Biodiesel Quality in Germany

Results of the Sampling Campaigns
at AGQM Production Plants
and Warehouse Operators

2014

Project Management and Report:

Nicola Prinz, Maren Dietrich (AGQM)

Translation by Christiane O'Connor

Analytics performed by:

SGS Germany GmbH
Fuel Technology Centre
Am Neuen Rheinhafen 12A
D-67346 Speyer / Germany

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

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1 Introduction

In Germany Biodiesel or FAME (**F**atty **A**cid **M**ethyl **E**ster) is still the most important fuel based on renewable raw materials. In the future it will also continue to be an important element to maintain mobility and to fight the climate change. Particularly with regard to the instable political situation in some of the oil producing countries and the high dependency from some individual oil supplying countries, Biodiesel can contribute significantly to the reduction of Europe's dependency from oil imports.

Arbeitsgemeinschaft Qualitaetsmanagement Biodiesel e.V. (AGQM) is the alliance of Biodiesel producers and traders who joined forces to market a product which safely complies with the requirements of the standard. Moreover, AGQM's additional and more stringent quality criteria assure that the best possible fuel is put on the market.

AGQM's quality management concept (QM concept), which has been successfully implemented by AGQM members for many years, is the basis for any quality assurance measures. As an important element of the QM concept, the fuel quality of the AGQM members is checked at regular intervals. To ensure the QM concept's compliance with the increasing requirements imposed by the standardization organizations it is continually revised by AGQM's Quality Assurance Committee (QA Committee). The QA Committee members are experts in the field of quality management and most of them come from AGQM member companies; however they may also be experts from companies outside AGQM like commercial laboratories for example.

Today Biodiesel is marketed predominantly as blend component to Diesel fuel which means it is almost exclusively sold as admixing component to produce B7 fuel. While in other European countries there are considerable quality issues, in Germany, where about 62 % of all Biodiesel is produced by AGQM members, the operation of engines with the B7 blend runs smoothly due to the good quality management.

While up to a few years ago Biodiesel was almost exclusively produced from rapeseed oil, the raw materials Biodiesel is based on today, have markedly changed. Reasons for that are high price fluctuations for raw materials, an increased offer of other types of oil such as soybean oil at comparably low prices, and the increased use of fatty acids and used cooking oils and fats which until the end of 2014 was politically supported by their double consideration for the fulfilment of the quota obligation.

The use of other raw materials has an impact on the fatty acid profile of the esters produced with considerable consequences for various parameters of the standard which then also lead

to necessary amendments. In 2011 for example, the application range of DIN EN 14103 for the determination of the ester content of originally C14 to C24 was extended to C6 to C24. In addition the internal standard was exchanged (C19 instead of C17) in order to make the method also applicable for FAME from animal fats which naturally contains C17.

By regularly monitoring our members' products, a unique data pool could be obtained for the verification of the constantly improving quality of Biodiesel. In 2011 the results of the unannounced sampling of all AGQM members was published in a quality report[1]. The results collected since 2011 document the high quality level of Biodiesel marketed by the AGQM members and its continuing improvement.

2 Description of Sampling

Member sampling is one of AGQM's most important quality assurance measures. Sampling without prior announcement is of crucial importance since it assures that the results reflect our members Biodiesel production and handling. 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. 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 Mineralöl- und Brennstoffnormung (FAM) im DIN*. In 2014 there were four unannounced sampling campaigns.

The Biodiesel parameters to be tested are determined by the QA Committee in the QM concept. 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 AGQM's quality check, i.e. the standard limits demanded as well as their related rejection limits comply with DIN EN 14214:2012 which substituted DIN EN 14214:2010 in November 2012. In addition more stringent requirements, so-called 'AGQM limits', were determined for some parameters; thus AGQM documents its particular quality commitment. Referring to DIN EN 14214:2010 is of importance insofar as the German 10th BImSchV – which stipulates the properties of Biodiesel – has only been adapted to the 2012 version of the standard in December 2014. So it may well be that such a product complies with the legal requirements for blending according to the German 10th BImSchV but its quality does not live up to the AGQM requirements.

[1] http://www.agqm-biodiesel.de/files/1213/2880/1660/20110530_Herstellerbepr_Final_dt.pdf

Table 3 of the attachment lists all tested parameters with their limits according to DIN EN 14214:2012. All adjustments to the previous version are marked in blue font.

Following Table 4 shows the parameters as required by AGQM which exceed the current standard. For parameters ‚water content', ‚total contamination', and 'CFPP', AGQM's requirements for the Biodiesel quality of its members are stricter than required by law.

However, AGQM also supports the needs of its members. In 2013 special regulations were made for Biodiesel produced from used cooking oils and fats. Biodiesel produced thereof is exempted from the determination of parameters 'sulfur content', 'CFPP', and 'Cloud Point' and is not sanctioned if the limits of these parameters are exceeded. However, it cannot be marketed directly but only as blend component to Biodiesel.

In 2014 eighteen Biodiesel producers and two traders participated in AGQM quality assurance measures; beside the production plants three fuel depots of the traders were sampled. Spread throughout the year four sampling campaigns took place in different seasons when 73 Biodiesel samples were taken, analysed and then evaluated – 37 less than in 2013. The reason for the reduced number of checked samples is the fact that in 2014 there were only four instead of six sampling campaigns.

The sampling dates were selected so that the AGQM member companies were sampled both in summer and in winter because for summer and winter grades there are different limits for parameters 'Cold Filter Plugging Point (CFPP)' and 'Cloud Point' which are stipulated in 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:	3 March to 14 March	Intermediate grade
K2:	5 May to 16 May	Summer grade
K3:	11 August to 22 August	Summer grade
K4:	17 November to 28 November	Intermediate and winter grades

3 Individual Results and Evaluation

In the following section the test method used, the limit, the rejection limit and a brief description can be found for every parameter followed by a graphical illustration of the evaluated measuring values.

The results were made anonymous and do not reveal the origin of the sample. Internally AGQM numbered all samples; this individual number is only given in the report so that conspicuous features of individual samples can be pointed out, should a rejection limit have been exceeded (see table 2).

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 by a black line, the rejection limits calculated by taking account of the precision of the method by a red line. These rejection limits are relevant for customs as well as for the assignment of sanction points according to AGQM's QM concept. In the diagrams of parameters 'total contamination', 'water content', and 'CFPP' the AGQM limit and rejection limit is given additionally.

For the parameters ‚sulfur content', ‚CFPP', and ‚Cloud Point', as mentioned in the previous chapter, there is an exception. 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 due to the fact that the production of fuel made from used cooking oils and fats complying with the standard is impossible with regard to the above parameters. Therefore, Biodiesel produced thereof must not be marketed directly but be admixed to other Biodiesel so that on the whole standard-conform Biodiesel is achieved. The measuring values referring to such an exception are marked accordingly.

In the following section the results of the sampling for every parameter are represented graphically and discussed individually.

3.1 Fatty Acid Methyl Ester (‚FAME') Content

Test method: DIN EN 14103:2011
Limit of DIN EN 14214:2012: ≥ 96,5 % (w/w)
Minimum rejection limit: 94,0 % (w/w)

The content of fatty acid methyl esters, briefly ester content, is a measure for the purity of Biodiesel. Fatty acid methyl ester is either produced by the reaction of fats and oils with methanol in the presence of an alkali catalyst (e.g. potassium hydroxide, sodium hydroxide, potassium methylate, sodium methylate) or from fatty acids and methanol in the presence of an acid catalyst (e.g. sulfuric acid). It differs with regard to the chain lengths of the fatty acid residues and the number of existing double bonds. The ester content is determined by gas chromatography and given as sum of all fatty 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 lower than 96,5 % can be an indication for the admixture of other substances or the presence of side products resulting from the Biodiesel production. Additionally, it is possible that other substances e.g. oligomers got into the Biodiesel with the raw material. In general, the ester content of a final product is higher after distillation subsequent to (trans-) esterification.

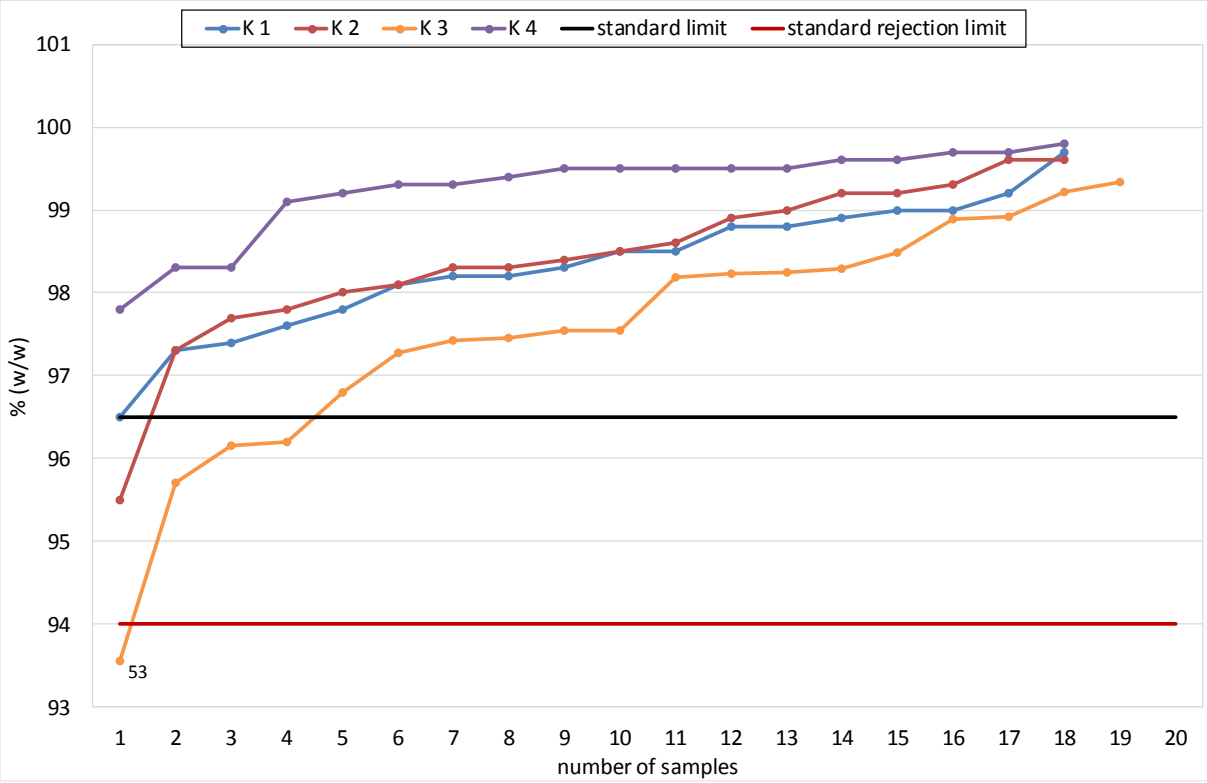

Diagram 1: Fatty Acid Methyl Ester Content according to DIN EN 14103.

The evaluation of the results of diagram 1 shows that all samples (but one) fulfil the requirements of DIN EN 14214. Non-standard-conform sample 53 of campaign K3 is significantly below the limit but with 93,6 % (w/w) only just below the rejection limit of 94 % m/m). According to the producer this Biodiesel consists of a mixture of distilled FAME and UCOME (Used Cooking Oil Methyl Ester). When the two components were mixed there was a maladjustment resulting in the admixture of too much UCOME with a high percentage of oligomeres which led to a decrease of the methyl ester content. Upon detection of this limit violation, correction measures were taken immediately and the amount of distillate in the mixture was increased.

In four additional cases the values were below the limit though they were far above the rejection limit.

3.2 Density at 15 °C

Test method: DIN EN ISO 12185:1997

Limit of DIN EN 14214:2012: between 860 and 900 kg/m³

Minimum rejection limit: 859,7 kg/m³; maximum rejection limit: 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 must be between 860-900 kg/m³ at 15 °C. The density is thereby dependent on the FAME composition and the purity of the Biodiesel; the shorter the carbon chain (C chain) and the more double bonds the higher the density. So, first cautious conclusions may be drawn with regard to the used raw material (see table 1).

Table 1: Selected Fatty Acid Methyl Esters and their Density.[2]

Fatty Acid Methyl Ester	Temperature	Density
C 6:0	15 °C	889 kg/m³
C 8:0	15 °C	881 kg/m³
C 10:0	15 °C	876 kg/m³
C 12:0	15 °C	873 kg/m³
C 14:0	20 °C	867 kg/m³
C16:0	20 °C	884 kg/m³
C 18:0	38 °C	852 kg/m³
C 18:1	20 °C	874 kg/m³
C 18:2	15 °C	894 kg/m³
C 18:3	15 °C	904 kg/m³

The density can also be influenced by contamination, e.g. methanol, which would decrease the density.

