SAND2012-0333P

Solar Thermochemical Fuels

Ivan Ermanoski

Sandia National Laboratories

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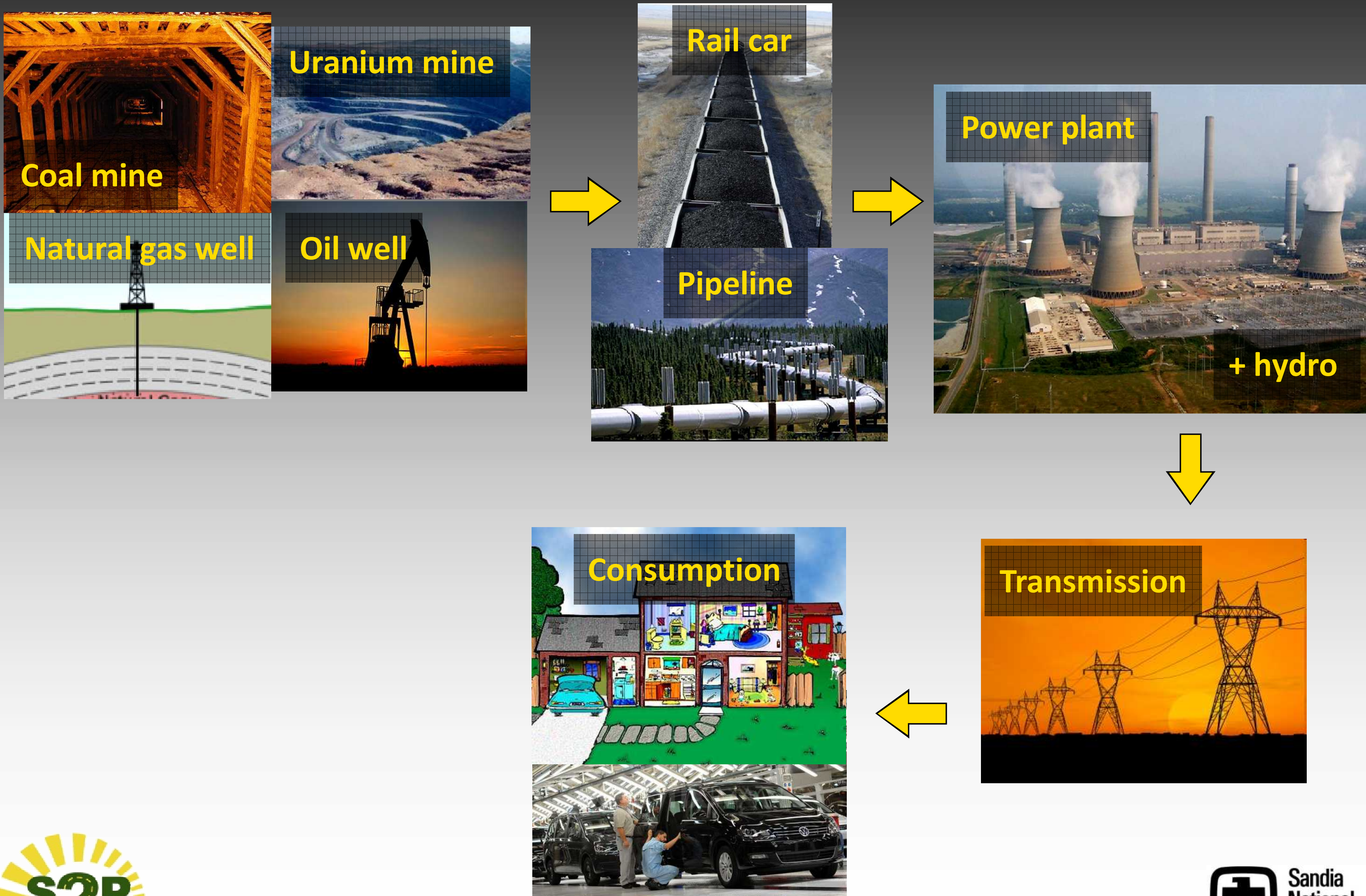
Outline

- The role of fuels in today’s energy landscape
- Concentrated solar power and solar fuels
- Packed bed particle reactor for solar fuel production
- Final thoughts

The 19th & 20th Century US Electricity Paradigm



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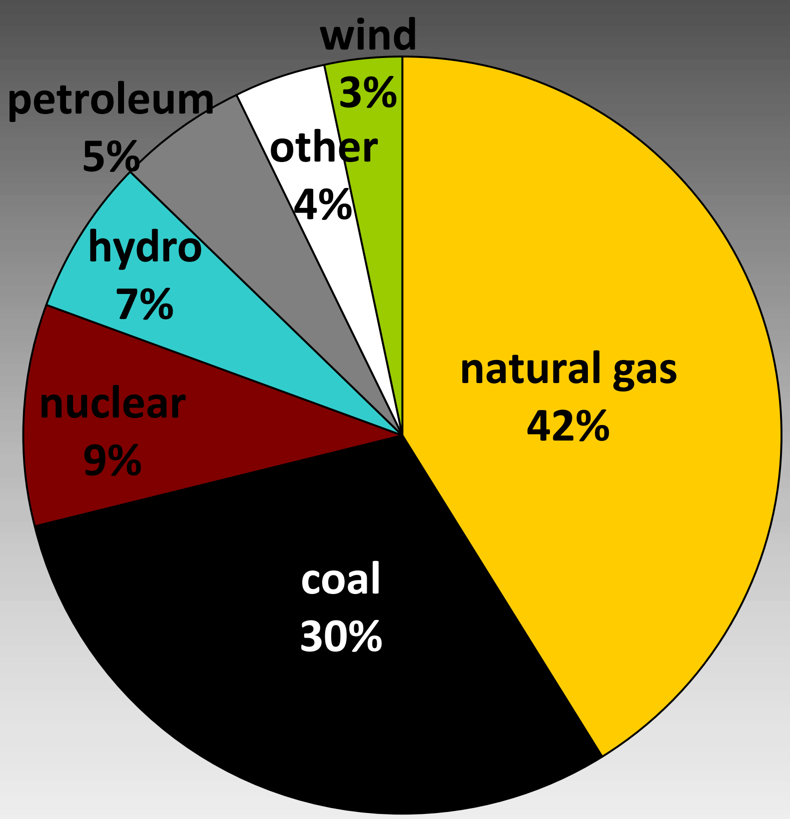
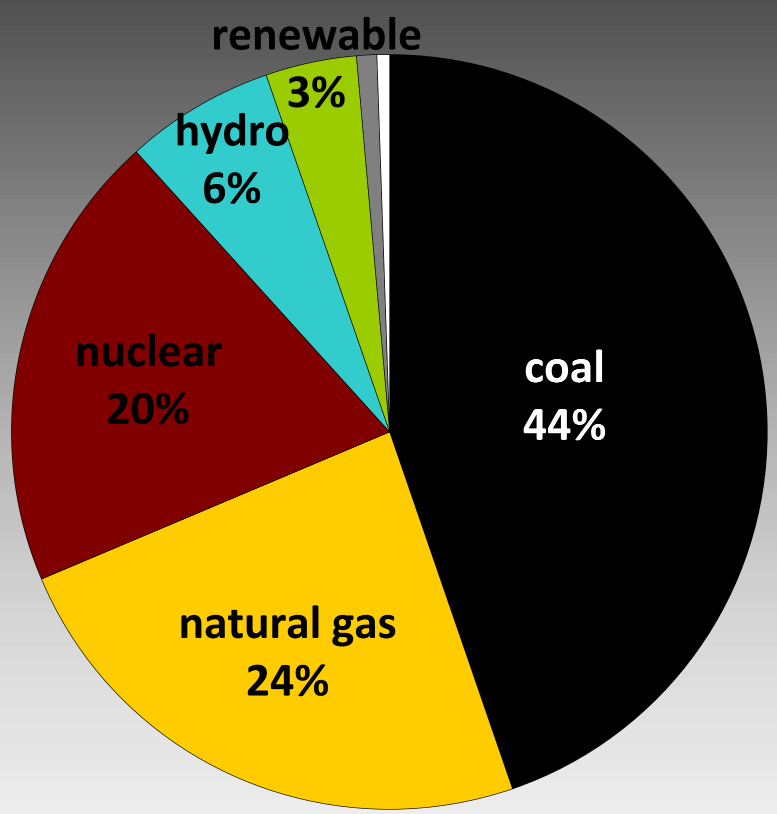
US Electricity Sources: Mostly Fuels



