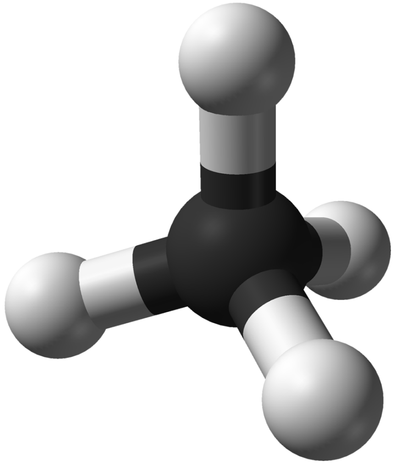
Membrane bioreactors for in situ carbon upcycling

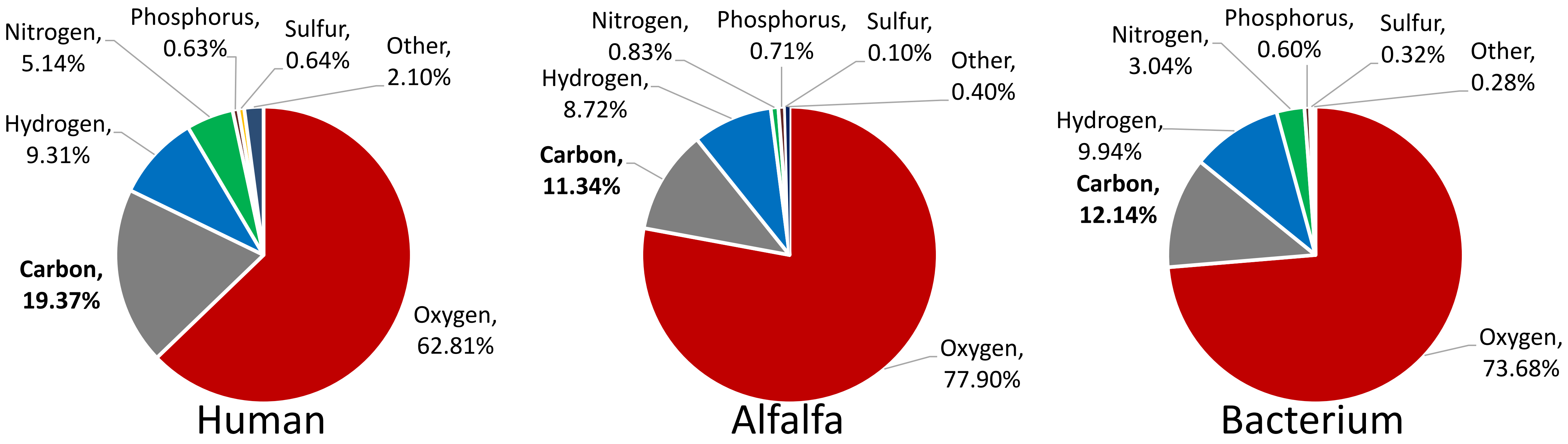
Johan Vanneste[1], Christopher Marks[1], Chelsea Billingsley[1], Allison Pieja[2], Molly Morse[2], Tzahi Cath[1], Junko Munakata Marr[1]

[1] Advanced Water Technology Center (AQWATEC), Colorado School of Mines
[2] Mango Materials, Oakland, CA



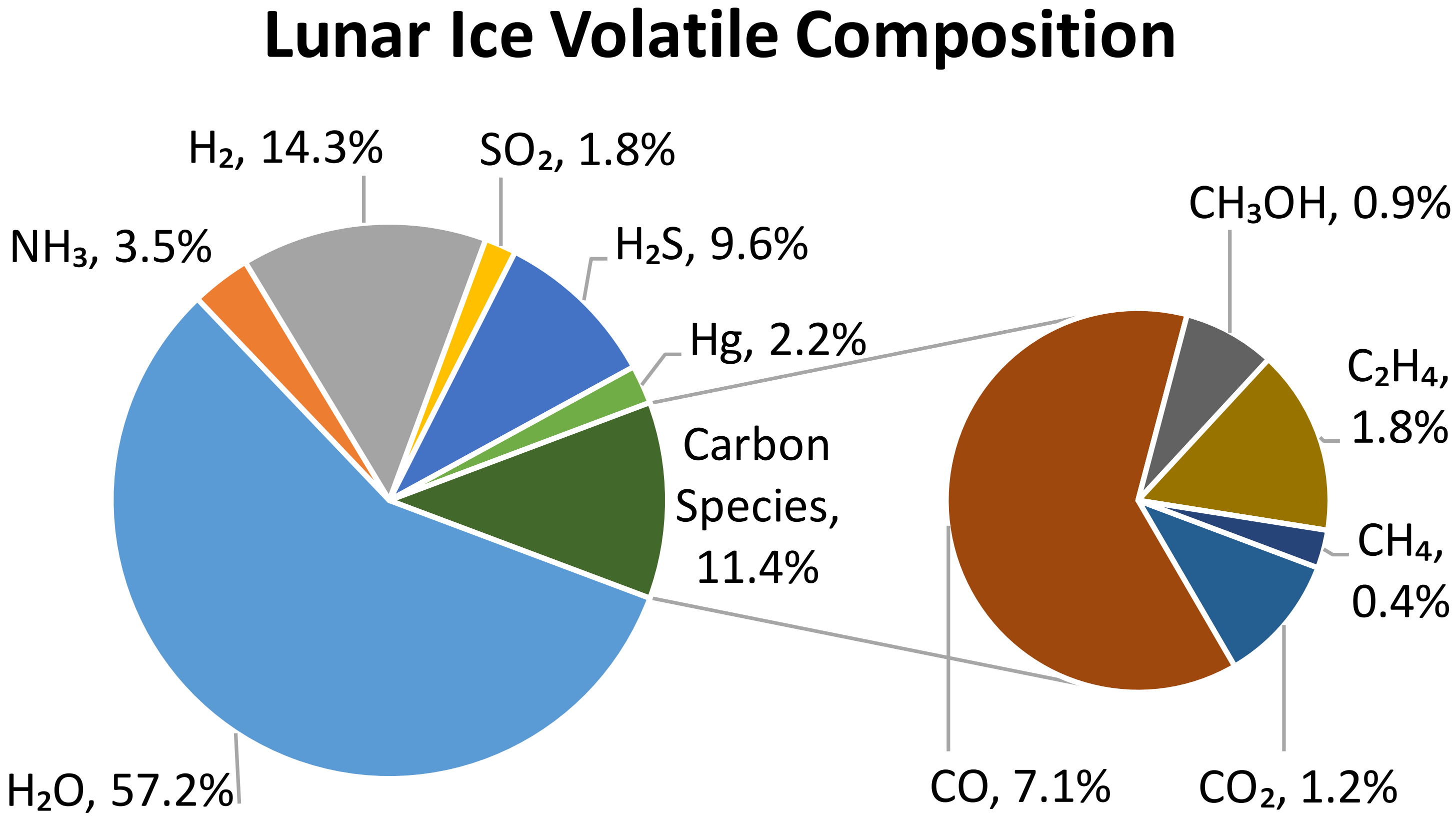
10th Space Resources Roundtable, June 12, 2019

Beyond water: Elemental composition of life



Martian and lunar carbon sources

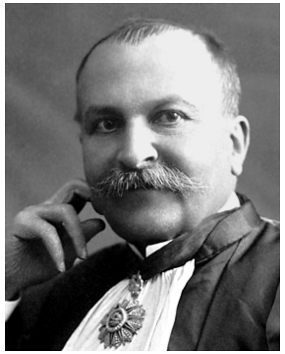
- Martian atmosphere
  - 95.3% carbon dioxide @ 6mbar
  - 25% condenses seasonally
  - 1.9% nitrogen gas
- Lunar ice
  - LCROSS mission found 11.4% carbon species in volatiles fraction
  - 3.5% NH_3

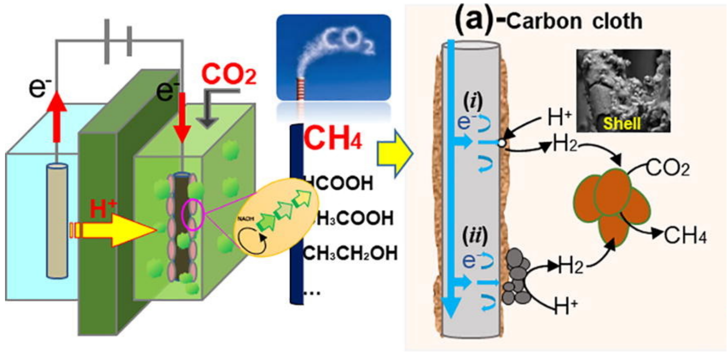


The case for life-supported space exploration

- Advantages of biological/biomimetic processes for carbon upcycling
  - Operate at mild temperature, pressure and chemical environment
  - Highly selective → High conversion rates and efficiency
  - Always produce biodegradable/recyclable products/waste streams
  - Don`t use exotic materials
  - Compact
- Example: Carbon dioxide to methane conversion

