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Lubricity of Canadian Diesel Fuels

Canadian Fuels Association
W. Stuart Neill and Shouvik Dev

Energy, Mining and Environment Research Centre, Low Carbon Fuels

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1 Introduction

The fuel injection equipment in diesel engines is protected against excessive wear by the lubricating properties of diesel fuel. Lubricity is the term used to describe the ability of a fluid to minimize friction between surfaces and so reduce damage due to wear. Diesel fuel pumps and injectors will experience significantly reduced durability when exposed to fuels with poor lubricity. Thus, lubricity is an important fit-for-service property of diesel fuels.

The desulphurizing processes used to produce ultra-low Sulphur diesel (ULSD) fuels tend to reduce the natural lubricating properties of diesel fuel. Since diesel fuel must provide lubrication to diesel fuel injection systems, fuel suppliers often use commercial lubricity improver additives (LIAs) to restore the lubricity of ultra-low sulphur diesel (ULSD) fuels.

Diesel fuel lubricity is commonly evaluated using the high-frequency reciprocating rig (HFRR). This laboratory rig was developed to evaluate the boundary lubrication properties of diesel fuel and was incorporated into ASTM D6079 Test Method [1] in 1999. This method involves rubbing a loaded steel ball against a stationary steel disk completely submerged in the test fuel for 75 minutes and measuring the wear scar diameter (WSD) on the steel ball at the conclusion of the test. This method is accepted in the United States and Canada as stated in ASTM D975 [2] and CAN/CGSB-3.517 [3] diesel fuel specifications, respectively. The method was revised in 2011 to specify the use of a microscope with digital camera for measuring the WSD and the original method using a microscope for visual observation of the WSD became ASTM D7688 Test Method [4]. Both of the ASTM Test Methods state that “It is not known that this test method will predict the performance of all additive/fuel combinations.”

In late 2011, Ken Mitchell reported that cetane improver additives (CIAs) interfere with the HFRR test causing an increase in the measured WSD, which did not correspond to increased wear in pump rig tests using the same fuel [5]. Subsequently, NRC researchers identified a bias in ASTM D6079 Test Method when it was used to evaluate the lubricity of renewable diesel blends containing lubricity improver additives (LIAs) [6]. A significant fuel sample loss was often observed when testing volatile diesel fuels, which led to an increase in the effective LIA treat rate as the test proceeded. This could lead fuel producers to underestimate the LIA treat rate required to provide adequate lubricity.

In July 2018, NRC presented lubricity data for one A-ULS and one B-ULS diesel fuel with ester- and monoacid-type lubricity improver additives to ASTM International, D02 Subcommittee E’s Lubricity Task Force. The experimental data highlighted the observed deficiencies with the existing HFRR Test Methods. In particular, 32% sample loss by mass was observed for one A-ULS diesel fuel during a HFRR test using the standard 2 ml fuel sample holder. The sample loss with the same fuel was reduced by approximately 80% using a 15 ml sample holder supplied as a “gasoline conversion kit” by PCS Instruments and a custom cover designed by NRC. These results were also published in a 2019 IASH paper [7].

The feedback from the ASTM Lubricity Task Force was that experimental data with additional fuels would be needed to support a potential revision to the Test Method. More recently, ISO has assembled a group of experts (ISO/TC22/SC34/AG1) to investigate paraffinic diesel fuel lubricity. The objective of this project is to collect the additional experimental data as requested by the Lubricity Task Force.

2 Experimental Apparatus

The high-frequency reciprocating rig specified in ASTM D6079-11 test method was used to evaluate lubricity. Figure 1 depicts the experimental apparatus installed at NRC. The method involves rubbing a loaded steel ball against a stationary steel disk completely submerged in the test fuel at a frequency of 50 Hz for a period of 75 minutes. The standard (2 ml) fuel sample holder and a partially-covered 15 ml fuel sample holder, similar to the one that the instrument manufacturer sells as a gasoline conversion kit but with a reduced slot area, were investigated in this study. The test balls and disks are made from SAE-AMS 6440 steel. The test ball has a diameter of 6 mm and Rockwell hardness "C" scale number of 58-66. The softer test disk is machined from an annealed 10 mm diameter rod, has a Vickers hardness of "HV30", a scale number of 190-210, turned, lapped and polished to a surface finish of less than 0.02 µm. At the conclusion of a test, the major and minor axes of the wear scar generated on the harder steel ball are measured using a microscope equipped with a digital camera. HFRR test conditions are listed in Table 1.

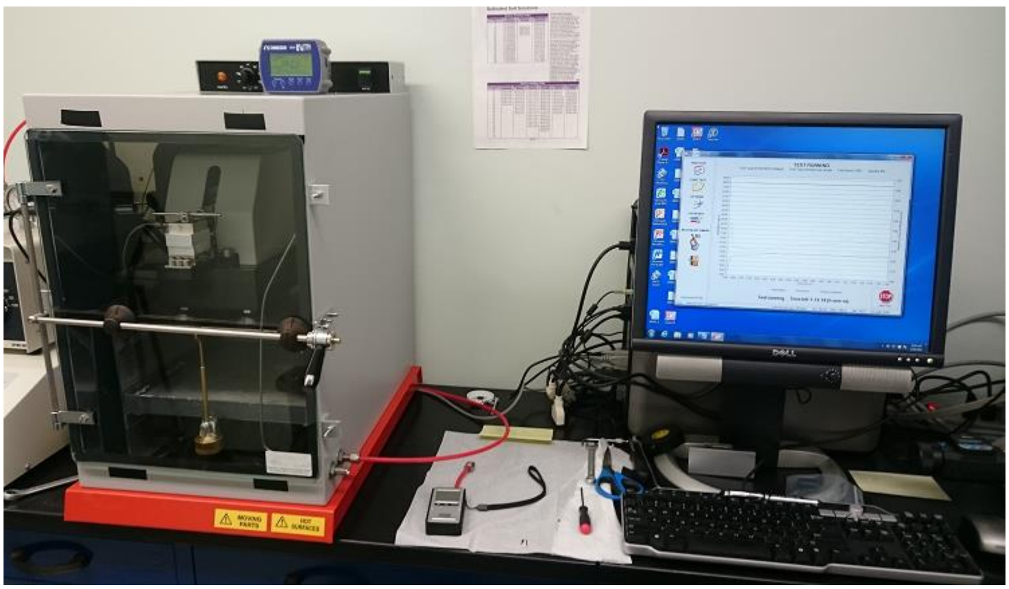

Figure 1 High-Frequency Reciprocating Rig

Table 1 HFRR Test Conditions

Fluid volume	2; 15 ± 0.20 ml
Fluid temperature	60 ± 2°C
Test duration	75 ± 0.1 min
Stroke length	1 ± 0.02 mm
Frequency	50 ± 1 Hz
Applied load	200 ± 1 g
Relative humidity	30% < RH < 85%

3 Diesel Fuels and Fuel Additives

3.1 Diesel Fuel Properties

A total of six Canadian diesel fuels and two hydrogenation-derived renewable diesel (HDRD) blending components were investigated. The Canadian diesel fuels consisted of three Type A-ULS and three Type B-ULS diesel fuels. The diesel fuels were produced by several Canadian refineries from crude oil and/or oil sands derived crude slates and reflect the range of conventional diesel fuels typically sold in Canada. The A-ULS diesel fuels are lighter middle distillates applicable for use where the low temperature operability properties of B-ULS diesel fuels are insufficient. The B-ULS diesel fuels are heavier middle distillate fuels that have been seasonally adjusted to meet the low temperature operability requirements for the period and location of intended use. NRC requested that the diesel fuels be supplied without a LIA. The two HDRD blending components were also supplied by a Canadian diesel fuel producer for this study.

