SAND2009-3668P

ENERGY, RESOURCES and NONPROLIFERATION

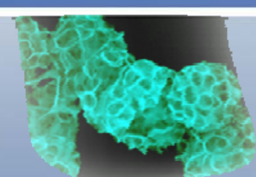
energy, water, and security . . . enabled by science & technology

Sunshine to Petrol

Kathryn Clay Visit

1 June 2009

Ellen B. Stechel
Manager, Emerging Energy Technologies



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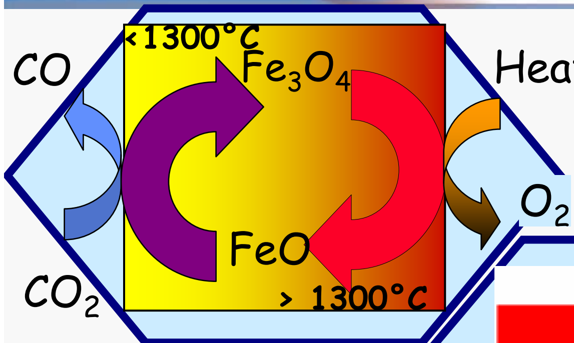
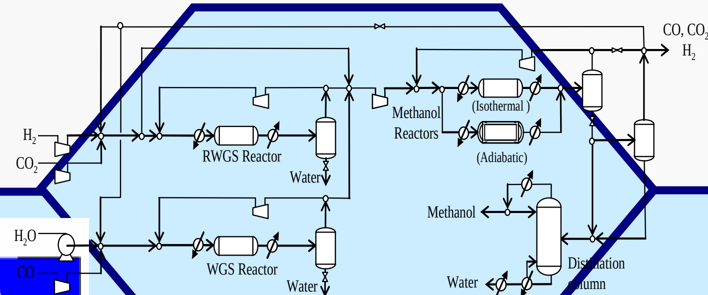
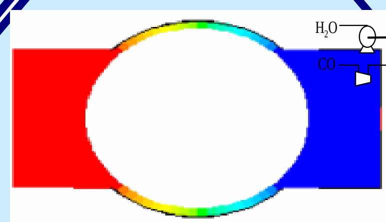
Sandia National Laboratories

We Have Assembled a Multi-Disciplinary Team Necessary for Success





Systems Engineering & Economics

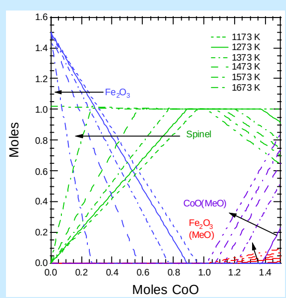


Multi-scale Rxn & Transport Modeling

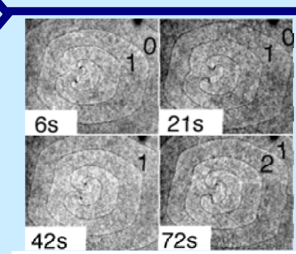
Materials Engineering & Fabrication

Solar Engineering

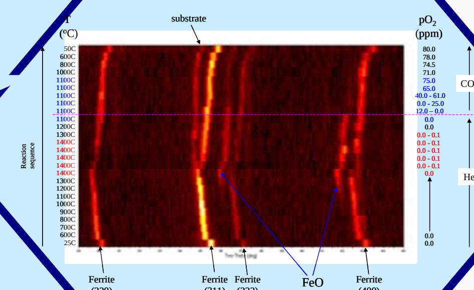
Engine Design & Build



Thermodynamics & Kinetics



Basic Science



Materials Science

Large Investment at Sandia

- **SNL – S2P Team**
  - James E. Miller, PI
  - Richard B. Diver, Task Lead
  - Nathan P. Siegel, Task Lead
  - Andrea Ambrosini, Task Lead
  - Mark D. Allendorf, Task Lead
  - Gary L. Kellogg, Task Lead
  - Roy E. Hogan, Task Lead
  - Daniel Dedrick, Task Lead
  - Stephanie Livers
  - Eric Coker
  - Ivan Ermanoski
  - Tony McDaniel
  - Ken Chen
  - Terry Johnson
  - Chad Staiger
  - Plus more

SNL-Other

- *Rush D. Robinett*
- *Margie Tatro*
- *Jeff S. Nelson*
- *Justine Johannes*
- *Duane Dimos*
- *Steve Roehrig*
- *Julie Phillips*
- *Les Shepherd*
- *Robert Hwang*
- *Andy McIlroy*
- *Ron Stoltz*
- *Andy Lutz*
- *Adam Simpson*
- *Phil Pohl*

- ***University Partners***
  - *Christos Maravelias, University of Wisconsin*
  - *Chris Wolverton, Northwestern University*
  - *Darryl James, Texas Tech University*
  - *Alan Weimer, University of Colorado*

- **Sponsors**
  - SNL-LDRD
  - DOE-EERE
  - DARPA Seedling

Motivation to "Recycle" CO_2

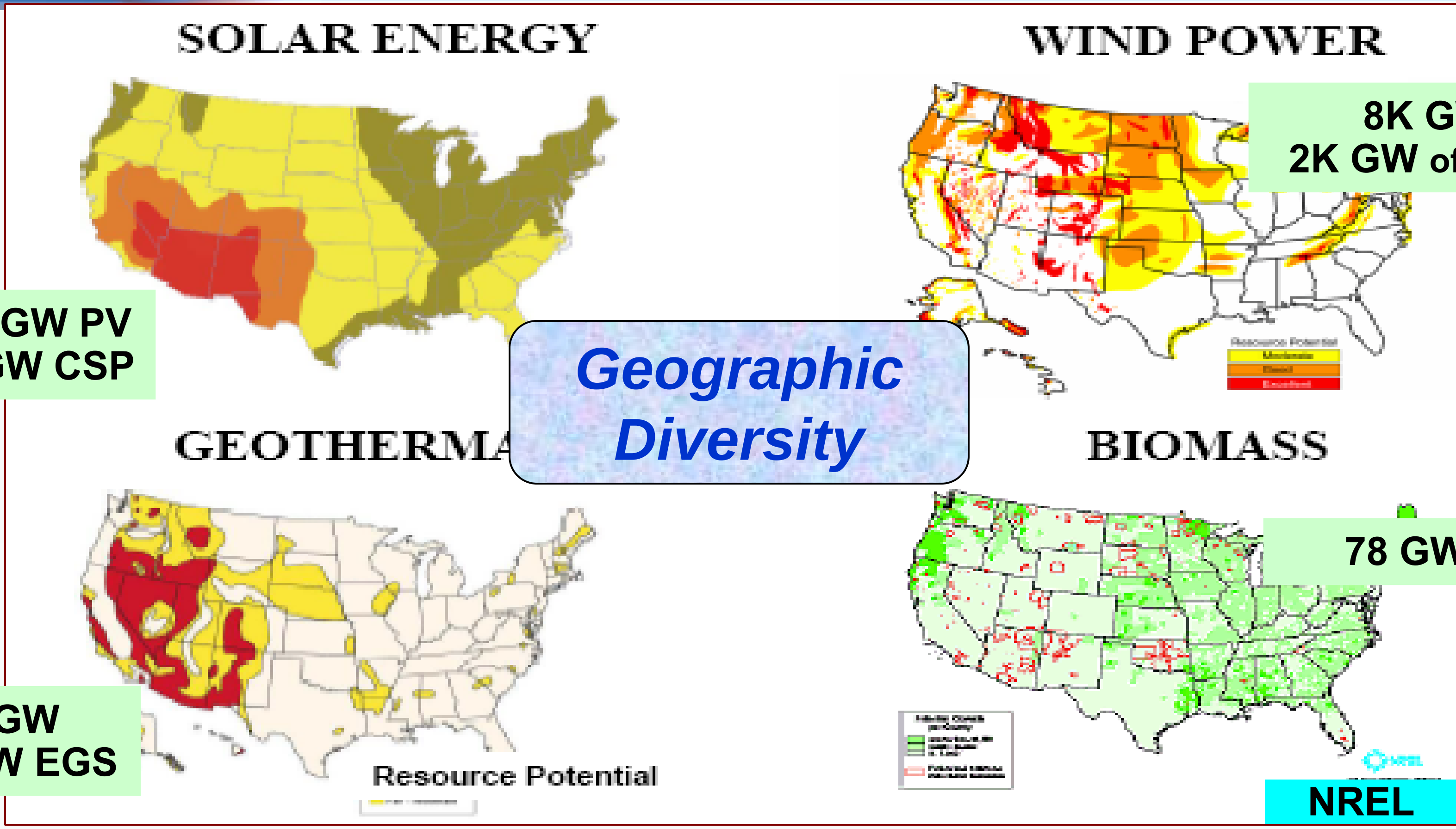
- **Assuring Energy Security**
  - Decrease the strategic importance of Petroleum and vulnerability to Supply Disruptions
  - Diversify Supply and use geographically and domestically available dispersed resources
  - Infrastructure Compatible: Fungible, Drop-In Fuels
- **Mitigating Climate Change**
  - E.g., Reduce GHG emissions, especially CO_2
  - Increase uses for and create value from CO_2

