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Title: Transient Control of Carbon Monoxide with Staged PrOx Reactors

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Los Alamos
NATIONAL LABORATORY

Transient Control of Carbon Monoxide with Staged PrOx Reactors

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Introduction

Fuel Processor systems generate hydrogen for fuel cell systems from hydrocarbon fuels such as gasoline for automotive fuel cell systems and natural gas for stationary fuel cell systems. These fuel processor systems must remove any contaminants to levels that won't poison the fuel cell before the outlet hydrogen-rich gas stream can be used by the fuel cell to generate electricity.

Carbon monoxide is a contaminant that must be removed to levels of < 100 ppm or < 10 ppm depending on the CO tolerance of the fuel cell. Typically, the last unit operation in a fuel processor is a preferential oxidation reactor or a selective oxidation reactor, which removes CO by oxidizing it to form CO_2. These are catalytic reactors where the catalyst and operating conditions are selected so that the oxidation rate of the carbon monoxide is higher than the oxidation rate of hydrogen, even though the hydrogen is present at much higher concentrations (> 30%) than carbon monoxide which is present at trace concentrations (< 1%).

Multiple stages of preferential oxidation are used for removal of CO concentrations from 1-2% to below 10 ppm. Because the CO and H_2 oxidation reactions are exothermic and selectivity for CO decreases with increasing temperature, achieving high CO conversions can increase the parasitic loss of hydrogen. Multiple stages with lower CO conversion per stage can be used to achieve a higher overall conversion with reduced parasitic loss of hydrogen by maintaining the catalyst in each stage in a temperature range where it is more selective for CO oxidation.

Transient control of the fuel processor outlet CO concentration also is critical for the fuel cell system to generate electric power in response to changing load demands. Both automotive and stationary power fuel cell systems will require transient CO control, although the characteristics of those transients will differ. A power transient is a change in the total flow through the fuel processor as it responds to changes in the hydrogen demand of the fuel cell. A composition transient is a change in the gas composition such as variations in the CO concentration caused by instabilities or variations in the fuel processor inlet flows. A key transient for automotive applications is the startup transient.

The Fuel Cell Team at Los Alamos National Laboratory has been researching and developing preferential oxidation (PrOx) technology for the removal of CO for automotive fuel processor systems. Previous work focused on developing laboratory and demonstration PrOx reactor hardware for gasoline fuel processing systems. Recent research has focused on expanding the fundamental knowledge of the CO removal process through steady-state and transient experiments conducted on well-characterized laboratory PrOx reactor hardware. We report here on the response and control of PrOx reactors to simulated power transients and to a simulation of a fuel processor startup.

Experimental Approach

PrOx Reactor. The PrOx reactor used in these experiments is based on a laboratory PrOx reactor design incorporating staged catalytic adiabatic reactors with interstage heat exchange. In each stage, air is metered and injected into the primary gas stream from either a low-temperature shift reactor or a previous PrOx stage. The main gas stream then passes through a heat exchanger to control the inlet temperature to the catalyst volume. Gas distribution elements such as porous foams or frits are used to distribute the flow evenly across the catalyst inlet. Catalysts are selected based on a desired operating temperature and inlet CO concentration. This scheme was implemented in a modular laboratory reactor with interchangeable catalyst holders so that various catalysts and catalyst supports could be tested. Lightweight internal components were used to enhance its transient response.

PrOx Reactor Test Facility. PrOx reactor components were tested in a facility capable of simulating the outlet stream and conditions from a fuel processor. The major components of reformate, hydrogen, nitrogen, carbon dioxide, and water (as steam) along with carbon monoxide as a trace component, were metered with mass flow controllers. The reformate flow was heated with inline gas heaters to simulate the outlet temperatures from a fuel processor. Fuel processor operating pressures were obtained using a back pressure regulator. Computer control and measurement of these functions allowed for simulation of a variety of fuel processor configurations and transient operating conditions. CO, CO_2, and CH_4 concentrations were measured with NDIR analyzers and O_2 concentrations were measured with a paramagnetic O_2 analyzer.

Power Transient Experiments. The response of PrOx reactor components to a simulated fuel processor transient was measured in both a 4-stage PrOx reactor and in a single-stage PrOx reactor. In the 4-stage reactor, the power transient response and CO control were complicated by interactions between the stages. To better characterize the response of PrOx components to power transients, a PrOx single-stage reactor was subjected to step transients in total reformate flow. These step transients were between 10 kW and 30 kW (based on the LHV of the H_2 flow) in a simulated gasoline reformate with 37% H_2, 28% N_2, 17% CO_2, 17% H_2O and 2000 ppm CO. Air injection and its timing was varied to investigate the conversion and control of CO through the transient.

Startup Transient Experiments. A 4-stage PrOx reactor was used in a set of experiments to investigate the feasibility of using a PrOx reactor to reduce system startup time by removing high CO concentrations. A 10 kW (LHV H_2) simulated gasoline reformate flow with 5% CO was heated to 200 °C in bypass around the PrOx reactor. The flow was then switched to flow through the PrOx. Air injection flows were started at the same time and were set to achieve a maximum setpoint temperature at the outlet of each stage. CO concentrations at the outlet of each stage were monitored by NDIR analyzers.

Results and Discussion

Power Transient Experiments. Figure 1 shows the CO flow and air injection flow into the PrOx single-stage reactor through two cycles of the step transient between 10 kW and 30 kW total flow. The air injection is programmed to step between the flows that give the desired CO outlet concentration at the steady-state 10 kW and 30 kW conditions. In this case, the air injection is programmed to lead the up transient by 1 second and then lag by 1 second on the down transient. Figure 2 shows the outlet CO concentration for the two cycles of the step transient. The outlet CO concentration is maintained below 100 ppm through the transient, which is the current specification for an automotive fuel processor.

When the air injection is programmed to step coincident with the step transient, the outlet CO concentration shows peaks above 400 ppm corresponding to the down transient. These peaks probably result from formation of CO through reverse water-gas shift reaction.

The time resolution of these experiments is on the order of 1 second, both in the measurement of the CO concentration and temperatures and in the control of the reformate and air injection flows. Thus, we could not refine further the transient controls without modifying the experimental apparatus for faster response times.

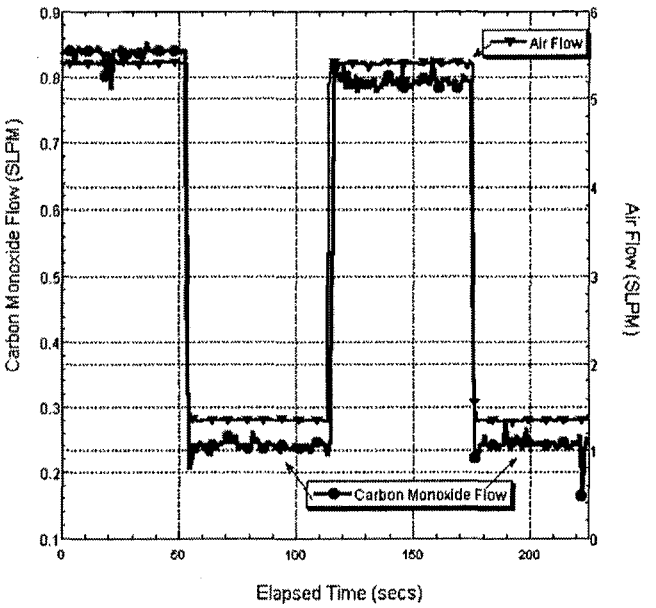

Figure 1. CO and air injection flows during step transients between 10 kW and 30 kW total flows of simulated gasoline reformate.

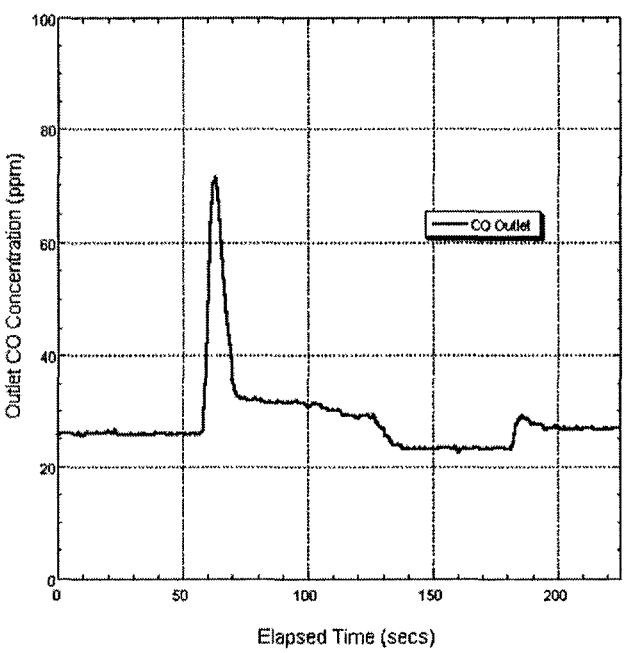

Figure 2. Outlet CO concentration measured during step transients between 10 and 30 kW total flows of simulated gasoline reformate.

Startup Transient Experiments. Figure 3 shows the response of the 4-stage PrOx reactor during the simulated startup transient . Oulet CO concentrations from each of the four stages is is shown as a function of elapsed time from the start of flow to the reactor. The final stage outlet CO concentration reached the target level of 10 ppm in 225 s from startup. Outlet CO concentrations increased after dropping below 10 ppm indicating that the control algorithm will require further refinement to maintain the low outlet CO. Further improvement also is required to reduce the startup time to 30 s. This reactor configuration used pellet catalysts. Switching to monolith supported catalysts may reduce the startup time significantly.

