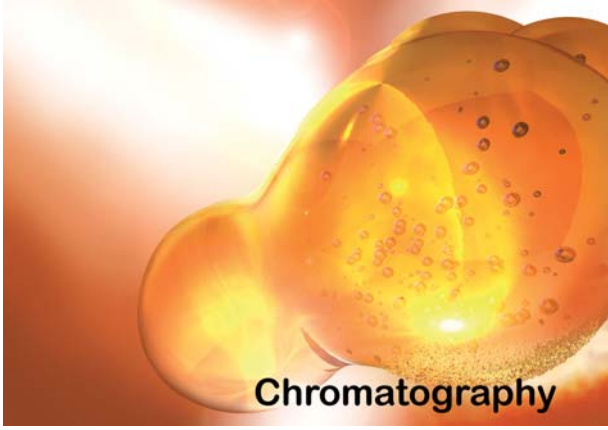
Application Note



Biodiesel Quality Control

according to DIN EN 14105
Determination of free and total glycerol and mono-, di, triglyceride contents (reference method)

Introduction

Biodiesel is an interesting alternative to the decreasing resources for mineral fuels. It can be manufactured from all kinds of plant oils or even fats from fryers. Because of the high viscosity the direct usage of those regenerative energy resources in diesel cars requires expensive modifications on motor and tank. Therefore the transesterification (Fig. 1) of the glycerol esters to Fatty Acid Methyl Esters (FAME) is preferred. FAMEs are less viscous and remain fluid even at low temperatures. They can be used in many diesel cars instead of mineral diesel without changes to the car. Presently the biggest market for biodiesel is the addition to mineral fuels (e.g. B5; up to 5% biodiesel in mineral diesel)

Biodiesel mainly consist of methyl esters of the following fatty acids:

Palmitic acid C_{16} (saturated)
Stearic acid C_{18} (saturated)
Oleic acid C_{18} (unsaturated)
Linoleic acid C_{18} (poly unsaturated)

The distribution changes depending on the plant oil used (see table 1). In principal all fatty acids with chain lengths from C_{14} to C_{24} might be found (in case of plant oils only the even numbers).

Property Fatty acid in %	Rape seed	Sun flower	Palm tallow	Beef
Palmitic	5	6	42	28
Stearic	1	4	5	19
Oleic	60	28	41	45
Linoleic/Linolenic	30	61	10	5

Tab. 1: Approximate content of fatty acids in different oils and fats.

FAMEs are the products of the following reaction:

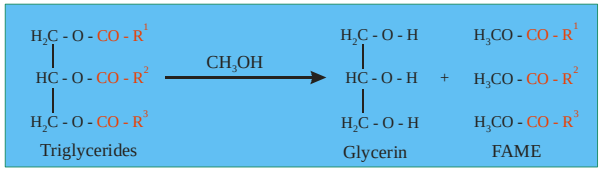


Fig. 1: Transterification of Tri-glycerols to FAME

Depending on the process parameters the transesterification is more or less quantitative. Generally a certain amount of mono-, di-, and tri-glycerides remains in the biodiesel. Additionally the surplus of methanol and the by-product glycerine must be removed during the biodiesel production. In the quality control procedure according to DIN EN 14105 or ASTM D 6584-00 the contents of the glycerine, mono-, di-, and tri-glycerides are determined. The methanol content is measured with headspace technique described in the DIN EN 14110.

Sample preparation

Preparation of standard solutions

Gas chromatography is a relative technique. Every component must be calibrated before it can be quantified in unknown samples. In case of biodiesel one mono-, di, and triglyceride is calibrated as a representative of the other components of each group.
According to DIN EN 14105 an Internal Standard Calibration based on two components is used with this application.

Derivatisation of the samples with MSTFA is crucial for improvement of peak shape and chromatographic separation.

The different levels contain the following concentrations in mass % for the given components:

Calibration Level	Glycerin	Mono-	Di-	Tri-

Conc. in mass %		olein	olein	olein
1	0.005	0.2	0.05	0.05
2	0.02	0.8	0.2	0.2
3	0.035	1.4	0.35	0.35
4	0.05	2	0.5	0.5

Tab. 2: Compound concentrations of the four calibration levels (given in mass %)

Fig. 2 shows the typical chromatogram of such a Biodiesel standard solution.

