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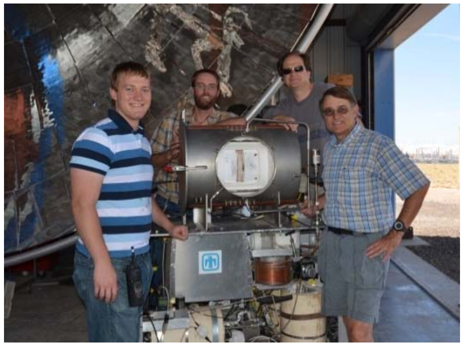

Sunshine to Petrol

Reimagining Liquid Transportation Fuels

Presented by James E. Miller

U.S. DEPARTMENT OF ENERGY NNSA National Nuclear Security Administration

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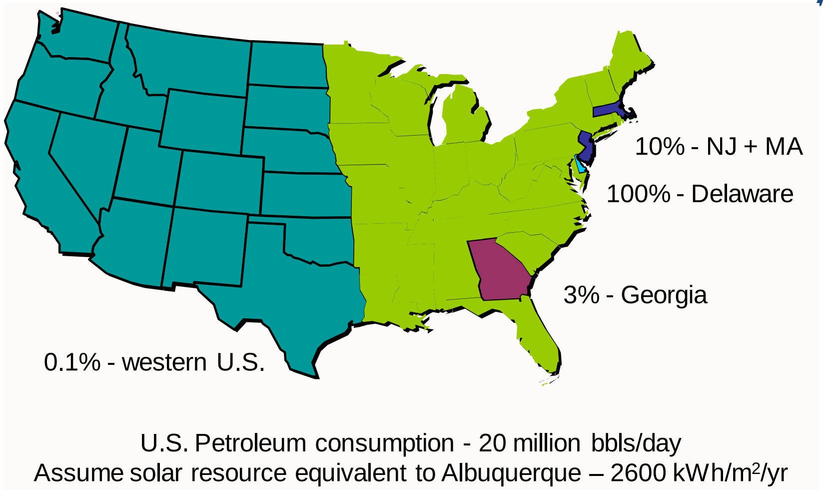
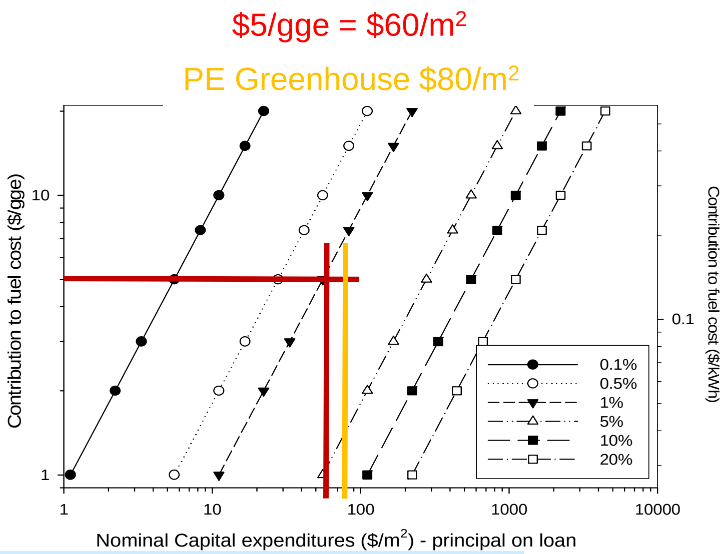
Setting the Stage

- Energy security and climate change are critical issues.
- Availability and price of transportation fuels linked to economic and national security.



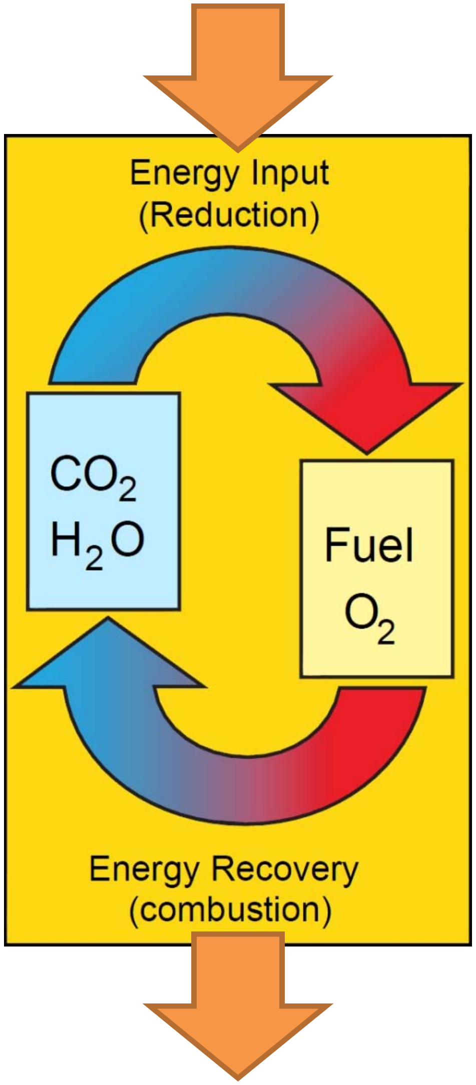


Meeting a significant fraction of global fuel demand with solar fuels is a plausible option.

Only highly efficient processes (> 10%) are scalable to impactful sizes (cost, land, materials)

- **High impact opportunity for CO_2. Water consumption relatively low.**
- **Consistent with other human activities that have occurred over several decade time scale.**
- **12.5% LCE: 10% of US petroleum demand met with 12.5% of available resource.**

Sunshine to Petrol



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.***

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

Route to Liquid Fuels

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

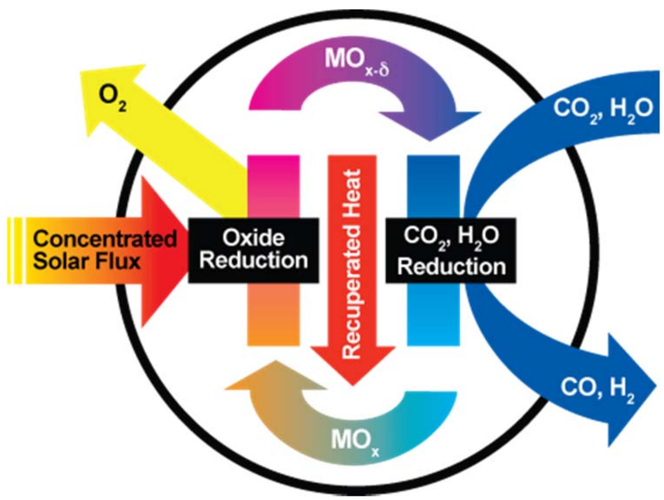
$$CO + H_2O \leftrightarrow CO_2 + H_2$$

Models suggest highest efficiency when splitting both

Thermochemical Cycles: A Simple Concept …

Divide an unfavorable reaction into two favorable reactions.

1) $1/\delta\ MO_x \rightarrow 1/\delta\ MO_{(x-\delta)} + ½\ O_2$



2) $1/\delta\ MO_{(x-\delta)} + CO_2 \rightarrow 1/\delta\ MO_x + CO$

3) $CO_2 \rightarrow CO + ½\ O_2$

Essentially a heat engine that converts heat directly stored chemical energy (work). Efficiency gains are possible as initial conversion to mechanical work and electricity are avoided.

