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B50 and B100 Re-additization for Prolonged Storage

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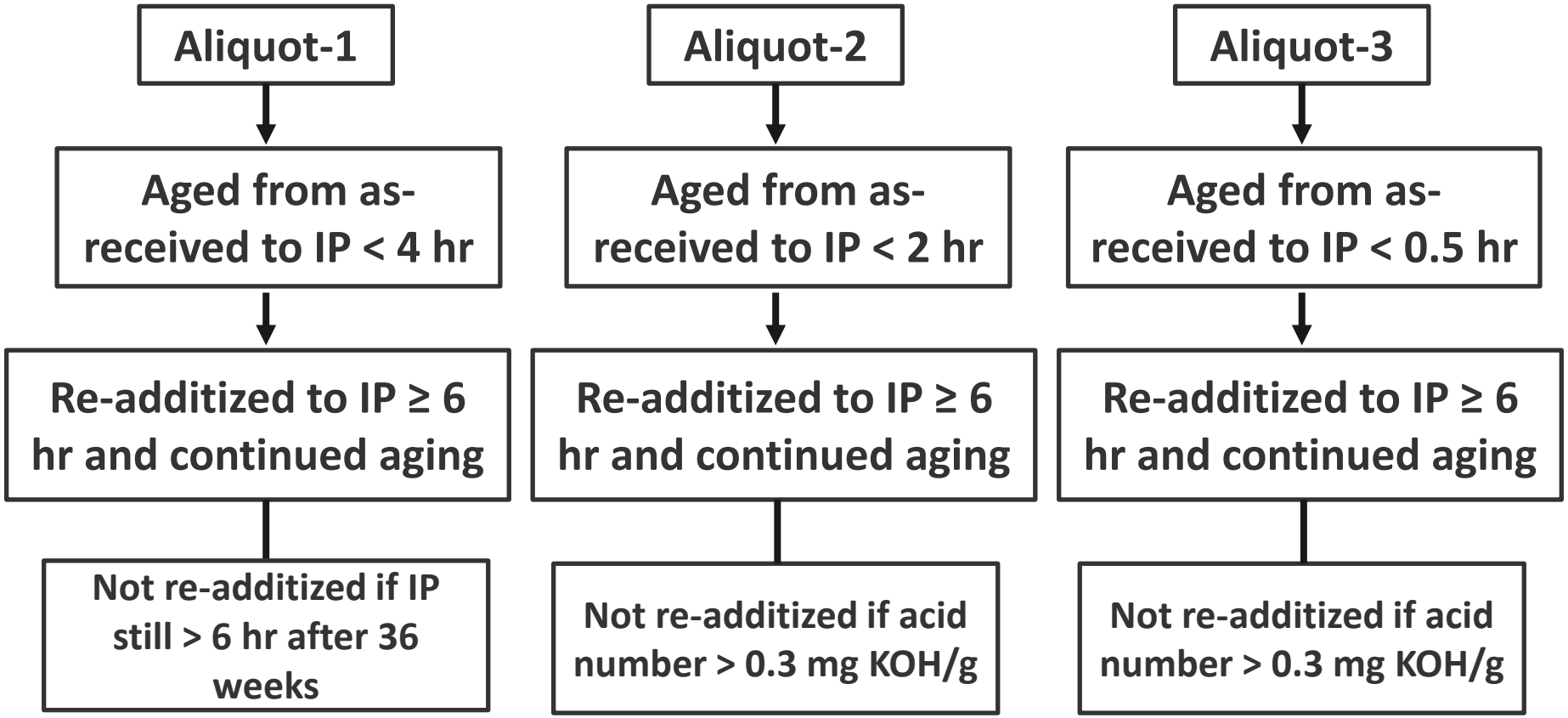
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Previous B20 Readd Study

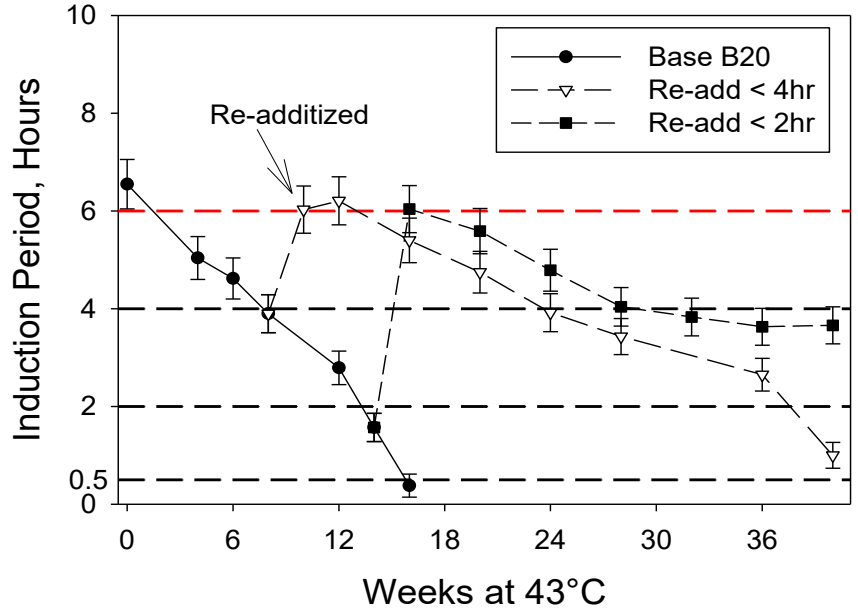
- Designed study based on previous work on B20 from 2018
- New study will investigate B50 blends rather than B20 blends

