Biodiesel Quality in Germany

Sampling results of Biodiesel producers and warehouse operators of

Arbeitsgemeinschaft Qualitaetsmanagement Biodiesel e.V. (AGQM)

2016

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1 Introduction

Arbeitsgemeinschaft Qualitaetsmanagement Biodiesel e.V. (AGQM) was founded in 1999 at the initiative of leading Biodiesel producers and traders with the intention to improve the quality of Biodiesel. All relevant topics concerning Biodiesel are covered by AGQM, from feedstocks used to production and application.

In Germany, Biodiesel – also known as FAME (**F**atty **A**cid **M**ethyl **E**ster) – is still the most important fuel based on renewable resources. Nowadays it is almost exclusively marketed as B7, which means as admixture of up to 7 % to Diesel fuel. Rapeseed oil is still the raw material predominantly used to produce Biodiesel in Germany. In addition, **u**sed **c**ooking **o**ils and fats, so-called UCO, are used as well as soybean and palm oils.

To assure the Biodiesel quality of AGQM member companies a quality management system (QM system) was developed which has been implemented successfully for many years. It is continually revised by AGQM's Quality Assurance Committee (QA Committee) to assure that the increasing requirements regarding the quality of Biodiesel are always met. QA Committee members are experts in the field of quality management and come from AGQM member companies as well as non-AGQM companies like commercial laboratories.

A core element of quality management is unannounced sampling of the Biodiesel produced and marketed by member companies; the results of which are presented in this report.

While in some other European countries there are massive quality issues when Biodiesel is blended, in Germany such problems have not been known for many years. The introduction of AGQM's QM system with its unannounced sampling of member companies has contributed significantly to this development. In 2010 the results of the unannounced sampling of AGQM member companies was published in a quality report[1] for the first time. The extremely positive quality development of AGQM members' products can thus be observed and clearly tracked.

Within the EU there are two decisive directives for the use of Biofuels: the 'Renewable Energy Directive' (RED) and the 'Fuel Quality Directive' (FQD). In Germany both directives are put into practice as part of the 'Bundes-Immisionsschutzgesetz' (BImSchG).

As per the current RED, the proportion of renewable energy must be at least 20 % in all sectors in 2020; in the transport sector, it should be at least 10 % in 2020. On 30 November 2016, the

[1] http://www.agqm-biodiesel.de/de/downloads/berichte/

European Commission presented the draft of a revised Renewable Energy Directive (RED II) which shall stipulate the European goals for renewable energy and the reduction of greenhouse gas (GHG) by 2030. It also provides a reduced cap for conventional Biofuels which are based on raw materials which may also be used to produce food. This cap shall be reduced from currently 7 % to 3.8 % at the most in 2030. For 'advanced renewable fuels', a separate quota will be stipulated which will rise from a maximum of 1.5 % in 2021 to a maximum of 6.8 % in 2030. A sub-quota of at least 3.8 % is planned for fuels based on straw, organic and wood waste, etc. Biofuels based on used cooking oils and fats as well as animal fats may have a maximum proportion of 1.7 % as part of the above 6.8 %. Renewable fuels based on ptx/ptl and renewable energy are also considered; however, there is no stipulated proportion.

Such a regulation may have profound consequences for the Biodiesel industry since it is foreseeable that the sale of conventional biofuels would decrease significantly.

The FQD stipulates the reduction of greenhouse gas (GHG) for emissions of fuels by the implementation of Biofuels. By 31 December 2020 the GHG reduction shall be 6 %. At the beginning of 2015 the German Biofuel Quota was adjusted accordingly. A minimum percentage of biofuels was stipulated in the (German) *Bundes-Immisionsschutzgesetz* (BImSchG) to achieve the GHG reduction; from 2015 the percentage was 3.5 %; 4 % must be saved since 2017 and from 2020 it will be 6 %. The Biofuels used can only be considered if they comply with the Biofuel Sustainability Ordinance. With this adjustment Germany is the first country to integrate the FQD specifications into national law.

For every kind of Biofuel, the FQD assigns a specific default value to save GHG of biofuels which can be used if the balance cannot be self-determined. However, the default value is not very attractive; for example, the default value for Biodiesel produced from rapeseed oil is only 38 %. Thus, Biodiesel producers observe and add up the GHG emissions along the production chain step by step, starting with the agricultural cultivation. By implementing appropriate measures to keep emissions as low as possible, the Biofuel industry succeeded in raising GHG savings to a percentage of about 70 %. For waste and residual materials, a GHG preload of 0 g CO_{2eq}/MJ is used which means UCOME can achieve a GHG savings potential of 80 to 90 %. However, on the downside the effect is that the fuel amount necessary to fulfill the quota is reduced correspondingly. Consequently, the Biodiesel sales volume in Germany has decreased considerably since the introduction of the GHG quota.

2 Description of Sampling

In 2016 there were four sampling campaigns. Member sampling is one of the most important AGQM quality assurance measures. Sampling without prior announcement is of crucial importance since it's the only way to assure that the results reflect the actual Biodiesel production and handling by AGQM members. Sampling is not carried out by AGQM itself but there is an annual call for tenders which leads to the assignment to an independent laboratory accredited for Biodiesel analytics. In addition, the laboratory must have successfully participated in AGQM's annual Round Robin Test for fatty acid methyl ester (FAME), jointly carried out by AGQM and *Fachausschuss für Mineralöl- und Brennstoffnormung (FAM) im DIN*.

The Biodiesel parameters to be tested are determined by the QA Committee in the QM system. All parameters essential for the verification of the fulfilment of the standard according to the legal stipulations of the 36th BImSchV are included.

The relevant current version of the standard always forms the basis of AGQM's quality check, i.e. the required standard limits as well as their related acceptance limits comply with DIN EN 14214:2014. In addition, more stringent requirements, so-called 'AGQM limits', were determined for some parameters which documents AGQM's particular quality commitment.

Table 2 of the attachment lists all tested parameters and their limits according to DIN EN 14214:2014. Subsequently Table 3 shows the parameters with AGQM's requirements which are higher than those of the current standard. For parameters 'Water Content', 'Total Contamination', and 'Cold Filter Plugging Point (CFPP)' AGQM's requirements for the Biodiesel quality of its members are more stringent than those demanded by legal stipulations.

AGQM also supports special needs of its members. In 2013 a special regulation was established for Biodiesel as intermediate product made from used cooking oils and fats. Biodiesel produced thereof is exempted from the determination of parameters 'Sulfur Content', 'CFPP' and 'Cloud Point' if the producer reported it to AGQM in advance as intermediate product for admixture to Biodiesel. Therefore, such Biodiesel must not be marketed directly but only as blend component for Biodiesel. This means it is blended to other fuel so that generally standard-conform Biodiesel is produced. Consequently, such products are not sanctioned if the limits of the above parameters are exceeded.

In case of doubt concerning the results of the analysis member companies are entitled to address AGQM to apply for arbitration proceedings. For that, the member assigns an independent laboratory accredited for Biodiesel analytics. The arbitration sample is one of the two retain samples taken during the sampling campaign. The result of the arbitrational analysis is binding for both parties.

In 2016, fifteen Biodiesel producers and traders participated in AGQM's quality assurance measures. Spread throughout the year four sampling campaigns took place in different seasons; a total of 64 Biodiesel samples were taken, analysed and then evaluated.

The sampling dates were selected so that the AGQM member companies were sampled in summer, during the intermediate period and in winter because for summer, intermediate and winter grades there are different limits for parameters 'CFPP' and 'Cloud Point' which are stipulated in the national Attachment NB of the standard and differ from country to country since their climatic conditions are also different. The individual campaigns are named K1 to K4. The sampling periods are listed below:

K1:	25 January to 5 February	Winter grade
K2:	18 April to 29 April	Summer grade
K3:	4 July to 15 July	Summer grade
K4:	10 October to 21 October	Intermediate grade

3 Individual Sampling Results and Evaluation

In the following section the test method used, the limit, the acceptance limit and a description can be found for every parameter followed by a graphical illustration of the measured values as well as their evaluation.

The results given in this report were made anonymous and do not reveal the origin of the sample. Internally AGQM numbered all samples. However, this individual number is only given in the report so that conspicuous features of individual samples can be highlighted, if an acceptance limit was exceeded.

The measuring values for every sampling campaign are given in ascending order to illustrate the spread. The axis 'Number of Samples' illustrates how many samples were taken in the relevant campaign; the internally assigned numbers are not given. In the diagrams the limits are marked with a black line, the acceptance limits – determined considering the precision of the method – with a red line. The acceptance limits are the decisive factor when it comes to Customs matters as well as to the assignment of sanction points according to AGQM's QM system. In the diagrams of parameters 'Total Contamination' and 'Water Content' both AGQM limit and AGQM acceptance limit are given additionally.

As mentioned in the section before, there is an exception for parameters 'Sulfur content', 'CFPP', and 'Cloud Point': AGQM members producing Biodiesel from used cooking oils and fats may exceed the quality parameters of the standard if they apply for exemption at the AGQM office in advance. The measuring values referring to such an exception are marked accordingly in the diagrams.

3.1 Fatty Acid Methyl Ester Content

Test method: DIN EN 14103:2015

Limit of DIN EN 14214:2014: min. 96,5 % (w/w)

Acceptance limit: min. 94,0 % (w/w)

Information on the purity of Biodiesel can be derived from the content of fatty acid methyl esters, briefly ester content. Dependent on the type and condition of the raw material and the type of reaction control, the ester content of the Biodiesel can be reduced if by-products form or substances ingress the final product.

FAME can be produced by a reaction of fats and oils with methanol in the presence of an alkaline catalyst (e.g. potassium hydroxide, sodium hydroxide, potassium methylate, sodium methylate). Another way is direct transesterification of fatty acids and methanol in the presence of an acidic catalyst (e.g. sulphoric acid). Dependent on the raw material the fatty acid methyl esters differ regarding the chain lengths of the fatty acids and the number of double bonds.

The ester content is determined by gas chromatography and given as sum of all fatty acid methyl esters from C6:0 to C24:1 in weight by weight [% (w/w)]. DIN EN 14214 demands a minimum fatty acid methyl ester content of 96,5 % (w/w). An ester content of below 96,5 % (w/w) may be an indication for admixture of other substances or the presence of by-products of the Biodiesel production process. It is also possible that other substances like oligomers, for example, got into the Biodiesel with the raw material. As a rule, the ester content of a product that was distilled after esterification or transesterification is higher, since unwanted substances can thus be separated.

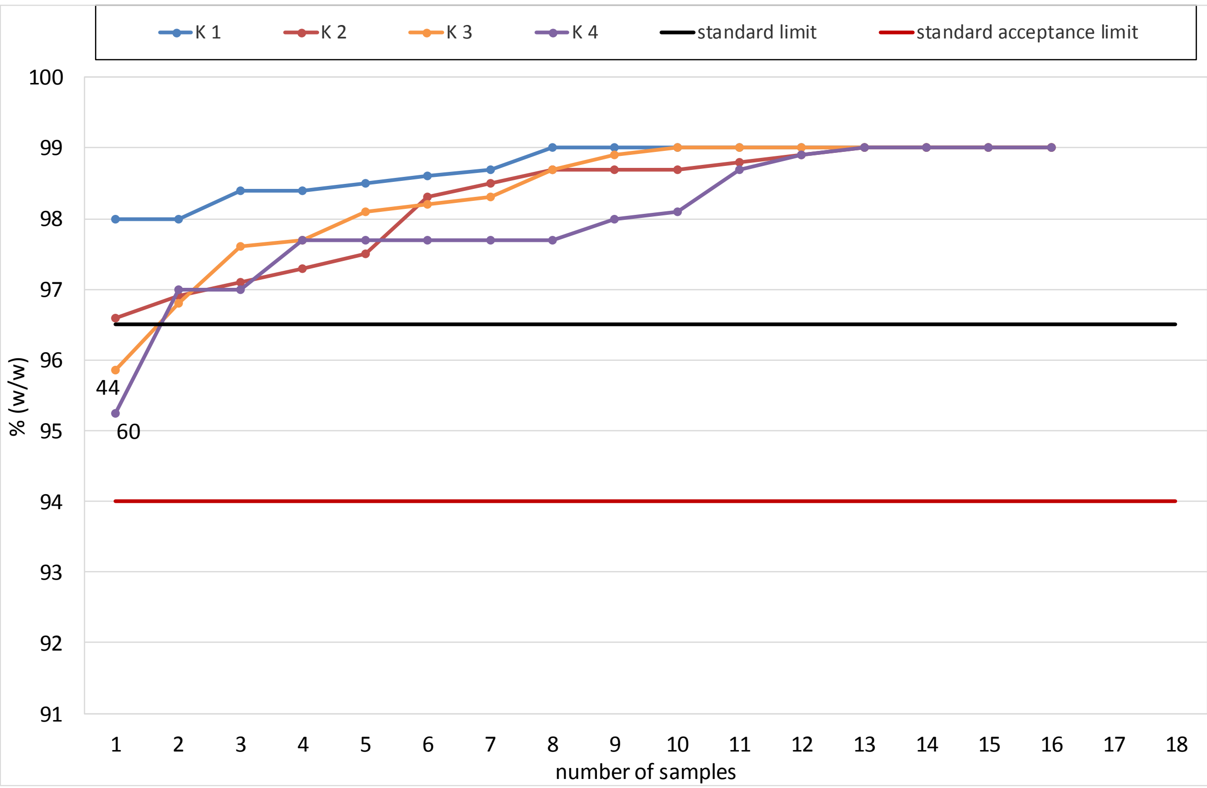

Diagram 1: Content of fatty acid methyl ester according to DIN EN 14103.

Diagram 1 shows the values of the fatty acid methyl ester content of the tested samples. The ester content of sample 44 of 95,25 % (w/w) in campaign 3 is too low; in campaign 4 sample 60 of the same producer only achieved an ester content of 95,85 % (w/w). Both values stay below the limit of the standard of 96,5 % (w/w); however, they are within the acceptance limit (94 % (w/w).

