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USING TERAHERTZ TIME-DOMAIN SPECTROSCOPY TO DISCRIMINATE AMONG WATER CONTAMINATION LEVELS IN DIESEL ENGINE OIL

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ABSTRACT. *Terahertz time-domain spectroscopy (THz-TDS) in the range of 0.5 to 2.0 THz was evaluated for discriminating among water contamination levels (0%, 0.1%, and 0.2%) in diesel engine oil (SAE 15W-40). The absorption coefficient demonstrated potential to discriminate among the three water contamination levels with significant differences among all three levels across the 1.111 to 1.332 THz and 1.669 to 1.934 THz ranges. At each of these frequency ranges, each water contamination level was significantly different from the other two. The 0% water contamination level had the lowest absorption coefficient, while 0.2% water had the highest absorption coefficient. The refractive index demonstrated greater potential to discriminate among water contamination levels with significant differences among all three water levels across the 0.5 to 1.5 THz range. The refractive index of 0% water was the lowest and 0.2% water was the highest across the THz range. Linear regression analysis of the refractive index as a predictor of water contamination level yielded a highly significant equation (p < 0.0001, R^2 = 0.99, RMSE = 0.01) when using the refractive indices at 0.5 THz. The refractive indices of these oil samples were promising for discrimination of water contamination. THz spectroscopy should be evaluated for discriminating other engine oil contaminants.*

Keywords. *Diesel, Engine oil, Terahertz spectroscopy, Water contamination.*

Agricultural equipment users regularly waste diesel engine oil that still has useful life or unknowingly continue use of contaminated engine oil to the detriment of internal engine components. Internal combustion engines rely on a thin film of oil for lubrication of metal-to-metal contact points. Modern diesel engine oils contain additives to clean, bind contaminants, improve sealing, resist oxidation, and inhibit corrosion (Mackney et al., 2012). Diesel engine oil has a finite life and is subjected to contamination and oxidation that impact its efficacy. Engine manufacturers recommend an oil change interval that is generally appropriate under normal operating conditions, but normal operating conditions vary from one engine application to another. In one case, a tractor may be stationary and providing PTO power at about 70% of engine rated speed in a relatively dust-free environment, and the engine oil may be able to perform satisfactorily for multiple times longer than the manufacturer's recommended change interval. In another case, a tractor may be used for a tillage operation and operating at near full power on dry ground, producing clouds of dust. In this case, the useful life of the engine oil may be consumed in a fraction of the recommended oil change interval. In other cases, coolant or air induction system leaks can lead to excessive contaminants and catastrophic engine system failure. In the first case, maintenance costs are unnecessarily increased and useful oil is wasted. In the other cases, the engine may experience accelerated wear and substantially greater costs are required to renew the engine. A convenient, scientific method is needed to monitor engine oil for contaminants and useful life. ASTM standards include oil analysis methods, but these methods require a suitable laboratory. Companies offer oil analysis services using ASTM standard or modified methods, but these services require collecting an engine oil sample and sending it for analysis. While some commercial equipment owners use these services, these services are not commonly used by agricultural producers due to the requirement of properly withdrawing an oil sample and the delay in receiving results. Diesel engines in agricultural equipment are a very high cost component, and better technology is required to allow on-board or at least on-site oil analysis.

Water is a common contaminant of engine oil as a result of burning fuel in a cold engine and from condensation (Lansdown, 2003). Although water can evaporate from oil at higher operating temperatures, even small amounts can lead to problems. Najjar (1987) reported that water has an adverse effect on foaming, sludge formation, and oxidation and should not exceed 0.2%. Smolenski and Schwartz

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(1994) listed water concentrations in engine oil of greater than 0.1% as a warning threshold for short operation. For this reason, it is imperative to discriminate water contamination levels.