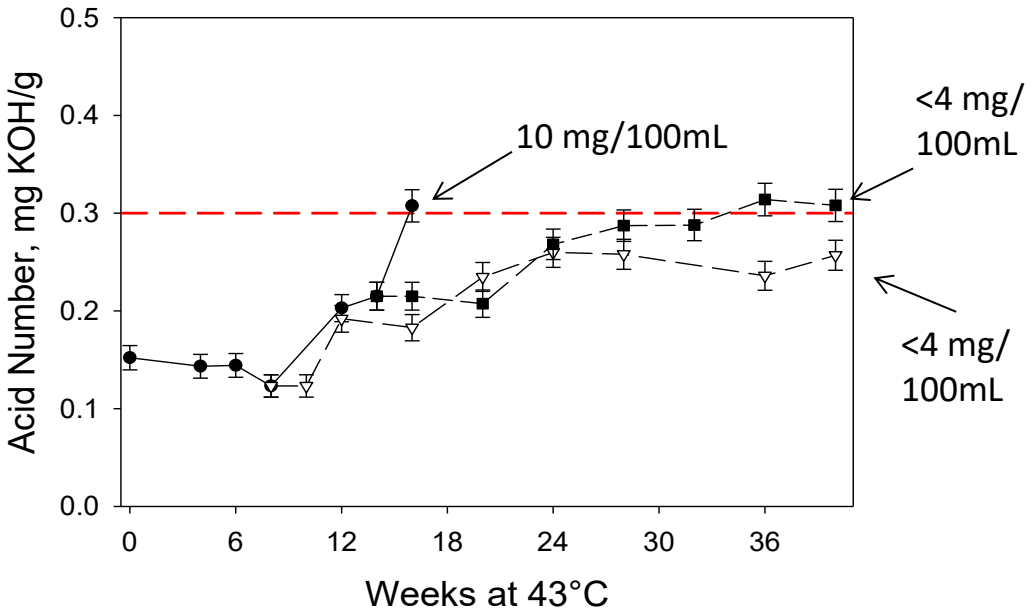
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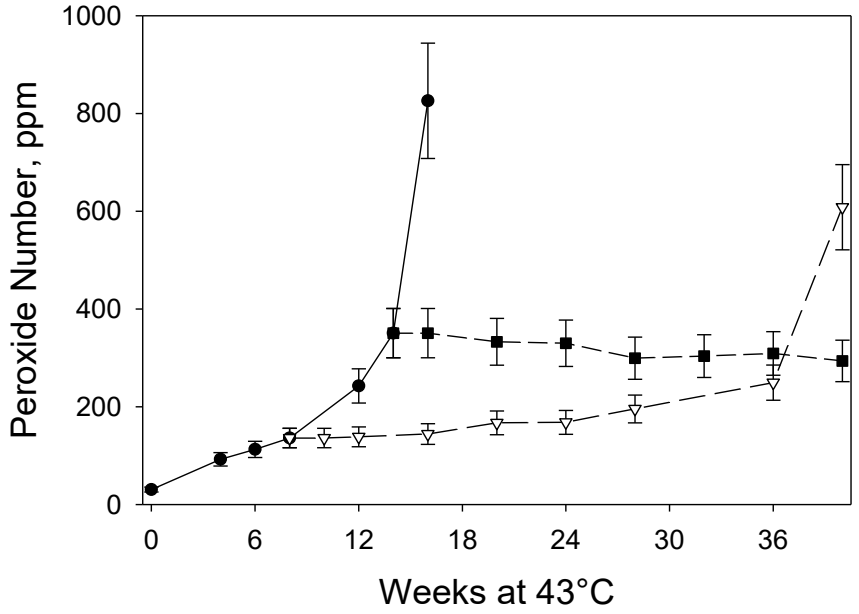
As-received B20 subdivided into 3 separate aliquots



Re-Additization of Just on Spec B20







- 16 months potential storage time without re-add
- Re-add at 4 hr, > 40 months – more than 3 years
- Re-add at 2 hr ~ 36 months

Christensen, E., Alleman, T.L., McCormick, R.L. "Re-additization of commercial biodiesel blends during long-term storage" Fuel Proc Techn 177 56-65 (2018).

