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Biodiesel Quality in Germany

AGQM Sampling Campaigns 2011

Introduction

Being the most important fuel based on renewable resources, Biodiesel is a supporting pillar when it comes to achieving the climate protection targets defined by the EU Commission for the traffic sector.

The increasing requirements of DIN EN 14214, the abidance by which is the prerequisite for a trouble-free operation, reflect the change in use from pure fuel to blend component as well as modified engine requirements. At the same time the significance of quality assurance increased. The Arbeitsgemeinschaft Qualitaetsmanagement Biodiesel e.V. (AGQM) was founded with the objective to improve the quality of Biodiesel and to provide producers and traders with an instrument in the form of a quality assurance concept which is suitable to assure the quality and capable to adjust to the constantly changing requirements. Meanwhile, about 90 % of the Biodiesel produced in Germany today are produced according to AGQM's stringent guidelines which in some points even exceed those of the requirements of DIN EN 14214. The aim is to safeguard the high German quality level achieved and to impart the necessary confidence in the product to Biodiesel users.

In Germany, meeting the requirements of DIN EN 14214 is the qualification for the granting of any tax relief and/or the consideration of Biodiesel for the Biofuel Quota. Customs Authorities are thus obliged to make random checks of the Biodiesel quality. Due to the quality assurance measures AGQM members profit from a special privilege: in negotiations with the Federal Ministry of Finance AGQM could achieve that such checks may be forgone if a company regularly (every other month) participates in the sampling and testing by AGQM.

Meanwhile the results of this regular monitoring have created an important and internationally unique data base for the development of the Biodiesel quality in Germany. In 2010 they were first published in a quality report[1] and prove the high quality level of AGQM's members.

Sampling – Execution and Scope

AGQM assigns an accredited and independent test laboratory six times a year to carry out the external monitoring of the production quality on its behalf. Biodiesel is sampled at production sites or trading companies and checked with regard to

[1] http://www.agqm.de/downloads/pdfs/20110530_Herstellerbepr_Final_eng.pdf

meeting the requirements stipulated in the QM concept. Basis for that is DIN EN 14214, although even more stringent limits than those of the standard may apply.

The following parameters are tested:

Parameter	Method
Ester content	DIN EN 14103
Sulphur content	DIN EN ISO 20846 DIN EN ISO 20884
Water content	DIN EN ISO 12937
Total contamination	DIN EN 12662
Oxidation stability	DIN EN 14112
Acid number	DIN EN 14104
Iodine number	DIN EN 14111
Glycerine/Glycerides	DIN EN 14105
Content of Alkali metals (Na + K)	DIN EN 14538
Content of Alkaline earth metals (Ca + Mg)	DIN EN 14538
Phosphorous content	DIN EN 14107
CFPP	DIN EN 116
Fatty acid profile	DIN EN 14103

The individual parameters and their significance are gone into in detail in the leaflet ‚Biodiesel Analytic – Important Parameters and their Meaning'[2].

Sampling and analytics are put out to tender and assigned anew every year. For that only test laboratories are considered which are accredited for Biodiesel analysis and successfully partook in AGQM's annual RRTs.

Additionally to the regular RRTs, the comparison of the analysis results of the external laboratory with the results of their in-house laboratory enables members to check the quality of their own analysis and to make necessary modifications in time.

Evaluation 2011

In 2011, 129 samples of AGQM members were tested in six sampling campaigns (production and trading companies). The campaigns are named K1 to K6. The following table shows the time of sampling.

K 1: February
K 2: March/April
K 3: May
K 4: July
K 5: September
K 6: November/December

[2] http://www.agqm.de/downloads/pdfs/Merkblatt_Analytics_2011.pdf

The following evaluation describes the individual parameters tested; the results are illustrated graphically. The results are anonymous and do not give any indication as to the samples' origin.

For every campaign the results are given in increasing order to illustrate the spread of the results; the individual limits are shown by a red line.

