

# Ensuring High Quality Biodiesel Product through Analytical Testing

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Multiple influences, including government mandates, environmental concerns, a quest for energy independence, and a desire to support the agricultural community are all encouraging communities around the world to increase their use of biofuels. Bioethanol that is blended with petroleum-produced gasoline has received widespread acceptance in many parts of the world. Biodiesel, which has been used for several years throughout Europe and Latin America, is now gaining new attention in China, Malaysia, South Africa, Canada and the United States. If consumers around the world are to

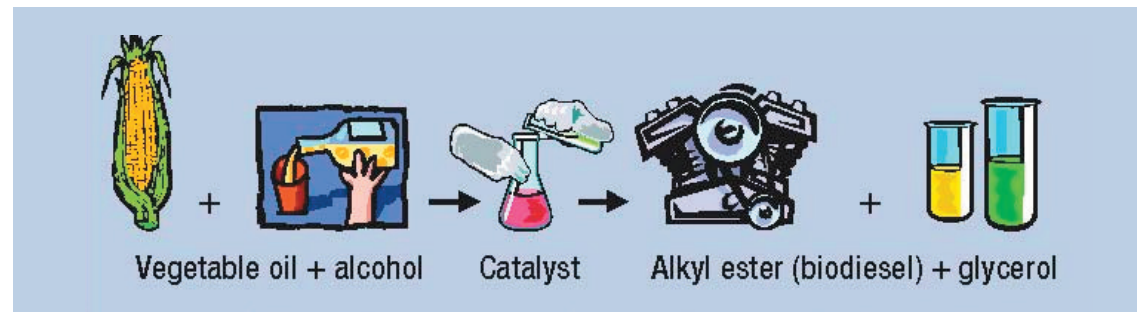


Figure 1. Simplified transesterification of vegetable oil into biodiesel (alkyl ester).

will focus on the tests set for the determination of free and total glycerin by gas chromatography (GC) and the determination of Group I and II metals as well as phosphorous by inductively-coupled plasma-optical emission spectroscopy (ICP-OES).

### Free and Total Glycerine

Biodiesel is manufactured from a variety of naturally occurring fats or oils. The process, which is called transesterification, is shown in Figure 1 and produces the bi-product glycerin. High levels of glycerin in biodiesel can result in deposits in the bottom of storage tanks, clogging of engine fuel filters, and the damage of injectors in the diesel engine. To meet the ASTM standard D 6751 or EN 14105 for total glycerin, biodiesel must contain no more than 0.020 weight percent of free glycerin and no more than 0.240 weight percent of total glycerin (the sum of free and bound glycerin).

A gas chromatograph equipped with a flame ionization detector (FID) is the technology recommended by both ASTM and EU for the analysis of free and total glycerin. To determine free and total glycerin, the sample is first derivatized with a silylating agent and then injected into an open tubular GC column packed with a 5% phenylpolydimethylsiloxane. Calibration is achieved with two internal standards (butanetriol and tricaprin) and four reference materials. Mono-, di- and triglycerides are determined by comparison with mono-olein, di-olein and tri-olein, respectively. Conversion factors are then applied to

the results for mono-, di- and triglycerides to calculate the sample's bonded glycerin content. The total glycerin represents the sum of the free and bonded glycerin. The peaks associated with the free and those associated with the bound glycerin are shown in Figure 2.

### Elemental Analysis

A second important test that must be performed on biodiesel if the end product is to perform as expected is the analysis of Group I and Group II metals. The transesterification reaction is quite close to the reaction used for making common soap. If the levels of Group I (Na and K) and Group II (Ca and Mg) metals are not kept at sufficiently low levels, the reaction will indeed make an unacceptable amount of soap. This soap can cause problems as the biodiesel is being used that are similar to the problems created by high levels of glycerin. Both ASTM D 6751 and EN 14538 specify the use of ICP-OES for the analysis of these metals. This analysis requires very little sample preparation. A 1-g aliquot of the sample is diluted to a volume of 25 mL using high purity kerosene. Since ICP-OES is a relative technique, the instrument is to be calibrated using non-aqueous standards in a concentration range that will bracket the anticipated concentration of the sample. At this point, the sample is simply aspirated into the instrument and the concentration read directly.

