What We Know About Biodiesel

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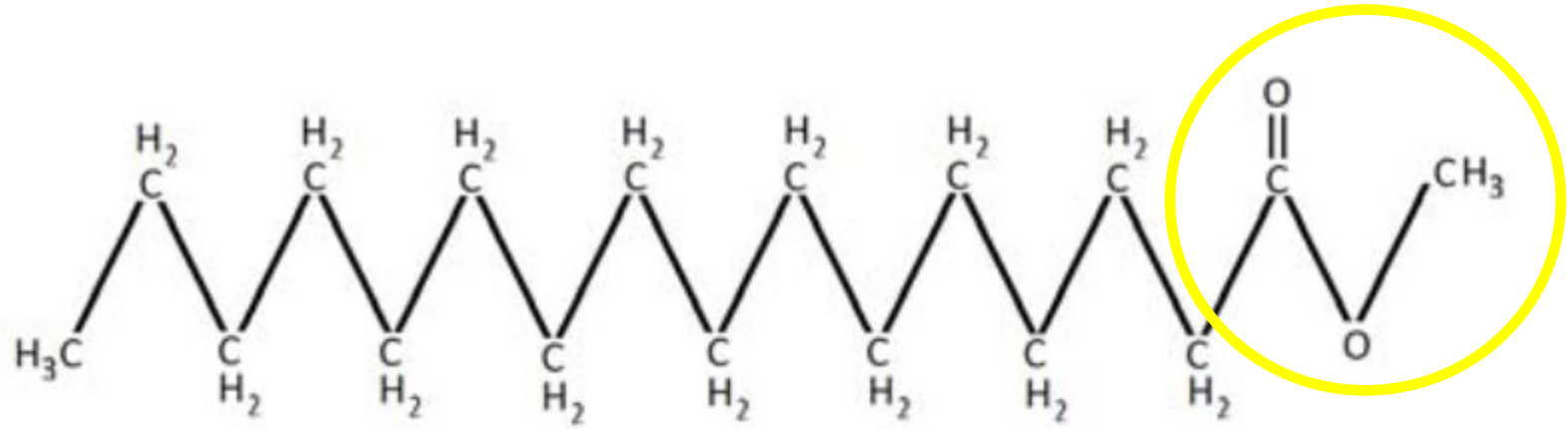
National Oilheat Research Alliance

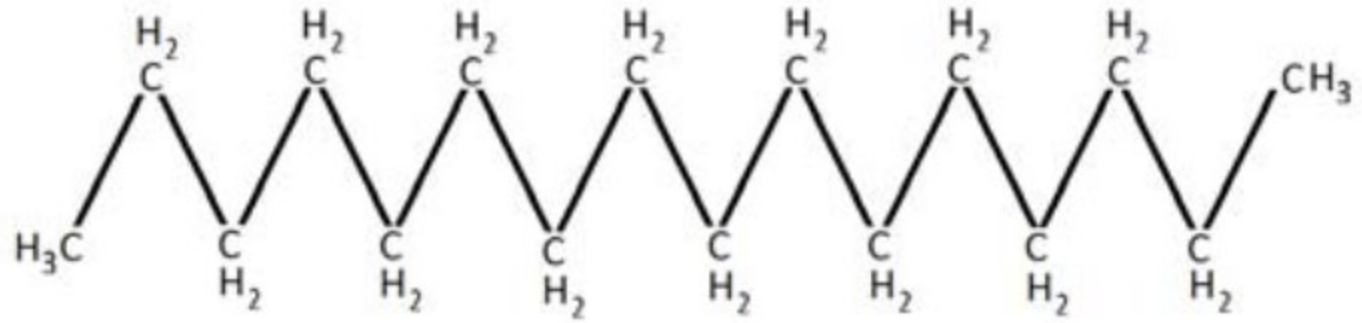
The Future of Liquid Fuel Heating
Tuesday October 25, 2022
Hartford, CT

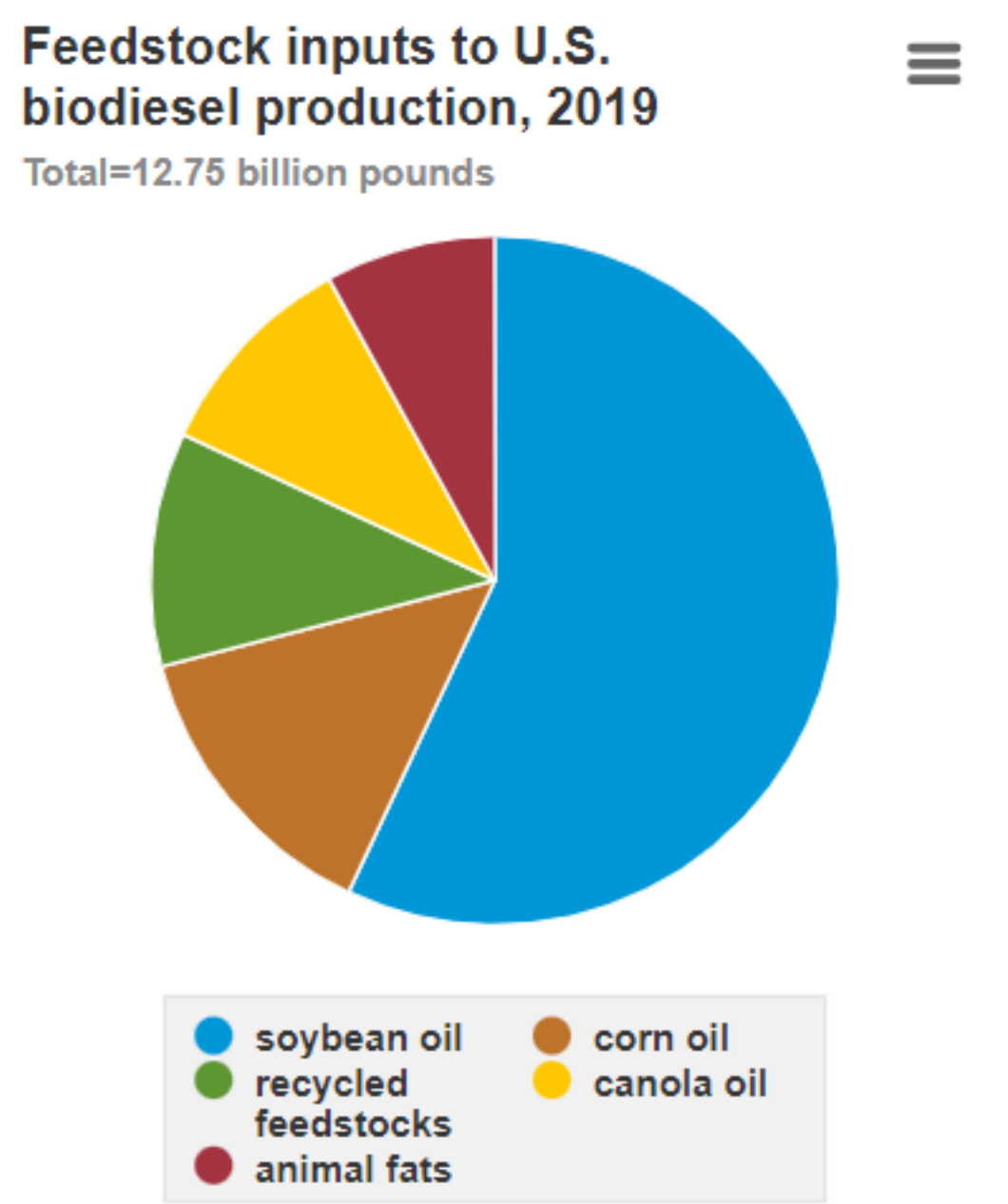
NORAweb.org
NATIONAL OILHEAT RESEARCH ALLIANCE

Biodiesel



Petro-No. 2





Source EIA for 2021

Typical Properties

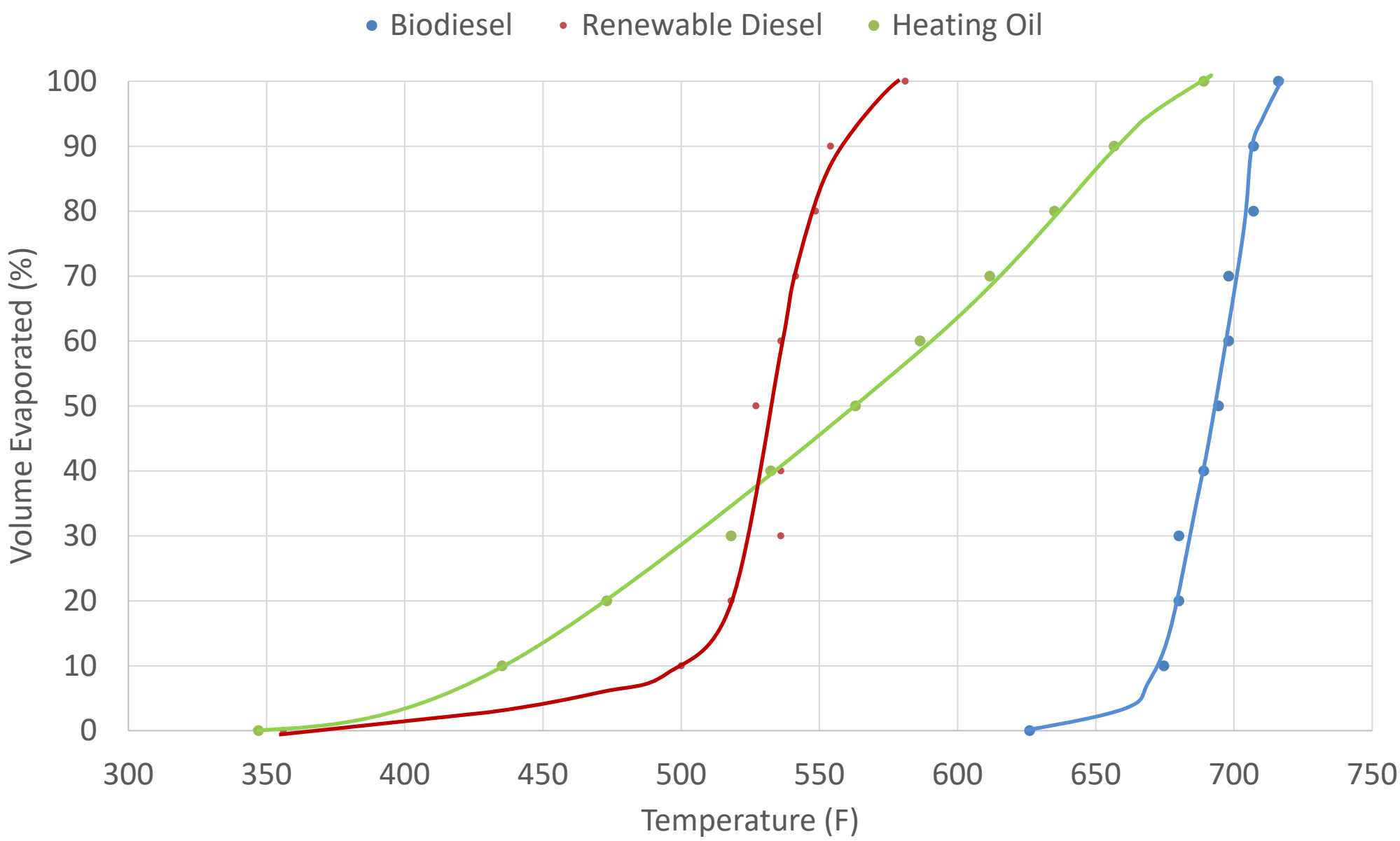
	Petroleum No. 2 Fuel Oil	Biodiesel	Renewable Diesel (HVO)
C (w%)	86.8	75.8	85.0
H (w%)	13.2	12.6	15.0
O (w%)	0	11.6	0
HHV[2] (Btu/gal)	138,300	125,300	132,800
Density (lb/gal)	7.09	7.34	6.51
Water Vapor Saturation[3] (F)	120	121	121

