Biodiesel patterns reflect

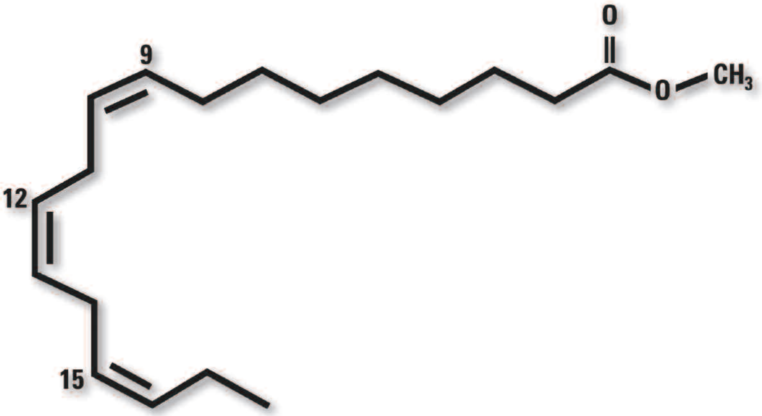

Figure 1: Structural formula for linolenic acid methyl ester (methyl cis,cis,cis-9,12, 15-octadecatrienoate)

Figure 2: GC-2010AF with AOC-20i+s

In the last years, biofuels have become well established as an independent source of energy in the industrial countries. The percentage of biofuels in the energy mix is expected to increase considerably within the next 10 to 15 years in order to reduce dependence on fossil fuels and to maintain energy prices at long-term affordable levels. Biofuels will also have a positive impact on CO_2 levels and climate change.

Bio-ethanol and biodiesel are presently the most important liquid biofuels. So-called “second-generation biofuels” are still under development. Via BTL (**B**iomass **T**o **L**iquid), biofuel production processes are designed to convert the greatest possible energy content from the plant to the liquid fuel.

Increasing importance of biofuels

Based on the amount of freight transportation, the need for diesel fuels and consequently biodiesel, is significant compared to other biofuels in the European Union. Should the European Parliament agree with the proposal of the European Commission, EU member states will add at least 10 % biofuel to fossil fuels before the year 2020. In Europe, the demand for biodiesel will further increase, leading to a continuous search for suitable plant oils and animal fats that can be used as raw material. Experience shows that the quality of the starting materials has an enormous impact on the quality of biodiesel. Continuous quality control therefore remains necessary in order to meet the demands of modern diesel generators.

“Pattern” of fatty acid methyl esters

The composition of biodiesel varies depending on the plant oil applied. When animal fats are also used in the production process, the number of different fatty acid methyl esters (FAME, for an example see Figure 1)

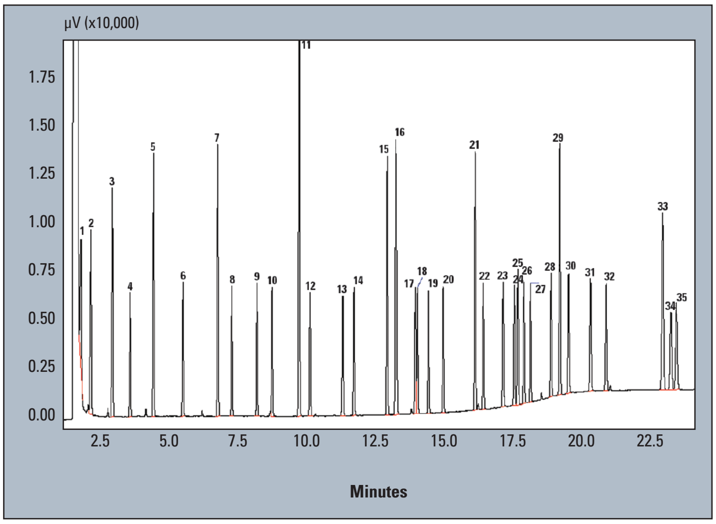

Figure 3: Supelco standard “37 Component FAME Mix” separated on a Restek FAME-WAX column. Not separated are the cis/trans isomers C18:1 (16). The signals (1)-(6) of fatty acid methyl esters C6:0 up to C13:0, C4:0 were not separated from the solvent. Method: carrier gas helium; linear velocity mode 35 cm/s; split injection 1:20; oven 150 °C 1 min; 5 °C/min up to 240 °C 5 min; FID 250 °C.