Sensor systems have been evaluated for on-site or *in situ* oil analysis as alternatives to sending oil samples to oil testing labs. Sensor systems studied have included electromechanical (Cheek and Mowery, 1989; Duchowski and Mannebach, 2006; Price and Clarke, 1991; Soleimani et al., 2013; Wang et al., 1994; Wang, 2002) and resonating sensors (Agoston et al., 2005; Jakoby et al., 2003; Milpied et al., 2010; Mohammed and Hassan, 2013). Infrared (Blanco et al., 1998; Borin and Poppi, 2005; Kasberger et al., 2011) and hyperspectral (Lulu et al., 2014) spectroscopy techniques have also been used. The oil conditions these sensors attempted to monitor were acidity (Agoston et al., 2005; Moon et al., 2006; Soleimani et al., 2013; Wang et al., 1994; Wang, 2002), antioxidants (Cheek and Mowery, 1989; Price and Clarke, 1991), viscosity (Duchowski and Mannebach, 2006; Jakoby et al., 2003; Schmitigal and Moyer, 2005), and contaminants of fuel, water, or antifreeze (Borin and Poppi, 2005). No single sensor has been preferred, and researchers have indicated that some combination would be required for monitoring oil condition (Milpied et al., 2010; Schmitigal and Moyer, 2005). To date, engine manufacturers have not widely implemented oil condition monitoring sensors. Algorithms have been implemented by automobile manufacturers using input from other engine sensors as a proxy for oil condition. These algorithms tend to serve more as a reminder for owners to change the oil rather than to accurately assess the remaining useful life of the oil. A new method of monitoring engine oil that has the potential to be miniaturized and ruggedized for on-board or on-site engine oil monitoring would be an important step in providing equipment use-specific data to schedule maintenance operations for agricultural engines.

A recent technology for characterizing various substances including fluids is terahertz (THz) spectroscopy. THz technology is a rapidly expanding field (Jepsen et al., 2011), and several agricultural applications have been identified, including measuring plant drought stress (Born et al., 2014) and leaf dehydration (Castro-Camus et al., 2013), estimating aflatoxin in peanut oil (Chen and Xie, 2014), and other applications summarized by Mathanker et al. (2013). Various methods (Tonouchi, 2007) have been developed to generate and detect THz waves, but THz time-domain spectroscopy (THz-TDS) (Vieweg et al., 2014; Withayachumnankul and Naftaly, 2014) is considered the most powerful and widely used scheme. THz-TDS uses ultrashort laser pulses and photoconductive antennas (Hunsche et al., 1998; Moreno et al., 2014; Tani et al., 1997) or nonlinear crystals (Moreno et al., 2014). THz-TDS has been used to characterize solids (Jiang et al., 2014; Lloyd-Hughes et al., 2006; Misochko et al., 1998; Nickel et al., 2014; Wietzke et al., 2011), liquids (Wang et al., 2014), liquid crystals (Reuter et al., 2013; Vieweg et al., 2010), gases (Harde et al., 1995; Mittleman et al., 1998), and plants (Born et al., 2014; Castro-Camus et al., 2013).

THz-TDS has been used to differentiate among fuel-related products, including grades of gasoline (Al-Douseri et al., 2006), gasoline and ethanol mixtures (Arik et al., 2014b), gasoline and diesel fuel (Arik et al., 2014a; Jin et al., 2008), diesel fuel grades (Zhao et al., 2012c), diesel fuel solidifying point (Zhao et al., 2012a), and biodiesel and base stocks (Zhao et al., 2012b). Lubricating oil characterization with THz-TDS includes polyglycol oils with water (Gorenflo et al., 2006), mineral oil with additives (Naftaly et al., 2005), six grades of lubricating oil (Tian et al., 2009), oil base stock and additive (Tian et al., 2012), and vegetable oils (Hu et al., 2005; Li, 2010). Our recent study was able to distinguish among three grades of unused gasoline engine oil (SAE 5W-20, 10W-40, and 20W-50) and predict viscosity (Abdul-Munaim et al., 2015). None of these studies evaluated the potential for THz-TDS to discriminate among unused engine oil samples with levels of water contamination below 0.4%.

