IASH 2022, the 17TH INTERNATIONAL CONFERENCE ON STABILITY, HANDLING AND USE OF LIQUID FUELS
Dresden, Germany
11-15 September 2022

MONITORING BIODIESEL BLENDS IN HEATING APPLICATIONS – EFFECTS OF EXPOSURE CONDITIONS

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***Keywords*:** heating oil; biodiesel; copper; oxidation reserve; oxidative stability; Rancimat

ABSTRACT Petroleum distillate fuel has been used for many years for building heating applications. This market is now increasingly using biodiesel blended with petroleum fuel. While copper is not recommended for conventional diesel engines and fuel systems, the use of copper lines in the heating oil industry in the U.S. is common due to their lower cost and ease of manipulation and installation. This study focused on the potential impacts of copper on the fuels used in today's home heating oil systems (i.e. ultra low sulfur No. 2 petroleum distillates and their blends with biodiesel) and showed the effects depend largely on the surface to volume ratio of the exposure to copper, access of the copper-exposed fuel to oxygen, residence time of the fuel in contact with copper, and the overall time before the fuel is burned. The practical implications of this research are that the presence of copper in heating systems should not present significant formation of acids or filterable insolubles that could adversely affect system operation of over time with either ultra-low sulfur No. 2 petroleum distillates or their biodiesel blends. This is likely due to the specific exposure conditions to copper in normal heating oil systems and the relatively small amounts of fuel exposed to both copper and oxygen for extended periods of time. To the extent conditions do exist where changes over time could occur, the changes observed with biodiesel blends were found to be similar or less than those with conventional No. 2 petroleum distillate fuel oil. However, exposure to copper can dramatically impact the measured oxidative reserve and this has important implications when sampling for monitoring fuel quality in this application.

Introduction

The heating oil market is an important consumer of distillate fuel in the U.S. with about 5 million homes using this fuel. Most of this consumption is in the Northeast. The heating oil market is currently in a period of transition to ultralow sulfur fuel (i.e. less than 15 parts per million sulfur) and increased use of biodiesel in blends with petroleum distillate (No. 2 heating oil)[1]. Some fuel marketers have taken the initiative to blend 20% biodiesel into No. 2 heating oil. Still others are exploring higher blend levels. Other biofuels are also being explored[2], but biodiesel is the most widely available and the lowest cost, so it is currently of the most commercial interest to the heating oil market in the U.S.

Figure 1 provides an illustration of a typical, residential fuel storage and burner supply system. This shows a storage tank indoors and at about the same elevation as the burner. Fuel storage tanks can also be outdoors, above ground or, less commonly, buried under ground. Tanks are most commonly made of carbon steel and have a typical storage volume of 1041 liters (275 gallons). This figure also shows the fuel line running from the tank to the burner under the foundation and coated with plastic. However, it is also common for the fuel line to be uncoated and to run inside the living or basement space. Copper fuel lines are most often 3/8-inch (9.5 mm) nominal diameter.

