National Laboratory of the Rockies

Long-Term Storage Results for Market B50 and B100

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Clean Fuels Technical Workshop

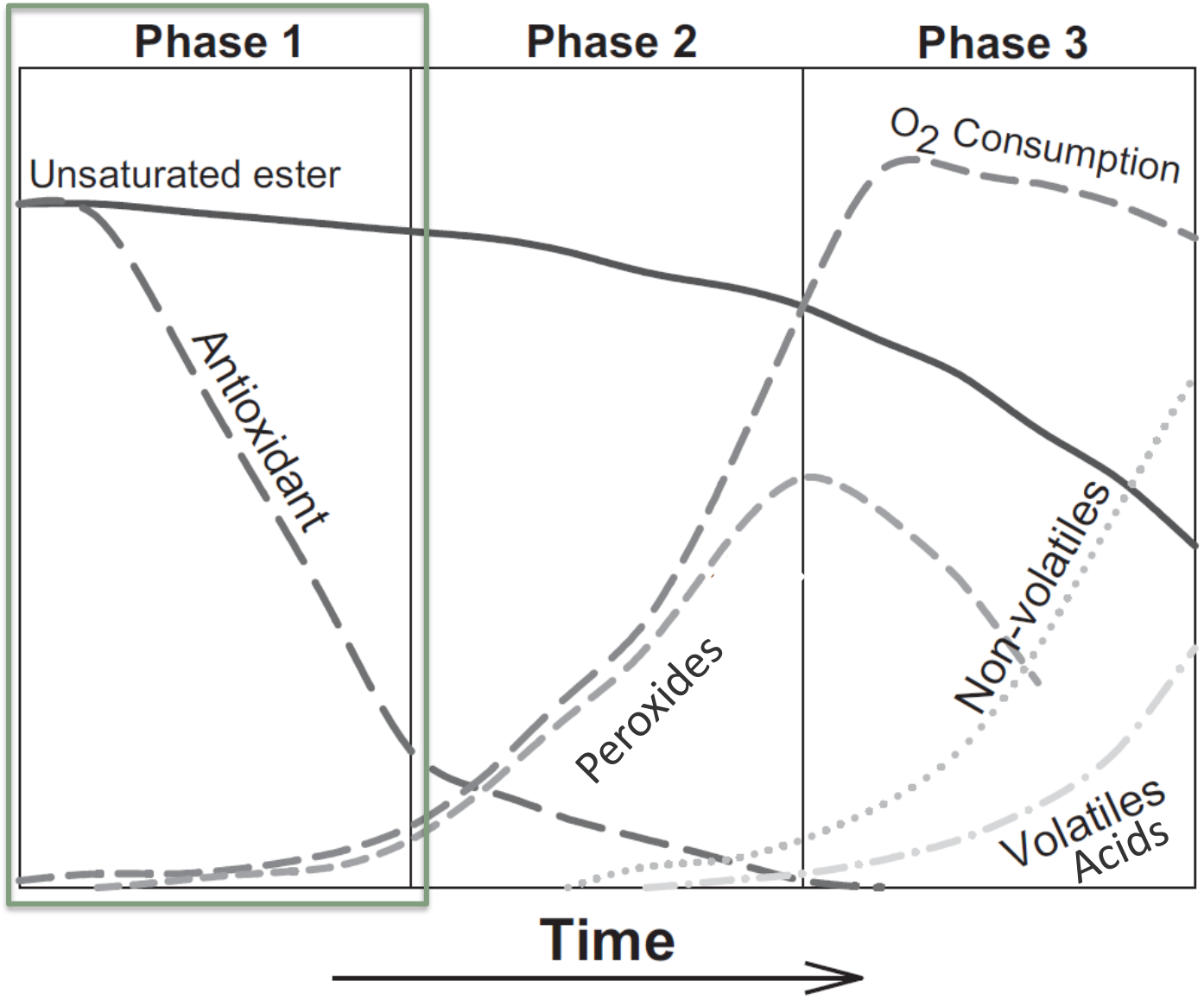
Kansas City, MO

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Biodiesel Stability Basics

Biodiesel Oxidation in Storage

Christensen, E., McCormick, R.L. “Long-Term Storage Stability of Biodiesel and Biodiesel Blends” Fuel Processing Technology 128 339–348 (2014).



- Oxidation in storage can lead to formation of gums and acids (failing TAN)
- Oxidation is a slow process that can take several weeks before negative effects are observed
- The goal of oxidation stability research is to understand how to maintain the fuel in Phase 1 – where minimal fuel changes have occurred

Rancimat Induction Time

- A measure of oxidation reserve:

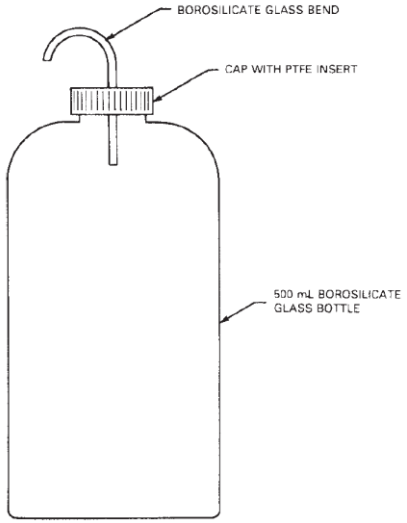
$$\propto \frac{Antioxidant\ Concentration}{Radical\ Initiator\ Concentration + Bisallylic\ Site\ Concentration}$$

- 110°C, high flowrate of bubbling air
  - Highly accelerated conditions – both high T and high oxygen availability
  - When induction time is reached, oxidation 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 Long-Term Storage

