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The Analysis of Biodiesel Blends by Fourier Transform Infrared Spectroscopy (FT-IR)

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Abstract

The increasing importance of sustainability in energy production worldwide has led to a recent global effort in the reduction of our dependence on fossil fuels and a commitment to the use of fuels derived from renewable biological sources such as biodiesel produced from plant based crops. Biodiesel consists of fatty acid methyl esters (FAME) that are produced from a catalyzed transesterification reaction involving methanol and triglycerides obtained from vegetable oils such as soybean and rapeseed. Considering biodiesel has many desirable diesel fuel properties, such as very low sulphur content, reduction in engine wear, and is cleaner burning than fossil based diesel, it has become of considerable importance to be able to accurately verify the FAME content of various biodiesel fuel blends while they are in production and/or in distribution chains. To that end, this experiment worked to precisely and accurately determine the FAME content of commonly available biodiesel blends through the use of the instrumental analysis technique Fourier transform infrared (FT-IR) spectroscopy. Here FAME concentrations where found using regression analysis techniques such as Beer's Law and/or principal component regression with correlation coefficients (R^2) values often being found to be ≥ 0.999 . Precision in terms of percent relative standard deviation (%RSD) and accuracy in terms of percent relative error (%RE) were also determined. Additionally, sample handling and data acquisition optimization procedures of the FT-IR instrument, that utilized an integrated 9 bounce (reflection) diamond attenuated total reflectance (ATR) sample interface, were also explored. All calibration standards, quality controls (QC), and samples were run in triplicate sets.

Keywords: Biodiesel, FT-IR, Beer's Law

1. Introduction

With the increase in importance of sustainability in energy production worldwide there has been a drive in the effort to reduce our current dependence on fossil fuels and a commitment to the use of fuels derived from renewable and/or biological sources such as biodiesel produced from plant based feedstocks. Biodiesel consists of fatty acid methyl esters (FAME), compounds that are produced from a catalyzed transesterification reaction involving triglycerides obtained from vegetable oils such as soybean, rapeseed, palm and coconut as shown below.



Figure 1. Transesterification reaction of triglycerides

Here, in Figure 1, $R = C_8-C_{18}$ with 0-3 double bonds. Biodiesel, depending upon the relative amounts of FAME compounds present, has been shown to have many desirable fuel properties such as being cleaner burning than fossil based diesel fuel, contain a lower sulphur content, and help in the advancement of reduction in engine wear. With this in mind, it has become of considerable importance to be able to accurately verify the amount FAME compounds present in various biodiesel fuel blends while they are still in production and/or in distribution chains. Presently, commercially pure FAME biodiesel designated as B100 is blended with Number 2 diesel to create biodiesel fuels with a range of 1 to 20 percent by volume total FAME compounds content, or B1 to B20, respectively. To that end, in this experimental laboratory approach the determination of the FAME compounds concentration in commonly available B5 and B20 biodiesel samples, as well as, B6 and B23 quality control (QC) biodiesel standards, was explored through the use of a six point calibration curve and a fourier transform infrared (FT-IR) spectrometer utilizing a novel integrated 9 bounce (reflection) diamond attenuated total reflectance (ATR) sample interface.¹

The FT-IR data that is obtained from this type of experimental approach is processed with a modified form of the Beer's Law relationship that takes place between the absorbance of an individual analyte being directly proportional to the concentration of that analyte, and the transmittance (fraction of light passing through the analyte) being logarithmically related to that analyte's concentration as shown in equation (1) below:

$$A = \log\left(\frac{P_0}{P}\right) = -\log T = \varepsilon bc \tag{1}$$

Here A is the absorbance, P_0 is the incident radiant power, P is the transmitted radiant power, ε is the molar absorptivity at a specific wavelength, b is the light path length through the sample cell containing the analyte, and C is the concentration of the analyte.²⁻⁴ However, since the FT-IR spectrophotometer is utilizing an integrated 9 reflection diamond ATR sample interface, there is no sample cell, and the light path length, b, can be thought of as the product of the light penetration depth, d_p , as shown in equation (2) below and the contact area, a_c , on the surface of the diamond ATR sample interface.

$$d_{p} = \frac{\lambda_{c}}{2\pi \left[\sin^{2}\theta - (n_{s} / n_{c})^{2}\right]^{1/2}}$$
(2)

