Agricultural Methane Capture and Use

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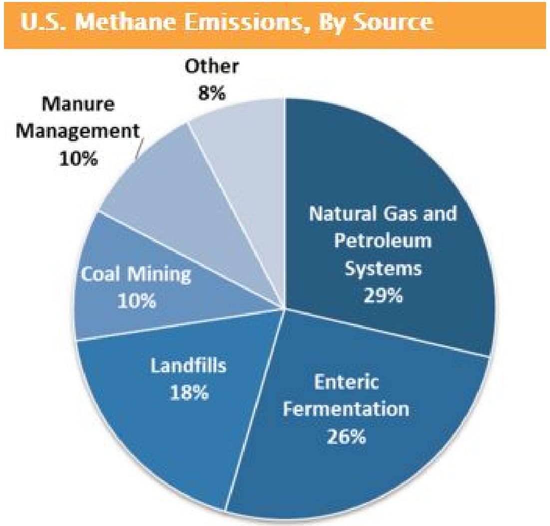
Motivations



- Agriculture has a huge environmental impact.
  - In addition to 9% of CO_2, livestock contribute 37% of worldwide anthropogenic methane emissions [1].
- Most of the methane produced through agriculture goes into the atmosphere where it has a lifetime of ~10 years and a very powerful greenhouse effect
- The Global Methane Initiative estimates that 26% of anthropogenic methane is produced by enteric fermentation. Of this, about 90% is produced by cattle (including both beef and dairy).

Figure: "U.S. Greenhouse Gas Inventory Report: 1990-2013." *U.S. Greenhouse Gas Inventory Report: 1990-2013*. United States Environmental Protection Agency, 4 Nov. 2015. Web. 06 Dec. 2015.

[1] Livestock's Long Shadow: Environmental Issues and Options. Food and Agriculture Organisation of the United Nations. 2006.

Our Proposal—An Advanced Farm

- The cows will be housed in large semi-enclosed buildings. Their emitted methane gases will be captured in vents in the roof.
- The methane will be separated from the air using cutting edge technologies.
  - Pressure Swing Adsorption using Nanoporous Zeolite filters
  - Methanotrophic Bacteria
- As needed, methane will be combusted on site to power the farm.
- Any surplus captured methane will be converted to methane hydrate for transportation and eventual use.
  - This way, small to medium amounts of methane can be transported to use in other areas without the need to install pipelines
- Existing biogas (anaerobic digestion) techniques will also be used extensively, but we do not propose to innovate in this area.

Our Proposal—An Advanced Farm

- Key risks include:
  - Capture: explosive depressurization of high pressure systems
  - Transport: assuring the stability of hydrates at atmospheric pressure
  - Public may not accept the products from the farm (preferences for free range or organic living conditions)
- All of the technologies we plan to implement can be tested on a very small, low-risk scale as we prepare to install them on the actual farm.
- We will collect data on the energy production and use as well as the economic impact of the farm.
- In the short term, strive for energy neutrality. In the long term, we would hope for an energy surplus.

Methane Capture

Relevance:

- Capture of enteric fermentation methane.
- Capture of methane from melting hydrates at high latitudes.
- Large scale atmospheric methane removal.

Methane source classification:

- High purity (>90%): market-grade natural gas.
- Medium purity (5–75%): landfill gas, anaerobic digester gas, low-grade natural gas.
- Dilute (<5%): animal feeding house gas, manure storage headspace, coal-mine ventilation.

Dilute $\xrightarrow{\text{Methane sorbent}}$ Medium Purity

Medium Purity $\xrightarrow{H_2S \text{ \& } CO_2 \text{ sorbent}}$ High Purity

Capture Techniques

CO_2 has a quadrupole moment, CH_4 is non-polar

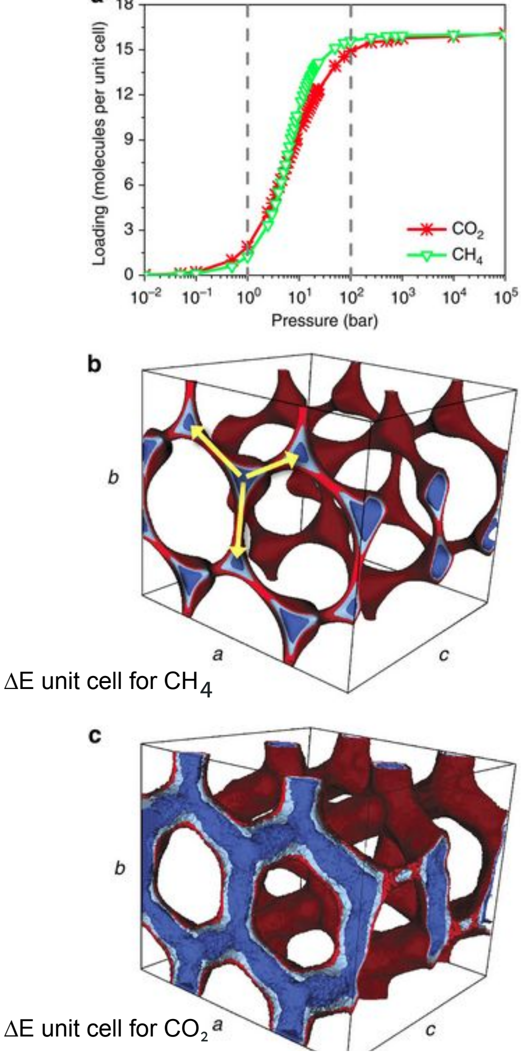
$\Rightarrow$ Typical liquid solvents or porous solids used in CO_2 capture are ineffective.

