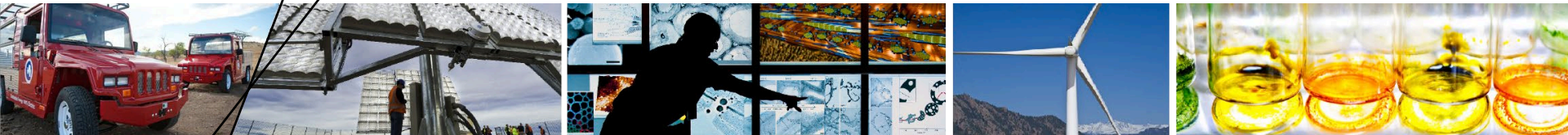


Benefits and Hurdles for Biological Methane Upgrading



Fei, Qiang

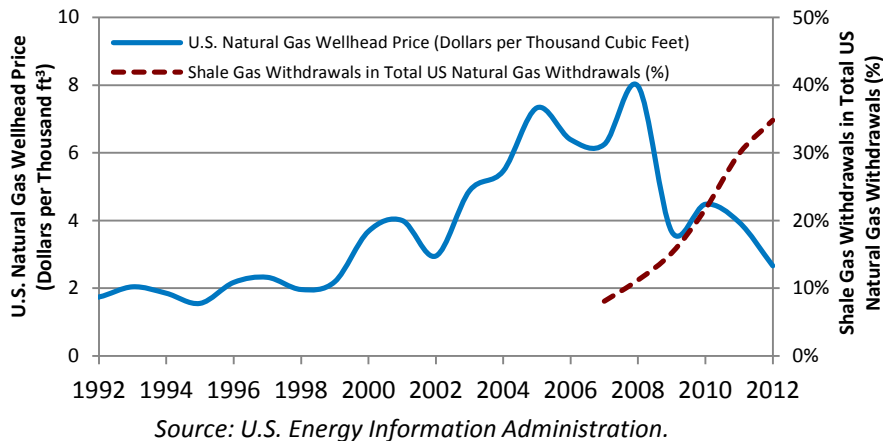
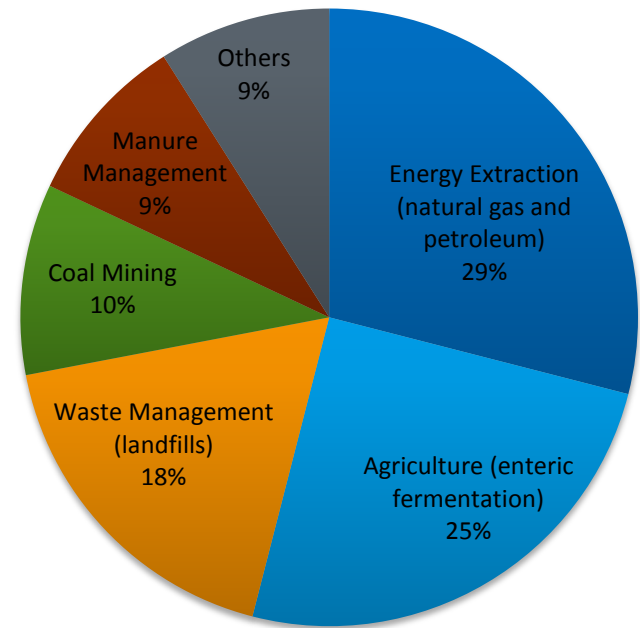
**Sustainable Chemicals & Plastics
Adoption & Applications Summit**

**San Diego, California
September 1-3, 2015**

Methane Source

- ❖ **Most energy dense alkane: 55 MJ/kg**
- ❖ **Extraction: Natural gas (90% CH₄)**
- ❖ **Anaerobic digestion: Biogas (60% CH₄)**
- ❖ **Global-warming potential (GWP) of CH₄ :**
 - CH₄ lifetime is 12 years
 - 100-year GWP: 21 times of CO₂
 - 20-year GWP: 72 times of CO₂
- ❖ **Methane Cost**
 - Natural gas: pipeline NG vs. industrial waste stream (flaring gas)
 - Biogas: associates with plant size

U.S. Methane emissions by sources from 1990-2012 (US_EPA 2015)



Biogas source	\$/MMBTU	Reference
Landfill	2-4	California Energy Commission, 2012
Livestock manure	6-10	CALSTART, 2010
Wastewater treatment plants	2-8	Nicholas Institute report, 2014
Biomass	6-8	Nicholas Institute report, 2014
Dairy farm	11	NRRL report, 2010

