

**2013 NDIA GROUND VEHICLE SYSTEMS ENGINEERING AND TECHNOLOGY
SYMPOSIUM
POWER & MOBILITY (P&M) MINI-SYMPOSIUM
AUGUST 21-22, 2013 - TROY, MICHIGAN**

**A FUEL FLEXIBLE REFORMING SYSTEM FOR PORTABLE SCALE
SOFC**

**Chien-Hua Chen, PhD and
Howard Pearlman, PhD**
Advanced Cooling Technologies, Inc.
Lancaster, PA

**Shakya Sur,
Jordan Thayer,
Shrey Trivedi, and
Paul Ronney, PhD**
Department of Aerospace and
Mechanical Engineering
University of Southern California
Los Angeles, CA

**Ioannis Valsamakis, PhD
Maria Flytzani-Stephanopoulos, PhD**
Department of Chemical and Biological Engineering
Tufts University
Medford, MA

ABSTRACT

An innovative, non-catalytic, thermal partial oxidation (TPOX) based fuel-flexible reformer for use with solid oxide fuel cells (SOFC) has been developed and demonstrated by Advanced Cooling Technologies, Inc. (ACT). Experimental results show that reforming efficiency comparable to that associated with catalytic based reformers can be achieved via effective heat recirculation. Moreover, challenges associated with the use of catalysts for reforming (including poisoning and degradation caused by impurities in military logistic fuels) can be avoided. The non-catalytic reformer is also self-sustained (does not require external energy sources) nor does it involve complicated subsystems. Fuel flexibility has been demonstrated by reforming rich propane, n-heptane, and JP-8-air premixtures. Sulfur compounds (H_2S , COS, etc.) are removed downstream by a high temperature H_2S sorbent that shows very high sulfur removal efficiency at temperatures similar to SOFC working temperatures. This eliminates the need for heat exchangers and therefore further reduces the system size and increases the overall system efficiency. The compactness and simplicity of the non-catalytic reformer and high temperature sorbent reforming system is well-suited for portable fuel cell applications.

INTRODUCTION

The high sulfur content and aromatic compounds in military logistic fuels create a significant challenge for catalytic based fuel reforming. This task becomes even more difficult for portable applications, where the overall system size, weight, and parasitic losses play very important roles. Several reforming and desulfurization techniques have been developed including noble metal based catalytic reformers that achieve high reforming efficiency with military logistic fuels [1]. However to avoid the sulfur poisoning and carbon deposition issues, complicated subsystems such as a pre-reformer desulfurization stage,

steam and water management system, etc. are usually needed, which increases the overall size, weight, power consumption, and complexity of the system and may limit their applicability for small scale portable applications.

An innovative, compact, and relatively simple, fuel-flexible, TPOX-based reforming system is proposed by ACT in collaboration with USC and Tufts University. The reformer works by first partially-oxidizing the fuel using a sulfur-tolerant, non-catalytic reformer and generates hydrogen-rich syngas with sulfur species converted to their equilibrium state products (i.e. H_2S , COS, etc.). Then, the sulfur compounds are removed using a high temperature

sorbent so that the reformat can directly used by the SOFC (Figure 1). Compared to other systems that require desulfurization upstream of the catalyst, for example, this TPOX-based system does not need such relatively complicated subsystems. In addition, the high temperature sorbent allows for desulfurization of the hot reformat without the need to first cool it; this eliminates the need for heat exchangers required for lower operating temperature sorbents such as zinc oxide. Consequently, the non-catalytic reforming system can be compactly integrated into the “hot box” of an SOFC system thus minimizing the system size and simplifying the thermal management requirements. In this paper, the two major components of the proposed reforming system are described including the non-catalytic reformer and the high temperature sorbent.

