

DIESEL FUEL DERIVED FROM VEGETABLE OILS, VI: SPECIFICATIONS AND QUALITY CONTROL OF BIODIESEL

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Abstract

Due to the rising importance of biodiesel as alternative fuel in many countries, it is absolutely necessary to establish standards for the description of the quality of the product. The parameters and the corresponding threshold values defining the quality of rapeseed-oil methyl esters (RME) used as biodiesel according to the latest Austrian standardization (Ö-NORM) are presented and discussed. The difference is distinguished between general fuel parameters, which already exist for mineral diesel fuel, and vegetable-oil-specific parameters, which have to be additionally defined. Correlations between parameters like Conradson carbon residue, sulfate ash and phosphorus content are outlined. Problems concerning the inclusion of parameters, which have not yet been taken up in the Austrian standards, like iodine number and water content, are discussed. In the second part, analytical aspects for the determination of free and bonded glycerol, as well as mono-, di- and triglycerides are described. Well tested methods for the analysis of glycerol and glycerides are presented, including the description of the advantages and disadvantages of each method. © 1996 Elsevier Science Ltd.

Key words: Vegetable oils, diesel fuel, analysis, standardization.

INTRODUCTION

For almost 10 years, fatty acid methyl esters have been produced in Austria for use as diesel fuel. As early as 1985, the first pilot-plant for the production of rapeseed-oil methyl esters (RME) was installed in Styria in southern Austria. Meanwhile, four decentralized plants, which are owned by cooperatives, and two industrial-scale production plants are producing an average of 30000 tons of rapeseed-oil methyl esters per year. One industrial-scale plant for the production of biodiesel from used frying oil is under construction. Because of the fact that biodiesel is produced in quite differently scaled plants from vegetable oils of varying origin and quality, it was necessary to install a standardization of fuel

quality to guarantee engine performance without any difficulties. Therefore, in 1992, Austria was the first country in the world to define and approve standards for rapeseed-oil methyl esters as diesel fuel (Ö-NORM, 1992). In 1995 these standards were changed slightly and enlarged according to the latest findings and, most recently, general standards for fatty acid methyl esters, derived from different fats and oils, have been established. As standardization is a prerequisite for the successful market introduction and penetration of biodiesel, standards or guidelines for defining the quality of biodiesel have also been defined in other countries, like Germany (DIN V 51606, 1994), Italy, France, the Czech Republic and in the United States (National Soy-Diesel Development Board, 1994). In this paper, the most important parameters for the quality of biodiesel, the correlation between specific parameters, as well as suitable analytical methods, will be presented and discussed. This contribution should provide a basis for further discussion and development in the standardization of biodiesel.

PARAMETERS DEFINING THE QUALITY OF BIODIESEL

The parameters which are selected and established to define the quality of biodiesel can be divided into two groups. One group contains general parameters which are also used for mineral-oil-based fuels, and the other group especially describes the chemical composition and purity of fatty acid methyl esters. Table 1 contains the general and Table 2 the vegetable-oil-specific parameters and the corresponding values for the quality of rapeseed-oil methyl esters according to the Austrian standards.

Correlations between specific parameters

Some general parameters, like density, cetane number and content of sulfur, mainly depend on the choice of vegetable oil and cannot be influenced by different production methods or purification steps. The flash point, however, strictly corresponds to the

content of methanol and the viscosity correlates with the content of unreacted triglycerides.

One parameter has proven to be one of the most important indicators for the quality of biodiesel—the Conradson carbon residue. Despite the fact that the experimental procedure for determination seems to be an old-fashioned method compared to modern analytical techniques, it can be shown in different investigations that this parameter is an excellent indicator for the quality of biodiesel (Hödl & Schindlbauer, 1994); it corresponds strictly to the content of glycerides (Mittelbach *et al.*, 1992), as well as free fatty acids, soaps, remaining catalyst and other impurities. An interlaboratory test with five different RME samples from different production plants involving six laboratories has shown that all values are within the required 95% confidence.

