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Research Article

Predicting Cold Flow Properties of Diesel by Terahertz Time-Domain Spectroscopy

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The frequency-dependent absorption characteristics of conventional diesel fuel have been researched in the spectral range of 0.2–1.5 THz by the terahertz time-domain spectroscopy (THz-TDS). The absorption coefficient increased monotonically with the solidifying point of diesel. A nonlinear regression model was established, and the cold flow properties of fuel were presented quantitatively. The results made the solidifying point prediction possible by THz-TDS technology and indicated the bright future in practical application.

1. Introduction

Diesel fuel is one of the commercial and industrial fuels, produced by refining crude oil. Because of being heavier and having more carbon content, diesels have some problems when being used in an engine. One of the important problems is a high freezing point that causes block age of filters, and hence, there are some difficulties when they are used in cold conditions. Solidifying point (SP), by which diesel has been classified as different grades of 0#, −10#, and −20#, is the highest temperature of diesel loses fluidity in engine, determined on the BSN(S)-4 solid point instruments according to GB/T510-83 [1]. SP is one of the key indicators ensuring the performance of diesel at low temperature, and it should be measured and controlled precisely in practical applications. However, the traditional method for SP has recognized that the test suffered from many disadvantages, some of which include a relatively large fuel sample volume requirement, significant time consumption, and a relatively high reproducibility error. For this reason, there have been many attempts to develop methods to estimate the indexes economically, rapidly, and effectively [2–4].

Serious applications in organism analysis have been proposed in the literature demonstrating that terahertz time-domain spectroscopy (THz-TDS) is an achievable method to detect the diesels via chemical analysis [5–7]. In this work, THz-TDS has been used to investigate the cold flow properties of diesel due to the reason that most terahertz spectrum contains rich physical, chemical, and structural information of the organism, and low-frequency vibrational and rotational spectra of organism are responsible for the cold properties and lie in terahertz frequency range. The results demonstrated the possibility of SP prediction of diesel by THz-TDS.

2. Experimental

A repetition rate of 80 MHz, diode-pump mode-locked Ti:sapphire laser (MaiTai, Spectra Physics) provided the femtosecond pulses with duration of 100 fs and center wavelength of 810 nm [8, 9]. A p-type InAs wafer with <100> orientation was used as the THz emitter, and a 2.8 mm thick <110> ZnTe was employed as the sensor. A standard lock-in technology was used in this system. A femtosecond laser pulse was split into two beams. The pump beam was used to generate THz radiation, and the probe beam acted as a gated detector to monitor the temporal waveform of THz field. A silicon lens and parabolic mirrors were used to collimate and focus the THz beam through free space onto the detector. A balanced photodiode detector detected the probe beam, and the signal was amplified by a lock-in amplifier and sent to the computer for processing. The THz beam path was purged with dry nitrogen to minimize the absorption of water vapor and enhance the signal-to-noise ratio (SNR). The humidity was kept less than 1% and the temperature was kept at 298 K. Here, the focus diameter of the THz beam is about 1 mm.

The diesels used in this work were collected from refinery with different SPs, located in the focus of the two Si lens, and are held in a 3 mm thickness polyethylene cells, which are transparent for visible light and have a low refractive index and THz absorption. Both the time-domain sample and reference spectra were obtained by testing the polyethylene cell holding the sample and empty cell, respectively. After applying fast Fourier transform, we get the frequency-domain sample and reference spectra and calculate the absorption characters of samples [10].

3. Results and Discussion

Diesel consists of n-alkanes, olefins, branched alkanes, and aromatic hydrocarbon, and n-alkanes are well known to be responsible for the paraffin deposit formation. When surface temperatures are below the temperature at which the waxes are soluble and a temperature-gradient exists between the diesel and colder deposition surface, long chain n-alkanes deposited to be wax crystals. As more and more wax precipitates, the formation and growth of the wax crystal gel network occurs. If the network becomes extensive enough, the diesel viscosity will increase significantly and lose fluidity in engine [11, 12]. The diesel with high alkanes content showed a higher SP and worse flow properties at low temperature.

Figure 1 is the absorption spectra of diesels with the SP ranging from −2.5 to −32.9 in 0.2–1.5 THz, showing that the absorption coefficients (α) of diesel increased regularly with its SP because of the differences on the content of diesel. As mentioned prviously, high-alkanes-content diesel showed a higher SP. And comparing to other compositions in diesel, n-alkanes have a lower carbon-chain-branched degree and greater intermolecular forces, which resulted in the stronger terahertz absorption due to that terahertz wave is sensitive to intermolecular forces. Thus, with the increasing of n-alkanes concentration in diesel, both SP and α increased. The n-alkanes in diesel are normal alkanes with the number of carbon ranging from 11 to 26. According to the Lambert-Beer law, which can be expressed as $\alpha = \sum_{i+1}^{n} b_i \alpha_i$ [13], where α is the absorption coefficient of the diesel and b_i and α_i are the weight ratio and absorption coefficient of the components, the absorption curve of the diesel can be understood as the superposition of different components, including n-alkanes, olefins, branched alkanes, and aromatic hydrocarbon. Therefore, there were not strong peaks in absorption curve of diesel for its complex components and concentrations, as shown in Figure 1. There are some oscillations in the absorption curves, manifesting the existence of Fabry-Perot reflection, which was inevitable for liquid samples [14].