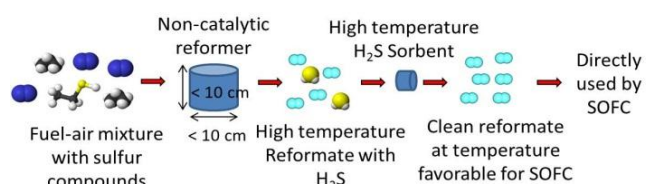
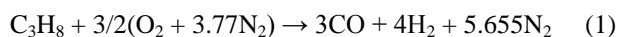


Figure 1: Schematic of the proposed non-catalytic reforming system.

Non-Catalytic “Swiss-roll” Fuel Reformer

Partial oxidation with air as the oxidizer is considered the simplest way to convert hydrocarbon fuels to hydrogen rich syngas for fuel cell usage. Ideally, no significant energy losses occur during the exothermic reaction. For example, partial oxidation of a propane-air mixture shown in Equation (1) has a reforming efficiency (chemical energy contained in the reformat / chemical energy of the parent fuel) around 90% $((283\text{kJ/mol}_{\text{CO}} \cdot 3\text{mol} + 286\text{kJ/mol}_{\text{H}_2} \cdot 4\text{mol}) / 2220\text{kJ/mol}_{\text{C}_3\text{H}_8} \approx 90\%)$.



If we further consider the equilibrium state composition of the reformat for a fuel-to-air ratio of Equation (1) (equivalence ratio, $\Phi = 3.3$), the reforming efficiency is $\sim 87\%$. In practice, however, the heat release from the partial oxidation process does not raise the reaction temperature to a sufficient extent for the reformat to achieve its equilibrium composition. As a result, the kinetics are slowed (for $\Phi = 3.3$, the adiabatic flame temperature is 748°C) and undesired non-equilibrium products (H_2O , CO_2 , C_2 species, etc.) are formed; this significantly reduces the reforming efficiency. One common method is using catalysts that accelerate the reaction rate and maximize the syngas (H_2 and CO) yields. Or alternatively, increase the temperature associated with the reforming process by effective heat recirculation. Catalysts

are effective, yet have challenges associated with impurities in the military logistic fuels (especially sulfur) and other issues (coking, degradation, etc.). Other methods such as plasma reforming that creates a radical pool that enhances the reaction rate has also been considered [2] but the need of additional electricity and complicated subsystems is perhaps not suitable for portable applications.

Our approach is to increase the reaction rate without using catalysts or external energy sources and instead increase the reaction temperature via efficient heat recuperation. The concept is illustrated in Figure 2. Blue and Purple lines represent the temperature profiles as a function of spatial location along the reformer channel without and with heat recirculation, respectively. For the case without heat recirculation, the reaction temperature increases due to the chemical energy release; in contrast, with heat recirculation, the reactants are heated by both the chemical energy release associated with the partial oxidation process in addition to heat recirculation from the hot reformat stream. Therefore, the reaction temperature is higher and can be higher than the adiabatic flame temperature; in this case, it is called super-adiabatic [3]. At this higher temperature, the reaction rate is faster enabling the reformat composition to more closely approach that of the equilibrium state.

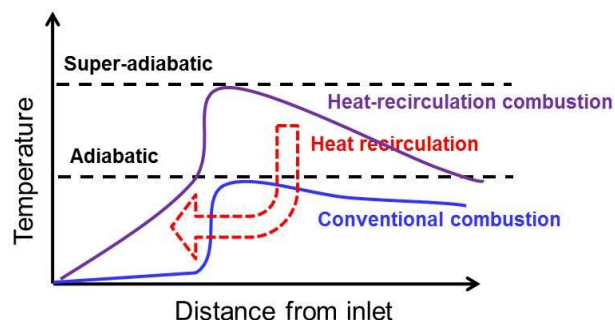


Figure 2: Illustration of super-adiabatic temperatures achieved with efficient heat recirculation.

