Biomass Fuel Cell Systems

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Colorado School of Mines
Golden, Colorado, USA

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Colorado Fuel Cell Center

Project ID: FC076

Overview: Improve robustness of hydrocarbon- and biomass-fueled solid-oxide fuel cells and systems

- **Timeline**
  - Project start date: 10/1/2009
  - Project end date: 9/30/2012
  - Percent complete: 85%
- **Budget**
  - Total project funding:
    - DOE Share: $1,665,125
    - CSM Share: $425,018
  - Funding received in FY11: $0
  - Planned Funding for FY12: $0
- **Industrial Partners**
  - CoorsTek, Inc. (Golden, CO)
    - Tubular SOFC supplier
    - Ceramic heat exchanger / fuel reformer
- **Project Lead:**
  - Colorado School of Mines

Barriers

- **Durability**
  - Broaden SOFC operating windows under hydrocarbon / biomass fuels
- **Performance**
  - Increase efficiency through system optimization / BoP integration
  - Optimize fuel-processing strategies
    - Biogas fuels of anaerobic digesters
- **Transient operation**
  - Develop model-predictive control algorithms
- **Balance-of-Plant costs**
  - Integrate BoP components
  - Decrease BoP fabrication costs
  - Decrease BoP materials costs

Objectives / Relevance: Improve durability and performance of SOFC systems while lowering costs

- **Task 1: SOFC materials and architectures for robust operation**
  - A. Integrate barrier-layer architecture into tubular SOFCs (completed)
  - B. Develop nickel-free, perovskite-based anode supports
- **Task 2: Fuel processing of bio-derived fuels**
  - A. Develop fuel-reforming strategies for biogas (completed)
  - B. Decrease cost of fuel-processing balance-of-plant hardware
    - Integrated ceramic microchannel heat exchangers / fuel reformer
- **Task 3: Modeling and simulation**
  - A. Develop chemically reacting flow models of fuel-processing hardware
    - Create design tools for microchannel heat exchanger / reformer
    - Utilize model-predictive control to integrate system hardware
    - Improve APU dynamic response, reduce supplementary-storage need
  - B. Conduct thermal modeling of hot-zone system components (completed)
  - C. System modeling: explore tradeoffs in biogas-processing approaches
    - Use of cyrogenic oxygen on-site at waste-water treatment facilities

Task 1 Approach: Develop materials and architectures to improve SOFC durability under biomass-derived fuels

A. Barrier-layer architecture in tubular SOFC geometries (completed)

- Inert barrier layer within anode support to improve durability
  - Reduce gas-transport rates
  - Increase local steam concentration within anode-support structure
  - Promote internal reforming over carbon-deposit formation
- ~ 1-kW APU target application – tubular geometries for fast start-up
- Milestone: 50-hrs continuous operation on hydrocarbons (100%)
  - 300 hours of trouble-free operation achieved

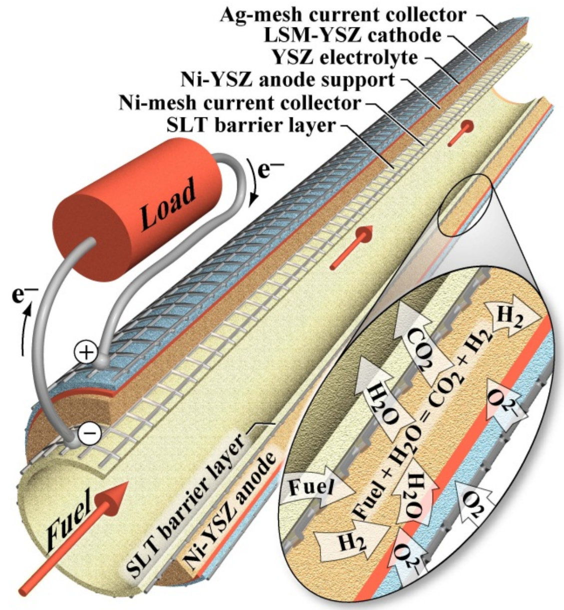
B. Develop perovskite-based, next-generation tubular anode supports

- Pros: perovskites more tolerant to sulfur, redox, and heavy hydrocarbons
  - Broaden the range of deposit-free SOFC operation
- Cons: perovskite electro-catalytic activity lower than existing solutions
  - Utilize nickel-based anode function layer to promote internal reforming
- Milestone: 50-hrs continuous operation on hydrocarbons (75%)

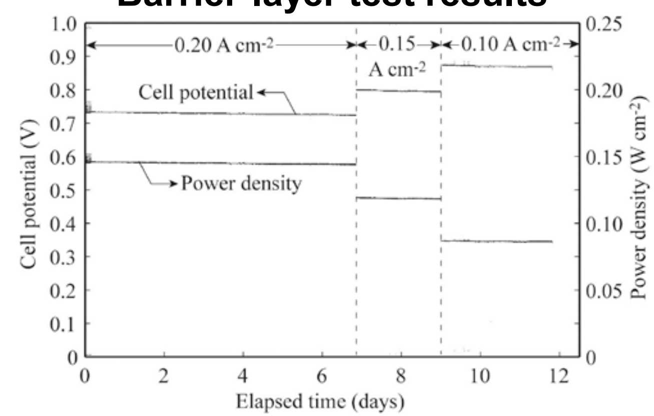
Task 1A Results: Barrier layers synthesized, integrated, and operated with CoorsTek tubular SOFCs (completed)

- **Tubular perovskite barrier layers synthesized**
  - $Sr_{0.8}La_{0.2}TiO_3$ (SLT) materials
  - ~ 40% porosity
  - ~ 15 S / cm conductivity
- **Integrated with CoorsTek SOFC**
  - Traditional Ni-YSZ anode materials
  - Low-cost "reaction-sintering" fabrication
- **> 12 days continuous operation demonstrated**
  - Biogas fuel: 65% CH_4 / 35% CO_2
  - Current density: 0.1 – 0.2 A / cm^2
  - Minimal degradation; no deposits observed
- **Extending effort to perovskite-based SOFCs**
  - SLT-based anode support
  - Ni-YSZ anode functional layer
  - Cell development ongoing

Barrier-layer architecture



Barrier-layer test results



Task 2A Approach: Develop biogas fuel processing strategies for SOFC integration (completed)

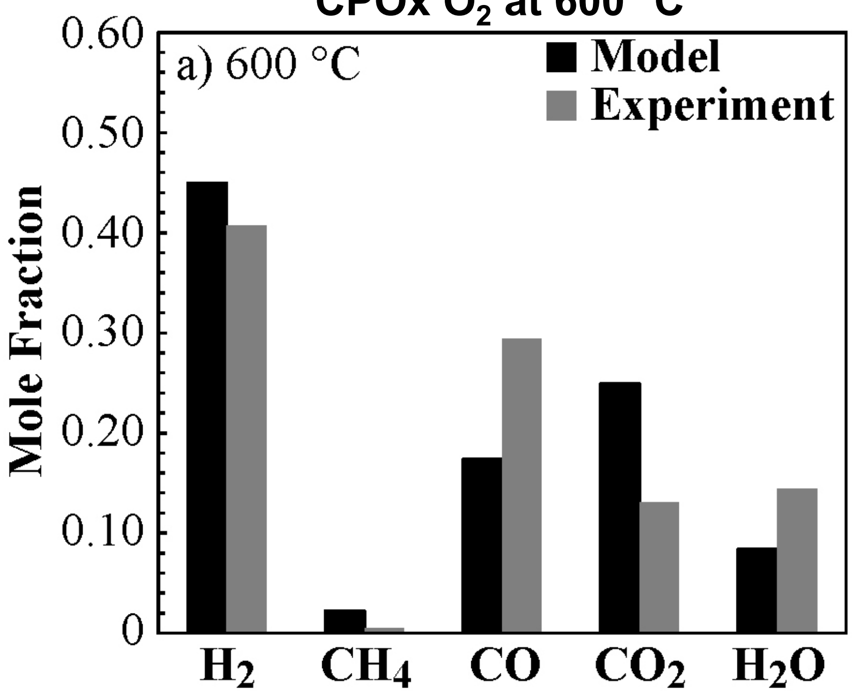
- Biogas fuels: anaerobic digesters at waste-water treatment facilities
  - Low-quality methane stream: 65% CH_4 / 35% CO_2
  - Requires clean-up of sulfur and siloxanes upstream of reformer & stack
    - Commercial clean-up technology exists (e.g. Xebec desiccant system)
  - Target MW-scale power generation
- Explore fuel-reforming options to convert biogas to syngas (H_2 + CO)
  - Catalytic partial oxidation (CPOX - air and / or O_2)
    - Simplest approach, lower capital cost, but lower system efficiency
      - Utilize cryogenic O_2 on-site at waste-water treatment facilities
  - Steam reforming
    - Endothermic, high capital cost, but improved system efficiency
- Milestone: Complete analyses of biogas external-reforming (100%)
- Biomass-derived liquid fuels: butanol (C_4H_9OH)
  - Reduced effort at direction of 2010 DOE AMR reviewers
- Integrate with ceramic microchannel reactor technology
  - Increased effort at direction of 2010 DOE AMR reviewers