Phosphorous is considered a carry over element that is typically found in the feedstocks used in pro-

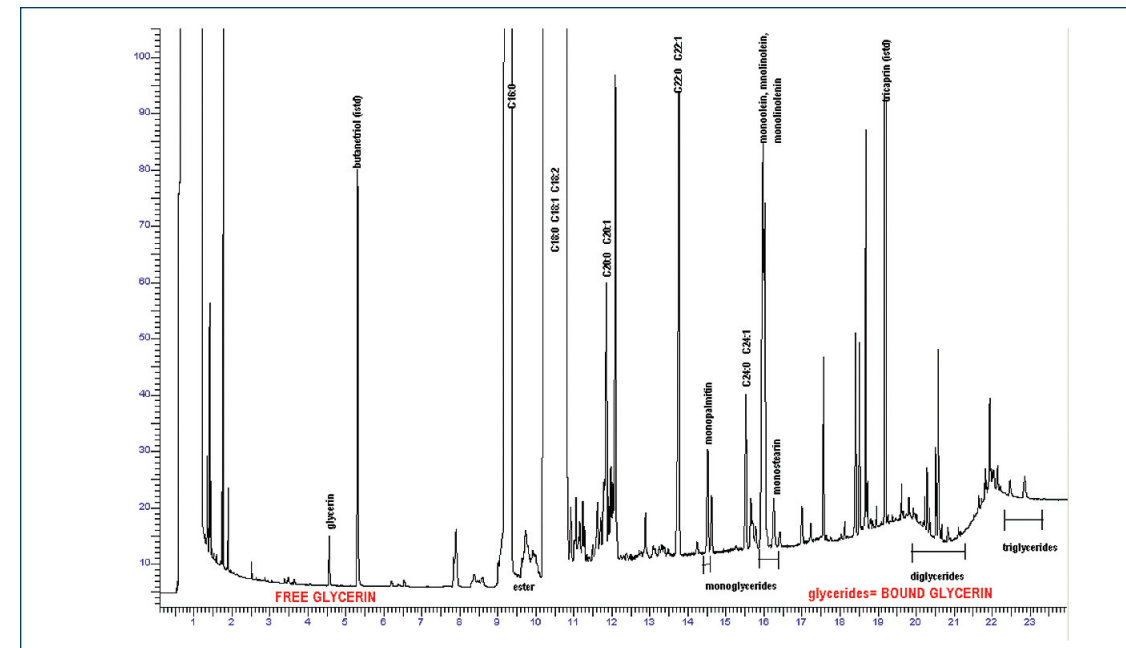


Figure 2: A chromatogram of biodiesel showing the peaks used to determine free and bound glycerin.

ducing biodiesel. If the level of phosphorous in the final product is not controlled, the catalytic converter of the diesel engine can be damaged. ASTM D 4951 and EN 14107 do specify the use of an ICP-OES instrument for the determination of phosphorous in biodiesel. Sulphur is also a carryover element that can create difficulties with the catalytic converter of a diesel engine and can create environmental issues

	Detection Limit using ICP-OES in ppm	Levels in Biodiesel set by EN in ppm	Levels in Biodiesel set by ASTM in ppm
Sulphur	0.01	10	15
Phosphorus	0.04	10	10
Sodium	0.0005	5(Sum Na + K)	5(Sum Na + K)
Potassium	0.001		
Calcium	0.00005	5(Sum Ca + Mg)	5(Sum Ca + Mg)
Magnesium	0.00004		

Figure 3: Detection limits using ICP-OES.

including the production of acid rain. At this time, both ASTM and EU recommend technologies other than ICP-OES for the determination of sulphur. While not taking issue with that recommendation, it has been found that ICP-OES instruments can readily determine sulphur in biodiesel at the levels required by both ASTM and EU. Since many biodiesel laboratories own an ICP-OES system for the analyses described above, there can be a real savings in the investment made in the laboratory if ICP-OES could be used for the determination of sulphur.

### Conclusion

As the world increases its use of biodiesel, it will remain increasingly important that the quality of

biodiesel produced meets consistently high quality standards. Meeting such standards will assure acceptance by the consumer and will assure that environmental benefits possible from increased use of biodiesel are indeed achieved. The testing of free and total glycerin can be achieved with full compliance with ASTM and EU standards by the use of GC while the testing of Group I and Group II metals, as well as

phosphorous, can be achieved in full compliance with ASTM and EN standards by the use of ICP-OES. The analysis of sulfur is achievable with ICP-OES; however, it is not yet in compliance with the ASTM or EU methods. Discussions are planned with both ASTM and EN to show the merits of using ICP-OES for the analysis of sulfur because it is expected that most well-equipped biodiesel laboratories will already have such a system in their laboratory for the analysis of Group I and II metals as well as phosphorous.

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