In the literature, the concept of heat recirculation has been used to extend flammability limits [4]. Here, this concept is applied to perform non-catalytic TPOX reforming. Amongst the heat-recirculating combustor designs, the Swiss-roll combustor, in which the reactants are preheated by the products via a spiral heat exchanger that surrounds the center combustion zone, has been shown to be thermally efficient and compact due to the large heat recirculation to heat loss area ratio (Figure 3). Notably, the Swiss-roll combustor has shown superior performance in terms of the reducing lean flammability limits by a factor of ~ 10 compared to combustion without heat recirculation [5-10]. Conveniently, the pressure drop created by the channels is not significant

and the device only requires a small pumping power to drive the system. When the combustor/ reformer operates with a fuel-rich reactant stream (partial oxidation), the superadiabatic reaction temperature and the long preheated inlet channel (long residence time controlled by the geometry/ size of the reformer) enable the reformat to reach the equilibrium state, hence the high syngas yield can be achieved without the need for catalysts [11].

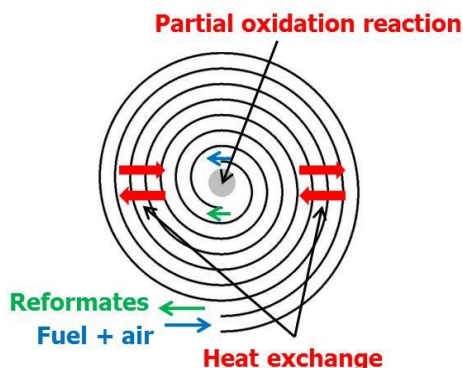


Figure 3: A schematic of the Swiss-roll combustor/reformer showing the two parallel streams (reactant/reformat) in a compact platform.

High Temperature Sulfur Compounds Sorbent

The Swiss-roll reformer is not affected by the sulfur compounds in the fuels, yet the eluted species (H_2S , COS) can poison the SOFC anode downstream and therefore need to be removed. With minimum heat loss, the temperature of the downstream reformat from the Swiss-roll reformer could be close to the adiabatic flame temperature prior to entry into the SOFC. This temperature is similar to the SOFC working temperature. Conventional zinc oxide based sorbents however operate at a temperature around $350^\circ C$ requiring heat exchangers to cool the reformat stream for desulfurization, and then reheat it for SOFC utilization. This is inconvenient, increases system size and complexity and reduces efficiency. Therefore, a high temperature lanthanum oxide (La_2O_3) based sorbent developed by Tufts University is considered to be integrated downstream of the reformer [12-14]. By eliminating the need of heat exchangers, the whole reforming system can be compact and more thermally efficient (Figure 4). Experiments that demonstrate the high temperature absorption capability of lanthanum oxide based sorbents have been evaluated in this work.

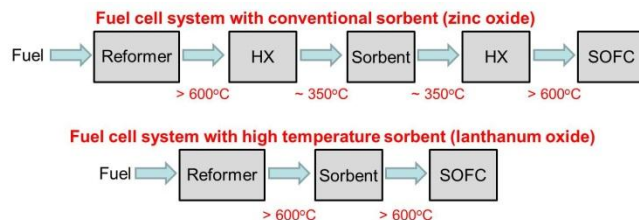


Figure 4: Comparison of the system components (HX: heat exchanger) needed for a zinc oxide sorbent and the high temperature lanthanum oxide sorbent considered here.

NON-CATALYTIC REFORMER TESTS

To assess the feasibility of using Swiss-roll combustors to reform hydrocarbon fuels, a 6-turn combustor with dimensions about 5 cm in height and 8 cm wide was used. Figure 5 shows a schematic diagram of the testing setup. The flow rates of fuel and air into the reformer were controlled by mass flow controllers connected to a data acquisition (DAQ) system. K-type thermocouples were used to measure the center and exhaust temperatures. The exhaust/ reformat was sampled using a syringe and analyzed with an SRI Gas Chromatograph (GC) Thermal Conductivity Detector (TCD) using argon for the carrier gas. Due to condensation of water during the sampling process, all data reported are dry-based (without including the concentration of water). At the exit from the reformer, the reformat was combusted for safety reasons to avoid syngas buildup in the exhaust ductwork. To start the reaction, an electrical ignitor (Kanthal resistance wire) located in the center of the reactor was used. After the gas-phase reaction was initiated, the ignitor was turned off and the reaction was self-sustained by its own exothermicity (heat release from the reforming process) taking advantage of the heat recirculation from the hot reformat.

