REMEDY- Reducing Emissions of Methane Every Day of the Year

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Brief History of REMEDY

- Part of larger investigation into non-CO_2 GHG abatement

- "Preventing or Abating Anthropogenic Methane Emissions"
  - Gas-fired engines
  - Flares (presumptive 98% methane destruction)
  - Wells and mines
  - Landfills
  - Enteric (ruminants)
  - Direct removal from air

- 10/20/2020 Workshop/links to presentations

https://arpa-e.energy.gov/events/preventing-abating-anthropogenic-methane-emissions-workshop

REMEDY: Engines, Flares, Coal Mines

- 3 yr, \$35MM program, diverse technologies/teams, systems approach
- Point source emissions
  - ~250 coal mine ventilation shafts
  - 50,000+ natural gas-fired engines in oil and gas and CHP/electric generation
  - 300,000 flares for oil and gas "routine" operations – not flares "temporarily" burning associated gas
- Ensure 99.5% methane reacted to CO_2; field tests in year 3
- Program update https://arpa-e.energy.gov/2023-repair-annual-meeting

CHANGING WHAT'S POSSIBLE

Awardees

Coal Mine VAM (Catalysts)
Johnson Matthey, Inc. $4.3MM
Massachusetts Institute of Technology $3.7MM
Precision Combustion, Inc. $3.7MM

Natural Gas Engines (Engine modifications, catalysts, plasma-enhanced combustion)
MAHLE Powertrain $3.3MM
Colorado State University $1.5MM
Marquette University $4.0MM
INNIO's Waukesha Gas Engines $2.2MM
Texas A&M University $2.8MM

Flares (Advanced burners, integrated heat exchange, catalysts, plasma-enhanced combusiton
Advanced Cooling Technologies, Inc. $3.3MM
Cimarron Energy, Inc. $1MM
University of Michigan $2.9MM
University of Minnesota $2.1MM

Observations re: methane removal from air

- Need to treat a lot of air
  - Need passive system, and/or leverage existing assets moving air

- Reacting dilute methane
  - Mimic nature's strategies
    - Atmospheric chemistry (free radical chain reactions)
    - Biology (subsurface, soil, atmospheric suspensions)
  - Catalysts need a lot of heat (>300 C)
    - Leverage waste heat/thermal integration

- Destroy, don't try to capture/recover
  - Incremental costs exceeds incremental revenue (10 MM ton = ~$1B)

- Adsorption/absorption likely ineffective
    - Low working capacity (difference in adsorption/desorption isotherms

- Do no harm
  - Potential co-emissions could be worse than methane
  - Keep track of energy and material inputs

It’s a Lot of Air

- *An ounce of prevention is worth a ton of cure*
- Accumulation 10MM ton/ yr
- Removing 10MM ton @ 2 ppm, need to “treat” 6 Pm^3 air/ yr assuming 100% destruction
  - 10 m high layer of air across the globe

