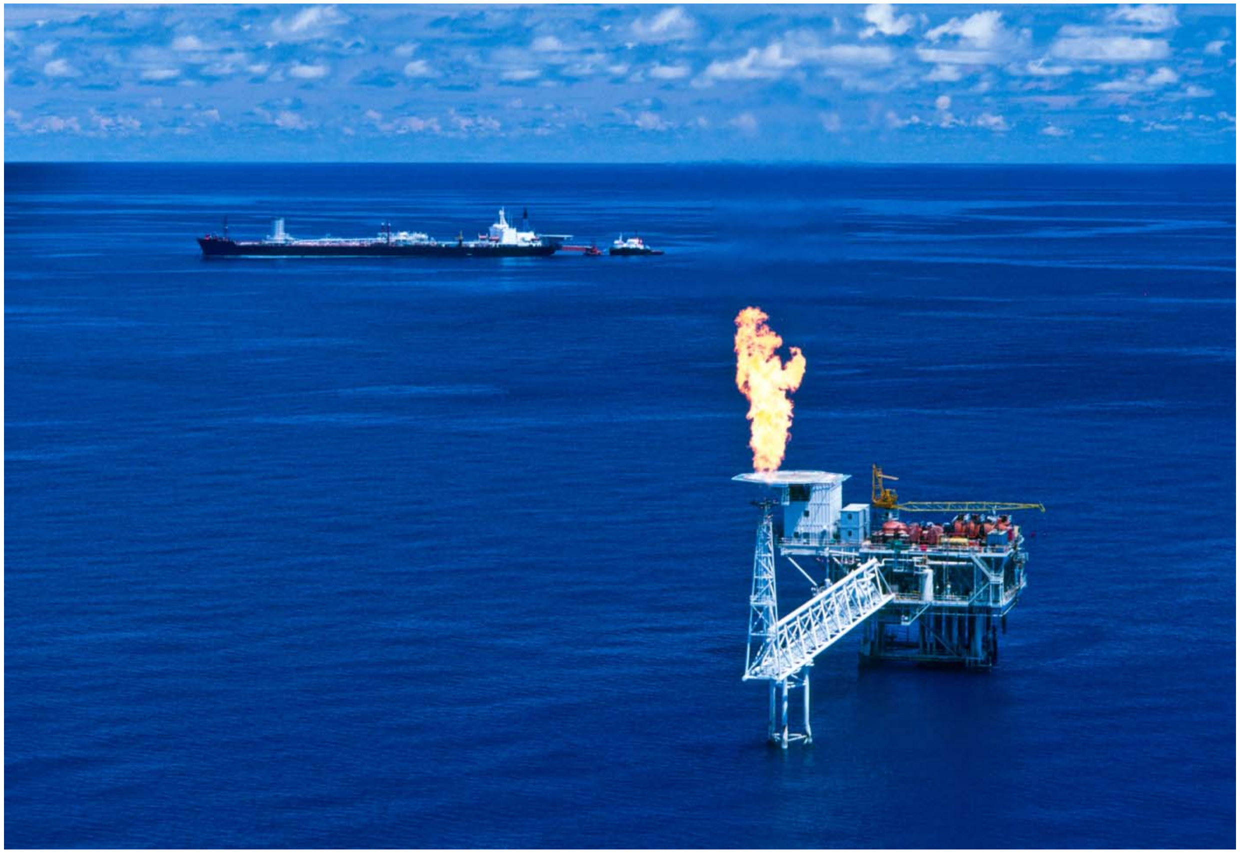
Small Modular Methane Utilization Workshop



September 6, 2012

arpa·e

Welcome and Safety Moment

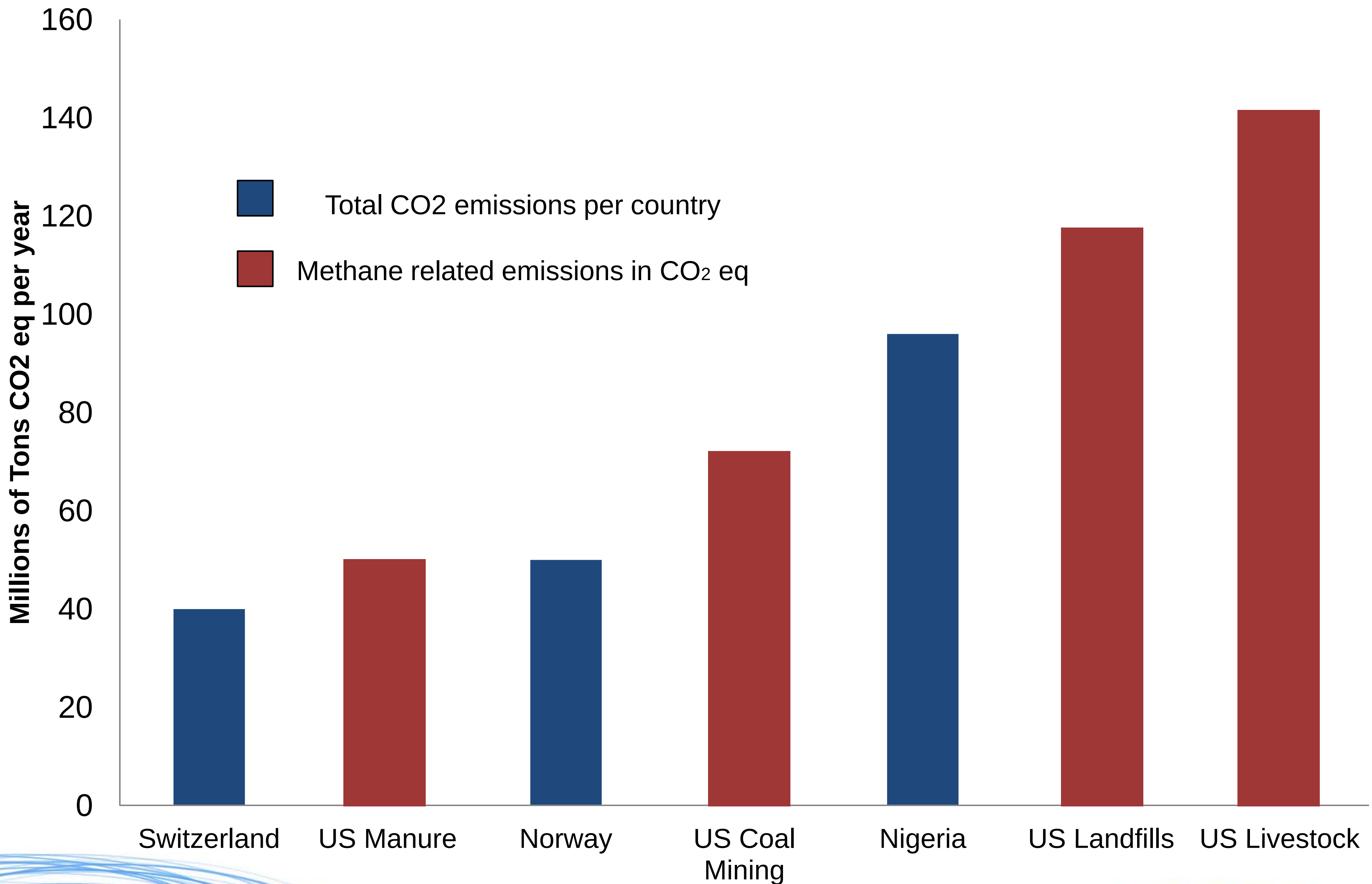
Workshop Schedule

9:00	Welcome and Opening Remarks – Methane Utilization Team
9:20	Guest Presentations
10:45	Break
10:55	Breakout Session #1
11:45	Breakout Session Report Out
12:05	Lunch – Franklin Conference Room
12:50	Breakout Session #2
1:40	Breakout Session #2 Report Out
2:00	Break
2:10	Brainstorm Challenge
3:30	Brainstorm Challenge Report Out and Discussion
4:05	Break
4:10	Open floor for general discussion
4:45	Closing Remarks – Eric Toone, Principal Deputy Director

Problem

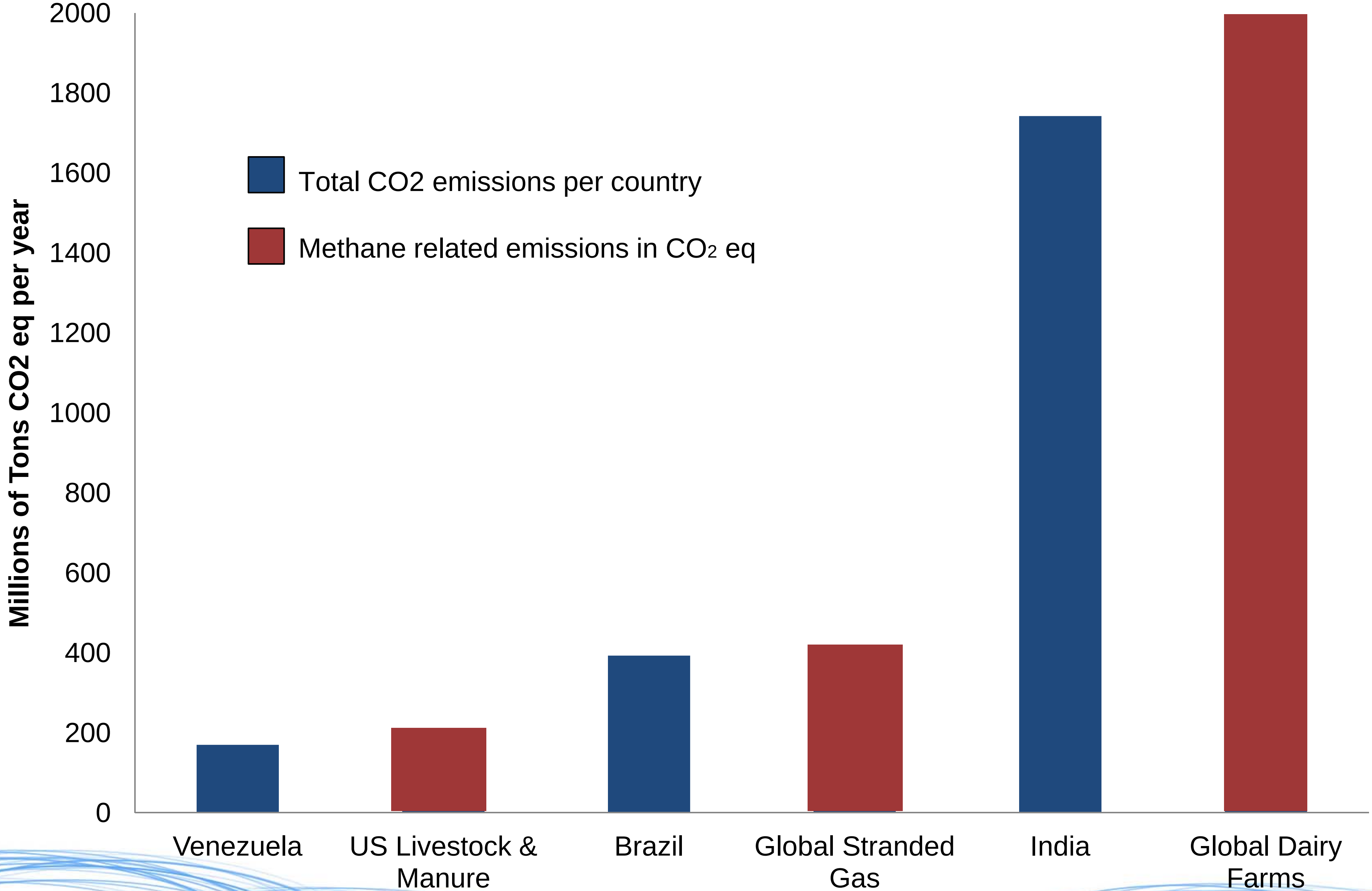
- Lots of methane is being wasted
  - Gas is hard to transport
  - Methane is low value
- Worldwide emissions in tons CO_2 eq.
  - 400 million from stranded petroleum gas worldwide
  - 2 billion tons from dairy farms worldwide
- Domestic emissions in tons CO_2 eq.
  - 100 million tons from stranded gas
  - 140 million tons from livestock and dairy
  - 60 million tons from manure
  - 170 million tons from landfills

Emissions By Source - Domestic Opportunity



Sources: World Bank, EPA, UN

Emissions by Source - Global Opportunity



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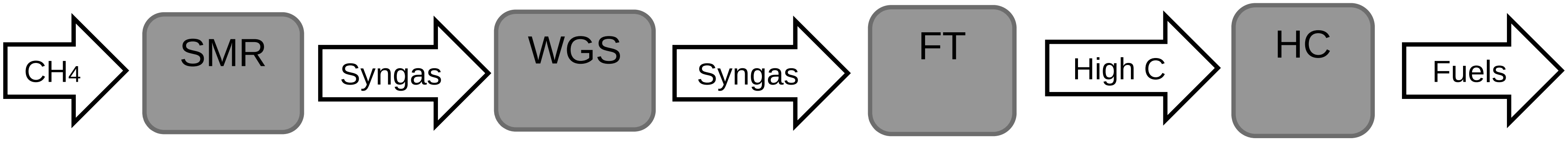
State of the art



Shell Pearl GTL
Capex: $135,000 per barrel per day

Workshop Objectives

- Potential technologies
- Current metrics
- Goal metrics
- Innovations needed

Expect different pathways to yield different challenges

Teaser Workshop Questions

- What are the different pathways?
  - Methane radical?
  - First C-C bond?
- How do pathways compare?
- What are optimal reactor and process designs?