quality

increases due to fatty acids with even carbon number in addition to animal fats containing uneven carbon number FAMES. Quality control according to DIN EN 14103 is carried out to determine the "pattern" of fatty acid methyl esters and to guarantee that the main biodiesel components are within a defined boiling point range. The content of polyunsaturated linolenic acid is also determined. While this compound is a welcome essential acid in salad oils, it is an interfering reactive compound in biodiesel that can influence long-term stability.

A Shimadzu GC-2010AF with AOC-20i autosampler (Figure 2) was used for FAME analysis. Figure 3 shows a chromatogram of the fatty acid methyl esters of the Supelco standard "37 Component FAME Mix" (Cat. No. 47885-U), used for the identification of the individual components. The standard contains fatty acid methyl esters C4:0 up to C24:1. The designation Cx:y refers to the carbon number or C-number (x) of the corresponding fatty acid as well as the number of double bonds (y). When y is larger than 0, it is an unsaturated fatty acid. Accordingly, the polyunsaturated linolenic acid (Figure 1) is designated as C18:3.

Animal fats differ from plant oils

Using the special Restek FAMEWAX column (FAMEWAX 30 m; ID 0.25 mm; df 0.25 µm; Cat No. 12497) it is possible to completely separate all fatty acid methyl esters, with the exception of the oleic acid methyl ester C18:1 cis/trans isomers. The analysis time of approximately 24 minutes can be shortened to less than 16 minutes if the complete C18:2 cis/trans separation is omitted.

For analysis according to DIN EN 14103, a complete separation is not required, since only the mass percentage of all fatty acid methyl esters within the range of C14:0 up to C24:1 is measured. It is important to take into account signal superposition of the sample components with those of the added internal standard C17:0. For plant oils this is not a problem, as only even-numbered chain lengths occur. For animal fats, however, which also consist of unevenly numbered fatty acids, co-elution with the internal standard must be corrected for if necessary.

Figure 4 shows the measurement of a biodiesel sample using the same method as described under Figure 3. For evaluation, the sum of all signal areas of C14:0 and C24:1 is calculated, which also takes into account the areas of unidentified signals. Using the following formula, the fatty acid methyl ester content C in % (m/m) can be calculated according to DIN EN 14103:

$$C = \frac{(\Sigma A) - A_{ISTD}}{A_{ISTD}} x \frac{C_{ISTD} x V_{ISTD}}{m} x\ 100\ \%$$

ΣA	total signal area of all methyl esters from C14:0 up to C24:1 (15734000 µV*s)
A_{ISTD}	signal area of the internal standard heptadecanoic acid methyl ester C17:0 (2644200 µV*s)
C_{ISTD}	concentration of the heptadecanoic acid methyl ester in the internal standard solution used (10 mg/mL)
V_{ISTD}	volume of the internal standard solution added (5 mL)
m	mass of the weighed biodiesel sample (250 mg)

