Association Quality Management Biodiesel e.V.

20 YEARS

AGQM LEAFLETS

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- an 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 (www.agqm-biodiesel.com).

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 fat-soluble 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.

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.

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 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).

BIODIESEL – TANK AND STORAGE

This leaflet should provide you with guidance on legal regulations and how to proceed with the storage of biodiesel, fuels mixed from diesel and biodiesel, and bio heating oil.

It is recommended to use biodiesel as a liquid energy carrier in nature conservation areas and the areas protected against sewage pollution, because biodiesel does not have hazardous material properties and has the lowest water hazard class (Wassergefährdungsklasse – WGK I).

Biodiesel or FAME (Fatty Acid Methyl Esters) consists of fatty acid methyl esters of different chain lengths. Due to the chemical and physical properties of FAME (polarity, functional groups, oxidation stability) it is necessary to maintain consistent quality assurance measures. Proper storage has a decisive influence on the quality of biodiesel.

The basics

Tank and storage installations in which combustibles, flammable or highly flammable materials (or mixtures thereof) are stored or transferred are treated as areas requiring supervision and subject to the BetrSichV[1] regulation, which in most cases envisages, among others, regular checks and the possibility of withdrawal of the authorization by the competent control authorities. Although pure biodiesel (B100) does not qualify as a dangerous substance, these and further provisions are valid for mixtures of diesel and biodiesel or bio heating oil.

For the assessment related to the commissioning and setting up of the tank, the WHG[2] – and the AWSV[3] regulation are of decisive importance for water hazard materials. The AwSV ordinance provides for the general obligation of a specialist company (Fachbetriebspflicht) for installations with a total volume of over 1,000 liters. All technical rules (TRwS[4], list of construction rules and standards) are defined as commonly recognized technical rules. In addition, depending on the location and volume of tanks, it is also obligatory to report and control them. For the storage of fuels, the principle is that in the case of a permitted mixture, the requirements for storing a fuel component with the higher water hazard class, in this case diesel fuel, must be respected. The installation marking is an important component of the safety markings for hazardous materials and is legally prescribed on the tank (or in the exposed area).

Above-ground and underground tanks

Basically, only tanks that have pattern approval or are compliant with the standard in the list of building rules (or from VV TB[5]) (§33 of the BImSchG[6]) can be operated. The corresponding lists must be clearly assigned to a given tank. Safety devices such as overfill protection (maximum value limiter), leak indicating devices, liquid alarm detectors in collecting containers or all installed components must have proof of their suitability in accordance with construction law. Overground tanks, regardless of their volume, must be constructed either with double walls and have a leak indicator, or they must be placed in a sufficiently large, airtight and durable room. In the case of aboveground tanks (capacity < 1,250 l), overfill protection or the maximum value limiter are not obligatory if it is filled using the self-locking hose end. Underground tanks must always have a double wall and be equipped with a leak indicator and fill level bar. Underground tanks of all sizes must be

controlled at their commissioning, withdrawal from use, in the event of significant changes and at regular time intervals. All installations or parts of installations that are partly or completely embedded in the ground are considered to be underground. All other installations (also in accessible underground rooms) are considered to be above-ground.

Construction material for tanks

In general, it should be taken into account that all used materials are appropriate for tanks, seals and construction products (construction products regulation, list of construction rules), as well as for the use of biodiesel or biodiesel mixtures.

The manual DIN-Taschenbuch 183 *Containers for liquids that are hazardous to water, flammable and non-flammable,* cites different standards for tanks. From DIN 6601 standard, containing a list of positive liquids for steel tanks, it can be read that all steels are suitable for biodiesel storage (item 292). In addition, various polymeric reservoir materials such as polyamide (PA) polyetheretherketone (PEEK)[7] and fiberglass reinforced plastic (GRP)[8] are suitable for biodiesel storage. Copper and other non-ferrous metals, or their alloy are in a complete tank and pipe system useful only under certain conditions and should rather be replaced.[9] This action aims to avoid corrosion, the formation of metal soaps and a negative impact on a long-term stability, which could deteriorate the quality of fuel and propellants. In addition, tanks or galvanized containers are not appropriate from the point of view of today's technology. Galvanic anodes must be removed before filling with biodiesel.