Samples of the diesel fuels and blending components were sent to InnoTech Alberta for analysis. Select properties of the A-ULS and B-ULS diesel fuels are provided in Tables 2 and 3, respectively. Select properties of the two renewable blending components are shown in Table 4. All of the fuel properties in Tables 2-4 were measured by InnoTech Alberta with the exception of ASTM D6890 derived cetane number, which was measured by NRC.

The six diesel fuels have a fairly wide range of densities (809 to 860 kg/m^3), kinematic viscosities (1.4 to 3.0 cSt) and cloud points (-14° to -54°C). The diesel fuels would meet the CAN/CGSB-3.517-2017 diesel fuel specification after being additized with an appropriate level of LIA. The T90 distillation temperature of A-ULS #3 diesel fuel slightly exceeds the 288°C limit in the ASTM D975 specification for Grade No.1-D S15.

Table 2 Selected Properties of A-ULS Diesel Fuels (as received)

Fuel Property	**ASTM Method**	**A-ULS #1 (NRC #19001)**	**A-ULS #2 (NRC # 19002)**	**A-ULS #3 (NRC # 19005)**
Density, kg/m^3	D4052	808.7	825.6	820.0
Kin. Viscosity, cSt	D7042	1.37	1.63	1.53
Flash point, °C	D93	48.0	51.0	45.5
Lubricity (WSD), µm	D6079	640	680	640
Cloud Point, °C	D5773	-51.2	-54.5	-38.1
Derived Cetane Number	D6890	43.0	43.9	41.7
Distillation	D86			
IBP, °C		147.8	155.3	143.7
10% Recovered, °C		177.5	181.7	169.8
50% Recovered, °C		212.2	221.1	220.5
90% Recovered, °C		248.0	272.2	289.1
FBP, °C		260.7	293.2	322.9

Table 3 Selected Properties of B-ULS Diesel Fuels

Fuel Property	ASTM Method	B-ULS #1 (NRC # 19003)	B-ULS #2 (NRC #19006)	B-ULS #3 (NRC #19007)
Density, kg/m³	D4052	849.3	844.7	860.4
Kin. Viscosity, cSt	D7042	3.01	2.46	2.76
Flash point, °C	D93	68.0	63.5	62.0
Lubricity (WSD), µm	D6079	570	570	530
Cloud Point, °C	D5773	-26.8	-13.9	-24.0
Derived Cetane Number	D6890	43.3	42.6	42.9
Distillation	D86			
IBP, °C		176.5	164.8	171.5
10% Recovered, °C		216.0	195.4	210.7
50% Recovered, °C		273.2	256.3	262.2
90% Recovered, °C		321.5	335.1	328.7
FBP, °C		343.9	365.3	358.3

Table 4 Selected Properties of HDRD Diesel Blending Components (as received)

Fuel Property	ASTM Method	HDRD #1 (NRC #19004)	HDRD #2 (NRC #19008)
Density, kg/m³	D4052	780.8	787.5
Kin. Viscosity, cSt	D7042	3.01	2.87
Flash point, °C	D93	81.0	73.0
Lubricity (WSD), µm	D6079	590	590
Cloud Point, °C	D5773	-15.4	-35.6
Derived Cetane Number	D6890	77.1	68.1
Distillation	D86		
IBP, °C		209.5	180.1
10% Recovered, °C		269.6	250.1
50% Recovered, °C		283.0	279.1
90% Recovered, °C		294.3	294.0
FBP, °C		308.7	318.3

HDRD is typically composed of n-paraffinic and iso-paraffinic hydrocarbons in the diesel boiling range. The densities of the HDRD blending components are lower than those of the six diesel fuels. The main difference between the two HDRDs is that HDRD #2 has a lower cloud point due to higher iso-paraffinic content. The two HDRDs have higher IBP and T10 distillation temperatures than the A-ULS and B-ULS diesel fuels.

Figure 2 shows the ASTM D86 distillation curves of the diesel fuels and blending components investigated. The three A-ULS diesel fuels have 50% distillation temperatures (T50) below 225°C, whereas the three B-ULS diesel fuels have T50 temperatures above 250°C. The two HDRD blending components have very flat distillation curves with a large fraction of the hydrocarbon sample distilling between 270-300°C.

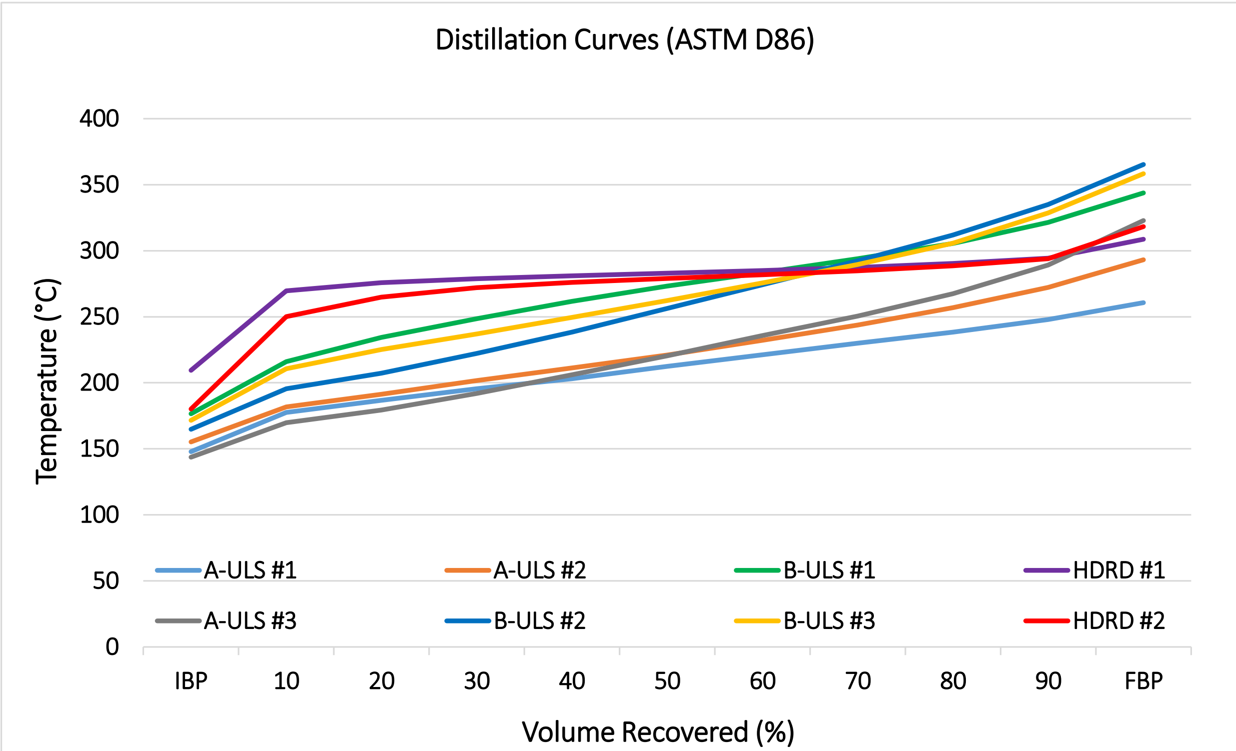

Figure 2 D86 Distillation Curves of the Diesel Fuels and Blending Components

3.2 Fuel Additives

LIAs with two different chemistries were employed to meet the lubricity requirement in the ASTM D975 diesel fuel specification[1]: a monoacid-type LIA (Afton Chemical Corp, HiTEC® 4142); and an ester-type (Infineum USA LP, R691).

2-ethylhexyl nitrate (2-EHN) is a commonly used cetane improver additive (CIA) in Canada when there is a requirement to raise the cetane number of a diesel fuel. Functionally, 2-EHN begins to decompose at a temperature of 130°C and serves to increase the combustion radical pool prior to ignition. For this study, a quantity of 2-EHN was procured from MilliporeSigma Canada (CAS Number 27247-96-7).

