Innovative Instrumentation Design for Measuring Multiple Fuel Properties in Diesel Fuel

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ABSTRACT

The efficiency, economy, and reliability of diesel engines has made it popular for use in transportation, manufacturing, power generation, construction, and farming. In 2004, 60 percent (%) of trucks in the United States was recorded to consume diesel fuel. In fact, the sales of diesel fuel are an indicator of economic strength, as diesel engines are commonly used to move goods from manufacturer to consumer. It is advantageous to the end-user or consumer to have a reliable and effective way to quickly determine properties of a fuel. However, determining the properties of fuel can be a time-consuming process. Therefore, the Portable Fuel Property Analyzer (PFPA) is an innovative technique developed for fuel quality assessment for in-field analysis of diesel fuel that can be compared to the governing ASTM requirements.

The PFPA combines Near Infrared Spectroscopy with Advanced Chemometric Analysis to determine key fuel properties that must meet specification standards. The PFPA correlates a database of NIR spectra to fuel properties that were determine with traditional ASTM methods using partial least squares (PLS). The PLS models were then compared to a validation set of fuel samples. The predicted values of PFPA exhibit comparable accuracy to ASTM methods and the repeatability values often-exceeding ASTM repeatability values. In contrast to standard ASTM test methods, which require a specific instrument for each property and a large volume of fuel sample, the PFPA can determine multiple fuel properties of diesel fuel in 10 seconds using only 2ml of sample. This allows end-users to test diesel fuel rapidly, and to quickly determine if it meets fuel specification requirements.

INTRODUCTION

A new technique has been developed for quick, in-field analysis of Diesel Fuel properties that can be compared to the governing ASTM requirements. ASTM D975 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 measured values. Correlation models for diesel 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

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

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

Table 1. Properties measured of diesel fuel.

Figure 1. PFPA

MODEL DEVELOPMENT

The fuel property models were built by measuring the NIR spectra (Figure 2) and ASTM properties of 166 diesel samples. 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); 4) a multiplicative scatter correction (MSC); and 5) Mean Center was applied to remove y-axis magnitude influences. 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.

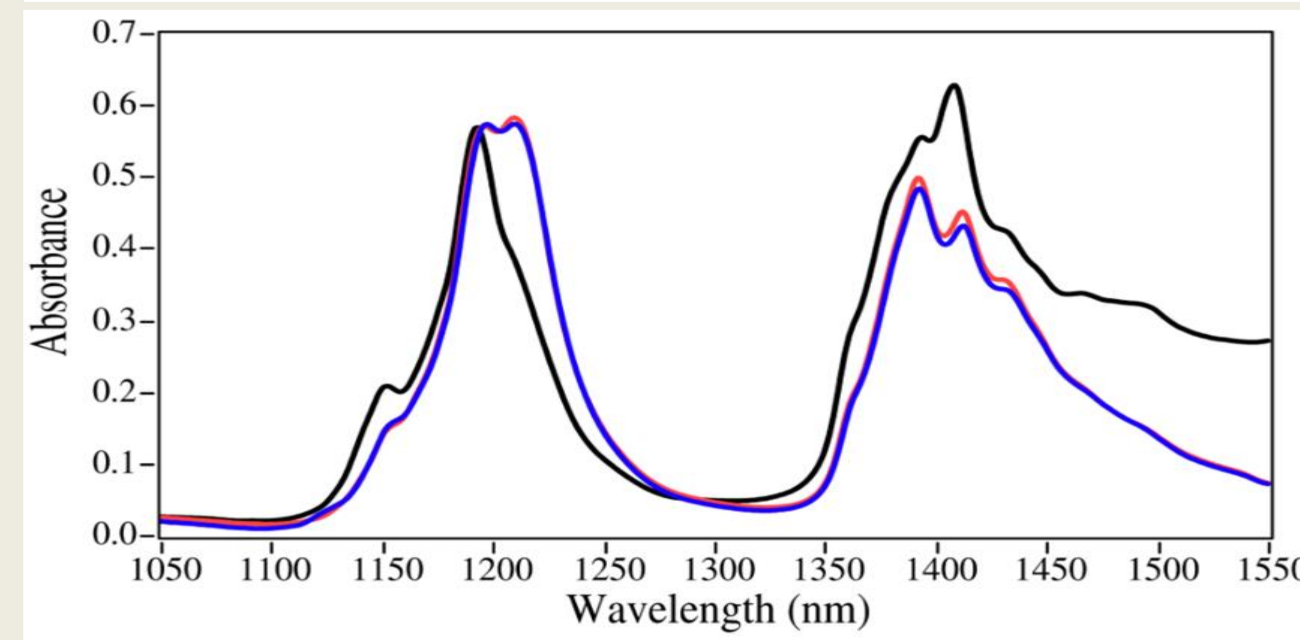

Figure 2. NIR Spectra

RESEARCH AND RESULTS

The performance of the model is shown in a plot of the ASTM measured values versus the NIR predicted values (Figure 3). 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 calibration (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.