3.2 Density at 15 °C

Test method: DIN EN ISO 12185:1997

Limit of DIN EN 14214:2014: min.860 and max. 900 kg/m³

Acceptance limit: min 859,7 kg/m³ and acceptance limit: max. 900,3 kg/m³

The density of a substance is the quotient of its mass and volume at a stipulated temperature. It is a substance-specific property and is determined by means of an oscillating u-tube density meter. According to DIN EN 14214, the density of Biodiesel at 15 °C must be between 860-900 kg/m³.

Both FAME composition and Biodiesel purity have an influence on the density. The shorter the carbon chain (c-chain) of the fatty acid and the more double bonds, the higher the density. Thus, first careful conclusions can be drawn regarding the raw material used. The density may also be influenced by contamination. For example, a higher methanol content would reduce the density.

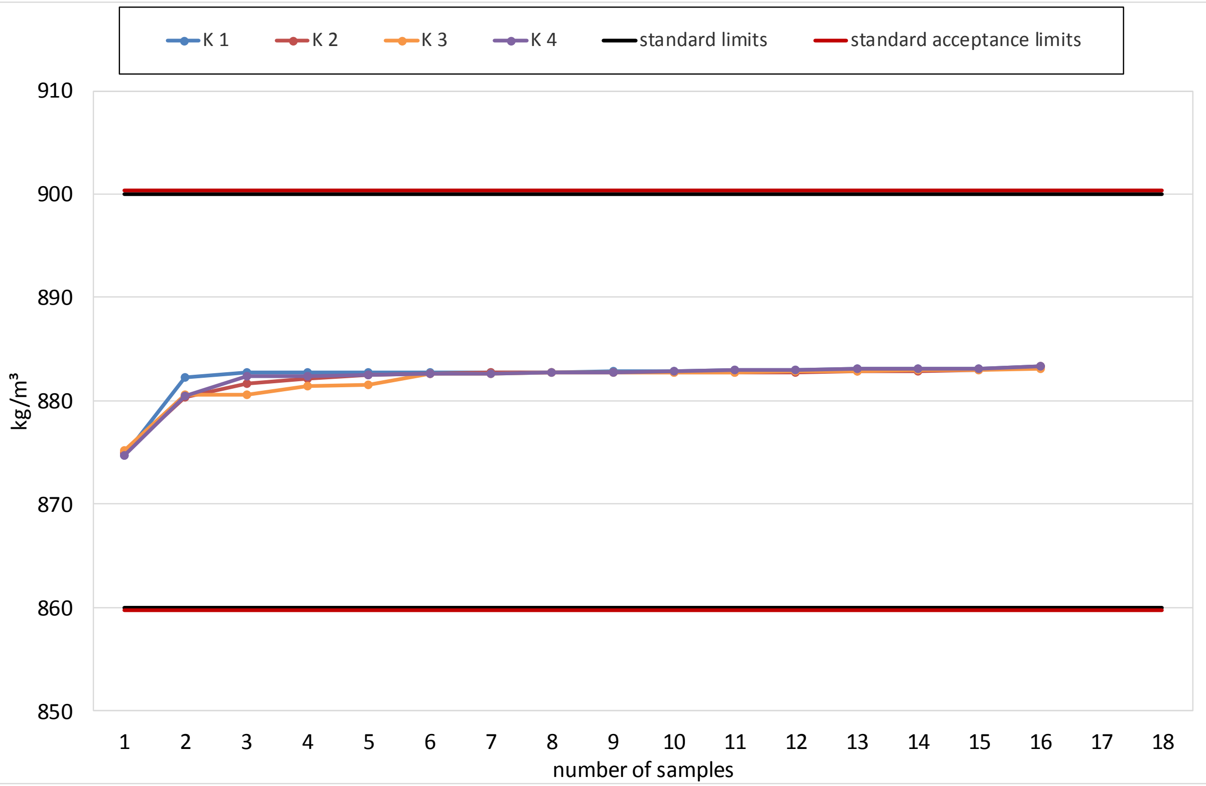

Diagram 2: Density at 15 °C according to DIN EN ISO 12185.

Diagram 2 shows the determined density values. All analyzed samples stay within the density range required by the standard. Almost all samples are in the tight range between 881 and 883 kg/m³. The value of the majority is exactly 883 kg/m³ which is that of Biodiesel produced of pure rapeseed oil. The samples of one producer always have a density of about 875 kg/m³; here, rapeseed oil was at least partly replaced by other raw materials.

During the summer campaigns K2 and K3 some samples had a somewhat lower density which can probably be attributed to the use of other raw materials. For example, increasing admixture of Biodiesel produced of used cooking oils and palm oil is possible in summer due to lower requirements for parameter CFPP.

3.3 Sulfur Content

Test method: DIN EN ISO 20846:2011

Limit of DIN EN 14214:2014: max. 10 mg/kg

Acceptance limit: max. 11,3 mg/kg

Sulfur can already be contained in raw materials used for the Biodiesel production. Plants can, for example, absorb sulfur compounds during growth, which usually results in a sulfur content of between 2 and 7 mg/kg. Animal and used cooking oils and fats can contain sulfur in the form of protein compounds. Here, the sulfur content can be up to 30 mg/kg. The sulfur content can be reduced if Biodiesel is distilled. Furthermore, by blending sulfur containing Biodiesel (blend component for Biodiesel) and Biodiesel low in sulfur, standard-conform Biodiesel can be generated.

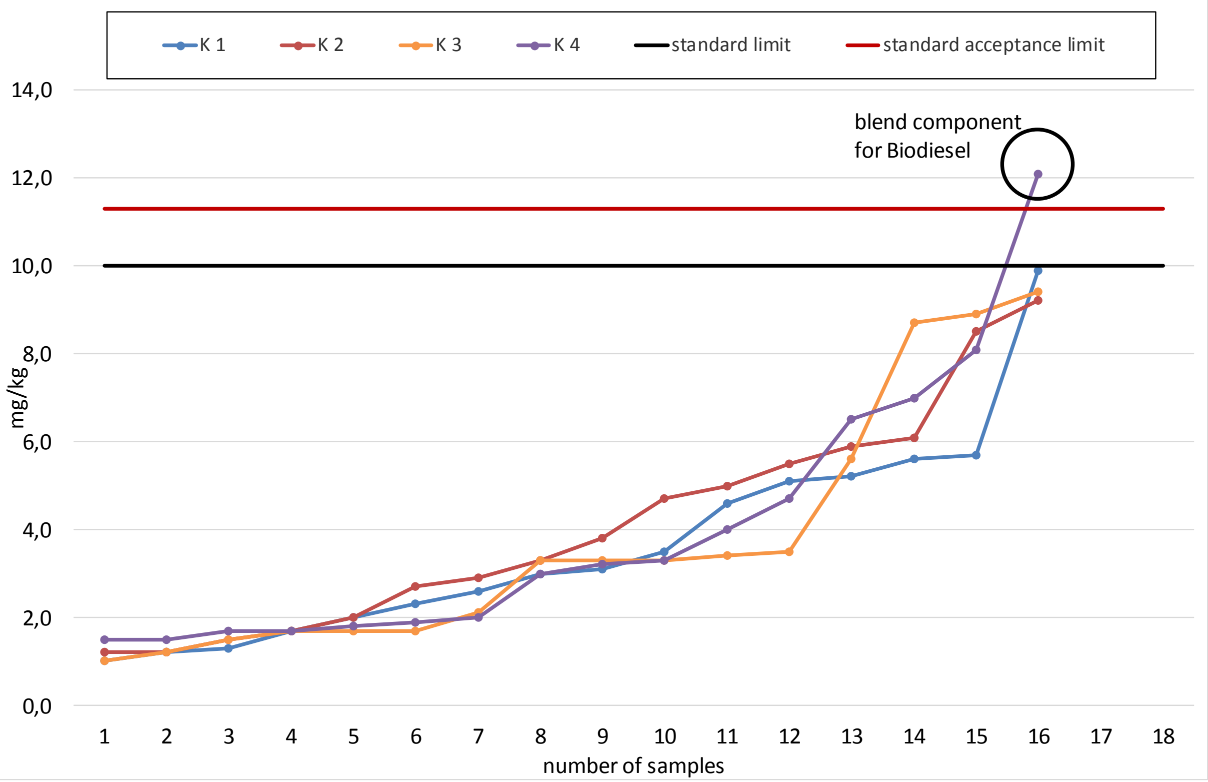

Diagram 3: Sulfur Content according to DIN EN ISO 20846.

As can be seen from diagram 3 most samples have a sulfur content of below 7 mg/kg; therefore, it can be concluded that vegetable oils were used as raw material for the Biodiesel production. Higher values are due to the use of UCO as raw material, since for UCOME (**U**sed **C**ooking **O**il **M**ethyl **E**ster) an acid catalyzed process is often used. Catalysts typically used are sulfur-based. Decomposition products thereof can get into the Biodiesel. Furthermore, UCOME can contain sulfur from animal proteins.

The sample circled black in diagram 3 is a blend component for Biodiesel, which means that this fuel is not marketed directly but admixed to other Biodiesel so that the fuel resulting from the mixture complies with the specification.

3.4 Water Content

Test method: DIN EN ISO 12937:2002
Limit of DIN EN 14214:2014: max. 500 mg/kg
Acceptance limit: max. 591 mg/kg

AGQM limit: max. 220 mg/kg for producers
Acceptance limit: max. 280 mg/kg
AGQM limit: max. 300 mg/kg for warehouse operators
Acceptance limit: max. 370 mg/kg

As last refining step almost all Biodiesel production processes use water wash to remove free glycerol, soaps, and other contamination. Other than carbon-based fuels, Biodiesel can physically dissolve large amounts of water due to its polar properties; which is why the product must be dried subsequently.

Also, due to air humidity, water can ingress into Biodiesel so that its storage conditions must be selected accordingly. Under normal conditions Biodiesel is saturated at about 1500 mg water/kg Biodiesel. Fossil Diesel fuels can only absorb very small amounts of water which means, when mixed with Biodiesel, the water dissolved therein may precipitate. It can freeze and thus block piping systems, cause corrosion and promote microbial growth.

DIN EN 14214 demands a maximum water content of 500 mg/kg. Due to the difficulties described above, AGQM's quality standards are stricter and require a maximum water content of 220 mg/kg (producers) and 300 mg/kg (warehouse operators).

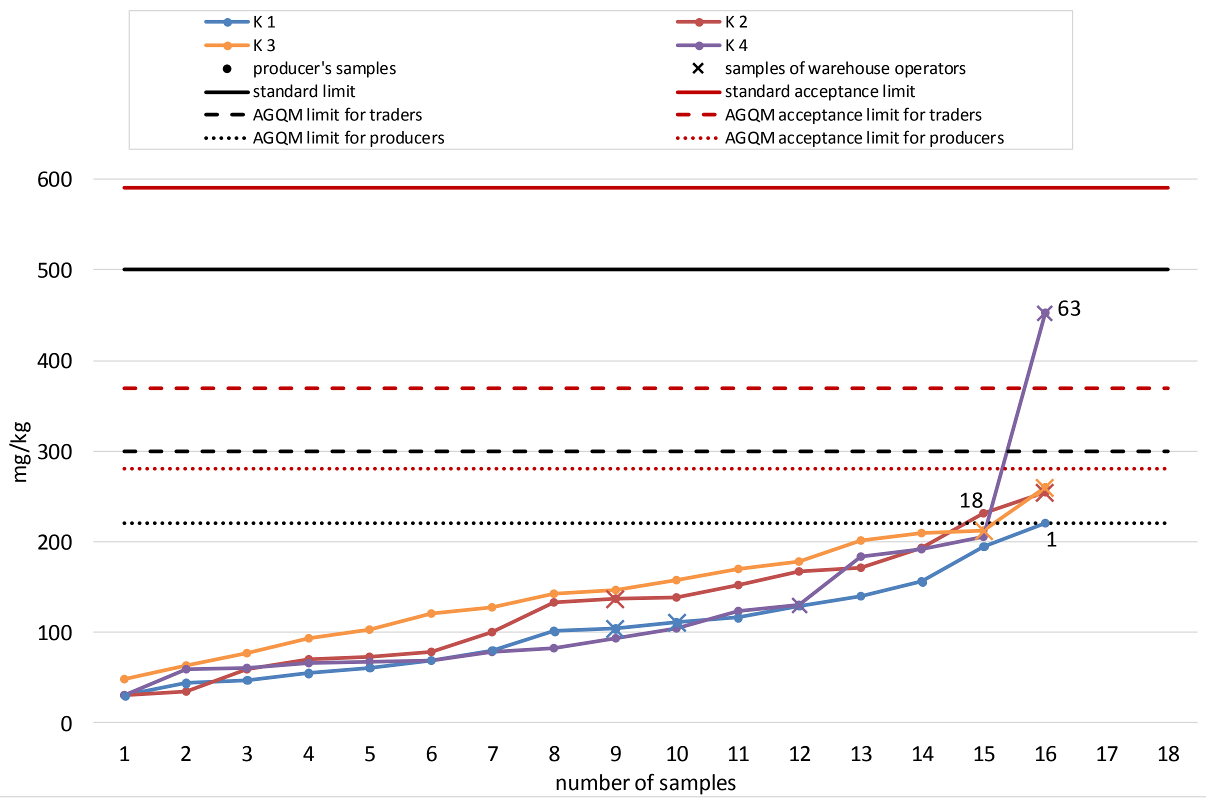

Diagram 4: Water Content according to DN EN ISO 12937.

According to diagram 4, all tested samples are below the standard limit. However, the evaluation shows that in K2 samples 1 (221 mg/kg) and 18 (232 mg/kg), which stem from different producers, slightly exceed the AGQM limit (220 mg/kg); however, both values range within the AGQM acceptance limit (280 mg/kg).