		Climate Change		
		Makes Worse	Neutral	Mitigates
Energy Security	Assures			
	Neutral			
	Makes Worse			

Non-Optional: We must find solutions that address both challenges simultaneously

The scale is large – but not too large

Renewable Energy Sources – No Lack of Resources, So what is the problem?



8K GW
2K GW offshore

206K GW PV
11K GW CSP

Geographic Diversity

78 GW

39 GW
520 GW EGS

NREL

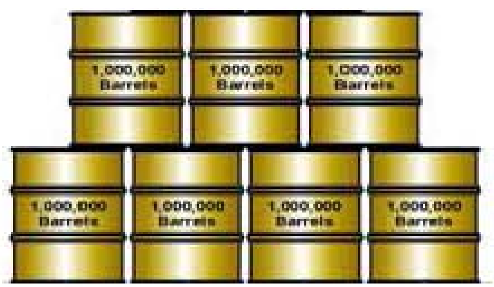
"Stranded" resources not necessarily close to major loads

Alternative to building out transmission lines - Make High Energy Density Fuels

Fuel: Stored Energy that can easily be used whenever & wherever, especially if liquid

Transportation Sector Consumes a Great Deal of Petroleum

Every day the U.S. consumes ~20.7 million barrels of petroleum (2006)
(that's ~10K gallons per second)



8.5 Billion Vehicle Miles/Day

All Substitutes face significant risks, barriers, and uncertainties: one or more from technical, economic, societal, political, regulatory

Over 2/3 (68.3%) of the petroleum consumed in the US is used for transportation
- **84.1% Highway; 65.2% Light Duty**

58% is imported

243M vehicles on the road in the US:
- **Median age ~8 yrs; cars ~9 yrs**
- **Median Lifetime of 1990 vehicles is ~17yrs**

*Transportation Energy Data Book, Edition 27-2008

What are Options for Transportation Energy?

No Silver Bullets
We will likely need all these options and maybe more
It is too soon to constrain the solution space

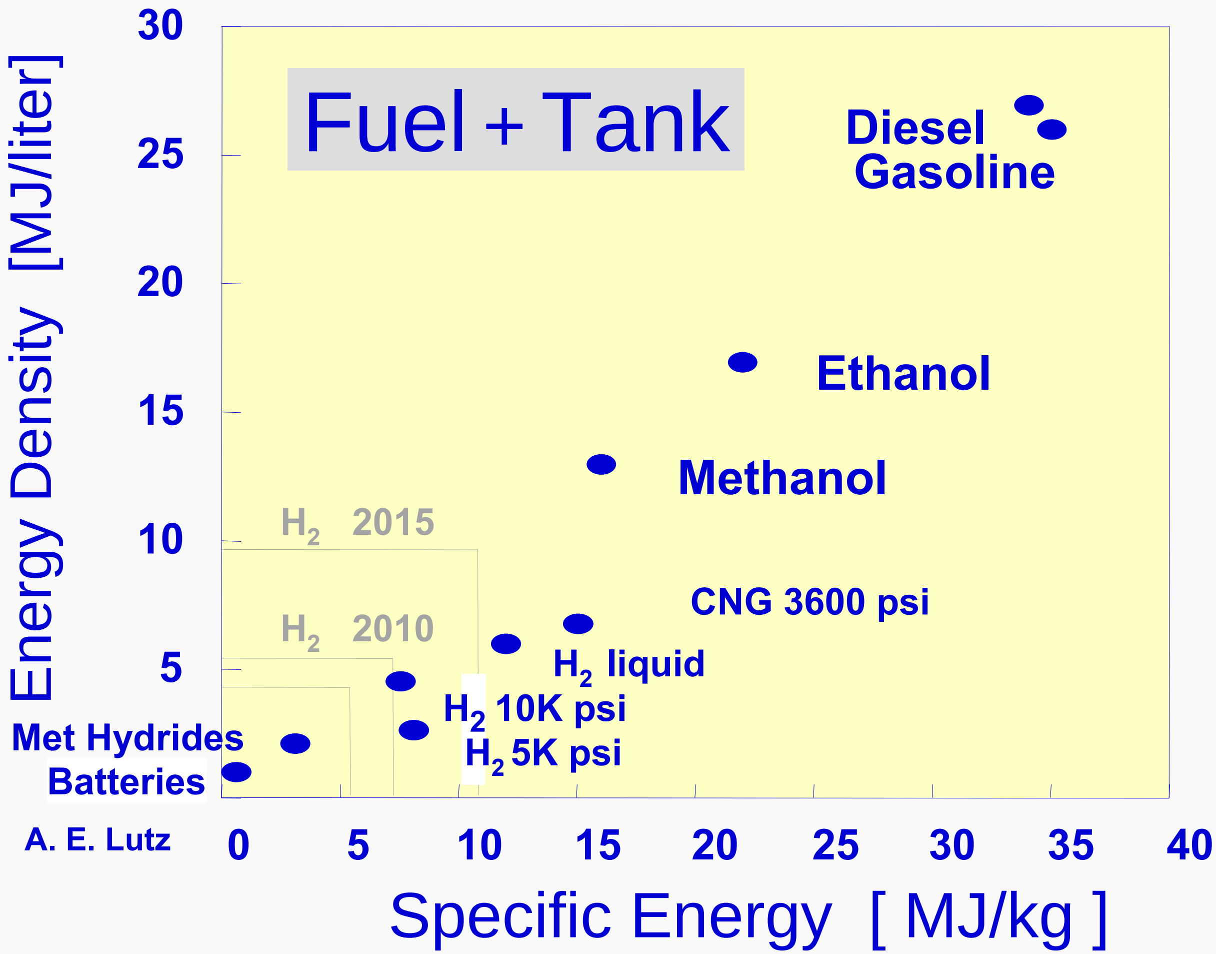
- **Coal to Liquids with Carbon Capture and Storage**
- **Unconventional Fossil**
  - with H_2 upgrading
- **Biomass to Liquids**
- **Bio-alcohols, Bio-diesel**
- **Algal Crude**
- **Hydrogen**

Partial and Full Electrification of Personal Vehicles,

e.g. Plug-in Electric Hybrids
Battery Electric
Ultra-capacitors

- **Solar Fuels or Low (Net) Carbon Synthetic Fuels**
  - ✓ **Not really on the radar screen yet, very little attention**
  - ✓ **Non-biological routes, high technical and economic risk**
  - ✓ **Government investment is needed to buy-down risk before we can expect industry or venture capital to "play."**