Pipes

In the area of the tank, pipelines are usually made of carbon steel. Attached or installed parts of colored metal (copper, brass, bronze) or galvanized materials should be replaced with equivalent parts made of steel or aluminum or be dismantled, if possible and acceptable from a functional point of view. In the area occupied by fuel oil, copper pipes are often found as suction pipes. The use in a onepipe system should be perceived as less critical.[10] However, copper wires should be replaced as much as possible with steel pipes. It is not advisable to use biodiesel in a double pipe arrangement with copper pipes, where unburnt fuel goes back to the tank. Such a system should be switched, according to the accepted technical rules, to work in a one pipe arrangement.

Seals

Already at the beginning of biodiesel use, compatibility problems were found when using existing EPDM and NBR seals. Due to their polar nature, biodiesel molecules deposit in these plastics and cause swellings leading to leaks. Sealing materials and membranes were identified as appropriate plastics for fluorinated rubber materials such as FKM and FFKM and PTFE[7,8].

Sealing surfaces and drainage devices

For safe storage, the correct functioning of the sealing surfaces (stones/joints) is essential. They should be checked visually, however any damage should be immediately removed in a professional manner.

Based on the documentation, please check whether the sealing materials (paint primer and sealing tape) and concrete stones for the upstands are suitable for use in the case of biodiesel. This also applies to diesel fuels with a higher proportion of biodiesel. Some paint primer for seals are not resistant to biodiesel or they undergo decomposition later. Stones with a layer of delicate mortar applied separately proved to be useless in a long-term exploitation.

In addition, for the use of biodiesel, check installed light liquid separators and other evacuation devices – according to the type/size of materials used. The settings should be made at an apparent product density of 0.95 g/cm^3, so that the automatic shut-off device works properly and the separator can be used as an additional retention volume. The DIN 1999-101 standard relating to light liquid separators with a certain biodiesel content should be used. In general, for new installations and changes, the manufacturers of construction products or a specialist plant should be consulted.

Cleaning, tank check

Although under the statutory regulations, checks of the tank are generally only necessary after 5 years (and do not necessarily imply prior purification of the tank), in the interest of preserving good biodiesel and avoiding product liability tanks should be cleaned every 2 years. The existing control obligation (Prüfpflicht) is regulated by the AWSV. When cleaning and checking the tank, it is especially necessary to check for corrosion pits and deformation of the tank walls or changes in the tank material. If a coating is used, it should be checked for a biodiesel-proof property.

Biodiesel storage

When storing fuel and propellants, and thus also biodiesel, the common rules of "good house-keeping" included in the guide of good system maintenance – DIN CEN / TR 15367-112 must be observed.

When biodiesel is stored, it is also necessary to pay attention to the high output quality of biodiesel. The most important quality parameters for biodiesel storage include oxidative stability and water content.

Ensuring oxidation stability
The addition of appropriate stabilizers to biodiesel usually takes place in the production process and is necessary for safe storage in order to achieve the required oxidation stability of 8 hours. If storage is to be carried out over a longer period, it is reasonable to increase the stability beyond the required minimum of 8 hours. It is possible to use additives with old biodiesel, however, the stabilizing properties of the additives may be reduced.

Notice acid number
The corrosive effect of free fatty acids is small. However, due to the aging process, the acid number of FAME during storage may increase, due to which it is not possible to completely rule out the impact on metal structural parts. However, under conditions free of non-ferrous metals, this effect is almost imperceptible.

Low water content
The hygroscopic properties of biodiesel lead to the fact that during storage, water can be absorbed from moisture contained in the air. Pure biodiesel can physically dissolve up to 1,500 mg/kg of water (DIN EN 14214: max

500 mg/kg). At lower temperatures, primarily in mixtures with non-polar fuels, a free aqueous phase can be formed. Free water causes corrosion and serves as a nutrient solution for microorganisms, which in turn create biofilms.[11] In order to avoid free aqueous phase, always fill storage tanks in such a way that only a small volume of air remains. Before filling with biodiesel, tanks should be as clean and dry as possible. The use of a water separator should also be considered. It is practically impossible to store biodiesel so that it does not come into contact with water (moisture). Based on the above-described properties, AGQM sets stricter requirements to be followed by its members (producers: max. 220 mg/kg, traders: max. 300 mg/kg). In general, it should be noted during storage that contamination with other fuels, and in particular the introduction of water into the product, can be excluded by appropriate measures.

