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Measurement of gasoline composition for real-time control

Key Words

- Aromatics
- Benzene
- T50, T90
- Mid-infrared
- FTIR
- Real-time monitoring
- Gasoline
- Petrochemicals

Abstract

The static optics IRmadillo has been successfully calibrated to measure regulated chemical and physical properties (aromatics, benzene, T50 and T90) in a gasoline product. Once installed on-line the IRmadillo will be able to continuously output measurements for these species in real-time, for enhanced process monitoring and control, replacing the need for frequent and laborious traditional testing techniques.

Introduction

Environmental and health concerns over the use of traditional petrochemical and fossil fuel-based energy sources have led to a global effort to reduce harmful emissions and improve air quality. To reduce the impact of utilising such fuel sources, regulations have been introduced by numerous authorities to improve fuel quality and engine efficiency. Gasoline is an example of a fuel that is a product of refined crude oil, mainly used for vehicles (including aircraft), but which can also be used for generators and an assortment of other equipment.

Gasoline contains constituents that are hazardous to the environment and health, and there are strict regulations for the content of gasoline fuels. Agencies, such as the United States Environmental Protection Agency (EPA), have set maximum concentrations for constituents, such as aromatics and benzene, to limit the exposure of these harmful chemicals. Other regulated gasoline properties include T50 and T90, defined as the temperature at which 50% or 90% of the fuel distils respectively. In fuels with too low a volatility, poor atomization causes reduced power output and fuel economy, whereas fuels with too high a volatility can cause engine vapor locks, which also leads to poor vehicle performance, power output and fuel economy. Therefore, the minimum and maximum values for T50 and T90 are regulated for adequate fuel quality and engine performance, also contributing to a reduction in emissions.

To demonstrate compliance to federal and environmental regulations, gasoline must be tested to ensure it meets the specifications outlined. Traditional analysis techniques include gas chromatography or mass spectrometry to measure the concentrations of aromatics and benzene, and simple batch distillation to measure T50 and T90. These techniques add delay, are labour intensive, and only give a single indication of the process for the exact time that a sample was withdrawn. Continuous real-time analysis of these properties, from an on-line installation, can enable effective process control and provide more understanding of the process, to produce quality gasoline.

This application note presents a static-optics FTIR spectrometer, for analysis of aromatics, benzene, T50 and T90 in a gasoline product. Once installed in-line and calibrated, the instrument can provide real time measurements, reducing the need for frequent offline sampling, and providing fast feedback.

Experimental

This work was performed on an IRmadillo spectrometer that was operating in a laboratory to undertake initial calibrations before being installed on-line for real-time process monitoring. The data was collected at a refinery in California, measuring various chemical and