Liquid Hydrocarbon Fuels: The Gold Standard

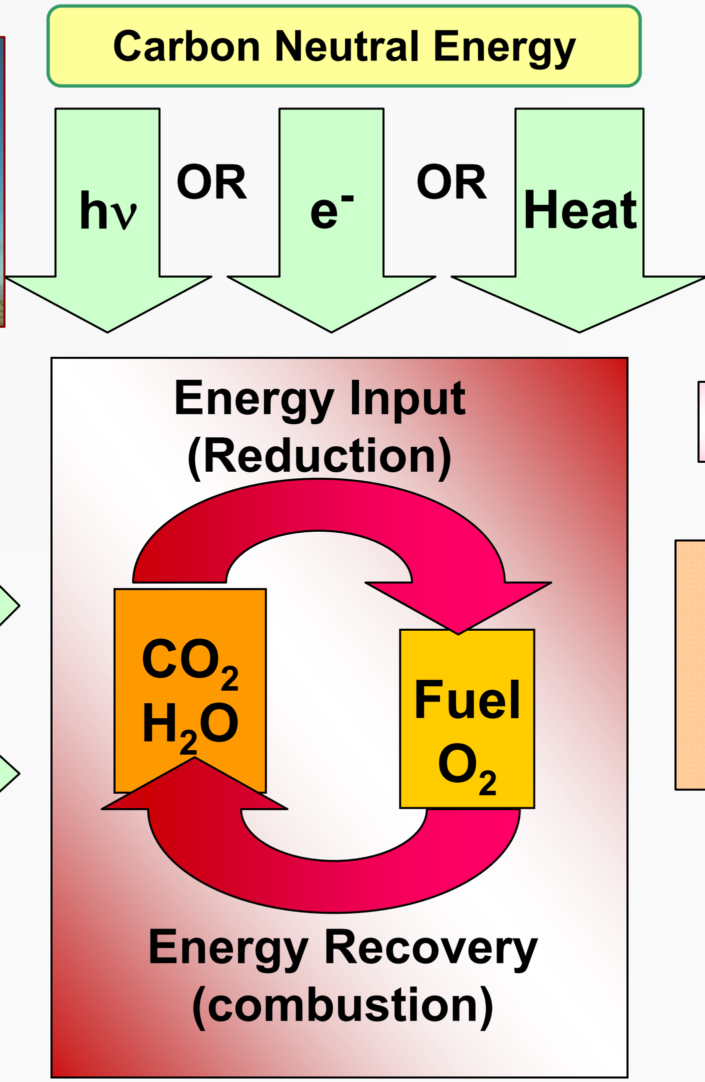


- Energy Density
- Infrastructure
- Fueling Rate
- Airplanes
- Heavy Duty Vehicles

Fuel	Energy/ Mass	Energy/ Volume
Gasoline	1	1
Li Ion Battery	0.019	0.035

For the foreseeable future & for transportation fuels, liquid hydrocarbons are the "Gold Standard" will not run out anytime soon, although "peak oil" implies demand might soon exceed supply – makes a fungible alternative very attractive

CO_2 to Fuels "Black Box"



Electro-Chemical
Photo-(Electro)-Chemical
Thermo-Chemical
Catalytic
Bio-chemical

Direct Chemical Routes

Capitalize on decades of Synfuel technology, e.g.

$$CO + 2H_2 \rightarrow CH_3OH \rightarrow C_2H_6O(DME) + H_2O$$

Focus on the critical conversions:

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

$$CO_2 + \text{energy} \rightarrow CO + \tfrac{1}{2}O_2 \text{ (carbon dioxide splitting)}$$

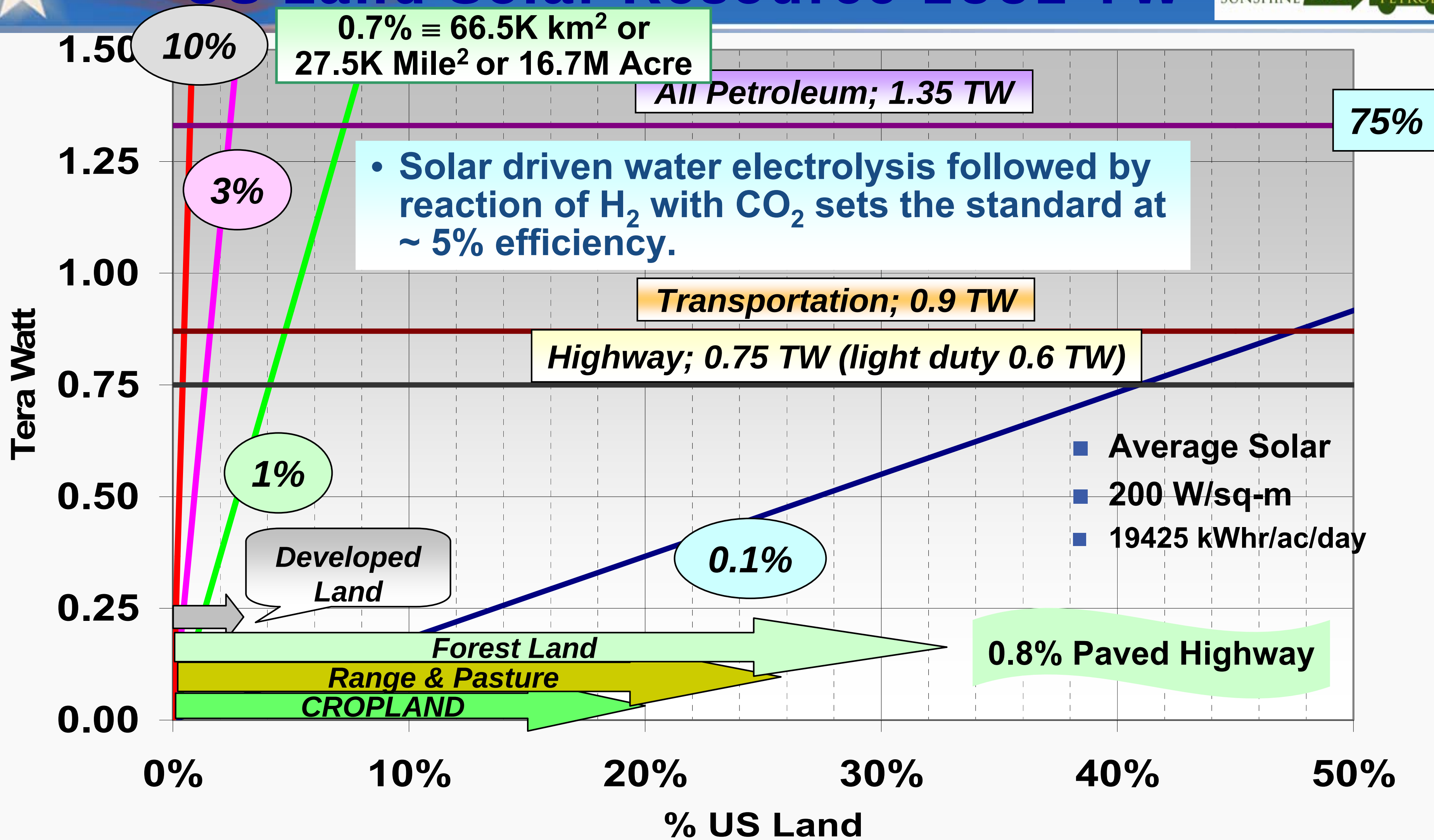
$$CO_2 + 2H_2O + \text{energy} \rightarrow CO + 2H_2 + {}^3/_2O_2$$

