Short communication

Comparison of reforming performance of JP-8 and HRJ-5 for fuel cell applications

Mark R. Walluk a,*, Michael A. Bradley a, Thomas A. Trabold a, Daniel F. Smith a, Christian Junaedi b, Subir Roychoudhury b

a Rochester Institute of Technology, Golisano Institute for Sustainability, 111 Lomb Memorial Drive, Rochester, NY 14623, United States
b Precision Combustion, Inc., 410 Sackett Point Road, North Haven, CT 06473, United States

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A B S T R A C T

A comparative study of fuel reformation using petroleum-based aviation jet fuel (JP-8) versus hydro-treated renewable jet fuel (HRJ-5) in an oxidative steam reforming process was performed in a single-tube reformer using a Precision Combustion, Inc. (PCI) Microlith® catalyst. The primary parameters compared during the study were reformate composition, carbon concentration in the effluent, and reforming efficiency versus catalyst temperature. This report illustrates an initial contrast between the reformation results for JP-8, a fossil fuel, as compared to HRJ-5, which is a plant-based fuel derivative. HRJ-5 showed improved fuel conversion with less carbon formation, higher reforming efficiency, and a lower catalyst operating temperature, as compared to 100% JP-8, and a 50%:50% blend of JP-8 and HRJ-5.

1. Introduction

In recent years, the armed services of the United States have placed additional emphasis on the reduction of petroleum based fuels. Several aspects of Department of Defense (DOD) operations are considered when defining this fuel reduction directive. First, the DOD is the largest single consumer of energy in the U.S., and approximately $16.7 billion was expended in 2013 on liquid fuel alone [1]. Aside from the upfront cost that is readily quantified, there are additional costs to deliver fuel to ships, forward operating bases, and personnel in conflict zones. The cost estimate for a gallon of fuel delivered to remote battlefields can be as high as $400 per gallon [2]. The DOD aims to reduce consumption through increased equipment efficiency, employing new technologies, and using renewable energy sources, thereby lessening the burden of fuel plus delivery cost and providing more funding to enhance other military capabilities. Use of biofuels is one potential path for attaining this goal, while having the added benefit of decreasing the dependence of the military on foreign oil suppliers. The U.S. Navy has performed trials with hydro-processed renewable diesel (HRD-76) and hydro-treated renewable jet fuel (HRJ-5) from feed stocks, such as algae, that do not compete with food supplies [3].

This paper reports the results of reformation experiments conducted with HRJ-5 and JP-8 in a single tube catalyst test cell at RIT’s Golisano Institute for Sustainability (GIS). The objective is to demonstrate the differences and potential benefits of HRJ-5 compared to the current military logistic fuels in an oxidative steam reforming process. Prior testing by GIS on a traditional rhodium wash-coated monolith catalyst showed benefits of HRJ-5 that included reduced need for water, lower air flow, lower operating temperatures, lower carbon production, higher efficiency, and an ability to operate the reformer at a higher space velocity. For this study, Precision Combustion, Inc. (PCI) supplied a Microlith®-based catalyst developed for various applications including fuel reforming for syngas production and provided operating parameters that would highlight the differences between reforming of HRJ-5 and JP-8 during evaluation in the GIS test cell [4].

2. Materials and method

Two tests, an oxidative steam reforming test sequence to ascertain the temperature effects on the fuel types and a fuel switch from HRJ-5 to JP-8, were performed on a 31.75 mm diameter nickel reactor tube containing PCI’s Microlith®-based catalyst. The catalyst bed was comprised of the Microlith® substrate coated with alumina supported platinum group metal-based catalyst according to PCI’s proprietary formulations and washcoat/catalyst application procedures. Active metal surface area of >50 m²/g and metal
dispersion of 20–25% were measured by H₂ chemisorption prior to this testing.