Samples marked with an 'X' in diagram 4 are samples of warehouse operators. For those an AGQM limit of 300 mg/kg and an AGQM acceptance limit of 370 mg/kg apply. In K4 sample 63 of a warehouse operator exceeds the AGQM limit with 452,5 mg/kg. This value is the result of an arbitration sample. The AGQM member had demanded an arbitration analysis due to massively exceeding the AGQM limit with 413,5 mg/kg.

The arbitration analysis of the sample resolved that with a value of 452,5 mg/kg the sample significantly exceeded AGQM's acceptance limit for warehouse operators. Since the required limit of the standard of 500 mg/kg was complied with, the sample may be marketed as standard-conform commodity but not as AGQM product.

3.5 Total Contamination

Test method: DIN EN 12662:1998

Due to the fact that the current version of DIN EN 12662:2014 is unsuitable for FAME concerning the determination of parameter 'Total Contamination', DIN EN 12662:1998 applies for AGQM's checks. This procedure is based on a recommendation by CEN TC19 – JWG 1 of 13 July 2014.

Limit of DIN EN 14214:2014: max. 24 mg/kg

Acceptance limit: max. 32 mg/kg

AGQM limit: max. 20 mg/kg (AGQM's limit for parameter 'total contamination' is also AGQM's acceptance limit.)

'Total contamination' is a measure for the content of insoluble particles ('rust and dust'). Upon filtration of a heated sample it is determined gravimetrically by weighing the filters. For mineral oil based Diesel fuel total contamination is of little relevance since there are hardly any insoluble particles because of the distillation steps during production. Biodiesel is usually not distilled which is why 'total contamination' is an important quality feature for it. Rust, dust but also organic solids like sterylglycosides, polymer particles or soaps may be found in Biodiesel. High proportions of insoluble particles can cause filter blocking and wear of the injector system. AGQM set its own more stringent acceptance limit of 20 mg/kg to improve the application security of Biodiesel and to account for the imprecision of the method.

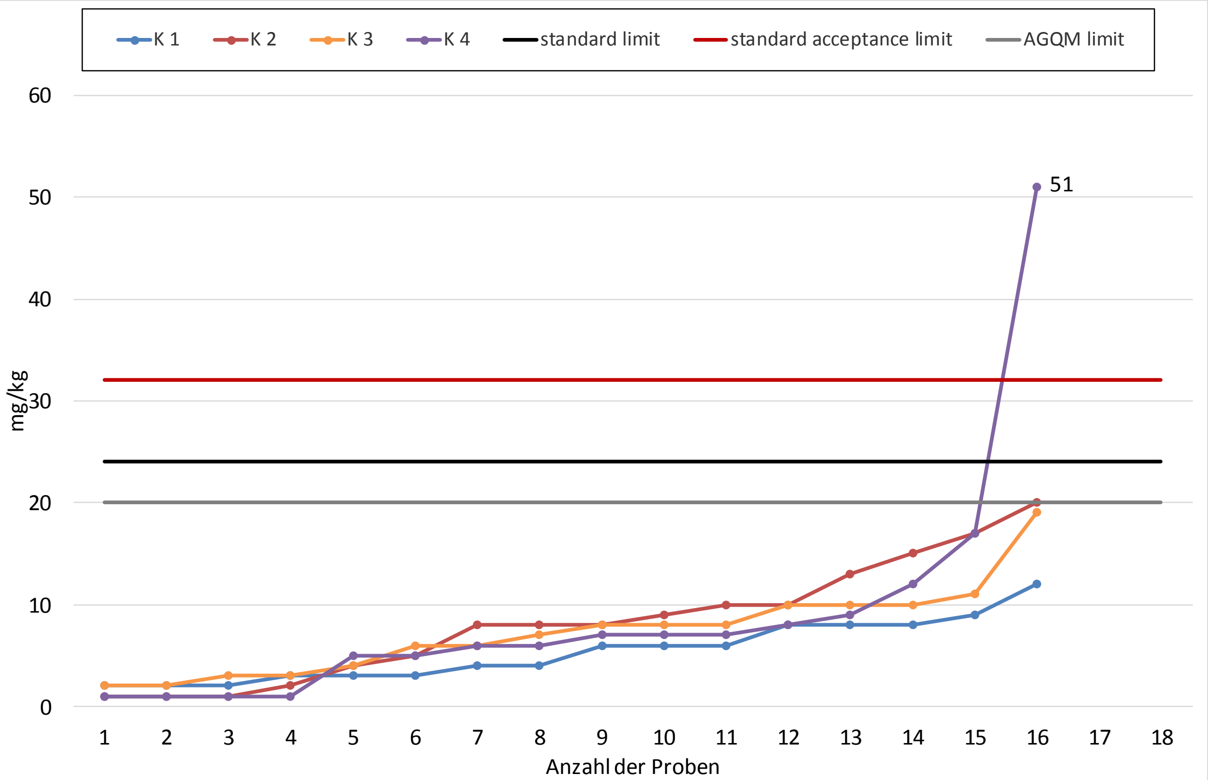

Diagram 5: Total Contamination according to DIN EN 12662.

Diagram 5 shows that except for one sample all values range within the AGQM limit for total contamination. With a total contamination of 51 mg/kg, sample 51 also clearly exceeds the standard limit (24 mg/kg). The member company communicated that the value exceeding the limit had already been determined in their own laboratory and that the fuel was only marketed after admixture to standard-conform Biodiesel.

3.6 Oxidation Stability

Test method: DIN EN 14112:2014
Limit of DIN EN 14214:2014: min. 8 h
Acceptance limit: min. 6,6 h

The oxidation stability of Biodiesel is the measure for the resilience against oxidative processes. Test method for Biodiesel is the so-called 'Rancimat test'. At 110 °C a constant air stream is passed through the test sample. Upon degrading the oxidation reserve (natural reserve plus additives) of the sample, large amounts of volatile oxidation products form which – together with air – are passed through the test liquid of the measuring vessel where they increase the conductivity. The time until such oxidation products are detected is called induction period. DIN EN 14214 stipulates a minimum oxidation stability of 8 hours.

Especially Biodiesel with a high proportion of polyunsaturated fatty acid methyl esters is more prone to oxidation processes because of their chemical structure; double bonds react with oxygen thus forming peroxides. Subsequent reactions may break up molecule chains; in addition, short-chain carbonic acids and polymer structures can form. Corrosion and deposits in fuel-carrying components are possible impacts.

In addition to natural antioxidants (e.g. tocopherols) which are contained in vegetable oils and slow down the ageing process, synthetic stabilizers are used.

To achieve the demanded oxidation stability of 8 h the use of additives to stabilize FAME is mandatory. Upon request of interested additive producers AGQM annually tests products which can be used to enhance the Biodiesel oxidation stability. Additives passing the test are published in the so-called 'No-Harm List' on AGQM's homepage.

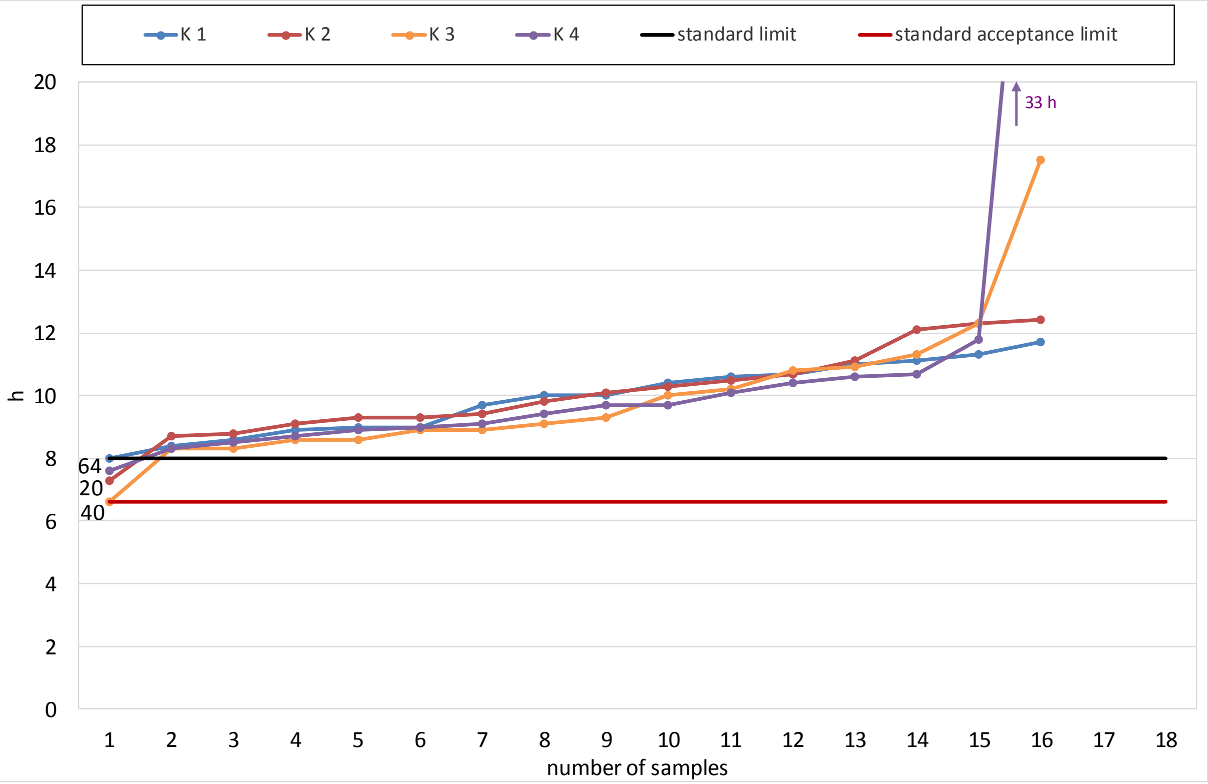

Diagram 6: Oxidation Stability according to DIN EN 14112.

Diagram 6 illustrates that for the majority of AGQM member companies there are no issues to meet the requirements for oxidation stability. One Sample of K4 even achieved an oxidation stability of 33 h. However, with measurements between 7,6 h and 6,6 h, three sample (20, 40 and 64) fall below the limit, but all values are still within the acceptance limit (6,6 h).

3.7 Acid Number

Test method: DIN EN 14104:2003
Limit of DIN EN 14214:2014: max. 0,5 mg KOH/g
Acceptance limit: max. 0,54 mg KOH/g

The acid number is the measure for free acids (especially fatty acids) in Biodiesel and thus indirectly for its corrosive properties also. Fatty acids are weak acids and therefore only little corrosive. During the transesterification of fats very small amounts of alkaline metal soaps may form because of the alkaline saponification of fats. They are removed from the product by physical separation. If washed with inorganic acids small soap residues are separated and the free fatty acids thus forming remain in the Biodiesel. The acid number may also rise during the storage of FAME when ageing processes (primarily oxidation) cause ester cleavage and the formation of short-chain carbon acids. However, this effect can hardly be observed under regular storage conditions. Also, the inorganic acids used for washing, which have a stronger corrosive effect, may contribute to the acid number. DIN EN 14214 stipulates a maximum acid number of 0,5 mg KOH/g.

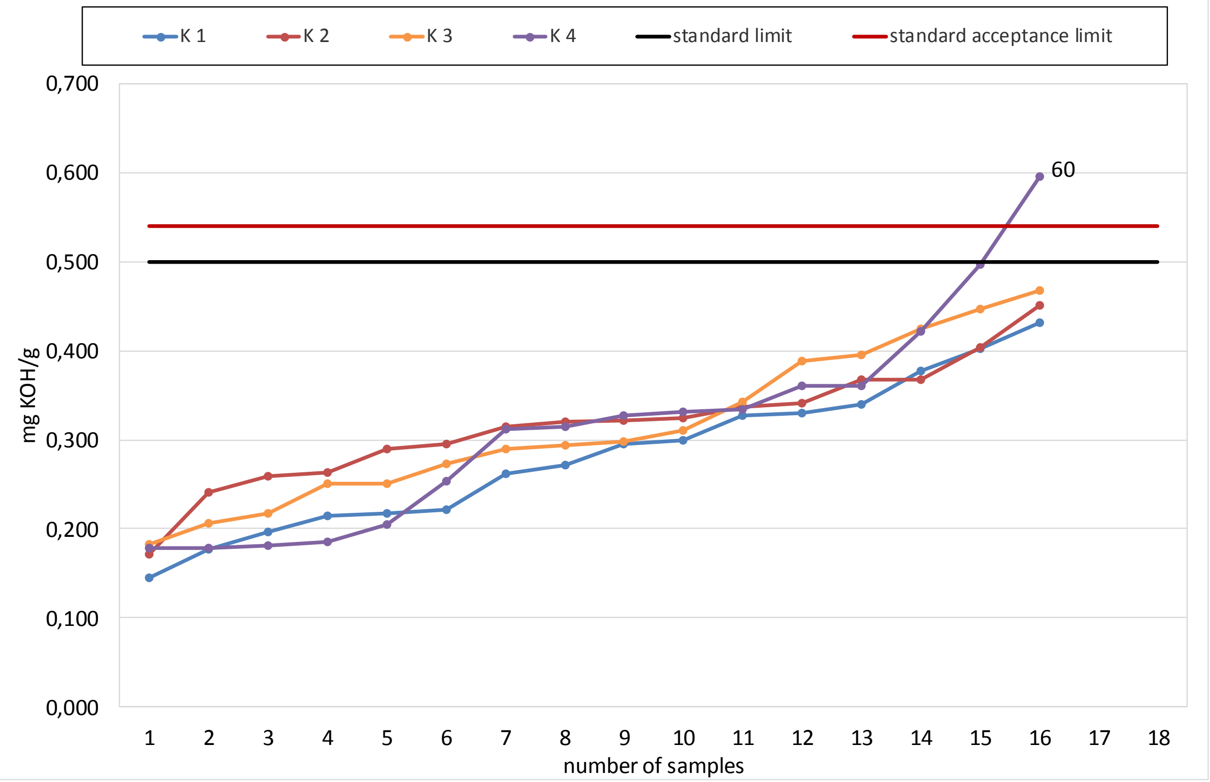

Diagram 7: Acid Number according to DIN EN 14104.