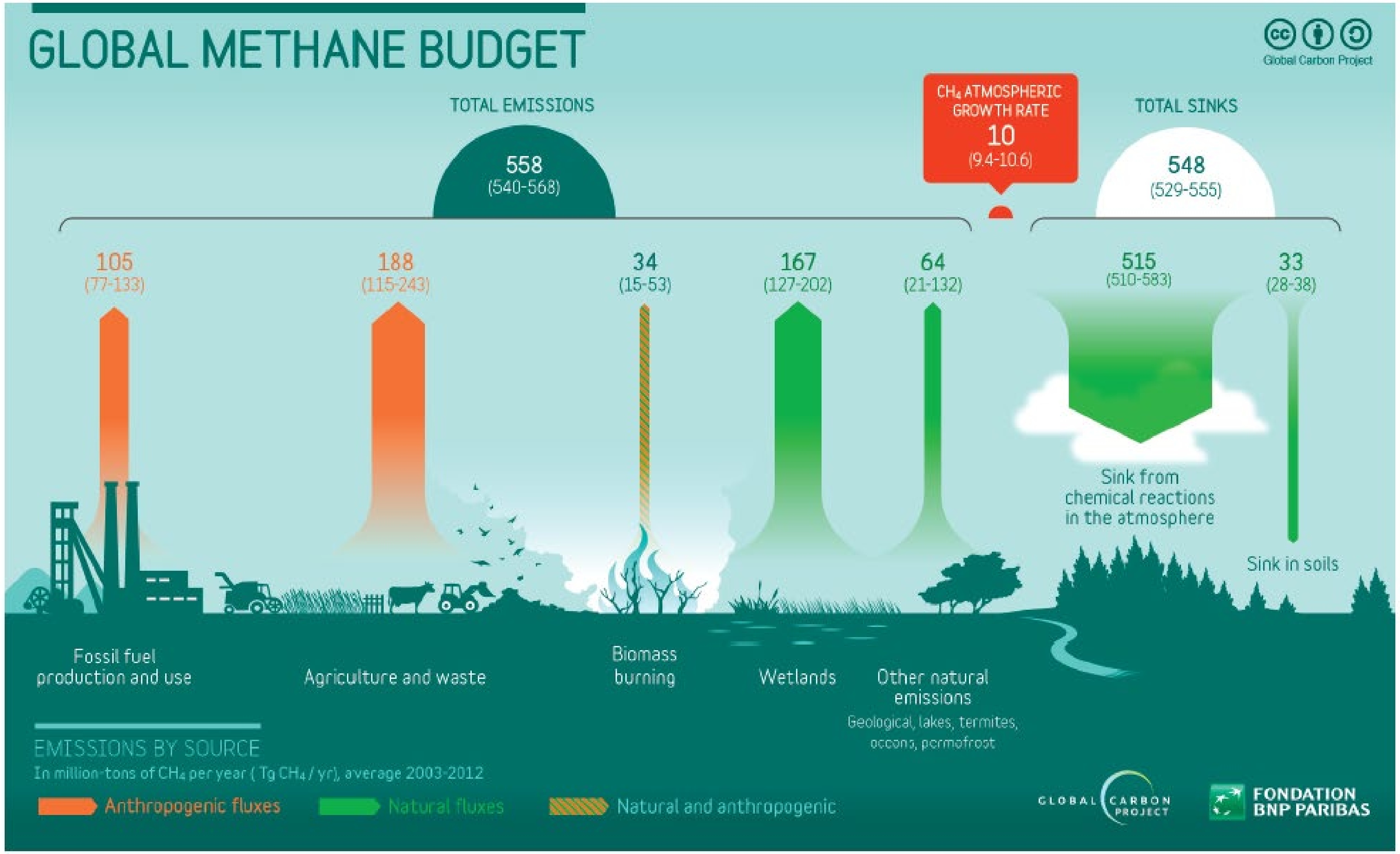


FIGURE S.1 Schematic of sources and sinks of methane globally. SOURCE: Global Carbon Project, http://www.globalcarbonproject.org/.

Passive and Leveraged Air Contacting

- Built infrastructure – lots of area
- Caves and abandoned mines – “diurnal breathing”

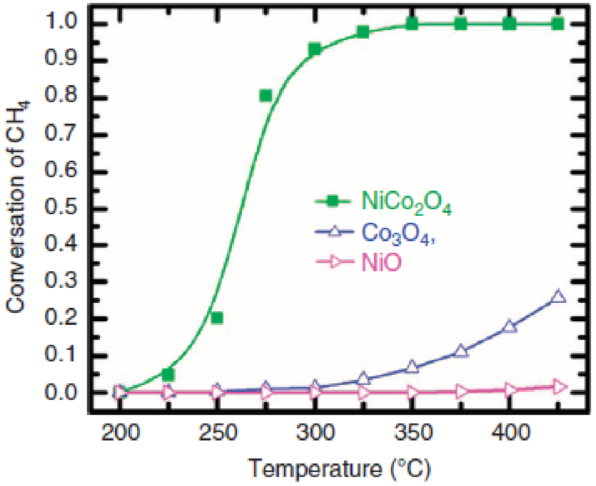
Viable methanotrophic bacteria enriched from air and rain can oxidize methane at cloud-like conditions

