TASK 2. TECHNOLOGY FOR SYNTHETIC FUELS PRODUCTION

2.2 Plasma Arc Processing

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Introduction

Recently, the alternative energy sector has experienced rapid growth because of increasing pressure from climate change awareness, rising fuel costs, and a need for domestic energy security [1, 2]. New technologies have focused on producing energy that is accessible, environmentally friendly, sustainable, secure, and can meet current and future projected energy needs [3]. Hydrogen is expected to play a large role in the energy economy of the future as it can be utilized in fuel cell applications, and in the synthesis of alternative fuels [1, 3, 4]. This work explored the use of a non-thermal reverse vortex flow (RVF) gliding-arc reformer for liquid fuels. Tests were conducted using dodecane as a model diesel compound and hydroprocessed renewable diesel fuel. Parametric tests determined the effects of various system parameters, while factorial tests were utilized for system optimization.

Hydrogen is expected to be a prominent fuel in the future [1, 3, 4]. However current production methods are expensive, require complex and large machinery or costly catalysts, and require an expensive distribution infrastructure [1, 3, 5]. Steam, partial oxidation, and autothermal reforming constitute the major reforming technologies [2, 3]. Hydrogen production via steam reforming of natural gas utilizes roughly one third of the fuel to support the parasitic energy requirement of the process. Ultimately this leads to an specific energy requirement (SER) of 325 to 354 kJ mol\(^{-1}\) of hydrogen produced [6, 7].

Since the late 90’s, interest in plasma reforming has grown [8]. Plasma reformers can operate in thermal equilibrium or non-thermal equilibrium. Thermal plasma reformers operate at high temperatures (5,000 – 10,000 K) [9], require power inputs of 1 kW to 50 MW [9, 10], require extensive measures to prevent electrode wear [9], and are most commonly used for metallurgical applications [11].

Non-thermal reformers can utilize various plasma forms such as glow discharge, corona discharge, silent discharge, dielectric barrier discharge, gliding arc, etc. Non-thermal plasma can operate near room temperature, at lower power inputs than thermal plasmas, and at or near atmospheric pressure [10]. They commonly have a much smaller physical footprint than traditional reforming technologies and can be used in onboard applications [12], all while maintaining high energy densities required for hydrocarbon reforming [13]. Within a non-thermal plasma, electrons exist at high temperatures, ranging from 10,000 to 100,000 K [2], while the protons and neutrons remain near room temperature [10, 13]. Intermediate, ‘warm’ plasmas, however, with gas temperatures ranging from 2,000 to 4,000 K can also be utilized for controlled gas reforming [11]. Petitpas et al. produced an extensive comparison of plasma technologies highlighting various reformer efficiencies, fuel conversion rates, and energy requirements [2]. Gutsol et. al.’s review of reforming technologies concluded that hydrogen must be produced for less than 109 kJ mol\(^{-1}\) [6] to be economically feasible. Many technologies are approaching this point [2].

Previous work explored parameters affecting the performance and optimization of non-thermal, reverse vortex flow, stabilized gliding-arc plasma reforming of methane [14]. Under this subtask, the performance and optimization of the same system adapted for the reforming of
selected liquid fuels. Liquid fuels can be distributed via existing fuel infrastructure and then reformed to produce hydrogen on site.

The two fuels of particular interest for ship board applications are marine diesel (F-76) and hydprocessed renewable diesel (HRD-76). Dodecane was chosen as a model liquid diesel compound in the development of a liquid fuel injection system. HRD-76 was the primary biofuel used in the recent Great Green Fleet exercises [15]. Reforming F-76, HRD-76, or their blends, could allow the Navy to transport a liquid fuel that could be reformed into hydrogen rich gas for shipboard applications.

**Materials and Methods:** Figure 2.2.Error! No text of specified style in document.-1 shows the test bed for RVF non-thermal, gliding-arc plasma reforming of liquid fuels. The system used for methane reforming previously described [14] was modified to accommodate liquid fuels. Changes to the three major component groups, reactant delivery, reformer and power supply, and product conditioning, are highlighted below.