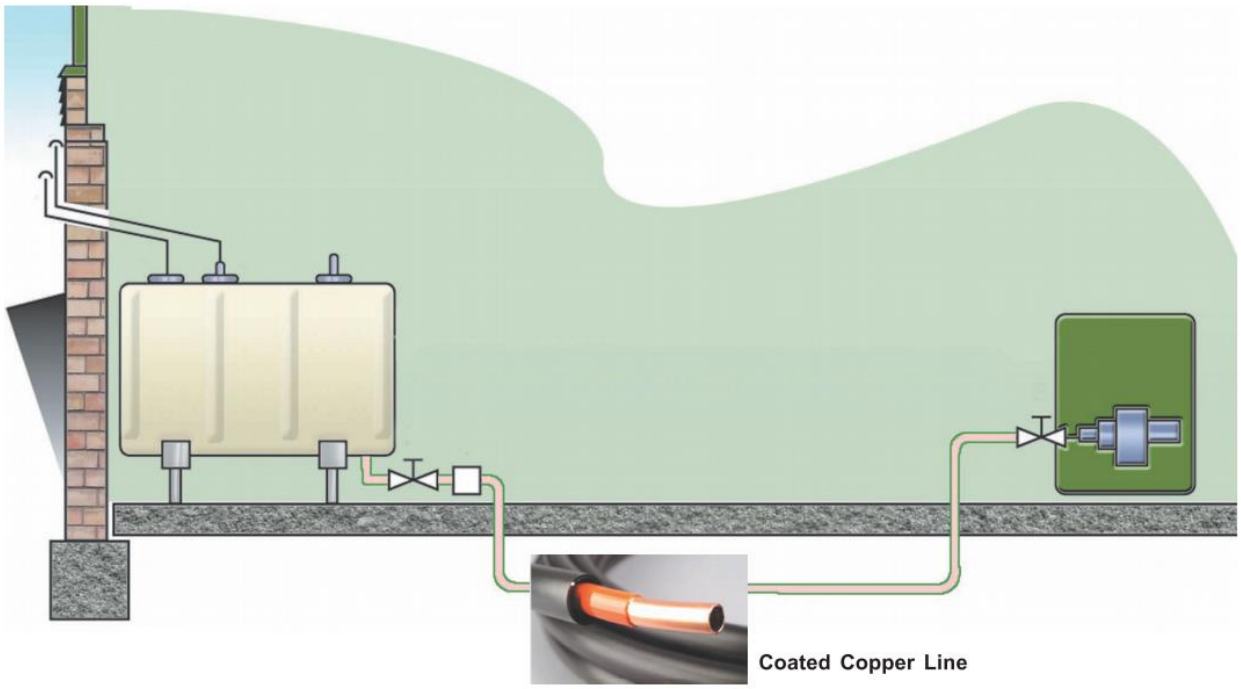

Figure 1. Illustration of a typical residential, oil-fired heating system fuel arrangement.

During normal winter operation, fuel flows from the tank to the burner periodically as the burner fires. When the burner is off, fuel is stagnant in the line, but during regular operation the residence time in the copper fuel line is only a few seconds.

Some boiler-based heating systems also operate during the summer for domestic hot water service. In this case, the fuel has the potential to be exposed to copper in the lines for longer time periods, but this rarely exceeds a few hours. In systems which are fully out of service during the summer, such as warm air furnaces, fuel can remain in the copper fuel line for up to 3-6 months.

The system in Figure 1 is termed a "one-pipe system". The burner fuel pump has an integral pressure regulator which bypasses excess fuel from the pump discharge internally back to the pump suction. In an alternative configuration, this bypass flow is directed back to the storage tank in a second copper line that runs parallel to the supply line. Fuel in these "two-pipe systems" can have greater exposure of the fuel to copper than the one-pipe systems. Two-pipe systems are typically only used when the fuel storage tank is at an elevation significantly below the burner and there is potential for air ingress into the fuel system due to the higher pump suction needed for these applications. In the U.S. market, it is estimated that 80 percent of the installations are of the one-pipe configuration, while the remaining are two-pipe.

Within common burner systems, fuel is directed at high pressure from the discharge of the pump through a short, small-diameter copper line to the atomizing fuel nozzle. The nozzle is the highest temperature component in the system. While stainless steel nozzles are available, most nozzles are brass. Nozzles are typically replaced annually but fuel lines are rarely replaced.

In the storage and handling of distillate fuel oil, it is often recognized that exposure to metals and the presence of dissolved metals in the fuel can accelerate oxidative degradation[3,4,5,6,7,8]. Some products of oxidation are relatively harmless in fuel while others that can form such as gels, particulates, or acids can be problematic. Copper is one such metal and it is generally recommended that copper should not be used in distillate fuel systems. The ASTM D975 standard for on/off road diesel states, "The formation of degradation products can be catalyzed by dissolved metals, especially copper and zinc. When dissolved copper and zinc are present it can be deactivated with metal deactivator additives." It goes on further to state, "Copper, copper-containing alloys, and zinc-coated or galvanized equipment should be avoided. Copper can promote fuel degradation and can produce mercaptide gels. Zinc coatings can react with water or organic acids in the fuel to form gels that rapidly plug filters." In general, copper is not recommended for either distillate fuel oils nor for biodiesel due to these factors.

In oil-fired home heating systems, however, copper fuel lines are commonly used due to their lower cost and ease of manipulation and installation. With the introduction of higher blends of biodiesel into home heating oil systems, questions have arisen about any potential differences in fuel performance of biodiesel blends vs. those of conventional petroleum-based distillates with the higher presence of copper in U.S. home heating oil systems vs. those commonly used for on- and off-road diesel fuel.

Currently, the ASTM D396 standard specification for fuels commonly used in home heating systems in the U.S. allows for up to 5% biodiesel by volume in the No. 1 and No. 2 grades, and also provides specifications for 6% to 20% biodiesel blends as heating fuels under the B6-B20 grade[9]. All three grades contain a specification for copper strip corrosion using the ASTM D130 test method of No. 3 maximum rating, as does the ASTM D6751 standard specification for B100. According to ASTM D396, "The corrosion test serves to indicate the presence or absence of materials that could corrode copper, brass, and bronze components of the fuel system." This parameter serves to help control potential corrosion of metal by the fuel, but it does not, however,

control potential adverse impacts of metal contact on the properties of the long term storage of the fuel.

The Rancimat Induction Period (IP) provides a rapid measure of fuel oxidation reserve and is specified as the indicator of storage stability in the ASTM D396 fuel specification for biodiesel blends. The oxidative reserve values mentioned throughout the remainder of this paper are those provided by the fuel version of the Rancimat test, EN15751 as per ASTM D396.

