The introduction of the ASTM D7591 standard at the beginning of this year has created a space for a new kind of detection within the quality control of biodiesel

Amperometric detection

Today many biodiesel manufacturers use an alkali catalyst in the transesterification process as reaction rates under acid or enzyme catalysts are relatively slow in comparison.

Incomplete reaction leads to the formation of residual glycerol intermediates such as mono-, di- and triglycerides (bonded glycerols). In contrast, complete conversion creates highly water-soluble glycerol (free glycerol) which is separated from the final product at the end of the production process.

Once separated, glycerol has uses in a number of industries, including the food sector as a sweetener, preservative or thickening agent; in the pharmaceutical sector; or in the personal care industry, found in toothpaste for example.

Despite this separation process, traces of glycerol are frequently found in the ester phase. Both free and bonded glycerols (total glycerol) lead to severe problems.

Alfred Steinbach, technical writer for precision instrument manufacturer Metrohm, says: 'The production of biodiesel creates co-products like glycerol, which can lead to problems in the engines. In particular, it leads to the formation of deposits, speeds up the aging of the fuel and causes blocked filters, lowering engine performance. Therefore, the idea is to reduce the glycerol content to a minimum.'

The US *ASTM D6751, Standard specification for biodiesel fuel blend stock (B100) for middle distillate fuels*, specifies a maximum total glycerol content of 2,400 ppm (0.24%), while the European *EN 14214, DIN 14214, Automotive fuels – fatty acid methyl esters (FAME) for diesel engines – requirements and test methods* stipulates 2,500 ppm (0.25%). In both standards, the free glycerol content is limited to 200 ppm (0.02%). Any biodiesel containing more than this cannot be sold.

Metrohm's amperometric detector

Choices, choices

Biodiesel quality is reflected in free and bonded glycerol content: a high percentage of free glycerol could prove problematic during storage or in the fuel system as a result of glycerol separation, while high total glycerol content can lead to injector fouling and may also result in deposits forming at injection nozzles and valves.

Glycerol levels in biodiesel can be measured using a range of technologies, including:

- Ion chromatography mass spectrometry (IC MS)
- Gas chromatography mass spectrometry (GC MS)
- Liquid chromatography mass spectrometry (LC MS)
- Titration

The *ASTM D6584, Standard test method for determination of total monoglyceride, total diglyceride, total triglyceride, and free and total glycerine in B100 biodiesel methyl esters by gas chromatography*, test method covers the quantitative determination of total monoglyceride, total diglyceride, total triglyceride, and free and total glycerol in B100 methyl esters by gas chromatography. This procedure still encounters coelution problems with biodiesel samples produced from or containing lauric oils, such as coconut oils and palm kernel oil.

At the beginning of this year, a new standard for biodiesel analysis was introduced: *ASTM D7591, Standard test method for determination of free and total glycerol in biodiesel blends by anion exchange chromatography*. This test method covers and describes an anion exchange chromatography procedure for determining free and total glycerol content of biodiesel (B100) and blends (B0-B20) with diesel fuel oils defined by the D975 specification grades 1-D, 2-D and low sulphur 1-D and 2-D, and specification D6751 (for B100 feedstocks).

IC-PAD

Ion chromatography followed by pulsed amperometric detection (IC-PAD) is a different, established method to test biodiesel and analyse the free and total glycerol content.

Metrohm's newly designed amperometric detector is an alternative to conductivity and UV/VIS detectors and is suitable when electroactive – i.e., oxidizable and reducible – compounds need to be determined. For the glycerol determination, the detector cell is equipped with a gold working electrode, a solid-phase reference electrode and a stainless-steel auxiliary electrode.

Its high selectivity and measurement sensitivity allows the precise determination of concentrations down to the ng/L range. The amperometric detector is available as a detector block (the 850 IC Amperometric Detector) and as a stand-alone device (the 896 Professional Detector). As well as in pulsed amperometric mode, the detector can also be operated in direct current mode (DC), flexible integrated pulsed amperometric mode (flexIPAD) or in cyclic voltammetric mode (CV).

PAD is used when analytes, such as glycerol, form a deposit on the surface of the working electrode. By applying a multistep potential waveform, the surface of the gold working electrode is continuously cleaned.

A total of up to 40 different potentials can be applied for this potential wave. In this way, the application can be optimised, so there is always a fresh working electrode surface available.

The equipment works for glycerol determination in all kinds of oil methyl esters. It includes a straightforward extraction and saponification-extraction for determining the free and bound glycerol content, respectively. With an MDL of 0.5 ppm by mass for total glycerol, IC-PAD exceeds the requirements of ASTM and DIN standards. ●

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