Note that WS and CDS are linked by the Water Gas Shift reaction

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

Only <u>required</u> to carry out one reaction - WS or CDS

Efficiency Matters: US Land Solar Resource 1832 TW



9.2M km² or 2.3 Giga Acre or 6% of the ~150M km² world-wide

What are Efficiencies of Some Solar Fuels

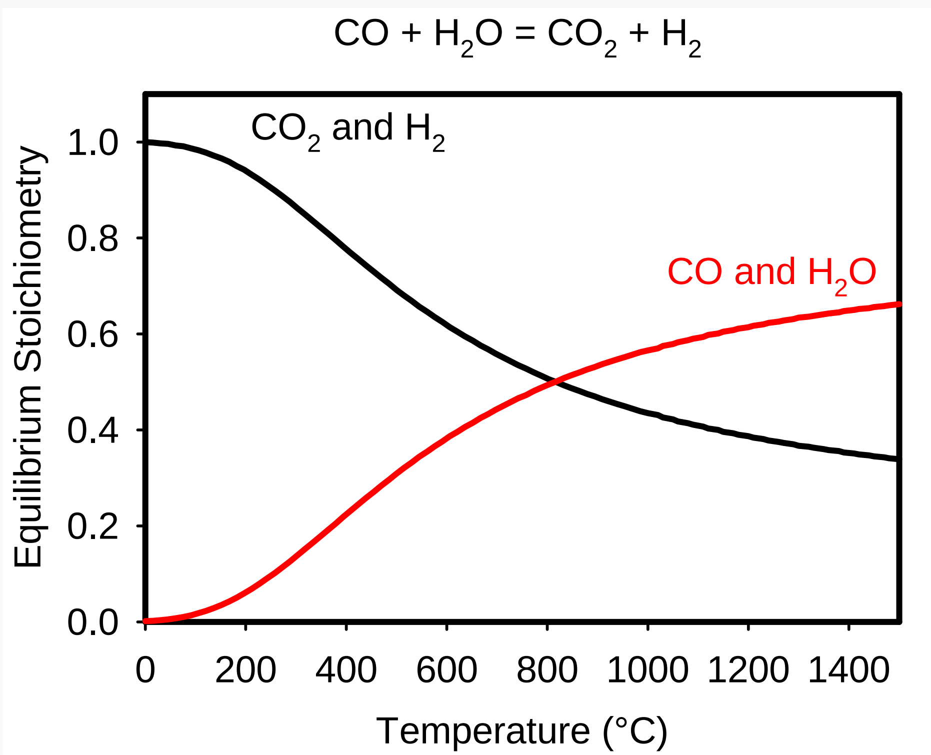
SUNSHINE 2 PETROL

Average Solar 1.35 TW Petroleum Consumption	HC Produced	Energy Flux	Efficiency	Land	% US
	kG/ac/day	kWhr/ac/day	%	Giga Acres	%
Petroleum [1] Stored Sunlight, Sequestered Carbon	3.3×10^{-3}	0.04	2×10^{-4}	833	368
Corn-based Ethanol [2] (Solar only)	3.53	26.25	0.14	1.25	55
Algae Crude [3] (Solar only)	52.5	569	2.9	0.057	2.5
Sunshine to Petrol [4] (lifecyle target)	155.4	1942	10	0.017	0.7

[1] JEFFREY S. DUKES, *Climatic Change* 61: 31–44, 2003.
[2] Based on the 2008 USDA-NASS corn yield of 153.9 Bushel/acre/yr and 2.8 Gallon Ethanol/Bushel
[3] WEYER, K., "Theoretical Maximum Algal Oil Production," 2008 Algae Biomass Summit, Seattle, WA
[4] S2P is a Target Efficiency counting all energy inputs

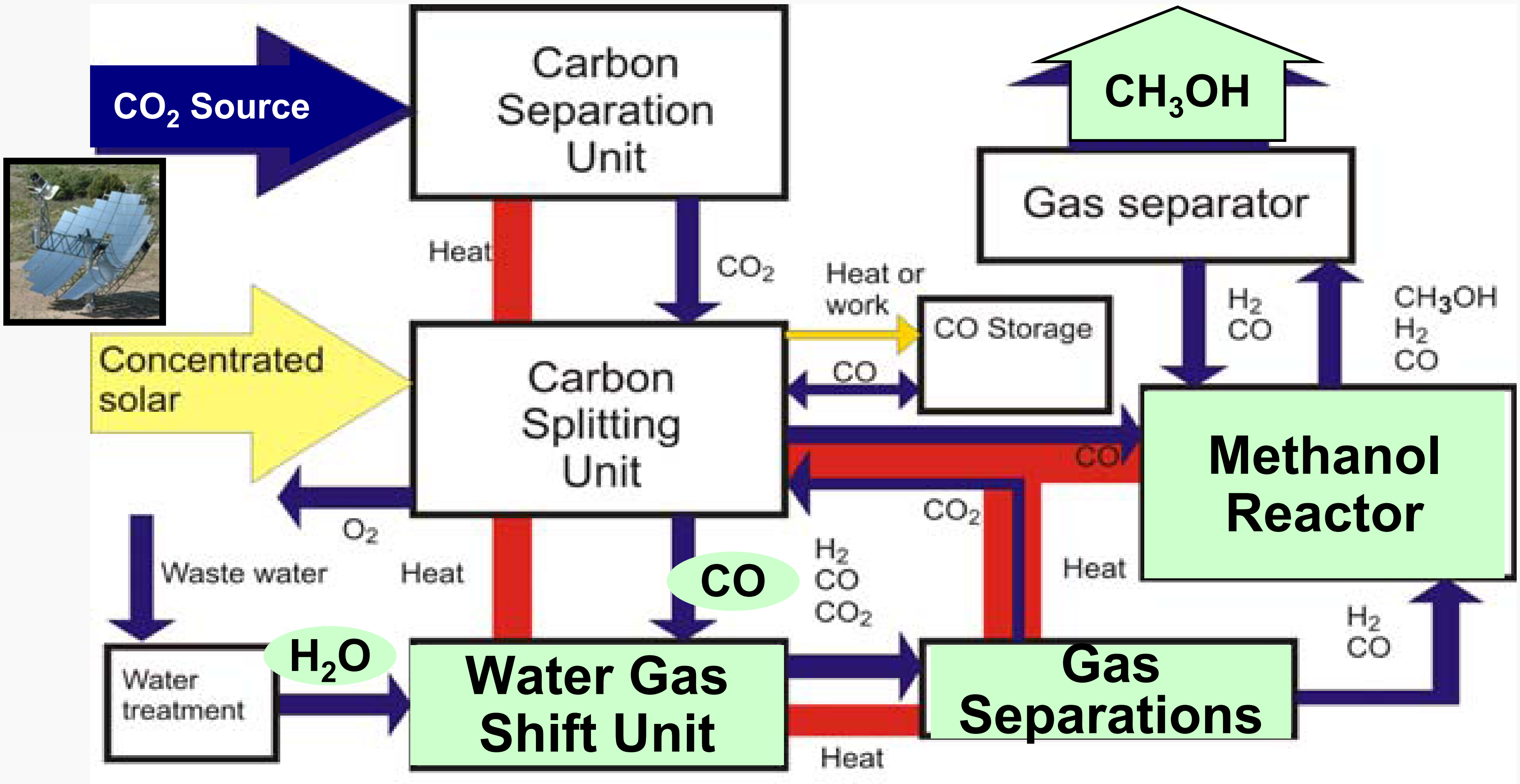
Setting the Standard: The Electrochemical Option

Efficiency	Electrical (%)	H_2 (%)	Elec. to Fuel (%)	Sun to Fuel (%)
PV	10-15	65-75	35-50	3.5-6.5



Limiting factors include photon to electric conversion and thermodynamics (RWGS).