For liquid fuels (n-heptane and JP-8) testing, the fuel was first injected into an electrically heated chamber (vaporizer) through a spray nebulizer, and then the vaporized fuel was mixed with the mainstream air and delivered to the reformer. A programmable syringe pump was used to control the liquid fuel injection rate. Typically the vaporizer temperature was set to about $20^\circ C$ higher than the liquid fuel boiling temperature to ensure the downstream mixture had a sufficient liquid fuel vapor pressure and did not condense before entering the Swiss-roll reformer. During cold start operation, to prevent the liquid fuel from condensing in the inlet channels of the Swiss-roll reformer, gaseous fuel (propane) was used for the initial ignition. After the reformer warmed up, the switch from gaseous to liquid fuel was accomplished by keeping a constant equivalence ratio to ensure the reaction zone was stable.

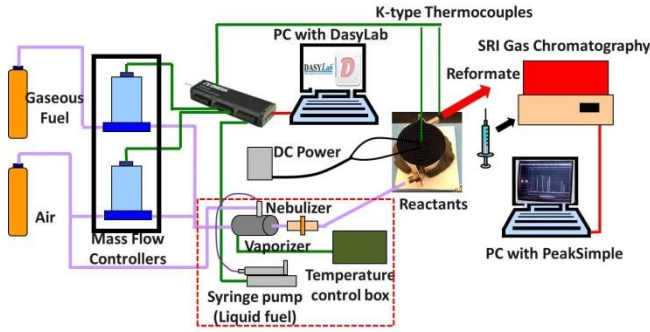


Figure 5: Experimental setup for bench-scale testing of the non-catalytic Swiss-roll reformer.

Reforming Efficiency

Gaseous fuel propane was first tested to study the reforming efficiency of the non-catalytic reformer. Four different Reynolds numbers (Re , defined based on the cold-flow inlet velocity, channel width and viscosity of the cold incoming mixture) were applied with fixed $\Phi = 3$. The corresponding flow rates and thermal power inputs are listed in Table 1.

Table 1: Input conditions (with the same $\Phi = 3$).

| Re | U (cm/s) | V (cc/s) | Input power (W) |
|-------|------------|------------|-----------------|
| 78.7 | 50 | 62.5 | 575.7 |
| 157.3 | 100 | 125 | 1151.5 |
| 236.0 | 150 | 187.5 | 1727.2 |
| 314.7 | 200 | 250 | 2303.0 |

Figure 6 shows that H_2 and CO yields measured at steady state increase with increasing Re . This is because at the low Re (thus low chemical enthalpy input), heat loss significantly affects the center reaction temperature (i.e., the temperature is lower at lower Re due to increased role of heat loss). It was found that the center temperature increased from $1183^\circ C$ at $Re = 78.7$ to $1310^\circ C$ at $Re = 157.3$, both of which greatly exceed the adiabatic flame temperature of $808^\circ C$, thereby confirming the benefit of heat recirculation for these cases. Without heat recirculation, supplemental thermal enthalpy would need to be supplied to the reformer to obtain such temperatures. (Temperatures at higher Re could not be measured due to the thermocouple material limitations.) Higher Re results in higher heat release to loss ratios and therefore the benefit of heat recirculation is greater. A comparison with the chemical equilibrium state (dashed lines in Figure 6) shows that the yield efficiencies (actual yield / equilibrium yield) are 60% for H_2 and 87% for CO . The lower H_2 yield suggests that some water formation is inevitable for the current test conditions.

