Improving biofuels profitability through NIRS and MIRS quality control

Better processes, better products

Biofuels quality is related to the inherent characteristics of the feedstock raw-materials (RMs) and operating conditions used in their production. However to be used as fuel in engines biofuels must meet certain specifications regulated by ASTM or EN standards regardless of the manufacturing processes and / or the type of RMs used in the production process. Failure to comply with these specifications can lead to various problems such as deterioration of the fuel, corrosion of metal parts and rubber, deposit formation and the clogging of filters.

Biofuels characterisation by conventional analytical methods such as Karl-Fisher titrations, GC chomatography or viscometry is slow and very costly. Therefore there is an opportunity for other analytical techniques, such as the near-infrared and mid-infrared spectroscopies (NIRS and MIRS), which are well established in other industrial areas.

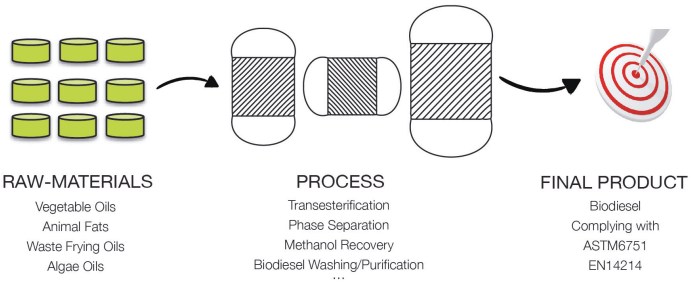
These techniques have gained interest in recent years and are considered as a simple, fast, reliable and accurate way to perform quality control of RMs and the final product. Moreover, the fact that NIRS and MIRS are able to perform multi-parametric analysis in multi-component samples in a rapid and nondestructive way makes them particularly suitable for use as online analytical techniques in industrial processes.

ASTM 1655 and 1790: standard practices for MIRS and NIRS quantitative and qualitative Analysis

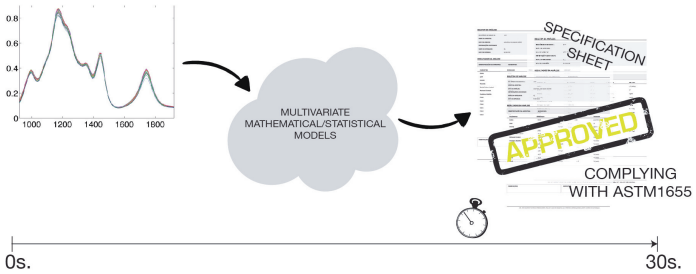
In the last five years ASTM has published two standards specifically addressing MIRS and NIRS use for quantitative (ASTM 1655) and qualitative (ASTM 1790) analysis.

ASTM 1655 describes methods to establish and validate calibration models to be used to predict chemical and physical properties in solid or liquid samples based on their spectra. A calibration model relates a sample spectrum with their chemical and physical properties, via multivariate mathematical/ statistical models (training set).

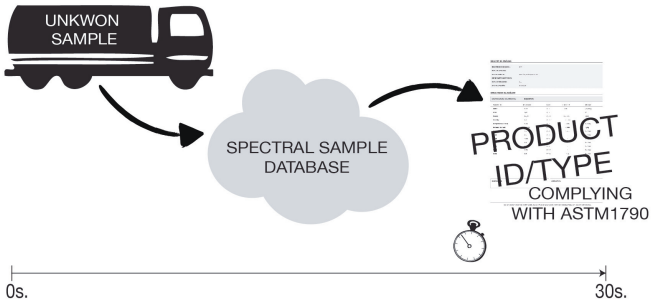
After training and validating the models with samples not used in calibration, it can be used to predict several parameters at once from one spectrum for an unknown sample. Since taking a spectrum takes less than 30 seconds, these technologies represent a huge opportunity to implement on-line or at-line monitoring, with supervisory control of all process from the arrival of feedstocks to the release of the end product.



MIRS/NIRS based quality control, according to ASTM1655



Feedstock or blended product identification/classification based on NIRS/MIRS according to ASTM 1790



Feedstock or blended product identification/classification based on NIRS/MIRS according to ASTM 1790

In addition, ASTM 1790 describes the methods used to sample identification or classification. These methods compare sample spectrum with a large spectral database to identify their similarities using a statistical software package. Samples with similar chemical/ physical properties will present similar spectra and would be classified as belonging to the same group. These databases can be created with a few samples and proper know-how and can be specific for a desired characteristic (e.g., type of oil).

Raw materials qualification and characterisation

Several biodiesel properties are determined by the quality of RMs (e.g., cold filter plugging point, iodine value, oxidation stability, etc.). It is therefore very important to choose RMs well and control them routinely as both seasonal variations, inconsistent processing at suppliers or counterfeiting may lead to significant variability.

A supervisory system not only allows quality control of incoming RMs but also advises and guides in formulating mixtures for a pre-defined biodiesel specification.

Portugal-based NIRS and MIRS based solutions provider 4TUNE Engineering has developed such a system and is now expanding it with features related to purchasing and pricing of RMs and also production recipe management as process conditions should be adjusted according to some RMs properties (e.g., water and free fatty acids content).