A piston pump (SmoothFlow Pump 100 (LF), Microfluidica, Glendale, WI) provided precise fuel flow control to a nozzle injection system. The fuel is atomized upon injection at the top of the reaction chamber by an ultrasonic nozzle system powered by a digital signal generator (model HT40K50T, Sonaer Ultrasonics, Farmingdale, NY). The system atomized liquid fuel into 25 µm diameter droplets using 1.15 to 2.25 W power input over a range of fuel flow rates from 0.44 to 1.65 ml min^{-1}. Droplet sizes were measured using a phase-Doppler particle sizing system (Aerometrics, Sunnyvale, CA). Increasing power to the nozzle tip decreased the mean droplet diameter while increasing axial and radial droplet velocity, and resulted in liquid accumulation on the reactor walls and/or excessive unreacted fuel directly exiting the reactor. Particles with 25 µm diameter were entrained within the interior vortex of the reverse vortex flow, and were transported along the flow lines through the plasma arc.
The power supply for the reactor underwent minor changes when the reformer was adapted for use with liquid fuels. The only change to the power supply section was the substitution of an updated variable transformer (Model 3PN1510B-DVAM, ISE, Inc., Cleveland, OH).
Figure 2.2. Non-thermal gliding arc plasma RVF reformer (42 mm internal diameter) for liquid fuels, dimension in mm.

Figure 2.2. shows the updated reformer, modified for the introduction of liquid fuels into the reaction chamber. A non-conducting, top electrode mount made from zirconia ceramic (AmZirOx 86, Astro Met Zirconium Oxide, Cincinnati, OH) electrically insulated the ultrasonic nozzle from the upper electrode. AmZirOx 86 zirconia ceramic was chosen due to its electrical resistivity, low thermal expansion, and chemical inertness. Removing the upper electrode mount from the Macor top plate allowed radial insertion of the upper electrode into the reaction chamber. The 42 mm ID quartz tube reactor body is sealed at all mounting points with silicone O-rings.

The stainless steel tangential inlet plate used in the earlier study was replaced by one made of zirconia (AmZirOx 86, Astro Met Zirconium Oxide, Cincinnati, OH) to avoid electrical discharge between it and the top electrode. The bottom electrode lead was inserted through a pilot hole on the side of the plate (not shown in Figure 2.2.2) and made radial contact with the Inconel bottom electrode. All gas ports were 316 stainless steel Swagelok fittings inserted into the ceramic with pipe thread connections.

The ultrasonic nozzle was attached to an aluminum mounting plate fixed to the Macor™ top plate with PTFE threaded rods and sealed with a Kalrez® o-ring.
A funnel shape was added to the bottom of the quartz post reaction chamber to drain any unreformed liquids out of the reactor. A high temperature three-way valve (model MPT100-SS-T-SSS-N-15, Control Resources, Salisbury NC) at the reactor exit directed the product stream into the reformate conditioning and analysis section or into a bypass to exhaust during non-steady state periods. This allowed the system to come to steady state without contaminating the impinger train used for liquid analysis.

The gas phase analysis section of the test bed remained unchanged. The reformate conditioning system was modified to accommodate liquid fuels. Unreformed liquid fuel and liquid byproducts were condensed, trapped, and removed from the reformate stream exiting the reactor. Following the post reaction chamber and the bypass valve, the product stream flowed into a set of four, 500 ml stainless steel impingers in series (SN-5C set, Apex Instruments, Apex, NC). The first three contained 100 ml of isopropyl alcohol (A416 2-Propanol Certified ACS Plus, Fisher Scientific, Hanover Park, IL) and the fourth impinger was left empty. Upon exiting the impinger train, the gaseous reformate passed through a coalescing filter (Model 31G, Balston, Haverhill, MA) to remove any remaining aerosol or particulate matter.

For each operating condition the system was allowed to come to steady state with the reformate bypassing the analysis section. Once steady state was reached, reformate was directed through the analysis section for 40 minutes. The reformate stream was analyzed for CH$_4$, CO, CO$_2$ (Ultramat 23, Siemens, Washington, D.C.), O$_2$ (Oxymat 6E, Siemens, Washington, D.C.), and H$_2$ (Calomat 6E, Siemens, Washington, D.C.) by three on-line gas analyzers. Reformate was analyzed every ten gas chromatograph (GC) (Model 14A, Shimadzu, Columbia, MD) equipped with a 1.52 m x 3 mm Carbonex™ 1000 column (SUPELCO, Bellefonte, PA) and a thermal conductivity detector in accordance with ASTM D1946-90 [16]. After a 40 minute sampling period the flow was diverted to the bypass and exhaust. The impinger train could be removed and replaced prior to characterizing a different reactor operating point.

The final mass and volume of liquid recovered from the impingers was recorded and a sample of the liquid stored for later analysis using a GC (Autosystem GC, Perkin Elmer, Waltham, MA) equipped with a 60 meter capillary column (Rtx-1, 60m-0.53-7 μm, Restek Corporation, Bellefonte, PA) and a flame ionization detector.

