Determining Biodiesel Content in Fuel Blends Using FT-NIR

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Key Words
Biodiesel, Biofuels, FT-NIR Spectroscopy, Fuel Blends, Renewable Energy

Introduction

The movement toward renewable energy sources has led to an increased production and use of biofuels, specifically biodiesel. Biodiesel provides an attractive alternative to traditional petroleum-based diesel fuel. The Environmental Protection Agency (EPA) estimates that over 2 billion gallons of biodiesel were utilized in 2015.[1] Biodiesel is produced by the trans-esterification of vegetable oils or animal fats. These oils and fats, which contain triglycerides, are reacted with methanol and an acid or base catalyst to produce biodiesel, also known as fatty acid methyl esters, or FAME, as shown in Figure 1. The resulting biodiesel is often blended with petroleum-based diesel at a variety of concentration levels. The most common biodiesel blend in the United States is referred to as B20 (20% biodiesel, 80% petroleum diesel). B20 is a popular biodiesel mixture because it represents a good balance of fuel cost, emission levels, cold-weather performance, and engine compatibility. Concentrated biodiesel blends, such as B80 or B100 (80% or 100% biodiesel), are less commonly used because, while they are compatible with most modern diesel engines, they cannot be used in many older vehicles. High level biodiesel blends also have lower energy content per gallon, perform poorly in cold weather, and carry a premium price. The non-uniform performance of biodiesel mixtures creates the need for accurately determining biodiesel concentration in fuel blends.

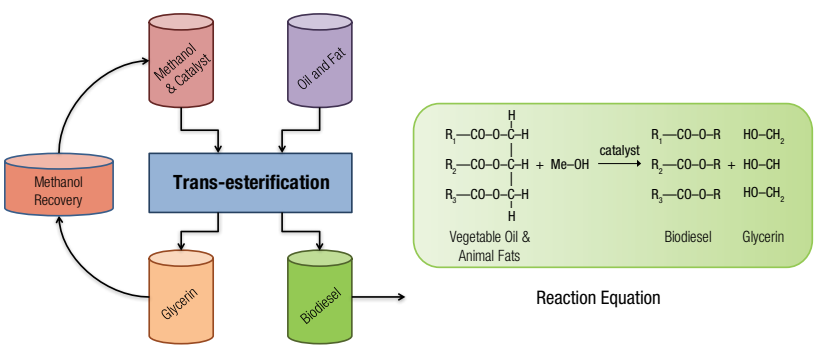

Figure 1: Biodiesel reaction pathway

Fourier transform near-infrared (FT-NIR) spectroscopy is a reliable analytical technique used to rapidly determine chemical concentrations in a broad range of commercial products. FT-NIR spectroscopy can measure the biodiesel content of a fuel blend with only one milliliter of sample in less than one minute. While this measurement is commonly performed in the mid-IR region, per ASTM D7371-14, near-IR spectroscopy can often provide more rapid and automated analysis.[2] This application note describes a method used to analyze a wide range of biodiesel fuel blends using the Thermo Scientific™ Nicolet™ iS™5N FT-NIR spectrometer configured with the iD1H Heated Transmission accessory.

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Experimental Conditions

A quantitative calibration used to determine the biodiesel concentration in fuel blends was developed with a set of 20 biodiesel fuel blend standards ranging from B0 (pure petroleum diesel) to B100 (pure biodiesel). Aliquots of these samples were transferred into 8 × 40 mm glass vials having an approximate sample pathlength of 6 mm. The vials were placed into the iD1H Heated Transmission accessory, which holds the sample temperature constant at 40 °C to provide more consistent results by reducing sample temperature variability. The samples were allowed to stabilize for one minute before analysis on the Nicolet iS5N FT-NIR spectrometer, as seen in Figure 2. The instrument was configured with a CaF_2 beamsplitter, tungsten-halogen light source, and a high sensitivity indium gallium arsenide (InGaAs) near-IR detector. Spectra were acquired from 11,000 to 4000 cm^{-1} in less than one minute (90 scans at 8 cm^{-1} resolution).

