Hydrogen Generation

Analyzing the viability of Hydrogen as a mobile energy carrier

Why Are We Interested in Hydrogen?

- It is abundant and can be produced locally
- No pollution
- Hydrogen is a clean energy carrier
- Fossil fuels are limited
- Renewable resource

Hydrogen Technologies

- Steam Reforming
- Electrolysis
- Thermochemical

Hydrogen Generation

- Steam reforming of methane accounts for the 50 million tons of hydrogen used world-wide
- Electrolysis is a mature technology and is used primarily for the production of high purity oxygen and hydrogen
- Hydrogen produced by high temperature thermo-chemical processes has not been demonstrated on a commercial scale
  - Promises high efficiency production in the future

Relative Cost

- H_2 produced by methane reforming –$0.80/kg
- H_2 produced by electrolysis –$3.00/kg @ $0.06/kWh
- H_2 expectations for nuclear & thermo chemical – $1.30/kg

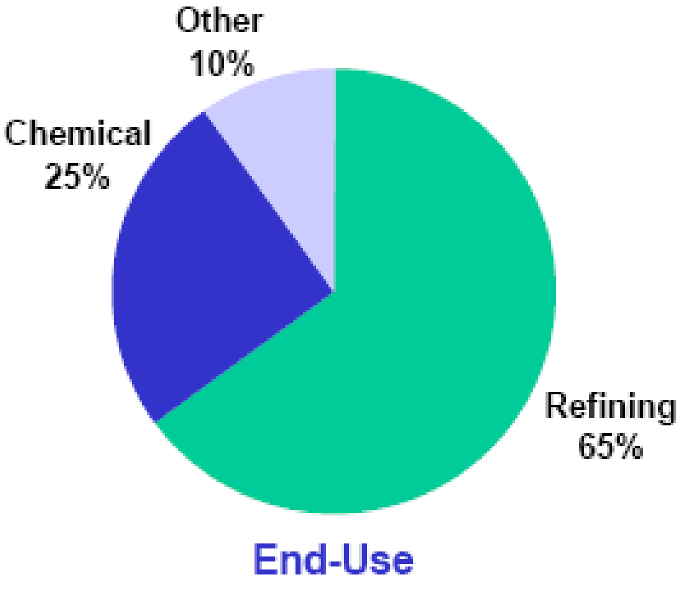
Advantages of Hydrogen

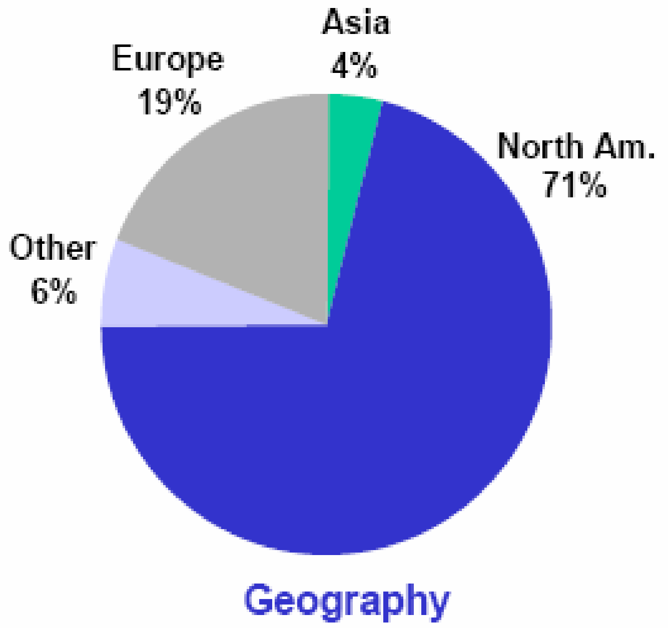
- Hydrogen can be totally non-polluting (water is the exhaust).
- Hydrogen can be economically competitive with gasoline or diesel.
- Hydrogen is just as safe as gasoline, diesel, or natural gas.
  - The self-ignition temperature of hydrogen is 550 degrees Celsius.
  - Gasoline varies from 228-501 degrees Celsius
- Hydrogen can help prevent the depletion of fossil fuel reserves.
- Hydrogen can be produced in any country.

Disadvantages of Hydrogen

- Hydrogen production is energy intensive
- Low density, resulting in:
  - large volumes
  - low temperatures
  - high pressures
- Complex systems required for storage

Market Environment-Global Purchased Hydrogen





Market Environment-Our Target

- Hydrogen Fuel Cell Cars
  - Why HFC Cars?
    - No byproducts concerning the environment
    - Gas equivalent value of hydrogen is $4.75/kg

- Why not the current users of hydrogen?
  - Not competitive with steam reforming
  - Steam reforming will not work for this market
    - More profitable to sell the CNG directly
    - CNG has environmental issues (CO_2, NO_x, Inefficiency of internal combustion engine)

