



# ***Biodiesel Quality in Germany***

## ***AGQM Sampling Campaigns 2010***

### ***(Producers and Warehouses)***

#### **Introduction**

Biodiesel is a composition of fatty acid methyl esters (FAME). It is made of diverse vegetable oils or animal fats by transesterification with methanol. In Germany rapeseed oil is used predominately apart from much smaller amounts of soybean and palm oil. Most of the Biodiesel produced is used as blend component for Diesel fuel with a ratio of 7 % (v/v) (B7 fuel).

In Germany, significant amounts of Biodiesel have been on the market since the mid-1990s. Since those early years, the quality of this fuel has been subject to ever increasing requirements; new producers, further developments in engine techniques and not least the blending of fossil Diesel fuel, introduced in Germany in 2004 also, call for strict compliance with the Standards and custom-made specifications. Since 2004, meeting the requirements of DIN EN 14214 is also a prerequisite for any tax exemption and/or tax relief for Biodiesel as well as eligibility for the Biofuel Quota. The deciding factor for that is the fulfillment of the requirements stipulated in the latest revision of the *10. BImSchV*. In practice, according to the parameters laid down therein, German Customs executes random checks of the marketed Biodiesel.

The Arbeitsgemeinschaft Qualitätsmanagement Biodiesel e.V. (AGQM) was founded in 1999. Since then, AGQM members profit from a quality management system which is permanently adapted to any changing requirements. Unannounced and independently carried out monitoring of all member companies is an integral part of that system. The results enable conclusions concerning the effectiveness of internal quality management measures and at the same time they are valuable information for the member companies themselves. The objective has always been the assurance of the high quality level achieved in Germany and to give Biodiesel consumers the necessary confidence in the product.

With the introduction of a standard for Biodiesel as a criterion for tax exemption and/or the consideration for Quota eligibility, those quality assurance measures provide AGQM members with a special advantage:

In negotiations with the Federal Ministry of Finance (BMF), AGQM achieved for its members that Main Customs Offices may refrain from random quality checks if their regular (every other month) sampling and monitoring of the parameters listed herein can be guaranteed.

Meanwhile the data gained due to AGQM's regular monitoring feeds an important and internationally unique data base for the development of Biodiesel quality in Germany. Being the first of its kind, this report illustrates the development of selected parameters in recent years – apart from the current situation – and thus documents the positive development of the German Biodiesel quality.

## **Sampling – execution and scope**

One of the main pillars of the QM (quality management) concept is the monitoring of the production quality by an accredited independent laboratory assigned by AGQM. The sampling is mandatory for AGQM members; six times a year and without prior notification samples are taken, analyzed and checked for compliance with the requirements of the standard. To some extent requirements which exceed those of the standard and which are laid down in the QM Concept also apply. The scope of the checks equates to the requirements defined in the QM Concept. The following parameters are measured:

<b>Parameter</b>	<b>Method</b>
Content of fatty acid methyl ester	DIN EN 14103
Sulphur content	EN ISO 20846 EN ISO 20884
Water content	DIN EN ISO 12937
Total contamination	DIN EN 12662
Oxidation stability	DIN EN 14112
Acid value	DIN EN 14104
Iodine value	DIN EN 14111
Glycerol/Glycerides	DIN EN 14105
Alkali metals (Na + K)	DIN EN 14108 DIN EN 14109
Alkaline earth metals (Ca + Mg)	DIN EN 14538
Phosphorus content	DIN EN 14107
CFPP	DIN EN 116
Fatty acid profile	DIN EN 14103

The individual significance of the parameters is described more explicitly in a separate document.

Sampling and analytics are put out to tender and assigned anew every year. For that only laboratories accredited for Biodiesel analysis and successfully partaking in the annual AGQM RRTs (round robin tests) are considered.

## Evaluation 2010

In 2010, a total of 139 samples of AGQM members (producers and traders) was examined in six campaigns. The campaigns are denominated c 1 to c 6. The following evaluation graphically illustrates and assesses the individual results for the parameters. All results are made anonymous and give no indication as to the origin of the sample.

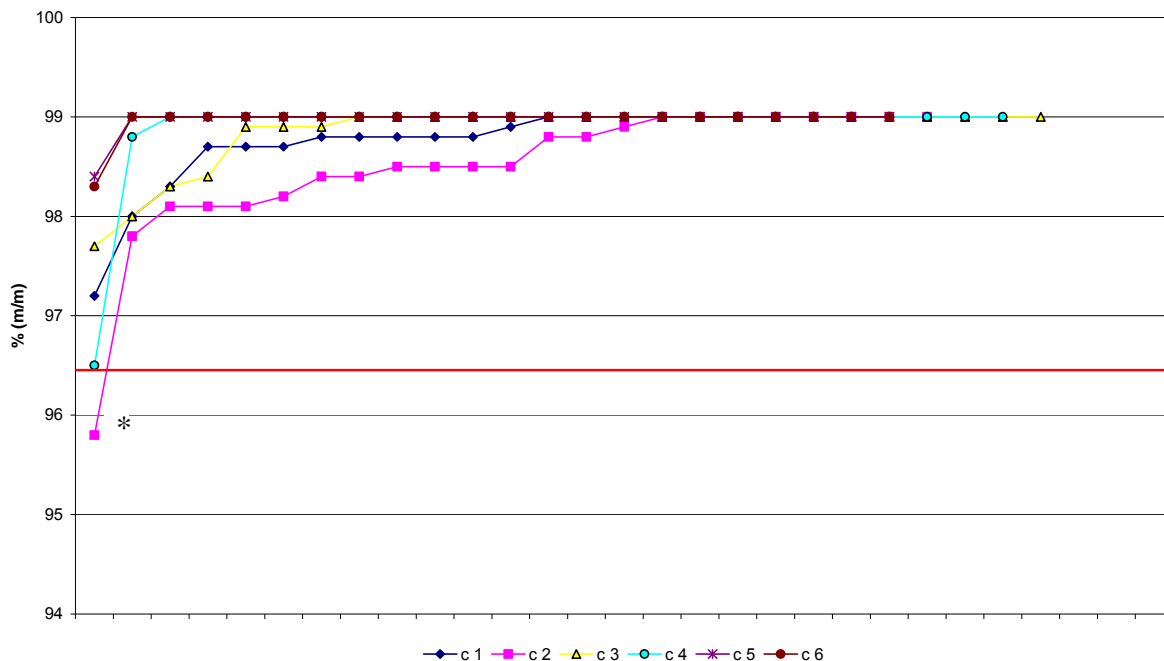
Below each determined parameter is described and the results are illustrated graphically. The values are for each campaign arranged in increasing order to illustrate the measured values and to facilitate comparison between the different campaigns. The order of the producers varies in each single curve due to the arrangement according to the measured values even within the same parameter.

