Advanced Sensors & Controls FWP: Raman Gas Analyzer Testing

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NATIONAL ENERGY TECHNOLOGY LABORATORY

April 9, 2019

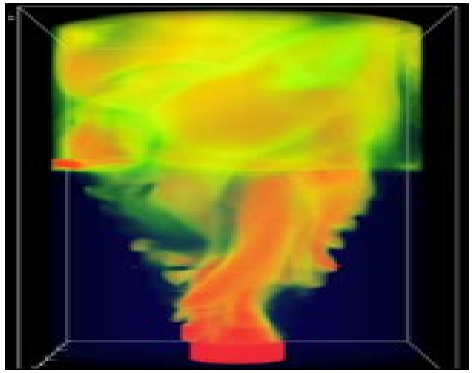
Crosscutting Research Review Meeting

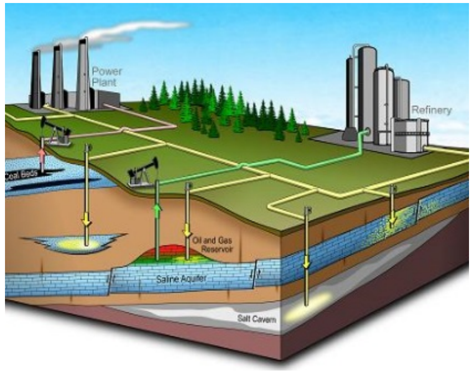
U.S. DEPARTMENT OF ENERGY

Overview

- **Introduction**
- **Overview of R&IC Sensors & Controls research**
- **Raman Gas Analyzer**
    - How it works
    - Recent field test results
    - Future work

R&IC Core Capabilities





APPLIED MATERIALS SCIENCE & ENGINEERING

Developing and deploying affordable, high-performance materials designed for severe service applications.

DECISION SCIENCE & ANALYSIS

Utilizing multi-scale computational approaches to provide in-depth objective analyses in support of the DOE mission.

CHEMICAL ENGINEERING

Pioneering efficient energy conversion systems that can enable sustainable fossil energy utilization.

SUBSURFACE SCIENCE

Enabling the sustainable production and use of fossil fuels through engineering of the subsurface.

SYSTEMS ENGINEERING & INTEGRATION

Accelerating technology innovation, development and deployment to enable new clean energy technologies to gain market acceptance.

Changing Landscape for Fossil Energy Power

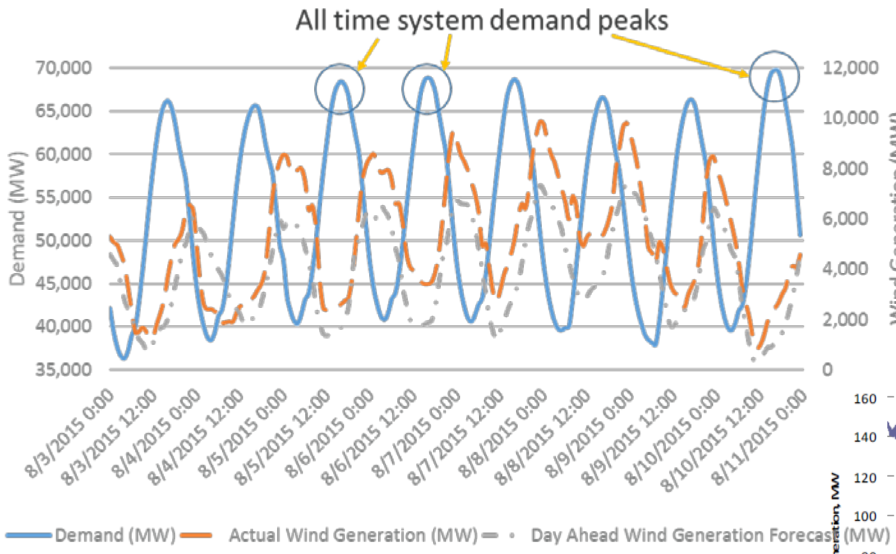
Changing Role

Fossil energy power generation is needed now and in the future, **but its role is shifting** from baseload operation to fulfilling **dispatchable power** needs in regions of the United States.

Novel sensors and controls will help to **increase efficiency**, **minimize emissions**, and **reduce operating costs** of existing power generation technologies under this increased load following role; and help enable next generation power systems with high efficiency and greater operational flexibility.

Renewables Increase Net Load Variability

Sensors and Controls Can Help Dispatchable Power Respond



Texas is has large swings in dispatchable power demand with wind variation.

Passing clouds can cause fast variations in PV output.

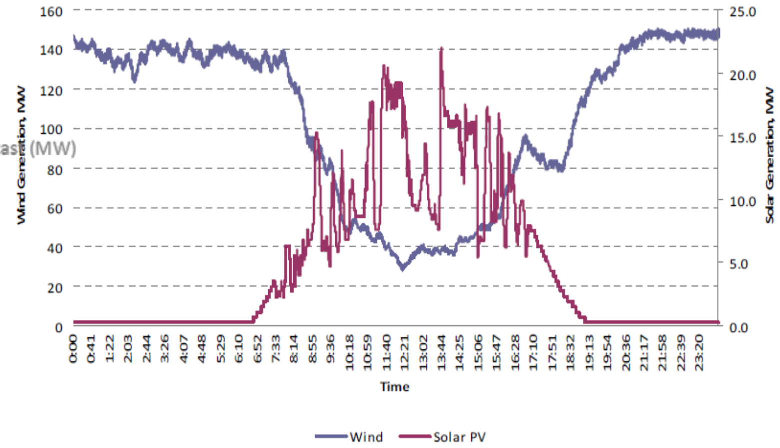
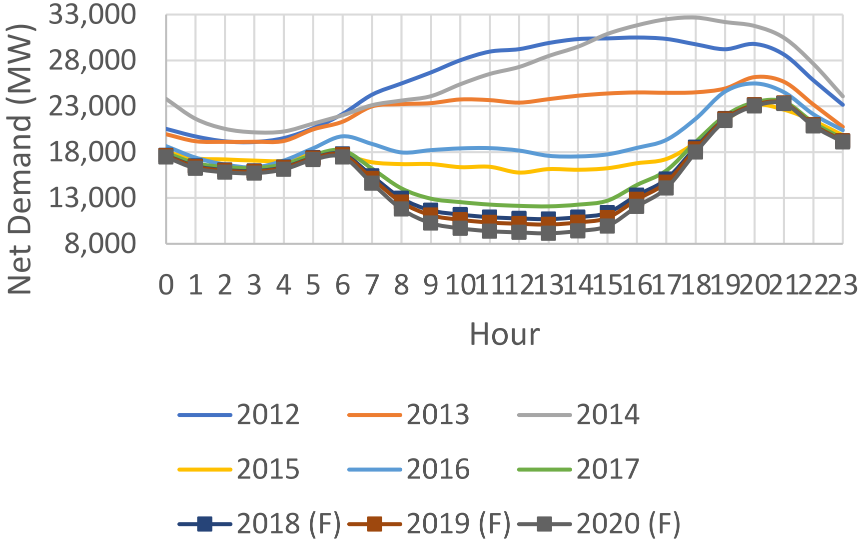


Figure 1-2: Sub-hourly wind and solar generation for a day for a 150 MW wind generator and a 24 MW Solar PV plant

2010 report by the California ISO, *Integration of Renewable Resources: Operational Requirements and Generation Fleet Capability at 20% RPS*



(F) = Forecasted

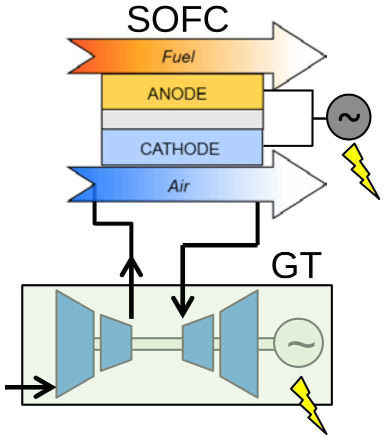
The highest level of renewable production to date for 2017 (13,664 MW) in CAISO was registered on May 26 at 1300 PDT

CAISO Duck Curve becomes more pronounced.
Similar net demand curve in North Carolina.

Data Sources: ABB Velocity Suite – Hourly Generation by Fuel Type Intelligent Query , Forecast Periods developed using California Energy Demand 2016 – 2026 Adopted Forecast Mid Case Final Baseline Forecast, http://www.energy.ca.gov/2015_energypolicy/documents/index.html#adoptedforecast

Technology Challenges

- **Harsh Environments: Temperature, Pressure, Corrosive, Erosive**
- **Cross-Cuts Fossil Energy Power Generation & Systems**
- Advanced S&C: cost effective implementation in existing plants, and enabling performance of Advanced Energy Systems



Hybrid systems
- 800°C in fuel cell
- 1500°C in GT

Meas. Challenges
- T and H_2 dist in SOFC
- Transient control

REMS
- Radically engineered modular systems for gasification
- 1100 - 1500°C

Meas. Challenges
- Multipoint temp
- Species
- NDE of adv. manuf. components
- Multiphase flow

Coal-fired Boilers
- Steam 1110°F (600°C), 4000 psig
- Fire side 2500°F (1370°C) +
- Ash / slag / SOx

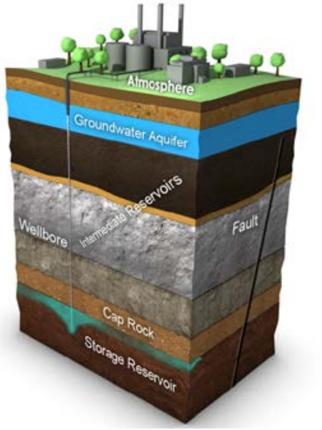
Meas. Challenges (*cycling)
- Tube temperatures / flow
  Corrosion/erosion/exfoliation
- Steam chemistry
- Coal particle size
- Temperature / species dist.