United States 2010
nameplate capacity



United States 2010
net generation

Source: Energy Information Administration

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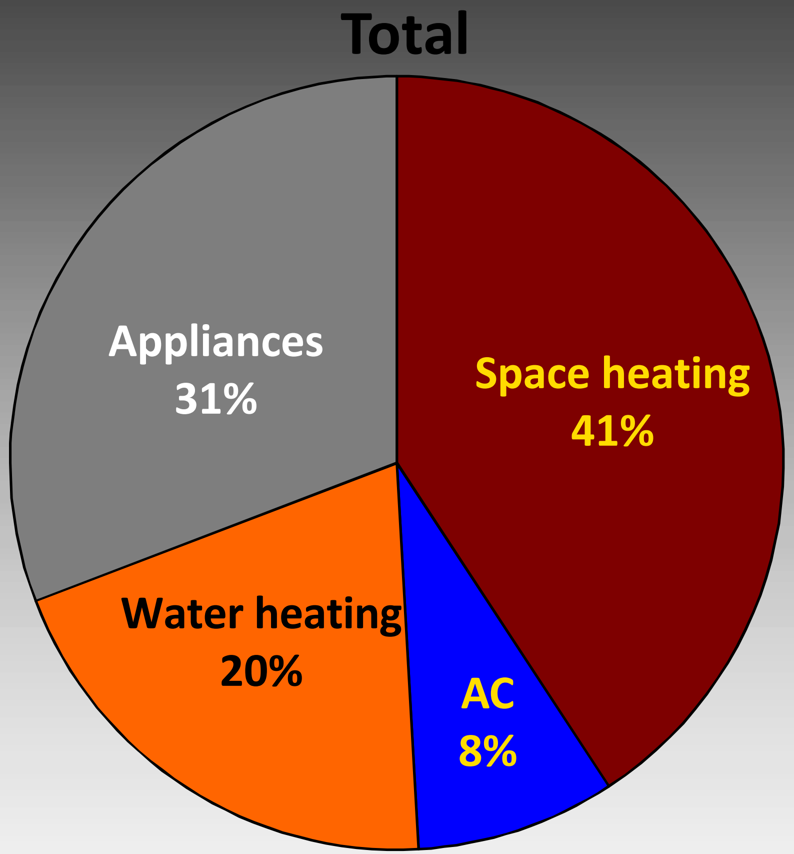
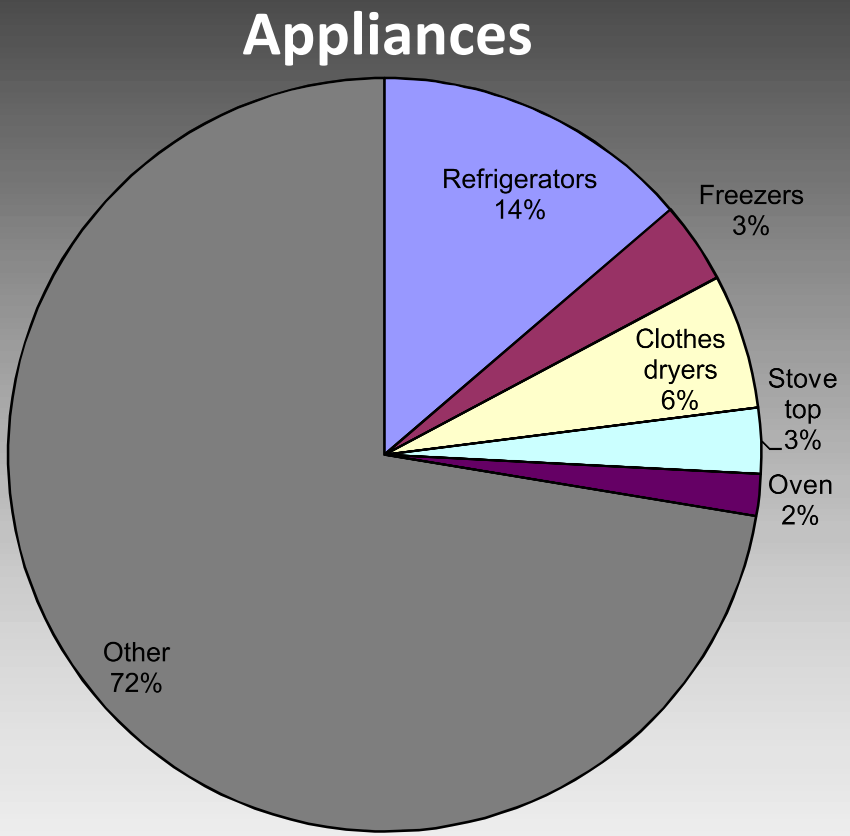
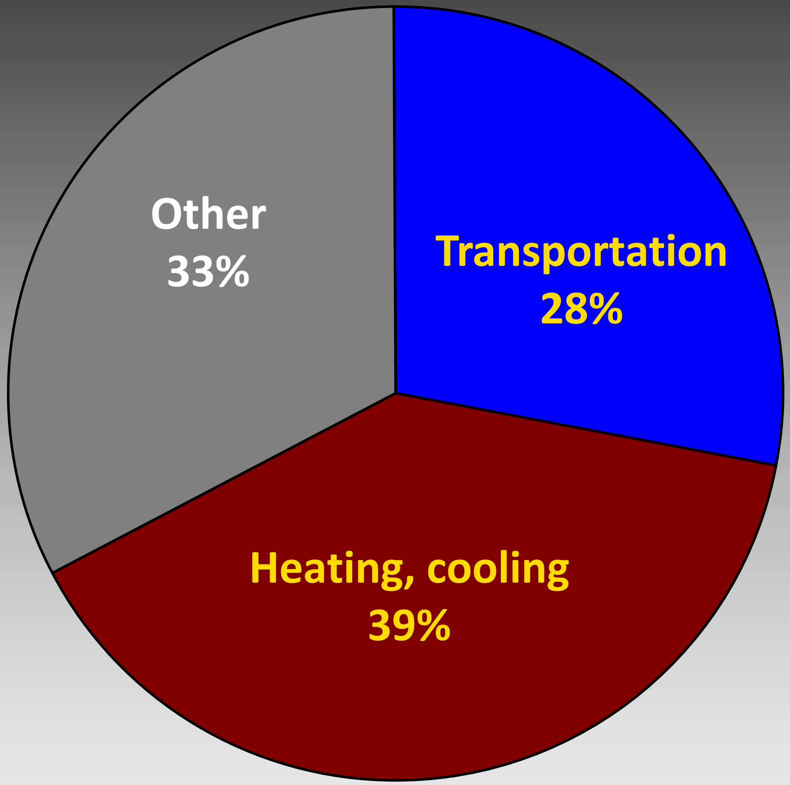
Residential Energy Needs: Mostly Heating and Cooling





US residential energy consumption: 78% heating and cooling

US Energy Needs: Mostly Heating, Cooling, and Fuels



Total US energy consumption

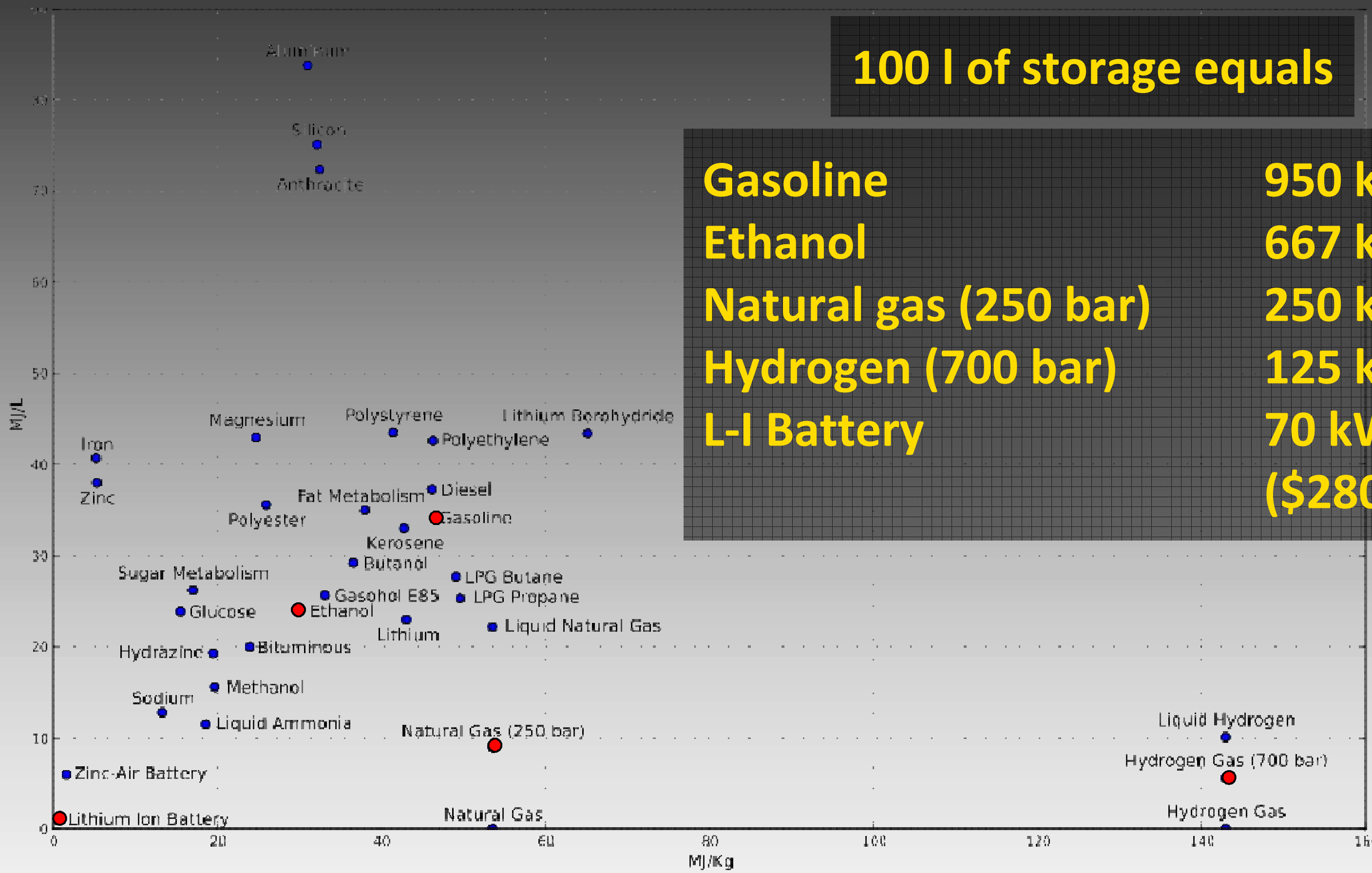
Why Fuels? Energy and Transport Efficiency

Energy efficiency	
Conventional thermal	35%
Combined cycle	60%
Cogeneration/Micro CHP	80%
Trigeneration	>85%

Transport losses	
Oil pipeline	0.8%
Natural gas pipeline	3%
Electricity T&D	9%

Most efficient approach: Deliver fuel close to point of use

Why Fuels? Storage



100 l of storage equals

Gasoline	950 kWh
Ethanol	667 kWh
Natural gas (250 bar)	250 kWh
Hydrogen (700 bar)	125 kWh
L-I Battery	70 kWh ($28000)

Days of power reserve from a comparatively small tank

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So, Why Fuels?

- Good fit for energy end-use: in transportation, heating, cooling
- Fuels can be transported efficiently
- Efficient when used localy (cogeneration/trigeneration)
- Fuels are easy (and inexpensive) to store

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Concentrated Solar Power: Full Solar Sprectrum Use

Parabolic trough

Power tower

Parabolic dish

Why Solar Thermochemical Fuels?

