Oxidation Stability of Biodiesel and Biodiesel Blends

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Steve Goguen and Dennis Smith, Managers

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Objectives

- Determine if B100 stability can be predicted by accelerated tests
- Determine if B100 stability is predictive of the stability of B5 and/or B20 blends
- Relate accelerated stability test results to more real world scenarios
- Recommend stability test methods and limits for B100, B20, and B5 blends

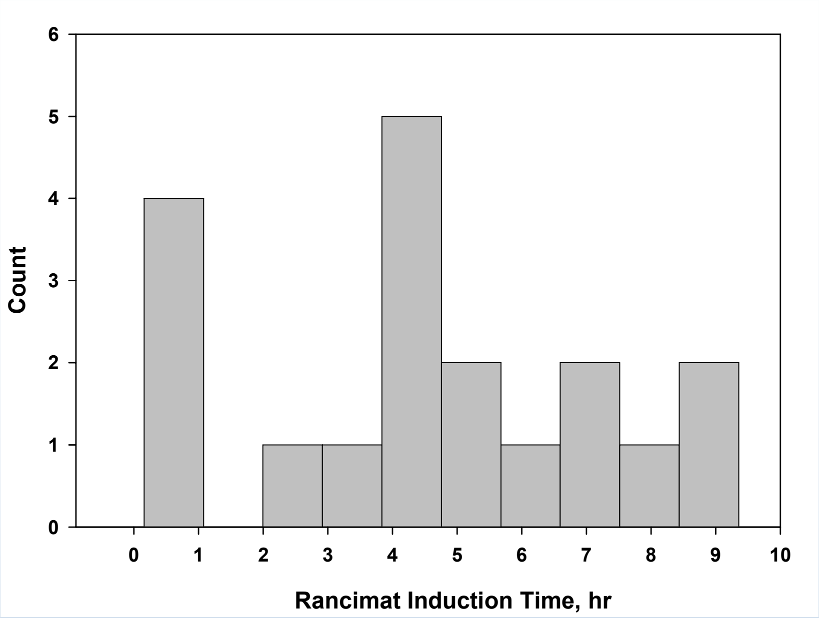
Stability Study Approach

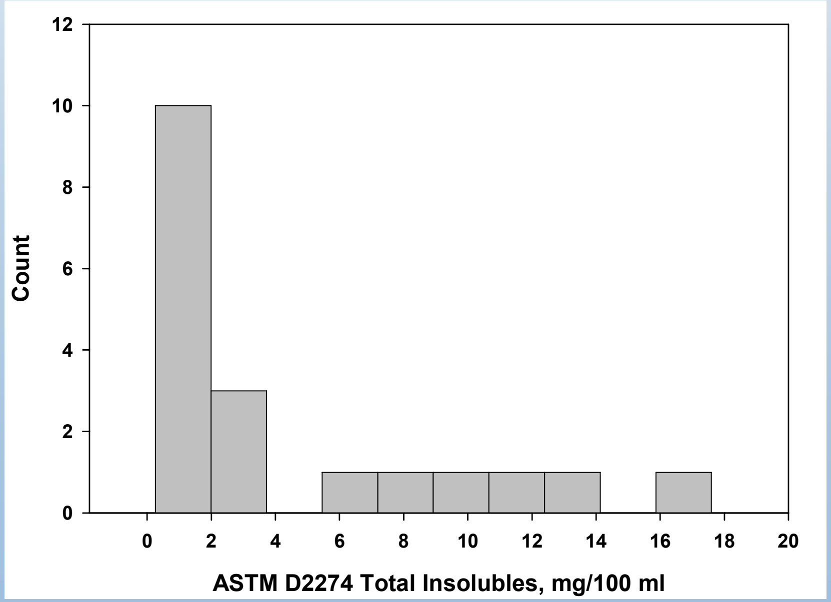
- Perform accelerated stability tests on 19 B100 samples covering the range available in US
- Select 8 B100 covering the range of stability for:
  - 12 week storage tests
  - Blending with 6 diesel fuels to produce 48 B5 and 48 B20 blends
  - Perform accelerated stability tests on the B5 and B20 blends
- Select 8 B5 and 8 B20 blends for:
  - 12 week storage test
  - One week test simulating fuel tank ageing
  - 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 - How long till oxidation starts?
  - Deposit formation – How much gum or deposit forms after oxidation for a fixed time?

B100 Stability





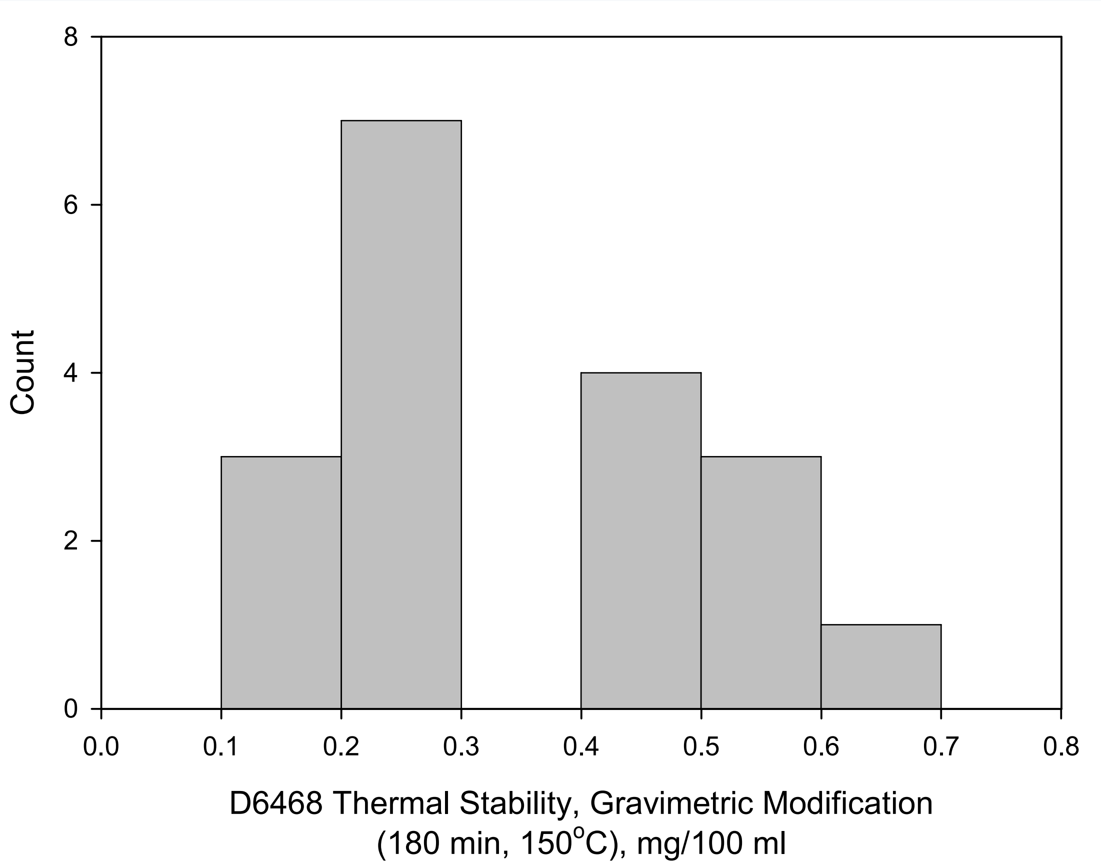
Induction Time

- Rancimat test, EN14112 (110°C/air)
- Measures induction time for volatile acid formation (hr)
  - May be related to resistance to oxidation or oxidation reserve, or time for start of deposit formation
- Included in European biodiesel quality specification