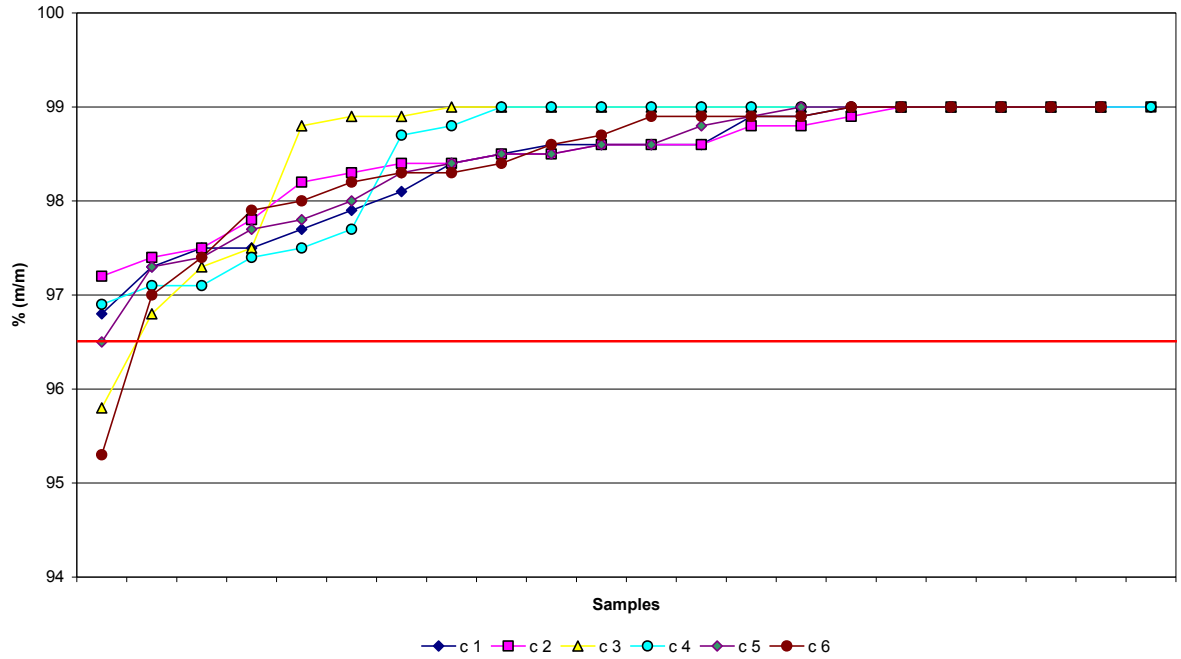
Individual Results

Content of Fatty Acid Methyl Ester (‚FAME')

Test method: DIN EN 14103

Limit DIN EN 14214: ≥ 96.5 % m/m

The content of fatty acid methyl esters – usually abbreviated 'ester content' – is an indication of the degree of transesterification and the purity of the Biodiesel; the higher the value, the better the quality. DIN EN 14214 stipulates a FAME content of at least 96.5 %.



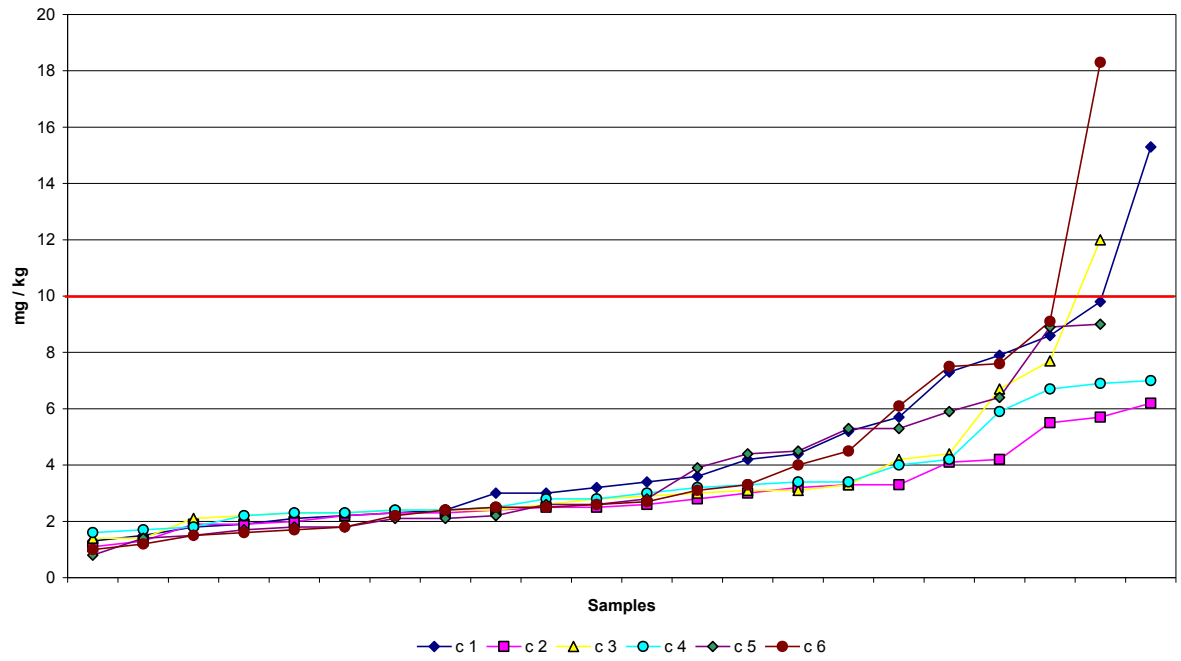
The graph shows that the limit of the standard is observed with the exception of two values. Considering the precision of the test method, all values meet the requirements of DIN EN 14214. Measuring values given as ‚> 99.0 %' are shown in the graph as ester content of 99 %.

Sulphur Content

Test method: DIN EN ISO 20846 / DIN EN ISO 20884

Limit DIN EN 14214: ≤ 10 mg/kg

The following graph shows the sulphur values of the production samples tested.



