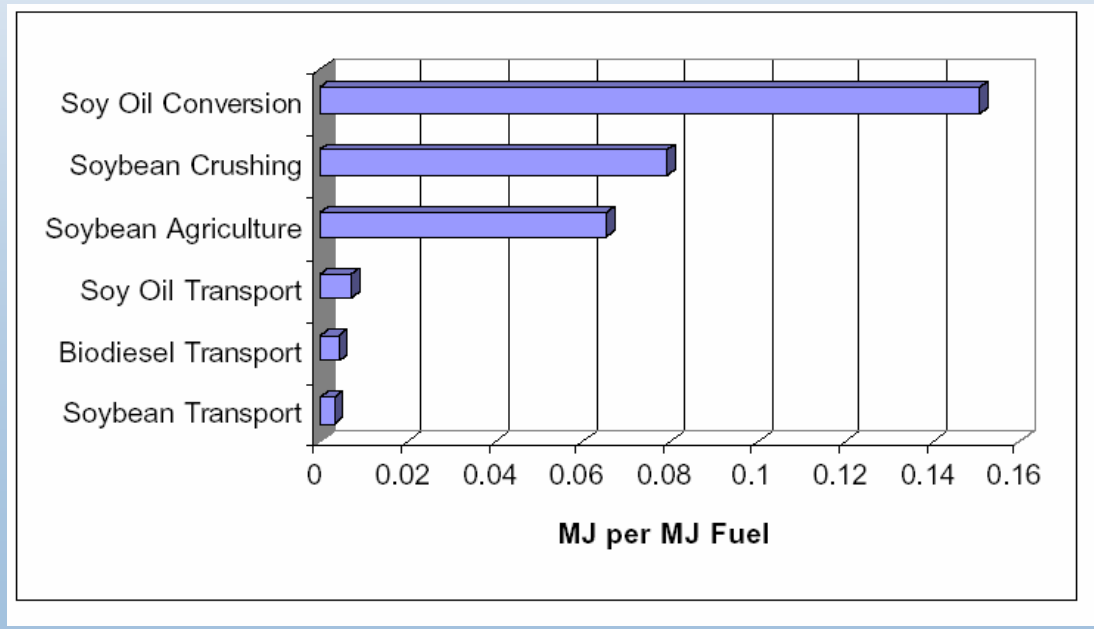
Energy Security and Global Warming Benefits

$$\text{Fossil Energy Ratio (FER)} = \frac{\text{Energy Delivered to Customer}}{\text{Fossil Energy Used}}$$

For soybean-based biodiesel = 3.2 (urban bus assessment)

Fossil energy used in production is similar to petroleum, small fraction of fuel energy-truly renewable





Analysis from NREL/TP-580-24772, May 1998

Biodiesel Quality Specification

- ASTM D6751 specifies the quality of biodiesel to be used for blending in the US
  - Two grades, S500 and S15
  - Notably does not include oxidation stability
  - Currently no standards for biodiesel blends

Property	Test Method[B]	Grade S15 Limits	Grade S500 Limits	Units
Flash point (closed cup)	D 93	130.0 min	130.0 min	°C
Water and sediment	D 2709	0.050 max	0.050 max	% volume
Kinematic viscosity, 40°C	D 445	1.9-6.0[C]	1.9–6.0[C]	mm^2/s
Sulfated ash	D 874	0.020 max	0.020 max	% mass
Sulfur[D]	D 5453	0.0015 max (15)	0.05 max (500)	% mass (ppm)
Copper strip corrosion	D 130	No. 3 max	No. 3 max	
Cetane number	D 613	47 min	47 min	
Cloud point	D 2500	Report[E]	Report[E]	°C
Carbon residue[F]	D 4530	0.050 max	0.050 max	% mass
Acid number	D 664	0.80 max	0.80 max	mg KOH/g
Free glycerin	D 6584	0.020	0.020	% mass
Total glycerin	D 6584	0.240	0.240	% mass
Phosphorus content	D 4951	0.001 max	0.001 max	% mass
Distillation temperature, Atmospheric equivalent temperature, 90 % recovered	D 1160	360 max	360 max	°C