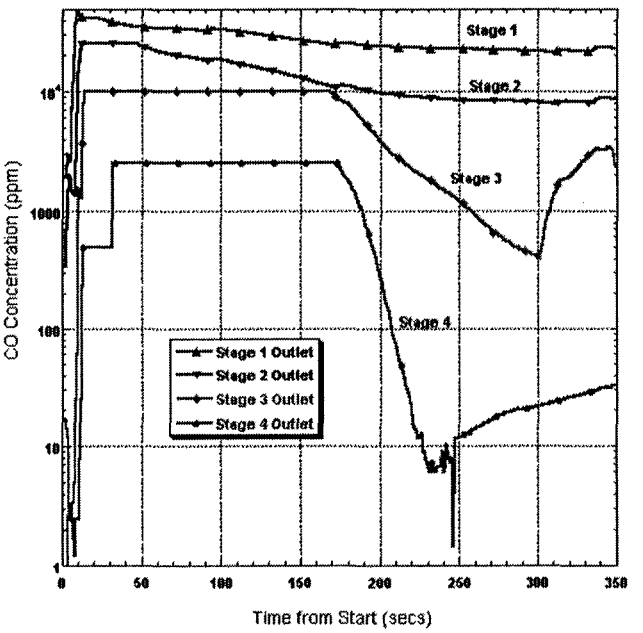

Figure 3. Outlet CO concentrations from each stage of a 4-stage PrOx reactor during startup with an inlet 5% CO concentration in simulated gasoline reformate.

Conclusions

The response of PrOx reactor components to step power transients has been measured. A possible control strategy has been identified where the air injection is increased before the total flow is increased and the air injection is decreased following the total flow decrease. This strategy may be feasible where the fuel processor outlet CO response is predictable and responses to changing load demands can be programmed. Efficient control of the outlet CO concentration would be more difficult where the fuel processor outlet CO composition is not predictable. In this case, a CO sensor may be required for transient control.

The time resolution of the transient experiments is on the order of 1 second and needs to be improved for better characterization of the transient response. We are in the process of implementing a tunable diode laser absorption measurement system to make in-situ CO concentration measurements at time scales of < 100 ms with a 1 ppm CO resolution. Along with improvements in data acquisition and control speeds this system should allow better characterization of the transient response of PrOx reactors for CO removal.

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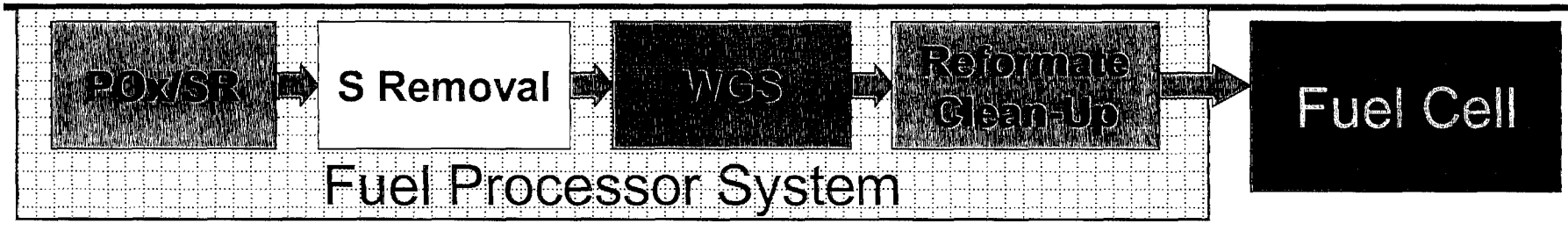
Reformate Clean-up:
Catalytic Clean-up of Impurities from Fuel Processor Streams



- Reformate Clean-Up is the last unit operation in the fuel processor process stream.
- Function - Remove contaminants to levels that do not compromise the performance of the fuel cell stack
- Operates in system context of the fuel processor system
- Meet fuel processor targets for energy efficiency, power density, specific power, cost, durability, and transient performance

Reformate Clean-up: Performance Requirements

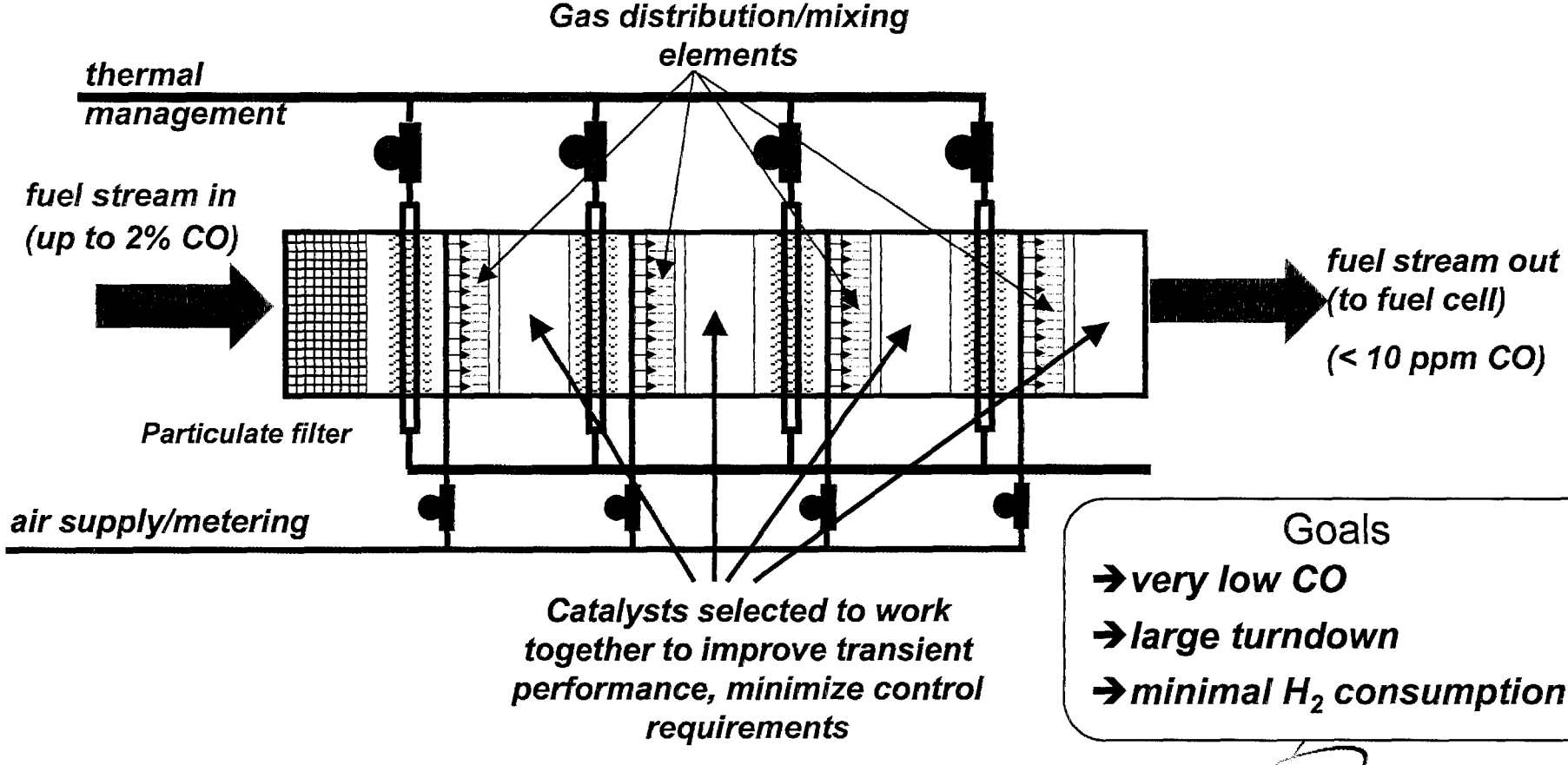
- Meet technical targets for the fuel processor system
  - Contaminant removal
    - CO < 10 ppm steady-state; < 100 ppm transient
    - NH_3 < 1 ppm, H_2S < 0.1 ppm
    - Other contaminants, hydrocarbons, soot
  - Transients
    - Power 10% to 90% - 1 second
    - Cold start – < 30 seconds (20 °C), < 60 seconds (- 20 °C)
  - Energy efficiency
    - Minimize hydrogen consumption, parasitic loads – air injection
  - Cost, volume, weight, durability
    - Catalysts on rugged supports
    - Reduce number of components, actuators, and sensors

CO Removal – Preferential Oxidation (PrOx)

- PrOx - Preferential Oxidation of CO in H_2 atm.
  - Non-equilibrium reactor (Reduce CO below equilibrium)
  - 2 % CO (20,000 ppm) to < 20 ppm CO (3 orders of mag.)
- Competing Oxidation Reactions
  - $CO + 1/2\ O_2 \rightarrow CO_2$ (the desired reaction)
  - $H_2 + 1/2\ O_2 \rightarrow H_2O$ (want to minimize)
- Water-gas shift reaction – $CO + H_2O \leftrightarrow CO_2 + H_2$
  - [CO] below equilibrium – prevent reverse W.G.S.
  - [CO] above equilibrium – use W.G.S. to further reduce [CO]
- Methanation Reactions
  - $3H_2 + CO \rightarrow H_2O + CH_4$ (can be used to reduce [CO], but consumes H_2)
  - $4H_2 + CO_2 \rightarrow 2H_2O + CH_4$ (avoid because of added H_2 consumption)

