High Temperature Solar Splitting of Methane to Hydrogen and Carbon

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2003 Hydrogen and Fuel Cells Merit Review Meeting
May 19-22, Berkeley, CA

Thermal Decomposition of Methane

- Demonstrated by Thagard in late 70’s
  - electrically heated, porous wall reactor
- Simple in concept
  - essentially single step to end products
- Extremely high reaction rates at 1600-2000^{o}C
- Various end-product configurations possible
- Co-products both have economic value

ΔH_{1800^oC} = -76 kJ/mole

-394 kJ/mol C

CH_4 +  $\rightarrow$ C + $2H_2$

-890 kJ/mol CH_4

-572 kJ/2mol H_2

Project Goals

- Near term
  - Current status:
    - 70-95% CH_4 conversion to H_2 @ 1850°C
    - $0 -12/kg depending on process configuration and co-product value
  - Targets:
    - 70% conversion on a continuous basis
    - $3/kg for fleet fueling station with carbon black at tire market price
- Long-term
  - < $2/kg for water-splitting cycles

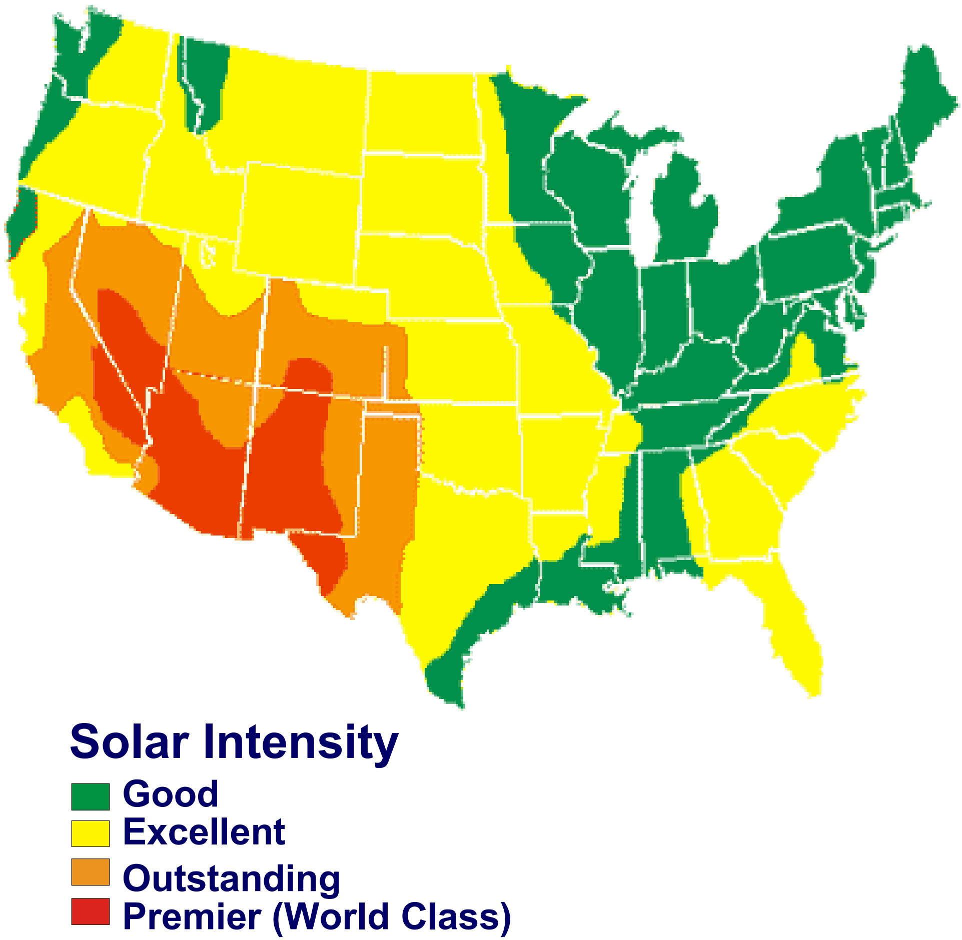
Historical Perspective

- Initiation of Project: FY2000
  - University of Colorado awarded competitive DOE GO subcontract
- Significant Results:
  - FY00: demonstrated proof-of-concept at HFSF
  - FY01: achieved 80% conversion in new reactor
  - FY02: demonstrated fluid-wall (aerosol) reactor
  - FY03: achieved 94% conversion
    - Limited funding to complete Ph.D. thesis experimental work
  - Overall:
    - very high reaction rates demonstrated
    - no technical showstoppers
    - near-term commercialization opportunities

Why Use Solar Energy?

- Environmentally benign energy source
  - little or no CO_2 emissions (depending on process)
- High concentrations possible (>1000 W/cm^2)
  - high temperatures easily achieved (>3000 ^oC)
  - reduced reactor size; low thermal mass
- Rapid heating rates (>>1000 $^oC/s$)
  - quick start/stop operation
- Abundant resource (both US and worldwide)
  - Sufficient to power the world (if we choose to)
- Advantages tradeoff against collection area
  - this is true for all technologies using sunlight
  - heliostat costs are significant fraction of capital
    - importance depends on overall process efficiency

World Class Direct Resource in US



- World Class area in US: 5.8×10^5 km^2
  - >6 kWh/m^2/day
- Annual US Energy Usage: 2.9×10^{13} kWh (Year 2000 EIA data)
  - At η=10%, area required: 1.3×10^5 km^2 (50% of Arizona)
- Annual World Energy Usage: 1.2×10^{14} kWh
  - At η=10%, area required: 5.5×10^5 km^2 (95% of Arizona +Nevada)

Vision for Solar Thermal Processing

- Apply advantages to a clean hydrogen economy producing hydrogen from water
- Near-term (0-5 years): Methane as transition fuel
  - Identify/develop promising processes
    - e.g. NG dissociation, dry reforming
  - Develop aerosol flow reactor and process understanding
    - technical and economic
  - Introduce solar technology on small scale in appropriate markets/locations (SW United States)
    - HCNG fleet fueling stations
- Longer-term (3-15 years): Move to water as the fuel
  - Initially through thermochemical cycles
    - e.g. 2-step metal oxide reduction, others as identified
  - Eventually to direct, high-temperature splitting/separation
    - significant materials separation issues need to be overcome
  - If renewable electric power is ever cheap enough: electrolyzers

Potential Application Areas

- Bulk Hydrogen
  - large-scale systems, pipeline feeds
- Distributed Fleets
  - fueling stations
  - HCNG a near-term possibility
- Industrial User/Supplier
  - Semiconductor industry
- Syngas
  - add reformer to system
- Utility plants
  - power and hydrogen
- Carbon black plant
- Stranded gas/capped wells

