Hydrogen Recovery by Methane Pyrolysis to Elemental Carbon

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Increased O₂ recovery via H₂ recovery

Sabatier: \[ CO_2 + 4 H_2 \rightarrow CH_4 + 2 H_2O \]
Electrolysis: \[ 2 H_2O \rightarrow 2 H_2 + O_2 \]
Pyrolysis: \[ CH_4 \rightarrow 2 H_2 + C \]
Net reaction: \[ CO_2 \rightarrow O_2 + C \]

- Sabatier reaction is limited to 50% recovery of oxygen from CO₂ because hydrogen is lost in the form of methane.
- Converting methane to carbon and hydrogen restores the stoichiometric balance.
- No separation steps needed to purify hydrogen.
- Carbon in the form of non-sooty durable dense solid.
Methane pyrolysis

- Chemical vapor deposition of carbon is used routinely to make carbon composites.
- Generally run at low conversion to adjust properties of the product.
- Ideally suited for hydrogen recovery since gas phase byproduct concentrations can be low.
- Hard durable non-sooty carbon product.

Honeywell’s experience with industrial scale CVD enabled rapid development of the pyrolysis process.
Methane pyrolysis rxn conditions

- Pyrolysis has a long series of intermediates between methane and carbon.
- Reaction is endothermic and occurs only at >1000°C and low pressures.
- Product distribution is strongly dependent on substrate surface area.

- Selectivity to CVD carbon increases as number of substrates increases.
- Non-methane hydrocarbon byproducts decrease.
Methane pyrolysis kinetics

- Detailed knowledge of pyrolysis kinetics were required for design.
  - Effects of temperature, pressure, substrate surface area.
  - Conversion increases with residence time, but reaction order is complex.
- Kinetics also determines the distribution of carbon vs. distance from inlet.
- Adjust parameters like temperature distribution, substrate design to prevent reactor from “front-loading”, increasing the overall loading the reactor.
Reactor model

- Differential model used to use reaction kinetics for reactor design.
  - Model predicts conversion and cumulative carbon deposition vs. temperature, pressure, residence time, hours on stream.
- As reaction proceeds, conversion decreases and part density increases.
- Objective is to maximize average density before conversion <50% or maximum density >1.8 g/cc.


Closing the loop

- Closing the ECLSS loop is required to get 100% recovery of oxygen from carbon dioxide.
- Mass balance model assumes all units are “on” all the time, and conversion for Sabatier & electrolysis reactions is 100%.
- Incomplete pyrolysis conversion increases the volumetric flow around the loop and the CH4 concentration at the Sabatier inlet.
- Since flow rate is determined by conversion, residence time in the reactor depends on reactor volume.
- Optimum conversion is 50-80%. 

\[
\text{Methane Pyrolysis: } \text{CH}_4 \rightarrow \text{C} + 2 \text{H}_2
\]

\[
\text{Sabatier: } \text{CO}_2 + 4 \text{H}_2 \rightarrow \text{CH}_4 + 2 \text{H}_2\text{O}
\]

\[
\text{Electrolysis: } 2 \text{H}_2\text{O} \rightarrow 2 \text{H}_2 + \text{O}_2
\]
Reactor size

- Reactor internal volume must meet two criteria:
  - Adequate residence time, since flow rate is fixed by mass balance.
  - Adequate capacity for reasonable maintenance interval.
- Reactor sized for 4 crew must accumulate 1 kg/day of carbon.
- Maintenance interval: How frequently must operator cool reactor down and change out the substrates.