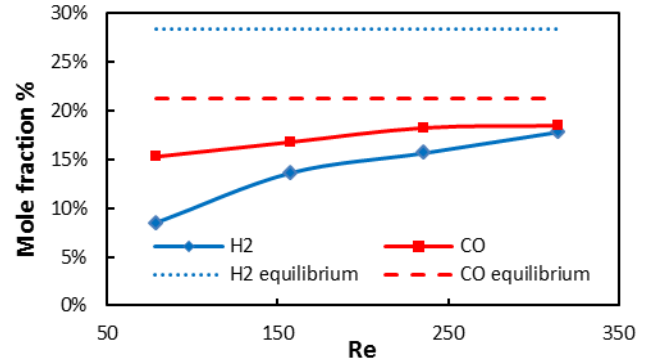


Figure 6: Composition of major species (H_2 and CO) in the reformat at different input Re . Dashed line is the theoretical value at equilibrium state ($\Phi = 3$).

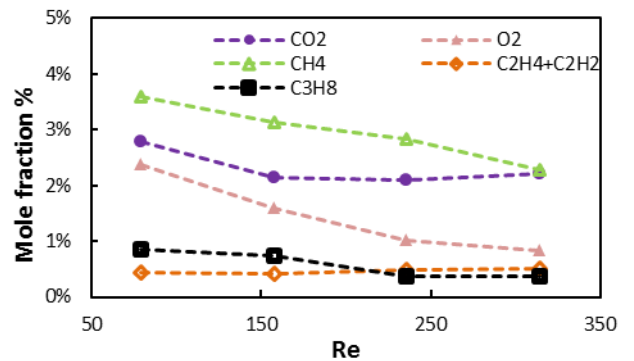


Figure 7: Composition of minor species of reformat gas at different input conditions.

The minor species in the reformat include small hydrocarbons (CH_4 , C_2H_4 and/or C_2H_2 (peaks overlap in column used)), CO_2 , O_2 , and unreformed C_3H_8 are shown in the Figure 7. The decreasing concentrations of the minor species as Re increases are consistent with the increased H_2 and CO yields as Re increases. A calculation of the energy remaining in the reformat shows a $\sim 71\%$ reforming efficiency can be achieved at the highest Re considered in the current test conditions. Further optimization should be able to increase this efficiency.

Fuel Flexibility

To assess fuel flexibility, two liquid fuels (n-heptane and JP-8) were tested in addition to propane. Table 2 shows a comparison of the reformat composition of the three different fuels at the same equivalence ratio ($\Phi = 3$) and flow conditions ($Re = 157$). Currently, the liquid fuel tests are limited to relatively low Re due simply based on our testing facilities. Also, the column used for the GC did not detect higher hydrocarbons (C_6 and above) so these species are not

shown in Table 2. Nevertheless, the results clearly show that H₂ and CO are the major species in the reformat.

Table 2: Comparison of the reformat gas composition of three different fuels at the same flow condition ($\Phi = 3$, $Re = 157$).

| Species | C ₃ H ₈ - air | n-C ₇ H ₁₆ - air | JP-8 - air |
|-------------------------------|-------------------------------------|--|------------|
| H ₂ | 13.6% | 14.86% | 10.22% |
| CO | 16.78% | 14.8% | 18.45% |
| O ₂ | 1.58% | 3.69% | 0.75% |
| CH ₄ | 3.14% | 1% | 1.61% |
| CO ₂ | 2.14% | 3.46% | 4.27% |
| C ₂ H ₄ | 0.42% | 0.14% | 0.26% |
| C ₃ H ₈ | 0.74% | 0.04% | <100 ppm |

Soot formation has been reported to be an issue for many thermal partial oxidation systems [15], especially when reforming higher hydrocarbons. Based on visualization of the reformat flare, the steady blue flame of the n-heptane reformat (Figure 8, left) suggests that soot formation was insignificant during for the current test conditions. However, for JP-8 tests, instead of a (preferable) steady blue flare (Figure 8, middle), an intermittent yellowish flare of the reformat stream was observed (Figure 8, right). This is maybe due to the presence of aromatic compounds in the JP-8, which are more difficult to reform and may instead form soot in the non-premixed exhaust flare. Improving heat recirculation effect via increasing input enthalpy (increasing heat release to loss ratio) may help to crack the aromatic compounds into smaller hydrocarbons and therefore mitigate the soot formation/ coking in SOFC's. In addition, the C₂ soot precursors have been observed in most of the reformat in current testing conditions. Methods such as further increasing heat recirculation or integrating a post reformer [16] after the high temperature sorbent will be explored in the future to mitigate these issues.