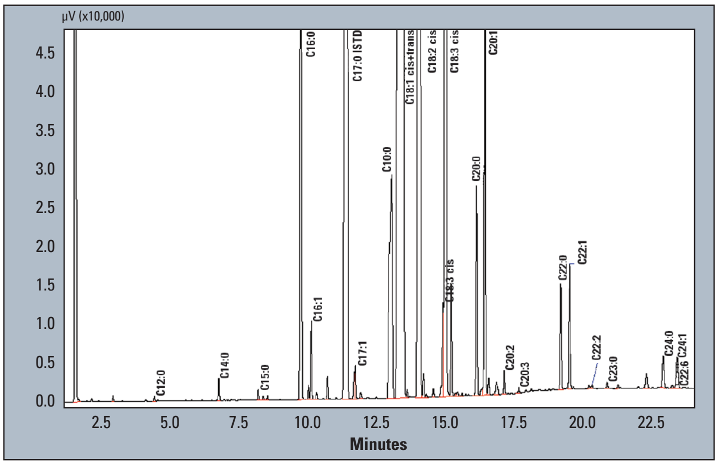

Figure 4: Biodiesel sample measured using the same method as described under Figure 3. The split ratio was increased to 1:50.

For the measured biodiesel sample (Figure 4), a fatty acid methyl ester content of 99.0 % is determined. A fatty acid methyl ester content of greater than 90 % is required. The linolenic acid methyl ester content L is calculated using the following equation:

$$L = \frac{A_L}{(\Sigma A) - A_{ISTD}} x\ 100\ \%$$

A_L	signal area of linolenic acid methyl ester C18:3 (991200 µV*s)
ΣA	total signal area of all methyl esters from C14:0 to C24:1 (15734000 µV*s)
A_{ISTD}	signal area of the internal standard heptadecanoic acid methyl ester C17:0 (2644200 µV*s)

The result is 7.6 % linolenic acid and this is well within the allowed range of 1 % up to 15 % (m/m). For determination of the iodine number the mass percentage of the marked fatty acid methyl esters can be calculated with the same formula (see components indicated with an asterisk in table 1, page 6). The weighting factors for these compounds are listed in DIN EN 14214 appendix B. When the respective percentage of the methyl ester is multiplied with the assigned factor and the results are summarized, the iodine number is obtained. In this case the result is 109 g iodine/100 g (limit value 120 g iodine/100 g).

Reproducibility of the measurements

When the same biodiesel sample is measured repeatedly with the same instrument, DIN EN 14103 allows a maximum difference in methyl ester content of 1.6 % (m/m) for two arbitrary results. Using the GC-2010 in combination with the AOC-20i autosampler, 24 measurements resulted in a range over all results of 0.2 % (m/m) – the difference between the largest and the smallest measured value was therefore 8 times less than the required value in the norm.

Peak No.	Name	
7	Tetradecanoic acid methyl ester	C14:0
8	cis-9-tetradecenoic acid methyl ester	C14:1
9	Pentadecanoic acid methyl ester	C15:0
10	cis-10-Pentadecenoic acid methyl ester	C15:1
11	Hexadecanoic acid methyl ester	C16:0
* 12	Methyl cis-9-Hexadecenoate	C16:1
13	Heptadecanoic acid methyl ester	C17:0
14	Methyl cis-10-heptadecenoate	C17:1
15	Methyl Octadecanoate	C18:0
* 16	Methyl cis-9-octadecanoate and Methyl trans-9-octadecenoate	C18:1cis+trans
* 17	cis,cis-Octadeca-9,12-dienoic acid methyl ester	C18:2 cis
* 18	trans,trans-Octadeca-9,12-dienoic acid methyl ester	C18:2 trans
* 19	trans-6,9,12-Octadecatrienoic acid methyl ester	C18:3 trans
* 20	Methyl cis,cis,cis-9,12,15-Octadecatrienoate Linolenic acid methyl ester	C18:3 cis
21	Eicosanoic acid methyl ester	C20:0
* 22	cis-11-Eicosenoic acid methyl ester	C20:1
23	cis-11,14-eicosadienoic acid methyl ester	C20:2
24	cis-11,14,17-ecosatrienoic acid methyl ester	C20:3
25	cis-8,11,14-Eicosatrienoic acid methyl ester	C20:3
26	cis-5,8,11,14-Eicosatrienoic acid methyl ester	C20:4
27	cis-5,8,11,14,17-Eicosapentaenoic acid methyl ester	C20:5
28	Heneicosanoic acid methyl ester	C21:0
29	Docosanoic acid methyl ester	C22:0
* 30	Methyl cis-13-Docosenoate	C22:1
31	cis-13,16-Docosadienoic acid methyl ester	C22:2
32	Tricosanoic acid methyl ester	C23:0
33	Methyl Tetracosanoate	C24:0
34	cis-4,7,10,13,16,19-Docosahexaenoic acid methyl	C22:6
35	Methyl cis-15-tetracosenoate	C24:1

