Comparison of Multiple Performance Properties of Diesel Fuel Using an Innovative Near-Infrared Analyzer Designed for Field Analysis

Authors: *Stuart Farquharson, Wayne Smith, Vincent Colantuoni, Cindy Galdamez, Dr. Raj Shah*

Real Time Analyzers, Inc. Middletown, CT & Koehler Instrument Company, Inc. Holtsville, NY

BACKGROUND INFORMATION

The need for fuel is growing worldwide along with the industrialization of many Asian and African countries. Along with this growth is an increase in fuel theft in the form of dilution. Dilution can range from water to lower grade fuels. While water dilution can easily be determined, low grade fuel dilution requires sophisticated analyzers that determine various fuel properties. Unfortunately, such analyzers are confined to laboratories, and the measurements can take hours to perform. In an effort to meet the need for rapid verification of fuel at ports and depots, we have developed a field-portable analyzer that can determine multiple properties within 10 seconds. The portable fuel analyzer measures the near-infrared (NIR) spectrum of a fuel sample, which is correlated to the properties using multivariate statistics and a fuel sample data base consisting of previously measured NIR spectra and ASTM properties. Twenty-two correlation models have been developed for diesel, gasoline, and jet fuels that predict fuel properties comparable to ASTM reproducibility values. The analyzer accurately determined properties for 16 diesel samples previously characterized at two ASTM certification laboratories. The analyzer design, model development, and the sample measurements are described.

INSTRUMENTATION AND DEVELOPMENT

The portable fuel property analyzer (PFPA) was designed and built to measure the diesel, gasoline, and jet fuel samples. The PFPA employed 2 mL glass sample, a transmission grating to spread the spectrum, and a 256 channel InGaAs array to detect the transmitted NIR radiation from 1000 to 1600 nm.

Table 1

Properties	Diesel
Density	166
Cetane Index	141
Viscosity @ 40 C	134
Aromatics	35
Saturates	35
Cloud Point	111
Flash Point	107
Distillation Values	163

Figure 1

Model Development

The fuel property models were built by measuring the NIR spectra (Figure 2) and ASTM properties of 166 diesel samples (Table 1). Then each spectrum was pre-processed as follows: 1) the 1st derivative was taken to remove baseline tilt and offset; 2) an 11-point, 3rd degree polynomial (Savitsky-Golay) was applied to remove noise; 3) the range was clipped to 1050 to 1550 nm (2nd overtone and combinations, 6500 to 9000 cm-1); and 4) a multiplicative scatter correction (MSC) was applied to remove y-axis magnitude influences (Figure 3A). Then partial least squares (PLS) modeling was used to develop correlations between the processed spectra as a function of wavelength and ASTM measured property values.

For example, a model was developed to correlate the diesel spectra of 141 diesel samples to their known cetane indexes measured according to ASTM D976 (Figure 3). The first-order correlation (or latent variable, LV) consists of regression coefficients, both negative and positive, as a function of wavelength (Figure 3B). This first LV for the cetane index model captured 77.78% of the variance, i.e. most of the correlation. Additional LVs, which represent higher order relationships between the spectra and properties, can be used to improve the models. This process was continued until the next latent variable did not improve the model (Figure 3C).