In a recent study[10], the impact of copper exposure on diesel fuel with 7% biodiesel was investigated at both low (12°C) and high (30°C) storage temperatures. One-liter samples were stored for up to 4 weeks in borosilicate glass flasks with and without copper plates. At one-week intervals samples were taken for evaluation of oxidative reserve or fuel property changes by three methods: oxidation reserve/Induction Period (EN15751), rapid small-scale oxidation test (EN 16091), and a gravimetric method (EN ISO 12205, the European version of ASTM D2274). All three measures indicated more changes that may impact fuel performance over time for the fuel samples stored with copper compared to those without copper. This effect was most pronounced at the highest storage temperature. The copper content of the fuel exposed to copper after the 4-week test was measured using an ICP-OES technique and found to increase only slightly from <0.1 ppm to 0.2 ppm for the fuel at 12°C, and 0.4 ppm for the fuel at 30°C.

In another study[11], the impact of different metal-containing additives on the measured oxidation reserve/Induction Period was studied over a range of biodiesel blend levels. Oxidation reserve was found to be reduced for metal contents up to 2.5 ppm, with copper having the most significant impact. Above 2.5 ppm, oxidation reserve was found to be unaffected by metal concentration. Antioxidant (storage enhancing) additives were found to improve the oxidation reserve for metal containing fuel blends. Similar results were found by Sarin et. al. for different biodiesel types[12,13]. Knothe and Steidly[14] extended studies of this type to a much wider range of metals and confirmed that copper stands out as having the most impact on oxidation reserve and potential changes in the fuel over time.

Öl-Wärme-Institute (OWI) in Aachen, Germany studied the long-term stability of samples of No. 2 heating oil and 20% biodiesel/80% heating oil blends with and without copper wire coils and additives. Their results showed a consistent decrease in oxidation reserve after exposure to copper. These tests were done in two series at 40°C, each lasting for 24 months. Storage enhancing additives were found to be effective in reducing the apparent rate of degradation. Gum formation was found on the copper coils for the samples that had them[15]. Chendynski et al.[16] and Kugelmeier et. al.[17] also demonstrated a strong reduction in the measured oxidative reserve of biodiesel fuels with exposure to copper. Squissato et. al. developed a new method for the measurement of free Cu (II) ions in biodiesel and found a strong negative correlation with oxidation reserve.

Myers et al, evaluated the response of different petroleum distillate fuels to copper exposure. This team concluded that the property changes of low-sulfur fuels was impacted by copper to a greater degree than high-sulfur fuels[18]. Storage additives were found to be effective in reducing the impact of copper exposure.

Despite the potential for adverse effects, residential oil-fired heating systems in North America almost universally use copper pipe to connect the fuel tank to the burner and for some components in the burner itself. The authors of this study have a strong interest in understanding the quality of

fuel actually being used in these small heating systems and the impact that the growing use of biodiesel has on this quality. The goal of this study was to evaluate the practical impact of the presence of copper on these modern fuels and the implications this impact has on fuel sampling for quality monitoring.

Experimental

A variety of fuel experiments were conducted to evaluate copper exposure impact. This included exposure of small fuel samples to copper under static conditions at ambient temperature, exposure and storage under warm conditions, and circulation of larger fuel samples in a tank-pump-tubing loop arrangement. The conditions were designed to simulate common conditions of exposure level of the fuel to copper in common fuel oil systems in the U.S.

Petroleum No. 2 heating oil samples meeting ASTM D396[9] were obtained from local heating oil distributors. Each sample was checked for biodiesel content using an InfraCal 2 ATR-B Biodiesel-in-Diesel Analyzer. It is common, presently, for heating oil to have some biodiesel in it and all of the samples referred to as petroleum No. 2 heating oil samples used in this work contained 2-4% biodiesel by volume. The 100% biodiesel used in this study for producing blends was a commercial fuel produced by Renewable Energy Group, Inc. (REG) and met the requirements of ASTM D6751[19]. Table 1 provides a summary of selected properties the biodiesel fuel used. The production facility for this fuel confirmed that additives were used with this fuel, as is common practice, to ensure acceptable stability.

Blends of the petroleum No. 2 heating oil and biodiesel mentioned above were prepared to determine the impact of copper exposure on fuel blends. The fuels were blended on a volumetric basis such that 20% and 50% biodiesel was blended into petroleum No. 2 heating oil.

