FIELD APPLICATION REPORT

ICP-OPTICAL EMISSION SPECTROMETRY

Phosphorus, Calcium and Magnesium Analysis of Soybean Oil-Feedstock for Biodiesel Production Using the Optima Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES)

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Introduction

Biodiesel consists of mono-alkyl esters of fatty acids derived from vegetable oil (or animal fat) and is rapidly gaining momentum in the US as an alternative fuel source for diesel engines. In Europe it is already well established. As demand for biodiesel increases in all parts of the world, new manufacturing facilities are being built at an extraordinary rate. Compared to petroleum diesel, biodiesel is environmentally friendly and is government mandated. It reduces carbon monoxide (CO), carbon dioxide (CO_2), sulfur dioxide (SO_2), hydrocarbons (HC) and other particulate matter emissions that cause respiratory damage. Biodiesel also eliminates the cloud of dense, black smoke normally associated with diesel vehicles. The exhaust fumes from an engine running biodiesel may smell like popcorn or French fries. It also has better lubricity than diesel fuel because of its higher viscosity.

Some of the benefits biodiesel has over petroleum-based diesel include:[1]

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- **Requires less energy to produce:** the fossil fuel energy required to produce biodiesel from soybean oil is only 30% of the energy contained in one gallon of the fuel
- **Reduces harmful emissions:** burning biodiesel produces less CO_2, moreover, as soybeans grow they take-up CO_2. In addition, tailpipe particulate matter emissions are reduced with the use of biodiesel
- **Lower sulfur content:** most biodiesel fuels contain less than 15 ppm sulfur
- **Improved lubricity:** biodiesel is twice as viscous as petroleum-based diesel
- **Implementation is easy:** conventional diesel engines can run up to 20% biodiesel blends with no modifications

Soybean oil is fast becoming the principal feedstock to many biodiesel plants being built in the United States. However, natural variation in oil quality can affect its conversion into biodiesel. One method of determining the quality of the soybean oil is to quantify its natural occurring metallic elements. These elements principally include phosphorus, calcium and magnesium. These elements, if allowed to vary in concentration in the oil, can result in poor separation of the biodiesel esters from its co-products such as glycerin and fatty acids during production. Swiftly and accurately measuring these elements is important in verifying oil quality.

In the US, ASTM standard D6751 and in Europe, EN 14214 are used for guidance on acceptable levels of metals that may affect the performance of the final product. Table 1 summarizes the metallic content specified in the final product to ensure proper engine performance.

Table 1. Consensus Standards for Maximum concentrations of P, Ca, and Mg.

Element	ASTM D6751	EN 14214:2003
P	10 mg/kg	10 mg/kg
Ca + Mg	5.0 mg/kg	5.0 mg/kg
Na + K	5.0 mg/kg	5.0 mg/kg

* ASTM also specifies the method for determination of the elements. Recent expansions in the methodology specified include ICP-OES for the measurement of all five elements indicated in Table 1.(2) Sulfur must also be measured in the final product and although ICP-OES is not currently specified, it may be allowed in the future.

Experimental

The analytical operating conditions are listed in Table 2. Approximately 1 gram of soybean oil was weighed into a 25-mL flask. The samples and standards were diluted with kerosene (Premisolve) by a factor of 10 to 20 times. The calibration curve was created using a multi-element organo-metallic standard (Conostan® S-21). Cobalt was added as an internal standard to all samples and standards.

Table 2. Instrumental Conditions

Analytical Instrumentation

- Optima™ 2100 Dual View ICP-OES
- GemCone Nebulizer
- Quartz Cyclonic Spray Chamber
- Quartz Torch for Optima 2100
- 1.2 mm I.D. Alumina Injector for Oil Analysis

Plasma Conditions

- Plasma Flow = 18 L/min
- Auxiliary Flow = 1.4 L/min
- Nebulizer Flow = 0.45 L/min
- RF wattage = 1500 W
- Pump Flow Rate = 1.50 mL/min
- Read Delay = 15 seconds
- Plasma Condition = Wet

Spectral Conditions

- Background Correction = 2 point
- BGC1: P = -0.048; Ca = -0.068; Mg = -0.61; Co = -0.048
- BGC2: P = 0.045; Ca = 0.068; Mg = 0.61; Co = 0.041
- Phosphorus wavelength = 213.62
- Cobalt wavelength (Used as Internal Standard) = 228.619
- Calcium wavelength = 317.933
- Magnesium wavelength = 285.213

The plasma was viewed in the radial mode. Additional sensitivity was not required since this is a quick survey method to roughly approximate the concentration of the elements for process control. Calibration standards of 0, 0.1, 1.0 and 10 mg/kg of each element were used.

