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by

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This work is supported by the U.S. Department of Energy, Office of Advanced Automotive Technologies, in the Office of Automotive Technologies, under Contract No. W-31-109-ENG-38.
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FUEL-FLEXIBLE PARTIAL OXIDATION REFORMING OF HYDROCARBONS FOR AUTOMOTIVE APPLICATIONS

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KEYWORDS partial oxidation, fuel-flexible reforming, hydrogen production

INTRODUCTION

Research is underway to develop fuel cells for ultra-low-emission vehicles. However, automotive and petroleum companies have pointed out that the successful commercialization of fuel-cell-powered electric vehicles in the near future will depend, to a large extent, on the availability of a refueling infrastructure. This infrastructure is completely lacking for hydrogen. To tap into the existing fuel infrastructure, fuel processors capable of converting liquid hydrocarbon fuels into hydrogen are required. Fuels of interest include gasoline, diesel, methanol, ethanol, and natural gas.

There is some debate about which hydrocarbon fuel is optimal for fuel cell systems. Methanol and ethanol are widely available commodity chemicals and have numerous advantages as fuel (easy to reform, water soluble, renewable, etc.). Gasoline and diesel have the advantage over the alcohols of existing refueling infrastructures and higher energy density. However, they are blends of different kinds of hydrocarbons and are believed to be more difficult to reform. Kumar et al., at Argonne National Laboratory, have developed a partial oxidation catalyst that can convert a broad range of alcohols and hydrocarbon fuels into a hydrogen-rich product gas. Tests in micro-reactors have shown high conversion and hydrogen yields from methane, methanol, ethanol, 2-pentene, cyclohexane, i-octane, hexadecane, gasoline, and diesel.

The overall partial oxidation reaction can be written as:

\[
\text{C}_n\text{H}_{2n+2} + (2n+1)\text{O}_2 + n\text{CO}_2 + (2n+1)\text{H}_2\text{O}
\]

This can be thought of as an exothermic oxidation reaction combined with an endothermic steam-reforming reaction.

\[
\text{C}_n\text{H}_{2n+2} + \frac{1}{2}(3n+1)\text{O}_2 = n\text{CO}_2 + (3n+1)\text{H}_2\text{O}
\]

The overall partial oxidation or autothermal catalytic reforming can be exothermic or endothermic. The main factor determining the heat balance for the reaction is the oxygen-to-carbon ratio. The thermal neutral point (where enthalpy of the reaction is zero) varies from an x/n ratio of 0.23 for methanol to 0.37 for iso-octane. For autothermal reforming, it is advantageous to run in the exothermic region, but at a low x/n ratio to maximize the yield of H₂. The experiments reported here were performed with an x/n ratio of 0.5, except for methanol and ethanol experiments, which were performed at a lower x/n (0.32 and 0.25) to compensate for the oxygen already present in the alcohol.

EXPERIMENTAL APPROACH

The catalytic partial oxidation reforming of hydrocarbon fuels was demonstrated in a series of experimental activities, beginning with micro-reactor studies and progressing up to bench-reactor-scale investigations. Since gasoline and diesel fuels are blends of different types of hydrocarbons, the studies were initially carried out with representatives of the different types of hydrocarbons present in these fuels, e.g., iso-octane for paraffins and toluene for aromatics. A schematic of the micro-reactor apparatus is shown in Fig. 1. The liquid fuel and water are pumped through separate vaporizer coils. The vapors then combine with oxygen to form the reactant mix that flows into the micro-reactor. The reactor is a 10.6 mm-ID tube packed with ~2 g of catalyst. The temperature is controlled by a surrounding furnace. Samples are drawn from the product stream and analyzed with a gas chromatograph or gas chromatograph–mass spectrometer. Temperatures and pressures are measured above and below the catalyst bed. In order to facilitate comparisons between the
various fuels, micro-reactor tests were generally run with a fixed carbon-to-oxygen ratio and a slight excess of water with respect to equation 1 \([H_2O > (2n - 2x - p)\]).

