Technologies for Hydrogen Economy

A Seminar Presented at

Department of Energy Science and Engineering
Indian Institute of Technology Bombay

April 6, 2016

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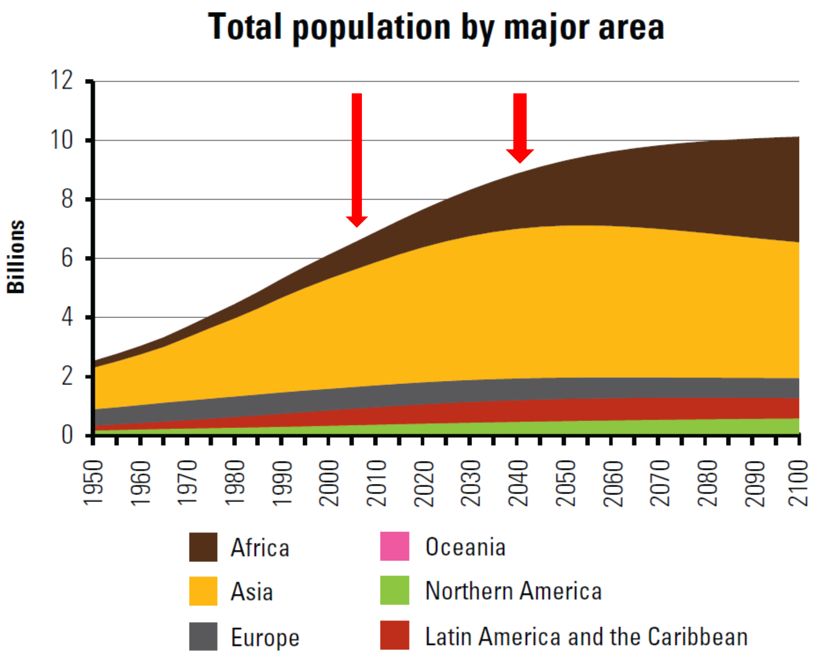
Outline

- The World Energy Picture and Issues
- Hydrogen Economy
- Challenges and Opportunities
- Hydrogen Production
  - Photolysis H_2
  - Bio-catalysts H2
  - Thermochemical H2
- Hydrogen Storage
  - Chemical Storage
- Hydrogen Conversion
- Conclusions

Humanity's Top Ten Problems for next 50 years

1. ENERGY
2. WATER
3. FOOD
4. ENVIRONMENT
5. POVERTY
6. TERRORISM & WAR
7. DISEASE
8. EDUCATION
9. DEMOCRACY
10. POPULATION

*Source: **R. E. Smalley**, Rice University, 2004,Presented at Purdue University*



2012	**7**	**Billion People**
2050	**8-10**	**Billion People**

Source: United Nations, Department of Economic and Social Affairs, Population Division (2011): World Population Prospects, the 2010 Revision. New York