The penetration depth, d_p , depends on the wavelength of the beam (i.e., peak of interest), λ_c , the angle of incidence, θ , the diamond prism refractive index, n_c , and the sample refractive index, n_s . Note that once θ , n_c , and n_s are set for the ATR instrumental setup only λ_c will affect your penetration depth. In fact, the wavelength dependence on the penetration depth increases by a factor of ten between 4000 and 400 cm⁻¹, yielding, for most diamond ATR sample interfaces a penetration depth of 1-2 µm at 1000 cm⁻¹. The contact area, a_c , value depends upon the sample contact coverage on the face of the diamond prism. Consequently, once the wavelength, or the peak of interest, is determined and the contact area between the analyte and the surface area of the diamond prism remain constant the analyte peak absorbance intensity then becomes directly proportional to the analyte concentration as shown in equation (3) below, yielding:

$$A = kC$$

Where, *k*, is the combined single absorptivity constant of, ε , d_p , and a_c . This proportionality relationship now relates *A* and *C* for any given analyte at a particular wavelength. Thus for a plot of *A* versus *C* (i.e., a Beer's Law plot), *k* is now the slope of the line. Additionally it was also important to remember that for Beer's Law to be valid for quantitation purposes the slope of the line must be linear. In practice, we found, as was also noted in literature, that FT-IR ATR calibration curves commonly exhibit excellent linearity (e.g., $R^2 = 0.999$) for liquid samples when they completely cover the entire face of the diamond ATR prism during measurements.⁵

2. Methodology

2.1. Absorption Spectra

A number 2 diesel fuel working solution standard, that was considered to be traditional diesel fuel derived from fossil fuel feedstock, was prepared by transferring approximately 1.0 mL of number 2 diesel fuel stock solution to a 1.5-mL snap top Eppendorph tube. This was followed by a B15 biodiesel fuel working solution standard, which was derived from 15% by volume plant fuel feedstock to 85% by volume fossil fuel feedstock, being prepared by transferring with a mechanical pipette a 150 μ L of B100 biodiesel fuel stock solution with 850 μ L of number 2 diesel fuel stock solution to a 1.5-mL snap top Eppendorph tube and mixing well with a vortexer. The absorption spectra for the two working solution standards (i.e., number 2 diesel fuel and B15 biodiesel fuel), as shown in Figure 2, was then taken with a Perkin Elmer Spectrum Two FT-IR fitted with a 9 reflection diamond ATR sample interface (Waltham, MA) from 4000 cm⁻¹ to 400 cm⁻¹. Spectral resolution was set to 4.0 cm⁻¹, data interval set to 1 cm^{-1} , and the number of accumulations set to 6 scans per integration to determine by inspection if these two working solution standards absorption spectra showed a wavelength region where there was a strong absorption of FAME compounds. More specifically, to explore if there was a wavelength region where there was a strong absorption of FAME compounds present in the B15 biodiesel fuel working solution standard and ideally no absorption of FAME compounds in that same region present in the number 2 diesel fuel working solution standard. Once this wavelength region of interest was found for the FAME compounds this was followed by obtaining a second set of individual absorption spectra from 1900 cm⁻¹ to 1600 cm⁻¹ under the same instrumental parameters listed above for each of the two working solution standards.



Figure 2. Number 2 diesel fuel and B15 biodiesel fuel working solutions.

2.2. Direct Calibration Curve

Six sets of biodiesel fuel direct calibration standards (i.e., B2, B7, B12, B17, B22, and B27) were prepared by transferring with a mechanical pipette 20, 70, 120, 170, 220, and 270 µL of the B100 biodiesel fuel stock solution with 980, 930, 880, 830, 780, and 730 µL of the number 2 diesel fuel stock solution to 1.5-mL snap top Eppendorph tubes, respectively and mixing well with a vortexer. Then the absorption spectra for each of the 6 biodiesel fuel direct calibration standards, as shown in Figure 3, was taken from 1900 cm⁻¹ to 1600 cm⁻¹ under the same instrumental parameters listed in section 2.1 above. The data that was generated from this was then used to build a linear Beer's Law regression plot (i.e., A vs. C) via two different direct calibration data analysis methods. The first data analysis method employed a peak height method at which the wavelength of maximum absorption of the FAME compounds peak heights for each of the direct calibration standards was determined by the carbonyl band at or near 1745 cm⁻¹ measured to a baseline drawn between 1820 to 1670 cm⁻¹(i.e., instrumentally baseline 1 was set at 1820 cm⁻¹ and baseline 2 was set at 1670 cm⁻¹) as shown in Figure 4. The second data analysis method employed a peak area method at which the peak areas representing the maximum absorption of FAME compounds for each of direct calibration standards were obtained from the peak area taken from the region between 1820 to 1670 cm⁻¹ in which a baseline was also drawn between that region of 1820 to 1670 cm^{-1} (i.e., again as was the case above baseline 1 was set at 1820 cm⁻¹ and baseline 2 was set at 1670 cm⁻¹) as shown in Figure 5. Additionally, it is important to note that all of the direct calibration standards were immediately scanned by the FT-IR instrument once the diamond ATR sample interface surface was covered with the liquid standard to reduce the effects of evaporation of biodiesel fuel.



Figure 3. B2, B7, B12, B17, B22, and B27 biodieselfuel direct calibration standards.



Figure 4. Peak height method with B27 biodiesel fuelat 1745 cm⁻¹ with baseline from 1820 cm⁻¹ to 1670 cm⁻¹.



