

Performance of Microlith Based Catalytic Reactors for an Isooctane Reforming System

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ABSTRACT

Use of catalytically coated short contact time (SCT) design approaches for application in mass transfer controlled reactors such as Auto Thermal Reformers (ATR's) is an area of much recent interest. Precision Combustion, Inc. (PCI) has developed an efficient and compact ATR using ultra-short channel length, high cell density SCT substrates (Microlith®). PCI has also extended this Microlith technology to other fuel processor reactors that operate at lower temperatures and are not mass transfer limited. Namely, reactors for the Water Gas Shift (WGS) and Preferential Oxidation (PROX) of CO have been developed. Due to the higher surface area per unit volume of the Microlith substrate compared to conventional monoliths, size advantages have been observed for these reactions, which are more kinetically controlled. This results not only in shortened startup times and quick load following capability but also allows much smaller and lighter reactors – required attributes for automotive fuel cell applications. In this paper, experimental data on the performance of Microlith based ATR, WGSR and PROX reactors for reforming isooctane is presented. Transient and durability characteristics have also been included and compared to Department of Energy (DOE) targets.

INTRODUCTION

One of the major obstacles in widespread use of fuel cells is the lack of a hydrogen supply infrastructure, which is constrained by significant technical and economic hurdles. On-board or localized reforming of liquid fuels, such as gasoline, which have extensive supply networks, is a sensible approach until a hydrogen supply infrastructure is available. To realize this goal there have been a number of attempts to develop on-board fuel processors. Although significant progress continues to be made, major remaining hurdles need to be overcome before on-board fuel processing technology can be successfully implemented. Current fuel processors are limited by low power density, sluggish transient response and slow startup time mostly as a consequence of large size and weight. The required size

and weight goals for a practical system have been outlined in the DOE PNGV targets.

Short Contact Time (SCT) reactor design approaches offer the potential for development of advanced fuel processors with a high likelihood of overcoming these barriers. Precision Combustion, Inc. (PCI), using a SCT Microlith technology has developed extremely compact, lightweight and efficient fuel processor reactors – Auto Thermal Reformers (ATR), Water Gas Shift Reactors (WGSR) and Preferential Oxidation Reactors (PROX) – with very fast transient response capability. While These reactors have been demonstrated over a range of conditions and fuels. In this paper we report the performance of these reactors under conditions suggesting consecutive operation, i.e. same H_2O/C and O_2/C ratio with the objective of demonstrating feasibility of a compact and fast transient response integrated reformer system.

SHORT CONTACT TIME APPROACH

Short contact time approach to chemical reactor design essentially consists of passing a reactant mixture over a catalyst at very high flow velocities, such that the residence time of the gas mixture inside the catalyst bed is on the order of milliseconds). Such SCT processes have commercially been used for a long time, for example in ammonia oxidation reaction in nitric acid production, where a mixture of ammonia and air is passed over precious metal gauzes. Near 100% conversion of ammonia with very high selectivity to the desired product is achieved. PCI has been developing application of similar catalytic systems based upon wire mesh coated with precious metal catalysts for many applications [1]. In more recent years Prof. Lanny Schmidt has proposed application of this system to a range of partial oxidation reactions by using either monolith supported catalysts [2] or a single gauze of bulk precious metal catalyst [3]. A research group at Shell performed similar partial oxidation over catalyst coated on a foam substrate with high porosity and tortuosity [4].

Using coated metal screen catalytic systems (Microlith) we have designed reactors operating at very high gas hourly space velocities for both mass transfer

and kinetically controlled reactions. This provides many advantages over traditional packed bed or monolith bed approaches e.g. smaller reactor size and improved selectivity over conventional substrates. For example in mass transfer limited reactions (e.g. ATR) SCT Microlith catalyst and substrate designs show higher selectivity to partial oxidation reactions, allowing operation within the material limits of commonly available materials. In kinetically controlled reactions (e.g. WGSR) near equilibrium operation at high space velocities (i.e. small reactor sizes) with lower selectivity to methanation has been observed. This is due to the higher Geometric Surface Area (GSA) per unit volume of the reactor combined with a high Specific Surface Area of the catalyst support/washcoat.

The Microlith technology consists of a series of discrete, ultra short channel length, low thermal mass metal monoliths [1]. Figure 1 shows magnified pictures of a conventional monolith and the Microlith substrates to give a conceptual understanding of its physical attributes. The effectiveness of the Microlith technology and long-term durability of PCI's proprietary catalyst coatings have been demonstrated in many applications e.g. exhaust aftertreatment [5], trace contaminant control [6, 7], catalytic combustion [8], partial oxidation of methane [9], and hydrogen peroxide decomposition. The ultra short channel length avoids the boundary layer buildup observed in conventional long channel monoliths and is justified in the following paragraph.