Task 2A Results: Kinetic models used to guide definition of external-reforming operating windows

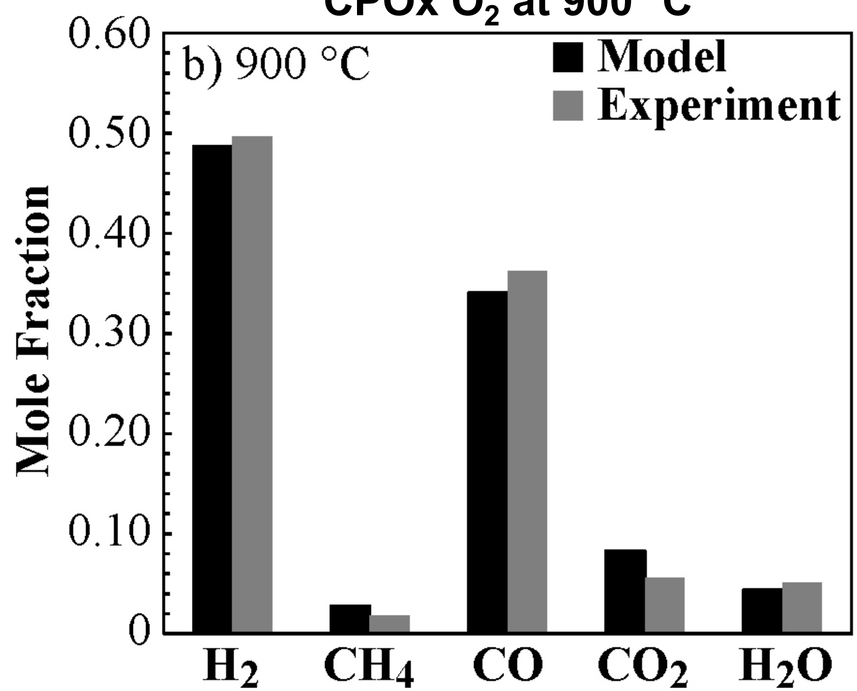
- Reacting-flow model with multi-step elementary reaction chemistry
- Exercised across numerous reforming approaches
- Validated with experiments utilizing Rh on porous Al_2O_3 foam
  - High-temperature reforming enables conversion of CO_2 to CO
  - Kinetic models generally underpredict CO_2 conversion

Biogas reformate composition

CPOx O_2 at 600 °C



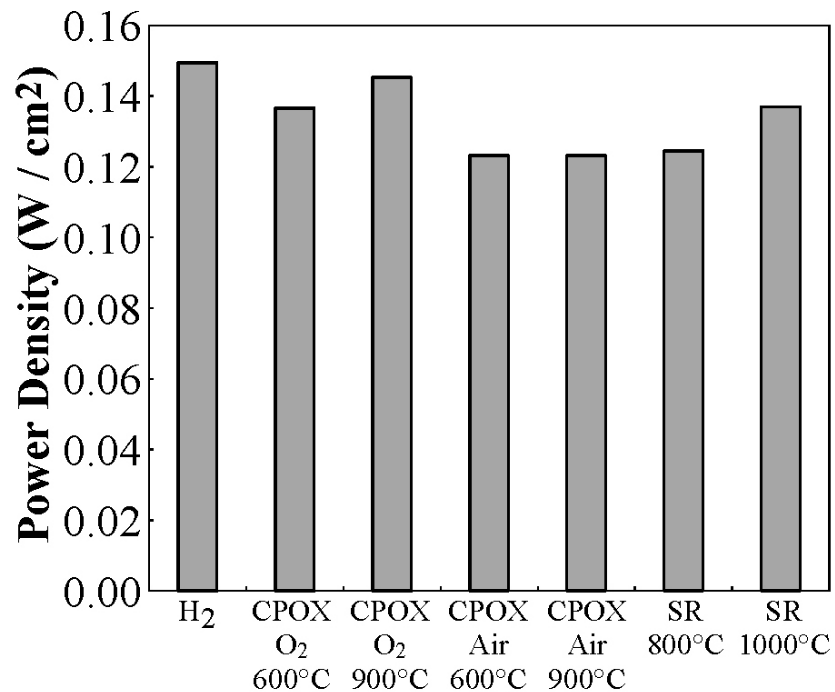
CPOx O_2 at 900 °C



Task 2A Results: SOFC electrochemical performance under reformed biogas can rival that of humidified H_2

- Reformate fed to CoorsTek SOFC
- Electrochemical performance
  - Current density at 800 °C
  - Cell potential = 0.65 V
  - Fuel utilization = 70 %
- Humidified H_2: *P”* = 0.15 W / cm²
- CPOX-O_2
  - 900 °C: *P”* = 0.145 W / cm²
  - 600 °C: *P”* = 0.137 W / cm²
- Steam reforming
  - 1000 °C: *P”* = 0.137 W / cm²
  - 600 °C: *P”* = 0.125 W / cm²
- System performance under study (Task 3C)

SOFC performance under biogas reformate, baselined to H_2 fuel



Task 2B Approach: Develop low-cost ceramic micro-channel reactive heat exchangers for fuel reforming

