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

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Outline

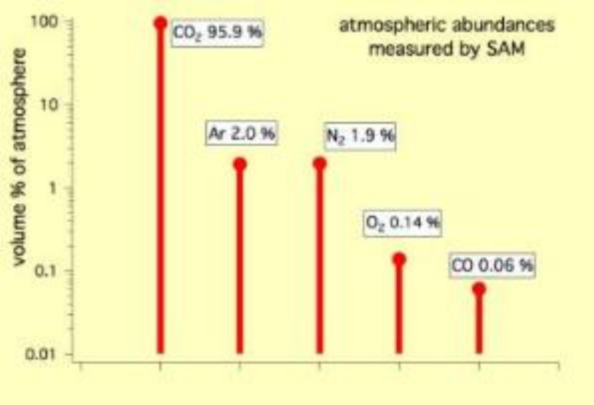
- Projects and Team Members
- Martian Resources
- Mars Atmospheric Processing Module
- Mars Propellant Production with Ionic Liquids
- Self-Cleaning Boudouard Reactor for Full Oxygen Recovery
- Conclusions

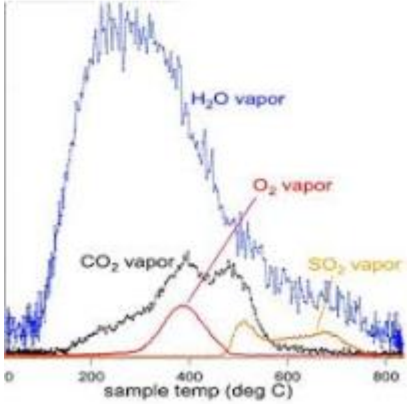
Projects and Team Members

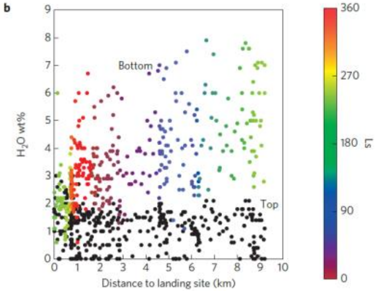
- **Mars Atmospheric Processing Module:** Paul Hintze, Anne Meier, and Jon Bayliss (KSC)
- **Ionic Liquids:** Paul Hintze, Tracy Gibson, Jan Surma (KSC), Laurel Karr, Steve Paley (MSFC), and Matt Marone (Mercer University, GA)
- **Self-Cleaning Boudouard Reactor for Full O_2 Recovery:** Paul Hintze, Anne Meier, Jon Bayliss, Tracy Gibson, James Captain, Griffin Lunn, Robert Devor, (KSC), Matt Mansell (MSFC), and Mark Berggren (Pioneer Astronautics)

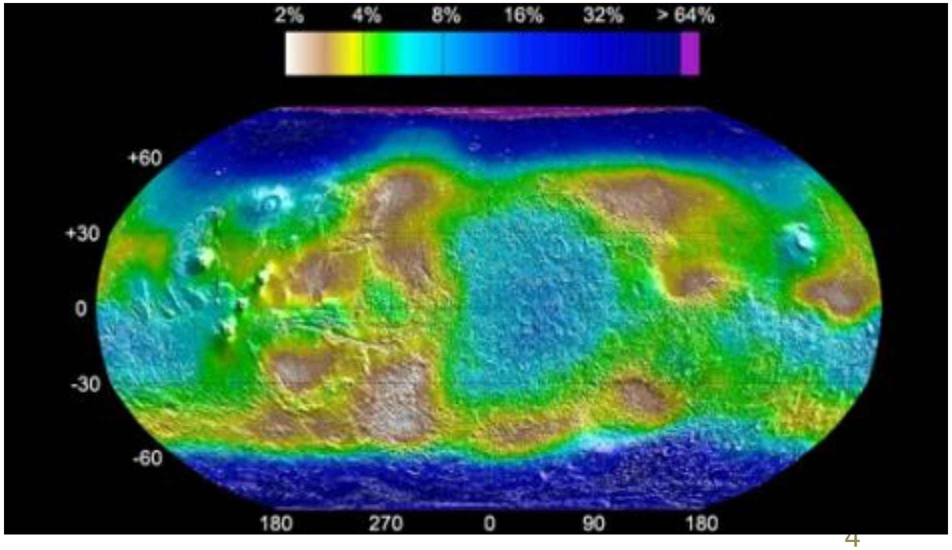
Martian Resources

- **Atmosphere of Mars**
  - 95.9% CO_2
  - 2% Ar, 1.9% N_2
  - <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





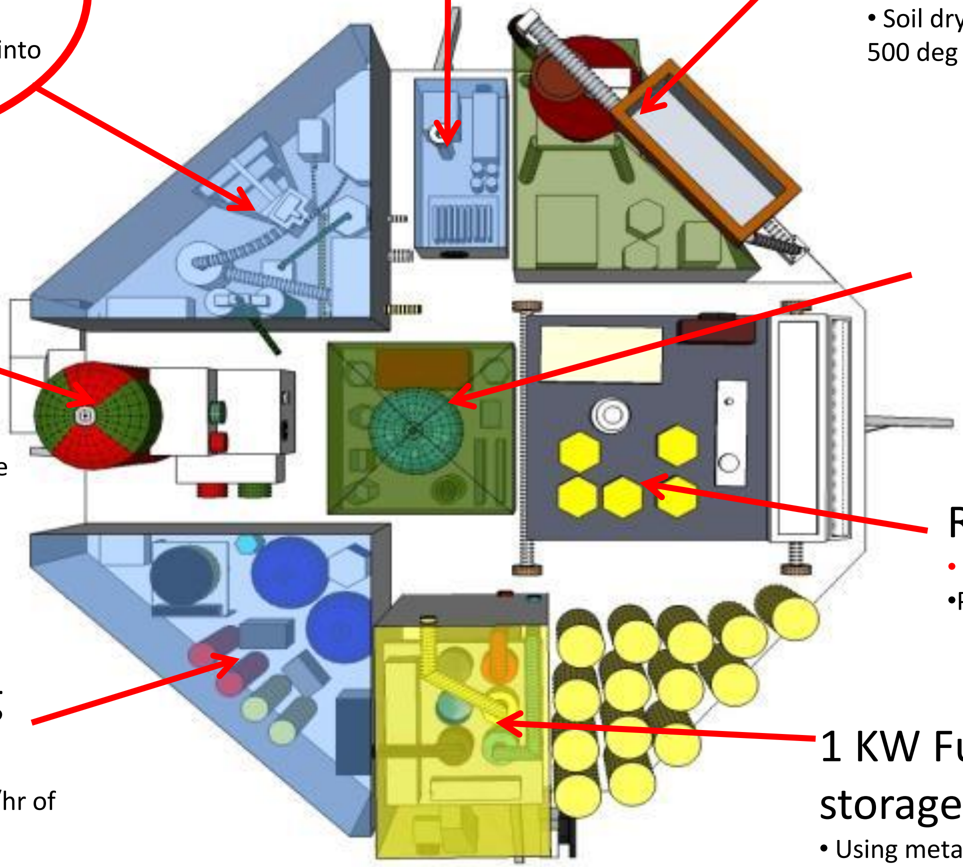




MARCO POLO Project

- **ISPP: In Situ Propellant Production**
  - Demonstrate production of Mars Sample Return propellant
  - Reduce risk for human Mars missions
- **MARCO POLO - M**ars **A**tmosphere and **R**egolith **CO**llector/**P**r**O**cessor for **L**ander **O**perations
  - Started in 2011
- The **A**tmospheric **P**rocessing **M**odule (**APM**)
  - Mars CO_2 Freezer Subsystem
  - Sabatier (Methanation) Subsystem
- Collect, purify, and pressurize CO_2
- Convert CO_2 into methane (CH_4) and water with H_2
- Other modules mine regolith, extract water from regolith, purify the water, electrolyze it to H_2 and O_2, send the H_2 to the Sabatier Subsystem, and liquefy/store the CH_4 and O_2