Fig. 1
Schematic of Experimental

RESULTS AND DISCUSSION
Hydrogen production from the partial oxidation reforming of several of the fuels tested is shown in Table 1. The table lists the hydrocarbon feed, the reactor temperature at which complete conversion of the hydrocarbon was achieved and the percentages of hydrogen, carbon monoxide, and carbon dioxide measured in the product gas. The last three columns list the calculated percentages of the gases that would exist at equilibrium at the different temperatures. Using the Argonne catalyst, we were able to convert these hydrocarbons at less than 700°C. Comparison between the experimental and equilibrium gas compositions indicates that the use of the catalyst allows for lower carbon monoxide and slightly higher hydrogen concentrations than what might be achieved at equilibrium at these temperatures.

Table 1. Experimental Product Gas Composition Compared with Equilibrium Compositions Calculated for the Given Feed Mixture and Experimental Temperature

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Temperature for complete conversion, °C</th>
<th>Experimental (% dry N2 free)</th>
<th>Equilibrium (% dry N2 free)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>H2</td>
<td>CO</td>
</tr>
<tr>
<td>Iso-octane</td>
<td>630</td>
<td>60</td>
<td>16</td>
</tr>
<tr>
<td>Toluene</td>
<td>655</td>
<td>50</td>
<td>8</td>
</tr>
<tr>
<td>2-Pentene</td>
<td>670</td>
<td>60</td>
<td>18</td>
</tr>
<tr>
<td>Ethanol</td>
<td>580</td>
<td>62</td>
<td>15</td>
</tr>
<tr>
<td>Methanol</td>
<td>450</td>
<td>60</td>
<td>18</td>
</tr>
</tbody>
</table>

Table I also indicates that the two alcohols (methanol and ethanol) are reformed at substantially lower temperatures than the other species. Of the fuels considered for partial oxidation reforming, alcohols should be considerably easier to reform since they are already partially oxidized.

There is a substantial difference in the temperature at which complete conversion of the hydrocarbons was achieved, even between the two alcohols studied. Figure 2 illustrates the temperature dependence of hydrogen production from the partial oxidation reforming of methanol and ethanol using the Argonne partial oxidation. The two alcohols behave quite differently.
Methanol was easily reformed throughout the temperature range investigated. This fuel yielded a product gas that had hydrogen concentrations in the 55 to 65% range (on a dry N\textsubscript{2} free basis), with the product gas varying only slightly in composition with changes in temperature. The temperature dependence of ethanol reforming was quite different, with the product composition varying strongly with temperature in the range of 410 to 525°C. At 470°C, the product gas from ethanol reforming contained only about 35% hydrogen, compared to about 60% hydrogen for methanol reforming at the same temperature. For temperatures greater than 525°C, hydrogen production from ethanol was almost identical to that from methanol. However, the maximum hydrogen yield for the reactant mix with methanol was 70.2%, while that for ethanol was 71%. Defining hydrogen selectivity as the measured hydrogen yield divided by the maximum, we find slightly lower hydrogen selectivity for ethanol in the high temperature region (88.9%) than for methanol (91%). This was due to the formation of methane in the ethanol reforming. The ethanol reformate contained substantial amounts of methane over the entire temperature range investigated, with the reformate containing about 5% methane at 640°C, while the methanol reformate contained an order of magnitude less methane at this temperature.

The effect of temperature on hydrogen production from reforming of methane, iso-octane, and 2-pentene is shown in Fig. 3. These hydrocarbons were more difficult to reform autothermally than the alcohols, as expected. Temperatures of nearly 650°C were needed to approach 60% hydrogen in the product gas. Hydrogen selectivities of 90% for methane and 88% for iso-octane and 2-pentene were obtained. The hydrogen concentration at a given temperature was similar regardless of the hydrocarbon. The data for methane, iso-octane, and 2-pentene all fall on the same regression line (see
Fig. 3). Hydrocarbon length over the range of C1 to C8 and the presence of unsaturation appear to have little affect on the product composition.

Increasing the hydrocarbon length to C16 (hexadecane) was observed to lead to lower hydrogen content in the product gas. Hexadecane reforming showed a temperature dependence similar to that observed for methane, iso-octane, and 2-pentene (i.e., similar slope in Fig. 3). However, higher temperatures were needed to reach comparable hydrogen content in the product gas. This appears to be due to increased methane formation from hexadecane. At 650°C, the product gas from hexadecane reforming contained 6% methane (dry, nitrogen free), while that from iso-octane reforming contained only about 2% methane.

