IV.C Fuel Processing Subsystem and Components

IV.C.1 Next Millennium Fuel Processor^{TM} for Transportation Fuel Cell Power System

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Objectives

- Validate Argonne National Laboratory (ANL) computer models by integrating existing fuel processing technology into a 10 kWe multi-fuel power system.
- Utilize integrated STAR (Substrate based Transportation application Autothermal Reformer) fuel processor, MPR (Modular Pressurized Reformer – a disintegrated fuel processor), high temperature material test facility, and microreactors to perform endurance testing that will identify and address component and fuel processor degradation mechanisms.
- Design and test the 50kWe STAR fuel processor.

Approach

- Integrate fuel processing (existing Model B based technology) and fuel cell sub-systems.
- Develop control strategies on 10 kWe fully automated fuel cell power system (FCPS) and deliver to ANL.
- Perform automotive system analysis and identify strategies for STAR to meet FreedomCAR targets.
- Set targets and develop key technologies and components to be used in STAR.
- Design and test STAR on four fuels and investigate efficiency, emissions, steady state and transient performance, and reformate purity.
- Integrate STAR fuel processor and fuel cell, investigate the performance of the power system, and identify system level integration issues. Deliver the integrated fuel processor system to ANL.
- Investigate and address degradation and durability issues of STAR fuel processor both on the component and integrated fuel processor level.

Accomplishments

- Tested the fuel cell sub-system and fuel processor sub-system.
- Developed sub-system and integrated power plant control strategies.
- Performed steady state and transient testing on gasoline and delivered integrated FCPS to ANL.
- Developed design criteria for scrubber media and validated them during full-scale operation of fuel processor and STAR systems.
- Selected materials for high temperature zones of the fuel processor and designed test facility to investigate long term stability of such materials.
- Performed deactivation studies of the STAR catalyst suite in microreactor.
- Tested >100 catalysts for STAR and selected final candidates.
- Designed substrate-only fuel processor and devised control strategies for fuel processor and FCPS.
- Tested partially integrated fuel processor (version 1) and demonstrated 74% H_2 efficiency (at high temperature shift exit).
- Tested partially integrated fuel processor (version 2) and demonstrated improvements in thermal stress and serviceability over version 1, and 80% syn gas efficiency (at high temperature shift exit).
- Designed and characterized reformate tolerant fuel cell on hydrogen.

Future Directions

- Support ANL's testing efforts and modeling studies, and provide necessary assistance.
- Bring the high temperature material test facility on-line.
- Complete the long term stability studies of the STAR catalyst suite and deduce equations to describe degradation.
- Perform long term stability studies of the integrated STAR fuel processor with gasoline.
- Demonstrate ≥50 kWe power from an integrated FCPS and characterize fuel processor on four fuels.
- Perform emission characterization of integrated FCPS.
- Deliver fuel processor system to ANL.

Introduction

Nuvera is working with the Department of Energy to develop efficient, low emission, on-board multi-fuel processors for the transportation application. The fuels include gasoline, methanol, ethanol, and natural gas.

In the first part of the project, Nuvera integrated an existing fuel processing technology into a 10 kWe multi-fuel power system in order to allow validation of computer models developed by ANL. This integrated fuel cell power system was delivered to ANL in June 2002.

The Substrate based Transportation application Autothermal Reformer (STAR) will contain high-activity, low-cost, transportation specific catalysts and substrates to address power density, specific power, and start-up tie issues. To address the issue of system durability, we are developing fuel purification (sulfur removal) and reformate clean-up technologies.

Results

Based on component technologies produced in previous years, we completed design of the STAR fuel processor in the reporting period (Figures 1 and 2). The design shown contains all the reaction zones and has a volume of ~70 L. This fuel processor also has the shape factor necessary for installation in the fuel cell vehicle.

We have collected operation data from the partially integrated STAR fuel processor (Figure 3). Gasoline was used as a fuel in this testing at 175 kWth feed rate and we expect the maximum feed rate to be ~200 kWth. The H_2 efficiency and CO concentration approach equilibrium values

Figure 1. Conceptual Design of STAR Fuel Processor

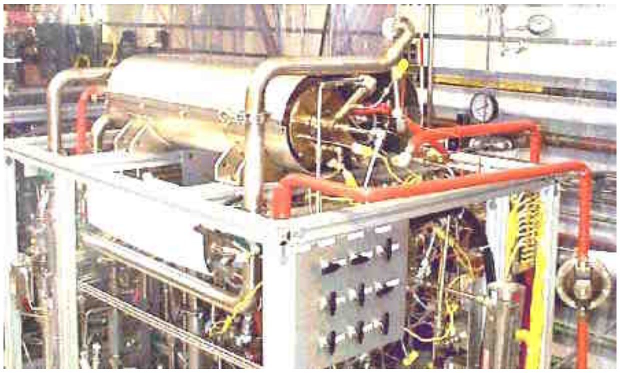

Figure 2. STAR Fuel Processor on Test Cart

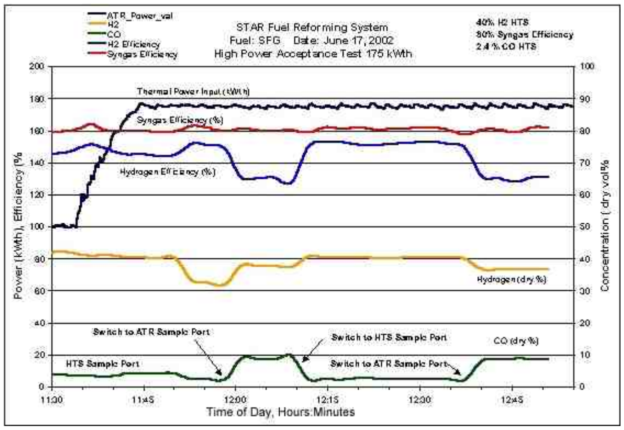

Figure 3. Performance Data of Partially Integrated STAR Fuel Processor

Technical targets: fuel processors[a] to generate hydrogen-containing fuel gas from reformulated gasoline containing 30 ppm sulfur, average, for 50 kWe (net) fuel cell systems

(Excludes fuel storage; includes controls, shift reactors, CO cleanup, heat exchangers)

Characteristics	Units	Calendar year		
		2001 status[b]	2005	STAR 2002[c]
Energy efficiency[d]	%	78	78	78
Power density	W/L	500	700	836
Specific power	W/kg	450	700	585
Cost[e]	$/kW	85	25	65
Cold start-up time to maximum power @+20 °C ambient	min	<10	<1	<10
Transient response (time for 10% to 90% power)	sec	15	5	15
Durability[f]	hours	1000[g]	4000[h]	1000
Survivability[i]	°C	TBD	–30	TBD
CO content in product stream[j]				
steady state	ppm	10	10	<50
transient	ppm	100	100	<100
H_2S content in product stream	ppb	<200	<50	<100
NH_3 content in product stream	ppm	<10	<0.5	<1

[a] With catalyst system suitable for use in vehicles.

[b] Projected status for system to be delivered in late 2002: 80% efficiency, 900 W/L, 550 W/kg.

[c] Projected status for STAR fuel processor in 2002.

[d] Fuel processor efficiency = total fuel cell system efficiency/fuel cell stack system efficiency, where total fuel cell system efficiency accounts for thermal integration. For purposes of testing fuel-processor-only systems, the efficiency can be estimated by measuring the derated heating value efficiency (lower heating value of $H_2 \times 0.95$/ lower heating value of the fuel in) where the derating factor represents parasitic system power losses attributable to the fuel processor.

[e] High-volume production: 500,000 units per year.

[f] Time between catalyst and major component replacement; performance targets must be achieved at the end of the durability period.

[g] Continuous operation.

[h] Includes thermal cycling.

[i] Performance targets must be achieved at the end of an 8-hour cold-soak at specified temperature.

[j] Dependent on stack development (CO tolerance) progress.

Table 1. Comparison of FreedomCAR Targets and STAR Performance Projections

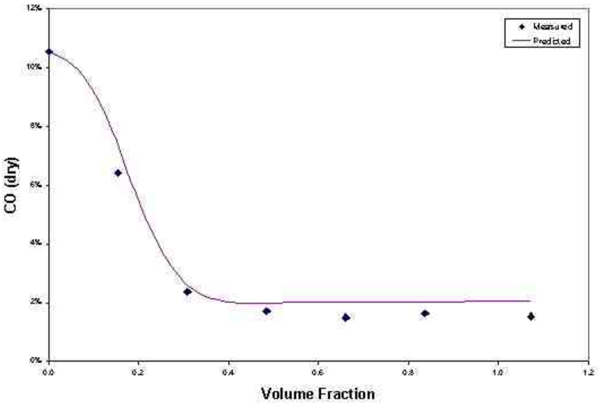

Figure 4. Comparison of Expected vs. Obtained Performance of WGS Catalyst in MPR

suggesting the validity of our design basis. We have accumulated >50 hrs of gasoline operation on STAR fuel processor (version 2) and have subjected it to >30 thermal cycles. Table 1 compares Nuvera's projections of the STAR fuel processor performance and FreedomCAR targets.

The STAR fuel processor represents a culmination of three years of intensive R&D and design efforts. Prior to their use in the integrated fuel processor, all components were tested in the MPR. Figure 4 compares the expected and obtained performance of the water-gas-shift catalyst in the MPR. Similarly, the MPR testing validates the desulfurizer performance data collected on the bench scale reactor (Table 2). The sulfur capacity was the same in both the MPR and the bench scale reactor.

Parameter	Bench-Scale	MPR
Adsorbent Weight (g)	9	3330
Physical Form	Powder	Structured

Table 2. Comparison of Bench-Scale and MPR Performance of Desulfurizer

The STAR fuel cell stack, shown in Figure 5, was characterized via H_2/air operation (Figure 6). Figure 6 data are limited to 66 kWe although the stack is capable of higher power – load bank limitations have prevented us from higher power operation.

The performance of adsorbent clean-up media was evaluated and validated. We anticipate the use of such media between the fuel processor and fuel cell sub-systems to safeguard the fuel cell from various trace species generated and/or present in gasoline. Figure 7 shows the performance of medium "A" after being used on the fuel cell power system for 30 hrs. We have also carried out extensive short-term and long-term durability testing of the STAR catalyst suite (Figure 8).

Figure 5. STAR Fuel Cell Stack

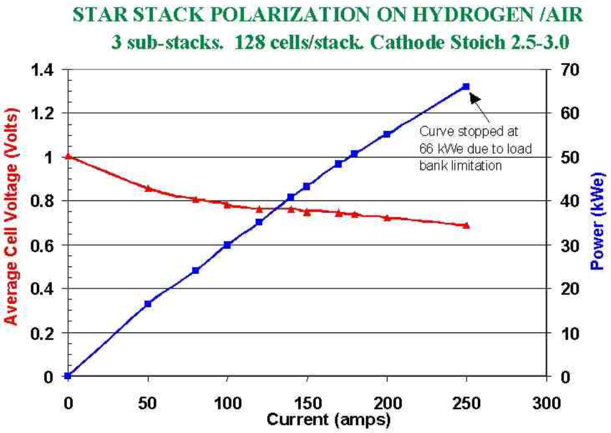

Figure 6. Polarization Data on STAR Fuel Cell for H_2/ Air Operation

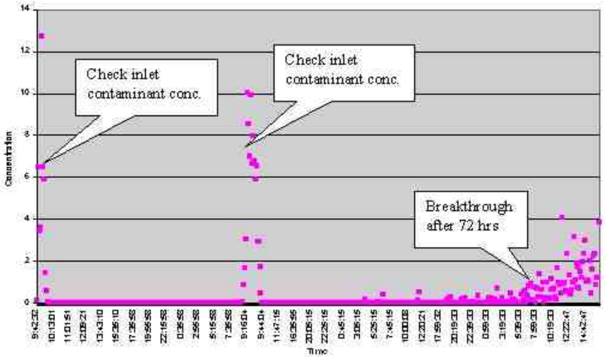

Figure 7. Performance of Adsorbent "A" after Being Used on Fuel Cell Power System for 30 hours

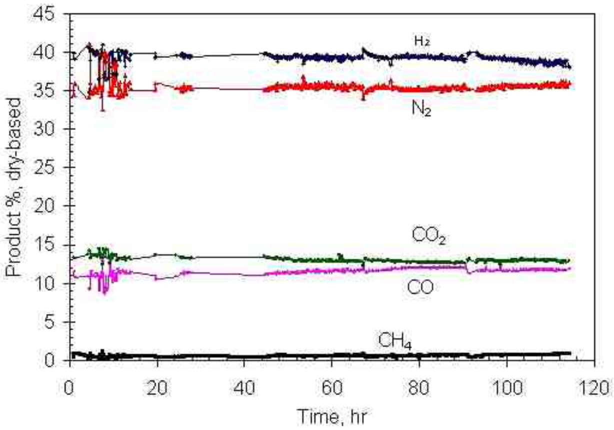

Figure 8. Longevity of STAR ATR Catalyst

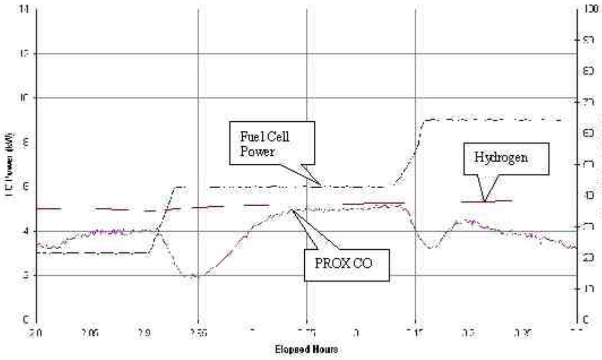

Figure 9. Fuel Cell Power System Performance on Gasoline

Over the last year, we retrofitted the existing fuel processor sub-system, designed the fuel cell sub-system, and integrated the two units. The integrated power plant was delivered to ANL in June 2002. Figure 9 shows typical performance of the integrated system on gasoline.

Conclusions

- A substrate only multi-fuel processor has been designed and tested. Preliminary data on gasoline indicate 80% efficiency (at HTS exit). Detailed testing is expected to validate the performance projections of specific power, power density, and emissions.
- Thermal stress and fluid flow distribution constitute major design challenges with such fuel processors.

IV.C.2 Multi-fuel Processor for Fuel Cell Electric Vehicle Applications

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Main Subcontractors: Catalytica Energy Systems and NexTech Materials, Ltd. (NexTech)

Objectives

- Design, build and demonstrate a fully integrated, 50-kilowatt electric (kWe) catalytic autothermal fuel processor system. The fuel processor will produce a hydrogen-rich gas for direct use in proton exchange membrane (PEM) fuel cell systems for vehicle applications.

Approach

- Develop preliminary design of 50-kWe fuel processor system and performance goals for individual components.
- Evaluate alternate approaches for the major catalytic components (e.g., desulfurizer, reformer, shift reactor and selective oxidation reactor).
- Conduct subsystem testing of major components utilizing best catalyst approach.
- Develop final design of overall system and design specifications for individual components.
- Assemble 50-kWe fuel processor system.
- Perform demonstration testing on gasoline and methanol.
- Ship fuel processor system to Argonne National Laboratory.

Accomplishments

- Completed peer review of final design.
- Produced required amount of Catalytica Energy System's autothermal reformer (ATR) catalyst.
- Produced required amount of NexTech platinum (Pt)/ceria medium-temperature-shift (MTS) catalyst.
- Obtained Los Alamos National Laboratory preferential oxidation (PROX) reactor.
- Obtained Battelle/Pacific Northwest National Laboratory micro-channel steam generator.
- Obtained Precision Combustion, Inc. dual-fuel catalytic burner.

- Completed fabrication and assembly of fuel processor system.
- Completed checkout of components, controls and instrumentation.

Future Directions

- Conduct performance tests of fuel processor system.
- Ship fuel processor system to Argonne National Laboratory for further evaluation and testing.

Introduction

Development of a compact, efficient and low-cost processor for converting carbon-based fuels to hydrogen is an important aspect of the successful implementation of fuel cells for transportation applications. A catalyst-based reforming approach for fuel processing can provide fast start-up and transient response, high efficiency and compactness. When coupled with a liquid-fuel desulfurizer, the multi-fuel processor under development by McDermott Technology, Inc./Catalytica Energy Systems promises to approach the FreedomCAR fuel processor targets.

Approach

The fuel processor consists of a liquid-phase desulfurizer, a catalytic reformer, two stages of water-gas-shift reaction, a selective oxidizing unit, and ancillary components including pumps, heat exchangers and controls [1]. A general arrangement concept drawing of the fuel processor system is shown in Figure 1. The project consists of 5 major tasks: preliminary design, catalyst development, subsystem testing, final design, and prototype assembly and demonstration.

The liquid fuel desulfurizer reduces sulfur in gasoline to less than 3 parts per million (ppm). The reformer unit operating at an average temperature of 800°C produces a hydrogen-rich gas from the fuel feed. Two reformer approaches were evaluated - a packed bed comprising a single catalyst and a plate-based catalyst system. A bi-functional ATR catalyst developed by Catalytica Energy Systems was selected for use over the plate-based design. The plate design showed possible advantages in size but could not be developed in the contract time frame. The ATR is followed by a shift reactor consisting of two stages. The first stage contains a medium-temperature-shift catalyst developed by NexTech. The second stage contains a commercial low temperature shift (LTS). The shift reactors reduces the CO concentration in the reformate gas to approximately 2,000 ppm. Final reduction of CO is achieved in a preferential selective oxidation reactor.

McDermott Technology, Inc. developed the overall system design including heat integration, mechanical design, ancillary equipment, and instrumentation/controls. Catalytica Energy Systems developed the catalytic components, including a state-of-the-art autothermal reforming catalyst. NexTech contributed its expertise and technology in the area of shift catalysts.

Results

During this reporting period, a peer review of the final design was completed. The review was performed by independent experts and was attended by DOE and team members. The reviewers approved the final design. Following the review, general arrangement drawings for the system and detailed fabrication drawings of the U-tube pressure vessel and internal components were completed.

The predicted performance of the system is summarized in Table 1. Three loads were used to develop the design. The maximum efficiency design point is 25% load (12.5 kWe). Thermal integration was optimized around the 60% load (30 kWe) case. The maximum continuous rated design point is 50 kWe. The predicted fuel processor efficiency is 80.6% at 25% load assuming 80% hydrogen utilization and 50% efficiency in the fuel cell.

Size and weight predictions are summarized in Table 2. The system power density and specific power are 283 W/L and 165 W/kg, respectively. The size and weight are actual size and weight using commercially available components or

Table 1. Predicted Performance for Authothermal Processor System

Characteristic	Units	Predicted Performance		
		Nominal	Design	Maximum
Load	kWe (net)	12.5	30	50
Reformer S/C Ratio		2.00	2.00	2.00
Total S/C Ratio		2.58	2.89	3.31
Total A/F Ratio (includes PrOx)		13.4	14.5	16.1
Reformer Stoichiometry		0.23	0.25	0.28
Fuel Equivalence Ratio		4.31	3.98	3.58
Fuel Value of Gasoline, LHV	kW	35.1	92.7	167.2
Fuel Value of H_2 to Fuel Cell, LHV	kW	31.2	80.4	141.0
Electrical Output	kWe (gross)	13.97	35.81	62.86
Electrical Output	kWe (net)	12.74	30.68	50.38
Carbon Conversion	%	99.82	99.45	99.76
Cold Gas Efficiency (LHV)	%	88.92	86.74	84.37
Fuel Processor Efficiency	%	80.58	82.42	81.99
Overall System Efficiency (LHV)	%	32.84	31.43	29.26
Compressor Efficiency	%	67.0	74.4	73.0
Expander Efficiency	%	75.7	81.8	85.0
Expander Output	kWe	0.4	2.3	4.0
Parasitic Loads	kWe	1.6	7.5	16.5
Radiator Heat Rejection	kW	13.8	34.6	63.5
Fuel Cell Operating Temperature	°C	60	60	60
Fuel Cell Voltage (Assumed)	V	0.7	0.7	0.7
Fuel Cell H_2 Utilization	%	80.11	79.83	79.86
Fuel Cell O_2 Utilization	%	50.07	49.90	49.91
Fuel Cell Efficiency, LHV	%	44.78	44.54	44.58
PrOx O_2/CO Ratio		0.98	0.98	0.98
PrOx Selectivity		0.51	0.51	0.51
PrOx CO Conversion	%	99.78	99.66	99.47
Sy Pressure Drop	KPa	6.74	15.75	38.69

Table 2. Summary of Sized and Weights of Components and System

Subsystem Totals	Size (L)	Weight (kg)
Reformate Generator	128.00	28-.0.25
Steam Regenerator	6.50	7.70
Reformate Conditioner	45.00	30.00
Fuel Supply	11.28	22.63
Water Supply	18.80	40.70
Controls & Piping (1/10 demonstration unit)	19.48	15.15
Overall Total	222.38	380.63
Power kWe (Gross	62.86	62.86
Power Density/Specific Power	283	165
DOE FreedomCAR 2000 Target (W/L, W/kg)	600	600
DOE FreedomCAR 2004 Target (W/L, W/kg)	750	750

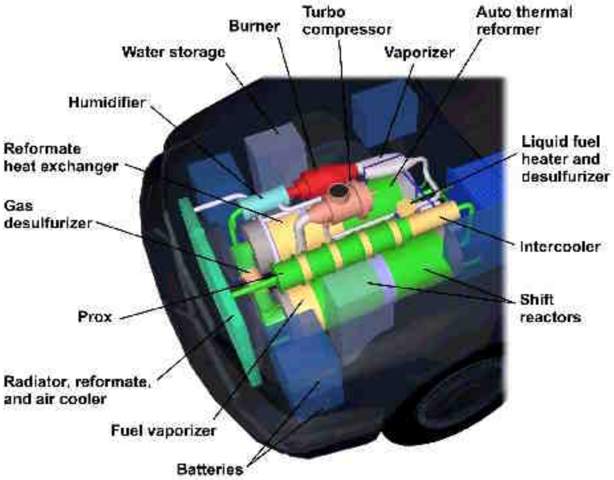

Figure 1. Schematic of McDermott's Fuel Processor

developmental components for control and thermal management. The compressor/expander and start-up burner are excluded from the totals. A humidifier is included in the fuel processor scope as part of the water management system.

The catalyst scheme is summarized in Table 3. The required amount of Catalytica Energy Systems ATR catalyst was produced and installed in the reactor. The required amount of NexTech shift catalyst was produced and installed in the first stage shift reactor. The NexTech shift catalyst is a medium-temperature shift catalyst that remains active in the oxidized or reduced state and is less sensitive to condensed moisture [2]. All catalysts are currently in pellet form; however, noble metal wash coating on monolith substrates is existing technology. Therefore, once the catalyst and system performance are verified, it will be straightforward to convert these catalysts to monoliths. The reactors have been designed to accommodate standard monolith sizes.

Table 3. Catalyst Scheme

	Catalyst Beds				**Clean-up Beds**	
Parameter	**ATR**	**MTS**	**LTS**	**PROX**	**Sulfur Removal**	**NH_3 Removal**
Temperature (°C)	807	399	263	94	322	None
Catalyst	Rh	Pt	Cu/ ZnO	Pt	ZnO	None
Support	Alumina	Ceria/ Zirconia	ZnO/ Al_2O_3	Alumina	None	None
GSHV (1 hour)	9.165	13,833	13,623	25,000	134,405	None
Bed Volume (L)	10.0	10.0	11.2	7.4	1.0	None
Bed Weight (kg)	14.4	15.0	15.0	2.23	1.4	None

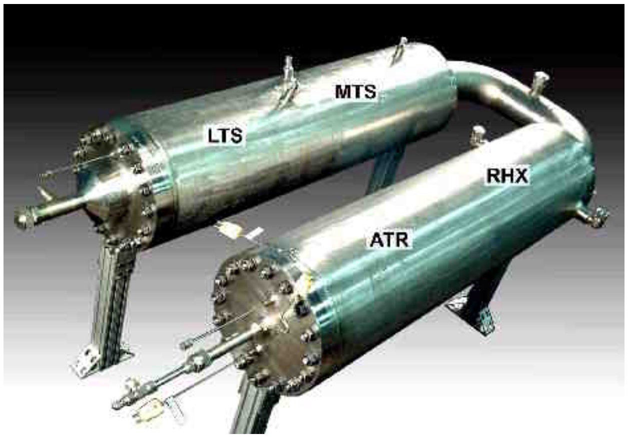

Figure 2. Fuel Processor Tube Pressure Vessel

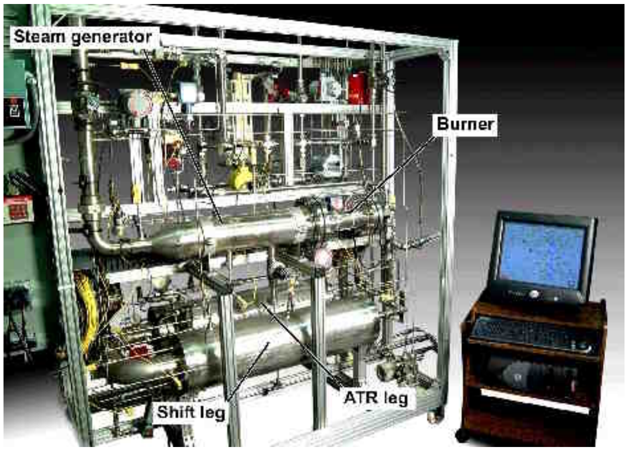

Figure 3. Integrated Fuel Processor Test Stand

Los Alamos National Laboratory provided a preferential oxidation reactor suitable for demonstration with monolith catalysts. Pacific Northwest National Laboratory provided a steam generator based on micro-channel heat exchanger technology. Precision Combustion, Inc. provided a dual-fuel catalytic burner.

The tube pressure vessel and its internals were fabricated and assembled as shown in Figure 2. The tube pressure vessel thermally integrates many major components including the ATR reactor, reformate heat exchanger, gas desulfurizer, fuel vaporizer, and MTS and LTS reactors. In addition, internal water spray cooling is used for temperature control. Upon completion of the pressure vessel and receipt of vendor-supplied components, the fuel processor system was assembled on a test stand as shown in Figure 3 with controls and instrumentation. To date, all components, controls and instrumentation have been checked out.

Conclusions

A fully integrated autothermal fuel processor based on a bi-functional ATR catalyst has been designed, fabricated and checked out. The unit continues to show progress towards the FreedomCAR targets and will be tested in the summer of 2002.