### Content of Fatty acid methyl esters („Ester content“)

*Test method: EN 14103*

*Limit value EN 14214:  $\geq 96.5$  % m/m*

The content of fatty acid methyl esters, mostly abbreviated ‚ester content‘, is a measurement of the transesterification rate and the purity of the Biodiesel; the higher the value, the better the quality. DIN EN 14214 determines the FAME content as at least 96.5 % (see Annex A).



\* Measured value is still within the tolerance range of the method, product tradable

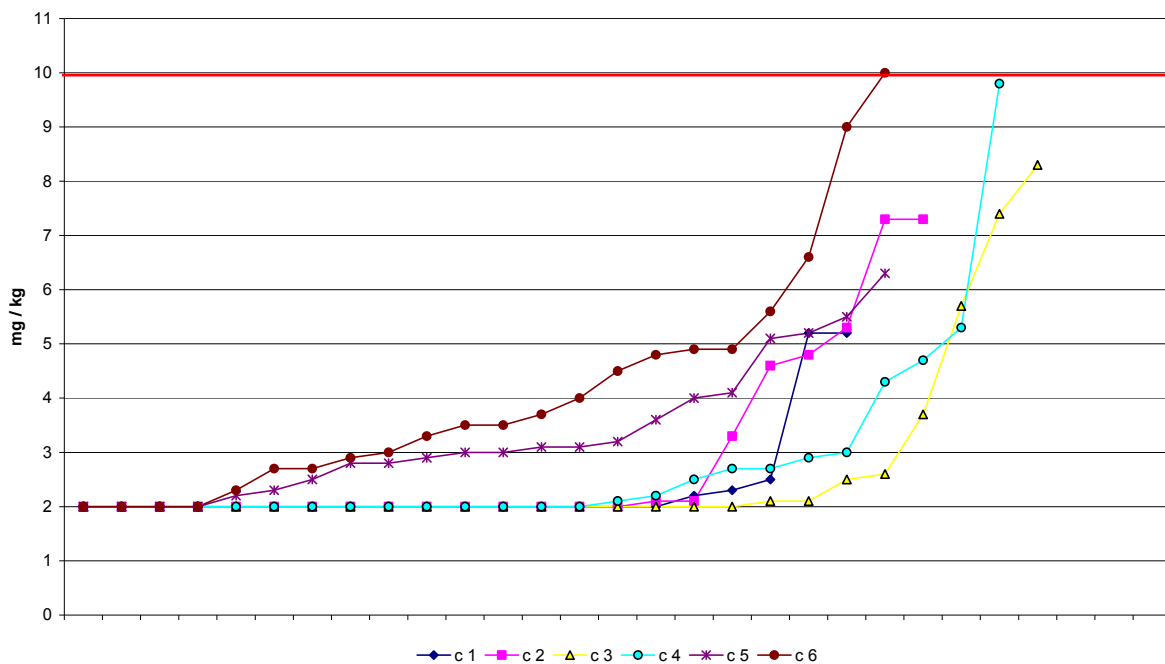
The graph shows that virtually all measurements meet the requirements of EN 14214; measurements given as „> 99.0%“ are shown in the graph as 99 % ester content. With 95.7 %, the only outlier is still within the tolerance range of the test method so that there is no reason for action or complaints.

## Sulphur Content

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

*Limit value EN 14214:  $\leq 10$  mg/kg*

There are only traces of sulphur to be found in Biodiesel and usually the standard limit of 10 mg/kg is not exceeded. The following graph shows the sulphur values of the production samples tested. Since the precision of the method does not suffice any more for an accurate indication below 2 mg/kg, the graph shows contents of less than 2 mg/kg as '2 mg/kg'.



Two samples of the last six campaigns had sulphur values close to the limit value which was probably caused by oils the seed of which contains sulphur. Indeed higher sulphur proportions are to be found in animal fats than in vegetable oils but there is no indication for that in their fatty acid profiles. Furthermore, it is striking that the values of campaigns 5 and 6 are higher compared with those of the other campaigns. Apart from the analytics (different laboratory) this effect may have been caused, for example, by an increased use of sulphur-containing fertilisers.