The breakup of the boundary layer in the Microlith substrate (due to the very small L/D ratio) enables higher heat and mass transfer coefficients than that for long channel monoliths or foam substrates, as shown in Figure 2. This Figure shows the results of a prediction of mass transfer coefficients as function of channel length to channel diameter (L/D) ratio and flow velocity for monoliths with a channel diameter of 3 mm. The mass transfer coefficients are determined by using Reynold's analogy between heat and mass transfer coefficients and correlation given for heat transfer coefficients in Shah and London [10]. Conventional monoliths have L/D ratio much greater than 10, whereas for Microlith substrate the L/D ratio is in the range of 0.1 to 0.5. The 3-D plot suggests that while increasing the flow velocity over conventional monolith substrates does provide some increase in mass transfer rate, a similar increase can be obtained over the Microlith substrate at

much lower flow velocities due to the lower L/D ratio. As an example, consider a Microlith substrate with L/D of 0.1 and monolith with L/D of 10. In order to achieve a mass transfer coefficient, K_g , of 100 cm/sec, the flow velocity would have to be much greater than 200 ft/sec. However the Microlith could operate at a K_g of 100 cm/sec at only 75 ft/sec. The data also suggests that the higher the velocity, the greater the difference between the mass transfer coefficients Microlith and Monolith substrates. Higher mass transfer coefficients also imply higher heat transfer coefficients. At a velocity of 150 ft/sec, the correlation predicts mass transfer coefficient of 228 k_g (cm/sec) for Microlith substrate (L/D of 0.1) versus 28 for monolith substrate (L/D of 10). The implication therefore is that short contact time coupled with high mass transfer coefficients are available only for low L/D substrates.

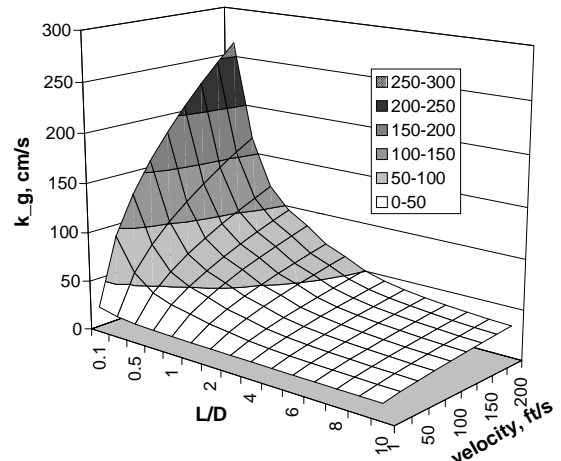


Figure 2: Plot of mass transfer coefficient (k_g) vs. length to diameter ratio (L/D) vs. velocity.[9]

Convective heat exchange with the gas phase is also strongly dependent on the boundary layer buildup. A Lumped Sum Capacitance analysis yielded time constants of 0.12 and 3.4 sec for the Microlith and ceramic monolithic substrate, respectively; which is a 30-fold improvement in thermal response [11]. A theoretical prediction of the heat up of the substrate in a non-reacting gas stream shows excellent convective heat transfer. Additionally the low thermal mass of the Microlith substrate results in rapid heat exchange with the gas, allowing equilibrium conditions to be quickly achieved. The fast startup potential of the Microlith substrate has also been seen in automotive tests [12].

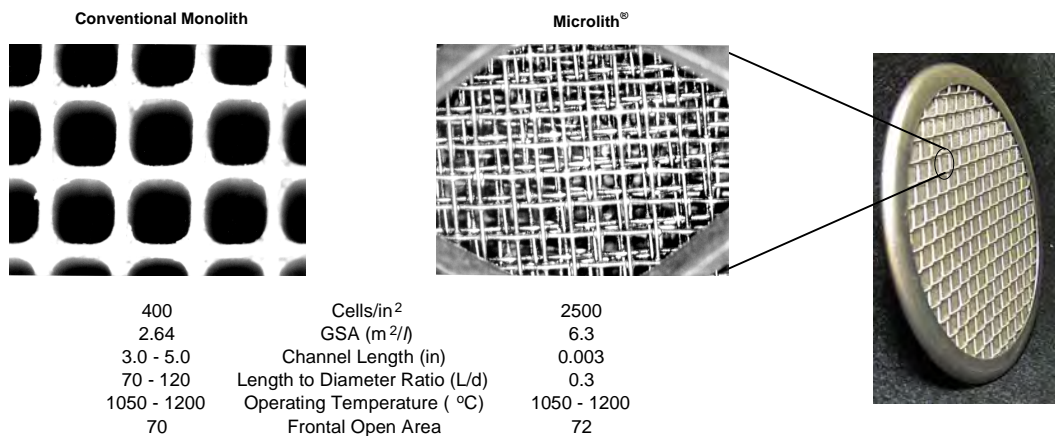


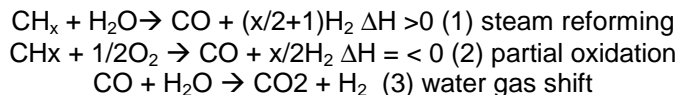
Figure 1: Physical characteristics of conventional monolith and Microlith substrate.

In exothermic reactions control of reactor temperature is a primary concern. The Microlith substrate is well suited for applications where control of reactor temperature is critical. One of the issues with on-board hydrogen generation for automotive applications is the presence of transients during startup, sudden accelerations and decelerations that can lead to abrupt changes in load demands (throughput) on the reactor. The enhanced transport properties of the Microlith combined with the lower overall mass offers the potential for improved transient response. Tests have shown that Microlith bed temperatures track inlet temperatures to within 2- 3 sec.