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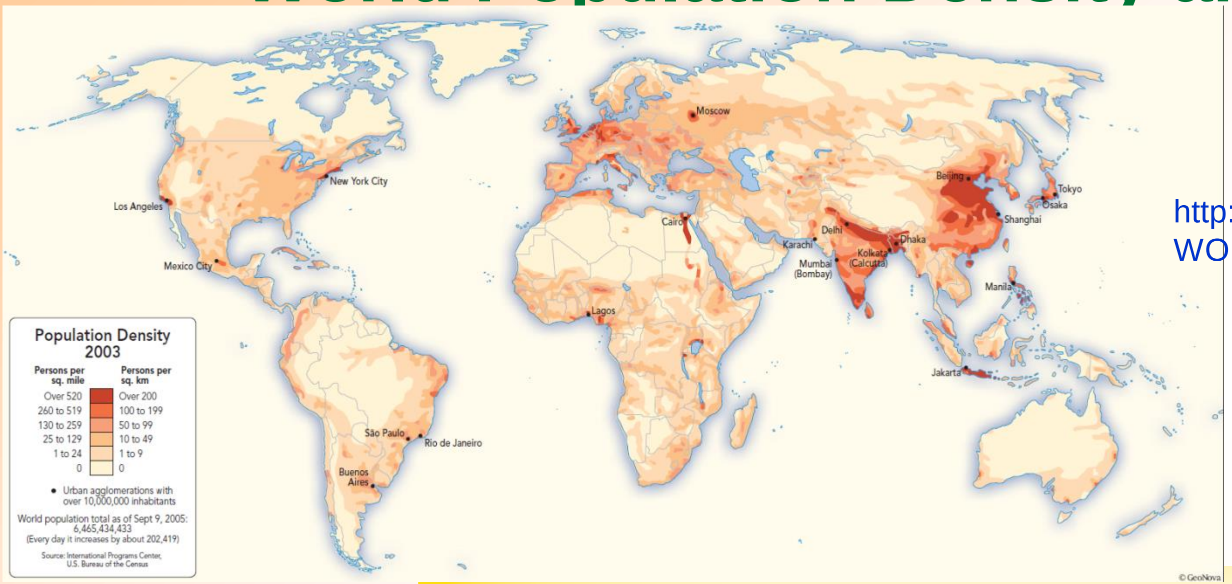
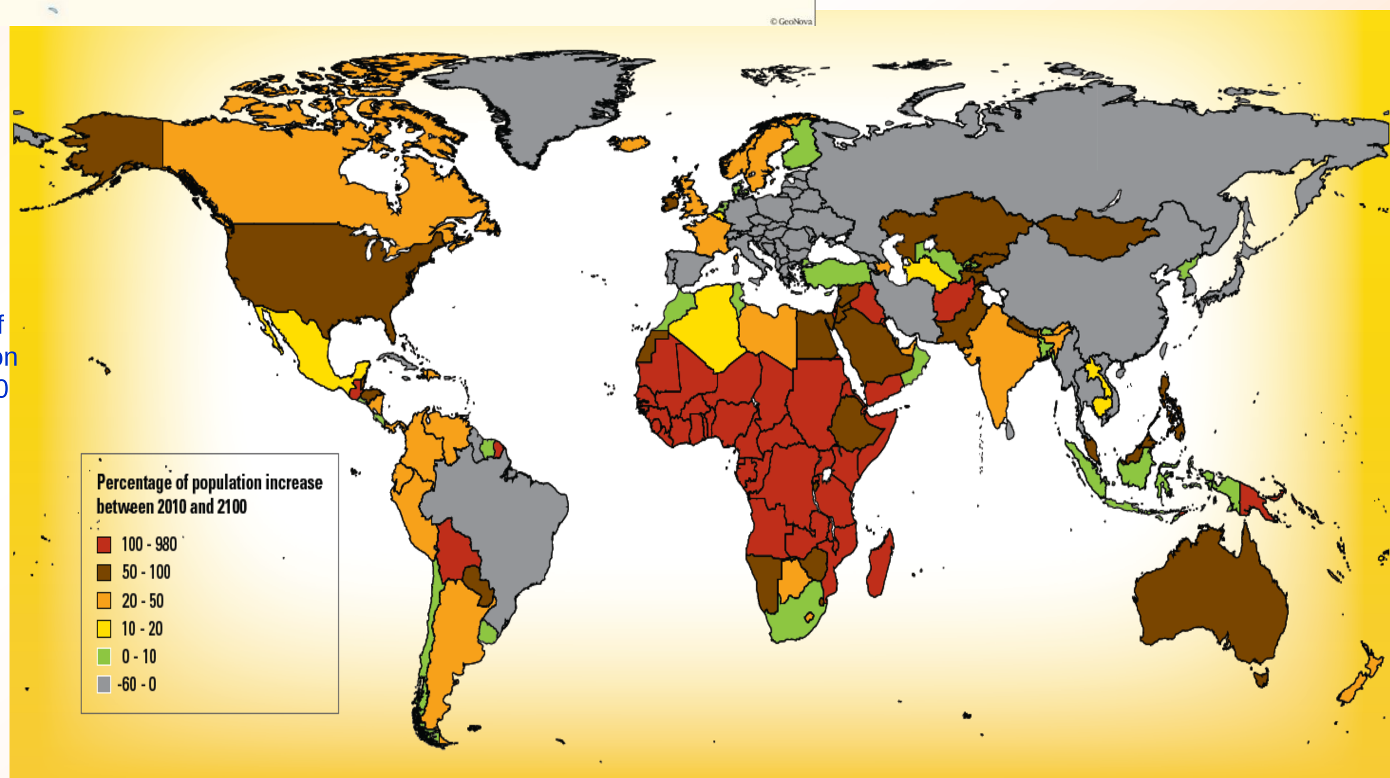
World Population Density and Growth