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)

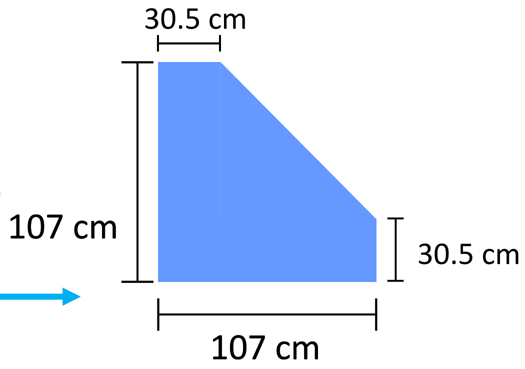
1 KW Fuel Cell and consumable storage (JSC & GRC)

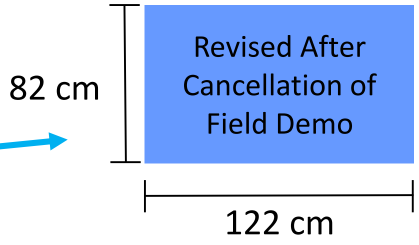
- Using metal hydride for H2 storage due to available
- 1 KW No Flow Through FC (GRC)
- 10 KW main power FC not shown (JSC)

3m x 3m octagon lander deck

APM Goals/Requirements

- **Collect and purify 88 g CO_2/h (>99%)**
  - From simulated Martian atmosphere
  - 10 mbar; 95.4% CO_2, 3% N_2, 1.6% Ar
- **Supply 88 g CO_2/h at 50 psia to the Sabatier reactor**
- **Convert CO_2 to 32 g CH_4/h and 72 g H_2O/h**
- **Operate autonomously for up to 14 h/day**
- **Minimize mass and power**
- **Fit within specified area and volume**
  - 9,000 cm^2 pentagon
  - 10,000 cm^2 rectangle for easier lab operations
  - 44 inches tall (112 cm, same as Water Processing Module)