The iso-octane and hexadecane experiments also pointed out some potential difficulties in reforming longer hydrocarbons. The product gas from iso-octane and hexadecane reforming contained small amounts of benzene. This is illustrated in Table II, which compares the output from thermal reforming (no catalyst present) and catalytic reforming (catalyst present) of iso-octane. Benzene was present in the product gas at concentrations of about 0.1-0.2% for temperatures from 600 to 725°C when the catalyst was present; however, no benzene was detected in the product gas when the catalyst was absent. This suggests that benzene is formed as a side product during the reforming of C8 hydrocarbons. Studies on the formation of aromatics from C8 hydrocarbons have indicated that the most likely mechanism for benzene production involves formation of xylene, which then form benzene by trans alkylation reactions.

Table 2. Effect of Catalyst on Product Composition

<table>
<thead>
<tr>
<th></th>
<th>Product Composition at 725°C, % (dry, N₂ free)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H₂</td>
</tr>
<tr>
<td>No Catalyst</td>
<td>0.0</td>
</tr>
<tr>
<td>Catalyst</td>
<td>57.9</td>
</tr>
</tbody>
</table>

We have also investigated the reforming of cyclohexane, a possible benzene precursor, and toluene, a benzene derivative. The hydrogen production from partial oxidation reforming of cyclohexane and toluene did not exhibit the same temperature dependence as did that from reforming the alkanes and the alkene discussed previously. The product composition was much less sensitive to temperature for these cyclic compounds (see Fig. 4). Hydrogen selectivity was still high, but slightly lower for toluene (82%) than for cyclohexane (91%) and the non-cyclic alkanes (88%). The lower temperature dependence suggests that a different mechanism may be controlling the reforming of cyclohexane and toluene.

![Fig. 4](image-url)

Hydrogen Production from Partial Oxidation Reforming of Cyclohexane and Toluene

![Graph](image-url)
The results from reforming toluene suggest that if benzene, xylene, or other aromatics are formed at low levels as side products in the reforming of branched hydrocarbons they can be reformed. Increasing the temperature will increase the conversion of these aromatics to hydrogen, but not as effectively as it increases the rate of conversion of alkanes to hydrogen.

The ability of the Argonne catalyst to reform several types of hydrocarbons suggested that this catalyst would be able to reform commercial petroleum fuels. Therefore, we proceeded with tests of commercial gasoline and diesel fuel. The product composition from autothermal reforming of a commercial premium gasoline is shown in Fig. 5. Hydrogen concentrations in the product gas approaching 60% on a dry N₂ free basis were obtained at temperatures ≥700°C. The slope of the plot of inverse temperature versus hydrogen content in the product gas is similar to that found for the reforming of methane, iso-octane, and 2-pentene, suggesting a similar mechanism. However, methane concentrations in the product gas are higher than what we have seen from reforming the simple hydrocarbons. Commercial gasoline contains sulfur, a known catalyst poison, at levels of over 100 ppm. However, no change was observed in the product composition after 40 h of intermittent gasoline reforming, indicating it has some resistance to sulfur poisoning.

Reforming of diesel fuel proved slightly more difficult. Methane was observed in higher concentrations in the product gas from diesel reforming than in the product from gasoline reforming. Higher reforming temperatures were needed to decrease the methane and increase the hydrogen in the product gas. At 850°C we were able to obtain a product gas with hydrogen concentrations >50% on a dry N₂ free basis (see Fig. 6).

CONCLUSIONS
Micro-reactor tests indicate that our partial oxidation catalyst is fuel-flexible and can reform conventional (gasoline and diesel) and alternative (ethanol, methanol, natural gas) fuels to hydrogen rich product gases with high hydrogen selectivity. Alcohols are reformed at lower temperatures (<600°C) while alkanes and unsaturated hydrocarbons require slightly higher temperatures. Cyclic hydrocarbons and aromatics have also been reformed at relatively low temperatures, however, a different mechanism appears to be responsible for their reforming. Complex fuels like gasoline and diesel, which are
mixtures of a broad range of hydrocarbons, require temperatures of > 700°C for maximum hydrogen production.

ACKNOWLEDGMENTS
This work was supported by the U.S. Department of Energy, Office of Advanced Automotive Technologies, in the Office of Automotive Technologies, under contract No. W-31-109-ENG-38.

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