Solution: Stack of fibrous substrates large enough to hold >7 days of carbon in cylindrical shell.

\[
\text{Capacity} = \frac{\rho_f - \rho_i}{\rho_i}
\]

Lower initial density increases capacity & decreases number of substrates needed.
Substrate requirements

- Supply of substrates required depends on mission length and substrate design.
- Methane pyrolysis is best suited for longer missions when higher recovery of oxygen trades well against substrate requirements.
- Can substrates be woven or made in space?
- Filled substrates are hard durable soot-free solids with re-use potential.
  - Construction material
  - Radiation shielding

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Baseline Substrate</th>
<th>Developmental Substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity (g Carbon/g substrate)</td>
<td>0.8</td>
<td>1.3</td>
</tr>
<tr>
<td>Maintenance interval (days)</td>
<td>6.5</td>
<td>10.9</td>
</tr>
<tr>
<td>Cartridges (1000 day mission)</td>
<td>155</td>
<td>92</td>
</tr>
<tr>
<td>1000 day Storage Volume (m³)</td>
<td>1.8</td>
<td>1.1</td>
</tr>
<tr>
<td>1000 day Storage Weight (kg)</td>
<td>787</td>
<td>280</td>
</tr>
</tbody>
</table>

ISS Express Rack
0.57 m³
Proposed brassboard design

- Brassboard reactor will be delivered to NASA for testing and demonstration.
  - Stand-alone
  - Integrated with existing Sabatier reactor
- Sized for 4-crew load (1.5 kg/day methane)
- High temperature alloy shell is heated by light weight annular heater.
- Insulation (not shown) surrounds reactor limiting power requirement.
- Cartridge of substrate media in the form of a stack of disks collected the CVD carbon.

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Internal volume</td>
<td>10.9 L</td>
</tr>
<tr>
<td>Weight</td>
<td>27 kg</td>
</tr>
<tr>
<td>Maintenance interval</td>
<td>7-11 days</td>
</tr>
<tr>
<td>Average temperature</td>
<td>1120°C</td>
</tr>
<tr>
<td>Pressure</td>
<td>100 torr</td>
</tr>
<tr>
<td>Power requirement</td>
<td>730 W</td>
</tr>
</tbody>
</table>
Proposed brassboard design

• Proposed skid holds two reactors in parallel, configured for one to operate while the second is cooling for substrate replacement and heating back up.
• Vacuum pump modulated with throttle valve.
• Inlet and outlet flowmeters used to measure conversion
• System controlled and monitored via cDAQ controller.
Integration with Sabatier

- Integration of pyrolysis reactor with Sabatier requires understanding the concentrations of all constituents in the output stream.
- System model, coupled with lab results, used to predict concentrations, after dilution with hydrogen, at inlet to Sabatier.
- Low concentrations of acetylene, benzene etc. expected.
- Water content assumes 95% removal by condensation between the Sabatier and pyrolysis units.

### Inlet of Sabatier Reactor (assuming molar H2/CO2 of 4.4)

<table>
<thead>
<tr>
<th>Compound</th>
<th>CH4 conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>65%</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>73.95%</td>
</tr>
<tr>
<td>Methane</td>
<td>5.59%</td>
</tr>
<tr>
<td>Water</td>
<td>3.10%</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.17%</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>0.34%</td>
</tr>
<tr>
<td>Acetylene</td>
<td>0.01%</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.03%</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>16.81%</td>
</tr>
<tr>
<td>Flow rate (sccm)</td>
<td>8915</td>
</tr>
</tbody>
</table>

\[ CH_4 + H_2O \rightarrow CO + 3H_2 \]

Methane steam reforming conversion 10% in absence of catalyst

**What is effect of this stream composition on Sabatier performance and catalyst material?**
Catalyst Challenge Testing: Short Duration

• Goals:
  1. To determine fate of non-CH4 hydrocarbons in Sabatier reactor
  2. To determine effect of exposure to challenge mixtures on catalyst performance
  3. To determine if carbon deposited on catalyst

• Materials & Methods
  • Collins Aerospace Sabatier catalyst
  • Evaluation conducted on Carbon Dioxide Reduction Catalyst Test Stand at NASA MSFC
  • Four simulant mixtures prepared based on predicted outlet composition from methane pyrolysis (0% humidity)
  • H2:CO2 ratios of 4.5:1 or 4.9:1 H2 – CO2 at 2-crew and 4-crew rates
  • Baseline tests conducted between each challenge test to evaluate catalyst performance