Chemical Looping
- > 1000°C
- Pressurized
- Erosive

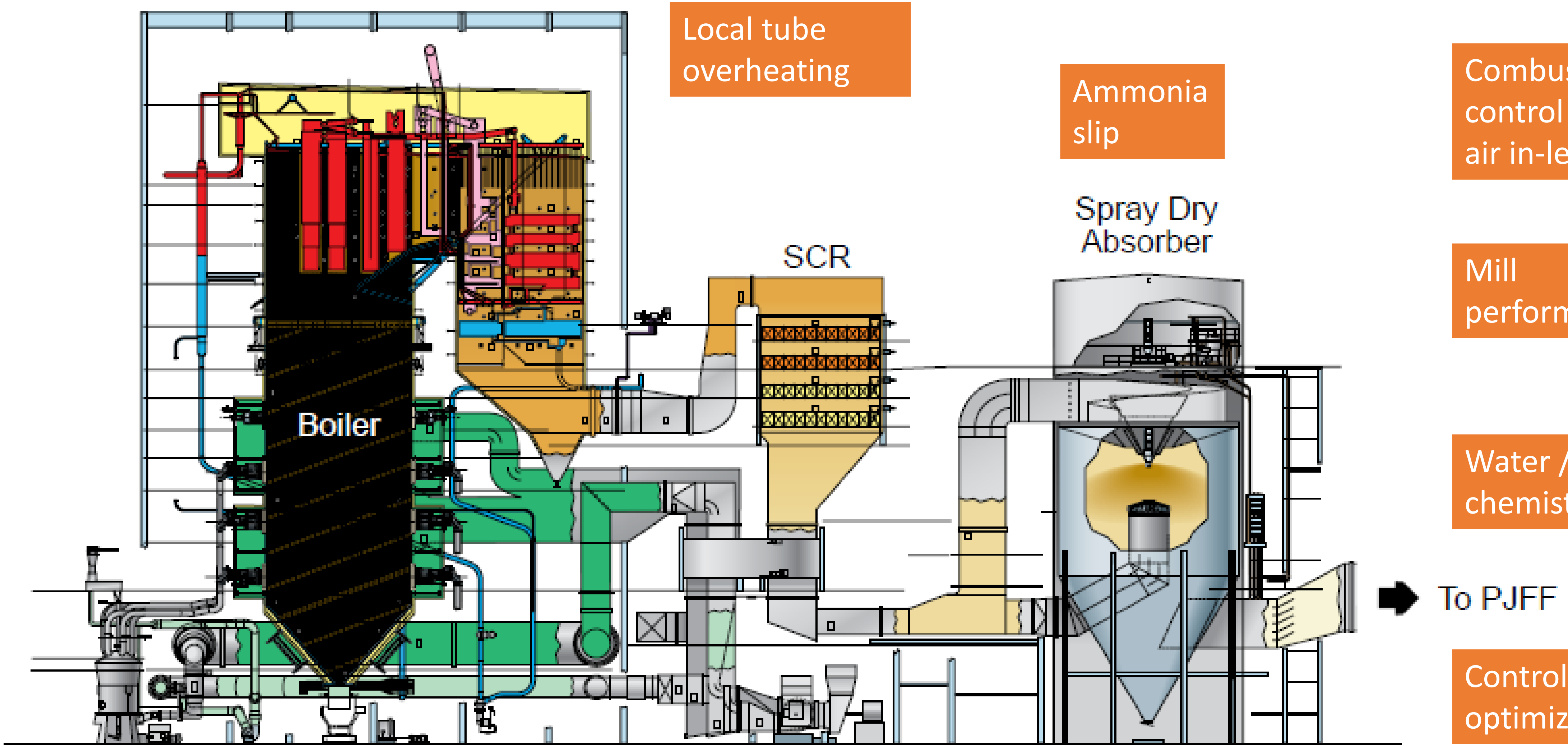
Meas. Challenges
- Solids circulation
- Oxidation state
- Multipoint temp

Subterranean chemistry monitoring
- High pressure brine

Meas. Challenges
- Salts in water
- Wellhead measurement
- Downhole measurement



Some Challenges in Existing Plants



Local tube overheating

Ammonia slip

Combustion control and air in-leakage

Mill performance

Water / WW chemistry

Controls optimization

Cross-section of John W. Turk Jr. USC Plant. Courtesy of Babcock & Wilcox. All rights reserved.

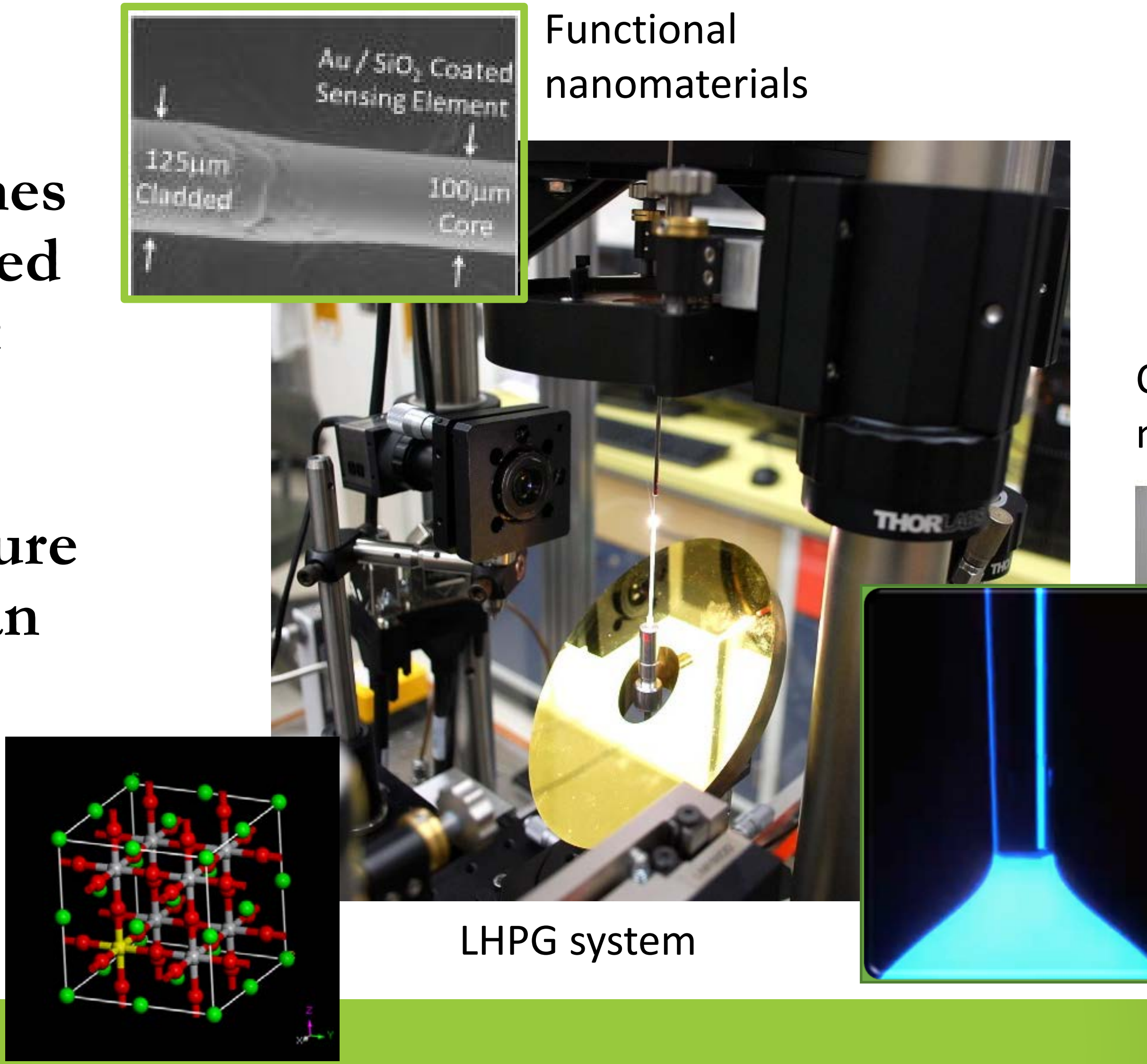
Overview of R&IC Research in Sensors & Controls

- **Sensors and Instrumentation**
  - High temperature optical fiber sensors
  - Embedding of optical fibers in metal parts
  - LIBS
  - Raman gas analysis
  - Solids circulation rate
- **Controls**
  - Real time hybrid system control for load following
  - Agent-based controls
  - Control strategies for sCO2 systems
- **Techno-Economic Analysis**

Optical Fiber Sensing for Harsh Fossil Energy Applications

PIs: Paul Ohodnicki, Michael Buric, Yuhua Duan

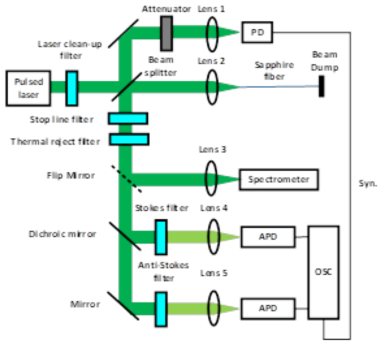
Developing materials and sensing approaches to develop a fiber-based sensing concepts that can provide spatially resolved chemical species and temperature measurements from an optical fiber at above 800°C