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

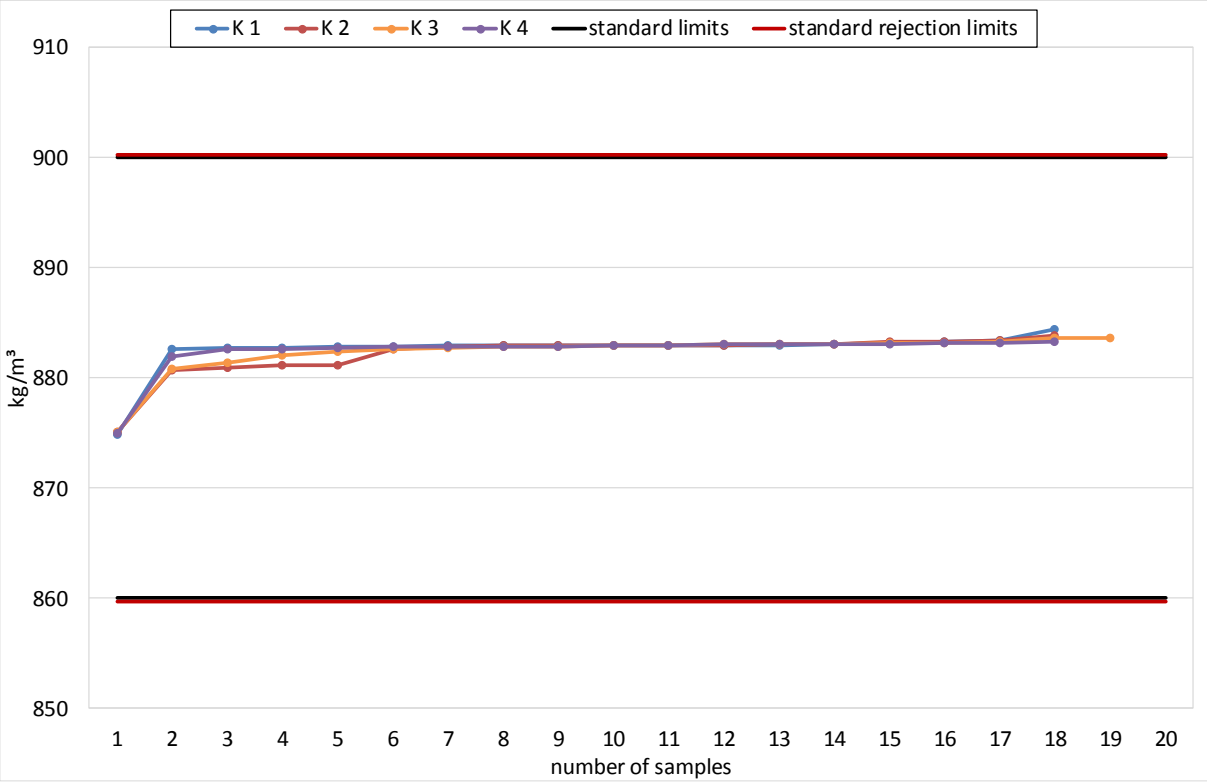

Diagram 2: Density at 15 °C DIN EN ISO 12185.

Diagram 2 shows that all accept one analysed samples range very closely between 881 and 883 kg/m^3 and that again the predominant majority exactly meets the value of 883 kg/m for Biodiesel from rapeseed oil which is used by customs for conversion of weight into volume. During summer campaigns K2 and K3 some lower densities were measured compared to K1 and K4. The cause is presumably the use of other raw materials (e.g. palm oil). In summer the admixture of Biodiesel stemming from used cooking oils is possible due to less stringent requirements with regard to the CFPP.

3.3 Sulfur Content

Test method: DIN EN ISO 20846:2011
Limit of DIN EN 14214:2012: ≤ 10 mg/kg
Maximum rejection limit: 11,3 mg/kg

Fuels with high sulfur content have a detrimental impact on human health and the environment. If vehicles are operated with fuel rich in sulfur more sulfur dioxide and particulates are thus emitted which can lead to a higher mutagenic potential for all living beings. For that reason the sulfur content in Biodiesel is limited to 10 ppm.

Biodiesel can contain sulfur compounds of different sources: on the one hand from the use of a sulfurous catalyst for the production and on the other hand from the raw materials used. During growth plants can absorb sulfurous compounds. Usually the sulfur content ranges between 2 and 7 mg/kg. Animal fats can contain sulfur in the form of protein compounds. Normally a sulfur content of up to 30 mg/kg can be expected. There are different approaches to achieve a reduction of this high sulfur content. For example the suflur content of the biofuel can be lowered by distillation. Another option is to mix strongly sulfurous Biodiesel with low sulfurous Biodiesel and to thus lower the sulfur concentration of the resulting mixture underneath the limit.

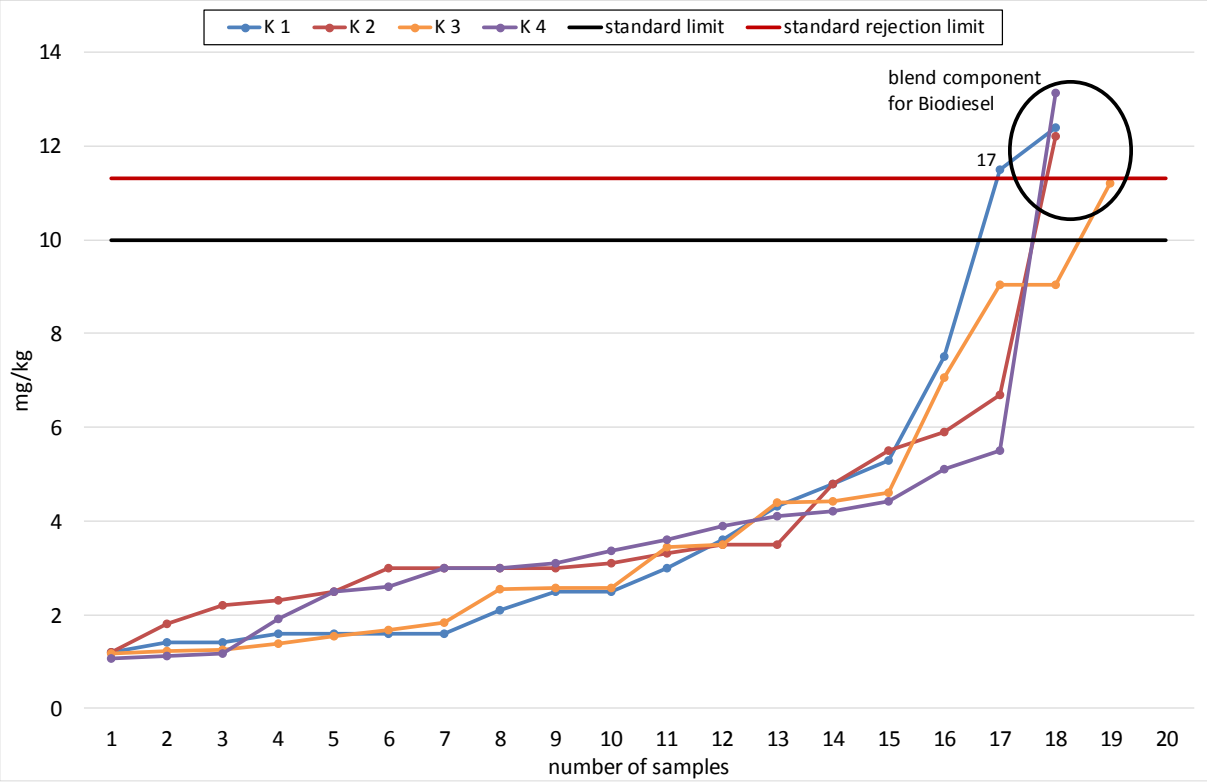

Diagram 3: Sulfur Content according to DIN EN ISO 20846.

The majority of samples has a sulfur content of less than 7 mg/kg which may be indicative of the use of vegetable oils as raw material for the Biodiesel production. The higher values can be explained with the use of UCOME because on the one hand the transesterification process of UCOME is based on acid catalysts (e.g. sulfur) and on the other hand sulfur from animal proteins can be contained in UCOME. The samples circled in black font of diagram 3 are blend components to standard-conform Biodiesel which means the fuel is not marketed directly but admixed to other Biodiesel.

If the circled samples are left unconsidered, only sample 17 of campaign K1 exceeds the limit. This sample originates from a member who also repeatedly violated limits of other parameters in the different campaigns. Due to this fact the member was excluded from AGQM. Unfortunately the reasons for those numerous limit violations stay unresolved.

3.4 Water Content

Test method: DIN EN ISO 12937:2000
Limit of DIN EN 14214:2012: ≤ 500 mg/kg
Maximum rejection limit: 591 mg/kg

AGQM limit: ≤ 220 mg/kg for producers
Rejection limit: 280 mg/kg
AGQM limit: ≤ 300 mg/kg for warehouse operators
Rejection limit: 370 mg/kg

Due to its polar properties Biodiesel can physically dissolve large amounts of water as opposed to carbon-based fuels. Since almost all Biodiesel production processes use water to remove free glycerol, soaps and other contamination as last refining step, the product must be dried subsequently.

Due to high air humidity water can ingress into Biodiesel so its storage conditions must be selected accordingly. Under standard conditions the saturation concentration of Biodiesel is ca. 1500 mg water/kg. However, with lower water contents and at lower temperatures, water may already precipitate which may then freeze and block piping systems, cause corrosion, and encourage the growth of microbes. Furthermore, conventional Diesel fuels can store significantly smaller amounts of water so that the water dissolved therein can precipitate when they are mixed with Biodiesel.

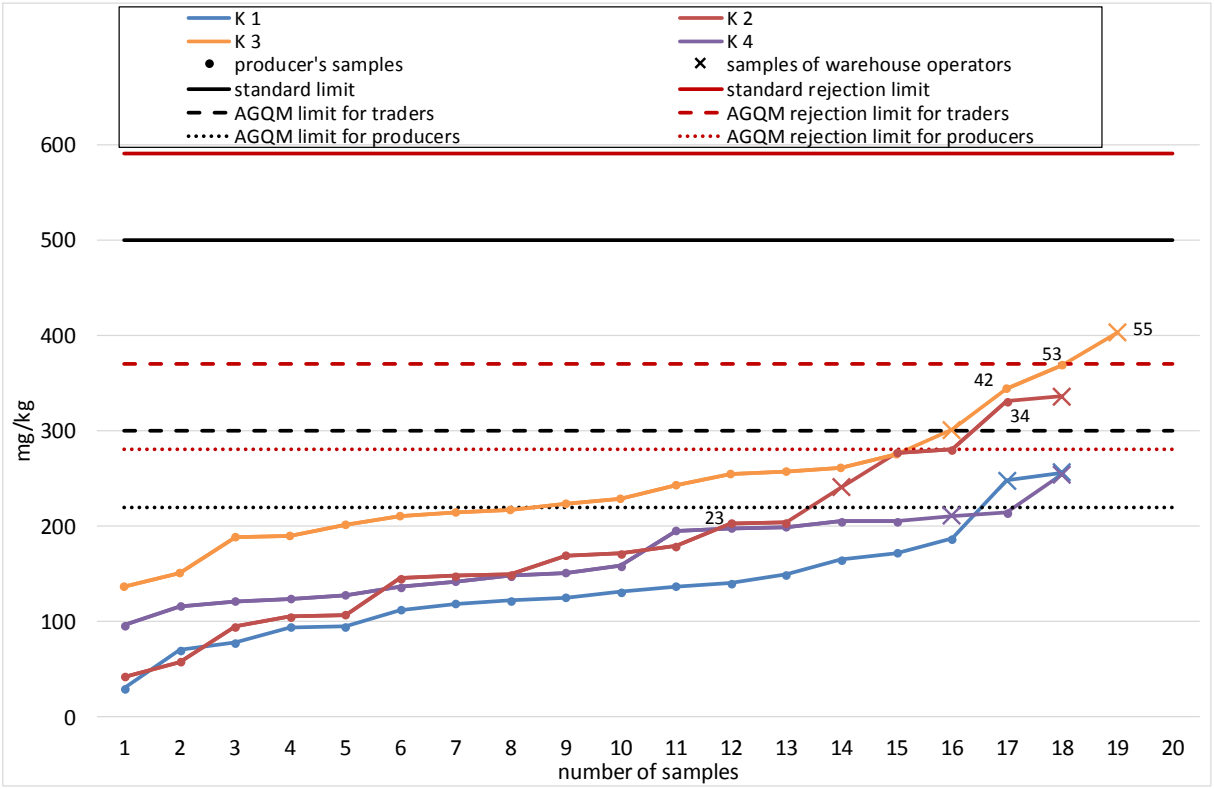

Diagram 4: Water Content according to DIN EN ISO 12937.