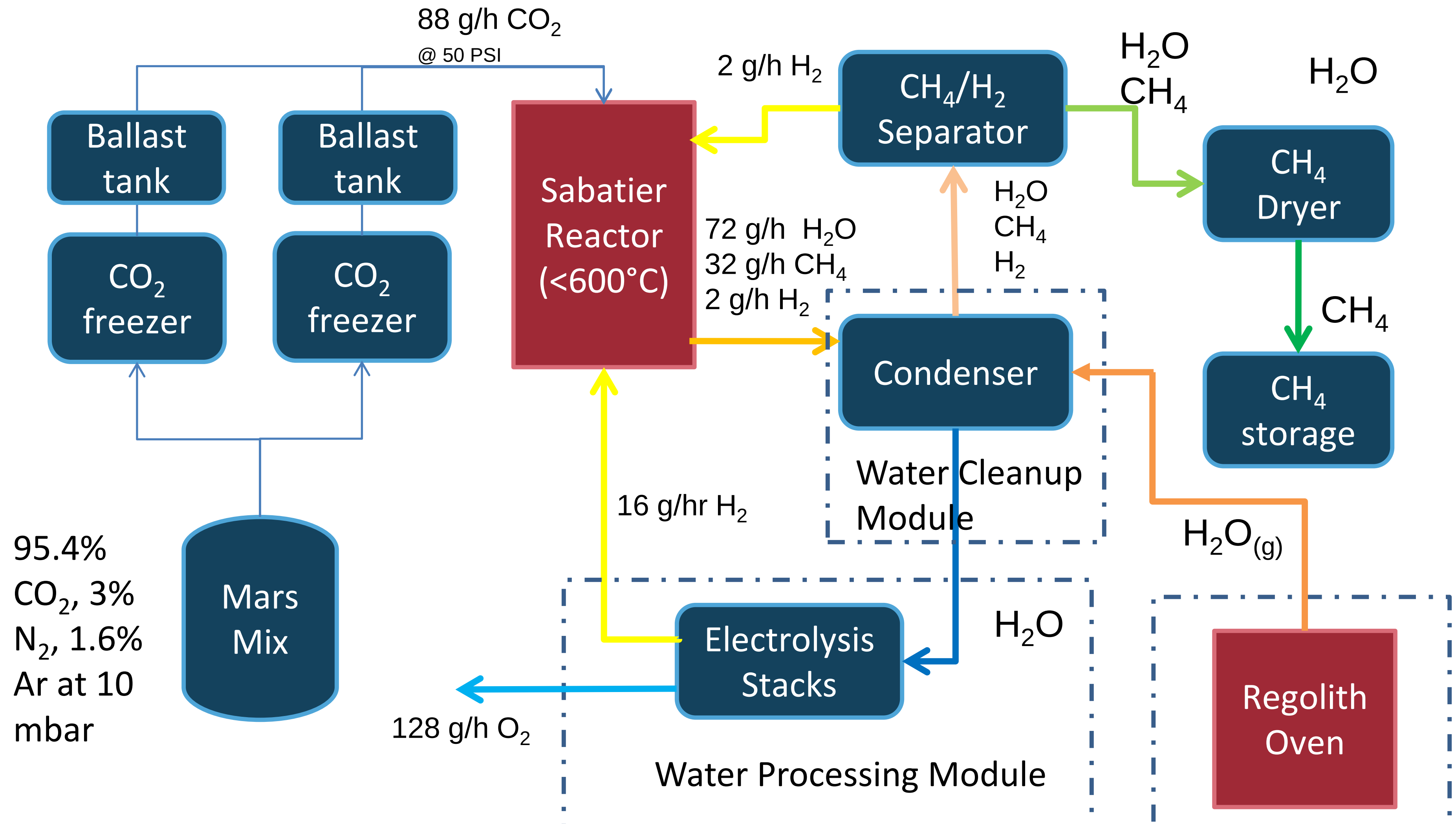




Revised After Cancellation of Field Demo

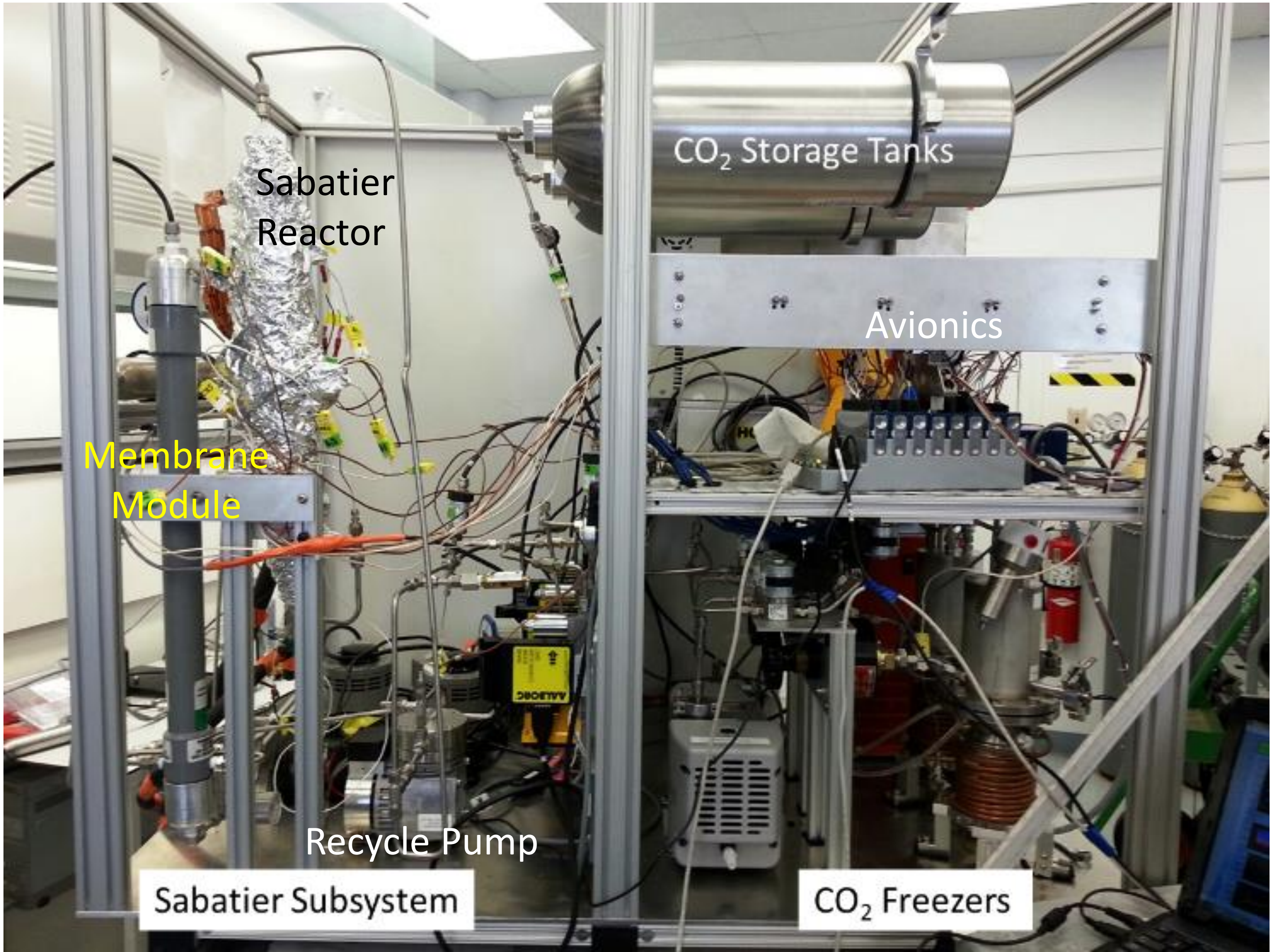
- **Support MARCO POLO production goals of 0.032 kg CH_4/h and 0.128 kg O_2/day (50% of O_2) for a total of 2.22 kg propellant/14 h day**
- **Sufficient for a Mars Sample Return Mission**
- **~17% of full-scale O_2 production goal for human Mars Missions (0.75 kg O_2/h/module x 3 modules = 2.2 kg O_2/h), i.e. 1/6th scale**

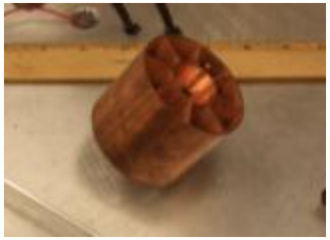
Atmospheric Processing Operations



95.4% CO_2, 3% N_2, 1.6% Ar at 10 mbar

Atmospheric Processing Module

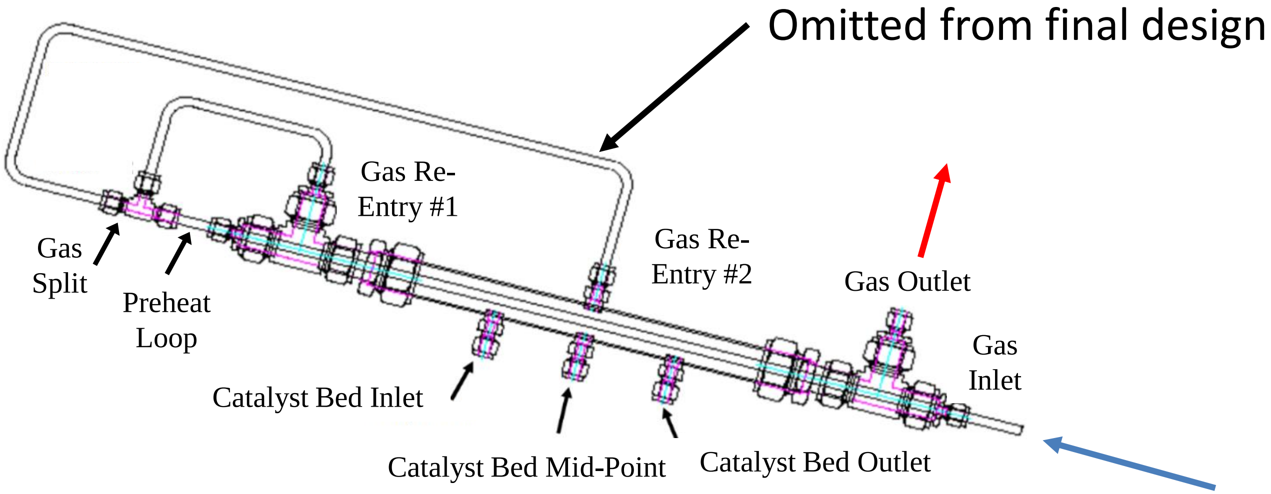




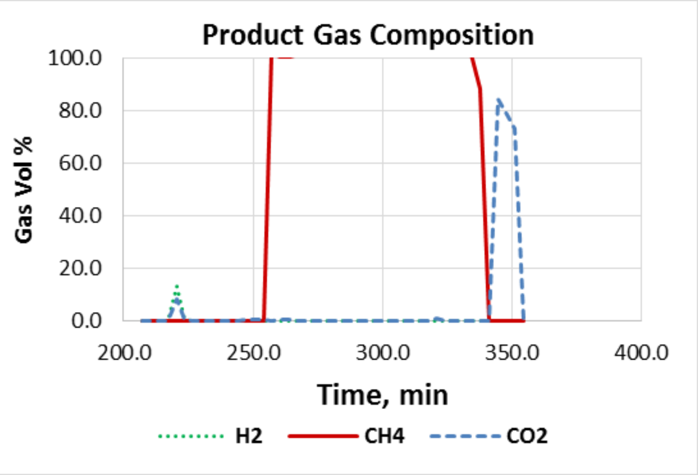
Copper Heat Exchanger

CO$_2$ 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 CO_2/h + 3.5:1 H_2/CO_2
- Based on Pioneer Astronautics design for steam oxidation of trash to methane
- 1.5 h integrated test with CO_2 Freezers and recycling system showed 100% conversion to pure CH_4

