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Application News

Gas Chromatograph

Determination of Ester and Linolenic Acid Methyl Ester Contents in Biodiesel According to EN 14103:2020

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User Benefits

- Nexis™ GC-2060 provides reliable analysis of biodiesel samples regarding their ester and linolenic acid methyl ester contents using hydrogen as a cost-effective carrier gas
- It delivers excellent repeatability and provides appropriate safety measures for the use of hydrogen as carrier gas
- The optional multi-mode injection unit (MMI) offers performance equivalent to a conventional split-splitless injection unit (SPL), significantly reducing maintenance downtime

■ Introduction

Biofuels play an important role in enabling countries to meet their greenhouse gas reduction targets. They can be produced from a range of raw materials, including plant oils, animal fats, and used cooking oils. Biodiesel is mainly being produced from rapeseed, soybean, and palm oils. Due to this diversity of feedstocks, continuous quality control is necessary as the quality of the raw material has an enormous impact on the quality of the biodiesel.

The EN 14103:2020 describes the determination of total ester content and linolenic acid methyl ester content in biodiesel by means of gas chromatography with flame ionization detection (GC-FID). The total ester content covers a range of fatty acid methyl esters (FAME) from C6 to C24, and linolenic acid methyl ester is investigated separately as interfering reactive compound that might influence long-term stability of the biodiesel. According to the standard, the total ester content must be greater than 90 % (m/m) and the linolenic acid methyl ester content shall be between 1 and 15 % (m/m)[1].

This study shows the analysis of biodiesel originating from rapeseed, soybean, and palm oil using the Nexis GC-2060.

■ Sample Preparation and Calculations

250 mg of the homogenized FAME sample was mixed with 100 mg of nonadecanoic acid methyl ester (C19:0) as internal standard (ISTD) and diluted with 10 mL of toluene. 1 µL of this solution was analyzed via GC-FID.

The ester content was calculated as mass percentage using the following formula:

$$\frac{\sum(A_x \times R_x) - A_{ISTD}}{A_{ISTD}} \times \frac{W_{ISTD}}{W} \times P \times 100$$

with

- A_x : Peak area of the individual methyl ester X in the sample
- R_x : Theoretical FID correction factor (TCF) for FAME X relative to the ISTD C19:0 (as given in EN 14103:2020)
- A_{ISTD} : Peak area of the ISTD C19:0
- P : Purity of the ISTD C19:0 standard
- W_{ISTD} : Weight of the ISTD C19:0 standard (in mg)
- W : Weight of the sample (in mg)

The linolenic acid methyl ester (C18:3) content was calculated as mass percentage using the following formula:

$$\frac{(A_L \times R_L) - A_{ISTD}}{A_{ISTD}} \times \frac{W_{ISTD}}{W} \times P \times 100$$

with

- A_L : Peak area of C18:3 in the sample
- R_L : TCF for C18:3 relative to C19:0 (as given in EN 14103:2020)

Other variables are alike the first equation

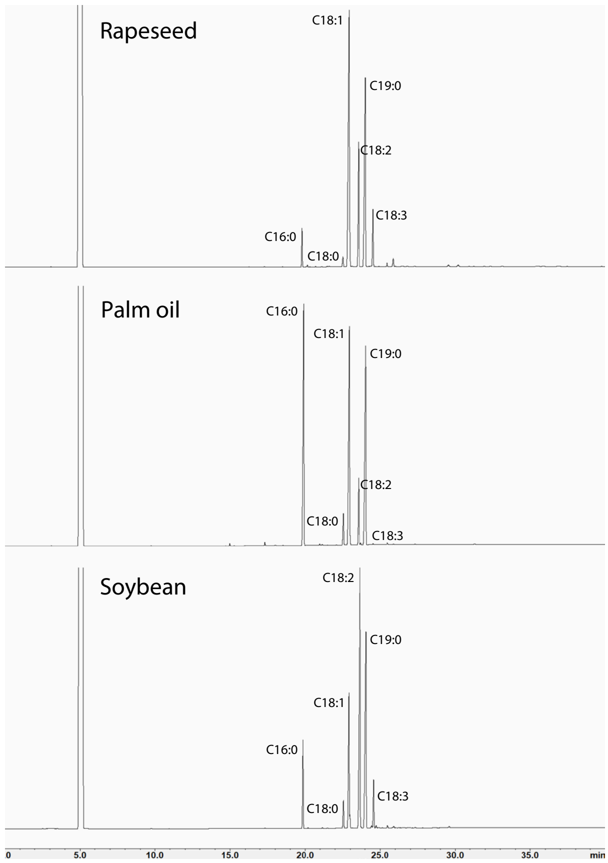

Fig. 1 Chromatograms of exemplary biodiesel samples: rapeseed-based (top), palm oil-based (middle), and soybean-based (bottom)

■ Results

Figure 1 shows exemplary chromatograms of the biodiesel samples analyzed. Table 1 summarizes the ester and linolenic acid methyl ester contents determined for the three samples. All tested biodiesels showed an ester content above 97 % and their linolenic acid methyl ester content remained well below the 15 % limit.