NRC performed HFFR lubricity determinations to determine appropriate LIA treat rates to decrease the HFRR WSD produced by the six diesel fuels below 520 µm. It was relatively easy to determine the treat rates for the diesel fuels additized with the monoacid-type LIA because the WSD measurements were repeatable. On the other hand, the WSD measurements for the diesel fuels additized with ester-type LIA were significantly less repeatable due to the waterfall response curve of ester-type LIA. At low treat rates, the ester-type LIA has minimal effect on the HFRR WSD produced by a ULSD fuel. As the treat rate is increased, a point is reached where a small increase in the ester-type LIA significant decreases the HFRR WSD by approximately 60 µm. This makes it difficult to establish the minimum LIA treat rate to meet the 520 µm WSD limit as the rapid decline in WSD occurs in this region of the LIA response curve.

[1] The lubricity requirement in ASTM D975 is a maximum WSD of 520 µm as measured in the HFRR test.

The NRC HFRR lubricity determinations for the six diesel fuels are shown in Table 5. The HFRR WSDs produced by NRC are higher by 10 μm on average than those measured by InnoTech Alberta, but the lubricity rankings for the six diesel fuels were fairly consistent between the two laboratories. Raw lubricity data is included in Appendix A.

Monoacid- and ester-type LIA were added to each of the six fuels to meet the maximum 520 μm WSD limit in ASTM D975. Table 5 provides the selected treat rates for the monoacid- and ester-type LIAs, as well as the lubricity (HFRR WSDs) of the additized diesel fuels. The monoacid-type LIA treat rates for the A-ULS and B-ULS diesel fuels were 100 ppmv and 50-75 ppmv, respectively. The selected treat rates for the ester-type LIA were not as consistent. The ester-type LIA treat rates for the A-ULS and B-ULS diesel fuels varied from 200-300 ppmv and 100-275 ppmv, respectively.

The monoacid- and ester-type LIA treat rates required for B-ULS #3 diesel fuel to meet the ASTM D975 lubricity limit were much lower than those for the other diesel fuels. This led NRC researchers to check all of the diesel fuel samples for the presence of lubricity or cetane improver additives. One ml samples of the diesel fuels and additives were run through a Nicolet 6700 FT-IR analyzer with an Attenuated Total Reflectance (ATR) accessory. The ATR cell was made of a horizontal ZnSe crystal. Analysis of the FT-IR spectra led to the conclusion that diesel fuel B-ULS #3 was additized with ester-type LIA and 2-EHN CIA. In addition, it was found that A-ULS #2 diesel fuel was additized with 2-EHN CIA.

The HFRR WSD produced by A-ULS #2 was higher than the WSDs produced by A-ULS #1 and #3. The higher WSD is likely due to decomposition of the 2-EHN CIA during the HFRR test in the diesel fuel supplied to NRC. The smaller WSD produced by B-ULS #3 is due to the presence of ester-type LIA in the base fuel, however, the reason that the base fuel did not meet the 460 μm WSD limit in CAN/CGSB-3.517 can be taken to be due to 2-EHN decomposition during the HFRR test.

Table 5 LIA Treat Rates for A-ULS and B-ULS Diesel Fuels

	A-ULS #1	A-ULS #2[1]	A-ULS #3	B-ULS #1	B-ULS #2	B-ULS #3[2]
Base Fuel						
Lubricity, μm	649	668	641	582	590	558
Monoacid-Type LIA						
Treat Rate, ppmv	100	100	100	75	75	50
Lubricity, μm	483	505	492	484	509	410
Ester-Type LIA						
Treat Rate, ppmv	300	250	200	275	250	100
Lubricity, μm	415	467	435	489	434	419

[1] A-ULS #2 diesel fuel was supplied containing 2–EHN CIA.

[2] B-ULS #3 diesel fuel was supplied containing both 2-EHN CIA and an ester-type LIA.

4 Results and Discussion

4.1 A-ULS Diesel Fuels

The three A-ULS diesel fuels were tested in their base form as supplied to NRC, then additized with a monoacid- or ester-type LIA to meet the lubricity standard in ASTM D975, and finally additized with both an LIA and 500 ppmv of 2-EHN CIA. The HFRR test was performed with 2 ml samples as specified in ASTM D6079 and D7688, as well as with 15 ml covered samples to reduce the percentage of fuel sample loss.

Figure 3 and Table 6 show the HFRR WSD produced for the different A-ULS diesel fuel/additive combinations with monoacid-type LIA. Please note that A-ULS #2 diesel fuel was supplied containing 2-EHN CIA, which was not included in the 2-EHN calculations. The following observations may be made:

- The base A-ULS diesel fuels produced 51-89 µm larger WSDs with the 15 ml covered samples compared to the standard HFRR test with 2 ml samples. The test with 15 ml covered samples is considered more severe because the loss of volatile hydrocarbons is reduced to 5-6% by mass, compared to approximately 30% by mass with the standard 2 ml sample holder. This minimizes the increase in LIA concentration in the fuel sample as the HFFR test proceeds;
- The HFRR provided repeatable results for the diesel fuels additized with monoacid-type LIA. It was fairly easy to determine minimum monoacid-type LIA treat rates for the A-ULS diesel fuels to meet the 520 µm WSD specification for lubricity in the ASTM D975 standard;
- The HFRR WSD increased by an average of 30 µm when 500 ppmv of 2-EHN was added to the A-ULS diesel fuels. The increase was similar for HFRR lubricity tests performed with the 2 ml and 15 ml covered fuel samples; and
- Since the monoacid-type LIA treat rates were selected to produce close to 520 µm WSD, some A-ULS diesel fuels didn't meet the lubricity specification when additized with 500 ppmv of 2-EHN.

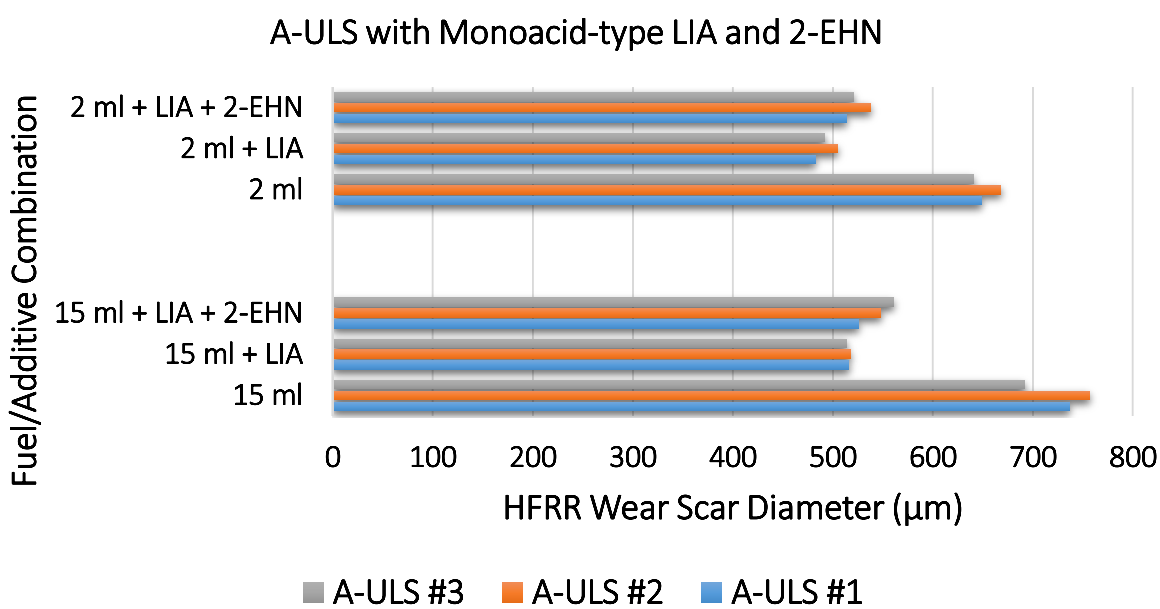

Figure 3 HFRR WSD of A-ULS Diesel Fuels with Monoacid-Type LIA and 2-EHN CIA

Table 6 HFRR WSD of A-ULS Diesel Fuels with Monoacid-Type LIA and 2-EHN CIA

Fuel Sample Volume (ml)	LIA	CIA (500 ppmv)	A-ULS #1	A-ULS #2	A-ULS #3
2	No	No	649	668	641
2	Yes	No	483	505	492
2	Yes	Yes	514	538	521
15	No	No	737	757	692
15	Yes	No	516	518	514
15	Yes	Yes	526	548	561

NB Fuel A-ULS #2 was supplied containing 2-EHN CIA.

