Topic 18F – Clean Coal and Carbon Management

Solar Energy Powered Materials-Based Conversion of CO_2 to Fuels

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Precision Combustion, Inc.
North Haven, CT

- Privately-held small business
  - Est. 1986; ~40 FTE employees
- Functional focus: Innovation and product development
  - Clean Energy
  - Compact, high-efficiency
- Product focus: Catalytic reactors/systems for Energy Sector
  - Novel architectures, new/improved performances
  - Enables new products and capabilities
- Collaborators include: U.S. Govt., large & small companies, universities, network
  - esp. DOD, DOE, NASA
- Bootstrapped financing – SBIRs, gov’t/industrial funding sources

44 SBIR Phase 2 wins
3 Tibbetts awards
9 SBIR success stories
2 Army SBIR Achievement awards (top 2%)

Outline

- Background
- Technical Approach and Phase I Summary
- Phase II
  - Overview and Goals
  - Partners and Focus Areas
  - Task Plan Overview

Considerations for Solar Power to Fuels and Chemicals

☀ + CO_2 → hydrocarbon fuels and/or chemicals

- Requires H_2 source

- Replaces petroleum-sourced equivalents
- Distributed, small-scale

- Desired products:
  - Gasoline
  - Jet fuel
  - Diesel fuel
  - C4+ olefins possible

- Product slate dependent on:
  - Source of hydrogen
  - Method of solar energy conversion
  - Thermodynamics / kinetics

	$\Delta H^{\circ}_{f,298K}$
H_2O(g)	-241.8 kJ/mol
CO_2	-393.5
CH_4	-74.9

C-O bond breaking requires most energy
(process controlling step)
C-H much less than H-O

Raw Materials Considerations

- Carbon dioxide:
    - From carbon capture or sequestered carbon
    - Not free, ~20-60 $/metric ton
    - Plentiful, relatively pure, relatively inexpensive

- Hydrogen:
    - From water electrolysis – low efficiency (~50 %, but getting better)
    - From methane steam reforming – energy intensive, large infrastructure, net CO_2 producer
    - Use natural/shale gas – plentiful, inexpensive, ~85% CH_4, contains usable energy

- Carbon monoxide reaction intermediate:
    - Water-gas shift (WGS) from H_2/CO_2 – hydrogen consumer
    - CO_2 electrolysis – low efficiency
    - Solid oxide electrolytic cell (SOEC) – high temperature (~750 °C), 50-60% eff. CO_2 conv.
    - Methane dry reforming – higher temperature (~850 °C), 90 % eff. CO_2/CH_4 conv.

Product Fuel/Chemicals Formation Considerations Considering Two-Step Processes Via Syngas Intermediate

Two step process from CO_2 to liquids:

1) Syngas via CH_4 reforming; or CO_2 and/or H_2O electrolysis; or combination
   - Water-gas shift may be needed to adjust H_2/CO syngas ratio
   - Without further processing, syngas will contain CO_2 & H_2O

2) Methanol, dimethyl ether – low single-pass yields, requires further processing for C-C bond formation

-or-

2) C_6-C_{20+} paraffins via Fischer-Tropsch synthesis – high yields, highly exothermic
   - Not commercially viable at very small scales
     - Address via reactor design (process intensification)
   - Negatively impacted by H_2O, CO_2 - lowers eff. from 90 to 50%
     - Address via catalyst selection

