More Advances in the use of Fourier Transform Infrared Spectroscopy for the Biodiesel Quality Analysis

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- Brief introduction to FT-IR
- Current capabilities
- Potential new capabilities

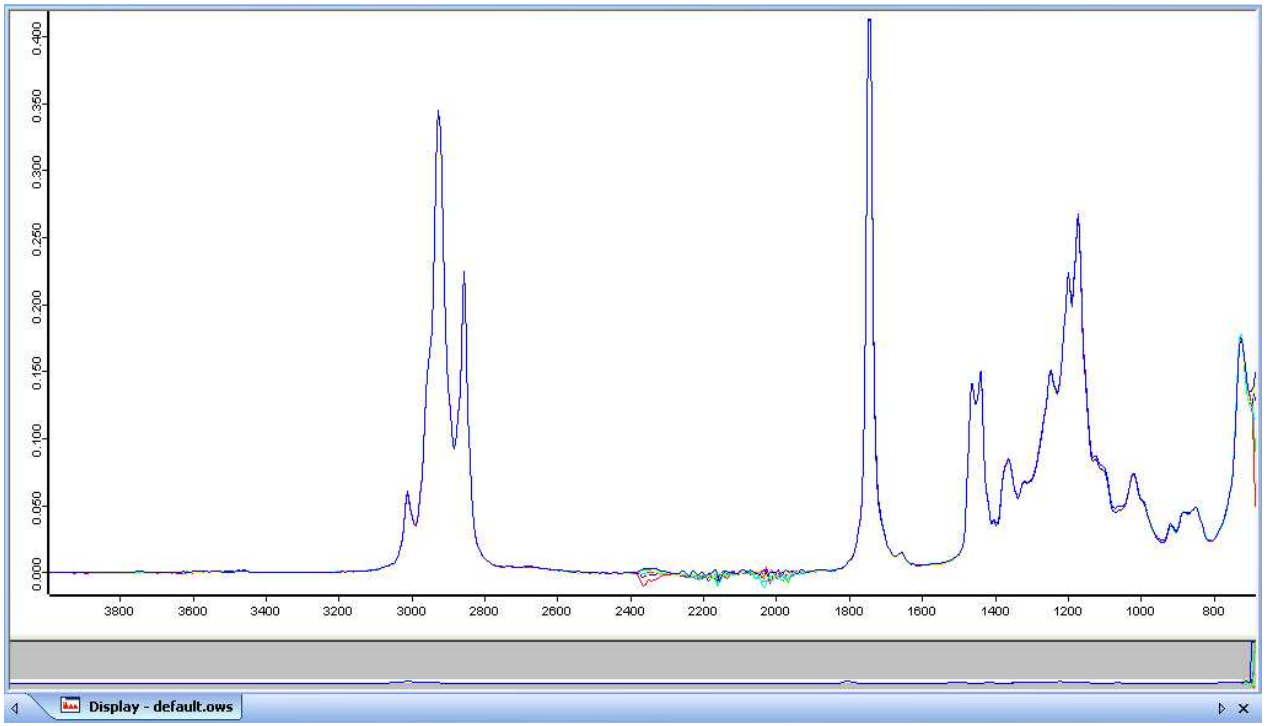
Uses of FT-IR for analysis

- Qualitative analysis: fingerprinting of samples for ID purposes only
- Quantitative analysis using specific functional group IR absorption regions
  - e.g. C-H or O-H, or C=O
- Quantitative analysis using chemometrics
  - Use of full spectral region, 680 - 4000 cm^{-1}
  - Correlation to primary methods, wet chemistry or chromatographic
  - Complex mathematical algorithms to correlate spectra to primary data

Quantitative FT-IR using Chemometrics

- Training set of at least 50 samples, but can be up to several hundred
- Primary data measured for the training set
- Spectra collected for training set
- Chemometric algorithm developed to count the interferences and correlate the primary data to the spectra
- Algorithm used to predict future samples having similar chemical matrix
- Specific spectral features not necessarily defined for specific traits
- Traits correlated can be either chemical components, properties or even physical properties

