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 ºC 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.

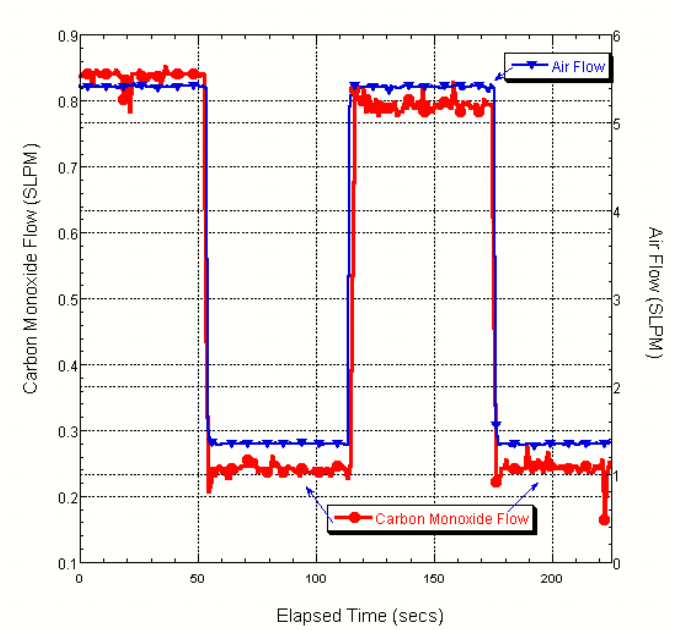

Figure 1. CO and air injection flows during step transients between 10 kW and 30 kW total flows of simulated gasoline reformate.

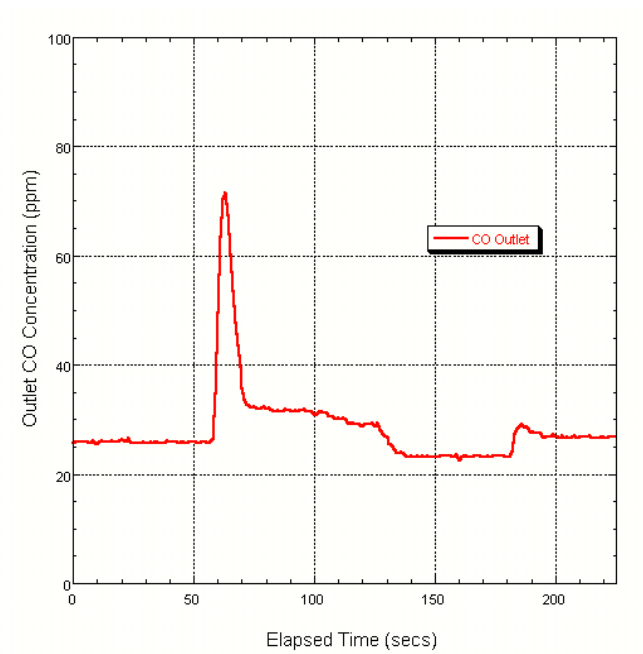

Figure 2. Outlet CO concentration measured during step transients between 10 and 30 kW total flows of simulated gasoline reformate.

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.

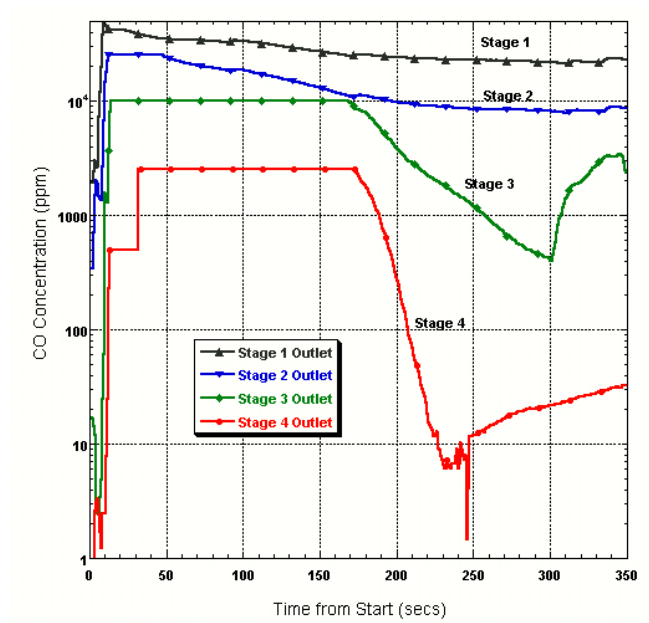

Figure 3. Outlet CO concentrations from each stage of a 4-stage PrOx reactor during startup with an inlet 5% CO concentration in simulated gasoline reformate.

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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