



Mars Atmospheric In Situ Resource Utilization Projects at the Kennedy Space Center

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Outline

- **Projects and Team Members**
- **Martian Resources**
- **Mars Atmospheric Processing Module**
- **Mars Propellant Production with Ionic Liquids**
- **Self-Cleaning Boudouard Reactor for Full Oxygen Recovery**
- **Conclusions**



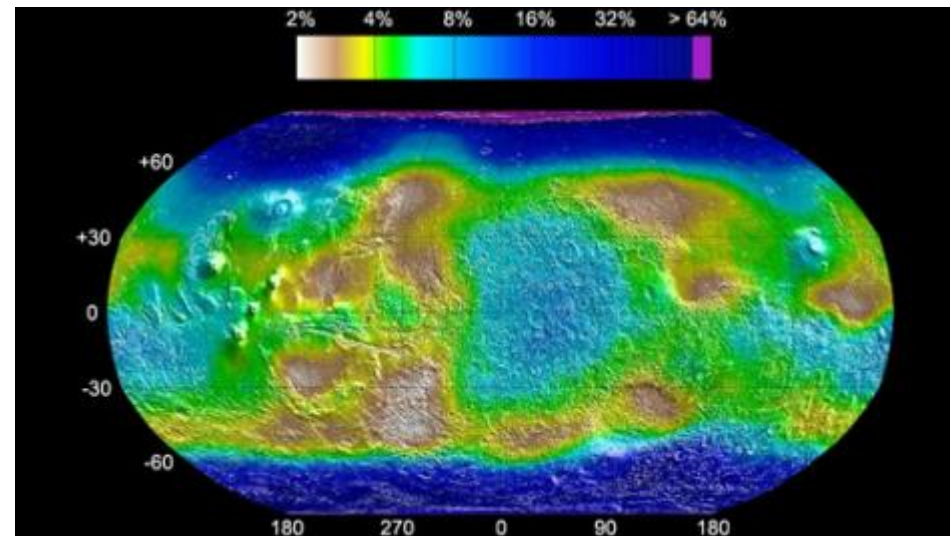
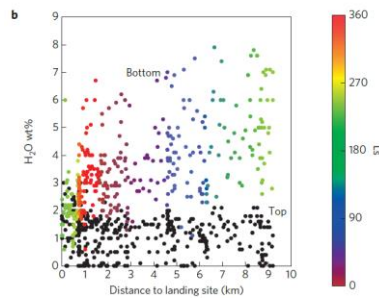
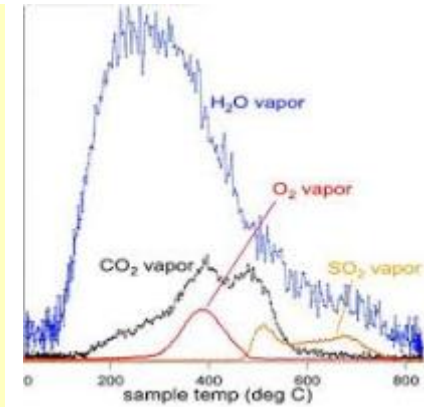
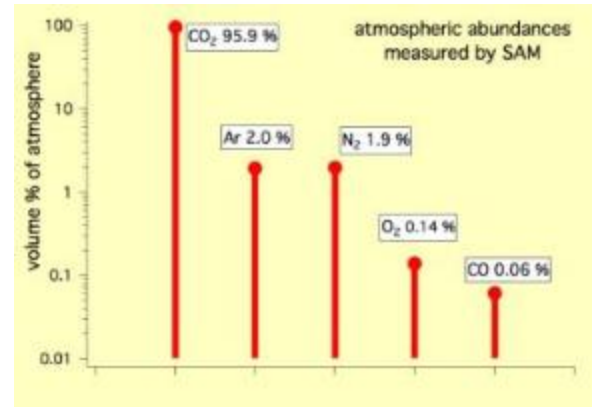
Projects and Team Members

- **Mars Atmospheric Processing Module:** Paul Hintze, Anne Meier, and Jon Bayliss (KSC)
- **Ionic Liquids:** Paul Hintze, Tracy Gibson, Jan Surma (KSC), Laurel Karr, Steve Paley (MSFC), and Matt Marone (Mercer University, GA)
- **Self-Cleaning Boudouard Reactor for Full O₂ Recovery:** Paul Hintze, Anne Meier, Jon Bayliss, Tracy Gibson, James Captain, Griffin Lunn, Robert Devor, (KSC), Matt Mansell (MSFC), and Mark Berggren (Pioneer Astronautics)



Martian Resources

- **Atmosphere of Mars**
 - 95.9% CO₂
 - 2% Ar, 1.9% N₂
 - <1% pressure of Earth's atmosphere (~7 mbar)
- **Significant Amounts of Water in the Top 1-Meter of Regolith**
 - Water ice caps at the poles
 - ~2% at least everywhere else
 - ~10% even at equatorial regions
 - Curiosity rover ground truth:
 - 1.5-3% water in surface regolith (SAM)
 - Average 2.9% water (DAN), up to 7% in top 60 cm of regolith in some locations-seasonal variation
 - Transient liquid water at night in the top 5 cm of regolith





MARCO POLO Project

- **ISPP: In Situ Propellant Production**
 - Demonstrate production of Mars Sample Return propellant
 - Reduce risk for human Mars missions
- **MARCO POLO - Mars Atmosphere and Regolith Collector/Processor for Lander Operations**
 - Started in 2011
- The Atmospheric Processing Module (APM)
 - Mars CO₂ Freezer Subsystem
 - Sabatier (Methanation) Subsystem
- Collect, purify, and pressurize CO₂
- Convert CO₂ into methane (CH₄) and water with H₂
- Other modules mine regolith, extract water from regolith, purify the water, electrolyze it to H₂ and O₂, send the H₂ to the Sabatier Subsystem, and liquefy/store the CH₄ and O₂



Lander Design Concept

Atmo Processing Module:

- CO2 capture from simulated Mars atmosphere (KSC)
- Sabatier converts H2 and CO2 into Methane and water (KSC)

C&DH/PDU Module: (JSC)

- Central executive S/W
- Power distribution

Soil Processing Module:

- Soil Hopper handles 30 kg (KSC)
- Soil dryer uses CO2 sweep gas and 500 deg C to extract water (JSC)

Liquefaction Module: (TBD)

- Common bulkhead tank for Methane and Oxygen liquid storage

Water Cleanup Module: (KSC)

- Cleans water prior to electrolysis
- Provides clean water storage

RASSOR 2.0: (KSC)

- Excavator
- Provides feed to Soil Dryer

Water Processing Module: (JSC)

- Currently can process 520g/hr of water (max 694 g/hr)