- Standard Test Method for Middle Distillate Fuel Storage Stability at 43°C
- 1 week nominally equivalent to 1 month in clean dry storage 21°C
- 500 mL bottles, open to air via “U”-tube, 400 mL of fuel
- 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

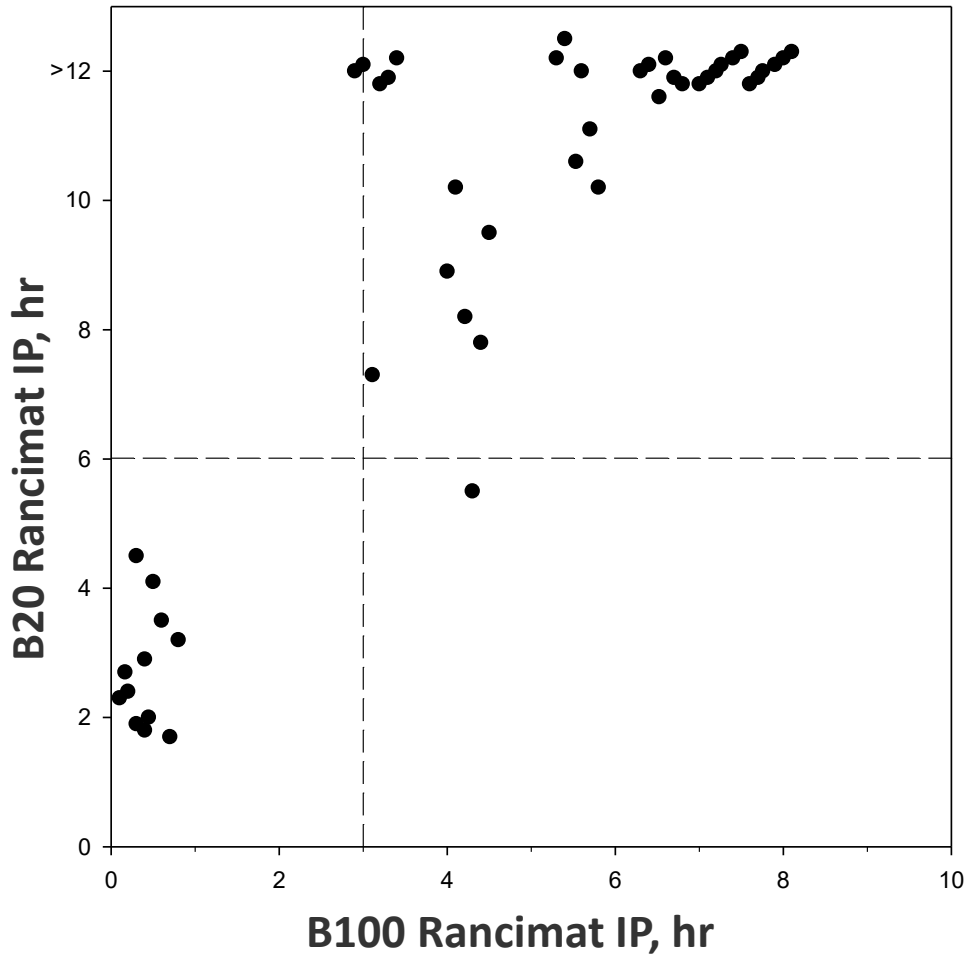






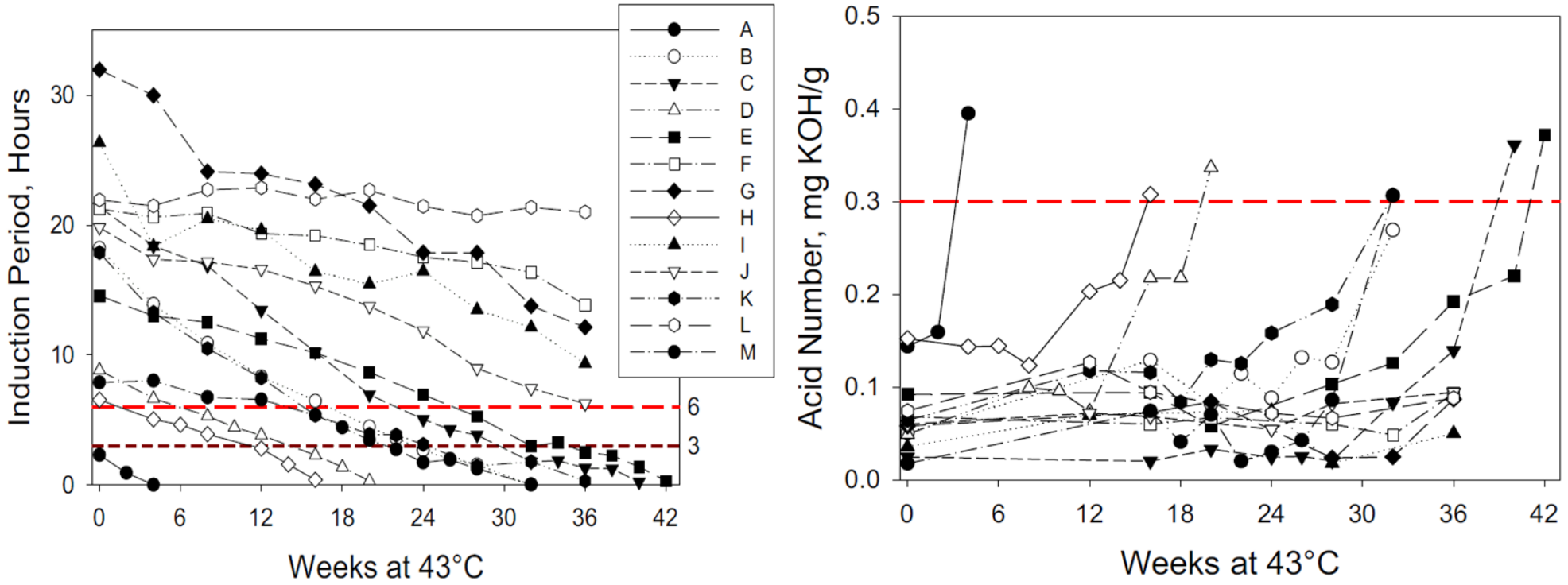
Basis for Current Biodiesel Stability Requirements