Deposit Formation

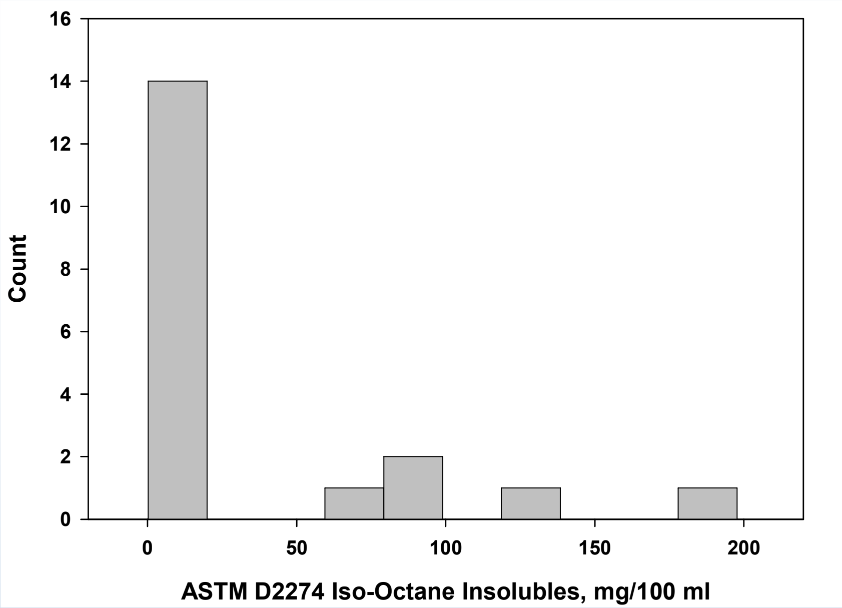
- ASTM D2274M (95°C/Oxygen/16 hr)
- Filter sample to measure insoluble formation
- Wash vessel and filter to measure gum formation
- Total insoluble=filterable+gum (mg/100 ml)
- Commonly used to specify diesel stability for pipeline transport

Thermal Stability

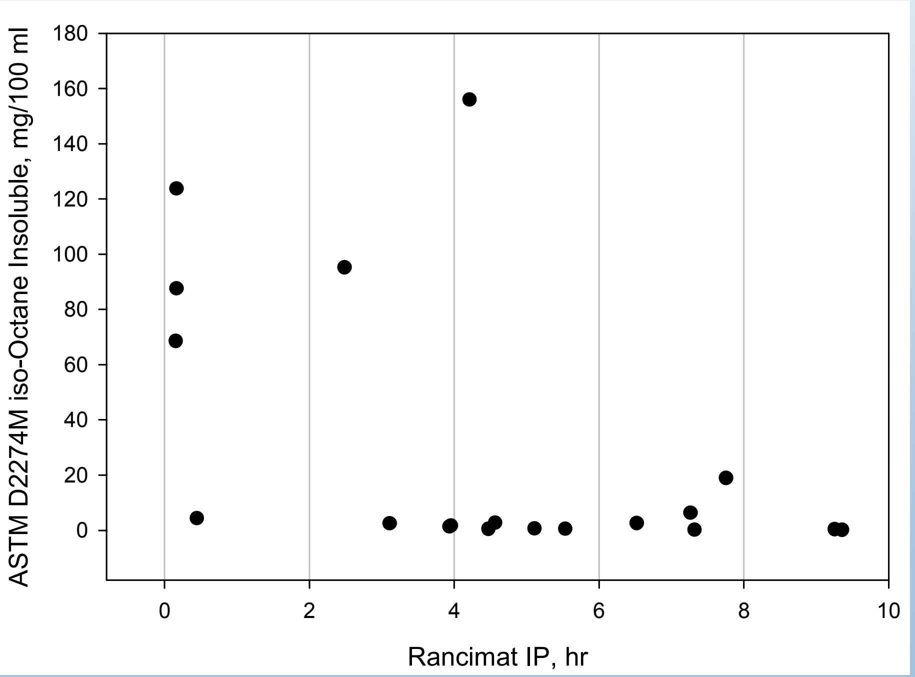


- Reflectance all over 90%
- B100 is thermally stable on this test
- Independent of oxidation stability

Distinguishing Stable and Unstable Samples

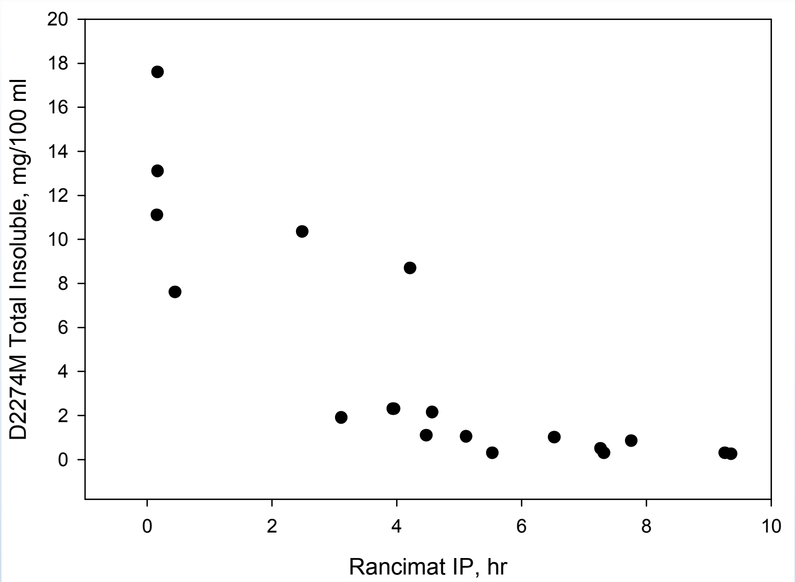


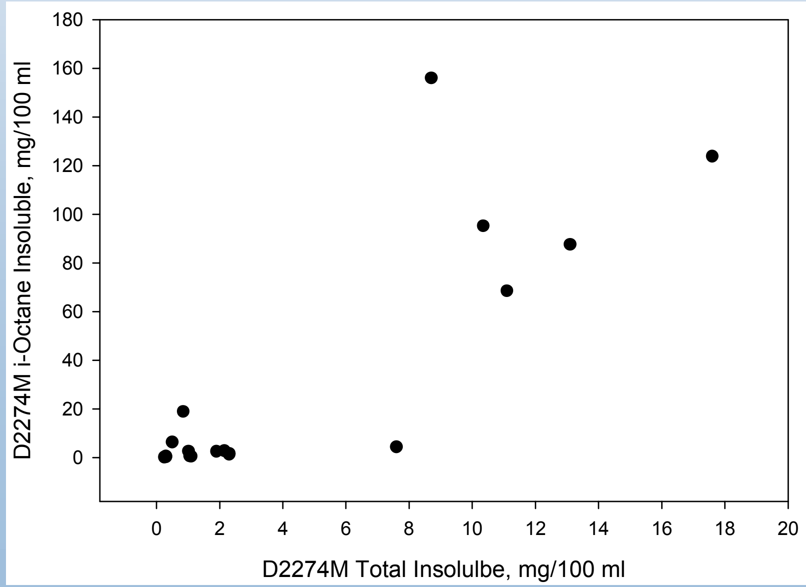
- i-Octane insoluble may be more predictive of what happens in diesel blends
- Bimodal distribution, 14 stable samples, 5 unstable