Aerobiologia **vol 29**, pages373–384 (2013)

- “Forced convection” – cooling towers, HVAC
- Turbines – reduced boundary layers/enhanced mass transfer

Methane Catalysts: Need cheap, active, robust

- **Mixed oxide catalysts** such as $NiCo_2O_4$ are promising cost-effective catalyst candidates for methane oxidation in the temperature >300 C[1].
- **Electric field enhancement** of MnCo catalyst for ultra-lean (0.2% CH_4) combustion
- REMEDY's **Precision Combustion Inc.** demonstrated 98% methane destruction for 17,000 and 20,000 hrs @100 ppm
- Preferably couple with waste heat source



[1] Tao, F., Shan, Jj., Nguyen, L. et al, *Nature Communications* 6, 7798 (2015). https://doi.org/10.1038/ncomms8798

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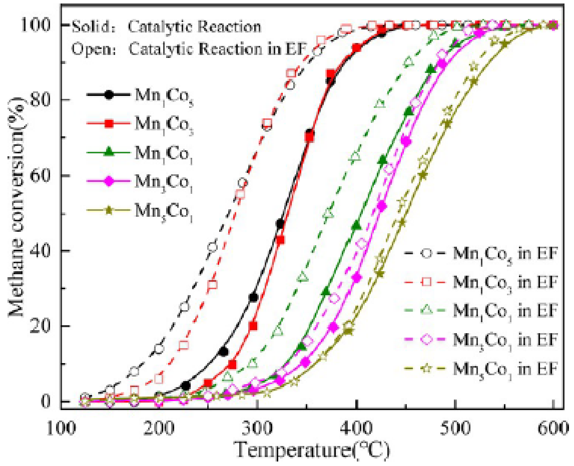


Figure 2. CH_4 conversion efficiency over Mn_xCo_y catalysts with different ratios of Mn/Co. Reaction conditions: $[CH_4] = 0.2$ %; $[O_2] = 1$ %; N_2 as balance gas; GHSV = 30,000 h^{-1}. The input current is 20 mA.

CHANGING WHAT'S POSSIBLE

Photo-catalysts – Resetting CO_2 Targets

Addition of noble or transition metals (Ag, Pd, V, Fe, Ga, Ce, Co, Cu and Zn) to HPW/TiO2 strongly affects the rate and selectivity of methane oxidation. Much higher activity was observed over the catalysts containing noble metals (Fig. 1a), however, this higher activity was accompanied by significant carbon dioxide production. *Note that only CO_2 was detected in methane photo-oxidation over the Pd containing catalyst.*

NATURE COMMUNICATIONS | (2019) 10:700 |
https://doi.org/10.1038/s41467-019-08525-2