Methane Production and Use in the US

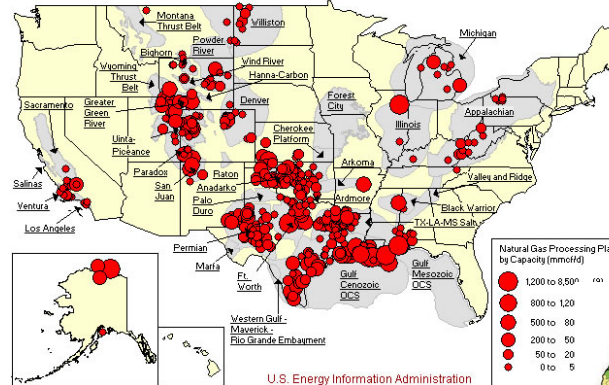
❖ Methane production

- Natural gas: 65.9 billion Bcf/d
- Biogas: 1.79 billion Bcf/d

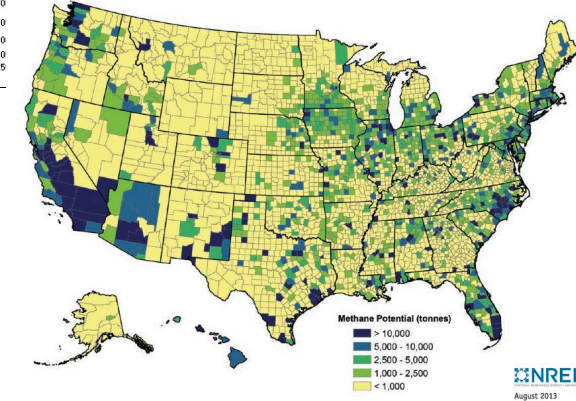
❖ Methane use

- Boiler: 85% heat and 15% lost
- Combined heat and power (CHP):
 - 50% heat, 35% electricity and 15% lost
 - 1m³ biogas=2 kWh (35% ECE)
- Upgrading (chemical and biological):
chemical, nutrient and transportation fuel

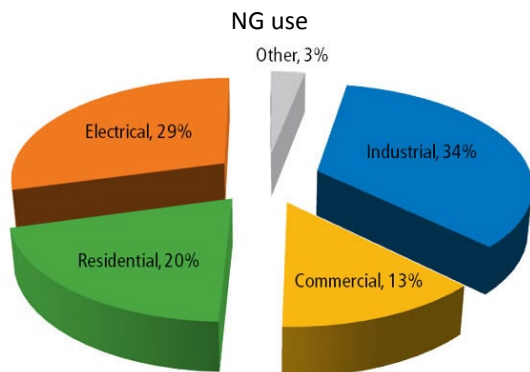
Natural gas production map



Biogas production map

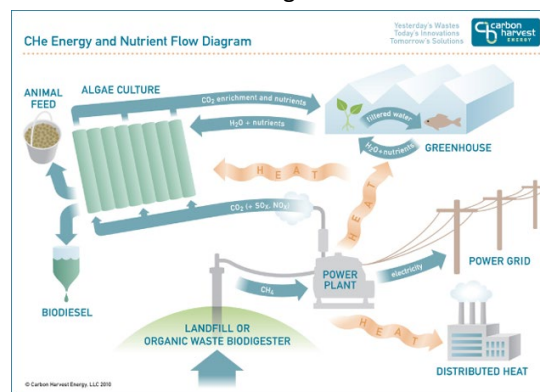


NREL
August 2013

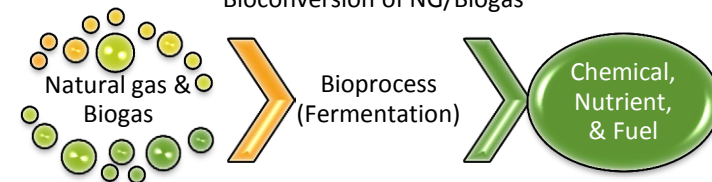


Source: Modern Shale Gas Development in the United States, US Department of Energy