- Current stability requirements added to D6751 in 2007 and D7467 (B6-B20) in 2008
- **3 hr minimum IP for B100** is based on providing 6 hr minimum IP for B20, and longer for lower-level blends
- **6 hr minimum B20 IP** was OEM request
- Supported by D4625 measurements
  - Lack of acid / insoluble formation
- Adopted for D396 B6-B20 grade in 2015
- No IP requirement for up to B5 (D975, D396)



Stability of Market B20 in 2017: 12 Week D4625 Accelerated Aging

- Twelve B20 samples acquired from 12 different states in 2017
- B20 samples meeting 6 hour minimum IP did not show acid number over 0.3 mg/100 ml or significant insolubles at 12 weeks (12 months of simulated storage)



Induction periods and acid numbers of as-received blends during accelerated aging.

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).

Observations From 12-Week D4625 Aging: 2017 B20

- B20 acid number over 0.3 mg KOH/g was not observed for aged samples with 6 hour minimum initial IP
  - One B20 sample with initial IP <3 hr showed acid number of 0.4 mg KOH/g at 4 weeks (simulated 4 months)
- Total insoluble > 4 mg/100 mL (detection limit) only if aged sample had TAN >0.3 mg KOH/g
  - But aged samples w/ TAN over 0.3 mg KOH/g did not necessarily show insolubles
- Aged samples maintaining IP over 3 hours did not show significant acid or insoluble formation
- Monitoring of IP and acid in storage over time can be used for successful long-term storage of B20 and lower blends

New Study on Higher Blend Levels of Biodiesel

B50 / B100 Stability Study Scope of Work

- Use similar protocols as previous work
  - D4625 with measurement of Rancimat IP, peroxide, TAN, and insoluble at end of test
- 7 B100s and 2 B0s selected from a larger group, prepare B50s
  - Varied B100 and B0 sources that represent the entire market
  - 14 B50s, 3 B20s, plus baseline fuels (9) = 26 (400 mL D4625 jars)
- Age for 12 weeks at 43°C (simulated 12 months) with property monitoring
  - D4625 aging protocol
  - IP, TAN, peroxide run on samples taken from D4625 jar at 2 week intervals
  - Total insolubles at end of test