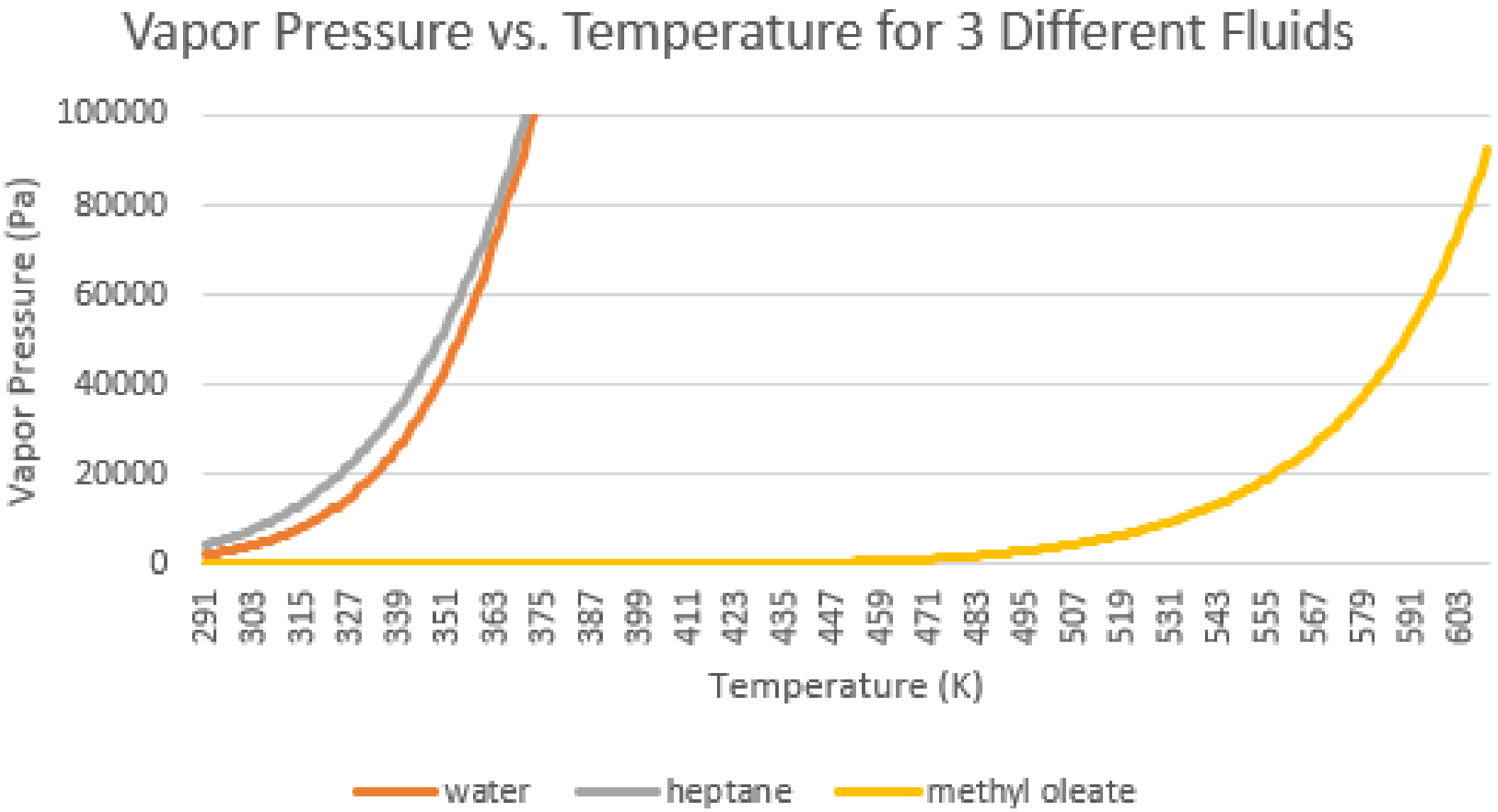
1. Higher Heating Value
2. Saturation temperature of flue gas water vapor at 30% excess air

ASTM Property Limits

Fuel	**No. 2**	**B20**	**B100**
Standard	ASTM D396	ASTM D396	ASTM D6751
Distillation Temperature (max -F)[1]	640	649	680
Stability (min - hrs)	---	6	3
Acid Number[2]	---	0.3	0.5
Flash Point (F)	100	100	199
Viscosity[3]	1.9-4.1	1.3-4.1	1.9-6.0
Carbon Residue (%)	0.035	0.035	0.05

1. Temperature for 90% recovery
2. mg KOH/g
3. mm2/s at 40 C


Biodiesel
Renewable Diesel
Heating Oil
Volume Evaporated (%)
100
90
80
70
60
50
40
30
20
10
0
300
350
400
450
500
550
600
650
700
750
Temperature (F)


Vapor Pressure vs. Temperature for 3 Different Fluids
Vapor Pressure (Pa)
100000
80000
60000
40000
20000
0
291
303
315
327
339
351
363
375
387
399
411
423
435
447
459
471
483
495
507
519
531
543
555
567
579
591
603
Temperature (K)
water
heptane
methyl oleate

Cold Flow General

Biodiesel Feedstock	Cloud Point °F	Pour Point °F
Soy	32	28
Canola	34	16
Palm	55	61
Jatropha	46	43
Tallow	53-63	43

Table 4. Cold Flow Data for Various B100s[14]				
Degree of saturation	B100 Cloud Point ASTM D2500		B100 Pour Point ASTM D97	
	°F	°C	°F	°C
Low	26	-3	25	-4
	32	0	25	-4
Mid	46	8	43	6
	56	13	55	13
	61	16	59	15
High	66	19	60	16

Source: NREL Biodiesel Handling and Use Guide, Fifth Edition

Elastomers

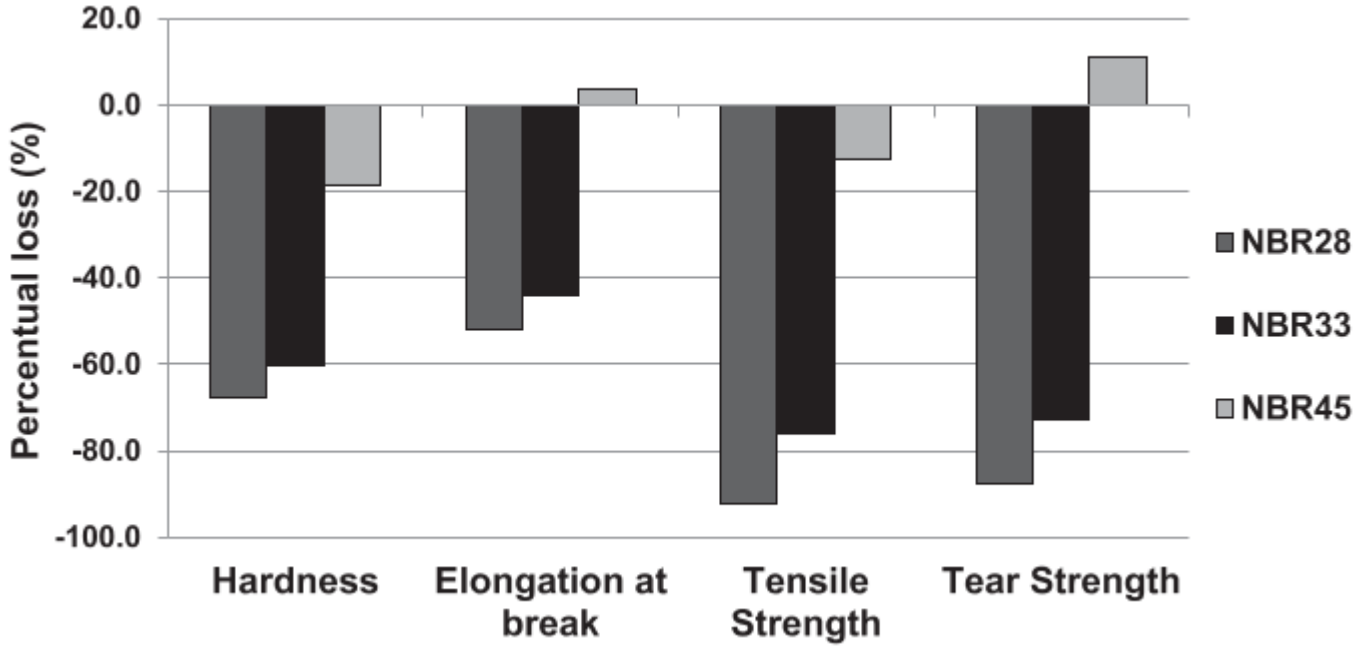
"Nitrile rubber" or Buna-N or NBR refer to the elastomer of interest

Nitrile rubber refers to a family of copolymers of (generally) acrylonitrile (ACN) and various butadiene monomers.

One very important factor in the properties of the produced elastomer is the "nitrile (ACN)/butadiene ratio. The higher this ratio the more resistant the product is but also the less flexible.

A range of other components are used in the elastomer production process including emulsifiers, catalysts, radical generating activators, reaction termination additives, antioxidants, coagulating agents and others.

Processing temperature and time also have strong impacts on the properties of the produced elastomer.



NBR45 = nitrile with 45% acrylonitrile content

Example – Three different “nitriles” exposed to coconut oil biodiesel.
Source – Linhares, F.N. et. al., Study of the compatibility of nitrile rubber with Brazilian biodiesel, Energy, 49, pp. 102-106 (2013).

“..the mechanical properties of the NBR sample comprising 45% acrylonitrile appeared unchanged even after immersion in biodiesel oils.”

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Biodiesel Nitrile

Biodiesel is a clean burning alternative fuel produced domestically. Biodiesel is nontoxic, biodegradable and can be used in diesel engines usually with no modifications.

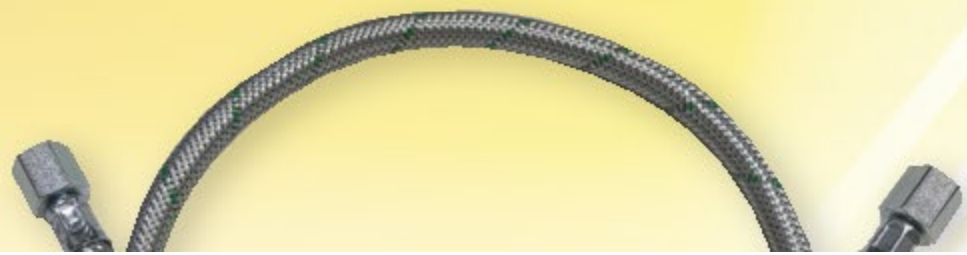
Biodiesel Nitrile is specially designed and developed for use in environments where alternative fuels are present. Immersion test results indicate that these materials are compatible with alternative fuels and are suitable for Bio-Diesel B20 (20% Bio-Diesel and 80% Petroleum Diesel) and Bio-Diesel B100 (100% Bio-Diesel).