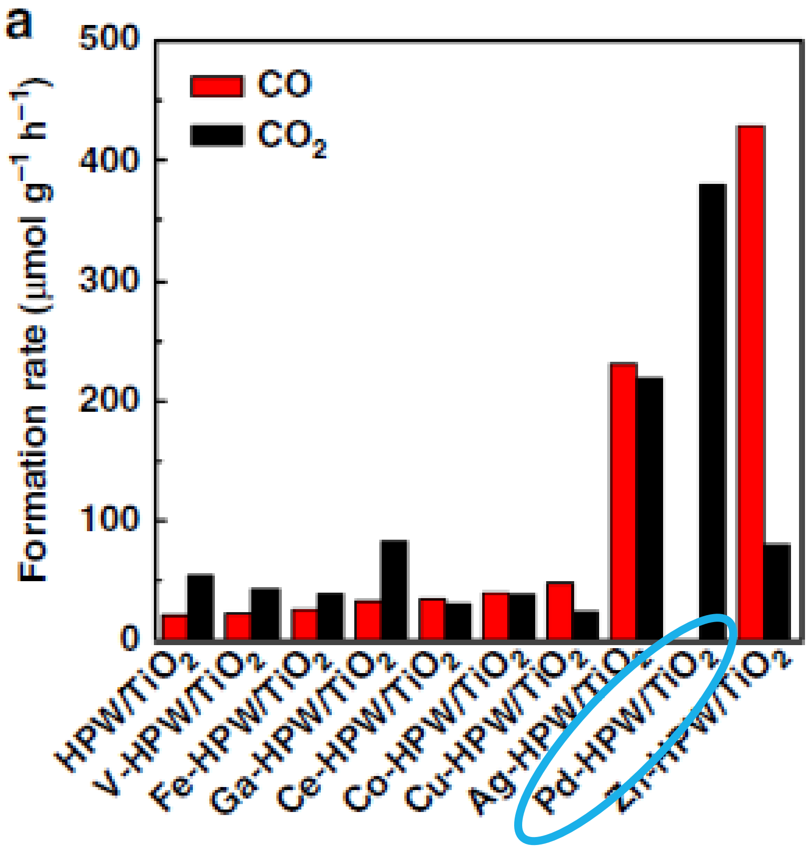


Fig. 1 Methane photocatalytic oxidation on different catalysts. a Metal-HPW/TiO2 composite Reaction conditions: catalyst, 0.1 g; gas phase pressure, CH4 0.3 MPa, Air 0.1 MPa; irradiation time, 6 h

Plasma/Hydroxyl/Reactive Accelerators– What’s New

- Methane oxidation promoters:
  - Hydroxyl radicals > oxygen radicals > ozone > hydrogen > C2+ hydrocarbons
- Plasma reduces CH_4 ignition temp 100K
- Plasma and plasma/catalyst effective for ~100 ppm VOC control.
- Elijah Thimsen (Wash U St. Louis) preliminary tests, 1 ATM, just below LEL, able to achieve 85% conversion at ~$150/ton. Believes plasma/catalyst integration required for high conversion/lower concentrations.

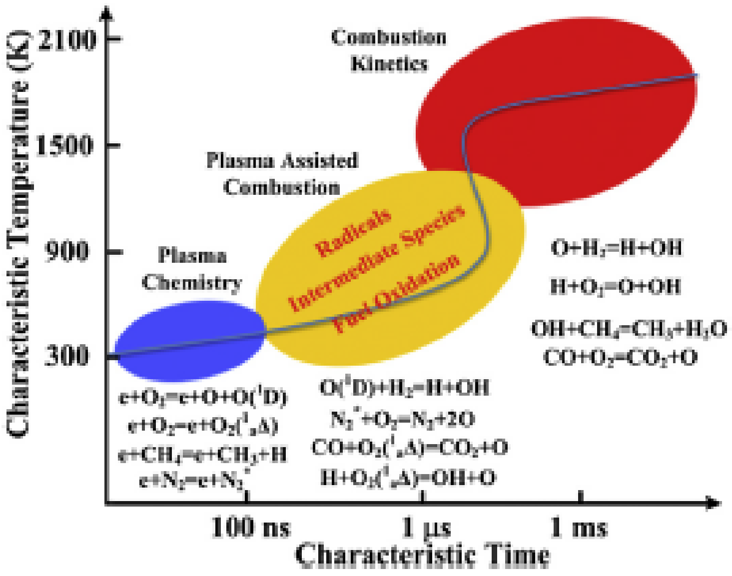
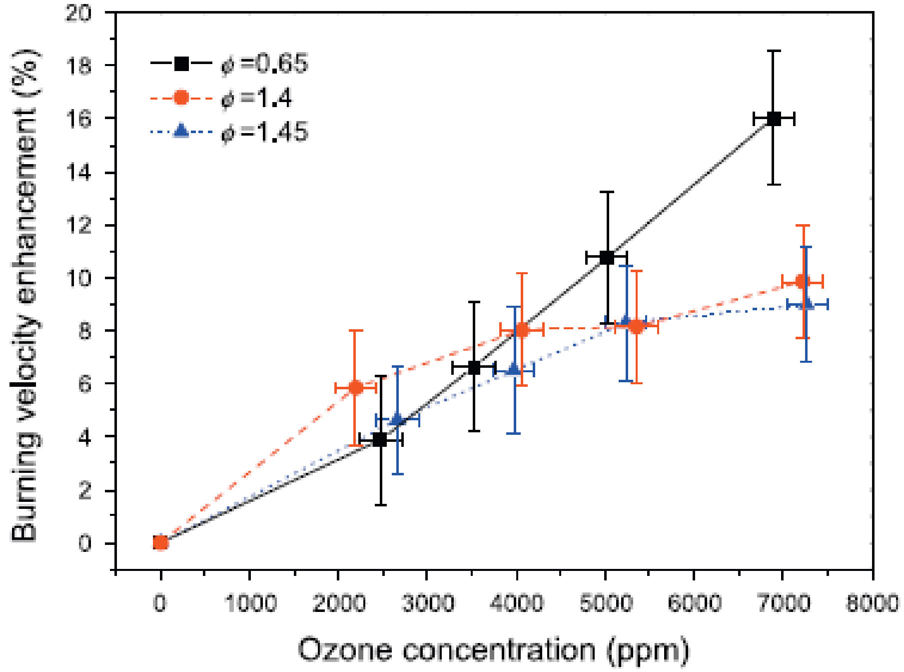


