

Determining the Blend Level of Mixtures of Biodiesel with Conventional Diesel Fuel by Fiber-Optic Near-Infrared Spectroscopy and ^1H Nuclear Magnetic Resonance Spectroscopy

Gerhard Knothe*

USDA, ARS, NCAUR, Peoria, Illinois 61604

ABSTRACT: Biodiesel, defined as the alkyl esters (usually methyl esters) of vegetable oils, is miscible with conventional diesel fuel at all blend levels. Until the present time, no rapid and reliable analytical method has existed for determining the blend level of biodiesel in conventional diesel fuel. In the present work, near-infrared (NIR) and nuclear magnetic resonance (NMR) spectroscopies were used to determine the blend level of biodiesel in conventional diesel fuel. Several regions in the NIR region (around 6005 cm^{-1} and $4800\text{--}4600\text{ cm}^{-1}$) are suitable for this purpose. The method is rapid and easy to use, and does not require any hardware changes when using the same instrument for monitoring the biodiesel-producing transesterification reaction and determining biodiesel fuel quality. In ^1H NMR spectroscopy, the integration values of the peaks of the methyl ester moiety and the aliphatic hydrocarbon protons in biodiesel and conventional diesel fuel were used for determining blend levels. The results of NIR and NMR blend level determinations are in good agreement.

Paper no. J9859 in *JAACS* 78, 1025–1028 (October 2001).

KEY WORDS: Biodiesel, biodiesel blends, diesel fuel, fiber-optic probe, methyl soyate, near-infrared spectroscopy, nuclear magnetic resonance spectroscopy.

Biodiesel is an alternative diesel fuel defined as the mono-alkyl esters of vegetable oils and animal fats (1,2). It is derived from vegetable oils through a transesterification reaction with the appropriate alcohol, usually methanol. Both in neat form and in blends with conventional petroleum-derived diesel fuel (DF), initial stages of biodiesel commercialization have been successful in many countries around the globe. In the United States, biodiesel is derived mainly from soybean oil (methyl soyate), in Europe from rapeseed oil, and in countries with a tropical climate from tropical oils, although waste frying and cooking oils are also possible feedstocks. In the United States, both neat biodiesel and “B20” (a blend of 20% biodiesel in conventional DF) are recognized as alternative fuels under criteria of the Energy Policy Act (EPACT).

Although numerous methods have been developed for assessing fuel quality of biodiesel and monitoring the transesterification reaction (3), at the present no report exists on de-

termining the blend level of biodiesel with conventional DF. Addressing this problem has become more urgent with the definition and increased use of B20 as an alternative diesel fuel, as well as the potential use of other biodiesel blend levels. Consequently, it is necessary to instill confidence in users of biodiesel blends that the fuel they are using indeed conforms to regulations, standards, and expected blend levels.

Recently, we reported that near infrared (NIR) spectroscopy using a fiber-optic probe could be used to rapidly and easily assess biodiesel fuel quality as well as to monitor a progressing transesterification reaction (4,5). ^1H Nuclear magnetic resonance (NMR) spectroscopy is also suitable for monitoring the transesterification reaction (5,6). NIR results can be correlated to those obtained from ^1H NMR spectroscopy (5). In this paper, NIR spectroscopy, again using a fiber-optic probe for acquiring spectra, and ^1H NMR spectroscopy were used for determining the blend level of biodiesel in conventional DF.

EXPERIMENTAL PROCEDURES

Biodiesel (methyl soyate) that complied with biodiesel fuel specifications was obtained from Ag Environmental Products (product name Soy GoldTM; Lenexa, KS). Methyl ester quality was checked by NMR spectroscopy (Bruker ARX-400 spectrometer; Bruker, Rheinstetten, Germany; 400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR; solvent CDCl_3) because this method will yield information on all possible contaminants from one sample. No significant contaminants were observed, and this material was treated as 100% methyl esters for purposes of this study. The NIR spectrum also corresponded to that reported previously (4). Off-road No. 2 diesel fuel (with red dye) was obtained from Cady Oil Co. (Peoria, IL). The dye (32.5% Solvent Red 164 in xylene with 13.5% other ingredients) was present at a low level (12 ppm) and thus did not affect the present results.