All these parameters are regulated by DIN EN 14214 standard. Further information on these and other important quality parameters can be found in the leaflet *Biodiesel Analytics* (page 4).

Cold and dark conditions

Generally, all fuels and propellants should be stored in cold and dark conditions. All reactions leading to the deterioration of the quality of liquid energy carriers proceed faster at elevated temperatures. This should be avoided by cold storage. Degradation induced by light leads to faster aging of fuels and propellants and therefore should be excluded.

Research projects have shown that long-term stability under good storage propellants conditions and with sufficient addition/stabilization of B100 can be over six months, and in the case of B20 mixtures many years.[12,13] If storage out of prescribed conditions is expected (e. g. in emergency aggregates, network replacement devices), the use of biodiesel or mixtures with biodiesel is discouraged.[14]

1 BetrSichV – Regulation on operational safety – German implementation of guideline 2009/104 / EG.
2 WHG – Water Ressources Act
3 AwSV – Ordinance on Installation for the handling of water hazardous substances
4 TRwS – Technical rules for water hazardous materials; TRwS 791 for installations using fuel oil
5 VV TB – Administrative provision of Technical Requirements for Construction Works
6 BImSchG – Federal law on protection against emissions
7 Bürkert Fluid Control Systems – durability table
8 Institute of Heat and Oil Techniques e. V., Project Resistance of materials, 2009
9 German Society for Petroleum and Coal Science and Technology e. V. – Project 729
10 Institute of Heat and Oil Techniques e. V. – construction parts of oil fuelling
11 German Society for Petroleum and Coal
12 R. L. McCormick, E. Christensen, Fuel Processing Technology, 128, 2014, 339 – 348.
13 German Society for Petroleum and Coal Science and Technology e. V. – Project 714
14 German Federal Office of Civil Protection and Disaster Assistance – emergency power supply in enterprises and public authorities

RECOMMENDATION ON ADDITIONAL REQUIREMENTS FOR FAME AS BLEND COMPONENT

Preamble

Biodiesel (FAME) is a fuel component important for the achievement of the legally set targets concerning the reduction of GHG emissions generated by road traffic. Worldwide, biodiesel is used as blend component to conventional Diesel fuel.

Today, the standard for Diesel fuel, EN 590, sets uniform European requirements. It allows the blending with FAME up to 7% (V/V). Every EU member state implements the standard in national requirements. In Germany this standard is put into force by DIN EN 590:2017-10.

All stipulations mentioned for biodiesel were based on the application of EN 14214 for the definition of requirements concerning FAME as blend component. In the meantime, however, there has been a demand regarding diverse additional quality requirements for this component beyond those stipulated in EN 14214, in order to ensure the final product quality of the Diesel fuel. Among others there is also the requirement to verify quality assuring measures during the production as well as the purchase of biodiesel which essentially base on obligatory in-house documentation. Additionally, customers must be given confirmation and verification that the internal documentation requirements are met and checked externally (e. g. by audits).

For that, the following aspects must be observed and/or verified:

- Compilation and observation of an explicit quality management manual,
- Internal and external checks of the product's quality parameters at regular intervals,
- Application of measures which reduce and alleviate unfavourable influences due to storage and transport
- Application of measures which ensure that inferior products are not marketed
- Proof of competence and qualification for a sound product control, i.e. by participation in Round Robin tests.

Objectives

This recommendation is meant to close gaps in the existing requirements for FAME used as blend component beyond DIN EN 14214:2014. The recommendation presented is based on the assessment of technical facts and the analysis of the risk that a produced blend fuel may not be 'fit for purpose'.

It is a compendium of the results of comprehensive scientific/technical research reports and monitoring of product properties of FAME as well as field studies in Germany and findings of experts.

Additionally, with the implementation of this recommendation it is intended to simplify the pooling of data of any parameters to be viewed in the future, in order to improve the data situation for any advancement of EN 14214. The additional requirements suggested here are checked periodically in line with any further development of EN 14214 and adjusted if necessary. This recommendation applies for blending with up to 7.0 % (V/V) FAME.