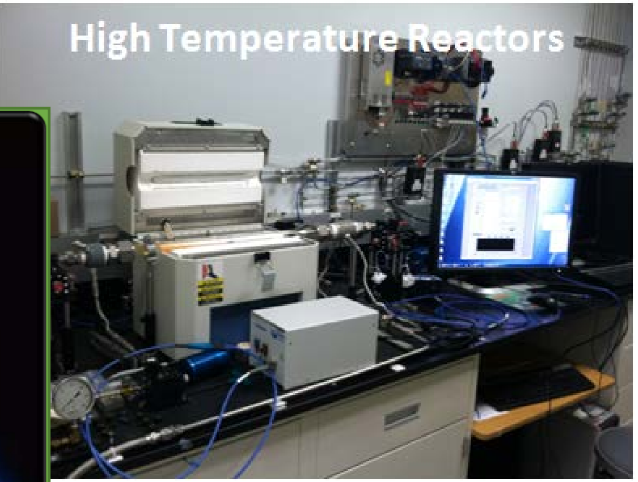
Functional nanomaterials

LHPG system

Atomic level material modeling

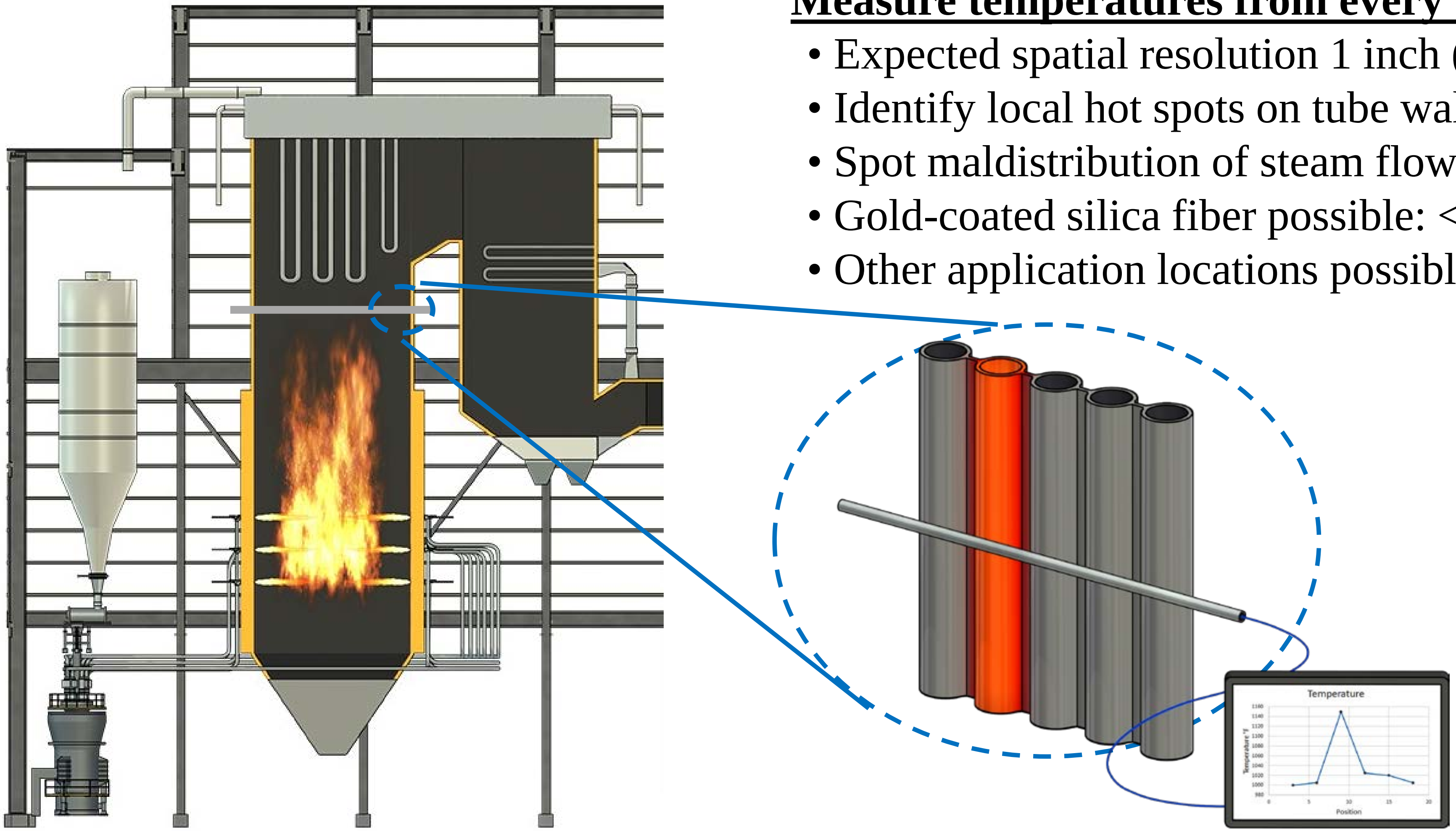


Commercial and novel multipoint interrogation



Fossil energy relevant gases

Multipoint Boiler Tube Temperature Monitoring



Measure temperatures from every tube

- Expected spatial resolution 1 inch (200 ft long)
- Identify local hot spots on tube wall
- Spot maldistribution of steam flow at low power
- Gold-coated silica fiber possible: <1200°F (650°C), air
- Other application locations possible

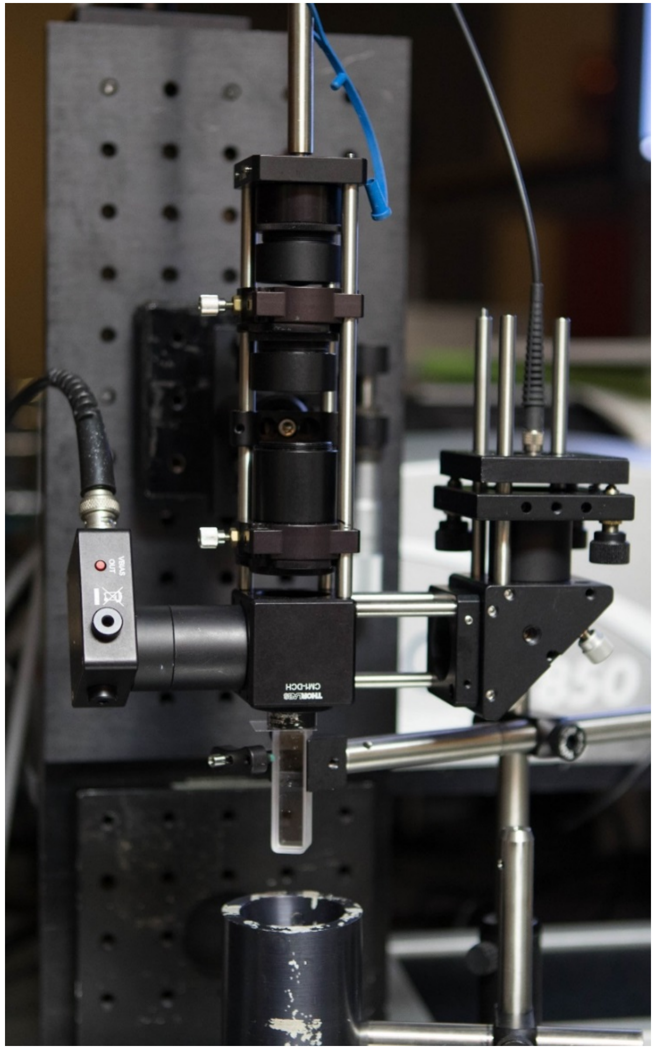
Apply commercial optical fiber readout instrument (silica fiber)

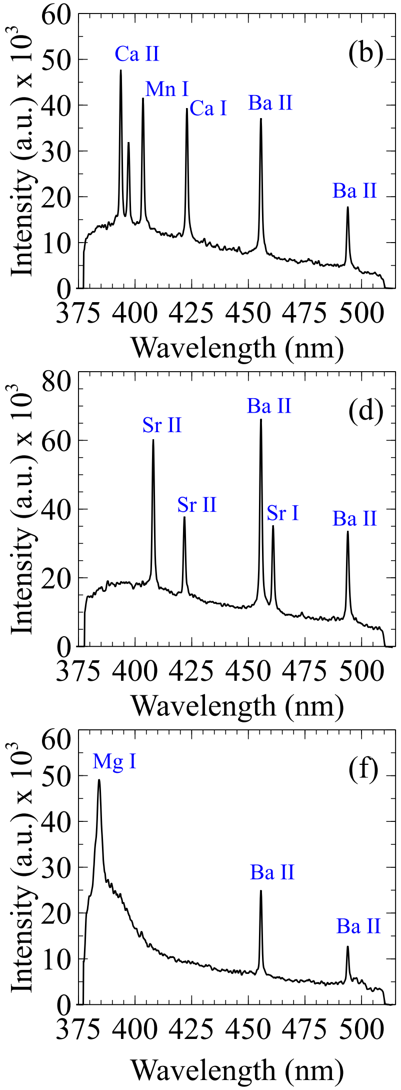
LIBS for Subsurface & Wastewater Chemical Measurement

PI: Dustin McIntyre

- **Demonstrated concurrent LIBS sensing of Ca^{2+} , Mg^{2+}, Mn^{2+}, Sr^{2+} as a function of CO_2 pressure up to 400 bar on the lab bench, from chloride solutions**
  - An important step toward in-situ subterranean measurements of carbonate dissolution.
  - 400 bar (5900 psia) spectra at right
- **Constructed proof-of-concept split laser LIBS system prototype to test key custom components**
  - Step toward field use system
  - TCF with Applied Spectra to help commercialize

Woodruff, S.D., McIntyre, D.L., Jain, J.C., “A method and device for remotely monitoring an area using a low peak power optical pump,” U.S. Patent 8,786,840 July 22, 2014.
D. A. Hartzler, J.C. Jain, D. L. McIntyre, “Development of a subsurface LIBS sensor for in situ groundwater quality monitoring with applications in CO2 leak sensing in carbon sequestration,” Scientific Reports, v.9, Article 4430, 2019.





LIBS for Subsurface & Wastewater Chemical Measurement

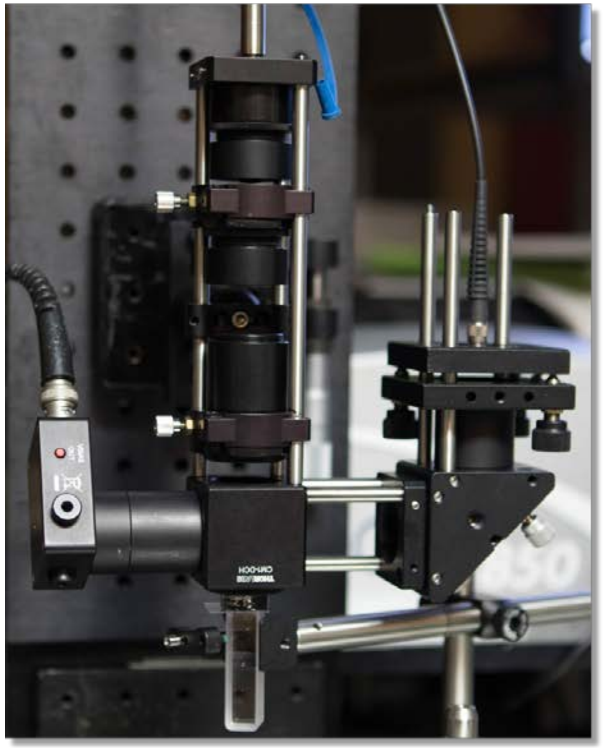
PI: Dustin McIntyre

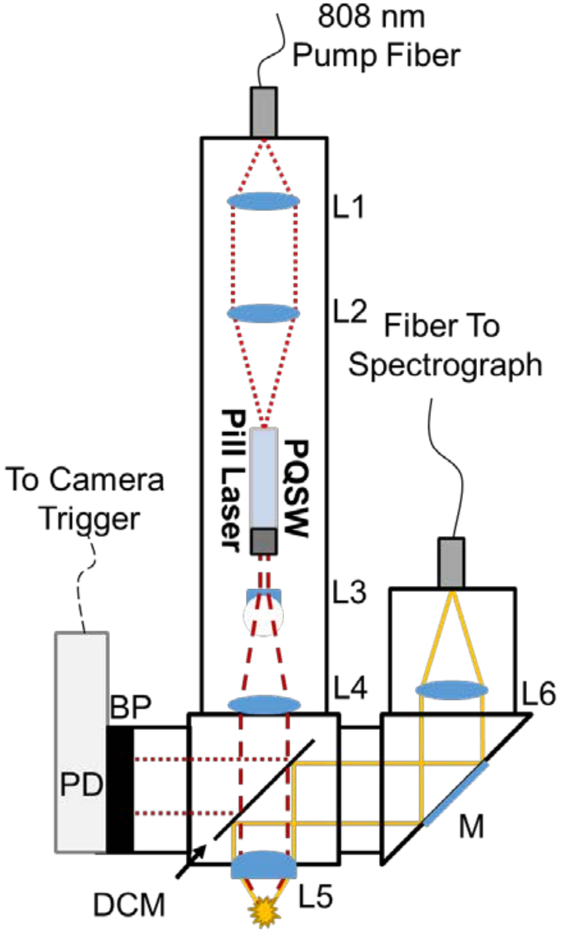
Technical Progress:

