Hydrogen Purification and Recycling for an Integrated Oxygen Recovery System Architecture

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Overview

• Background
• Hardware
• Test Setup
• Results
• System Architectural Options
• Conclusion
• Acknowledgements
State-of-the-Art

• Sabatier Reactor
  – $\text{CO}_2 + 4\text{H}_2 \rightarrow 2\text{H}_2\text{O} + \text{CH}_4$
  – Water product electrolyzed for oxygen
  – Methane product vented resulting in loss of hydrogen reactant
  – Theoretical recovery of $\sim 54\%$ of $\text{O}_2$ recovered from metabolic $\text{CO}_2$
Sabatier Plus Post-Processing

• ~91% O₂ recovery from CO₂ possible
PPA Technology Description

- Developed by UMPQUA Research Co.
- Methane converted to hydrogen and acetylene by partial pyrolysis in microwave generated plasma
- Targeted PPA Reaction:
  \[2\text{CH}_4 \leftrightarrow 3\text{H}_2 + \text{C}_2\text{H}_2\]
- Other reactions:
  - CH\(_4\) Conversion to Ethane
    \[2\text{CH}_4 \leftrightarrow \text{H}_2 + \text{C}_2\text{H}_6\]
  - CH\(_4\) Conversion to Ethylene
    \[2\text{CH}_4 \leftrightarrow 2\text{H}_2 + \text{C}_2\text{H}_4\]
  - CH\(_4\) Conversion to Solid C
    \[\text{CH}_4 \leftrightarrow 2\text{H}_2 + \text{C}(s)\]
  - CO Production
    \[\text{C}(s) + \text{H}_2\text{O} \leftrightarrow \text{CO} + \text{H}_2\]
  - CO Production
    \[\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2\]
Metal Hydride Hardware

- Hydrogen Components, Inc. Metal Hydride Canister
- LaNi$_{4.6}$Sn$_{0.4}$ metal hydride
- Designed for hydrogen storage
Electrochemical Hardware

• Electrochemical hydrogen separation
  – $H_2$ electro-oxidized to protons and electrons
  – Protons are electro-reduced, recombined with electrons, in another chamber producing purified $H_2$

• Basic technology was well developed but not compatible with CO
  – CO would preferentially adsorb on catalytic electrodes and interfere with $H_2$ oxidation

• Sustainable Innovations developed electrolyte materials capable of operating above 150°C CO thermal desorption temperature
  – “Basic” and “Advanced” cell stacks delivered to MSFC
Test Configurations

• Stand alone
  – Metal hydride to verify safety
    • Literature indicated other metal hydrides had potential to cause violent acetylene decomposition or metal-carbide formation
  – Tested with gas mixture containing 7% C₂H₂, 1% CH₄, and 92% H₂
  – Tested in Marshall Space Flight Center’s Component Development Area, usually used for rocket engine component testing
Test Configurations

- **PPA + H$_2$ Purification**
  - Cell stacks integrated with 2$^{nd}$ Gen. PPA
  - PPA operated with ultra-high purity H$_2$ and CH$_4$ bottles
  - 1 Crew Member processing rate
  - 4:1 ratio of H$_2$:CH$_4$
  - 52 torr
  - 550 W microwave power

- PPA products contained H$_2$, C$_2$H$_2$, unreacted CH$_4$, C$_2$H$_4$, and C$_2$H$_6$
- No CO
- 100 standard milliliters per minute (SmLPM) to cell stack
- Evaluated H$_2$ product and process effluent
Test Configurations

- **Sabatier Development Unit (SDU) + PPA + H₂ Purification**
  - Precision Combustion, Inc. SDU integrated upstream of PPA
  - SDU operated to produce 350 SmLPM CH₄ with no unreacted CO₂
  - Methane product containing 80 mol% hydrogen
  - Water vapor content dew point of 31°C
- PPA operated identically to PPA + H₂ testing
- PPA products contained all previously indicated components and CO and H₂O

![Diagram showing the flow of gases through SDU and PPA](image)

- **Electrochemical Cell Stack**
  - Inputs: H₂, C₂H₂, CH₄, C₂H₄, C₂H₆, CO, H₂O
  - Outputs: Anode Out, H₂
Metal Hydride Performance

• No measurable pressure or temperature difference between pure H₂ runs and acetylene mixed gas runs
• No safety risk under expected operating conditions
PPA effluent composition as a function of configuration
H₂ separation performance comparison between Basic and Advanced cell stacks

- Varied gas feed from PPA, stack temperature, inlet composition, and applied voltage
  - Conditions for each data point were identical
- All recovered H₂ pure within measurable limits of μGC
Hydrogenation

- Expected similar gas mix (minus $H_2$) leaving anode as entering
- High levels of $C_2H_4$ and $C_2H_6$ were observed with minimal or no $C_2H_2$
- Overall chemical equations:
  - $CH_4$ Conversion to Ethane: $2CH_4 \leftrightarrow H_2 + C_2H_6$
  - $CH_4$ Conversion to Ethylene: $2CH_4 \leftrightarrow 2H_2 + C_2H_4$
- Ethane Formation from $CH_4$ with free radical intermediates:
  - $CH_4 + CH_4 \leftrightarrow CH_3^* + CH_3^* + H^* + H^* \leftrightarrow C_2H_6 + H_2$
  - $CH_4$ forms $CH_3^*$ free radicals which then recombine to form $C_2H_6$
  - $C_2H_6$ is converted to $C_2H_4$ and $C_2H_4$ is converted to $C_2H_2$
  - Reverse reactions also occur providing a mechanism for $C_2H_2$ hydrogenation to the other hydrocarbons
Effect of temperature on $\text{C}_2\text{H}_2$ hydrogenation, Advanced Cell Stack
Acetylene conversion to methane in Advanced cell stack as a function of voltage and anode feed rate.
Acetylene conversion to ethylene in Advanced cell stack as a function of voltage and anode feed rate.
Acetylene conversion to ethane in Advanced cell stack as a function of voltage and anode feed rate.
Effect of water vapor and CO on hydrogenation of C₂H₂.
SI Cell Stack Architecture

- CO₂ from crew
- H₂O
- O₂ to crew

CRA

CH₄ + H₂

Flow Meter

PPA

Flow Controller

Accumulator Tank

Flow Controller

H₂

C₂H₂ + CH₄ + H₂O

to space

H₂ + C₂H₂ + H₂O + CH₄...

H₂

Electrochemical Cell Stack

CRA PPA

OGA

Carbon Capture
Sorbent Architecture

CO₂ from crew → CRA → CH₄+H₂ → Flow Meter → PPA → Flow Controller → Accumulator Tank → Carbon Capture → Compressor → Sorbent to space

H₂O → Flow Meter → OGA → O₂ to crew

H₂+ residual CH₄ → Flow Meter → PPA
Metal Hydride Architecture

CRA

CO₂ from crew

CH₄ + H₂

Flow Meter

PPA

Flow Controller

Accumulator Tank

Carbon Capture

H₂ + C₂H₂ + H₂O + CH₄...

Flow Meter

H₂

OGA

H₂O

O₂ to crew

C₂H₂ + CH₄ to space

Metal Hydride

Space Vacuum
Conclusion

• Effective acetylene separation technology is essential for Sabatier + PPA architecture

• Future work:
  – Reduce acetylene hydrogenation in cell stacks
  – Test UMPQUA sorbent based hydrogen separation system
  – Test metal hydride
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