<u>Sabatier Process (1897)</u>
- 400 °C
- Elevated pressure
- Nickel catalyst



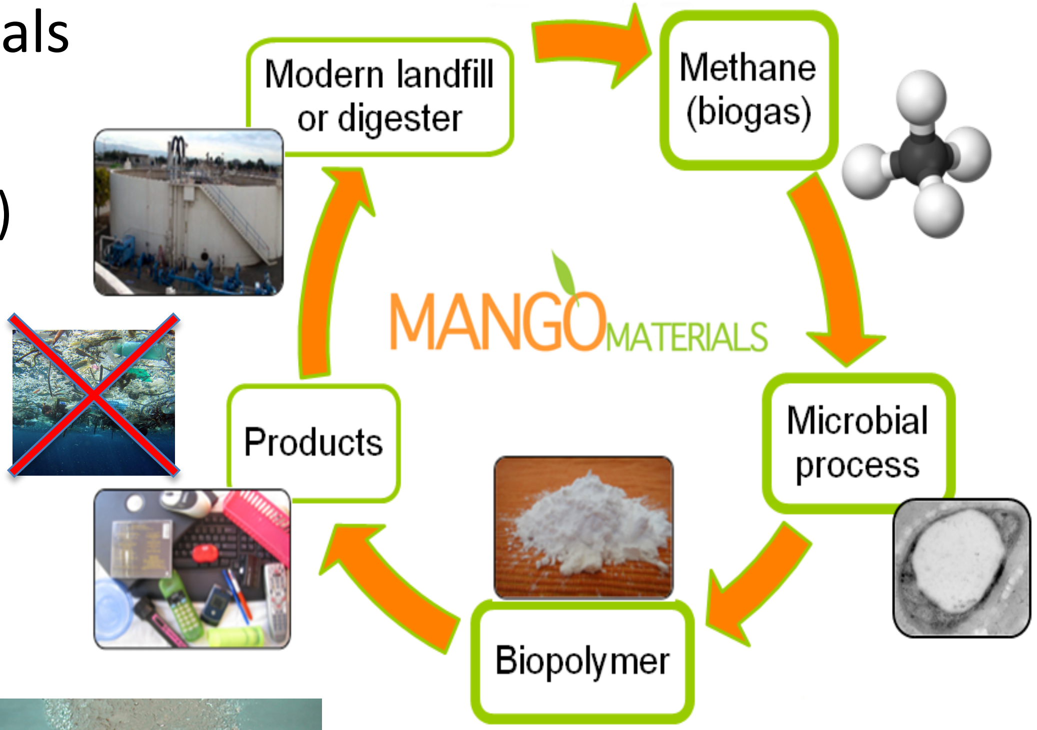


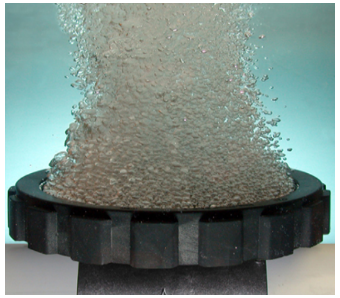
<u>Bioelectro-methanogenesis</u>
- 20 °C
- 1 atmosphere
- Carbon electrodes

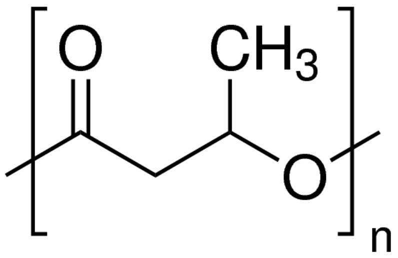
(Zhen et al. 2018)

Beyond fuels: From methane to bioplastics

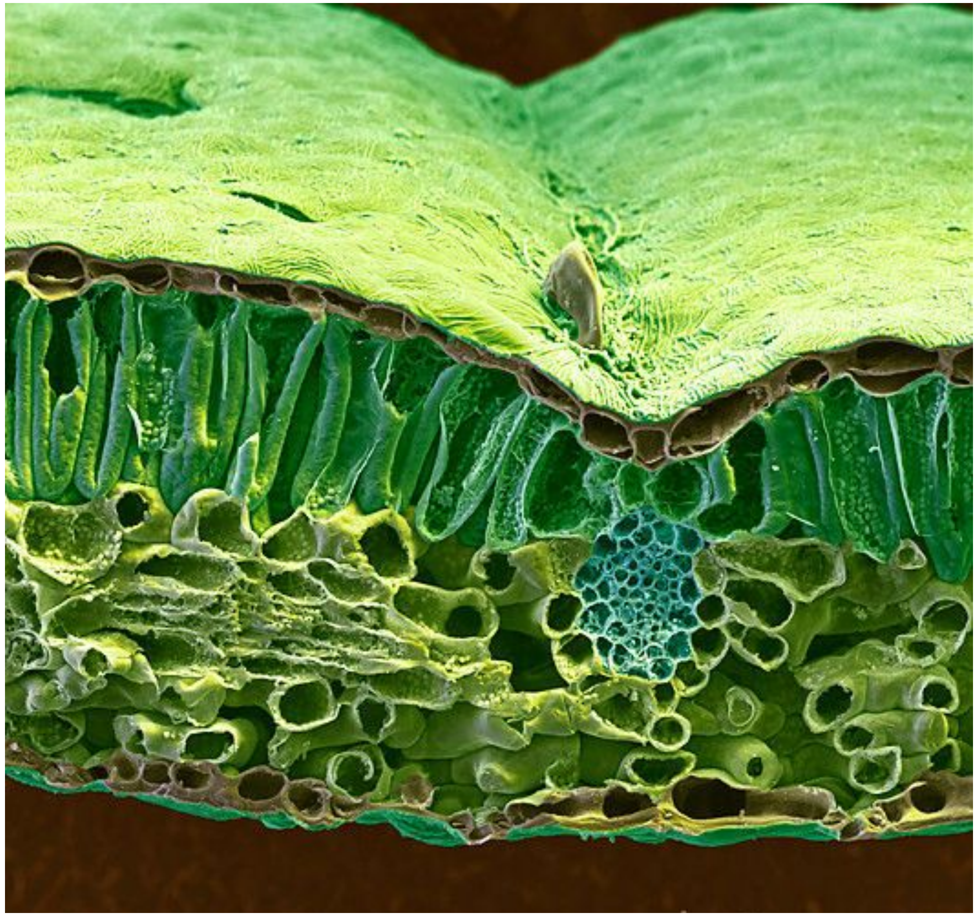
- Biocondensation by methanotroph type II to Polyhydroxybutyrate (PHB)
  - Biologic growth optimization by Mango Materials
  - PHB similar to polypropylene (PP)
    - Production temperature: 37°C versus 80°C (PP)
    - Production pressure: 1 atm versus 40 atm (PP)
    - Biodegradable
    - Nitrogen starvation triggers PHB production
    - Has good 3D print quality mixed with Polylactic acid (= another biopolymer)
  - Currently gas delivery through gas sparging
    - Non-uniform gas distribution which is **even worse in low-gravity environment**