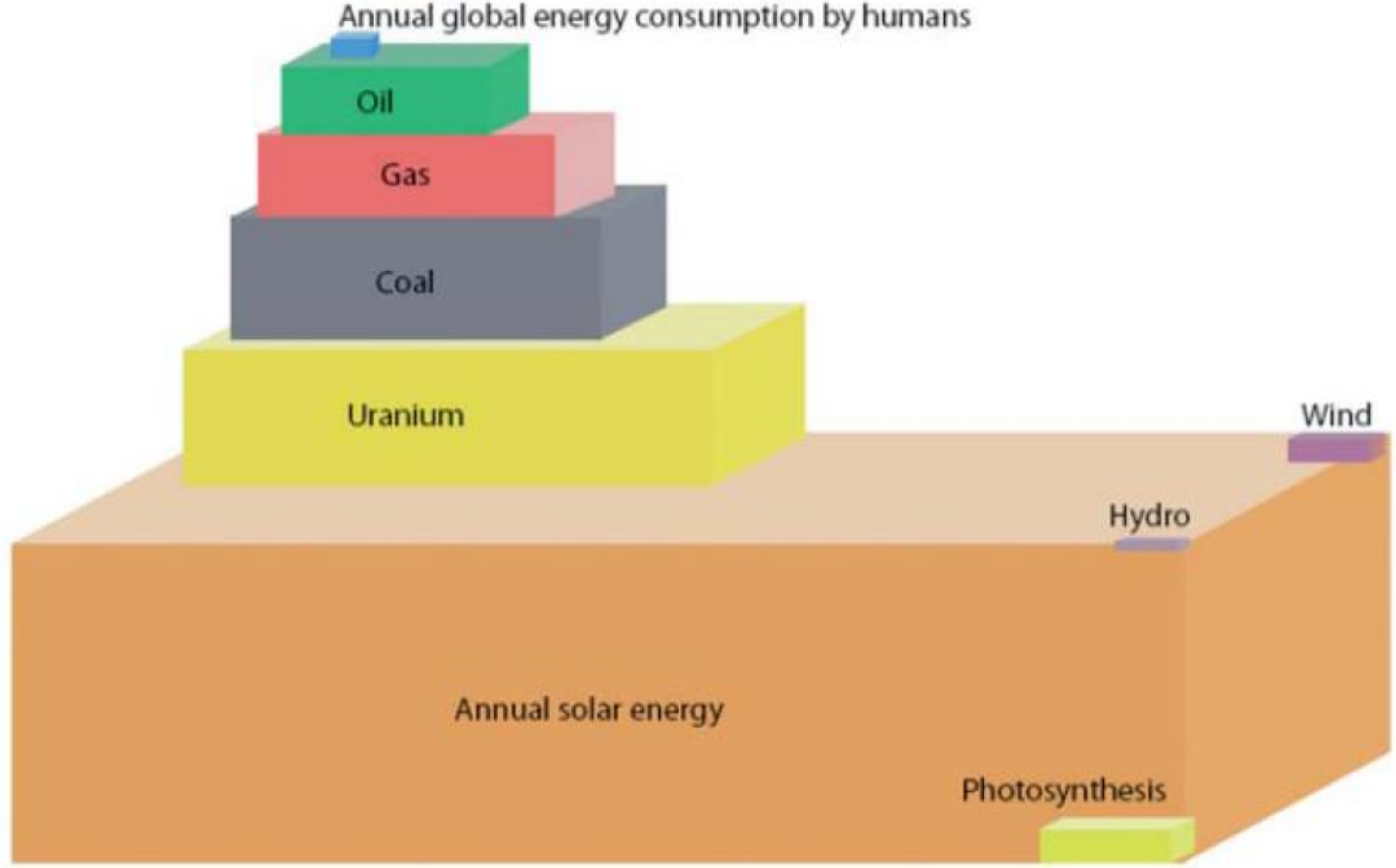


http://static.ddmcdn.com/gif/maps/pdf/WOR_THEM_PopDensity.pdf

Source: United Nations, Department of Economic and Social Affairs, Population Division (2011). World Population 2010 (Wall Chart). ST/ESA/SER.A/307.