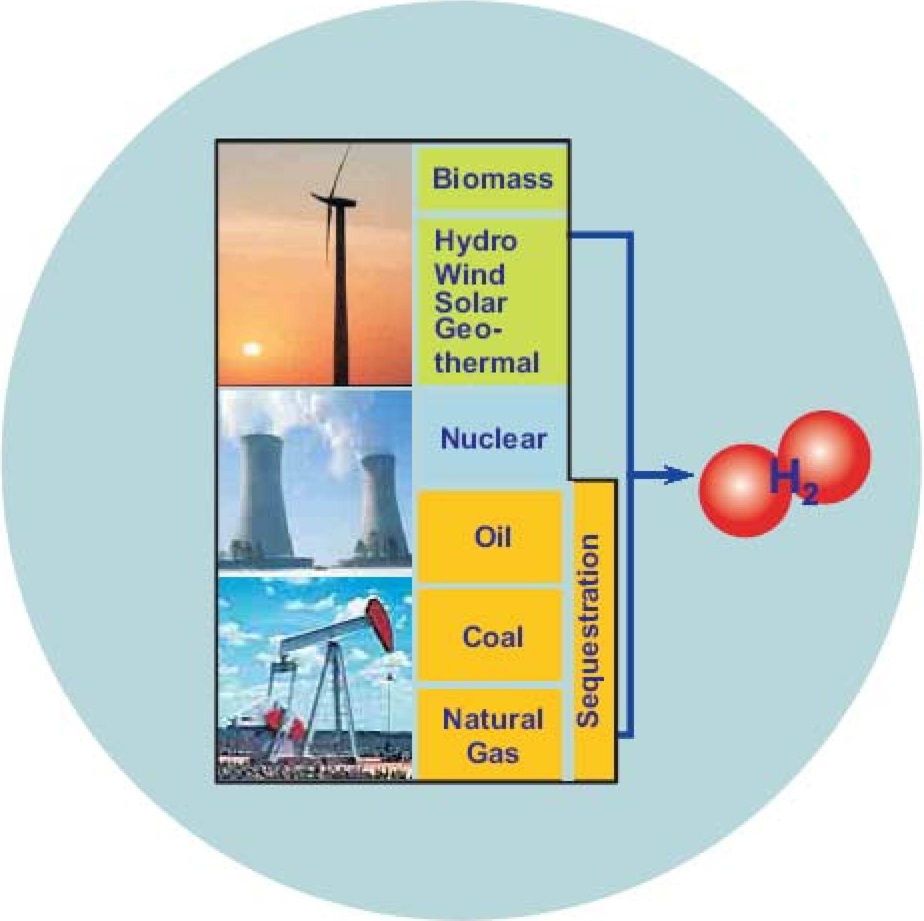
Market Environment-Hydrogen Prices

- Historical (1997 - 2002) Steam Reformed Methane
  - High, $ 2.60 per 100 SCF, compressed gas, tube trailer
  - Low, $1.25, same basis.

- Current: $1.70 to $2.60 same basis;
  - $1.15 to $1.80 per 100 SCF, cryogenic liquid, tank truck
  - $0.18 to $0.80 compressed gas, pipeline

- Hydrogen market prices vary depending on the form of delivery, consumed volume, and location.

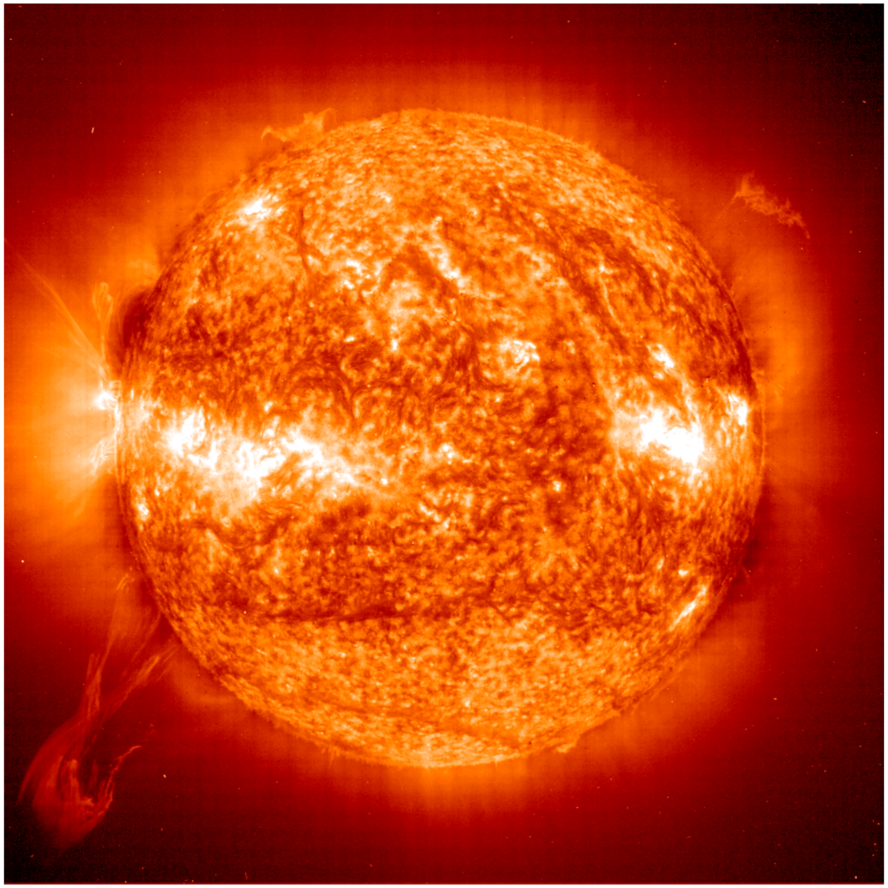
Sources of Energy to Produce Hydrogen



Sources of Energy to Produce Hydrogen-Solar

Solar

- Solar input is interrupted by night and cloud cover
- Solar electric generation inevitably has a low capacity factor, typically less than 15%
- Expensive to make
- Materials are environmental concern: crystalline silicon and gallium arsenide

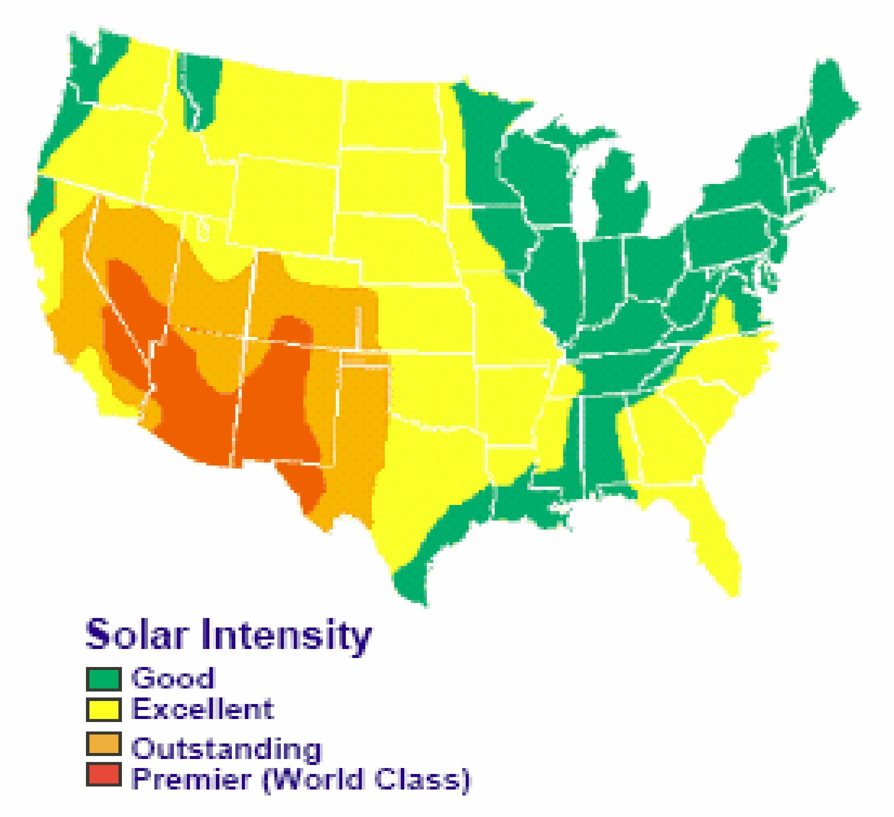


Sources of Energy to Produce Hydrogen-Solar

Solar

- To produce enough energy as a 1,000-megawatt nuclear reactor, panels would have to occupy 127 square miles of land
  - Solar Power from Sun is 1 kW/m^2