Sid Harvey's®

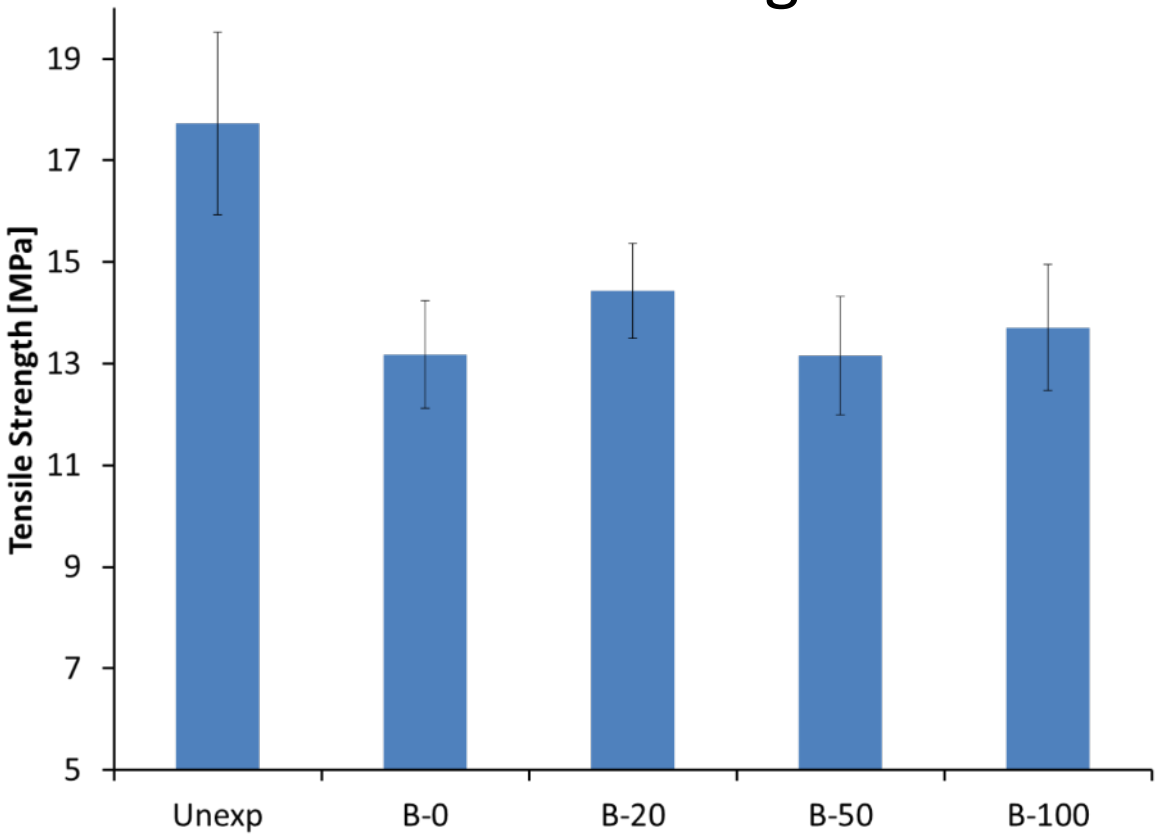
bio B100

B100 COMPATIBLE FLEXIBLE OIL LINES

- Flexible braided steel outer casing
- HNBR rubber compound

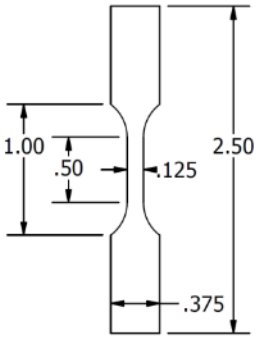


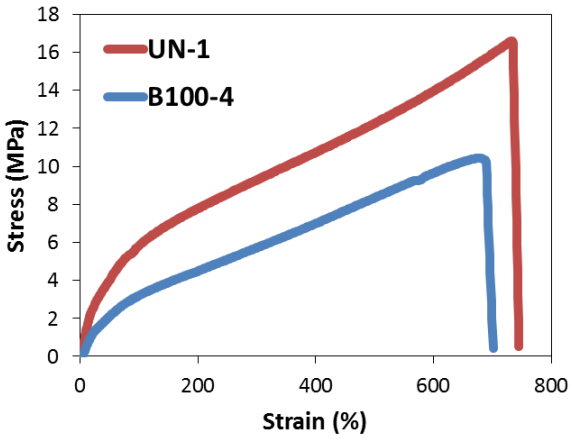
Tensile Strength – Biodiesel Blends



- ASTM D412
- ASTM D471
- TiraTest 26005 Load Frame (0.5 kN)
- Immersion: 670 h @125F

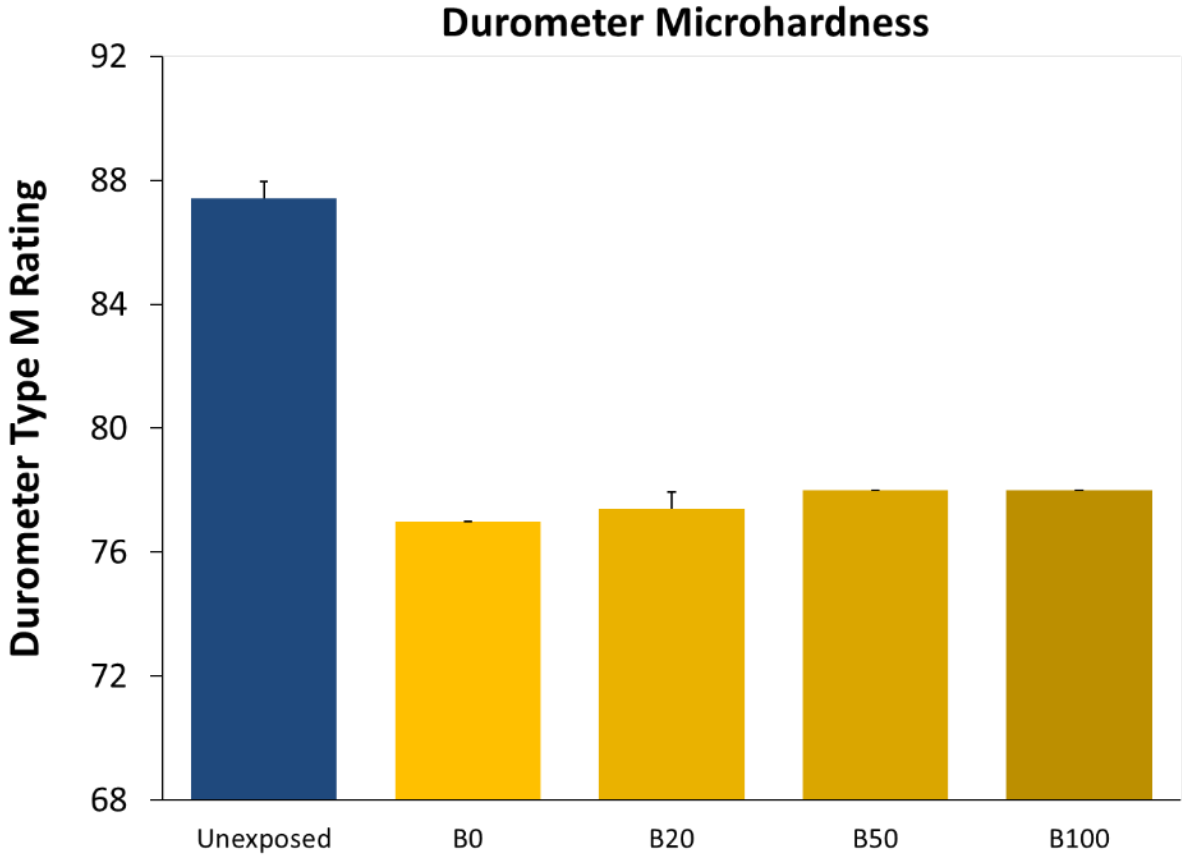
- Nitrile dogbone specimens
- Gage length = 20 mm
- Rate = 500 mm/min





Durometer Microhardness – Biodiesel Blends

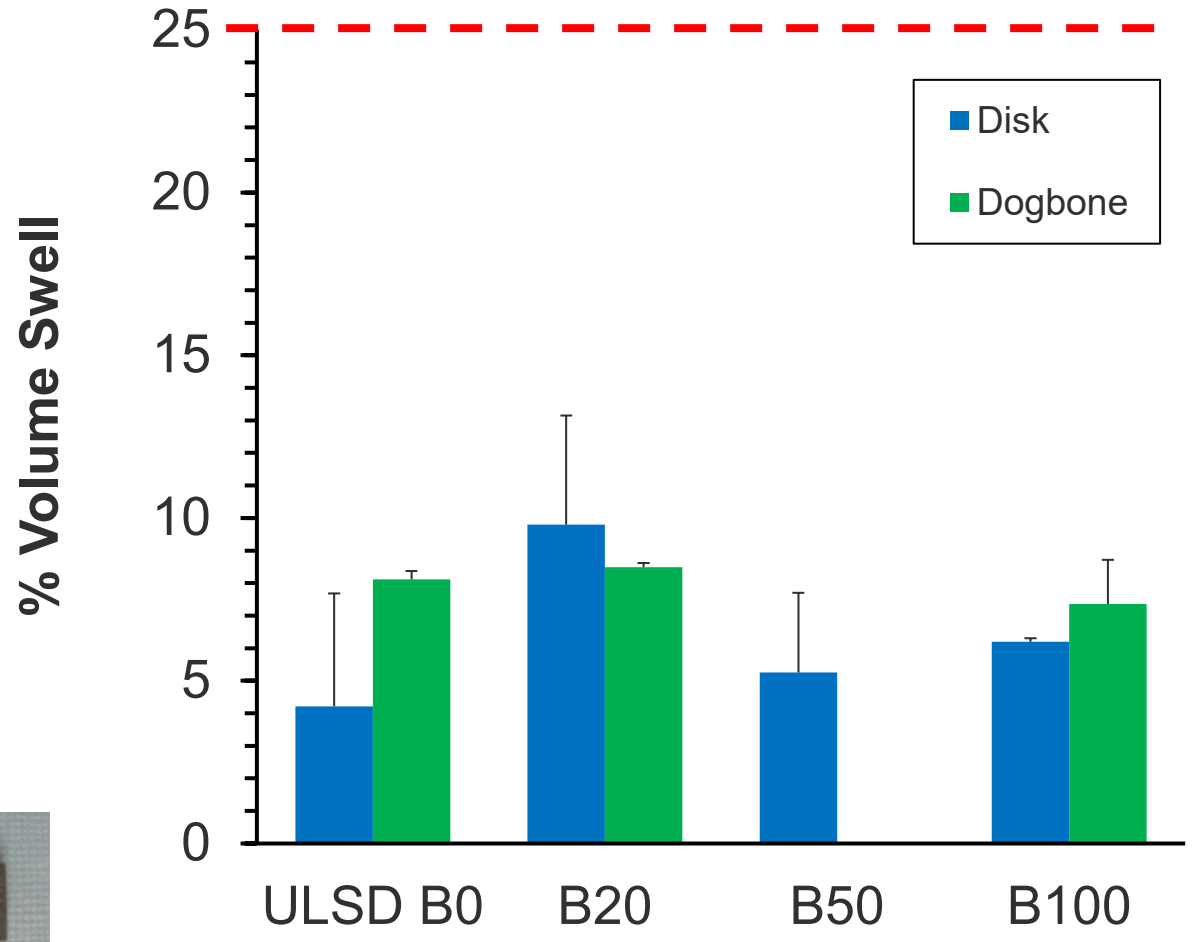
- Type M Durometer
- ASTM D2240
- ASTM D471
- Immersion:
  670 h @125F
  840 h @RT
  = 1510 h Total



Exposure	Unexposed	B0	B20	B50	B100
Durometer Type M Rating	87.4	77.0	77.4	78.0	78.0
standard deviation	0.5	0	0.5	0	0