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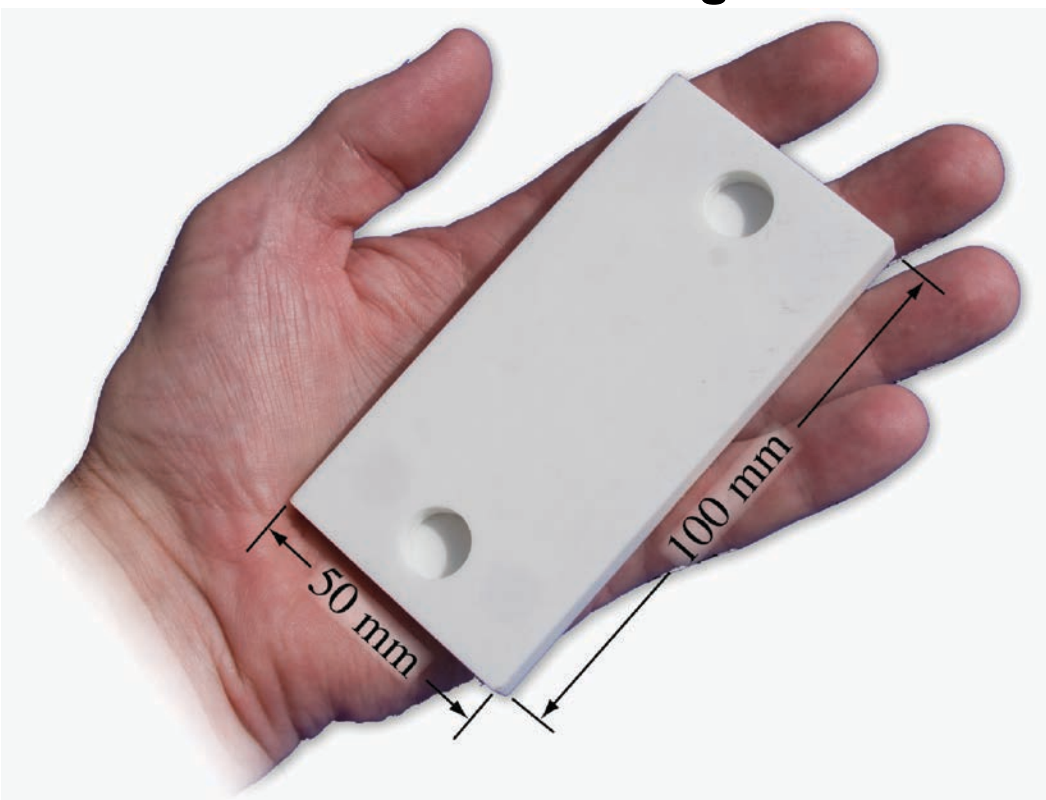
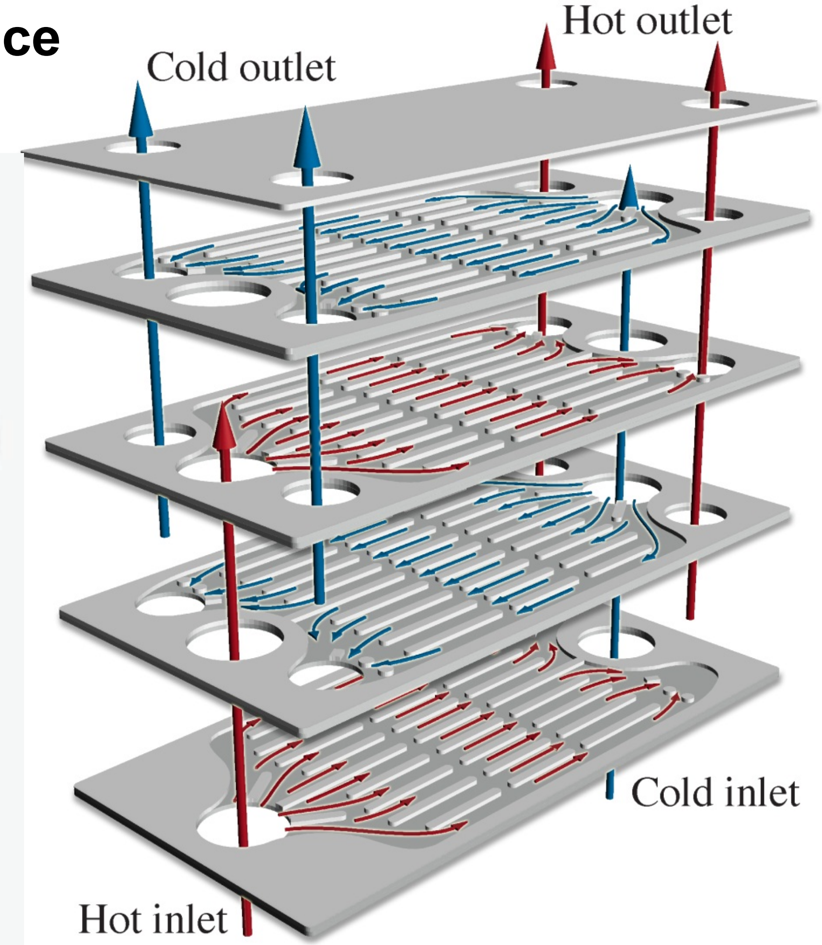
- Low-cost alumina materials
- Co-sintered layers: Single-body device
- Low-cost manufacturing





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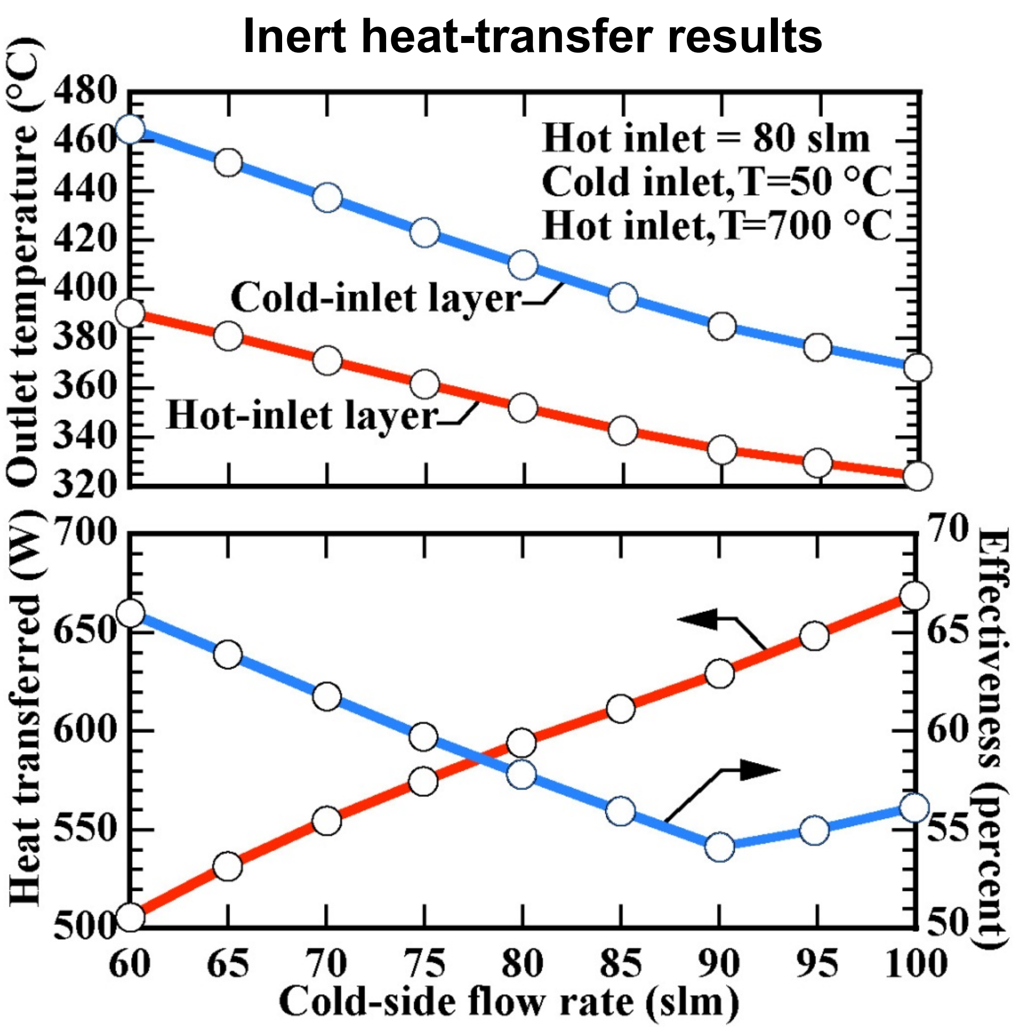
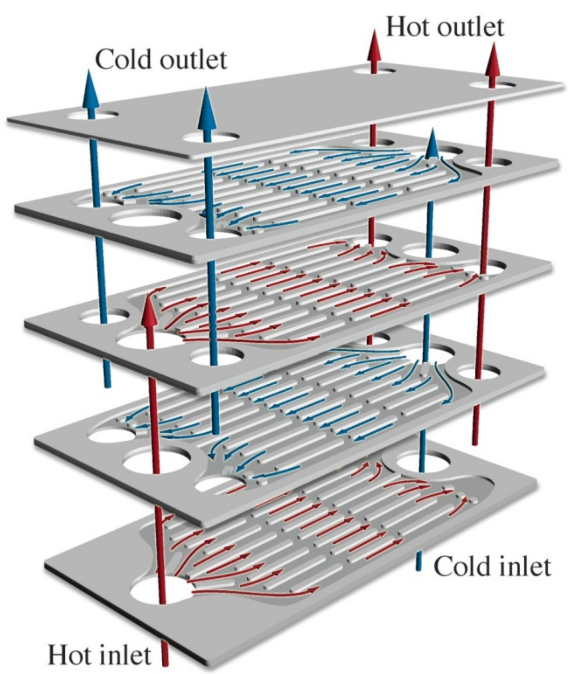
Generation-5 design