- There is a low intensity of incoming radiation and converting this to electricity
  - Inefficient (12 – 16%)



Sources of Energy to Produce Hydrogen-Wind

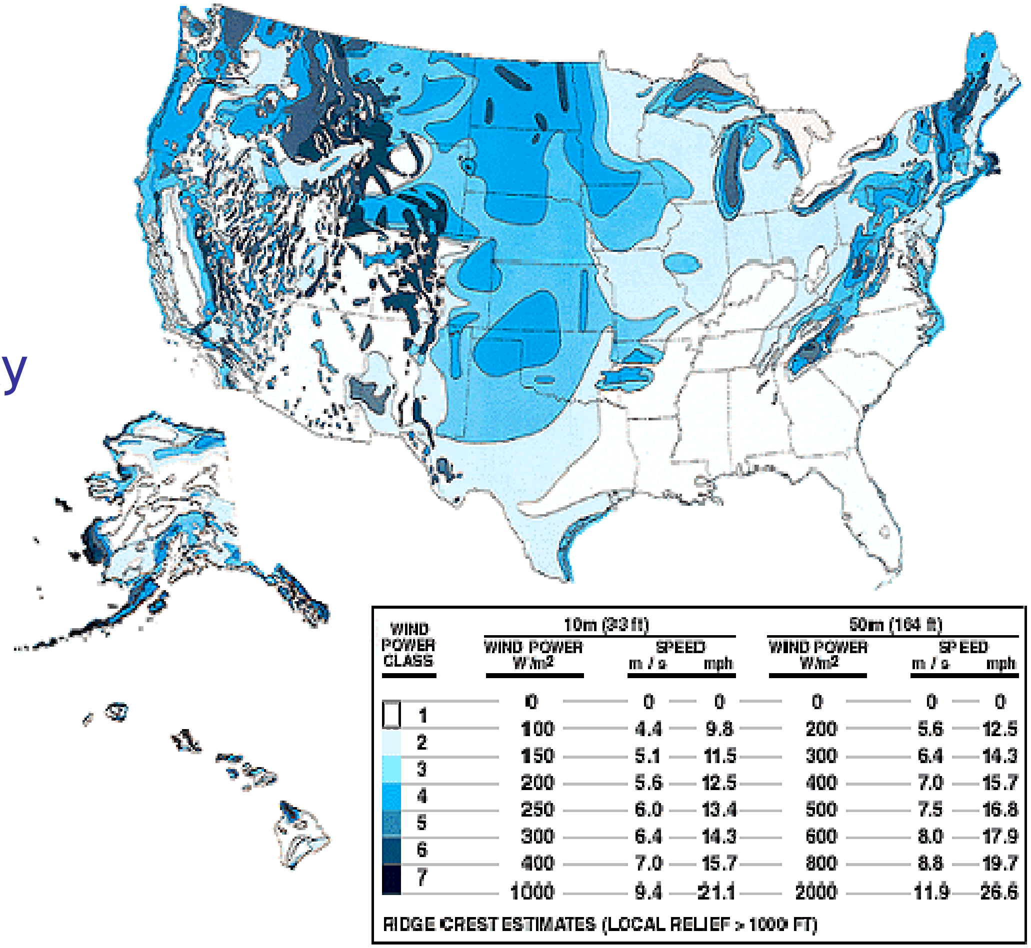
Wind

- Average wind speed of 14 mph is needed to convert wind energy into electricity economically
- Average wind speed in the United States is 10 mph
- Higher initial investment than fossil-fueled generators
- 80% of the cost is the machinery, with the balance being the site preparation and installation

Sources of Energy to Produce Hydrogen-Wind

Wind

- Irregular and it does not always blow when electricity is needed
- Based on the average wind speed
  - 50,000 wind turbines
  - 300 square mile area
  - For the same amount of electricity of one 1000 MW nuclear power plant produces



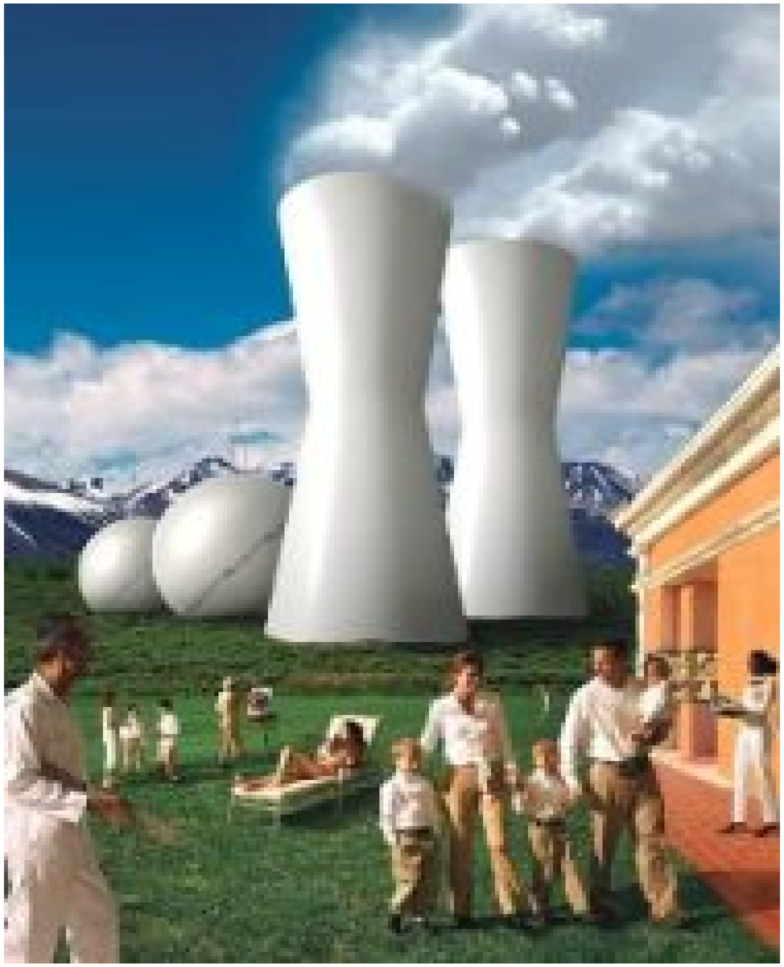
WIND POWER CLASS	10m (33 ft) WIND POWER W/m2	10m (33 ft) SPEED m / s	10m (33 ft) SPEED mph	50m (164 ft) WIND POWER W/m2	50m (164 ft) SPEED m / s	50m (164 ft) SPEED mph
	0	0	0	0	0	0
☐ 1						
	100	4.4	9.8	200	5.6	12.5
2						
	150	5.1	11.5	300	6.4	14.3
3						
	200	5.6	12.5	400	7.0	15.7
4						
	250	6.0	13.4	500	7.5	16.8
5						
	300	6.4	14.3	600	8.0	17.9
6						
	400	7.0	15.7	800	8.8	19.7
7						
	1000	9.4	21.1	2000	11.9	26.6

