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Redox-Active Metal Oxide-Based Solar Thermochemical Fuels

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30 June 2016

ASU LightWorks
ARIZONA STATE UNIVERSITY

*ASU campus wide initiative on light inspired research for energy and sustainability

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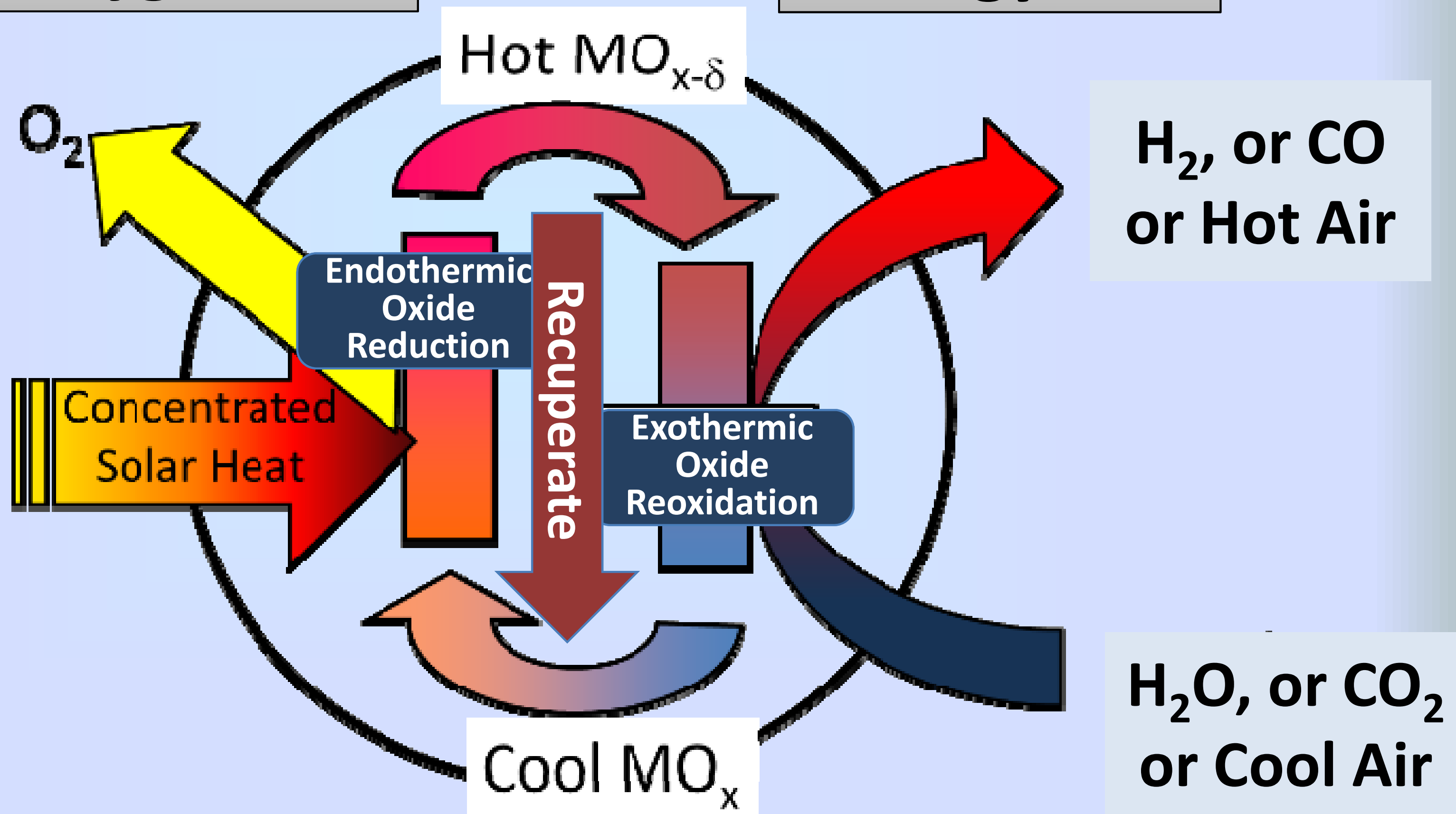
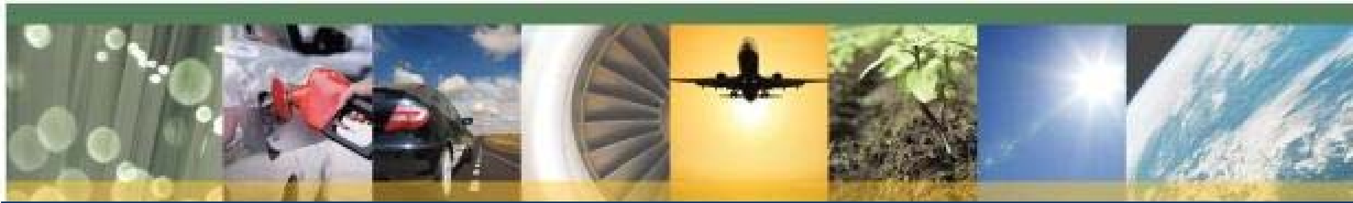
Metal oxide thermal redox chemistry

Energy in, Oxygen out

Oxygen in, Energy out



Materials, Reactors, and Systems Challenges to operationalize the cycle



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Solar thermochemical CO_2 and H_2O splitting with redox active metal oxides

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

$$MO_{x-\delta} + H_2O \rightarrow MO_x + H_2$$

$$MO_{x-\delta} + CO_2 \rightarrow MO_x + CO$$

Reduction on Sun

$$O_{(s)}^{-2} \leftrightarrow 2e^{-}_{r,(s)} + \tfrac{1}{2} O_{2,(g)}$$

Re-oxidation off Sun

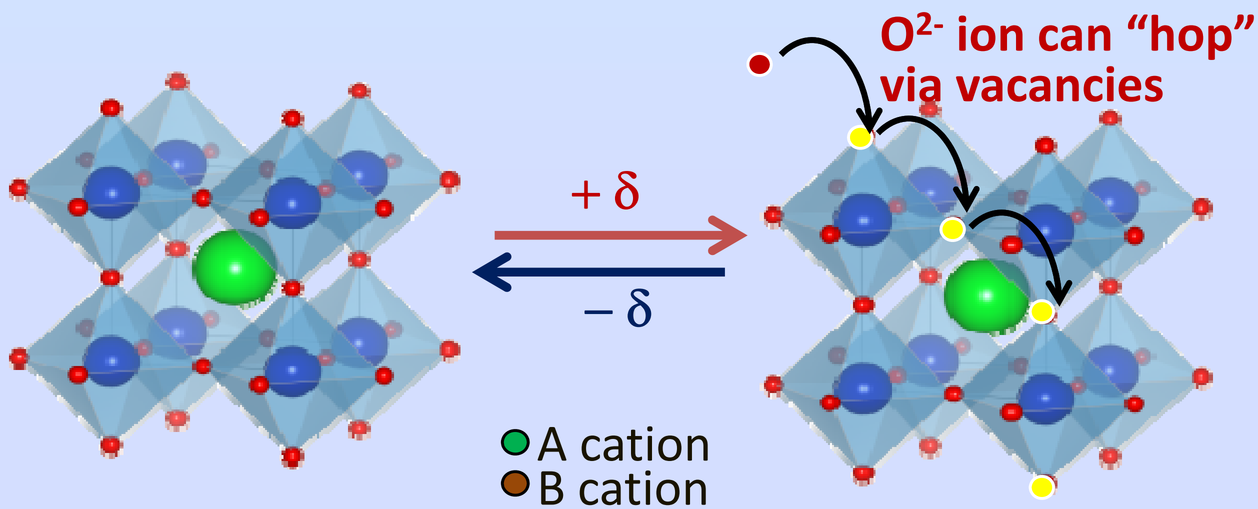
$$2e^{-}_{r,(s)} + CO_{2,(g)} \leftrightarrow O_{(s)}^{-2} + CO_{(g)}$$

$$2e^{-}_{r,(s)} + H_2O_{(g)} \leftrightarrow O_{(s)}^{-2} + H_{2,(g)}$$

(Co) Design of materials for the operating space

- Mixed Ionic-Electronic Conducting (MIEC) Perovskites oxides have several properties of significance: high temperature stability, redox-active (**like charging a battery**), and phase "stable"
  - $ABO_{3-x} \leftrightarrow ABO_{3-x-\delta} + \delta/2\ O_2(g)$
  - Continuous reduction reaction allows storage/extraction of heat at high temperatures

- **No major crystallographic phase change occurs during redox**
- **Vacancies facilitate oxide ion transport**
- **Redox activity is continuous over a range of T and pO_2**
- **SOA is Ceria CeO_2**



A cation
B cation
Oxygen anion
Vacancy on anion lattice

Like $SrTiO_3$ – not redox active.
$SrMnO_3$

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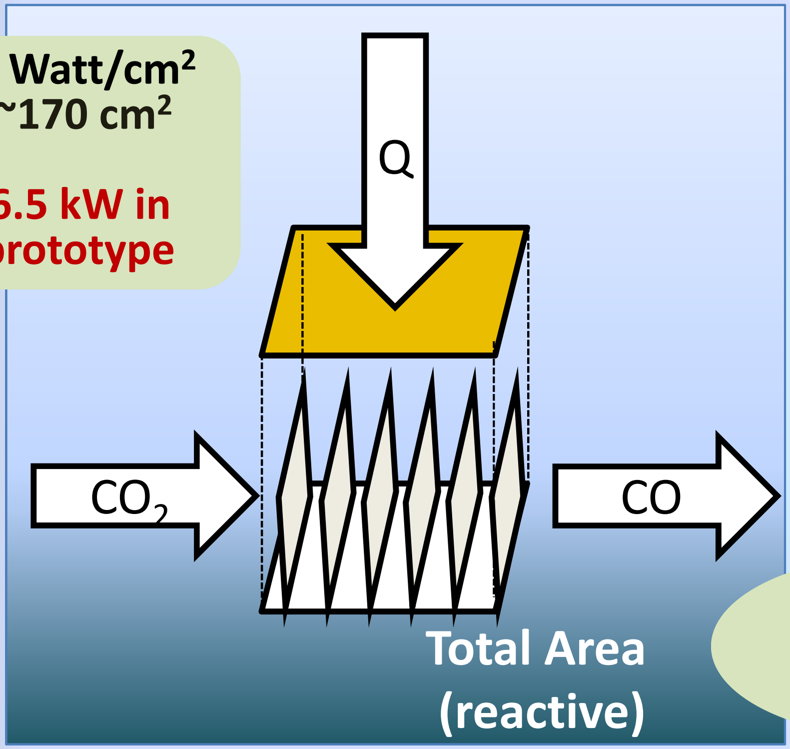
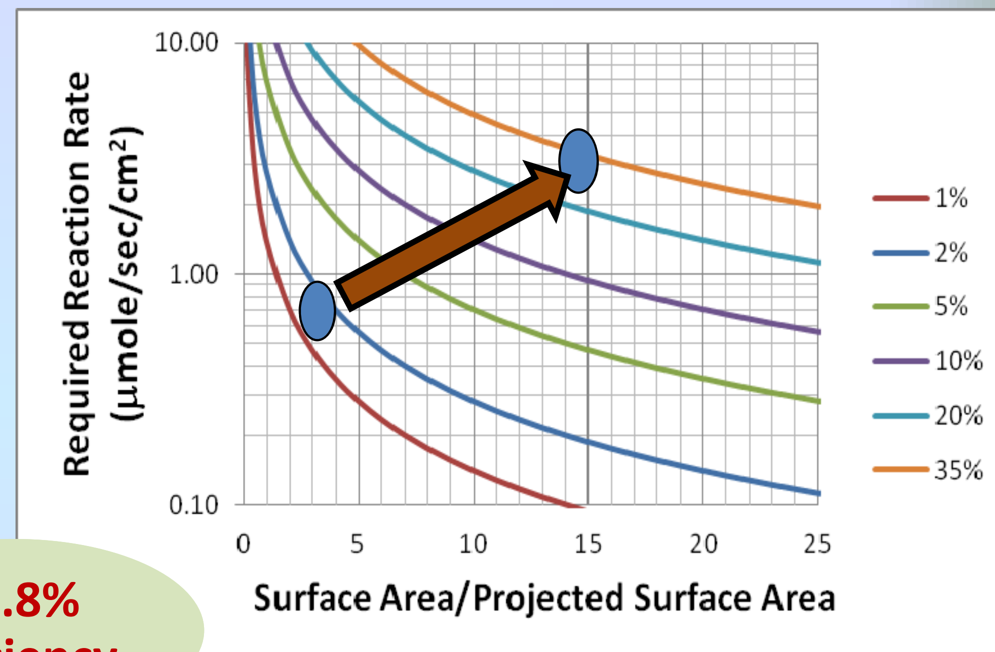
Efficiency is related to the reaction rate: must be able to keep up with solar flux

