V.K.3 Biomass Fuel Cell Systems*

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Fiscal Year (FY) 2012 Objectives

- Utilize ceramic microchannel reactor technology for reforming of natural gas and biogas fuels for subsequent electrochemical oxidation within a solid-oxide fuel cell (SOFC).
- Employ system modeling to optimize SOFC system configurations for biogas systems.
- Extend model-predictive control strategies to integrate system hardware for improved load following and dynamic response in biogas-fueled SOFC systems.

Technical Barriers

- Durability: Broaden SOFC operating windows under hydrocarbon and bio-derived fuel streams.
- Balance-of-plant costs: Integrate fuel reforming and heat recuperation hardware into a single low-cost ceramic micro-channel reactive heat exchanger.
- Performance: Increase efficiency and decrease costs through system optimization and balance-of-plant component development and integration.
- Transient operation: Develop model-predictive control algorithms for use in dynamic control.

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability

(C) Performance

Technical Targets

In this project, we conduct a range of studies to improve the durability, efficiency, and transient operation of SOFC systems. Fuel streams for these systems include anaerobic digester-derived biogas. Insights gained from these studies will be applied toward the design and synthesis of SOFC materials and systems to meet the DOE 2015 technical target for durability (40,000 hours), start-up time (30 minutes), and degradation with cycling (0.5%/1,000 h). Targets are taken from the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan, Table 3.4.5 Technical Targets: 1–10 kWe Residential Combined Heat and Power and Distributed Generation Fuel Cell Systems Operating on Natural Gas.

FY 2012 Accomplishments

- Demonstrated steam-methane reforming in ceramic microchannel reactor with greater than 90% conversion and 70% hydrogen selectivity at 10,000 hr^{-1} space velocity.
- Utilized state-of-the-art hybrid computational fluid dynamics (FLUENT)/chemical kinetics (CHEMKIN) models of steam-methane reforming (SMR) in ceramic microchannel reactor.
- Utilized system-level models to understand inefficiencies in MW-scale SOFC systems for use in wastewater treatment facilities.
- Developed model-predictive controller for dynamic load following in a SOFC system.

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Introduction

The objective of this project is to advance the current state of technology of SOFC systems to improve performance when operating on biomass-derived fuel streams. The target fuel stream is "biogas" (~65% CH_4/35% CO_2) generated by the anaerobic digesters that are widely used for treatment of sludge in municipal wastewater treatment facilities. In this project, we are developing new SOFC materials and architectures to improve the robustness of systems operating under biogas. Additionally, modeling and experimentation is being conducted to examine performance tradeoffs across numerous fuel-processing strategies for this fuel. Fuel-reforming processes are being integrated with exhaust-gas recuperation processes through development of a single low-cost ceramic microchannel reactive heat exchanger, created in collaboration with industrial partner CoorsTek, Inc. System-level models are being used to predict SOFC system efficiencies under biogas fuels utilizing the fuel-reforming microchannel-reactor integration strategies under development. Model-predictive control strategies are being developed and applied to improving the dynamic response of the biogas-fueled system, with particular focus placed on reforming components.

Approach

The Colorado School of Mines has assembled a strong and diverse team of scientists and researchers with broad skill sets applicable to fuel cell development. Coordinated through the Colorado Fuel Cell Center, this team examines both the fundamental underpinnings and the key technical problems facing SOFC operation under biomass-derived fuel streams. We develop new SOFC materials and architectures to address the technical challenges and operating windows associated with SOFC operation on biomass-derived fuels. Through development of low-cost ceramic microchannel reactive heat exchangers with industrial partner CoorsTek, Inc., we create system-integration strategies to combine balance-of-plant processes into single hardware units, reducing system complexity and decreasing cost. A range of computational models are developed to examine the physical processes underway during SOFC and fuel-reformer operation. Model-predictive control strategies are created and applied to fuel-reforming hardware in an effort to improve the dynamic response of SOFC systems.