FT-IR spectra of B100

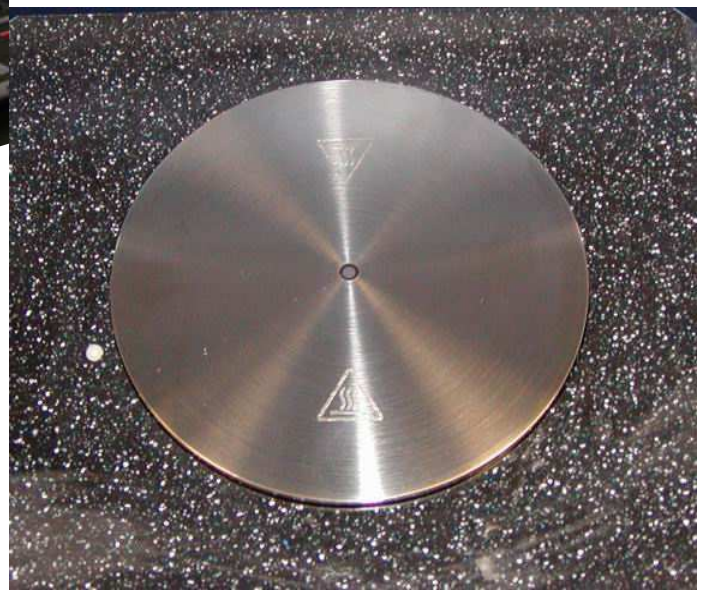


The QTA® System: Networked FT-IR Systems

- Calibration algorithms are developed for many users, many systems, many feedstocks and production processes
  - Calibrations are more robust
  - Real world samples are used; artificially produced samples are not suitable
- Multiple FT-IR instruments in remote locations are networked to use a single, central calibration
  - All FT-IR instruments provide consistent results
  - No instrument specific or site specific calibration adjustments are required

The QTA® System: Networked FT-IR Systems

- Sample surface requires only one drop
- No sample preparation fo homogeneous samples



- Multiple component analyses obtained with a single spectra

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Current use of networked FT-IR Systems

- Networked FT-IR systems are currently in use at over 30 biodiesel production facilities in the U.S., Europe and South America
- Feedstocks include:
  - Soybean
  - Tallow
  - Choice White Grease
  - Waste Vegetable Oil
  - Rapeseed
  - Canola
  - Poultry
  - Palm oil

And mixtures of the above

Current QTA® System Applications

	Reference method	Range	Std. error
B100 (NA)			
Free Glycerin, %	D6584	0 – 0.03	0.003
Total Glycerin, %	D6584	0 to 0.50	0.025
Cloud Point, deg C	D2500	-6 – 12	1.7
Acid Number, mg KOH/g	D664	0 – 1.25	0.08
Moisture, %	KF	0 – 0.1	0.007
Methanol, %	EN 14110	0 – 3	0.03
B100 (EN)			
Ester, %	EN 14103	93 – 100	0.45
Iodine Value	EN 14111	45 to 135	1.1
Density, Kg/m^3	EN 12185	875 – 890	0.5
Viscosity, mm^2/sec	EN ISO 3104	3 – 6	0.1
Monoglycerides, %	D6584	0 – 0.9	0.06
Diglycerides, %	D6584	0 – 0.55	0.04
Triglycerides, %	D6584	0 – 0.24	0.03

Current QTA® System Applications

	Reference Method	Range	Std. error
In-process biodiesel			
Monoglycerides, %	D6584	0 – 3	0.11
Diglycerides, %	D6584	0 – 5	0.1
Triglycerides, %	D6584	0 – 7.5	0.15
Incoming Oil			
FFA, %	AOCS Ca 5a-40	0 to 12	0.2
Moisture, %	KF	0 – 1.3	0.05
Crude Glycerin			
MeOH, %	GC	0-12	0.28
Moisture, %	KF	0.5 to 25	0.6
Methanol			
Moisture, %	KF	0-20	0.25

