

Free and Total Glycerin in B100 Biodiesel by Gas Chromatography

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Introduction

Rudolph Diesel originally designed his 1892 prototype of the diesel engine to run on a renewable fuel made from peanut oil and other vegetable oils. That fuel could be produced by the farmers of his day. But petroleum-based distillates of the early 1900s proved to be a cheaper, readily available alternative fuel. As a result, the petroleum-based fuel industry became the standard of the world and Diesel's dream of cheap, renewable fuel was lost. Fuel shortages in the 1970s, however, re-kindled interest in alternative fuels. Today, as oil prices continue to climb, once again, the world's interest in alternative fuels is stronger than ever. One of the most popular fuel alternatives today is biodiesel.

Biodiesel is a renewable fuel from natural oils like soybean oil, rapeseed oil or animal fats and can be used as a substitute for diesel fuel. Biodiesel made from vegetable oil or animal fat works just like petroleum diesel, but with far lower toxic air emissions. It is cleaner burning than petroleum diesel and has less sulfur content, reducing emissions. It is also made from renewable resources so it is less taxing on petroleum supplies. Biodiesel fuel can be mixed with petroleum diesel fuel at any dilution level to create a biodiesel-blended fuel. Biodiesel refers to the pure fuel before blending. Common nomenclature for blended fuel is noted as the percentage of biodiesel in the blend. B100 is 100% biodiesel. B20 is 20% biodiesel and 80% petroleum diesel.

Combustion of fossil fuels adds carbon dioxide to the atmosphere, promoting the buildup of greenhouse gases and global warming. Photosynthesis from plants removes carbon dioxide from the atmosphere – therefore

the combustion of biodiesel fuel from vegetable-oil feedstock adds no net carbon dioxide to the atmosphere.

In addition to the environmental advantage that biodiesel provides, the U.S. Energy Pollution Act of 1992 and 1998 offers tax incentives to users of biodiesel fuel. So, biodiesel can fuel the consumer's pocketbook as well as his car.

Several mechanisms for the conversion of the free fatty acids (lipids) to fatty acid esters have been published. These mechanisms would include saponification, transesterification, hydrolysis and esterification. Esterification is carried out by the reaction of the carboxylic acids (free fatty acids), alcohol and a catalyst. The fatty acid methyl ester (FAME) is the reaction typically used for manufacturing biodiesel fuel, with water and glycerin as by-products.

Glycerin content can indicate the quality of biodiesel. Glycerin can be in the form of free glycerin or bound glycerin in the form of glycerides. Total glycerin is the sum of free glycerin and bound glycerin. A high content of free and total glycerin can lead to buildup in fuel tanks, clogged fuel systems, injector fouling and valve deposits.

ASTM method D-6751 specifications serve as the benchmark which identifies the standards that pure biodiesel (B100) must meet before being used as fuel or being blended with petrodiesel. The U.S. National Biodiesel Board has adopted the ASTM biodiesel specification and analytical methodology. ASTM recommends test method D-6584 for the analysis of glycerin in biodiesel fuel by gas chromatography (GC).

Gas chromatography can also serve as a tool for process troubleshooting during biodiesel production to ensure trouble-free operation of the fuel in diesel engines. Monitoring the level of free glycerin and any unrelated mono-, di- and triglycerides will indicate the efficiency and progress of the chemical reaction during the process of making biodiesel. Glycerides can appear in samples taken during the esterification process but ideally should not remain in the final product. Unrelated glycerides and free glycerin make the product behave more like soap rather than fuel. The length of the carbon chain in the fatty acid methyl ester is not of primary importance. Most biodiesel contains carbon chains ranging from C₁₂ to C₂₄, with a median chain length of C₁₈ as the carboxylic acid methyl ester (FAME).

Experimental

Table 1. System.

Gas Chromatograph:	PerkinElmer® Clarus® 500 GC with Autosampler
Injector:	Programmable On Column (POC), 5.0- μ L syringe with 0.47-mm ID needle
Detector:	FID
Pneumatics:	PPC for POC Carrier Gas (Helium), PPC FID Gases (Air and Hydrogen)
Guard Column:	8-12 in. x 0.53 mm ID connected to analytical column with column union
Analytical Column:	15 m x 0.32 mm ID x 0.10 μ m Elite-5HT

Table 2. Conditions.