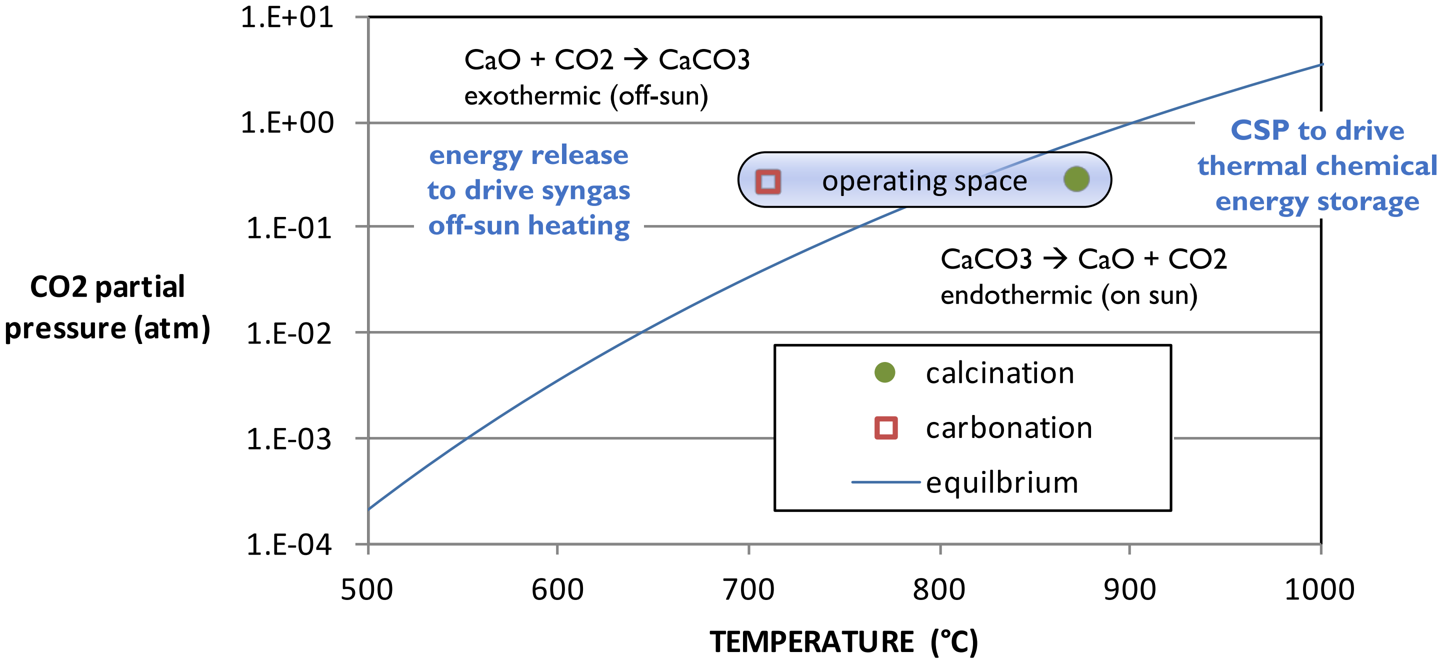
Solar Energy Considerations

- Photovoltaic – low efficiency (15%) – provides electricity only
  - can be supplemented with off-peak/excess power, wind, etc…
- Concentrating Solar Power (CSP)
  - liquid / molten salt: 300-500 °C, trough or tower
  - sCO2 solar collector: ~850-925 °C, tower / collector, ~40 % eff.

Operational Considerations:
WGS/FT – continuous, some turn down OK
CH_4/CO_2 supply – always on
Solar – discontinuous - daily / diurnal / seasonal variations

CaO-Based Energy Storage and Release

- $CaCO_3 \Leftrightarrow CaO + CO_2$ equilibrium based energy storage
- CO_2 is used in process to:
  - Drive thermal energy storage reaction cycle



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Process Considerations

Electrochemical approaches – less efficient use of sun power

H_2O electrolysis	$H_2O \rightarrow H_2$	RT	50% eff.
WGS	$H_2 + CO_2 \rightarrow H_2O + CO$	300 °C	equil.
FT	$2H_2 + CO \rightarrow$ HC's	350 °C	90% eff.