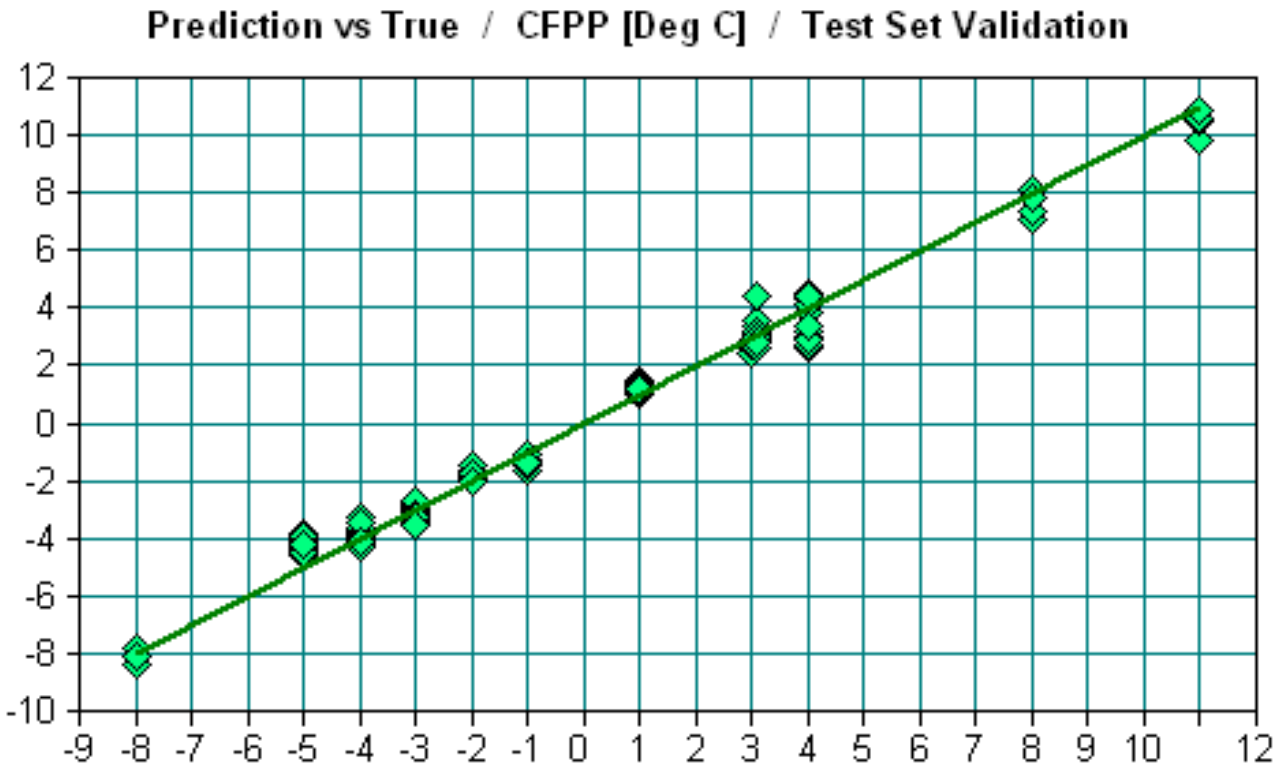
New developments with networked FT-IR systems

- Cold Filter Plugging Point, EN 116
- Cetane number, D613
- Pour Point, D97
- Biodiesel Blend concentrations, D7371
- Oxidative stability, EN 14112

New developments in FT-IR: CFPP

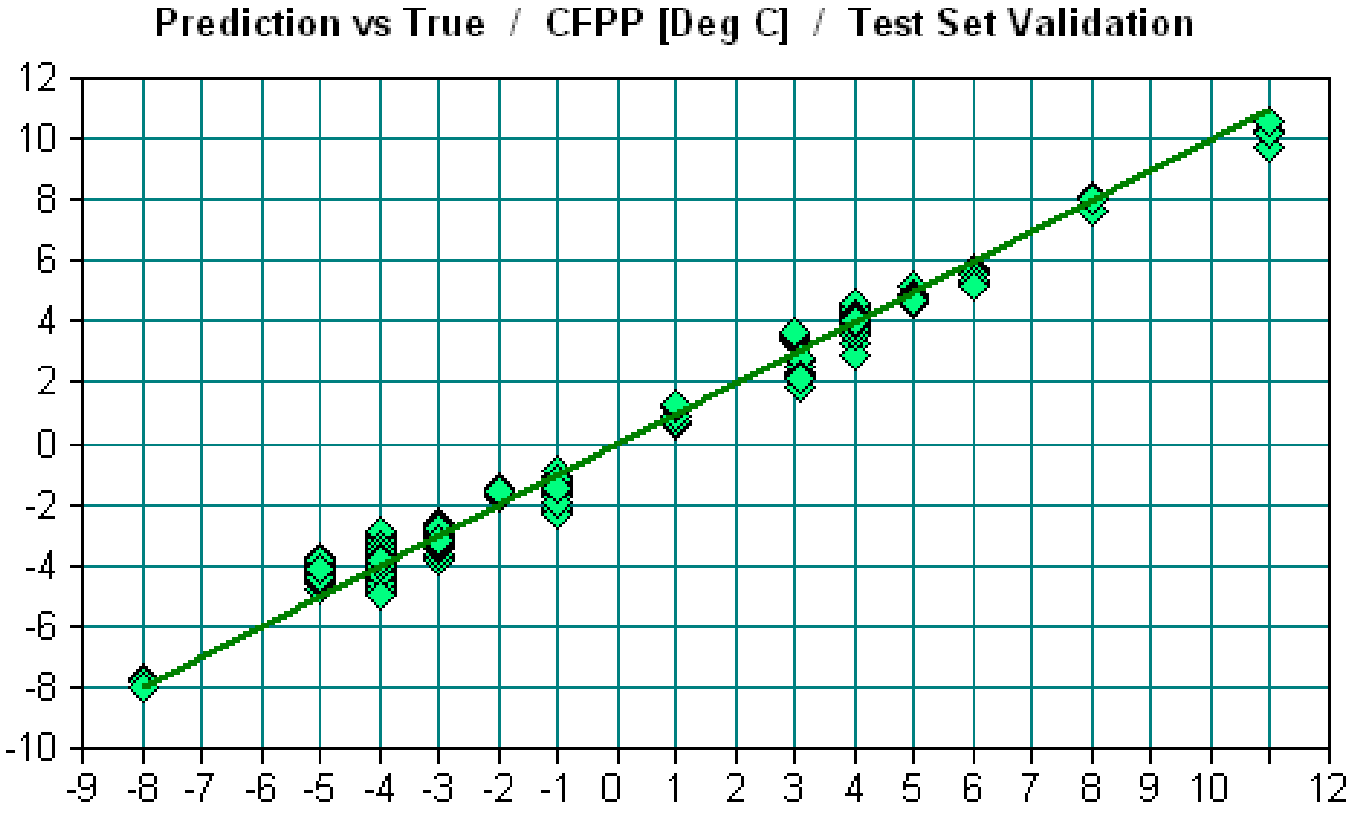
- CFPP data obtained from two sources
- Total of 50 samples encompassing at least 7 feedstocks

