PERFORMANCE OF A DIESEL, JP-8 REFORMER

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ABSTRACT

Under a U. S. Army program, Precision Combustion, Inc. (PCI) has developed and demonstrated an ultra compact and lightweight 2 – 5 kW<sub>e</sub> diesel reformer and desulfurizer producing <1 ppm sulfur in reformate. The prototype includes a steam generator, fuel/air/water pumps, premixer, atomizer, igniter, sulfur cleanup and a controller to enable stand-alone operation. The reforming reactor was based on a small, modular catalytic reactor, which utilized patented Microlith substrates and catalyst technology. It uses an auto thermal reforming (ATR) approach. The reformer has been tested with JP-8 and Jet-A fuels. It can also be adapted and thermally integrated to use various fuels and fuel cells. The primary characteristic of PCI’s ATR is that it operates on very low water flows (S:C ≤ 1) without coking and the reforming catalyst is sulfur tolerant. This permits meeting water needs via recycling from the stack exhaust as well as the long-term use of a ZnO desulfurizer. The reforming efficiency is >70%. Two brassboard prototypes were developed – a 5 kW<sub>e</sub> (12 kW<sub>th</sub>) and a 2 kW<sub>e</sub> (5 kW<sub>th</sub>) sized unit and tested over hundreds of hours.

1. INTRODUCTION

Fuel cells are one of most favorable technologies for power and energy source for the Army’s Transformation and have potential for automotive and auxiliary power unit (APU) applications. However, the key barrier to exploiting the potential of fuel cells for automotive and APU applications is the technology for processing and reforming practical fuels to generate a hydrogen rich reformate gas that can be directly used by the fuel cells. To reduce logistics problem, the Army has one logistic fuel (Diesel or JP-8) policy. Diesel and/or JP-8 are heavy fuels that are difficult to reform, especially with its aromatic and organosulfur compounds.

Current work with Diesel/JP-8 reformers has shown that auto thermal reforming is the best low risk choice of technology to maintain a balance between size, weight, performance, durability and logistics. PCI has developed and demonstrated such a reactor that starts up in partial oxidation mode and transitions to ATR mode, operating at low steam to carbon ratios.

These reformers can be used to generate SOFC-quality reformate or coupled with a WGS and CO cleanup reactor can generate PEM-quality reformate. In addition to permitting “silent-watch” operations, fuel cell powered systems have the opportunity for significantly higher fuel to electrons efficiency. More detailed results will be presented at the conference.

2. MICROLITH TECHNOLOGY

The heat and mass transfer coefficients depend on the boundary layer thickness. For a conventional long channel honeycomb monolith a fully developed boundary layer is present over a considerable length of the catalytic surface, limiting the rate of reactant transport to the active sites. This is avoided when short channel length catalytic screens are used.

The Microlith substrate is a mesh-like structure coated with catalyst. It has high mass and heat transfer properties as well as high surface area. Use of catalyst substrates with high mass transfer rates, high surface area and low pressure-drop has a significant impact on reactor performance and size. PCI has developed a Microlith-based (trademarked by PCI) approach. The catalyst and reactor are based on PCI’s patented Microlith technology. The Microlith substrate consists of a series of ultra-short-channel-length, low thermal mass, catalytically coated metal meshes with very small channel diameters. The short channel length minimizes boundary layer buildup and results in remarkably high heat and mass transfer coefficients compared to other substrates (e.g. monoliths, foams, pellets). The substrate provides about three times higher geometric surface area over monoliths with equivalent volume and open frontal area. PCI’s proprietary catalyst coatings, with high surface area washcoats, allow for very low catalyst usage with rigorously demonstrated mechanical and performance durability. These include exhaust aftertreatment [1], trace

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contaminant control [2, 3], catalytic combustion [4], partial oxidation of methane [5, 6], hydrogen peroxide decomposition, as well as liquid fuel reforming [7], preferential oxidation of CO and water gas shift reactors in fuel processors [8].