Technical Challenges

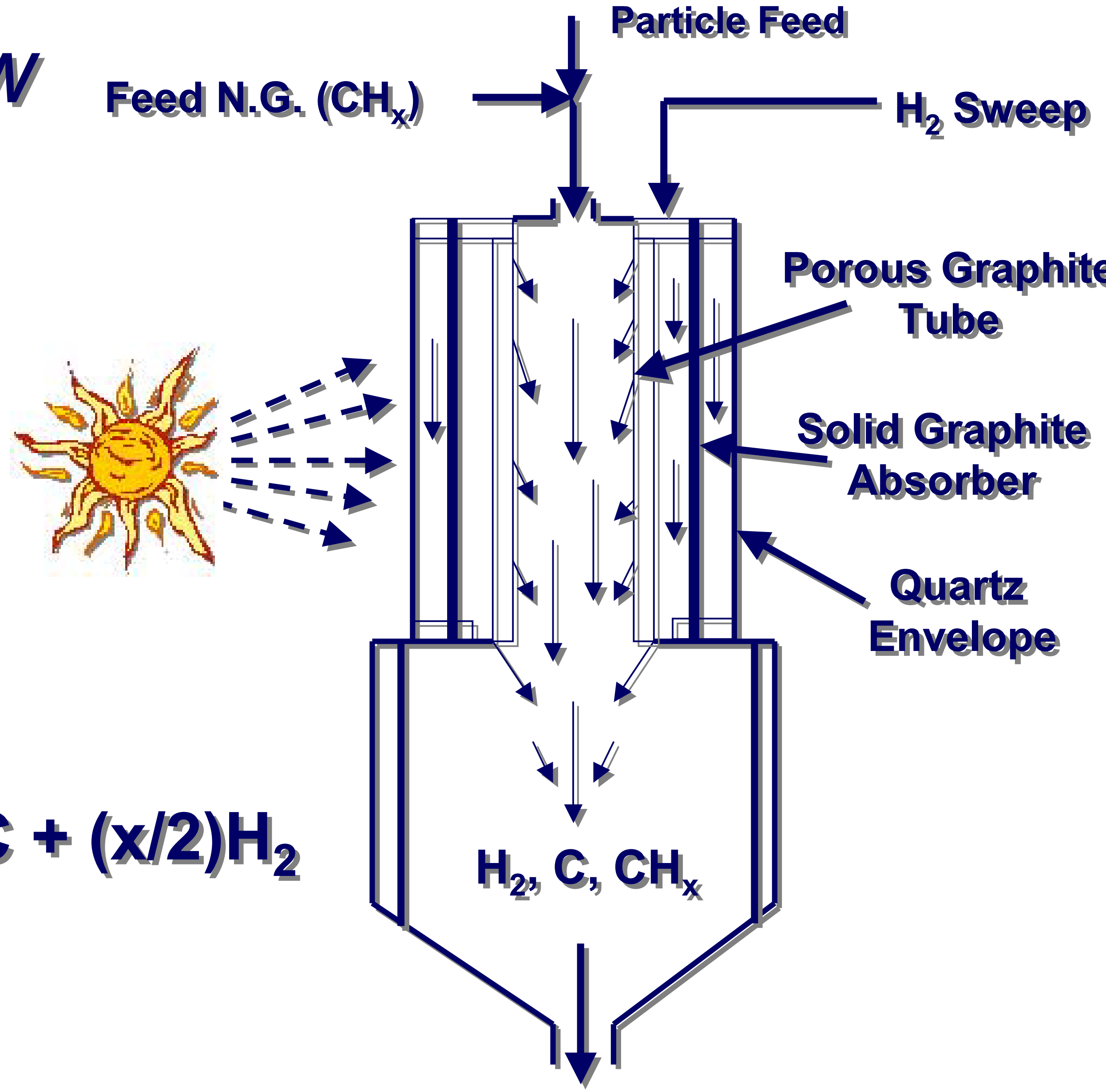
- Compatibility with on/off nature of sunlight
  - short start-up & shut-down times
  - semi-continuous operation
- High efficiency reactor design for high temperature
- Materials of construction
- Thermophoretic deposition of carbon black

