An alternative, broad-scope approach to ISRU plans for Mars

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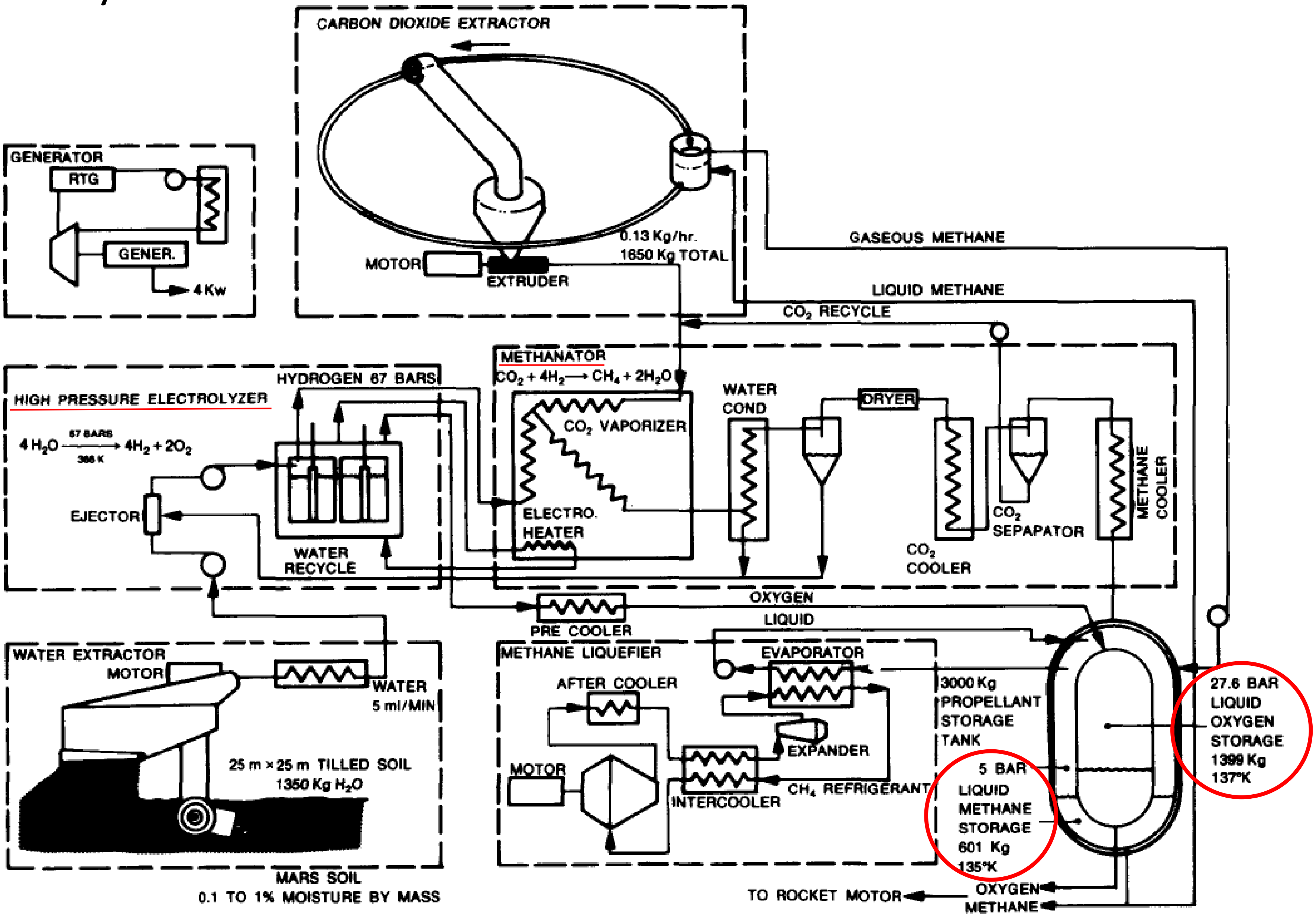
Alternative ISRU Approach