CO_2 electrolysis	$CO_2 \rightarrow CO$	RT	50% eff.
WGS	$CO + H_2O \rightarrow H_2O + CO$	300 °C	equil.
FT	$2H_2 + CO \rightarrow$ HC's	350 °C	90% eff.

also, H_2O/CO_2 co-electrolysis followed by FT

Thermochemical approach – better overall efficiency

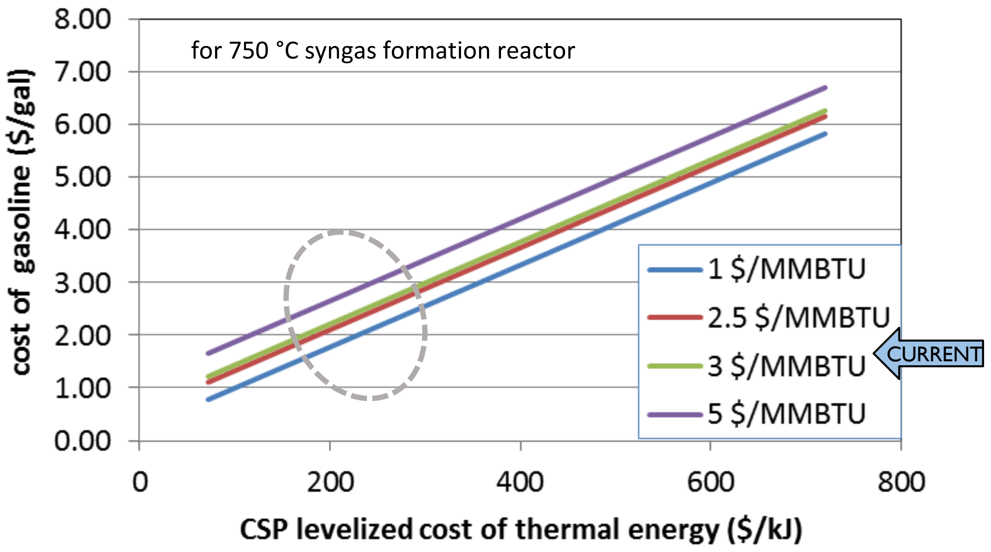
CO_2/CH_4 reforming	$CO_2 + CH_4 \rightarrow 2CO + 2H_2$	850 °C	90% eff.	(endothermic)
add water to minimize/prevent carbon deposits, adjust H_2/CO ratio				
WGS to adjust H_2/CO ratio to ~ 2:1		300 °C	equil.	(~thermoneutral)
FT		350 °C	90% eff.	(exothermic)

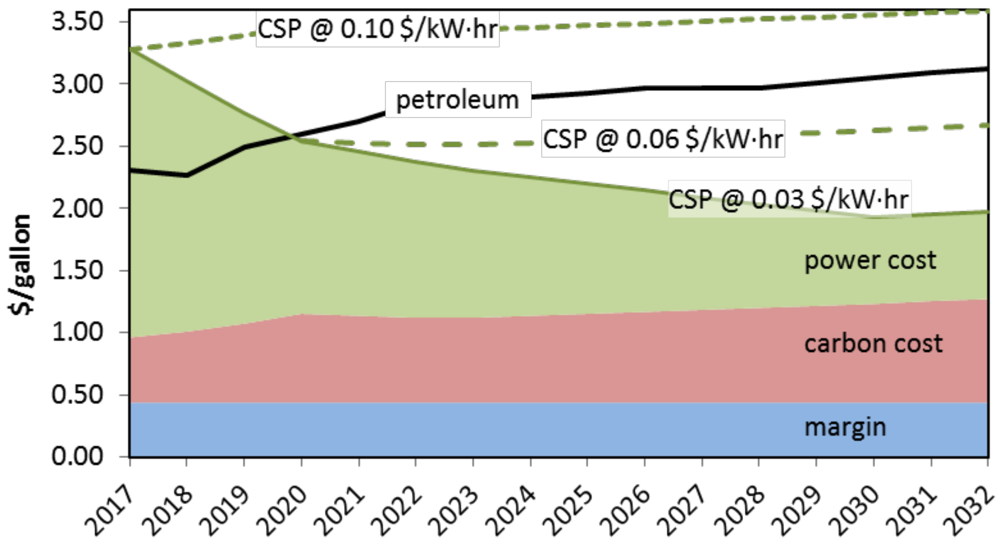
Phase I Outcomes

- Thermochemical approach to CO_2 conversion proven viable
  - CO_2/CH_4 conversion to syngas over Rh or Pt on Al_2O_3 catalyst at 99% of equilibrium
  - Clean syngas from either methane or natural gas; no evidence for carbon deposition
    - All C2+ in NG converted, not detectable (<0.0001%) rxn T > 850 °C
- Demonstrated effectiveness of $CaO/CaCO_3$ thermal energy storage material
  - Washcoated onto mesh substrate for enhanced thermal performance
    - Less than 10% loss of CO_2 capacity as compared to powder after coating
- Developed novel strategy to integrate reforming / energy storage functions
- Added development partners for Ph II
- Preliminary economics favorable