Global Energy Resources

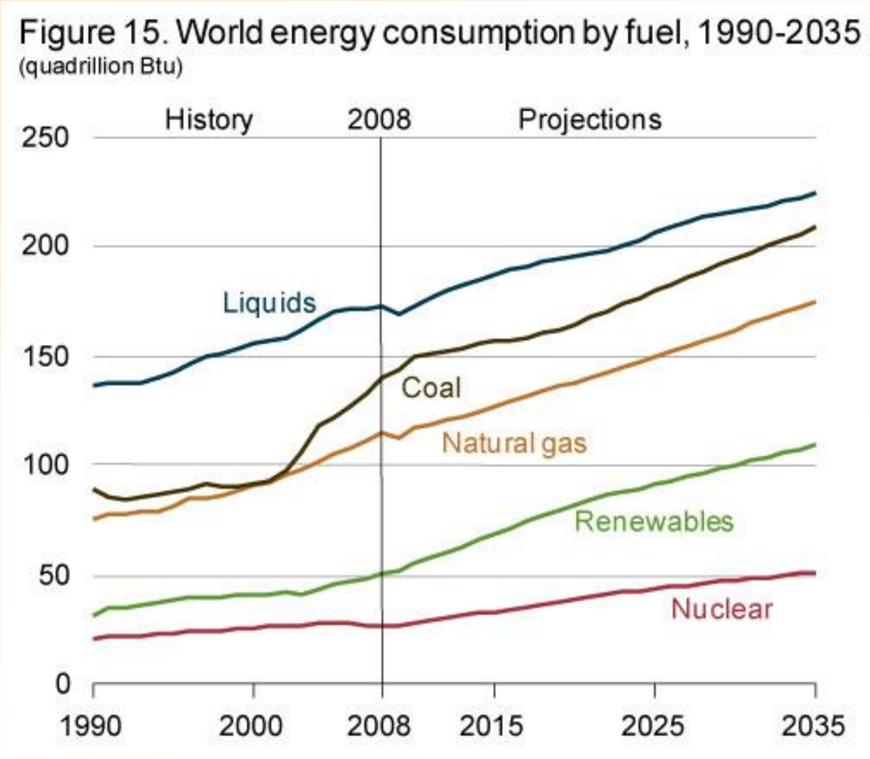


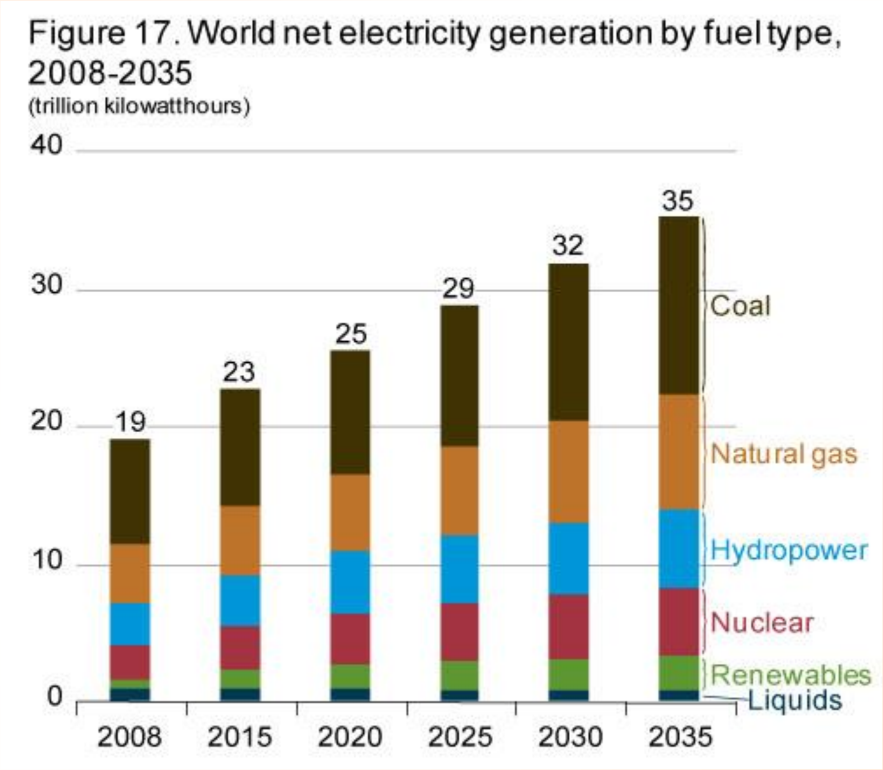
Graph 1 - Theorical Potential conventional and non-renewable energies reserves[5]

Source: National Petroleum Council, 2007 after Craig, Cunningham and Saigo

World Primary Energy Consumption by Fuel Type

Quadraillion BtU





Quadrillion BtU (10^{15} BTU), = Exajoule (1.055×10^{18} J)