Biogas use



Bioconversion of NG/Biogas

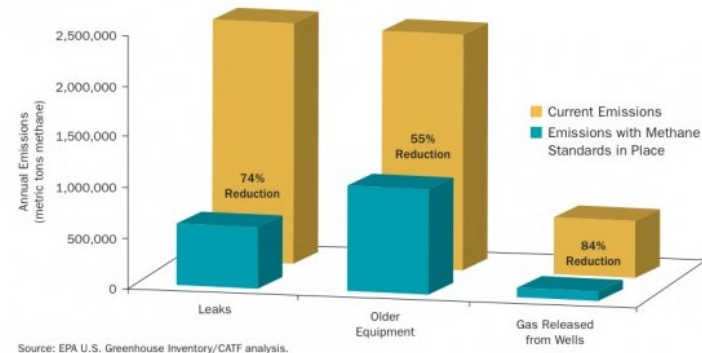


Rule of Methane Production and Use

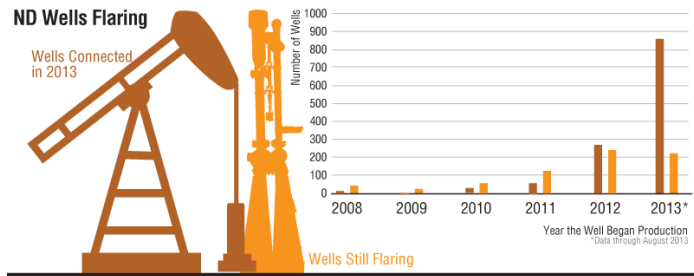
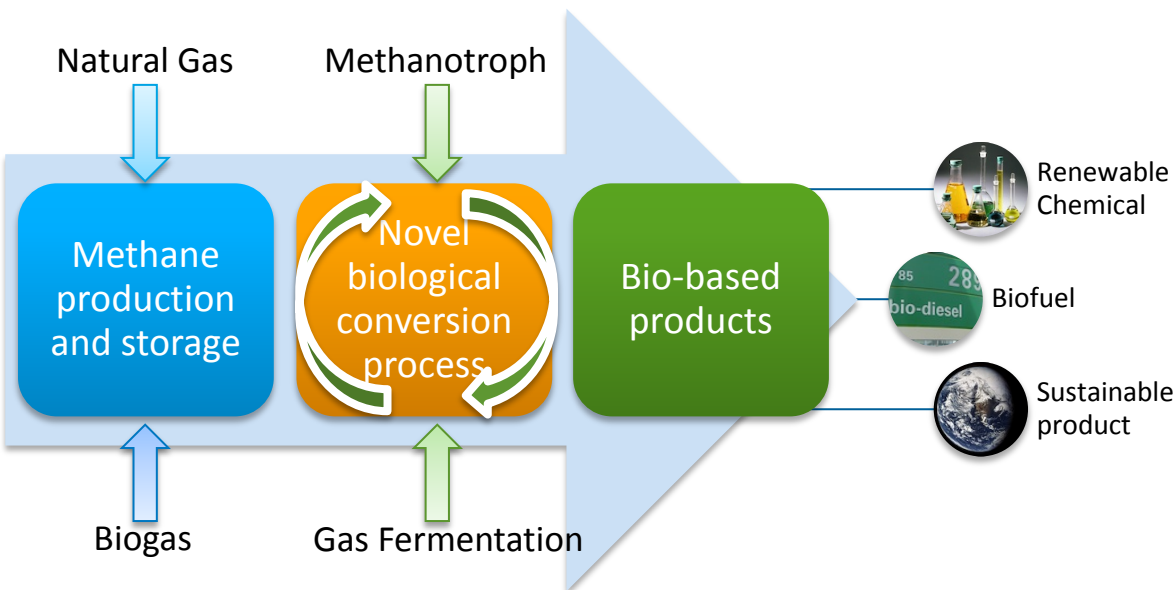
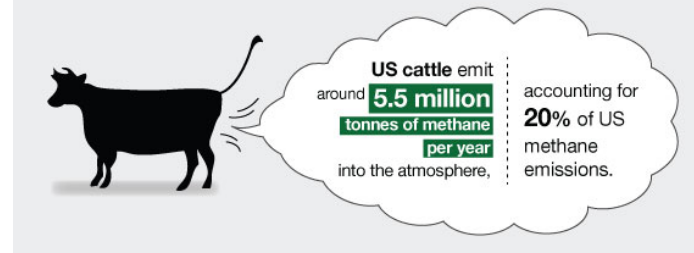
❖ Regulation

- Methane availability: Control and Storage
- Technology demand: Conversion Process
- Product: Bio-base Fuel and Chemical
- Player: EPA, USDA, DOE, American Biogas Council, DOD, State government, North Dakota Industrial Commission (NDIC), etc.
- Rule: Renewable Fuel Standard II, Low Carbon Fuel Standard, 2007 Energy Bill, Farm Bill, Treasury Grants, Clean Air Act, Climate Action Plan, etc.

