Natural Gas Conversion Technologies Workshop

OUTPUT REPORT

Program Director: Dane Boysen

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Houston, TX

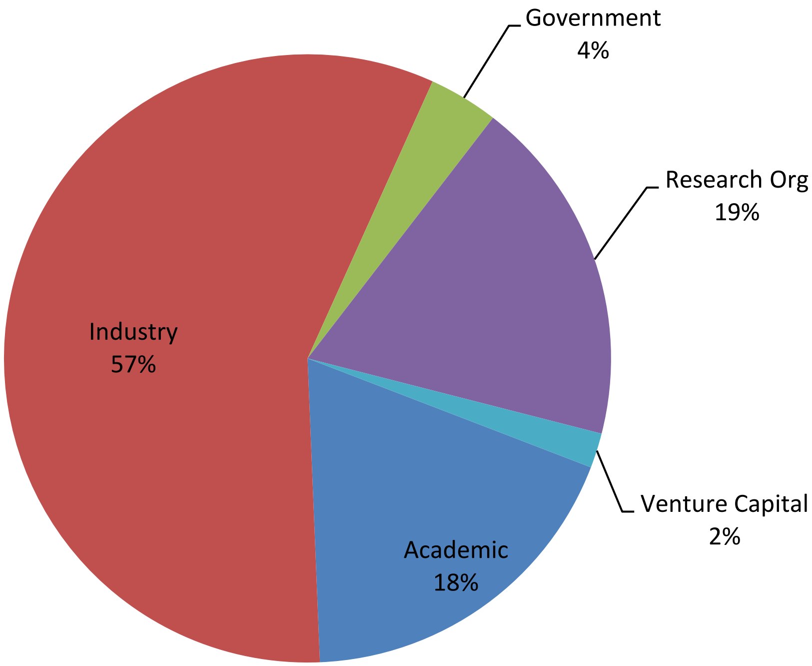
Workshop Attendees

Attendee	Organization
Arun Basu	Gas Technology Institute
Richard Boardman	Idaho National Lab
Dane Boysen	ARPA-E
Emilio Bunel	Argonne National Lab
Jonathan Burbaum	ARPA-E
Jack Chen	Ceramatec
Dolly Chitta	Ceramatec
Luke Coleman	RTI
Rob Conrado	ARPA-E
Wyndham Cook	Albemarle Corp.
Burtron Davis	University of Kentucky
Richard Deal	BASF
Arno DeKlerk	U Alberta
David Denton	RTI International
Richard Doctor	Argonne National Lab
Dan Driscoll	NETL
S. (Elango) Elangovan	Ceramatec
Christodoulos A. Floudas	Princeton
Karl Gerdes	Chevron
Daniel Ginosar	Idaho National Lab
Paul Grimmer	Eltron Research
Marina Kalyuzhnaya	University of Washington
Mark Kaminsky	Dow
Mukund Karanjikar	Ceramatec
Steven Kaye	Wildcat Discovery Technologies
Theodore Krause	Argonne National Lab
Marty Lail	RTI
Philippe Larochelle	ARPA-E
Stephen LeViness	Velocys/Oxford Catalyst
Jack Lewnard	GTI
Wei Liu	PNNL
Ajay Madgavkar	(Independent Consultant)