Fig. 1.5. Schematic of timescales and key kinetic pathways at different stages of plasma assisted ignition and combustion.

Combustion Chemistry Implications for Additives

W. Sun, X. Gao and B. Wu et al./Progress in Energy and Combustion Science 73 (2019) 1–25

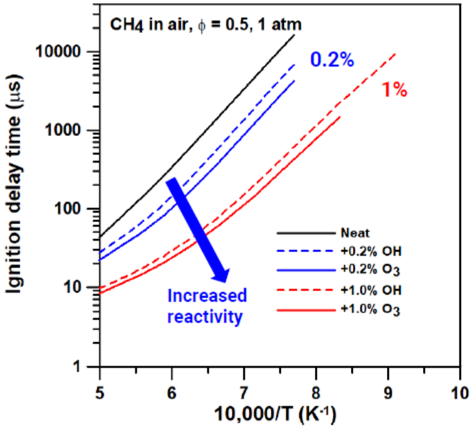


- **Fig. 5.** Enhancement of CH_4 /air flame speeds as a function of O_3 concentration, where φ is the equivalence ratio

Eric Peterson – Workshop Combustion Fundamentals

OH Radical and Ozone Seeding

Models can be used to estimate effect of OH and O_3 addition to CH_4-Air combustion process



- Calcs using AramcoMech model
- CH_4 – Air at ϕ = 0.5
- OH represents infusion of radicals, for basic trend
- O_3 submechanism taken from Ju et al. (2016)

Catalyst and "Accelerant" Issues

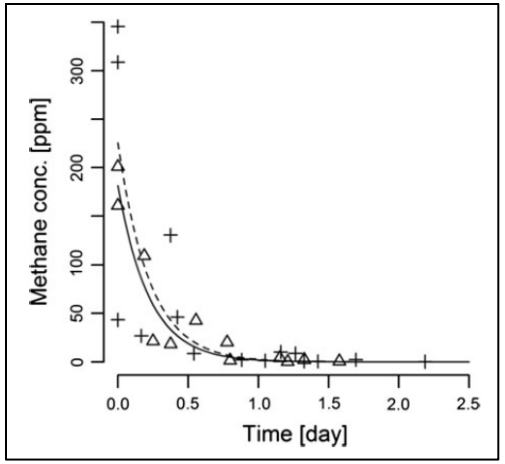
- Parasitic energy load
  - Electricity, heat