Significant Methane Reductions are Possible at Sources Identified in this Report



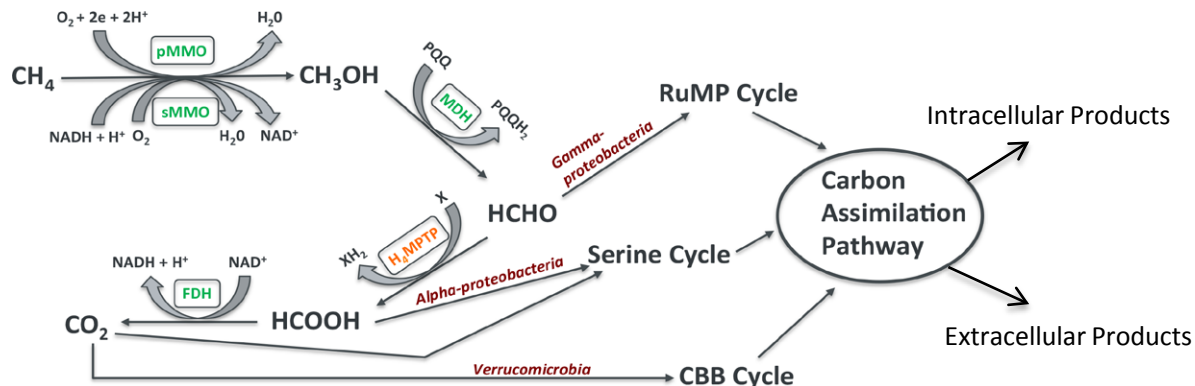
Cattle methane emissions



Source: North Dakota Petroleum Council

Biological Conversion of Methane

❖ Methanotrophic bacteria (Aerobic cultivation)

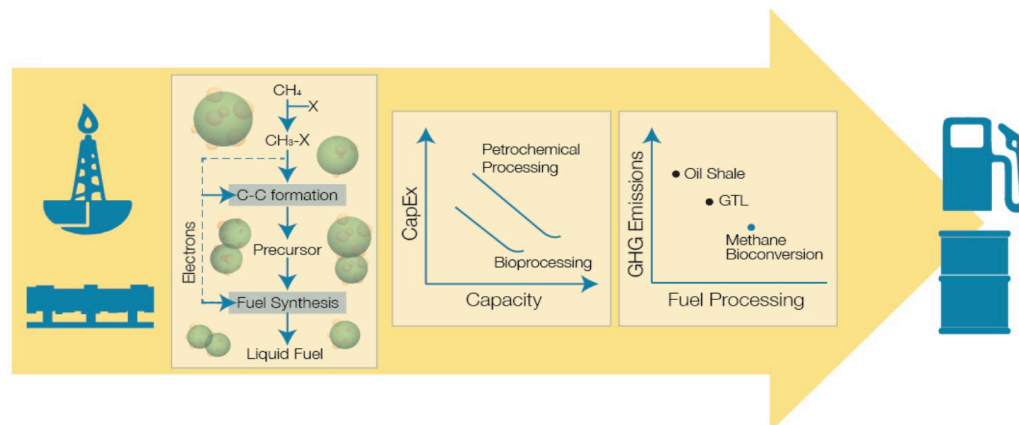


❖ Selected products

Product	Formula	Application
Fomate	CH ₂ O ₂	Chemical
Glycogen	C ₆ H ₁₂ O ₆	Chemical
Ectoine	C ₆ H ₁₀ N ₂ O ₂	Healthy care
Astaxanthin	C ₄₀ H ₅₂ O ₄	Healthy care
Sucrose	C ₁₂ H ₂₂ O ₁₁	Chemical
Isoprene	C ₅ H ₈	Fuel/Rubber
Lactic acid	C ₃ H ₆ O ₃	Chemical
Lipid	C ₁₅ -C ₁₈	Fuel
PHB	C ₄ H ₈ O ₂	Fuel/plastic
Single cell protein*		Nutrient

*, including glutamic acid, aspartic acid, alanine, leucine, valine, glycine, lysine, isoleucine, threonine, serine etc.

❖ Biological routes chemical route for fuel



Source: Conrado & Gonzalez, 2014. *Science*, 343: 621/Haynes & Gonzalez, 2014. *Nat. Chem. Biol.* 10: 331

