Rapid Monitoring of Transesterification and Assessing Biodiesel Fuel Quality by Near-Infrared Spectroscopy Using a Fiber-Optic Probe

Gerhard Knothe*
ARS, USDA, NCAUR, Peoria, Illinois 61604

ABSTRACT: Vegetable oil esters, particularly methyl esters, are being explored and used as alternative diesel fuel (biodiesel). The transesterification reaction which yields the methyl esters can be monitored for completion by near-infrared (NIR) spectroscopy using a fiber-optic probe. Although the NIR method is less sensitive than gas chromatography (GC) for quantifying minor components, by correlation with existing GC or other analytical data, biodiesel fuel quality can be assessed through the NIR method. The NIR method is easier and faster to use than GC. Paper no. 19071 in JAOS 76, 795–800 (July 1999).

KEY WORDS: Biodiesel, fiber-optic probe, fuel quality, near-infrared spectroscopy, transesterification.

Biodiesel, defined as the monoalkyl esters of fatty acids from vegetable oils and animal fats (1), neat and blended with conventional diesel fuel has significant potential as alternative diesel fuel (2,3). Initial stages of commercialization have been successful. Biodiesel is usually obtained from the neat vegetable oil by transesterification with an alcohol, usually methanol, in presence of a catalyst, usually a base such as KOH (Fig. 1). Glycerol is a by-product of the reaction. Other possible materials in biodiesel include residual alcohol, moisture, unreacted feedstock (triacylglycerides), incompletely reacted monoo- and diglycerides, and free fatty acids.

Fuel standards have been developed in Austria (ÖNORM C1190), Germany (DIN 51606) and Italy (UNI 10635:1997), and in the United States a provisional ASTM (American Society for Testing and Materials) standard has been completed. The fuel standards address quality issues of biodiesel by limiting materials such as free and total glycerol (total glycerol is the sum of free glycerol and glycerol bound as mono-, di-, and triacylglycerides), water (moisture), free fatty acid (by limiting the acid number), and residual alcohol (by limiting the flash point). These materials need to be limited in biodiesel because their presence can lead to fuel deterioration during storage as well as to significant operational problems such as engine deposits. The rationale for various quality test methods in biodiesel standards (United States, Austria) has been discussed (4,5).

The analysis of biodiesel for various contaminants is usually conducted by gas chromatography (GC). Originally, a method for analyzing mono-, di-, and triacylglycerides together with methyl esters in one run was developed (6). This method was extended to include glycerol (7). Other papers also report on the GC analysis of biodiesel for determining contaminants such as methanol, glycerol, and glycerides (8–13). Biodiesel was also analyzed by GC for minor components such as sterols (14,15). Preseparation of biodiesel and its contaminants by high-performance liquid chromatography (HPLC) prior to GC was reported (16). However, other methods have been utilized in the analysis of biodiesel, including HPLC with density detection (17) or pulsed amperometric detection for determining glycerol (18), and viscosity (19).

On the other hand, spectroscopic methods are being increasingly utilized for quality control purposes. Near-infrared (NIR) spectroscopy is among the methods finding increased use. Operational ease, rapidity of measurement, and nondestructiveness are among the chief reasons for this development besides accuracy and reliability. NIR spectroscopy is now being used routinely for analyzing the fatty acid composition of oilseeds besides finding other applications in the field of fats and oils (20,21). To the best of our knowledge, the NIR spectra of numerous fatty compounds were first reported more than 40 yr ago (22). Several other papers discuss NIR spectra of long-chain compounds (23–25). Here we report differences in the NIR spectra of vegetable oils (soybean oil used as example here) and their methyl esters as well as

![FIG. 1. Transesterification reaction.](attachment:image.png)

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*To whom correspondence should be addressed at NCAUR, ARS, USDA, 1815 N. University St., Peoria, IL 61604.
E-mail: knothe.g@ncaur.usda.gov

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initial results on the potential use of these spectral differences to monitor progress and endpoint of the transesterification. A model system consisting of defined concentrations of contaminants in biodiesel was used. By induction, biodiesel fuel quality can be assessed. NIR can be an alternative not only to GC but to other methods in biodiesel standards, for example flash point. Testing biodiesel for every such specification in the standard is a lengthy and extremely expensive process. A method such as NIR can shorten this process and render it considerably less expensive. Spectra were obtained with the aid of a fiber-optic probe, which makes the use of NIR spectroscopy particularly easy.