Q ~38 Watt/cm²
PSA ~170 cm²

Q ≅ 6.5 kW in the prototype



~1.8% Efficiency



- **Sandia's "Sunshine to Petrol" team demonstrated on sun 430 µmol/sec CO ≡ 116 Watt**
- **~470 g ceria (CeO_2) & SA~500 cm² SA/PSA ≈ 3 in the prototype**
- **0.86 µmol/sec/cm²**
- **~1 RPM ring rotation**
- **<1% CO flux to cerium cation flux means low utilization**

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High efficiency solar thermochemical reactor for hydrogen production Gen 3

<u>Planned Demo</u>

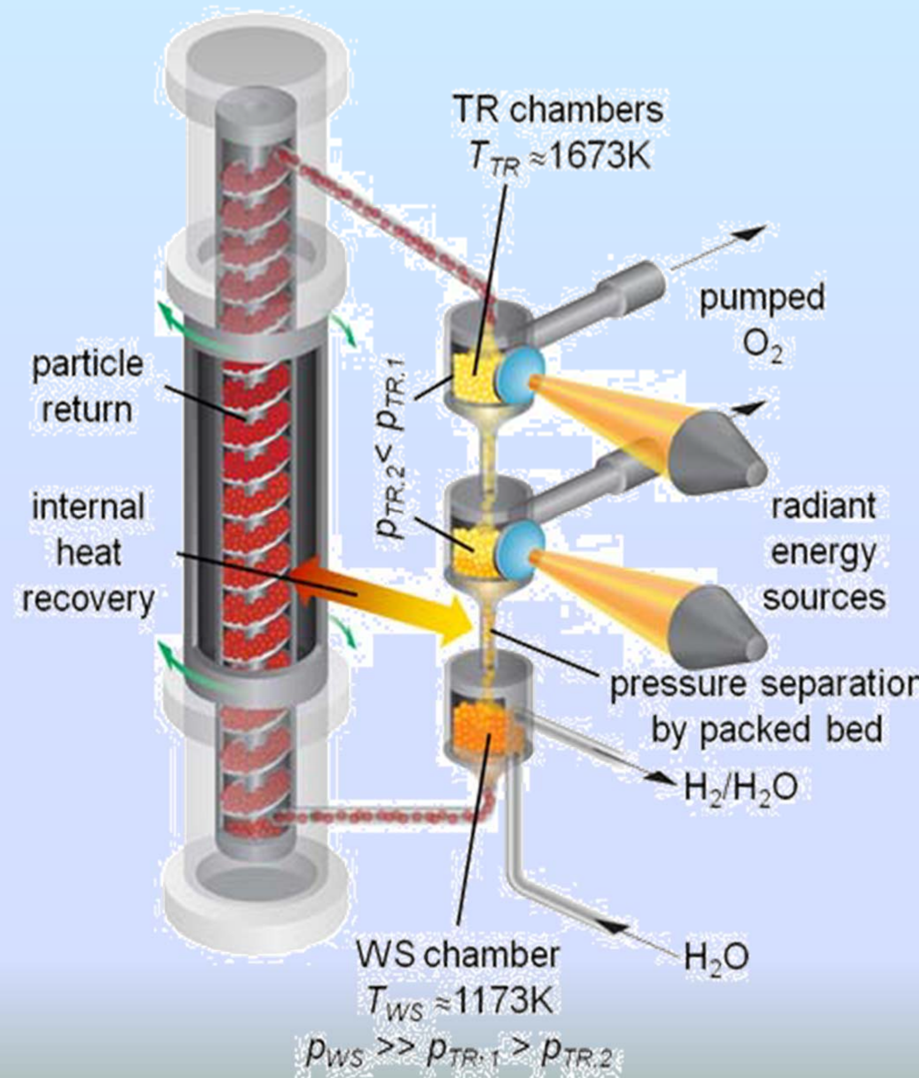
3 kW, 8 hours, or 86.4 MJ

> 3L H_2 or 38.3 kJ

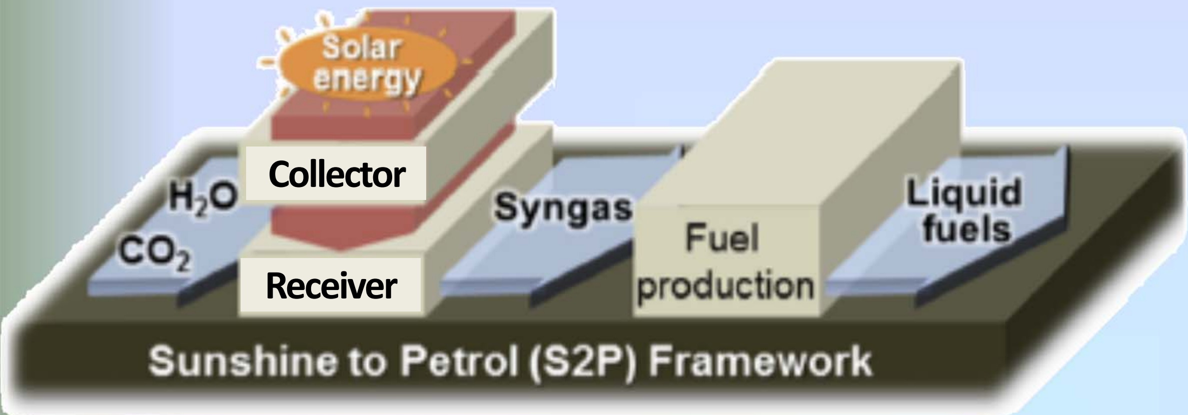
DOE FCTO Funded

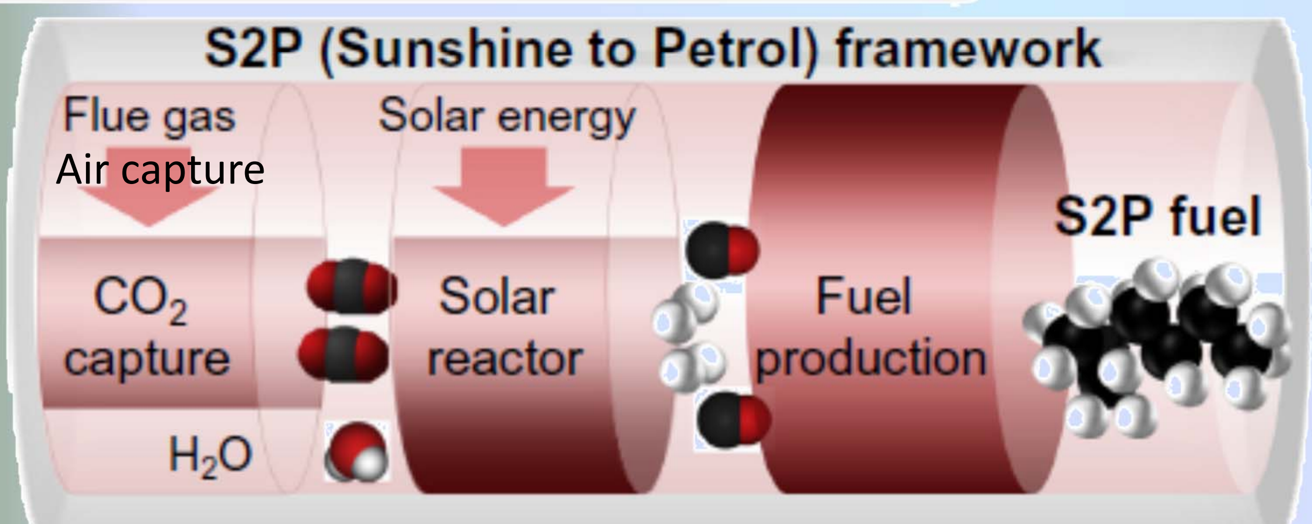
Roadmap projection to <$2.30/kg and >20%

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy



Can also make CO and therefore liquid hydrocarbons





Techno-economics
Lifecycle Analysis
No showstoppers but lots of challenges & opportunities

300 Barrels/day = 21.25 MW

- ~604400 m^2 mirrors
- @12.5% annual average and 6.75 $kWh/m^2/day$ sunlight
- ~2.4 km^2 Land Area & 25%
- ~6900 parabolic mirrors
- (88 m^2): Each ~7 Liter/Day
- ~10000 L/d Liquid (62 bpd) (@12.5%)

50000 kg H_2/day = 82 MW

- ~1.5 Million m^2 mirrors
- Small Towers 20-50 MW_{th}
- 4000-10000 kg H_2/day (@20%)

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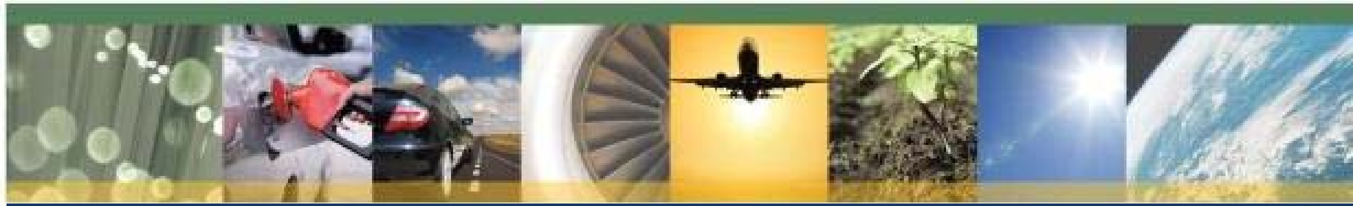
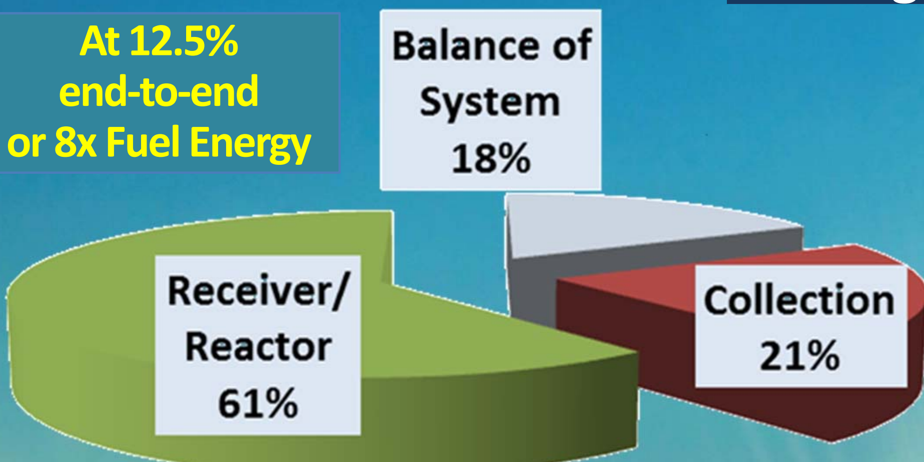


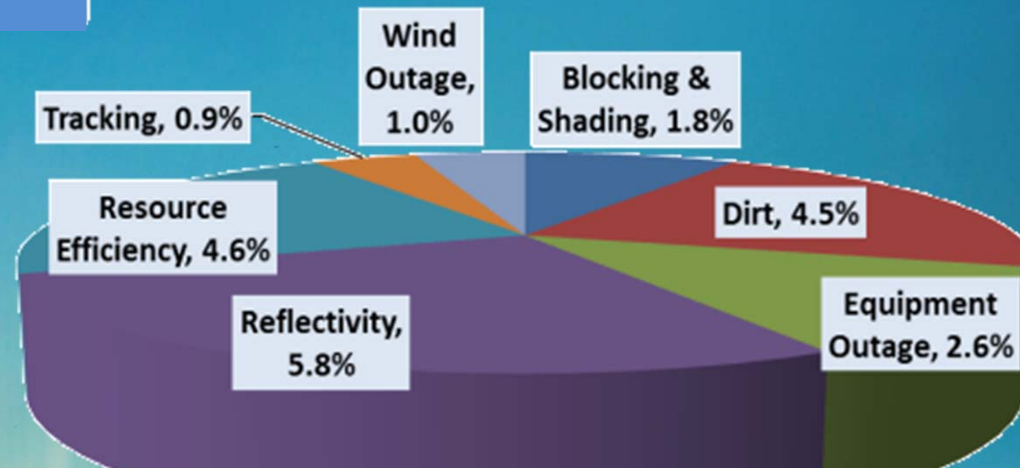
What is feasible?

