Monitoring Biodiesel Blends in Heating Applications – Effects of Exposure Conditions

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Biofuels in the U.S. Heating Market

- Over 5 million homes and businesses use liquid fuels for heating in the U.S.;
- Annual consumption ~ 5 billion gallons, residential and commercial combined;
- This industry has committed to a conversion to biofuels:
  - 40% GHG reduction by 2030
  - Net zero GHG by 2050
- Currently biodiesel (FAME) is the only biofuel used;
- Renewable diesel (HVO) and other fuels are future candidates.

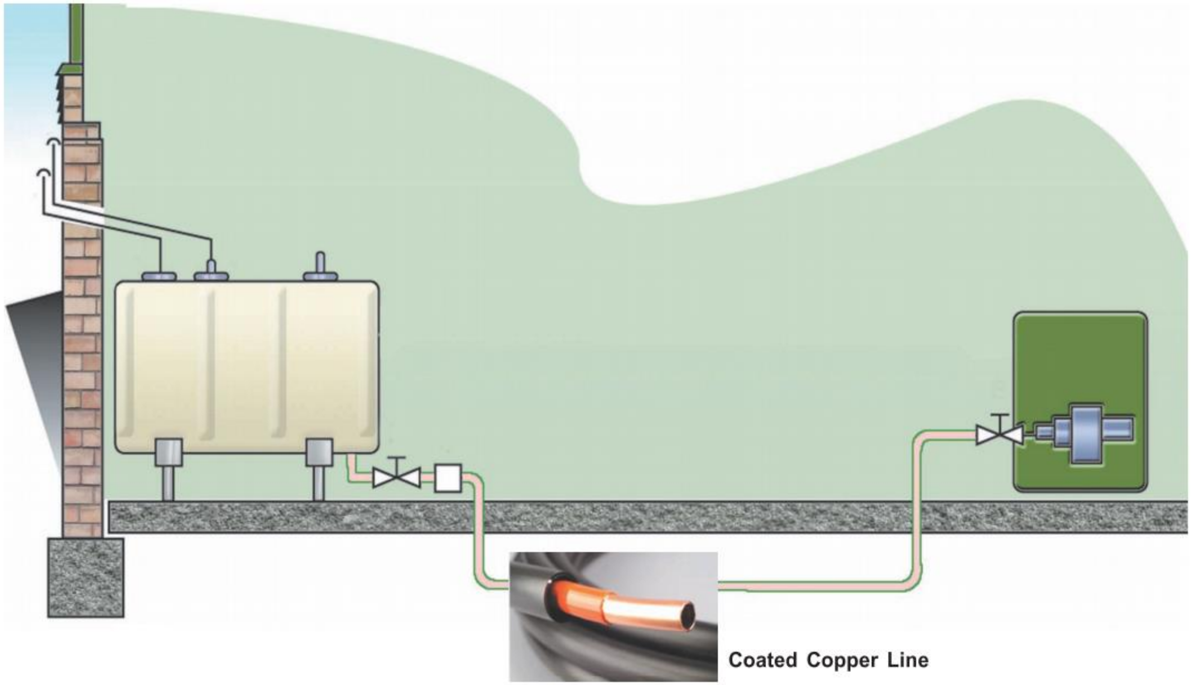
Biodiesel Status in the U.S.

- B100 specifications formally defined (ASTM D6751);
- Standard heating oil can contain up to 5% biodiesel, B5-B20 is a defined fuel (ASTM D396);
- Equipment approval standards in place for up to B20, in progress for fuels up to B100 (UL 296)
- Beyond traditional specs, Stability (Rancimat) and Acid Number added for B100 and blends;
- B5 blends are now routinely used;
- B20 now commonly used by several fuel marketers

  One marketer has committed to B20 use in 400,000 homes;
- One marketer now delivers B50 to over 8,000 customers;
- B100 now routinely used in Seattle in 150 homes;
- B100 pilots underway in Vermont, New York and other locations.

Typical Residential Systems

- Most home systems have 275 gallon steel tanks;
- Indoor tanks most common but outside and buried tanks also used;
- Fuel deliveries typically 3-4 times each year;
- Many tanks are older than 20 years;
- Tanks are not cleaned;
- Flexible copper lines commonly used to deliver fuel to burner.