RIDGE CREST ESTIMATES (LOCAL RELIEF > 1000 FT)

Sources of Energy to Produce Hydrogen-Nuclear

Nuclear

- 1,000 MWe power station consumes about 2.3 million tonnes of black coal each year
- Nuclear: 25 tonnes of uranium
- No CO_2 emissions



Sources of Energy to Produce Hydrogen-Comparison of Energy

One kilogram (kg) of firewood can generate 1 kilowatt-hour (kW·h) of electricity.

1 kg coal:	3 kW·h
1 kg oil:	4 kW·h
1 kg uranium:	50,000 kW·h

Consequently, a 1000 MWe plant requires the following number of tonnes (t) of fuel annually:

2,600,000 t coal:	2000 train cars (1300 t each)
2 000 000 t oil:	10 supertankers
25 t uranium:	Reactor Core (10 cubic metres)

Sources of Energy to Produce Hydrogen-Comparison of Land Use

1000 MW system with values determined by local requirements and climate conditions (solar and wind availability factors ranging from 20 to 40%):

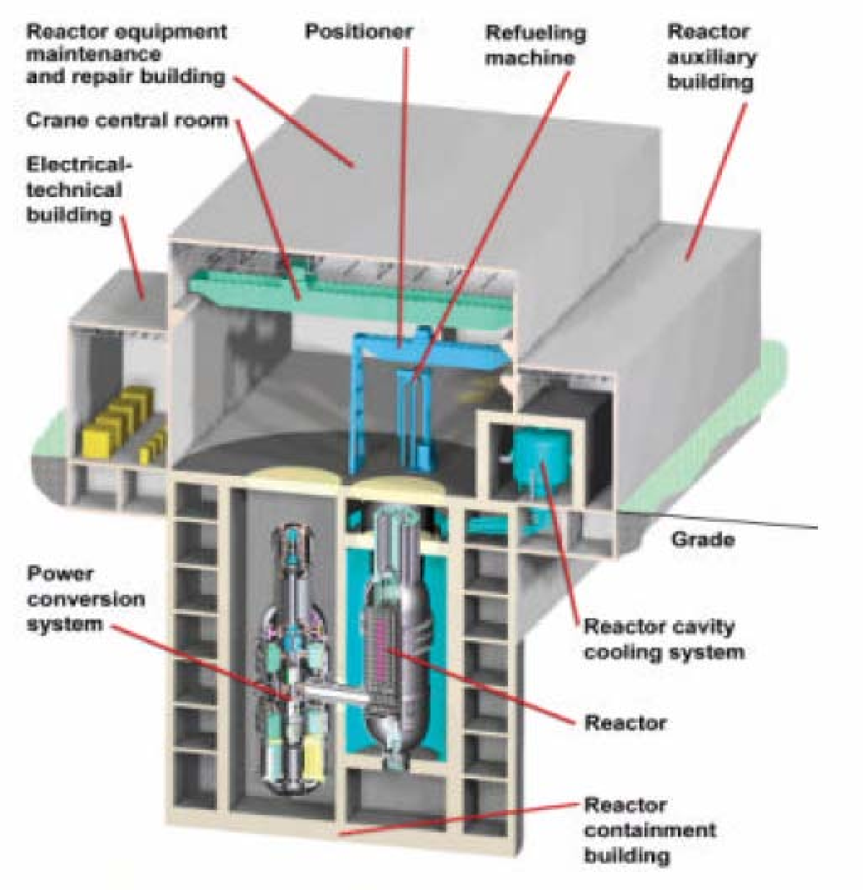
Fossil and Nuclear sites:	1–4 km^2
Solar thermal or photovoltaic (PV) parks:	20–50 km^2 (a small city)
Wind fields:	50–150 km^2
Biomass plantations:	4000–6000 km^2 (a province)

Power Sources

- Nuclear power costs about the same as coal, so it's not expensive to make.
- Does not produce smoke or carbon dioxide, so it does not contribute to the greenhouse effect.
- Produces huge amounts of energy from small amounts of fuel.
- Produces small amounts of containable waste.