Contrary to lab-based quality control, NIRS and MIRS based-

Vegetable oils calibration performance using NIRS in compliance with ASTM 1655

Parameter	Calibration range	NIR accuracy	ASTM method accuracy
Iodine value (gI2/100g)	60-140	1.1	3
Density (kg/m^3)	905-925	0.6	0.5
Soybean (%)	0-100	3.7	-
Rapeseed (%)	0-100	5.0	-
Palm (%)	0-100	2.1	-
FFA (%)	0-100	0.8	1
FFA (%)	0-17	0.2	0.5
Dynamic Viscosity (cP)	48.7-72.3	0.5	0.5
C14:0 (%)	0.06-1.21	0.02	0.01
C16:0 (%)	4.9-39.9	0.8	0.9
C18:0 (%)	1.6-4.1	0.2	0.1
C18:1 (%)	26.4-66.1	2.1	2
C18:2 (%)	10.8-49.7	1.8	1.7
C18:3 (%)	2.2-8.3	0.2	0.6

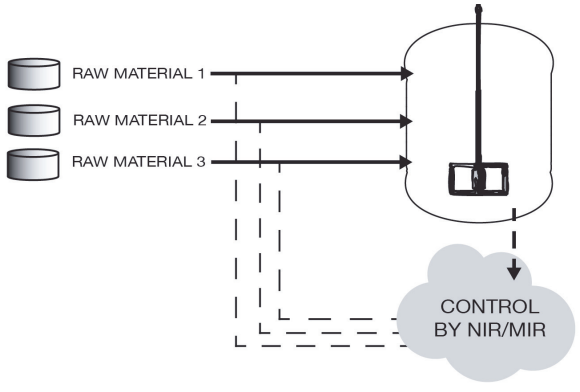
The table shows an example of 4TUNE Engineering's package capabilities in controlling the quality of incoming RMs based on a vendors low-resolution handheld NIR spectrometer with MEMS technology, although the results obtained using other systems (FT-NIR, FT-MIR, Variable Filter Array MIR, etc.)

systems take the lab near the truck-tanker, pipeline or tank farm, giving in less than a minute a multi-parameter specification sheet for each sample or lot of RMs and enabling decisions (accept/reject/blend) to be taken.

Another interesting opportunity for NIRS and MIRS is their use to establish supervisory systems for vegetable oils blends (cf. ASTM 1790). Vegetable oils must meet certain specifications so that the biodiesel produced complies with EN 14214 or ASTM 6751. Oil samples that comply with those specifications will have similar spectra. Therefore one can define thresholds on acceptable/unacceptable lot-to-lot variability, and NIRS and MIRS be used in optimisation of oils blends to meet desired specifications. Also feedstocks trading could be based on their production potential value and not on their labelled origin or quality. That is the principle of a modern feedforward control strategy

Process monitoring and supervision

For most biofuels pre-established process recipes are used, although RMs and process conditions have a huge influence on process performance. Processes are also operated with a reduced number of parameters monitored (e.g., temperature, flows, pH) at low sampling frequency, resulting in relatively low process knowledge and frequent reprocessing of products (e.g., blending of biodiesel with different quality to meet ASTM/EN specifications). One possible supervisory strategy to minimise costs and increase throughput would involve monitoring intensification (on- or at-line monitoring of several quality parameters with MIRS/NIRS instead of a few controlled parameters) and multivariate tools to better map production process conditions. Such strategies would allow the early identification of process deviations (e.g., due to incoming feedstocks), better end-point determination of different processing stages, and overall a significant reduction of reprocessing costs and increased productivity.



Adjusting process conditions to match feedstock properties: feedforward control or process recipe management

End product multi-parametric release

ASTM and European standards (ASTM D-6751 and EN 14214) impose limits on several quality parameters of biodiesel (25 parameters in EN 14214 and 20 parameters in ASTM) and their analyses are expensive and time consuming.

However, after calibration according to ASTM 1655, NIRS or MIRS make it possible to speed up the release of biodiesel lots according to the required specifications on at least half of those specifications, bringing investment in analytical instrumentation down by a factor of 10 and the running costs (e.g., consumables and personnel) down to a bare minimum.

The green goal

The biodiesel industry's main goal is, as with any other industry, to produce a high quality product from a wide range of feedstocks in the most flexible and reliable way possible at a competitive price.

One proven way to do that is through modern cost-effective monitoring solutions that have a payback time of weeks or a few months, such as mature technologies like NIRS and MIRS.

Other industries such as pharma and refining have adopted these technologies, and the opportunity exists now for them to spread to the biofuels sector. ●

For more information:
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Biodiesel calibration performance using MIRS complying with ASTM 1655

Parameter	Calibration range	NIR accuracy	ASTM method accuracy
Iodine value (gI2/100g)	57-130	1.4	3
Density (kg m-3)	905-925	1.1	0.5
Methyl Esters Content (%)	0-100	1.7	1.5
Methyl Esters Content (%)	0-100	1.0	1.5
Methanol Content (%)	0-100	255	100
CFPP (o C)	0-17	1	1
C14:0 (%)	0.06-1.21	0.03	0.01
C16:0 (%)	4.9-39.9	1.3	0.9
C18:0 (%)	1.6-4.1	0.2	0.1
C18:1 (%)	26.4-66.1	2.0	2
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A typical biodiesel analysis based on a portable variable filter array MIR spectrometer (acquired on 4TUNE Engineering package using industrial samples)