Pure water has been studied using different techniques to observe its properties at THz frequencies (Zafar et al., 1973; Thrane et al., 1995; Wang et al., 2014). These studies revealed refractive index values of >2 and high absorption coefficients of >150 cm^{-1} at 1 THz. The polar nature of the relatively small water molecule is believed to be responsible for this high absorption at THz frequencies. As a consequence, water delivers a strong contrast mechanism. Due to the completely different THz properties of water and oil samples THz radiation shows high sensitivity to water, and THz-TDS is therefore a potential method to detect small amounts of water in engine oil.

RESEARCH OBJECTIVE

The objective of this study was to determine if THz-TDS could discriminate among fresh diesel engine oil samples with three levels of water contamination (0%, 0.1%, and 0.2%). If successful, this study would provide evidence that THz-TDS could be an alternative for determining water content of engine oil and potentially other oil contaminants.

EQUIPMENT AND PROCEDURES

THZ TIME-DOMAIN SPECTROMETER

The THz time-domain spectrometer (fig. 1) used a Nd:YVO$_4$ frequency doubled laser to optically pump a Ti:sapphire laser with a repetition rate of 80 MHz and a center wavelength of 800 nm. The sub-100 fs pulses emitted by the laser were used to excite charge carriers in pho-
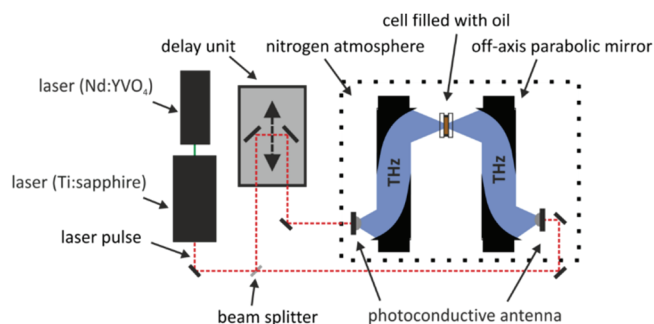

Figure 1. Schematic of THz time-domain spectrometer

toconductive antennas. At the emitter antenna, an electrical field was applied, which accelerated the generated carriers. The accelerated carriers emit an electrical field with frequency components in the range from about 0.3 to 4.5 THz. This THz pulse was detected by a similar photoconductive antenna. The carriers generated by the fs laser pulse were accelerated by the incident THz field. This led to a current that was proportional to the THz field strength. Since the fs pulse was short in comparison to the THz pulse, a delay unit allowed for sampling the THz field. The THz radiation was collimated and focused by off-axis parabolic mirrors. The oil sample was positioned in the intermediate focus between the antennas. Jepsen et al. (2011) provide additional details.

OIL SAMPLE PREPARATION

Three 946 mL containers of Shell Rotella T SAE 15W-40 heavy-duty diesel engine oil rated for API service CJ-4/SM were purchased from a local retailer (Carbondale, Ill.). The 15W-40 grade was selected because it was representative of common multiviscosity oil used in agricultural diesel engines. Each water concentration level was prepared by pouring the contents of the 946 mL container into a blender (model 58130, Proctor-Silex, Inc., Southern Pines, N.C.). Then distilled water was added in the amounts of none, 1 mL, or 2 mL for 0%, 0.1%, or 0.2% water contamination, respectively. These low water levels were selected because levels above 1% may not achieve solubilization in oil (Dobrinski et al., 2007). The 0% water sample served as the control. The lid was secured to the blender jar, and the blender was set at the highest speed setting (17,500 rpm, no load) and operated for 90 s, resulting in a thorough mixing of the water in the oil, or just mixing the oil in the case of the 0% sample, as evidenced by an even distribution of air bubbles throughout the solution. The oil samples were then poured back into the original containers.