References

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1. Flynn, T. J., Privette, R. M., Perna, M. A., Kneidel, K. E., King, D. L. and Cooper, M., "Compact Fuel Processor for Fuel Cell-Powered Vehicles," International Congress and Exposition, Detroit, MI, March 1-4, 1999, SP-1425, pp 47-53.

IV.C.3 Quick-Starting of Fuel Processors

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Objectives

- Develop strategies to meet the rapid-start targets for on-board fuel processors in gasoline-fueled fuel cell vehicles.

Approach

- Identify constraints that limit fuel processors from reaching rated hydrogen production capacity within 30 seconds.
  - Identify the fundamental technical barriers – thermal mass, fuel consumption, feed limitations, etc.
  - Set up component and hardware models, and validate with experimental study of rapid heat-up behavior.
- Develop a heat-up strategy to enable 30-second start-up of the fuel processor.
- Demonstrate fast-start strategy in a laboratory-scale fuel processor.

Accomplishments

- Evaluated burner feeds and heat load required to warm up the fuel processor to full capacity.
  - The mid-temperature (200-400°C) zones represent ~70% of the total heat load.
  - Air flows required at the burner for meeting the appropriate hot gas temperatures in the various zones are nearly five times that required for operation in reforming mode at rated power.
  - Parallel heating of the various components is preferable to sequential heating, since parallel heating allows better temperature control of the hot gas and permits starting the fuel processor at partial capacity.
- Developed a computational fluid dynamics (CFD) model to simulate heat-up of individual reactor zones.
- Designed, fabricated, and installed a generic fuel processor and test stand to study the heat transfer characteristics of monolith loaded reaction zones.
  - Initiated experiments to validate the CFD model.

Future Directions

- Study the effect of hot gas temperature, gas hourly space velocity, adjacent environments, and flow patterns (adjacent zones with co- or counter-current flow, parallel vs. series heating, etc.) on the heat-up rates.
- Validate model with experimental data and use model to design a fuel processor capable of rapid start.
- Establish a start-up strategy (identify necessary components, hot gas and flow specifications, heating sequence, etc.) to achieve fast start
- Demonstrate rapid start-up of an engineering-scale (~5 kilowatts electrical [kWe]) fuel processor.

Introduction

To achieve significant market penetration, fuel cell vehicles will have to meet or exceed the performance baseline established by today's spark-ignition engine vehicles. These performance criteria include improved gas mileage, rapid acceleration, and turn-key start-up. The goal of this work is to develop strategies that will result in demonstration of a fuel processor for fuel cell vehicles that starts rapidly. The Department of Energy has set a start-up time of 30 seconds (from 20°C to maximum power) for the year 2010.

Approach

This project will identify the constraints that prevent existing fuel processors from reaching rated capacity in 30 seconds or less. A fundamental technical barrier is the thermal mass of the catalysts and structural materials. Reductions in thermal mass require improvements in catalyst materials and effective heat transfer. Other limiting factors are related to auxiliary equipment and process design, such as available gas blowers and burners, the fuel injection system, sensor response, and hot gas distribution within the processor.

The development approach will be to set up component and hardware models for rapid heat-up and to validate the models experimentally. The models will then be used to determine optimal feed distributions, anisotropies in gas flow, and patterns of heat transfer. Further experiments will be conducted to validate the models. The initial goal is a thorough understanding of the heat transfer characteristics of monolithic catalysts. Studies will include the effect of geometry, flow and distribution of the heating medium, and material compositions.

Fundamental studies of heat transfer, combined with a basic understanding of the underlying kinetics of the combustion process, will be used to develop a model of the fast-start reactor. The model will then be used to design a fast-start reactor that can meet the prescribed operational targets.

Accomplishments

As a first step in development, the heating requirements for a fast-start reactor were defined.

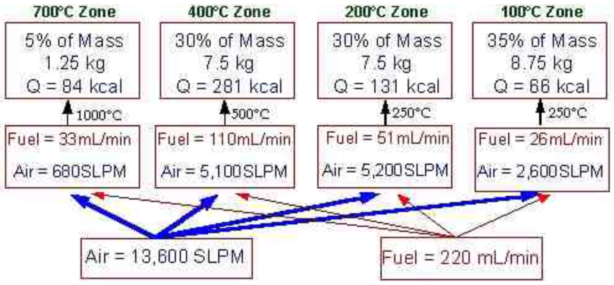

Figure 1. Fuel Requirements for a 50-kW Processor

The processor was sized according to existing catalyst technology, and the design was based on our previous fuel processor's test systems.

The processor can be divided into four zones based on the operating temperature: reformer, scrubber-high temperature shift (S-HTS), low temperature shift (LTS), and preferential oxidation (PROX). Operating temperatures are nominally 700°C in the reformer, 400°C in the S-HTS, 200°C in the LTS, and 100°C in the PROX. In actual operation, temperatures are not discrete; rather, there is a gradual decrease between each zone. The middle zones, S-HTS and LTS, comprise ~70% of the total heat required during start-up. The fuel requirements and heat flow for a 50-kilowatt (kW) processor are shown in Figure 1.

Two primary options for heating the fuel processor were considered: heating the different components in sequence or in parallel. Heating the components in parallel is preferable to heating them sequentially since it allows direct temperature control of the hot gas within each zone. A parallel system also avoids sending all of the hot gas through the reformer catalyst. A negative feature is the requirement of multiple injection points.

For a parallel system with a central burner, the air flow required to achieve the appropriate temperatures during start-up is nearly five times that required for steady operation at the rated reforming capacity. The additional air is required to maintain temperatures within allowable ranges for each of the various zones. A possible design for a parallel heating system utilizing a fuel burner is shown in Figure 2.

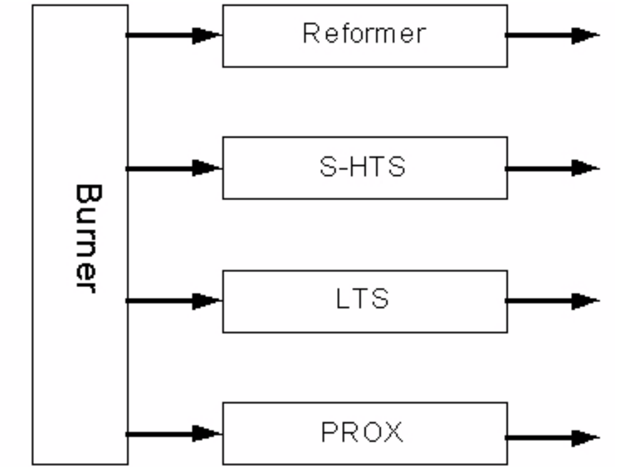

Figure 2. Parallel Heating of the Fuel Processor Components

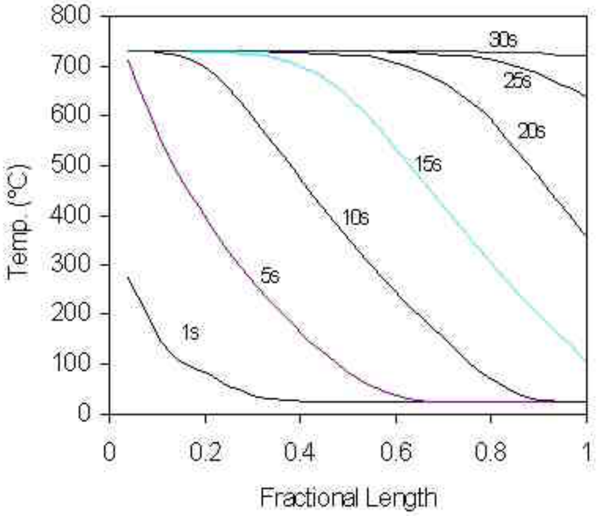

Figure 3. Initial Temperature Progression in Reformer

A CFD model was developed to simulate heat-up of a generic fuel processor based on a cylindrical geometry. The model was based on a simplified fuel processor design that consisted of three concentric zones bounded and separated by three concentric cylinders. The adjacent zones can represent either a layer of insulation or another catalyst bed. The heat transfer characteristics are studied by varying the weight of catalyst in each zone, the temperatures of the hot gases used to heat up the zones, and the direction (co- or counter-current) of flow of the hot gases in adjacent zones.

Figure 4. A test reactor is used to validate the CFD model.

Figure 3 shows the temperature progression from the CFD model for a cylindrical reactor containing a cordierite monolith that is heated to 700°C. This result suggests that the reformer monolith can attain its desired temperature in 30 seconds if a hot gas at 730°C is fed at a space velocity of 45,000 per hour (h^{-1}), assuming no heat losses. Similar start-up scenarios can be obtained for the other zones.

To validate the CFD model, a generic reactor, shown in Figure 4, was fabricated and is being used for the heating studies. Electrically heated air rather than hot combustion gas, is used to heat the catalyst beds.

As in the CFD model, the three concentric zones were loaded with monoliths and insulation. Other structural forms such as heat exchangers can be installed as needed to study their heat-up characteristics (rate, heat transfer effectiveness, temperature distribution, etc. The model is being updated to account for deviations between simulated and experimental data.

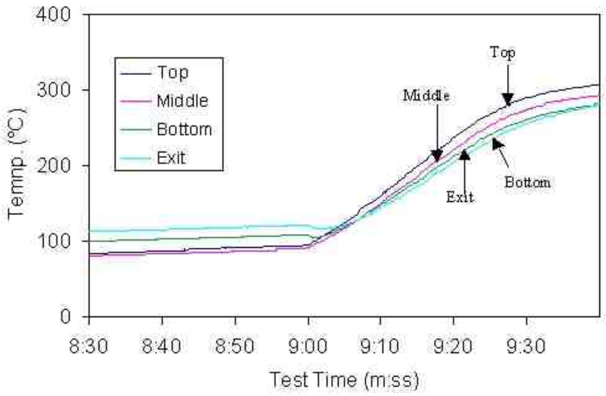

Figure 5. Heat-up of a Cylindrical Zone using Hot Gas, Flowing at a Space Velocity of 60,000 h^{-1}

Conclusion

Analysis of thermal requirements to attain operating temperatures in the fuel processor indicates that, at the space velocities required in fuel processors typical today, the shift reactor zone represents the largest thermal mass. The hot zones in the fuel processor can be heated up with hot combustion gas. Parallel heating of the various zones is preferable to sequential heating because it allows individual control of the hot gas streams into each zone. The total air required to limit the combustion gas temperatures within the bounds of tolerance of the catalyst zones is significantly higher than during reforming operations, and the air blower needs to be sized accordingly. Similarly, the cross-sectional area of each zone must be large enough to accommodate the larger flow during heat-up.

Future Directions

The fast-start test reactor will be used to determine the effect of hot gas temperature, gas hourly space velocity, adjacent environments, and flow patterns on the heat-up rates of catalysts and materials. The temperature progression within the reactor will be a function of the effectiveness of heat transfer between the hot gas and the catalyst. Variations in flow patterns that will drive the design of a fast-start processor include the effect of counter-current versus co-current flow of the gas streams in adjacent zones and of heating the zones in series versus parallel. The temperature distributions in adjacent zones will determine the insulation requirements and drive the design of the heat exchangers.

The results of these tests will be used to validate the heat transfer model. Once the heat transfer characteristics are understood, the model will be expanded to include the effects of using a fuel:air combustion mixture to generate the hot gas to heat up the system. An overall start-up strategy will be defined that will achieve rapid start and transition to steady-state operation. The strategy will identify the necessary components, the hot gas flow specifications, and the heating sequence. These data will be incorporated into the design of a 5-kWe engineering-scale fuel processor that will demonstrate a start-up time of 2 minutes or less.

Fy 2002 Publications

1. C. Pereira, S.H.D. Lee, T.D. Kaun, S. Ahmed and M. Krumpelt, "Fuel Processor for Fuel Cell Systems," presented at the Annual Meeting of AIChE, Reno, NV, November 2001.

2. C. Pereira, S. Ahmed, S.H.D. Lee, and M. Krumpelt, "Integrated Fuel Processor Development," 2002 Future Car Congress Proceedings, Arlington, VA, June, 2002.

IV.C.4 Microchannel Fuel Processor Development

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Objectives

- Develop a compact, steam reformation-based fuel processing system for the onboard reformation of hydrocarbon fuels that meets FreedomCAR performance targets for energy density, efficiency, residual CO content, durability, rapid start-up, and transient response.
- Develop highly effective reactors, fuel and water vaporizers, recuperative heat exchangers, and condensers broadly applicable to fuel processing and fuel cell systems.

Approach

- Emphasize endothermic steam reformation to best take advantage of unique heat and mass transfer advantages available in engineered microstructures.
- Utilize a differential temperature approach for the water gas shift reactor to provide an optimum balance of rapid kinetics at high temperature and favorable thermodynamics at lower temperature.
- Use a two-stage preferential oxidation reactor to reduce CO concentrations to acceptable levels, with active heat exchange for superior temperature uniformity.
- Achieve high efficiency through integration of steam reforming, water gas shift, and preferential oxidation reactors with microchannel recuperative heat exchangers, fuel and water vaporizers, condensers, and separators.

Accomplishments

- Fuel flexibility of the fuel reforming subsystem was demonstrated using methane, propane, butane, methanol, ethanol, isooctane, and benchmark gasoline. A 1000-hour catalyst and reactor durability test was completed using benchmark gasoline. Warm transient response of less than 5 seconds was achieved for 10 to 90% of full reformer capacity. A three-fold increase in reformer productivity was achieved compared to the previous year, due to improved catalyst performance and more uniform flow within the reactor. Reactor concepts that would meet FreedomCAR's rapid start-up targets were developed.
- A differential temperature water gas shift reactor was designed based on tests performed with engineered catalysts in a microchannel configuration. Conversion rates in the differential temperature reactor were higher than achievable in two isothermal stages.
- Residual CO concentrations less than 15 ppm were achieved in two microchannel preferential oxidation stages at gas hourly space velocities greater than 200,000 using catalysts obtained from commercial developers.

- Heat exchangers and vaporizers with very low pressure losses have been developed and are being supplied to interested collaborators for evaluation. A low pressure-drop water vaporizer sufficient to supply a 50 kWe autothermal reformer was designed, constructed, and delivered to McDermott Technology, Inc. Vaporizers and heat exchangers were provided to other industrial partners as well.

Future Directions

- Demonstrate rapid reformer start-up based on low pressure-drop concepts. This reactor design should also provide improved transient response characteristics.
- Incorporate a sulfur management subsystem into the steam reformer.
- Complete optimization of the reformer, water gas shift, and preferential oxidation catalyst compositions and forms.
- Complete integration of the steam reforming, water gas shift, and preferential oxidation subsystems.
- Conduct lifetime testing of reactors, heat exchangers, and catalysts using transportation fuels.
- Continue to engage industrial partner(s) to facilitate reformer system development.

Introduction

Steam reforming is an attractive fuel processing option for several reasons. Steam reforming is endothermic and thus can make use of heat from the catalyzed combustion of unutilized fuels in the fuel cell exhaust. The hydrogen content in the reformate stream is higher than obtained using other fuel processing options because it is not diluted by nitrogen from air. High reformate pressures can be efficiently generated by pumping fuel and water in liquid form; compression of air is not necessary. While conventional hydrocarbon steam reformation requires long residence times and relatively large reactor sizes because of heat transfer limitations, the heat and mass transfer advantages offered by engineered microchannels allow steam reformation to be conducted in a compact, energy-efficient system. Rapid kinetics for steam reforming in heated microchannels was first demonstrated by PNNL in 1999. Steam reforming reactors in the 10-20 kWe range were later demonstrated, coupled with a network of microchannel heat exchangers that significantly improved energy efficiency (Whyatt et al. 2001).

Approach

A modular, steam-reforming test stand with an internal volume of 51 cc that would support fuel processing rates in the 50 to 1000 We range was designed to conduct fuel flexibility and long-term durability testing (Figure 1). A network of microchannel heat exchangers was included in the test stand for water and fuel vaporization, recuperation of reformate to preheat reactants and for preheating of combustion air using the combustion exhaust. The heat exchangers were fabricated as

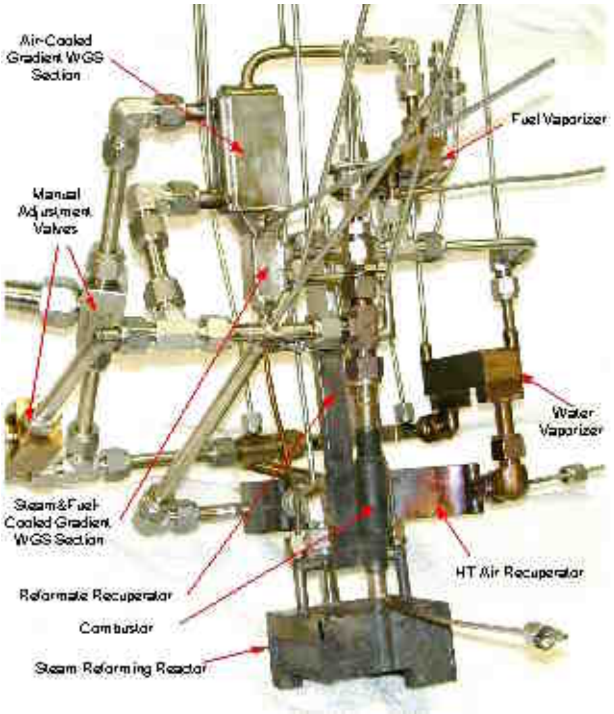

Figure 1. Modular Steam Reforming Test Stand Capable of Testing in the 100 to 1000 We Capacity Range

individual components and then connected via tubing.

The superior heat transfer achievable in engineered microchannels can be used to optimize temperature profiles in a reactor, which can lead to smaller reactor sizes and improved conversion. For reversible exothermic reactions such as water gas shift, the microchannels make it possible not only to remove the heat of reaction, but also to reduce the reaction temperature. By maintaining heat transfer length scales on the order of 100 microns, minimal temperature gradients across the catalyst were maintained while achieving precise control of temperature down the reactor. This approach provides an optimum balance between rapid kinetics at high temperature and favorable thermodynamics for conversion as the temperature is reduced.

Results

Steam Reforming Subsystem

Through improvements in gas flow characteristics and engineered catalyst performance, the volumetric productivity of the steam reforming reactor was improved by approximately a factor of three compared to our previous efforts. The catalyst that was used in these tests is a proprietary formulation obtained from Battelle Memorial Institute. For a full-sized, complete fuel processing system, projected power densities are more than double FreedomCAR targets, as shown in Table 1. To meet FreedomCAR targets for specific power, the mass of the system will need to be reduced, expected to be met through further improvements in reactor productivity and the use of lightweight alloys where appropriate.

The steam reforming subsystem was shown to exhibit good fuel flexibility. Tests were conducted using multiple fuels, including methane, propane, butane, methanol, ethanol, isooctane, and benchmark gasoline, a mixture of isooctane, xylene, methyl cyclohexane, and 1-pentene. The results of these tests are given in Figure 2, which shows conversion versus gas hourly space velocity (GHSV). The steam to carbon ratio was maintained at 3 to 1 for all non-alcohol fuels. For alcohols, the oxygen to carbon ratio was maintained at 3 to 1. Methanol was the most easily reformed, and was completely reacted to the highest space velocities tested. A conversion greater than 99.9% is necessary for fuels such as gasoline to prevent downstream condensation, whereas lower conversion may be acceptable for volatile fuels such as methane.

Performance Criteria	**Current Performance**	**2005 FreedomCAR Target**	**Explanation**
50 kWe System Volume	<1 cubic foot (<28 L)	2.5 cubic feet (71 L)	Projected from tests conducted on a smaller scale.
Energy Efficiency	81%	78%	High efficiency is the result of extensive thermal integration using effective heat exchangers.
Durability	>1000 h	4000 h	Testing beyond 1000 hours not conducted; expanded durability testing planned for FY 2003.
Power Density, Specific Power	1800 W/L, 320 W/kg	700 W/L, 700 W/kg	Improvements in specific power expected from improved productivity and use of lightweight alloys for components intended for low temperature operation.
Transient Response	5 s	5 s	Further improvements expected with incorporation of low pressure-drop components.
Start-Up to Full Power, 20^{o}C	30 s (low dP) projection 15 min current	<1 min	Low combustion-side pressure drop is key to start-up; redesign of reactors using low pressure-drop concepts is expected to meet start-up goals.

Table 1. Comparison to FreedomCAR Performance Targets

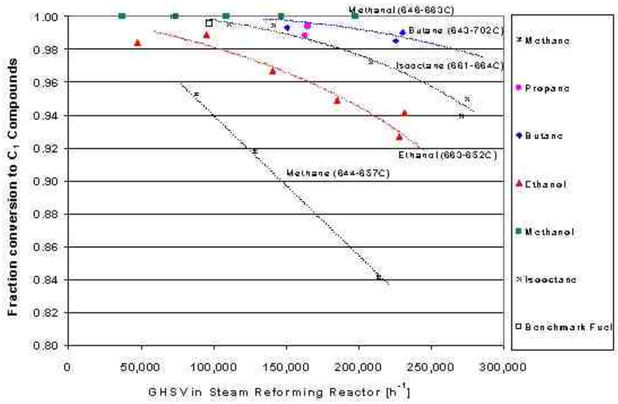

Figure 2. Conversion versus Space Velocity for Multiple Fuels

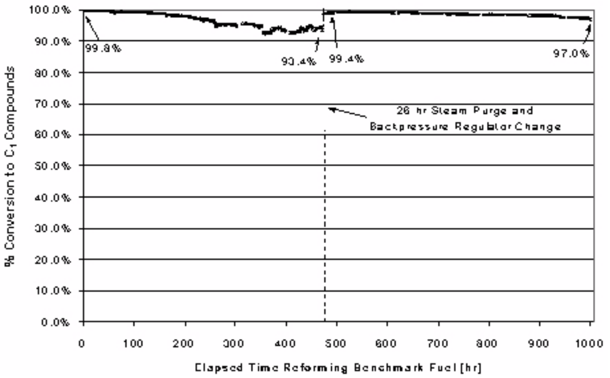

Figure 3. Conversion of Benchmark Gasoline versus Time in a Steam Reforming Reactor

To evaluate the durability of both the reactor and reforming catalyst, a 1000-hour test was performed using benchmark gasoline containing 10 ppm sulfur. The space velocity was chosen to obtain a small fraction of unconverted fuel (0.2%) at the start of the test, which aided in tracking changes in conversion versus time. Conversion fell by several percent over the first 500 hours, as shown in Figure 3, believed due to the effects of sulfur. The catalyst was then re-activated in clean hydrogen and steam, which returned the performance to near initial levels.

Warm transient response characteristics of the steam reforming subsystem were evaluated, shown in Figure 4. Fuel inflow was varied from 10 to 100% of full-scale, and reformate outflow was measured versus time. Because the residence time for fuel in this reactor and heat exchangers is very short, these portions of the system are capable of very rapid transient response. Major limiting factors are associated with fuel and water vaporizers. Scale-up is not expected to diminish transient response characteristics since a greater number of microchannels with similar aspect ratios would be used.

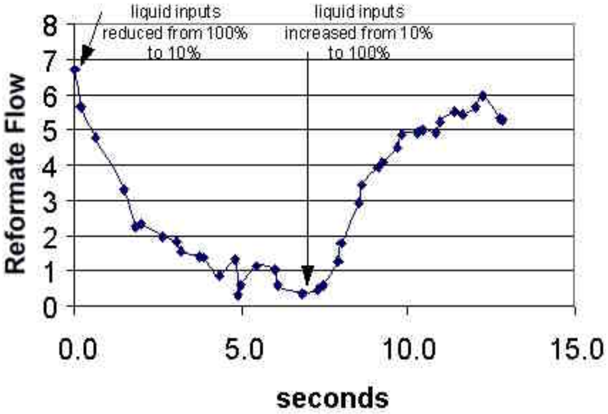

Figure 4. Warm Transient Response of the Steam Reforming Reactor from 10 to 100% of Full Capacity

Water Gas Shift Subsystem

Research supporting the development of a compact water gas shift (WGS) reactor subsystem included catalyst screening studies, kinetic model development, and test reactor design and performance evaluation. Water gas shift catalysts obtained from commercial and other developers were converted into an engineered form and tested versus temperature, space velocity, and steam-to-gas ratio in single-channel reactors. Both base metal and precious metal catalyst formulations were included in the studies.

While both base metal and precious metal catalyst formulations performed well in a simulated high temperature WGS feed stream (~15% CO), precious metal catalysts were clearly superior when tested with a low temperature WGS feed stream (~5% CO). Results for a Süd-Chemie copper zinc catalyst (T2650) and a Süd-Chemie precious metal-ceria catalyst (PMS5) are shown in Figure 5, tested in a simulated low temperature WGS feed stream. Equilibrium was achieved for the PMS5 catalyst for

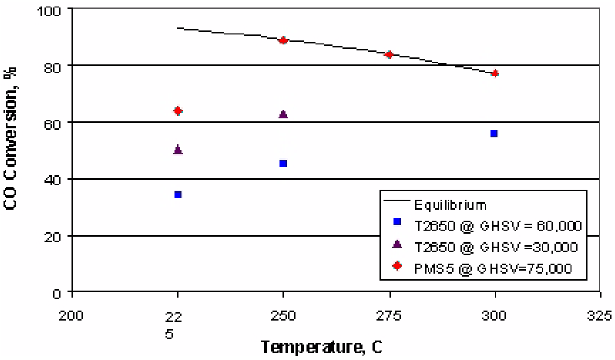

Figure 5. Conversion of CO versus temperature for engineered forms of Sud-Chemie T2650 (copper-zinc) and PMS5 (precious metal ceria) catalysts. Results correspond to a simulated low temperature WGS feed stream at a steam to gas ratio of 0.5.

temperatures greater than 250°C at a gas hourly space velocity of 75,000, whereas the T2650 copper-zinc catalyst gave more modest performance. Thus, the PMS5 catalyst was used primarily in additional testing.

A kinetic model was developed from the results of catalyst screening studies that relates reaction rates to temperature, space velocity, and steam to gas ratio. A finding of kinetic modeling studies is that conversion of carbon monoxide could be enhanced in a thermal gradient compared to reactions conducted isothermally. By managing the temperature profile of a reactor, reactants can be fed at a high temperature where rapid kinetics promotes an initial approach to equilibrium. As the reaction mixture is cooled, conversion is increased due to more favorable thermodynamic driving forces.