Guest Presentations

The History of the World of Oxidative Coupling of Methane (OCM) in 5 minutes…

History and Status

- Methane + "Ox" → Ethylene + H_2O
  Ethylene → Liquid Fuel
- Reaction Discovered ~1980
  (Union Carbide, ARCO, Phillips)
- Potential for higher thermal efficiency and product specificity than GTL
- ARCO spent ~$35 million in 1980's
- >150 ARCO patents (>300 others)
- >Thousand of papers (>270,000 "Google hits")
- To date - No commercial units built

Challenges

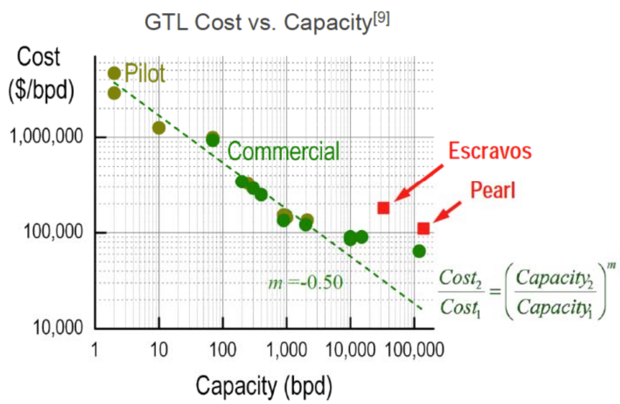
- ~25% OCM per pass yield limit
- High temperature reaction AND
  cryogenic separations
- OCM reaction rate too slow for conventional reactors
- Big technology scale-up risk compared to known GTL technologies

Opportunities

- Lower temperature catalyst
- Higher yield catalyst
- Novel reactor concepts
- Ethylene "tweezers"
- Low cost oxygen

Bi O_2 Electric

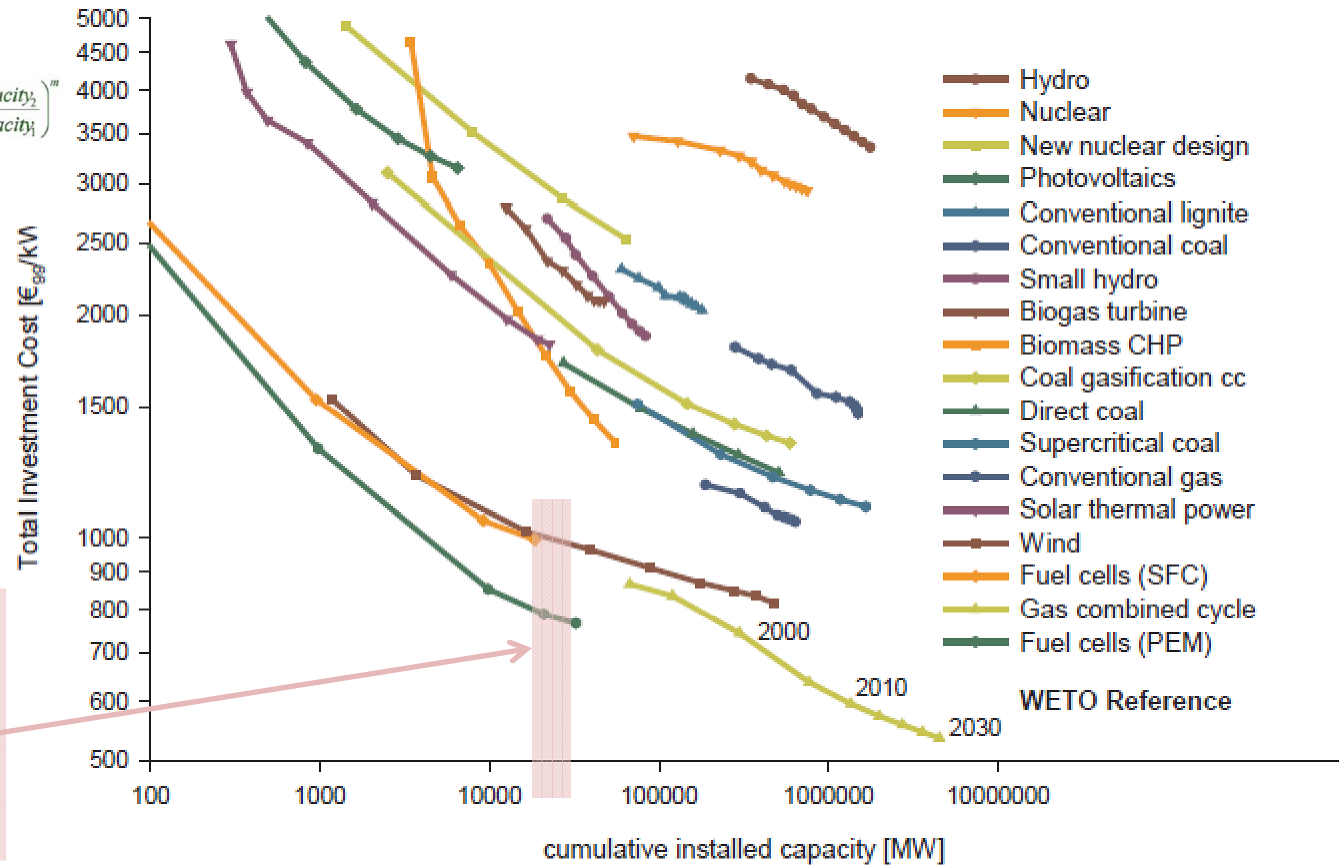
The Learning Experience of Energy Conversion Technologies can improve by both increasing scale and/or increasing unit volume.



PJA Tijm, "Gas to Liquids, Fischer-Tropsch, Advanced Energy Technology, Future Pathways" Feb. 2010

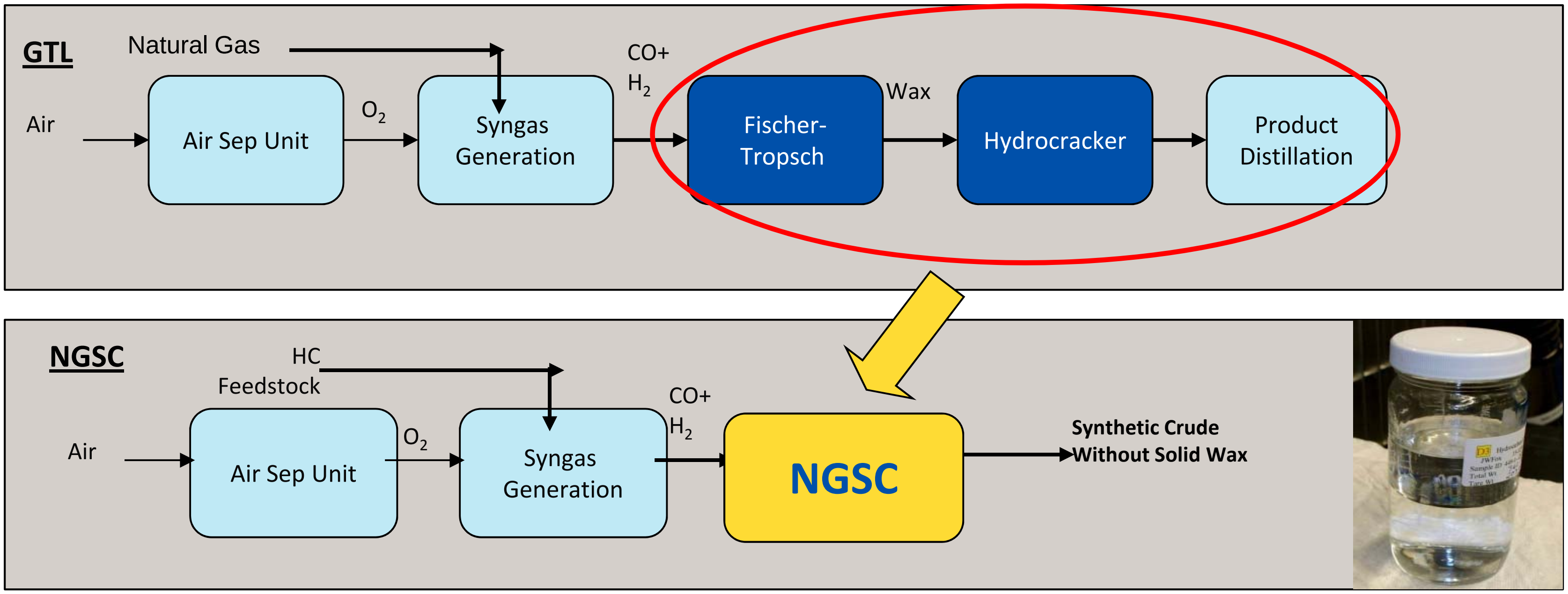
Project	Capacity, bpd	Cost, $ bpd
Bintulu	15,000	68,000
Escrovos	33,000	180,000
Pearl	140,000	110,000
Orxy	34,000	30,000
Cumulative	~300,000	?

Assume syn crude = 1,800 kWhr/BL



"World Energy, Technology and Climate Policy Outlook 2030" WETO, Eur 20366, 2003.

Chevron's NGSC™ is a Wax-Free GTL Process
A Significant Improvement Over Conventional GTL



***N**ext **G**eneration **S**yngas **C**onversion Advantages over conventional GTL:*

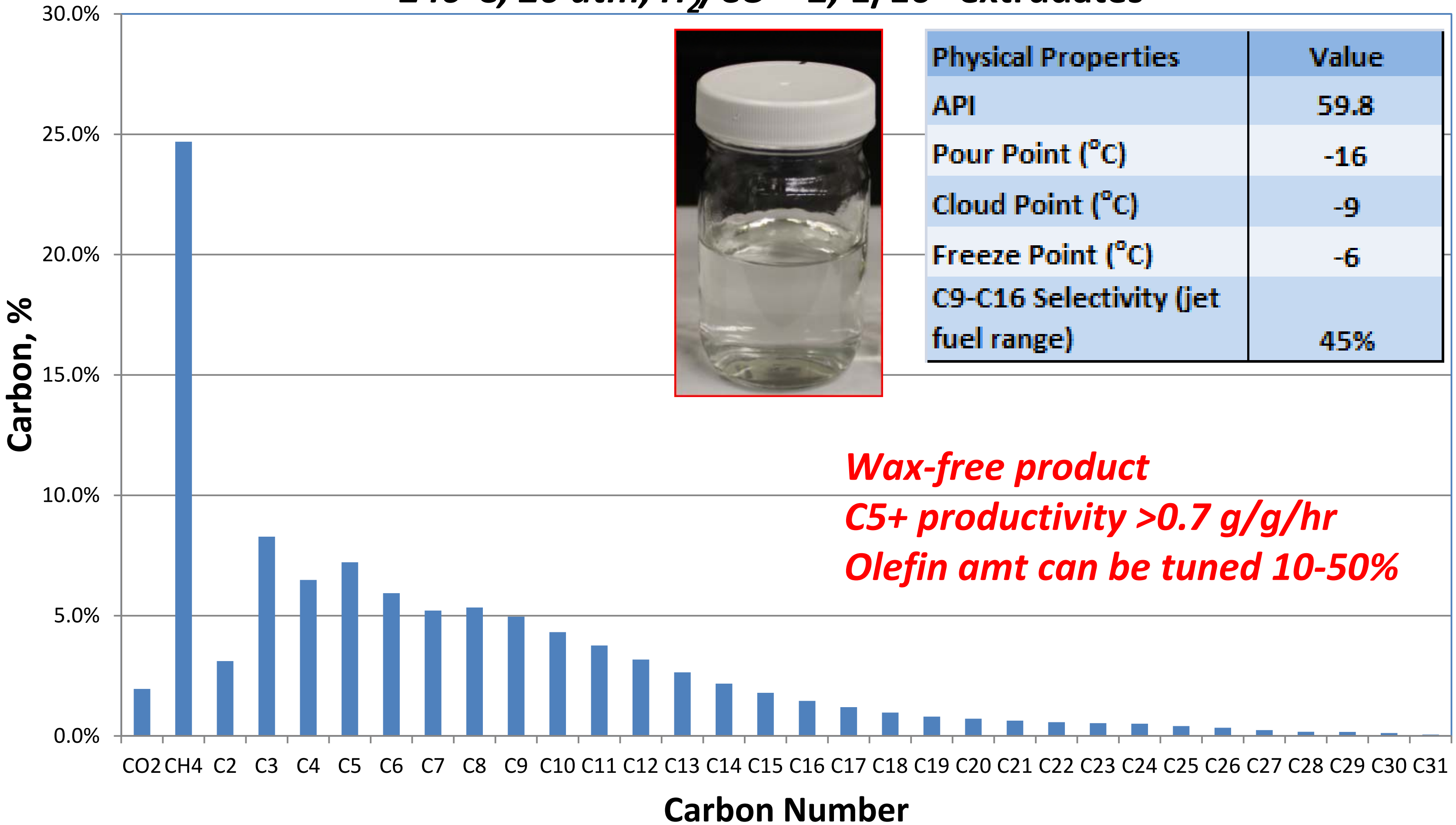
- -Commercial catalyst and process conditions
- -Wax-free product, no hydrocracker required
- -Simpler process with smaller plot area
- -Lower capital and operating expenses
- -Product is a true syncrude: completely blendable, transparent with crude

Feedstock alternatives for syngas generation include natural gas, coal and biomass.

