Sulphur and Phosphorus Analysis in Vegetable Oil and Beef Tallow for Biodiesel Production Using the Optima Inductively Coupled Plasma-Optical Emission Spectrometer

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Introduction

Renewable biological wastes, such as animal fats and vegetable oils, are gaining interest in the energy industry sector as potential alternative fuel sources for diesel engines. Feasibility of use depends on many factors including:

1. Physical Properties

The specific energy densities (energy content per fuel mass) of vegetable oils and animal fats (~40MJ/kg) are approximately 80% of diesel (~48MJ/kg). Minimum temperatures at which biodiesels are useable increases at higher concentrations (10-20%)[1]; these temperatures and viscosities also increase with greater degrees of saturation, going from vegetable to animal sources. Hence, biodiesel is often used and blended with diesel. Besides reducing fuels costs, when added in small quantities (<3%) to petroleum-based diesel, biodiesels provide better lubricity, improve operation of diesel equipment and extend component life. At these low quantities, cold temperature properties (i.e., cloud point, cold filter plugging and pour point) are not affected. Biodiesels also exhibit low reactivity with other materials such as reduced copper corrosion[2].

2. Environmental Impact and Safety

Unlike virgin vegetable oils, rendered products such as edible and inedible tallow, greases and lard, are recycled waste products and they will not increase demand of raw materials. In general, biodiesels emit less HC, COx, and SOx, than petroleum-based diesel for the same amount of fuel used. Biodiesels have high boiling points and flash points, very low vapor pressures, and a lesser tendency to smoke. This indicates a high level of safety in handling[2].

3. Costs[3]

Market price of raw materials, transportation costs, quality, supply and reliability are some of the obvious costs of procurement. Compared to petroleum-based diesel, raw material and production costs per gallon of animal-based and grease-based biodiesels are similar or lower; brown grease is about half the cost. Plant material (corn, soy, canola) costs, however, are higher; corn is about twice the cost. Unlike refined oils, animal fats require prior degumming, bleaching, thermal deacidification and esterification. Biodiesel yield, storage, oxidation stability, disposal cost, labor and infrastructure are some of the other costs of operating a biodiesel plant.

4. Testing

Given the diversity of sources of biofuels, testing of raw materials is an important first step in assuring consistent quality of the final product. Fuel sulphur is converted to sulphur oxides and sulphuric acid. Although raw materials may not contain large quantities of sulphur, some processing methods use sulphur catalysts to utilize fatty acid feedstocks[2].

Phosphorus damages catalytic converters used in emission control systems. Since catalytic converters are becoming more common in diesel powered equipment, maintaining low or no S and P levels will be of increasing importance.

European and U.S. Biodiesel Specifications for some elements are listed in Table 1.

Table 1. European and U.S. Biodiesel Specifications (% mass units).

	ASTM D-6751	pr EN 14214	E DIN 51606
Phosphorus	0.001	0.001	0.001
Sulphur	0.05	0.01	0.01
Ca + Mg	—	0.0005	0.0005
Na + K	—	0.0005	0.0005

Procedures for determining S and P in beef tallow and canola oil are described below.

Experimental

1. Polypropylene centrifuge Tubes, 50 mL, Sarstedt or equivalent
2. Vortex – Fisher Scientific Ltd. Model-G560 or equivalent
3. Transfer pipette, disposable or otherwise.
4. Mettler-Toledo, Model PG 1003-S weighing balance or equivalent

Reagents

The calibration standard for P, S and Mn was made using Conostan® standards. (Conostan Division, Conoco, Inc. P.O. Box 1267, Ponca City, OK 74601). A 10 ppm calibration standard was used.

The solvent used in all cases was a mixture of 90% PremiSolv kerosene (Conostan) and 10% hexane (A.C.S. Reagent, Anachemia, 45126-540, UN-1208) for beef tallow. Hexane was not necessary for canola oil.

Sample preparation

Transfer 2 g of tallow using a spatula to a 50 mL centrifuge test tube. Using a Pasteur pipette, add 2 g of hexane to the tube. Add 0.2 g 100 ppm Mn and add PremiSolv to 20 g total. Vortex until the tallow is completely dissolved, approximately 1 to 2 minutes. Let solution stand until all bubbles are dissipated and the solution clarifies, about 3 minutes. All samples, standards and controls for tallow were diluted with kerosene/hexane (90/10) prior to measurement.

Preparation of canola oil is a dilution of 1 g canola oil and 9 g PremiSolv, followed by vortex. All samples, standards and controls for canola oil were diluted with kerosene prior to measurement.

A final concentration of 1 ppm Mn was used as an internal standard to correct for physical interferences affecting P and S. This was added to the kerosene/hexane solvent for tallow, and kerosene only for canola oil. A higher concentration may be required for other systems; a minimum of 100,000 counts per second is required. The Mn solution is stable for three days.

Instrument conditions

All ICP-OES data were collected using the PerkinElmer® Optima™ 2100 DV ICP-OES and an AS 93plus autosampler.

1. Low flow GemCone™ Nebulizer (N069-0671)
2. Standard single slot torch (N077 0338)

Modifications to the standard system are as follows:

1. 2 mm ID ceramic injector was replaced with a 1.2 mm ID straight bore injector (N077 6093)
2. 2 mm ID injector adapter holder was replaced with a 1.2 mm ID injector adapter holder (N077 6091)
3. Standard cyclonic spray chamber was replaced with the 4 mm baffled cyclonic spray chamber (N077 6090) which requires a black holder (N077 0614) if currently using a Scott spray chamber

Solvent flex peristaltic pump tubing is used: black/black for sample and red/red for the drain. The flush was not used. Read times were 2 seconds minimum and 5 seconds maximum. Three replicate measurements were used.