Note:
Not all limitations of test parameters, which would objectively be desirable in principle (e. g. reduced limits for metal contents), can be achieved due to the current status of the test methods. Furthermore, requirements with a fixed limit should not be included if standardised or sufficiently validated test methods are not available. Ultimately, such requirements would rather produce new uncertainties instead of improving the marketing situation of FAME.

Requirements

FAME used as blend component should comply with the following additional conditions beyond the fulfilment of the requirements of DIN EN 14214:

Parameter	Test method/Criterion	Value/Condition	
General			
Clear & bright	Appearance: „At 15 °C at least clear and bright of undissolved water and visible contamination“	Condition must be observed	(1)
Water content	DIN EN ISO 12937	max. 300 mg/kg for traders max. 220 mg/kg for producers	(2)
Cold property and filterability			
Pourpoint (PP)	DIN EN ISO 3016	16.11. to 28./29.02. max. 6 °C and min. - 18 °C	(3)
Total contamination	DIN EN 12662:1998	max. 20 mg/kg	(4)
Optionally			
Content of Steryl-glycosides (SG)	DIN EN 16934:2017	Measuring value must be given (no limit)	(5)
Saturated Mono-glycerides (SMG)	DIN EN 17057:2018	Measuring value must be given (recommended limit max. 1,200 mg/kg)	(6)
Oxidation stability and Stabilisers			
Oxidation stability	DIN EN 14112	min. 9 h	(7)
Proof of observance of the no-harm criteria and proper dosage of the oxidation stabilisers (min./max.)	Recommendation of the no-harm criteria and determination of the relative efficiency according to the description of the methodology of the no-harm test (available on request at AGQM). (See also no-harm list of AGQM under www.agqm-biodiesel.com)	Requirements must be complied with; supplier must give confirmation thereof. On request supplier reveals data supporting his confirmation.	(8)

Explanation of the requirements

(1) The parameter "clear & bright" is easy to determine and with its use mineral oil products have been successfully characterised for a long time. It averts the acceptance of obviously faulty products which may contaminate storage facilities for example.

(2) FAME is hygroscopic and can solve up to 1,500 mg water/kg. From a multitude of investigations it is known that the exhaustion of the maximum water content of FAME stipulated as 500 mg/kg by DIN EN 14214 can have various detrimental consequences for blend fuels. These include e. g. precipitation of water when mixing with very non-polar arctic Diesel fuels which may lead to corrosion and microbial growth. The suggested limits of 220 mg/kg for producers and of 300 mg/kg for traders may avert these risks.

(3) The Pourpoint (PP) secures that FAME can be handled safely until it is blended. This is only relevant during the winter period. The lower limits are set in order to restrict the use of additives with a potential for incompatibility.

(4) The reduction of the limit of the total contamination compared with that of DIN EN 14214 provides a 'safety buffer' which improves the application security of the product. At European level, CEN TC19 WG31 is currently working on a new method for the determination of total contamination in FAME. At present, method EN 12662:2008 is recommended. However, it was shown that EN 12662:1998 gives excellent results with low effort and sample volume. In the national foreword of DIN EN 12662:2008 the use of the method from 1998 is recommended.

(5) In multiple examinations it was shown that sterylglycosides are one of the main sources for poor filterability of FAME and blend fuels made thereof. But next to the connection between filterability and the sterylglycoside content further impacts have to be taken into account. Moreover, the blend fuel made from FAME with a poor filterability does not automatically have a poor filterability itself. A complete refining of the crude oil usually leads to a FAME with no significant amounts of sterylglycosides. In 2017, a test method for the determination of sterylglycosides (DIN EN 16934) was validated.

(6) Saturated monoglycerides (SMG) are hardly soluble in mineral Diesel due to their physicochemical properties, they accumulate in the cold and may lead to precipitations. Higher concentrations of those components cause a deterioration of the filterability of blend fuels up to a point of risking filter blocking in vehicles. In 2018, DIN EN 17057 was released, a method to measure the SMG content directly. Alternatively, the SMG content was calculated via the monoglyceride content and the Cloud Point (CP). Until now no limit value for SMG content could be defined because neither a correlation nor the actual contents were determined yet. On a basis of FAME monitoring and determined concentrations thereof, AGQM recommends a maximum SMG content of 1,200 mg/kg.