Chevron's Integral Fischer-Tropsch Catalyst

Hydrocarbon Liquid Properties – Entire C_{5+} Product

***240°C, 20 atm, H_2/CO = 2,* 1/16" extrudates**



Physical Properties	Value
API	59.8
Pour Point (°C)	-16
Cloud Point (°C)	-9
Freeze Point (°C)	-6
C9-C16 Selectivity (jet fuel range)	45%

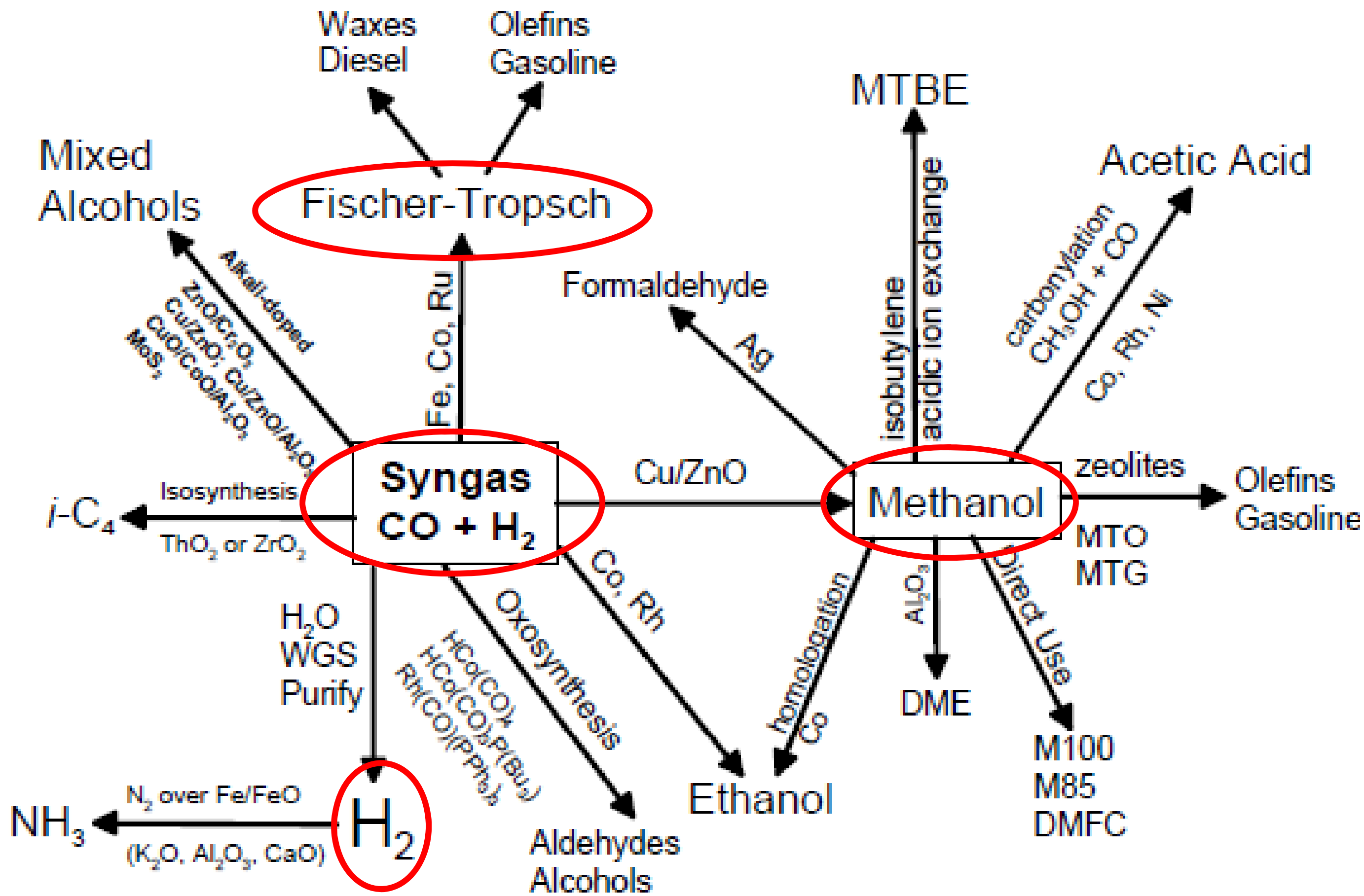
Wax-free product

C5+ productivity >0.7 g/g/hr

Olefin amt can be tuned 10-50%

Light Gas C1-C3 can be tuned to <15% at lower productivity (<0.2 g/g/hr)

Generalized Syngas Reaction Scheme



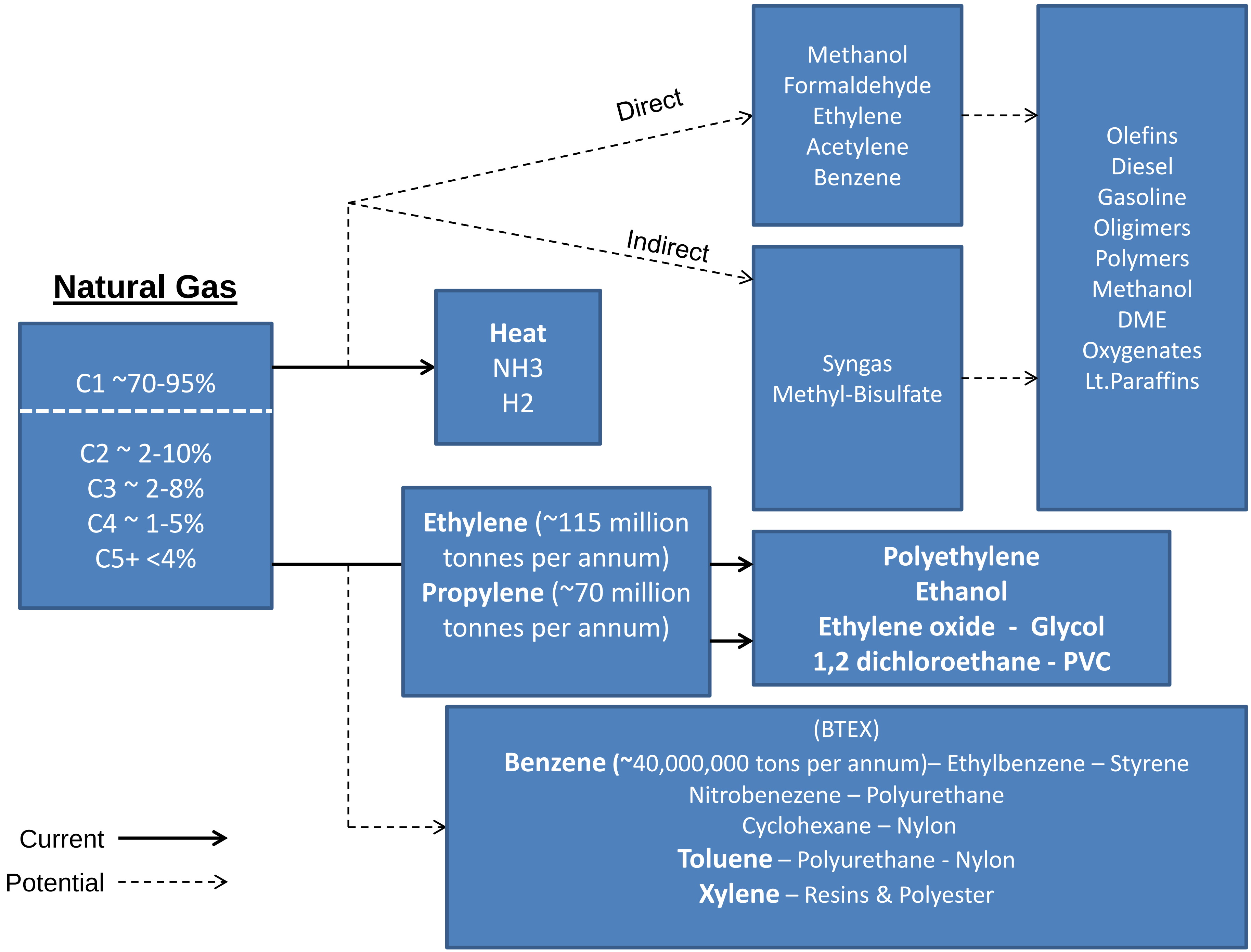
NETL Research Expertise

Core Competencies and Capabilities to enable R&D in support of the Department of Energy mission for Sustainable Domestic Energy Security:

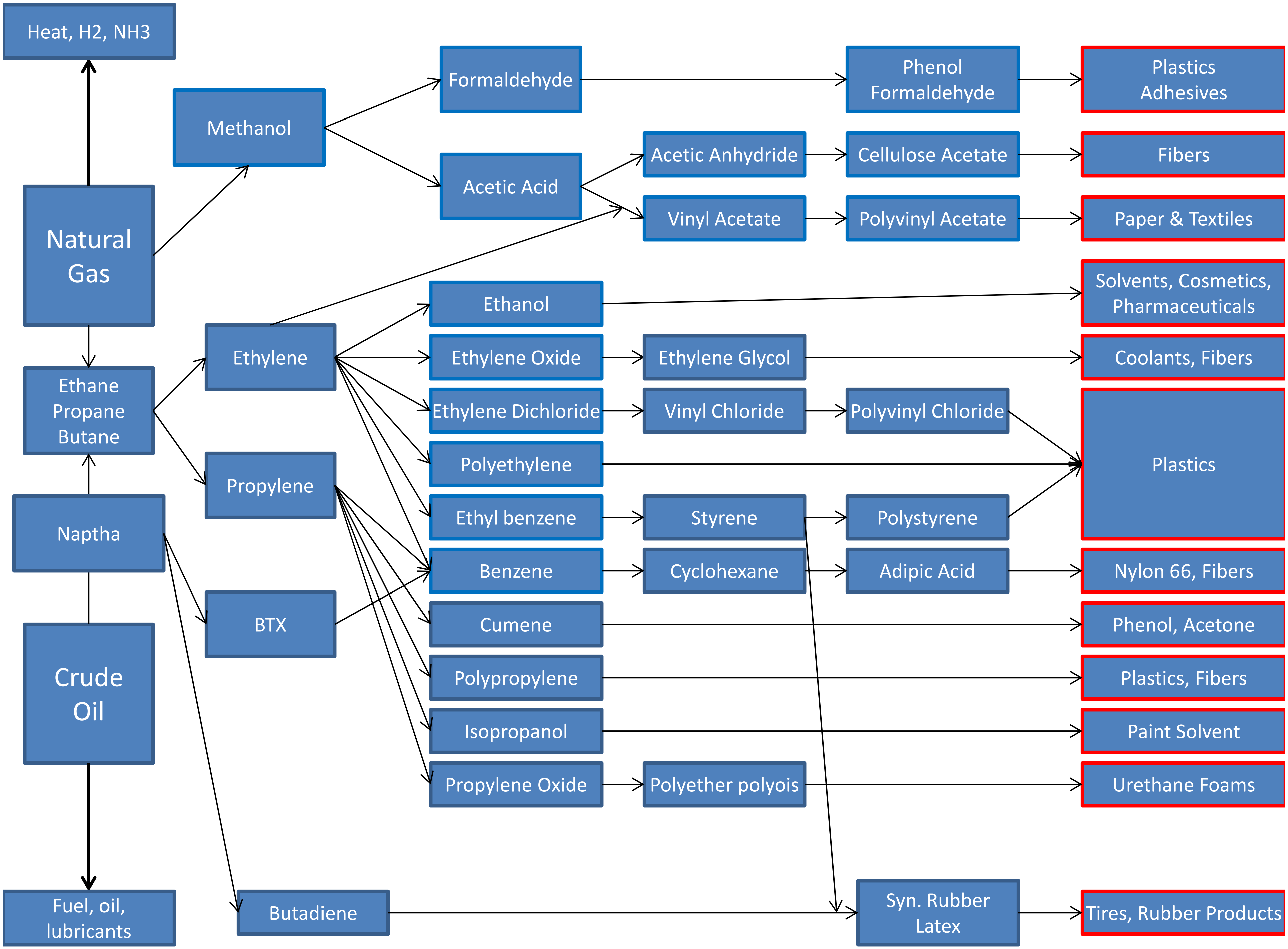
- Validated Simulation-based Science & Engineering to Accelerate Energy Technology Development.
- Materials Discovery, Characterization & Deployment, to Enable the Nation's Energy Future.
- Development & Optimization of Engineered Systems to Enable the Sustainable Production & Utilization of the Nation's Fossil Fuel Resources:
  - Efficient Energy Production.
  - CO_2 Sequestration/Utilization.
  - Access to Unconventional Resources.

Historical Methane Conversion Technologies

- **Electrophilic Methane Conversion**
- **Conversion of Methane into Ethylene, Acetylene and Ethane by the CCOP Process**
- **Electrocatalytic Conversion of Light Hydrocarbons to Synthesis Gas**
- **Direct Methane Conversion**
  - **Direct Methane Conversion to Methanol by Ionic Liquid-dissolved Platinum Catalysts,**
  - **Methane to Methanesulfonic Acid**
- **Oxyhydrochlorination of Methane**
- **Plasma Conversion**
- **Oxidative Coupling**
- **Halogenation of Methane**
- **Dehydroaromatization of Methane to Benzene**
- **Biological Conversion of Methane**



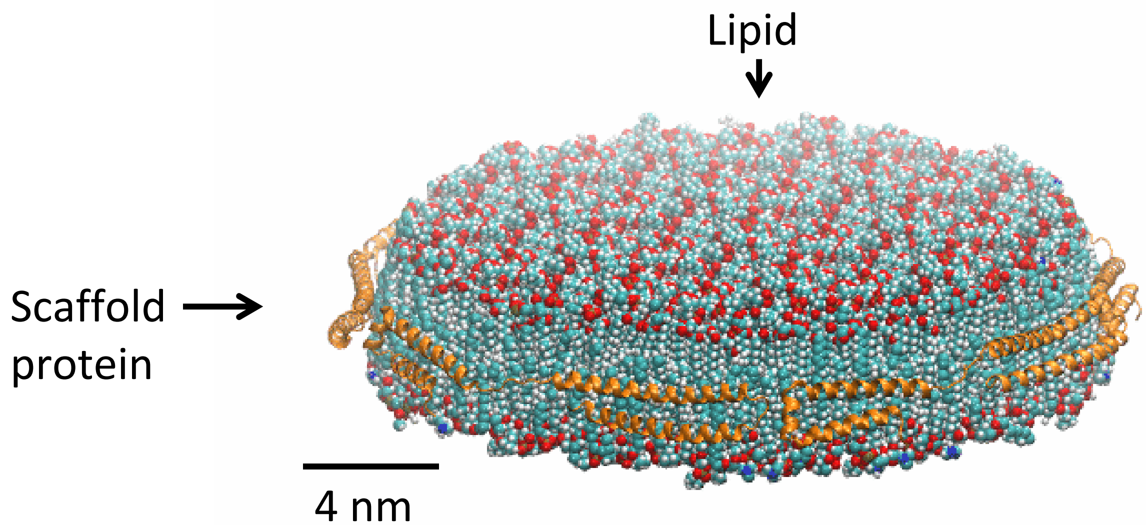
Natural Gas
C1 ~70-95%
C2 ~ 2-10%
C3 ~ 2-8%
C4 ~ 1-5%
C5+ <4%
Direct
Indirect
Heat
NH3
H2
Methanol
Formaldehyde
Ethylene
Acetylene
Benzene
Syngas
Methyl-Bisulfate
Olefins
Diesel
Gasoline
Oligimers
Polymers
Methanol
DME
Oxygenates
Lt.Paraffins
Ethylene (~115 million tonnes per annum)
Propylene (~70 million tonnes per annum)
Polyethylene
Ethanol
Ethylene oxide - Glycol
1,2 dichloroethane - PVC
(BTEX)
Benzene (~40,000,000 tons per annum)– Ethylbenzene – Styrene
Nitrobenezene – Polyurethane
Cyclohexane – Nylon
Toluene – Polyurethane - Nylon
Xylene – Resins & Polyester
Current
Potential


Heat, H2, NH3
Methanol
Formaldehyde
Phenol Formaldehyde
Plastics Adhesives
Acetic Acid
Acetic Anhydride
Cellulose Acetate
Fibers
Vinyl Acetate
Polyvinyl Acetate
Paper & Textiles
Natural Gas
Ethanol
Solvents, Cosmetics, Pharmaceuticals
Ethylene
Ethylene Oxide
Ethylene Glycol
Coolants, Fibers
Ethane Propane Butane
Ethylene Dichloride
Vinyl Chloride
Polyvinyl Chloride
Polyethylene
Plastics
Propylene
Ethyl benzene
Styrene
Polystyrene
Naptha
Benzene
Cyclohexane
Adipic Acid
Nylon 66, Fibers
BTX
Cumene
Phenol, Acetone
Crude Oil
Polypropylene
Plastics, Fibers
Isopropanol
Paint Solvent
Propylene Oxide
Polyether polyois
Urethane Foams
Syn. Rubber Latex
Fuel, oil, lubricants
Butadiene
Tires, Rubber Products

Opportunity: pMMO in Artificial Cell Membranes

Sarah Baker
Lawrence Livermore National Laboratory

- Nanolipoprotein Particles (NLPs) are self-assembling artificial cell membranes that stabilize and solubilize membrane proteins.
- LLNL has pioneered the use of NLPs to preserve enzymatic activity of hydrogen-producing and light-harvesting enzymes outside the native membrane



Nanolipoprotein Particle (NLP)

Successful NLP-protein systems (LLNL)

- Hydrogenase
- Human GPCRs
- Human cytochrome p450
- Bacterial cytochrome 572
- Y. pestis YopB
- Y. pestis YopD
- Bacteriorhodopsin

- Enable purified, active pMMO in soluble particles outside native membrane.
- pMMO in discrete, uniform nanoparticles that can be tethered to solid supports for re-use and optimized mass transfer
- Bioinspired: Organism uses lipid to concentrate methane. Use NLPs to concentrate methane.