The reactor was heated by an electric tube furnace to obtain the desired catalyst temperatures. An Applied Instrument Technologies, Inc. fixed magnetic sector mass spectrometer and an AVL LIST GMBH Micro Soot Meter were installed to sample the effluent from the reforming process, shown schematically in Fig. 1, please refer to our previous works for a more detailed description of a similar test configuration [5,6]. Vaporization of fuel and de-ionized water were performed using internally-coated stainless steel coils wrapped with feedback-controlled heat tapes. Nitrogen and air were also introduced through mass flow controllers to act as carrier gas for more efficient reactant mixing. Fuel and de-ionized water were delivered to the coils using high performance liquid chromatography (HPLC) pumps and the mass flow rate was calculated and recorded by the data acquisition system based on changes in scale readings.

UOP LLC provided the HRJ-5 fuel through a partnership with Sustainable Oils LLC which typically uses oil from the camelina plant as feedstock. The JP-8 fuel used for testing was provided by PCI (as obtained from Wright-Patterson Air Force Base) and contained approximately 298 ppmw of sulfur as documented in the fuel certificate. The testing was performed at an existing fuel cell and bio-fuel research facility at GIS, and leveraged the laboratory’s significant prior experience in diesel, bio-fuel blends, and reforming processes [5,6].

Fuel reforming testing was performed in accordance with a multi-parameter matrix, including fuel type and catalyst temperature. The test points were chosen to compare the performance and carbon generation of the catalyst/fuel combinations where the differences between the HRJ-5 and JP-8 are apparent but do not result in irreversible catalyst degradation. Therefore, the operating condition was selected with a maximum catalyst temperature of ~935 °C, steam-to-carbon ratio (H₂O/C) and diatomic oxygen (from air)-to-carbon ratio (O₂/C) of 1.0 and 0.46, respectively. This equaled a total oxygen-to-carbon ratio (O/C) of 1.92 where the oxygen was the total contribution from both inlet air and water. The fuel mass flow rate was kept constant as the net heat of combustion for HRJ-5 and JP-8 are within 1% of each other based on data from the fuel certifications. The mass flow rate for air and water were adjusted to maintain the O₂/C and H₂O/C ratios for each fuel while the nitrogen flow was held constant for all test points. The combined reactant flow dictated the effective gas hourly space velocity (GHSV) at standard temperature and pressure of approximately 2000 h⁻¹.

A break-in test was performed at the beginning of the test sequence, with 8 h of catalyst exposure to ultra low sulfur diesel (ULSD) fuel having less than 7 ppm of sulfur. The subsequent steps in the test sequence involved a temperature sweep for each fuel. The furnace was controlled for each step by a Watlow module to reach the desired catalyst temperature. The initial condition was a catalyst temperature near 930 °C followed by test points at 900, 850, and 800 °C. Once the test point temperature was attained, the condition was held for approximately one hour to obtain steady-state operation from which average values of the results were calculated and presented herein. HRJ-5 was the next fuel tested after ULSD as it does not have any significant sulfur or aromatic compounds and therefore is believed to impart less damage to the catalyst than JP-8. After HRJ-5, a 50%:50% mixture of JP-8 and HRJ-5 was tested since this ratio has been used in recent documented military operations, including the U.S. Navy’s Great Green Fleet trials [7]. After the blended fuel testing, the catalyst was tested with JP-8 containing 298 ppmw sulfur. After the test sequence, the catalyst was tested again with HRJ-5 to determine if the test setup or catalyst had degraded due to the temperature sweep or exposure to sulfur containing JP-8 fuel. After this last operation on HRJ-5, the fuel type was immediately switched to JP8 to capture a continuous data sample containing results with both fuels. For all tests, the reforming efficiency calculation was based on the sum of the energy content of the hydrogen and carbon monoxide flows in the reformate stream divided by the energy content of the fuel input. Lower heating values of the fuels were used for each mass-to-energy conversion.

3. Results

Using the effluent gas concentrations recorded by the mass spectrometer, the efficiency of the reforming process was calculated for each catalyst temperature, assuming the end use is a solid oxide fuel cell (SOFC), or similar, consuming both H₂ and CO. The pivot graph, Fig. 2, shows the reforming efficiency for each fuel as a function of catalyst temperature in the order it was tested. The graph shows that HRJ-5 has the highest reforming efficiency and JP-8 has the lowest efficiency at the operating conditions (e.g., temperatures) performed in this study. The graph also shows that when reforming JP-8 fuel, the reforming efficiency decreased by almost 13% as the catalyst temperature was reduced from 935 °C to 813 °C.