The Induction Period (IP or "oxidative reserve") of fuel blends was measured to evaluate oxidative stability in storage, following EN 15751 using a Metrohm 893 Professional Biodiesel Rancimat instrument. In addition, long term storage impacts of fuel blends were measured following ASTM D4625[20]. In this test, 400 ml of sample were placed in an incubator set to 43 ± 1°C. The samples were left in the incubator, open to the air, for a predetermined amount of time. Heating the samples to 43°C increases degradation approximately fourfold compared to degradation at ambient temperature such that 1 week in the incubator is equal to approximately 1 month at ambient temperature. After the planned amount of time, samples were removed from the incubator and both filterable and adherent insolubles were measured. Filterable insolubles were measured by forcing each sample through a nylon membrane filter with a nominal pore size of 0.8 µm and determining the mass of filtered insolubles. The adherent insolubles, which are the materials remaining on the sample container walls, were then measured by washing the container twice with a solvent comprised of equal parts acetone, methanol, and toluene. The solution was then heated to 160°C to drive off the solvent. The residual mass is taken as that of the gum. Fuel acid numbers were measured via manual titration following ASTM D664[21].

Trace metals analysis of the fuel samples before and after exposure to copper was conducted at REG using a Spectro Arcos inductively coupled plasma optical emission spectrophotometer (ICP-OES). The ICP-OES was calibrated to measure copper below 1 ppm levels. A 2-ppm check standard was included intermittently between each fuel sample to check for instrument drift.

Table 1. Properties of the Biodiesel Fuel (B100) Used in this Study

Property	Value	Units	Test Method
Cloud point	-1.1	°C	D7397
Free Glycerin	0.01	% mass	D6584
Total Glycerin	0.11	% mass	D6584
Acid Number	0.34	mg KOH/g	D664
Oxidation Reserve (IP)	9.0	hours	EN 15751
Cold Soak Filtration	102	seconds	D7501
Sulfur	0.6	mg/kg	D5453
Sodium & Potassium Combined	0.2	mg/kg	EN 14538
Calcium & Magnesium Combined	0.0	mg/kg	EN 14538
Kinematic Viscosity at 40°C	4.13	mm^2/sec	D445
Distillation at 90% Recovered	352	°C	D1160

Exposure of fuel blends to copper was done using several methods as follows:

Exposure Method 1 – A section of copper tubing commonly used in fuel systems with a length of 291 mm, was capped on one end and positioned in a vertical orientation. The tubing has an inside diameter of 6.76 mm and an outside diameter of 9.36 mm. A volume of 14 ml of fuel was then added to the tubing and maintained at ambient temperature for 24 hours. This arrangement provided a surface area to volume ratio of 5.92 cm^2/cm^3.

Exposure Method 2 – A section of the standard copper tubing described in Exposure Method 1, was cut into short (8 mm) pieces. For each test, 50 pieces were combined with 400 ml of each fuel blend. In this case the fuel was exposed to the inside, outside, and end of each piece. Exposure time to copper was again 24 hours at ambient temperature. The ratio of surface area of copper tubing to volume of fuel was 0.59 cm^2/cm^3. This exposure level is more than found in the bulk fuel tank in Exposure Method 4 but provides a means to accelerate the potential impacts of copper.

Exposure Method 3 – This is the same as in Exposure Method 2 except the total number of pieces was reduced to just 8 but the pieces were longer, giving the same surface to volume ratio as in

Exposure Method 2. This provides a slightly different avenue for accelerating the impacts of copper.

Exposure Method 4 – This method involved a much larger volume of fuel and an exposure arrangement which more closely emulated field conditions. A commercially available plastic fuel storage tank with a total volume of 379 liters (100 gallons) was used in combination with a standard oil burner pump configured to simulate a two-pipe arrangement. The pump was connected to the storage tank with two coils of copper tubing, each with a total length of 7.86 m. A pump operated continuously for a period of two months. Based on the total volume of oil in the tank and the total internal surface area of the copper tubing, the surface area to volume ratio in this arrangement was 0.018 cm^2/cm^3.

Exposure Method 5 – This method was designed to simulate a summer shutdown field situation, where fuel could be stationary in a copper line for many months. A copper tube with a total length of 9.14 m was filled with a volume of 420 ml of fuel. This copper tube was then capped at both ends to prevent air exposure. The copper tube with the fuel inside was then left at ambient temperature for 6 months. The ratio of surface area of copper tubing to volume of fuel was 5.92 cm^2/cm^3.

Results

Table 2 shows the results of a series of tests with different fuel blends exposed to copper using Method 1. All of these tests were conducted at the NORA laboratory in Plainview, N.Y. A sample of each fuel was held in a glass beaker without exposure to copper to serve as a control. Table 2 compares the IP of the control samples and those exposed to copper using Method 1. Each fuel showed a significant drop in oxidation reserve after copper exposure compared to the control sample with no copper. Specifications for the properties of heating oil blends with 6 to 20% biodiesel content in the ASTM D396[9] standard require a minimum oxidation reserve of 6 hours at the time of manufacture which has been shown to provide a consistent lack of fuel degradation products for a minimum of at least 6 months. All of the No. 2 heating oil, B20, and B50 fuels tested using this exposure method had measured IP below 6 hours after exposure to copper. Similarly, the B100 sample also has measured IP below the 3-hour value for as-manufactured B100 in ASTM D6751[19].