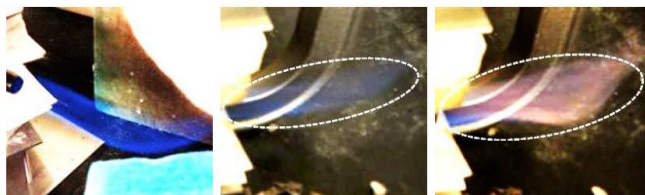


Figure 8: Direct images of the flame color of the n-heptane (left) and JP-8 (middle and right).

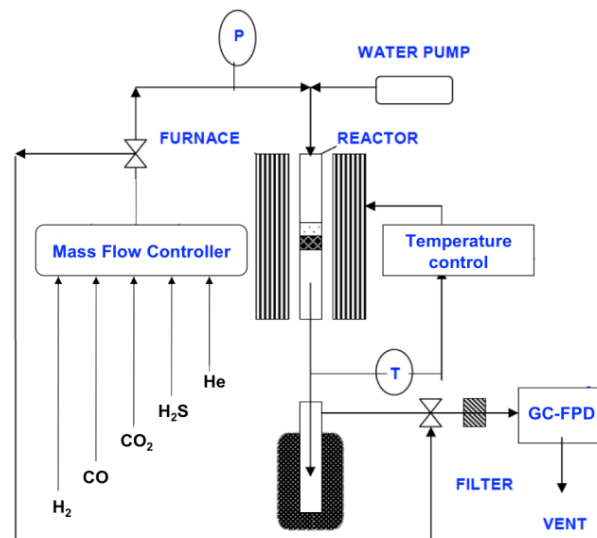


Figure 9: Schematic of sulfidation testing.

HIGH TEMPERATURE SORBENT TESTS

To demonstrate the performance of the high-temperature sorbent, sulfidation tests were performed using hardware schematically shown in Figure 9. Five different particle size lanthana sorbents (> 425, 250-425, 150-250, 53-150, and < 53 micron) were tested at 800°C. The packed bed experiments were carried out with a constant contact time (approximately 0.29 g s / mL) to avoid an effect of the sorbent amount on the breakthrough time, t . A simulated reformat stream with 250 ppm H₂S by volume was used, which is roughly equal to 2500 ppm by weight of sulfur in the fuel. The experimental conditions are shown in Table 3.

Table 3: Experimental conditions for sulfidation test of high-temperature lanthanum oxide sorbent.

| | |
|--------------------------------|--------|
| Temperature [°C] | 800 |
| Contact time [g s / mL] | ≈ 0.29 |
| Flow Rate [mL/min] | 100 |
| Amount of Sorbent Used [g] | ≈ 0.48 |
| <i>Gas Composition [vol %]</i> | |
| H ₂ | 20 |
| CO | 25 |
| H ₂ S [ppm] | 250 |
| H ₂ O | 5 |
| CO ₂ | 5 |

Breakthrough Curve

Figure 10 shows the breakthrough curve for different size sorbent particles. High sulfur adsorption efficiency was observed at the testing temperature of 800°C. Overall, no significant particle size effect was found for the breakthrough (at < 2 ppm) sulfur capacity of the tested

samples, which suggests that larger particles can be used to reduce the pressure drop of the sorbent bed.