Economics - $2.50/gallon Gasoline Possible

- Assuming overall process efficiency of ~40 %
- 90% conversion of syngas to gasoline
- CSP levelized cost accounts for all cost factors
    - currently at 0.13 $/kW-hr, DOE target is 0.06 for electricity production
- Assume project life 5-20 years, equipment costs become negligible





Phase II – Overview and Goals

- Primary Goal – Demonstrate performance and economics to attract Phase III funding
- Technical Goals:
    - Improve capacity/durability of CaO storage material – charge/discharge modes
    - Optimize performance/durability of CO_2/CH_4 reforming catalyst
    - Achieve robustness to natural/shale gas variations/impurities
        - Similarly, for CO_2 impurities (depends on CO_2 source)
    - Determine on-/off-sun duty cycles
    - Integrate CSP into process
    - Economic, process, and reactor modeling to support above

Phase II Work Plan Overview

	Quarter							
Task	1	2	3	4	5	6	7	8
1 – Catalyst/material optimization	🟥	🟥	M1					
2 – Durability testing			🟥	M2	🟥			
3 – Process modeling	🟥	🟥	M3					
4 – Simulated on-/off-sun cyclic durability testing					🟥	🟥	M4	🟥
5 – System modeling and cost analysis				🟥	🟥	🟥	🟥	M5
6 – Reporting								

M1: Select catalyst/material compositions that meet performance metrics of activity and CO_2 capacity.

M2: Demonstrate catalyst durability via maintenance of performance metrics.

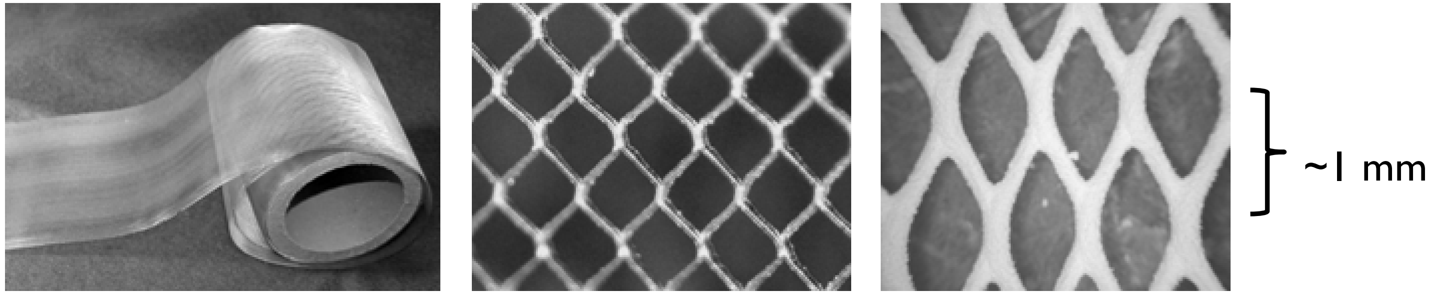
M3: Develop a process model that accurately predicts experimental measurements and design parameters.

M4: Demonstrate little to no loss of catalyst activity and CO_2 capacity as a result of pilot-scale simulated on-/off-sun cycle testing.