Average end-to-end efficiency can be reasonably high

At 12.5% end-to-end or 8x Fuel Energy

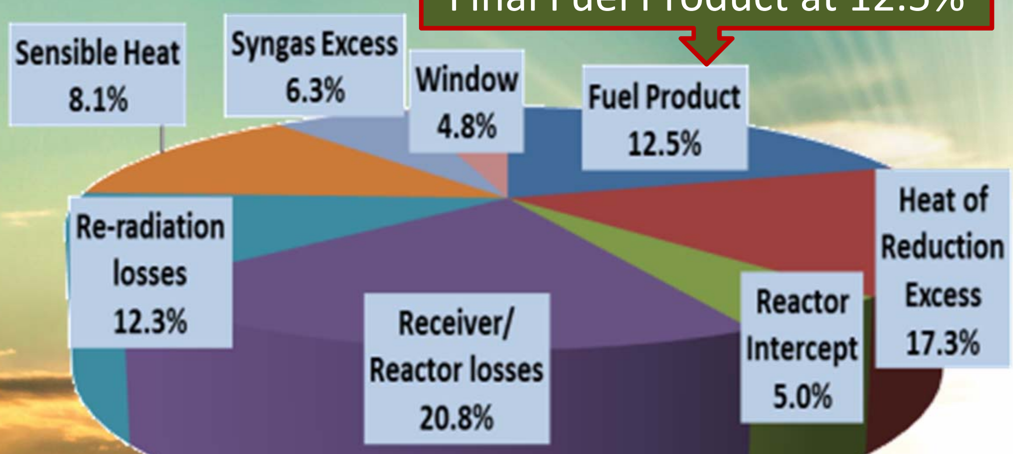


Full System

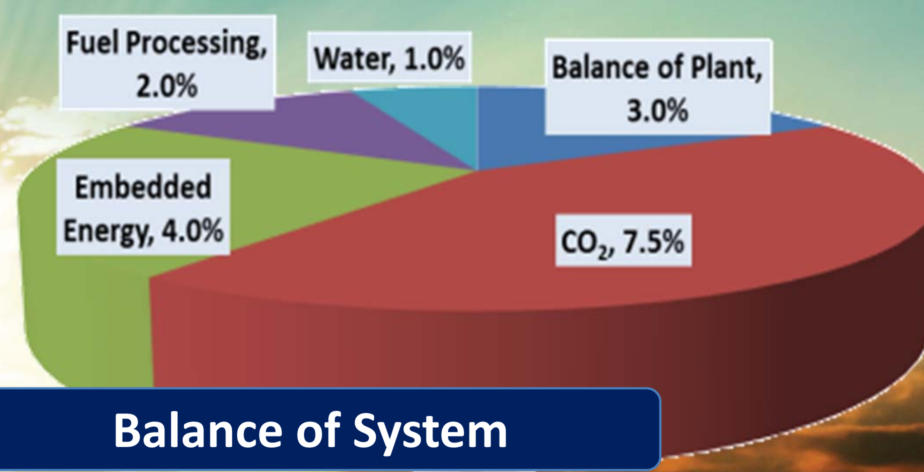


Collection: Common to all components if concentrated solar is the primary energy

Final Fuel Product at 12.5%

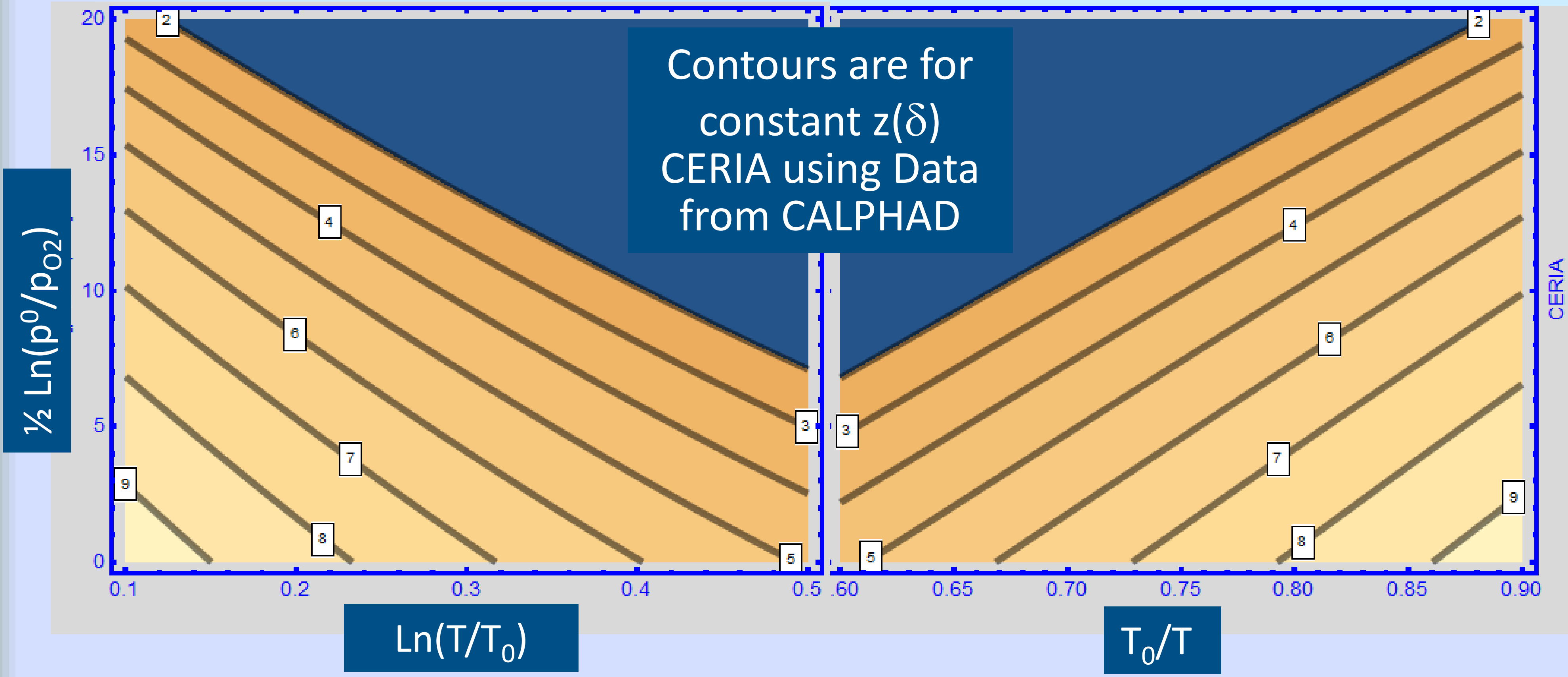


Receiver / Reactor: Produces Syngas



Balance of System

Fitted response surfaces and derivatives determine enthalpy and entropy of incremental reaction



Negative of the slope determines $\frac{\partial \Delta s(\delta;T)}{\partial \delta}$

Slope determines $\frac{\partial \Delta H(\delta;T)}{\partial \delta}$

9

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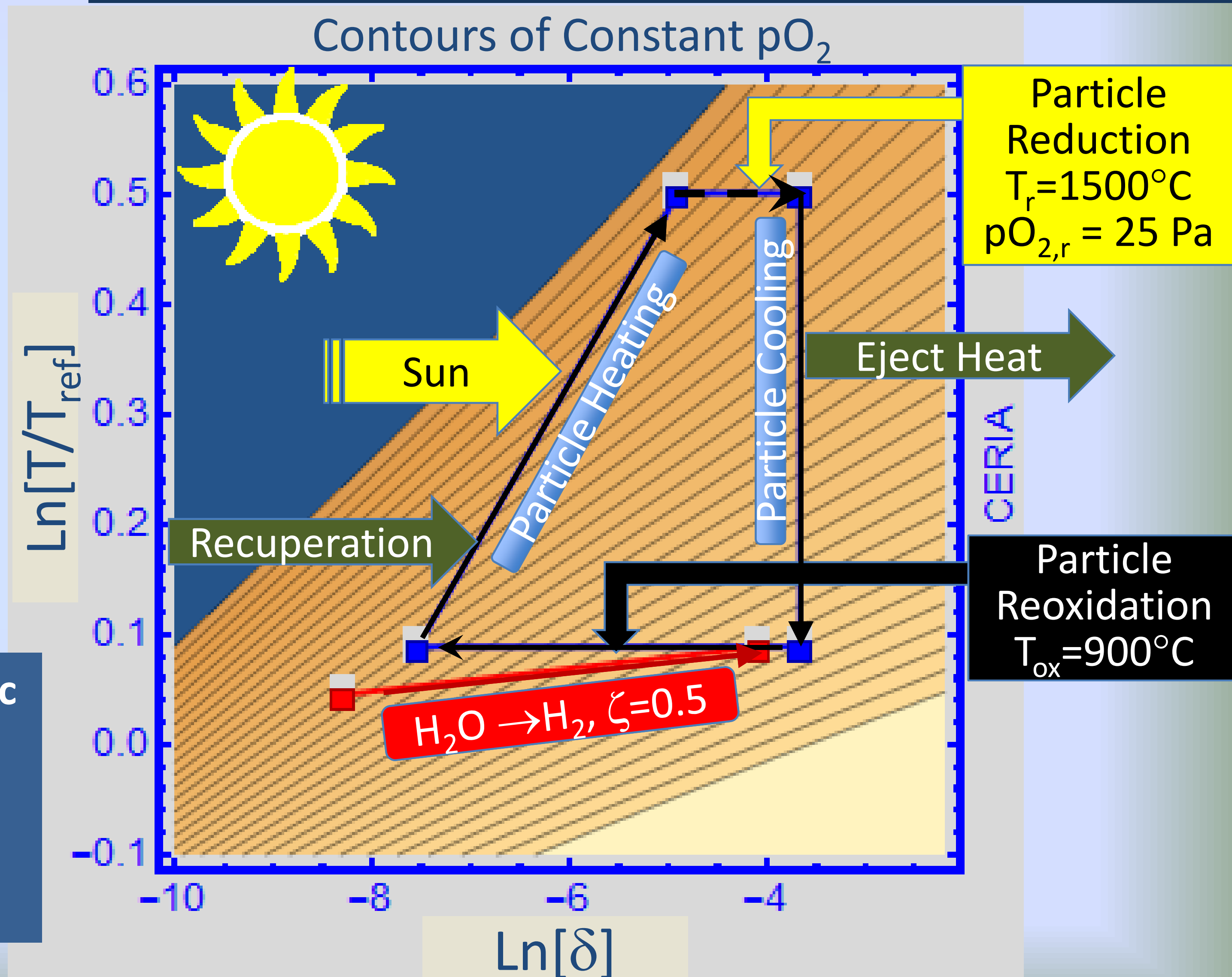
$$CeO_{2-\delta ox} \rightarrow Ce_{2-\delta r} + 1/2\,\Delta\delta\, O_2$$
$$\Delta\delta\,(\zeta+1)\, H_2O + Ce_{2-\delta r} \rightarrow CeO_{2-\delta ox} + \Delta\delta\,(\zeta\, H_2O + H_2)$$

Operating Variables

1. **Reduction Temperature, T_r**
2. **Re-oxidation Temperature, T_{ox}**
3. **Reduction Partial Pressure, $pO_{2,r}$**
4. **Excess H_2O, ζ**



Contours Materials Specific
5^k Pascal, $-22 \le k \le 8$
4×10^{-21} up to ~4 Atm
Tref = 800°C
Pref=0.21 Atm