Prepared by LLNL under Contract DE-AC52-07NA27344

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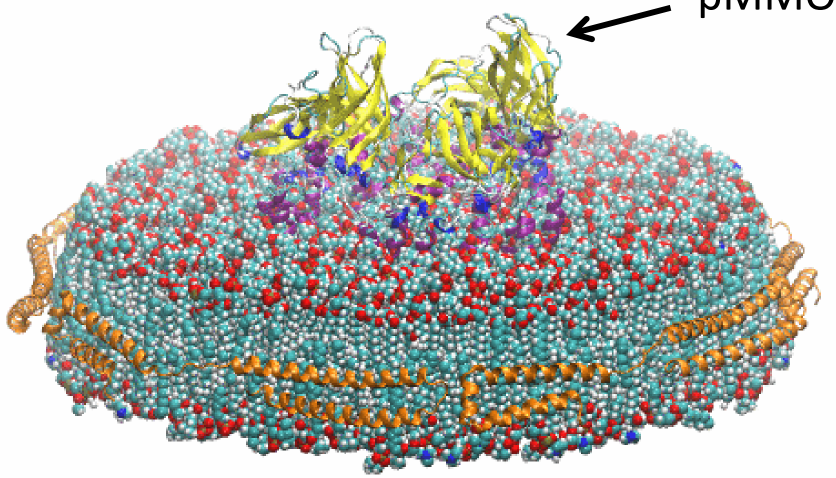

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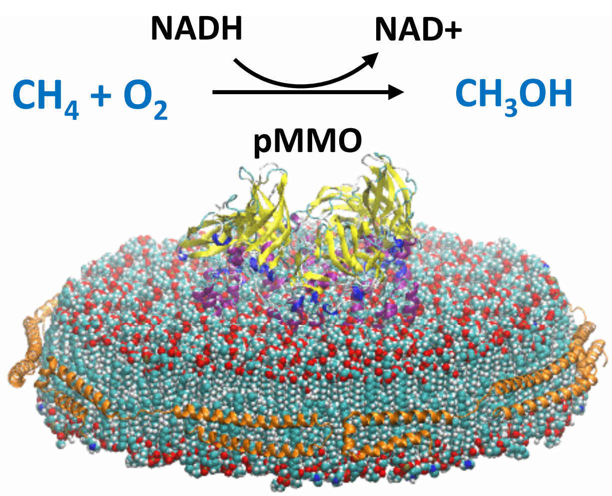
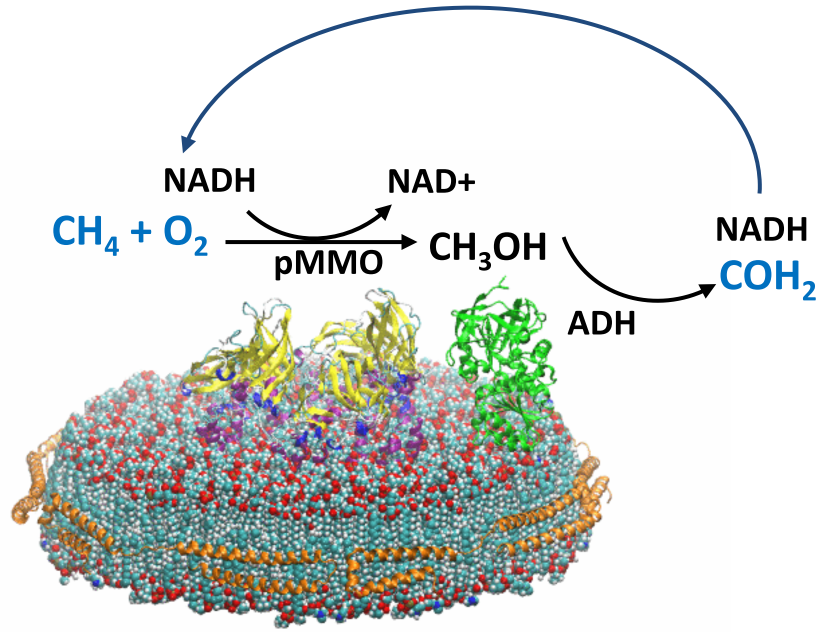
Hybrid Biocatalyst Approach: Use NLPs to co-localize coenzyme for **Self-sustaining** pMMO particles



pMMO alone in NLP requires cofactor

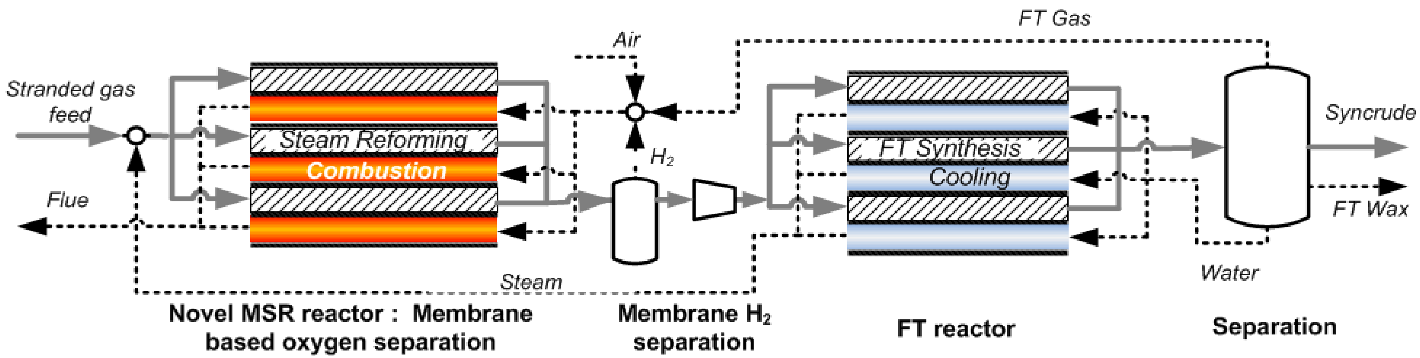


Co-localized enzyme concept: ADH (Alcohol Dehydrogenase) removes cofactor requirement

- **Co-localized enzyme concept**: cofactor regeneration necessary for practical use of pMMO.
- Broadly applicable to industrial biocatalysis
- Coenzyme can be changed based on system requirements. E.g. phosphite dehydrogenase replaces ADH if methanol desired product.
- pMMO in NLPs will enable pMMO kinetic and mechanistic studies (previously impossible)
  →New active site mimics based on pMMO

Optimal Integration and Intensification of Modular GTL Processes

Michael Baldea, Department of Chemical Engineering, The University of Texas at Austin, Austin, TX 78712



Process intensification with microchannel reactors: excellent scale-dowr

Specific challenges

- **water management:** scarce, location-dependent resource; steam needed/generated at multiple pressures
- **hydrogen management:** reforming product H_2:CO ratio is not optimal for FT synthesis: separation or high recycling?
- **process control:** integration and intensification reduce number of degrees of freedom
  - determine minimal sensor set required for operation (lower cost)
  - startup, shutdown: reduce time, complexity

Optimal Integration and Intensification of Modular GTL Processes

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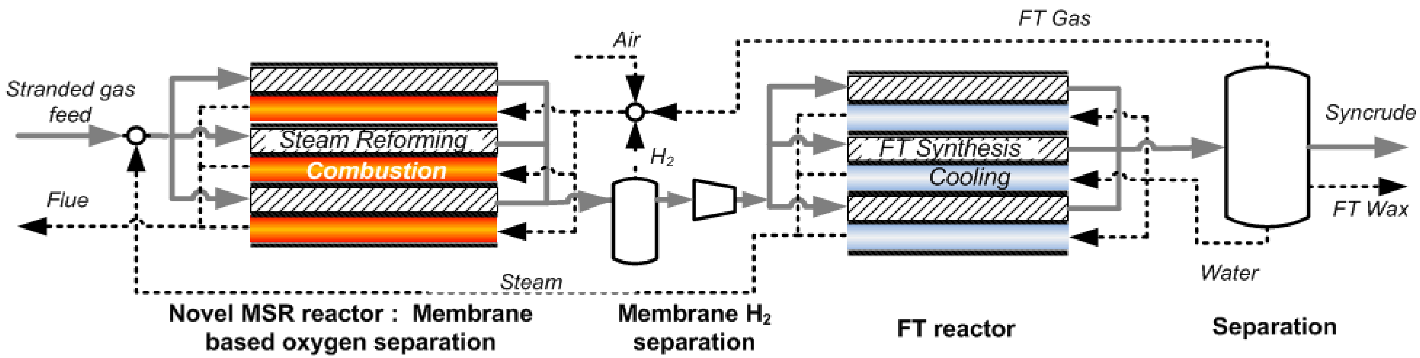
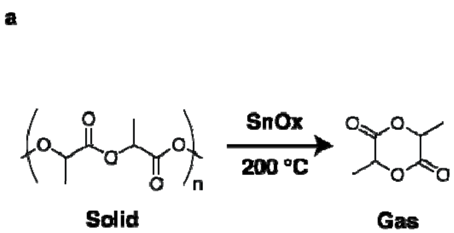


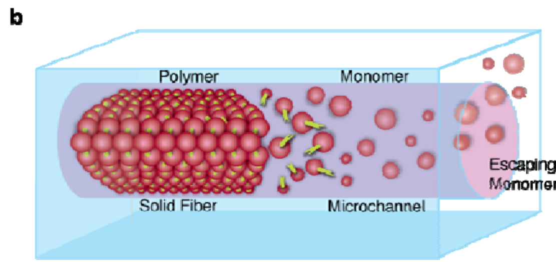
Modular GTL : generic challenges

- **Process <u>integration</u>: <u>simultaneous</u> <u>optimal</u> design of reactors (key unit operations) <u>and</u> process**
  - separation, balance-of-plant units, ancillary equipment
  - material and energy recycle structure
- **Intuitive approach:** incorporate **detailed models of key units** in **flowsheet model,** then solve **optimization problem**
  - Not possible with current (sequential modular) process simulators

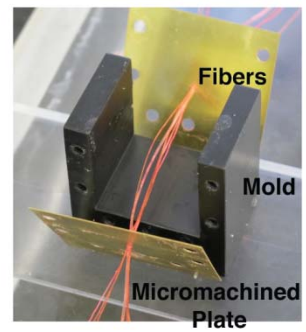
Need: robust, equation-oriented, optimzation-ready process modeling tools

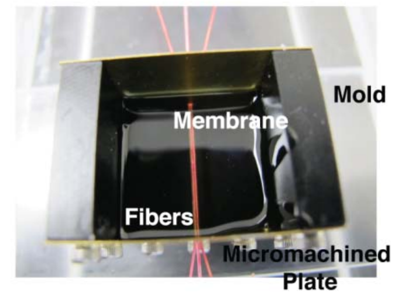
VaSC – Vaporization of a Sacrificial Component





