INVESTIGATION OF PROPERTIES OF DIESEL WATER MIXTURES WITH AND WITHOUT EMULSIFIER BY TERAHERTZ SPECTROSCOPY

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ZÜHRA ÇINAR

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Approval of the thesis:

INVESTIGATION OF PROPERTIES OF DIESEL WATER MIXTURES WITH AND WITHOUT EMULSIFIER BY TERAHERTZ SPECTROSCOPY

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ABSTRACT

INVESTIGATION OF PROPERTIES OF DIESEL WATER MIXTURES WITH AND WITHOUT EMULSIFIER BY TERAHERTZ SPECTROSCOPY

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Additives such as alcohol, water are used in petroleum products for different purposes. Aim of the thesis is to determine water content in diesel water mixtures in THz region. The samples with and without emulsifier were analyzed in THz region. Besides, different kinds of oils (olive oil, sunflower oil, frying oil and engine grease #10) were measured in THz region because mixed of oils can be used instead of regular diesel. For this reason, we aimed to show distinguishability of regular diesel and mixed fuel. Then, FTIR spectrum of all diesel water mixtures and oils were collected in order to compare THz results. Meaningful results were obtained for diesel water mixtures by using both techniques. It has been shown that THz-TDS and FTIR are complementary techniques. However, FTIR was not a suitable technique for oils measurements because no marker could be seen to distinguish oils. On the other hand, THz-TDS was an effective technique because it enabled us to calculate refractive indexes of oils. When oils' refractive indexes were compared, the differences between them could be seen clearly. These results gave a hint to us about distinguishability of diesel and mixed fuel by THz-TDS.

Keywords: Terahertz, Terahertz Time Domain Spectroscopy, Fuel Oil Additives, Diesel Water Emulsions

ÖZ

EMÜLGATÖR İÇEREN VE İÇERMEYEN DİZEL SU KARIŞIMLARININ ÖZELLİKLERİNİN TERAHERTZ SPEKTROSKOPİ İLE İNCELENMESİ

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Tez Yöneticisi: Doç. Dr. Okan Esenturk
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Alkol, su gibi katkı maddeleri petrol ürünlerinde farklı amaçlar için kullanılmaktadır. Bu tezde, dizel su karışımları içinde bulunan su mikatarının Terahertz bölgesinde belirlenmesi amaçlanmıştır. Örnekler emülgatörlü ve emülgatörsüz iki farklı şekilde THz bölgesinde incelenmiştir. Bunun yanısıra, farklı türde yağlar (zeytin yağı, ayçiçek yağı, kızartma yağı ve motor yağı) THz bölgesinde ölçülmüştür çünkü yağların karışımı normal dizel yerine kullanılabilmektedir. Bu nedenle, normal dizel ve karışım olan yakıtın ayrıt edilebilirliğini göstermek amaçlanmıştır. Daha sonra, hem dizel su karışımlarının hem de yağların FTIR spektrumları THz sonuçları ile karşılaştırmak amacıyla toplanmıştır. Dizel su karışımları için her iki tekniği de kullanarak anlamlı sonuçlar elde edilmiştir. THz-TDS ve FTIR'ın birbirini tamamlayan teknikler olduğu gösterilmiştir. Ancak, FTIR yağ ölçümleri için uygun bir teknik olmadığı gösterilmiştir çünkü yağları ayırt edebilmemizi sağlayacak herhangi bir işaret görülmemiştir. Öte yandan, THz-TDS yağları ayırt edebilmek için etkili bir yöntem olduğu gösterilmiştir çünkü THz-TDS yağların kırılma indisini hesaplamamıza imkan sağlamıştır. Yağların kırılma indisini karşılaştırıldığında da, yağlar arasındaki fark açık bir şekilde görülmüştür. Bu sonuçlar bize THz-TDS kullanarak karışım olan yakıt ile normal dizelin ayırtedilebilirliği hakkında ipucu vermiştir.

Anahtar kelimeler: Terahertz, Zamana Dayalı Terahertz Spekroskopi, Akaryakıt katkı maddeleri, Dizel Su Emüsyonları

To my lovely sister Serap Berivan

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LIST OF SYMBOLS AND ABBREVIATIONS

THz : Terahertz
THz-TDS : Terahertz Time Domain Spectroscopy
FTIR : Fourier Transform Infrared Spectroscopy
PCA : Photoconductive Antenna
iPCA : Interdigitated Photoconductive Antenna
SNR : Signal-to-noise ratio
DR : Dynamic range
Ti:Sapphire : Titanium Sapphire
GaAs : Gallium Arsenide
ZnTe : Zinc Telluride
FFT : Fast Fourier Transform
fs : Femtosecond
OAPM : Off-axis parabolic mirror
eV : Electronvolt
mW ; Milliwatt
ms : Millisecond
dB : Decibel
GaAs : Gallium Arsenide
TPX : Polymethylpentene

CHAPTER 1

INTRODUCTION

Petroleum products are still main energy sources of world although there are many alternative energy sources such as bioenergy and solar energy. However, as it is known petroleum reserves are running out day by day so it is necessary to use existing sources as efficiently as possible in addition to finding alternative energy sources. Thus, studies on petroleum products are still a hot topic in scientific world. Addition of water to diesel is one of such solutions to reduce the consumption of fuel oil while not losing from overall efficiency. Moreover, it decreases price of diesel per gallon which is the driving economic force. However, addition of water to diesel should be controlled because it can damage vehicles' engines in the long run. There are numerous ways by which water can be combined with diesel. Two most common ways are i) mixing at the engine and ii) premixing in the fuel with emulsifier. Addition of water to diesel with emulsifier is a common and preferred method because it can be stored and used directly with the existing infrastructure and the current diesel engines without a need for modification. In addition it is environmentally friendly because diesel water mixtures containing emulsifier decreases emission of dangerous gases such as NO_x. However, determination of water amount in mixtures with or without emulsifier is important point since the excess amount of water can cause damage. It is also important to control whether mixtures contain water at the stated amount. Therefore, study on determination of water amount in diesel by Terahertz spectroscopy was carried out in this thesis. In addition to water addition, mixture of diesel and lubricating oil, hydraulic oil, waste oil or raw oil are also preferred instead of regular diesel. However, production of this kind of fuel should be under control. Currently there are regulations; however, the control is very limited. Uncontrolled use would be dangerous for not only health but also to the environment. Therefore, distinguishing diesel and diesel mixture with oils is important. Possibility of use of THz spectroscopy on differentiation of various oil types was also studied. In this thesis, the applicability of FTIR and time domain terahertz spectroscopy (THz-TDS) for determination of the water content of diesel in water diesel mixtures with or without emulsifiers for observation of their strength in distinguishing diesel with oil mixtures were tested.

1.1 THz Radiation

The electromagnetic (EM) spectrum includes all types of EM radiation and terahertz (THz) is located between the microwave and infrared as shown in **Figure 1**. Tera is prefix which connotes 10^{12} Hz and Hertz is SI unit of frequency (s^{-1}). Therefore, 1 THz equals to 10^{12} Hz. In terms of units, 1 THz corresponds to 33.33 cm^{-1} wavenumber, 4.1 meV photon energy, 300 μm wavelength, 48 K temperature.

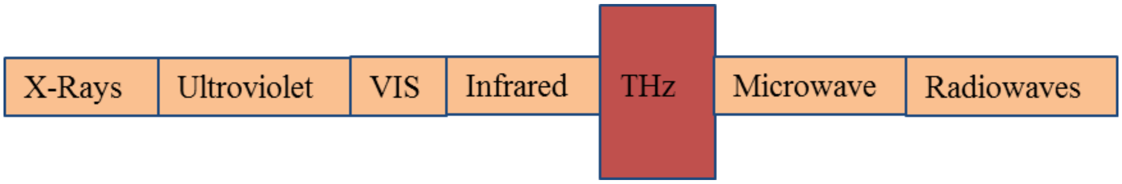


Figure 1. Electromagnetic spectrum

In the 1960s, although the advantages of terahertz radiation were known by scientists, it was not used commonly because there were no such suitable sources and detectors working in this range. THz radiation was begun to use more frequently in 1970s. In the following years, nonlinear crystals were used to generate THz beam. Dan Grischkowsky, David Auston, and Martin Nuss generated and detected THz beam.[1] The first terahertz time domain spectrometer was built by Auston and Cheung in 1985.[2] In 1988, THz wave generation and detection via photoconductive antenna (PCA) was done successfully by Smith, Auston and Nuss.[3] Terahertz technology has become popular and widespread all over the world thanks to studies carried out by many scientists. Currently, it finds application in many areas such as security screening, medical imaging, quality control and petroleum industry.

1.2 THz Generation Techniques

There are two main techniques to generate THz radiation; nonlinear optical process and photo conductive antenna (PCA) generation. PCA is the oldest method in these two techniques for the THz generation.[4] In a PCA, antenna is made up of two metal electrodes coated by semiconductor substrate. There is a micrometer size gap between these two electrodes. A connected bias voltage is applied to the two electrodes and then charge carriers are generated.[5] The carriers move on the same direction and accelerate with bias voltage.[4] With the acceleration of carriers electromagnetic radiation is emitted in THz range.

In spite of the fact that nonlinear optical process is not as efficient as PCA in producing THz, it is more common technique than PCA. In this method, nonlinear crystals such as ZnTe, GaAs or GaP are used to generate THz.

1.3 THz Detection Techniques

PCA and free space electro optic (EO) sampling are two main techniques to detect THz radiation. The detection of THz by using a PCA is basically similar to generation of THz. The semiconductor is excited by a laser pulse and then charge carriers are generated. Here, THz radiation is used to accelerate charge carriers instead of bias voltage. Acceleration of carriers results in current generation and the current overtime is detected by lock-in amplifier.

Another common method is electro optic sampling (EO) for detection of THz. In this method, generated THz beam and probe beam are focused on a nonlinear crystal at the same time.[6] When THz beam hits crystal, birefringence occurs on the crystal. Then, the polarization of probe beam is changed by the birefringence. Finally, it is possible to detect the change in polarization of probe beam by using the balance photodiode detector with the help of Wollaston prism and quarter waveplate.[7]

1.4 Application of THz Wave

Since 1965, studies on the generation and detection of THz waves have drawn attention with the spread of lasers. With the development of mode-lock lasers, the THz technique has kept developing and become available in many areas. THz Spectroscopy gives extensive information about physical and chemical properties of the materials.[8,9]

Molecular spectroscopy of gases[10], liquids[11,12], isomers[13–17], and biological samples such as DNA and protein can be studied at THz frequencies of 0.1-3.0 THz. THz rays have very low energy compared to IR, NIR or visible region and do not heat or ionize the sample. Therefore, they present an opportunity to do analysis safely and without harming the sample.[18] They can be also used in detecting explosive detection[12,19,20], quality control, and drug analysis[21] due to their low energy. In addition, THz technology is used in astronomy[22] and communication[23].