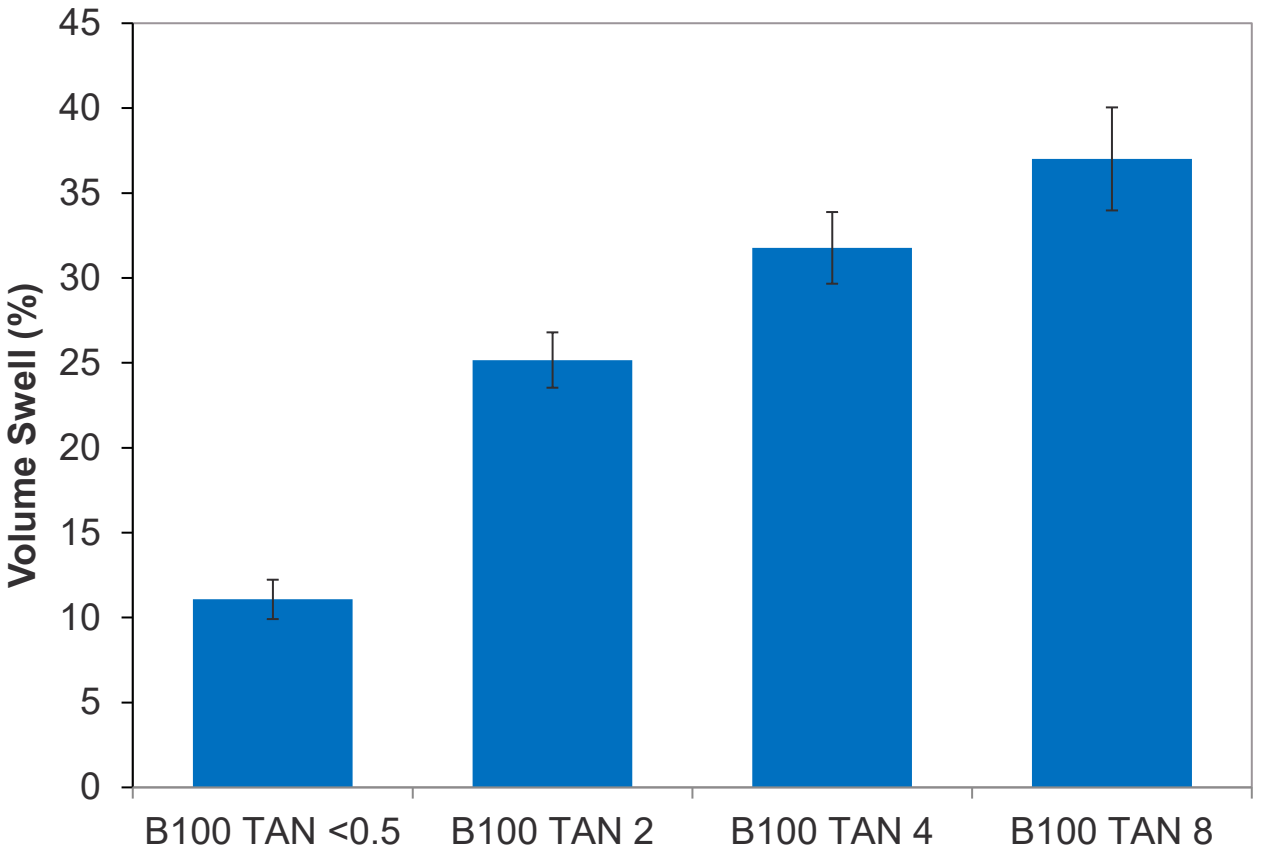
Volume Swell – Biodiesel Blends

- ASTM D471
- Water Displacement Method
- Immersion: 720 h @125F



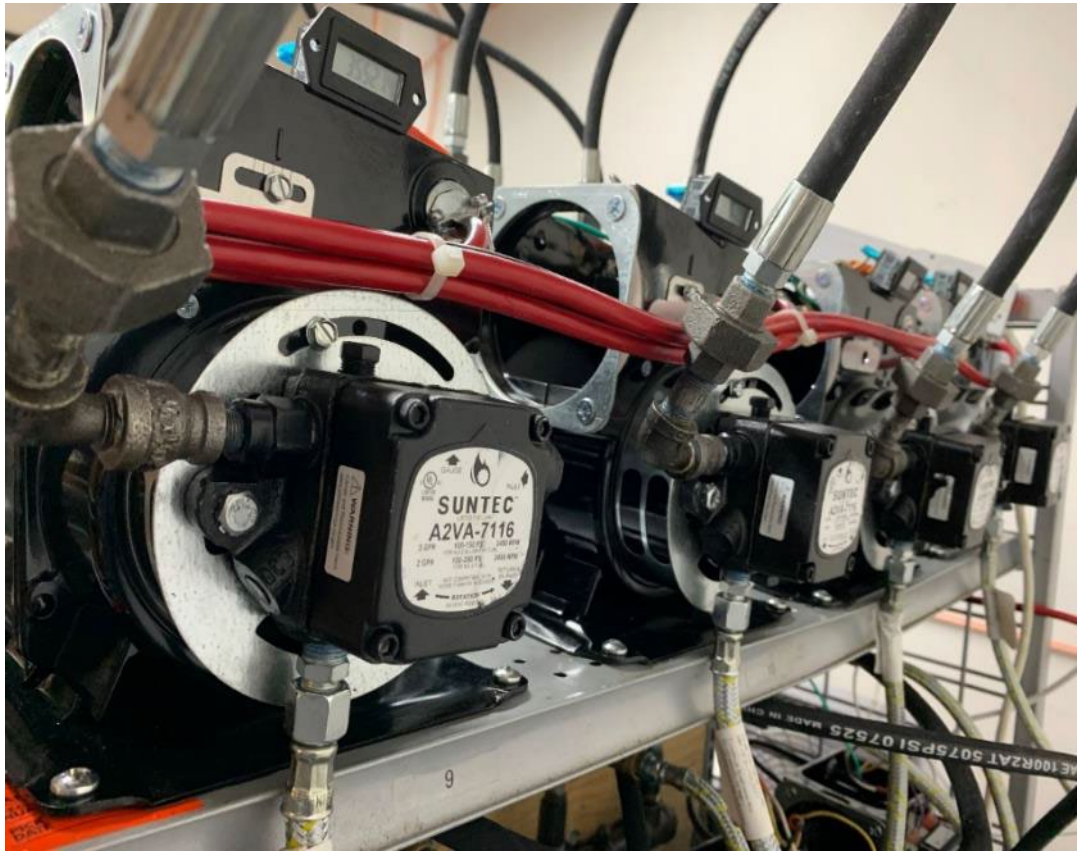
Volume Swell – Acid Number Effect

- ASTM D471
- Water Displacement Method
- Immersion: 720 h @125F
- Decanoic Acid (Total Acid Number(TAN) = 2, 4, 8)



Legacy Pump Testing B0/B5 to B100

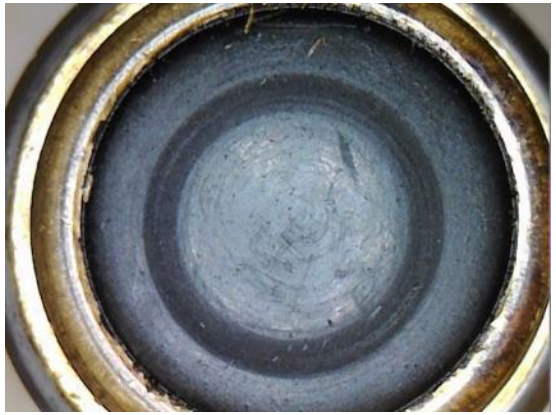
- Goal – evaluate durability and failure modes of legacy oil burner pumps when using biodiesel blends ranging from B0/B5 to B100;
- Focus planned on pressure regulator piston seal but included whole pump;
- “Exposure” based on number of cycles with target of 500,000 cycles (equivalent to 50 years in the field).

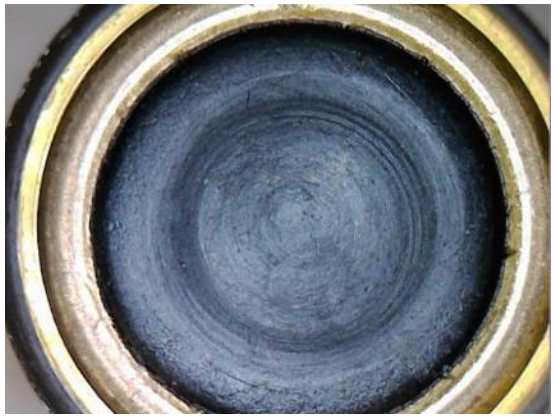


Measuring Impact on Pumps

- Observation of any “seized” pumps or shaft seal failures;
- Planned stops at 100K, 200K, 350K, and 500K cycles;
- Shaft seal and pressure regulator piston face examined for all pumps;
- Diaphragm valve inspected for some cases;
- Full tear-down for inspection at 500,000 cycles all pumps;
- Cutoff test for all pumps at each stop point
  - Installation on a burner;
  - Detailed measurement of cut-off time based on cad cell transient.