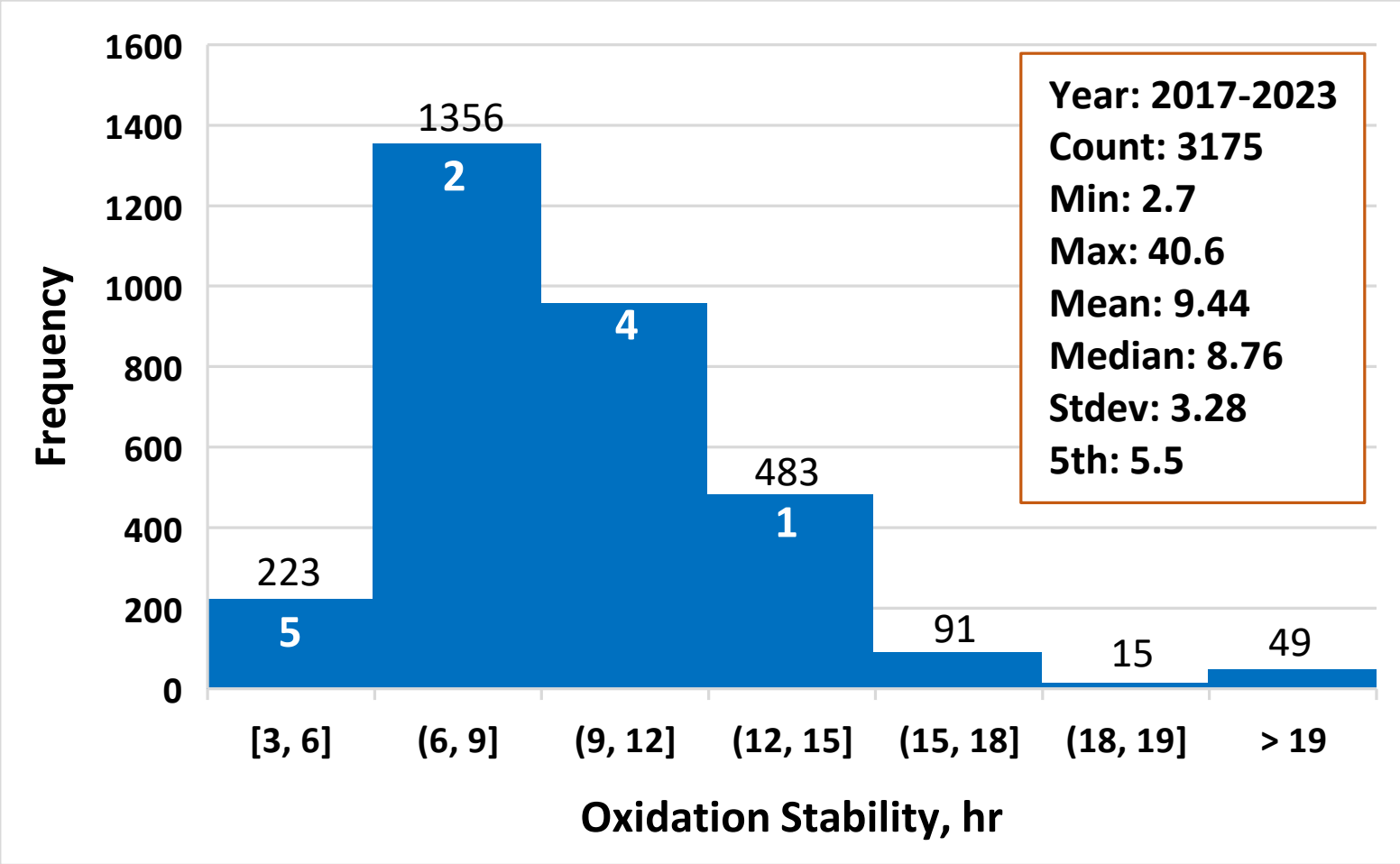
Fuel Selection: 2 Diesel Fuels

			Canadian Diesel	Mid Con #1 Diesel	Mid Con #2 Diesel
Density at 15C	D4052	g/ml	0.8596	0.8355	0.8300
Flashpoint	D6450	C	61.7	59.7	60.7
Kinematic Viscosity at 40C	D7042	mm2/s	2.639	2.605	2.413
Cloud point	D5773	C	-20.3	-10	-8.7
Cetane Number (ICN)	D8183		42	49.7	51.8
Total Aromatics	D5186	Mass%	37.2	23.0	21.0
MonoAromatics	D5186	Mass%	28.7	19.3	18.1
Polynuclear Aromatics	D5186	Mass%	8.5	3.6	2.9
Carbon Residue, 10% bottoms	D524	wt%	0.13	0.09	0.06
Sulfur	D5453	ppm	10.94	9.35	8.38
Distillation					
IBP	D86	C	162.8	156.3	162.6
5% (Diesel)		C	192.2	189.1	187.7
10% (Diesel)		C	203.0	201.5	196.7
15% (Diesel)		C	211.7	210.3	204.1
20% (Diesel)		C	219.6	219.4	211.2
30% (Diesel)		C	235.3	234.4	225.3
40% (Diesel)		C	249.6	249.4	240.4
50% (Diesel)		C	263.6	263.4	255.9
60% (Diesel)		C	277.3	277.6	271.4
70% (Diesel)		C	292.1	292.7	288.2
80% (Diesel)		C	307.9	309.9	307.6
90% (Diesel)		C	328.7	332.8	333.3
95% (Diesel)		C	346.8	351.1	351.6
FBP		C	359.9	362.7	360.4