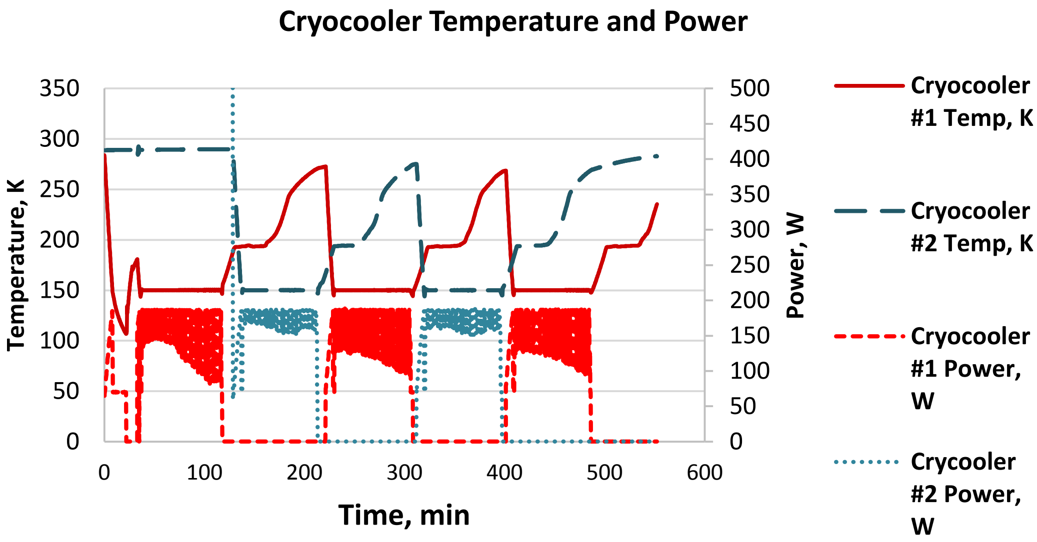


Long-Duration Tests Were Successful

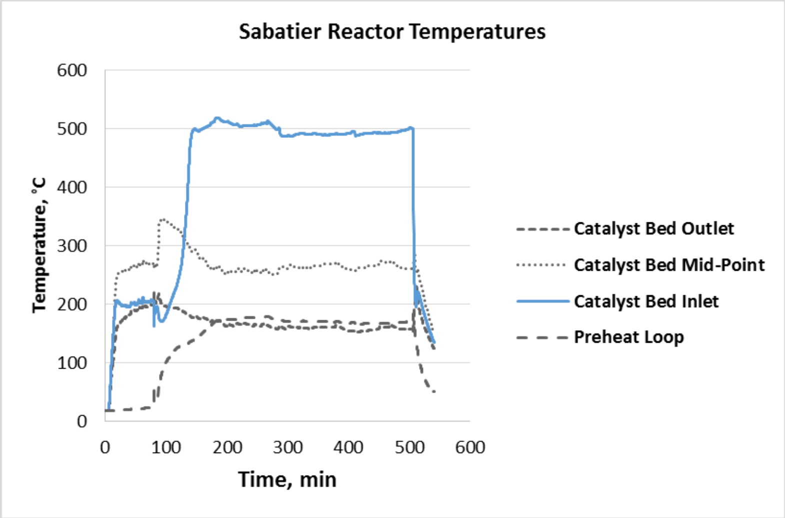
Run No.	*1*	*2*	*3*
Sabatier Run Duration	7.0 h	7.0 h	7.0 h
Gas Composition	CO_2	CO_2	Mars Gas
Average CO_2 Freezing Rate	102 g/h	100 g/h	102 g/h
Average Fraction of CO_2 Frozen	79%	76%	72%
Average Cryocooler Power	139 W	150 W	158 W
Average energy needed to Freeze CO_2	4917 J/g	5051 J/g	5655 J/g
Average 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_2O 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



CO_2 Freezer Cold Head Temperatures and Cryocooler Power Consumption during the Third Run of the 7-h Integrated Test Series



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

Conclusions from the Long-Duration Tests

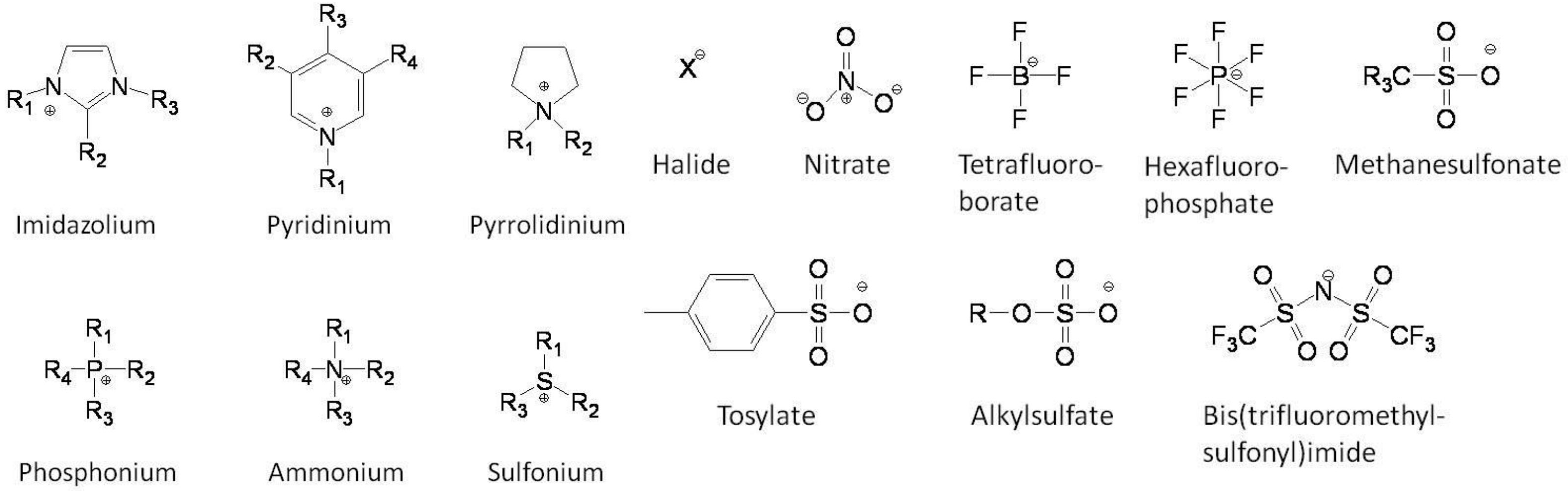
- **CO_2 Freezer Subsystem operates well**
  - Exceeds 88 g/h freezing and supply rate
  - Freezes ~70% of incoming CO_2
  - Provides valuable data for power to freeze CO_2 at Mars pressure
    - Averages 0.22 W/g CO_2 frozen = only 108% of theoretical
  - Contributes to Human Mars Mission ISRU system designs, e.g. 680 W lift for 3.1 kg CO_2/h
- **Sabatier Subsystem also operates well**
  - New reactor is efficient
  - Recycling system (membrane module + recycle pump) works well
  - Pure CH_4 obtained at expected rate
  - ~7% of water is missing (<1% of loss is in CH_4)