Table 1 Ester contents of exemplary biodiesel samples

Biodiesel	Ester Content (%)	Linolenic Acid Methyl Ester Content (%)
Rapeseed	97.4	8.5
Palm oil	97.3	0.3
Soybean	97.8	7.3

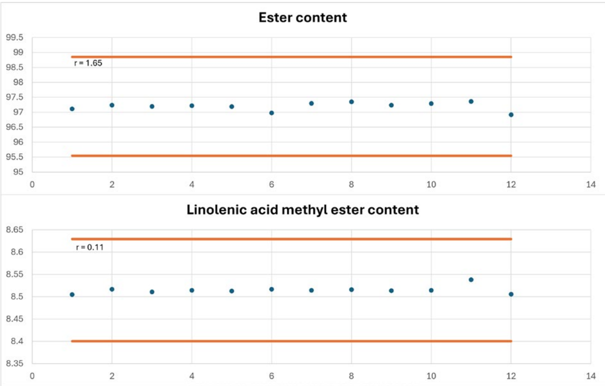

Fig. 2 Repeatability of ester content (top) and linolenic acid methyl ester content (bottom) for 12 injections of an exemplary biodiesel sample

To investigate reliability of the analysis, the same sample was measured 12 times. The %RSD values for the ester and the linolenic acid methyl ester content were found to be 0.1 %. The repeatability *r* was calculated based on EN 14103:2020 requirements. For the ester content, an *r* value of 1.65 is given in the standard, whereas the *r* value for linolenic acid methyl ester is calculated for the respective data set based on the following formula:

$$r = 0.0092 \times (X + 3.9180)$$

with X: Average of the test results being compared

Figure 2 shows the repeatability of a rapeseed-based biodiesel sample, which is well within the limits given by the standard for the ester content (top) and the linolenic acid methyl ester content (bottom).

■ Multi-Mode Injection Unit as Alternative

Shimadzu's multi-mode injection unit (MMI) offers reliable split-splitless mode functionality over a broad range of carbon numbers. It allows analysis of biodiesel samples with high repeatability and provides chromatographic results comparable to those measured with SPL as dedicated split-splitless injection unit. The use of MMI significantly shortens maintenance downtime from tens of minutes for a classical split-splitless injection unit to just a few minutes. Figure 3 gives a direct comparison of an exemplary rapeseed-based biodiesel sample measured with SPL (top) and MMI (bottom).

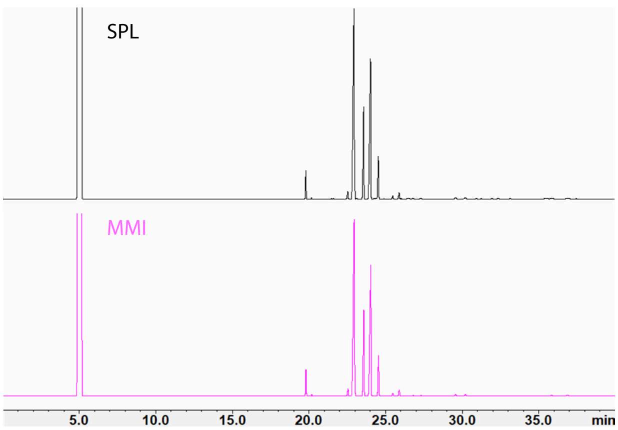

Fig. 3 Chromatograms of exemplary rapeseed-based biodiesel samples measured via SPL injection (top) and MMI injection (bottom)

Fig. 4 Gas chromatograph Nexis™ GC-2060 with autosampler AOC™-30i

■ Configuration and Analysis Conditions

Table 2 summarizes the instrument configuration (Fig. 4) and the analysis conditions used in this study.

Table 2 Instrument configuration and analysis conditions

Model	: Nexis GC-2060 with AOC-30i
Column	: SH-PolarWax (30m x 0.25 mm x 0.25 µm)*
Inj. Temp.	: 250 °C
Inj. Mode	: Split 1:50
Carrier Gas	: Hydrogen
Linear Velocity	: 20.8 cm/s
Column Temp.	: 60 °C (2 min) – 10 °C/min – 200 °C – 5 °C/min – 240 °C (16 min)
Det. Temp.	: 250 °C
Det. Gas Flows	: Default Values
Analysis time	: 40 min

* P/N: 227-36305-02

■ Conclusion

Nexis GC-2060 provides reliable analysis of biodiesel samples regarding their ester and linolenic acid methyl ester content according to EN 14103:2020, covering the various ester types commonly in use. It allows repeatable analysis using hydrogen as a cost-effective carrier gas. The optional multi-mode injection unit (MMI) can be selected as alternative to a classical split-splitless injection unit (SPL).

<Acknowledgments>

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<References>

1) EN 14103:2020, Fat and oil derivatives - Fatty Acid Methyl Esters (FAME) - Determination of ester and linolenic acid methyl ester contents

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