Gas Clean-Up Approach: PrOx Schematic

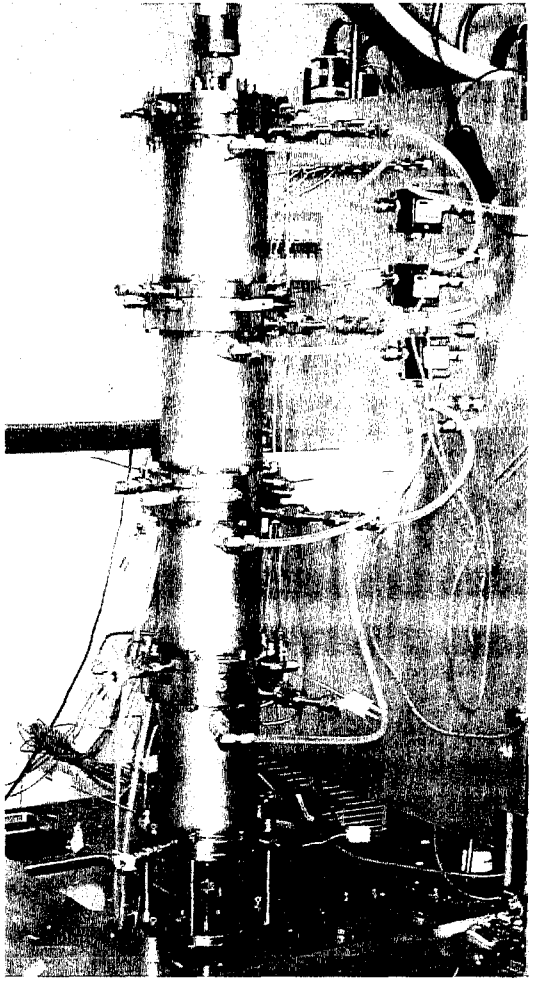
PrOx operates as a series of short residence time reactors, each with thermal management, gas mixing and catalyst volume



Goals

- very low CO
- large turndown
- minimal H_2 consumption

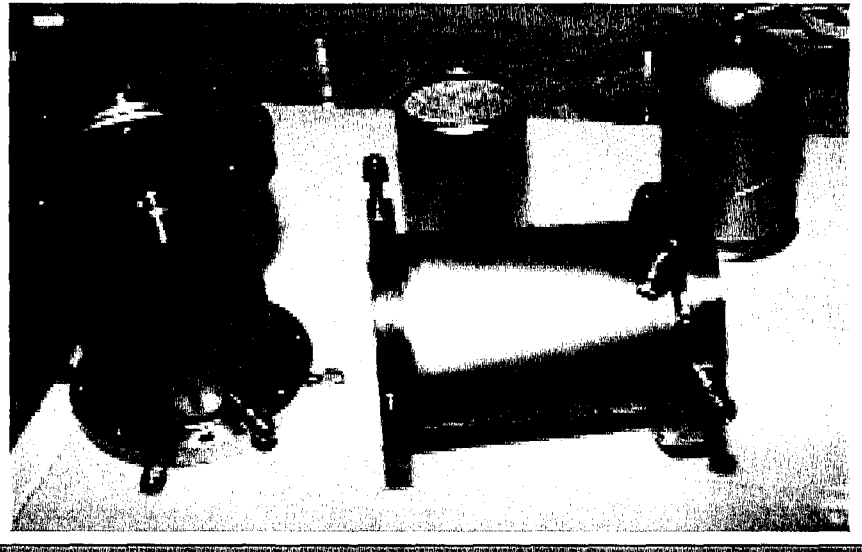
Laboratory PrOx Works as Baseline System for Testing Concepts



- 2% CO inlet to 10 ppm CO outlet
  - Simulated gasoline reformate
  - Natural gas system at Energy Partners
- Modular laboratory design gives flexibility to test:
  - Catalysts
  - Configuration options
  - Control schemes
- Design and lightweight internal components enhance transient performance
- Uniform air distribution and mixing
- Inlet temperature control

LANL Laboratory PrOx Reactor Components

Manufacturable components while still maintaining ease and flexibility of use for laboratory investigations

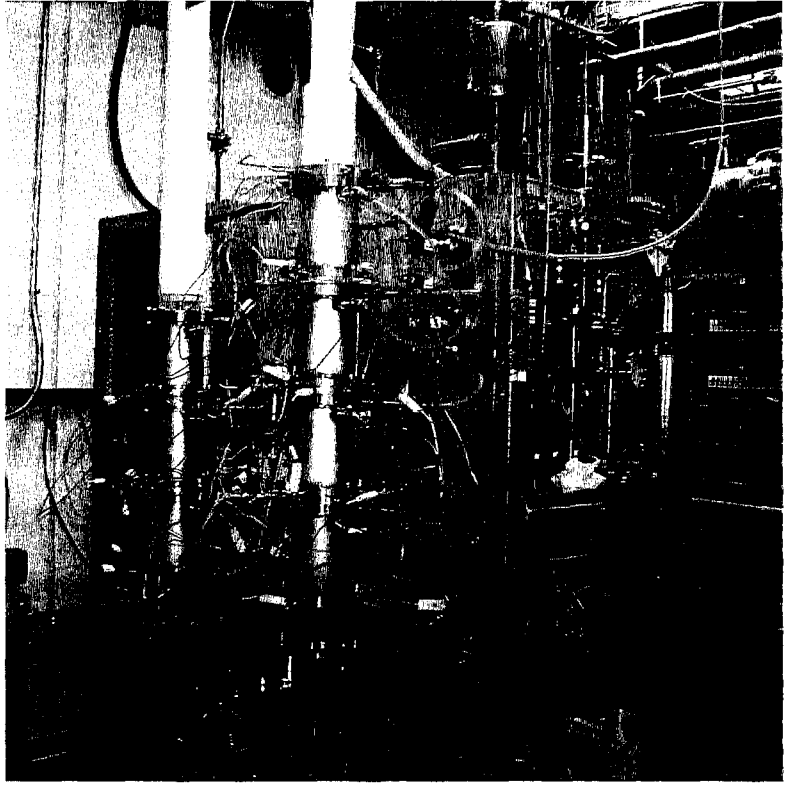


Catalyst cartridge - replaceable monoliths, pellets, foams, screens

HEX insert - replaceable insulating or cooling

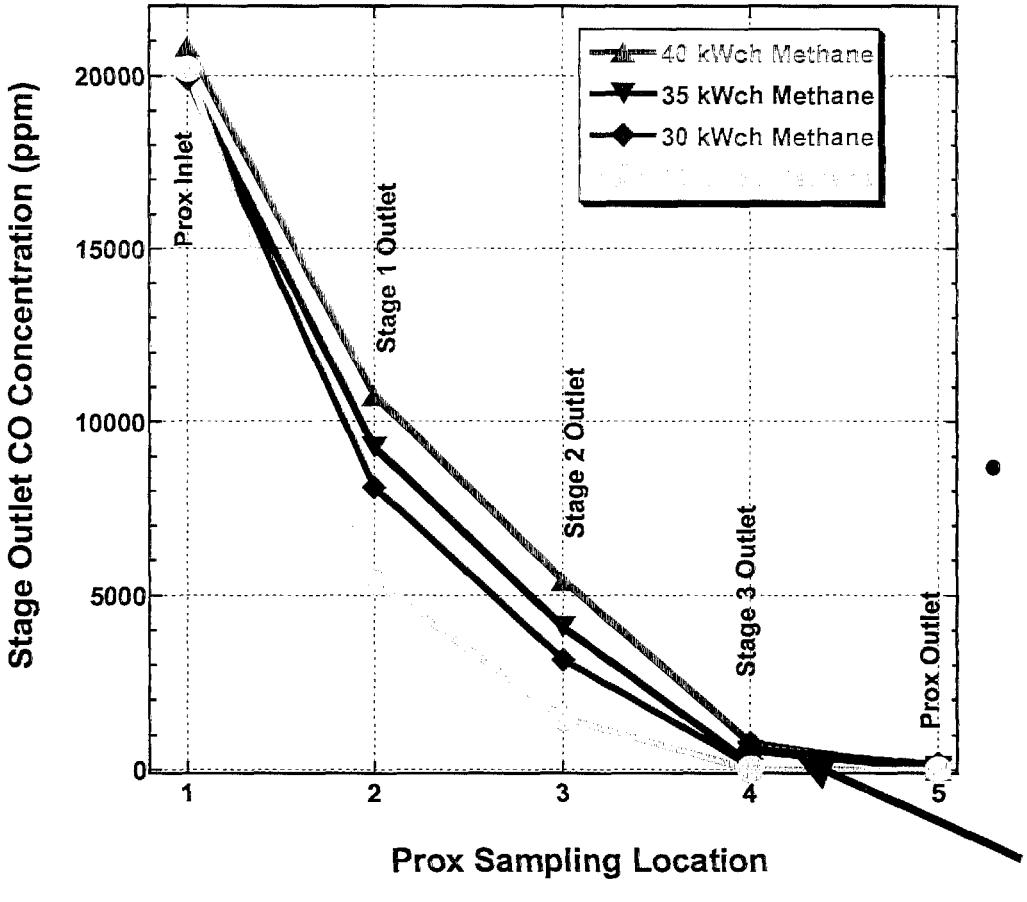
PrOx Test Facility

- Function: Benchmark testing of PrOx hardware to characterize and simulate performance in an automotive system.