(7) The increase of the limit of the oxidation stability compared with that of DIN EN 14214 provides a 'safety buffer' which improves the application security of the product.

(8) DIN EN 590 contains a strong recommendation for the use of stabilisers for FAME. The assumption is that proper dosage applies because both excess and reduced dosages cause detrimental effects. Against this background, a no-harm test for oxidation stabilisers for FAME was developed which at the same time provides the option to assess the relative efficiency of stabilisers, thus enabling a proper dosage by the user. The no-harm list with all successfully tested additives can be found on AGQM's homepage under www.agqm-biodiesel.com.

Not recommended as additional requirement

It is not recommended to limit the colour of FAME since it is no true quality feature. Potentially critical products are safely excluded by means of the other characteristics of DIN EN 14214 with the combination of 'clear and bright'.

There is no intention to create requirements for an additional limitation of the Na, K, Ca, Mg and P contents below the limits stipulated in DIN EN 14214; also, there will be no additional limitation of other metal contents. Such specifications cannot be supervised and monitored with the precision data of the existing test methods with legal reliability. However, it should be noted that the values measured in the field lie far below the limits of DIN EN 14214.

It is not recommended to limit the filter blocking tendency (FBT), because the precision of the method (IP 387[1]) is not sufficient. Until now, neither correlations between FBT and occurrences in the field (e. g. dead vehicles) nor between FBT and other parameters like sterylglycosides or saturated monoglycerides could be found. Additionally, a multitude of factors (e. g. storage, transport) have an influence on the FBT.

[1] https://publishing.energyinst.org/topics/fuel-quality-and-control/ip-test-methods/ip-387-determination-of-filter-blocking-tendency

TAKING RETAIN SAMPLES

The aim of taking retain samples is the documentation of the current quality status of the product. As a rule, certain causes of problems with the product can be identified and complaints about their accuracy can be checked. The informative value of a retain sample depends largely on the circumstances during the sampling.

This leaflet describes the key points about organization and requirements for sampling.

Requirements for sampling

In principle, the requirements of **DIN EN ISO 3170** – *Petroleum Liquids – Manual sampling* must be adhered to when sampling liquid fuels.

Take a representative sample (draw a flow quantity dependent on the sampling point to ensure that actual fuel is freshly withdrawn from the tank). If taken directly from tanks, use the prescribed draft method or make a mixed sample from the start, middle and end of the discharge (for example, for vehicles with bottom-only loading).

The **sample containers** must be suitable, clean and dry. Never use test tubes intended for use with food. Fill the vessels as completely as possible and with as little air entrapment as possible. For biodiesel and mineral diesel fuel tin canisters with press-fit lids are well-proven.

Take a **sufficient sample quantity** (at least 1 l) to ensure that all tests can be carried out in accordance with standards.

Organisation of Sampling

Sampling should always be recorded in a sampling protocol. A special form is not defined for this purpose. Nevertheless, the following minimum information should be included:

- Reason of sampling
- Place of sampling
- Date of sampling
- Type of sampling (outlet, put-through, bottom sample, etc.)
- Name of the sampler
- Sample taken (also divided in different vessels)
- Special circumstanced when taking samples (weather, statements from other persons, etc.)
- Reciprocal agreements to recognize a sample as “representative”
- Signature of the sampler and at least one witness on the sampling protocol

An example of such a sampling protocol can be found at the end of this leaflet.

The sample containers must be labelled unambiguously and legibly (ensure assignment to the sampling protocol) and sealed in such a way that subsequent changes to the sample are clearly visible, possibly seale.

In each case, three similar samples should be prepared (1 sample for the own company, 1 sample for the trading partner, 1 arbitration sample). Store samples in a dry place at temperatures between 8 – 15 °C. The retention period should be at least 3 months. A sample storage beyond 6 months does not make sense.