Recent Work and Current Status

- **Additional integrated tests performed**
- **Faster and slower production rates tested**
  - 1.0-1.6 SLPM feed to CO_2 Freezers (87-71% frozen; 4800-5400 J/g)
  - Sabatier works at 0.3 to 1.2 SLPM CO_2 (0.75 SLPM nominal, 550°C max T)
  - Some CO observed in CH_4 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

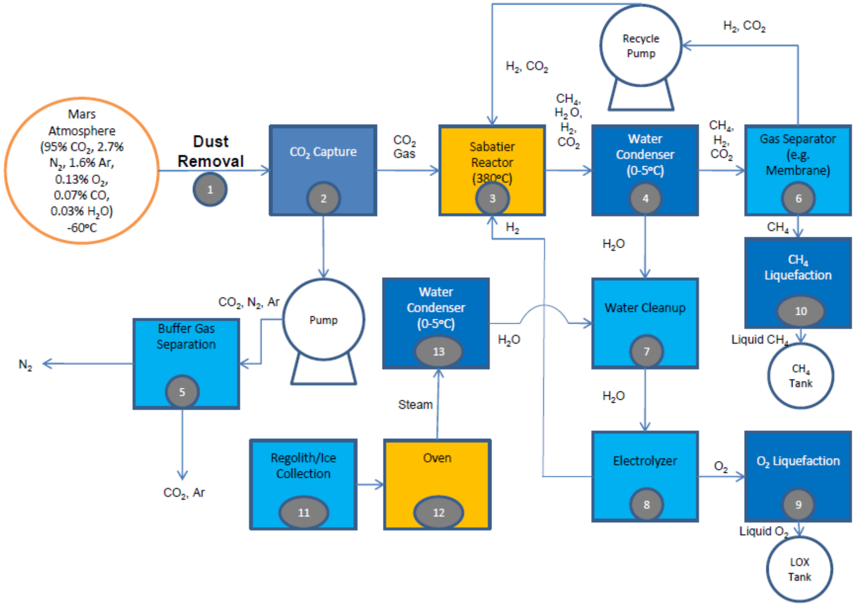
- Ionic Liquids (ILs) are organic salts that have melting points near room temperature
- Certain ILs adsorb CO_2 at low partial pressures and provide a medium for electrolysis to useful compounds