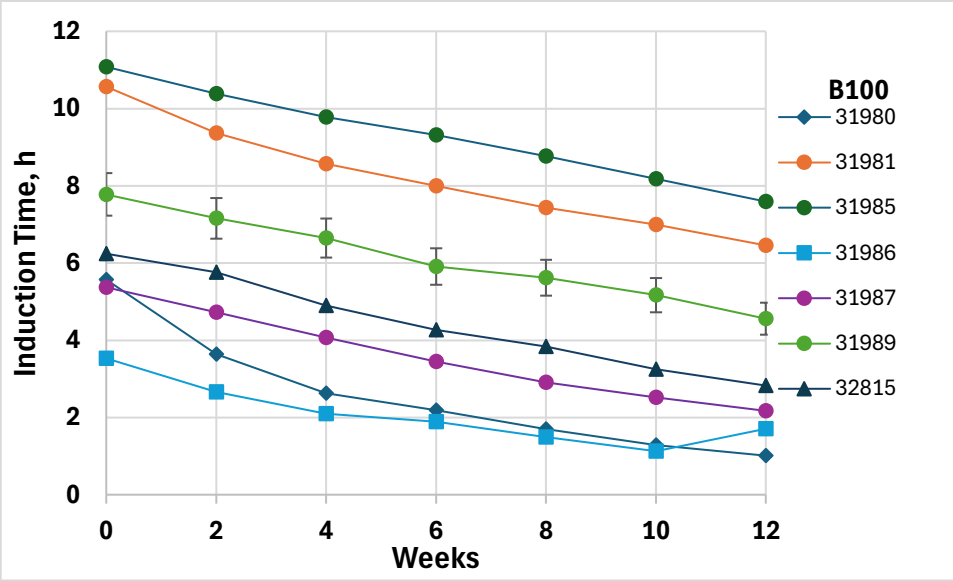
Fuel Selection: 7 B100

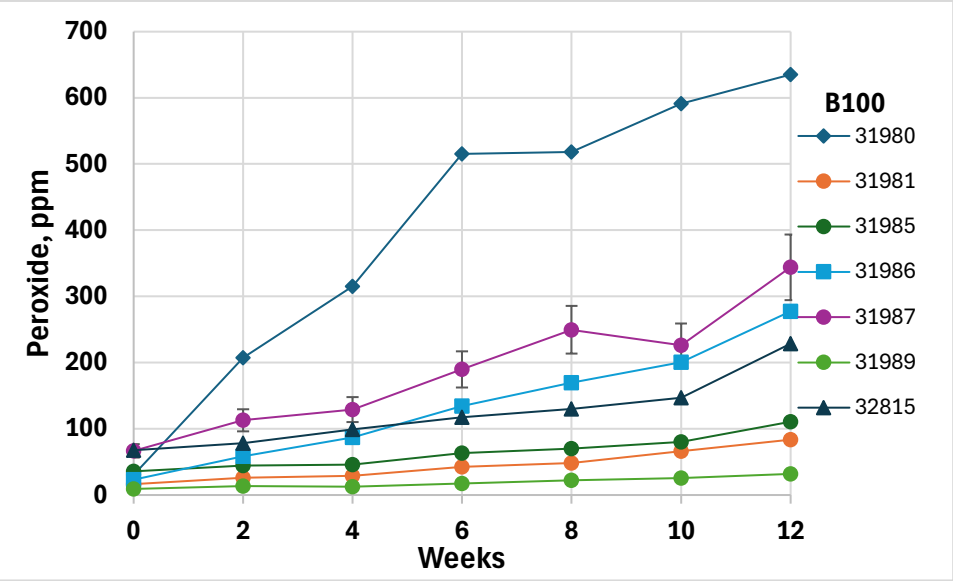
CAN#	S ppm	CSFT, s	FP, C	Visc, cSt	CP, C	TAN, mg KOH/g	FG, wt%	TG, wt%	Mono G, wtT	P, ppm	T90, C	Na+K, ppm	IP, hr
31980	0.5	95	115	4.028	-1	0.07	0.001	0.098	0.349	0.41	351	0.1	5.7
31981	6.8	118	153	4.498	2	0.43	0.008	0.129	0.312	0.36	353	0.8	10.8
31982	1.9	103	127	4.437	-3	0.39	0.001	0.091	0.294	0.93	353	0	12
31984	0.4	89	165	4.018	-1	0.37	0.001	0.058	0.176	0.13	351	0.3	5.9
31985	1.3	99	177	4.248	-4	0.26	0.002	0.018	0.048	0.23	352	0.3	11.4
31986	6.7	96	165	4.097	2	0.09	0.006	0.024	0.068	0.78	350	0	2.8
31987	14.6	101	157	4.585	1	0.25	0	0.111	0.349	0.43	354	0.8	4.8
31988	0.5	156	157	4.066	-2	0.27	0	0.107	0.349	1.61	351	0.1	7.8
31989	3.0	123	175	4.305	7	0.29	0.003	0.028	0.098	0.73	349	0.1	9.2
32811	0.4	87	151	4.043	0	0.21	0.001	0.052	0.15	0.51	351	0	6.2
32812	11.0	109	145	4.474	1	0.41	0.001	0.096	0.330	0.27	354	0.6	14
32815	4.2	107	149	4.354	0	0.29	0.011	0.136	0.388	0.42	354	0.6	6

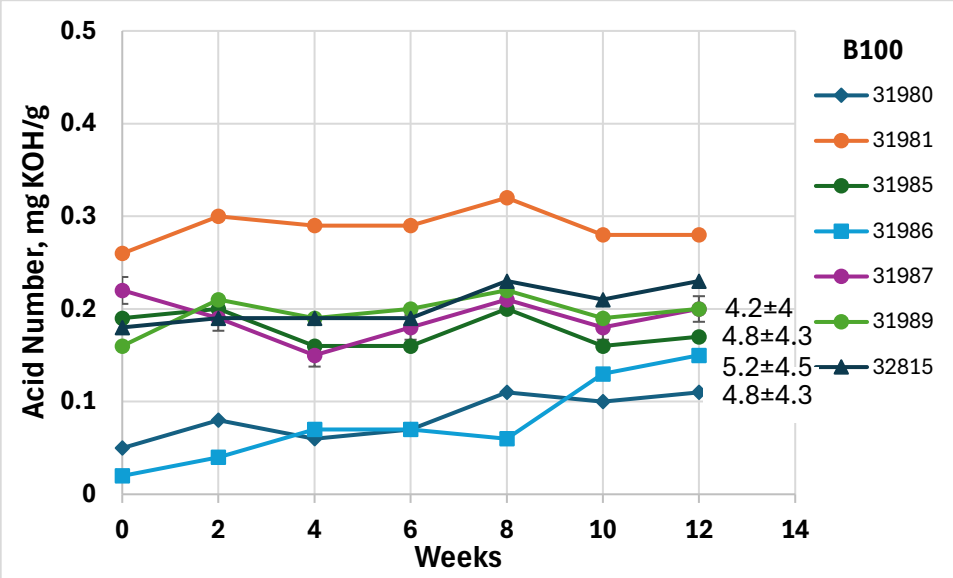
Stability of B100 at Point of Production