In this paper we report the results of separate testing of the three Microlith based reactors, comprising the principal components of a fuel processor system, namely, an ATR reactor, a WGS reactor and a PROX reactor. All reactors were tested using synthesized gas mixtures in a rig setup with mass flow controllers and heaters providing specified inlet conditions. These conditions were picked for each reformer component test such that the effluent of a previous reactor corresponds to the inlet to the following reactor. We realize that some additional conditioning of the stream between the consecutive reactors may be required, such as cooling and addition of extra steam between the ATR and WGS and cooling and air addition between the WGS and PROX. Integration with balance of plant components such as pumps, heat exchangers, anode gas burners, etc. are not reviewed in this study since these are often system-specific and is an outcome of system optimization analysis. The objective of this paper is to show the advantages of using Microlith based reactors for each of the reformer components and to demonstrate feasibility of a complete reformer, which exceeds current DOE size and weight targets.

THE AUTO THERMAL REFORMER

Hydrocarbons may be converted to H₂ either through steam reforming (reaction 1) or partial oxidation (reaction 2) usually followed by a water gas shift reaction (3), which converts CO formed on the first step to additional hydrogen.



The steam reforming reaction is endothermic and requires external heat, while traditional non-catalytic partial oxidation of liquid hydrocarbons proceeds through a complete oxidation step, such that very high temperatures are reached on the front of the reactor. For improved efficiency and control of the process it is desirable to operate a primary reformer in the autothermal regime through combined steam reforming and partial oxidation in one reactor.

Typically if an autothermal reformer is operated at a stoichiometry close to that of the ideal reforming process, with good thermal integration, high reactor efficiency can be achieved e.g. PCI's experience with autothermal reforming of methanol suggests that efficiency of up to 87% can be obtained in these

processes. In addition to high efficiency the autothermal reaction can be very fast, carried out in a small volume under adiabatic conditions (without external heat) and at high space velocities (~500,000 hr⁻¹).

An autothermal reactor (ATR) based on the Microlith catalyst substrate technology was tested for reforming isooctane into hydrogen. The reactor was made of stacked Microlith screens coated with La-stabilized alumina washcoat and a precious metal based catalyst. A schematic diagram of the reactor is shown in Figure 3. The reactor diameter was ~ 4 cm and length ~1.2 cm, which corresponds to a volume of about 15 cm³ (~1 in³) and a mass of ~12 gms for the catalyst and substrate. The isooctane feed rate corresponded to about 3.4 kW_t of thermal energy input and water and airflow were regulated to provide the specified steam to carbon and oxygen to carbon ratios. This implies a power density of 160 kW/L and 200 kW/kg. Several thermocouples and gas sampling probes were placed between the screens along the axis of the reactor to elucidate the reaction sequence. This allowed measuring axial temperature and gas composition profiles along the reactor. In this test the reactor feed comprised of isooctane (2,2,4-trimethylpentane), steam and air with H₂O/C ratio of 2.0 and O₂/C ratio of 0.5. Upstream of the reactor water was vaporized into superheated steam by an electrically heated vaporizer and mixed with pre-heated air. Fuel was injected into the stream as liquid upstream of a static mixer, where it was vaporized and mixed with the stream before entering the catalyst bed. The heat required to vaporize the water in the test would be expected to come from a thermally integrated system. Calculations of the amount of heat needed to vaporize the water and fuel indicate no external energy input would be needed for a complete processor system.

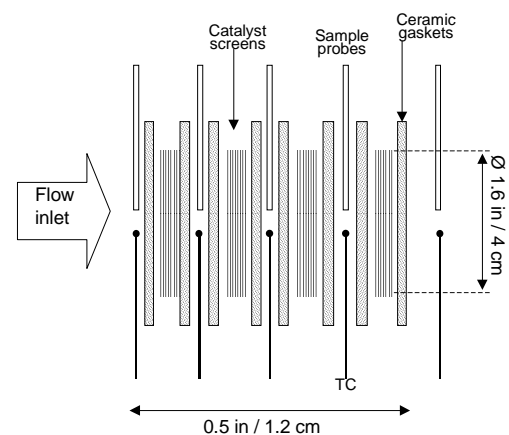


Figure 3. Schematic of a Microlith based isooctane ATR.

The catalyst was initially preheated to about 200 °C by flowing hot air through the reactor. The water vaporizer was preheated to ~200°C without water flow. Water and fuel flows were simultaneously started leading to lightoff of the catalyst bed. Thermocouple readings of the catalyst temperature during the start up process are shown in figure 4. Fuel and water flows were started at t = 0, after which the catalyst bed temperature rapidly increased to a steady state value. Lightoff of the reactor started at the front of the bed and rapidly propagated

towards the back. From the figure 4 it can be seen that the start up process, from lightoff to steady state, takes less than 30 seconds, with the front of the reactor being fully operational after less than 10 seconds. Finally, based on previous data from similar reactors and the transient response of the WGS and PROX reactors, the ATR is anticipated to meet DOE targets of 5-second response time for 25% to 100% load transient.

