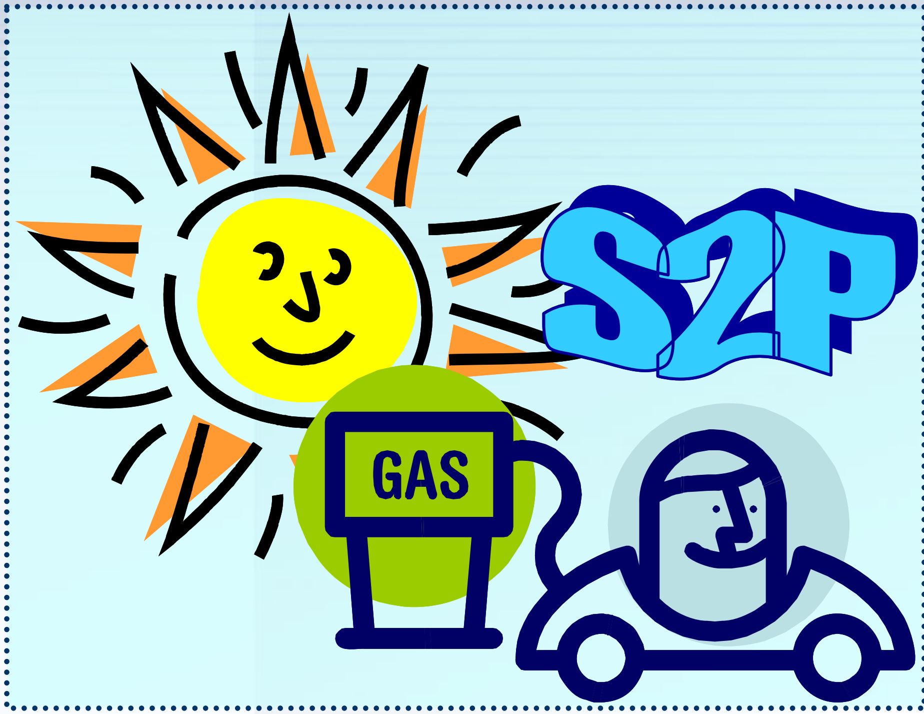
SAND2008-1712P

Sunshine to Petrol

Potentially Game Changing

Disruptive Solar –Sustaining Petrol Technologies



Liquid Solar/Nuclear Fuels

Alternative Feedstocks

Alternative Processing

Not Alternative Fuels

P.O.C: Ellen B. Stechel
Program Manager
ebstech@sandia.gov
(505) 845-1277
Cell: (505) 401-9871

Carbon Utilization (Recycling)

An Alternative to Carbon Sequestration

Sandia National Laboratories

Solar Fuels: Sunshine to Petrol

S2P

GAS

Our Goal:

To directly, efficiently, and cost effectively produce <u>infrastructure compatible</u> liquid fuels employing the same resources as nature (Sunlight, CO_2 and H_2O).

Sunlight + CO_2 + H_2O = Fuel + O_2

Sunlight + CO_2 + $2H_2O \rightarrow CO + 2H_2 + (3/2)O_2 \rightarrow$ CnH(2n+2) or "Green Gasoline"

<u>Target</u>

10-100x sunlight to fuel efficiency compared to fuels from biomass
Competitive Cost with other Alternative Fuels

All Fuels are Essentially Stored Sunshine
Fossil Fuels – Stored Buried Sunshine

- Each gallon of gasoline is equivalent to 100 tons of prehistoric biomass, processed at low temperature for millions of years (ancient stored solar energy)
- Effective Conversion Efficiency ~2×10^{-4} %
  - We don't have millions of years to make what we are burning in centuries
- Corn Ethanol Conversion Efficiency ~0.1%
  - Lot better
- But can we improve on that efficiency even more by using chemical processes? 10%?
  - E.g. Solar driven thermo-chemical processes

Solar Driven CO2 to Fuel and Back
Biofuels Without the Biology

hν OR e^- OR Heat

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

CO_2

H_2O

Energy Input
(Reduction)

CO_2
H_2O

Fuel
O_2

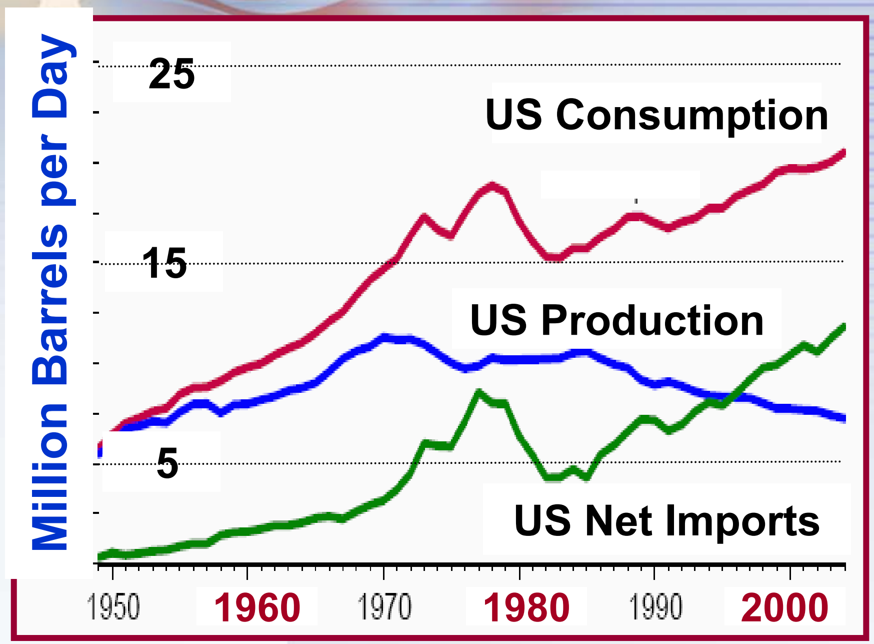
Energy Recovery
(combustion)

Transportation Fuels (Gasoline, Diesel, Jet Fuel)
Natural Gas (CH_4)
Chemical Precursors

O_2

Sandia National Laboratories

Demand for Petroleum (or suitable alternatives) will keep increasing

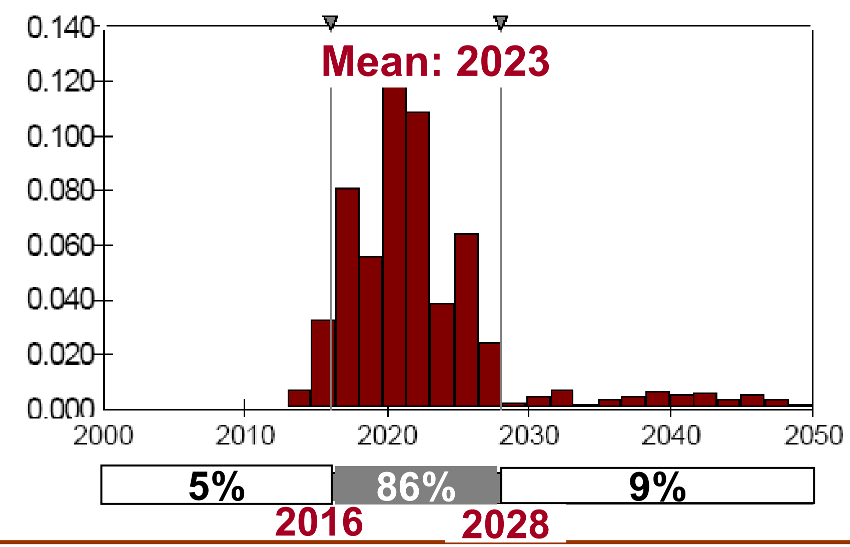


Trends indicate that U.S. will Need 30% more Transportation Fuels by 2030

Increased Electrification of the Vehicle is one way to reduce this demand

Opportunity for greater "cross-talk" between transportation and electrical sector

Peak Year of ROW Conventional Oil Production: Reference/USGS



ROW – Rest of World

Multitude of Concerns

National Security

Energy Security

Competition for Resources

Climate Change

Economic Competitiveness &Shocks

Growing Trade Imbalance

Source: DOE/EIA-0384 (2004), Sam Baldwin, DOE

Sandia National Laboratories

Is it possible to gracefully phase out of fossil-based fuels into something just as good, but with much less downsides?