Several common techniques that are in use to distinguish petroleum products and their additives are GC, X-ray florescence and UV-florescence spectroscopy. Recently, Terahertz Spectroscopy is also being developed to characterize and distinguish petroleum and petroleum products. When it is compared to other common techniques such as visible, UV and x-ray, it is cost-efficient, reproducible, safe, nondestructive and time-efficient.[9] Also, THz-TDS gives an opportunity to determine absorption coefficient and refractive index of a sample at the same time. Obtaining of absorption coefficient and refractive index at the same time makes it more sensitive than other techniques. For this reason, studies about petroleum products with THz spectroscopy are increasing day by day. Qin et al. had shown that amount of sulfur in gasoline can be determined accurately by THz-TDS.[9] In 2006, Al-Douseri et al. showed the potential application of THz and Far-IR on petroleum products.[24] They calculated the frequency-dependent absorption coefficients, refractive indices, and complex dielectric constants of gasoline and xylene isomers in the spectral range from 0.5 – 3.0 THz. Also, their research group reported the THz spectra of gasoline (#87, #89, #93) and related BTEX (benzene, toluene, ethylbenzene, and xylene) compounds by using FTIR in the 1.5-20 THz. In similar studies carried out by Jin et al. and Kim et al., petroleum products (gasoline, diesel, kerosene etc.) and their mixtures with organic solvents (xylene, toluene, benzene etc.) were analyzed in the THz region where refractive index and absorption coefficient of these samples were determined.[25,26] Jin's study also demonstrated that refractive index of mixtures can be found from arithmetic mean of pure substances.[25] Cetane number (CN) and solidifying point (SP) are two important parameters for diesel and expensive techniques are needed to determine these parameters. Zhao et al. had shown that CN and SP can be determined by using THz spectroscopy.[27] In addition to diesel and gasoline, THz spectroscopy is used for detection of CH_4, C_2H_6, C_3H_8, CO_2 and mixture of CO and CO_2 in natural gas.[28] Adbul-Munaim et al. used THz spectroscopy to distinguish gasoline engine oils of different viscosities. Amount of zinc isopropyl-isooctyl-dithiophosphate (T204) used as additive was determined successfully by using THz spectroscopy, too. [29,30] Addition to these, in a study carried out by Jin et al. Cenox known as illegal diesel which is mixture of thinner, toluene, and methanol was analyzed by using THz spectroscopy. At the end of their study, difference between Cenox and diesel was clearly revealed.[25]

Petroleum products continue to be one of the world's main energy sources, although many other energy sources, including alternative energy sources, have become more available.[31] In petroleum products, additives are used for several purposes. It was observed that some fuel additives enhance fire performance of fuel and decrease emission.[32,33] Alcohols such as ethanol or butanol, ethers are also used as oxygenated fuel additives.[32] Amount of additives allowed in petroleum products can change by depending on a country. Corsetti et al. characterized gasoline with ethanol as additive by using IR spectroscopy.[34] In another study, Conklin et al. firstly dissolved ethanol in hexane at various ratios and then plotted a calibration curve by using these mixtures to determine amount of ethanol in gasoline.[35] In addition to these ethanol studies, a study by Enis et al. on determination of ethanol content in gasoline was carried out in our research group.[36] THz-TDS was used to measure dielectric properties of pure gasoline, ethanol and their 5-50% (v/v) mixtures. The samples have been differentiated with one percent sensitivity. Li et al. determined octane grades in gasoline using terahertz metametarials.[37] The spectral analysis of number of oils, including lubricants, gasoline and diesel, with different additives were done by Zhan et al by THz spectroscopy.[38] Optical properties of different kind of lubricating oils were analyzed by Tian et al. in terahertz range.[39] Juisheng et al. showed that different kind of vegetable oils can be distinguished by using terahertz spectroscopy.[40] Optical properties of gasoline and diesel were reported by Enis et al. by a study carried in our research group.[18] Mixtures of gasoline and diesel were also investigated by Li et al. and this study showed that there is a linear relationship between absorption coefficient and amount of gasoline.[41]

1.5 Aim of Study

Additives are used in petroleum products for different purposes. Primary purpose of additives is lowering the price of fuel per gallon while secondary purpose is decreasing emission of harmful gases and increasing engine performance.[42] Petroleum companies use ethanol, butanol and other oxygenated compounds as additives. Recent studies have shown that emulsified water can be an additive for diesel to enhance engine performance and decrease NO_x emissions while lowering combustion temperature.[43,44] Alahmer et al. showed that 5% (v/v) water concentration in diesel is the best for maximum break power. They have also shown that 30% water concentration can be comparable with 5 % water concentration.[45] Zaid et al. found that 20% water concentration gives optimum engine performance in their study.[46] In studies carried out by Park et al. and Henningsen et al., they showed that emulsion diesel fuel has a positive effect on NO_x emission. Park et al. found that 20% water concentration reduces NO_x emission by 20% [47]while Henningsen et al. found that 25% water concentration reduces NO_x emission by 30%[48]. However, studies have shown that uncontrolled addition of water can affect engine performance and emissions negatively. In addition to emulsified water addition, water can be added in diesel directly in order to decrease price of diesel. Until 0.1% (v/v) can be acceptable amount of water in diesel.[49] However, higher water amount in diesel can cause corrosion on engine, blockage of injection system, and microbial growth so water addition without emulsifier should be controlled as well.[42] Therefore, controlled addition of water and its detection in diesel with or without emulsifier are important. In this study, we present a study on detection of water amount in diesel with or without emulsifier by Terahertz spectroscopy. The same samples were also measured by FTIR in order to compare with THz results.

In addition to water diesel mixtures study, we also collected spectra for different kinds of oil (olive oil, sunflower oil, fried oil and engine grease #10). Diesel is mixed with lubricating oil, hydraulic oil, waste oil and raw oil and this mixed oil is also used instead of regular diesel. Production of this kind of fuel should be controlled. Although it is dangerous, consumers prefer this mixed fuel because of its very low price. Uncontrolled production causes evasion of taxes. Burning of it causes emission of sulfur and heavy metal to air because it contains waste oils. Therefore, it causes environmental pollution and also these gases are dangerous for not only human but also environment. Unfortunately, it is difficult and time consuming to distinguish diesel and this mixed fuel by using common techniques including FTIR. Our purpose is to present a preparatory work to distinguish diesel and mixed fuel. In this thesis, we showed that oils can be differentiated by using THz-TDS.

CHAPTER 2

EXPERIMENTAL

2.1 THz Time Domain Spectrometer

In this study, Terahertz Time-Domain Spectrometer located in Laser Spectroscopy Group at Chemistry Department at Middle East Technical University was used. Components of setup are listed in **Table 1**.

Table 1. Components of THz-TDS setup

Item	**Manufacturer**	**Model**
Ti.Sapphire Mode-locked laser	Coherent	Mantis-5
iPCA antenna	BATOP	iPCA-21-05-1000-800-h
Wollaston prism	Thorlabs	WP10
PCA antenna	BATOP	PCA-40-05-10-800-h-l
ZnTe crystal	MTI corp	
Quarter wave plate	Thorlabs	WPQ10M-808
OAPMs		
Dielectric mirrors	Thorlabs	BB1-E03
Beam splitter	Thorlabs	BSF10-B
Lenses	Thorlabs	LA1908-B and LA1172-B
TPX plate		
Large Area Balanced photodiode	Thorlabs	PDB-210-A
Function generator	HM8030-6	HM8030-6
Motorised microstage and its controller	Standa	8MT167-100 and 8SMC1-USBHBHF-B2-2MC)
Voltage amplifier	BATOP	
Oscilloscope	Tectronix	DPO2014
Lock-in Amplifier	Stanford Research Systems	45347A
Multifunction Data Acquisition	National Instruments	NI USB 6251 and USB X SERIES 6361

The setup used in this study is schematized in **Figure 2**. Ti-Saphire mode locked laser is used as a source. Generated Laser pulses are guided towards beam splitter (1) with the help of plane mirrors. Laser pulses are divided into two by beam splitter (1) in a ratio of 90 to 10. Laser pulses with the higher power generation arm are used to generate THz beam and the other one is used for detection of THz beam. Generated THz beam is guided and focused to sample with help of parabolic mirrors (4). Then THz beam that is passed through a sample is focused to a ZnTe crystal (7) for detection, also the detection arm is guided to the same ZnTe crystal by a TPX beam combiner (6). Delay stage is used to obtain THz profile in time domain. This stage changes the gating time of laser pulse used for detection and THz pulse coming from sample. THz profile in time domain is recorded by using quarter waveplate (8), Wollaston prism (9), lockin amplifier, and balanced photodiode (10).

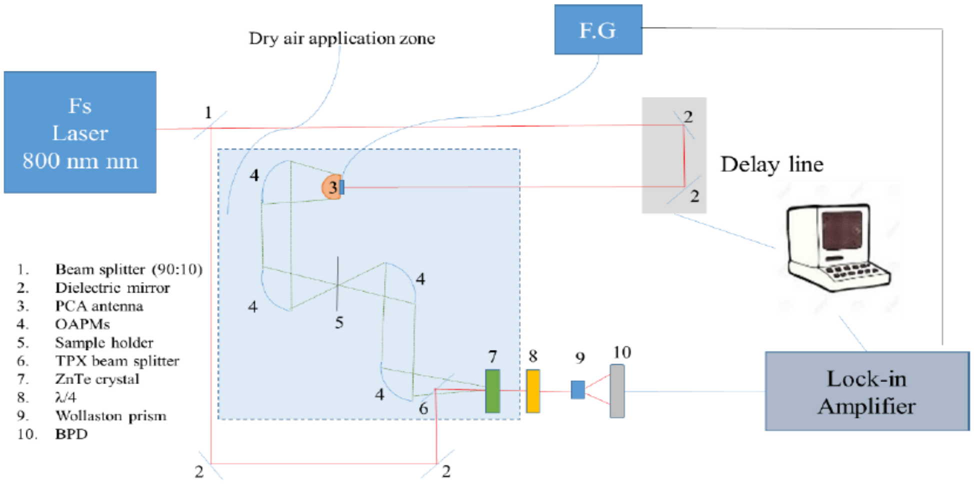


Figure 2. THz-TDS system in our laboratory[50]

2.3 General Information on Main Components of the System and Their Properties

2.3.1 Laser Source

In this thesis, optical source is a Ti-Saphire mode locked laser for THz-TDS. These kinds of lasers are usually preferred for ultrafast studies because they can be tuned easily and it is suitable to generate ulta-short pulses. In Ti-Sapphire laser Ti^{3+} ions dope the lasing medium of sapphire crystal (Al_2O_3). A source green laser light pumps this crystal with 5.5 W pump power at 532 nm wavelength. Green light is absorbed by Ti-sapphire crystal to produce red light having a center wavelength about 800nm. After beam is mode-locked, 80 fs pulses with 600 mW average power at 80 MHz repetition rate are obtained.

This laser system is very sensitive to temperature and humidity so these parameters should be kept stable. For this reason, temperature and humidity should be under control and recorded regularly. In order to control these parameters an air conditioning system and a chiller are used.

2.3.2 THz Generation via Interdigitated Photoconductive Antenna (iPCA)

iPCA antenna contains GaAs semi-conductor chip and Au electrodes deposited on this semi-conductor as it is schematized in **Figure 3**. In iPCA antenna there are more than one antenna gap formed by finger electrodes lie on the antenna chip. The gap between the electrodes is 5 μm in width. Laser beam is focused on the gap by a lens. Electron carriers are excited by laser beam. After excitation process carriers are accelerated by bias voltage of 15V in this study.

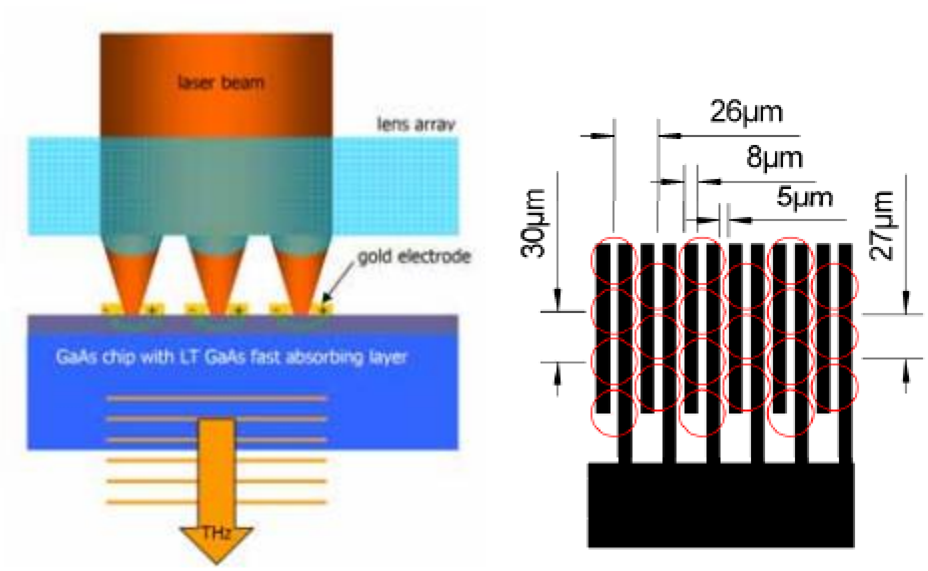


Figure 3. iPCA antenna[51]

2.3.3 THz Detection via Electro-Optic Sampling

In this thesis, THz radiation is detected via electro-optic sampling. The THz beam coming from sample and the probe beam are focused on <110> ZnTe crystal at the same time. This kind of nonlinear crystal possesses birefringence properties under THz field. Birefringence results in a change in polarization of probe beam under THz field. Polarization change of probe beam is detected by a balance photodiode detector with the help of quarter waveplate and Wollaston prism. Then THz waveform in time domain is obtained as shown in **Figure 4a** as the delay between THz and probe beam are changed.