- Potential for high efficiency:
  - Use the entire solar spectrum
  - Efficient conversion of solar to chemical energy
  - Production of H_2 and CO avoids reverse water gas shift reaction in hydrocarbon synthesis
- Majority of cycles are two-step metal oxide based
  - Thermal reduction (T>1300°C): $\frac{1}{\delta}MO_x \rightarrow \frac{1}{\delta}MO_{x-\delta} + \frac{1}{2}O_2$
  - Fuel production (T<1200°C): $\frac{1}{\delta}MO_{x-\delta} + H_2O \rightarrow \frac{1}{\delta}MO_x + H_2$

    $\frac{1}{\delta}MO_{x-\delta} + CO_2 \rightarrow \frac{1}{\delta}MO_x + CO$
- Key elements: reactive materials and reactors

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Comparison of Solar Fuel Technologies

- Molten salt power tower with 65% electrolysis efficiency
  - 11% annual average solar efficiency (solar to H_2)
- Dish-Stirling with electrolysis
  - 16% annual average solar efficiency (solar to H_2)
- PV with electrolysis
  - 10% annual average solar efficiency (solar to H_2)
- Corn ethanol
  - approximately 0.12% annual average solar efficiency (solar to ethanol)

These are the targets that need to be exceeded

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System Level View: Many Energy Losses to Consider

Resource efficiency = 95% for Daggett, CA (DNI > 300W/m^2)

Operational ~ 94%

Equip. Availability = 97%, Blocking&Shading = 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 heat: ~58%

Reactor <60%

H_2 CO

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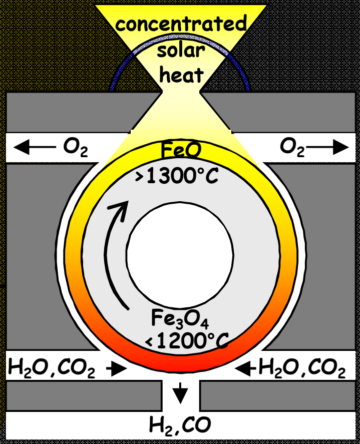
System Level View: Many Energy Losses to Consider

- Lots of places to lose energy
  - Solar collection is mature, improvements will be small

- The reactor is the single least efficient component
  - Improve materials
  - Improve reactor: key attributes

- Lessons learned from CR5:
  - Mechanical stability of reactive structures
  - Materials kinetics as source of efficiency limits

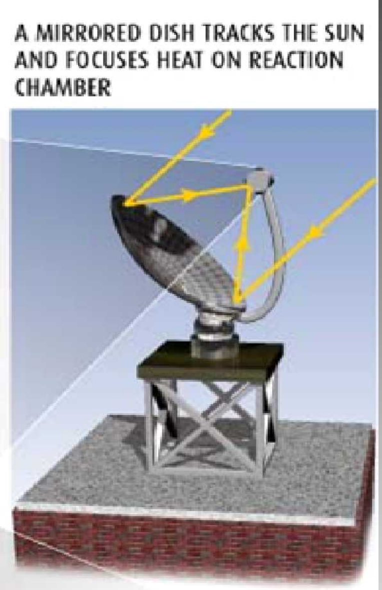


Solar-to heat: ~58%

Reactor 20-50%

H_2 CO

The CR5



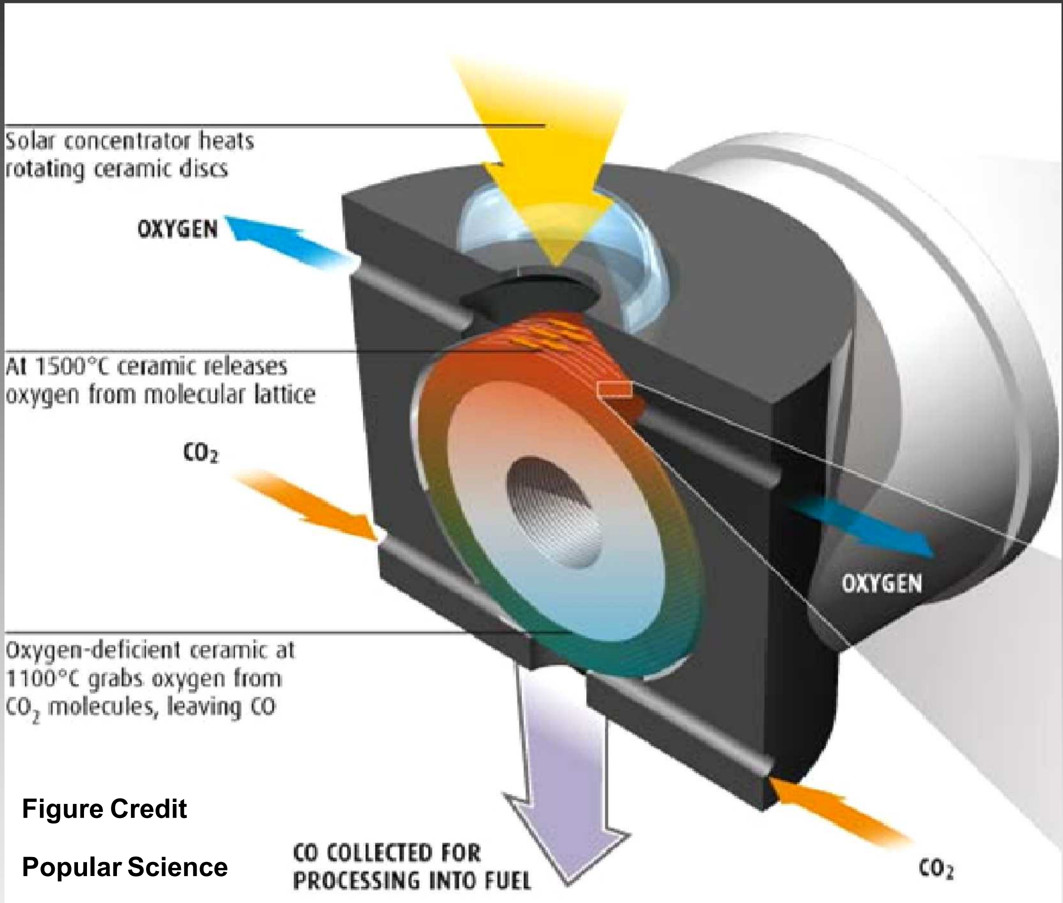


Figure Credit

Popular Science

Counter-Rotaring-Ring Receiver Reactor Recouperator

R.B. Diver, J. E. Miller, M. D. Allendorf, N.P. Siegel, R. E. Hogan, J. Solar Energy Engineering (130), 2008

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Desirable Reactor Attributes: Efficiency Driven

- Direct solar absorption by the working material
- Sensible energy recovery between T_H and T_L
- Continuous on-sun operation
- Pressure, temperature and product separation

- **Lessons learned:**
  - **– Reactive structures durability**
  - **– Material kinetics limitations**

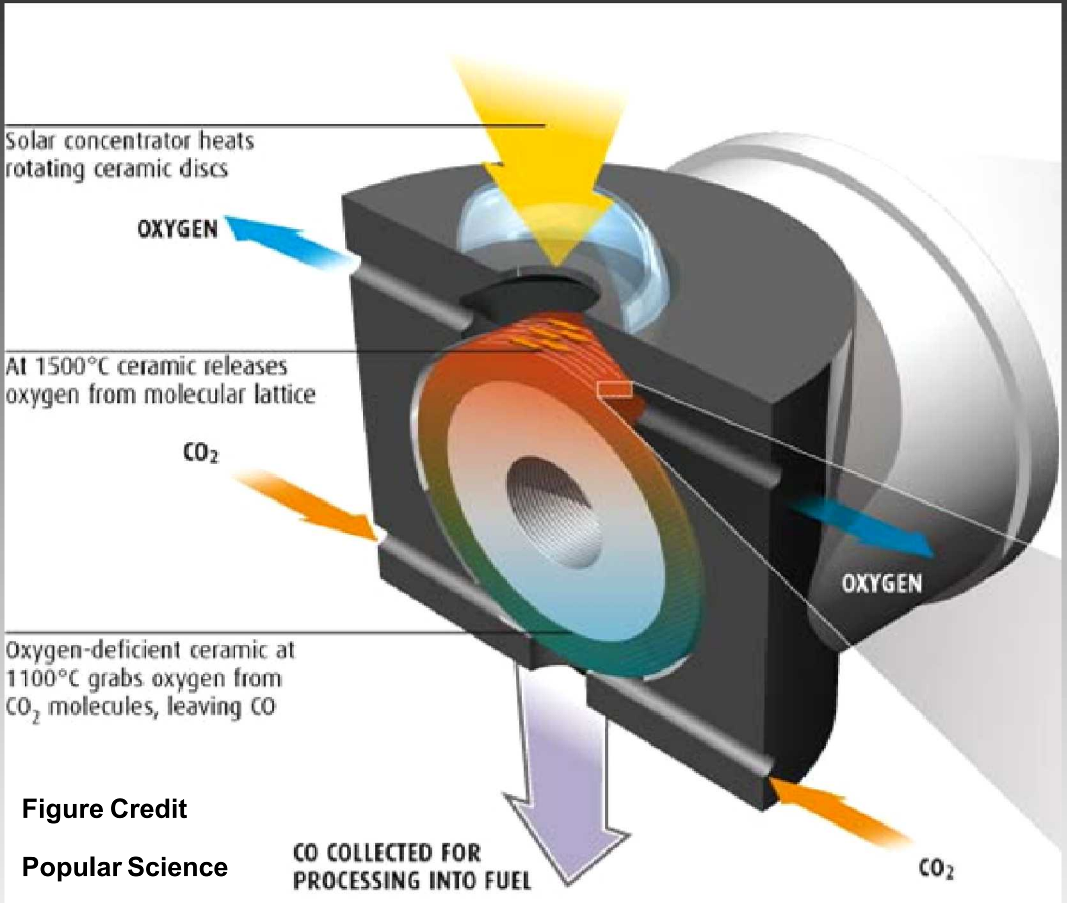


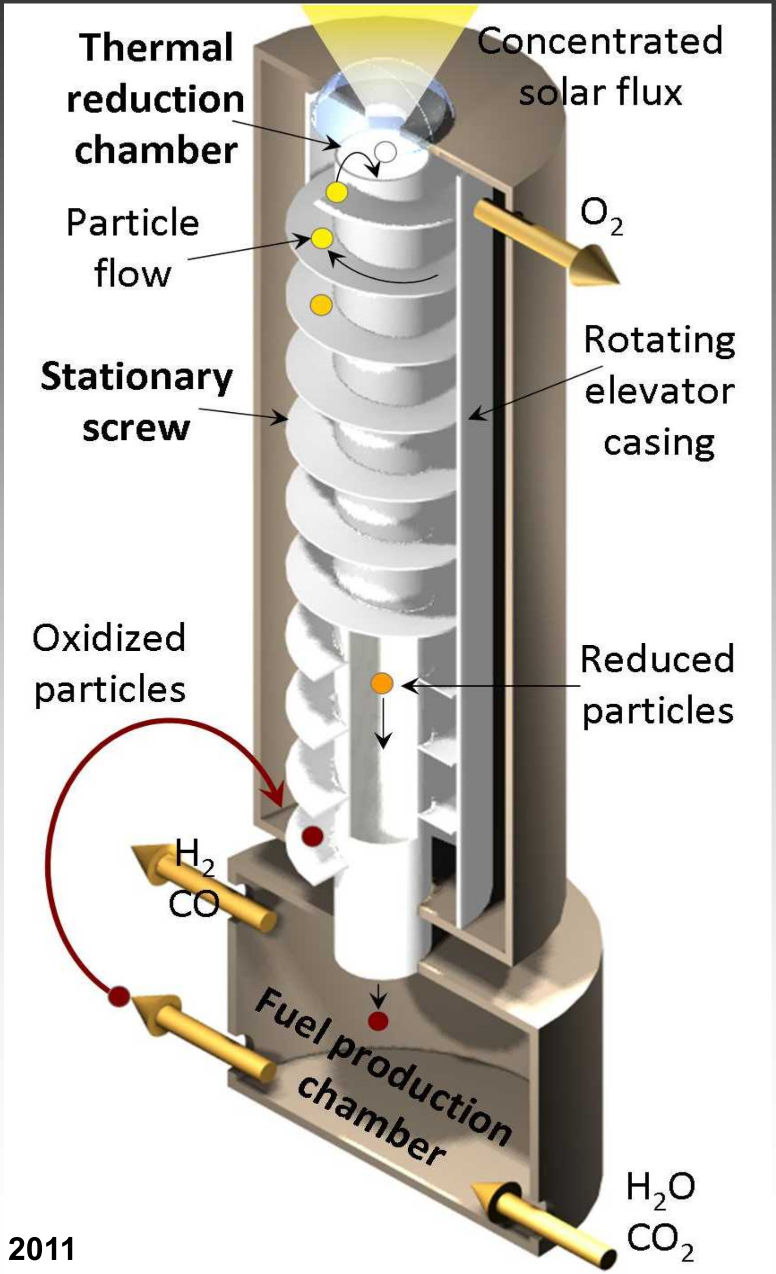
Figure Credit

Popular Science

Packed Bed Particle Reactor

- Direct solar absorption by the working material
- Sensible energy recovery between T_H and T_L
- Continuous on-sun operation
- Pressure, temperature and product separation