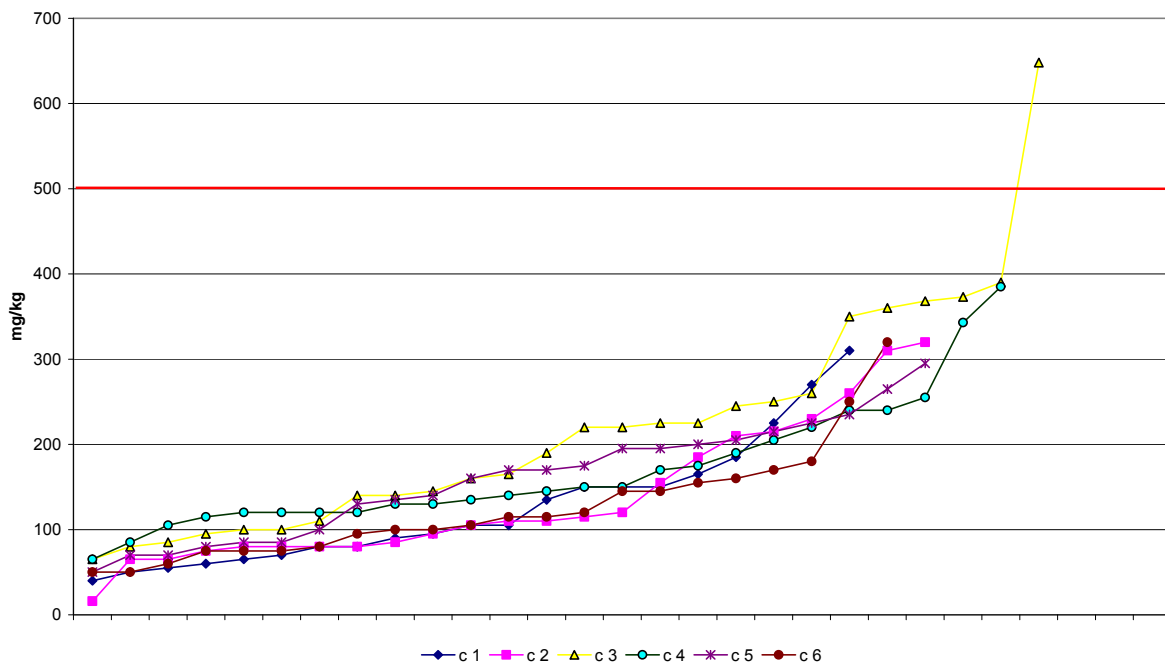
## Water Content

Test method: EN ISO 12937

Limit value EN 14214:  $\leq 500$  mg/kg

Limit value AGQM:  $\leq 220$  (300) mg/kg

Two limits must be considered for the assessment of the water content: on the one hand the maximum content of 500 mg/kg as defined by EN 14214 and on the other hand the value stipulated by the QM Concept at 200 mg/kg for producers and/or 300 mg/kg for traders. The tolerance range is defined by the maximum/minimum permissible values which can be found in the 10. BImSchV (fuel quality directive).



The majority of the samples contains less than 200 mg water/kg which is even significantly below the AGQM definition. Just one sample exceeds the limit of EN 14214; however, the product was not put on the market; due to the result adequate corrections measures were undertaken.

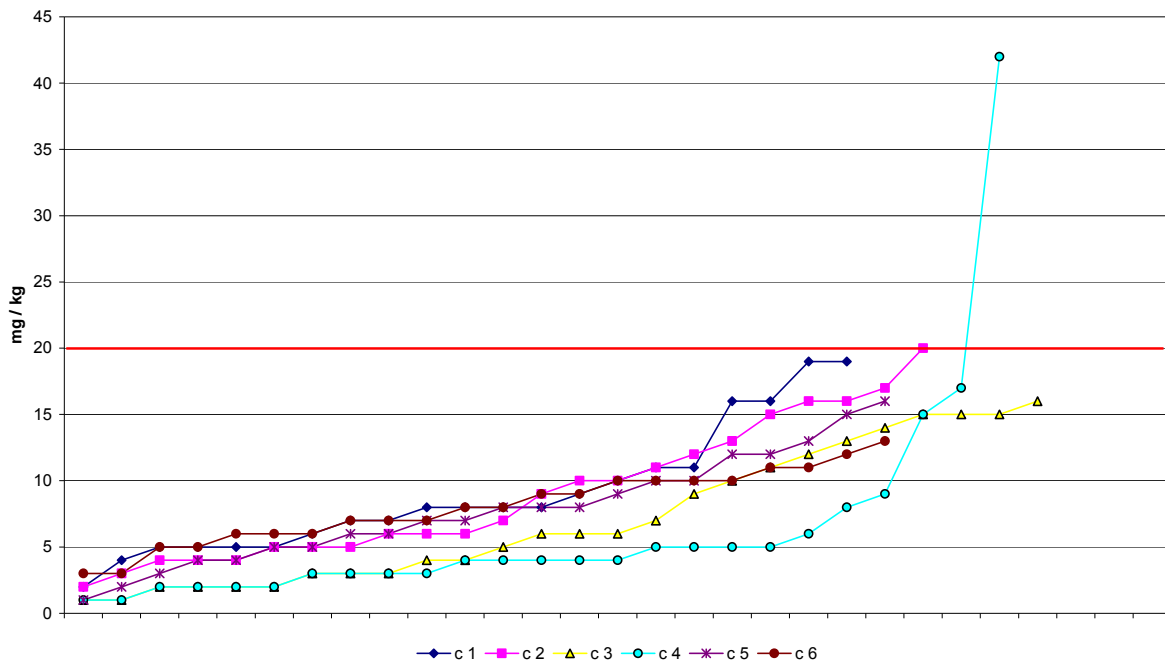
## Total Contamination

Test method : EN 12662

Limit EN 14214:  $\leq 24$  mg/kg

Limit AGQM:  $\leq 20$  mg/kg

In the past, particles contributing to the total biodiesel contamination were frequently the cause for queries and dysfunction which is the reason why their number is restricted by the standard. The AGQM limit value was reduced to 20 mg/kg in accordance with the German draft of Standard E DIN 51606, which means a tightened requirement compared with that of EN 14214.



