

Stability of Biodiesel and Biodiesel Blends with Ultra Low Sulfur Diesel

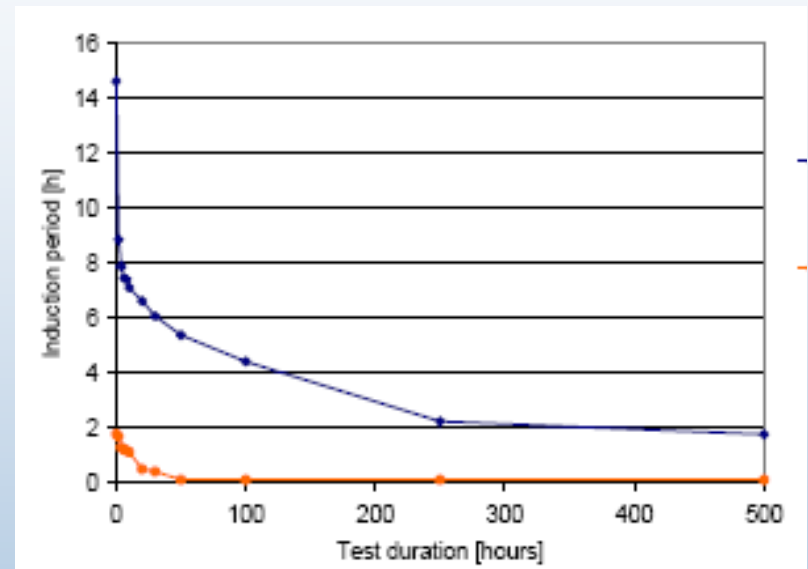
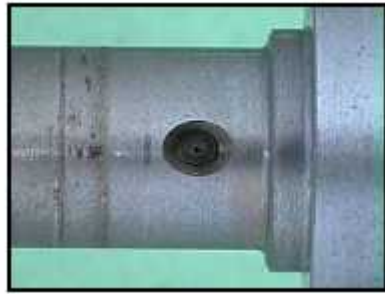
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Steve Westbrook (SwRI)*

*National Biodiesel Conference
Orlando, February 4, 2008*

*Study sponsored by National Biodiesel Board
and
US Department of Energy*

Why do we need a specification on stability?

- 500 hr bench test comparing stable and unstable B100:
 - 9 hr vs 2 hr induction time initially
 - Induction time decayed during study
- Poorly stable biodiesel produced substantial injector deposit



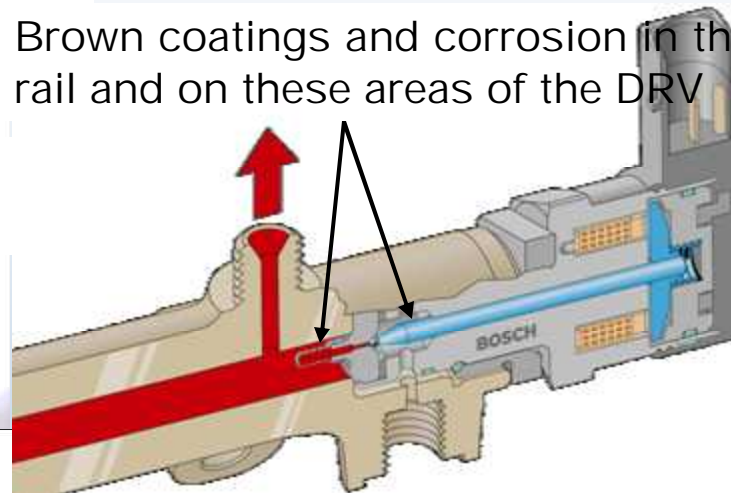
Blassnegger, J. in *Stability of Biodiesel Used as a Fuel for Diesel Engines and Heating Systems*, Presentation of the BIOSTAB Project Results, July 2003, Graz, Austria.

Why do we need a specification on stability?

DRV with Deposits – fuel B5



Brown coatings and corrosion in the complete rail and on these areas of the DRV



- Induction Period $IP = 0$
→ no more ageing reserve
- Vehicle no longer operational
- Also deposits and corrosion on fuel pump

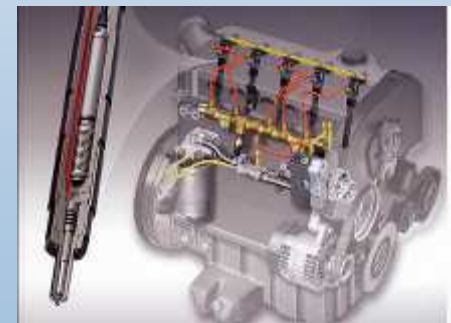
Courtesy of Tom Livingston, Robert Bosch LLC

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

Approach: Three Aging Scenarios

1. In storage and handling
 - Applies to B100 and blends
 - No longer than 6 month storage of B100 is recommended today
2. In vehicle fuel tank
 - Recirculation at low fuel level
 - Applies to biodiesel blends only
3. Aging (reacting) in high temperature engine fuel system
 - Deposit formation from unstable or pre-aged fuel
 - Applied to biodiesel blends only



Tests to Simulate Aging Scenarios

1. *Aging in storage: D4625*

- Quiescent aging at 43°C for 12 weeks
- One week equivalent to one month for petroleum fuel
- Measurement of total insoluble plus other fuel properties

2. *Vehicle tank aging: D4625 (heavily modified)*

- Quiescent aging at 80°C for 1 week
- With ullage purge to insure test is not oxygen limited
- Measurement of total insoluble plus other fuel properties

3. *High temperature fuel system aging (reacting):*

- Thermal stability test on un-aged blend (D6468)

Stability Study Plan

- Perform accelerated stability tests on 19 B100 samples covering the range available in US
- Select 8 B100 covering the range of stability for:
 - 12 week storage tests
 - Blending with 6 diesel fuels to produce 48 B5 and 48 B20 blends
 - Perform accelerated stability tests on the B5 and B20 blends
- Select 8 B5 and 8 B20 blends for:
 - 12 week storage test
 - One week test simulating fuel tank aging
 - High temperature test simulating conditions in an engine fuel injection system
- Interpret results to address study objectives