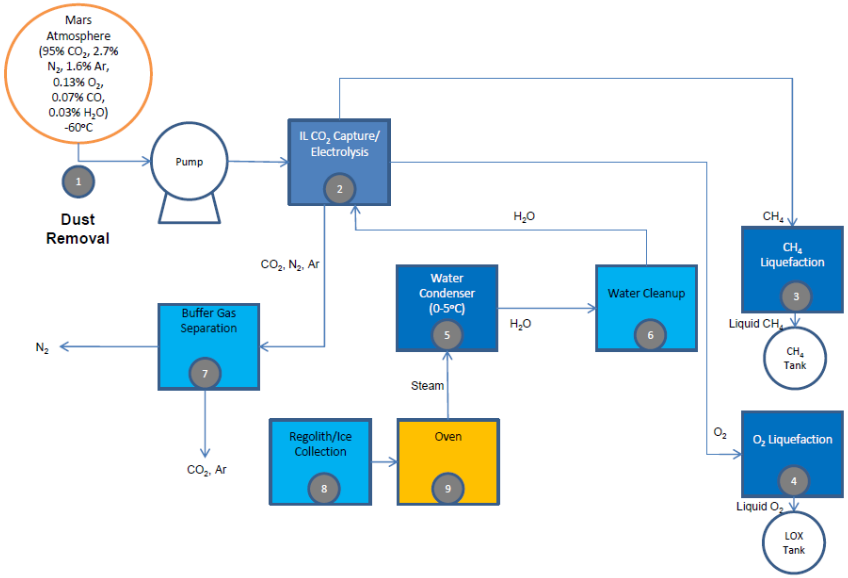
Typical Ionic Liquid Cations and Anions

Potential Benefits for ISRU

Current Mars Propellant Production Process Diagram

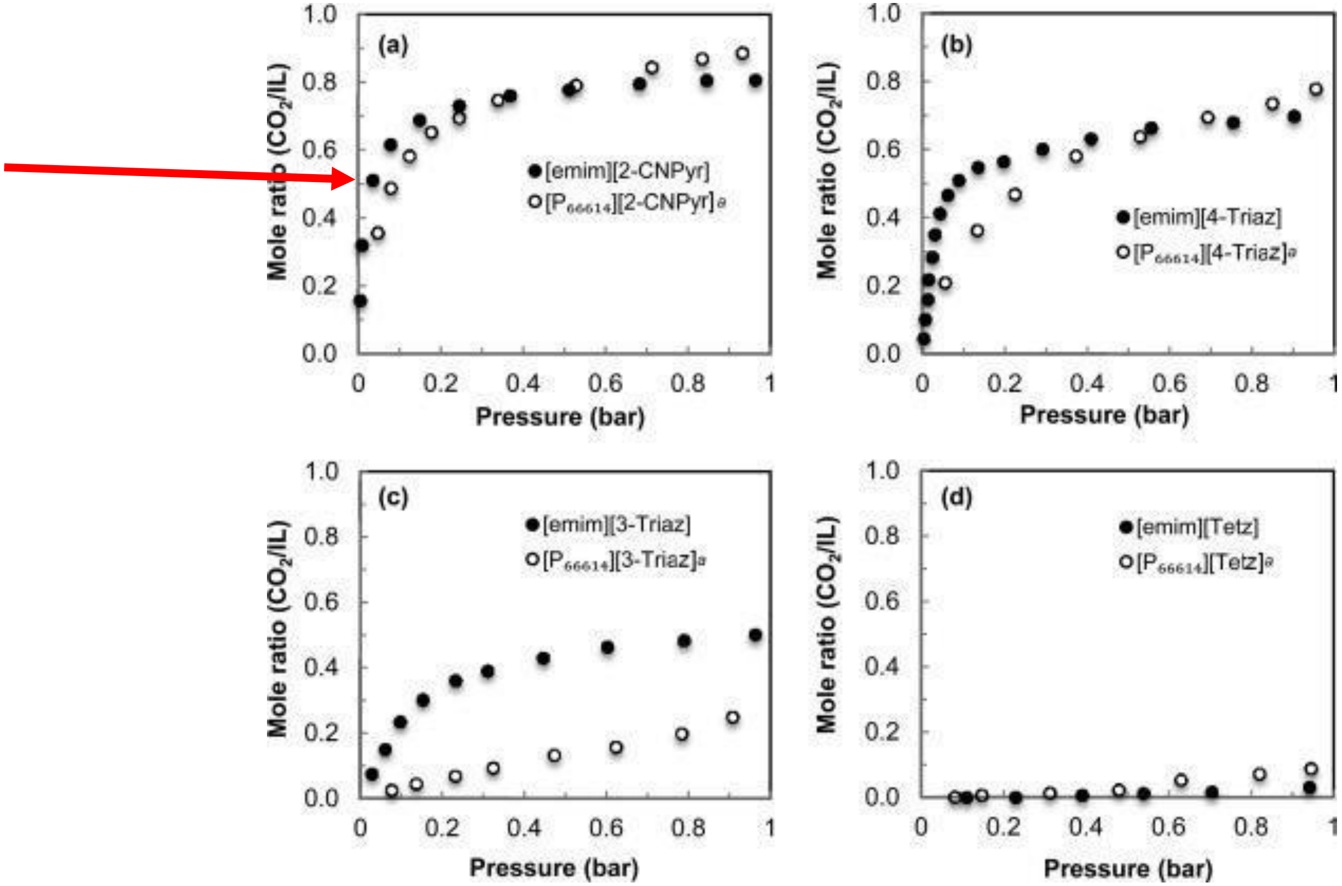


Mars Propellant Production Process Diagram with IL Electrolysis



- **Advantages of IL capture/electrolysis:**
  - No high temperature processing of CO_2
  - One less pump and no cryocoolers
  - Four fewer major process steps
  - Estimated ~50% less mass and ~25% less power

CO$_2$ Uptake at Low Partial Vacuum
~50% Mole Fraction at ~10 mbar



"CO$_2$ absorption capacity in (a) [emim][2-CNPyr], (b) [emim][4-Triaz], (c) [emim][3-Triaz], and (d) [emim][Tetz] at 22 °C. The CO$_2$ solubility in [P$_{66614}$]+ counterparts from ref 10 are also shown for comparison." (Brennecke, 2014)

Technical Approach

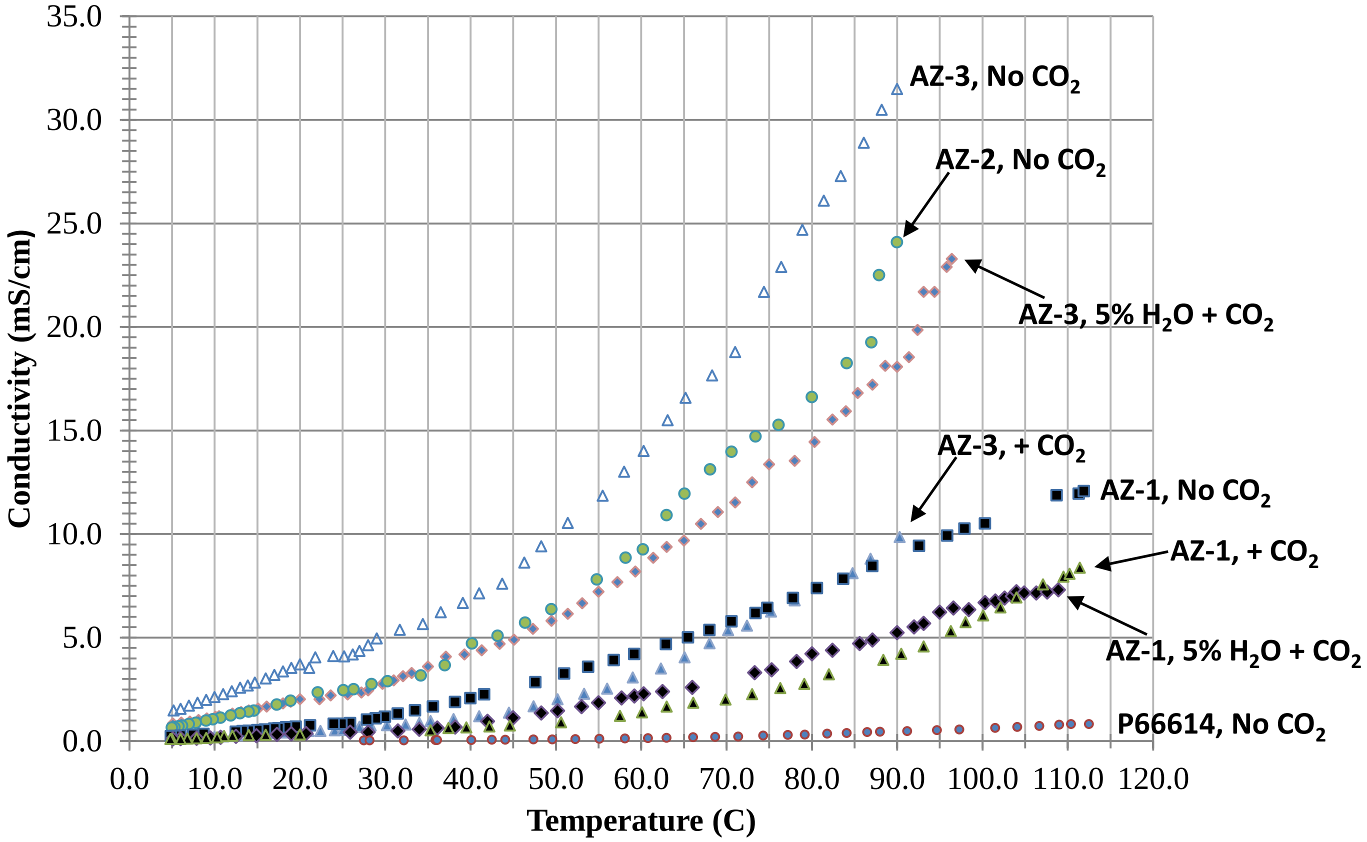
- Select best available candidate COTS ILs and electrocatalysts (KSC)
  - Based on literature review
- Prepare new task-specific ILs (AZ Technology/MSFC)
- Determine CO_2 capture efficiency and conductivity of ILs (Mercer University and KSC)
- Measure electrochemical windows (KSC)
- Design/build electrochemical cells (KSC)
- Test electrolysis of $CO_2 + H_2O$ to $CH_4 + O_2$

Results

- COTS IL candidates: [EMIM][BF$_4$], [BMIM][BF$_4$], [BMIM][TFMSI], [BMIM][PF$_6$] and [HMIM][B(CN)$_4$]
- Electrocatalysts: Copper cathode/Pt anode, TiO$_2$ cathode/Pt anode
- Several ILs have good electrochemical windows and conductivity
- Two-compartment cell w/Nafion membrane
  - Polycarbonate not suitable: CaCO$_3$ precipitate,
  - Switched to glass cell

- Three TSILs prepared: AZ-1, AZ-2, and AZ-3 (code named to protect IP)
  - High CO$_2$ sorption and conductivity

AZ-3 Shows High IL Conductivity with CO_2 and $CO_2 + H_2O$



Conductivity of AZ-1, AZ-2, AZ-3 and [P_{66614}] [3-CF_3Pyra] vs. time for CO_2 uptake with and without 5% dissolved water