To confirm these results, a copper tube was prepared per Exposure Method 1 and sent to the REG lab in Iowa for repeat testing at a B50 blend level using different samples of No. 2 heating oil and biodiesel. REG also left portions of the B50 blend in both the copper tube and a glass beaker for 24 h at room temperature. In addition to IP, each sample was analyzed by ICP-OES to measure trace metals. The results from these tests are shown in Table 3. The IP values from REG are close to the B50 induction times obtained in the tests at the NORA lab even though the fuels were different. Results of the ICP test also show a small but measurable increase in the amount of copper in the exposed sample compared to the unexposed sample, with the copper value increasing more than that of lead or zinc.

Table 2. Oxidation Reserve (Rancimat Induction Period) for Fuel Samples Held in a Vertical Copper Tube and the Control Samples held in a Glass Beaker without Copper Exposure. Each was held for 24 hours at room temperature (~22°C) at the NORA Lab.

Copper Exposure	No.2 Oil	B20	B50	B100
Not Exposed to Copper	18.29	8.16	7.82	6.13
Exposed to Copper	3.07	0.98	0.11	0.11

Table 3. Oxidation Reserve (Rancimat Induction Period - hours) and Selected Trace Metals for a B50 Blend Exposed and not Exposed to Copper in a Vertical Tube for 24 hours at Room Temperature (22°C) at the REG lab.

	B50 (control)	B50 (copper)
Induction Period (hr)	7.6	0.18
Copper Content (ppm)	0.1	4.1
Lead Content (ppm)	0.1	1.3
Zinc Content (ppm)	0.1	1.6

The first long term-storage stability test following ASTM D4625 involved eight samples, two control samples of No. 2 heating oil not exposed to copper, two samples of No. 2 heating oil exposed to copper, two control samples of a B20 blend not exposed to copper, and two samples of a B20 blend exposed to copper. The exposure in this test followed Exposure Method 2. Fuels were separated from the copper prior to starting the long-term storage test. All of the samples were filtered through a 0.8 micron filter before testing to remove any initial particles. The samples were removed after 9 weeks and IP, acid number, filterable insolubles and adherent insolubles were measured. Results are shown in Table 4. When comparing the control samples to those that were exposed to copper, the oxidation reserve values were reduced to similar values for both the No. 2 heating oil samples and the B20 samples. After aging the control samples all remained above 3 hour Induction Period which has been used in previous research as an acceptable performance indicator for aged fuel. Similar results were observed for acid number; the samples exposed to copper showed elevated acid numbers compared to the control samples although all control results remained low and all aged results remained below 1 mg KOH/g. Filterable insolubles and adherent insolubles also increased noticeably for the samples exposed to copper, although the increase was about 5 times less for the B20 compared to No. 2 oil. This could be the result of the presence of

oxidation reserve specifications for B100 and for B20, leading to introduction of stability-additives during commercial production, while none exist for No. 2 oil.

Table 4. Results of Long-Term Storage Test #1. Four Samples of No. 2 oil and Four Samples of B20 Blends. Half of the Samples were Exposed to Copper for 24 hours Before Starting the Long-Term Storage Test.

Sample ID	IP (hr)	Acid Number (mg KOH/g)	Filterable Insolubles (mg/100 mL)	Adherent Insolubles (mg/100 mL)
No. 2 heating oil #1, (initial)	30.58	-	-	-
No. 2 heating oil #1, (control)	10.66	0.01	0.5	5
No. 2 heating oil #1, (copper)	0.02	0.81	12	93.25
No. 2 heating oil #2, (control)	10.92	0.05	0.25	6
No. 2 heating oil #2, (copper)	0.03	0.75	5.5	95
B20 #1, (control)	3.58	0.13	0.25	6.5
B20 #1, (copper)	0.02	0.87	5.25	17.75
B20 #2, (control)	4.49	0.13	0.25	6.5
B20 #2, (copper)	0.01	0.87	6	12.75

In the second long-term test, eight samples of No. 2 heating oil were exposed to copper for 24 hours using exposure Method 3 in duplicate before starting the long-term storage test. Again, all samples were filtered through a 0.8 micron filter before testing to remove any initial particulate contamination. Every three weeks from the beginning of the test (at weeks 3, 6, 9 and 12) one set of duplicates was removed and analyzed for oxidation reserve, acid number, filterable insolubles and adherent insolubles. A control sample of No. 2 heating oil, stored in a glass beaker and not exposed to copper, was also held in the incubator for the full 12 weeks. Results are listed in Table 5. All of the samples exposed to copper showed a large decrease in oxidation reserve with respect to the control sample. The initial oxidation reserve of the No. 2 heating oil was 23.6 hours. By the end of 12 weeks, the oxidation reserve fell below 0.06 hours for the samples exposed to copper. The acid number of the samples exposed to copper also increased with time, with the samples from week 12 going slightly over 1 mg KOH/g. The filterable insolubles amount increased for each sample as the test progressed up to week 9 but fell slightly in the samples removed at 12 weeks. The adherent insolubles increased substantially through the 12-week period. In contrast, the control sample showed only minor changes for the four quality metrics analyzed.

