A Non-Catalytic Fuel-Flexible Reformer

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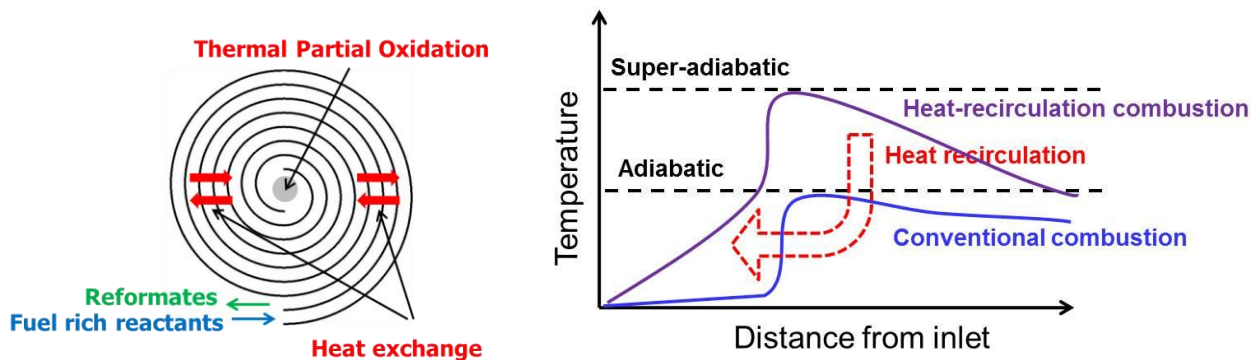Los Angeles, CA 90089*

A compact, non-catalytic, thermal partial oxidation fuel reformer was developed based on the Swiss-roll heat-recirculating combustor concept with the reforming reactions take place at elevated temperature in the centrally-located combustion chamber of a spiral heat exchanger. In this reformer, the reactants (hydrocarbon fuel and air) are preheated by the partial oxidation products of combustion resulting in a reaction temperature that is higher than the adiabatic flame temperature which accelerates chemical reaction rates and leads to partial oxidation product compositions approaching the chemical equilibrium state, yielding high H_2 and CO (syngas) concentrations without requiring an external heat source. No catalyst is needed, thus eliminating undesirable issues associated with catalytic based reformers including sulfur poisoning and carbon deposition. In addition, the Swiss-roll combustor is compact and thermally efficient due to the high effectiveness of the spiral heat exchanger. Using a 6-turn Swiss-roll reformer (5 cm tall, 8 cm overall diameter) and a rich propane-air premixed feedstock with equivalence ratio = 3, experiments showed about 73% of input chemical enthalpy remains in the reformate (18% H_2 and 18% CO). Consequently, of the total input chemical enthalpy of 2400 W, only about 650 W is released as thermal enthalpy during partial oxidation to self-sustain the reaction. The effect of fuel-to-air ratio was studied to evaluate its effect on the H_2 and CO yields. Fuel flexibility was tested using different fuels (propane, n-heptane and JP-8); at the same equivalence ratio and flow rate, similar results were obtained for all three fuels. No visible soot formation was observed in the flame/flare at the exit from the reformer when reforming propane or n-heptane. Current work aims to optimize the reformate product for portable solid oxide fuel cell generators.

1. Introduction

Electrical power generation devices using hydrocarbons such as propane, heptane and JP-8 as the energy storage medium have several advantages over batteries in terms of energy density, transportation, supply infrastructures, etc. One promising method for converting hydrocarbon fuel into electrical energy is by reforming the hydrocarbon into syngas (a mixture of H_2 and CO) and using this to fuel a Solid Oxide Fuel Cell (SOFC) that is able to efficiently convert the syngas to electricity [1], or enhance performance of an internal combustion engine [2]. The simplest fuel reforming technology is partially oxidizing a rich hydrocarbon-air mixture resulting in H_2 and CO products instead of H_2O and CO_2. Since the heat release of this exothermic reaction is usually not sufficient to achieve high reaction temperature and thus rapid reaction rate, different catalysts are usually involved to lower the effective activation energy so that the products are able to reach their chemical equilibrium state (maximum H_2 and CO yield). This is the well-known Catalytic Partial Oxidation (CPOX) method, however, a significant challenge for CPOX is that impurities (e.g. sulfur) or higher hydrocarbons in the fuel can easily poison or deposit carbon on the catalyst, which degrades performance and shortens the reformer lifetime. One method of avoiding these issues and achieve syngas yield without using catalysts is the Thermal Partial Oxidation (TPOX) method in which the mixture is preheated to achieve higher reaction temperature and enable the products to reach their chemical equilibrium state. To preheat the reactants for TPOX operation several methods such as filtration waves, heat recirculation, etc., have been proposed [3, 4, 5].