Diagram 4 shows that all tested samples are significantly below the standard limit. Still, the evaluation reveals that in K3 about half of the producers' samples exceed the AGQM limit for producers (220 mg/kg); however, only two of those samples exceed the AGQM rejection limit for producers (280 mg/kg). In K2 only three producer samples violated the AGQM limit, one of which also exceeded the rejection limit. Those three products (samples 34, 42 and 53) exceeding the AGQM rejection limit for producers may be marketed as standard-conform commodity but not as AGQM product.

In case of doubt concerning the analytical results of the sampling, members can address AGQM to apply for arbitration. For that purpose the member designates an independent laboratory accredited for Biodiesel analytics. One of the two retain samples taken during sampling functions as arbitration sample and the result of the arbitrational analysis is binding for both parties. One member demanded two arbitrational analyses, due to massive limit violations in K2 (sample 23: 377 mg/kg) and K3 (sample 42: 367 mg/kg).

The arbitrational analysis of sample 23 in campaign 2 revealed that with 203 mg/kg it fulfils the AGQM requirements. However, the second arbitrational analysis (sample 42) showed a value

of 344 mg/kg which is significantly above AGQM's rejection value for producers. This sample must not be marketed as AGQM product.

Samples marked ‚X' in diagram 4 are samples of warehouse operators. For such samples an AGQM limit of 300 mg/kg and an AGQM rejection limit of 370 mg/kg apply. One of those samples exceeded the AGQM limit and with a value of 403 mg/kg sample 55 exceeded the AGQM rejection limit. The fuel of sample 55 must not be marketed as AGQM product.

Overall it is apparent that during the summer months it is more difficult to restrict the water content. The reason is not only the higher absolute humidity in summer but it can also be explained by higher temperatures in the vacuum systems required to dry Biodiesel.

3.5 Total Contamination

Test method: DIN EN 12662:1998
Limit of DIN EN 14214:2012: ≤ 24 mg/kg
Maximum rejection limit: 32 mg/kg
AGQM limit: ≤ 20 mg/kg
(AGQM's limit for parameter 'total contamination' is also AGQM's rejection limit.)

Due to the fact that the current version of DIN EN 12662 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 8 March 2012.

'Total contamination' is a measure for the content of insoluble particles which are obtained by filtration of a heated sample. It is determined gravimetrically by weighing the filter. For Diesel fuel 'total contamination' is of little relevance since there are hardly any insoluble particles due to distillation steps during production. Biodiesel is usually not distilled which is why 'total contamination' is an important quality feature. Rust, dust but also organic solid substances like Sterylglycosides, polymer particles or soaps may be found in Biodiesel. A high proportion of insoluble particles may cause filter plugging, wear on the injection system, and leaks on valves. Therefore, AGQM set its own more stringent limit of 20 mg/kg to improve the application security of Biodiesel and to account for the imprecision of the method.

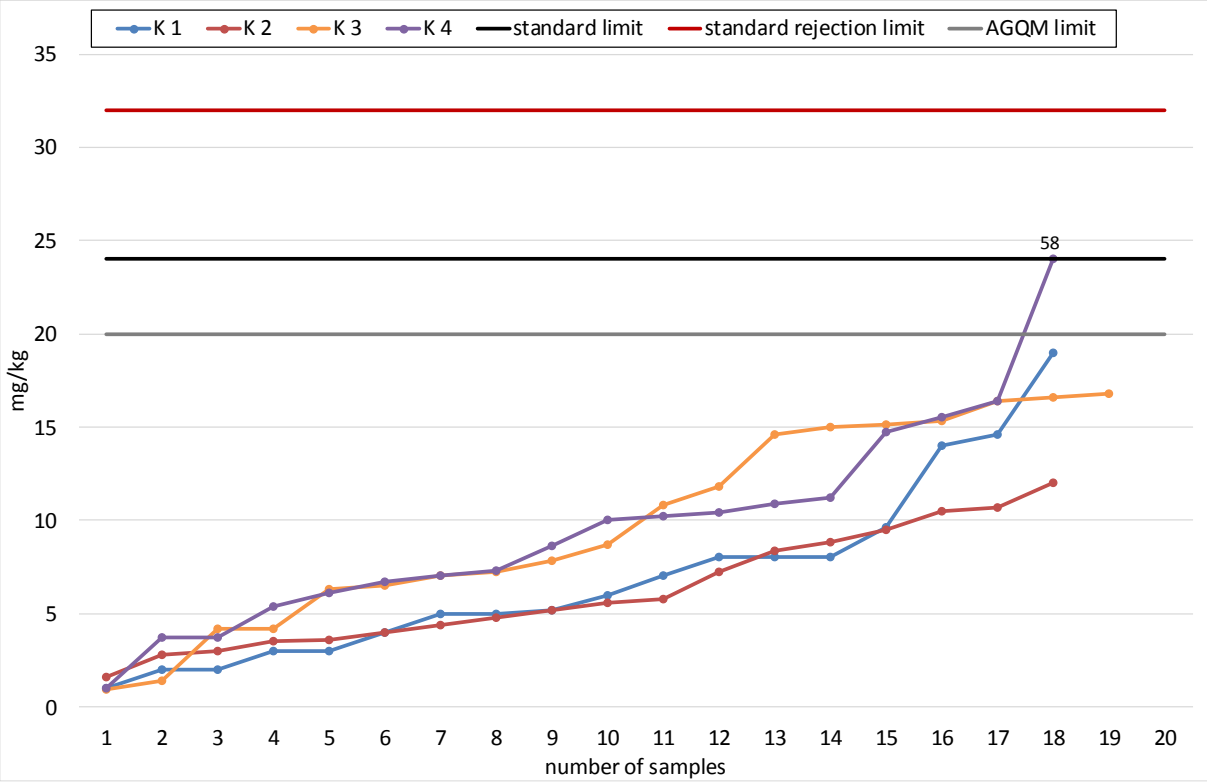

Diagram 5: Total contamination according to DIN EN 12662.

With the exception of one sample all values range within the AGQM limit (see diagram 5). Three members demanded arbitration samples the result of which was in favour of the members in two cases. According to the arbitration sample also, the third sample (58) exceeds the AGQM limit with 24 mg/kg; however, it meets the requirements of DIN EN 14214 and may thus be marketed as standard-conform commodity though not as AGQM product.

3.6 Oxidation Stability

Test method: DIN EN 14112:2003
Limit of DIN EN 14214:2012: ≥ 8 h
Minimum rejection limit: 6.6 h

The oxidation stability of Biodiesel is the measure for the resilience against oxidative processes. Test method is EN 14112, the so-called 'Rancimat test" when a constant stream of air is led through a sample at high temperature. When all antioxidants are used up, volatile oxidation products form which increase the conductivity in the measurement cell. The period until oxidation products are detected is called induction time. The limit for the oxidation stability of DIN EN 14214:2010 was raised from 6 to 8 hours when DIN EN 14214: 2012 came into force.

Especially Biodiesel with a high proportion of polyunsaturated fatty acid methyl esters is – due to their chemical structure – more prone to oxidative processes since the double bonds form peroxides when reacting with oxygen. Subsequent reactions may cause chain fracture, formation of short-chain carbon acids and polymer structures. Plugging of fuel filters, corrosion and deposits in fuel-containing components are possible consequences. Vegetable oils contain natural antioxidants like tocopherols which slow down the ageing process. Synthetic stabilizers are used in addition. 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.

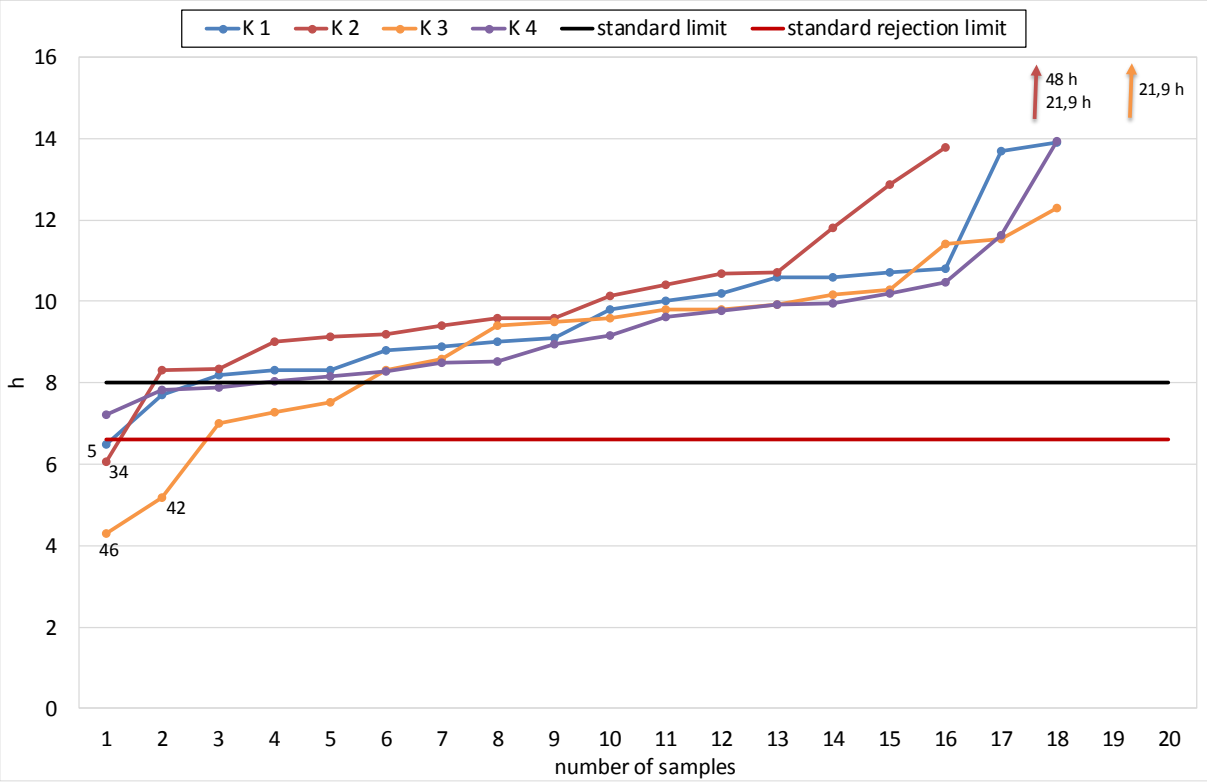

Diagram 6: Oxidation Stability according to DN EN 14112.

The test result in diagram 6 illustrates that for the majority of AGQM members the increased requirements for the oxidation stability do not pose a problem. With >48 h und 21,9 h, some samples are even way above the required 8 h. However, samples 5, 34, and 42 fall below the rejection limit of 6,6 h with values between 6,5 and 5,2 h. Since according to 10th BImSchV, DIN EN 14214:2010 with a limit of 6 h and a rejection limit of 4,9 h still applies in Germany, those products may not be marketed as AGQM commodity but they are standard-conform. Only sample 46 falls below the legal limit with an oxidation stability of 4,3 h and must not be marketed.

3.7 Acid Number

Test method: DIN EN 14104:2003

Limit of DIN EN 14214:2012: ≤ 0,5 mg KOH/g

Maximum rejection limit: 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. However, fatty acids are weak acids and thus only little corrosive. An impact on metal components can yet not be ruled out. But also residues of inorganic acids used for washing and short-chain carbon acids (e.g. formic acid, acetic acid), which form during the ageing of Biodiesel and have a stronger corrosive effect, may contribute to the acid number.

Alkali metal soaps form in a side reaction of the transesterification process when free fatty acids of the raw materials react with the catalyst and by soaping of the fats. They are removed from the product by physical separation. By washing with inorganic acids the small residual soap contents are split and the forming free acids thus remain in the Biodiesel.