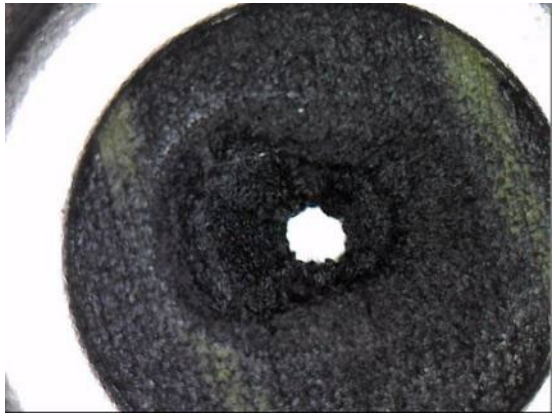
Four pumps, 500K cycles, B100

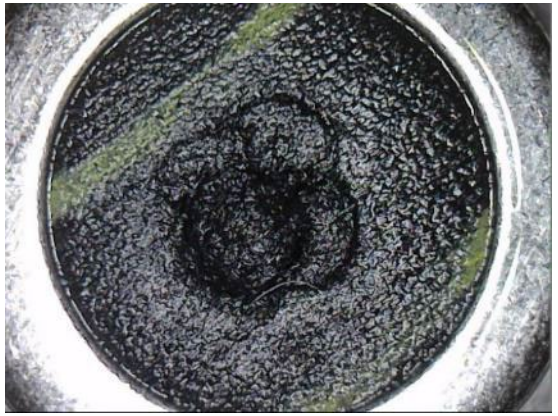




Example Results –worst case, 500K cycles, diaphragm valve

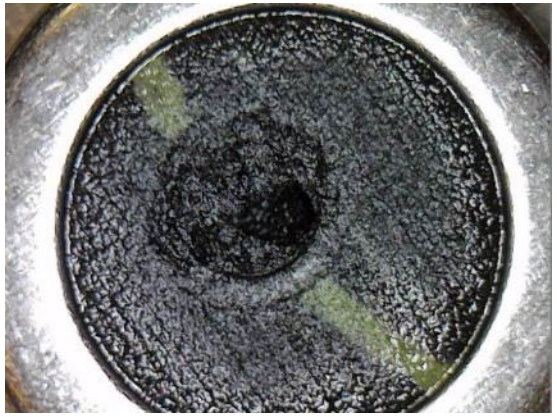
B0/B5

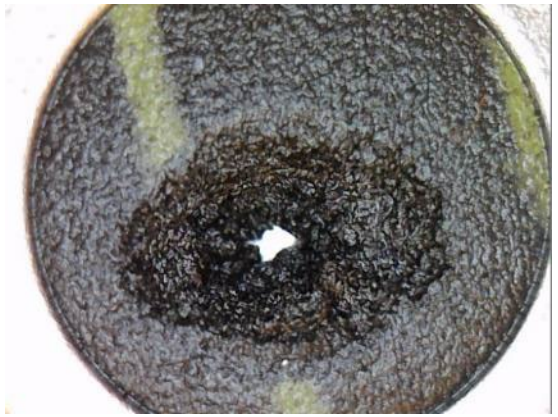




B50

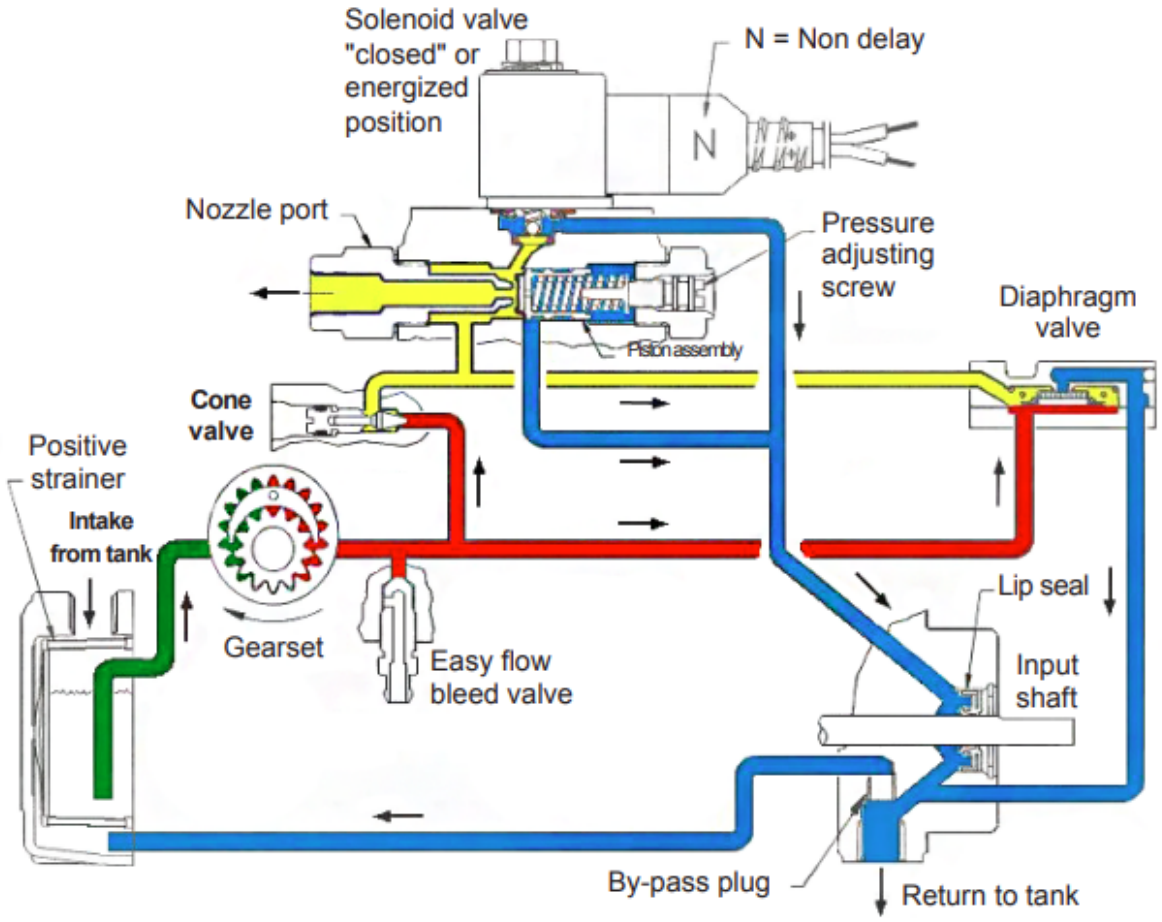
B20





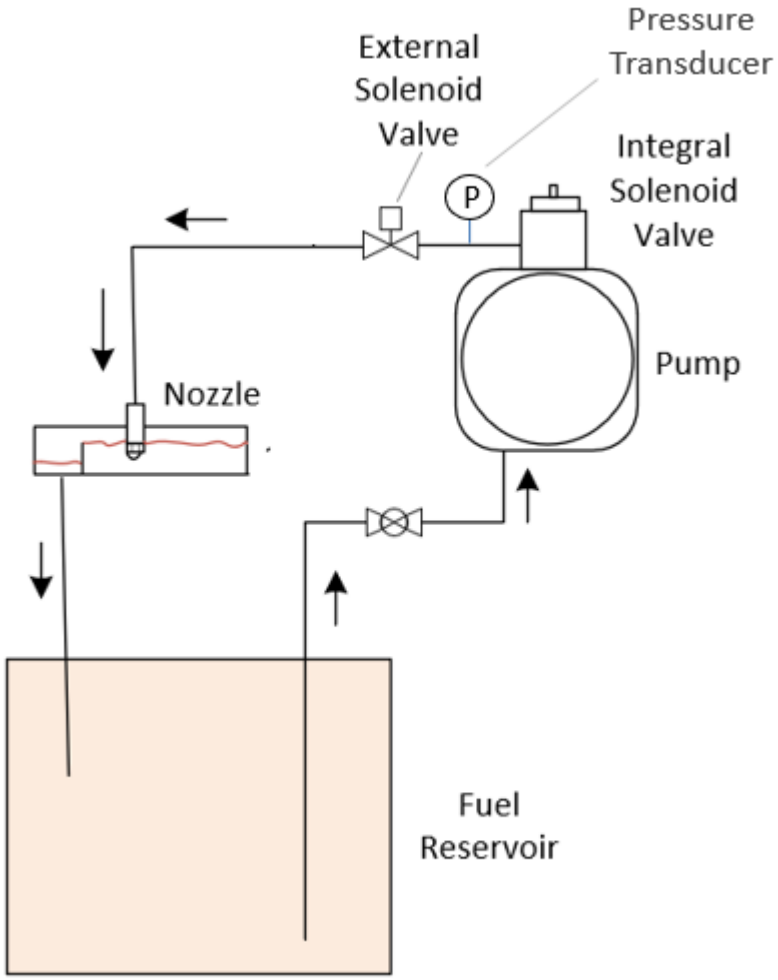
B100

Next Generation Pump Testing



Test Stand Setup

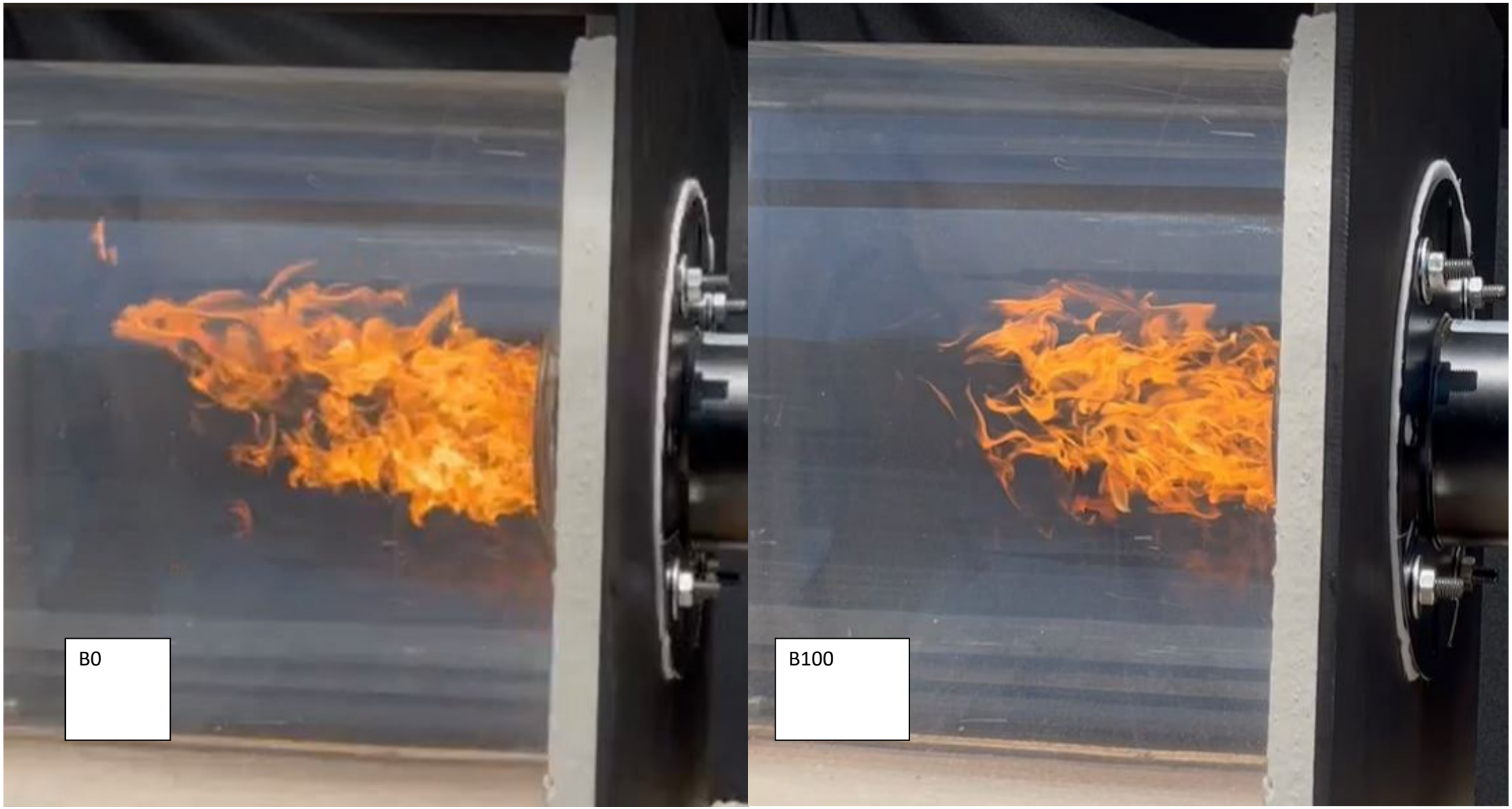
- Test set up at external site in Wantagh, NY
- 3 test stands, 10 pumps each – B0, B20 and B100
- All pumps in each stand draws from same fuel bank of ~4 gallons
- Secondary solenoid valve and transducer installed on the outlet side of each pump
- All exiting fuel is returned to reservoir via radiator, which is cooled by fan
- Temperature sensors in reservoir and inside bottom left pump of each stand



Conclusions – Next Gen Pump Tests

- New seal materials have been qualified for B20 and B100
- Pump robustness have been improved towards blend with high biofuel content, latest findings will help to go one step further
- Technical solutions for « B100 ready » Fuel Units are defined and will be deployed within few months
- Standards (ASTM, UL) need to be updated, and tests for certification need to be performed to market official B100 rated Fuel Unit

Combustion Performance



Combustion Testing

Cast iron boiler, standard burner

Fuel	B0	B100	% change
Burn Rate lb/hr	6.85	7.32	6.9
Heating Value, Btu/lb	19,500	17,062	-12.5
Heating Value, Btu/gal	138,490	127,960	
Input Rate Btu/hr	133,497	124,894	-6.4
T flue gas, °F	528	530	0.4
T blr, °F	158	157	-0.6
Excess Air, %	22.6	26.7	18.1
Flue O2 measured, %	4.7	5.4	14.9
Flue Water Vapor Saturation, °F	119.9	121.7	1.5
Cad Cell Resistance, ohms	132	520	293.9

Combustion Testing

Cast iron boiler, standard burner

Fuel	B0	B100	% change
Burn Rate lb/hr	6.15	6.55	6.2
Heating Value, Btu/lb	19,500	17,062	-12.5
Heating Value, Btu/gal	138,490	127,960	-7.6
Input Rate Btu/hr	119,925	111,756	-6.8
T flue gas, °F	472	464	-1.7
T blr, °F	161	161	0
Flue CO2 measured, %	12.2	11.9	-2.4
Flue Water Vapor Saturation, °F	119.9	121.7	1.5

Biodiesel Field Testing Goals

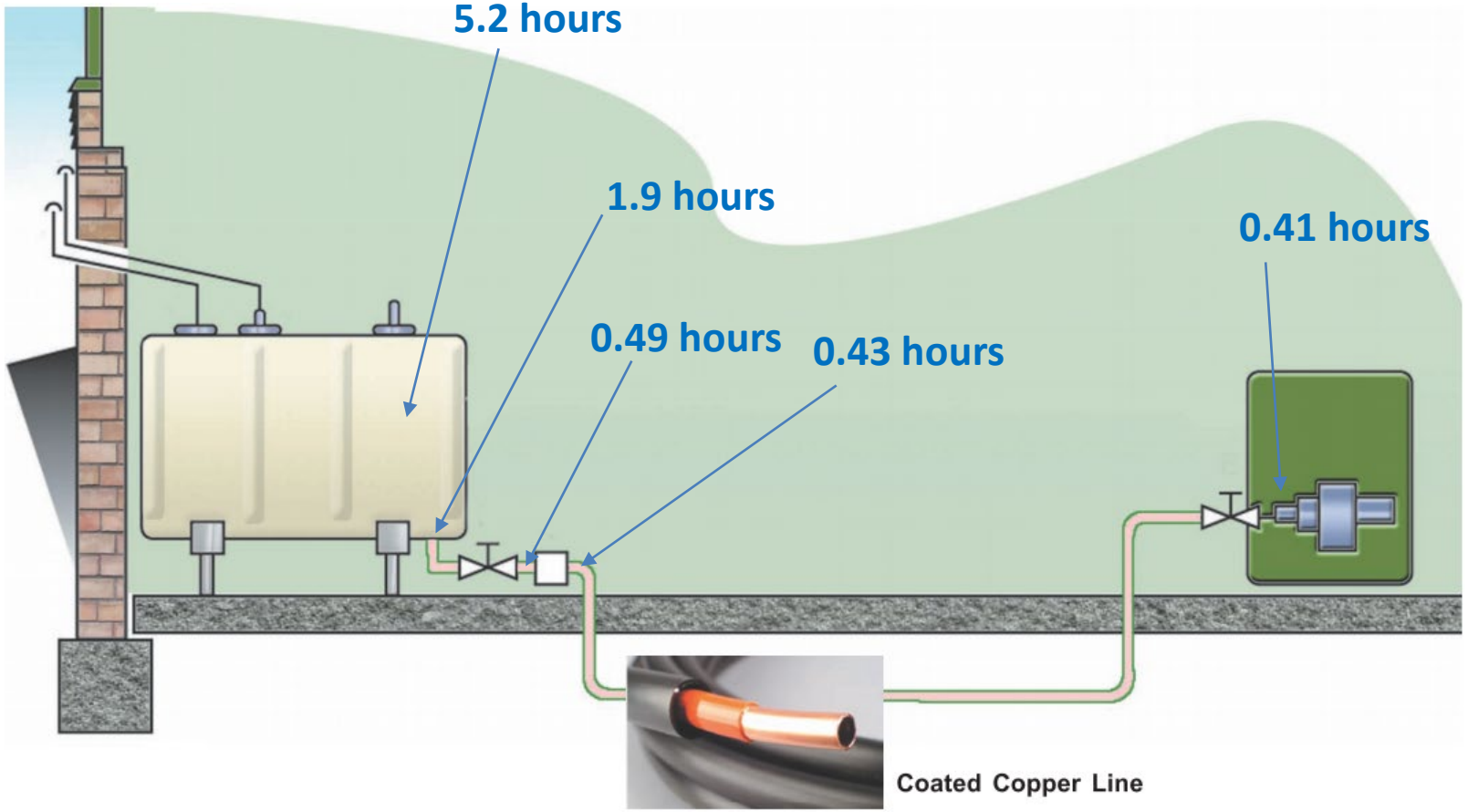
Does biodiesel maintain its quality over time in home tanks?

When changing from low blends to high blends how much is excess air or CO_2 impacted?

Over extended periods, in normal use, how does biodiesel impact the heating system?

General observations from several field campaigns

B20 to B100 sites;
Sites with up to 5 years of biodiesel blend use;
Acid numbers can exceed 0.5 but rarely over 0.8;
Measured oxidative reserve often very low but depends on sampling location;
In some sites very high filterable particulates at the pump bleeder point.



Measured oxidative reserve (stability / Rancimat) Field site with B100 fuel. Summer – low use period. This site has special sampling taps before and after the filter.