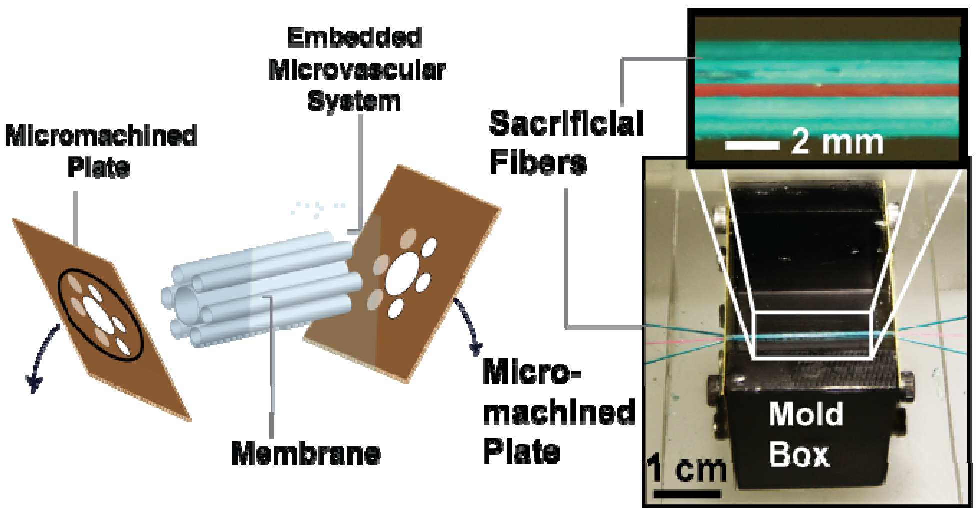
200 °C

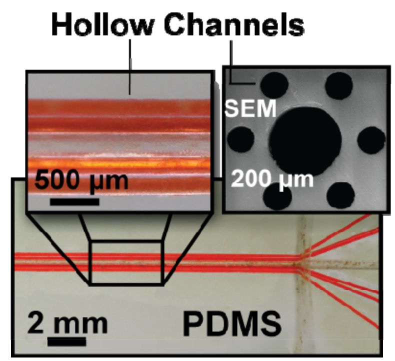


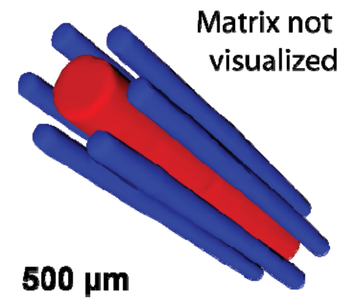


PLA Degradation

Empty Char





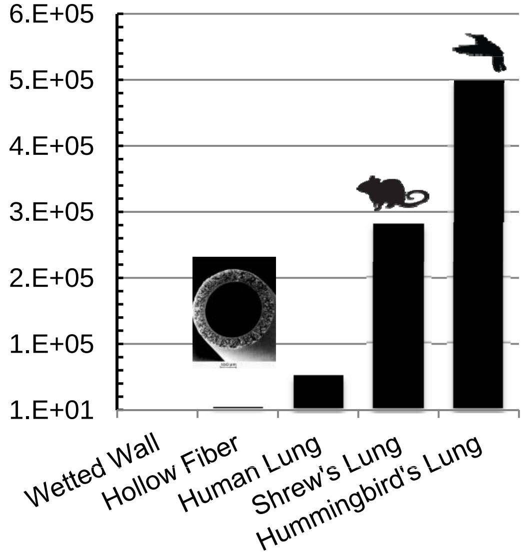


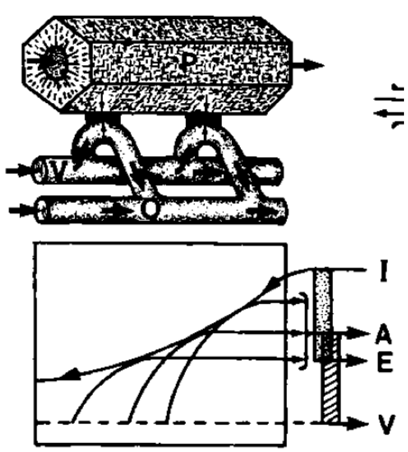
Aaron Esser-Kahn UC Irvine

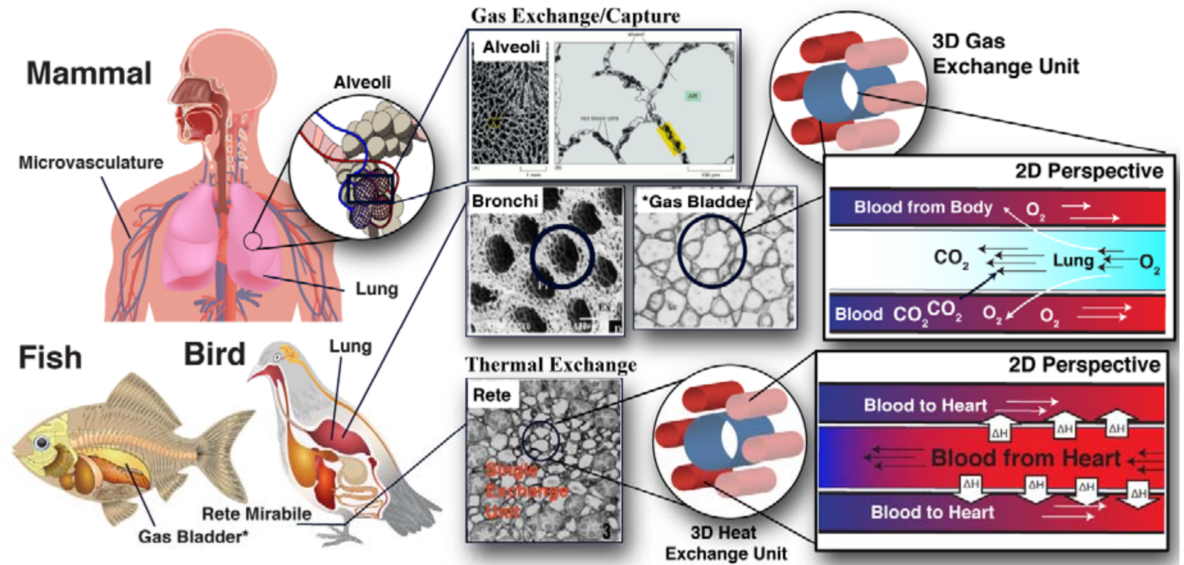
Esser-Kahn, A. P.; Thakre, P. R.; Dong, H.; Patrick, J. F.; Vlasko-Vlasov, V. K.; Sottos, N. R.; Moore, J. S.; White, S. R. *Advanced Materials* ***2011, 23, 3654–3658***

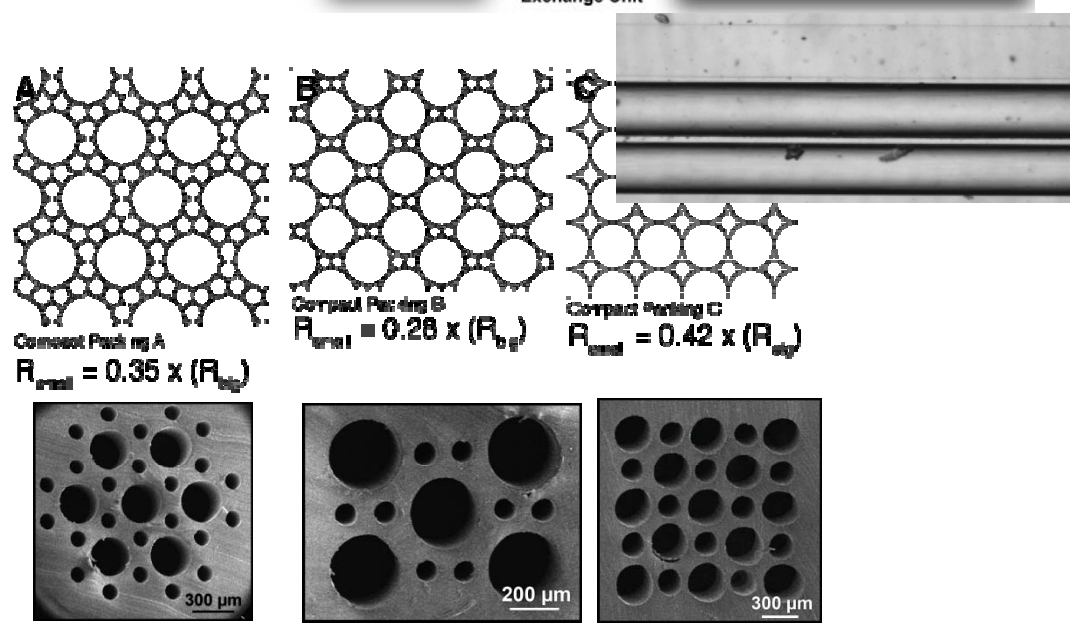
Man-Made Contactors vs. Natural Exchangers

Specific Surface Area
$(m^2 \cdot m^{-3})$







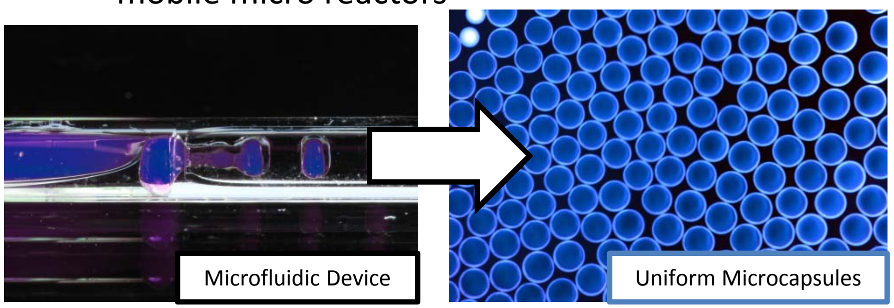


Multiple fabrication techniques for designed materials

Jennifer A. Lewis
University of Illinois at Urbana-Champaign
Lawrence Livermore National Laboratory

Microfluidic Encapsulation

Flow focusing devices create mobile micro reactors



Flow focusing microfluidic devices yield highly uniform microcapsules with control over structure and materials

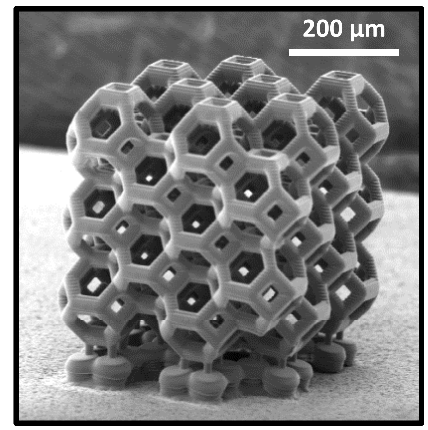
Solvent chemistry can be chosen to exhibit desired traits, while encapsulation increases surface area and aids transportation of media

Projection Microstereolithography (PµSL)

A photochemical and optical technique for exquisite structure control

Complex, designed architectures with high repeatability and uniformity

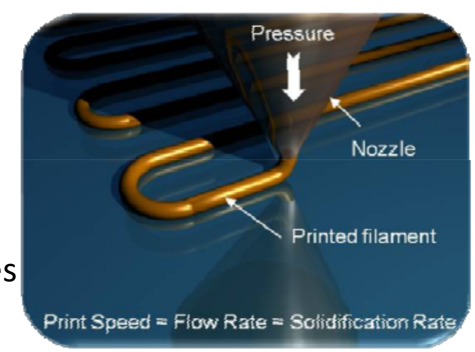
Materials such as ceramic nanoparticles can be incorporated during fabrication or introduced in post processing steps

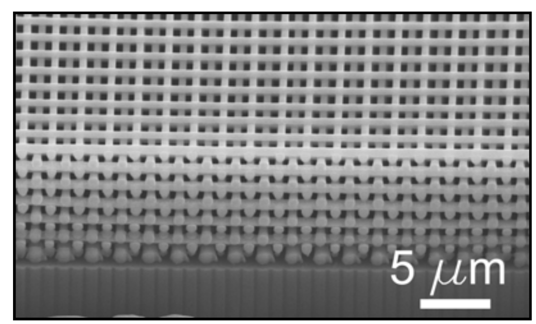


Direct Ink Writing (DIW)

Utilizes flow and gelling properties with a broad materials set

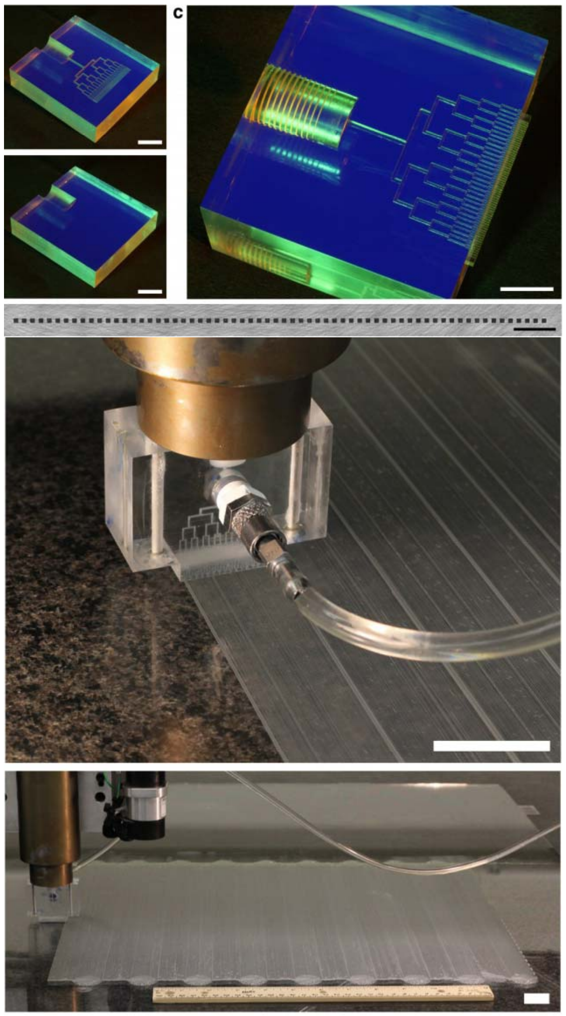
Library of materials available with ability to incorporate dopants, additives and catalysts.



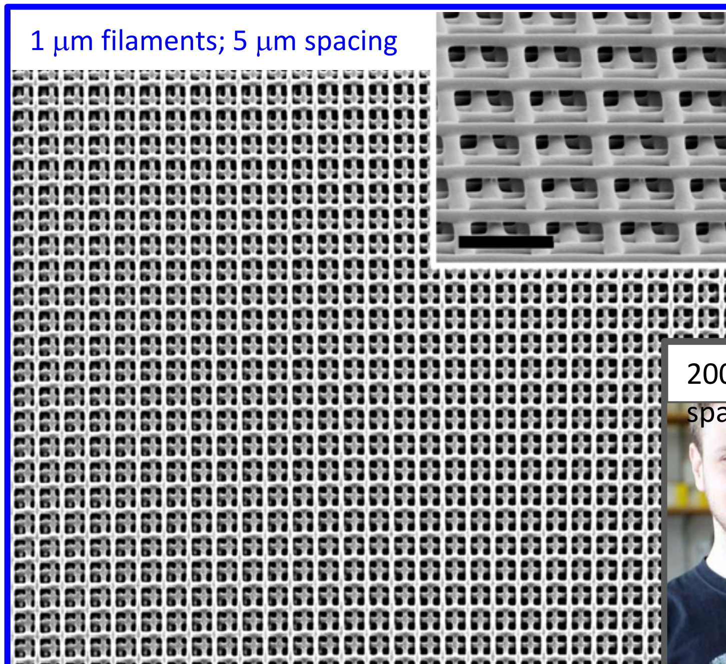


High Throughput Printing of 3D Catalyst Supports

Jennifer A. Lewis
University of Illinois at Urbana-Champaign



Multinozzle arrays for high-throughput printing of 3D catalytic supports



Precise control over 3D structure

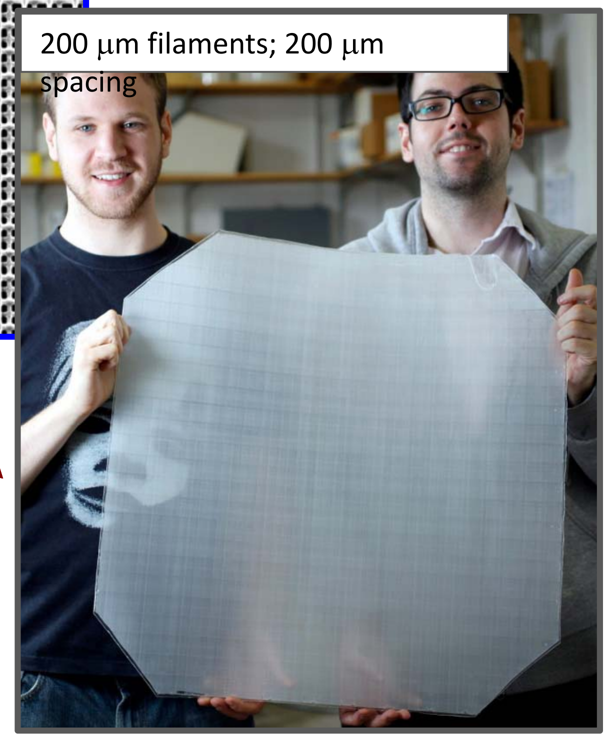
High surface area/volume ratio

Open architecture allows gas flow at modest pressures

Fine-scale to large-area 3D micro-periodic supports

Ability to print supports from broad array of substrate materials, e.g., polymers, biomolecules, etc.