1 KW Fuel Cell and consumable storage (JSC & GRC)

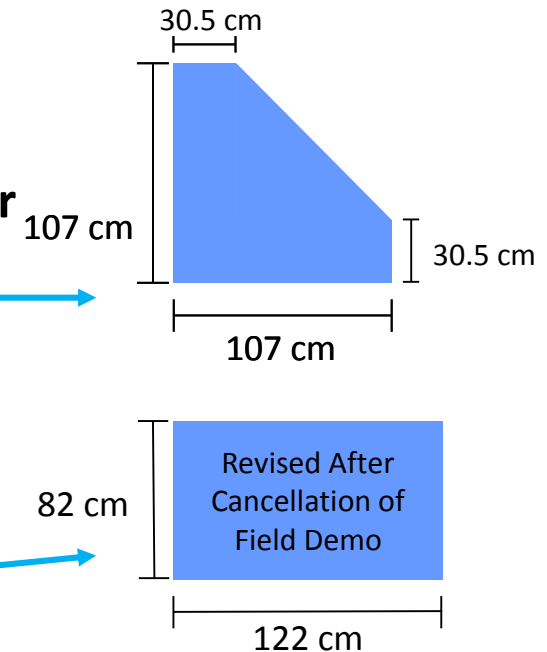
- Using metal hydride for H2 storage due to available
- 1 KW No Flow Through FC (GRC)
- 10 KW main power FC not shown (JSC)