GC Oven:	50 °C (1) 15 °C/min 180 °C (0) 7 °C/min 230 °C (0) 30 °C/min 380 °C (10)
Carrier Gas:	Helium at 3 mL/min constant flow
Injector:	Cold on column: Oven tracking mode Injection Volume: 1.0 μ L Speed: Slow Viscosity: 2
Detector:	FID Range: x1 Attn: x4 Temp: 380 °C Air: 450 mL/min H ₂ : 45 mL/min
Wash Solvent:	n-Heptane Rinse: 5 Pump: 5 Wash: 5

Note: Cold on-column injection represents true ratios in the sample better than split or splitless techniques.

Reagents

- n-Heptane
- Pyridine
- Derivatization reagent: n-methyl-n-trimethylsilyltrifluoroacetamide (MSTFA) (Pierce Chemical)

- Glycerin
- Monoglyceride standards: monopalmitin, monoolein, monolinolein, monolinolenin and monostearin
- Diglyceride standard: diolein
- Triglyceride standard: triolein
- Internal standard components: butanetriol, tricaprin

Internal standard solution

Prepare a combined solution of 1-mg/mL butanetriol and 8-mg/mL tricaprin in n-heptane.

Sample preparation

Standards are prepared in pyridine. Standards and samples are treated in an identical manner. Into 2.0-mL disposable autosampler vials, weigh approximately 100 mg of sample or standard, record actual weight.

Add ISTD. Add 100 μ L MSTFA.

Allow to stand 20 min at room temperature.

Add 1.5-mL heptane, cap vial and shake.

Analysis

Inject 1- μ L derivatized sample into cold on column injector. Collect chromatogram for processing.

Results and discussion

Typical chromatograms for standards and a biodiesel sample prepared from soybean oil are shown in Figures 1 and 2 (Page 3). A typical calibration curve for glycerin is shown in Figure 3 (Page 4), demonstrating excellent linearity. Total monoglycerides are calculated with a summed peak group including all 5 monoglyceride peaks, but do not include the C₂₄ carboxylic acid methyl ester peak eluting between the monoglycerides. Summed time group must not be used due to coelution of the C₂₄ ester between the monoglycerides.

Total diglycerides are calculated as a summed time group including all peaks eluting with diolein \pm 0.35 min. Total triglycerides are calculated as a summed time group including all peaks eluting with triolein \pm 1 min. Free glycerin is calculated by the area of the glycerin peak. ASTM D-6751 limits free glycerin to 0.020% by mass. Total glycerin is calculated by the sum of free glycerin plus a percentage of total mono-, di- and triglycerides, as formulated in ASTM D-6584. Specifications in ASTM D-6751 limits total glycerin to 0.240% by mass. A typical report for a biodiesel sample in compliance with the ASTM specifications is shown in Table 3 (Page 4).