Previous studies have shown that "Swiss-roll" combustors [6, 7] has superior heat recirculation capability in that it is able to recycle 5 times more thermal enthalpy than the enthalpy released from the reaction itself [8]. This feature makes the Swiss-roll combustor a potential candidate to perform TPOX in small-scale power generation systems. Figure 1 (left) shows the working principle of the Swiss-roll combustor: the incoming cold reactants (a fuel-air premixture) are

preheated by the outgoing hot combustion products via the spiral-wrapped counterflow heat exchanger. This concept is further explained in Figure 1 (right). The reactants therefore obtain a higher total enthalpy (sum of thermal and chemical enthalpies) than that of the cold reactants, resulting in a higher reaction temperature than the adiabatic flame temperature. One of the advantages of Swiss-roll combustor compared to other types of heat-recirculating combustors is the high ratio of internal heat transfer area to external heat loss area, which makes it extremely thermally efficient. Also, the reaction zone is easily stabilized in the center, where the most heat recirculation can be obtained, and thus does not have a reaction zone stabilization issue that occurs in some other gas phase TPOX systems [3].

Figure 1. Left: Schematic diagram of the proposed Swiss-roll fuel reforming process. Right: Comparison of the temperature profile between combustion with and without heat-recirculation.

2. Methods

To assess the feasibility of using Swiss-roll combustors to reform hydrocarbon fuels, a 6-turn combustor was made by manually rolling two strips of Inconel 625 sheet (0.002" (0.05 mm) thick) with an temporary internal spacer (soft rubber strips) to maintain a fixed gap size between adjacent windings. Ceramic adhesive (Cotronic Resbond 907GF) was then used to seal the end plate(s) made from ceramic board. Figure 2 (left) shows a top view of the six-turn Swiss-roll reformer (5 cm height, 8 cm diameter) with the top insulation removed to show the internal structure.

Figure 2 (right) shows a schematic diagram of 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/reformate was sampled using a syringe and analyzed with an SRI Gas Chromatograph (GC) Thermal Conductivity Detector (TCD) using argon as a carrier gas. Due to the condensation of water during the sampling process, all the data reported are dry-based (without including the concentration of water). At the exit from the reformer the reformate 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 combustion products.

For liquid fuel (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°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 stability of the reaction zone.
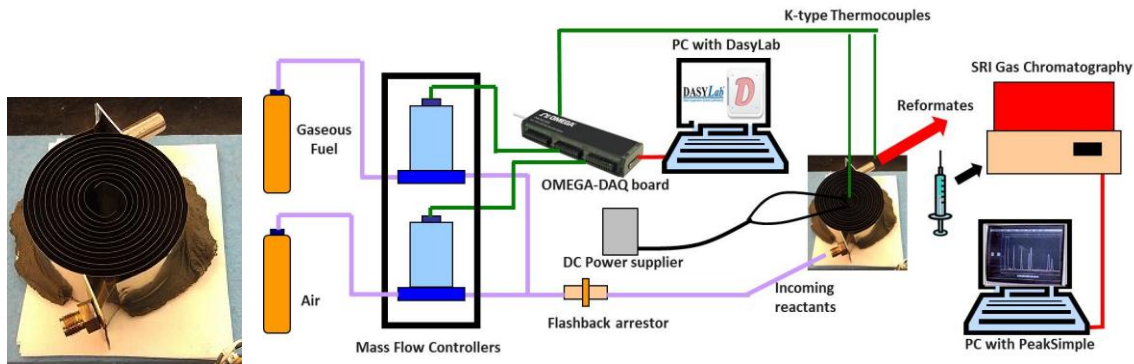
Figure 2. Left: Six-turn Swiss-roll combustor mounted on a ceramic board. The top insulation is removed to show the internal structure. Right: Schematic diagram of the experimental apparatus (for gaseous fuel).