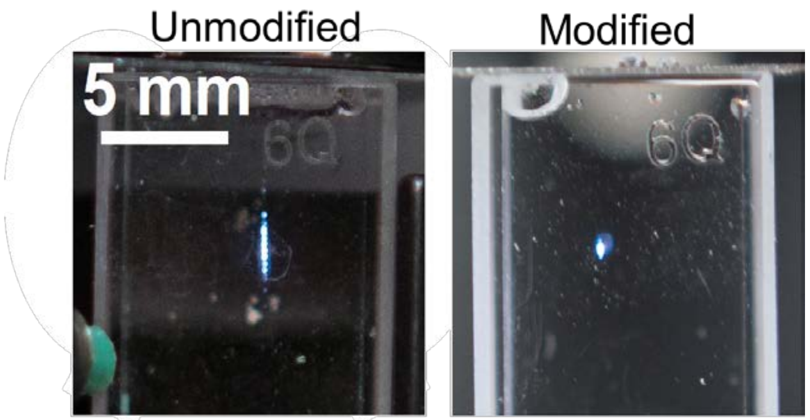
- Online LIBS measurements were taken during exposure of synthetic rock (contained Ca, Mg, Sr, and Mn) to high pressure carbonated water over several days
- Online LIBS measurements taken during exposure of Mt. Simon sandstone to high pressure carbonated water over several days.
- Optics tested and optimized

Outlook:

- Fabrication and initial validation of watertight prototype
- Planning for initial field testing







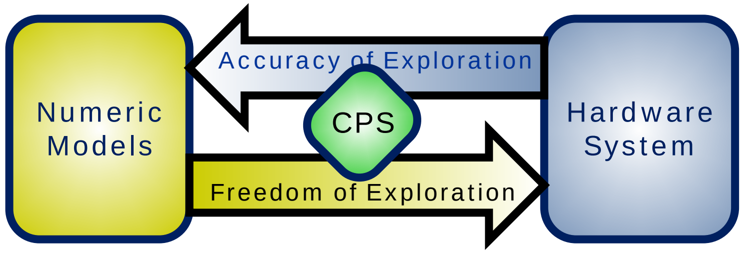
See poster tonight for more information

Advanced Controls:

Agent Based Controls for Power Systems

PI: David Tucker

Development and testing of advanced controls for highly-coupled advanced power generation systems which are often plagued with non-linear actuator response



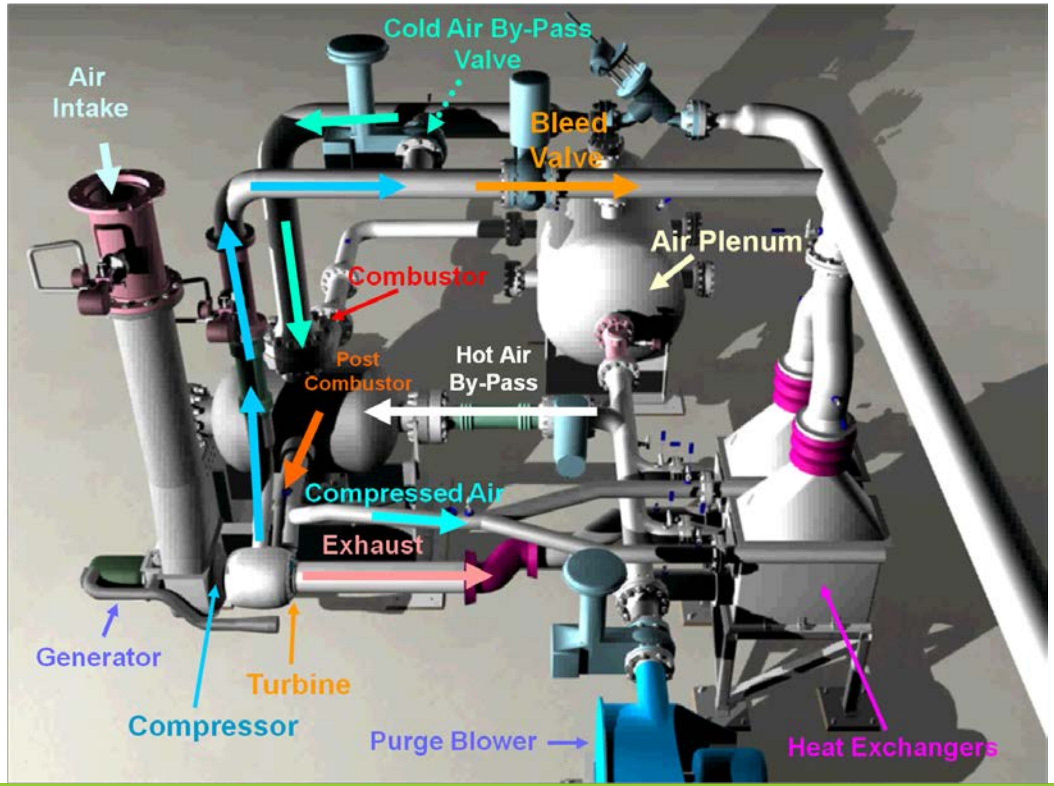
Numeric Models

Accuracy of Exploration

CPS

Freedom of Exploration

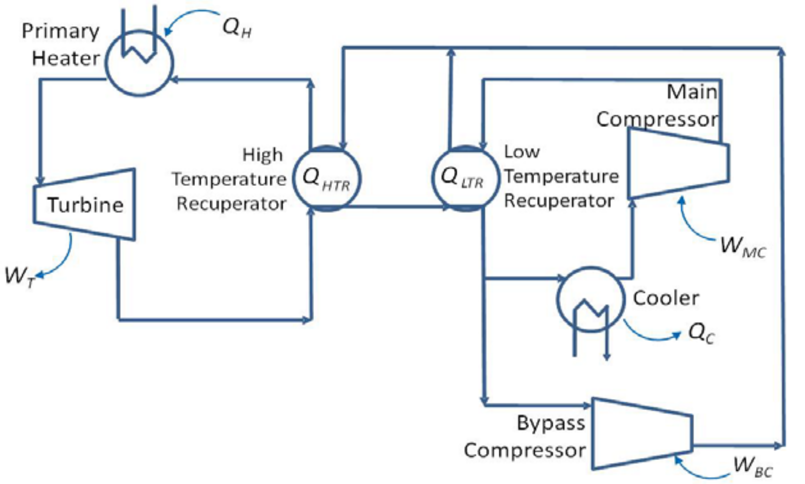
Hardware System



- Applying ***cyber-physical systems*** to reduce the risk and cost of control system development
- Real APU gas turbine and system volume exhibits complex dynamic behavior
- Team has destroyed hundreds of ***virtual*** SOFCs, in transient testing of hybrid fuel-cell turbine systems

Advanced Controls:
Control Strategies for a 10 MW sCO2 Power System

PI: Eric Liese



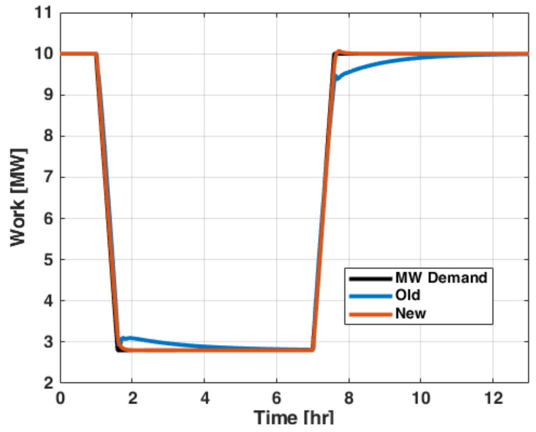
Objective: Use a dynamic process model to study operational and control strategies for a 10 MWe indirect-fired supercritical CO_2 (sCO_2) recompression Brayton closed cycle (RCBC) with emphasis on the DOE experimental Supercritical Transformational Electric Power (STEP) facility.

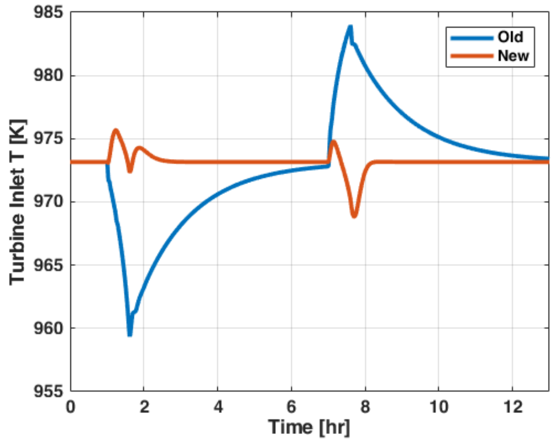
Technical Progress:

- Discussed previous NETL control studies and future interests with STEP development team (GTI, SwRI, GE)
- Implemented turbine inlet temperature control by manipulating external combustor and load setpoint tracking using inventory management control.
- Investigated cooler exit CO_2 temperature control. Details to be presented at ASME Turbo Expo conference†

In Progress/Future Work:

- Update model with current STEP design data (e.g. equipment sizes)
- Simple Cycle model (first year of STEP operation will be in a Simple Cycle configuration)





Figures: Updated control improves Work and Turbine Inlet Temperature setpoint tracking

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†Liese E., Mahapatra, P., and Jiang, Y., “Modeling and Control of a Supercritical CO_2 Water Cooler in an Indirect-fired 10 MWe Recompression Brayton Cycle near Supercritical Conditions”, To be presented at the ASME Turbo Expo, Phoenix, Arizona, June 17-21, 2019

Fast Raman Gas Analyzer

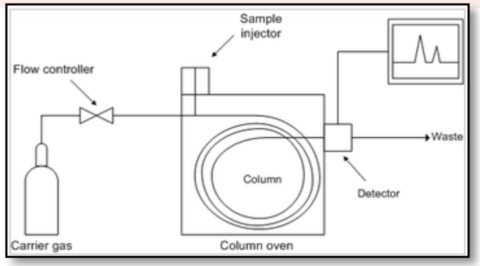
- How it works
- Recent field test results
- Future work

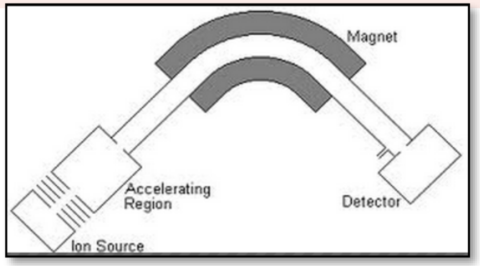
Benefit of Fuel Gas Analysis:
Maximizing Efficiency and Minimizing Emissions