CFPP: primary data from one lab



R2 = 97% RMSEP = 0.66 degC

CFPP: primary data from multiple labs



R2 = 97% RMSEP = 0.74 hr

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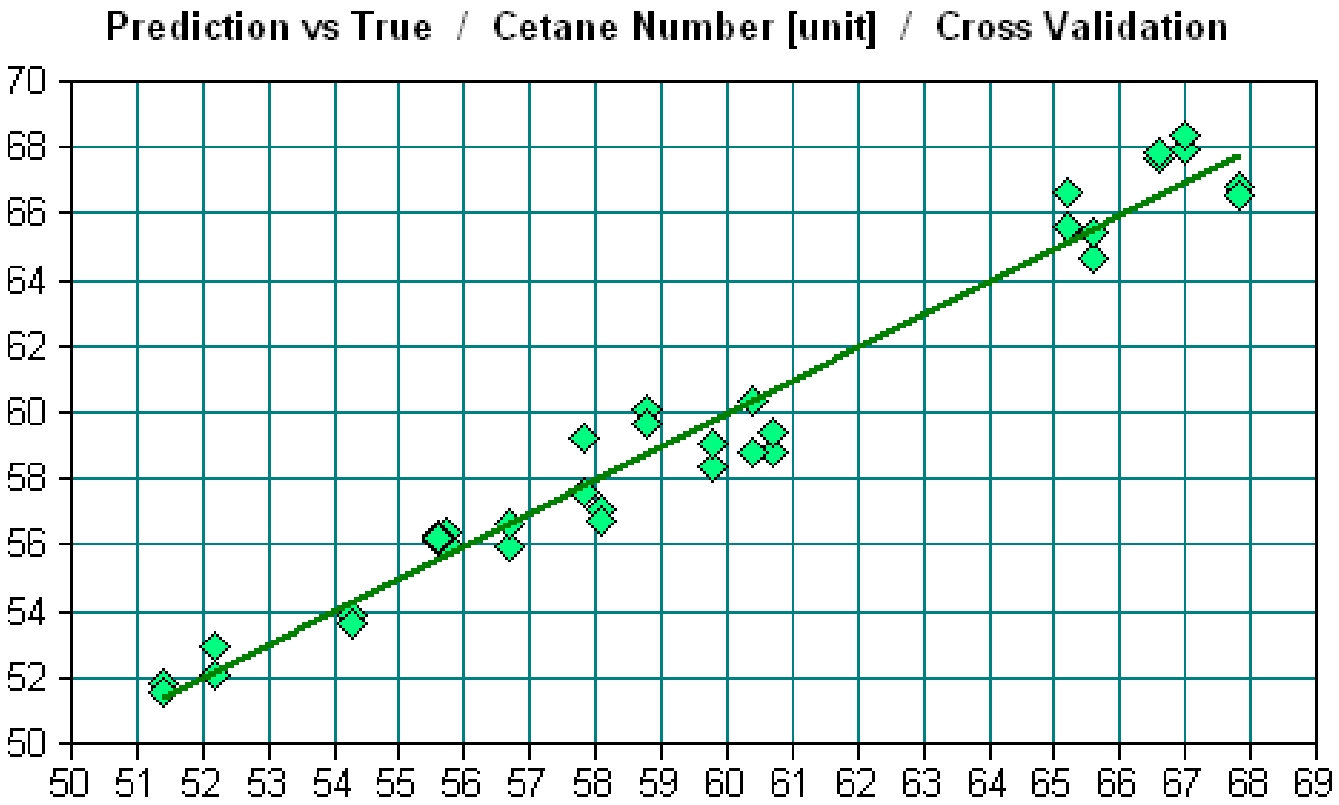
Next steps: CFPP