Source: Energy Information Administration / Annual Energy Outlook 2008

Energy Supplies –Demand, Oil Example

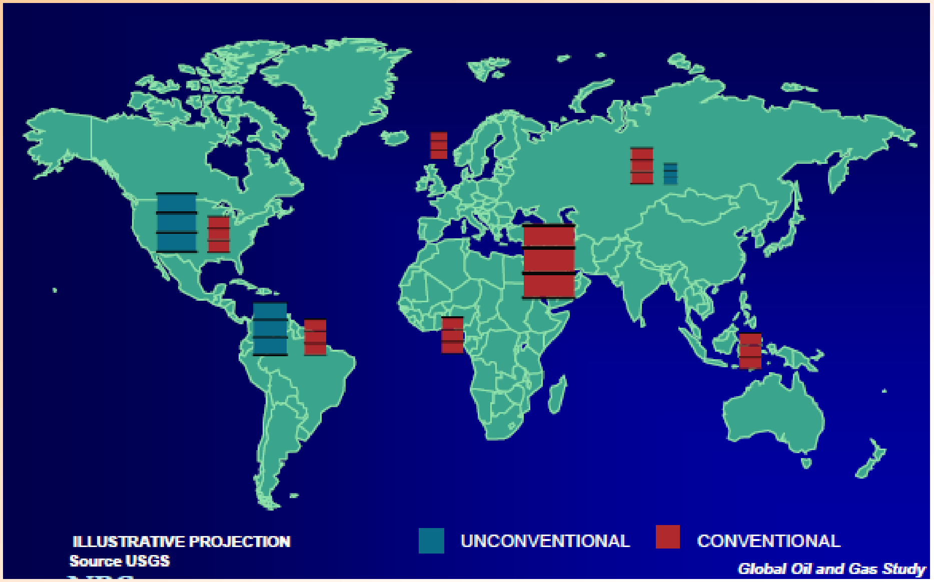
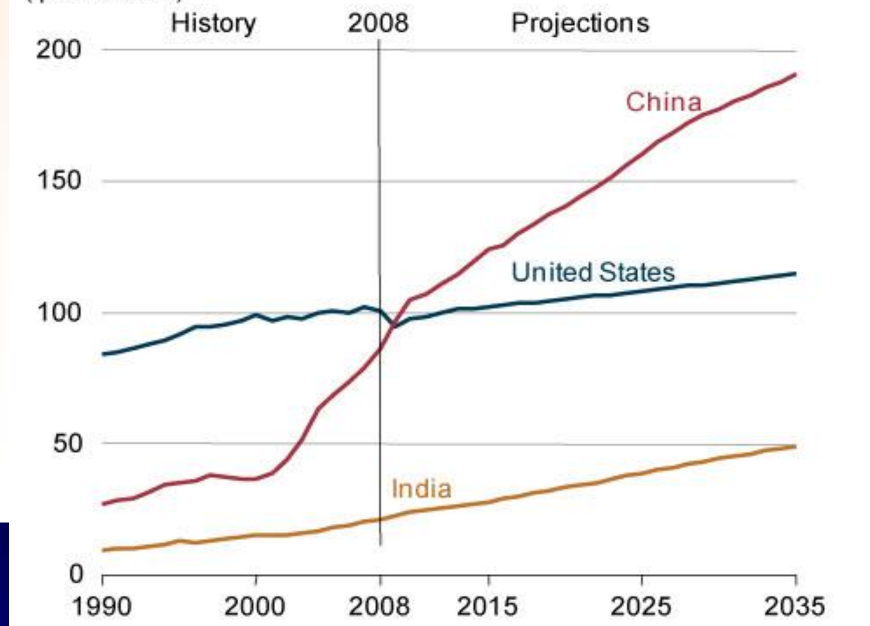
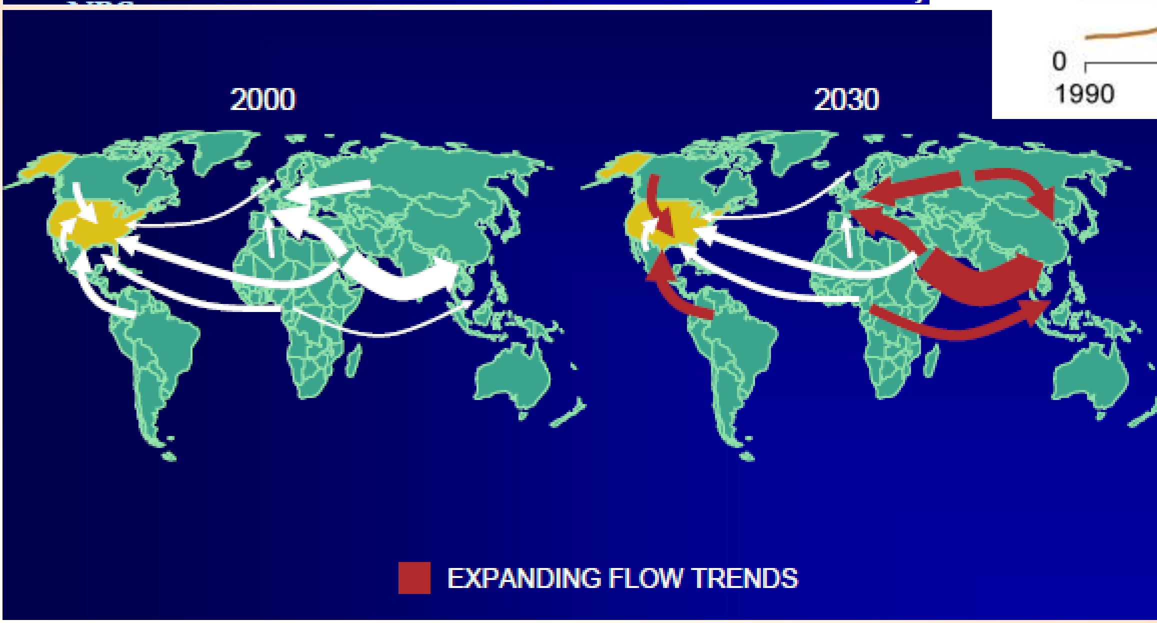


Figure 13. Energy consumption in the United States, China, and India, 1990-2035
(quadrillion Btu)