To optimize the performance of a microchannel-based water gas shift reactor, the temperature profile of the reactor was adjusted as a means to provide the best trade-off of rapid kinetics at high temperature and favorable thermodynamics at low temperature. A schematic for one microchannel configuration is shown in Figure 6, where catalytic monoliths are located at the center of an array of reaction channels, interleaved with heat exchange channels. A heat exchange fluid flowing co- or counter-current (shown in Figure 6) to the reaction flow removes the heat of reaction and cools the gas, thereby establishing a temperature trajectory for the reaction. The choice of coolant, the temperature and flow of the coolant, and the geometry are all design variables for achieving an optimal temperature profile to maximize the productivity of the catalyst.

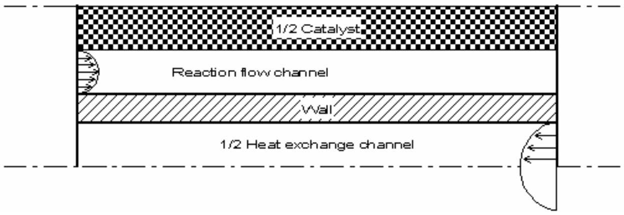

Figure 6. Two-dimensional schematic of a repeat unit for a microchannel reactor with counter-current heat exchange. Dashed lines indicate symmetry planes.

An experimental validation of modeling predictions is given in Figure 7, comparing the performance of a reactor run in a differential temperature mode versus isothermally. This experiment was performed using a low temperature feed stream, corresponding to an initial CO concentration of 4.9% (wet basis). For a space velocity of 76,000 hr^{-1}, as steam to dry gas ratio of 0.52, and an initial temperature of 350°C dropping to 280°C, a CO concentration at the outlet of 0.84% was achieved. Conversion was always less when performed isothermally in the same reactor at an identical space velocity.

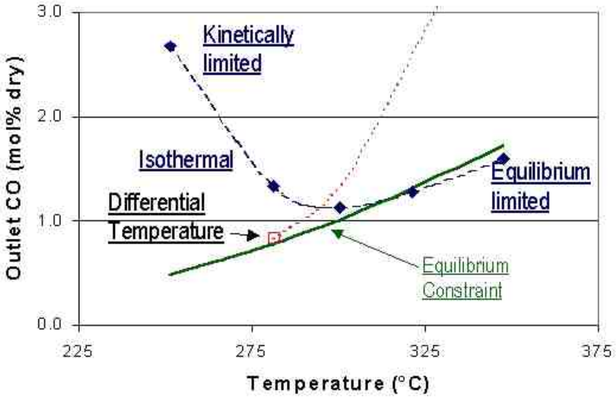

Figure 7. Comparison of a Microchannel WGS Reactor Run in Isothermal and Differential Temperature Modes on a Simulated Low Temperature Feed Stream

Preferential Oxidation Subsystem

Microchannel reactor designs may hold advantages for use in the preferential oxidation subsystem because of the ability to operate under strictly isothermal conditions and because of the ability to suppress undesired reactions (methane formation and reverse water gas shift) through the use of short residence times. Engineered forms of precious metal and base metal preferential oxidation catalysts obtained from commercial suppliers were evaluated in a microchannel reactor to show whether this approach is a viable means to meet FreedomCAR targets for conversion and selectivity. We have shown that less than 15 ppm CO in a 2 stage microchannel reactor can be obtained. For the first stage, operation at approximately 200^{o}C, oxygen to carbon ratio = 1.0, and GHSV greater than 200,000 resulted in a reduction of CO from approximately 1% to approximately 500 ppm (0.05%). For the second stage, operation at 100^{o}C, oxygen to carbon ratio = 4.0, and GHSV = 200,000 resulted in conversion of CO to below 15 ppm. To date, these two stages have not been tested together, nor has the catalyst durability been established. Discussions with catalyst vendors indicate that improved catalysts over what we have already tested are available, and such catalysts will be evaluated.

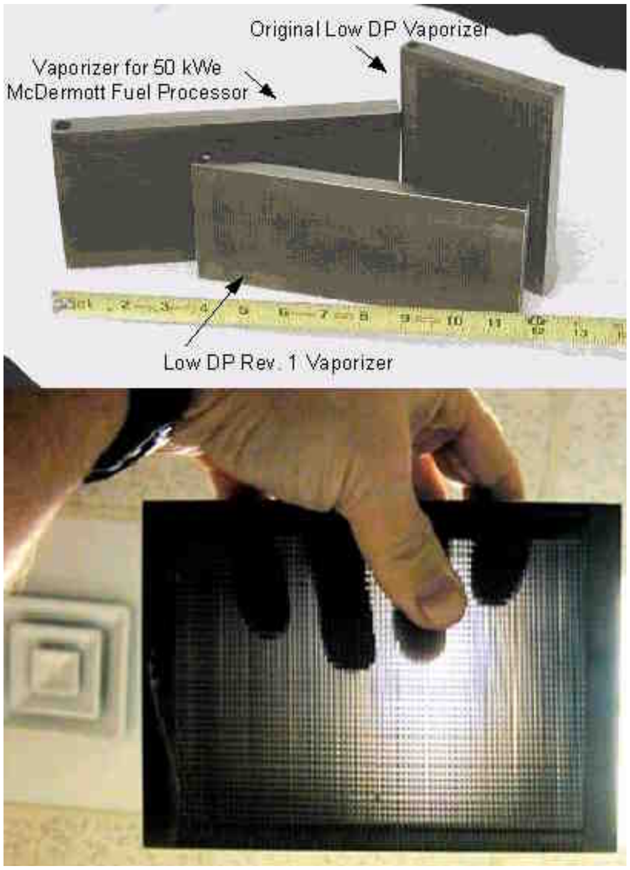

Figure 8. Microchannel Steam Generator Panel Sufficient to Support a 50 kWe Autothermal

Water Vaporizer

A full-scale water vaporizer exhibiting extremely low gas-side pressure drop has been developed during the past year and provided to industrial collaborators for evaluation. Sufficient to support a 50 kWe autothermal reforming system, the dimensions of the vaporizer panels are 22.2 cm x 10 cm x 1.8 cm, with a weight of 2.4 kg when constructed using 316L austenitic stainless steel, as shown in Figure 8. At the maximum operating point, the heat exchanger duty is 24.6 kW, with a heat exchange intensity of 60 W/cm^3. The pressure drop on the gas side was minimized by making the flow distance very short and by providing a large cross-sectional area for gas flow. Multiple vaporizer panels were fabricated in a single diffusion bonded stack, separated using wire electric discharge machining methods. One of the steam generator panels is currently undergoing testing by McDermott Technology Inc. in a 50 kWe autothermal steam reforming system. This particular panel was designed to vaporize more than 4 g/s water to produce steam at 225^{o}C and 425 kPa. The expected combustion-side pressure drop is approximately 250 Pa.

Conclusions

- Power densities in excess of FreedomCAR targets, fuel flexibility, greater than 1000-hour reactor and catalyst life, and less than 5 second transient response have been demonstrated in a microchannel-based steam reformer. Future development activities will focus on rapid start-up and improving specific power.
- A differential temperature water gas shift reactor was developed that provides an optimum balance between fast kinetics at high temperatures and favorable thermodynamics at low temperatures.
- Residual CO concentrations less than 15 ppm were achieved in two microchannel preferential

oxidation stages at gas hourly space velocities greater than 200,000.

- Heat exchangers and vaporizers exhibiting very low pressure losses have been developed and are being supplied to interested collaborators for evaluation, including a unit sufficient to supply a 50 kWe autothermal reformer provided to McDermott Technology, Inc.

References

1. Whyatt, G. A., W. E. TeGrotenhuis, J. G. H. Geeting, J. M. Davis, R. S. Wegeng, and L. R. Pederson. "Demonstration of Energy Efficient Steam Reforming in Microchannels for Automotive Fuel Processing," Proceedings of the 5th International Conference on Microreaction Technology, May 27-30, 2001.

2. Van Herwinen, T. and W. A. DeJong. J. Catalysis 63, 3 (1980).

FY 2002 Publications/Presentations

1. TeGrotenhuis, W. E., D. L. King, K. P. Brooks, B. J. Golladay, and R. S. Wegeng. "Optimizing Microchannel Reactors by Trading-Off Equilibrium and Reaction Kinetics Through Temperature Management," IMRET 6 – 6th International Conference on Microreaction Technology, AIChE, New Orleans, March 10-14, 2002.

2. Whyatt, G. A., C. M. Fischer, and J. M. Davis. "Progress on the Development of a Microchannel Steam Reformer for Automotive Applications," IMRET 6 – 6th International Conference on Microreaction Technology, AIChE, New Orleans, March 10-14, 2002.

Special Recognitions and Awards/Patents Issued

1. "Active Microchannel Fluid Processing Unit and Method of Making", USP 6,192,596

IV.C.5 Plate-Based Fuel Processing System

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Subcontractors: National Fuel Cell Research Center, Irvine, CA

Objectives

- Design, build and demonstrate a fully integrated, plate-based fuel processor system that will convert EPA Tier 2 gasoline into a hydrogen-rich gas for direct use in proton exchange membrane (PEM) fuel cell systems for vehicular applications.

Approach

Phase 1

- Complete conceptual design of plate-based reformer, water gas shift and preferential oxidation reactors and simulation models of each reactor using available catalyst kinetics. Begin optimization studies and parametric sensitivity analysis.
- Obtain catalyst performance data and kinetic data as required, including initial data on catalyst deactivation rate.
- Assess feasibility of reactor configurations, understand performance advantages, and develop initial cost analysis of reactor components.

Phase 2

- Perform prototype proof of concept testing at about 2-kW scale for laboratory component reactors.

Phase 3

- Develop 50-kW component reactors and assemble complete integrated fuel processor. Evaluate performance.

Accomplishments

- Identified sources of high local stresses in the plate reformer design that would result in short cyclic life. Developed improved designs with cyclic life approaching 250,000 cycles.
- Identified the need for a unique reactor design that would allow close control of reaction temperature under conditions typical of the reactor concepts being developed.
- Developed detailed reactor models for steam reforming, water gas shift and preferential oxidation reactor designs.

- Developed new proprietary catalyst for the water gas shift reaction that is non-noble metal, non-pyrophoric, and does not require pre-reduction.
- Began development of a fuel processor simulation tool to assess the overall integration and performance of the complete fuel processor utilizing the novel component reactors being developed.

Future Directions

- Establish kinetic models for the primary catalyst candidates for each of the component reactors (steam reforming, water gas shift, and preferential oxidation). Update the reactor models for the component reactors and establish performance for the various reactor configurations.
- Use the fuel processor simulation tool to evaluate the performance of a fuel processor based on the reactor design and establish catalyst performance criteria required for optimum performance of the component reactors and desired performance of the fuel processor.
- Complete initial catalyst stability studies for each of the component reactors. Establish catalyst stability improvement targets if required.
- Develop mechanical design for a steam reformer meeting the durability requirements including cyclic life.

Introduction

The Catalytica Energy Systems, Inc. (CESI) project is directed at developing unique reactor designs and the associated catalyst materials that will provide advantages toward meeting the DOE performance goals. The general approach is to utilize where feasible a plate-based reactor design that closely integrates heat exchange with the catalytic process to optimize component and system performance. The program consists of 3 phases as described above, with the first phase concentrating on component conceptual design and catalyst development.

Approach

The approach taken in this project is to utilize 1) steam reforming of gasoline as the first step to produce a reformate that has a high concentration of hydrogen, followed by 2) sulfur removal, 3) water gas shift, and 4) preferential oxidation to yield PEM fuel cell quality hydrogen. Work is ongoing on each of these four catalytic processes, including the development of a process simulation model that includes catalyst reaction kinetics, heat and mass transfer effects, etc. to adequately model the important aspects of the reactor design. Kinetics are either taken from the literature or are measured experimentally.

Results

Plate Reactor Design Development

In previous work, a prototype plate reactor was developed for methane steam reforming. This unit was operated for 400 hours at 100% load but with minimal (approximately 20) slow start-up cycles. An automotive fuel processor would have to demonstrate significantly higher levels of durability, including a large number of fast start-up cycles. It was assumed that the system would undergo 250,000 start-up and load transients as a worst case scenario (5,000 hours fuel processor life, one cycle every 1.2 minutes and similar stress levels from start-up and load transients). For a typical ferritic steel, this would require that the strain levels remain below 0.25%. Finite element analysis of a very fast start-up transient (30 seconds) resulted in high local stresses, in the range of 0.5 to 0.8% in the baseline reactor design. Alternative mechanical designs were evaluated, including designs that would provide a more realistic gas flow path and flow distribution. A derivative design was developed that gave a calculated strain of 0.28%, close to the target value and in an acceptable range.

Gasoline Steam Reforming Catalyst Evaluation

Initial catalyst development for direct steam reforming of gasoline was done in an integral reactor system operating at design conditions including pressure and space velocity as shown below. In these tests, the H_2 and CO levels at the reactor exit are near the expected equilibrium values.

Conditions

Gasoline flow rate (as C_8H_{18})	0.522 mmol/min
Steam to carbon ratio (S/C)	3.1
Pressure	3 atm
Catalyst amount	2.0 g
Weight hourly space velocity	1.75 g/g/hr
Reactor outlet temperature	795°C

Results

Conversion (based on C species)	95.6%
Carbon mass balance	100.6%
Product composition (dry basis)	mole fraction
H_2	0.666
CO	0.158
CO_2	0.160
$CH_4 + C_{2+}$	0.016

It should be noted that these space velocities are similar to those typically found in autothermal reforming (ATR) so that catalyst volumes will not be excessive compared to autothermal reforming processes. Catalyst activity was found to be reasonably stable for the short duration tests in this work. However, the extremely endothermic nature of the reaction and the integral operation of the test reactor made it difficult to extract reaction kinetics. A new test reactor design was developed and fabricated, and work is in progress to obtain simplified kinetics for the gasoline steam reforming reaction adequate to model the catalytic process in the plate reactor simulation.

Water Gas Shift Catalyst Development

CESI is developing an improved water gas shift catalyst formulation that targets transportation applications with catalyst characteristics such as 1) no pre-conditioning requirement, 2) no air sensitivity, 3) preferably non-precious metal based, and 4) low sensitivity to condensed water. For the data analysis, the integral fixed bed reactor design equation was used with an empirical rate expression and a first-order deactivation model. Catalysts were quantitatively compared on the basis of the initial activity, *k'* [=] moles/(gram cat.-hr-atm^2), and the deactivation constant, k_d [=] hr^{-1}. The best Pt-based material tested did exhibit reasonable initial activity (*k'* = 0.287 at 250ºC), but rapid deactivation was observed throughout the temperature window of 250ºC to 350ºC. The value of $k_d = 0.008$ for that catalyst indicates a 50% loss of activity in just 87 hours time-on-stream, implying a very rapid loss in activity with time, making these catalysts inappropriate for commercial application [1-2].

Significant work during this period was directed at developing a non-precious metal-based or base metal water gas shift catalyst (Figure 1). The initial activity, *k'*, and the deactivation rate, k_d, are determined from a fit of the measured conversion curve shown in Figure 1 after the first 5 to 10 hours. These k_d and *k'* values for these catalysts are summarized in Table 1 with the Pt catalyst reported in Reference 2 included for comparison.

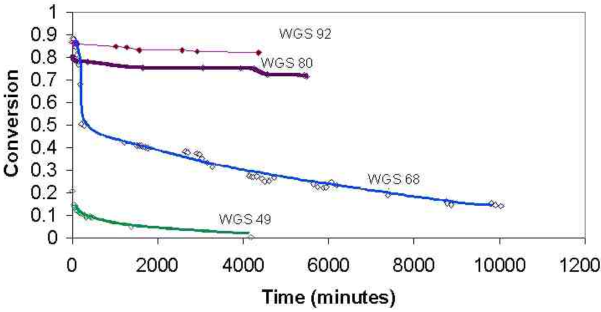

Figure 1. Catalyst Performance Test Results for Water Gas Shift Catalyst Materials

Catalyst	**k_d**	***k'***	**Half life**
	hr^{-1}	**mol/(g-hr-atm^2)**	**hr**
WGS 49	0.0812	0.014	8.5
WGS 68	0.0047	0.44	147
WGS 80	0.0022	1.39	315
WGS 92	0.0016	1.21	433
Pt-catalyst	0.008	0.287	86.6

Table 1. Performance of Base-Metal and Pt-Based Water Gas Shift Catalysts after 5 to 10 Hours on Stream

Currently, the best base-metal catalyst developed by CESI possesses much better activity and stability than the reported Pt-based catalyst and is comparable to commercial catalysts in long term activity. However, while the WGS 92 catalyst shows very good stability, the k_d value of 0.0016 still implies a half life of about 433 hours, and if this deactivation rate is maintained throughout 2,000 hours of operation, the catalyst activity would decrease by 25 fold. Work is in progress to develop static aging procedures to measure activity out to 5,000 hours and to accelerate the development of more stable catalyst systems.

Preferential CO Oxidation

A detailed computational model was developed for several different innovative designs for the preferential carbon monoxide (CO) oxidation reactor using a kinetic mechanism and reaction sequence derived from a micro-kinetic model and literature data for the specific adsorption coefficients and kinetic parameters for a platinum-based catalyst. The course of the reaction calculated by such a kinetic model is shown in Figure 2, where the space time is varied over a wide range in an isothermal reactor operating at 150°C. At nearly 100% CO conversion, the selectivity is high due to the selective adsorption of CO over H_2; it drops as H_2 begins to oxidize.

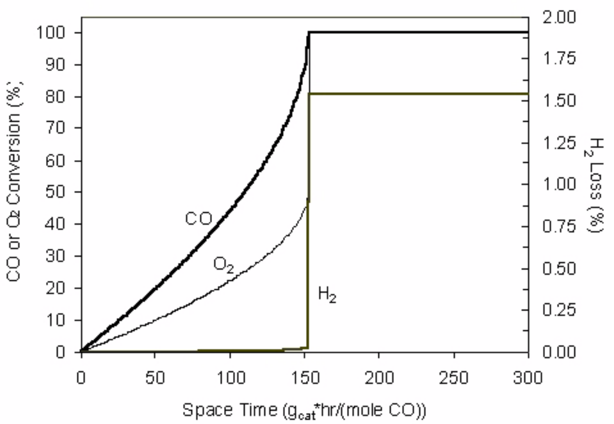

Figure 2. Reaction profile during the preferential oxidation of CO using the simulation model described in the text. This models an isothermal reactor operating at 150°C with a 1% CO reformate stream typical of the exit composition from the water gas shift reactor.

The results of a parametric study exploring the effect of mass transport limitations on this reaction gave the results shown in Figure 3. For this study, the reactor was assumed to be isothermal, and the conversion data of Figure 3 show the final composition exiting the reactor. The ideal (kinetics only) result gives the expected high conversion and selectivity due to the selective CO reaction. As mass transport limitation is added, the maximum CO conversion drops (Table 2) due to CO depletion near the surface since O_2 is in excess.

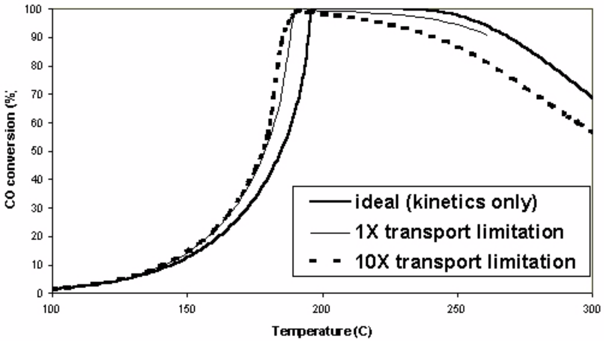

Figure 3. Simulation model results showing the effect of transport limitations on the preferential oxidation of CO. This models an isothermal reactor operating at 150°C with a 1% CO reformate stream typical of the exit composition from the water gas shift reactor.

Simulation conditions	Minimum CO level
Kinetics only	~0 ppm
1X mass transport limitations	30 ppm
10X mass transport limitations	140 ppm

Table 2. Effect of Mass Transport Limitations on the Minimum Level of CO that Can Be Obtained in the Preferential Oxidation of CO

These results and other parametric studies show the importance of the reactor and catalyst design. However, some of these results deviate from measured kinetics and CO selectivity and suggest that the assumed kinetics may not be fully representative of reality. The strong dependence of the results on the kinetic and equilibrium parameters suggest that it is absolutely essential that the kinetic parameters be validated by experimental tests, and this work is in progress.

Conclusions

Initial work on the steam reforming of Tier 2 gasoline demonstrated that equilibrium composition reformate can be obtained with space velocities typical of autothermal reforming catalysts, supporting the feasibility of a compact and effective gasoline steam reforming reactor. A new reactor design has been developed to obtain kinetics under well controlled conditions for highly exothermic or endothermic reactions.

A water gas shift catalyst has been developed that is very active and reasonably stable, does not require pre-reduction, is non-pyrophoric, and does not contain precious metals. The kinetics of this catalyst are being more fully explored to allow process and reactor modeling, including modeling in a plate reactor configuration, and work has been initiated to develop a long-term, cost effective aging process to estimate performance at the target 2,000 to 5,000 hour life.

A process simulation tool for the full fuel processor has been developed, and parametric studies have shown the importance of catalyst and reactor design in obtaining the target CO levels of 10 ppm.

References and Publications

1. Zalc, J.M., Park, T., Sokolovskii, V.D., and Löffler, D.G., "Optimal Design of a Water-Gas Shift Reactor for Use in Automotive Applications," American Institute of Chemical Engineers Annual Meeting, Reno, Nevada, November 6, 2001, Paper 167a.

2. Zalc, J.M., Sokolovskii, V.D. and Löffler, D.G., "Are Noble Metal-Based Water-Gas Shift Catalysts Practical for Automotive Fuel Processing?" Journal of Catalysis, 206[1], 169-171, 2002.

IV.C.6 Fuel Processors for PEM Fuel Cells

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Objectives

The key objectives of this project are to:

- Demonstrate high performance desulfurizer, catalyst, microreactor and microcombustor/ microvaporizer concepts that will enable production of compact fuel processors for proton exchange membrane (PEM) fuel cells;
- Design, fabricate and evaluate a 1 kW fuel-flexible (including EPA Phase II reformulated gasoline) fuel processor; and
- Design, fabricate and evaluate a fuel-flexible (including EPA Phase II reformulated gasoline) fuel processor capable of producing a hydrogen-rich stream for up to a 10 kW PEM fuel cell.

The 1 kW fuel processor will be completed during the first 36 months of the project. Following a go/no-go decision, the larger fuel processor will be completed within 48 months.

Approach

Tasks devised to accomplish the program objectives include:

- Component design and modeling;
- Sorbent development;
- Catalyst development and catalyst/microreactor integration;
- Microcombustor/microvaporizer development;
- Microchannel reactor system development;
- Component evaluations;
- Fuel processor design, modeling, fabrication and evaluation; and
- Cost analysis.

Accomplishments

- Models have been developed for the entire fuel processor system (ASPEN) and several of the microchannel reactors (FEMLAB and FLUENT).
- Demonstrated that π-complexation sorbents out-perform commercial sorbents by a wide margin for the adsorption of model sulfur compounds like thiophene.
- High activity carbide and supported gold water gas shift (WGS) catalysts have been demonstrated. Some of the materials possess rates that exceed those for Cu-Zn-Al commercial catalysts.
- Fabricated and tested several micro-reactors.

Future Directions

- We are in the first year of the project. We have not identified better strategies; therefore, we plan to execute the tasks outlined above.

Introduction

Fuel cells are being developed to power cleaner, more fuel efficient automobiles. The fuel cell technology favored by many automobile manufacturers is proton exchange membrane (PEM) cells operating with H_2 from liquid fuels like gasoline and diesel. A key challenge to the commercialization of PEM fuel cell based powertrains is the lack of sufficiently small and inexpensive fuel processors. Improving the performance and cost of the fuel processor will require the development of better performing catalysts and new reactor designs, as well as better integration of the various fuel processing components.

Approach

Prototype gasoline fuel processors will be produced and evaluated against the Department of Energy technical targets. Significant improvements over the present state-of-the-art will be achieved by integrating low-cost microchannel systems, high activity catalysts, π-complexation sorbents, and high efficiency microcombustors/microvaporizers being developed at the University of Michigan. The microchannel system will allow (1) more efficient thermal coupling of the fuel processor components and minimization of the heat exchanger requirements, (2) improved catalyst performance due to optimal reactor temperature profiles and increased heat and mass transport rates, and (3) better cold start and transient responses. The project will be accomplished in 3 phases. The Phase I effort will focus on demonstrating compact desulfurizer, microreactor and microcombustor/microvaporizer components for a 1 kW fuel processor, and developing low-cost microdrilling and micromilling methods for the production of microchannel systems. The components will be third-party tested and will provide the basis for design and fabrication of an integrated 1 kW ethanol or gasoline fuel processor during Phase II. We will scale-up the smaller processor to 10 kW during Phase III.

Results

Component design and modeling. ASPEN, a chemical process simulator, is being used to model the fuel processor system. These simulations will allow determination of the equilibrium constraints and heat duties for the different components in the fuel processing system. Performance of the microreactors is being simulated using FEMLAB, a finite-element software package, and FLUENT, a package that is capable of handling multi-component transport in a flow fluid simultaneously with surface reactions. The FEMLAB simulations demonstrated that one can control heat transfer in microchannel reactors by properly designing thermal bridges within the microfabricated system. The FLUENT results are being cross-validated against the FEMLAB results.

Sorbent development. During liquid-phase experiments, π-complexation sorbents adsorbed more sulfur (e.g. thiophene) at low concentrations than commercial sorbents. Table 1 compares the performance of selected sorbents.

	NaY (commercial)	π-Complexation Adsorbent
Solvent	Saturation Amount (mmol/g)	
Benzene	0.102	0.171
n-Octane	----	0.898

Table 1. Thiophene Adsorption Amounts upon Saturation

Catalyst development and catalyst/ microreactor integration. Several ATR, WGS, and PrOx catalysts have been prepared. The ATR catalysts include beta-alumina supported nickel. These catalysts are being evaluated. Transition metal carbide and oxide supported gold catalysts were demonstrated to be highly active for the WGS reaction. The carbide catalysts were more active and durable than the oxide supported catalysts. The oxide supported gold catalysts deactivated dramatically during the first 10 hours on stream (see Figure 1). The deactivation appears to be a consequence of over-reduction of the support by CO. We are modifying the supports to improve their durability. Preferential oxidation catalysts consisting of 5% Pt/15% ceria-85% alumina wash-coated onto honeycomb monoliths have been prepared. These materials are currently being tested.