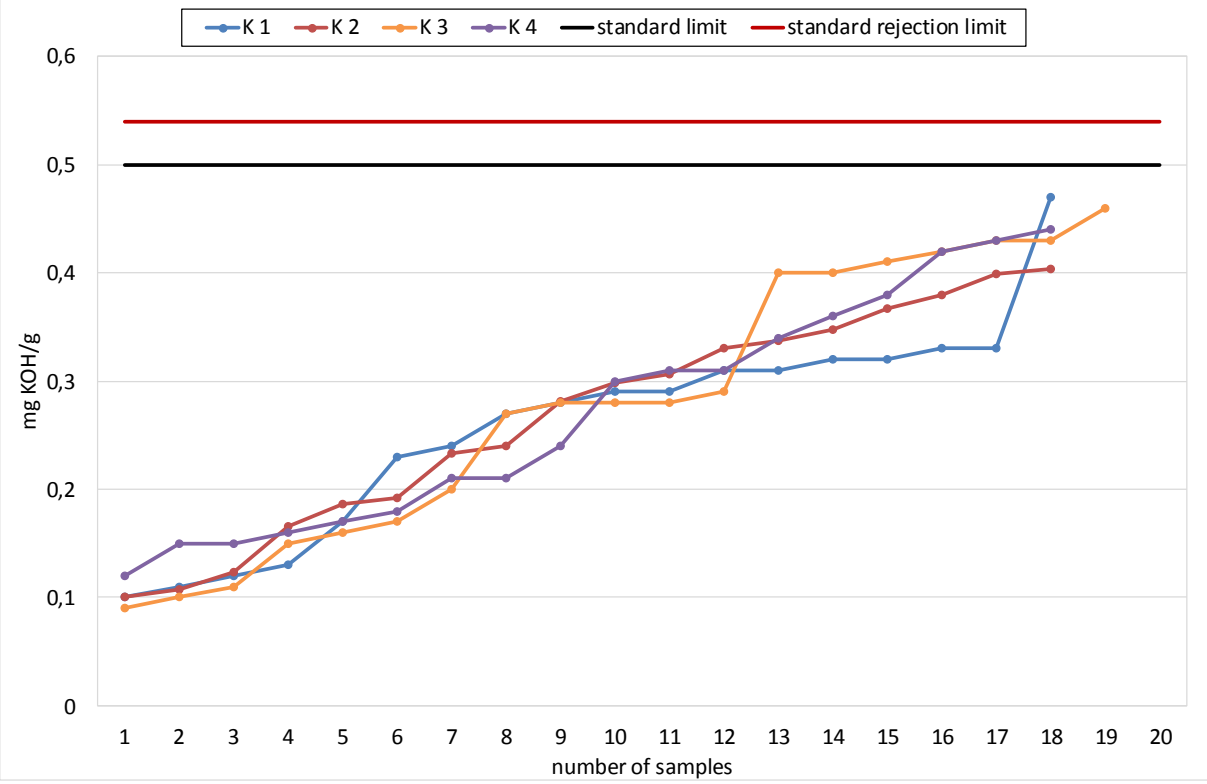

Diagram 7: Acid Number according to DIN EN 14104.

Diagram 7 shows the measurements for the acid number. All samples are below the standard limit (0,5 mg KOH/g). During the storage of FAME the acid number can rise when ageing processes (primarily oxidation) cause ester cleavage and the formation of short-chain carbon acids. However, this effect can hardly be observed under normal storage conditions.

3.8 Iodine Number

Test method: DIN EN 14111:2003
Limit of DIN EN 14214:2012: 120 g iodine/100g
Maximum rejection limit: 123 g iodine/100g

Test method: DIN EN 16300:2012
Limit of DIN EN 14214:2012: 120 g iodine /100g
Maximum rejection limit: 124 g iodine /100g

The iodine number is a measure for the proportion of double bonds in the fatty acids found in fats and oils and in Biodiesel. It varies dependent on the raw material used. There are two different methods for its determination: on the one hand wet chemical determination according to DIN 14111; on the other hand arithmetical determination based on the fatty acid profile measured by gas chromatography according to DIN EN 16300. The result is given in g iodine/100 g of Biodiesel.

Since unsaturated fatty acids are more prone to oxidative reactions, it applies that the Biodiesel stability decreases with the rising number of double bonds thus also rising iodine consumption. Therefore, apart from the oxidation stability, the iodine number is an indication for the stability of Biodiesel.

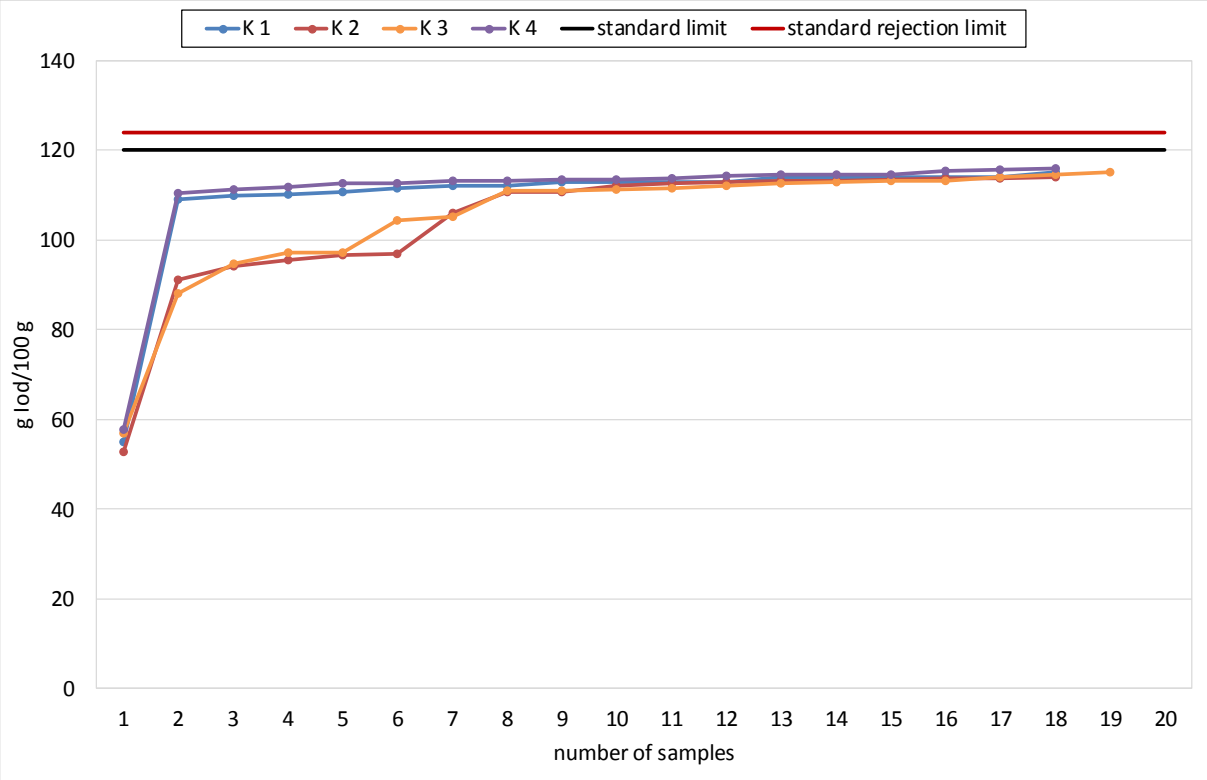

Diagram 8: Iodine Number according to DIN EN 16300 (determined from the methyl ester profile).

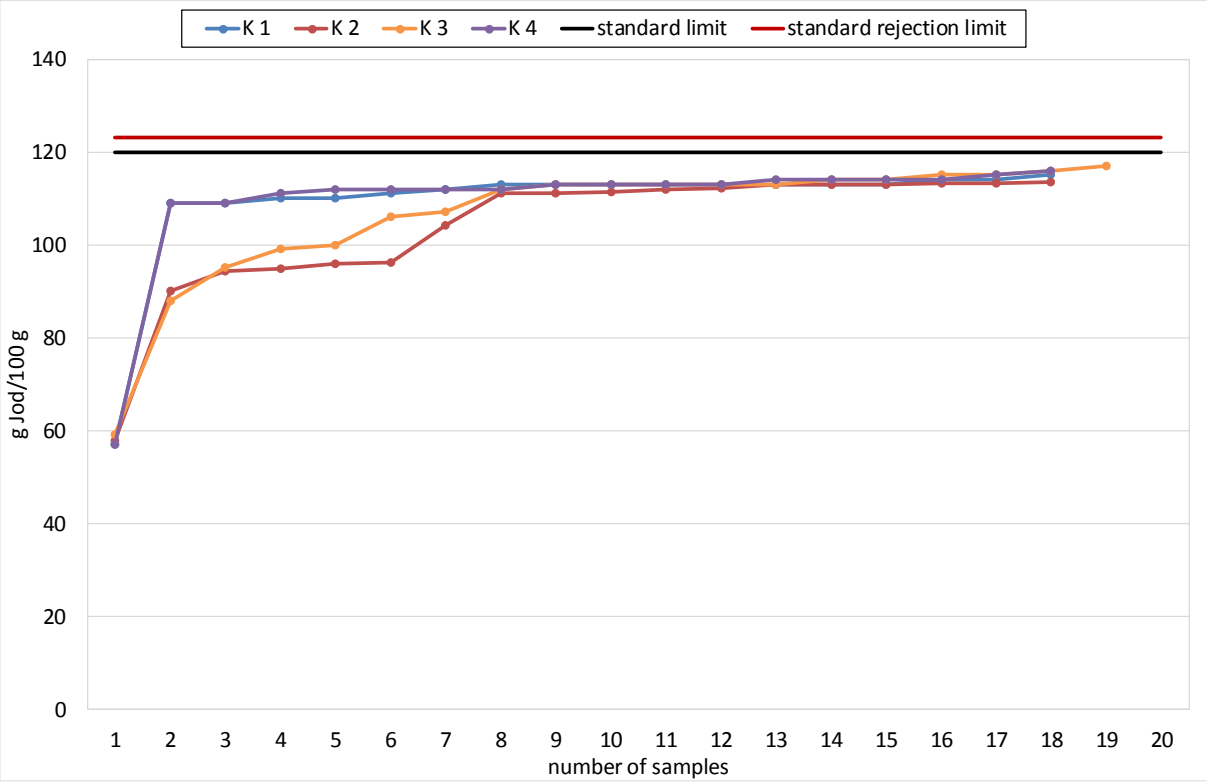

Diagram 9: Iodine Number according to DIN EN 14111 (titrated).

The results of the two test methods for the iodine number (arithmetical determination from the methyl ester composition and titrated) illustrated in diagrams 8 and 9 do not show any difference worth mentioning. All tested samples fulfil the requirements of DIN EN 14214:2012. In K2 and K3 partially lower acid numbers were measured which can be ascribed to the use of raw materials with a higher saturation level. In the summer months this is not a problem due to the lower requirements to the cold properties. Some samples show an iodine number of <60 g iodine/ 100g which can be explained by the raw material used (e.g. used cooking oil or palm oil).

3.9 Glycerides / Free Glycerol

Test method: DIN EN 14105:2003-10
Test method: DIN EN 14105:2011-07

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 adjusts in any case. Glycerides can only be completely removed by distillation. Upon publication of DIN EN 14214:2012 the test method was restructured and the precision of the method improved.

3.9.1 Monoglycerides

Limit of DIN EN 14214:2012: ≤ 0,70 % (w/w)
Maximum rejection limit: 0,82 % (w/w)

With 0,7 % (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.

A large content of monoglycerides can be the cause for coking and deposits in the injector system. In addition, especially saturated monoglycerides have a relatively high melting point which already leads to precipitation at temperatures above the Cloud Point and is considered one of the main causes for bad cold properties and filter plugging.

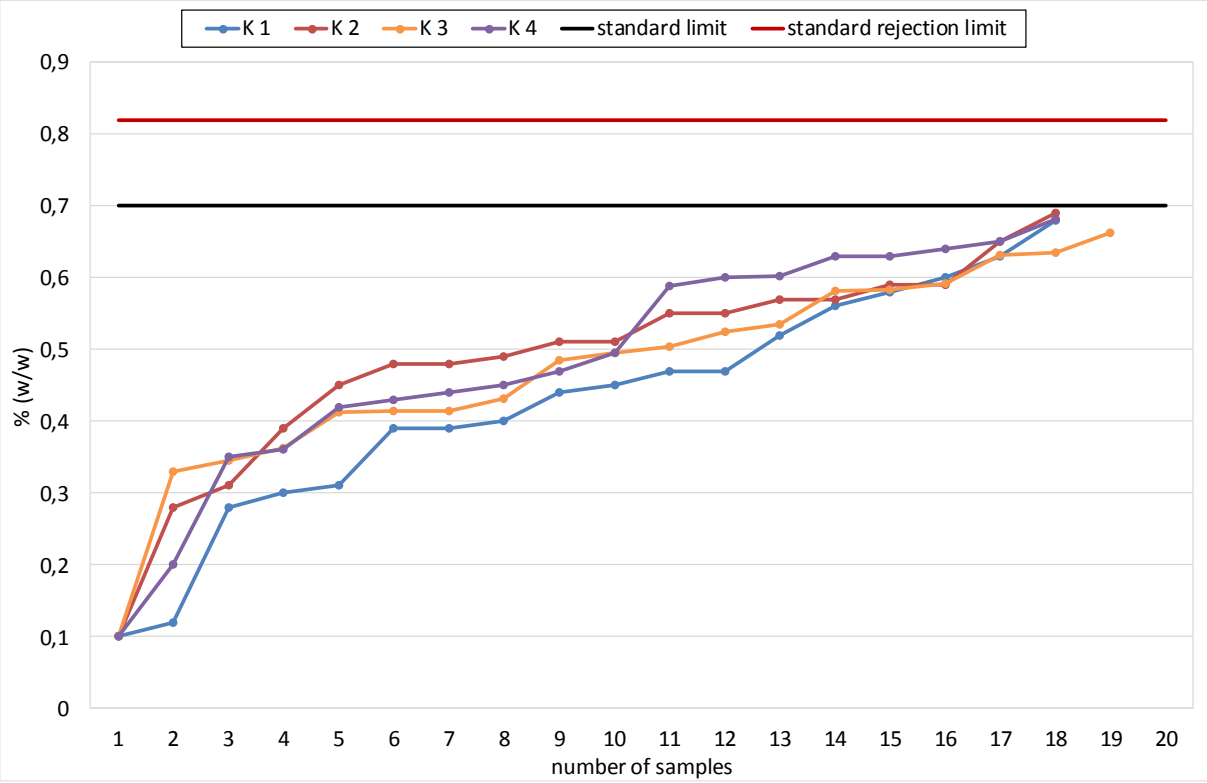

Diagram 1: Monoglycerides according to DIN EN 14105.

