A review on the Spectroscopic Analyses of Biodiesel

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Abstract: The study of the interaction between matter and radiation is known as spectroscopy and it is seen as a suitable and precise analytical method in quality control analysis. Spectroscopy is vital in analysis of biodiesel given that biodiesel has gained considerable attention in recent years due to its merits: biodegradable, renewable, non-toxic, less emission of gaseous and particulate pollutants with higher cetane number than normal fossil fuels. Spectroscopic methods could be atomic or molecular though modern techniques of acoustic, mass and electron spectroscopy do not involve the electromagnetic radiation. In this review, we studied various spectroscopic methods that have been used to evaluate the quality of biodiesel as well as observe the process of transesterification. Infrared, Nuclear magnetic resonance, Ultra-violet-Visible, Thermal lens and Mass spectroscopies are important analytical tools reviewed in this paper.

Keywords: Spectroscopy, Nuclear magnetic resonance, Ultra-violet-Visible, Thermal lens, Mass spectroscopy, Biodiesel analysis

1.0 Introduction
Spectroscopy is the study of the interaction between matter and radiation. It measures radiation intensity as a function of wavelength. Spectroscopic analyses are based on measuring the amount of radiation produced or absorbed by molecular or atomic species of interest (Skoog, West, Holler and Crouch, 2004). Spectroscopy is a common technique used in analytical chemistry for the identification of substances through the spectrum emitted from or absorbed by them (Lewis, Lee and Kidder, 2004). Spectroscopic methods can be classified...
according to the region of the electromagnetic spectrum involved in the measurement. The regions that have been used include gamma-ray, X-ray, Ultraviolet (UV), Visible, Infrared (IR), Microwave and Radio frequency (RF). Indeed current usage extends the meaning of spectroscopy to include techniques that do not even involve electromagnetic radiation, such as acoustic, mass and electron spectroscopy (Skoog et al, 2004).

Spectroscopic methods are mostly classified as atomic, molecular or ionic based on whether or not they apply to atoms, molecules or ions. The nature of their interactions can also be used to classify spectroscopic methods (Lewis, Lee and Kidder, 2004). These can be divided in three categories; the absorption spectroscopy which uses the range of the electromagnetic spectra in which substance absorbs photons. Infrared, ultraviolet, visible and microwave spectroscopy are molecular techniques of absorption spectroscopy. Second category is the emission spectroscopy that uses the range of electromagnetic spectra in which photons are emitted by the substance. The last category is scattering spectrometry where the amount of light that a substance scatters depends on polarization angles and wavelength. An example of the application of light scattering spectroscopy is Raman spectroscopy.

Spectroscopy is seen as a suitable and precise analytical method in quality control analysis hence; this review covers the applications of various spectroscopic methods in the analyses of biodiesels given that biodiesel has gained considerable attention in recent years due to its merits: biodegradable, renewable, non-toxic, less emission of gaseous and particulate pollutants with higher cetane number than normal fossil fuels. Biodiesel has good fuel properties: high flash point and good lubricity (Kouzu and Hidaka, 2012). Emphasis in this review is made on Infrared spectroscopy: Fourier transform (FT-IR) and Near-Infrared (NIR), Nuclear Magnetic Resonance Spectroscopy (NMR), Ultraviolet-Visible Spectroscopy (UV), Thermal lens spectroscopy (TLS) and Mass spectroscopy (MS).

2. Literature Review
2.1 Infrared Spectroscopy
FT-IR is being employed as a modern analytical technique for detecting the conversion of biodiesel because it is a fast and easy detection method. Raw oils and the methyl esters are noted as fairly strong absorbers in the infrared region of the electromagnetic spectrum. From a study of the literature, there are units that use an integration of the side (1750 – 1760 cm\(^{-1}\)) of the carbonyl peak (~ 1744 cm\(^{-1}\)) to monitor the progress of the reaction. Lin-vienet al. (1991) studied this method to be effective in a known system but noted its limitation because it is not specific for the end product and there could be a number of interferences. This method is however, being used because spectral resolution is not needed for more specific analysis. They pointed out that the peak typical of the methyl ester (OCH\(_3\)) at 1436 cm\(^{-1}\) is very narrow and moves along the raw oil peak. These characteristics were noted to make the peak unattractive for monitoring the progress of the biodiesel reaction. However, they observed the peak measurement to give a direct indication of the attachment of the alkyl group of the alcohol with the fatty acids of the triglycerides but the peak is not influenced by the alkyl group (-CH\(_3\)) (Lin-Vien, Colthup, Fateley and Grassellil, 1991)