RESULTS AND DISCUSSION

The NIR spectra were determined with a fiber-optic probe, which makes their acquisition especially easy and provides the possibility of developing on-line reaction monitoring. Fiber-optic probes are currently used for monitoring commercial reactions (27–29) in applications similar to the one presented here. In conjunction with biodiesel, fiber-optic technology has up to the present only been used for determining the amount of biodiesel in lubricating oil by monitoring carbonyl absorption at 1820–1860 cm⁻¹ in the mid-infrared region (30).

Spectra were determined of solutions of predetermined concentration of feedstock (or other contaminants) in methyl soyate. The solution (approximate volume 100 mL) was prepared in a beaker into which a fiber-optic probe was immersed so that the path of the beam passed through the solution. This method proved advantageous in terms of ease of sample preparation. Concentration ranges of contaminants were also considered beyond those specified in biodiesel standards in order to demonstrate the potential of the method for monitoring the transesterification reaction. All spectra were recorded at ambient temperature (22–24°C), although the transesterification reaction is usually conducted at an elevated temperature (60°C). Temperature dependence of NIR spectra has been discussed but this affects mainly determinations of hydroxyl values as these are influenced more by temperature-sensitive hydrogen bonding (27) and less by the peaks used here for quantitation.

While the mid-range infrared spectra of triacylglycerides (vegetable oils) and their corresponding methyl esters are very similar, the NIR spectra of triacylglycerides (soybean oil used here) and the corresponding methyl esters (methyl soya te) reveal two distinct possibilities for distinguishing them. While one of the distinguishing signals, at 4425–4430 cm⁻¹, was indicated in an early paper on NIR of fatty compounds (22), a second signal at 6005 cm⁻¹ has apparently not been reported previously. Figure 2 depicts the NIR transmission spectra of soybean oil (also referred to as feedstock in this paper) and methyl soya te as well as methyl soya te containing some contaminants in the range of 4300–7300 cm⁻¹. In both regions, the methyl ester displays peaks while the triacylglyc eride-containing soybean oil exhibits shoulders [note that ethyl esters apparently display a strong shoulder at 4425–4430 cm⁻¹ (22)].

Both peak regions, 4425–4430 (indicated as 4428 cm⁻¹ in Fig. 2) and 6005 cm⁻¹, can be used for quantitation. Partial least-squares (PLS) analysis of the NIR spectra converted to the absorbance mode (note that transmission spectra are depicted in Fig. 2) was applied for quantitation. The software used offered the choice of two PLS approaches for calibration. The first PLS calibration models the spectra by a different set of factors for each component and the concentration values by the respective factors (i.e., the number of calibrations corresponds to the number of sample components). The second PLS calibration models the spectra by one set of factors and each component is modeled by relating the concentration values to those factors. The first PLS calibration

EXPERIMENTAL PROCEDURES

Biodiesel (methyl soya te) complying with biodiesel fuel specifications and the corresponding feedstock (soybean oil) were obtained from NOPEC Corp. (Lakeland, FL) or Ag Environmental Products ("Soy Gold;" Lenexa, KS) or Twin Rivers Technology (Quincy, MA). These materials were used as received. Methyl ester quality was checked by nuclear magnetic resonance (NMR) spectroscopy (Bruker ARX-400 spectrometer; Bruker, Rheinstetten, Germany; 400 MHz for 1H NMR and 100 MHz for 13C NMR; solvent CDCl₃) because this method will yield information on all possible contaminants from one sample. No significant contaminants were observed and these materials were treated as 100% methyl esters for purposes of this study. Free fatty acids were obtained from Nu-Chek-Prep (Elysian, MN; purity >99%). Methanol and glycerol were from Fisher Scientific (Fairlawn, NJ).

NIR spectra were obtained on a Perkin-Elmer (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; Perkin-Elmer). Method calibrations were carried out automatically by using the corresponding software feature.

Samples were prepared in a beaker by mixing methyl esters with defined quantities of contaminants. After each addition of contaminant within a series of measurements, the mixture was stirred for 5 min and again for several minutes with the probe immersed. Then the spectrum was recorded. After every series of measurements, the fiber-optic probe was cleaned by successive treatment with ethanol and acetone by immersing into each stirred solvent for several minutes.