AZ-3 Shows High CO_2 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

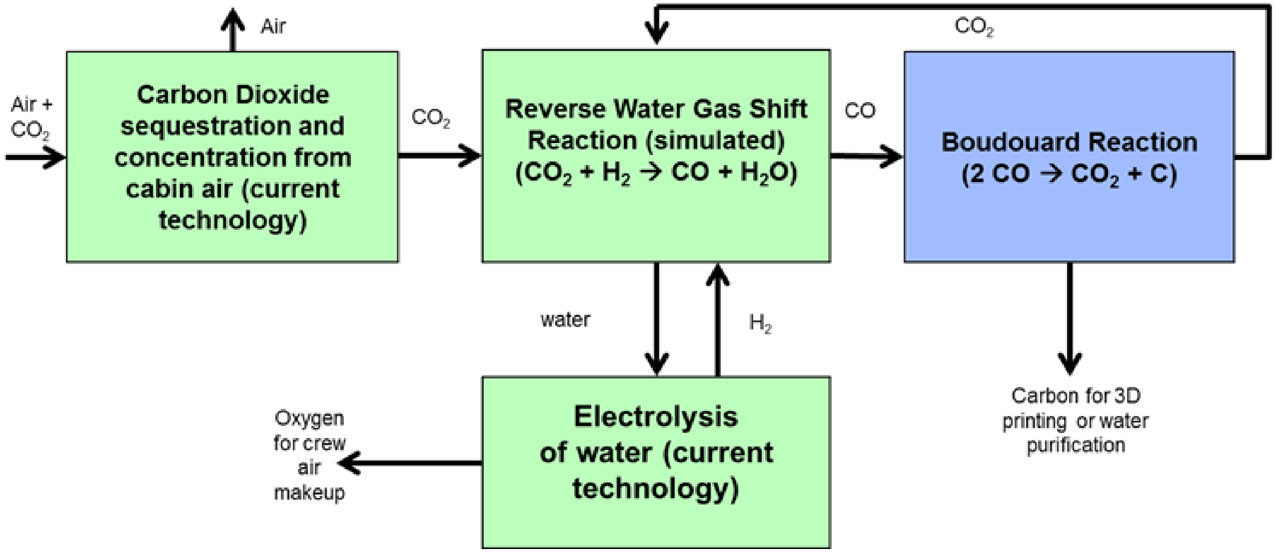
Summary
(Underlined ILs = Candidates)

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
[BMIM][PF_6]	0.50	2.4		Yes	Precipitate, Cu darkened		0
[BMIM][BF_4]	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
AZ-2	9.6	2.4		Yes	IL darkened		0
AZ-3	15.6		1.2	Slow color change	Precipitate	5	Possible CH_4 and CO (TiO_2 only)

Self-Cleaning Boudouard Reactor for Full O_2 Recovery from CO_2

- Initiated by NASA RFP for “GAME CHANGING DEVELOPMENT PROGRAM, ADVANCED OXYGEN RECOVERY FOR SPACECRAFT LIFE SUPPORT SYSTEMS APPENDIX NH14ZOA001N-14GCD-C2”
- Only 50% of O_2 can recovered from respiratory CO_2 on the ISS
- Sabatier reactor makes CH_4 and H_2O
- CH_4 is vented, losing H_2
- H_2O from cargo limits H_2 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

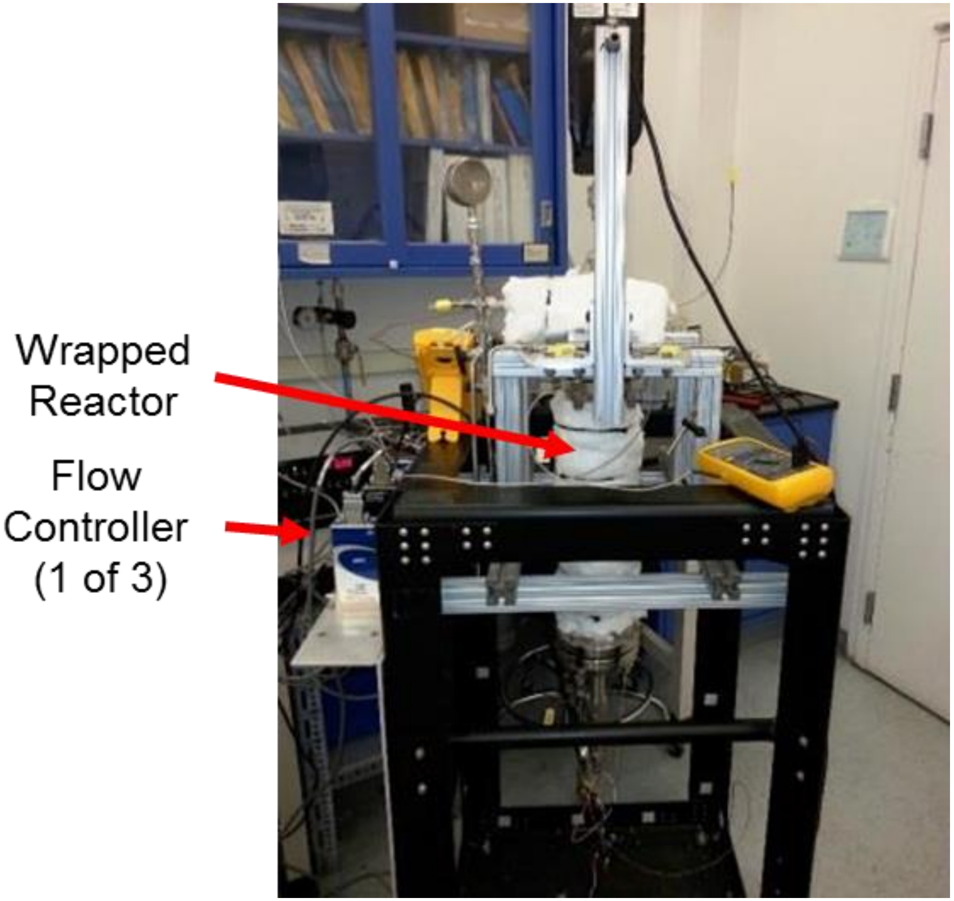
Approach - Break Bosch Reaction into Two Parts (Demo'd by MSFC)



- Bosch Reaction: $CO_2 + H_2 \rightarrow C_{(s)} + 2\,H_2O$ ($\rightarrow 2\,H_2 + O_2$)
- RWGS: $CO_2 + H_2 \rightarrow CO + H_2O$ ($\rightarrow H_2 + \frac{1}{2}\,O_2$)
- Boudouard: $2\,CO \rightarrow C_{(s)} + CO_2$ (Fe catalyst, H_2 enhancer)
- Need a method to remove C from catalyst as it forms
- Several concepts developed and one tested so far with encouraging results