The content of inorganic matter, like impurities of remaining catalyst, is limited by the value of the

Table 1. General parameters for the quality of rapeseed-oil methyl esters (Ö-NORM C-1190, 1995)

Parameter	Unit	Value
Density at 15°C	g/cm ³	0.87–0.89
Viscosity at 20°C	mm ² /s	6.5–8.0
Flash point	°C	> 100
Sulfur %	m/m	≤ 0.02
Conradson carbon residue	% m/m	≤ 0.05
Sulfate ash %	m/m	≤ 0.02
Cetane number		> 48
Neutralization number	mg KOH/g	≤ 0.8

Table 2. Vegetable oil specific parameters for the quality of rapeseed-oil methyl esters (Ö-NORM C-1190, 1995)

Parameter	Unit	Value
Methanol	% m/m	≤ 0.2
Free glycerol	% m/m	≤ 0.02
Total glycerol	% m/m	≤ 0.24
Phosphorus	ppm	≤ 20

ash content. In the Austrian standards for RME, the determination of the sulfate ash is preferred to that of the oxide ash because the remaining alkaline catalysts are transformed into alkali sulfates, which have lower volatility at higher temperatures than the corresponding oxides, and, therefore, will be better recovered. When performing transesterification of fully refined oils using alkaline conditions, the sulfate ash content is mainly determined by the concentration of remaining soaps. When using unrefined oils, the value also correlates with the content of phosphorus, which, for RME in Austria, is limited to 20 ppm. A higher content of phosphorus in the fuel can lead to higher particulate emissions, which may influence the operation of a catalytic converter. The phosphorus content of the vegetable oil depends mainly on the grade of refined oil. So, fully refined oils have a phosphorus content of only several ppm phosphorus, whereas unrefined or water-degummed rapeseed oil can have a phosphorus content over 100 ppm, which corresponds to a content of phosphatides over 0.25%. During transesterification using alkaline catalysts, the phosphorus content, however, can be lowered from over 100 ppm to approximately 20–30 ppm. This leads to a sulfate ash content of approximately 0.04%. Further reduction of the phosphorus content can only be achieved by additional purification steps. A correlation between the phosphorus content and the content of sulfate ash from RME samples at different refining steps is shown in Fig. 1.

Water content

In the Austrian standards for RME, the water content is limited by the definition that RME should be free from separated water. Due to the fact that a higher content of water in biodiesel might reduce the storage ability or lead to the separation of water when blending with mineral diesel, the German standards limit the water content to 300 ppm.

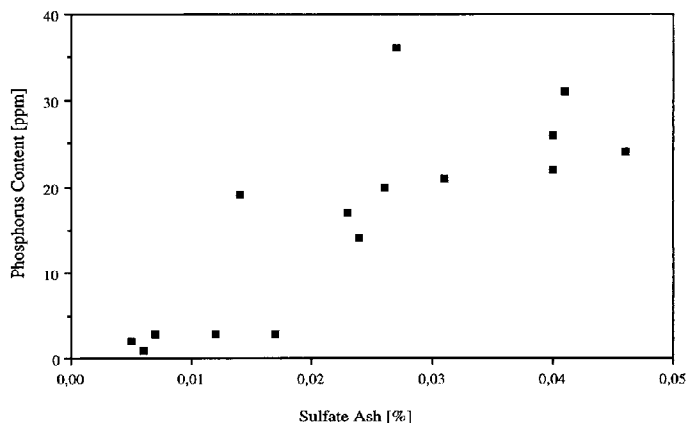


Fig. 1. Correlation between phosphorus content and sulfate ash in RME samples.

It is known that RME is more hygroscopic than mineral-oil-based fuels and, during storage, it can absorb water up to a concentration of approximately 1000 ppm. The maximum concentration of soluble water in RME with a methanol content of 0.2% (m/m) lies at 1500 ppm. Therefore, it does not seem reasonable to limit the concentration of water with a specific value that cannot be met during longer storage without installation of very expensive technical equipment.

