Hydrogen Recovery by Methane Pyrolysis to Elemental Carbon

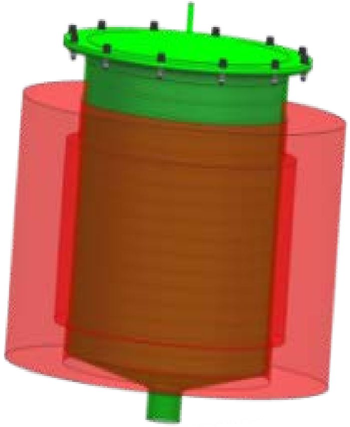
ICES Paper 2019-103

Stephen F. Yates, Amanda Childers, Nicholas Brom,
Sean Skomurski, Charles Lo

Honeywell Aerospace

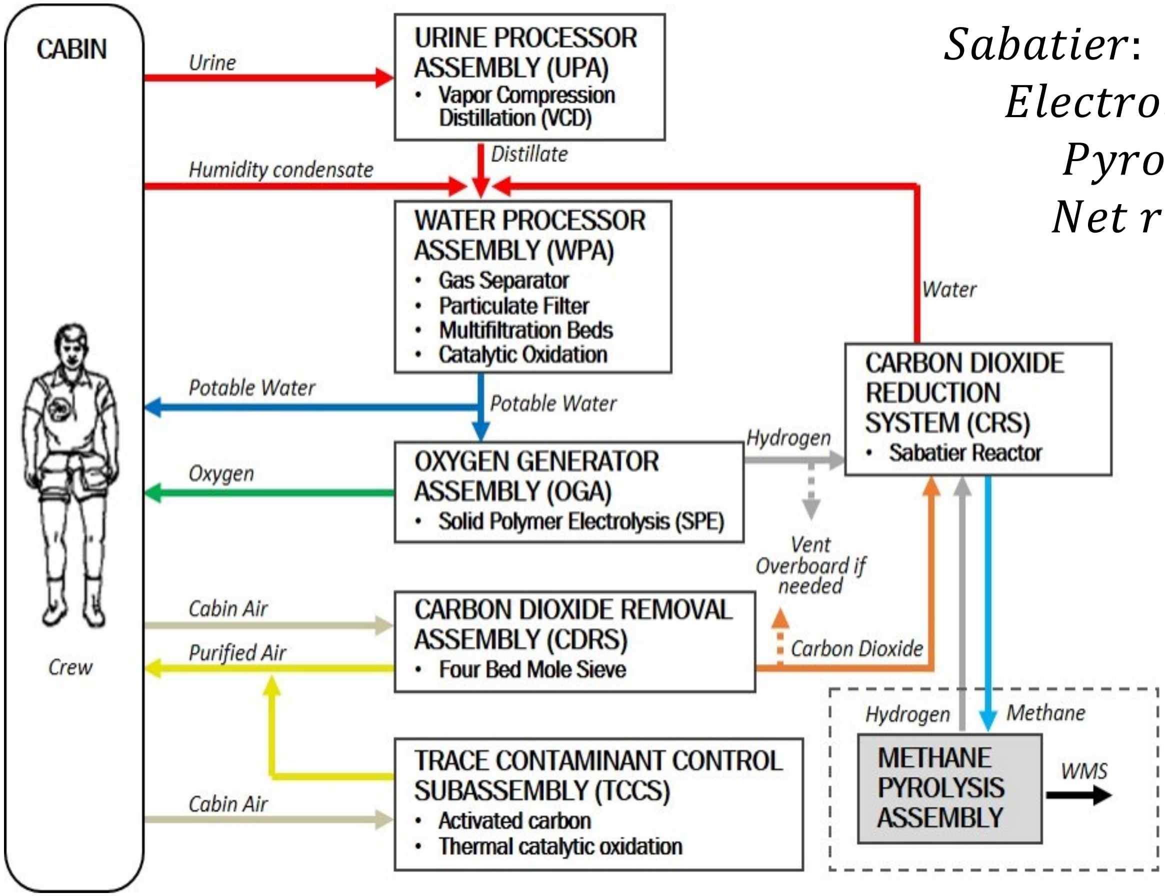
Morgan B. Abney

NASA Marshall Space Flight Center



International Conference on Environmental Systems,
Boston, MA 2019

Increased O_2 recovery via H_2 recovery



$$Sabatier:\quad CO_2 + 4\,H_2 \rightarrow CH_4 + 2\,H_2O$$

$$Electrolysis:\quad 2\,H_2O \rightarrow 2\,H_2 + O_2$$

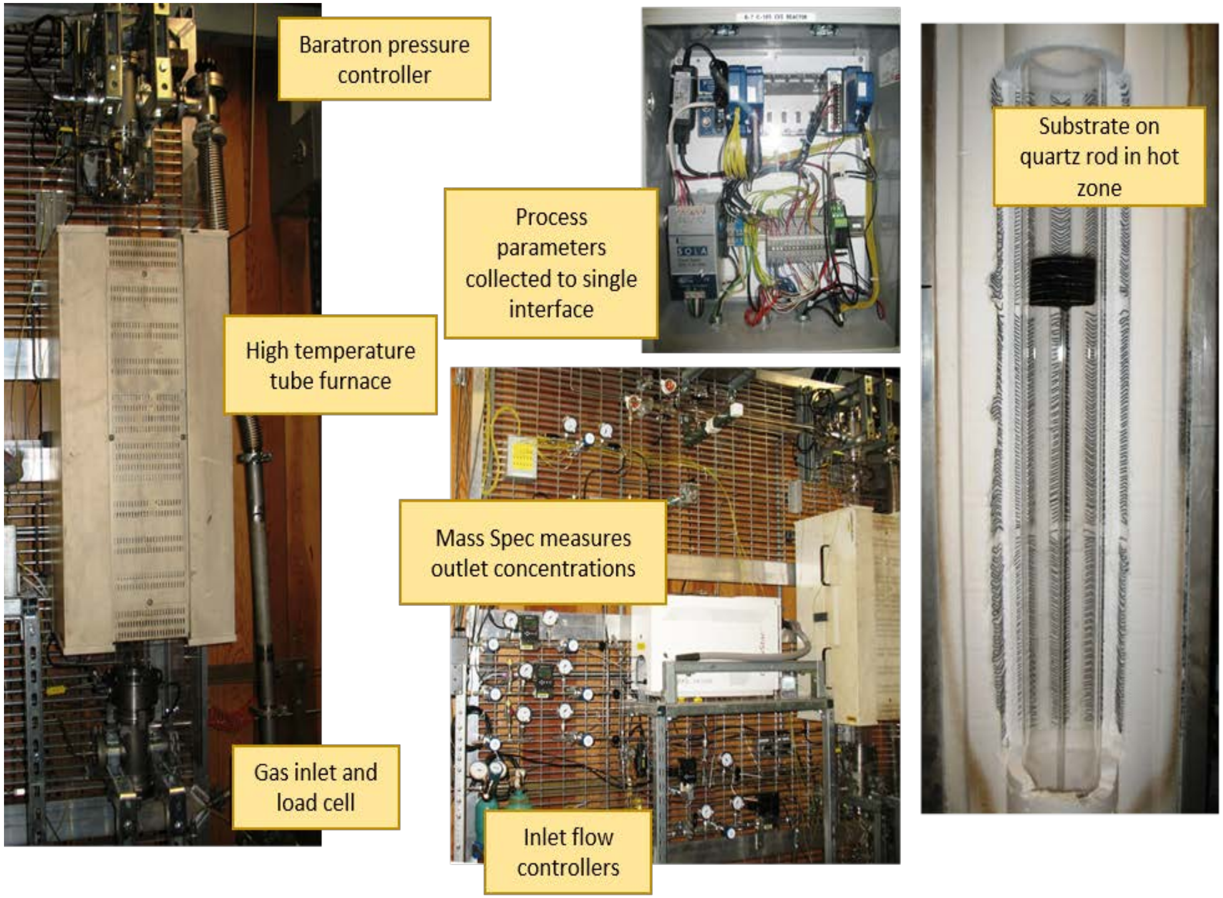