New B100 and B50 Study

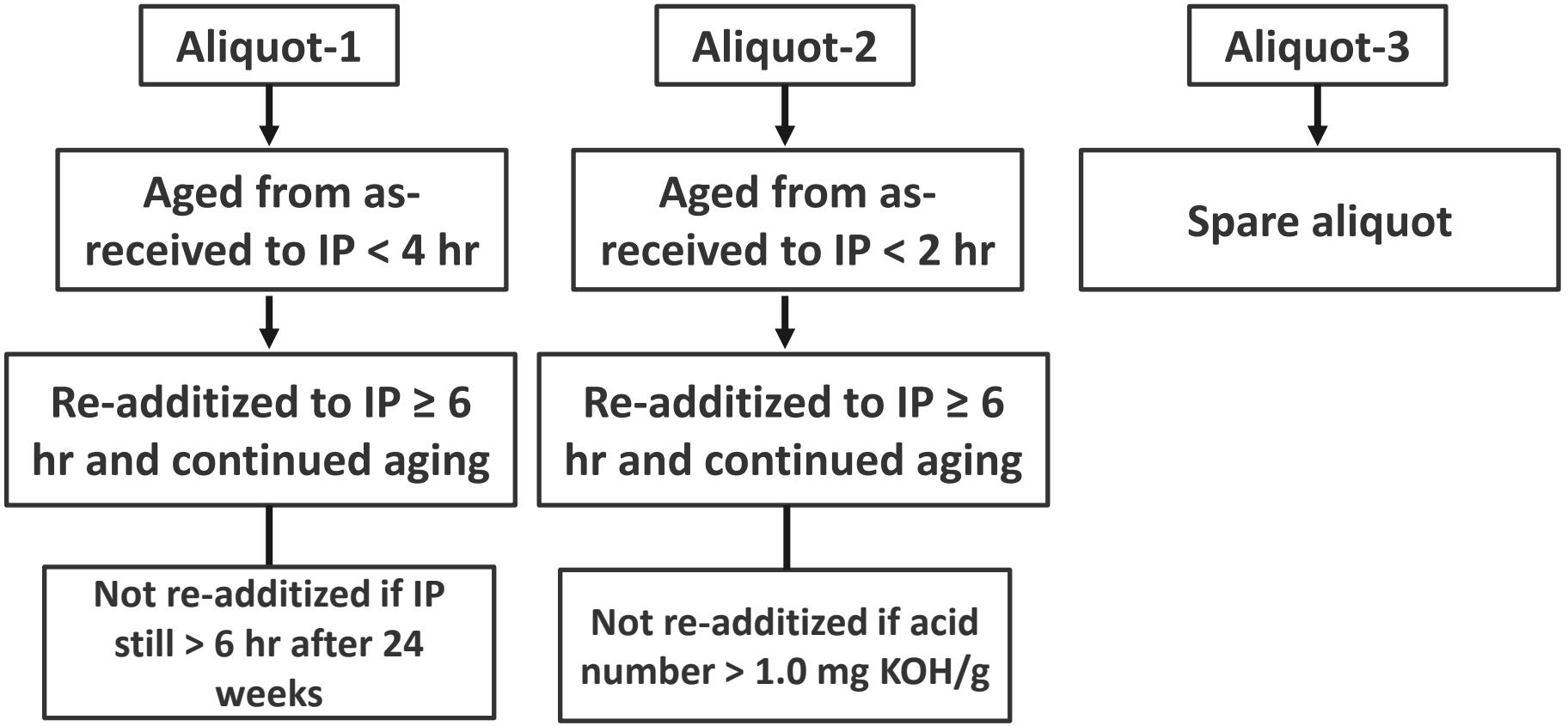
Phase 2: Re-additization

- B50 samples chosen from those tested in Phase 1
  - Fuels stored during Phase 1 under nitrogen at room temperature
- Aging for up to 24 weeks (2 years simulated storage)
  - IP, TAN, peroxide run on samples taken from D4625 jar at 2 week intervals
  - Total insoluble at end of test
- Re-additization up to 6 hr Rancimat induction time when aging samples reach 4 hr and 2 hr
- Antioxidant used is BHT

Phase 2 – New Readd Study

- Used same samples received for Phase 1 long-term storage stability study (previous presentation)
- Selected 4 B100 and 1 B0 for preparation of B50 blends