- Excellent correlation and error using both single lab and multi-lab primary data
- CFPP calibrations have been commercialized
- Continue to expand calibration training set and validate

New developments in FT-IR: Cetane number

- Cetane data obtained from one source
- Total of 20 samples encompassing at least 4 feedstocks
- Primary analysis done in triplicate

Cetane number: primary data from one lab



R2 = 97% RMSEP = 0.66 degC

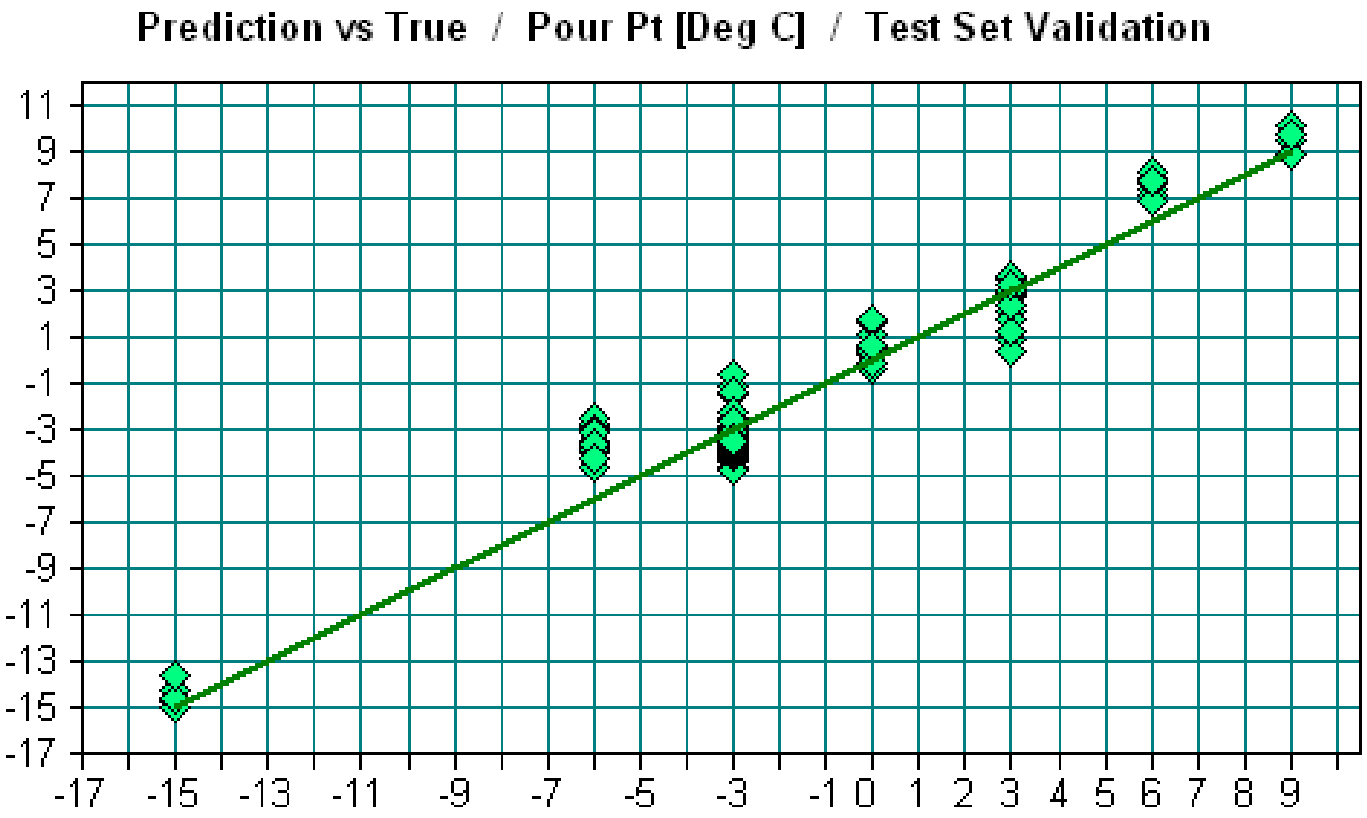
Next steps: Cetane number

- Excellent correlation with a limited number of samples
- Additional 30 samples are underway for primary data analysis in triplicate – using 3 additional feedstocks