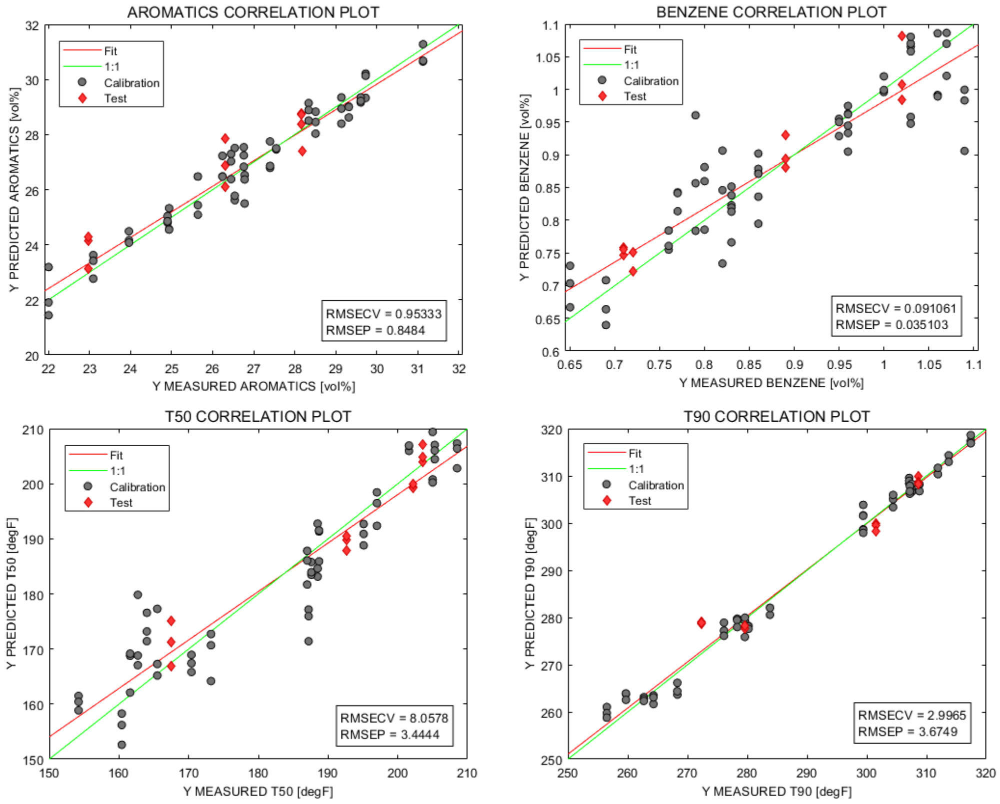

Figure 1: Correlation plots for aromatics, benzene, T50 and T90

physical properties in the final gasoline product. Each sample was measured in triplicate. Spectra were acquired at a resolution of 16 cm^{-1}. and averaged over 120 seconds. Reference data was supplied by the customer using their standard analytical techniques. Models were developed using chemometric modelling software and using partial least squares regression (PLS).

Results

The IRmadillo was set up in a laboratory so that multiple applications at the refinery could be explored. Here we display some results from the gasoline application. For the components modelled, all show a good agreement between the measured value (supplied by traditional reference measurements) and the predicted value (output from the model), as can be seen in Figure 1. The data used for model development was split into calibration data to train the model, and validation data to test the model. The correlation plots are shown in Figure 1, where the black dots represent the calibration data, and the red diamonds the validation data.

All components modelled well with partial least squares regression (PLS). Models were evaluated based upon the root mean squared error of cross validation (RMSECV) and root mean squared error of prediction (RMSEP) which represent the average error across the training and testing dataset (samples that were unseen by the model) respectively. We define the accuracy as +/- RMSECV of model across the range of the component of interest. The table below (Table 1) summarises these average errors for each species, which are also displayed in the correlation plots in Figure 1.

The models developed can inform the plant as to whether the gasoline meets their required standards and adheres to regulations, thus ensuring a quality gasoline product. Models can be uploaded to the instrument software and, once installed on-line, the IRmadillo will output continuous real-time measurements. The IRmadillo will continuously collect spectra and output measurements of every modelled chemical species or property every few minutes, or seconds, dependent on the plant's requirements. Model prediction outputs can be used to monitor and observe any changes and give actionable chemical insights for increased process understanding and control. The outputs from the instrument can also be sent to the plant DCS for remote analysis.

Table 1: Summary of model performances for developed models for aromatics, benzene, T50 and T90

	Aromatics	Benzene	T50	T90
Data range	22 - 31 vol%	0.65 - 1.10 vol%	154.2 - 208.5 °F	258 - 320 °F
Model type	PLS	PLS	PLS	PLS
Number of factors	5	5	3	3
RMSECV	0.95 vol%	0.09 vol%	8.05 °F	3.00 °F
RMSEP	0.85 vol%	0.04 vol%	3.44 °F	3.68 °F

Conclusions

The use of a static-optics mid-infrared spectrometer, as a means for gasoline analysis, has been successfully presented in this work. The ability to install the IRmadillo on-line, for real-time measurements, enables the replacement of traditional time-consuming and expensive sampling and off-line analysis. Gaining actionable chemical insights into the process enables improved process understanding, continuous monitoring and process control.

Although this work focuses on aromatics, benzene, T50 and T90, the IRmadillo has also been proven to be able to measure other species in gasoline, including, but not limited to, sulfur, octane and Reid vapor pressure (RVP). The IRmadillo can also be implemented in other applications within the renewable fuel industry, including feedstock monitoring, distillation, and biodiesel production, further displaying the robustness and versatility of the IRmadillo.

Keep in Mind

The IRmadillo is a static-optics FTIR (mid-infrared) instrument, not NIR (near infrared), and can provide more meaningful information than NIR, particularly in the petrochemicals industry. NIR looks at overtones and combination vibrations of molecules, which means it can be difficult to differentiate between similar molecules and may not give the level of information that is required to accurately monitor your application. The IRmadillo FTIR spectrometer directly measures features of interest, meaning similar molecules can be identified and quantized, thus can provide substantially more information for interpretation than NIR.

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