APPLICATION NOTE

ASTM D6584 Determination of Free and Total Glycerol, mono-, di,- tri-glycerides in FAME with AC Biodiesel All in One Solution

- **Compliant to ASTM D6584-10a**
- **Included QC materials**
- **Dedicated Software for Biodiesel specific reporting**

Keywords:
FAME, ASTM D6584, Biodiesel All-in-one, Free and Total Glycerol, Mono-, di-, and triglycerides.

INTRODUCTION

Biodiesel is the “green” equivalent for petroleum diesel or petrodiesel. Biodiesel is a renewable fuel derived from algae, vegetable oils, animal fats or cooking oils. The most important environmental benefit of biodiesel is that it is biological degradable, less poisonous and does not contain aromatics and very low sulfur. Therefore, burning biofuels release less sulfur oxides and carbon monoxide.

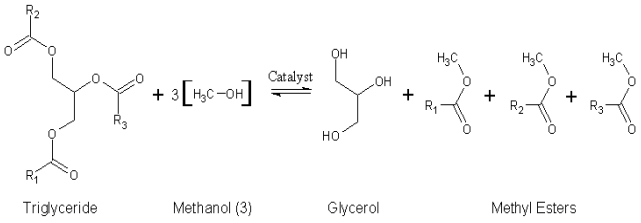


Figure 1: Trans esterification of triglyceride to FAME.

Quality requirements of biodiesel for use as pure biofuel or blending stock for diesel fuel are defined in ASTM D6751 and EN 14214 specification. The standards ensure that important factors in the fuel production process are monitored: reaction conversion yield, removal of glycerol, absence of Poly Unsaturated Fatty Acids (PUFA), removal of alcohol and absence of free fatty acids.
Method ASTM D6584 is mandated for the determination of Free & Total Glycerol, mono-, di- and triglycerides in Fatty Acid Methyl Esters (FAME).

SOLUTION

The AC Biodiesel All in One fully complies with the latest version of ASTM D6584. It combines all major Biodiesel methods in one complete solution.

After derivatisation with MSTFA, the sample is introduced into the Temperature Programmable Inlet (TPI), where it is mixed with clean carrier gas and directed to the analytical PDMS column. The capillary column separates the individual components in a temperature programmed oven after which they are detected by the FID. Instrumental conditions are inserted in Fig 3.
Calibration is achieved by the use of two internal standards and four reference materials (Fig 1). Mono-, di-, and triglycerides are determined by comparing to monoolein, diolein, and triolein standards respectively. Average conversion factors are applied to the mono-, di- and triglycerides to calculate the bonded glycerin content of the sample.

Solution	Component	Approximately Wt concentration [µg/ml]
1	Glycerol	5
	Triolein	50
	1-monooleoyl-rac-glycerol (monoolein)	100
	1,3-diolein	50
2	Glycerol	15
	Triolein	100
	1-monooleoyl-rac-glycerol (monoolein)	250
	1,3-diolein	100
3	Glycerol	25
	Triolein	200
	1-monooleoyl-rac-glycerol (monoolein)	500
	1,3-diolein	200
4	Glycerol	35
	Triolein	350
	1-monooleoyl-rac-glycerol (monoolein)	750
	1,3-diolein	350
5	Glycerol	50
	Triolein	100
	1-monooleoyl-rac-glycerol (monoolein)	1000
	1,3-diolein	500
ISTD #1	Butanetriol	1000
ISTD #2	Tricaprin	8000