3. FUEL REFORMER DESIGN

The fuel processing prototype demonstrated is described here. It consists of an ATR reactor packaged with a fuel/air/steam injector, igniter, steam generator and desulfurizer. It has connections for controlled fuel, air and water inlet. The ATR operates at H₂O:C ratios of ~1 and O:C of 1, to minimize water need while achieving complete conversion of the fuel to C1 products and fuel-sulfur to H₂S at sustainable temperatures. A photo of the 5 kWth unit developed at PCI under ARL and TACOM support is shown in Figure 1. The internal schematic is shown in Figure 2. The flow through the ATR is indicated by arrows. Water, fuel and air (all at ambient temperatures at startup) are fed to the fuel processor. The ATR is started up with fuel and air in CPOX mode and operated in this mode until steam is available. It is then transitioned to ATR mode. When integrated thermally with a stack, the air and/or steam may be preheated by heat exchange with the stack before entering the ATR. A soda bottle is shown next to it to reference the size. The Balance of Plant components such as pumps and controller are separately packaged and are controlled via a laptop interface. A photo of the fuel reformer hardware is shown in Figure 3. A 2-liter soda bottle is shown next to it to reference the size.

The conceptual layout is shown in Figure 4. Note that after the ATR exit the temperature is dropped to 350 – 400 °C for sulfur removal. While some might argue that dropping the temperature and raising it up again hurts efficiency, initial analysis indicates that it may be insignificant. Given the practical considerations of high temperature flow control (e.g. lack of easily available valves for control of high temperature flows) and loss of fuel using alternative desulfurization approaches, the proposed approach is arguably both practical and efficient. In our discussions with SOFC manufacturers and modeling experience with implementing integrated (reformer + SOFC) systems, we have found that for implementing effective controls, it is not desirable to implement hot reformate directly from the reformer into the stack. Rather using a cooled reformate (~350°C) works best because it can be reheated, albeit with an additional HX, to suit the temperature and flow.
requirements of SOFC stacks (which are sensitive to startup temperature ramps). Since controlling two interdependent reactors (ATR and SOFC) is a control challenge, it is best done in an isolated fashion at the expense of negligible efficiency penalty and minor weight penalty.

![Figure 4: Component layout in the reformer.](image)

4. ATR PERFORMANCE

Dependence of the reformer performance on O:C and H₂O:C ratios was studied with both JP-8 and diesel. The reformate gas was analyzed by a GC at various S:C and O:C ratios, inlet temperatures and flow rates to measure the gas composition and the reactor performance. Relevant results (O:C = 1 and H₂O:C = 1) show that complete conversion of JP-8 was achieved.

In addition to running hundreds of hours of ATR durability tests, PCI has also run a durability test with Jet-A fuel containing 1100 ppm sulfur 1000 hours. Stable, sulfur tolerant performance was demonstrated. A precious metal based formulation supported on an oxide support with appropriate binders and additives was used. Washcoat/catalyst/support combinations and additives were selected to optimize catalyst performance. Temperatures, fuel conversion and hydrogen concentration in the reformate stream for one of the catalysts tested is shown in Figure 5. Reforming efficiency (LHV_reformate/ LHV_fuel) ranged from 70 – 80% and H₂ and CO concentrations were 28 and 22 % respectively. The small variations in the fuel conversion and H₂ and CO concentrations were due to controller drifts in the O:C and S:C ratios in the reactor feed. This graph show stable performance of the catalyst over the test duration of 150 hours. A prototype reactor was also subjected to severe thermal cycling. It was cycled between 50 and 1050 °C at 1000 °C per minute for 500 start/stop cycles without degradation.

![Figure 7: ATR performance w. JP-8 (80 ppm sulfur) @ 5 kWt feed rate](image)

The reason for the lack of significant catalyst coking has not been conclusively determined. However, since the Microlith surface operates close to the bulk gas temperature, due to its high heat transfer coefficients, and since the transport rates over Microlith are high, it is likely that if high molecular weight carbon species were to build up on the surface, they would be in contact with considerable amounts of oxidizers that would inhibit carbon formation.

