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EVALUATION OF DIESEL FUEL HAZE RESULTING FROM WATER CONTENT

Final Report

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Evaluation of Diesel Fuel Haze Resulting from Water Content

CRC Project No. DP-06-20

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Acknowledgements

This report represents results and conclusions from an effort between representatives of Coordinating Research Council, Inc. (CRC) Diesel Performance Group (DPG) Fuel Cleanliness Panel and the Southwest Research Institute (San Antonio, Texas) with assistance from an anonymous sponsor. The members of the Fuel Cleanliness Panel include representatives from industry associations, equipment manufacturers, fuel & additive vendors, and service/contractor organizations.

This project was conducted by CRC with the goal of determining actual relationship between haze rating methods of Haze Clarity Index test method (ASTM D8148) and the commonly use ASTM Haze number method (ASTM D4176) for typical levels of water content seen in the marketplace compression ignition fuels.

Program: Evaluation of Diesel Fuel Haze Resulting from Water Content

Objective

Apply the new ASTM Haze Clarity Index (HCI) test method, ASTM D8148 to investigate relationship of HCI to water levels in diesel fuel that cause diesel to become hazy. Several diesel types at various water levels were included to evaluate whether HCI haze has any correlation to total water in a hazy sample.

Background

Engine, auto, injection equipment manufacturers, and other users of diesel fuel believe that additional controls to reduce amount of water and solids in diesel fuel is beneficial to the operation of modern high-pressure common-rail fuel systems. Several avenues such as ASTM, Top Tier, Worldwide Fuel Charter, and NCWM have been pursued but in most cases credible research data to set limits do not exist.

ASTM D975 standard specifications for diesel fuel allows a combined water and sediment level of 0.05 % max by volume. It also has required workmanship statement that states; ‘The diesel fuel shall be visually free of undissolved water, sediment, and suspended matter.’

There are concerns with the current ASTM requirements for water control as determination of visually free is very subjective and temperature of the fuel evaluated is not specified. To comply with workmanship requirement the fuel may have to be cleaner than the ASTM specification for “Water and Sediment” of less than 0.05 volume percent.

A new ASTM Haze Clarity Index (HCI) test method, ASTM D8148, has been developed which can generate useful data quantifying appearance of haze for different fuel types at various water levels. This test method provides an objective analytical means for providing a haze rating that does not depend on subjective visual ratings that typically vary with operator and lighting conditions.

This project was conducted to generate data that can be used by other groups in industry to propose limits on water levels, use of filters, or any other measure relevant to their application.

This project is not a study of all the factors that might affect haze formation in diesel fuel. These factors include, but are not limited to, temperature, additives, fuel type, interfacial tension, and water separation characteristics.

Experimental Procedures

Fuel Type: Following market representative fuels were provided by fuel producers for this study:

Fuel Sample Description	Test Sample ID
Diesel No . 1	CL19-3841
GTL Diesel	CL19-3914
CARB Diesel	CL19-3915
Diesel No.1	CL19-4215
Diesel No.2 – 29 % Aromatics	CL19-4216
Diesel No.2 – 32 % Aromatics	CL19-4217
Renewable Diesel	CL19-4218

All the fuels tested were expected to contain typical additives such as corrosion inhibitor, conductivity, and lubricity additives at normal treat rates while the biodiesel portion of biodiesel blends was expected to contain antioxidant additive. There was no pre-treatment of the fuels before testing and no specific restrictions were made for presence of additives in the selected test fuels as the study was not about the effects of these constrains on the haze formation. Also, these restrictions were not expected to have a great impact on the outcome of the study.

Water Level: The baseline water content in the selected fuels was measured using Karl Fischer test method. The fuels were then dosed with deionized water at 50 ppm, 200 ppm, and 500 ppm by weight/weight and final water content was measured again. Efforts were not made to have exact water contents in the test fuels, since the objective of this study was to vary amount of water and perform measurements of haze ratings.

Temperature: The original test plan proposed measuring haze at couple of temperatures as temperature affects level of haze in the fuels. The proposed test temperatures were room temperature range (22 ± 2°C) as specified in the ASTM D8148 standard and a cold temperature of -4°C (average temperature in Chicago in January).

However, it is very difficult to control temperature of the sample and take all needed measurement steps at the same time. The samples were small and there was a good chance the sample would change before the HCI measurement can be taken at cold temperatures. Thus, a decision was made to measure haze ratings at the room temperature only (22 ± 2°C).

Test Methods

D8148 Test Method for Spectroscopic Determination of Haze in Fuels (Haze Clarity Index)

D6304 Test Method for Determination of Water in Petroleum Products, Lubricating Oils, and Additives by Coulometric Karl Fischer Titration

D2709 Test Method for Water and Sediment in Middle Distillate Fuels by Centrifuge

D4176 Test Method for Free Water and Particulate Contamination in Distillate Fuels (Visual Inspection

Procedures), Procedure 2
D7261 Test Method for Determining Water Separation Characteristics of Diesel Fuel by Portable Separometer (DSEP)

Test Procedure and Analysis

For test measurements, one-liter samples were pulled from each fuel to serve as a base fuel for blending. About 200 grams of fuel was dosed with deionized water at 50 ppm, 200 ppm, and 500 ppm by w/w. The sample blends were then sonicated for 5 minutes with intermittent hand swirling/dunking into sonicator bath before making test measurements. Blends were analyzed immediately by Karl Fischer, followed by measurements of Haze Clarity Index and Haze number. Figure 1 shows representative samples prepared for Haze rating measurements.