Task 2B Result: Performance of ceramic microchannel heat exchanger measured over a broad range



- Large temperature gradient
  - 700 °C hot inlet
  - 50 °C cold inlet
- Effectiveness near 70%
- ~ 660 W transferred
  - Over 1 kW possible



Task 2B Result: Rhodium catalyst addition enables methane steam reforming with high conversion

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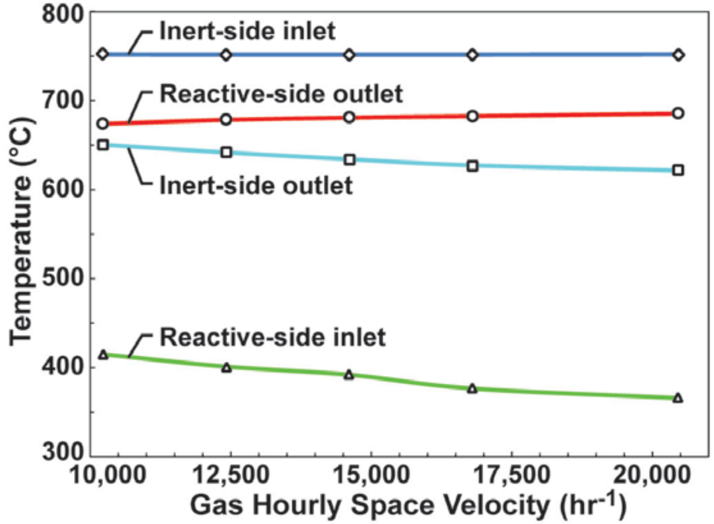
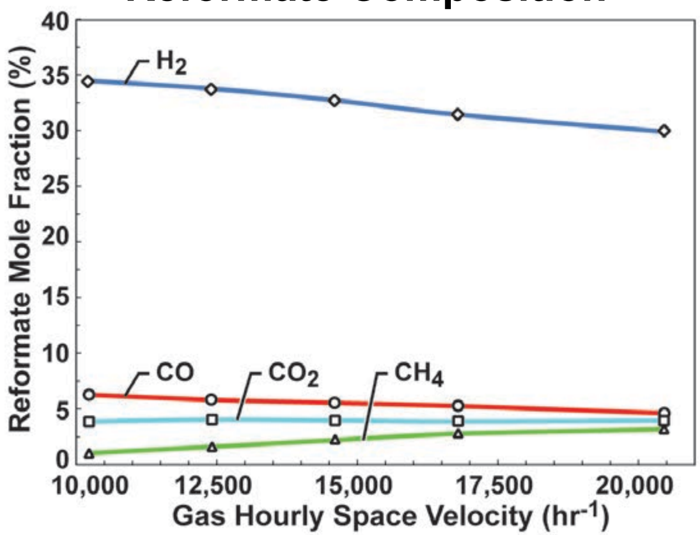
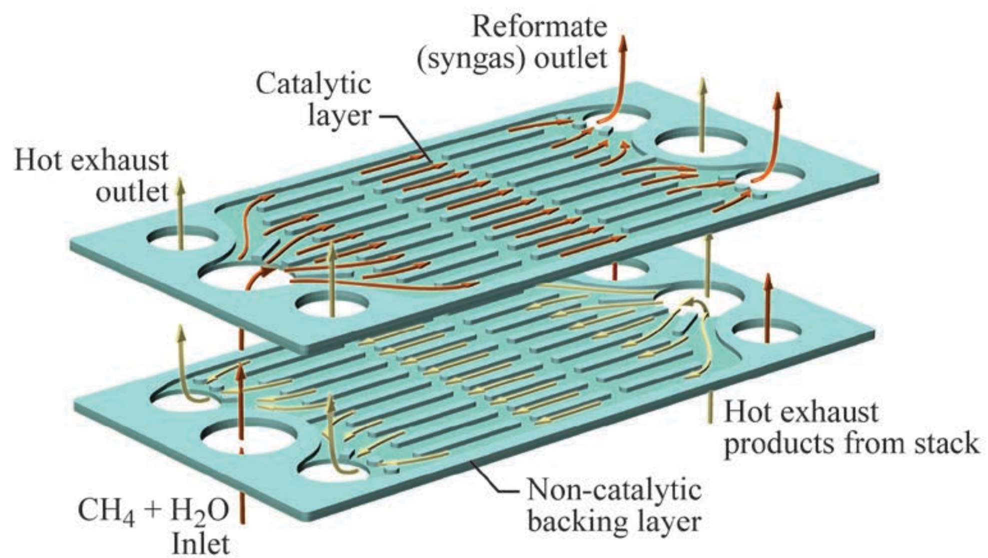
Temperatures – Inlet and Outlet



Reformate Composition



- Rh catalyst on Ce-Al_2O_3 support
  - Washcoated onto reactive layers
- CH_4 conversion > 90%
- H_2 selectivity up to 70%
- 750 °C inert hot-inlet temperature



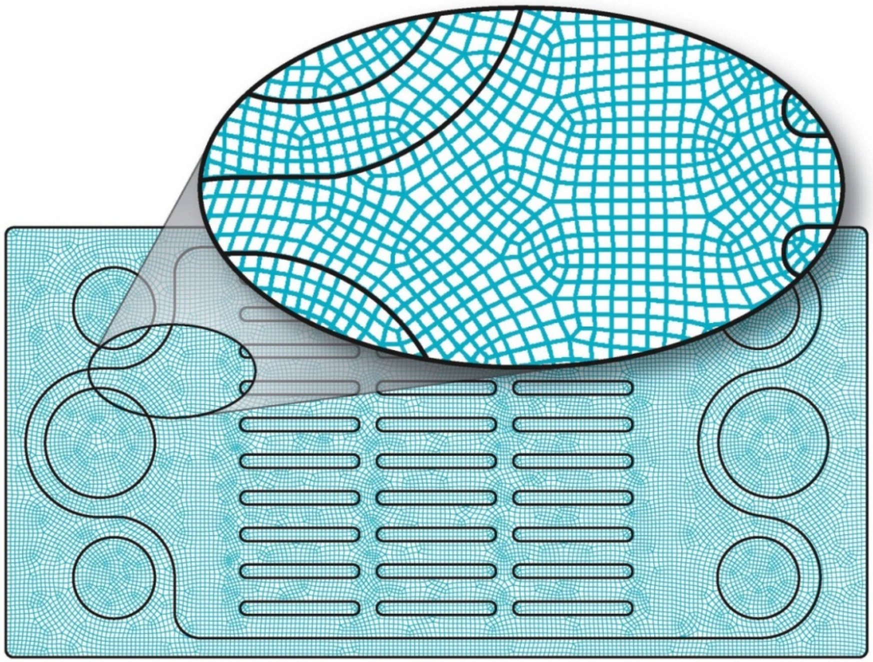
Task 3 Approach: Provide modeling support for Tasks 1 and 2 using CFD and chemically reacting-flow tools