To further reveal the correlation of SP and α, the α at 0.4, 0.6, 0.8, 1.0, and 1.2 THz has been collected as independent variable, and SP as dependent variable. As shown in Figure 2, α and SP exhibited nonlinear features at different frequencies, and a fitted regression equation has been presented as follows:

$$SP = a + b * \exp\left(\frac{(-x)}{c}\right), \quad (1)$$

where x is the absorption coefficient, and the parameters a, b, and c for different frequencies are listed in Figure 2.

Equation (1) will be a predictive model for SP based on terahertz spectrum of the diesel fuel and will quantitatively describe the effect of pour-point depressant (PPD) on the SP

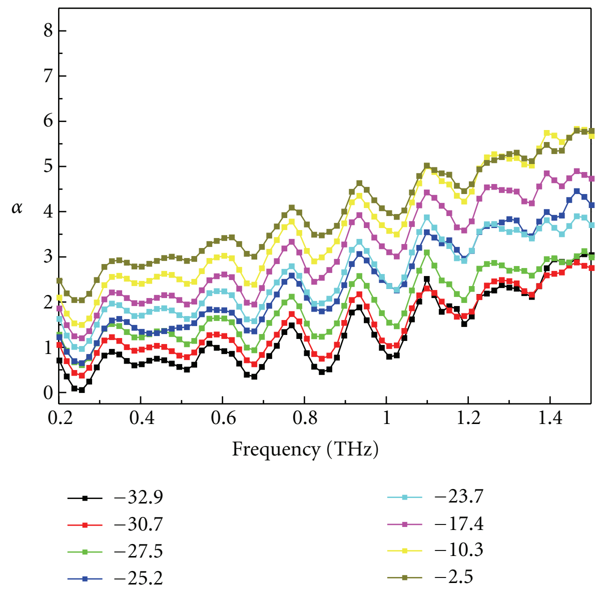

FIGURE 1: Terahertz absorption coefficient (α) of diesel with different solidifying point (SP).

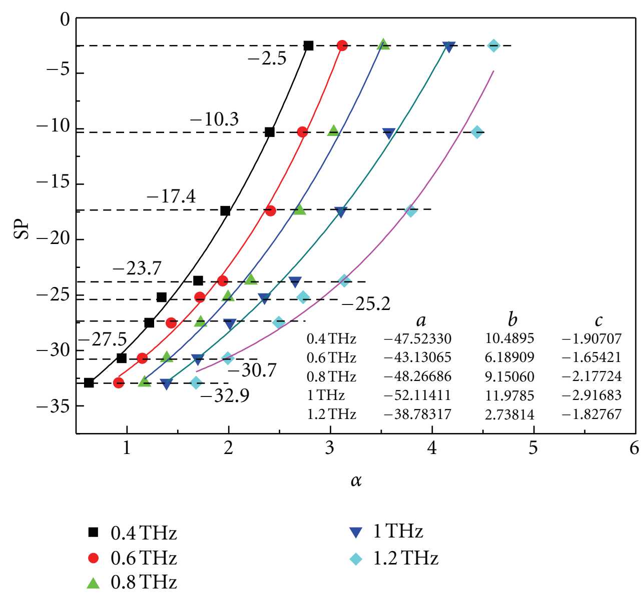

FIGURE 2: The nonlinear relationship between solidifying point (SP) and absorption coefficient (α), and a, b, and c are parameters of regression equation.

Table 1: Solidifying point (SP) and cetane number (CN) of diesels.

Volume fraction of MMA	0.2%	0.4%	0.6%	0.8%	1.0%	1.2%	1.4%
Calculated SP	−5.45177	−16.45461	−23.79484	−25.72656	−29.57764	−30.69636	−32.21498
Measured SP	−6.3	−15.3	−21.7	−26.9	−28.1	−30.6	−31.5
Measured CN	62.4	54.9	49.6	48.4	47.3	46.7	46.2