Dodecane and HRD-76 were used to test the liquid reforming performance of the reactor. Dodecane (99.9% purity, Arcos Organics No. 117595000, Fisher Scientific, Hanover Park, IL) was chosen as a model compound for diesel [17, 18]. Parametric tests with dodecane were conducted to determine the effects of system parameters. Factorial tests were used to approach optimal operating conditions for dodecane and HRD-76.

HRD-76 was provided by the Naval Fuels and Lubricants Cross Functional Team. It was shipped with a bulk composition by mass of 84.63% carbon and 15.37% hydrogen, and a density of 0.781 g ml$^{-1}$. Figure 2.2.Error! No text of specified style in document.-3 shows the GC mass spectrometry (MS) analysis of HRD with the y-axis truncated. 3% of the peak area is octane, but the large majority of the fuel’s components fall between pentadecane and octadecane. Heptadecane composes 24% of the peak area, and octadecane 18%. Gowdagiri et.al report that HRD-76 has an equivalent hydrocarbon formula of C$_{15.4}$H$_{32.7}$ [19] and molecular weight of 218 g
mol\(^{-1}\), which corresponds well with the GCMS data. Higher heating value was measured with an adiabatic bomb calorimeter (Model 6200, Parr Instruments, Moline, IL) and found to be 46.7±0.3 MJ kg\(^{-1}\) (95% confidence interval), with a calculated lower heating value of 43.40 MJ kg\(^{-1}\).

Figure 2.2. GCMS chromatograph of HRD components

Dodecane input was varied from 0.44 ml min\(^{-1}\) to 1.32 ml min\(^{-1}\), corresponding to equivalence ratios of 0.70 to 0.26. Subsequent HRD test conditions were based on dodecane test equivalence ratios. The equivalence ratio is defined as the oxygen to fuel ratio of the reaction divided by the stoichiometric oxygen to fuel ratio (Equation 2.2.1) where \(\dot{n}\) is the species molar flow rate.

\[
\text{Equivalence Ratio} = \frac{\dot{n}_{O_2}^{\text{Reaction}}}{\dot{n}_{O_2}^{\text{Stoich.}}} = \frac{\dot{n}_{fuel}^{\text{Reaction}}}{\dot{n}_{fuel}^{\text{Stoich.}}} \tag{2.2.1}
\]

Parametric tests on dodecane investigated the system response while altering one independent variable at a time. Equivalence ratio, power input, and steam to carbon ratio were investigated. Initial set points and their range for the parametric tests are presented in
Table 2.2.1.
Table 2.2.1 - Independent variables, initial conditions, and value ranges for parametric tests.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Initial Set Point</th>
<th>Parametric Range of Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor Length</td>
<td>112.4 mm</td>
<td>fixed</td>
</tr>
<tr>
<td>Reactor Diameter</td>
<td>40 mm</td>
<td>fixed</td>
</tr>
<tr>
<td>Axial Exit Diameter</td>
<td>12.7 mm</td>
<td>fixed</td>
</tr>
<tr>
<td>Electrode Gap</td>
<td>35 mm</td>
<td>fixed</td>
</tr>
<tr>
<td>Nitrogen Flow</td>
<td>2 slpm</td>
<td>fixed</td>
</tr>
<tr>
<td>Oxygen Flow</td>
<td>0.56 slpm</td>
<td>fixed</td>
</tr>
<tr>
<td>Dodecane Flow</td>
<td>0.66 ml min⁻¹</td>
<td>0.44 to 1.32 ml min⁻¹</td>
</tr>
<tr>
<td>Equivalence Ratio</td>
<td>0.47</td>
<td>0.70 to 0.23</td>
</tr>
<tr>
<td>Steam Input</td>
<td>0.6 g min⁻¹</td>
<td>0.1 to 0.6 g min⁻¹</td>
</tr>
<tr>
<td>Steam : Carbon Molar Ratio</td>
<td>0.96</td>
<td>0.16 to 0.96</td>
</tr>
<tr>
<td>Power Input</td>
<td>180 W</td>
<td>140 to 250 W</td>
</tr>
</tbody>
</table>

A $2^3$ factorial experimental design (8 points per test) was used to optimize dodecane reforming using SER (see definition in Equation (2.2.2)) as the performance variable, i.e. identifying the minimum SER operating point of the process. The SER definition in Equation (2.2.2) is based on the assumption that CO in the product gas can be used to produce additional H$_2$ using the water gas shift reaction. The input power is measured in kW, and $\dot{n}$ is the molar flow rate in mol s⁻¹.

$$SER = \frac{\text{Input Plasma Power}}{\left(n_{\text{CO}^*} + n_{\text{H}_2}\right)_{\text{produced}}} \quad (\text{kJ mol}^{-1}\text{H}_2 \text{ produced}) \quad (2.2.2)$$

High and low values of operating parameters were selected using the results from the parametric tests as a center point (Table 2.2.2). The factorial tests also identified system operating limits and higher order interaction effects between the independent variables. The order of individual test points was randomized and data at each test point were collected four times to provide an average value and estimate error. Reported error and error bars on charts reflect a 95% confidence interval.