<table>
<thead>
<tr>
<th>Component</th>
<th>Challenge Gas (mol %)</th>
<th>Mix A</th>
<th>Mix B</th>
<th>Mix C</th>
<th>Mix D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td></td>
<td>0.20</td>
<td>0.01</td>
<td>0.02</td>
<td>0.02</td>
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<tr>
<td>Methane</td>
<td></td>
<td>9.98</td>
<td>25.10</td>
<td>5.68</td>
<td>17.90</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td></td>
<td>0.00</td>
<td>0.00</td>
<td>3.82</td>
<td>3.29</td>
</tr>
<tr>
<td>Acetylene</td>
<td></td>
<td>0.10</td>
<td>0.50</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>Hydrogen</td>
<td></td>
<td>89.72</td>
<td>74.39</td>
<td>90.44</td>
<td>78.75</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run</th>
<th>Rate</th>
<th>Feed</th>
<th>Exposure Time (hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,3,5,7,9</td>
<td>2-CM</td>
<td>BT</td>
<td>22.8</td>
</tr>
<tr>
<td>2</td>
<td>2-CM</td>
<td>Mix A</td>
<td>2.9</td>
</tr>
<tr>
<td>4</td>
<td>2-CM</td>
<td>Mix B</td>
<td>4.5</td>
</tr>
<tr>
<td>6</td>
<td>2-CM</td>
<td>Mix C</td>
<td>3.2</td>
</tr>
<tr>
<td>8</td>
<td>2-CM</td>
<td>Mix D</td>
<td>2.4</td>
</tr>
<tr>
<td>10,12,14,16,18</td>
<td>4-CM</td>
<td>BT</td>
<td>4.7</td>
</tr>
<tr>
<td>11</td>
<td>4-CM</td>
<td>Mix A</td>
<td>0.0</td>
</tr>
<tr>
<td>13</td>
<td>4-CM</td>
<td>Mix B</td>
<td>1.3</td>
</tr>
<tr>
<td>15</td>
<td>4-CM</td>
<td>Mix C</td>
<td>0.9</td>
</tr>
<tr>
<td>17</td>
<td>4-CM</td>
<td>Mix D</td>
<td>1.1</td>
</tr>
</tbody>
</table>
Catalyst Challenge Testing: Goal 1
Fate of Hydrocarbons

**Expectation:**
- If no reaction of hydrocarbons, byproduct concentrations would have increased due to reduction in number of moles of product vs. reactant and water removal

**Observations:**
- Acetylene entirely consumed in Sabatier reactor in all but one run. No hydrogenation products (ethylene, ethane) detected
- Benzene partially removed under same conditions
Catalyst Challenge Testing: Goals 2 & 3

- **Goal 2: Effect on Catalyst Performance**
  - Baseline testing shows no significant change in performance over duration of the test after repeated exposure to challenge mixtures

- **Goal 3: Carbon Deposition**
  - SEM-EDX shows higher concentration of surface carbon on catalyst
  - Source of observed carbon might be deposited solid carbon, adsorbed CO$_2$, adsorbed CO or adsorbed hydrocarbons
  - Carbon deposition may be suppressed by higher hydrogen ratio or presence of water

Continued evaluation using more realistic water-containing feed recommended.
Summary and next steps

- Almost quantitative recovery of oxygen from carbon dioxide is enabled by pyrolysis of methane to carbon and hydrogen.
- Pyrolysis kinetics have been measured, and models used to specify the temperature, pressure, substrate characteristics and reactor volume for a compact reactor.
- Opportunities to reduce the number of substrates required per mission interval are being explored.
- Possibility that trace byproducts from pyrolysis may cause carbon deposition on the Sabatier catalyst is being investigated.
- Brassboard pyrolysis system to be delivered to NASA in June 2020.
Acknowledgements

Game Changing Development Program Spacecraft Oxygen Recovery Project

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