Copper Exposure Test -1 (at NORA)

Common copper tube
Vertical, sealed at bottom
I.D. = 6.75 mm
O.D. = 9.36 mm
Fuel Volume = 14 ml
Exposure time = 24 hours
Ambient temperature
Control sample without copper exposure
Exposure 5.9 cm^2/cm^3

Sample	Oxidative Reserve (Rancimat – hrs)
No. 2 oil (control)	18.3
No. 2 oil (copper)	3.1
B20 (control)	8.2
B20 (copper)	1.0
B50 (control)	7.8
B50 (copper)	0.1
B100 (control)	6.1
B100 (copper)	0.1

Note: No. 2 heating oil contains nomially 5% biodiesel.

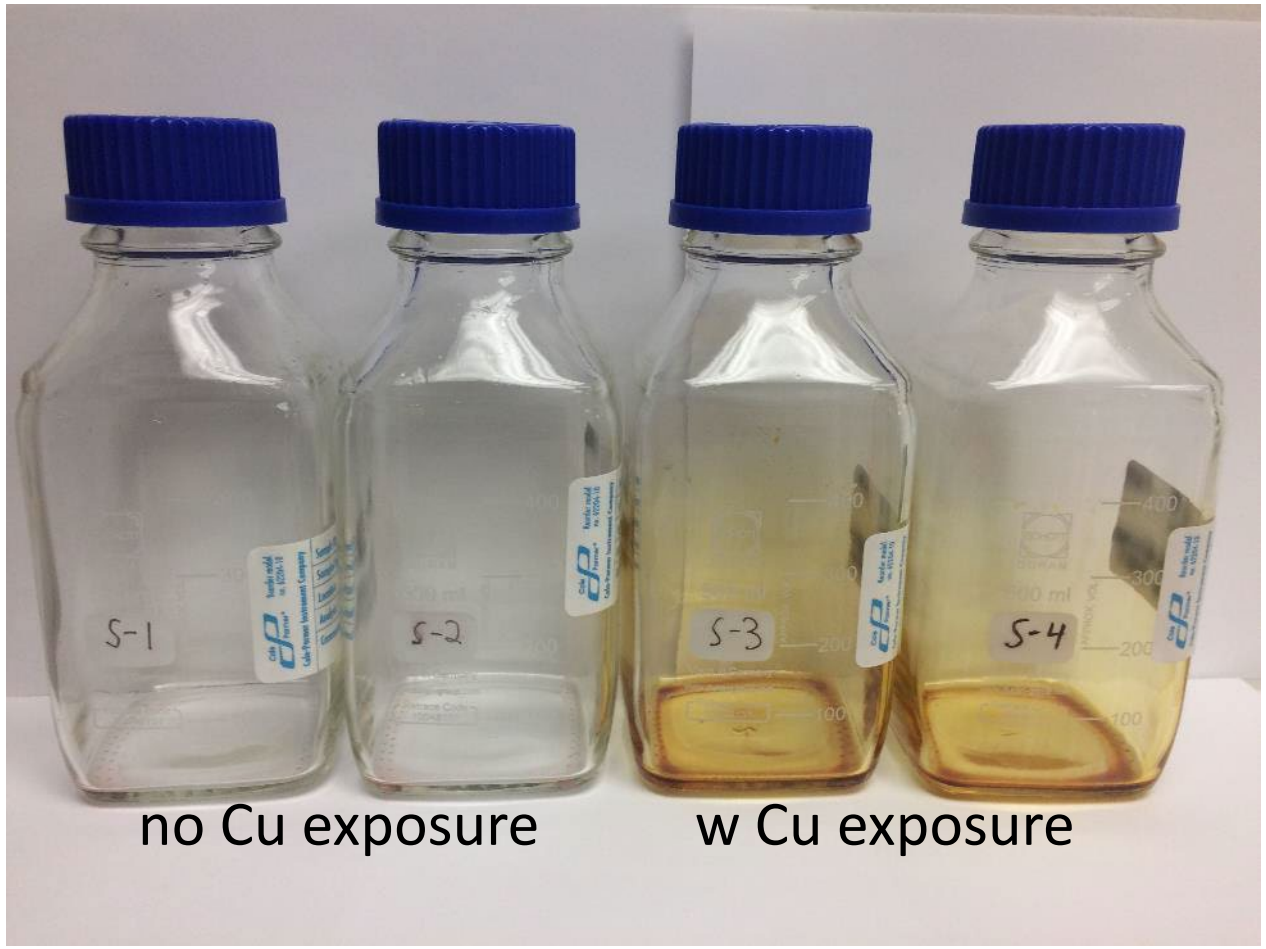
Copper Exposure Test -2 (at REG)

- Same exposure conditions as test 1
- B50 only
- Different fuels, done at REG lab
- Added metals analysis by ICP

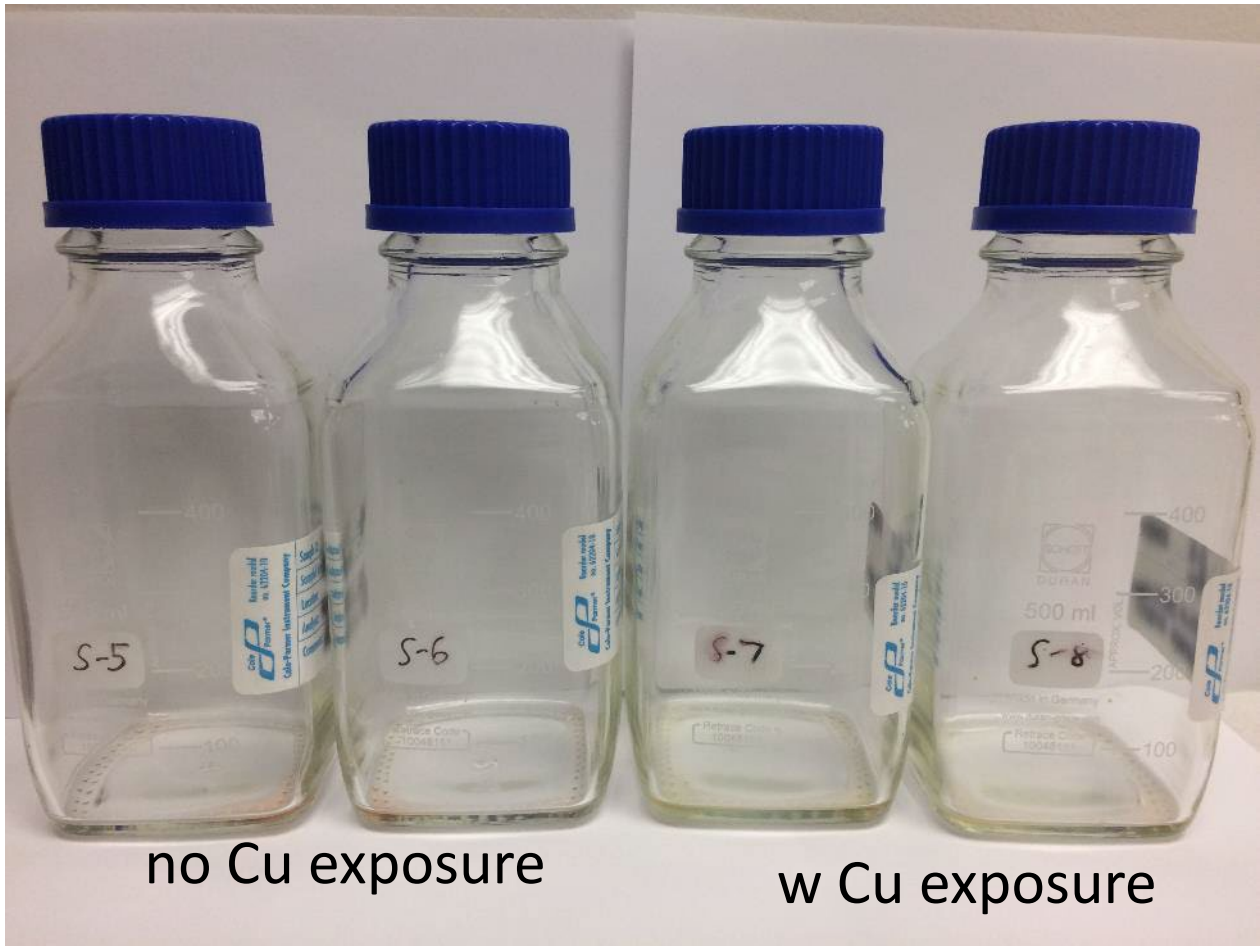
Sample	Oxidative Reserve (Rancimat – hrs)	Copper content (ppm)	Lead content (ppm)	Zinc content (ppm)
B50 (control)	7.6	0.1	0.1	0.1
B50 (copper)	0.2	4.1	1.3	1.6

Long Term Storage Stability Test (ASTM D4625)

- Glass containers at 43 °C, 9 weeks;
- Analysis for filterable insoluble and adherent insolubles;
- 0.8 micron filter, vacuum filtration;
- Solvent – acetone, methyl alcohol, toluene;
- Acid number and Oxidative reserve before and after as added metrics;
- Fuel samples exposed to copper for 24 hours using cut copper pieces in glass beaker. Fuel then separated from copper prior to the start of the test.
- Exposure 0.59 cm^2/cm^3

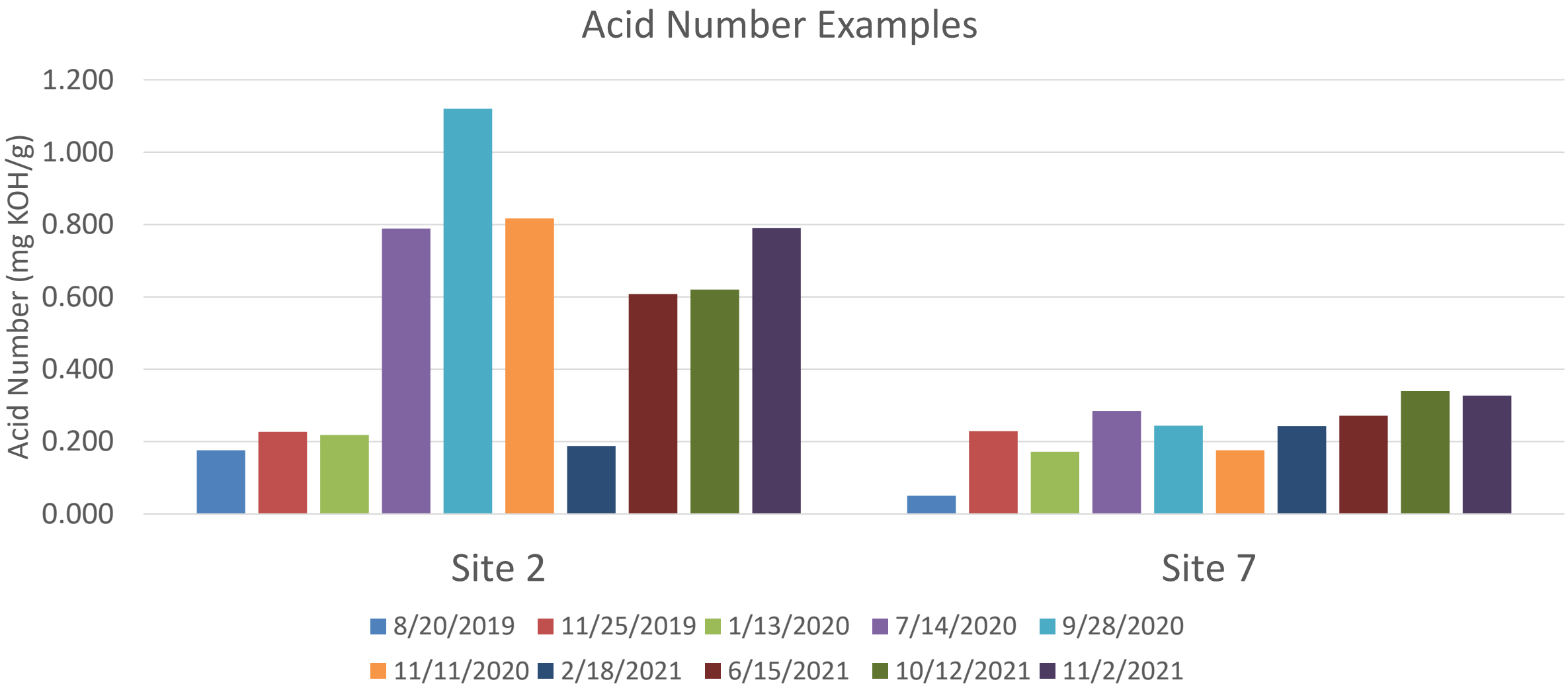


No. 2 heating oil (nominal B5)



B20 Blend

Acid Number Over Time



Summer Fuel Stability B50

Over the summer, no deliveries are made. Is the fuel stability decreased over this summer period? And does the stability improve with a new delivery?