Figure 2: Nicolet iS5N FT-NIR spectrometer equipped with the iD1H Heated Transmission accessory

Once the spectra from the biodiesel standards had been collected, they were opened in the Thermo Scientific™ TQ Analyst™ chemometric software for quantitative model development. In the TQ Analyst software, calibration curves can be built using a variety of quantitation models, from single variable methods to the most robust multi-variate statistical analysis algorithms. In this case, Simple Beer's Law (SBL) and Classical Least Squares (CLS) models were both used for method calibration.

Results and Discussion

The SBL model uses a specific spectral region to build the calibration. TQ Analyst software employs a region selection tool, which automatically selected the wave number region that best correlated to changes in biodiesel concentration (6078 to 6043 cm^{-1}). As seen in Figure 3, the selected region contained a high amount of variation and the peak intensities directly correlated to the concentration of biodiesel in the fuel blend standards.

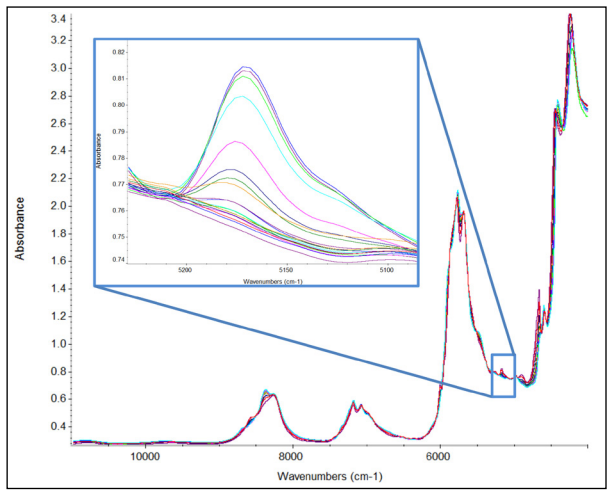

Figure 3: Automatically selected biodiesel spectral region

The calibration result using the SBL model is shown in Figure 4. The actual biodiesel concentrations are plotted on the x-axis and the calculated concentrations are plotted on the y-axis. The correlation coefficient of greater than 0.99 is indicative of a strong correlation model. However, the data points in the calibration show some curvature due to the wide calibration range. In this calibration, the low end biodiesel concentrations are relatively linear, but the high end biodiesel concentrations display non-linearity.

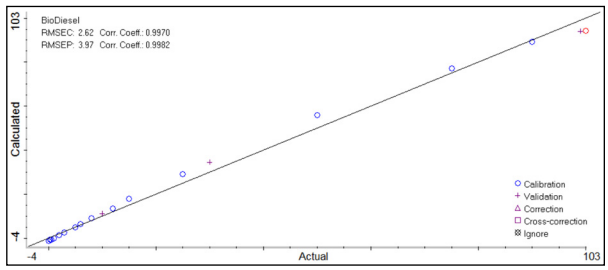

Figure 4: Biodiesel fuel blend calibration curve – SBL model

To optimize this calibration over a wide concentration range, the CLS calibration model was used. This model allows the user to specify multiple regions of interest and apply mathematical corrections to the results. The CLS model was created from the same biodiesel data set with the identical region of interest. A polynomial correction was applied to the resulting calibration curve, which produced a higher correlation value that was linear throughout the calibration range, as seen in Figure 5.

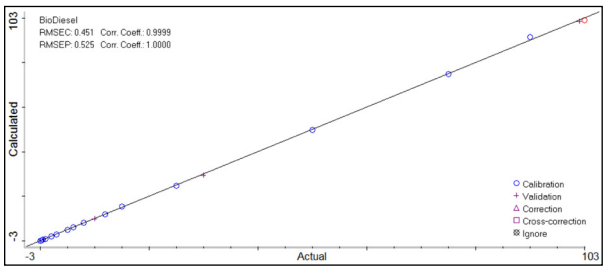

Figure 5: Biodiesel fuel blend calibration curve – CLS model

To determine the accuracy and precision of the Nicolet iS5N FT-NIR spectrometer and the iD1H Heated Transmission accessory, four fuel blend samples of known biodiesel concentration were measured multiple times over the course of two hours. To make analysis more efficient, an automated collection process was developed using the Thermo Scientific™ OMNIC™ Macros\Basic™ workflow generator. Macros\Basic software is often used in the process environment to automate standard operating procedures (SOPs). The workflow and result for a single measurement of the 5% biodiesel fuel blend is shown in Figure 6.