Figure 2

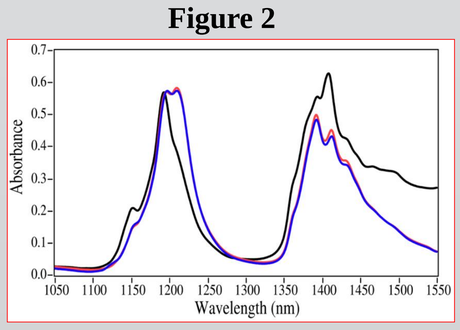
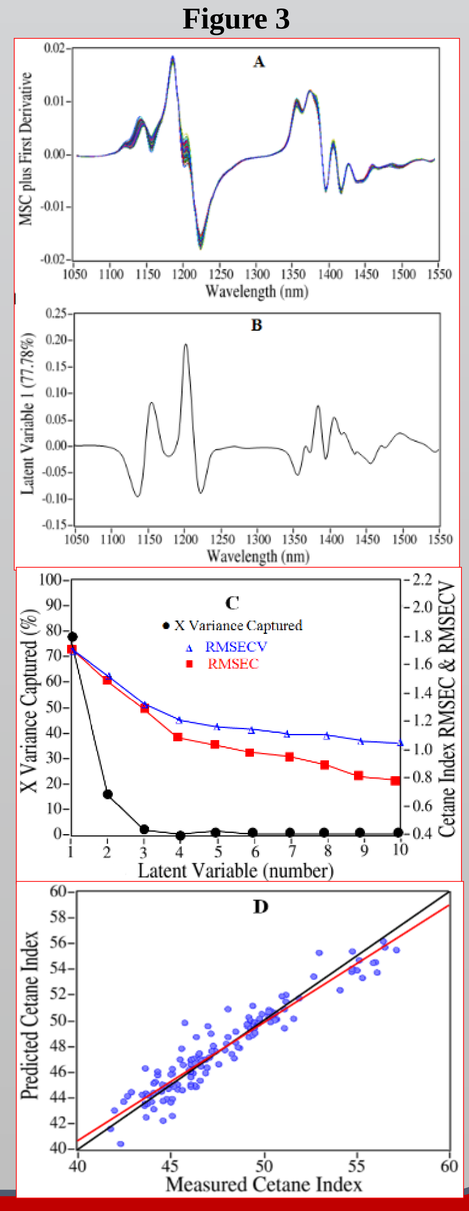


Figure 3



RESEARCH AND RESULTS

The performance of the model is shown in a plot of the ASTM measured values versus the NIR predicted values (Figure 3D). A linear least squares fit to the data, here referred to as the correlation coefficient of calibration, R2, has a value of 0.92 (1.0 would be a perfect correlation). The root mean squared error of correlation (RMSEC) was then cross validated using the "venetian blinds" method to yield a cross-validated correlation coefficient (R2-CV) and a RMSECV of 0.91 and ±1.1, respectively. This process was performed for all of the diesel properties. The R2-CV and RMSECV values are listed in Tables 2.

Table 2

Performance Specifications for Diesel Fuel								
Property	ASTM			PFPA				
	Method	Reproduc-ibility	Repeat-ability	Lv	R^2-CV	2x RMSECV	2x StdDev	Calibration Range
Density (15 C), g/mL	D1298	0.0012	0.0001	6	0.95	0.0045	0.001	0.82 to 0.88
Cetane Index	D976	2	-	5	0.93	1.5	0.4	43 to 57
Viscosity (40 C), cSt	D445	0.042	0.022	6	0.85	0.34	0.058	2.0 to 4.5
Aromatics, % vol*	D1319	3.0	1.4	3	0.92	5.2	0.9	20 to 55
Saturates, % vol	D1390	4.0	1.2	3	0.89	6.2	1.4	45 to 80
Cloud Point, C	D2500	4	2	5	0.68	7.2	0.7	-25 to 15
Flash Point (P-M), C	D93	6	2	3	0.37	13.4	1.4	65 to 95
Pour Point, C	D5297	6.8	3.4	4	0.45	9.4	1.6	-28 to -6
Distillation 0%, C	D86	8.5	3.5	5	0.35	21.4	1.9	160 to 210
Distillation 10%, C	D86	8.5	3.5	6	0.72	12.6	1.8	200 to 250
Distillation 20%, C	D86	8.5	3.5	6	0.85	12.5	1.8	180 to 270
Distillation 50%, C	D86	8.5	3.5	6	0.78	10.2	1.8	240 to 300
Distillation 90%, C	D86	10.5	3.5	6	0.53	14.2	1.5	300 to 360

The 16 test samples were measured at ASTM certification laboratories in Houston, TX, and New Haven, CT. The comparison was limited to density, cetane index, viscosity, flash point, and cloud point, and distillation points at 90% for which all of the samples had ASTM values, except cloud point which had values for 13 samples. The PFPA predicted all of the properties very close to the measured ASTM values (Table 3). Statistically, twice the standard deviation of the average difference between the ASTM and PFPA values for each property (2xStdDev), indicative of the 95% confidence level for this data set, was better than twice the RMSECV calculated by the models (2xRMSECV), except for a minor difference in the cetane index of Sample 11 (highlighted yellow). Removal of this sample from the analysis greatly improved the 2xStdDev, reducing it from 2.4 to 1.7.