$$Pyrolysis:\quad CH_4 \rightarrow 2\,H_2 + C$$

$$Net\,reaction:\quad CO_2 \rightarrow O_2 + C$$

- 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.

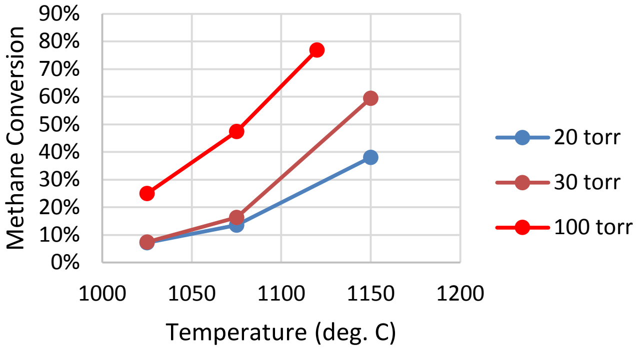
Methane pyrolysis

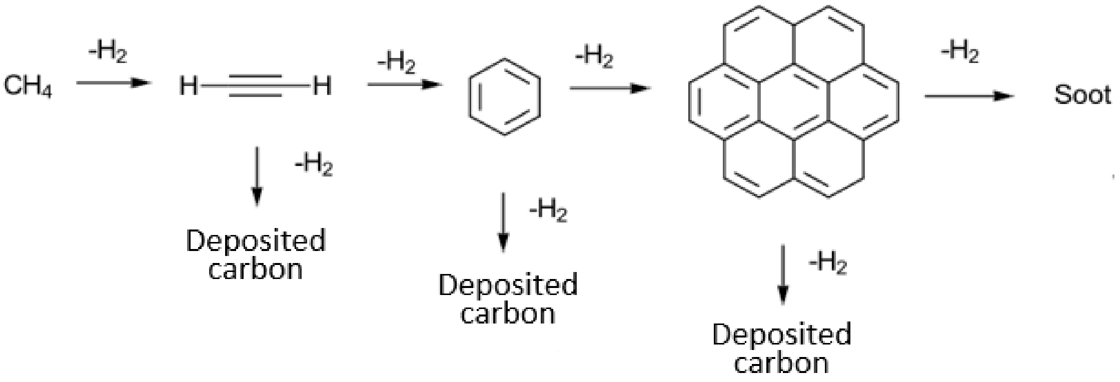
- Chemical vapor deposition of carbon is used routinely to make carbon composites.
- Generally run at low conversion to adjust properties of the product.
- Ideally suited for hydrogen recovery since gas phase byproduct concentrations can be low.
- Hard durable non-sooty carbon product.