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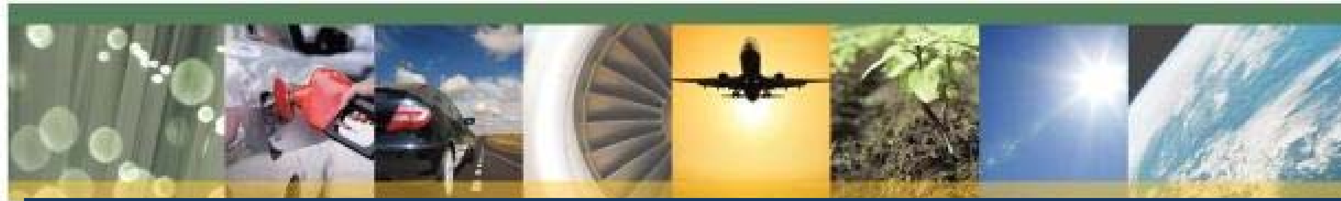
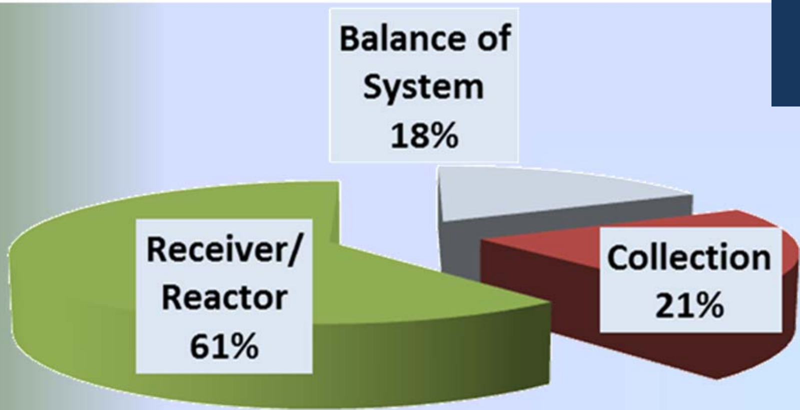
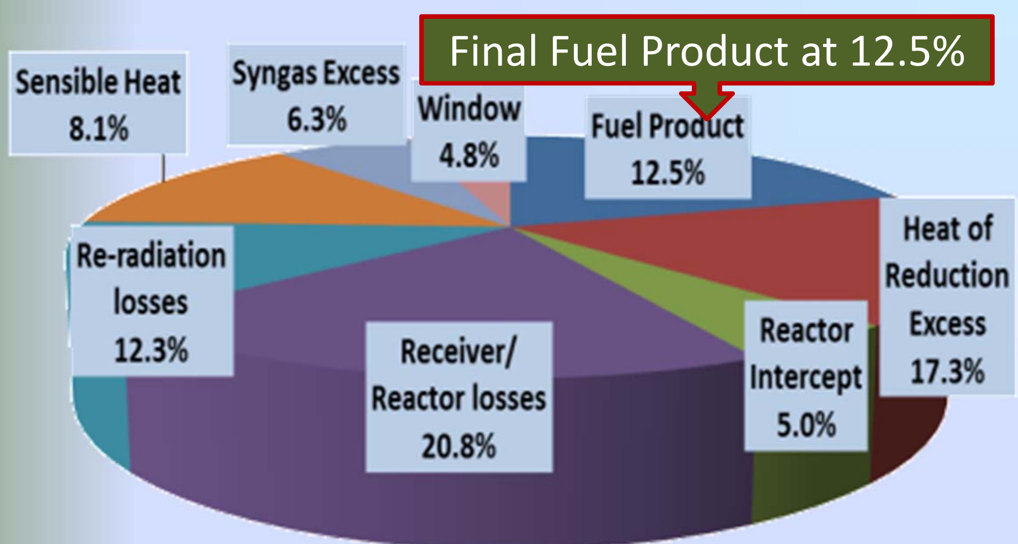


Achieving economics and scale on earth will require high efficiencies – are they achievable?



Could we imagine scaling up to 75M barrels of oil equivalent per day – 5.3 TW, 167.5 EJ/yr, ~64B GGE?

Embedded energy in the materials correlate with the mass of steel and concrete



Receiver / Reactor: Produces Syngas

<u>Conclusion:</u>

To achieve scale and reasonable economics ties to the efficiency

~12.5% life cycle sunlight to liquid HC fuel (8x sun energy to product energy)

<u>Still requires:</u>

Materials, reactor, and systems advances in design

On systems we are now focusing on co-producing fuel, electricity, and clean water

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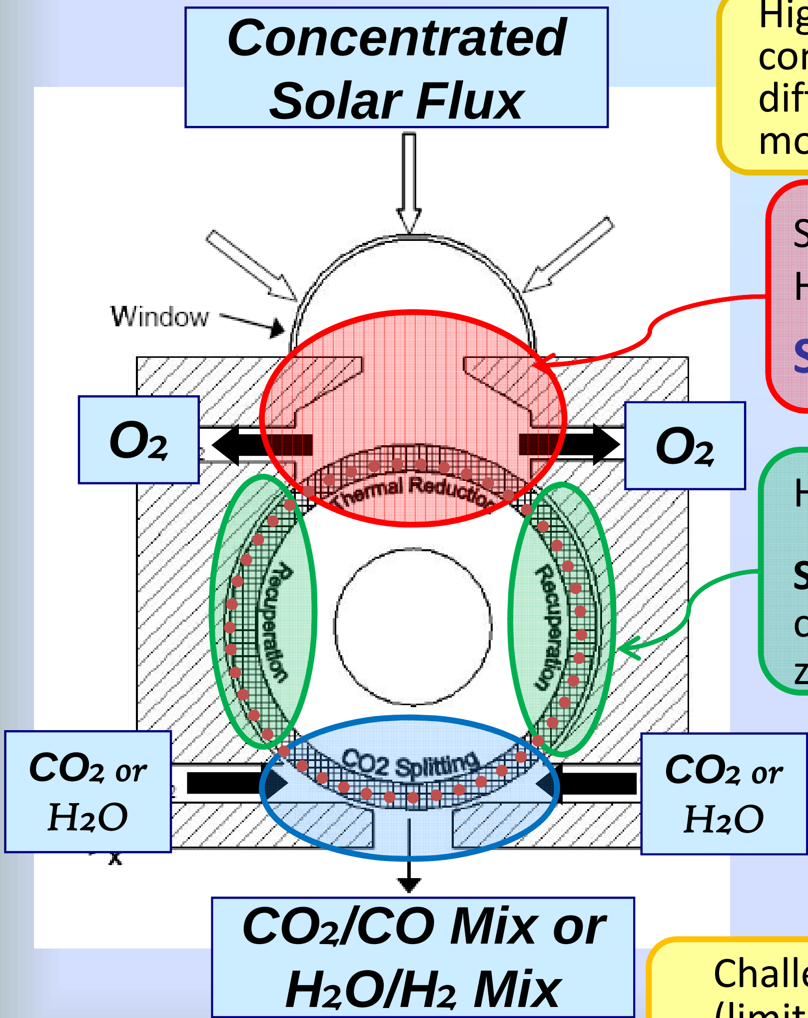
Work is mostly done by numerous colleagues especially Jim Miller at Sandia National Laboratories, the STCH Team (led by Tony McDaniel at Sandia), and an Australian led Initiative ASTRI and an International Solar Thermochemical Fuels Road-mapping team.

Extra Slides

Lots Going On



Highly coupled problem: thermal radiation, heat conduction and convection, gas-phase flow and species transport, solid-state diffusion of charged species, and redox chemical reactions within moving reactant rings

Solar Flux in $\dot{E} \approx CA_a I$ less Re-radiation losses $\dot{Q}_a \approx A_a \sigma T_r^4$
Heat & mass exchange across the solid/gas interface

Solid Reduction: $O_{(s)}^{-2} \leftrightarrow 2e_{r,(s)}^{-} + \frac{1}{2} O_{2,(g)}$

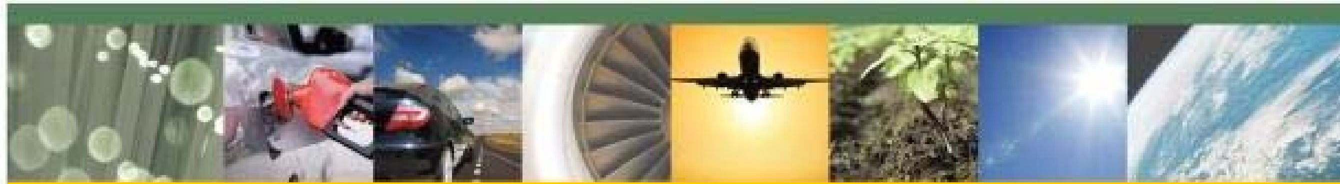
Heat exchange through a recuperator

Spatial Separation: Flow strategies must limit crossover of product chemical species (O_2,CO) between the reduction and oxidation zones and provide temperature and possibly pressure spearation

Re-Oxidation: CO_2 (or H_2O) injection, and heat & mass exchange across the solid/gas interface in the oxidation zone

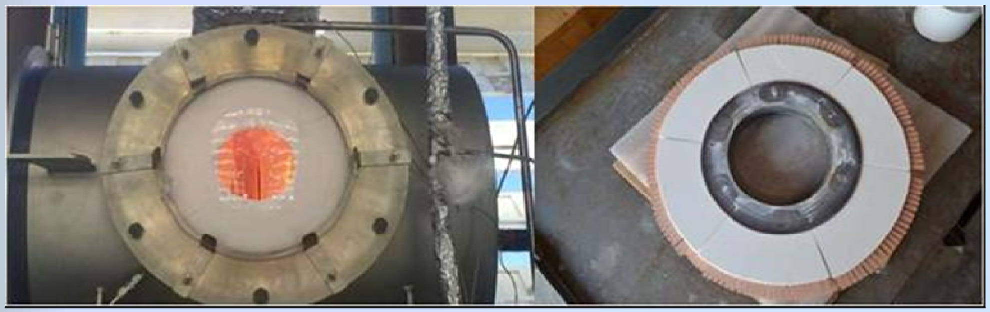
Gas Reduction: $2e_{r,(s)}^{-} + CO_{2,(g)} \leftrightarrow O_{(s)}^{-2} + CO_{(g)}$

Challenge is to balance incident solar flux, redox chemical kinetics (limited by thermodynamics), reactant/product species transport, and heat recuperation to maximize efficiency and through-put.

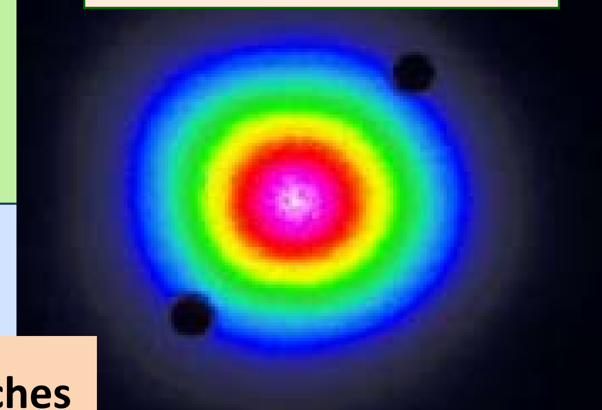


On Sun Testing Provides a Realistic Operating Environment

- **Sandia solar furnace used for material testing & prototype reactor testing**
  - **~6750 suns peak concentration, ~3000 average;**
  - **~ 18 kWt**
- **Provide control of solar power input**



Focal Plane



Holes are 3 inches (7.62 cm) apart

Peak flux 675 W/cm^2

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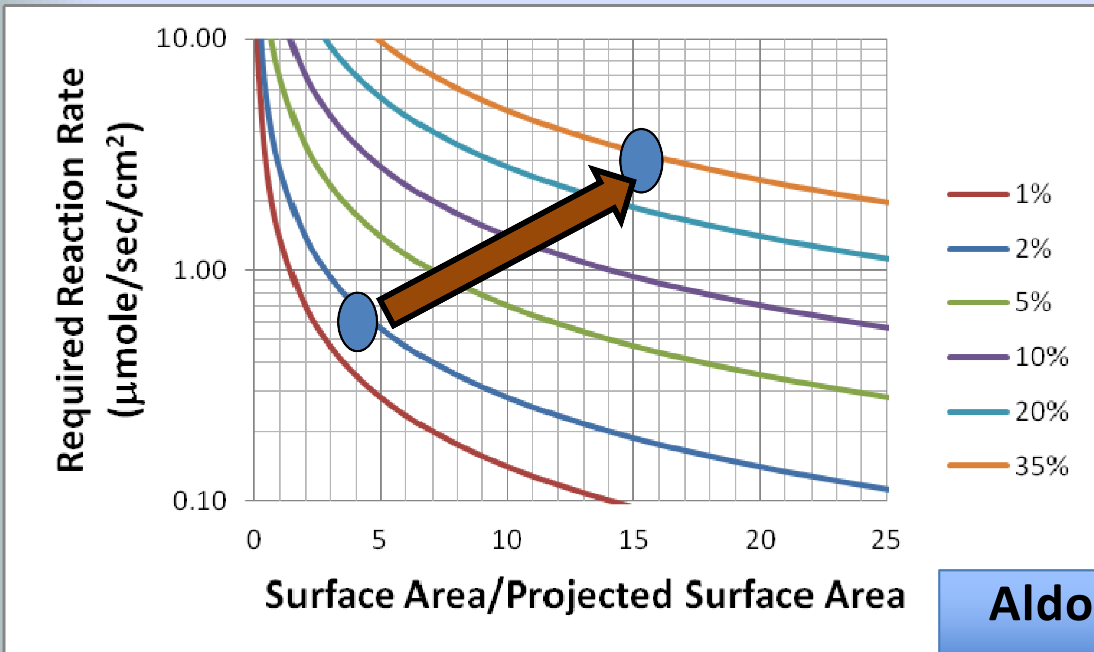
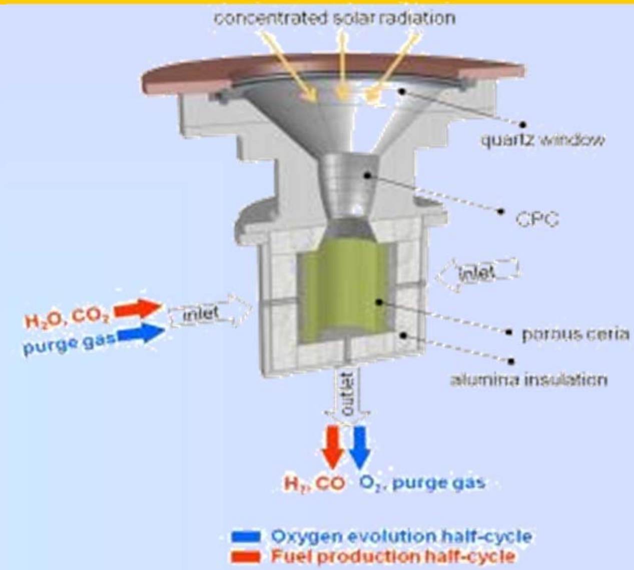
What will it take to achieve 30% efficiency?