Table 5. Results of Long-Term Storage Test #2. Eight Samples of No. 2 Heating Oil were Exposed to Copper for 24 Hours Using Exposure Method 3 in Duplicate. Each Set of Duplicates were

Removed at Weeks 3, 6, 9 and 12. One Control Sample of No. 2 Heating Oil was Stored in a Glass Beaker and not Exposed to Copper. This Sample was Held for the Full 12 Weeks.

Sample ID	Duration (weeks)	IP (hr)	Acid Number (mg KOH/g)	Filterable Insolubles (mg/100 mL)	Adherent Insolubles (mg/100 mL)
No. 2 heating oil (initial)	0	23.59			
No. 2 heating oil (copper)	3	1.86	0.10	0.8	9.5
No. 2 heating oil (copper)	3	0.03	0.01	1.3	9
No. 2 heating oil (copper)	6	0.06	0.13	5.5	14.5
No. 2 heating oil (copper)	6	0.06	0.29	12.5	16.25
No. 2 heating oil (copper)	9	0.02	0.40	13.8	31
No. 2 heating oil (copper)	9	0.02	0.37	13.3	27.8
No. 2 heating oil (copper)	12	0.02	1.14	5.5	317.5
No. 2 heating oil (copper)	12	0.02	1.10	7.5	764.3
No. 2 heating oil (control)	12	10.61	0.06	0.5	14.3

The oxidation reserve measurements taken for the two-pipe system of Exposure Method 4, are shown in Figure 2. In this exposure technique, the fuel is constantly recirculating, so it is not stagnant. Samples were pulled from the pump bleed valve about every 7 days. The oxidation reserve of the No. 2 heating oil in the tank was 24.9 hours before the start of the test. For a sample taken from the pump bleeder, which in this case is a good representation of the fuel in the bulk tank since it is constantly recirculating, one day after the start of the test, the oxidation reserve fell to 19.8 hr. The next collection at day 8 fell again to 15.0 hours, and all collections after this were relatively similar to this measurement, varying from 14.2 to 16.3 hours. The final sample was collected at 57 days. Interestingly, ICP-OES indicated that no significant amount of copper was present in this sample.

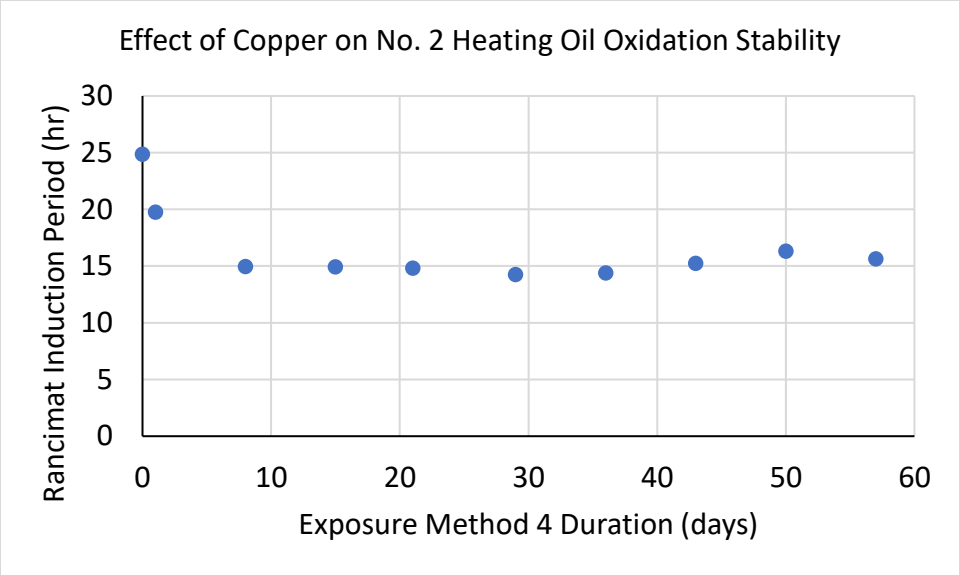

Figure 2 Results of periodic Rancimat IP measurements of No. 2 heating oil exposed to copper for 57 days using Exposure Method 4.