- Simulate reformate output from gasoline, natural gas, or methanol fuel processors:
  - Major constituents: H_2, CO_2, N_2, H_2O
  - Minor constituents: CO, CH_4, others
  - Up to automotive-scale flow rates, 50 kW net electric equivalent
- Transient experiments
  - Computer-controlled transients and sequencing
  - Total flow (power level) and composition can be varied simultaneously
  - Transient instrumentation
  - Online gas analyzers

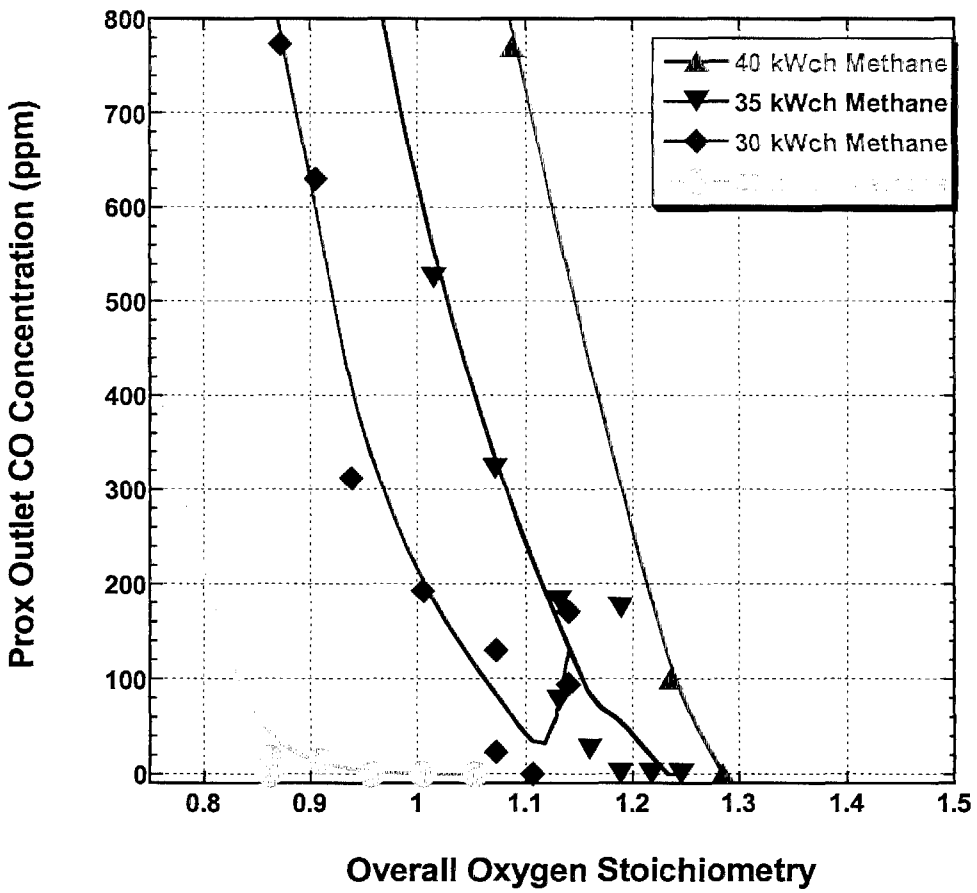
Performance of 4-stage PrOx – Outlet CO From Each Stage



- Simulated methane POx reformate at 4 total flows and specified equivalence and steam-to-carbon ratios
  - 20,000 ppm CO at inlet
- Operating points identified for each stage to produce low outlet CO (< 10 ppm)

At 20 kWch flows, 3 stages are sufficient

Performance of 4-Stage PrOx:
Outlet CO as a function of Oxygen Stoichiometry

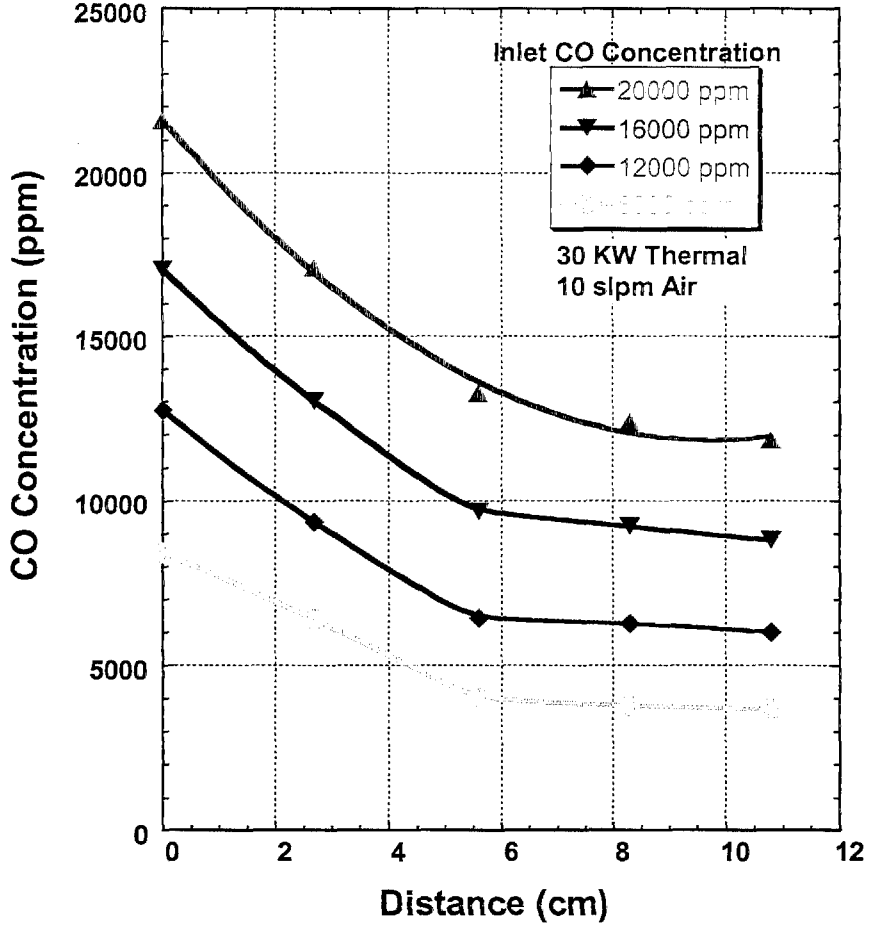


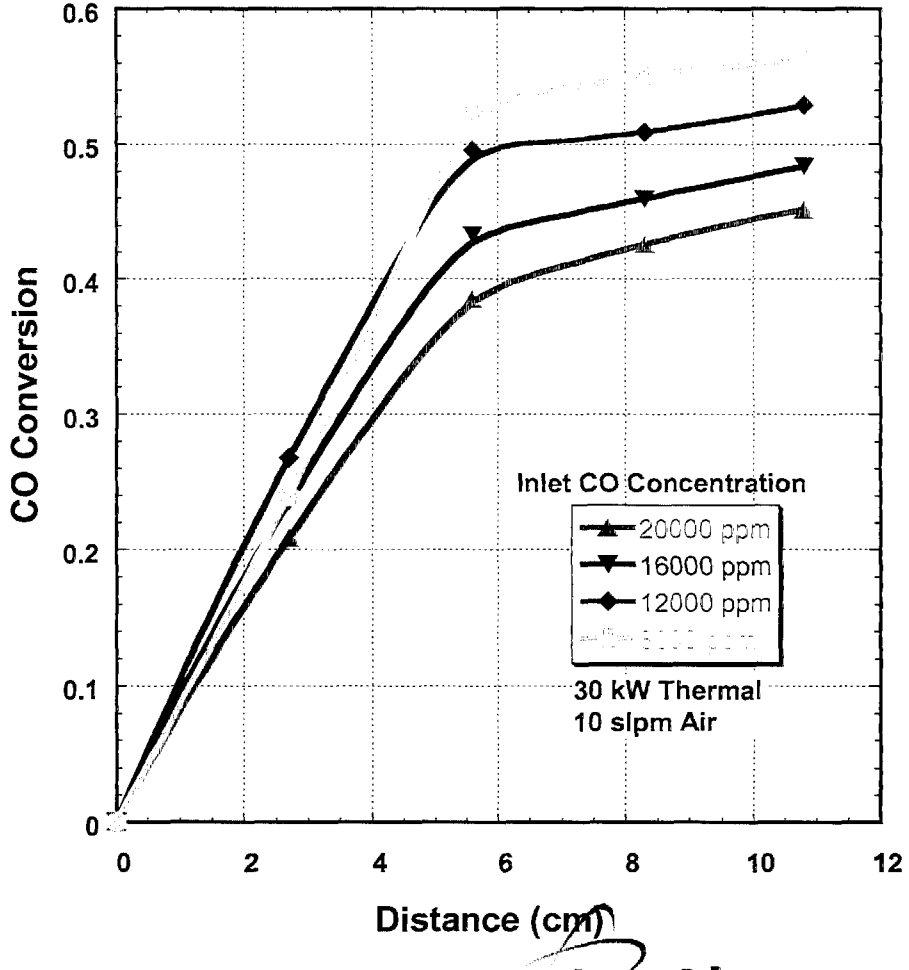
- Low outlet CO (< 10 ppm) demonstrated
- Oxygen stoichiometry reduced to below 1.3 at highest flow
- Parasitic hydrogen loss greatly reduced with new PrOx configuration

$$O_2st = 2 \cdot \left(\frac{[O_2]}{[CO]} \right)_{actual}$$

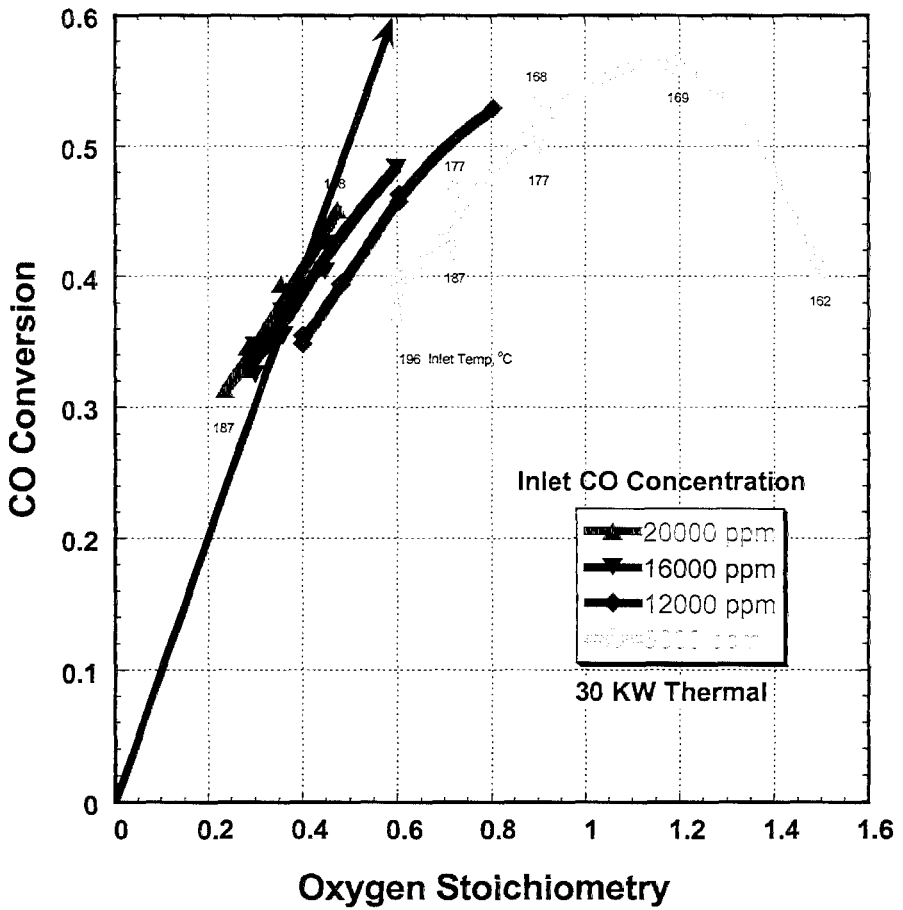
PrOx Single-Stage Characterization:

CO as a function of catalyst depth



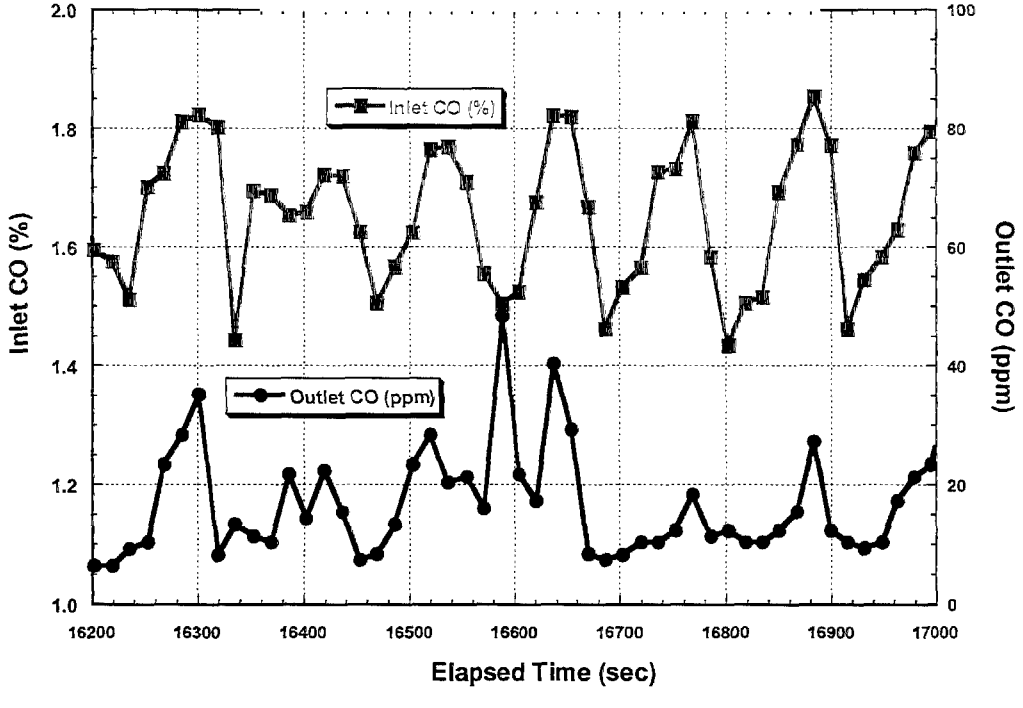


PrOx Single-Stage Characterization:
CO Conversion vs Oxygen Stoichiometry



- CO conversion as a function of oxygen stoichiometry for a first stage PrOx configuration
- Black line shows ideal for no parasitic hydrogen loss
- Data provides input to model for optimization of PrOx staging and operating conditions

PrOx Performance in a Natural Gas Fuel Processor System



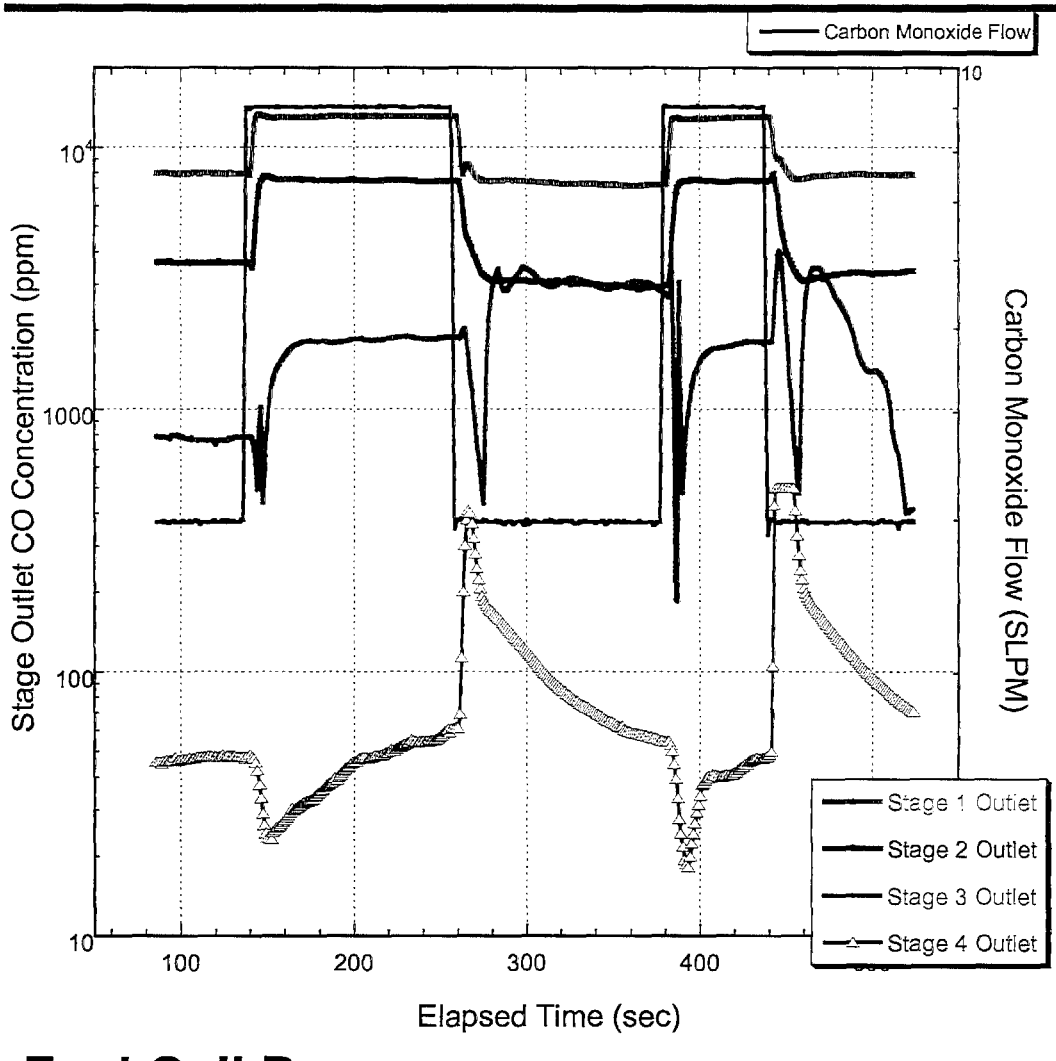
- PrOx in a natural gas fuel processor and operated on methane reformate
- Data snapshot shows Prox inlet and outlet CO concentration as a function of time at a steady reformer power level and constant PrOx control settings
- Low outlet CO (< 50 ppm) demonstrated

- Sensitivity to inlet CO concentration fluctuations greatly reduced (outlet CO < 50 ppm with inlet CO variations ~ 0.4%)

PrOx Response and Control in Transients and Startup

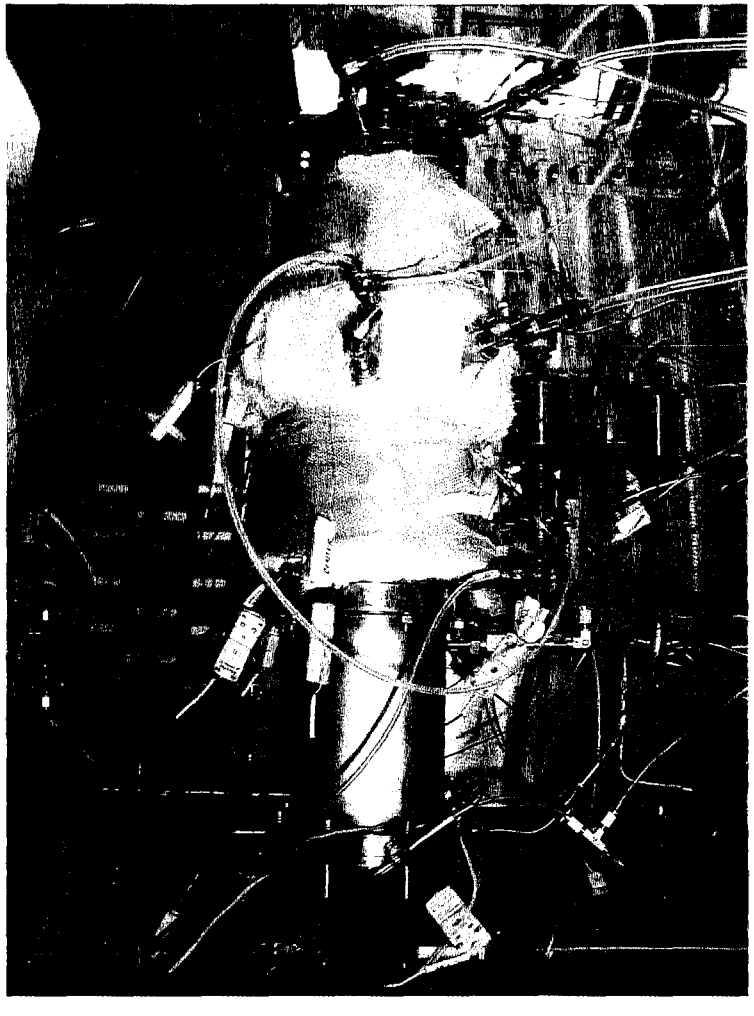
- Quantify PrOx behavior during transient operation
  - Power transient response
    - Single and multi-stage configurations
    - CO and temperature profiles
    - Information to identify control requirements
  - Sensitivity to CO variation (Composition transient)
    - Information to identify control requirements
    - Identify required detection limits for CO sensors
  - Provide data for transient modeling and trade-off studies
- Explore PrOx concepts to reduce overall fuel processor startup time
  - Short-term PrOx operation at higher inlet CO concentrations