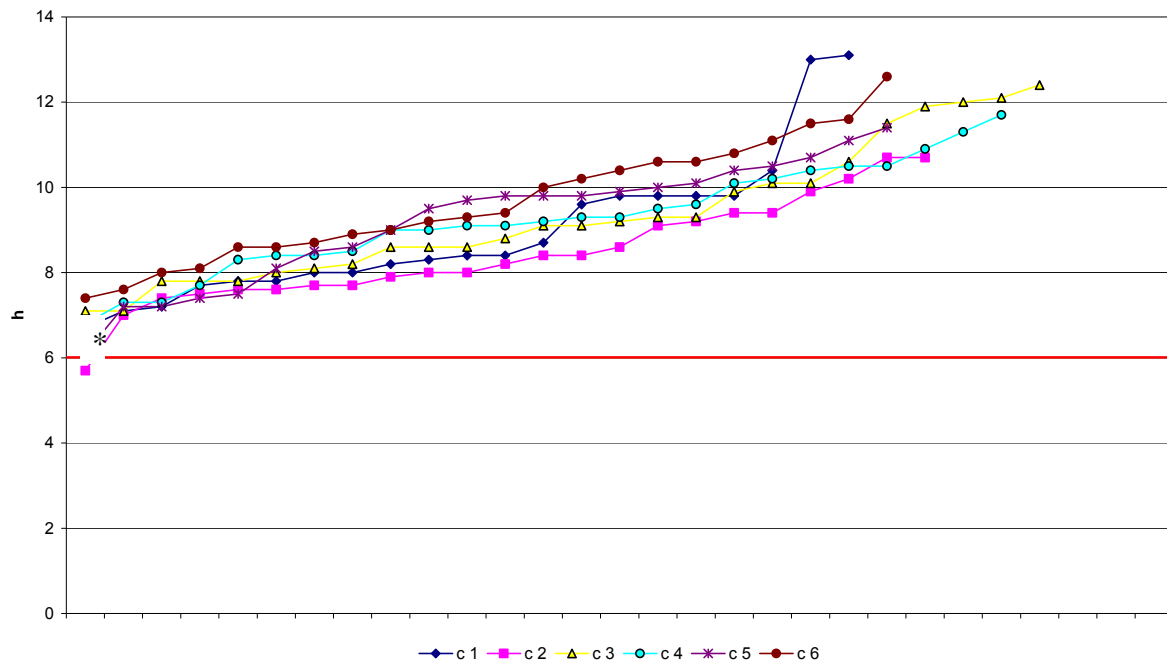
The result of the sampling is pleasing: the predominant share of the samples by far contains less than 10 mg/kg of “dirt”; only one sample exceeded the AGQM limit but the product concerned had already been banned from shipping by its producer.

## Oxidation Stability

*Test method: EN 14112*

*Limit value EN 14214:  $\geq 6$  h*

According to DIN EN 14214 the oxidation stability of biodiesel, defined by the induction time, must be at least 6 hours; the increase to 8 hours is an element of the current revision. Frequently the mineral oil industry already demands a higher stability; by now the use of stabilizers has become common routine and AGQM's recommendation for blend fuels also includes an induction time of 8 hours.



\* Measured value is still within the tolerance range of the method, product tradable

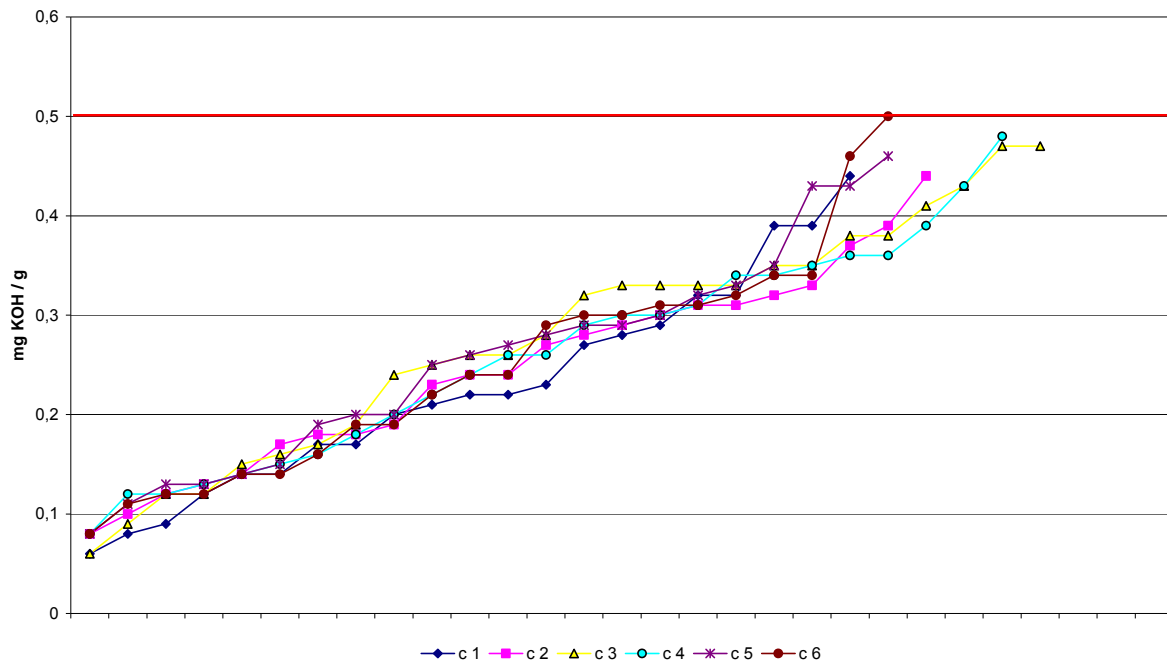
Again, the results of the sampling show that the quality requirements are also met in this respect; in most cases an induction time of 8 hours is reached, too. Significant seasonal deviations cannot be observed; obviously the good quality is primarily achieved by selecting suitable feedstock and using additives.

## Acid value

*Test method: EN 14104*

*Limit value EN 14214:  $\leq 0,5$  mg KOH/g*

Free fatty acids in biodiesel may cause minor corrosion but they can also form soaps with alkaline compounds which may lead to adhesion and filter plugging. Also, short chain carbon acids (formic acid, acetic acid) which increase the acid value, can form due to the aging of the Biodiesel. Therefore, the limit according to EN 14214 is fixed at 0.5 mg KOH/g.



The evaluation of the sampling shows that no limits were exceeded and only few samples are marginal, with most acid values below 0.4 mg KOH/g.

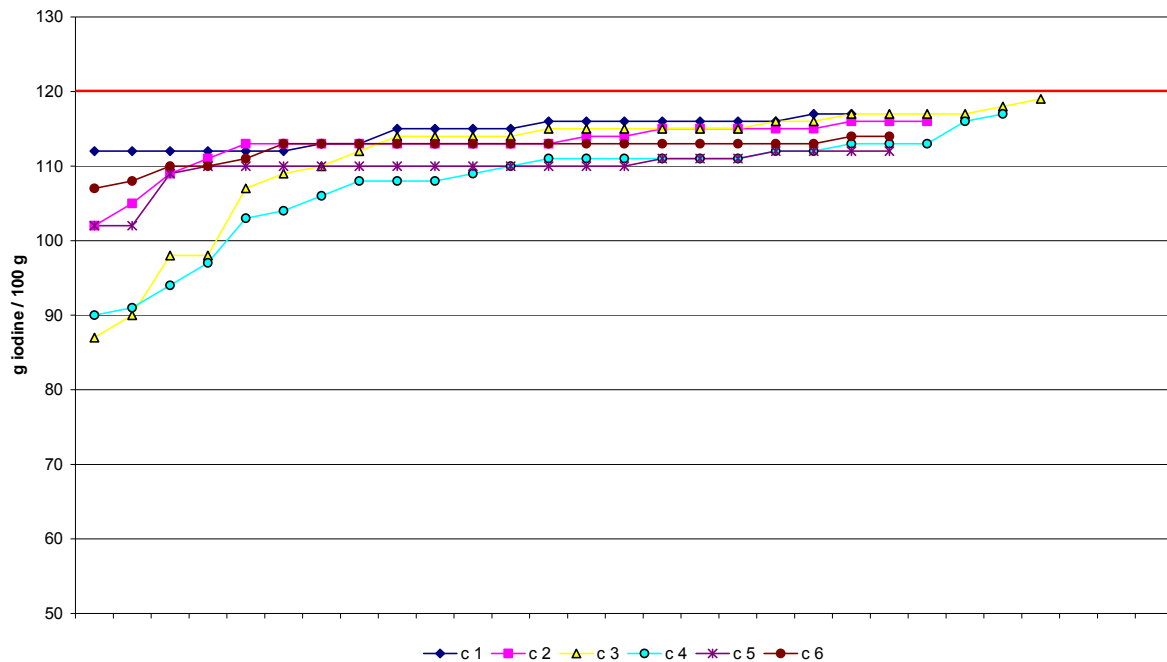
## Iodine value

*Test method: EN 14111*

*Limit value EN 14214: 120 g/100g*

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





The graph shows that the iodine value of the predominant number of samples ranges between 110 and 120. There is no indication for any limit exceedance. Campaigns c3 and c4, carried out in the summer months, show significantly lower values, whereas in the winter months the value of the iodine value is almost exclusively  $\geq 110$ . The reason for that is that due to the climate-dependant requirements in summer a limited amount of palm oil can also be used for the Biodiesel production while during the winter months RME (rapeseed oil methyl ester) and blends with SME (soybean methyl ester) can almost only be used. However, conclusions as to the feedstock cannot be safely based on the iodine value alone.