As-received samples subdivided into 3 separate aliquots

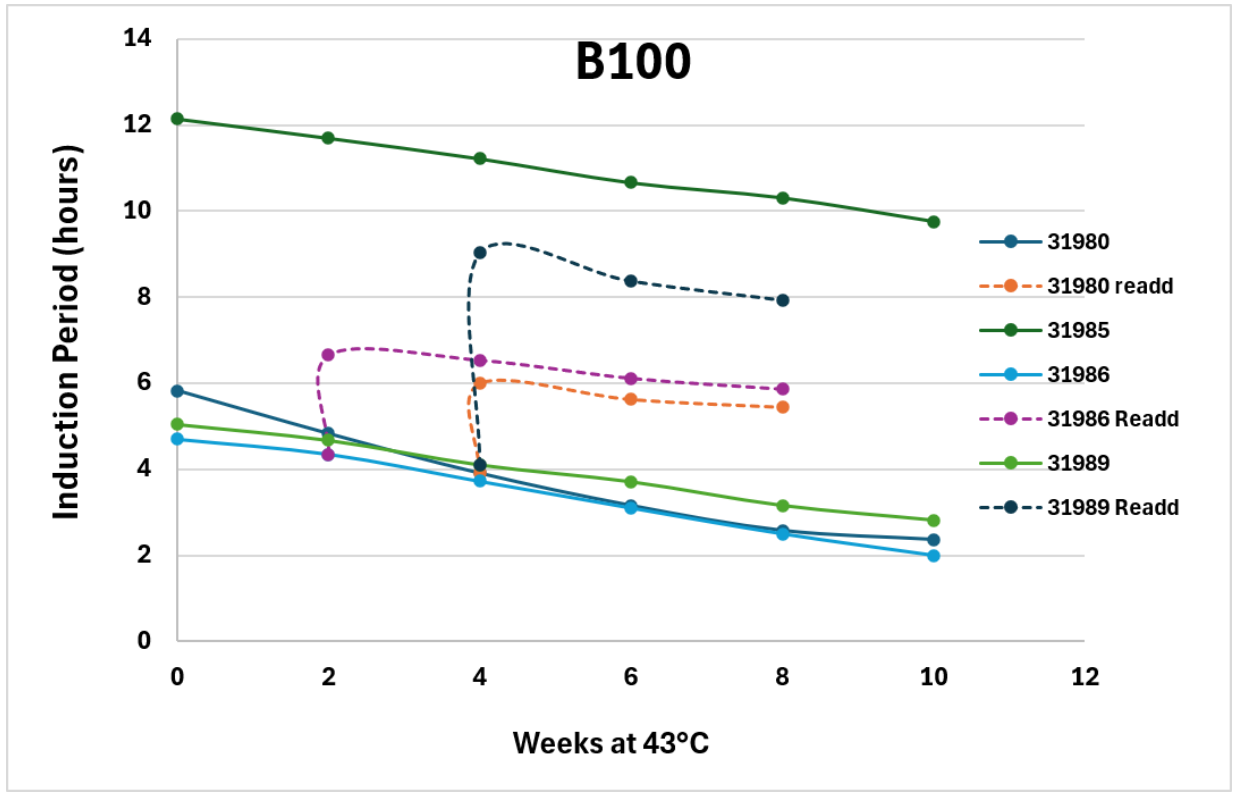


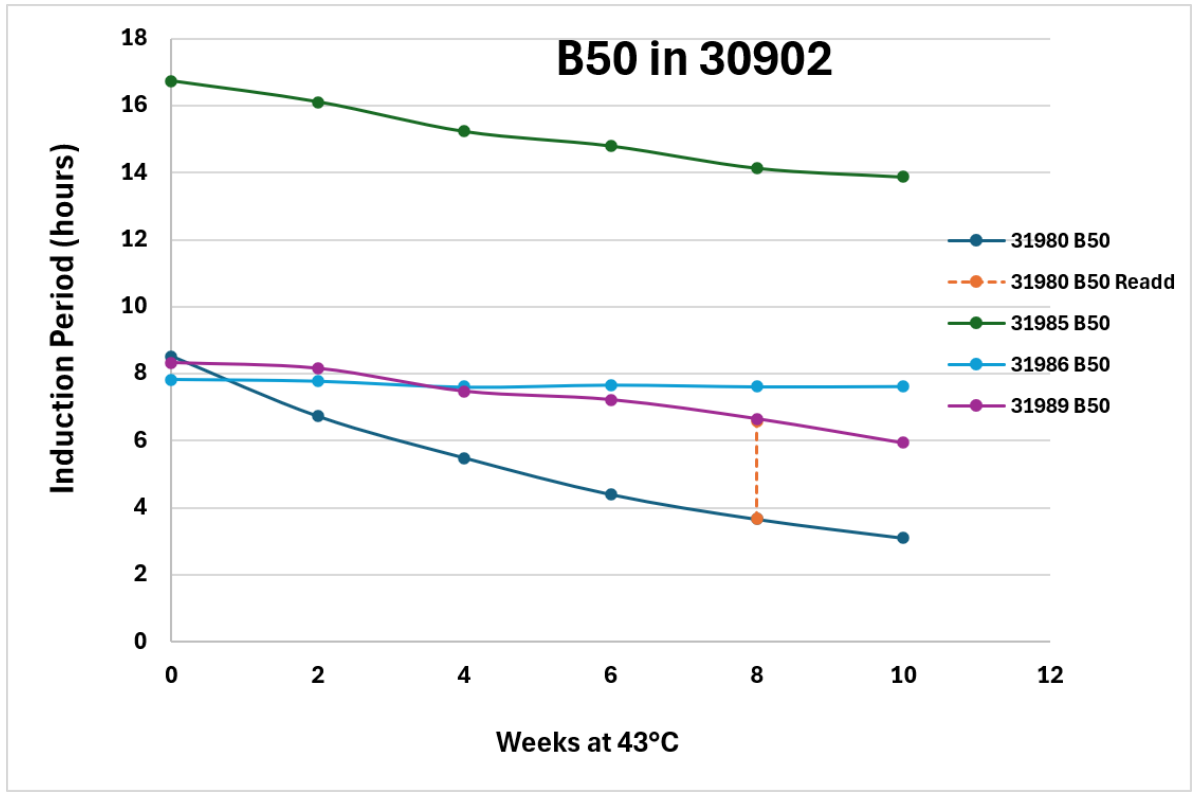
Final Selection – Phase 2 B100

- Three with high IP (14, 11.4, 10.8)
- Two with medium IP (9.2 and 5.7)
- Two with low IP (4.8 and 2.8)
- Cloud point from -4 to 7
- TAN from 0.07 to 0.43
- B0 used for Phase 2 was 30902

CAN#	S ppm	CSFT, s	FP, °C	Viscosity, cSt	CP, °C	TAN, mg KOH/g	TG, wt%	Mono G, wt%	P, ppm	T90, °C	Na+K, ppm	IP, hr
31980	0.5	95	115	4.028	-1	0.07	0.098	0.349	0.41	351	0.1	5.7
31981	6.8	118	153	4.498	2	0.43	0.129	0.312	0.36	353	0.8	10.8
31985	1.3	99	177	4.248	-4	0.26	0.018	0.048	0.23	352	0.3	11.4
31986	6.7	96	165	4.097	2	0.09	0.024	0.068	0.78	350	0	2.8
31987	14.6	101	157	4.585	1	0.25	0.111	0.349	0.43	354	0.8	4.8
31989	3.0	123	175	4.305	7	0.29	0.028	0.098	0.73	349	0.1	9.2
32812	11.0	109	145	4.474	1	0.41	0.096	0.330	0.27	354	0.6	14