The procedure in Haze Number method involves placing the fuel into a one-liter clear glass jar and visually inspecting for clarity. Fuel clarity is rated by placing a standard bar chart behind the sample and comparing its visual appearance with the standard haze rating photos. For lab testing, the procedure is performed after the sample has equilibrated at the test temperature of interest.

Figure 1. Representative test fuel sample with and without addition of water

Results of Analysis

The plots in Figure 2 through Figure 8 compares the haze rating for individual fuel samples as measured by haze number and HCI for varying amounts of water content. Overall, the results show predictable trend of increasing haze number and drop in HCI with increasing amount of water. However, there are variances in the haze rating values when comparing individual fuel samples for same amounts of water content. These variances could be attributed to the differences in the ability of the individual fuel samples to dissolve water at the test temperature. The ability of individual fuel sample to dissolve water is influenced by its composition primarily linked to level of aromatics and polar components like biodiesel content. For example, a fuel with high aromatics content or higher biodiesel content can have potential to dissolve higher amounts of water than a fuel that is highly paraffinic with no biodiesel or other polar contents. NOTE: It should be noted that regarding both aromatics and biodiesel, the ability to dissolve water is much less than compounds like ethanol that are highly polar therefore miscible with water.

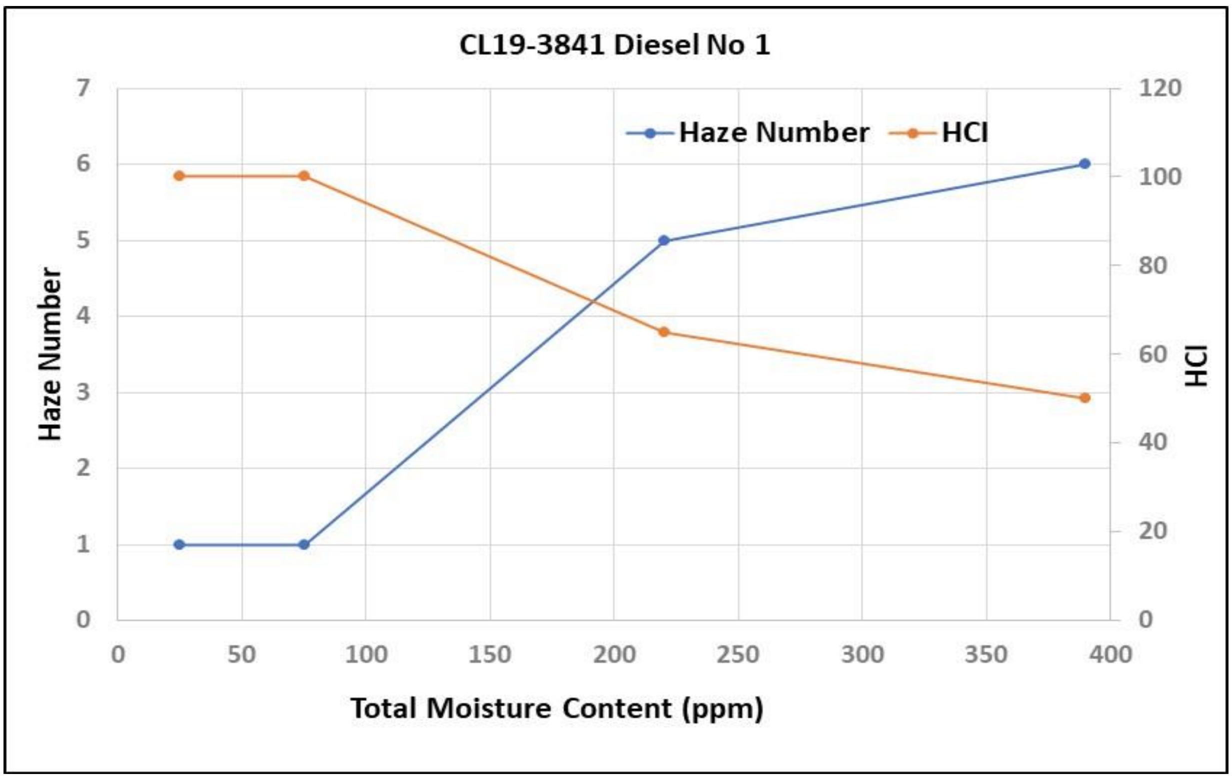

Figure 2. Comparison of Haze ratings by Haze Number and HCI for CL19-3841 Sample

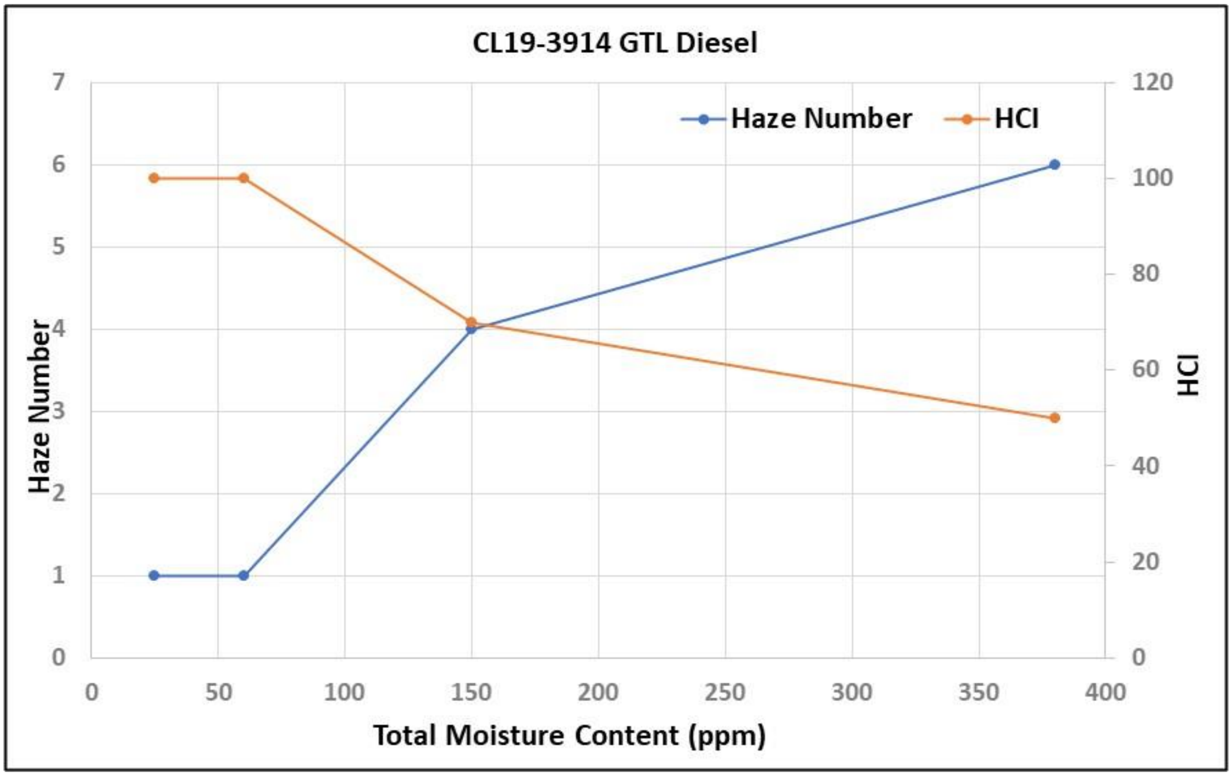

Figure 3. Comparison of Haze ratings by Haze Number and HCI for CL19-3914 Sample

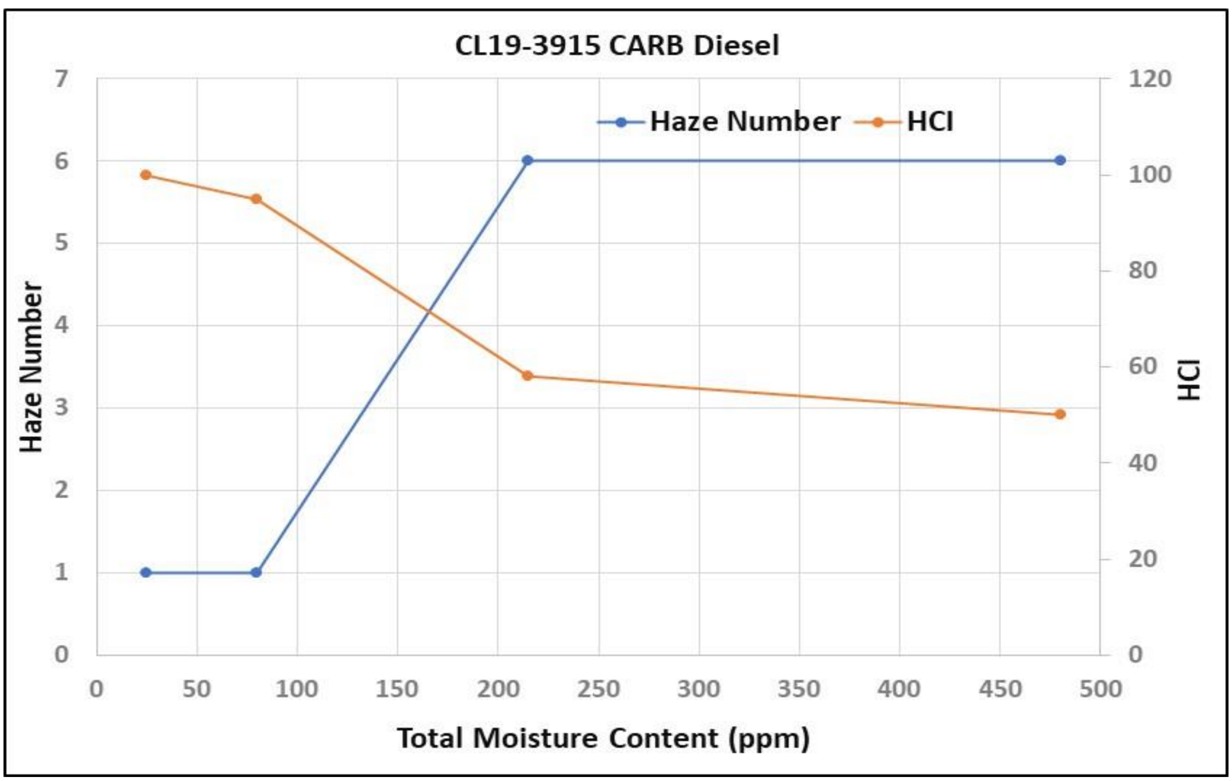

Figure 4. Comparison of Haze ratings by Haze Number and HCI for CL19-3915 Sample

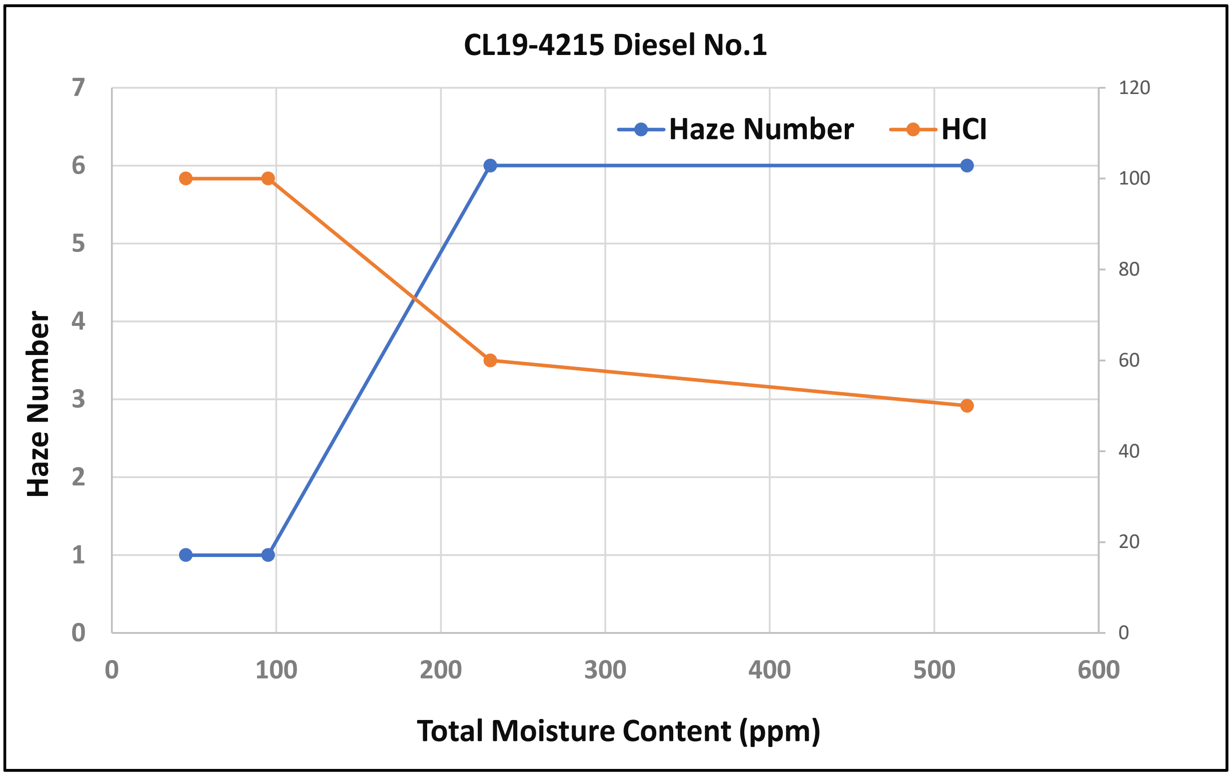

Figure 5. Comparison of Haze ratings by Haze Number and HCI for CL19-4215 Sample

