RAPID ONLINE ANALYSIS OF ACETYLENE FOR HYDROGENATION REACTOR CONTROL OPTIMIZATION

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ABSTRACT

Rapid analysis of acetylene ($C_2H_2$) in crack gas has been a significant technology gap in the olefin's industry for many years. Currently, the accepted best practice in the industry is on-line Gas Chromatography (GC); however, it suffers from a slow response time. A much faster, near real-time, analysis would allow tighter acetylene hydrogenation process control (patent pending).

Since 1999, The Dow Chemical Company has been aggressively pursuing solutions to this unmet need. To catalyze a commercial solution, Dow formed a strategic partnership with several external partners (Analytical Specialties, Dept. of Energy and Los Gatos Research). These collaborations have led to the development and commercialization of a near real-time analyzer capable of measuring $C_2H_2$ in cracked gas at the part-per-billion level. This technology is based on Off-Axis Integrated Cavity Output Spectroscopy (ICOS). The presentation will outline the ICOS technology, application feasibility study, and analyzer performance and field validation undertaken by Dow.
INTRODUCTION

In 2002, Dow’s Process Analytical group commenced a collaborative effort with an industry supplier, Analytical Specialties, Inc. (ASI), and a small research company, Los Gatos Research (LGR) to develop and commercialize an Off-Axis Integrated Cavity Output Spectroscopy (ICOS) analyzer for rapid on-line acetylene (C$_2$H$_2$) measurements. The specific technical objectives for the Off-Axis ICOS platform are pathlength enhancement for sensitivity improvement and to provide near or real-time data for improving advanced process control (APC) and product quality control (PQC).

The speed, reliability and accuracy of C$_2$H$_2$ analysis for hydrogenation reactors are critical to process control optimization, safety and environmental drivers, and product quality specifications. However, the fastest process Gas Chromatography (GC) methods—the industry accepted best practice at present—have a 90-second to 5 minutes response-time, much less than optimum which are 15 seconds or less.

This laser-based technology development effort has been funded through the Department of Energy [DOE] under a cost-share grant and their Small Business Innovation Research (SBIR) program grant. The work proceeded from laboratory testing and “proof-of-concept” to prototype construction and field validation, and commercial implementation. Developmental concepts and aspects such as the application economic impact, technology fundamentals and evaluation, application spectroscopy and chemometric feasibility, and field on-line validation and implementation are addressed and reported.

TECHNOLOGY DESCRIPTION

Off-Axis ICOS is an optical absorption spectroscopic technique which is based on the principle that when a molecule interacts with a light beam at a specific wavelength it will cause the molecule to vibrate/rotate, and thereby absorb the energy (the light source). The wavelengths at which these absorptions occur are unique and are a function of the analyte and its molecular bond types. Utilizing the measured absorption light intensity, the concentration of the probed species can be determined from Beer’s Law.

The basic operating concept of the Off-Axis ICOS is based on injecting the laser light into the optical cavity in an off-axis configuration with respect to the on-axis cavity alignment formed by the two highly reflective dielectric mirrors $^{1,2}$, as illustrated in Figure 1.

Unlike traditional absorption measurements, the optical pathlength in the Off-Axis ICOS method is effectively infinite as the entering laser light bounces back and forth retracing the same path on each cycle. The effective pathlength of the cavity is given by the mirror reflectivity. Therefore, using highly reflective astigmatic mirrors with $R > 99.99\%$ the laser beam can travel 10,000 passes, lengthening a 20cm long cavity to an optical pathlength of 2,200 meters. This allows Off-Axis ICOS to have very high sensitivity and low detection limit $^3$. 
In addition, by implementing LGR patented off-axis alignment configuration Off-Axis ICOS is intrinsically robust. The cavity effective pathlength does not depend on the exact laser beam alignment, only on the losses in the cavity, and thus it’s not necessary to meticulously align the input beam or the optical cavity allowing for a high degree of mechanical vibration tolerance.

The absorption intensity signal is acquired as the injection laser light wavelength is scanned over the entire spectral feature of absorption peak. Quantitative measurement of the probed species; concentration, can be derived from the transmitted intensity signal, the analyte absorption line-strength, sample temperature and total pressure, and the cavity’s effective optical pathlength. The detector, electronics and laser software control module process the detected amplitude signal and analyze the acquired spectra to derive the targeted gas concentration in real-time.

**PROOF-OF-CONCEPT TECHNOLOGY EVALUATION**

Off-Axis ICOS is employed to perform quantitative trace gas detection by means of a high-finesse (low loss) optical cavity. The cavity is formed by two high reflectivity (HR) (typical reflectivity is > 99.9%), dielectric-coated fused silica mirrors. The technology detection sensitivity would be impaired if the mirrors are fouled (reduction of mirror reflectivity) when exposed to process sample streams. Thus, it was pertinent to determine if this condition could potentially be an unacceptable factor of reliable performance.

Figure 2 shows the testing apparatus to determine potential mirror fouling of the Off-Axis ICOS sample cavity under process conditions. The mirrors were installed on a typical extractive GC sample flow system for a 1-week, 1-month, and 6-month long term studies to verify if there was any affect on the window’s reflectivity and/or its coating’s integrity from the exposure to hydrocarbon process gas line contents. To determine the mirror’s reflectivity before and after exposure to the process, LGR calculated the mirror loss from the measured the cavity’s ring-down time parameter.
APPLICATION FEASIBILITY STUDY

Besides the target acetylene analyte, there are several other gases present in the ethylene cracked process steam. Figure 3 is a plot of several spectra corresponding to the major constituents present in the stream.
Conventional laser sensors are incapable of performing quantitative analysis of process gas samples with spectroscopic interference backgrounds. Utilizing chemometrics as an analytical prediction tool enables the same laser-based technology to analyze and monitor analyte concentrations in the presence of spectral interferences. Chemometrics model spectral data illustrated in Figure 4 allows the Off-Axis ICOS analyzer to accomplish the following, which conventional spectrometry cannot:

- Ability to monitor near real-time component(s) in process streams with complex compositions by incorporating the model algorithm into the laser spectrometer.
- Ability to predict multi-components.
- Ability to provide concentration estimates in the presence of spectral interferences and non-linear effects including pressure and temperature effects.

![Model Parent Spectra](image)

**FIGURE 4-CHEMOMETRIC MODEL PARENT SPECTRA**

**PROCESS OFF-AXIS ICOS PROTOTYPE**

The prototype analyzer, shown in Figure 5, consisted of an electronic control unit, sample optical cavity unit, and sample handling system (SHS) equipped with a vacuum-pump. The data acquisition and operation of the analyzer was achieved through the use of the software module as shown in Figure 6.
FIGURE 5- OFF-AXIS ICOS PROTOTYPE

FIGURE 6- ICOS PROTOTYPE SOFTWARE CONTROL MODULE
RESULTS

CHEMOMETRIC MODEL VALIDATION

Seven gas mixtures with various concentration ranges for acetylene, methylacetylene, ethylene, methane, and ethane were obtained to perform model validation based on process operating conditions.

Figure 7 illustrates data of the model performance validation where Mixture 1 was in use. The upper graph shows acetylene and methylacetylene precision with auto calibration time-stamp for each day, and the lower graph shows each component prediction residual results. The first graph segment of 1 to 200 data point represents the model uncertainty in the comparison between measured Mixture 1 spectra and the model prediction spectra for acetylene component, and the segment data point of 201 to 561 is for methylacetylene component.

FIGURE 7- MODEL PERFORMANCE PRECISION DATA AND PREDICTION RESIDUAL FOR MIXTURE 1 SAMPLE
Summarized in Table I is the performance specification (precision and accuracy) of the ICOS. For comparison with the GC, the model validation data were grouped by concentration range. The GC specifications for acetylene measurement were from the Dow optimum GC method. As shown in Table I, the accuracy and precision of the ICOS prototype (with 6 second analyzer response time) for C$_2$H$_2$ application are as good or improved over GC specifications. Due to GC slow response-time for the existing methylacetylene analysis, this parameter has not been previously used to aid in the acetylene hydrogenation process optimization control. Thus, the methylacetylene measurement required specifications are not available for comparison.

**TABLE I- MODEL VALIDATION PERFORMANCE SPECIFICATION COMPARISON WITH GC**

<table>
<thead>
<tr>
<th>BOC Reported (ppm)</th>
<th>ICOS Ave. (ppm)</th>
<th>Precision @ 95% RSD (± ppm)</th>
<th>Accuracy/Bias (± ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ICOS</td>
<td>* Expected GC Spec.</td>
<td>ICOS</td>
</tr>
<tr>
<td>0.50</td>
<td>0.49</td>
<td>0.03</td>
<td>0.06</td>
</tr>
<tr>
<td>0.96</td>
<td>0.88</td>
<td>0.07</td>
<td>0.06</td>
</tr>
<tr>
<td>0.99</td>
<td>1.02</td>
<td>0.04</td>
<td>0.06</td>
</tr>
<tr>
<td>1.48</td>
<td>1.51</td>
<td>0.07</td>
<td>0.14</td>
</tr>
<tr>
<td>2.86</td>
<td>2.58</td>
<td>0.06</td>
<td>0.14</td>
</tr>
<tr>
<td>8.00</td>
<td>7.74</td>
<td>0.14</td>
<td>0.14</td>
</tr>
</tbody>
</table>

**Acetylene (Sep 5-20, 04)**

| BOC Reported (ppm) | ICOS Ave. (ppm) | Precision @ 95% RSD (± ppm) | Accuracy (%)
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1017</td>
<td>1020.9</td>
<td>5.8</td>
<td>0.4</td>
</tr>
<tr>
<td>1021</td>
<td>1021.1</td>
<td>13.9</td>
<td>0.0</td>
</tr>
<tr>
<td>3022</td>
<td>3082.3</td>
<td>63.0</td>
<td>2.0</td>
</tr>
<tr>
<td>5349</td>
<td>5144.0</td>
<td>130.7</td>
<td>3.8</td>
</tr>
</tbody>
</table>

**Methylacetylene (Sep 5-20, 04)**

**ON-LINE FIELD TRIAL PERFORMANCE**

The field test installation compared the ICOS with the GC in parallel, as illustrate in Figure 8, at Dow, Oyster Creek Hydrocarbon plant.
FIGURE 8- ICOS AND GG ARE IN PARALLEL FIELD COMPARISON

Plant operation protocol generally prohibits making changes to process conditions until a sufficient number of data points (minimum 2 to 3) indicate a consistent or trending alarm condition. Note that the analyzer input to the plant’s process control system is once per minute. Every GC measurement (5 minute cycle) in Figure 9 repeats the same data point 5 times.

FIGURE 9- REACTOR ACETYLENE SPIKE

Because of the batch process nature of a gas chromatograph (GC), an excursion may be well underway before the GC can detect it. The continuous measurement made by the ICOS analyzer provides near real-time results and updates measurements quickly enough to make a reliable determination.
Figure 10 illustrates a process methylacetylene spike simultaneously measured by the ICOS analyzer and a GC (data rate of 1 data point per ~20min). In this example, the GC reported a measurement exceeding alarm condition almost ten minutes after the excursion took place and with only two measurements exceeding alarm value. The measurement was not considered reliable. The ICOS analyzer detected the excursion as it was occurring and made approximately 200 measurements during the twenty minute period of the excursion. Therefore, the measurement quality of the ICOS gives plant operations confidence that the data reflects actual process conditions to take action to control and optimize reactors.

The continuous measurement and speed of the ICOS analyzer also allows more accurate process measurements. In the example shown in Figure 10, the ICOS analyzer measured and reported changes in process conditions much more quickly and accurately than the GC. While this process spike does not represent a plant upset or excursion, it did indicate that process conditions fluctuated. No matter how accurate the GC method was, it did not accurately reflect actual process conditions, primarily because of its intrinsic slow response time.

![MA On-Line Process Sample](image)

**FIGURE 10- REACTOR METHYLACETYLENE SPIKE**

In addition to speed and accuracy, the ICOS analyzer’s signal to noise ratio enables it to be sensitive enough to reliably report small changes in measured values. The sensitivity of the GC measurement is such that small changes in the process are difficult or impossible to differentiate a process spike from baseline noise. Some process spikes, like those in Figure 11, are not large enough to warrant process control actions, but can be useful for correlating other process events for troubleshooting.
While the ICOS analyzer prediction model was optimized for a measurement range of 0-10 ppm, the measurement range extends to 1,000 ppm. During the plant restart, the analyzer recorded measured values far above the reporting range of the GC as shown in Figure 12, thus providing additional data about the plant during the startup process.

The ICOS analyzer recorded measurement results, diagnostic and event data with every measurement. Additionally, the analyzer was set to record spectra at a rate of about one per hour during normal run conditions and at a higher rate during warning or fault alarm conditions.

**FIGURE 11- MEASUREMENT SENSITIVITY**
During the plant startup, at approximately 11:04 pm, a downward spike occurred in the acetylene and methylacetylene measurements as magnified in Figure 13. It is not uncommon to doubt the validity of a GC measurement during the pressures of a plant startup because of the reliability of GC’s under these conditions. However, because an alarm condition existed, the ICOS analyzer recorded additional spectral data that was used to confirm the reliability of the measurement.

Spectral data was extracted from files stored by the analyzer, tabulated and charted at different intervals representing different measurement values. An example of a spectra data table and chart are shown in Figure 13.
The acetylene spectra shown in Figure 15 was extracted at intervals representing 1) the high concentration before the downward spike, 2) the concentration at the lowest point of the downward spike and 3) normal concentration as measured before the plant upset occurred.
The peak height and area indicate that the measurement depicted in Figure 15 accurately represents process conditions and is not an instrument issue. Because the spectra can be used to validate the analyzer measurement, spectra data records become a powerful troubleshooting and diagnostic tool.

CONCLUSION

Under a variety of process conditions, the ICOS analyzer proved to be much more accurate, precise and durable than current gas chromatography methods. The speed and reliability of analysis provided insight into process run conditions that were previously unavailable and unexpected. Powerful diagnostic tools designed into the ICOS capabilities allowed for validation of reported results.

The continuous measurement method and speed of analysis of the ICOS analyzer proved to be more valuable than gas chromatography because, no matter how accurate the GC method was, it did not correctly reflect real-time process conditions, primarily because of the GC’s intrinsically slow response time. The speed, reliability and accuracy of acetylene (C$_2$H$_2$) analysis for hydrogenation reactors are critical to process control optimization, safety and environmental drivers, and product quality specifications.

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