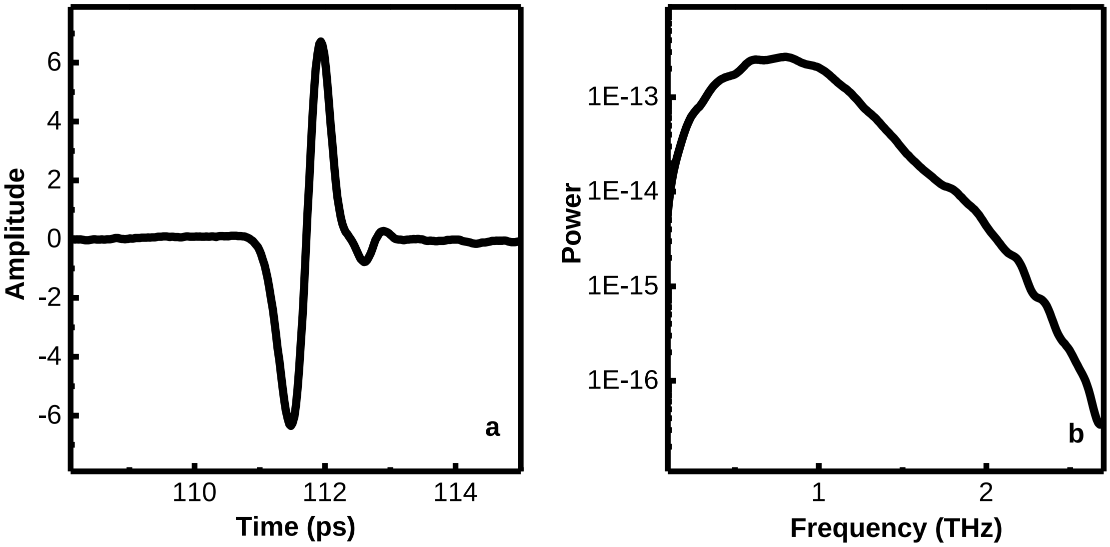


Figure 4. Typical a) time and b) frequency domain waveform

2.4 Sample Preparation

In this thesis, our samples were diesel-water mixtures and four different kinds of oils (sunflower oil, olive oil, fried oil and engine grease #10). Diesel was received from METU Petroleum Research Center. Oils were obtained commercially. Diesel-water mixtures were prepared by distilled water. Sorbitan monoolate (Span80) and polyoxyethylene (20) sorbitan monooleate (Tween80) were used as emulsifiers in diesel water mixtures to disperse water in diesel much better and they were obtained from Sigma Aldrich, Germany. Their properties are given in **Table 2**. Also, chemical structure of surfactant are given in **Figure 5**.

Table 2. Properties of surfactants

Surfactant	Physical State	Density (g/mL at 25 °C)	Molecular Formula	Formula Weight	Hydrophilic Lipophilic Balance (HLB)
Span 80	Liquid	0.994	$C_{24}H_{44}O_6$	428	4.3
Tween 80	Liquid	1.08	$C_{24}H_{44}O_6$	1309.63	15

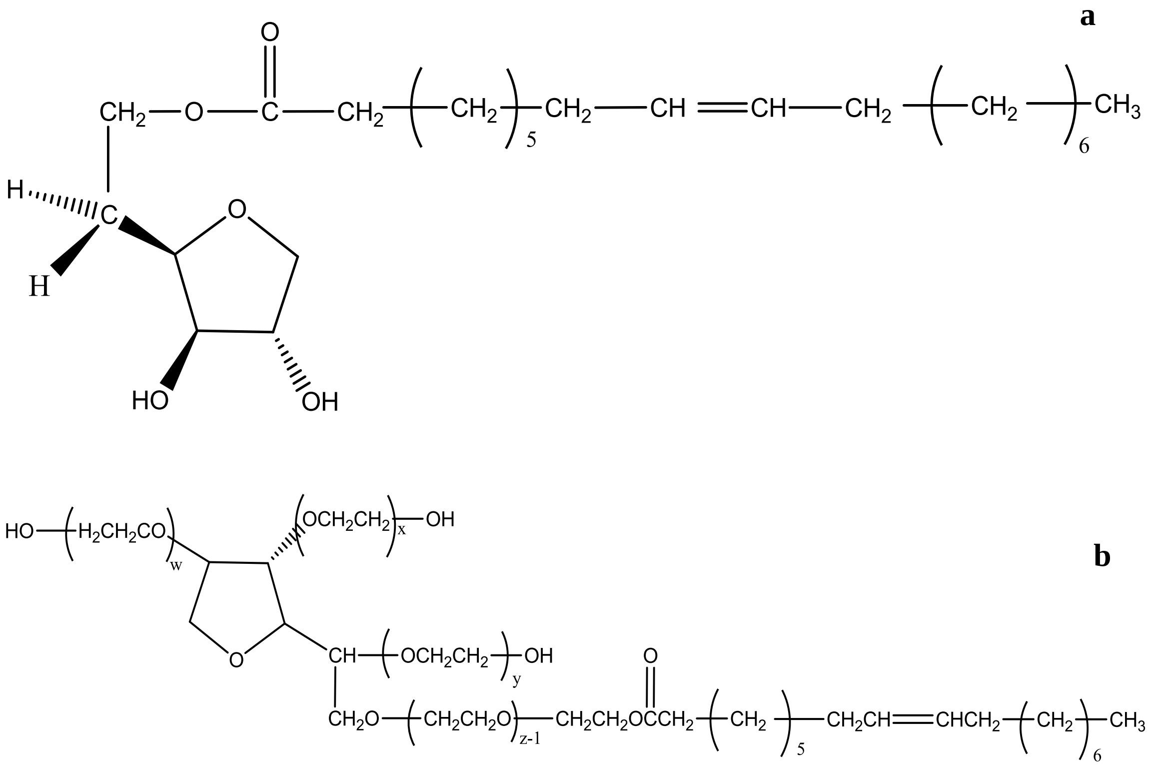


Figure 5. Chemical structure of a) Span 80 b) Tween 80

Firstly, 0.01%, 0.02%, 0.03%, 0.04%, 0.05%, 0.1%, 0.2%, 0.3%, 0.5% (v/v) diesel water mixtures without emulsifier were prepared and their spectra were measured by THz-TDS and FTIR. The same samples were also prepared with emulsifier. The same amount of Span80 and Tween80 were mixed and mixture of emulsifier was added to diesel water mixtures as 5% (w/w). The reason of using two different emulsifiers is that while Span 80 is soluble in oil and Tween 80 is soluble in water so mixture gives perfect emulsion.[52] Then, water diesel mixtures were prepared at higher concentrations (1%, 2%, 5%, 10%, 15%, 20%, and 25% (v/v)) with the same amount of emulsifier. Before measurements, samples without emulsifiers were sonicated for 10 minutes to disperse water in diesel as much as possible. Samples with emulsifiers were stirred for 15 minutes to disperse water in diesel before each measurement, too.

2.5 Data Collection

Unfortunately, direct detection of THz beam is not possible in our laboratory. Therefore, we need to detect change in polarization of probe beam to obtain THz profile in time domain as it was explained in part of working principle of the system. For this purpose, a balanced photodiode, quarter waveplate, Wollaston prism and lock-in amplifier are used to detect change in polarization. Locking amplifier is connected to balanced photodiode and a function generator. Labview is used as software to control the system and collect the data. In this software, there are two options which are continuous and step scan to control traveling stage. In this thesis, continuous scan mode was preferred because of its advantages. In continuous scan mode, the translational stage of the optical set-up moves between the initial set position and final set position continuously with a certain velocity without stopping. Data are collected with defined window range and velocity of microstep stage. The number of points, settings of lock-in amplifier, and total number of data points in the scan window are dependent to each other. Time constant of lock-in amplifier and total number of data points restrict the number of points. In step scan mode, the stage travels in steps with certain step sizes and stops for a time determined previously to collect data at each step point. In previous study carried out our research group, continuous scan mode and step scan mode were compared.[50] It was observed that continuous scan mode is more practical than step scan. It resulted with similar resolution and signal to noise level in a much shorter time**.** Information received from balance photodiode transferred to Labview software by lock-in amplifier, and THz profile in time domain is obtained. Our scan settings are 13 ps total window with 512 data points. The lock-in amplifier was set on 100 μV sensitivity setting, 100 ms at 24 dB time constant, 500 μV sensitivity, normal reserve setting, and 2x line filters.

At the beginning of the study, various lock-in settings were tested and the one with best the signal to noise was chosen. TPX windows are used for liquid cell. After some time, it was noticed that diesel diffuses into TPX windows and they were changed to Teflon windows. By using this system, time domain data of reference and samples were obtained. Sample and reference cause a change in THz pulse as shown in Hata! Başvuru kaynağı bulunamadı..

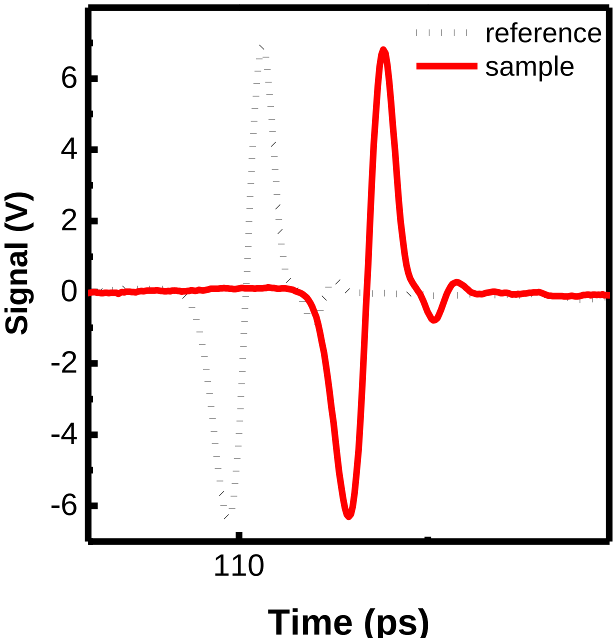


Figure 6. Time domain THz waveform of reference and sample

2.6 Data Analysis and Calculations

Data obtained from THz-TDS are in time domain and Fast Fourier Transform (FFT) of the time domain data converts to frequency domain. Time domain waveforms and their corresponding frequency domain data are given in **Figure 7** as an example.

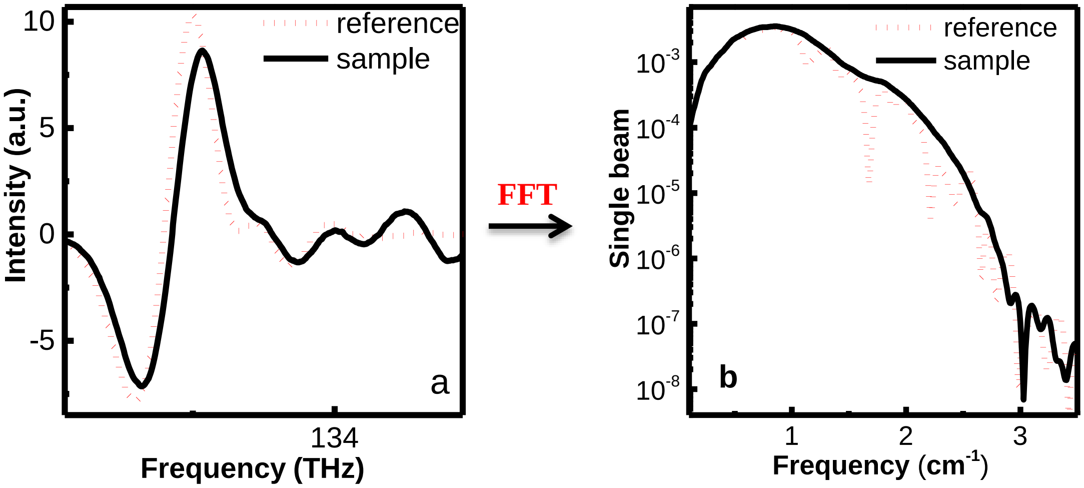
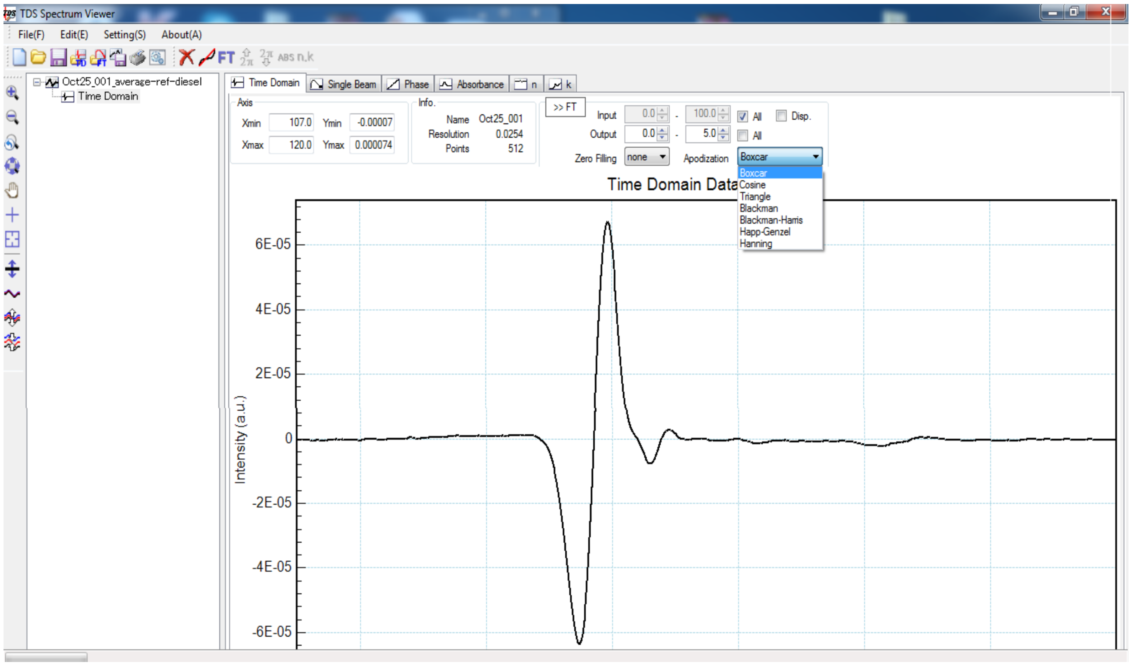