Non-technical Challenges

- Co-product marketing (outlet for carbon black)
- Poor fit to a single business

Aerosol Flow Reactor Concept

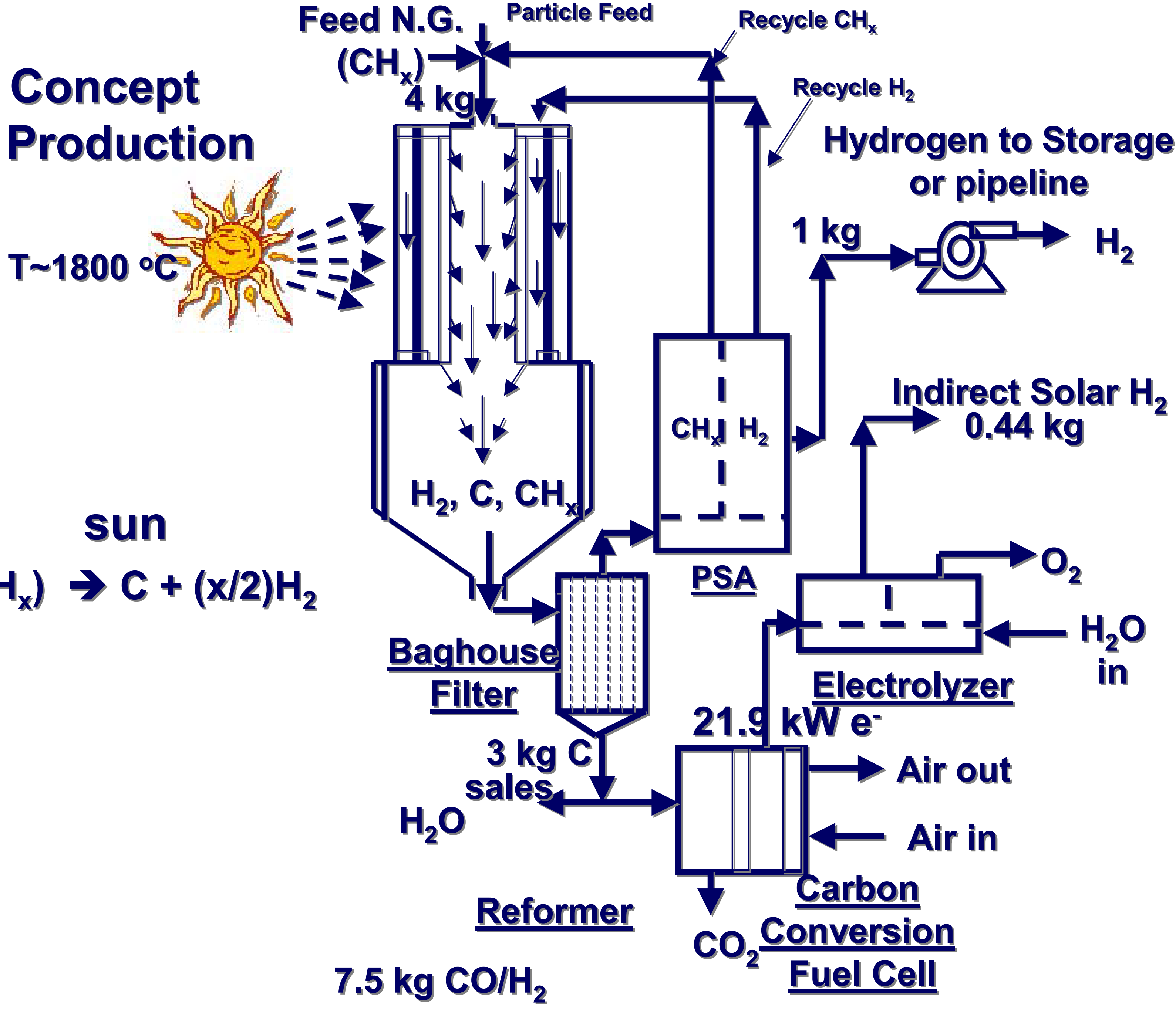
T~1800 °C



Sun

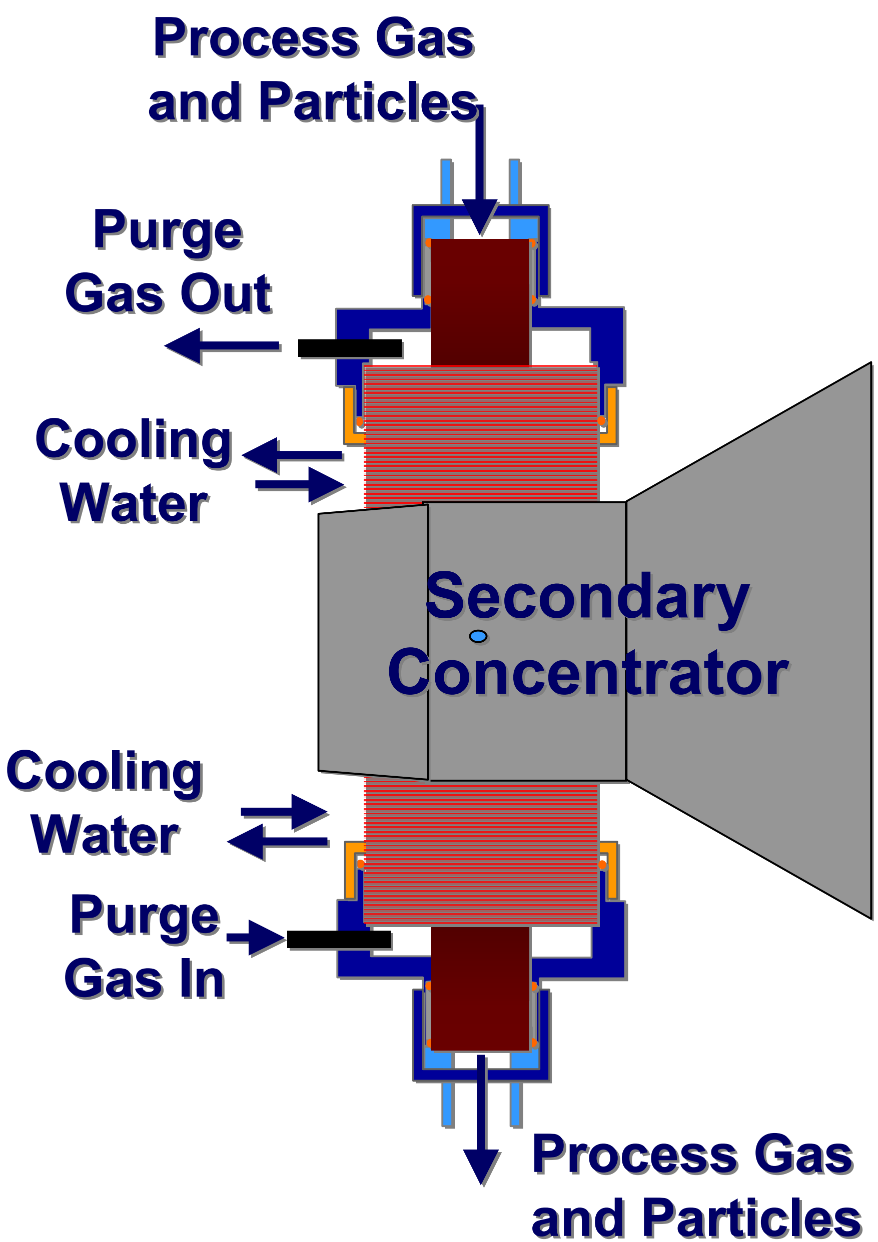
$$\text{N.G.}(CH_x) \rightarrow C + (x/2)H_2$$