B100 12-Week Aging



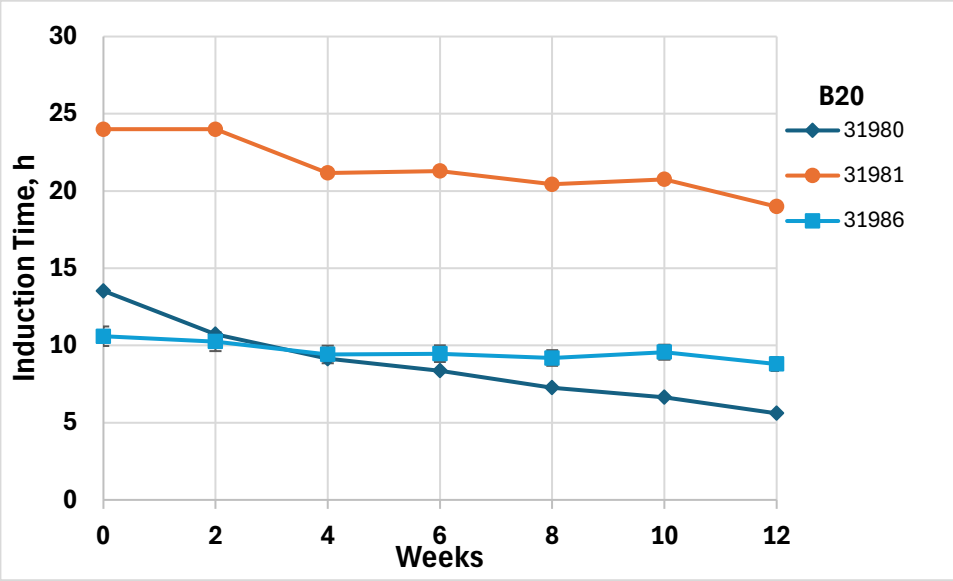


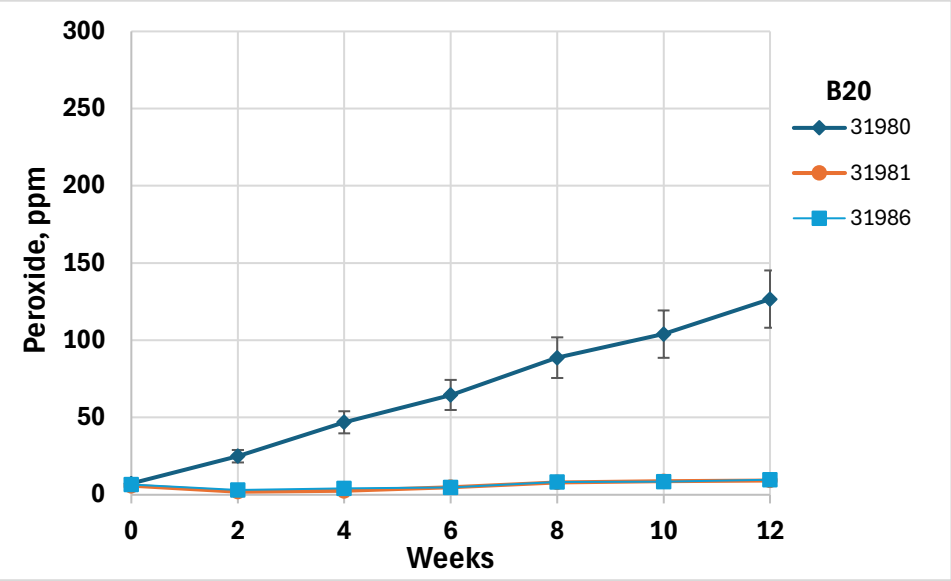


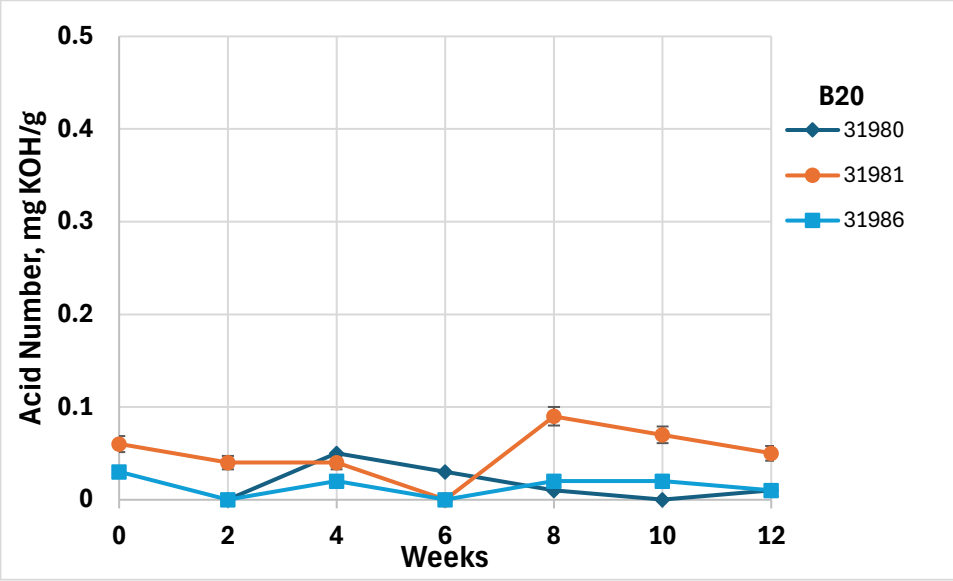
- Induction time decreased to < 3 hr for 4 samples
- Peroxide development for 1 sample (31980)
  - Peroxides of 500-1500 are not necessarily an issue if acids or insoluble have not yet formed
- All samples in spec for TAN after 12 weeks (<0.5 mg KOH/g)
- 4 samples showed measurable insoluble after 12 weeks