Early Focus of ISRU on Mars

- Generate O_2 for Mars Ascent Vehicle (MAV) using CO_2
  - Focus mainly on use of solid oxide electrolysis (CO_2 reduction)
    - $2CO_2 \rightarrow 2CO + O_2$
  - Alternate approach through use of recycled H_2O via water electrolysis
    - Combination of water electrolysis and reverse water gas shift (RWGS) reactions
      - Electrolysis ($2H_2O \rightarrow 2H_2 + O_2$) and RWGS ($CO_2 + H_2 \rightarrow CO + H_2O$)
      - Water is recycled from RWGS to electrolyzer for 'closed' system operation
- Generate CH_4 and O_2 for MAV
  - Apply combined Sabatier process and Proton Exchange Membrane (PEM) Electrolysis (Ash – 1978)
    - $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$ and $2H_2O \rightarrow 2H_2O + O_2$
- Only minor consideration for other uses for extant carbon (CO_2)
  - Methanol production described (Zubrin - 1997)
  - Ethylene and acetylene also considered (Zubrin 1997 and Linne 1991)
  - Fischer-Tropsch liquids discussed (Zubrin 1999)
- Little consideration for other needs or use of carbon (CO_2) resource

Alternative ISRU Approach

Early Focus of ISRU on Mars



“Feasibility of rocket propellant production on Mars”, R.L.Ash, et al, Acta Astronautica 1978, Vol. 5, pp 705-724

Alternative ISRU Approach

Focus on CH_4 production from CO_2 results in certain limitations and poses questions

- Production of CH_4 for propulsion requires certain demands
  - Storage of CH_4 requires high electrical demand for liquefaction
  - Robotic transfer of liquid CH_4 requires special operational demands
  - Required amount of H_2 for CH_4 production necessitates high demand on H_2O recovery from Martian sources (2H_2 for every C)
  - Separation of H_2 from CH_4 in Sabatier process operation is not resolved
  - Expanded use of CH_4 for other uses requires additional processing
- How does CH_4 fit into longer term ISRU operations?
  - Human and equipment operations on Mars will demand production of materials applicable to manufacturing of replacement parts, etc.
  - Chemical processing of CH_4 to produce hydrocarbon materials (e.g., plastics) requires additional high energy demands (i.e., steam reforming of CH_4 {$CH_4 + 2H_2O \rightarrow CO + 3H_2 + H_2O$} for synthesis gas [CO and H_2] production)
  - Systems aspects associated with combining propellant production AND synthesis of fabrication materials are important to long range planning

Alternative ISRU Approach

Consider Alternative ISRU Approaches on Mars

- Production of various hydrocarbon materials from CO_2 and H_2O
  - Synthesis gas (CO/H_2) production necessary as first step
    - Solid oxide electrolysis (SOXE) offers an efficient method for CO and H_2 production from combined CO_2 and H_2O feed in addition to production of pure O_2
    - Reverse water gas shift (RWGS) process ($CO_2 + H_2 \rightarrow CO + H_2O$) exemplified in the past
  - Methanol (MeOH) synthesis is a source for production of various hydrocarbons
    - Either of two synthesis processes is applicable
      - $CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$ or $CO + 2H_2 \rightarrow CH_3OH$
    - Methanol easily stored as a liquid under most Martian conditions
  - Dimethyl ether (DME) synthesis offers a range of advantages
    - Produced via several methods from synthesis gas and source for other hydrocarbons
    - Offers excellent possibility as a MAV propellant
  - Fischer-Tropsch process is also a source of a propulsion fuel
    - Production of liquid hydrocarbon similar to RP-1 is part of product mixture
    - No problem with sulfur as a contaminant in fuel produced on Mars
    - Hydrocarbon mixture can provide initial material for other useful hydrocarbon products
- Significant advances in process development over the last 20 years