Based on the optimal operating conditions for dodecane a $2^2$ factorial test investigated HRD-76 reforming while minimizing SER. For the HRD factorial treatments, power input was held constant at the maximum value identified from the dodecane factorial tests. The operating values are summarized in Table 2.2.2.

Table 2.2.2 - Center points and step sizes for dodecane and HRD-76 factorial tests

<table>
<thead>
<tr>
<th>Parameter</th>
<th>1st Dodecane Factorial Test</th>
<th>2nd Dodecane Factorial Test</th>
<th>HRD-76 Factorial Test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel Input</td>
<td>0.66 ml min⁻¹, 0.11 ml min⁻¹</td>
<td>1.32 ml min⁻¹, 0.11 ml min⁻¹</td>
<td>1.27 ml min⁻¹, 0.11 ml min⁻¹</td>
</tr>
<tr>
<td>Steam Input</td>
<td>0.4 g min⁻¹, 0.1 g min⁻¹</td>
<td>1.1 g min⁻¹, 0.1 g min⁻¹</td>
<td>1.1 g min⁻¹, 0.1 g min⁻¹</td>
</tr>
</tbody>
</table>
Calculation of performance indicators from experimental data conformed to those used by Petitpas et al. [2]. System performance for dodecane parametric tests and factorial tests were characterized by hydrogen yield, fuel conversion, hydrogen selectivity, efficiency, and specific energy requirements. Differentiating reaction products from original fuel components in HRD was not possible, as higher hydrocarbons present in the fuel could react to form smaller molecules also present in the original fuel, e.g. octadecane reformed to heptadecane. Therefore system performance indicators for HRD omitted fuel conversion and selectivity.

Hydrogen yield is defined by the number of hydrogen atoms in hydrogen gas in the reformate divided by the total amount of hydrogen atoms in the reactant fuel (Equation 2.2.3) [2].

\[
\text{Hydrogen Yield} = \frac{\text{Hydrogen Atoms in } H_2 \text{ in reformate}}{\text{Hydrogen Atoms in Feed Fuel}} (\%) \tag{2.2.3}
\]

Fuel conversion is defined as the amount of fuel converted in the reactor divided by the total fuel input to the system (Equation 2.2.4).

\[
\text{Dodecane Conversion} = \frac{n_{\text{dodecane in fuel}} - n_{\text{dodecane in reformate}}}{n_{\text{dodecane in fuel}}} \times 100 \, (\%) \tag{2.2.4}
\]

Selectivity is defined as the hydrogen yield divided by the fuel conversion as shown in Equation 2.2.5. This provides an index of the system’s ability to reform the fuel into hydrogen with the assumption that unreformed fuel could be recovered, utilized by other processes, or reintroduced into the reformer.

\[
\text{Selectivity} = \frac{\text{moles of } H_2 \text{ produced}}{13(\text{moles of dodecane converted})} \times 100 \, (\%) \tag{2.2.5}
\]

Efficiency is defined in Equation 2.2.6 as the amount of hydrogen energy in the reformate divided by the total system energy input from both the plasma and reactant fuel [2].

\[
\text{Efficiency } \eta = \frac{LHV_{H_2\text{gas}} \times (n_{H_2} + n_{CO})_{\text{reformate}}}{\text{Plasma Power} + LHV_{\text{fuel input}} \times m_{\text{fuel input}}} \tag{2.2.6}
\]

\(LHV\) is the lower heating value (MJ kg\(^{-1}\)) and \(m\) is the mass flow rate of a given species. The efficiency definition assumes, according to convention [2, 21], that any CO present in the reformate could be converted to \(H_2\) by the exothermic water gas shift reaction (Equation 2.2.7) [22].

\[
H_2O + CO \rightarrow H_2 + CO_2 \quad \Delta H = -41 \, kJ \, mol^{-1} \tag{2.2.7}
\]

Results and Discussion: Results from the parametric and factorial tests of dodecane and HRD-76 are summarized below.