Site	Jan 2020	July 2020	Sept 2020	Nov 2020
Site 1	8.4	5.04	3.17	1.96
Site 2	10.4	2.82		0.52
Site 3	1.0	0.68	0.57	0.45
Site 5	8.6	5.80	4.83	9.54
Site 6	10.3	8.16	6.37	9.55
Site 7	10.5	9.28	5.25	10.22
Site 8	11.5	6.78	5.91	11.94
Site 9	6.2	0.04	0.81	2.44
Site 10	4.7	7.24	4.63	3.92
Site 11	2.9	2.19	2.71	5.02
Site 12	5.2	1.44	0.85	9.73

Note: Last delivery in spring done on May 14, first delivery of fall done on Oct 21

B50 Field Test Summary

ASTM Limits

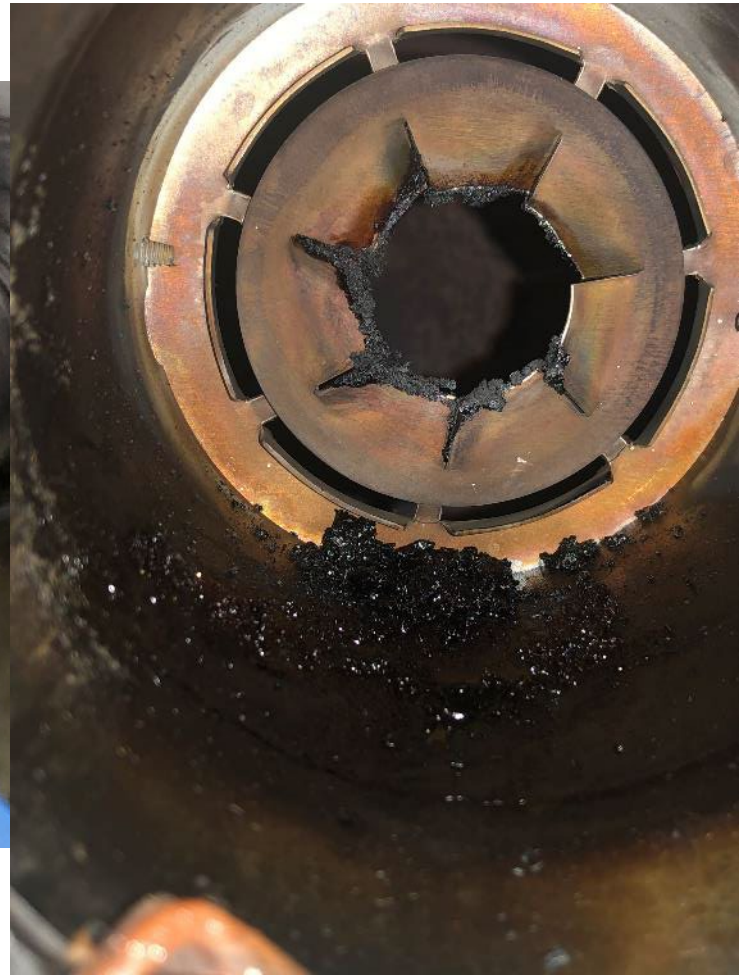
	B20	**B100**
Rancimat (hrs)	6	3
TAN (mg/kg)	0.3	0.5
Carbon Residue (%)	0.035	0.05

	Rancimat	**TAN**
End of Heating Season	0% > 6 hours	70% > 0.3
	90% > 3 hours	20% > 0.5
End of Summer	0% > 6 hours	90% > 0.3
	40% > 3 hours	40% > 0.5

Carbon Buildup

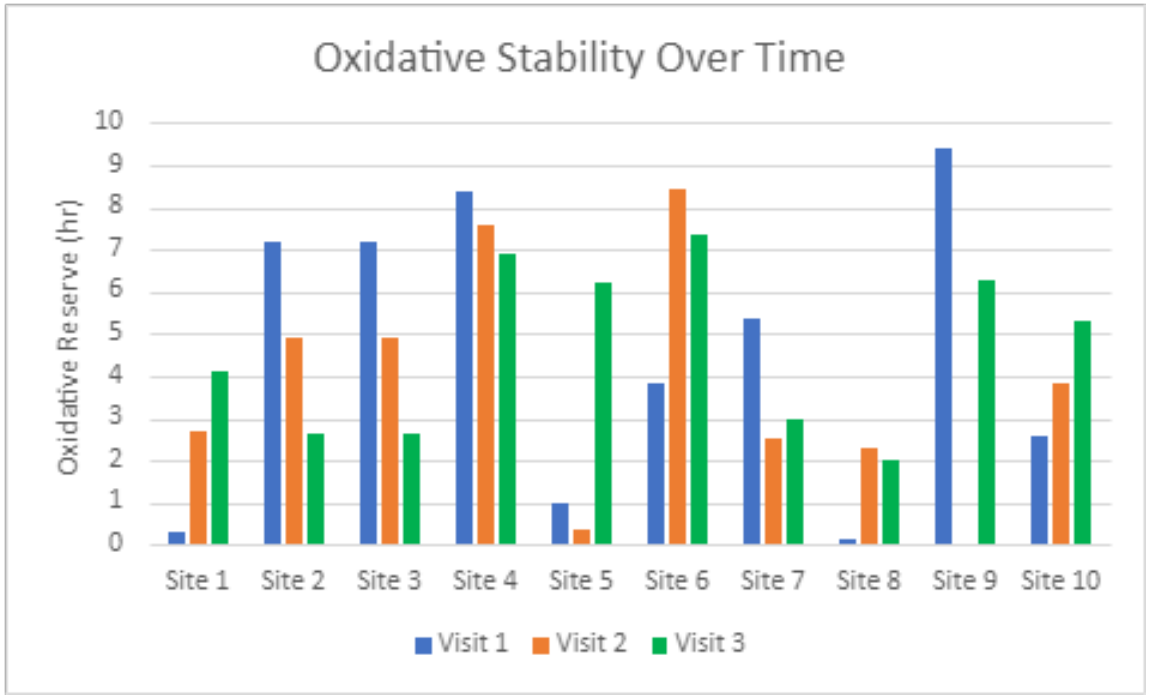
- Some sites in the test showed a buildup of carbon on the burner head or in the air tube

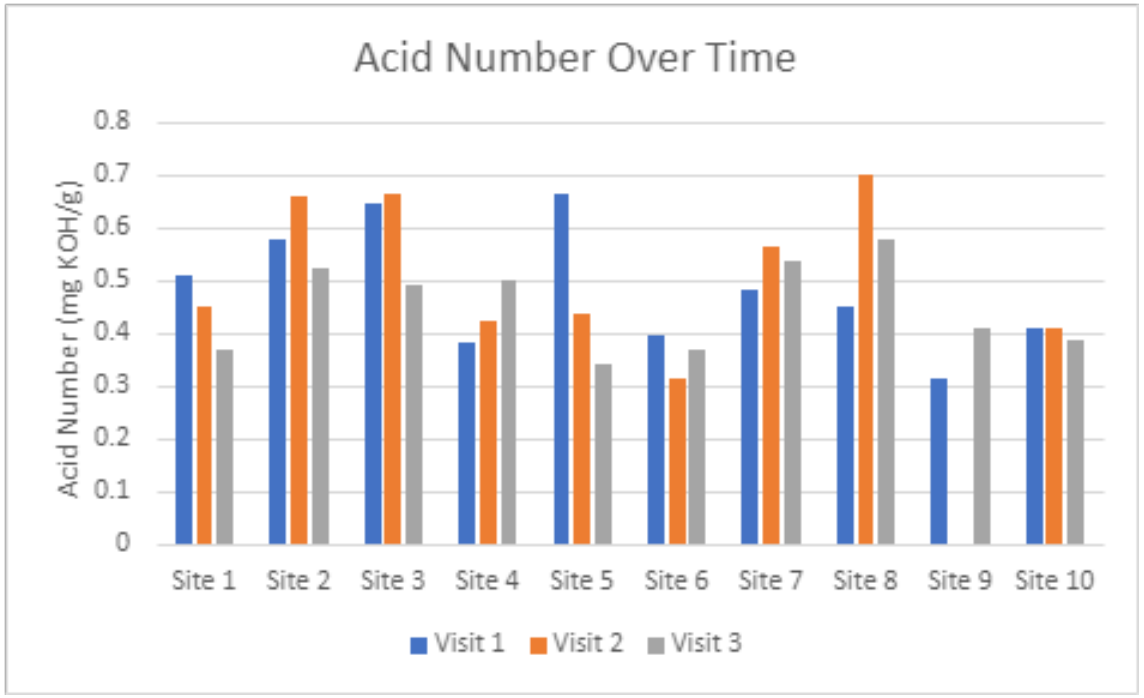
- Investigations into the root cause and preventative measures for this issue are ongoing



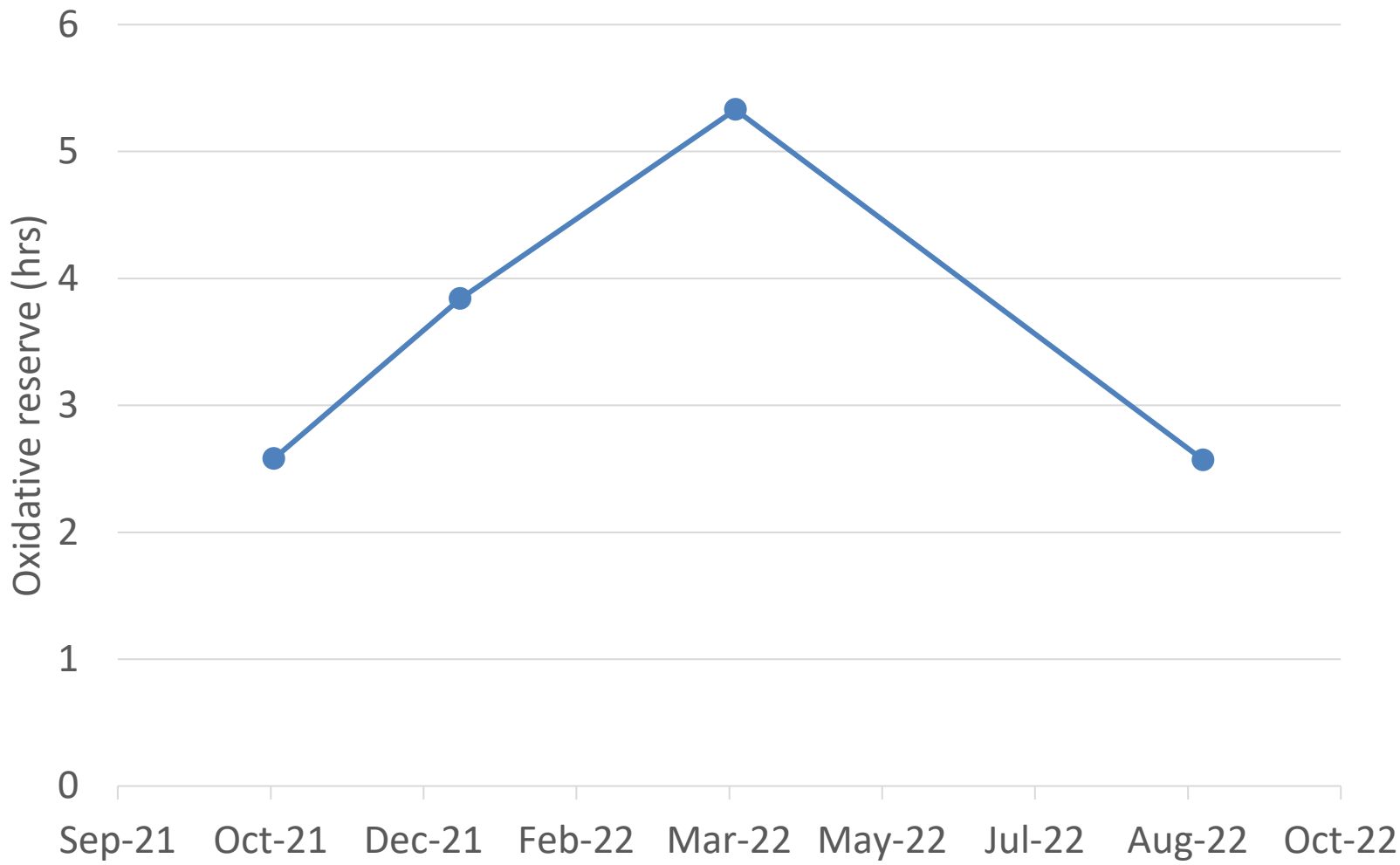
B100 Test

- B100 Field Test at Hart Home Comfort is Continuing. Started Nov. 2021. 10 Sites. End of Summer Samples Recently Collected. Analysis in Progress.