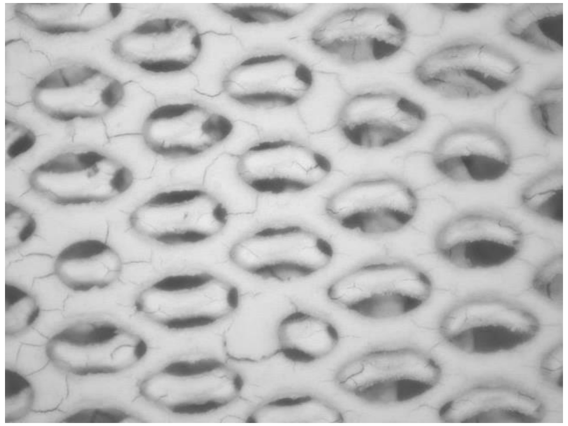
M5: Model performance of a full-scale plant the can product gasoline at or below 3.00 $/gallon

Advantages of Microlith® Mesh Substrate

- As compared to packed/pellet beds or honeycomb / microchannel / metallic substrates
  - 2-10x increased rates of heat/mass transfer and reactions
  - Due to boundary layer disruptions and enhanced mixing

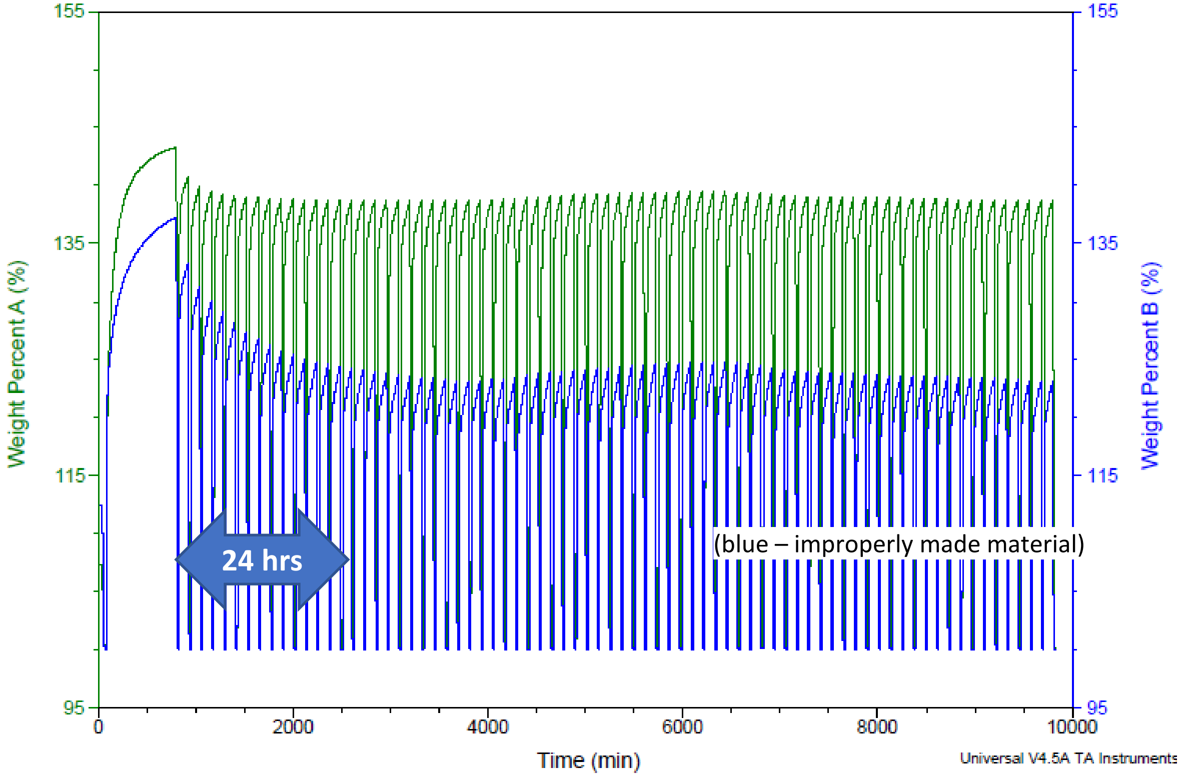


CaO-based material after 4 carbonation cycles



CO_2 Sorbent Improvements

- Optimize CaO content, binder content
- Rapid screening via fully-automated TGA
  - TGA has multi-gas capability, can introduce CO_2 impurities (S, tar, etc.)
  - Rapidly determines performance and durability