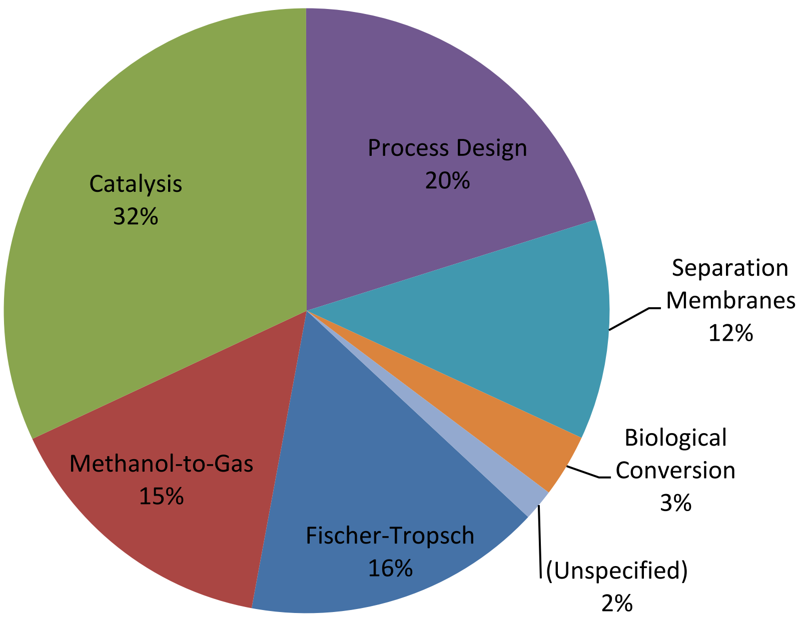
Attendee	Organization
Cheryl Martin	ARPA-E
Jon McCarty	SRI, RTI, and Catalytica
Jeff Miller	Argonne National Lab
Robert Motal	Chevron
Olayinka Ogunsola	DOE, Fossil Energy
Ah-Hyung Alissa Park	Columbia University
Abhimanyu Patil	ExxonMobil
Lawrence Peck	LBP Consulting
Roy Periana	The Scripps Research Institute
Phil Pienkos	NREL
Simon Podkolzin	Stevens Institute of Technology
Joe Powell	Shell
Karma Sawyer	ARPA-E
Erik Scher	Siluria Technologies
Mark Siddoway	Dow Chemical
John A Sofranko	Bio2Electric
James Spivey	LSU
Peter Stair	Northwestern University
Brien Stears	Dow Chemical
Sven Strohband	Mohr Davidow
Dave Studer	Air Products
Sam Tam	Office of Clean Coal
Greg Tao	Materials & Systems Research Inc.
Eric Toone	ARPA-E
Niel Udengaard	Haldor Topsoe, Inc.
Anil Virkar	University of Utah
Robert Weber	PNNL
Ken Whitmire	Rice University
Bang Xu	Dason Technology
DJ Zaziski	Siluria Technologies