Data from the reformers have been used to generate the performance specifications shown in Table 1.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>PCI’s Reformer Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>System Net Rated Power (kWₑ)</td>
<td>2 – 5</td>
</tr>
<tr>
<td>Energy Efficiency (LHV basis)</td>
<td>75% (fuel quality dependent)</td>
</tr>
<tr>
<td>Power Density (We/L)</td>
<td>&gt;600</td>
</tr>
<tr>
<td>Specific Power (We/kg)</td>
<td>&gt;600</td>
</tr>
<tr>
<td>Start-up (Cold start)</td>
<td>≤10 min</td>
</tr>
<tr>
<td>Transient Response</td>
<td>≤1 min</td>
</tr>
<tr>
<td>Thermal Cycles</td>
<td>1000°C/min; 500 cycles</td>
</tr>
<tr>
<td>Lifetime (w/o replacement)</td>
<td>Projected to be &gt;2000 hrs</td>
</tr>
<tr>
<td>Maximum H₂S in product stream</td>
<td>&lt;1 ppm</td>
</tr>
<tr>
<td>Turn Down Ratio</td>
<td>3:1</td>
</tr>
<tr>
<td>Acoustic Signature (dBₐ @ 1m)</td>
<td>&lt;50</td>
</tr>
</tbody>
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Table 1: Fuel Processor Performance Metrics (ATR, steam generator, injector, mixer, igniter, sulfur cleanup).
5. SULFUR CLEANUP

The ATR catalysts tested appear to be resistant to fuel sulfur. We have observed that sulfur content affects the H₂/CO concentration ratios in the reformate and overall reforming efficiency. Higher sulfur results in lower H₂ and higher CO concentrations as well as lower reforming efficiency and vice-versa with lower sulfur fuels. Note that ~1500 ppm(w) of sulfur in the fuel corresponds to ~150 ppm(v) of sulfur, mainly in the form of H₂S, in the reformate. This is due to dilution upon mixing with the other feed components and molar expansion upon reaction in the ATR. ZnO beds, which can readily adsorb H₂S, were tested with both simulated reformate as well as actual JP-8 reformer outlet.

The kinetics of sulfur absorption in the ZnO bed was first tested with synthetic mixtures of 115 ppm H₂S in methane and nitrogen (dry and with 20 % steam addition). Space velocity was varied and sulfur uptake was measured to estimate the sorption rate and the required ZnO bed size. Test data suggested that under the actual processor operating conditions the H₂S concentration could be decreased to below 1 ppm. The ZnO adsorption capacity was tested by flowing the same mixture containing 20% steam and 115 ppm H₂S at 350°C through a ZnO bed for an extended period of time. The results showed that the system could operate effectively. The desulfurizer bed lifetime will depend on the fuel-sulfur content. E.g. more than 1000 hours with either Tier 2 diesel or JP-8 with 100 ppm sulfur before sulfur breakthrough occurred. This bed could be periodically replaced or it could be made regenerable. The prototype desulfurizer currently being tested in-line with JP-8 and diesel reformate exiting the ATR indicates similar trends. However care has to be taken to ensure complete conversion of the sulfur to H₂S rather than to carbonyl sulfides.

6. SYSTEM CONTROLS

Fuel conversion and catalyst exit temperature in the ATR have a nearly linear dependence. The reformate temperature was a good indicator of reactor performance and product quality. Airflow rate was therefore used to control the ATR performance at a fixed S:C ratio and was based on the ATR exit gas temperature. The fuel, air and water flows were controlled by varying the control signal to a power conditioning circuit. Algorithms required for startup, transitioning to steady state operation, and shutdown, as well as the ability to detect reactor malfunction and make appropriate control adjustments were implemented. Currently a National Instruments based system operated via a laptop-based Labview® is used for control and data acquisition.

CONCLUSIONS

An ATR-based 5 kWth brassboard diesel fuel processor and sulfur cleanup prototype was designed, developed and successfully tested for operation on JP-8, and Diesel. Sulfur tolerance and coke resistance of the catalyst was examined over hundreds of hours. Fuel sulfur was converted to H₂S in the ATR and a sulfur trap was used to remove the H₂S and reduce sulfur concentrations to <1ppm in the reformate. SOFC quality reformate was generated from a compact and lightweight package. A fuel-air-steam mixing and injection system was also developed. The volume of the Fuel Processor containing the atomizer, mixer, igniter, glow plug, ATR, steam generator and desulfurizer was 3 liters (i.e. 0.3 ft³) and it weighed 5 kg.

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REFERENCES