- There will be no big increase in i-octane insoluble if EN14112 (Rancimat) is above about 3 to 4

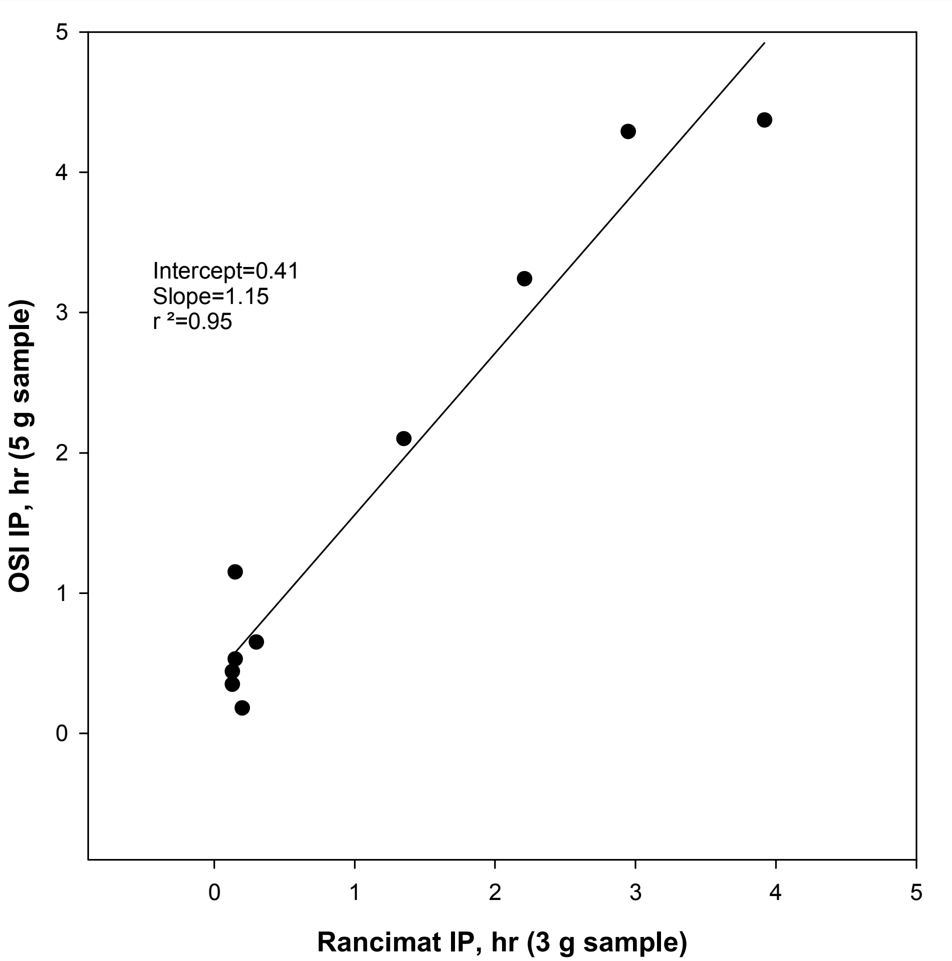
Correlation Between Methods for B100





- EN14112 IP and D2274 Total Insoluble
  - Approximate correlation
  - Rancimat of 3 – 4 hr ensures insoluble below 2.5 mg/100 ml (with one exception)
- Total Insoluble and i-Octane Insoluble
  - Samples with high total insoluble have high i-octane insoluble
  - If total insoluble is below roughly 2.5 mg, i-octane insoluble is low (limit may actually be as high as 7 to 8)

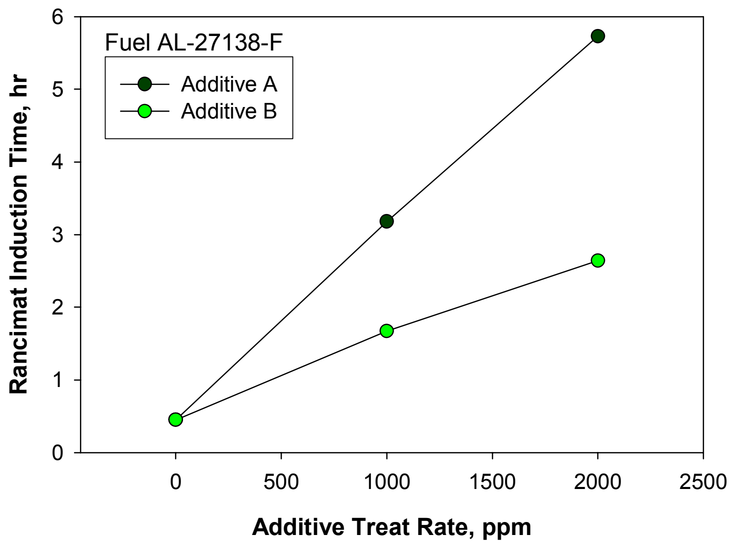
Rancimat vs OSI

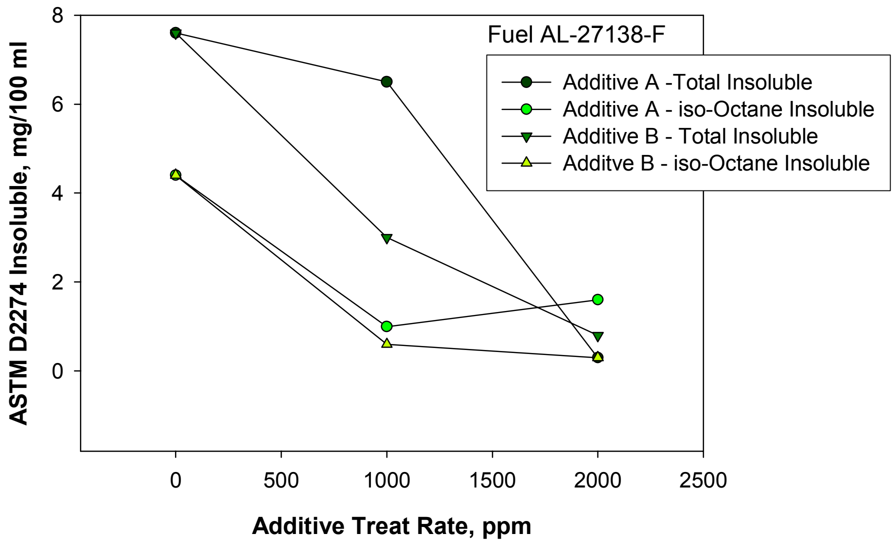


- Rancimat (EN14112) and OSI are similar instruments made by two different manufacturers
  - operate on identical principle
  - Bubbling air through sample, capturing volatile oxidation products in water, measuring change in water conductivity
- Results are similar but not identical
- With some OSI method refinement it seems likely that identical results could be obtained