Attendee Statistics

Attendee Affiliation



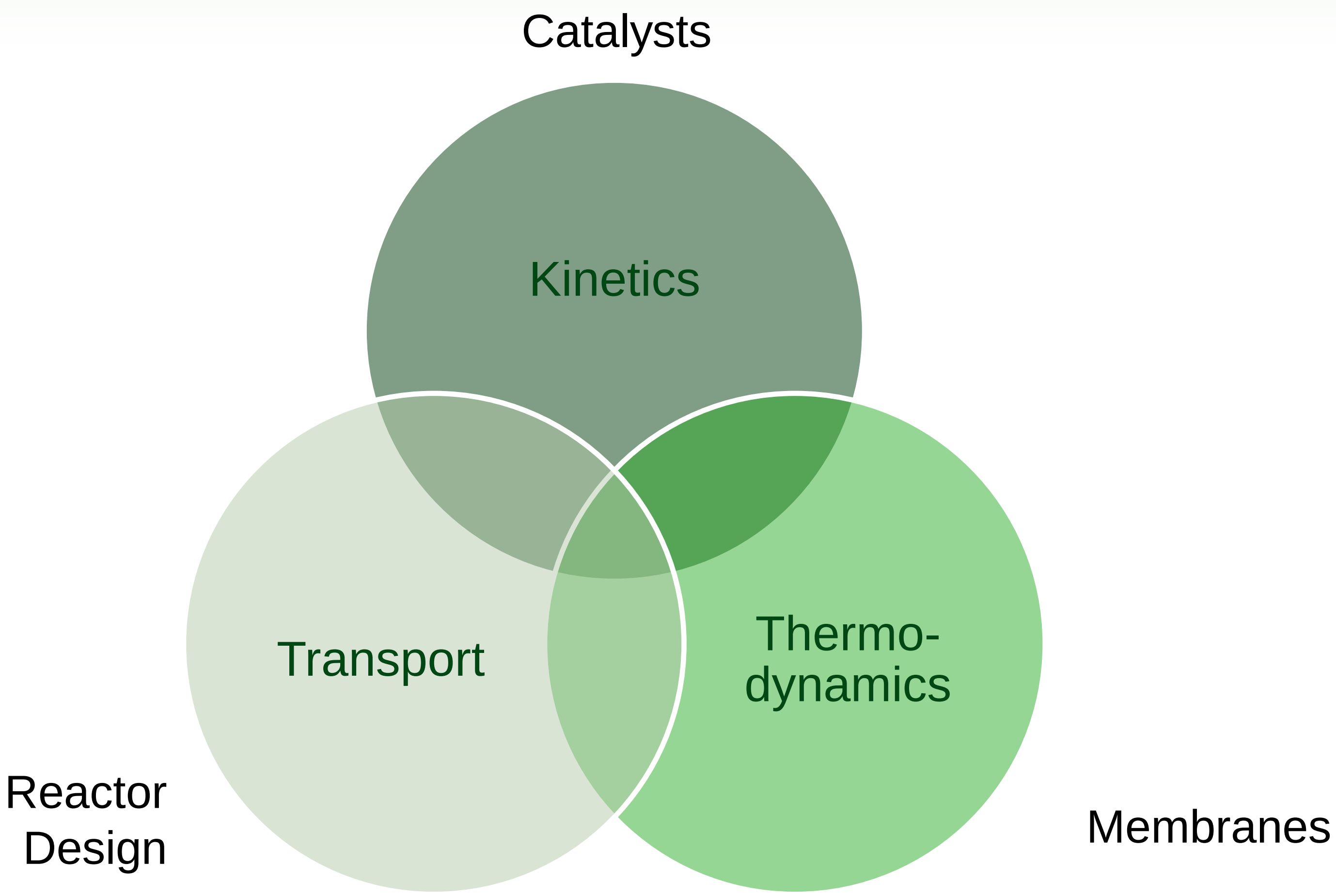
Attendee Expertise



Workshop Introduction Overview

- Natural gas prices are nearly 5x less than petroleum prices. Is this a short-term arbitrage opportunity or long-term market trend?
- Is increasing use of natural gas in the transportation sector the right direction?
- Is using natural gas directly more efficient that converting it to liquid fuels?
- Why develop natural gas conversion technologies?
- The global problem of flared/vented associated natural gas presents the clearest near term opportunity for natural gas conversion technologies
- What is the grand challenge in methane conversion to liquids and where are the opportunities?

Challenges for methane conversion to liquid fuels



Starting premise for workshop discussions

Identify technological whitespace, new research directions, and opportunities that could enable natural gas conversion to liquid hydrocarbons with the following characteristics:

Criterion	Target
Scale	Small (< 1000 boe/day)
Carbon Efficiency	High (>60%)
Cost	Low (simple/few unit operations)

For the purposes of this workshop, the following will <u>not</u> be discussed:

- Regulation and policy
- Coal, biogas, carbon dioxide feedstocks (XTL)
- Ethane, propane, butane (LPG) separation and conversion

Agenda

08:15	Welcome and Opening Remarks	Eric Toone, Deputy Director, ARPA-E
08:30	Workshop Overview and Objectives	Dane Boysen, Program Director, ARPA-E
08:45	Gas to Liquids Overview	Arno de Klerk, U. Alberta (formerly Sasol)
10:00	Morning Breakout Sessions	
12:15	Lunch – review morning session results	
01:00	Commercialization Considerations for Gas Conversion Technology Development	Rob Motal, Chevron
	Center for Catalytic Hydrocarbon Functionalization (DOE Energy Frontier Research Center)	Roy Periana, The Scripps Research Institute
02:20	Afternoon Breakout Session	
04:30	Review afternoon break session results	
05:30	Concluding Remarks	

Discussion Questions

1. What is the state of the art?
2. What advances/breakthroughs (if any) have there been in the last 10 years?
3. What are the technical and economic barriers for this approach?
4. What are the advantages and disadvantages of this approach?
5. How does this approach simplify/reduce the cost of gas to liquids processes? (minimize T, P changes)
6. What needs to happen for this approach to be commercially viable?
7. What novel/unique approaches could be enabling for this technology?
8. Who would you use to validate test results externally? How would they verify your results?
9. What specific research avenues for the identified technical areas do you believe are the most promising?