B20 12-Week Aging

Blends into Diesel 31956

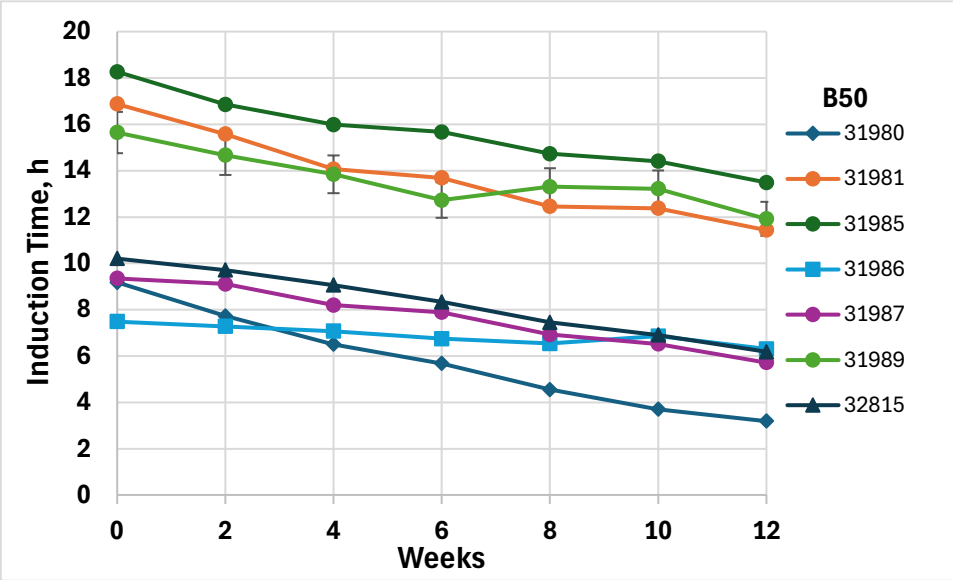


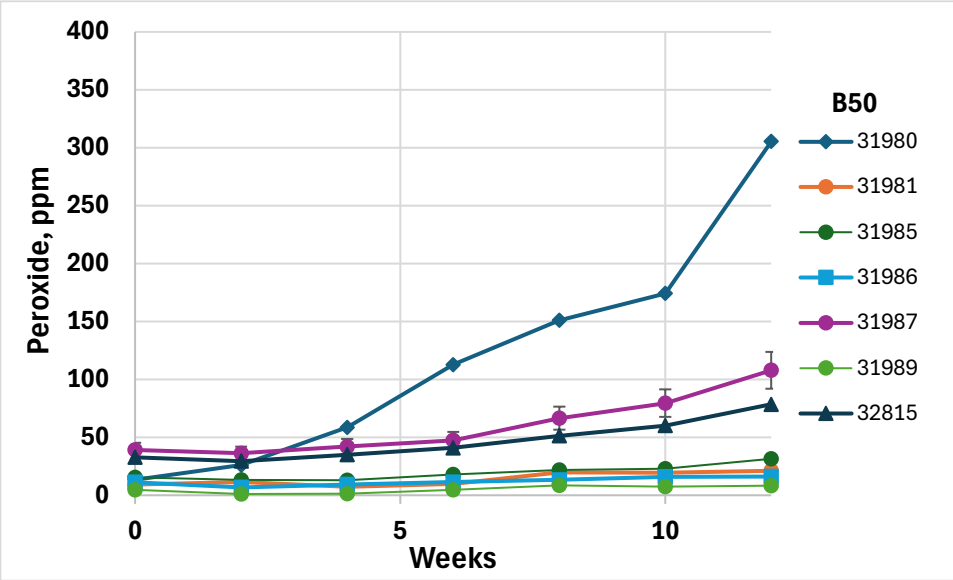


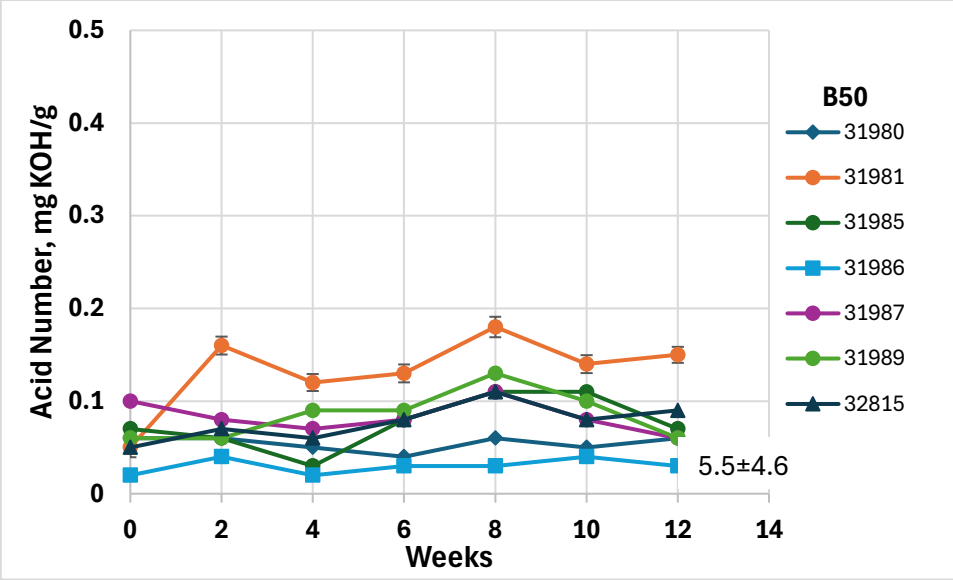


- Very slow oxidation, 1 sample below 6 hr IP (31980)
- Minimal peroxide increase
- Essentially no change in TAN
- Insolubles all below detection at end of test
- Very similar to older study for samples with similar initial IP

B50 12-Week Aging (Diesel 30902)

