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\textsubscript{2} eq.
  - 400 million from stranded petroleum gas worldwide
  - 2 billion tons from dairy farms worldwide
- Domestic emissions in tons CO\textsubscript{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

- Total CO2 emissions per country
- Methane related emissions in CO2 eq


Sources: World Bank, EPA, UN
Emissions by Source - Global Opportunity

- Total CO2 emissions per country
- Methane related emissions in CO2 eq

Sources: World Bank, EPA, UN
State of the art

CH4 → SMR → Syngas → WGS → Syngas → FT → High C → HC → Fuels

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 + H₂O
  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
The Learning Experience of Energy Conversion Technologies can improve by both increasing scale and/or increasing unit volume.

![Graph showing cost vs. capacity for GTL projects](image)

**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

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

Next Generation Syngas Conversion 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.

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Chevron’s Integral Fischer-Tropsch Catalyst
Hydrocarbon Liquid Properties – Entire C_{5+} Product

240°C, 20 atm, \( \text{H}_2/\text{CO} = 2, \) 1/16” extrudates

<table>
<thead>
<tr>
<th>Physical Properties</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>API</td>
<td>59.8</td>
</tr>
<tr>
<td>Pour Point (°C)</td>
<td>-16</td>
</tr>
<tr>
<td>Cloud Point (°C)</td>
<td>-9</td>
</tr>
<tr>
<td>Freeze Point (°C)</td>
<td>-6</td>
</tr>
<tr>
<td>C9-C16 Selectivity (jet fuel range)</td>
<td>45%</td>
</tr>
</tbody>
</table>

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)

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Generalized Syngas Reaction Scheme

[Diagram showing various reactions and products related to syngas, including Fischer-Tropsch, Methanol production, and hydrogen and ammonia synthesis.]
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:
  o Efficient Energy Production.
  o CO₂ Sequestration/Utilization.
  o 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%

Heat
- NH3
- H2

Ethylene (~115 million tonnes per annum)
Propylene (~70 million tonnes per annum)

Polyethylene
Ethanol
Ethylene oxide - Glycol
1,2 dichloroethane - PVC

Benzene (~40,000,000 tons per annum)– Ethylbenzene – Styrene
Nitrobenzene – Polyurethane
Cyclohexane – Nylon
Toluene – Polyurethane - Nylon
Xylene – Resins & Polyester

Current

Potential
Opportunity: pMMO in Artificial Cell Membranes

- 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.

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.
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Prepared by LLNL under Contract DE-AC52-07NA27344
**Hybrid Biocatalyst** Approach: Use NLPs to co-localize coenzyme for **Self-sustaining** pMMO particles

- **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
Process **intensification** with microchannel reactors: excellent scale-down

**Specific challenges**

- **water management**: scarce, location-dependent resource; steam needed/generated at multiple pressures
- **hydrogen management**: reforming product H₂: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

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

Modular GTL: generic challenges

- **Process integration**: simultaneous optimal design of reactors (key unit operations) and 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, optimization-ready process modeling tools
VaSC – Vaporization of a Sacrificial Component

PLA Degradation

200 °C

Man-Made Contactors vs. Natural Exchangers

Specific Surface Area (m² • m⁻³)

- Wetted Wall
- Hollow Fiber
- Human Lung
- Shrew's Lung
- Hummingbird's Lung

<table>
<thead>
<tr>
<th>Surface Area</th>
<th>Wetted Wall</th>
<th>Hollow Fiber</th>
<th>Human Lung</th>
<th>Shrew's Lung</th>
<th>Hummingbird's Lung</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>6.0E+05</td>
<td>1.0E+05</td>
<td>2.0E+05</td>
<td>3.0E+05</td>
<td>4.0E+05</td>
</tr>
</tbody>
</table>

Blood from Heart → CO₂ → Lung → O₂ → Blood

2D Perspective

- Gas Exchange/Capture
- Thermal Exchange
- 3D Gas Exchange Unit
- 3D Heat Exchange Unit

Compacted Packing A
\[ R_{eq} = 0.35 \times R_{bg} \]

Compacted Packing B
\[ R_{eq} = 0.28 \times R_{bg} \]

Compacted Packing C
\[ R_{eq} = 0.42 \times R_{bg} \]
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

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.