Accelerated Stability Tests

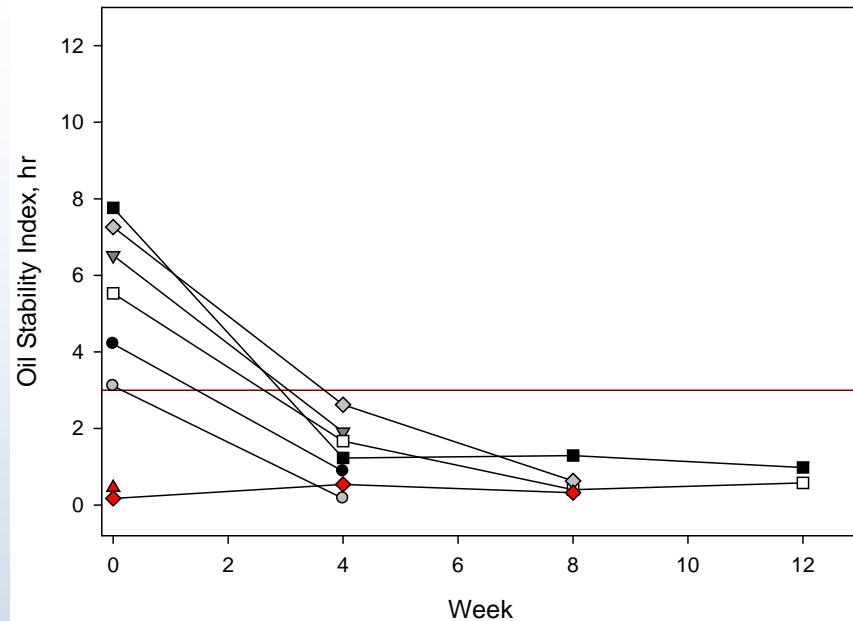
- Lab tests that reveal if a sample is stable or unstable in a short time
 - Oxidize under severe or “accelerated” conditions
- Two main approaches:
 - Induction period (Rancimat, OSI)
 - How long till oxidation starts?
 - Measured as time to initial formation of acids by oxidative degradation at 110°C in air
 - Relevant to storage stability
 - Deposit formation (D2274)
 - How much gum or deposit forms after oxidation for a fixed time?
 - Measured as deposits formed after 16 hr at 90°C in oxygen
 - Relevant to engine compatibility

B100 Selection

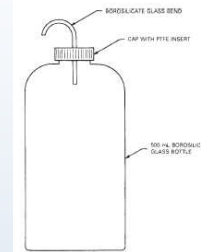
- Cover range on accelerated tests
- Cover all feedstocks
- Samples to be used in:
 - 12-week storage test
 - Preparation of B5 and B20 blends

	Feedstock	Rancimat	D2274 Total
Observed Range:		0.2 – 7.8 hr	0.3 – 17.6 mg/100 ml
AL-27128-F	Canola	4.2 (med)	6.5 (med)
AL-27129-F	Palm Stearin	3.1 (med)	1.9 (low)
AL-27137-F	Soy	6.5 (high)	1.0 (low)
AL-27138-F	Soy	0.5 (low)	7.6 (med)
AL-27141-F	Soy	5.5 (high)	0.3 (low)
AL-27148-F	Grease	7.8 (high)	0.9 (low)
AL-27152-F	Rapeseed	7.3 (high)	0.5 (low)
AL-27160-F	Tallow	0.2 (low)	17.6 (high)