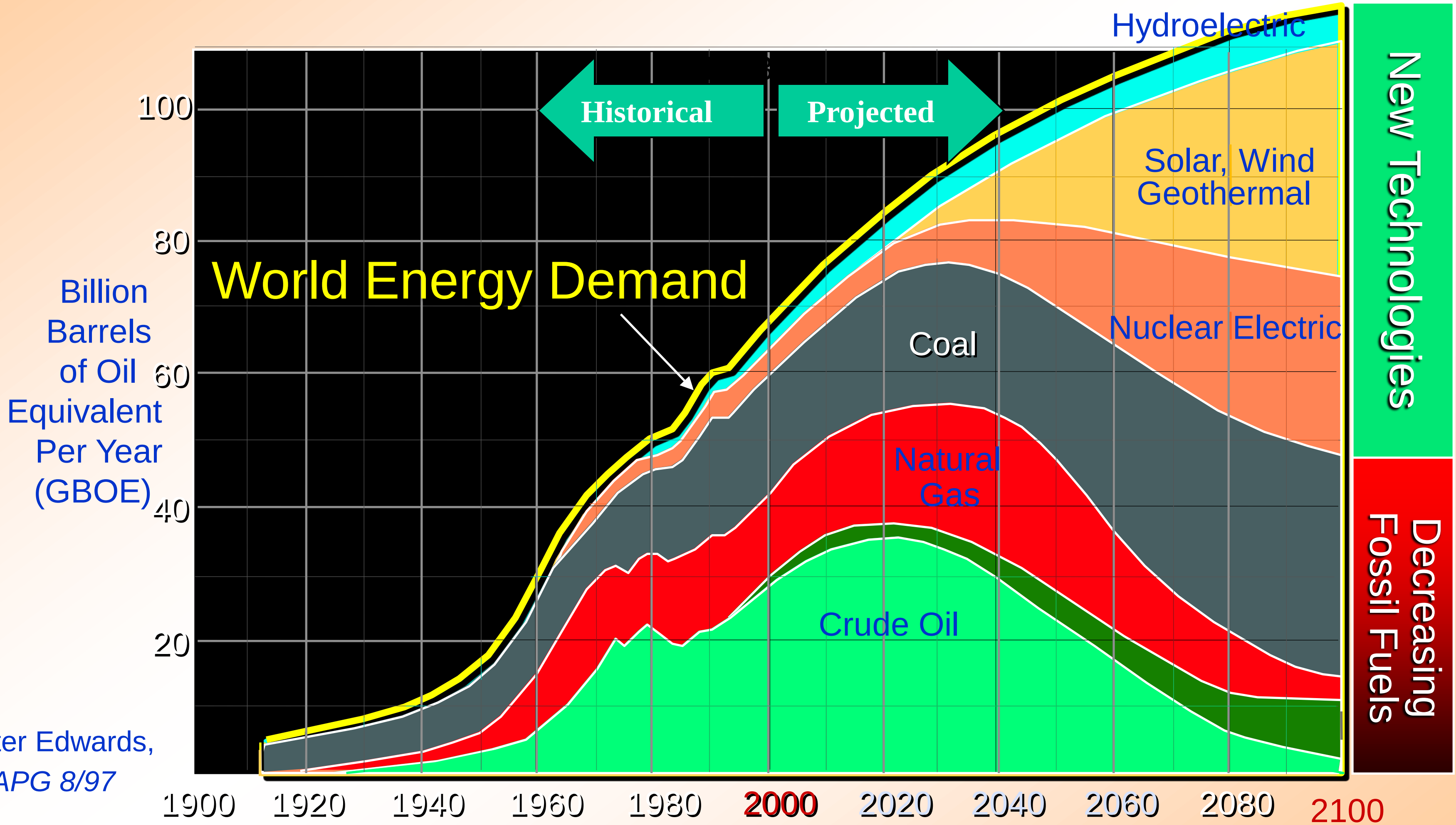


Source: Energy Information Administration / Annual Energy Outlook 2008



Source: National Petroleum Council 2007

World Energy Supplies: One Vision



after Edwards, *AAPG 8/97*