Ivanoiu and others (2011) performed a comparative study on biodiesel synthesis from different vegetable oils and used infrared spectroscopy using KBr plates in the range of 4000-400 cm\(^{-1}\). Figure 1 displays the infrared spectra of biodiesel from palm oil, soybean oil and sunflower oil they obtained. The ester carbonyl group stretching vibration at 1740 cm\(^{-1}\) is shown by strong bands, esteric –COC vibration at 1171 and 1207 cm\(^{-1}\) reveals medium intensity bands, and the presence of the (CH\(_2\)_n) group vibration band is seen at 724 cm\(^{-1}\). They observed the absence of a broad band at the 2500-3300 cm\(^{-1}\) region which confirms the low moisture and free fatty acid content of the sample (Ivanoiu, Schmidt, Peter, Rusnac and Ungurean, 2011)
Furthermore, Bergougnou et al. (2009) produced biodiesel from jatropha curcas oil using potassium carbonate as the catalyst and Bruker IFS 55 FT-IR was used for analysis with an ATR (Attenuated Total Reflectance) cell made of ZnSe. They monitored the progress of the transesterification reaction by measuring the FT-IR area (1446-1428 cm\(^{-1}\)) under the methyl (O-CH\(_3\)) peak (1436 cm\(^{-1}\)). This area reflected the methyl esters of all types of fatty acids in the biodiesel. They also qualitatively evaluated the presence of soap by measuring the area of a single FT-IR peak in the 1597 – 1544 cm\(^{-1}\) range of the “unwashed sample” spectrum. They took precautions to ensure that the spectra were not saturated when performing the analysis because the raw oil and the methyl esters are fairly strong absorbers in the infrared region. They observed that saturated spectra exist when none of the IR light is transmitted at a particular wavelength and all the light is absorbed (Bergougnou, Chinmoy and Ernest, 2009). They discussed that under this circumstance, it is impossible to make a quantitative analysis based on the peak. In saturated spectra however, the peaks either have the same height or appear to be “grassy”. The spectra they obtained are shown below in figures 2 and 3.

Zhang reported on the infrared study of biodiesel (Zhang, 2012) and figure 4 illustrates the functional groups absorbed in the mid-IR regions while figure 5 compares the spectra of biodiesel and petrodiesel.

Knothe (1999) used Near Infrared spectroscopy (NIR) in monitoring the transesterification reaction (Knothe, 1999). He used the difference in the NIR spectra of the compounds as the basis for quantifying the turnover from triacylglycerol feedstock to methyl ester products. He observed that at 6005 cm\(^{-1}\) and at 4425–4430 cm\(^{-1}\), the methyl esters display peaks, while only shoulders were exhibited by the triacylglycerols. He also distinguished Ethyl esters in a similar way (Knothe, 1999). He noted that the mid–range IR spectra of triacylglycerols and methyl esters of fatty acids are almost identical and very difficult to differentiate. He observed that ethyl esters, and maybe even higher esters, may be differentiated similarly by NIR from triacylglycerols, but did not report any results.

Furthermore, Knothe in another work applied NIR spectroscopy to a transesterification reaction in progress on a 6 L scale. Here, he obtained spectroscopic results using both \(^1\)H–NMR and NIR (Knothe, 2000). The results of both spectroscopic methods, which can be correlated by simple equations, did concur. He used two NMR approaches, one being the use of the methyl ester protons (peak at 3.6 ppm) and the protons on the carbons next to the glyceryl moiety (α–CH\(_2\); peaks at 2.3 ppm) (Knothe, 2000), and gave the equation for determining conversion (given as a %) as:

\[
C_{ME} = 100 \times \frac{5I_{ME}}{5I_{ME} + 9I_{TAG}} \quad \text{Equation 1 (Knothe, 2000)}
\]

where \(I\) refers to integration values, while ME and TAG refer to methyl esters and triacylglycerol. The second approach was the use of the methyl ester protons and the protons of the glyceryl moiety (peaks at 4.1–4.3 ppm) in the triacylglycerols (Knothe 2000). His results are shown in figures 6 and 7.

Sadeghi–Jorabchi et al. (1994) discussed about determining the amount of biodiesel in lubricating oil (Sadeghi-Jorabchi et al., 1994). The problem they investigated is significant because biodiesel blended with lubricating oil can cause dilution of the lubricant, which can ultimately result in engine failure. They observed that dilution was attributed to the higher boiling range of biodiesel (Sadeghi-Jorabchi et al., 1994; Siekmann et al., 1982) compared to conventional diesel fuel, whose more volatile components have less chance to dilute the lubricant. These authors used mid–range IR spectroscopy with a fiber–optic probe to
determine biodiesel content in lubricating oil. The spectra range 1820–1680 cm\(^{-1}\), which is typical for carbonyl absorption was used and this range is not observed in conventional diesel fuel nor in the lubricating oil (it is important to understand that this range is not suitable for distinguishing vegetable oils and their methyl esters because of their identical carbonyl absorptions in the mid–IR range). Previously, other authors also reported the use of IR spectroscopy (without the aid of a fiber–optic probe) in the range 1850–1700 cm\(^{-1}\) to analyze biodiesel in lubricating oil (Siekmann et al., 1982). They found that the absorption of oxidation products at 1710 cm\(^{-1}\) did not disturb the carbonyl absorption at 1750 cm\(^{-1}\).