Thermodynamics Requires:

High temperatures for simple two-step cycles → concentrating solar power

The two reactions are only favorable at ***different temperatures.***

Fe_3O_4/FeO is the archetypical cycle

…With Multiple Technical Challenges

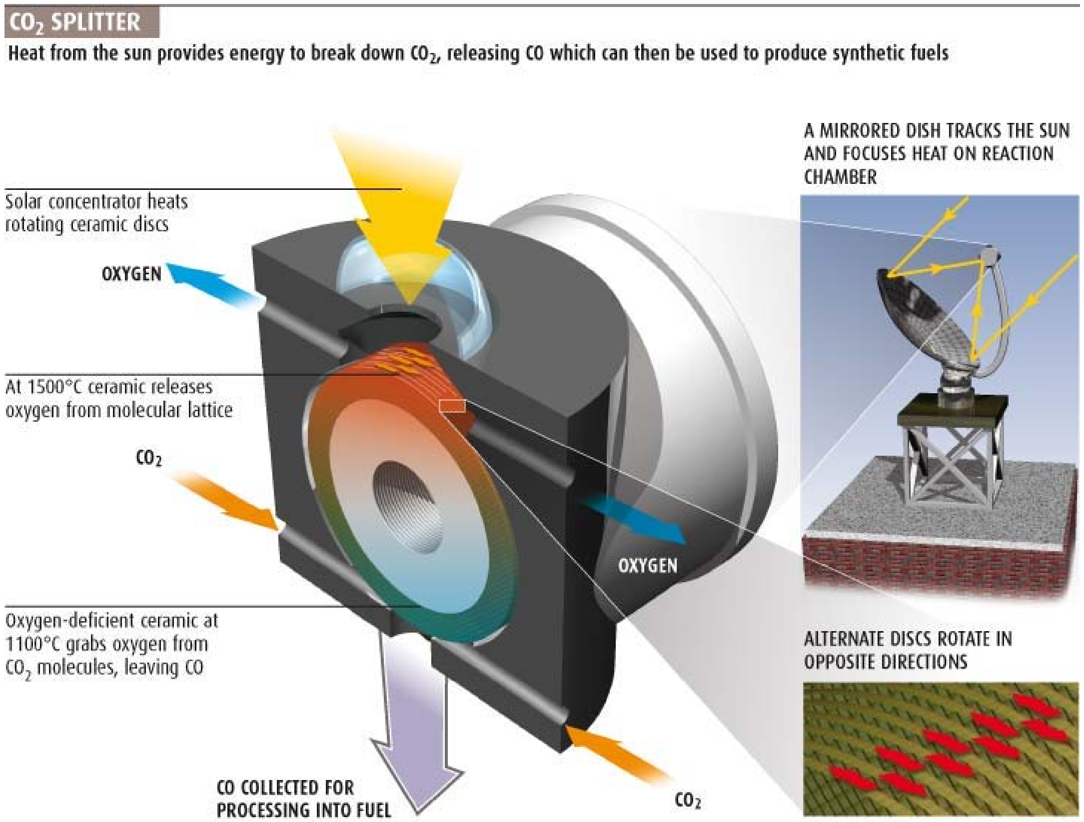
Exploiting complex materials and systems to carry out highly coupled, multi-scale (time, dimensions) dynamic processes under extreme conditions.

- **Reactors**
  - **Maximizing Energy usage (continuous operation, sensible energy recovery i.e. recuperation)**
  - **Interfacing Solar with chemistry**
  - **Minimal parasitic work input**
  - **Decoupling steps (products, conditions, rates)**
- **Materials**
  - **Thermodynamics**
  - **Kinetics**
  - **Durability**
- **Systems**
  - **Setting targets, process optimization , economics, life cycle impacts etc.**

Our multidisciplinary team has done work to address each of these areas.

CR5 : First-of-a-kind approach to thermochemistry

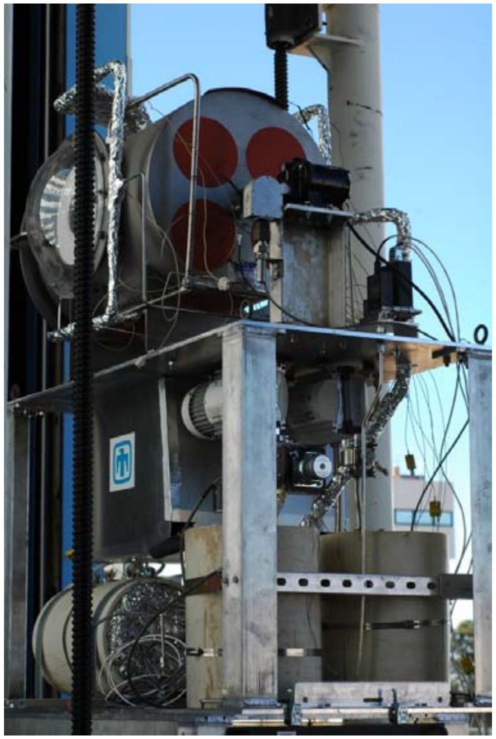
Counter-Rotating-Ring Receiver/Reactor/Recuperator (CR5)

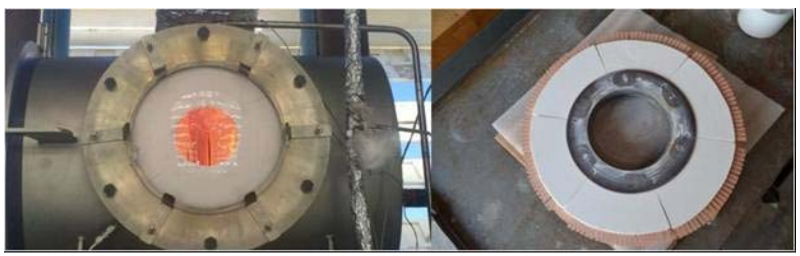


"Reactorizing a Countercurrent Recuperator"

