Biodiesel Analytics

Important Parameters and their Meaning

Content of fatty acid methyl esters ("ester content")

Test method: EN 14103 (GC)
Limit value: min. 96.5% (m/m)

The content of fatty acid methyl esters, frequently called ester content, is a measure for the purity of the FAME. Fatty acid methyl esters, produced by the reaction of fats and oils or fatty acids with methanol, differ regarding the chain length of the fatty acids and the number of double bonds. The ester content is determined as a total of the fatty acid methyl esters of C6:0 to C24:1 and indicated in percent by mass % (m/m). It is determined by gas chromatography in accordance with EN 14103. The biodiesel standard EN 14214 requires a minimum content of methyl esters of 96.5% (m/m).

Fatty acid profile

Test method: EN 14103 (GC)
Limit values:
Content of linolenic acid (C18:3) max. 12% (m/m)
Content of polyunsaturated FAME (≥ 4 double bonds) (PUFA) max. 1% (m/m)

The fatty acid profile indicates the distribution of fatty acids in oils and fats and the products resulting thereof. The distribution of the different FAME provides information on the feedstock used. It is used to determine the ester content and the also limited content of linolenic acid methyl ester, as well as for the calculation of the iodine value. The abbreviated designation of the fatty acids comprises the number of carbon atoms and the number of double bonds (e.g. C18:2 for a carbonic acid with 18 carbon atoms and two double bonds). The distribution of the various fatty acid methyl esters is indicated in percent by mass %(m/m), in relation to the total amount of fatty acid methyl ester. The limit value for linolenic acid of max. 12% (m/m) and PUFA of max. 1% is intended to contribute to the stability of the biodiesel, as tri- and polyunsaturated fatty acids in particular are extremely prone to oxidative attacks.

Sulphur content

Test methods: EN ISO 20846 (UVF)/
EN ISO 20884 (wdXRF)
EN ISO 13032 (edXRF)
Limit value: max. 10 mg/kg

Sulphur compounds can be absorbed by plants during growth, while animal fats can contain sulphur in the form of protein compounds. FAME produced from vegetable feedstocks usually contains 2 to 7 mg sulphur/kg. Animal fats with up to 30 mg/kg must be refined in order to remove the Sulphur by suitable processes (e.g. distillation). The sulphur content of diesel fuels has been limited to 10 mg sulphur/kg in Europe since 2003 to reduce SO_2 emissions from road traffic and to protect sensitive exhaust gas aftertreatment systems against poisoning. The same requirement was already incorporated in EN 14214 at the beginning of the standardisation work.

Water content

Test method: EN ISO 12937 (Karl-Fischer titration) Limit values: max. 500 mg/kg (EN 14214)
AGQM: max. 300 mg/kg for traders
max. 220 mg/kg for producers

Almost all biodiesel processes use a water wash as the final refining step for the removal of free glycerol, soaps and other impurities. As FAME, in contrast to hydrocarbon-based fuels, can bind relatively large amounts of water on account of its polar properties, the product must be dried before the final completion.

Owing to the high affinity to water, FAME can also absorb water under the effect of high air humidity; the storage conditions therefore have to be chosen so that this is extensively prevented. Under normal conditions the saturation concentration of FAME is 1,500 mg water/kg. At low temperatures especially in mixtures with non-polar fuels free water can precipitate. It can also cause corrosion and accelerate microbial growth. The water content is limited to 500 mg/kg in EN 14214. Due to the properties outlined above AGQM requirements are significantly stricter here with max. 300 mg/kg for traders and max. 220 mg/kg for producers.

Total contamination

Test method: EN 12662
Limit value: max. 24 mg/kg
AGQM: max. 20 mg/kg

The total contamination is a measurement for the content of filterable solid particles so called "Rust and Dust" in diesel or biodiesel. It is determined gravimetrically by filtration and weighing of the filters. High contents of insoluble particles can lead to filter blockages, wear to the injection system and valve leakage. Because of the relatively bad precision of the method, AGQM has specified a stricter limit of max. 20 mg/kg.

Oxidation stability

Test method: EN 14112 ("Rancimat")
Limit value: min. 8 h min.

The oxidation stability is a measurement for the resistance to oxidative processes. EN 14112, the so called Rancimat, serves as test method: an air stream is passed through the sample at high temperature. Volatile oxidation products form after any present antioxidants are used up. These volatile compounds increase the conductivity in the measuring cell. The time until determination of this oxidation products is called induction time or oxidation stability.