Diagram 10 shows the measurements for monoglycerides. All tested samples fulfil the requirements of the standard and fall below the limit of 0,7 % (w/w).

3.9.2 Diglycerides

Limit of DIN EN 14214:2012: ≤ 0,2 % (w/w)

Maximum rejection limit: 0,24 % (w/w)

Due to their high boiling points, diglycerides are not fully combusted. Thus coking in the injector system and the cylinder can be caused. The limit for the content of diglycerides is 0,2 % (w/w).

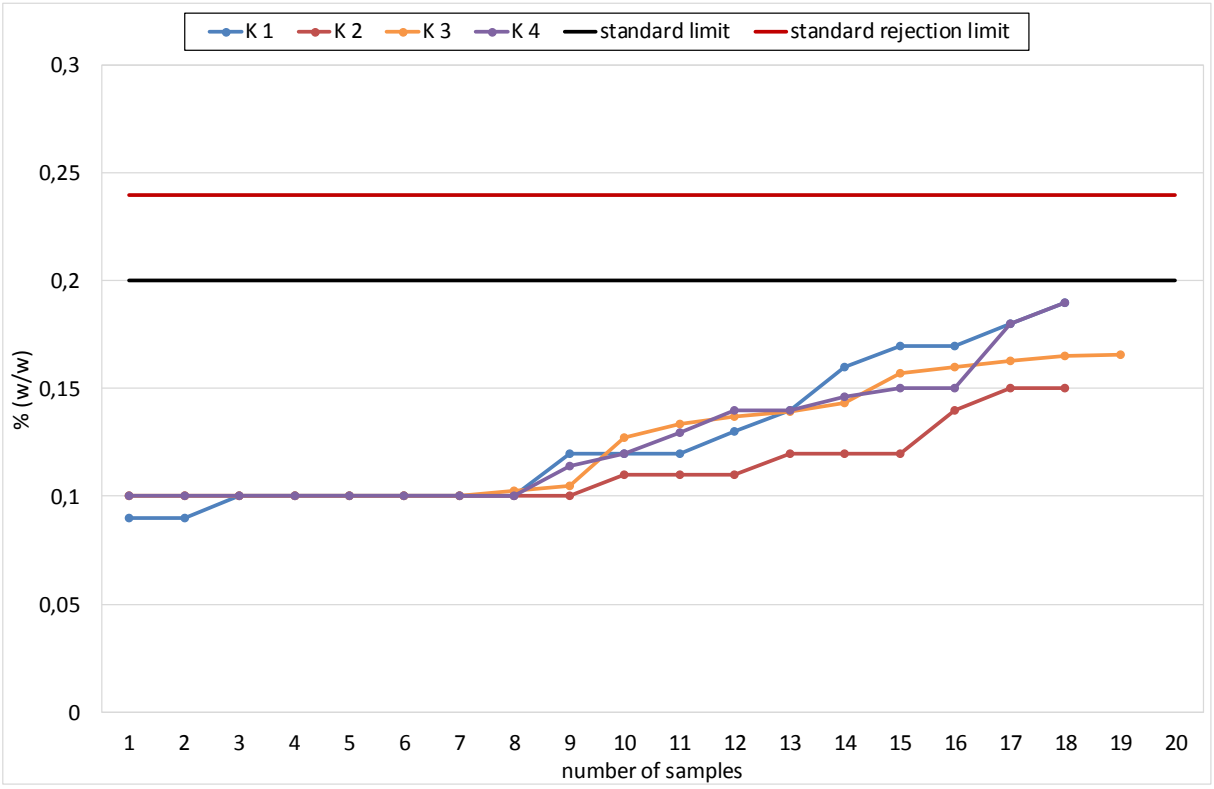

Diagram 11: Diglycerides according to DIN EN 14105.

Diagram 11 shows the measurements for the content of diglycerides. All values are below the limit of 0,2 % (w/w).

3.9.3 Triglycerides

Limit of DIN EN 14214:2012: ≤ 0,2 % (w/w)

Maximum rejection limit.: 0,27 % (w/w)

The high boiling points and low cetane numbers of triglycerides lead to incomplete combustion and may thus also cause coking in the injector system and the cylinder. In addition, triglycerides have a high viscosity which may be the reason for increased wear of the injector system. High contents of triglycerides in combination with low contents of mono and diglycerides are an indication for mixtures of Biodiesel with oils or fats (e.g. in the logistics chain).

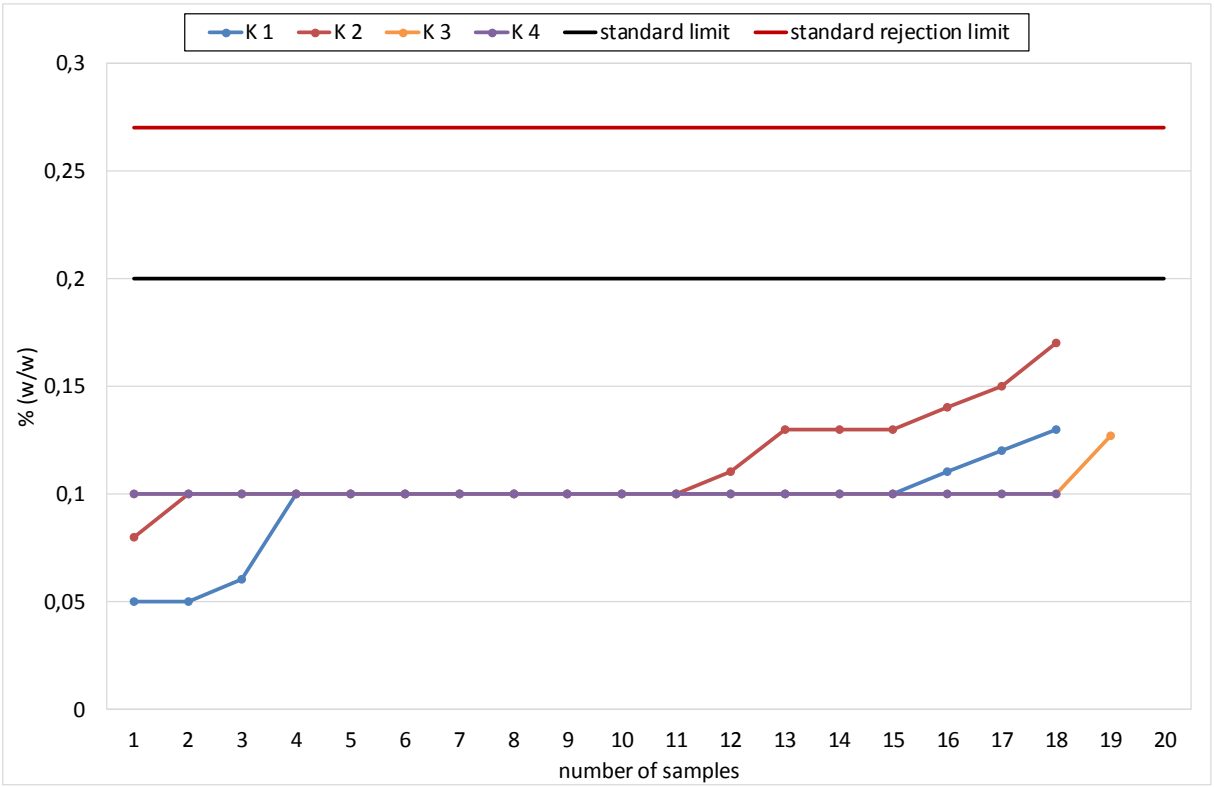

Diagram 12: Triglycerides according to DIN EN 14105.

Diagram 12 shows the measuring results of the triglyceride content. All tested samples clearly fall below the limit.

3.9.4 Free Glycerol

Limit of DIN EN 14214:2012: ≤ 0,02 % (w/w)

Maximum rejection limit: 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.

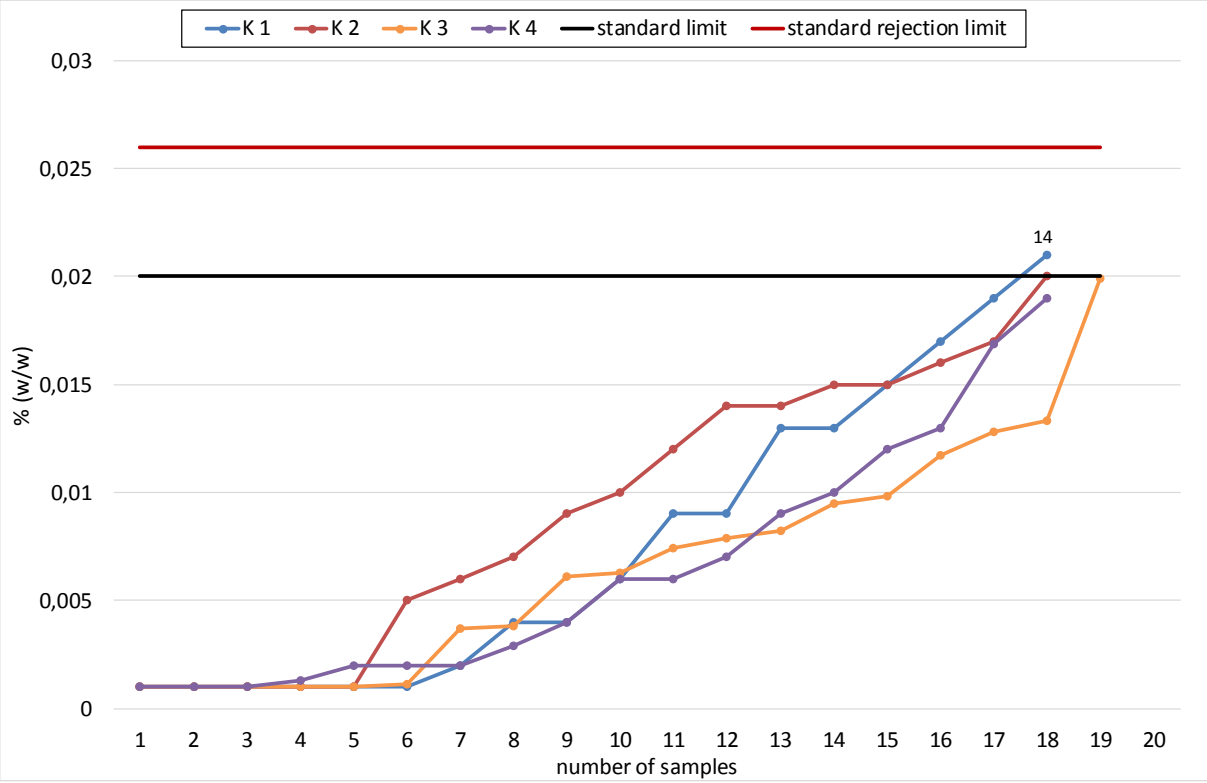

Diagram 2: Free Glycerol according to DIN EN 14105.

As can be seen from diagram 13 in K1 only sample 14 exceeds the limit for the content of free glycerol with 0,021 % (w/w). However, the value is within the rejection limit. The member concerned commented that the washer had had a technical defect which was repaired.