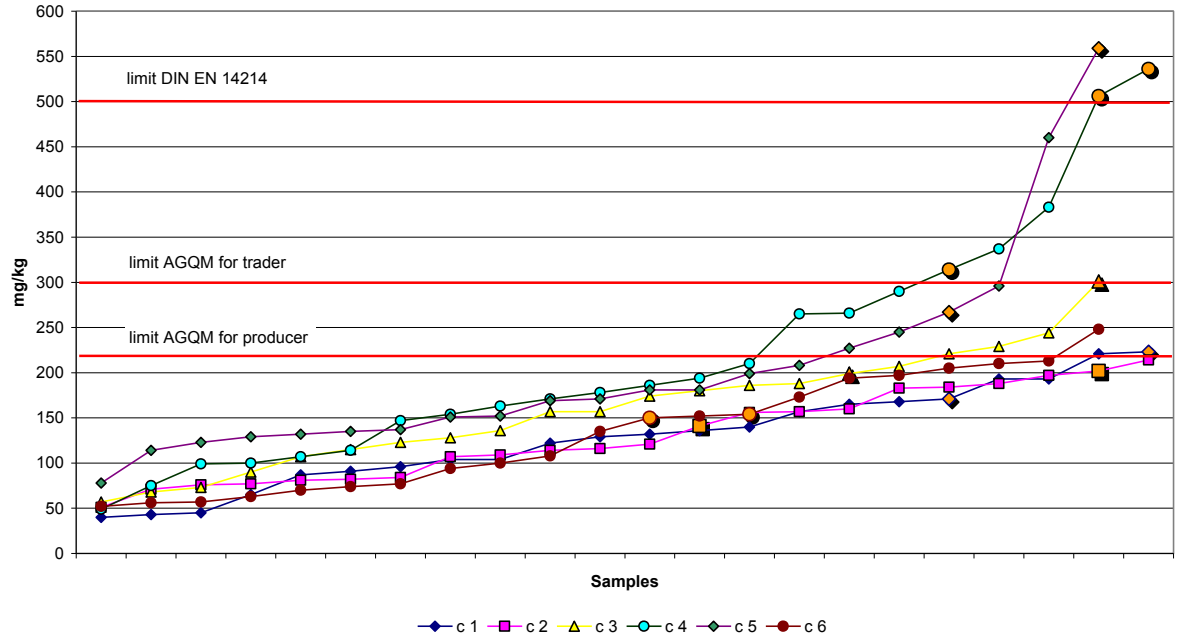
Three samples of the last six campaigns show sulphur values of above the limit. In two cases the cause for that was identified as increased use of sulphuric acid (H_2SO_4) during production, in the third case the cause could not be finally resolved. Appropriate corrective measures were taken.

Water Content

Test method: DIN EN ISO 12937

Limit DIN EN 14214: ≤ 500 mg/kg
Limit AGQM: ≤ 220 mg/kg for production plants
Limit AGQM: ≤ 300 mg/kg for storage facilities/trading companies

For the assessment of the water content two limits must be taken into account: first the maximum content of 500 mg/kg as stipulated by DIN EN 14214 and second the values of AGQM's quality concept defined for producers at 220 mg/kg and 300 mg/kg for storage facilities/trading companies, thus considering the fact that – due to Biodiesel being hygroscopic – the water content rises along the transport chain.



The majority of samples contain less than 200 mg of water/kg which is even significantly below AGQM's stipulation. All results meet the limit of DIN EN 14214 considering the precision of the test method. It is notable that the values of campaigns 4 and 5 are higher than those of the other campaigns and that all those exceeding the AGQM limit of 300 mg water/kg stem from these two campaigns. The reasons for that are the high summery temperatures with increased absolute humidity.

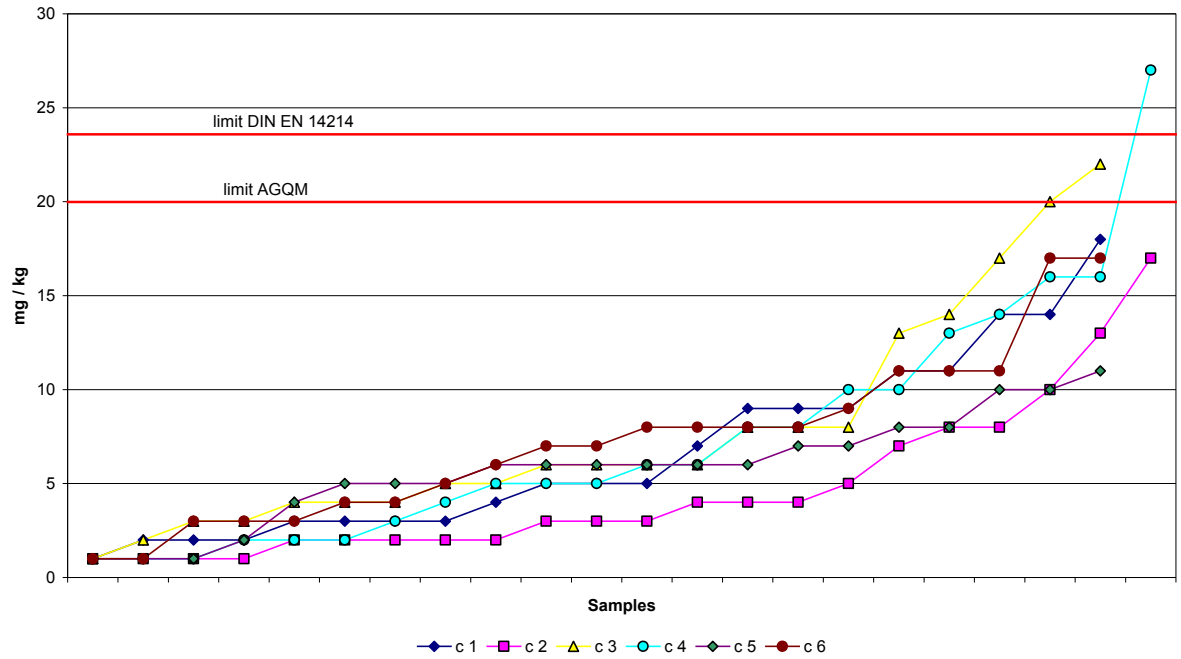
As shown by the individual assessments, this affects primarily trading companies. The results obtained from trading companies are the orange ones in the graph. In contrast to production sites there are many possibilities for water ingress along the logistics chain and thus higher water contents dependent on the environmental circumstances.

