TDL syngas sensor for *in situ* monitoring of CO, CH_4 , CO_2 , & H_2O in an engineering-scale high-pressure coal gasifier

Ronald K. Hanson, Ritobrata Sur, Kai Sun, Jay B. Jeffries High Temperature Gasdynamics Laboratory, Stanford University

> NETL's Crosscutting Research Review Meeting May 19-23, 2014, Pittsburgh, PA



Gasifier in Wilsonville, Alabama USA

- Vision for gasifier sensing
- Absorption sensor fundamentals
- NCCC gasifier facility
- Stanford optics design
- Results for CO, CH₄, CO₂, & H₂O
- Summary and further work







Supported by DOE NETL – Dr. Susan Maley

Stanford's Vision for TDL Sensing in IGCC



Vision: Sensor for control signals to optimize gasifier output and gas turbine input

- 1st generation laser absorption sensor for CO, CO₂, CH₄, and H₂O
 - Stanford sensor tested in a pilot-scale (1 T/day coal) gasifier (U Utah 2009-2012)
- 2^{nd} generation CO, CO₂, CH₄, and H₂O sensor developed
 - Tested in an engineering-scale (30,000 lb/hr syngas) gasifier at NCCC (December 2012 & March 2014)

Absorption sensing: How does it work?



- Scanned-wavelength *line-of-sight* direct absorption
 - Beer-Lambert relation $T_v \equiv \frac{I_t}{I_o} = \exp(-k_v \cdot L)$
 - Spectral absorption coefficient $k_V = S(T) \cdot \Phi(T, P, \chi_i) \cdot \chi_i \cdot P$
 - Wavelength-scanning yields χ

$$\int_{v} k_{v} L \cdot dv = S(T) \cdot \chi_{i} \cdot P \cdot L$$

Integrated absorbance

3

Two Absorption Sensor Strategies: Direct Absorption (DA) & Wavelength Modulation Spectroscopy (WMS)



- Direct absorption: Simple, if absorption is strong and isolated
- WMS: More sensitive especially for small signals (near zero baseline)
 - WMS with TDLs improves noise rejection
 - Normalized WMS, e.g. 2f/1f cancels scattering losses!

What wavelengths for syngas detection?

Gas Species Important to Combustion/Gasification Absorb Light in the Near-Infrared



- Important gasification species can be monitored (e.g., CO, CO₂, CH₄, H₂O)
- Select 2-2.3µm to minimize H₂O interference for CO, CO₂, CH₄

What does the facility look like?

NCCC Gasifier Large-Scale DoE Demo

NCCC transport gasifier based on a circulating fluidized bed concept
 Goal:

Laser absorption *in situ* measurements of syngas products composition *Where is sensor located?*

- TDL sensor monitors syngas flow 30m downstream of the PCD
- Flow laden with particulate (< 0.1% transmission) at sensor location

How do we measure 4 species?

Detection Strategy: Time Demultiplexing Wavelength Scanned WMS-2f with 1f Normalization

Connections of Stanford Sensor to NCCC Facility

- Electronics in the control house ~30m to measurement location
- Lasers near measurement location (~ 2m away)
- Sensor operated remotely (alignment, detector gain, laser scanning)
 Next: Further details of optical system

Optics Design: Multiplex Four Lasers

- Fiber bundle delivers light from four lasers
- Optics combine all beams onto common line-of-sight w/ only one detector
- Large beam size reduces beam steering noise

Next: Data from gasifier warm-up

Time-Resolved H₂O During Gasifier Warm-up

- In situ measurements of syngas moisture content capture transient events
 - Propane used for slow heating of ceramic linear
 - Pulsed coal feeding begins at hour 38
 - Reactor shut down at hour 54 (before transition to stable gasification)

Next: Transition to gasification

H₂O and CO₂ During Transition to Gasification

- CO₂ fluctuations damped when reactor transitions to gasification
- GC time resolution does not capture transients, only average mole fraction

Sensor Captures Onset of Gasification via CO & CH₄

- Rapid jump in CO and CH₄ at onset of gasification
- GC data have large time lag (shifted here by 20 minutes for comparison with laser)
- GC data also have poor time resolution (note slow CO response vs laser)

Next: Data from "Stable Gasification"

Four Species Measurements After Gasifier "Stable"

- Laser sensor provides simultaneous CO, CH₄, CO₂, and H₂O
- Correlation of CO with CH₄ confirms that fluctuations are real
- GC time resolution does not capture temporal fluctuations

Next: Long unattended monitoring

18 Days of H₂O Unattended Monitoring

- Continuous, stable measurements for 18 days (terminated by NCCC)
- Periodic liquid H₂O samples taken from syngas agree with laser sensor
- Laser sensor show small fluctuations in the H₂O mole fraction

Are sensor fluctuations real or noise?

H₂O Sensor Captures Fluctuations in Gasifier Reactor

- H_2O fluctuation tracks the reactor thermocouple (note small ΔT)
- H₂O fluctuation tracks the reactor coal feed pulse
- Laser sensor captures small H_2O change (Δ mole fraction ~ 0.1%)

Summary

- Laser sensor yields successful measurements in syngas
 - First-ever *in situ* laser absorption in pilot scale gasifier (Utah, 2010)
 - First-ever *in situ* laser absorption at NCCC (2012)
 - Successful in harsh environment, even with large (>99.9%) transmission losses due to scattering & pressure ~15atm
- Demonstrated excellent detection sensitivity at 1-second (1Hz):
 - H₂O : 200ppm m
 - CO: 200ppm m
 - CH₄: 300ppm m
 - CO₂: 800ppm m
- Unattended operation (>435 hours demonstrated)
- Sensor strategy useful for other applications, especially at elevated pressure and/or dusty gases

Recommendations for future work

- Add additional species important to specific application, for example
 - NH₃, H₂S, SO₂,
- Improve data processing
 - Provide real time readout compatible with facility record
 - Provide web-based monitoring for unattended operation
- Refine optical engineering and repackage in smaller containers

Acknowledgements

- DoE, NETL: Dr. Susan Maley and Mr. Charles Miller
- National Carbon Capture Center, Southern Company Services, Mr. John Socha
- Stanford team:

Ritobrata Sur

Dr. Kai Sun

Dr. Jay Jeffries