Application of Wilks Enterprise InfraSpec VFA-IR Spectrometer to test for bound glycerin in biodiesel.

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Abstract

A Wilks Enterprise InfraSpec VFA-IR Spectrometer was used to measure the bound glycerin (mono-, di- and triglycerides) in samples of biodiesel. The potential application and limitations of this approach were evaluated and a method developed to enable pass/fail determinations given the ASTM D 6751 limit on total glycerin of 0.240 mass %.

Background

Imperial Western Products (IWP) is a manufacturer of alkyl methyl esters, better known as biodiesel. IWP utilizes multiple feedstocks, including yellow grease, soybean oil and corn oil. IWP has been producing biodiesel for over 5 years and we are a BQ-9000 accredited manufacturer.

Our process is a batch process. There are several reactors in which the feedstock oil is transesterfied into biodiesel. The transesterfication reaction in our process takes 3-4 hours. To determine when the reaction is complete, a sample must be taken from the reactor and the mass % of bound glycerin (mono-, di- and triglycerides) determined on the sample. The ASTM standard D 6751, specifies that the total glycerin, which is the sum of free and bound glycerin, must be below 0.240 mass %. Since virtually all of the free glycerin is removed downstream in our process we are concerned only with the bound glycerin. Therefore, if bound glycerin is below 0.240 mass % it is considered to have passed and will move on to the next step in the process. If greater than 0.240 mass % it is allowed to react for an additional amount of time or additional reactants will be added.

Before testing the sample, the excess methanol and sodium hydroxide catalyst must first be removed. This is accomplished by washing the sample several times and then drying the sample on a hotplate. After the sample has been washed and dried it is ready for testing by either gas chromatography or the InfraSpec VFA-IR Spectrometer (referred to hereafter as InfraSpec). The procedure for running a gas chromatograph on the sample is approximately 45 minutes. The sample can be run on the InfraSpec in less than 5 minutes.

Instrumentation

The InfraSpec represents a new concept in portable mid-infrared instrumentation that provides spectral, quantitative or qualitative information. The InfraSpec incorporates a patented design consisting of an Attenuated Total Reflection (ATR) sample plate with an electronically modulated source on one end and a linear variable filter (LVF) and linear variable array on the other (Figure 1). The result is a compact spectrometer with no moving parts and no optical path exposed to air that is portable and rugged. The exposed ATR plate makes sample presentation and cleaning quick and simple. The software includes an internal calibration program that allows for simplified screen interface that give a digital readout in total glycerides for non-technical end users.

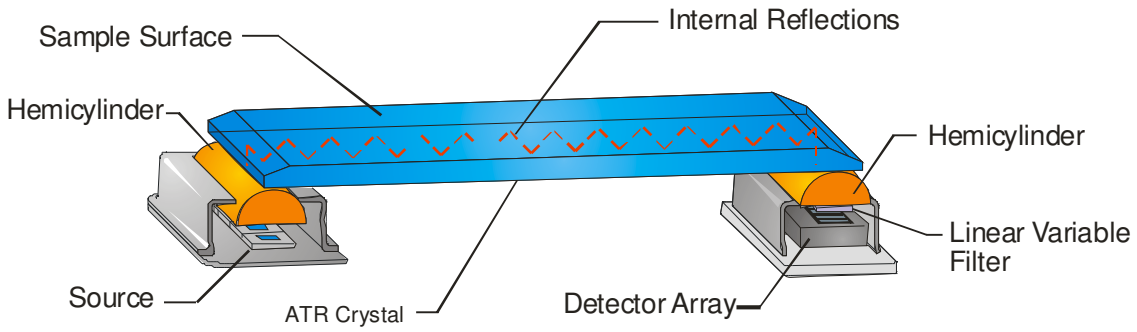

Figure 1 Optical schematic of the InfraSpec VFA-IR Spectrometer

Photo: InfraSpec VFA-IR Spectrometer

Data and Analysis

The InfraSpec was calibrated by obtaining spectra on 20 samples of biodiesel, derived from yellow grease, with varying levels of bound glycerin. The calibration was based on Partial Least Squares Regression analysis of the spectra.

One of the first observations was that the InfraSpec read samples with lower levels of bound glycerin slightly higher than the actual value and samples with higher levels of bound glycerin slightly lower than actual value. This in effect compressed the actual

range of bound glycerin. When running the identical sample repeatedly it was found that the InfraSpec results varied an average of 0.02 mass % at levels below 0.280 mass %. When running different samples with the same bound glycerin it was found the InfraSpec results varied an average of 0.03 mass % at levels below 0.280 mass %. The InfraSpec results varied from the actual bound glycerin by an average of 0.03 mass % at levels below 0.280 mass % bound glycerin. These values are derived from the data shown in Table 1 and Figure 2 below.