Continuous flow, Spatial separation of products, Thermal recuperation

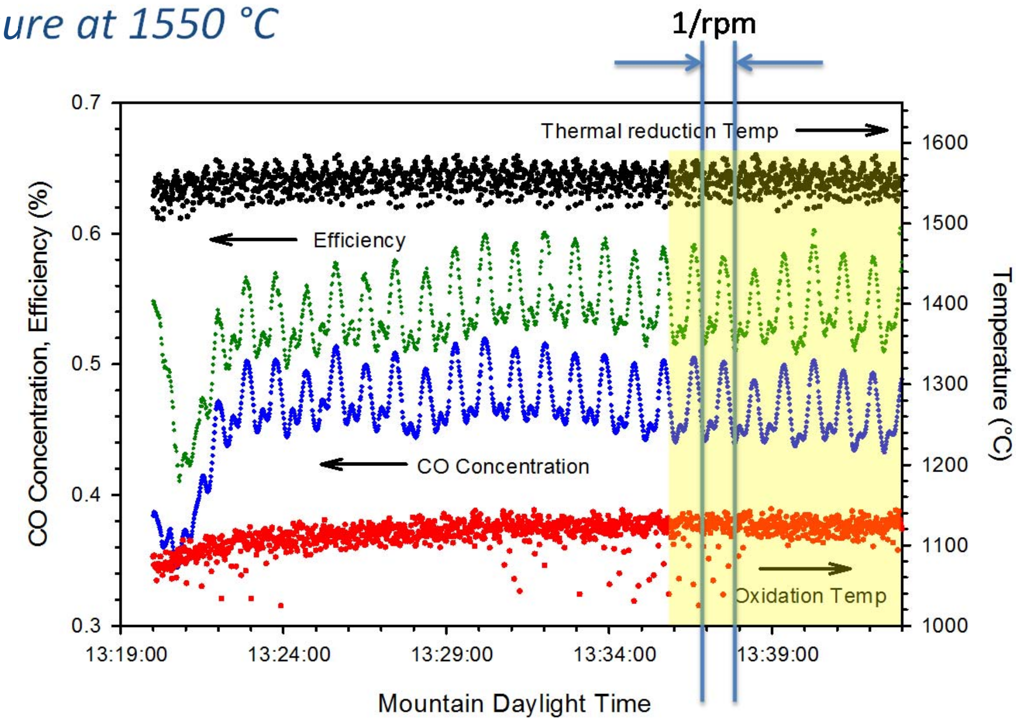
Performance Map of Gen-1 Prototype

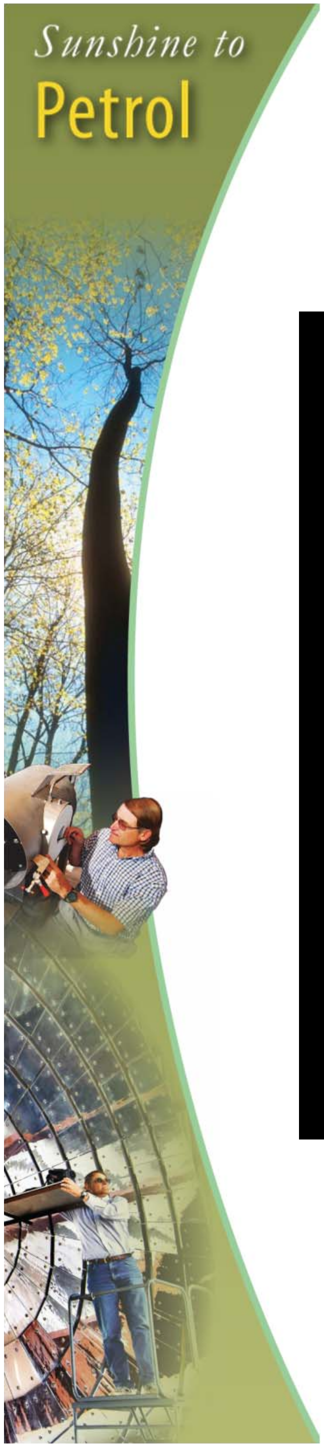




Collect data to validate models, guide improvements

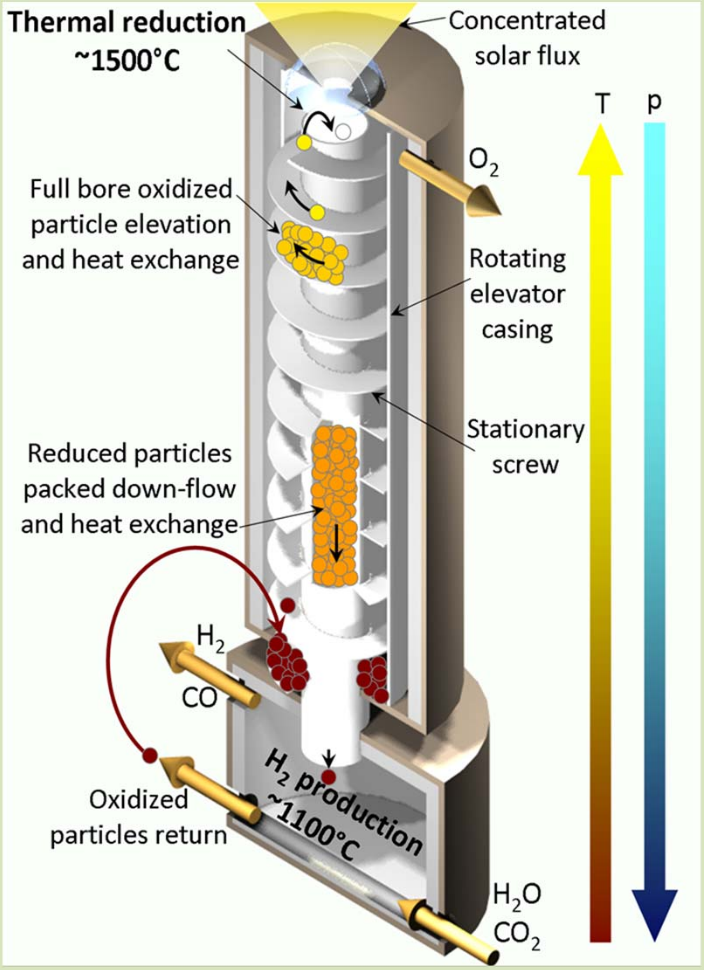
- *Ceria-based fins on rings*
- *6 Data Sets: Cold, 2@ 1450 °C, 2@ 1550 °C, 1620 °C*
- *3 ring rotation speeds, 3 CO_2 flow rates for each*
- *Constant Ar flow, Pressure = 0.5 atm*
- *Floating Pressure at 1550 °C*





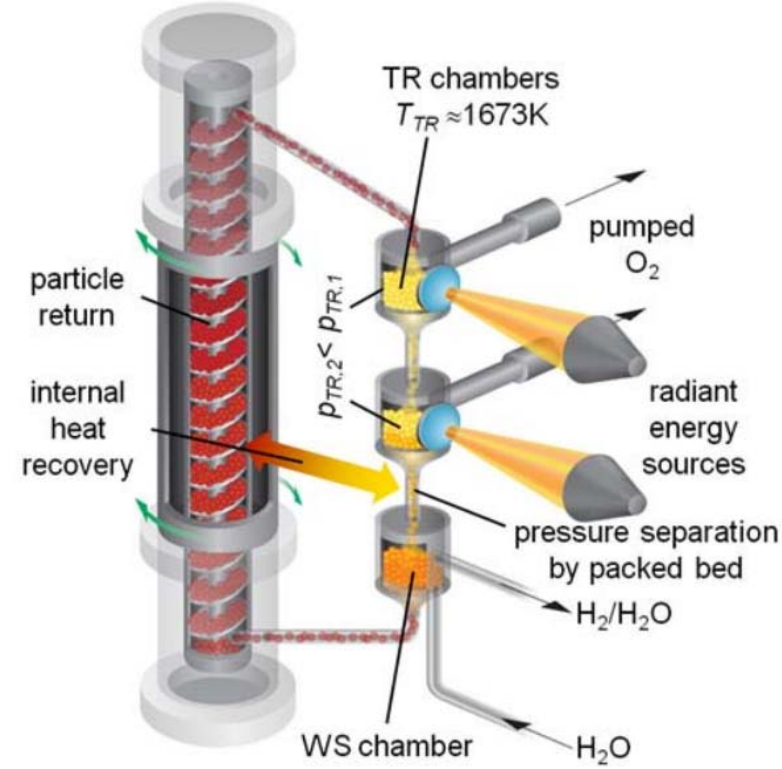
Operating with 22 Rings

Gen 2: Packed Bed Particle Reactor



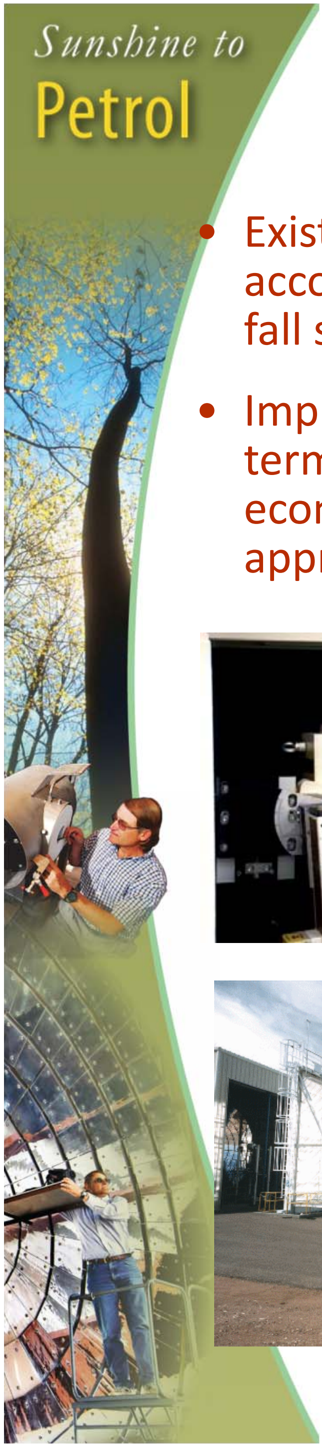
- **Counter-current heat exchange incorporated into particle lift apparatus**
- **Particle bed provides gas and pressure separation (redox pressures decoupled)**
- **Independent optimization of unit ops**

Gen 2.1: Cascading Pressure PBR



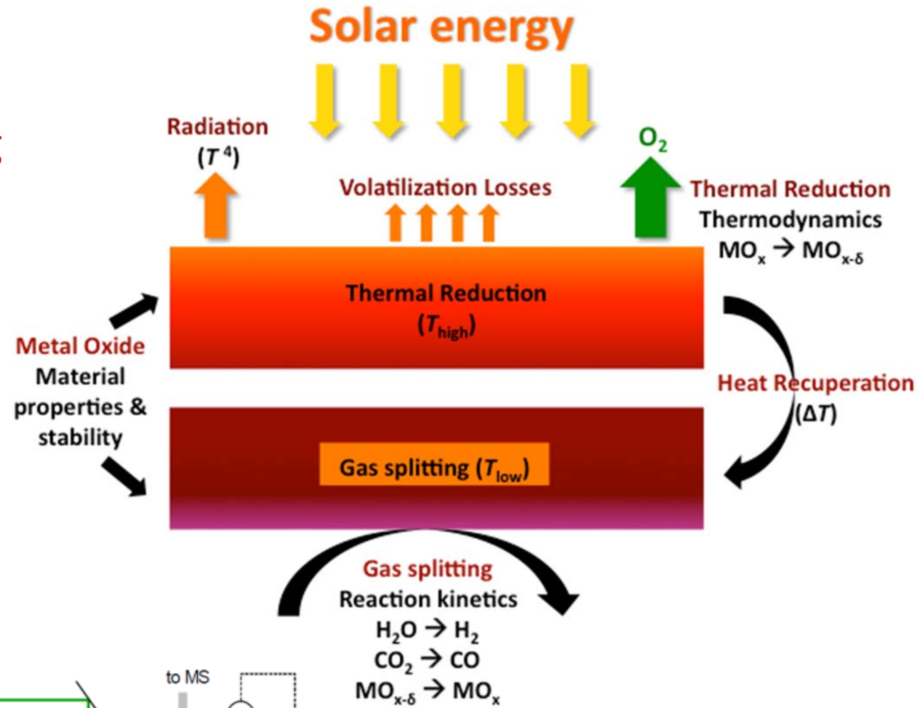
- **Similar features and heat exchange concepts to PBR**
- **Pressure-Staged thermal reduction to facilitate high conversion , maximize efficiency**