Table 1: Fatty acid methyl esters of C14:0 up to C24:1 (in accordance with the DIN EN 14103 predetermined range). *unsaturated methyl esters, used for determination of the iodine number in accordance with DIN EN 14214 appendix B.

Measuring value	Methyl ester content	Linolenic acid content
Mean value % (m/m)	98.9	7.55
Standard deviation % (m/m)	0.06	0.06
Maximum value % (m/m)	99.0	7.56
Minimum value % (m/m)	98.8	7.55
Difference max.-min.-value % (m/m)	0.2	0.01

Table 2: Reproducibility over 24 measurements of the same biodiesel sample using Shimadzu's GC-2010 und AOC-20i. The table shows the statistical data including the relative standard deviation and range of all results (max.-min.-value).

For the determination of linolenic acid, a similar result is obtained. Over 24 measurements the range over all results was only 0.01 % (m/m). The norm allows for a value ten times higher of 0.1 % (m/m). All statistical results of the performed measurement sequence are summarized in Tab. 2.

Summary

The strongly increasing demand for biofuels inevitably leads to a shortage of the required raw materials until world agriculture production will be able to accommodate the growing demand. Independently of this development, the fast-rising energy costs will require new and independent energy sources. This means for biodiesel that in addition to the plant oils presently used, new raw materials will have to be applied in order to cover the growing demand in the future. The requirements on measuring technology and applications will focus on the continuous adaptation to new developments in order to guarantee a steady quality of biofuels also in the future. Shimadzu has been involved in biofuel quality control for almost 10 years and will also work on new solutions together with its customers.

TELEGRAM

On the safe side

ZVEI user-forum "RoHS in daily practice"

Although RoHS regulations have applied since 1 July 2006, they have not suffered from any lack of current attention. This became convincingly evident to the 100 participants from the electrical and electronics industry during a user meeting on the topic "RoHS in daily Practice" organized by the ZVEI (Zentralverband Elektrotechnik- und Elektronikindustrie e.V. – Association of the Electrical and Electronics Industry in Germany) on November 17, 2007 in Frankfurt am Main, Germany.

Many aspects of the RoHS guidelines were hotly discussed. Phrases such as "homogeneous material" or "mechanical disjointing" still lead to misinterpretation and must, therefore, be defined in legally binding terms in order to create certainty. The ZVEI pointed out that in addition to the European RoHS regulations, similar legislation applies in countries such as Korea, China, Australia, Japan and several US states.

In order to avoid economic disadvantage for manufacturers or importers, reliable analytical determinations are indispensable. False analyses of construction elements based on incorrect measurements can lead to rejection of complete instruments by enforcement authorities at the borders. Seamless analyses with hardware and software for the reliable determination of "RoHS elements" as well as competence and know-how, as offered by Shimadzu, will help manufacturers and processing companies to remain on the safe side.

RoHS (2002/95/EG):
Since 1 July 2006, the **R**estriction **o**f **H**azardous **S**ubstances" (RoHS) regulations are in place within the EU, limiting the use of certain hazardous compounds in electronic devices. According to the RoHS guidelines, lead, cadmium, mercury, chromium (VI) and certain bromine-containing flame retardants (PBB and PBDE) may not be applied in amounts exceeding the established maximum value.