Power Sources: GT-MHR

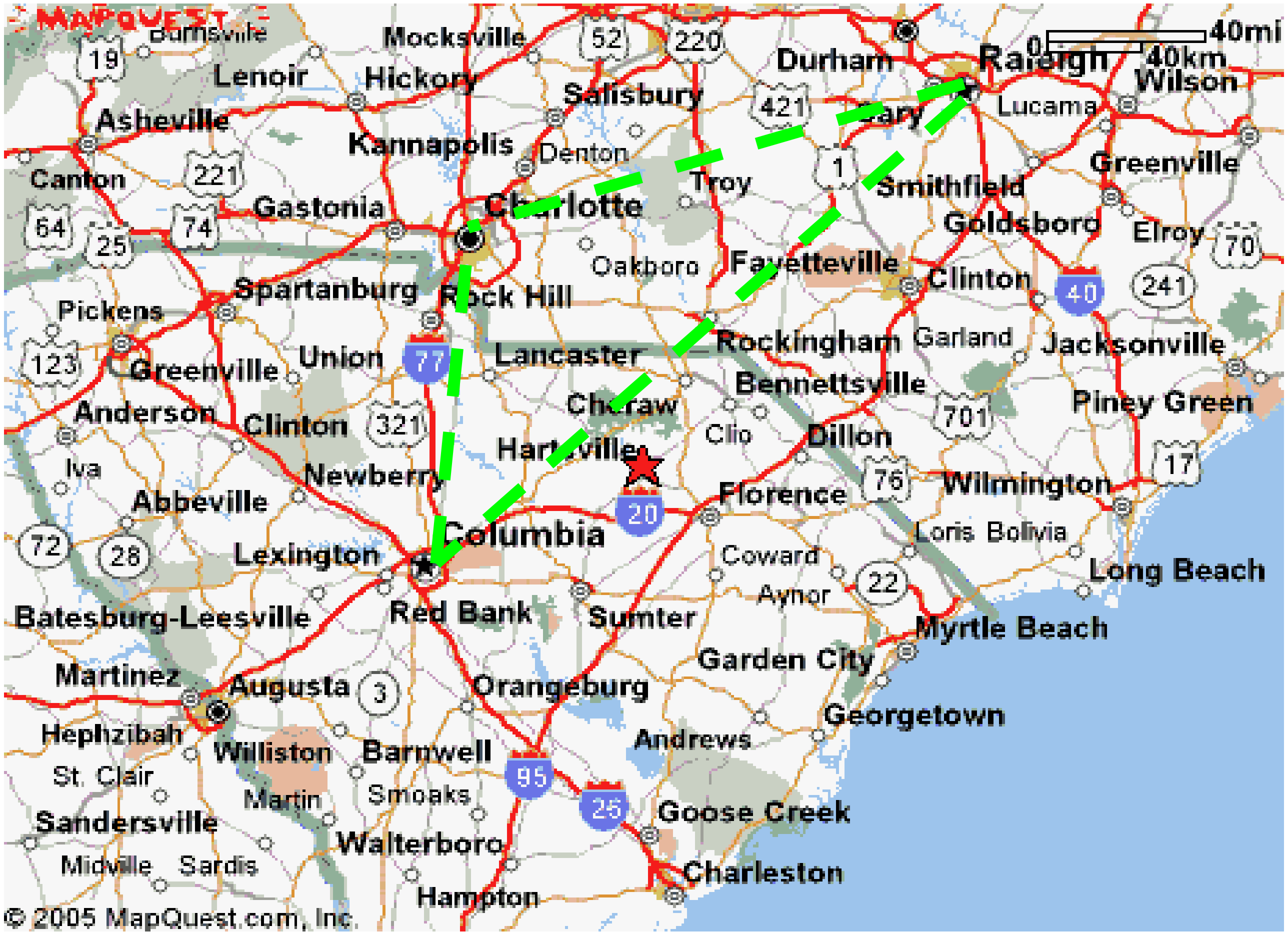
- Reactor power, MWt 600
- Core inlet/outlet temperatures, 491/850 °C
- High thermal efficiency
- Low environmental impact
- Competitive electricity generation costs.



Decision of Location

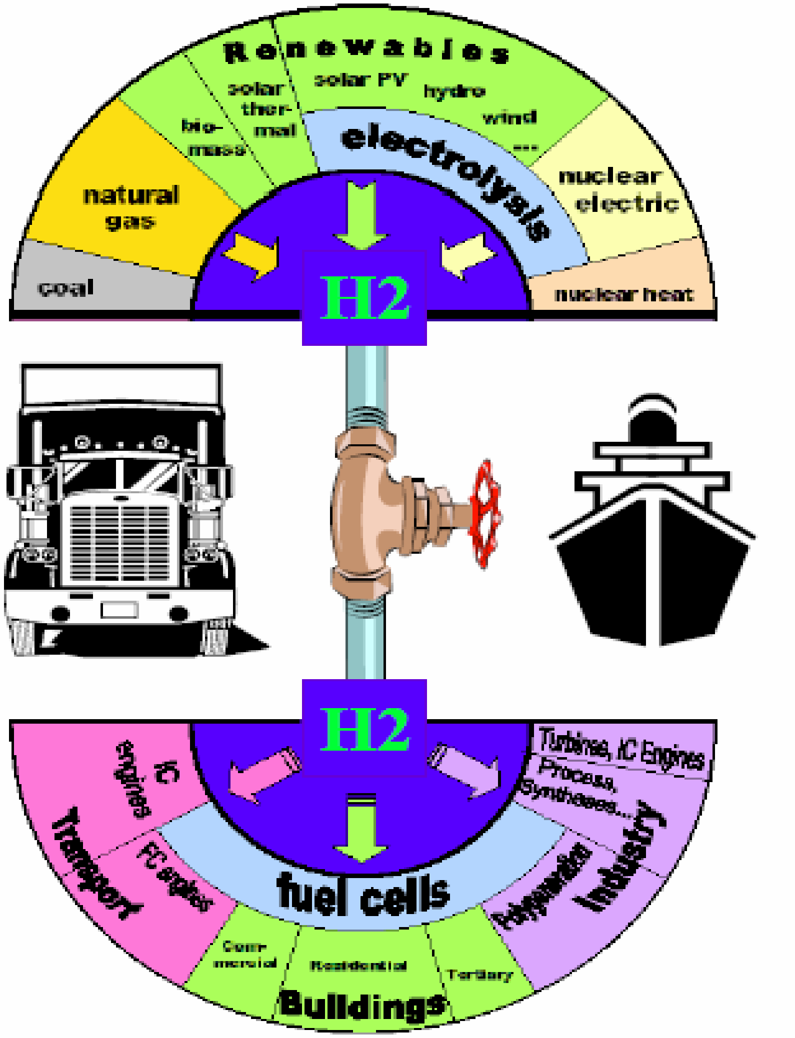
- Exelon, Entergy, and Dominion Resources
  - Plans to build new nuclear power plants using a GT-MHR
  - Exelon – Clinton, Illinois
  - Entergy – Port Gibson, Mississippi
  - Dominion – North Anna Power Station
    Sixty miles NW of Richmond, VA

Decision of Location



Transportation

- Gaseous hydrogen can’t be treated the same as natural gas
- Important hydrogen-related concerns for pipelines:
  - Fatigue cracking
  - Fracture behavior
  - Performance of welds
  - High pressure hydrogen
  - Gas purity



Transportation-Tube Trailers

- Compressed gas tube trailers
  - Fill at plant, swap for empty at fueling station
  - Holds 400 kg of H_2 at 7000 psi
  - Pumping is required to transfer from trailer to tank (~3.1 kWh/kg)

Transportation

- Compressed gas tube trailers
  - Fill at plant, swap for empty at fueling station
  - Holds 400 kg of H_2 at 7000 psi
  - Pumping is required to transfer from trailer to tank (~3.1 kWh/kg)

- Cryogenic liquid trailers
  - Holds 4000 kg of H_2
  - Liquefaction energy ~13.75 kWh/kg
  - Boil-off occurs

Transportation-Pipelines

- Environmental impacts
- Compatibility with land uses
  - Availability of rights of way and permitting
- Cost
- Maintenance and operation of the completed pipeline

Transportation-Trucks/Pipeline

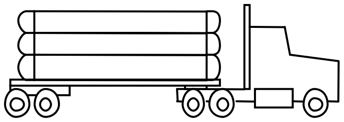
Central production is more efficient. Getting the hydrogen to market is a challenge. Assuming production rate of 500 tonnes/day.