Figure 4 and Table 7 show the HFRR WSD produced for the different A-ULS diesel fuel/additive combinations with ester-type LIA. The following observations may be made:

- The waterfall response curve for ester-type LIA made it challenging to establish the minimum treat rate to meet the 520 μm WSD specification for lubricity in the ASTM D975 standard. As a result, the HFRR WSD produced by the A-ULS diesel fuels were between 415 and 467 μm;
- The HFRR WSD of the A-ULS diesel fuels increased by an average of 45 μm and 42 μm when additized with 500 ppmv of 2-EHN CIA for the standard 2 ml and 15 ml covered tests, respectively. The larger increase in HFFR WSD, compared to the monoacid-type LIA, is due to the waterfall response of ester-type LIA;
- Since the ester-type LIA treat rates were conservative due to the waterfall response curve, the A-ULS diesel fuels met the lubricity specification when additized with 500 ppmv of 2-EHN; and
- HFRR WSDs were higher for the A-ULS diesel fuels with ester-type LIA when using 15 ml covered samples compared to the standard 2 ml samples. This is likely due to a reduction in sample loss with 15 ml covered samples on a mass percentage basis in conjunction with the waterfall response curve of ester-type LIA.

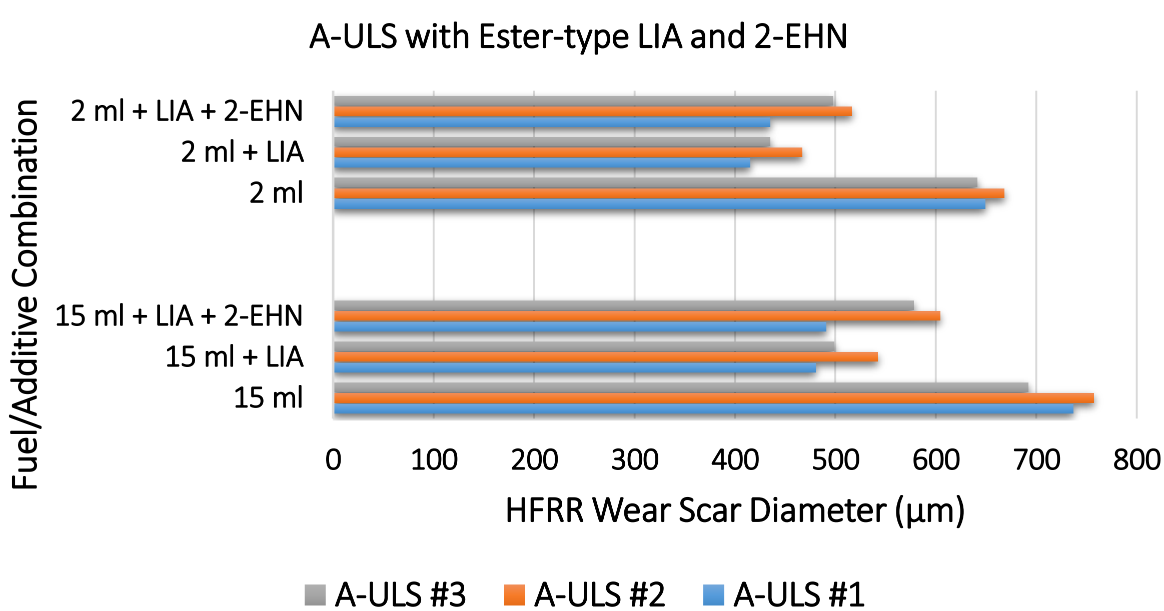

Figure 4 HFRR WSD of A-ULS Diesel Fuels with Ester-Type LIA and 2-EHN CIA

Table 7 HFRR WSD of A-ULS Diesel Fuels with Ester-Type LIA and 2-EHN CIA

Fuel Sample Volume (ml)	LIA	CIA	A-ULS #1	A-ULS #2	A-ULS #3
2	No	No	649	668	641
2	Yes	No	415	467	435
2	Yes	Yes	435	516	498
15	No	No	737	757	692
15	Yes	No	480	542	499
15	Yes	Yes	491	604	578

NB Fuel A-ULS #2 was supplied containing 2-EHN CIA.

4.2 B-ULS Diesel Fuels

Figure 6 and Table 8 show the HFRR WSD produced for the different B-ULS diesel fuels with monoacid-type LIA. Please recall that B-ULS #3 diesel fuel was supplied containing both an ester-type LIA and 2-EHN CIA and was not included in the 2-EHN effect calculations. The following observations may be made:

- The base B-ULS diesel fuels produced HFRR WSDs that were 31 µm higher when tested with 15 ml covered samples compared to standard 2 ml samples. The effect of fuel sample size on HFRR WSD was much smaller with the B-ULS diesel fuels due to their lower volatility compared to the A-ULS diesel fuels;
- The HFRR provided repeatable results for the diesel fuels additized with monoacid-type LIA. It was fairly easy to determine minimum monoacid-type LIA treat rates for the B-ULS diesel fuels to meet the 520 µm WSD specification in the ASTM D975 standard;
- The HFRR WSD increased by an average of 81 µm (2 ml samples) and 57 µm (15 ml covered samples) when 500 ppmv of 2-EHN was added to the B-ULS diesel fuels;
- Two of the B-ULS diesel fuels did not meet the 520 µm HFRR WSD specification when additized with 500 ppmv of 2-EHN; and
- The B-ULS #3 base diesel fuel that was supplied with ester-type LIA and 2-EHN CIA did not meet the 520 µm WSD specification. This was likely due to 2-EHN decomposition occurring during the HFRR test.