3. Results and Discussion

Effect of Re

Propane-air premixtures with fixed equivalence ratio ($\Phi = 3$) were tested for four different Reynolds numbers (Re, defined based on the cold-flow inlet velocity, channel width and viscosity of the cold incoming mixture). The corresponding flow rates and thermal power inputs are listed in Table 1. Figure 3 plot 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 heat recirculation and therefore center reaction temperature (i.e., the temperature is lower at lower Re due to increased impact of heat losses). It was found that the center temperature increased from $1183^{o}C$ at Re = 78.7 to $1310^{o}C$ 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 ratio and therefore more benefit of heat recirculation. Comparison with the chemical equilibrium state (dashed lines in Figure 3), the reforming efficiencies (actual exhaust concentration / equilibrium concentration) are 60% for H_2 and 87% for CO in the 6-turn Swiss-roll reformer at $\Phi = 3$. The lower H_2 yield suggests that some water formation is inevitable for the current testing conditions. The minor species in the reformate including small hydrocarbons (CH_4, C_2H_4 and/or C_2H_2 (peaks overlap in current GC)), CO_2, O_2, and unreformed C_3H_8 were shown in the Figure 4. The decreasing concentrations of the minor species as Re increases is consistent with the increasing H_2 and CO yields as Re increases.

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

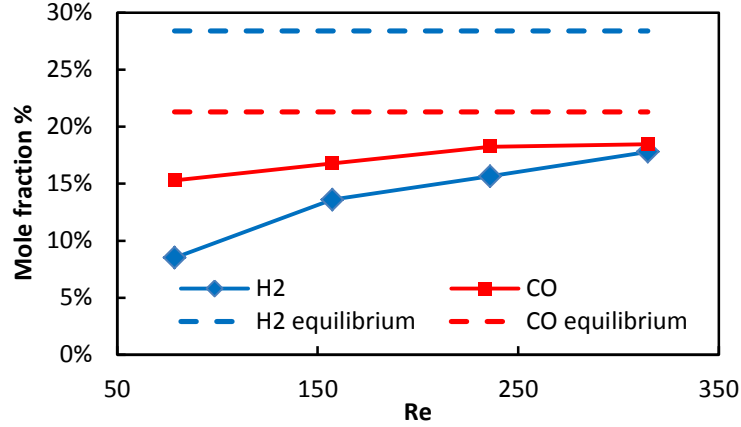**Table 1. Test conditions for propane/air mixtures at equivalence ratio $\Phi = 3$**

Figure 3. Comparison of the H_2 and CO yields at different input flow rates to their equilibrium values. Feedstock: Propane air premixture, $\Phi = 3$.
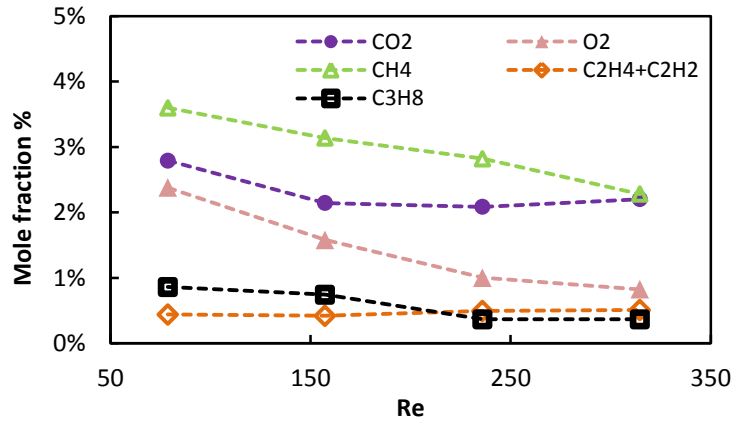

Figure 4. Minor species in the reformate at different input flow rates. Feedstock: Propane air premixture, $\Phi = 3$.