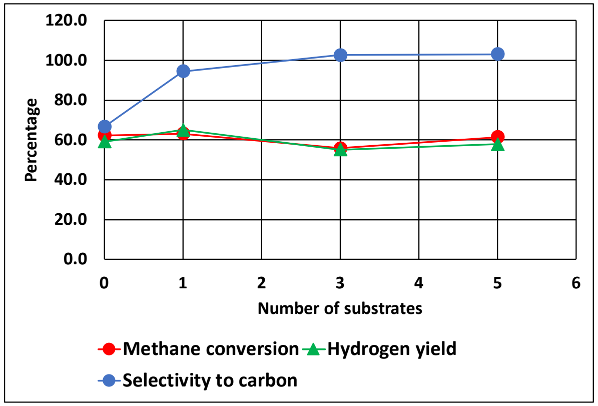
Honeywell’s experience with industrial scale CVD enabled rapid development of the pyrolysis process.

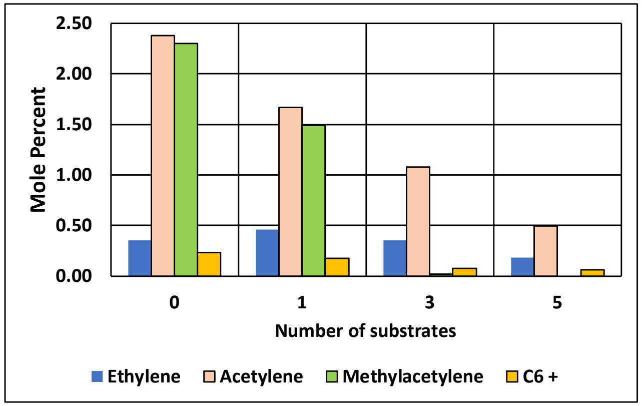
Methane pyrolysis rxn conditions





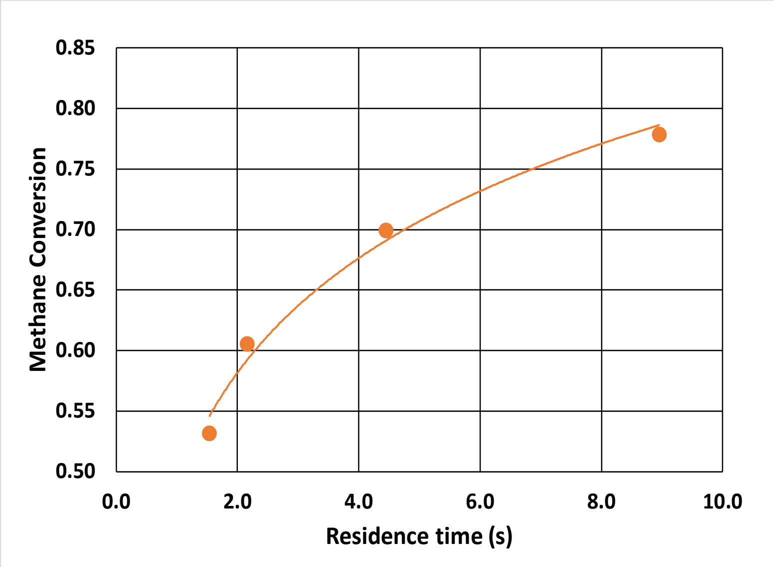
- Pyrolysis has a long series of intermediates between methane and carbon.
- Reaction is endothermic and occurs only at >1000°C and low pressures.
- Product distribution is strongly dependent on substrate surface area.

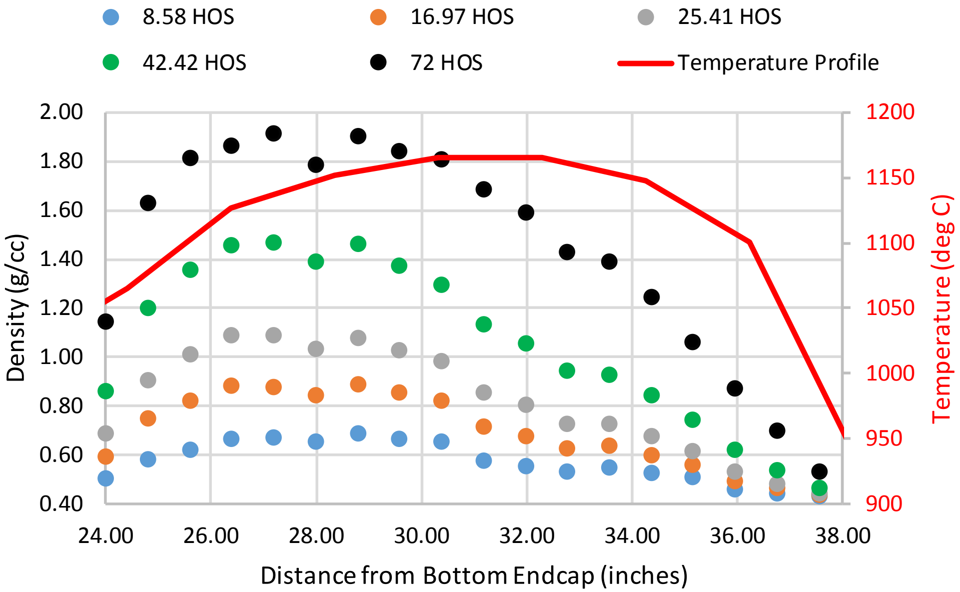




- Selectivity to CVD carbon increases as number of substrates increases.
- Non-methane hydrocarbon byproducts decrease.