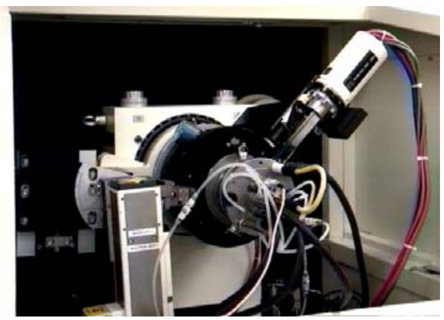
I. Ivan Ermanoski, Nathan P. Siegel and Ellen B. Stechel "A New Reactor Concept for Efficient Solar-Thermochemical Fuel Production" J. *Sol. Energy Eng.* 135(3), 2013.
Ermanoski, International Journal of Hydrogen Energy, in press DOI: 10.1016/j.ijhydene.2014.06.143



Addressing Materials Challenges

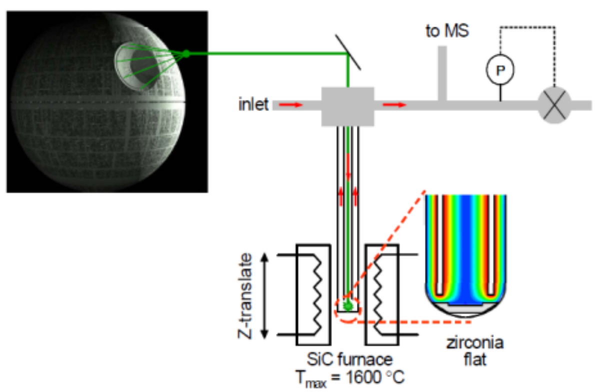
- Existing materials are appropriate for accomplishing short term goals, but fall short in one or more category.
- Improvements needed to meet long term targets as defined by systems, economics, and competing approaches.





HT-XRD

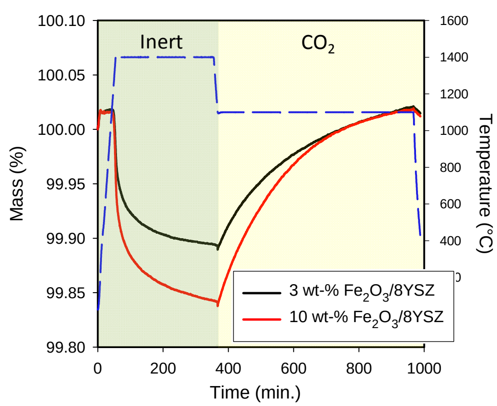
NSTTF

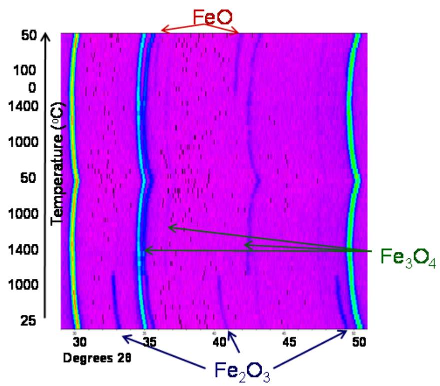


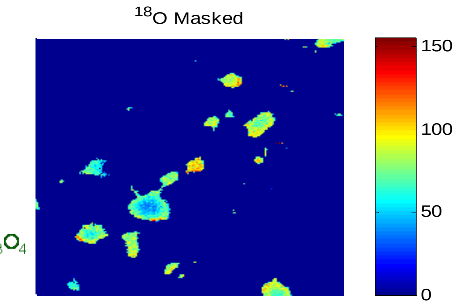
500 W CW near IR laser/STFR

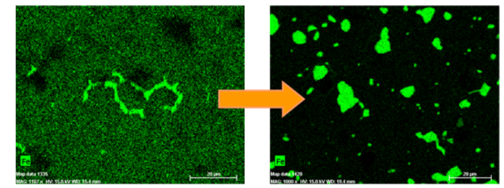
We have developed unique capabilities over the course of the S2P program

Conventional approaches coupled with unique capabilities led to detailed understanding of complex materials (Fe/zirconia) behavior

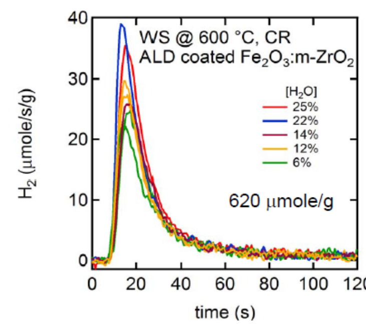


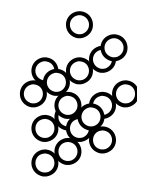


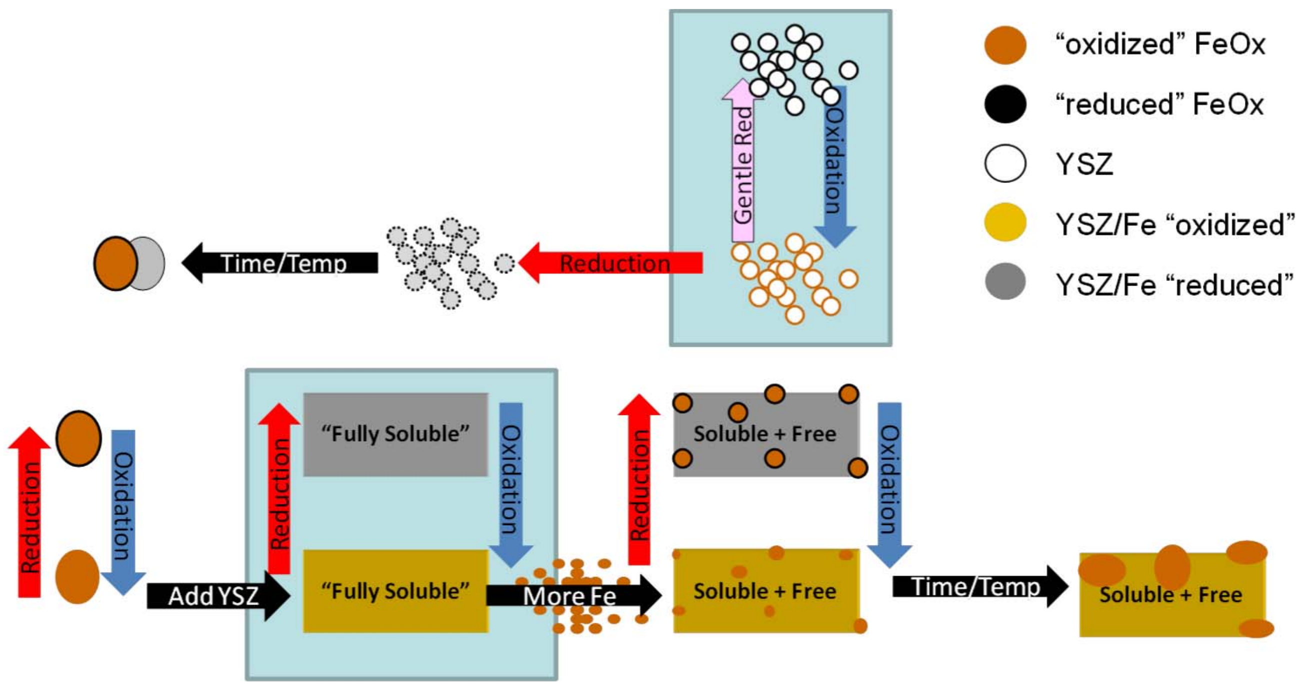




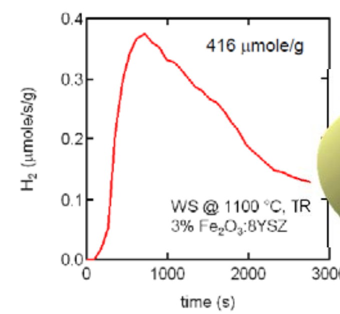
Chemically reduced ALD $Fe:ZrO_2$ nanoparticles