Breakout Group Summaries

Group 1	*biocatalysis, homogeneous catalysis, halogenation*
Group 2	*oxidative coupling, partial oxygenation, (other activation routes), membranes*
Group 3	*membranes, oxidative coupling, cracking, dehydroaromatization, electrochemical, test equipment*
Group 4	*syngas, Fischer-Tropsch, reactor design*
Group 5	*methanol-to-fuels, Fischer-Tropsch, reactor design*
Group 6	*Fischer-Tropsch, water separation, process design*

BREAKOUT GROUP 1 – Morning Session

Discussion Topics: *biocatalysis, homogeneous catalysis, halogenation*

Summary Points

- Opportunity 1: Methanotrophs to higher chain hydrocarbons
  - Advantage: Direct conversion, highly specific, with no air separation
  - Disadvantage: Low productivity and carbon efficiency
  - Challenges include matching reaction rates within the cell, heat transfer without refrigeration, and culture stability
- Opportunity 2: Bio-Catalysis and Biomimetic Catalyst Control
  - Advantage: High Active-Site Loading, can couple to non-biological membranes, very specific
  - Disadvantage: Expensive and unstable catalysts
  - Challenges: Enzyme immobilization, and the pMMO structure is not well known
- Opportunity 3: Homogeneous Catalysis (Hg, ligated Pt)
  - Advantage: Can tolerate sulfur, operates at only 100-200C, produces MeOH/DME feedstock
  - Disadvantage: Requires circulating SO_2
  - Challenges: Separation required with Hg carryover, along with 10-1000x increase in rate to reduce platinum catalyst cost

BREAKOUT GROUP 1 – Morning Session

Discussion Topics: *biocatalysis, homogeneous catalysis, halogenation*

Summary Points

- Opportunity 4: Methane to ethane coupling with H2 production
  - Advantage: Product compatible with regular petroleum streams
  - Disadvantage: Low driving force
  - Challenges: Big coking problems, H2 removal
- Opportunity 5: Sulfonation of Methane
  - New research topic, uses expensive persulfate, has significant corrosion issues
- Opportunity 6: Halogenation as an alternative oxidant
  - Advantage: Can directly produce MeOH
  - Disadvantage: Chlorine contamination of product
  - Challenges: Difficult to stop at mono-halide/control other products
- Opportunity 7: Bromine based process as an oxidant
  - Advantage: Can directly produce Methanol
  - Disadvantage: Low selectivity, bromine in the product stream
- Opportunity 8: Super Acid catalyzed oligomerization of methane
  - Advantage: Can directly produce MeOH
  - Disadvantage: Chlorine contamination of product
  - Challenges: Difficult to stop at mono-halide/control other products

BREAKOUT GROUP 1 – Afternoon Session

Discussion Topics: *biocatalysis, homogeneous catalysis, halogenation*

Summary Points

- Super-Acid Catalysis was mainly discussed as a research direction

- Product catalysts should have the following attributes
  - Halogen-free final product
  - Selectivity to C5+ compounds
  - Maximum information possible regarding mechanism
  - Productivity of 1E-06 mol/cc/s
  - Carbon Efficiency >25%
  - Mass-Energy Balance less than “N” process steps (unknown exact number)
  - Has upper limit for T,P
  - Minimal byproducts
  - Catalyst cost is less than $.01/gallon product

BREAKOUT GROUP 2 – Morning Session

Discussion Topics: *oxidative coupling, partial oxygenation, (other activation routes), membranes*

Summary Points

- GTL through direct oxidative or reductive processes is transformative
  - Lower plant capital cost
  - Capable of more facile, smaller-scale design
- Most of the processes discussed are only at laboratory scale
  - Improvements needed in catalyst, membrane, and reactor materials to scale systems at 1000 bbl/d target set in this workshop.
- Inexpensive source of oxygen is a game changing technology
  - Electrolysis or advanced membrane technology cited
- Better intermediate product separations and separations technology is a key enabler
  - Heat management, systems integration, and manufacturability of components also important.

BREAKOUT GROUP 2 – Afternoon Session

Discussion Topics: *oxidative coupling, partial oxygenation, (other activation routes), membranes*

Summary Points

- Small-scale GTL approaches have several engineering advantages
  - Heat, power, and process elements integration (where appropriate)
  - Lower overall capital and operations costs
  - Higher efficiencies.

- Advanced catalysts or membrane reactors with high conversion efficiencies and high selectivity are critical enablers

- Variable natural gas feed processing (i.e. from different wells) is a key requirement
  - Unit should be controllable, tunable to the gas feed, and be a refinery drop-in.

- Assembly line-made GTL units would lower capital costs overall.
  - Parts modularity and manufacturability are key to manufacturing effectively.