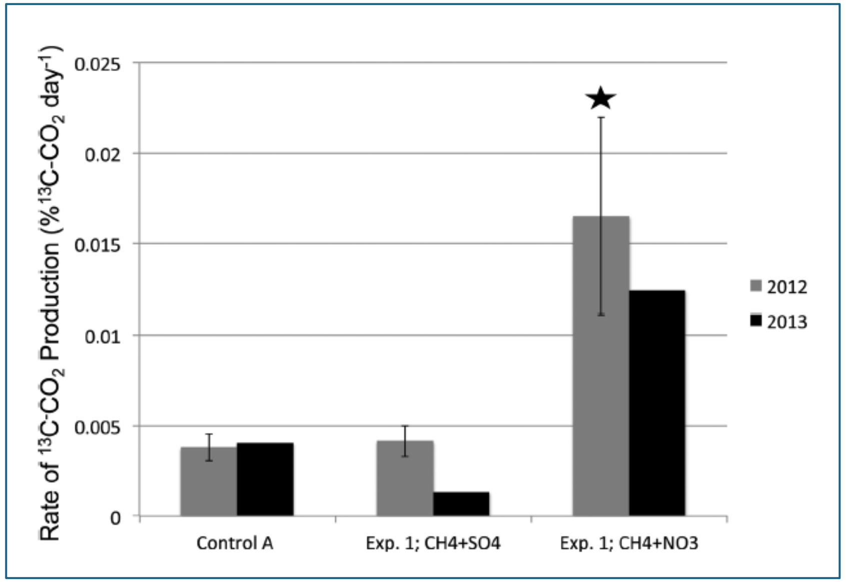
- Environmental
  - Potential for NOx, ozone-forming emissions
  - Potential for HAPS (ie formaldehyde) emissions
  - Mining, etc, esp for noble metals

Methanotrophs/ Biofilters – What's New

- Sampling, metabolism, strain isolation, genetic sequencing
  - Atmospheric suspensions
    - Dispersed methanotrophs are potentially large methane sink
  - Vietnamese cave biofilm
    - Removes 150,000 mt/yr methane; coal mine analog?
  - Soils
    - Isolated and characterized strain that grows on 2 ppm methane, role of pMMO
  - Coal bed methane
    - USGS site, likely methanotroph biofilm
  - Subsurface
    - South African study correlates methanotrophs activity with reducing equivalents in saline formation at 1340m