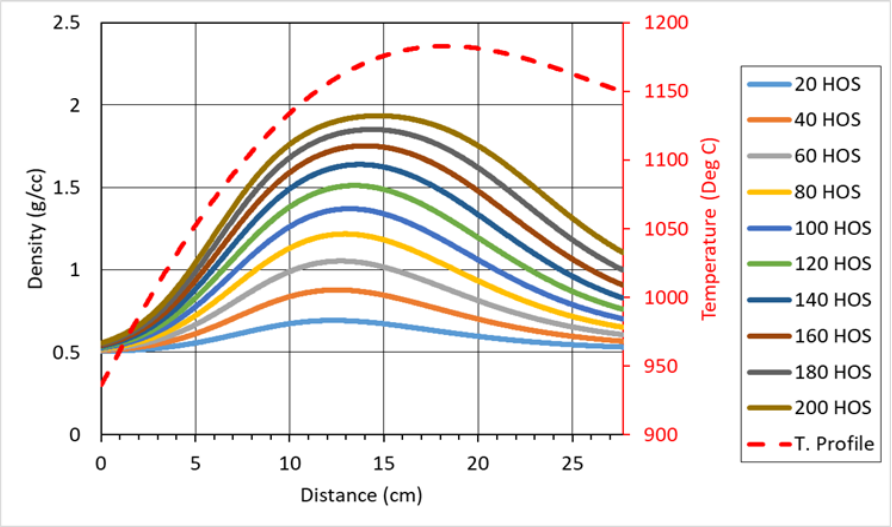
Methane pyrolysis kinetics

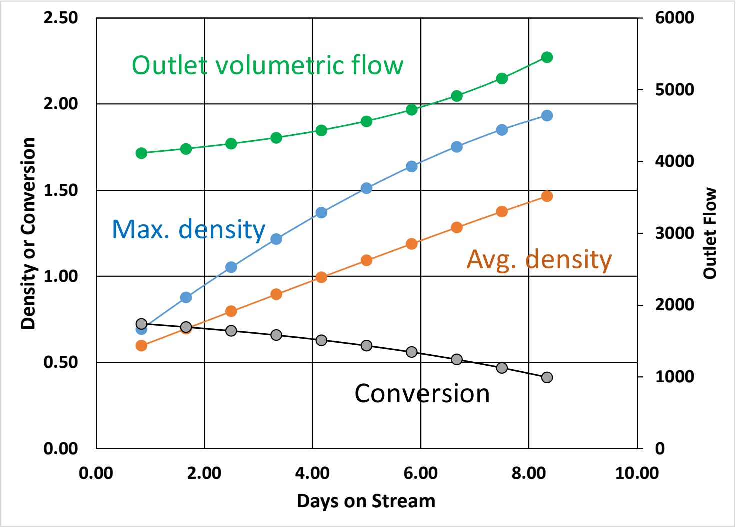


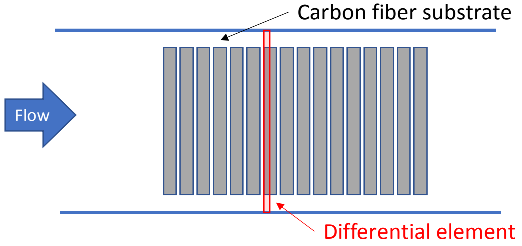


- Detailed knowledge of pyrolysis kinetics were required for design.
  - Effects of temperature, pressure, substrate surface area.
  - Conversion increases with residence time, but reaction order is complex.
- Kinetics also determines the distribution of carbon vs. distance from inlet.
- Adjust parameters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

