U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Agricultural Utilization Research Institute – Renewable Energy Roundtable

St. Paul, MN

August 23, 2017

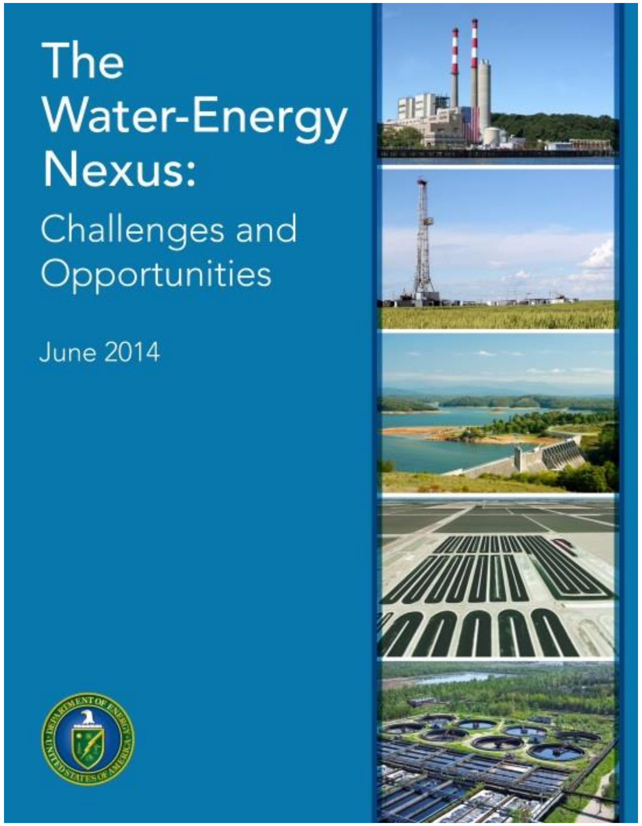
Biofuels and Bioproducts from Wet and Gaseous Waste Streams: Challenges and Opportunities

Mark Philbrick

U.S. Department of Energy

Water-Energy Nexus: DOE Engagement

- GAO issued report in Fall 2012, fifth in a series on energy-water nexus
- GAO found that the DOE was not doing enough to meet its obligations under the Energy Policy Act of 2005
- DOE agreed with the GAO, launched a cross-cutting Water-Energy Tech Team (WETT)
- Water-Energy Nexus a priority for Secretary Moniz
- WETT produced a comprehensive report in June, 2014
- Intended as a first step, an invitation to dialogue with stakeholders at multiple levels



Download the full report at energy.gov

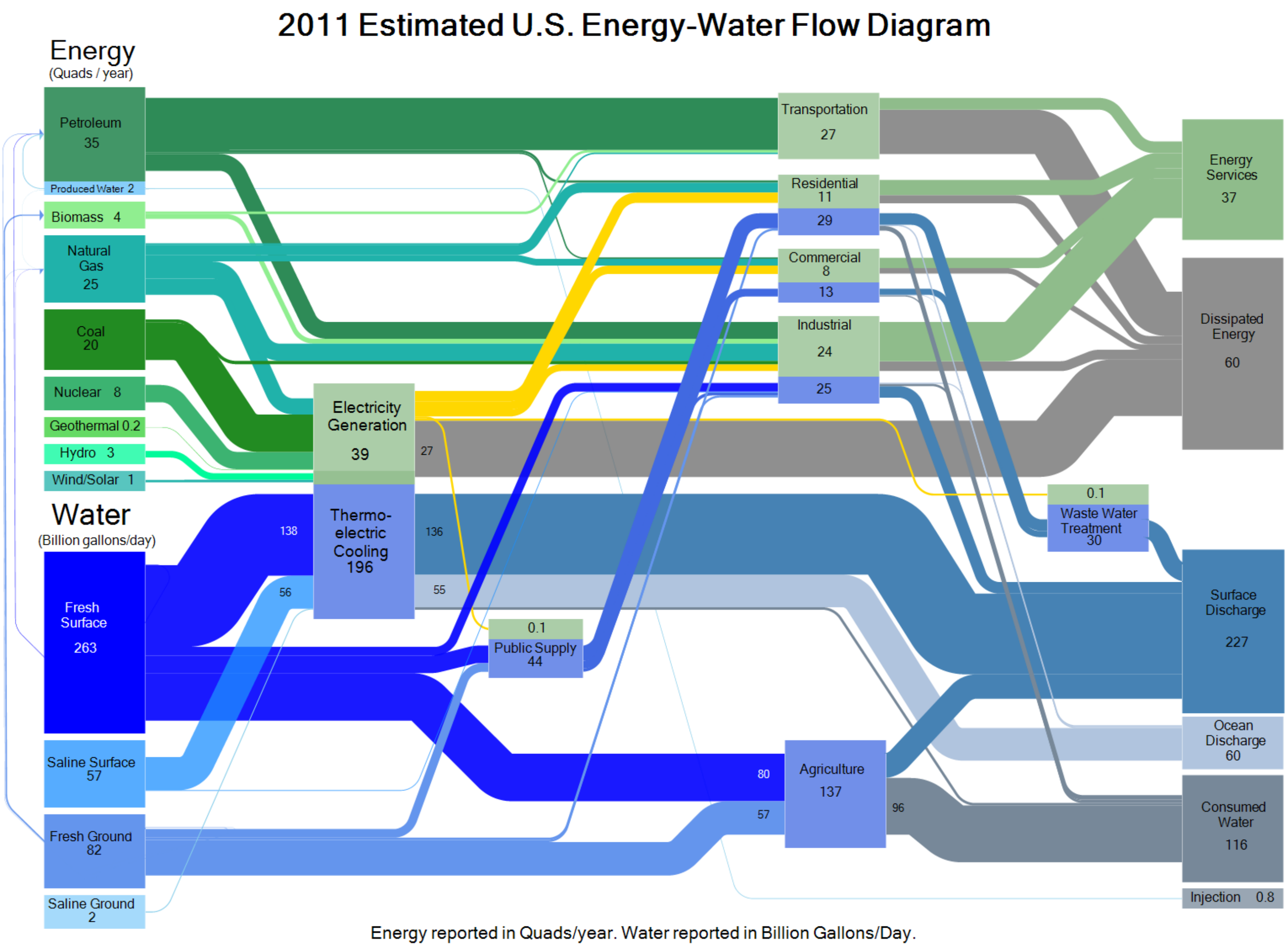
U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable E

Water-Energy Nexus: Critical National Need

- Energy and water are interdependent.
- Water scarcity, variability, and uncertainty are becoming more prominent.
  - Leading to vulnerabilities in the U.S. energy system
- We cannot assume the future is like the past in terms of climate, technology, and the evolving decision landscape.
- Replacing aging infrastructure brings an opportunity to make some changes.
  - **$600 billion** needed in water infrastructure investment over the next 20 years
- Energy and water issues are gaining international prominence.

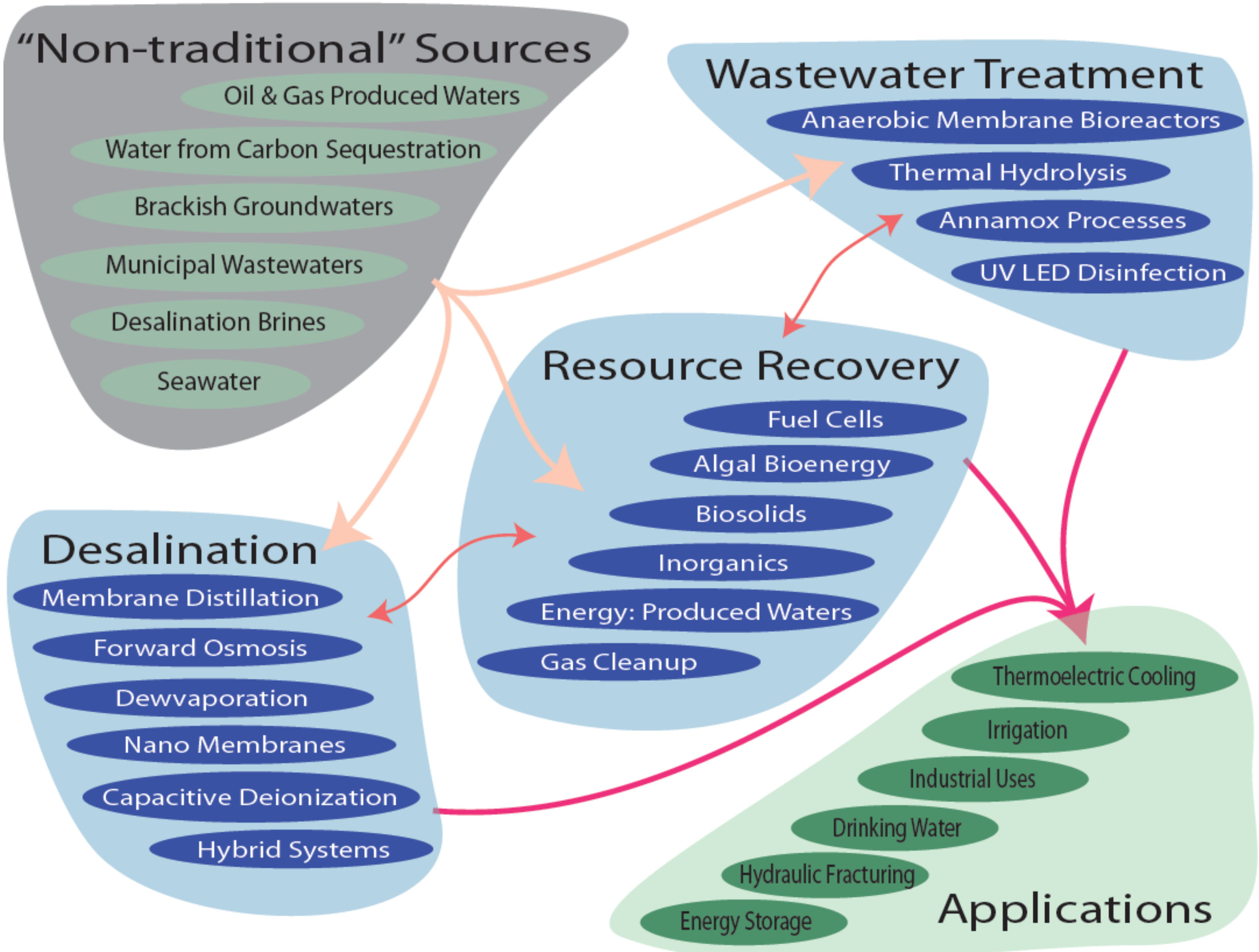
U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable E

Interconnected Energy and Water Systems



U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Technology RDD&D: Energy for and from Water



Bioenergy Technologies Office (BETO) Mission & Vision

A thriving and sustainable bioeconomy fueled by innovative technologies

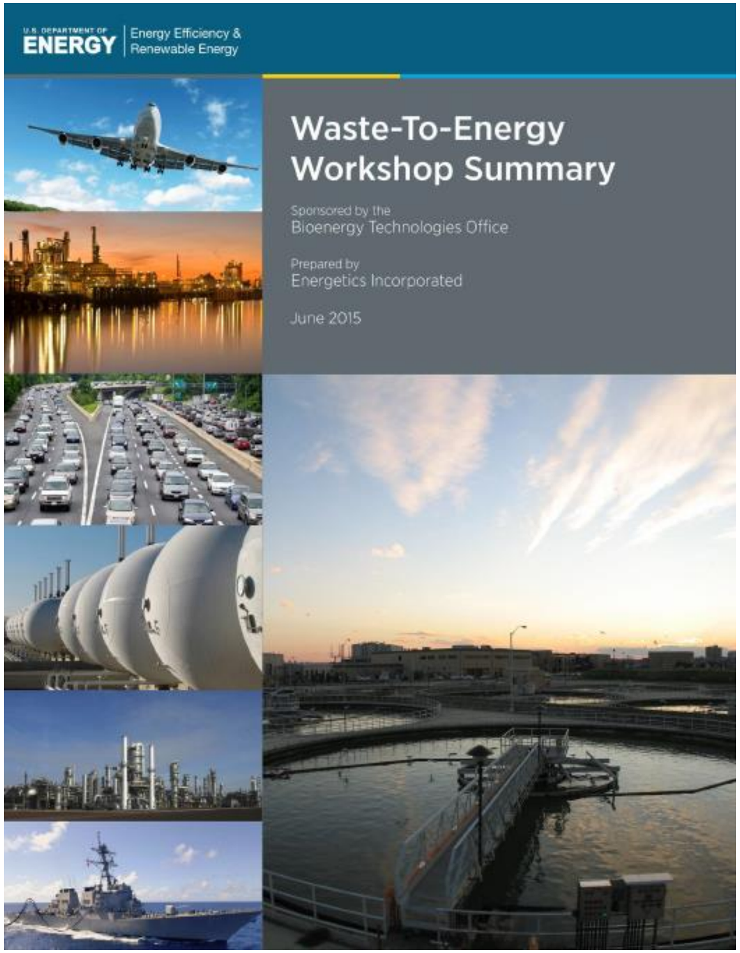
Developing and demonstrating transformative and revolutionary sustainable bioenergy technologies for a prosperous nation

Develop industrially relevant technologies to enable domestically produced biofuels and bioproducts without subsidies

BETO reduces risks and costs to commercialization through RD&D.