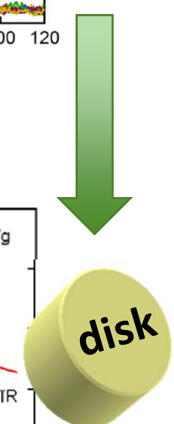






Bulk Fe:YSZ

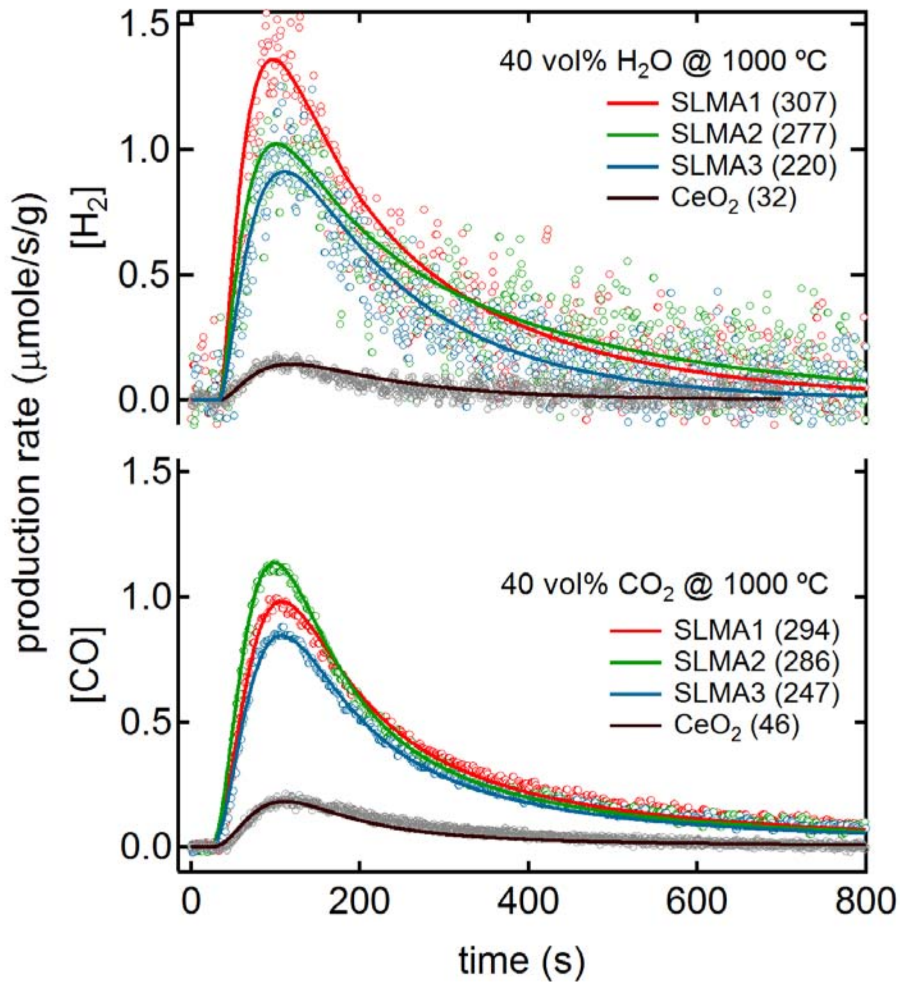


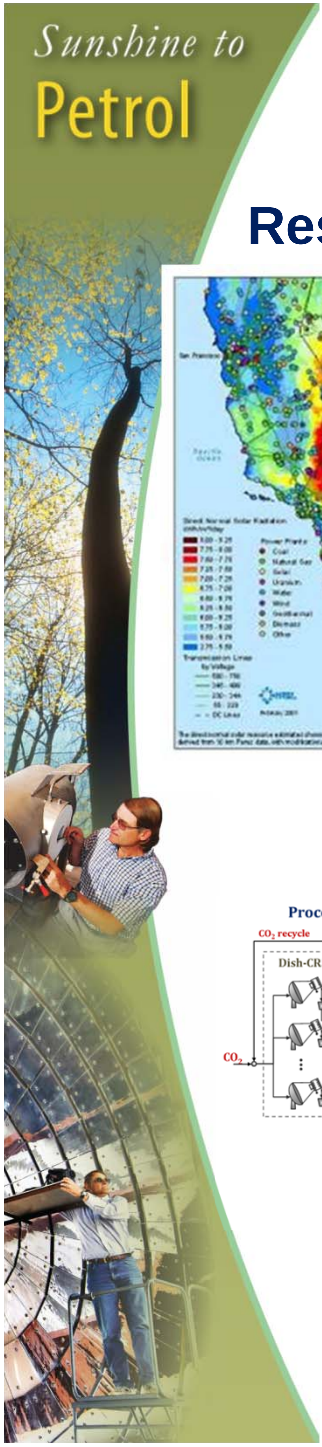


Insights led to Next Gen Materials: *$Sr_xLa_{1-x}Mn_yAl_{1-y}O_{3-\delta}$*

- Perovskite compounds oxidize to split H_2 and CO_2.
- Comparable kinetics.
- Produce more fuel at lower Reduction onset Temp.
  - 9× more H_2, 6× more CO

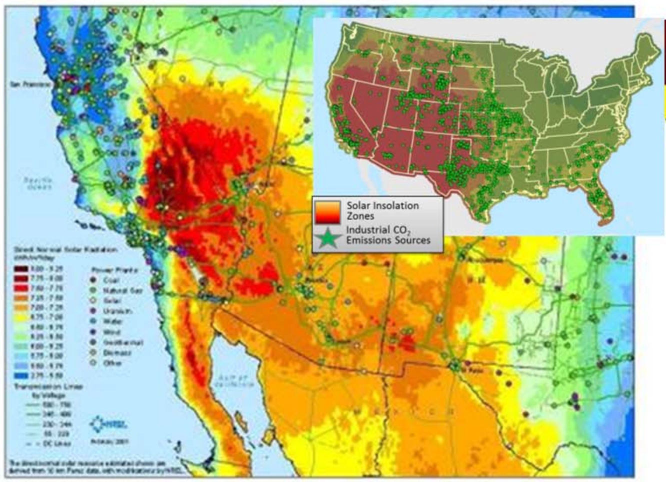
compound	CO (µmole/g)	H_2 (µmole/g)
LSAM1	294	307
LSAM2	286	277
LSAM3	247	220
$CeO_{2-\delta}$	46	32

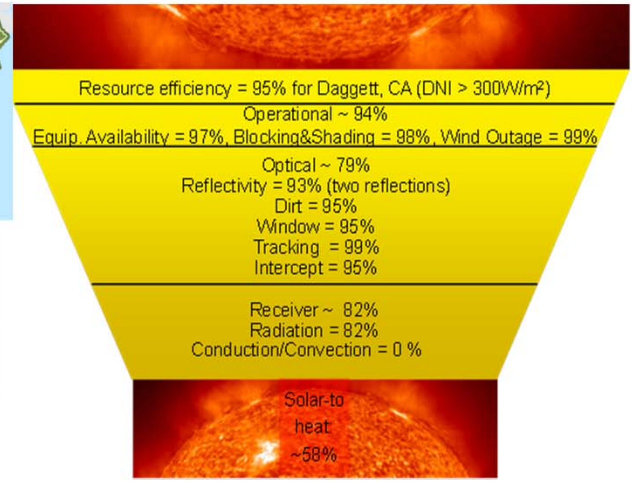


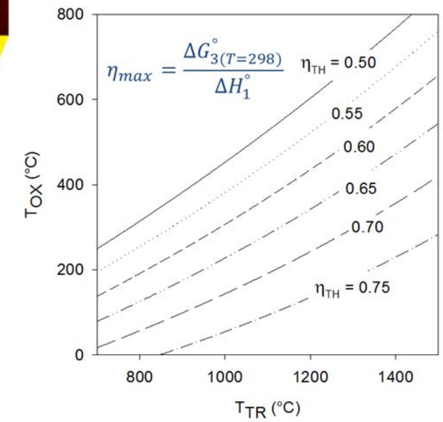


Impact, Systems, Technoeconomics, ...