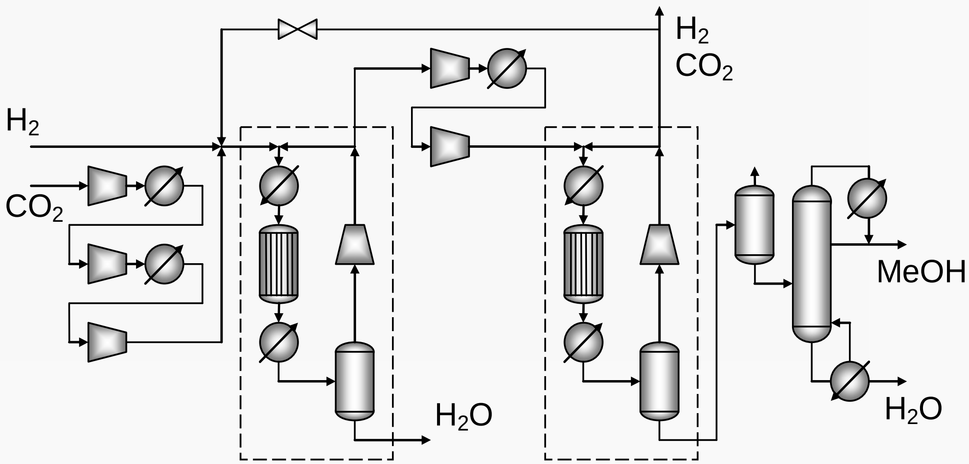
S2P System Concept



This represents one possible S2P configuration.

Preliminary Results Indicate Significant Benefit for Methanol from CO & H_2O

Methanol from H_2 and CO_2

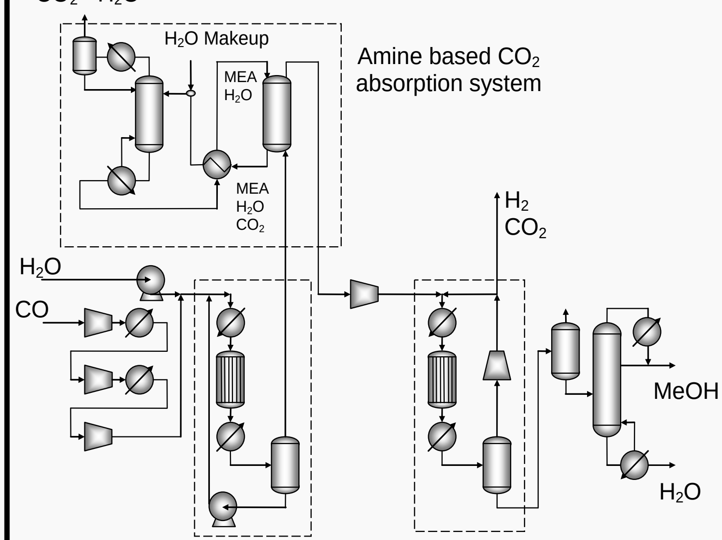


Reverse WGS reaction loop

Methanol synthesis reaction loop

49% ***energy efficient***

Methanol from H_2O and CO



WGS reaction loop

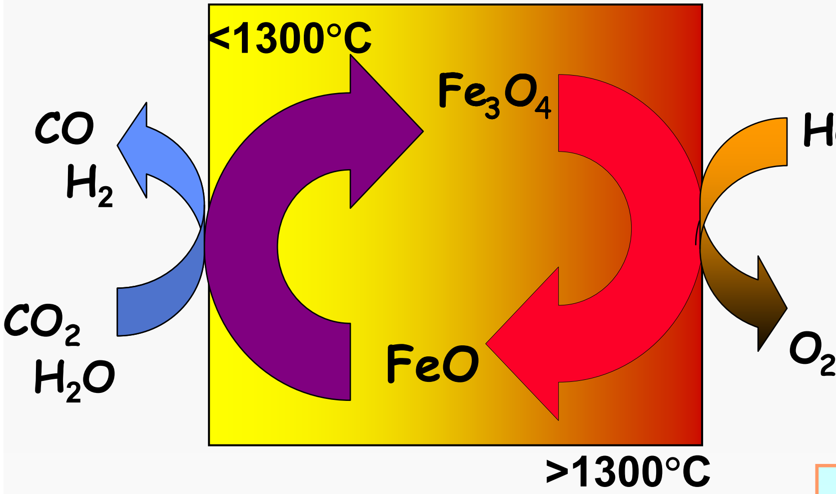
Methanol synthesis reaction loop

62% ***energy efficient***

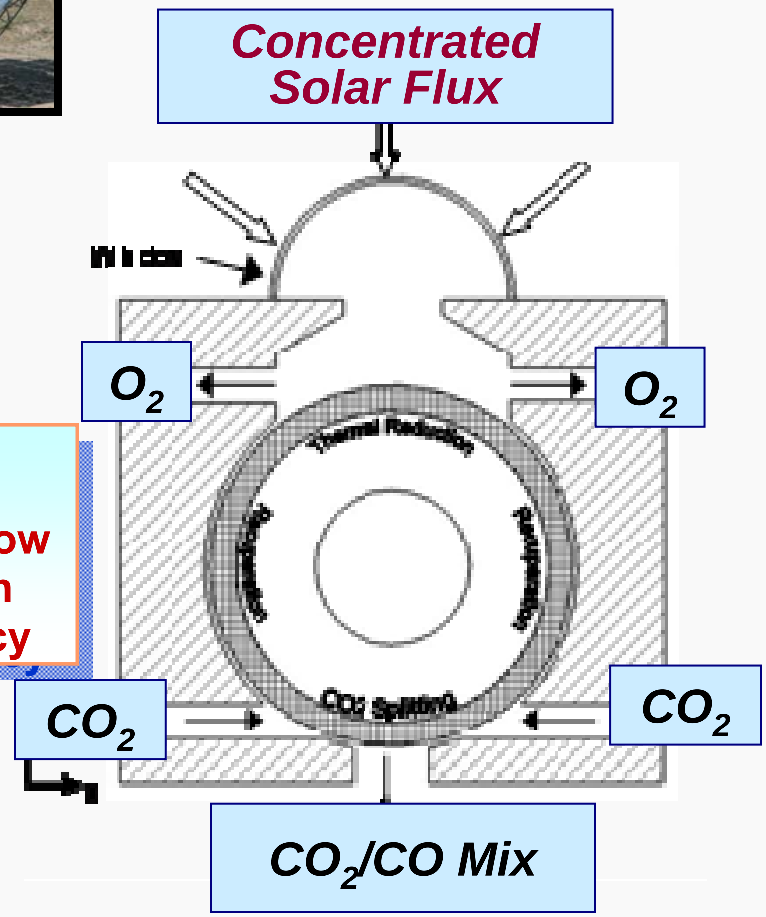
$$Efficiency = \frac{Methanol}{Feedstock + Process}$$

Henao, Maravelias, Miller and Kemp, to be presented @ FOCAPD 2009.

Thermo-Chemical Splitting



Cross-Section Illustration



Reaction Separation
Continuous Flow
Recuperation
High Efficiency

Two step solar-ThermoChemical process based on iron-oxide to split CO_2 (or H_2O):

1) Fe_3O_4 + Heat $\Rightarrow$ 3FeO + ½ O_2

2) 3FeO + $CO_2 \Rightarrow Fe_3O_4$ + CO

Net: $CO_2 \Rightarrow CO + ½O_2$
Similarly $H_2O \Rightarrow H_2 + ½O_2$

Program Structure

Overall
Baseline with known materials, Understand and Develop Models & Improve Efficiency Durability Manufacture Economics

University Contracts
Add Strength, Fill Gaps Extend Breadth Build Allies

Reactor Modeling
Create & Validate Predictive Models at a range of scales

Thermo-dynamics & Kinetics
Determine & Quantify

Integrated Systems
Design Tool for System's Performance & Economics What if's Separations

Reactor
Demonstrate Proof of Concept Baseline Performance Refine Design to Improve

Bulk & Surface
Observe & Quantify Critical Processes @ the Atomic Scale

Reactive Structures
Design for Performance, Fabrication & Demonstrate Durability Milestone

Reactive Materials Design
Performance (chemical) Screen, Understand, Find New

Designed to meet challenges in the areas of materials, reactor design, and systems. Any breakdown tends to obscure the large degree of connectedness within and between the three focus areas.