3.10 Alkali Metals: Sodium and Potassium

Test method: DIN EN 14538:2006

Limit of DIN EN 14214:2012: ≤ 5 mg/kg

Maximum rejection limit: 6,1 mg/kg

For the production of Biodiesel sodium and potassium hydroxides are used as catalysts. Their residues in Biodiesel are often present as soaps which were not completely removed during washing. On the one hand soaps can cause filter plugging and clogging of injectors and nozzle needles. On the other hand alkali metals are also associated with ash formation. Sodium as well as potassium deposit on the surface of particulate filters and oxidising catalytic converters and thus reduce the effectiveness and service life of the systems.

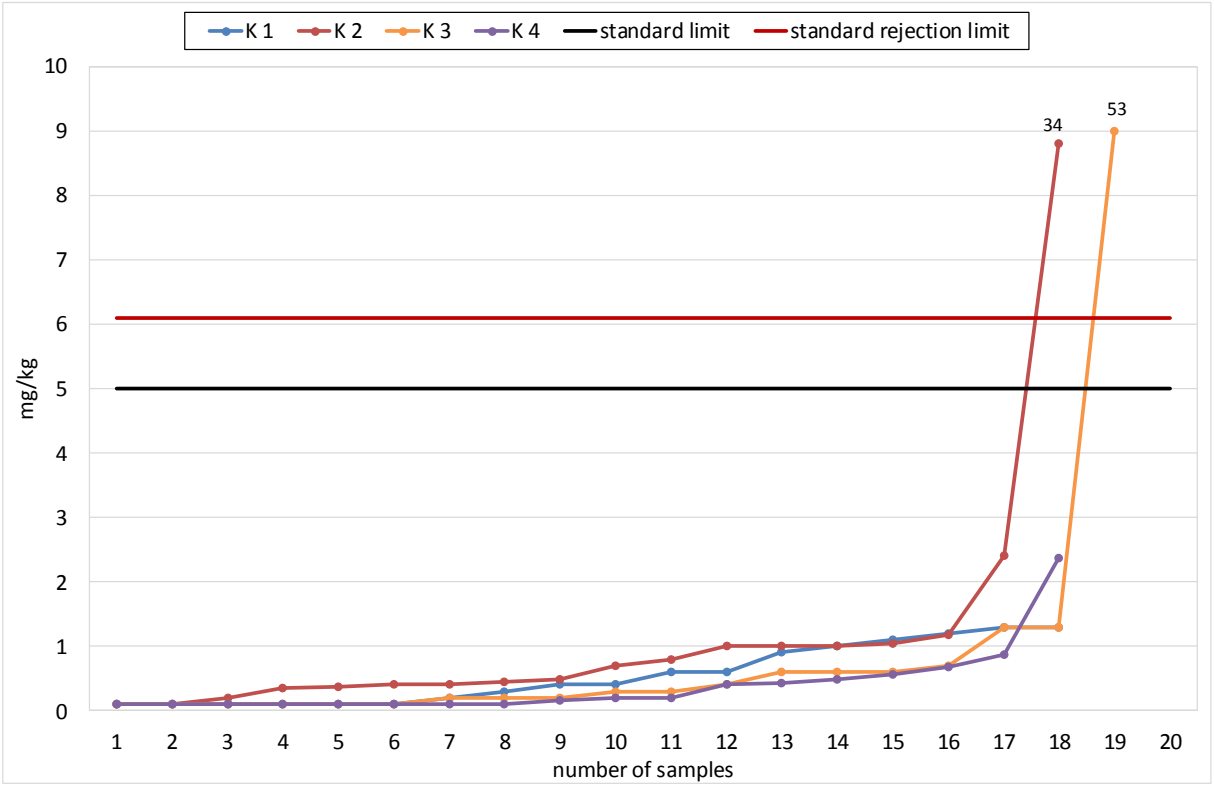

Diagram 3: Sum of Alkali Metals Sodium and Potassium according to DIN EN 14538.

Diagram 14 shows the sum of the alkali metals sodium and potassium. The majority of samples show an alkali content of way below the limit. 78 % of the measured values are below 1 mg/kg. Samples 34 and 53 both belonging to the same member show massive limit violations with 8,8

and 9,0 mg/kg. Upon inspection of the individual values for sodium and potassium it is noticeable that the potassium content of these samples is very high which is due to potassium used as catalyst.

3.11 Earth Alkali Metals: Calcium and Magnesium

Test method: DIN EN 14538:2006
Limit of DIN EN 14214:2010/2012: ≤ 5 mg/kg
Maximum rejection limit: 6,1 mg/kg

Earth alkali metals calcium and magnesium are either introduced into the process by the 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. They can cause filter plugging and clogging of injector pumps. The use of softened water can reduce the ingress of earth alkali metals into Biodiesel.

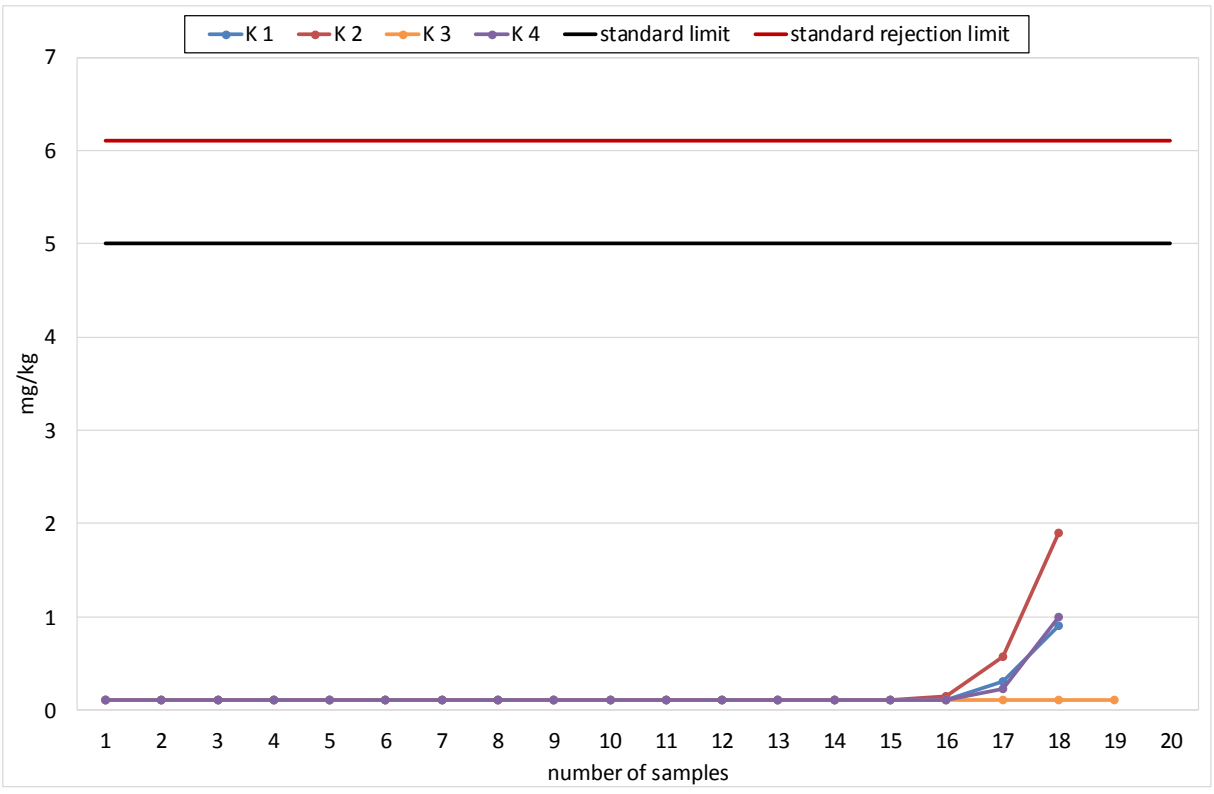

Diagram 4: Sum of Earth Alkali metals Calcium and Magnesium according to DIN EN 14538.

The sum of the earth alkali content given in diagram 15 does not reach the limit in any case. Almost all values are below the determination limit of 1 mg/kg as stipulated by the standard.

3.12 Phosphorus Content

Test method: DIN EN 14107:2003
Limit of DIN EN 14214:2012: ≤ 4 mg/kg
Maximum rejection limit: 4,5 mg/kg

Phosphorus is a catalyst poison which can disrupt the effect of exhaust gas after-treatment systems irreversibly. Already small phosphorus contents may lead to long-term impact during continuous operation. The phosphorus content must already be considered when the raw material is selected or be reduced to low residual contents by a refining process. The transesterification process is influenced if the content of phospholipids is too high because phospholipids can work as emulsifiers and thus interfere with the phase separation. Remaining phosphorus residues can be separated from the final product by distillation. Phosphorus is contained in vegetable oils in form of phospholipids as well as in animal fats. There is evidence that the phosphorus content of cold-pressed oils is lower than that of hot-pressed oils.
Phosphorus can also be introduced into Biodiesel during the production process if phosphoric acid is used for the cleavage of soaps. In general however, used phosphoric acid can be well removed from Biodiesel with water.

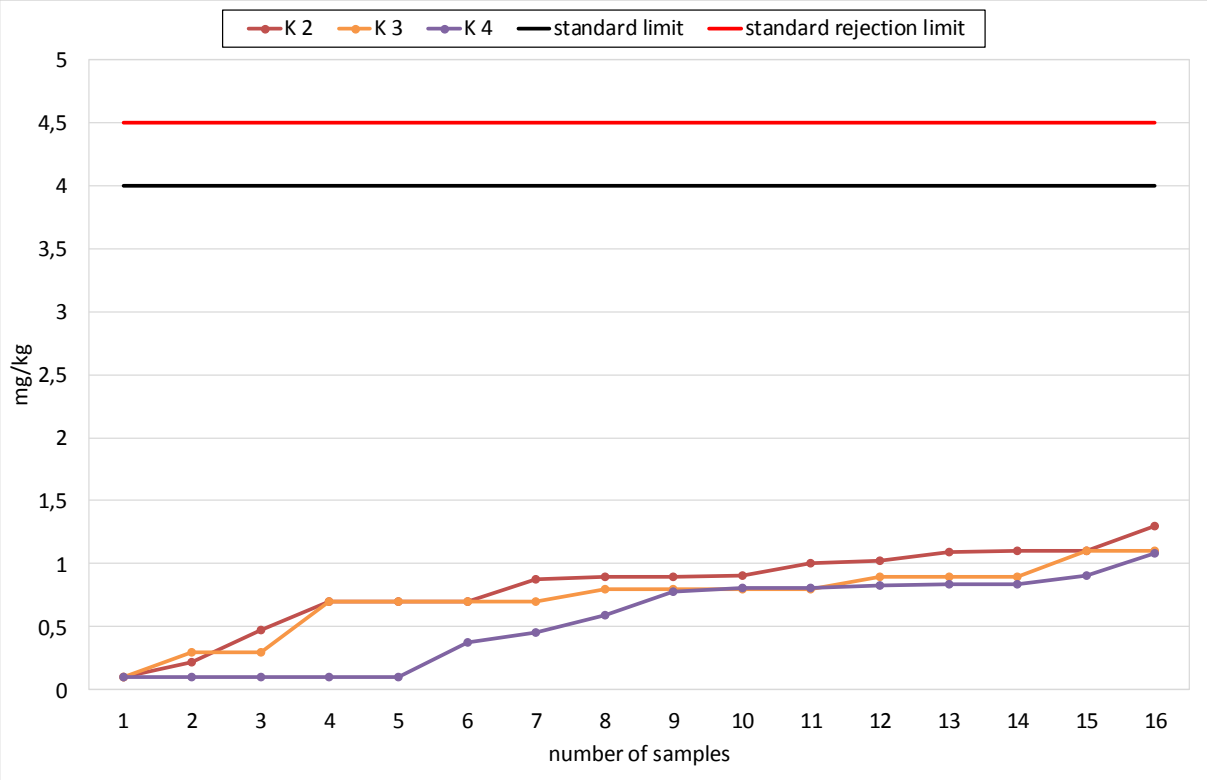

Diagram 16: Phosphorus Content according to DIN EN 14107, K2 to K4.

Diagram 16 shows the results of K2 to K4. Due to technical difficulties there were great deviations between K1 and the values determined in the years before. For that reason K1 is not considered for the evaluation (see diagram 17). Fortunately, the values of the samples of K2 to K4 are all far below the limit of the standard. The maximum limit is 4 mg/kg; however, so far the precision of the method does not allow for any additional tightening of the limit.