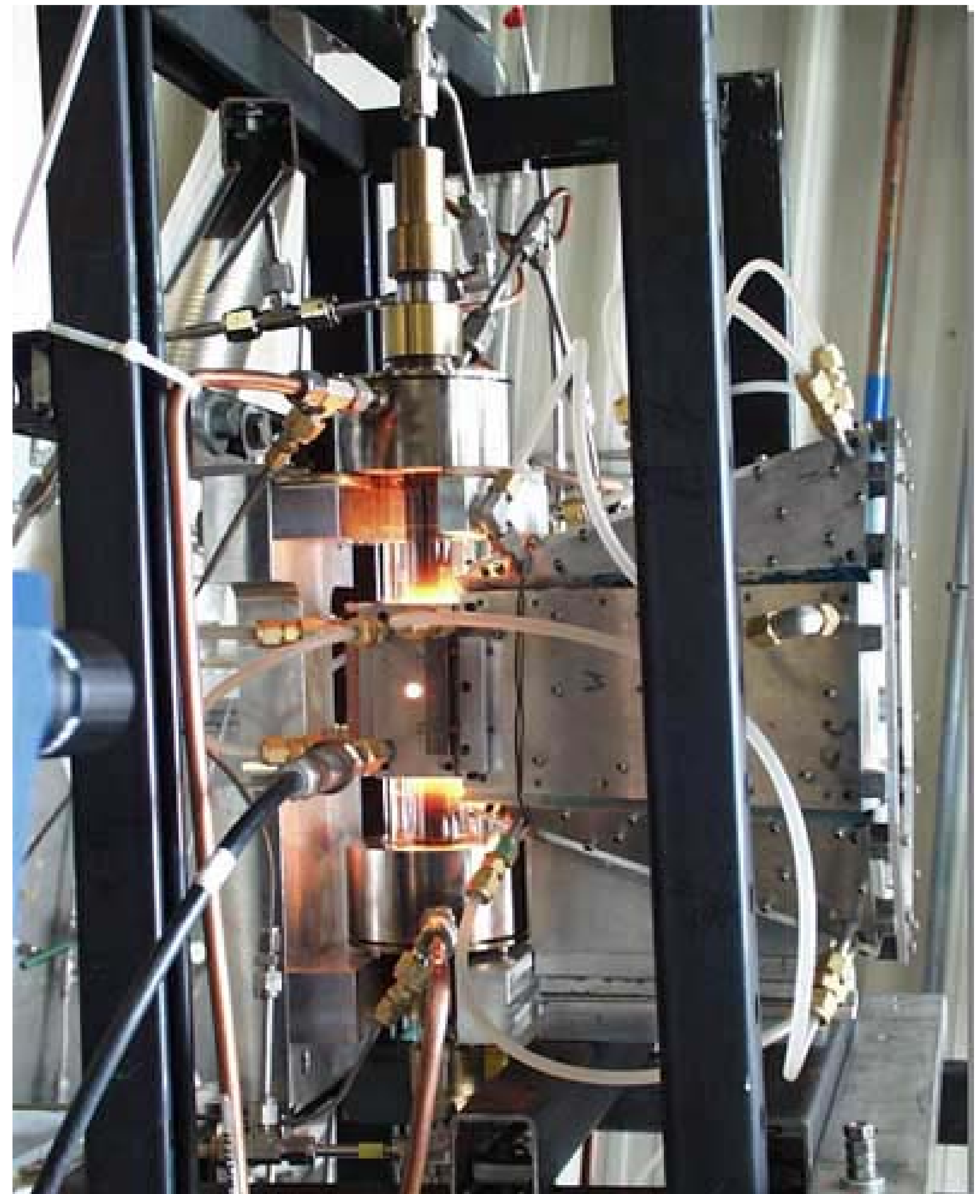
System Concept
Hydrogen Production



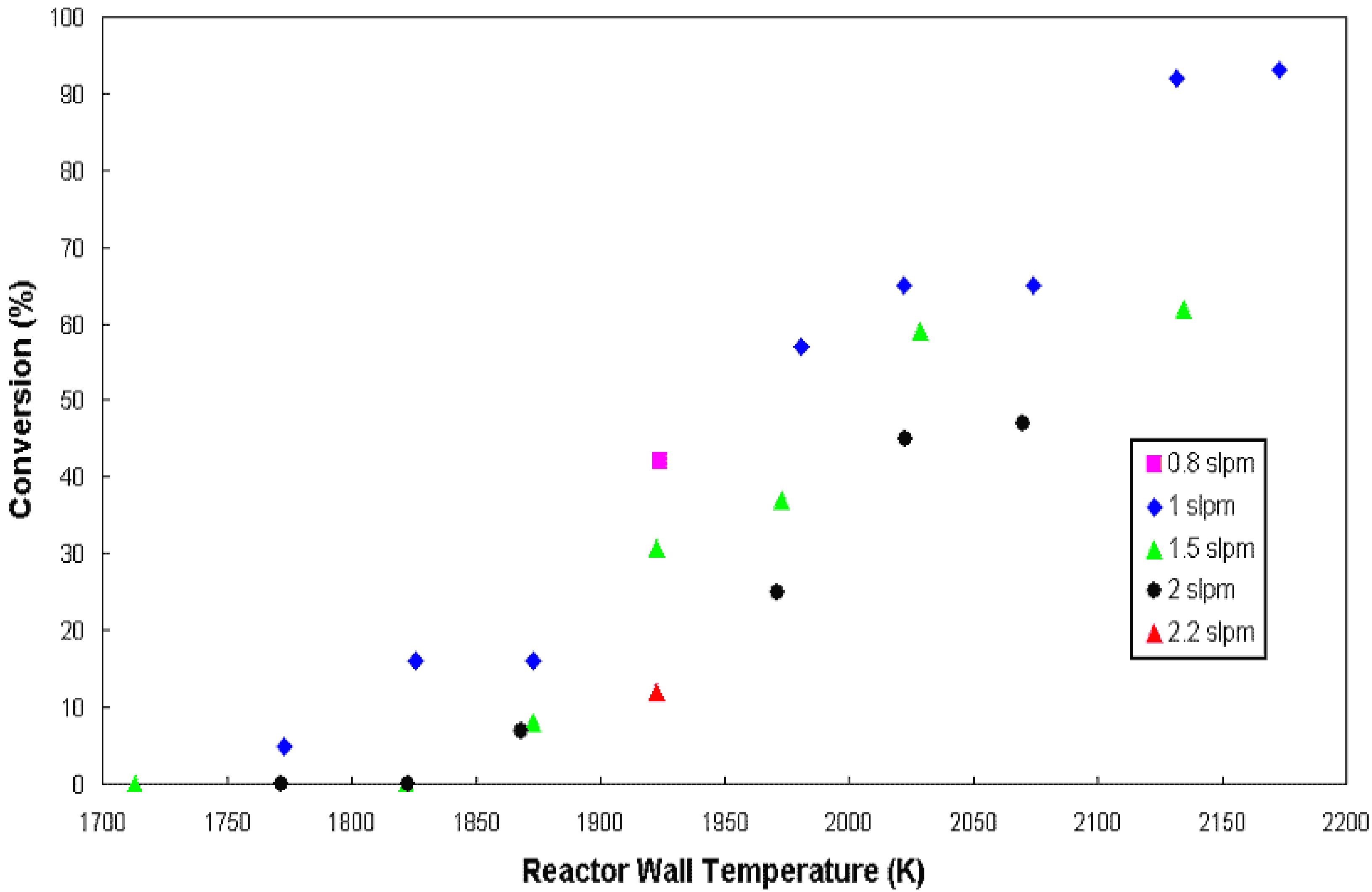
$$\mathrm{N.G.(CH_x)} \xrightarrow{\text{sun}} \mathrm{C} + (x/2)\mathrm{H_2}$$

Reactor System





Conversion as a Function of Reactor Wall Temperature for Various Initial Methane Flow Rates



Energy use and GHG Emissions
(H_2 Supplied as High-pressure Gas)