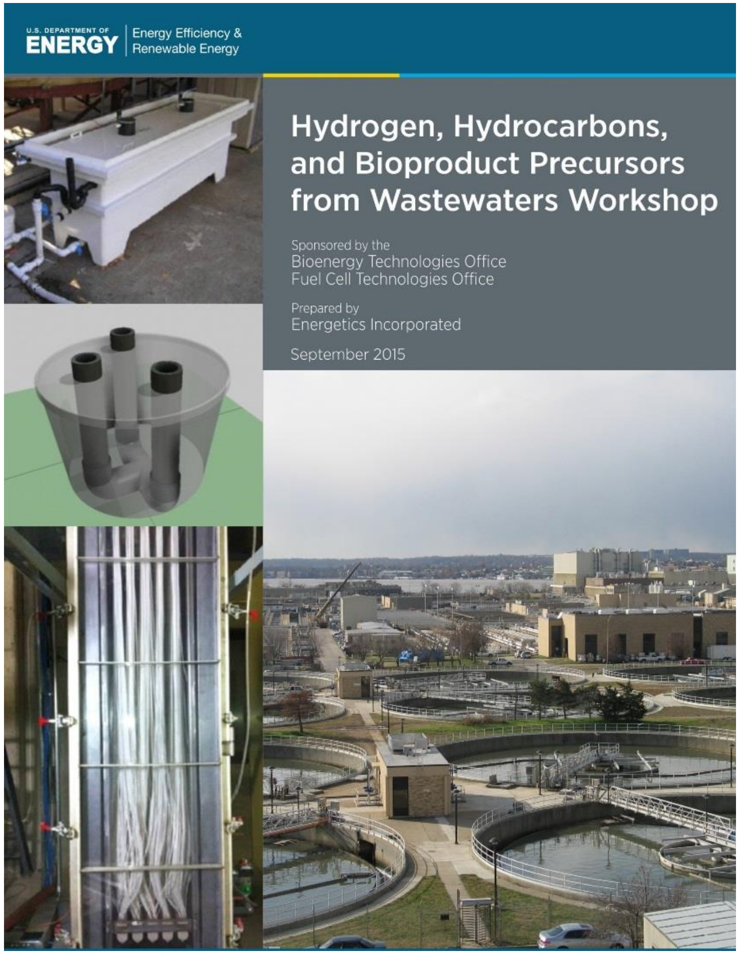
November 2014 Wet Waste-to-Energy Workshop

- Five summary conclusions:
  - Pre-processing
  - Conversion process research
  - Alternative anaerobic reactor designs
  - Biogas may not be the best intermediate for biofuels and bioproducts
  - Detailed and comprehensive resource assessment lacking, and essential
- Report available: http://www.energy.gov/eere/bioenergy/waste-energy-workshop



March 2015 Joint Fuel Cells-Bioenergy Workshop

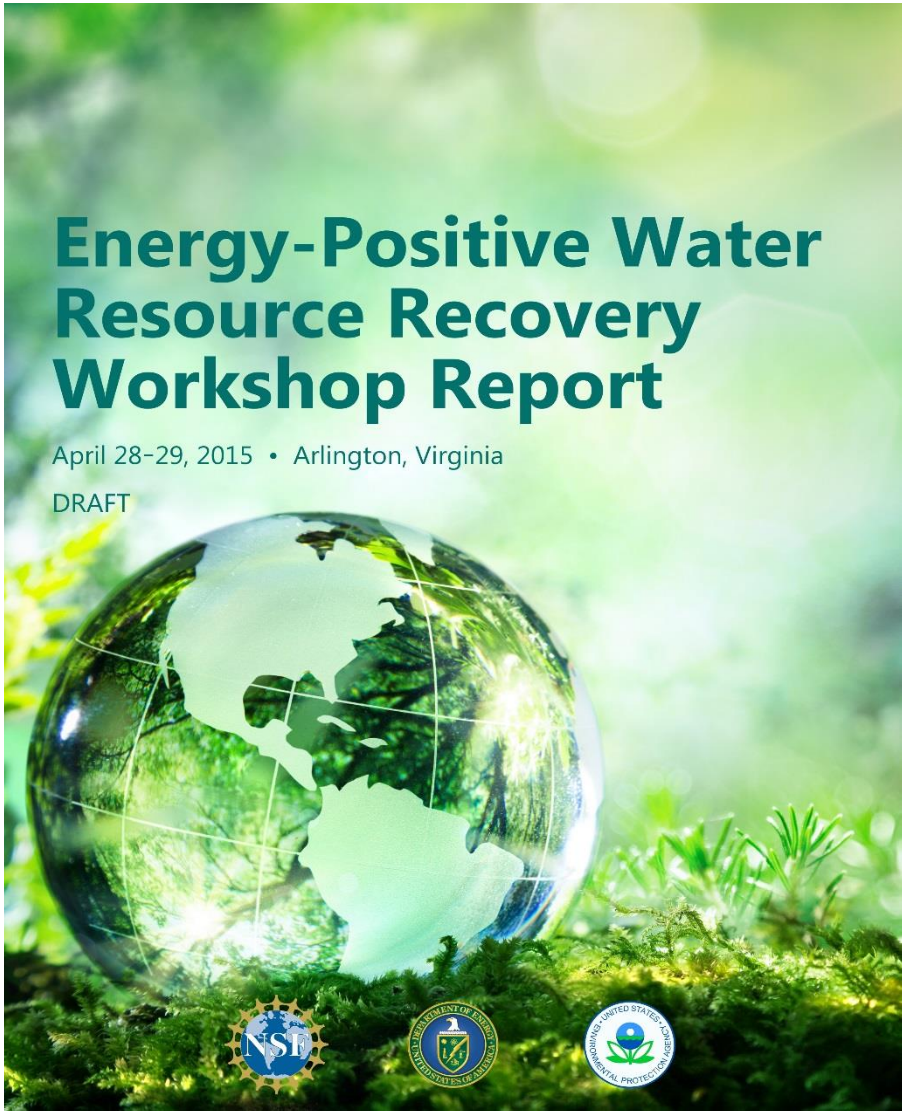
- **AnMBRs**
  - Membrane fouling and methane permeation key issues
  - Combination of fluidized-bed reactors with granular activated carbon one promising solution
    - Other options are possible
  - Energy-positive solutions have been demonstrated at pilot scales
  - Larger pilots under way at Stanford and in Singapore
- **MxCs**
  - Scalability always the question
  - Skid-mounted systems are in commercial test for flowback/produced water from Oil and Gas operations
- Targeted industrial wastewater markets are probably the best candidates for initial niche commercialization (true for both AnMBRs and MxCs)
- Distributed Processing Systems to produce transportable product intermediates



- Presentations available at: http://energy.gov/eere/fuelcells/hydrogen-hydrocarbons-and-bioproduct-precursors-wastewaters-workshop

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

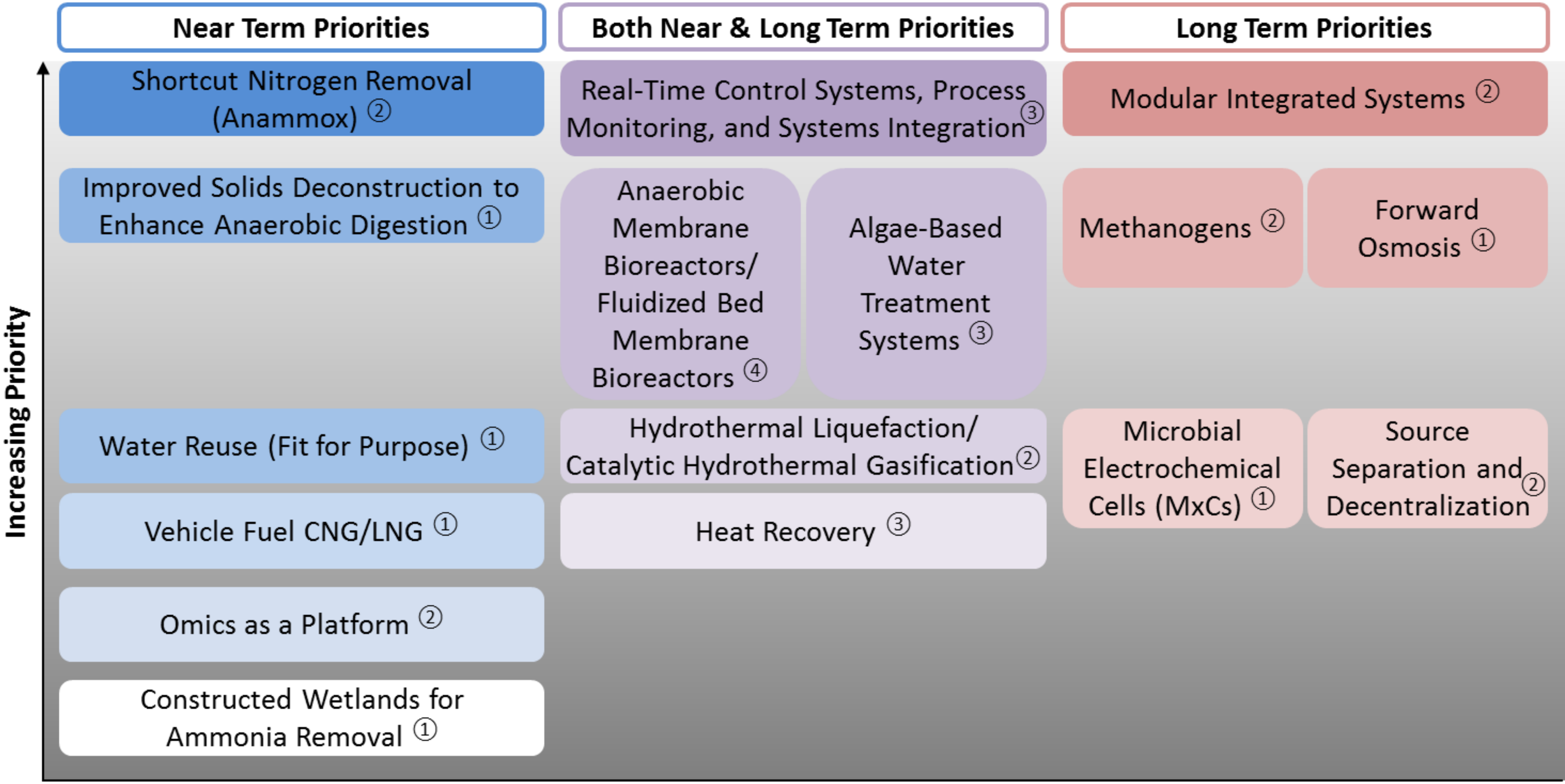
April 2015 Energy-Positive Water Resource Recovery Workshop (w/NSF & EPA)



- Building on previous work from WEF/WERF/NACWA (and EPRI)
- Opportunity for collaboration among NSF, EPA, and DOE, together with external stakeholders
- Joint between BETO and WETT

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

April 2015 Workshop Participant Priorities

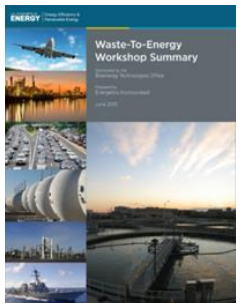


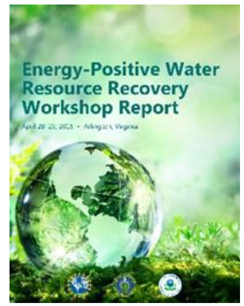
①Research area prioritized by a single breakout group; ②Research area prioritized by two different breakout groups; ③Research area prioritized by three different breakout groups; ④Research area prioritized by all four breakout groups