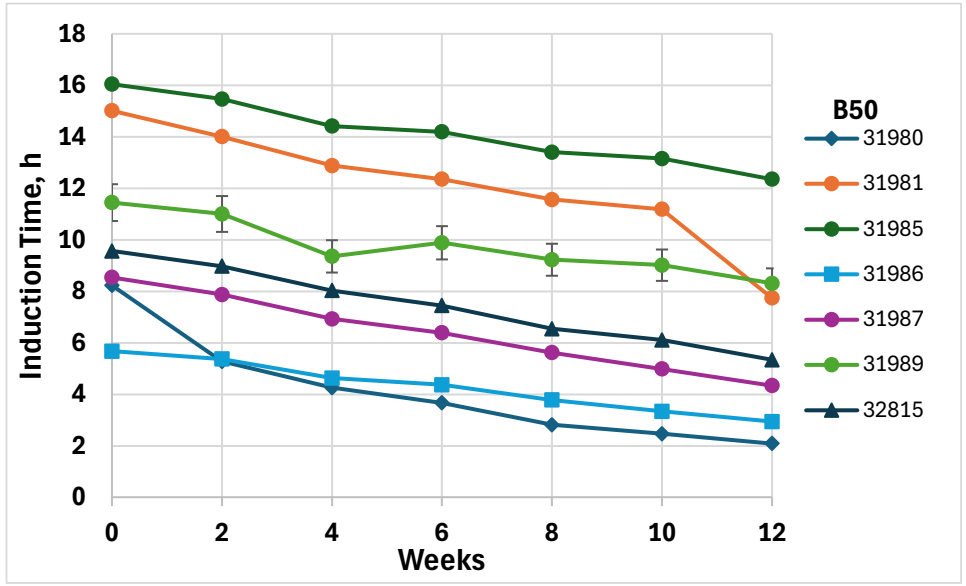


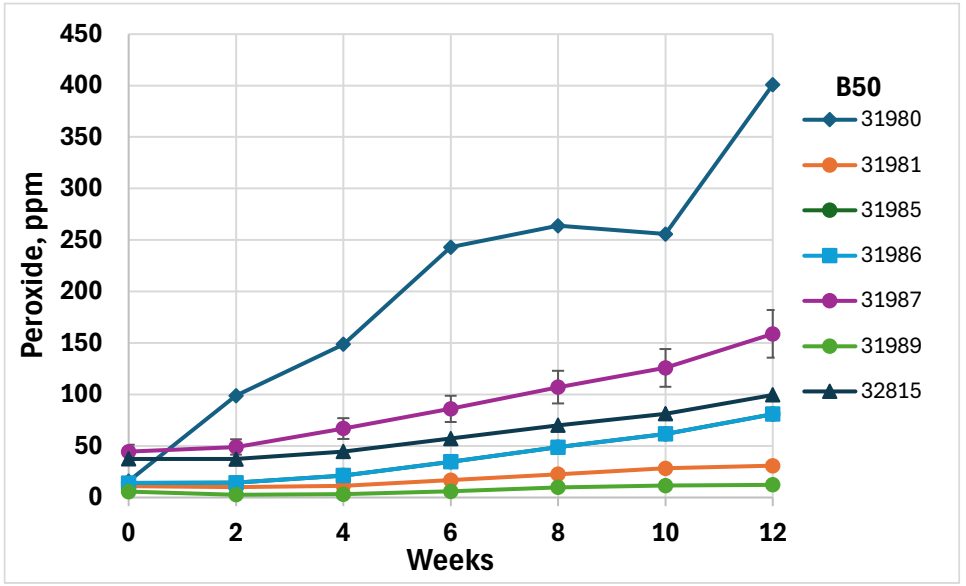


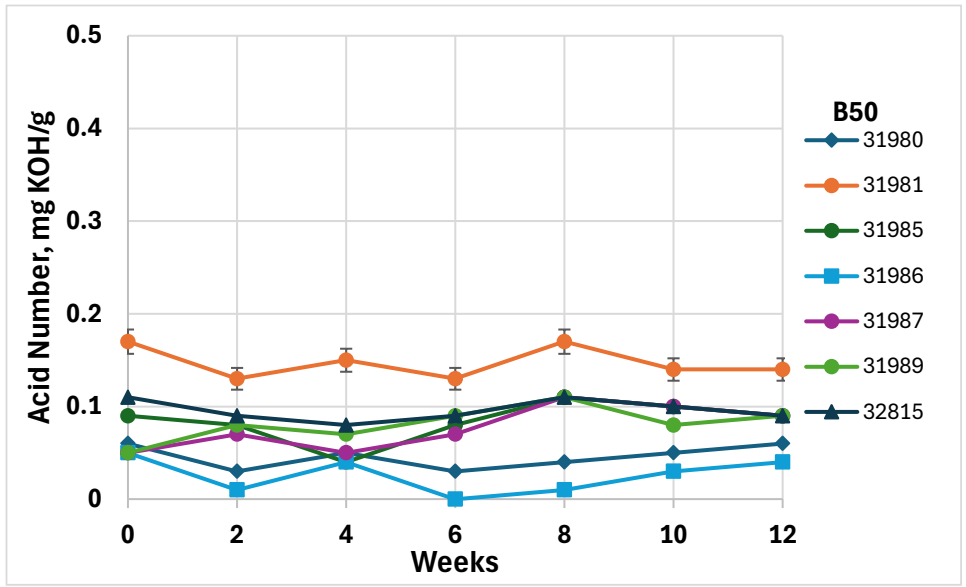


- 2 samples had lower IP than 6 hr at 12 weeks
- The least stable sample experienced some peroxide growth (31980)
- Essentially no change in TAN
- One sample exhibited measurable insoluble at the end of the test

B50 12-Week Aging (Diesel 31956)







- 4 samples were below 6 hr IP at end of test
- The least stable sample experienced some peroxide growth (31980)
- No change in TAN
- No insoluble observed

Diesel Fuel (B0) Results

- Peroxide below 4 ppm at all points during 12 week aging
- TAN below detection at all points during test
- Petroxy (ASTM D7545) shows no change between beginning and end of test (all > 90 min)
- Insolubles below detection at end of test

Comments on Results

- The main difference with prior studies is the formation of barely measurable insoluble for aged B100 and B50 samples

- If B100 IP > 6, then no insoluble forms for B50s after 12 months simulated aging
- B50s with initial IP over 6 hours show no insolubles—if made with B100 that had an IP over 6 hours

Summary

- These data support a 6 hr minimum IP for B100 for B50 blends, to produce a B50 with 6 hr minimum IP – as these will not form acids or insoluble over 12 weeks of storage – or 12 months of simulated storage
- A 3 hr B100 could still be used for B20 or lower blends

National Laboratory of the Rockies

Thank you!

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