Figure 5. Peak area method with B27 biodiesel fuel with baseline from 1820 cm⁻¹ to 1670 cm⁻¹

2.3. Samples And Quality Controls

Two sets of certified reference material (CRM) biodiesel fuel samples (i.e., B5 and B20) were prepared by transferring approximately 1.0 mL of solution to a 1.5-mL snap top Eppendorph tubes. This was followed by two sets of biodiesel fuel quality control samples (i.e., QCB6 and QCB23) being prepared by transferring with a mechanical pipette 60 and 230 μ L of the B100 biodiesel fuel stock solution with 940 and 770 μ L of the number 2 diesel fuel stock solution to 1.5-mL snap top Eppendorph tubes, respectively and mixing well with a vortexer. Then the absorption spectra for the B5 and B20 biodiesel fuel samples and the QCB6 and QCB23 quality control biodiesel fuel samples were taken from 1820 cm⁻¹ to 1670 cm⁻¹ under the same instrumental parameters listed in section 2.1 above. The data that was generated from this was then used to analyze the FAME compound content found from

both the peak height and peak area data analysis methods out lined in section 2.2 above for the linear Beer's Law regression plot (i.e., A vs. C) calibration curves, shown in Figures 6 and 7, respectively.



Figure 6. Peak height method direct calibration curve.



Figure 7. Peak area method direct calibration curve.

3. Results

Here, in Table 1 below, it was important to not only calculate the FAME compound concentrations of the B5 and B20 biodiesel fuel samples and the QCB6 and QCB23 quality control biodiesel fuel samples for both the peak height and peak area direct calibration methods shown in Figures 6 and 7 in section 2.3 above, but to also provide a measure of comparative accuracy between the two methods in the form of a percent relative error (%RE) calculation for the experimentally calculated FAME compound concentrations found in the B5 (%RE = 0.84) and B20 (%RE = 0.05) biodiesel fuel samples and theQCB6 (%RE = 1.51) and QCB23 (%RE = 0.28) quality control biodiesel fuel

samples when compared to what the true concentration values for both of these were originally (i.e., 5%, 20%, 6% and 23% by volume FAME).

Biodiesel Samples and Biodiesel QC Samples	B5	B20	QCB6	QCB23
Biodiesel Fuel (v%)	5	20	6	23
Biodiesel Fuel (v%) by Peak Height Method	4.81	19.83	5.67	22.91
Error in peak height method (%RE)	3.36	0.87	5.51	0.39
Biodiesel Fuel (v%) by peak Area Method	5.01	20.01	5.91	22.94
Error in peak area method (%RE)	0.84	0.05	1.51	0.28

Table 1. Biodiesel fuel samples and biodiesel fuel quality control samples.

4. Conclusion

This experiment has provided an experiment to precisely and accurately determine the FAME content of commonly available biodiesel blends through the use of the instrumental analysis technique Fourier transform infrared (FT-IR) spectroscopy. Here FAME concentrations for B5, B20, QCB6, and QCB23using the peak area of absorption method from 1820 to 1670 cm⁻¹ was found to be more accurate in all cases than using the peak height method at or near 1745 cm⁻¹. An example of this increase in accuracy with the peak area method can be seen in the comparison of QCB6 %RE of 1.51 for the peak area method to that of 5.51 for the peak height method. Moreover, the Beer's Law regression analysis that was employed in this experiment has also shown to have a high degree of correlation and/or fitting with the data set as shown by the correlation coefficients (R²) value of 0.9998 being obtained for the peak area method. Typically R² values of 0.9999 are considered to be an excellent fit to the data. Lastly, throughout the progression of this experiment, the application of learned Quantitative Analysis and Instrumental Analysis laboratory skills for the proper handling of samples, standards, and instrumentation were found to be especially rewarding given the quality of results shown in this experiment.

5. Future Work

The use of a chemometric analysis to analyze the whole spectrum should be explored with a full principle component regression in a comparative way to a Beer's Law regression to determine if a more statistically accurate concentration of FAME compounds can be found for biodiesel samples.

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7. References

1. Perston, B.; Harris, N. Biodiesel Blend Analysis by FT-IR, *Application Note*, Perkin Elmer Incorporated, Seer Green, UK, **2009**, 008859-1.

2. Harris, D.C. Fourier Transform Infrared Spectrophotometry, *Quantitative Chemical Analysis Eighth Edition*, W. H. Freeman and Company, **2010**, 467-472.

3. Skoog, D.A.; Holler, F.J.; Crouch, S.R. Infrared Spectroscopy, *Principles of Instrumental Analysis Sixth Edition*, Thomson Brooks and Cole, **2007**, 430-480.

4. Sawyer, D.T.; Heineman, W.R.; Beebe, J.M. Infrared Spectroscopy, *Chemistry Experiments for Instrumental Methods*, John Wiley & Sons, **1984**, 222-241.

5. Williams, S.; Sellors, J.; Wells, S. Biodiesel Concentration Measurements Using Attenuated Total Reflectance (ATR), *Application Note*, Perkin Elmer Incorporated, Shelton, CT, USA, **2009**, 007845B-1.