Aldo Steinfeld, et al, demonstrated ~4% by increasing surface areas

Kinetics, Thermodynamics, and Reactor Design

- Structuring materials, Increase Surface Area
- Improve kinetics per unit exposed surface area while decreasing oxidation temperature
- Increase amount of reactive material – optimize flux to material ratio
- Improve utilization – decrease non-recovered sensible heating, increase active (reducible cation) loading, larger reduction extent $\Delta\delta$ and probably larger solid-solid recovery
- Better thermodynamics - materials modification & new materials discovery

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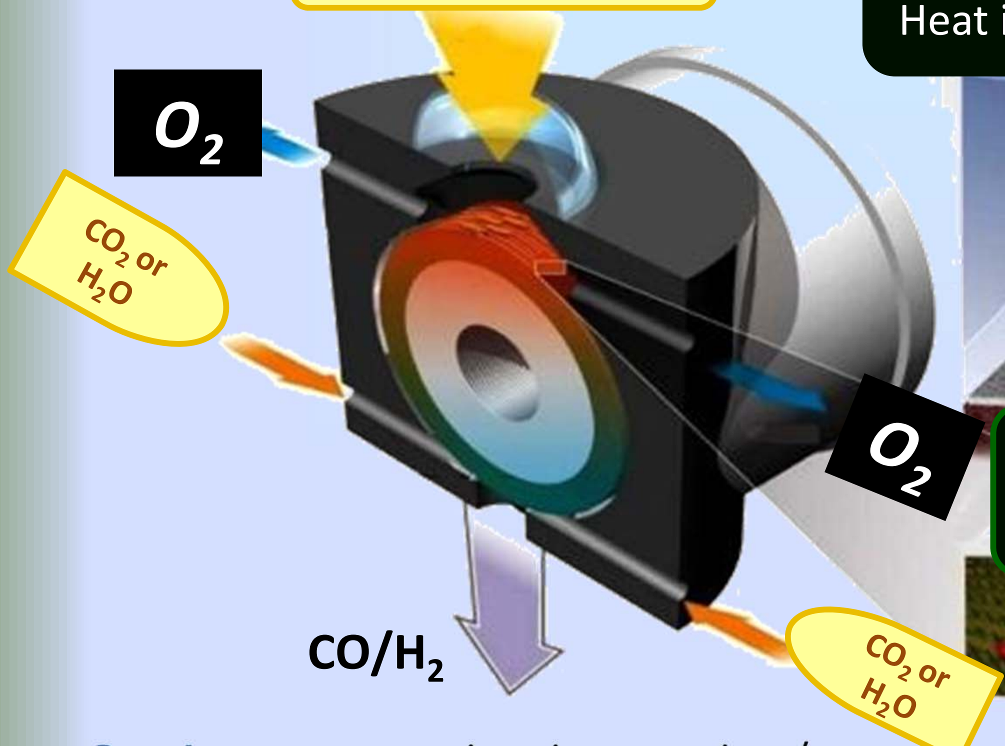
Novel reactor designs to realize high efficiency design attributes: Sandia National Labs – Sunshine to Petrol Team

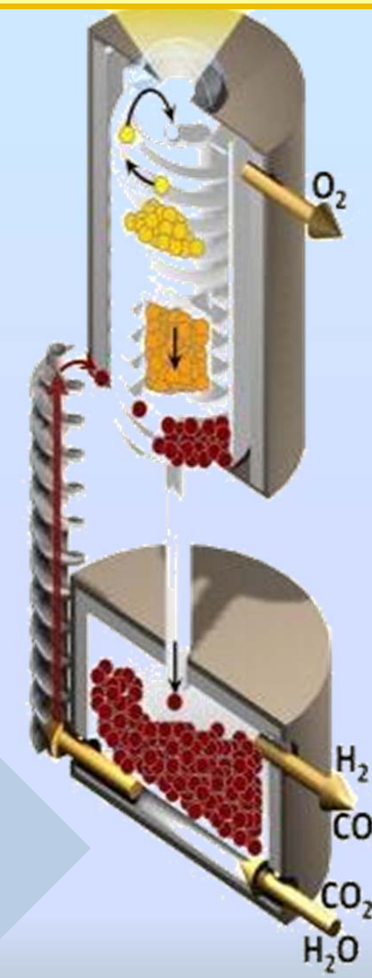
Solar Heat

Mirrored Dish Tracks the Sun and Focuses Heat into the Chamber



Alternate discs rotate in opposite directions

Solar Heat



- **Gen 1** counter-rotating rings receiver/reactor recuperator CR5
- Operational
- Continuous flow, Internal recuperation, product separation
- Diver and Miller inventors

Gen 2:
packed bed particle reactor

Ermanoski & Siegel

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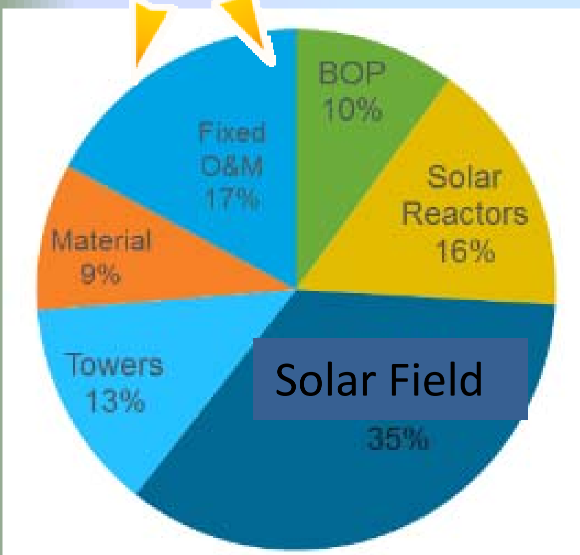
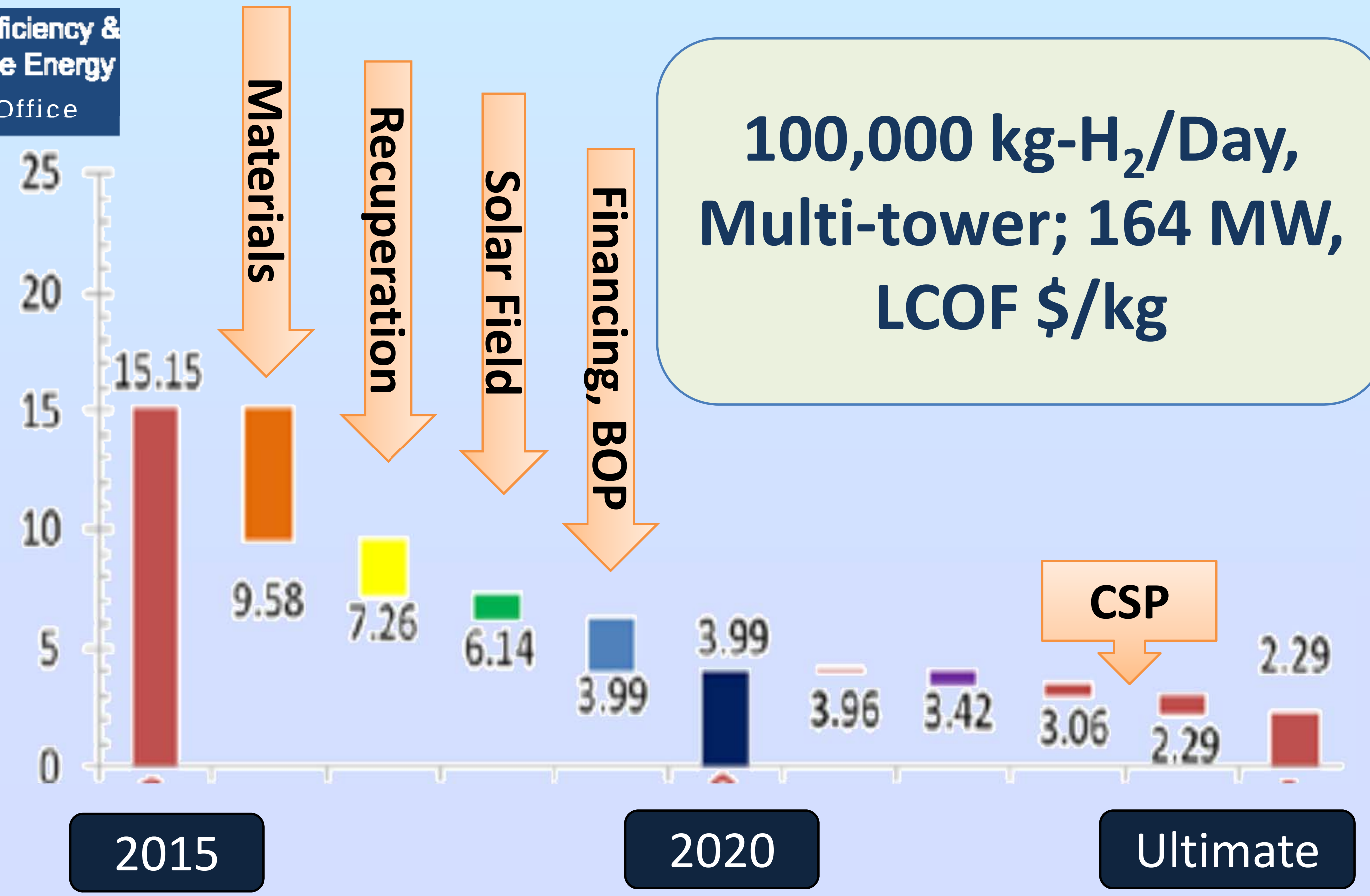
Roadmap to efficiency, affordability and scalability

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy
Fuel Cell Technologies Office



STCH
Solar-thermochemical



100,000 kg-H_2/Day,
Multi-tower; 164 MW,
LCOF $/kg

Solar-to-hydrogen conversion efficiencies > 20-30% likely needed to meet cost targets and that is true if photo-electrochemical or Solar Thermochemical.