Alternative ISRU Approach

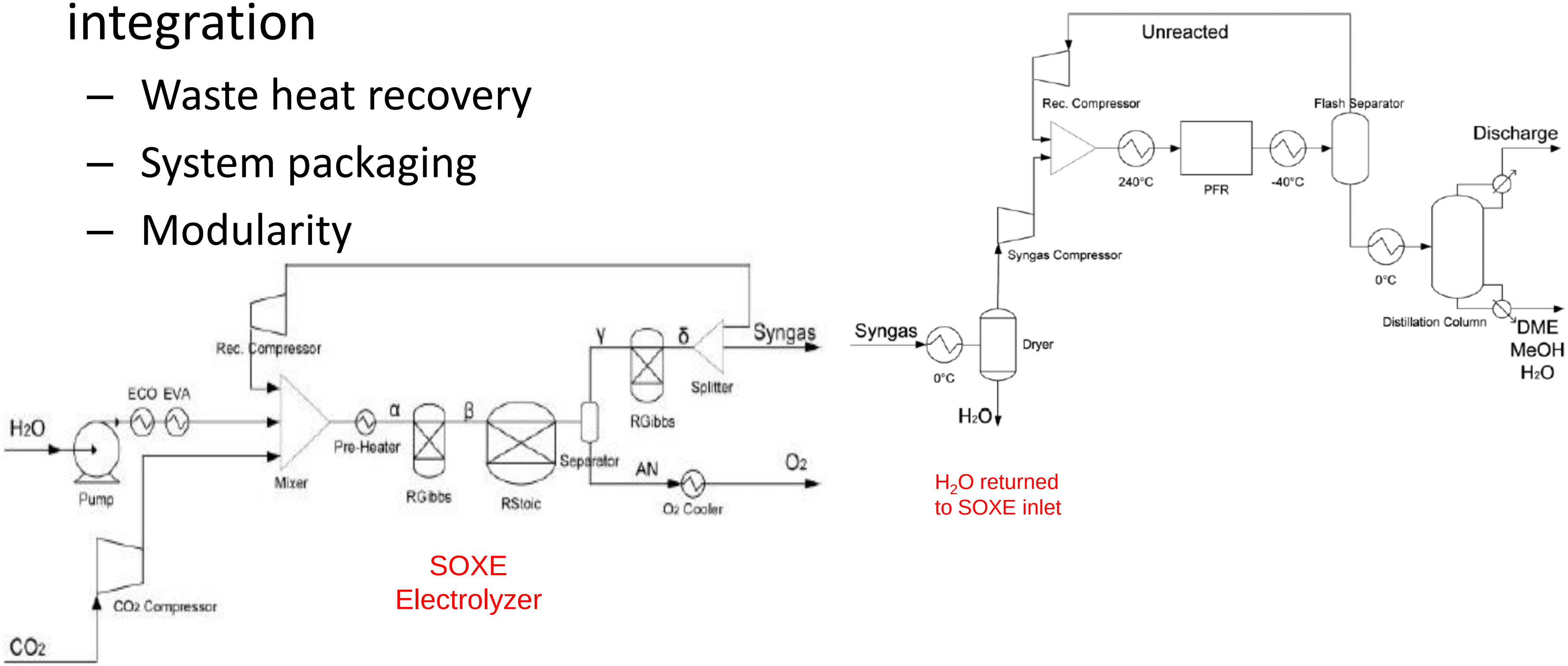
Use of SOXE offers many advantages over RWGS

- SOXE can operate efficiently with a combined CO_2 and H_2O feedstock to simultaneously produce synthesis gas and O_2
  - Operation with H_2O increases the overall efficiency of the SOXE compared to CO_2 electrolysis
    - CO_2 electrolysis is considered as source of oxygen source on Mars
    - Primary electrochemical reaction is associated with H_2O electrolysis
      - Lower overpotential [1.25v (H_2O) vs 1.47v (CO_2)]
    - Reduced possibility of carbon production in cathode compared to dry CO_2 electrolysis
  - Ratio of CO_2/H_2O can be varied for optimum H_2/CO production
  - Continuous operation not dependent on availability of either H_2O or CO_2
    - Oxygen is produced throughout operation
  - Operational pressure can be varied according to process demands
    - For increase in O_2 demands, pressurized operation can provide advantage in O_2 compression efficiency
- RWGS must be combined with separate H_2O electrolyzer for syngas production
  - $2H_2O \rightarrow \underline{2H_2} + O_2$ (electrolysis) and $CO_2 + H_2 \rightarrow \underline{CO} + H_2O$ (RWGS)

Alternative ISRU Approach

Industrial SOXE Co-electrolysis Process Schematic

- System designed for terrestrial operations (thermal integration)
- Single step synthesis operation simpler than two step (via MeOH)
- Aspen model used in system performance evaluation
- Martian operations would require modifications to system integration
  - Waste heat recovery
  - System packaging
  - Modularity



H_2O returned to SOXE inlet

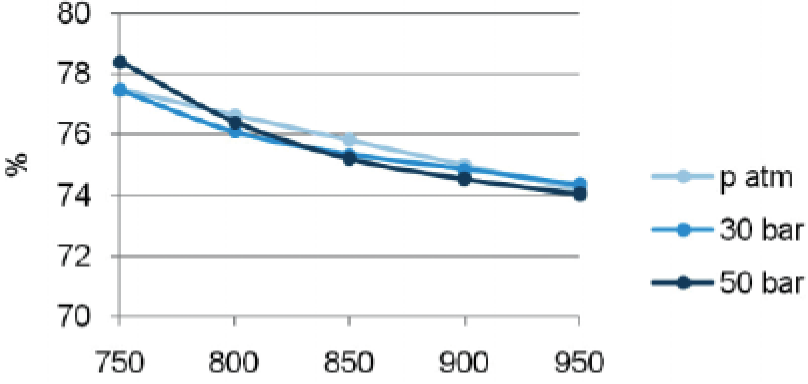
SOXE Electrolyzer

"Thermodynamic Analysis of Coupling a SOEC in Co-Electrolysis Mode with the Dimethyl Ether Synthesis", G. Botta, M. Solimeo, P. Leone, P.V. Aravind, Fuel Cells 15, 2015, No. 5, 669-681