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NORA Interest in Biodiesel Blends in the Field

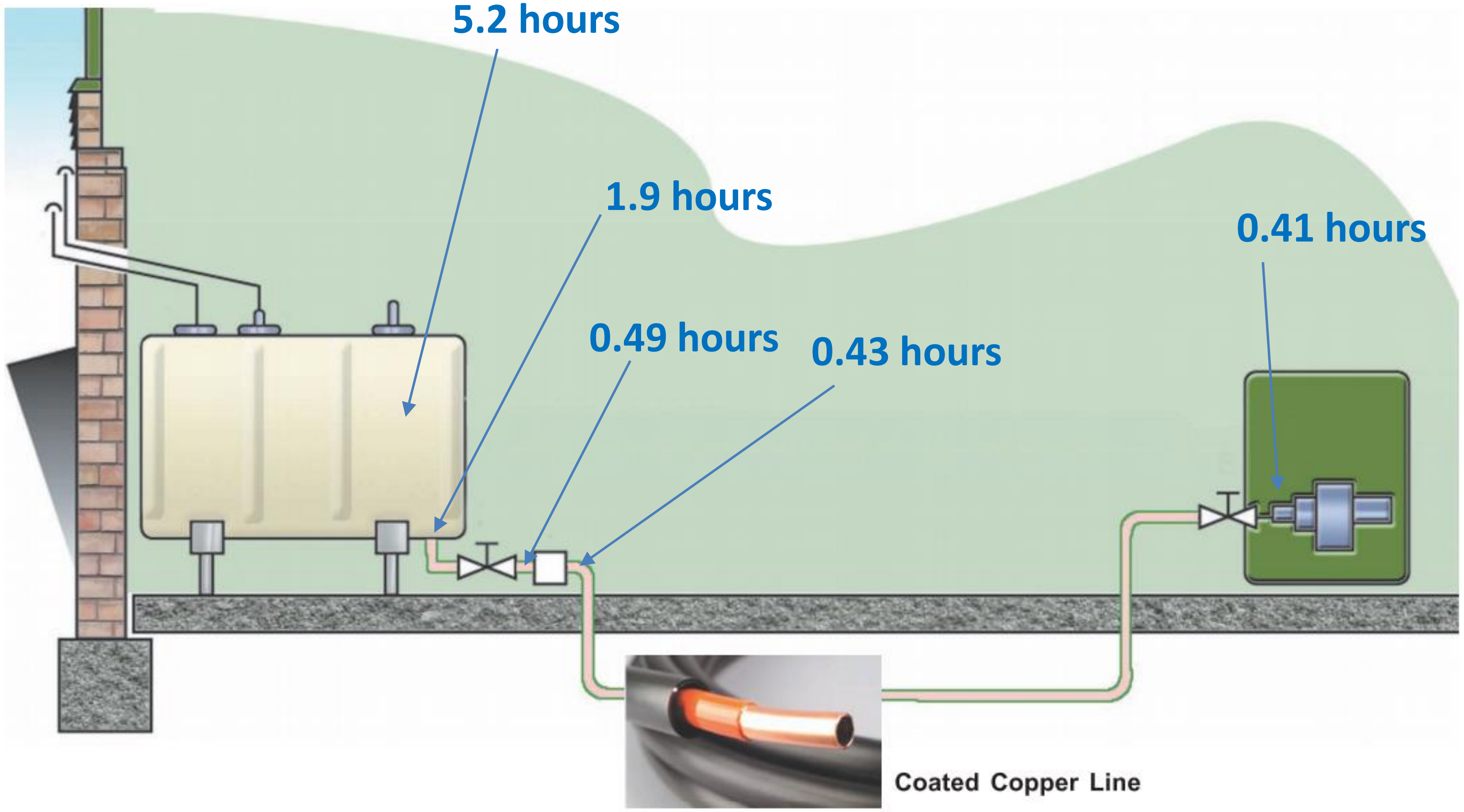
The storage and use environment in heating applications is somewhat unique; Many home tanks have significant degradation products and some water on the bottom.

Questions we are interested in:

Are biodiesel blends in routine service healthy?
Is oxidative degradation of biodiesel blends over summer storage a concern?
Will additives delivered with “fresh” fuel keep even older fuel protected?
Can in-use acid numbers reach levels that could impact elastomers?
When testing equipment for approval how “aggressive” a test fuel should be used?

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.