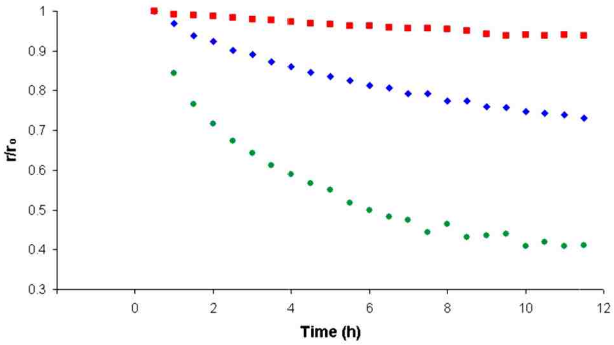

Figure 1. Deactivation Patterns for the Oxide Supported Gold Catalysts

Microchannel reactor system development. A prototype micro-reactor with concentric tubes has been fabricated. The main body is made of aluminum with 4 channels produced by deep hole micro-drilling. These channels have diameters of 3 mm and depths of 50 mm. Tubes with outer diameters of 650 µm and inner diameters of 300 µm were fitted into the channels. The structure included 4 stainless steel end caps made by milling and micro-drilling processes. The prototype reactor is illustrated in Figures 2 and 3.

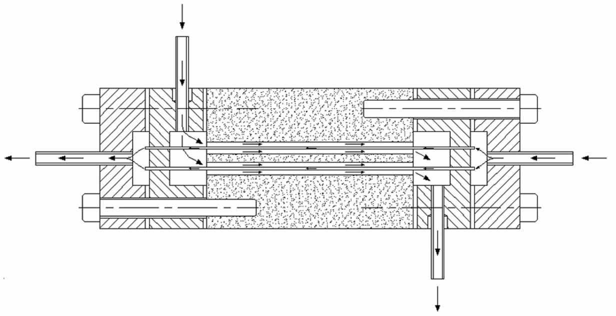

Figure 2. Schematic of the Prototype Micro-Reactor

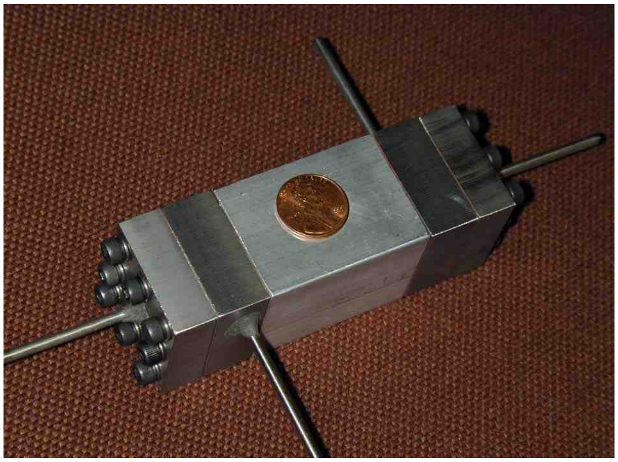

Figure 3. Photograph of the Prototype Micro-Reactor

Conclusions/Future Work

While this project is relatively new, significant progress has been made regarding the component design and modeling, sorbent and catalyst development and microchannel system development tasks. We will continue to focus on these tasks and microcombustor/vaporizer development. In addition, methods will be demonstrated to integrate catalysts into the micro-reactors.

IV.C.7 Evaluation of Partial Oxidation Fuel Cell Reformer Emissions

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Subcontractors: Nuvera Corporation, Cambridge, MA; Air Toxics, Ltd., Sacramento, CA; Clean Air Vehicle Technology Center, Hayward, CA

Objectives

- Measure the emissions from a partial oxidation/autothermal fuel processor for a proton exchange membrane (PEM) fuel cell system under both cold-start and normal operating conditions.
- Assess the feasibility of meeting emissions standards for automobiles and light-duty trucks through the use of a fuel cell vehicle with a gasoline reformer.

Approach

- Define a representative test cycle consisting of both cold-start and normal operating conditions.
- Use the established test cycle to quantify emissions from a partial oxidation reformer before and after anode-gas-burner treatment.
- Measure emissions with continuous monitor measurements supplemented with laboratory analyses of speciated hydrocarbons.
- Use reasonable approximations and estimates to convert emissions data from a grams/unit fuel basis to a predicted grams/mile basis.

Accomplishments

- Measured emissions from a fuel processor (without fuel cell) over several operating conditions including cold-start.
- Speciated total hydrocarbon data before and after the anode gas burner.
- Assessed the sensitivity of monitoring equipment over a range of operating conditions.
- Analyzed data to report emissions on a g/kg fuel basis.
- Established testing plans for two additional reformer systems.

Future Directions

- Perform extensive emissions testing of a fuel cell/reformer system to include particulate, formaldehyde, and ammonia as well as NO_x, hydrocarbons, and CO.
- Develop control strategies to minimize emissions.
- Test emissions from McDermott Technologies fuel processor in August 2002.
- Evaluate on-road emissions from fuel cell vehicles with on-board reformers.

Introduction

Fuel reformer operation is generally divided into two operating modes: start-up and normal partial oxidation. During start-up, the fuel processor burns fuel at near stoichiometric conditions until critical system temperatures and pressures stabilize to target values. Once the target conditions are reached, the reformer operates in normal mode in which the fuel processor burns fuel at very rich conditions. Since these modes are comprised of considerably different operating conditions, it follows that the emissions associated with each of these modes are also considerably different.

Since the combustor is typically cold under start-up conditions, the emissions produced during this brief period (target times are under 30 seconds) can be substantially higher than those produced during the remaining, much longer portion of the driving cycle. The pollutant emissions produced during this operating mode include NO_x, CO, formaldehyde, and organic compounds. These organic compounds, which include hydrocarbons, alcohols, and aldehydes, are regulated in California and referred to as non-methane organic gases (NMOG).

Under normal operating conditions, in which the combustor is sufficiently warm and operated under fuel rich conditions, virtually no NO_x is formed, although the formation of ammonia is possible. Most hydrocarbons are converted to carbon dioxide (or methane if the reaction is incomplete); however, trace levels of hydrocarbons can pass through the fuel processor and fuel cell. The shift reactors and the preferential oxidation (PrOx) reactor reduce CO in the product gas, with further reduction in the fuel cell. Thus, of the criteria pollutants (NO_x, CO, and non-methane hydrocarbons [NMHC]), NO_x and CO levels are generally well below the most aggressive standards. NMOG concentrations, however, can exceed emission goals if these are not efficiently eliminated in the catalytic burner.

Approach

In this study, a gasoline fuel processor is operated under conditions simulating both cold start and normal operation. Emissions are measured before and after the anode gas burner in order to quantify the effectiveness of the burner catalyst in controlling startup emissions. The emissions sampling system includes continuous emissions monitors (CEMs) for O_2, CO_2, CO, NO_x, and total hydrocarbons (THC). Also, integrated gas samples are collected in Tedlar bags for hydrocarbon speciation analysis via gas chromatography (GC). This analysis yields the concentrations of the hydrocarbon species required for the California NMOG calculation. The particulate matter (PM) concentration in the anode burner exhaust is measured through either isokinetic sampling or the placement of a filter in the exhaust stream.

Concentrations of the aforementioned species are obtained using the emission sampling system shown in Figure 1. Since emissions vary significantly between startup and normal operation, a wide range of analyzer capability is required.

Emission data will be used to assess on-road emissions from fuel cell vehicles and will be characterized in terms of cold-start on reforming modes. Current fuel processor technologies are not configured to follow a vehicle load and may be

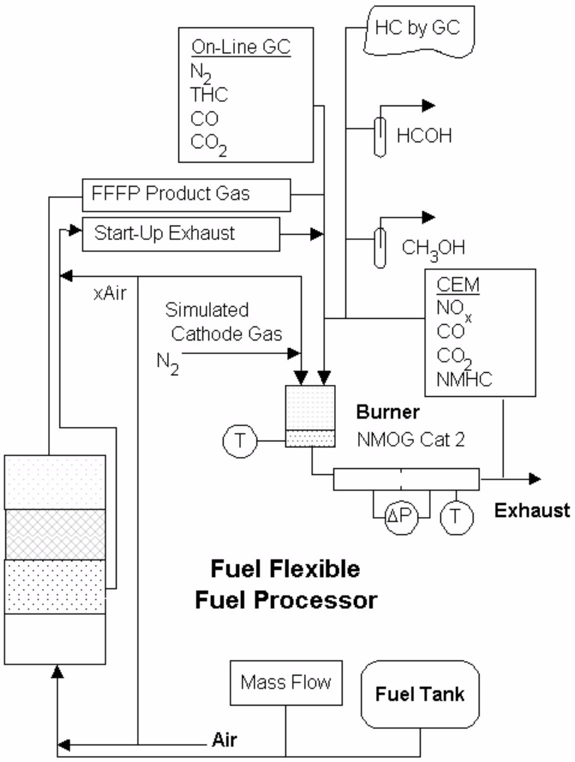

Figure 1. Fuel Processor Schematic

integrated with a hybrid vehicle. For this project, the fuel processor is operated at several steady-state points while emissions are monitored for the steady-state conditions and transients between load changes. The combination of data during start-up, different loads, and transients will be inputs to a vehicle emissions model. The model for determining vehicle emissions estimates the emissions for each second in a driving cycle based on load. Start-up emissions are also added to the total driving emissions. The data will also be provided to the National Renewable Energy Laboratory to support their efforts in vehicle emissions modeling.

Results

Our previous report summarized the results of a preliminary emissions test of an autothermal fuel processor operating without a fuel cell. The test focused on NO_x and hydrocarbon emissions, including speciation of hydrocarbon components. Figure 2 shows NO_x and THC emission levels as the reformer was started up and operated over a duty cycle. The testing did not attempt to follow a vehicle driving cycle but rather followed a series of steady-state conditions with load changes. THC emissions were high during start-up and then varied during the test, with spikes occurring when the load was increased.

During reforming, over 90 percent of the THC emissions were methane. The composition of the hydrocarbons was analyzed and the presence of toxic contaminants determined. Figure 3 shows the hydrocarbon fractions from fuel processor tests in terms of methane and NMHCs. Samples from these tests were also analyzed to determine the speciated hydrocarbon emissions profile over various operating loads. Figure 4 shows the results of the speciation analysis, in terms of the fraction of olefins and saturated and aromatic hydrocarbons that comprise the NMHCs. Aromatics and saturated hydrocarbons comprise almost all of the NMHC emissions. The fraction of NMHC as aromatics was close to the fraction of aromatics in the test gasoline for several samples taken from the PrOx and the tail gas combustor (TGC). The TGC burned reformer product gas.

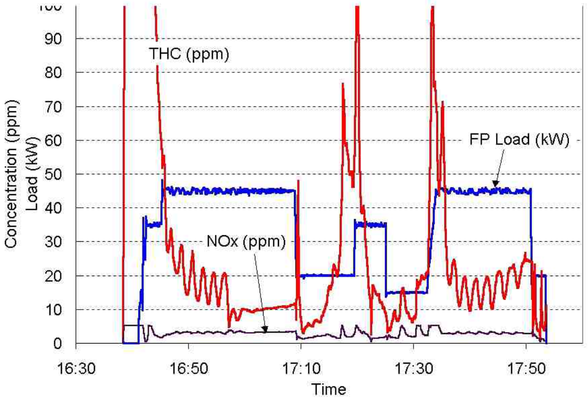

Figure 2. THC and NOx Concentrations Compared with Fuel Processor Load over Time

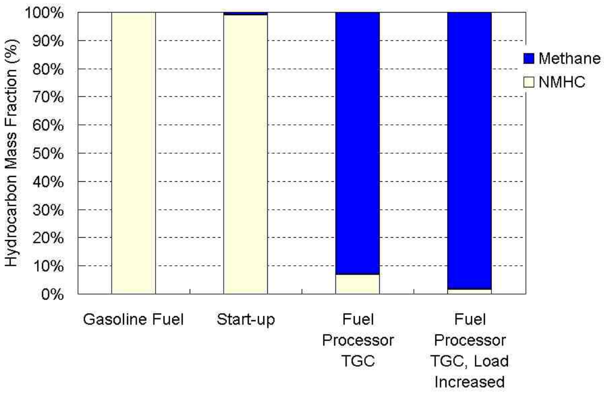

Figure 3. Hydrocarbon Mass Fraction of Fuel Processor Emissions at Various Stages

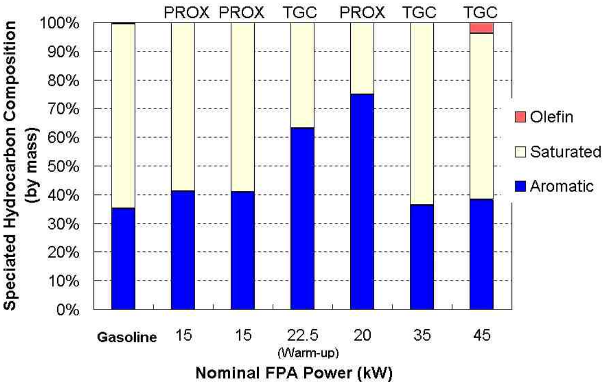

Figure 4. Speciated Hydrocarbon Composition of Air Toxics Samples from the Fuel Processor or Tail Gas Combustor at Various Fuel Processor Loads

During warm-up and one mid-power PrOx sample (20-22.5 kW), the fraction of NMHC as aromatics was higher. Olefins were typically less than 1 percent of NMHC in the PrOx and TGC samples and also represented less than 1 percent of the gasoline. However, for one test point, olefins comprised 4% of the NMHC. The presence of the toxic components benzene and 1,3-butadiene were less than 1 ppm.

Conclusions

Preliminary emissions data were measured from the PrOx and a TGC that combusted all of the reformer products. The fuel processor and the combustion of reformer products did not represent an optimized fuel cell vehicle configuration. Even with these limitations, the following conclusions can be drawn from the data.

NO_x emissions measured from a TGC ranged from less than 1 ppm to 5 ppm. These emission levels would correspond to approximately 0.01 g/mi of NO_x over a vehicle driving cycle. These emissions would be as low if the TGC were burning hydrogen-depleted anode gas.

NMHC emissions during start-up were over 100 ppm. In order to meet stringent emission standards, the start-up duration will need to be minimized. More data on start-up with an optimized fuel processor is required before on-road NMHC emissions can be estimated.

During reforming, hydrocarbon emissions are typically 90 percent methane, which will help reduce the NMHC contribution of the fuel processor.

IV.C.8 Catalysts for Autothermal Reforming

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Objectives

- Improve catalytic activity and reduce the cost of autothermal reforming (ATR) catalyst to decrease the size of the fuel processor and reduce start-up time.
- Develop a better understanding of reaction mechanisms in order to optimize catalytic activity, minimize deactivation, and improve sulfur tolerance.

Approach

- Synthesize materials that meet Argonne National Laboratory (ANL) selection criteria and DOE cost goals.
- Determine H_2, CO, CO_2, CH_4, and C_nH_m yields versus temperature and space velocity.
- Work with catalyst manufactures to optimize catalyst performance and to support the catalyst on structured forms such as a monolith.
- Conduct fundamental studies to gain insight into reaction mechanisms.

Accomplishments

- Demonstrated the performance of Rh-, Ni-, and Pt-CGO (gadolinium-doped ceria) supported on a cordierite monolith.
- Demonstrated that the oxidation and reforming reactions are “decoupled.”
- Transferred technology to Süd-Chemie, Inc. under a CRADA to optimize the performance of the CGO-based catalyst.
- Demonstrated that modified $LaNiO_3$ and $LaCoO_3$ perovskites are active for autothermal reforming and appear to be structurally stable under autothermal reforming conditions.

Future Directions

- Optimize the choice of metals and metal loadings for the CGO-based catalysts supported on structured forms, such as monoliths or foams.
- Work with Süd-Chemie, Inc. to optimize the performance of the CGO-based catalysts.
- Increase the activity of the perovskite catalysts.
- Improve the sulfur tolerance of non-Pt catalysts.
- Continue to work with academic collaborators to gain better insight into reaction mechanisms.

Introduction

Catalytic autothermal reforming (ATR) of hydrocarbon fuels was first proposed by Argonne National Laboratory (ANL) several years ago and has been widely accepted as the most promising route to meet the efficiency, volume, and cost goals of the DOE Hydrogen, Fuel Cells and Infrustructure Technologies Program. ANL has developed a new family of reforming catalysts that are modeled after solid oxide cathode materials. Unlike typical industrial steam-reforming catalysts that consist of nickel supported on a modified alumina substrate, the ANL catalyst consists of selected Group VIII transition metals, such as platinum, rhodium, or nickel, supported on an oxide ion-conducting substrate, such as gadolinium- or samarium-doped ceria. The ANL catalyst has demonstrated near-equilibrium yields of H_2 from a number of hydrocarbon fuels, including natural gas, gasoline, and diesel, exhibiting high catalytic activity and resistance to coking. The platinum catalyst has been shown to exhibit long-term tolerance to sulfur at a concentration of 50 ppmw, which is typical of the sulfur content in Tier II gasoline. Süd-Chemie, Inc., of Louisville, Kentucky, produces the ANL catalyst under a licensing agreement. Because of concern over the cost of platinum and rhodium, we have initiated an effort to develop mixed non-noble metal oxides with the ABO_3 stoichiometry and the perovskite structure as reforming catalysts. Perovskites were selected because many are good oxygen ion conductors and/or good mixed electronic conductors.

High reforming activity has been exhibited by lanthana-based perovskites that have been doped on the A-site to improve catalytic activity and on the B-site to provide structural stability in reducing environments.

Approach

Gadolinium-doped ceria (CGO) substrates are prepared from nitrate salt precursors by either coprecipitation or glycine-nitrate combustion techniques. Pt, Rh, or Ni is loaded onto the CGO using the incipient wetness technique. Typical weight loadings are 1 wt% or less for Pt and Rh and up to 10 wt% for Ni. Pt-, Rh-, and Ni-CGO supported on cordierite monoliths were prepared by Süd-Chemie. Core samples from the monoliths were tested in a microreactor system for the reforming of isooctane and benchmark fuel (74 wt% isooctane, 20 wt% xylenes, 5 wt% methylcyclohexane, and 1 wt% 1-pentene). Temperature-programmed reaction studies were performed by exposing powder samples (~50 mg) of the catalysts to isobutane (C_4H_{10}), O_2, H_2O, and N_2 at the desired feed ratios over a temperature range of 100-800ºC using a Zeton Altamira Chemisorption Instrument Model AMI-100 equipped with a mass spectrometer. Lanthana-based perovskites were prepared by mixing selected nitrate salt precursors at the appropriate ratios using the glycine-nitrate combustion technique. Powder samples were tested for isooctane and benchmark fuel reforming in a microreactor system. The structural stability of the materials was evaluated by comparing the X-ray diffraction pattern of samples before and after reforming.

Results

Rh-, Ni-, and Pt-CGO Catalysts Supported on a Cordierite Monolith

As shown in Figure 1, Rh- or Ni-CGO supported on a cordierite monolith were observed to be more active than Pt-CGO supported on a cordierite monolith based on the higher H_2 yield observed with

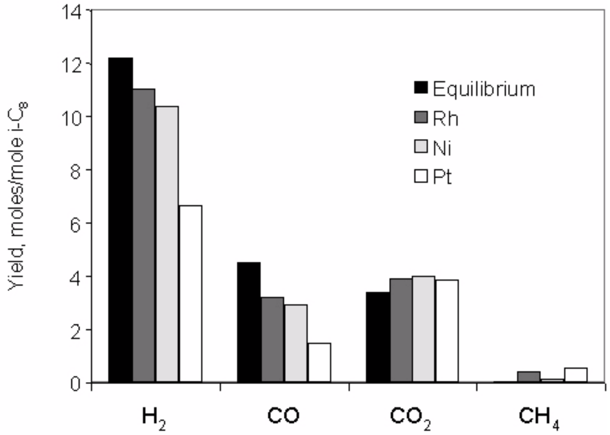

Figure 1. Yields of H_2, CO, CO_2, and CH_4 (mole/mole of isooctane) from Reforming Isooctane Catalyzed by Rh-, Ni-, or Pt-CGO Supported on a Cordierite Monolith. Conditions: 700°C, O_2/C=0.5, H_2O/C=1.2, GHSV=11,000 h^{-1}.

Rh-CGO (11.0 moles/mole of isooctane) or Ni-CGO (10.4 moles/mole of isooctane) compared with Pt-CGO (6.7 moles/mole of isooctane) for isooctane reforming at 700°C. The 11.0 moles of H_2 per mole of isooctane produced by Rh-CGO were slightly less than the 12.2 moles of H_2 predicted by thermodynamic equilibrium at 700°C. The higher H_2 yield observed with Rh- or Ni-CGO compared to Pt-CGO is attributed to Rh and Ni being more active than Pt for steam reforming. A comparison of the temperature-programmed isobutane reforming reaction profiles for Rh-, Ni-, and Pt-CGO (Figure 2) shows that the temperature at which 50% of the maximum H_2 yield is observed for Rh-CGO (381°) or Ni-CGO (512°) is considerably lower than for Pt-CGO (615°C). For Rh-, Ni-, and Pt-CGO, the oxidation reactions involving O_2 occur at a lower temperature than the reforming reactions, which produce H_2 and CO (not shown in Figure 2). While it is possible that H_2 and CO may be produced by partial oxidation reactions, they are rapidly oxidized to H_2O and CO_2, respectively, as long as O_2 is still present. For isooctane reforming, the fact that the CO_2 yield for all three metal catalysts is essentially the same (3.9-4.0 moles per mole of isooctane), as shown in Figure 1, and the lack of O_2 in the reformate suggest that all three metals are very active oxidation catalysts.

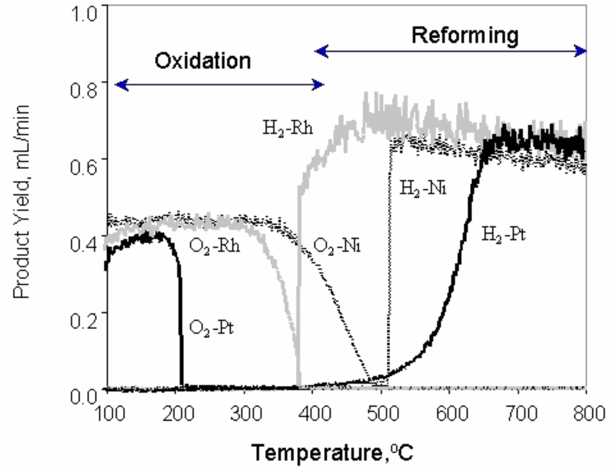

Figure 2. Temperature-Programmed Reaction Profile for the Flowrate of O_2 and H_2 in the Reformate Produced from Reforming Isobutene Catalyzed by Rh-, Ni-, or Pt-CGO in Powder Form. Conditions: O_2/C=0.5, H_2O/C=1.0, GHSV=~50,000 h^{-1}, total flowrate is 50 mL/min (balance He).

In long-term testing, Rh-CGO supported on a cordierite monolith exhibited relatively stable performance over a 1000-hr period, producing a reformate containing ~30-38 vol% H_2 from the benchmark fuel at 700°C, as shown in Figure 3. Initially, Pt-CGO supported on a cordierite monolith exhibited activity similar to Rh-CGO, producing a reformate containing ~38 vol% H_2 at 675°C (Figure 3); however, the concentration of H_2 in the reformate decreased by ~50% after only a few hours on stream. This initial rapid decrease in activity was followed by a much slower, continuing decrease in activity. After 250 hr, the concentration of H_2 in the reformate was <10 vol%. Increasing the reaction temperature to 725°C resulted in an increase in the H_2 concentration to ~20 vol%.

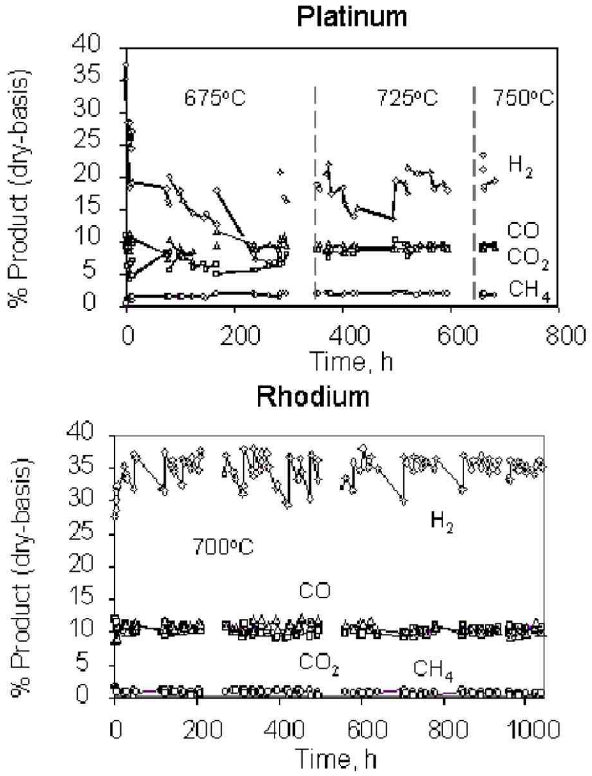

Figure 3. Yields of H_2, CO, CO_2, and CH_4 (mole/mole of fuel) from Reforming Benchmark Fuel Catalyzed by Rh- or Pt-CGO Supported on a Cordierite Monolith. Conditions: O_2/C=0.44, H_2O/C=1.6, GHSV=9,000 h^{-1}.

Mixed Metal Oxides with the Perovskite Structure

Simple lanthana-based perovskites ($LaNiO_3$, $LaCoO_3$, $LaCrO_3$, $LaFeO_3$, and $LaMnO_3$) were tested for reforming activity using isooctane at 700°C. Yields of 14.3 and 11.3 moles of H_2 per mole of isooctane were observed with $LaNiO_3$ and $LaCoO_3$, respectively. The X-ray diffraction patterns of $LaNiO_3$ and $LaCoO_3$ after testing suggested that the oxides had decomposed into La_2O_3 and metallic Ni and Co, respectively, under the reaction conditions. Yields of 2.6 and 2.5 moles of H_2 per mole of isooctane were observed with $LaCrO_3$ and $LaMnO_3$, respectively, while the H_2 yield of $LaFeO_3$ was 6.4 moles per mole isooctane. The X-ray diffraction patterns of $LaCrO_3$, $LaFeO_3$, and $LaMnO_3$ after testing suggested that these compounds maintained the perovskite structure under the reaction conditions.