Biodiesel Quality Survey

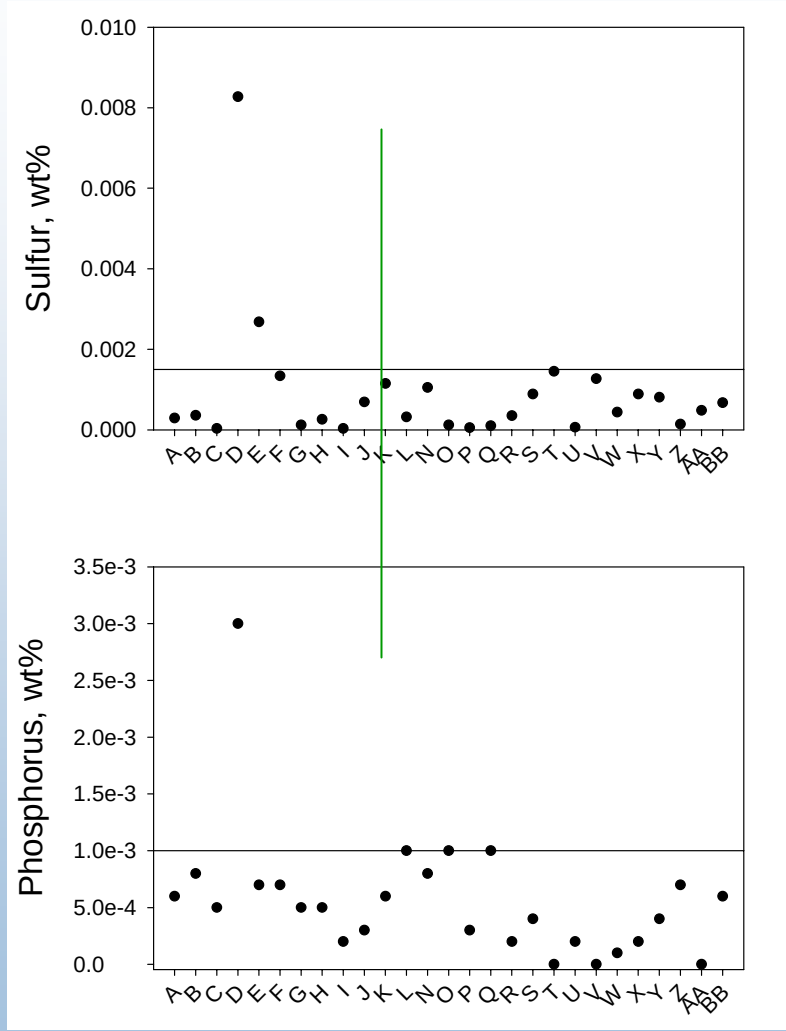
- Samples obtained nationwide from biodiesel blenders (27 samples)
- Tested using methods in D6751 as well as stability tests
- 85% of samples tested met the ASTM D6751 specification
- Four samples failed because they exceeded limits on:
  - phosphorus
  - total glycerin
  - acid number
  - acid number and total glycerin
- Blenders/distributors depend completely on producers to insure quality
  - Only “visual” quality checks were made, no sample testing