Diagram 7 shows the measurements for the acid number. All samples but one comply with the requirements of the standard. With 0,60 mg KOH/g sample 60 clearly exceeds the standard limit of 0,50 mg KOH/g as well as the acceptance limit of 0,54 mg KOH/g; therefore, it cannot be marketed as standard-conform. The member company concerned communicated that they had already detected the exceeding value and taken appropriate steps to blend the commodity at a standard-conform ratio.

3.8 Iodine Number

Test method: DIN EN 16300:2012
Limit of DIN EN 14214:2014: max. 120 g iodine/100g
Acceptance limit: max. 124 g iodine/100g

Test method: DIN EN 14111:2003
Limit of DIN EN 14214:2014: max. 120 g iodine /100g
Acceptance limit: max. 123 g iodine /100g

The iodine number is a measure for the proportion of double bonds in fats and oils as well as fatty acid methyl esters. It varies dependent on the raw material used. The standard stipulates two different methods for its determination: first the arithmetical determination based on the fatty acid profile measured by gas chromatography according to DIN EN 16300; second, wet-chemical determination according to DIN 14111. The result is given in g iodine/100 g of Biodiesel.

Since unsaturated fatty acids are more prone to oxidative reactions, the oxidation stability of Biodiesel decreases with the rising number of double bonds which means rising iodine number. Therefore, apart from the oxidation stability, the iodine number is an indicator for the stability of Biodiesel.

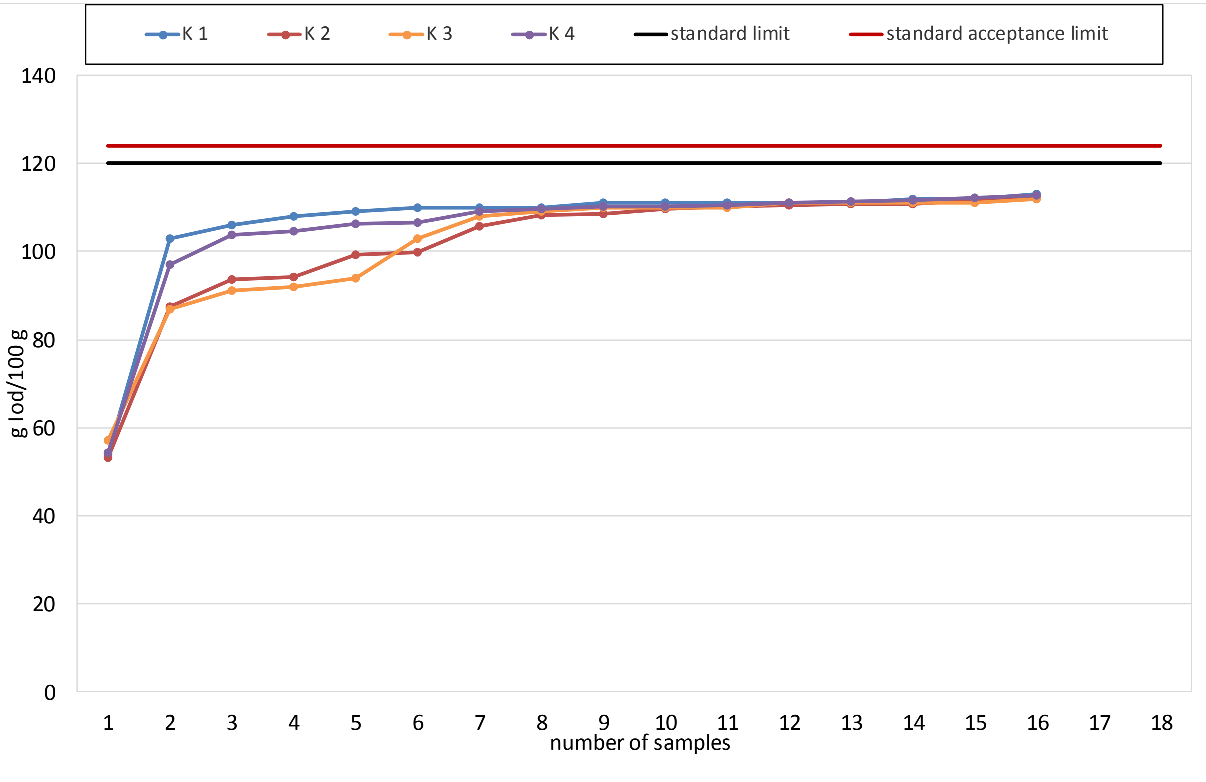

Diagram 8: Iodine Number according to DIN EN 16300 (determined from the methyl ester profile).

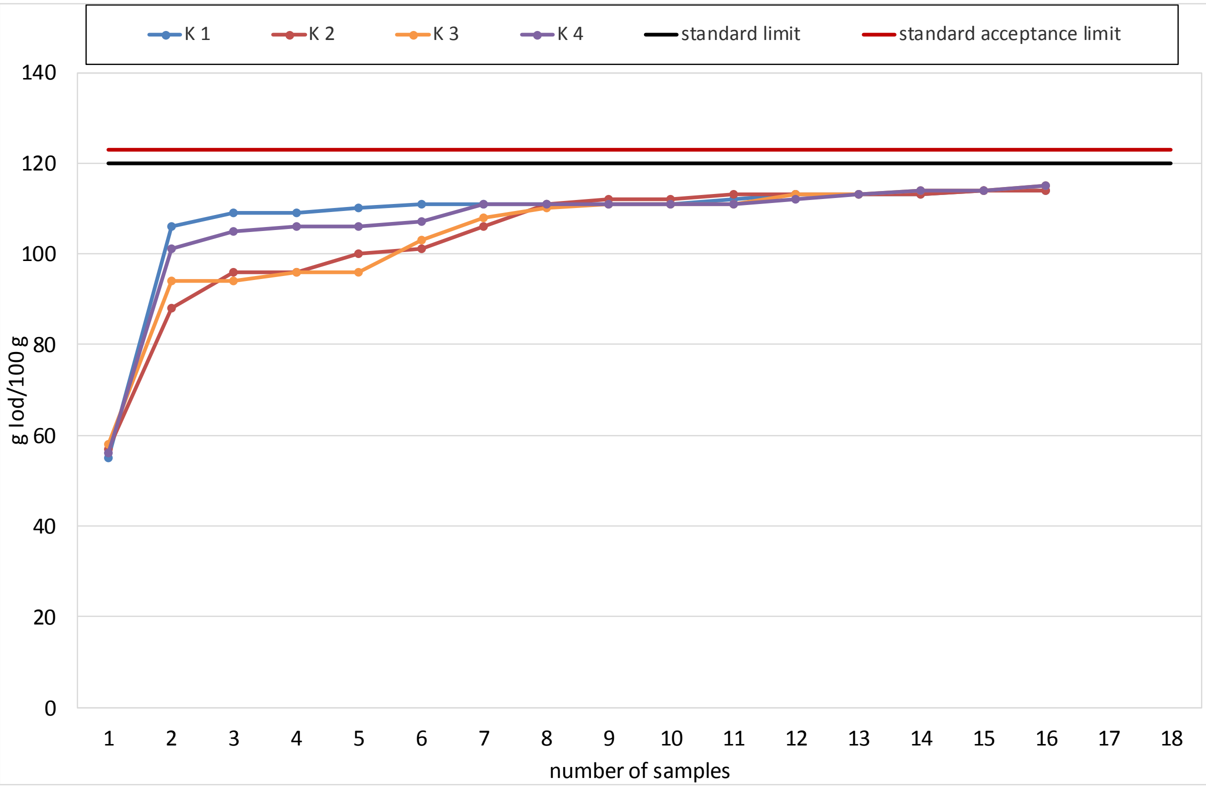

Diagram 9: Iodine Number according to DIN 14111 (wet-chemical determination).

The results of the two methods (arithmetical determination from the methyl ester profile and titrated) to determine the iodine number as illustrated in diagrams 8 and 9 do not differ significantly. All tested samples fall below the limit of the standard. In campaigns K2 and K3 some notably lower iodine numbers are measured. This can be attributed to the use of raw materials with a higher saturation level. High saturation levels cause reduced cold properties (regarding CFPP and Cloud Point) which is of minor importance during the summer months. The samples of one producer have an iodine number of under 60 g iodine/100 g all year round, which can also be attributed to the raw material used; here presumably used cooking oils and fats.

3.9 Glycerides / Free Glycerol

Test method: DIN EN 14105:2011

Dependent on the type of reaction control during the transesterification of vegetable oils with methanol, apart from the main product ‘fatty acid methyl ester’, intermediate products (monoglycerides and diglycerides) and unprocessed vegetable oil (triglycerides) can be found. Therefore, the contents of mono, di-, and triglycerides are a measure for the completeness of the transesterification reaction. In general, the concentration increases in the order ‘triglyceride < diglycerides < monoglycerides’ since the cleavage of the last fatty acid residue is the slowest step of the reaction. With reasonable effort, the glyceride content can only be reduced to a certain degree, since chemical equilibrium between products and educts adjusts in any case. Glycerides can only be completely removed by distillation.

3.9.1 Monoglycerides

Limit of DIN EN 14214:2014: max. 0,70 % (w/w)

Acceptance limit: max. 0,82 % (w/w)

With 0,70 % (w/w) a significantly higher value was selected as limit for monoglycerides compared to those for di- and triglycerides. The reason is that the cleavage of the last fatty acid residue is the slowest step of the transesterification reaction. Here, it is most difficult to achieve a complete reaction.

A high proportion of monoglycerides can be the cause for coking and deposits in the injector system. In addition, especially saturated monoglycerides have relatively high melting points which can favour precipitation and is considered one of the main causes for bad cold properties and filter plugging.

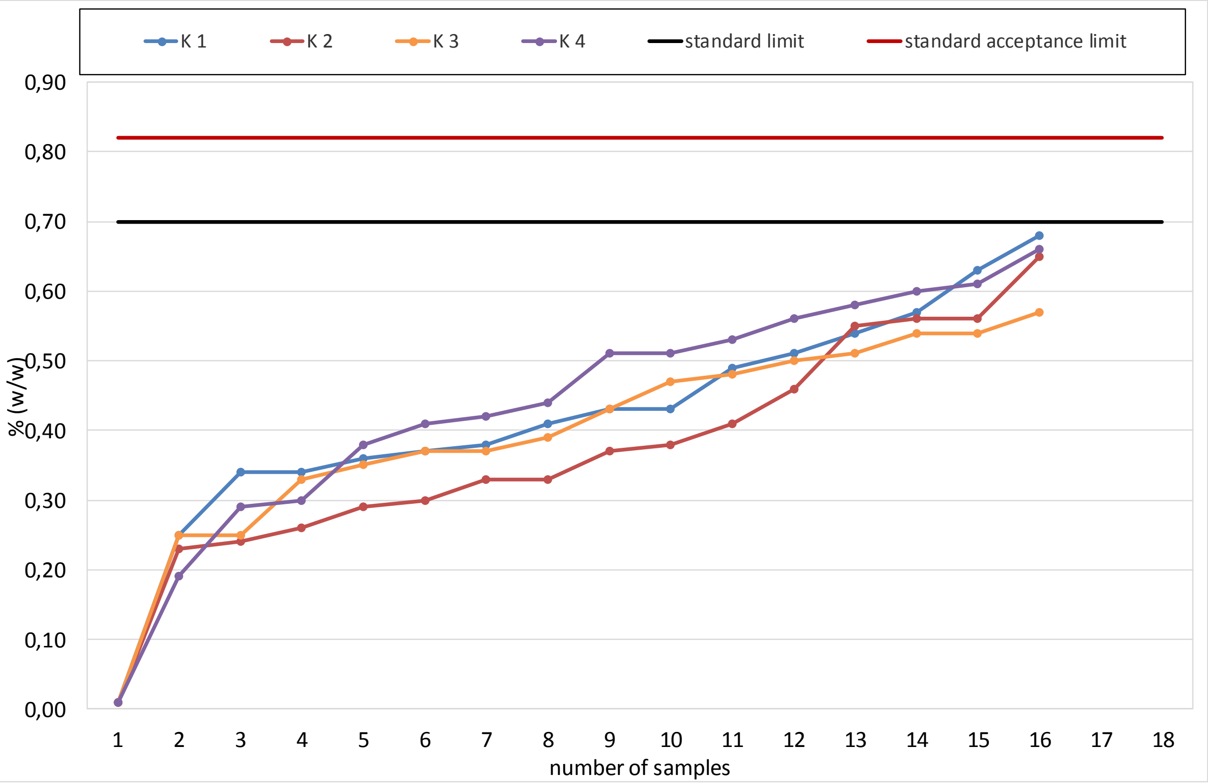

Diagram 10: Monoglycerides according to DIN EN 14105.

Diagram 10 shows the measurements for monoglycerides. All tested samples fall below the limit of 0,70 % (w/w). The samples of one producer show values near 0 % (w/w) which suggests that the production process includes a distillation step.

3.9.2 Diglycerides

Limit of DIN EN 14214:2014: max. 0,20 % (w/w)

Acceptance limit: max. 0,24 % (w/w)

Due to their high boiling points, diglycerides are not fully combusted. Thus, coking in injector system and cylinder can be caused. The limit for the content of diglycerides is 0,20 % (w/w).