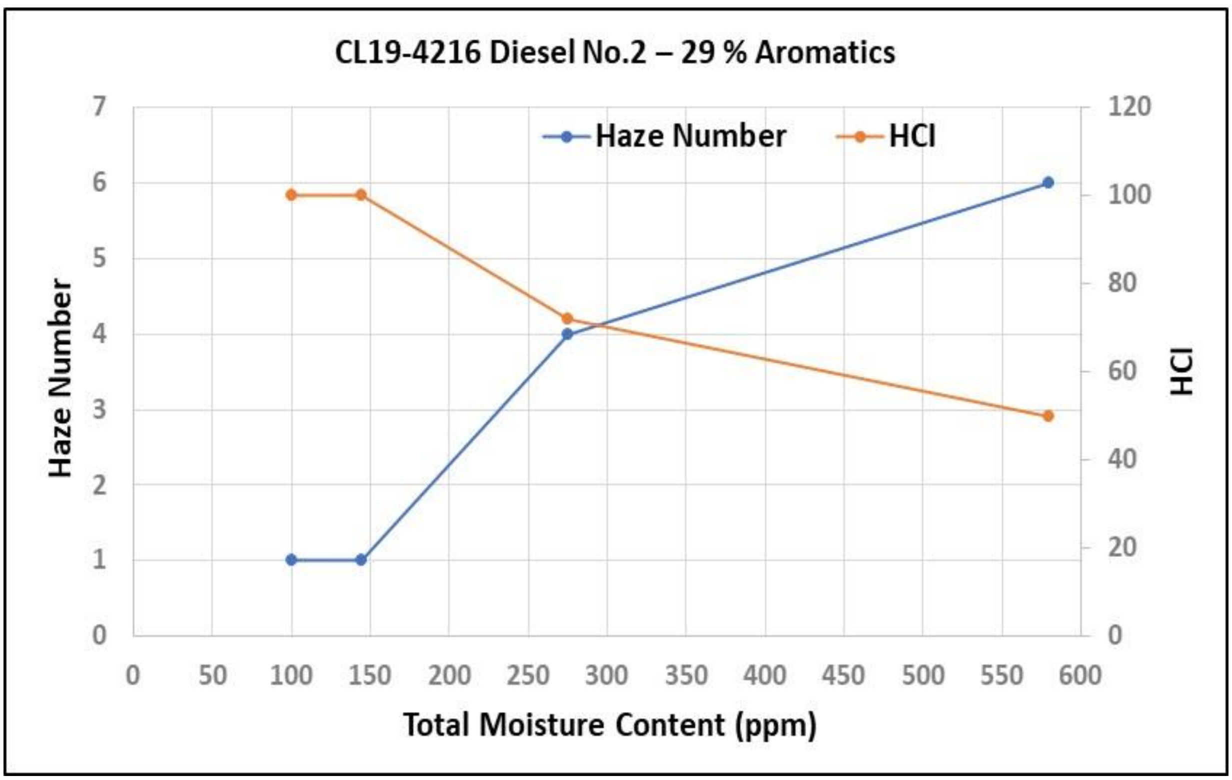

Figure 6. Comparison of Haze ratings by Haze Number and HCI for CL19-4216 Sample

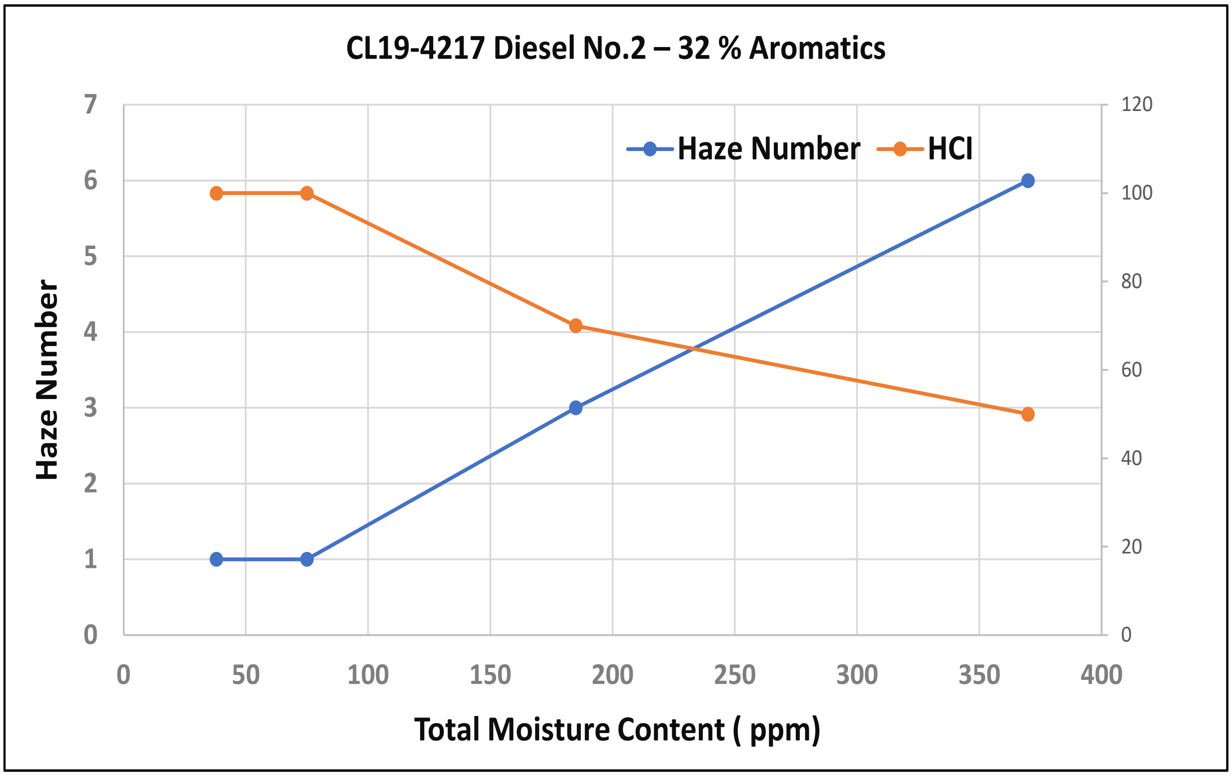

Figure 7. Comparison of Haze ratings by Haze Number and HCI for CL19-4217 Sample

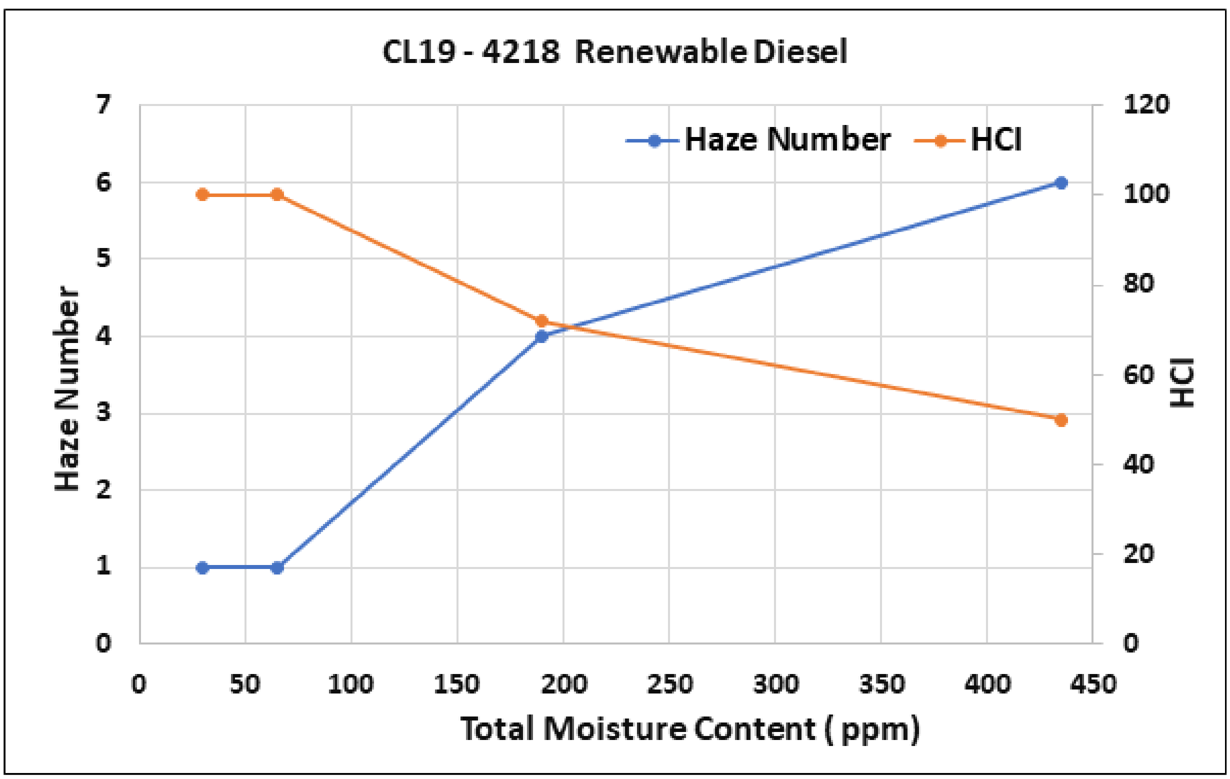

Figure 8. Comparison of Haze ratings by Haze Number and HCI for CL19-4218 Sample

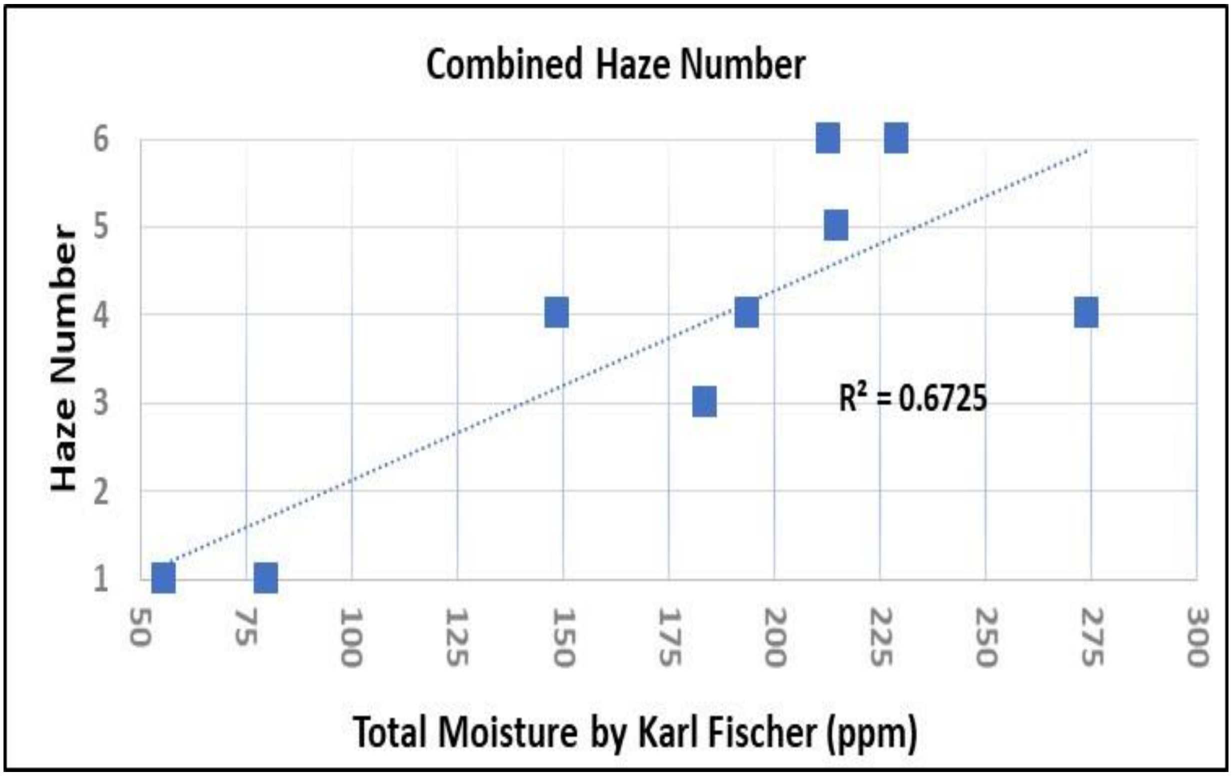

Figure 9. Combined results of Haze Number for all samples (except for ones with HCI of 100 and total water content below 50 ppm)