B100 Sampling Locations

-green flags

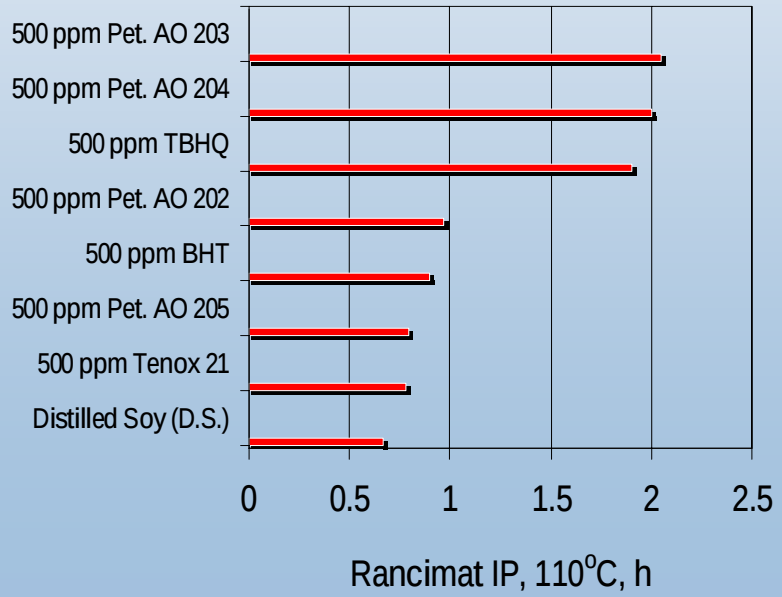
Biodiesel Quality Survey: Sulfur

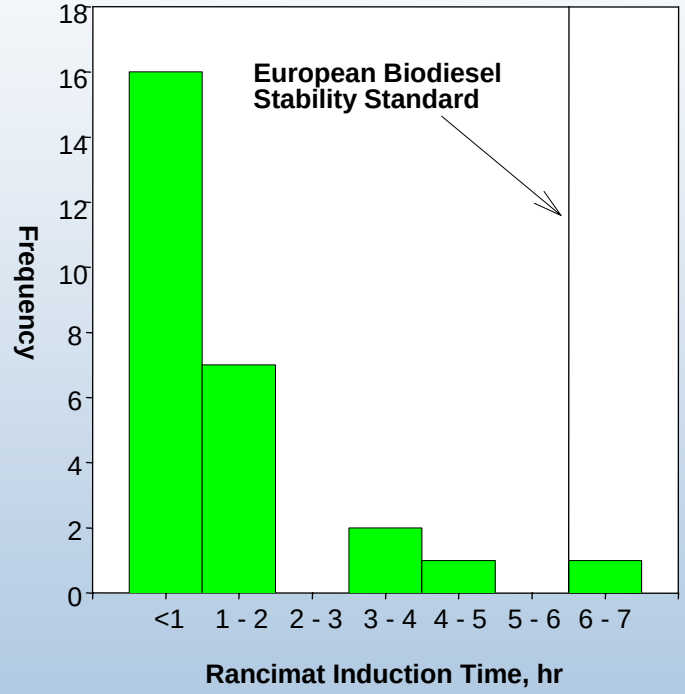
- Distributors have generally not yet begun to distinguish between S15 and S500 grades
- All but two samples met S15
- One sample exhibited 83 ppm Sulfur *and* 3x the allowable Phosphorus
  - Speculate lube oil contamination?



Oxidation Stability – Rancimat (EN14112)

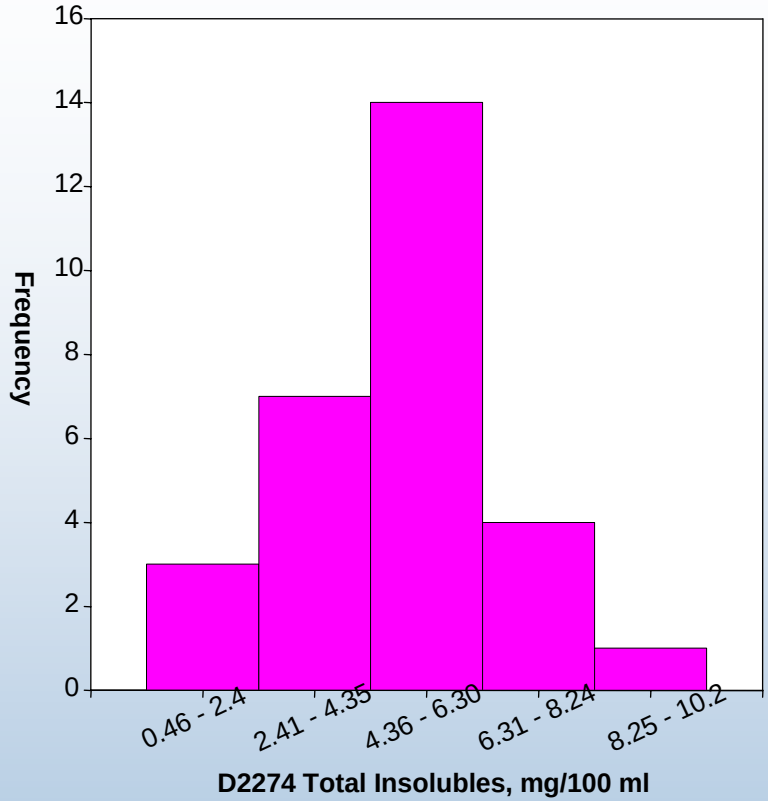
- Air bubbled through sample at 110°C.
- Measures formation of volatile acids-not directly related to fuel performance
- EN14214 requires min. 6 hr induction time
- Only one US sample would meet this requirement - 6 hr induction time may not be appropriate for US biodiesel
- Antioxidants can increase induction time