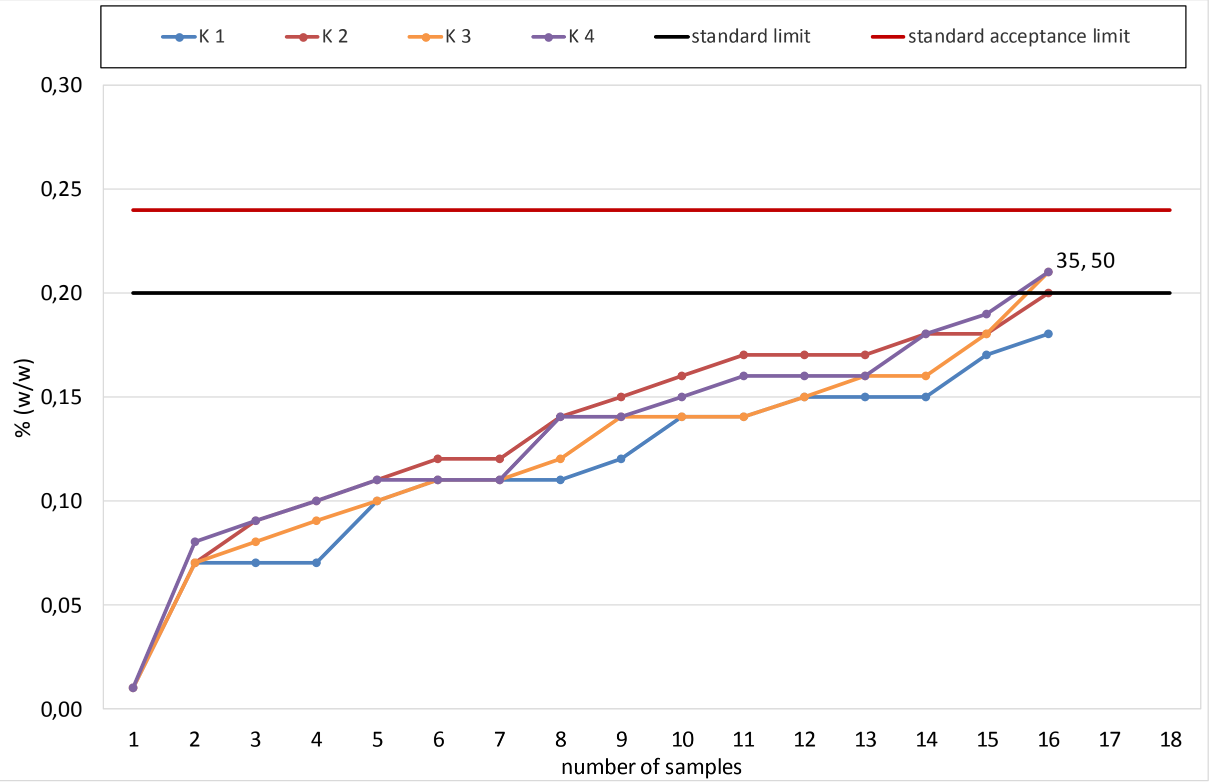

Diagram 11: Diglycerides according to DIN EN 14105.

Diagram 11 shows the measurements for the content of diglycerides. In both campaigns 3 and 4 one sample (samples 35 and 50) exceeds the standard limit of 0,20 % (w/w). However, both limit violations (0,21 % (w/w) each) comply with the acceptance limit of 0,24 % (w/w).

3.9.3 Triglycerides

Limit of DIN EN 14214:2014: max. 0,20 % (w/w)

Acceptance limit: max. 0,27 % (w/w)

High contents of triglycerides in combination with low contents of mono and diglycerides are mostly an indication for mixtures of Biodiesel with oils or fats (e.g. in the logistics chain). The limit for the content of triglycerides is also 0,20 % (w/w).

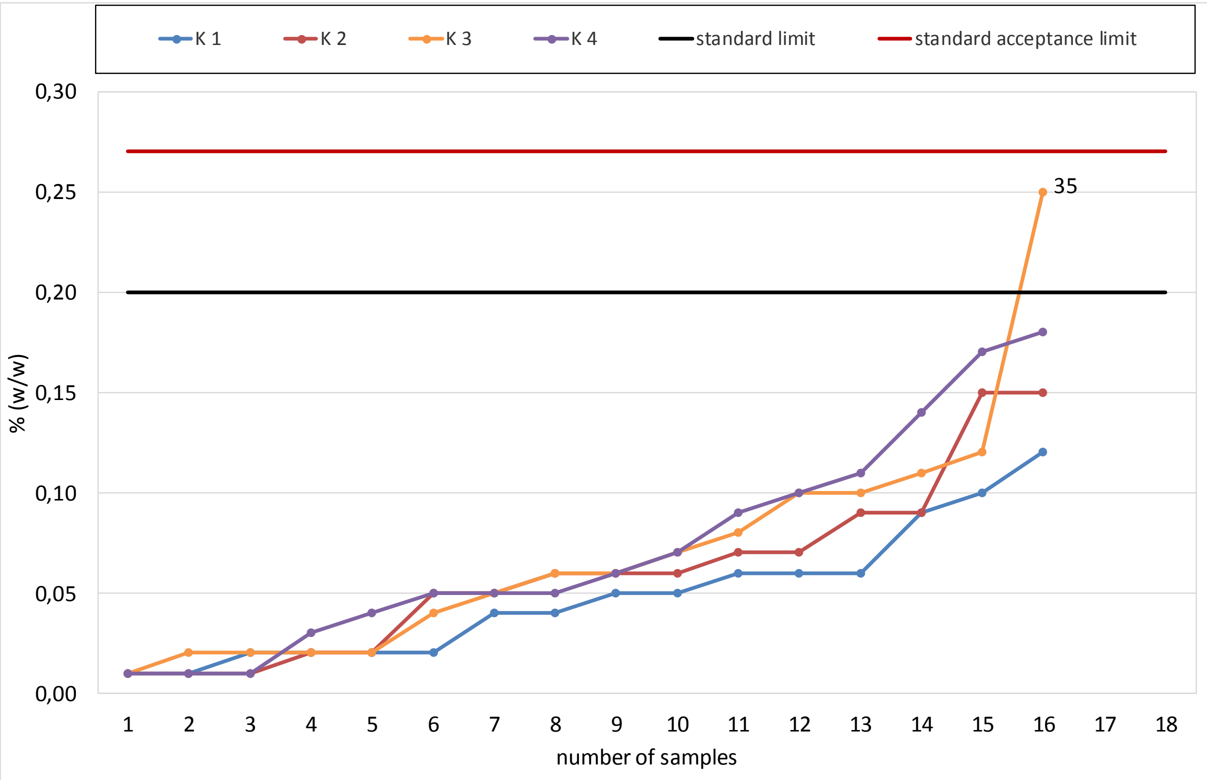

Diagram 12: Triglycerides according to DIN EN 14105.

Diagram 12 shows the measurements for the content of triglycerides. All but one tested samples stay below the limit. With 0,25 % (w/w) sample 35 exceeds the limit of DIN EN 14212 of 0,20 % (w/w); however, it ranges within the acceptance limit of 0,25 % (w/w).

3.9.4 Free Glycerol

Limit of DIN EN 14214:2014: max. 0,02 % (w/w)

Acceptance limit: max. 0,026 % (w/w)

Glycerol is generated during the transesterification of fats and oils to fatty acid methyl esters. Since glycerol is practically insoluble in Biodiesel it can be separated almost completely by decantation and subsequent water wash.

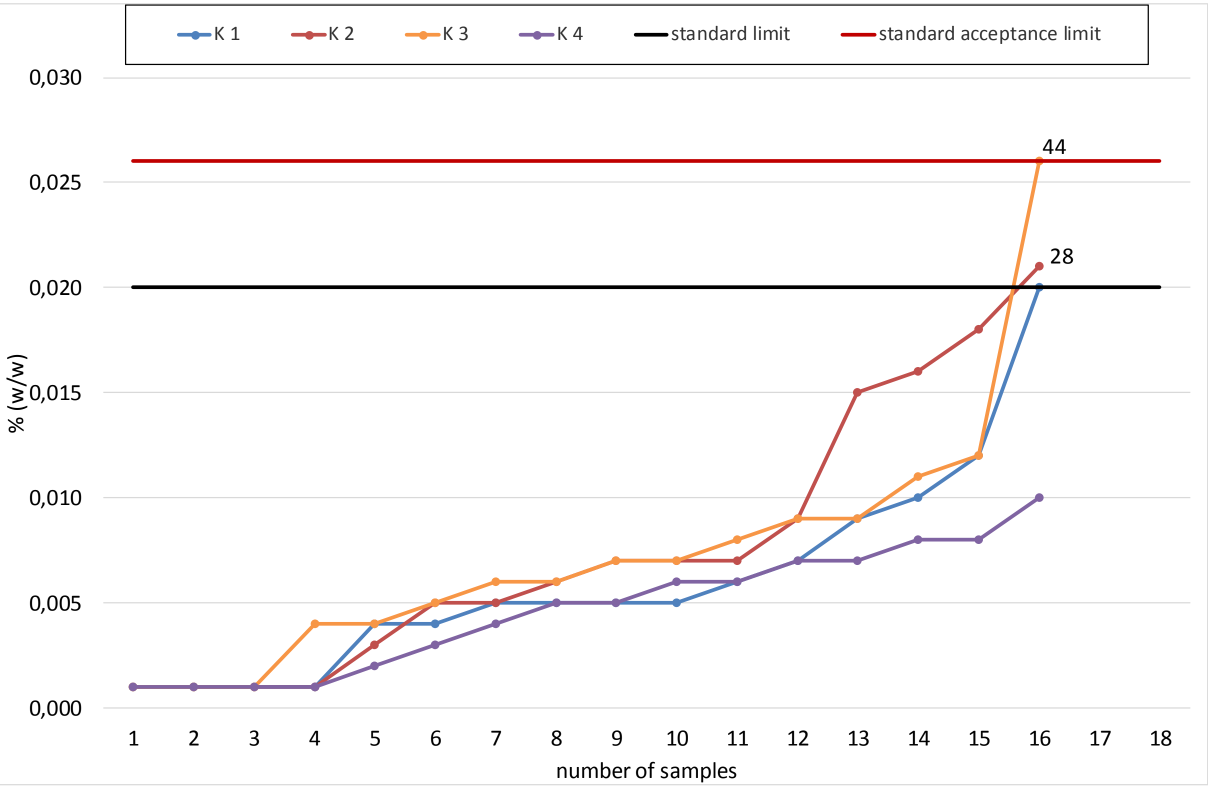

Diagram 13: Free Glycerol according to DIN EN 14105.

The content of free glycerol of all samples but two stays below the standard limit (see diagram 13.) Samples 28 and 44 with increased contents of free glycerol belong to the same member. In K2, the limit of 0,020 % (w/w) is exceeded with a value of 0,021 % (w/w), yet it complies with the acceptance limit. In K3 the value of the member's sample of 0,026 % (w/w) is exactly that of the acceptance limit. This value is the result of an arbitration sample. Originally, with 0,0265 % (w/w), the sample had exceeded the acceptance limit. By means of the arbitration sample the member company could avert the assignment of a sanction point. In K4 the member company had no negative results, so the mistake could most likely be detected and adjusted.

3.10 Alkali Metals: Sodium and Potassium

Test method: DIN EN 14538:2006

Limit of DIN EN 14214:2014: max. 5 mg/kg

Acceptance limit: max. 6,1 mg/kg

Sodium and potassium hydroxides or methylates are used as catalysts for the production of Biodiesel. Residues thereof are often present in Biodiesel as soaps which were not completely removed during washing. Soaps can cause filter plugging and clogging of injector pumps and nozzle needles. Alkali metals are also associated with formation of ash. Sodium as well as potassium deposit on the surface of particulate filters and oxidising catalytic converters and thus reduce the effectivity and service life of the systems.

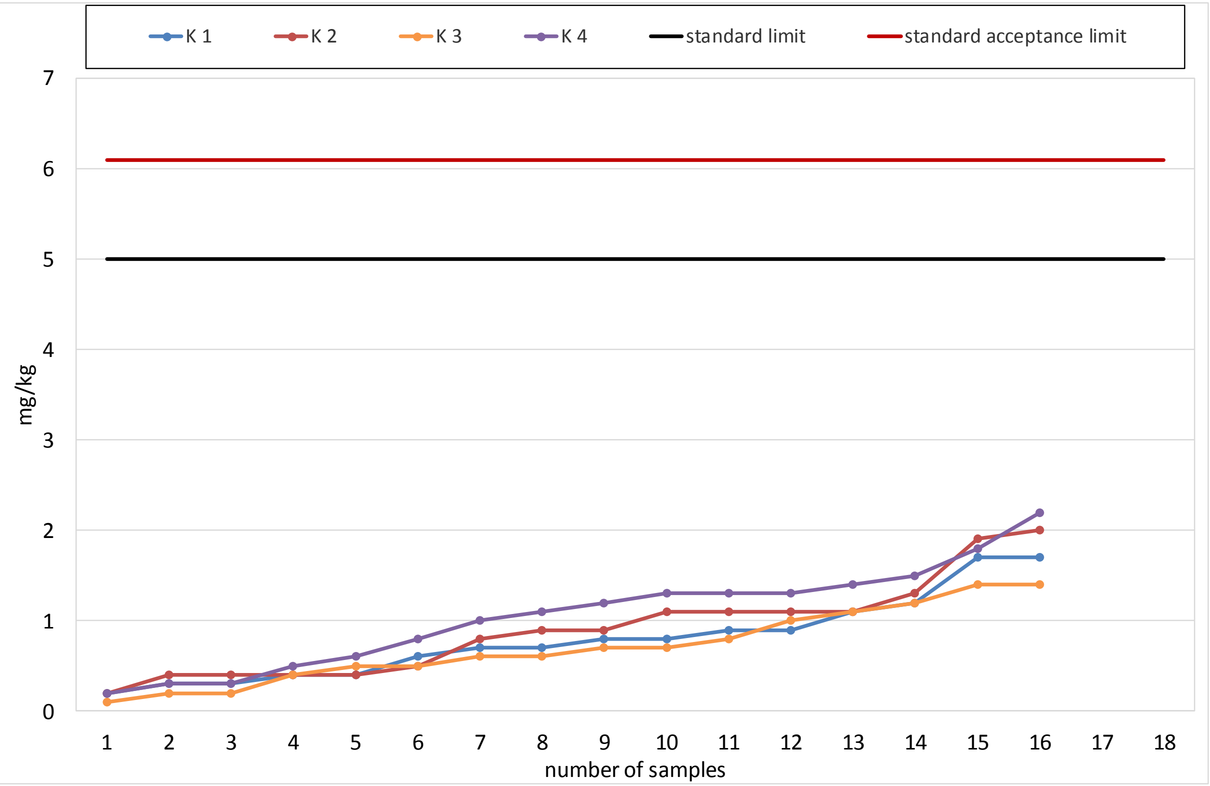

Diagram 14: Sum of Alkali Metals Sodium and Potassium according to DIN EN 14538.