3m x 3m octagon lander deck

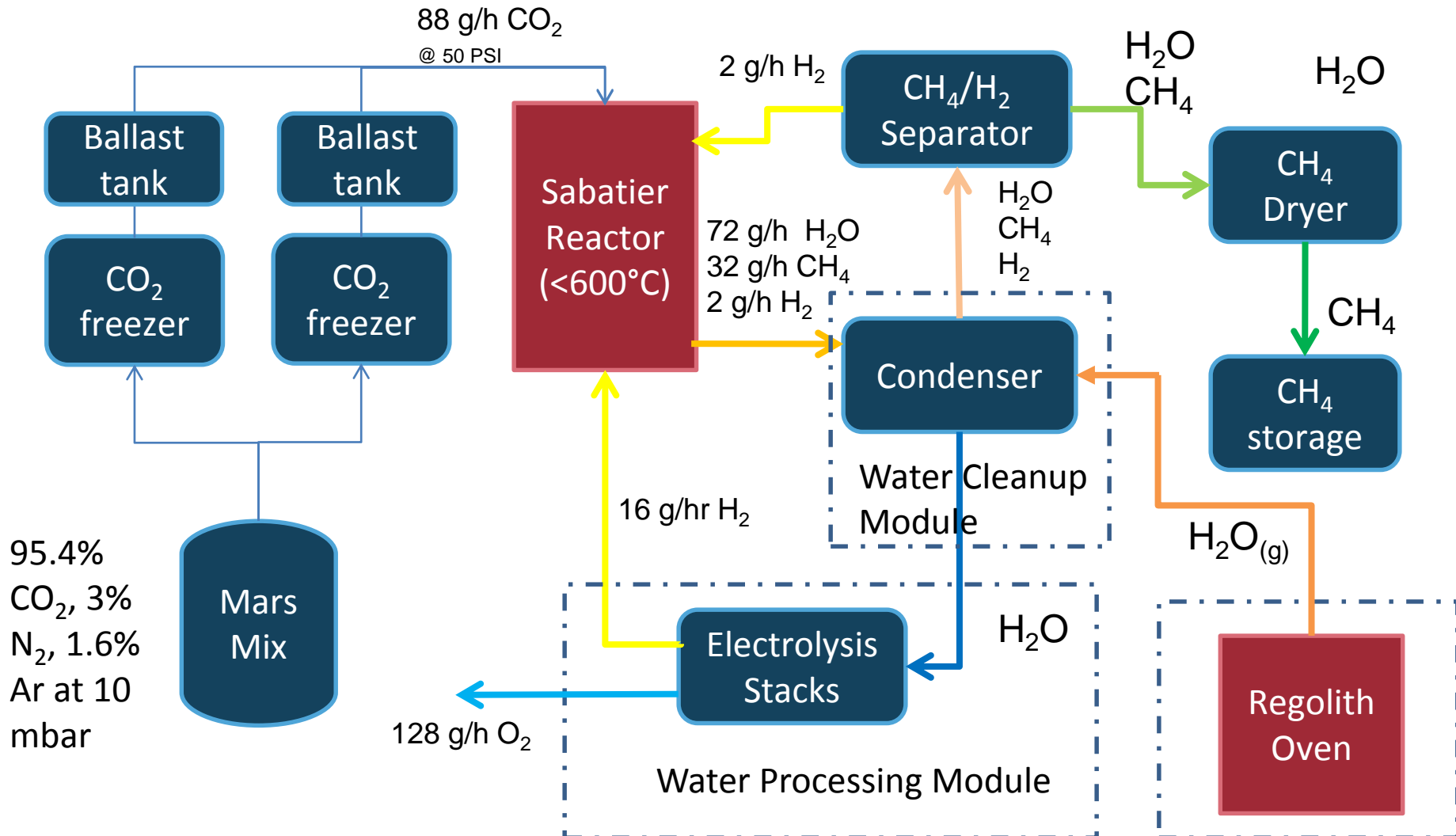
APM Goals/Requirements



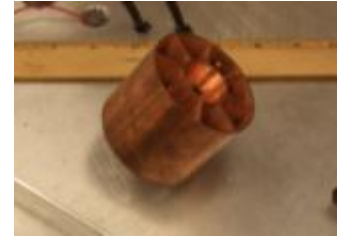
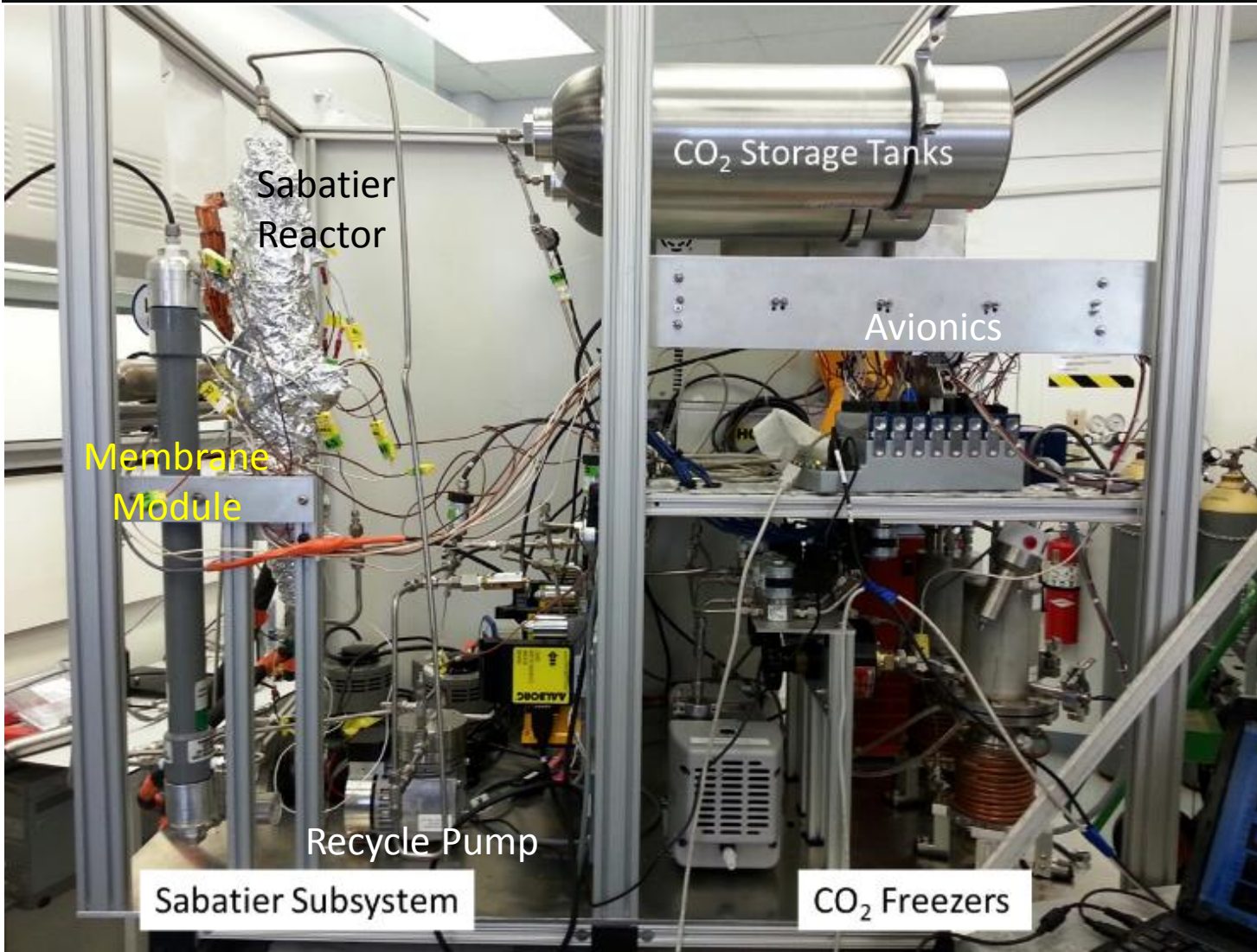
- **Collect and purify 88 g CO₂/h (>99%)**
 - From simulated Martian atmosphere
 - 10 mbar; 95.4% CO₂, 3% N₂, 1.6% Ar
- **Supply 88 g CO₂/h at 50 psia to the Sabatier reactor**
- **Convert CO₂ to 32 g CH₄/h and 72 g H₂O/h**
- **Operate autonomously for up to 14 h/day**
- **Minimize mass and power**
- **Fit within specified area and volume**
 - 9,000 cm² pentagon
 - 10,000 cm² rectangle for easier lab operations
 - 44 inches tall (112 cm, same as Water Processing Module)
- **Support MARCO POLO production goals of 0.032 kg CH₄/h and 0.128 kg O₂/day (50% of O₂) for a total of 2.22 kg propellant/14 h day**
- **Sufficient for a Mars Sample Return Mission**
- **~17% of full-scale O₂ production goal for human Mars Missions (0.75 kg O₂/h/module x 3 modules = 2.2 kg O₂/h), i.e. 1/6th scale**



Atmospheric Processing Operations



Atmospheric Processing Module

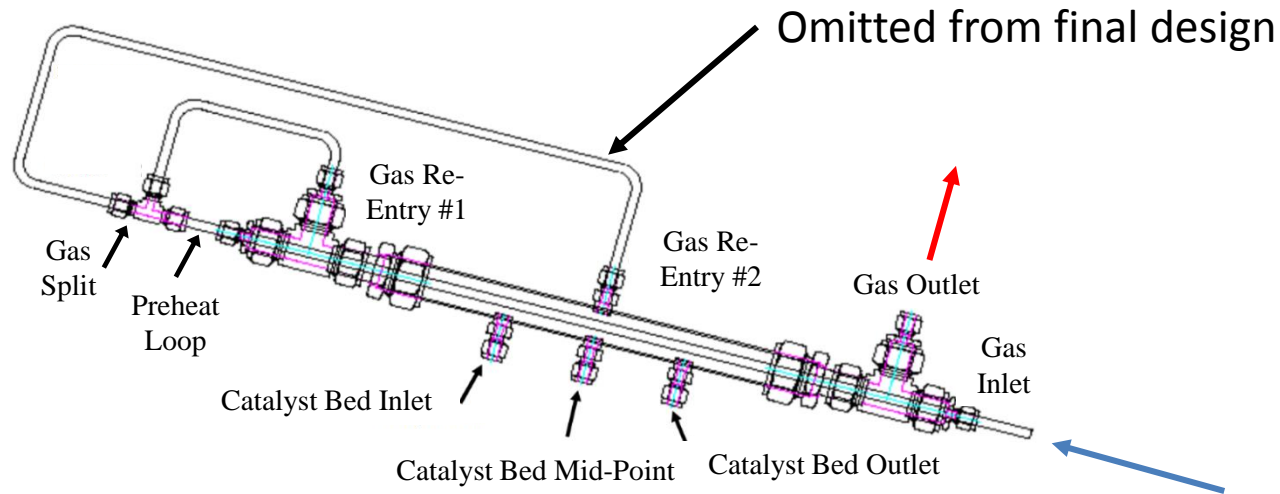


Copper Heat Exchanger

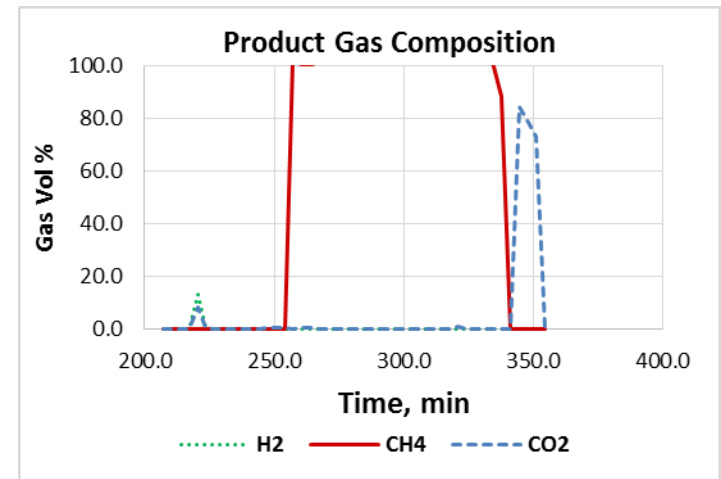


CO₂ Freezers and Chiller

Design of KSC Sabatier Reactor



- 30 cm long stainless steel tube with an OD of 2.54 cm and a wall thickness of 0.21 cm Twelve tests at various flow rates overheated
- Single-pass conversion = 90% @ 88 g CO₂/h + 3.5:1 H₂/CO₂
- Based on Pioneer Astronautics design for steam oxidation of trash to methane
- 1.5 h integrated test with CO₂ Freezers and recycling system showed 100% conversion to pure CH₄



