

Optical property of biodiesel and its base stock in terahertz region

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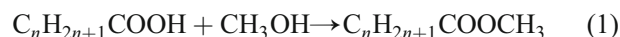
Abstract Biodiesel (BD) is the product of catalysed transesterification reaction, in which fatty acid (FA) is transformed to fatty acid methyl ester (FAME), named BD. The frequency-dependent absorption and refractive characters of BDs and its base stocks have been researched in the spectral range of 0.2–1.5 THz by terahertz time-domain spectroscopy (THz-TDS). The BDs showed higher absorption value than those of its base stocks because of the concomitant, and the increasing of absorption coefficients of three BDs differed with the different transesterification technology. The results suggested that THz-TDS can be a promising method to the quality control and ester transfer efficiency analysis of BD.

Keywords terahertz time-domain spectroscopy (THz-TDS), biodiesel (BD), fatty acid methyl ester (FAME)

1 Introduction

Major energy demand is fulfilled by conventional energy resources like coal, petroleum and natural gas. Petroleum-based fuels are limited reserves concentrated in certain regions of the world. These sources are in the verge of getting extinct. The scarcity of petroleum reserves will make renewable energy resources more attractive than before. As a bio-fuel, biodiesel (BD) has several advantages used in diesel motors, such as the reduction of greenhouse gases emissions and the increasing of eco-efficiency. At the same time, engine performance can be remained constant or decrease slightly compared to the use of diesel fuel [1,2]. The production of BD may be achieved by a homogeneous (sodium hydroxide or methoxyde) catalysed transesterification reaction between vegetable and animal oils (fatty acid (FA)) and a short chain alcohol,

such as methanol, which can produce fatty acid methyl ester (FAME), the main component of BD. The reaction is expressed as follows:



This reaction occurs stepwise, and intermediate products are mono and diglycerides [3]. At the end of the reaction period, BD phase is contaminated with mono, di and triglycerides, methanol, catalyst, free glycerol and soaps. And it has to be purified to comply with the European Standard EN 14214 [4]. Therefore, quality control tests of BD are necessary, including conversion rate from FA to FAME, the residue of contamination and so on.

BD analyses are very expensive and time consuming before. The method of terahertz (THz) spectroscopy as a cheaper and faster alternative can be used to control the quality of BD. Result of THz spectroscopy contains rich physical, chemical, and structural information of materials. Most low-frequency vibrational and rotational spectra of organics and related compounds lie in this frequency range. Recently, there has been remarkable effort in employing THz time-domain spectroscopy (THz-TDS) for investigating the properties of materials, including environment pollutants, semiconductors, polymers, explosive materials, oil-water complexes, and gases [5–14].

In this paper, the THz spectrum of three types of BDs and its base stocks have been studied. Distinguished absorption and refractive characters suggested the promising applications of quality control of BD using THz-TDS.

2 Experiment section

All measurements were performed with a conventional transmission TDS system based on a p-type InAs with <100> orientation emitter and a 2.8 mm-thick <110> ZnTe sensor. The repetition rate of diode-pump mode-locked Ti:sapphire laser (MaiTai, Spectra Physics) was 80

MHz, and the duration of femtosecond pulses was 100 fs, and its center wavelength was 810 nm [15,16].

For analysis, several types of BD and FA have been collected. Three FAs derived from drainage oil I, drainage oil II and rap oil, which were numbered for FA1, FA2 and FA3 respectively. The three BDs are the final products of transesterification reaction of FA1, FA2 and FA3, named BD1, BD2 and BD3, and the main component of BD was named as FAME1, FAME2 and FAME3 accordingly. The samples are located in the focus of 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 a low 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 will get the frequency-domain sample and reference spectra and calculate the absorption characters of samples [17].

3 Results and discussion

Reference pulse of free cell without sample is shown in Fig. 1 with dotted line. The THz signals, amplified in inset Fig. 1, showed distinguishing decrease in amplitude and delay in time, suggesting that there are some differences of physical and chemical properties among the samples [18].