Iodine number

One parameter which has not yet been included in the Austrian standards for RME, but might be necessary when defining general standards for fatty acid methyl esters is the iodine number, which describes the content of unsaturated fatty acids and is only dependent on the origin of the vegetable oil. In Germany a value of 115 is defined, which corresponds to rapeseed oil, but would exclude different kinds of oils, like sunflower oil and soybean oil. A limitation of unsaturated fatty acids may be necessary, due to the fact that heating higher unsaturated fatty acids results in polymerization of glycerides. This can lead to the formation of deposits or to deterioration of the lubricating oil. This effect increases with the number of double bonds in the fatty acid chain. Therefore, it seems better to limit the content of higher unsaturated fatty acids, like linolenic acid, than to limit the degree of unsaturation with the iodine number.

ANALYTICAL ASPECTS: GLYCEROL AND GLYCERIDES

In the Austrian standards for RME, there are limitations for the content of free and total glycerol. With the determination of total glycerol, which means the sum of free and bonded glycerol, the content of the sum of mono-, di- and triglycerides is determined. In Germany, the content of individual glycerides is limited as follows: monoglycerides to 0.8%, diglycerides to 0.1% and triglycerides to 0.1%.

Free and bonded glycerol, mainly depending on the technical process of transesterification, are the main parameters for defining the quality of biodiesel. During the transesterification process, free glycerol can easily be removed by washing steps, whereas a low content of glycerides can only be achieved by the use of specific catalysts and reaction conditions or by further distillation of the product. A higher content of free glycerol may cause problems during storage or in the fuel system, due to separation of glycerol, or can lead to injector fouling or the formation of higher aldehyde emissions. A higher content of glycerides, especially triglycerides, may cause formation of deposits at the injection nozzles, at the piston and at the valves (Mittelbach *et al.*, 1983; Moser *et al.*, 1991). As the limits of free

glycerol and glycerides are very low, there is a need for precise and reliable analytical methods for the determination of free and bonded glycerol, as well as the individual glycerides.

Free glycerol

Two non-chromatographic methods for the determination of free glycerol in vegetable-oil products have been described in previous work. Glycerol in toilet soaps can be determined by aqueous extraction, oxidation with periodic acid and titration of the resulting formic acid (AOCS, 1989). This method has not yet been evaluated for biodiesel. A photometric determination based on enzymatic reactions using commercially available test kits was developed especially for biodiesel samples (Bailer & de Hueber, 1991).

Several gas chromatographic methods for the determination of free glycerol in fatty acid methyl esters have been developed. The method using direct determination without extraction and derivatization has a detection limit of approximately 0.02% (Bondioli *et al.*, 1992). This seems to be insufficient to control the quality of biodiesel according to the standards. A concentration step using extraction of glycerol with water and gas chromatographic separation on a Carbowax-coated capillary column leads to a detection limit of approximately 0.002% (Hödl & Schindlbauer, 1994). The most sensitive method, with a detection threshold of $10^{-4}\%$, uses derivatization of the sample and separation on a methyl silicone fluid-coated capillary column with FID- or MS-detection (Mittelbach, 1993). This method has the advantage of high sensitivity and simple sample preparation. The method including extraction has the advantage of separation of glycerol from the organic matrix prior to gas chromatographic determination.

Both gas chromatographic methods, as well as the enzymatic method, have been thoroughly tested and evaluated in recent years with a large number of different samples. As a result of interlaboratory studies, it can be shown that the accuracy and the precision of these methods are comparable. The mean standard deviation for the gas chromatographic methods was found to be 0.003% mass and that for the enzymatic method 0.002%.

The right choice of the method depends mainly on the analytical equipment which is available. The gas chromatographic methods can be operated fully automatically, which is a prerequisite for routine analysis. If gas chromatographic equipment is not available, the more time-consuming enzymatic method can also be used.

Bonded glycerol; mono-, di- and triglycerides

One method for the determination of glycerides as a sum parameter, called bonded glycerol, includes saponification of the sample and analysis of the total glycerol following the enzymatic method (Bailer &

de Hueber, 1991). This method, especially developed for the analysis of RME-samples, cannot distinguish between mono-, di- and triglycerides. The ratio of these components can vary significantly depending on the transesterification process and might have an important influence on the combustion characteristics.