Mobile Delivery/Tube Trailer

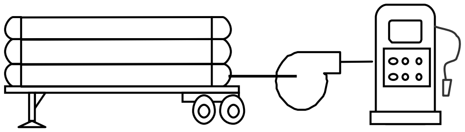
- 2500 trailers
- Annual Costs: $408 million

Hydrogen Pipeline

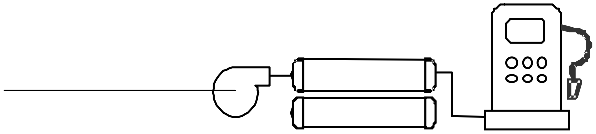
- Lower fueling station storage and equipment requirement
- $800/m
- 419 km
- Total Cost: $335 million
- Less Dangerous



TRUCK DELIVERY



COMPRESSED HYDROGEN TUBE TRAILER



HYDROGEN PIPELINE

1 Introduction

2 Sources of Energy

3 Power Source

4 Decision of Location-Nuclear

5 Cycles and Previous Studies

- Water Splitting Cycle
- Literature Proposed Cycles

6 Thermodynamic Analysis

7 Molecular Discovery

8 Plant Design Analysis

9 Conclusions

Water splitting cycle

- Splits water into constitute elements

$$2H_2O \rightarrow 2H_2 + O_2$$

- The reaction is not thermodynamically favorable, with Gibbs Energy: 237.1 kJ/mol

- A set of reactions can achieve the overall result, with favorable thermodynamics.

Literature Proposed Cycles

The following 2 examples were included in our investigation based on cycle efficiency

Hallett Air Products

Reaction		Temperature
$Cl_2 + H_2O \rightarrow 2HCl + \frac{1}{2}O_2$		800 ^oC
$2HCl \rightarrow Cl_2 + H_2$	(electrolysis)	25 ^oC

Literature Proposed Cycles

Sulfur - Iodine

Reaction	Temperature
$H_2SO_4 \rightarrow SO_2 + H_2O + ½O_2$	850 °C
$2HI \rightarrow I_2 + H_2$	450 °C
$I_2 + SO_2 + 2H_2O \rightarrow H_2SO_4 + 2HI$	120 °C

This cycle is being seriously considered by the DOE, a pilot plant is being planned

Thermodynamic Analysis

- The heat cascade analysis allows for a preliminary method of selection of a given cycle
- The final efficiency of a cycle will be obtained after a detailed analysis has been performed

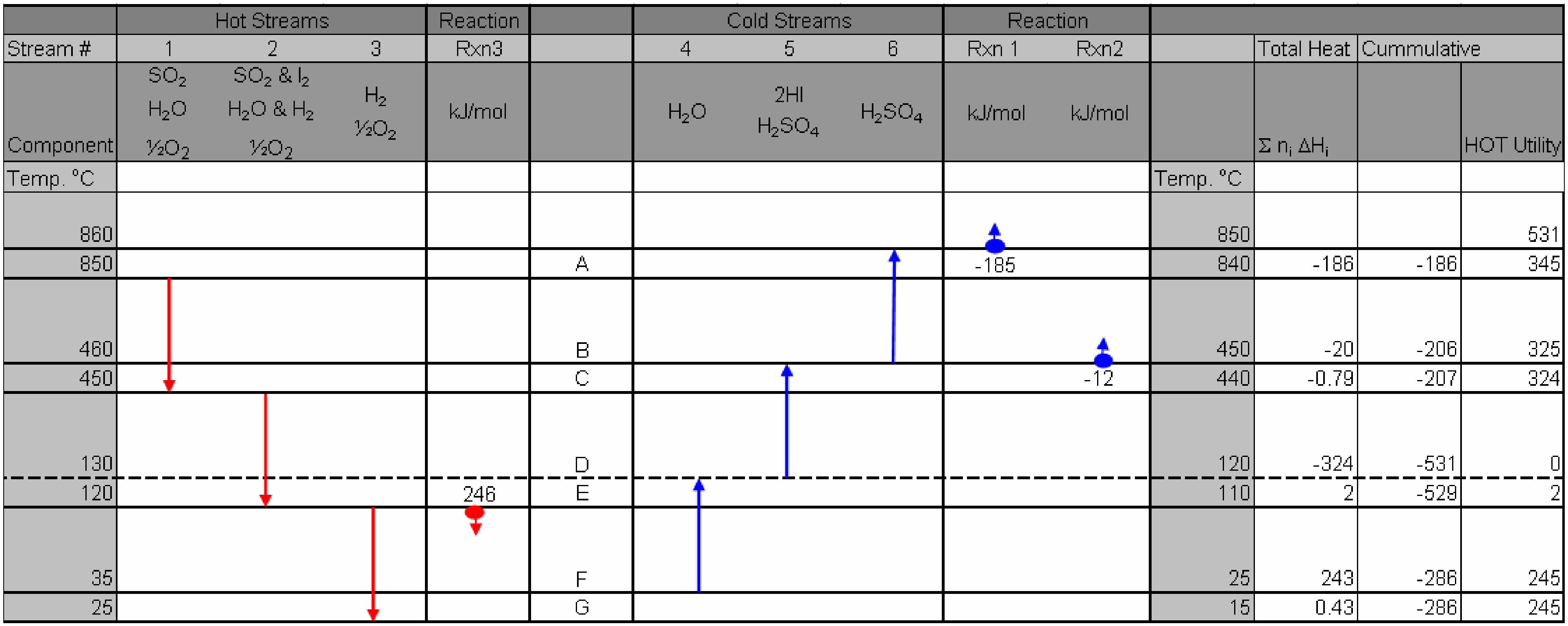
Heat Cascade Efficiency

- The cycle heat cascade efficiency is defined as

$$\varepsilon = {\Delta H_{RXN}}\big/{HU}$$

- The hot utility, HU, was found using a heat cascade analysis using an approach temperature of 10 degree Celsius

Temperature Interval Diagram plus Heat of Reaction for Sulfur-Iodine



	Hot Streams			Reaction		Cold Streams			Reaction					
Stream #	1	2	3	Rxn3		4	5	6	Rxn 1	Rxn2		Total Heat	Cummulative	
Component	SO_2 H_2O ½O_2	SO_2 & I_2 H_2O & H_2 ½O_2	H_2 ½O_2	kJ/mol		H_2O	2HI H_2SO_4	H_2SO_4	kJ/mol	kJ/mol		$\Sigma n_i \Delta H_i$		HOT Utility
Temp. °C											Temp. °C			
860											850			531
850					A				-185		840	-186	-186	345
460					B						450	-20	-206	325
450					C					-12	440	-0.79	-207	324
130					D						120	-324	-531	0
120				246	E						110	2	-529	2
35					F						25	243	-286	245
25					G						15	0.43	-286	245