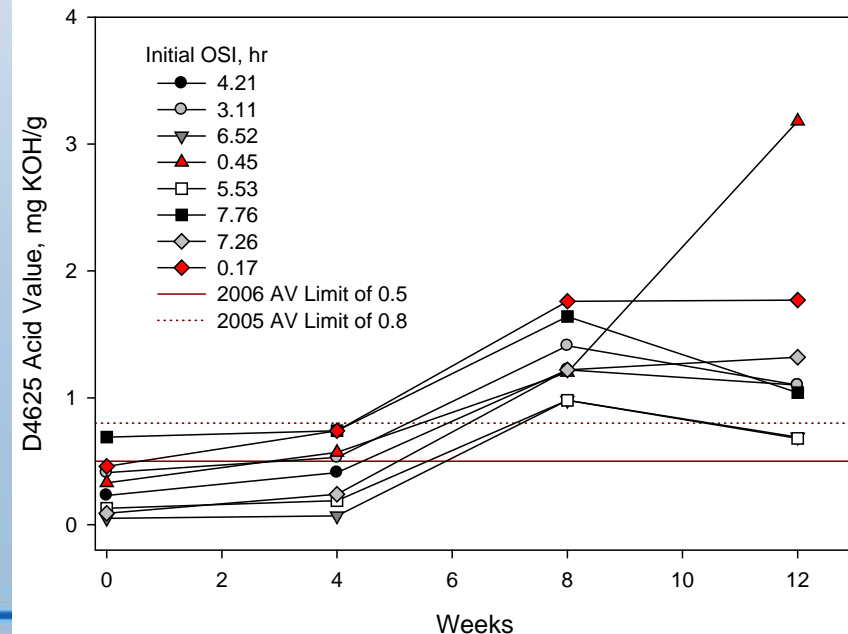
B100 Long Term Storage: D4625



- 12 weeks at 43°C, vessel open to air

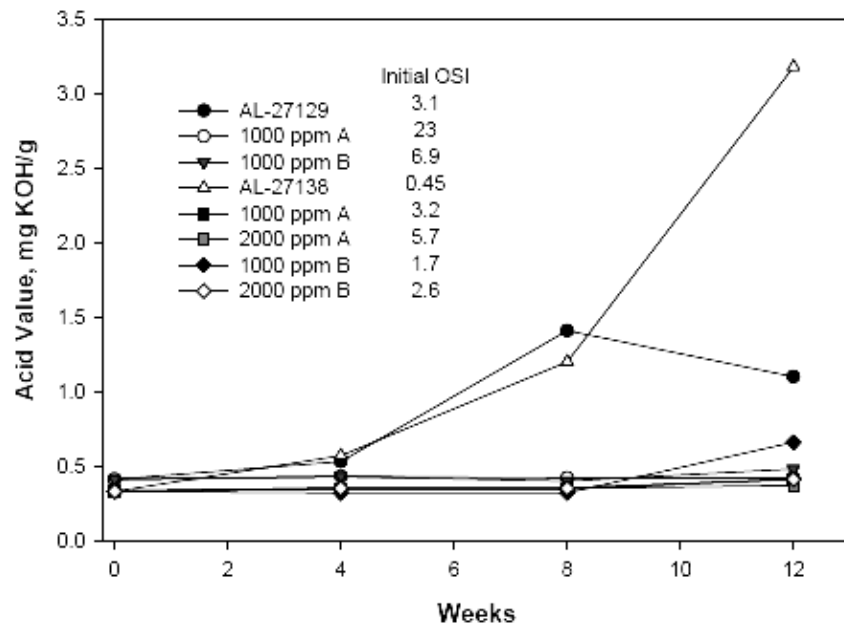
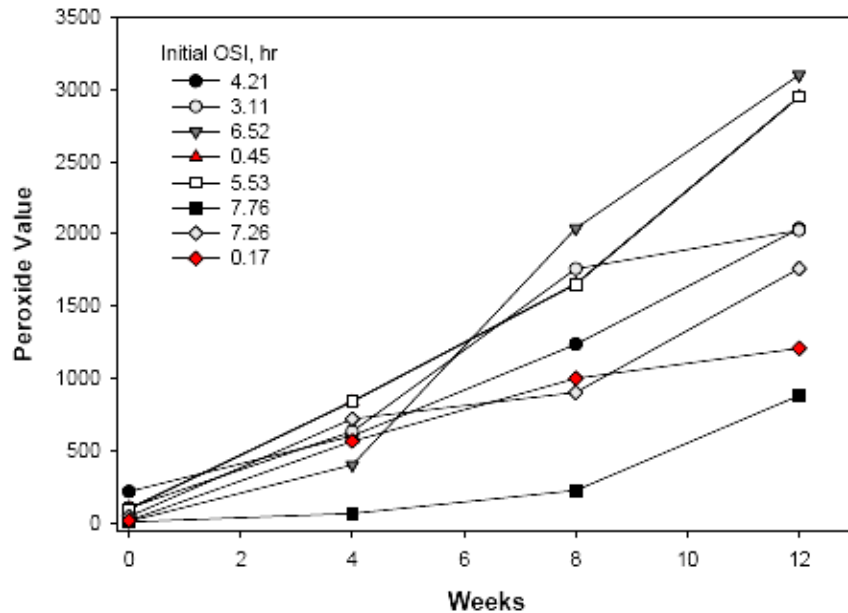


500 ml bottle
Filled to 400 ml



- IP deteriorates to less than 3 hr in less than 4 weeks (3 month storage limit?)
- Acid value increases slightly over 4 weeks, and rapidly beyond 4 weeks
- Are samples degrading or just losing “oxidation reserve”?

B100 Long Term Storage – D4625



- Peroxide value increase shows that B100 are degrading
- Synthetic antioxidant additives (TBHQ, BHT) are effective at stabilizing B100 in storage

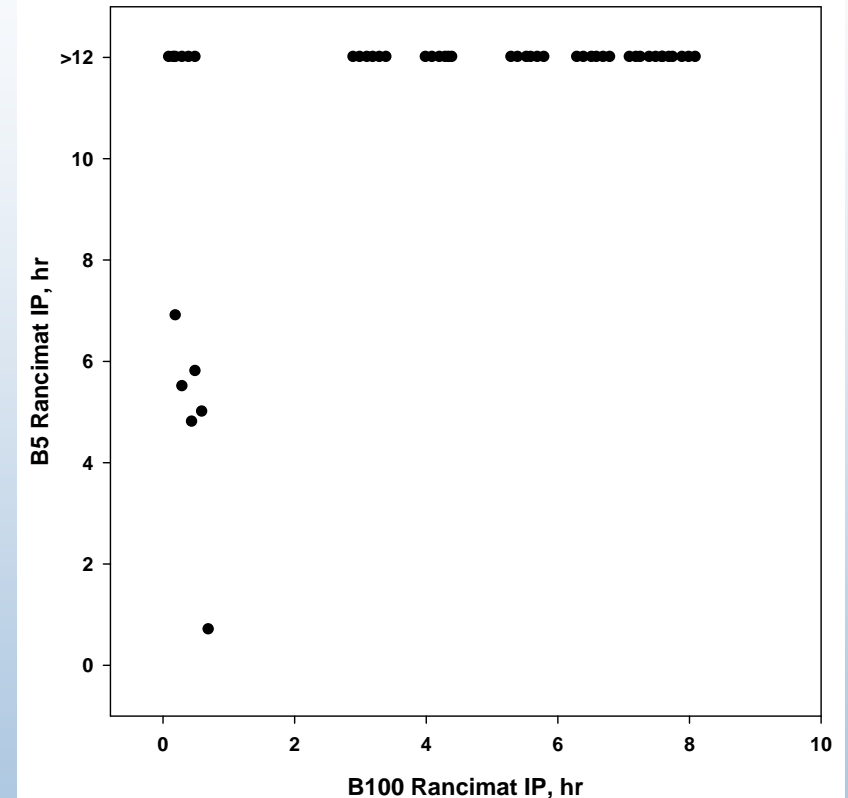
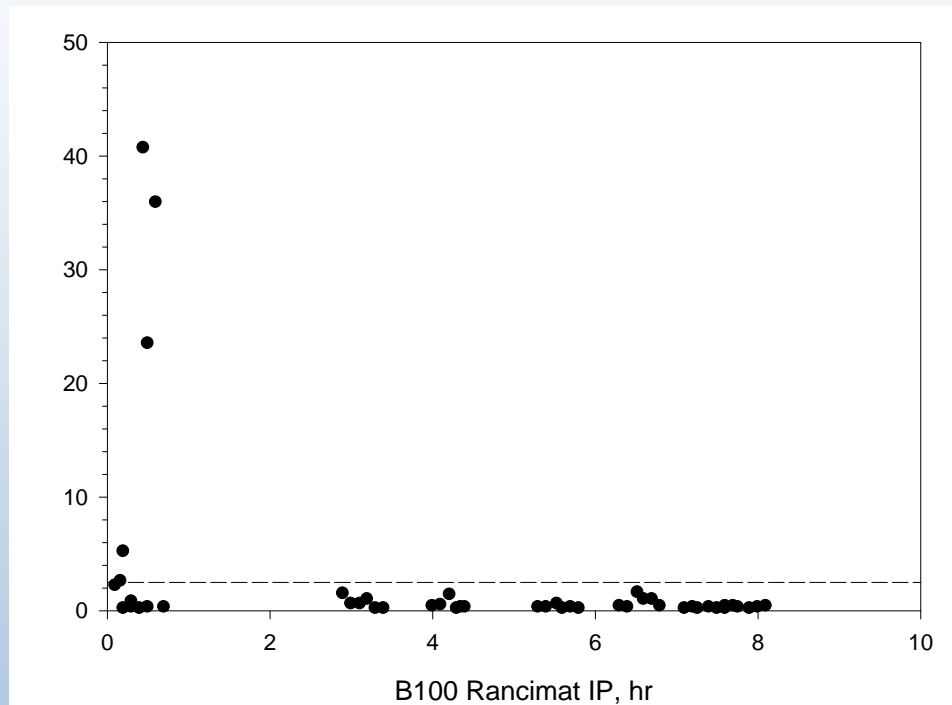
Blending Diesel Fuel Properties