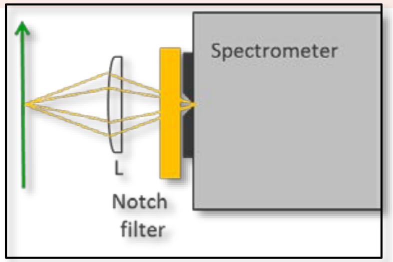
- **Natural gas: 85-95% CH_4, 3-8% C_2H_6, <7% C_3H_8**
  - Liquefied Natural Gas: Similar, but ratio varies during vaporization
  - Variations randomly fluctuate in pipeline because of season, source, and temperature driven fuel dropout
- **Coal-derived syngas and biogas: H_2, CO, CO_2, H_2O, CH_4, N_2, …**
- **Turbines and reciprocating engines**
  - Fuel composition affects efficiency and pollutant emissions
    - Flame temperature and optimal fuel/air ratio
  - Fuel composition affects operation and maintenance costs
    - Flame speed and combustion stability
  - Optimal control requires ~1 sec, better than 1% measurement

Current, Conventional Technology

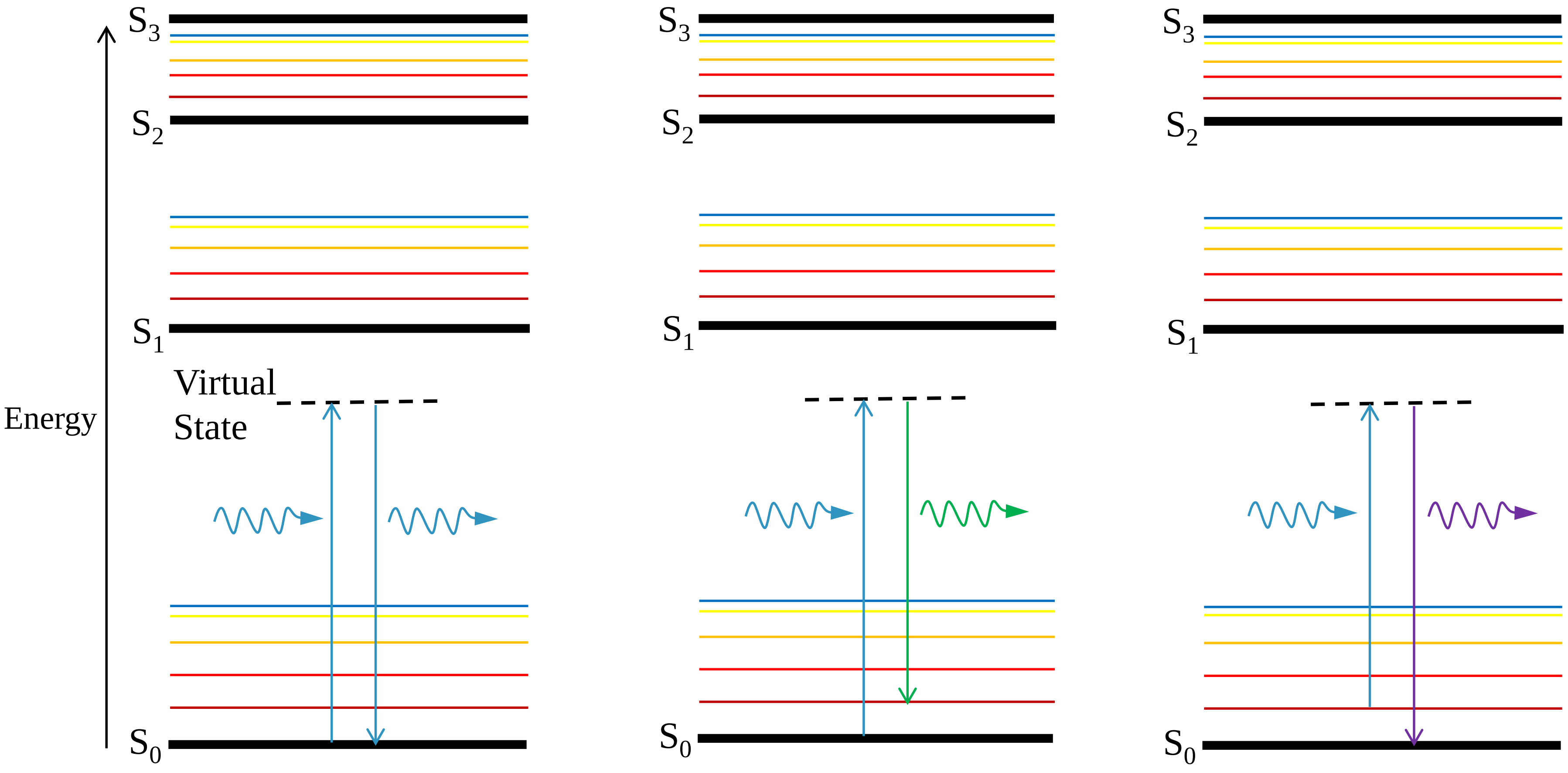
	Gas Chromatography	Mass Spectrometry	Conv. Raman Spectroscopy
Method	Separates based on affinities for adsorbent and a carrier gas – used in conjunction with a detector	Electron beam ionizes particles that get placed in a magnetic field – velocity of components reveals identity	Electromagnetic radiation is scattered by collisions with molecules – each species produces a specific shift
Use	Identification & quantification	Identification & structure	Identification & quantification
Read-Out Time	**Minutes**	Real time, if only one mass	**About a minute**
Results	Gas chromatograph	Mass spectrum	Raman spectrum
Limitations	Retention time overlap. Molecule interactions. Frequent recalibration.	**Vacuum required for ions.** **Resolution of same-mass species**	Weak signal in gases. Fits results to 100%
Advancements	Multidimensional GC	GC-MS	In progress







Principle of Raman Spectroscopy



Rayleigh Scattering

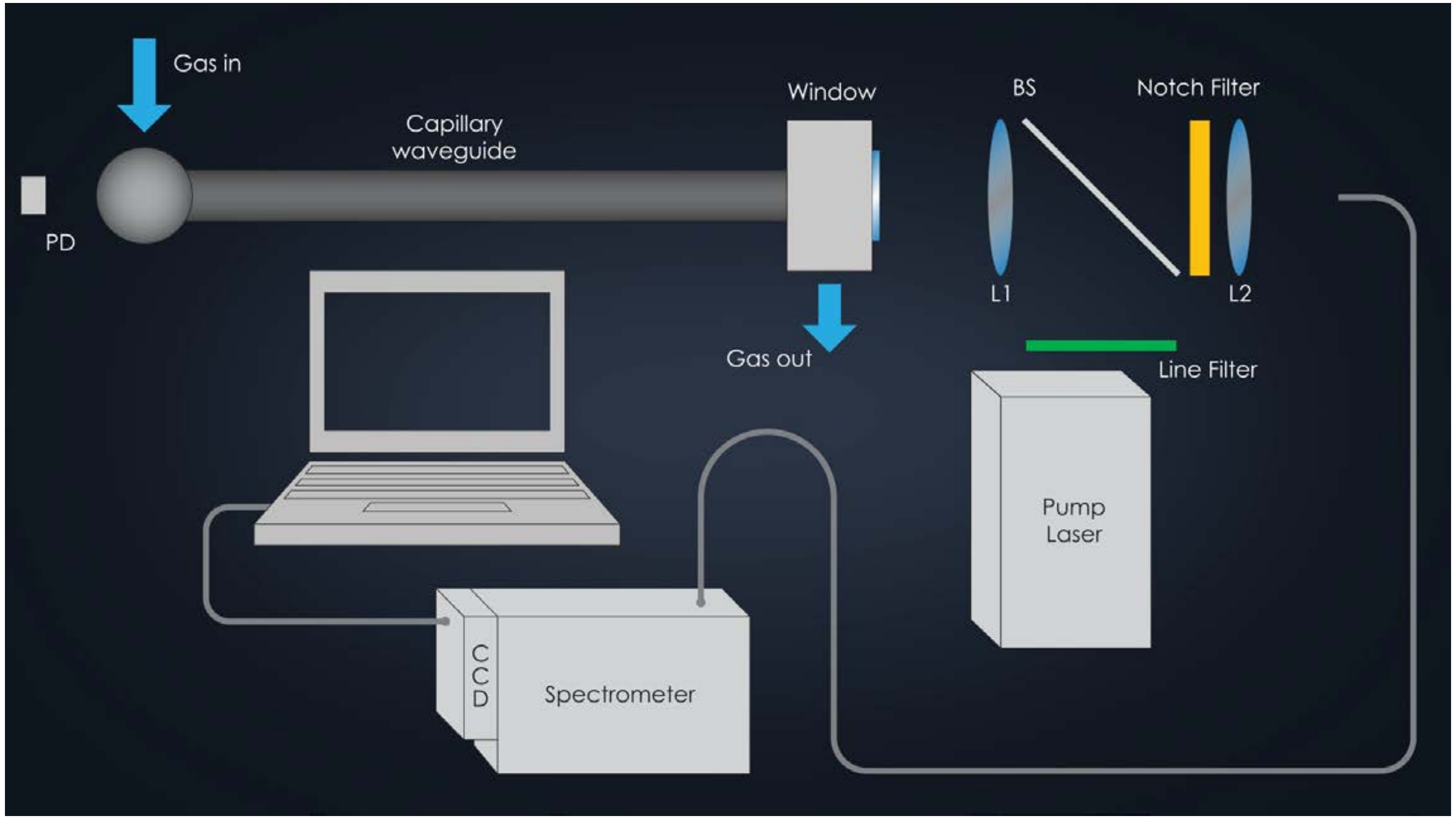
Raman Scattering (Stokes)

Raman Scattering (Anti-Stokes)

S_0, S_1, S_2, and S_3 are electronic energy levels

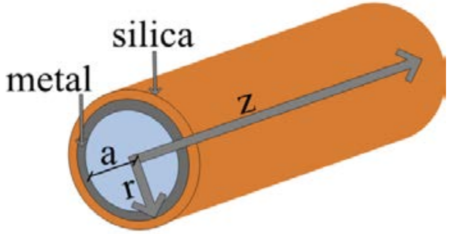
Waveguide Enhanced Raman System

- **SPEED**: One-second response time
- **ACCURACY**: Sub-percent for all species with little cross sensitivity
- **SIMPLICITY/STABILITY**: Obtains all species at once with no tunable lasers, no pump power control