Dodecane testing: Power input was varied parametrically from 120 to 225 W in nominal 20 W increments. The highest point was 225 W instead of 220 due to the sensitivity of power input controls. Below 120 W, a continuous arc could not be maintained.
Parametrically increasing power input had very little effect on hydrogen yield, hydrogen selectivity, fuel conversion, and efficiency as seen in Figure 2.2. As the power increased the fuel conversion remained relatively constant at \(~90\%\). Gains in hydrogen yield, which rose from 32.1 to 35.73\%, and selectivity, which rose from 35.7 to 42.6\%, were realized. Increases in H\(_2\) and CO yields maintained efficiency at near constant values of \(~19\%\) across all power input levels. At 120 W power input, the plasma power corresponded to 23\% of the total energy input (plasma plus fuel), increasing to 37\% at 225W. The increasing power input to the system yielded increasing specific energy requirements, ranging from 319.9 to 486.0 kJ mol\(^{-1}\) of H\(_2\) produced. Therefore the lower the plasma power input to the system the better the reformer performed as measured by SER.

Figure 2.2. - Dodecane parametric test results for power input. Error bars indicate 95\% confidence interval. Error bars that are not visible are equal in size to the data point symbol.

The fuel input tests effectively decreased the equivalence ratio by increasing the fuel input (Equation 2.2.1). Soot formation occurred when the equivalence ratio decreased below 0.25. Figure 2.2. shows fuel conversion remained constant at \(~95\%\) while the equivalence ratio decreased. As the fuel input increased the hydrogen yield and selectivity both increased from 34 to 47\% and 36 to 49\% respectively. At 0.29 equivalence ratio, both the hydrogen yield and selectivity were slightly higher than at 0.25 equivalence ratio. Over the equivalence ratio test range, the efficiency varied from 13 to 30.3\% with the latter value measured at equivalence ratio of 0.29. This is strongly due to the large increase of H\(_2\) and CO production. At an equivalence ratio of 0.29 and efficiency of 33.2\%, the reformate contains H\(_2\) (17.0\%) and CO (16.2\%). A significant rise in SER resulted from increasing fuel input while the fuel conversion percentage remained constant. The SER of 763 kJ mol\(^{-1}\) of H\(_2\) produced at an equivalence ratio of 0.71 decreases to 184 kJ mol\(^{-1}\) at 0.25.
However these gains have diminishing returns and approach a lower limit as the equivalence ratio drops below 0.30.

Figure 2.2. Dodecane parametric test results for equivalence ratio. Error bars indicate 95% confidence interval. Error bars that are not visible are equal in size to the data point symbol.

Steam input helps prevent soot formation within the reactor, however the excess water molecules absorb energy introduced to the system [23]. Steam input to the system was varied from 0.1 to 0.6 g min\(^{-1}\) corresponding to a steam:carbon molar ratios of 0.16 to 0.96, respectively. Figure 2.2 shows the effects of increasing steam input to the reformer. The increase in steam does little to change the fuel conversion, which remains near 94%, and efficiency, which remains around 17%. Slight gains are realized in hydrogen yield and hydrogen selectivity as the steam input increases. Hydrogen yield increases 18% (relative) from 28.3 to 33.5%, while selectivity increases by 14% (relative) from 31.2 to 36.4%. Gains realized over this low range of steam input indicate that steam was a limiting reactant in some H\(_2\) producing reactions. Further increases in steam input dilute the plasma power with negative results [14]. These gains are reflected in the SER which decreased from 493 to 434 kJ mol\(^{-1}\) of H\(_2\) produced. The effect of steam input was further investigated in the factorial treatments.
Dodecane reforming was further investigated using a $2^3$ factorial experiment design which investigated effects of plasma power input, fuel input, and steam input. The center point and step sizes for the first factorial test were chosen to ensure the reactor system operated (i.e. no soot formation or arc extinction) and to produce measurable differences in the dependent variables. Data from the factorial tests allowed a path of steepest descent to be mapped across the operating response surface toward a set of independent variable control points that minimized SER.

Table 2.2.3 shows the effects of independent variables changing between high and low values. Third order effects (ABC) are assumed to be an estimate of the error [24] thus first and second order effects of greater magnitude are significant. None of the control parameters have a significant effect on dodecane conversion, confirming the parametric test results. Increasing power did not affect the performance metrics except for its negative effect on SER; a 20 W increase in power input increased the SER by 60 kJ mol$^{-1}$ H$_2$. Dodecane input significantly increased both hydrogen yield and selectivity, however it did not have a significant effect on either efficiency or SER. Steam input had the greatest effect on all of the metrics. The increase from 0.3 to 0.5 g min$^{-1}$ improved both hydrogen yield and selectivity by 13%, and increased
efficiency by 10.5%. The greatest performance gains came in the SER, decreasing by 276 kJ mol\(^{-1}\) H\(_2\) produced.