Hurdles of Bioconversion of Methane

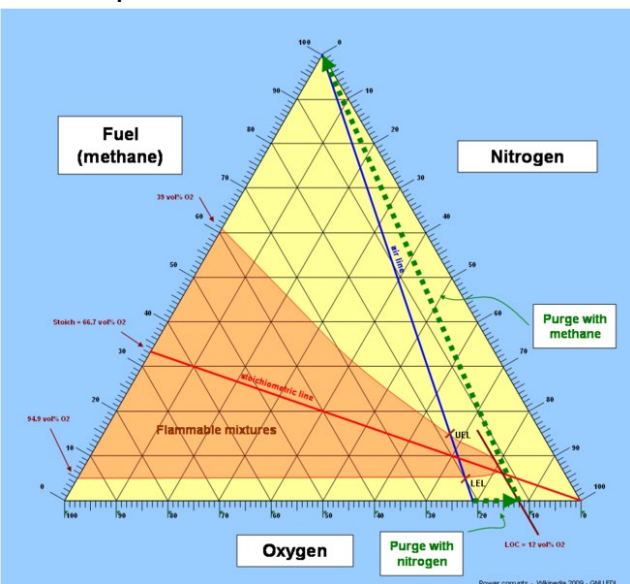
❖ Safety consideration

Limiting Oxygen Concentration (LOC) = 12 vol % O₂

UEL of CH₄: 15% in Air (v/v)

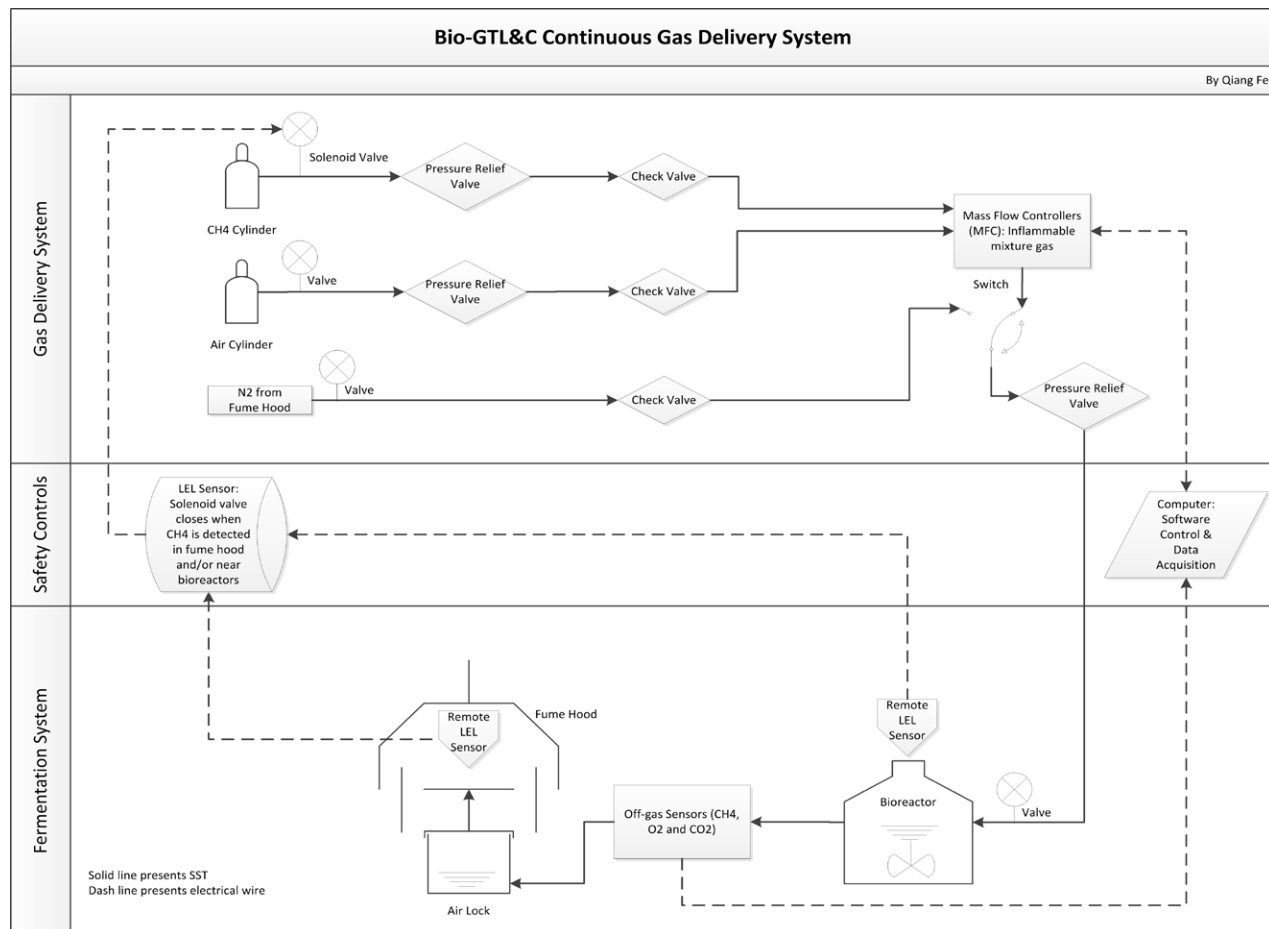
LEL of CH₄: 5% in Air (v/v)