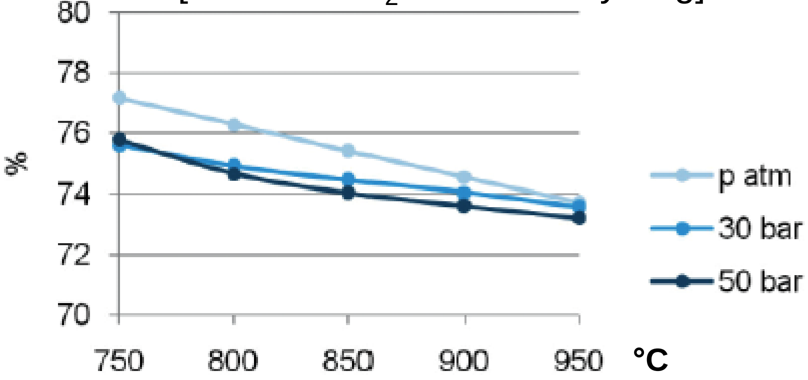
Alternative ISRU Approach

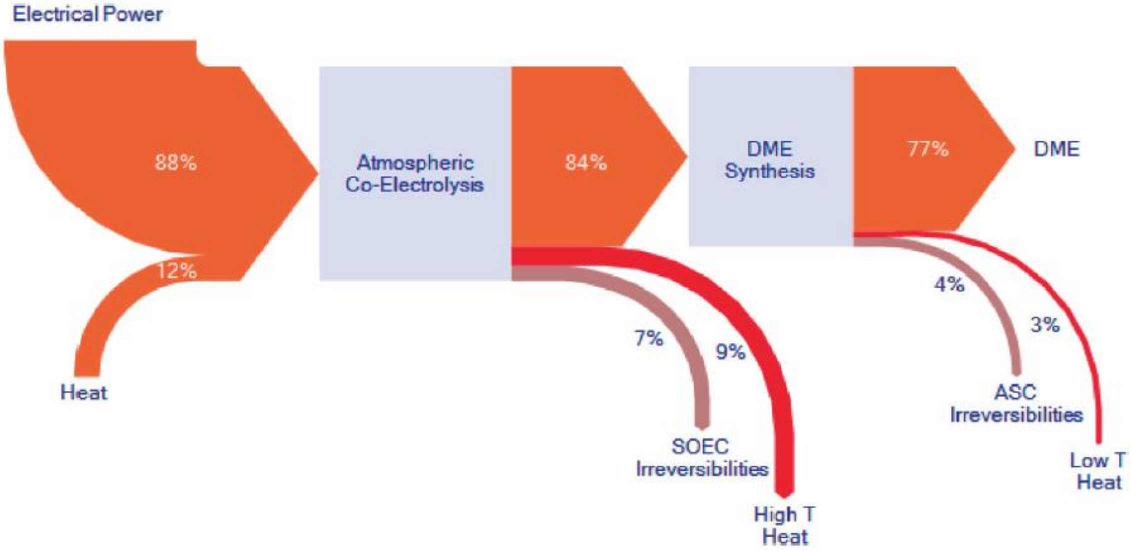
Recent DME/SOXE co-electrolysis design for commercialization

SOXE Efficiency
(pressure and temperature)



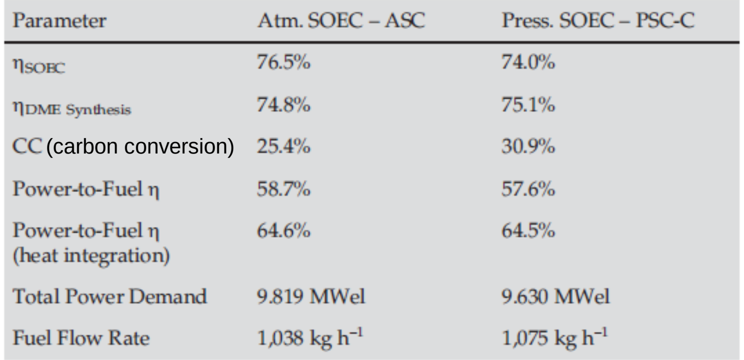
SOXE Efficiency
(@ pressure and temperature)
[With 10% H_2 and CO recycling]