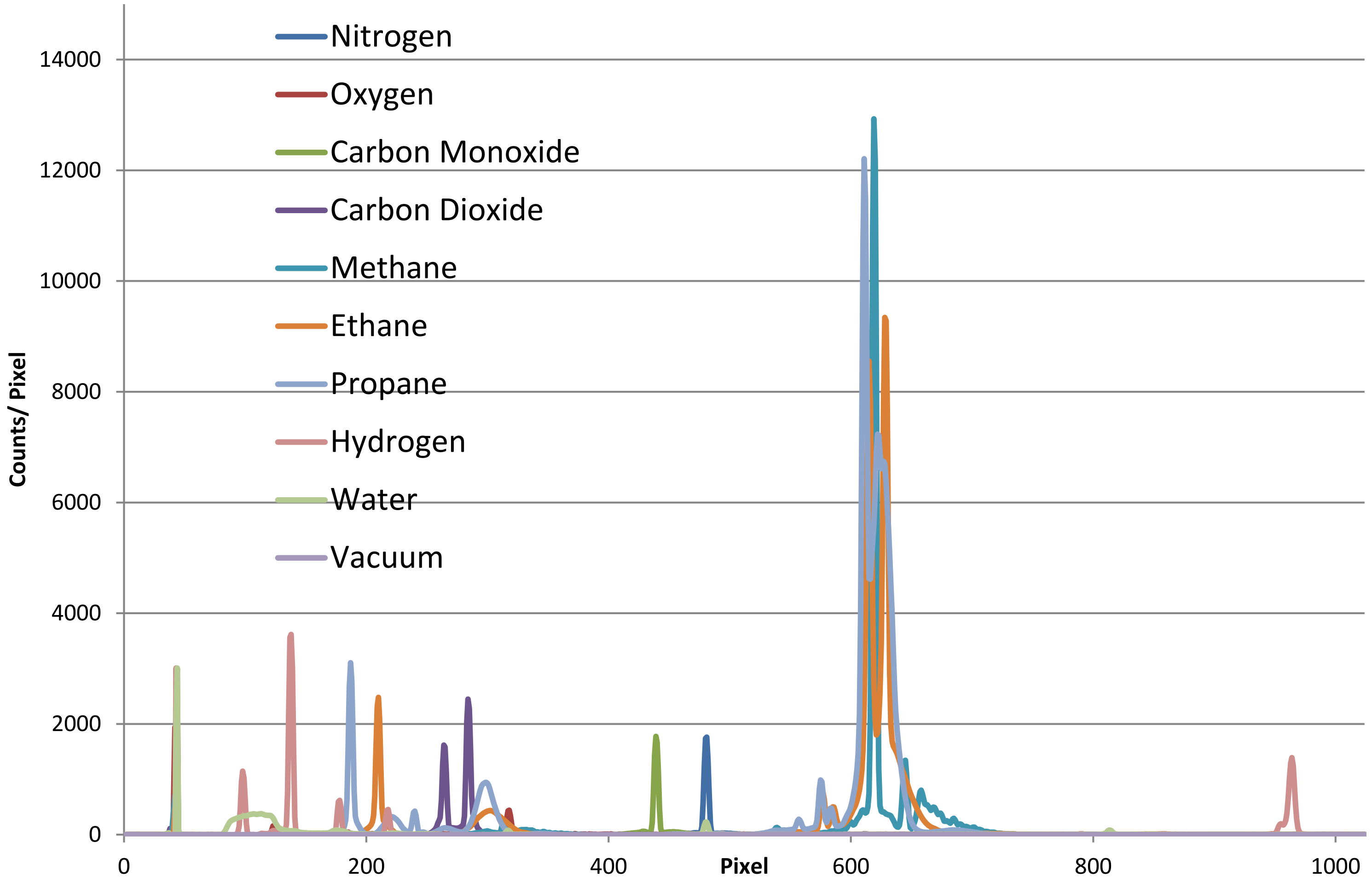


Novel configuration with capillary waveguide enables speed and accuracy.

US Patent 8,674,306, NETL and University of Pittsburgh



Raman Spectroscopy of Gases



All major species simultaneously (no noble gases)

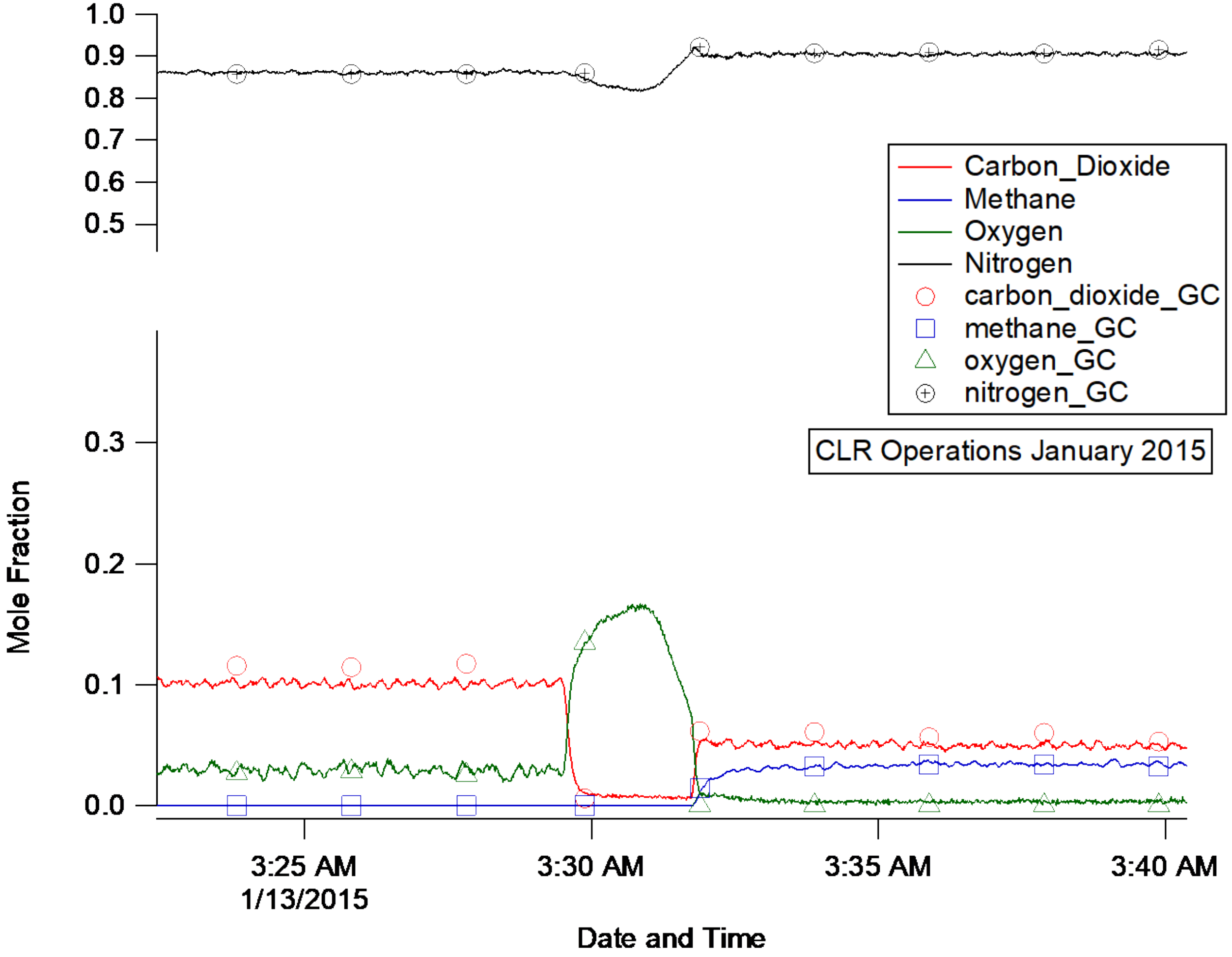
Measures difficult gases: H_2, N_2, O_2 (they have no IR transitions)

Easily distinguishes CO from N_2 (difficult for mass spectrometer)

Operates at process pressure

US Patent 8,674,306, NETL and U. of Pittsburgh

Example Application: Chemical Looping Fuel Reactor Gas Monitoring

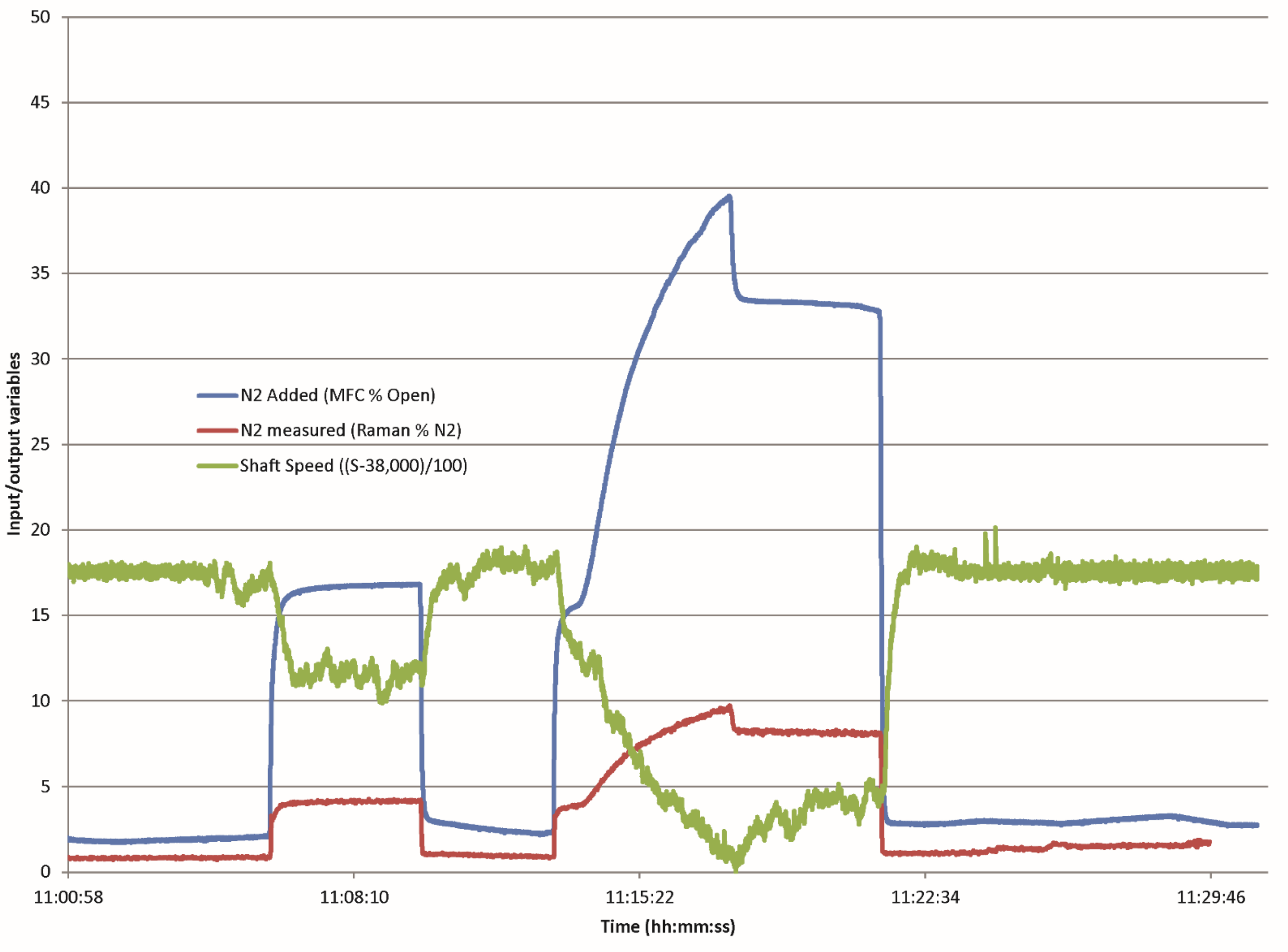


Much faster response than gas chromatograph (GC) enables smarter process control

B. Chorpening, M. Buric, S. Woodruff, J. Weber, and D. Straub. 2015, "Raman gas analysis for chemical looping," AIChE Annual Meeting, Nov. 11, 2015, Salt Lake City