Long-Duration Tests Were Successful



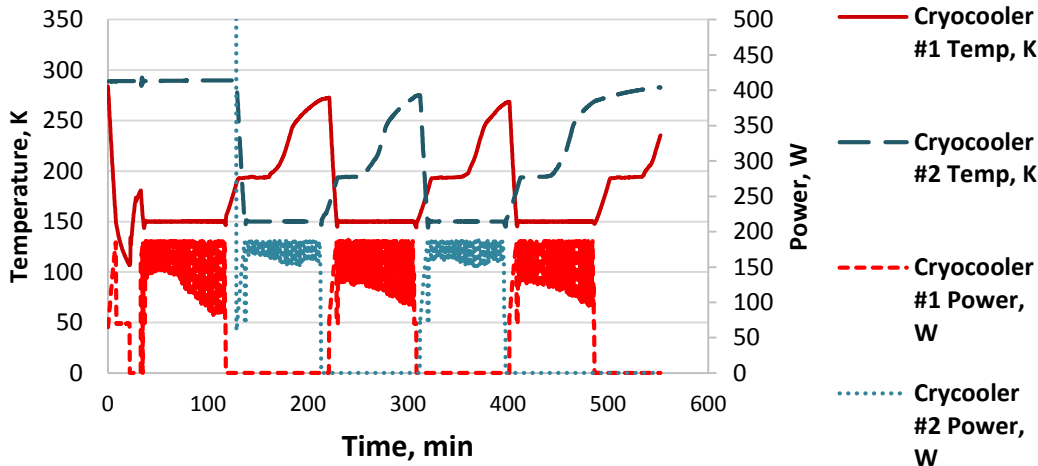
<i>Run No.</i>	<i>1</i>	<i>2</i>	<i>3</i>
Sabatier Run Duration	7.0 h	7.0 h	7.0 h
Gas Composition	CO ₂	CO ₂	Mars Gas
Average CO ₂ Freezing Rate	102 g/h	100 g/h	102 g/h
Average Fraction of CO ₂ Frozen	79%	76%	72%
Average Cryocooler Power	139 W	150 W	158 W
Average energy needed to Freeze CO ₂	4917 J/g	5051 J/g	5655 J/g
Average CO ₂ Supply Rate to Freezers	128 g/h	142 g/h	146 g CO ₂ /h
Average CH ₄ Production Rate	32 g/h	32 g/h	32 g/h
Average CH ₄ Purity	~99.9%	~99.9%	96.0%*
Average H ₂ O Produced	67 g/h	69 g/h	64 g/h

*Due to pressure losses during manual draining of Sabatier water condenser

Selected Results from Long-Duration Tests

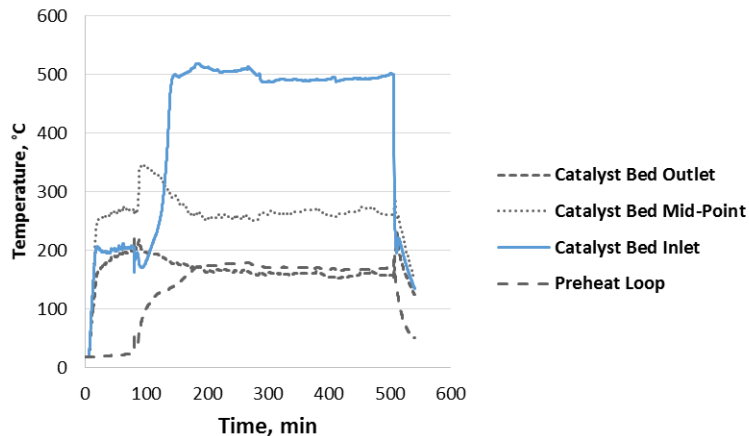


Cryocooler Temperature and Power



CO₂ Freezer Cold Head Temperatures and Cryocooler Power Consumption during the Third Run of the 7-h Integrated Test Series

Sabatier Reactor Temperatures



Sabatier Reactor Temperatures during the Second Run of the 7- Hour Integrated Test Series

Conclusions from the Long-Duration Tests



- **CO₂ Freezer Subsystem operates well**
 - Exceeds 88 g/h freezing and supply rate
 - Freezes ~70% of incoming CO₂
 - Provides valuable data for power to freeze CO₂ at Mars pressure
 - Averages 0.22 W/g CO₂ frozen = only 108% of theoretical
 - Contributes to Human Mars Mission ISRU system designs, e.g. 680 W lift for 3.1 kg CO₂/h
- **Sabatier Subsystem also operates well**
 - New reactor is efficient
 - Recycling system (membrane module + recycle pump) works well
 - Pure CH₄ obtained at expected rate
 - ~7% of water is missing (<1% of loss is in CH₄)

Recent Work and Current Status



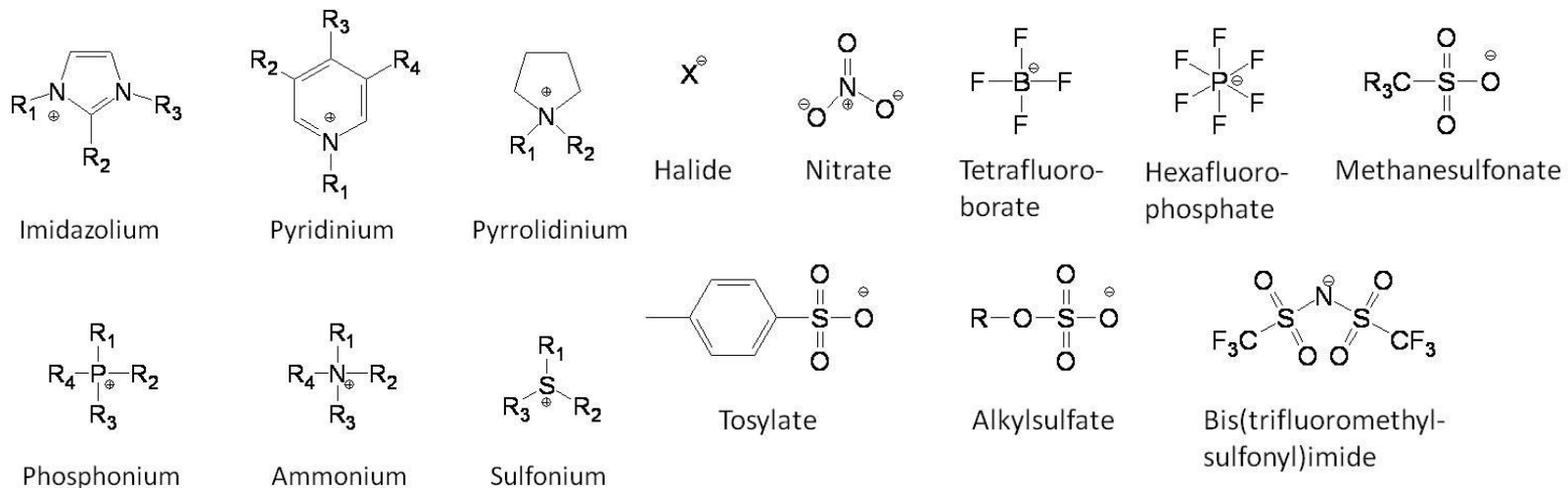
- **Additional integrated tests performed**
- **Faster and slower production rates tested**
 - 1.0-1.6 SLPM feed to CO₂ Freezers (87-71% frozen; 4800-5400 J/g)
 - Sabatier works at 0.3 to 1.2 SLPM CO₂ (0.75 SLPM nominal, 550°C max T)
 - Some CO observed in CH₄ after higher flow rates (now testing catalyst)
- **Better LabVIEW automation implemented (sequences)**
- **Plan “virtual” integrated MARCO POLO tests with other systems at KSC and JSC in May and September – Hardware integration in FY17**
- **Testing is supporting Mars ISRU design studies**
- **Long Term Goal is to continue to refine ISRU technologies for potential robotic Mars missions using SpaceX “Red Dragon” (date TBD) and Mars Pathfinder in 2026/28**