Table 1: Data comparing InfraSpec to Actual Bound Glycerin

Sample ID	Actual Bound Glycerin	InfraSpec Result
R4 #2, 10-24-06	0.101	0.163
R1, 10-24-06	0.104	0.145
ME 5, 8-31-06	0.130	0.157
ME 4, 10-3-06	0.134	0.132
R7, 10-26-06	0.134	0.164
R4, 10-30-06	0.147	0.170
R5, 10-26-06	0.153	0.174
R8, #2, 10-24-06	0.155	0.176
R4, 10-26-06	0.159	0.210
R5, 10-25-06	0.160	0.188
R2, 10-4-06	0.166	0.178
R5, 10-3-06	0.169	0.213
R-7,10-13-06	0.170	0.200
R9, 10-30-06	0.173	0.196
R5, 10-30-06	0.183	0.169
R9, 10-4-06	0.184	0.220
R7, 10-30-06	0.185	0.126
R-4, 10/13/06	0.186	0.192
R8, 10-2-06	0.189	0.166
ME 5, 9-5-06	0.189	0.175
R3, #2 10-31-06	0.190	0.197
R4, 10-3-06	0.197	0.159
ME 4, 8-15-06	0.207	0.165
ME 4, 8-14-06	0.211	0.180
R2, #2, 10-31-06	0.213	0.142
R2, 10-25-06	0.213	0.234
R4, 10-11-06	0.214	0.151
R-1, 10/12/06	0.214	0.189
R4, 10-31-06	0.222	0.200
ME 5, 7-12-06	0.225	0.205
R-2, 10/13/06	0.235	0.240
R8, 10-25-06	0.236	0.192
R6, 10-25-06	0.244	0.254
R4, 10-24-06	0.248	0.243
R8, 10-10-06	0.252	0.226
R9, #2, 10-10-06	0.284	0.234
R2, 10-24-06	0.303	0.359

R9, 10-5-06	0.364	0.260
R-1, 10/13/06	0.395	0.276
R8,10-31-06	0.447	0.307
ME 5, 8-7-06	0.463	0.273
R1, 10-3-06	0.496	0.292
R8, 10-24-06	0.738	0.408
R2, 10-31-06	1.382	0.739
R9, 10-2-06	1.721	0.575
R3, 10-31-06	6.502	1.061