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

Materials such as ceramic nanoparticles can be incorporated during fabrication or introduced in post processing steps.
High Throughput Printing of 3D Catalyst Supports
Jennifer A. Lewis
University of Illinois at Urbana-Champaign

- 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

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

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**
- **Selectively 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** (*Methylocordobium* 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**

- Ability to convert C\textsubscript{1} into C\textsubscript{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 (C1)**

\[
\text{P-sugars} \quad \text{C6} \quad \text{C4} \quad \text{C2} \\
\text{Glucose} \quad \text{Succinate} \quad \text{Acetyl-CoA} \\
\text{Fermentation feedstock} \quad 1,4\text{-butanediol} \quad \text{FAEs, FAMEs, Alkenes/Alkanes, 1-butanol, Isobutanol, 3-Hydroxypropionate, Isopentanol, Bisabolane, Farmesane} \\
\]

**TEM images of Methylomicrobium sp. cells**

*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 (700-900°C) and under an oxygen chemical potential gradient, \( \text{O}_2 \) selectively permeates across membrane.
- Economic and energetic \( \text{O}_2 \) separation penalty lower than conventional \( \text{O}_2 \) separation technologies.
- \( \text{CH}_4 \) can be used as sweep gas for oxy-combustion, partial oxidation of methane (POM), or oxidative coupling.

Diagram:
- Air enters at high \( p'_{\text{O}_2} \) on the left, and \( \text{O}_2 \)-depleted air exits on the right.
- \( \text{CH}_4 \) enters at low \( p''_{\text{O}_2} \) on the left and reacts to form \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) on the right.
- ITM: \( T=700-900^\circ \text{C} \), Non-Porous.
ITM for Small Modular Methane Utilization

- Benefits over conventional co-feed reactors:
  - Feed gas streams are CH₄ and air; high heating value syngas without requiring separate air separation unit
  - Distributed introduction of reactant (O₂) prevents deep oxidation, increases CO yield, and reduces temperature spikes¹
- Modular/scalable reactor concepts have been proposed for POM and separation processes
- Pilot plants have demonstrated technology feasibility

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

Environmental competitiveness of ironmaking processes:
CO2 intensity (t CO2 / t product)
Blast furnace 1.25-1.5
Methane-based <1

What are the fundamental scientific issues?

Source: steelonthenet.com; Japanese coastal plant
Fundamental issue: direct reaction between methane and metals / metal oxides; soot (carbon) formation

Graphene grown on liquid copper surface (2% CH₄ in H₂, 1120°C, 30 min)

Reduction of chromite at 1100°C

HYL process to reduce iron ore: no reformer
Small Modular Methane Utilization

Jason S Norman
jnorman@rti.org
919-541-6788
Balancing the key issues

Small Modular Methane Utilization

- QREX vs. CAPEX
- POX vs. SMR
- Efficiency
- Productivity
- Integration with Existing Technologies
- Economics
- Standalone Technology
- Balance
- Supply Channels
- Distributed Markets
- Displacements
- Optimal Size
- Modularity
- Manufacturing
- Product Integration
- Portability
- Deployment
- Operations
- Reliability
- Feed Flexibility
- Automation & Control
- Safety
- Poisons
- Catalysts
- Sintering
- Flexibility
- Reactors
- Heat Management
- Throughput
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°C) temperature operation**
  
  Ability to scale-down effectively
  Improved safety, lower CO₂, 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*
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.

>1000X Improvement in ~300 assays

Machine learning and DOE methods build knowledge of the system to inform designs.
Conversion to methanol can aid global methane mitigation

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.
### Biocatalysis: path to better methane conversion

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

\[
\text{CH}_4 \rightarrow \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{O} \rightarrow \text{CO}_2 \text{ or proteins}
\]

- **High temperature, high pressure, low yield.**
- **Soluble (sMMO)**
  - characterized only recently
  - no co-enzymes needed
  - higher methane solubility in lipid membrane
  - membrane enzymes generally harder to work with

### Methanol production 89%

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

### Conversion

- **Methanotrophs** oxidize methane from 2ppm to 60% concentration at ambient conditions.

### Chain of reactions:

\[
\begin{align*}
\text{CH}_4 & \rightarrow \text{CH}_3\text{OH} \\
\text{CH}_3\text{OH} & \rightarrow \text{CH}_3\text{O} \\
\text{CH}_3\text{O} & \rightarrow \text{CO}_2
\end{align*}
\]

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

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Carbocation Generation – The Key to Direct Oligomerization of Methane

Chemical Route ↔ 70 yard Field Goal

Nuclear Route ↔ One-inch Field Goal

Willard Libby  George Olah

Jerry Spivey  Sean McDeavitt
Prepare for the Critics

Direct conversion of methane to higher hydrocarbons using AlBr₃–HBr superacid catalyst

Sivakumar Vasireddy, a Sreemoyee Ganguly, a Joe Sauer, b Wyndham Cook b and James J Spiveyac

Received 14th June 2010, Accepted 19th October 2010
DOI: 10.1039/c0ee01886d
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