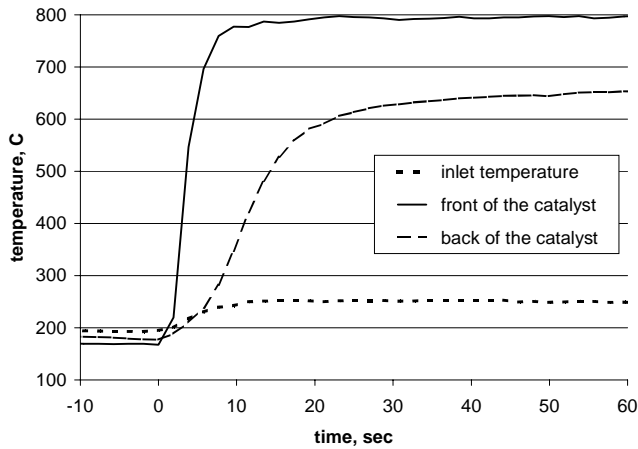


Figure 4. ATR reactor lightoff characteristics.

Results of the test of the Microlith based ATR reactor under the specified condition is shown in figure 5. The figure shows the catalyst temperature profile, hydrogen and oxygen concentrations in the reformate mixture on a dry basis and fuel conversion. These data show that complete conversion of fuel to primarily H₂ and CO was achieved at a peak catalyst temperature of ~ 850°C. In addition, the reactor achieved nearly 90% of the final, or equilibrium, hydrogen concentration within 2 mm into the reactor. Exit mixture composition on a dry basis was 34 % H₂, 7.7 % CO, 14 % CO₂, 0.5 % CH₄, 44 % N₂ and trace amounts of higher hydrocarbons. Note the low amount of methane produced in the ATR reactor under these conditions. This is an important advantage of the Microlith based catalyst, as the methanation reaction irreversibly consumes hydrogen, such that it cannot be extracted in the downstream reactors. There was no evidence of coke formation in the reactor after about 5 hours on stream.

Assuming a 1 to 1 conversion of CO into H₂ in a downstream water gas shift reactor, the thermal efficiency of the tested reactor (based on the ratio of lower heating values of product hydrogen to input fuel, as defined by the DOE fuel cell handbook [13]) was ~70 %. Note, that using this definition the maximum achievable efficiency for isooctane reformation is 90 %.

While long-term ATR durability data for the reactor described above is currently unavailable, the durability of a nearly identical reactor was tested for the partial oxidation of methane for 500 hours. No performance degradation was observed during that test which was aged at much higher temperatures, which can be considered a severe aging condition. More importantly the washcoat was adherent even in the hottest portions of the reactor [9].

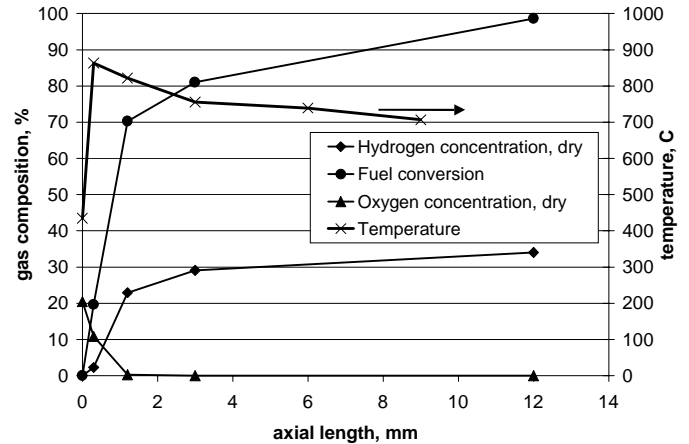


Figure 5: Temperature and Gas composition profile along the reactor.

THE WATER GAS SHIFT REACTOR

A compact and lightweight water-gas shift reactor has been developed that can be operated in both single and dual stage configurations as per system requirements. These attributes arise from the high operating space-velocities ranging from 11,000 hr⁻¹ in a two-stage configuration to 40,000 hr⁻¹ in a single stage. These two configurations achieved outlet CO concentrations of 1.0% to 0.5%, which then are processed in a PROX reactor for further reduction to permissible levels for PEM fuel cells, usually between 50 and 10 ppm. The formulations used for operating in these configurations, produced a WGS rate constant of 684 mol/(min-l catalyst). This allows operation at even higher space velocities of 30,000 hr⁻¹ to 70,000 hr⁻¹ at 280°C (subject to inlet concentrations, especially the water to CO ratio). In comparison, other reactor/catalyst combinations have shown WGS rate constants of about 17.5 mol/(min-l catalyst) at the same temperature [14].

Currently, the PCI WGSR exceeds DOE 2004 primary performance targets. Table 2 compares the goals achieved by PCI's WGSR with DOE's targets for

Table 1: Performance comparison of Microlith-based ATR vs. DOE targets.

| Parameter | ATR | DOE ATR Targets |
|--|----------|-----------------|
| ¹ Power Density (catalyst only), (kW/L) | 160 | >77 |
| Weight (catalyst only), (kW/kg) | 200 | >67 |
| Durability, (hrs) | underway | 5000 |
| Fuel conversion, (%) | > 99 | > 99.9 |
| Startup,(sec) | <30 | <60 |

1: Based on thermal energy input, reactor volume/weight and efficiency.

the shift reactor. All calculations were done for simulated conditions of a 75 kW PEM fuel cell automotive application. Two different concepts were explored, a single stage unit that would operate adiabatically and a dual stage unit that would employ an inter-stage heat exchanger. This translates into a specific power density of more than 25 kW/L for a representative WGSR. Note that these configurations are considered un-optimized, yet demonstrate the potential of the Microlith substrate to be used for lightweight compact applications.