Sampling Protocol - Example

	ID:
Company	
Street	
Postal Code, City	

Information on Sampling

The manufacturer makes use of the derogation according to chapter 2.2.1.2 of the QM system of AGQM with low production.	Yes ☐	No ☐
Due to the derogation, the sampler took two retain samples of the last batch produced in the last three months (a third sample of the batch sampled remains in the company as retain sample).	Yes ☐	No ☐

Designation of the samling point	*Sampler*	*Date of Sampling*	*Time*
Operational description of the batch	*Responsible person in the company*		

Further Information

Purpose	☐ B100 ☐ Blend component for diesel fuel ☐ Blend component for biodiesel	
Feedstock		
The sampling point is the one reported to AGQM.	Yes ☐	No[1] ☐
The condition of the sampling point is suitable for carrying out the sampling (free from contamination and adhering water, correct operability, safety at work).	Yes ☐ Retain sample ☐	No[1] ☐
The samples for operational quality assurance are also taken at this point.	Yes ☐	No[1] ☐
Retain sample was given to the company.	Yes ☐	No[1] ☐
The plant or analysis certificate of the tested batch is attached.	Yes ☐	No[3] ☐

[1]Please briefly explain below. [2] Volume per retain sample mind. 1 l
[3]will be handed in within 5 working days

Other comments / specifics:

The sampling was carried out in the presence of a representative of the company. All circumstances relevant to sampling (including the name of the sample) are recorded in the log.

Signature Sampler *Signature of the representative of the company*

COLD PROPERTIES OF BIODIESEL

The cold properties of fuels have always been an important quality criterion. For fuels with insufficient cold properties, partial or complete crystallization may occur at low temperatures. As a result, lines and filters in the vehicle can be blocked and lead to break down. The requirements for the cold properties of fuels vary according to the country, depending on the prevailing climatic conditions and the season. This leaflet is intended to give an overview of the national requirements and the cold properties of biodiesel (fatty acid methyl ester – FAME).

Regulatory Base – Parameters

Both the diesel fuel standard EN 590 and the biodiesel standard EN 14214 define requirements for the fuel depending on the climate. The climatic requirements are defined in the national annex on the basis of meteorological data and provide the requirements for a summer and a winter class as well as two intermediate classes.

The Cold Filter Plugging Point (CFPP, EN 116) is defined as a requirement for diesel fuel as well as for biodiesel as pure fuel (B100) and as blend component for diesel fuel. The CFPP is considered a measure of cold filterability. A sample is cooled in 1 °C steps and sucked through a filter. If the sample is no longer filterable within 60 seconds, the limit of filterability is reached.

In addition, for biodiesel as a blend component for diesel fuel, the cloud point (CP, EN 23015) is defined. The Cloud Point indicates the temperature at which the first precipitates ("clouds") form in a clear, liquid product when cooled under specified test conditions. (Detailed information on the two parameters can also be found in the leaflet *Biodiesel Analytics* (page 4).)

The following table lists the limit values for CFPP and CP for B100 and biodiesel as blend component, which apply in Germany depending on the period:

Period	B100 (CFPP)	FAME as blend component (CFPP/CP)
15.04. – 30.09.	0 °C	0 °C / 5 °C
01.10. – 15.11. and 01.03. – 14.04.	- 10 °C	- 5°C / 0 °C
16.11. – 28./29.02	- 20 °C	- 10 °C / -3 °C

Influence of different FAME Types/Fatty Acid Patterns

Biodiesel consists of fatty acid methyl esters, which differ in chain length and degree of saturation. Their composition varies depending on the raw material used. Methyl esters of saturated fatty acids have significantly higher melting points than those of unsaturated fatty acids.

The melting points of the fatty acids and their share allow conclusions about the cold properties of the corresponding biodiesel. In palm oil or animal fats, the share of saturated fatty acids is very high. Biodiesel from these raw materials has correspondingly lower cold properties than biodiesel from e. g. rapeseed oil with a high content of unsaturated fatty acids (see table).[1]

From the table it can be seen that the use of a pure palm methyl ester is not possible in the summer months, since the climatic requirements cannot be met. A blend of different FAME types is therefore common. Due to the high requirements on the CFPP, predominantly FAME blends

Fatty Acid Methyl Ester	Melting Point	Share Palm Methyl Ester (PME)	Share Rapeseed Methyl Ester (RME)	Share Soja Methyl Ester (SME)
C12:0	+ 5 °C	0,5 %	–	–
C14:0	+ 19 °C	1 – 2 %	–	–
C16:0	+ 31 °C	40 – 48 %	3 – 5 %	11 – 12 %
C18:0	+ 39 °C	4 – 5 %	1 – 2 %	3 – 5 %
C18:1	- 20 °C	37 – 46 %	55 – 65 %	23 – 25 %
C18:2	- 35 °C	9 – 11 %	20 – 26 %	52 – 56 %
C18:3	- 46 °C	0,3 %	8 – 10 %	6 – 8 %
Resulting CFPP		PME appx. + 13 °C	RME appx. - 14 °C	SME appx. - 2 °C

with rapeseed methyl ester as main component are used in winter.