- **Pros:**
  - **– Small reactive particles (~100mm)**
  - **– Only particles are thermally cycled**
  - **– Independent component optimization**
  - **– Easy material replacement**
- **Cons:**
  - **– Particle conveyance**
  - **– Beam-down optics**



U.S. Patent Filed, Ermanoski, 2011

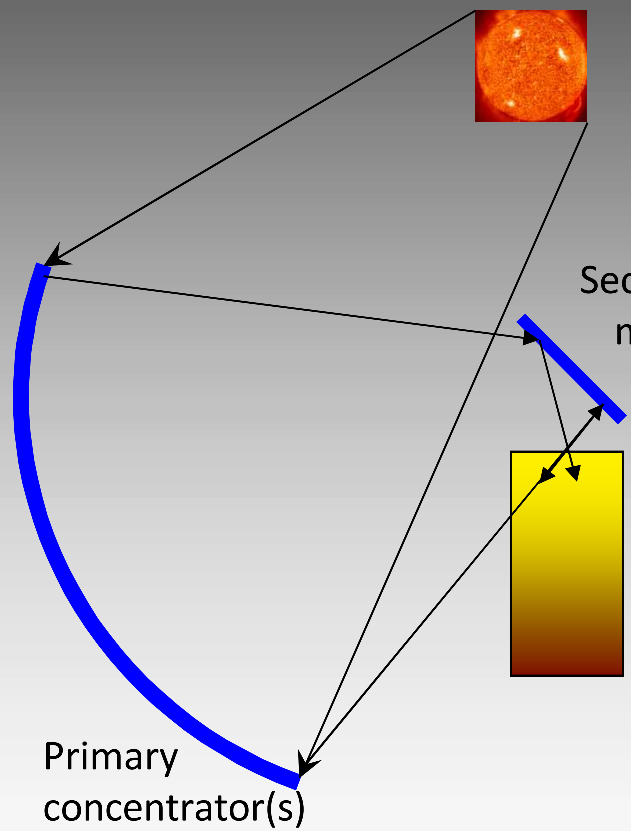
Solar Efficiency: An All Inclusive Metric

$$\eta = \frac{\dot{n}_{H_2/CO} \cdot HHV_{H_2/CO}}{P_S}$$

- *Collection losses (concentrator, re-radiation)*
- Metal oxide heating
- Metal oxide thermal reduction
- Feedstock heating (steam)
- Pumping
- Electrical/mechanical

$$CeO_2 \rightarrow CeO_{2-\delta} + \frac{\delta}{2} O_2$$

$$CeO_{2-\delta} + \delta \cdot H_2O \rightarrow CeO_2 + \delta \cdot H_2$$

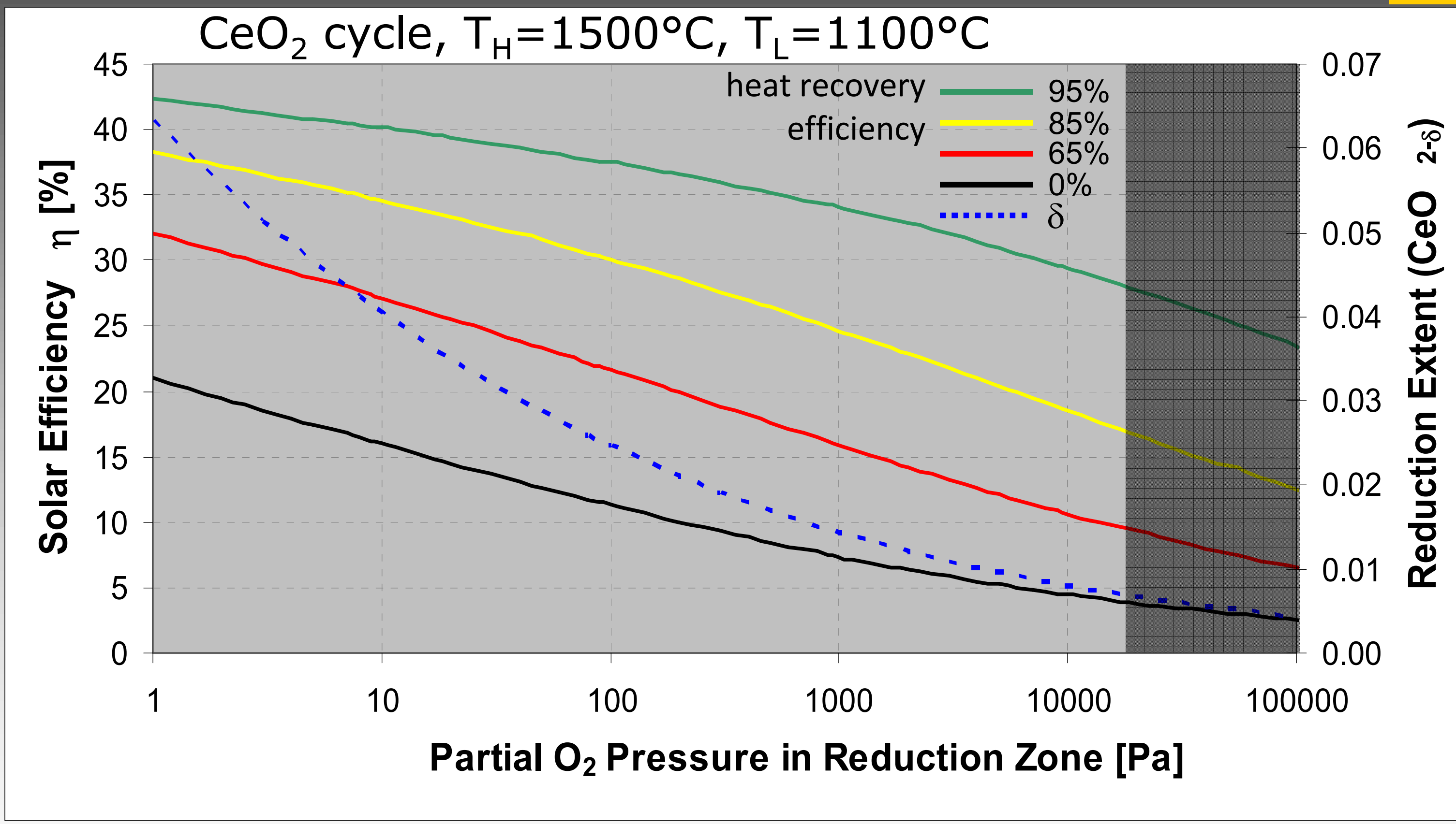


Solar is the *only* primary energy used

Packed Bed Reactor Performance Model

$$\eta = \frac{\dot{n}_{H_2/CO} \cdot HHV_{H_2/CO}}{P_S}$$

All mechanical work included, excess waste heat not included



Most important: Oxide chemistry, heat recovery, pressure (p_{O2})

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I. Ermanoski, N.P. Siegel, in prepearation

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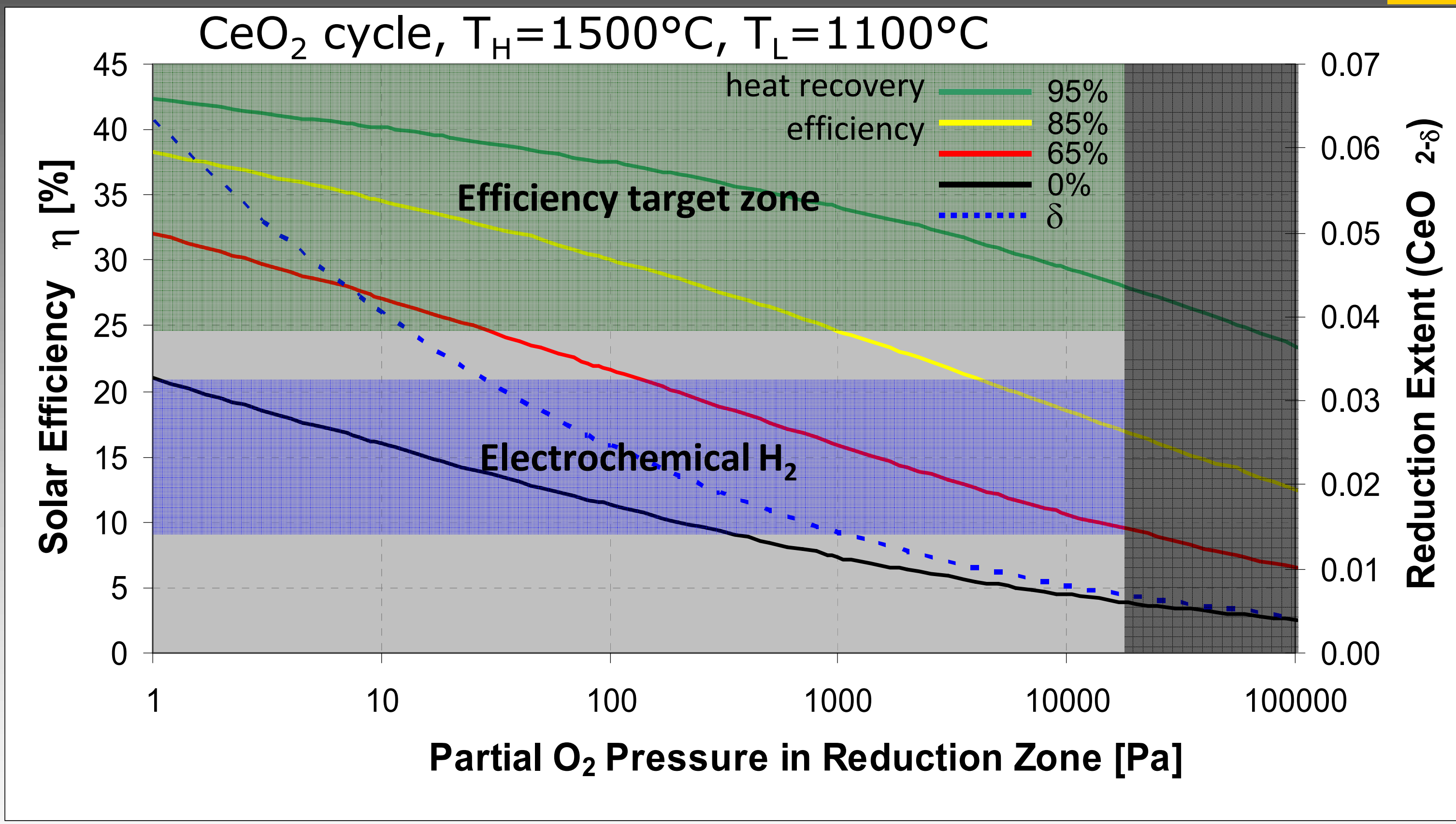
Packed Bed Reactor Performance Model