Figure 7. a) Signal in time domain b) Signal in frequency domain

THz spectrum viewer software was used to analyze THz time domain data.[53]

Figure 8 presents a screenshot of the software. This software is very practical to apply FFT and calculate refractive indices and absorbance in a very short time. There are different options for zero padding and window type (boxcar, blackman, hanning etc.). In this thesis, boxcar and 8x zero padding was used during FFT calculations. Complex THz electric field is obtained as **Equation 1.** After FFT, frequency dependent phase ($\emptyset$) and amplitude (A) data are obtained. Using **Equation 2**, the frequency-dependent refractive index ($n(\omega)$) of the sample can be calculated by utilizing the phase difference between the sample ($\emptyset_{sample}$) and reference ($\emptyset_{ref}$). Here, n(ω) is refractive index of sample, c is speed of light, d is thickness of sample and ω is angular frequency. In **Equation 3**, frequency dependent absorption coefficient ($\alpha(\omega)$) can be calculated by proportioning amplitudes of sample and reference. Another optical parameter is complex dielectric function ($\hat{\varepsilon}(\omega)$) and is composed of real and imaginary parts as **Equation 5** and **Equation 6**, respectively. $\hat{\varepsilon}(\omega)$ equals to $\hat{n}^2$ where $\hat{n}^2(\omega) = n + ik(\omega)$ where $k(\omega) = \frac{c\alpha}{2\omega}$.



Axis

Xmin 107.0 Ymin -0.00007

Xmax 120.0 Ymax 0.000074

Info.

Name Oct25_001

Resolution 0.0254

Points 512

Input 0.0 - 100.0 ☑ All ☐ Disp.

Output 0.0 - 5.0 ☐ All

Zero Filling none

Apodization Boxcar

Figure 8. Screen shot of software

$$\tilde{E}(\omega) = A(\omega)e^{i\emptyset(\omega)}$$ **Equation 1**

$$n(\omega) = n_{ref} + (\emptyset_{sample} - \emptyset_{ref})\,\frac{c}{\omega d}$$ **Equation 2**

$$\alpha(\omega) = -\frac{2}{d}\ln\left(\frac{A_{sample}}{A_{ref}}\right)$$ **Equation 3**

$$\hat{\varepsilon}(\omega) = \varepsilon'(\omega) + \varepsilon''(\omega)i$$ **Equation 4**

$$\varepsilon'(\omega) = n^2(\omega) - k^2(\omega)$$ **Equation 5**

$$\varepsilon''(\omega) = 2nk$$ **Equation 6**

2.7 FTIR Instrument

In this thesis, all FTIR measurements were carried out by Thermo Nicolet 6700 FT-THz spectrometer as shown in **Figure 9.** Effective working range was 50-600 cm^{-1} for our measurements. Working range of FTIR is an important parameter for us since we want to collect spectra at Far-IR region to compare FTIR results with THz-TDS. It is nearly overlap to THz range. This FTIR instrument offers unique Smart Purge option. It is important for our measurements because we needed to purge measuring environment before each measurement because excess water in air attenuates far-IR and it can prevent sensitive measurement. Light source was IR-turbo and beam splitter was Si coated mylar. DTGS PE was used as detector for our study.

Figure 9. Thermo Nicolet 6700 FT-THz spectrometer

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Diesel Water Mixture Measurements by FTIR

Before measurement of samples, system measurement capabilities were determined. Unfortunately, the light source is a comparably weak one. Therefore, thickness becomes a very important issue. Another parameter that needs to be optimized is the purging time. Measuring environment should be as dry as possible because water attenuates the far-IR very strongly and we try to determine water content in diesel. For this reason, we firstly optimized these parameters and used octane as sample during optimization. The reason of choosing octane is that diesel is mixture of hydrocarbons that includes alkanes between 8 and 21 carbon atoms. Firstly four different thicknesses were tried. These are 110µm, 240µm, 450µm and 730µm. The spectra collected for each thickness are compared in **Figure 10a**. 240 µm is considered to be the most proper thickness for diesel measurement among these. 110µm were not chosen because filling the liquid into the cell was very difficult. 730µm could be chosen for measurement, too. However, 730µm thickness means using about 3 times more samples for each measurement. After cell thickness optimization, purging time was optimized to minimize humidity in the measurement environment and eliminate interference as much as possible. For this purpose, octane spectrum was collected at 5 minutes, 10 minutes and 15 minutes after sample placement while the system is continuously purged. Beyond 15 minutes system is dry enough to do the measurements. (**Figure 10b)**

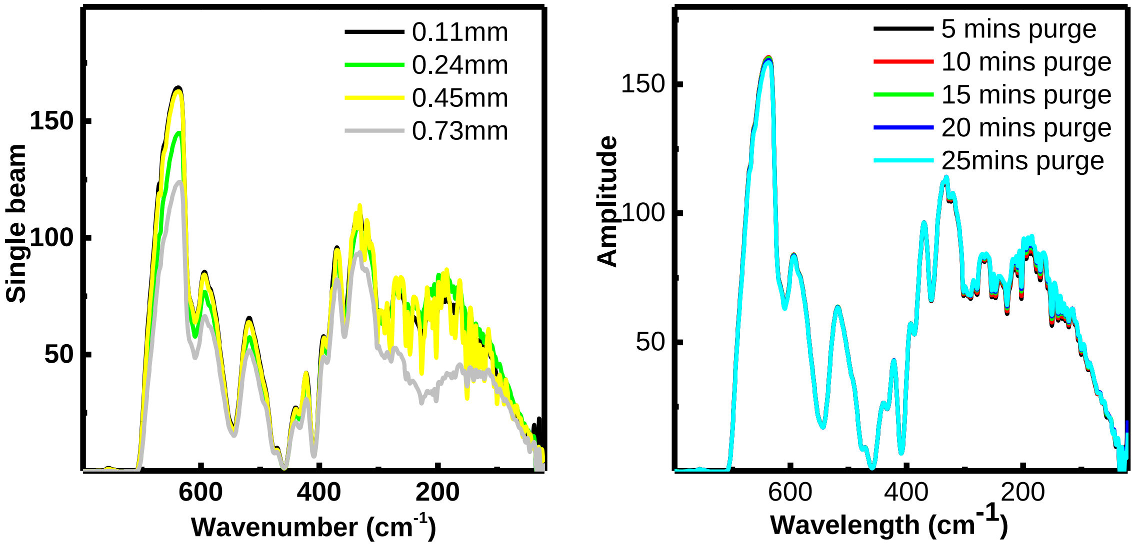


Figure 10. a) Thickness optimization b) purging time optimization

After cell thickness and purging time had been optimized, firstly diesel water mixtures without emulsifier were measured in FTIR. Concentrations of mixtures were chosen to be 0.01%, 0.02%, 0.03%, 0.04%, 0.05%, 0.1%, 0.2%, 0.3% and 0.5% (v/v). Right before each measurement, the sample measurements samples were placed in a sonicator for 10 minutes to disperse water in diesel as much as possible. Once the sample is filled into sample holder, the FTIR was purged for 15 minutes to dry the system. A spectrum was collected at each 5 minutes for 15 minutes because water diesel did not form stable mixture although they were sonicated and spectra were compared. After the measurement, three regions which are 270-185 cm^{-1}, 203-150 cm^{-1} and 163-117 cm^{-1} were selected. The primary reason for choosing these regions is that water has absorption lines in here. On the other hand, regions were selected by taking into consideration of easy determination of base line. Areas of these regions were calculated for each purging time and were divided to its peak point in order to normalize to day by day change of light source signal level. Then area vs concentration was plotted. The **Figure 11-13** show the regions and the base line.

First region (270-185cm^{-1})

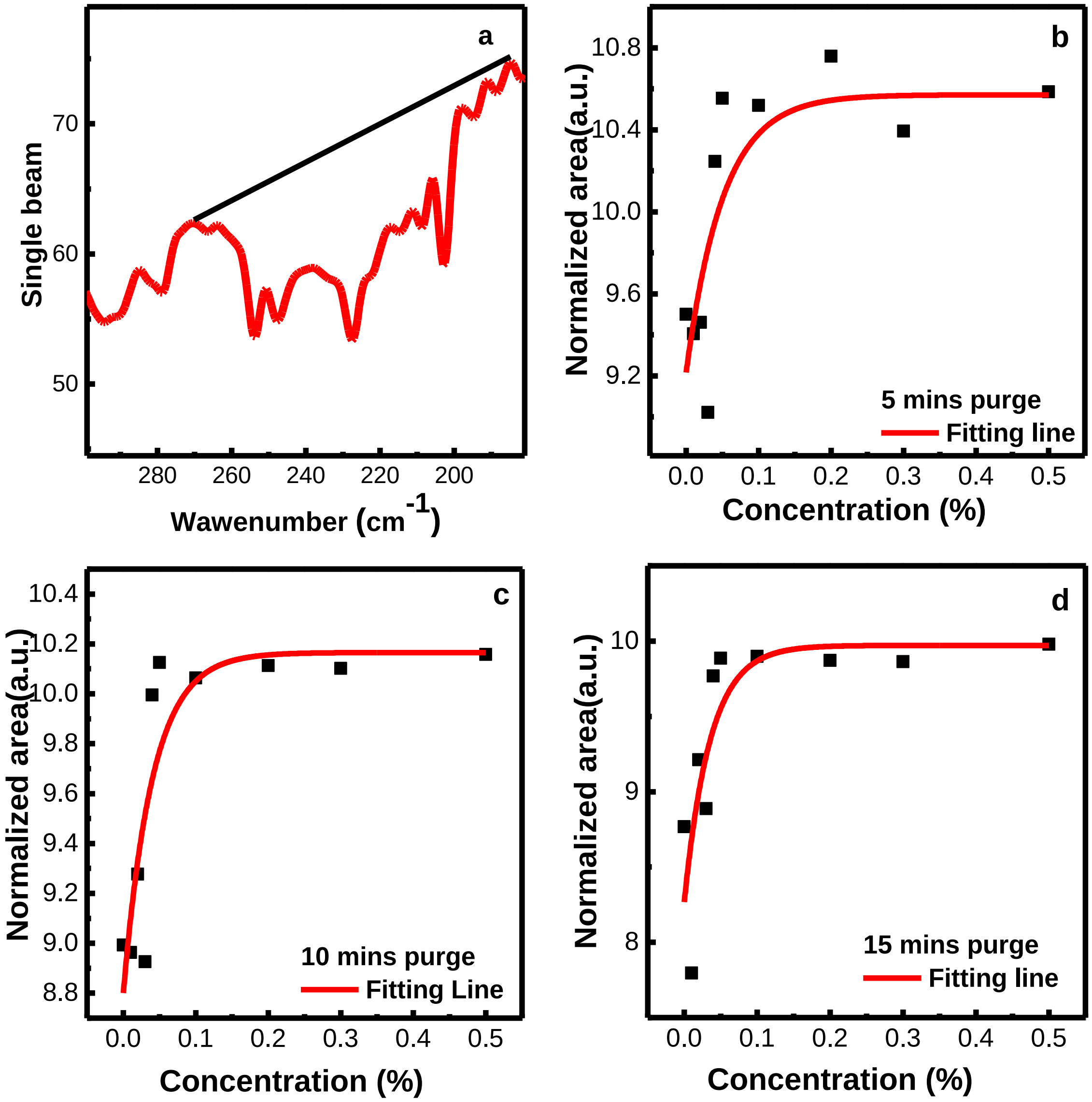


Figure 11. a) FTIR single beam data between 270-185 cm^{-1} b) concentration vs area graph for 5 minutes purge c) for 10 minutes purge d) 15 minutes purge