- Multi-lab variability will be investigated
- Continue to expand calibration training set and validate

New developments in FT-IR: Pour Point

- Pour point data obtained from one source
- Total of 36 samples encompassing at least 4 feedstocks

Pour point: primary data from one lab



R2 = 91% RMSEP = 1.5 degC

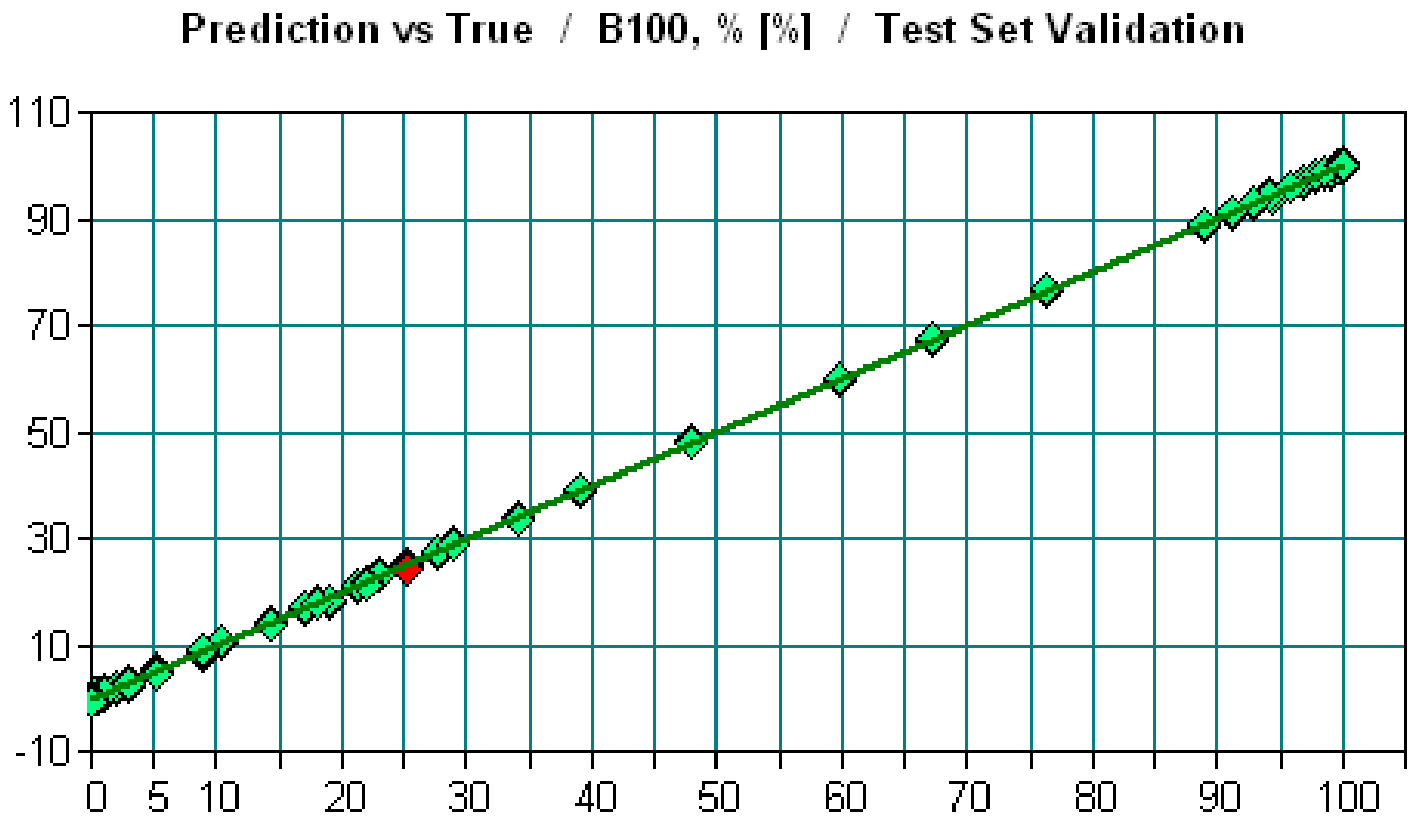
Next steps: Pour point

- Very good correlation with a limited number of samples
- Additional 30 samples are underway for primary data analysis – using 3 additional feedstocks
- Multi-lab variability will be investigated
- Continue to expand calibration training set and validate