The operating condition selected for showcasing the WGSR in this paper is representative of the composition that would be delivered from many types of reformers operating on various fuels. The condition consists of about 6% CO, 30% H₂, 34% H₂O and 10% CO₂ with N₂ making up the balance with an operating temperature of about 300°C. This is usually considered a high temperature shift stage and would normally be followed by a low temperature shift stage to further reduce the CO. Yet, the Microlith-based design requires only the high temperature stage reactor since the effluent contains less than 1% CO and can safely be introduced into the PROX reactor. Two additional important constraints for reactor design are the transient response capability and durability. The transient capability manifests itself in the ability to rapidly respond to changes in load, which is particularly critical in automotive applications. In addition, durability is essential to the long term, low maintenance operation of the reactor within the system. To address these concerns and determine where improvements are needed, a promising water gas shift formulation, a precious metal on a stabilized alumina support, in terms of performance was chosen and tested. Observations and calculations indicate that the durability of the water gas shift reactor is mostly dependent on the catalyst formulation whereas the transient behavior is a combination of reactor substrate design and formulation.

A durability test, alternated between low and high temperature shift conditions, was done on the same formulation. Equilibrium CO concentrations for the high and low temperature conditions are 2.0% and 1.0% respectively, from inlet concentrations of 5.65%. This testing produced an aggregate of 215 hours of operation, 123 hours at low temperature conditions and 92 hours at high temperature conditions. In addition, these tests cycled the reactor about 5 times which can be thought of as a simulation of start-stop cycles. Each time the reactor was started for a new durability run, it immediately arrived at its steady-state operational level. The activity was very stable for the high temperature conditions, but a slight decrease in activity was measured for the low temperature conditions.

Transient response tests were done to determine the ability of the Microlith WGS reactor to follow load conditions. The concentrations and flow rates chosen simulated a nominal 25% and 100% load for a 75 kW automotive fuel cell application (Figure 6). Figure 7 is an exploded view of one cycle from Figure 6 to allow a clear idea of the time response for steady state to be achieved after a load switch. It can be seen that the system reacts immediately to the changing influent

and takes about 10 seconds to settle out and achieve steady state operation (this includes rig response time and has not been separately called out). If the transient condition is considered complete when the reactor achieves 90% of steady state, the response time is 25% faster.

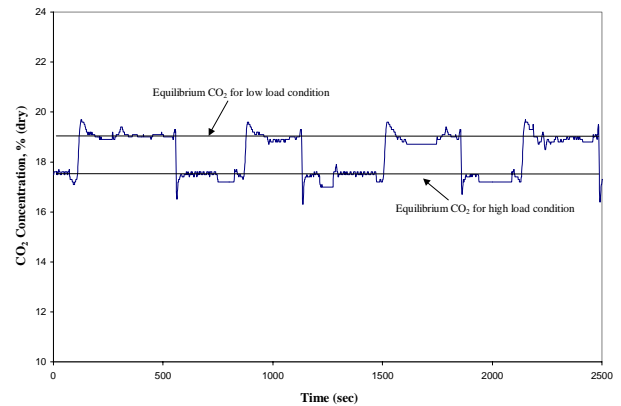


Figure 6: Composite plot showing reproducible behavior of Microlith WGSR for load following transients between 25% and 100% load simulations.

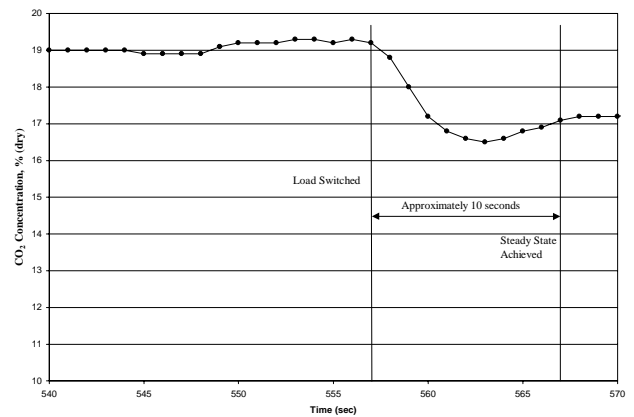
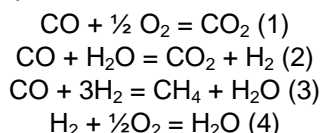


Figure 7: Expanded view of a 25% to 100% load transient. Response time to steady state is ~10 sec.

In this test, an NDIR CO₂ analyzer was coupled to the reactor effluent to measure the transient change in CO₂ concentrations when a solenoid valve switched conditions. The NDIR was used because the response time of the unit enabled multiple data points to be taken during the transients. The available CO analyzer had too long of a response time to track performance. Once the reactor achieved steady state, GC measurements were taken to confirm the CO₂ NDIR data. The plot in Figure 6 below shows CO₂ concentrations on a dry basis for a set of switches done to confirm reproducibility of the reactor system. Equilibrium CO₂ concentrations for both load conditions are shown on the plot as well. This experiment clearly demonstrates the potential for the Microlith WGSR to continually convert CO at constant levels for a given influent while responding to rapid changes that could be experienced in an automotive application.

