EN 14105 Using a Multi-Mode Inlet and Agilent J&W Select Biodiesel for Glycerides

Application Note

Energy and Chemicals

Authors

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Abstract

B100 biodiesel, a cleaner-burning alternative fuel produced from renewable resources such as plant oils, was assayed for free and total glycerol content using a cool on-column inlet according to industry standard method DIN EN 14105:2011-07. The GC column was an Agilent J&W Select Biodiesel for Glycerides with UltiMetal. The optimized MMI inlet was linear for all the derivatized components in the volatility range for glycerol along acceptable relative response factors. The inlet parameters were optimized for heptane as dilution solvent and injection mode was cold-splitless.

Introduction

One of the advantages of biodiesel over petroleum-derived diesel fuel is that it contains no sulfur, which when emitted into the air produces acid rainfall. Modern petroleum diesel engines must be fitted with selective catalytic reduction (SCR) recovery systems to reduce emissions. Diesel blends of up to 20% biodiesel (B20) in regular diesel fuel can be used safely in most current engines. The conversion of free fatty acids and alcohols from biofuel feed stocks is accomplished by forming fatty acid methyl esters (FAMEs). Incomplete esterification will produce a fuel that has poor flow qualities in cold weather and can absorb water, making it burn poorly or cause a pre-ignition condition known as knocking. The CEN specifications (EN 14214) are < 0.02 mass% glycerol and < 0.25 mass% total glycerin [1]. The quantification range of this method for glycerol is 0.005 to 0.05% and for total glycerides is 0.05 to 0.5% [2].

Agilent Technologies

The Multi-Mode Inlet (MMI) has gained in popularity and is the most versatile inlet system. It offers the ability to introduce a sample onto a GC column in modes similar to split/splitless, while mimicking on-column with cold-splitless capability. Agilent J&W UltiMetal columns provide an even broader range of temperature options, with stability at temperatures well beyond that of polyimide-coated fused silica columns. Combining these two tools and leveraging premeasured calibration solutions manufactured to cover the assay range, allows Agilent to offer the most complete single-vendor source for determining the quality of biofuels and feedstock.

Materials and Methods

An Agilent 7890A GC was fitted with an Agilent MMI inlet and FID detector. The B100 biodiesel was an SRM2772 soybean biodiesel from NIST. Heptane > 99% was from Sigma-Aldrich Corp.

Agilent kits contain the reagents/components in a standard range suitable for the assay.

- MSTFA Derivatization kit (p/n 5190-1407)
- Standard Glycerides kit (p/n G3440-85018)
- Glycerol Standards kit (p/n G3440-85028)
- Butanetriol Internal Standard kit (p/n 5982-0024)

Sample preparation was according to the method. Add 100 mg accurately weighed sample into a 22 mL vial, followed by 200 µL glycerides, 200 µL pyridine, 200 µL MSTFA, and 80 µL butanetriol ISTD. Cap hermetically and mix well. Allow to react for 15 minutes at room temperature. Finally, add 8 mL heptane, mix well, and transfer a 1 mL aliquot to an autosampler vial for injection.

Conditions [3]

Column:	Agilent Select Biodiesel for Glycerides, 15 m × 0.32 mm, 0.10 µm (p/n CP9079)
Carrier:	Helium 5.6 mL/min constant flow
Oven:	50 °C (hold 1 minute), then to 180 °C at 15 °C/min, then to 230 °C at 7 °C/min, then to 380 °C at 30 °C/min (hold 10 minutes)
Injection:	MMI Cold-Splitless, initial temperature 88 °C for 0.1 minutes, then to 350 °C at 250 °C/min (hold 1 minute)
Purge time:	1.0 minute
Purge flow:	9.6 mL/min
Detector:	FID at 380 °C
Sampler:	Agilent 7693A Automatic Liquid Sampler, 1 µL volume injection

Supplies

Vials:	22 mL (p/n 5183-4313), caps (p/n 5183-4303)
Autosampler vials:	Amber screw-cap (p/n 5182-0716), caps, blue screw-cap (p/n 5282-0723)
MMI inlet liner:	2 mm id, 200 µL dimpled liner (p/n 5190-2296)
Autosampler syringe:	5 µL tapered (p/n 4513-80206)
PTFE tip syringes:	250 µL (p/n 5190-1517) (4 recommended)
Pipet:	8 mL volumetric
Tube cutter:	for UltiMetal capillary (p/n CP 8099)
Magnifier:	20 × (p/n 430-1020)

Results and Discussion

As can be seen in Figures 1 and 2, the reaction of MSTFA with the hydroxyl groups produces good symmetrical peak shape, and the peak for ISTD glycerol is nicely uniform, indicating completeness of derivatization reaction in pyridine at room temperature. To evaluate the MMI inlet system for carryover due to incomplete volatilization, a heptane blank was injected after samples, which showed no peaks eluting, indicating the heavy fraction was completely injected and eluted from the column during the sample run. A comparison of the column performance control, as shown in the trend line in Figure 3, graphs the ratio of glyceryl dinonadecanoate (Di C38) versus glyceryl trinonadecanoate (Tri C57). The result of the relative response factor or RRF must be lower than 1.8 or the system is not suitable for analysis and will require operator intervention/troubleshooting. Figure 4 shows that the linearity was excellent for the range of concentration required by the assay. Table 1 demonstrates a direct comparison of the MMI inlet to a data set generated for the same sample using cool on-column.