Diagram 14 shows the sum of the alkali metals sodium and potassium. All samples fall way below the limit. The highest value measured of all 64 samples was just above 2 mg/kg.

3.11 Earth Alkali Metals: Calcium and Magnesium

Test method: DIN EN 14538:2006

Limit of DIN EN 14214:2010/2014: max. 5 mg/kg

Acceptance limit: max. 6,1 mg/kg

Earth alkali metals calcium and magnesium are either introduced into the process by raw material or they can get into the final product during the production process when tab water is used for washing. Calcium and magnesium soaps, which are more voluminous than alkali metal soaps, form by reacting with free fatty acids. The use of softened water for the washing process can reduce the ingress of earth alkali metals into Biodiesel.

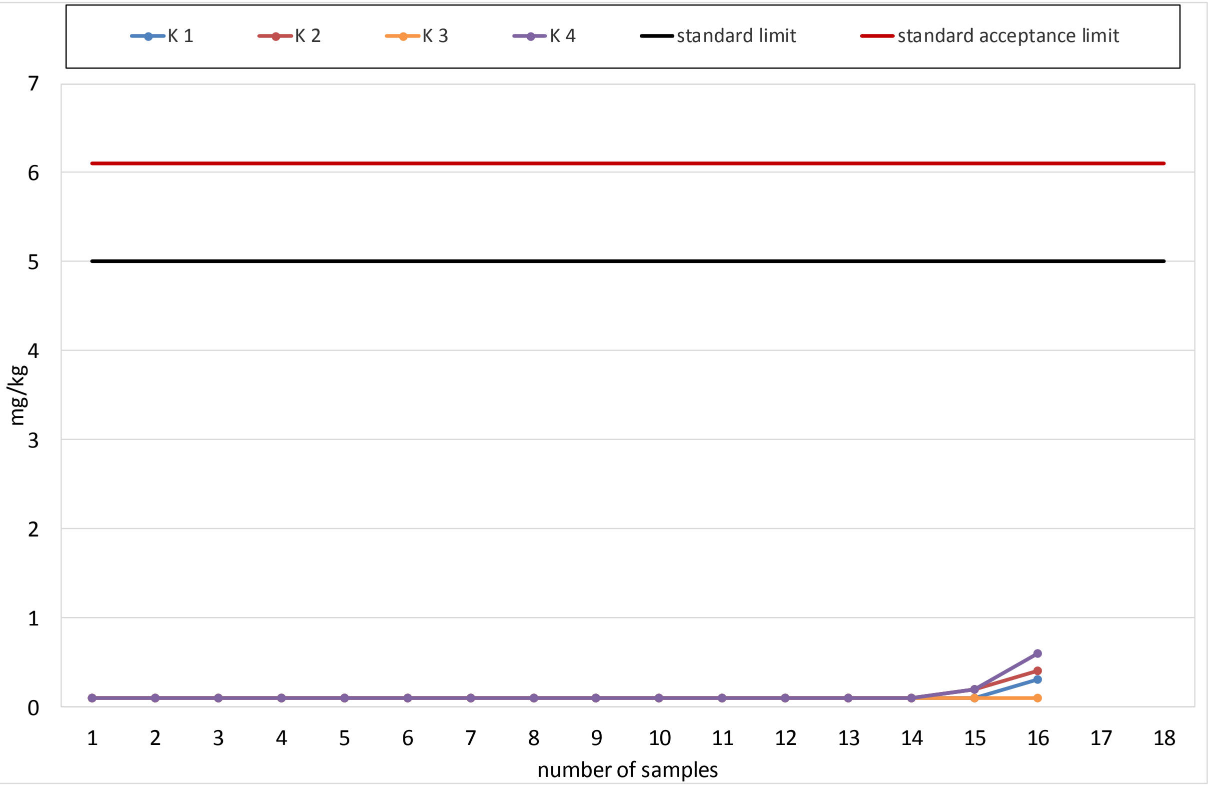

Diagram 15: Sum of Earth Alkali Metals Calcium and Magnesium according to DIN EN 14538.

The sum of the earth alkali content is given in diagram 15. All samples have values of far below the limit and significantly below the determination limit of 1 mg/kg.

3.12 Phosphorus Content

Test method: DIN EN 14107:2003

Limit of DIN EN 14214:2014: max. 4 mg/kg

Acceptance limit: max. 4,5 mg/kg

Phosphorus is a catalyst poison which can interfere irreversibly with the effectivity of exhaust gas after treatment systems. Phosphorus can contaminate Biodiesel via both vegetable oils in form of phospholipids and animal fats. Furthermore, the transesterification process deteriorates if the content of phospholipids is too high because these act as emulsifiers and thus interfere with the separation of the phases. Therefore, the phosphorus content must already be considered when the raw material is selected or it must be reduced to a minimum residual content by a refining process before the transesterification. Phosphorus can also be introduced into Biodiesel during the production process when phosphoric acid is used to separate soaps. In general, however, used phosphoric acid can be well removed from Biodiesel with water. Any residual phosphorus can be separated from the final product by distillation.

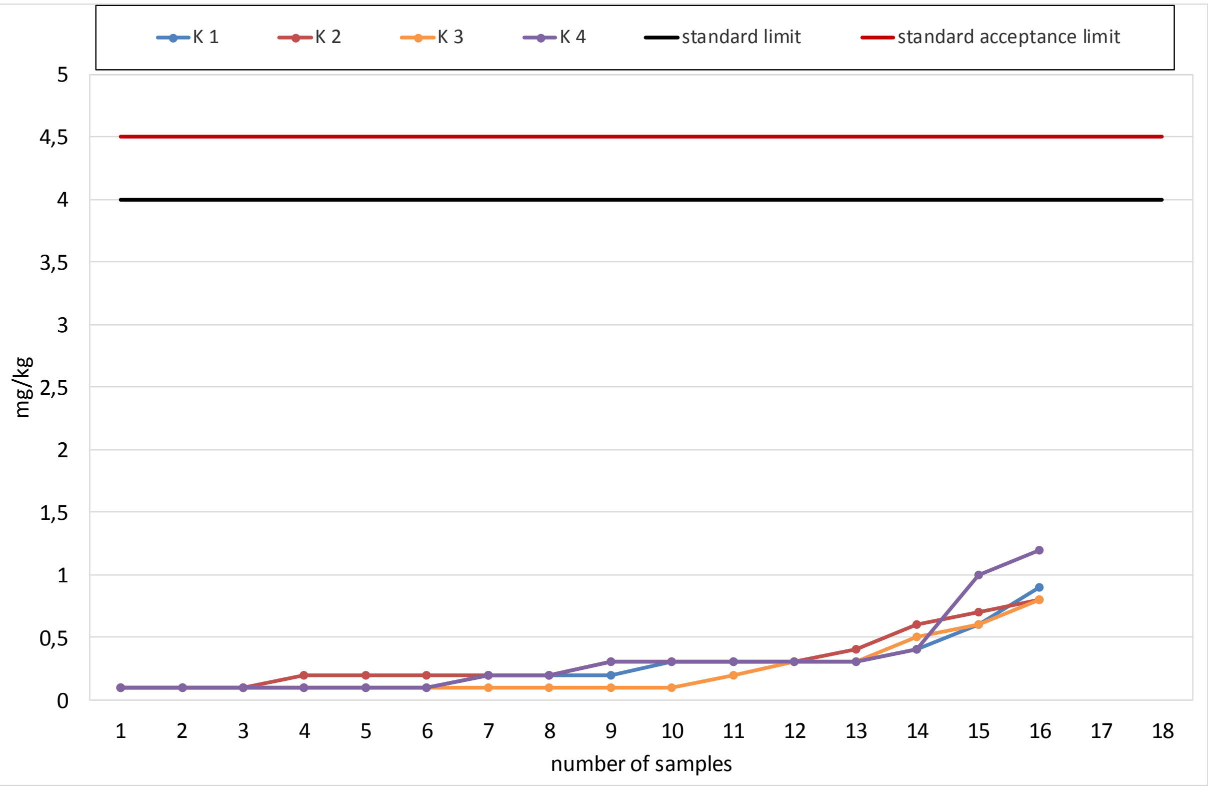

Diagram 16: Phosphorus Content according to DIN EN 14107.

Diagram 16 illustrates the results of the phosphorus content. The values fall way below the limit; 62 of all 64 samples even have a value of less than 1 mg/kg. The maximum limit is 4 mg/kg; at present the precision of the method does not allow for any additional tightening of the limit.

3.13 Content of Linolenic Acid Methyl Ester

Test method: DIN EN 14103:2015

Limit of DIN EN 14214:2014: max. 12,0 % (w/w)

Acceptance limit: max. 14,9 % (w/w)

The content of linolenic acid is determined by gas chromatography from the fatty acid profile. Linolenic acid is a triple unsaturated fatty acid with 18 carbon atoms (C18:3). Due to its chemical structure, it is extremely prone to oxidative attacks which is why the content of linolenic acid in Biodiesel is limited to 12 % (w/w).

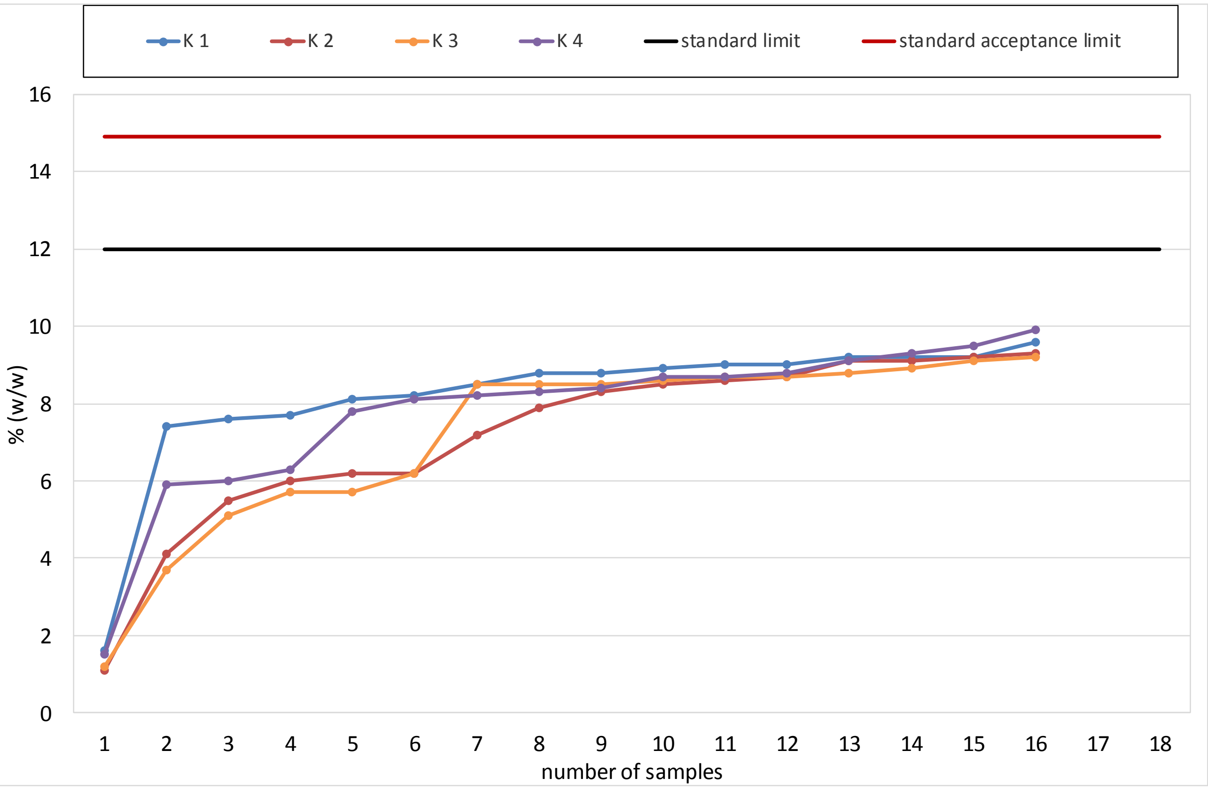

Diagram 17: Content of Linolenic Acid Methyl Ester according to DIN EN 14103.

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Qualitaetsmanagement Biodiesel e.V.
Claire-Waldoff-Str. 7
D-10117 Berlin / Germany

As shown in diagram 17 all analysed samples have a content of linolenic acid methyl ester which complies with the requirements of the standard. Usually the content of pure linolenic acid of rapeseed oil is between 8 and 10 %[2]. The low contents of linolenic acid of a large number of samples of summer campaigns K2 and K3 as well as transition campaign K4 show that the raw material 'rapeseed oil' usually used for the production of Biodiesel was at least partly substituted by other oils.