Total Contamination

Test method: DIN EN 12662:1998

Limit DIN EN 14214: ≤ 24 mg/kg
Limit AGQM: ≤ 20 mg/kg

Solid impurities, forming the total contamination of Diesel fuels, are time and again cause for queries and failure and are therefore also restricted for Biodiesel. The AGQM limit was reduced to 20 mg/kg which is a more stringent requirement compared to that of DIN EN 14214.



The result of the sampling campaign is pleasing: only two samples exceed AGQM's limit while the majority of samples contains less than 10 mg/kg of 'dirt' by far. Considering the precision of the test method DIN EN 14212 is observed in all cases.

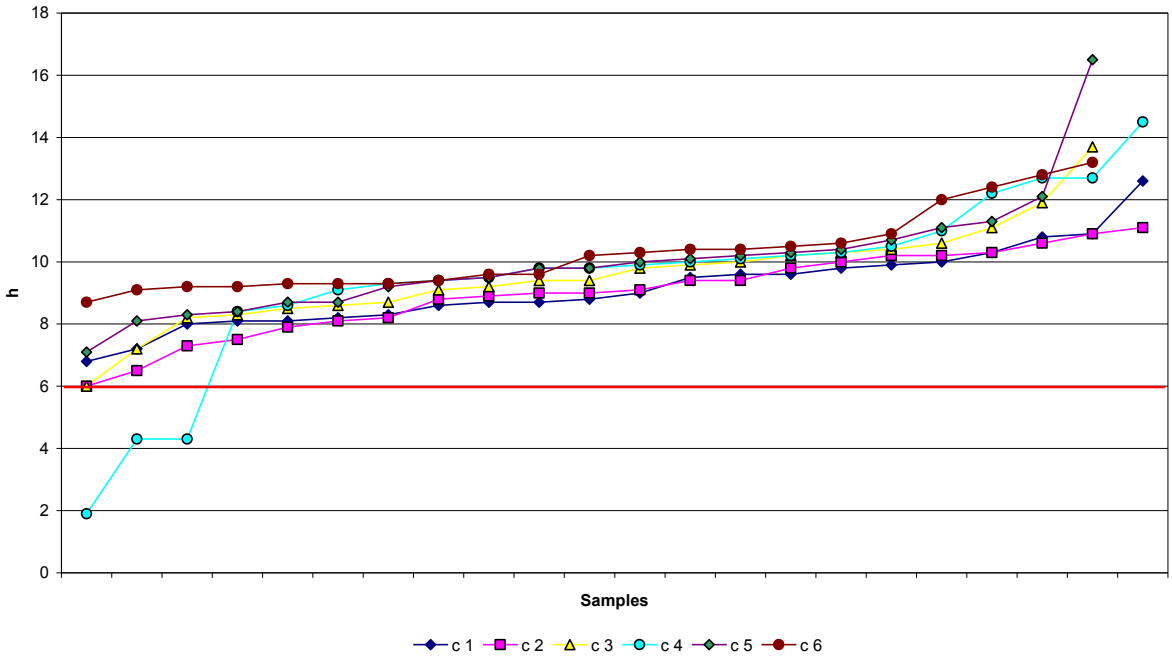
Oxidation Stability

Test method: DIN EN 14112

Limit DIN EN 14214: ≥ 6 h

According to DIN EN 14214, the oxidation stability of Biodiesel, defined by the induction time, must be at least six hours; the increase to eight hours is part of the revision currently underway. Frequently, higher stability is already called for by the mineral oil industry; meanwhile the use of stabilisers is customary and AGQM's recommendation[3] for blend fuels also includes an induction time of eight hours.

[3] http://www.agqm.de/downloads/pdfs///FAME_Blendkomp_final_161110.pdf



The results of the sampling campaigns show that the quality requirement of six hours is met with the exception of three samples and that in most cases even an induction time of eight hours is achieved. In one of the three cases of deviation an unsuitable place of sampling could be verified as cause; the commodity itself was in line with the specification. The problem was solved by relocating the place of sampling.

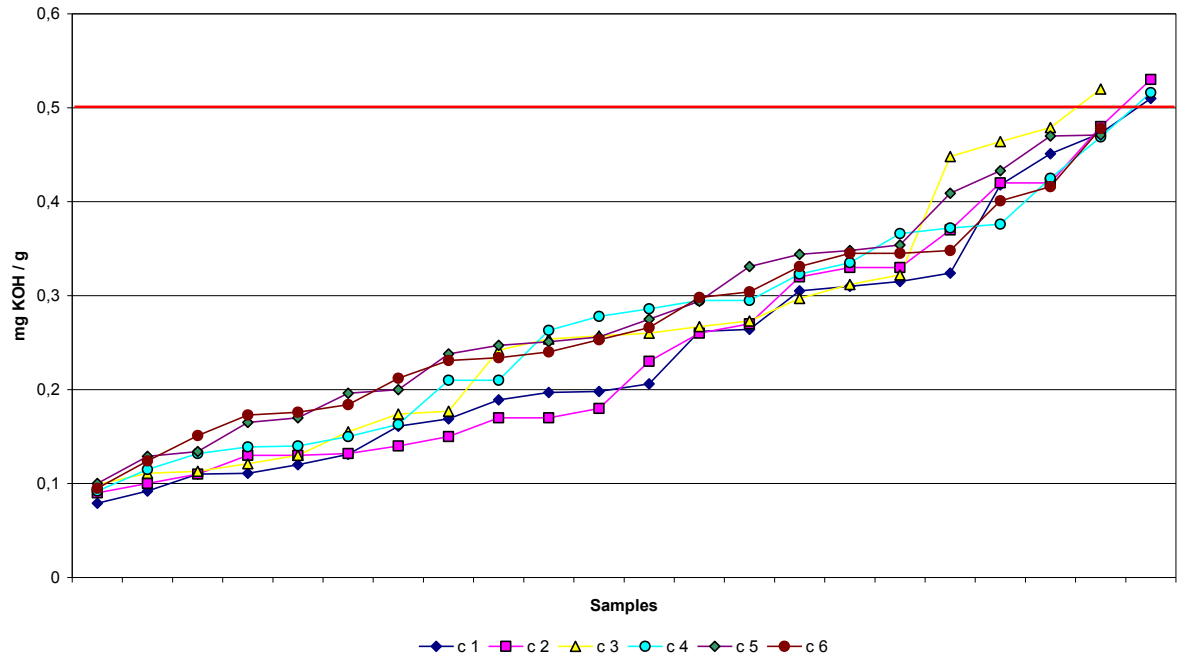
Apart from the fact that all three deviations were detected in campaign 4, no other significant seasonal variations could be found; obviously the good quality is basically achieved due to adequate selection of feedstock and the use of additives.

Acid Number

Test method: DIN EN 14104

Limit DIN EN 14214: ≤ 0,5 mg KOH/g

Free fatty acids in Biodiesel may cause corrosion but they may also form soaps with basic compounds which may lead to gumming and filter plugging. In addition, short-chain carboxylic acids (formic acid, acetic acid) with a potentially stronger corrosive effect may form due to Biodiesel ageing. Therefore, the limit stipulated in DIN EN 14214 is 0.5 mg KOH/g.



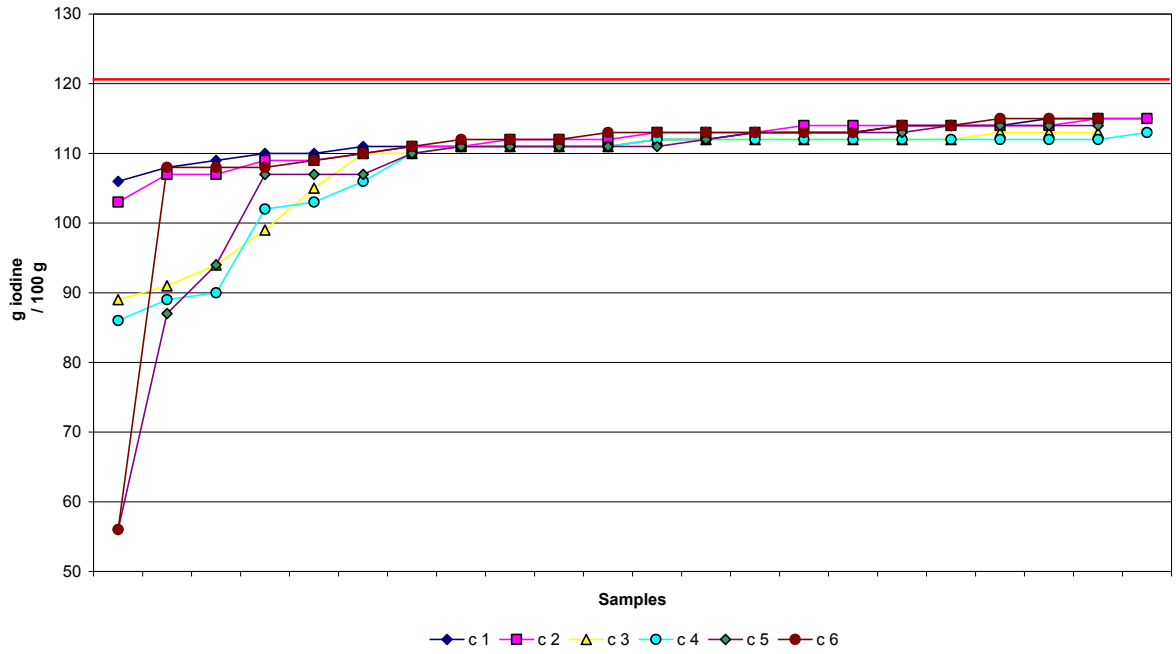
With the exception of four cases the limit of DIN EN 14214 was observed. However, the four exceeding values were so small that with regard to the precision of the test method the standard was observed.

Iodine Number

Test method: DIN EN 14111

Limit DIN EN 14214: 120 g/100g

The Iodine number is a measure for the proportion of unsaturated fatty acids in Biodiesel and is limited to 120 g of iodine/100g by DIN EN 14214. Along with the oxidation stability it is considered an indicator for the stability of Biodiesel.



The graph shows that the iodine number of the majority of samples ranges between 110 and 120; there is no indication for any exceeding of the limit. Campaigns 3 and 4 show significantly lower values for a large number of producers. The reason for that is that due to climate-related requirements in summer (CFPP: 0°C) a limited quantity of palm oil can also be used for the production of Biodiesel, whereas during the winter months rapeseed oil methyl ester and blends with soybean methyl ester can be used almost exclusively. However, the iodine number alone does not allow a safe inference with regard to the feedstock.