Additives

Through the use of additives, the cold properties of fuels can be improved. In fossil diesel fuel, typically Middle Distillate Flow Improvers (MDFI) and Wax Anti-Settling Agents (WASA) are used. In biodiesel flow improvers (Biodiesel Flow Improver, BDFI) are used as well.

All flow improvers (MDFI and BDFI) work in the same way. When middle distillates are cooled to temperatures below the Cloud Point, flaky crystals are typically formed in rhombic form. Due to their size and shape, these can block filters or assemble into a larger wax structure. Flow improvers modify the crystals into smaller sized needles so that the formed crystals cannot block filters or coalesce. Flow improvers only have an influence on the CFPP, the Cloud Point of the fuel remains untouched. There are known additives that can lower Cloud Point and pour point (see Additional Parameters). However, these are suspected to adversely affect other properties of the fuel.

AGQM together with the mineral oil industry is currently developing a no-harm test for BDFI, which will test the additives for trouble-free use and possible negative interactions.

Additional Parameters

The **Pourpoint** (PP, EN ISO 3016) is not required in EN 590 and EN 14214, but it provides additional information about the cold properties of the fuel. It indicates the temperature to which the sample can be cooled without losing its fluidity.

Sterylglycosides (SG, EN 16934) can be a major cause of poor filterability of FAME. At the end of 2017, EN 16934 was published to determine the content of SG. Complete refining of the crude oil usually results in no significant levels of sterylglycosides in the resulting FAME. Therefore, currently there are few reported problems associated with sterylglycosides.

Saturated monoglycerides (SMG, EN 17057) are difficult to dissolve in fossil diesel because of their physicochemical properties. They accumulate in the cold and can lead to precipitation. Since 2018, there is a method to directly determine the content of saturated monoglycerides. An implementation in EN 14214 is planned, but so far no limit value for the content of saturated monoglycerides has been established.

The AGQM recommends not to exceed a level of 1,200 mg/kg for saturated monoglycerides based on independently performed FAME tests.

The **Filter Blocking Tendency** (FBT, IP 387[2]) was developed as a performance test on the filterability of fuels in the cold. AGQM does not recommend the designation of a limit value for FBT because the method does not have sufficient precision. So far no correlation between FBT and field events (e. g. filter blocking) has been established. Moreover, no correlation could be found between FBT and other parameters such as sterylglycosides or saturated monoglycerides, although the latter have a significant influence on the cloud point of FAME. In conclusion, there are a variety of factors (e. g. storage, transport) that affect the FBT value.

Different committees are currently working on methods derived from the FBT, Cold FBT and Cold Soak FBT. The problems of the original FBT remain however.

[1] Biodiesel the comprehensive handbook, Martin Mittelbach, Claudia Remschmidt

[2] https://publishing.energyinst.org/topics/fuel-quality-and-control/ip-test-methods/ip-387-determination-of-filter-blocking-tendency

TRANSPORT OF BIODIESEL

Biodiesel or FAME consists of fatty acid methyl esters of different chain lengths. In addition to storage, the transport of biodiesel has a decisive influence on its quality.

Due to the chemical-physical properties of FAME (polarity, functional groups, saturation), consistent compliance with simple quality assurance measures should be ensured so that the quality of biodiesel is not adversely affected by transport.

This leaflet is intended to give you information on legal regulations, transport regulations and the handling of biodiesel on the transport route.

Classification, Labelling and Packaging – CLP[1]-Regulation

The classification, labelling and packaging of substances and mixtures has been regulated in a uniform manner throughout Europe by Regulation (EC) No. 1272/2008 (CLP Regulation) since the end of the transition periods on 1 June 2015. There is no classification from the CLP regulation and therefore no specific identification for biodiesel. Biodiesel is classified as water hazard class 1 (WGK 1).