PREFERENTIAL OXIDATION OF CO REACTOR

Following the WGS reactor is a preferential oxidation reactor (PROX) to reduce the CO further. In order to achieve the sub-10 ppm CO levels needed for the PEM fuel cell application, CO conversions of 90% or more are needed in the PROX unit. Representative values of shifted reformate were taken from equilibrium calculations to allow determination of the constraints imposed on the PROX reactor. CO conversions, in the PROX reactor, computed for a range of inlet temperatures for the shifted reformate show that thermodynamics do not favor 100% selectivity of O₂ to convert CO and reverse water gas shift reactions need to be avoided. Even at temperatures of 25°C, the calculations show that all the O₂ is converted mostly reacting with H₂ to form water. At higher temperatures, the reverse water-gas shift reaction occurs which increases CO concentration in the effluent. The most dominant reactions that can occur within the reactor for this type of composition are:



The catalyst formulation chosen has to be selective toward CO oxidation (reaction 1) over methane and water production reactions (reactions 3 and 4), as well as be active at low temperatures where the reverse rate of reaction 2 is slow. The formulation also needs to be highly active for reaction 1, thus allowing the use of near stoichiometric amounts of O₂. Stoichiometric amounts of O₂ are desirable to keep the selectivity toward CO conversion high. Any O₂ remaining after conversion of CO will react with H₂, thus decreasing the effectiveness of the reactor. Typical formulations that can operate within these constraints are precious group metal formulations on stabilized alumina supports of which PCI has developed a proprietary formulation that achieves nearly 50% selectivity toward CO conversion.

Since the oxidation of CO and H₂ are highly exothermic ($\Delta H = -67$ kcal/mol and -58 kcal/mol, respectively), control of reactor temperature becomes a

critical issue. A calculation of the adiabatic temperature rise for a typical reformate stream exiting a water gas shift reactor with 5000 ppm CO and with 2500 ppm added O₂ was ~ 45 °C (assuming 100% selectivity to CO oxidation). The Microlith catalyst substrate is especially suited for applications where control of reactor temperature is critical. This enables the reactor to run closer to the gas phase temperature than conventional monolithic or pellet bed reactors before the onset of bulk mass transfer controlled reaction.

The durability of the PROX catalyst has been tested for 500 hours to allow reasonable extrapolation of long term operation (5000 hr) and to investigate possible deactivation mechanisms. As evidenced by Figure 8, there was no degradation observed over 500 hours. Temperature scans, shown on Figure 8 (a), were done to evaluate the performance of the catalyst with time over an operational window for catalyst surface temperature. The data falling on the same general curve indicated that the performance is not affected over the entire operating window by aging. The graph in Figure 8 (b) shows the composite 500 hours of aging at a constant surface temperature, again with no evidence of decay. These two tests were done to ensure the ability of the catalyst to perform well over a range of conditions.

To begin the elucidation of a decay mechanism, BET measurements and XRD analysis were done for the fresh catalysts and compared to the aged catalysts from the durability study, which were exposed to PROX reaction conditions for 510 hours. The results from N₂ adsorption BET measurements indicate that the specific surface area decreased by ~ 28% from the fresh catalyst measurements when compared to the final measurement after 510 hours of operation. The catalyst surface area was still considered to be relatively high. This is an indication that the γ -Al₂O₃ structure did not collapse under PROX reaction condition, remaining fairly stable during reactor operation. Both techniques BET and XRD, indicated that precious metal agglomerates and forms larger crystallites with time on stream. Despite the agglomeration process no decrease in the catalyst activity in terms of CO/CO₂ conversion and selectivity was observed after 510 hours of testing.

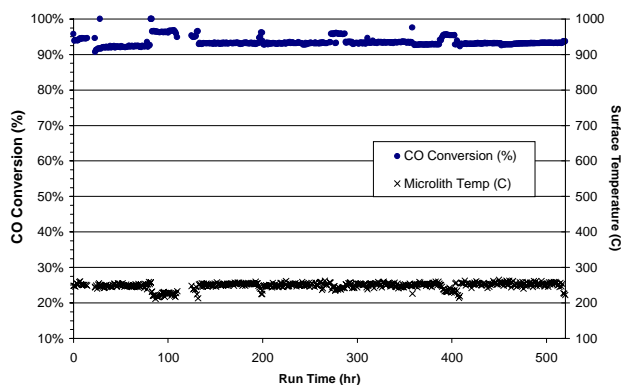
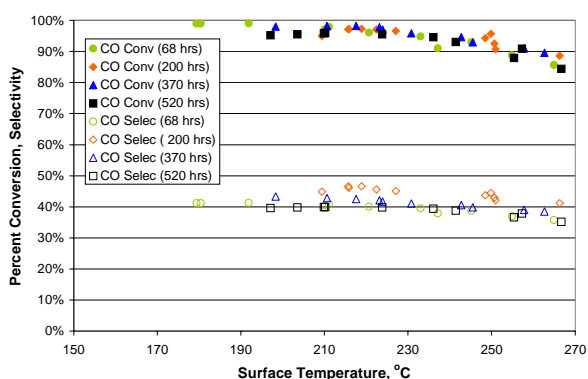


Figure 8 (a), (b): Results of 500-hour PROX test. 8 (a) on the left shows the performance versus catalyst surface temperature vs. time. 8 (b) on the right shows composite aging at a constant surface temperature.