- 5 ULSD, 1 LSD
- Fuels that were available in Dec. 2005 – may not be fully representative of today's ULSD
- Wide range of aromatic content

	Sample	ASTM D975 Limit (No. 2 Diesel)	AL27150F	AL27151F	AL27166F	AL27171F	AL27175F	AL27176F
ASTM D93	Flash point, °C	52	58	69	59	73	59	69
ASTM D5453	Sulfur, ppm	15 or 500	7.4	6.7	5.8	339.6	2.9	7.4
ASTM D86	BD, °C	282 min 338 max	274	313	289	319	333	236
ASTM D524	Carbon residue (on 10% distillation residue), mass%	0.35	0.07	0.04	0.06	0.13	0.05	0.08
ASTM D664	Acid number, mg KOH/g	none	0.01	0.03	0.01	0.01	0.01	0.01
ASTM D3703	Peroxide number	none	<1	<1	<1	<1	<1	<1
ASTM D2709	Water and sediment, vol%	0.05	0.01	0.01	0.01	0.01	0.01	0.01
ASTM D482	Ash content, mass%	0.01	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
ASTM D5186	Total Aromatics, mass%	none	15.7	22.1	18.1	36.2	8.2	19.3
	Monoaromatics, mass%	none	14.4	19.9	17.1	27.6	7	17.4
	Polynuclear aromatics, mass%	none	1.3	2.1	1	8.7	1.2	1.9
ASTM D6217	Particulate contamination, mg/l	none	0.5	0.4	0.8	0.8	1.2	0.3
ASTM D2274	Total Insolubles, mg/100 ml	none	0.25	0.25	0.5	0.2	0.1	0.05
ASTM D6488	Thermal stability, 150°C/180 min % reflectance	none	100	100	100	98	95	100
ASTM D4625	Modified, 80°C, air purge, 1 week	none						
	Adherent insoluble, mg/100 ml		0.3	0.4	0.1	0.1	0.2	0.2
	Flocculent insoluble, mg/100 ml		0.7	0.2	0.1	0.1	0.4	0.2
	Total insoluble		1.1	0.6	0.2	0.2	0.6	0.4

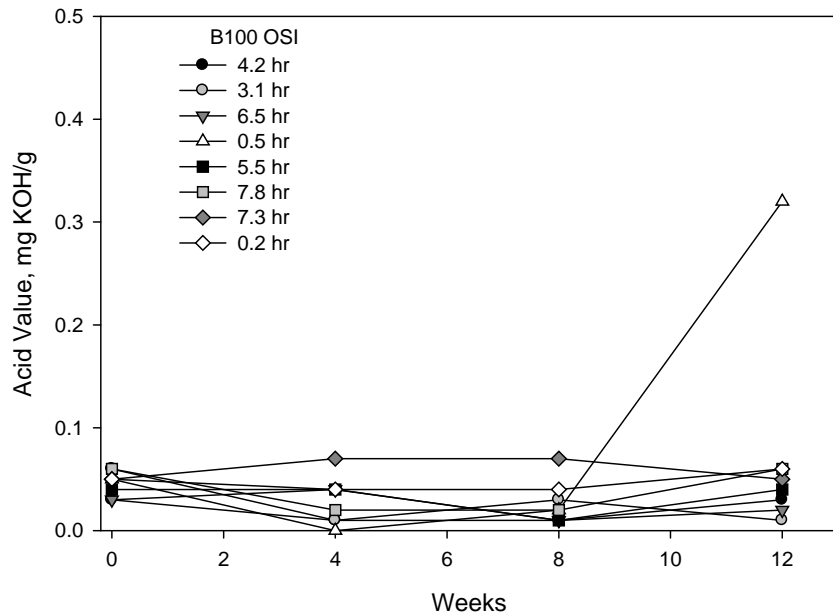
Impact of B100 Stability on B5 Stability: Accelerated Tests

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

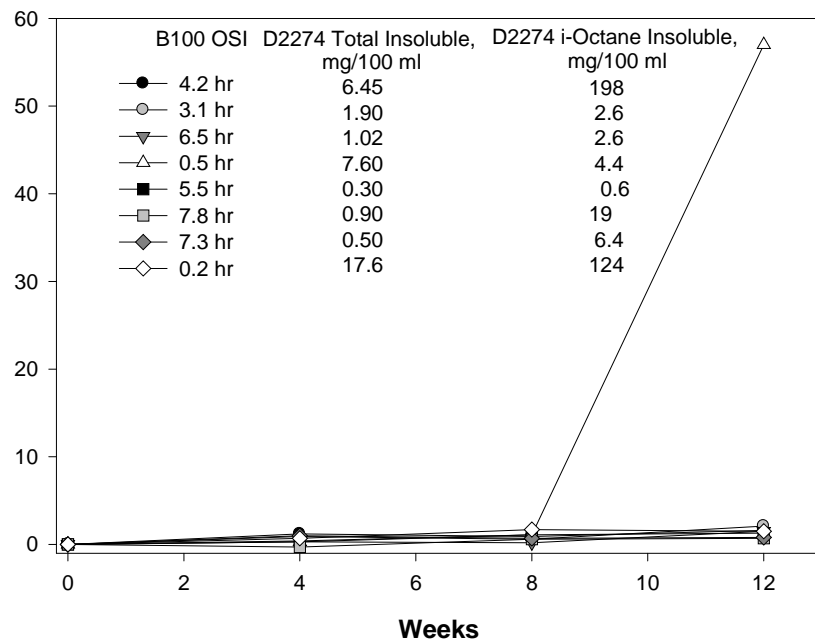


B100 stability appears to be an excellent predictor of blend stability, an IP of 3 hr ensures low deposits and long induction time for the blend