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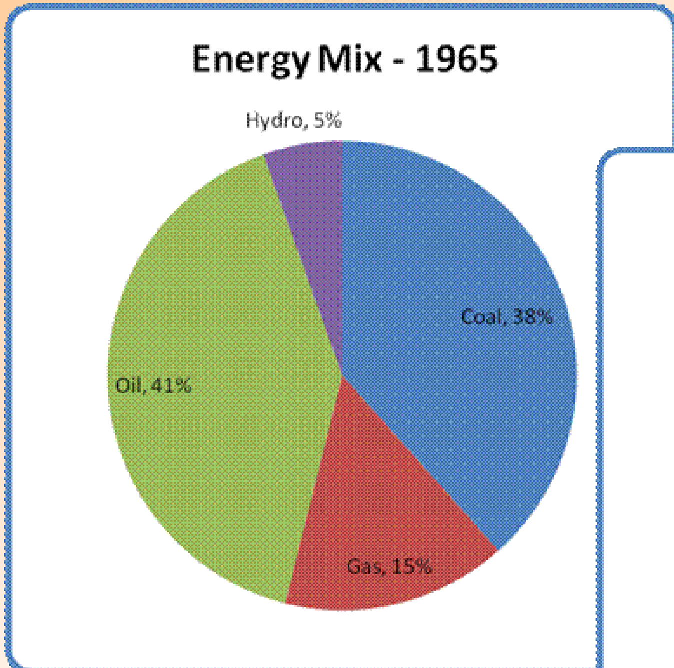
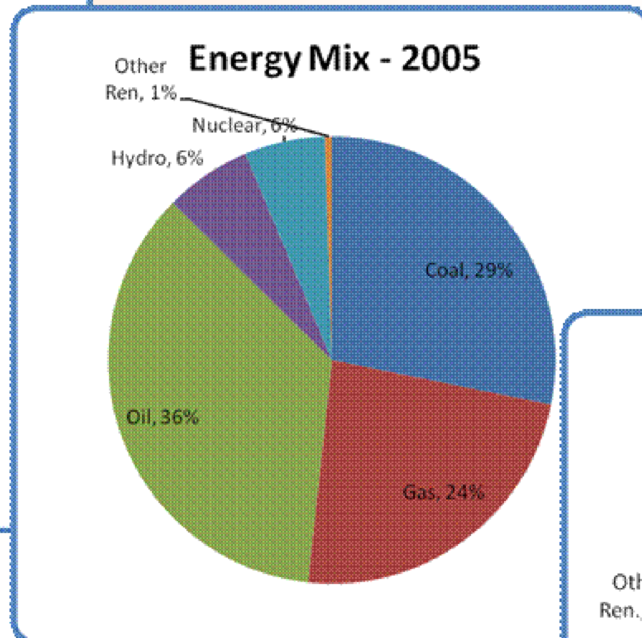
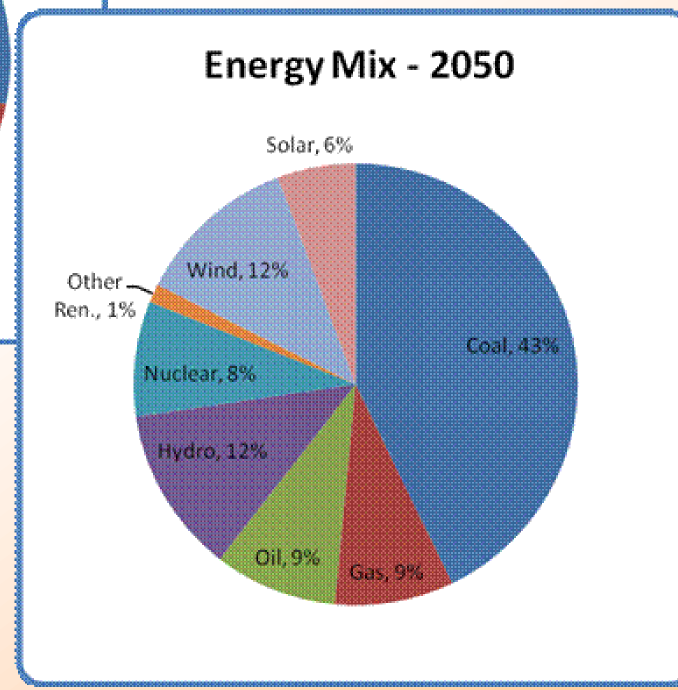
World Primary Energy Consumption by Fuel Type