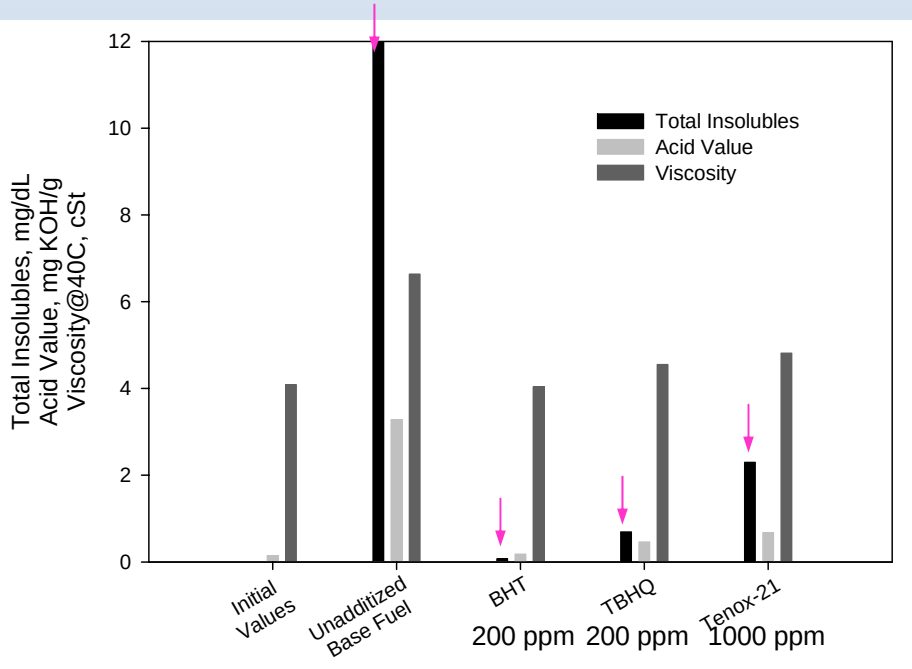




Oxidation Stability – D2274

- Exposure to oxygen at 95°C for 16 hours
- Filtration and weighing of deposits – directly related to fuel performance
- Limits for this test have not been determined for biodiesel
- Antioxidants are effective for reducing deposits

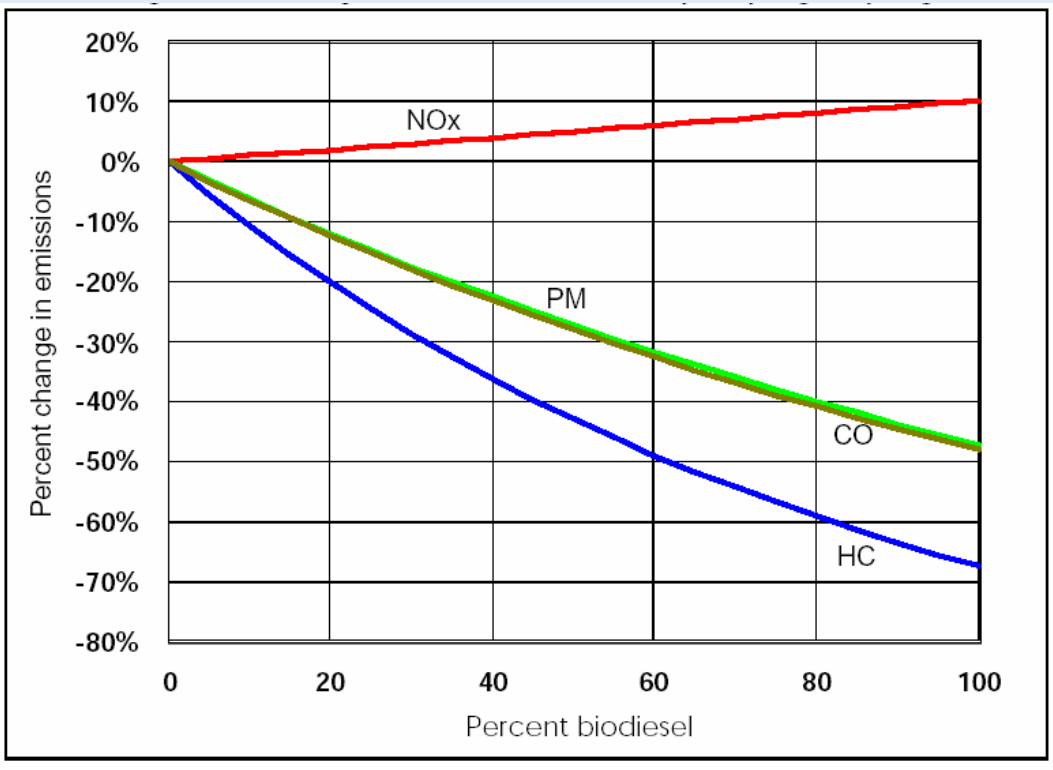




Considerable work remains to determine an appropriate test and limit for biodiesel oxidation stability

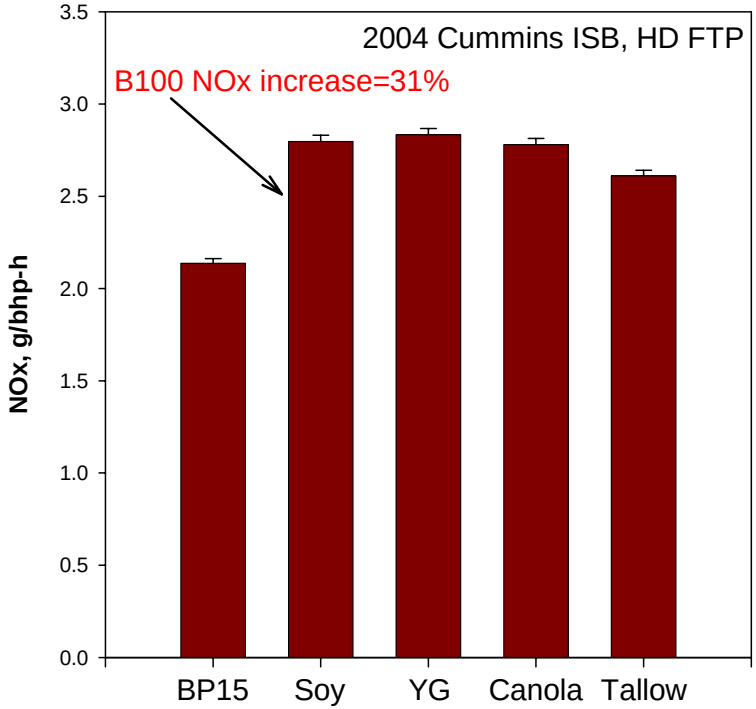
Emissions in Older Engines

- EPA analysis:
  - data from many studies
  - engine models through 1997
- NOx 2% increase B20, 10% for B100
- PM 10% decrease for B20, 50% for B100