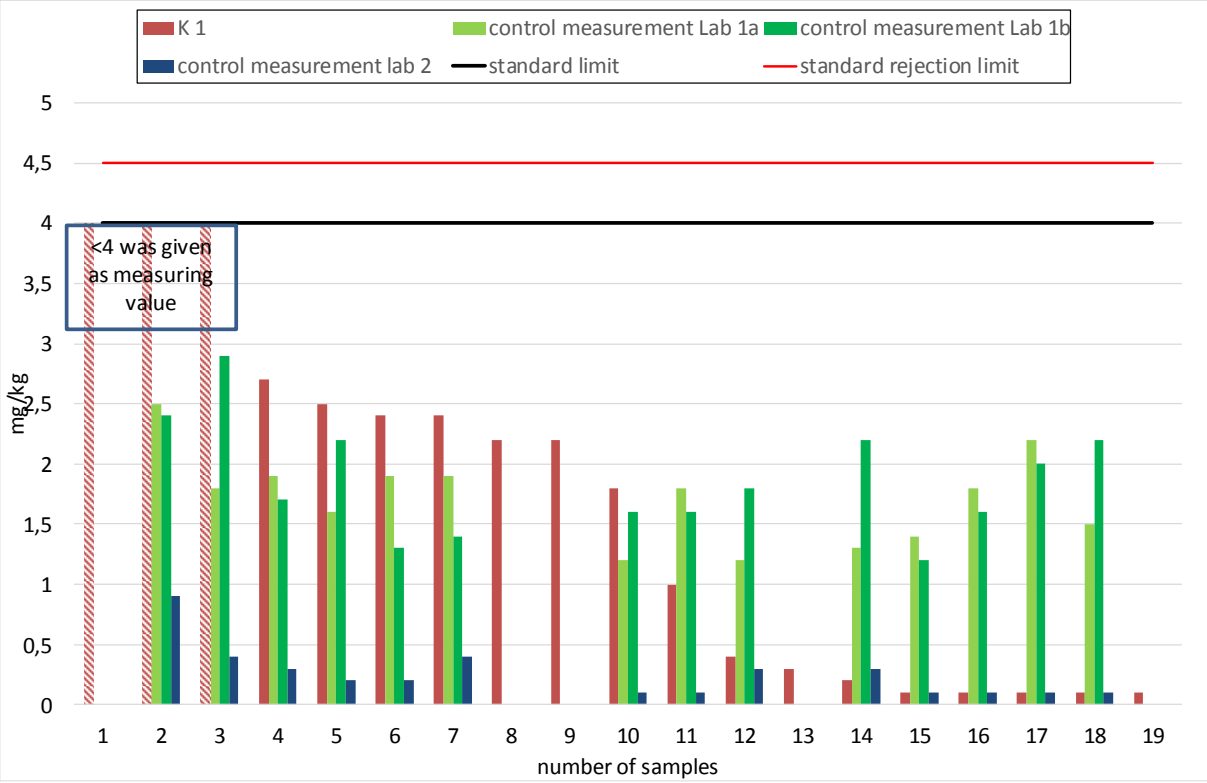

Diagram 17: Phosphorus Content according to DIN EN 14107, K1.

Due to technical problems values of the phosphorus content were measured during K1 which were far above the usual measurements. Therefore, control measurements were commissioned. Diagram 17 shows the phosphorus values measured in K1. The values measured originally and afterwards by laboratories 1 and 2 are both illustrated. The control measurements by laboratory 2 revealed that all values are far below 4 mg/kg and in the usual range.

3.13 Content of Linolenic Acid Methyl Ester

Test method: DIN EN 14103:2011

Limit of DIN EN 14214:2012: ≤ 12,0 % (w/w)

Maximum rejection limit: 14,9 % (w/w)

The content of linolenic acid is determined with the fatty acid profile by gas chromatography. 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). For example, rapeseed oil has a linolenic acid content of 8 to 10 %.

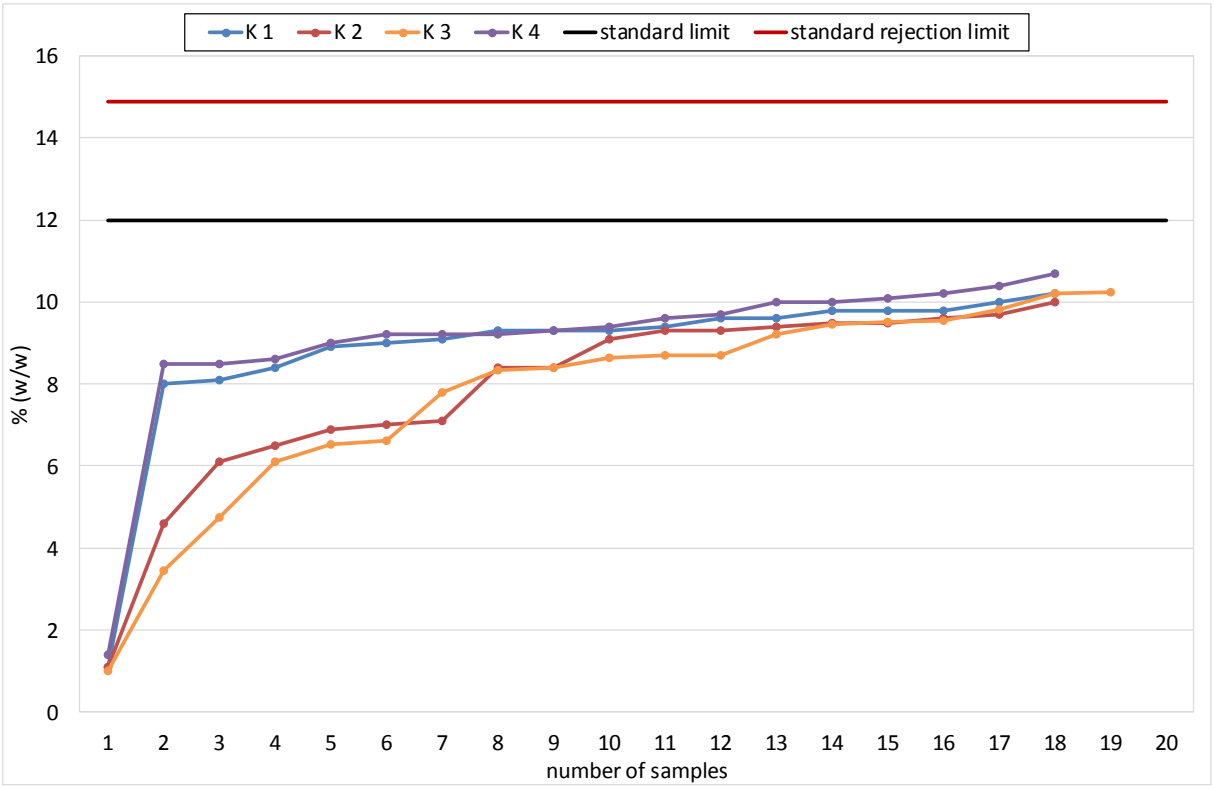

Diagram 18: Content of Linolenic Acid Methyl Ester according to DIN EN 14103.

As shown in diagram 18 all analysed samples fulfil the requirements of DIN 14214:2012. Rapeseed oil as raw material for the production of Biodiesel was at least partly substituted by other oils which is demonstrated by the low content of linolenic acid at a big part of the samples

of summer campaigns K2 and K3. Pure rapeseed oil has a content of linolenic acid between 8 and 10%.[3]

3.14 Cold Filter Plugging Point (CFPP)

Test method: DIN EN 116:1997
Limit according to DIN EN 14214:2012

	Limit	*Rejection Limit*
15 April to 30 September	*0° C*	*1,5 °C*
1 October to 15 November	*-10 °C*	*-7,9 °C*
16 November to 28/29 February	*-20 °C*	*-17,3 °C*
1 March to 14 April	*-10 °C*	*- 7,9 °C*

AGQM Limit: max -20°C from 19 October to 28/29 February

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

For the determination of the CFPP the sample is cooled down in 1-grade-steps and sucked through a filter. The CFPP is reached as soon as the sample is no longer filterable. The distribution of the fatty acid methyl esters – and thus the raw materials used – influence the cold properties of Biodiesel. The freezing points of saturated fatty acid methyl esters are significantly above those of unsaturated compounds which remain liquid even far below 0 °C. The cold properties of Biodiesel can be improved if flow improvers are implemented.

Nowadays Biodiesel is used almost exclusively as blend component for Diesel fuel which is why the use of additivation is often dispensed with. According to the German legal regulations applicable to the cold properties, Biodiesel as blend component only needs to adhere to a CFPP value of -10 °C between 16 November and 28/29 February if the value of - 20 °C as demanded by DIN EN 14214 can be achieved by additivation.

The results of the summer and winter campaigns were depicted separately in two diagrams to enable a more clearly presentation of the determined data.

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

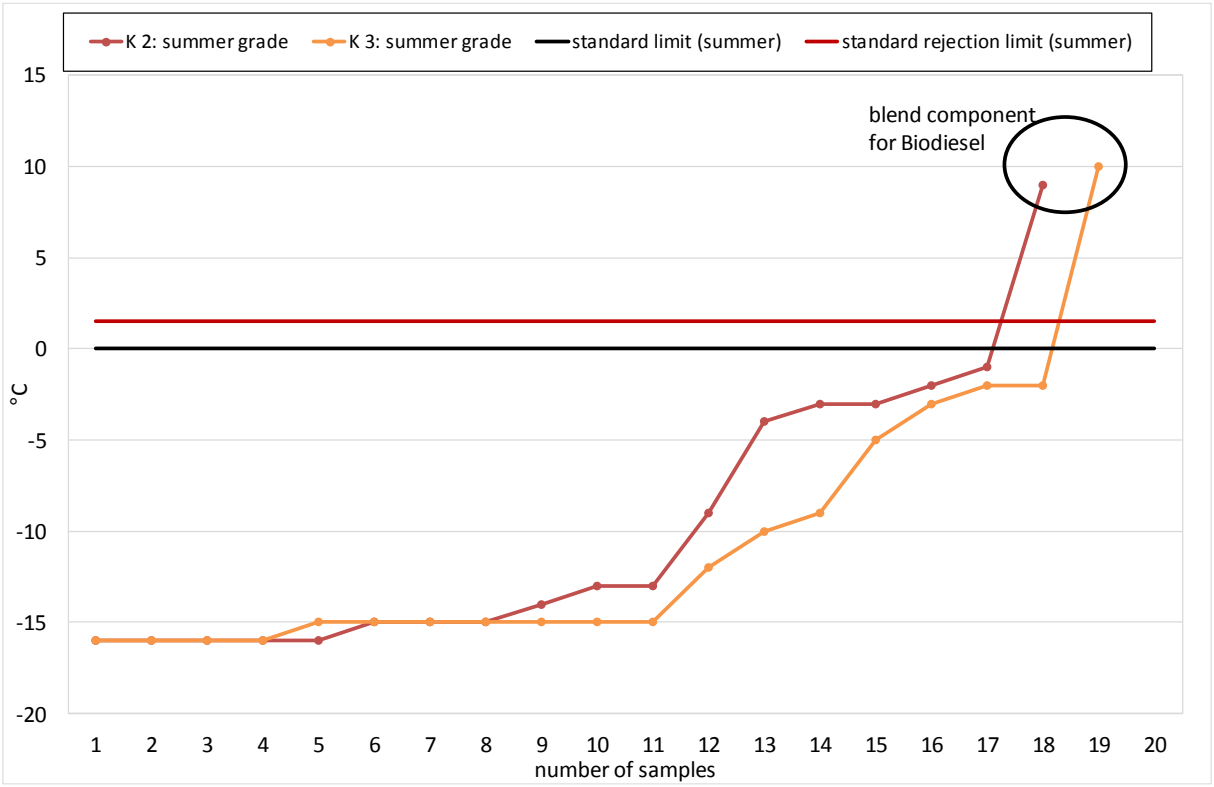

Diagram 19: CFPP (summer grade) according to DIN EN 116.

In K2 the samples were taken during the period May 5 to 16; K3 took place from August 11 to 22 which means that the samples were taken in summer. With the exception of 2, all samples tested fulfil the requirements of the standard (see diagram 19). The two samples circled in diagram 19 are blend components for Biodiesel (as noted in the diagram already) which can only be marketed after adjustment of the quality by mixing with Biodiesel having a correspondingly low CFPP.