All mechanical work included, excess waste heat not included

$$\eta = \frac{\dot{n}_{H_2/CO} \cdot HHV_{H_2/CO}}{P_S}$$



Most important: Oxide chemistry, heat recovery, pressure (p_{O2})

I. Ermanoski, N.P. Siegel, in prepearation

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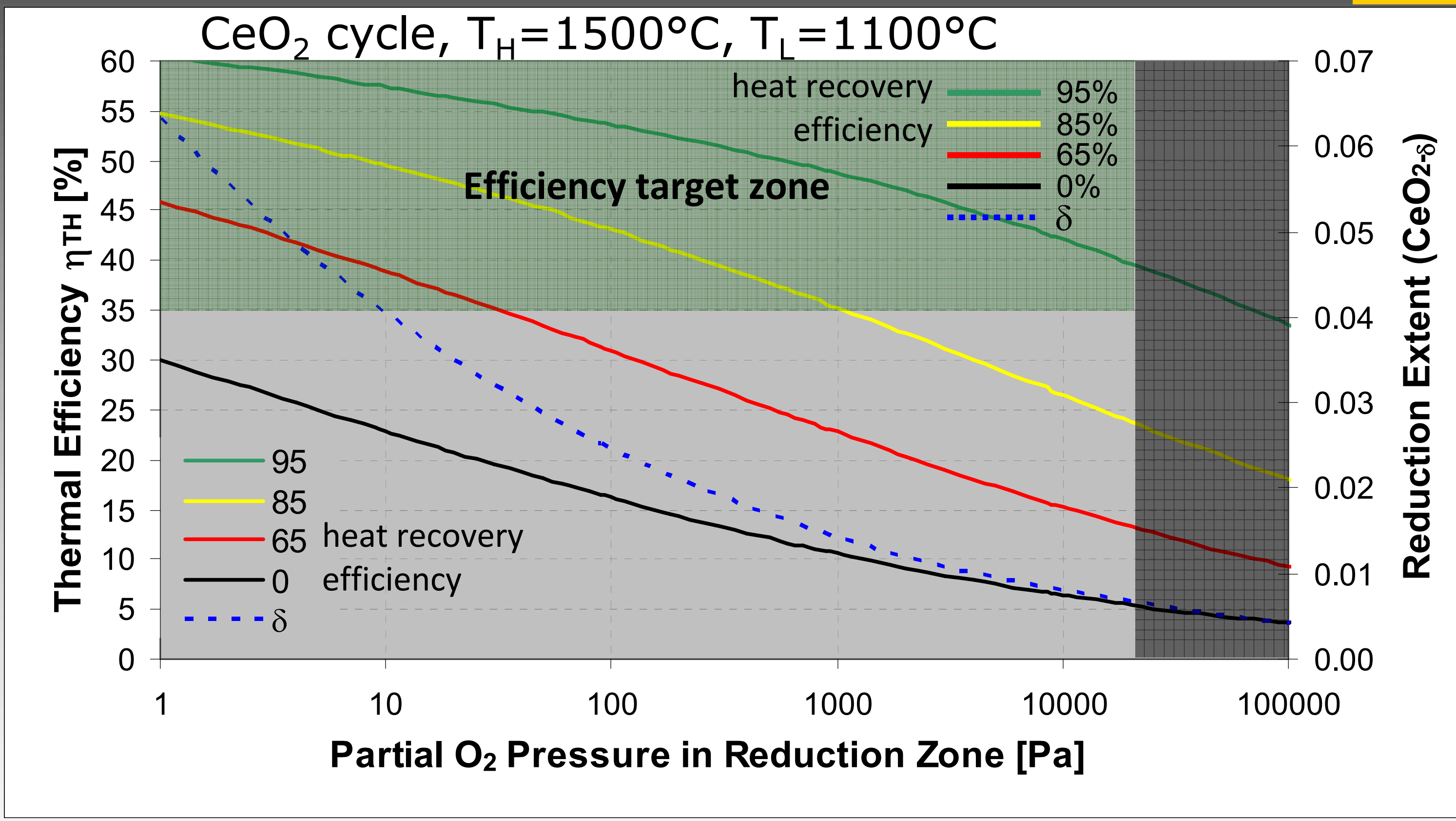
Performance Model Predicts High Thermal Efficiency

Collection losses excluded

All mechanical work included, excess waste heat not included

$$\eta_{TH} = \frac{\dot{n}_{H_2/CO} \cdot HHV_{H_2/CO}}{P_{TH}}$$



- **Thermal Efficiency > 50% possible even with CeO_2**
- **Great materials and efficient reactors needed for success**

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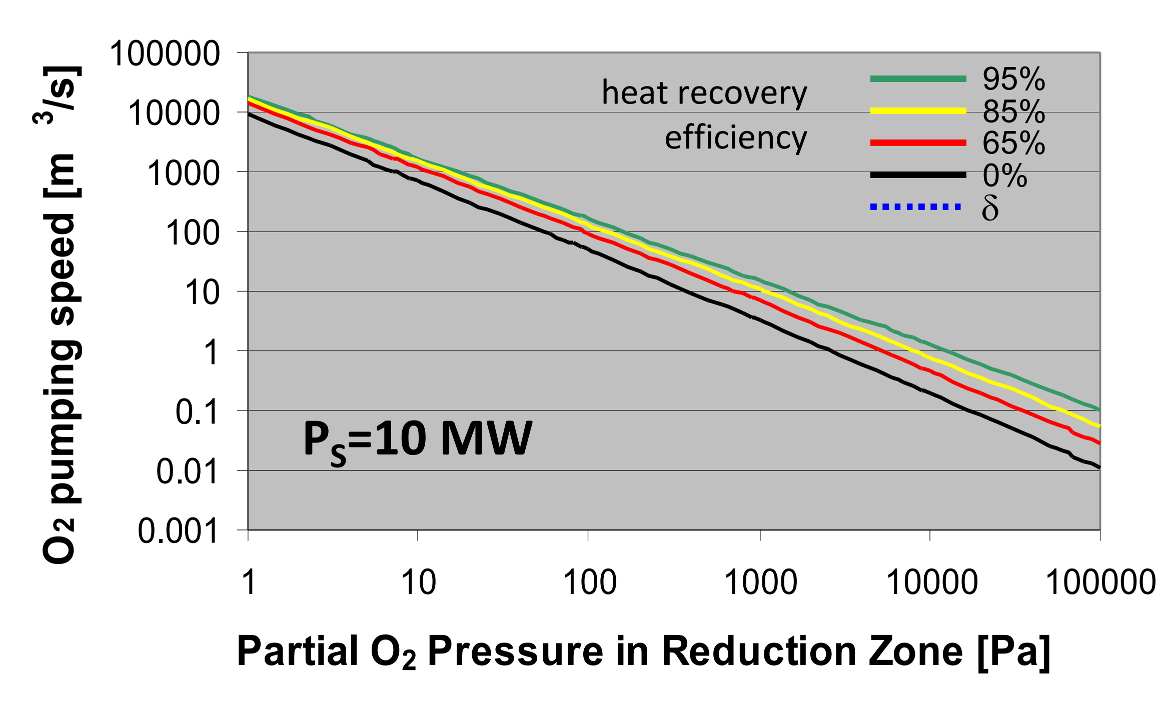
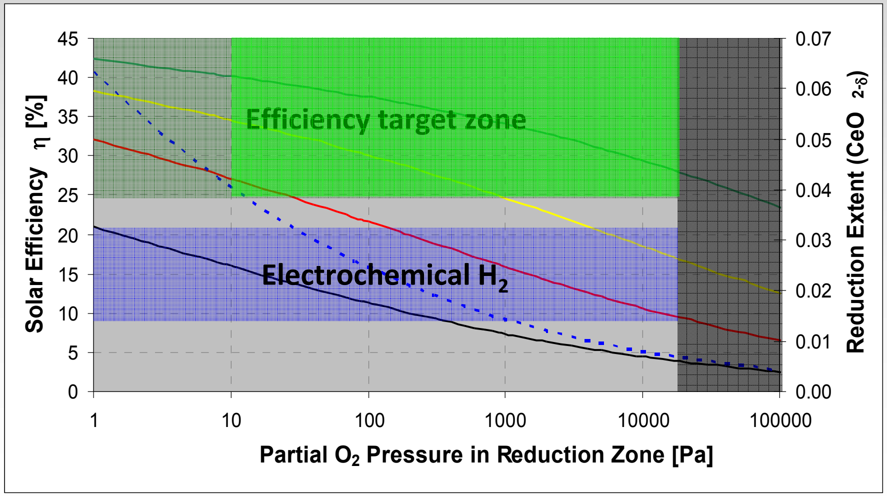
Low Pressure Limit: Pumping Speed