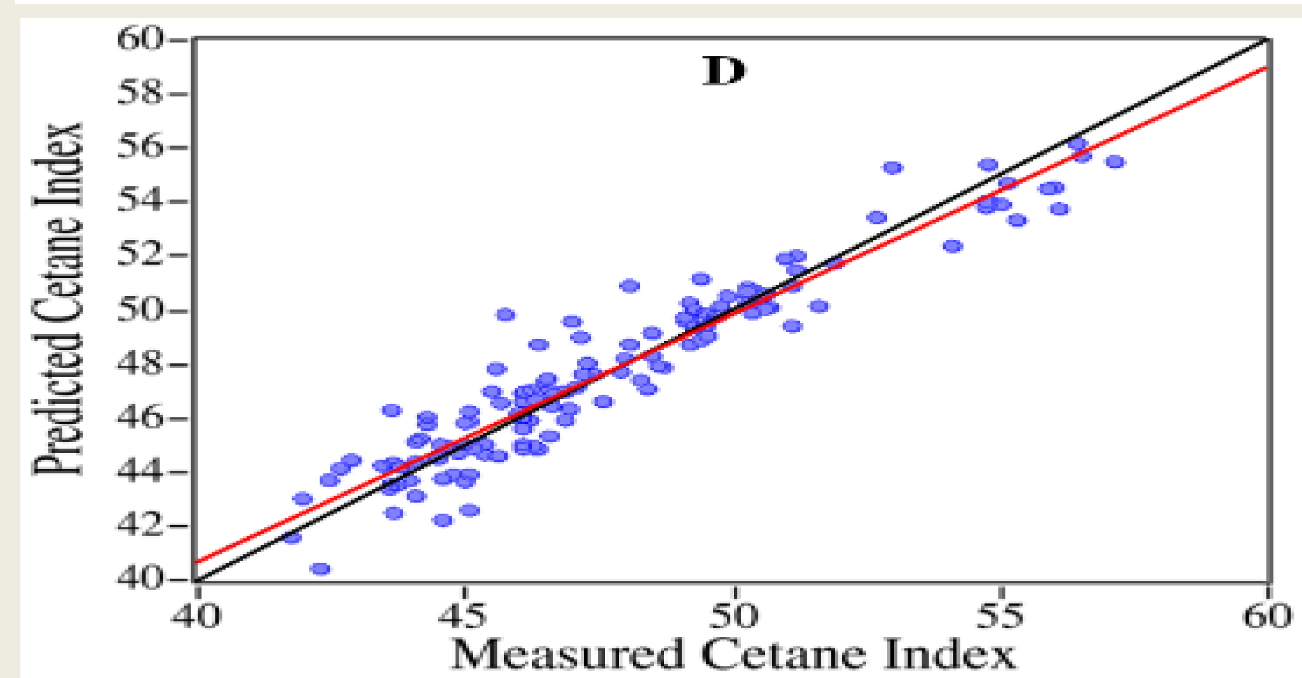

Figure 3. ASTM measured values versus NIR predicted Values

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 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

Table 2. Performance Specifications

Diesel	Jet Fuel	Gasoline
Density / API Gravity	Density / API Gravity	Density / API Gravity
Distillation Fractions (IBP, 10%, 50%, 90%, FBP)	Distill Fractions (IBP, 10%, 50%, 90%, FBP)	Distill Fractions (IBP, 10%, 50%, 90%, FBP)
Cetane Index	Cetane Index	Octane (RON, MON, AKI)
Viscosity (+40 C)	Viscosity (-20C, +40C)	Reid Vapor Pressure
Flash Point	Flash Point	Ethanol
Cloud Point	Freeze Point	MTBE
Aromatics / Saturates	FIS-II	Benzene, Toluene, Ethylbenzene, Xylenes
Biodiesel Content	Aromatics	
	Hydrogen Content	
	Net Heat	

Figure 3.Fuel properties measured by PFPA for different fuels

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.

REFERENCES

- **ASTM D975** "Standard Specification for Diesel Fuel Oils" (West Conshohocken, PA: ASTM International).
- **Pittcon Poster 2018** "Fuel Property Model Transfer for Fielded Near-infrared Spectrometers" (Real-Time Analyzers, CT).

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