The catalyst showed no irreversible degradation, returning to near baseline performance after exposure to the matrix of various fuels and temperatures which is evident from test #12 in Fig. 2. The observed change in the reforming efficiency on HRJ-5 from the beginning to end of the temperature test sequence was approximately 4%; however, this is within the uncertainty of the temperature and flow measurements. This result confirmed that the data were repeatable and minimal long term catalyst degradation had occurred from the use of both HRJ-5 and JP-8 during the 9-hr of testing. The soot meter readings on HRJ-5 at the end of the test occurred from the use of both HRJ-5 and JP-8 during the 9-hr of testing. The soot meter readings on HRJ-5 at the end of the test sequence also returned to their baseline values.

The reformate quality, as evidenced by the concentrations displayed in Fig. 3, decreased for JP-8 as the temperature was reduced from 935 °C to 813 °C; however, HRJ-5 showed a more stable output as a function of temperature in the range evaluated in this work. Thus, operating the catalyst in this temperature range validates the results from our previous testing indicating that HRJ-5 can be more easily reformed at a lower catalyst temperature. By operating the catalyst at a temperature between 810 °C and 930 °C, the performance differences between the reformation of HRJ-5 and JP-8 were clearly highlighted and could be easily distinguished; refer to Fig. 3. At these catalyst temperatures, the reforming efficiency observed from JP-8 reformation was lower than that from HRJ-5 reformation, in part because the methane and ethylene concentrations were higher for the former.

After the temperature test sequence, a simple method to illustrate the difference in reforming performance of HRJ-5 and JP-8 fuels was performed to capture a transition between the two fuels in consecutive data. As illustrated in Fig. 4, a switch from HRJ-5 to JP-8 occurs over time and the resulting effect on the reformate quality on a dry basis is observed at a catalyst temperature of ~930 °C. The hydrogen concentration drops after the transition, shown within the dotted area in the figure, while the CO level.
increases slightly. Methane, soot, and ethylene concentrations all increase with the transition from HRJ-5 to JP-8, indicating a dramatic contrast between the two fuels at the operating temperature evaluated in this study.

4. Discussion

To understand the results of the catalyst testing, a review of the fuel properties, shown in Table 1, is pertinent. In the material safety data sheets for the two fuels, the main components are C9 to C15 paraffins for HRJ-5, and C9 to C16 kerosene for JP-8. Kerosene is a petroleum-based fuel that may contain normal, branched, and ring hydrocarbons. Ring hydrocarbons such as naphthenes and aromatics typically have lower cetane numbers than normal paraffins [8]. Since the cetane number is higher for HRJ-5, it is assumed there are more branched paraffins or aromatics in JP-8. The maximum specification limit for aromatic content in JP-8 is 25%, with significant samples reported with a content near 18% [9]. In previous reports, we have shown that heavier hydrocarbon chains have a high likelihood of carbon formation [6,10].
For many catalysts, sulfur in the inlet fuel and carbon formation temporarily decrease reactor efficiency by blocking active catalyst sites [6,11]. As observed in the testing on the PCI catalyst, the HRJ-5 did not produce significant amounts of carbon in the reformate stream within the range of temperatures tested, corresponding to stable catalyst performance. The lower concentration of sulfur in HRJ-5 is also a factor in improved reformer performance in comparison to JP-8. Shekhawat et al. showed a rapid decrease of approximately 20% in hydrogen yield for rhodium catalysts with the addition of 1000 ppm sulfur to the fuel [11]. Similarly, in our testing of JP-8 with 298 ppmw sulfur, the reforming efficiency was decreased by approximately 10% from baseline HRJ-5 levels at the operating temperatures and conditions evaluated in this study. Howell also showed that removing sulfur from JP-8 before the reactor yielded efficiencies greater than 58, a synthetic fuel similar to HRJ-5 [12]. The use of ULSD in the current experiments with 7 ppmw of sulfur and 30.3% aromatics for the break-in test provided results between those of HRJ-5 and JP-8. This is consistent with Howell’s results and indicates sulfur may be one of the major contributors to the lower performance observed with JP-8 reformation.