- **What do we like about fossil-based fuels?**
  - High Energy Density by Mass (BTU/kG)
  - High Energy Density by Volume (BTU/Liter)
  - High Power Density (kW/Liter)
  - Easy to transport, store, & feed into energy conversion device (e.g. internal combustion engine)
  - Abundant and Affordable
    - Nature's Gift (stored ancient sunlight)
  - Relatively Non Toxic, Can be low in air-polluting by-products
  - Relatively Low Explosion Hazard
  - 100 years of learning, infrastructure, industry support

- **What do we dislike about fossil-based fuels**
  - Strategic Resource
    - Those with derive power and advantage over those without
  - Geographically localized
    - Center of gravity shifting to middle east oil
  - High Environmental Impact (from mining, drilling, refineries, air pollution)
  - Large GHG footprint
  - Large and growing trade imbalance in oil
  - Price volatility for oil and NG
  - Peak Oil coming? Finite Resource
    - Geopolitical risks & uncertainties, possible supply disruptions

Sandia National Laboratories

What are Some Competing or Complementary Options for Transportation Fuel?

No Silver Bullets – We will probably need them all – It is too soon to constrain the solution space!!

- **Coal to Liquids with Carbon Capture and Storage (CCS)**
- **Biomass to Liquids**
- **Bio-ethanol, Bio-diesel**
- **Algal Crude**
- **Hydrogen**

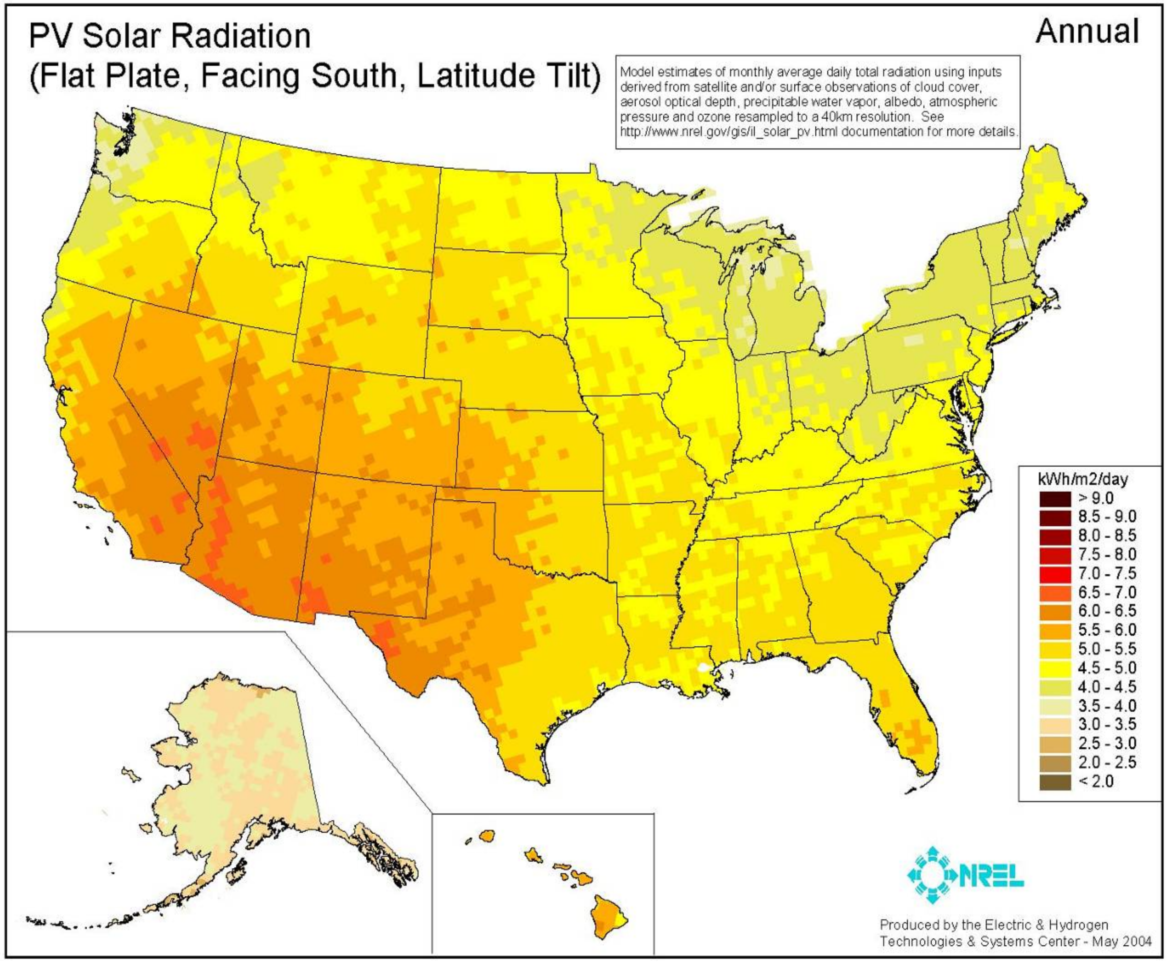
Plus Partial Electrification of the Vehicle, e.g. Plug-in Electric Hybrids

---

- **Solar Fuels**
  - **New kid on the block**
  - **Non-biological routes are very early in technology maturity, hence still have elements of high technical and economic risk**

Sandia National Laboratories

Why Solar? U.S. and World-Wide Solar Resources Greatly Outweigh the Energy Used



120 Peta Watts

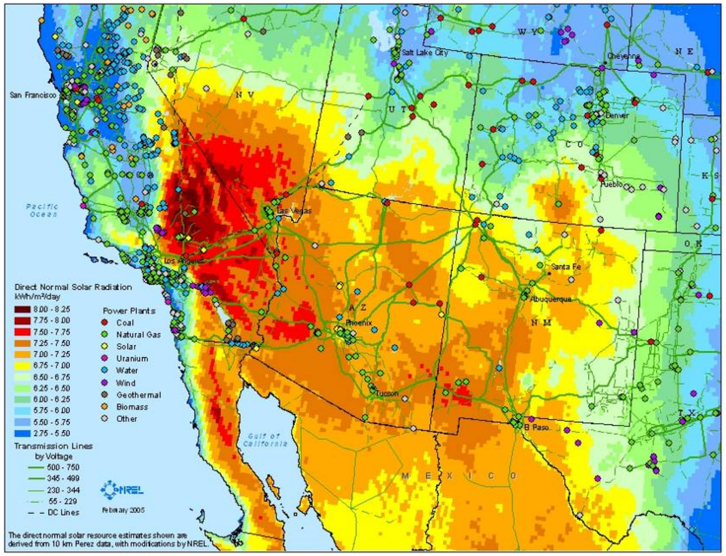
- ✓ **Currently, solar provides less than 0.1% of the electricity used in the U.S.**
- ✓ **Covering less than 0.2% of the land on the earth (115K sq-mi) with 10%-efficient solar cells would provide (~6 TW) twice the power used by the world.**
- ✓ **For the U.S., a 100-mi by 100-mi area in the Southwest could generate as much electricity as we use (0.72 TW.)**
- ✓ **The same amount of area could provide nearly all (~85% or 174B Gal/yr) the US transportation fuels with 10% efficient Solar to a transportation fuel.**