Coat supports with catalytic agents



24”x24” lattice; build time < 30 min

More details @ http://colloids.matse.illinois.edu

Methane Fermentation

Biological Conversion

Methanotrophy (methane utilization) is a widespread natural process

Advantages

- **Efficient** (CCE=62%)
- **Low T /Pressure**
- **Selective toward methane**
- **Scalable**
- **Low-complexity** (few modules, easy to assemble/disassemble)
- **Low environmental impact**
- **Biomass -** animal feed (SCP)

Limitations

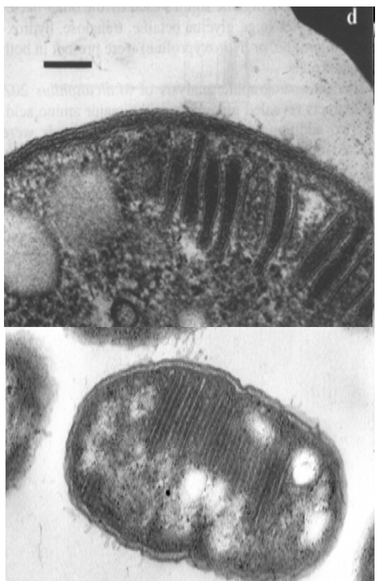
- **Strains not robust**
  - ✓ Less studied
  - ✓ Unstable (spontaneous lysis/loss of viability)
  - ✓ Sensitivity to C_{2-4} alkanes (can't be used for natural gas fermentation)
  - ✓ Contamination (grow better in consortia)
- **Processes mass-transfer limited for methane**

Recent progress

- **New strains (*Methylomicrobium* spp.)**
  - ✓ High rate of methane oxidation
  - ✓ Low K_s for methane
  - ✓ Simple cultivation requirements
  - ✓ Stay active at a wide range of chemical parameters
- **Enabling system level approaches for genetic alterations**
  - ✓ Genomes
  - ✓ Metabolic reconstruction
  - ✓ Genetic tools

Methane Fermentation

Biological Conversion



TEM images of *Methylomicrobium* sp. cells

Methane (C1)

↓

P-sugars

↓ ↓ ↓

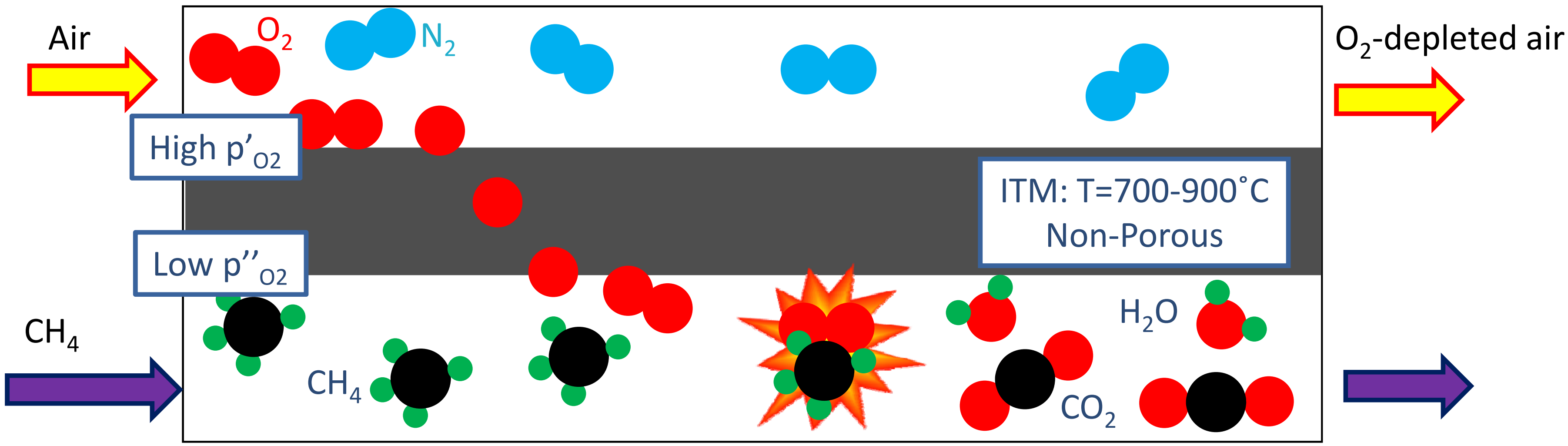
C6	C4	C2
Glucose	**Succinate**	**Acetyl-CoA**
↓	↓	↓
Fermentation feedstock	1,4-butanediol	FAEEs FAMEs Alkenes/Alkanes 1-butanol Isobutanol 3-Hydroxypropionate Isopentanol Bisabolane Farmesane

- Ability to convert C_1 into C_n compounds requires the presence of specific metabolic networks and complex cell architecture
- Efficient methane oxidation pathways can not be easily integrated into metabolic framework of well characterized microbes (*E .coli*)
- Biosynthetic modules for the production of advanced fuels or chemicals, developed for *glucose-based fermentation* in *E. coli* could potentially be implemented in the methane-utilizing strains

Methane fermentation by methanotrophic bacteria to generate value-added products is a potential GTL system that is now ready to exploit

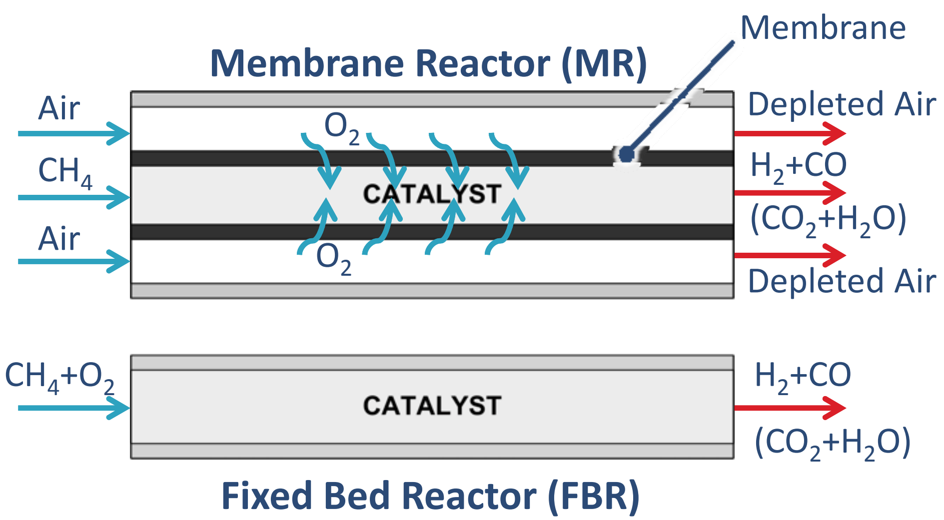
Ion Transport Membranes (ITM)

- At high temperature (700-900C) and under an oxygen chemical potential gradient, O_2 selectively permeates across membrane
- Economic and energetic O_2 separation penalty lower than conventional O_2 separation technologies
- CH_4 can be used as sweep gas for oxy-combustion, partial oxidation of methane (POM), or oxidative coupling



ITM FOR SMALL MODULAR METHANE UTILIZATION

- Benefits over conventional co-feed reactors:
  - Feed gas streams are CH_4 and air; high heating value syngas without requiring separate air separation unit
  - Distributed introduction of reactant (O_2) prevents deep oxidation, increase CO yield, and reduces temperature spikes[1]
- Modular/scalable reactor concepts have been proposed for POM and separation processes
- Pilot plants have demonstrated technology feasibility

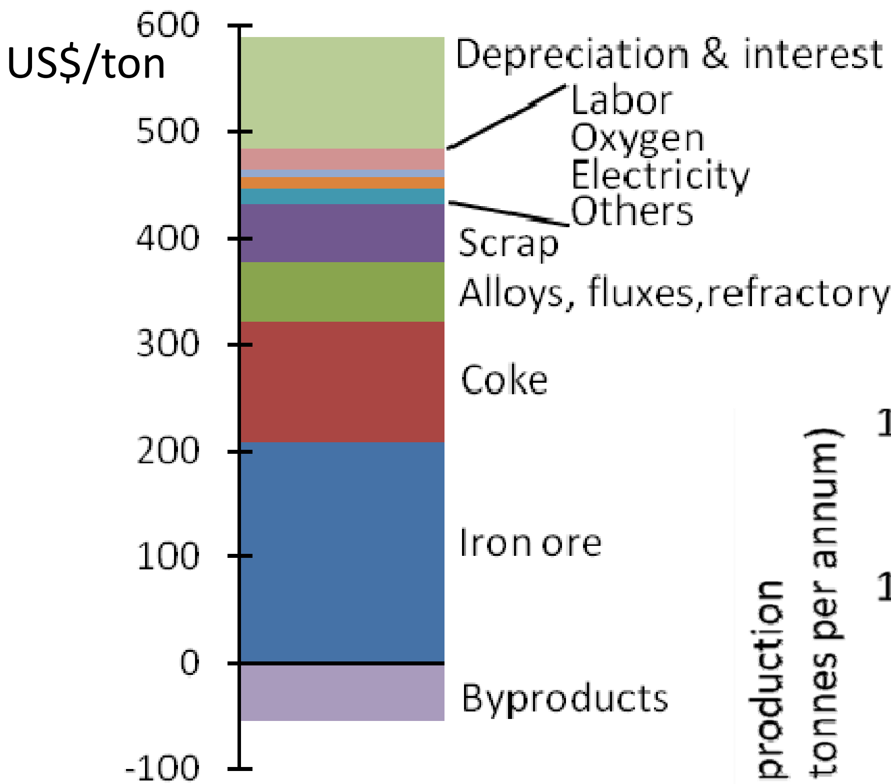


- **Current challenges:**
  - Reactor design and maximizing performance
  - Fundamental knowledge of processes
  - Sealing
  - Material longevity

1. X. Tan and K. Li. AIChE Journal, 55(10), 2009.

Opportunity for bulk, scalable methane use: metal production

Steelmaking cost:
Energy and capital are large components



source: steelonthenet.com;
Japanese coastal plant

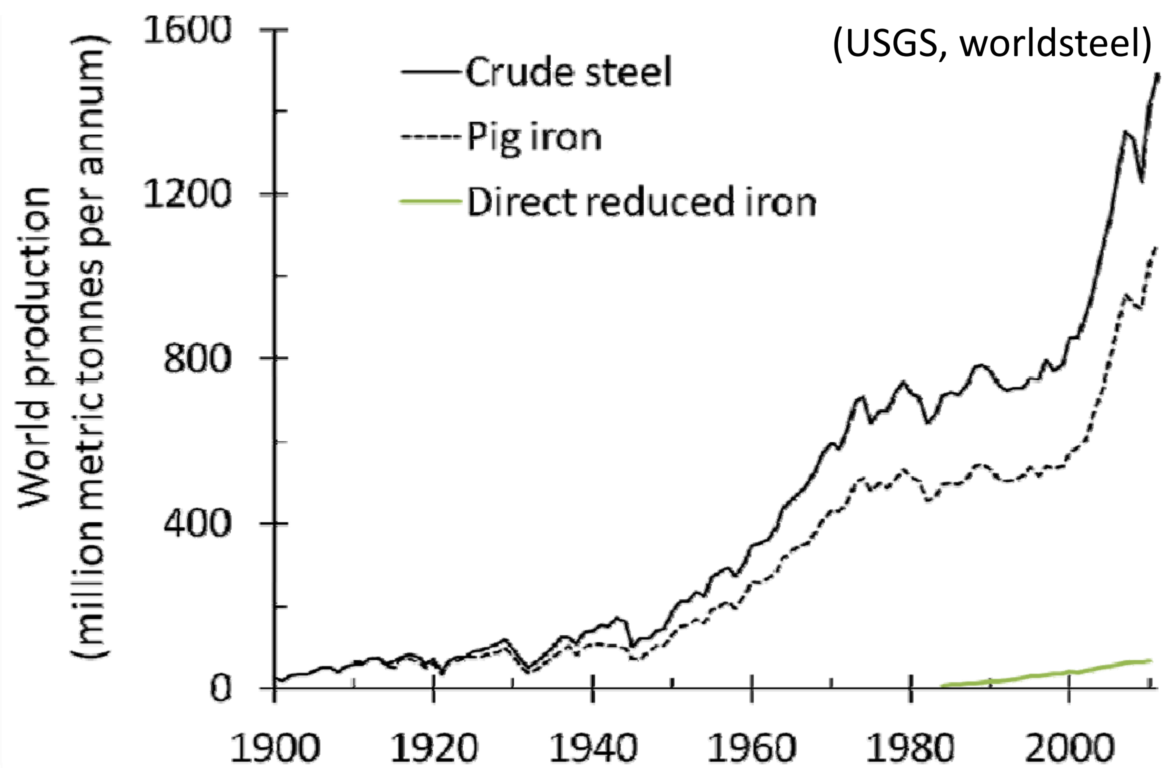
What are the fundamental scientific issues?