Approximately 100 mL of each of the three oil-water samples were poured into a separate amber, round bottle (Qorpak GLC-01935, Fisher Scientific, Pittsburgh, Pa.). The sample bottles were generically coded as T6, T2, and T1 and shipped to the Experimental Semiconductor Physics Laboratory at Phillips University (Marburg, Germany) for THz-TDS analysis. About three months passed before the oil samples were analyzed with THz-TDS. A syringe was used to remove oil from the center of the bottles, without any additional mixing, and inserted into a customized cell. No oil-water separation of the sample was observed, and the samples were assumed to be homogeneous for THz-TDS. While the ratio of water in each subsample used for THz-TDS may not have been equal to the original ratio, this method was used to detect water that was solubilized, rather than water that had separated.

THz TIME-DOMAIN SPECTROSCOPY

Customized cells consisting of two windows of 700 µm thick fused silica plates (Vieweg et al., 2010), which were nearly transparent at THz frequencies, were used to hold the oil samples for THz-TDS. Prior to building the cells, the silica plates were separately subjected to THz-TDS, and multiple reflections were used to determine the material parame-

ters (Scheller et al., 2009). The cell was built by separating the two windows with two copper plates that were 5.9 mm apart. Due to the relatively low absorption of oil samples, these relatively thick cells were chosen to improve the interaction length of the THz radiation. After measurement of one oil sample, the cell was cleaned and the same cell was used for the next sample. The time-domain data were recorded in the THz spectrometer. The material parameters of the oil samples and windows were determined using Teralyzer software (Menlo Systems GmbH, Martinsried, Germany). Teralyzer incorporates the algorithms described by Wilk et al. (2008) and Scheller et al. (2009).

THz-TDS DATA ANALYSIS

For the data analysis, each of the three samples was measured three times. Teralyzer software was used to retrieve the refractive index and absorption coefficient for each measurement. The arithmetic average of the three measurements of each of the three oil-water samples was further analyzed. The mean, standard deviation, and 95% confidence interval of the refractive index and absorption coefficient were calculated for each sample at each frequency and plotted. Analysis of variance (ANOVA) was used to determine if there were significant differences ($\alpha = 0.05$) in the refractive index or absorption coefficient among the samples at each frequency.

Regression analysis was completed on the best potential predictor value (refraction index or absorption coefficient) using data at multiple frequencies (0.5 to 2.0 THz at 0.25 THz intervals) (Zhao et al., 2012a). The linear models were evaluated with the coefficient of determination (R^2) and root mean square error (RMSE). SAS Enterprise Guide 6.1 (SAS Institute, Inc., Cary, N.C.) was used for ANOVA and linear regression analysis.

RESULTS AND DISCUSSION

The THz time-domain spectrometer delivered spectrally resolved data about the refractive index and absorption coefficient in the range from 0.5 to 2.0 THz with a resolution of approximately 5 GHz. These data were used for further analysis.

REFRACTIVE INDEX

The refractive indices for each of the three levels of water contamination in diesel engine oil are shown in figure 2. The curves are distinct from each other with relatively consistent spacing, particularly across the 0.5 to 1.5 THz range. Increased water contamination resulted in an increased refractive index at all frequencies. Across the 0.5 to 1.5 THz range, the refractive index differences between the 0% and 0.1% water contamination samples ranged from 0.0006 to 0.0008 with a mean of 0.0007. Across the same range between the 0.1% and 0.2% samples, the refractive index ranged from 0.0003 to 0.0007 with a mean of 0.0006. The 95% confidence intervals generally increased slightly with higher water contamination. For all three curves, the confidence interval generally increased slightly at higher frequencies. This is a consequence of the lower signal-to-
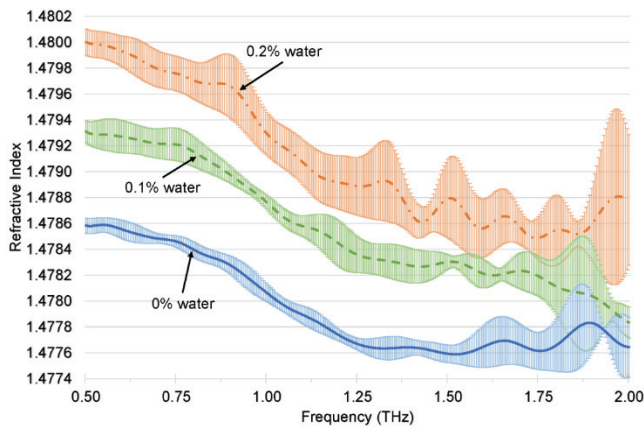
Figure 2. Mean refractive index (*n* = 3) of diesel engine oil samples with three levels of water contamination with 95% confidence intervals.