- Adsorption to filters using Nanoporous Zeolites
  - Adsorbent lattices that “trap” CH_4 molecules.
- Methanotrophic Bacteria
  - Oxidize methane into methanol at atmospheric levels.
- Enzymatic/Catalytic systems
  - Oxidize methane into methanol.
- Cryogenic separation
  - Condense other hydrocarbons in mixture onto a suitably cold surface.

None of the existing technologies are economically or energetically suitable for a large scale implementation.

Nanoporous Zeolites

- Porous material that can be used as a filter in Pressure Swing Adsorption processes
    - process during which certain gases in a mixture are adsorbed at high pressures, and then released at low pressures after other gases have been removed
- Free-energy profiling and geometric analysis to understand how the distribution and connectivity of pore structures and binding sites can lead to enhanced sorption of methane while being competitive with CO_2 sorption at the same time [2].
- Kim *et al.* identify one specific zeolite (see Figure) , dubbed SBN, which captured enough medium purity source methane to turn it to high purity methane.
- Other zeolites, named ZON and FER, were able to concentrate dilute methane streams into moderate concentrations.



[2] Kim, Jihan, Amitesh Maiti, Li-Chiang Lin, Joshuah K. Stolaroff, Berend Smit, and Roger D. Aines. "New Materials for Methane Capture from Dilute and Medium-concentration Sources." *Nature Communications Nat Comms* 4 (2013): 1694. Web.

Methanotrophic Bacteria

CH_4 $\xrightarrow{\text{Digestion}}$ Methanol

- Bacteria use an enzyme called Methane monooxygenase (MMO), to oxidize CH_4.
- Balasubramanian *et al.* recently discovered MMO has 2 Cu atoms at its center [3].

⇒ Enhanced capture through bioengineering and/or Cu based catalysts.

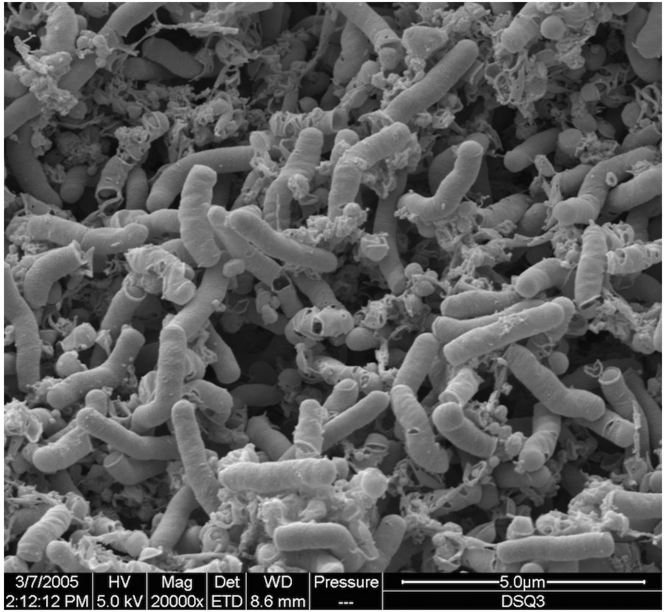
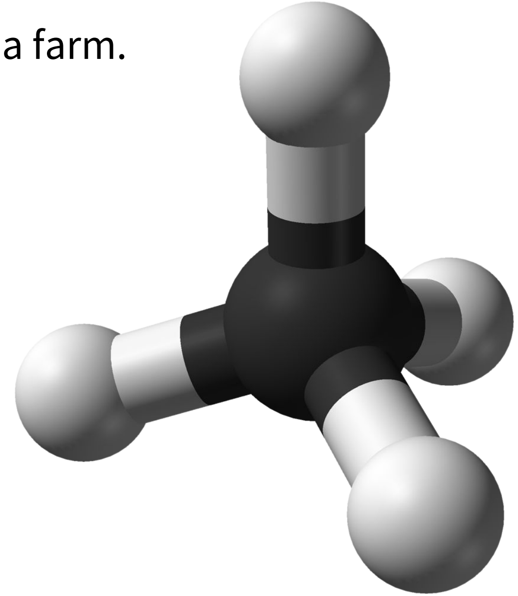


Image credit : Boden, Rich, Thomas, Elizabeth, Savani, Parita, Kelly, Donovan P. and Wood, Ann P. . (2008) *Novel methylotrophic bacteria isolated from the River Thames (London, UK).* Environmental Microbiology , Vol.10 (No. 12). pp. 3225-3236. ISSN 1462-2912

[3] Balasubramanian, Ramakrishnan, Stephen M. Smith, Swati Rawat, Liliya A. Yatsunyk, Timothy L. Stemmler, and Amy C. Rosenzweig. "Oxidation of Methane by a Biological Dicopper Centre." *Nature* 465.7294 (2010): 115-19. Web.