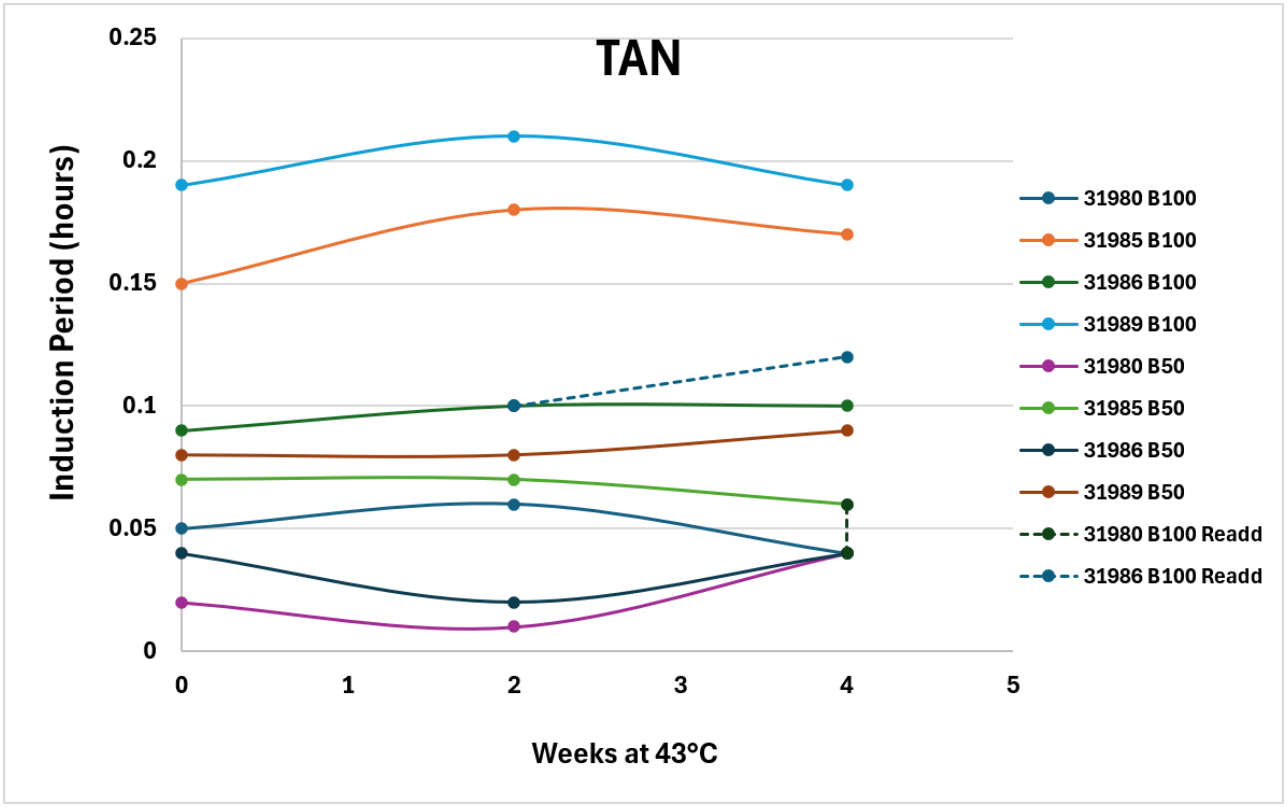
B100 and B50 Rancimat

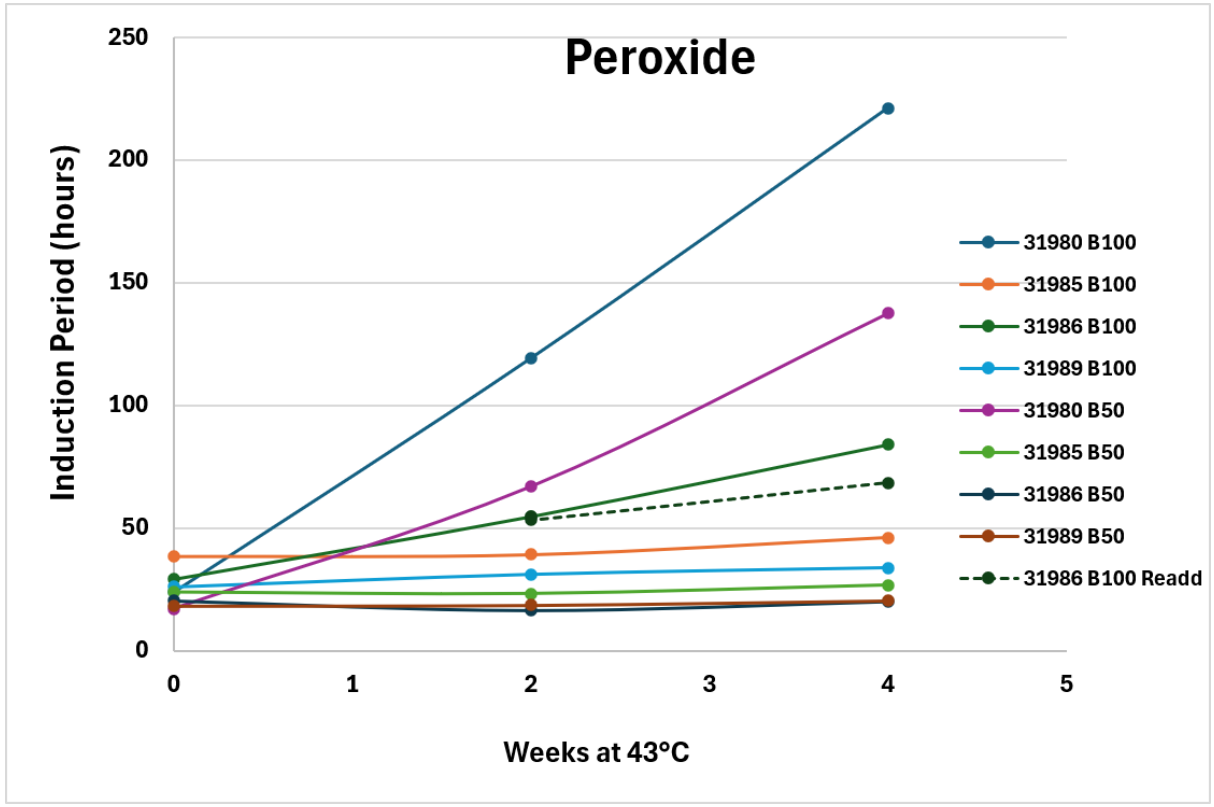




- Three of four B100 have been readditized as of week 10
- One B50 has been readditized as of week 10
- Treat rates ranged from 150 ppm up to 1200 ppm of BHT to achieve 6-hour Rancimat

TAN and Peroxide Results





- TAN and peroxide measurements completed through 4 weeks
- Starting to see peroxide formation for 31980 as B100 and B50 (was lowest stability sample in Phase 1)
- TAN is still very low for all samples

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Thank you!