Steam-reforming Plant + Liquid H_2 + Transport

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$$

+310 MJ/kg of H_2
+20.42 kg CO_2-eq/kg H_2

(Spath and Amos, 2002)

Solar-thermal NG Dissociation Distributed Plant

$$CH_4 \rightarrow C + 2H_2$$

(carbon is sold)

+38 MJ/kg of H_2
+3.46 kg CO_2-eq/kg H_2

Fossil fuel avoided = 272 MJ/kg H_2
CO_2 avoided = 17 kg CO_2/kg H_2

(carbon is converted to H_2)

+218 MJ/kg of H_2
+14.2 kg CO_2-eq/kg H_2

Fossil fuel avoided = 82 MJ/kg H_2
CO_2 avoided = 6.22 kg CO_2/kg H_2

Economic Studies

(Spath and Amos 2002)

Fueling Stations

(H_2 @ 3000psig; $0.66/kg C)

Collector Area (m^2)	Capital Cost ($M)	H_2 Selling Price ($/kg) "Out the Gate"	Compressed/Stored
2,188 (1.8 acres)	4.42	-----	12.30 (250 kg/day)
	2.15	3.35 (462 kg/day)	-----
8,750 (7 acres)	8.93	-----	8.04 (750 kg/day)
	4.34	2.61 (1141 kg/day)	-----

Basis: $3.92/1000 scf NG; 15% IRR, 20 yr life, Equity funded

Economic Studies

(CU analysis)

Semi-conductor Plant

(300 psig, \$4.35/kg current contract price)

Collector Area (m^2)	Capital Cost (\$M)	H_2 Selling Price (\$/kg)
985 (0.8 acre)	**\$ 1.46**	**3.92** (240 kg/day total; 75 kg/day stored)

Small Utility

(co-gen 1.6 MW electricity & H_2 out the gate)

Collector Area (m^2)	Capital Cost (\$M)	H_2 Selling Price (\$/kg)
7,800 (6.2 acres)	**\$ 4.96**	**3.22** (1743 kg/day; electricity @ 5 ¢/kWh)

Basis: \$3.92/1000 scf NG; 15% IRR, 20 yr life, Equity funded

Collaborations

- In the US
  - 10 industrial partners (in-kind cost share)
  - BP, ChevronPhillips, GM, EPRI, Harper International, Siemens, Pinnacle West, ChevronTexaco, Plug Power
- Outside of the US
  - IEA SolarPACES, Task II, Solar Chemistry (AL is US Coordinator)
  - Paul Scherrer Institute, Switzerland
  - Swiss Federal Institute of Technology (ETH), Zurich

2002 Review Panel Comments

- Team took exception to the use of a carbon fuel cell to extend hydrogen production into dark hours
  - Response: the carbon fuel cell is a long-term technology that was considered as an option for use of the carbon byproduct and is not essential to the overall concept technically or economically.
- "…inclusion…in the hydrogen program portfolio is important in that it keeps the technology area broad, maximizes options for commercial use, and complements other dissociation technologies."

HCNG Fleet Opportunity in Desert SW United States

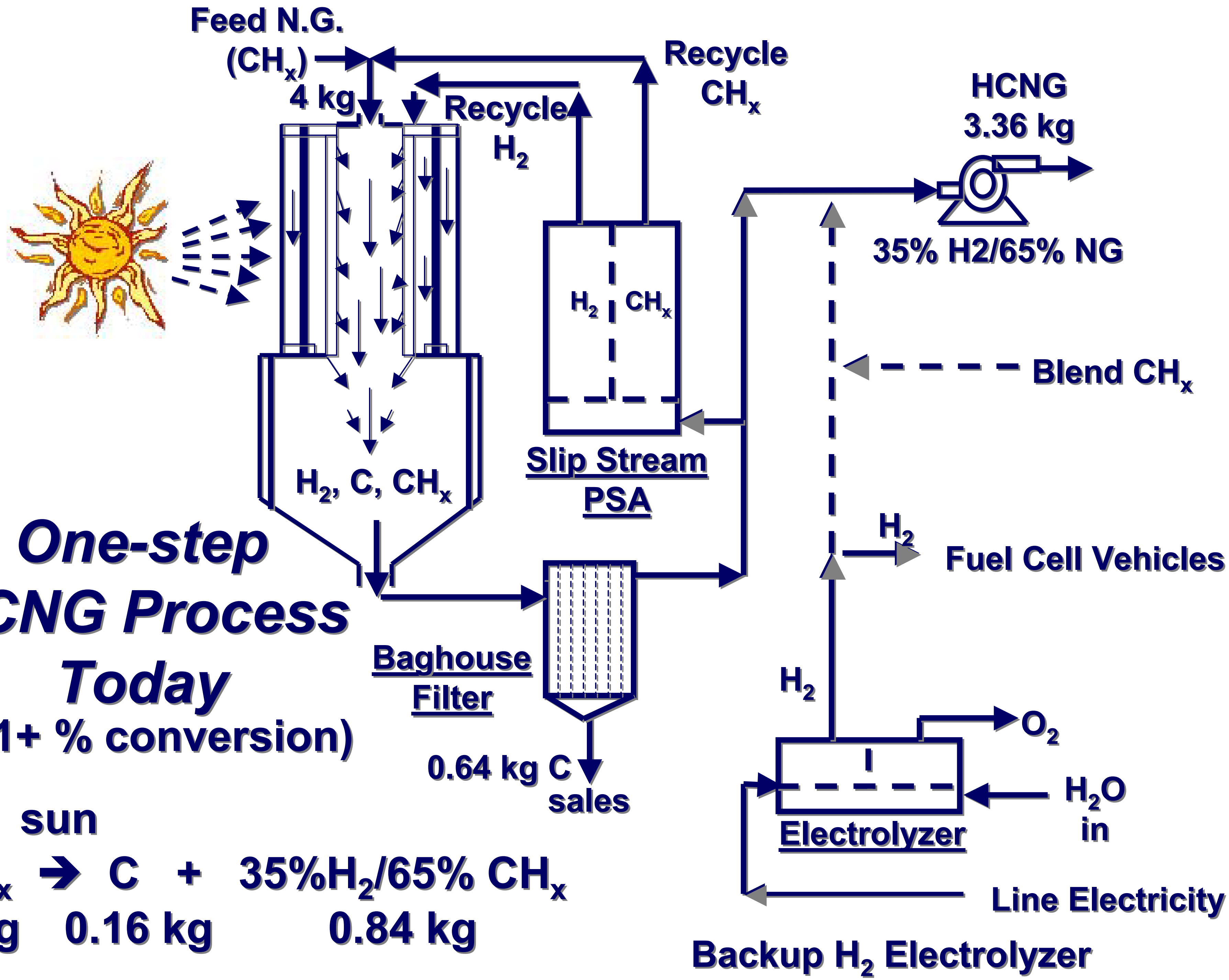
- First Fueling Station: Phoenix Area
  - Pinnacle West is already in business
    - HCNG, NG, H_2; H_2 by electrolysis w/off-line e^-
  - Arizona Public Service, Municipal Vehicles, Taxis, Bus Lines, …