US Patent 8,674,306, NETL and U. of Pittsburgh

Example Measurements (Hyper turbine)



Fuel mixing measured in real time; turbine shaft speed affected

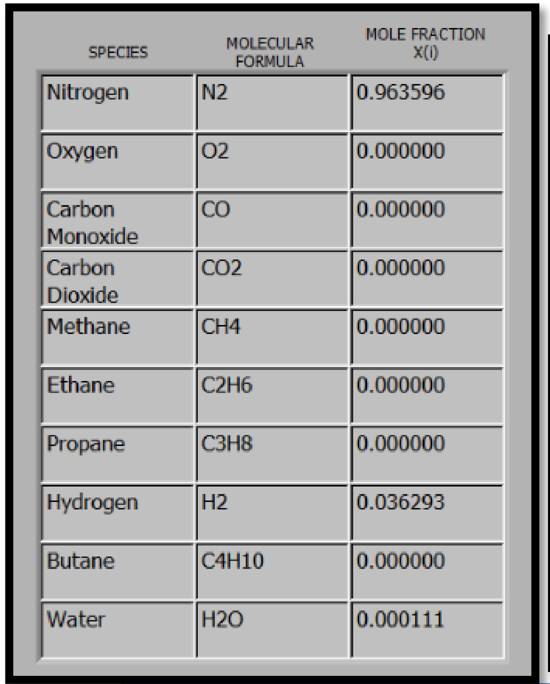
Nitrogen blended into fuel for test; manual time sync between computers

M. Buric, S. Woodruff, B. Chorpening, D. Tucker., "Fuel flexibility via real-time Raman fuel-gas analysis for turbine system control", Proceedings of SPIE Vol. 9482, 94820S (2015)   SPIE Digital Library

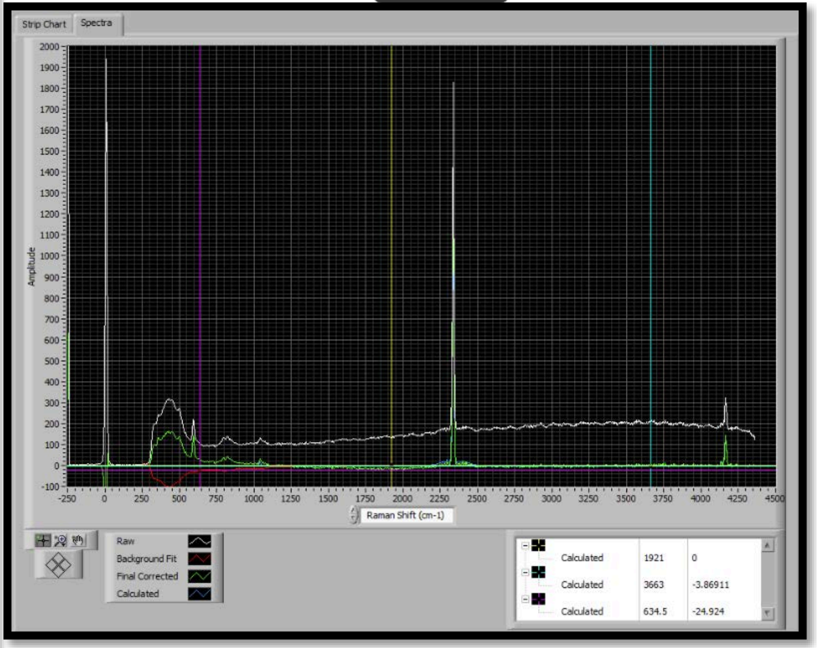
US Patent 8,674,306, NETL and U. of Pittsburgh

Status/Accomplishments

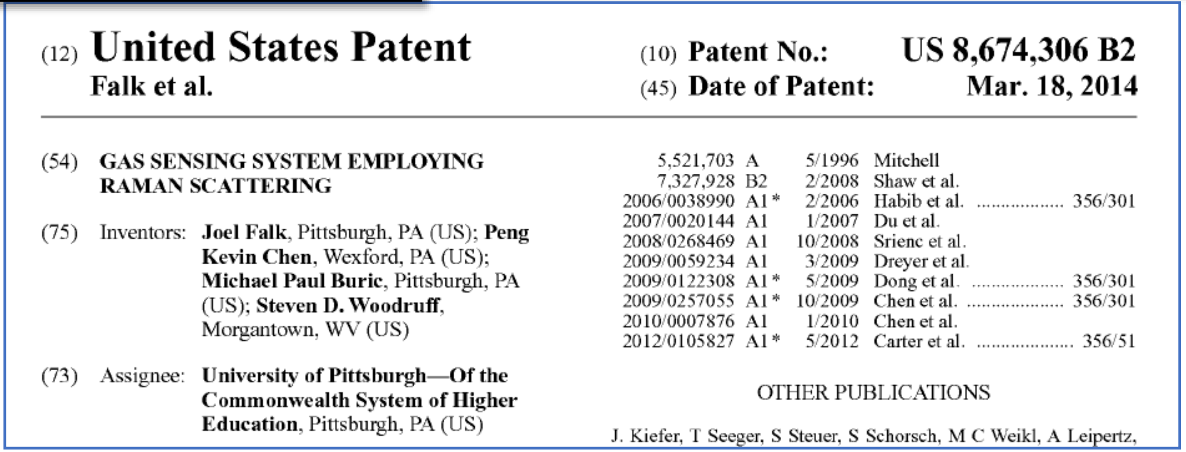
- **Status**
  - US Patent 8,674,306, U. of Pittsburgh and NETL – **Available to License**
  - Labview-based Software
  - Field prototype constructed and operated
    - NEC Class 1 Division 2 compatible
    - Operated at NCCC
    - Operated at NETL – Hyper
    - Operated at NETL – High pressure combustion facility
    - Operated at NETL – Chemical Looping Reactor
  - CRADA with Oxergy, Inc. on specific application (non-exclusive)
  - CRADA with Solar Turbines, field testing



SPECIES	MOLECULAR FORMULA	MOLE FRACTION X(i)
Nitrogen	N2	0.963596
Oxygen	O2	0.000000
Carbon Monoxide	CO	0.000000
Carbon Dioxide	CO2	0.000000
Methane	CH4	0.000000
Ethane	C2H6	0.000000
Propane	C3H8	0.000000
Hydrogen	H2	0.036293
Butane	C4H10	0.000000
Water	H2O	0.000111



Calculated	1921	0
Calculated	3663	-3.86911
Calculated	634.5	-24.924



(12) **United States Patent**
Falk et al.

(10) **Patent No.:** **US 8,674,306 B2**
(45) **Date of Patent:** **Mar. 18, 2014**

(54) **GAS SENSING SYSTEM EMPLOYING RAMAN SCATTERING**

(75) Inventors: **Joel Falk**, Pittsburgh, PA (US); **Peng Kevin Chen**, Wexford, PA (US); **Michael Paul Buric**, Pittsburgh, PA (US); **Steven D. Woodruff**, Morgantown, WV (US)

(73) Assignee: **University of Pittsburgh—Of the Commonwealth System of Higher Education**, Pittsburgh, PA (US)

5,521,703	A	5/1996	Mitchell	
7,327,928	B2	2/2008	Shaw et al.	
2006/0038990	A1 *	2/2006	Habib et al.	356/301
2007/0020144	A1	1/2007	Du et al.	
2008/0268469	A1	10/2008	Srienc et al.	
2009/0059234	A1	3/2009	Dreyer et al.	
2009/0122308	A1 *	5/2009	Dong et al.	356/301
2009/0257055	A1 *	10/2009	Chen et al.	356/301
2010/0007876	A1	1/2010	Chen et al.	
2012/0105827	A1 *	5/2012	Carter et al.	356/51

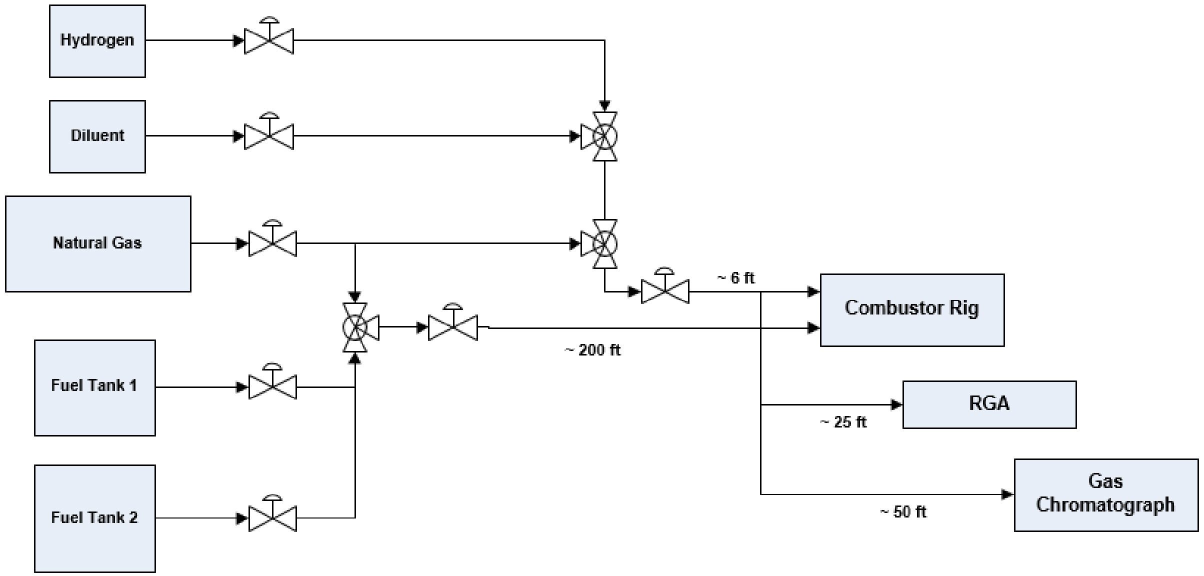
OTHER PUBLICATIONS

J. Kiefer, T Seeger, S Steuer, S Schorsch, M C Weikl, A Leipertz,

RGA Field Test at Solar Turbines
Operation with Pressurized Natural Gas Blends

- **Blends of San Diego natural gas with other gases to vary composition**
- **RGA connected near combustor fuel inlet**
- **Pressure varied, up to 185 psig inlet**
- **Limited to non-condensing mixtures at 50 C**