Table 2.2.3 – Summary of first dodecane factorial test results

<table>
<thead>
<tr>
<th>Control Parameter</th>
<th>Performance Indicator</th>
<th>Dodecane Conversion change in %</th>
<th>Hydrogen Yield change in %</th>
<th>Hydrogen Selectivity change in %</th>
<th>Efficiency change in %</th>
<th>SER change in kJ mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (Power)</td>
<td></td>
<td>0.45</td>
<td>0.70</td>
<td>0.54</td>
<td>-1.35</td>
<td>60.16(^1)</td>
</tr>
<tr>
<td>B (Steam)</td>
<td></td>
<td>0.36</td>
<td>13.25(^1)</td>
<td>13.75(^1)</td>
<td>10.47(^1)</td>
<td>-276.51(^1)</td>
</tr>
<tr>
<td>C (Fuel)</td>
<td></td>
<td>1.27</td>
<td>4.81(^1)</td>
<td>4.45(^1)</td>
<td>1.45</td>
<td>-39.44</td>
</tr>
<tr>
<td>AB</td>
<td>1.16</td>
<td>-2.47</td>
<td>-1.97</td>
<td>-1.64</td>
<td>3.07</td>
<td></td>
</tr>
<tr>
<td>AC</td>
<td>0.98</td>
<td>2.39</td>
<td>2.07</td>
<td>1.15</td>
<td>-39.48</td>
<td></td>
</tr>
<tr>
<td>BC</td>
<td>-1.18</td>
<td>-1.77</td>
<td>-1.33</td>
<td>-0.80</td>
<td>32.76</td>
<td></td>
</tr>
<tr>
<td>ABC</td>
<td>-1.25</td>
<td>-2.34</td>
<td>-1.85</td>
<td>-1.32</td>
<td>42.32</td>
<td></td>
</tr>
</tbody>
</table>

\(^1\) Indicates significant effect

To move toward operating conditions that improve (reduce) the SER, a path of steepest descent was calculated from the results of the first factorial test. As shown in Table 2.2.2, the path pointed toward a center point for the second factorial tests characterized by increased steam input, increased dodecane input, and a slight increase in arc power input.

The second factorial test point with high dodecane and steam inputs, and low power input, experienced multiple failures due to arc extinction. While the arc was extinguished, unreformed fuel passed through the reactor and into the impingers. Therefore the impinger data needed to calculate dodecane conversion and selectivity was not available. However, the GC and online gas analyzers provided reformate gas stream composition when the arc was established and the remaining metrics could be calculated.
Table 2.2.4 shows the system responses from the second factorial test. Only dodecane input continued to have a significant effect on the system performance. Changing levels of power and steam input with respect to the center point no longer had an effect on system performance. Based on the results of the second factorial test, the path of steepest descent for SER required increasing dodecane input with constant steam and power inputs.
Table 2.2.4 - Second dodecane factorial test results

<table>
<thead>
<tr>
<th>Control Parameter</th>
<th>Performance Indicator</th>
<th>Dodecane Conversion change in %</th>
<th>Hydrogen Yield change in %</th>
<th>Hydrogen Selectivity change in %</th>
<th>Efficiency change in %</th>
<th>SER change in kJ mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st Order Effects</td>
<td>A (Power)</td>
<td>NA</td>
<td>3.88</td>
<td>NA</td>
<td>0.34</td>
<td>18.85</td>
</tr>
<tr>
<td></td>
<td>B (Steam)</td>
<td>NA</td>
<td>-3.07</td>
<td>NA</td>
<td>-2.35</td>
<td>13.87</td>
</tr>
<tr>
<td></td>
<td>C (Fuel)</td>
<td>NA</td>
<td>3.66</td>
<td>NA</td>
<td>3.30</td>
<td>-37.79</td>
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<tr>
<td>2nd Order Effects</td>
<td>AB</td>
<td>NA</td>
<td>-2.85</td>
<td>NA</td>
<td>-1.56</td>
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<tr>
<td></td>
<td>AC</td>
<td>NA</td>
<td>-3.36</td>
<td>NA</td>
<td>-1.90</td>
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<td></td>
<td>BC</td>
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<td>-0.14</td>
<td>NA</td>
<td>-0.09</td>
<td>-0.12</td>
</tr>
<tr>
<td>3rd Order Effects</td>
<td>ABC</td>
<td>NA</td>
<td>-6.36</td>
<td>NA</td>
<td>-3.52</td>
<td>17.57</td>
</tr>
</tbody>
</table>