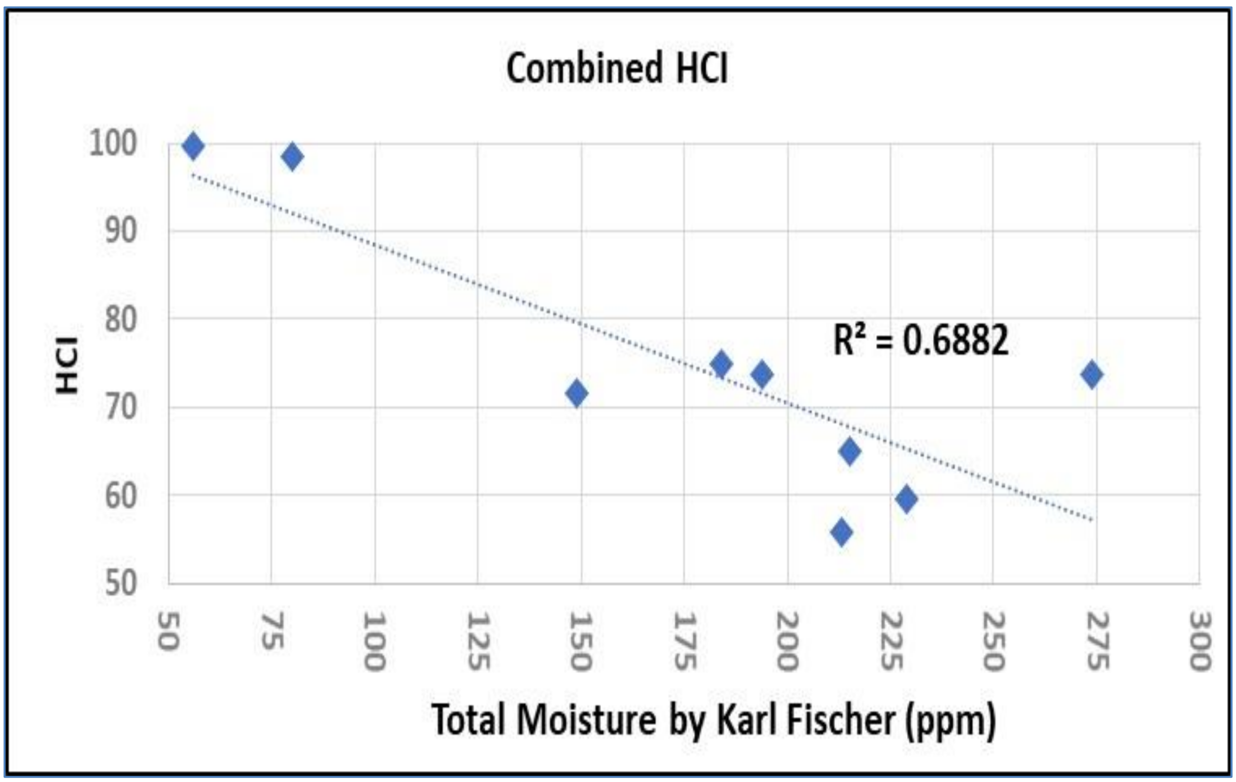

Figure 10.Combined results of Haze Number for all samples
(except for ones with HCI of 100 and total water content below 50 ppm)

Figure 9 and Figure 10 shows overall plot for Haze number and HCI for fuel samples excluding samples with an HCI of 100 and below 50. The test method D4176 measures haze rating from 1 to 6 which corresponds to range of Haze Clarity Index (HCI) from 50.0 to 100.0. Thus, Haze Clarity Index (HCI) from 50.0 to 100.0 is used to evaluate haze intensity in general and samples beyond these ranges were not considered.

The data indicates that there is similar correlation for Haze number (R^2 =0.67) and HCI (R^2 =0.68) with increasing water content. Figure 11 shows plot for HCI versus Haze number and indicates strong correlation between these values with R^2 =0.97 and indicates that either method could be used for Haze rating of the diesel and biodiesel blended fuels. Workmanship requirements in the fuel standards for diesel and biodiesel blends requires the fuel to be free of undissolved water, sediment, and suspended matter. However, the workmanship section in the fuel standards does not specify a test method, temperature or other factors associated with the determination of fuel meeting this requirement. When comparing the two haze methods in this study, it appears that HCI method provides more objective quantitative measure of dispersed undissolved water. HCI method is independent of the operator assessment of the haze, and requires measurement at specified temperature and, thus could be a preferred method.