2.2 Nuclear Magnetic Resonance Spectroscopy
Gelbard et al. (1995) reported on spectroscopic determination of the yield of a transesterification reaction using \(^1\)H–NMR (Gelbard et al., 1995). Their results depict the \(^1\)H–NMR spectrum of a transesterification reaction in progress. These authors used the protons of the methylene group adjacent to the ester moiety in triglycerols and the protons in the alcohol moiety of the product methyl esters to monitor the yield. The conversion is illustrated by the equation given below. (Their terminology is slightly modified here):

\[
C = 100 \times \frac{2A_{ME}}{3A_{\alpha–CH2}} \quad \text{Equation 2 (Gelbard et al, 1995)}
\]

Where \(C\) = conversion of triacylglycerol feedstock (vegetable oil) to the corresponding methyl ester.

\(A_{ME}\) = integration value of the protons of the methyl esters (the strong singlet peak).

\(A_{\alpha–CH2}\) = integration value of the methylene protons.

They derived the factors 2 and 3 from the fact that the methylene carbon possesses two protons and the alcohol (methanol–derived) carbon has three attached protons.

Furthermore, Dimmig et al. (1999) studied the reaction rates of the transesterification of rapeseed oil with methanol by \(^{13}\)C–NMR (Dimmig, Radig, Knoll, and Dittmar, 1999) using benzene–\(d6\) as solvent. For the internal quantification standard, they used the signals at approximately 14.5 ppm of the terminal methyl groups since they are not affected by the transesterification reaction. They observed that the product methyl esters showed signal peaks at around 51 ppm, and the glyceridic carbons of the mono–, di–, and triacylglycerols showed peaks at 62–71 ppm (Dimmig, Radig, Knoll, and Dittmar, 1999). Further analysis of the latter peak range allowed them to determine the transesterification kinetics, and they found the formation of partial acylglycerols from the triglycerols as the slower, rate–determining step.

2.3 Ultraviolet-Visible Spectroscopy
Ultraviolet – Visible (UV) spectroscopic analysis is fast becoming a common technique for providing analytical data on degradation of biodiesel. Souza et al. (2011) in their study of Oxidative degradation of Sunflower Biodiesel using UV spectroscopy used three antioxidants (blend (hydrogenated cardanol + 5-n-pentadecyl-2-tert-butylphenol), 5-npentadecyl- 2-tert-butylphenol and ionol BF200) to evaluate if they can decrease the rate of oxidation of biodiesel from sunflower oil under thermal stress. Changes in peroxide values were studied using iodometry and UV-Vis spectroscopy to check for oxidative degradation. Their values reveal the blend and 5-n-pentadecyl-2-tert-butylphenol to be of important potentiality when compared with ionol BF200. 5-n-pentadecyl-2-tert-butylphenol and the blend decreased the absorbance around 31% (Souza et al., 2011). In their results, sunflower biodiesel/A2, sunflower biodiesel/A3 and sunflower biodiesel/AC formulations gave better results when compared with the biodiesel that has no antioxidant as illustrated by figures 8 and 9.
2.4 Thermal Lens Spectroscopy
Another modern spectroscopic method used in the analysis of biodiesel is Thermal lens (TL) spectroscopy applied by Ventura et al. (2012) to biofuels to test its potential to distinguish diesel from biodiesel in blended fuels. Both the heat and mass diffusion effects observed using a TL procedure provide significant information about biodiesel concentrations in blended fuels. The results indicate that the mass diffusivity decreases 32% between diesel and the blend with 10% biodiesel added to the diesel (Ventura et al., 2012). This simple TL procedure has the potential to be used as an analytical method of analysis to certify the mixture and quality of biodiesel-diesel blends.

2.5 Mass Spectroscopy
Amaiset al. (2010) reported an analytical procedure for direct introduction of biodiesel samples into an inductively coupled plasma mass spectrometer (ICP-MS) by using micro emulsion for sample preparation. They evaluated the accuracy of the procedure by using addition-recovery experiments for biodiesel samples from different sources. Their report shows the attainment of optimum performance using oxygen while correcting transport disturbances. They concluded that the method based on the formation of micro emulsion was ideal for the introduction of biodiesel samples in ICP-MS (Amais et al., 2010). Furthermore, Amaiset al. (2010) observed that Ti and Zn were the elements present in the highest concentrations for different biodiesel samples, varying from 145.8 to 180.0 ng mL$^{-1}$ and from 64.7 to 184.3 ng mL$^{-1}$ for Ti and Zn, respectively. They noted contamination and variability of Zn to be responsible for its wide concentration range (Amais et al., 2010). Their studies also showed relatively high concentration observed for Ti probably originating from the use of solid-based catalysts such as TiO$_2$ employed in the biodiesel production process. For other analytes, they observed all concentrations determined were lower than those found for Ti and Zn. The lowest concentrations they obtained in the different biodiesel samples were determined for Cd as shown in table 1.