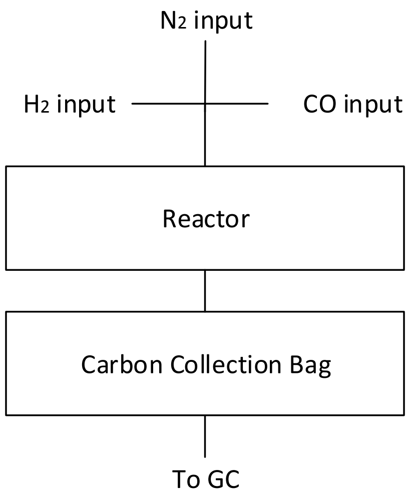
Self-Cleaning Boudouard Reactor

- Used CO/H_2/N_2 feed
- Tested steel wool reactor for comparison
- Tested 1" and 2" ID reactors
- Collected carbon in HEPA filter bag as it was generated



Results Are Encouraging

Reactor Schematic



N_2 input

H_2 input

CO input

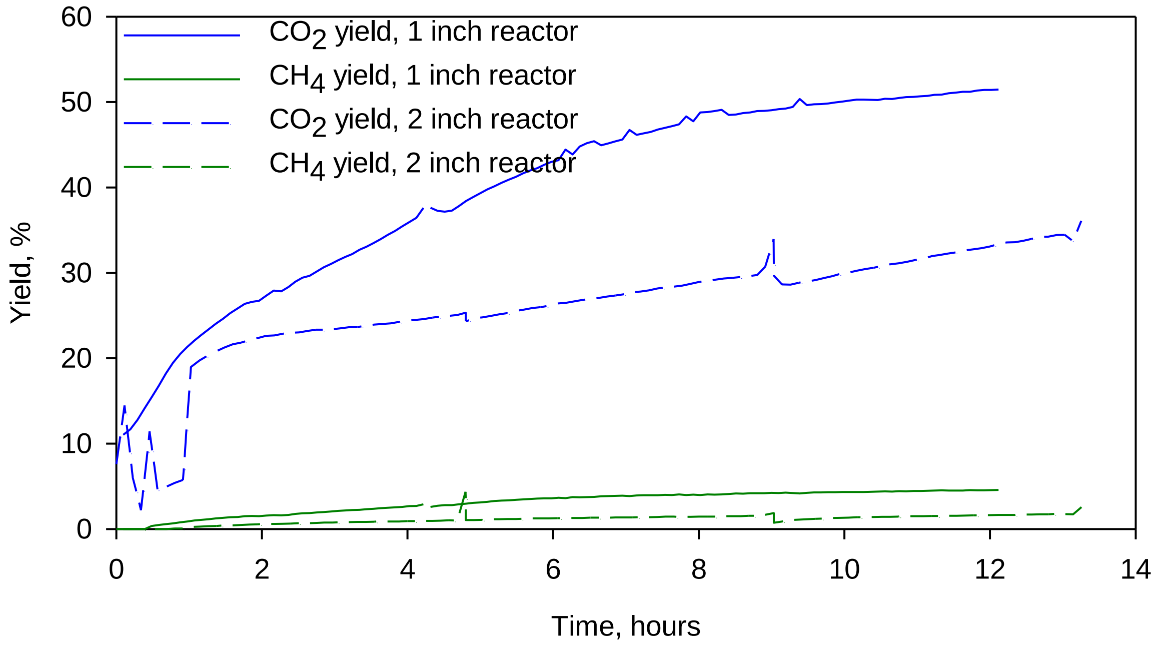
Reactor

Carbon Collection Bag

To GC

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



CO_2 and CH_4 Yields for Both Reactors

Boudouard Summary

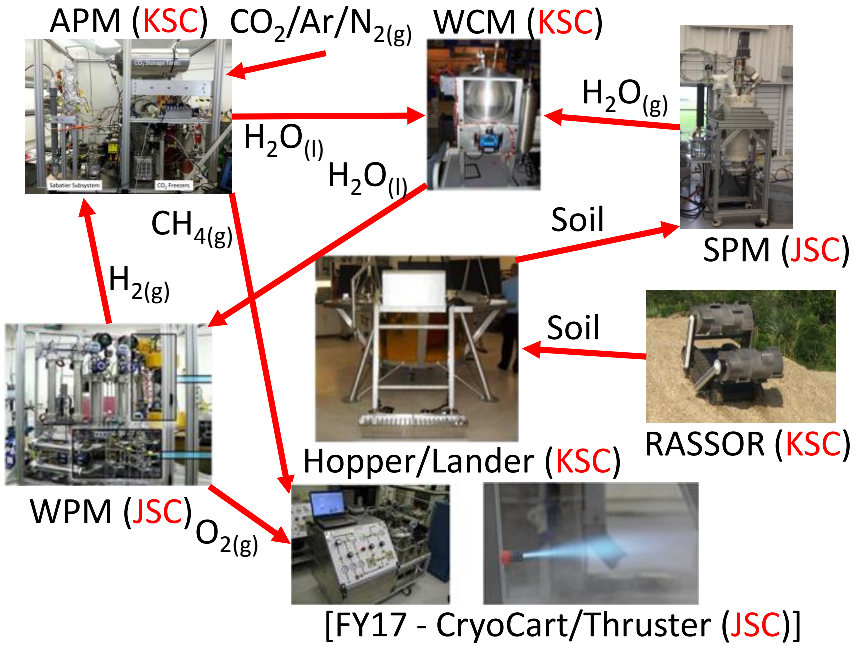
- 1” reactor ran for 12 h
  - Reached 47% conversion, collected 27% of C in bag
  - Found to be damaged upon disassembly
- 2” reactor run for 35 h
  - Reached 40% conversion, collected 60% of C in bag
  - Equivalent to ~45% of 1 crew $CO_2 \rightarrow O_2$/day
  - Damage was similar to 1” reactor
  - 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 CO_2/H_2O 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



APM (KSC)

$CO_2/Ar/N_{2(g)}$

WCM (KSC)

$H_2O_{(g)}$

$H_2O_{(l)}$

$H_2O_{(l)}$

Soil

SPM (JSC)

$CH_{4(g)}$

$H_{2(g)}$

Soil

RASSOR (KSC)

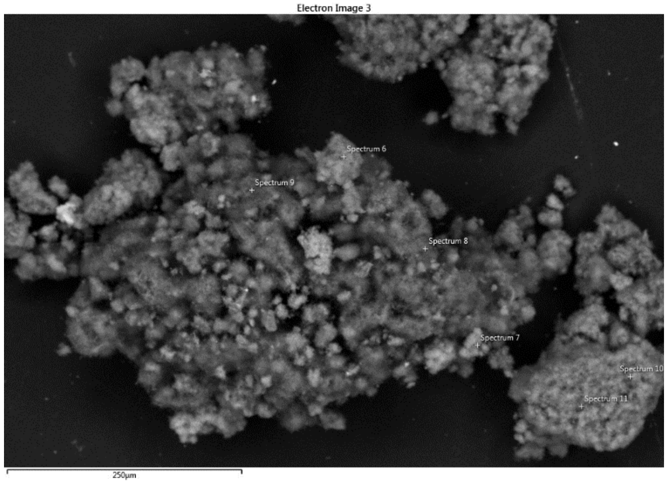
Hopper/Lander (KSC)

WPM (JSC)

$O_{2(g)}$

[FY17 - CryoCart/Thruster (JSC)]

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



Experimental setup for testing the Pine Research Instrumentation H-cell