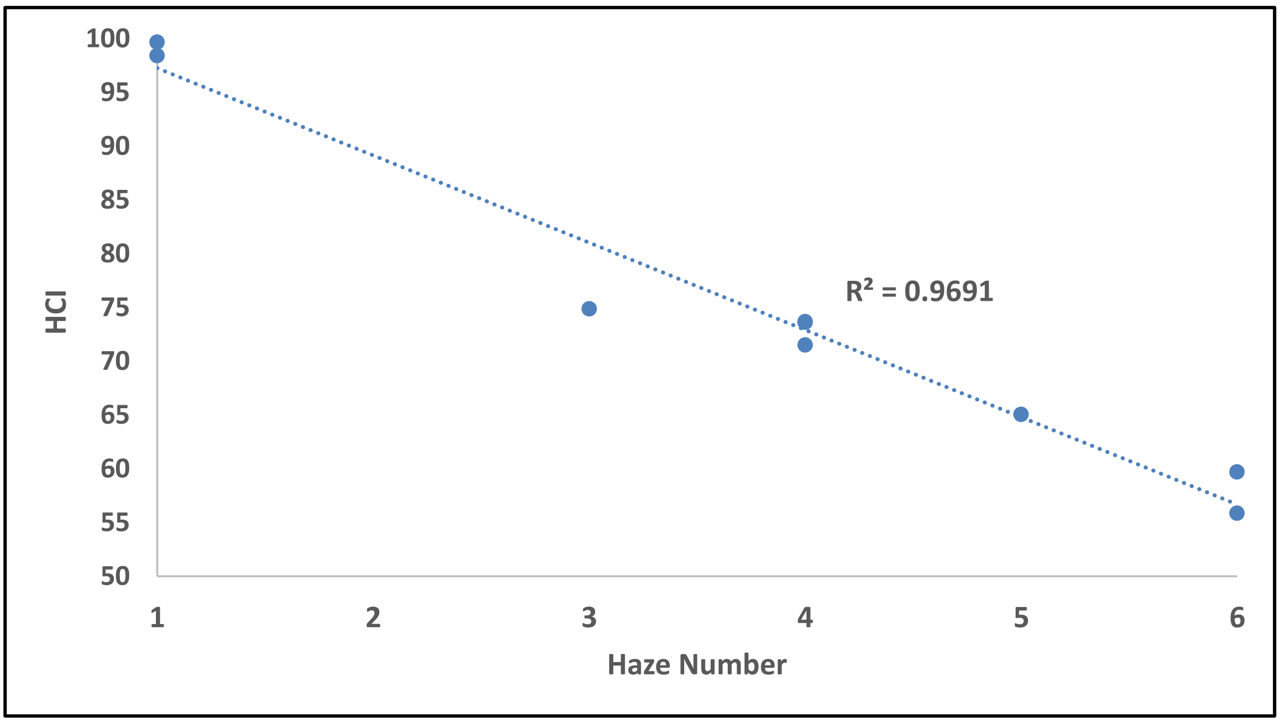

Figure 11. Correlation of HCI and Haze Number for all the samples (except for ones with HCI of 100 and below 50)

Select few samples were re-tested after 4 weeks of storage interval at room temperature to evaluate water settling by performing same measurements for haze ratings and water content as the original tests. Results are summarized in Table 1 and indicates a significant loss of water during the storage period, which improved the haze ratings of all the samples relative to the initial testing. These observations show variability in the haze ratings that can be introduced by sample storage times and conditions. This also demonstrates practical usefulness of the common industry practice of placing a hazy fuel in a tank overnight to let it settle and drop out water from a fuel phase to improve haze ratings. Note: The value of reported initial water content for fuel sample CL19-3914 (GTL Diesel) is lower compared to other fuels with similar spiked water content. This is likely to be attributed to non-polar nature of the GTL fuel which makes it difficult to hold water content in the fuel. However, this sample follows similar trend of significant loss of water during the storage period.

Table 1. Impact of water settling after certain duration

Sample Name	Water Spike	Initial Testing			3 - 4 Weeks Post Testing			Change		
		Reported Value Water (ppm)	Haze Number	HCI	Reported Value Water (ppm)	Haze Number	HCI	Reported Value Water (ppm)	Haze Number	HCI
CL19-4217	200 ppm	184	3	75	55	1	100	***-129***	***-2***	***25***
CL19-4215	200 ppm	229	6	60	64	2	94	***-165***	***-4***	***34***
CL19-3841	200 ppm	215	5	65	66	1	100	***-149***	***-4***	***35***
CL19-3915	200 ppm	213	6	56	84	2	90	***-129***	***-4***	***34***
CL19-3914	200 ppm	149	4	72	40	1	99	***-109***	***-3***	***27***

Summary and Conclusions

The study evaluated impact on haze ratings by two different methods in a variety of fuel samples for a range of water content (<500 ppm) typically seen in the marketplace diesel and biodiesel blended fuels. These experiments were conducted in a manner intended to simulate haze with realistic levels of water contamination in real world fuels. In this study, the two haze rating test methods, Haze number and HCI, showed predictable trend of poor haze ratings with increasing amounts of water. The two test methods showed very strong correlation for the range of water levels and the fuel types tested in this study. The results showed that a haze rating is influenced by the fuel composition as well as the storage time.

The study did not evaluate other factors like sediment or suspended matter on haze rating nor did it test extreme levels of water content which could be present in the fuel. It is possible that other factors influencing haze rating may produce different results for the two test methods evaluated in this study and as such the results of this study may not apply to all scenarios related to hazy fuels encountered in the field. However, these results do provide some confidence that the ASTM D8148 HCI method could be used to test and implement the haze rating related to water contamination for the typical levels of water content present in the marketplace fuel. Also, the ratings by HCI measurements are comparable to the ASTM D4176 Haze number method commonly used for haze rating.

Recommendations for future work could include further validation of HCI method using various factors that can impact haze rating of fuel such as sediments, suspended matter, biodiesel blends impact, impact of low temperatures and higher water content.