

Methods of biodiesel analysis vary, but one mid infrared option may be what the industry is looking for

Infrared shines bright

High feedstock prices are driving producers to try out lesser quality raw materials.

These can still produce quality fuels but it makes the need for analysis even greater to ensure an on-spec end product. Many producers are now relying on mid infrared spectroscopy (MIR) for their quality testing.

When compared to other methods of analysis, such as gas chromatography, titrations and other wet chemical methods, mid infrared spectroscopy wins in terms of speed, ease of use, and often accuracy.

Infrared spectroscopy uses the interaction between the radiation (infrared) and matter (the molecules in the biodiesel) to analyse samples; in layman's terms, different molecules vibrate differently when exposed to infrared light. These changes in vibration define the molecular structure and can be used to quantify the concentrations of components and the properties of the biodiesel.

Mid infrared is inherently more sensitive than the other infrared regions (near IR and far IR), and therefore can be used to measure components at lower concentration levels, such as the levels of free glycerine in biodiesel. Quantification of low free glycerine levels can usually not be accomplished using near infrared spectroscopy (NIR), another common analytical tool that is particularly useful for bulk component analysis (>0.1%). However, it should be noted that MIR is generally suitable only for homogeneous liquids, whereas NIR can measure both homogeneous

and inhomogeneous samples. NIR is also best for solid samples like grains, and granular products.

Fourier Transform IR spectrometers

Fourier Transform mid-Infrared (FT-IR) utilises a light source, sampling chamber, detector, and an interferometer, the latter being unique to FT forms of IR spectroscopy. All FT-IR instruments utilise the interferometer, the most common of which is the Michelson Interferometer, consisting of a beam splitter, a moving mirror and a stationary or fixed mirror.

FT-IR utilises multivariate analysis, a form of statistics encompassing the simultaneous observation and analysis of more than one statistical variable, which combines features from principal component analysis and multiple regression techniques for constructing predictable models. Multi-linear regression (MLR), classical least squared (CLS) and partial least squared (PLS) are all examples of multivariate analysis, although PLS is most commonly used for FT-IR calibration modelling.

Unlike a dispersive instrument which interrogates a sample one wavelength at a time, an FT-IR spectrometer passes all frequencies of energy from the source through the sample. The raw signal is collected as amplitude vs. time (called an interferogram) rather than amplitude vs. wavelength. A computer performs a Fourier transform algorithm to convert the time domain interferogram to a frequency

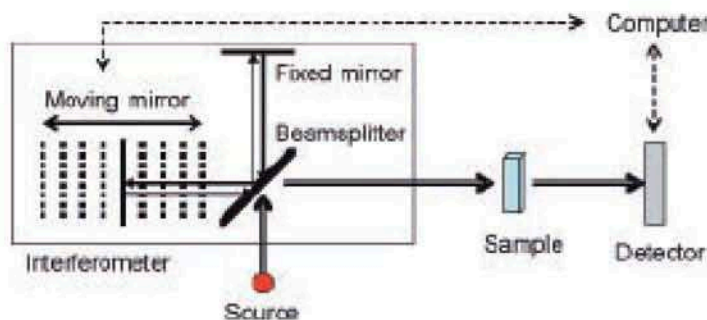


Figure 2: FT-IR spectrometer with Michelson Interferometer

domain single beam sample spectrum. Because detectors cannot sample IR interference patterns fast enough, the entire signal is first modulated to a lower frequency using an interferometer. An FT-IR absorbance spectrum is computed from two single beam spectra; the first is a reference (background) spectrum in the absence of sample. The second spectrum is collected when the sample is in the path of the beam. For ease of use, the sample can be presented using an ATR (attenuated total reflectance), a simplified IR sampling technique which enables liquid sample to be analysed directly on a crystal instead of pumping the sample into a flow through cell.

The benefits of FT-IR

FT-IR has inherent benefits over other types of IR spectroscopy. Since the light source energy is more powerful (containing all rather than a select few wavelengths), more light reaches the sample and detector, thus providing more and better information about the sample. Because sample information is collected at all wavelengths simultaneously,

this allows for multiple spectra to be collected rapidly, then averaged, thus giving greater accuracy. And FT-IR has higher inherent wavelength accuracy and precision, making the spectra and corresponding results much more consistent over time.

The use of FT-IR for analysis of materials is quick and easy once calibration algorithms are developed for interpretation of the light spectra collected as described above. However, the development of calibration algorithms is not trivial. The process is as follows:

1. A sample set is defined for calibration building that includes all expected variability in the product being analysed. For example, for biodiesel, the calibration sample set should include all possible feedstocks, produced using a variety of production processes, and having the broadest concentration range of the components of interest, particularly including samples that are above and below the specification limits. For example, for developing a calibration algorithm for total glycerine (TG), it is desirable