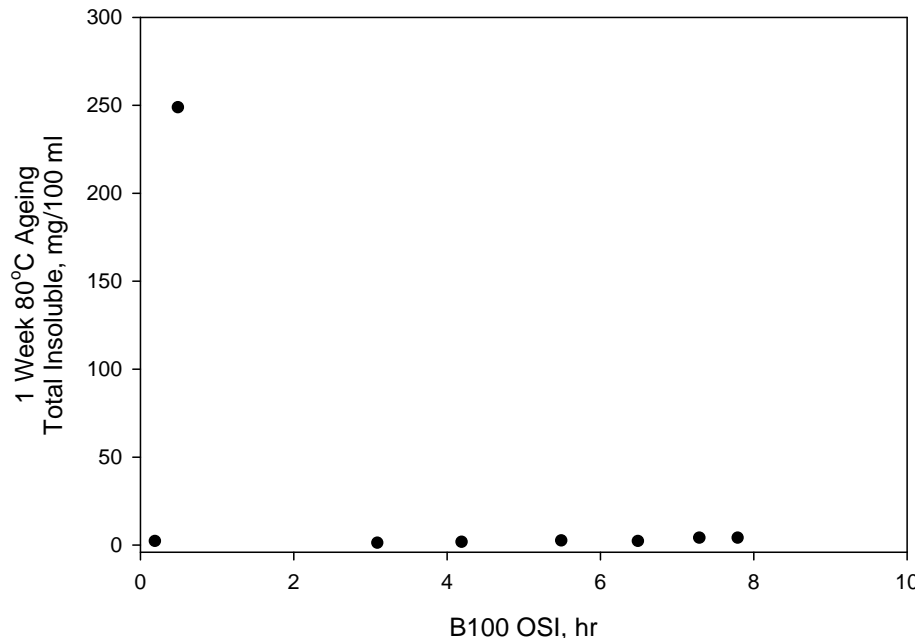
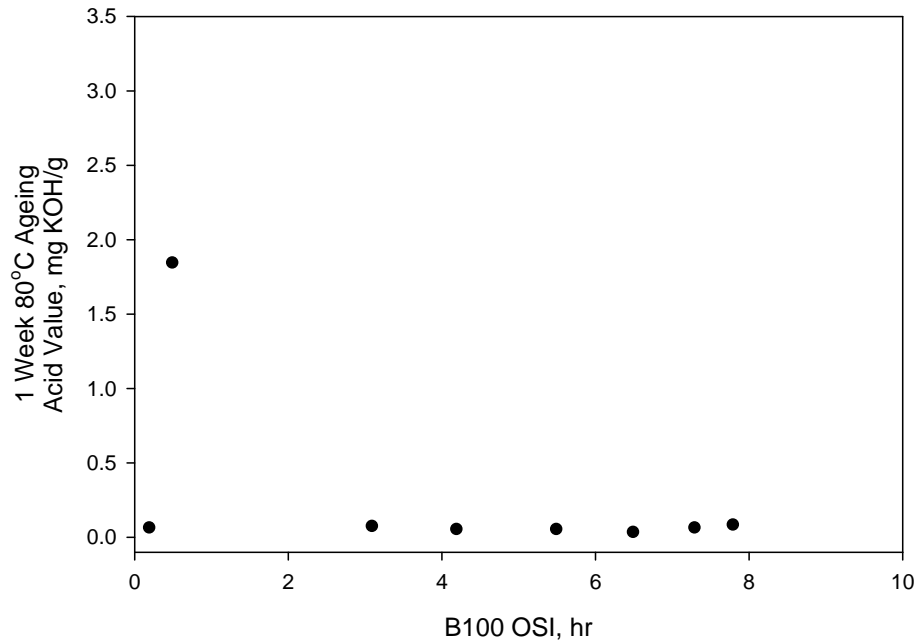
B5 Blends Long Term Storage: D4625



- 12 weeks at 43°C, vessel open to air
- The only B5 that experienced an increase in AV or insoluble was for B100 with IP < 3 hr
- Other samples are not degrading – no increase in peroxides for stable B100
- 3 hr IP adequately protects B5 blends under these conditions