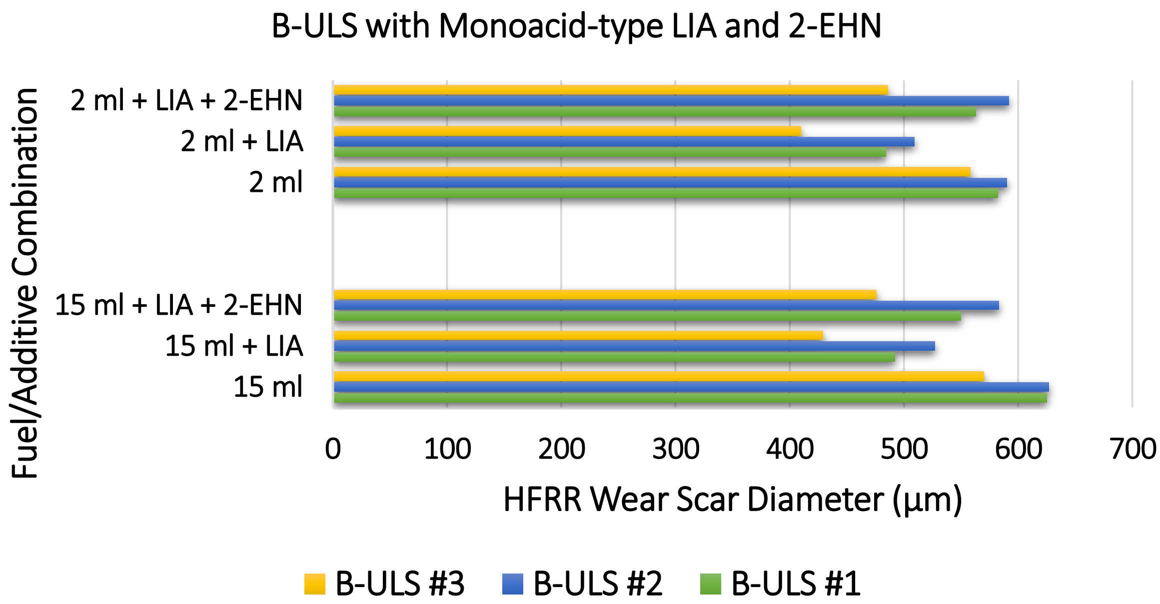

Figure 5 HFRR WSD of B-ULS Diesel Fuels with Monoacid-Type LIA and 2-EHN CIA

Table 8 HFRR WSD of B-ULS Diesel Fuels with Monoacid-Type LIA and 2-EHN CIA

Fuel Sample Volume (ml)	LIA	CIA	B-ULS #1	B-ULS #2	B-ULS #3
2	No	No	582	590	558
2	Yes	No	484	509	410
2	Yes	Yes	563	592	486
15	No	No	625	627	570
15	Yes	No	492	527	429
15	Yes	Yes	550	583	476

NB Fuel B-ULS #3 was supplied containing both LIA and 2-EHN CIA.

Figure 6 and Table 9 show the HFRR WSD produced for the B-ULS diesel fuels with ester-type LIA.

- The B-ULS diesel fuels were slightly over-additized with ester-type LIA due to the waterfall response curve with this LIA type. The HFRR WSDs produced by the B-ULS diesel fuels with ester-type LIA ranged from 419 to 489 µm;
- B-ULS #3 diesel fuel showed a smaller 2-EHN effect as the fuel was additized with LIA by both the supplier and NRC;
- The HFRR WSD increased by an average of 83 µm (2 ml samples) and 67 µm (15 ml covered samples) when 500 ppmv of 2-EHN was added to B-ULS diesel fuels #1 and #2. The 2-EHN effect would have likely been larger if the diesel fuels had not been conservatively additized; and
- B-ULS #1 and #2 diesel fuels did not meet the 520 µm HFRR WSD specification when 500 ppmv of 2-EHN was added.

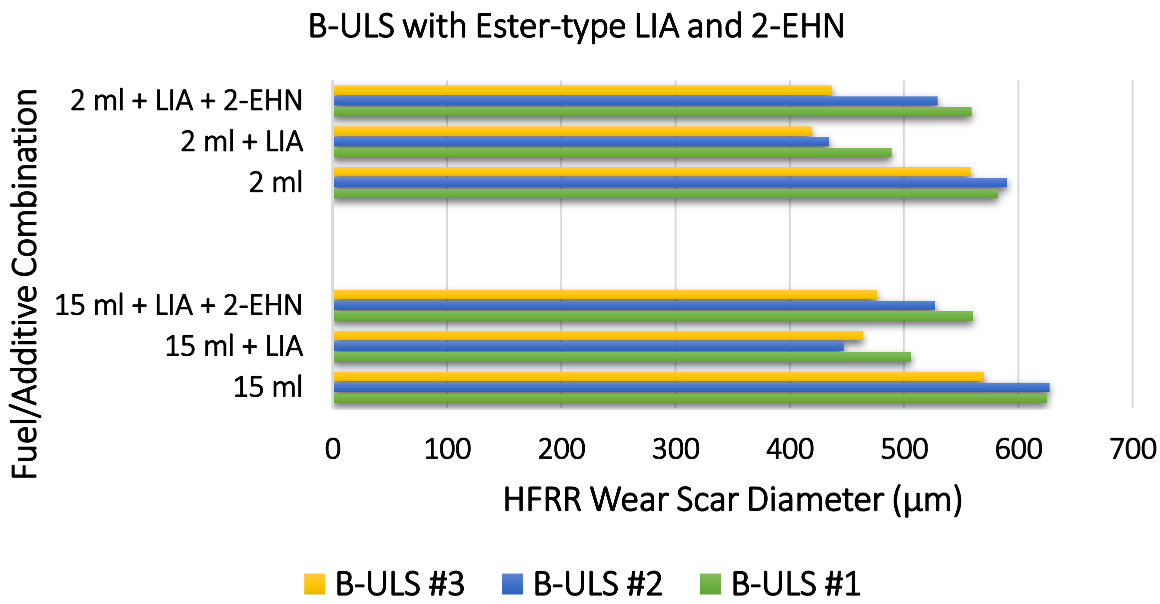

Figure 6 HFRR WSD of B-ULS Diesel Fuels with Ester-Type LIA and 2-EHN CIA

Table 9 HFRR WSD of B-ULS Diesel Fuels with Ester-Type LIA and 2-EHN CIA

Fuel Sample Volume (ml)	LIA	CIA	B-ULS #1	B-ULS #2	B-ULS #3
2	No	No	582	590	558
2	Yes	No	489	434	419
2	Yes	Yes	559	529	437
15	No	No	625	627	570
15	Yes	No	506	447	464
15	Yes	Yes	560	527	476

NB Fuel B-ULS #3 was supplied containing both LIA and 2-EHN CIA.

4.3 HDRD Blending Components

Since HDRD is generally composed of paraffinic hydrocarbons, its composition is significantly different from typical Canadian diesel fuels. Figure 7 shows the effect of monoacid-type LIA treat rate on the HFRR WSD produced by HDRD #1 using standard 2 ml samples. The following observations may be made:

- The monoacid-type LIA was ineffective in reducing the HFRR WSD produced by HDRD #1 at treat rates up to approximately 80 ppmv; and
- The response curve appears to be flattening at monoacid-type LIA treat rates of 100-125 ppmv, which suggests that relatively high treat LIA rates would be required for neat HDRD #1 to meet the CAN/CGSB-3.517 lubricity specification (a maximum WSD of 460 µm in the HFRR test).