Introduction – Ionic Liquids

- Ionic Liquids (ILs) are organic salts that have melting points near room temperature
- Certain ILs adsorb CO₂ at low partial pressures and provide a medium for electrolysis to useful compounds

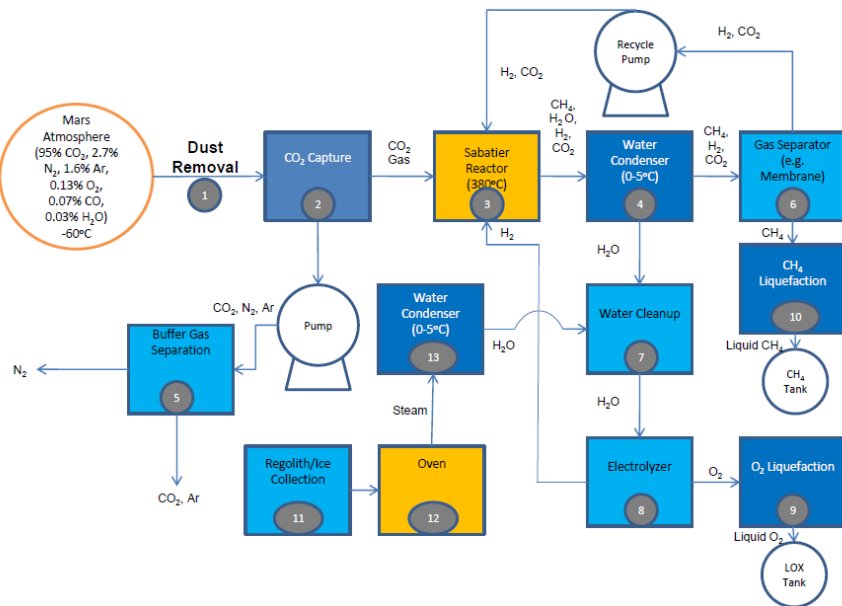


Typical Ionic Liquid Cations and Anions

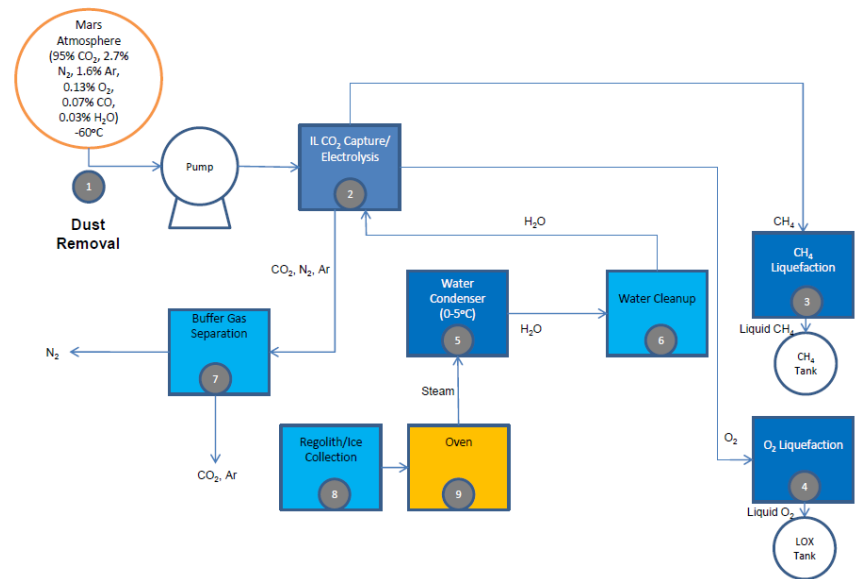


Potential Benefits for ISRU

Current Mars Propellant Production Process Diagram



Mars Propellant Production Process Diagram with IL Electrolysis

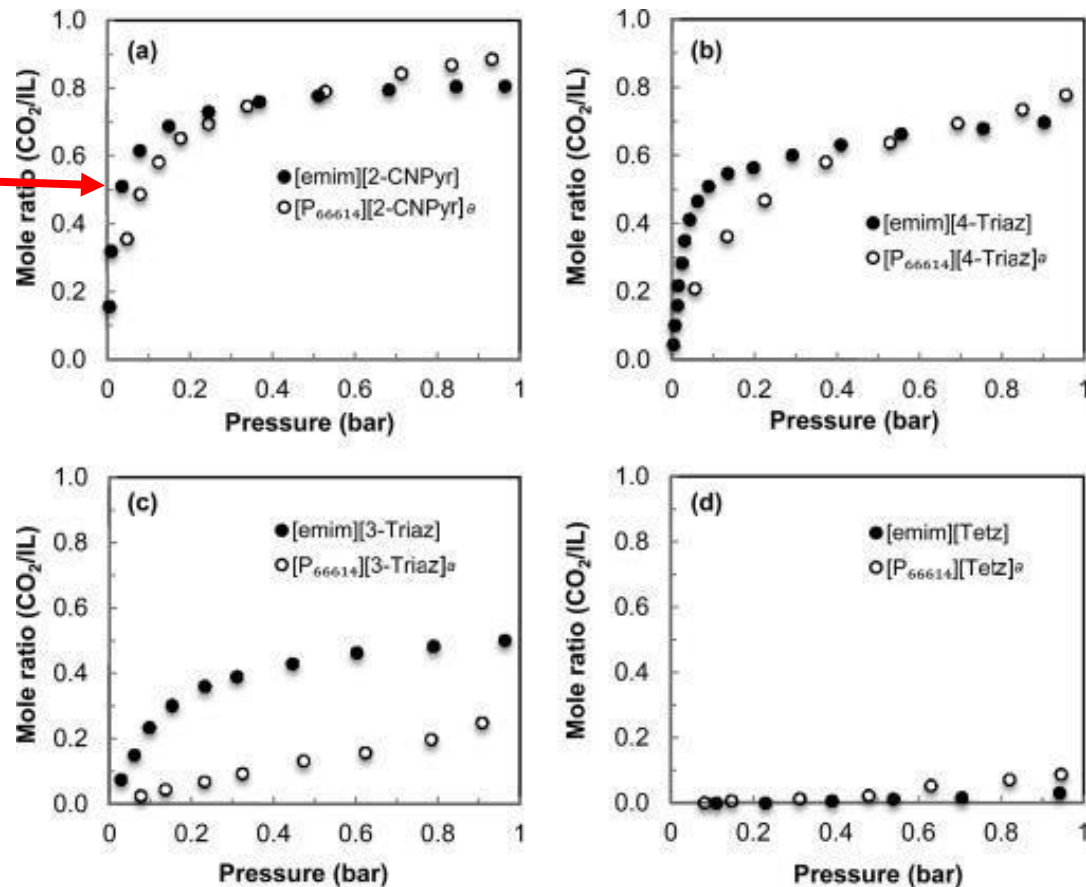


- **Advantages of IL capture/electrolysis:**

- No high temperature processing of CO₂
- One less pump and no cryocoolers
- Four fewer major process steps
- Estimated ~50% less mass and ~25% less power