Second region (203-150 cm^{-1})

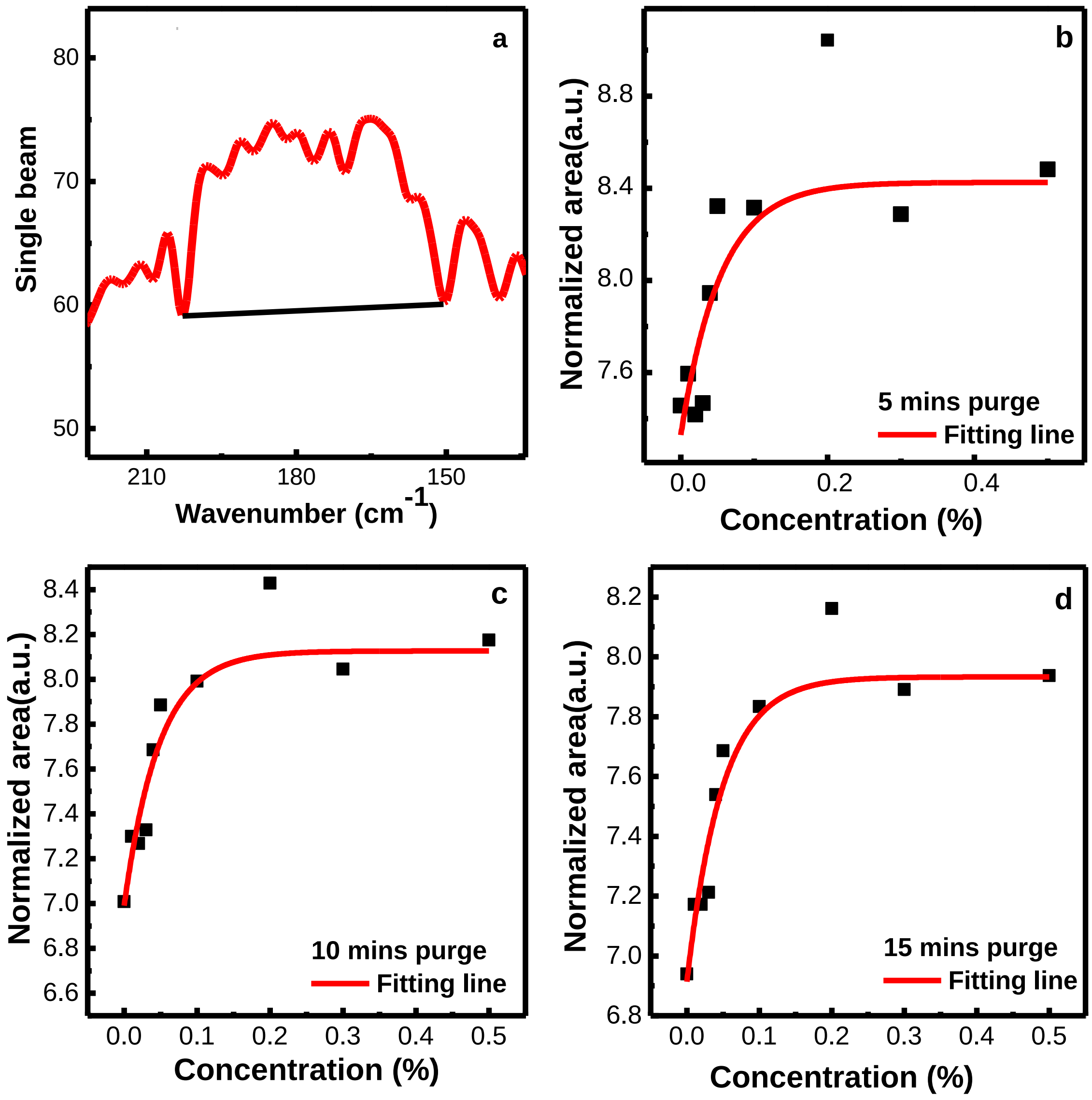


Figure 12. a) FTIR single beam data between 203-150 cm^{-1} b) concentration vs area graph for 5 minutes purge c) for 10 minutes purge d) 15 minutes purge

Third region (163-117 cm^{-1})

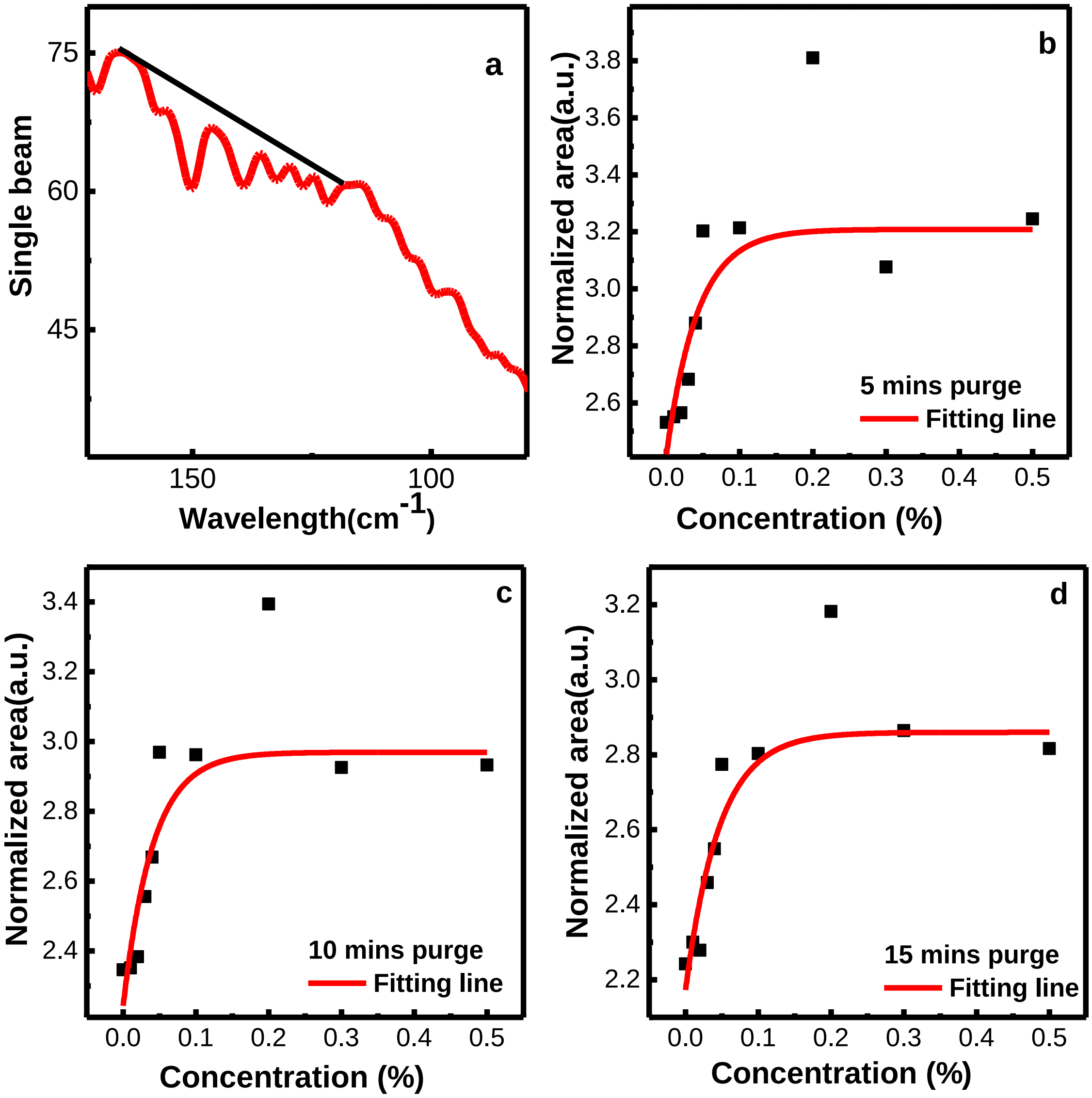


Figure 13. a) FTIR single beam data between 163-117 cm^{-1} b) concentration vs area graph for 5 minutes purge c) for 10 minutes purge d) 15 minutes purge

In all regions, 5 minutes purge resulted the least consistent reading among three. Thus, the spectra collected at 5 minutes after sample placement was discarded. Here, 15 minutes purge gives us slightly better results than 10 minutes purging time and different concentrations can be separated more sensitively. Both for first and third region, linearity are observed until 0.1%. The second region (203-150 cm^{-1}) is slightly better for separation among different concentrations until 0.2 %. In general, it can be said that lower concentrations than 0.05% can be detected by FTIR but there is saturation after this concentration. Overall, FTIR is not sensitive enough to distinguish the samples with different water amounts very well. Also, there is a problem for 0.2% concentration in all regions and all purging times.

It was noticed that water does not disperse very well in diesel even at very low concentrations so emulsifier was added to the samples to disperse water in diesel. Two sets of samples were prepared; i) with low concentrations and ii) with high concentrations according to procedure given in the experimental part. **Figure 14a** represents absorbance of low concentrations (0.01%-0.5%) where purple, yellow, green and blue are absorbance of 0.1%, 0.2%, 0.3% and 0.5%, respectively. It can be seen from the figure, the absorbance increases with concentration. The observed increase appears to be featureless and may be characterized with the slope of absorption lines between 60 and 150 cm^{-1}. **Figure 13b** shows slopes vs concentrations. Addition of emulsifier enabled to disperse water in diesel better. Therefore, mixtures with concentrations higher than 0.05% can be distinguished while mixtures with less than 0.05% could not.

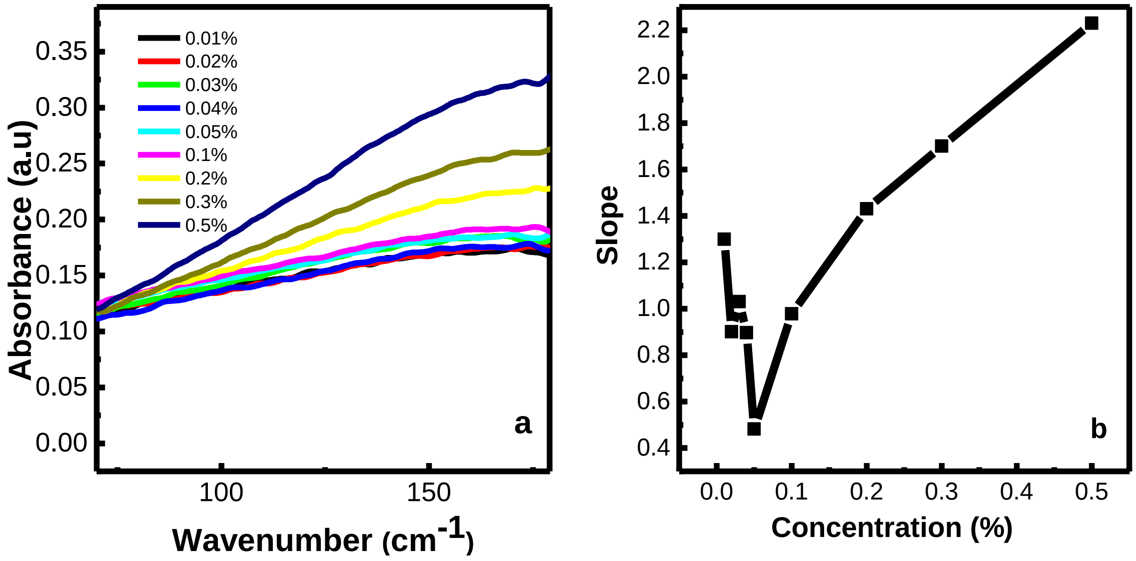


Figure 14. a) Absorbance of emulsified diesel water mixtures among 0.01% and 0.5% b) concentration vs slope graph for these mixtures

Figure 15a shows FTIR single beam spectra of emulsified mixtures with higher concentrations (0.2%-25%). As the concentration increases, intensity of single beam signal decreases. Absorbance of samples is given in **Figure 15b**. Slopes were calculated from the data between 70 and 140 cm^{-1}. **(**Hata! Başvuru kaynağı bulunamadı.**c)** There is linear change until 2% which appears to be a turning point. As from 2% concentration, there is a new linear behavior between concentration and slope again up to 20%. Concentrations higher than 20% cannot be measured by FTIR because light does not pass throughthe sample. The behavior can be used to determine the water content of a diesel water mixture with an unknown concentration.