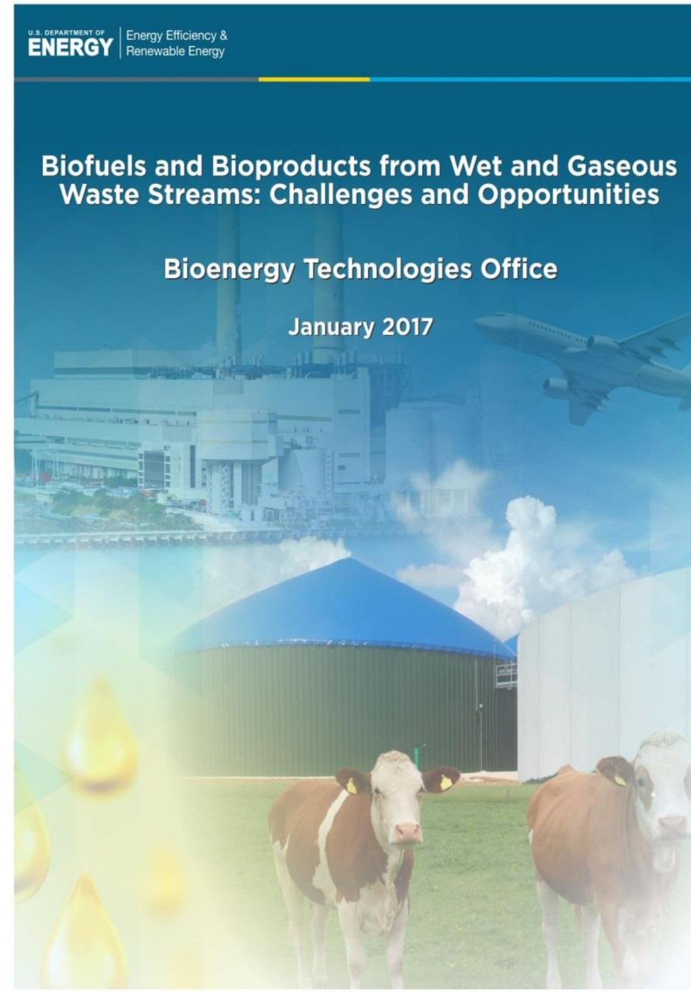
U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Biofuels and Bioproducts from Wet and Gaseous Waste Streams

Building off of series of four workshops and other recent interagency collaborations.







U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

U.S. Wet and Gaseous Waste Streams Contain Substantial Chemical Energy

	Annual Raw Resource Generation[1]		
Feedstocks	Estimated Annual Resources	Inherent Energy Content (Trillion Btu)	Inherent Fuel Equivalent (MM GGE)[2]
Wet Feedstocks	77.17 MM Dry Tons	1,078.6	9,290.8
Wastewater Residuals	14.82	237.6	2,046.6
Animal Waste	41.00	547.1	4,713.0
Food Waste[4]	15.30	79.6	685.3
Fats, Oils, and Greases	6.05	214.3	1,845.9
Gaseous Feedstocks		733.6	6,319.8
Biogas[5]	420 BCF	430.5	3,708.6
CO_2 Streams	3,142 MM Tons	-	-
Associated Natural Gas	289 BCF	303.1	2,611.2
Other Waste Feedstocks		526.1	4,531.6
Glycerol	0.6 MM Tons	8.7	75.1
Black Liquor	44 MM Tons	517.4	4,456.5
DDGS	44 MM Tons	n/a	n/a
Total		**2,338.3**	**20,142.2**

As Received, 32 wt% Solids, autoclaved

Processed Biocrude

[1] Data from Table ES.1 of "Biofuels and Bioproducts from Wet and Gaseous Waste Streams: Challenges and Opportunities." (Revised), published by the Bioenergy Technologies Office.
[2] 116,090 Btu/gal. This does not account for conversion efficiency.
[3] Petroleum consumption data from Table 3.5, Table 3.6, Table 3.7c, and Table 3.8c of EIA Monthly Energy Review, 2015 Total Values
[4] The moisture content of food waste varies seasonally, ranging from 76% in the summer to 72% in the winter.
[5] Methane potential. This does not include currently operational landfill digesters (>1,000 billion cubic feet [Bcf] annually).

Estimated Production of HTL Bio-Crude from Waste Streams is Equivalent to 147 MM BBL (26.0%) of 2015 U.S. Jet Fuel Consumption

Feedstocks	Estimated Annual HTL based Bio-Fuel[1]	2015 Consumption[2]	
		Jet Fuel	Diesel
Manure	63.33 MM BBL	11.21%	4.34%
Fattened Cattle Manure	17.62	3.12%	1.21%
Dairy Cow Manure	23.78	4.21%	1.63%
Swine Manure	21.93	3.88%	1.50%
Publicly Owned Treatment Works (POTW)	33.55 MM BBL	5.94%	2.30%
POTW (Primary + Secondary Sludge)	33.55	5.94%	2.30%
Food Waste	22.38 MM BBL	3.96%	1.54%
Food Waste	22.38	3.96%	1.54%
Fats, Oils, and Greases (FOG)	27.61 MM BBL	4.89%	1.89%
Animal Fats (Livestock + Poultry)	14.79	2.62%	1.01%
Brown Grease	7.71	1.37%	0.53%
Yellow Grease	5.11	0.90%	0.35%
Total	**146.87 MM BBL**	**26.00%**	**10.07%**

Jet Fuel Consumption (2015):

565 MM BBL

Diesel Consumption (2015):

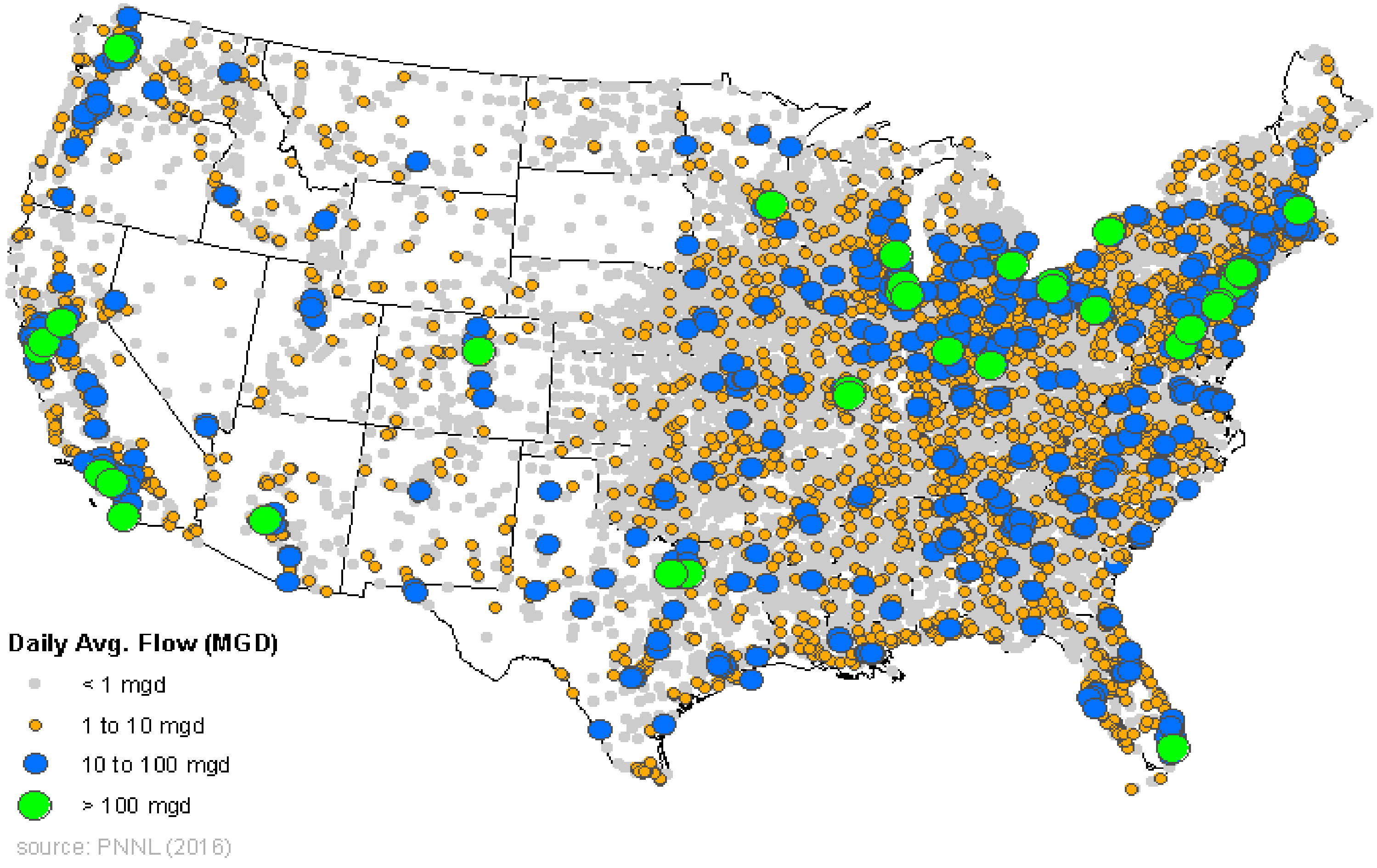
1,458 MM BBL

Assumes 1:1 conversion of HTL Bio-Oil to Diesel or Jet Fuel by volume

[1] Estimated annual bio-crude production assessment for each waste feedstock in the conterminous United States. Values from "Waste-to-Energy Biofuel Production Potential for Selected Feedstocks in the Conterminous U.S." by Skaggs, Richard L., et al. A reasonable estimate of the V:V conversion from HTL bio-oil to diesel or jet fuel is 1:1.

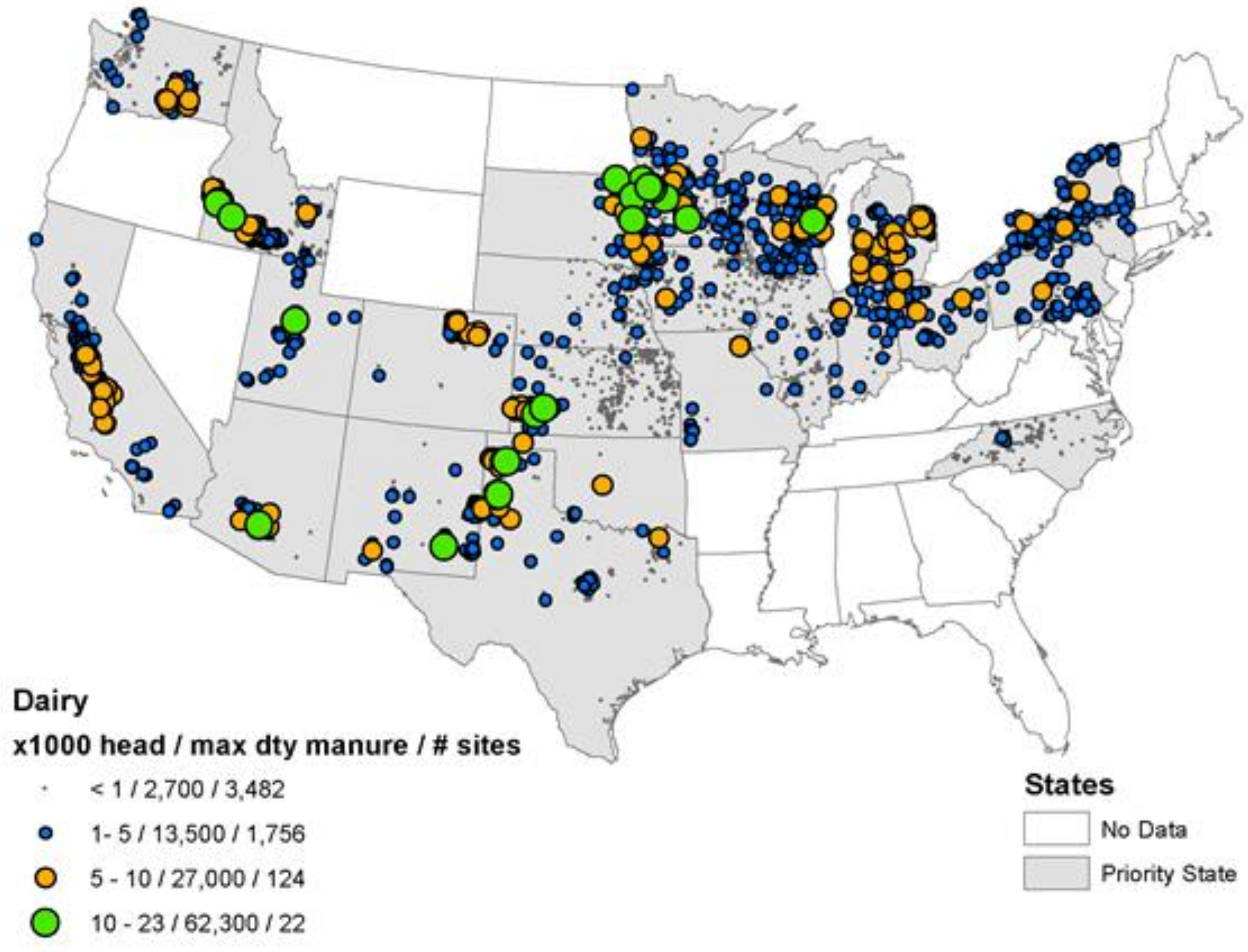
[2] Jet Fuel and Diesel total from Table 3.5 of EIA Monthly Energy Review. Diesel consumption is taken from Distillate Oil consumption which consists of fuel oil and diesel fuel.