For the determination of glycerides in different matrices, a series of analytical methods are practicable, but only three chromatographic methods have proven to be applicable for biodiesel analysis. The first method described for the analysis of transesterification mixtures used thin-layer chromatography/flame-ionization detection (TLC/FID) with an Iactroscan instrument (Freedman *et al.*, 1984). Separation of transesterification mixtures can also be performed by HPLC with light-scattering detection (Bruns, 1988) or density detection (Trathnigg & Mittelbach, 1990). Using a conventional refractive-index detector, a high dependence of the response factors on the fatty acid composition can be observed (Trathnigg, 1991). Both TLC- and HPLC-methods have the advantage of little sample preparation, a quick analysis time, and the possibility of performing automatic analyses. Furthermore, the different glycerides are separated as a sum of each of the glyceride species, therefore, no further separation according to the chain length occurs. The major disadvantage of these methods is the lower accuracy and precision compared to gas chromatography. The detection threshold is 0.1–0.2% and this might be also too high for the analysis corresponding to the limits proposed in several standard specifications. These methods, however, are excellent for the rapid analysis of reaction mixtures during transesterification processes.

Therefore, several gas chromatographic methods have been developed for the analysis of glycerides in transesterification mixtures. The methods include derivatization with a silylating reagent and separation on capillary columns (Freedman *et al.*, 1986; Mariani *et al.*, 1991). Further development led to a detailed description of a fast and reliable gas chromatographic procedure for biodiesel analysis (Plank & Lorbeer, 1992). The method can also be used for the simultaneous determination of glycerides and free glycerol (Plank & Lorbeer, 1995). Therefore, only gas chromatography meets all demands for an analytical method for the determination of low contents of mono-, di- and triglycerides in biodiesel. The required analytical

Table 3. Factors for conversion of content of glycerides (% m/m) into content of bonded glycerol (% m/m)

Species of glyceride	Mean molecular mass	Conversion factor
Monoglycerides	355.4	0.259
Diglycerides	618.7	0.149
Triglycerides	882.0	0.104

Table 4. Maximum concentrations of individual glycerides leading to a content of bonded glycerol of 0.22%

Species of glyceride	Maximum concentration
Monoglycerides	0.85%
Diglycerides	1.48%
Triglycerides	2.12%

hardware is standard instrumentation in nearly all analytical laboratories. Analyses can be fully automated. As interlaboratory tests have shown, one crucial point, however, is the purity of commercially available standard substances, especially monoglycerides, which can lead to inaccurate analyses. The purity of the standard substances should be checked by HPLC prior to analysis of biodiesel.

Out of the gas chromatographic data, concerning the content of mono-, di- and triglycerides, one can easily calculate the amount of bonded glycerol. In Table 3 the factors for the conversion of content of individual glycerides into bonded glycerol are listed based on the mean molecular mass of the fatty acids in rapeseed oil (281.3 g/mol)

According to the Austrian Ö-NORM the content of total glycerol is limited to 0.24% and free glycerol to 0.02%. This indirectly limits the concentration of bonded glycerol to 0.22%. Table 4 gives the maximum concentrations of the individual glycerides, each leading to the threshold limit of 0.22%, on the assumption that only one species of glyceride exists in the sample.

CONCLUSIONS

As production and utilization of biodiesel is increasing in different countries all over the world, there is a need for the installation of standards defining a quality which guarantees long-term operation of a diesel engine without any difficulties. It is also a prerequisite for the clearance of engines from engine manufactures. Particularly when using different oils and fats, including waste cooking oil or animal fat for the production of biodiesel, it is necessary to meet specific standards. The limits of the parameters defining the quality of biodiesel are quite similar in different countries; still in discussion are the limitations for the content of water, of glycerides and of higher unsaturated fatty acids. Particularly for the determination of the content of free glycerol and the different glycerides, it is necessary to develop and define standardized analytical procedures.

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