Pump size, not efficiency may limit p_{O2}



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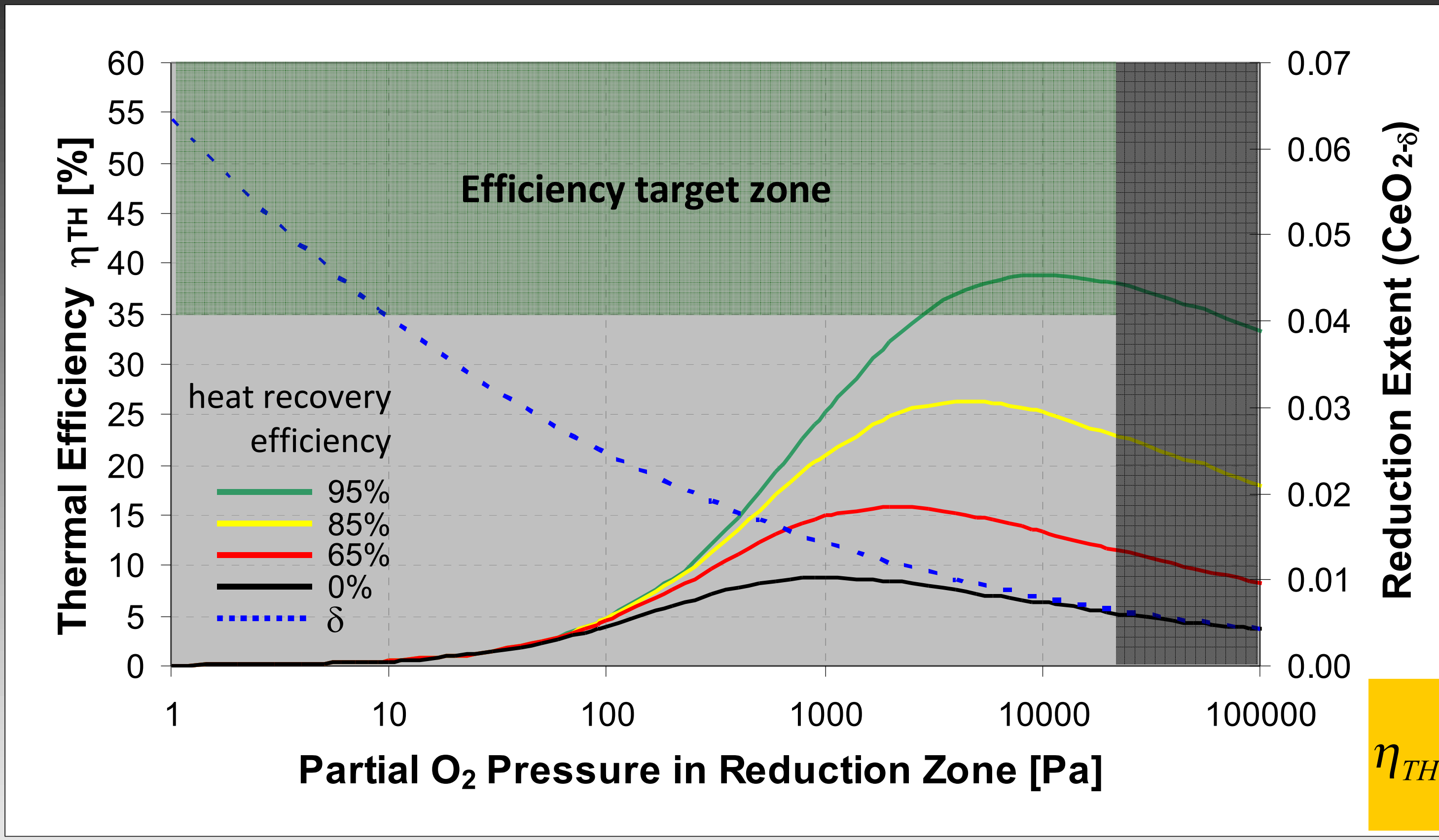
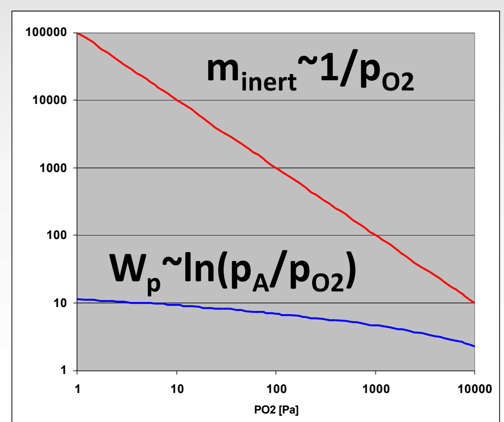
Inert Sweep Limit: Efficiency



$$\eta_{TH} = \frac{\dot{n}_{H_2/CO} \cdot HHV_{H_2/CO}}{P_{TH}}$$

Inert gas production and heating limit efficiency



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Weakly Coupled Design and Operational Flexibility

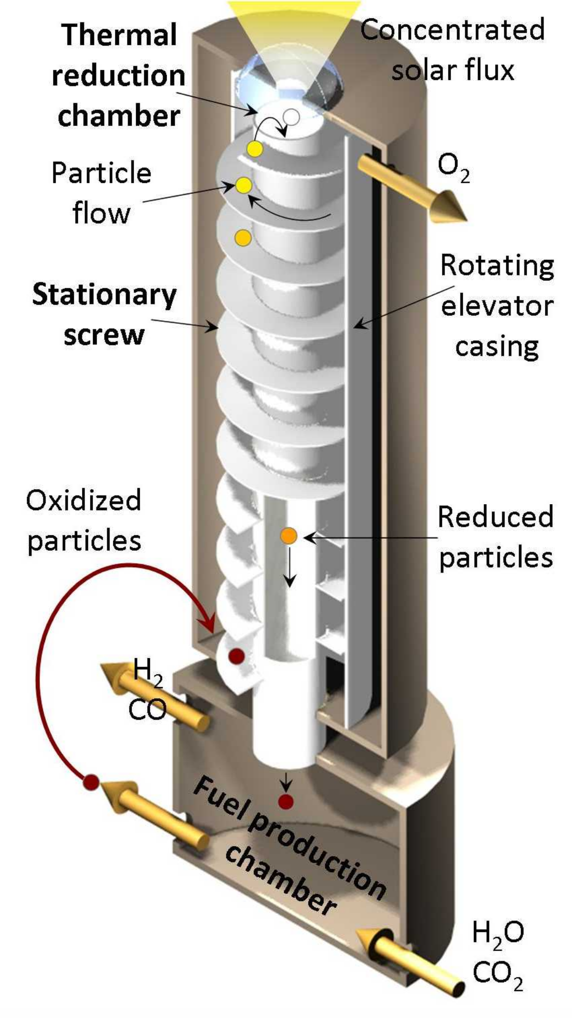
Independent component optimization allows a design point efficiency choice

Identify working oxide

Set T_H, residence time, p_{O2}

Set η_{HR} (size exchanger)

Set T_L, residence time



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Weakly Coupled Design and Operational Flexibility

Independent component optimization allows a design point efficiency choice

Identify working oxide

↓

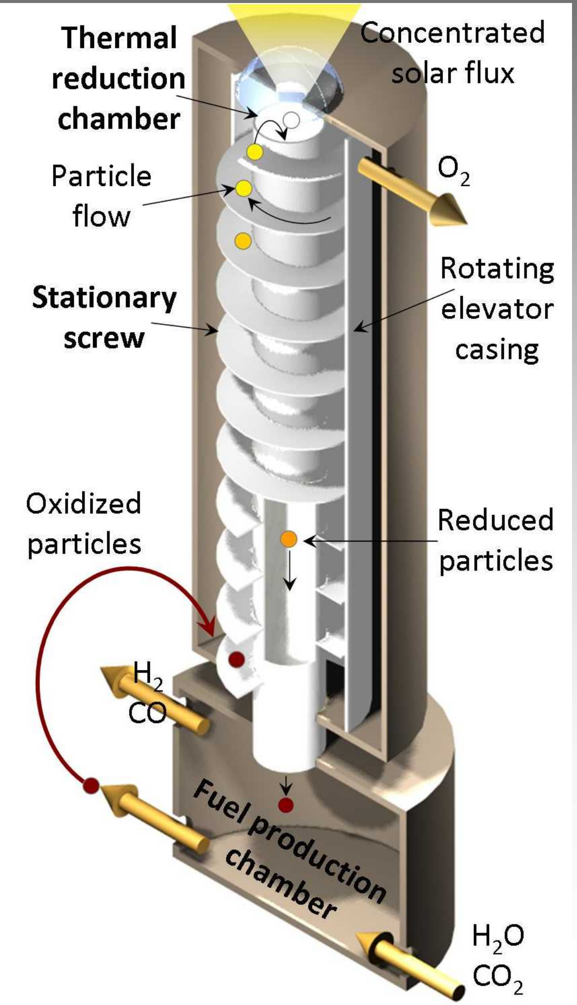
Set T_H, residence time, p_{O2}

↓

Set η_{HR} (size exchanger)

↓

Set T_L, residence time



Operational flexibility allows design point efficiency for δP_S~33%

Low P_S

↓

Decrease oxide flow to maintain T_H → increases η_{HR} → η is unchanged

High P_S

↓

Increase oxide flow to maintain T_H → decreases η_{HR} → η is unchanged

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Reduction to Practice

- Demonstrating a good "paper design" is not always easy

- Technical challenges being addressed
  - Reactant properties
  - Material chemical durability
  - Material compatibility

Packed Bed Reactor: Summary and Next Steps

- The packed bed particle reactor embodies all of the efficiency-driven attributes
- It has the potential to exceed considerably electrochemical efficiency for H_2 production
- Lowest p_{O2} probably limited by pumping speed, not efficiency
- Efficiency through design, independent component optimization, and operational flexibility
- Conveyor/heat exchanger detailed design
- Gradually increasing temperature prototypes