Distributed Resources: Water Resource Recovery Facilities



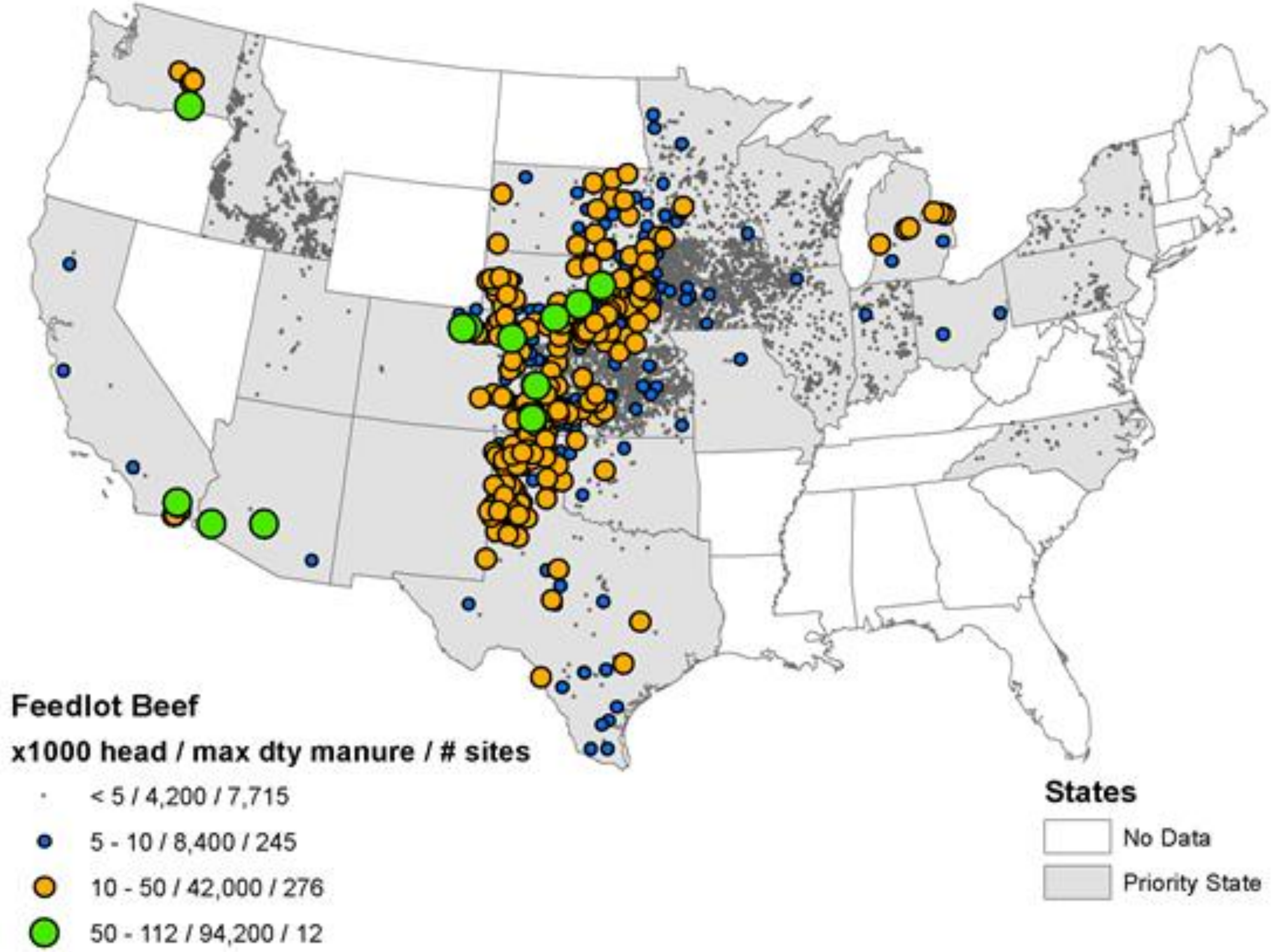
Spatial distribution and influent range of 14,581 U.S. EPA CWNS 2012 catalogued treatment plants