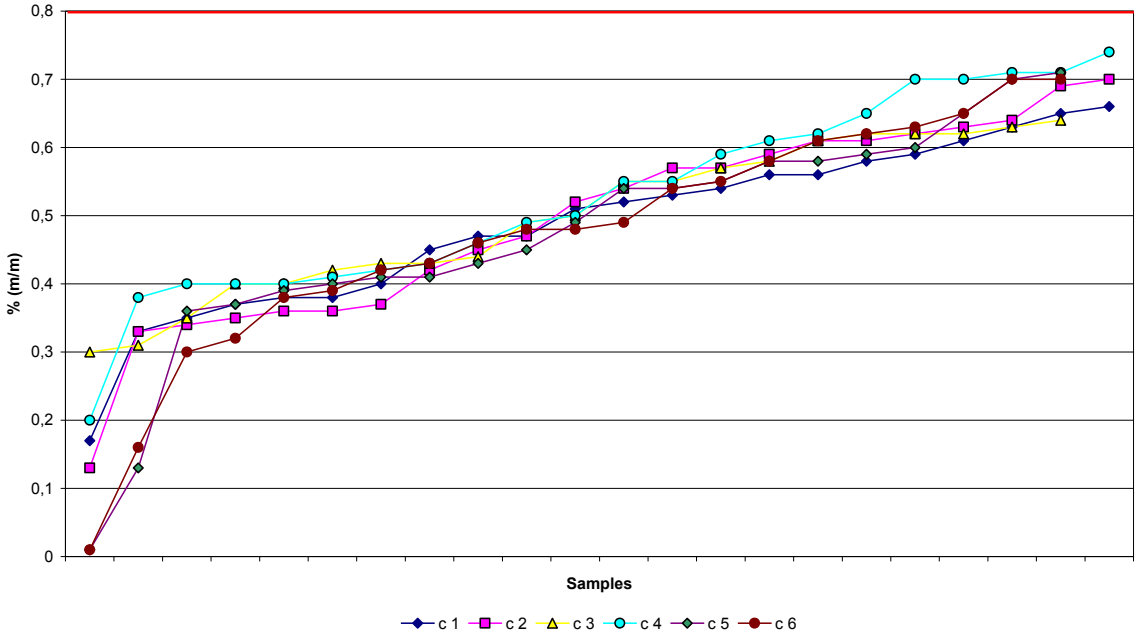
Glycerides / Free Glycerol

Test method: DIN EN 14105

Partial glycerides and Triglycerides are an indication for complete transesterification. Their contents can be influenced by the process conditions; usually they occur in the order triglycerides < diglycerides < monoglycerides because the split-off of the last fatty acid is the slowest transesterification step. High triglyceride concentration, despite correspondingly lower mono and di values, is mostly an indication for contamination with oils and fats e.g. along the logistics chain. The data for the individual components of the sampling campaigns is evaluated as follows:

Monoglycerides

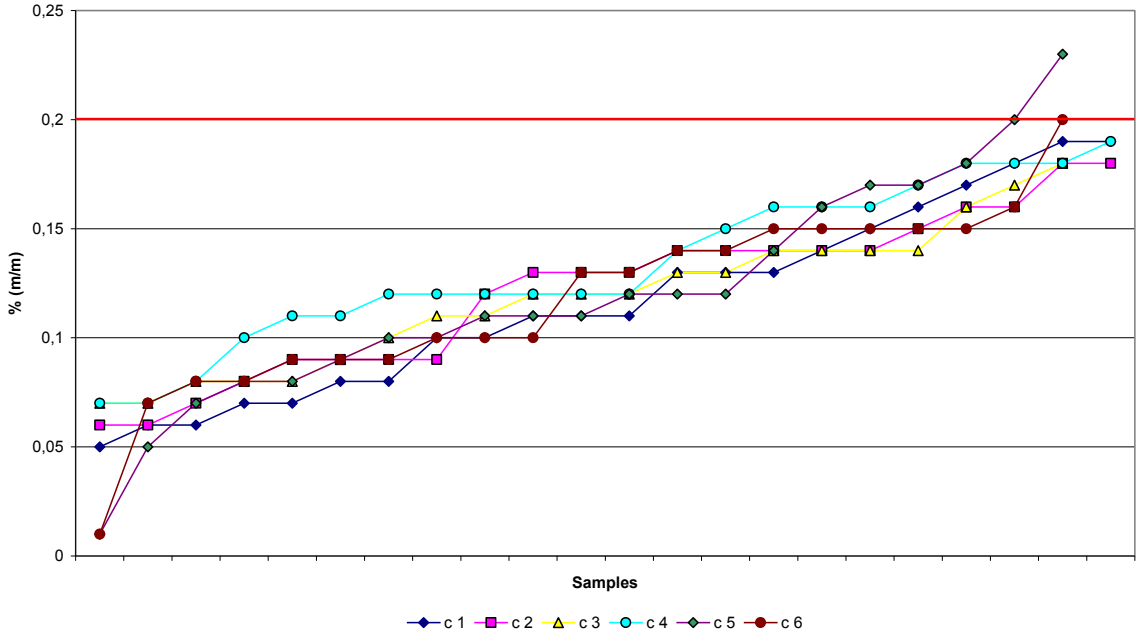
Limit DIN EN 14214: ≤ 0,8 % m/m



FAME according to DIN EN 14214 may contain a maximum of 0.8 % (m/m) of monoglycerides. The graph shows that all tested samples stay below the limit and that most producers are already in a position to meet the lower limit for FAME as pure fuel of 0.7 % (m/m), which will take effect with the next revision of DIN EN 14214.

