KOEHLER INSTRUMENT COMPANY, INC.

Development of an NIR Analyzer for Measuring Multiple Fuel Properties of Commercial and Military Grade Jet Fuel in the Field

Authors: *Stuart Farquharson, Cindy Galdamez, Dr. Raj Shah*

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

BACKGROUND INFORMATION

When it comes to Aviation fuel of both commercial and military grade, quality and safety are of the utmost importance. A new technique has been developed for quick, in-field analysis of Jet Fuel properties that can be compared to the governing ASTM requirements. ASTM D1655 is the standard specification for aviation turbine fuels, the new portable near-infrared (NIR) analyzer that will be discussed in this poster can give results with comparable reproducibility to some of the key tests required by this standard.

The new Portable Fuel Quality Analyzer uses optics, detectors, and a light source that are cost effective allowing there to be more fuel checks during the shipment process at fuel ports and depots. Through experimental research it was determined that an NIR analyzer that measures in the 1000 to 1600 nm spectral range with 5 nm resolution and a 1 cm path length would give results meeting ASTM repeatability and reproducibility for testing certain fuel properties.

Through the use of multivariate statistics and a fuel sample data base the values given by the Portable NIR Analyzer were correlated to the ASTM proven values. Twenty-two correlation models for diesel, gasoline, and jet fuels were developed with the help of ASTM certified laboratories to compare repeatability and reproducibility values. The analyzer determined properties had reproducibility values that compared favorably to the ASTM values and the repeatability values of the analyzer properties often exceeded ASTM repeatability values. Therefore, for jet fuel in particular, the user can quickly and easily determine Density, API Gravity, Distillation Fractions, Flash Point, Viscosity (at -20°C), Freezing Point, Pour Point and Fuel System Icing Inhibitor values.

INSTRUMENTATION AND DEVELOPMENT

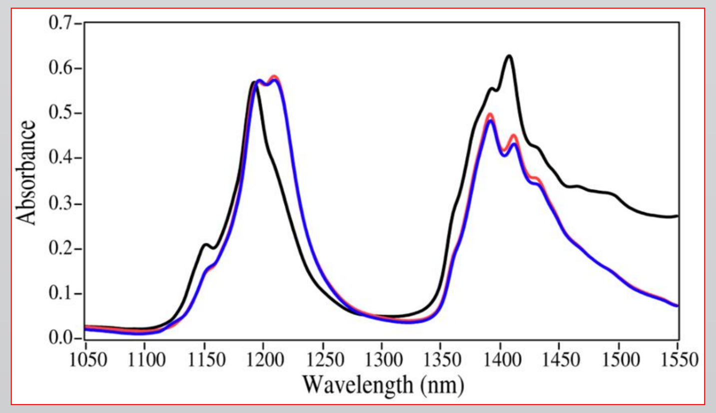
The portable fuel property analyzer (PFPA) was designed and built to measure the diesel, gasoline, and jet fuel samples. The PFPA employed 2 mL glass sample, a transmission grating to spread the spectrum, and a 256 channel InGaAs array to detect the transmitted NIR radiation from 1000 to 1600 nm.

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

Figure 2

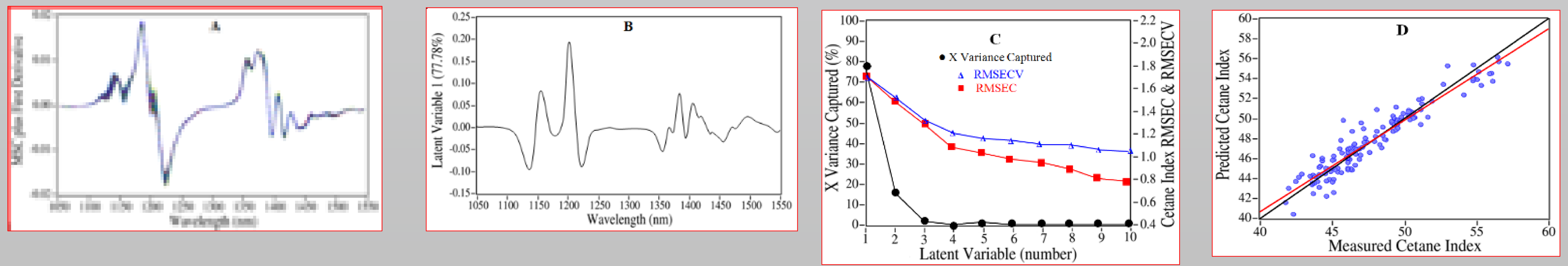


Model Development

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 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