BREAKOUT GROUP 3 – Morning Session

Discussion Topics: *membranes, oxidative coupling, cracking, dehydroaromatization, electrochemical, test equipment*

Summary Points

- Improved oxygen membrane reactors for syngas production would offer many benefits
  - No oxygen separation or
  - No external heat input and
  - Improved scalability towards smaller units.
  - Cost, membrane stability, and integration are significant concerns.
- Oxidative coupling with systems integration offer improved implementation at small scales over standard FT reactors
  - Challenges are reactor design integration, heat management and incorporating membrane technologies with large oxygen mobility
- Non-oxidative dehydroaromatization would produce a transportable liquid product without needing an oxygen separation unit.
  - Low yields of desirable products and complex unit integration are challenges.
  - Benzene (the predominant product) may not have significant enough value to justify the plant costs.
- Primary challenges overall are low yields and product separation
  - Catalyst and membrane technology (particularly membranes that can withstand higher temperatures) are target areas for improvement

BREAKOUT GROUP 3 – Afternoon Session

Discussion Topics: *membranes, oxidative coupling, cracking, dehydroaromatization, electrochemical, test equipment*

Summary Points

- Thermally stable membranes and materials (>600 °C) are potentially enabling technologies for oxygen membrane reactors.

- Membrane integration with advanced catalysts and overall process design integration (i.e. heat, power, etc.) will benefit reactor efficiency and system cost.

- Smaller-scale modular GTL plants should ideally be self-sustaining, able to operate unattended and use energy derived exclusively from the well. There may be opportunities for co-generation of electricity.

- Need to develop accurate testing and validation equipment and facilities to confirm and normalize the performance of future developments.

BREAKOUT GROUP 4 – Morning Session

Discussion Topics: *syngas, Fischer-Tropsch, reactor design*

Summary Points

- Autothermal catalytic partial oxidation (CPOX) reformers
  - Could produce methanol for small-scale GTL
  - Problems include oxygen costs, materials, coatings, and process integration
  - Conversion to create a compliant fuel and methanol transportation are important.

- Fischer-Tropsch and product cracking catalysts could be combined to make a low wax, high quality product (mostly light olefins)
  - Current processes produce a large quantity of methane.
  - Catalyst and separations technology improvements needed

- New materials advances are enablers for smaller, more efficient GTL processes.
  - Higher temperatures or large temperature gradient capable systems

BREAKOUT GROUP 4 – Afternoon Session

Discussion Topics: *syngas, Fischer-Tropsch, reactor design*

Summary Points

- Modular, mass-manufactured, skid-mounted CPOX and oxygen separation units could reduce plant capital cost and also overall plant size.

- Reactor improvement technologies include
  - High temperature metal reformers (>1000°C) and chemical looping
  - Integrated reforming and oxidation steps
  - High temperature metal reformers
  - Ceramic microchannel reactors
  - ITM syngas reactors

BREAKOUT GROUP 5 – Morning Session

Discussion Topics: *methanol-to-fuels, Fischer-Tropsch, reactor design*

Summary Points

- Opportunity 1: Direct Methanol and Dimethylether (DME) (non-syngas)
  - Top most promising area to investigate
  - Challenging compatibility between process and product
  - Difficult to see how new efforts will get past 40 years of technology barriers
- Opportunity 2: Heat Integrated reforming and synthesis
  - Advantage: Compact, manufacturable, simple integration, avoids air separation unit
  - Disadvantage: High maintenance
  - Challenges: Design refinements needed to meet operability, safety, and maintainability goals
- Opportunity 3: Small fixed-bed translation of complex large scale systems
  - Advantage: Heat management on a small scale
  - Disadvantage: Requires integration of several disciplines
  - Challenges: Heat management on a small scale, stable hydrodynamics on a small scale
- Opportunity 4: Plasma to syngas (low priority)
  - Advantage: High energy density
  - Disadvantage: complex system, energy-inefficient
  - Challenges: Selectivity and efficiency improvements required

BREAKOUT GROUP 5 – Afternoon Session

Discussion Topics: *methanol-to-fuels, Fischer-Tropsch, reactor design*

Summary Points

- Integrated, small scale reactors (or better to say processing) is a focus for disruption
  - Devise new manufacturing methods to scale down plant size.
  - Volume for Heat Transfer vs. Volume For Reaction
  - Mass of Structure/Production Capacity
  - Adjust catalyst for smaller scale systems
  - Create new controls and automation for the system
  - Low yield is acceptable, since feedstock is "free"