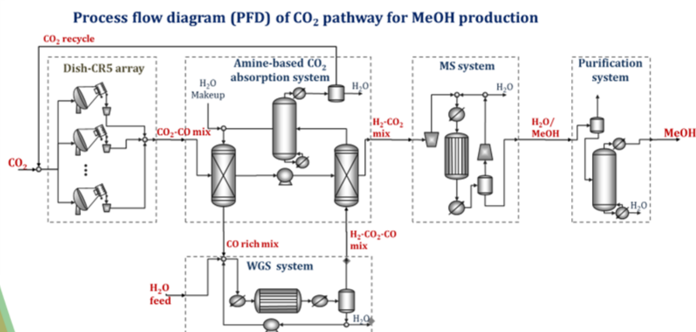
Resources → Solar Components → Materials

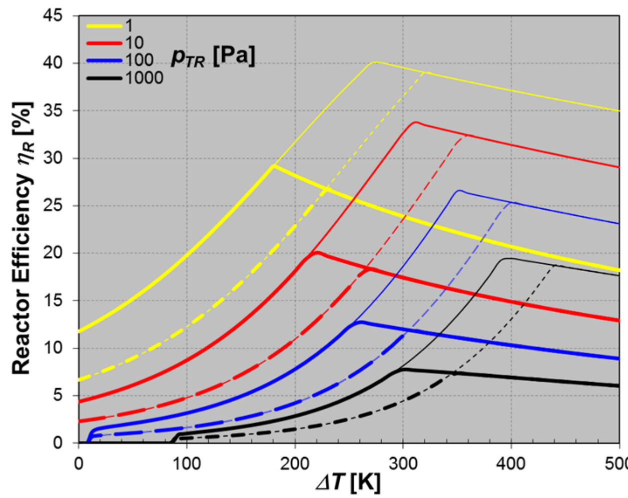


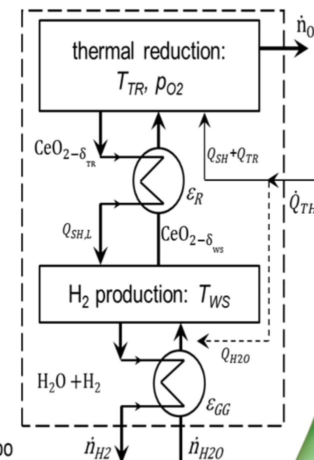




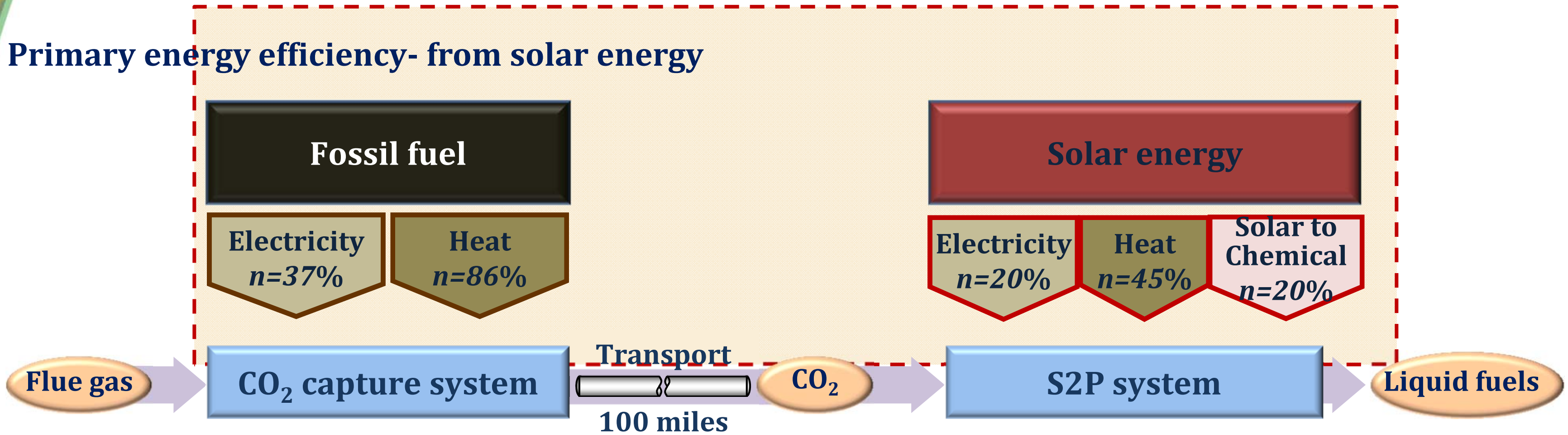
Processes ← Reactors

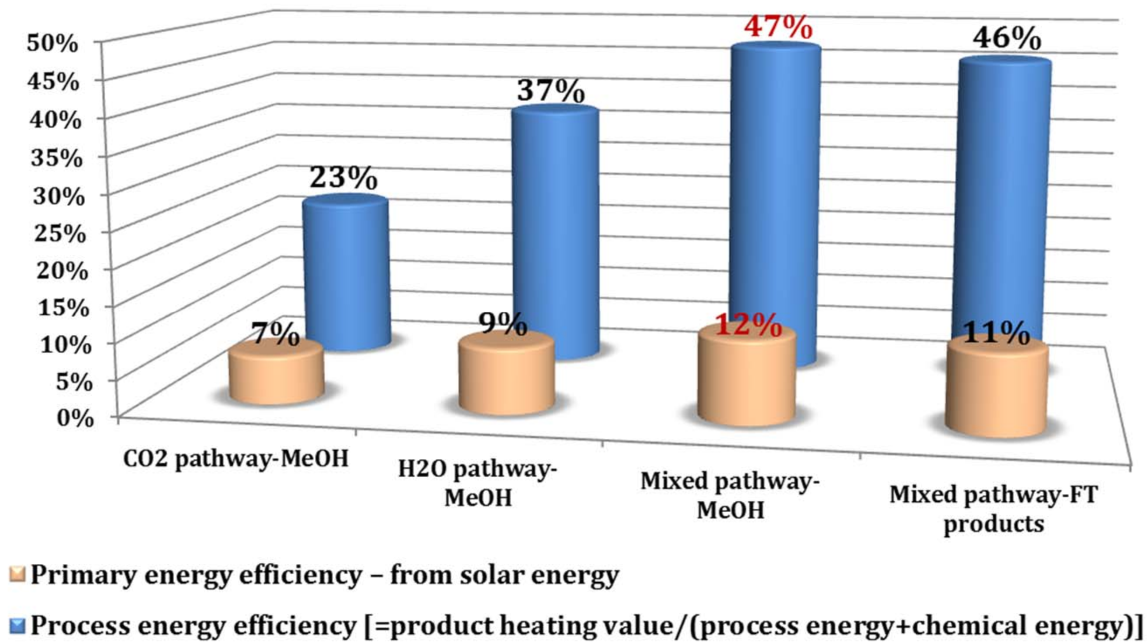






Process models demonstrate viability, identify areas for improvement





Capital investment is a primary driver of economics

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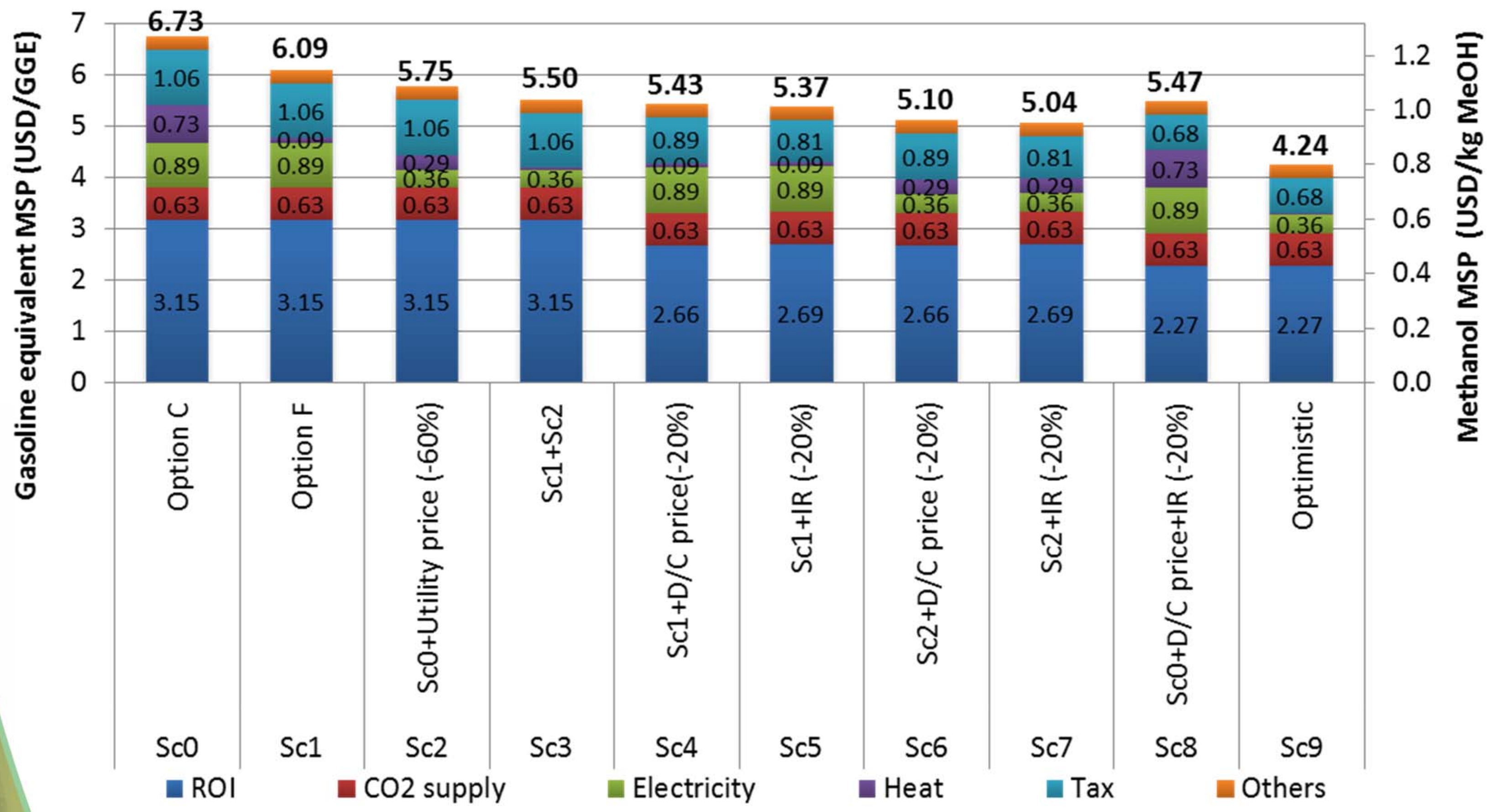
Mixed pathway to MeOH



Sensitivity Analysis to Identify High impact areas

Take home points

- For any approach to Solar Fuels- Efficiency is key for cost and scalability
  - 10% solar to hydrocarbon minimum
  - Sunlight is the high cost feedstock (capital cost to capture it)
  - Avoid resource limits
- Thermochemical approaches have great promise and potential for large impact
  - Potential for high efficiency
  - Systems studies support claims for eventual economic viability
  - Adjacency to other technologies (e.g. solar electric, solar reforming) can help move technology forward
  - Small global community has made significant advances in recent years
- Materials, Reactors, and Systems are all areas of opportunity and need.
  - All impact efficiency, all relatively immature for this technology.
  - Large multidisciplinary efforts with close collaboration between materials developers, reaction engineers, system modelers, etc. are ideal to move the technology forward

Producing solar fuels via thermochemical processes has the potential for transitional impact in our future energy mix of liquid transportation fuels