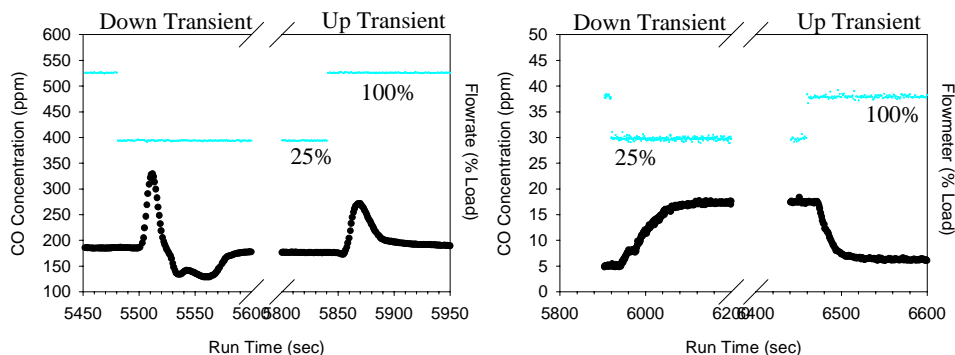


Figure 9: Transient response of PROX 1 (a) and PROX 2 (b) reactors. While there is a CO breakthrough in PROX 1 it is not seen in PROX 2.

The PROX reactor was tested to determine its performance under realistic transient operation via a simulated load change from 25% to 100%. Figure 9 shows the transient response results of the PROX reactor stages for a 4 to 1 turndown in load. The inlet and outlet conditions are given in Table 3. The outlet CO concentrations from PROX 1, Figure 9 (a), is the input concentration to PROX 2, Figure 9 (b).

It is seen that the PROX 1 reactor responds very rapidly to the change in flow conditions. The lag time between the load change and CO concentration change is test-stand limited and is attributed to the time required for the new flow conditions to reach the reactor. Once the new conditions reach the reactor, there is a small CO concentration spike of ~150 ppm, however it quickly returns to the previous steady state CO concentration, indicating that the activity of the reactor is unaffected. This behavior is indicative of O₂ limited conversion. In addition, a change in selectivity occurs with the change in space velocity. That is, the lower space velocity has a lower selectivity toward CO conversion, and thus the H₂ consumption increases slightly. The combination of the two types of behavior keep the CO conversion constant for a 4 to 1 change in space velocity.

For the PROX 2 reactor, there is a steady approach to the step changes in load. The approach to steady state occurs when the new flow conditions enter the reactor and achieve steady state operation in about 40 seconds. In addition, there is no evidence of a CO spike during this change. It can be concluded that any CO spike that occurs in PROX 1 is greatly damped, or eliminated in PROX 2. A simple calculation of conversion efficiency demonstrates this damping effect. The CO

spike in PROX 1 amounts to a maximum of 150 ppm. PROX 2 conversion efficiency being near 99%, the 150 ppm spike entering PROX 2 will be reduced to a 1.5 ppm spike, if it is not totally eliminated.

Startup performance of the WGS and PROX reactors has not been explicitly tested thus far. However, based on lightoff data from similar reactor configurations and the transient test results, it is anticipated that these Microlith reactors will achieve DOE startup targets of less than 60 seconds.

INTEGRATED ATR, WGSR, PROX REACTORS:

A conceptual fuel processor train is depicted in Figure 10, with placement of heat exchangers. The experimentally obtained data from the separate reactors presented above were combined in Table 3 for examination of an integrated prototype fuel processor arrangement. Since the reactors were tested separately, the effluent from each reactor does not exactly match the influent for the subsequent reactor. However, the critical species, such as carbon monoxide and hydrogen, were closely matched. It is recognized that balance of plant and ancillary equipment needs to be incorporated to produce a complete fuel processor and the integration of those pieces are not a trivial task. However, the technology that is needed for the balance of plant components currently exists and is assumed to be available, once defined. From the patchwork of data, the overall fuel processor size for a 75 kW system, without heat exchangers and balance of plant components is estimated to be 6 liters (~0.2 ft³). This small size arises from the ability of the Microlith reactors to operate at very high space velocities (40,000 – 220,000 hr⁻¹).

Table 2: Performance comparison of Microlith-based WGSR and PROX vs. DOE targets.

| Parameter | WGSR | PROX | 2004 DOE Targets |
|---|---------------------|-------------------------|------------------------------------|
| Power Density, (kW/L) | > 25 | > 30 | 2.25 |
| Specific Power, (kW/Kg) | > 28 | > 35 | 2.25 |
| CO conversion (%) | >92 [6% to 0.5%] | 99.8 [0.5% to 10ppm] | > 90 |
| Selectivity [H ₂ in product/H ₂ extractable from feed] | > 99% | <3% H ₂ lost | >99% & <20% H ₂ lost |
| Durability, (hrs) | 200 proven | 500 proven | 4000 |
| Transient: 10-90% Power (sec) | 3 | 3 | 5 |