According to the REACH Regulation (EC) No. 1907/2006, fatty acid methyl esters are likewise not classified as hazardous. As a result, the substance information does not necessarily have to be made available in form of a safety data sheet (SDS).

Nevertheless, manufacturers usually provide their customers with substance information on chemical-physical properties, toxicity, degradability and water hazard via voluntary safety data sheets.

Transport routes and naming

Regardless of the transport route, in any case, an identification of biodiesel with the official name is required. For land transport (ADR/RID)[2,3], inland transport, sea transport and air transport (IATA DGR)[4], the official name for carriage of biodiesel is **FAME (biodiesel)**. Due to the high flash point of at least 101 °C (EN 14214), biodiesel is classified under consideration of other safety-relevant characteristics neither as a hazardous substance nor as a dangerous good for land transport or by shipping (Pollution Category Y).

For the transport of biodiesel by land, tank vehicles, carrier vehicles for attachment tanks and battery tanks < 1000 l as well as vehicles for the transport of tank containers and rail tank cars can be used.

As a minimum standard, the vehicles should also have a valid type approval, an ADR/RID approval and an examination in accordance with §29 StVZO (Road Traffic Licensing Regulation). For materials that are suitable for the transport of biodiesel, please refer to the leaflet *Tank and Storage* (page 9).

Caution

Even low levels of contamination or mixing with products with a low flash point such as gasoline, diesel or methanol can lower the flash point significantly below 100 °C, which results in a classification as hazardous or dangerous goods.

The measures for quality assurance in the transport of biodiesel are geared to ensuring that no residues of systems and, above all, no product residues from previous loads lead to a mixing

and thus a deterioration of the biodiesel quality or a change in the safety-relevant properties. Inadvertent filling of tanks with other fuels can be avoided by appropriate labelling.

Handling biodiesel during transport

During transport, problems may arise due to contamination with other fuels or through the entry of water. Special attention should therefore be placed on transport vehicles and containers. The following measures and points should therefore be particularly noted:

» The entry of water into the product must be excluded at every point in the transport chain by appropriate measures (e. g. covered filling stations). When delivering the goods to the gas station, the dome shaft must be free of water. Unnecessary refilling operations should be avoided.

» Non-ferrous metals or their alloys should be avoided throughout the transport system. Even galvanized tanks or containers are not suitable.

» Inadvertent mixing of biodiesel with mineral fuel must be excluded.

» For tank trucks with a full hose system, flush the system including the test section before loading with a sufficient quantity of biodiesel. The control of this measure takes place via the receipt printing, which can be used in case of a complaint to prove the correct procedure.

» Transport containers or vehicles in which previously acids or alkalis (also as mixtures), chemicals, oxidizing substances, glycerol, vegetable oils or products with a flash point < 60 °C (flammable liquids Cat. 1 – 3) were transported must be thoroughly cleaned before loading with biodiesel. If cleaning is not possible, a loading must always be rejected for safety reasons.

» In the case of ship transports, particular care must be taken to ensure that no remains of subcharge, water or solid impurities are present in the tanks. If necessary, an independent inspector should be consulted here.

» The chambers/tanks of the transport device must not contain water or any contamination. This also applies to the chambers/tanks, which should not be filled.

For taking reference samples when loading biodiesel, please refer to the leaflet *Taking Retain Samples* (page 17).

[1] **CLP:** Classification, Labelling, Packaging
[2] **ADR:** European Agreement on the International Carriage of Dangerous Goods by Road
[3] **RID:** Regulation governing the international carriage of dangerous goods by rail
[4] **IATA DGR:** Dangerous Goods Regulations of International Air Transport Association

20 YEARS

All presented standards have been published by Beuth-Verlag and can be obtained there (www.beuth.de).

Note

The leaflet brochure is a summary of the experience of the AGQM and its members and has been compiled with the utmost care. Nevertheless, no guarantee can be given for the accuracy, completeness and timeliness of the content provided. For this reason, we exclude any liability in connection with the use of the leaflet broschure.

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Association Quality Management Biodiesel e. V. (AGQM)

Claire-Waldoff-Str. 7
10117 Berlin
phone: +49 30/31904433
e-mail: info@agqm-biodiesel.de
internet: www.agqm-biodiesel.de