CO₂ Uptake at Low Partial Vacuum ~50% Mole Fraction at ~10 mbar



“CO₂ absorption capacity in (a) [emim][2-CNPyr], (b) [emim][4-Triaz], (c) [emim][3-Triaz], and (d) [emim][Tetz] at 22 °C. The CO₂ solubility in [P₆₆₆₁₄]+ counterparts from ref 10 are also shown for¹⁷ comparison.” (Brennecke, 2014)

Technical Approach



- Select best available candidate COTS ILs and electrocatalysts (KSC)
 - Based on literature review
- Prepare new task-specific ILs (AZ Technology/MSFC)
- Determine CO₂ capture efficiency and conductivity of ILs (Mercer University and KSC)
- Measure electrochemical windows (KSC)
- Design/build electrochemical cells (KSC)
- Test electrolysis of CO₂ + H₂O to CH₄ + O₂

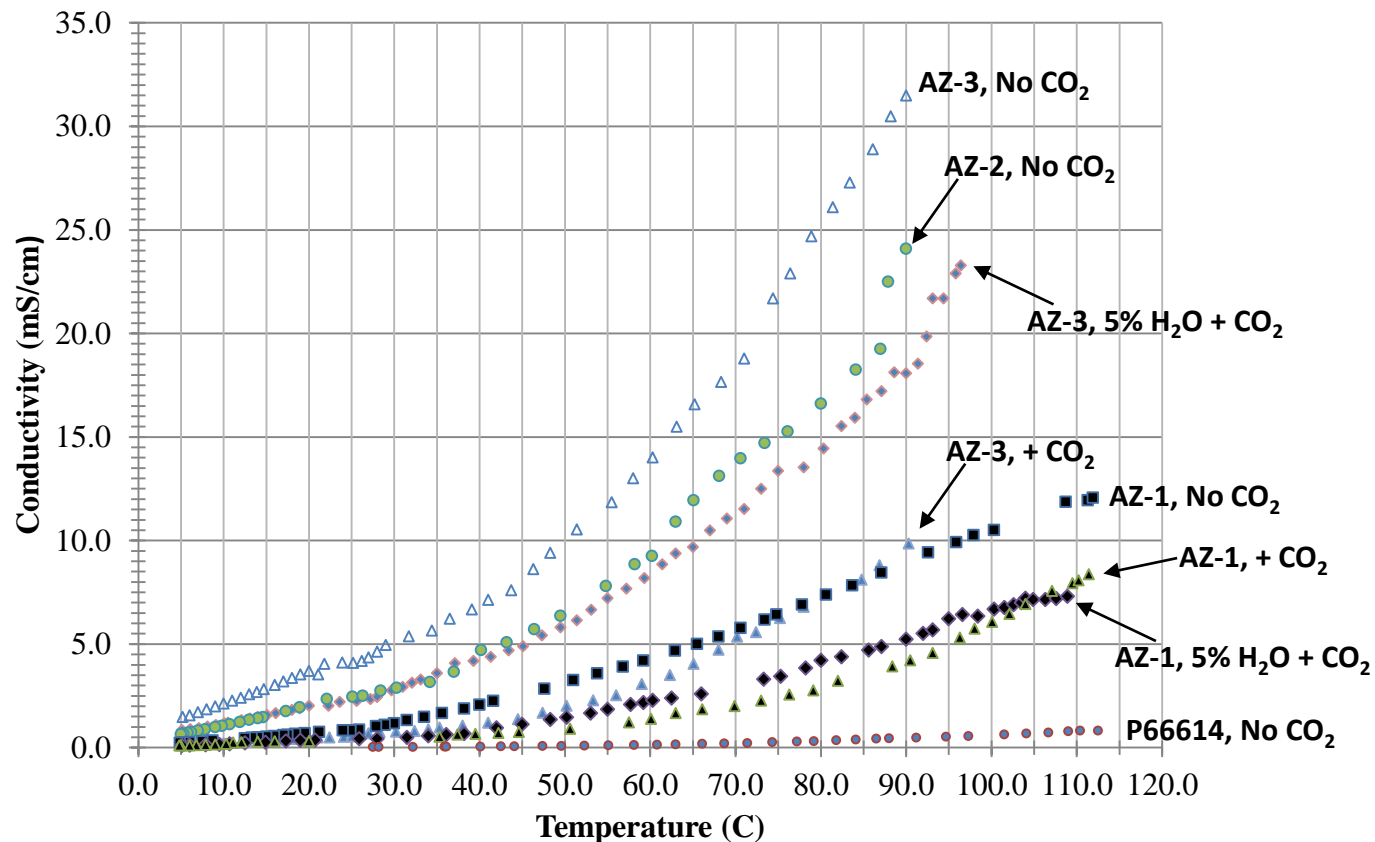


Results

- COTS IL candidates: [EMIM][BF₄], [BMIM][BF₄], [BMIM][TFMSI], [BMIM][PF₆] and [HMIM][B(CN)₄]
- Electrocatalysts: Copper cathode/Pt anode, TiO₂ cathode/Pt anode
- Several ILs have good electrochemical windows and conductivity
- Two-compartment cell w/Nafion membrane
 - Polycarbonate not suitable: CaCO₃ precipitate,
 - Switched to glass cell
- Three TSILs prepared: AZ-1, AZ-2, and AZ-3 (code named to protect IP)
 - High CO₂ sorption and conductivity



AZ-3 Shows High IL Conductivity with CO₂ and CO₂ + H₂O



Conductivity of AZ-1, AZ-2, AZ-3 and [P₆₆₆₁₄] [3-CF₃Pyra] vs. time for CO₂ uptake with and without 5% dissolved water

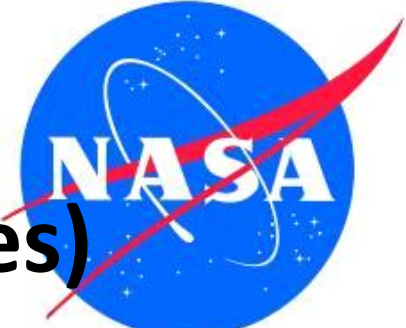
AZ-3 Shows High CO₂ Uptake (No Water Added)



Ionic Liquid	CO ₂ Uptake at ~25°C, wt%	CO ₂ Uptake at 60°C, mol%	Viscosity Increase
AZ-1	9.0	NA	High (m.p. = 18°C)
AZ-2	9.6	9.1	High
AZ-3	15.6	NA	High
[BMIM][PF ₆]	0.50	NA	Low
[HMIM][BF ₄]	0.70	NA	Low
[EMIM][BF ₄]	2.6	NA	Low
[BMIM][BF ₄]	0.6	NA	Low
[BMIM][TFMSI]	0.5	NA	Low

Summary

(Underlined ILs = Candidates)