Basic Thermodynamics Reveals that Recuperation is Key

Diver, et al - Journal of Solar Energy Engineering November 2008, Vol. 130

Assumptions

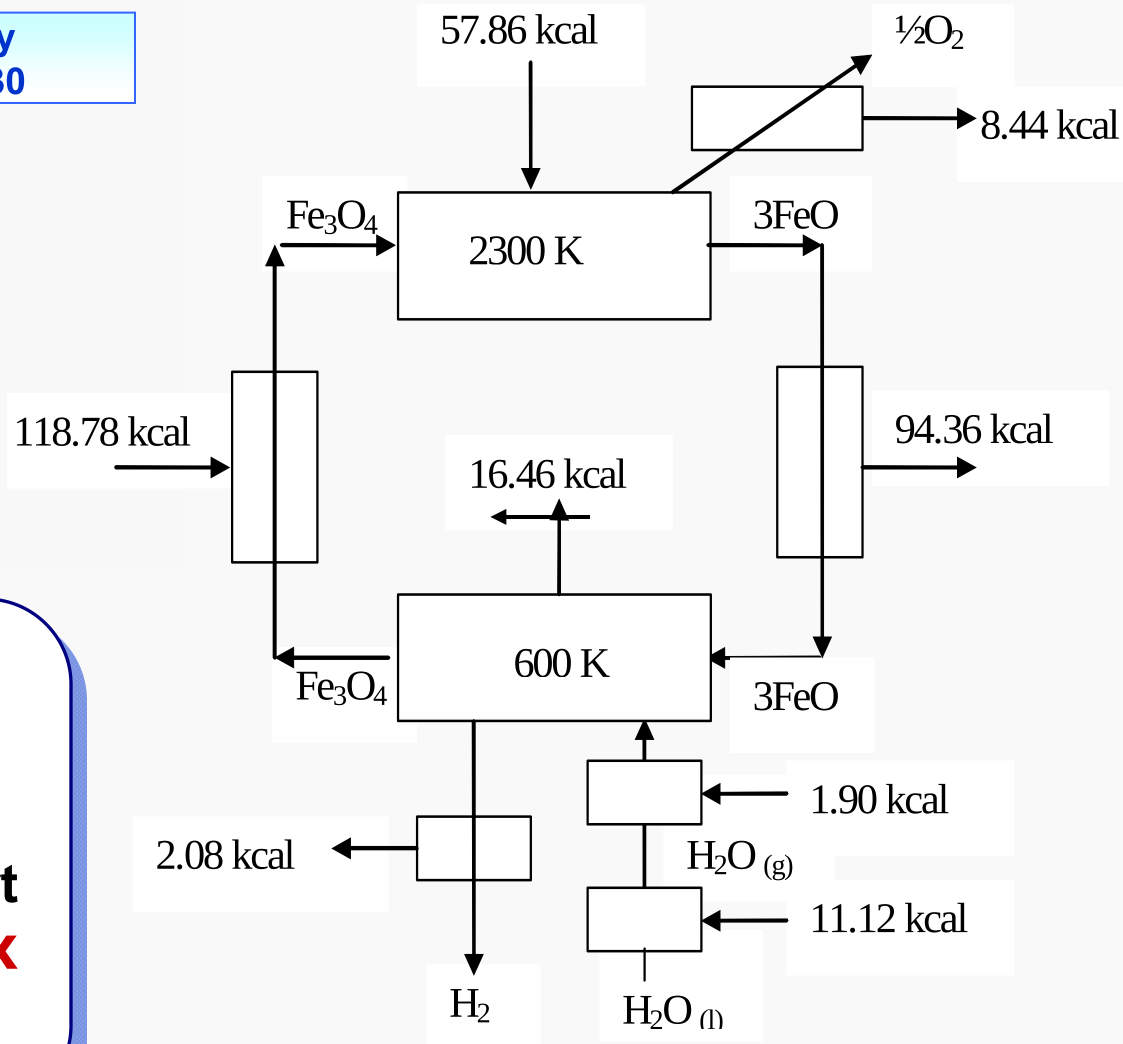
- 100% reaction extent magnetite to wustite and reverse
- Pure iron oxide material. No support such as YSZ

Without Recuperation max efficiency = 36%

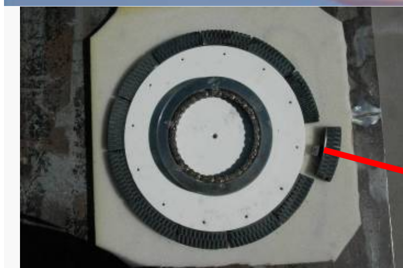
Less if Reaction Extent <100%

Even less with inert support

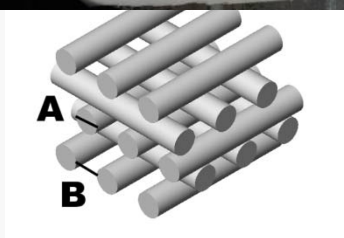
With Recuperation max efficiency = 76%

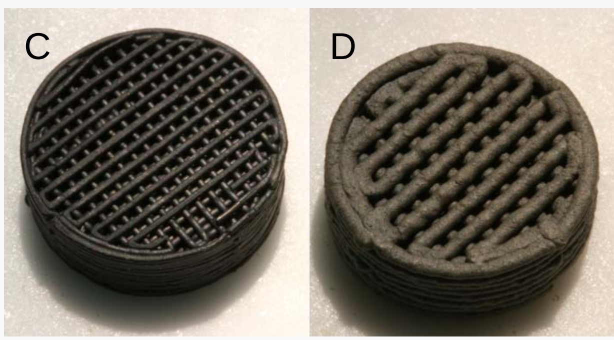


From Powders to Parts

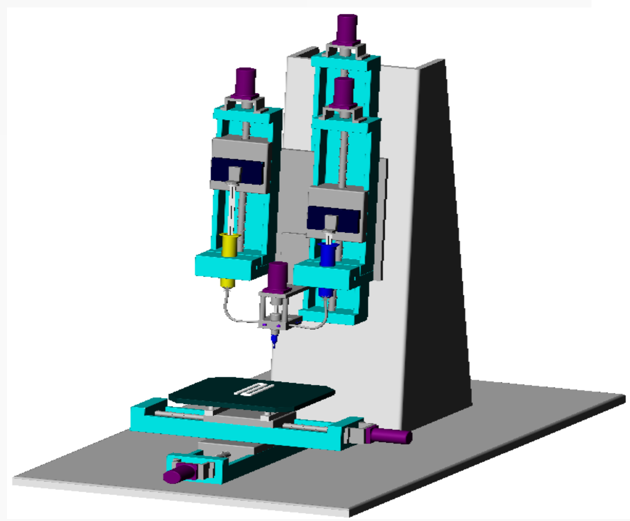


- Direct fabrication of high surface area geometries.
- Avoid degradation via chemical and mechanical mismatch.
- Kodama (Niigata Univ,) Tamaura (Tokyo Institute of Technology) showed the way by mixing powders with Zirconia
- Dense $Co_{1-x}Fe_{2+x}O_4$/YSZ (1:3) Monolith