For quantitation in wt% (most contaminants in biodiesel are limited in wt%), densities were taken into account by determining the weight of 10 mL material (average of three measurements; temperature 22°C) or using literature data. Densities were 0.87104 for methyl soya te and 0.9092 for soybean oil. Values for glycerol (1.26132⁰¹⁰⁴) and methanol (0.7914²⁰⁴) were taken from the literature (26). Our measurements for glycerol and methanol agreed excellently with these values, thus indirectly confirming the validity of the determinations for methyl esters and soybean oil feedstock.
method was applied with excellent results. PLS calibration for NIR spectra obtained by means of a fiber optic probe has been applied to other (trans-)esterification reactions. These include the synthesis of di- and trifunctional esters from multifunctional alcohols and excess fatty acid or methyl ester by monitoring the hydroxyl and, in case of acids, the acid value (27), determining the shift of the OH absorption band in NIR during polyester production (28), monitoring the transesterification of methyl esters with polyethylene glycol 300 (PEG 300) to give the corresponding PEG 300 ester (29), and monitoring epoxide and hydroxyl values in polymerization of a polyol (31). Polyol production monitoring by NIR using a fiber-optic probe and PLS calibration was also the subject of a patent application (32). Other authors determined various fat index values by NIR principal component analysis (33).

The region of the spectrum around the peaks giving the best results for calibration needs to be determined empirically. The

\[ m = \binom{n}{n} + \binom{n}{n-1} + \binom{n}{n-2} + \cdots + \binom{n}{n_{\text{min}}} \]  

when the minimum number of spectra required for a method is \( n_{\text{min}} \). With adjustments to wavenumber range and other parameters, the number of theoretically possible methods increases considerably. Many of these methods will yield similarly excellent calibration and prediction results. Only a few methods were developed and some examples are reported here. Table I compares specified values of methyl ester/feedstock samples not contained in the method (but run in the same sample series) with values predicted (the term “pre-
TABLE 1

Specified and Predicted Amounts of Feedstock (soybean oil) in Methyl Soyate (biodiesel)\textsuperscript{a}

<table>
<thead>
<tr>
<th>Peak (cm\textsuperscript{-1})</th>
<th>Specified Methyl esters (wt%)</th>
<th>Predicted Methyl esters (wt%)</th>
<th>Specified Feedstock (wt%)</th>
<th>Predicted Feedstock (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6005</td>
<td>56.09</td>
<td>55.67</td>
<td>44.44</td>
<td>43.91</td>
</tr>
<tr>
<td>6005</td>
<td>95.04</td>
<td>95.76</td>
<td>4.96</td>
<td>4.24</td>
</tr>
<tr>
<td>6005</td>
<td>97.96</td>
<td>98.06</td>
<td>2.04</td>
<td>1.94</td>
</tr>
<tr>
<td>6005</td>
<td>98.97</td>
<td>98.66</td>
<td>1.03</td>
<td>1.34</td>
</tr>
<tr>
<td>6005</td>
<td>99.93</td>
<td>99.90</td>
<td>0.07</td>
<td>0.10</td>
</tr>
<tr>
<td>4428\textsuperscript{b}</td>
<td>56.09</td>
<td>55.02</td>
<td>43.91</td>
<td>44.98</td>
</tr>
<tr>
<td>4428</td>
<td>97.96</td>
<td>97.99</td>
<td>2.04</td>
<td>2.01</td>
</tr>
<tr>
<td>4428</td>
<td>98.96</td>
<td>98.69</td>
<td>1.03</td>
<td>1.31</td>
</tr>
<tr>
<td>4428</td>
<td>99.98</td>
<td>100</td>
<td>0.02</td>
<td>0</td>
</tr>
<tr>
<td>6005\textsuperscript{c}</td>
<td>89.38</td>
<td>89.14</td>
<td>9.33 + 1.29\textsuperscript{d}</td>
<td>10.86</td>
</tr>
<tr>
<td>6005\textsuperscript{c}</td>
<td>90.08</td>
<td>92.23</td>
<td>4.70 + 5.22\textsuperscript{d}</td>
<td>7.77</td>
</tr>
<tr>
<td>6005\textsuperscript{c}</td>
<td>98.26</td>
<td>99.14</td>
<td>1.03 + 0.71\textsuperscript{d}</td>
<td>0.86</td>
</tr>
<tr>
<td>6005\textsuperscript{c}</td>
<td>99.96</td>
<td>100</td>
<td>0.02 + 0.01\textsuperscript{d}</td>
<td>0</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Method calibration for peak at 6005 cm\textsuperscript{-1}. Results obtained by method described in the text.

\textsuperscript{b}Spectral region used for calibration 4600–4330 cm\textsuperscript{-1}.