In order to stabilize $LaNiO_3$ or $LaCoO_3$, we substituted a portion of Ni or Co with selected transition metals, termed "B-site modifying". Although the B-site-modified $LaNiO_3$ appeared to be structurally stable under reducing conditions (based on a comparison of the X-ray diffraction pattern of the oxide before and after testing), a decrease in the H_2 yield was observed compared with the unmodified $LaNiO_3$, as shown in Table 1. The H_2 yield of the B-site-modified $LaNiO_3$ could be improved by substituting a portion of the La with a lower valent cation, termed "A-site modifying," which introduces oxide ion vacancies (Table 1). An "A,B-site-modified" $LaNiO_3$ exhibited relatively stable performance over a 300-hr period, producing a reformate containing ~35 vol% H_2 from the benchmark fuel at 700°C, as shown in Figure 4. The "A,B-site-modified" $LaNiO_3$ deactivated rapidly when exposed to the benchmark fuel containing 50 ppmw sulfur added as benzothiophene.

Perovskite	Moles of H_2/Mole of Isooctane	
	700°C	600°C
$LaNiO_3$	14.3	10.8
B-site modified $LaNiO_3$	12.6	10.0
A,B-site modified $LaNiO_3$ (I)	13.1	13.5
A,B-site modified $LaNiO_3$ (II)	13.2	11.3

Table 1. Effect of A- and B-Site Modification of $LaNiO_3$ on the Moles of H_2 Produced per Mole of Isooctane for Reforming Isooctane. Conditions: $O_2/C=0.5$, $H_2O/C=1.2$, GHSV=~5,000 h^{-1}.

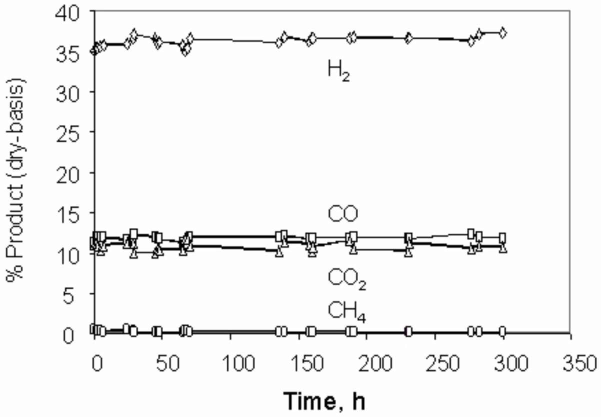

Figure 4. Yields of H_2, CO, CO_2, and CH_4 (mole/mole of fuel) from Reforming Benchmark Fuel Catalyzed by an A,B-Site-Modified $LaNiO_3$ in Powder Form. Conditions: $O_2/C=0.44$, $H_2O/C=1.6$.

Conclusions

Rh- or Ni-CGO supported on a cordierite monolith produced reformates with a higher H_2 concentration than Pt-CGO supported on a cordierite monolith. The better performance of the Rh- and Ni-CGO compared with Pt-CGO is attributed to the higher steam reforming activity of Rh and Ni. Sulfur tolerance is still an issue, since only Pt-CGO has shown sulfur tolerance when reforming fuels with sulfur concentrations in the 30-80 ppmw range. We are working with Süd-Chemie under a CRADA to optimize the activity of the CGO-based catalysts.

A,B-site modified $LaNiO_3$ and $LaCoO_3$ were demonstrated to be active autothermal reforming catalysts and appear to be structurally stable under the reducing reaction conditions. Sulfur tolerance is still an issue based on the rapid decrease in the H_2 concentration in the reformate when reforming sulfur-containing fuels. Future work will focus on improving the activity and the sulfur tolerance of these perovskite catalysts.

Publications/Presentations

1. M. Krumpelt, T. R. Krause, J. D. Carter, J. P. Kopasz, and S. Ahmed, "Fuel Processing for Fuel Cell Systems in Transportation and Portable Power Applications," *Catalysis Today* (submitted for publication).

2. T. Krause, J. Kopasz, C. Rossignol, J. D. Carter, and Michael Krumpelt, "Catalytic Autothermal Reforming of Hydrocarbon Fuels for Fuel Cell Systems," 224th American Chemical Society National Meeting, Boston, MA, August 18-22, 2002.

3. A. L. Wagner, J. P. Wagner, T. R. Krause, and J. D. Carter, "Autothermal Reforming Catalyst Development for Fuel Cell Applications," 2002 Future Car Congress, Arlington, VA, June 3-5, 2002.

4. C. Rossignol, T. Krause and M. Krumpelt, "Role of Metal-Support Interactions on the Activity of Pt and Rh Catalysts for Reforming Methane and Butane," American Institute of Chemical Engineers Spring National Meeting 2002, New Orleans, LA, March 10-14, 2002.

5. M. Krumpelt, T. Krause, J. Kopasz, J. D. Carter, and S. Ahmed, "Catalytic Autothermal Reforming of Hydrocarbon Fuels For Fuel Cells," American Institute of Chemical Engineers Spring National Meeting 2002, New Orleans, LA, March 10-14, 2002.

Patents

1. K. W. Kramarz, I. D. Bloom, R. Kumar, S. Ahmed, R. Wilkenhoener, and M. Krumpelt, "Steam Reforming Catalyst," US Patent 6,303,098 issued October 16, 2001.

2. S. Ahmed, R. Kumar, and M. Krumpelt, "Methanol Partial Oxidation Reformer," US Patent 6,244,367 issued June 12, 2001.

Special Recognitions & Awards

1. R&D Magazine – R&D 100 Award (2001) for Autothermal Reforming Catalyst Technology; Federal Laboratory Consortium Award (2002) for excellence in technology transfer.

IV.C.9 Fuel Processing of Diesel Fuel for Auxiliary Power Units

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Objectives

- Develop understanding of system integration issuesfor diesel fuel powered auxiliary power units (APUs) and provide necessary tools (models) and information to fuel cell/fuel process developers and system integrators for performance optimization and system control.

Approach

- Conduct a systems analysis to understand reformer integration and operational requirements.
- Utilize computational fluid dynamics (CFD) models to understand and address heat and mass transfer issues and reactor performance for steady-state and transient analysis.
- Conduct kinetic rate determination studies in the laboratory to allow for predictive modeling and design of diesel fuel reformers.

Accomplishments

- Identified diesel-based 5-kWe fuel cell auxiliary power unit (APU) system with >50% electrical conversion efficiency
- Developed a prototype CFD model including all the key elements of auto-thermal reforming (ATR)
- Developed a model that accounts for fuel atomization and vaporization, partial oxidation, steam gasification, and anode exhaust gas combustion
- Tested the convergence behavior of the model
- Conducted laboratory kinetic experiments
- Tested platinum (Pt), palladium (Pd), and ruthenium (Ru) catalysts
- Initial rate measurements made for hexadecane and diesel fuel

Future Directions

- Develop a predictive CFD model (Fluent) for diesel reforming
- Conduct steady-state simulations and validate model with ATR experimental data
- Conduct transient analysis
- Use benchmark fuel for kinetic modeling experiments
- Develop a complex reaction model and validate with CFD
- Ultimately, develop a kinetic rate methodology for diesel autothermal reforming catalyst systems

Introduction

The U.S. Department of Energy is sponsoring development of high temperature fuel cell power systems based on solid oxide technology through its Solid State Energy Conversion Alliance (SECA) program. The program is geared at mass manufacturing of fuel cells for high volume markets and multiple applications. One of those markets/applications is a diesel-fueled auxiliary power unit (APU) for long-haul truck transportation. The fuel processor is a critical component of this system and must be able to provide a clean, tailored synthesis gas to the fuel cell stack for long-term operation. Key characteristics desired for the processor (and the system) include low cost, high efficiency, maximum thermal integration, low maintenance intervals, and acceptable startup and transient response. There are several barrier issues that must be overcome to achieve these characteristics. Carbon formation, particularly upon startup, must be minimized to avoid coking of the catalysts in the reformer and downstream fuel cell. Fuels containing sulfur can poison both the reforming catalysts and the fuel cell anode. High thermal mass components (some of which may have heat-ramp restrictions) can limit startup times and transient response. Finally, cost targets must be achieved to ensure commercial success. Depending on the system approach taken, technology is needed to resolve these barriers.

Approach

The objective of this work is to develop understanding of system integration issues for diesel fuel powered APUs and provide the necessary tools (models) and information to fuel cell/fuel process developers and system integrators for performance optimization and system control. A systems analysis was the first activity conducted to help understand reformer integration and operational requirements for the system. One of the more important underlying assumptions of the study is that the reforming catalyst can handle any sulfur content of the fuel, but the sulfur must be removed prior to the fuel gas entering the fuel cell. This may or may not be eventually achieved, but there is some evidence that a viable degree of sulfur tolerance can be attained in the reformer, especially as sulfur content of the diesel itself is being dramatically reduced through Environmental Protection Agency regulations. This assumption could greatly impact the cost/efficiency trade-off of dealing with sulfur in the system. One goal of the systems analysis is to reduce the number of components to keep the system compact and economical, while still having the enough thermal integration to maximize system efficiency.

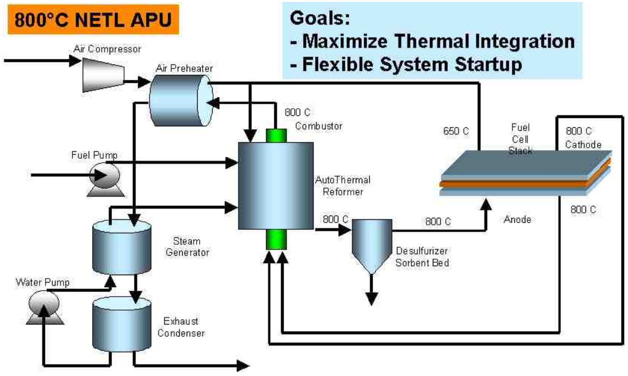

Figure 1. High Efficiency Integral Combustor/Reformer

The next task was to model the reformer itself to understand design issues and be able to predict performance of various reactor/catalyst types and transient behavior. However, upon trying to obtain kinetic rate expressions for the reforming reactions, it was found that very little information existed in the public domain. This led to the decision/need to develop reaction kinetics for catalytic partial oxidation and steam reforming at National Energy Technology Laboratory's (NETL's) onsite research facility.

Results

Systems Analysis: Figure 1 shows a concept identified by NETL for a integrated fuel processor/fuel cell system targeted for diesel APUs. There are several favorable attributes of this system. For example, startup occurs by firing an internal combustor in the dual reactor reformer. This provides heat to the ATR reformer (via conduction) as well as supplying heat to the fuel cell cathode via direct exhaust from the combustor or preheated air from the heat exchanger (optional). If necessary, the ATR is fired in a partial oxidation mode to aid in heatup and to provide heat to the anode side of the fuel cell. At steady-state, all fuel is diverted to the reformer, and the internal combustor acts as a polishing bed to fully oxidize any remaining unburned hydrocarbons from the fuel cell. The figure also depicts a bed of zinc oxide that serves as a polishing bed to remove sulfur from the fuel gas entering the fuel cell. This is just one of several configurations that is being evaluated for this particular system. Depending on the rate of technology development (e.g., sulfur-tolerant reforming catalysts), the system could evolve along one of several pathways. Table 1 shows the effect of system integration of the fuel processor on the efficiency of the overall fuel cell system when compared to stand-alone reformer with external (non shared heat) combustion of anode exhaust. The comparison shows an approximate 7% efficiency improvement due primarily to better thermal integration in the shared heat reformer concept. Fuel flow was kept constant, but it was necessary to vary the fuel/air (F/A) ratio of the non-shared heat system in order to keep the reformer and fuel cell at reasonable temperatures. Increased efficiency of the non-shared case could also be obtained with the addition of another heat exchanger for independent preheat of the reformer and fuel cell inlet air. Unfortunately, this leads to higher cost, footprint, and complexity.

Table 1. Effect of System Analysis on System Efficiency

	Shared Heat	Non-Shared Heat
Fuel (kg/hr)	0.834	0.834
Air – stoichiometric units in	5	5.2
ATR F/A Ratio	9	3.5
Steam/Carbon Ratio	0.8	0.8
Efficiency	50.21	42.39
Net Power	5.0	4.221
ATR Temperature	800	800
Fuel Cell Temperature	805	813

Reformer Modeling: NETL is also developing a CFD model in Fluent to understand and address the heat and mass transfer issues and reactor performance for steady-state and transient analysis.

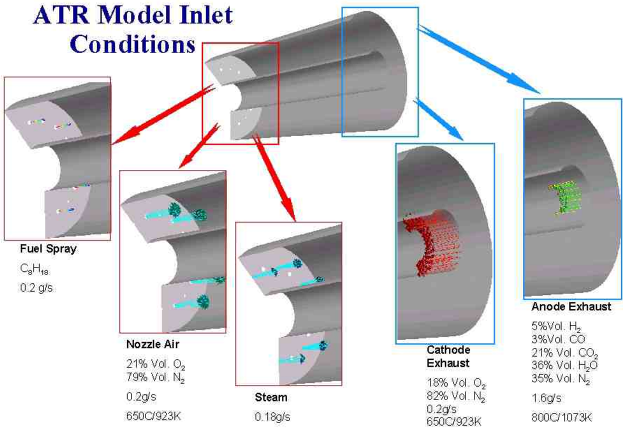

Figure 2. ATR Model Inlet Conditions

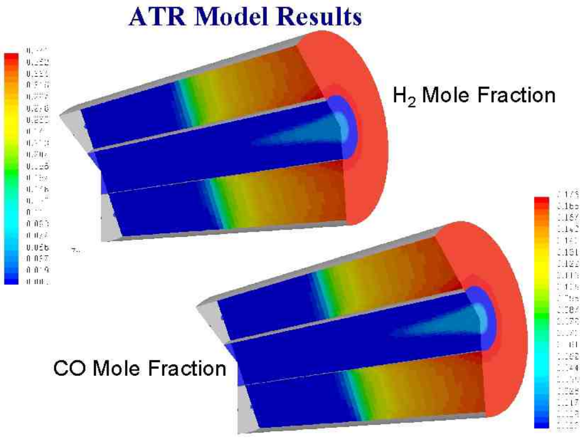

Figure 3. ATR Model Results

This model accounts for fuel atomization and vaporization, partial oxidation, steam reforming, and anode exhaust combustion. It is asumed that the partial oxidation reaction is very fast and occurs at the top of the catalyst bed along with fuel atomization and vaporization. It is also assumed that the steam reforming initiates after all O_2 is consumed in the partial oxidation reaction. Therefore, the reactor will initially be considered as two plug-flow reactors in series. Figure 2 and 3 depict the inlet conditions for the ATR model and results from the model, respectively.

Kinetic Measurements: Preliminary studies have been conducted for the kinetic model development for the autothermal reforming of diesel fuel. Three different catalysts (g-alumina supported Pt, Pd, and Ru) were evaluated to obtain data for the ATR kinetic modeling.

A fixed bed reactor system was used to conduct the diesel ATR experiments. The reactor was operated continuously at steady state. The temperature was varied between 750 – 850°C, oxygen/carbon ratio was 0.6, steam/carbon ratio was 1.5, and the gasl hourly space velocity was 25,000 - 200,000 hr^{-1}. Table 2 shows the surface area, porosity, pore size distribution, metal loading, and metal dispersion of the catalysts used in the study.

Table 2. Physicochemical Properties of Catalyst used in Diesel ATR

Catalyst	N_2 BET Surface area (m^2/g)	Dispersion (%)	Pore Volume (cc/g)	Avg. Pore Size (A)
0.611 wt% Pt on γ-alumina	103	60	0.27	104
0.699 wt% Pd on γ-alumina	103	88	0.28	107
0.423 wt% Ru on γ-alumina	122	33	0.27	87

Figure 4 compares the product distribution from ATR of diesel from three different catalysts at 850 °C. The γ-Alumina supported ruthenium catalyst proved to be the most active catalyst in producing synthesis gas from diesel ATR.

Kinetic modeling of diesel autothermal reforming is extremely complicated. Diesel fuel consists of a complex variable mixture of hundreds of hydrocarbon compounds containing paraffins, isoparaffins, naphthenes, aromatics, and olefins. To simplify the model, a steady-state power law rate expression for the diesel reforming over each type of catalyst used in this study was developed. A linearized least-squares method of data analysis was used to determine the power law parameters from a series of diesel ATR experiments. The power law rate model for diesel autothermal reaction may be written as:

$$-r_{HC} = ke^{\frac{-E_A}{RT}} C^a{}_{HC} C^b{}_{H_2O} C^c{}_{O_2} \qquad \text{(I)}$$

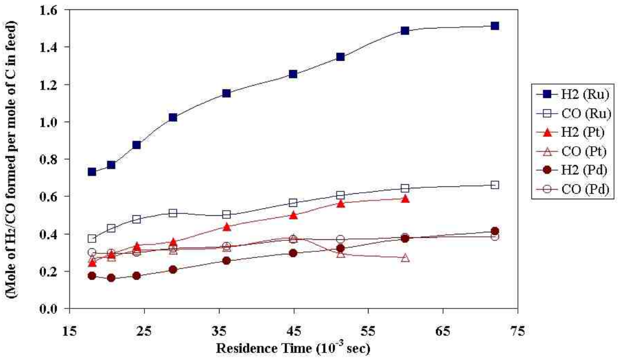

Figure 4. Product Distribution from ATR of Diesel (T=850°C, O_2/C=0.3, S/C=1.5)

Equation (I) is linearized so that a linear least square approach could be employed to solve for the activation energy, E_A, and the reaction orders in hydrocarbon (HC), a, H_2O, b, and O_2, c.

$$\ln(-r_{HC}) = \ln(k) - \frac{E_A}{RT} + a\ln(C_{HC}) + b\ln(C_{H_2O}) + c\ln(C_{O_2}) \qquad \text{(II)}$$

The resulting activation energy, preexponential factor, and the reaction order with respect to each reactant are presented in Table 3. A comparison of data predicted from the power law model to the experimental data shows the goodness of fit (correlation factor: ~92% for Pt and Pd, and ~72% for Ru). The ATR rate shows a non-monotonic dependence with respect to oxygen varying from positive to negative. By looking at the very low reaction orders with respect to oxygen from each kind of catalyst used in this study, it can also be concluded that the rate of diesel ATR is almost independent of oxygen. Good agreement has been found between Pd and Pt catalysts with respect to reaction order and activation energy. The negative order with respect to water shows that the water present in the system strongly inhibits the rate of reaction.

Autothermal reforming of single components such as n-hexadecane and toluene was also performed at the same reaction conditions as the diesel ATR to understand the reaction mechanisms and pathways for the ATR system.

Table 3. Kinetic Parameter for Diesel Reforming from Three Different Catalysts

Catalyst	Pre-Exponential Factor[1]	Activation Energy[2]	a	b	c
Pt/γ-Al_2O_3	18.4	16.5	0.87	1.02	0.13
Pd/γ-Al_2O_3	44.7	16.4	0.74	1.07	0.10
Ru/γ-Al_2O_3	0.02	9.7	0.50	1.39	0.03

Units: [1]$(L/mol)^{a+b+c-1}$/sec; [2]kcal/mol

Conclusions

A novel fuel processor is configured at NETL to integrate the fuel cell system for process optimization and system control. In the proposed system, startup occurs by firing an internal combustor in the dual reactor reformer, which provides heat to the ATR reformer via conduction as well as supplying heat to the fuel cell cathode via direct exhaust from the combustor.

A CFD model in Fluent was also developed by NETL to understand and address the heat and mass transfer issues and reactor performance for steady-state and transient analysis.

A power law-type kinetic model for diesel ATR has also been presented, which provides preliminary insight into reaction kinetics and will provide direction for future high level kinetic modeling.

FY 2002 Presentations/Publications

1. Gardner, T. H., Berry, D. A., James, R. E., Lyons, K. D., Monahan, M. J. "Fuel Processor Integrated H_2S Catalytic Partial Oxidation Technology for Sulfur Removal in Fuel Cell Power Plants". FUEL, Vol. 81, issue 17, September 2002.

2. Berry, D. A., Gardner, T. H., James, R. E., Rogers, W., Shekhawat, D., "Processing of Diesel for Fuel Cell Auxiliary Power Systems", 3rd Annual Department of Defense Logistic Fuel Reforming Workshop, Panama City, Florida, August 26 – 29, 2002.

3. Surdoval, W. A. and Berry, D. A, "Solid State Energy Conversion Alliance", 3rd Annual Department of Defense Logistic Fuel Reforming Workshop, Panama City, Florida, August 26 – 29, 2002.

4. Berry, D. A., Gardner, T. H., James, R. E., Rogers, W., Shekhawat, D., "Fuel Processing of Diesel Fuel for Fuel Cells", 2002 SECA Core Review Conference, Pittsburgh, Pennsylvania, June 18 – 19, 2002.

5. Berry, D. A., Gardner, T. H., James, R. E., Rogers, W., Shekhawat, D., "Fuel Processing of Diesel for Fuel Cells", 2002 Fuel Cells for Transportation Program / Lab R&D Review, Department of Energy Office of Transportation Technology, Denver, Colorado, May 6 – 10, 2002.

IV.C.10 Testing of Fuels in Fuel Cell Reformers

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Objectives

- Explore effects of fuels, fuel components, additives and impurities on the performance of hydrogen generation technologies
  - Examine fuel composition effect on energy efficiency, durability, cold startup, transients, NH_3 concentration, cost, and power density
  - Understand the parameters that affect fuel processor and fuel cell lifetime and durability

Approach

- Examine fuel effects on fuel processing by testing fuels in automotive scale, adiabatic reactors
  - Examine individual fuel components
  - Examine fuel component blends
  - Examine ‘real’ fuels (reformulated gasoline, naptha)
  - Examine fuel additives (anti-oxidants, detergents, impurities)
- Model fuel reforming chemistry
  - Model carbon formation
  - Model equilibrium gas composition
  - Model thermodynamic properties

Accomplishments

- Tested iso-octane, iso-octane/xylene, methylcyclohexane, naptha, reformulated gasoline, diesel components, anti-oxidants, and nitrogen containing hydrocarbons; monitored ammonia formation with
  - Aliphatic and napthenic hydrocarbons
  - Catalytic and homogeneous oxidation
  - Nitrogen bound compounds (anti-oxidants)
- Monitored carbon formation with *in situ* laser diagnostics
  - Monitored carbon formation for various fuel components
  - Monitored carbon formation during start-up and shut-down

Future Directions

- Evaluate effects of fuel constituents on fuel processor operation
  - Monitor carbon formation *in situ* with an adiabatic reactor and laser scattering

    - Monitor carbon formation during start-up and reactor transients
    - Define methods of operation for fast, repetitive start without carbon formation
  - Develop capabilities to monitor carbon formation with *in situ* gravimetric analysis steam reforming apparatus
    - Delineate carbon formation mechanisms
    - Measure carbon effect on reforming kinetics
    - Measure carbon formation kinetics
  - Measure fuel additive and impurity effects on performance and carbon formation
    - Sulfur effect
    - Oxygenated hydrocarbons
- Integrate fuel cell stack testing with fuel processor operation to evaluate system integration effects of fuels

Introduction

This report describes our FY02 technical progress in examining the effects of fuel on hydrogen generation for proton exchange membrane (PEM) fuel cells for transportation. The goal of this research is to explore the effects of fuels, fuel constituents, additives and impurities on the performance of on-board hydrogen generation devices and, consequently, on the overall performance of a PEM fuel cell system using a reformed hydrocarbon fuel. Understanding the fuel effects on the durability of PEM fuel cell systems is key for their commercial use.

Different fuels and components have been tested in automotive scale, adiabatic reactors to observe their relative reforming characteristics with various operating conditions. Ammonia (NH_3) formation was monitored, and conditions were varied to observe under what conditions NH_3 is made. Nitrogen-bound hydrocarbons were added to fuels to determine their effect on NH_3 formation. Carbon formation was monitored during fuel processor operation by *in situ* laser measurements of the effluent reformate. Fuel composition effects on carbon formation were measured.

Approach

To examine the effect of the fuel on hydrogen production devices, various fuel components and real fuels have been tested in autothermal reformers (ATRs) and fuel reforming systems. Fuel reformers used for these experiments are automotive-scale reactors, and are operated adiabatically, such as systems likely will operate in vehicles. The analysis of the fuel effect on the product composition stream is conducted by various analytical techniques, specifically laser scattering and laser flourescence, gas chromatography, FTIR (fourier transform infrared), NDIR (non-dispersive infrared), paramagnetic oxygen and GC/MS (gas chromatography/mass spectrometry). Ammonia formation from various fuels and for different operating conditions was measured by FTIR. Carbon formation for different operating conditions and fuel components was monitored by *in situ* laser scattering. Mapping of the onset of carbon formation for different fuel components as a function of operating conditions has been conducted with these techniques. The reactor with catalyst observation windows, laser extinction, and scattering facilities is shown in Figure 1. Expected outlet concentrations of the fuel reformer and the relative fuel component effects on the fuel reformer outlet have been modeled. In particular, modeling of equilibrium carbon formation has been used to predict the operating conditions for the onset of carbon formation for various fuel blends.

Specific fuel compositions and components measured include iso-octane, xylene, methylcyclohexane, naptha and California reformulated gasoline. Additives examined include anti-oxidant No. 29 (2,6-Di-Tert-Butyl-4-methylphenol), anti-oxidant No. 22 (N, N’-Di-Sec-Butyl-P-Phenylenediamine) and DMA-548.

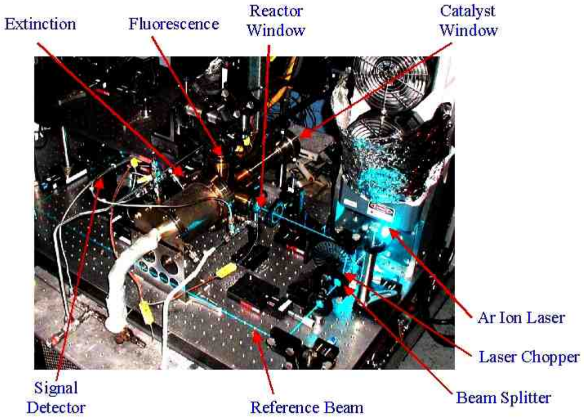

Figure 1. Catalytic partial oxidation with facilities for laser extinction and scattering measurements with catalyst observation.