As shown in Figure 2, this test exhibited some reduction in oxidation reserve over the two-month test period but showed no decrease after the first week. After this test was completed, a sample of the fuel was removed and exposed to copper at much higher surface to volume ratio using Exposure Method 1. After 24 hours at room temperature in the vertical tube, the Rancimat Induction Period fell to 1.4 hours, confirming results of the earlier tests.

After the completion of the two-pipe system test, the pump was shut down and remained off. Fuel remained stagnant in the copper pipes for 2 months to simulate leaving fuel in the copper pipes of a 2-pipe system at the end of a heating season. In this case, the fuel inside the copper pipes is not being constantly exposed to fresh oxygen. A fuel sample was taken at the end of the 2-month period and analyzed for IP, acid number, and copper content. IP was 13.5 hours, similar to the IP measured for samples in the two-pipe system test. The acid number was 0.03 mg KOH/g, and the copper concentration was 0.2 ppm.

After the test was concluded, the fuel removed from the 2-pipe set-up was left at room temperature for 1 month in an open-top glass beaker where it was exposed to fresh oxygen. After this month it was observed that a large amount of adherent insoluble had formed on the bottom of the glass beaker. The filterable and adherent insoluble were measured. The filterable insolubles were measured as 8.5 mg/100 ml, while the adherent insolubles were measured at 16.5 mg/100 ml.

Based on these results, a test protocol was developed to study the effect of summer shutdown on a fuel. A sample of No. 2 oil was prepared in copper according to Exposure Method 5 and was left at room temperature for 6 months. In this exposure technique fuel inside a long copper line is held without exposure to oxygen, as would be the case in the field. An identical sample of No. 2 heating oil was also stored in a sealed epoxy-lined metal can for 6 months to serve as a control. The IP of this fuel was measured before the start of the test. Both samples were filtered through a 0.8 micron

filter before the start of the test. At the end of the 6 months, both fuels were removed from storage and analyzed for IP, acid number, and filterable particulates. The results for this are shown in Table 6. These results show that the only major difference between the two samples is the IP, which fell heavily for the sample exposed to copper.

After testing was complete on both samples, each was stored in a glass beaker with an open top. This was done to see how the fuels would degrade over time when exposed to air. Both samples were left at ambient temperature for 15 weeks. After this time, both samples were again analyzed for IP, acid number, filterable particulates and adherent insolubles. These results are shown in Table 7. While both samples saw a decrease in IP and an increase in acid number and filterable particulates, the change for the fuel stored in the copper tubing was much greater. The amount of adherent insolubles formed between the two samples was also very different, with the sample exposed to copper forming much more particulates on the glass beaker.

Table 6. Results of Simulated Summer Shutdown Test. One Sample of No. 2 Oil Exposed to Copper Using Exposure Method 5. One Sample of No. 2 Oil Stored in an Epoxy-Lined Metal Can and Not Exposed to Copper.

Sample ID	IP (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

Table 7. Results of Simulated Summer Shutdown Test #2. One Sample of No. 2 Heating Oil Exposed to Copper Using Exposure Method 5, Then Left for 15 Weeks. One Sample of No. 2 Oil Stored in an Epoxy-Lined Metal Can and Not Exposed to Copper, Then Left for 15 Weeks.

Sample ID	IP (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

Discussion

In traditional diesel engine fuel systems, the presence of copper can be problematic. The presence of copper can catalyze the formation of degradation products and produce mercaptide gels in petroleum-based diesel fuels. For these reasons, copper is not normally used or recommended in diesel engine fuel systems with petroleum distillates or biodiesel blends. Copper tubing and brass nozzles are commonly used in heating oil, however, due to lower cost and ease of manipulation and installation. The adverse impacts of copper particularly pertinent to home heating oil fuel systems are potential increases in acid number and increases in filterable or adherent solids from degradation products or their complexes with sulfur.

This study showed that the potential impacts of copper on the fuels used in today's home heating oil systems (i.e. ultra low sulfur No. 2 petroleum distillates and their blends with biodiesel) depend largely on the surface to volume ratio of the exposure to copper, access of the copper-exposed fuel to oxygen, residence time of the fuel in contact with copper, and the overall time before the fuel is burned. Potential impacts of copper can also be mitigated by the presence of storage enhancing additive packages, metal deactivators, and natural or synthetic antioxidants although this study did not specifically control or evaluate them.

The conventional fuel specifications for petroleum distillates do not have controls for acid number or filterable insolubles other than those measured as sediment in the D2709 water and sediment test. Biodiesel (B100) on the other hand, has the same water and sediment specifications but it also has specifications for acid number, oxidative reserve, and cold soak filtration which is a measure of sediments after cold-soaking the fuel using a 0.7 micron filter.