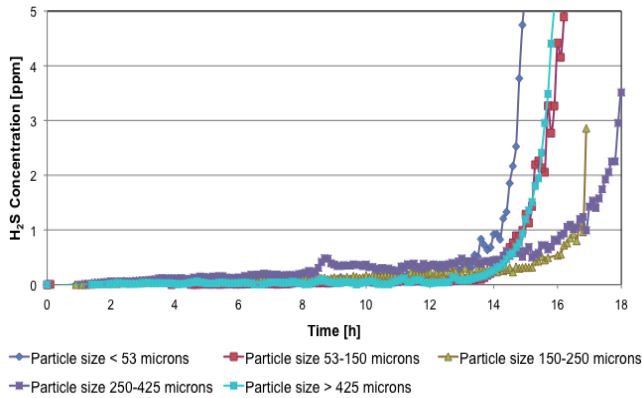
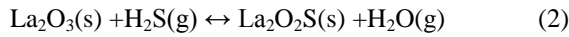


Figure 10: Sulfidation test for lanthanum oxide particles with different size.

Sulfur Loading

The sulfidation performance of the samples is expressed in terms of sulfur loading, defined as mg of sulfur absorbed per gram of sorbent [mg S / g_{sorbent}]. The amount of sulfur absorbed by the sample is measured as the difference of the total amount flowed over the sample and the area underneath the H₂S breakthrough curve from the beginning of the sulfidation to the 2 ppm breakthrough. The theoretical sulfur loading corresponding to complete bulk sulfidation of the oxides to the respective oxysulfide phases is calculated from Equation (2):



98.4 mg of S g_{sorbent}⁻¹ is the maximum attainable sulfur capacity for La₂O₃. The measured sulfur capacities and the percent of utilization for all the samples examined are reported in Table 4. The results obtained here indicate that the sulfur capacities are not significantly affected by the increase in the sorbent particle size, and 70% to 85% sample utilization is achieved.

Table 4: Experimental conditions for sulfidation test.

| Particle Size microns | Sulfur Capacity [mg S/g _{sorbent}] | Sorbent Utilization % |
|--------------------------|---|-----------------------------|
| < 53 | 70 | 71 |
| 53-150 | 72 | 73 |
| 150-250 | 80 | 81 |
| 250-425 | 84 | 85 |
| > 425 | 74 | 75 |

CONCLUSION

A non-catalytic fuel flexible reformer has been demonstrated and experiments show that high H₂ and CO yields can be achieved via effective heat recirculation. A reforming efficiency greater than 70% was shown to date in a very compact size with thermal input ~2000 W_t. Higher reforming efficiency can undoubtedly be achieved with further optimization. Also, it is expected higher input power will be easier to result in higher efficiencies as the heat generation to loss ratio increases and therefore more heat recirculation effect.

Fuel flexibility was also demonstrated by reforming three different fuels: propane, n-heptane, and JP-8. At same input conditions (Φ and Re), the reformate compositions of the three different fuels were similar. No yellowish flare was observed in the propane and n-heptane reformate flares indicating no visible soot formation during the reforming process. However, an intermittent yellowish flare was observed in the JP-8 reformate flare probably due to the presence of aromatics in the fuel that are more difficult to be thermally decomposed. Due to our facility limitations, current liquid fuels tests are limited to relatively low thermal input conditions (≈ 1000 W_t), which limited the benefit of heat recirculation owed to a larger heat loss effect. To further decompose aromatics in JP-8, higher thermal input and improve reformer design will be considered in future studies.

Experimental data show the lanthanum oxide based sorbent is able to effectively remove H₂S at temperatures similar to SOFC operation temperature (800°C). This eliminates the need for heat exchangers and allows the reforming system to be more compact and integrated into a portable SOFC system. No significant effect of particle size on the breakthrough curve suggests that larger size particles could be used to reduce the pressure drop of the sorbent bed without compromising performance. Moreover, high sulfur loading can be achieved with the lanthanum oxide based sorbent reducing the amount of sorbent required.