1.6 Bar pressure operation

50 Bar pressure operation



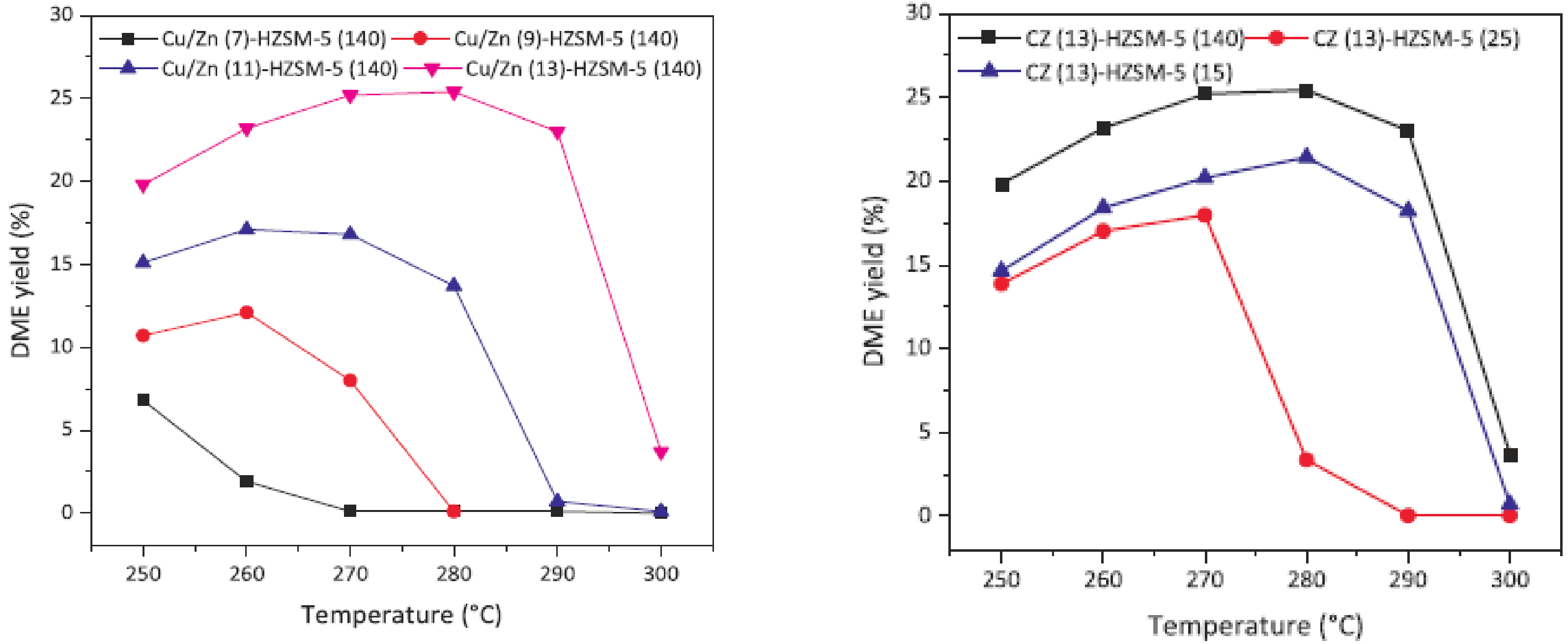
Parameter	Atm. SOEC – ASC	Press. SOEC – PSC-C
η_{SOEC}	76.5%	74.0%
$\eta_{DME\ Synthesis}$	74.8%	75.1%
CC (carbon conversion)	25.4%	30.9%
Power-to-Fuel η	58.7%	57.6%
Power-to-Fuel η (heat integration)	64.6%	64.5%
Total Power Demand	9.819 MWel	9.630 MWel
Fuel Flow Rate	1,038 kg h^{-1}	1,075 kg h^{-1}

"Thermodynamic Analysis of Coupling a SOEC in Co-Electrolysis Mode with the Dimethyl Ether Synthesis", G. Botta, M. Solimeo, P. Leone, P.V. Aravind, Fuel Cells 15, 2015, No. 5, 669-681