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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

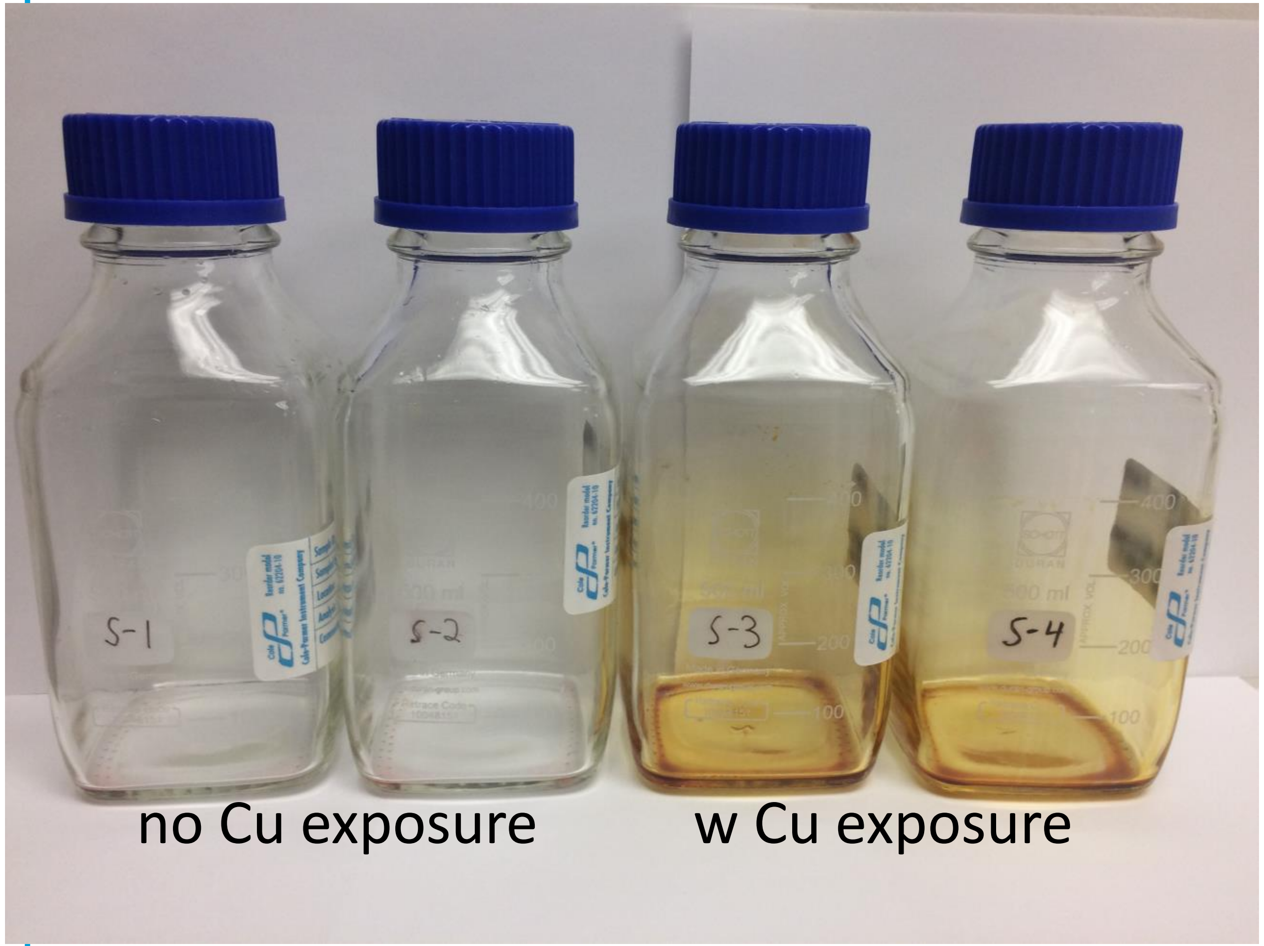
Long Term Storage Stability Test (ASTM D4625)