noise ratio of the spectrometer for higher frequencies. The refractive indices at 1.0 THz for 0%, 0.1%, and 0.2% water contamination were 1.4781, 1.4788, and 1.4793, respectively, with standard deviations of 0.00006, 0.00004, and 0.00015, respectively. Across the 0.5 to 1.5 THz range, the standard deviation among the replications for each of the 0%, 0.1%, and 0.2% water contamination samples peaked at 0.00008, 0.00016, and 0.00027, respectively.

The curve patterns of refractive index indicate good repeatability among the same samples and distinct differences among the water levels for all but the highest of the THz range measured. ANOVA results confirmed a significant difference ($p < 0.05$) in refractive index among each of the three water contamination levels across the 0.5 to 1.5 THz range ($p < 0.01$ across 0.5 to 1.1 THz range). At each frequency, the refractive index of a water contamination level was significantly different from the other two. In all cases, the refractive index of 0% water was the lowest and 0.2% water was the highest.

The differences in the refractive indices of these water contamination levels were promising for identification and distinction of water contamination levels in 15W-40 diesel engine oil. The overall refractive indices were in good agreement with a study of polyglycol oils with water levels ranging from 0.43% to 3.28% (Gorenflo et al., 2006), in that higher water concentrations resulted in higher refractive indices with relatively distinct, equidistant curves. Most studies of oils have resulted in refractive indices that decrease as frequency increases. Examples of refractive indices decreasing across the 0.5 to 1.5 THz range are polyglycol oils by about 0.04 (Gorenflo et al., 2006), four vegetable oils by about 0.02 (Li, 2010), and five plant oils by 0.01 to 0.035 (Ying et al., 2005). Conversely, a gasoline engine oil of service category SF but unreported grade had a refractive index curve that increased by about 0.025 over the range of 0.5 to 1.6 THz (Tian et al., 2009). Although figure 2 appears to show a descending trend with increasing frequency, this is more a function of the *y*-axis scale. The refractive index curve of 0.2% water contamination in the range 0.5 to 1.5 THz had the highest difference between minimum and maximum values of the three water levels, and it was only 0.0014, which is relatively flat compared to

most studies. A recent study of three gasoline engine oils found even flatter curves, with refractive indices decreasing by only 0.0002 to 0.0005 across the same range (Abdul-Munaim et al., 2015). The study of three gasoline oils used the same THz spectrometer as the current study.

Refractive indices among studies are commonly compared at 1.0 THz. In this study, the values were 1.4781 to 1.4793, with 0% water having the lowest value and 0.2% water having the highest value. These values were higher than the values of 1.240 to 1.375 for three grades of diesel fuel (Zhao et al., 2012c) and 1.455 (Jin et al., 2008) or 1.465 (Arik et al., 2014a) for a single grade of diesel fuel, but they were lower than 1.48 to 1.49 for four vegetable oils (Li, 2010) and 1.475 to 1.62 for five plant oils (Ying et al., 2005). The differences between the refractive indices of diesel engine oil and diesel fuel indicate potential to differentiate concentrations of diesel fuel in diesel engine oil. The refractive index of soybean oil at 1.0 THz of about 1.485 (Li, 2010) is higher than that of diesel engine oil, indicating potential for THz to distinguish soybean oil contamination of diesel engine oil.

