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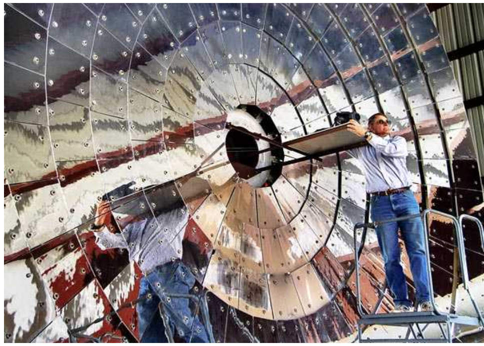

Solar Thermochemistry for Producing Fuels from Carbon Dioxide and Water

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Sandia National Laboratories

Advanced Materials Laboratory

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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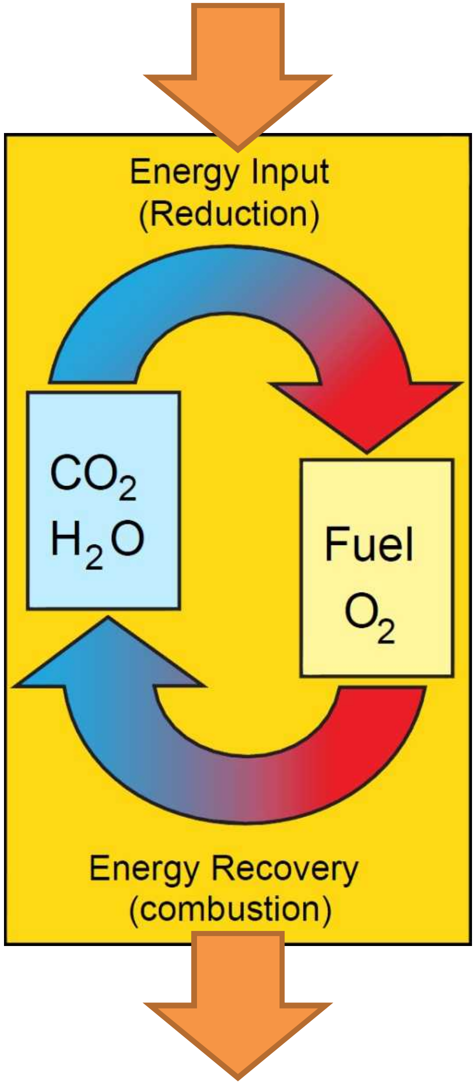
Closing the Cycle



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

Vision: ***Achieving many of the benefits of hydrogen while preserving the advantages of the Hydrocarbon Economy*** by effectively and efficiently reversing combustion, i.e. "energizing" CO_2 and H_2O back into hydrocarbon.

$$Sunlight + CO_2 + H_2O \rightarrow Fuel + O_2$$

Process should be analogous to, but more efficient than, those that produce bio and fossil fuels.

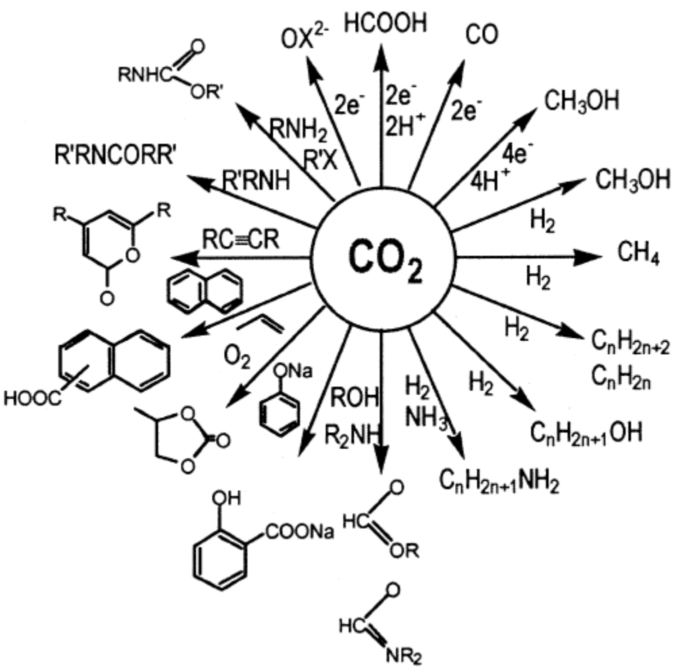
Capitalize on decades of Synfuel technology, e.g.