(Gordon *et al.*, 2012)

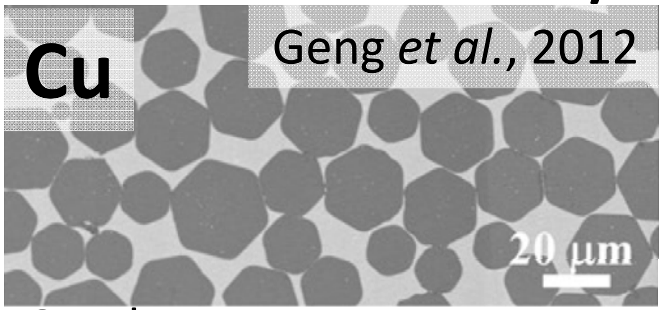
Environmental competitiveness of ironmaking processes:

CO_2 intensity (t CO_2 / t product)

Blast furnace	*1.25-1.5*
Methane-based	*<1*

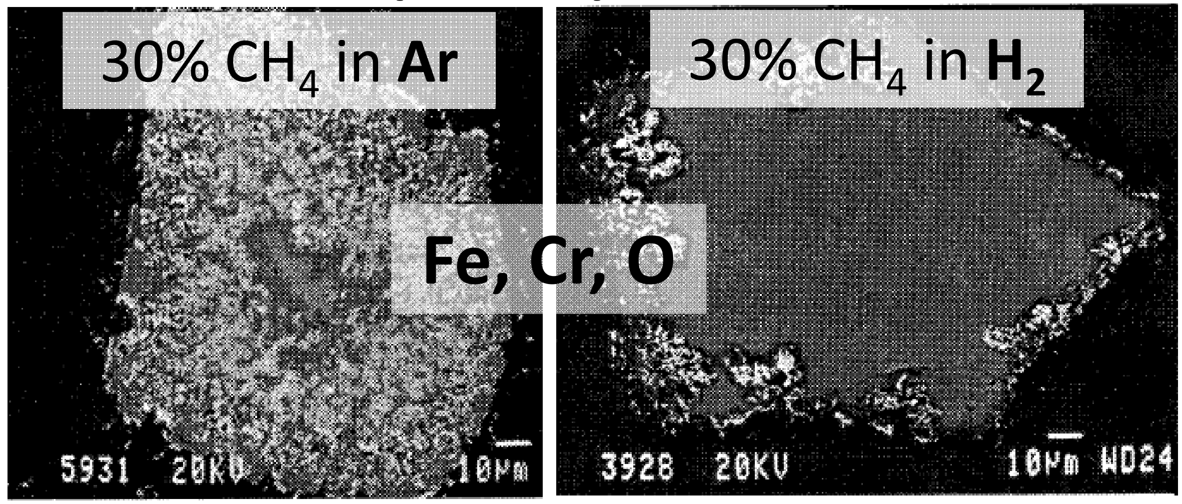


Fundamental issue: direct reaction between methane and metals / metal oxides; soot (carbon) formation

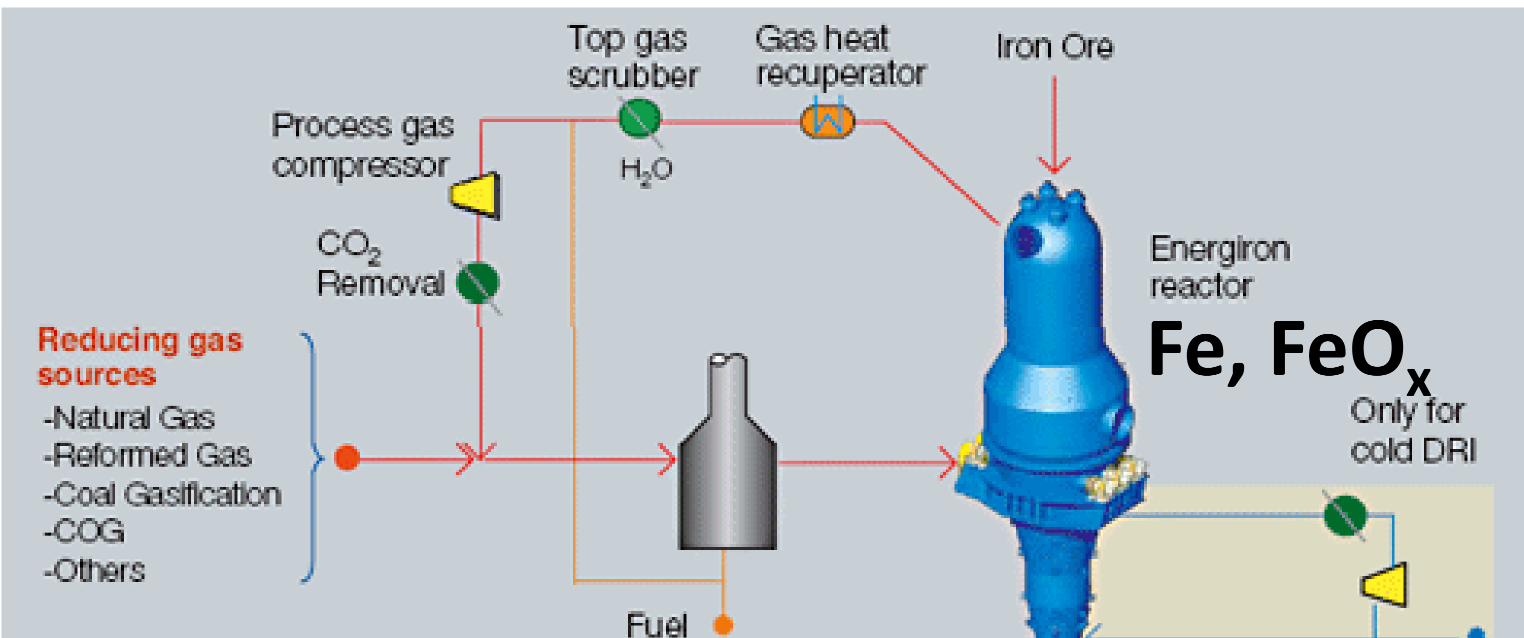


Graphene grown on liquid copper surface (2% CH_4 in H_2, 1120°C, 30 min)

(de Campos, 2003)



Reduction of chromite at 1100°C



HYL process to reduce iron ore: no reformer

Small Modular Methane Utilization

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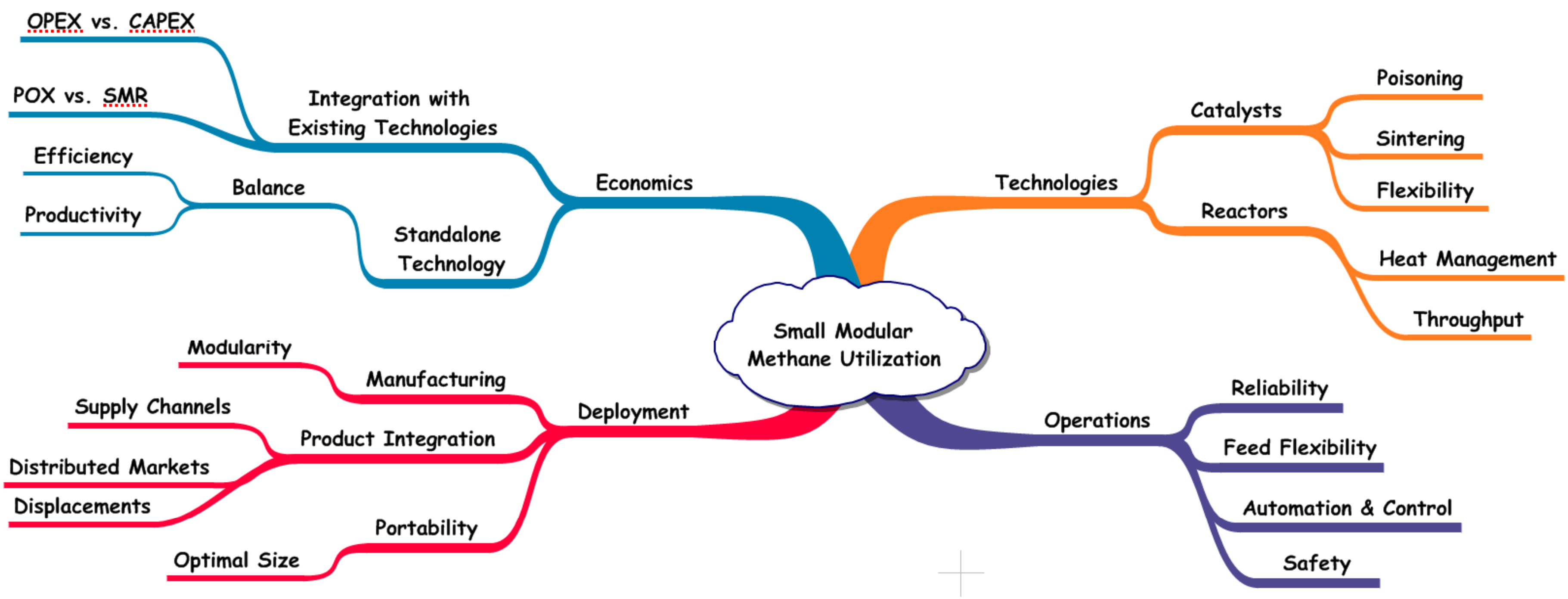
Balancing the key issues



Jason S Norman jnorman@rti.org

Biological Gas to Liquids

Advances in biological engineering provide new routes for catalyst development in a wide range of petrochemical applications and processes.

Key advantages for F-T alternatives and stranded gas

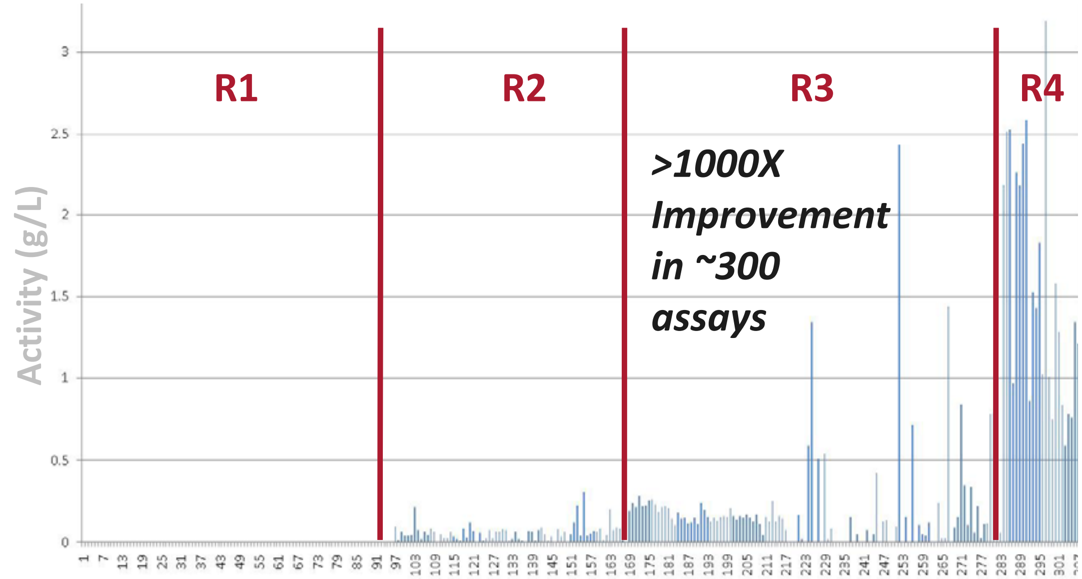
- ✓ High specificity
  - Controlled oxidation of methane to defined products
  - Carbon-carbon bond formation; pathways to high-value products
- ✓ Low (< 120^{o}C) temperature operation
  - Ability to scale-down effectively
  - Improved safety, lower CO_2, lower CapEx
- ✓ Lower sensitivity to common gas contaminants
  - Standard technology for a broad range of gas sources
  - Reduce/Eliminate need for gas scrubbing

Controlled oxidation of methane to defined products at break-through economics

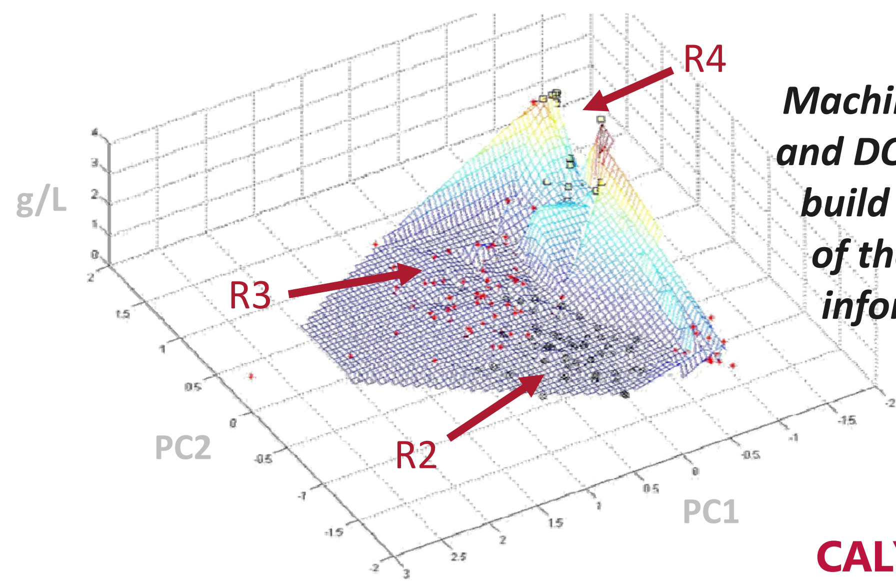
Catalyst Engineering Technology

Robust technology for catalyst optimization, e.g.:

- Operating Temperature
- Conversion Efficiency
- Conversion Specificity
- Reaction Rate
- Process Stability / Lifetime