NIR spectra were obtained on a PerkinElmer (Norwalk, CT) Spectrum 2000 spectrometer equipped with a Galileo (Sturbridge, MA) transmission-type fiber-optic probe. Quantitation methods were developed on a personal computer (Spectrum 2000 and Quant+ software; PerkinElmer). Method calibrations were carried out automatically by using the corresponding software feature. Spectra were converted to absorbance values when developing a method. As the algorithm

*Address correspondence at USDA, ARS, NCAUR, 1815 N. University St., Peoria, IL 61604. E-mail: knothegh@mail.ncaur.usda.gov

for quantitation, principal component analysis was used instead of the partial least squares regression used in the previous work (4). When determining the blend level of a sample, several statistical parameters (*M*-distance and residual ratio) were checked to verify that the sample whose composition was being predicted was representative of the samples used in the calibration set (4).

Samples (100 mL) were prepared in beakers by mixing the methyl soyate with the diesel fuel to defined blend levels. The fiber-optic probe was immersed into the sample so that the path of the beam passed through the solution. All spectra were recorded at ambient temperature (22–24°C). Besides neat methyl soyate and neat DF, the spectra of blends of 1–10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30, 32, 34, 36, 38, 40, 42, 44, 46, 48, 50, 55, 60, 70, 75, 80, 85, 90, and 95% methyl soyate with conventional DF were recorded. For checking reproducibility, an additional series of 10, 20, 30, 40, 50, 60, 70, 80, and 90% methyl soyate with conventional DF was prepared, and the spectra were recorded. After recording a spectrum, the fiber-optic probe was cleaned by successive treatment with ethanol and acetone by immersion in each stirred solvent for several minutes. NMR spectra of blends were obtained as indicated above.

RESULTS AND DISCUSSION

Spectroscopic or chromatographic methods have been used most often for assessing biodiesel fuel quality and monitoring transesterification (3). In a few cases, hyphenated techniques combining the advantages of both types of analyses have been reported. However, for determining the blend level of biodiesel in conventional DF, chromatographic methods appear less suitable due to the complex mixture of compounds conventional DF represents. Especially in gas chromatography (GC) analyses, it can be expected that that complexity will make it difficult to determine the nature of a compound causing a specific peak. This is especially the case if a detector such as a flame-ionization detector is used, which does not provide any direct structural information on the nature of the eluting compounds. Thus the use of a mass selective detector appears advisable, but this increases cost and requires more complex interpretation, and peak overlapping may still cause problems. High-performance liquid chromatography is likely more suitable for blends than gas chromatography because classes of compounds may elute instead of individual compounds. Methods based on physical properties may also warrant additional study.

Spectroscopic methods, on the other hand, give results in which all components of a mixture contribute simultaneously to the resulting spectrum. They can only be used for quantitation if appropriate components in the mixture exhibit unique peaks well separated from those of other components. The sensitivity is usually reduced compared to chromatographic methods. Acquisition of the information using spectroscopic methods is often more rapid and facile compared to chromatographic methods.

In NIR spectroscopy, peaks at 6005 cm^{-1} and 4425–4430 cm^{-1} were shown to be suitable for distinguishing vegetable oils and their methyl esters, as described previously (4). The exact wavenumber range suitable for quantitative determination was determined empirically. In order to simplify analyses by not requiring hardware changes on the spectrometer such as changing beam splitters, in the present work, the NIR region was investigated for its suitability in distinguishing vegetable oil methyl esters (in this case, methyl soyate) from conventional DF. The NIR region was selected for another reason. Theoretically, the mid-IR region could be used for distinguishing vegetable oil methyl esters from conventional diesel fuel due to the carbonyl peak 1740–1750 cm^{-1} displayed by esters and lacking in conventional DF. The mid-IR carbonyl absorption has been used for determining biodiesel contamination in lubricating oil (7,8). However, the carbonyl peaks in the mid-IR range have the drawback that they are virtually identical for vegetable oils and their methyl esters as both contain the carbonyl functionality in ester form. Thus, from the carbonyl absorption it may not be possible to distinguish whether conventional DF was blended with methyl esters (biodiesel) or vegetable oil feedstock.