Sandia National Laboratories

Do we have the Resource?
Direct Normal Incidence Solar Resource in the Southwest

Filters applied:

- Direct-normal solar resource.
- Sites > 6.75 kwh/m^2/day.
- Exclude environmentally sensitive lands, major urban areas, etc.
- Remove land with slope > 1%.
- Only contiguous areas > 10 km^2 or > 500MW
  - ~2500 Acres or 4 sq-Mile
- 5 Acre/MW or ~18% to MW Solar Capacity
- 27% to Generation Capacity, Net is ~5%



Data and maps from the Renewable Resources Data Center

at the National Renewable Energy Laboratory

State		Land Area (mi^2)	Solar Capacity (MW)	Solar Generation Capacity GWh
AZ	17%	19,279	2,467,663	5,836,517
CA	4%	6,853	877,204	2,074,763
CO	2%	2,124	271,903	643,105
NV	5%	5,589	715,438	1,692,154
NM	12%	15,156	1,939,970	4,588,417
TX	<1%	1,162	148,729	351,774
UT	4%	3,564	456,147	1,078,879
Total	6%	53,727	6,877,055	16,265,611

Bottom Line:
Conservative ~7 TW (Peak) Available Resource
>16000 Tera Watt Hours/Year
US Energy Consumed ~29000 TWh/yr

Sandia National Laboratories

Major Challenges With Widespread Adoption of Renewable Energies

- **Cost**
  - Not necessarily an issue in the near future, but major advances needed to continue adoption and reach ~$0.02 / KWhr
- **Intermittency**
  - → Major issue, and will require fundamental new approaches to grid management and storage
- **Geographic Diversity**
  - Transmission constraints
  - → Significant issue, but regional optimization coupled with storage in the form of liquid fuels or hydrogen could provide some solutions
- **Infrastructure Evolution**
  - → Major issue, and solutions should take maximum advantage of 100 years of infrastructure investments

Sandia National Laboratories

At 10 % Conversion Efficiency, Can it scale to the size of the Problem?

What resources would we need to operate?

1. Land and Sunshine – How much?
   - Estimates indicate little impact on land usage
     - 25 FT x 25 Ft per vehicle of sunny land or <27 Ft x 27 Ft of average sunshine
     - Assuming 32 mpg and 12500 Miles/Year
     - 100M vehicles – 2242 sq-miles (300M vehicles – 6726 sq-miles)
2. CO_2 – Is there enough?
   - More than enough CO_2 – Coal emitted 580 MMT-Carbon in 2006
     ~105 MMT-Carbon/Year* for 100 M Vehicles (315 MMT –C/yr for 300M)
   - More Interesting if we "mine" the CO2 from the air
3. H_2O – Is there enough?
   - Less than 1% of current domestic use of water
   - Can also be "mined" from the air, while mining CO2

MMT: Million Metric Tons, * Based on 2006 emissions

Sandia National Laboratories

Primary sources of CO_2

Total = 5.8 Gt

Source	Percentage	US 2000 (Gt)
Fossil fuel combustion [Electricity generation] [Transportation]	**96.7%** [38.0%] [32.8%]	**5.6** [2.2] [1.9]
Iron and steel production	1.1%	0.066
Cement manufacture	0.7%	0.041
Waste combustion	0.4%	0.022
Ammonia manufacture	0.3%	0.018
Lime manufacture	0.2%	0.013
Limestone/dolomite use	0.2%	0.009
Natural gas flaring	0.1%	0.006
Aluminum production	0.1%	0.005
Soda ash manufacture/consumption	0.1%	0.004
Fermentation Plants – growing source		
Coal to Liquids or Biomass to Liquids – new source		

Increases the Atom Efficiency from 50-66% to 100%

Source: EPA, EIA and SPCC TAR

Sandia National Laboratories

Reuse or Recycle of CO2: Delays the Release of CO_2 to the Atmosphere

Present Primary Industrial Uses of CO_2

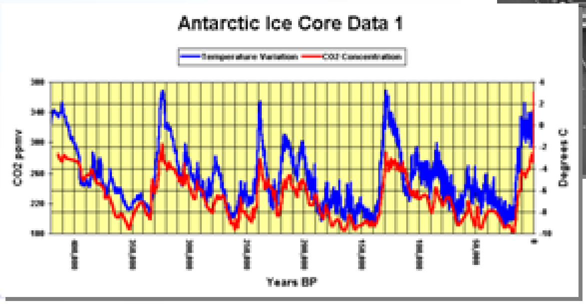
	Market (Gt/yr)	Lifetime
Fertilizer (urea)	0.090	Six months
Methanol	0.024	Six months
Inorganic carbonates	0.008	Decades to centuries
Organic carbonates	0.003	Decades to centuries
Polyurethanes	0.010	Decades to centuries
Technological	0.010	Days to years
Food	0.008	Months to years
Enhanced Oil Recovery	0.017 (estimate)	Decades to centuries, longer?

Total = 2.9% of the 5.8 Gt/yr

"A large proportion of all CO_2 recovered is used at the point of production to make further chemicals of commercial importance, chiefly urea and methanol" *IPCC* report 2005

Convert and Reuse:
Only Fuel Scales to the CO_2 Problem

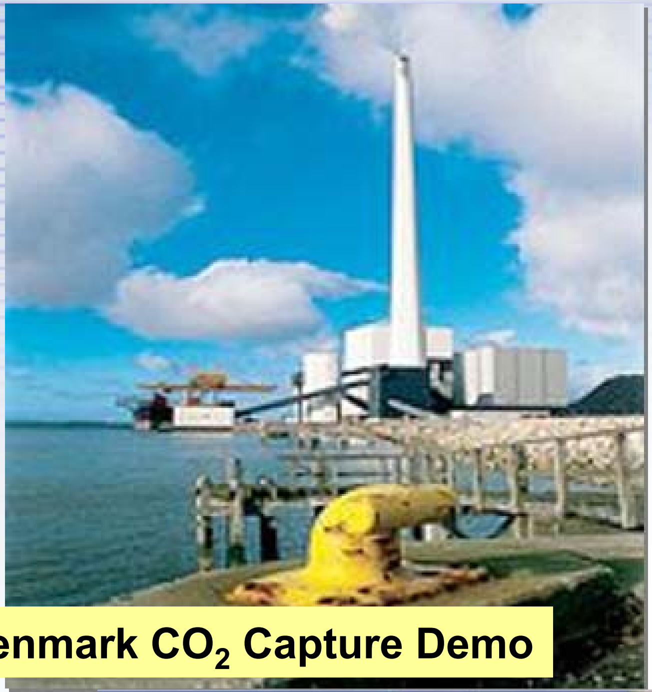
- ‘Problem’ CO_2 came from fuels
- In principle, it can be recycled into fuels
- BUT, where can we get the energy to convert CO_2 back to fuel?
  - Solar (biofuels from biomass… or is there something possibly better)
  - Nuclear



Sandia National Laboratories

Capturing the CO_2 for Re-use rather than waste management or burial?