Effect of Equivalence Ratio

The effect of equivalence ratio on H_2 and CO yields were studied via three different values of the equivalence ratio Φ for propane-air mixtures with fixed Re = 314.7. The results are shown in Table 2. In this table, the output chemical enthalpy (Q_{output}) was obtained by calculating:

$$Q_{output} = V_{output,\,298K} \times C \times E$$

where $V_{output,\,298K}$ is the output volumetric flow rate at 298K, C is mole fraction, and E is volumetric enthalpy density. The $V_{output,\,298K}$ was calculated via assuming constant N_2 flow rate for input and output conditions at the same temperature (298K):

$$V_{input,\,298K} \times C_{N2,\,input} = V_{output,\,298K} \times C_{N2,\,output}$$

where $C_{N2,\,input}$ and $C_{N2,\,output}$ were obtained from GC measurements.

While the H_2 and CO concentrations with different values of the input equivalence ratio Φ are similar (Table 2), the stronger mixture (lower Φ, i.e. closer to stoichiometric) shows better reforming efficiencies due to less enthalpy input (Figure 5). However, an optimal Φ in terms of maximum enthalpy of H_2 and CO in the reformate should exist since there should be almost no enthalpy in the form of CO or H_2 remaining if $\Phi = 1$. Currently, reforming efficiencies of about 75% for H_2 and 95% for CO are achieved at $\Phi = 2.6$.
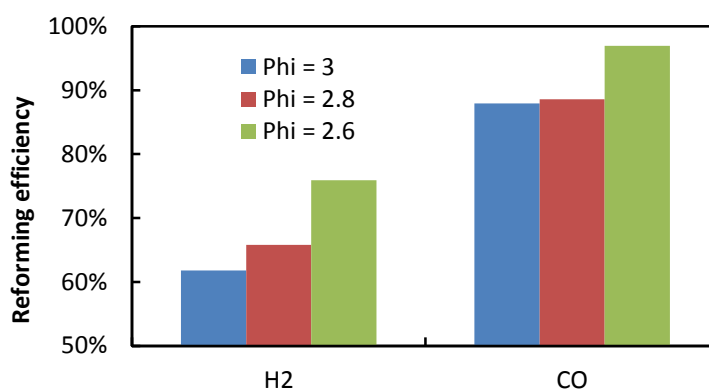
One interesting observation was that the CO and H_2 yields were nearly identical for different equivalence ratios. This observation suggests that the reaction pathway for equivalence ratios in excess of $\Phi = 2.5$, i.e. $C_3H_8/O_2 = \frac{1}{2}$ as shown below, favors the production of stable species other than CO and H_2.

$$C_3H_8 + 2O_2 + 2(3.77)N_2 \rightarrow 3CO + 3H_2 + H_2O + 2(3.77)N_2$$

More tests will be conducted to test this hypothesis.

Output	$\Phi = 3$	$\Phi = 2.8$	$\Phi = 2.6$
H_2	**17.8%**	**17.51%**	**18.22%**
CO	**17.96%**	**17.45%**	**17.87%**
Adiabatic flame T	808°C	901°C	1008°C
Chemical enthalpy input	**2303 W**	**2173 W**	**2039 W**
Chemical enthalpy in the reformate	1737 W	1618 W	1564 W
Chemical enthalpy in the form of H_2 and CO	**1215 W**	**1185 W**	**1219 W**
Enthalpy$_{reformate}$ / Enthalpy$_{total}$	71.33%	68.5%	73.22%
Enthalpy$_{H2+CO}$ / Enthalpy$_{total}$	**52.75%**	**54.53%**	**59.78%**

Table 2. Comparison of the reformate compositions of 3 different equivalence ratios ($\Phi = 3$, 2.8, and 2.6) for Re = 314.7.