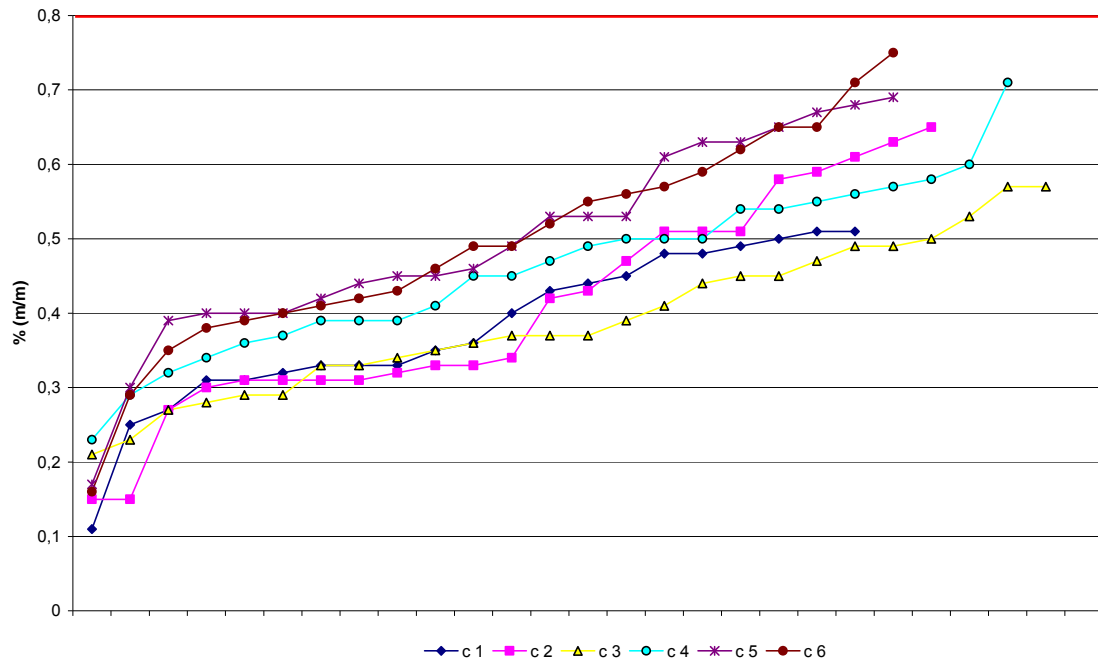
## Glycerides / Free Glycerol

*Test method: EN 14105*

Partial glycerides and triglycerides are measurements for complete transesterification. Their contents can be influenced by the reaction management. Usually they occur in the order 'monoglycerides > diglycerides > triglycerides' because the split-off of the last fatty acid is the slowest transesterification step. High triglyceride concentration in spite of lower mono and di values are an indication for intermixture with the feedstock. The data for the individual components gained from the production samplings is given below.

## Monoglycerides

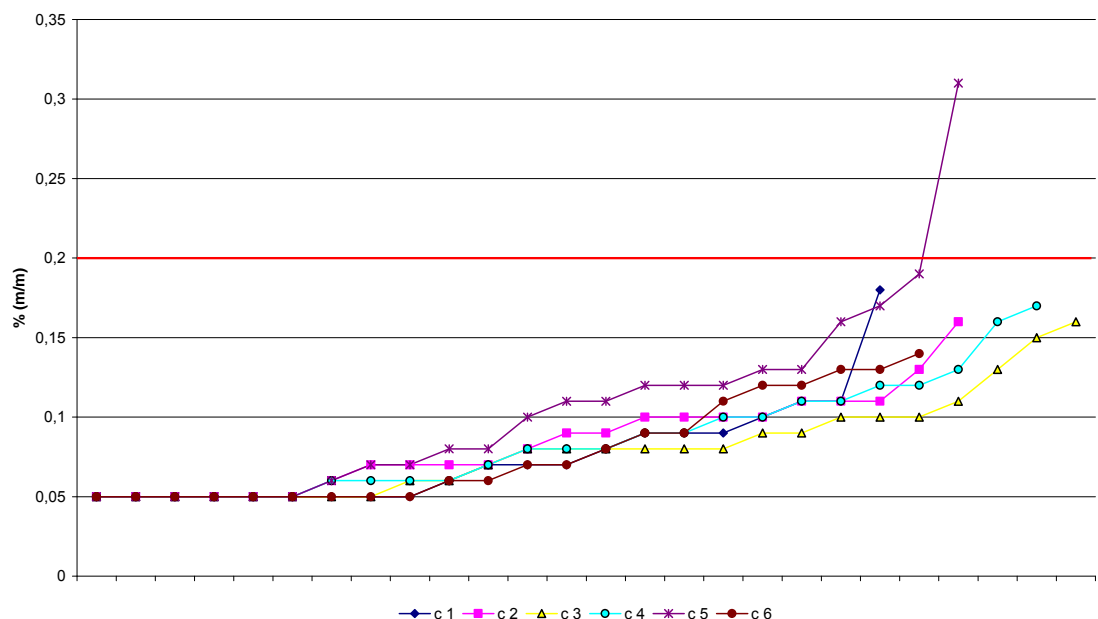
Limit value EN 14214:  $\leq 0,8 \text{ \% m/m}$



FAME according to EN 14214 may contain a maximum of 0.8 % (m/m) of monoglycerides. The graph shows that most producers are already able today to satisfy the demand for reduced monoglyceride values.

## Diglycerides

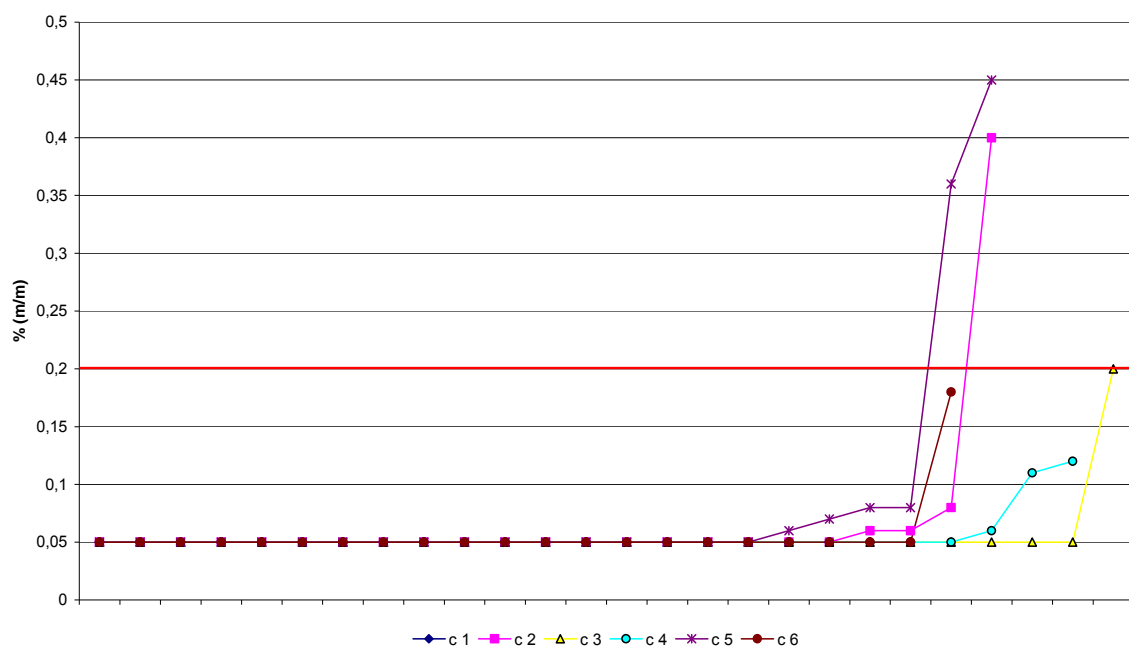
Limit value EN 14214:  $\leq 0.2 \text{ \% m/m}$



As it is the case with monoglycerides, the graph reflects that the Biodiesel producers have the transesterification process under control. Dysfunction and ensuing exceedance of limits almost only occur when the plants are started up and/or in case of technical faults. Generally such problems are detected during in-house operational checks. In the case of the value exceeding the limit the product was not traded and corrective measures taken.