Rancimat from Bosch, OSI from Eastman

Antioxidant Effectiveness





- Simple demonstration that AO can be effective for both induction time and deposits
- Ongoing work to determine impact on blends

B100 Downselection

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

	Feedstock	Rancimat	D525	D2274 Total	D2274 i-Octane
Observed Range:		0.2 – 9.4 hr	34 - >780 min	0.3 – 17.6 mg/100 ml	0.2 – 198 mg/100 ml
AL-27128-F	Canola	4.2 (med)	341 (med)	6.5 (med)	198 (high)
AL-27129-F	Palm Stearin	3.1 (med)	169 (med)	1.9 (low)	2.6 (low)
AL-27137-F	Soy	6.5 (high)	retesting	1.0 (low)	2.6 (low)
AL-27138-F	Soy	0.5 (low)	80 (low)	7.6 (med)	4.4 (low)
AL-27141-F	Soy	5.5 (high)	335 (med)	0.3 (low)	0.6 (low)
AL-27148-F	Grease	7.8 (high)	325 (med)	0.9 (low)	19 (med)
AL-27152-F	Rapeseed	7.3 (high)	418 (med)	0.5 (low)	6.4 (low)
AL-27160-F	Tallow	0.2 (low)	159 (low)	17.6 (high)	124 (high)

Additional B100 Properties

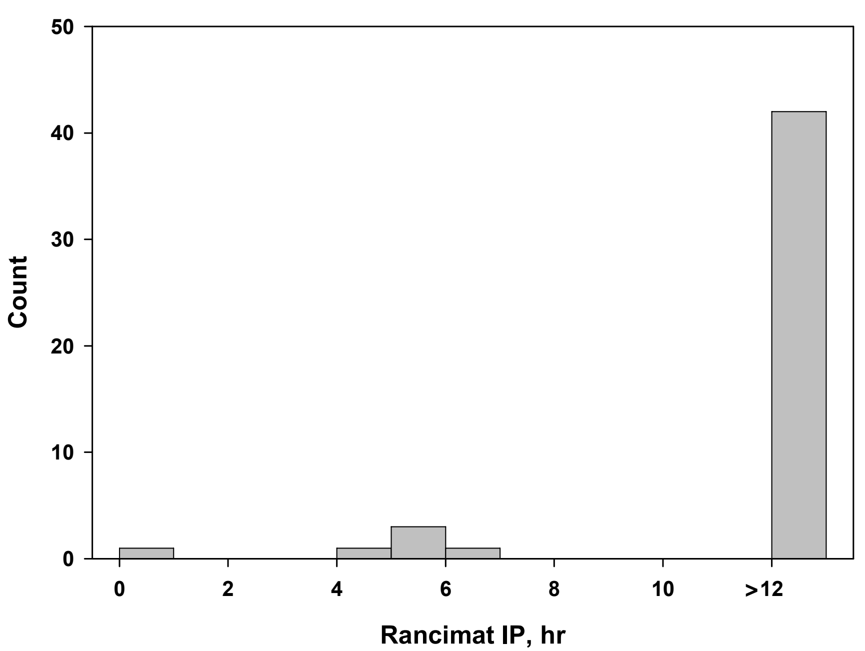
			AL-27128-	AL-27129-	AL-27137-	AL-27138	AL-27141-	AL-27148-	AL-27152-	AL-27160-I
Particulate Contamination	D 6217, mo	mg/l	14.7	0.2	103.9		3.5	19.5	5.1	17.6
Total Water	D 6304	ppm	656	217	149		131	118	298	1092
Flash Point	D 93	°C	160	177	179		152		169	178
Acid Number	D664	mg KOH/g	0.23	0.41	0.05	0.33	0.13	0.69	0.09	0.46
Free Glycerin	D6458	wt%	0.009	<0.001	0.002	0.002	0.005	<0.001	0.001	0.002
Total Glycerin	D6458	wt%	0.103	0.081	0.144	0.016	0.121	0.121	0.150	0.188
Elemental Analysis	D 5185	ppm								
	P		<1	<1	<1		<1	<1	<1	<1
	Na		<5	<5	<5		<5	<5	5	5
	K		<5	<5	<5		<5	<5	<5	<5
	Ca		1	<1	<1		<1	<1	<1	2
	Mg		<1	<1	<1		<1	<1	<1	<1
	Cu		<1	<1	<1		<1	<1	<1	<1
	Zn		<1	<1	<1		<1	<1	<1	<1
IsoOctane Insoluble	D 4625, mo	mg/100 ml	3.9	0.1	1.9		2.3	0.1	0.1	0.5
Peroxide Value	D 3703		217.28	105.33	12.8		98.21	8.78	43.84	17.18
Viscosity@40°C	D 445		4.45	5.12	4.10		4.09	4.67	4.47	4.86
Polymer Content	ISO 16931		2.63	0.17	0.82		1.03	1.46	2.17	4.91

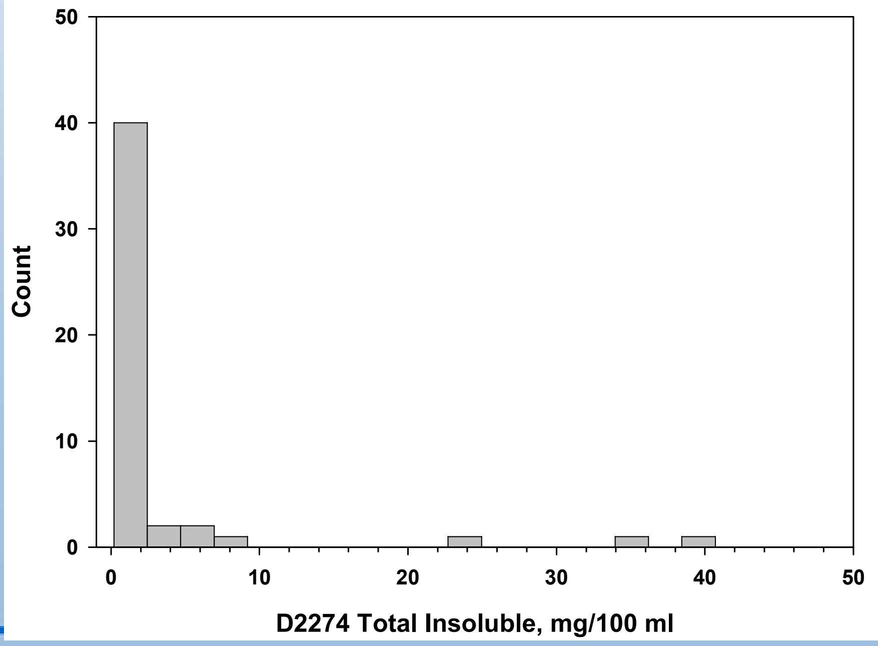
Diesel Fuel Properties

- 5 ULSD, 1 LSD
- Fuels that were available in Dec. 2005 – may not be fully representative of what ULSD will actually look like
- 3 ULSD look more like No. 1 fuels than No. 2