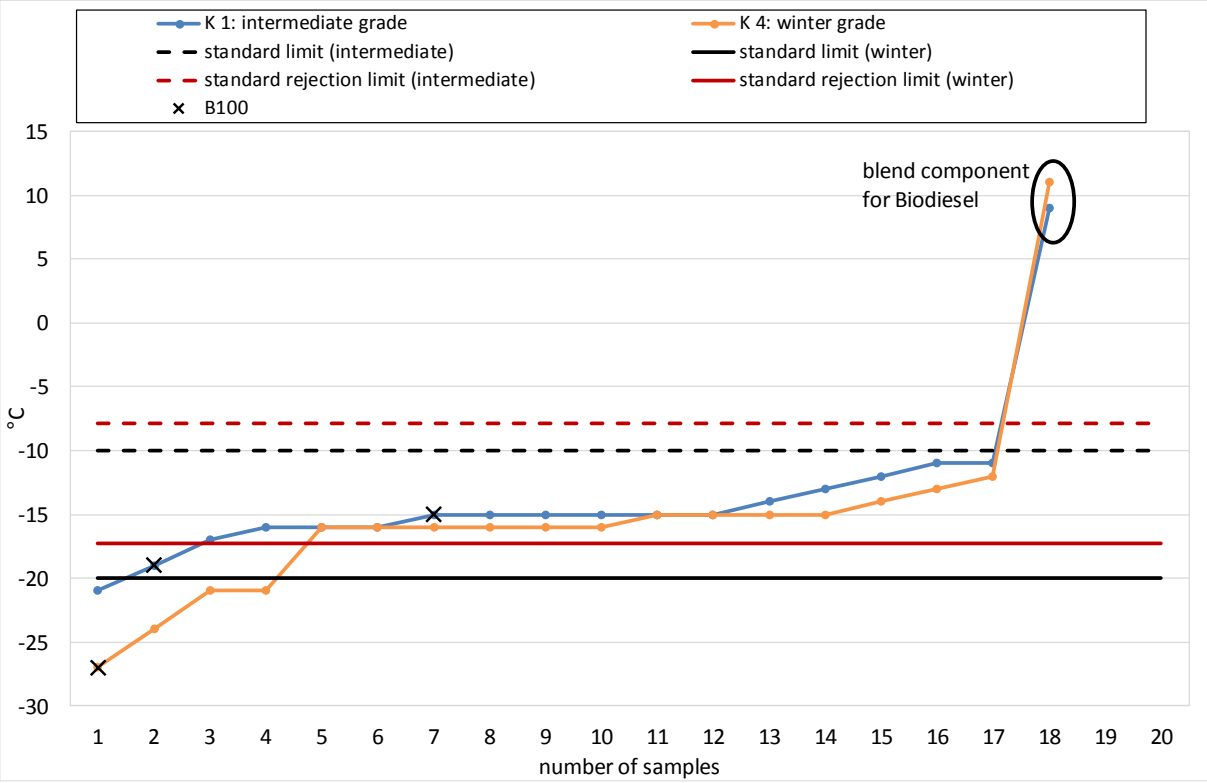

Diagram 5: CFPP (intermediate and winter grades) according to DIN EN 116.

Sampling of K1 took place in the period March 3 to 14; therefore, the samples are intermediate grade fuel. In K4 the samples were taken between November 17 and 28 which means the samples are winter grade fuel.

The limit for pure Biodiesel (B100) in the winter period is -20 °C which is illustrated by an uninterrupted line. In the intermediate period the limit for B100 is -10 °C shown by a dotted line. The limit for Biodiesel used as blend component for Diesel fuel in the winter period is -10 °C as well if a CFPP of -20 °C can be achieved by additivation.

Except three samples marked with an X and two samples circled all samples are blend components for Diesel fuel. Diagram 20 shows that all samples – except the two circled ones – fulfil the requirements.

The two samples circled in diagram 20 are blend components for Biodiesel (as noted in the diagram already). This Biodiesel cannot be marketed directly but has to be admixed to other Biodiesel.

3.15 Cloud Point (CP)

Test method: DIN EN 23015:1994

Limits according to DIN EN 14214:2012:

	Limit	*Rejection Limit:*
15 April to 30 September	*5° C*	*7,4 °C*
1 October to 15 November	*0 ° C*	*2,4 °C*
16 November to 28/29 February	*-3° C*	*-0,6 °C*
1 March to 14 April	*0° C*	*2,4 °C*

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. For pure Biodiesel this parameter is not required yet.

As for the CFPP, the results of the summer and winter campaigns were depicted separately in two diagrams to enable a more clearly presentation.

Diagram 6: Cloud Point (summer grade) according to DIN EN 23015.

As described for parameter CFPP, sampling of K2 and K3 was arranged in the summer time. There are two limit violations. As mentioned above already, those samples are blend components for Biodiesel which will only be marketed subsequent to adaquate blending.

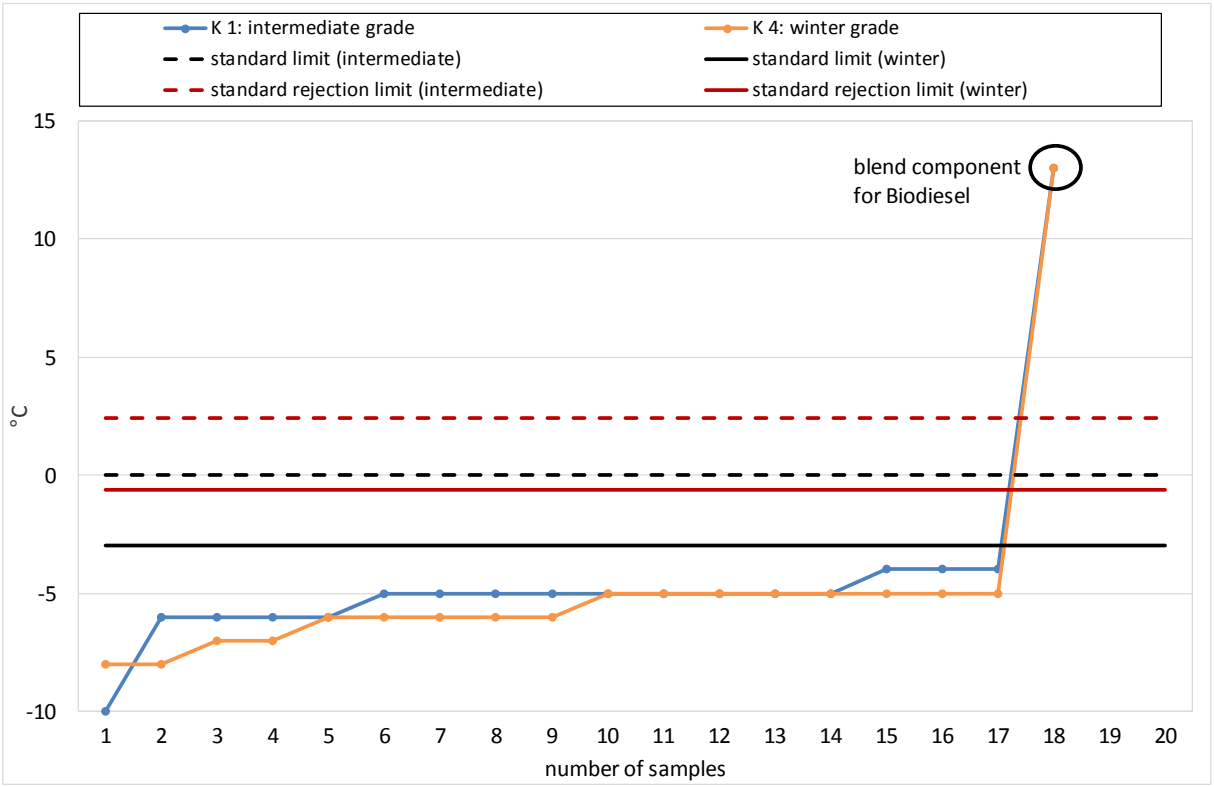

Diagram 7: Cloud Point (intermediate and winter grades) according to DIN EN 23015.

There were also two limit violations in the winter and intermediate periods. Again this is blend fuel for Biodiesel which is not intended for direct marketing.

4 Summary

The result of the four sampling campaigns in 2014 shows that all 73 tested Biodiesel samples except for only 5 fulfil the requirements of DIN EN 14214. Six samples did not reach the AGQM limits. Two of those six samples already show violations of the standard limits. For another 6 samples the exception for Biodiesel from used cooking fats and oils was availed of. Disregarding those six samples of blend fuel for the overall evaluation and considering the relevant precision of the test method, about 93 % of the samples tested fulfil the requirements of DIN EN 14214. The following table 2 serves as an overview of the limit violations.

Table 2: List of samples violating limits.

Parameter	Method	Sample number								
		5	14	17	34	42	46	53	55	58
Fatty Acid Methy Ester Content	DIN EN 14103									
Sulfur Content	DIN ISO 20846									
Water Content	DIN EN ISO 12937									
Total Contamination	DIN EN 12662									
Oxidation Stability 110 °C	DIN EN 14112									
Content of free Glycerol	DIN EN 14105									
Alkali Metals Sodium and Potassium	DIN EN 14538:2006									

Violations of the rejection limit of DIN EN 14214:2012
Violations of AGQM's rejection limit

Samples 34 and 53 (which are samples of the same member) are particularly striking. They violate more than one limit. Obviously the reasons are mistakes in the production process. Meanwhile the member concerned has left AGQM.

For some members the oxidation stability poses problems; there are four values falling below AGQM's limit (samples 5, 34, 42 and 46). Since in Germany DIN EN 14214:2010 is still in force in 2014 due to 10th BImSchV, three of the four members may still market their product as standard-conform. Only sample 46 falls below the standard limit and must not be marketed.

Four of the samples tested violate the limit for water content. Samples 42, 53 and 55 cannot fulfil AGQM's more stringent requirements. The products concerned may be marketed despite violating AGQM's limit because they still comply with the legal requirements. However, in such a case members are not allowed to declare their Biodiesel as AGQM-conform product. Sample 34, however, violates the standard limit and may not be marketed.

There is one violation of the limit for total contamination. Sample 58 cannot fulfil AGQM's more stringent requirements but can be marketed as standard conform.

Unannounced sampling to check the product quality of AGQM members is an important element of AGQM's quality management system. So on the one hand compliance with legal regulations can be monitored and on the other hand the companies' internal control is supported. The data compiled over the years form the basis of a database unique in the world for the development of the Biodiesel quality. Therefore, AGQM impressively documents the continuing improvement and optimization of production processes and quality assurance measures in the Biodiesel trade. The result of the four sampling campaigns in 2014 again shows that the products of AGQM members meet very high quality standards.

5 Annex

5.1 Limits and Test Methods

Table 3: Limits and Test Methods for the Parameters tested according to DIN EN 14214:2012

Test Parameter	Method	Year of Publication	Measuring Unit	Standard Limit		Rejection Limits	
				min.	max.	min.	max.
Content of Fatty Acid Methyl Ester	DIN EN 14103	2011	% (w/w)	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	2003	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	2011	% (w/w)	-	12,0	-	14,9
Content of free Glycerol	DIN EN 14105	2011	% (w/w)	-	0,02	-	0,026
Content of Monoglycerides		2011	% (w/w)	-	0,70	-	0,82
Content of Diglycerides		2011	% (w/w)	-	0,20	-	0,24
Content of Triglycerides		2011	% (w/w)	-	0,20	-	0,27
Overall Glyceride Content		2011	% (w/w)	-	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

[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.

CFPP	DIN EN 116	1997	°C	15 April to 30 September 1 October to 15 November 16 November to 28/29 February 1 March to 14 April	0 -10 -20 -10	- - - -	1,5 -7,9 -17,3 -7,9
Cloud Point	DIN EN 23015	1994	°C	15 April to 30 September 1 October to 15 November 16 November to 28/29 February 1 March to 14 April	5 0 -3 0	- - - -	7,4 2,4 -0,6 2,4

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

Test Parameter	Method	Year of Publication	Measuring Unit	AGQM Limits		Rejection 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	1997	°C	19 October to 28/29 February	-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	**A**rbeits**g**emeinschaft **Q**ualitaets**m**anagement Biodiesel e.V.
B7	Short for blended fuel permissible according to DIN EN 590 with a proportion of 7 % Biodiesel
B100	Short for pure Biodiesel
BImSchV	**B**undes-**Im**missions**sch**utz**v**erordnung *(German Federal Emission Protection Directive)*
ca.	circa
CEN	**C**omité **E**uropéen de **N**ormalisation *(European Standardization Committee)*
CFPP	**C**old **F**ilter **P**lugging **P**oint
DIN	**D**eutsches **I**nstitut für Normung *(German Institute for Standardization)*
e.g.	For example
FAM	**F**ach**a**usschuss **M**ineralöl- und Brennstoffnormung (FAM) im DIN
FAME	Fetty Acid Methyl Ester
JWG	**J**oint **w**orking **g**roup
K.F.	Karl Fischer
K1	Campaign 1
K2	Campaign 2
K3	Campaign 3
K4	Campaign 4
QA Committee	Committee for Quality Assurance
QM concept	Quality Management-Concept
TC	**T**echnical **C**ommittee
UCOME	**u**sed **c**ooking **o**il **m**ethyl **e**ster (fatty acid methyl ester from used cooking oils and fats)