The general trend of increased refractive index for higher levels of water contamination can be explained as follows. Pure water has a considerably higher refractive index than oil (2.2 at 1 THz per Hirori et al., 2004). What can be seen in figure 2 is the transition from pure oil to an oil-water mixture, which has a higher refractive index.

ABSORPTION COEFFICIENT

The THz-TDS results for the absorption coefficients of the three levels of water in diesel engine oil are shown in figure 3. The three curves exhibit similar patterns, with increased water contamination resulting in higher absorption coefficients. The absorption coefficient ranged from 0.4 to 3.3 across the 0.5 to 2.0 THz range. The 95% confidence intervals generally increased with frequency. The curve patterns indicate good repeatability among the same samples and differences among the water contamination levels, except for 0% and 0.1% water at lower frequencies. ANOVA results confirmed a significant difference ($p < 0.05$) in absorption coefficient among each of the three
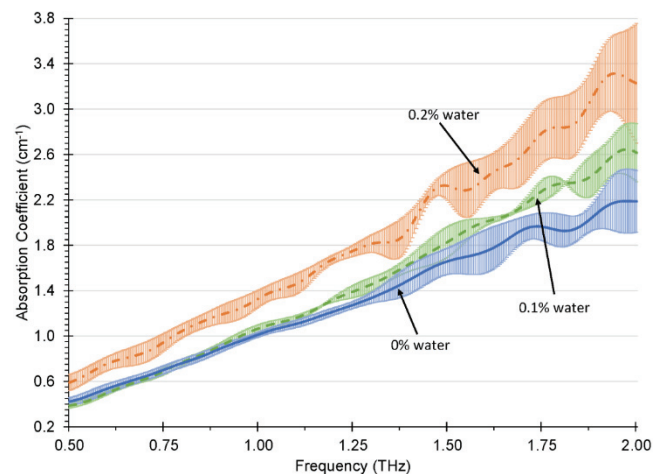

Figure 3. Mean absorption coefficient (*n* = 3) of diesel engine oil samples with three levels of water contamination with 95% confidence intervals.

water contamination levels across the 1.111 to 1.332 THz and 1.669 to 1.934 THz ranges ($p < 0.01$ across the 1.165 to 1.224 THz range). In each of these frequency ranges, each water contamination level was significantly different from the other two. The 0% water contamination level had the lowest absorption coefficient, while 0.2% water had the highest absorption coefficient. The 0.2% sample was significantly different ($p < 0.05$) from the 0% and 0.1% samples across the entire range of 0.5 to 1.96 THz.

Compared to the refractive index, water contamination level had a lesser effect on THz absorption (Abdul-Munaim et al., 2015; Naftaly et al., 2005). The absorption coefficients demonstrated potential for identification and discrimination of water contamination levels of diesel engine oil, particularly at the higher contamination level. The pattern of increasing absorption coefficient with increasing frequency was consistent with studies of other oils, such as transmission fluid (Gorenflo et al., 2006), gasoline engine oil of SF service category (Tian et al., 2009), vegetable oils (Hu et al., 2005) (Li, 2010), and three gasoline engine oil grades (Abdul-Munaim et al., 2015).

As discussed for the refractive index, the absorption coefficient of water is also higher than that of oil (200 cm^{-1} at 1 THz per Hirori et al., 2004). This leads to a higher absorption coefficient for oil-water mixtures.