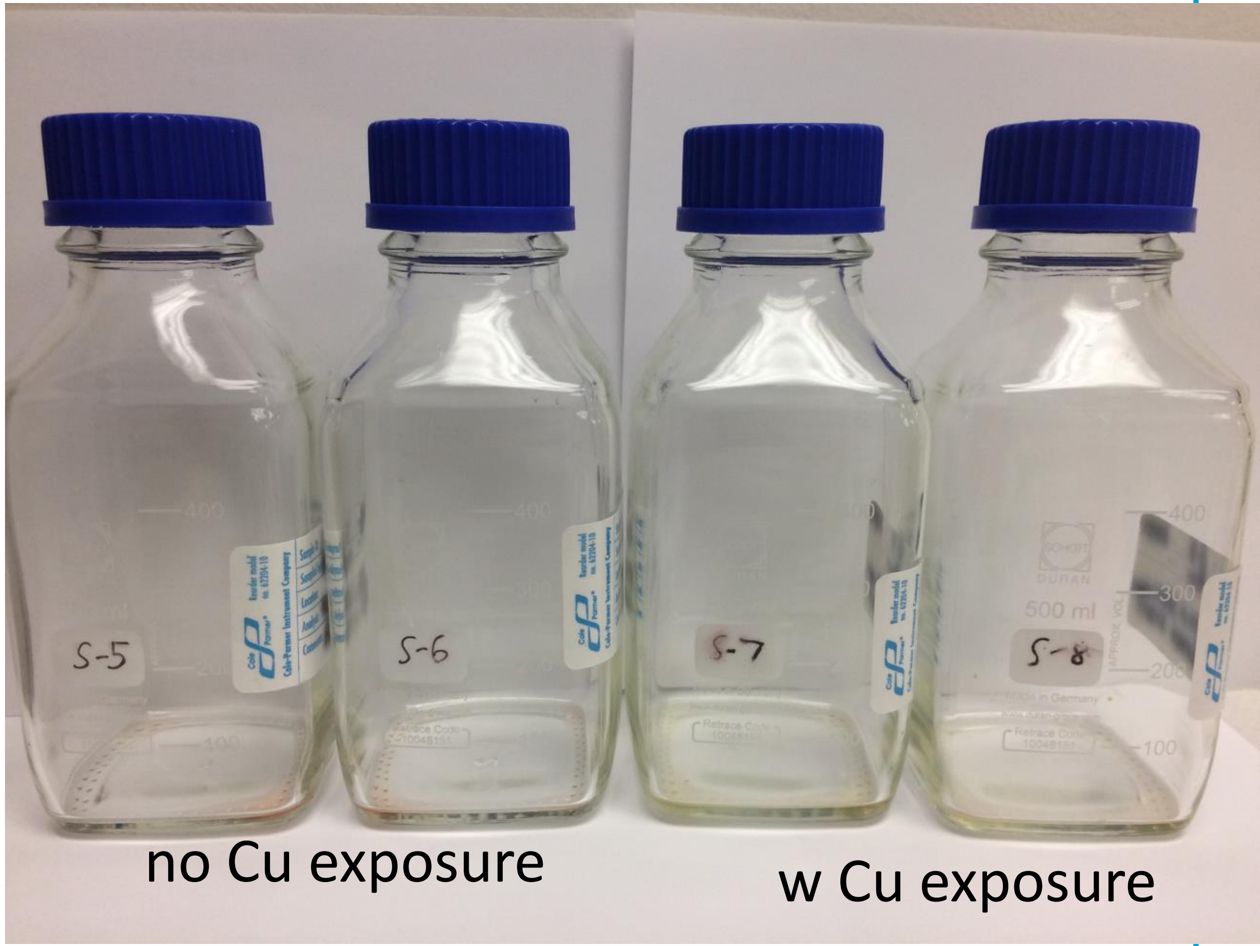
- Glass containers at 43 °C, 9 weeks;
- Analysis for filterable insoluble and adherent insolubles;
- 0.8 micron filter, vacuum filtration;
- Solvent – acetone, methyl alcohol, toluene;
- Acid number and Oxidative reserve before and after as added metrics;
- Fuel samples exposed to copper for 24 hours 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

Long Term Storage Stability Test (ASTM D4625)

Sample ID	Oxidative reserve (Rancimat – hrs)	Acid Number (mg KOH/g)	Filterable Insolubles (mg/100 mL)	Adherent Insolubles (mg/100 mL)
No. 2 heating oil #1, (initial)	30.6			
No. 2 heating oil #1, (control)	10.7	0.01	0.5	5.0
No. 2 heating oil #1, (copper)	0.02	0.81	12	93.2
No. 2 heating oil #2, (control)	10.9	0.05	0.25	6.0
No. 2 heating oil #2, (copper)	0.03	0.75	5.5	95
B20 #1, (control)	3.6	0.13	0.25	6.5
B20 #1, (copper)	0.02	0.87	5.25	17.8
B20 #2, (control)	4.5	0.13	0.25	6.5
B20 #2, (copper)	0.01	0.87	6	12.8

Note: No. 2 heating oil contains up to 5% biodiesel.