Thermodynamic Results

Cycle	Name	Temperature	Reaction	Δ G	K	Efficiency
1	US -Chlorine	850	2Cl2(g) + 2H2O(g) → 4HCl(g) + O2(g)	-17.43	6.466	**99.9%**
		200	2CuCl + 2HCl → 2CuCl2 + H2(g)	-5.79	2.462	
		500	2CuCl2 → 2CuCl + Cl2(g)	143.68	1.37534E-16	
2	Hallett Air Products	800	2Cl2(g) + 2H2O(g) → 4HCl(g) + O2(g)	-14.02	4.811	**99.7%**
		25	2HCl → Cl2(g) + H2(g)	162.32	3.64892E-29	
3	Westinghouse	850	2H2SO4(g) → 2SO2(g) + 2H2O(g) + O2(g)	-68.36	1510	**81.7%**
		77	SO2 (g) + 2H2O(a) → H2SO4(a) + H2(g)	44.23	2.52718E-07	
4	Ispra Mark 4	850	2Cl2(g) + 2H2O(g) → 4HCl(g) + O2(g)	-17.43	6.466	**77.9%**
		100	2FeCl2 + 2HCl + S → 2FeCl3 + H2S	189.21	6.178E-10	
		420	2FeCl3 → Cl2(g) + 2FeCl2	15.94	0.06296	
		800	H2S → S + H2(g)	105.34	1.796E-15	
5	Gaz de France	725	2K + 2KOH → 2K2O + H2(g)	159.47	2.600E-08	**56.2%**
		825	2K2O → 2K + K2O2	141.86	3.770E-08	
		125	2K2O2 + 2H2O → 4KOH + O2(g)	-217.89	3.84112E+28	
6	Julich Center EOS	800	2Fe3O4 + 6FeSO4 → 6Fe2O3 + 6SO2 + O2(g)	-91.00	26879	**54.1%**
		700	3FeO + H2O → Fe3O4 + H2(g)	19.29	0.09222	
		200	Fe2O3 + SO2 → FeO + FeSO4	-18.04	98.03	
7	Sulfur-Iodine	850	2H2SO4(g) → 2SO2(g) + 2H2O(g) + O2(g)	-68.36	1510	**53.8%**
		450	2HI → I2(g) + H2(g)	23.59	0.019770129	
		120	I2 + SO2(a) + 2H2O → 2HI(a) + H2SO4(a)	-36.79	77134	
8	Ispra Mark 7B	1000	2Fe2O3 + 6Cl2(g) → 4FeCl3 + 3O2(g)	141.87	1.513E-06	**51.6%**
		420	2FeCl3 → Cl2(g) + 2FeCl2	48.63	0.001771369	
		650	3FeCl2 + 4H2O → Fe3O4 + 6HCl + H2(g)	23.90	0.01580	
		350	4Fe3O4 + O2(g) → 6Fe2O3	-39.37	1135	
		400	4HCl + O2(g) → 2Cl2(g) + 2H2O	-76.64	2657047.645	

Thermodynamic Results

Cycle	Name	Temperature	Reaction	Δ G	K	Efficiency
9	UT-3 Univ. Tokyo	600	2Br2(g) + 2CaO → 2CaBr2 + O2(g)	101.8900379	6.28583E-06	**47.6%**
		600	3FeBr2 + 4H2O → Fe3O4 + 6HBr + H2(g)	-37.95	186.28	
		750	CaBr2 + H2O → CaO + 2HBr	-95.07	461816604	
		300	Fe3O4 + 8HBr → Br2 + 3FeBr2 + 4H2O	122.93	4.42731E-08	
10	Ispra Mark 13	850	2H2SO4(g) → 2SO2(g) + 2H2O(g) + O2(g)	-68.36	1510	**46.6%**
		77	2HBr(a) → Br2(a) + H2(g)	-125.55	5.36365E+18	
		77	Br2 (l) + SO2(g) + 2H2O(l) → 2HBr(g) + H2SO4(a)	169.78	4.71168E-26	
11	Ispra Mark 9	420	2FeCl3 → Cl2(g) + 2FeCl2	48.63	0.001771	**44.2%**
		150	3Cl2(g) + 2Fe3O4 + 12HCl → 6FeCl3+6H2O+O2(g)	23.90	0.015799	
		650	3FeCl2 + 4H2O → Fe3O4 + 6HCl + H2(g)	-19.98	292.2	
12	GA Cycle 23	800	H2S(g) → S(g) + H2(g)	-136.71	2279787.497	**36.0%**
		850	2H2SO4(g) → 2SO2(g) + 2H2O(g) + O2(g)	189.21	6.178E-10	
		700	3S + 2H2O(g) → 2H2S(g) + SO2(g)	-230.20	2.270E+12	
		25	3SO2(g) + 2H2O(l) → 2H2SO4(a) + S	-290.18	6.86346E+50	
		25	S(g) + O2(g) → SO2(g)	-300.12	3.78213E+52	
13	Mark 7A	420	2FeCl3(l) → Cl2(g) + 2FeCl2	47.29	0.01148	**30.2%**
		650	3FeCl2 + 4H2O(g) → Fe3O4 + 6HCl(g) + H2(g)	48.63	0.001771369	
		350	4Fe3O4 + O2(g) → 6Fe2O3	23.90	0.01580	
		1000	6Cl2(g) + 2Fe2O3 → 4FeCl3(g) + 3O2(g)	-76.64	2657047.645	
		120	Fe2O3 + 6HCl(a) → 2FeCl3(a) + 3H2O(l)	69.65	5.573E-10	

Summary of Results

- Positive Gibbs Energy prevents high conversion
  - Le Chatelier’s Principle

- Two cycles chosen for further investigation
  - Hallett Air Products: 99.7% 163 kJ/mol
  - Sulfur-Iodine: 53.8% 24 kJ/mol

Discussion of Results

- Thermodynamic analysis is not done until separation processes are included

- Ideal cycle
  - Best heat cascade efficiency
  - Most efficient separation process
  - Lowest total capital investment

What is Molecular Discovery?

- An algebraic model
  - A series of constraints solved by GAMS
  - Minimizes / Maximizes an objective function
  - Performs an exhaustive search within the molecular data entered
  - Can find undiscovered water splitting cycles

What is Molecular Discovery?