The reformer performance of the JP-8 and HRJ-5 oxidative steam reforming can be predicted in the range of catalyst temperatures evaluated in this study. Efficiency decreased for both fuels, but not as significantly for HRJ-5 where the efficiency achieved was near 85% and was less sensitive to temperature. The ethylene and ethane concentrations did not change for HRJ-5 as they did for JP-8 at lower catalyst temperatures, as expected, thus indicating a decrease in hydrocarbon conversion efficiency of the JP-8 due to heat transfer and reaction kinetics limitations. Howell also showed a similar decrease of 12% between reactor temperatures of 1100 °C and 900 °C with JP-8 [12]. Likewise, Kang and Bae showed that thermal transfer efficiencies between the partial oxidation and steam reforming portions of the catalyst can affect catalyst performance during reduced furnace temperature [13]. These results may vary depending on the H2O/C and O2/C ratios employed and their net effect on the endothermic nature of the reactions.

Shekhawat et al. stated that aromatics require higher contact time to yield H2 and CO than the higher reactivity paraffins [14]. The paraffins will react with the oxygen first and therefore the aromatics are left to breakdown by pyrolysis and steam reforming. This helps explain the results observed where the reforming efficiency and conversion of JP-8 decreased, especially at the lower operating temperatures. Based on the results from our prior study with a monolith catalyst, the effects of space velocity and heat transfer within the catalyst resulted in a lower conversion efficiency and therefore more carbon precursors present downstream, such as methane and ethylene [6]. For the fuels tested herein, the data indicates a strong correlation between reformer efficiency, and both the mass of soot in the effluent stream per mass of input fuel (mg/g), as shown in Fig. 5, and hydrocarbon conversion efficiency for these operating points.

5. Conclusion

The results of the fuel reformation experiments reported in this paper demonstrate the benefits of HRJ-5 as compared to JP-8. They include lower permissible operating/catalyst temperatures, lower carbon production, and higher reforming efficiencies. Using a PCI Microlith®-based catalyst, a reforming efficiency of 85% was obtained using HRJ-5 fuel with O2/C and H2O/C ratios of 0.46 and 1.0, respectively. Use of HRJ-5, or other synthetic fuels such as coal derived JP8 that do not contain significant aromatic content and sulfur species [15], may afford fuel cell developers greater design flexibility, longer system life due to lower catalyst temperatures, higher efficiencies, lower operating costs, and potentially smaller/lighter systems.

Without large quantities of sulfur, the typical sulfur trap in an SOFC system may be removed or at least reduced in size. Additionally, the higher reformer quality and reforming efficiency possible with HRJ-5 at a lower reforming temperature (i.e., lower air flow) will allow slightly smaller balance-of-plant components for fuel delivery, air supply, and water/recycle flows. A secondary benefit of HRJ-5 may include an increased reformer lifetime due to the reduction of the operating temperature needed to obtain complete fuel conversion and to avoid formation of higher hydrocarbons (i.e., ethane, ethylene). Additional increases in system efficiency may be possible from a more thermally integrated reformer, desulfurizer, heat exchanger, and stack assembly. Further research is needed to optimize O2/C and H2O/C ratios, space velocity, and operating temperature during the reforming of HRJ-5 and other biofuels. There is additional need to perform long term degradation testing with biofuels, analyze the effect of sulfur in blended fuels, and separate the effects of aromatics versus sulfur for systems in military applications.

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References


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Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>HRJ-5</th>
<th>JP-8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iso/n paraffin (% mass)</td>
<td>97</td>
<td>30</td>
</tr>
<tr>
<td>Sulfur (ppm)</td>
<td>&lt;0.08</td>
<td>298</td>
</tr>
<tr>
<td>Net heat of combustion (MJ/kg)</td>
<td>43.99</td>
<td>43.63</td>
</tr>
<tr>
<td>Hydrogen (wt%)</td>
<td>15.23</td>
<td>14.13</td>
</tr>
<tr>
<td>Cetane number</td>
<td>57.6</td>
<td>44.7</td>
</tr>
</tbody>
</table>