Outlet CO Response through a Power Transient in a 4-Stage PrOx



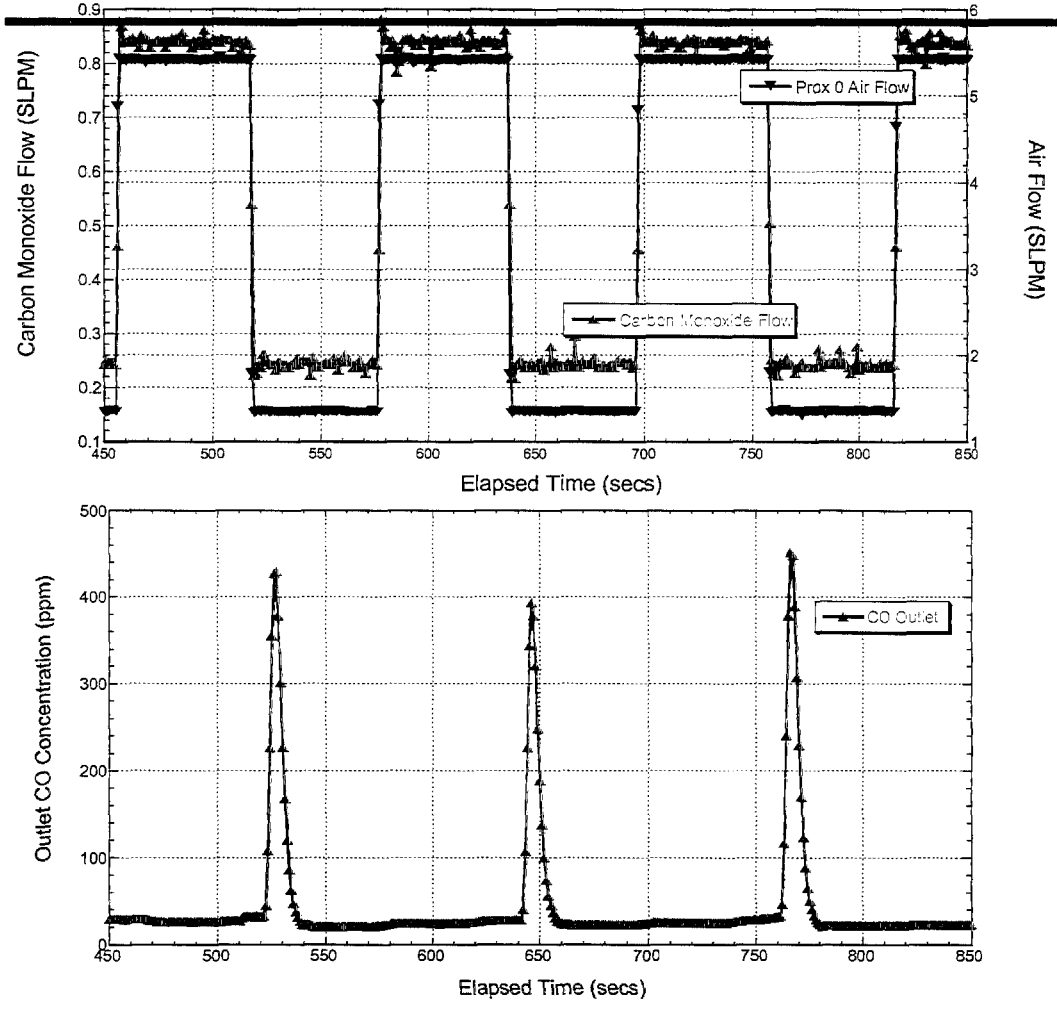
- Measurement of Outlet CO in response to a step transient
  - Nominal 20000 ppm CO Inlet
  - 10 kWth to 30 kWth LHV H_2 total flow, gasoline reformate
  - Pellet catalysts
  - CO flow shows the step transient
- Outlet CO response
  - Does not remain below 100 ppm (transient spec)
  - Stage 4 sees both power and composition transient
  - Stage 3 shows instabilities

Measurement of Power Transients in a Single PrOx Stage



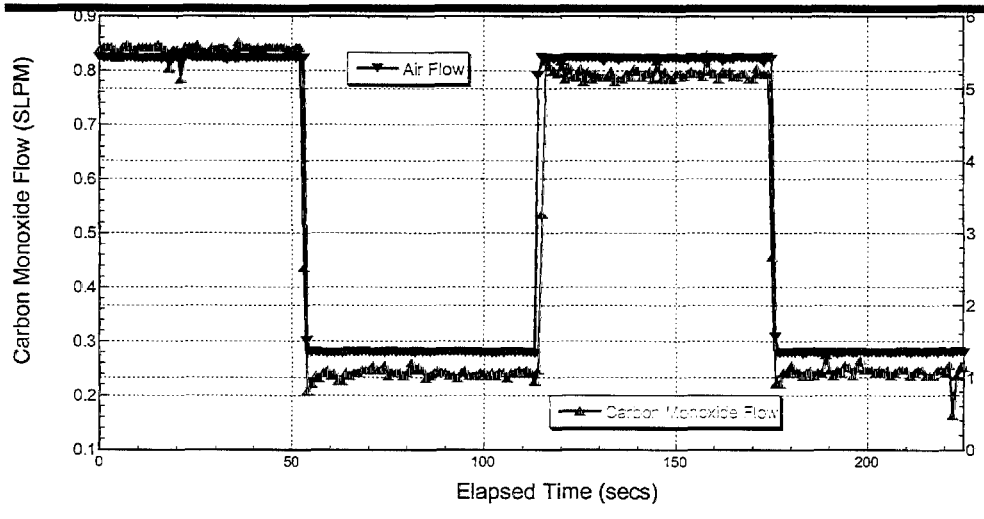
- Measurement of Outlet CO in response to step transients in total flow
  - –Single-Stage Monolith
    - Platinum-based catalyst
    - 400 cpsi
    - 3 in dia x 4 in long
  - –Gasoline Reformate
    - 37% H_2, 28% N_2, 17% CO_2, 17% H_2O
  - –Nominal 2000 ppm CO Inlet
  - –Step between 10 kWth and 30 kWth LHV H_2 total flow

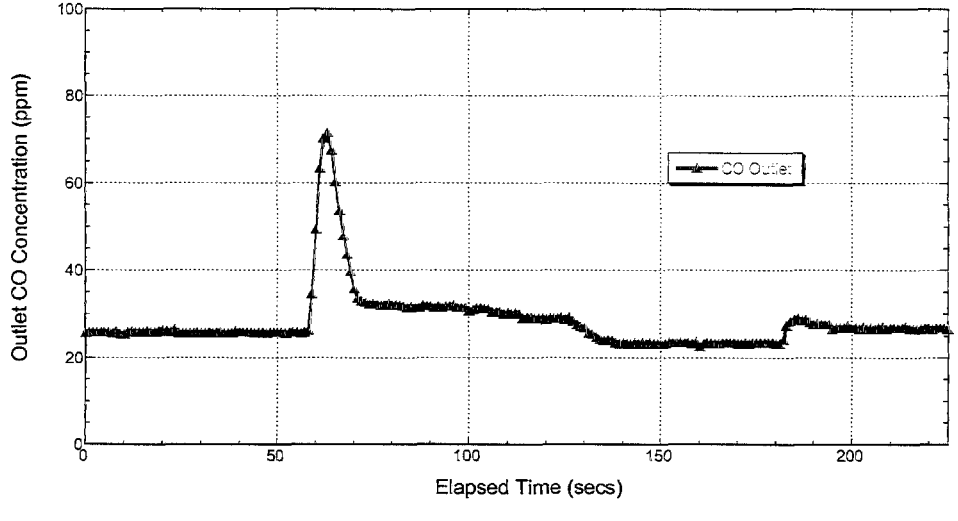
Outlet CO Response:
CO and Air Flows Changed Simultaneously



- Outlet CO response
  - Air injection tracks change in CO flow during the step flow change
  - CO peaks observed above 400 ppm on the down transient
  - Does not fall within 100 ppm transient specification
- Experiment Resolution - ~ 1 second