Results

Fuel Effects Comparisons in Catalytic Partial Oxidation

The relative rates for catalytic partial oxidation for different fuels have been measured for various operating conditions. Figure 2 shows relative reaction rates for various fuel components, mixtures, and a Phillips Petroleum Hydrotreated Naptha stream at a S/C of 1.0. The relative reaction rates vary as the O/C ratio varies due to temperature changes. At lower O/C ratios, the adiabatic temperature rise is lower, thus the overall reaction rate is lower. The reaction rate for all components are higher at higher O/C, and subsequently, higher temperatures. The oxidation rates for O/C's of 0.7 and 0.8 are fastest for iso-octane. The addition of aromatics such as xylene slows the kinetics and conversion. Real fuel composition mixtures such as the Phillips Naptha and California reformulated gasoline show an oxidation rate faster than that of iso-octane/xylene mixtures even though the relative aromatic concentration is approximately the same. At high O/C ratios (O/C = 1.0), the real fuel mixtures show an equal or faster oxidation rate compared with pure iso-octane. The resulting decrease in kinetics due to the presence of aromatic hydrocarbons indicates that the fuel composition will have an effect on the required size (and cost due to catalyst loading) of the fuel processor. If it is possible to make a non-aromatic containing fuel available, the fuel processing size and cost would be positively effected.

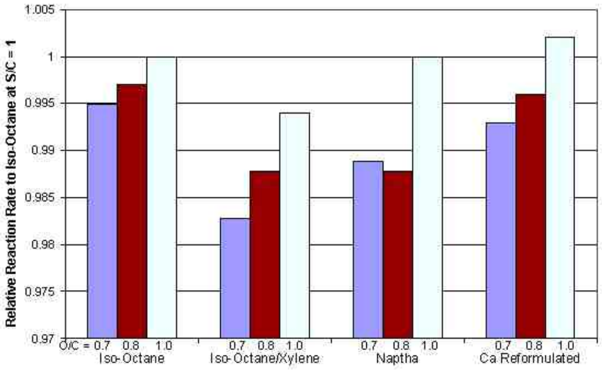

Figure 2. Relative oxidation rates of iso-octane, iso-octane/20% xylene, Phillips Naptha and California reformulated gasoline.

Ammonia Formation

Ammonia formation in the fuel processor is a concern, as NH_3 is a poison to PEM fuel cell membranes and ionomer.[1] As ammonia is known to degrade the performance of fuel cells, the DOE has targeted the outlet concentration for ammonia formation is < 0.5 ppm for 2005 and < 0.1 ppm by 2010. However, little has been published about the generation of NH_3 in ATR reactors. To examine this issue, an FTIR was set up to monitor the reactor effluent and calibrated to a detection limit of 400 ppb (parts-per-billion) of NH_3 with the presence of ethylene. Without the presence of ethylene, the detection limit of NH_3 is significantly lower, < 100 ppb. Figure 3 shows FTIR spectra for NH_3 calibration and of reformate from the partial oxidation and reforming of MCH (methylcyclohexane). Small amounts of NH_3 are easily measured in a pure N_2 background with the major peak at 967 cm^{-1}; however, with the addition of ethylene, the sensitivity is greatly reduced, since ethylene has a minor peak near 967 cm^{-1}. With the addition of 100 ppm ethylene, the NH_3 sensitivity is reduced to about 400 ppb. Normal catalytic partial oxidation of fuel components does not show a measureable NH_3 concentration (see curve 3(c)).

Precombustion can occur in a reformer due to mixing air/fuel at high temperatures; this is essentially homogeneous combustion before the catalyst surface and typically an operation mode

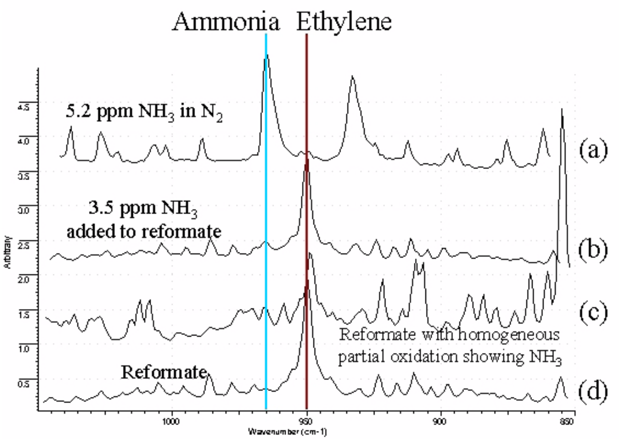

Figure 3. FTIR spectra of (a) 5.2 ppm NH_3 in N_2, (b) 3.5 ppm NH_3 added to MCH reformate, (c) reformate from homogeneous partial oxidation of MCH showing ethylene and 11 ppm NH_3, and (d) reformate from the catalytic partial oxidation of MCH showing ethylene and 0 ppm NH_3.

which is avoided. However, when pre-combustion of fuels occurs (homogeneous combustion upstream of the catalyst) as in 3(c), NH_3 is observed, in this case at a concentration of 11 ppm.

Nitrogen-containing hydrocarbons are present in gasoline fuels. These can be small amounts of naturally occurring hydrocarbons, or they can be anti-oxidants or detergents with amine groups added to the fuel, such as Anti-oxidant No. 22 (N, N'-Di-Sec-Butyl-P-Phenylenediamine). To determine the conversion products of nitrogen-containing hydrocarbons, 50 ppm of Anti-oxidant No. 22 was added to MCH to observe potential NH_3 formation. In addition, pyridine was added to a pure fuel to observe whether NH_3 formation would occur at higher concentrations of nitrogen-containing hydrocarbons. Figure 4(a) shows FTIR spectra of reformed MCH with 10% pyridine added. The measured NH_3 in the reformate was 414 ppm NH_3. When 1% pyridine was added to MCH, the reformate analysis measured 54 ppm NH_3. When 50 ppm of the nitrogen containing anti-oxidant was added, no NH_3 was observed (Figure 4(c)).

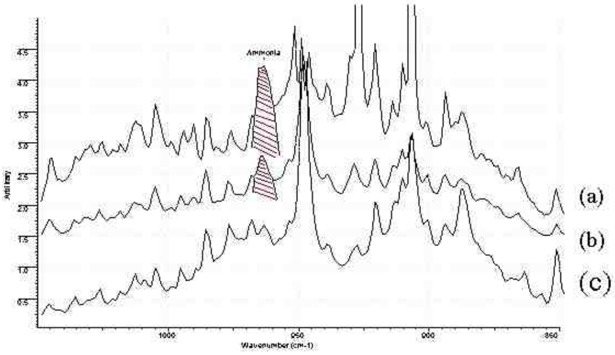

Figure 4. FTIR spectra of reformed (a) MCH (methylcyclohexane) with 10% pyridine, (b) MCH with 1% pyridine, and (c) MCH with 50 ppm of anti-oxidant.

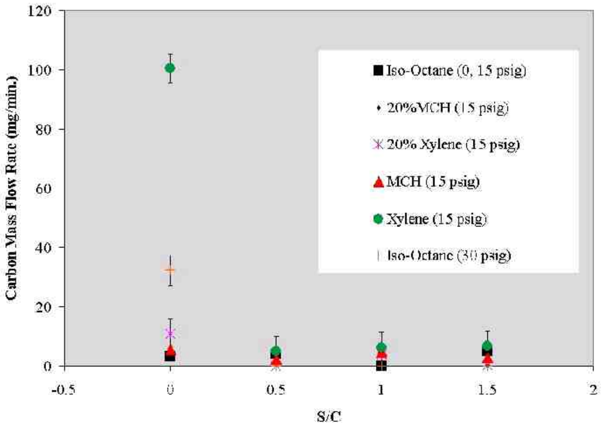

Figure 5. Equilibrium modeling of carbon formation for various fuels and conditions. The dashed conditions are potential start-up scenarios, depending upon whether water is available during reactor start-up.

Carbon Formation

Carbon formation is recognized to be a potential limiter of fuel processor ATR durability. Equilibrium calculations can identify proper operating conditions to prevent carbon formation; however, during the start-up of the fuel processor, avoiding non-zero carbon equilibrium is difficult. Laser extinction measurements have been conducted to observe carbon formation for different fuel components. An example of this is shown in Figure 5. The residence time of this reactor was short, about 10 msec. As the S/C ratio is decreased, carbon formation is detected by a decrease in the laser extinction signal, which is converted to a mass flow rate of carbon formed. Little measurable carbon was formed until equilibrium conditions predicted carbon formation.

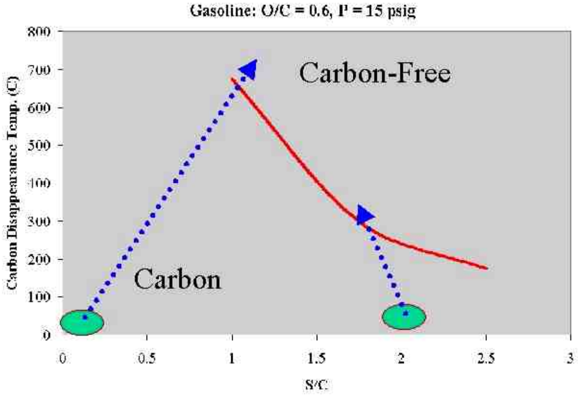

Figure 6. Mass flow rate of carbon formation for various fuel components and component blends. O/C = 0.65.

Aliphatic hydrocarbons such as iso-octane could be reformed without significant carbon formation even when equilibrium predicted carbon formation. However, the addition of aromatic hydrocarbons caused significant carbon formation. The addition of anti-oxidants to the fuel stream did not make any measurable difference in carbon formation.

Figure 6 shows the minimum temperature at which the equilibrium concentration of carbon is zero as a function of S/C ratio. During start-up, water may not be available to suppress carbon formation. In this case, lighting off a partial oxidation reactor without water could result in large amounts of carbon formation. Figure 7 shows the lightoff of a partial oxidation reactor with low amounts of water. As the temperature approaches normal operating conditions, large amounts of carbon are observed via laser scattering.

Carbon formation has been observed to occur both in the partial oxidation/steam reforming catalyst and in the reformate after it exits the catalyst. Analysis of carbon formed in the steam reformer catalyst found that the carbon was mostly carbonaceous carbon with an approximate H/C ratio of 0.2 – thus about 97% carbon. Carbon that formed in the reformate after it exited the catalyst (probably from unconverted hydrocarbons) has been analyzed to contain 30% by weight solidified hydrocarbons.

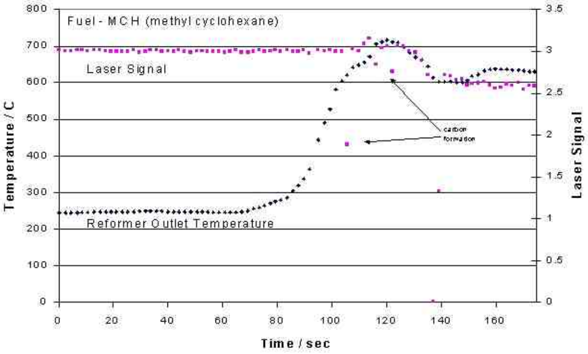

Figure 7. Carbon formation during ATR start-up. Reactor was preheated to 250^{o}C, and started up with an O/C=1.0 and S/C = 0.0.

Conclusions

Fuel component effects are being examined to determine their effect on hydrogen generation technologies. Measurements show that the fuel composition does effect the design and operation of the fuel reformer, and fuel blends low in aromatic content show higher reforming kinetics, which result in a reduced fuel processor size (and thus cost). The fuel composition effect also effects the relative carbon formation, which will effect the fuel processor durability.

Various fuel components and fuels have been tested with various O/C and S/C ratios in partial oxidation/steam reforming reactors. The addition of aromatics slows the overall reaction rate for catalytic oxidation. Real fuels have similar oxidation rates at high O/C compared with iso-octane, but lower oxidation rates at O/C < 1.0.

Ammonia formation was not observed at a measurable concentration for normal operating conditions with expected fuel compositions. Pre-combustion of fuels lead to the formation of NH_3 measured at 11 ppm NH_3. Large concentrations of nitrogen-containing hydrocarbons lead to higher amounts of NH_3 formation.

Laser extinction measurements mapping the onset of carbon formation have been conducted. Carbon formation was quantified by the laser extinction measurement. Post analysis of carbon formed indicates the method and cause of carbon formation lead to different carbonaceous species.

Carbon formed in the steam reformer was mostly carbonaceous carbon with an approximate H/C ratio of 0.2, while carbon formed downstream from the reformer consisted of high amounts of solidified hydrocarbons.

Acknowledgments

The authors would like to thank Fred Cornforth of Philips Petroleum for supplying the fuels and anti-oxidants used in this testing.

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IV.C.11 Sulfur Removal from Reformate

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Objectives

- Adapt proven technologies for on-board fuel processing to be capable of reducing the H_2S concentration to <1 ppm in reformate.
- Develop new technologies or improve existing technologies to meet the DOE targets for H_2S removal: (1) H_2S concentration of <10 ppb in reformate (FY 2010), (2) a reactor size of <0.06 L/kWe (<0.06 kg/kWe), and (3) GHSV of 50,000 h^{-1}.

Approach

- Predict the H_2S equilibrium partial pressure for candidate adsorbents (metal sulfide-H_2S equilibrium) and identify candidate materials.
- Synthesize mixed metal oxides consisting of CuO/Cu_2O and another first-row transition metal oxide based on thermodynamic calculations.
- Conduct experimental studies in a microreactor system to evaluate the H_2S concentration in the effluent as a function of temperature and the gas composition for candidate mixed metal oxides.

Accomplishments

- Synthesized various mixed metal oxides consisting of CuO/Cu_2O and screened them for H_2S uptake in a microreactor system.
- Determined that competitive adsorption between H_2O and H_2S inhibits H_2S uptake by these mixed metal oxides.

Future Directions

- Work to improve the H_2S uptake performance of mixed metal oxides containing predominantly Cu oxides.
- Evaluate the use of metal doping to increase the rate of H_2S uptake by ZnO.
- Evaluate the impact of using liquid-phase sulfur adsorption on the H_2S removal requirements of the fuel processor.
- Better define the sulfur removal requirements for the fuel processor based on sulfur tolerance studies for the ATR and WGS catalysts.

Introduction

New EPA regulations will significantly lower the sulfur content of gasoline from the current average of 300 ppmw to an average of 30 ppmw with a maximum of 80 ppmw by the year 2006. For on-board fuel processing for transportation applications, reformate produced by autothermal reforming of these gasolines will contain 3-8 ppmv of H_2S. Even at these low concentrations, H_2S is known to poison many of the catalysts being developed for use in the fuel processor and in the fuel cell anode for PEMFC systems. For example, an H_2S concentration of <50 ppb is recommended for copper-zinc oxide water-gas shift catalysts. Studies have shown that the Pt-anode catalyst in the PEMFC is irreversibly poisoned at an H_2S concentration as low as 50 ppb (Uribe et al. 2002).

Two different approaches are being considered for on-board sulfur removal. The first approach involves liquid-phase desulfurization of the fuel prior to reforming using a nickel-based adsorbent to remove organosulfur compounds (Bonville et al. 2000). While liquid-phase desulfurization can significantly reduce the sulfur content of the fuel, it is not clear whether the extent of desulfurization achieved by this process will meet the requirements for the fuel processor and fuel cell stack without additional removal of sulfur in the fuel processor. The second approach involves gas-phase desulfurization of reformate in the fuel processor using a metal oxide adsorbent, typically ZnO, to remove H_2S. Gas-phase desulfurization requires that the reforming catalyst be sulfur tolerant at least to the concentration of sulfur present in the fuel.

Gas-phase desulfurization using ZnO is the approach that we have pursued in past years. ZnO is an attractive adsorbent for on-board fuel processing because of its favorable sulfidation thermodynamics (<1 ppmv). The sulfidation equilibrium for ZnO ($ZnO + H_2S \Leftrightarrow ZnS + H_2O$) is a function of the temperature and the ratio of the partial pressure of H_2O/H_2S. To reduce the H_2S concentration to <0.1 ppmv requires a temperature of 300-350°C based on the typical range of H_2O concentrations present in the reformate (Carter et al. 2001). However, it has been observed that although the equilibrium becomes more favorable as the temperature is lowered, the concentration of H_2S in the reformate after contacting ZnO actually increases with decreasing temperature because of a significant decrease in the rate of H_2S uptake (Carter et al. 2001).

We have begun to investigate mixed metal oxide systems predominantly based on copper oxide. Copper oxides (CuO and Cu_2O) have sulfidation equilibrium constants among the highest of all metal oxides and could potentially achieve sub-ppb concentrations of H_2S in reformate, as shown in Figure 1. Unfortunately, CuO/Cu_2O is readily reduced to metallic Cu in reformate, which significantly reduces the desulfurization efficiency. In order to maintain Cu in the +1/+2 oxidation state, researchers have focused on combining CuO/Cu_2O with other metal oxides (Li and Flytzani-Stephanopoulos 1997), which is the approach that we are investigating.

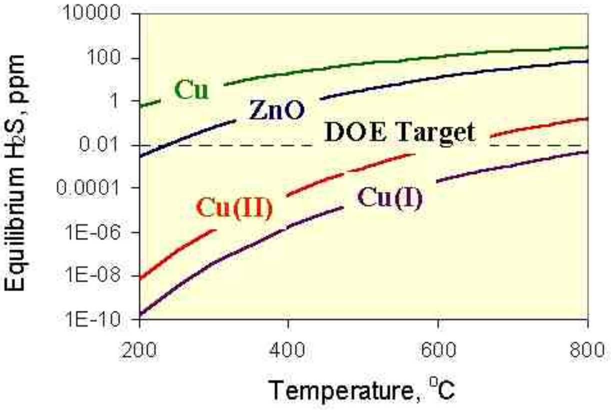

Figure 1. Equilibrium concentration of H_2S as a function of temperature in the presence of 20 vol% H_2O or H_2 for Cu_2O, CuO, Cu and ZnO.

Approach

Mixed metal oxides consisting of a combination of Cu and another first-row transition metal oxide, such as Co, Mn, and Ni, were synthesized by various techniques, including coprecipitation and glycine-nitrate combustion. Some of the mixed metal oxides were dispersed on a high-surface-area δ-alumina. The H_2S uptake of the candidate metal oxides was evaluated using a microreactor system with an on-line gas chromatograph equipped with a flame photometric detector and an on-line H_2S analyzer equipped with a lead acetate detector. The typical experimental protocol involved exposing a sample of the mixed metal oxide to four different gas compositions (50 ppm H_2S/N_2, 50 ppm H_2S/reformate [dry], 10 ppm H_2S/10%H_2O/reformate, and 50 ppm H_2O/20% H_2O/reformate) at temperatures ranging from 150 to 550ºC using a heating rate of 2ºC/min. The GHSV was 5,000 h^{-1}. The gas composition was varied to study the effect of the various components in reformate (H_2O, CO, and CO_2) on the uptake of H_2S by the mixed metal oxide.

Results

Figure 2 shows the H_2S concentration in the effluent from the microreactor for the four different gas compositions as a function of temperature for a Cu-Co oxide. The H_2S concentration in the effluent was <1 ppm over a temperature range of 250-450ºC for the gas composition containing only H_2S and N_2. When the gas composition was changed to a dry reformate containing CO, CO_2, and H_2 in addition to N_2, an H_2S concentration of ~1-2 ppm was observed at 330-380ºC. At 240-280ºC, the H_2S concentration was ~5 ppm, which is slightly higher than at 330-380ºC; however, it appears that a significant portion of the H_2S was converted to COS (Figure 3). It is not known whether COS is produced by the reaction with CO ($CO + H_2S \Leftrightarrow COS + H_2$) or with CO_2 ($CO_2 + H_2S \Leftrightarrow COS + H_2O$); however, assuming that some of the oxidized Cu or Co is reduced to metallic Cu or Co, the CO pathway is more probable due to the higher affinity of these metals for CO than CO_2. The presence of H_2O in reformate (10 or 20 vol%) resulted in higher H_2S concentrations in the effluent than in the absence of H_2O (Figure 2). The observation that the H_2S concentration in the effluent increased with increasing H_2O concentration suggests that competitive adsorption between H_2O and H_2S inhibits H_2S uptake by the oxide. As shown in Figure 3, the presence of water inhibits the formation of COS.

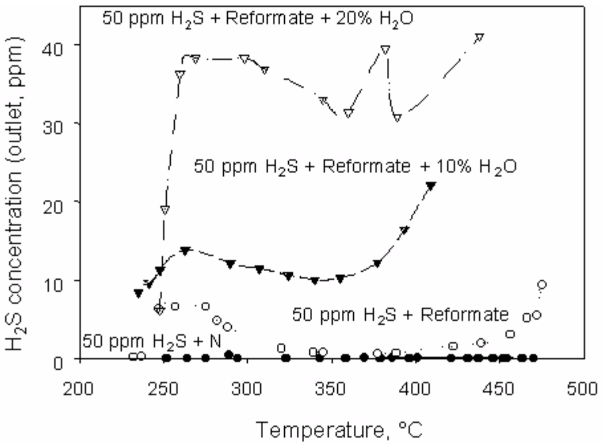

Figure 2. Concentration of H_2S in the effluent as a function of temperature for four different gas compositions, each containing 50 ppm H_2S. The adsorbent is a Cu-Co oxide.

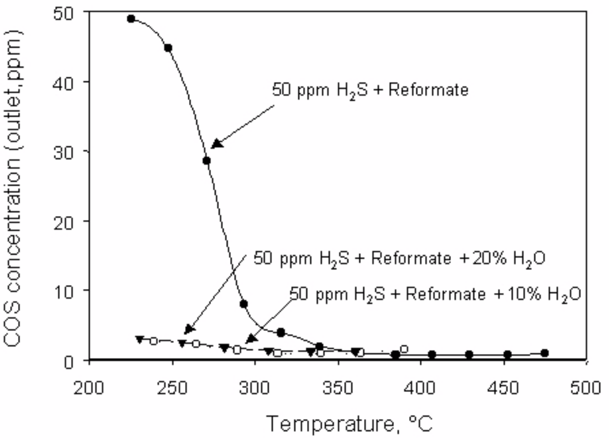

Figure 3. Concentration of COS in the effluent as a function of temperature for four different gas compositions, each containing 50 ppm H_2S. The adsorbent is a Cu-Co oxide.

Although H_2S uptake data are presented for only one Cu-containing composition, i.e., Cu-Co, similar behavior has been observed, in terms of the effect of H_2O and CO/CO_2 on H_2S uptake, for other Cu-containing oxides investigated.

Conclusions

Although the sulfidation equilibria suggest that CuO/Cu_2O should be able to reduce the H_2S concentration in reformate below the 10 ppb DOE target, initial screening of various Cu-containing mixed metal oxides suggests that competitive adsorption between H_2O and H_2S may inhibit H_2S uptake. As a consequence, the H_2S concentration that is predicted by the sulfidation equilibrium may not be achieved. Future work will focus on confirming that (1) oxidized Cu can be stabilized in reformate under fuel processing conditions, (2) sulfidation is occurring at oxidized Cu, and (3) competitive adsorption between H_2O and H_2S inhibits H_2S uptake.

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IV.C.12 Nanoscale Water Gas Shift Catalysts

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Main Subcontractors: University of Pennsylvania, Catalyte, LLC, Süd-Chemie, Inc.

Objectives

- Develop synthesis methods for highly active water-gas-shift (WGS) catalysts based on platinum supported on nanoscale ceria-based oxides.
- Develop and scale up washcoating process for depositing Pt/ceria catalysts on monolithic supports, and demonstrate high WGS activity in monolith-supported catalysts.
- Demonstrate that Pt/ceria catalysts can meet application-specific requirements for the WGS reactors of automotive fuel processors, which include: resistance to degradation by exposure to air; ability to withstand repeated temperature cycles during operational transients; and stable operation over a wide temperature range.
- Demonstrate that DOE technical targets for size, weight and cost of water-gas-shift reactors can be met using monolith-supported Pt/ceria catalysts.

Approach

- Use wet-chemical synthesis methods to prepare aqueous suspensions of nanoscale ceria-based oxides and to incorporate platinum onto ceria nano-particle surfaces.
- Optimize of catalyst synthesis methods and formulations through extensive micro-reactor testing and use of characterization techniques such as temperature programmed reduction and CO chemisorption.
- Collect of long-term micro-reactor test data to assess catalyst deactivation rates, and correlate catalyst activity and deactivation rates with catalyst formulation and synthesis methods.
- Collect micro-reactor data at different temperatures and gas compositions to determine kinetics of Pt/ceria WGS catalysts. Use these kinetic data in a model for estimating the size, weight and cost of monolith-supported catalysts for 50-kW scale WGS reactors.
- Modify Pt/ceria catalyst suspensions with surfactants and binders, and washcoat catalysts onto ceramic honeycomb monoliths.
- Conduct extensive sampling of Pt/ceria catalyst powders, pellets, and washcoated monoliths for evaluation by Süd-Chemie, HydrogenSource, and other fuel processor developers.

Accomplishments

- A number of highly active and stable Pt/ceria catalyst formulations have been demonstrated, with performance sufficient for the automotive fuel processor application.
- A washcoating process has been developed for monoliths with catalyst loadings up to 400 grams per liter, and excellent performance has been demonstrated in these monoliths.

- A fundamental understanding of WGS kinetics for Pt/ceria catalyst system has been established, and a kinetic model has been developed to allow realistic comparisons of data obtained under different test conditions.
- Based on the kinetic model, it is estimated that for a 50-kW scale WGS reactor, CO levels can be reduced to less than one percent using a monolith with a weight of less than a kilogram, a volume of less than a liter, and a cost of less than $150.

Future Directions

- This project ends March 31, 2003. Plans for the remainder of the project include scale-up of the monolith washcoating process and testing of a 10-kW scale monolith at HydrogenSource.