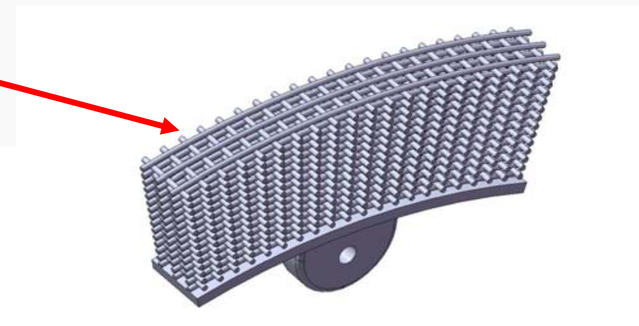


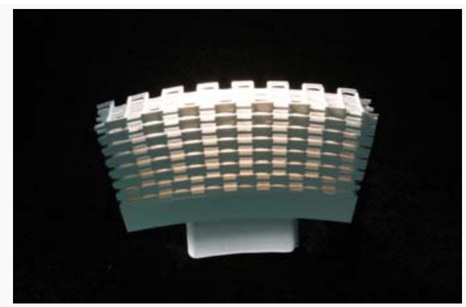


Laboratory test pieces



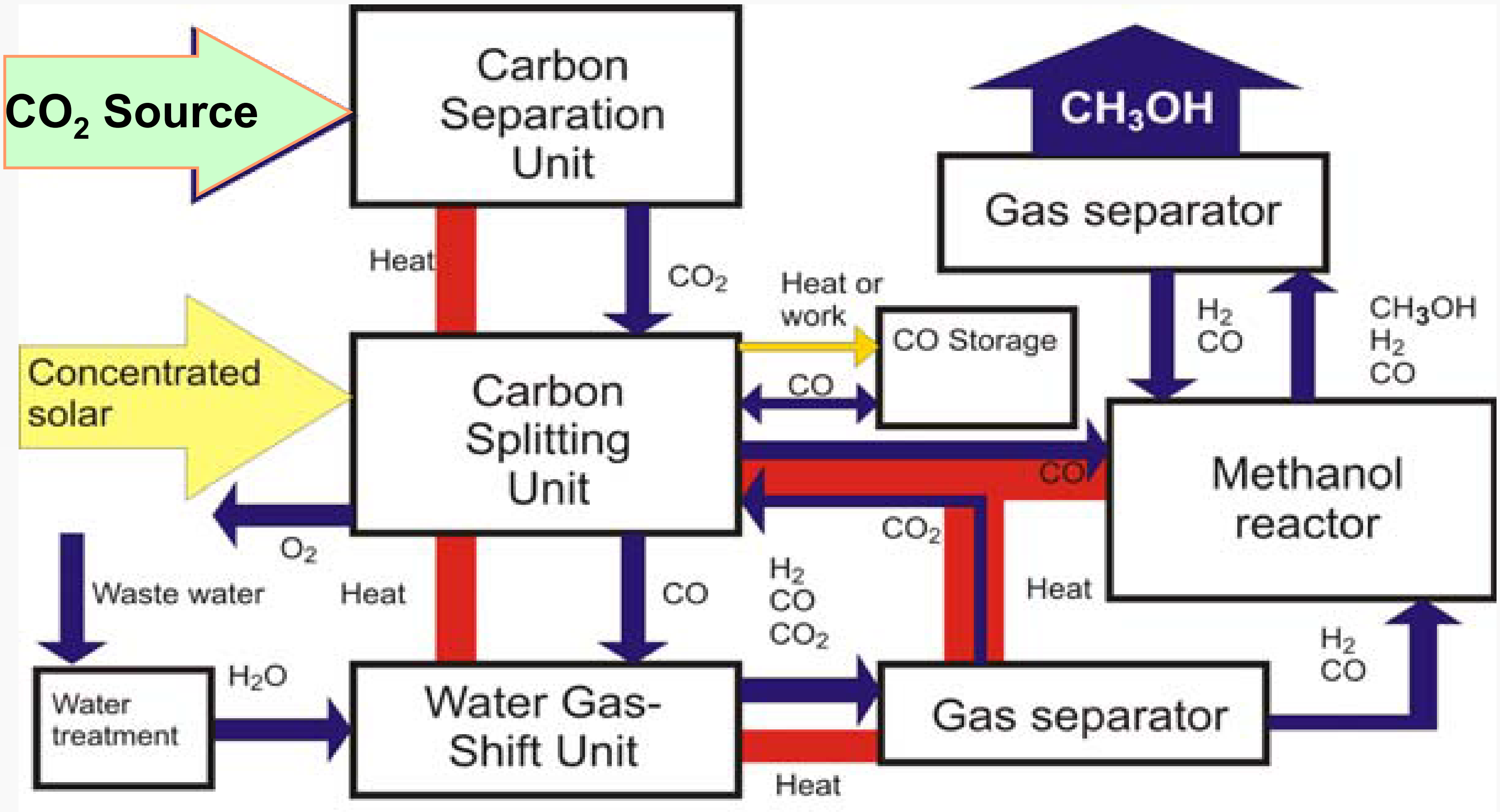
Cesarano, J. III and Calvert, P., "Freeforming Objects with Low-Binder Slurry," US Patent No. 6,027,326.





Open structure provides effective light penetration

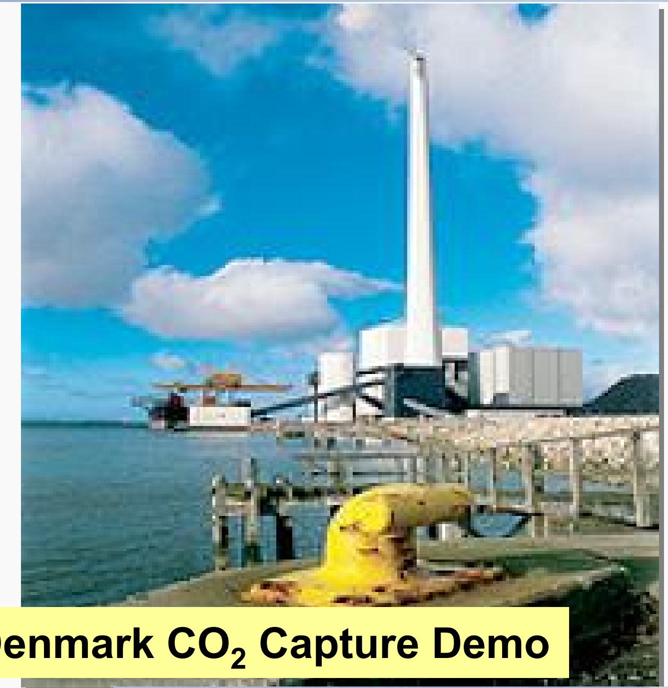
S2P System Concept



CO_2 Capture from Air

- **Two major possibilities**
  - √Capture it at the source (initially)
    - Most practical for stationary sources, e.g. flue gas
    - Demonstrations now underway
    - Fermentation plants, biomass gasification
  - √**Not Necessarily Carbon-Neutral until we can remove it from the atmosphere**
    - Challenging, but not impossible
    - Potential to disconnect capture from source
    - Not yet demonstrated at scale or in field
    - \$50-75/Tonne CO_2 ~\$0.44-66/gallon

Air Capture is a Hard Problem Outside the Direct Focus of S2P, but not an obvious cost or energy show-stopper