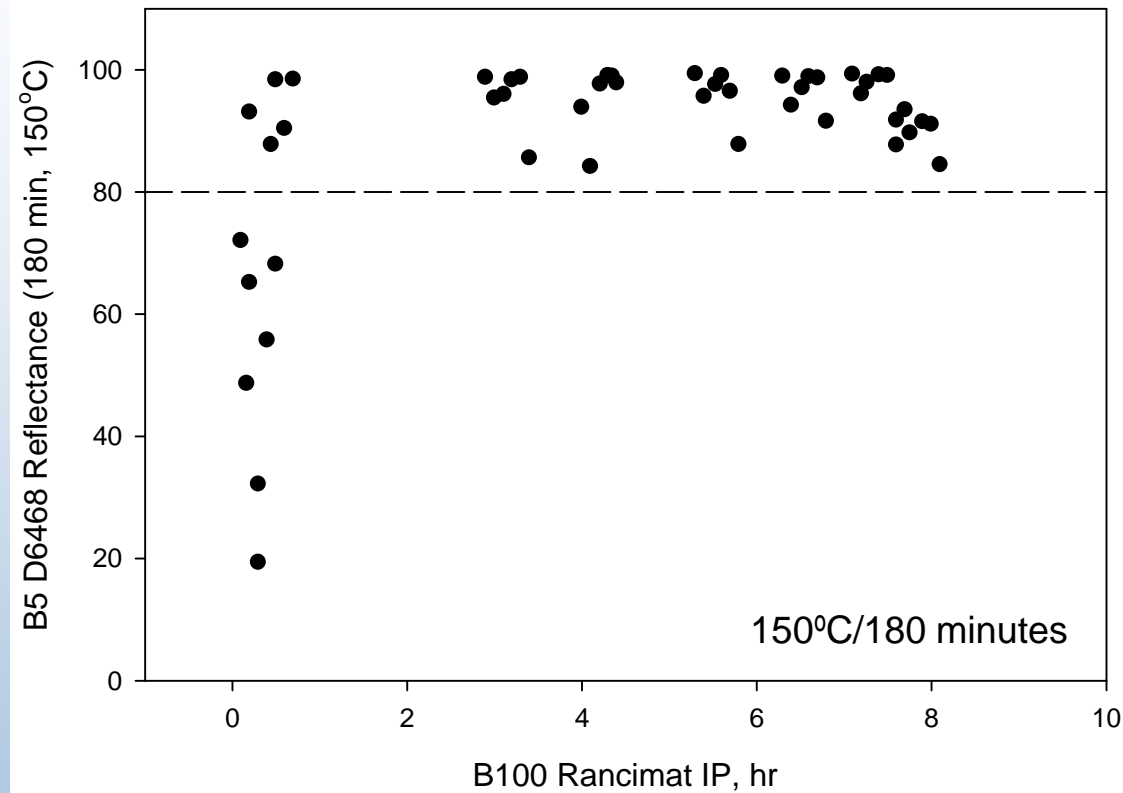


B5 Blends Fuel Tank Simulation



- 1 week at 80°C with ullage purge intended to simulate aging in vehicle tank
- B5 blends from B100 with 3hr+ IP show little increase in AV or insoluble
- 3 hr IP adequately protects B5 blends under these conditions
- Caveat: new test, meaning uncertain

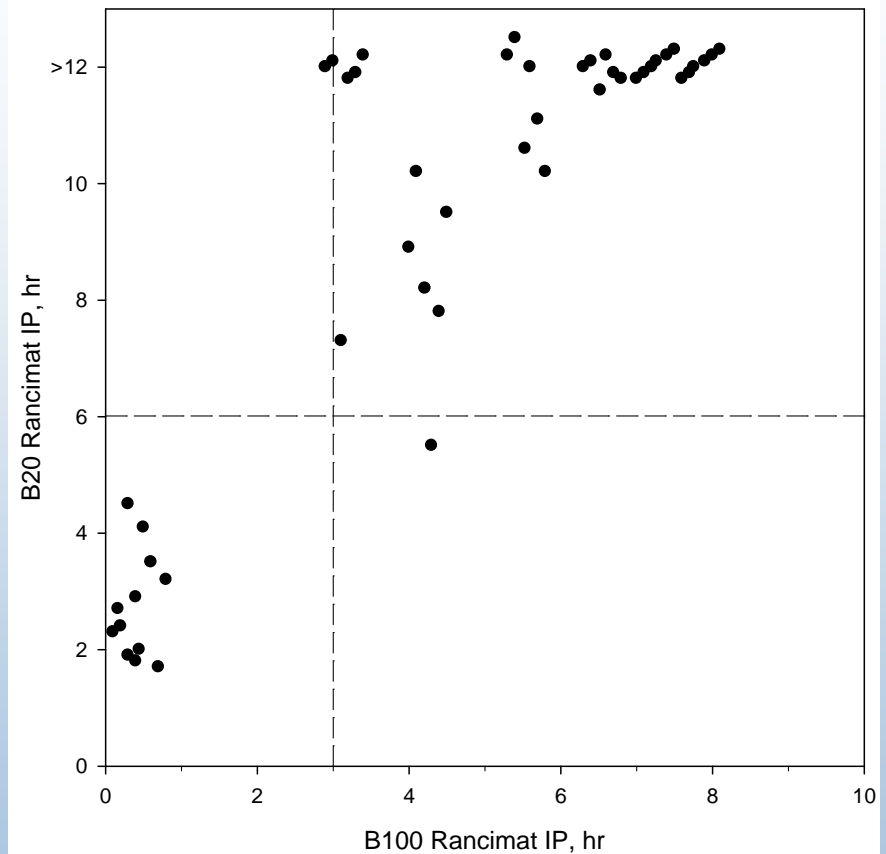
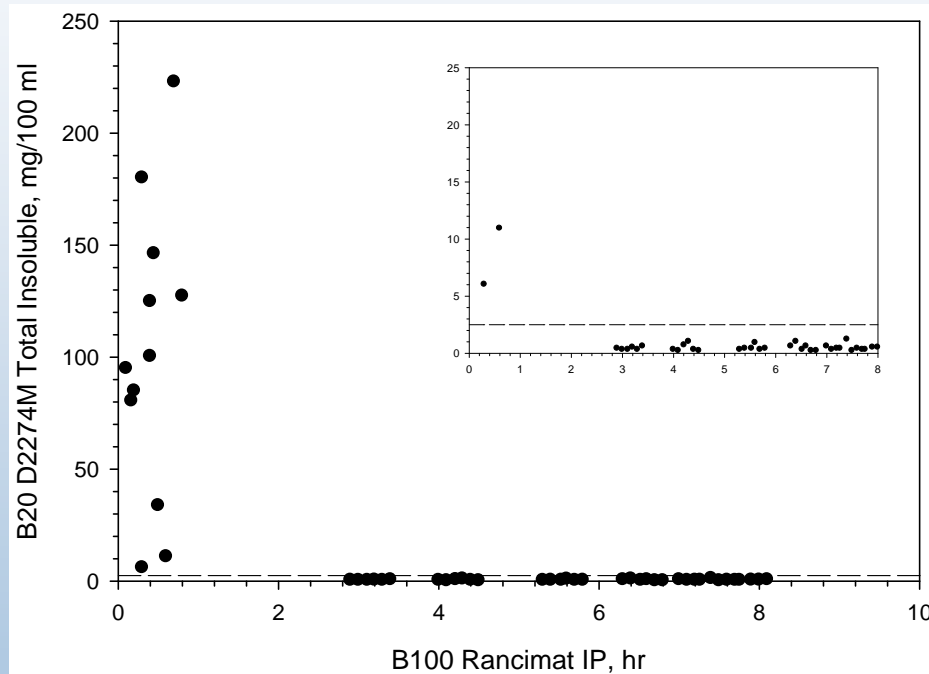
B5 High Temperature Stability



B5 blends are thermally stable if produced from oxidatively stable B100 (IP > 3 hr)