1 Indicates significant effect

Figure 2.2. Error! No text of specified style in document. 7 shows the last path of steepest descent, which terminated at the optimal operating condition for dodecane reforming. The optimal reactor operating point was defined by an input of 2 slpm N₂ and 0.26 slpm O₂, power input of 240 W, fuel input of 1.65 ml min⁻¹ of dodecane (EQ ratio = 0.18), and steam input of 1.0 g min⁻¹ (S:C ratio = 0.63). These inputs yielded a SER of 134.1 kJ mol⁻¹ H₂ produced, a hydrogen yield of 65%, and an efficiency of 37%. Throughout the path of steepest descent the SER continually dropped while the hydrogen yield and efficiency remained nearly constant. Continuing beyond this point on the path of steepest descent was unsuccessful due to extinction of the arc.

The 37% efficiency at the operating conditions identified by minimizing SER can be compared to the efficiency predicted by thermodynamic equilibrium. The state of the reactant system was described using the N₂, O₂, C₁₂H₂₆, and H₂O input flowrates detailed above, a mass averaged input temperature of 50 °C, and 0.1 MPa pressure. The change in enthalpy between reactants and products was based on the 240 W power input to the plasma arc. Reactant flow rates and arc power were converted to units of moles and Joules using a common time basis. The product composition at equilibrium, calculated using FactSage™ (CRCT, Montreal, Quebec, Canada), yielded an efficiency of 77%, with 86% of the input carbon predicted to be present as CO and the remainder (>13%) largely present as CH₄, CO₂, and solid C. Differences between the measured and equilibrium efficiencies are the result of non-idealities in the plasma system such as heat loss, incomplete mixing of reactants, and inadequate reaction time. This single-pass reactor efficiency would be improved by recovering and recycling unreacted liquid hydrocarbons (described in the next section) as might be expected to occur in a fully integrated reformer unit. Gallagher et al. [21] reported ~35% efficiency for a lab scale plasmatron reformer using n-tetradecane at an oxygen to carbon reactant ratio of 0.9, similar to the conditions reported here as optimal conditions.
Figure 2.2. Error! No text of specified style in document. - Final dodecane path of steepest descent and optimal operating condition based on minimized SER. Error bars indicate 95% confidence interval. Error bars that are not visible are equal in size to the data point symbol.

Analysis results of the liquid product recovered from impingers downstream of the reactor for test conditions of 0.55 ml dodecane min$^{-1}$, steam input of 0.3 g min$^{-1}$, and power input of 200 W, are presented in Figure 2.2. Error! No text of specified style in document. -8. In addition to unreacted dodecane, six alkenes from 1-hexene to 1-undecene were identified and quantified. Concentrations determined from the GC-FID analysis and the impinger liquid volumes were used to calculate analyte mass. Figure 2.2. Error! No text of specified style in document. -9 summarizes the distribution of dodecane input carbon among reforming products. The alkene species from Figure 2.2. Error! No text of specified style in document. -8 as a group (Alkenes) in Figure 2.2.9 account for 1.3% of the input carbon. Identified products accounted for 96.3% of the carbon input to the system. C3 to C5 hydrocarbons were not measured in either the GC-TCD or GC-FID analysis due to co-elusion with the IPA/acetone trapping solution.
Figure 2.2. TCD analysis of liquid samples from impingers 1 - 4. IPA/acetone and dodecane saturated the detector. 1.54 g of unreformed dodecane was recovered in the impingers, analysis was performed at 10% dilution.

Figure 2.2. Distribution of dodecane input carbon among measured products.

HRD-76 testing
Based on the parametric and factorial test results for dodecane, a factorial test was performed to identify the optimal SER reactor operating conditions for HRD-76.
During the preliminary HRD-76 tests a cloud of fuel vapor was observed in the top of the reaction chamber. Insulation was added to the top section of the reaction chamber, above the upper electrode mount to improve vaporization. Tests were conducted before and after the insulation was added to the reaction chamber with operating conditions of 260 W, 1 g min\(^{-1}\) of steam input, and 1.16 ml min\(^{-1}\) of HRD. Prior to adding insulation, the average SER was 218.7 ± 2.5 kJ mol\(^{-1}\) of H\(_2\). With the added insulation on the reactor, this operating point was revisited intermittently throughout the ensuing test campaign to provide an indicator of performance repeatability. Using SER data from 12 independent measurements yielded an average value of 183.3 ± 4.5 kJ mol\(^{-1}\) of H\(_2\) produced or 2.5% error.