Results

Ceramic Microchannel Reactors for Biogas Fuel Processing

Ceramic microchannel reactors are being developed to convert biogas into syngas for subsequent electrochemical oxidation within SOFCs. A schematic and photograph of this reactor is shown in Figure 1. The reactor is fabricated by industrial partner CoorsTek, Inc. using low-cost ceramic materials (Al_2O_3) that are joined in a single high-temperature sintering process. After sintering, rhodium catalysts are wash-coated over ceria-alumina catalyst supports within the microchannels; a scanning electron micrograph of the catalyst support is shown in the inset of Figure 1. In the exploded image, hot inlet gases generated by a tail-gas combustor are fed to the inert layers of the reactor and used to drive endothermic steam reforming reactions on the catalytically active side of the reactor. These ceramic microchannel reactors offer great cost and performance advantages over

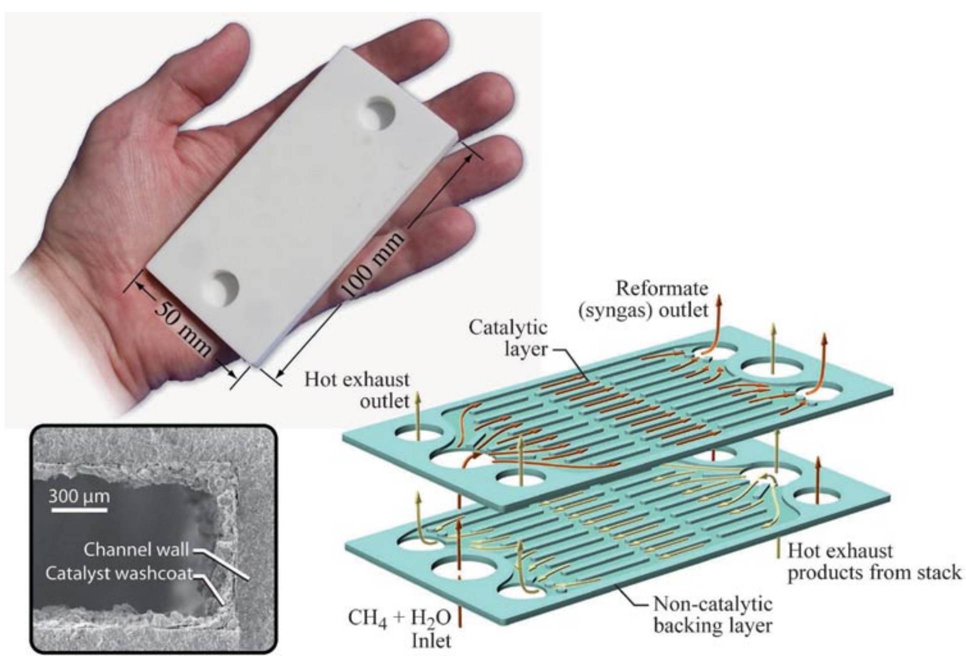

FIGURE 1. Photograph and exploded view of ceramic microchannel reactor, including inert and reactive gas streams. Inset shows high-resolution electron micrograph of ceria-alumina catalyst support wash-coated onto walls of microchannels.

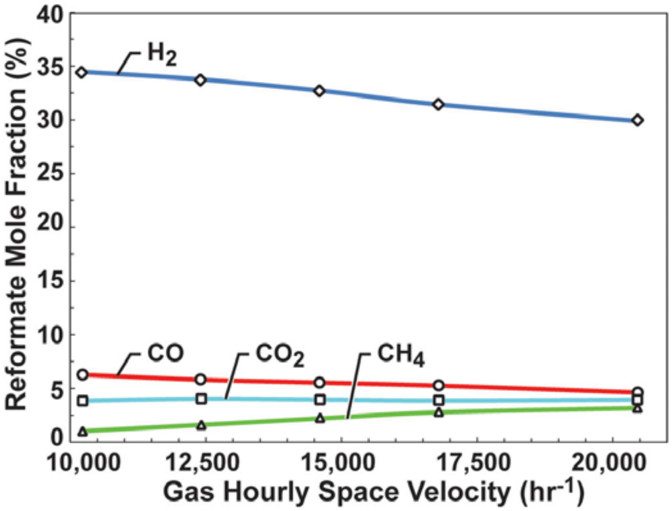

FIGURE 2. Reformate composition as a function of GHSV (reactant flow rate) for steam-methane reforming within the ceramic microchannel reactor.

conventional shell-and-tube reactors through improved heat transfer and thermal regulation of reforming processes.

During the past FY, methane steam reforming was demonstrated within this microchannel reactor over a range of operating conditions. Results are shown in Figure 2; reformate composition is shown as a function of reactive inlet gas hourly space velocity (GHSV, flow rate between 1 and 4 slpm). The inert layers are fed with nitrogen at a constant flow rate of 40 slpm and inlet temperature of 750°C. High methane conversion and reasonable hydrogen selectivity is observed at GHSV of ~10,000 hr^{-1}. Excellent methane conversion is observed at GHSV of <10,000, with some CH_4 slip observed at higher GHSVs. Hydrogen formation is also quite high, but drops off as more methane slips through unreacted. Carbon dioxide formation is higher than desirable, possibly due to the relatively low reforming temperatures used in this series of experiments. These steam-reforming results are an important milestone for the microchannel-reactor efforts. Reactor design is currently being modified to improve performance through the application of Fluent computational fluid dynamics software.