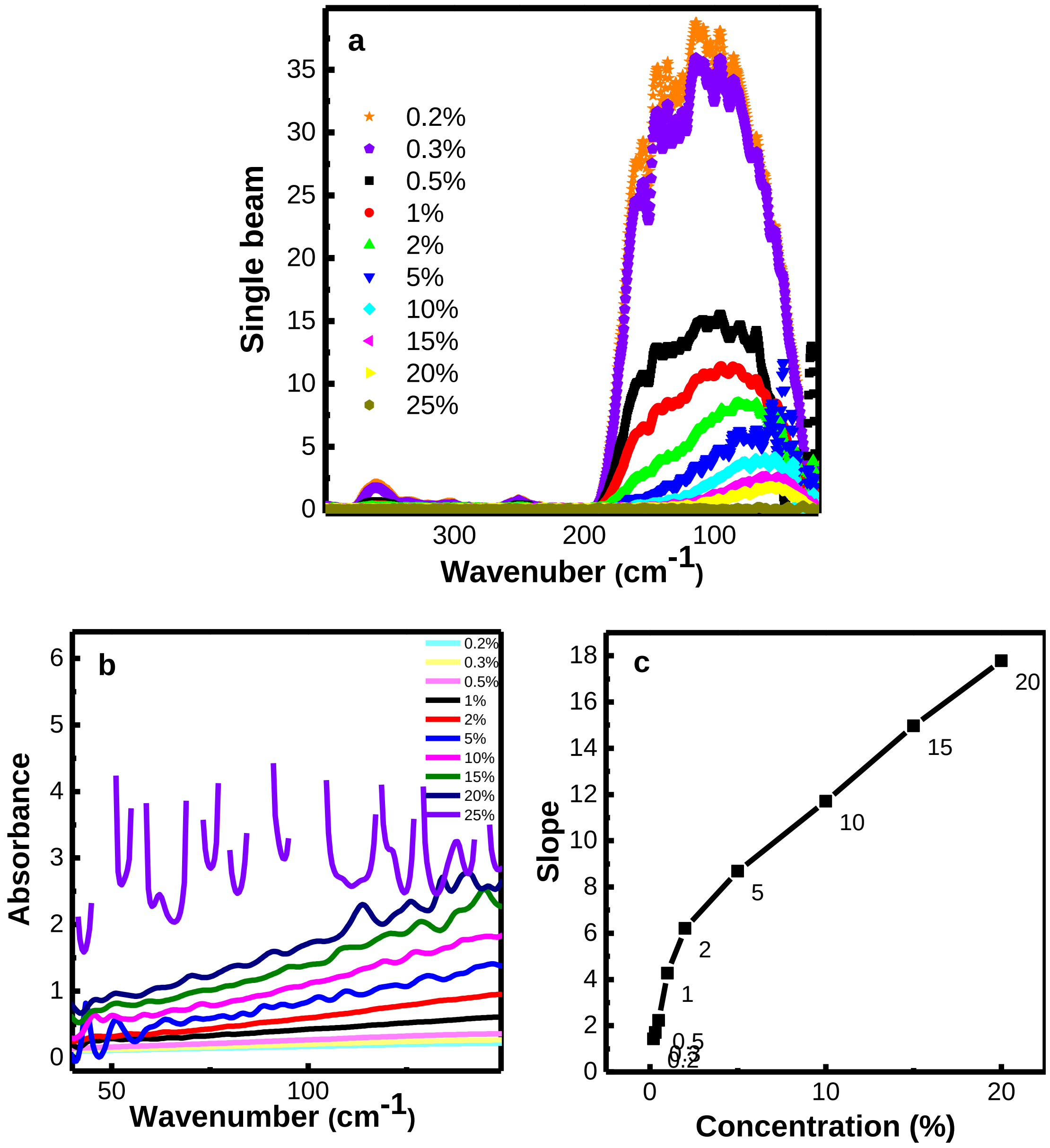


Figure 15. a) FTIR single beam data for emulsified mixtures with 0.5% and 25% concentrations b) absorbance of these mixtures c) concentration vs slope graph for emulsified higher concentration

3.2 Diesel-Water Mixtures Measurements by THz-TDS

The FTIR appears to be sensitive enough up to 0.05% for samples without emulsifier but after this concentration cannot be measured because of saturation. Also, results of emulsified samples showed us that concentrations between 0.05% and 20% can be distinguished but above 20% light transmittance is attenuated too much to do measurements. Measurement of samples with concentration up to 20% is not enough because the studies reported in the literature around 25% water in diesel an acceptable amount.[45,48] Therefore, a new technique is needed and similar measurements were carried out with THz-TDS. Before data collection, the system was needed to be modified for our study to obtain better and stable signals. Measurement environment should also be dried during the measurements. In order to change the sample, liquid cell has to be taken from dry air zone to fill. However, it is not an effective method because it causes unstable signal and increases the measurement time a lot. For this reason, a very simple but effective flow cell design was employed as shown in **Figure 16**. In addition, an aluminum bridge presented in **Figure 16** was necessary in order to place liquid cell with aim of obtaining a stable signal.

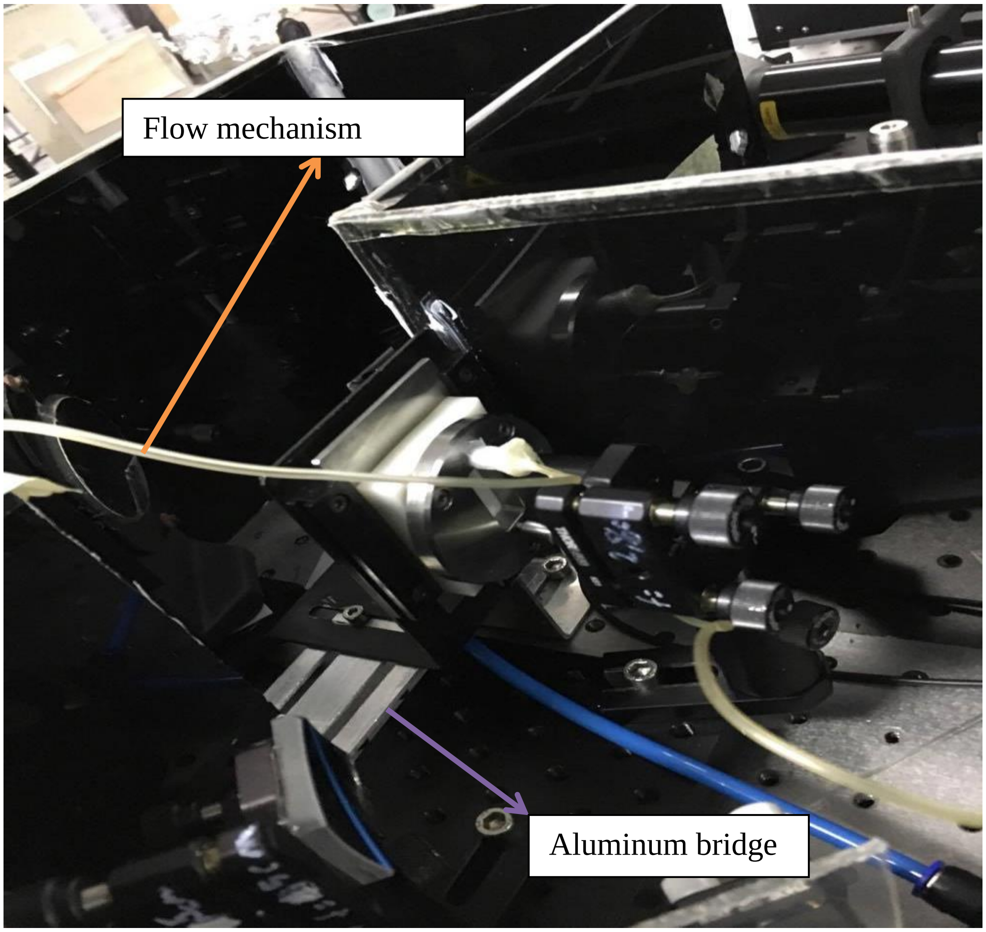


Figure 16. Designed mechanism to fill liquid from outside and bridge to obtain stable signal

After those, number of scan and number of data points were optimized to obtain a better signal-noise ratio. Determined number of scan should give us enough SNR and should be time efficient at the same time. Noise level and dynamic range of three consecutive scans and, two and three averages were calculated and compared in **Table 3.** The spectra are given in **Figure 17.** Average of three scan gives better result than others because it is less noisy and has higher dynamic range thus, average of three scan was used in our measurements.

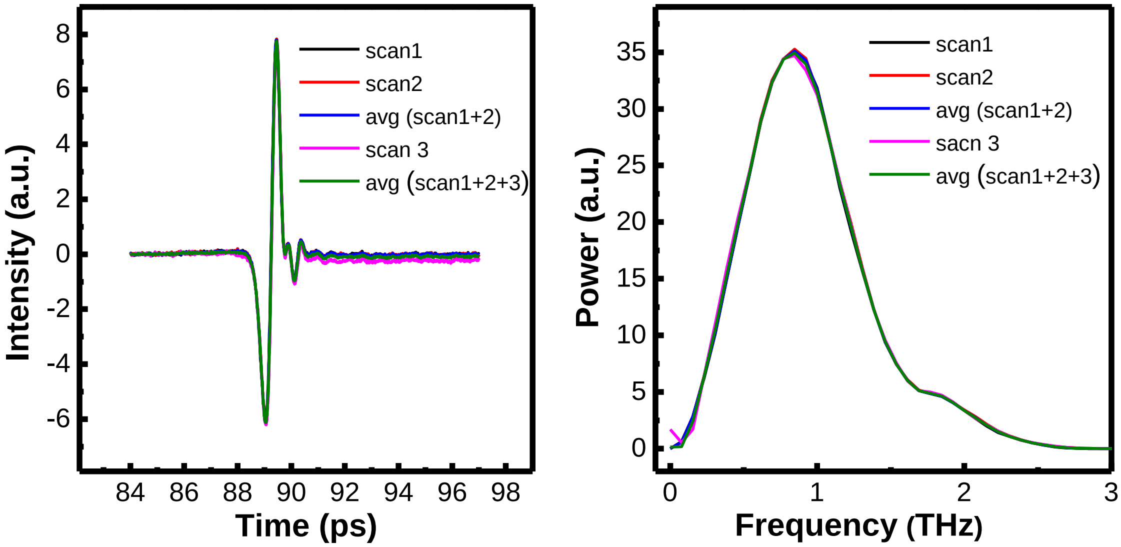


Figure 17. a) Time and b) frequency domain profiles of chosen different scan number

Table 3. Noise levels and dynamic ranges of chosen different scan number

	Scan 1	Scan 2	Scan 3	Avg (Scan 1 and 2)	Avg (scan 1, 2 and 3)
Amplitude	13.9x10^{-5}	13.9x10^{-5}	13.9x10^{-5}	13.9x10^{-5}	13.8x10^{-5}
Noise Level	2.0x10^{-7}	2.5x10^{-7}	2.7x10^{-7}	1.7x10^{-7}	1.3x10^{-7}
Dynamic Range	677	557	513	842	1043

Number of points is defined as points per each picosecond. It determines the speed of stage with the help of time constant setting on lock-in amplifier so it is an important parameter. It changes the amount of time to collect a full scan. Many numbers of data points have been tried, here time profiles of two (lowest 512 and highest 1950) are shown in **Figure 18.** In **Table 4**, noise level and dynamic range of those are compared. Noise level of waveform with 512 point is little higher than the one with 1950 point. There is a very small difference in their noise levels and dynamic ranges. For this reason, 512 number of points was preferred during our measurements because it is time efficient. When 1950 is used as number of points instead of 512, it takes four times more for each measurement.