The transmittance NIR spectra of methyl soyate, conventional DF, and a 50:50 blend thereof are depicted in Figure 1. The spectra display differences at 6005 cm^{-1} and 4600–4800 cm^{-1} , which permit determination of the blend

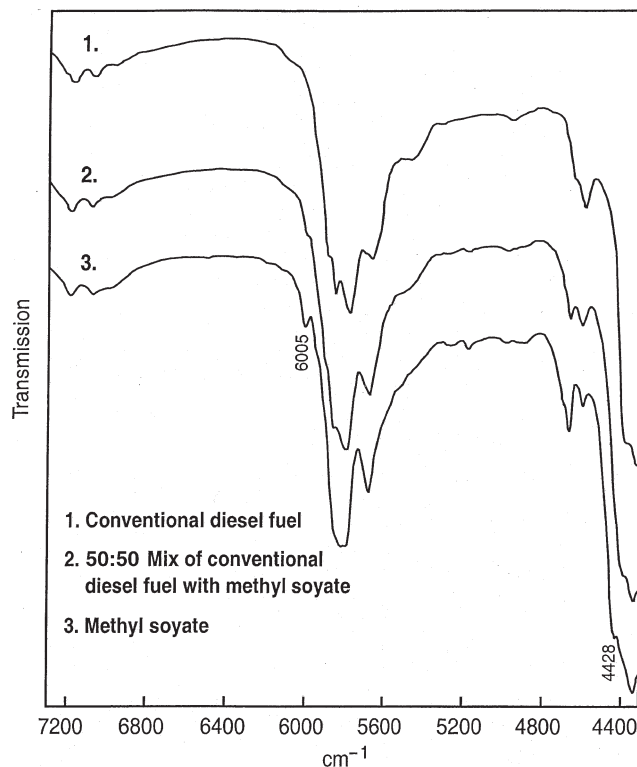


FIG. 1. Near-infrared (NIR) spectra in the region 7300–4300 cm^{-1} of: (1) neat conventional, petroleum-derived diesel fuel; (2) a 50:50 mixture of conventional diesel fuel with methyl soyate (biodiesel); and (3) neat methyl soyate (biodiesel).

level of biodiesel blends with conventional diesel fuel. Spectra were determined of solutions of predetermined blend levels of methyl soyate (biodiesel) with conventional DF. For validation of the NIR method, arbitrarily selected spectra were used for building quantitation methods, and all samples were then treated as being of unknown concentration when determining blend levels in a procedure similar to that applied previously to monitoring transesterification and assessing fuel quality (4,5).

As mentioned above, ¹H NMR is also suitable for monitoring the transesterification reaction, and NMR and NIR results can be correlated. Note that ¹³C NMR also has been applied to monitoring the transesterification reaction (9). Therefore, it was straightforward to apply ¹H NMR to the determination of biodiesel blend levels with conventional DF. The ¹H NMR spectra of methyl soyate and No. 2 conventional DF are depicted in Figure 2. Note that the ¹H NMR spectrum of conventional DF exhibits a multitude of peaks at 7–8 ppm that arise from the aromatic compounds present in that fuel. Those peaks were not taken into account in biodiesel blend level determinations.

For blend level determination by ¹H NMR spectroscopy, the peak of the methyl ester protons in the region of 3.6–3.7 ppm was selected as one standard peak area, and the second standard peak area was the cluster of peaks between 0.8 and 3.0 ppm, which arises from the methylene and terminal methyl protons of the hydrocarbon moieties in conventional DF and biodiesel, and the peaks at 5.3–5.4 ppm arising from the protons attached to the olefinic carbons in biodiesel. The integration value of the methyl ester protons should be set to 3 in all spectra regardless of blend levels. Otherwise, determining the blend level is carried out by first calculating the normalization factor N derived from setting the integration value $I_{ME,blend}$ of the peak of the methyl ester protons in a blend to 3 (Eq. 1).