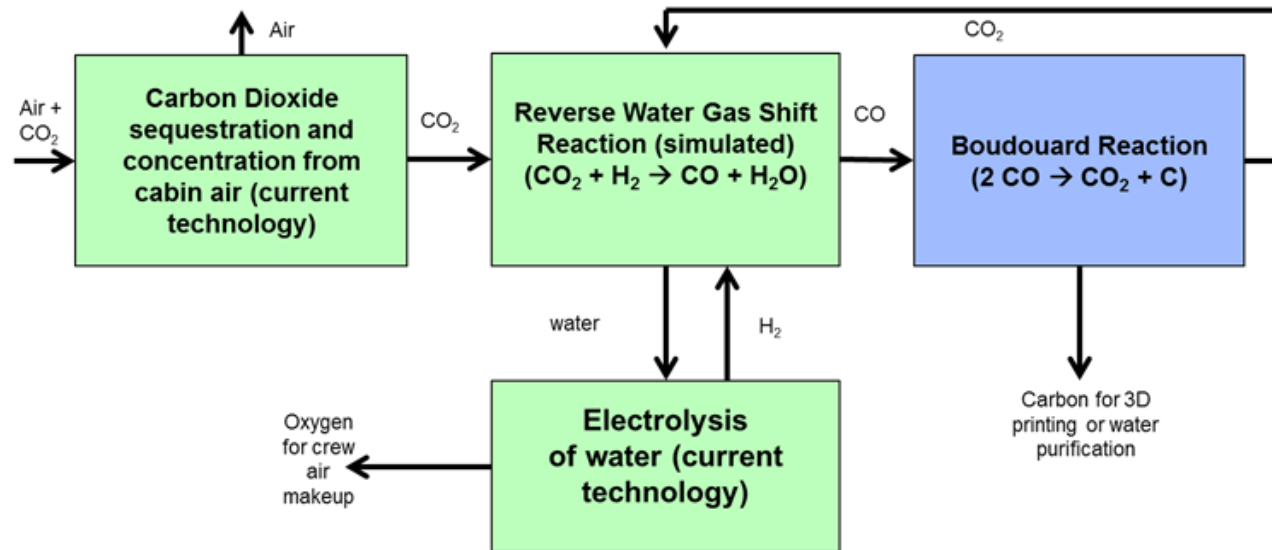
Ionic Liquid	CO ₂ Capacity, wt.% (R.T., 1 atm, dry)	Electro-chemical Window, V	Conduc-tivity with CO ₂ (mS/cm, 40°C)	Compatible with Cu	Other Issues	Tested Solubility of Water, v/v%	Methane Production Rate
[BMIM][TFSI]	0.46	2.1		No			X
<u>[BMIM][PF₆]</u>	0.50	2.4		Yes	Precipitate, Cu darkened		0
<u>[BMIM][BF₄]</u>	0.55	1.8		Yes			Small
[HMIM][B(CN) ₄]	0.70	0.6		No			X
[EMIM][BF ₄]	2.6	1.6		No			X
AZ-1	9.0	4.4	0.67	No		5	X
<u>AZ-2</u>	9.6	2.4		Yes	IL darkened		0
<u>AZ-3</u>	15.6		1.2	Slow color change	Precipitate	5	Possible CH ₄ and CO (TiO ₂ only)

Self-Cleaning Boudouard Reactor for Full O₂ Recovery from CO₂



- Initiated by NASA RFP for “GAME CHANGING DEVELOPMENT PROGRAM, ADVANCED OXYGEN RECOVERY FOR SPACECRAFT LIFE SUPPORT SYSTEMS APPENDIX NH14ZOA001N-14GCD-C2”
- Only 50% of O₂ can recovered from respiratory CO₂ on the ISS
- Sabatier reactor makes CH₄ and H₂O
- CH₄ is vented, losing H₂
- H₂O from cargo limits H₂ availability to 50% recovery
- RFP seeks at least 75% recovery
- Deep space missions (Moon, Mars moons, Mars surface, asteroids, etc.) need closer to 100% recovery
- Joint KSC/FIT/ORBITEC/Pioneer Astronautics proposal was not selected, but received encouragement from STMD GCD
- KSC funded a FY14 CIF project
- Completed in July 2015

Approach - Break Bosch Reaction into Two Parts (Demo'd by MSFC)



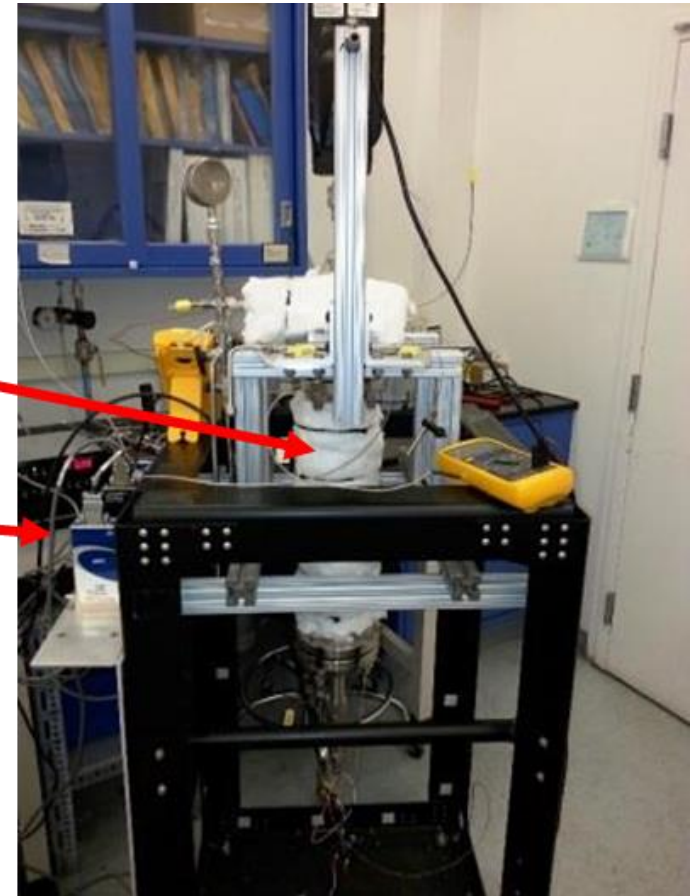
- Bosch Reaction: $\text{CO}_2 + \text{H}_2 \rightarrow \text{C}_{(s)} + 2 \text{H}_2\text{O} (\rightarrow 2 \text{H}_2 + \text{O}_2)$
- RWGS: $\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O} (\rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2)$
- Boudouard: $2 \text{CO} \rightarrow \text{C}_{(s)} + \text{CO}_2$ (Fe catalyst, H₂ enhancer)
- Need a method to remove C from catalyst as it forms
- Several concepts developed and one tested so far with encouraging results

Self-Cleaning Boudouard Reactor



- Used CO/H₂/N₂ feed
- Tested steel wool reactor for comparison
- Tested 1" and 2" ID reactors
- Collected carbon in HEPA filter bag as it was generated