\textsuperscript{c}Methyl esters contaminated with feedstock and glycerol. Feedstock values reflect total contaminants (wt% feedstock + wt% glycerol). Same calibration method used as in the nonglycerol entries for 6005 cm\textsuperscript{-1}.

\textsuperscript{d}The first value reflects feedstock, the second one glycerol. For purposes of prediction in the next column, both materials treated as one contaminant. For the effect of glycerol and mono- and diglycerides on the near-infrared spectra, see text.

The quality of the predicted values was checked in the prediction report generated by the quantitation software by the M-distance and residual ratio. Ideally, these values should be <1 and <3, respectively, indicating that the sample whose composition is being predicted is representative of the samples used in the calibration set. In most examples investigated here, these conditions were met but even in samples where one (or both) parameters exceeded the ideal values, excellent correlations of specified with predicted values could be attained.

Table 1 contains some results from the quantitation of soybean oil feedstock in methyl soyate. Most specified and predicted values are in excellent agreement. At low contamination levels as prescribed in biodiesel standards, it must be kept in mind that even statistically excellent results can translate into deviations from the desired fuel specifications. Although, as discussed above, different kinds of contaminants can be present in the product of the transesterification reaction, they do not alter the peak regions for distinguishing methyl esters and feedstock triacylglycerides (see Fig. 2). However, effects such as baseline depression apparently play a role at higher concentrations of additional contaminants and can play a role in quantitation. Baseline depression is observed in the spectra obtained with amounts of glycerol significantly beyond those in biodiesel fuel specifications. This is a result of the very low solubility of glycerol in biodiesel (13) which leads to a two-phase system. Similar observations hold for samples containing mono- and diglycerides. These observations would need to be accounted for when considering NIR spectroscopic online monitoring of the transesterification reaction. Thus, the results when taking the additional contaminants into consideration show somewhat higher deviation from specified values with the deviation being lower when the additional contaminants are present in low concentrations. This deviation is likely due to the insolubility of some of these contaminants (e.g., glycerol) in the methyl esters. The deviation is lower when the additional contaminants are present in low concentrations. Some examples of methyl ester/feedstock samples containing glycerol as additional contaminant are also listed in Table 1. Nevertheless, the results show that for purposes of reaction monitoring and endpoint determination, the problem can be largely reduced to determining the turnover from feedstock to methyl esters without determining all contaminants.

Methanol in methyl esters can be determined in a fashion similar to feedstock. Curve 3 in Figure 1 depicts methyl soyate biodiesel containing a significant amount of methanol [actually the spectrum contains an overload of methanol (18.5 wt%) which is not attained at any stage of the transesterification reaction when using the molar ratio as described in the literature (35,36)]. It serves to show, however, that when carrying out on-line monitoring, the spectra of the feedstock and the methyl ester will not be “overpowered” by a strong methanol spectrum. The methanol causes a relatively broad peak at 4480–4885 cm\textsuperscript{-1}, as well as a depression of the baseline in the range of 7000–6200 cm\textsuperscript{-1}. The peak at 4480–4885 cm\textsuperscript{-1} can be used for quantitation in the fashion discussed above by converting the spectra to absorbance with subse-
NIR MONITORING OF TRANSESTERIFICATION AND BIODIESEL QUALITY

TABLE 2
Specified and Predicted Amounts of Methanol in Methyl Soyate

<table>
<thead>
<tr>
<th>Methyl esters (wt%)</th>
<th>Methanol (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specified</td>
<td>Predicted</td>
</tr>
<tr>
<td>Specified</td>
<td>Predicted</td>
</tr>
<tr>
<td>81.49b</td>
<td>82.98</td>
</tr>
<tr>
<td>99.55</td>
<td>99.28</td>
</tr>
<tr>
<td>99.73</td>
<td>99.52</td>
</tr>
<tr>
<td>99.82</td>
<td>99.64</td>
</tr>
<tr>
<td>99.95</td>
<td>99.93</td>
</tr>
</tbody>
</table>

aCalibration region 5500–4600 cm⁻¹. Samples in calibration method: 88.01, 99.10, 99.55, 99.91, 99.99 wt% methyl soyate, remainder methanol.
bMethanol “overload” (18.51 wt%). The molar ratio methanol/vegetable oil of 6:1 used in transesterification reactions (see text) corresponds to approximately 17.9 wt% methanol at the beginning of the reaction.

REFERENCES


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