New developments in FT-IR: Biodiesel blends

- 92 biodiesel blends with various diesel sources & various BD sources prepared in the lab to build calibrations
- Low, high and ultra high cetane diesel used
- Biodiesel concentrations varied from 0% - 100%, with particular focus on B5, B20 and B99 ranges
- Correlations developed with concentration level
- Initial correlations developed for total glycerin, acid number and cloud point for B100 used to make the blend

Biodiesel blends: analysis of BD concentration



R2 = 100% RMSEP = dependent on range

Biodiesel blends: comparison with ASTM D7371

Biodiesel Concentration,%	D7371 Reproducibility	QTA Reproducibility
1	0.76	0.12
2	0.81	0.14
5	0.95	0.19
10	1.19	0.13
20	1.66	0.29

B20: analysis of starting B100

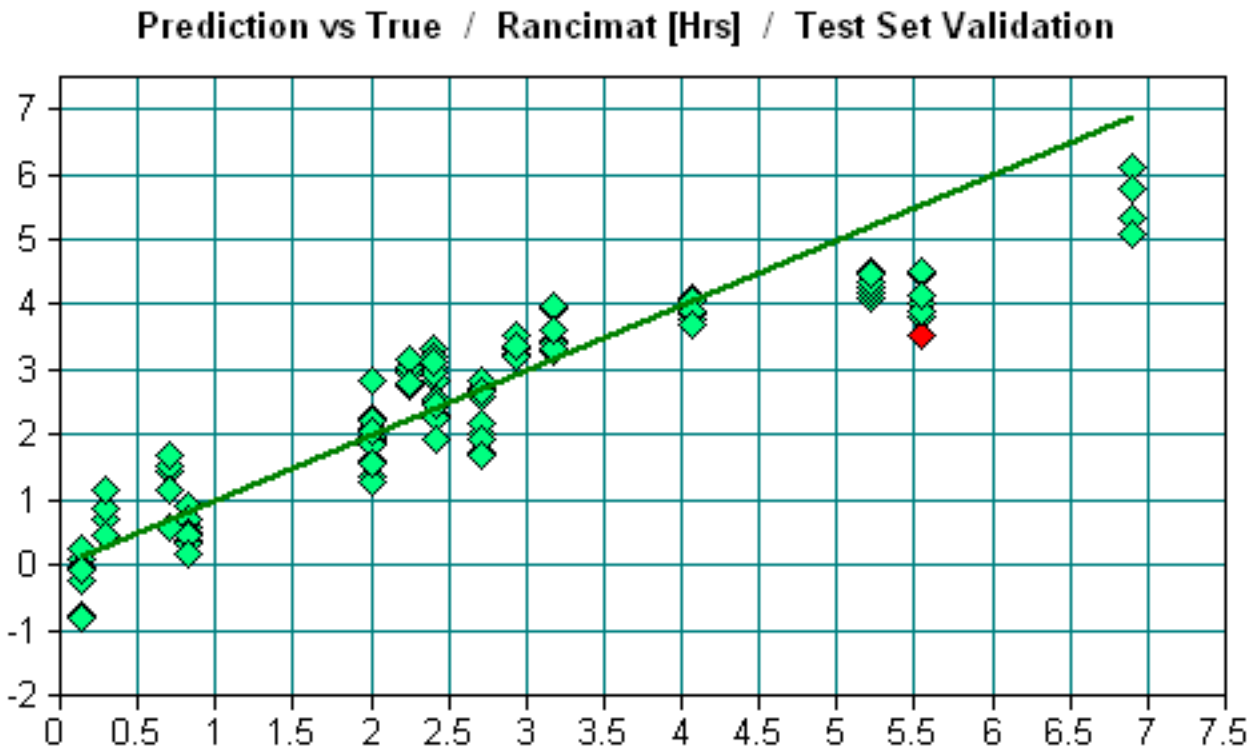
- FT-IR Capability established for total glycerin, acid number and cloud point
- Free glycerin analysis is not possible, due to very low concentrations in B20
- Moisture feasibility is underway