- Combined Fleet Facility with Industrial H_2 users
  - Intel & Motorola are heavy users
  - Tucson, Albuquerque, Las Vegas, Denver, Colorado Springs, Salt Lake City, …

- Potential scale-up scenario
  - H_2 Enriched NG (HCNG) (20 – 35% H_2) for Fleets
  - Increased H_2 Content HCNG (50% or more)
  - Fuel Cell Vehicles (100% H_2) or IC engines running on H_2
    - Carbon Conversion Fuel Cell Marketed

One-step HCNG Process Today

(21+ % conversion)



$$\begin{array}{lcl} CH_x & \xrightarrow{\text{sun}} & C \quad + \quad 35\%H_2/65\%\ CH_x \\ 1\text{ kg} & & 0.16\text{ kg} \qquad\qquad 0.84\text{ kg} \end{array}$$

Economic Impact of Fleet Station Development

Number of 327 fill-up HCNG Fleet Stations	*Total Annual Revenue ($M)**	*% North American Carbon Black Market*
40	141	1%
200	706	5%
400	1,413	10%
1600	5,648	40%

*based on capital cost of $3.2M per station and operating costs of $2.3M/year

Carbon Black Market

- **World Market: ~ 8 billion kg/year**
- **Tire & industrial rubber: 92%of World Market**
  - **7.3 billion kg/yr**
- **North American Market: 25% of World Market**
  - **1.8 billion kg/year**


Al's Quik Serv
Hydrogen
HCNG
NG
STT

Solar Examples

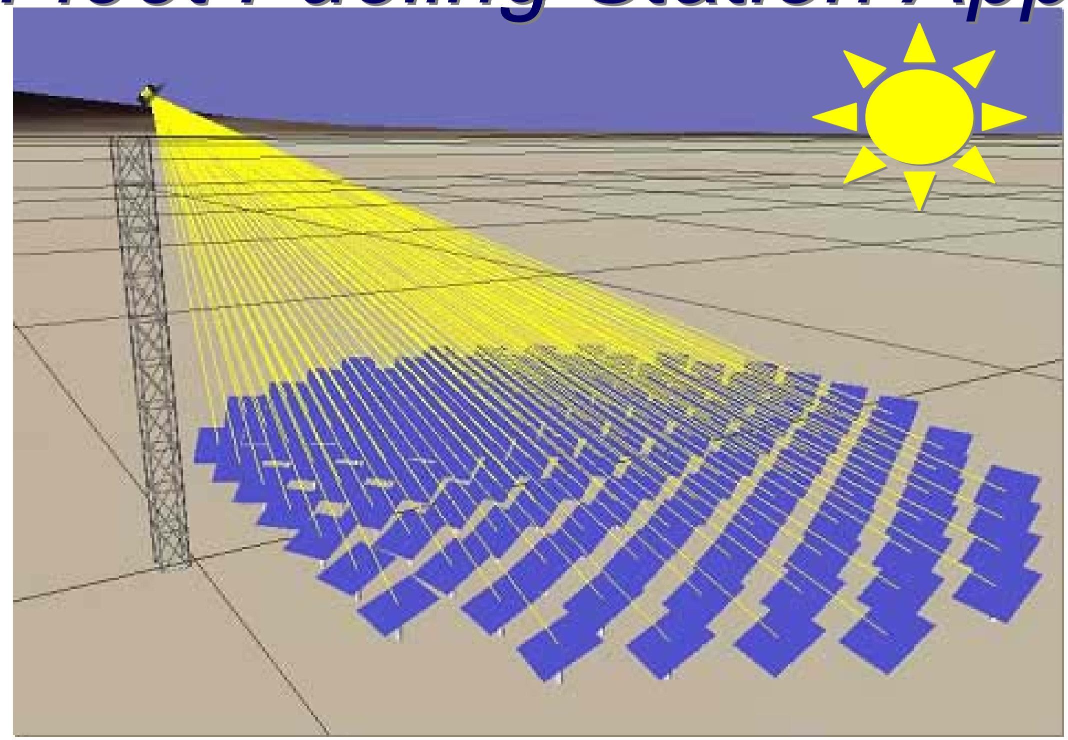
Enhanced oil recovery, early 80's

Large solar furnace, France

Small central receiver, Israel

30 MW_{th} Solar Plant, CA

Preliminary HCNG Field Design for Fleet Fueling Station Application



- Phoenix Area
- ~ 6,546 kg/day HCNG
- ~ 327 fill-ups/day
  (@ 20 kg/fill-up)
- ~ 1250 kg C/day
- ~ 0.57 hectares (1.4 acres)