CH₄ Flammability Diagram



❖ Source: wikipedia.com

NREL lab-scale continuous gas delivery system

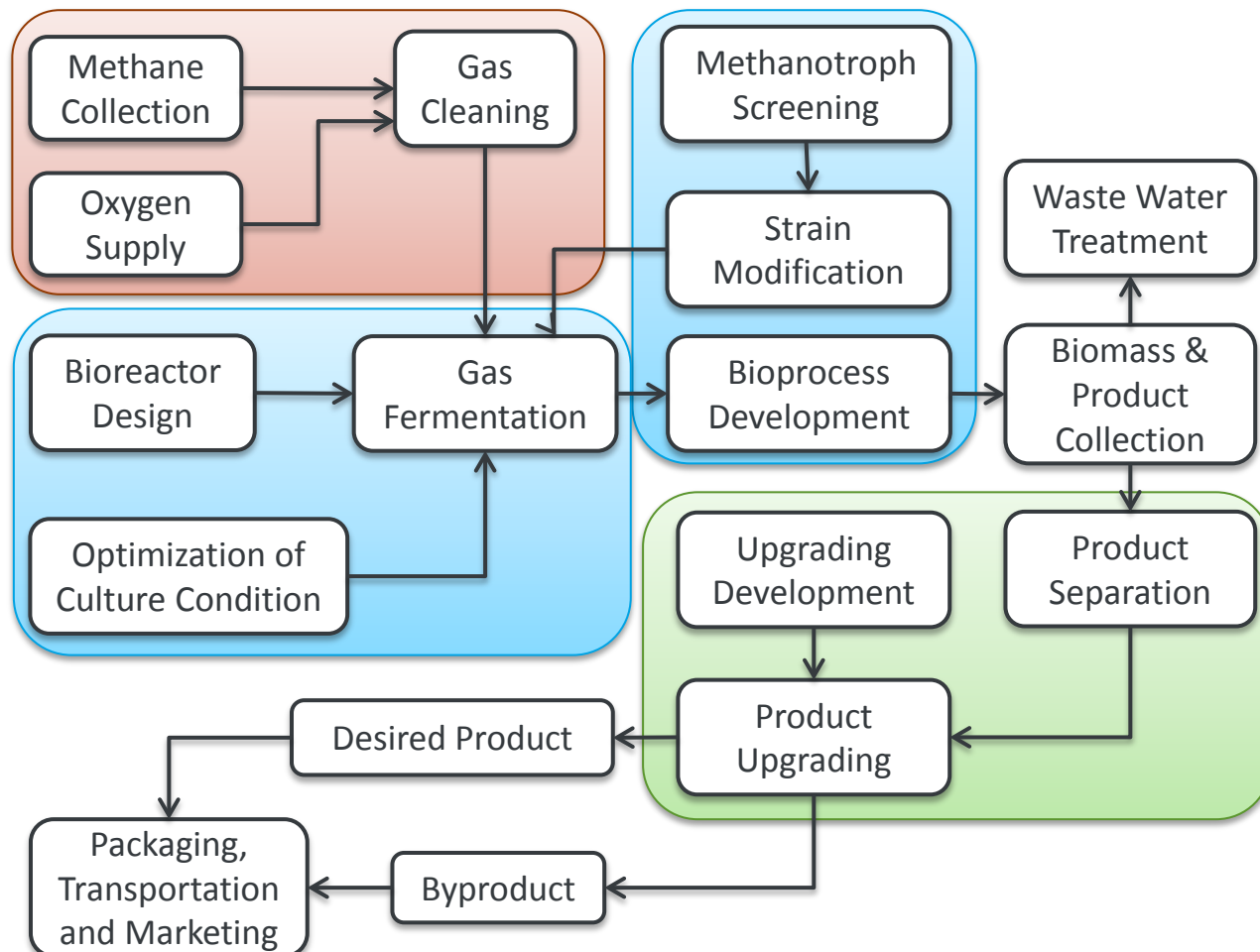


Source: *Extremophilic Bioprocessing of Lignocellulosic Feedstocks to Biofuels, Value-Added Products, and Usable Power. Chapter: Bioconversion of Methane for Value Added Products*

Hurdles of Bioconversion of Methane

❖ Technical hurdles (R&D Map for Bioconversion of Methane)

- Gas Supply & Cleaning
- Bioprocess Development
- Product Separation & Upgrading