Bucknell, ASU, Sandia Nat'l Labs

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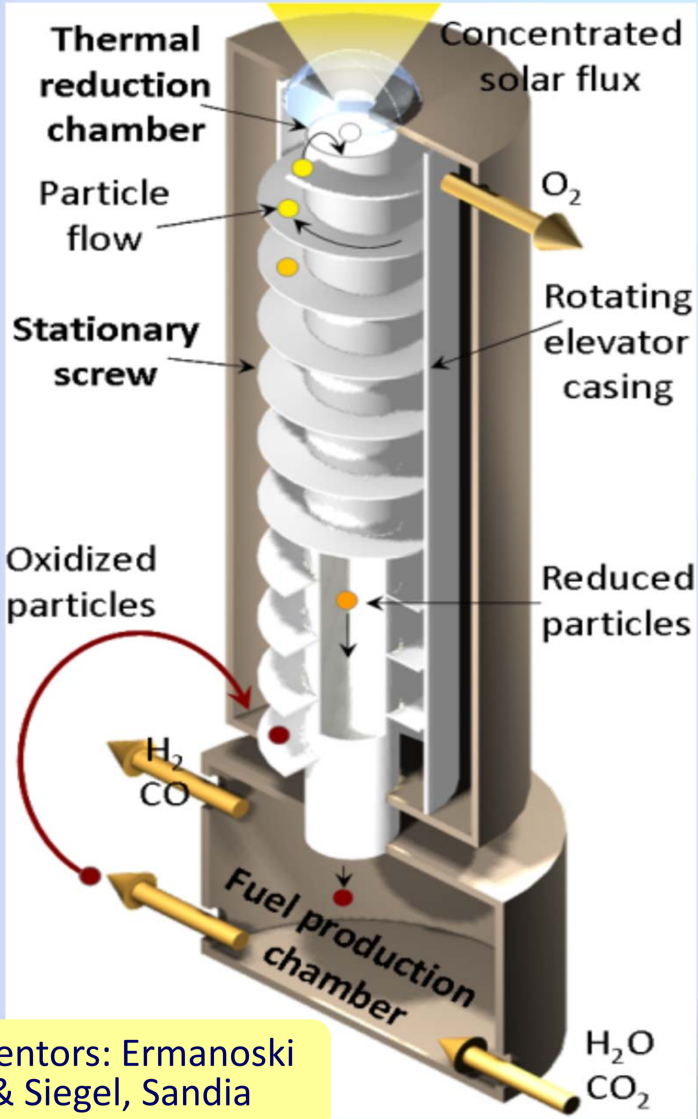
2nd GENERATION Reactor Concept Preserves Key Attributes And Mitigates Some Risks, But Brings In New Engineering Challenges



Inventors: Ermanoski & Siegel, Sandia

Packed-bed particle reactor

Advantages

- Inherent pressure, temperature and product separation
- Small reactive particles
- Only particles are thermally cycled
- Easy material replacement
- Independent component optimization
- Can operate under vacuum thus no sweep gases

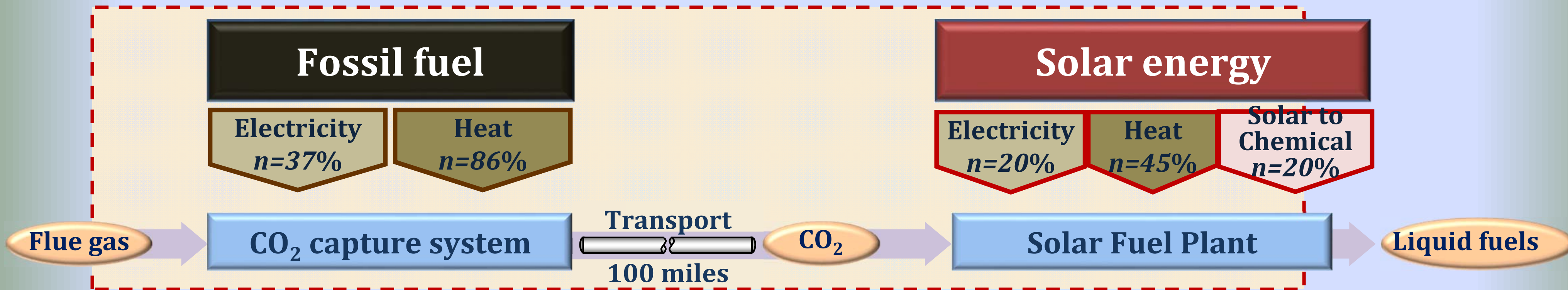
Disadvantages

- Particle conveyance
- Beam-down optics

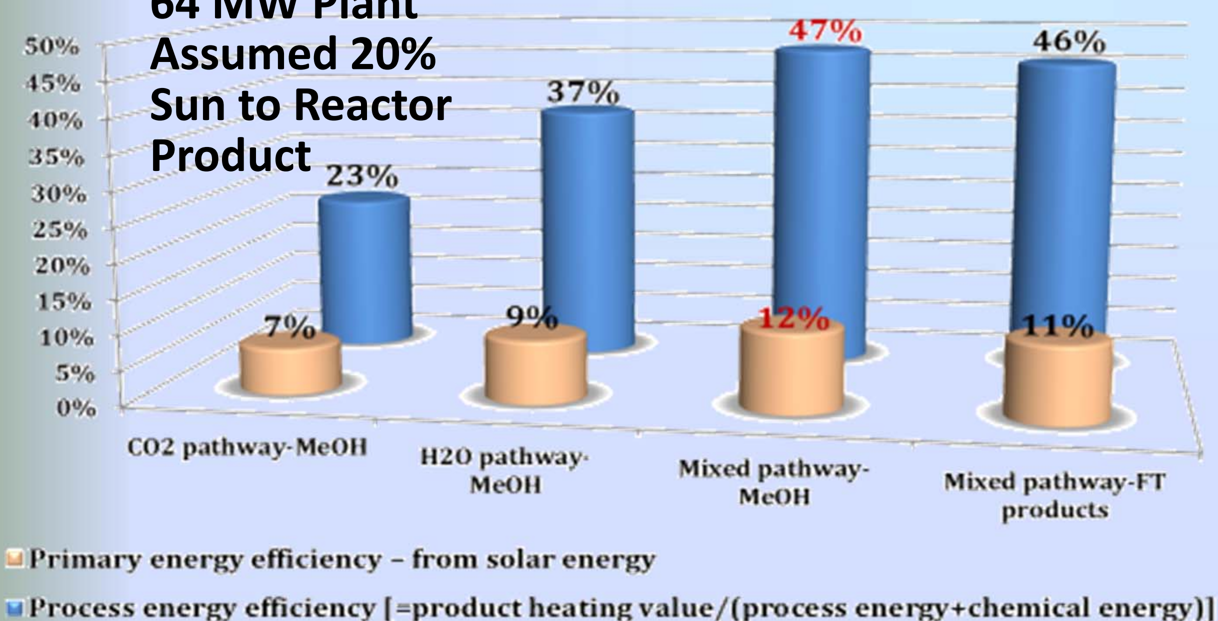
Ermanoski, Siegel, Stechel, JSEE, AUGUST 2013, Vol. 135

A Baseline Solar Fuels Plant: Identifying Opportunities To Economic Viability And Scale

Sandia Nat'l Labs, U.WI, ASU



64 MW Plant
Assumed 20% Sun to Reactor Product



1000 bpd ~70MW fuel
~ 8 km^2 at target efficiency

Kim, et al "Methanol production from CO_2 using solar-thermal energy: process development and techno-economic analysis" Energy Environ. Sci., 2011, 4, 3122.

"Fuel production from CO_2 using solar-thermal energy: system level analysis" Energy Environ. Sci., 2012, 5, 8417.

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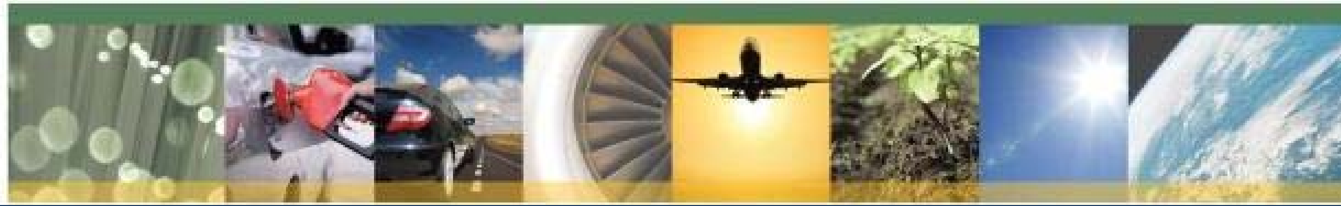
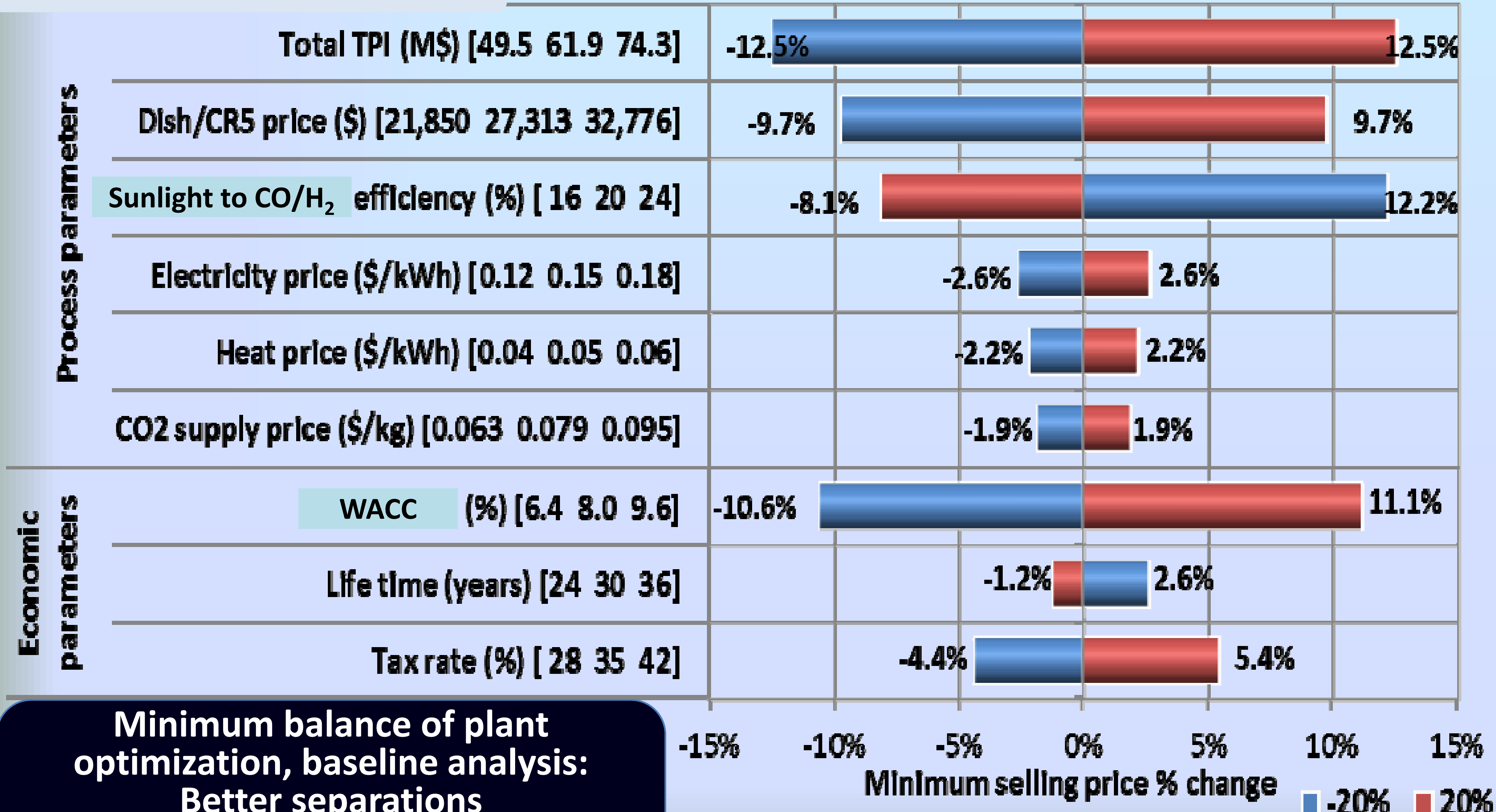


Preliminary economic evaluation: Sensitivity analysis

Sandia Nat'l Labs, U.WI, ASU



Minimum balance of plant optimization, baseline analysis:
Better separations
Heat integration
One step syngas to fuel synthesis