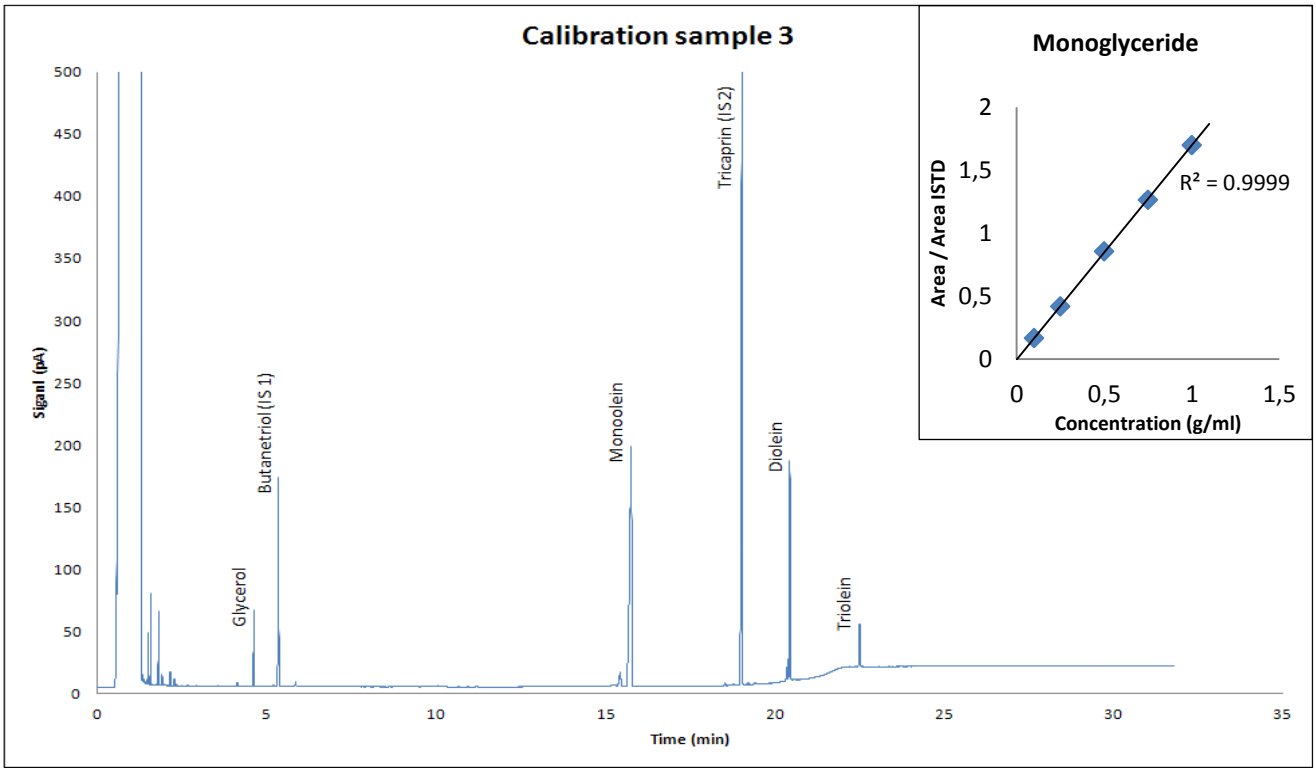
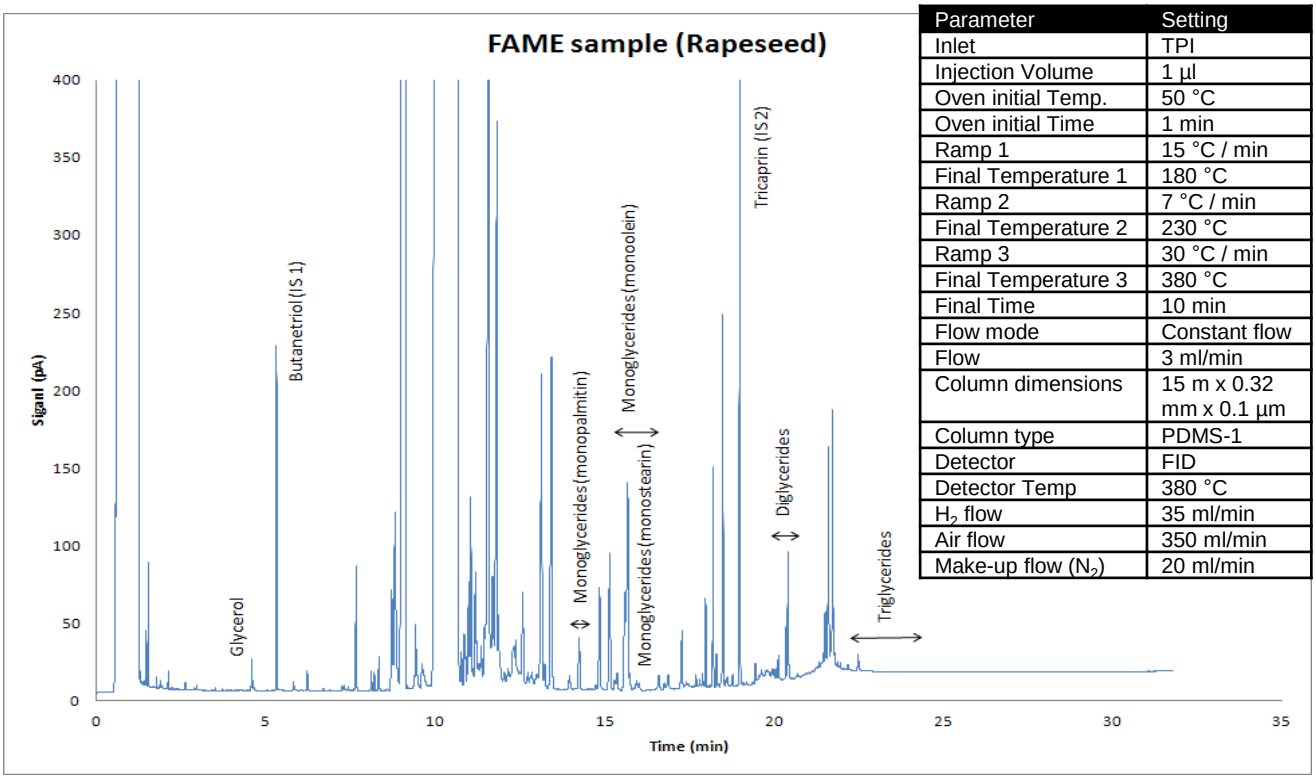