More works need to be conducted to address issues such as the presence of C₂ soot precursors in the reformate. Method such as optimizing the reformer design or including a “post reformer” after the sulfur sorbent will be explored in the future. Nevertheless, the combination of non-catalytic “Swiss-roll” reformer and high temperature sorbent provides a feasible solution for portable scale SOFC power generation application.

ACKNOWLEDGEMENTS

This work was funded by DoD Army CERDEC under the contract no. W15P7T-12-C-A127. The author thanks for the useful discussion with Dr. Swartz at NexTech Materials.

REFERENCES

- [1] Roychoudhury, S., Lyubovsky, M., Walsh, D., Chu, D., Kallio, E., "Design and Development of a Diesel and JP-8 Logistic Fuel Processor," *J. Power Sources*, 160, 510-513 (2006).
- [2] Bromberg, L., Cohn, D. R., Rabinovich, A., and Heywood, J., "Emissions Reductions Using Hydrogen From Plasmatron Fuel Converters," *Int. J. Hydrogen Energy*, 26, 1115-1121 (2001).
- [3] Schoegl, I. and Ellzey, J., "A Mesoscale Fuel Reformer to Produce Syngas in Portable Power Systems," *Proceedings of the Combustion Institute*, 32, 3223-3230 (2009).
- [4] Jones, A., Lloyd, S., and Weinberg, F., "Combustion in Heat Exchangers," *Proceedings of the Royal Society of London Section A*, 360, 97-115 (1978).
- [5] Weinberg, F., "Combustion Temperature: The Future?" *Nature*, 233, 239-241 (1971).
- [6] Lloyd, S. and Weinberg, F., "A Burner for Mixtures of Very Low Heat Content," *Nature*, 251, 47-49 (1974).
- [7] Ronney, P., "Analysis of Non-adiabatic Heat-recirculating Combustors," *Combustion and Flame*, 135, 421-439 (2003).
- [8] Chen, C. and Ronney, P., "A Compact, Light Weight, Combustion-Driven Air-Purification System," *Chemical and Biological Defense Science and Technology Conference*, Poster # 111 (2010).
- [9] Chen, C. and Ronney, P., "Three-dimensional Effects in Counterflow Heat-recirculating Combustors," *Proceedings of the Combustion Institute*, 33, 3285-3291 (2011).
- [10] Chen, C. and Ronney, P., "Scale and Geometry Effects on Heat-recirculating Combustors," to appear in *Combustion Theory and Modelling* (2013) (DOI: 10.1080/13647830.2013.812807).
- [11] Chen, C. Sur, S, Thayer, J., Pearlman, H, and Ronney, P., "A Non-Catalytic Fuel Flexible Reformer," *8th US National Combustion Meeting*, Park City, Utah, May 19-22 (2013).
- [12] Li, Z. and Flytzani-Stephanopoulos, M., "Cu-Cr-O and Cu-Ce-O Regenerable Oxide Sorbents for Hot Gas Desulfurization," *Ind. Eng. Chem. Res.*, 36, 187-196 (1997).
- [13] Flytzani-Stephanopoulos, M., Sakbodin, M., and Wang, Z., "Regenerative Adsorption and Removal of H₂S from Hot Fuel Gas Streams by Rare Earth Oxides," *Science*, 312, 1508-1510 (2006).
- [14] Valsamakis, I., R. Si and Flytzani-Stephanopoulos, M., "Stability of Lanthanum oxide-based H₂S sorbents in realistic fuel processor/fuel cell," *J. Power Sources*, 195, 2815-2822 (2010).
- [15] Dixon, M. J., Schoegl, I., Hull, C. B., Ellzey, J. L., "Experimental and Numerical Conversion of Liquid Heptane to Syngas through Combustion in Porous Media," *Combustion and Flame*, 154, 217-231 (2008).
- [16] Yoon, S. and Bae, J., "A diesel fuel processor for stable operation of solid oxide fuel cells system: I. Introduction to post-reforming for the diesel fuel processor," *Catalysis Today*, 156, 49-57 (2010).