A Snapshot of the S2P Project Team

Principal Investigator – James E. Miller
Project Managers - Ellen B. Stechel and 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), Jonathan Scheffe (student)


Merci pour votre intérêt!
Thank you for your interest.

Backup slides

Research Opportunities

- Materials
  - Despite our success, the possible palette of materials has barely been explored -opportunities for good science and engineering are nearly endless.
  - Oxide ion conductors with redox centers.
  - Low risk: modifying known materials – composition and structure.
  - High risk (high payoff): developing new materials altogether.
- Reactors
  - Materials improvements will not likely completely close the gap.
  - Recuperating reactors, integrated systems.
- Systems
  - Full Life cycle analysis, Targeted development
- Ideal: close collaboration of materials developers, reaction engineers, system modelers, etc.

No substitute for actual on-sun operation

Interplay of Materials and Systems determine Reactor Efficiency

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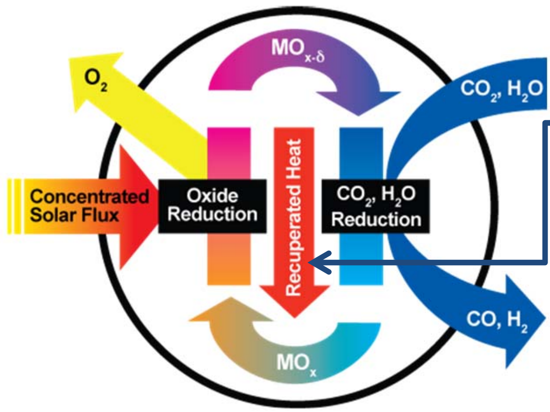
$MO_x \rightarrow MO_{x-\delta} + \delta/2\ O_2$ (ΔH_1, T_{high}, e.g. 1500 °C)



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

T_{low}, e.g. 800 °C

<u>Efficiency is a function of:</u>

Thermodynamics: ΔH_1 (T_{high} & T_{low}), δ

Kinetics: δ

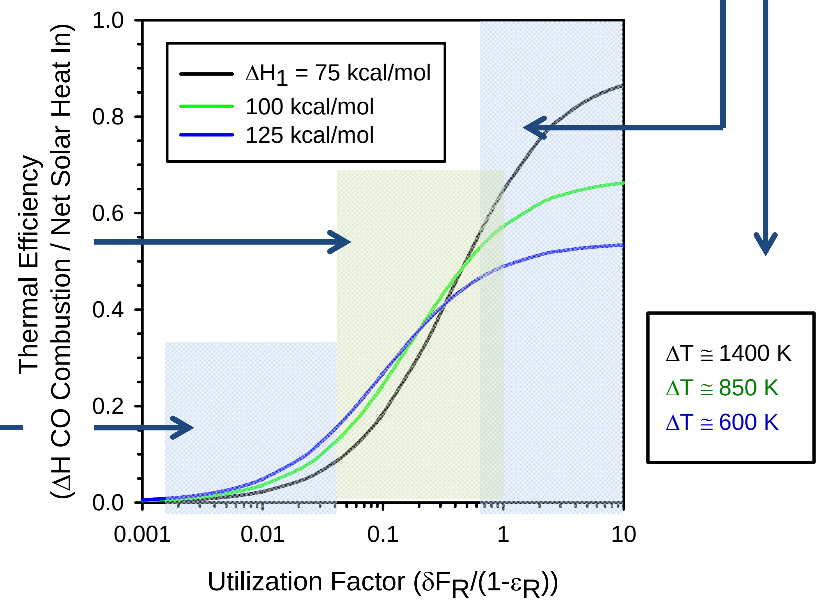
The reactor: recuperation effectiveness & pressures, sweep etc. (work input)

The maximum possible efficiency is limited by ΔH_1.