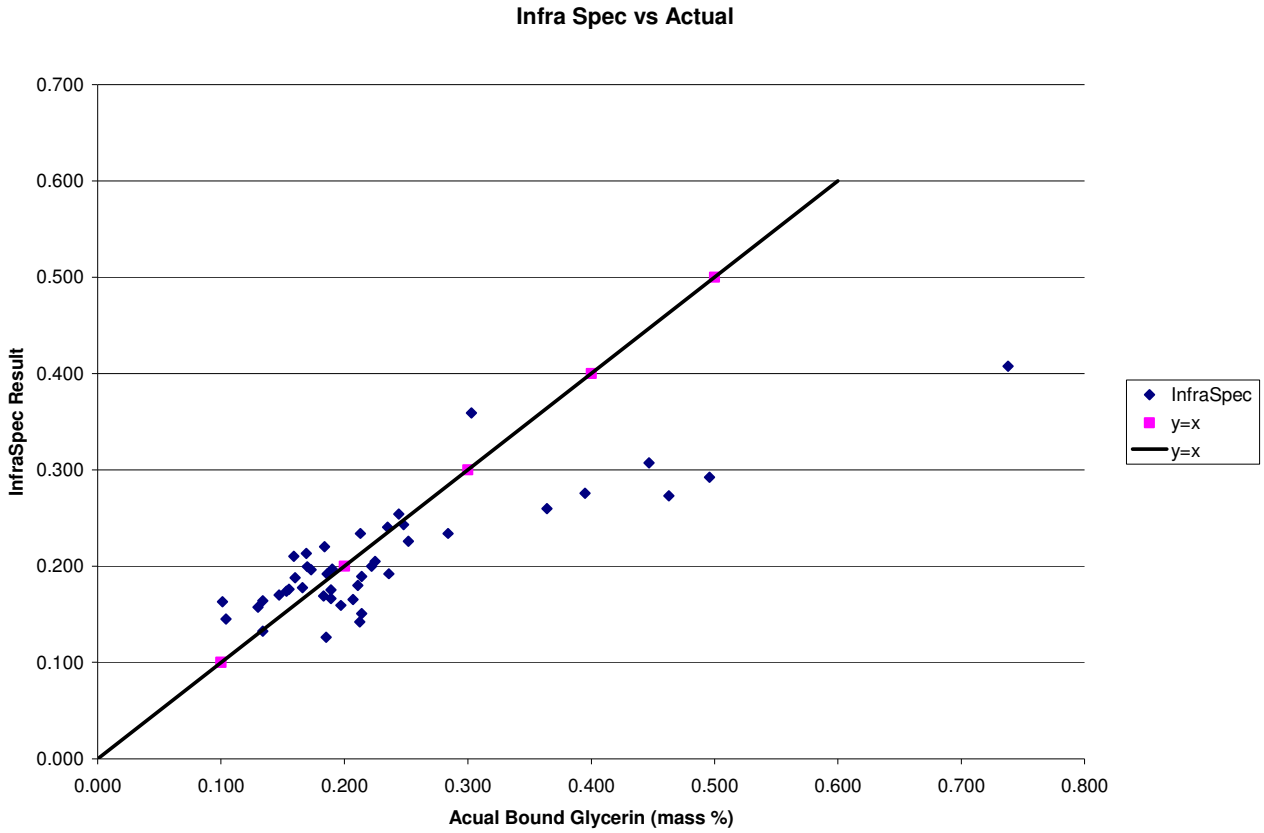

Figure 2 Chart of InfraSpec Result versus Actual Bound Glycerin

Due to these aforementioned limitations in the accuracy of the InfraSpec it was concluded that the best approach would be to empirically establish three ranges in which to categorize the results given by the InfraSpec. Below a certain value the sample would be deemed passing. Above another value it would be deemed failing and between these two values it would be indeterminate. If deemed indeterminate, a gas chromatograph would be necessary. Refer to Table 2 for the limits derived for yellow grease biodiesel.

Table 2: Limits for Pass/Fail Determination

	Bound Glycerin Limits
Passing	X < 0.220
Indeterminate	0.220 < X < 0.260
Fail	X > 0.260

Determining where to set these limits needs to be determined empirically from the data and should be updated on a regular basis. These limits were established to assure that no samples which actually pass bound glycerin are interpreted as failing by the InfraSpec and vice versa. It was found that biodiesel derived from other feedstocks (soy, corn) gave very different results than yellow grease derived biodiesel.

The effect of the pH of the sample on the result generated by the InfraSpec was also investigated. It was found that pH has a significant effect on the result. Samples at a high pH (8-9) gave results that were about +/- 0.06 mass % higher than those samples at low pH (6-7). To minimize this variance it is necessary to adjust all samples to the same predetermined pH during the wash step. In our case, we adjust the samples to a pH of 6-7, which is checked with a pH strip.

Conclusions/Recommendations

Use of the InfraSpec for making pass/fail determinations can significantly reduce analysis time, by about 40 minutes in our case, and thereby decreasing wait time and increasing throughput. It is estimated that use of the InfraSpec will increase our reactor throughput by 15 -20 %.

There are limitations to the accuracy and precision obtainable using the InfraSpec. The InfraSpec by no means can achieve the performance of a gas chromatograph, but can be useful for quickly giving a pass/fail determination for biodiesel while in-process. Testing by gas chromatography per ASTM specifications is still necessary for finished lots of biodiesel.

All the factors which limit the accuracy and precision are not understood but the following are a couple possibilities. The analytes in our case are the triglyceride, diglyceride and monoglyceride molecules, which collectively constitute the bound glycerin. Having multiple analytes makes developing a correlation more complicated as the absorbance at each wavelength is the composite of the absorbance of all analytes. For example, say two samples may have the same bound glycerin value but different ratios of mono-, di-, and triglycerides. The InfraSpec may be more sensitive to monoglycerides than triglycerides and so it would measure the bound glycerin as being higher for the sample with the higher concentration of monoglyceride than the sample with higher triglyceride concentration.

Another factor is the type of feedstock the biodiesel is derived from. Different kinds of oil have different ratios of free fatty acids. Even a certain type of oil will have some variance in the free fatty acid composition. For this reason the focus of the study so far

was limited to develop criteria for making a pass/fail determination on yellow grease derived biodiesel.

It should be possible to establish criteria for analyzing biodiesel derived from other feedstocks using the same basic approach as used for yellow grease.