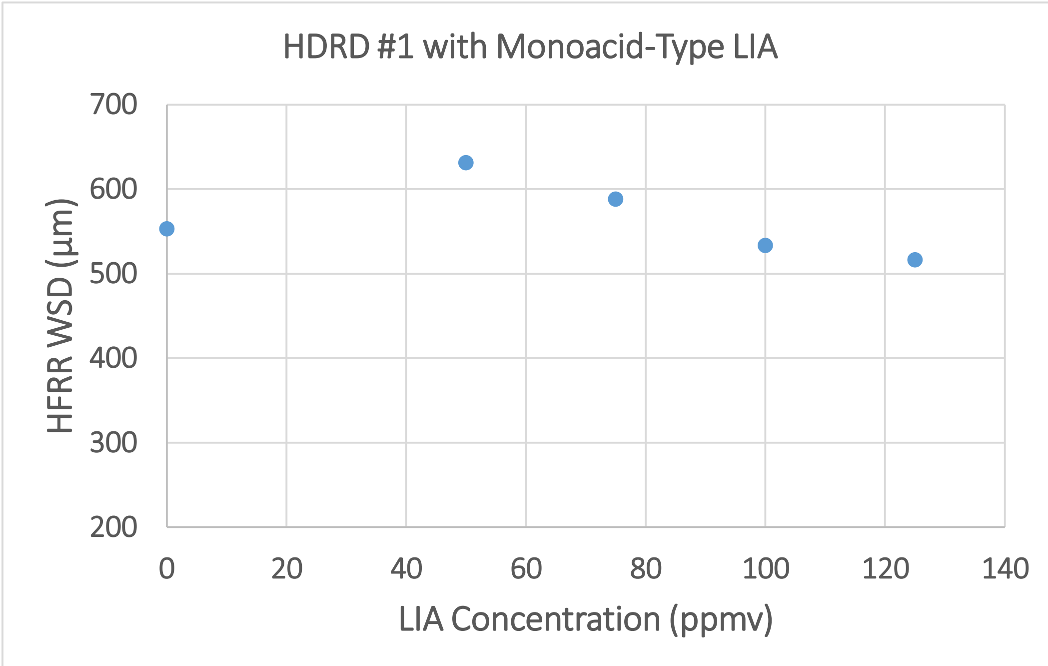

Figure 7 Effect of Monoacid-Type LIA on HFRR WSD

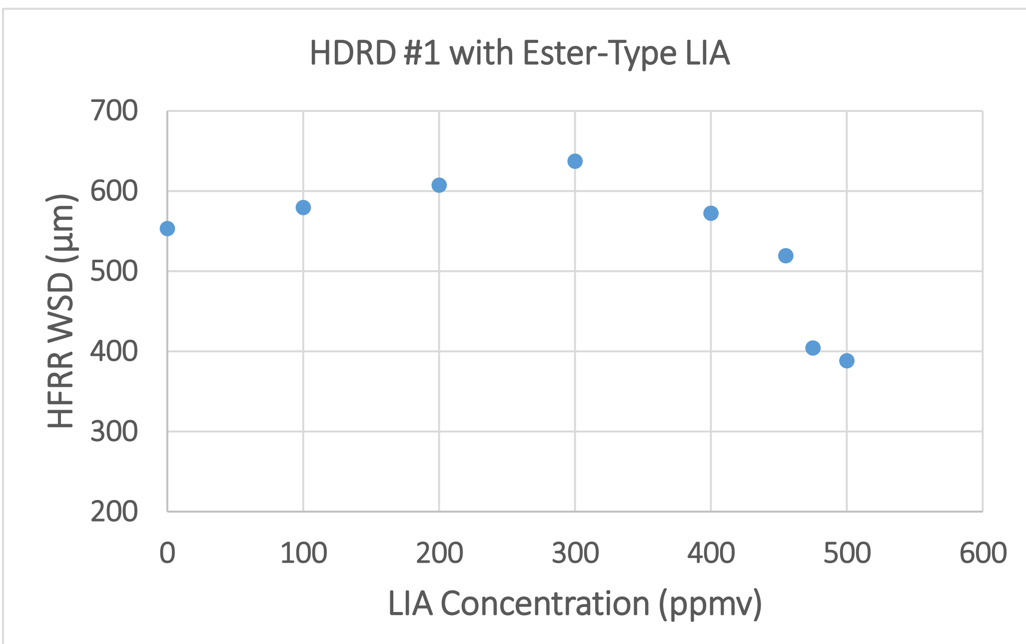

Figure 8 shows the effect of ester-type LIA treat rate on HFRR WSD of HDRD #1. The following observations may be made:

- The response curve for HDRD #1 with ester-type LIA is different from what is typically observed for commercial diesel fuels;
- The HFRR WSD increased with increasing treat rate of ester-type LIA up to ~300 ppmv;
- The typical waterfall response curve for ester-type LIAs occurred at a relatively high treat rate of 450 ppmv; and

- A treat rate of 450-500 ppmv of ester-type LIA was needed to reduce the HFRR WSD produced by HDRD #1 below the 520 µm limit specified in ASTM D975 and approximately 500 ppmv to meet the maximum 460 µm limit specified in CAN/CGSB-3.517.

4.4 Discussion

In this study, HFRR lubricity data was collected with six Canadian diesel fuels, one renewable diesel blending component, two LIAs and 2-EHN CIA. Two different HFRR fuel sample holders were investigated. Following is a discussion of the lubricity results obtained.

Effect of Fuel Sample Size

NRC has previously shown that the standard 2 ml fuel sample size specified in ASTM Test Methods D6079 and D7688 can lead to biased lubricity results due to excessive fuel sample loss during a HFRR test. The fuel sample loss may be reduced by approximately 80% by mass by switching to a 15 ml covered fuel sample holder.

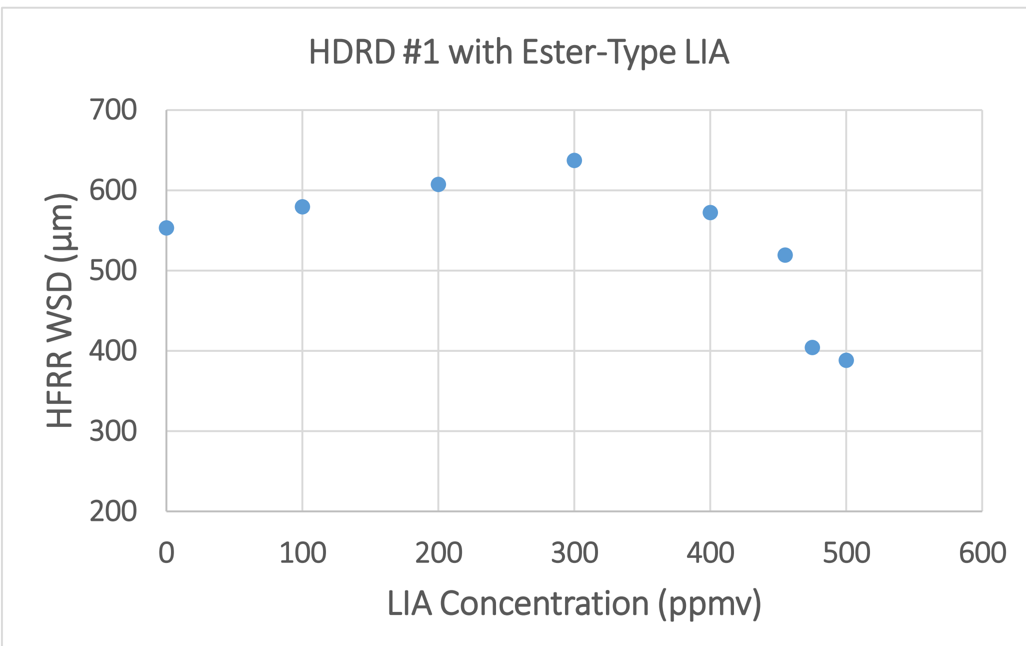

Figure 8 Effect of Ester-Type LIA on HFRR WSD

In this study, additional lubricity data was collected with a range of Canadian diesel fuels. The more volatile A-ULS diesel fuels #1 and #3 produced HFRR WSD's that were 70 µm larger for 15 ml covered samples compared to 2 ml samples. In comparison, the less volatile B-ULS diesel fuels #1 and #2 produced HFRR WSD's that were 40 µm larger with the 15 ml covered samples compared to the standard 2 ml samples.

The larger increase in WSD for the HFRR tests with 15 ml fuel samples compared to 2 ml samples with the A-ULS diesel fuels relative to B-ULS diesel fuels is due to a bias in the standard 2 ml test. Approximately 30% of A-ULS diesel fuel vaporizes during a HFRR lubricity test. The loss of the volatile fraction from the fuel sample increases the concentration of the heavier fractions remaining, which typically contain the lubricating agents. This provides a downward bias in the HFRR lubricity results for A-US diesel fuels with 2ml fuel samples. For this reason, the authors recommend that ASTM Test Methods D6790 and D7688 be revised to specify the utilization of 15 ml covered fuel samples to reduce this bias.