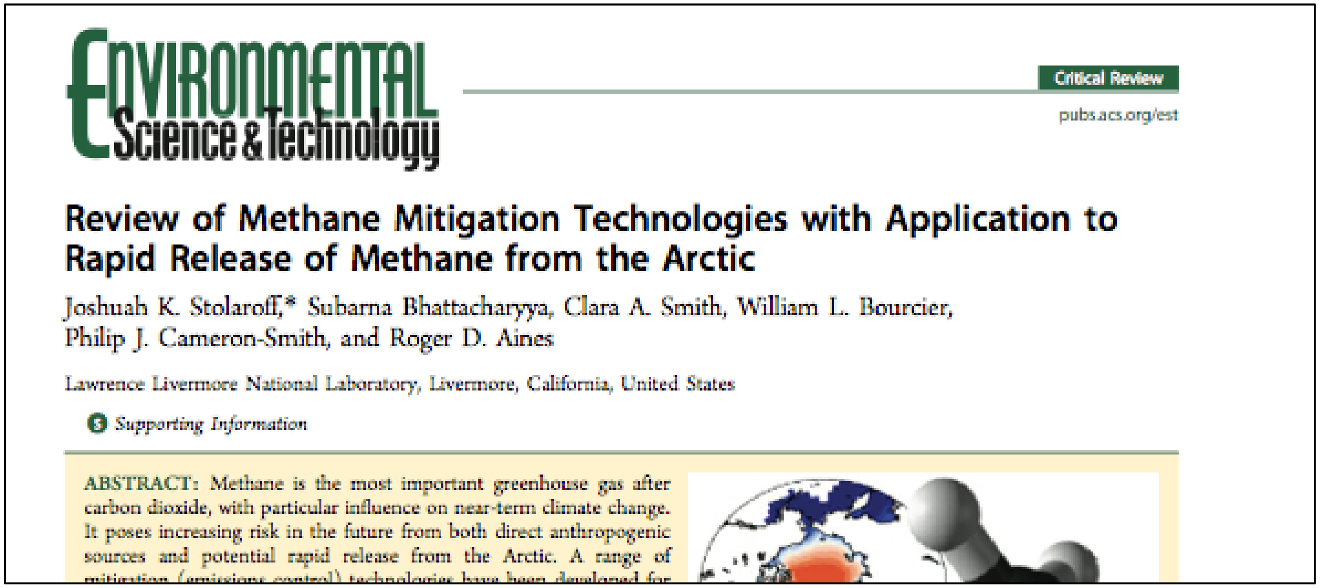
Calysta's approach to bioengineering combines well-established multivariate optimization methods with cutting-edge synthetic biology capabilities to develop biocatalysts and pathways for industrial applications.



Machine learning and DOE methods build knowledge of the system to inform designs.

Conversion to methanol can aid global methane mitigation

Joshuah Stolaroff
Lawrence Livermore National Laboratory


Environmental Science & Technology
Critical Review
pubs.acs.org/est

Review of Methane Mitigation Technologies with Application to Rapid Release of Methane from the Arctic

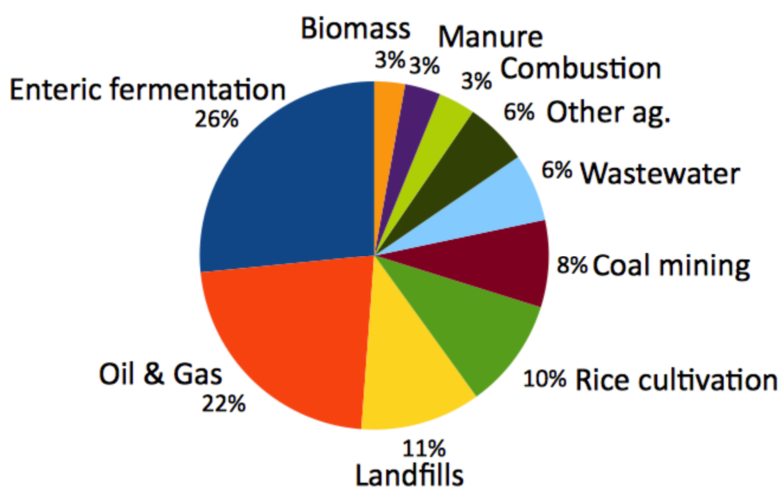
Joshuah K. Stolaroff,* Subarna Bhattacharyya, Clara A. Smith, William L. Bourcier, Philip J. Cameron-Smith, and Roger D. Aines

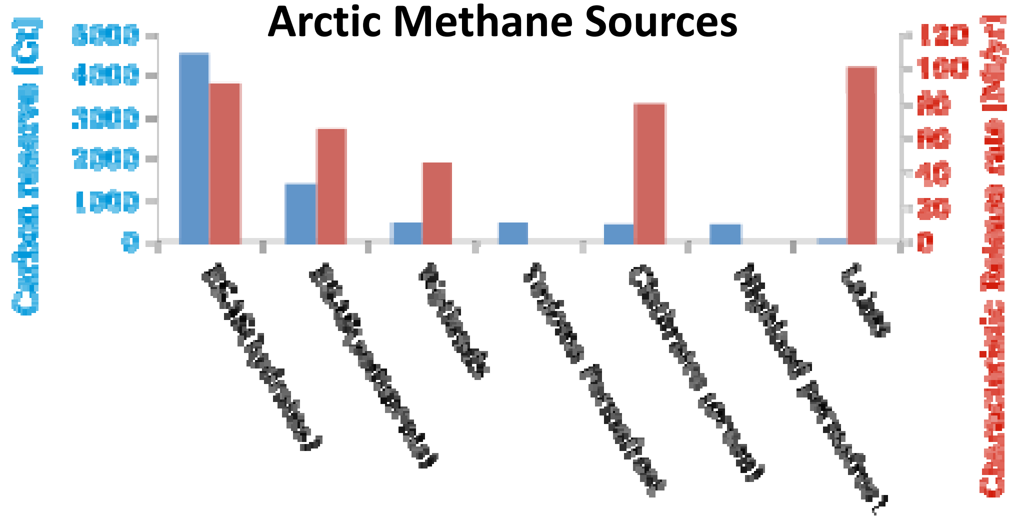
Lawrence Livermore National Laboratory, Livermore, California, United States

Supporting Information

ABSTRACT: Methane is the most important greenhouse gas after carbon dioxide, with particular influence on near-term climate change. It poses increasing risk in the future from both direct anthropogenic sources and potential rapid release from the Arctic. A range of

⇒Technologies are needed for current and Arctic methane sources of varying size and concentration.





- •Particular need to address small & remote sources, low concentration sources.
- •Methane-to-liquids could address these economically.

Existing technologies	Min. conc.	
Methanol production	89%	Conversion
Carbon black production	84%	Conversion
Purification by N2, O2 removal	40%	Energy
Spark ignition / internal combustion engine	40%	Energy
Gas or steam turbine	30%	Energy
Fluidized bubbling bed combustion	6%	Energy
Homogeneous charge gas engine	5%	Energy
Open flare	5%	Remediation
Lean-burn gas turbine	1.60%	Remediation
Catalytic lean-burn gas turbine	1%	Remediation
Catalytic Monolith Reactor	0.40%	Remediation
Concentrator (activated C)	0.40%	Remediation
Thermal Flow Reversal Reactor	0.20%	Remediation
Catalytic Flow Reversal Reactor	0.10%	Remediation
Bioreactors	**2 ppm**	Remediation
Combustion air in coal plant	--	Remediation
Combustion air in gas turbine	--	Remediation
Combustion air with waste coal production	--	Remediation

Biocatalysis: path to better methane conversion

High temperature, high pressure, low yield.

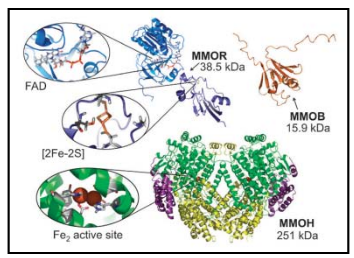
Methanotrophs oxidize methane from 2ppm to 60% concentration at ambient conditions along chain:

$CH_4 \rightarrow CH_3OH \rightarrow CH_3O \rightarrow CHOO^- \rightarrow CO_2$ or proteins

(methanol) (formaldehyde) (formate)

The first step is achieved by the enzyme Methane Monooxygenase (MMO), the only known catalyst at ambient conditions.

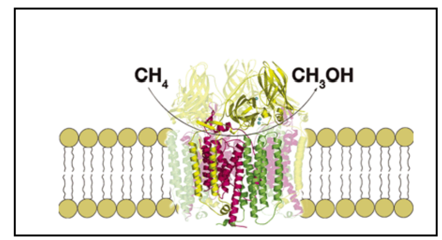
Soluble (sMMO)



Friedle, S., Reisner, E. & Lippard, S. *Chemical Society Reviews* **39**, 2768 (2010).

- long-studied with ongoing (decades) attempts at mimics.
- Requires multiple co-enzymes for function
- Structure mostly known

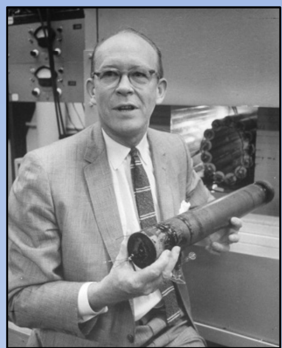
Membrane-bound (pMMO)



Lieberman, R. L. & Rosenzweig, A. C. *Dalton Transactions* 3390 (2005)

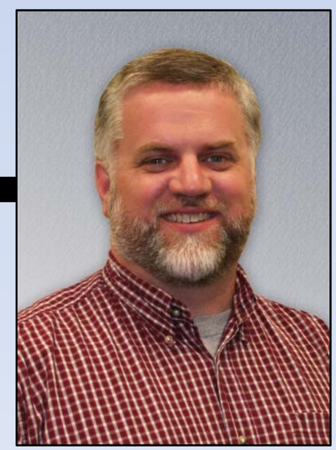
- characterized only recently
- no co-enzymes needed
- higher methane solubility in lipid membrane
- membrane enzymes generally harder to work with

Carbocation Generation – The Key to Direct Oligomerization of Methane



Willard Libby

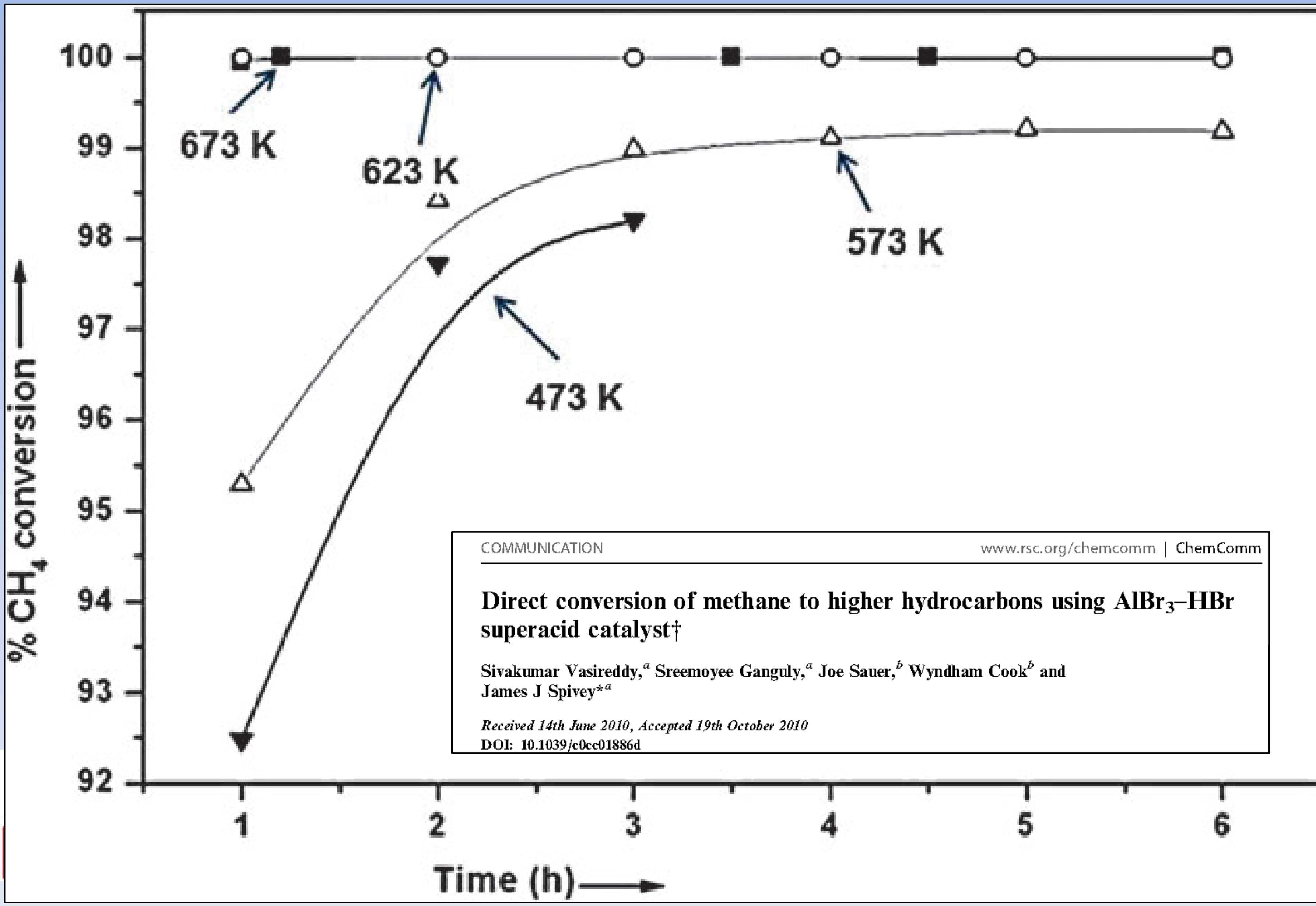
George Olah



Sean McDeavitt

Jerry Spivey

Prepare for the Critics



COMMUNICATION www.rsc.org/chemcomm | ChemComm

Direct conversion of methane to higher hydrocarbons using $AlBr_3$–HBr superacid catalyst†

Sivakumar Vasireddy,[a] Sreemoyee Ganguly,[a] Joe Sauer,[b] Wyndham Cook[b] and James J Spivey*[a]

Received 14th June 2010, Accepted 19th October 2010
DOI: 10.1039/c0cc01886d

Breakout session Brief

Report out from breakouts

Brainstorm Overview

- 90 minute challenge
- Choose a scenario
- Come up with a system that will convert methane.
- 10 minute presentation at the end
- Computer and internet allowed

Wrap up