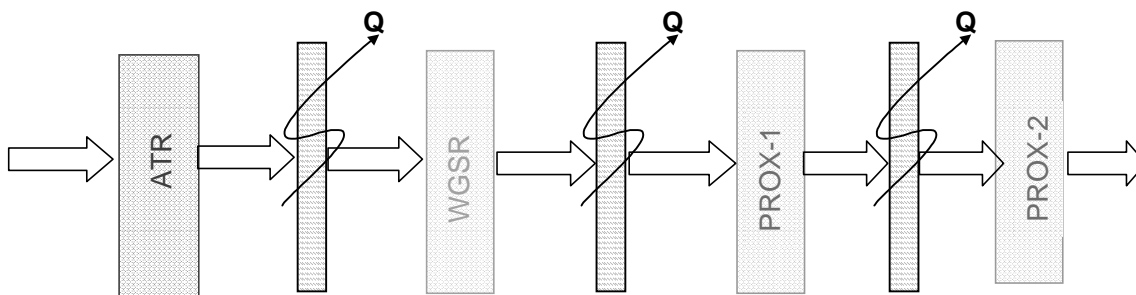


Figure 10: Schematic of integrated reactors.

Table 3: Reformate concentrations with integrated fuel processor reactors.

| | ATR in | ATR out | WGS in | WGS out | PROX 1in (lambda=2.4) | PROX 1out | PROX 2in (Lambda=8) | PROX 2out |
|----------------------|---------|---------|--------|---------|--------------------------|-----------|------------------------|-----------|
| O/C | 1.06 | | | | | | | |
| H ₂ O/C | 2.01 | | | | | | | |
| Sp vel (hr)-1 | 175,000 | | 40,000 | | 150,000 | | 220,000 | |
| N ₂ | | 32.6 | 21.5 | 21.5 | 20.1 | 20.2 | 20.5 | 20.5 |
| H ₂ | | 25.9 | 34.1 | 29.3 | 32.9 | 33.8 | 33.6 | 33.6 |
| H ₂ | | 25.1 | 29.1 | 33.9 | 32 | 31.5 | 31.3 | 31.3 |
| CO | | 5.7 | 5.7 | 0.85 | 0.55 | 0.019 | 0.018 | 0.0001 |
| CO ₂ | | 10.3 | 9.7 | 14.5 | 13.9 | 14.5 | 14.4 | 14.4 |
| O ₂ | | ~0 | | | 0.66 | 0.05 | 0.16 | 0.13 |
| T _{in} (C) | 237 | | 320 | | 170 | | 132 | |
| T _{out} (C) | | ~700 | | 340 | | 250 | | 150 |

CONCLUSIONS

The results of this paper demonstrate that the performance of the short contact time based Microlith catalytic reactors is beneficial for ATR, WGS and PROX stages of an isooctane reforming system and exceeds DOE size and transient response targets with the potential of meeting startup targets. While each reactor was tested separately, the conditions allow conceptual integration with a high likelihood of success. This provides a strong basis for achieving the DOE performance targets for an integrated fuel-reforming system capable of efficient on-board reforming of gasoline into PEM cell quality hydrogen. Challenges expected during integration of these reactors will include heat exchange for flow conditioning between the reactors, flow distribution, system startup, transient response, tolerance to poisoning, minimization of parasitic losses e.g. pressure drop, and control issues.

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REFERENCES

1. U.S. Patent # 5,051,241, September 24, 1991.
2. U.S. Patent # 5,648,582, July 15, 1997.
3. U.S. Patent #5,654,491, August 5, 1997.
4. U.S. Patent # 5,510,056, April 23, 1996.

5. S. Roychoudhury, J. Bianchi, G. Muench, W.C. Pfefferle SAE 971023, SAE Intl, 1997.
6. R. Carter, J. Bianchi, W. Pfefferle, S. Roychoudhury, J.L. Perry, SAE 972432, SAE Intl, 1997.
7. J.L. Perry, R.N. Carter and S. Roychoudhury, SAE 1999-01-2112, SAE International, (1999).
8. G Kraemer, T. Strickland, W.C. Pfefferle and J. Ritter, Proc., International Joint Power Generation Conference, ASME International 1997.
9. M. Lyubovsky, et al., *Catalysis Today*, Proc. of "The 5th Intl. Workshop on Cat. Comb", April 2002, *in print*.
10. Shah, R. K. and London, A. L., Laminar flow forced convection in ducts, *Advances in Heat Transfer*, Academic Press, New York, (1978).
11. R.N. Carter, S. Roychoudhury, W. Pfefferle, G. Muench, H. Karim. *MRS Symposium*. Proc. Vol. 454 1997 Materials Research Society.
12. R. N. Carter, P. Menacherry, W. C. Pfefferle, G. Muench, S. Roychoudhury, SAE 980672, SAE Intl, Warrendale, PA, 1998.
13. Fuel Cell Hand Book 5th ed., by EG&G Services Parsons, Inc. Contract No. DE-AM26-99FT40575 (2000).
14. Alternative Water-Gas Shift Catalysts; D. Myers, J. Krebs, T. Krause, and M. Krumpelt; Argonne National Laboratory; Annual National Laboratory R&D Meeting, DOE Fuel Cells for Transportation Program, June 2000.

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