The HFRR test with 15 ml covered fuel samples is a more severe test as a result of reducing fuel sample loss by approximately 80% by mass. NRC researchers have shown that the test severity can be reduced by a combination of ramping up the reciprocating speed from 10-50 Hz over a 10 minute period rather than maintaining a constant 50 Hz reciprocating speed for the entire HFRR test and by slightly reducing the fuel sample temperature from 60°C to 50°C [7].

Effect of LIA Type

Both monoacid- and ester-type LIAs are used in Canadian diesel fuels. Each LIA type has their benefits and disadvantages. Monoacid-type LIAs typically require lower treat rates to meet lubricity specifications than ester-type LIAs. On the other hand, acidic LIAs can react with basic compounds, if they are present, to form salts. This has led to fuel filter clogging and fuel injector sticking issues in the field [8].

Diesel fuels treated with an ester-type LIA produced less repeatable HFRR lubricity results than fuels treated with monoacid-type LIA. This observation is believed to be due to the waterfall (or reverse sigmoidal) response curve of diesel fuels treated with ester-type LIA, whereby the HFRR WSD is insensitive to low LIA treat rates and then rapidly decreases once a critical treat rate of ester-type LIA is present (“waterfall curve”). The HFRR lubricity of a diesel fuel treated with ester-type LIA is not very repeatable when the treat rate is close to this critical range.

Diesel fuels treated with monoacid LIA produced very repeatable HFRR lubricity determinations. This is due to the more gently sloping HFRR WSD response to increasing monoacid-type LIA treat rate. As a result, it was much easier to select the minimum treat rate of monoacid-type LIA to meet the lubricity specifications.

Effect of 2-EHN CIA

2-EHN CIA is used to increase the cetane number of a diesel fuel, when required, to meet the minimum cetane number of 40.0 as specified in CAN/CGSB-3.517. 2-EHN rapidly decomposes shortly after being injected into the combustion chamber of a diesel engine and increases the combustion radical pool, which assists in the autoignition process.

The HFRR lubricity test involves rubbing a loaded steel ball against a steel disk at a reciprocating frequency of 50 Hz for 75 minutes. The lubricity tests conducted with diesel fuels additized with 2-EHN CIA have been shown to usually produce higher HFRR WSD’s. This suggests that the HFRR test could be too severe because some 2-EHN decomposes as the test proceeds. Although the 2-EHN decomposition mechanism [9] is fairly well known, knowledge is lacking about how 2-EHN decomposition increases the HFRR WSD during a lubricity test. In this study, the focus was to acquire knowledge about the impact of fuel sample size and fuel properties on 2-EHN decomposition during a HFRR lubricity test.

In this study, the B-ULS diesel fuels additized with 2-EHN CIA produced a larger increase in HFRR WSD than the A-ULS diesel fuels. This result is believed to be due to two factors. Firstly, A-ULS diesel fuels are more volatile than B-ULS diesel fuels. Approximately 30% of A- ULS diesel fuel can vaporize during a standard HFRR test, which concentrates the lubricating compounds found in the remaining heavier hydrocarbon fractions and LIA of the fuel sample. This results in decreased the localized temperatures due to the wear process and less 2-EHN decomposition. Secondly, the heat of vaporization needed to vaporize the lighter hydrocarbon fractions is provided by frictional heat from the wear process. The heat absorbed during the vaporization process reduces the localized high temperature regions, which reduces 2-EHN decomposition.

For the B-ULS diesel fuels, the fuel sample loss is much lower with the standard 2 ml test (approximately 10% by mass) compared to A-ULS diesel fuels. As a result, fuel sample size is a much less of a significant factor. Surprisingly, the 2-EHN effect for the B-ULS diesel fuels appears to be slightly lower with the 15 ml covered samples even though the HFRR test is more severe when using this configuration. The larger heat capacity of the 15 ml fuel samples may play a beneficial role in reducing localized high temperatures that lead to 2-EHN decomposition.

Effect of HDRD Blending Components

A limited number of HFRR lubricity tests were performed with neat HDRD #1, a renewable diesel blending component, additized with monoacid and ester-type LIAs. HDRD #1 would not normally be used as a neat diesel fuel due to its high cost relative to conventional diesel fuel. Figures 7 and 8 show that HDRD #1 produced different response curves for monoacid- and ester-type LIAs than what one would typically observe for a conventional diesel fuel. In particular, the monoacid-type LIA was not effective in reducing the HFRR WSD of HDRD #1 at treat rates up to 125 ppmv. This result may be due to the absence of aromatic hydrocarbons in HDRD #1, which are known to be excellent solvents for polar additives. Further studies with higher treat rates of monoacid-type LIA are needed.

When HDRD #1 was additized with ester-type LIA, treat rates up to 400 ppmv did not have any beneficial effect in reducing the HFRR WSD produced by HDRD #1. However, a treat rate of 450-500 ppmv was sufficient to meet the lubricity standards in North America. The ester-type LIA demonstrated the waterfall response curve with HDRD #1, albeit at a higher treat rate.

Although only HDRD #1 was investigated with LIA and CIA’s in this study, similar HFRR results for the two HDRD’s would be anticipated. This assessment is based on the identical HFRR WSD of the two neat HDRD’s and the relatively high IBP and T10 distillation temperatures of the HDRD’s compared to the B-ULS diesel fuels. The limited results for HDRD #1 suggest that caution should be exercised when moving to higher renewable content in Canadian diesel fuels as HDRD is less compatible with LIAs.

5 Conclusions

HFRR lubricity determinations have been undertaken with a large number of diesel fuel/additive combinations to better understand the deficiencies in ASTM Test Methods D6079 and D7688. A total of six A-ULS and B-ULS conventional diesel fuels originating from both crude oil and oil sands sources in Canada were investigated, as well as one HDRD renewable diesel blending component. The diesel fuels were additized with monoacid and ester-type LIAs and 2-EHN CIA. HFRR lubricity determinations were carried out using standard 2 ml fuel samples and 15 ml covered samples. The following conclusions may be drawn from the lubricity data collected in this study:

1. The current HFRR Test Methods with a 2 mL sample produce lower WSDs for A-ULS diesel fuels as compared to the same test methods using a 15 mL sample.
2. The HFRR lubricity test produces higher WSDs when 15 ml covered fuel samples are employed due to an 80% reduction by mass in the loss of volatile fuel compounds, which typically have relatively poor lubricity.
3. ASTM Test Methods D6079 and D7688 should be revised to specify the use of 15 ml covered fuel samples in place of the current standard 2 ml samples to reduce fuel sample loss as the test proceeds.
4. The laboratory test data suggests that diesel fuels additized with 2-EHN produce higher HFRR WSDs due to 2-EHN decomposition, which increases the HFRR WSD.
5. The severity of the HFRR lubricity test could be decreased slightly to reduce 2-EHN decomposition [7]. Suggested modifications are ramping up the reciprocating frequency from 10 Hz to 50 Hz over a 10-minute period at the start of the test and reducing the fuel sample temperature from 60° to 50°C.
6. Due to the paraffinic nature of HDRD, higher LIA treat rates may be needed to meet existing HFRR limits when blending higher levels of HDRD with diesel fuel.