3.0 Summary and Conclusion
Several spectroscopic analytical methods have been investigated for fuel quality assessment and production monitoring of biodiesel. However, physical properties-based methods have been explored less, and it appears that this may be an area for further study. However, no method can simultaneously satisfy all criteria of determining all trace contaminants with minimal investment of time, cost, and labor. A fast and easy-to-use method that may be adaptable to production monitoring, such as NIR can be used for routine analysis while NMR and mass spectroscopy are more advanced techniques that should be further studied to enable quality control of biodiesel and its blends. Determining the blends and contaminants in biodiesel need further studies. Advanced spectroscopic techniques should be applied in the study of biodiesels and their blends to provide more reliable references.
Figures and Table

Figure 1. The Infrared spectra of biodiesel obtained from palm (POB), sunflower (SFOB) and soybean (SOB) oils, (Source: Ivanoiu, A et al.2011, Comparative Study on Biodiesel Synthesis from Different Vegetables Oils)

Figure 2: FTIR - ATR Spectra of pure biodiesel produced from jatropha (JTC) oil and raw jatropha oil. (Source: Bergougnouet al. 2009, Biodiesel Production from JatrophaCurcas Oil using Potassium carbonate as an unsupported catalyst)
Figure 3: Change in methyl peak (O-CH3) with molar concentration of Fatty Acid Methyl Esters in the standard solution (Source: Bergougnouet al. 2009 Biodiesel Production from JatrophaCurcas Oil Using Potassium Carbonate as an Unsupported Catalyst.)

Figure 4: Functional group absorptions in the mid-IR region. (Source: Zhang, 2012. Review on analysis of biodiesel with infrared spectroscopy)

Figure 5. Diesel and Biodiesel IR spectra.(a) The mid-IR spectra and (b) The spectra in near-IR region.(Source: Zhang, 2012. Review on analysis of biodiesel with infrared spectroscopy)
Figure 6: $^1$H–NMR spectrum of a progressing transesterification reaction. Mono–, di–, or triacylglycerols show signals at 4.1-4.3 ppm. Methyl ester formation shows a strong singlet at 3.6 ppm. The signals at 2.3 ppm result from the protons on the CH2 groups adjacent to the methyl or glyceryl ester moieties (–CH2CO2CH3 for methyl esters). The indicated signals are for quantification purposes. (Source: Knothe, G 2000.)

Figure 7: NIR spectra of methyl soyate (SME), soybean oil (SBO), and SME containing significant amounts of methanol. Quantification and distinguishing of spectra is made possible through the inscribed wave numbers. (Source: Knothe, G 2000.)
Table 1. Concentrations of various metals in biodiesel samples

<table>
<thead>
<tr>
<th>Isotope</th>
<th>African Palm</th>
<th>Castor beans</th>
<th>Palm</th>
<th>Unknown sample</th>
<th>Soybeans</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>0.14±0.01</td>
<td>&lt;0.08</td>
<td>&lt;0.08</td>
<td>0.25±0.04</td>
<td>&lt;0.08</td>
</tr>
<tr>
<td>Co</td>
<td>5.94±0.44</td>
<td>6.04±0.49</td>
<td>5.87±0.49</td>
<td>6.11±0.48</td>
<td>5.92±0.86</td>
</tr>
<tr>
<td>Mn</td>
<td>&lt;0.75</td>
<td>&lt;0.75</td>
<td>&lt;0.75</td>
<td>1.230±0.056</td>
<td>&lt;0.75</td>
</tr>
<tr>
<td>Pb</td>
<td>&lt;0.15</td>
<td>&lt;0.15</td>
<td>&lt;0.15</td>
<td>0.401±0.006</td>
<td>&lt;0.15</td>
</tr>
<tr>
<td>Ti</td>
<td>172.2±26.8</td>
<td>180.0±12.5</td>
<td>145.8±21.0</td>
<td>159.8±17.8</td>
<td>158.8±14.6</td>
</tr>
<tr>
<td>Zn</td>
<td>&lt;4.2</td>
<td>64.7±2.8</td>
<td>&lt;4.2</td>
<td>184.3±8.4</td>
<td>&lt;4.2</td>
</tr>
</tbody>
</table>


References