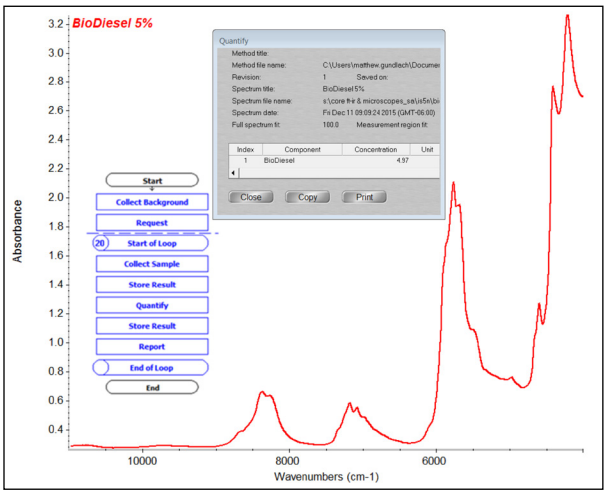

Figure 6: Biodiesel sample with quantitation result and workflow

Measurements were repeated 20 times for each of the four biodiesel blend samples at 2%, 5%, 25%, and 75% concentration levels. The standard deviation for repeated analysis of the samples was 0.05, 0.04, 0.10, and 0.12, respectively. As an example, data from the 5% biodiesel sample is plotted in a control chart, as shown in Figure 7. The standard deviation shown in the plot demonstrates a high degree of instrumental precision.

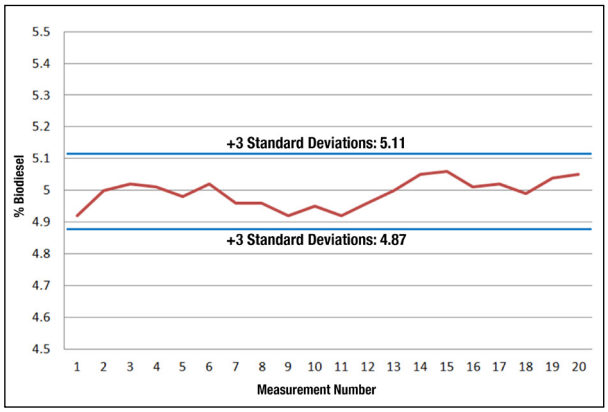

Figure 7: Consecutive measurements of 5% biodiesel fuel blend

While this biodiesel standard set could be modeled with the SBL and CLS calibrations, other near-IR calibrations can be more complex. In certain standard sets, the near-IR spectral features are broad, have regions of overlap, and exhibit interdependencies. In these more complex quantitative calibrations, multivariate statistical analysis techniques may be used to create a more accurate representation of the sample set. Popular statistical models include Partial Least Squares (PLS), Principal Component Regression (PCR) and Stepwise Multiple Linear Regression (SMLR). To determine the best approach, it is helpful to evaluate several models and see which performs best with the specific application and data set.

Conclusions

The Nicolet iS5N FT-NIR spectrometer and the iD1H Heated Transmission accessory provided exceptional accuracy and repeatability in the prediction of biodiesel fuel blend concentration. The automated workflow developed by Macros\Basic software allowed for an easy determination of instrumental precision and can be extended to routine sample analysis. As renewable energy use continues to grow in popularity, the Nicolet iS5N FT-NIR spectrometer provides an ideal solution for the accurate determination of biodiesel concentration in fuel blends.

References

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