- **Two major possibilities**
  - **Capture it at the source (initially)**
    - **Most practical for stationary sources**
    - **Easiest with pure oxygen combustion**
    - **Demonstrations now underway**
  - **Remove it from the atmosphere**
    - **Challenging, but not impossible**
    - **Wind naturally moves vast quantities of air**
    - **Feasible to build scrubbers that pull CO_2 directly from air**
    - **Potential to disconnect capture from source**
    - **Not yet demonstrated at scale or in field**



Denmark CO_2 Capture Demo

GRT LLC Synthetic Trees Concept

Sandia National Laboratories

Is 10% feasible? Thermodynamic Analysis: Efficiencies

Candidate Pathways	CO2 from a Concentrated Source such as Flue Gas		
	Reversible (%)	2nd Law Eff (%)	1st Law Eff (%)
H_2 by PV electrolysis react with CO_2	61.2	9.0	8.0
H_2 and CO by TC	69.7	20.1	17.9
H_2 by TC react with CO_2	61.2	18.7	16.6
CO by TC react with H_2O	65.6	19.0	16.9

TC Target: ~24% sunlight to CO conversion

Adam Simpson & Andy Lutz unpublished

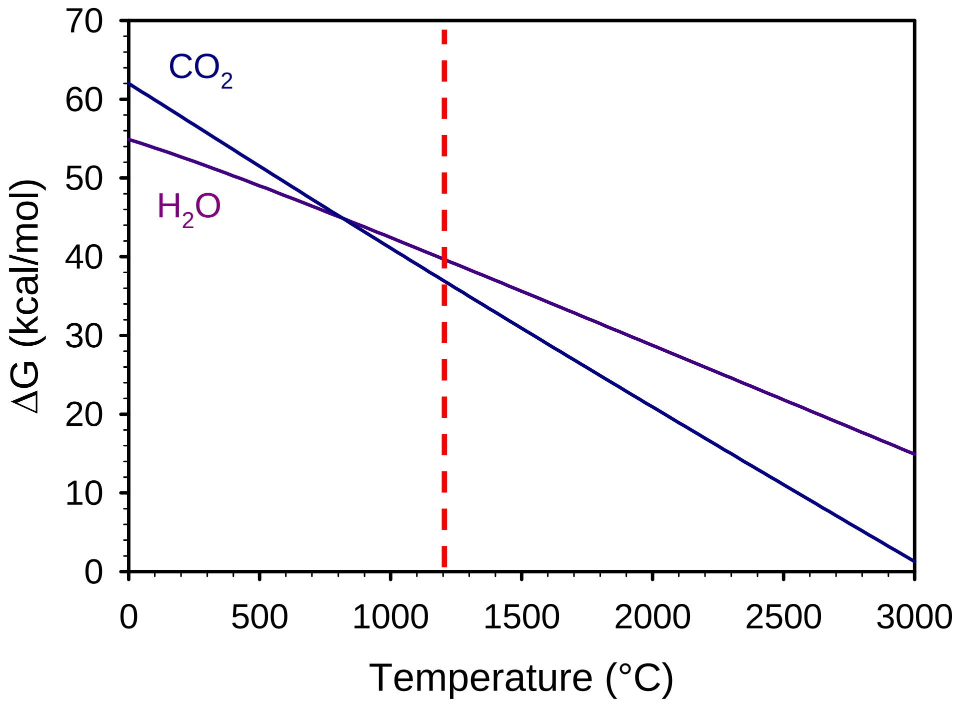
PV: Photovoltaics, TC: Thermochemical

Note: Assumed 100% conversion of CO2, hence underestimates separations and pumping

Sandia National Laboratories

Why Split CO_2?

Sunlight + CO_2 + H_2O → CO + $2H_2$ → CH_3OH → C_2H_6O(DME) + H_2O



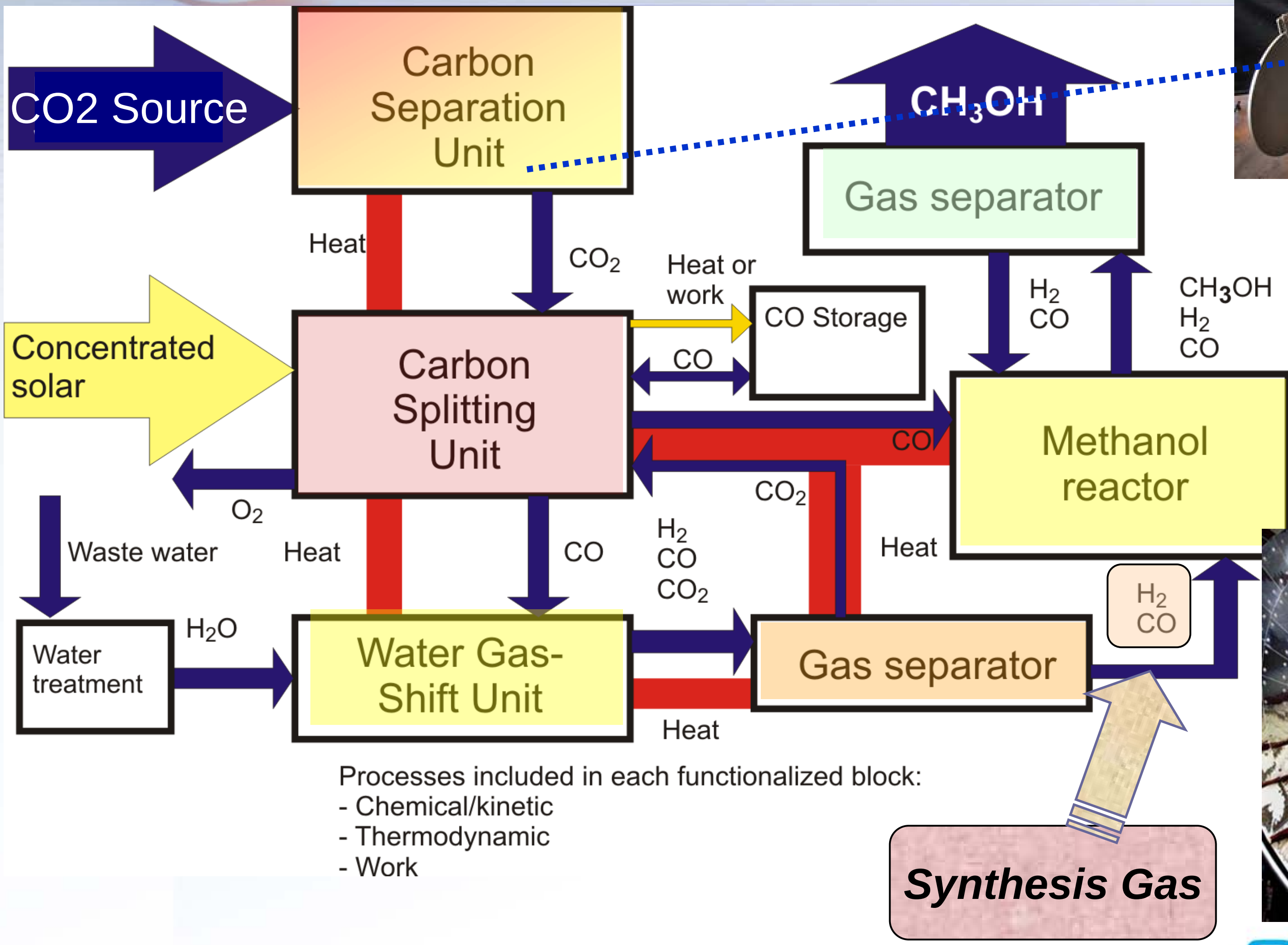
Splitting CO2 makes it fairly easy to make Syngas of any desired H2:CO ratio