- Key metrics will wind up being:
  - $/Joule of transportable energy
  - Minimal efficient scale (inflection point of the $/Joule vs. Capacity curve)
  - Heat transfer volume/reaction volume
  - Volume specialization and heat movement
  - Structural pounds of steel required

- Disruptively attack the stranded gas situations
  - "stranded" = gas has "no" value so any transportable conversion is good if it covers module cost
  - mass produce the modules to drive down cost
  - move up market by attacking large fields with the massively parallel approach

BREAKOUT GROUP 5 – Afternoon Session

Discussion Topics: *methanol-to-fuels, Fischer-Tropsch, reactor design*

Summary Points

- **Potential Areas of White Space:**
  - complex geometry high end heat exchangers and mass transfer equipment to allow for plug flow at small scale (you could not manufacturer these things 5 years ago, could not conceive of them 15 years ago)
  - membrane reactors modules (enabled by materials science and manufacturing advances, reduce the need for water-gas-shift and lower CO2)
  - self-regulation of heat and composition (enabled by intelligent design based on computational tools)
  - advanced controls
  - minimizing / eliminating the need for balance of plant components (drawing in O2 as needed from a membrane of silicon etched, CFD designed manifold)
  - combining the natural gas processing (a box between Nat Gas and Pipeline in your schematic) with the GT"L" conversion would be huge step skip and is conceptually possible

BREAKOUT GROUP 6 – Morning Session

Discussion Topics: *Fischer-Tropsch, water separation, process design*

Summary Points

- Process integration is the most important component to making new, small GTL plants
  - Processes must be simplified (membranes that can do Fisher-Tropsch, separation and syngas all-in-one)
  - Possibility to integrate fuel cells for cogeneration into system to prevent waste
- Membrane-based water separation from product stream at 240°C is also transformative
  - Some Nafion systems exist, but are expensive and unreliable
  - Subject to fouling
- Other opportunity areas include:
  - Liquid-Liquid Mass Separation
  - Distillation, Condensation/Decantation or centrifugation
  - Absorbants (new products desired with greater selectivity, lower swing energy, more durable)
  - Mass Separating Agents (Reduce cost, make more durable, understand fouling mechanisms)

BREAKOUT GROUP 6 – Afternoon Session

Discussion Topics: *Fischer-Tropsch, water separation, process design*

Summary Points

- **Efficiencies to consider in integrated unit and model include**
  - Heat/Power/Water Integration
  - Gas Cleanup/Oxygen and Steam Production
  - Reforming
  - Synthesis
  - Separation
  - Power
  - Water Cleanup
  - Process controls for Non-Expert Operation
- Optimal metrics for a small scale reactor are highly dependent upon the gas well site
- Goal is to meet current cost of delivering crude at 1000 bbl/day
- Conversion Efficiencies at 60% or greater
- Robust, low maintenance systems will be key, and plant design hasn't been done
- **Improvements for membrane based water separation include**
  - Devise alternative to large bubble reactors
  - Remove __% of water in situ from FT process at 220C and 30 bar
  - Improve catalyst life by 20-50%

Key Workshop Take Aways

Workshop Output

Small-scale GTL plants require new performance norms to be economical

… and the path to a paradigm shift in GTL requires improvements in many systems and technologies

Desired Metrics for <1000 bbl/day GTL Unit

Metric	Target
Capital Cost per output Capacity	< 100k $/bpd
Plant Output Capacity	100-1000 bpd
Plant size per input capacity	<10 ft^3/bpd
Carbon Efficiency	>50%
Reliability	> 5000 hours

Enabling Technologies with Significant "White Space"

- Reactor design
- Multifunctional membranes
    - Oxygen separation
    - Water separation
    - On-Membrane catalysis
- High-temperature heat transfer
- Corrosion-resistant materials
- Assembly-line manufacturing
- Sensors for process control

Workshop Output

- The most white space for exploration lies in implementation of a full system. Small advances in one area could lead to huge efficiency changes in another
- Very little is known about the mechanisms of GTL conversion chemistries, and some seed money should go to develop better insight into those reactions
- Successful teams should work with the engineering services community at an early stage to ascertain the utility of their programs
- New sensors to evaluate product quality, and to increase unit automation must be developed in tandem with other new technologies

Multiple technology areas are necessary to build manufacturable and economical, small scale GTL plants. Technological solutions will require a systems approach to open this new opportunity to exploit stranded natural gas resources.