Alternative ISRU Approach

Recent developments on direct DME synthesis from syngas

- Significant interest and progress in single step operation



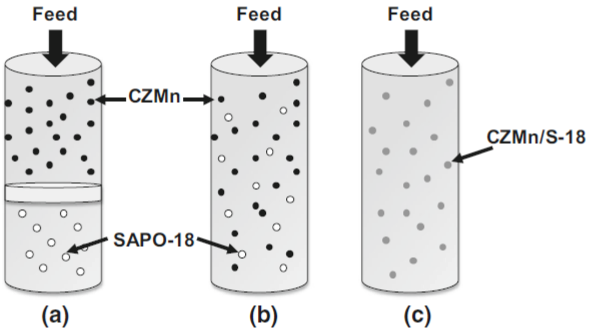
Determination of DME yields as a function of catalyst (Cu/Zn) and dehydration material (HZSM-5) loadings (constant pressure of 50 bar, $H_2/CO = 1$)

[Cu/Zn (Cu loading) catalyst, HZSM-5 zeolite (Si/Al ratio)]

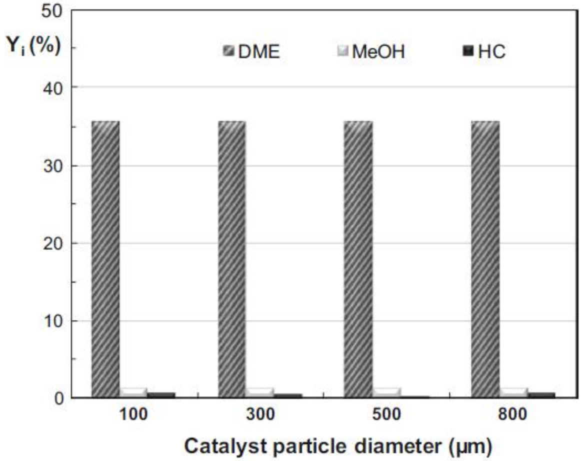
“Bifunctional catalysts based on colloidal Cu/Zn nanoparticles for the direct conversion of synthesis gas to dimethyl ether and hydrocarbons”, M. Gentzen, D.E. Doronkin, T.L. Sheppard, J.-D. Grunwaldt, J. Sauer, S. Behrens, Applied Catalysts A, General 557, 2018, 99-107

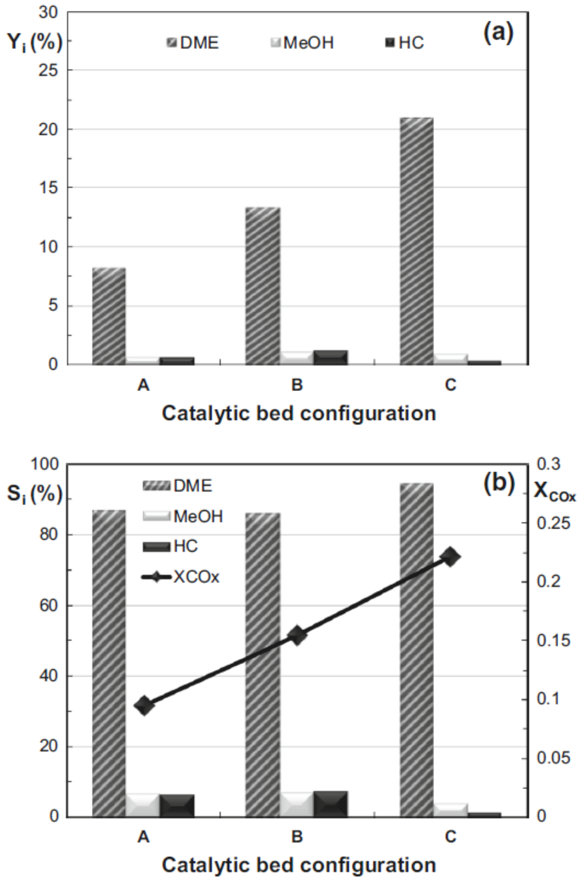
Alternative ISRU Approach

Recent developments on direct DME synthesis from syngas



Different catalyst bed configurations tested





Determination of DME yields with combined catalyst (Cu/Zn/Mn, 2:0.75:1.5) and dehydration material (SAPO-18) [cat/dehydration material ~2] with respect to particle size and catalyst bed configuration (constant pressure of 30 bar, T=275 C, H_2/CO = 3

"Catalyst configuration for the direct synthesis of dimethyl ether from CO and CO2 hydrogenation on CuO-ZnO-MnO/SAPO-18 catalysts", A. Ateka, M. Sanchez-Contador, J. Erena, A.T. Aguayo, J. Bilbao, Reac. Kinet. Mech. Cat, 124, 2018, 401-418