- **A mixture of CO and H_2 can be used to produce liquid fuels**
- **CO can be used to produce H_2 in an <u>exothermic</u> shift reaction**

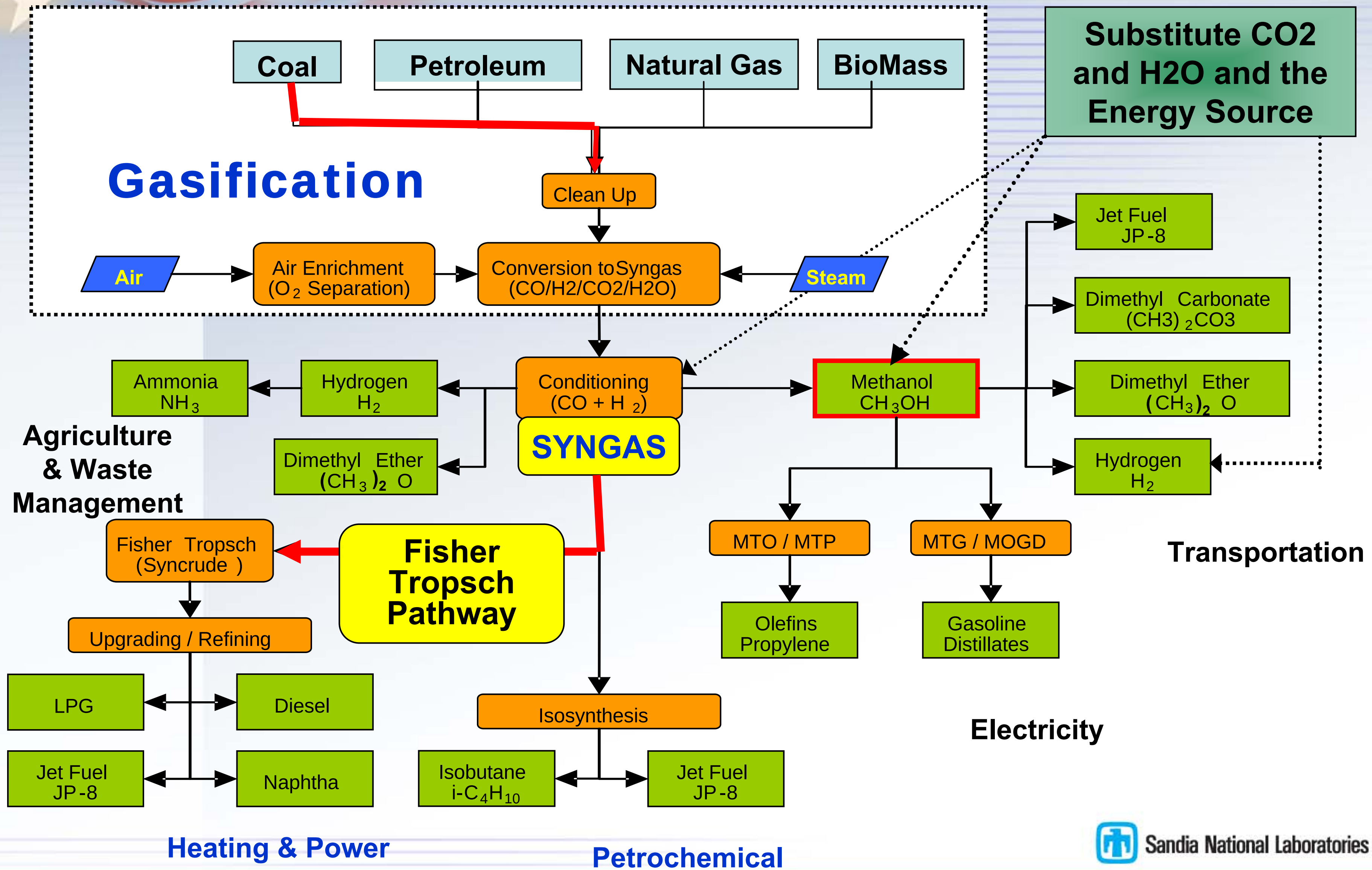
CO + H2O ↔ CO2 + H2

- **CO_2 decomposition may have advantages over H_2O decomposition**

The “Sunshine to Petrol” Concept



There are Known Pathways to Most Anything Desirable to Synthesize



Sandia National Laboratories

What is the base Solar Technology: Solar Dish Systems

- **Technology Features:**
  - **High efficiency (Peak > 30% net solar-to-electric)**
  - **Autonomous operation**
  - **High-Efficiency Stirling**
  - **Modularity (10, 25kW)**

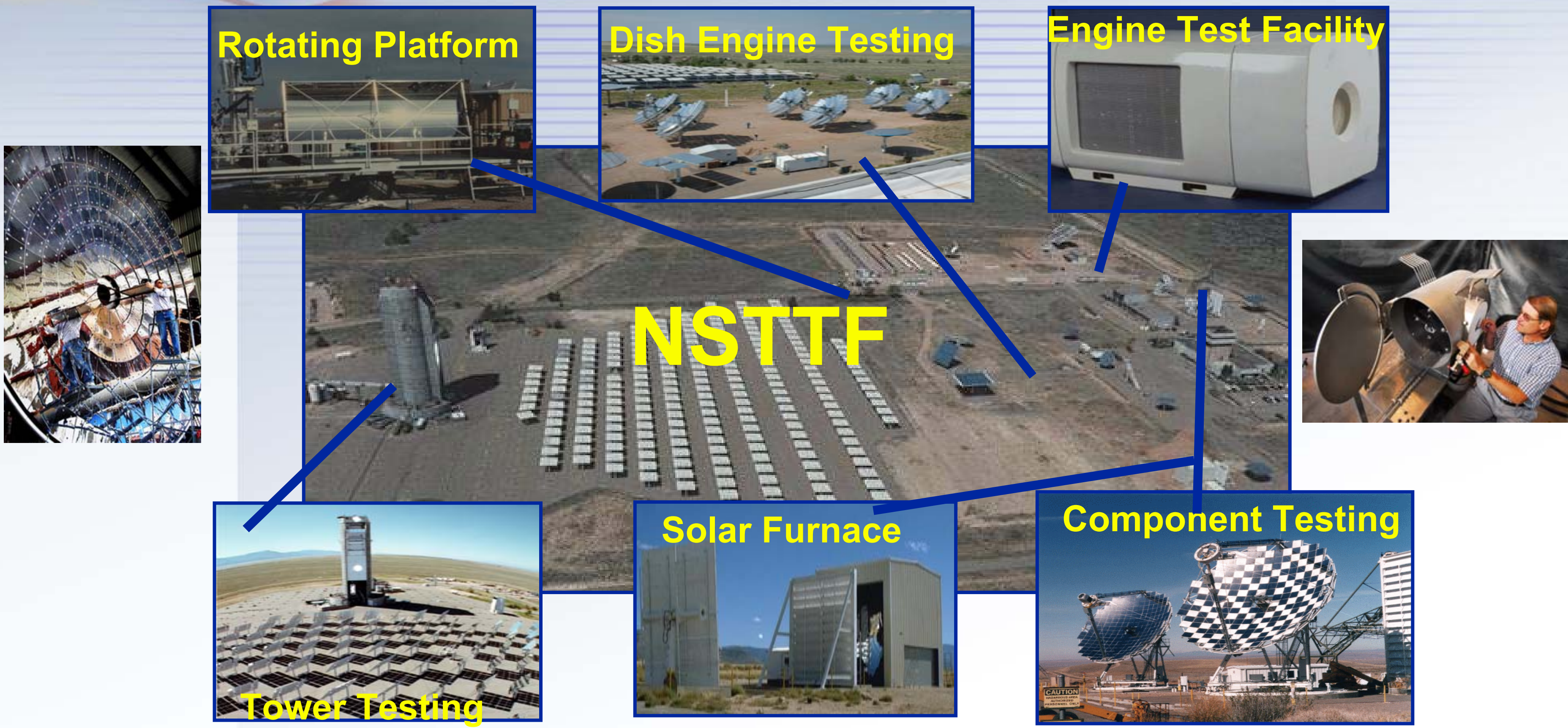
Current R&D focus for Dish Stirling is on Reliability improvement and cost reduction.