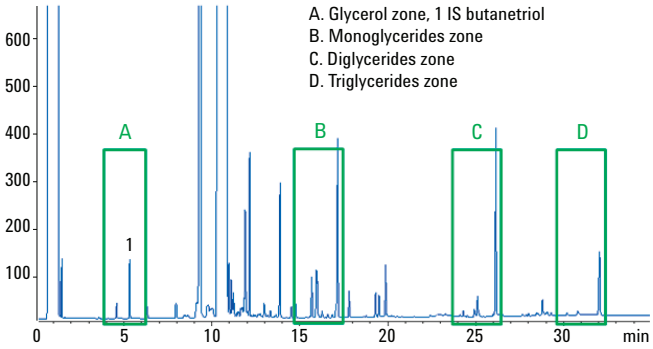

Figure 1. B100 biodiesel with internal standards kit solutions showing the zones of interest, separated on an Agilent J&W Select Biodiesel GC column.

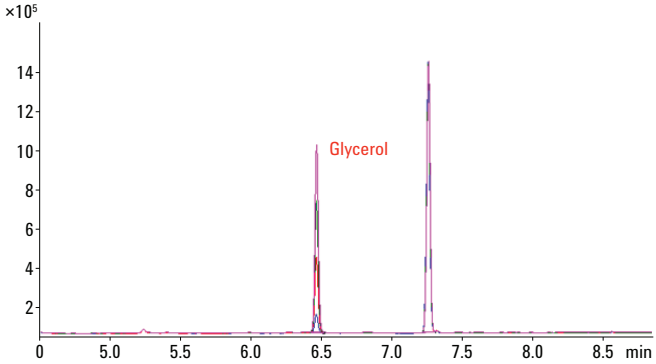

Figure 2. Glycerol and ISTD butanetriol showing linearity and complete reaction of glycerol with MSTFA indicated by single symmetric peak, using an Agilent J&W Select Biodiesel GC column.

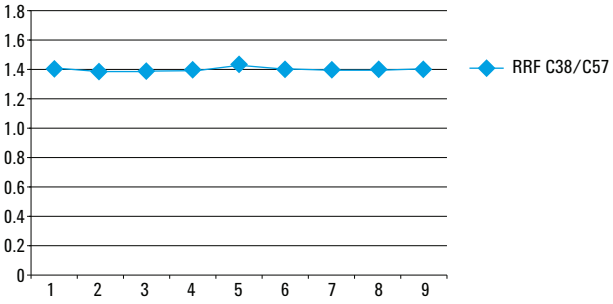

Figure 3. Trend line of relative response factors (RRF) for the ratio of glyceryl dinonadecanoate (Di C38) versus glyceryl trinonadecanoate (Tri C57).

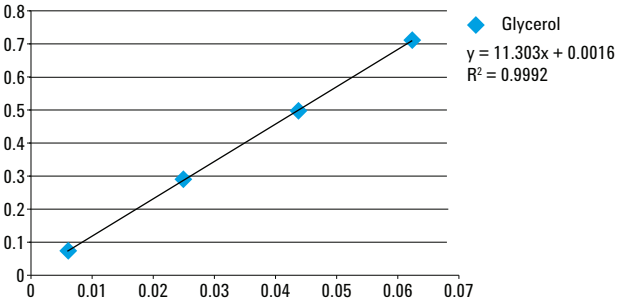

Figure 4. Linearity response for glycerol using the MMI inlet showing acceptable performance according to EN14105:2011-07.

Table 1. Good agreement between the cool on-column and Multi-Mode Inlet can be seen for this sample run in duplicate weighing on each setup. Additionally, the MMI repeatability measure, r (calc), exceeds the EN14105 specification, r (spec).

	wt% Glycerol		wt% Monoglycerides		wt% Diglycerides		wt% Triglycerides		wt% Total glycerin	
	COC	MMI	COC	MMI	COC	MMI	COC	MMI	COC	MMI
Run 1	0.146	0.147	0.25	0.25	0.10	0.10	0.05	0.04	0.230	0.231
Run 2	0.146	0.146	0.24	0.25	0.10	0.10	0.05	0.04	0.227	0.231
Average	0.146	0.147	0.25	0.25	0.10	0.10	0.05	0.04	0.229	0.231
r (calc)	0.000	0.001	0.01	0.00	0.00	0.00	0.00	0.00	0.003	0.000
r (spec)	0.024	0.024	0.03	0.03	0.01	0.01	0.02	0.01	0.028	0.041

Conclusions

The Agilent MMI inlet can be used in place of cool on-column for the assay of the glycerin content in B100 biodiesel with a high degree of confidence. By employing the Agilent J&W Select Biodiesel for Glycerides GC column with UltiMetal and test solutions, the task of quantifying biofuel glyceride content has been greatly simplified. Routine maintenance after a series of dirty samples will require replacing the inlet liner, the inlet ferrules, and trimming the metal column inlet end. All the needed tools and parts, including a metal capillary tubing cutter, can be readily sourced from the same supplier as well, which will improve up-time and throughput.

Acknowledgement

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References

1. CEN. DIN EN 14214 "Fatty Acid Methyl Esters (FAME) for Diesel Engines, Requirements and Test Methods" European Committee for Standardization, Management Centre, Brussels, Belgium (2009).
2. J. Oostdijk "Analysis of Free and Total Glycerol in B-100 Biodiesel Methyl Esters Using Agilent Select Biodiesel for Glycerides" Application note, Agilent Technologies, Inc., Publication number 5990-8993EN (2011).
3. ASTM. D6751 "Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuel" ASTM International, West Conshohocken, PA, USA (2012).

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