Table 3

	Density (15 C), g/mL			Cetane Index			Viscosity@40 C, cSt			Flash Point (P-M), C			Cloud Point, C			Distillation 90%, C		
Sample	ASTM	PFPA	Diff	ASTM	PFPA	Diff	ASTM	PFPA	Diff	ASTM	PFPA	Diff	ASTM	PFPA	Diff	ASTM	PFPA	Diff
1	0.832	0.832	0.000	49.4	51.9	2.5	2.43	2.36	0.1	65	57	8		-8.7		323	328	5
2	0.834	0.837	0.003	49.6	48.9	0.7	2.16	2.34	0.2	63	67	4		-17.3		318	322	4
3	0.845	0.842	0.003	52.2	52.2	0.0	3.11	3.33	0.2	73	71	2		-14.8		326	317	9
4	0.833	0.836	0.003	49.8	49.7	0.1	2.19	2.38	0.2	57	65	8	-18	-17.4	1	313	321	8
5	0.831	0.833	0.002	49.6	50.2	0.6	2.10	2.29	0.2	57	65	8	-14	-16.5	3	315	324	10
6	0.826	0.826	0.000	54.2	54.3	0.1	3.63	3.43	0.2	69	57	12	-14	-9	5	317	328	11
7	0.832	0.835	0.003	48.3	48.2	0.1	2.10	2.16	0.1	65	65	0	-14	-18.3	4	313	322	9
8	0.839	0.841	0.002	52	52.1	0.1	3.06	3.13	0.1	71	70	1	-11	-14.5	4	327	317	10
9	0.846	0.847	0.001	48.5	46.1	2.4	2.77	2.54	0.2	61	69	8	-23	-19.3	4	325	313	12
10	0.857	0.854	0.003	44.9	43.5	1.4	3.06	2.70	0.4	66	76	10	-9.6	-10.8	1	325	312	13
11	0.865	0.860	0.005	36.6	40.8	4.3	2.53	2.58	0.1	62	71	9	-9.4	-11.1	2	327	330	3
12	0.845	0.845	0.000	45.4	46.3	0.9	2.66	2.69	0.0	62	67	5	-15.4	-16.6	1	320	321	1
13	0.829	0.827	0.002	50.0	51.0	1.0	2.43	2.23	0.2	60	66	6	-7.7	-12.5	5	329	326	3
14	0.856	0.853	0.003	43.7	44.0	0.3	2.86	2.63	0.2	79	69	10	-13.6	-14.9	1	320	307	13
15	0.844	0.843	0.001	49.2	48.7	0.5	3.00	2.96	0.0	66	67	1	-15.2	-15.5	0	323	316	7
16	0.842	0.841	0.001	44.2	46.2	2.0	2.43	2.36	0.1	59	67	8	-14.9	-14.8	0	312	315	3
Ave Diff			0.002			1.1			0.15			6.3			2.3			7.6
2xStdDev			0.0028			2.4			0.19			7.4			3.5			7.9
2xRMSECV			0.0045			2.2			0.34			13.4			7.2			14.2

CONCLUSIONS

When transporting fuels, specifically diesel fuels, it is important to verify that the fuel shipments meet required specifications. Often in the transportation process, the shipments pass through custody at different depots, pipelines and ports where the fuel properties should be quickly checked. To meet this need of testing multiple properties in the field, a fuel analyzer based on near-infrared (NIR) spectroscopy was developed. The standard deviations between the values given by the analyzer and the ASTM laboratory instrument measured values for these samples were generally better than the model root mean squared error of correlation or, in other terms, the cross-validated values for each property. This innovative analyzer will be able to produce quick and accurate results correlated to ASTM methods for on-site fuel verification

ACKNOWLEDGEMENTS

Koehler Instrument Company, Inc. 85 Corporate Drive Holtsville, NY 11742 631-589-3800

rshah@koehlerinstrument.com, cklager@koehlerinstrument.com

Real-Time Analyzers, Inc. 362 Industrial Park Rd (#8) Middletown, CT 06457

stu@rta.biz, wayne@rta.biz