Economy of Scale by Numbering up – not Scaling up

Marry with chemical μ-reactors – achieve process intensification advantages

Sandia National Laboratories

Where are the S2P Experiments being Conducted?

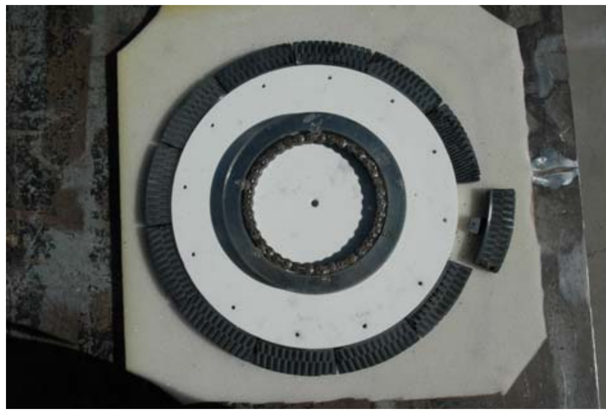


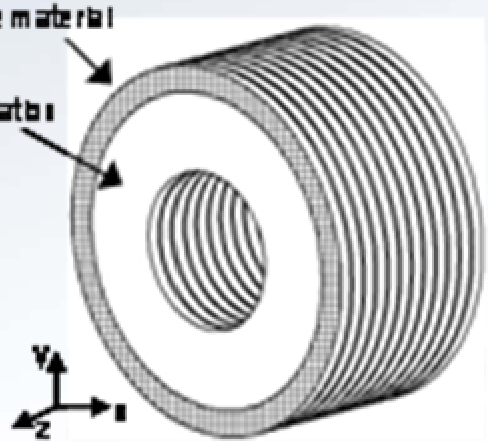
Sandia National Laboratories

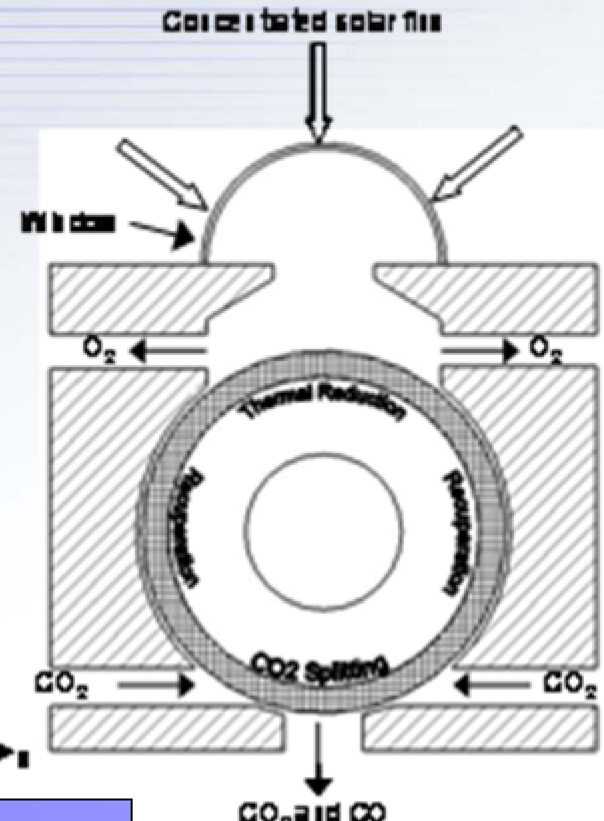
NATIONAL SOLAR THERMAL TEST FACILITY

Sandia National Laboratories

What is the enabling technical innovation? A "Thermo-Chemical Heat Engine"