Introduction

A major technical barrier to commercialization of PEM fuel cells in automobiles is the need for a fuel processing system to convert liquid fuels, including gasoline into a hydrogen-rich gas. The fuel processor must be small enough to fit into the confined spaces of a vehicle. The system must also be able to perform reliably under highly variable power loads, be capable of rapid start up, and deliver a gas stream containing very low levels of carbon monoxide. The water-gas shift (WGS) reactor is a critical component of the fuel processor. Its function is to reduce carbon monoxide levels to intermediate levels, which can then be further reduced in a subsequent preferential oxidation step. Commercial copper-based WGS catalysts are unsuitable for transportation applications because of the tendency of the catalysts used in these reactors to degrade under the severe conditions encountered in an automotive system.

NexTech Materials is collaborating with the University of Pennsylvania, Süd-Chemie, Catalyte, HydrogenSource, and McDermott Technology to develop catalytic water-gas-shift reactors that meet the needs of the automotive PEM fuel cell systems. The catalyst being developed is based on nanoscale mixtures of ceria-based oxides and uniformly incorporated platinum. Compared to existing copper-based catalysts, the Pt/ceria system offers several advantages: (1) operation at higher temperatures (where kinetics are more favorable); (2) no need for activation prior to use; (3) no degradation upon exposure to air; and (4) availability of conventional washcoating technologies for ceria-based catalysts (reduced size and weight, improved ruggedness).

Approach and Results

Results of work performed during the past year are summarized below:

Catalyst Characterization and Testing: NexTech's micro-reactor was refined to allow collection of reliable test data over extended time periods. Much of the catalyst testing work focused on long-term catalyst performance, to support the development of high-activity and stable catalysts. In parallel, catalysts were characterized by surface area, temperature-programmed reduction (TPR), and CO chemisorption methods. The results suggest that optimization of platinum dispersion (as measured by CO chemisorption) is important to achieving high activity and suppressing deactivation. Reducibility of the precious metal (as measured by TPR) does not appear to be related to WGS activity.

Formulation Development: Improvements in WGS performance were achieved by optimizing the ceria composition, synthesis processes for the nanoscale ceria support, and platinum incorporation methods. Long-term micro-reactor test results suggest that proper synthesis conditions are required to produce highly active and stable catalysts (Figures 1 and 2). Low de-activation rates were achieved by modifying the ceria support composition and by optimizing the precious metal dispersion. Pt/ceria catalysts can be regenerated by heating in air (Figure 3).

Monolith Washcoating and Testing: A process was developed for applying Pt/ceria catalyst coatings onto ceramic honeycomb monoliths (see Figure 4), and high catalyst loadings (>350 grams per liter) were achieved. Results obtained at Süd-Chemie indicate that these monoliths provide exceptional

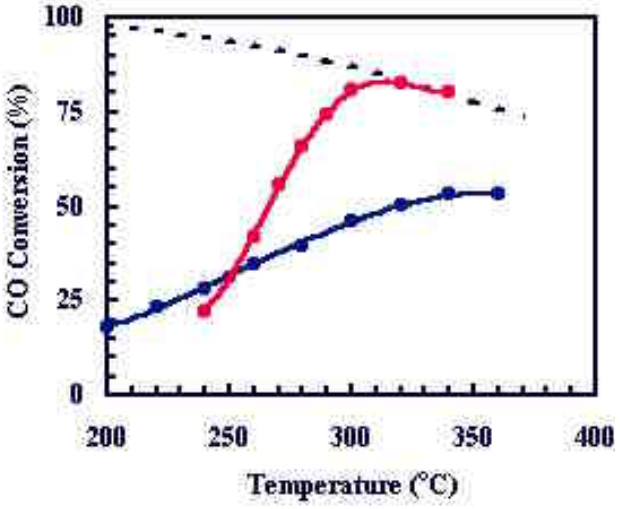

Figure 1. Comparison of temperature dependence of Pt/ceria and commercial (Cu/ZnO) catalysts.

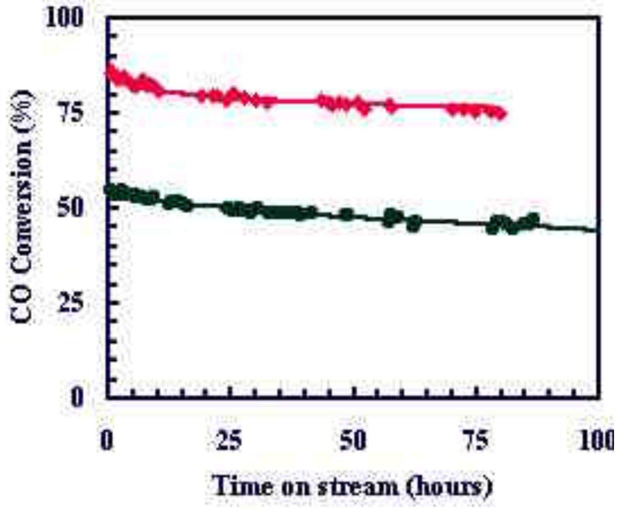

Figure 2. Comparison of long-term performance of Pt/ceria and commercial (Cu/ZnO) catalysts at 300ºC.

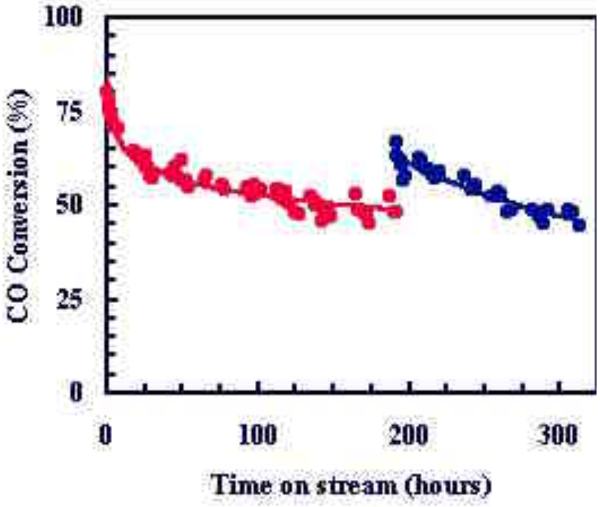

Figure 3. CO conversion versus time at 300ºC for a Pt/ceria catalyst sample, before and after regeneration by annealing in air at 375ºC.

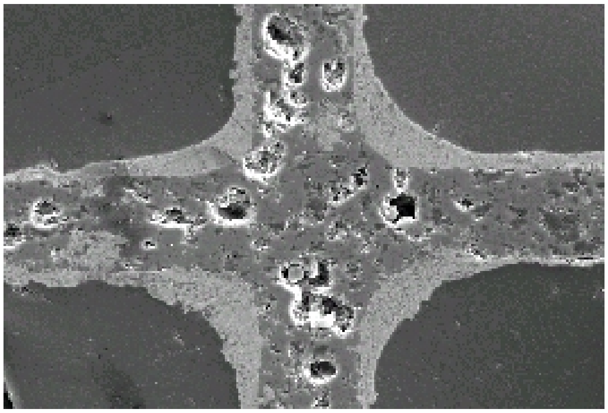

Figure 4. SEM micrograph of a washcoated Pt/ceria catalyst layer on a cordierite monolith.

performance (Figure 5). The construction and commissioning of NexTech's WGS monolith-testing reactor also was completed, with design support provided by Catalyte.

Size/Weight/Cost Modeling: A kinetic model was established for estimating the size, weight and cost of monolith reactors with washcoated Pt/ceria catalysts, using Arrhenius data obtained from micro-reactor tests. A reaction rate expression for Pt/ceria catalysts was derived from kinetic data, which was used to estimate the amount of catalyst required to achieve equilibrium conversions at a given temperature for any input reformate gas composition. This model (Figures 6 and 7) suggests that a WGS monolith reactor scaled to 50 kilowatts will have a volume of less than 1 liter, a weight of less than 1 kilogram, and a cost of less than $150. This reactor will operate at 350ºC and will provide an exit CO content of less than 0.9 percent.

Conclusions

- Pt/ceria water-gas-shift catalysts are sufficiently active and offer a number of

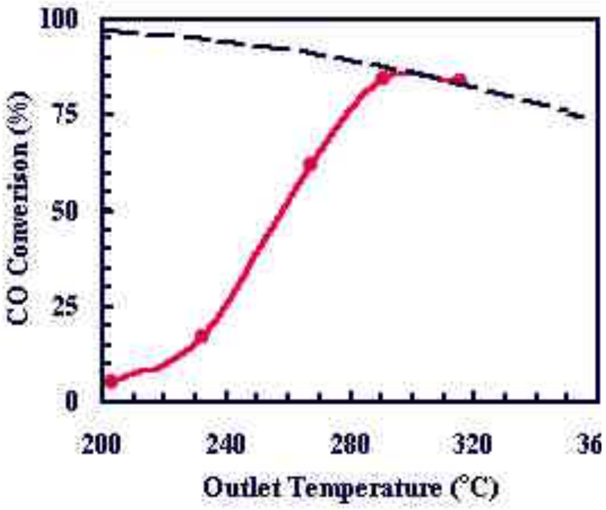

Figure 5. WGS performance of a Pt/ceria monolith

practical advantages for automotive fuel processors for PEM fuel cell systems.

- Pt/ceria catalysts are substantially more active than commercially available copper-based catalysts at temperatures above about 270ºC.
- Careful synthesis and processing is required to minimize long-term de-activation of Pt/ceria catalysts. Regeneration of deactivated catalysts can be achieved by heating in air.
- Washcoating of monoliths with Pt/ceria catalysts provides a viable path for achieving rugged and volumetrically efficient packaging of catalysts in WGS reactors of automotive fuel processors.
- Based on current performance levels, modeling suggests that a WGS reactor based on monoliths loaded with Pt/ceria catalysts will exceed DOE technical targets for reactor volume and weight. The reactor cost will be less than $3.00 per kilowatt.

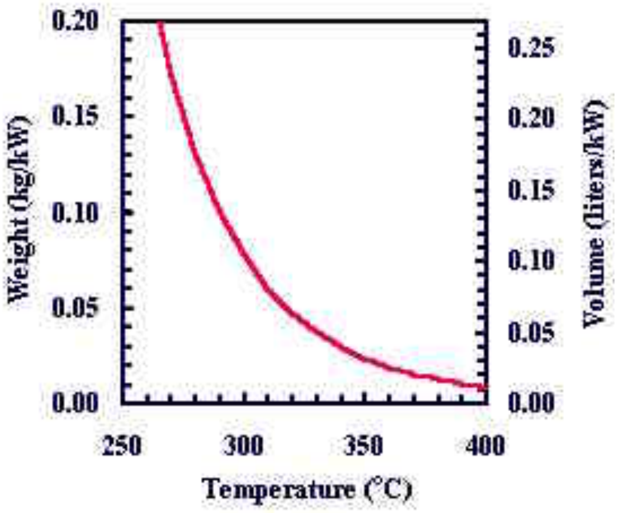

Figure 6. Estimated weight and volume of a WGS monolith washcoated with Pt/ceria catalysts.

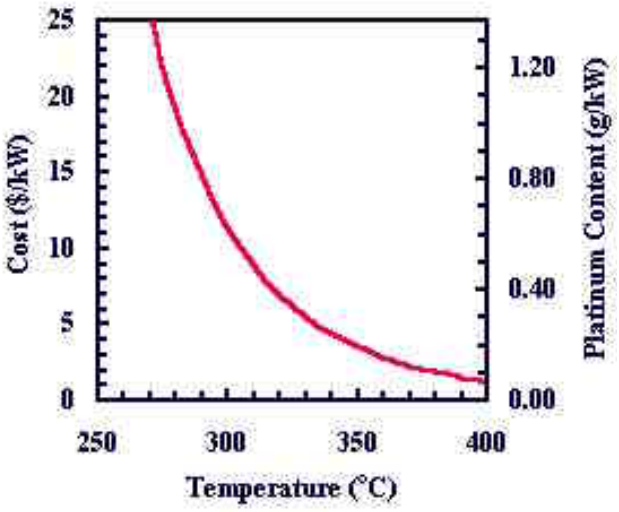

Figure 7. Estimated cost and platinum content of a WGS monolith washcoated with Pt/ceria catalysts.

IV.C.13 Water-Gas Shift Catalysis

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Objectives

- Develop water-gas shift catalysts that:
  - Meet the DOE goals of 90% CO conversion,
  - 99% selectivity, 30,000 hr^{-1} gas hourly space velocity (GHSV), <$1/kilowatt electric (kWe)
  - Eliminate the need for careful in situ catalyst activation
  - Are tolerant to temperature excursions
  - Have operating lifetimes of >5000 hours

Approach

- Develop metal-support combinations to promote bifunctional mechanism of catalyst action:
  - One component to adsorb carbon monoxide (CO), e.g., metal with intermediate CO adsorption strength
  - Another component to adsorb and dissociate water (H_2O), e.g., oxides with redox properties or oxygen vacancies under reformate conditions

Accomplishments

- Fabricated copper/mixed oxide catalyst as extrudates with no loss in activity
- Demonstrated <1% CO at 20,000 per hour) with Cu/mixed oxide vs 16,000 hr^{-1} for iron oxide-chromium oxide + copper/zinc oxide (Fe-Cr + Cu/ZnO)
- Determined sulfur tolerance of copper (Cu)/mixed oxide catalyst; catalyst loses all WGS activity after 45 hours on 4.5 ppm hydrogen sulfide (H_2S)
- Improved activity of ruthenium (Ru) and Co catalysts while suppressing methanation by using a promoter

Future Directions

- Demonstrate <1% CO out at 30,000 hr^{-1} using a structured non-precious metal catalyst
- Determine lifetime and durability of catalysts under actual reformate conditions
- Improve low-temperature activity (<300°C) of catalysts to >50 µmoles CO/sec-g catalyst (currently 11 at 230°C)
- Develop a catalyst that is tolerant to 3-4 parts per million volume (ppmv) H_2S in reformate

Introduction

The water-gas shift (WGS) reaction,

$CO + H_2O \quad CO_2 + H_2$,

is used to convert the bulk of CO in the raw reformate to carbon dioxide (CO_2) and additional hydrogen (H_2). In the chemical process industry, e.g., in the manufacture of ammonia, the shift reaction is conducted at two distinct temperatures. The high-temperature shift (HTS) is carried out at 350-450°C using an iron-chrome (Fe-Cr) catalyst. The low-temperature shift (LTS) is carried out at 160-250°C with the aid of a copper/zinc oxide catalyst (Cu/ZnO).

The commercial HTS and LTS catalysts require activation by careful pre-reduction in situ and, once activated, lose activity very rapidly if they are exposed to air. Further, the HTS catalyst is inactive at temperatures <300°C, while the LTS catalyst degrades if heated to temperatures >250°C. The automotive application, because of its highly intermittent duty cycle, requires alternative water-gas shift catalysts that (1) eliminate the need to sequester the catalyst during system shutdown; (2) eliminate the need to activate the catalyst in situ; (3) increase tolerance to temperature excursions; and (4) reduce the size and weight of the shift reactors. Another desirable property for an automotive WGS catalyst is tolerance to ppm levels of sulfur in the feed stream because sulfur species are present as contaminants or additives in conventional fuels (30 parts per million weight [ppmw] in future gasoline gets converted to 3 ppmv H_2S in reformate).

Approach

We are investigating bifunctional catalysts in which one component of the catalyst adsorbs or oxidizes CO and the other component dissociates water. Our present research is focusing on metal-support combinations to promote this bifunctional mechanism. The metallic component is chosen to adsorb CO at intermediate adsorption strengths (platinum [Pt], Ru, palladium [Pd], PtRu, PtCu, cobalt [Co], ruthenium [Ru], silver [Ag], iron [Fe], copper [Cu], and molybdenum [Mo]). The support is chosen to adsorb and dissociate water, typically a mixed-valence oxide with redox properties or oxygen vacancies under the highly reducing conditions of the reformate.

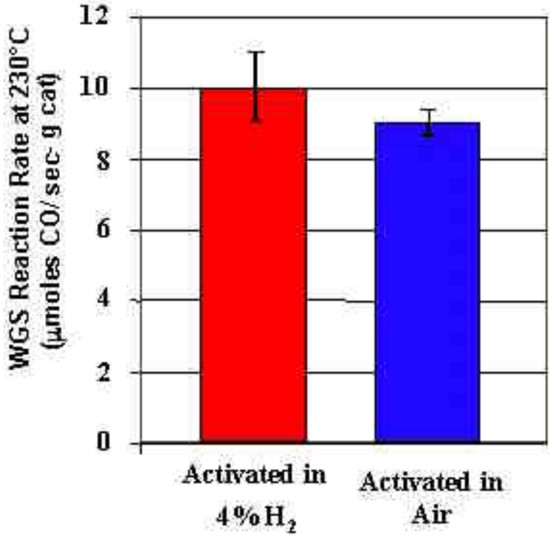

Figure 1. ANL's copper/mixed oxide catalyst can be activated in air rather than dilute hydrogen with no loss of WGS activity (within the error of the measurement). GHSV = 200,000 hr^{-1}, "High CO" reformate

Tests of the candidate catalysts' activities were conducted with simulated reformate using a micro-reactor. The micro-reactor was operated as a differential reactor for determining kinetic parameters and as an integral reactor for overall CO conversions. The concentrations of reactant gases were chosen to simulate the composition and concentrations of gases exiting an auto-thermal reformer ("High CO", dry composition: 10% CO, 13% CO_2, 43% H_2, balance diatomic nitrogen [N_2]) and exiting an HTS stage ("Low CO", dry composition: 5% CO, 15% CO_2, 45% H_2, balance N_2. A steam-to-dry gas ratio of 0.45 was chosen to simulate the additional amount of water necessary to cool the autothermal reforming gases to 400°C. Sulfur tolerance testing was conducted using simulated reformate containing 11% CO, 7.5% CO_2, 45.5% H_2, 6 ppmv H_2S, balance N_2, and a steam-to-dry gas ratio of 0.45.

Results

Last year a copper/mixed oxide catalyst was identified as a potential WGS catalyst with several desirable properties. As opposed to copper/zinc

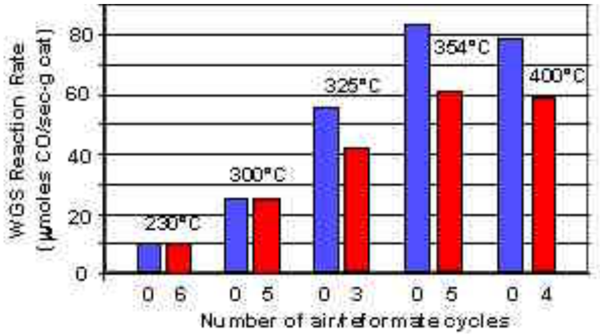

Figure 2. ANL's copper/mixed oxide catalyst does not lose WGS activity with multiple cycles between reformate and air at temperatures up to 300°C. GHSV = 200,000 hr^{-1}, "High CO" reformate

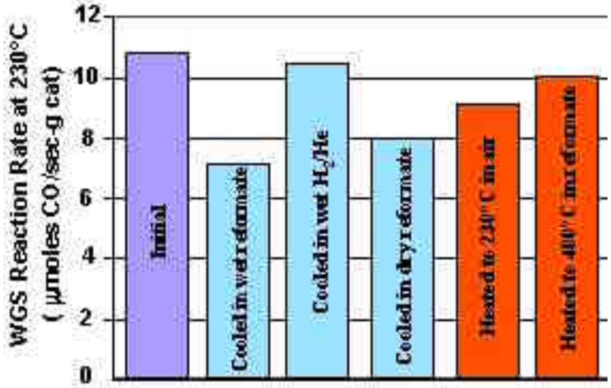

Figure 3. ANL's copper/mixed oxide catalyst does not lose WGS activity when exposed to water condensate in hydrogen/helium and reversibly loses activity when cooled to room temperature in wet or dry reformate. GHSV = 200,000 hr^{-1}, "High CO" reformate

oxide, this catalyst can operate above 260°C without loss of activity, does not have to be reduced in situ (Figure 1) and does not lose activity upon exposure to air up to 300°C (Figure 2). This catalyst also does not lose activity upon exposure to water condensate. It does lose activity when cooled down to room temperature in reformate; however, the activity can be regenerated by heating the catalyst to reaction temperature in air or to 400°C in reformate (Figure 3).

A WGS bed composed of the copper/mixed oxide catalyst powder was tested for its ability to reduce the CO in reformate from an inlet concentration of 10.2% (dry basis) to an outlet concentration of 1% (dry basis). This was accomplished in two steps, by first reducing the CO concentration to 5% and then to <1%. Figure 4A shows that the copper/mixed oxide bed can achieve 5% CO out (dry basis) at a temperature of 400°C and a gas hourly space velocity (GHSV) of 158,000 hr^{-1} compared with 45,000 hr^{-1} for the commercial iron-chrome catalyst. A dry outlet CO concentration of <1% can be achieved by the copper/mixed oxide catalyst at a temperature of 322°C and a GHSV of 23,000 hr^{-1} compared with 230°C and 25,000 hr^{-1} for the commercial copper/zinc oxide (Figure 4B). The temperature of the copper/zinc oxide bed was held at 230°C in order to avoid the deactivation of the catalyst that occurs above 260°C. Therefore, the copper/mixed oxide catalyst can achieve an outlet

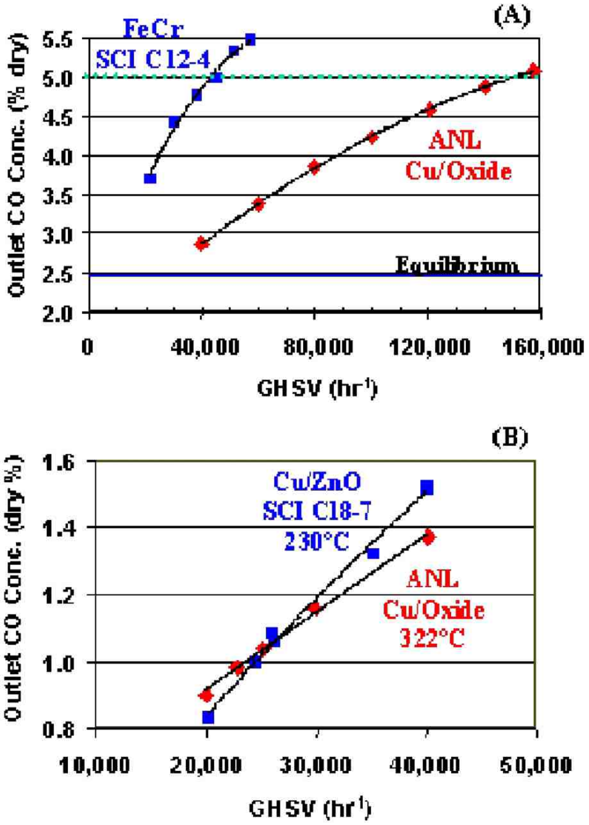

Figure 4. ANL's copper/mixed oxide catalyst can achieve CO conversions from (A) 10.2% in to <5% out at 400°C and 158,000 hr^{-1} (vs 45,000 hr^{-1} for Fe-Cr) and (B) 5% in to <1% out at 322°C and 23,000 hr^{-1} (vs 25,000 hr^{-1} at 230°C for Cu/ZnO).

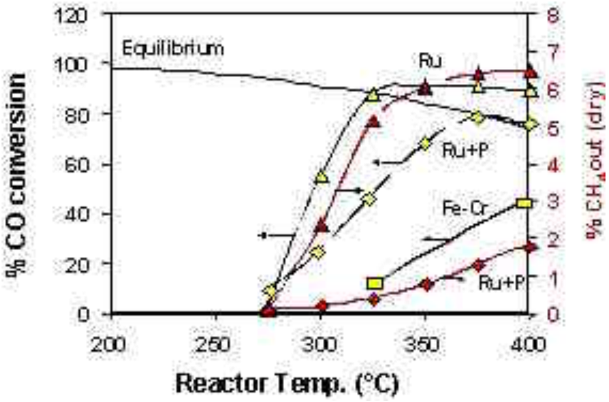

Figure 5. The addition of a promoter (P) to ANL's ruthenium/mixed oxide catalyst diminishes the conversion of CO to methane while maintaining WGS activity higher than commercial iron-chrome (Fe-Cr). GHSV = 30,000 hr^{-1}, "High CO" reformate

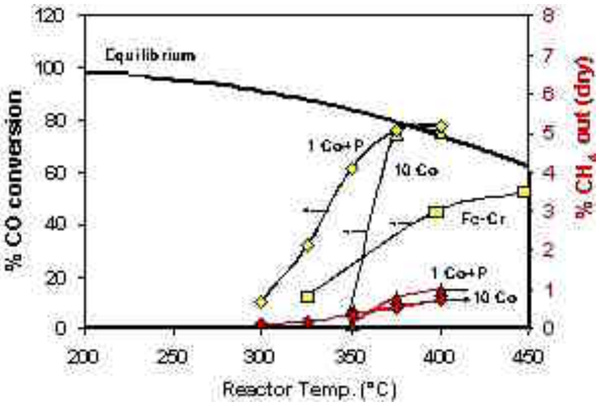

Figure 6. The addition of a promoter (P) to ANL's cobalt/oxide catalyst improves its WGS activity at temperatures below 350°C to give it higher activity than commercial iron-chrome (Fe-Cr). GHSV = 30,000 hr^{-1}, "High CO" reformate

CO concentration of <1% (90% conversion) at an overall GHSV of 20,000 hr^{-1} whereas a combination of iron-chrome and copper/zinc oxide requires a lower GHSV of 16,000 hr^{-1}.

The higher GHSV that can be achieved with the Argonne National Laboratory (ANL) copper/mixed oxide translates into a 20% reduction in the WGS catalyst volume compared with the commercial catalysts. The projected size, weight, and cost of copper/mixed oxide catalyst for an automotive fuel processor are 0.15 liter/kilowatt electric (L/kWe), 0.14 kg/kWe, and $0.9/kWe. The projected size and weight fall short of the DOE goals. Iprovements are needed in the catalyst's activity. Improvements are also needed in the sulfur tolerance of the catalyst, as it showed total deactivation after 45 hours on a stream of 4.5 ppmv H_2S in reformate.

We improved the WGS activity of cobalt- and ruthenium-based catalysts while suppressing the methanation activity by adding a promoter. As shown in Figures 5 and 6, these catalysts are more active than commercial iron-chrome at temperatures >300°C. Our results indicate that the cobalt and ruthenium catalysts would be suitable replacements for iron-chrome as an HTS catalyst.