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

Why Fuels for CO_2 Utilization:

Fuels are the high impact Opportunity Space,
Commensurate with CO_2 Production

CO_2 utilization chemistry (From Aresta, Studies in Surface Science and Catalysis 114,1998).

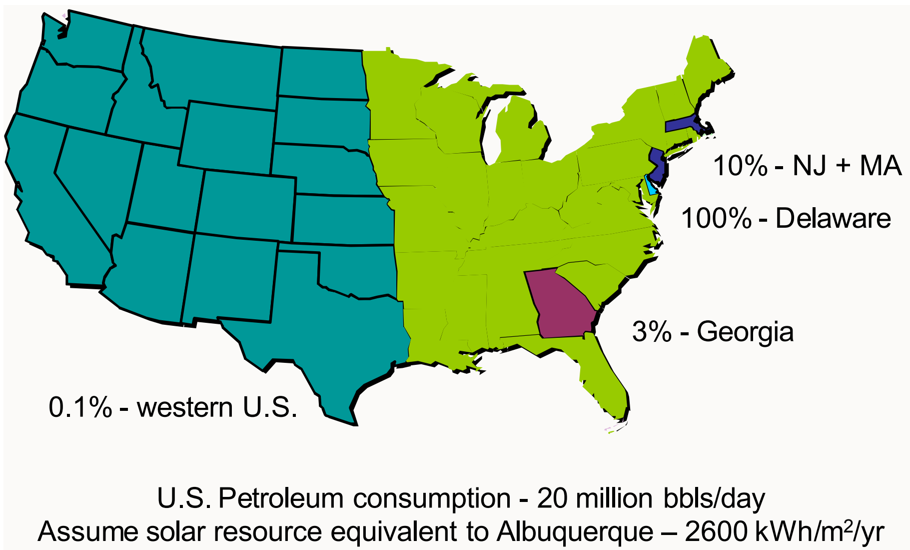


	2004 U.S. production (1,000 metric tons)	CO_2 equivalents* (1,000 metric tons)
Ethylene	25,682	80,641
Propylene	15,345	48,183
Ethylene dichloride	12,163	10,811
Top 3 U.S. Chemicals		139,635
U.S. Petroleum		2,458,000 (5.7%)
Petrol, Coal, NG		5,705,000 (2.4%)

Sources: C&E News July 2, 2007; Report DOE/EIA-0573 (2004).
* Assuming 100% conversion of CO2 into the hydrocarbon, e.g. 2 moles of CO_2 would supply the carbon for 1 mole of C_2H_4.

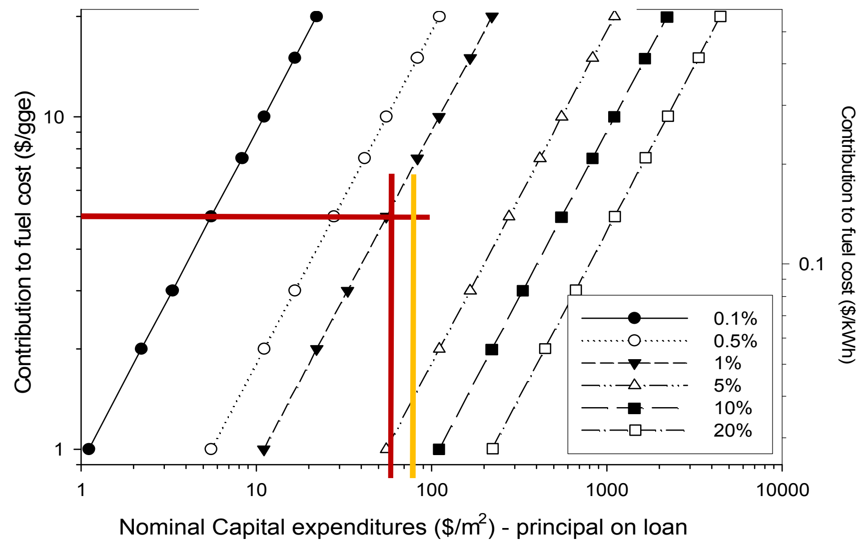
Meeting a significant fraction of transportation fuel demand with solar fuels is certainly plausible!