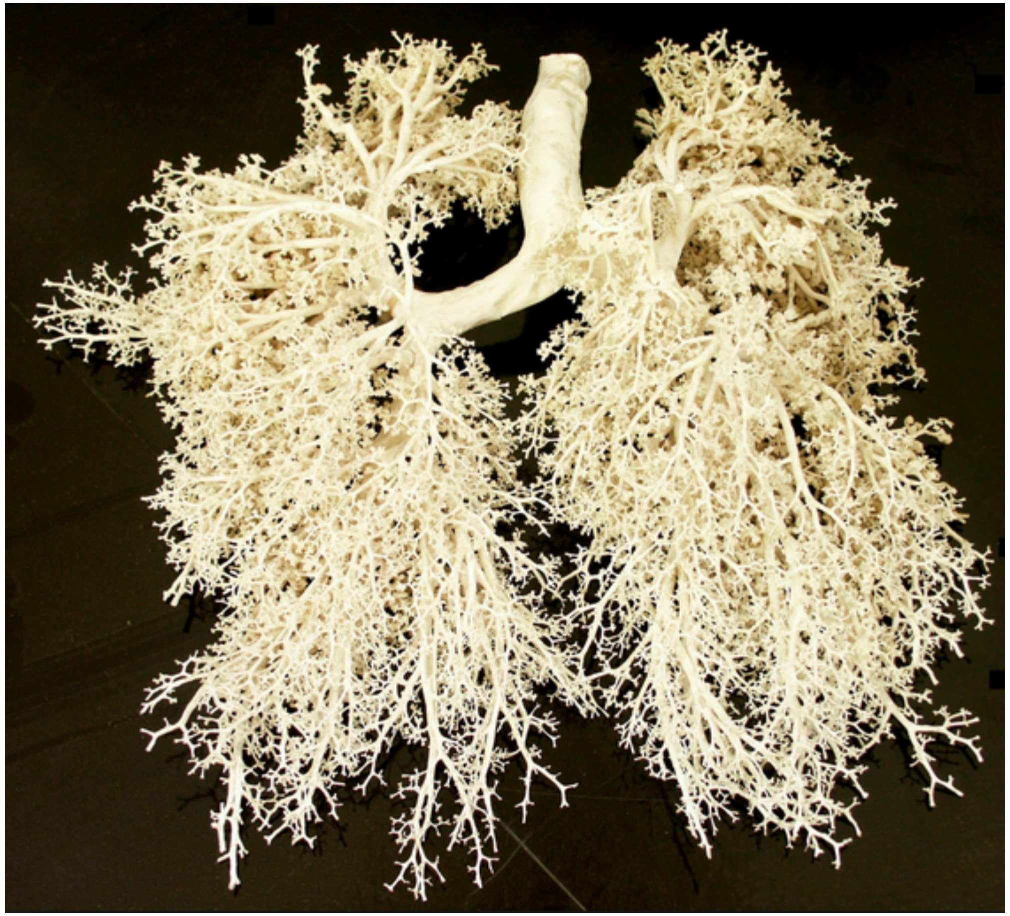






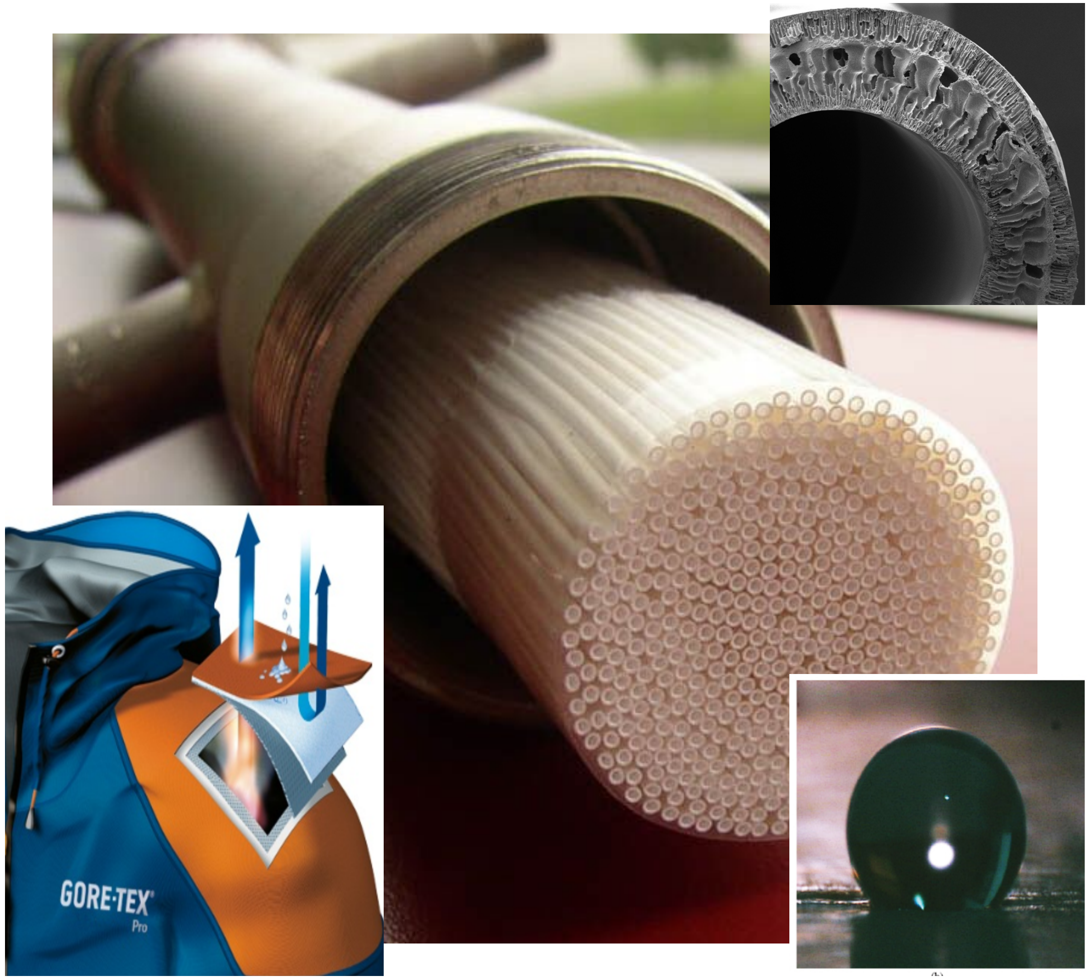
How do biological reactors breathe?





What are breathable membranes?

- Hydrophobic microporous materials
  - Up to 85% porosity
  - Pore size: 0.1 - 0.5 micron
  - Thickness down to 50 micron
  - Typical materials: PP, PVDF, PTFE, PE
  - Cannot handle pressure or surfactants
  - High vapor fluxes



- Dense polymeric membranes
  - Non-porous
  - Non-wettable
  - Typical materials: PDMS (silicone)
  - Low vapor fluxes, but can be pressurized and no problem with surfactants!

Goal and objectives

- Goal NASA STTR Phase II

  Design an automated membrane-aerated bioreactor (MABR) that can produce PHB

- Objectives
  - Membrane gas transfer characterization and selection procedure
    - Pure water and oxygen
    - During growth trial and mixed gases
  - Safety system for methane leakage
  - Selection of sensors and flow and pressure control valves
    - Gas utilization efficiency
    - Growth rate/PHB production monitoring and optimization
  - Implement control system
  - Implementation of gas recycle/intermittent gas delivery

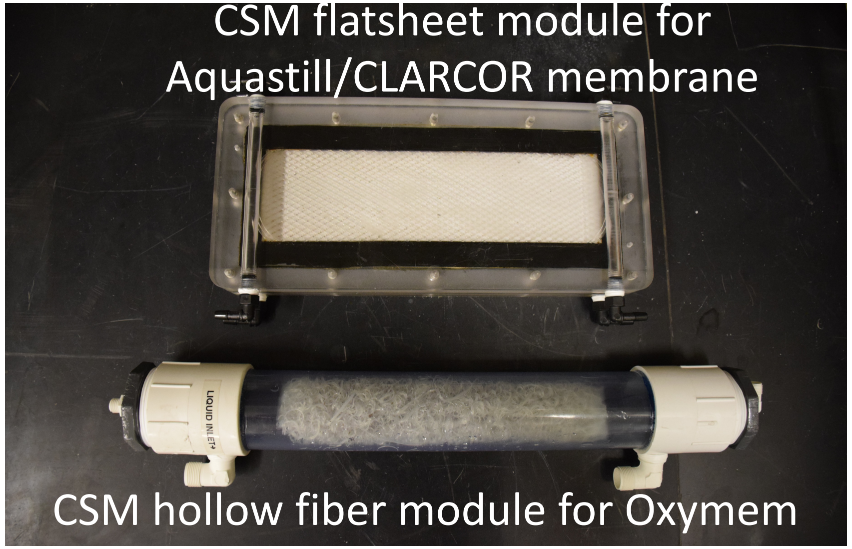
Materials and Methods

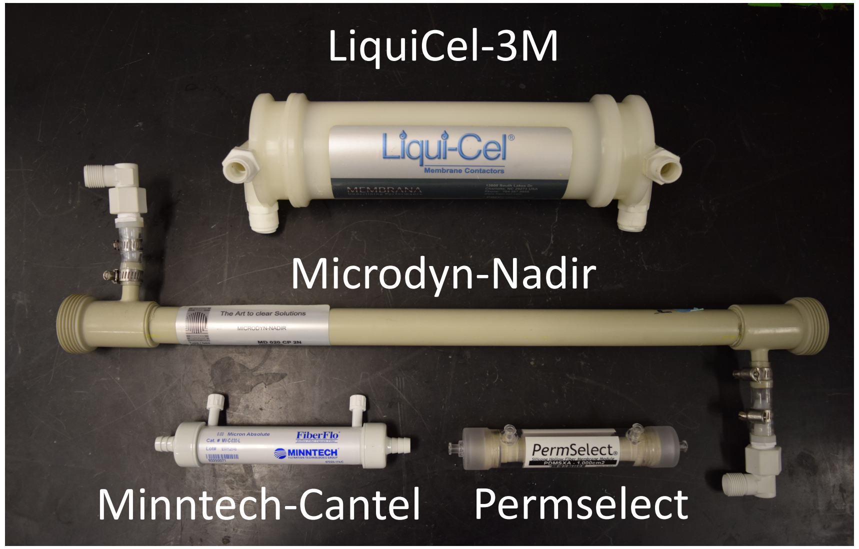
Membrane characteristics

Manufacturer	Model number	Material	Membrane type	Porosity (%)	Pore size (µm)	Thickness (µm)
Aquastill	0.3 micron	Polyethylene	Flat sheet	85	0.3	76
CLARCOR	QP952	PTFE	Flat sheet	70-85	0.2	225
LiquiCel-3M	X50 Fiber	Polypropylene	Hollow fiber	40	0.04	40
Microdyn-Nadir	MD 020 CP 2N	Polypropylene	Hollow fiber	-	0.2	500
Minntech-Cantel	MV-C-030-L	Polypropylene	Hollow fiber	40	0.03	28
Oxymem		PDMS (Silicone)	Hollow fiber	dense	dense	50
Permselect	PDMSXA-1000	PDMS (Silicone)	Hollow fiber	dense	dense	55