Fatty acid methyl esters are prone to oxidation processes owing to their chemical structure. Double bonds of unsaturated fatty acids react with oxygen forming peroxides, while consecutive reactions can cause the chains to break, leading to the formation of shortchain carbonic acids and polymeric structures. Natural antioxidants such as tocopherols, being present in significant quantities in vegetable oils, slow down the aging process. Synthetic stabilisers are also used on a broad basis. AGQM once annually analyses oxidation stabilisers for their efficiency and their trouble-free application. Additives that pass the test are released in the "no-harm list" on AGQM's homepage.

Acid value

Test method: EN 14104 (Titration)
Limit value: max. 0.5 mg KOH/g

The acid value is a measurement for the acid content and hence for potentially corrosive properties of biodiesel. The reaction of free fatty acids from the feedstock with the catalyst causes alkaline metal soaps formation in a secondary reaction of the transesterification. These soaps are removed from the product almost completely by physical separation. The low remaining soap residues are split by washing with inorganic acids, and the resultant free fatty acids remain as fatsoluble component in the biodiesel. Free fatty acids are very weak acids and hence only slightly corrosive; nevertheless, an effect on metallic components cannot be ruled out. The limitation of the acid value to 0.5 mg KOH/g, corresponding to a fatty acid content of approx. 0.25 % ensures that biodiesel does not induce corrosion caused by acids. Nevertheless, the acid value of FAME can rise during storage, if esters are split or short-chain carbonic acids are formed as a result of aging processes (see also: "Oxidation stability"). However, this effect can hardly be

observed under normal storage conditions.

Iodine value

Test methods: EN 14111 (Titration), EN 16300 (calculated)
Limit value: max. 120 g Iod/100g

The iodine number is a measurement for the content of unsaturated fatty acids in fats and oils and hence also in biodiesel. The iodine value varies with the type of feedstock used. It is either measured by titration or calculation from the fatty acid profile which is determined by gas chromatography according to EN 14103. The result is indicated in g iodine /100 g biodiesel. As unsaturated fatty acids are more sensitive to oxidation, biodiesel with a high iodine value is less stable against oxidation than more saturated FAME. The iodine value of biodiesel is therefore regarded as an additional stability parameter. Based on experience with rapeseed oil methyl ester, the maximum is specified at 120 g iodine/ 100 g in EN 14214. The iodine value can be set corresponding to the specifications by mixing various FAME.

Mono-, di- and triglycerides, free glycerol

Test method: EN 14105 (GC)
Limit values:
Monoglycerides max.0.70 % (m/m)
Diglycerides max.0.20 % (m/m)
Triglycerides max.0.20 % (m/m)
Free glycerol max.0.02 % (m/m)
Total glycerol max.0.25 % (m/m)

The transesterification of vegetable oils with methanol is an equilibrium reaction, as are all chemical reactions. Besides the main product FAME, the end product also contains the intermediate phases of the reaction (mono- and diglycerides) as well as non-converted vegetable oil (triglycerides), depending on the reaction conditions. As conversion of the monoglycerides to fatty acid methyl esters is the slowest partial reaction, the following concentration ratios can normally be found:
Monoglycerides > diglycerides > triglycerides. With appropriate effort, the glyceride content can only be influenced by the reaction conditions up to a certain degree, as a chemical equilibrium arises in all cases. More extensive removal of the by-products is only possible by distillation. Free glycerol is released from the oils and fats during the transesterification. As glycerol is insoluble in FAME but is easily soluble in water, it can be removed almost completely by decanting and subsequent water washing. The glycerides and glycerol are determined by gas chromatography in accordance with EN 14105.

Monoglycerides

A high content of monoglycerides can lead to coking and deposits in the injection system. Owing to their high melting points, monoglycerides, in particular the saturated ones are also suspected of being one of the main causes of precipitation and hence poor cold properties and filter blockages. The limit value for monoglycerides in EN 14214 is 0.70 % (m/m).

Saturated monoglycerides

Test method: EN 17057
Scope: 200 mg/kg – 1,500 mg/kg

Saturated monoglycerides (SMG) are suspected to lead to filter blocking and poor cold behaviour, particularly in diesel/FAME blends. However, the SMG content of biodiesel cannot be determined directly with the GC test method (EN 14105). As an alternative, it was calculated by using the monoglyceride content and the Cloud Point (EN 14214 Annex C) so far. This method was relatively inaccurate due to the precision of the respective methods and the error propagation. In the meantime, there is a GC-FID method (EN 17057) for the direct determination of SMG. Currently, no limit is

set for saturated monoglycerides. AGQM recommends a maximum content of 1,200 mg/kg in its guidelines for FAME as blend component.