SOFC System Modeling under Biogas Fuels

The potential of SOFC systems for enhancing the prospects of biogas utilization via co-production (or tri-generation) of heat, fuel, and power is being examined using system-level computational models. This effort involves a techno-economic performance evaluation of 'mature' SOFC combined-heat-and-power (CHP) systems fueled with biogas generated in small- (300 kW), medium- (1.5 MW), and large-scale (>5 MW) wastewater treatment plants. Representative biogas feedstock is established from compositional data for a large wastewater reclamation facility in Denver, Colorado. A steady-state SOFC-CHP system model is developed with Aspen Plus® for the integration with small (640 kW-lower heating value, LHV), medium (3 MW-LHV) and large (12 MW-LHV) biogas sources.

The proposed SOFC system concept includes anode-gas recirculation equipped with a biogas-pretreatment system and a waste-heat recovery unit. The system performance is evaluated at near atmospheric pressure with a 725°C nominal stack operating temperature and system fuel utilization of 80%. The SOFC-CHP system employs 80% internal reforming at a steam-to-carbon (S/C) ratio of 1.2.

During the past FY, modeling efforts have been used to show that the system concept is estimated to offer a net electrical efficiency of 51.6% LHV and a net CHP efficiency of 87.5% LHV. A characteristic result is shown in Figure 3, where the exergy destruction (inefficiency creation) is shown for each of the system components. The afterburner, waste-heat recovery unit, and air preheater present significant sources of inefficiency.

Additionally, the effect of operating parameters on system efficiency has been investigated with a parametric study. The economic performance is evaluated using a levelized cost of electricity (LCOE) and a levelized cost of heat. The results are compared with the LCOE from reciprocating internal-combustion engines, microturbines, gas turbines, and molten carbonate fuel cell technologies and grid electricity prices. The influence of economic parameters including biogas feedstock cost, system first cost, and stack operating parameters on the LCOE was also investigated.

The proposed SOFC-based cogeneration system concept for waste water treatment facilities offer a net electrical efficiency approaching 52% (LHV) even for small-scale facility applications. This efficiency is significantly higher compared with efficiencies offered by competing cogeneration technologies (with the exception of molten

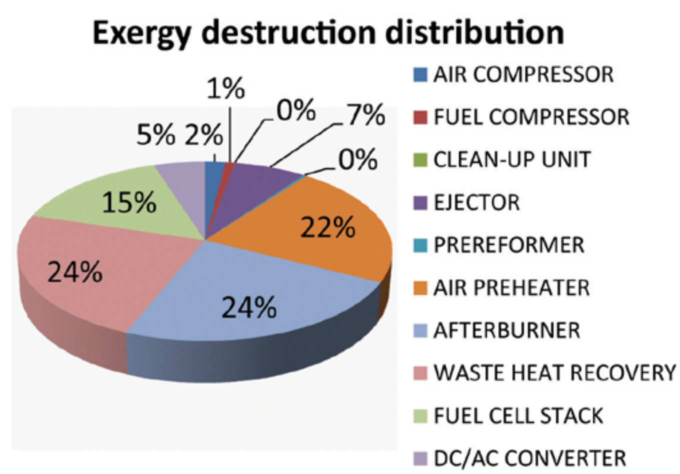

FIGURE 3. System-model predictions of exergy destruction and inefficiency creation from the multiple components making up the biogas SOFC system.

carbonate fuel cells). Moreover, the net electrical efficiency of the proposed SOFC system concept could be further increased by a few percentage points by optimizing the operating conditions (i.e. decreasing the steam-to-carbon ratio). The economic analysis based on the cost of electricity indicates that only medium- and large-scale SOFC systems could successfully compete against the grid electricity price without incentives. This is caused by a high unit capital cost of small SOFC units and the cost of the required biogas pretreatment system.

Model-Predictive Control of Biogas-Fueled SOFC System

The aim of this work is to develop a model-based controller that is capable of achieving variable current output while ensuring all operating constraints of the system are met, such as the required stack and reformer temperatures, fuel utilization, etc. To this end, a high-fidelity, non-linear model of an SOFC system was designed, consisting of two blowers, a fuel reformer, the SOFC stack, tail-gas burner, and a heat exchanger. This non-linear model is too complex and slow for model-predictive control. For controller development, a rapid, linear model is identified that accurately captures the dynamics found in the non-linear model. The comparative simplicity of the linear model enables rapid response to variations in electrical load, and is used to implement model-predictive control.