Outlet CO Response:
Air Injection Controlled to meet CO spec



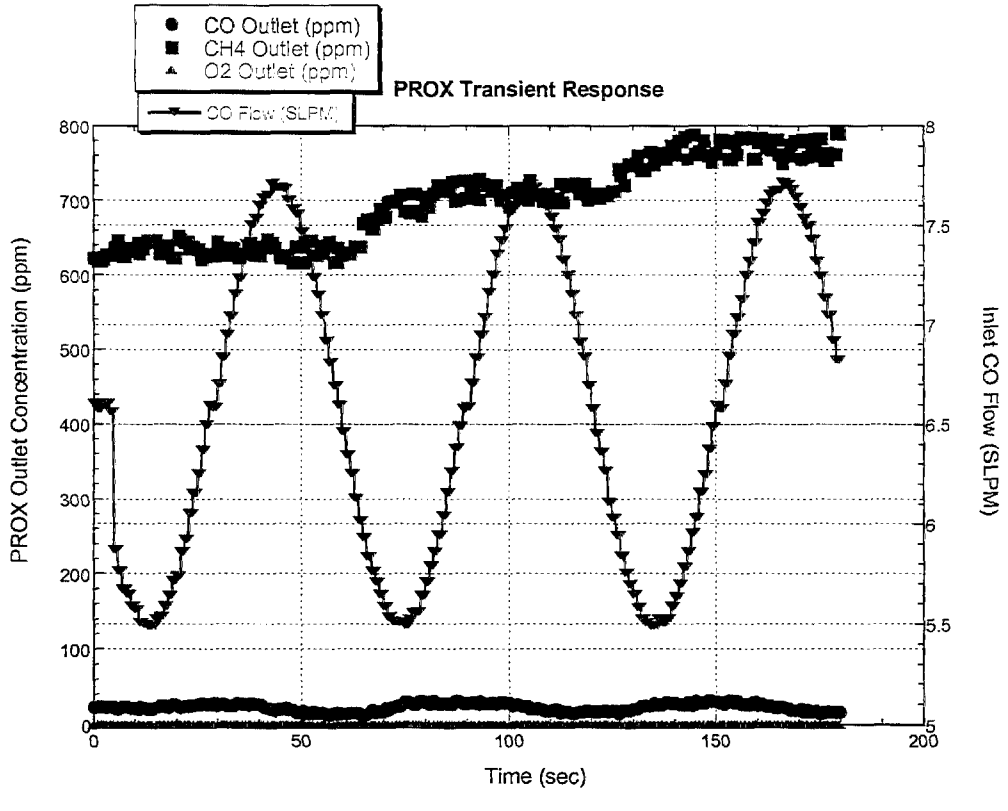


- Outlet CO response
  - Air injection leads CO by 1 sec on the up-transient
  - Air injection lags 1 sec on the down-transient
  - Maintained below 100 ppm peak
- Experiment Resolution - ~ 1 second

PrOx Transient Experiments - CO Modulation

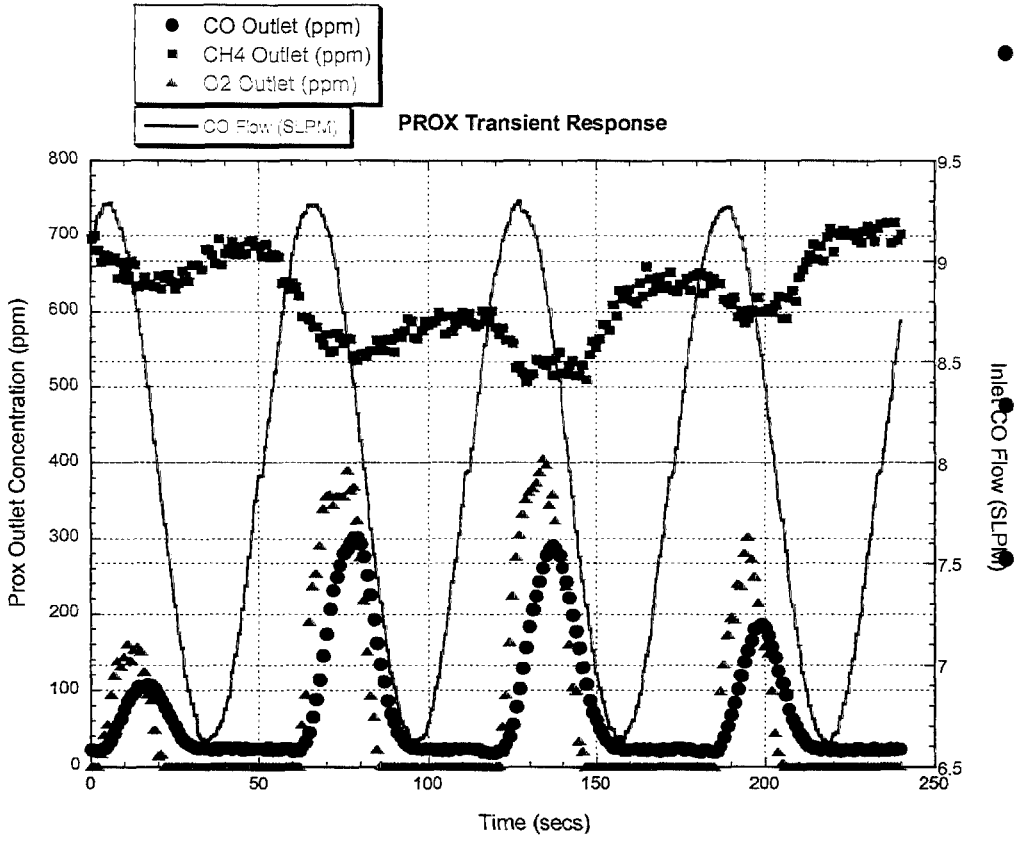
- Identify the PrOx response when the inlet CO concentration fluctuates at an overall steady flow
- Reproduce PrOx in-system performance with fuel processor on PrOx test stand with simulated reformate
- Test strategies for CO control
- Evaluate trade-offs - system complexity versus efficiency
  - For example, if the air injection is set for the maximum CO level, what is the hydrogen consumption penalty?
- Identify sensor requirements
  - Response time required?
  - Type of sensor?

PrOx Response to Modulated CO Input:
Air Injection Set for Maximum CO Level



- CO modulation with steady-state total flow
  - Simulated natural gas reformate, 30 kWth H_2
  - 15000 ppm ± 3000 ppm
- Outlet CO remains below 30 ppm
- Steady-state air injection for maximum CO input (18000 ppm)
  - Results in greater H_2 consumption, but handles the transient

PrOx Response to Modulated CO Input:
Air Injection Set for Mean CO Level

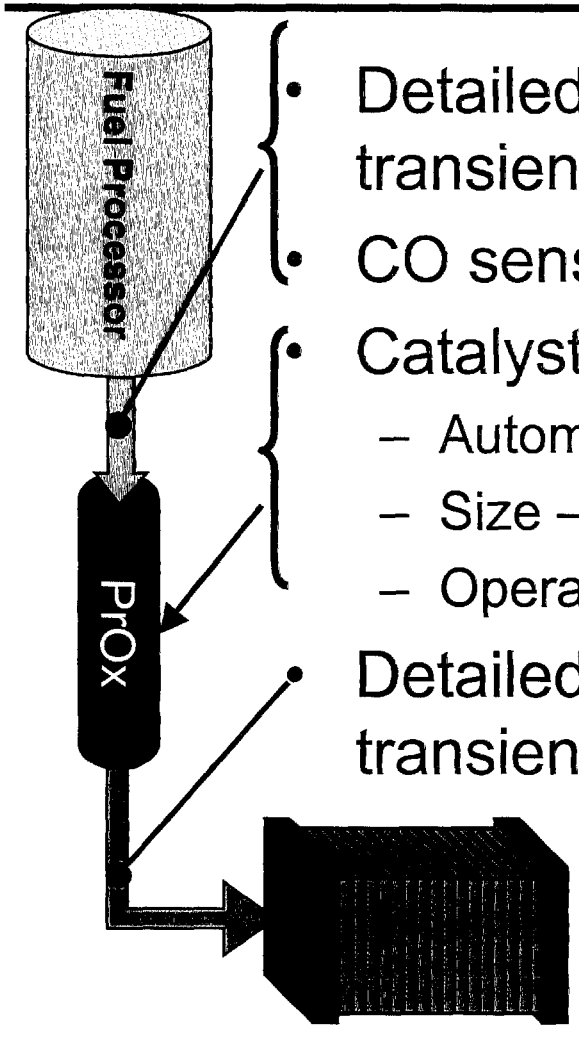


- CO modulation with steady-state total flow
  - Simulated natural gas reformate, 30 kWth H2
  - 18000 ppm ± 3000 ppm
- Outlet CO peaks at ~400 ppm
- Steady-state air injection for mean CO input
  - Does not handle transients above the mean, but does recover

CO Modulation Summary

- PrOx can handle transients when set for the maximum expected CO concentration, but at the expense of H_2 consumption.
- Required PrOx transient response may depend on fuel cell stack tolerance to CO transients.
- Measurement of other species such as O_2 may be an indicator of PrOx outlet CO concentration.