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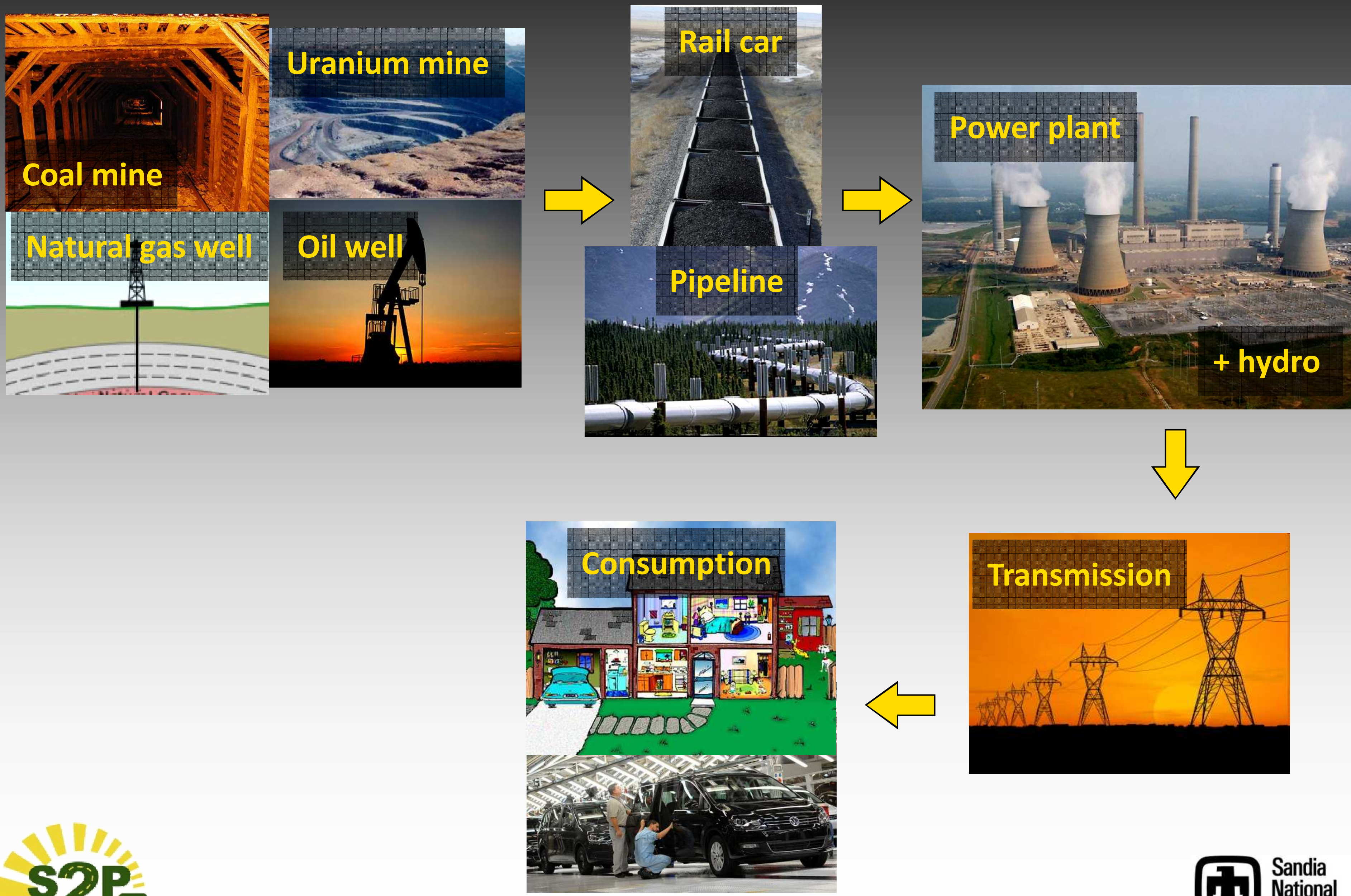
The 19th & 20th Century US Electricity Paradigm



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The 21st Century Energy Paradigm?

Local cogeneration and consumption

+ PV, wind, hydro

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Thank you for your attention.

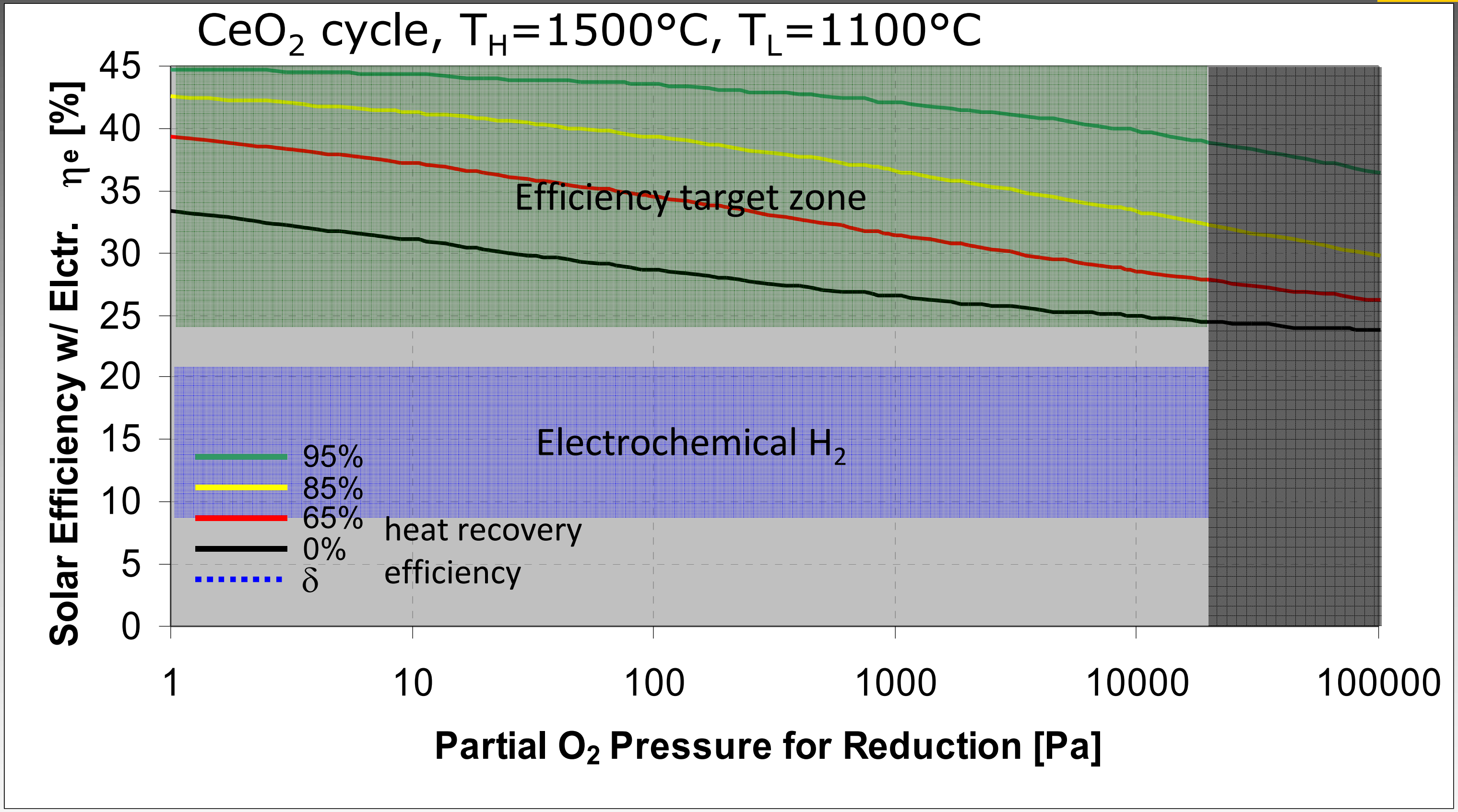
Questions?

Hybrid Solar Efficiency: Use Waste Heat

All mechanical work included

Excess waste heat used to produce electricity for electrolysis

$$\eta = \frac{\dot{n}_{H_2/CO} \cdot HHV_{H_2/CO}}{P_S}$$



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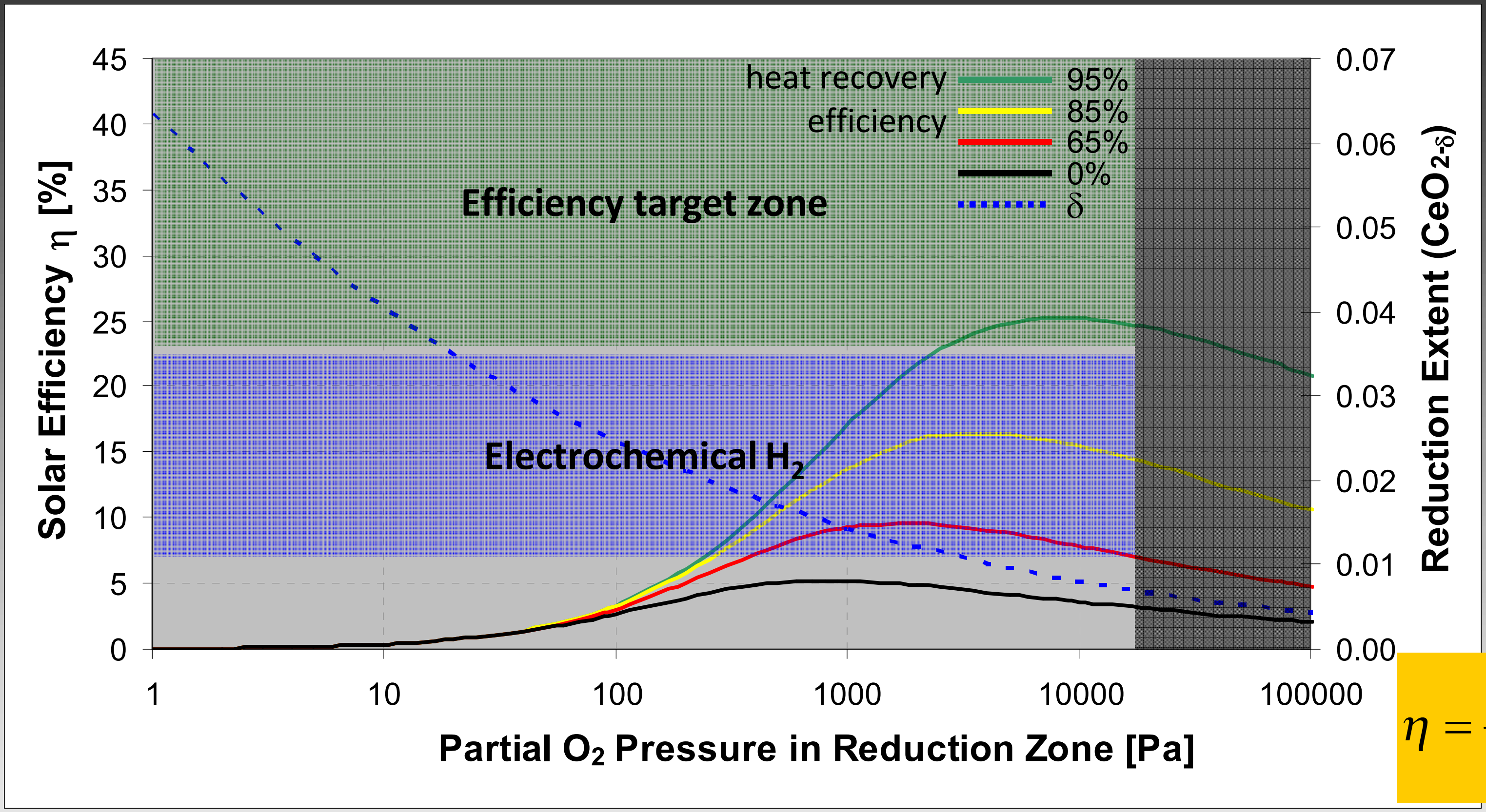
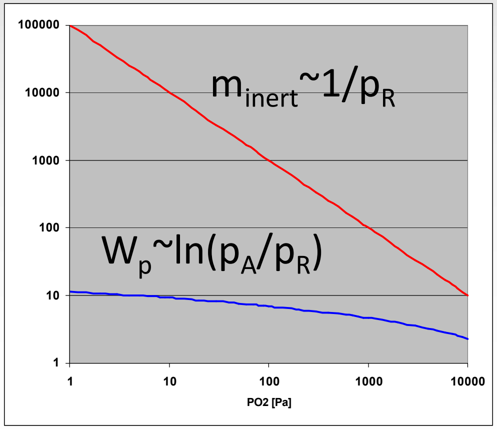
Inert Gas Sweep Limit: Efficiency