Enabling Attributes

- Thermal recuperation
- Reaction separation
- Continuous flow

Solar thermal to Chemical Work
Prototype in Build Phase

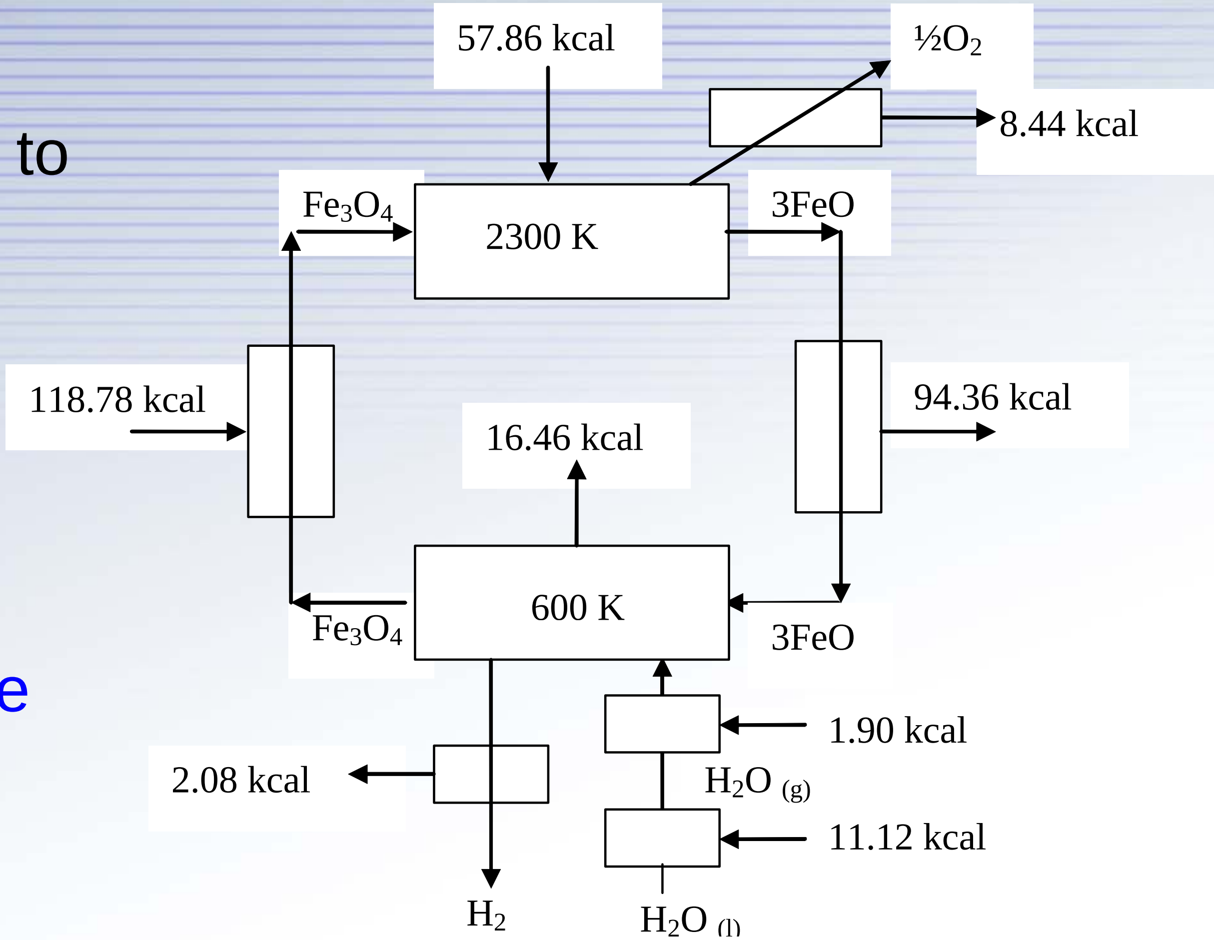
Sandia National Laboratories

Basic Thermodynamic Analysis Shows Recuperation is Key

Cycles are equivalent to a heat engine.

The prototypical "working fluid" is Fe_3O_4/Fe_3O_{4-y}.

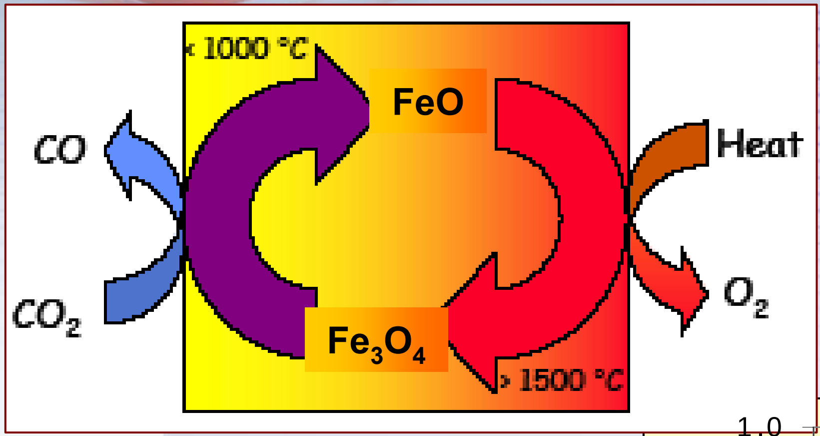
~1000-1500 °C is the "sweet spot" for coupling to CSP.

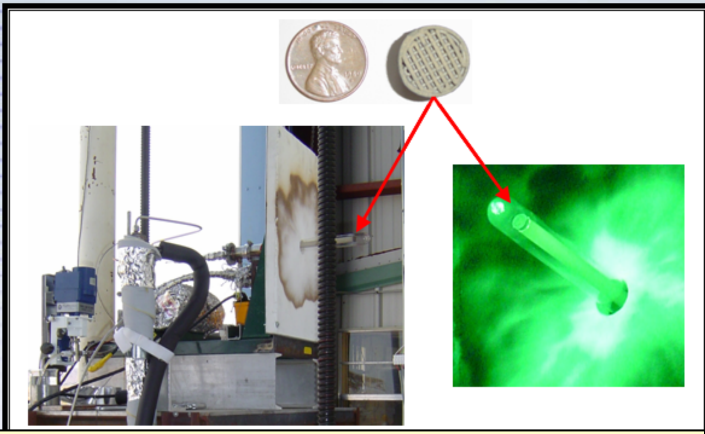


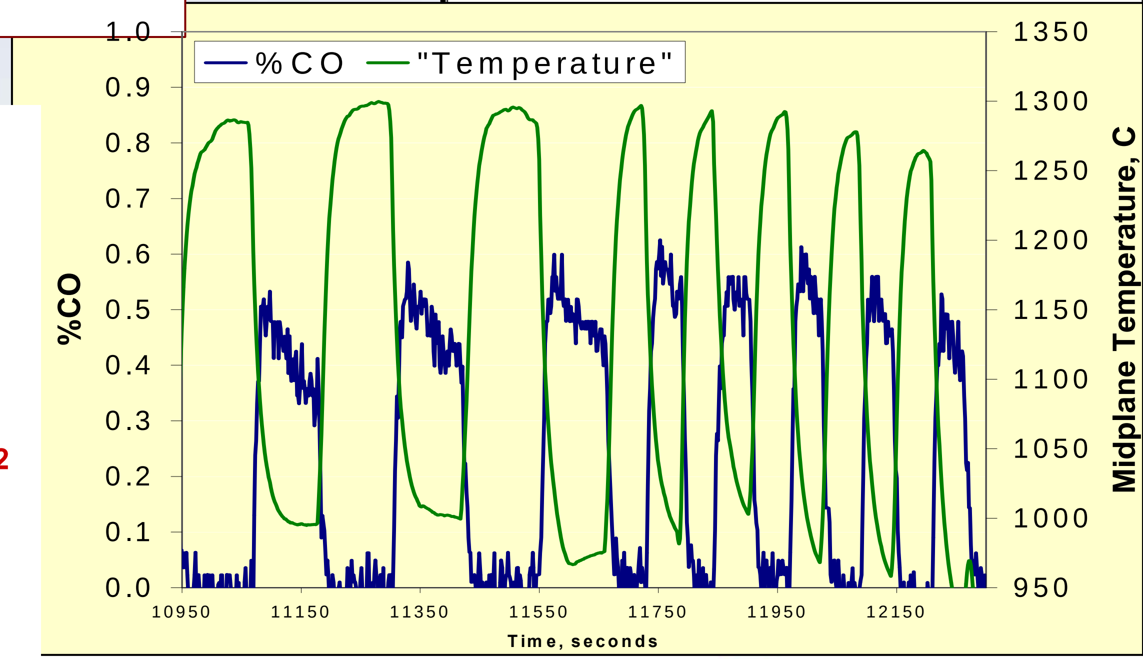
Without Recuperation max efficiency = 36%
With Recuperation max efficiency = 76%

Sandia National Laboratories

CO_2 Splitting Results at the NSTTF







Sandia-Invented device uses a relatively simple two step solar-thermochemical process based on iron-oxide to split CO2 (or H2O):