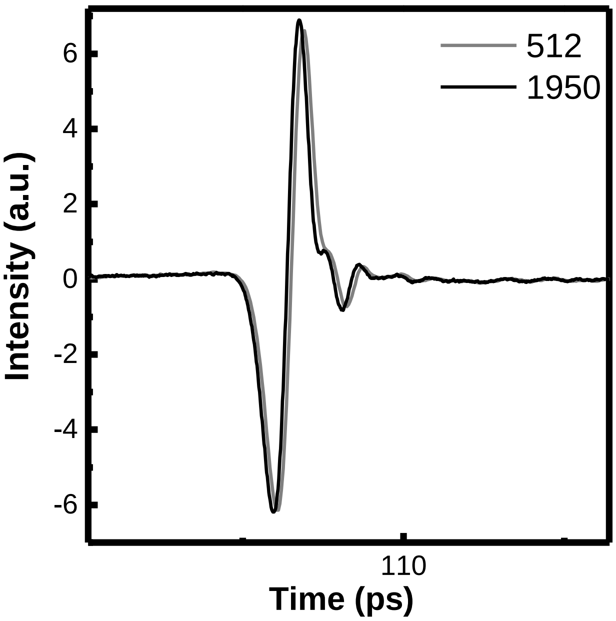


Figure 18. Time domain profiles of 512 and 1950 number of points

Table 4. Noise level and dynamic range of 512 and 1950 number of points

	512 data points	1950 data points
Amplitude	$1.3\text{x}10^{-4}$	$1.3\text{x}10^{-4}$
Noise Level	$1.54\text{x}10^{-7}$	$1.51\text{x}10^{-7}$
Dynamic Range	849	847

After optimization studies, diesel water mixtures were measured by THz-TDS. First of all, lower concentration mixtures without emulsifier were measured. Then, absorbance of mixtures was calculated and smoothed as shown in **Figure 19.** Lower concentrations than 0.04% cannot be distinguished very well but as from this concentration difference among absorbance can be seen clearly. **Figure 20a** shows absorption spectra of water vapor and it has strong absorption at about 0.9, 1.1, 1.4 and 1.7 THz. Absorbance vs concentration graphs were plotted at 0.9 and 1.1 THz as shown in **Figure 20b and Figure 20c.** The figures show the linear behavior of absorbance above 0.03%. At that point, these results show us that signal to noise ratio (SNR) is not enough to distinguish very low concentrations. For practical purposes, this is not very important since the water addition is generally critical above 0.1%.[49]

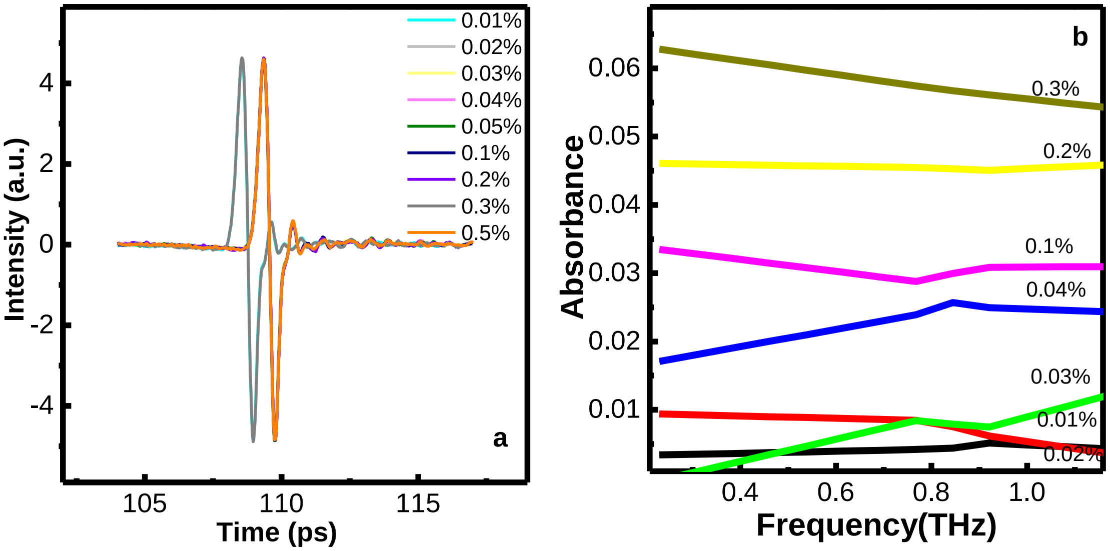


Figure 19. a) Time domain profile and b) absorbance of diesel water mixtures without emulsifier

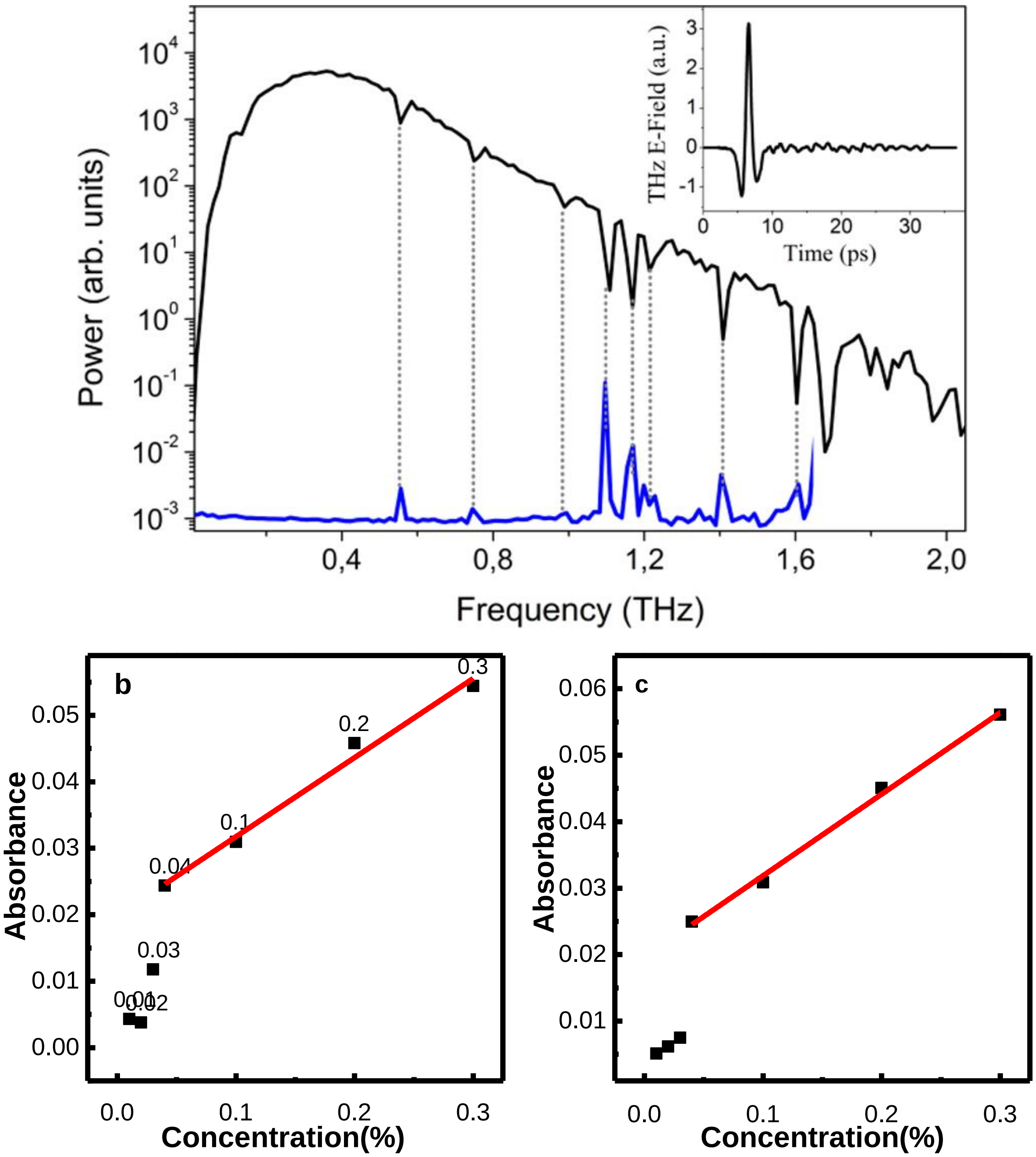


Figure 20. a) Absorbance of wet air and water vapor[36] b) concentration vs absorbance graph for mixtures without emulsifier at 0.9 THz and c) at 1.1 THz

Beyond 0.05%, it is not possible to disperse water in diesel very well even with sonication. Further concentrations require emulsifiers to disperse the water in diesel with the help of reverse micelle formation. Firstly, the emulsified mixtures were prepared for the same concentrations. Then, mixtures with emulsifier were measured by THz-TDS. **Figure 21a** presents absorbance of samples with different concentrations. The absorption spectra show featureless behavior similar to the absorption spectra obtained by FTIR. The behaviors are characterized by the slope of each spectrum. However, the behavior is inconclusive since it could not present the increased absorption of sample with increased concentration. The slightly better behavior was observed with absorbance data at 1.1 THz shown in **Figure 21b.** Amount of water in mixtures with emulsifier cannot be detected for concentrations lower than 0.04% although emulsifier is used. Here, linear behavior was observed after this concentration. We tried to distinguish lower concentrations with two different approaches. However, these results showed us that addition of emulsifier to mixtures did not help much to determine lower concentrations. It showed that signal to noise ratio of our system is not enough to measure very low concentrations. The system performance needs to be improved before carrying out such measurements.

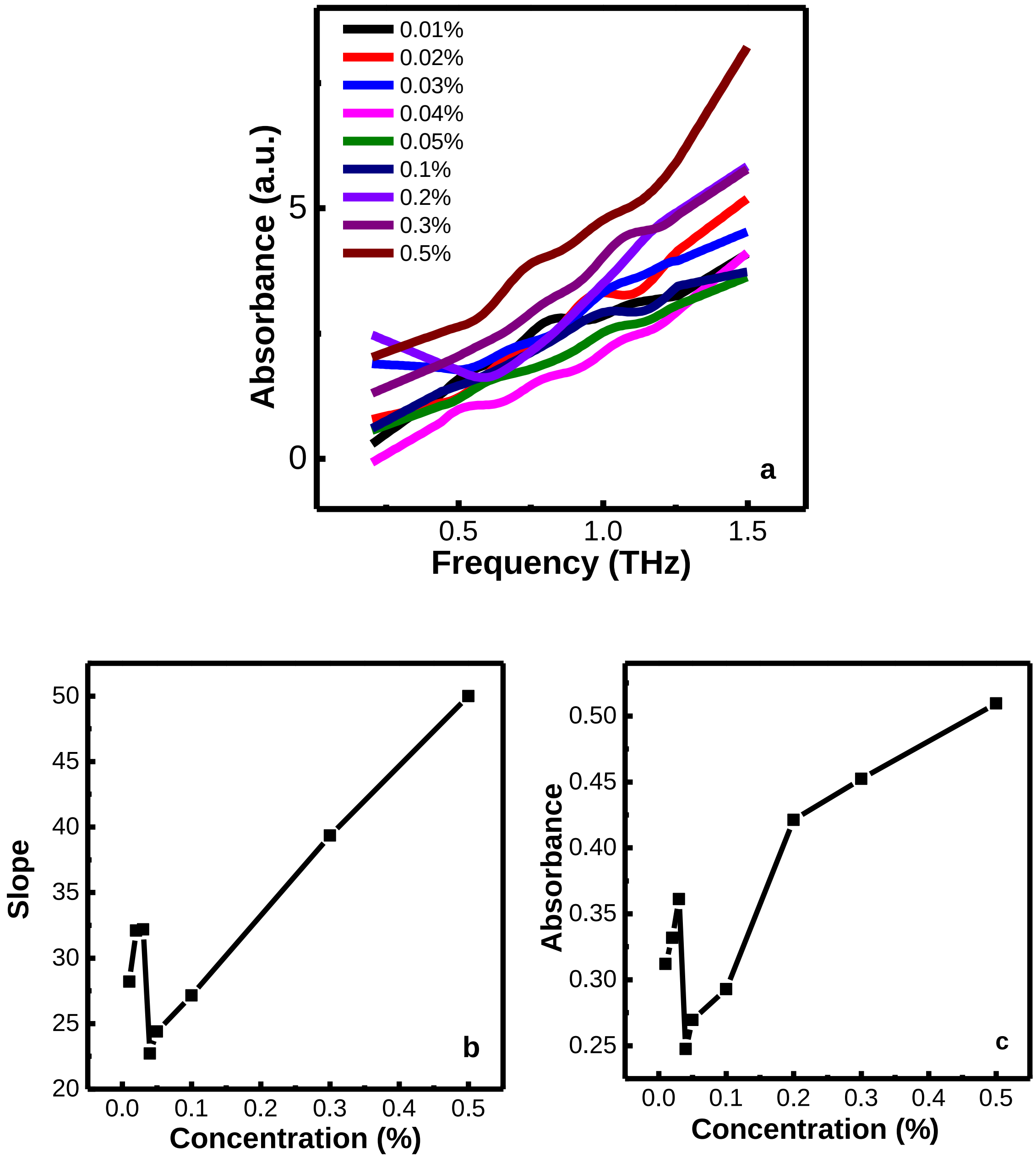


Figure 21. a) Absorbance of emulsified diesel water mixtures b) concentration vs slope graph of diesel water mixtures with emulsifier c) concentration vs absorbance graph at 1.1 THz

Later, higher concentrations were prepared (0.5%, 1%, 2%, 3%, 5%, 10%, 15%, 20% and 25%) with the same procedure and measured with THz-TDS. Absorptions spectra of mixtures with higher concentrations are given in **Figure 22a.** The absorption spectra are also featureless similar to the lower concentrations. The observed oscillations are due to strong attenuation of THz light at high concentrations. Slope vs concentration data were plotted in **Figure 22b.** The change in absorption between 0.5% and 25 % is a nonlinear behavior. However, the data may be divided in two linear regimes. First one is between 0.5% and 2%. After 2% there is a turning point and new linearity may be considered between 5% and 25%. Although there are two linear behaviors, these results showed us that THz-TDS is sensitive enough to measure emulsified samples higher than 0.5% even the mixtures with concentration higher than 20%.