3.14 Cold Filter Plugging Point (CFPP)

Test method: DIN EN 116:2015

Limit according to DIN EN 14214:2014

For Biodiesel as pure fuel	***Limit***	***Acceptance limit***	
from 15 April to 30 September	*0 °C*	*-1,5 °C*	*Summer Grade*
from 1 October to 15 November	*-10 °C*	*-7,9 °C*	*Intermediate Grade*
from 16 November to 28/29 Feb	*-20 °C*	*-17,3 °C*	*Winter Grade*
from 1 March to 14 April	*-10 °C*	*-7,9 °C*	*Intermediate Grade*

For Biodiesel as blend component	***Limit***	***Acceptance limit***	
from 15 April to 30 September	*0 °C*	*-1,5 °C*	*Summer Grade*
from 1 October to 15 November	*-5 °C*	*-3,2 °C*	*Intermediate Grade*
from 16 November to 28/29 Feb	*-10 °C*	*-7,9 °C*	*Winter Grade*
from 1 March to 14 April	*-5 °C*	*-3,2 °C*	*Intermediate Grade*

The CFPP is the measure for Biodiesel cold properties. As described before at the end of chapter 2, the requirements for 'resistance to cold' are regulated nationally according to the prevailing climatic conditions. As applicable for Diesel fuel, there are differing requirements for summer, intermediate and winter grades.

Since nowadays Biodiesel is almost exclusively used as blend component for Diesel fuel, additivation is often dispensed with. According to German legal regulations applicable for cold properties, Biodiesel as blend component only needs to adhere to the CFPP value of -10 °C

[2] M. Mittelbach, C. Remschmidt: Biodiesel The Comprehensive Handbook, 1. Edition, Graz 2004, ISBN 3-200-00249-2, S. 135.

between 16 November and 28/29 February if the value of -20 °C demanded by DIN EN 14214 can be achieved by additivation.

The results of the summer, intermediate, and winter campaigns were depicted in two separate diagrams to enable a clearer presentation of the determined data.

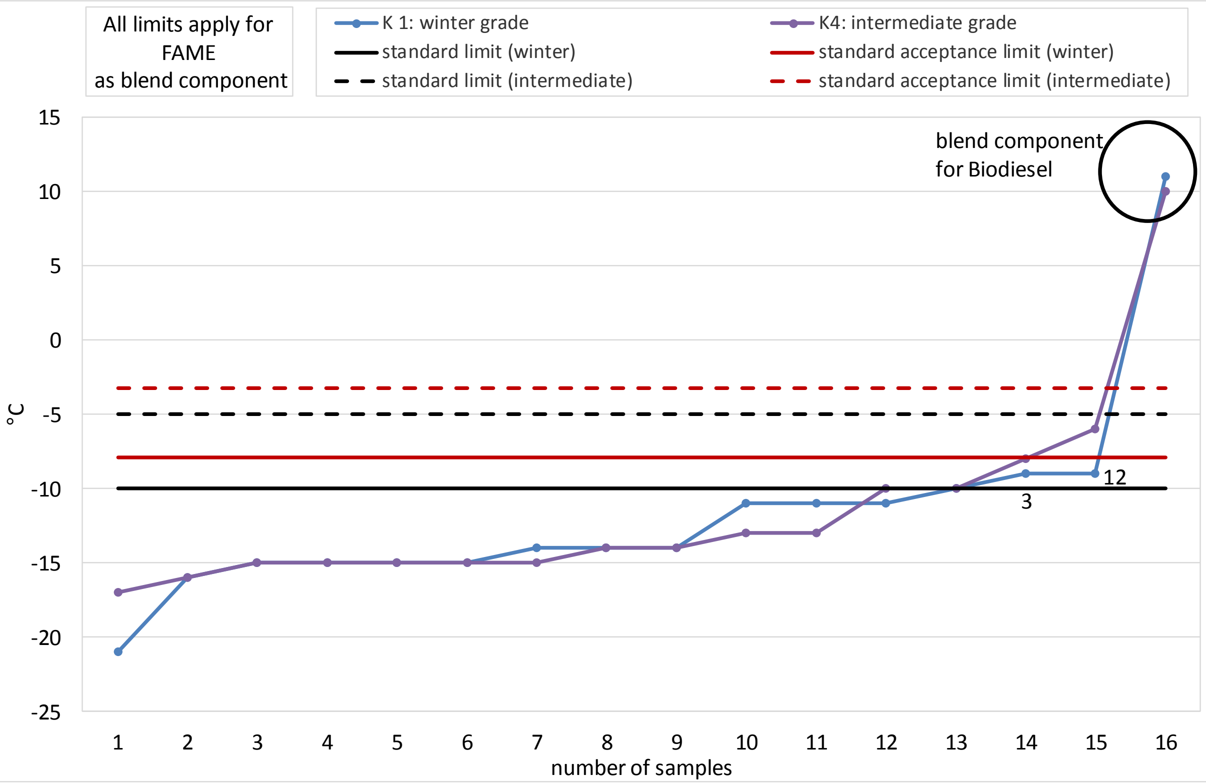

Diagram 18: CFPP (intermediate and winter grades) according to DIN EN 116.

In K1, samples were taken during the period 25 January to 5 February, so the samples are winter grade. Sampling in K4 took place from 10 to 21 October which makes the samples intermediate grade. In diagram 18 the limits for FAME as blend component are given because pure Biodiesel fuel is not marketed any longer by any AGQM member. The limit for the winter period is illustrated by an uninterrupted line; the limit for intermediate grade is given by a dotted line.

All but two samples (3 and 12) meet the relevant limit. With -9 °C samples 3 and 12 exceed the standard limit for the winter period (-10 °C) in K1; however, they still range within the acceptance limit (- 7,9 °C). The two samples circled black are blend components for Biodiesel, as noted in the diagram above; they cannot be marketed directly but only if blended to other Biodiesel to achieve a standard-conform product.

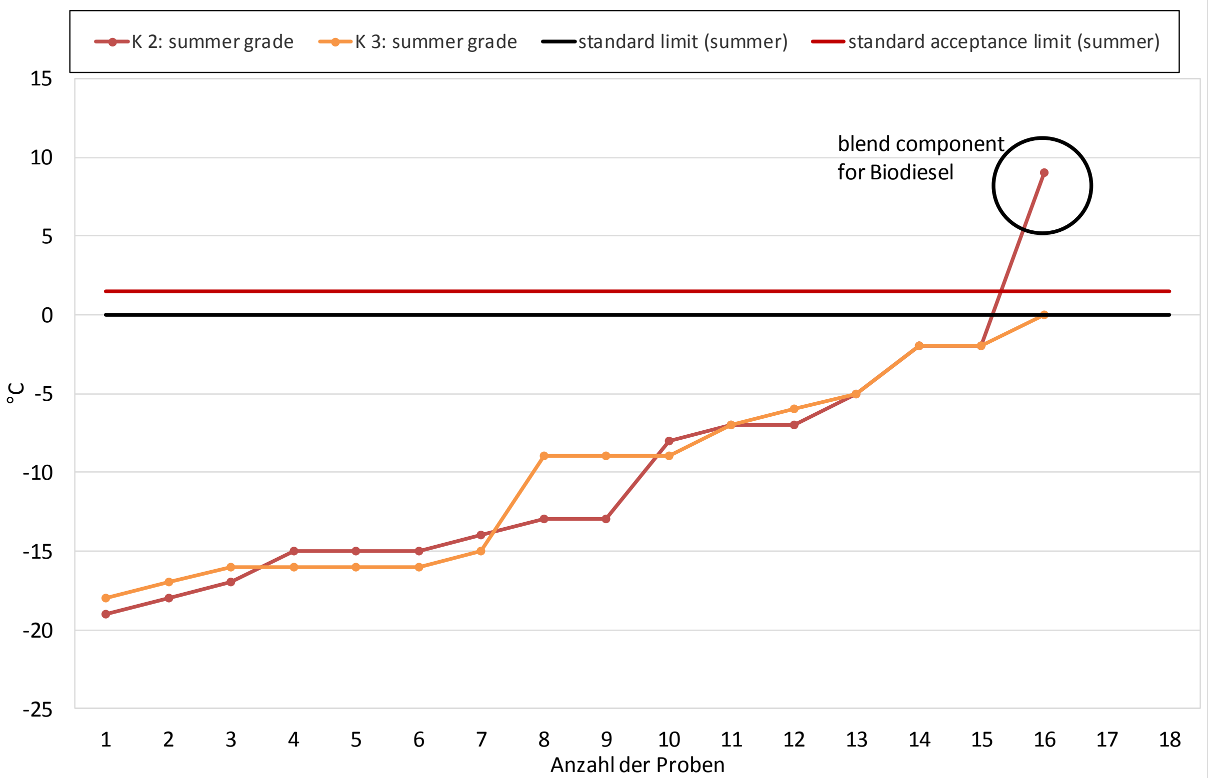

Diagram 19: CFPP (summer grade) according to DIN EN 116.

In K2, the sampling took place in the period 18 to 29 April; in K3 samples were taken from 4 to 15 July, which means that the samples were taken during the summer period. As shown in diagram 19 all tested samples fulfil the requirements of the standard. As noted in the diagram above, the samples circled black are blend components for Biodiesel, which can only be marketed after adjustment of the quality, e.g. by mixing with other appropriate fuel.

3.15 Cloud Point (CP)

Test method: DIN EN 23015: 2013

Limits according to DIN EN 14214:2014

For Biodiesel as blend component	***Limit***	***Acceptance limit***	
from 15 April to 30 September	*5 °C*	*7,4 °C*	*Summer Grade*
from 1 October to 15 November	*0 °C*	*2,4 °C*	*Intermediate Grade*
from 16 November to 28/29 Feb	*-3 °C*	*-0,6 °C*	*Winter Grade*
from 1 March to 14 April	*0 °C*	*2,4 °C*	*Intermediate Grade*

The Cloud Point is the temperature at which temperature-induced clouding (‘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.

As before for the CFPP, the results of the summer, intermediate, and winter campaigns were depicted in two separate diagrams to enable a clearer presentation.

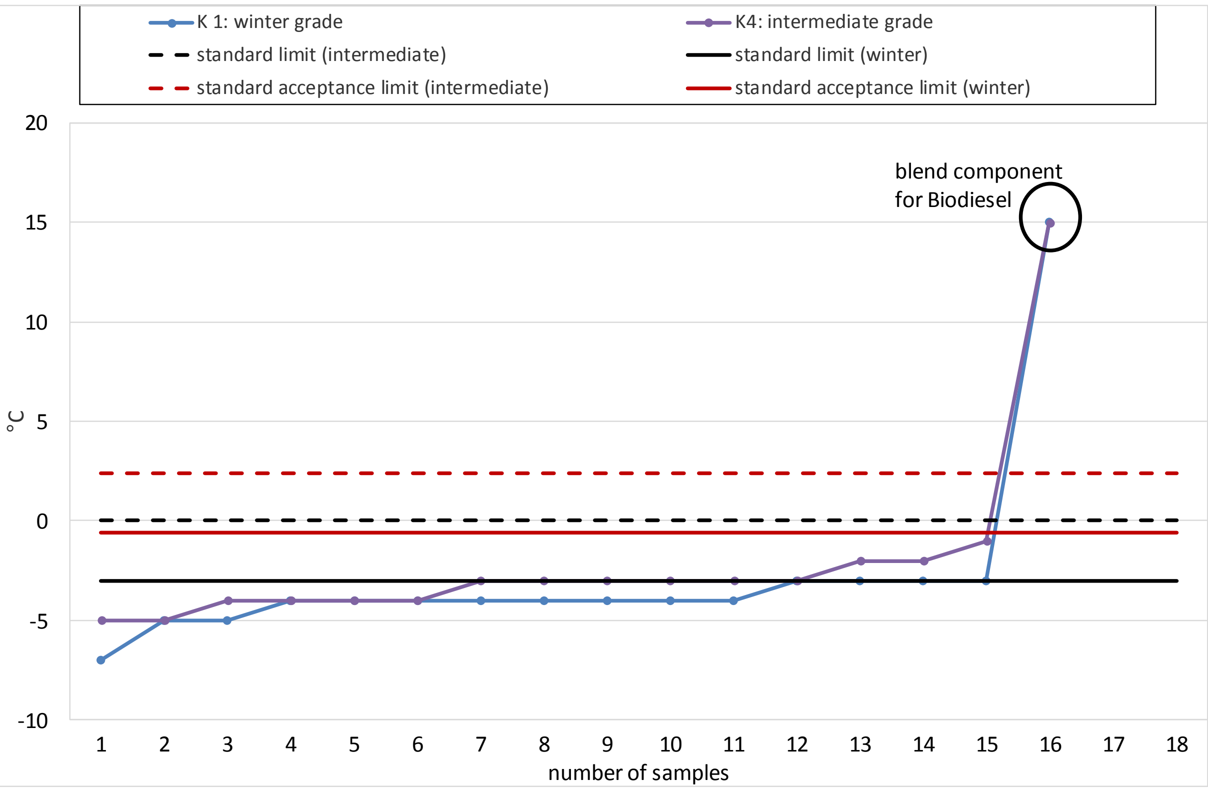

Diagram 20: Cloud Point (intermediate and winter grades) according to DIN EN 23015.

As illustrated by diagram 20, there was one limit violation each in the winter and intermediate periods. The samples circled black are blend components for Biodiesel.