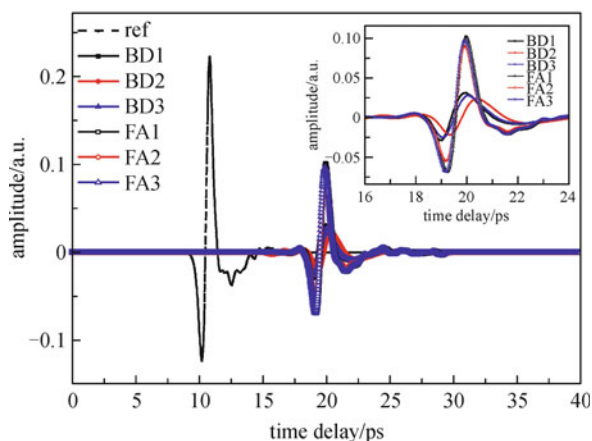


Fig. 1 THz pulses of reference, BDs and its base stocks

Figure 2 shows absorption characters of samples obtained within 0.2–1.6 THz. The absorption coefficients of BDs have higher values than those of FAs by about twice, which can be detected by the THz-TDS system.

THz wave is sensitive to changes of vibration and intermolecule forces. The molecule vibration modes of FAMES changed with carbon number from 12 to 18, which are the dominant chemical components in BD [19], as well as the corresponding FAs. The vibration frequency of FAMES and FAs have been observed by the density

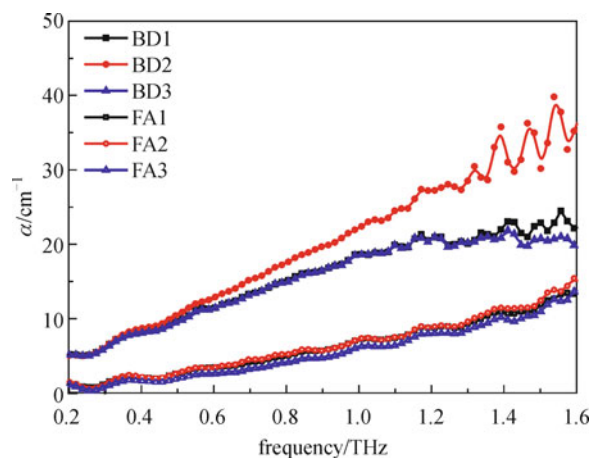


Fig. 2 Absorption coefficients of samples in 0.2–1.6 THz

functional theory using the GAUSSIAN 03 software package, the B3LYP method used conjuncting with the 6-31G (d) basis set. The results have been shown in Fig. 3, manifesting that FAMES showed similar absorption coefficients to FAs at 0.2–1.6 THz because that the skeleton vibration is a predominant manner in THz region, and the changed group at the end of carbon chain has less impact on the vibration modes of FA and FAME with same carbon number. Furthermore, compared to FAs, BDs have higher viscosity, therefore, there are much greater tension existing in the molecules, and stronger absorption by THz wave. The other nonnegligible factor stronger absorption by THz wave may be methanol and glycerol, the by-product of transesterification reaction. Methanol and glycerol have strong absorption, which have been reported [20–22]. Even a small quantity of methanol and glycerol in BD will cause the strong absorption in THz region.

Besides, FA1 and FA2 are drainage oils with different derivations, while FA3 is rap oil. The three FAs showed similar absorption curves and coefficients due to their similar compositions. After the transform of BDs, their absorption coefficients increased significantly, nearly 150% for BD1 and BD3, 200% for BD2. Although derived from different raw materials, BD1 and BD3 showed similar absorption coefficients because of their same manufacturing techniques. Compared with BD1 and BD3, BD2 is produced by another technology with different operating environment, conversion efficiency and products. Thus, there was various type and content of methanol and glycerol in BD2, which have been distinguished prominently by THz spectroscopy, as shown in Fig. 2.