Distributed Resources: Dairy Manure



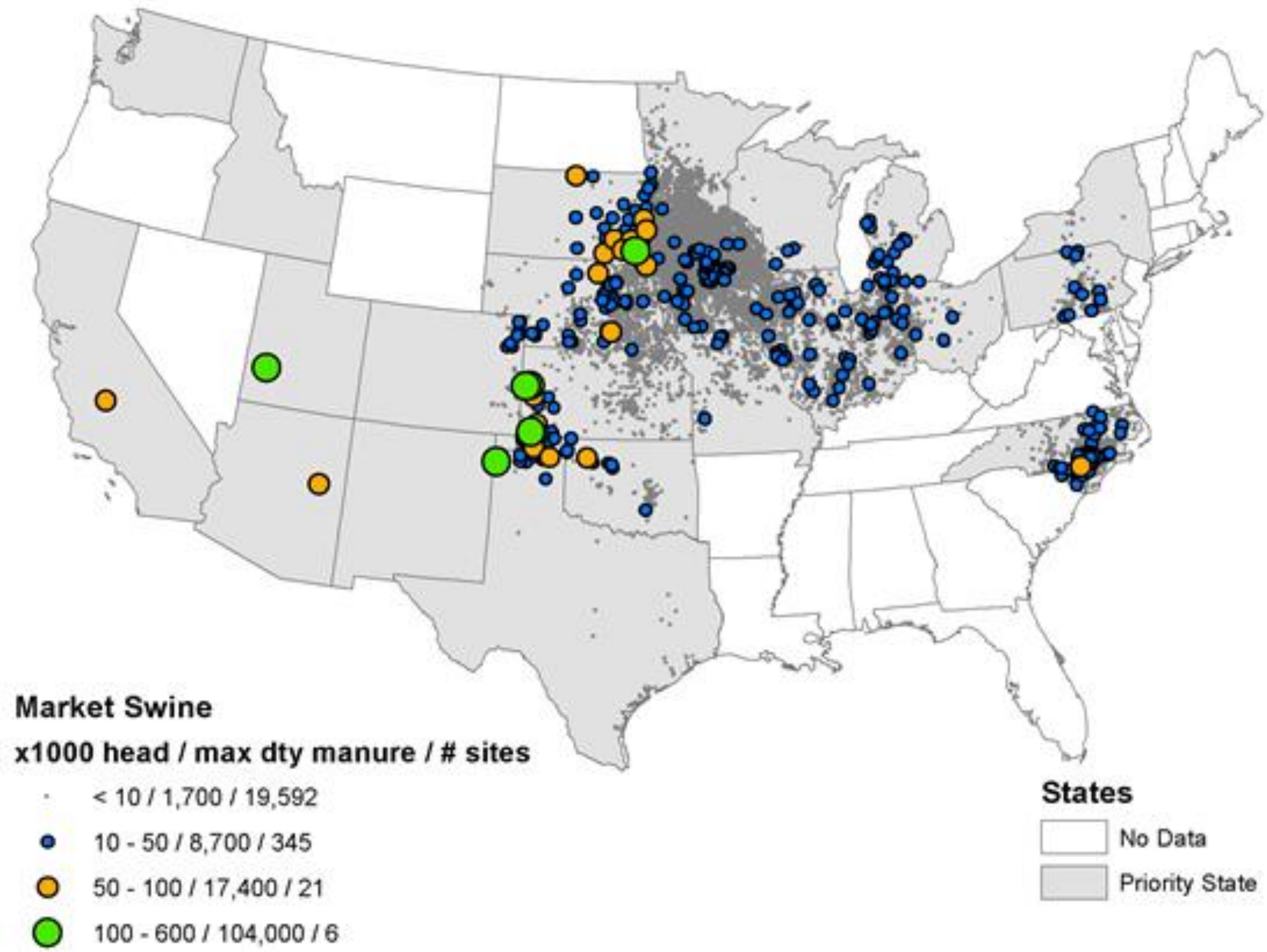
Recoverable Manure for Dairy Cows

Distributed Resources: Feedlot Beef



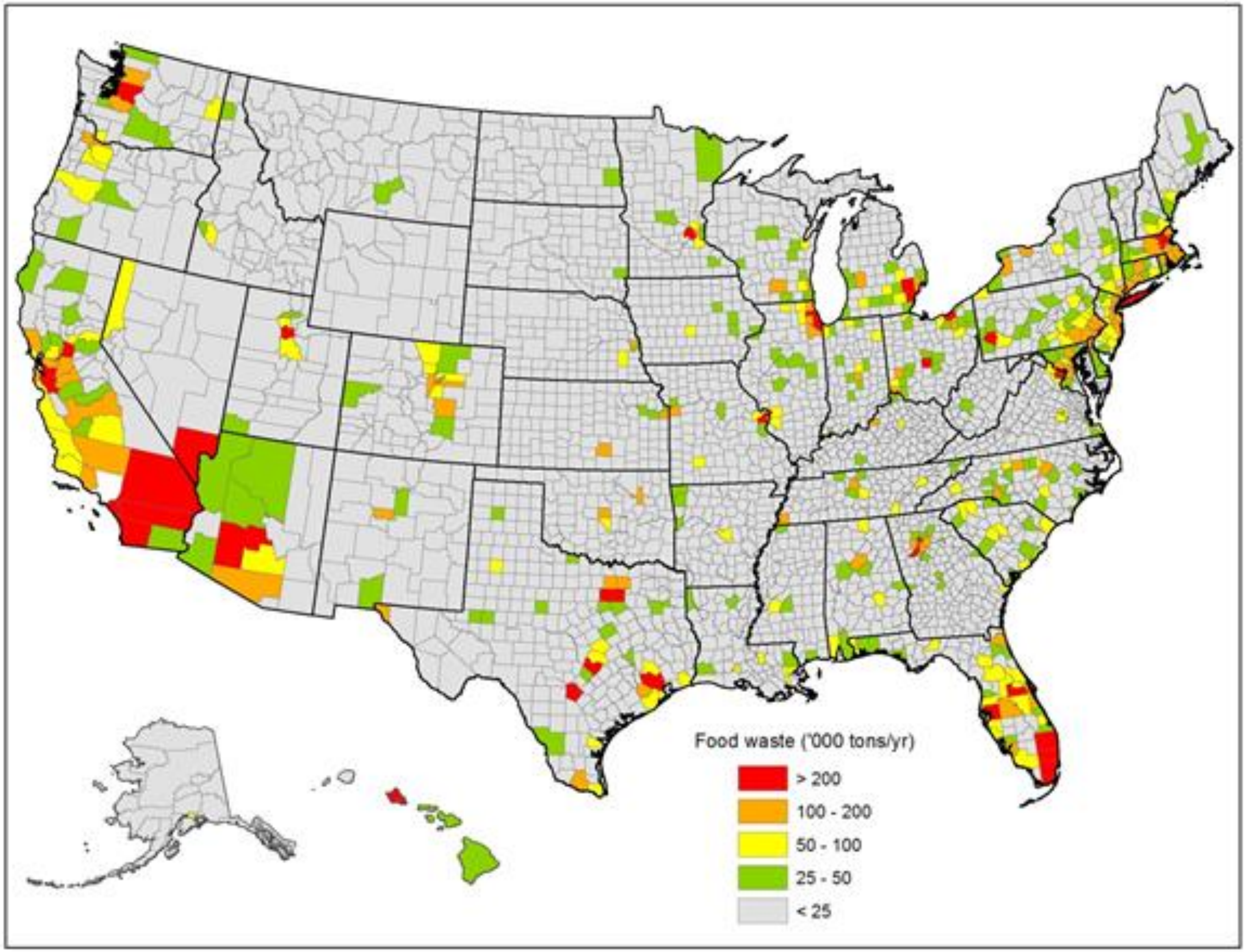
Recoverable Manure for Fed Beef Cattle

Distributed Resources: Swine



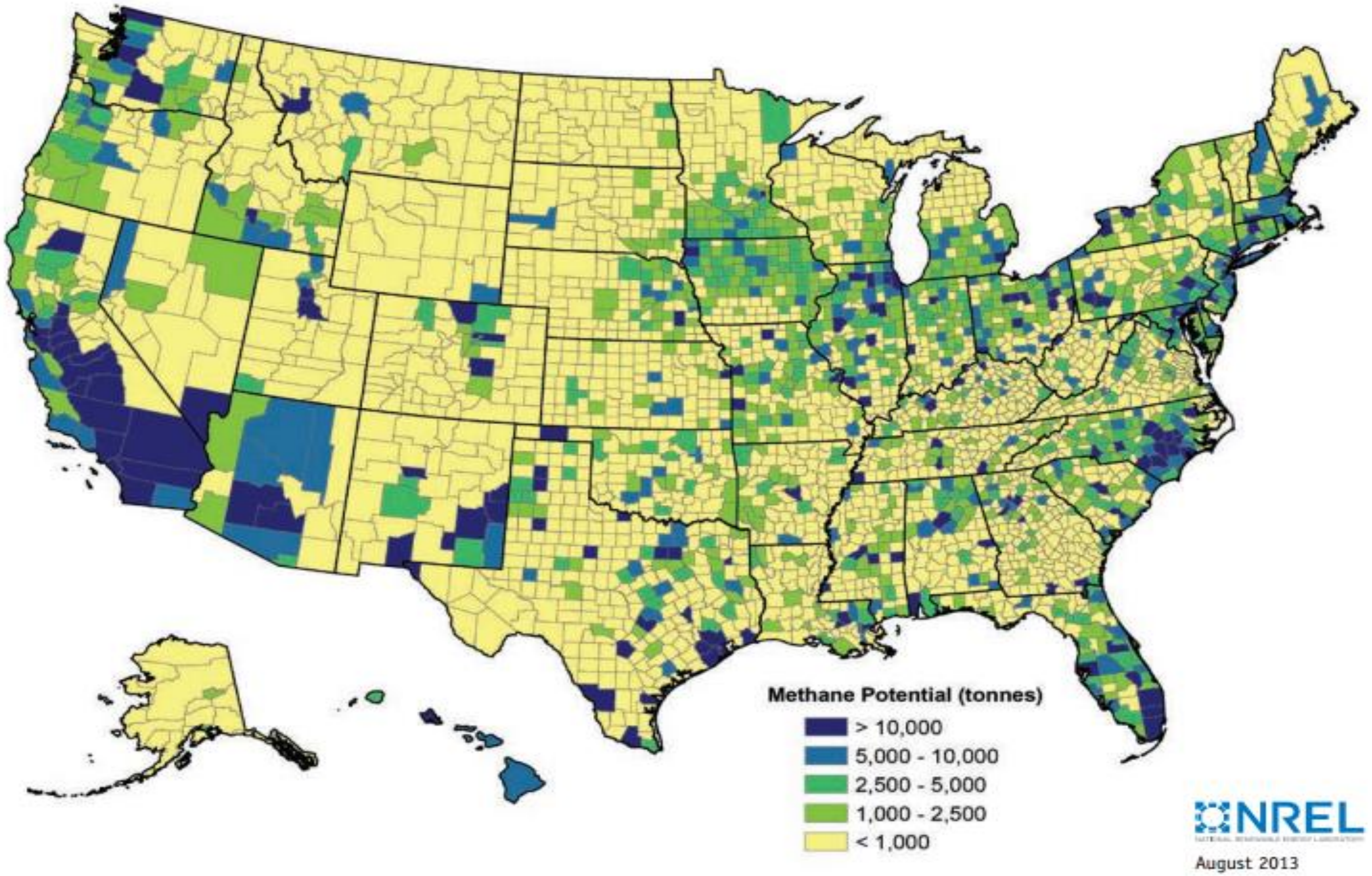
Recoverable Manure from Market Swine

Distributed Resources: Food Waste



U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Distributed Resources: Biogas Potential



Methane potential from landfill material, animal manure, wastewater and food waste in the United States, from (NREL 2013)

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

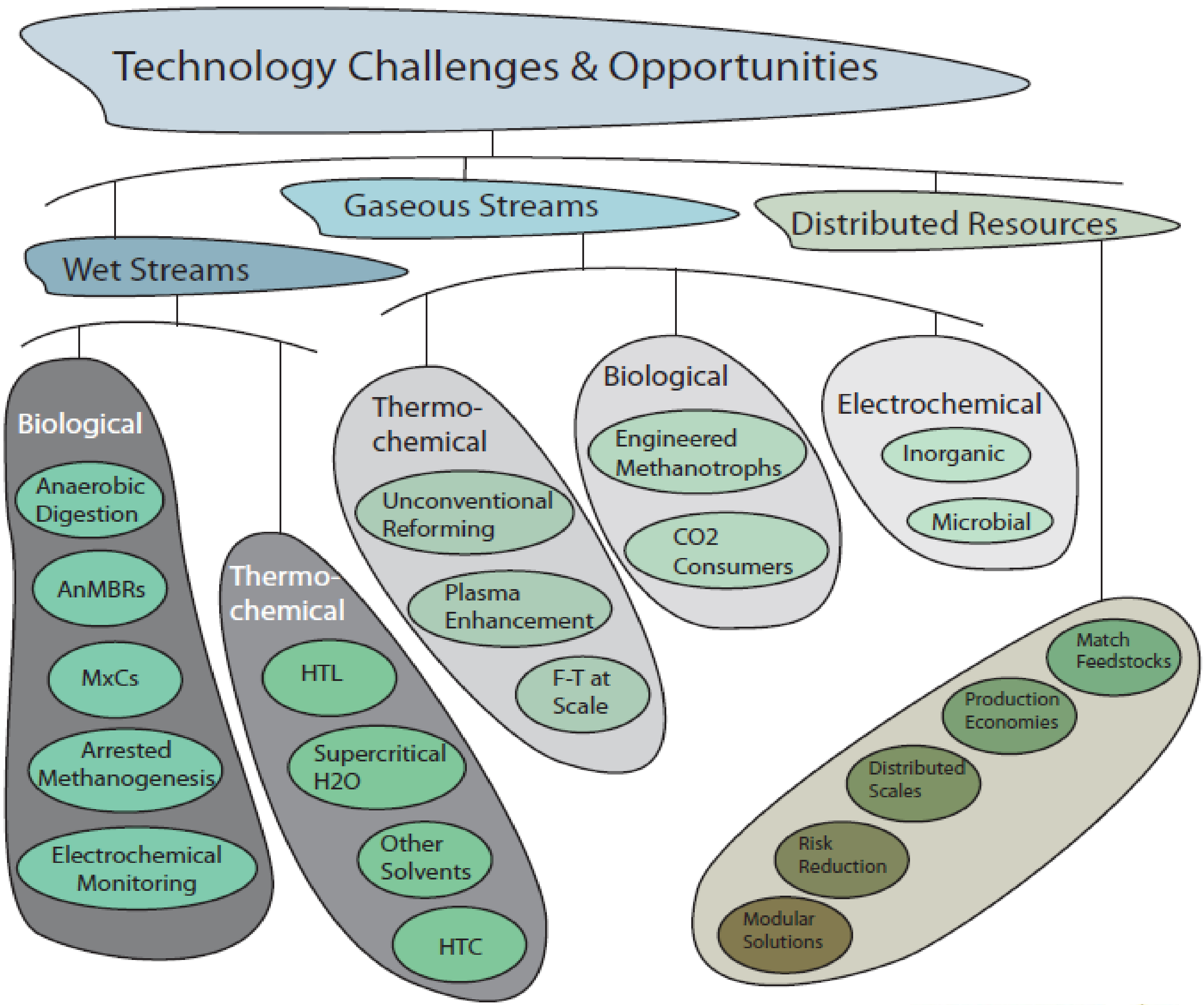
Distributed Resource Challenges

- Transportation of Wet Feedstocks Cost-Prohibitive
- Production of Transportable Intermediates
- Integration with Regional Upgrading Facilities
  - Pacific Northwest National Lab working on the techno-economics of this problem as one next step
- Conversion Technologies Must Match Scale of Feedstock Availability
  - Modular solutions one possibility
  - Economies of Mass Production instead of/in addition to Scale
  - Take Advantage of Learning Curves
- Not your Grandmother's Fuel Production Problem
  - Traditional Petroleum Refinery Scale is not an option
  - Bioproducts probably necessary to enable biofuels in short-to-medium term
  - Wet and Gaseous Feedstocks Require Different Conversion Technologies

Need to Consider Competing Uses

Food waste hierarchy taken from BSR (2012)

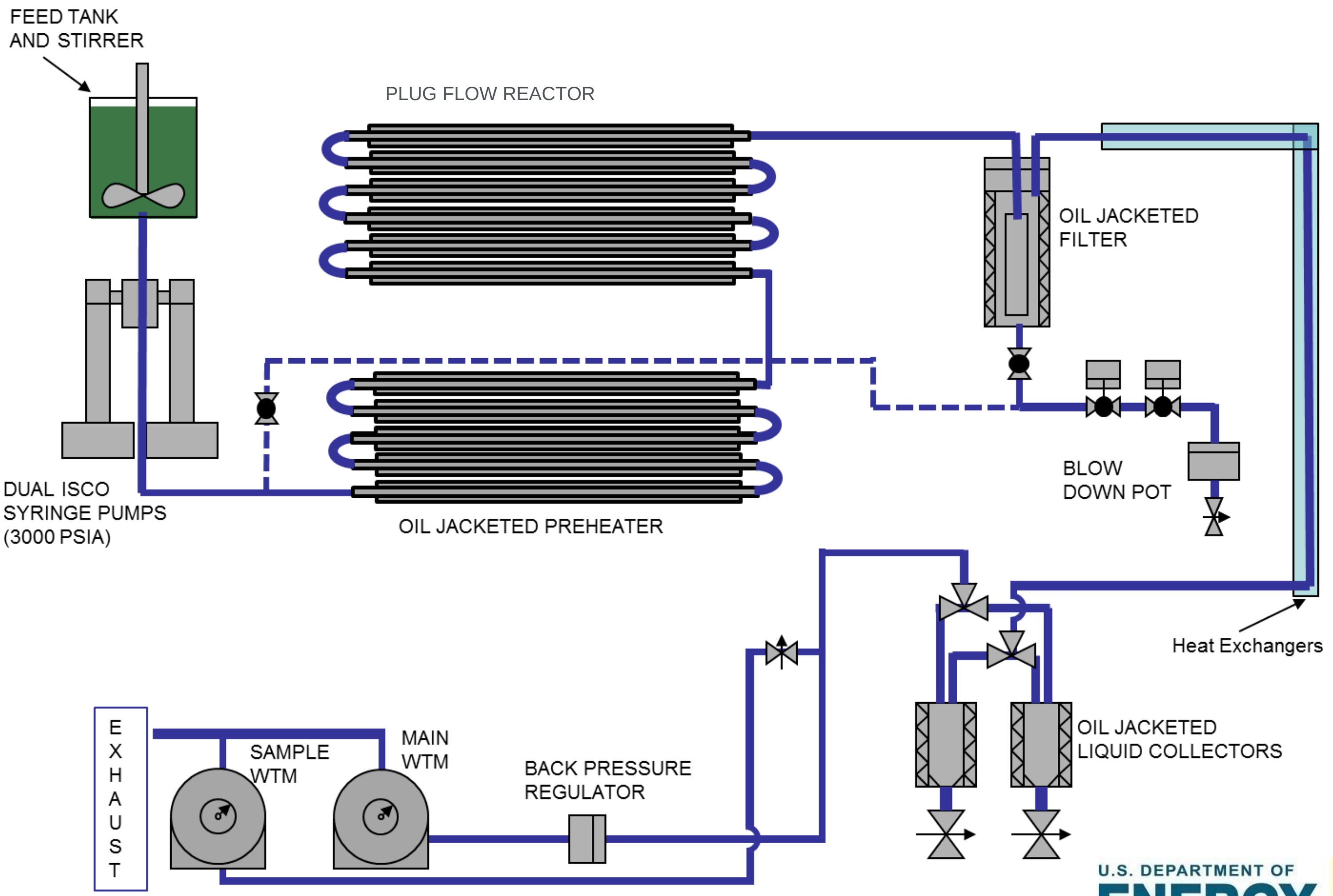
Potential Areas for Technology RDD&D



Current Waste-to-Energy R&D Vehicles

- National Laboratories
  - Resource Assessments
  - Future Market Modeling
  - Technology Development
    - Hydrothermal Liquefaction (HTL) of Sludge and other Wet Feedstocks
    - Biological Conversion of both CH_4 and CO_2 in Biogas to Bioproducts
    - Alternatives to Traditional Anaerobic Digestion
- Small Business Innovation Research (SBIR) grant program
  - Phase I, $150k for one year
  - Phase II, $1M over two years
  - 18 phase I and 6 phase II awards over last two years
  - First FY 18 solicitation currently open
- Pilot and Demonstration Funding Opportunity
  - Two Waste-to-Energy awards in FY 17