Module characteristics

Manufacturer	Membrane area (m^2)	Packing density (m^2/m^3)	Specific weight (kg/m^2)
Flatsheet CSM (CLARCOR/ Aquastill)	0.0154	6	181
LiquiCel-3M	1.4	1085	0.36
Microdyn-Nadir	0.1	244	2.08
Minntech-Cantel	0.23	2434	0.17
Permselect	0.1	973	0.86
Hollow Fiber CSM (Oxymem – 17”)	0.855	447	0.85
Hollow Fiber CSM (Oxymem – 27”)	0.855	273	1.27





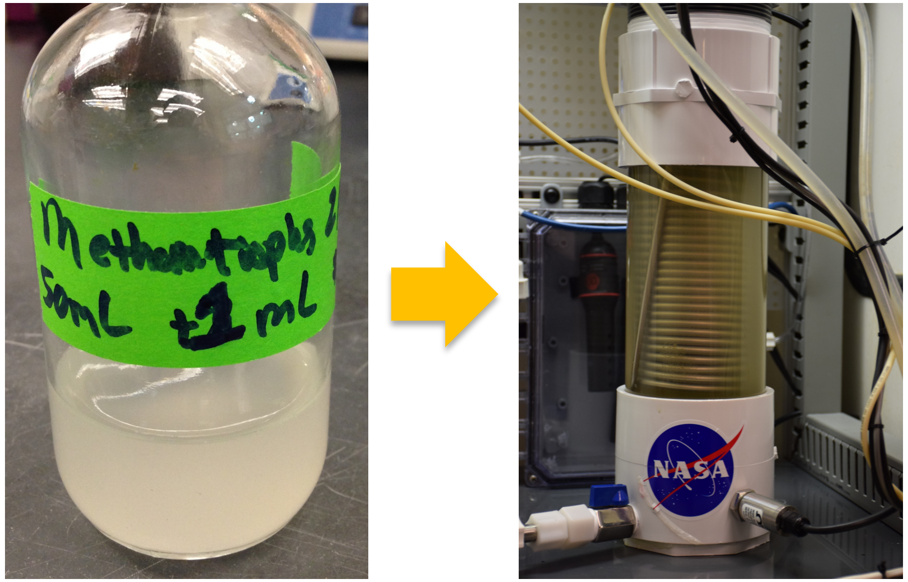
Gas transfer rate comparison membranes

- Oxygen transfer as an indicator for methane transport
  - Porous membranes are non-selective
  - Vernier oxygen sensors much less expensive than methane sensors
  - Validation required for dense membranes
- Flux determination
  - First oxygen removal by nitrogen sparging in reactor filled with DI
  - Flux calculation based on initial oxygen concentration increase over time

$$\mathrm{Flux} = \frac{dC_{O_2}}{dt.A_{membrane}.V_{reactor}} \left[\frac{mg\ O_2}{m^2.min}\right]$$

Growth trial operation

- Bacterial inoculum
  - 250 mL of inoculum per 4.5L growth trial
  - 5 mL from previous methanotroph type II microcosm with media from Mango Materials
  - Growth vial 50:50 headspace O_2/CH_4



- Operating conditions controlled by Labview
  - Temperature: 37 °C
  - pH: 7
  - Gas flows: 0.5 SLPM CH_4 and 0.1 SLPM O_2
- Monitoring: T, P, pH, DO, gas flows and concentrations (CH_4, O_2, CO_2&H_2O)
- Sampling: Ammonium (Hach TNT), Optical Density, Bleach ratio & FTIR (PHB)