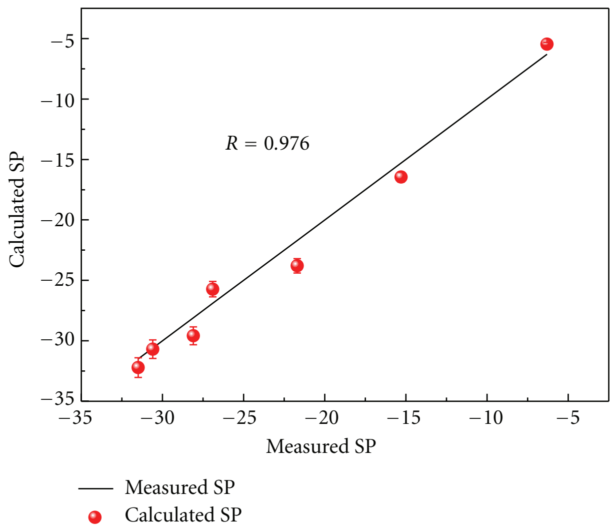

Figure 3: The comparison of experimental and calculated values of solidifying point (SP).

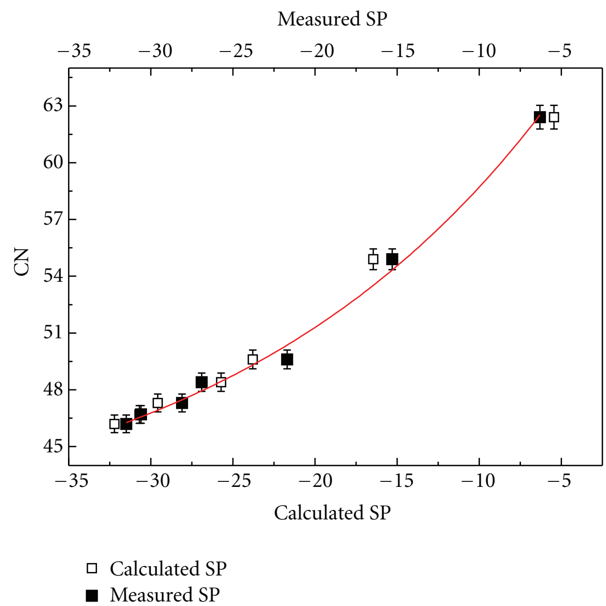

Figure 4: Relation between solidifying point (SP) and cetane number (CN).

of the fuel. PPDs are ester copolymer constituted by long line chain hydrocarbons and have been proven to be an effective and economic way of improving the cold flow properties of oils. When added into diesel, the long chain alkyl group can be inserted into the wax crystal in the fuels and the polar moiety exists on the surface of the wax crystal, which act as crystallization nuclei dangling from the polymeric matrix. Thereby the crystal lattice formation was inhibited and the wax's crystal size reduced to the region of 5–20/μm. Large number of crystallization nuclei correspond to less free paraffin that will hinder fluidity with the reducing temperature, so that more wax crystal can get through the filter, and SP will be lower [1, 15, 16].

Methyl methacrylate (MMA), one of the most widely used PPD [17], has been researched in this study, the structure of which has been shown in Figure 3. Blend MMA with base diesel (SP = −2.5) by the volume fraction of 0.2% to 1.4%, stirring 30 minutes. The SPs of blends have been listed in Table 1, measured by GB/T510−83 and exhibited good improvement performance so that SPs of blends decreased efficiently with the increasing content of MMA. THz absorption coefficients of mixtures, as testing set, have been measured in 0.2–1.2 THz. Putting α at 0.4, 0.6, 0.8, 1.0, and 1.2 THz into (1), the SPs will be calculated. Averaging the values at different frequencies, the calculated SPs were obtained, which were close to the measured results, demonstrating a good agreement and the effectiveness of the built model, as shown in Figure 3.

Figure 4 displays the relationship between SP and cetane number (CN) of blends. CNs have been listed in Table 1, which is the measure of the ignition quality of diesel, and have been measured by the American Society for Testing and Materials (ASTM D613) method [18, 19]. High CN of diesel ensures the combustion performance of fuel. It can be observed that CN decreased nonlinearly with the decreasing SP due to the injection of MMA. Diesel is a mixture of various organic compounds and every pure-component contributes to its CN. n-alkanes have the highest CN and multi-isoalkanes has the lowest. Regarding diesel as a whole organic system, the branch degree of diesel will affect the CN of diesel. The greater the branch degree is, the lower the CN is [18, 19]. When MMA was added into diesel, the SP decreased efficiently but the CN, meaning the combustion characteristic of fuel, decreased due to the higher isomerization degree. Enough attentions should be paid to this phenomenon on the usage of PPD.

4. Conclusions

In summary, the SPs of diesel have been researched using THz-TDS technology. The terahertz absorption coefficient of diesel increases regularly with the increasing SP, by which the SP will be calculated easily by the built absorption-SP models. The investigations have illustrated that THz-TDS is an effective method to predict SP of diesel and it will be a promising approach for quality control no matter on-line or field monitoring.

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