	Sample:	ASTM D975 Limit (No. 2 Diesel)	AL27150F	AL27151F	AL27166F	AL27171F	AL27175F	AL27176F
ASTM D93	Flash Point, ºC	52	56	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	T90, ºC	282 min 338 max	274	313	269	319	333	236
ASTM D524	Carbon Residue (10%), 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 D2274	Total Insolubles, mg/100 ml	none	0.25	0.25	0.5	0.2	0.1	0.05
ASTM D6468	Thermal Stability, 150ºC/180 min % Reflectance	none	100	100	100	--	95	100
ASTM D6217	Particulate Contamination, mg/L	none	0.5	0.4	0.8	0.8	1.2	0.3

Preliminary B5 Blend Data

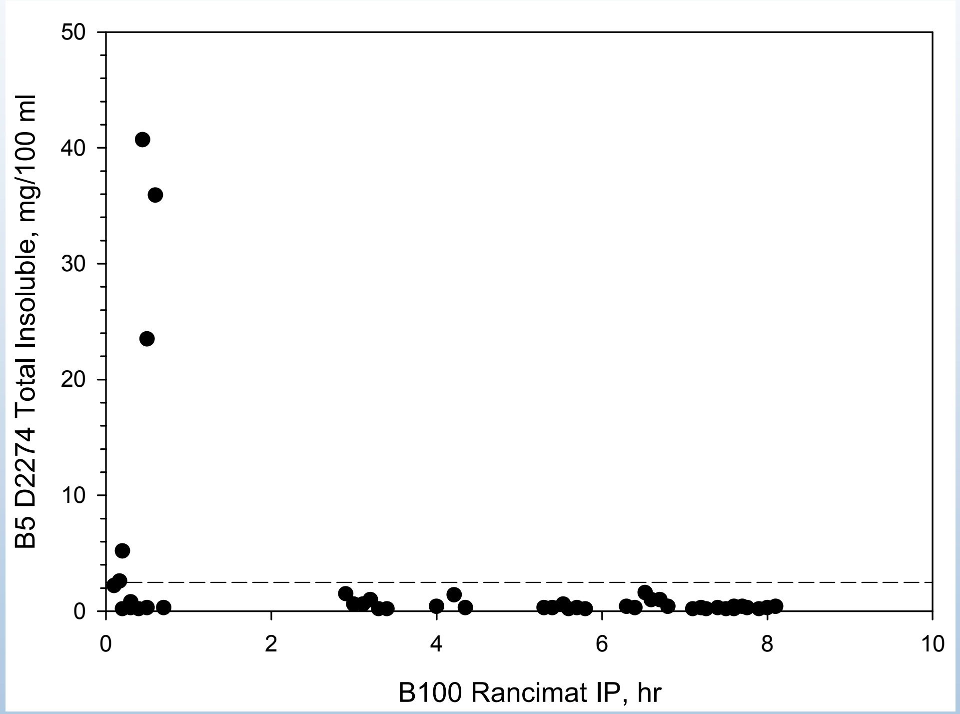


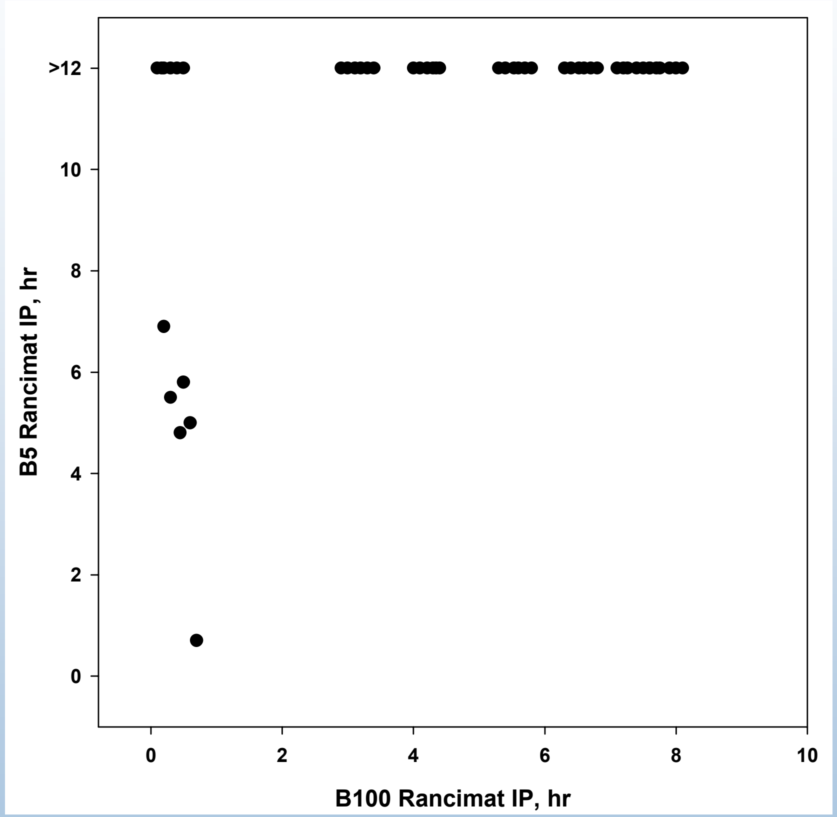


Most B5 samples highly stable for induction time or deposits

Can B100 Stability Ensure B5 Stability?

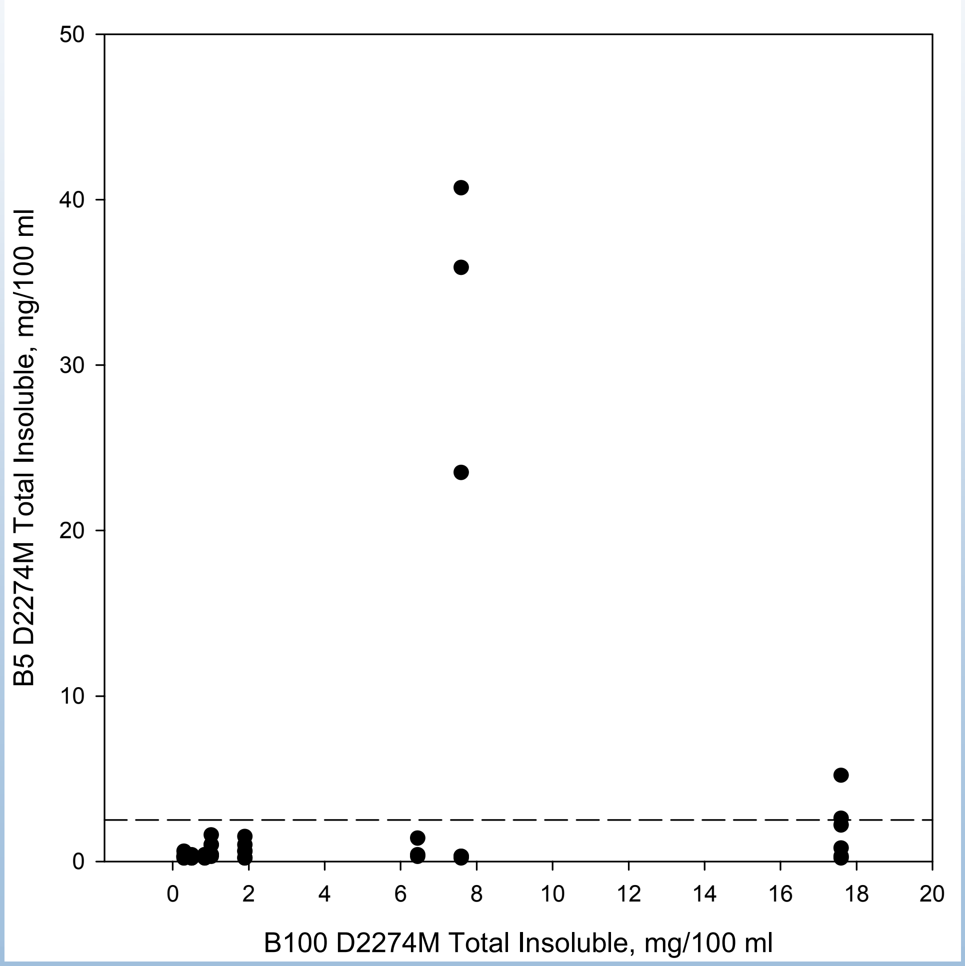
Note: data points artificially spread out so number of points is more evident