Table 2. Instrument Conditions.

RF Power	1500 W
Plasma Gas	15 L/min
Auxiliary Gas	2.0 L/min
Nebulizer Gas	0.3 L/min
Pump Speed	0.6 mL/min
Purge	High
Torch Cassette Position	-3.5
Read Delay	180 seconds

Spectral conditions

Emissions at low ultraviolet wavelengths (<185 nm) from the ICP are absorbed by oxygen in ambient air. The air is purged out of the optical path by means of a high purge of either argon or nitrogen which does not affect transmission of the low UV. Displacement of air by nitrogen to steady state conditions requires approximately 1.5 hours from system ready[4]. Determination of trace concentrations of S must be done axially in order to maximize the sensitivity. Absorption of low UV by the thin shear gas (air) that removes the plasma plume is negligible compared to the entire light path from ICP to detector. The shear gas also serves to considerably reduce material deposition on the entrance window.

A five point peak area is used for quantitation. Spectral interference correction was not required for this analysis.

Table 3. Operating Parameters.

Element	Wavelength (nm)	Background (nm)
P	213.617	-0.031
S	180.669	-0.048
Mn	257.610	-0.054

Physical interferences

Fats and oils have widely varying densities, viscosities and surface tension which result in different nebulization efficiencies. For accurate measurement, these differences must be corrected. Matrix matching of calibration standards and samples can be achieved fairly successfully by diluting samples with a solvent such as kerosene, or mixtures of kerosene and xylene, or in this case, kerosene and hexane. A commonly used dilution factor of 1 part sample and 9 parts solvent results in 10% of the testing material not exactly matched to the calibrant. This 10% can be accounted for to some extent with internal standardization. Prior studies using a reference material for edible oils indicated that manganese is a better internal standard than the commonly used Co or Y. The canola was used for COPA (Canadian Oilseed Processors Association) certification. Internal standards provide a monitor on changes of conditions in the sample introduction system. Samples that cause a greater than 25% difference from the calibrant are additionally diluted to reduce the matrix effect.

Results

There are no certified reference materials for P and S in tallow. Reference results for S in five separate samplings of a tallow sample were provided by POS Pilot Plant Corporation (118 Veterinary Road, Saskatoon, Sask. Canada, S7N 2R4) using an Optima 4300 DV ICP.

Reference results for P in one tallow sample was provided by Dr. A. Verwey Chemical Laboratories (Coolhaven 32, 3024 AC Rotterdam, The Netherlands, P.O. Box 6003,3002 AA Rotterdam, http://www.drverwey.nl) using ICP-OES.

Results compare well as shown in Table 4.

A crude degummed canola oil reference material (ID 05-183, Cargill Ltd., P.O. Box 190 Cheviot Rd., Clavet, Sask., S0K 0Y0, Canada) was utilized for QC purposes. Three aliquots of beef tallow were sampled and prepared separately. An additional sample was spiked with a final concentration of 9 ppm P and S. These results are shown in Table 5 and represent concentrations in the raw material. The actual concentrations measured are 10 times lower.

Table 4. Reference Material Results, ppm

	Sulphur 3P	Sulphur 8P	Sulphur 10P	Sulphur 8S	Sulphur 10S	Phosphorus
IMS	13.5	14	15	14	14	191
POS	13.9	14.1	14.3	13.5	14.2	—
Verwey	—	—	—	—	—	199

Table 5. Sample Results.

Sample	S (% mass)	P (% mass)	Mn (% recovery)
QC1	0.00144		120
Expected QC	0.0014		
QC2		0.0198	114
Expected QC		0.0200	
A1	0.00165	0.00424	106
A1 duplicate	0.00148	0.00423	105
A2	0.00135	0.00439	101
A2 spiked with 9 ppm P and S	0.00978	0.0125	100
Spike Recovery (%)	94	93	

Conclusion

The European Union leads the way to environmental protection and implementation of biodiesel production. At 100 ppm maximum tolerance for S and P, i.e., 10 ppm in the plasma after dilution, an axial view ensures the ICP system would be able to reliably meet anticipated lower regulation levels now and in the future. The Optima ICP-OES provides reliable and accurate analysis of sulphur and phosphorus in canola oil and beef tallow. In addition, the Optima can be easily set up to also measure Ca, Mg, Na, and K. Sodium and potassium must be measured radially to avoid any issues with ionization interferences amongst the alkali metals.

References

1. Biodiesel: A Renewable and Biodegradable Fuel, M. BOWMAN, D. HILLIGOSS and S. RASMUSSEN, PerkinElmer Life and Analytical Sciences, Shelton, Connecticut, and R. THOMAS, Scientific Solutions, Washington, DC.
2. Production of Biodiesels from Multiple Feedstocks and Properties of Biodiesels and Biodiesel/Diesel Blends. Report 1. J.A.Kinast, National Renewable Energy Laboratory, US Dept of Energy Laboratory, Colorado, 2003.
3. Economics of a Biodiesel Plant, Martin Kleber, mg engineering Lurgi PSI, AOCS, May 10, 2004.
4. Light and It's Measurement: Part 2 Sensitivity and Stability, Pamela Wee, PerkinElmer LAS Canada ICPOES /ICPMS Users Group Meetings held in Quebec City (2005), Toronto (2005), Edmonton (2006), and Vancouver (2006).

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