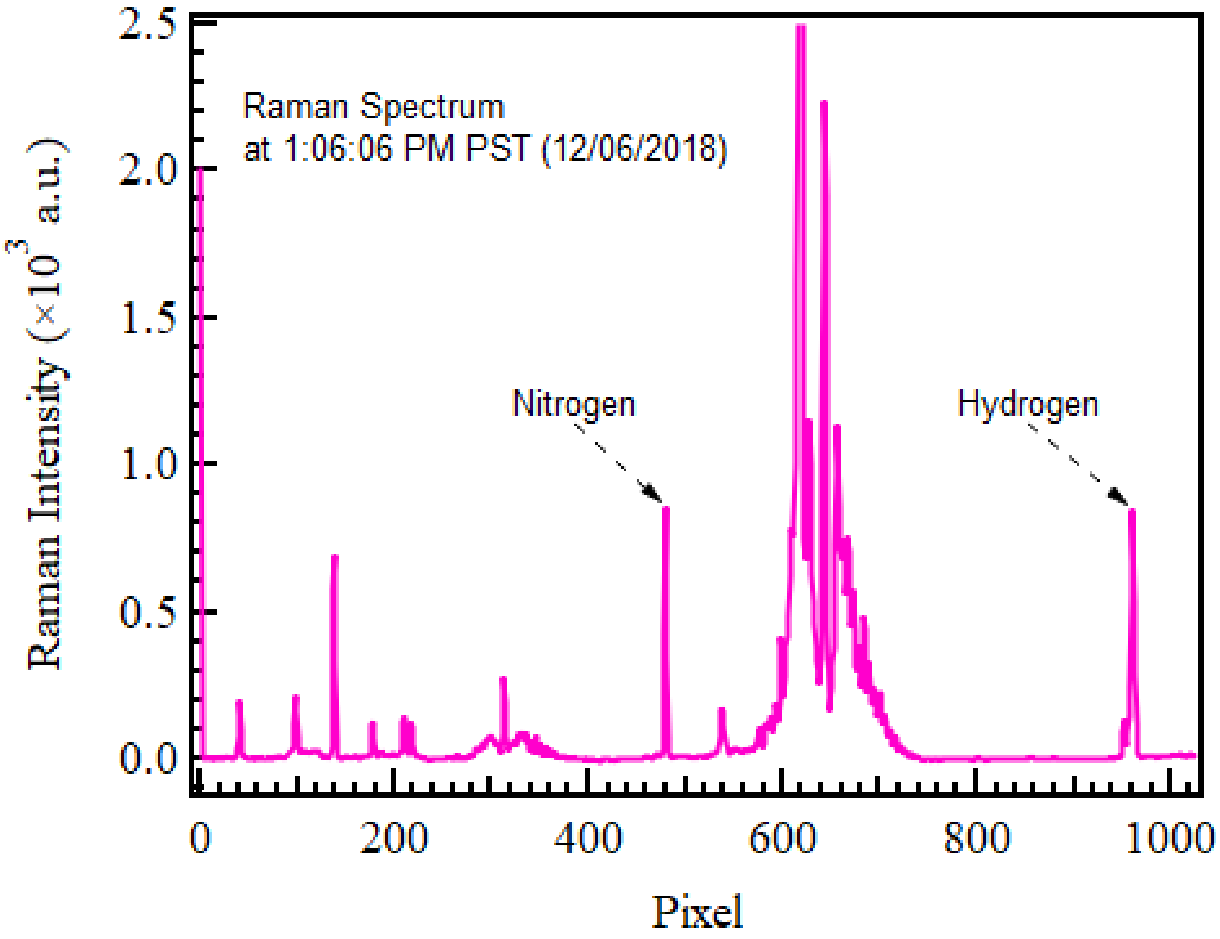
Test Configuration at Solar Turbines



Results of Steady Condition Natural Gas with 10% Hydrogen

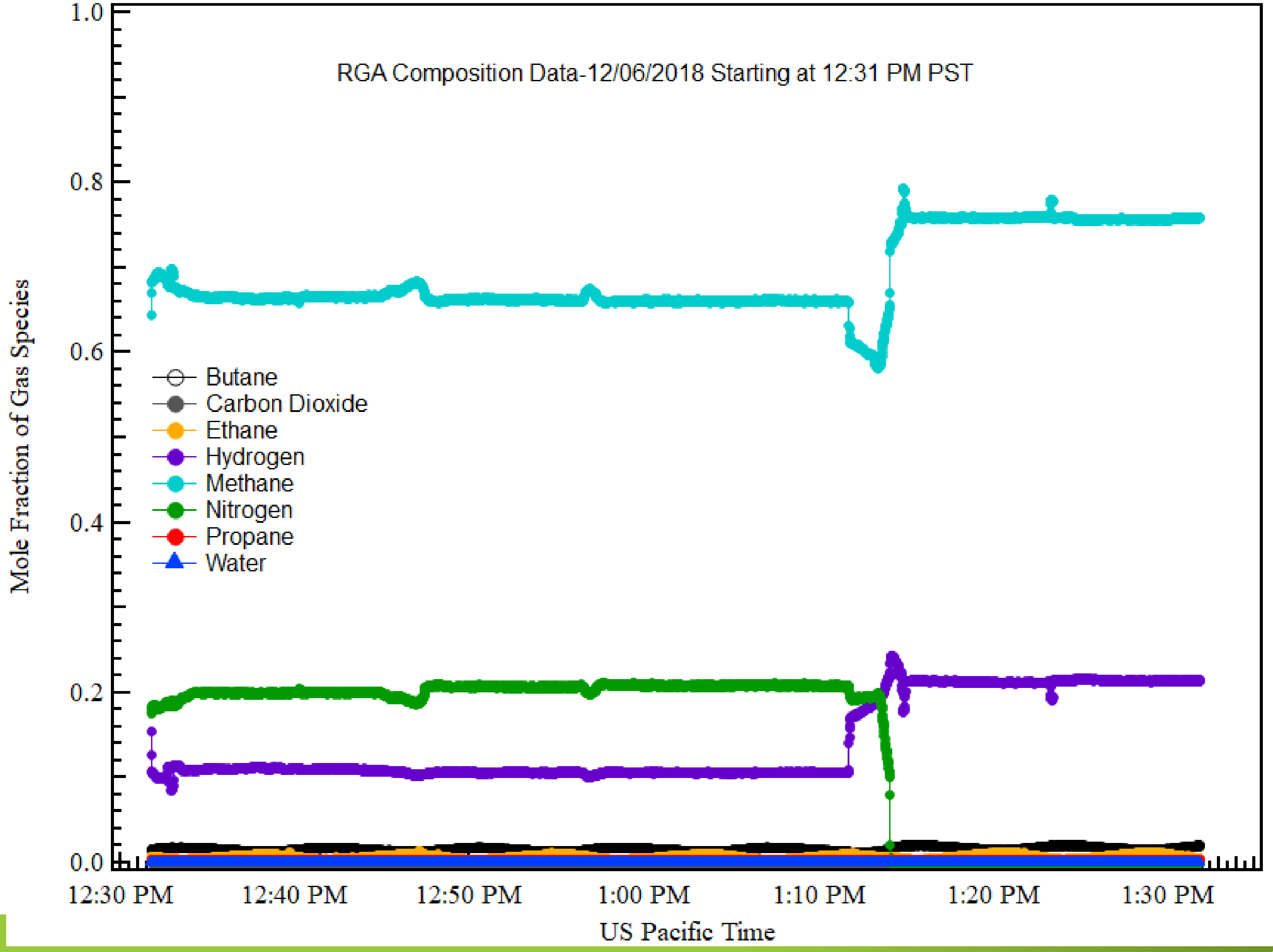
Gas species	Flow Meter Measurement (% vol)	GC (% vol)	RGA (% vol)
Natural Gas	69.207		
a. Methane (CH_4)		65.227	66.1061
a. Ethane (C_2H_6)	0	2.793	0.5522
a. Propane (C_3H_8)	0	0.293	0.2678
a. n-Butane (C_4H_{10})	0	0.045	1.6464
a. i-Butane (C_4H_{10})	-	0.028	NC
Nitrogen (N_2)	20.570	21.073	20.8547
Carbon Dioxide (CO_2)	0	0.505	0
Hydrogen (H_2)	10.223	10.015	10.5728
Wobbe (BTU/scf)		847.3	959.7

Wobbe calculated from LHV



Transient Response
Natural Gas with Hydrogen

- **RGA shows fast detection of composition changes**
- **GC samples took 6 minutes to report**



Results & Future Work

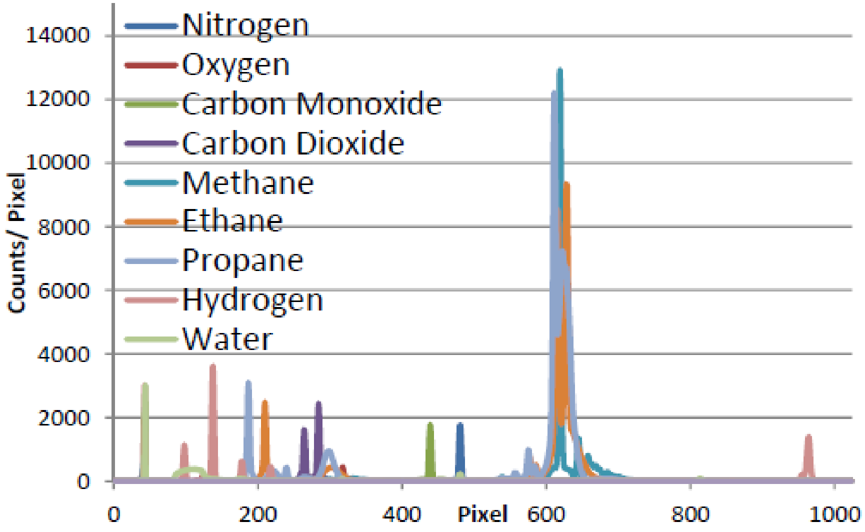
- **Potential benefits demonstrated**
  - Fast response
  - Pressurized operation
- **Challenges**
  - System durability
    - Shipping
    - Higher temperature operation
  - Improve hydrocarbon mixture quantification
    - Add isobutane to calibration
    - Adjust data processing

Special thanks to Solar Turbines staff Alejandro Camou, Gail Doore, and David Voss for work on the field test.

Fast Raman Gas Analyzer Summary

- Applications to **power generation** and **chemical process control**
- Prototype tested in pilot scale laboratory applications
- Fast - 1 second measurement time
- Species concentrations measured to 0.1%
- Optical waveguide technology boosts Raman signal more than 1000X
- No recalibration needed in normal operation
- **Seeking collaborative partners or licensees**

No commercial technology has this combination of speed, accuracy, and multi-gas capability.



US Patent 8,674,306, NETL and U. of Pittsburgh

Acknowledgements

This research was supported by the Department of Energy, Office of Fossil Energy, under the Crosscutting Research Program.

Questions?

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