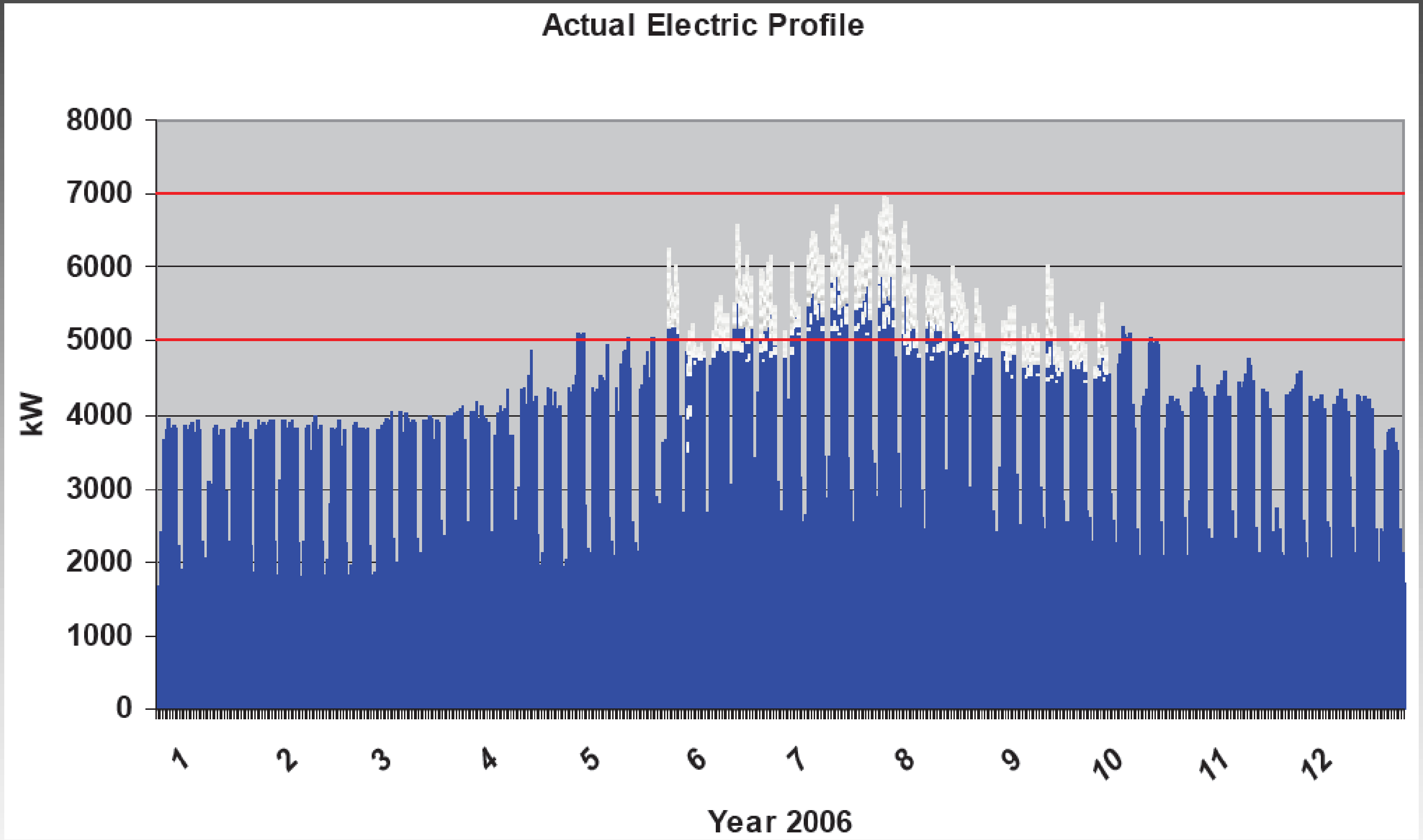


$$\eta = \frac{\dot{n}_{H_2/CO} \cdot HHV_{H_2/CO}}{P_S}$$

Inert gas production and heating limit efficiency



Using Heat for Cooling



Con Edison proposal for New York City steam cooling

Material Compatibility: High T Makes Reactions Easy

- The reactor and reactants should not react… With each other
- Ceria compatibility with
  - Alumina: 1550°C
  - Haynes 214 alloy: 1400°C
  - SiC: 1400°C
- Material strength is a concern
  - Creep in metals
  - Shock resistance in ceramics

CeO_2/HA214, 1200 C
10ppm O_2, 2h

CeO_2/HA214, 1400 C
10ppm O_2, 2h

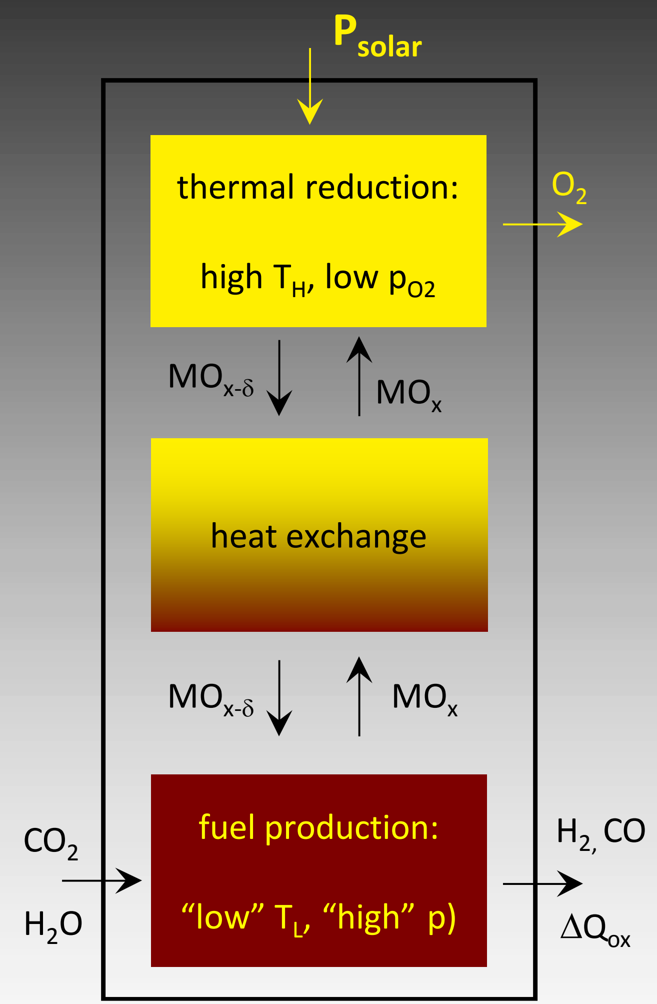
CeO_2/SiC Hexoloy, 1400 C
stagnant air, 3h

CeO_2/Al_2O_3, 1450 C
stagnant air, 3h

paint CeO_2/Al_2O_3/SiC, 1450 C
stagnant air, 3h

Desirable Reactor Attributes: Efficiency Driven

- Direct solar absorption by the working material
- Sensible energy recovery between T_H and T_L
- Continuous on-sun operation
- Pressure, temperature and product separation



Metal oxide cycle

Packed Bed Particle Reactor

- Direct solar absorption by the working material
- Sensible energy recovery between T_H and T_L
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- **Pros:**
  - **– Small reactive particles**
  - **– Only particles are thermally cycled**
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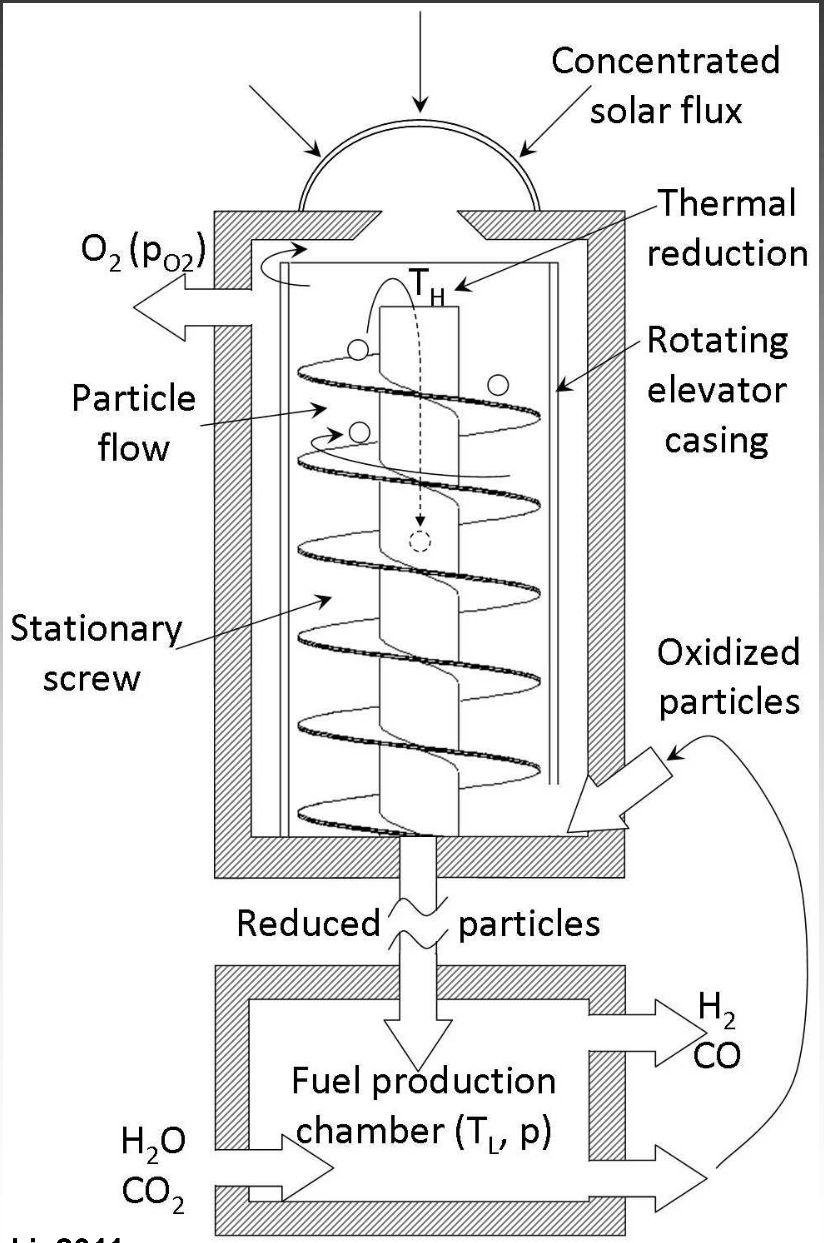

U.S. Patent Filed, Ermanoski, 2011

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