Using Captured Methane

- Methane can be used as an energy source to power a farm.
- Methane is the cleanest fossil fuel.
  - Coal: 0.963 kg CO_2/kWh
  - Oil: 0.881 kg CO_2/kWh
  - Methane: 0.569 CO_2/kWh [4]
- $CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$



[4] CO2 Carbon Dioxide Emissions from the Generation of Electric Power in the United States, DOE, EPA, 1999.

Using Captured Methane

- Many environmentally friendly farms already use methane as a power source.
- With current technologies and practices, most methane is obtained from anaerobic digestion of manure (biogas).
- Biogas produced in this way is about 50% to 70% methane [5].
- Per 1000 pound cow, we can get about 7.327 kWh per day [6].

[5] El-Mashad, H. M., & Zhang, R. (2010). Biogas production from co-digestion of dairy manure and food waste. *Bioresource technology*, *101*(11), 4021-4028.
[6] Amon, T., Amon, B., Kryvoruchko, V., Zollitsch, W., Mayer, K., & Gruber, L. (2007). Biogas production from maize and dairy cattle manure—influence of biomass composition on the methane yield. *Agriculture, Ecosystems & Environment*, *118*(1), 173-182.

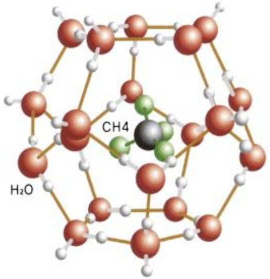
Using Captured Methane

- Cows produce about 10 pounds of volatile solids per day in manure.
- Anaerobic digestion can yield about 140 L of methane per kg of volatile solids, providing about 600 L of methane per animal per day [7].
- Cows emit a further 200–450 grams of methane a day, mostly from the mouth, offering a potential 450 L per day [8].

[7] Amon, T., Amon, B., Kryvoruchko, V., Zollitsch, W., Mayer, K., & Gruber, L. (2007). Biogas production from maize and dairy cattle manure—influence of biomass composition on the methane yield. *Agriculture, Ecosystems & Environment*, *118*(1), 173-182.
[8] Lassey, K. R. (2007). Livestock methane emission: from the individual grazing animal through national inventories to the global methane cycle. *Agricultural and forest meteorology*, *142*(2), 120-132.

Methane transport

- Methane/Natural Gas Hydrates (NGH) can be found in the permafrost or deep underwater but can also be synthesized artificially
- Between 150-180 cubic meters of natural gas can be contained in 1 cubic meter of hydrate (vs. 600 cubic meters methane/1 cubic meter of LNG)
- It is better than LNG (liquefied natural gas) for transport of small/medium volumes of natural gas since it doesn't have to be transported through a pressurized pipeline [99]
- Currently, NGH is being synthesized in a reactor with a water nozzle, methane gas, and a magnetic stirrer at high pressure (~50-70 bar/725 psi)
- Costs are quickly declining on production as the synthesis matures
- With the current technology, an engineering group in Norway has calculated transport of NGH instead of LNG is cheaper [9]
- If we could build small/medium-scale reactors in agricultural areas, methane hydrate would be the optimal way to transport excess methane to other areas for use without the need to install pipelines -- and it will be about 24% cheaper [10].



[9] Gudmundsson, Jon S. "Hydrate Non-Pipeline Technology for Transport of Natural Gas." Norwegian University of Science and Technology. *22nd World Gas Conference*, Tokyo 2003.
[10] J.S. Gudmundsson, A. Børrehaug. "Frozen Hydrate for Transport of Natural Gas." *2nd International Conference on Natural Gas Hydrate,* France 1996.

Environmental Impact

- Methane can be burned for electricity and is advantageous over coal- it releases up to 25% less CO_2 than burning the same amount
- Methane is a much more dense greenhouse gas than CO_2 → it has 23 times the global warming potential per volume [11]. This proposal removes what would become atmospheric methane.
- Through alternative methods of transport to LNG pipelines, natural gas usage can become more widespread, further eliminating coal burning.

[11] Livestock's Long Shadow: Environmental Issues and Options. Food and Agriculture Organisation of the United Nations. 2006.

Viability

- The methane separation process is the most expensive process (energy-wise and economically)
- As we demonstrate the viability of this method, further interest and development will make the process more and more efficient.
- This is a long term idea- many of the components still need to be optimized before it will be an economically attractive option to farms

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