Improving PrOx Transient Performance

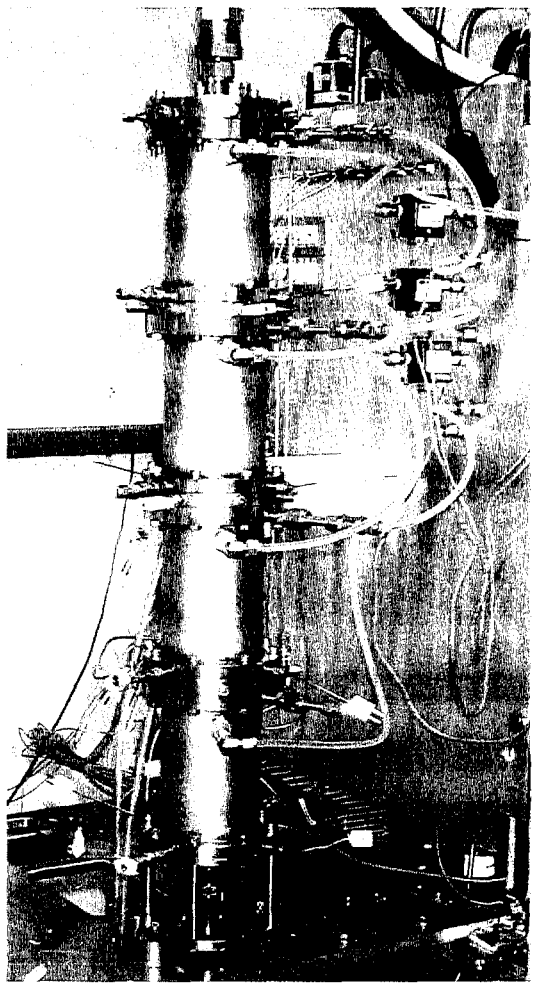


- Detailed understanding of fuel processor outlet transients – flow and composition
- CO sensor required?
- Catalysts – Improved performance
  - Automotive supports
  - Size – to reduce mass
  - Operating temperature and range
- Detailed understanding of fuel cell stack CO transient tolerance

PrOx Startup Issues

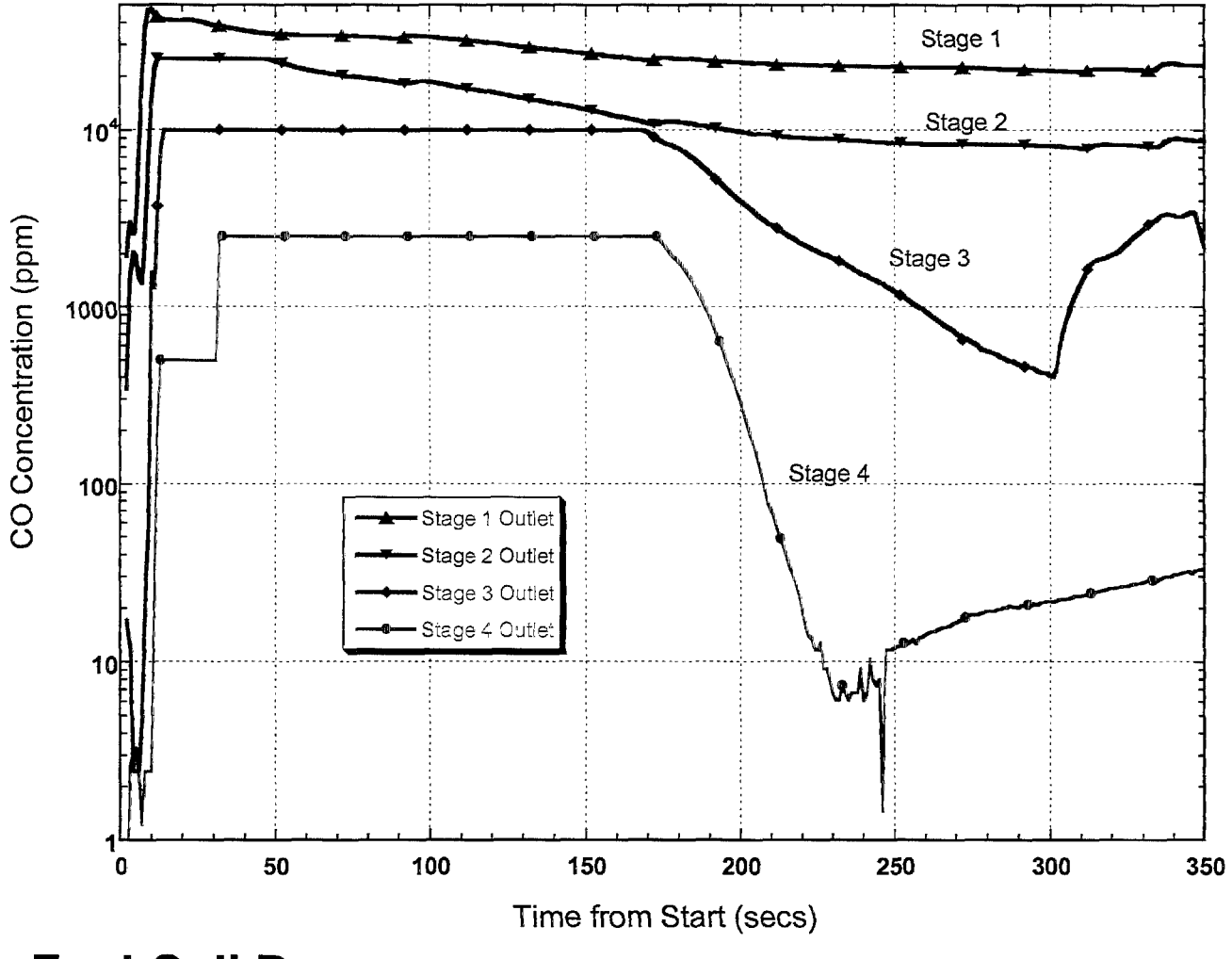
- Maintain fuel processor outlet CO concentration within fuel cell stack tolerances through the startup transient and transition to normal operation.
  - Low catalyst light-off temperature for CO oxidation
  - Wide temperature range for CO selectivity
  - Reduced thermal mass of catalysts and components in contact with the flow
  - Startup heating mechanisms
  - CO absorption during startup transient with regeneration during normal operation
  - High CO startup option
  - Control options with staged reactors

Simulation of PrOx High CO Startup



- 4-Stage Laboratory PrOx Reactor
  - Staged Adiabatic plug-flow reactors with interstage cooling
  - NDIR CO analyzers monitor outlet of each stage
  - Pellet catalysts
- Startup Conditions
  - 10 kW (LHV H_2) Simulated Gasoline reformate. 200 °C
  - 5 % CO (wet)
  - PrOx at Room temperature
  - Initial air flows set to achieve a maximum temperature at each stage outlet

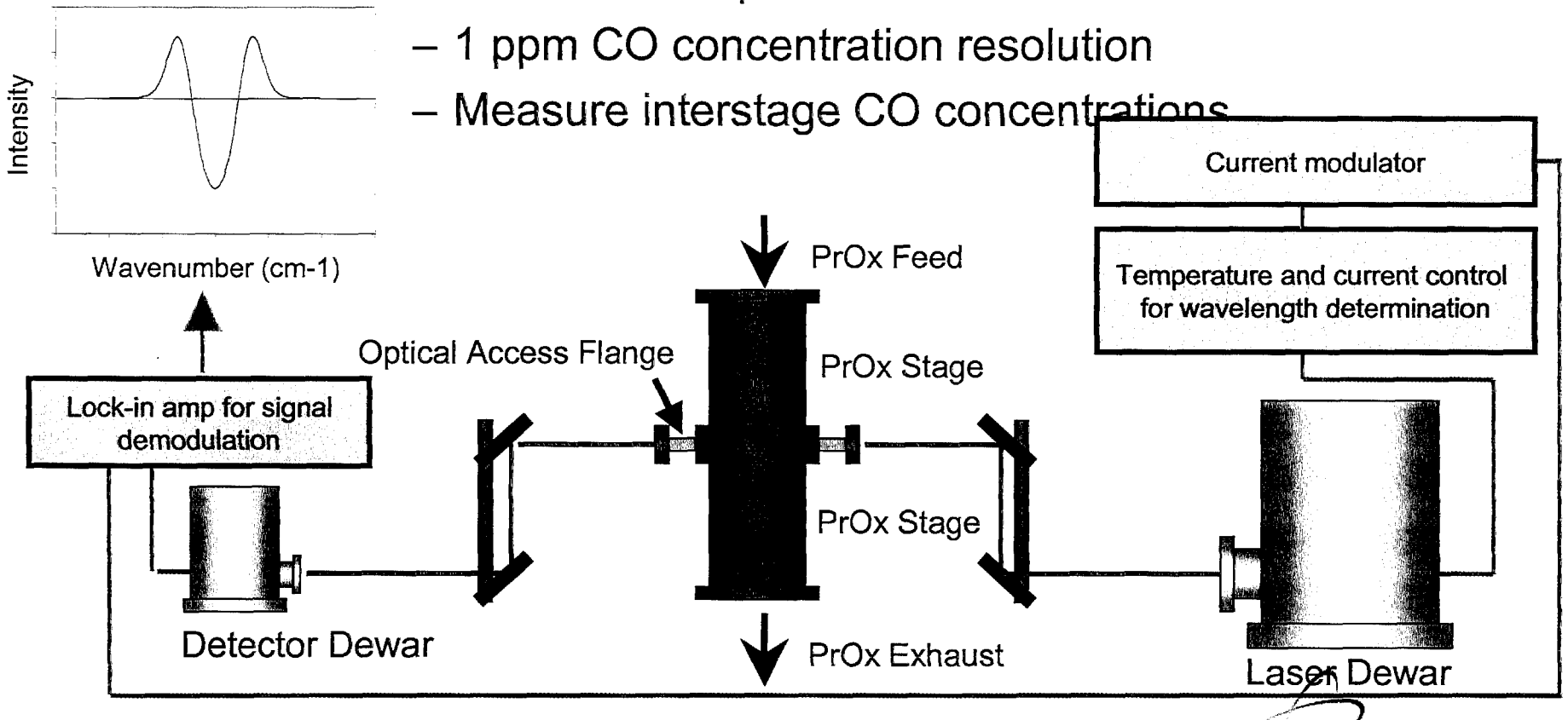
Stage Outlet CO Profiles during High CO Start-Up



- Initial test of concept drops outlet CO below 10 ppm in 225 secs
- CO starts to rise after initial minimum
- Requires fine-tuning of air flow control algorithm
- Faster response with monoliths?

Transient *in situ* CO Diagnostics

- Tunable Diode Laser Absorption System
  - 100 msec temporal resolution
  - 1 ppm CO concentration resolution
  - Measure interstage CO concentrations



Summary

- Transient performance – startup and power – are critical for automotive applications
- Working laboratory reactors and test facility developed to investigate the fundamentals of reformate cleanup technology
- Transients
  - Investigating strategies for cold-start and transient control – power and composition transients
  - Developing fast *in situ* CO diagnostics