PREDICTING WATER CONTAMINATION LEVEL

The refractive indices (fig. 2) were of more interest for predicting water contamination level than the absorption coefficients (fig. 3). Seven frequencies (0.5 to 2.0 THz at 0.25 THz intervals) were selected for linear regression analysis. Each of the seven models with intercept and coefficient was highly significant ($p < 0.01$). The R^2 values ranged from 0.99 to 0.71 and decreased with increased THz frequency. Similarly, RMSE increased with THz frequency from 0.01 to 0.05. The refractive indices at 0.5 THz (fig. 4) resulted in the best fit, with $R^2 = 0.99$ and RMSE = 0.01. The resulting linear equation was:

Water contamination (%) =

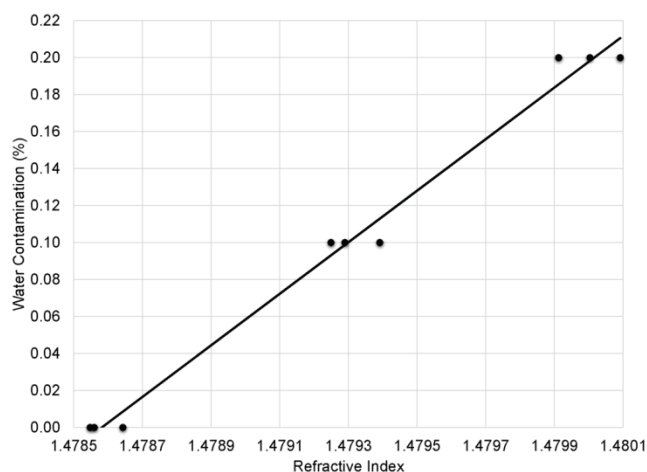$$-206.21 + 139.47(\text{refractive index}) \qquad (1)$$

Figure 4. Refractive indices (round markers) ($n = 9$) and predicted water contamination (%) based on linear regression of refractive indices at 0.5 THz ($R^2 = 0.99$, RMSE = 0.01).

The relatively consistent differences in refractive indices across the 0.5 to 2.0 THz range for the three water contamination levels and the increased refractive index as water contamination increased (fig. 2) resulted in a strong positive linear relationship for refractive index to predict water contamination. The consistent separation among refractive indices at 0.5 THz resulted in the best linear model.

This study assumed that the water distribution within the oil was homogeneous and consistent during the study. This may not have been the case, as the level of water within the samples for THz-TDS may not have been equivalent to the water in the initially prepared samples. Even with this limitation, THz-TDS demonstrated potential for discriminating among water contamination levels of SAE 15W-40 diesel engine oil. THz-TDS should be considered for additional research regarding discrimination of engine oil contaminants.

CONCLUSIONS

Diesel engine oil samples (SAE 15W-40) were contaminated with different levels (0%, 0.1%, and 0.2%) of distilled water. The samples were examined by THz-TDS to determine if they could be discriminated based on water contamination level. The refractive index increased with water contamination level and was a strong indicator of water contamination. The refractive index curves were similar to those of other studies but relatively flatter across the 0.5 to 2.0 THz range. ANOVA results confirmed a significant difference ($p < 0.05$) in refractive index among each of the three water contamination levels across the 0.5 to 1.5 THz range ($p < 0.01$ across 0.5 to 1.1 THz range). In this frequency range, the refractive index of each water contamination level was significantly different from the others. In all cases, the refractive index of 0% water was the lowest and 0.2% water was the highest.

The absorption coefficient increased with increased water contamination and frequency and was similar to those of other studies of oils. The absorption coefficient provided potential for discriminating water contamination levels, as significant differences existed among the three water contamination levels across the 1.111 to 1.332 THz and 1.669 to 1.934 THz ranges ($p < 0.01$ across the 1.165 to 1.224 THz range). In each of these frequency ranges, each water contamination level was significantly different from the other two. The 0% water had the lowest absorption coefficient, while 0.2% water had the highest absorption coefficient.

Linear regression analysis of the refractive index as a predictor of water contamination level yielded a highly significant equation ($p < 0.0001$, $R^2 = 0.99$, RMSE = 0.01) when using the refractive indices at 0.5 THz. The regression lines for higher THz frequencies were similar, but with reduced R^2 and increased RMSE.

THz spectroscopy is a new technology for potential application to oil condition analysis. The results of this study are promising for discrimination of water contamination of engine oil. Additional work should be completed with a range of engine oil ages and contaminants to further investigate the potential of THz for oil condition analysis.

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