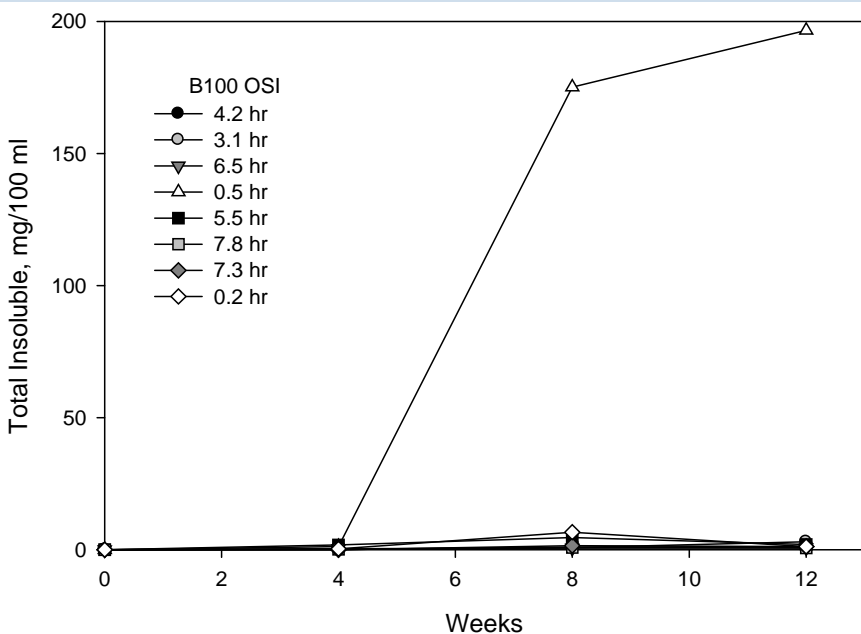
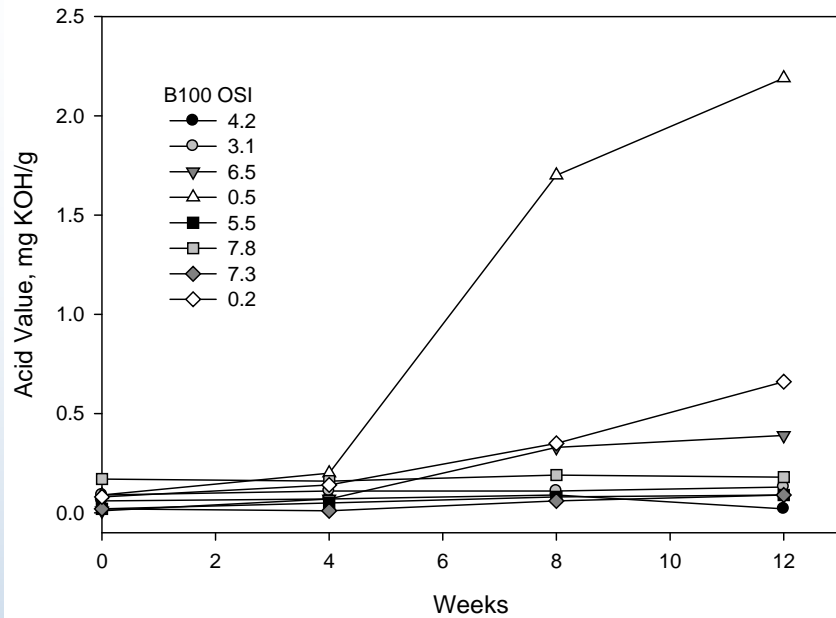
Impact of B100 Stability on B20 Stability: Accelerated Tests

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



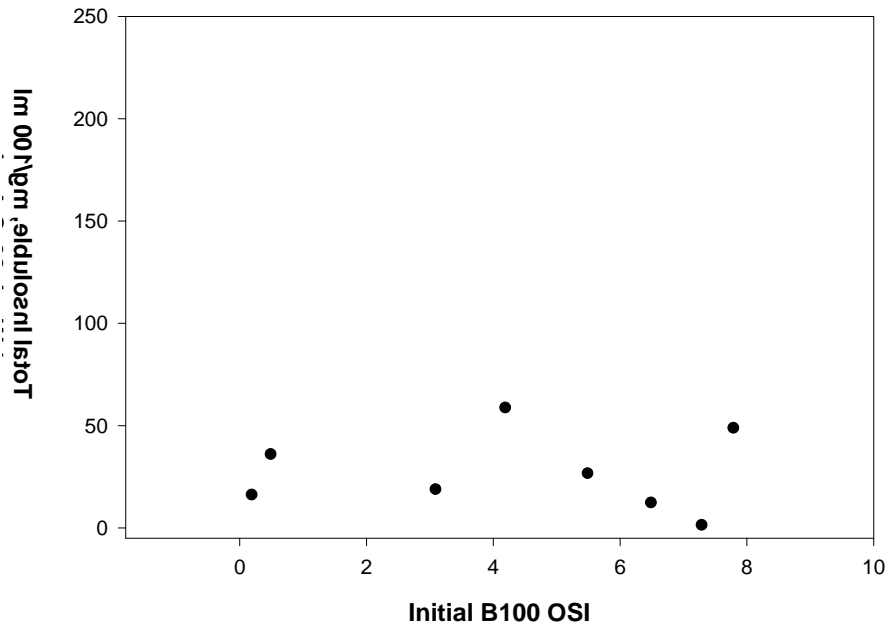
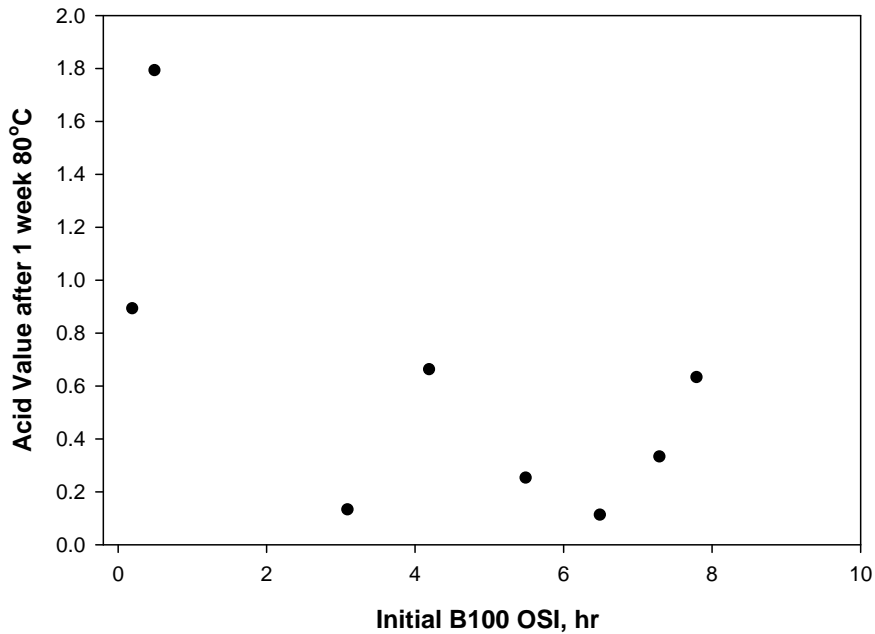
B100 stability appears to be an excellent predictor of blend stability, 3 hour IP ensures low deposits and 6 hr Rancimat in the blend (with one exception out of 48 samples)