Reactor model

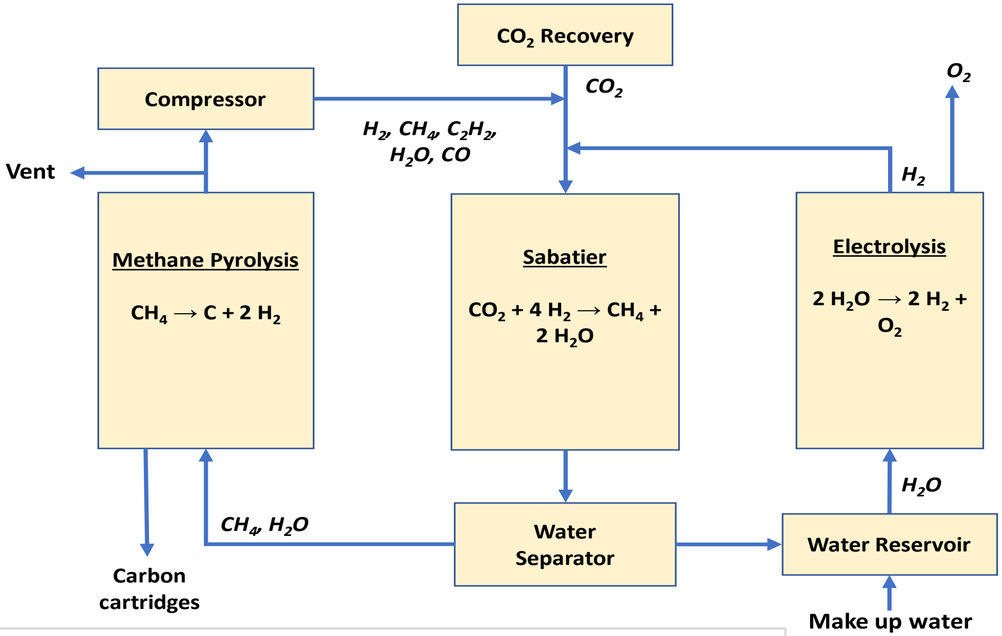






- Differential model used to use reaction kinetics for reactor design.
  - Model predicts conversion and cumulative carbon deposition vs. temperature, pressure, residence time, hours on stream.
- As reaction proceeds, conversion decreases and part density increases.
- Objective is to maximize average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

Closing the loop



CO$_2$ Recovery

CO$_2$

Compressor

H$_2$, CH$_4$, C$_2$H$_2$, H$_2$O, CO

O$_2$

Vent

H$_2$

Methane Pyrolysis

CH$_4$ → C + 2 H$_2$

Sabatier

CO$_2$ + 4 H$_2$ → CH$_4$ + 2 H$_2$O

Electrolysis

2 H$_2$O → 2 H$_2$ + O$_2$

H$_2$O

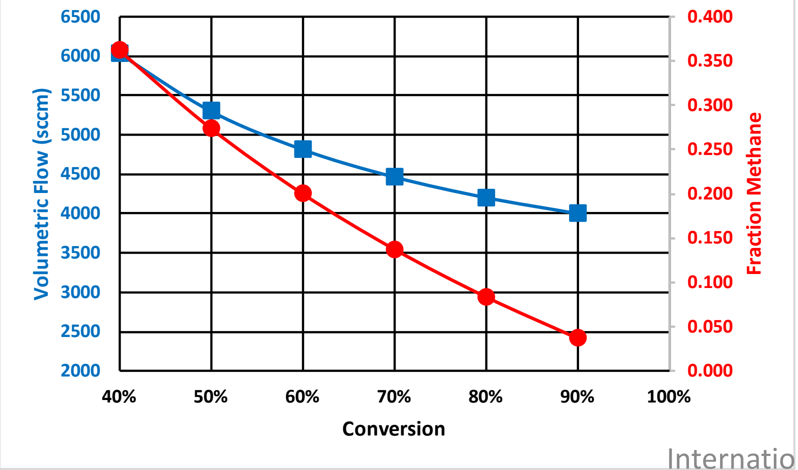
CH$_4$, H$_2$O

Water Separator

Water Reservoir

Carbon cartridges

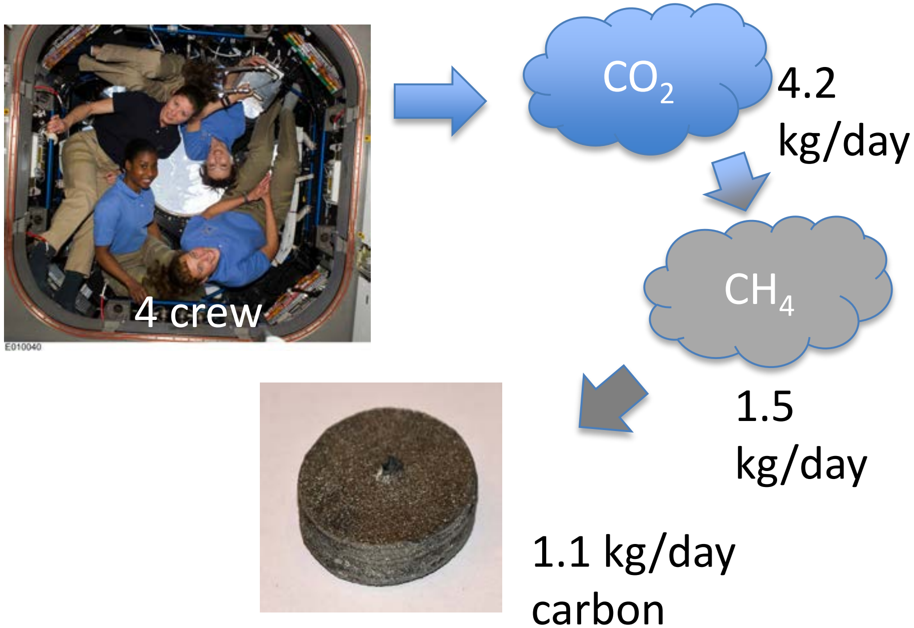
Make up water



- 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%.