Alternative ISRU Approach

Comparison of various fuels as MAV propellant options

- Assumed identical MAV performance
  - Basis used was the JSC sized MAV
    - Tank mass model that fits the JSC data from SOL 1 and SOL 5 for LOX / Methane was created
  - System comparison based on JSC 42.9 mT MAV liftoff mass
    - Tank estimates include mass of empty landing tank shell
  - DME offers significant advantages

Property		**LOX/Methane**	**LOX/DME**	**LOX/Methanol**
Delivered ISP – (H/C)		360 s (4)	344 s (3)	331 s (4)
MAV Comparison	Emtpy Mass [mT]	9.34	**9.06** [1]	9.21
	Volume of Tanks [m^3]	41.4	**34.8** [2]	36.8
	Liftoff Mass, LOX [mT]	25.5	21.3	21.6
	Liftoff Mass, Fuel [mT]	8.07	11.8	14.8
	Liftoff Mass, total [mT]	33.6	33.1	36.4
	LOX tank shell Mass [mT]	0.236	0.197	0.200
	Fuel tanks shell mass [mT]	0.212	0.190	0.203
Energy to liquefy	LOX [MJ]	5434	4539	4603
	Fuel [MJ]	4137	0.0	0.0
	Total [MJ]	9571	**4539** [3]	4603
Energy to store	LOX [MJ/day]	767	680	686
	Fuel [MJ/day]	608	8	0.0
	Total [MJ/day]	1375	**688** [4]	686

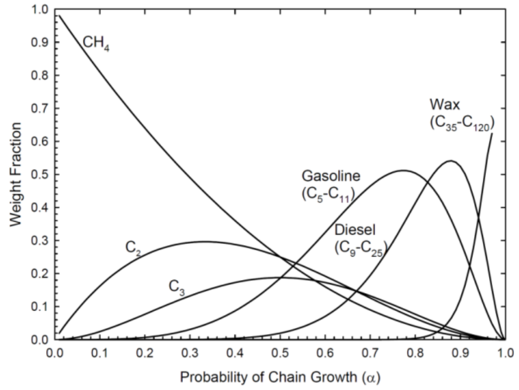
Compared to methane - based on projected same liftoff mass (~42.9 mT) on Mars:

1.**DME** comes out ahead on landed MAV dry mass (**3% better**)
2.**DME** comes out ahead on landed MAV tank volume (**16% smaller**)
3.**DME** comes out ahead on energy to liquefy the launched propellant load: (**53% less energy**)* [liquefaction included in fuel production]
4.**DME** comes out ahead on energy to store the launched propellant load: (**50% less energy/day**)