Conclusions

We further developed a temperature-stable copper/mixed oxide catalyst by fabricating it in a structured form that has the same activity as the powder. This catalyst can be activated in air and does not lose activity after exposure to air at temperatures up to 300°C. The ANL copper/mixed oxide catalyst has the potential to reduce the volume of the WGS reactor by 20% compared with the commercial catalysts. The copper catalyst showed susceptibility to poisoning by H_2S in the reformate feed. We have also developed cobalt and ruthenium catalysts with higher activity than commercial iron-chrome (325-400°C) by using a promoter to suppress methane formation.

FY 2002 Publications/Presentations

1. D. J. Myers, J. F. Krebs, J. D. Carter, R. Kumar, and M. Krumpelt, "Metal/Ceria Water-Gas Shift Catalysts for Automotive Polymer Electrolyte Fuel Cell Systems," Presentation, Abstract, and Presentation Record, American Institute of Chemical Engineers, 2002 Spring Meeting, Fuel Processing Session III, New Orleans, LA, March 10-14, 2002.

2. D. J. Myers, J. F. Krebs, J. D. Carter, R. Kumar, and M. Krumpelt, "Metal/Ceria Water-Gas Shift Catalysts for Automotive Polymer Electrolyte Fuel Cell Systems," Presentation and Preprint, 224th American Chemical Society Fall National Meeting, Boston, MA, August 18-22, 2002.

IV.C.14 Transition Metal Carbide Water Gas Shift Catalysts

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Objectives

The objective of the project is to demonstrate water gas shift (WGS) catalysts with:

- Rates in the absence of sulfur that are twice those for Cu-based shift catalysts,
- Activities in the presence of sulfur that are >85% of activities in the absence of sulfur,
- Projected stabilities and durabilities that are compatible for use in automobiles, and
- Costs that are competitive with Cu-based catalysts.

Approach

Tasks devised to accomplish the program objectives included:

- Develop monolith washcoat procedure.
- Optimize carbide formulation, microstructure and pretreatment.
- Fabricate prototype catalyst.
- Evaluate and model catalyst performance.
- Demonstrate performance in prototype fuel processor.
- Access commercial potential.

Accomplishments

- Methods were demonstrated to washcoat the carbide catalysts onto cordierite monoliths and ceramic foams. The adhesion of the carbides to the substrates was very good.
- Our best performing carbide catalysts outperformed the commercial Cu-Zn-Al catalyst by a factor of more than 2. Ninety percent CO conversion was achieved with an hourly space velocity in excess of 70,000 hr^{-1}, exceeding the present DOE WGS catalyst performance target.

Future Directions

- Evaluate carbide catalysts in the presence of sulfur.
- Produce >1 kg of catalyst for prototype work and third-party testing.
- Produce monolith supported prototype catalysts.
- Assess cost competitiveness via evaluations by an established fuel processor developer.

Introduction

Fuel cells are being developed to enable the commercialization of cleaner, more fuel efficient vehicles. The fuel cell technology favored by many vehicle manufacturers is proton exchange membrane (PEM) cells operating with H_2 from hydrocarbon steam reforming and/or partial oxidation. The water gas shift (WGS) is a critical step during fuel processing, and the associated reactor constitutes about a third of the mass, volume and cost of the fuel processor. While presently available catalysts work well in industrial petroleum refining and chemical plants, significantly improved catalysts are required to meet the transient operation and size constraints imposed by vehicular applications. Rather than seeking incremental improvements through the modification of existing formulations (e.g., Fe-Cr and Cu-Zn catalysts), we are developing new WGS catalysts based on transition metal carbides. Significant reductions in the WGS reactor size and cost are anticipated as a consequence of *high activities, durabilities and sulfur tolerance*.

The focus of Phase II of this project is to optimize formulations for the carbide catalysts and produce monolith supported prototype catalysts that substantially out-perform the commercial catalysts. In addition, we will evaluate the cost competitiveness of the monolith supported carbide catalysts. The performance of new monolith supported catalysts demonstrated in this effort will be confirmed by independent evaluations by established fuel processor developers.

Approach

The carbide catalysts were synthesized and washcoated onto substrates using a proprietary method. Water gas shift rates and product selectivities for the carbide powders were measured in a plug flow reactor using a feed gas that simulates the exhaust from the partial oxidation of gasoline. The individual gas phase constituents were delivered by mass flow controllers, and H_2O was added by bubbling the dry gas mixture through a heated saturator vessel. The CO was passed through a bed of alumina to remove any carbonyls. The resulting reactant contained 38.6% H_2, 15.9% N_2, 5.7% CO, 6.3% CO_2, and 30.0% deionized H_2O. The WGS rates were measured at 175-240°C and atmospheric pressure with CO conversions that typically ranged up to 30%. Prior to the rate measurements, the catalyst bed was pretreated either in H_2 or a mixture of 15% CH_4 in H_2 for 4 hours at 400-590°C.

Results

The reaction rates reached steady-state after approximately three hours on-stream and were reproducible to within 10% during subsequent runs. Small amounts of methane were produced over some catalysts; however, there was no evidence of methanation activity at steady-state.

The performance of selected catalysts that were pretreated at 450°C in the CH_4/H_2 mixture is illustrated in Figure 1 (the Cu-Zn-Al catalyst was pretreated at 200°C in a mixture of 2% H_2 in N_2 for 4 hours as recommended by the manufacturer). Several of the formulations substantially outperformed the commercial Cu-Zn-Al catalyst.

The performance of the carbide catalysts was a function of the pretreatment conditions employed. For example, pretreatment in the CH_4/H_2 mixture typically resulted in catalysts that were more active than those same catalysts pretreated in pure H_2 (Figure 2). For some materials, increasing the pretreatment temperature also resulted in significant improvements in the performance. The improved activities appear to be linked to the production of

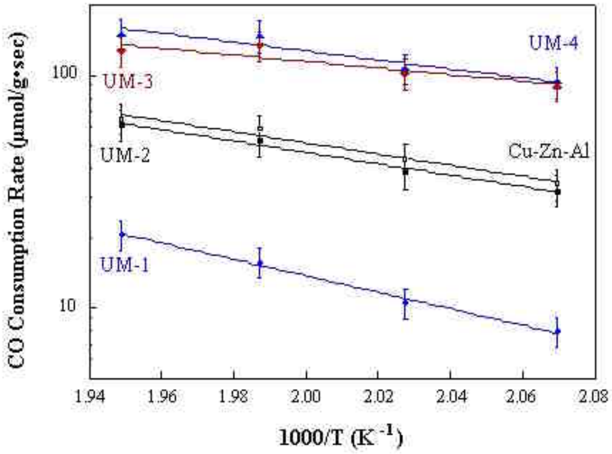

Figure 1. Comparison of Reaction Rates for the Carbide and Cu-Zn-Al Catalysts

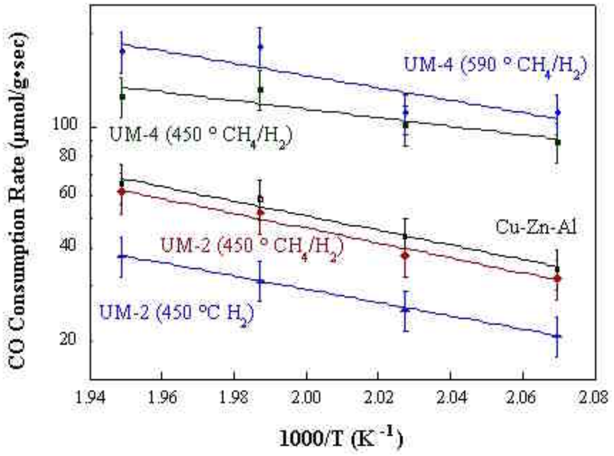

Figure 2. Effects of Pretreatment Gas and Temperature on Rates for the Carbide Catalysts

additional carbide sites based on the results of *in situ* x-ray photoelectron spectroscopic characterization.

We recently compared characteristics of the carbide catalysts to the DOE targets. As one can see from Table 1, the performance of one of our best catalysts, UM-3, exceeded important DOE targets.

Characteristic	Target	Cu-Zn-Al	UM-3
GHSV (hr^{-1})	30,000	30,800	>70,000
CO Conversion (%)	>90	76	89
H_2 Selectivity (%)	>99	>99	>99
Volume (L/kW_e)	<0.1		
Weight (kg/kW_e)	<0.1		
Durability (Hrs.)	5000		
Cost ($\$/kW_e$)	<1		
*Rates measured at 240°C. The equilibrium CO conversion under these conditions is 96.5%.			

Table 1. Progress Against DOE Performance Targets*

We demonstrated that the carbide catalysts could be washcoated onto cordierite monoliths and ceramic foams. Details regarding the methods are proprietary and were not disclosed. Examples of the monolith and foam supported catalysts are illustrated in Figures 3 and 4.

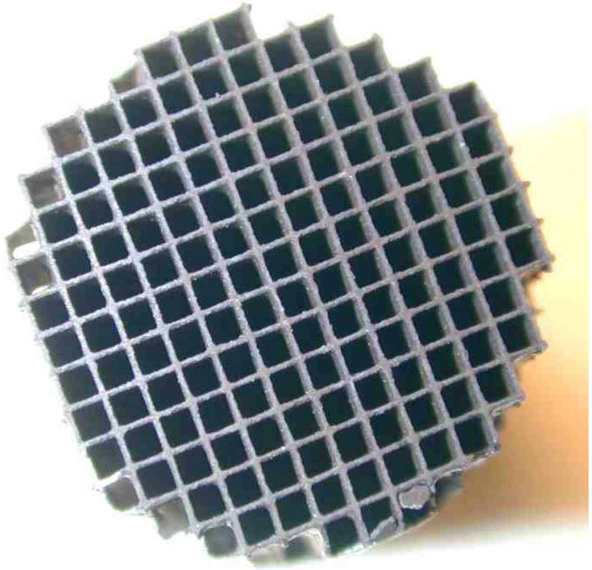

Figure 3. Carbide Washcoated Cordierite Monolith

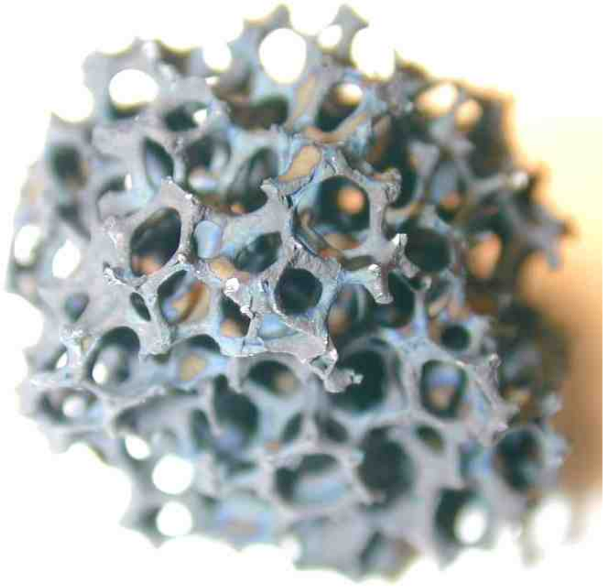

Figure 4. Carbide Washcoated Ceramic Foam

Conclusions/Future Work

The carbides have been demonstrated to be highly active WGS catalysts and are able to be washcoated onto monolith and foam substrates. To further differentiate the carbide catalysts and enhance their commercial potential, we will demonstrate that they are:

- more durable than the Cu-Zn-Al catalysts that are used commercially,
- much more tolerant to sulfur than other types of WGS catalysts, and
- cost effective.

Future work will focus on producing larger quantities (>1 kg) of the most active carbide catalysts, preparing and evaluating monolith supported prototype catalysts, and determining the cost competitiveness of the catalysts.

IV.C.15 Development of Novel Water-Gas-Shift Membrane Reactor

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Objectives

- Develop a mathematical model for the novel water-gas-shift (WGS) membrane reactor with a carbon dioxide (CO_2)-selective membrane to elucidate the effects of system parameters on the reactor and to show the feasibility of achieving hydrogen (H_2) enhancement via CO_2 removal and carbon monoxide (CO) reduction to 10 parts per million (ppm) or lower from the modeling study.
- Synthesize CO_2-selective membranes for the reactor.
- Develop the membrane reactor for achieving H_2 enhancement and <10 ppm CO.

Approach

- Develop a non-isothermal model for the novel WGS membrane reactor by taking material and energy balances and reaction into account.
- Use the model to study the effects of system parameters on the reactor, to carry out the technical analysis of the reactor for synthesis gases from steam reforming and autothermal reforming, and to guide/minimize experimental work.
- Synthesize and characterize of CO_2-selective membranes containing amino groups.
- Incorporate the membrane synthesized in the reactor to demonstrate H_2 enhancement via CO_2 removal and CO reduction to 10 ppm or lower.

Accomplishments

- Developed a one-dimensional non-isothermal model for the novel WGS membrane reactor with a CO_2-selective membrane in the hollow-fiber configuration using air as the sweep gas.
- Elucidated the effects of system parameters on the membrane reactor for synthesis gases from steam reforming and autothermal reforming.
- Showed the feasibility of achieving H_2 enhancement via CO_2 removal and CO reduction to 10 ppm or lower based on the modeling study.

Future Directions

- Analyze the effects of feed pressure on the membrane reactor for synthesis gases from steam reforming and autothermal reforming.
- Synthesize and characterize CO_2-selective membranes for the reactor.

- Conduct the proof-of-concept demonstration using the laboratory membrane reactor.
- Carry out the prototype membrane reactor demonstration for a 50 kilowatt (kW) fuel cell.

Introduction

A WGS reactor for the conversion of carbon monoxide and water to hydrogen and carbon dioxide is widely used in chemical and petroleum industries. The reactor is also critically needed for the conversion of fuels, including gasoline, diesel, methanol, ethanol, natural gas, and coal, to hydrogen for fuel cells. Since the WGS reaction is reversible, the reaction is not efficient, resulting in a high concentration of unconverted CO (about 1%) in the H_2 product and a bulky, heavy reactor.

The WGS reaction can be enhanced significantly through a CO_2-selective membrane, which removes the reaction product, CO_2, in order to beat the reaction equilibrium and shift the reaction towards the product side. The CO_2-selective WGS membrane reactor has advantages including (1) a high-purity H_2 product is recovered at the high pressure (feed gas pressure) and (2) air can be used as the sweep gas to remove the permeate, CO_2, on the low-pressure side of the membrane to have a high driving force for the separation. These advantages are especially important for fuel cell vehicles. The first advantage eliminates the need for an unwanted compressor. With the second advantage, the high driving force created by the air sweep can result in low CO concentration and high H_2 purity and recovery.

We have developed a mathematical model for the countercurrent WGS membrane reactor with a CO_2-selective membrane in the hollow-fiber configuration using air as the sweep gas. With this model, we have elucidated the effects of system parameters on the novel WGS membrane reactor for synthesis gases from steam reforming and autothermal reforming. The modeling results show that H_2 enhancement via CO_2 removal and CO reduction to 10 ppm or lower are achievable. For comparison and the completeness of the modeling work, we have also developed a similar model for the cocurrent WGS membrane reactor.

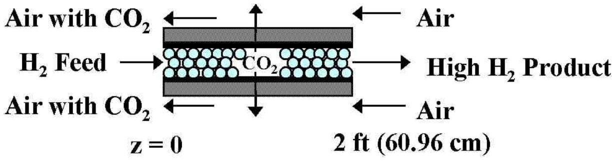

Figure 1. Schematic of a Countercurrent CO_2 Selective Membrane Reactor Containing Catalyst Particles

Results

Development of Mathematical Model

We have developed a one-dimensional non-isothermal model for the countercurrent WGS membrane reactor with a CO_2-selective membrane in the hollow-fiber configuration using air as the sweep gas. Figure 1 shows the schematic of each hollow-fiber membrane with catalyst particles in the reactor. The modeling study of the membrane reactor is based on: (1) the CO_2 / H_2 selectivity and CO_2 permeance reported by Ho [1, 2] and (2) low-temperature WGS reaction kinetics for the commercial catalyst copper oxide, zinc oxide, aluminum oxide ($CuO/ZnO/Al_2O_3$) reported by Moe [3] and others [4]. In this modeling study, the model that we have developed has taken into account critical system parameters including temperature, pressure, feed gas flow rate, sweep gas (air) flow rate, CO_2 permeance, CO_2/H_2 selectivity, CO concentration, CO conversion, H_2 purity, H_2 recovery, CO_2 concentration, membrane area, water (H_2O)/CO ratio, and reaction equilibrium.

For a 50 kW fuel cell system, two types of synthesis gases, one from the steam reforming of methane and the other from the autothermal reforming of gasoline with air, have been considered. The syngas from steam-reforming of methane consists of 18.63% CO (theoretical maximum value), 58.23% H_2, 0.78% CO_2, and 22.36% water (24% CO, 75% H_2, and 1% CO_2 on a dry basis). The syngas from autothermal reforming of gasoline with air consists of 18.63% CO (maximum), 20.96% H_2,

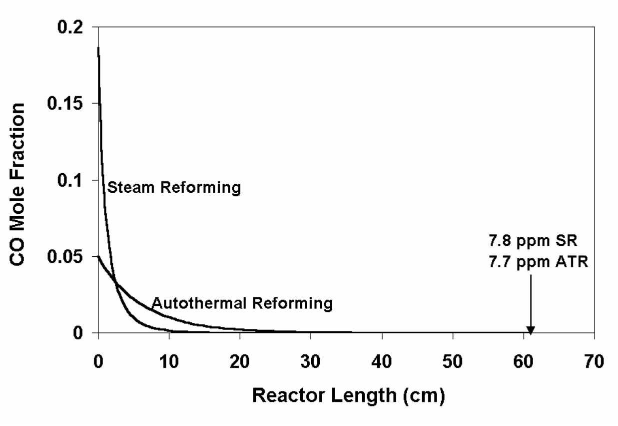

Figure 2. Profiles of Carbon Monoxide Mole Fractions in the Hydrogen Products Along the Countercurrent Membrane Reactors for the Synthesis Gases With (1) 18.63% CO from Steam Reforming and (2) 5% CO from Autothermal Reforming

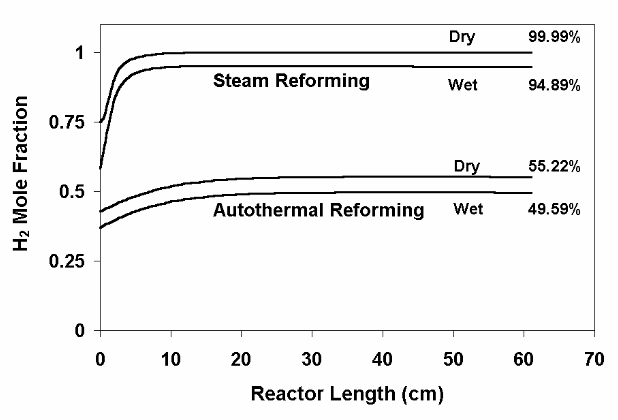

Figure 3. Profiles of Hydrogen Mole Fractions in the Hydrogen Products on Dry and Wet Bases Along the Countercurrent Membrane Reactors for the Synthesis Gases with (1) 18.63% CO from Steam Reforming And (2) 5% CO from Autothermal Reforming

0.78% CO_2, 37.27% diatomic nitrogen (N_2), and 22.36% water (24% CO, 27% H_2, 1% CO_2, and 48% N_2 on a dry basis).

Modeling for Syngas from Steam Reforming of Methane

For the syngas at 3 atm from steam reforming of methane, the modeling of the membrane reactor containing 20,500 hollow fibers was conducted. Figure 2 shows the profile of the CO concentration in the H_2 product in the reactor with an inlet feed temperature of 180°C for a total reactor length of 61 centimeters (24 inches). The syngas flow on the high-pressure side of the membrane (3 atmospheres [atm]) was countercurrent to the flow of air sweep at 1 atm on the low-pressure permeate side of the membrane (with 22°C inlet air). The molar flow rate ratio of the air sweep to the syngas was 0.75. As shown in this figure, the CO concentration in the H_2 product at the exit of the reactor was 7.8 ppm, which was better than the desired concentration of 10 ppm for fuel cells. The H_2 recovery was very good at 90.3%. A CO conversion of 99.997% was achieved.

Figure 3 depicts the profiles of the H_2 mole fraction in the H_2 product both on a dry basis and on a wet basis in the same membrane reactor. A high H_2 concentration of 99.99% on a dry basis resulted in the H_2 product, which was significantly higher than the original concentration of 75% in the syngas. In other words, the novel membrane reactor has given not only significant H_2 enhancement but also a H_2 product with a CO concentration of less than 10 ppm.

For the same membrane reactor, the effects of inlet feed temperature and sweep-to-feed molar ratio on CO and CO_2 concentrations and H_2 recovery were studied. For the inlet feed temperatures ranging from 160°C to 220°C at a sweep-to-feed molar ratio of 0.75, the CO concentrations in the H_2 product were all below 10 ppm, and the H_2 recoveries were about 90%. As the sweep-to-feed molar ratio increased from 0.5 to 1.25 at an inlet feed temperature of 180°C, the CO concentration in the H_2 product decreased from 12.5 ppm to 2.2 ppm as a result of a more favorable equilibrium at a lower outlet feed temperature. As shown in Figure 4, the H_2 recovery decreased significantly as the ratio increased. The H_2 loss to the sweep gas was a result of the higher H_2 driving force created from the higher ratio.

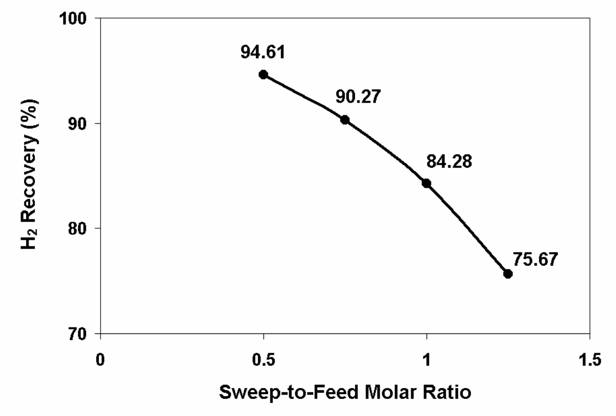

Figure 4. Effect of Sweep-To-Feed Molar Flow Rate Ratio on Hydrogen Recovery for the Countercurrent Membrane Reactor With the 18.63% CO Syngas From Steam Reforming

However, the CO_2 concentration (~100 ppm) in the H_2 product hardly changed with either the ratio or the inlet feed temperature since the CO_2 concentration was nearly equivalent to that in the sweep gas.

Modeling for Syngas from Autothermal Reforming of Gasoline with Air

Similarly, significant H_2 enhancement and a H_2 product with 10 ppm CO or lower were also obtained for the synthesis gases at 3 atm from the autothermal reforming of gasoline with air containing CO at concentrations of 18.63%, 10%, 5%, and 1%. As the CO concentration of the feed gas decreased, the temperature rise in the membrane reactor due to the WGS reaction decreased. At the feed gas CO concentration of 5% or lower, there was no temperature rise. For the feed gas CO concentration of 5% (5% CO, 37% H_2, 11% CO_2, 33.5% N_2, and 13.5% water), Figure 2 illustrates the profile of the CO concentration in the H_2 product for the reactor containing 20,000 hollow fibers with an inlet feed temperature of 180°C. The molar flow rate ratio of the air sweep to the syngas was 1. As shown in this figure, the CO concentration in the H_2 product at the exit of the reactor was 7.7 ppm. The H_2 recovery was excellent at 98.4%.

Figure 3 depicts the profiles of the H_2 mole fraction in the H_2 product both on a dry basis and on a wet basis in the same membrane reactor. A H_2 concentration of 55.22% on a dry basis resulted in the H_2 product, which was significantly higher than the original concentration of 42.8% in the syngas.

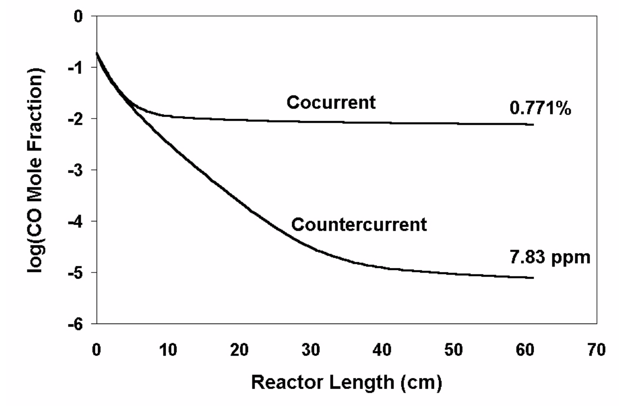

Figure 5. Comparison Between Cocurrent And Countercurrent Membrane Reactors in Terms of the Profiles of Carbon Monoxide Mole Fractions in the Hydrogen Products along the Reactors

Comparison with Cocurrent WGS Membrane Reactor

For comparison and the completeness of the modeling work, we have also developed a similar model for the cocurrent WGS membrane reactor. Figure 5 illustrates the comparison between the cocurrent and countercurrent WGS membrane reactors in terms of the profiles of CO mole fractions in the H_2 products along the reactors under the same conditions. As shown in this figure, the CO concentration in the H_2 product was 7.8 ppm for the countercurrent reactor whereas that was 0.77% (7,700 ppm) for the cocurrent reactor. Thus, the countercurrent reactor was much more effective than the cocurrent one. Future work will be on the countercurrent reactor only.

Conclusions

We have developed a one-dimensional non-isothermal model for the countercurrent WGS membrane reactor with a CO_2-selective membrane in the hollow-fiber configuration using air as the sweep gas. With this model, we have elucidated the effects of system parameters, including feed CO concentration, feed temperature, and sweep-to-feed molar ratio, on the reactor for synthesis gases from steam reforming and autothermal reforming. The modeling results have shown that H_2 enhancement (>99.9% H_2 for the steam reforming of methane and >49% H_2 for the autothermal reforming of gasoline with air on a dry basis) via CO_2 removal and CO reduction to 10 ppm or lower are achievable for both synthesis gases investigated. For comparison and the completeness of the modeling work, we have also developed a similar model for the cocurrent membrane reactor. The countercurrent reactor is much more effective than the cocurrent one.

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1. W.S. Winston Ho, "CO_2-Selective Membranes Containing Amino Groups", U. S. Patent Application Serial No. 10/145,297, filed on May 14, 2002.