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.



$$Capacity = \frac{\rho_f - \rho_i}{\rho_i}$$

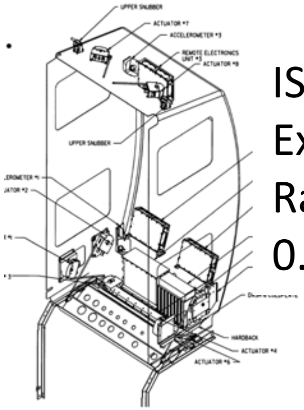
Lower initial density increases capacity & decreases number of substrates needed.

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

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

Parameter	Baseline Substrate	Developmental Substrate
Capacity (g Carbon/g substrate)	0.8	1.3
Maintenance interval (days)	6.5	10.9
Cartridges (1000 day mission)	155	92
1000 day Storage Volume (m^3)	1.8	1.1
1000 day Storage Weight (kg)	787	280

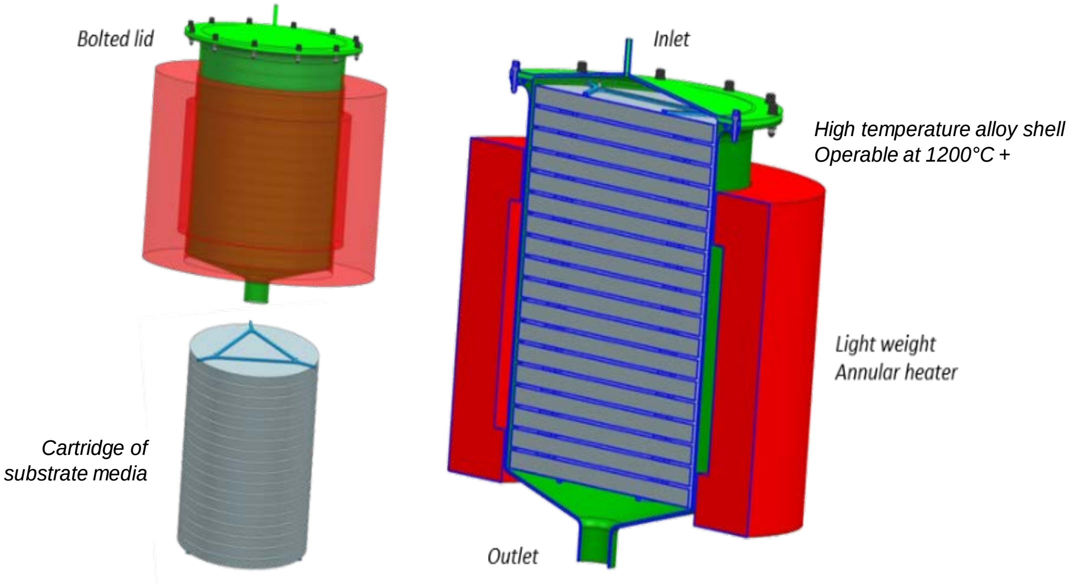


ISS Express Rack $0.57\ m^3$

$1\ m^3$

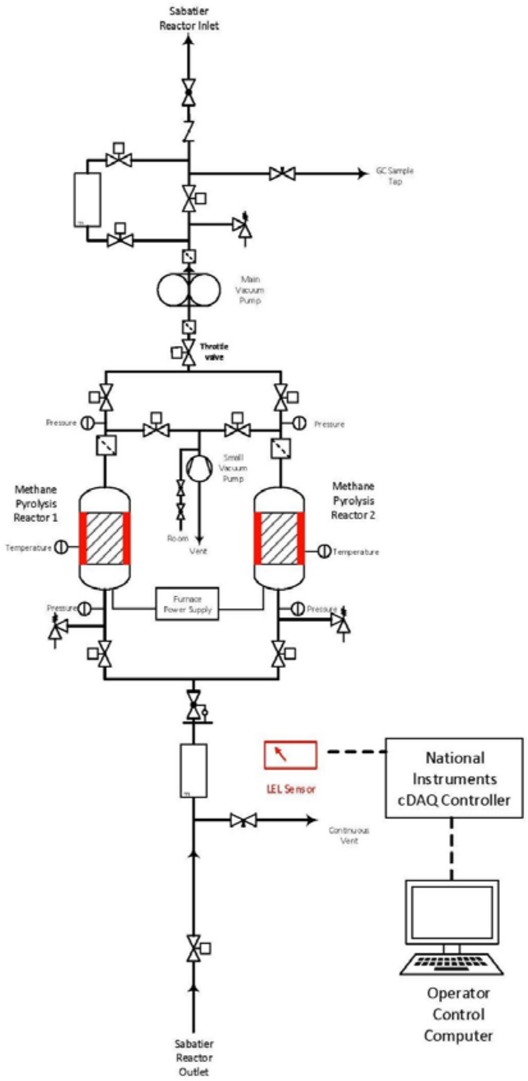
Proposed brassboard design

- 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.