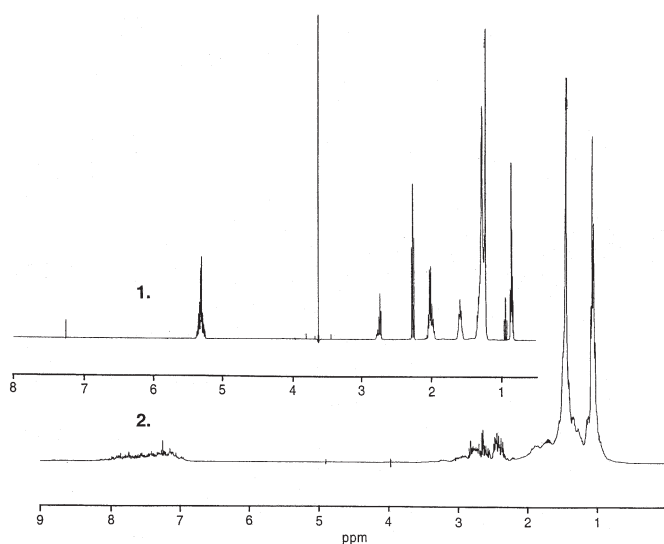


FIG. 2. ¹H Nuclear magnetic resonance (NMR) spectra of (1) methyl soyate (biodiesel) and (2) conventional, petroleum-derived diesel fuel.

$$N = \frac{3}{I_{ME,blend}} \quad [1]$$

Dividing the integration value $I_{CH,biodiesel}$ (the CH, CH₂, and CH₃ integration values in the hydrocarbon moieties of neat biodiesel) by the corresponding integration value $I_{CH,blend}$ of the peak cluster of all the hydrocarbon protons in the blend (including the integration value of the olefinic protons in biodiesel) multiplied by N , and then multiplying by 100 yields the blend level $C_{biodiesel}$ of biodiesel in conventional diesel fuel in percent.

$$C_{biodiesel} = 100 \times \frac{I_{CH,biodiesel}}{N \times I_{CH,blend}} \quad [2]$$

The value $I_{CH,biodiesel}$ depends on the fatty acid composition of the biodiesel used when taking into consideration the olefinic proton peaks at 5.3–5.4 ppm; thus, at least a reasonable approximation thereof must be known. Accordingly, for purposes of this work $I_{CH,biodiesel}$ was set to 32.5, taking into consideration the fatty acid composition of methyl soyate and resulting from the ¹H NMR spectrum of the neat methyl soyate used here. Note that taking the protons attached to the olefinic carbons into consideration may appear unnecessary, as the integration values of their signals appear to cancel out in Equation 2. However, considering the integration values of those signals improves accuracy of blend level determination. One reason may be that the use of the broad range of CH₂ and CH₃ signals includes background, and using a well-defined signal with a well-defined integration value in both the numerator and denominator decreases the influence of that background. Knowledge of fatty acid composition is not necessary for the NIR determinations.

Figure 3 is a plot of the blend level determination of biodiesel blends at 10% increments by NIR and ¹H NMR.

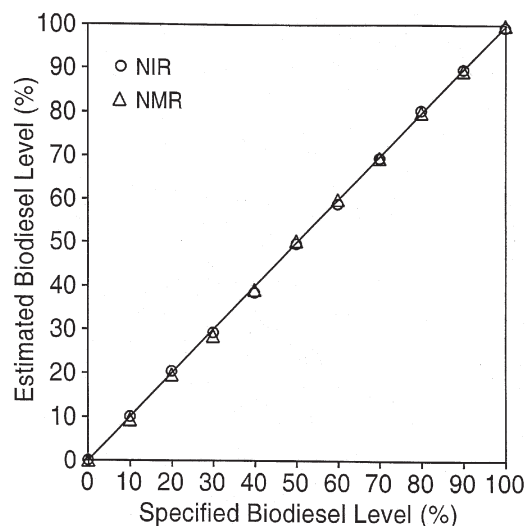


FIG. 3. Plot of estimated (by calibration) vs. specified values for a method quantitating the amount of biodiesel blended with conventional diesel fuel by NIR and ¹H NMR. Spectral region used for the method was 6050–5850 cm⁻¹. See Figures 1 and 2 for abbreviations.