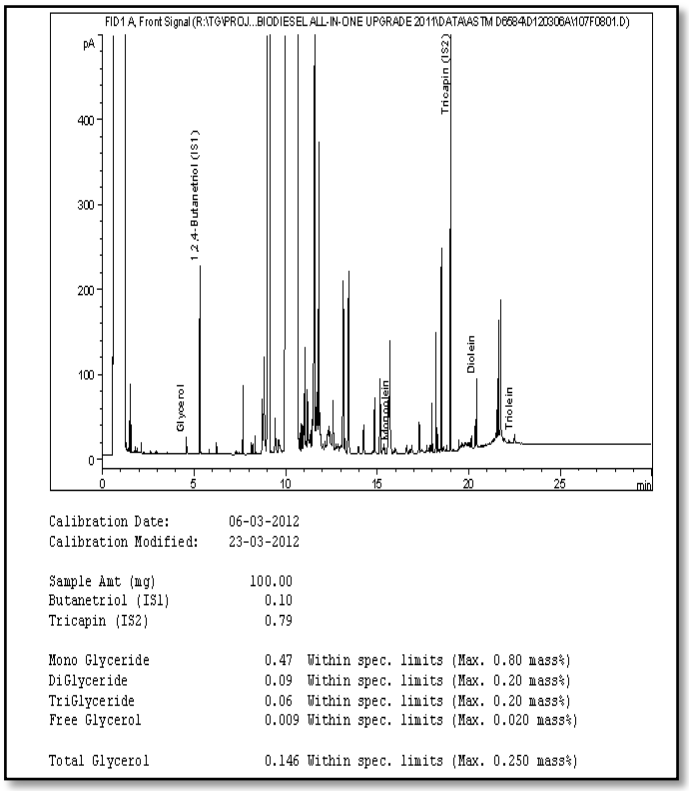