Results

A variety of oil batches were analyzed for the elements of interest and the results shown in Table 3. The three feedstock types represent progressively refined materials progressing toward the conversion process. There are no regulations for metals in feedstock materials so these analyses are done to ensure that the manufacturing process proceeds smoothly. The instrument results take less than two minutes per sample, after a short calibration period.

The wide dynamic range of the ICP-OES provides an advantage in that it allows for the measurement of a wide range of potential sample concentrations in one run. This provides rapid turnaround, important when a process may be halted, waiting for diagnostic analytical results.

Table 3. Analysis of Oil Feedstock for Metallic Elements (mg/kg).

	Plant Feed			Degummed Oil			Crude Oil		
Feed Stock	**P**	**Ca**	**Mg**	**P**	**Ca**	**Mg**	**P**	**Ca**	**Mg**
Batch 1	7.07	0.83	0.79	30.00	3.63	3.30	448.5	57.9	54.7
Batch 2	11.63	1.48	1.45	7.89	0.72	0.72	550.7	68.3	66.1
Batch 3	8.64	1.10	1.10						
Batch 4	8.97	1.00	1.01	6.36	0.67	0.79	521.0	60.7	61.5
Batch 5	6.32	0.86	0.89	6.87	0.79	0.82	625.7	73.3	67.0
Batch 6	6.01	0.84	0.86	10.04	1.11	1.04	447.4	55.7	51.5
Batch 7	6.33	0.88	0.83	12.92	1.39	1.21	507.4	63.4	57.0
Batch 8	11.55	1.38	1.51	61.75	6.40	6.90	545.1	60.4	68.8
Batch 9	11.55	1.38	1.51	61.75	6.40	6.90	545.1	60.4	68.8
Batch 10	37.81	4.42	4.95						
Batch 11	16.27	1.84	2.11						
Batch 12	12.23	1.43	1.53	24.70	2.69	2.88	584.3	68.7	74.4
Batch 13	7.92	1.02	1.01	10.00	1.12	1.04	583.3	66.8	61.6
Batch 14	7.37	0.95	0.91	7.93	0.97	0.86	639.0	77.5	71.0
Batch 15	7.96	0.87	0.87	9.39	0.95	0.86	589.1	63.9	60.1
Batch 16	16.80	1.94	1.77	9.16	1.21	1.00	814.0	99.6	87.7
Batch 17	16.20	1.77	1.55						
Batch 18	19.70	1.94	1.69						
Batch 19	15.10	1.40	1.20						
Batch 20	14.70	1.14	1.33	8.91	0.87	0.89	582.0	67.9	61.3
Batch 21	4.78	0.32	0.42						
Batch 22	36.50	4.87	4.37	115.90	15.00	11.80	1286.0	167.7	151.7
Batch 23	37.10	4.90	4.60	23.97	2.53	2.28	1218.0	157.2	149.5

Table 4 shows the precision for these elements measured in feedstock and refined feedstock. The samples are diluted by a factor of 10-20 so the concentrations actually measured are quite low in some cases and the precision would be expected to be poorer than at higher concentrations.

Conclusion

The analysis of soybean oil feedstocks using the Optima ICP-OES is a fast and accurate way to measure naturally occurring elements such as phosphorus, calcium and magnesium present within the soybean oil. The presence of these elements at certain concentrations is an indicator of the quality of the feedstock for processing. The concentration in the final product is also specified by consensus groups to ensure proper engine performance. Initial measurement and on-going monitoring is an important part of product quality control protocols.

References

1. M. Bowman, D. Hilligoss, and S. Rasmussen, and R. Thomas, Biodiesel: A Renewable and Biodegradable Fuel, Hydrocarbon Processing, February 2006, p. 103-106.
2. R. McCormick and S. Westbrook, Biodiesel and Biodiesel Blends, ASTM Standardization News, April, 2007.

Table 4. Precision for Biodiesel Feedstocks (n=5).

Sample	P (mg/kg)	%RSD	Ca (mg/kg)	%RSD	Mg (mg/kg)	%RSD
Soy crude 2216	1270	1.0	175	0.6	171	2.0
Soy refined 2218	9.1	5.2	ND	–	0.72	4.4
Corn oil	2.1	16	ND	–	0.28	8.4
Animal fat	234	2.6	170	3.6	20.9	2.6
Poultry	14.5	6.6	ND	–	0.15	43
Check sample	40.2	3.3	40.5	2.5	40.4	3.1

ND: not detected at an approximate detection limit of 0.4 mg/kg in the original sample.
Other elements such as sodium, potassium, and sulfur also have specifications in the final product and are not measured within the scope of this work.

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