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Key measurements for oxidation stability

- Rancimat induction time
  - Requires several hours to run
  - Used as a requirement in ASTM standards to address shelf life and long-term storage of biodiesel and biodiesel blends
- ASTM D4625 accelerated aging
  - Requires many weeks, simulates nominal storage conditions
  - Monitor Rancimat induction time, peroxide formation, acid number, and insoluble formation as the fuel ages

Rancimat Induction Time

- A measure of oxidation reserve:

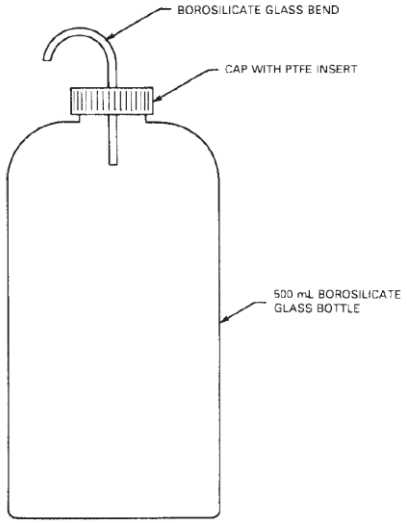
$$\propto \frac{Antioxidant\ Concentration}{Radical\ Initiator\ Concentration + Bisallylic\ Site\ Concentration}$$

- 110°C, high flowrate of bubbling air
  - Highly accelerated conditions – both high T and high oxygen availability
  - When induction time is reached, oxidation chain reaction begins forming volatile acid products
  - Volatile acids carried out by the air into a water vial, with conductivity detector
- Used in ASTM standards for biodiesel and biodiesel blends to address shelf life and long-term storage



D4625 Aging

- ASTM D4625 Standard Test Method for Middle Distillate Fuel Storage Stability at 43°C (110°F)
- 400 mL of fuel held for weeks (1 week nominally equivalent to 1 month in clean dry storage at ambient temperature)
- Open to air via “U”-tube
- Method as written measures insoluble by filtration at the end of the test, separate jar at each time
- We measure Rancimat, peroxide, TAN by withdrawing sample