Di- and triglycerides, free glycerol

High boiling points and incomplete combustion of these by-products can lead to coke formation in the injection system and in the cylinder. The maximum content of di- and triglycerides is consequently limited to 0.20 % (m/m), the content of free glycerol to 0.02 % (m/m). Triglycerides can also find their way into the end product via the logistics chain: this can generally be discerned by an atypical distribution of the mono-, di- and triglycerides.

Na/K content (alkali metals)

Test method: EN 14538 (ICP-OES)
EN 14108/EN 14109 (AAS)
Limit value: Na + K max. 5 mg/kg

Sodium and potassium hydroxides or methylates are used as a catalyst for biodiesel production. Residues thereof are usually present as soaps which are not fully removed in the wash. Soaps can lead to filter blockages and adhesions of injection pumps and nozzles. Another important aspect is ash formation: in particular sodium accumulates on the surface of particle filters and oxidation catalysts, thereby reducing the efficiency and service life of the systems. Suitable process conditions allow the alkali metal content to be reduced to concentrations below the determination limit of the specified test method.

Ca/Mg content (earth alkali metals)

Test method: EN 14538 (ICP-OES)
Limit value: Ca + Mg max. 5 mg/kg

Earth alkali metals enter the biodiesel when using tap water for the water wash. Calcium and magnesium soaps are formed by reaction with free fatty acids. Soaps of earth alkali metals are more voluminous than alkali metal soaps and can lead to filter blockage and adhesion of injection pumps. The entry of earth alkali metals into FAME can be prevented by using soft water (condensate, demineralised water).

Phosphorus content

Test method: EN 14107 (ICP-OES)
Limit value: max. 4 mg/kg

Phosphorus can be found in vegetable oils as well as animal fats as phospholipids. It is a typical catalyst poison which can irreversibly affect the function of exhaust gas aftertreatment systems. Even low phosphorus contents can already lead to longterm effects in continuous operation. The phosphorus content is reduced by degumming in vegetable oil production, distillation having to be carried out during the production of biodiesel from animal fats. If phosphoric acid is used in the process to remove the catalyst, phosphorus can also originate from there. However, phosphoric acid can usually be removed from the biodiesel very effectively with water. At present the precision of the method does not allow for any additional tightening of the limit.

CFPP

Test method: EN 116
Limit value as per DIN EN 14214 for biodiesel as blend component for Diesel fuel:

Summer:	max. 0°C from 15.04. to 30.09.
Intermediate:	max. -5°C from 01.10 to 15.11.
	max. -5°C from 01.03. to 14.04.
Winter:	max. -10°C max. from 16.11. to 28./29.02.

The cold filter plugging point (CFPP) is a measurement for the filterability at low temperatures. A sample is cooled in 1°C-steps and sucked through a filter. If the sample can no longer be filtered within 60 seconds, the CFPP is reached. There are national requirements with respect to the

Biodiesel Analytics

CFPP depending on the climatic conditions. In Germany, a distinction is made between the limit values for summer, intermediate and winter quality. Inadequate cold flow properties of the fuel can lead to blocked filters and engine problems or even failure of the injection pump. The cold flow properties of the biodiesel depend on the distribution of the fatty acid methyl ester and hence on the feedstock used: the freezing points of saturated fatty acid methyl esters are significantly higher than those of the unsaturated compounds, which also remain liquid at temperatures far below 0 °C. The cold properties of the biodiesel can be improved by the addition of flow improvers. As biodiesel is nowadays predominantly used as a blend component for Diesel fuel, additives are not used on a regular basis. In Germany, the regulation applies that between the 16.11. and 28./29.02. only a CFPP value of -10°C has to be maintained, but the supplied product has to be able to achieve the -20°C required in DIN EN 14214 when suitable additives are added. The fulfilment of this requirement is a prerequisite for the marketability of biodiesel pursuant to 36th Federal Immission Control Ordinance (36. BImSchV, §5).

Cloud Point

Test method: DIN EN 23015
Limit value as per DIN EN 14214 for biodiesel as blend component for Diesel fuel:

Summer:	max. 5°C from 15.04. to 30.09.
Intermediate:	max. 0°C from 01.10 to 15.11.
	max. 0°C from 01.03. to 14.04.
Winter:	max. -3°C max. from 16.11. to 28./29.02.

The Cloud Point is the temperature at which temperature-induced precipitation ('clouds') sets in when a clear liquid product is cooled down under stipulated test conditions. Upon publication of DIN EN 14214:2012 in November 2012 the Cloud Point has since been part of the requirements for biodiesel as blend component in Germany. There are also national requirements with respect to the Cloud Point depending on the climatic conditions. In Germany, a distinction is made between the limit values for summer, intermediate and winter quality.

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Note

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