The low-order linear model takes the form of a four-input, five-output state-space model. Inputs are taken as the power provided to the stack and reformer blowers, mass flow of biogas fuel to the reformer, and the stack voltage. Outputs are taken as stack and reformer temperature, stack H_2-exhaust concentration, current, and the proximity of the reformate composition from the thermodynamic carbon-deposition barrier. The results for the linear model fit over a variety of current set points are shown in Figure 4. Reasonable agreement with the high-fidelity model is observed. The risk of carbon formation has proven to be a significant constraint to the response time. Rapid changes in fuel flow rate cannot be stoichiometrically matched by air blowers, so more modest response times are expected.

In the case of an operating change from very high mass flow to low mass flow, the discrepancy in transient response of the fuel and air flow rates can result in the current dropping suddenly before recovering to a nominal value. In the case of a rapid increase, the stack is fed almost pure biogas, causing a spike in the distance from the carbon deposition barrier. Both the non-linear and the identified linear model predict this transient mismatch, and thus the model-predictive controller can be designed to compensate.

The effect of this compensation is an increase in the time the current takes to reach a given set point, and an overall decrease in the rapidity of the controller dynamic response. It is exactly this kind of response that is interesting to analyze, as it provides a direct method to determine what kind of load sharing will be needed based off of the transient response desired. That is, if the SOFC system needs to provide extremely rapid current changes, the controller shows what is possible for the blowers and the fuel reformers to provide, the deficit indicating what is required of any battery that may supplement the SOFC system.

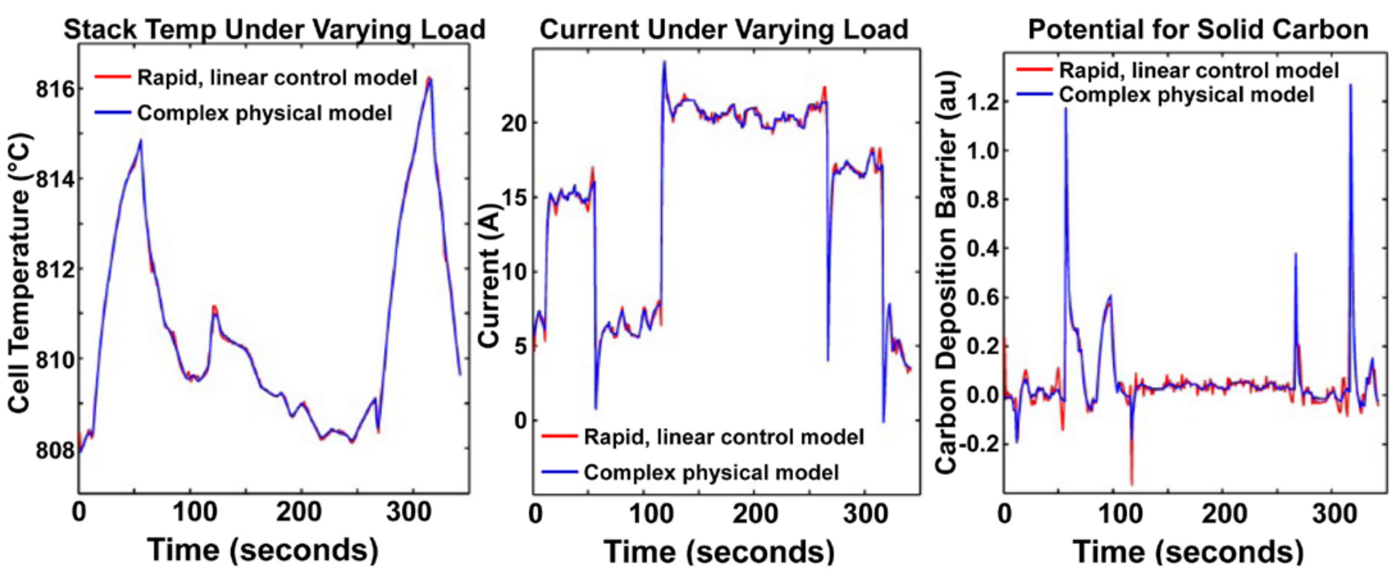

FIGURE 4. Comparison of model outputs from the multi-dimensional high-fidelity model with the rapid, lower-order linear model. Positive values for the carbon-deposition barrier (far right) indicate deposit-free operating conditions.