The term "specified biodiesel level" in Figure 3 pertains to the known composition of a sample vs. estimated values (in vol%). The term "estimated biodiesel level" in Figure 3 pertains to the analyzed blend level of samples of known composition being treated as unknown. In other words, a sample of known composition was treated as being of unknown composition, and then the values resulting from NIR and NMR analysis were compared to the known composition value. Agreement of the spectroscopically determined blend levels with the known blend levels in the samples is good to excellent. Maximum deviations between specified and estimated values are 1–1.5%, with most deviations considerably lower and within the experimental error range of sample preparation. Although the peak at 6005 cm^{-1} was used for NIR blend level determination (in a method using a range of 200 cm^{-1} around that peak), the range at $4600\text{--}4800\text{ cm}^{-1}$ was also suitable as a method using that range of the spectrum shown. Also note that the composition of the conventional DF (aliphatic hydrocarbons vs. aromatic hydrocarbons) did not influence the NMR results because the use of the integration values of the methyl ester and hydrocarbon peaks of biodiesel ensured constant reference values against which the integration values of the aliphatic hydrocarbon peaks of conventional DF were determined.

In summary, NIR and ^1H NMR spectroscopic methods can be used for determining the blend levels of biodiesel in blends with conventional DF. The results from both methods are in good agreement.

ACKNOWLEDGMENTS

The author thanks Daniel A. Knetzer for obtaining the NIR spectra, Dr. David Weisleder for recording the NMR spectra, and Cady Oil Co. for a free sample of off-road conventional diesel fuel.

REFERENCES

1. Knothe, G., R.O. Dunn, and M.O. Bagby, Biodiesel: The Use of Vegetable Oils and Their Derivatives as Alternative Diesel Fuels, in *Fuels and Chemicals from Biomass*, edited by B.C. Saha and J. Woodward, ACS Symposium Series 666, American Chemical Society, Washington, DC, 1997, pp. 172–208.
2. Dunn, R.O., G. Knothe, and M.O. Bagby, Recent Advances in the Development of Alternative Diesel Fuels from Vegetable Oils and Animal Fats, *Recent Res. Dev. Oil Chem. 1*:31–56 (1997).
3. Knothe, G., Analytical Methods Used in the Production and Fuel Quality Assessment of Biodiesel, *Trans. ASAE 44*:193–200 (2001).
4. Knothe, G., Rapid Monitoring of Transesterification and Assessing Biodiesel Fuel Quality by Near-Infrared Spectroscopy Using a Fiber-Optic Probe, *J. Am. Oil Chem. Soc. 76*:795–800 (1999).
5. Knothe, G., Monitoring a Progressing Transesterification Reaction by Fiber-Optic Near Infrared Spectroscopy with Correlation to ^1H Nuclear Magnetic Resonance Spectroscopy, *Ibid. 77*:489–493 (2000).
6. Gelbard, G., O. Brès, R.M. Vargas, F. Vielfaure, and U.F. Schuchardt, ^1H Nuclear Magnetic Resonance Determination of the Yield of the Transesterification of Rapeseed Oil with Methanol, *Ibid. 72*:1239–1241 (1995).
7. Sadeghi-Jorabchi, H., V.M.E. Wood, F. Jeffery, A. Bruster-Davies, N. Loh, and D. Coombs, Estimation of Biodiesel in Lubricating Oil Using Fourier Transform Infrared Spectroscopy Combined with a Mid-Infrared Fibre Optic Probe, *Spectrosc. Eur. 6*:16, 18, 20–21 (1994).
8. Siekmann, R.W., G.H. Pischinger, D. Blackman, and L.D. Carvalho, The Influence of Lubricant Contamination by Methyl Esters of Plant Oils on Oxidation Stability and Life, in *Vegetable Oil Fuels*, ASAE Publ. No. 4-82, St. Joseph, MI, 1982, pp. 117–122.
9. Dimmig, T., W. Radig, C. Knoll, and T. Dittmar, ^{13}C -NMR Spektroskopie zur Bestimmung von Umsatz und Reaktionskinetik der Umesterung von Triglyceriden zu Methylestern, *Chem. Tech. (Leipzig) 51*:326–329 (1999).

[Received January 2, 2001; accepted August 2, 2001]