Hurdles of Bioconversion of Methane

❖ Gas Supply & Cleaning

- Flow rate:
 - Plant capacity and productivity
 - Biogas: 20-11000 (1000m³/hr)
 - Natural gas:
- Location: transportation and water availability
- Impurity and cleaning method:
 - Natural gas vs. Biogas
 - CO₂, H₂S, higher chain hydrocarbons (in NG)
- Oxygen supply: Pure oxygen costs as much as methane on final product price
- Gas cleaning: Adsorption (PSA) vs. Membrane vs. Absorption vs. Cryogenic

❖ Bioprocess Development

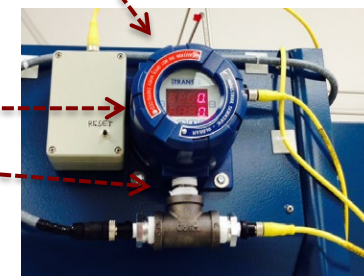
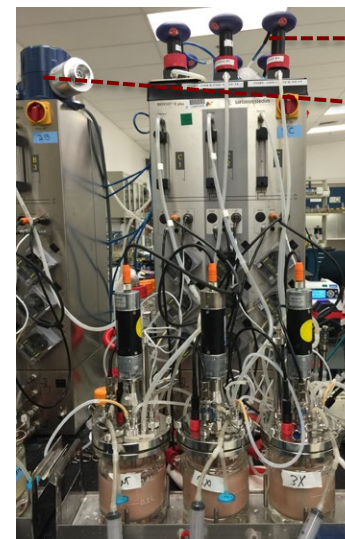
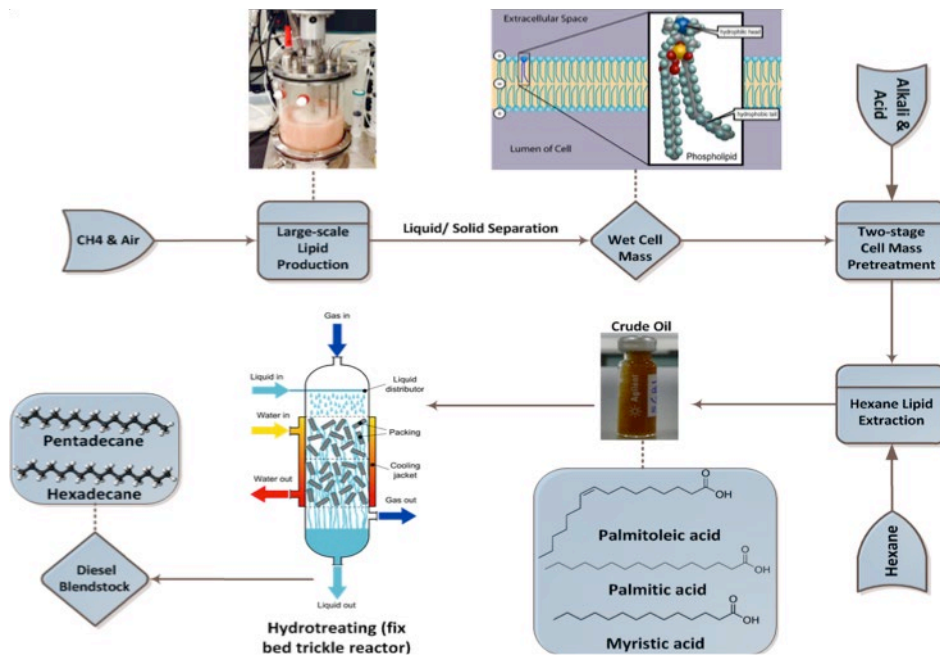
- Strain modification: carbon conversion efficiency, growth rate, pathway modification
- Culture condition: pH, T, Cu²⁺, CH₄/O₂ ratio, pO₂,
- Bioreactor design (gas transfer efficiency): CSTR/micro-bubble, loop/air-lift, bubble column, trickle-bed, membrane-based, nanoparticles gas substrate carrier