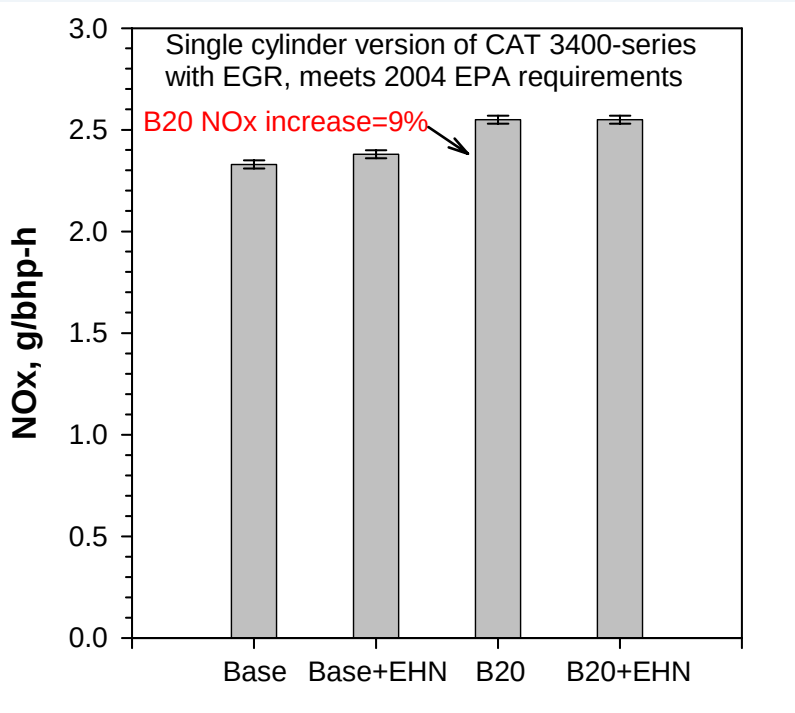
EPA420-P-02-001, October 2002

Newer Engines: 2004 Cummins ISB – B100



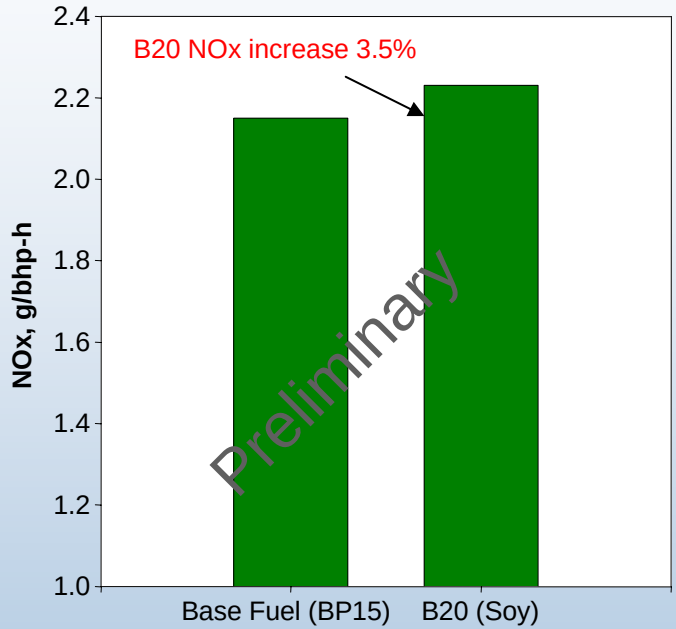
- HD FTP compared to ULSD
- Larger NOx increase than older engines
  - 31% vs 10%
- More saturated fuel (tallow) has somewhat lower NOx
- Large PM reduction than older engines
  - 75% versus 50%
- EGR valve opens less on B100 compared to ULSD

New Engines: Single-Cylinder Caterpillar Engine – B20



- 8-Mode SS compared to oil sands No. 2
- Single cylinder engine modified with EGR to meet 2004 standard.
- NOx increase larger than for older engines
  - 9% vs 2%
- PM reduction larger than for older engines
  - 25% vs 10%

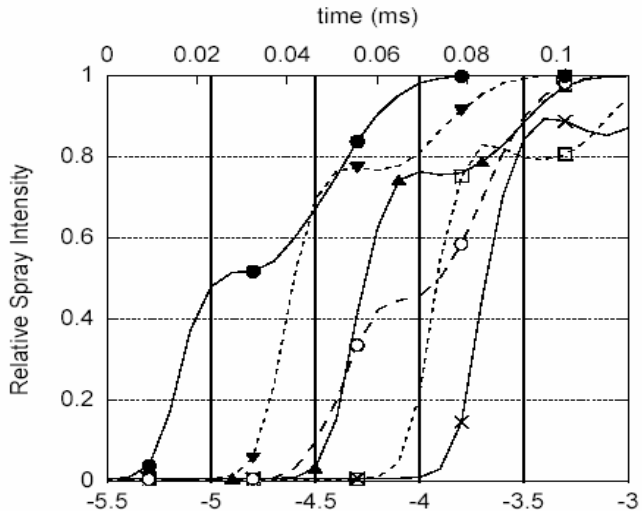
New Engines: 2004 DDC Series 60 – B20



- HD FTP compared to ULSD
- Similar NOx increase as older engines
  - 3.5% vs 2%
- Larger PM reduction than older engines
  - 28% versus 10%

Why Does Biodiesel Increase NOx?