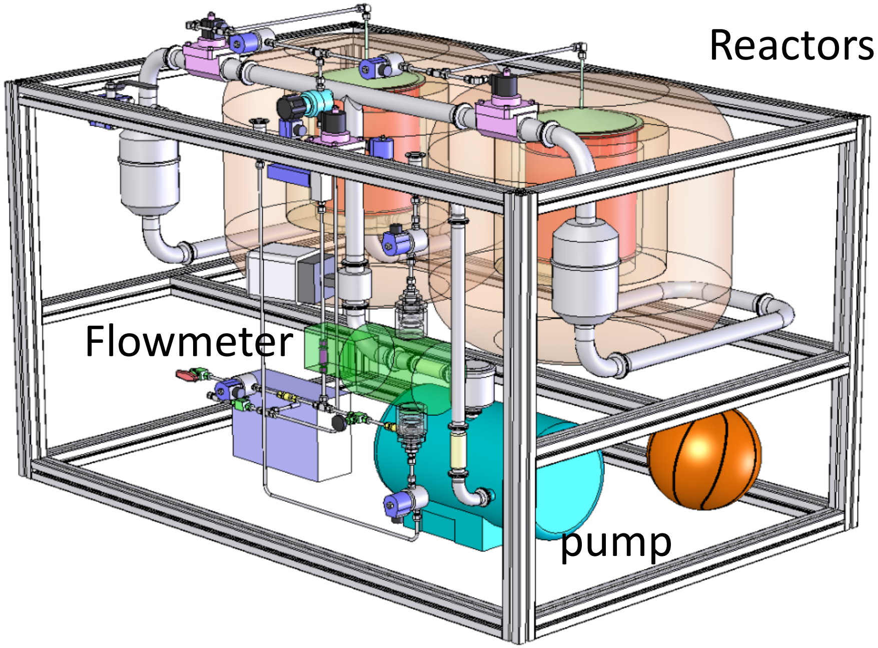


Specification	Value
Internal volume	10.9 L
Weight	27 kg
Maintenance interval	7-11 days
Average temperature	1120°C
Pressure	100 torr
Power requirement	730 W

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 H_2/CO_2 of 4.4)		
	CH_4 conversion		
Compound	**65%**	**75%**	**80%**
Hydrogen	73.95%	76.59%	77.71%
Methane	5.59%	2.23%	0.79%
Water	3.10%	3.21%	3.26%
Nitrogen	0.17%	0.17%	0.18%
Carbon monoxide	0.34%	0.36%	0.36%
Acetylene	0.01%	0.01%	0.01%
Benzene	0.03%	0.02%	0.03%
Carbon dioxide	16.81%	17.41%	17.66%
Flow rate (sccm)	8915	8611	8489

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

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

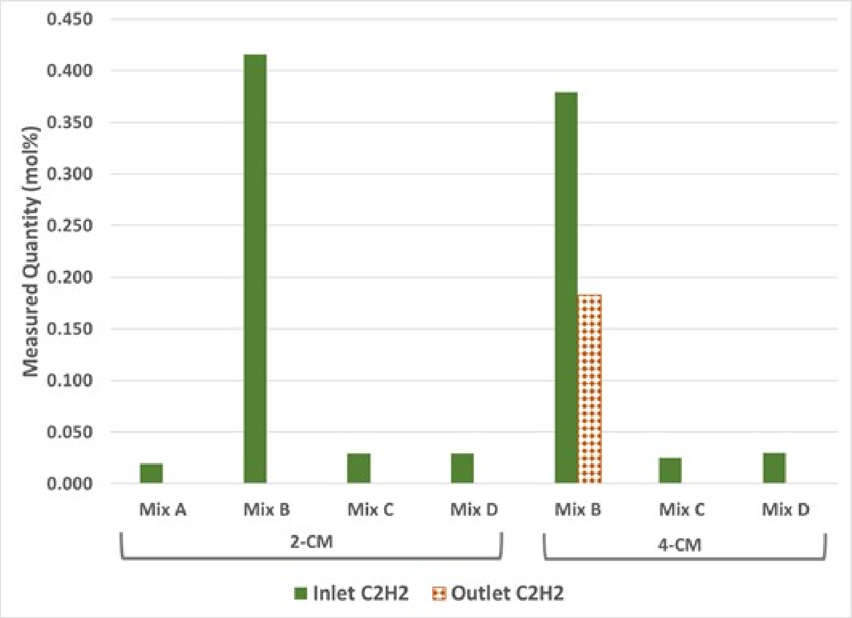
Component	**Challenge Gas (mol %)**			
	Mix A	Mix B	Mix C	Mix D
Benzene	0.20	0.01	0.02	0.02
Methane	9.98	25.10	5.68	17.90
Carbon monoxide	0.00	0.00	3.82	3.29
Acetylene	0.10	0.50	0.04	0.04
Hydrogen	89.72	74.39	90.44	78.75

- 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 $H_2 – CO_2$ at 2-crew and 4-crew rates
  - Baseline tests conducted between each challenge test to evaluate catalyst performance