Base Case; $312/bbl; $6.73/GGE; $51/GJ; Target <$45/GJ

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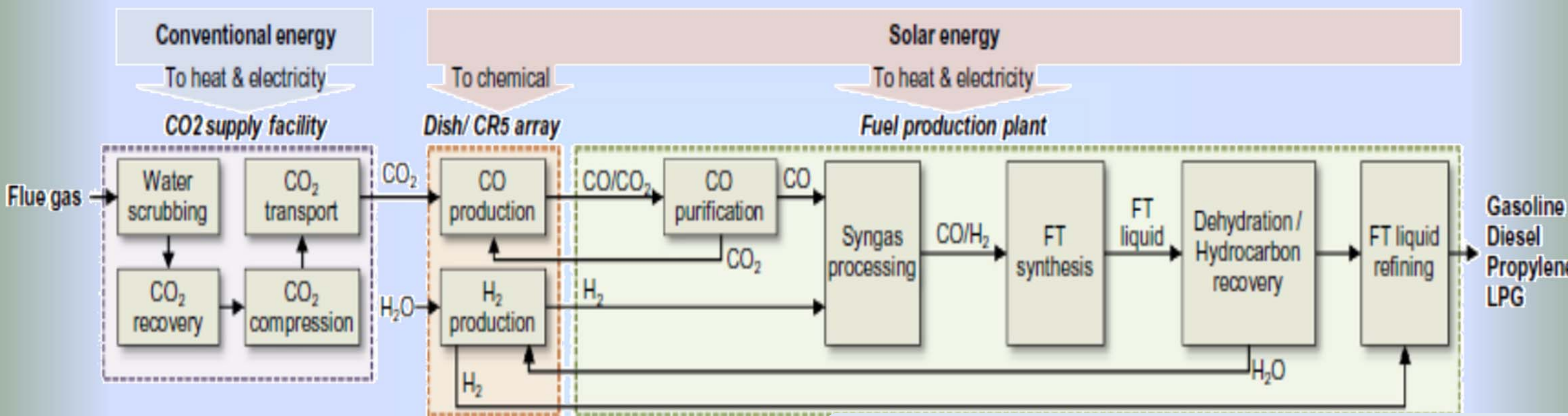
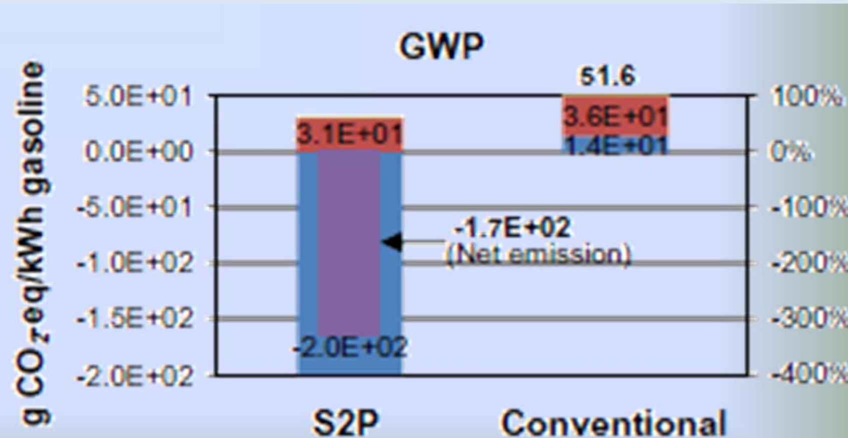
Sandia Nat'l Labs, U.WI, ASU

Life cycle analysis identifies most of the GHG footprint of production comes from capturing the CO_2



- **Energy Efficient Electrochemical CO_2 capture and release**
  - **DOE ARPAe project: Consortium: ASU, Proton Onsite, University of Colorado**
- **Redoing the Lifecycle analysis with a direct air capture front end**
  - **New ASU Center: Center for Negative Carbon Emissions and with Columbia Univ.**
- **Two energy services – policy issues**

Jiyong Kim, James E. Miller, Christos T. Maravelias, Ellen B. Stechel, Applied Energy 111 (2013) 1089–1098



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High efficiency solar thermochemical reactor for hydrogen production

Sandia National Laboratories

Dr. Anthony H. McDaniel (Principal Investigator)

Drs Ivan Ermanoski, James E Miller

Arizona State University

Profs. Ellen Stechel, Nathan Johnson

Bucknell University

Prof. Nathan Siegel

Colorado School of Mines

Profs. Ryan O'Hayre, Jianhua Tong

Stanford University

Prof. William Chueh

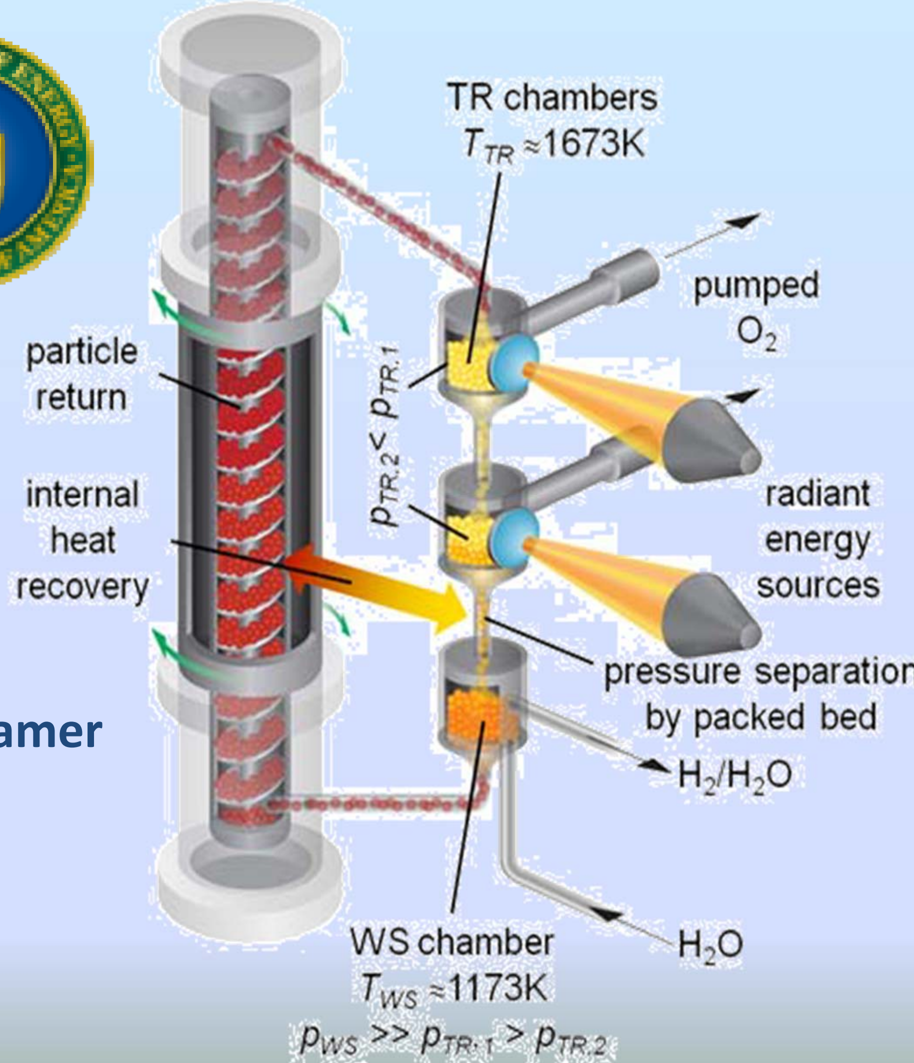
German Aerospace Center (DLR)

Dr. Martin Roeb, Dr. Martina Neises-von Puttkamer

Dr. Stefan Brendelberger, Dr. Christian Sattler

Northwestern University

Prof. Chris Wolverton



Solar Thermochemical Storage For High Temperature Power Cycles

Concentrating Solar Power: Efficiently Leveraging Equilibrium Mechanisms for Engineering New Thermochemical Storage (**CSP: ELEMENTS**)

Project Title: High Performance Reduction/Oxidation Metal Oxides for Thermochemical Energy Storage (**PROMOTES**)

Sandia National Laboratories

- **Dr. James E. Miller (Principal Investigator)**
- **Dr. Andrea Ambrosini**
- **Dr. Clifford Ho**
- **Dr. Eric Coker**

Georgia Institute of Technology

- **Prof. Peter Loutzenhiser,**
- **Prof. Sheldon Jeter**

Arizona State University

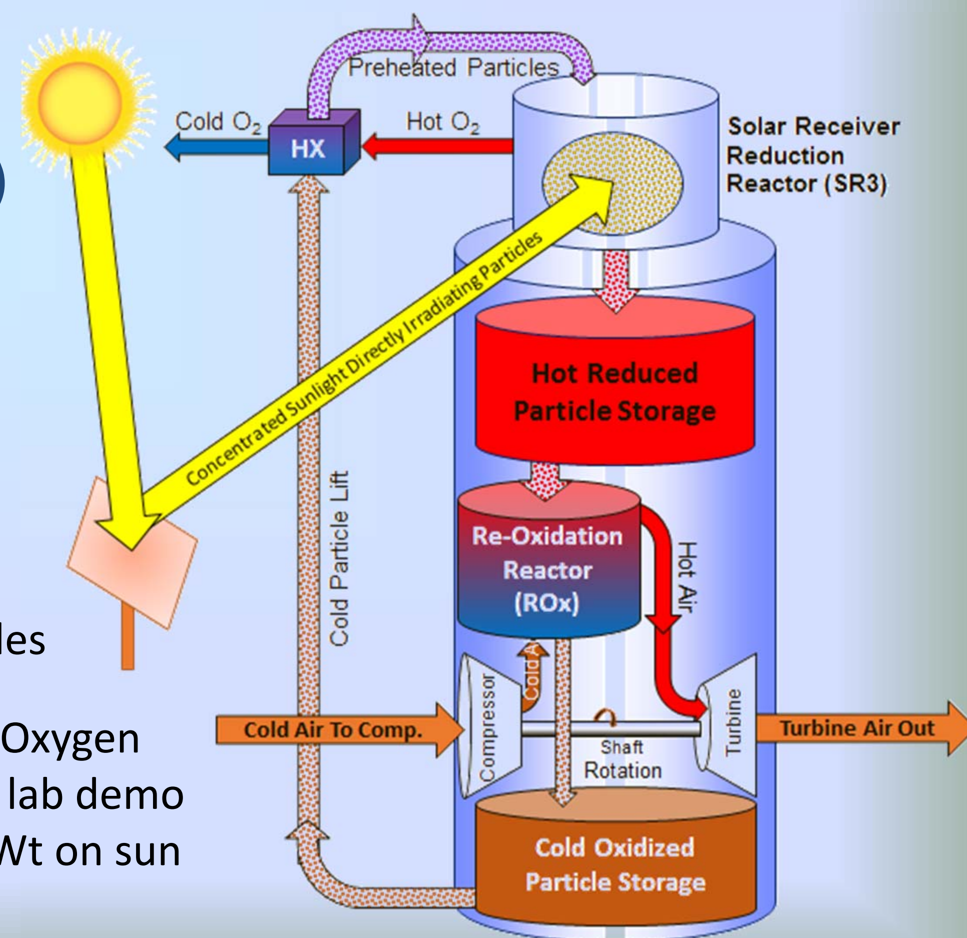
- **Prof. Ellen B. Stechel**
- **Prof. Nathan Johnson**

