FuelPro

Application Note: 1050

The Determination of Phosphorous, Sulfur, Sodium, Potassium, Calcium and Magnesium in Biodiesel using the Teledyne FuelPro

Introduction

Biodiesel is a renewable fuel produced from vegetable oil, animal fats, and waste cooking oils. Feedstocks such as soy, canola, mustard, sunflower, coconut, palm and cottonseed oil as well as beef tallow and fish oils have been used to manufacture biodiesel.

As a result of the world's energy demands, the use of biodiesel is increasing rapdily. Blends of biodiesel with conventional petroleum diesel represent a common use of biodiesel. In the United States, "B20" (a blend of 20% biodiesel and 80% petroleum diesel) is recognized as an alternative diesel fuel. Biodiesel has a number of advantages. Some of these include:

1. Reduction of toxic exhaust emissions – lower amounts of hydrocarbon (HC), carbon monoxide (CO) and particulate emissions (PM)
2. Greenhouse gas savings – Carbon Dioxide (CO_2) produced by burning biodiesel is used by subsequent crops used to produce the fuel
3. Fast biodegradability – Approximately 4-5 times as fast as petroleum diesel
4. Lower toxicity than petrodiesel
5. Higher flashpoint than petroleum diesel – 150^{o}C vs. 70^{o}C
6. Can be used in diesel engines with little or no modification

Since the presence of contaminants can lead to operational problems, the American Society for Testing and Material (ASTM) and European Standard (EN) have developed standards to which pure biodiesel (B100) can be tested. The ASTM Standard is D-6751 shown in **Table 1**.

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Property	ASTM Method	Biodiesel Specification (B100)	
		Limits	Units
Flash Point	93	130 min	°C
Water and Sediment	2709	0.05 max	% volume
Kinematic Viscosity (40°C)	445	1.9 – 6.0	mm^2/sec
Sulfated Ash	874	0.02 max	Max wt. %
Sulfur	5453	15 (S15) 500 (S500)	ppm
Copper strip Corrosion	130	No. 3 max	
Cetane Number	613	47	min
Cloud Point	2500	Report	°C
Carbon Residue	4530	0.050 max	wt%
Acid Number	664	0.080 max	mg KOH/g
Free Glycerol	6584	0.020	wt%
Total Glycerol	6584	0.240	wt %
Phosphorus	4951	10 max	ppm
Vacuum Distillation End Point	1160	360	°C
Total Combined Na + K	UOP -391	5	ppm
Total Combined Ca + Mg		5	ppm

Table 1   ASTM D-6751

Physical, chromatographic and spectroscopic methods are used to apply the standard. This application note will focus on the use of FuelPro Biodiesel Metals Analyzer to apply the ASTM standard.

Instrumentation

Accurate elemental analysis of biodiesel requires analytical methodology that is both sensitive and selective. FuelPro meets these requirements and has the capability of determining up to 70 different elements in a sample. FuelPro permits close monitoring of elemental content throughout processing, starting with the raw oil to the finished product. Trace metal analysis is an important part of quality control as well as quality checks of the finished products.

FuelPro can easily measure the elemental parameters of the D-6751 standards. The effects of the biodiesel not meeting the specification are listed below:

Phosphorus – Phosphorus has been shown to damage the ability of after-treatment systems to reduce exhaust emissions as intended. The influence of phosphorus is cumulative; and as a result, very low levels of contamination over the significant amount of fuel consumed by an engine may lead to unexpected deterioration of the after treatment system.

Alkali and Alkaline Metals – Sodium and potassium hydroxides are utilized as catalysts and magnesium and calcium as absorbents in the production of biodiesel and should be removed through the biodiesel production process. These residual metals can form deposits in fuel injection system components and poison emission control after-treatment systems.

Sulfur – Sulfur levels in fuel are regulated by various governmental agencies to assure compatibility with emission standard requirements. In the United States there are currently three sulfur grades: S5000, S500, and S15, for both D1 and D2 petroleum diesel fuel. Biodiesel blends may not exceed the applicable maximum sulfur levels as defined for petroleum diesel.

Method

Biodiesel samples were prepared by simply diluting 1:10 with kerosene. The FuelPro was calibrated with standards prepared by diluting Plasma-Pure biodiesel stock standards. Standard concentrations were at the 0.00 ppm, 10.0 ppm and 20.00 ppm levels for Na, K, Cu, Mg, P and S.

FuelPro's preprogrammed method was followed for the set-up and analysis of biodiesel.

Results

The values obtained as a result of the FuelPro analysis of a B100 biodiesel sample are shown in ***Table 2***. All concentrations are given in ppm. The concentrations in the original sample are listed in the column labeled "Final Concentration ppm" ("ND" indicated the analyte was not detected).

The results indicate this biodiesel sample passes the ASTM D-6751 standard. The result for sulfur indicates it successfully passes the S-15 low sulfur designation that all highway diesel fuels have to meet from 2007 onward.

	Final Concentration ppm
P 213.618 r	ND
Ca 317.933 r	0.129
Mg 285.213 r	0.039
S 180.731 r	8.226
K 766.491 r	0.511
Na 589.592 r	0.252

Table 2 Analysis Results

Table 3 contains typical detections limits (DL) obtained in the oil matrix. The DLs were determined by taking 3 replicates measurements in blank oil and multiplying the standards deviation by three. The detection limits indicate that the FuelPro can easily measure the analyte levels required for ASTM D-6751.

Element	DL, ppm
P 213.618 r	.0227
Ca 317.933 r	.0029
Mg 285.213 r	.0009
S 180.731 r	0.114
K 766.491 r	.070
Na 589.592 r	.0193

Table 3 Detection Limits

Conclusion

Biodiesel is easily analyzed using the FuelPro Biofuel Metal Analyzer. The detection limit capability of the instrument easily meets the requirements of the ASTM and EN Standards against which biodiesel must be measured.

Samples are easily prepared by dilution with a suitable solvent. Excellent recoveries are obtained from spiked biodiesel samples. This indicated that the method is suitable for the analysis of biodiesel fuels and that matrix interferences are not a problem.