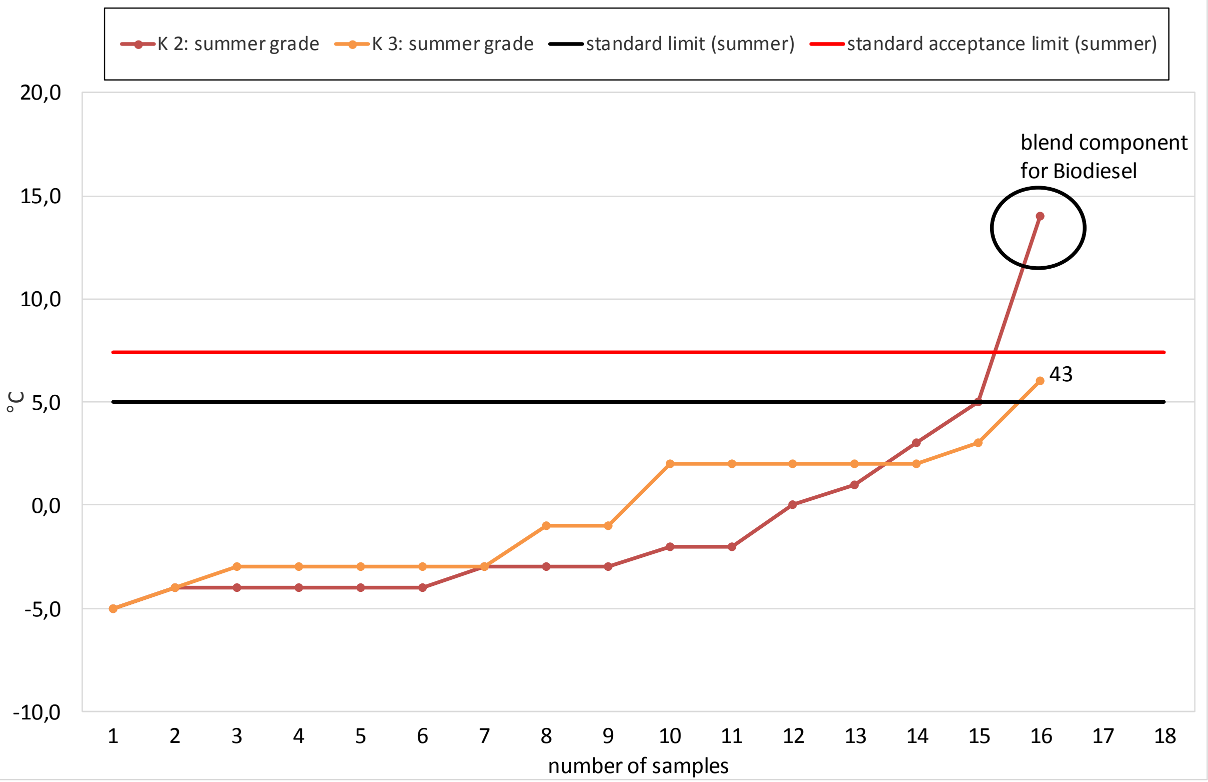

Diagram 21: Cloud Point (summer grade) according to DIN EN 23015.

As described for parameter CFPP, sampling of K2 and K3 was arranged in summer. As can be seen in diagram 21, there are also two limit violations. With 6 °C in K3 sample 43 exceeds the standard limit (5 °C) within the acceptance limit (7,4 °C). Again, the sample circled black is a blend component for Biodiesel which is not intended for direct marketing.

4 Summary

In this report the results of the unannounced sampling campaigns at AGQM producers and traders are illustrated. AGQM's sampling campaigns serve two purposes: to observe the compliance with the limits as stipulated by 10. BImSchV of the parameters laid down by 36. BImSchV; and to support the self-monitoring of its members.

Since 2010 AGQM has published an annual report[3] on the quality of the Biodiesel produced and traded by AGQM members. With the data obtained, the AGQM member companies' development of quality assurance measures can be observed and clearly tracked.

Compared with the previous year the Biodiesel quality has slightly deteriorated in 2016. However, 2015 showed outstanding results because the overall result revealed that considering the relevant precision of the test method no acceptance limit was violated, and there were only five violations of a limit. Compared to that three acceptance limits were violated in 2016. Another fifteen samples exceeded or fell below limits but considering the precision of the relevant test methods the violations were within the relevant acceptance limits. The following table 1 offers an overview of all limit violations.

Table 1: List of all samples violating limits.

Parameter	Method	Sample Number														
		1	3	12	18	20	28	35	40	43	44	50	51	60	63	64
Ester Content	DIN EN 14103															
Water Content	DIN EN ISO 12937															
Total Contamination	DIN EN 12662															
Oxidationstability at 110 °C	DIN EN 14112															
Acid Number	DIN EN 14104															
Content of Diglycerides	DIN EN 14105															
Content of Triglycerides	DIN EN 14105															
Content of free Glycerol	DIN EN 14105															
CFPP	DIN EN 116															
Cloud Point	DIN EN 23015															

Violations of limits within the acceptance limit
Violations of the acceptance limit of DIN EN 14214:2014
Violations of AGQM's acceptance limit

There were irregularities for parameters Ester Content, Water Content, Total Contamination, Oxidation Stability, Acid Number, Content of Di- and Triglycerides, Content of Free Glycerol, CFPP, and Cloud Point.

[3] http://www.agqm-biodiesel.de/en/downloads/reports/

The overview of all four sampling campaigns reveals that the number of violations rose from campaign to campaign: The number increased from two violations in K1 to four in K2 to six violations each in K3 and K4. In K4 three samples did not even meet the acceptance limit which resulted in the assignment of three sanction points.

A possible reason could be the economic situation and the political uncertainties which may cause companies to produce to an increasing extent on the verge of specification limits for financial reasons. The risk of limit violations is thus increased. Producers and storage operators should apply more attention to this quality assurance aspect.

In diagram 22 the number of limit and acceptance limit violations in the years 2010 to 2016 is juxtaposed to the overall number of tested parameters.

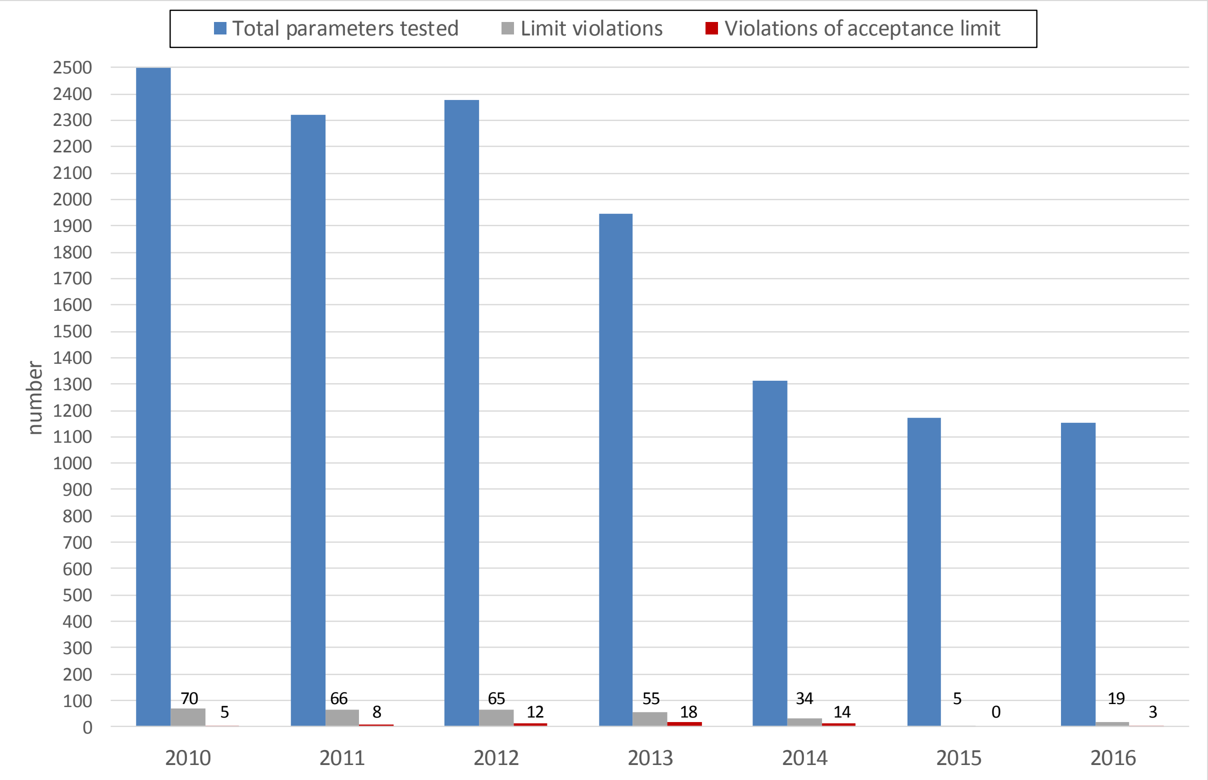

Diagram 22: Overview of all limit violations juxtaposed to the total number of tested parameters.

It is recognizable that the number of violations is very small if juxtaposed to the overall number of determinations. Furthermore, over the years a sharp decline of the number of violations is apparent. The slight increase of limit violations in 2016 compared to 2015 shows that the monitoring of AGQM's member companies will continue to be of importance.

In 2016, 61 of 64 tested samples complied with the requirements of DIN EN 14214 and the more stringent AGQM limits. Thus, the extremely high quality level of Biodiesel produced by AGQM members was verified anew.

5 Annex

5.1 Limits and Test Methods

Table 2: Limits and Test Methods for the Parameters tested according to DIN EN 14214:2014.

Test Parameter	Method	Year of Publication	Measuring Unit	Standard limits		Acceptance Limits	
				min.	max.	min.	max.
Content of Fatty Acid Methyl Ester	DIN EN 14103	2015	% (m/m)	96,5	-	94,0	-
Density at 15 °C	DIN EN ISO 12185	1997	kg/m³	860	900	859,7	900,3
Sulfur Content (UV)	DIN EN ISO 20846	2011	mg/kg	-	10,0	-	11,3
Water Content K.-F.	DIN EN ISO 12937	2000	mg/kg	-	500	-	591
Total Contamination	DIN EN 12662	1998[4]	mg/kg	-	24	-	32
Oxidation Stability (at 110 °C)	DIN EN 14112	2014	h	8,0	-	6,6	-
Acid Number	DIN EN 14104	2003	mg KOH/g	-	0,50	-	0,54
Iodine Number	DIN EN 16300	2012	g Iod/100g	-	120	-	124
Iodine Number	DIN EN 14111	2003	g Iod/100g	-	120	-	123
Content of Linolenic Acid Methyl Ester	DIN EN 14103	2015	% (m/m)	-	12,0	-	14,9
Content of free Glycerol	DIN EN 14105	2011	% (m/m)	-	0,02	-	0,026

[4] Due to the fact that the current version of DIN EN 12662 is not suitable for the determination of parameter ‘total contamination‘ in FAME, DIN EN 12662:1998 applies until further notice.

Content of Monoglycerides		2011	% (m/m)	-	0,70	-	0,82
Content of Diglycerides		2011	% (m/m)	-	0,20	-	0,24
Content of Triglycerides		2011	% (m/m)	-	0,20	-	0,27
Overall Glyceride Content		2011	% (m/m)	-	0,25	-	0,28
Content of Alkali Metals (Na + K	DIN EN 14538	2006	mg/kg	-	5,0	-	6,1
Sodium Content		2006	mg/kg	-	5,0	-	6,1
Potassium Content		2006	mg/kg	-		-	
Content of Earth Alkali Metals (Ca + Mg)		2006	mg/kg	-	5,0	-	6,1
Calcium Content		2006	mg/kg	-	5,0	-	6,1
Magnesium Content		2006	mg/kg	-		-	
Phosphorus Content	DIN EN 14107	2003	mg/kg	-	4,0	-	4,5
CFPP	DIN EN 116	2015	°C	15 April to 30 September	0	-	1,5
				1 October to 15 November	-10	-	-7,9
				16 November to 28/29 Feb	-20	-	-17,3
				1 March to 14 April	-10	-	-7,9
Cloud Point	DIN EN 23015	2013	°C	15 April to 30 September	5	-	7,4
				1 October to 15 November	0	-	2,4
				16 November to 28/29 Feb	-3	-	-0,6
				1 March to 14 April	0	-	2,4

Table 1: Limits and Determination Methods for the Parameters Tested according to AGQM's QM System.

Test Parameters	Method	Year of Publicatio	Measuring Unit	AGQM Limits		Acceptance Limits	
				min.	max.	min.	max.
Water Content K.-F. (for Producers)	DIN EN ISO 12937	2000	mg/kg	-	220	-	280
Water Content K.-F. (for Warehouse operators)	DIN EN ISO 12937	2000	mg/kg	-	300	-	370
Total Contamination	DIN EN 12662	1998[5]	mg/kg	-	20	-	20
CFPP	DIN EN 116	2015	°C	19 Oct to 28/29 Feb	-20 (applicable for use of Biodiesel as pure fuel (B100))	- - - -	-17,3

[5] Due to the fact that the current version of DIN EN 12662 is not suitable for the determination of parameter 'total contamination' in FAME, DIN EN 12662:1998 applies until further notice.

5.2 Abbreviations

AGQM	Association Quality Management Biodiesel e.V.
B7 Biodiesel	Short for blended fuel permissible according to DIN EN 590 with a proportion of 7 %
	BImSchG Bundes-Immissionsschutzgesetz (German Federal Emission Protection Act)
BImSchV	Bundes-Immissionsschutzverordnung (German Federal Emission Protection Directive)
ca.	Circa
CEN	Comité Européen de Normalisation (European Standardization Committee)
CFPP	Cold Filter Plugging Point
DIN	Deutsches Institut für Normung (German Institute for Standardization)
DIN EN 14214:2014	DIN EN 14214:2012+A1:2014
EN	European Standard
FAM	Fachausschuss für Mineralöl- und Brennstoffnormung (FAM) im DIN
FAME	Fatty Acid Methyl Ester
FQD	Fuel Quality Directive (2009/30 EG)
GHG	Green House Gas
JWG	Joint working group
K1	Campaign 1
K2	Campaign 2
K3	Campaign 3
K4	Campaign 4
ptx/ptl	Power to X / Power to Liquid
QM System	Quality Management System
QA Committee	Committee for Quality Assurance
RED	Renewable Energy Directive (2009//28/EG)
RME	Rapeseed Oil Methyl Ester
TC	Technical Committee
UCO	Used cooking Oils and Fats
UCOME	Used cooking oil methyl ester (fatty acid methyl ester from used cooking oils and fats)