Figure 2: Calibration sample 3



Parameter	Setting
Inlet	TPI
Injection Volume	1 µl
Oven initial Temp.	50 °C
Oven initial Time	1 min
Ramp 1	15 °C / min
Final Temperature 1	180 °C
Ramp 2	7 °C / min
Final Temperature 2	230 °C
Ramp 3	30 °C / min
Final Temperature 3	380 °C
Final Time	10 min
Flow mode	Constant flow
Flow	3 ml/min
Column dimensions	15 m x 0.32 mm x 0.1 µm
Column type	PDMS-1
Detector	FID
Detector Temp	380 °C
H_2 flow	35 ml/min
Air flow	350 ml/min
Make-up flow (N_2)	20 ml/min

Figure 3: FAME sample (Rapeseed)



Calibration Date: 06-03-2012
Calibration Modified: 23-03-2012

Sample Amt (mg)	100.00	
Butanetriol (IS1)	0.10	
Tricapin (IS2)	0.79	
Mono Glyceride	0.47	Within spec. limits (Max. 0.80 mass%)
DiGlyceride	0.09	Within spec. limits (Max. 0.20 mass%)
TriGlyceride	0.06	Within spec. limits (Max. 0.20 mass%)
Free Glycerol	0.009	Within spec. limits (Max. 0.020 mass%)
Total Glycerol	0.146	Within spec. limits (Max. 0.250 mass%)

Figure 4: Sample report

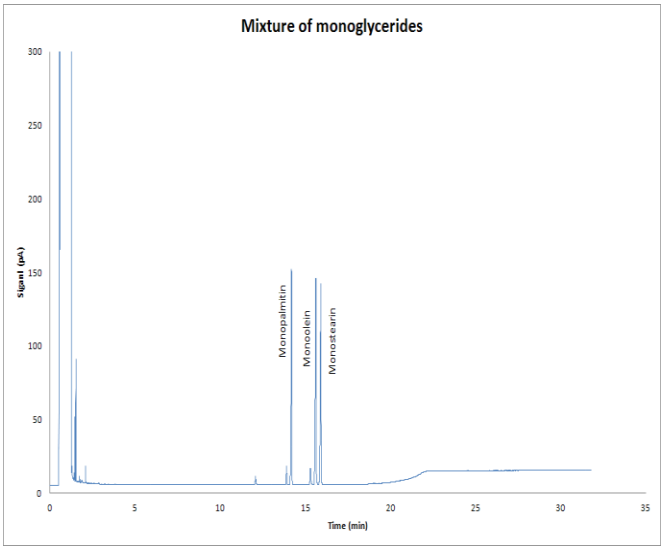


Figure 5: QC-Mixture of monoglycerides (used to locate relevant peaks).

RESULTS

A typical chromatogram for the mid level calibration standard is shown in figure 2. Good linearity is obtained for all calibrated peaks (R^2 > 0.995). Glycerol is quantified as a single peak, with butanetriol as the internal standard. The mono-, di-, and triglycerides are quantified as timed groups, with tricaprin used as an internal standard.

An example of a sample (rapeseed source) is shown in figure 3. Dedicated report templates will show all relevant results, information and chromatogram. Total glycerol is calculated by applying average conversion factors for the mono,- di-, and triglycerides. Reported Results are checked against specifications and reported within or out of spec. *(figure 4).*

CONCLUSION

The performance of the AC Biodiesel All in One is demonstrated for ASTM D6584-10a. All requirements as stated in method are met.

The AC Biodiesel All in One is also an excellent choice to analyze FAME feedstock according to EN 14103, EN 14105, EN 14110, prEN 16300 and EN 15779. Its innovative dual programmable oven design ensures optimal availability and flexibility towards various methods as no column changes are required when switching applications and the system is 'always ready', regardless the method that's needed for the sample .

The included reference materials & chemicals and the dedicated reporting makes the AC Biodiesel All in One very user friendly and easy to use for fastest adoption in any biodiesel lab.

AC Analytical Controls® has been the recognized leader in chromatography analyzers for gas, naphtha and gasoline streams and in crude oil refining since 1981. AC also provides technology for residuals analysis for the hydrocarbon processing industry. Applications cover the entire spectrum of petroleum, petrochemical and refinery, gas and natural gas analysis; ACs Turn-Key Application solutions include the AC Reformulyzer ® , DHA, SimDis, NGA, Hi-Speed RGA and Customized instruments.

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