Diglycerides

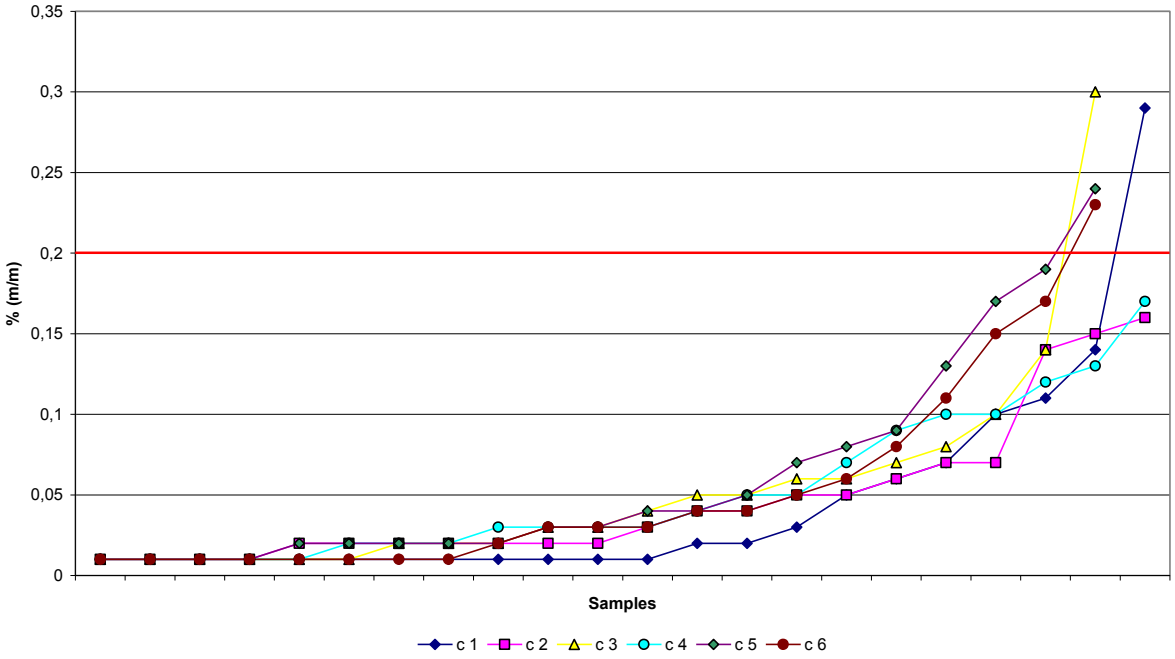
Limit DIN EN 14214: ≤ 0,2 % m/m



As it is the case with monoglycerides, the graph reflects that the Biodiesel producers have the transesterification process under control. Failure and ensuing exceedance of limits almost only occur when the plants are started and/or in case of technical faults. Generally such problems are detected during in-house operational checks. Despite the fact that the limit was exceeded in one single case, the standard was observed in all cases considering the precision of the test method.

Triglycerides

Limit DIN EN 14214: ≤ 0.2 % m/m



Again the evaluation shows that generally the contents are way below the permissible values and in most cases they are even below the determination limit of test method DIN EN 14103. The commodities of the two detected violations were not delivered and corrective measures were taken; considering the precision of the test method the limit was just observed in two cases. Limits are exceeded, with a simultaneous increase of diglyceride values, primarily in case of production plant failure.

Free Glycerol

Limit DIN EN 14214: ≤ 0.02 % m/m

Free Glycerol in Biodiesel is no longer a problem. All samples show extremely low contents and so the graphical presentation of the results was foregone.

Alkali metals: Sodium / Potassium

Test method: DIN EN 14538

Limit DIN EN 14214: ≤ 5 mg/kg

The Alkali metals sodium and potassium result from the catalyst used for the production of the Biodiesel. Any soaps forming during the reaction process must be removed from the final product by means of suitable cleaning steps. DIN EN 14214 restricts the sum of the sodium and potassium contents to 5 mg/kg (Na + K: ≤ 5 mg/kg).

The sum of the alkali contents does not reach the limit in any case, in most cases it is below 2 mg/kg. The graphical presentation was foregone because the precision of the method does not allow any more detailed data.

Alkali earth metals: Calcium / Magnesium

Test method: DIN EN 14538

Limit DIN EN 14214: ≤ 5 mg/kg

The Alkali earth metals calcium and magnesium get to the final product if ‚hard' water is used for the washing process; their reaction with free fatty acids leads to the forming of Ca and Mg soaps. DIN EN 14214 restricts the sum of the calcium and magnesium contents to 5 mg/kg (Ca + Mg: ≤ 5 mg/kg).

As it is the case with Alkali metals the sum of the Alkali earth metals does not reach the limit in any case. All cumulative values are below 2 mg/kg. Since the precision of the method does not allow any more detailed data either, the graphical presentation was foregone as well.

Phosphorous Content

Test method: DIN EN 14107

Limit DIN EN 14214: ≤ 4 mg/kg

Phosphorous residues in Biodiesel mostly result from phospholipids which are a natural part of the vegetable oils used. The phosphorous content must already be considered when choosing the feedstock because, if too high, it interferes with the transesterification process. During the normal transesterification process, jointly with the watery glycerol phase, any existing phosphatides are separated from the Biodiesel to the greatest possible extent. Phosphatides can impede the processing of

the glycerol phase to pharmaceutical glycerol which is another reason why the feedstock's phosphorous content is limited as far as possible.

None of the samples shows a content of above 2 mg/kg; with only one exception the contents are even below 1 mg/kg. As it is the case with Alkali and Alkali earth metal contents, the precision of the method does not allow more detailed information. The phosphorous content in Biodiesel is of great importance to the automotive industries and its OEMs since phosphorous is poisonous for catalysts and can damage exhaust aftertreatment systems. The low values found here show that the quality provided by the Biodiesel producers is significantly better than required by the standard.