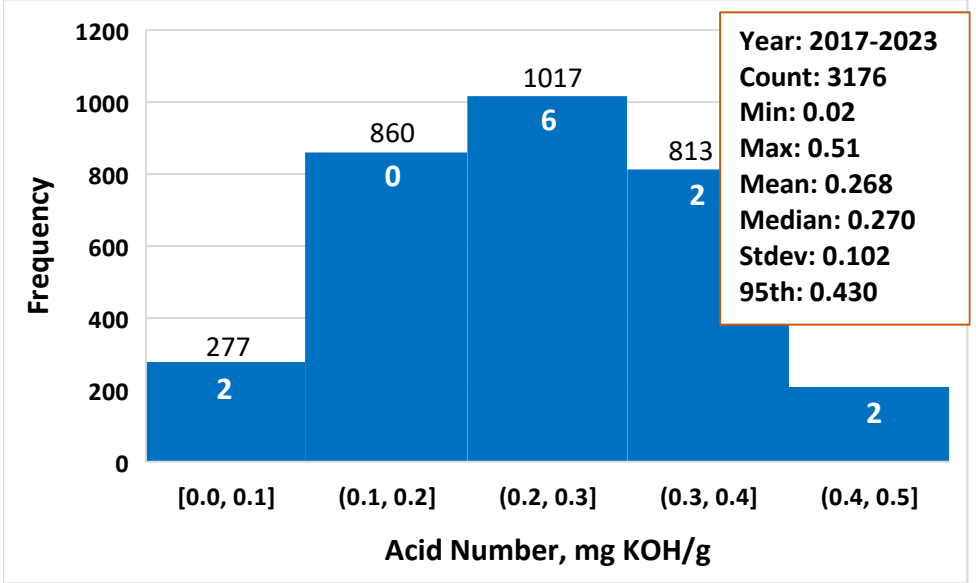


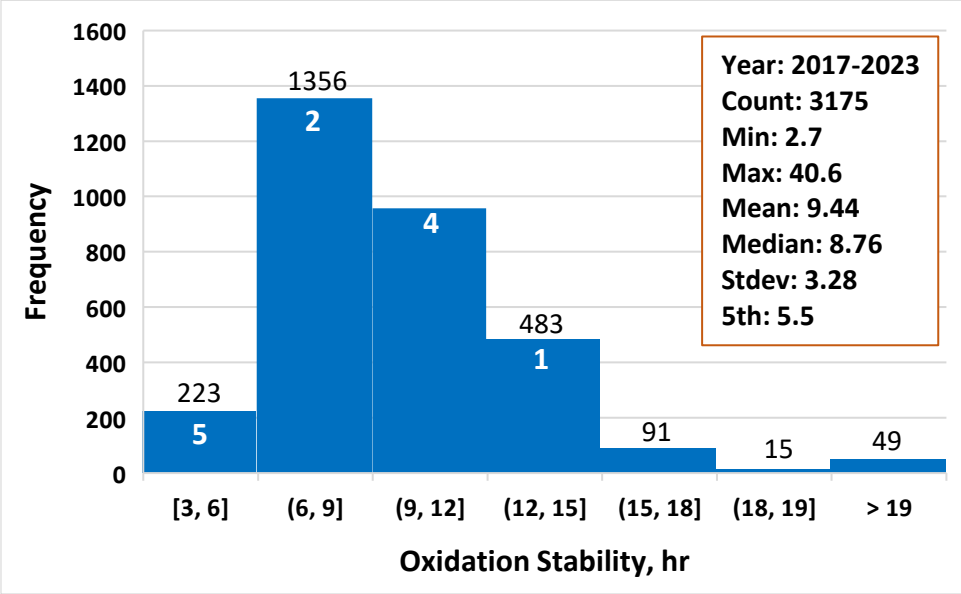


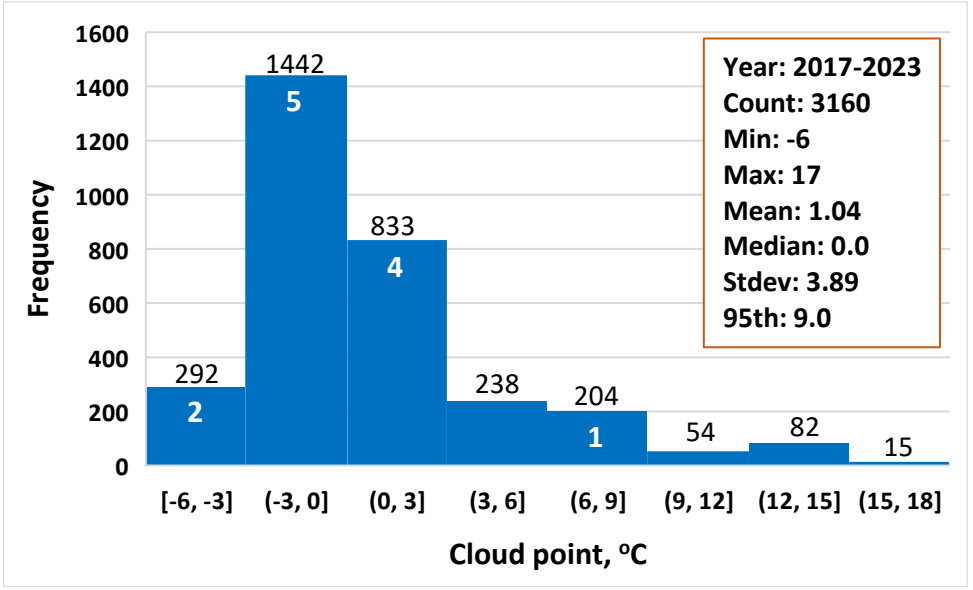


Stability and Relevant Properties

- Histograms from combined 2017-2023 BQ-9000 quality reports
- Samples span the distribution of stability in the market (white numbers are for the 12 B100 samples)
- Acid number may indicate prior oxidation
- Cloud point is related to unsaturated fatty acid content – polyunsaturates are the source of oxidation instability







Properties of Diesel Fuels

			Diesel A	Diesel B
Density at 15C	D4052	g/ml	0.8596	0.8300
Flashpoint	D6450	C	61.7	60.7
Kinematic Viscosity, 40C	D7042	mm2/s	2.639	2.413
Cloud point	D5773	C	-20.3	-8.7
Cetane Number (ICN)	D8183		42	51.8
Total Aromatics	D5186	Mass%	37.2	21.0
MonoAromatics	D5186	Mass%	28.7	18.1
Polynuclear Aromatics	D5186	Mass%	8.5	2.9
Cetane Index	D976		43.4	51.5
Carbon Residue, 10% bottoms	D524	wt%	0.13	0.06
Distillation T90	D86	C	328.7	333.3
PetroOxy Oxidation Stability	D7545	min	120	100