- **Task 3A: Design tools for ceramic microchannel reactive heat exch.**
  - ANSYS-FLUENT Computational Fluid Dynamics software
    - Flow through complex heat-exchanger channel geometries
  - CANTERA chemically reacting flow software
    - Open-source code under development at Sandia National Labs
    - Elementary chemical kinetics for fuel-reforming simulations
  - Two models integrated through FLUENT "User-Defined Functions" feature
    - Enables high-fidelity chemically reacting flow with high-fidelity CFD
- **Task 3B: Model-predictive control for dynamic-load following**
  - Map high-fidelity CANTERA model results to rapid low-order linear models
  - Apply to fuel-reformer hardware for dynamic control of pump and blower
- **Task 3C: System-level modeling tools to advance thermal integration**
  - Map ANSYS-FLUENT results to lower-order hot-zone thermal models
  - Utilize system tools to estimate benefits of thermal-integration strategies
    - Examine biogas fuel processing options

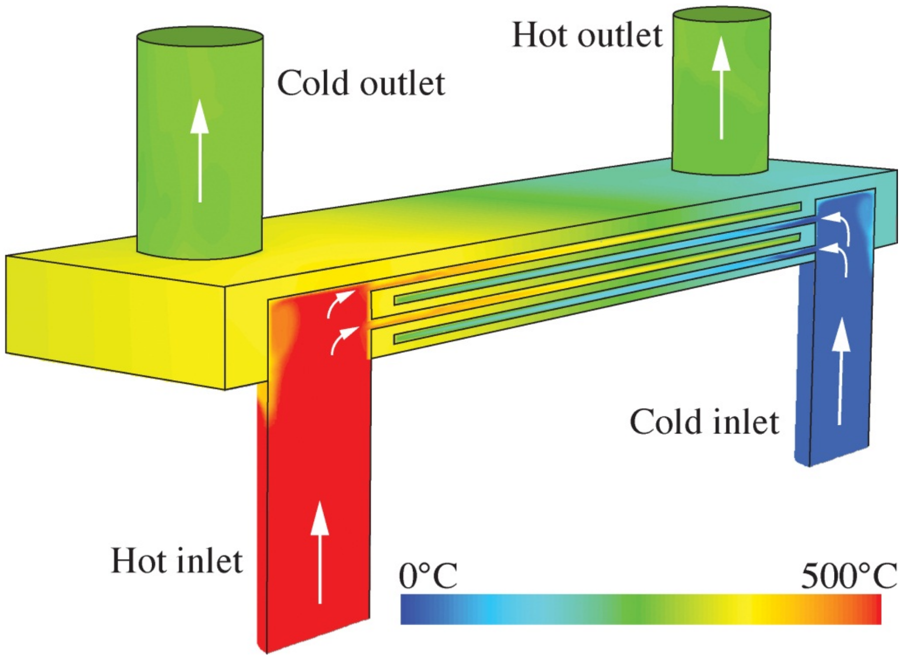
Task 3A Approach: CFD and chemically reacting-flow models integrated to provide HX-design guidance

- ANSYS-FLUENT software utilized for computational fluid dynamics
- CANTERA software developed for chemically reacting flow simulation
- Two models integrated in FLUENT "User-Defined Functions" feature
- Tight collaboration with developers at ANSYS / FLUENT

Numerical mesh used in FLUENT simulations



Characteristic ANSYS/FLUENT solution Thermal-field, non-reacting flow



Task 3A Result: CFD modeling aids in optimizing backing-side conditions for reactive testing

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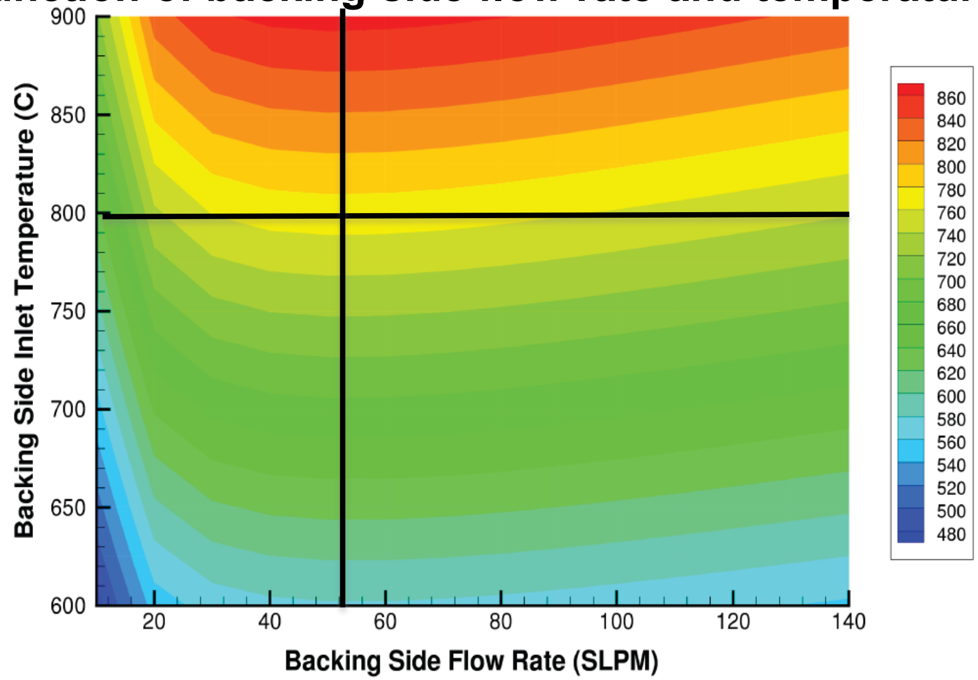
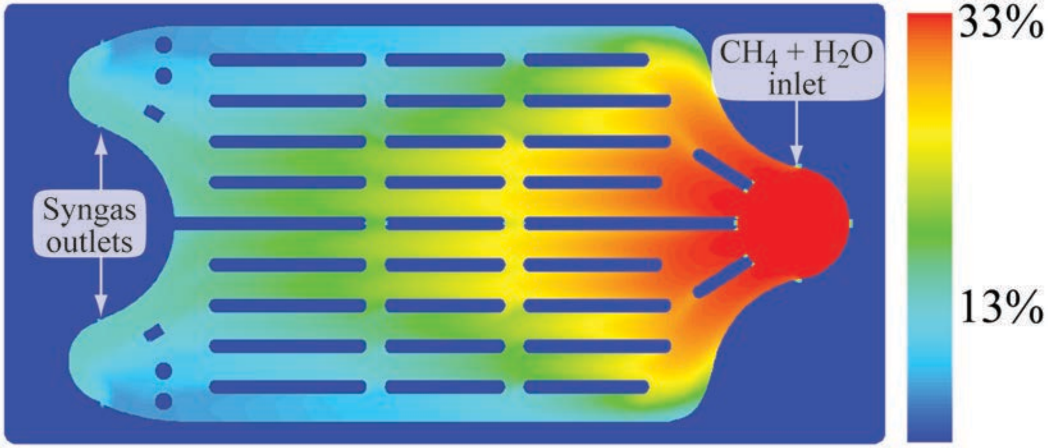
- 182 simulations
- Low backing-side flow
  - Limited thermal energy input
  - Low reactive-side temp
- High backing-side flow
  - High localized velocities
  - Poor flow distribution
- Optimal backing-side flow
  - 45 SLPM, 800 °C
  - Reactive-side conditions:
    - 750 °C reactive-surface
    - Good SMR conditions
    - GHSV ~ 10 hr^{-1}

Average reactive-side surface temperature as a function of backing-side flow rate and temperature