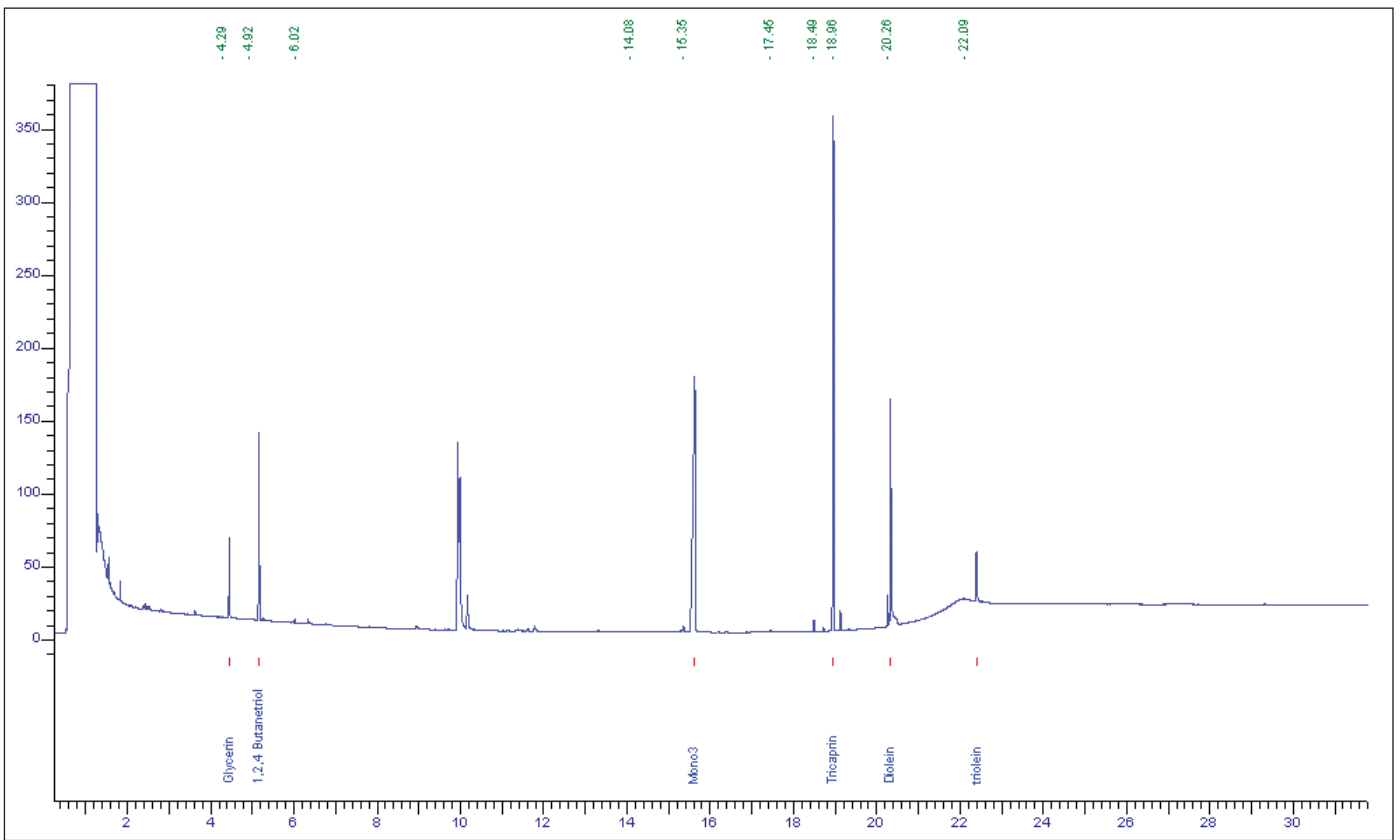


Figure 1. Typical chromatogram for biodiesel standards and internal standards.

