2014 NDIA GROUND VEHICLE SYSTEMS ENGINEERING AND TECHNOLOGY SYMPOSIUM
POWER & MOBILITY (P&M) TECHNICAL SESSION
AUGUST 12-14, 2014 - NOVI, MICHIGAN

IN-LINE FUEL SULFUR ANALYZER FOR IMPROVED MANAGEMENT OF DESULFURIZERS FOR FUEL CELL AUXILIARY POWER

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ABSTRACT

Combat vehicles have unmet needs for auxiliary power units (APUs) that reduce fuel consumption and offer improved operational effectiveness and soldier safety. Adoption of fuel cell APU technology is hindered by requirements for fuel desulfurization and reforming. Both solid-oxide and polymer-electrolyte-membrane fuel cells are poisoned by sulfur compounds in jet fuels. To more efficiently manage desulfurization processes, improved in-line methods of determining the sulfur content of fuel are required. Mainstream Engineering is developing a compact, in-line analyzer for measuring total sulfur in jet fuel for fuel cell applications. This analyzer enables less frequent desulfurizer regeneration events when compared to scheduling regenerations based on the assumed worst-case sulfur limit. The measurement technique uses multivariate analysis of Raman intensity spectra, which offers calibration robustness, contaminant detection, and identification of fuel type.

INTRODUCTION

Fuel cell auxiliary power units (APUs) would significantly reduce military fuel consumption and lead to improved operational effectiveness and solider safety. We estimated that a fuel cell APU could result in up to a 90% reduction in fuel consumption during idling for large combat vehicles [1, 2]. Considering the high fully burdened cost of delivered fuel (*ca.* $15/gal), the potential savings in fuel expenditures is substantial [3].

Both solid oxide fuel cells (SOFCs) and high-temperature polymer electrolyte membrane (PEM) fuel cells are poisoned by sulfur compounds. Current desulfurizers are regenerable, but the desulfurizers are forced to assume the worst-case fuel sulfur concentration at all times. The sulfur level in JP-8 is capped at 3,000 ppm (0.3 wt %) per the military fuel standard MIL-DTL-83133H [4]. Figure 1 shows the distribution of sulfur levels in fuel supplied by the Defense Logistics Agency in 2009 [5]. As shown, the peak in the distribution is at 1,000 ppm and the distribution is broad. The mean sulfur content varies somewhat from year to year; recently, the mean has been approximately 750 ppm, one fourth what must be assumed by current desulfurizers.

Sulfur compounds in JP-8 take several forms, including mercaptans (i.e., thiols), sulfides, disulfides, thiophenes, and benzothiophenes. Of these sulfur compound classes, by far the most prevalent species are various benzothiophenes because they are the hardest to remove by conventional refinery desulfurization processes. Most benzothiophenes in jet fuel have two or three methyl groups attached to the rings as described by Lee and Ubanyionwu [6]. Mercaptans, in particular, are capped at 20 ppm by the military standard and are a minor contributor to total sulfur. Quantification of the total sulfur in jet fuel spectroscopically is challenging because the sulfur is present as an assortment of organosulfur compounds in a complex hydrocarbon matrix.

Because desulfurizers are regenerated based on the assumed worst-case sulfur concentration and not the *actual* sulfur concentration, there is a potential for up to a four-fold average reduction in regeneration frequency by using an in-line sulfur analyzer for desulfurizer control. Regeneration is frequently done at high temperatures, incurring significant parasitic losses. A polisher is often needed after the adsorbent bed to get the sulfur down to the very low levels required for high-temperature PEM fuel cells. The polisher might not be regenerable. Also, desulfurization hardware presents a packaging problem. Centeck [1] reported that 10–20% of the current developmental JP-8 fuel cell APU space claim is consumed by the desulfurizer. The objective of this program is, therefore, to provide an intelligent means to detect the real-time fuel sulfur concentration, allowing less frequent desulfurizer regenerations or downsizing of the desulfurizer for the same regeneration frequency.