MABR 3.0

CH_4/O_2 mass flow controllers

0.85 m^2 Oxymem membrane module

Exhaust CH_4 sensor

Membrane outlet dissolved O_2 probe

CH_4 alarm with automatic gas shut-off

Inline Total Suspended Solids probe

Gas pressure relief valve

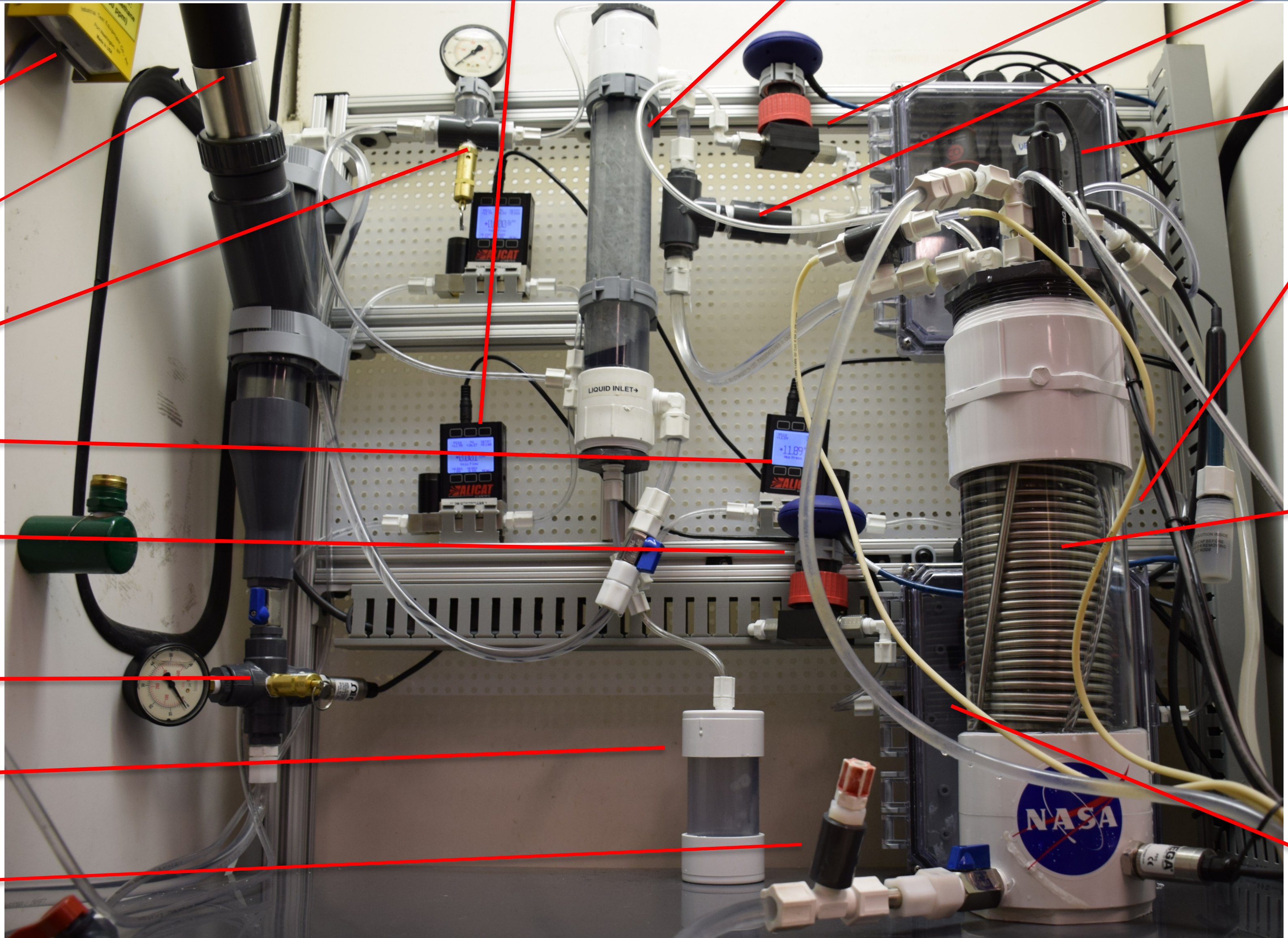
Back-pressure controller

Headspace CH_4 probe

Pressure sensor and liquid relief valve

Condensate collector

Gastight sampling port



Gastight box with
- Exhaust CO_2 sensor
- Relative humidity
- O_2 gas sensor

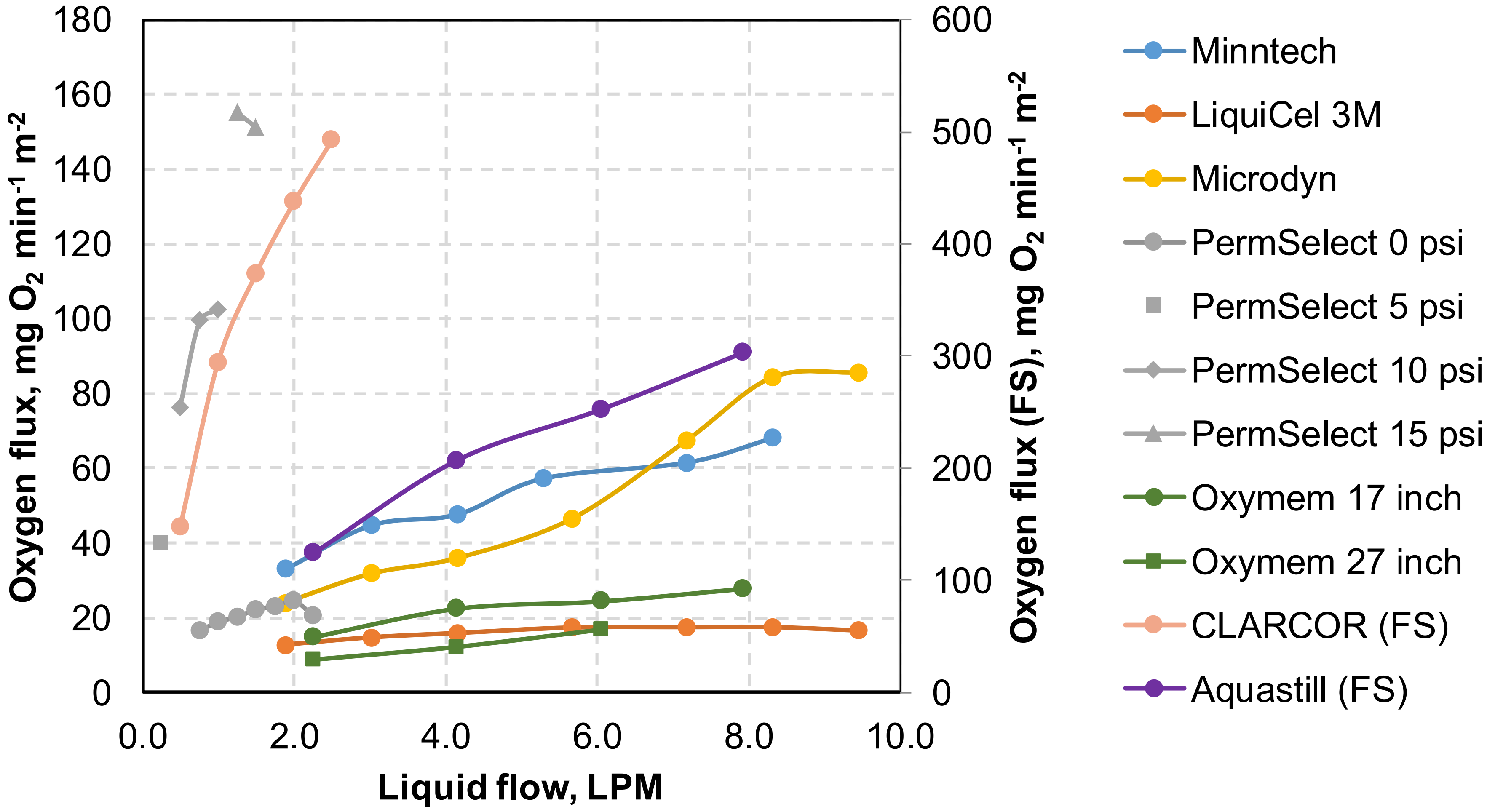
Exhaust flow meter (behind)

4.5 L Reactor with
- Dissolved Oxygen sensor
- Ammonium probe
- pH probe
- Temperature sensor
- Level sensor
- Cooling/Heating coil
- Base/nutrient dosing

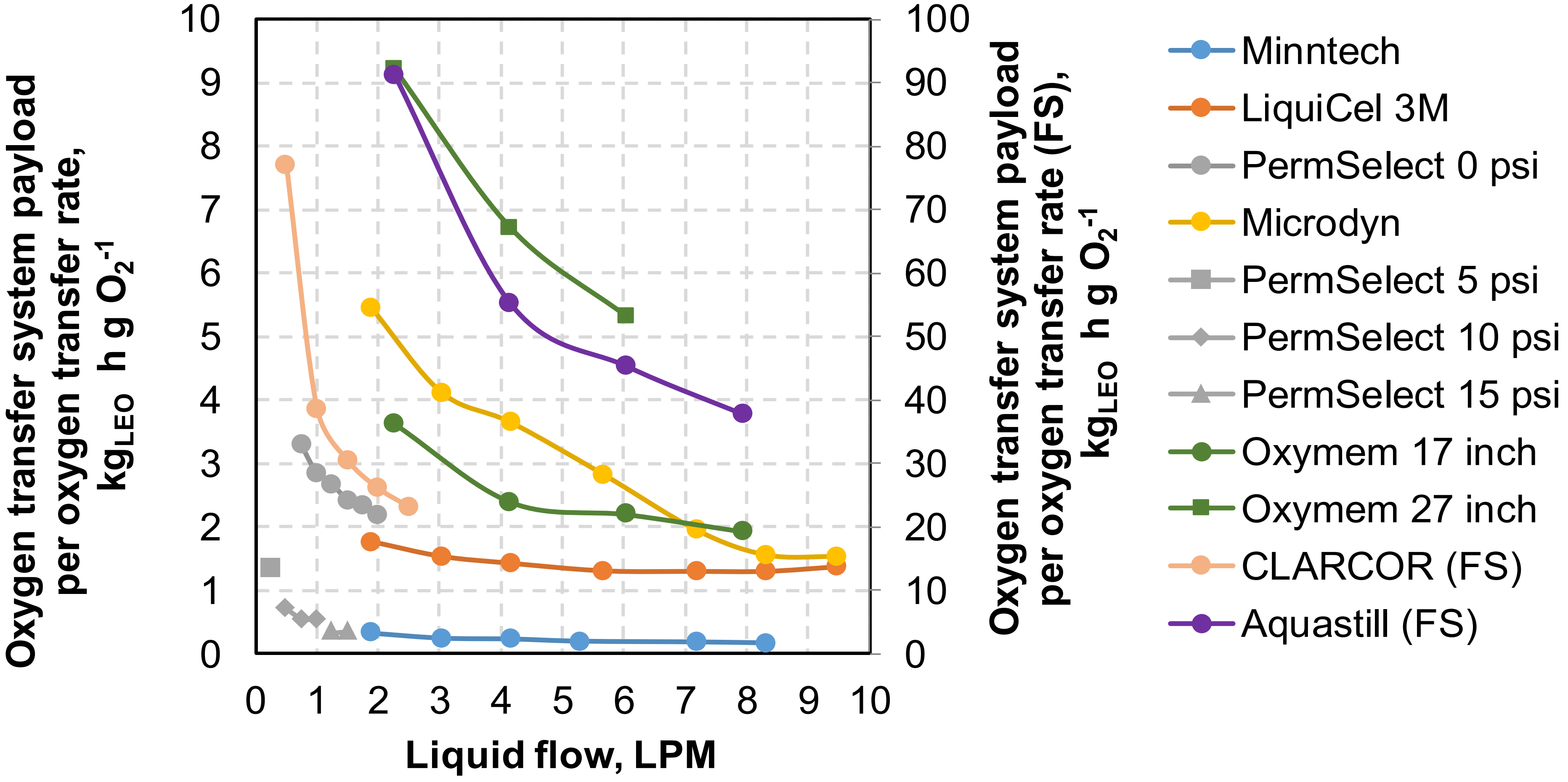
Gastight box with headspace CO_2, relative humidity, and O_2 probes

Results and Discussion

Membrane flux

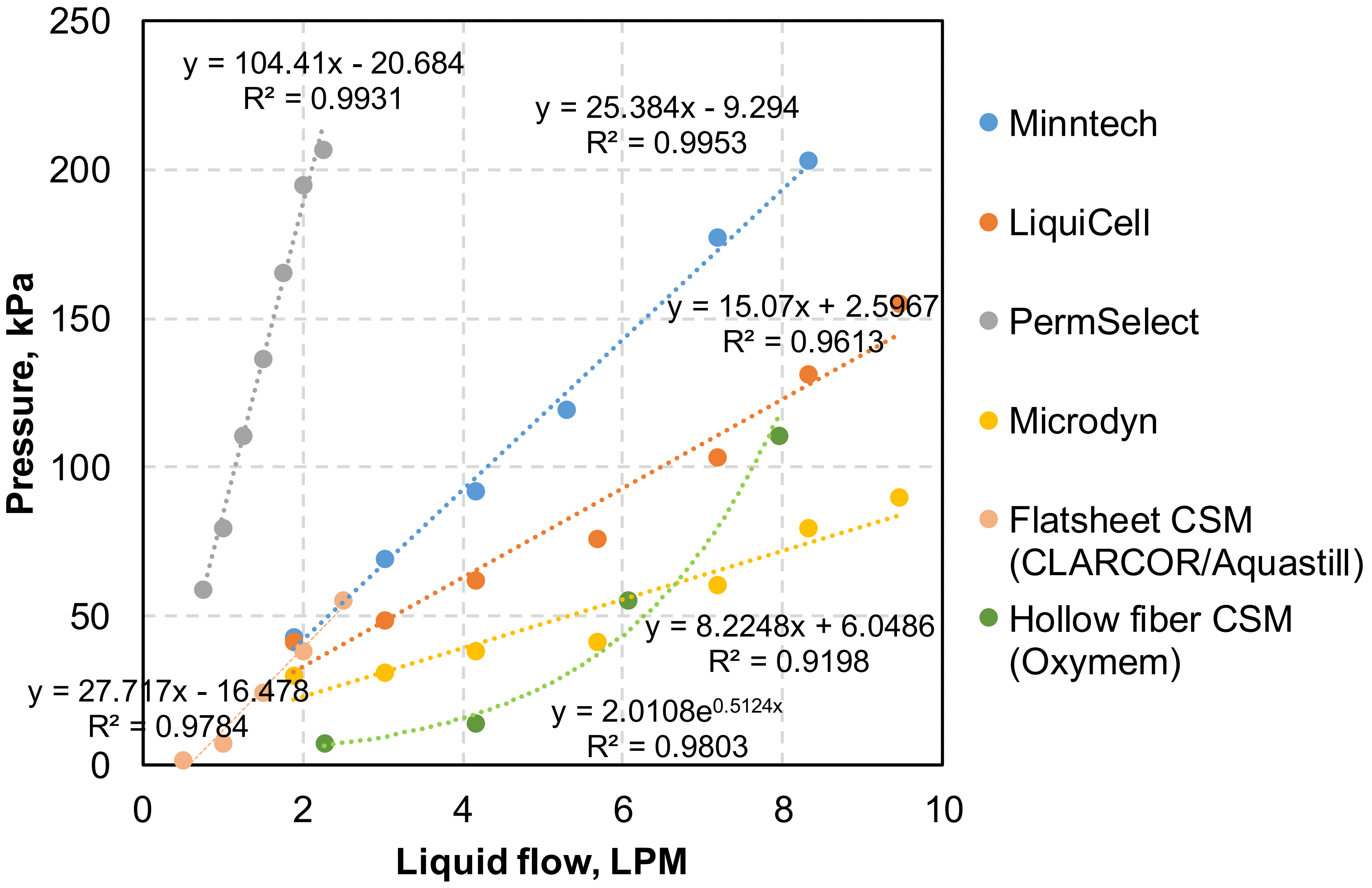


Equivalent system mass on Mars of gas transfer system

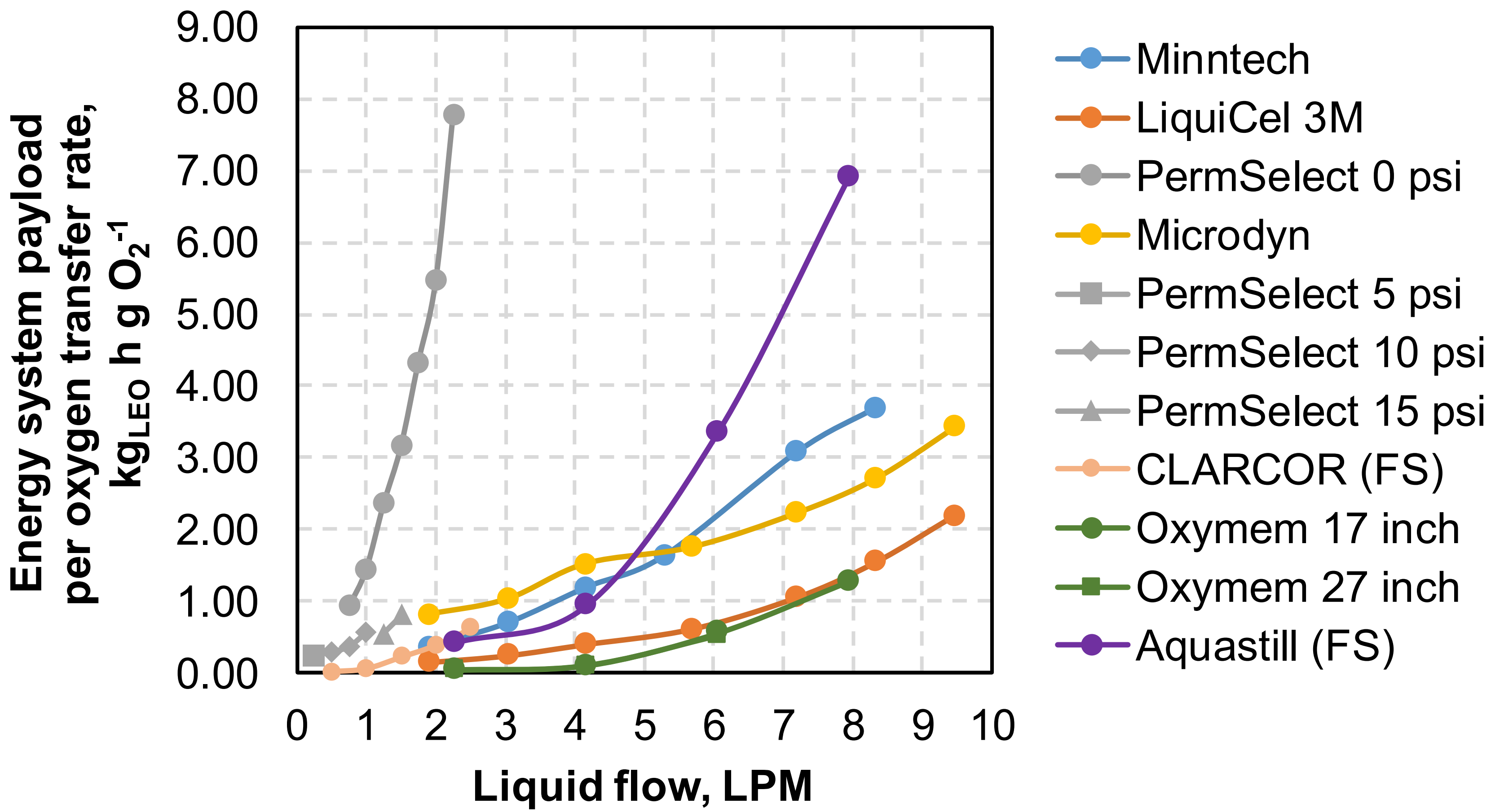


Based on packing density (m^2/m^3) and specific weight (kg/m^2) membrane modules and 3.77 kg_{LEO}/kg_{Mars} (Anderson et al. 2018)

Pressure drop in membrane module

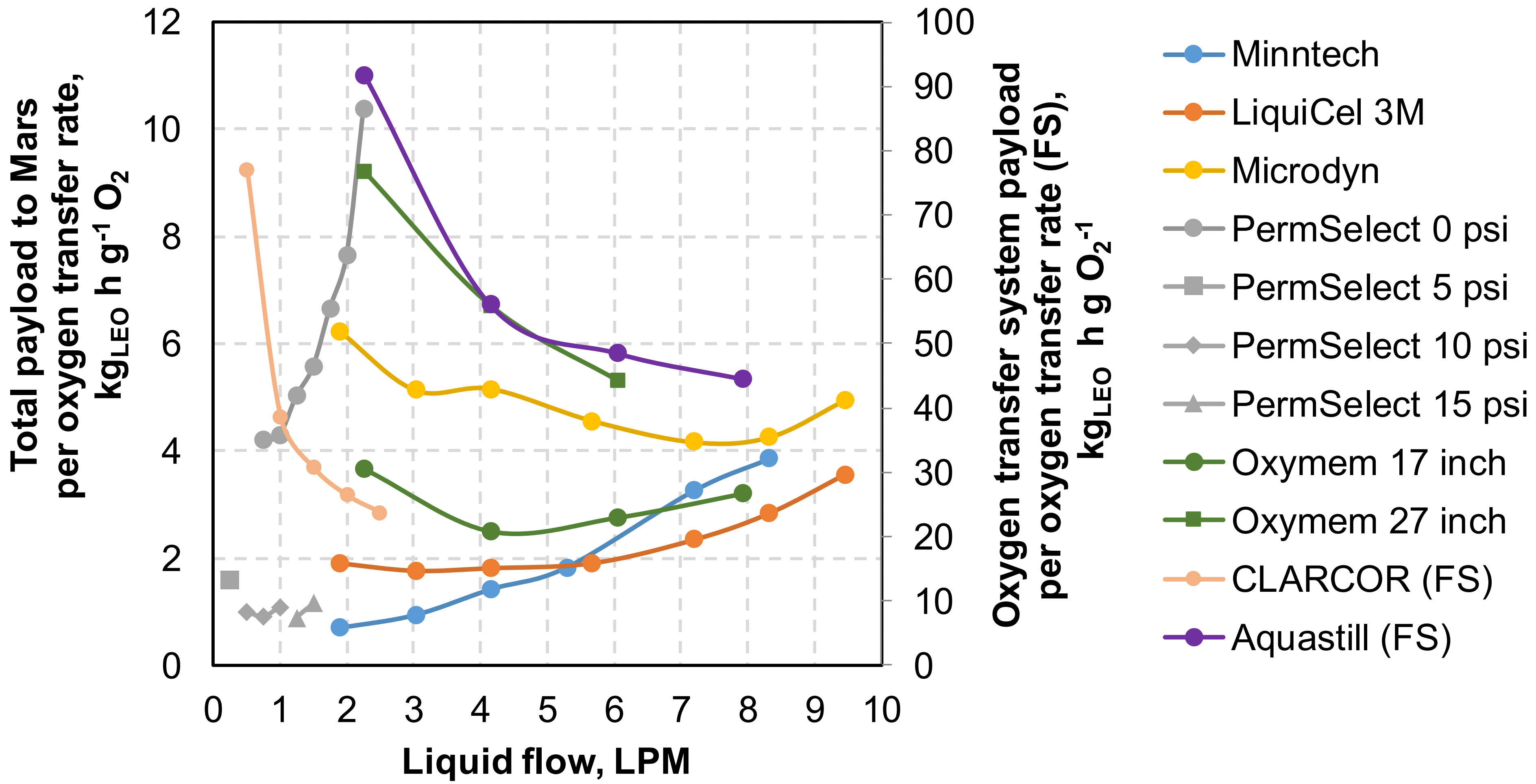


Equivalent system mass on Mars of energy system



Based on 70% pump efficiency and 87 kg_{LEO}/kW_{Mars} (Anderson et al. 2018)

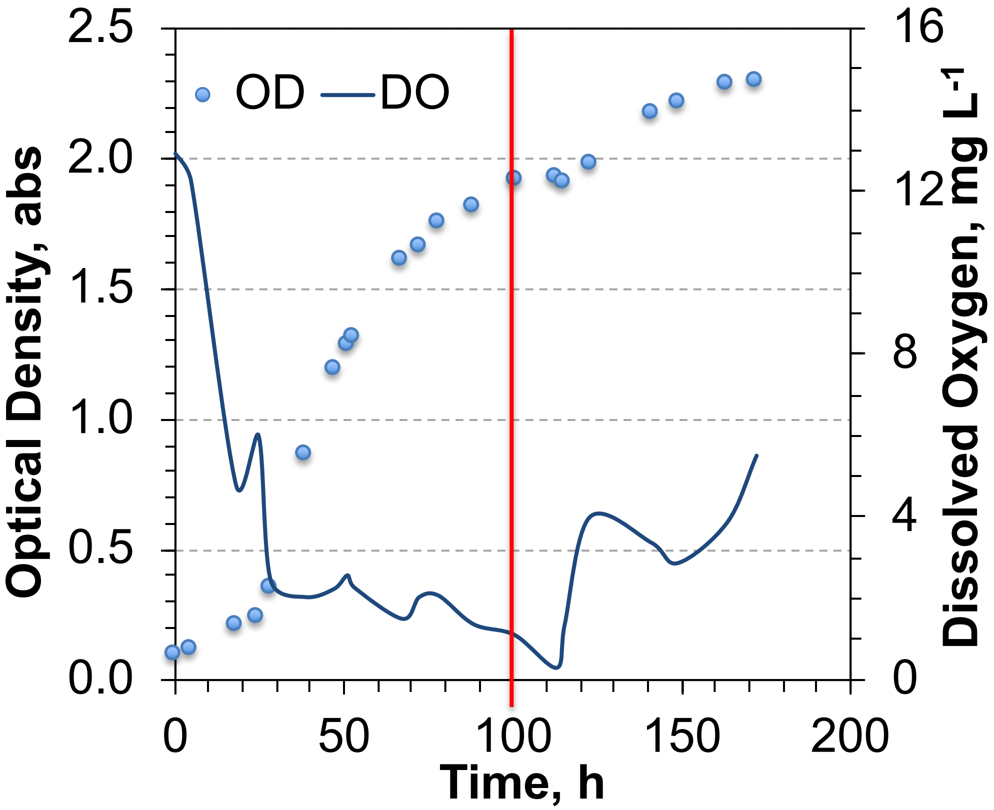
Equivalent system mass on Mars of total membrane system

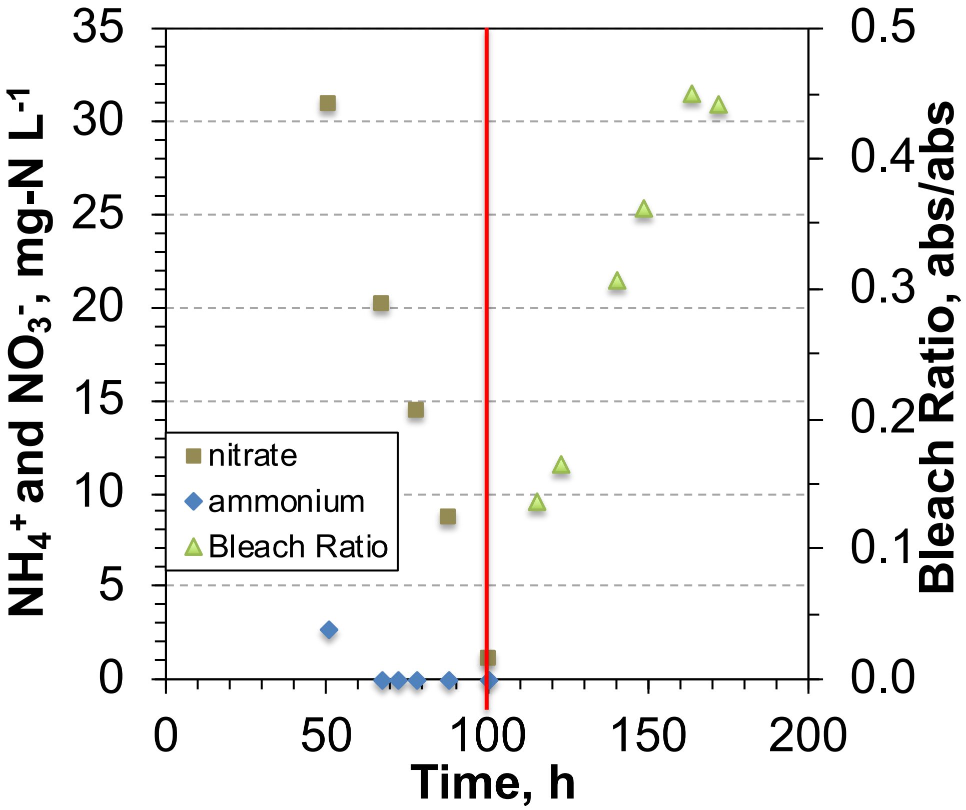


Based on 3.77 kg_{LEO}/kg_{Mars} and 87 kg_{LEO}/kW_{Mars} (Anderson et al. 2018)

Growth trial results

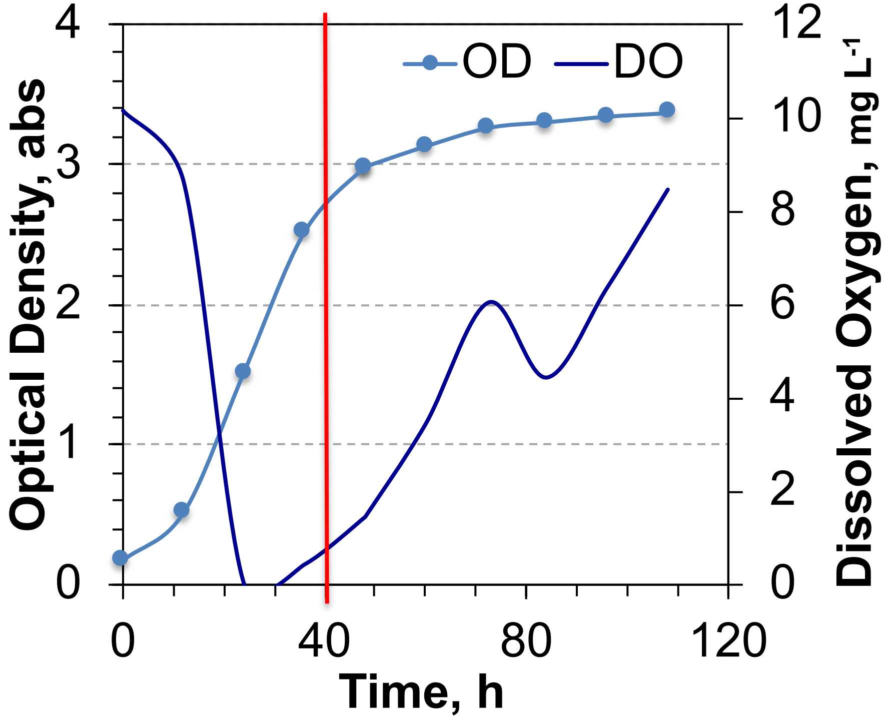
- Flatsheet CSM module with CLARCOR membrane
  - 2x0.0154 m^2 in parallel, 2 LPM liquid flow rate, 30°C
  - PHB production after 100h, 22 wt% PHB per dry cell mass (FTIR)

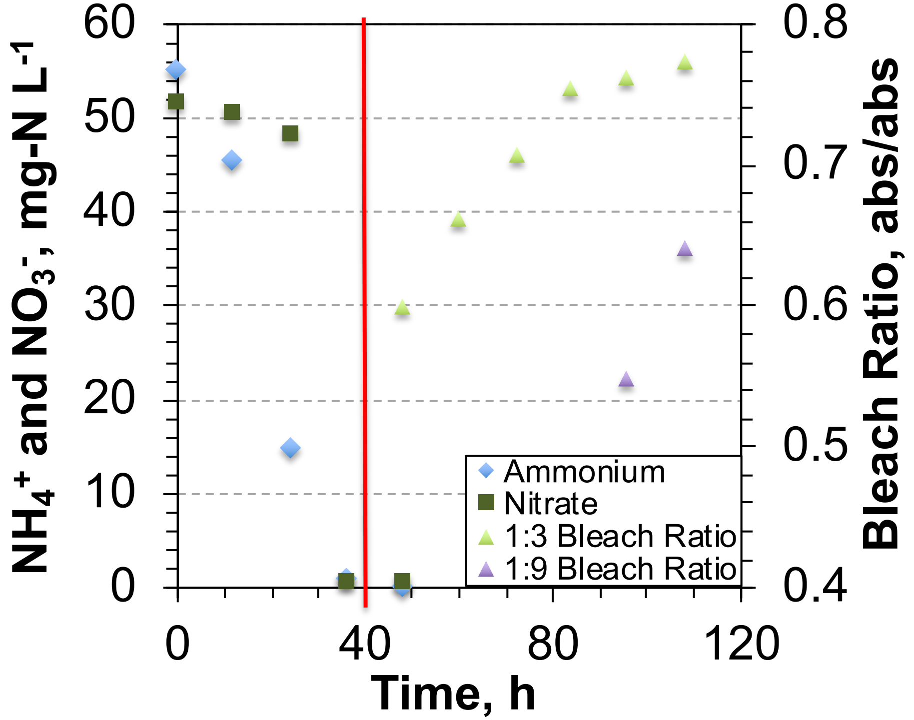




Growth trial results

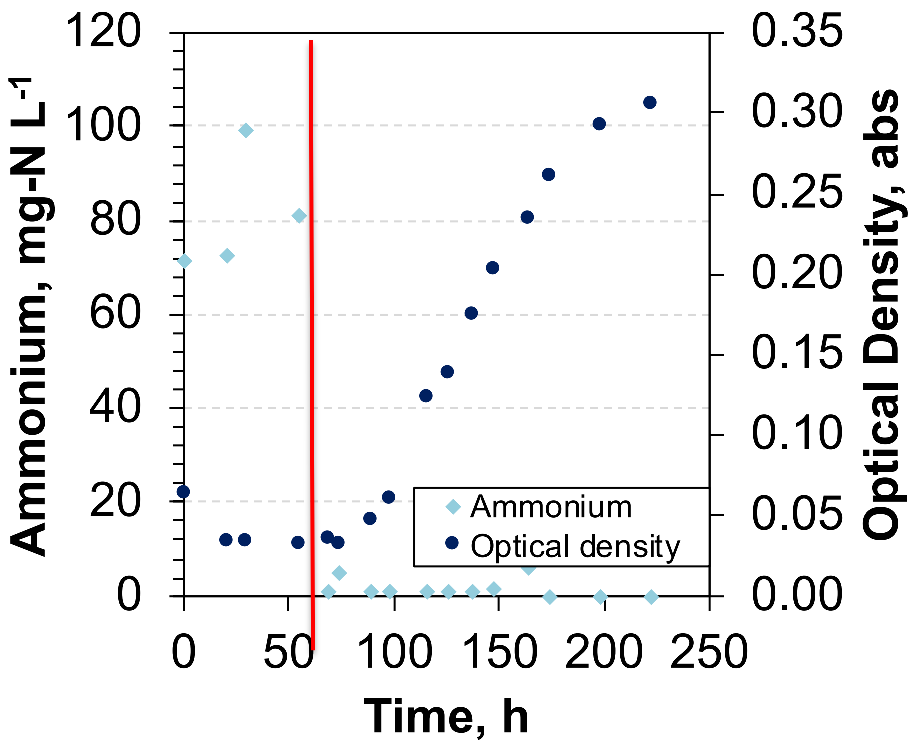
- Hollow fiber Minntech module
  - 0.23 m², 2 LPM liquid flow rate, 30°C
  - PHB production after 40h, 47 wt% PHB per dry cell mass (GC)
  - However, irreversible membrane wetting after 400h of operation!





Growth trial results

- Preliminary results CSM hollow fiber module with Oxymem membrane
  - 0.855 m^2, 2 LPM liquid flow rate, 37°C, 3 psi back pressure, nitrate-free recipe
  - Dense membranes don`t wet, can be pressurized and less water vapor loss
  - PHB production after 60h, 0.45 g H_2O h^{-1} m^{-2} water loss

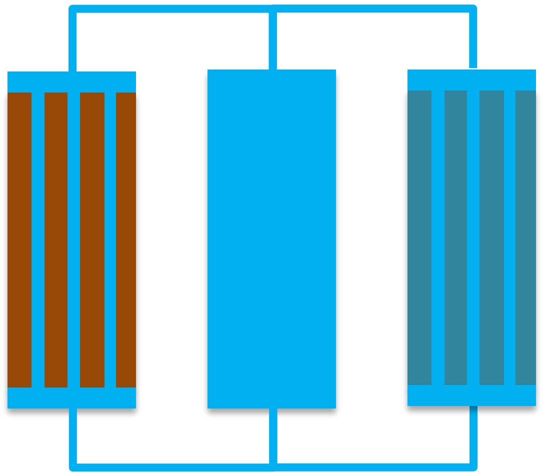


Conclusions

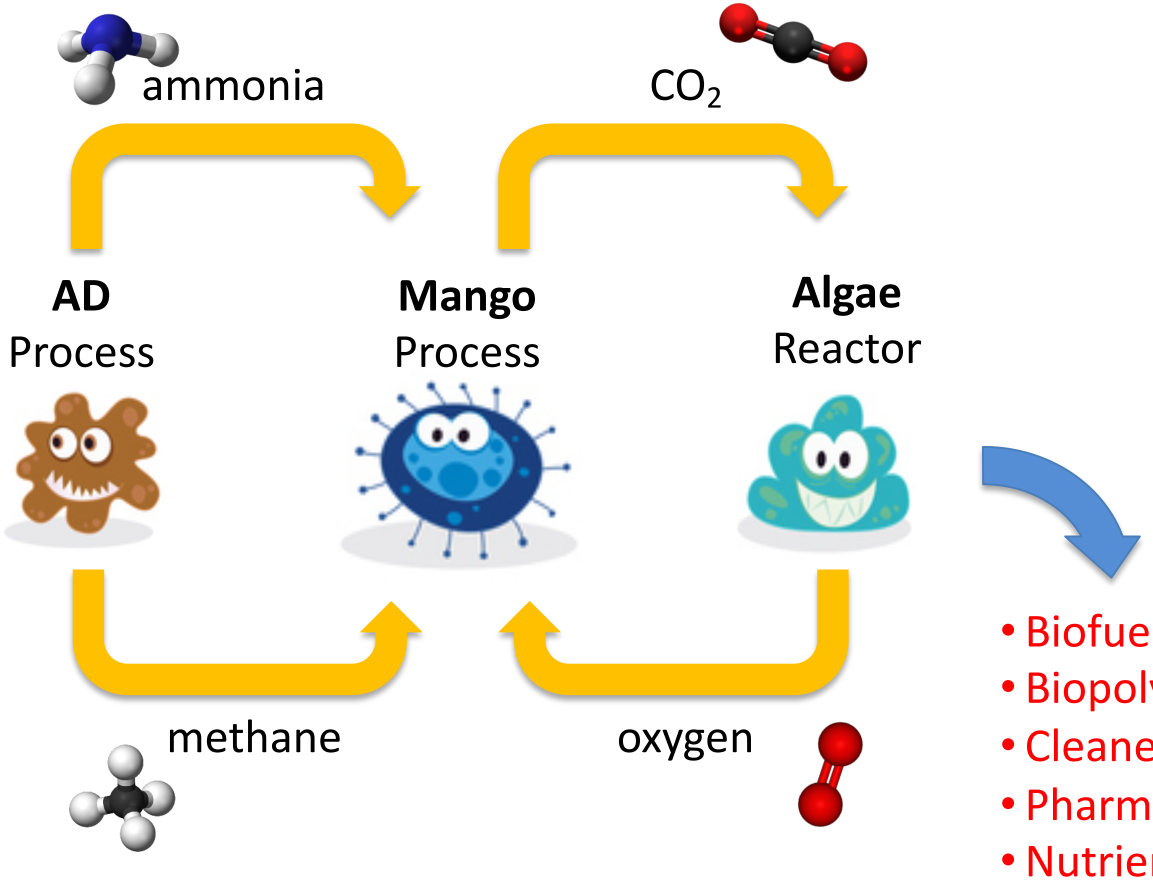
- Gas transfer and pressure drop of 7 different membranes was characterized
- Every membrane exhibited a liquid flow rate minimizing ESM to Mars
- Minntech, Permselect, Liqui-Cel and Oxymem (17”) had the lowest ESM
- PHB was successfully produced with three different membranes
- A maximum PHB content of 47 wt% per dry mass was obtained with the Minntech membrane
- However, the methanotrophs seem to produce a surfactant-like molecule that irreversibly wetted the Minntech membranes after >400h
- Further tests will be conducted with non-wettable dense Permselect and Oxymem membranes

The future? Breathing Reactor Networks!

- Microbial hybrid system with liquid-liquid membrane contactors
  - Half the contactor surface
  - No external gas input
  - No vapor condensation issues
  - Most gas remains dissolved
    - Safe
    - Energy efficient



- Manure
- Food waste
- Wastewater sludge



- Biofuels
- Biopolymers
- Cleaner water
- Pharmaceuticals
- Nutrients

Confidential

Acknowledgements

Industry

MANGO MATERIALS

OXYMEM SMARTER AERATION

Aqua|still

CLARCOR

3M

CANTEL

Funding

SBIR/STTR Phase I and II

NASA

ESF Edna Bailey Sussman Foundation INTERNSHIP PROGRAM

AQWATEC

Tani Cath

Juliana Anderson

Allesandra Smith

Kate Spangler

Rudy Maltos

AQWATEC Advanced Water Technology Center

Thank you!