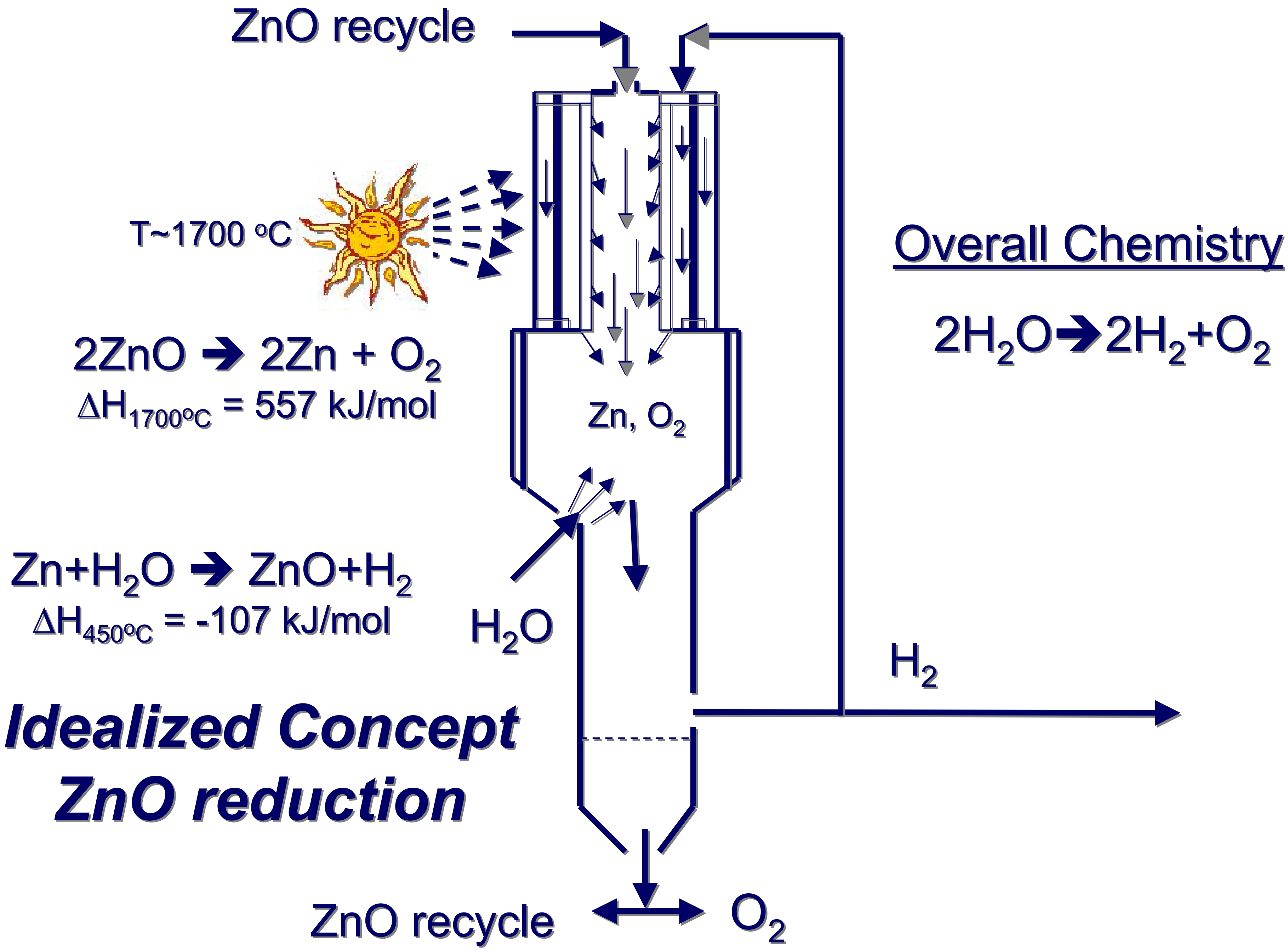
- ~ 1.1 MW_{th}
- ~ 5 cm ID x 48 cm reactor
- ~ 122 heliostats (~1770 m^2)
- Overall optical η~70%
  - peak flux >3000 suns

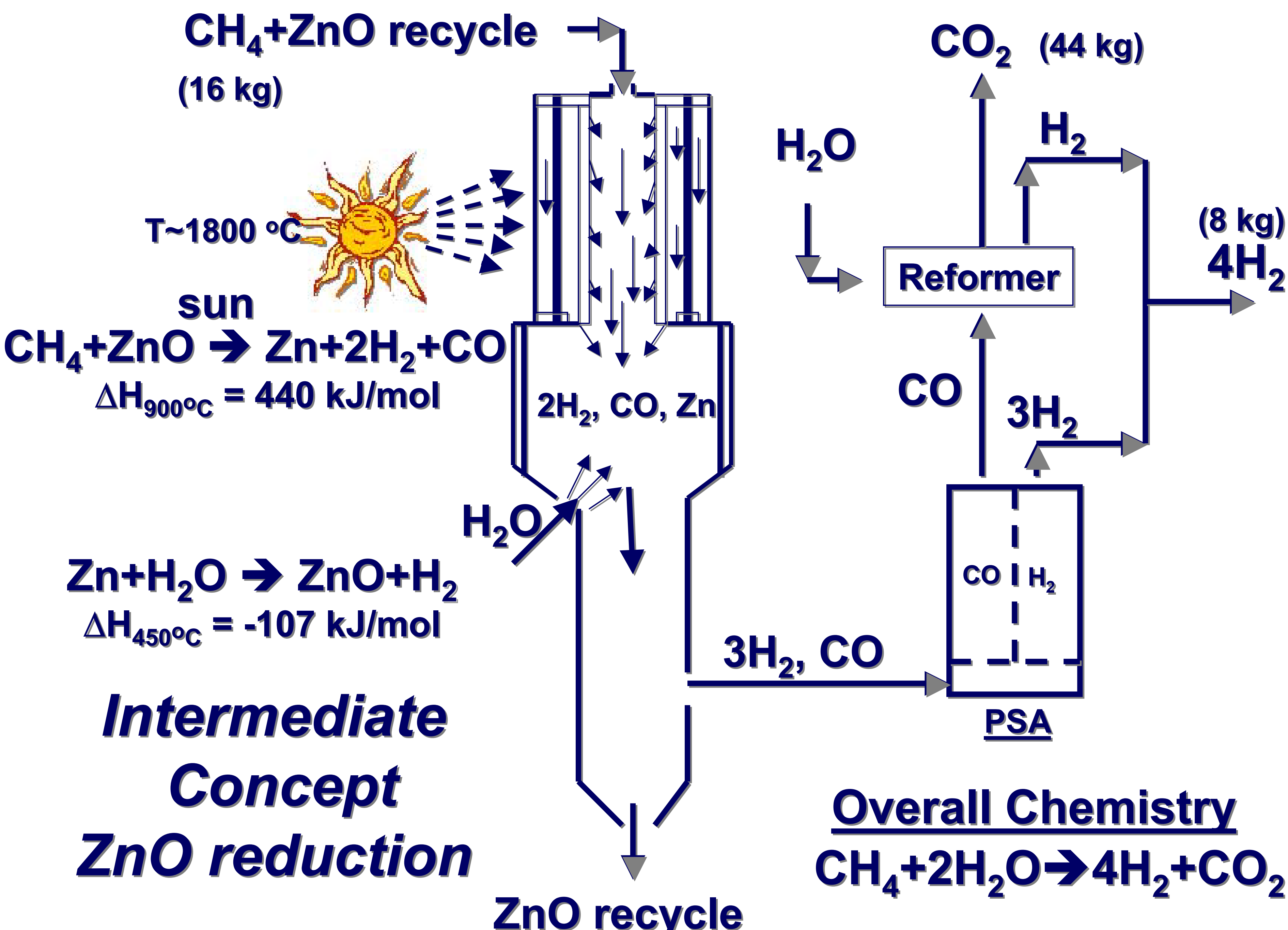
Next Step Applications/Options

- Industrial H_2 to Semi-conductor Plants in SW, etc.
- Co-generating Utilities
  - H_2 and electricity
- Coal Bed Methane Conversion
  - largest reserves in the world are in the Four Corners Region of the desert SW United States)
- Biogas Conversion
  - waste landfill biogas, etc.
- Dry Reforming of CO_2 Contaminated Gas Wells
- Water-splitting cycles