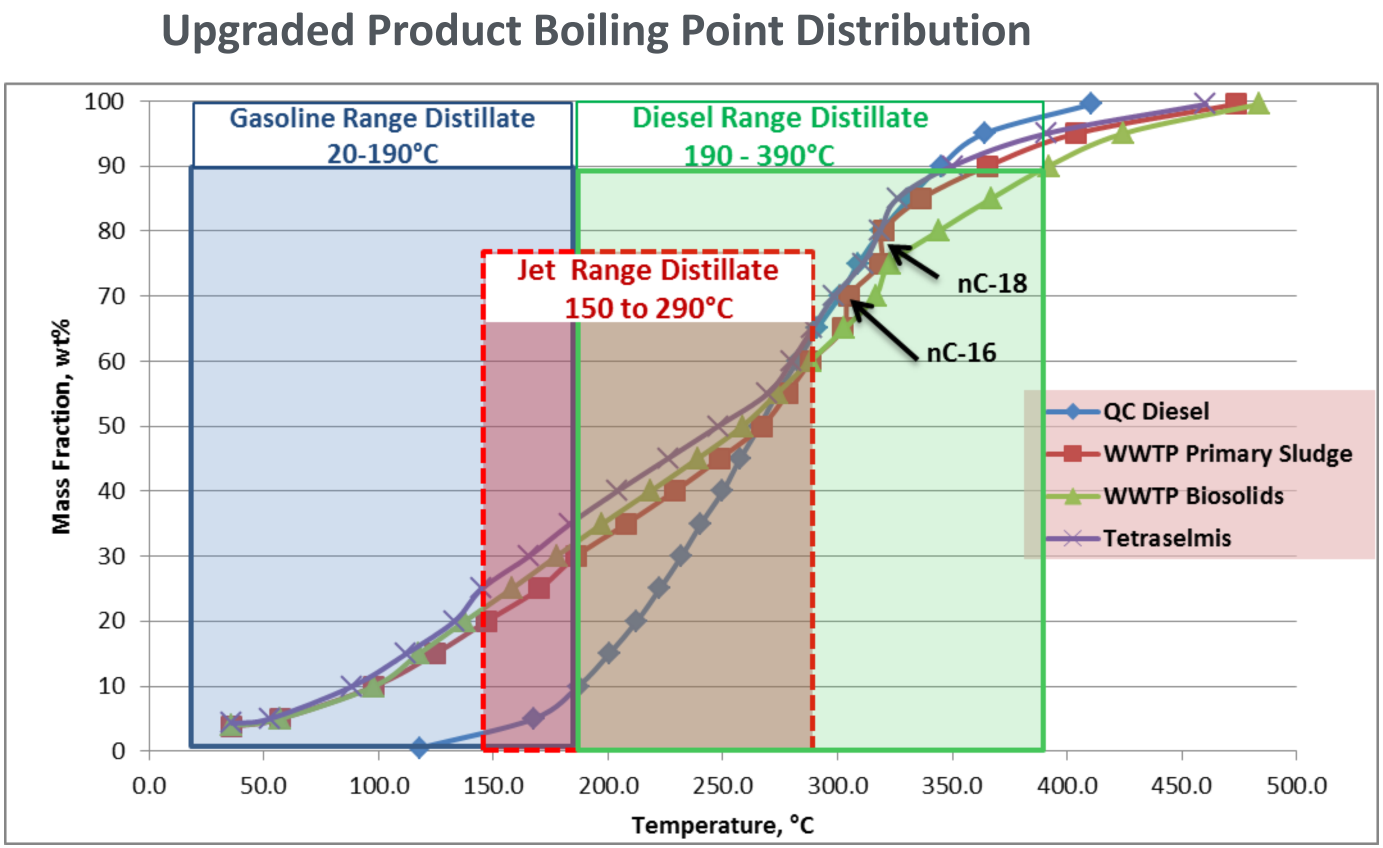
Hydrothermal Liquefaction (HTL) - PNNL



HTL Operating Conditions

- Average T, P: 330-350°C, 2900psig
- Slurry feed rate: 1-4 L/h (LHSV=1-6 L/L/h)

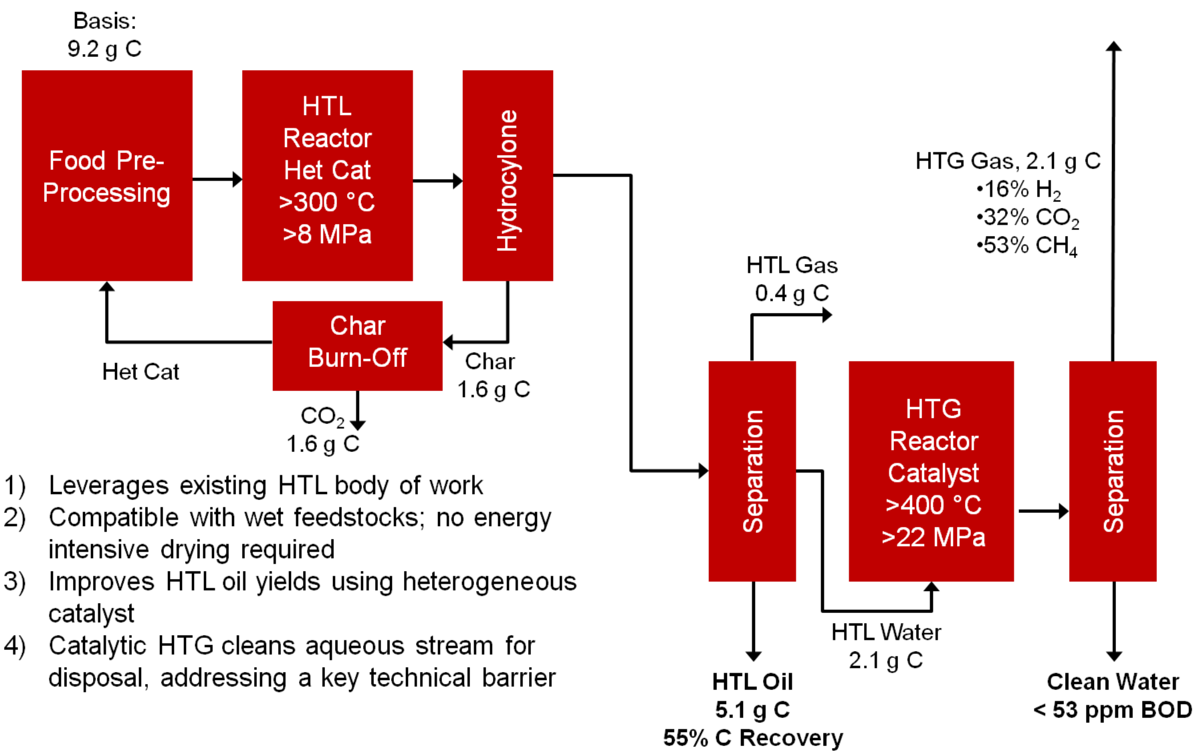
HTL: Jet and Diesel Blendstock from Sludge - PNNL



- Distillation curve for primary sludge similar to Algae (tetraselmis)
- Approximately 60% of hydrotreated product from HTL sludge biocrude similar to Diesel range distillate.

HTL of Food Waste (SBIR phase II)

- Use a heterogeneous catalyst (Het Cat) to improve HTL oil yield
- Catalyst converts aqueous organics to water insoluble compounds
- Gasify remaining aqueous organics to decrease disposal costs

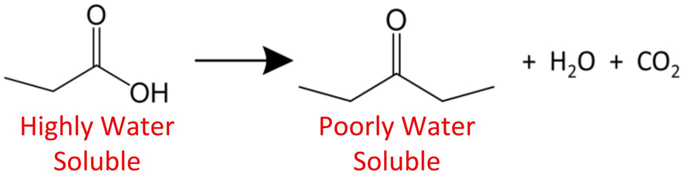


1) Leverages existing HTL body of work
2) Compatible with wet feedstocks; no energy intensive drying required
3) Improves HTL oil yields using heterogeneous catalyst
4) Catalytic HTG cleans aqueous stream for disposal, addressing a key technical barrier

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

HTL of Food Waste: SBIR Phase I Results

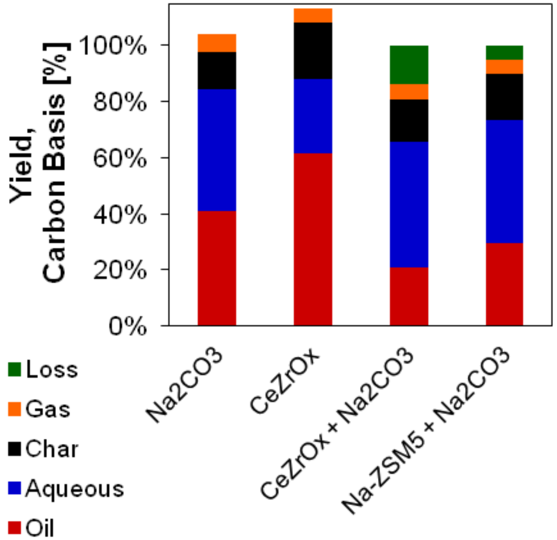
- Het Cat is stable under hydrothermal conditions for at least 165 hrs
- Het Cat ketonized propionic acid to 3-pentanone at 15-20% yield
- Het Cat increased HTL oil yield (from 41% to 61%, Carbon basis) and decreased aqueous organics



HTL Water →Na_2CO_3 Catalyst

HTL Water →Het Catalyst

HTG Water →HTG Catalyst

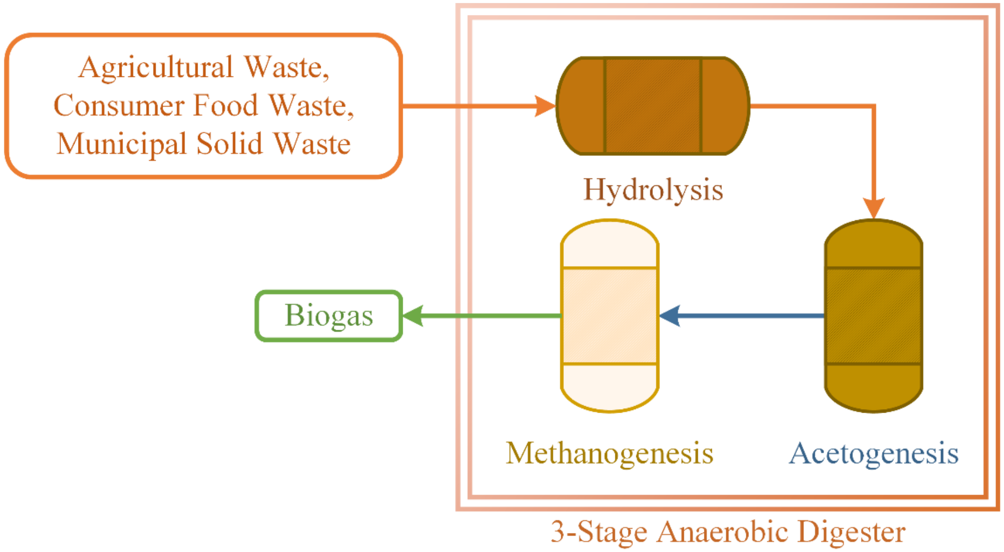


- **Het Cat reduced aqueous organics 50% compared to Na_2CO_3 (24,200 vs 12,500 ppm TOC)**
- **Catalytic HTG converts 98% of organic carbon to gases (24,200 to 550 ppm TOC)**

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Waste Biomass to High Value Chemicals – SBIR Phase I & II

Fuels and Products from Organic Wastes – SBIR Phase I and II



Process	2nd Gen Cellulosic	Petrochemical route	X Co. (projected)	AD-Biogas
Product	Ethanol	Fuels and Chemicals	Fuels and Chemicals	Methane
Production cost ($/kg)	2-5	0.5-3	1-2	0.5-1
Product Value ($/kg)	1	0.5-3	1-3	0.1
Capital Intensity ($/kg)	6-10	1.5-3	2-3	1-2
Minimum size ($M/plant)	250-500	1,000	15-25	5-7
Feedstock source	Biomass	Petroleum	Biomass	Biomass
Feedstock flexibility	Medium	Low	High	High

BROWN GREASE TO BIODIESEL – SBIR Phase I & II

Feed - FOG from WWTP after Debris Removal and Dewatering

Fats Extracted with SCCO2

Biodiesel Product (FAME) after Reaction with Methanol in SSC Process, and Removal of Glycol and Water

"This is the best looking waste derived bio-diesel I have ever seen!"
- Industry Consultant
April 2017

Step 1: Supercritical Fluid Extraction with Carbon Dioxide was successful in extracting the triglycerides and free fatty acids (TGA/FFA) from the contaminants in the brown grease.