Conclusions and Future Directions

Ceramic Microchannel Reactors for Biogas Fuel Processing

Building on the important milestone of demonstrating steam methane reforming within the ceramic microchannel reactor, goals for the upcoming year include:

- Explore effects of ceramic microchannel reactor design on increasing throughput for SMR conversion and hydrogen selectivity.
- Utilize computational modeling to guide reactor design for improved performance.
- Disseminate results in peer-reviewed journal publications.

SOFC System Modeling Under Biogas Fuels

System modeling efforts indicate:

- Net electrical efficiency approaches 52% (LHV) even for small-scale facility applications. This efficiency is significantly higher compared with efficiencies offered by competing cogeneration technologies (with the exception of molten-carbonate fuel cells).
- The economic analysis based on the cost of electricity indicates that only medium- and large-scale SOFC systems could successfully compete against the grid electricity price without incentives. This is caused by a high unit capital cost of small SOFC units and the cost of the required biogas pretreatment system.
- The sensitivity analysis of the cost of electricity from an SOFC system indicates high sensitivity to the biogas cost and the system-first cost.

Future goals for the system-level modeling work include dissemination of results in a peer-reviewed journal.

Model-Predictive Control of Biogas-Fueled SOFC System

The linear model accurately captures the dynamics found in the high-fidelity, multi-dimensional model. In the coming FY, this linear model will be used in numerical simulations to control the complete SOFC system.

FY 2012 Publications/Presentations

1. D.M. Murphy, A.E. Richards, A. Colclasure, W.A. Rosensteel, N.P. Sullivan, "Biogas fuel reforming for solid oxide fuel cells," *Journal of Renewable and Sustainable Energy* **4** (2012) http://dx.doi.org/10.1063/1.3697857.

2. R.J. Kee, B.B. Almand, J.M. Blasi, B.L. Rosen, M. Hartmann, N.P. Sullivan, H. Zhu, A.R. Manerbino, S. Menzer, W.G. Coors, J.L. Martin, "The design, fabrication, and evaluation of a ceramic counter-flow microchannel heat exchanger," *Applied Thermal Engineering* **31** (2011) 2004-2012.

3. D.M. Murphy, M. Parker, J. Blasi, A. Manerbino, R.J. Kee, H. Zhu, and N.P. Sullivan, "Fuel processing in ceramic microchannel reactors for SOFC applications," *European Fuel Cell Forum*, June 26 – June 29, 2012.

4. D.M. Murphy, M. Parker, J. Blasi, A. Manerbino, R.J. Kee, H. Zhu, N.P. Sullivan, "Fuel processing in ceramic microchannel heat exchanger reactors," *IMRET12 - The International Conference on Microreaction Technology*, Lyon, France, February 20-22, 2012.

5. A.E. Richards, M.G. McNeeley, R.J. Kee, N.P. Sullivan, "Gas transport and internal-reforming chemistry in Ni–YSZ and ferritic-steel supports for solid-oxide fuel cells," *Journal of Power Sources* **196** (2011) 10010– 10018.

6. W.A. Rosensteel, S.M. Babiniec, D.D. Storjohann, J. Persky, N.P. Sullivan, "Use of anode barrier layers in tubular solid-oxide fuel cells for robust operation on hydrocarbon fuels," *Journal Power Sources* **205** (2012) 108–113.

7. S. Babiniec, B. Gorman, and N.P. Sullivan, "Processing of lanthanum-doped strontium titanate anode supports in tubular solid oxide fuel cells," *European Fuel Cell Forum*, Lucerne, Switzerland, June 26 – 29, 2012.

8. K.J. Kattke, R.J. Braun, "Characterization of a novel, highly integrated tubular solid oxide fuel cell system using high-fidelity simulation tools," *Journal of Power Sources* **196** (2011) 6347–6355.

9. K.J. Kattke, R.J. Braun, A. Coclasure, G. Goldin, "High-fidelity stack and system modeling for tubular SOFC system design and thermal management," *Journal of Power Sources* **196** (2011) 3790–3802.

10. M.J. Kupilik, T.L. Vincent, "Estimation of biogas composition in a catalytic reactor via an extended Kalman filter," *2011 IEEE International Conference on Control Applications* (2011) 768–773.

11. M.J. Kupilik, T.L. Vincent, "Model Predictive Control of Reformate Composition for use in Solid Oxide Fuel Cells," *ASME 2012 Dynamic Systems and Control Conference*, Ft. Lauderdale, FL, USA, October 17–19 2012.