(blue – improperly made material)

CO2/CH4 Reforming Catalyst Improvements

- Select Pt or Rh
- Durability against natural gas composition variations / sulfur content
- Durability against duty cycle – need 1000’s of ‘warm’ starts
  - TGA can help, reactor testing best
    - Installing rapid catalyst screening test unit
- Measure kinetics and deactivation rates – predict lifetime durability

$$k = k_0 e^{-E_A/RT}$$

$$k = (\mathrm{SV})\ln(1 - \mathrm{X}_{\mathrm{CH}_4})$$

Task 1 Metrics

- Adhesion to Microlith mesh: no more than 1 wt. % loss as measured using our standard adhesion testing
  - Supplement with vibration testing (NASA requirement)
- CO_2 capacity, measured after ~100 cycles, of at least 0.3 g CO_2/g material, with a stretch goal of 0.35 g/g.
- 95% of activity for reforming of CO_2 and CH_4, at 900 °C, as compared to PCI's standard, after 20-40 hours short term durability testing.

Task 2 – Reactor Performance Studies

- Use optimized catalyst and sorbent from Task 1
    - Introduce CH_4 and CO_2 feed impurities
- 100-500 hours durability
    - Retain 0.27-0.32 g/g CO_2 capacity and 86% of reforming activity

Task 3 – System Optimization

- Simulate CSP
    - Address BOP for solar field
- Define on-/off-sun solar cycles for a variety of scenarios
    - Provide input into process model and bench-scale testing
- Select commercial CSP tech. for our application
    - Define P, T, flow rate, energy rates for input into process and cost models
- Specify aspect of CSP operation
    - Heat exchangers, recycle, thermal integration
    - Site-specific issues and prepare for Phase III field pilot

- Metric : Realistic process model that accurately predicts experimental measurements

Task 3A – Demonstrate FT Upgrading

- Determine inlet composition to FT reactor, based on Task 2 (later, 4 and 5)
- Initially, use modified Co-based catalyst
- 300-500 psi, 250-350 °C, gas and liquid GC analysis
- Fit results to Anderson-Schultz-Flory (ASF) carbon number distribution in order to determine chain-growth mechanism and deviations from non-ideal behavior
    - deviations will indicate greater extents of intra-pore mass transfer resistance
    - enable catalyst parameter optimization for ideal chain length
        - process parameters – T, P, SV, heat transfer, etc.

- Metric – Demonstrate feasibility, >50% yield of gasoline range hydrocarbons

Task 4 – Subscale Simulated Solar Cycle Testing

- Develop data for Phase III field trial
- Simulated heated CO_2/CH_4 feeds and flow fluctuations
  - Alternate with simulated syngas feed for validation of reheat performance
- Planning 20-40 cycles for each solar cycle defined

- Metric - Demonstrate little to no loss of catalyst activity and CO_2 capacity as a result of pilot-scale simulated duty cycle testing

Task 5 – Process Optimization and Economics

- Preparation for Phase III on-sun field trial
  - BOP requirements; flow rates; equipment sizes; etc.
  - Mass/energy balances
  - Inputs from Tasks 2, 3 and 4 for performance and durability
  - Cost models
- Metric - Model performance of a full-scale plant the can produce gasoline at/below 3.00 $/gallon

Task 6 - Reporting

- Annual, Final Reports as per contract
- Conferences, etc.

Solar CO2 Conversion Markets

- Strong Carbon Capture pull for technology
- The primary market need being addressed is the excess CO_2 currently being collected and stored that could be put to productive use in conversion to fuels.
- The global concentrated solar power (CSP) market will rapidly grow and reach US$8,675 million by the end of 2020 (19.4% CAGR between 2014 and 2020)
- Target Markets and Customers
    - CCS – global USD 4.25 Billion in 2016, and is projected to grow at a CAGR of 13.6% from 2016 to 2021
    - Cement – global 2.55 billion tons in 2006 to 3.7-4.4 billion tons by 2050
    - Syngas – in US, 20 MW in 2020, growing at a CAGR of over 5%

Thank you!