❖ Product Separation and Upgrading

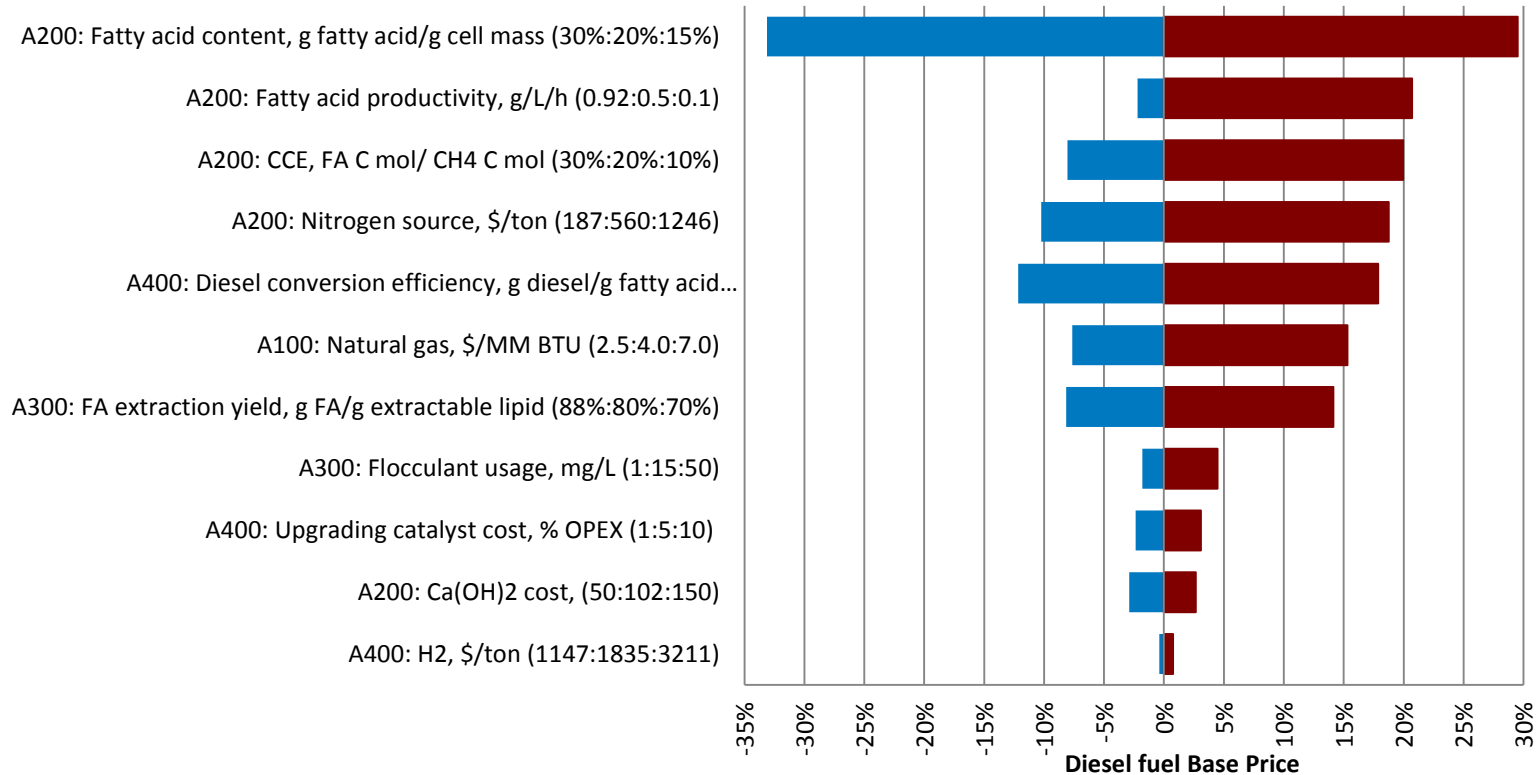
- Intercellular product (single cell protein, lipid/fatty acid, PHB): S/L separation, extraction, and upgrading
- Extracellular product (lactic acid, butanol, isoprene): purification, extraction (harvesting), and upgrading

Bioconversion of Methane at NREL

- ❖ **Methane source:** Natural gas and Biogas
- ❖ **Product:** Lipid, Carbohydrate, Lactic acid & Muconic acid
- ❖ **Bioprocess:**
 - Safety control system
 - Strain screening with continuous gas delivery
 - Seed train development
 - Batch production culture with continuous gas delivery
 - High cell density culture: Dry cell density up to 20 g/L
 - Scale up of fermentation: 50 mL to 5L



Techno-economic Analysis at NREL



Acknowledgements

❖ NREL

- Philip T. Pienkos
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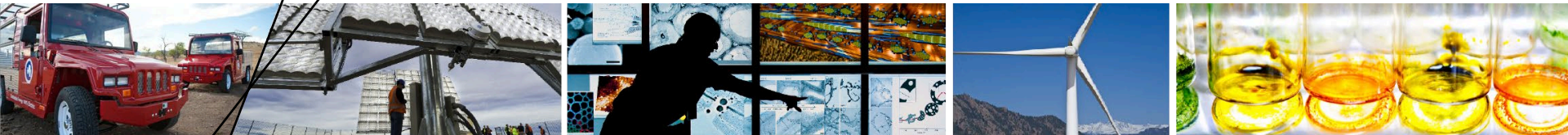
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Thank you for your time



NREL Campus
Golden, CO

