Mid IR Laser Sensor for Continuous SO$_3$ Monitoring to Improve Coal-Fired Power Plant Performance during Flexible Operations

Jason Kriesel (jason@oksi.com)
Camille Makarem
Richard Himes
Derek Dunn-Rankin
Andrea Biasioli
Alice Chien
Larry Muzio
Karol Schrems
Project Description and Objectives

Purpose:
- Produce and demonstrate a continuous $\text{SO}_3$ monitor for coal-fired power plants

Alignment to Fossil Energy objectives
- Real-time information to optimized additive injection and minimize catalyst deactivation
- Without an $\text{SO}_3$ monitor, power plants over use sorbent => waste (typical sorbent costs $1M/yr)
- Sensor would enable cost savings ($100k/yr – $200k/yr) and improved flexible operations

Driving questions
- Can the sensor provide sufficient sensitivity in a challenging environment?
- Do measurements accurately reflect the composition of the flue gas?
Sorbent Injection for SO$_3$ Mitigation

Lack of continuous SO$_3$ monitor limits ability to optimize sorbent injection rates
Alkali Sorbent Injection

**Alkali sorbent injection uses include:**
- Mitigation of $\text{H}_2\text{SO}_4$ ‘blue plume’
- Enhanced powdered activated carbon (PAC) efficiency in capturing mercury
- Mitigation of ammonium bisulfate (ABS) and $\text{SO}_3$ condensation impacts on air heater fouling
- Mitigation of duct corrosion due to $\text{SO}_3$ condensation

**Alkali sorbent injection locations moving upstream:**
- Originally downstream of air heater / upstream of particulate collection device
- Also between the Selective Catalytic Reduction (SCR) outlet and air heater
- Recently positioned upstream of the SCR

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Project Description and Objectives

Technology Benchmarking
- Accepted standard is controlled condensation: wet chemistry, off-line process (EPA method 8A)
- Breen probe being used, but it is a non-specific condensation probe with limitations

Current Status of Project
- Prototype laser absorption system tested/validated in laboratory tests of SO₂
- Working to generate SO₃ and H₂SO₄ for higher fidelity validation
- Industry feedback: “We need a solution now”
Spectroscopy System

Tunable Laser

IR Detector

Library

Species Concentration

2,3 Butanedione: 99.7 ppm
Acetaldehyde: 230.2 ppm
Acetone: 130.8 ppm
Methane: 259.3 ppm
Water: -38.8 ppm
Sulfur dioxide: 2.5 ppm
Mid-Infrared Wavelength Range

- Fundamental transitions in Mid-Infrared (λ: 2 - 12 µm) stronger than overtones in NIR (λ: 1 - 2 µm)
- Molecular species uniquely identified and precisely quantified
- But..... NIR benefits from developed components (telecom investments)
Prior Related Work Using FTIR

**EPRI funded work¹:**
- Both H₂SO₄ and SO₃ can be detected and quantified
- Multi-port cross-duct measurements found minimal (10%) variation in SO₃ quantity across the duct

**Danish EPA funded work²:**
- Verified Mid-IR spectroscopy in heated lab cells
- Generated SO₃ with ozone method
- Could not measure SO₃ in field

**Comparison to Current Effort:**
- Lasers are more intense than FTIR source enabling faster and more sensitive measurements
- Current system for SO₃ generation uses catalyst

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2. “Sulfur trioxide measurement technique for SCR units”, The Danish Environmental Protection Agency Project #1885 (2016).
Technology Development

- Dual laser approach for $\text{SO}_3$ and $\text{H}_2\text{SO}_4$
- Need “broad” wavelength tuning lasers
- Use close-coupled heated multi-pass cell
- Use inertial filter sampling
- Mid-IR Fiber Optics for remote laser delivery
• External-cavity Quantum Cascade laser with broad-tuning capabilities
• Custom laser developed at Pacific Northwest National Laboratory (PNNL) transitioned to OptoKnowledge
• Sensitive to multiple gas species and able to measure “large” and “small” molecules
• Better solution than standard “narrow-tuning” Distributed Feedback (DFB) lasers
Hollow Core Fiber Optics

Hollow Fiber (Waveguide)
- Technique developed by Rutgers
- Transitioned to OptoKnowledge
- Manufactured and sold by OptoKnowledge
- Full-line of hollow fiber optics products
- Used as gas cell for other applications

Commercial QC Laser

http://www.optoknowledge.com/fiberstore.html
Fiber Optic Delivery to Multi-pass Cell

- Investigate trade-off between transmission and beam quality
- Demonstrated remote delivery of laser with and L = 5 m fiber cable
- Sufficient transmission and beam quality for multi-pass measurements at 1 ppm level
- Also produced beam combiner for coupling two lasers into a single fiber

Measurement of Methane used to verify multi-path cell
Flue Gas Test Facility

- Heated vanadium catalyst bed reactor
- Heated optical cell with windows: T = 400°C (750°F)
- Controlled condensation setup for validation
- Still working on generating SO₃ and H₂SO₄ with known quantities
Measurements

- Laser systems demonstrated with heated multi-pass test cell
- 1 ppm level sensitivity for SO$_2$ at elevated temperatures
- No evidence of SO$_3$ (problems with catalyst?)

T = 390°C

Measured SO$_2$ spectra
Power Plant Testing

FirstEnergy Harrison Station host site

- 3 x 700 MW units equipped with:
  - SCR for NOx control
  - ESP for particulate control
  - FGD scrubbers for SO₂ control

Initial proof-of-concept testing scheduled in 2019

- First test conducted between economizer outlet and SCR ammonia-injection grid
- Second test conducted downstream of air heater focusing on H₂SO₄
- Controlled condensate wet chemical tests to be obtained in parallel (SO₃ + H₂SO₄)
Summary

- A continuous SO₃ monitor is needed to optimize sorbent injection
- Mid-IR Laser spectroscopy solution
- Advancing the state of the art
  - Broad tuning Mid-IR lasers
  - Hollow core fiber optics
  - Close-coupled, heated multi-pass cell
- Technology proven with 1 ppm sensitivity of SO₂
- Working to generate SO₃ and H₂SO₄
  - UCI flue gas facility need to understand catalyst function
  - Will also conduct tests at alternative facility (FERCo)