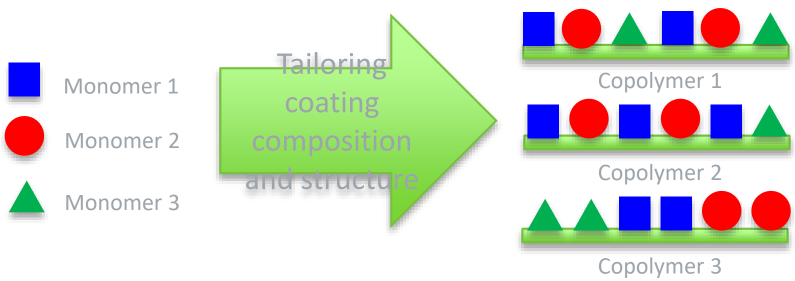
Step 2: React treated TGA/FFA lipids from Step 1 using the Supercritical Solid Catalyst (SSC) reaction process to produce Bio-Diesel or FAME (Fatty Acid Methyl Esters).

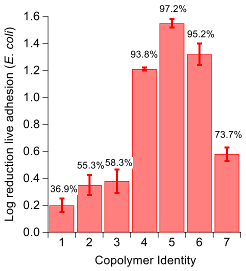
Company Y is developing a coating for PVDF ultrafiltration membranes to reduce biofouling in anaerobic membrane bioreactors at least 90% during biobutanol production.

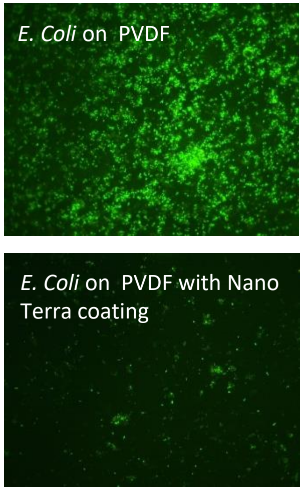
Reduced biofouling will lead to decreased operational and capital costs for an AnMBR plant and a more positive energy balance.

The coating is:

- An organic copolymer (non-metal)
- Covalently attached to the membrane (non-leaching)
- Non-toxic (does not interfere with cell viability in solution)
- Non-specific (resists fouling by proteins, sugars, bacteria)
- Optimizable for chosen conditions by modifying its composition and structure



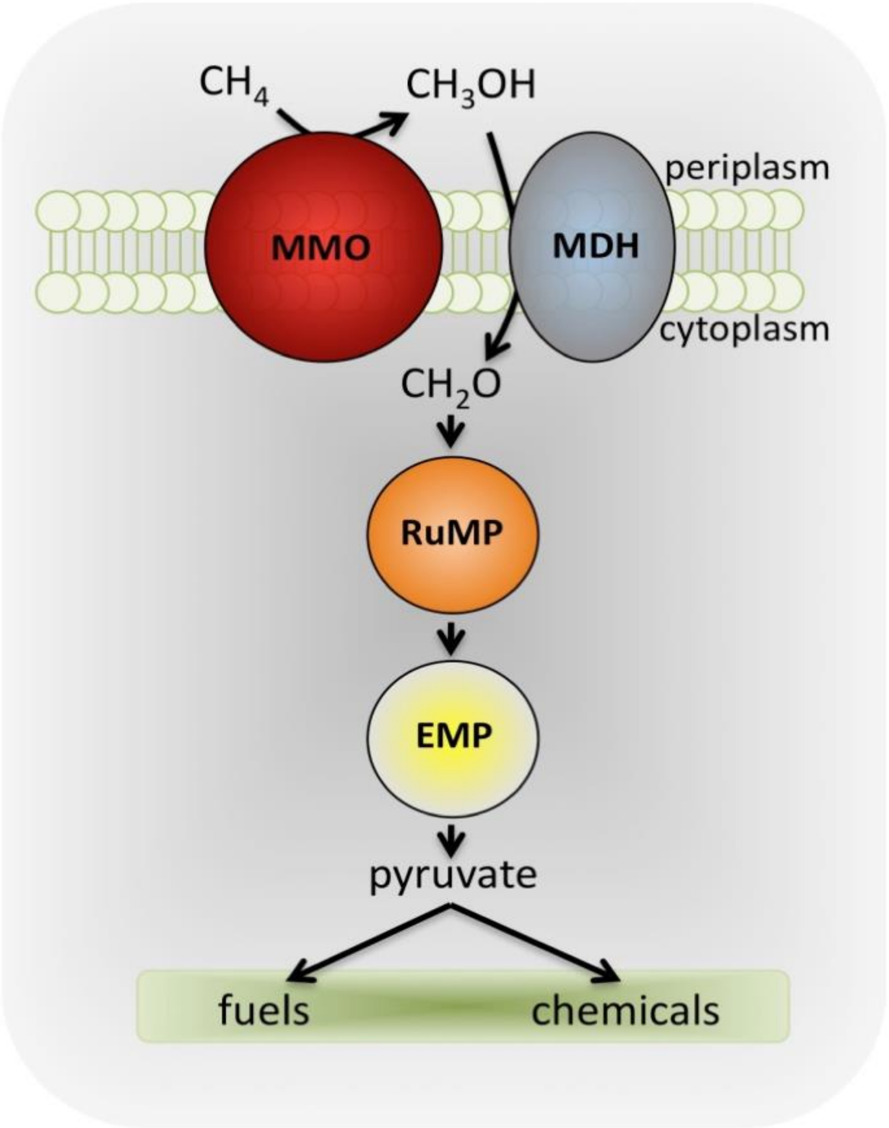




Left) Reduction of number of adhered *E. coli* cells on coated PVDF membranes compared to uncoated control. Right) Fluorescence microscope image of *E. coli* of untreated PVDF substrate (top) and on PVDF treated with antifouling coating (bottom).

Biological Upgrading of CH_4 and CO_2 in Biogas - NREL

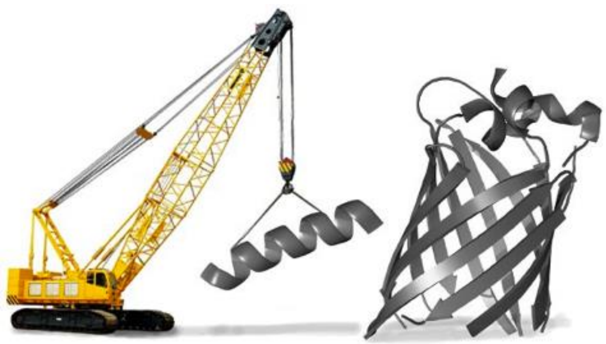
- The gaseous state of biogas prevents facile integration with current transportation and industrial infrastructure.
- Biological gas-to-liquid conversion offers a means to bypass conventional chemical and physical conversion strategies.
  - Modular, scalable, selective
- Methanotrophic bacteria can use CH_4 (and CH_3OH) as sole carbon and energy source.

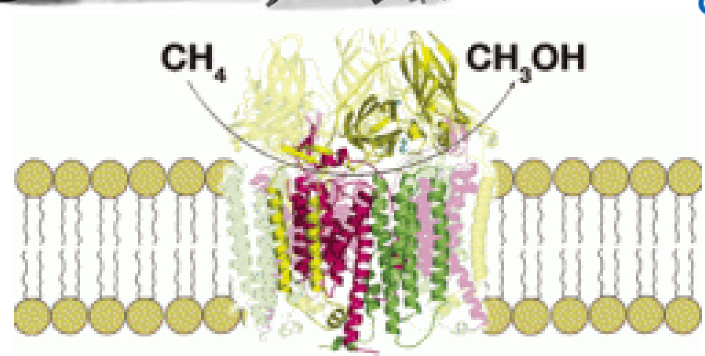


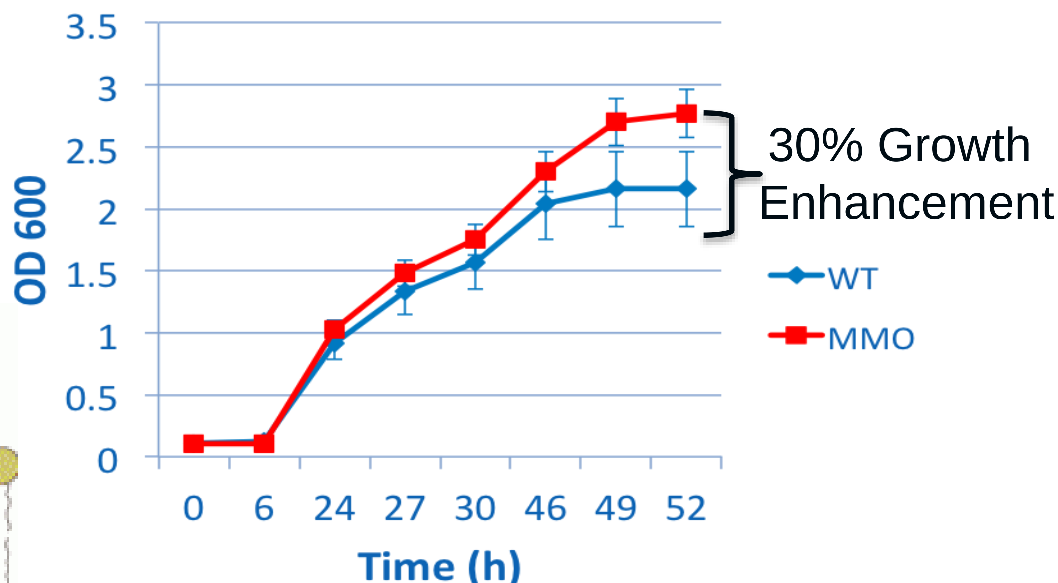
U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Enhanced Methane Activation via Protein Engineering

- **FY17 Target:** 20% enhancement in methane oxidation.
- Methane monooxygenase catalyzes oxidation of methane to methanol.
  - Unknown mechanism; low activity represents a potential bottleneck.
- **Approach:** Generation of MMO mutant libraries (>2,000 variants).
- **Result:** 30% growth enhancement with no alteration to composition.
  - *Represents highest growth/oxidation enhancement reported to date for methanotrophic bacteria.*
  - Combinatorial strain engineering approaches underway.