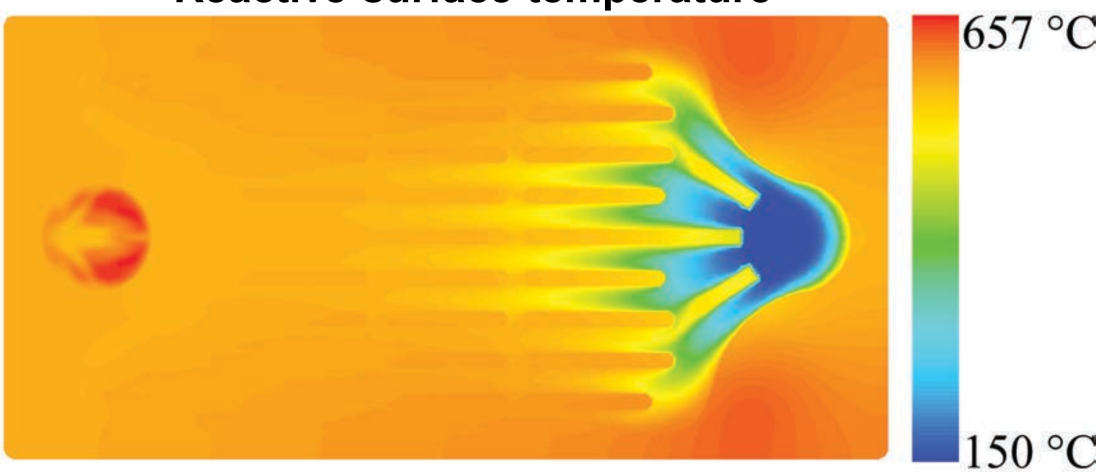


Task 3A Result: Chemically reacting flow models guide operating setpoints for high CH_4 conversion

Methane mole fraction



Reactive-surface temperature



- High-fidelity CFD
- Elementary catalytic chemistry

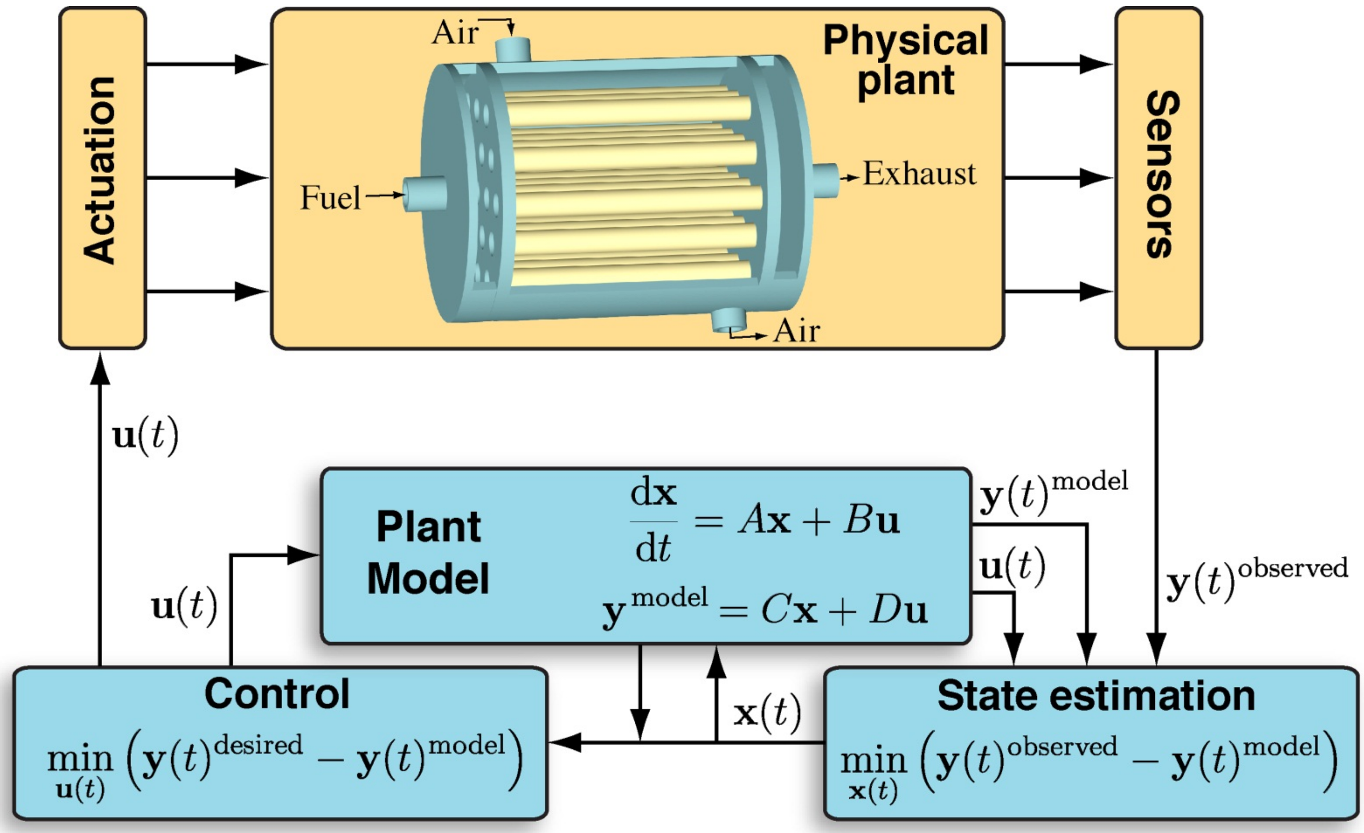
Kinetic reaction mechanism for heterogeneous reforming of CH_4 over Rh catalyst[1]

$$H_2 + Ni(s) + Ni(s) \rightarrow H(s) + H(s)$$
$$H(s) + H(s) \rightarrow Ni(s) + Ni(s) + H_2$$
$$O_2 + Ni(s) + Ni(s) \rightarrow O(s) + O(s)$$
$$O(s) + O(s) \rightarrow Ni(s) + Ni(s) + O_2$$
$$CH_4 + Ni(s) \rightarrow CH_4(s)$$
$$CH_4(s) \rightarrow Ni(s) + CH_4$$
$$H_2O + Ni(s) \rightarrow H_2O(s)$$
$$H_2O(s) \rightarrow Ni(s) + H_2O$$
$$CO_2 + Ni(s) \rightarrow CO_2(s)$$
$$CO_2(s) \rightarrow Ni(s) + CO_2$$
$$CO + Ni(s) \rightarrow CO(s)$$
$$CO(s) \rightarrow Ni(s) + CO$$

[1]N.E. Mcguire *et al.*, *Appl. Cat. A* (2011)

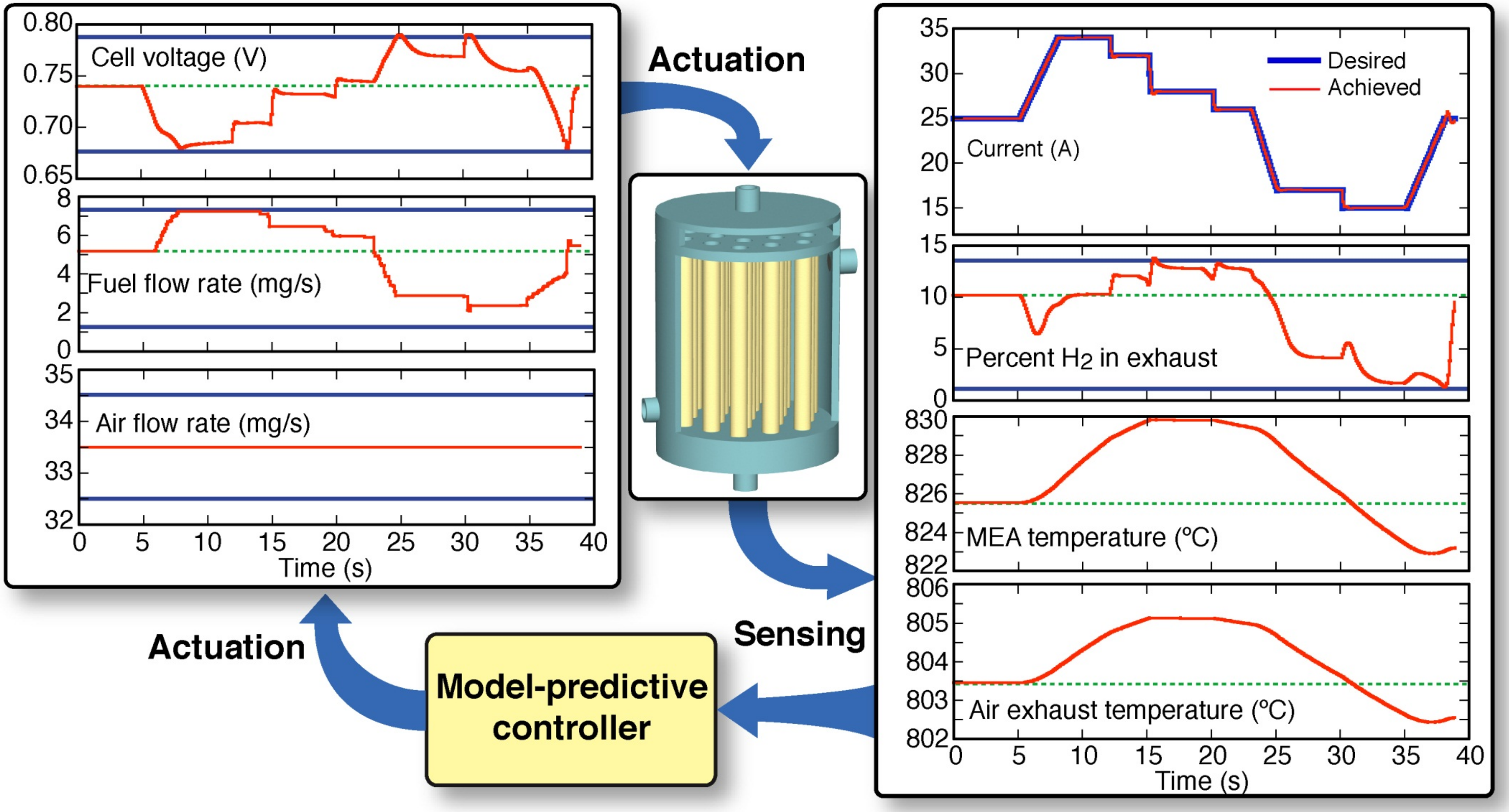
Task 3B Approach: Extend high-fidelity chemically reacting flow models to model-predictive control

- Map high-fidelity CANTERA model results to rapid linear models
- The model-predictive controller (MPC) enables real-time optimization
  - Controller satisfies constraints on actuation and observables
  - Multiple-input--multiple output (MIMO) enables sensor fusion



Task 3B Result: Controller makes a complex set of decisions to meet load demand, satisfy constraints

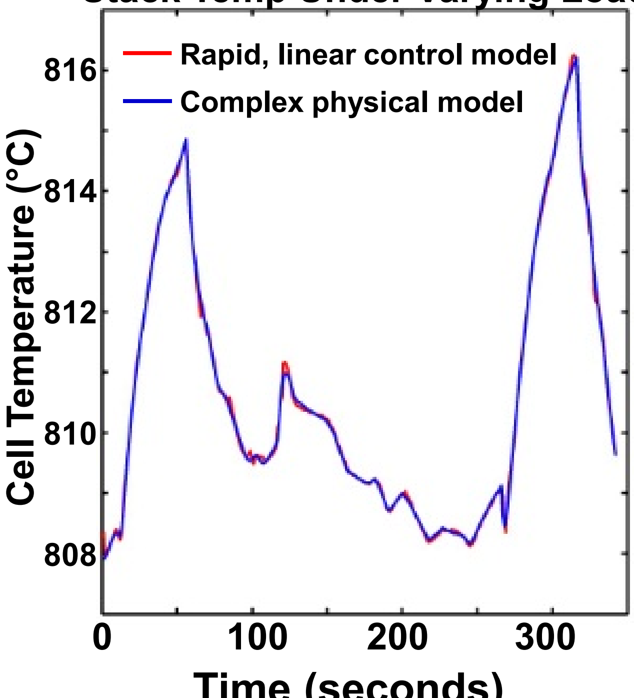
Dynamic response to varying load



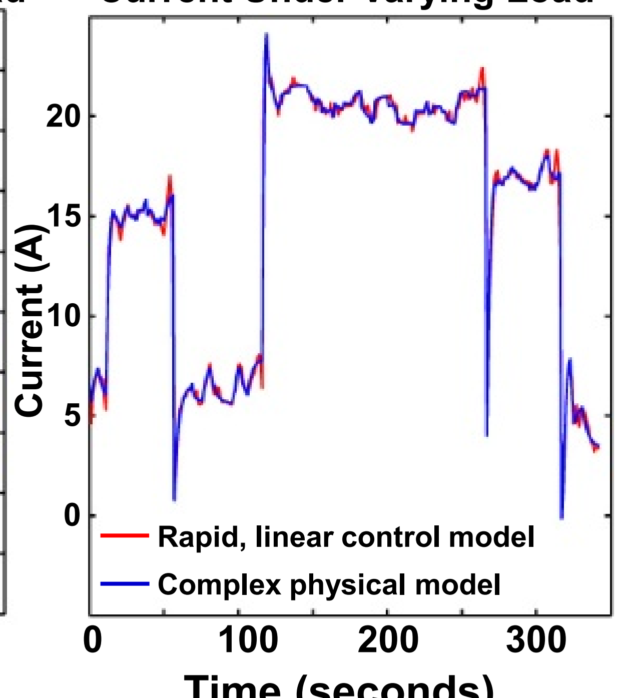
Task 3B Result: Controller makes a complex set of decisions to meet load demand, satisfy constraints

- **Model components**
  - Tubular stack
  - Cathode-air blower
  - CPOX-air blower
  - Tail-gas burner
  - Recuperator
- **Biogas fuel (65% CH_4, 35% CO_2)**
- **Controller performance**
  - Wide operating range (5 – 20 Amps)
  - Problematic operating conditions identified
    - Coke formation in CPOX reactor
    - CPOX-air blower response is too slow
  - Limitations addressed with battery buffer
- **Define load-sharing requirements**

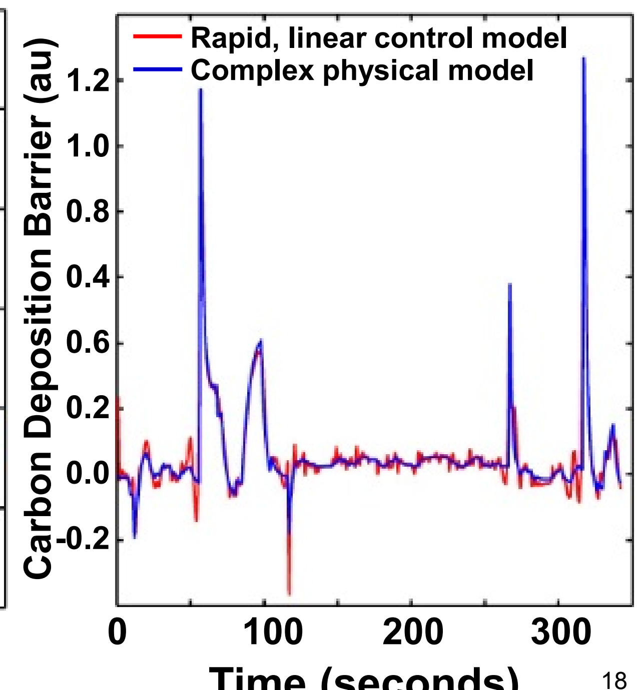
Stack Temp Under Varying Load



Current Under Varying Load



Potential for Solid Carbon



Task 3C Approach: System analysis of Metro Wastewater Reclamation Facility (Denver, CO, USA)

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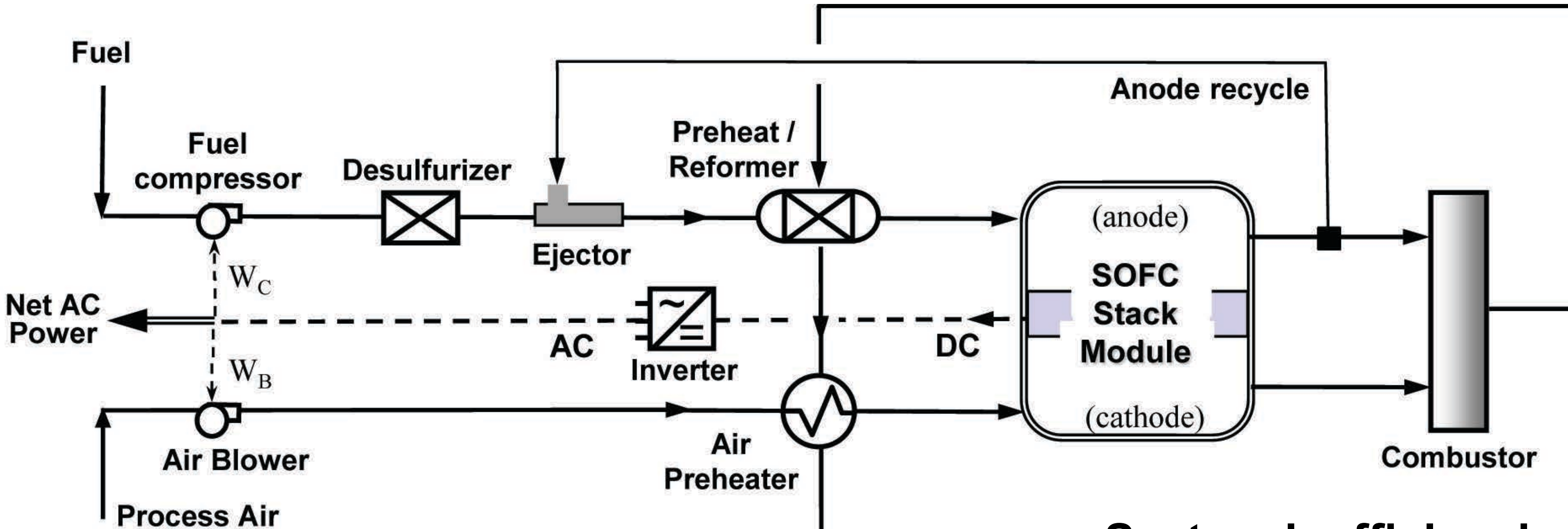
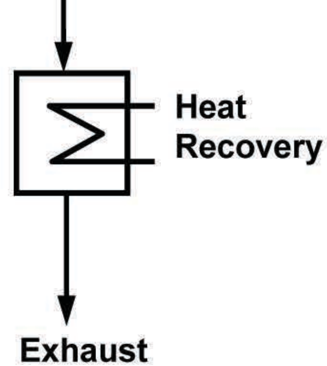
Metro Wastewater Reclamation Facility

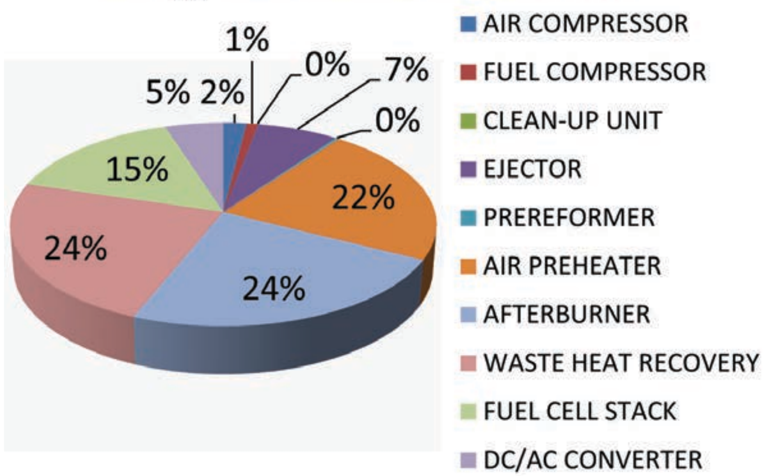
- **Wastewater Treatment Facility**
  - One of nation's largest
  - 140 million gallons per day
  - 15.5 MW biogas generated
  - Feeds two combustion turbines
    - Nominal 6 MW electrical
    - Average only 4.5 MW_e
    - Fluctuating biogas flow
- **Integrate SOFC system**
  - ASPEN model components
    - SOFC stack
    - Biogas fuel processing
      - Siloxane removal
      - Fuel pre-reforming (~ 20%)
    - Tail-gas burner
    - Recuperator

Task 3C Result:
Exergy analyses identify system inefficiencies





Exergy destruction distribution



- System inefficiencies
  - Recuperator
  - Tailgas combustor
  - Air preheater
  - Desulfurizer
- Future work
  - Operational optimization

Industrial collaborations: CoorsTek Inc., Golden, CO

- Largest ceramics company in the United States
  - Recently acquired Ceramatec and St. Gobain
- Supplier of SOFCs and materials for use across multiple tasks
  - Task 1: Provider of baseline Ni-YSZ materials (task completed)
    - CSM develops barrier layers to extend range of SOFC operation
    - CSM compares Ni-YSZ to next-generation perovskite anodes
  - Task 2A: Supplier of tubular SOFCs (task completed)
    - CSM evaluates cell performance under bio-fuel reformate streams
  - Task 2B: Fabricate ceramic microchannel heat exchangers
    - CSM adds catalyst to reactive side of microchannel heat exchanger
    - CSM develops test protocol, evaluates performance of reactive HX
    - CSM develops computational modeling to provide design guidance

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Future work

- Task 1B: Next-generation SOFC materials and architectures
  - Demonstrate operation of tubular perovskite-based solid-oxide fuel cell
  - Establish deposit-free operating windows under biogas fuel
- Task 2B: Reforming of biomass-derived fuels
  - Utilize ceramic microchannel reactor for biogas reforming
  - Modify microchannel design for improved conversion and selectivity
- Task 3: Modeling and simulation
  - Task 3A: Ceramic micro-channel reactive heat exchanger
    - Add metallic gas manifolding to FLUENT simulations
      - Improve model-to-experiment agreement
    - Explore alternate reactor designs and channel layouts
  - Task 3C: Model-predictive control of fuel-reforming BoP hardware
    - Develop control algorithms; validate using experimental facility
  - Task 3D: System-level modeling of Metro Wastewater Reclamation Facility
    - Explore system operation to optimize performance on biogas

Summary: CSM program is focused on improving system robustness, decreasing BoP costs

- **Relevance**
  - Improve durability: advanced materials, improved control strategies
  - Decrease costs: Develop low-cost integrated reactive heat exchangers
- **Approach**
  - Create next-generation SOFC materials and architectures
  - Utilize microchannel-reactor technology for tight thermal integration
- **Results**
  - Demonstrated extended operation of first tubular barrier-layer SOFC
  - Explored unconventional biogas fuel-reforming strategies
  - Developed ceramic microchannel reactors for methane steam reforming
  - Utilized modeling tools for optimizing system operation
- **Future work**
  - Establish SOFC operation using perovskite anode-support materials
  - Extend microchannel-reactor technology to biogas fuel reforming
  - Explore system operation to optimize performance on biogas