- ***High solar to fuel LC efficiency (>10%) is a requirement.***



$5/gge = $60/m² at 1% efficiency

PE Greenhouse $80/m²



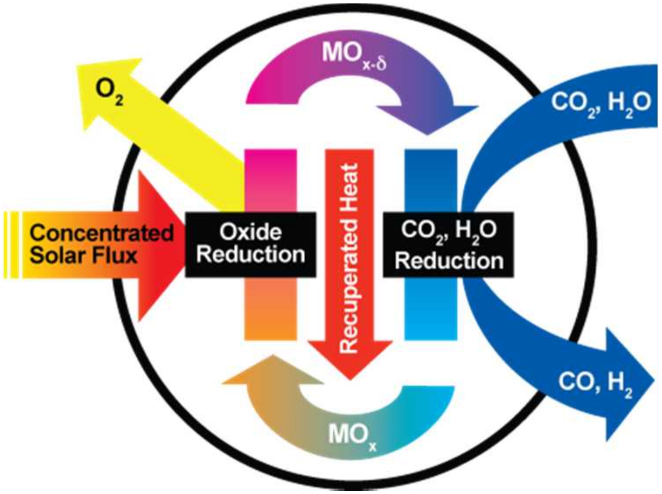
- ***Water, CO_2 are not limiting resources***
  - **Water consumption/cost relatively low – (may be spoken for)**
  - **High impact opportunity for CO_2 (short term stationary, long term air capture)**
- ***Consistent with other human activities occurring over multiple decades.***

E.B. Stechel and J.E. Miller "Re-energizing CO_2 to fuels with the sun: Issues of efficiency, scale, and economics" Journal of CO_2 Utilization, 1 (2013) 28–36.

Thermochemical Cycles: A Simple Concept …

Unfavorable reaction
e.g. $H_2O \rightarrow H_2 + ½ O_2$
divided into two more favorable reactions.

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



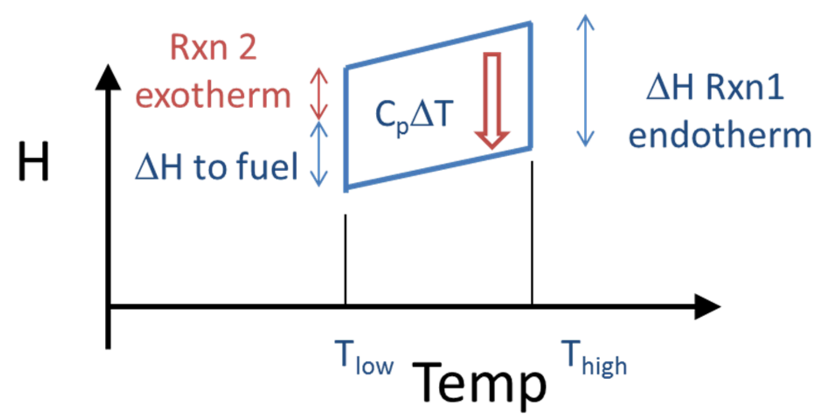
2) $1/\delta\ MO_{(x-\delta)} + CO_2 \rightarrow 1/\delta\ MO_x + CO$

3) $CO_2 \rightarrow CO + ½ O_2$

Fe_3O_4/FeO is the archetypical cycle

A thermochemical cycle is essentially an engine that converts heat into work in the form of stored chemical energy. ***Efficiency gains are possible as initial conversion to mechanical work and electricity are avoided.***

$$\Delta H_{endotherm} - \Delta H_{rxn\ exo} = \Delta H_{fuel}$$



Thermodynamics require a temperature difference for the two reactions.

… With A Lot of Nuances to Doing it Well.

Unfavorable reaction
e.g. $H_2O \rightarrow H_2 + ½\ O_2$
divided into two more favorable reactions.

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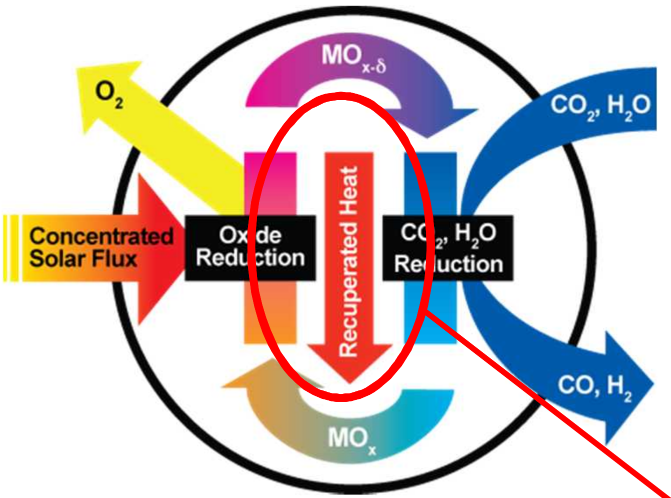