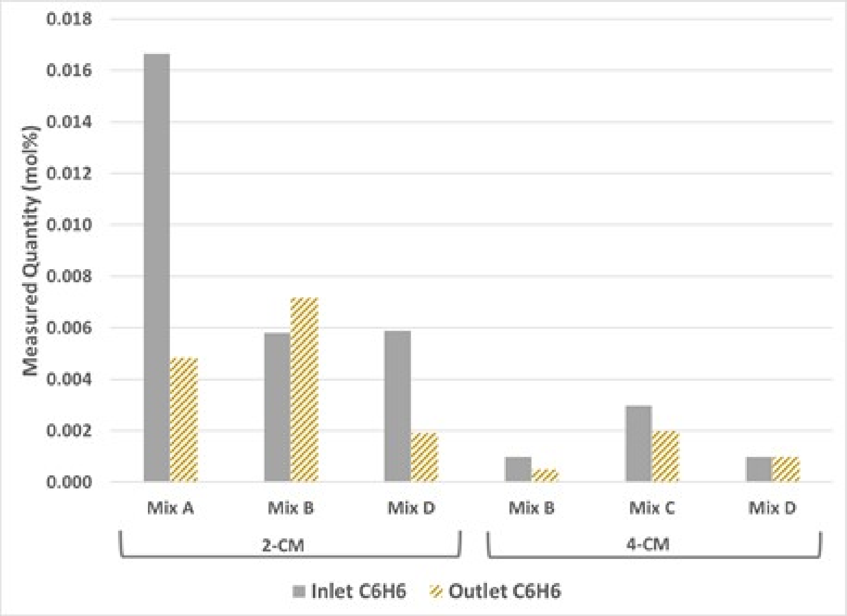
Run	**Rate**	**Feed**	**Exposure Time (hrs)**
1,3,5,7,9	2-CM	BT	22.8
2	2-CM	Mix A	2.9
4	2-CM	Mix B	4.5
6	2-CM	Mix C	3.2
8	2-CM	Mix D	2.4
10,12,14, 16,18	4-CM	BT	4.7
11	4-CM	Mix A	0.0
13	4-CM	Mix B	1.3
15	4-CM	Mix C	0.9
17	4-CM	Mix D	1.1

Catalyst Challenge Testing: Goal 1
Fate of Hydrocarbons

Acetylene Outlet Concentrations



Benzene Outlet Concentrations



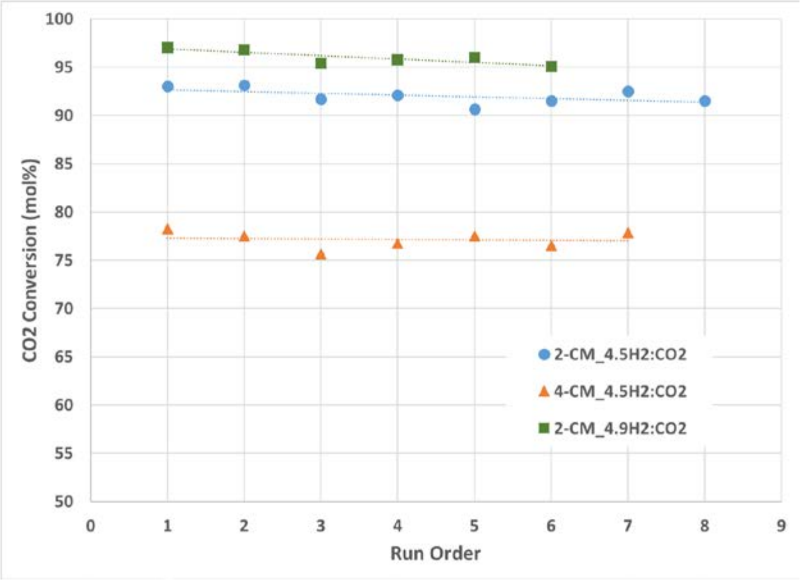
- Expectation:
  - If no reaction of hydrocarbons, byproduct concentrations would have increased due to reduction in number of moles of product vs. reactant and water removal
- Observations:
  - Acetylene entirely consumed in Sabatier reactor in all but one run. No hydrogenation products (ethylene, ethane) detected
  - Benzene partially removed under same conditions

Catalyst Challenge Testing: Goals 2 & 3

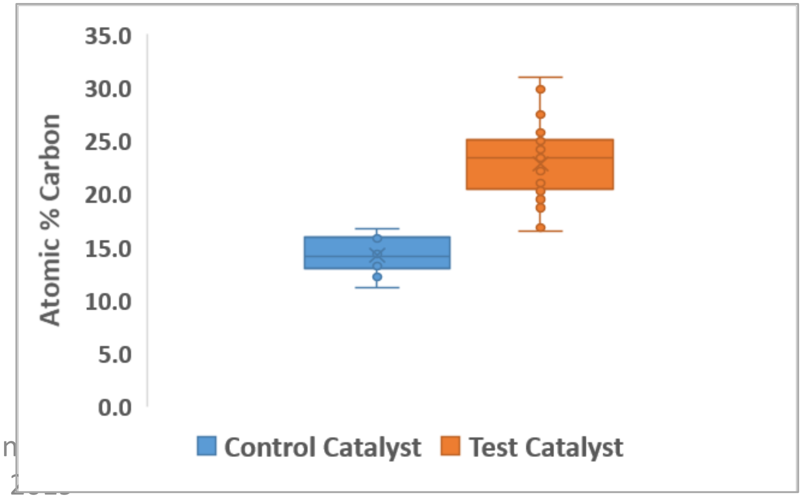
- Goal 2: Effect on Catalyst Performance
  - Baseline testing shows no significant change in performance over duration of the test after repeated exposure to challenge mixtures
- Goal 3: Carbon Deposition
  - SEM-EDX shows higher concentration of surface carbon on catalyst
  - Source of observed carbon 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.

CO_2 Conversion Using Baseline Conditions



SEM-EDX - % C on Catalyst



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

Daniel Barta

Jeff Mehan

Ellen Rabenburg