Based on dodecane test results, a 2\(^3\) factorial experiment was designed for the HRD-76 optimization with power input centered at 240 W and a 20 W step size. However, the system could not operate at 220 W due to arc extinction. Power input was removed as a variable in the optimization and the factorial test redesigned to investigate steam and HRD-76 (equivalence ratio) inputs while holding power constant at 260 W (see Table 2.2.2).

**Figure 2.2.** Results of first factorial test for HRD. The darkened symbols show the high steam input points and lighter symbols show the low steam input points. Error bars indicate 95% confidence interval. Error bars that are not visible are equal in size to the data point symbol.
The path of steepest descent from the first factorial test held both power and steam at constant values, while increasing fuel input. The power was set at 260 W in order to ensure reactor operation, while steam was held constant at an input of 1.0 g min$^{-1}$. As the fuel was increased past 1.38 ml min$^{-1}$, at an equivalence ratio of 0.22, soot and liquids deposited on the reactor walls, the latter appearing as a tacky brown film. With increasing deposit mass the arc discharged to the deposited material instead of the lower electrode and the test was terminated. Thus optimal operating conditions for minimum SER were identified at inputs of 2 slpm of N$_2$, 0.56 slpm of O$_2$, 1.0 g min$^{-1}$ of steam, 1.38 ml min$^{-1}$ of HRD-76, and 260 W of power. At these conditions the reactor operated with an H$_2$O:C ratio of 0.70, equivalence ratio of 0.21, SER of 176.1 kJ mol$^{-1}$ of H$_2$ produced, an efficiency of 35.0%, and a hydrogen yield of 64.2%.

Modifications to the non-thermal plasma reverse vortex flow methane reformer allowed for the reformation of liquid fuels. Ultrasonic atomization of the fuel was used to axially inject fuel into the reformer. Injected fuel vaporized due to elevated temperatures in the reactor, and vapor clouds were eliminated by insulating the upper half of the reaction chamber.

Parametric and factorial tests investigated the effects of varying the power input, dodecane input, and steam input to the system. Dodecane conversion remained fairly constant across all of the tests while the selectivity, hydrogen yield, efficiency, and SER of the system varied greatly. The system was optimized for SER. Decreasing power input, increasing fuel input, and increasing steam input up to a steam:carbon ratio of 0.73 decreased the SER and improved system performance. Optimal SER of 134.1 ± 1.08 kJ mol$^{-1}$ H$_2$ produced, with accompanying hydrogen yield of 65.0 ± 0.02 %, and efficiency of 37.0 ± 0.02 % was achieved for dodecane at inputs of 2

Table 2.2.5 – HRD-76 first factorial treatment system responses

<table>
<thead>
<tr>
<th>Control Parameter</th>
<th>Performance Indicator</th>
<th>Hydrogen Yield change in %</th>
<th>Efficiency change in %</th>
<th>SER change in kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A(Steam)</td>
<td>-3.12 $^1$</td>
<td>-1.28 $^1$</td>
<td>-0.45</td>
<td></td>
</tr>
<tr>
<td>B(HRD)</td>
<td>-0.04</td>
<td>1.62 $^1$</td>
<td>-36.50 $^1$</td>
<td></td>
</tr>
<tr>
<td>AB</td>
<td>1.72</td>
<td>0.29</td>
<td>6.09</td>
<td></td>
</tr>
</tbody>
</table>

$^1$ indicates significant effect
slpm N₂, 0.26 slpm O₂, 240 W, 1.65 ml min⁻¹ of dodecane (equivalence ratio = 0.18), with a steam input of 1.0 g min⁻¹ (H₂O:C ratio = 0.63).

HRD-76 reforming was optimized at SER of 176.1 ± 3.8 kJ mol⁻¹ of H₂ produced, a hydrogen yield of 64.2 ± 1.7%, and efficiency of 35.0 ± 1.0%, using operating parameters of 2.0 slpm of N₂, 0.56 slpm of O₂, HRD input of 1.38 ml min⁻¹ (equivalence ratio = 0.21), and steam input of 1.0 g min⁻¹ (H₂O:C ratio of 0.73).

SER values obtained for both fuels were below the ~340 kJ mol⁻¹ H₂ benchmark for steam reforming of natural gas but above the ~110 kJ mol⁻¹ H₂ identified as competitive for plasma based systems. SER could be improved by reducing heat loss, recovering and recycling unreacted liquid and gas phase hydrocarbons, and operating the reformer as a fully integrated industrial package.

References