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Appendix A

Table A- 1: HFRR WSD data of A-ULS #1 diesel fuel with monoacid-type LIA

Monoacid-Type LIA Treat Rate (ppmv)	2-EHN CIA Treat Rate (ppmv)	Fuel Sample (ml)	HFRR WSD (µm)
0	0	2	649
0	0	2	652
0	0	2	645
75	0	2	535
75	0	2	531
100	0	2	480
100	0	2	485
100	500	2	532
100	500	2	502
100	500	2	507
0	0	15	751
0	0	15	722
100	0	15	515
100	0	15	517
100	500	15	515
100	500	15	537

Table A- 2: HFRR WSD data of A-ULS #1 diesel fuel with ester-type LIA

Ester-Type LIA Treat Rate (ppmv)	2-EHN CIA Treat Rate (ppmv)	Fuel Sample (ml)	HFRR WSD (µm)
0	0	2	649
0	0	2	652
0	0	2	645
250	0	2	493
250	0	2	560
250	0	2	522
300	0	2	407
300	0	2	422
300	500	2	467
300	500	2	403
0	0	15	751
0	0	15	722
300	0	15	502
300	0	15	454
300	0	15	508
300	0	15	463
300	0	15	473
300	500	15	513
300	500	15	468

Table A- 3: HFRR WSD data of A-ULS #2 diesel fuel with monoacid-type LIA

Monoacid-Type LIA Treat Rate (ppmv)	2-EHN CIA Treat Rate (ppmv)	Fuel Sample (ml)	HFRR WSD (μm)
0	0	2	687
0	0	2	649
75	0	2	543
100	0	2	498
100	0	2	512
100	500	2	542
100	500	2	534
0	0	15	747
0	0	15	766
100	0	15	518
100	0	15	517
100	500	15	547
100	500	15	548

Table A- 4: HFRR WSD data of A-ULS #2 diesel fuel with ester-type LIA

Ester-Type LIA Treat Rate (ppmv)	2-EHN CIA Treat Rate (ppmv)	Fuel Sample (ml)	HFRR WSD (μm)
0	0	2	687
0	0	2	649
250	0	2	459
250	0	2	474
300	0	2	332
250	500	2	480
250	500	2	552
0	0	15	747
0	0	15	766
250	0	15	516
250	0	15	568
300	0	15	418
250	500	15	603
250	500	15	604

Table A- 5: HFRR WSD data of A-ULS #3 diesel fuel with monoacid-type LIA

Monoacid-Type LIA Treat Rate (ppmv)	2-EHN CIA Treat Rate (ppmv)	Fuel Sample (ml)	HFRR WSD (μm)
0	0	2	640
0	0	2	641
50	0	2	602
100	0	2	514
100	0	2	470
100	500	2	514
100	500	2	527
0	0	15	687
0	0	15	696
100	0	15	511
100	0	15	517
100	500	15	554
100	500	15	568

Table A- 6: HFRR WSD data of A-ULS #3 diesel fuel with ester-type LIA

Ester-Type LIA Treat Rate (ppmv)	2-EHN CIA Treat Rate (ppmv)	Fuel Sample (ml)	HFRR WSD (μm)
0	0	2	640
0	0	2	641
200	0	2	455
200	0	2	415
250	0	2	421
250	0	2	375
250	0	2	356
300	0	2	390
300	0	2	360
200	500	2	484
200	500	2	512
0	0	15	687
0	0	15	696
200	0	15	512
200	0	15	486
200	500	15	599
200	500	15	557

Table A- 7: HFRR WSD data of B-ULS #1 diesel fuel with monoacid-type LIA

Monoacid-Type LIA Treat Rate (ppmv)	2-EHN CIA Treat Rate (ppmv)	Fuel Sample (ml)	HFRR WSD (µm)
0	0	2	589
0	0	2	575
75	0	2	478
75	0	2	490
75	500	2	561
75	500	2	565
0	0	15	608
0	0	15	642
75	0	15	489
75	0	15	495
75	500	15	549
75	500	15	551

Table A- 8: HFRR WSD data of B-ULS #1 diesel fuel with ester-type LIA

Ester-Type LIA Treat Rate (ppmv)	2-EHN CIA Treat Rate (ppmv)	Fuel Sample (ml)	HFRR WSD (µm)
0	0	2	589
0	0	2	575
250	0	2	510
275	0	2	491
275	0	2	487
300	0	2	405
300	0	2	435
275	500	2	559
275	500	2	558
0	0	15	608
0	0	15	642
275	0	15	501
275	0	15	510
275	500	15	545
275	500	15	572

Table A- 9: HFRR WSD data of B-ULS #2 diesel fuel with monoacid-type LIA

Monoacid-Type LIA Treat Rate (ppmv)	2-EHN CIA Treat Rate (ppmv)	Fuel Sample (ml)	HFRR WSD (μm)
0	0	2	595
0	0	2	571
0	0	2	586
0	0	2	607
75	0	2	512
75	0	2	505
100	0	2	455
100	0	2	410
75	500	2	603
75	500	2	581
0	0	15	630
0	0	15	623
75	0	15	532
75	0	15	521
75	500	15	593
75	500	15	573

Table A- 10: HFRR WSD data of B-ULS #2 diesel fuel with ester-type LIA

Ester-Type LIA Treat Rate (ppmv)	2-EHN CIA Treat Rate (ppmv)	Fuel Sample (ml)	HFRR WSD (μm)
0	0	2	595
0	0	2	571
0	0	2	586
0	0	2	607
200	0	2	550
200	0	2	540
225	0	2	541
225	0	2	537
250	0	2	425
250	0	2	441
250	0	2	437
300	0	2	450
300	0	2	435
250	500	2	608
250	500	2	564
250	500	2	469
250	500	2	608
0	0	15	630
0	0	15	623
250	0	15	422
250	0	15	434
250	0	15	486
250	500	15	621
250	500	15	460
250	500	15	529
250	500	15	525

Table A- 11: HFRR WSD data of B-ULS #3 diesel fuel with monoacid-type LIA

Monoacid-Type LIA Treat Rate (ppmv)	2-EHN CIA Treat Rate (ppmv)	Fuel Sample (ml)	HFRR WSD (μm)
0	0	2	547
0	0	2	568
50	0	2	412
50	0	2	408
50	500	2	479
50	500	2	493
0	0	15	570
50	0	15	447
50	0	15	411
50	500	15	472
50	500	15	480

Table A- 12: HFRR WSD data of B-ULS #3 diesel fuel with ester-type LIA

Ester-Type LIA Treat Rate (ppmv)	2-EHN CIA Treat Rate (ppmv)	Fuel Sample (ml)	HFRR WSD (μm)
0	0	2	547
0	0	2	568
100	0	2	442
100	0	2	396
200	0	2	366
250	0	2	377
275	0	2	307
100	500	2	437
100	500	2	462
0	0	15	570
100	0	15	389
100	0	15	406
100	0	15	373
100	0	15	451
100	0	15	477
100	500	15	442
100	500	15	409
100	500	15	373
100	500	15	411

Table A- 13: HFRR WSD data of HDRD #1 with monoacid-type LIA

Monoacid-Type LIA Treat Rate (ppmv)	2-EHN CIA Treat Rate (ppmv)	Fuel Sample (ml)	HFRR WSD (μm)
0	0	2	549
0	0	2	542
0	0	2	569
50	0	2	637
50	0	2	625
75	0	2	577
75	0	2	599
100	0	2	543
100	0	2	524
125	0	2	526
125	0	2	489
125	0	2	533
150	0	2	478
150	0	2	476

Table A- 14: HFRR WSD data of HDRD #1 with ester-type LIA

Ester-Type LIA Treat Rate (ppmv)	2-EHN CIA Treat Rate (ppmv)	Fuel Sample (ml)	HFRR WSD (μm)
0	0	2	549
0	0	2	542
0	0	2	569
100	0	2	585
100	0	2	573
200	0	2	603
200	0	2	611
300	0	2	630
300	0	2	638
300	0	2	644
400	0	2	579
400	0	2	571
400	0	2	566
455	0	2	556
455	0	2	532
455	0	2	435
455	0	2	543
455	0	2	546
455	0	2	448
455	0	2	544
455	0	2	537
455	0	2	533
475	0	2	405
475	0	2	410
475	0	2	425
475	0	2	376
500	0	2	402
500	0	2	373