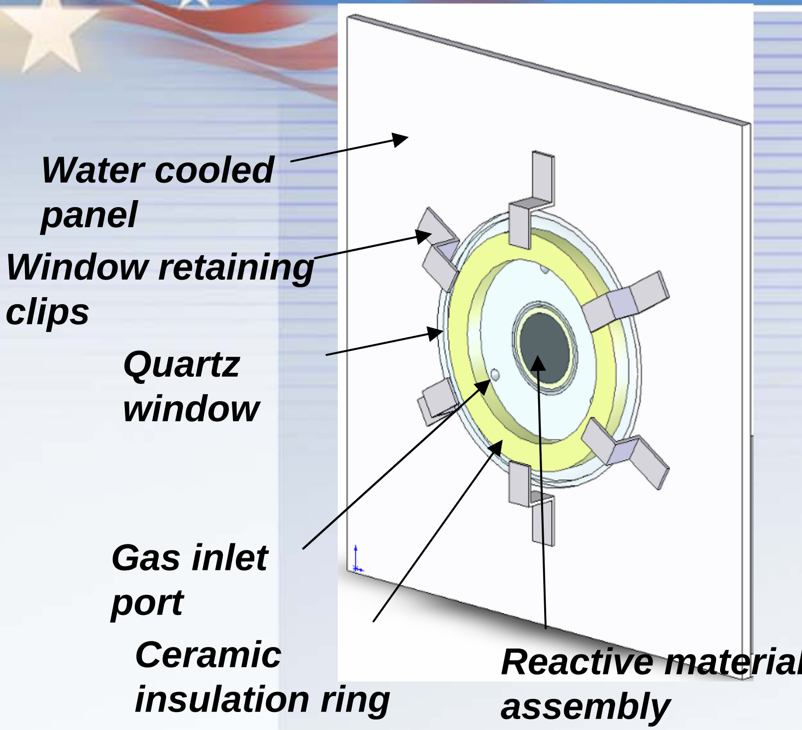
1) Fe_3O_4 + Heat $\Rightarrow$ Fe_3O_{4-y} + $y/2O_2$

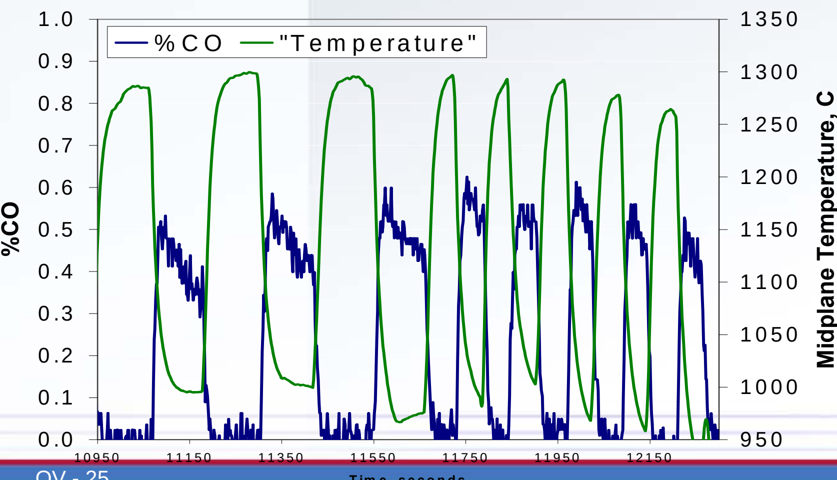
2) Fe_3O_{4-y} + yCO_2 $\Rightarrow$ Fe_3O_4 + yCO

Net: yCO_2 $\Rightarrow$ yCO + $y/2O_2$

Sandia National Laboratories

What is the status of the development? Critical Milestones have been achieved





- Two materials classes have demonstrated the ability to split both H_2O and CO_2
- Fast cycles (up to 1/2 RPM) have demonstrated significant splitting
  - Necessary for continuous operations
- Repeated cycles have demonstrated the reactive material can be regenerated each cycle without loss of chemical activity
  - Need to determine mechanical stability over thousands to millions of cycles.
- Measured a key performance gap
  - Needs about 20% reaction extent for 10% target
  - Demonstrated ~1.5% so far – in batch reactor

Sandia National Laboratories

Summarize why we like Thermo-chemistry

- Thermo-chemistry is an exciting alternative to electrolysis and expected to have a much higher energy conversion efficiency than either electrolysis or photo-electro-chemistry.
- Energy management is key (simplicity, high yields, recuperation).
- Ferrites Show Promise as a “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 potential advantages over H_2O.
- Ceria-based materials interesting, questions remain.
- Wide range of mixed-metal oxides to explore, using predictive simulation to find promising candidates.

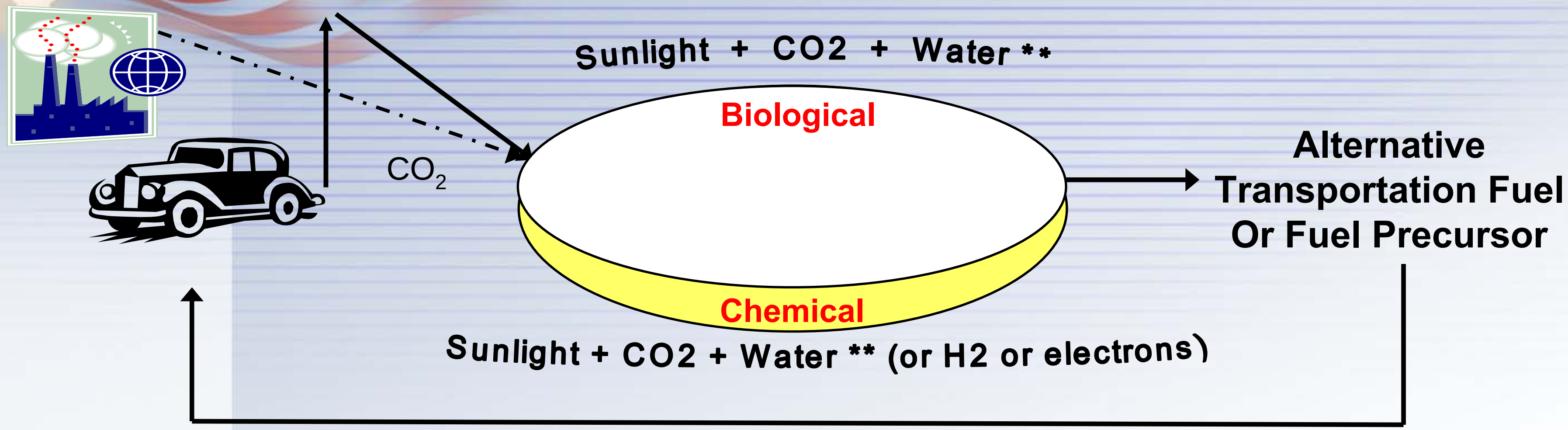
SANDIA NATIONAL LABORATORIES

Thank-you for your Attention

Questions

Backup Slides

Is it Realistic?
Liquid Solar Fuels: Bio-Inspired without the Extraneous Constraints



Frequent False First Impressions vs. Reality

- **Recycling CO2 Is "Perpetual Motion" or Thermodynamically Implausible**
  - **Completely Analogous to Bio-fuels, Just takes an** external energy source **(Solar)**
- **Cannot Be Done Efficiently**
  - Photosynthesis Is Very Inefficient **and Produces a Complex Product Mixture, Significantly greater efficiencies expected with chemical processing**
- **Cost Will Necessarily Be Outrageous**
  - **Compare to Sustainable Version of H2 Economy with Carbon Capture & Storage**
  - **Compare to Current Prices with the Cost of Externalities**
  - **Compare to Coal to Liquids with Carbon Capture & Storage & Cost of Externalities**
  - **Initial Estimates (without optimization) are Not Outrageous Compared to current Methanol Synthesis (~factor of 2) and we have just begun.**

Sandia National Laboratories