To our knowledge, there is no reported study on the water diesel emulsions by THz-TDS. However, Ji Wu-Jun et al. studied on determination of water content in crude oil by using terahertz spectroscopy and showed that there is a linear relationship between water content and absorption coefficient in water crude oil mixtures.[54] D.R. Emberson et al. examined water-diesel emulsions (10% and 20% water by mass) by using Shadograph. [55] In our study, we have shown that water content in diesel up to 25% by volume and possibility even higher can be determined by using terahertz spectroscopy. One advantage of THz-TDS is that it is less complicated than D.R. Emberson’s study. Gorenflo et al. used terahertz transmission spectroscopy to determine water content in polyglycol alcohol and they can distinguished concentration between to 0.3% and 3.3%.[56]

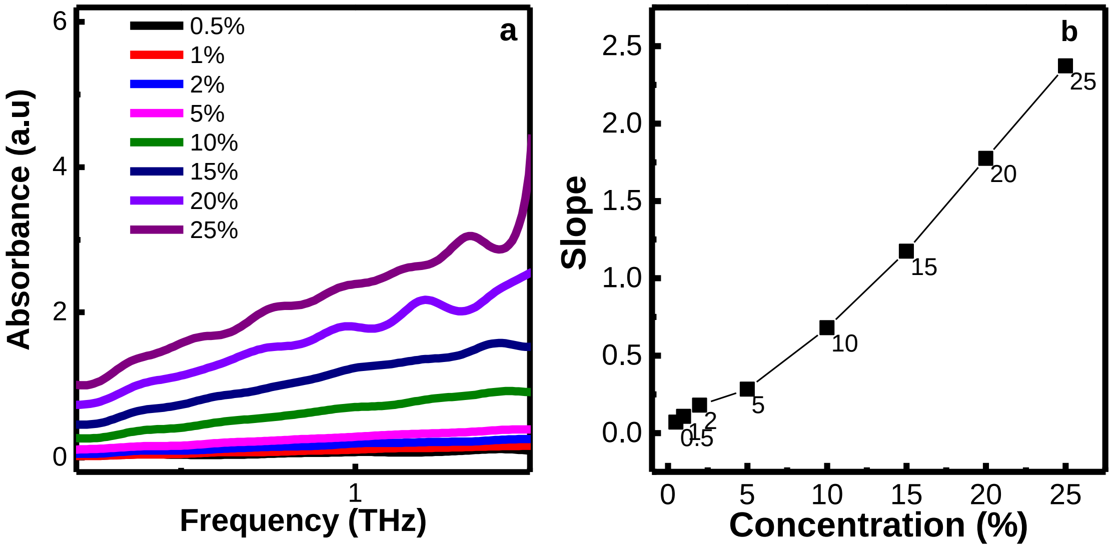


Figure 22. a) Absorbance of emulsified diesel water mixtures with higher concentrations b) concentration vs slope graph of them

Both FTIR and THz-TDS were used to distinguish diesel and water mixtures with and without emulsifier. Mixtures without emulsifier measured by using FTIR could be distinguished up to 0.05% concentration. After this concentration, there is saturation and FTIR is not sensitive enough to determine the small differences. Then, the same mixtures were measured by using THz-TDS and although concentrations lower than 0.04% could not be differentiated due to low SNR, samples with higher concentration were distinguished well enough. The results show that FTIR and THz-TDS are complementary techniques to each other for samples without emulsifier. However, THz-TDS is a better choice than FTIR for determination of water content in diesel without emulsifier because up to 0.1% concentration is an acceptable water amount in diesel in the industry.[49] For this reason, detection of more than 0.1% is important for mixtures without emulsifier. For mixtures with emulsifier, lower concentrations up to 0.05% could be distinguished by using FTIR. Then the same samples were measured by THz-TDS and similar results were also obtained by using THz-TDS. As from 0.04% concentration, water content in diesel could be detected. Also, concentrations between 0.2% and 25 % were measured by FTIR and linear behavior was observed for concentrations between 0.2% and 1%. 2% could be considered as the turning point and there is also linearity between 2% and 20%. However, after 20% FTIR could not be utilized because light did not pass through the sample. When we measured the same samples by THz-TDS, water content in mixtures with between 0.04%-25% could be detected. However, concentrations lower than 0.04% could not be differentiated by using THz-TDS because of low SNR of the system. For higher concentration, THz-TDS can be a better choice because THz-TDS enabled to us measure higher concentration than 20%. Measurement of samples with concentration up to 20% is not enough because the studies reported in the literature around 25% water in diesel an acceptable amount.[45,48]

3.3 Oil Measurements by FTIR

Recently, mixed oil is used instead of regular diesel due to its lower price. However, production and consumption of this kind of fuel should be controlled because it can be harmful to not only human health and but also to the environment. In this study on preliminary work about distinguishability of mixed fuel and regular diesel, sunflower oil, olive oil, fried oil and engine grease #10 were measured by using two different instruments. Firstly, FTIR was used to distinguish oils. Before the measurement, measuring environment was purged for 15 minutes like diesel water mixture case.

Figure 23 presents single beam of FTIR spectra and green, purple, black, red and blue represent diesel, engine grease #10, sunflower oil, frying oil, olive oil, respectively. Here, no marker could be seen in FTIR data that can be used to distinguish engine oil from diesel or to distinguish vegetable oils. However, there is a clear difference in attenuation of the light between diesel or engine grease #10 and vegetable oils.

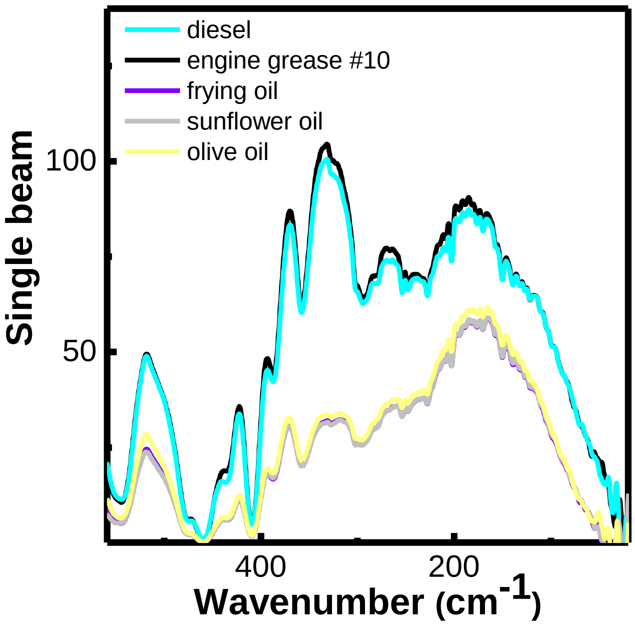


Figure 23. FTIR single beam data of oils

3.4 Oil Measurements by THz-TDS

After FTIR measurements, oil samples were measured by using THz-TDS. Absorbance and refractive index of oil samples were calculated and presented in the **Figure 24**. Similar to FTIR, the diesel and engine grease #10 overlap very well and would not be distinguished with absorbance data only. Similarly, olive oil, sunflower oil and frying oil cannot be distinguished from each other by using absorbance. On the other hand, refractive indices of samples calculated as compared in **Figure 24b**. Oil samples can be distinguished clearly by using refractive indices. Frying oil's refractive index is between olive oil and sunflower oil as expected because frying oil is mixture of those oils. Also there is a clear difference in refractive indices. This shows us that THz-TDS can be a powerful tool to distinguish regular diesel and mixed fuel by utilizing their indices or dielectric constants.

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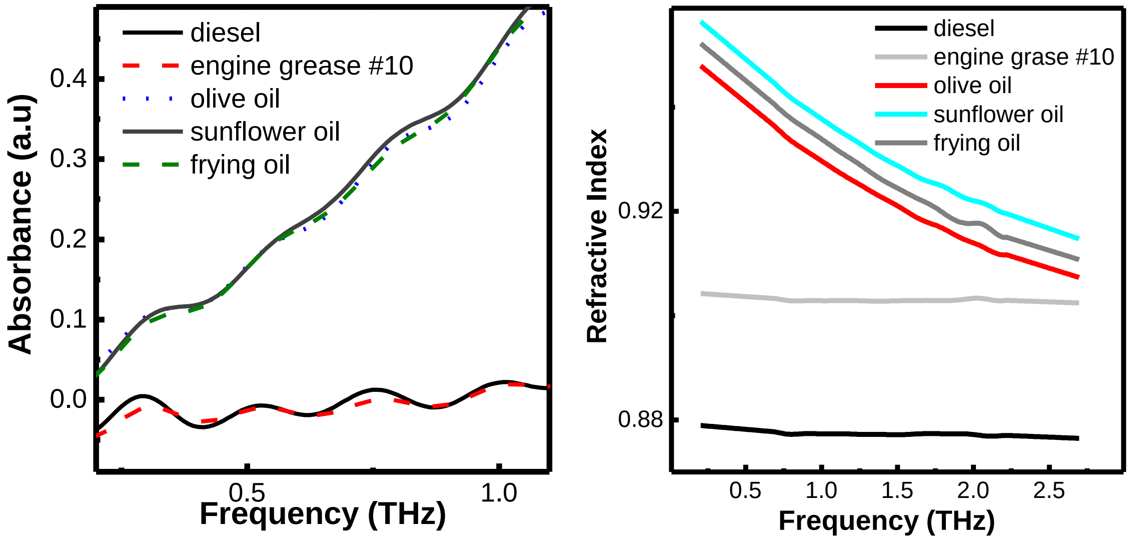

Figure 24. a) Absorbance and b) refractive indexes of five different oils

CHAPTER 4

CONCLUSIONS

In this study, we investigated the use of Terahertz waves for determination of water amount in diesel with and without emulsifier by FTIR and THz-TDS since emulsified diesel water mixtures are being a preferred product because of its lower price in the market. In addition, use of Terahertz waves to distinguish the various types of oils was also tested as a preliminary study since mixtures of oils are also being used instead of regular diesel. The results show that THz-TDS and FTIR are complementary techniques for diesel water mixtures without emulsifier. However, for diesel water mixtures with emulsifier THz-TDS appears to be a better choice. For oil measurements, it was shown that THz-TDS is a better technique than FTIR to distinguish diesel and oils using their frequency dependent indices at THz frequencies.

Firstly, diesel water mixtures without emulsifier were measured by using THz-TDS and FTIR. Results showed us that FTIR is slightly better technique than THz-TDS for samples up to 0.05% concentration. However, after this concentration samples could not be distinguished by using FTIR because of saturation. When THz-TDS results were considered, it was possible to distinguish samples at with concentrations higher than 0.04%. Distinguishing higher concentrations than 0.04% is more important because up to 0.1% is an acceptable water amount in diesel. After direct water addition studies, emulsifier was added to samples to disperse water in diesel better. In addition to lower concentrations, samples with higher concentrations were also prepared with emulsifier. Firstly, FTIR spectrums were collected for concentrations between 0.01% and 25%. Below 0.05% concentration mixtures could not be distinguished but between 0.05% and 20% they could be differentiated successfully by FTIR. After 20% light did not pass through the sample thus, FTIR is not a suitable technique for higher concentrations than 20%. In addition to FTIR measurements, the same samples were also characterized by

THz-TDS. However, even with addition of emulsifier it was not possible to distinguish very low concentrations and this showed us that signal to noise ratio of THz-TDS is not enough to see very small differences. However, distinguishing of higher concentrations between 0.5% and 25% could be done successfully. Two different linear trends at slope vs concentration graph were observed. First one is between 0.5% and 2% concentration and second one is between 5% and 25% concentration. The plot can be used for determination of water content in diesel-water mixtures with emulsifier.

In this thesis, oils (sunflower oil, olive oil, frying oil and engine grease # 10) were also measured by using FTIR and THz-TDS. No marker could be seen in FTIR spectra to distinguish the oils from each other. However, THz-TDS results showed us that oils can be distinguished very well. Although their absorbance did not have clear differences, they could be distinguished easily by using their refractive indices. This showed us that THZ-TDS is a more suitable technique than FTIR to distinguish oils. The results are preparatory work about distinguishability of diesel and mixed fuel.

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