Previous research used to set the ASTM standards for biodiesel and biodiesel blends indicated fuels with high Rancimat Induction Periods would not form problematic acids or filterable insolubles over time under normal use conditions with diesel engine fuel systems. These systems, however, do not normally contain copper. Low Rancimat values did not necessarily mean problematic acids or sediments would form over time, and Rancimat values twice as high may not mean storage life is doubled, but samples that met a relatively high value consistently had low acids and sediments. This made the fuel version of the Rancimat Induction Period test a conservative method—and one that was readily available and that provided relatively quick, precise, repeatable results—so it was adopted into the biodiesel specifications and is commonly used today. This previous research was used to inform and design the testing conducted in this study to understand the long-term implications of exposure to copper in modern heating oil systems.

This testing confirmed that copper can have adverse long-term effects if the fuel is exposed to copper under high surface-to-volume ratios and then has access to oxygen without being intermingled with a larger quantity of bulk fuel. In these cases, the high contact with copper can dramatically reduce the measured oxidation reserve and accelerate the formation of acids and filterable and adherent insolubles which could result in clogged strainers, coked nozzles, and problematic system deposits. The impacts observed under these conditions were similar or less for the biodiesel blends than the No. 2 petroleum distillates, likely due to oxidation reserve requirements for biodiesel and biodiesel blends that are not present in No. 2 fuel oil. Fuels in home heating oil systems, however, are not normally subject to these conditions.

Over a normal summer shutdown, the fuel is exposed to high surface-to-volume ratios inside the copper tubing but without access to oxygen for extended periods of time. The amount of copper tubing is approximately double for the two-pipe systems, but these systems are much less prevalent in the U.S. market. The fuel is also subject to the same high surface-to-volume ratio conditions inside copper lines during normal operation, although for much shorter periods of time. In these cases of high surface-to-volume copper exposure but without access to oxygen formation of potentially problematic acids or sediments inside the copper tubing were not substantially increased, even though the exposure to copper dramatically reduced the oxidation reserve value as measured by the Rancimat Induction Period. A location that experiences a summer shutdown and uses a 2-pipe system could see fuel stability issues, as the fuel that will rapidly degrade in the presence of oxygen will be recirculated to the tank.

Fuel in the bulk 275 gallon home heating oil bulk tank is exposed to oxygen but is not normally exposed to copper for a one pipe system. A notable exception to this would be the two-pipe system, where the fuel is subjected to the high surface-area-to-volume ratio in the copper tubing going to the burner as well as in the return line back to the tank. In tests simulating a one-pipe system, a two-pipe system under recirculation, and a two-pipe system under summer shutdown, fuel did not show problematic increases in acid number or filterable insolubles, or a substantial decrease in measured oxidative reserve. This is likely due to the dilution effect of the relatively small amount of high surface-area-to-volume fuel in the copper tubes co-mingling with the bulk fuel after summer shutdown, potential passivation of the copper tubing by the fuel in general, and the relatively low contact time with copper in the fuel lines during on-going operations.

Conclusions

The practical implications of this research are that the presence of copper lines in most home heating oil systems in the U.S. should not present significant formation of acids or filterable insolubles that could adversely affect system operation over time with either ultra low sulfur No. 2 petroleum distillates or their biodiesel blends. This is likely due to the specific exposure conditions to copper in normal heating oil systems and the relatively small amounts of fuel exposed to both copper and oxygen before being burned. To the extent conditions do exist where changes over time could occur, the changes observed with biodiesel blends were similar or less than those with conventional No. 2 petroleum distillate fuel oil. This is likely due to the oxidative reserve and acid number controls present in the biodiesel and biodiesel blend specifications that are not present in traditional heating oil specifications.

An additional practical implication of this research is the significant negative impact that high surface-to-volume contact with copper has on oxidation reserve testing methodology. Oxidation reserve, measured via the Rancimat Induction Period, is used with biodiesel and its blends as a convenient and conservative surrogate for deleterious fuel changes that could happen over time. Contact with copper, however, can cause a significant reduction in the oxidative reserve testing methodology with either No. 2 petroleum distillate or its blends with biodiesel even though problematic acids or filterable insolubles may not have formed. This can particularly be the case when sampling for troubleshooting purposes or periodic quality checks from a copper line or pump bleeder valve in the field. A low Rancimat Induction Period value from a sample from a copper line or pump bleeder may not represent problematic fuel in the line or in the bulk tank. In this case use of the acid number, filterable insolubles, or taking a sample of the bulk tank would be a better means to assess whether the fuel has changed to the point of being problematic.

Funding Sources and Acknowledgements

This work was sponsored by the National Oilheat Research Alliance and the National Biodiesel Board. The authors would like to acknowledge contributions to the experimental work by Jonathan McCutcheon, John Levey, and Robert O'Brien. We would also like to thank Steve Howell for his careful review of the manuscript and many helpful suggestions.

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