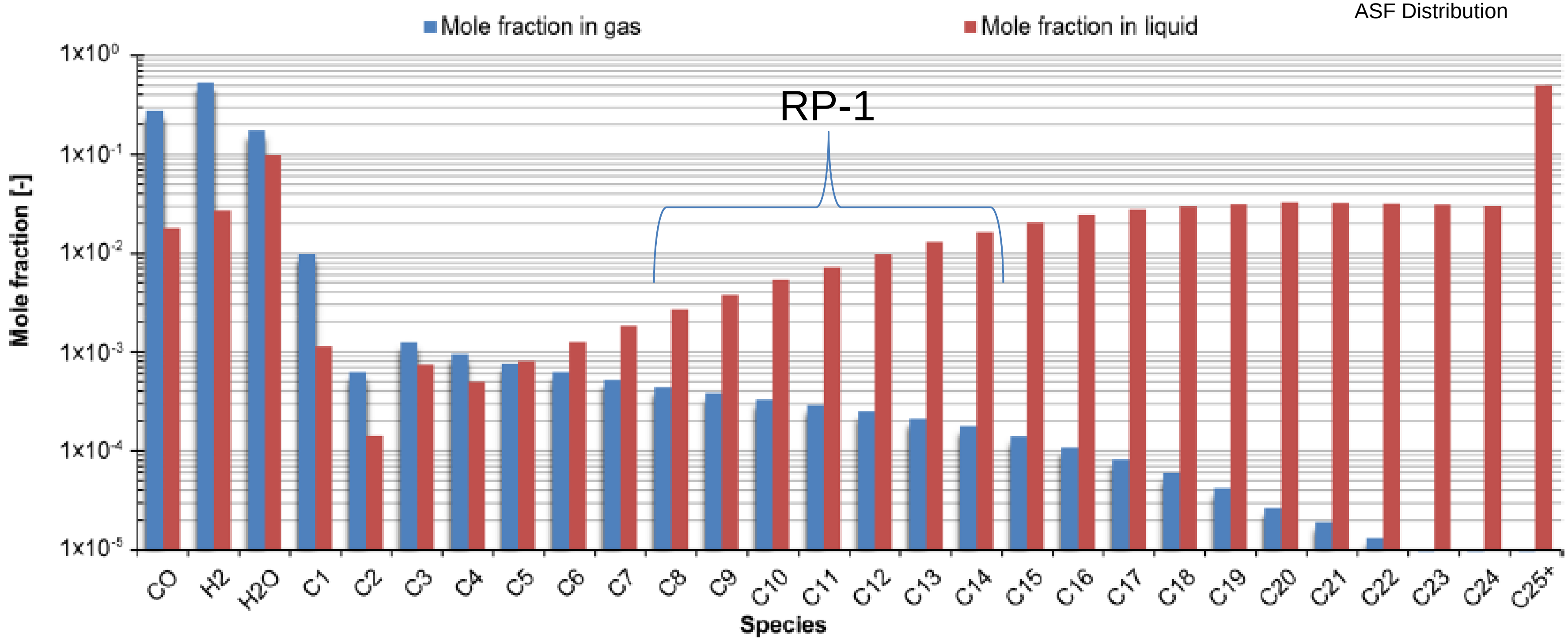
Alternative ISRU Approach

Anticipated product distribution from Fischer-Tropsch process unit

- Production of “RP-1” is a fraction of overall products
  - (+) Distillation column would provide the cut of hydrocarbons desired
  - (+) No sulfur in the fuel due to use of clean initial CO and H_2 reactants
  - (+) Other hydrocarbon species could provide material for other uses
  - (+) Extensive commercial experience exists in FT process operations
  - (-) Total amount of CO and H_2 required for RP-1 specifically is relatively high
  - (-) System required for capturing RP-1 spec fuel is relatively complex
  - (-) Energy efficiency on the order of 50-60 %



ASF Distribution



“Multiscale and Multiphase Model of Fixed Bed Reactors for Fischer−Tropsch Synthesis: Intensification Possibilities Study”, M. Stamenić, V. Dikić, M. Mandić, B. Todić, D. B. Bukur, and N. M. Nikačević, I&EC Res, 56, 2017, 9964-9979

Alternative ISRU Approach

Consider Broader Perspective of CO_2 and H_2O use on Mars

Long term operations on Mars benefits from operating synthesis processes which provide dual benefits, i.e. propellant fuel and oxygen AND feedstock for other useful materials

- Dimethyl ether production processes inherently include the ability to generate other useful hydrocarbons
  - Dehydration produces olefinic and paraffinic hydrocarbons
  - Methanol can be produced instead of dimethyl ether if advantageous
- Fisher-Tropsch process produces hydrocarbons that can be converted to other useful hydrocarbons
  - Additional separation and processing required
- Methane must be processed further (i.e., via steam reforming) in order to produce synthesis gas (CO and H_2) from which other useful hydrocarbons can subsequently be synthesized
- Oxygen production is considered a requirement in all systems

Alternative ISRU Approach

Outline for DME production from CO_2 and H_2O on Mars

1. Understand SOXE benefits from Mars 2020 MOXIE demonstration
    - MOXIE – Mars Oxygen ISRU Experiment (Solid Oxide Electrolyzer)
    - Small SOXE/CO_2 compressor system designed to illustrate production of O_2 via electrolysis of Martian CO_2
    - Initiates understanding of engineering aspects associated with operating on Mars
2. Scale up SOXE to include co-electrolysis on Mars
    - Complete design for DME production system
    - Fabricate modular DME production system
3. Demonstrate O_2 production and storage system for MAV/human use
4. Demonstrate modular O_2 and DME production on Mars
5. Demonstrate O_2 and DME production and storage for MAV and human operations on Mars

Alternative ISRU Approach

Conclusions

- Liquid oxygen (LOX) production is clearly necessary to include in any chemical processing of in situ resources on Mars
- While methane production as a MAV fuel appears simple in utilizing CO_2 and H_2O resources, additional processing of methane is required to generate other useful materials necessary to sustain long duration operations on Mars
- Synthesis processes which produce MAV fuels and oxidant, as well as feedstock for generating other useful hydrocarbon materials, provides a dual benefit to ISRU processes
- Dimethyl ether appears to offer significant benefits over methane as a fuel for MAV
- Methanol synthesis and Fischer-Tropsch process provide options worth considering as options to methane as a MAV fuel
- Additional details associated with processing equipment are needed to define overall benefits and trade-off value for alternative fuel choice

Alternative ISRU Approach

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