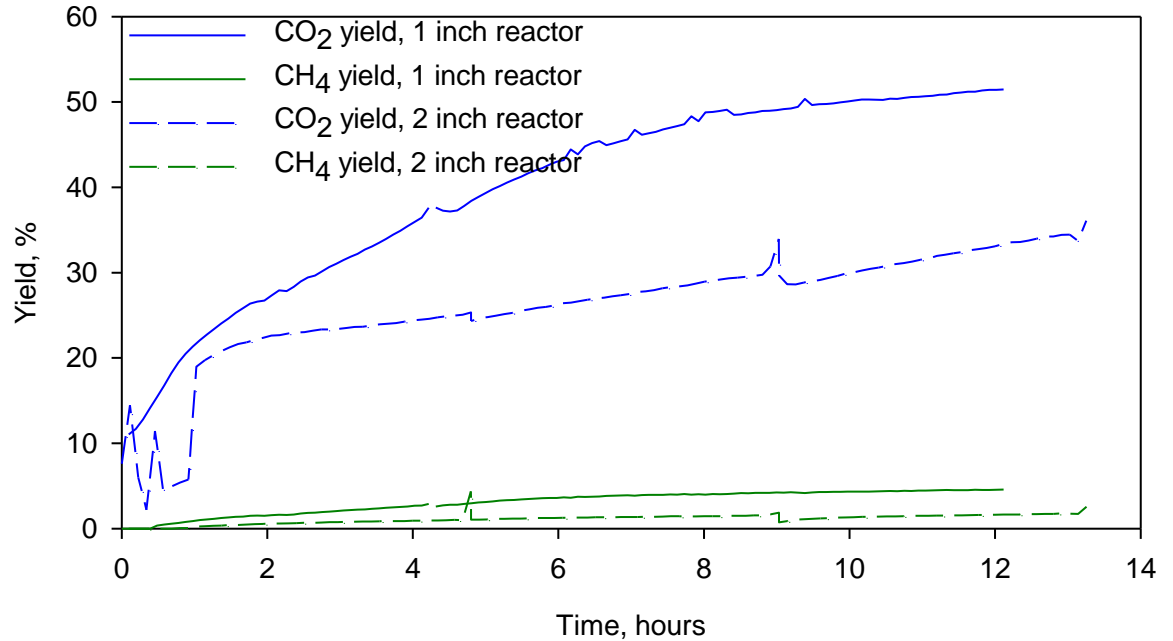
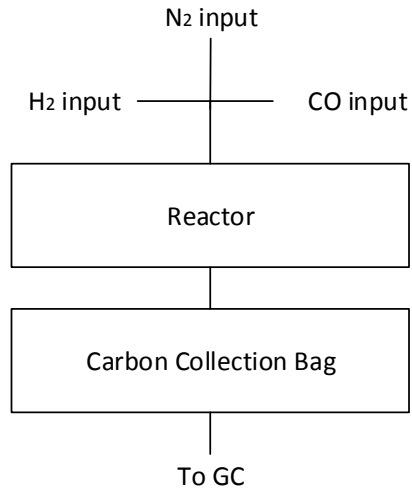
Wrapped
Reactor
Flow
Controller
(1 of 3)



Results Are Encouraging



Reactor Schematic



Parameters for Each Reactor

	1" REACTOR	2" REACTOR
REACTOR VOLUME, ML	76	300
CATALYST MASS, G	1.31	11.82
H ₂ FLOW, SCCM	232	909
CO FLOW, SCCM	232	909
N ₂ FLOW, SCCM	52	202

CO₂ and CH₄ Yields for Both Reactors

Boudouard Summary



- 1" reactor ran for 12 h
 - Reached 47% conversion, collected 27% of C in bag
 - Found to be damaged upon disassembly
- 2" reactor run for 35 h
 - Reached 40% conversion, collected 60% of C in bag
 - Equivalent to ~45% of 1 crew CO₂ → O₂/day
 - Damage was similar to 1" reactor
 - Evaluating improvements to reactor design
- Lasted much longer than steel wool reactors
- Fe, Ni, & Cr seen in carbon fines (corrosion of stainless steel wall)
- Will check ability to filter contaminants from air and water
- Relevance to Mars: carbon for filters, 3D printing, radiation shielding, dry lubricant (stable in vacuum), carbothermal reduction for metals production (Fe, Al, Si), diamonds?, terraforming?

Conclusions

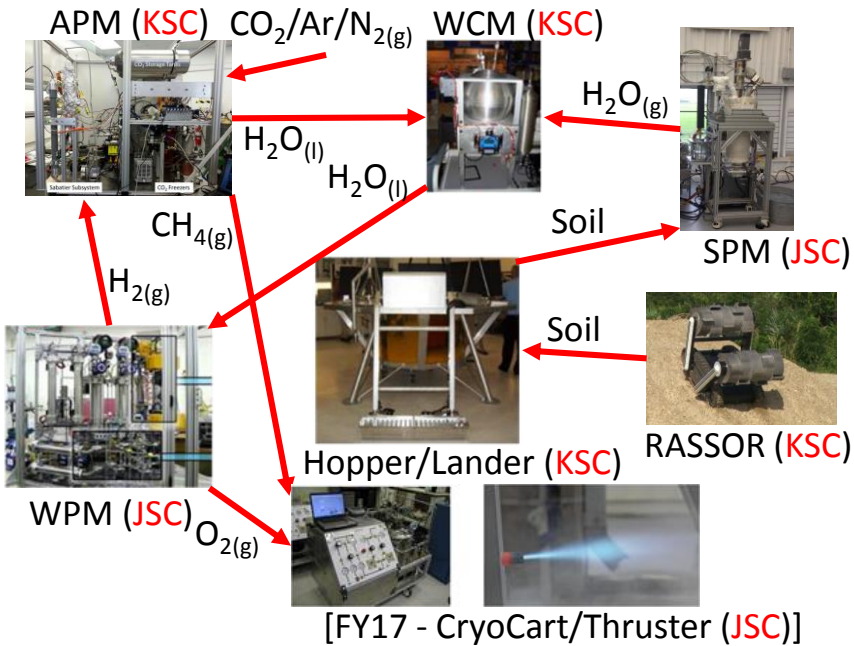


- KSC is developing both low and higher TRL Mars ISRU technologies
- Significant progress made on Atmospheric Processing Module for methane/oxygen production
- Initial $\text{CO}_2/\text{H}_2\text{O}$ electrolysis using Ionic Liquids shows more work is needed
 - NASA Graduate Fellow at KSC this fall
- Very encouraging results so far for Self-Cleaning Boudouard reactor for both O_2 recovery from CO_2 and carbon production

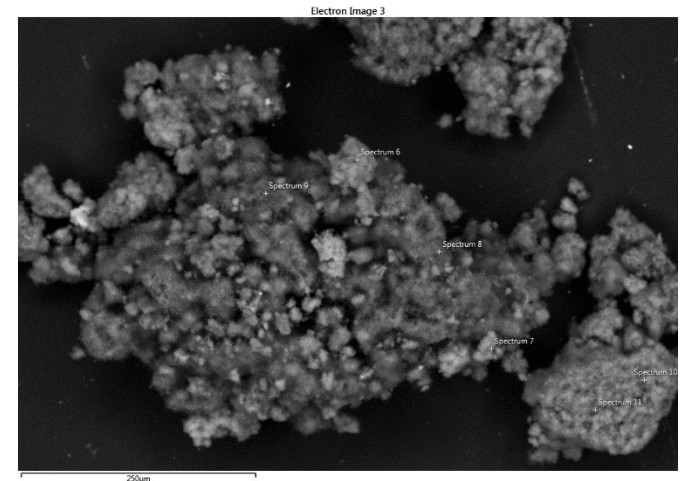


Questions?

MARCO POLO Modules



Scanning electron microscope image of carbon collected during the 1 inch diameter reactor test



Experimental setup for testing the Pine Research Instrumentation H-cell