Water-splitting Cycles

- 2 Step metal oxide reduction
  - high temperature endothermic reduction
  - lower temperature exothermic reaction with water
  - Ongoing European solar projects
- Thermochemical cycles
  - originally studied with nuclear reactors in mind
  - recent General Atomics study identified 2 candidates
    - adiabatic UT-3
    - Sulfur – iodine
  - GA proposing to identify others with higher temperature operation using solar thermal power
- Direct water splitting
  - requires $T>2500^oC$, high temperature separation
  - $\Delta H_{2500^oC} = 238$ kJ/mole


ZnO recycle
T~1700 °C
$2ZnO \rightarrow 2Zn + O_2$
$\Delta H_{1700°C} = 557$ kJ/mol
Zn, O_2
$Zn + H_2O \rightarrow ZnO + H_2$
$\Delta H_{450°C} = -107$ kJ/mol
H_2O
Overall Chemistry
$2H_2O \rightarrow 2H_2 + O_2$
H_2
Idealized Concept
ZnO reduction
ZnO recycle
O_2


CH_4+ZnO recycle
(16 kg)
T~1800 °C
sun
$CH_4 + ZnO \rightarrow Zn + 2H_2 + CO$
$\Delta H_{900°C}$ = 440 kJ/mol
$2H_2$, CO, Zn
H_2O
$Zn + H_2O \rightarrow ZnO + H_2$
$\Delta H_{450°C}$ = -107 kJ/mol
Intermediate Concept ZnO reduction
ZnO recycle
$3H_2$, CO
CO
H_2
PSA
CO
$3H_2$
H_2O
Reformer
CO_2 (44 kg)
H_2
(8 kg)
$4H_2$
Overall Chemistry
$CH_4 + 2H_2O \rightarrow 4H_2 + CO_2$

Dry Reforming Experiments

- **Application to high CO_2 containing gas wells and landfill gas processing**

$$CO_2 + 2CH_4 \rightarrow C + 2CO + 4H_2$$

Feed Gas: 0.90% CH_4; 0.45% CO_2

Flux (kW/m^2)	% CO_2	% CH_4	% CO	% H_2
none	0.45	0.84	0	0
1500	0.23	0.20	0.35	1.55
2000	0.11	0.07	0.62	1.60

Chemically-assisted Solar-thermal Water Splitting

$CH_4 + ZnO \rightarrow Zn + 2H_2 + CO$

$\Delta H@900^{o}C = 440$ kJ/mol

$Zn + H_2O \rightarrow ZnO + H_2$

$\Delta H@450^{o}C = -107$ kJ/mol

$CO + H_2O \rightarrow CO_2 + H_2$

$CH_4 + 2H_2O \rightarrow 4H_2 + CO_2$

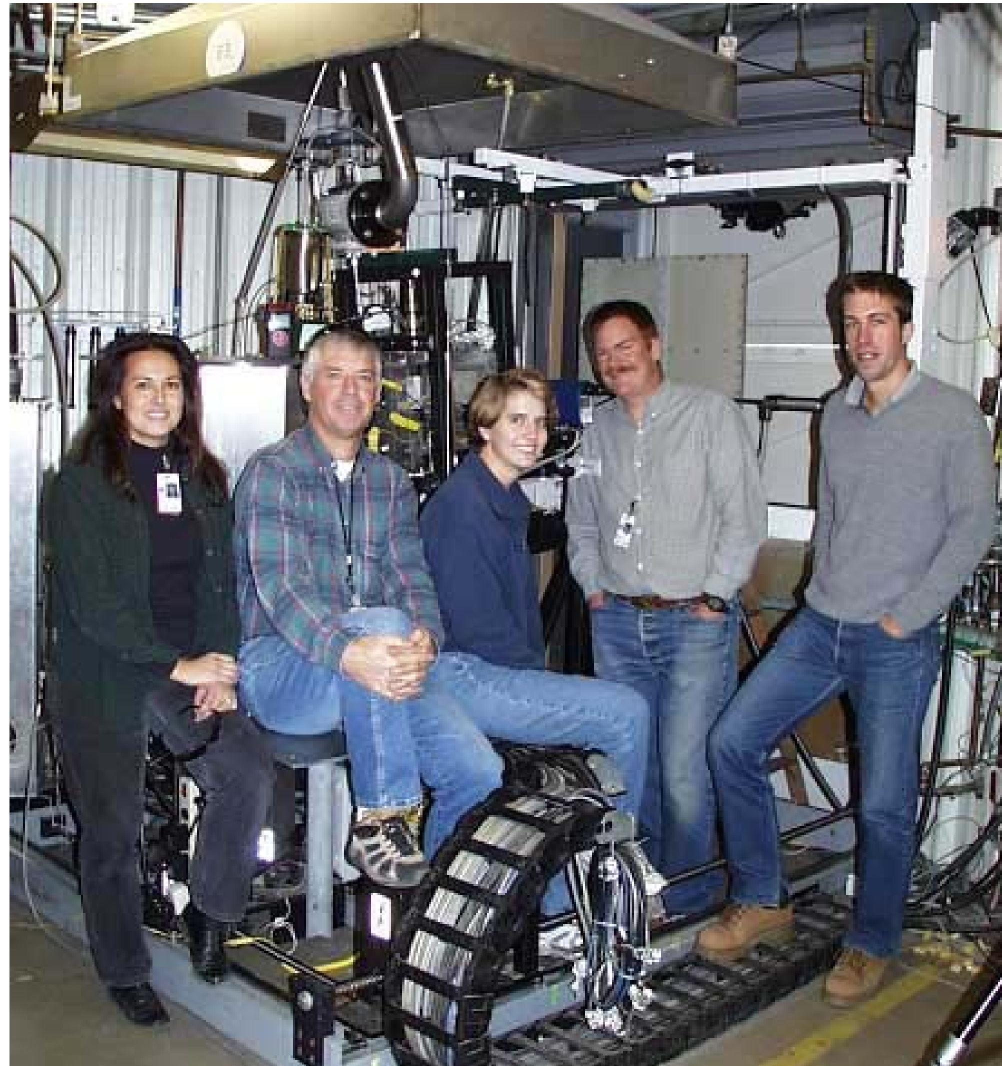
Summary

- Splitting methane using concentrated sunlight is technically feasible
- Various system configurations and applications have economic potential
- Technical concept can be extrapolated to other chemical reactions and to water splitting
- A near-term application, business opportunity and path forward have been identified
- Continued funding is warranted

Project Team

Al, Karen

Sarah



Judy, Al, Jaimee, Carl, Fabian