B20 Blends Long Term Storage: D4625



- 12 weeks at 43°C, 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

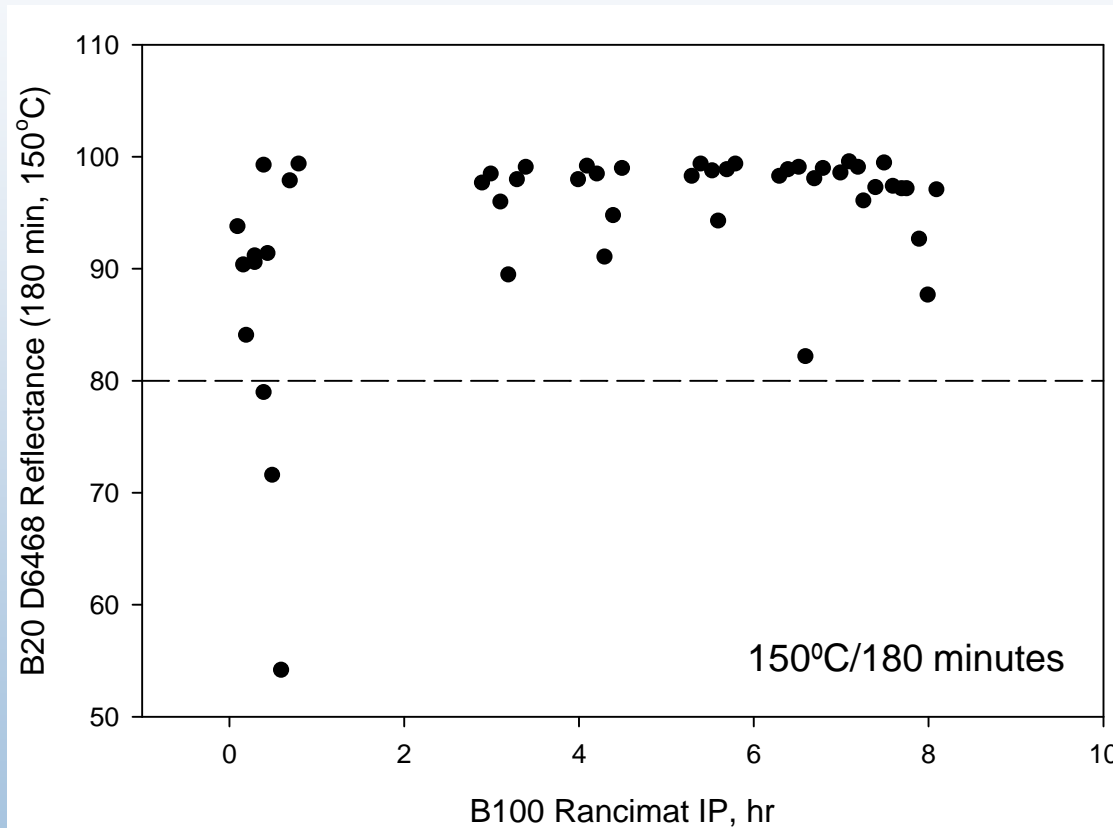
B20 Blends Fuel Tank Simulation



- 1 week at 80°C with ullage purge intended to simulate aging in vehicle tank
- Test does not appear to discriminate between stable and unstable blends for acid value or insoluble formation
- Caveat: new test, meaning uncertain

Diesel fuels produced up to 1 mg/100 ml on this test

B20 High Temperature Stability



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

Conclusions

- Blend stability is dominated by B100 stability – independent of diesel fuel stability, aromatic, or sulfur content
- Most B100 samples began to oxidize in storage, synthetic antioxidants and limited storage time recommended
- A 3 hr IP for B100 appears to be adequate to ensure stability of B5
- For higher biodiesel levels, measurement of blend stability would provide added user protection
- Conclusions apply to the specific test methods employed
- IP may need to be longer than 3 hr at point of production to insure stability at point of blending
- Hindered phenolic antioxidants prevented degradation of B100 and blends

Empirical Study of the Stability of Biodiesel and Biodiesel

Blends: <http://www.nrel.gov/docs/fy07osti/41619.pdf>

Biodiesel Stability Outcome

- 3 hr induction time requirement added to D6751 in January 2007 (D6751-07b)
- Cummins approves use of B20 in direct response:

“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>

Future Work

- Better define B100 degradation in storage:
 - D4625 for B100 over 4 weeks with weekly sampling for IP, PV, AV, and insoluble
- Tests with blends using commercial ULSD (previous samples acquired prior to October 2006)
- Tests to validate in actual storage and hardware
- Some in auto and oil industry will push to increase the induction time limit
- Other resources on stability and stability impacts:

McCormick, R.L., Ratcliff, M., Moens, L., Lawrence, R. “Factors Affecting The Stability Of Biodiesel In The United States” *Fuel Processing Technology* 88(7) 651-657 (2007).

Fang, H.L., McCormick, R.L. “Spectroscopic Study of Biodiesel Degradation Pathways” *SAE Technical Paper No.* 2006-01-3300 (2006).

Terry, B., McCormick, R.L., Natarajan, M. “Impact of Biodiesel Blends on Fuel System Component Durability” *SAE Technical Paper No.* 2006-01-3279 (2006).