- Some constraints imposed are:
  - Acceptable Gibbs energy of reactions
  - Number of species per half reaction
  - Number of each individual species
  - Overall result of cycle splits water

Application to Water Splitting

- Minimize cost
  - Reduction of energy required to run cycle per mole of H_2 produced
    - Hot utility requirement (heat cascade analysis)
    - Objective function can find a minimum hot utility requirement

Original Model by Holiastos and Manousiouthakis

- Temperature range is specified
  - Only searches for solutions within this range
- Objective function is arbitrary
  - Minimized number of chemical species in reaction set
- Gibbs energy calculations based on linear estimate

Modifications Made to Original

- More meaningful objective function
  - Minimizes hot utility requirement of heat cascade analysis
    - HU corresponds to operating costs
- Thermodynamics based on Shomate equation
  - Includes Gibbs energy for reactions

Model Setup Conditions

- Temperature range of 400K – 1400K
- One to four chemical species allowed per side of reaction
- A maximum of four of any one species per reaction

Model Setup Conditions

GAMS#	Species	GAMS#	Species
i1	Acetylene	i25	Potassium Peroxide
i2	1,1 Dichloroethane	i26	Copper(I) Oxide
i3	1,1,1-Trichloroethane	i27	Copper(II) Oxide
i4	Chloroethene	i28	Copper(II) Chloride
i5	Chloroethane	i29	Bromine Chloride
i6	Ethanol	i30	Dichloroethyne
i7	Carbon Monoxide	i31	Ketene
i8	Carbon Dioxide	i32	Bromoethene
i9	Chlorine	i33	Ethene
i10	Tetrachloroethene	i34	Bromoethane
i11	Hydrogen	i35	Ethane
i12	Water	i36	Ethylamine
i13	Oxygen	i37	Acetone
i14	Bromine	i38	Propane
i15	Hydrogen Bromide	i39	Formaldehyde
i16	Hydrogen Chloride	i40	Bromomethane
i17	Hydrogen Iodide	i41	Chloromethane
i18	Hydrogen Sulfide	i42	Methylamine
i19	Sulfur Dioxide	i43	Nitromethane
i20	Sulfuric Acid	i44	Methylnitrate
i21	Calcium Oxide	i45	Methanol
i22	Iron(II) Oxide	i46	Methane
i23	Iron(II) Sulfate	i47	Hydrogen Peroxide
i24	Iron(III) Oxide		

Current Results

$$\tfrac{1}{2}C_3H_6O \rightarrow \tfrac{1}{2}C_2H_2 + H_2 + \tfrac{1}{2}CO \qquad (1400K)$$

$$\tfrac{1}{2}C_2H_2 + H_2O + \tfrac{1}{2}CO \rightarrow \tfrac{1}{2}O_2 + \tfrac{1}{2}C_3H_6O \qquad (400K)$$

- Gibbs energies of reactions 1 and 2 are 9.33 kJ/mol and 18.9 kJ/mol respectively
- Heats of reactions 1 and 2 are 416 kJ/mol and 14.8 kJ/mol respectively
- Hot utility requirement is 414 kJ/mol H_2
- Cascade efficiency is 70.0%

Discussion / Limitations

- Only two reactions per set
- Cannot account for phase changes
  - Except water
  - Limits temperature range / species
- Reaction temperatures are specified by the user
- Reactions discovered might not really occur as written and therefore need further analysis
  - Side reactions, catalysts, etc… need to be considered

Future Work

- Automatic selection of applicable Shomate constants for a chemical species according to temperature
  - This will extend the temperature range that can be searched (allows for phase changes of species)
- Give list of top results
- Explore possibility of three reaction sets
- Exhaustive search of temperature range settings
  - Using a control loop

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8 Plant Design Analysis

- **Hallett Air Products**
- **Sulphur-Iodine**

9 Conclusions

Hallett Air Products

- Plant cost for daily production of 500 tonnes/day
  - $1.1 Billion Total Capital Investment
- Energy Costs
  - 14 kWh (t)/kg of H_2 produced
  - 38.7 kWh (e)/kg
- Cost of Hydrogen
  - $2.03/kg
- Selling Price of Hydrogen
  - $4.75/kg

Fabricated Equipment	
Electrolyzer	$143,000,000
Absorber Tower	$2,802,800
Heat Exchangers	$657,800
Distribution Pipes	$335,000,000
Reactor	$2,255,100
Total Fabricated Equipment:	$483,715,700
Process Machinery	
Pump	$1,287,000
Total Process Machinery:	$1,287,000
Storage	
Hydrogen Storage Tanks	$272,000,000
Total Storage:	$272,000,000

Sulfur-Iodine

- Plant cost for daily production of 500 tonnes/day
  - $1.5 Billion Total Capital Investment
- Energy Costs
  - 75.7 kWh (t)/kg of H_2 produced
- Cost of Hydrogen
  - $1.60/kg
- Selling Price of Hydrogen
  - $4.75/kg

Fabricated Equipment		
	Reactor	$429,000,000
	Distribution Pipes	$335,000,000
	Total Fabricated Equipment:	$764,000,000
Storage		
	Storage Tanks	$272,000,000
	Total Storage:	$272,000,000

Profitability

Hallett Air Product Cycle with Transportation & Storage

The Investor's Rate of Return (IRR) for this Project is: **10.28%**

The Net Present Value (NPV) at 10% for this Project is: **$ 30,605,100.00**

ROI Analysis (Third Production Year)

Annual Sales:	$390,270,200
Annual Costs:	-367,963,000.00
Depreciation:	-78,607,200.00
Income Tax:	$20,831,000
Net Earnings:	$43,138,200
Total Capital Investment:	$1,107,337,800
ROI:	**3.90%**

Profitability

Sulphur Iodine Cycle with Transportation & Storage

The Investor's Rate of Return (IRR) for this Project is:	**8.26%**
The Net Present Value (NPV) at 10% for this Project is:	**-247,152,500.00**

ROI Analysis (Third Production Year)

Annual Sales:	390,270,200.00
Annual Costs:	-388,301,600.00
Depreciation:	-107,578,200.00
Income Tax:	39,075,600.00
Net Earnings:	41,044,200.00
Total Capital Investment:	1,512,901,900.00
ROI:	**2.70%**

Conclusions

The economic analysis is based an “existing hydrogen economy.”

- Hallett Air Product
  - Low capital investment
  - High profitability
  - Lower thermal efficiency
- Sulfur-Iodine
  - High capital investment
  - Better thermal efficiency
  - Low profitability

Based on this we recommend the Hallett Air over the sulfur-iodine cycle

Recommended Future Studies

Investigate

- "Hydrogen Economy" startup planning
- Westinghouse difficulties can be overcome
- Transportation of Hydrogen
  - Trailers
    - Number of Hydrogen Stations
  - Railway
- Further study with Molecular Discovery using extended databases

Thank you for your attention!

Contact:
John.A.Coppock-1@ou.edu
prgerber@ou.edu
cramos@ou.edu
Nicholas.M.Anderson-1@ou.edu