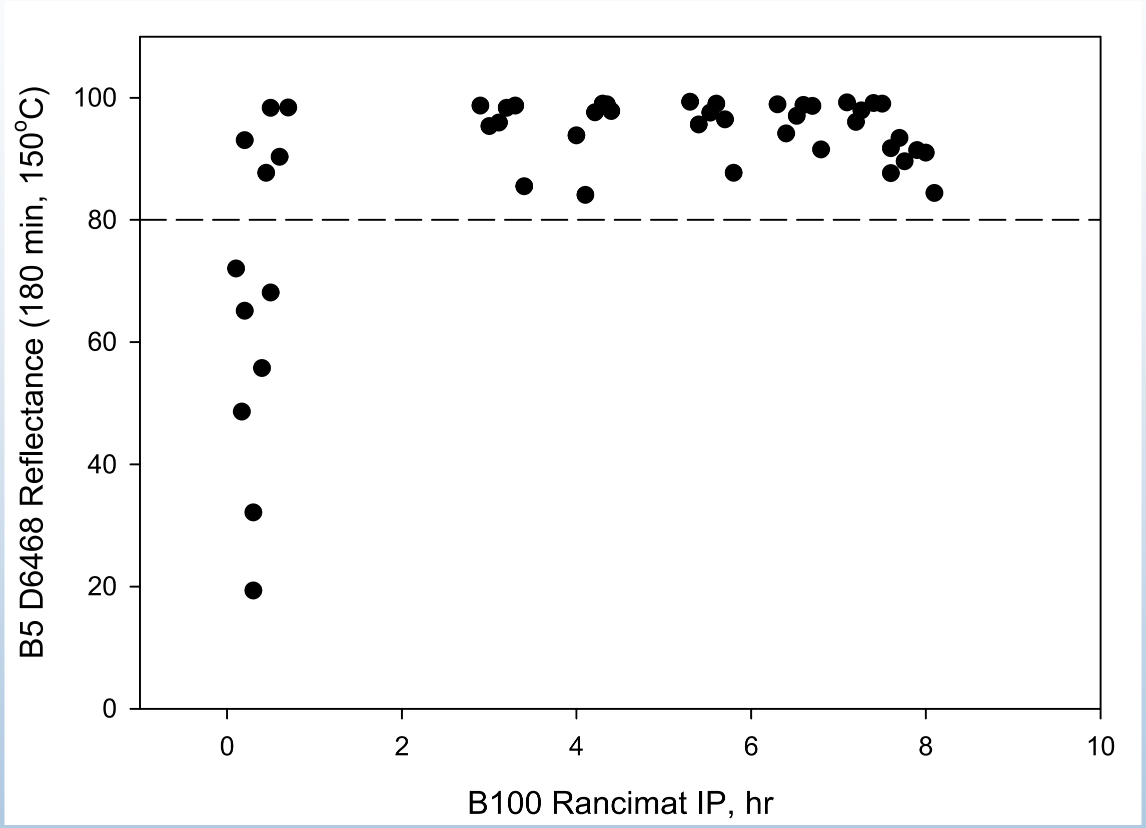
Yes, B100 stability appears to be an excellent predictor of blend stability, a Rancimat of 3 hr ensures low deposits and long induction time for the blend

Additional B5 Stability Data



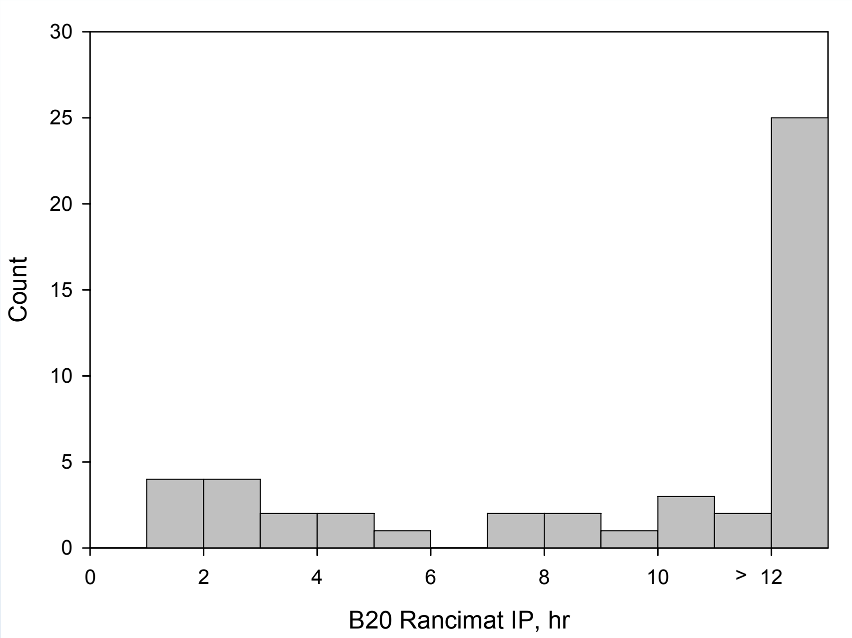
B100 samples producing less than 2.5 mg/100 ml on D2274M produce stable (<2.5 mg/100 ml) B5 blends