Denmark CO_2 Capture Demo

Synthetic Trees Concept, based on Klaus Lackner

A Word About Capture of CO_2 from Air

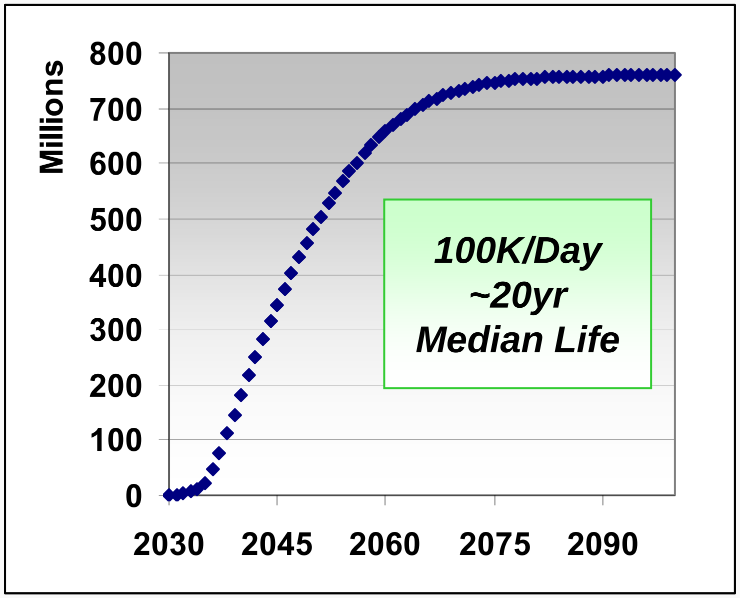
Capture Effectiveness	Air Flux		Collector Cross-Sectional Area	Equivalent Power	Equivalent Power from Wind
	mph	m/sec	Acres	GWH/ac/da	MWH/ac/da
20%	5	2.2	72242	0.44	0.39
20%	10	4.5	36121	0.89	3.14
50%	5	2.2	28897	1.11	0.39
50%	10	4.5	14448	2.22	3.14

To Capture 3 Gt/year of CO_2 – enough to make 1.35 TW of stored energy in petroleum-like hydrocarbons

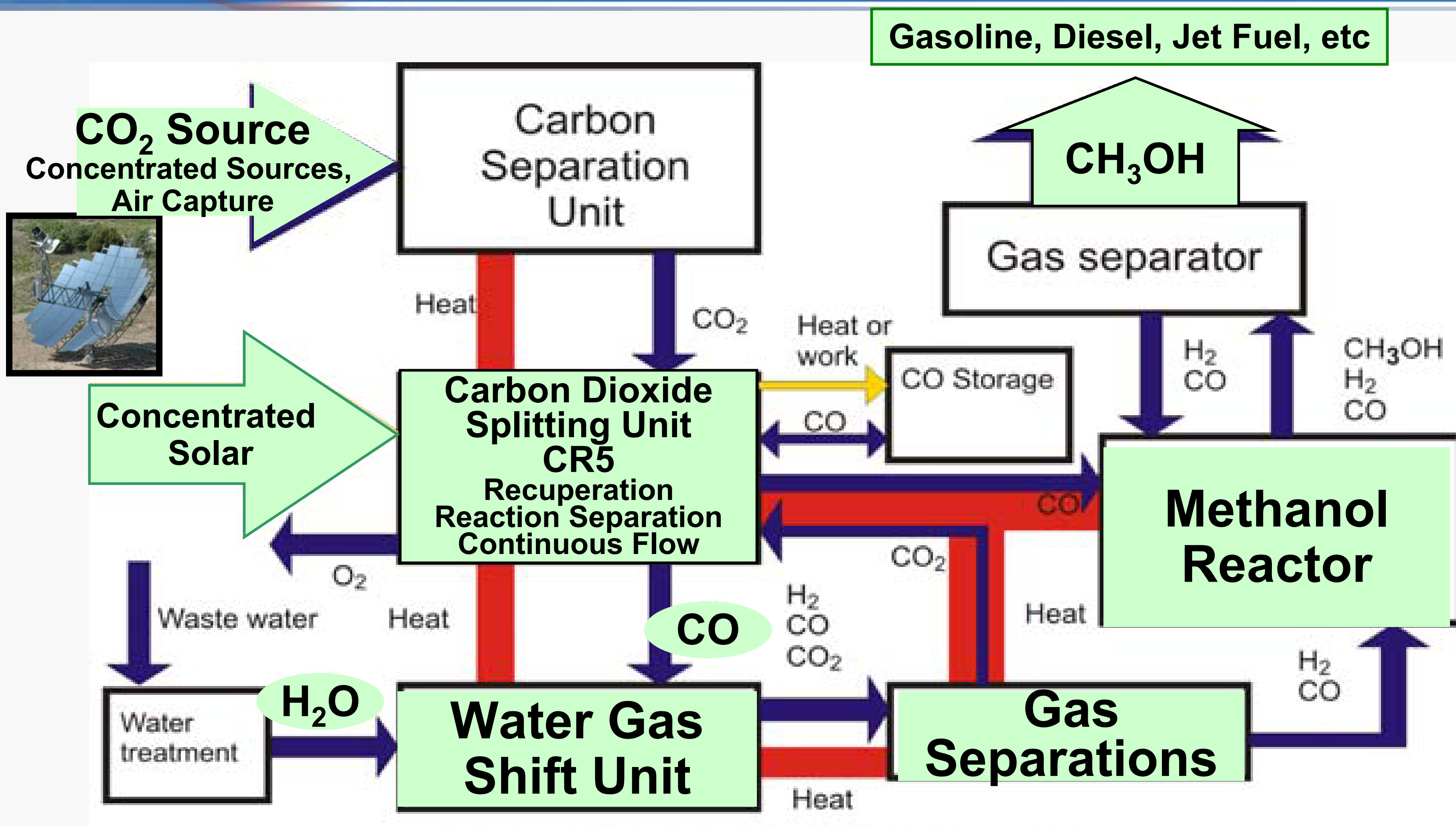
Scalability: No Obvious Show-Stoppers Land, CO_2, H_2O, Materials

- All Petroleum 1.35 Tera Watts
- 10% Solar to Fuels – 27.5K $Mile^2$
  - ~750 M Solar Dishes (88 $Meter^2$)
  - Average ~30K/Day from 2030-2100
  - ~100K/Day with Replacement; if ~20yr median lifetime
    - Comparable to the current capacity to make automobiles in the US (~40K/Day)
    - 6-20x the number of residential buildings per year
- 3 Giga Tonne CO_2/Year
  - 20% capture from Air, <Air Speed> = 5 mph
  - ~113 $Mile^2$ of capture media or ~73M 4 $Meter^2$ Units
    - Average ~32K/Day from 2030-2100 if ~5yr median life
- ~825 Billion Gallons H_2O/Year or 2.26B Gallons/Day or 7.5 Gallon/Capita/Day
  - Average Urban Water Use ~160 Gallon/Capita/Day
  - Total US Consumption ~1360 Gallon/Capita/Day

The Metrics that will Matter
Efficiency, Durability, Manufacturability, Economics, and SCALABILITY



S2P System Concept



Challenges in Thermo-Chemical Reduction of CO_2 to CO

- Extreme environments
  - High melting temperatures, low cation volatility, resistant to thermal shocking, small volumetric changes with temperature or phase, compatibility with other materials
- Thermodynamics requires cycling between two temperatures
  - Recuperation is critical
- Thermodynamics favorable for reduction and oxidation
  - At reasonable temperatures that couple with the energy source
- Efficient Separations
- Activity over 10^5 cycles without intermediate processing
- High Surface areas or Facile Bulk Transport
- Fast Kinetics
- Cost, Cost, Cost

Summarize What's to Like About Thermo-Chemistry

- **Thermo-chemistry is a promising alternative to electrolysis**
  - Underexplored, materials science understanding minimal at best
- **Energy management is key (high efficiency, recuperation).**
- **Ferrites Show Promise as the "working fluid"**
  - Thermodynamics, Repeatability, Fabrication reasonable.
  - Reaction Rates could use improvement (Surface).
  - Materials Utilization could be improved (Bulk Transport).
  - Processes are a lot more complex than discussed here.
- **CO_2 splitting has apparent advantages over H_2O in the targeted temperature range.**
  - The targeted temperature range is in the "sweet spot" for coupling to concentrated solar technologies.
- **Wide range of mixed-metal oxides to explore,**
  - Using predictive simulation to find promising leads.
- **It is a worthy challenge and "game-changing" if successful**

Thank-you for your Attention

I Welcome Your Questions