### Triglycerides

*Limit value EN 14214:  $\leq 0.2$  % m/m*



Here the evaluation also shows that the content is generally much below the permissible value and in most cases it is even below the measuring range of test method EN 14103. Like it is with diglycerides, limit exceedance occurs primarily in case of production plant dysfunctions; mistakes in the logistics supply chain are hardly ever observed any more. In the cases the values exceeded the limit the product was not traded and corrective measures taken.

### Free Glycerol

*Limit value EN 14214:  $\leq 0.02$  % m/m*

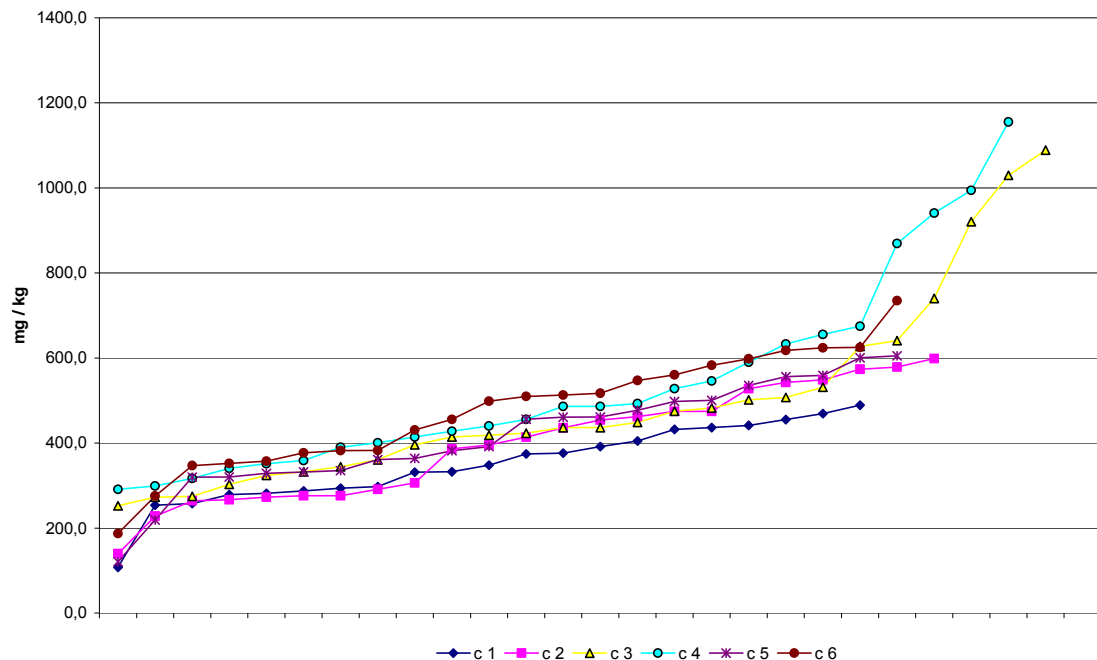
Free glycerol in Biodiesel is no problem any longer. All samples showed extremely low contents so the graphical presentation of the results was forgone.

## Saturated Monoglycerides

Test method: EN 14103/14105

Saturated monoglycerides (SMG), of all FAME components, have the highest freezing point and are therefore associated with filter plugging and vehicle breakdown. Since this parameter, which is not part of EN 14214, is discussed intensely at present, in 2010 it was integrated into the measuring scope of the sampling campaign for the first time. So far there is no standardized test method; the content of unsaturated monoglycerides was determined by calculating with the fatty acid profile and the overall monoglyceride content. Thus the content is determined with two independently obtained measuring values, each determined with the precision laid down for the test method. The accuracy of the methods is acceptable for the determination of the fatty acid profile and/or the monoglycerides; however, due to error propagation the measurement becomes imprecise for saturated monoglyceride values of < 1000 mg/ kg.

So far there is no fixed limit value. In the AGQM guideline for FAME as blend component a maximum content of 1200 mg/ kg is recommended, whereas the European mineral oil industry called for climate-related maximum contents ranging between 225 and 1200 mg/kg.



The test shows that all participants achieve very low levels of unsaturated monoglycerides when appropriate feedstock and/or refining methods are selected. The values of all samples tested are below the limit recommended by AGQM; more than 90 % contain less than 650 mg/kg, some even less than 200 mg/kg. High values are only detected during the summer months when the use of adequate methyl esters is possible.

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### **Alkali Metals: Sodium / Potassium**

*Test method: EN 14538*

*Limit value EN 14214:  $\leq 5$  mg/kg*

The alkali metals sodium and potassium arise from the catalyst used for the Biodiesel production. Soaps forming during the reaction (Reaction induced soaps) must be removed from the final product by suitable cleaning steps. EN 14214 limits the sum of the sodium and potassium contents to 5 mg/kg (Na + K:  $\leq 5$  mg/kg).

All values found for alkali metals are below 2 mg/kg (limit of detection). A graphical presentation of these results was forgone for lack of information value.