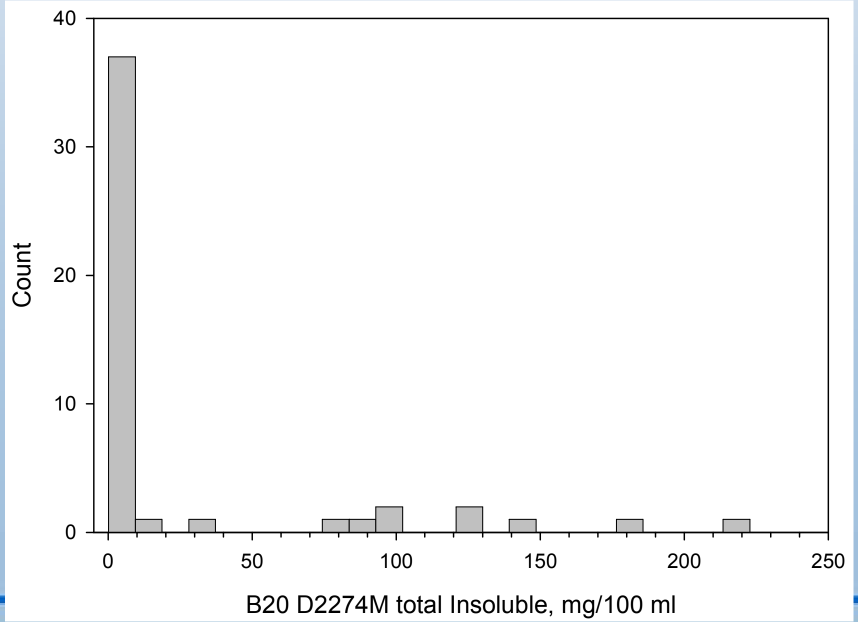
Additional B5 Stability Data



B5 blends are thermally stable if produced from oxidatively stable B100

Preliminary B20 Results

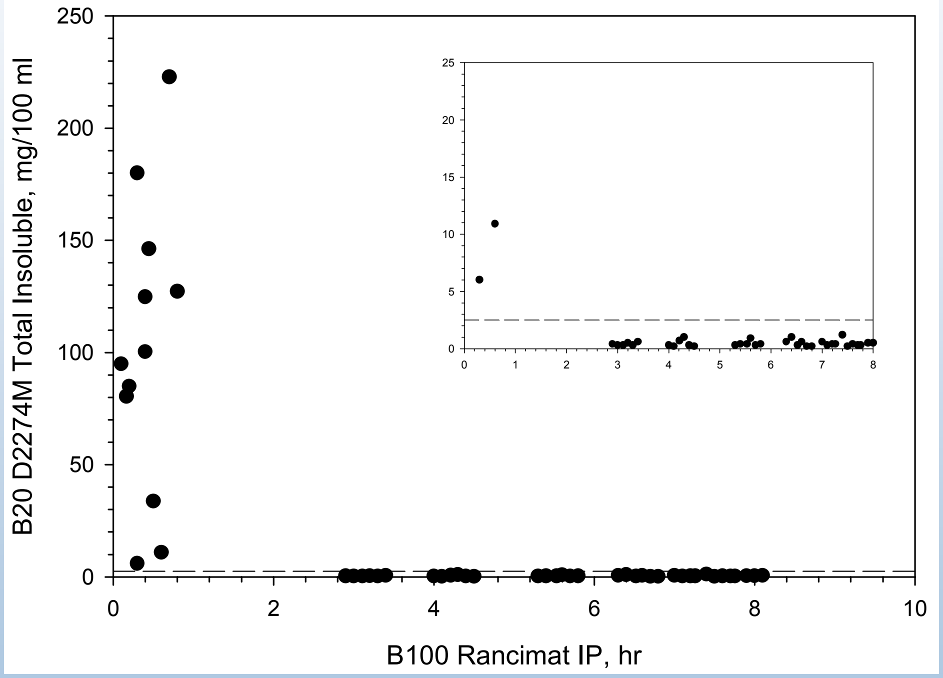


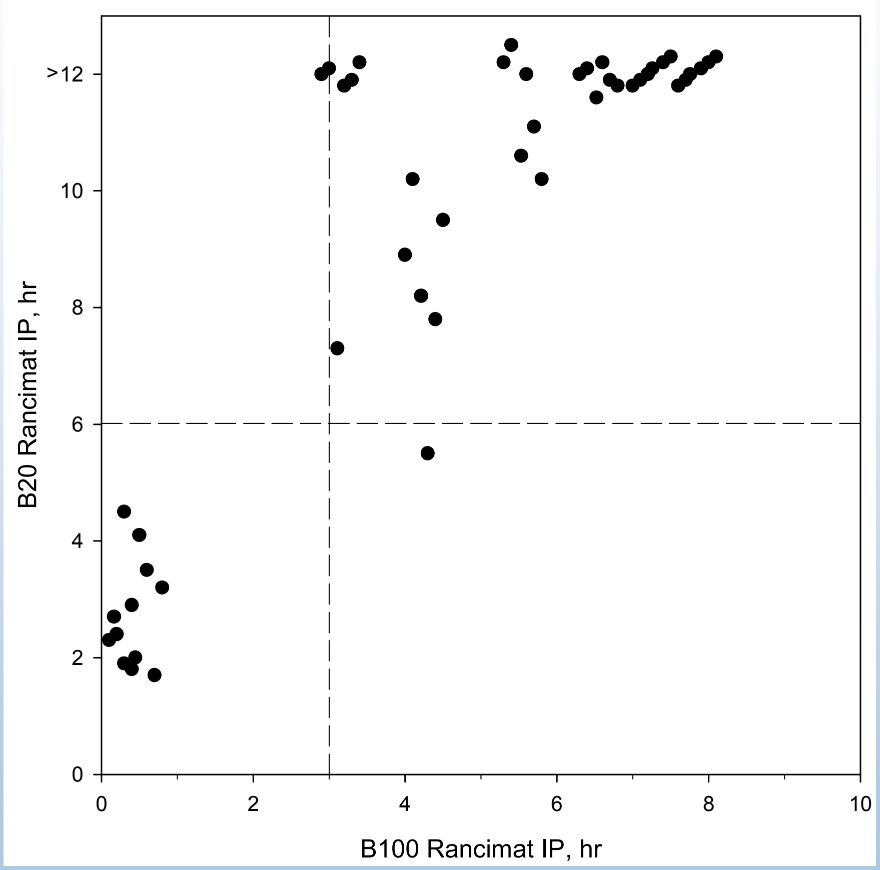


- Most samples are stable, but a range of stability is observed
- Consistent IP and deposit results

Can B100 Stability Ensure B20 Stability?