- to include samples that have TG levels greater than 0.24%, as well as numerous samples at low and mid range TG levels. Note that these samples should not be laboratory-prepared or spiked samples, as such samples will normally have different spectral features than real-world samples.
- The calibration sample set is then analysed using primary methods, i.e. traditional ASTM or EN methods. It is desirable to collect these data from multiple laboratories, to ensure the most accurate primary data.
 - Multiple IR spectra should be collected for each sample.
 - Using the correlated result from the ASTM or EN method and the IR spectra, a calibration algorithm is developed using a Partial Least Squares calibration modelling method.
 - Once the initial calibration algorithm is built, an iterative validation process ensues. The validation process consists of analysing additional samples (the validation sample set) using both the FT-IR method and the ASTM/EN methods. The results are compared, and the FT-IR calibration algorithm adjusted if needed. This process is repeated until the FT-IR result is within two standard deviations of the method 95% of the time.
 - The validation process is also repeated periodically, or when new feedstocks are added, or if significant process adjustments are made.
 - Once the validation process is complete, then samples can be analysed routinely using the FT-IR method, with the traditional ASTM/EN method used only for validations as described in #6 above.

FT-IR for biodiesel analysis

An early reported use of FT-IR for biodiesel analysis

was detailed in a 1997 report submitted to the National Biodiesel Board. Since then, much research has been conducted for FT-IR biodiesel reaction monitoring, or percent biodiesel analysis in diesel blends. Recently, ASTM has approved D7371, which uses FT-IR with an ATR for sample presentation and Partial Least Squares data treatment to analyse percent biodiesel in diesel blend samples without sample preparation. EN 14087, which pre-dates D7371, requires dilution of diesel blend samples in hexane, followed by analysis using FT-IR, using only peak height analysis and a transmission cell for sample presentation, so its ease of use and accuracy is comprised. Newer FT-IR techniques utilise no sample preparation.

Since the 1990s, Cognis Corporation has developed and implemented various FT-IR methods for multivariate quantitative analysis of oils, fats, methyl esters and related products for both in-process monitoring and finished product testing. Tests developed include free fatty acids, free glycerine, total mono-, di- and tri-glycerides, acid value, ester value, iodine value, sterols, tocopherols, and trans-fatty acids.

The QTA system for biodiesel analysis

With Cognis Corporation's QTA System all materials in the process can be analysed using a single analytical instrument. No solvents or reagents are required, and results are obtained in two minutes, so that process adjustments to improve quality and cut costs can be made in real time. It can analyse properties for B100, a wide variety of feedstocks, crude glycerine, recovered methanol, and biodiesel blends in diesel fuels or jet fuels.¹

Users need no specialised training or spectroscopic

knowledge. The typical analysis requires applying a drop of homogeneous biodiesel sample to the ATR surface. Results for multiple traits are displayed within less than two minutes. This system is advantageous since the calibration algorithms can be much more robust, covering the broadest sample matrix: more than 2,000 spectra are included in most QTA biodiesel calibrations, which include over ten different feedstocks, and blends thereof, countless production processes, samples from three continents, and over five years.

The QTA System's centralised calibration model also provides better industry standardisation: since all users access the same calibration algorithms, site to site reproducibility is significantly better than that of the ASTM/EN methods in many cases.

In early 2010, five years after commercialisation, the QTA method was approved and published as AOCS Standard Procedure Ck 2-09.

The National Renewable Energy Laboratory (NREL) is using the QTA System in-house for evaluation and testing with biodiesel survey samples. Work with the American Oil Chemists Society (AOCS) yielded the peer-reviewed published method AOCS Ck 2-09. Then working with ASTM, the QTA methods for critical biodiesel properties free and total glycerine (FG, TG), methanol content, acid number (AN), cloud point (CP), and moisture content were evaluated using the ASTM D6708 round robin methodology for comparison to the traditional ASTM/EN methods. The QTA method Ck 2-09 is being balloted for inclusion in ASTM D6751, as an alternative method for FG, TG, methanol, CP and AN. This balloting process will continue through December 2010; if approved, the QTA System could be used to certify biodiesel per D6751 for the approved tests, and

could be used as part of a BQ-9000 quality programme. Additionally, an AOCS collaborative study and D6708 round robin is being conducted to evaluate the QTA method for other BD tests including mono-, di- and tri-glycerides, oxidative stability, and sulphur content.

The QTA System also participates in the ASTM Interlaboratory Cross Check programme (ILCP). Under this programme, commercial samples of biodiesel are sent to as many as 60 laboratories for analysis. The results from these 60 labs are combined to provide a robust mean and standard deviation.

Since 2005, the QTA System has conducted over 1.8 million biodiesel analyses and has been used by over 60 different biodiesel producers. Northbend Biodiesel reported that through the use of the QTA System it was able to reduce the amount of catalyst used by 3-5%, resulting in annual savings of \$20,000 (€15,148). Other users include GEA Westfalia and Louis Dreyfus.

The results are in

With so many choices on the market, from near infrared to mid infrared, dispersive to Fourier Transform, they need to look for the most comprehensive and thorough solution.

FT-IR provides high quality and detailed spectral information about the sample because of its high light throughput and signal averaging ability, yielding greater accuracy.

What is more, producers need a system they can trust, one that has been extensively tested and set to standard such as the QTA system. ●

For more information:

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analysis

**European biodiesel
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