King Saud University

- **Prof. Hany Al-Ansary**

Particles

Air or Oxygen
5 kWt lab demo
100 kWt on sun



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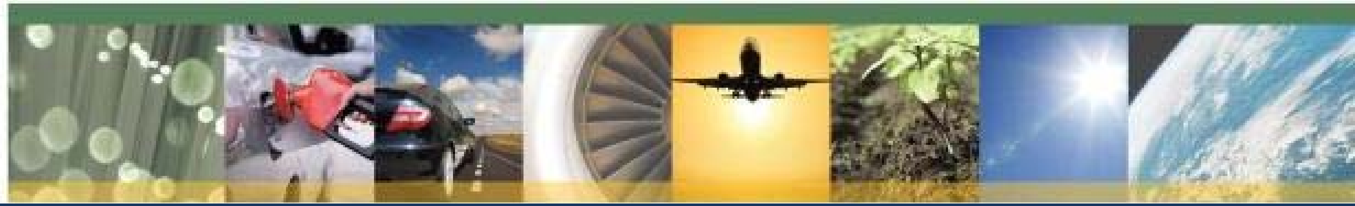
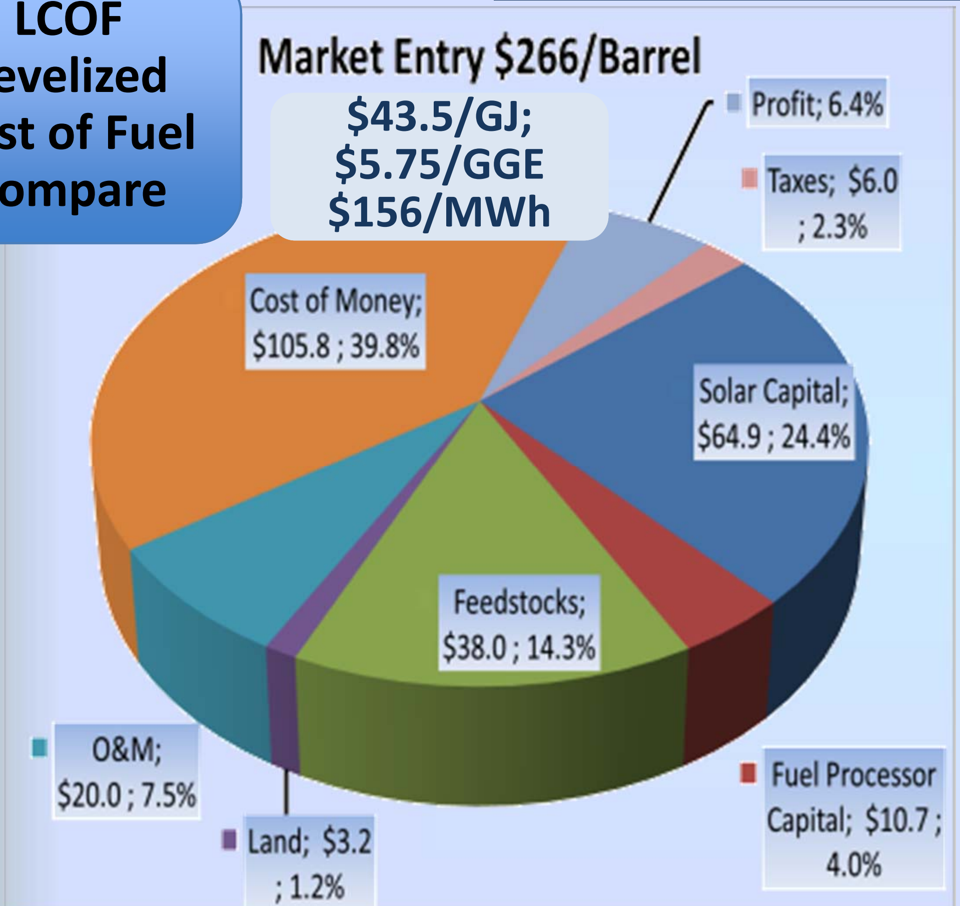
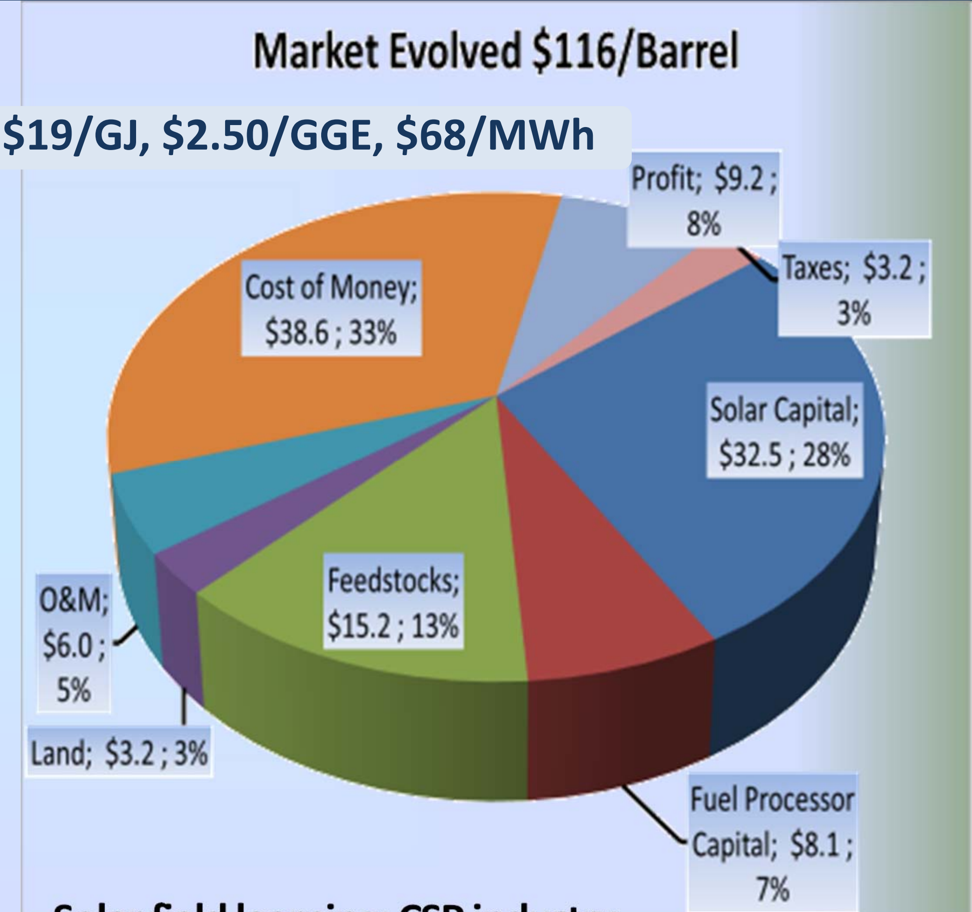


Similar roadmap to liquid hydrocarbon affordability

LCOF Levelized Cost of Fuel Compare





Based on 12.5% end-to-end sunlight to fuel efficiency

Ellen B. Stechel and James E. Miller "Re-energizing CO_2 to fuels with the sun: Issues of efficiency, scale, and economics" in press J. CO_2 Util. (2013), http://dx.doi.org/10.1016/j.jcou.2013.03.008.

- **Solar field learning: CSP industry**
- **Fuel processing learning: Distributed GtL, BtL**
- **Financing innovations for access to low cost of money**
- **Solar/Chemical interface: Learning from solar reforming and gasification, resolving storage issues**

ASU & Sandia Nat'l Labs

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Summary of popular material systems

Fe^{2+}/Fe^{3+} systems:

- Deep reduction at 1400 °C.
- High redox capacity (Δδ>0.1).
- Slow H_2O oxidation kinetics.
- YSZ, ZrO_2, Al_2O_3 matrix required.

Ce^{3+}/Ce^{4+} systems:

- Shallow reduction at 1500 °C.
- Low redox capacity (Δδ<0.08).
- Fast H_2O oxidation kinetics.
- Durable.

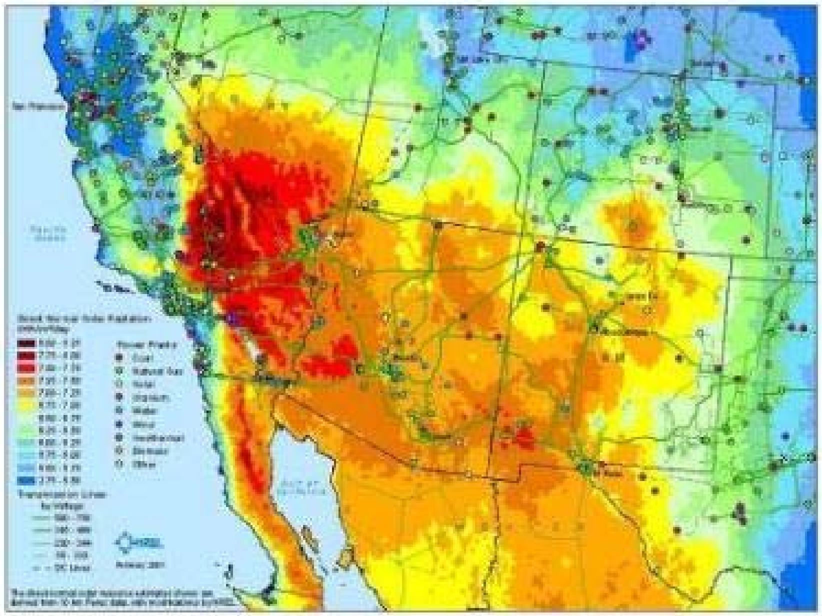
$TM^{2+}/TM^{3+}/TM^{4+}$ perovskite systems:

- Deep reduction at 1400 °C.
- High redox capacity (Δδ>0.1).
- Promising H_2O oxidation kinetics.
- Vast material space!

PROPERTY	FERRITE ($MFeO_x/ZrO_2$) ($MFeO_x/Al_2O_3$)	CERIA (CeO_2) Current State of the Art	PEROVSKITE (ABO_3)	IDEAL
Redox Kinetics	SLOW	FAST	?	FAST
Capacity (Δδ)	HIGH	LOW	HIGH	HIGH
T_{TR} @ Reduction	MED/HIGH	HIGH	LOW	LOW
H_2O/H_2 @ Oxidation	MED	LOW	?	LOW
Durability	MED/HIGH	HIGH	?	HIGH
Earth Abundance	HIGH	LOW/MED	HIGH	HIGH

Consider the scale at 12.5%

- Global 5.0 mbpd aviation fuels or the equivalent of 350 GW energy flux (2009) and growing
  - ~40 billion m^2 land area
- Global 88.3 mbpd petroleum consumption or the equivalent of 6.3 TW energy flux (2011) and growing
  - ~700 billion m^2 < 0.5% global land area



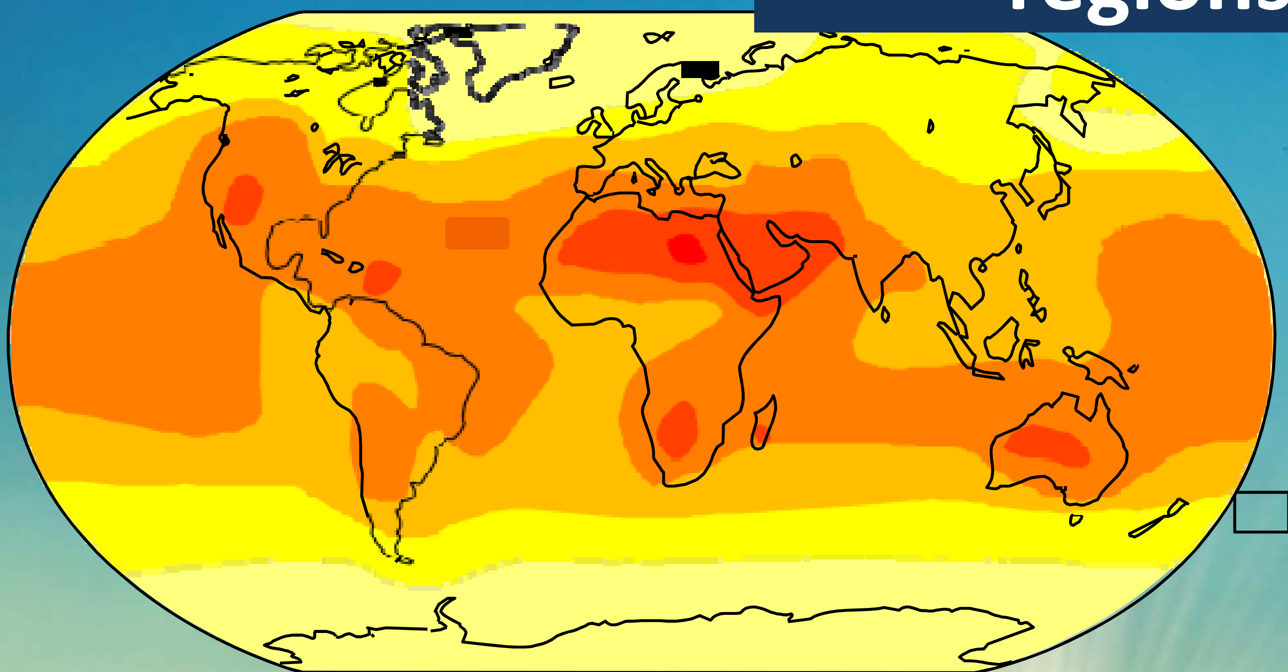
Filters applied (Resource analysis by NREL and SNL):

- Sites > 6.75 kwh/m^2/day – 280 Watt/m^2 - ~2450 kWh/m^2/yr
- Exclude environmentally sensitive lands, major urban areas,
- Remove land with slope > 1%.
- Assumes 25% packing density
- Only contiguous areas > 10 km^2 (675 $MW_{primary}$) sufficient for ~1200 boe/day **(at 12.5% sunlight to fuel efficiency)**

State	Land Area (10^9 m^2)	Solar Capacity (TW)	Fuel Capacity (GW)	Fuel Capacity (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
Similar to transportation infrastructure

Great potential in a number of regions in the world*



< 1000 | 1000 | 1500 | 2000 | 2300 | 2500
kWh/m²/yr

< 114	114	171	228	263	285 W/m^2
< 2.74	2.74	4.11	5.48	6.30	6.85 $kWh/m^2/d$

~ 25000 TW on land
~ 600 TW exploitable solar or ~2.5% of land area
For Concentrating Solar, Probably >2400 $kWh/m^2/yr$

Australia ~43 TW (>600 mbpd)

Middle East ~14 TW (190 mbpd)

Africa ~73 TW (1030 mbpd)

SW United States ~2.7 TW (38 mbpd)

- **Screened data from Trieb, et al SolarPACES 2009, Berlin**

If Land Utilization 12.5% × 25% = ~ 3.1%