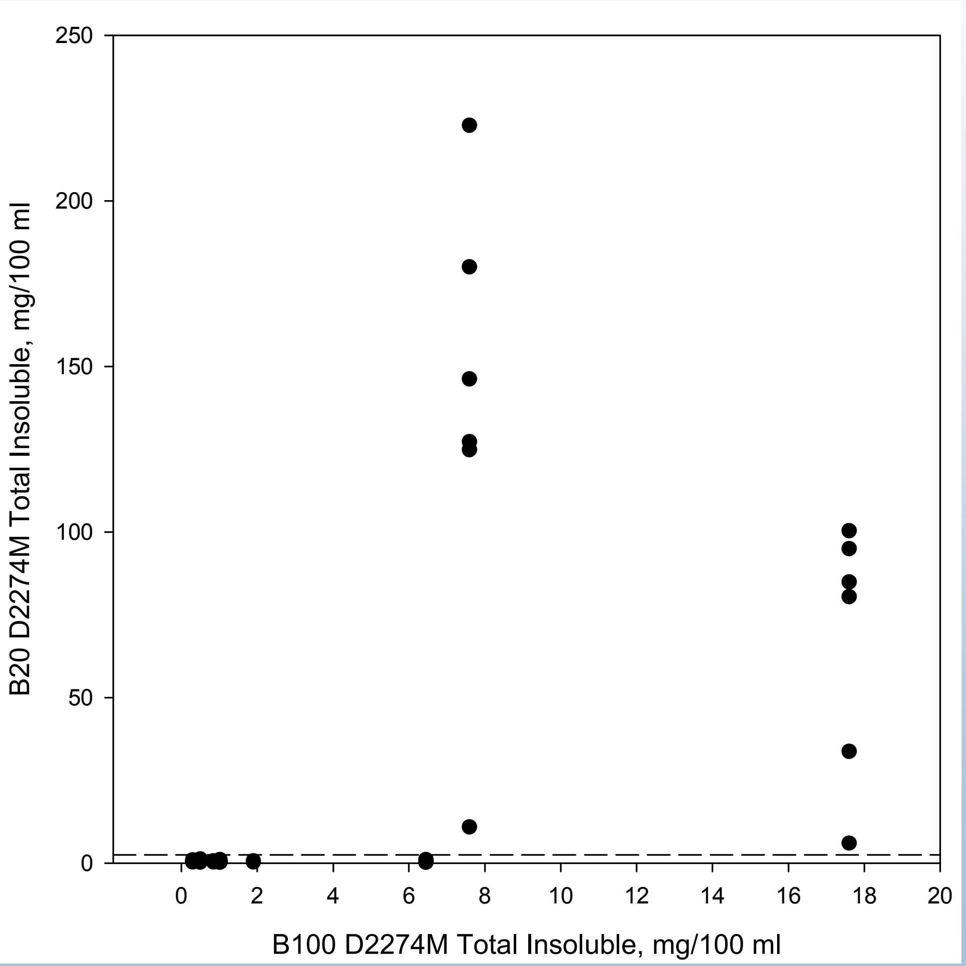
Note: data points artificially spread out so number of points is more evident





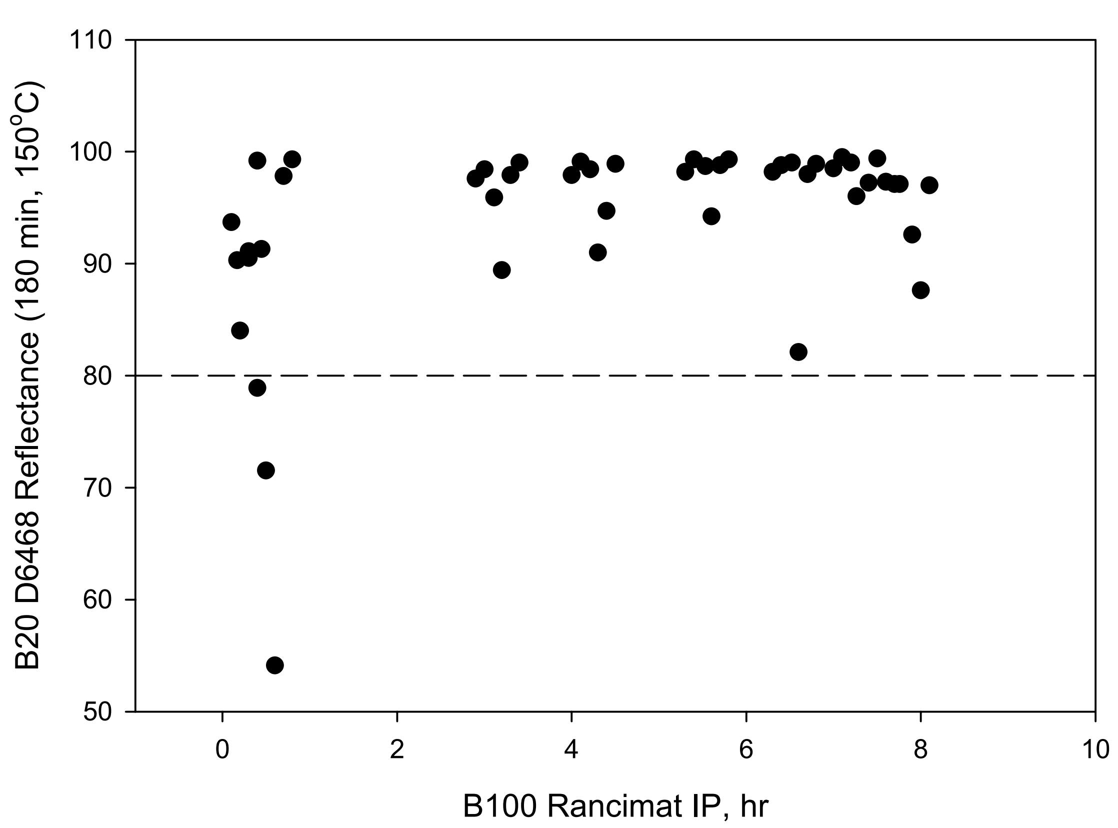
Yes, B100 stability appears to be an excellent predictor of blend stability, 3 hour Rancimat ensures low deposits and 6 hr Rancimat in the blend (with one exception out of 48 samples)

Additional B20 Stability Data



B100 samples producing less than 2.5 mg/100 ml on D2274M produce stable (<2.5 mg/100 ml) B20 blends

Additional B20 Stability Data



B20 blends are thermally stable if produced from oxidatively stable B100

Tentative Conclusions

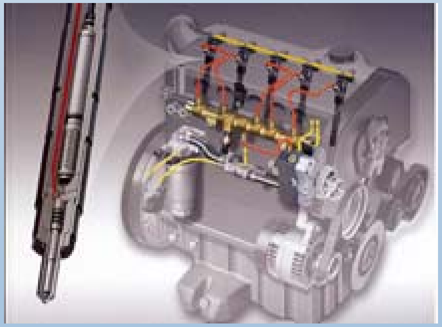
- Blend stability is dominated by B100 stability
- A 3 hr Rancimat IP for B100 appears to be adequate to ensure stability of both B5 and B20 blends
  - IP may need to be longer than 3 hr at point of production to insure stability at point of blending
- It is likely that OSI can be an alternative method to Rancimat
- Currently also investigating D525 as alternative

What is missing?

- Only accelerated stability test data reported to date
- Need results of more realistic tests

Ageing Scenarios

1. In storage and handling
   – Applies to B100 and blends
2. In vehicle fuel tank
   – Recirculation at low fuel level
   – Applies to biodiesel blends only
3. Ageing in high temperature engine fuel system
   – Deposit formation from unstable or pre-aged fuel
   – Applied to biodiesel blends only



Tests to Simulate Ageing Scenarios

1. *Ageing in storage:* D4625
   - Quiescent ageing at 43C for 12 weeks
   - Measurement of total insoluble plus other fuel properties
2. *Vehicle tank ageing:* D4625 (heavily modified)
   - Quiescent ageing at 80C 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 ageing*
   - Quiescent ageing at 80C for 1 week (as above)
   - Followed by ASTM D6468 at 150C/180 min/350 ml sample size
   - Gravimetric measurement of insoluble plus other fuel properties

Summary and Future Work

- Preliminary data suggests that ensuring B100 stability might also ensure the stability of B5 *and* B20 blends
- Realistic simulation tests are ongoing, anticipate full report published by October 2006

B100 results are available here:
http://www.nrel.gov/vehiclesandfuels/npbf/pdfs/39721.pdf

This presentation will also be posted on NREL's website within a few weeks