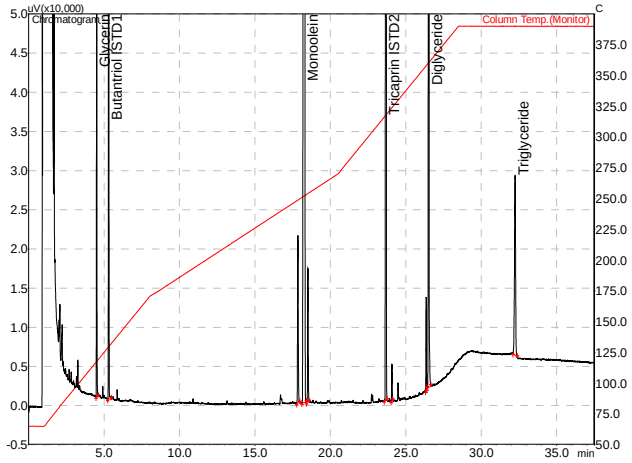


Fig. 2: Chromatogram of a Biodiesel standard

Preparation and derivatisation of unknown biodiesel samples

100mg biodiesel is given into to a 10ml flask the internal standard solution and 100µl of MSTFA are added. Close the flask, tighten, and shake it well. The derivatisation needs minimum 15 minutes at room temperature. After that time add 8ml of n-heptane to each flask and shake again.

After leak check and conditioning of the instrument a first sample can be injected. The DIN EN 14105 recommends a non-polar column with length of 10m, ID (inner diameter) 0.32mm, film thickness 0.1µm. This is a good column to start with but most operators prefer a longer column (12 to 25 m). With smaller ID a better resolution can be achieved even with a shorter column (e.g. Zebron ZB-5HT, 15m ID 0.25mm df 0.1µm). Generally smaller ID allows a faster chromatography but optimization of the gas chromatographic method might need more time.

Gas chromatographic Instrumentation and Method

GC:	GC-2010AF with OCI
Sampler:	AOC-20i
Column:	HT5, 25 m, ID 0.32 mm, df 0.1 µm
Carrier gas:	Helium
Control Mode:	constant linear velocity
Injection Mode:	direct
Linear velocity:	50 cm/s
Septum Purge:	3 ml/min

The injection technique used is “Cool on column” injection (OCI) to avoid discrimination effects. For OCI a wide-bore column (retention gap) has to be used and can then be coupled to a narrow-bore column for separation with better resolution. Fig. 3 shows a chromatogram of a biodiesel sample measured on a SGE 25 m HT5, ID 0.32 mm df 0.1 µm with retention gap.

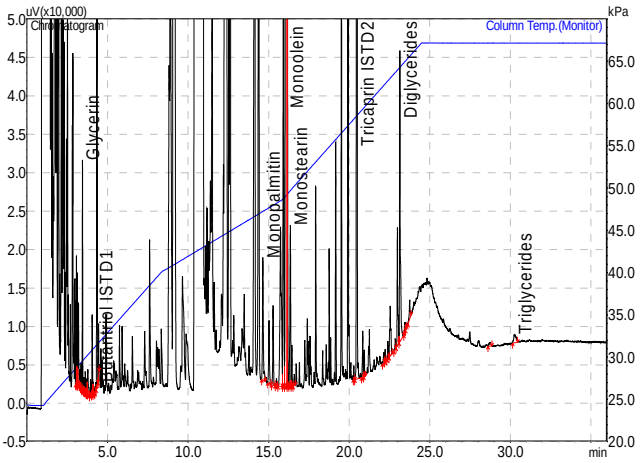


Fig. 3: Chromatogram Biodiesel sample

An alternative is the “Simple On Column” injection technique offered by Shimadzu. Instead of a retention gap a special deactivated glass liner is used. In this case no column connectors have to be used, which could become leaky, especially at the elevated temperatures used for this application.