### **Alkaline Earth Metals: Calcium / Magnesium**

*Test method: EN 14538*

*Limit value EN 14214:  $\leq 5$  mg/kg*

Due to the use of 'hard' water for the cleaning process, the alkaline earth metals calcium and magnesium are inserted into the final product; their reaction with free fatty acids leads to the forming of Ca and Mg soaps. EN 14214 limits the sum of the calcium and magnesium contents to 5 mg/kg (Na + K:  $\leq 5$  mg/kg).

All values found for these alkaline metals are below 2 mg/kg (limit of detection). A graphical presentation of these results was forgone for lack of information value.

### **Phosphorus Content**

*Test method: EN 14107*

*Limit value EN 14214:  $\leq 4$  mg/kg*

Residual phosphorus in the Biodiesel results from phospholipids which are a natural part of the vegetable oils used. Conventional Biodiesel production processes only influence the phosphorus content to a limited extent; this must already be taken into account when the feedstock is selected.

All values found range up to 2 mg/kg (limit of detection). A graphical presentation was forgone for lack of information value.

## CFPP

Test method: EN 116

Limit value according to DIN EN 14214:

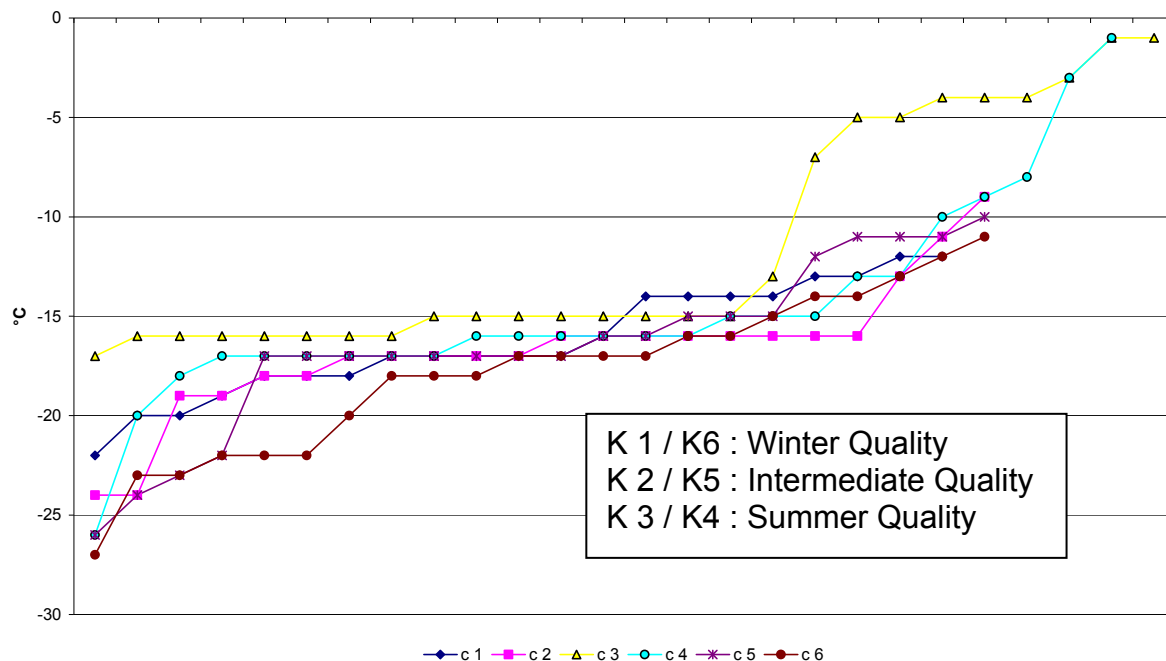
- 0°C from April 15 to September 30
- 10°C from October 1 to November 15.
- 20°C from November 16 to February 28/29
- 10°C from March 1 to April 14

Limit values according to AGQM:

- 10°C max. from October 1 to 18
- 20°C max. from October 19 to February 28/29

The Cold Filter Plugging Point (CFPP) is a measurement for the cold properties of Biodiesel. The national requirements of 'cold properties' are laid down dependent on the individual climatic conditions. In Germany – as it is the case with Diesel fuel – there are differing requirements for summer, intermediate and winter qualities.

There are special requirements due to the relevant provisions of the German Energy Tax Act: although the limit value for winter quality is deferred for the use of FAME as blend component, on request it must be proven that a CFPP for -20°C could basically be achieved with the use of suitable additives.



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

## Summary

As an important programme module, regular unannounced product checks are included in the AGQM quality management. The results obtained therewith are then evaluated by AGQM staff; that way the compliance with the requirements can be monitored and the member companies' self-control is supported. Furthermore, the data gathered over the years feeds a data base – unique in the world – for the development of the Biodiesel quality. The data base also impressively shows how production processes and quality assurance measures were continuously improved and optimized.

The evaluation of the 6 sampling campaigns in 2010 illustrates that the production of the AGQM member companies is of consistently good quality and that the results of the internal quality assurance are reliable. Apart from few exceptions all products tested meet the relevant parameters of the Standards' requirements and/or the sometimes even more rigid AGQM requirements (see table below). Necessary measures for the outliers were taken. In many cases the products already satisfy demands made for higher blends by the mineral oil industry and automotive producers.

The following table lists all parameters exceeding any limits. Only one parameter per batch exceeded the limit.

<b>Parameter</b>	<b>Number of samples exceeding the limit (of a total of 139 samples)</b>
Ester content	0
Sulphur content	0
Water content	1
Total contamination	1
Oxidation stability	0
Acid value	0
Iodine value	0
Glycerol/Glycerides	3
Content of Alkaline Earth Metals (Ca + Mg)	0
Phosphorus content	0
CFPP	0