No. 2 heating oil (nominal B5)

B20 Blend

Time Study - Nominal B5, Changes over 12 weeks

- No. 2 heating oil (nominal B5), exposed to copper with lengths of tubing in a beaker;
- This provides a lower surface to volume ratio than fuel-in-tube 0.59 cm^2/cm^3;
- Exposure for 24 hours and then fuel removed from copper exposure;
- Aged at 43°C as per ASTM 4625;
- Samples removed at 3,6,9,12 weeks for Oxidative Reserve (Rancimat); Acid Number; Filterable and Adherant Insolubles Analysis

Time Study - Nominal B5, Changes over 12 weeks

Sample ID	Duration (weeks)	Oxidative Reserve (hr)	Acid Number (mg KOH/g)	Filterable Insolubles (mg/100 mL)	Adherent Insolubles (mg/100 mL)
B5 Fuel (initial)	0	23.59			
B5 Fuel (copper)	3	1.86	0.10	0.8	9.5
B5 Fuel (copper)	3	0.03	0.01	1.3	9
B5 Fuel (copper)	6	0.06	0.13	5.5	14.5
B5 Fuel (copper)	6	0.06	0.29	12.5	16.3
B5 Fuel (copper)	9	0.02	0.40	13.8	31.0
B5 Fuel (copper)	9	0.02	0.37	13.3	27.8
B5 Fuel (copper)	12	0.02	1.14	5.5	317.5
B5 Fuel (copper)	12	0.02	1.10	7.5	764.3
B5 Fuel (control)	12	10.61	0.06	0.5	14.3

Two-Pipe Systems

Some burner systems are arranged as “two-pipe”. Here the relief flow from the pump pressure regulator returns to the tank through a separate copper tube.

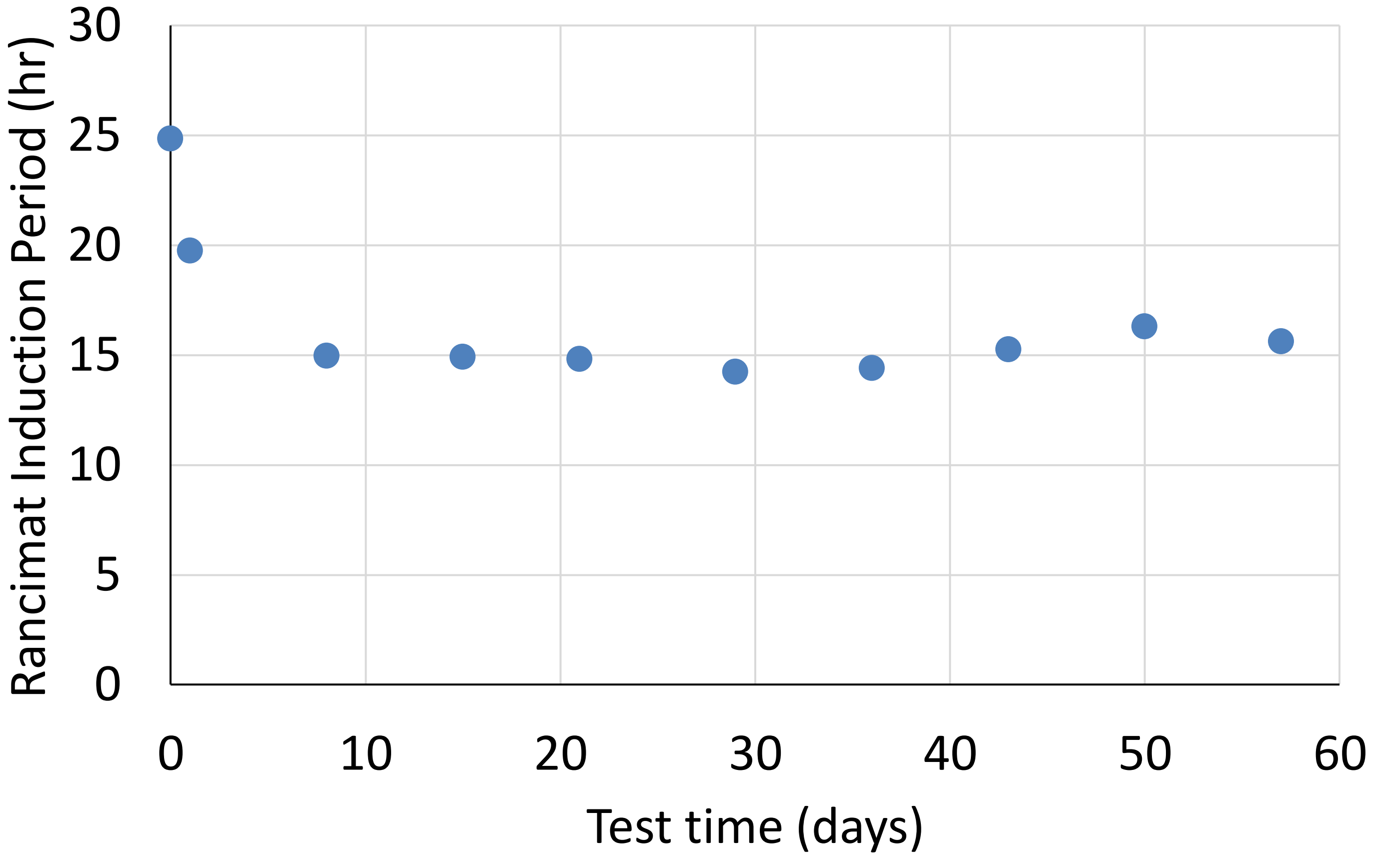
This approach leads to rapid priming and air elimination in high-lift situations but greatly increases the amount of fuel that must be filtered. This approach is becoming less common.