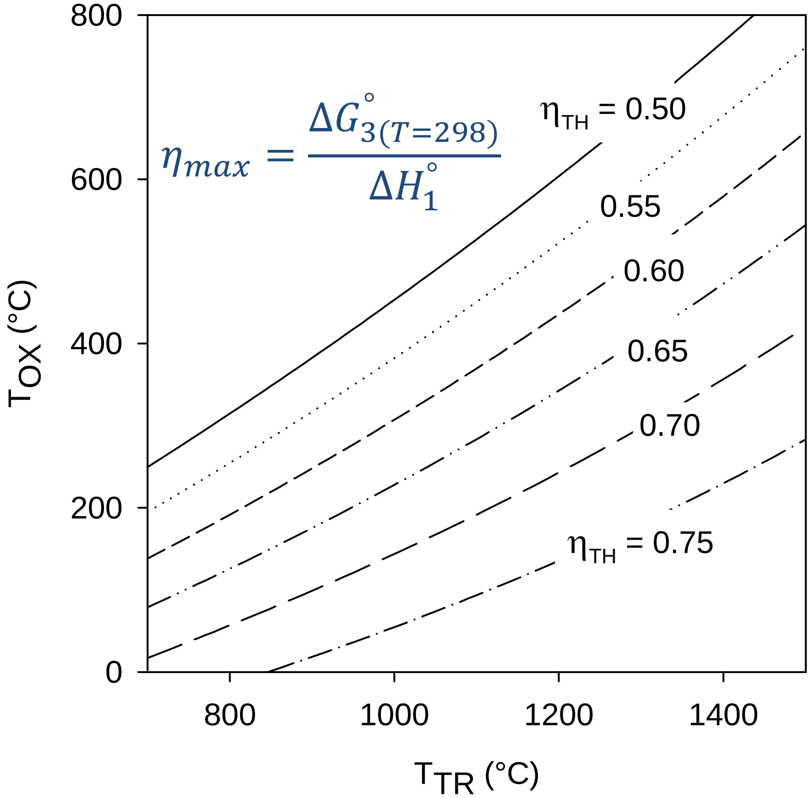
High efficiency (small ΔH_1) corresponds to a large T_{high}-T_{low}.

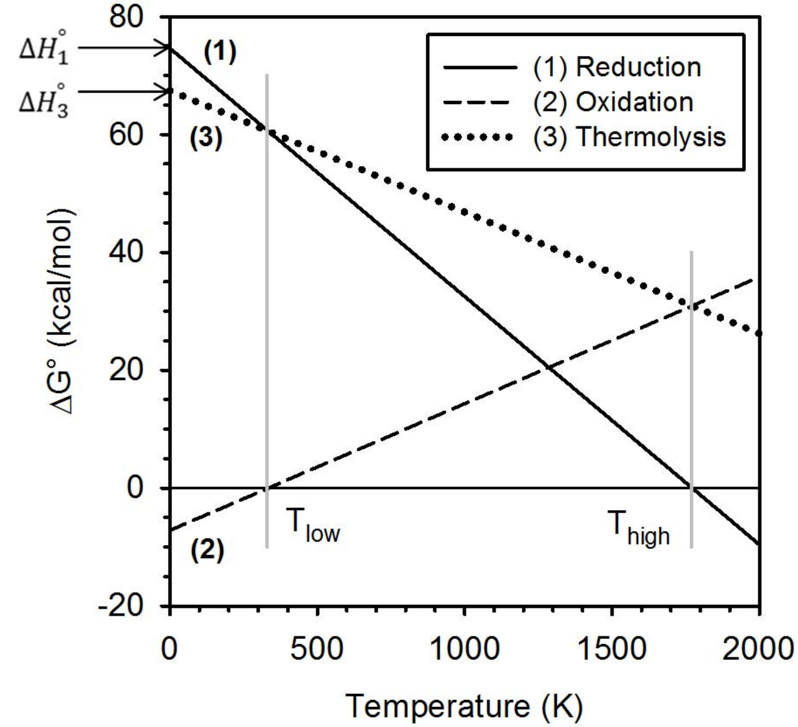
The possible efficiency increases with degree of reaction (δ) and/or effectiveness of recuperation.

When utilization is low, sensible heat demand becomes a more dominant factor than ΔH_1.



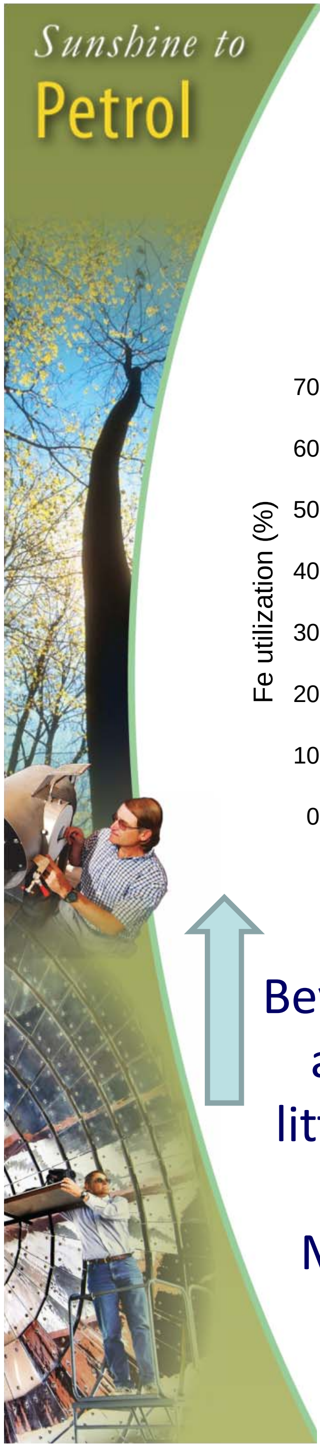
Thermodynamics and Efficiency





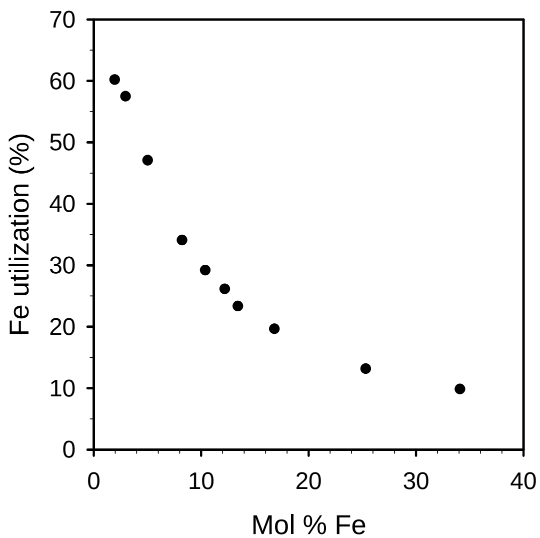
Ideal behavior assumed.

$$\eta_{max} = \frac{\left[1 - \frac{298}{T_{thermolysis}}\right]}{\left[1 - \frac{T_{low}}{T_{thermolysis}}\right]} \left[1 - \frac{T_{low}}{T_{high}}\right]$$

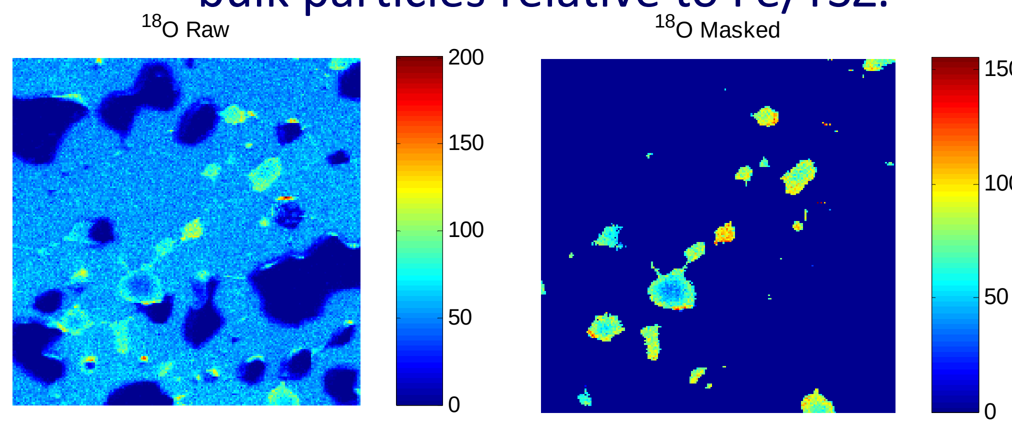


Fe redox centers, Zirconia transport

Pioneered by Kodama et. al. (ISEC) 2004, ISEC2004-65063, Portland, OR.



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



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

Maximizing Fe content through Y content