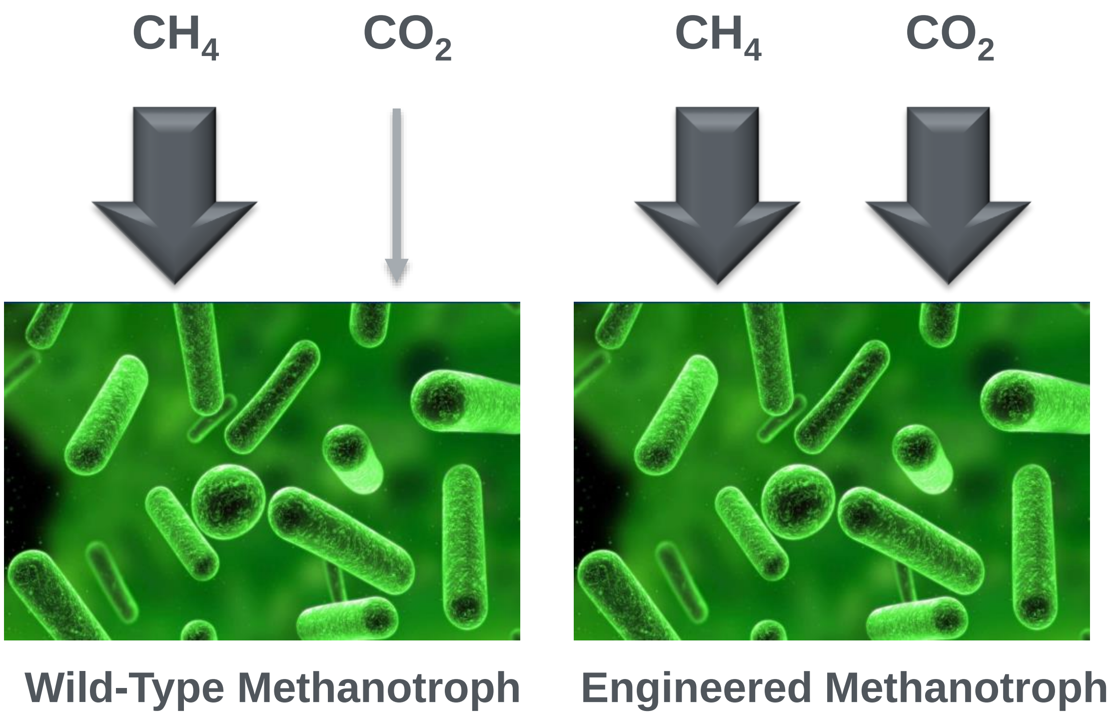


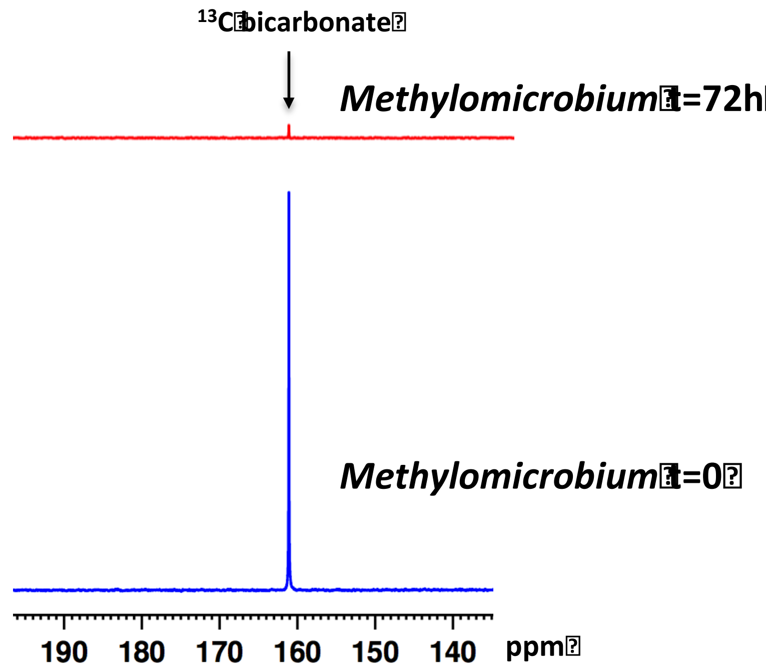




U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Complete Biogas Conversion: CH_4/CO_2 Co-utilization



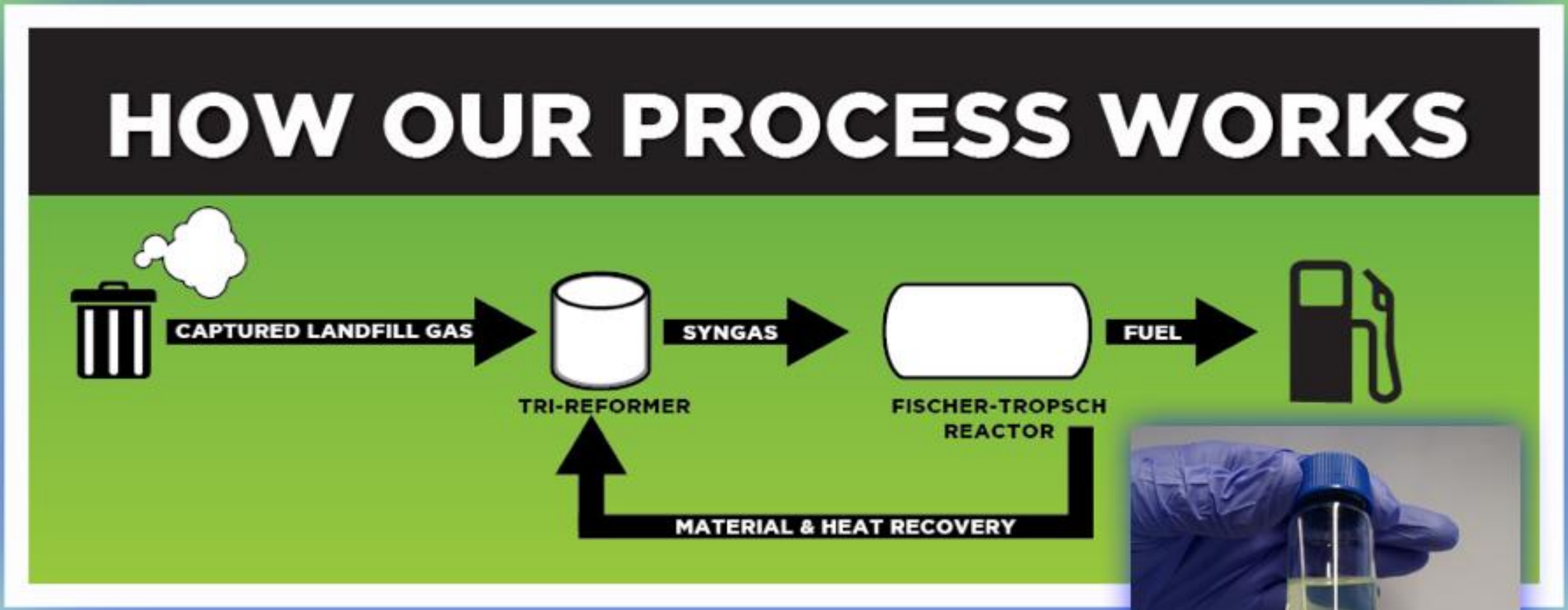


- We have established non-photosynthetic, non-RuBisCO-mediated CO_2 assimilation capacity in our methanotrophic biocatalyst.

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Landfill Gas to Diesel for Trash Collection Fleet - SBIR

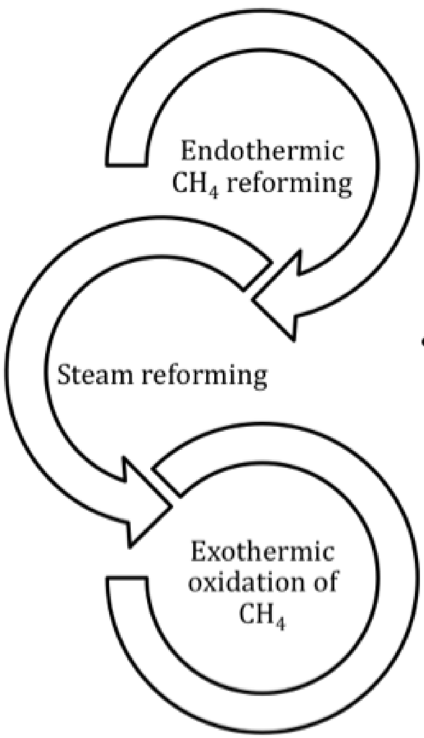
Demonstrate small scale GTL in economical and profitable manner



Project Overview – SBIR phase I & II

Tri-reforming:

- Minimize cleanup and pretreatment process
- Less energy consumption
- Produce high quality syngas (H_2:CO ~ 2)



- $CH_4 + CO_2 \rightarrow 2CO + 2H_2$
- $\Delta H^o_{298} = 247.3$ kJ/mol

→ **Utilize 100% of biogas as feedstock**

- $CH_4 + H_2O \rightarrow CO + 3H_2$
  - $\Delta H^o_{298} = 206.3$kJ/mol

→ **Control H2 and CO selectivity**

- $CH_4 + ½ O_2 \rightarrow CO + 2H_2$
  - $\Delta H^o_{298} = -35.6$ kJ/mol
- $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
  - $\Delta H^o_{298} = -880.3$kJ/mol

→ **Generate heat in-situ**

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

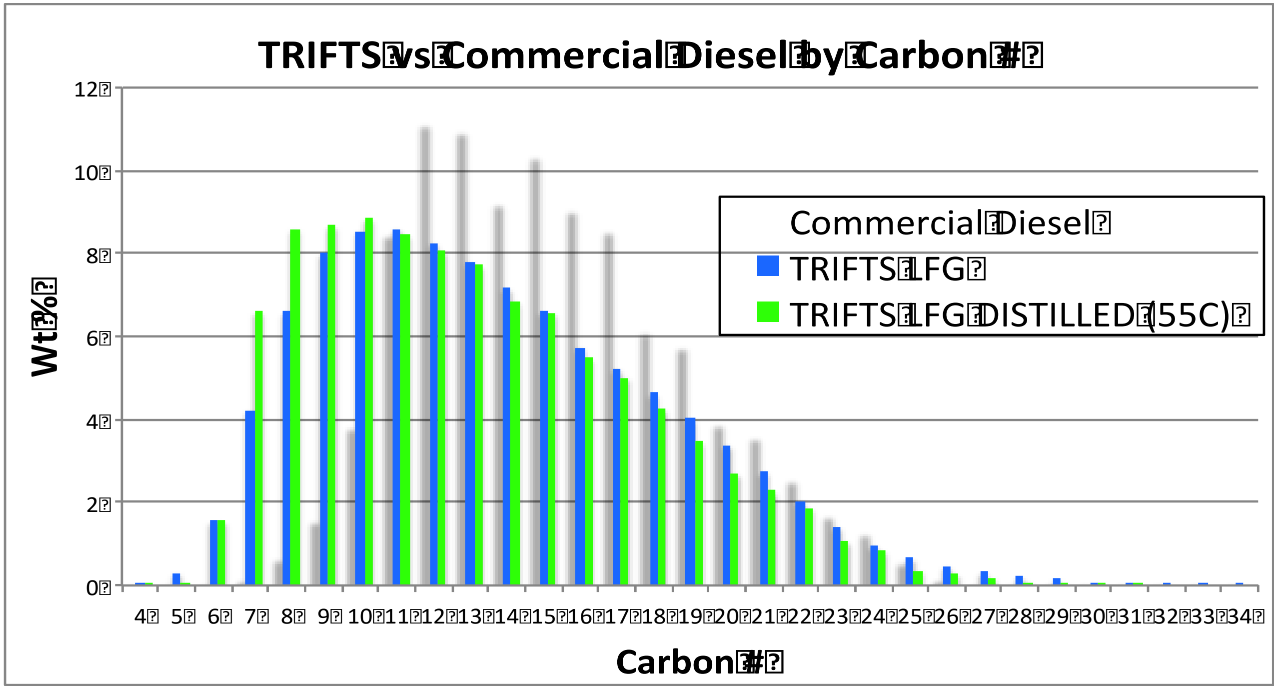
Project Overview – SBIR Phase I & II

Fuel Analysis

- Low aromatics improve net heat of combustion and reduce soot
- Isomers improve cold temp properties
- Further reduce olefin content w/ addition of catalyst promoters

Hydrocarbon Family	T2C-E (H2:CO=1.7)	Commercial Diesel
Paraffins	67.164	19.95
Isomers	28.243	31.6
Olefins	4.323	0.92
Aromatics	0.02	39.48
Cyclics	0.25	8.05

- Excellent middle distillate boiling point distribution
- Control phase separation temp to fractionate light ends
- Final boiling point aligns with commercial diesel



U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Key Wet and Gaseous Feedstocks Messages

- Wet and gaseous feedstocks constitute a significant resource
- These feedstock streams already exist, in distributed form
  - "Bring the refinery to the feedstock"
- In many cases, they constitute a clear and present problem to be solved
  - This problem has garnered serious congressional attention
  - The streams are only going to get larger as population grows
- Feedstock supply and conversion have cost advantages over agricultural and woody biomass resources
  - Already collected in many cases, avoid harvesting and dry transportation costs
  - Wet and gaseous materials easier to process physically than solids
  - Lower in recalcitrant lignin
- While challenges remain, these resources could present a leading-edge niche opportunity for the bioeconomy of the future

Questions?

Mark Philbrick
Mark.Philbrick@hq.doe.gov

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy