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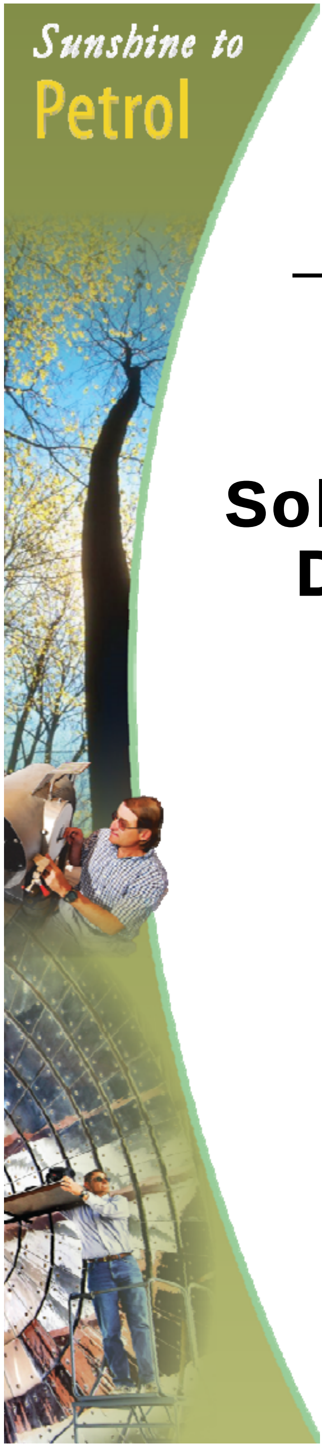

Sunshine to Petrol:
Solar Thermochemical Conversion of Carbon Dioxide and Water to Hydrocarbon Fuels

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Up to date as of February 2012
Generic viewgraph set to present to visitors

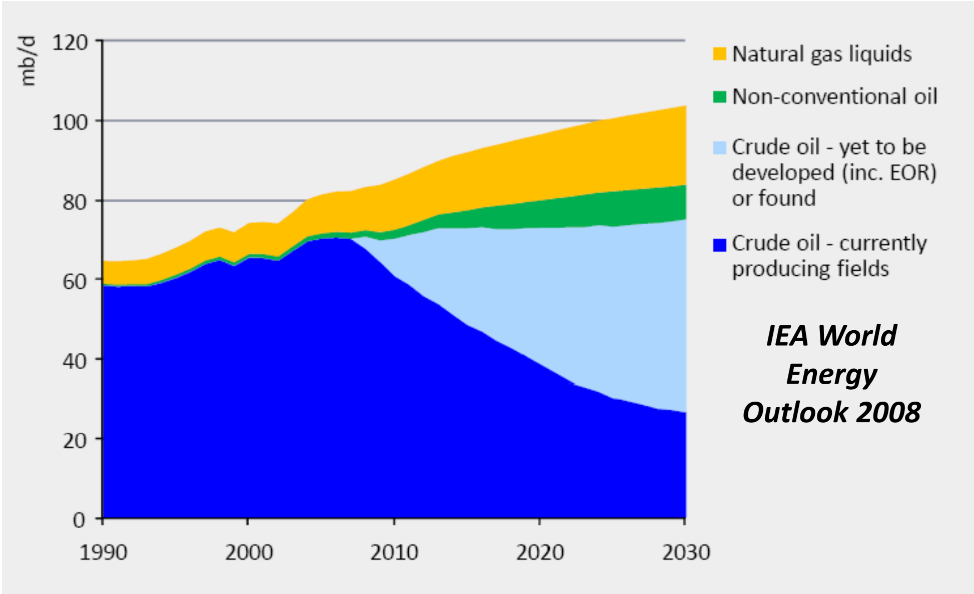
Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Sunshine to Petrol

Motivation: Assure Energy Security. Mitigate Climate Change Risk.

- *Energy consumption will continue to grow with development gains and population growth.*
- *Fossil fuels dominate energy picture and drive GHG emissions from energy sector.*
- *U.S. deeply dependent on foreign supplies of petroleum in the transportation sector.*
- *Energy and climate security are now a clear global priority.*

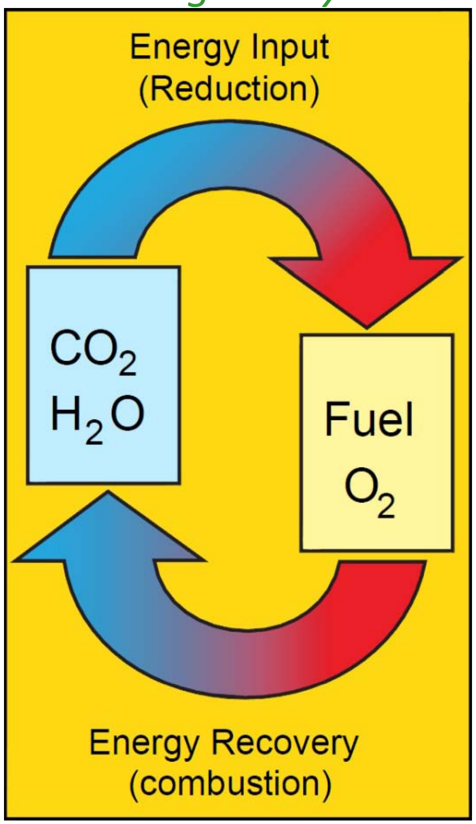
64 mb/d of gross capacity needs to be installed between 2007 & 2030 – six times the current capacity of Saudi Arabia – to meet demand growth & offset decline



Significant resources will be expended even if we only act to maintain the petroleum economy.

Sunshine to Petrol

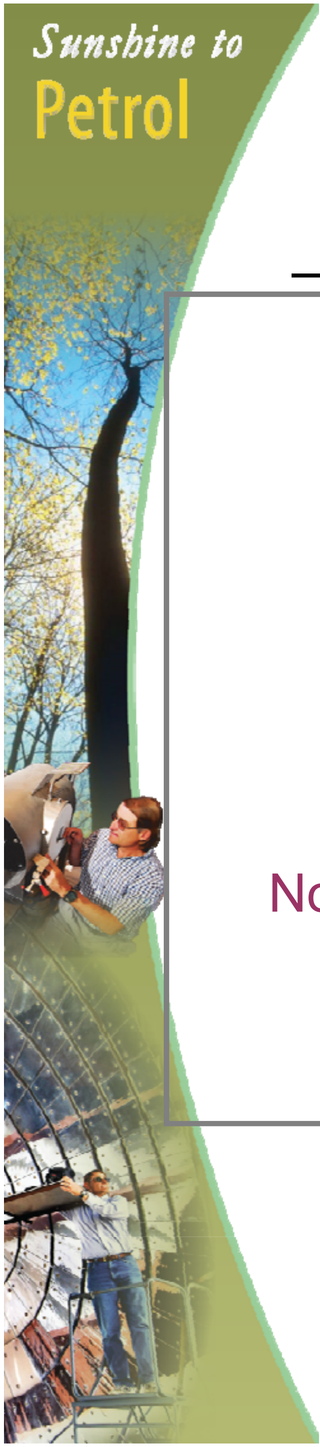
Closing the Cycle



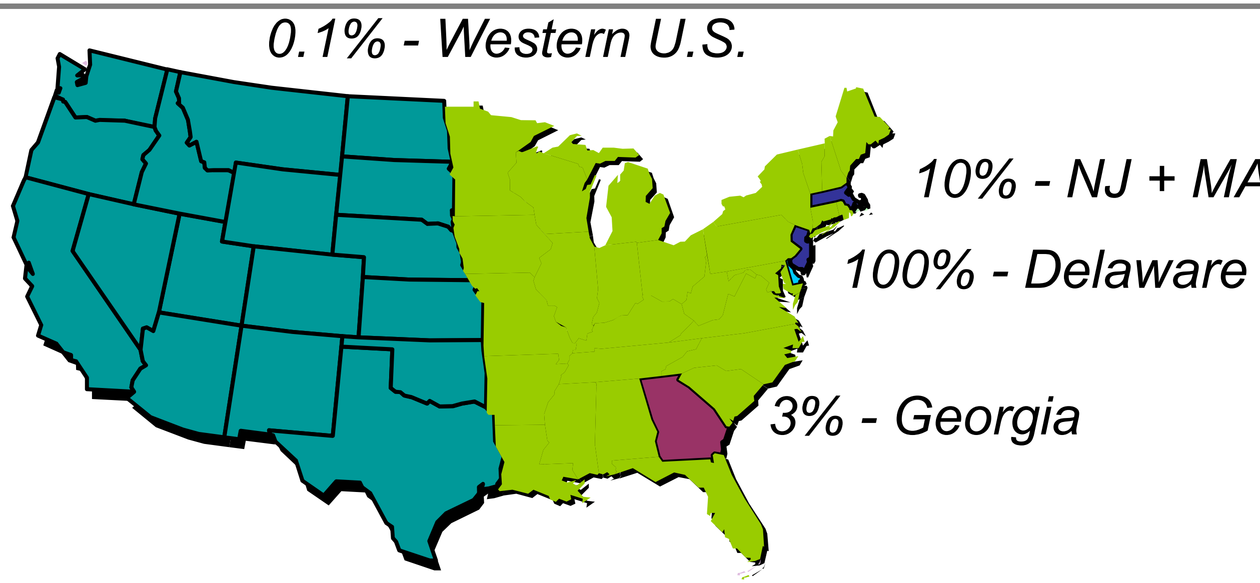
For now and for transportation fuels, liquid hydrocarbons are the "Gold Standard"

Vision: Directly apply a solar thermal energy source to effectively reverse combustion and "energize" CO_2 and H_2O into hydrocarbon form in a process analogous to, but more efficient than, the one that produces bio- and fossil fuels, therefore ***achieving many of the benefits of hydrogen while preserving the advantages of the Hydrocarbon Economy.***

$$\text{Sunlight} + CO_2 + H_2O \rightarrow \text{Fuel} + O_2$$



Can we make an impact?
Energy Efficiency (sunlight to fuel)



Nominal Equivalent Land Area Required to Produce 20 mbpd at a given efficiency.

Sunlight to fuel efficiency assuming solar resource equivalent to Albuquerque – 2600 kWh/m^2/yr.
U.S. Petroleum consumption - 20 million bbls/day

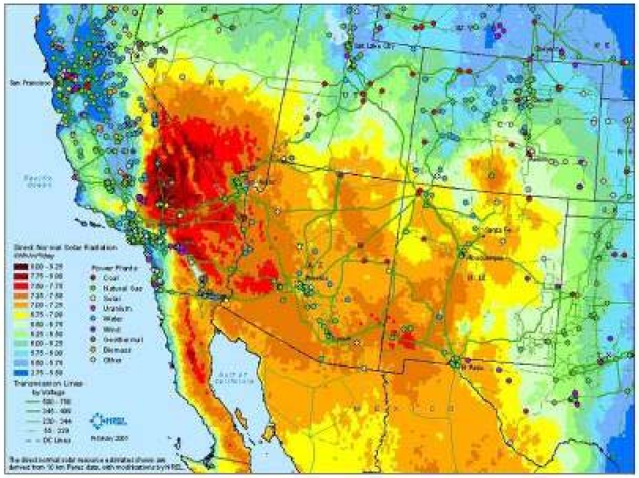
Fossil oil ~ 2x10^{-4}

Bioethanol routes currently < 1%

Photosynthesis < 6% (Theoretical)

Photosynthesis < 0.5% (actual, large area crops)

The Actual Resource.



Filters applied (Resource analysis by NREL): Over-filtered

- Sites > 6.75 kwh/m^2/day
- Exclude environmentally sensitive lands, major urban areas, etc.
- Remove land with slope > 1%.
- Assume 25% packing density
- Only contiguous areas > 10 km^2 (675 MW$_{primary}$) 10 km^2 = 10^7 m^2 = 3.86 mi^2

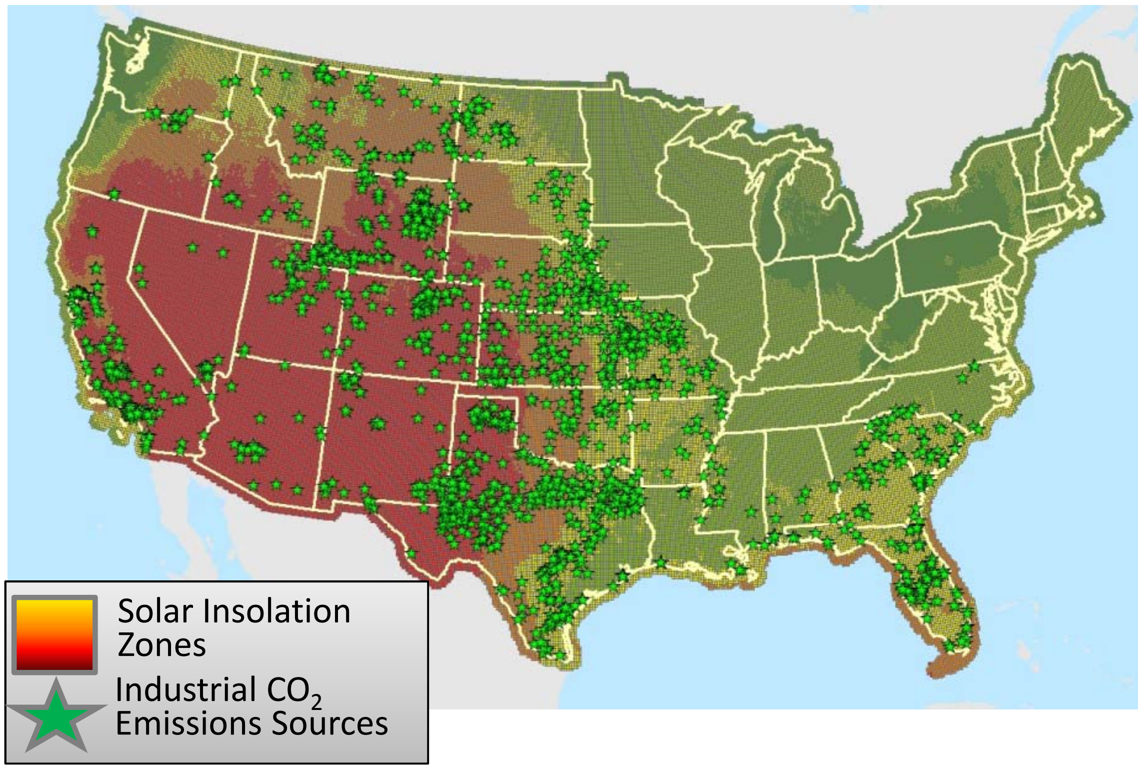
- U.S. Petroleum Demand is 20.7 mb/d (2007)
- **12.5%** lifecycle efficiency could produce 16.6 mb/d (**80%** of total U.S. demand)
- NM alone could produce **23%** of U.S. demand
- **12.5%** of available land (17.4 × 10^9 m^2) could provide **10%** of U.S. demand

State	Land Area (10^9 m^2)	Solar Capacity (TW)	Fuel Capacity (GW)	(mb/d)
AZ	49.9	3.37	421	5.9
CA	17.7	1.20	150	2.1
CO	5.5	0.37	46	0.7
NV	14.5	0.98	122	1.7
NM	39.3	2.65	331	4.7
TX	3.0	0.20	25	0.4
UT	9.2	0.62	78	1.1
Total	139.2	9.39	1,174	16.6

139 billion m^2 is 1.5% of total U.S. land

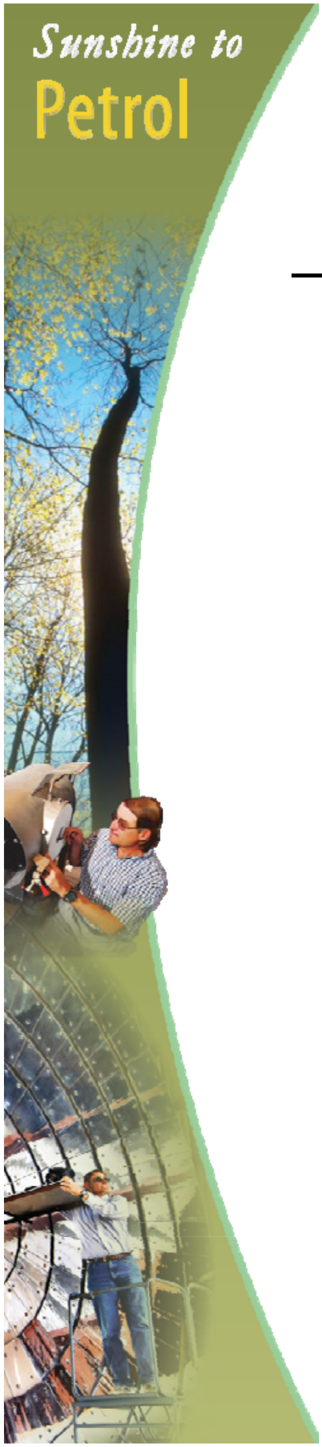
Sunshine to Petrol

Large CO_2 Sources Available

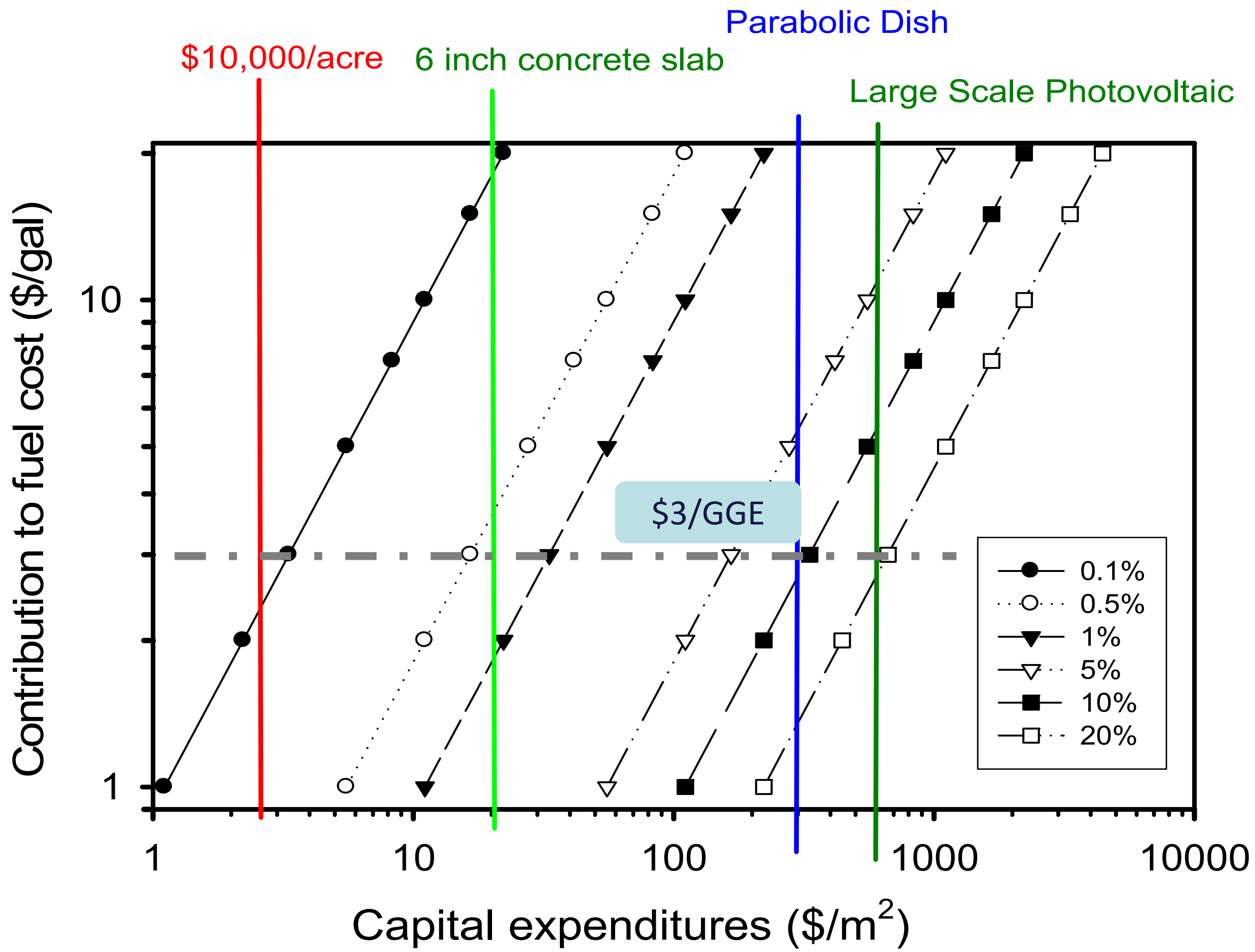


- Hundreds of large industrial CO_2 emissions sources exist in the United States in areas of high solar insolation.
  - 4-Corners Power Plant: 15.6 Mt/y and San Juan 13.4 Mt/y
  - At 81% utilization these two plants can supply fuel plants up to 9.8 GW (139 kb/d)
  - ~**25 plants** of comparable size to 4-Corners could supply US CO_2 for **10%** of U.S. demand.

Substantial resources can be tapped.
Infrastructure exists for CO_2 transport.



Can We Afford it? Efficiency → Cost



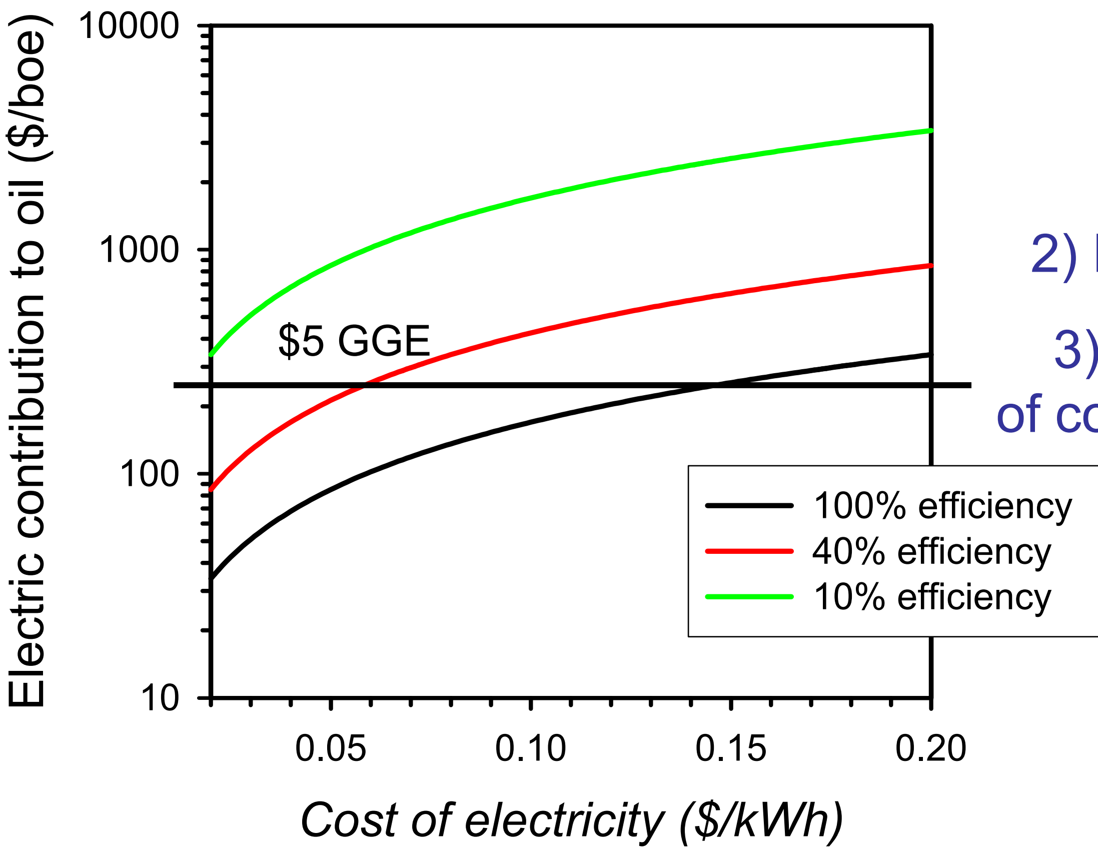
Assumptions: GGE = 36 kWh, Solar Resource = 2600 kWh/m²/yr, Favorable Financing (5% interest, 30 years)

Sunshine to Petrol

Renewable Electric to Hydrocarbon as the Baseline

Electrical to Fuel $\geq$ 40%

H_2 + utilities to MeOH ≈ 50%



Insights on how might we better this?

1) Economics of Thermal vs. electric

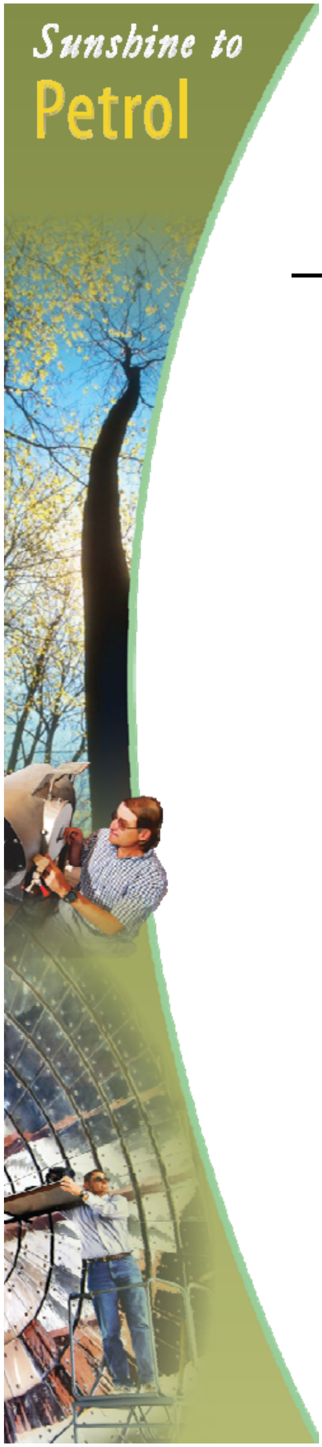
2) Efficiency of solar thermal

3) Avoid the efficiency loss of converting primary to electric

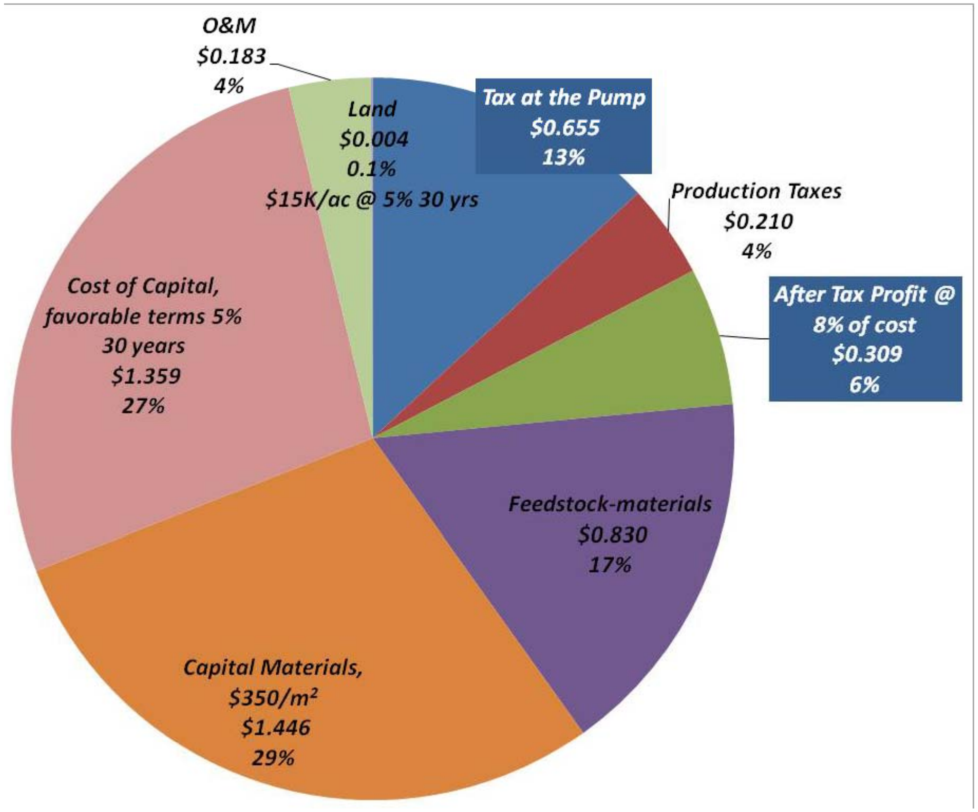
Divide by 46.4 to get $/gge

(1) Mignard and Pritchard Trans IChemE, Part A, September 2006.

(2) Henao, Maravelias, Miller and Kemp, presented @ FOCAPD 2009.



20% Solar to CO/H_2
\$5/GGE; S2P 12.5% LCE



- **Costs for S2P are in the ballpark of viability**
- **Learning curve will reduce the most expensive contributions**
- **Very sensitive to the cost of capital recovery**

How? Direct Chemical Routes.

Capitalize on decades of Synfuel technology, e.g.

$$nCO + (2n+1)H_2 \rightarrow C_nH_{2n+2} + nH_2O$$

Focus on the following critical conversions:

$$4H_2O + \text{energy} \rightarrow 4H_2 + 2O_2 \text{ (water splitting)}$$

$$2CO_2 + \text{energy} \rightarrow 2CO + O_2 \text{ (carbon dioxide splitting)}$$

$$2CO_2 + 4H_2O + \text{energy} \rightarrow 2CO + 4H_2 + 3O_2$$

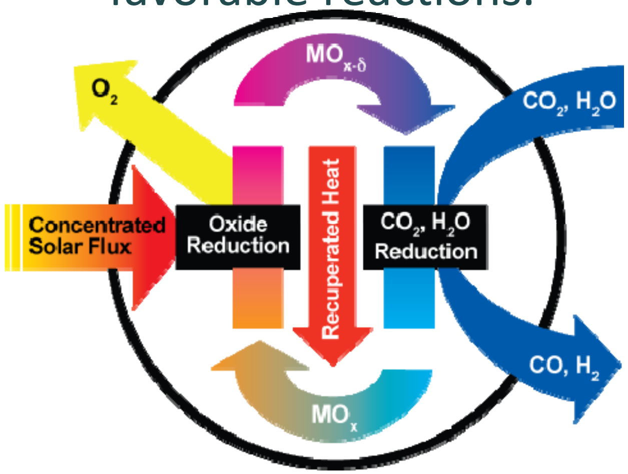
Although WS and CDS are linked by the Water Gas Shift reaction

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

Models suggest highest efficiency when splitting both

Direct Utilization of Thermal Energy

Unfavorable reaction
(e.g. $H_2O \rightarrow H_2 + ½ O_2$, or
$CO_2 \rightarrow CO + ½ O_2$)
divided into two or more
favorable reactions.



Without Recuperation
max efficiency = 36%

With Recuperation
max efficiency = 76%

A thermochemical cycle is essentially a heat engine that converts heat into work in the form of stored chemical energy.

In our case, the "working fluid" is a metal oxide (Ce- or Fe-based.)

High end temperatures of ~1300°C couple best with CSP.

Efficiency gains are possible as conversion to mechanical work and electricity are avoided.

Thermodynamics requires reactions be carried out at two temperatures.

Efficiency: Solar to Thermal

Sunlight

Resource eff.=(Resource>300 DNI)/Resource= **95%** for Daggett

Operational ~ 94%

Equip. Availability = 97%, B&S = 98%, Wind Outage = 99%

Optical ~ 79%

Reflectivity = 93%(two reflections), Dirt = 95%, Window = 95%, Tracking = 99%, Intercept = 95%

Receiver ~ 82%

Radiation = 82%

Conduction/Convection = 0 %

Solar to Available Heat = 58%

Reactor/Thermochemical ~ 35%

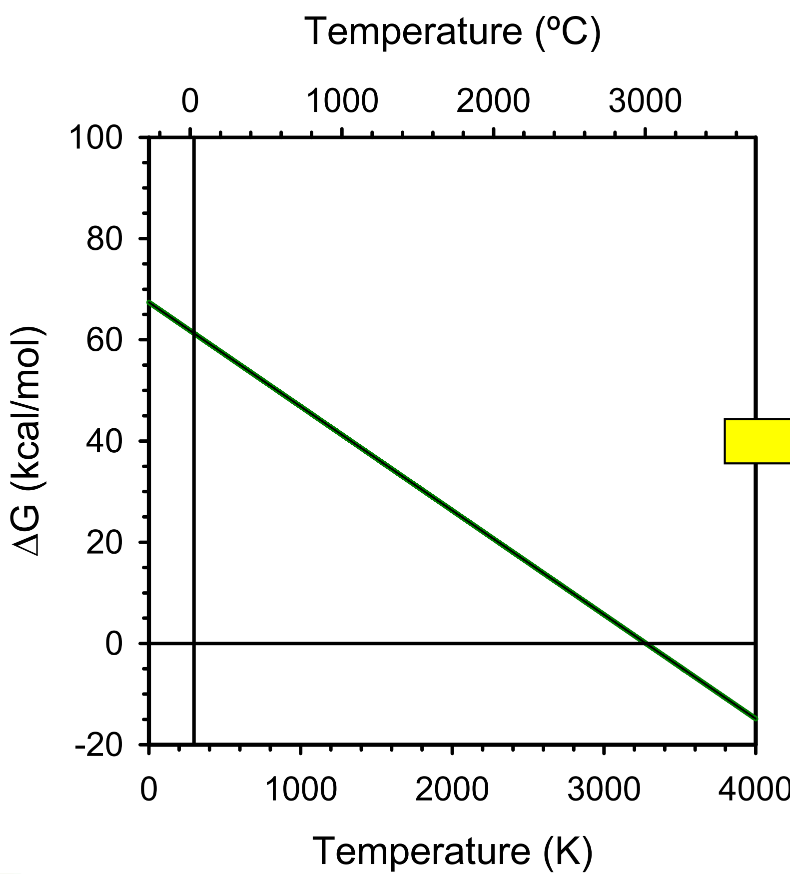
CO or H_2

Annual Average

Solar to H_2/CO

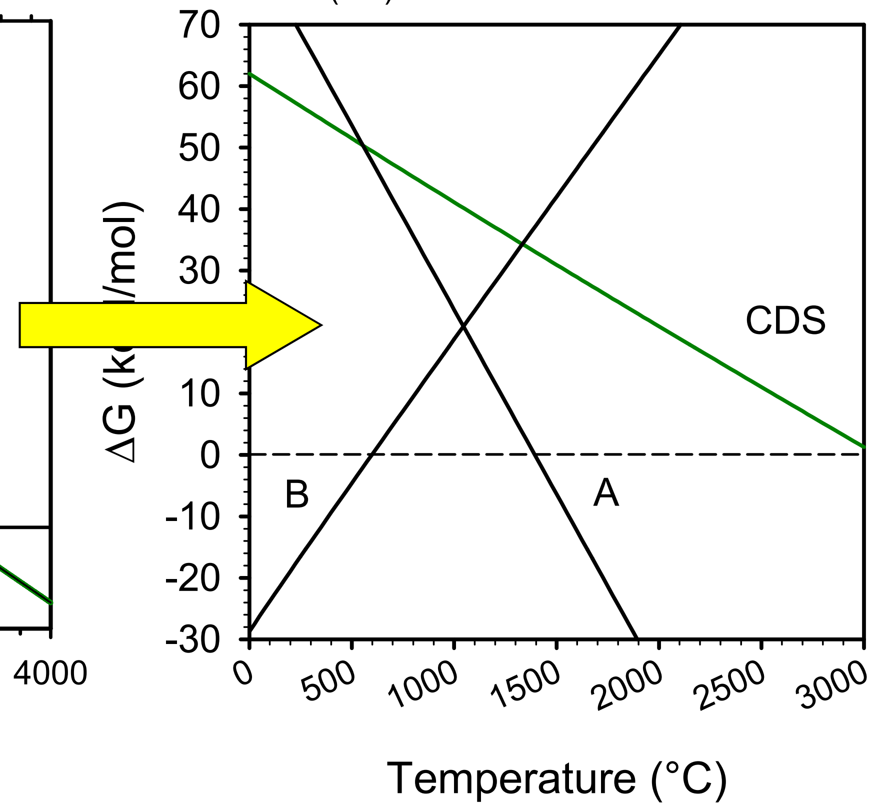
Design Point: 20%

Thermodynamics – Operating Temperatures



$AO_x \rightarrow AO_{(x-1)} + \frac{1}{2}O_2$

$AO_{(x-1)} + CO_2 \rightarrow AO_x + CO$



Assumptions: ΔH, $\Delta S \neq f(T)$, P=1 atm

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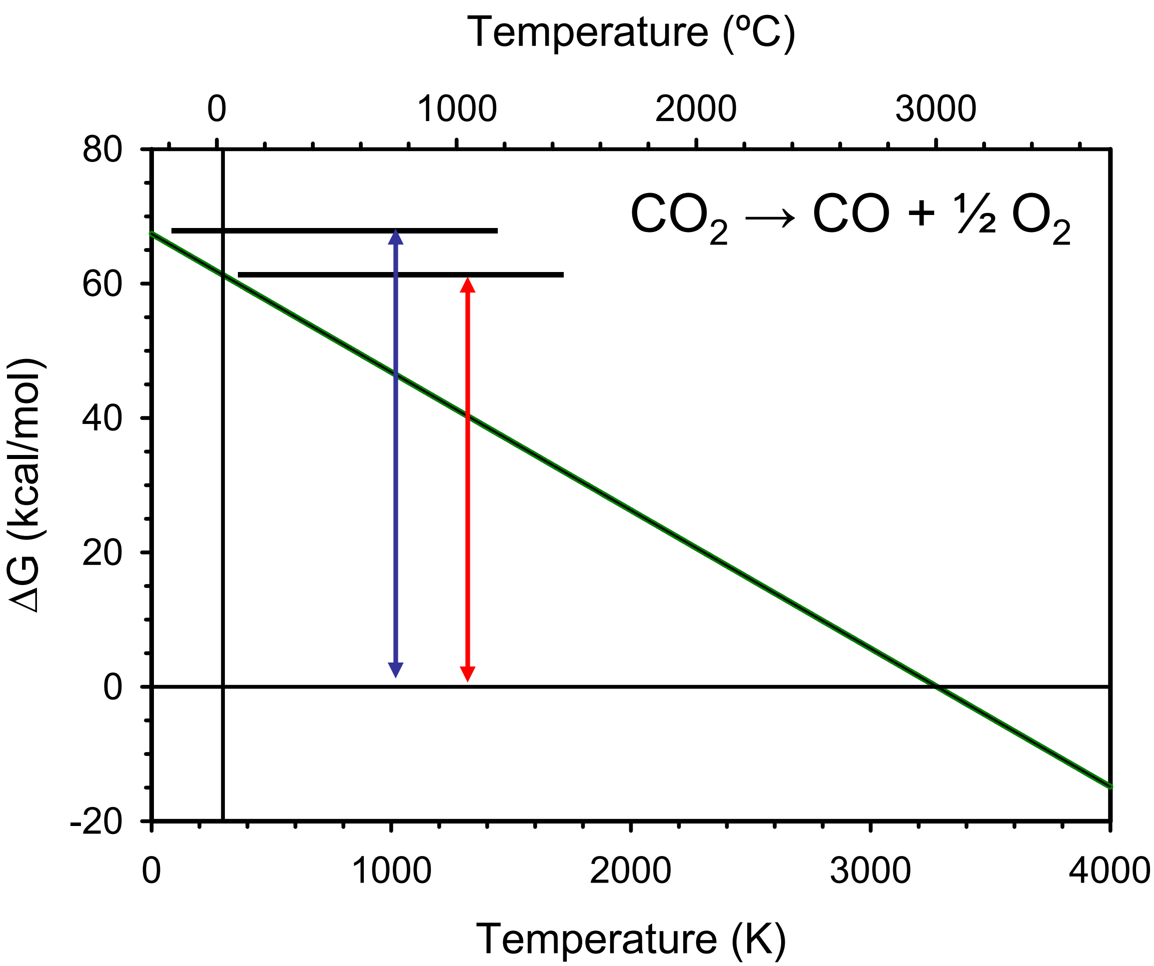
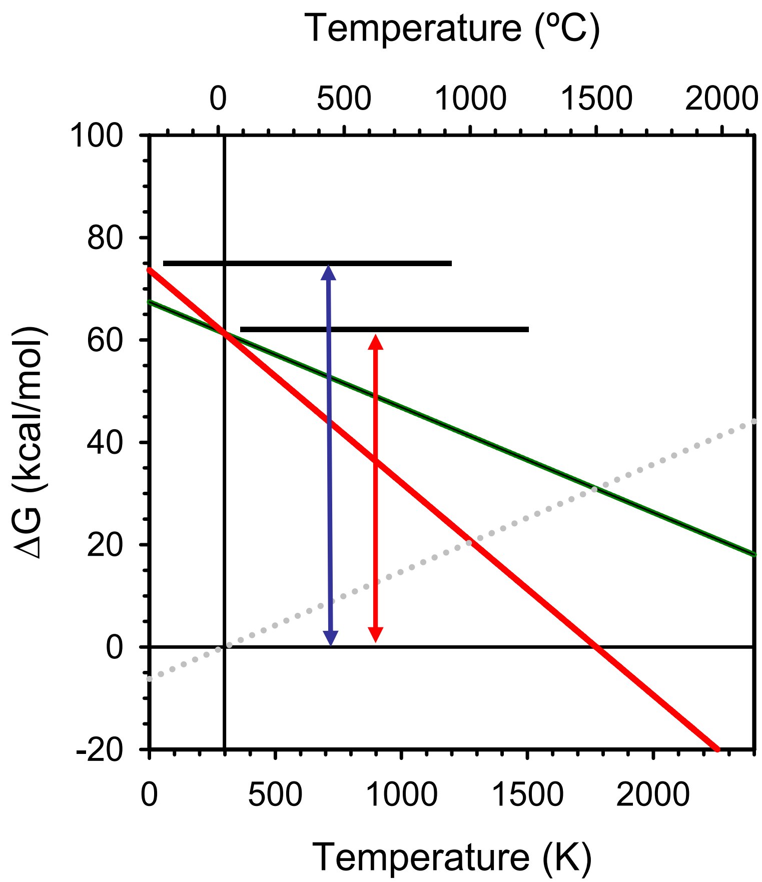
Efficiency Consideration

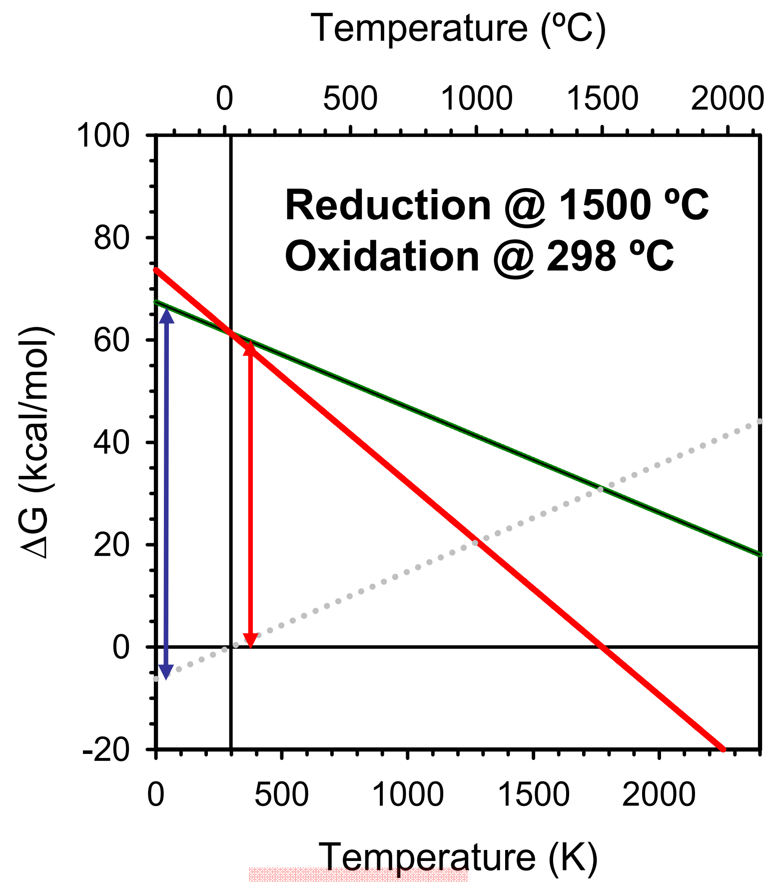


$$\eta = \frac{\Delta G_{CDS}^{298}}{\Delta H} = 0.91$$

Cycle Efficiency 1: Exotherm



$$\eta = \frac{\Delta G_{CDS}^{298}}{\Delta H_{MOx\ Reduction}} = 0.83$$



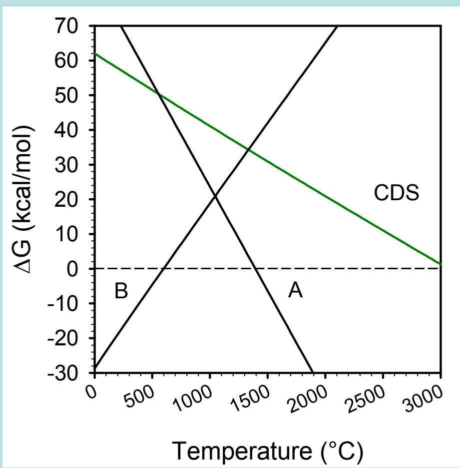
$$\eta = \frac{\Delta G_{CDS}^{298}}{\Delta H_{CDS} - \Delta H_{MOx\ Oxidation}} = 0.83$$

Efficiency 2: Utilization

Extent of reaction

$$1/\delta\ MO_x \rightarrow 1/\delta\ MO_{x-\delta} + \tfrac{1}{2}\ O_2$$

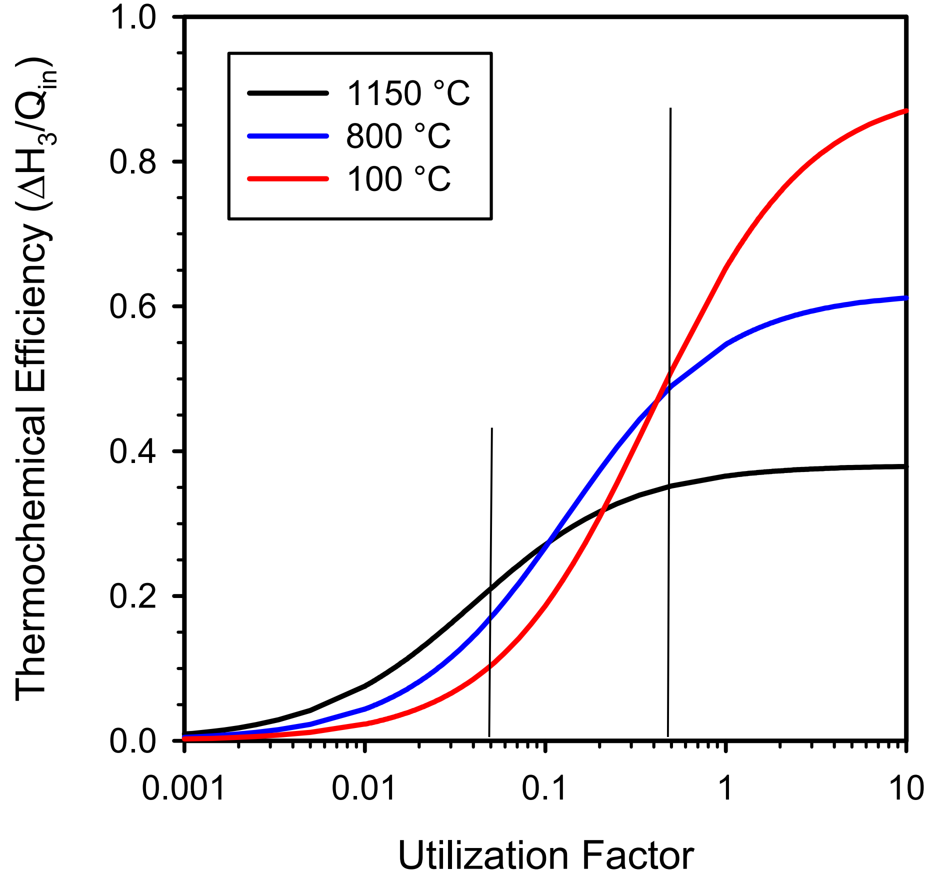
Recuperation



$$\chi = \frac{\delta}{1-eff}$$

$CO:CO_2 = 1:3$

T_{high} = 1500 °C, T_{low} as given



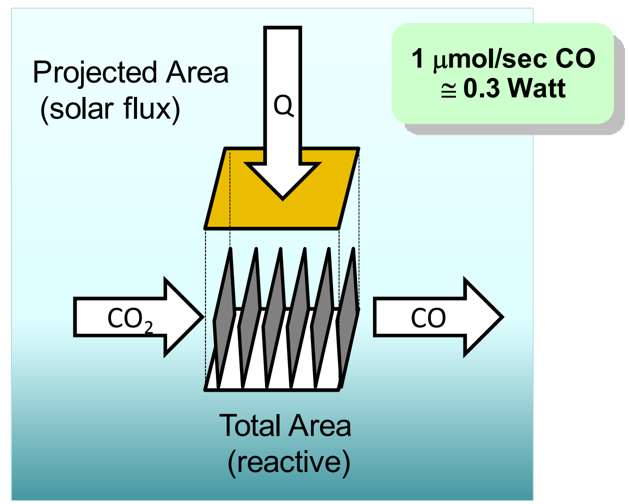
Efficiency 3: Kinetics

$$\eta = \frac{Chemical\ Energy\ Out}{Solar\ Energy\ In} = \frac{\int_0^t \left(CO\ Flux \times HHV \right) dt}{\int_0^t Solar\ Flux\ dt}$$

$$CO\ Flux = 2\ O_2\ Flux$$

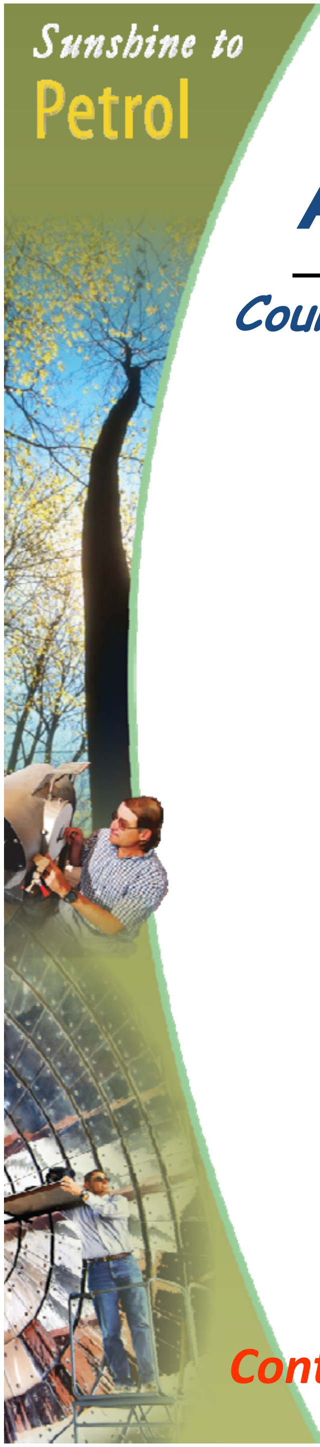
In order to achieve high efficiency the energy fluxes (solar and chemical) must match.

I.e. Reaction rates must be matched to the solar flux.



To the extent that the rates and flux do not match, heat is rejected.

Suitability of Current materials subject to surface area.



The CR5 is an Enabling Approach to Thermochemistry

Counter-Rotating-Ring Receiver/Reactor/Recuperator (CR5)

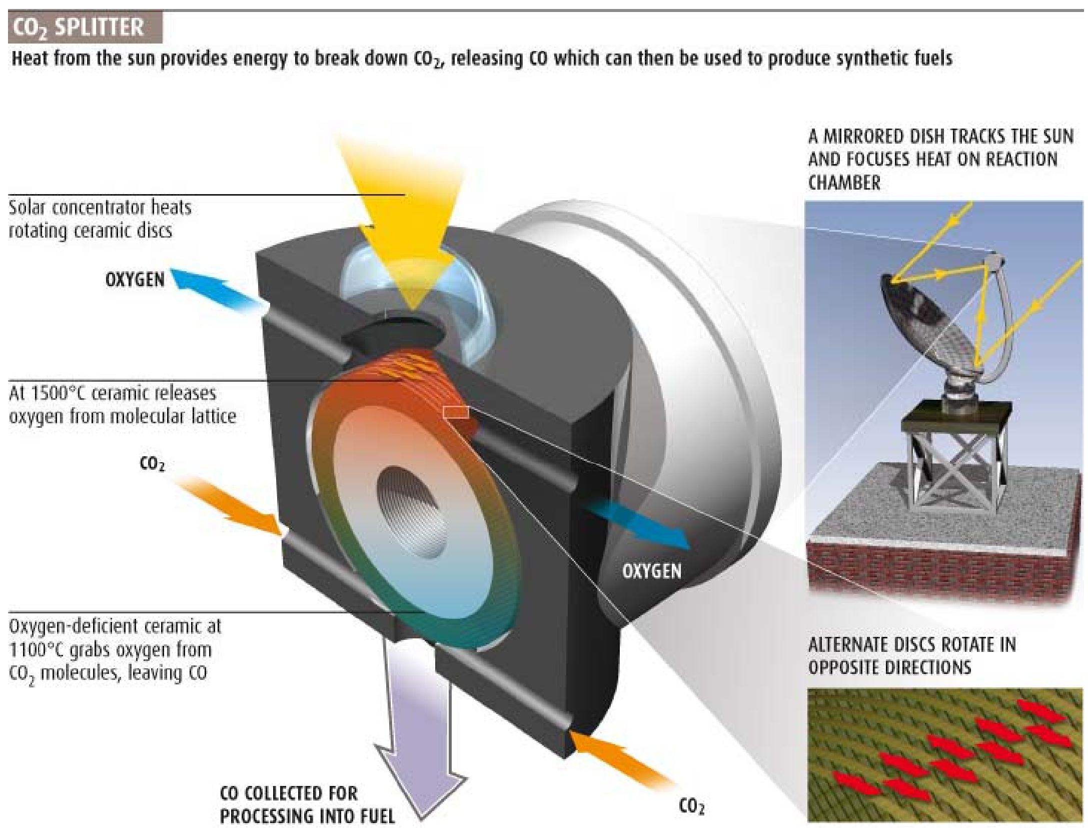
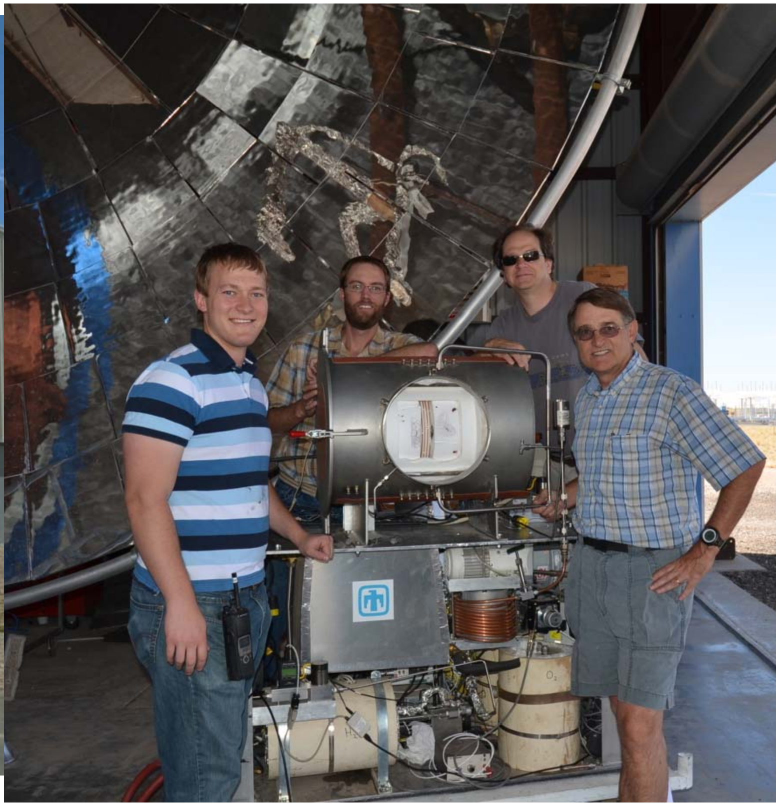


Figure Credit: Popular Science

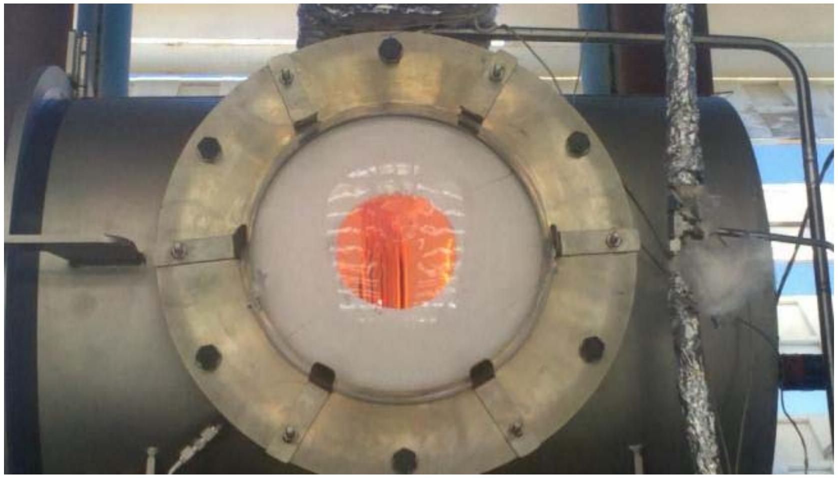
"Reactorizing a Countercurrent Recuperator"

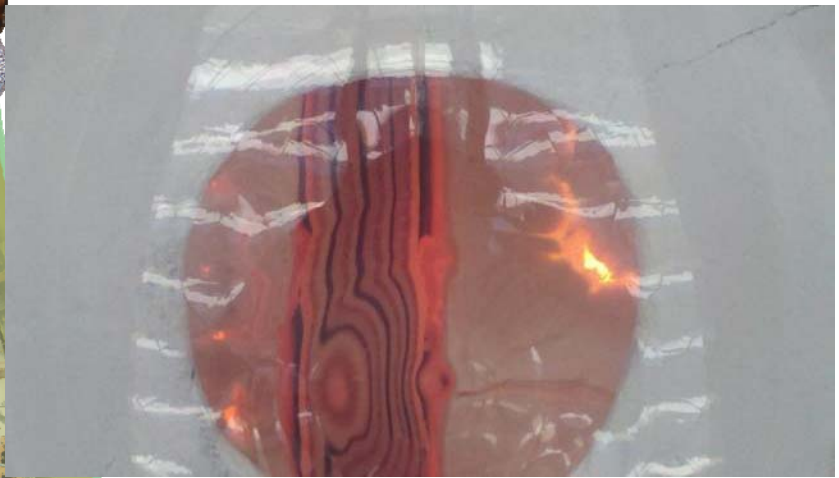
Continuous flow, Spatial separation of products, Thermal recuperation



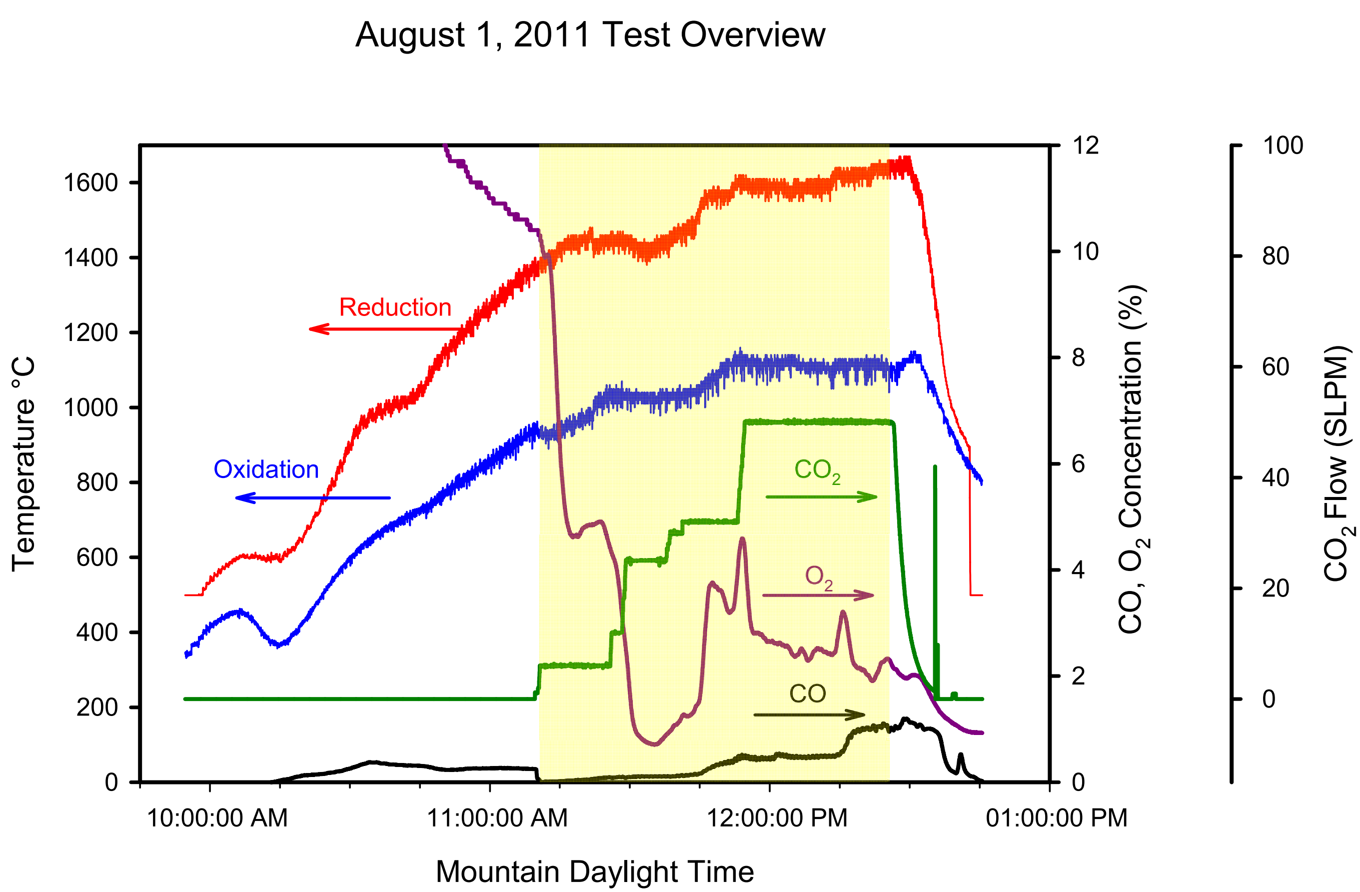
Operating with 22 Rings

Post Test Photos



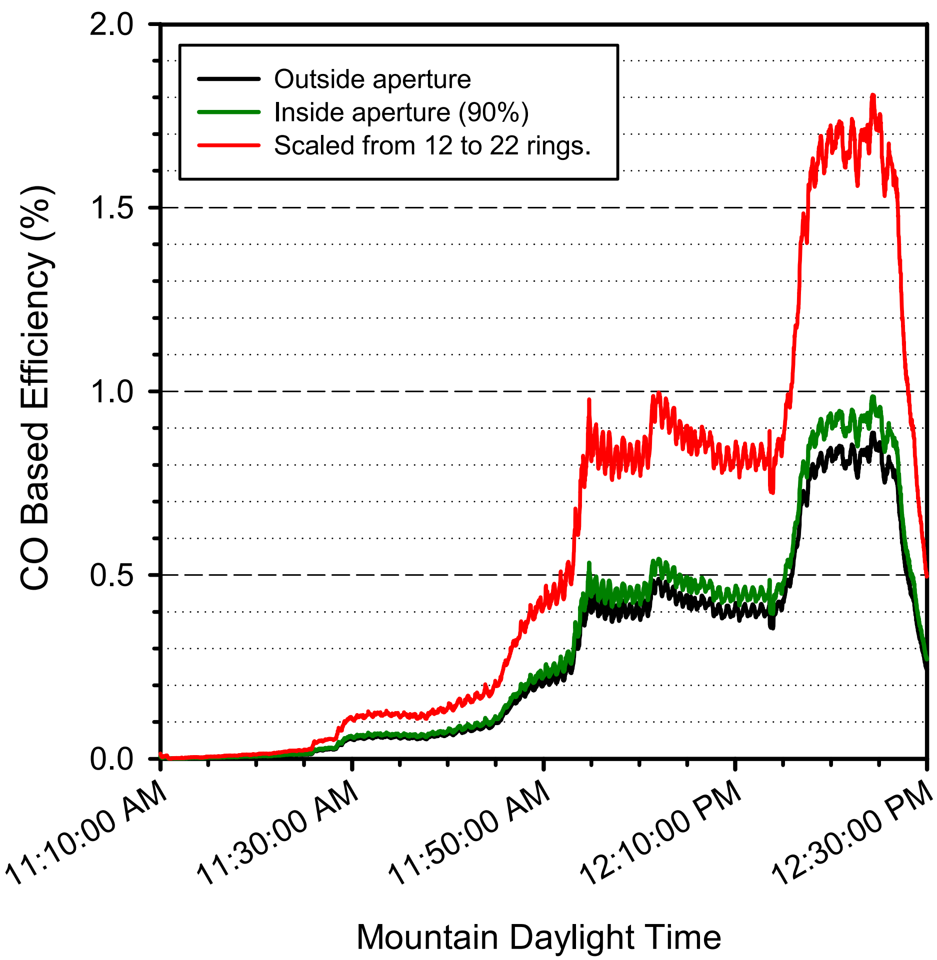


Successful 12 Ring Test



Test stopped when CO_2 supply was exhausted.

Approaching 2% Efficiency

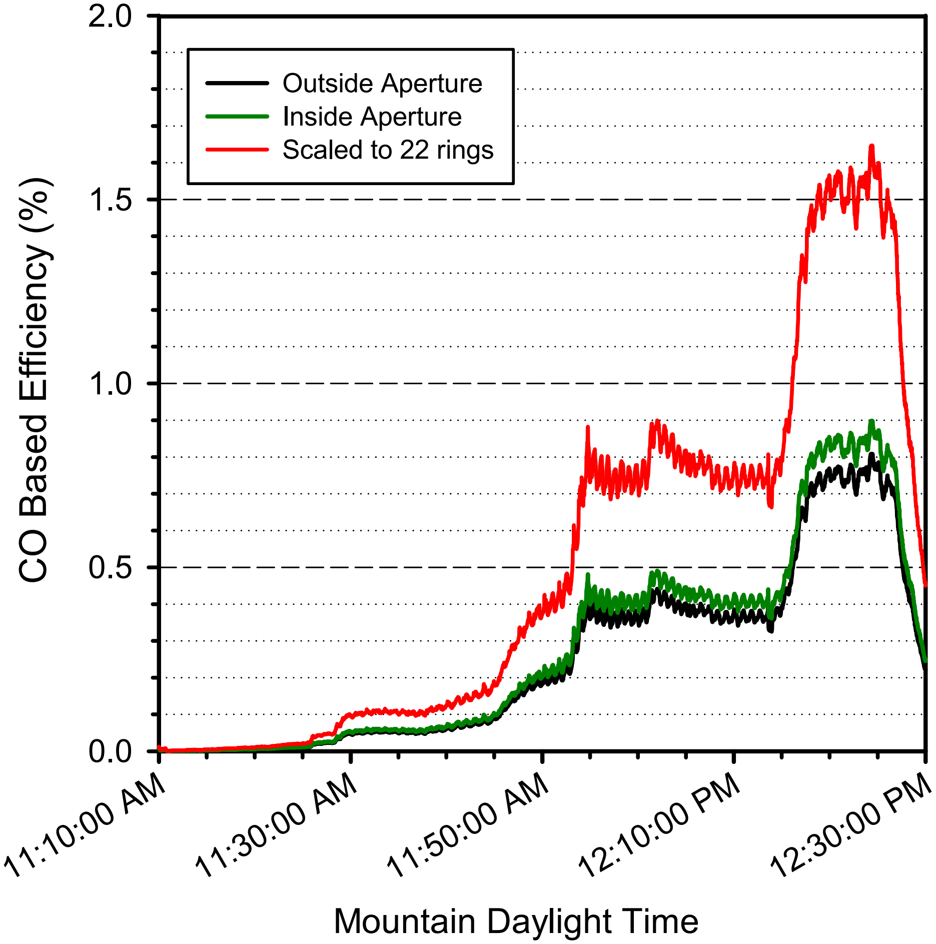


$$Eff = \frac{0.21\,(\text{W/sccm CO}) \times \text{CO flow}}{Q_{solar}}$$

$$Eff = \frac{0.21\,(\text{W/sccm CO}) \times \text{CO flow}}{0.90 \times Q_{solar}}$$

$$Eff = \left(\frac{0.21\,(\text{W/sccm CO}) \times \text{CO flow}}{0.90 \times Q_{solar}}\right) \times \frac{22}{12}$$

Accounting for Ar and Pumps



$$Eff = \frac{0.21(\text{W/sccm CO}) \times \text{CO flow}}{Q_{solar} + (20(\text{kJ/mol}) \times \text{Ar flow}) + (0.5\,\text{kW}/.4)}$$

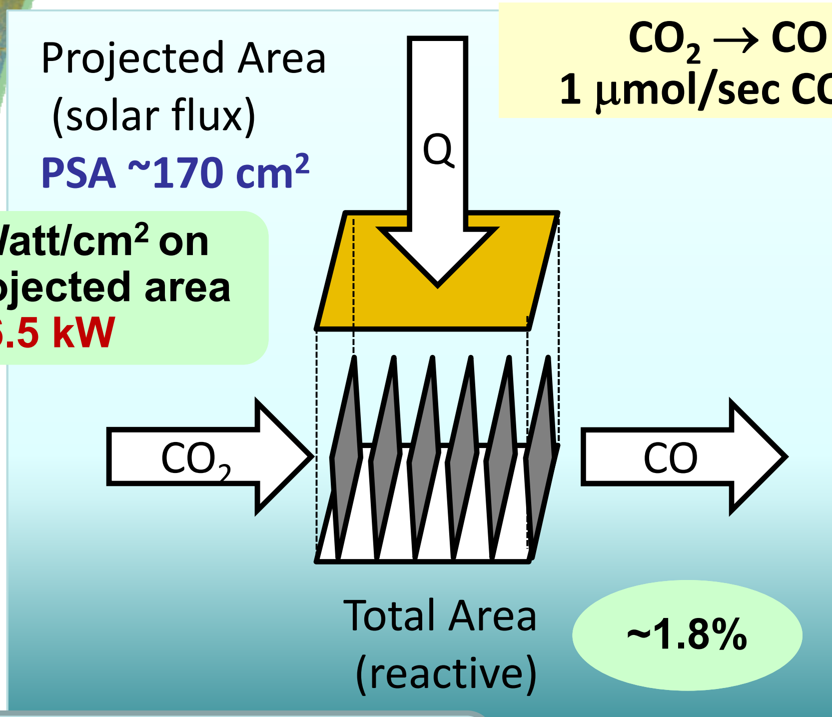
$$Eff = \frac{0.21(\text{W/sccm CO}) \times \text{CO flow}}{0.9 \times (Q_{solar} + (20(\text{kJ/mol}) \times \text{Ar flow}) + (0.5\,\text{kW}/.4))}$$

$$Eff = \left(\frac{0.21(\text{W/sccm CO}) \times \text{CO flow}}{0.9 \times (Q_{solar} + (20(\text{kJ/mol}) \times \text{Ar flow}) + (0.5\,\text{kW}/.4))}\right) \times \frac{22}{12}$$

Efficiency limited by δ (≈ 0.001) and kinetics

Sunshine Petrol

Larger geometric and active surface areas should lead to improvements.

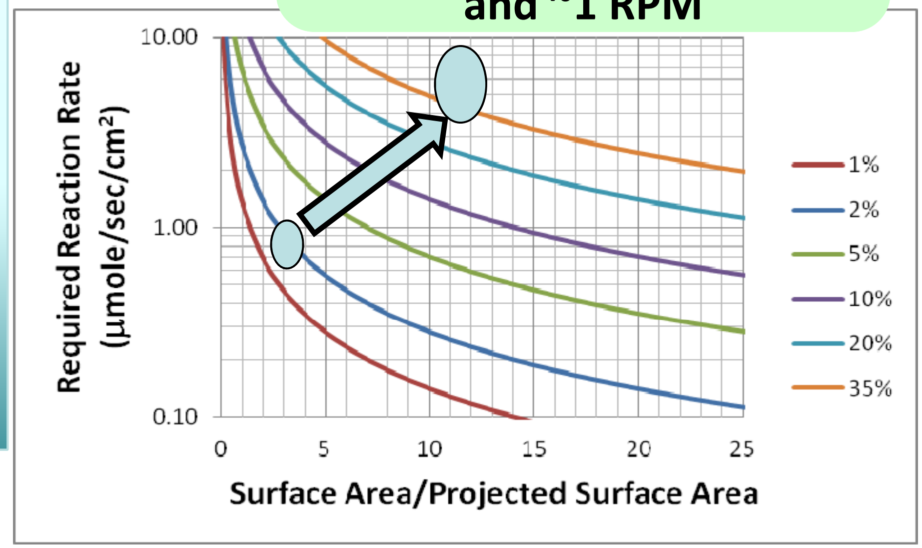


$CO_2 \rightarrow CO + ½\ O_2$
1 μmol/sec CO ≅ 0.27 W

~38 Watt/cm² on the projected area
6.5 kW

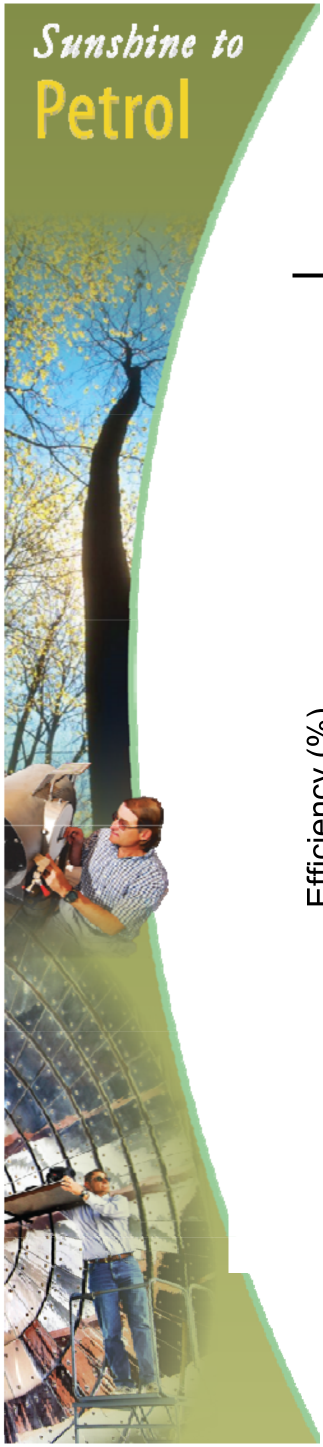
SA/PSA ≈ 3;
0.86 μmol/sec/cm²
<1% CO/cerium metal sites

Achieved 430 μmol/sec CO
≡ 116 Watt
~470 g ceria & SA~500 cm²
and ~1 RPM



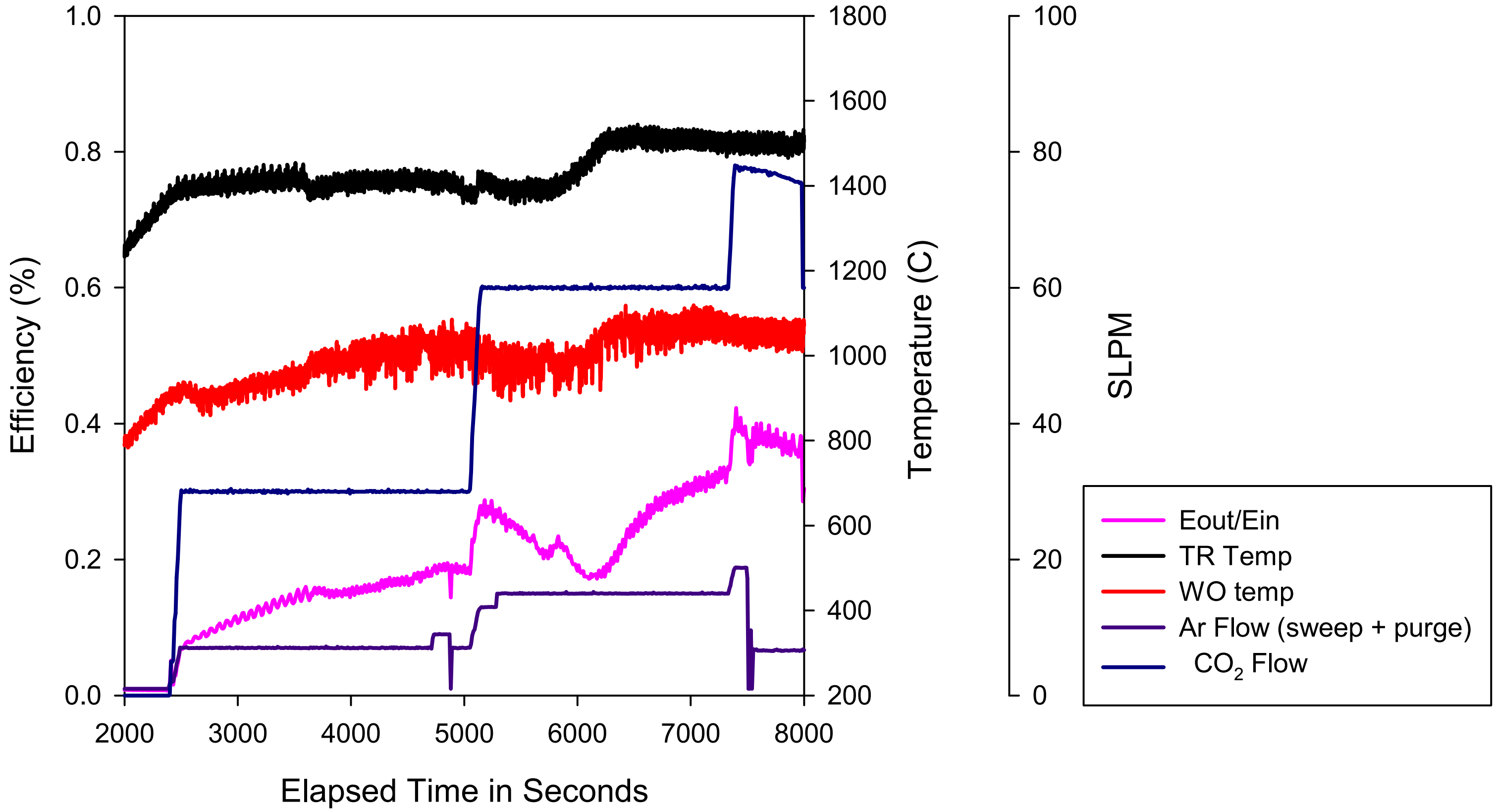
To Improve Efficiency

- Improve Kinetics per unit exposed surface area
- Structuring materials, Increase Surface Area (Assuming Rates ∝ Surface Area)
- Increase active (reducible metal) Loading (may have broader effects).
- Improved thermodynamics compositions – modification & discovery



Kinetics and Efficiency

11/30/2011
22 rings



Key Reactor Attributes For GEN2

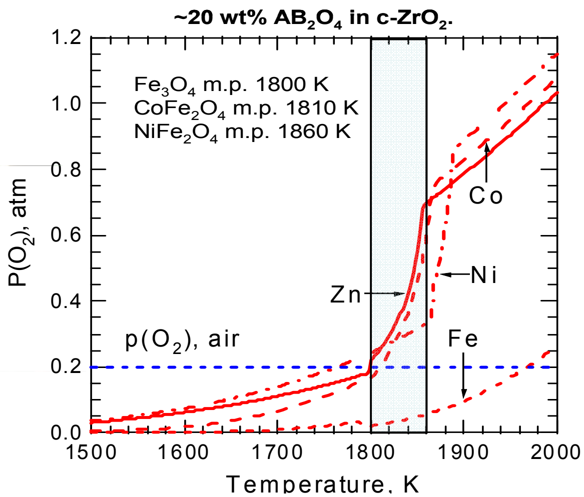
- Continuous operation on-sun
- Sensible energy recovery (recuperation)
- Direct solar absorption
- Inherent reaction product separation
- Chemical and mechanical durability
- Minimal work input
- Decouple Oxidation and Reduction pressures/rates

Ferrites as an Example

Idealized Chemistry

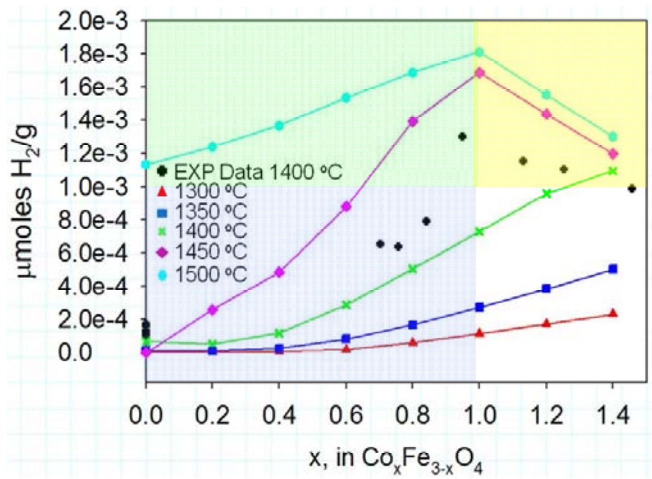
$Fe_3O_4 \rightarrow 3FeO + ½\ O_2$

$3FeO + H_2O \rightarrow Fe_3O_4 + H_2$



Favorable temperature range (thermodynamics) can be manipulated via metal substitutions in Fe_3O_4. Useful, e.g., to shift operating temperatures below the melting point.

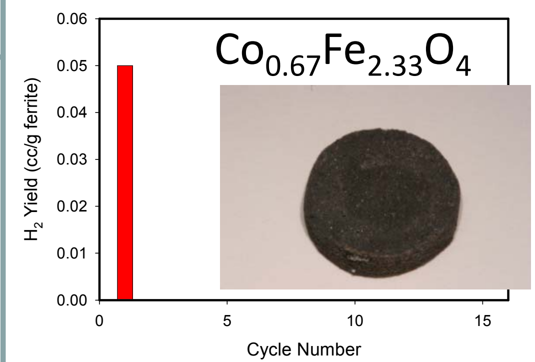
The effect of composition on gas yields can be predicted.



Modified Idealized Chemistry

$A_xFe_{2-x}O_4 \rightarrow 3A_{x/3}Fe_{(2-x)/3}O + ½\ O_2$

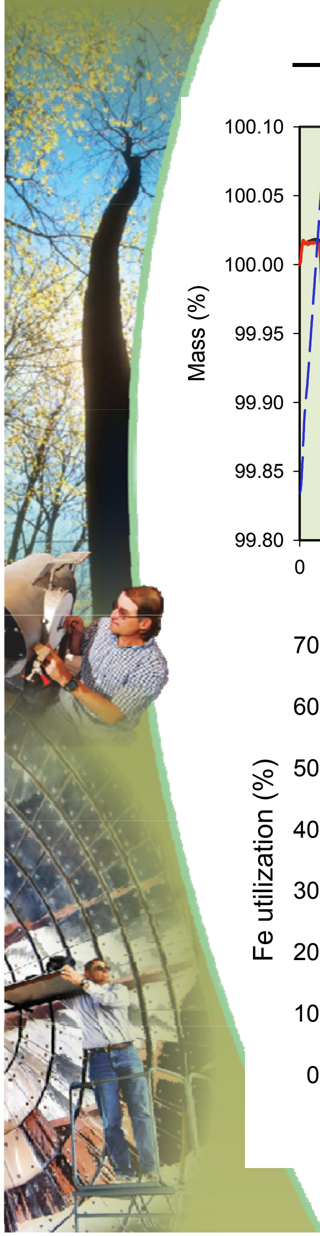
$3A_{x/3}Fe_{(2-x)/3}O + H_2O \rightarrow A_xFe_{2-x}O_4 + H_2$

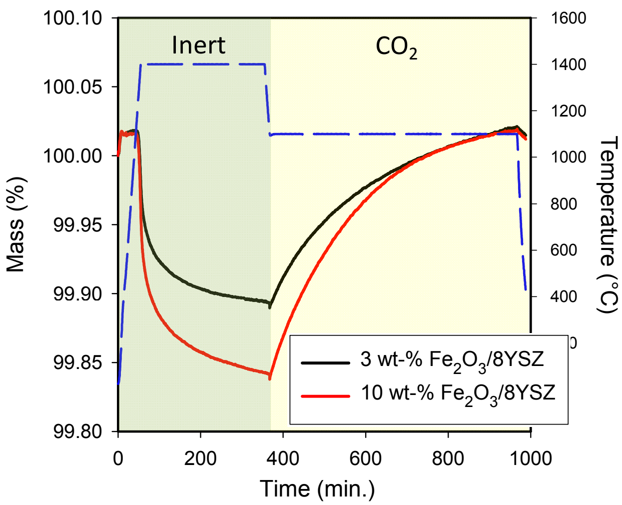


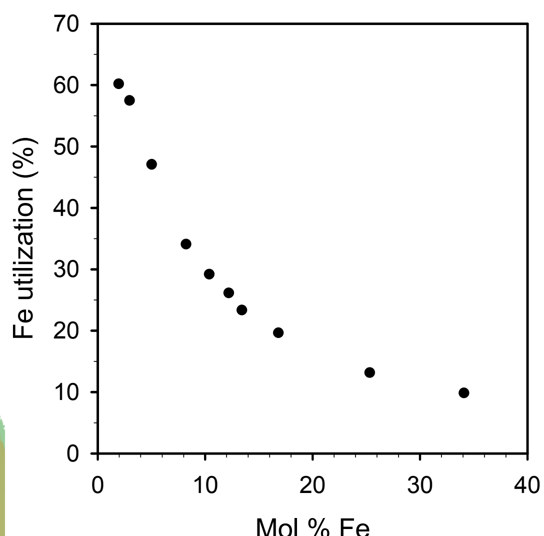
"Bulk" materials do not live up to their potential.

Sunshine to Petrol

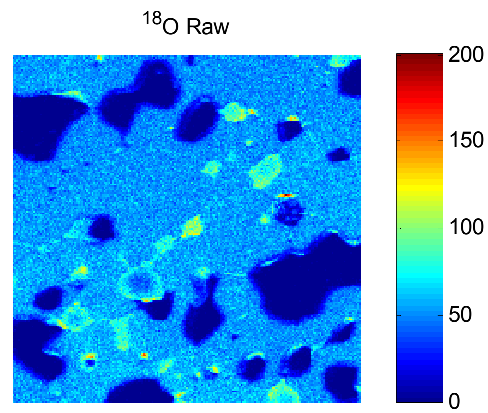
Monolithic Composites with YSZ are Cyclable – Why?

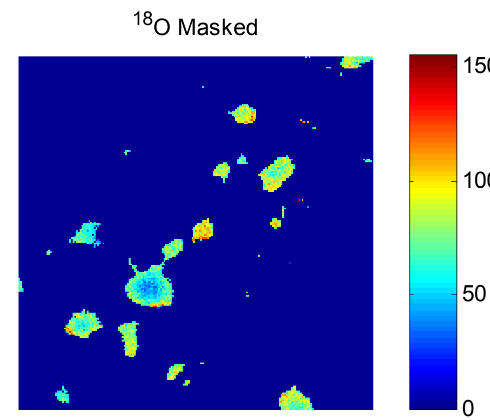




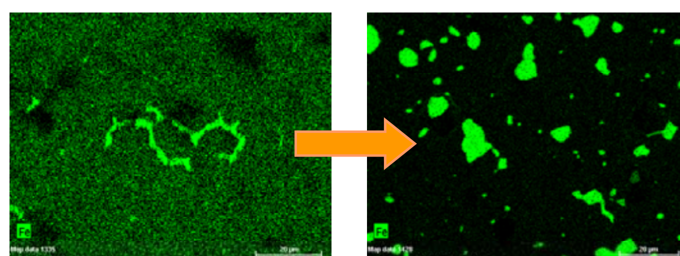


Beyond the solubility limit additional Fe contributes little to the overall gas yield.





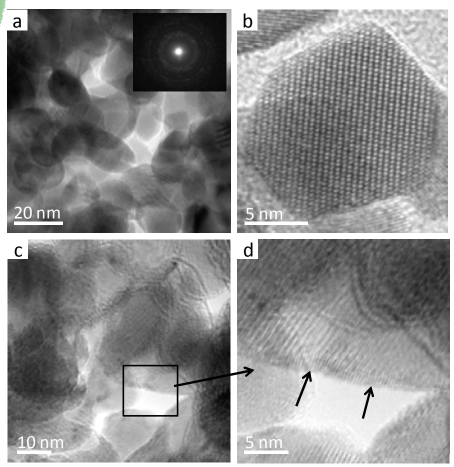
Reaction with ^{18}O-labelled CO_2 confirms limited utilization of bulk particles relative to Fe/YSZ.

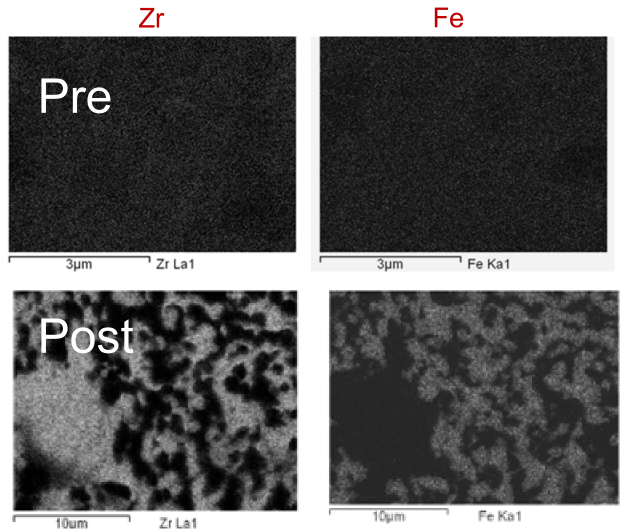


Fe EDS

Structured Ferrites?

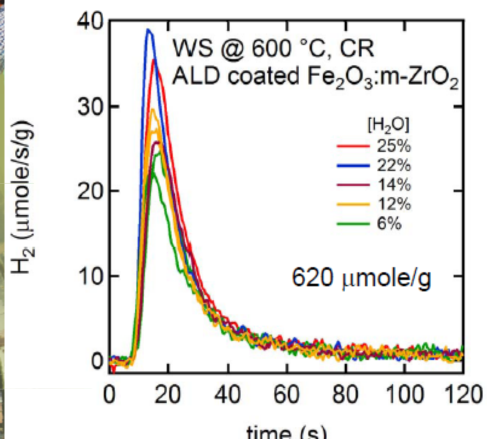
2 nm $CoFe_2O_4$ film after ALD synthesis



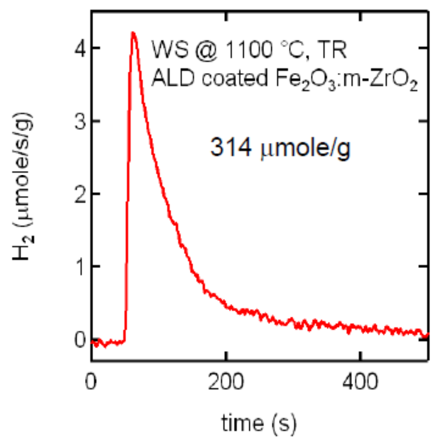


Development of a chemical reduction has allowed demonstration of rapid intrinsic kinetics for ferrites.

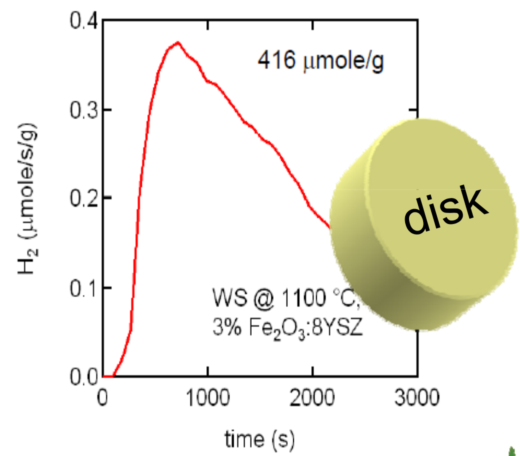
H_2 peak rates > 100x faster at 600 °C than Fe/YSZ at 1100 °C.



Chemically reduced ALD coated Fe:ZrO_2 nanoparticles

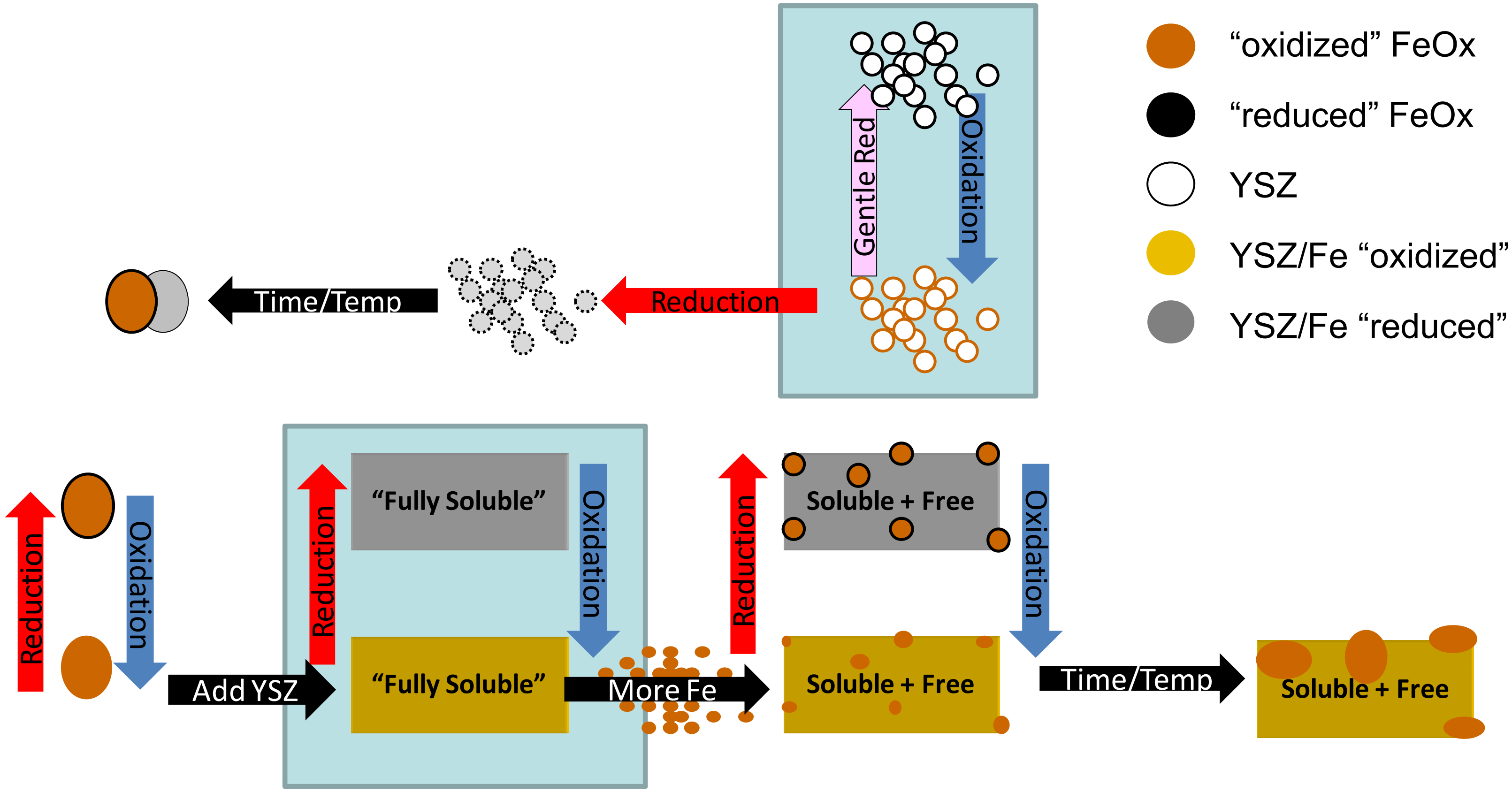


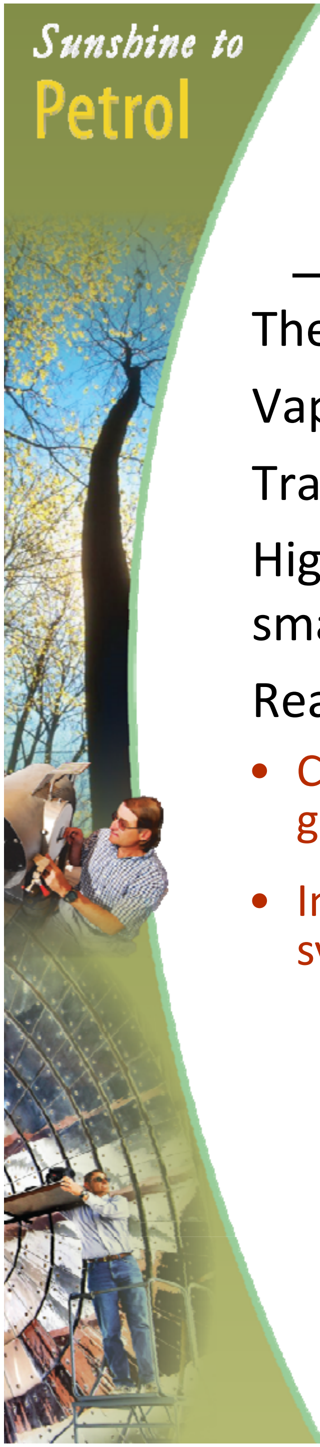
Thermally reduced ALD particles



Bulk Fe:YSZ

Ferrites Summary





Attributes of Ideal Material are Linked to Device

Thermodynamic Operating Window 500-1500 °C

Vapor Pressure of Working Oxide < $3x10^{-7}$ Torr

Transport $\geq$ the characteristic dimension (thickness) of fabricated parts

High melting Points, Low thermal expansion, Characteristic dimensions small to relieve stress.

Reaction Kinetics/Material Loading matched to Flux

- Current Materials are appropriate for accomplishing our short term project goals, but fall short in one or more category.
- Improvements will be needed to meet long term targets as defined by systems, economics, and competing approaches.

Three Aspects to the Path Forward

- Improved compositions – modification & discovery
- Structuring materials
- Matching the reactor to the material

Take home points

- There are many potential routes to "Solar Fuels"
  - Thermochemistry is a strong contender, advantages over others
- Efficiency is key for scalability (avoiding resource limits) and cost
  - Sunlight is the high cost feedstock (capital to capture)
  - Adjacency to other technologies (e.g. solar electric) offers benefits
- Thermochemical approaches have great promise.
  - Potential for high efficiency
  - Field is rapidly advancing
  - Systems studies support claims for eventual economic viability
- Opportunities and Need to develop the next generation of materials and systems
  - New materials with optimized thermodynamics, transport properties, structures, physical properties …
  - Thermally efficient reactors.

Project Team

Principal Investigator – James E. Miller
Project Manager - Ellen B. Stechel, Tony Martino

Systems

- Terry Johnson, Chad Staiger, *Christos Maravelias (U-WI),* Carlos Henao (student,) Jiyong Kim (PD), Daniel Dedrick

Reactor

- Solar Reactor - Rich Diver, Tim Moss, Scott Korey, Nathan Siegel
- Reactive Structures - Nathan Siegel, Terry Garino, Nelson Bell, Rich Diver, Brian Ehrhart
- Detailed Reactor Models - Roy Hogan, Ken Chen, Spencer Grange, Siri Khalsa, *Darryl James (TTU),* Luke Mayer (student)

Materials

- Reactive Materials Characterization & Development - Andrea Ambrosini, Eric Coker, Mark Rodriguez, Lindsey Evans, Stephanie Carroll, Tony Ohlhausen, William Chueh
- Bulk Transport & Surface Reactions - Gary Kellogg, Ivan Ermanoski, Taisuke Ohta, Randy Creighton
- Thermodynamics & Reaction Kinetics - Mark Allendorf, Tony McDaniel, *Chris Wolverton (Northwestern University),* Bryce Meredig (student), Heine Hansen (PD), Asegun Henry, *Al Weimer (CU),* Jon Scheffe (student)

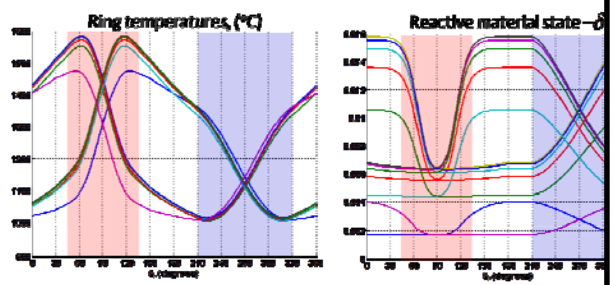
Models Provide Insight into Physics and Design Space

"Numerical Experiments"

- Operational parameters
  - Ring speed
  - Incident solar flux
  - Reactor pressure
- Reactor geometry
  - Fin/ring dimensions
  - Number of rings
  - Reactive material

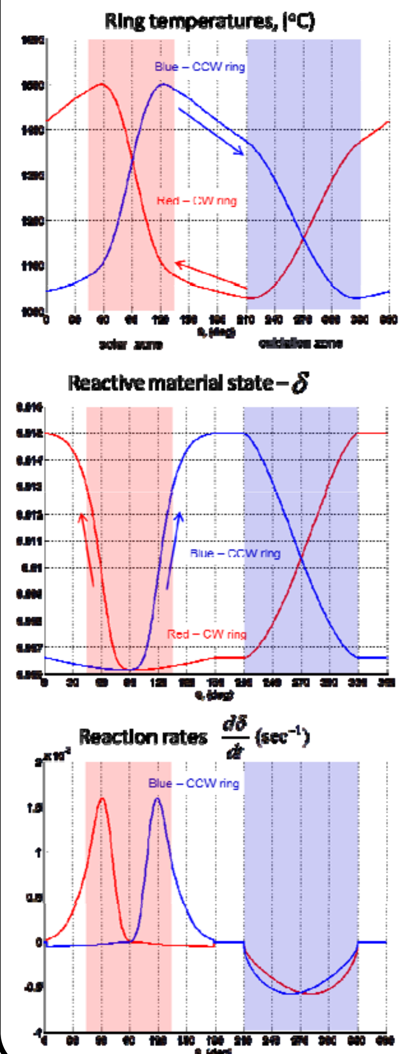
Improves our understanding of the important parameters and the details of reactor operation

12-Ring CR5 Performance



Ring	Max Temp (°C)	Min Temp (°C)	Max Delta	Min Delta	Diff in Delta	Conv. Eff
1 (edge)	1475	1089	0.0040	0.0017	0.0023	0.49
2	1553	1087	0.0106	0.0044	0.0062	1.04
3	1579	1010	0.0196	0.0056	0.0080	1.39
4	1580	1014	0.0145	0.0061	0.0088	1.45
5	1584	1016	0.0156	0.0063	0.0092	1.51
6 (center)	1585	1017	0.0158	0.0084	0.0083	1.53

2-Ring CR5 Performance



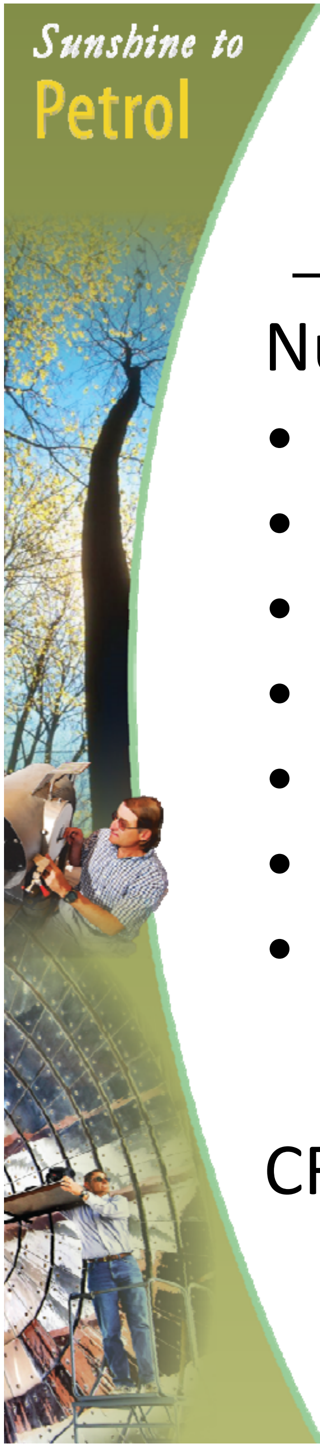
Parameter Sensitivities

Parameter Varied	Baseline Values	Perturbed Value	Temps (°C)	Diff in Temp (°C)	Delta Range
Baseline	—	---	1507.4 1031.7	475.7	0.0064 0.0028
Incident solar flux	245 kW/m²	257 kW/m² +5%	1564.3 1065.7	498.6	0.0136 0.0058
Ring speed	1 rpm	0.9 rpm -10%	1542.0 1007.1	534.9	0.0102 0.0038
O_2 partial pressure	1e-3 atm	1e-4 atm *33%	1499.5 1028.5	471.0	0.0150 0.0062
Recuperation effectiveness	—	+20%	1519.2 1027.5	491.7	0.0074 0.0032
Carrier ring density	4000 kg/m³	4400 kg/m³ +10%	1485.6 1046.6	439.0	0.0048 0.0021
Fin thickness	1.13 mm	1.70 mm +50%	1470.4 1055.1	415.3	0.0038 0.0017
Fin thickness & solar flux (match max T)	1.13 mm 245 kW/m²	1.70 mm 267 kW/m²	1507.3 1078.8	428.5	0.0067 0.0030

Scale-up from 12-inch to 36-inch Diameter

	CR5 Configuration (12-inch dia)			Full-Scale Configuration (36-inch dia)		
Number of Rings	4	12	24	4	12	24
Reactor Power (kW)	3.18	9.86	19.90	18.0	55.9	112.71
Average T_{max} (°C)	1499	1558	1573	1544	1553	1568
Average $\Delta\delta$	0.0033	0.0073	0.0085	0.0031	0.0068	0.0079
Chem Conv Efficiency (%)	0.59	1.23	1.40	0.71	1.49	1.71
CO Rate @ STP (L/min)	0.09	0.58	1.33	0.67	4.44	10.2

- ~3x efficiency benefit from increasing rings and loading
- Material utilization ($\Delta\delta$) is the "limiting factor" → options
  - Increase reduction temperature
  - Reduce operating pressure
  - Improve Ceria and/or develop new materials



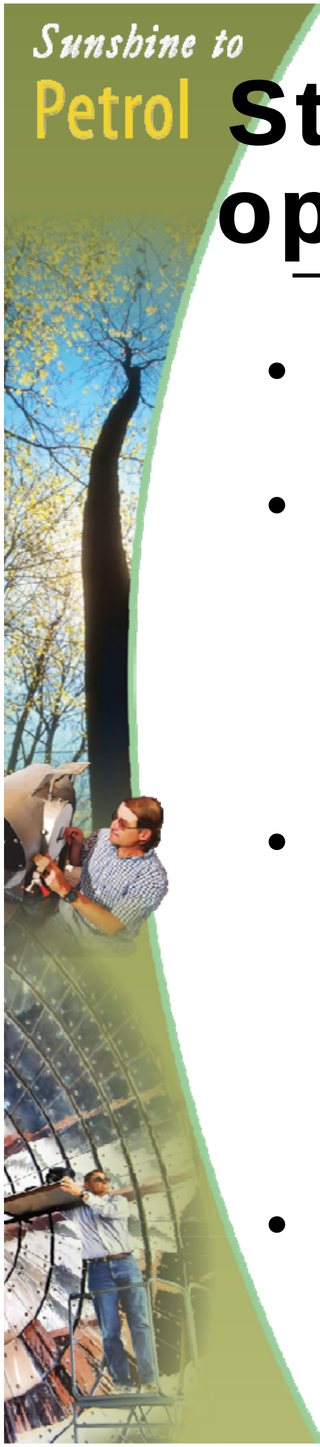
Modeling and Validation Accomplishments

Numerical modeling has provided insight into:

- Radiative environment
- Thermal stresses
- Species cross-over
- Recuperation
- Effective fin thickness (thermal penetration)
- Chemical conversion efficiency
- Important reactor physics and operating parameters
  - Temperature, reactant state, reaction rate distributions, chemical conversion, geometry and scale-up

CR5v will provide validation data and insight into:

- Species cross-over, sweep-gas effectiveness, recuperation effectiveness, reactor ring and gas temperatures

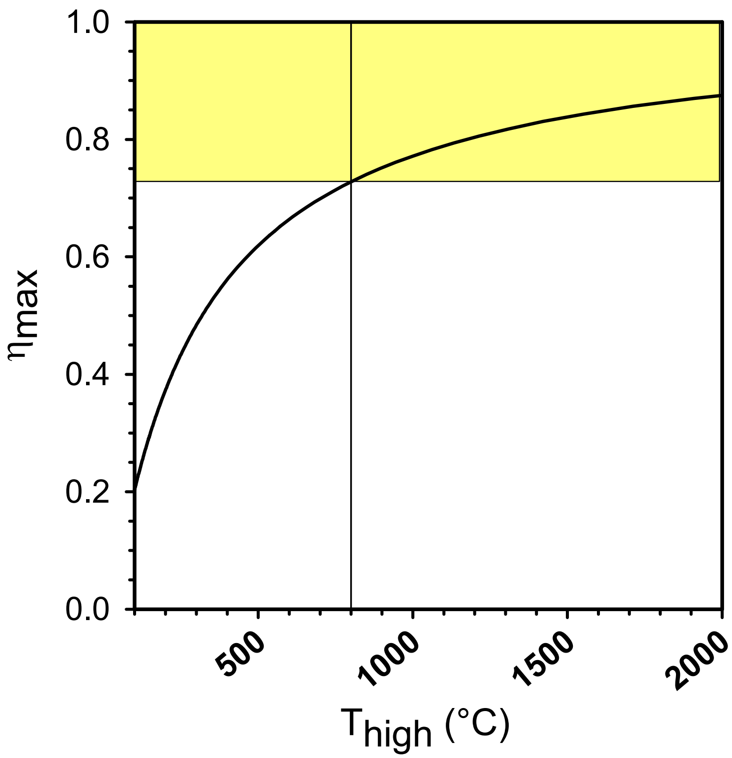


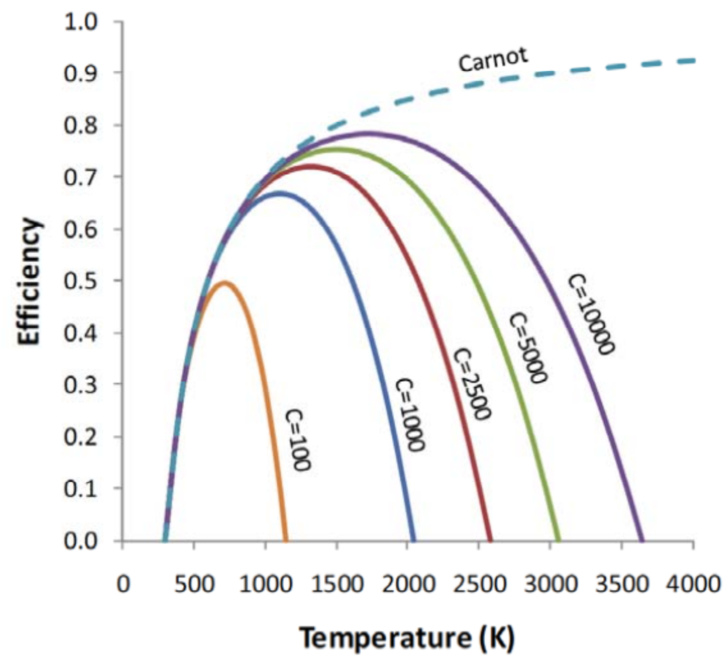
Strong and Capable Team operating at the Forefront

- Have demonstrated that they can set challenging technical goals and meet them
- Have put together a rigorous, comprehensive, and multi-perspective inventory of the challenge and determined:
  - There are no show-stoppers
  - This is a difficult challenge, and it demands depth and breadth of expertise that is hard to assemble – except at Sandia
- Have made smart use of thorough analytical modeling to complement experiment and have demonstrated:
  - A solid, plausible case that this technology can significantly impact the dual challenge of energy (petroleum) and climate (CO_2) security
  - This may be the only technology capable of this promise within a relevant timeframe.
- Have capitalized on unique and diverse capabilities at Sandia

Ideal Thermal Reduction 800-1500 °C

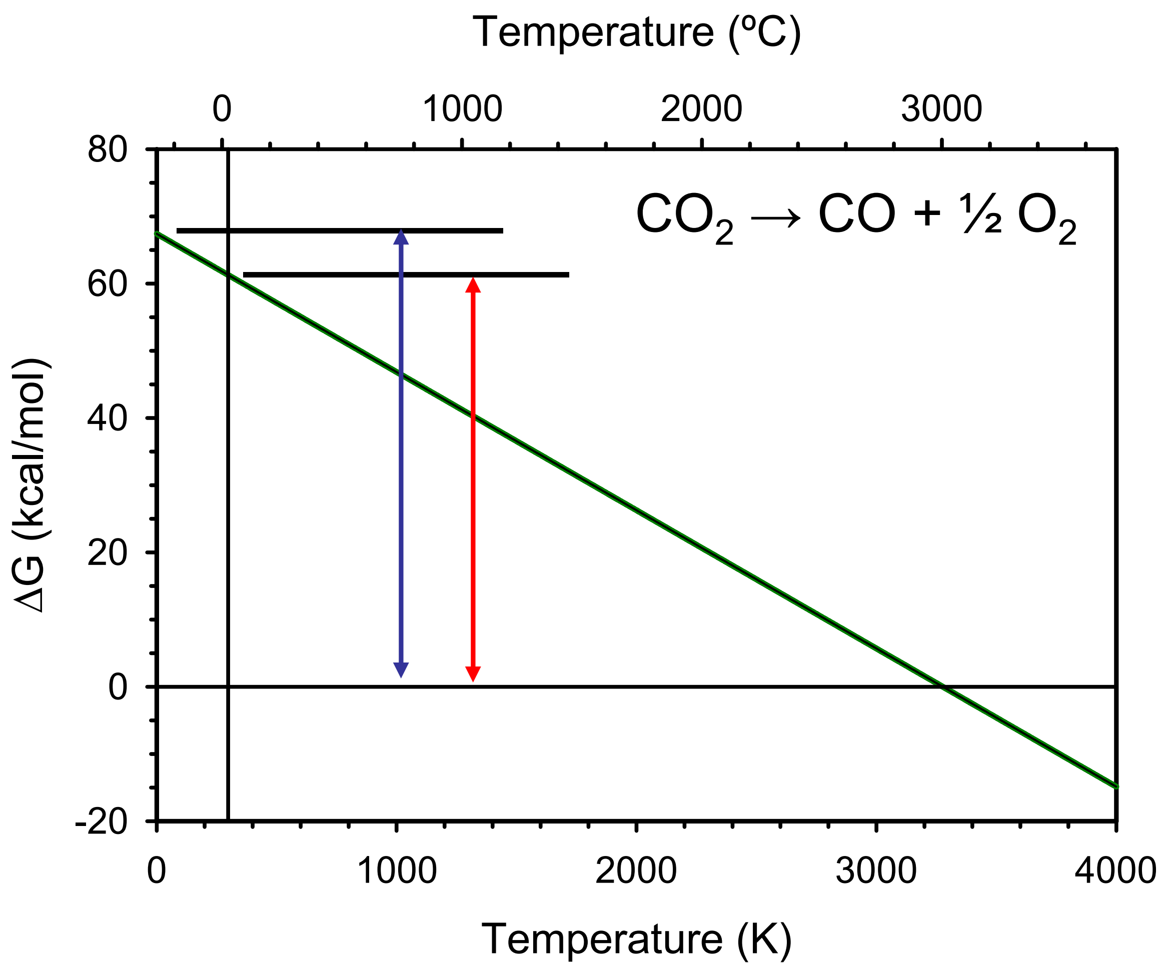
Carnot considerations suggest temperature should be as high as possible, but at least 800 °C





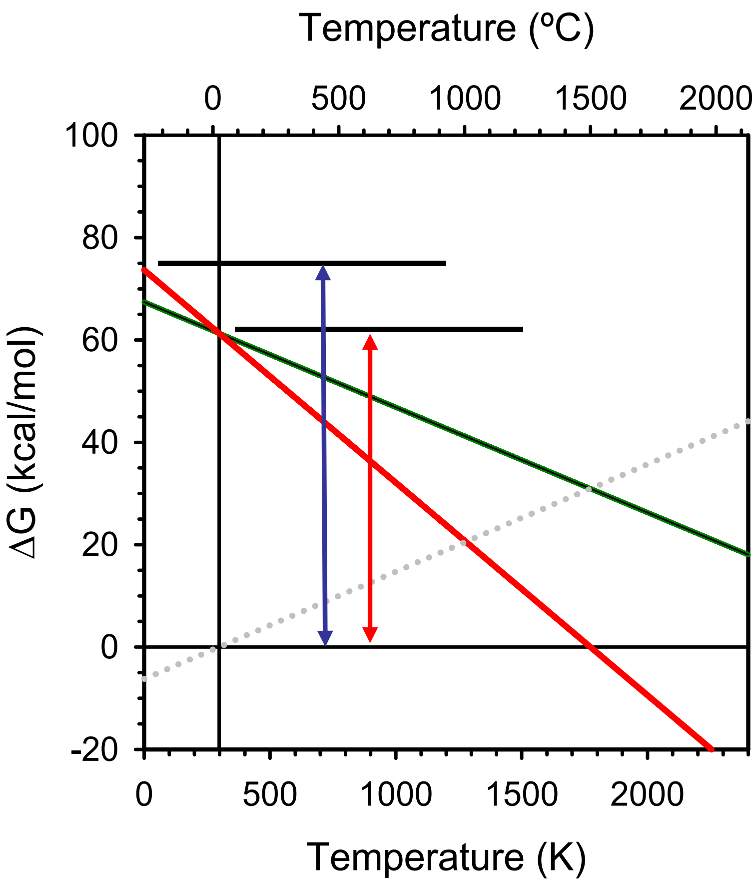
Radiation losses suggest temperature should be limited to < 1500 °C

Efficiency Consideration

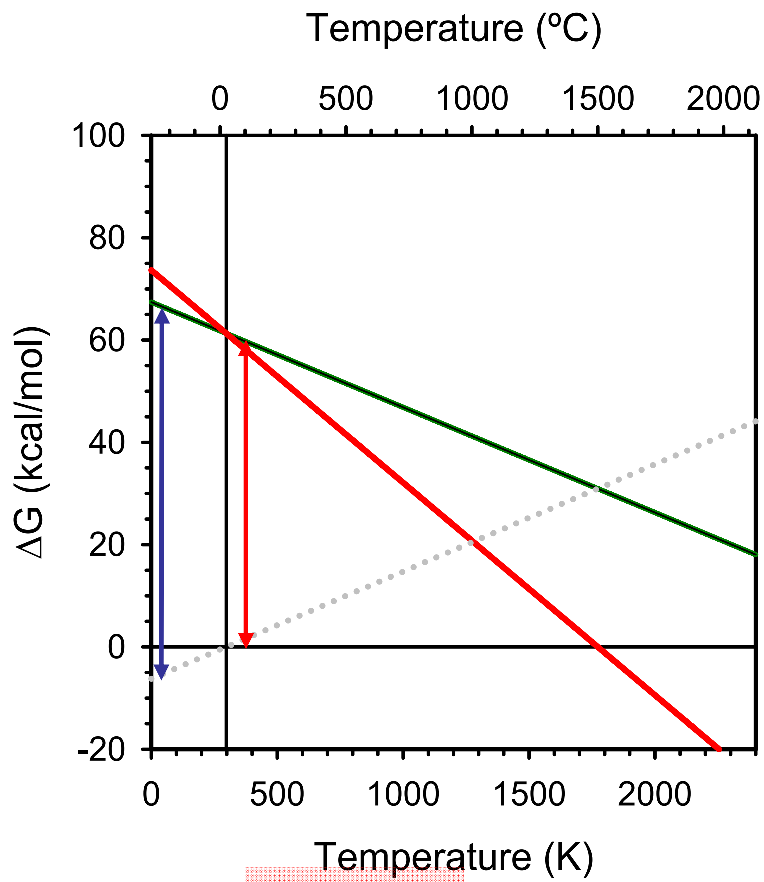


$$\eta = \frac{\Delta G_{CDS}^{298}}{\Delta H} = 0.91$$

Reduction @ 1500 ºC
Oxidation @ 298 ºC



$$\eta = \frac{\Delta G^{298}_{CDS}}{\Delta H_{MOx\ Reduction}} = 0.83$$

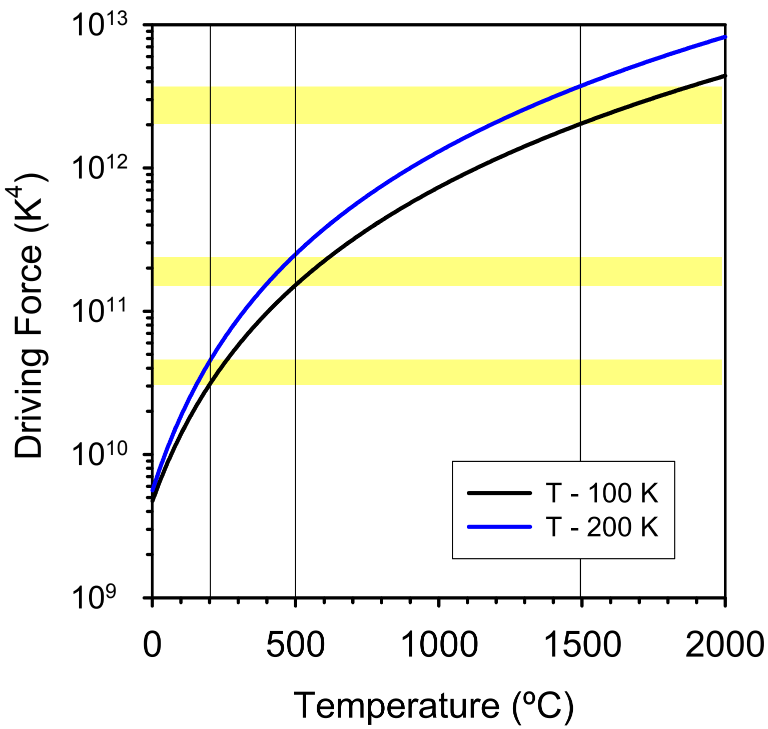


$$\eta = \frac{\Delta G^{298}_{CDS}}{\Delta H_{CDS} - \Delta H_{MOx\ Oxidation}} = 0.83$$

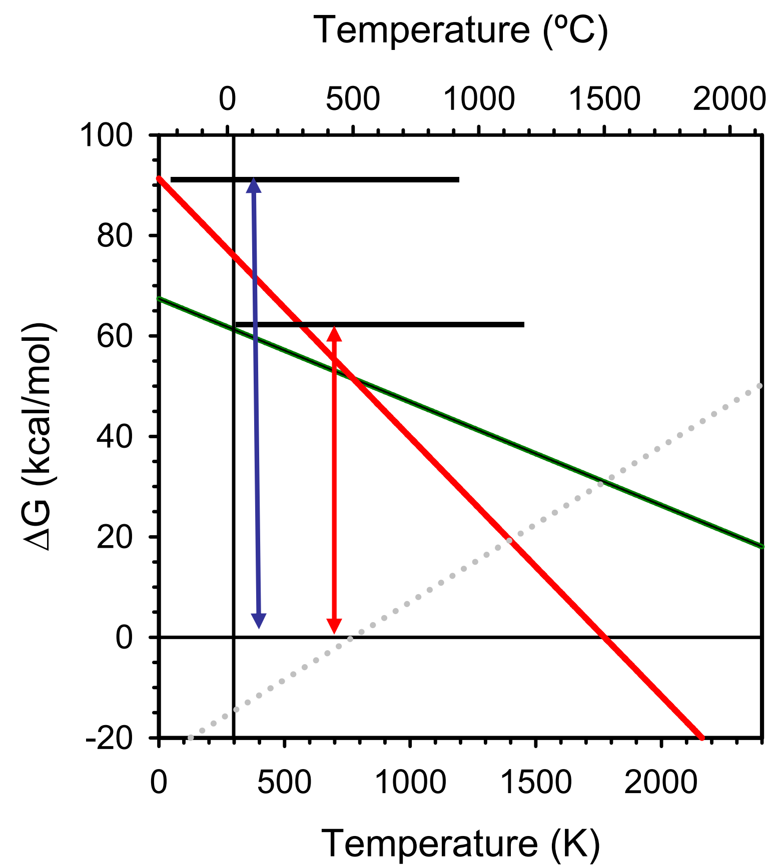
Ideal Oxidation

Reduction @ 1500, Oxidation @ 500 °C

$$Q_{12} = A_1 F_{12} \sigma \left(T_1^4 - T_2^4 \right)$$



Oxidation should be at as low a temperature as possible, but need for recuperation suggests temperature limited to > ca. 500 °C



$$\eta = \frac{\Delta G^{298}_{CDS}}{\Delta H_{MOxReduction}} = 0.67$$

Project Summary

Some Major Accomplishments:

- Demonstrated key operating features of the CR5 on-sun
  - continuous production of O_2 and CO from CO_2
  - recovery of O_2 and CO in separate streams
  - control over two distinct operating regions & temperatures
- Developed, for the first time, an in depth understanding of the dynamic Ferrite/YSZ composite system.
- Established credibility of high efficiency direct paths for solar fuels

Principal Goal for Remainder of the Year:

- Continuous steady state production of fuel intermediates at an average of at least 2% efficiency (chemical out/solar in).

Next?

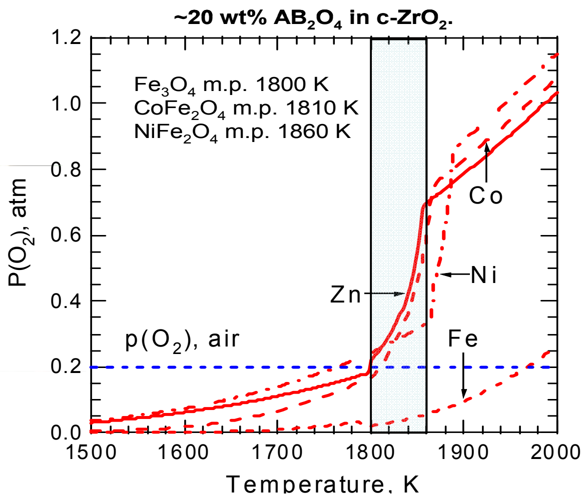
- Apply lessons of materials science to design and development of next generation of materials.
- Design /development of next generation reactor/system (η=5 $\rightarrow$25%)
- Sustained resources on the decade time scale
- >10% full-system life-cycle sunlight-to-fuel efficiency

Ferrites as an Example

Idealized Chemistry

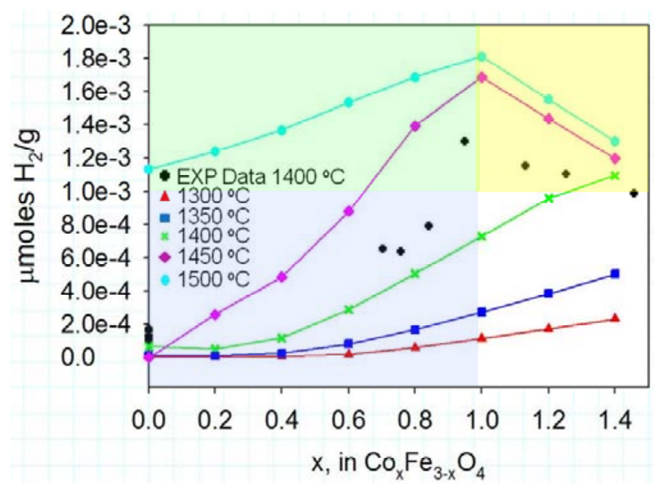
$$Fe_3O_4 \rightarrow 3FeO + \frac{1}{2} O_2$$

$$3FeO + H_2O \rightarrow Fe_3O_4 + H_2$$



Favorable temperature range (thermodynamics) can be manipulated via metal substitutions in Fe_3O_4. Useful, e.g., to shift operating temperatures below the melting point.

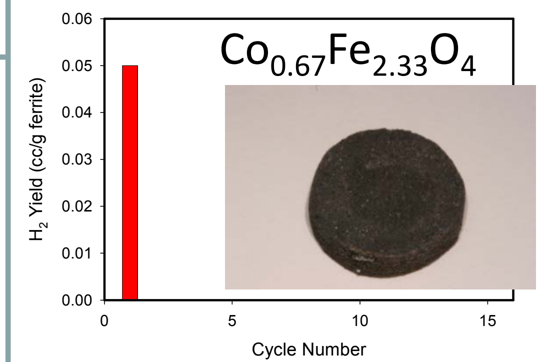
The effect of composition on gas yields can be predicted.



Modified Idealized Chemistry

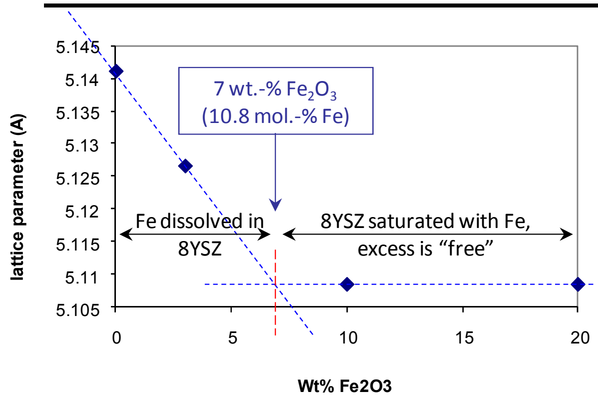
$$A_xFe_{2-x}O_4 \rightarrow 3A_{x/3}Fe_{(2-x)/3}O + \frac{1}{2} O_2$$

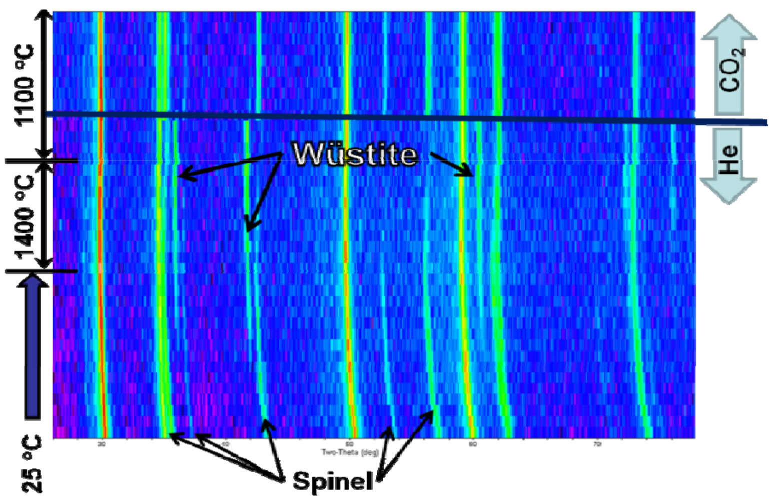
$$3A_{x/3}Fe_{(2-x)/3}O + H_2O \rightarrow A_xFe_{2-x}O_4 + H_2$$



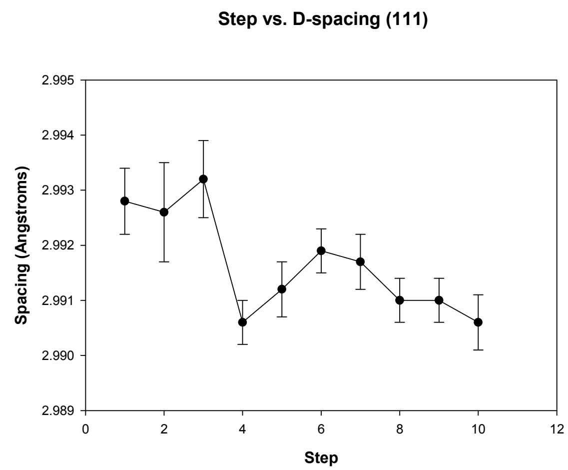
"Bulk" materials do not live up to their potential.

Monolithic composites with YSZ are cyclable – Why?

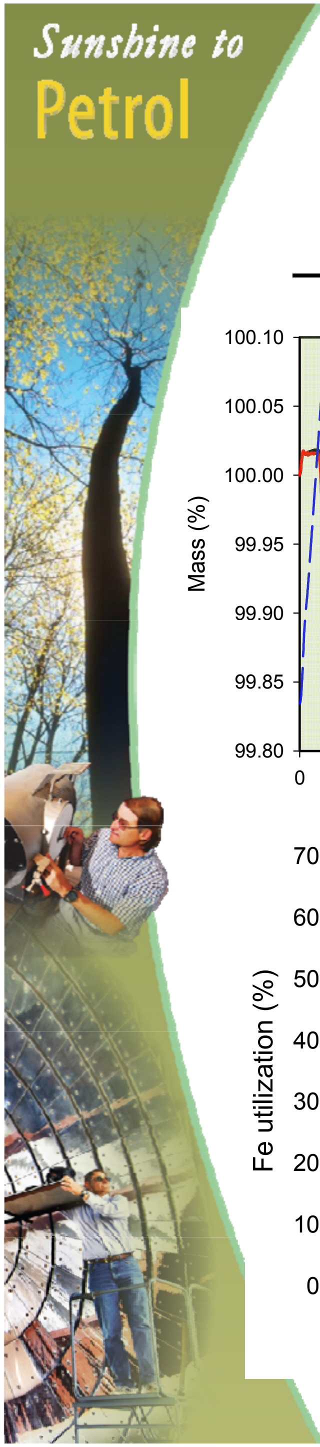




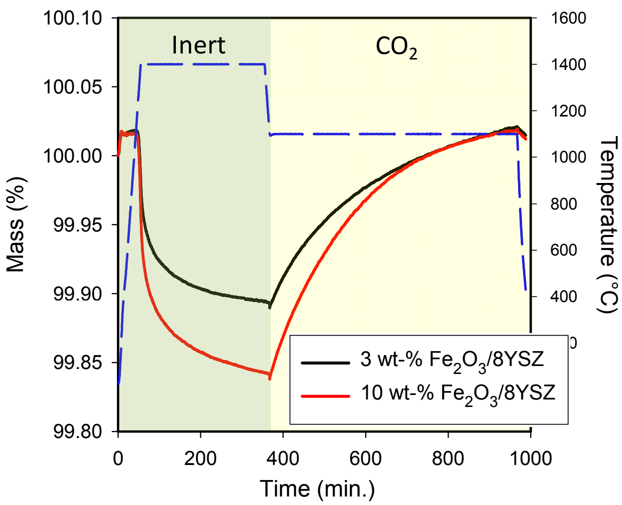
- Fe is soluble in 8YSZ
- Solubility is a function of both temperature and oxidation state.

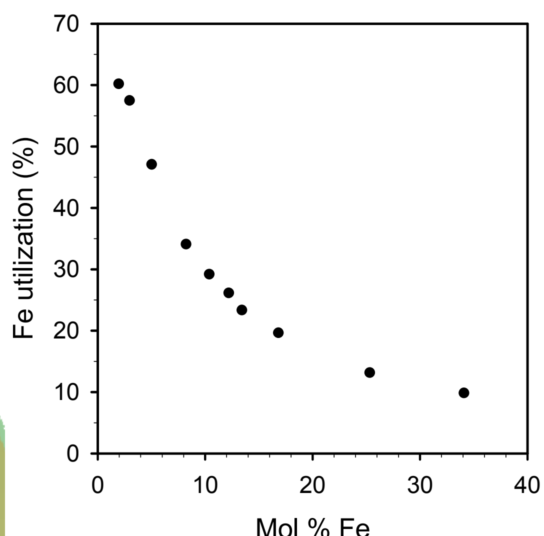


In situ observation of phases and 8YSZ lattice parameters reflect complex migration of Fe in/out of solid solution.

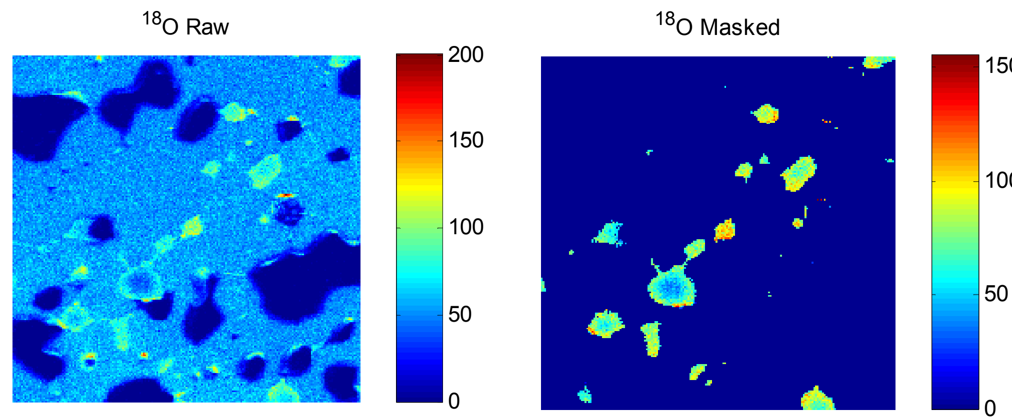


Monolithic composites with YSZ are cyclable – Why?

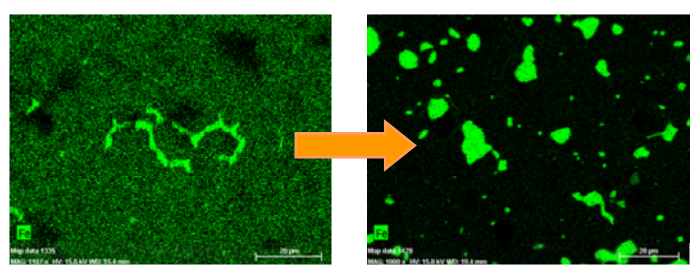




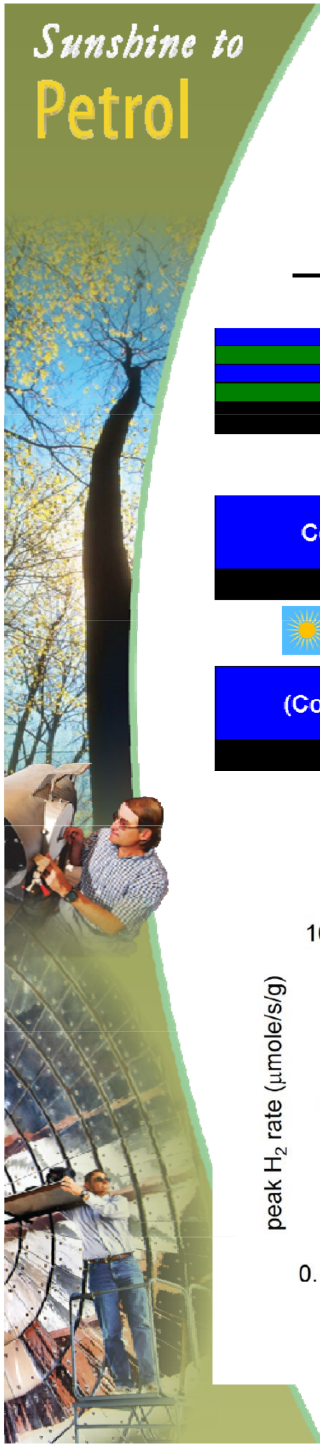
Beyond the solubility limit additional Fe contributes little to the overall gas yield.



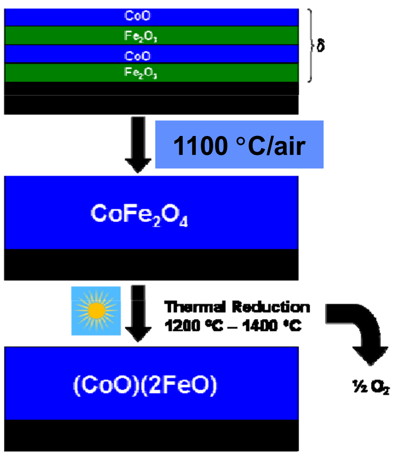
Reaction with ^{18}O-labelled CO_2 confirms limited utilization of bulk particles relative to Fe/YSZ.



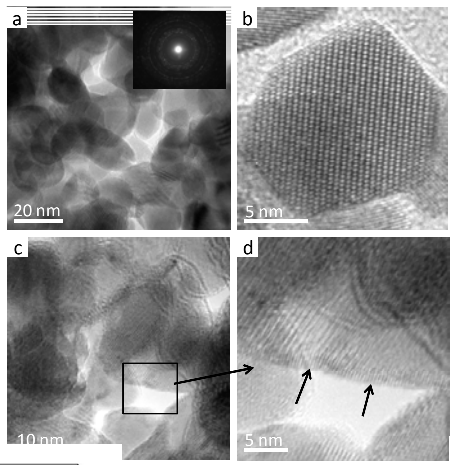
Fe EDS



Structured Ferrites?



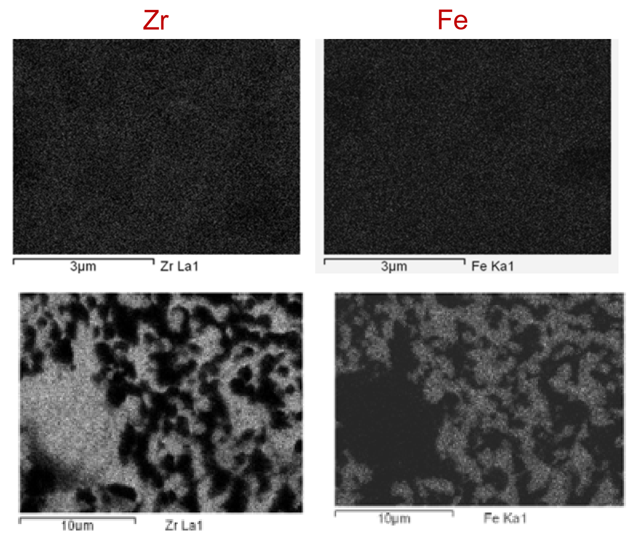
2 nm $CoFe_2O_4$ film
after ALD synthesis

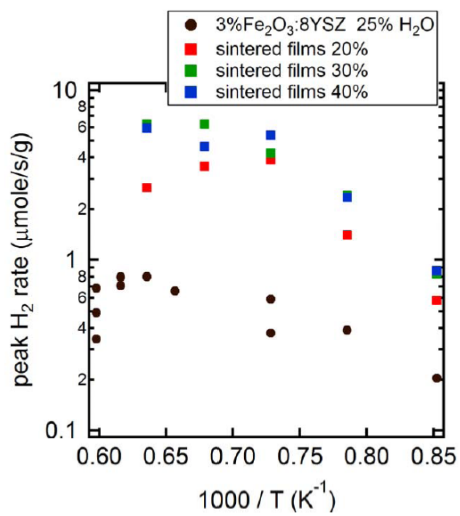


Phase Segregation

Pre-Processing

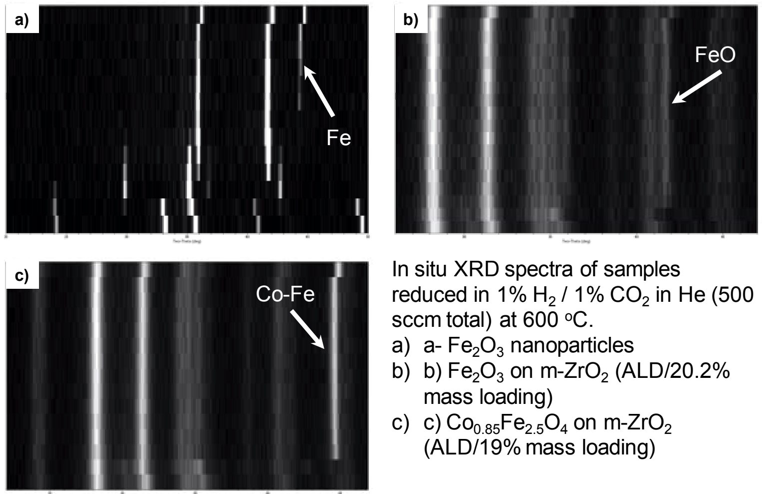
Post-Processing





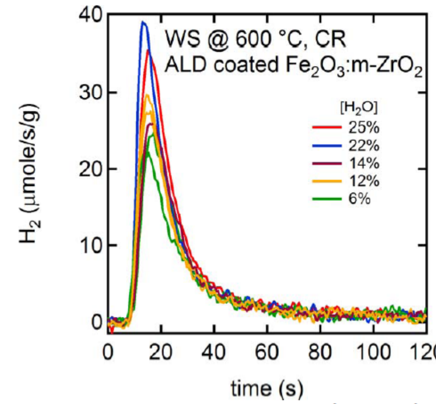
Aside from a higher surface area, after thermal reduction,
ALD films are chemically and physically similar to sintered structures.

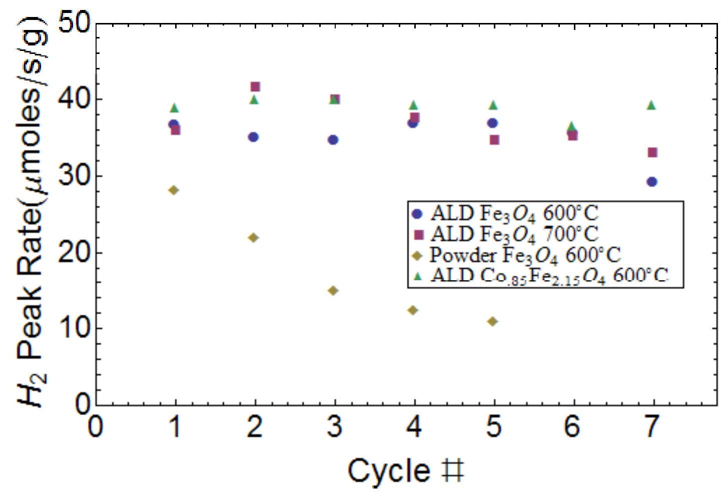
Structured Ferrites?



In situ XRD spectra of samples reduced in 1% H_2 / 1% CO_2 in He (500 sccm total) at 600 °C.

a) a- Fe_2O_3 nanoparticles
b) b) Fe_2O_3 on m-ZrO_2 (ALD/20.2% mass loading)
c) c) $Co_{0.85}Fe_{2.5}O_4$ on m-ZrO_2 (ALD/19% mass loading)



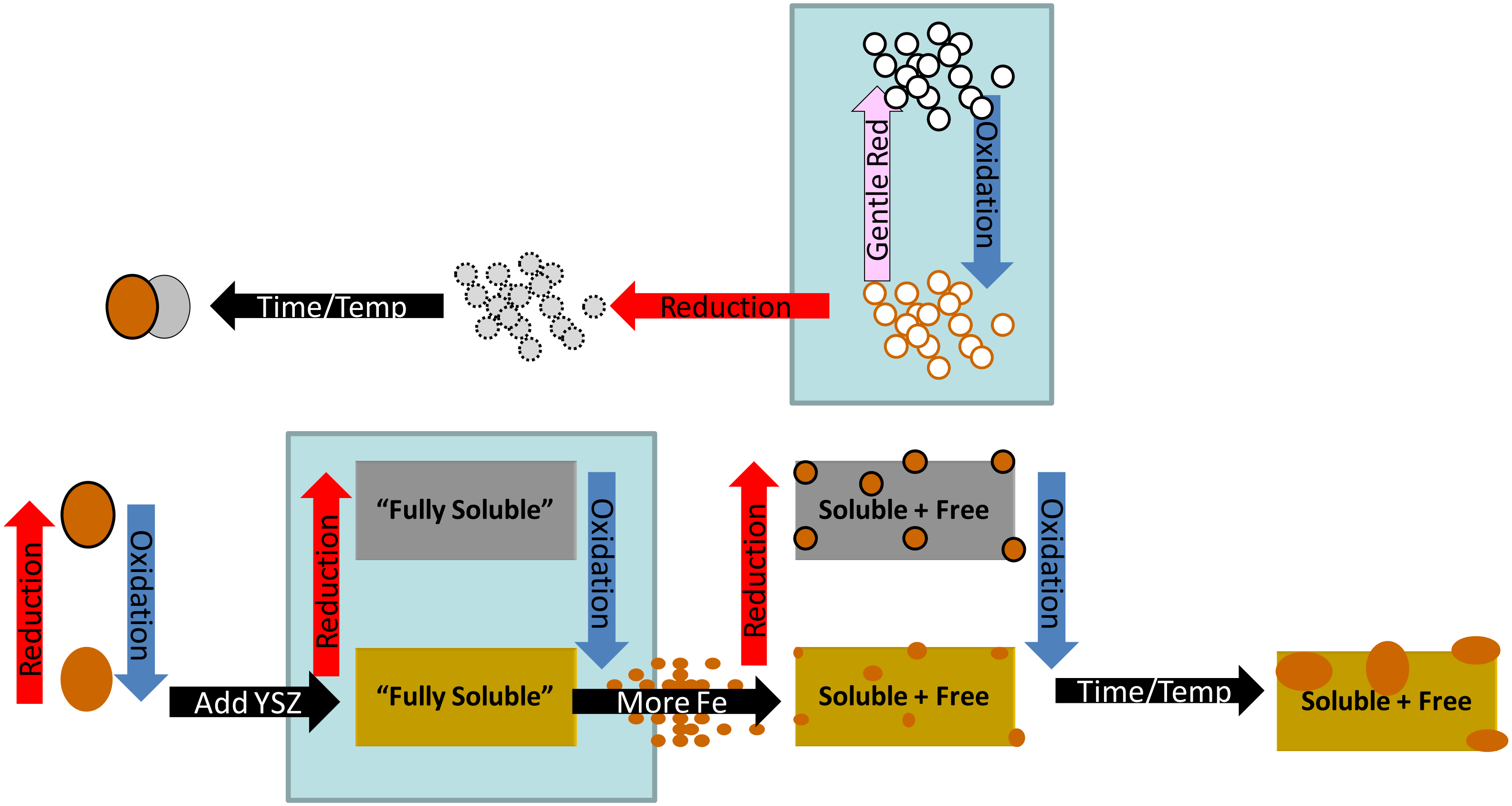


Development of a chemical reduction has allowed demonstration of rapid intrinsic kinetics for ferrites.

H_2 peak rates > 100x faster at 600 °C than Fe/YSZ at 1100 °C.

Sunshine to Petrol

Ferrites Summary



Attributes for Next Generation Materials

Operating Window 500-1500 °C

- Current materials can be improved upon

Vapor Pressure of Working Oxide < $3x10^{-7}$ Torr

- Ceria borderline, bulk ferrites are problematic, soluble Fe?

Melting Point > 3275 °C

- Unlikely to be met – highlights the challenge for structured materials

Thickness of Dense, Directly Illuminated Parts < 4 mm

- Assumes heating from all sides

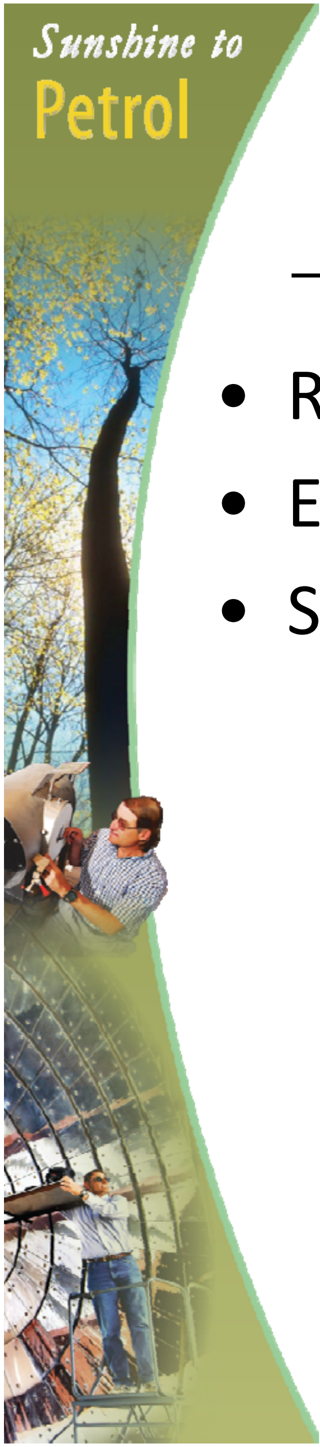
Diffusion Length $\geq$ the characteristic dimension (thickness) of fabricated parts

- Consistent with large geometries for ceria, Fe must be highly structured or coupled into a conductive matrix

Characteristic dimensions small to relieve stress.

Reaction Kinetics/Material Loading matched to Flux –

- For $\eta=0.36$ & 17 w/cm^2, > 20.4 μmol CO/cm^2 sec or 10.2 μmol O_2/cm^2 sec if linked



Briefly: Three More Themes

- Resource Demands and Scalability
- Efficiency Matters (Scalability and Costs)
- Systems/Economics

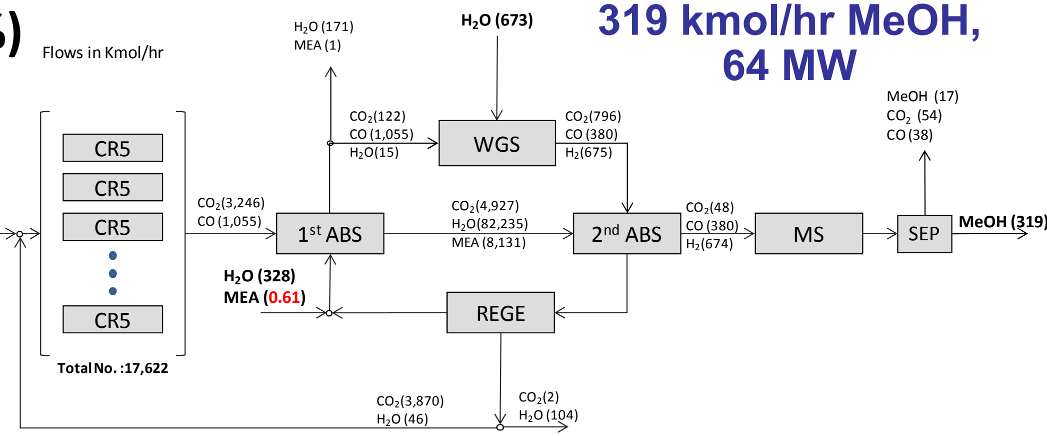
Sunshine to Petrol

Baseline System

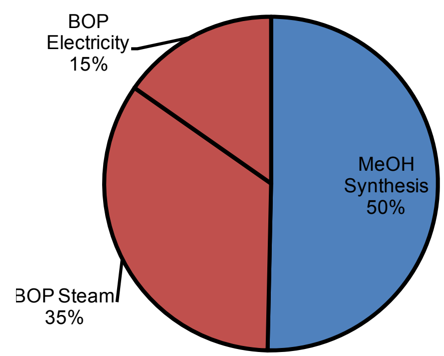
Baseline energy efficiency (7%)

- Dish/CSUs
  - 84% of the capital cost
  - 22.7% of operational cost
- Separations
  - MEA based CO_2
  - 48.7% of operational cost
  - 1.2% of the capital cost
- Water Gas Shift (WGS)
  - Minimal direct cost
  - Increases need for CO_2 separation
- Fuels synthesis
  - Minimal direct cost
  - Transition to higher value FT fuels from methanol

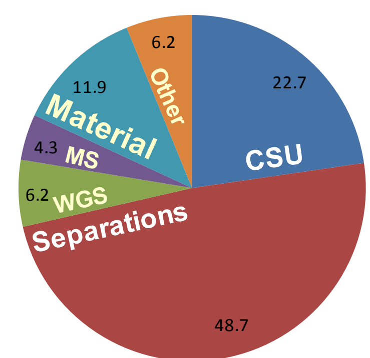
319 kmol/hr MeOH, 64 MW



Energy Balance:



System operating cost:



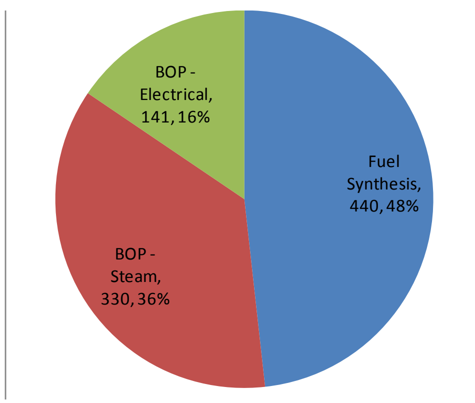
Current market price of methanol:
0.56 \$/kg (0.09 \$/kW-hr or 3.25 \$/GGE)

Cost of methanol from baseline system:
1.70 \$/kg (0.27 \$/kW-hr or 9.88 \$/GGE)

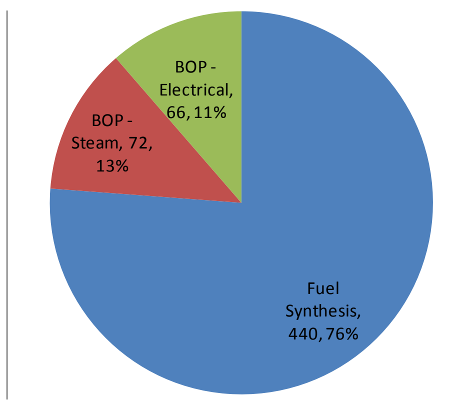
Improving the Balance of System

- The team has shown a pathway that:
  - Doubles the solar to chemical efficiency over the baseline system (from 7.1 to 16.2%)
  - Reduces the solar collection area by 51% (solar only system)
  - Produces end-use fuels at the S2P plant (FT)
  - Sets the stage for technology development, integration, and demonstration once the reactor is mature enough

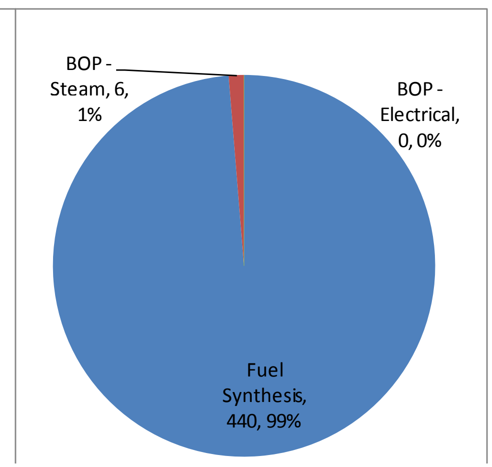
Energy to produce 65 MW Chemical:



Baseline System
911MW solar



Mixed Pathway
577MW solar

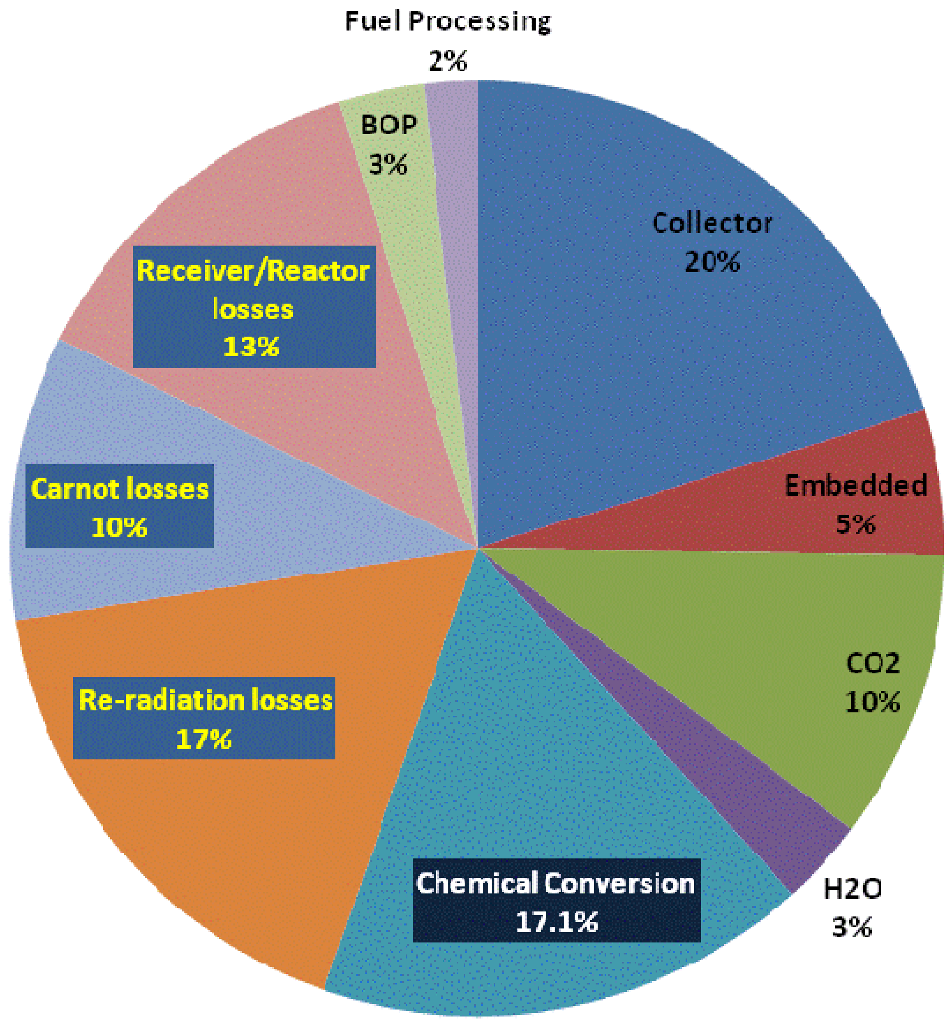


Advanced Sep/CR5
446MW solar

Next efficiency and cost opportunity: CO_2 and H_2O splitting efficiency

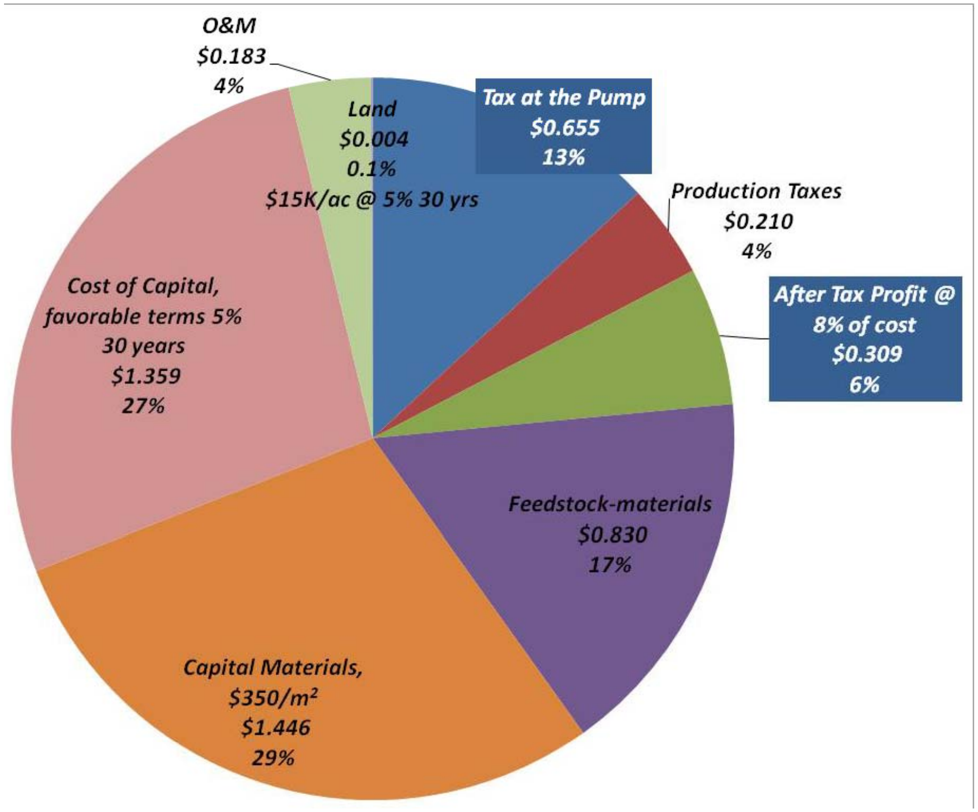
Sunshine to Petrol

Graphical View of Where the Energy Goes: 12.5 % LCE



- Re-radiation losses assumed 1450°C reduction and 3000-sun concentration
- Reactor assumed at 57% of theoretical and 30% first law efficient
- Lower temperature reduction will reduce losses
- Lower temperature reduction will reduce durability issues

Cost Breakdown For $5/GGE; S2P 12.5% LCE

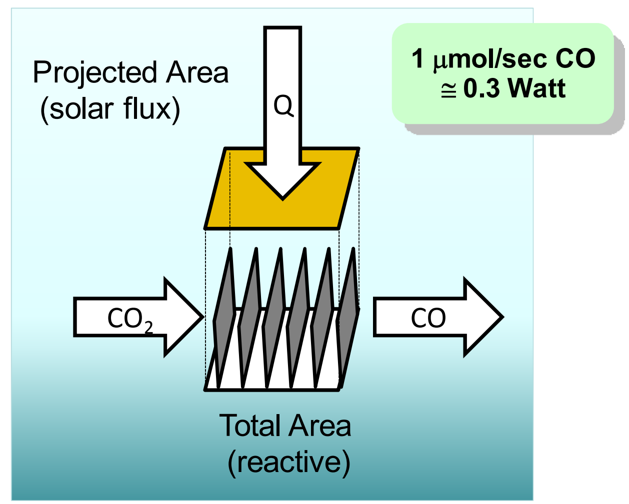


- **Costs for S2P are in the ballpark of viability**
- **Learning curve will reduce the most expensive contributions**
- **Very sensitive to the cost of capital recovery**

Kinetics Should be Matched to Solar Flux

$$\eta = \frac{Chemical\ Energy\ Out}{Solar\ Energy\ In} = \frac{\int_0^t (CO\ Flux \times HHV)\, dt}{\int_0^t Solar\ Flux\ dt}$$

$$CO\ Flux = 2\, O_2\, Flux$$



In order to achieve high efficiency the energy fluxes (solar and chemical) must match.

I.e. Reaction rates must be matched to the solar flux.

To the extent that the rates and flux do not match, heat is rejected.

Suitability of Current materials subject to surface area.