With two pipe systems the fuel has more opportunity to pickup copper in solution and this is returned back to the bulk tank.

Two-Pipe System Test Setup

- 379 liters of No. 2 heating oil with 5% biodiesel;
- Standard fuel pump – setup with two pipe arrangement;
- 7.9 m of copper fuel line on both supply and return;
- Continuous operation for 2 months;
- Exposure .018 cm^2/cm^3

Two –pipe system – Change in oxidative reserve (Rancimat) over time.



Note: Nominal B5

Summer shutdown

Some heating systems operate all year, providing domestic hot water in the summer. For systems which do not, fuel can be stagnant in a copper line for 6 months. If this fuel degrades heavily it can damage downstream fuel system components after startup.

To study this case a sample of No 2. heating oil (with up to 5% biodiesel) was stored in a copper line for 6 months. Tube length was 9.1 m, volume of fuel was 420 ml, 5.9 cm^2/cm^3, ambient temperature.

Control sample stored in a sealed, epoxy-lined container

Sample ID	Oxidative Reserve (hr)	Acid Number (mg KOH/g)	Filterable Insolubles (mg/100 mL)
No. 2 heating oil, (initial)	17.8		
No. 2 heating oil, (control)	15.2	0.025	0.2
No. 2 heating oil, (copper)	1.2	0.02	0.2

Note: Nominal B5.

Summer shutdown

Following this test these same fuel samples were stored for an additional 15 weeks, with open exposure to air

Sample ID	Induction Time (hr)	Acid Number (mg KOH/g)	Filterable Insolubles (mg/100 mL)	Adherent Insolubles (mg/100 mL)
No. 2 heating oil #1, (control)	8.9	0.04	0.6	11.7
No. 2 heating oil #1, (copper)	0.01	0.55	2	230

Note: Nominal B5.

Conclusions

- The impact of copper exposure on measured oxidative stability of distillate fuel samples is very strong;
- In these tests the impact on fuels with a low biodiesel content was found to be higher than with a higher biodiesel content;
- Continuous exposure to copper is not necessary for these effects. Exposure leads to dissolved copper in the fuel sample which causes instability;
- When evaluating the "health" of fuels in the field, samples not-yet-exposed to copper are a better indicator of the bulk fuel condition;
- Fuels exposed to copper for long times inside of lines may not degrade because of the absence of oxygen;
- In single pipe fuel systems, the fuel can be exposed to copper and become unstable but is quickly burned;
- These results overall do not make a case for replacement of existing copper fuel lines in existing systems.