Methanotrophs in cloud condition

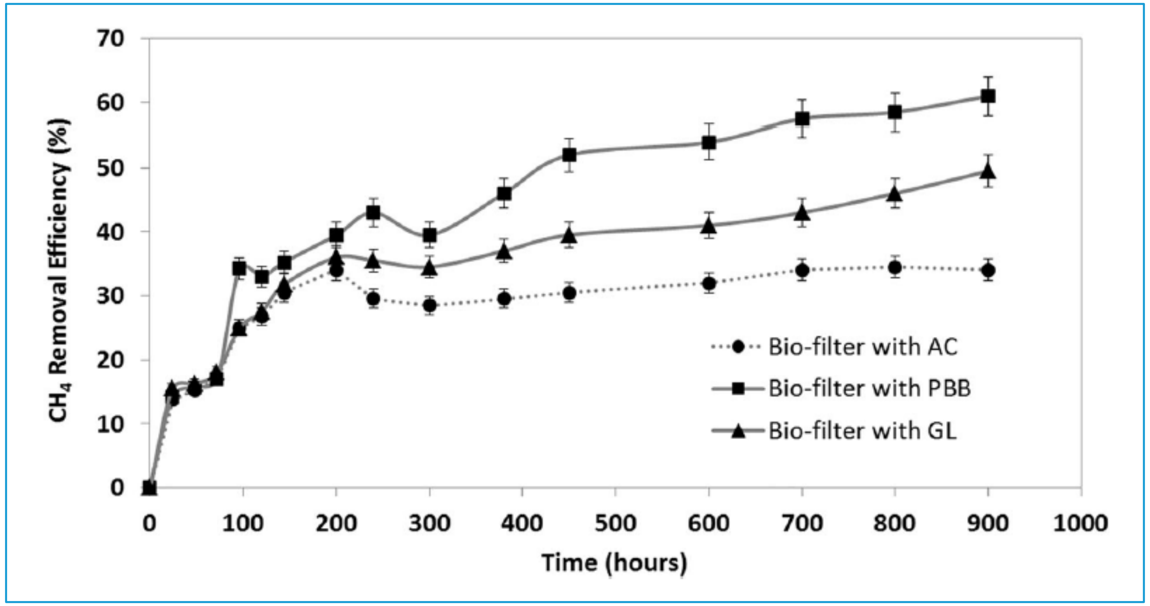


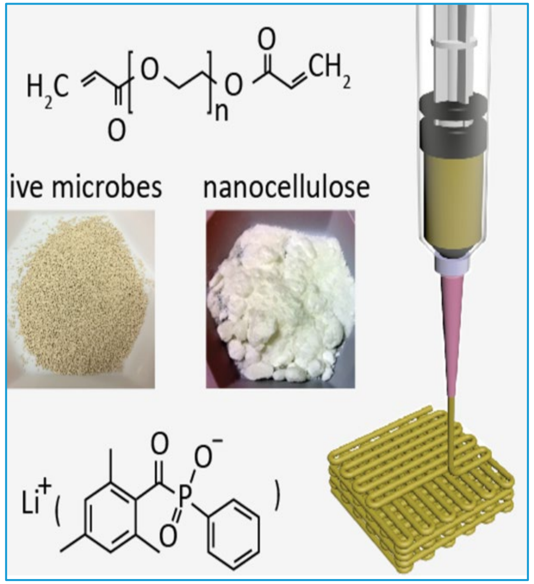


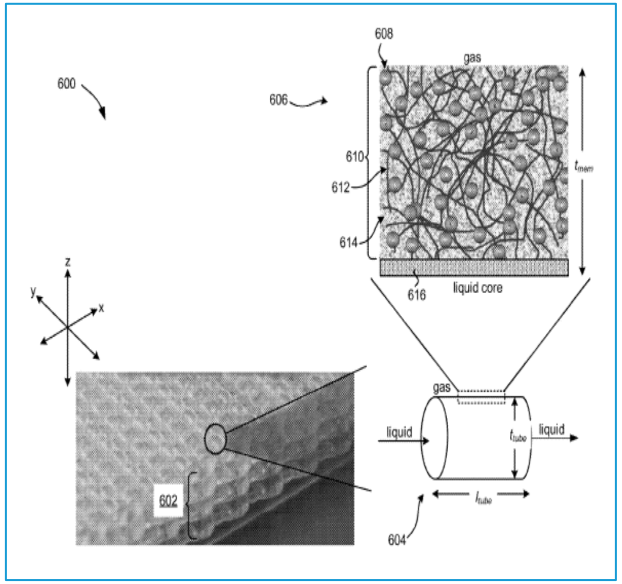
Methanotrophs in 1340 m deep fissure

Methanotroph/ Biofilters – What's New

- System developments
  - Russian tests injecting methanotrophs into coal seams reduced methane emissions >50%
  - Mixed marine sediment consortia on plastic balls in packed bed
  - LLNL
    - "Printed tunable living ink" biofilter has 10X productivity gain
    - Plastic encapsulation allow dispersion and protection from native environment







Summary

- Many potential routes
- Good scientific base for methane oxidation mechnisms
  - But few studies to apply science for methane removal from air in novel
- Look for out-of-the-box integration/deployment
- Be mindful of potential unintended consequences