Visit 1 – Nov 2021, Visit 2 – Feb. 2022, Visit 3 – April 2022



Oxidative reserve over time – site 10

NORA In-House Rapid Coking Test

- Peerless Boiler
- 1 hour of steady state followed by 1000 cycles; 15s on and 60s off
- Fuels used:
  - B5 from in-house tank
  - Soy based and part-UCO based B100
  - B50 made using part-UCO B100
  - Distilled B100
- Head pictures taken before and after test along with mass measurement
- 43 tests done on Peerless boiler under various conditions and fuels

NORA Rapid Coking Test – Observations to Date

- Increasing biodiesel content leads to more deposit
- Less deposit mass with added refractory
- Cycling as a key source of deposit mass
- Post-purge helps reduce deposits
- Distilled biodiesel less mass than non-distilled

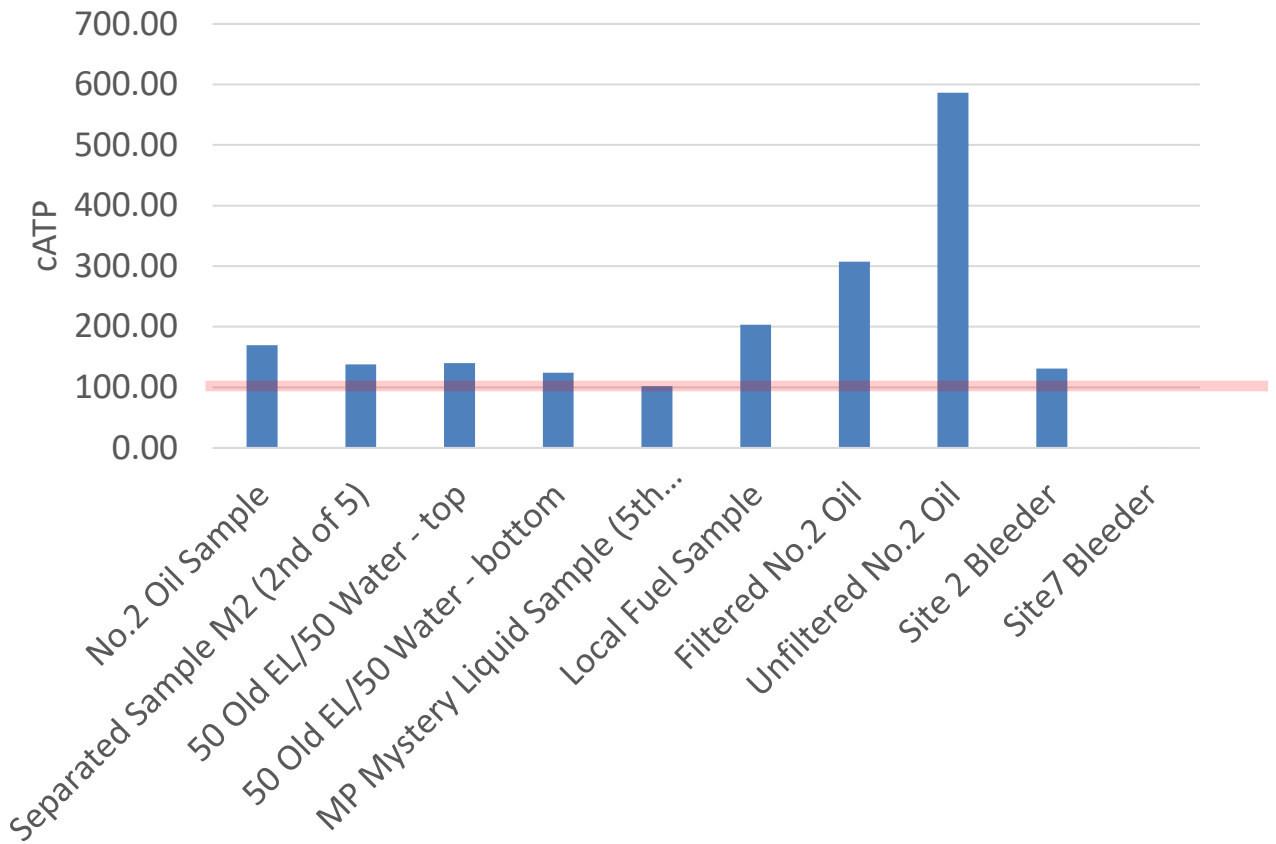
This work is ongoing. In parallel our Engineering Intern – Michael Persch is developing a concept for a Master's Thesis at Stony Brook University modeling the practical impacts of biodiesel's distillation characteristics on liquid fuel flow back to the burner head.

A limited field test of distilled biodiesel is also being started in collaboration with Cubby Oil.

Corrosion in Tanks

Recent published studies showed no significant impact of biodiesel or fuel sulfur level;
Water plus products of biological or oxidative degradation key factors;
Current NORA work focused on tools to evaluate how bad a tank environment is.

New instrument at NORA measures ATP a strong indicator of biological activity.



Possible ways to address biodiesel and biodiesel blend cold flow

- Specify biodiesel properties for location/season;
- Additives;
- Blend with No. 2 petroleum or kerosene;
- Winterization (fractional crystallization);
- Isomerization;
- Esterification with alternative alcohols;
- Control temperature environment / heating.

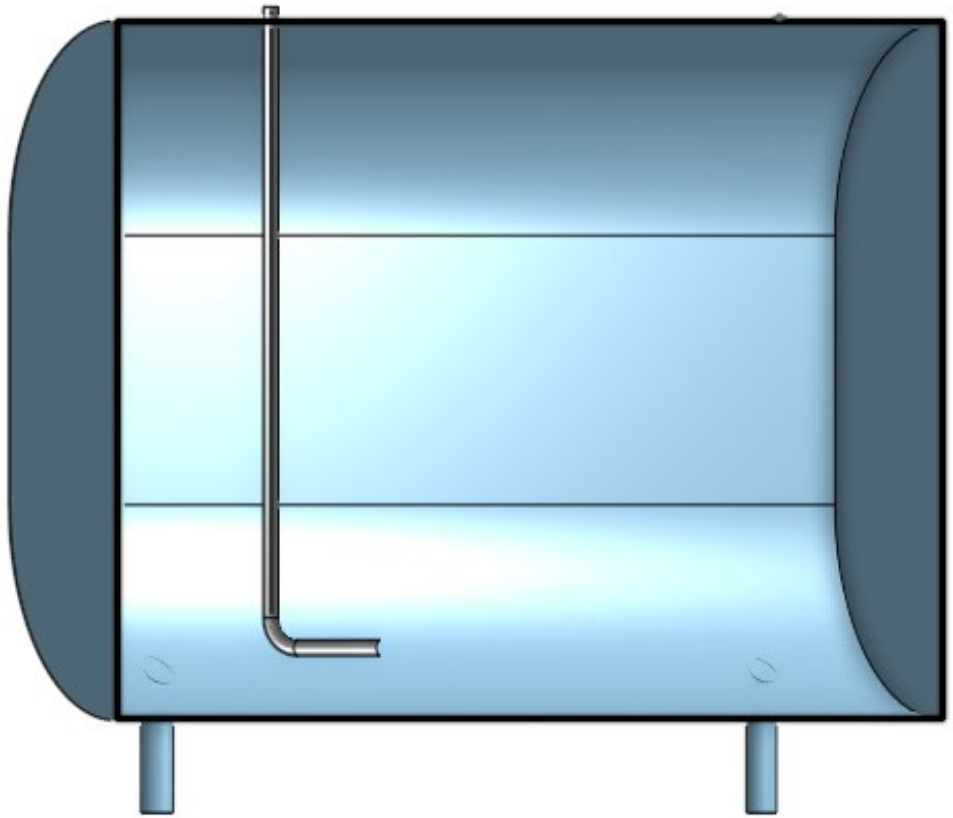
Solutions for Outside Tanks

- Almost 90% of home heating oil tanks in the U.S. are located inside the home (i.e., in the basement)
  - This essentially eliminates cold flow concerns with B50 or B100 for most homeowners

- For B50 proper management of fuel selection and additives will likely provide adequate cold flow for the 10% of outside home heating oil tanks

- For B100 (maybe some B50) alternative solutions will be needed for the 10% of tanks that are outside
  - Many tanks cannot practically be moved inside
  - Segregating deliveries not desired
  - Require heat or insulation of some sort

Horizontal Heating Element



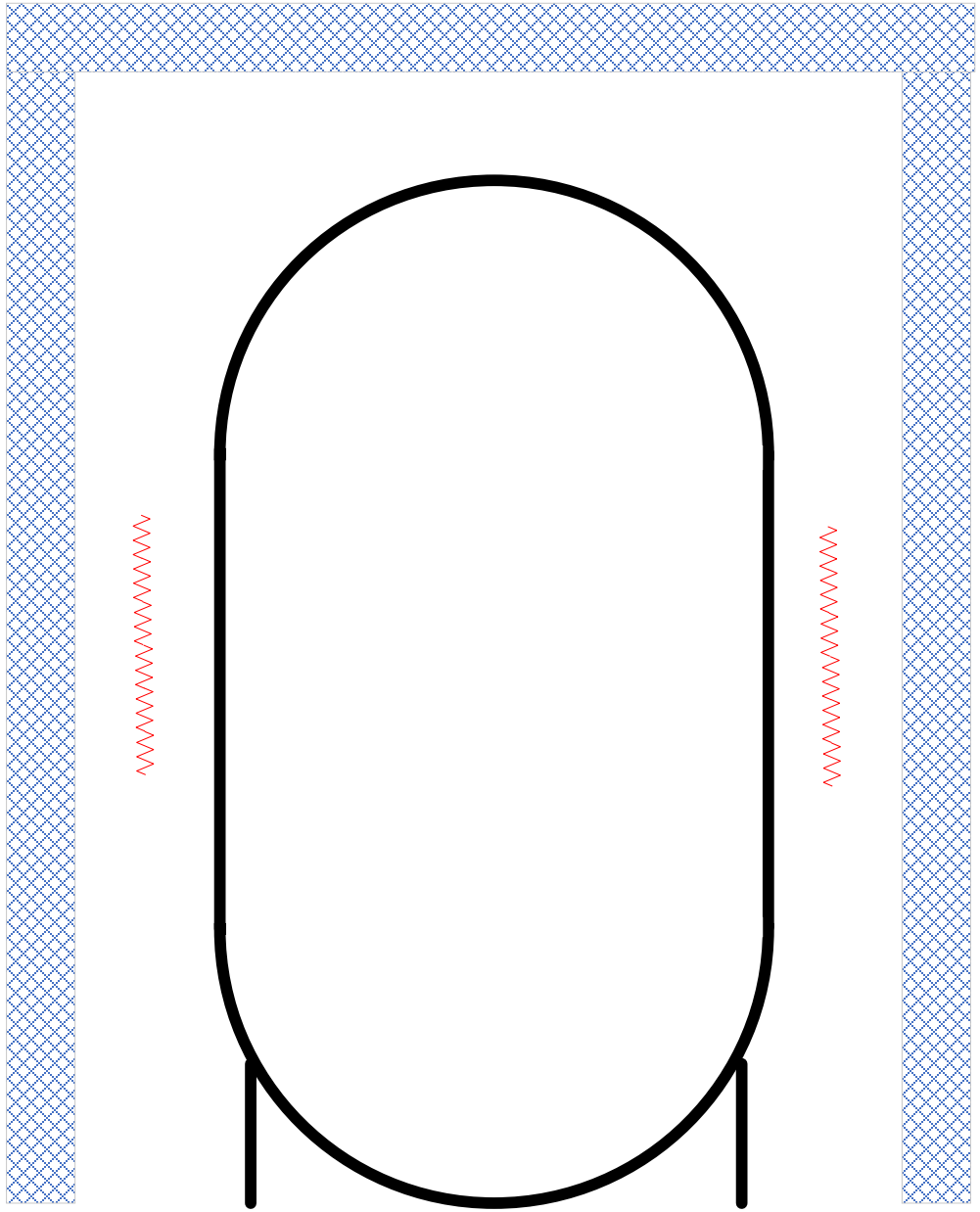
Failure of Test Visualized

2 hours

17 hours

23 hours

Insulated enclosure concept. R15 insulation.



Summary of Tank Heating Tests

- An in-tank, 200 watt heater is effective, can recover a gelled tank in about 8 hours;
- An insulated enclosure with heater in the air space very effective for maintaining tank but not for rapid recovery;
- Insulated “jackets” effective but concern about condensation between jacket and tank and corrosion. Need to be able to inspect tank.
- Solution will depend on region.

Thanks!

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More details: www.noraweb.org/technical-bulletins/