Figure 5. Comparison of H_2 and CO reforming efficiency (actual yield / equilibrium state) for 3 different equivalence ratios.
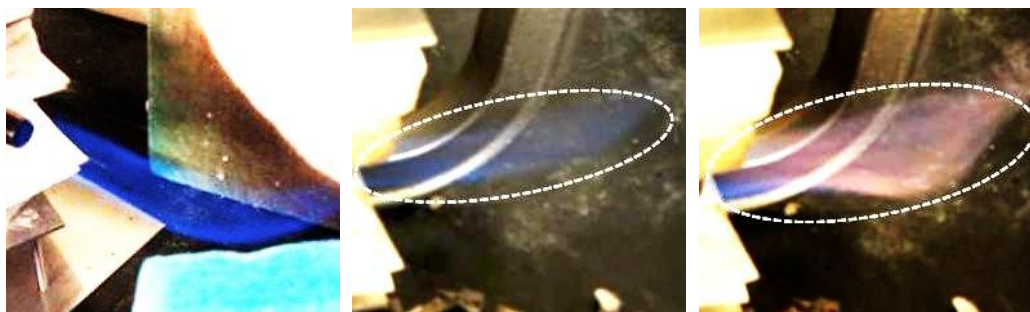
Fuel Flexibility

To assess fuel flexibility, two fuels (n-heptane and JP-8) were tested in addition to propane. Table 3 shows a comparison of the reformate composition of three different fuels at the same equivalence ratio ($\Phi = 3$) and flow rate (Re = 157). Since higher hydrocarbons (C_6 and above) cannot be measured by the current GC system, these species are not shown in Table 3. Also, current liquid fuel tests can only be performed at relatively low Re due to the limitation of the testing facilities. Nevertheless, all the tests show H_2 and CO are the major species in the reformate.

Soot formation has been reported as an issue for many thermal partial oxidation systems [3], especially when reforming higher hydrocarbons. Based on visualization of the reformate flare, the steady blue flame of the n-heptane reformate (Figure 6, left) suggests the soot formation was insignificant during the current test condition. However, for JP-8 tests, instead of a (preferable) steady blue flare (Figure 6, middle), intermittently a yellowish flare of the reformate stream was observed (Figure 6, right). This is probably because of 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 downstream soot formation.

Output Species	C_3H_8 - air	n-C_7H_{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_2H_4 and/or C_2H_2	0.42%	0.14%	0.26%
C_3H_8	0.74%	0.04%	< 100 ppm

Table 3. Comparison of the reformate composition of propane, n-heptane and JP-8 operated at the same mixture and flow conditions (Φ = 3, Re = 157).

Figure 6. Direct images of the flame color of the n-heptane (left) and JP-8 (middle and right).

4. Conclusions

The feasibility of the non-catalytic Swiss-roll reformer was demonstrated. Experimental results show H_2 and CO yields increase as Re increases because of higher release to loss ratio resulting more heat recirculation and thus higher reaction temperature. Tests of the effects of equivalence ratio show that stronger mixtures (less lean, closer to stoichiometric) yielding higher H_2 and CO output and suggest that Φ = 2.5 may be the optimal condition in terms of minimizing water formation. Current results show that for propane fuel, the H_2 and CO in the reformate contain about 60% of the input enthalpy, and more than 73% if all small hydrocarbons in the reformate are included. While the syngas yields have not as yet been optimized (as a function of mixture composition, flow conditions, reformer geometry), it is clear that the Swiss-roll reformer has several advantages: it is compact, lightweight, non-catalytic, self-sustaining and is able to provide higher power density syngas output for portable applications.

Fuel flexibility was demonstrated by reforming propane, n-heptane, and JP-8 into syngas-rich reformate. The soot formation from the reformer appears insignificant for propane and n-heptane tests. However, some JP-8 tests showed evidence of a yellowish flare in the reformate stream probably due to the presence of aromatic compounds that are difficult to decompose, thus forming soot in the non-premixed exhaust flare. Higher input flow rates and thus more preheat for the reactants should be able to mitigate this issue.

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