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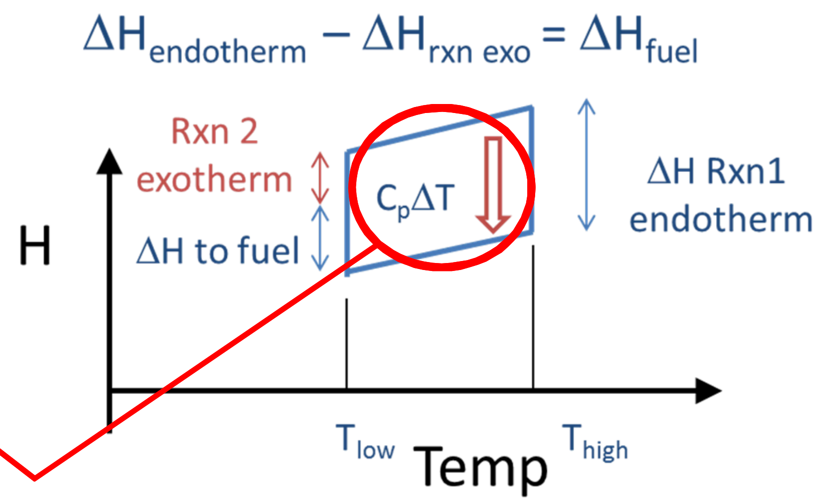
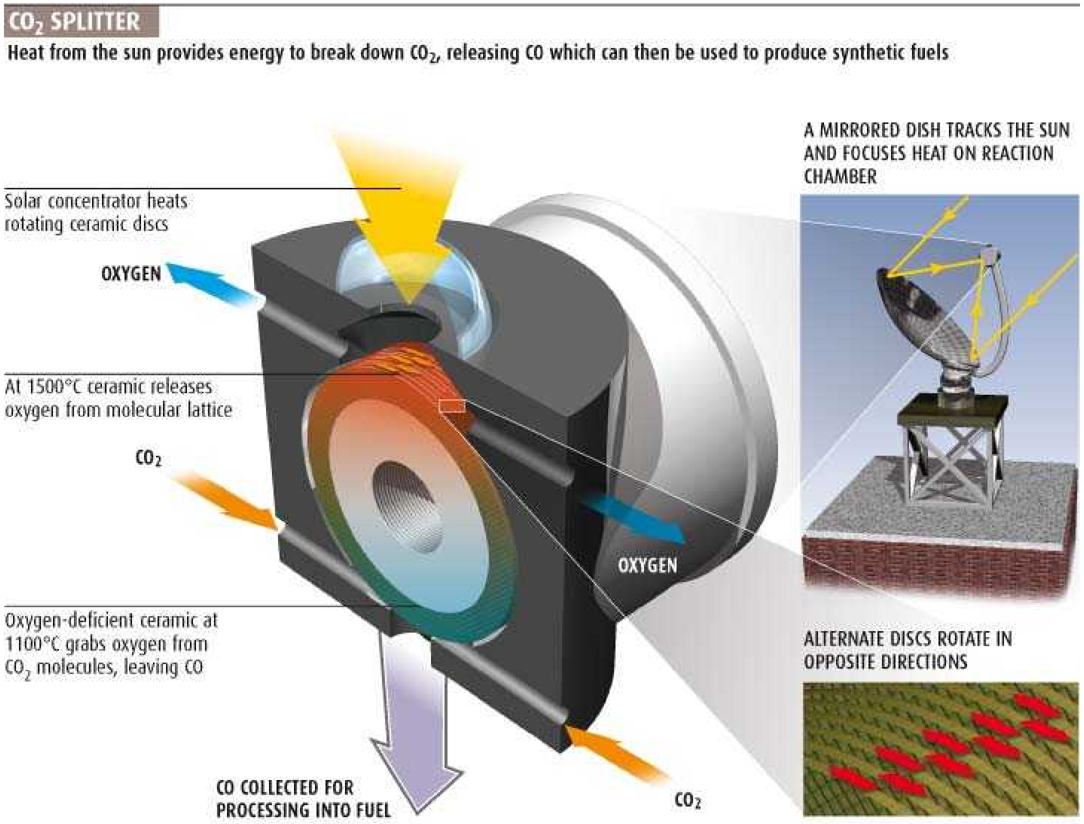


Example: Managing Sensible Heat is Essential to Efficiency

CR5 : First-of-a-kind approach and our attempt to apply the lessons.