- Biodiesel exhibits higher bulk modulus of compressibility than petro-diesel
- van Gerpen proposed that this causes advance in injection timing, increasing NOx (*J. Am. Oil Chemists Society, 2000. 77(3):285*).
- More recently, Boehman has shown this experimentally, and that the start of combustion is also advanced by up to 4 CA degrees *(SAE 2003-01-1039).*
- *Biodiesel NOx may increase because of advanced injection timing and start of combustion*

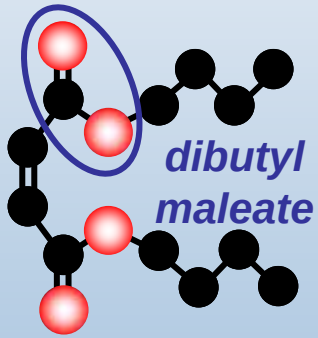


Start of injection timing by laser attenuation, 25% load. (X) Baseline, (□) B20, (▲) B40, (▼) B60, (○) B80, and (●) B100

Biodiesel PM Reduction Mechanism Revealed

Research at Sandia National Laboratories/California (Chuck Mueller)

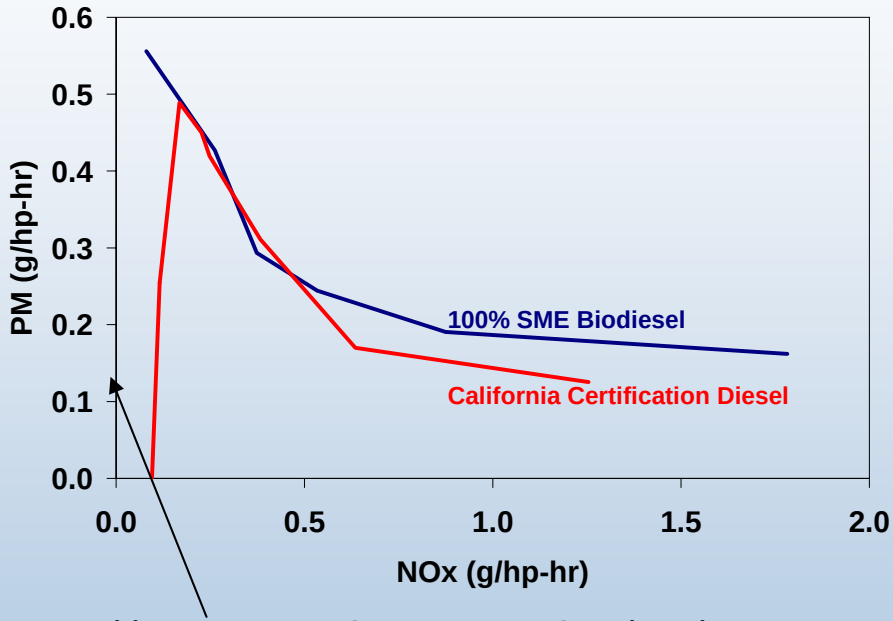
- Approach: Use optical-engine experiments to enhance fundamental understanding of biodiesel combustion and emissions formation
  - Complemented by kinetic modeling and carbon-14 isotopic labeling collaborations with Lawrence Livermore National Lab
- Recent result: Direct formation of CO2 from ester causes two O-atoms to be used to remove one C-atom
  - Ideally, each O-atom in fuel removes one
  - C-atom from soot-formation pathways
  - (i.e., one O-atom is wasted)
  - Ester structure found in biodiesel is less
  - effective than ether at suppressing soot emissions
  - SAE Papers: 2003-01-1791, 2004-01-1849
- Current focus: Determine reason(s) for elevated NOx emissions with biodiesel fueling
  - Collaboration with Prof. Ed Cheng of San Francisco State Univ.



Potential for Biodiesel in LTC Explored

Research at Oak Ridge National Laboratory (Wagner et al.)

- Biodiesel (B100) did not show a transition into high-efficiency clean combustion.
- Somewhat surprising, expected O_2 content to help.
- All three petroleum-based fuels (CERT, CARB, ECD1) behaved very similarly.
- B100 data was very erratic.
- ORNL hopes to repeat some experiments this FY to confirm earlier results.



Transition to Low-NO_x, Low-PM Combustion
Caused by increasing EGR to 55%, changing fuel injection

Mercedes 1.7-L engine
1500 rpm/25.9 ft-lb

Closing Remarks

- Survey results indicate that 85% of US biodiesel meets the ASTM quality standard
- Oxidation stability issues still being studied
  - Best test method not yet defined
  - Antioxidants appear to be effective
- Modern (2004) engines show NOx increase and PM reduction
  - Magnitude may be larger than in older engines
  - Cause of NOx increase and solutions to this problem are still under investigation