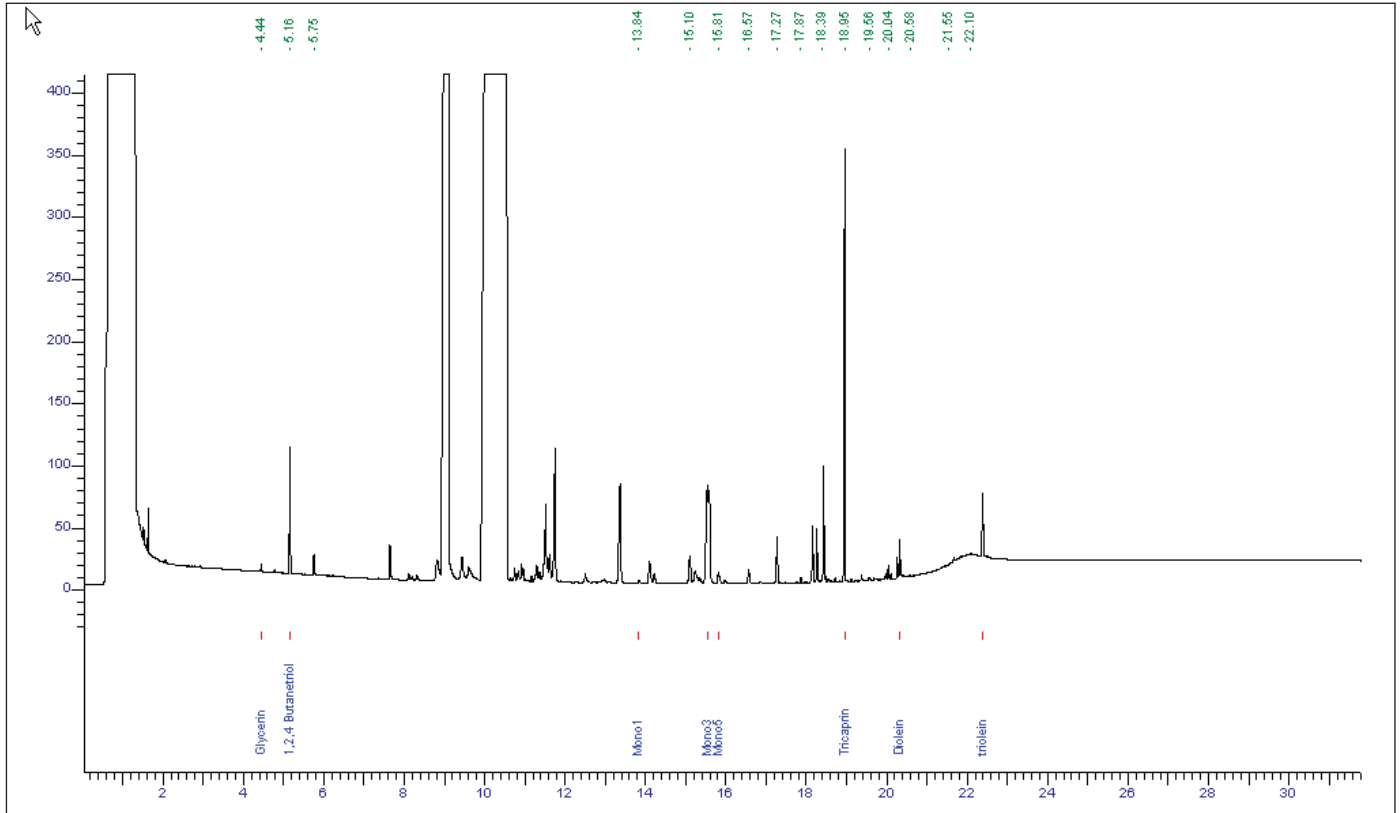


Figure 2. Typical chromatogram of soybean B100 biodiesel fuel.

Conclusion

Alternative fuel interest continues to increase with higher prices at the pump. With this increased interest, both established fuel suppliers and new entrepreneurs are doing their best to respond to this interest by producing quality, alternative fuel products. To measure that quality, there are a number of different laboratory techniques to evaluate different parameters. Gas chromatography (GC) is often used as the analytical method of choice for free and total glycerin analysis since it is simple, sensitive and reliable, requiring only a small amount of sample preparation. Infrared spectroscopy (FTIR) is often used for rapid on-line assessment of quality control, but is less sensitive to minor components. The two

techniques are often used in conjunction with each other for a more complete analysis. UV fluorescence has been used for sulfur determination, but inductively coupled plasma optical emission spectroscopy (ICP-OES) is rapidly gaining ground as the analytical method of choice for trace-sulfur determination.

This report has demonstrated the application of ASTM D-6584 methodology to a soybean oil-based biodiesel fuel. The method may need further optimization to apply to other sources of biodiesel which may produce other components in the final product. European producers typically use high performance liquid

Table 3. Typical Report For Free and Total Glycerin - ASTM D-6584 Report.

Time [min]	Component Name	Area [$\mu\text{V}\cdot\text{sec}$]	Total Mass %
4.442	Glycerin	7405.23	0.014
5.159	1,2,4-Butanetriol (ISTD)	144966.27	—
15.53	Total Monoglycerides	515808.44	0.142
18.95	Tricaprin (ISTD)	515249.64	—
20.31	Total Diglycerides	82765.76	0.011
22.44	Total Triglycerides	116084.59	0.004
	Total Glycerides		0.171

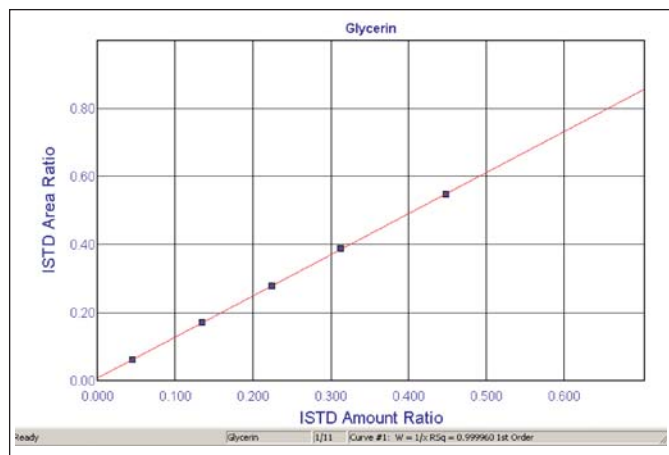


Figure 3. 5-point calibration curve for free unbound glycerin.

chromatography (HPLC) methodology for analysis of the final product for by-products. Further work will include evaluation of HPLC methodology and comparison with the GC method for comparability and wide application.

References

1. ASTM Method D-6751 03a, Standard Specification for Biodiesel Fuel (B100) Blend Stock for Distillate Fuels
2. ASTM Method D-6584, Test Method for Determination of Free and Total Glycerin in B100 Biodiesel Methyl Esters by Gas Chromatography
3. U.S. Energy Pollution Act of 1992

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