Refractive index of sample in 0.2–1.6 THz can be observed in Fig. 4, the left is the refractive index of FAs and the right is that of BDs. The FAs showed similar refractive frequency-dependent slope of nearly -0.004 and average refractive index of 1.90 before transesterification. After ester transfer, the BDs had distinguishing

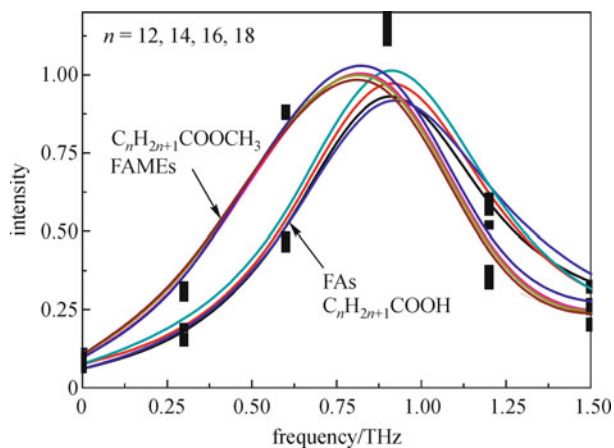


Fig. 3 Calculated absorption characters of FAMES and FAs with carbon number from 12 to 18 at 0.2–1.6 THz

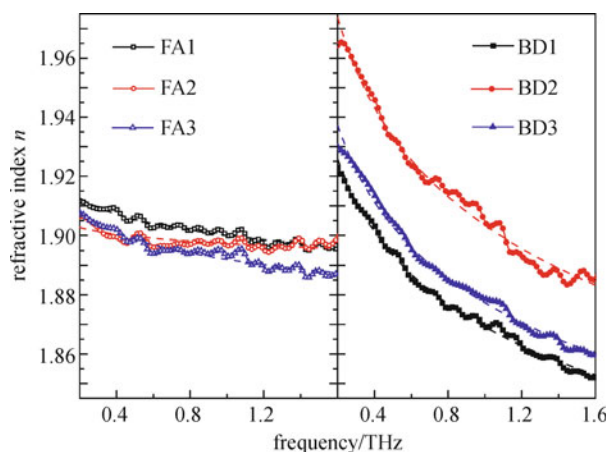


Fig. 4 Refractive indexes of samples in 0.2–1.6 THz

refractive slope of nearly -0.02 . Especially, the change of refractive indexes of BD2 is more remarkable than those of BD1 and BD3, suggesting that the composition and content of BD and its by-products are fairly different due to different technology, which can be easily distinguished in THz region.

These results implied the possibility of BD identification using THz spectrum. The increasing of absorption coefficient of BD compared to FA is due to two factors: One is the different intermolecule forces of its components; the other is the strong absorption of methanol and glycerol. Actually, methanol and glycerol are undesirable contaminants in BD. Excess of methanol decreases heating value and flash point and increases carbon deposits, while the presence of glycerol may cause injector tip coking and deposits in the combustion chamber [23]. The content of methanol and glycerol should be limited sternly in production process. Furthermore, the absorption coefficient is influenced by the content of pure compound according to Lambert-Beer law. The more methanol and

glycerol have been produced in transesterification period, the higher the absorption coefficient of BD is [24]. So the content of methanol and glycerol will be confirmed by the measurement of THz absorption spectra of BD compared to its base stocks.

4 Conclusions

In summary, the absorption and refractive characters of BD and its base stocks have been studied in 0.2–1.6 THz. Besides different intermolecule forces of BDs and FAs, the generation of undesirable by-products, methanol and glycerol, make BD stronger absorption than that of its raw materials. By this reason, BD and its base stocks will be analyzed by the THz absorption spectra. And this method exhibited a great prospect in practical application of harmful substance control and transform efficiency calculation on BD by THz-TDS for its simplicity, rapidity and availability.

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