	Std error
Total glycerin	0.04%
Acid number	0.16
Cloud point	2 deg

New developments in FT-IR: Oxidative stability

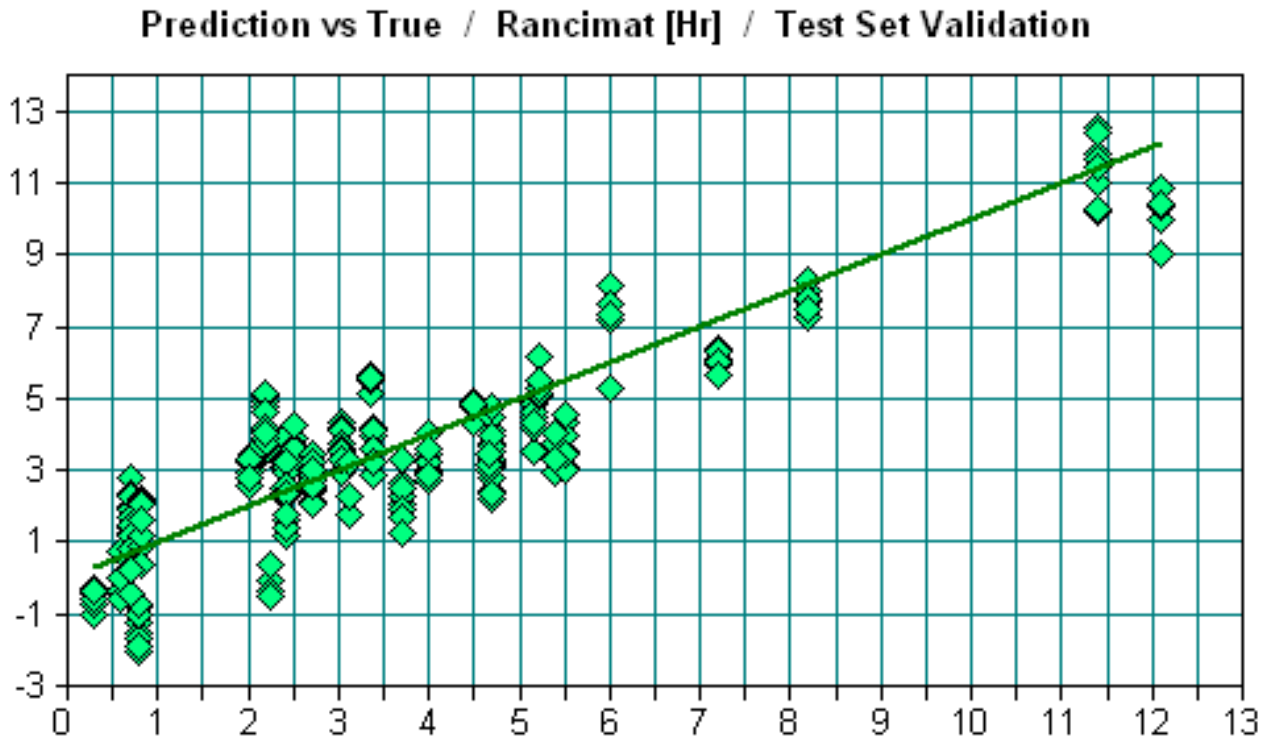
- Oxidative stability data obtained from two sources
- Total of 69 samples encompassing at least 7 feedstocks
- Unknown whether samples contained stabilizers or additives

Oxidative stability: primary data from one lab



R2 = 83% RMSEP = 0.87 hr

Oxidative stability: primary data from multiple labs



R2 = 77% RMSEP = 1.5 hr

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Next steps: Oxidative stability

- Good correlation and error when only one primary lab's data is used
- Correlation lessens and error becomes unacceptable when multiple primary labs are used
  - Investigate sources of primary method error via round robin
- Investigate impact of additives and stabilizers on the calibrations

New developments in FT-IR: Summary

- Networked FT-IR is highly capable of predicting CFPP, pour point and biodiesel blends and calibrations have been commercialized
- FT-IR correlations with cetane number look promising, and the calibrations will be made more robust prior to commercialization
- FT-IR correlations for B100 analysis within B20 and other blends requires more development, although capability looks good
- FT-IR correlations with rancimat data also look promising, although significantly more work is required to understand variables such as multi-lab variability of primary data, and impact of stabilizers and additives on the calibrations.

For more information:

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