The research reported in this document/presentation was performed in connection with contract/instrument W911QX-13-C-0005 with the U.S. Army Research Laboratory. The views and conclusions contained in this document/presentation are those of the authors and should not be interpreted as presenting the official policies or position, either expressed or implied, of the U.S. Army Research Laboratory or the U.S. Government unless so designated by other authorized documents. Citation of manufacturer's or trade names does not constitute an official endorsement or approval of the use thereof. The U.S. Government is authorized to reproduce and distribute reprints for Government purposes notwithstanding any copyright notation hereon.

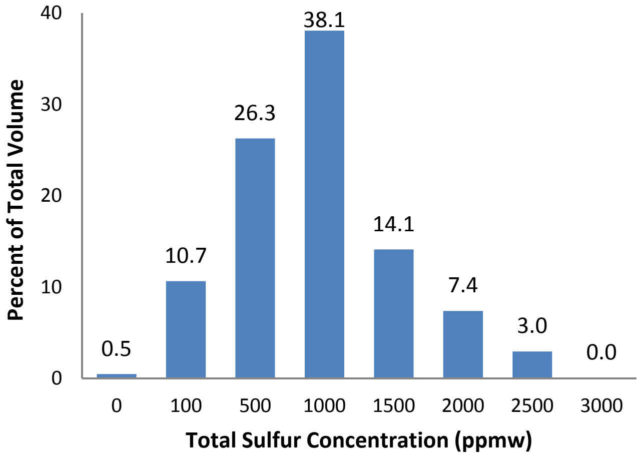

Figure 1. Sulfur in JP-8 distribution from 2009 [5]

FUEL PROPERTY ANALYZER DEVELOPMENT

Fuel Samples

The military procures JP-8 fuel from across the world for local and global use. Fuel that conforms to the military specifications must contain less than 3,000 ppm sulfur, but the average is much lower, 750 ppm, with a wide distribution. In addition, all the global regions sampled in 2009 reported samples ranging from near 0 ppm to over 1,500 ppm sulfur [5]. This sulfur variability, the degradation of fuel, and the retrieval and use of captured fuel with unknown sulfur content precludes a simple sulfur test at the place of origin to tune the desulfurizer.

A representative set of about 400 JP-8 fuel samples that ranged over 0–2,900 ppm sulfur was collected. As many samples as possible were obtained to maximize the diversity in fuel composition. However, because of the nature of the fuel distribution, the majority of the set of JP-8 samples had less than 1,500 ppm sulfur. In addition to sulfur, 35 other fuel properties were available (e.g., cetane number, flash point) for on average 60% of the samples. All samples conformed to military specifications and ASTM standards. Additional samples were obtained by collecting Jet-A from local airports, doping jet fuel with methylbenzothiopehenes, and desulfurizing JP-8, which brought the total number of fuel samples to over 500.

Raman Spectroscopy of Jet Fuels

Raman spectroscopy probes rotational and vibrational modes in molecules. The sample is illuminated with a laser beam, and a detector is used to measure the intensity and wavelength of inelastically scattered light. Raman spectroscopy provides a good characterization of compounds with polarizable bonds (e.g., C–C, C–S). The main sulfur compounds in JP-8, thiophene and benzothiophene, can be identified with this technique because of their aromatic groups and strong carbon–sulfur bonds.

Raman intensity spectra were collected by a portable Raman spectrometer (200–2780 Δcm^{-1}, 2.7 Δcm^{-1} resolution). A fuel sample was excited with a fiber-coupled 785 nm diode laser (350 mW), and scattered light was collected with a fiber-coupled Raman probe (7.5 mm focal length). The probe was inserted into a sample holder that blocked all stray light and fixed the distance to the sample during measurement. A single, ten-second scan was taken of the sample, and the spectra was not smoothed or preprocessed at the time of measurement. An example of the relevant portion of a JP-8 fuel spectrum that has been baseline corrected is shown in Figure 2. Many distinct peaks vary between the samples and can be analyzed for chemical information.

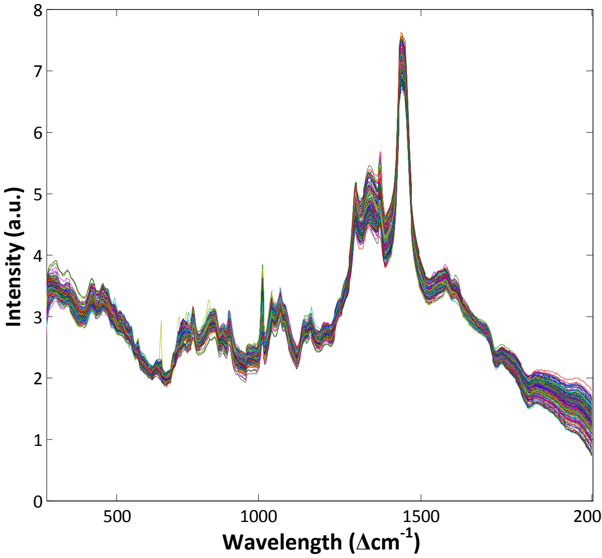

Figure 2. Baseline-corrected Raman spectra of JP-8 fuels

Chemometric Analysis of Raman Spectra

Chemometrics is the use of mathematical and statistical methods to provide maximum relevant chemical information by analyzing chemical data [7]. Although chemometrics of Raman and IR data have been used to predict sulfur in other hydrocarbons [8–10] and for various other fuel properties [11–15], it has not been used to predict jet fuel sulfur content with the desired accuracy and reproducibility for a predictive sensor [16, 17]. We have previously shown that near-IR absorption spectroscopy can be used for fuel sulfur quantification, although with less accuracy compared to the Raman spectroscopic method [18]. Using chemometric tools, large data sets are analyzed with statistical methods to determine linear combinations of independent variables (absorbance at various wavelengths) that best describe the response (sulfur). Regression methods such as principal component regression (PCR) and partial least squares (PLS) determine these "latent variables" (LVs). The LVs are by definition orthogonal and uncorrelated. Typical multivariate calibrations generated from PLS or PCR reduce the dimension of the problem from thousands of discrete absorbances in each spectrum to less than ten LVs. This multivariate approach has significant advantages over the univariate methods used in traditional Beer's law analyses. In particular, multivariate calibration reduces noise, handles interferences, and can help identify outliers. Other related chemometric methods allow recognition of patterns in the data (e.g., identification of sample contamination) and classification of samples (e.g., identification of an unknown fuel sample as diesel, JP-8, or some other fuel).

Chemometric analysis was conducted using PLS_Toolbox (Eigenvector Research, Inc.) in MATLAB (Mathworks). The spectral data were preprocessed with generalized least squares and mean centering to eliminate baseline offsets and highlight differences in the spectra. The corresponding sulfur property data was preprocessed using autoscaling. An unsupervised learning method (PCA) was used to classify JP-8 samples. An inverse method (PLS) was used to create regression models of the fuel sulfur. A venetian-blinds cross-validation test with seven splits was used to generate a root-mean-square error of cross validation (RMSECV) that characterizes the error in the model. Looking at the RMSECV is akin to defining multiple calibration and prediction sub-sets in the samples, separately testing each one, and determining how well the model can predict the samples not included in the calibration set. Cross validation provides a more accurate characterization of chemometric model robustness than arbitrarily defining a *single* calibration set and test set and calculating the analogous root-mean-square error of prediction (RMSEP). The RMSEP was also calculated for the samples that were never used in the model to validate predictive model performance. These regression models were optimized using inverse partial least squares variable selection (50 wavelength window), which omits data at certain wavelengths to improve the model. The acceptable number of latent variables was analyzed using principal component regression, predictive power over time, and signal-to-noise tests.

Interferent (peak width up to 20 wavelengths) and shift (up to 1 wavelength) analyses were conducted on the regression models to determine resistance to sample contamination and detector drift. Calibration drift analysis was conducted on spectra taken over a period of months by determining the change in the RMSEP. Permutation tests were conducted to help identify over-fit models or chance correlation. For this test, the sulfur data was randomly reassigned to the spectral data, and regressions were built using this mismatched data. Fifty permutations were used with this test.

Regression Model Accuracy

The main spectral regions used in the model were around 500–1500 Δcm^{-1}. This region includes aromatic C–C and C–S functional groups that can be found in the sulfur molecules containing thiophene rings [19]. A regression model made from preprocessed spectra is shown in Figure 3. The spectra were split into a calibration set of 227 samples and a validation set of 164 samples. The model has 3 latent variables and a RMSECV of 160 ppm. The RMSEP for this calibration/prediction set split was 180 ppm. For reference, the ASTM reproducibility, *R*, for the laboratory fuel sulfur measurement (ASTM D4294) used to generate the "reference" sulfur data is 165 ppm at a nominal 1,000 ppm sulfur level. The model error is similar to *R*, with 58% of the sample predictions falling inside the ASTM reproducibility bounds. Many of those predictions not within the bounds are on the low range where the laboratory ASTM method clearly outperforms the sensitivity of the deployable Raman method. Over 90% of the predicted sulfur concentrations fall within ±250 ppm of the values measured via the ASTM method; those samples not predicted accurately can be identified as potential outliers based on the spectral data. A separate model can be made for the poorly determined samples. Using a tiered sampling approach, the sulfur of these samples can be determined albeit with more error, but still providing an advantage compared to assuming 3,000 ppm sulfur.

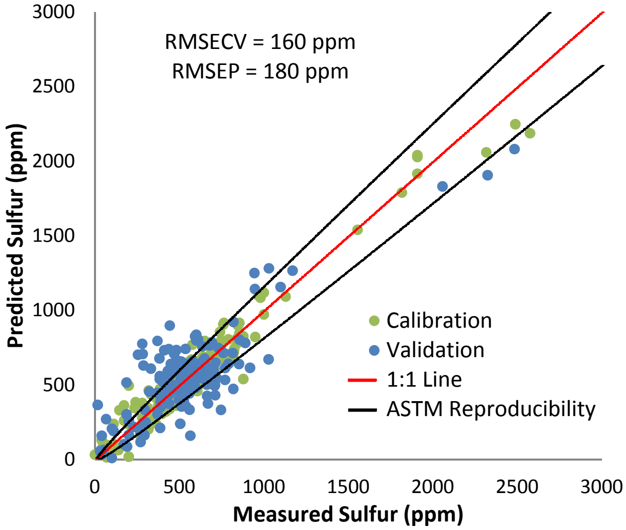

Figure 3. Parity plot of Raman PLS regression model

The model was tested for signal-to-noise ratio, interferents, wavelength shifts, and significance. The choice of three latent variables was deemed appropriate based on these metrics. The regression model was most susceptible to interferents around 625 Δcm^{-1}, 1,000 Δcm^{-1}, and 1,400 Δcm^{-1}. Wavelength shifts did not impact the model in either direction by a significant amount. A permutation test was conducted with 50 permutations that showed the model was significant with at least a 99.5% level of confidence.

PCA classification models were successfully made from these spectra that were able to distinguish fuel types (diesel and JP-8). Other fuel properties such as density, cetane number, and aromatic content were predicted successfully with PLS, as expected from previous studies [13]. By examination of the spectral data, outliers could be easily detected and selectively removed.

Real-time Desulfurization Tests

Desulfurization experiments were conducted with a custom, fixed-volume adsorbent bed to evaluate the use of the analyzer *downstream* of the desulfurizer. Fuel was pumped into a bed filled with adsorbent, through a flow cell (connected to the portable spectrometer), and into a sample vial for off-line sulfur analysis. The fuel collected in the sample vial was diluted 3:1 with heptanes and analyzed off-line for sulfur via X-ray fluorescence (XRF) according to ASTM D4294. Six sulfur-in-kerosene standards spanning 0 to 3,000 ppm were used to calibrate the XRF instrument. The fuel was pumped through the bed until the effluent reached a sulfur concentration similar to the feed concentration, yielding a full saturation curve for the adsorbent.

Chemometric techniques were used to analyze the desulfurization runs. Before each run, the flow cells were cleaned with isopropyl alcohol and purged with nitrogen. Spectra were gathered every 10 seconds during all desulfurization runs. Some spectra had to be excluded because of interference caused by air bubbles in the lines. Later a bubble trap was installed that eliminated the interference problem. During every desulfurization run, 10–20 fuel samples were collected for off-line XRF analysis. Spectral data from the in-line spectrometer were assigned to each off-line sample for accuracy comparisons. The results from a desulfurization experiment from our previous work with near-IR absorption is shown in Figure 4 [18].

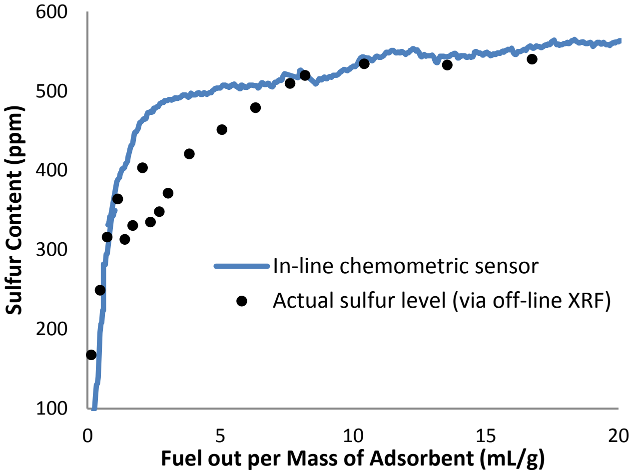

Figure 4. Chemometric sensor predicting breakthrough of sulfur in an adsorbent column in real time [18]

Size, Weight, and Power Requirements

The fuel sulfur analyzer consists of a portable spectrometer, flow cell chamber, fiber optics, laser source, microcontroller, and software. The packaging of the main components is shown in Figure 5. Fiber optics connect to an in-line flow cell (not shown) that is attached directly in the APU fuel line. The dimensions of the analyzer is currently 19.7 cm × 8.4 cm × 13.3 cm (7.8 in. × 3.3 in. × 5.2 in.), taking up 1.95 L (119 in^3) of space. Packaging improvements are being examined that could reduce the volume by 25%. The APU space claim for the M1A1 Abrams is 213 L (13,000 in^3) [20]. The desulfurizer consumes up to 20% of the space claim, or 42.6 L (2,596 in^3). The analyzer takes up less than 1% of the APU space claim.

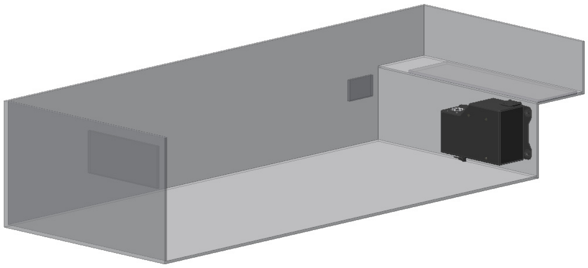

Figure 5. Initial packaging of the fuel sulfur analyzer and its size relative to the M1A1 Abrams APU space claim

DESULFURIZER CONTROL STRATEGIES

Battlefield Day Simulations

A Monte Carlo (MC) method was used to estimate actual desulfurization regeneration requirements based on a simulated battlefield day (BFD) using the sulfur fuel distribution from 2009 [5]. The battlefield day, defined by TACOM, consists of 3.4 hours of secondary road travel, 3.3 hours of cross country road travel, and 11.3 hours of idle for a total 18 hours of use in a day as shown in Table 1 [2].

Table 1. Time and Fuel Consumption for Tasks in the BFD Simulation

Battlefield Day Task	Task Time (hr)	Fuel Consumption (gal/hr)	
		Without Fuel Cell	With Fuel Cell
Low Idle/Silent Watch/Electric Power	4.4	11.8	1.5
High Idle	6.9	15.6	1.5
Secondary Roads	3.4	78.0	78.0
Cross Country	3.3	92.6	92.6

A desulfurizer capacity was determined based on the APU space claim and the assumption that the desulfurization equipment accounts for 10–20% of the available space [1]. Regeneration losses of the adsorbent were modeled after data from TDA Research [21]. The fuel tank in the simulation was 500 gallons as per the M1A1 specification. To determine the simulated sulfur reading, the sulfur was first randomly sampled from the 2009 distribution. Then a random, Gaussian regression model error based on the RMSEP was assigned along with a random, Gaussian repeatability-based sensor error based on data taken during the real-time experiments. Finally, the sulfur prediction was time-averaged to reduce noise and an offset was applied as a safety factor. An example of the output from the MC analysis is shown in Figure 6 for three battlefield days where the jumps in fuel tank sulfur constitute a tank refill from a new source. In the simulation, the actual sulfur in the tank was predicted by the regression model; the raw sulfur prediction is a noisy signal that was sometimes below the true sulfur value. However, the control signal that was used is both time-weighted to reduce noise, and contains a safety offset so that the desulfurizer never experiences breakthrough, preventing sulfur from ever reaching the fuel cell.

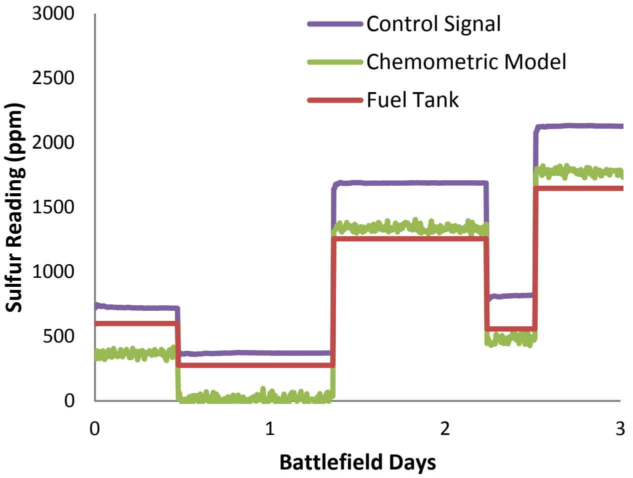

Figure 6. Time-series of simulated M1A1 use and refueling over three 18-hour battlefield days

Feed-forward/Feedback Controls

Regeneration events could be timed based on feed-forward, feedback, or combined feed-forward/feedback control as shown in the schematic in Figure 7. A selector valve is used to cycle between adsorbent beds allowing regeneration of the bed not in use. A flow meter is used to totalize the mass of sulfur challenged to the adsorbent bed. In the feed-forward arrangement, the sensor would be only a predictive instrument, calculating the total amount of sulfur in the fuel passed into the bed. This would allow for a regeneration gauge, like a fuel level gauge, that would tell when the bed needs to be regenerated based on the amount of sulfur challenging the bed. In the feedback set-up, the sensor would be on the effluent of the bed and tell when sulfur above an acceptable threshold was released. The feedback method is advantageous because this method allows measurement of adsorbent bed capacity in the field and therefore does not require large factors of safety to account for potential bed degradation over time. A downside is that the bed regeneration events could not be anticipated, requiring a back-up "catch" bed to avoid sulfur poisoning the downstream fuel cell. Using a combined feed-forward/feedback controller maintains all of the control advantages of both strategies at the expense of a modest cost increase for a second flow cell, optical switch, and additional fiber-optic cables.

The feed-forward/feedback controller could be based on tailored chemometric models to maximize the accuracy for nascent JP-8 at the inlet and desulfurized JP-8 at the outlet. The feed-forward model would be a full-range model for fuels from 0 to 3,000 ppm sulfur, whereas the feedback model would focus on desulfurized fuels with very low sulfur. The accuracy of the low-sulfur model would be higher at low concentrations, allowing for a less conservative safety factor.

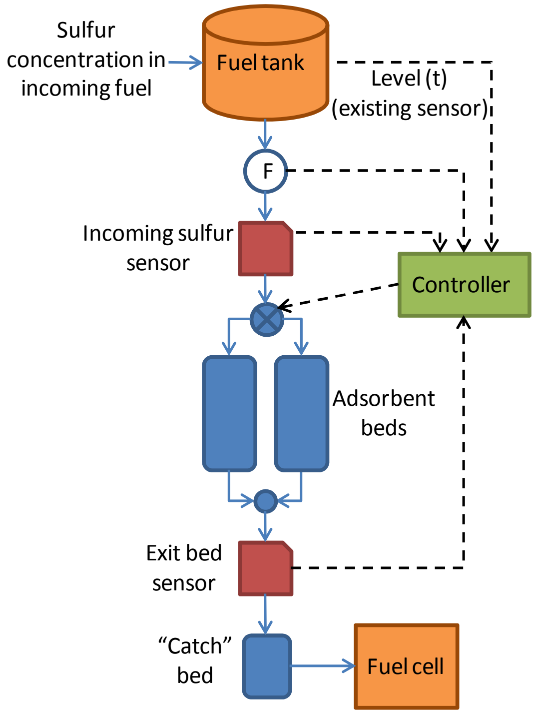

Figure 7. Control schematic for feed-forward and feedback desulfurizer control

Reduction in Regeneration Frequency

The benefit of applying the control schemes was evaluated with the battlefield day simulations. The improvements based on the average fuel sulfur content were also calculated to determine the expected overall increase in regeneration efficiency. Figure 8 shows where the current technology lies with the current model accuracy.

The plot shows how the reduction in regeneration frequency scales with sensor error for the feed-forward (red line) and feedback (blue line) control strategies. From strictly a regeneration standpoint, the feedback and hybrid feed-forward/feedback strategies offer the same benefit. The symbols indicate the benefit based on the accuracy of the current prototype analyzer (square and diamond) and what is reasonably attainable with future enhancements to the analyzer (circle). Raman feed-forward control can reduce regeneration events or bed size by 65%, but requires adsorbent deactivation to be well understood. The best solution uses the feedback (or combined feed-forward/feedback) control system that can reduce regeneration events by over 70%. As discussed, the feedback strategy requires the additional catch bed and cannot judge the remaining capacity of the bed, but this strategy can measure adsorbent deactivation in the field. The combined feed-forward/feedback approach achieves the regeneration reduction of the feedback controller with the predictive power of the feed-forward controller, but requires a catch bed and additional optical components. The combined feed-forward/feedback approach also offers the option to periodically probe the bed capacity while otherwise operating in a feed-forward scheme to preserve the catch bed.

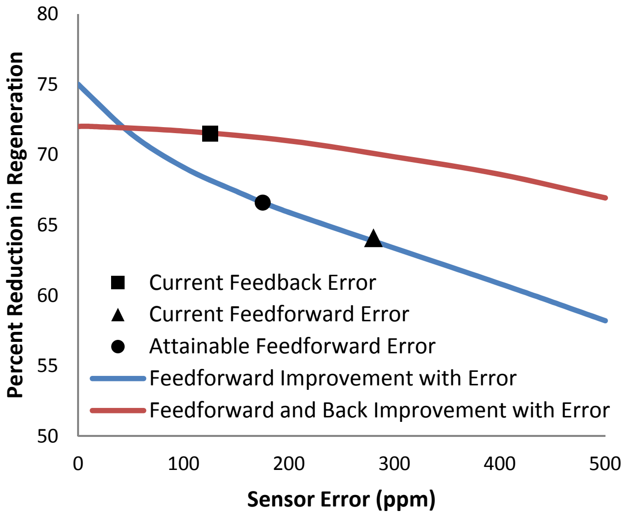

Figure 8. Reduction in the frequency of regeneration events for different control strategies

SUMMARY

With the high and variable sulfur content of JP-8 jet fuel, intelligent management of desulfurizers is critical to the adoption of next-generation fuel cell APUs. An in-line chemometric fuel sulfur sensor has the potential to reduce costs, improve combat effectiveness, and reduce overall fuel consumption. The fuel sulfur analyzer needs to be compact, low-power, and robust—a chemometric, Raman-based analyzer appears to satisfy these mission requirements. Regeneration events could be timed based on feed-forward, feedback, or a hybrid control strategy. The analyzer can either be used to downsize the desulfurizer or reduce the regeneration frequency by 65–70% compared to current systems based on the accuracy of our prototype analyzer.

ACKNOWLEDGEMENTS

We would like to thank the U.S. Army for supporting this work under Contract No. W911QX-13-C-0005. We are grateful to Charles Rong (U.S. Army Research Laboratory) and Joel Schmitigal (U.S. Army Tank Automotive Research, Development and Engineering Center) for helpful discussions, property data, and fuel samples.

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