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

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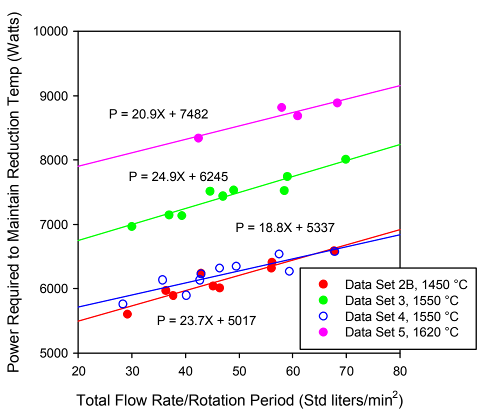
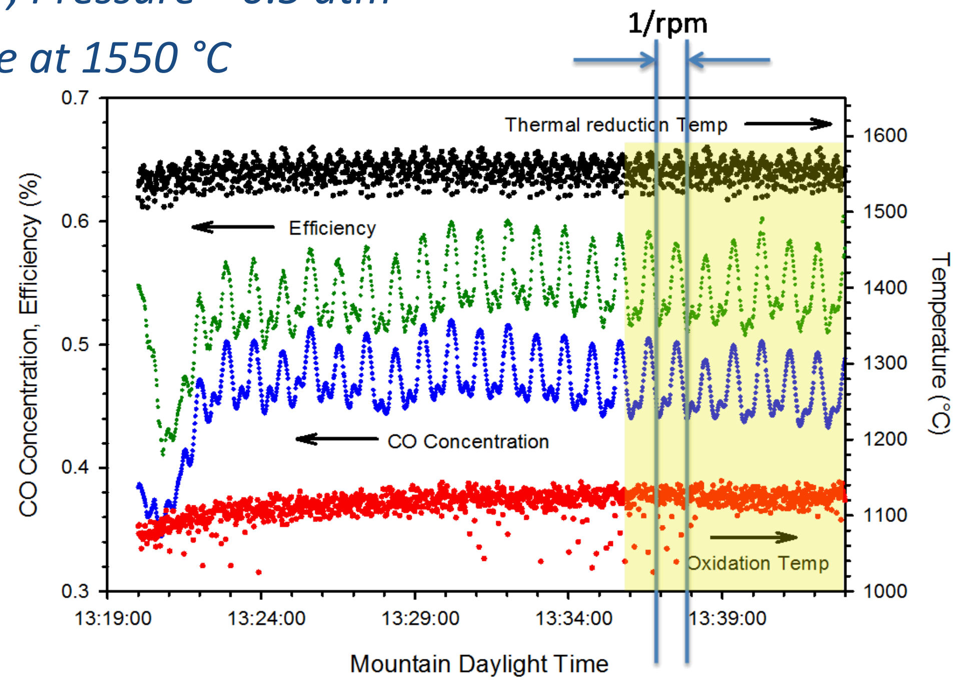
Collect data to validate models, guide improvements

- *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*





J.E. Miller, M.A. Allendorf, A. Ambrosini, E.N. Coker, R.B. Diver, I. Ermanoski, L.R. Evans, R.E. Hogan, and A.H. McDaniel "Development and Assessment of Solar-Thermal-Activated Fuel Production: Phase 1 Summary" SAND2012-5658, July 2012

Take-home points

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- For any approach to Solar Fuels- Efficiency is key for cost and scalability – 10% solar to fuel minimum (lifecycle)
  - Often it is unappreciated that sunlight is a “high cost” feedstock (capital cost)
  - Low efficiencies increase scale, further challenge efficiency and stretch resources.
  - CO_2 and water (and associated energy costs) are not limiting
- Thermochemical approaches have potential for high efficiency and thus high impact
  - Systems studies support idea of eventual economic viability – difficult but not implausible
  - 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.
  - Adjacency to other technologies (e.g. solar electric, solar reforming) can help move technology forward, but focused cross-discipline efforts are also needed.

Solar fuels have the potential for transformational impact in our future energy mix.


Thank You.