CFPP

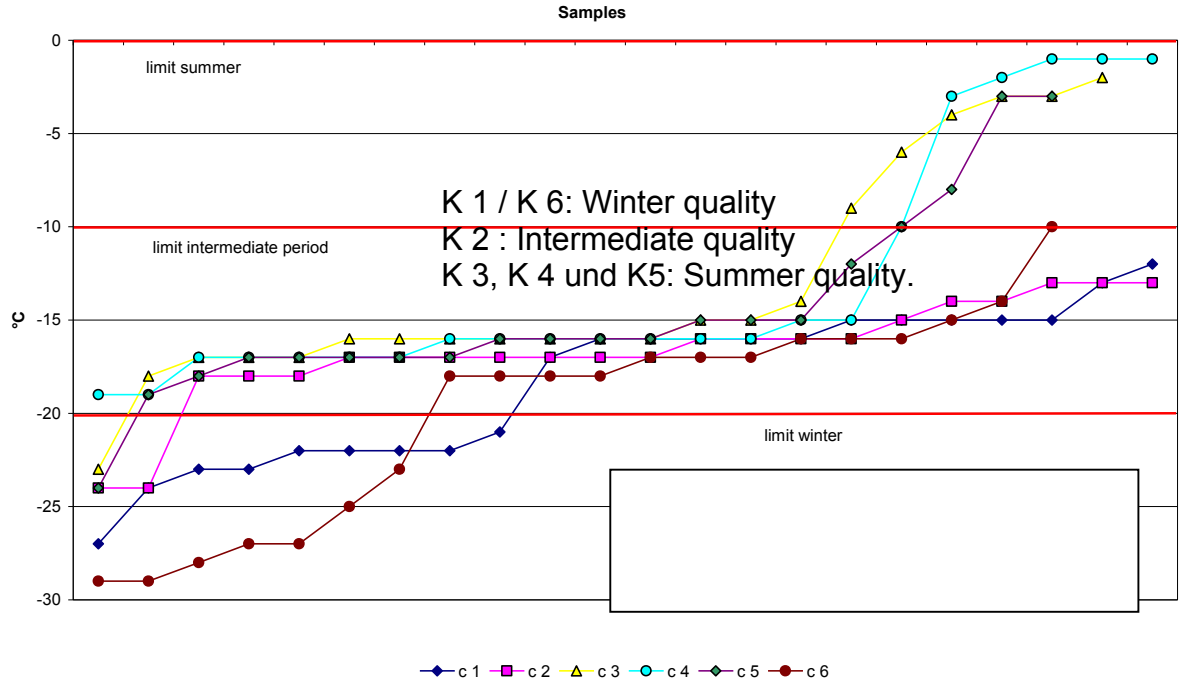
Test method: DIN EN 116

Limit according to DIN EN 14214:
0°C from April 15 to September 30
-10°C from October 1 to November 15
-20°C from November 16 to February 28/29
-10°C from March 1 to April 14

AGQM's additional limits:
-10°C max. from October 1 to October 18
-20°C max. from October 19 to February 28/29

The Cold Filter Plugging Point (CFPP) is a measure for the cold properties of Biodiesel. Due to the applicable climate situation the requirements for 'cold properties' are stipulated nationally. Analogous to Diesel fuel, different requirements apply for summer, intermediate and winter qualities.

Due to specific Energy Tax Law regulations, special requirements apply in Germany: though for the use of FAME as blend component there is only a limit of -10° C for winter quality, it must be possible to verify on demand that a CFPP of -20° C can be achieved by suitable additivation.



Considering the individual sampling periods all samples comply with the requirements of the standard. The graph shows that a significant share of the FAME produced in summer is also of winter quality.

Summary

AGQM's quality management concept comprises the regular monitoring of the product quality by unannounced checks as an integral part. The results thus obtained are assessed by AGQM; this measure serves two purposes: to observe the abidance by the specifications and additionally to support the companies' own monitoring. Also, the data compiled over the years forms the foundation of a database for the development of Biodiesel quality unique in the world, which impressively verifies the continuous improvement and optimisation of production processes and quality assurance measures.

The evaluation of the six sampling campaigns carried out in 2011 shows that the AGQM member companies produce consistently good quality and that internal quality assurance provides reliable results.

The following table impressively shows that the share of limit violations is very low:

Parameter	**Number of samples exceeding the limit** (of a total of 129 samples)	**Samples exceeding the limit (in %)**
Ester content	0	0
Sulphur content	3	2.3 %
Water content	0	0
Total contamination	0	0
Oxidation stability	3	2.3 %
Acid number	0	0
Iodine number	0	0
Glycerine/Glycerides	2	1.6 %
Content of Alkaline metals (Na + K)	0	0
Content of Alkaline earth metals (Ca + Mg)	0	0
Phosphorous content	0	0
CFPP	0	0

Apart from few exceptions all products tested fulfil the requirements of the relevant parameters of the standard and/or the sometimes even more stringent ones by AGQM; in case of deviations from the requirements necessary measures were taken immediately. In many cases the products already comply with requirements for higher blend rates called for by the mineral oil industry and car manufacturers.

A detailed evaluation of the contents of Alkali, Alkaline earth, phosphorous and sulphur from the years 2000 to 2010 was published recently[4]. The results of 2011 confirm the positive development during the past years.

[4] T. Wilharm, H. Stein, A short study to assess the metal, phosphorus and sulfur content in biodiesel **2011**, http://www.agqm.de/downloads/pdfs/20110825_Abschlussbericht_ENG_pdf.pdf.