Quadraillion BtU

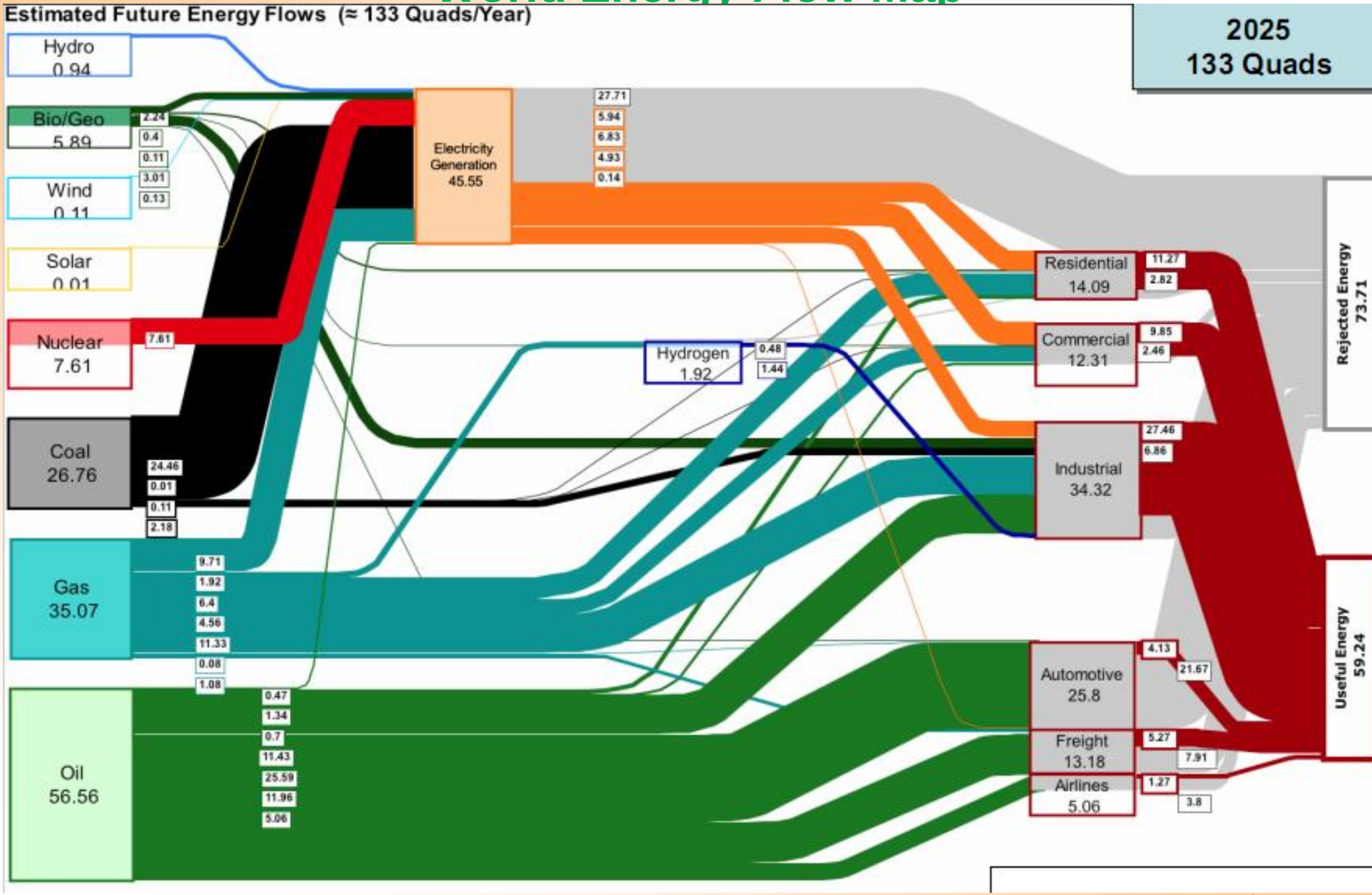






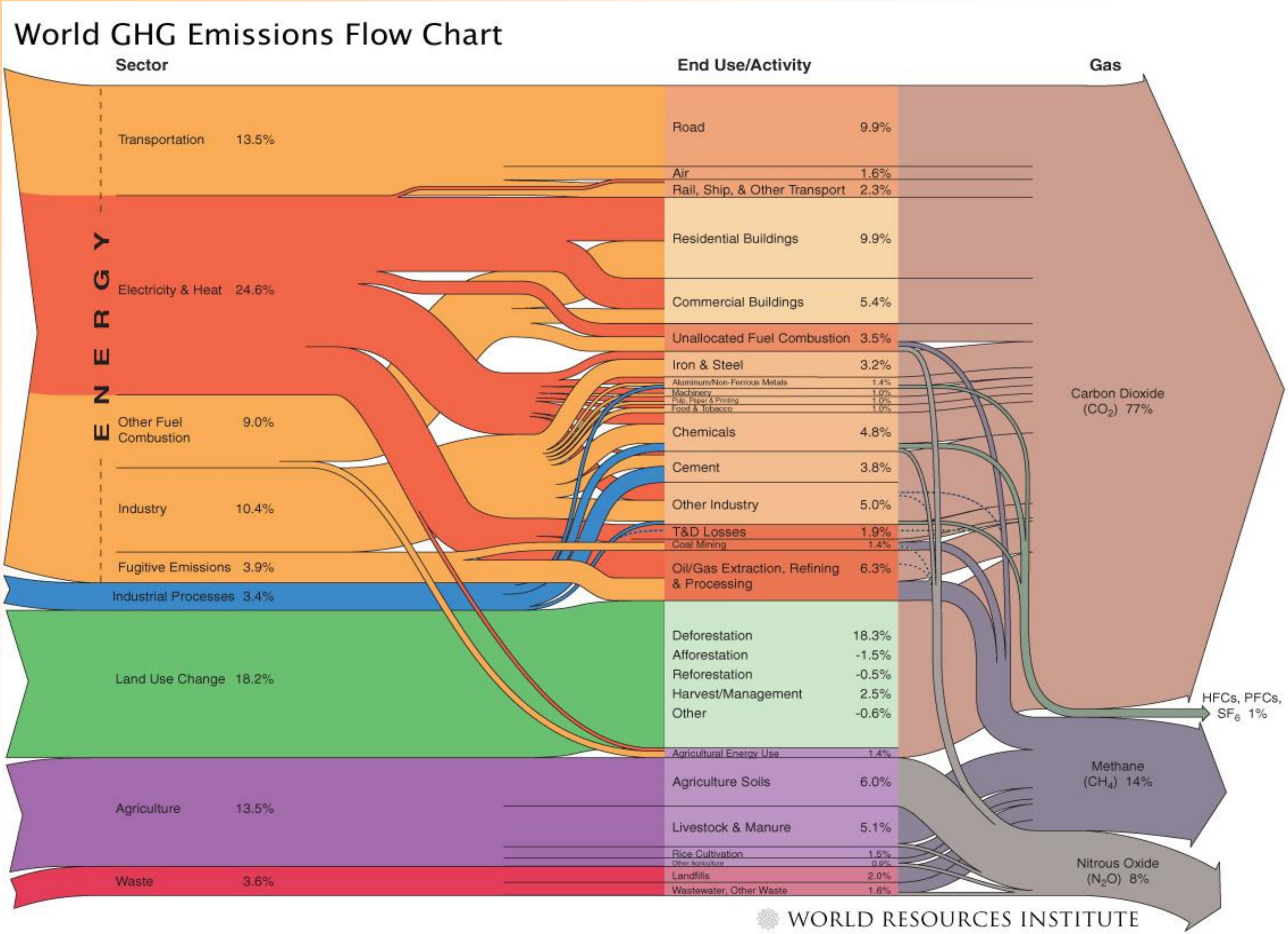
Source: Energy Information Administration / Annual Energy Outlook 2010

World Energy Flow Map



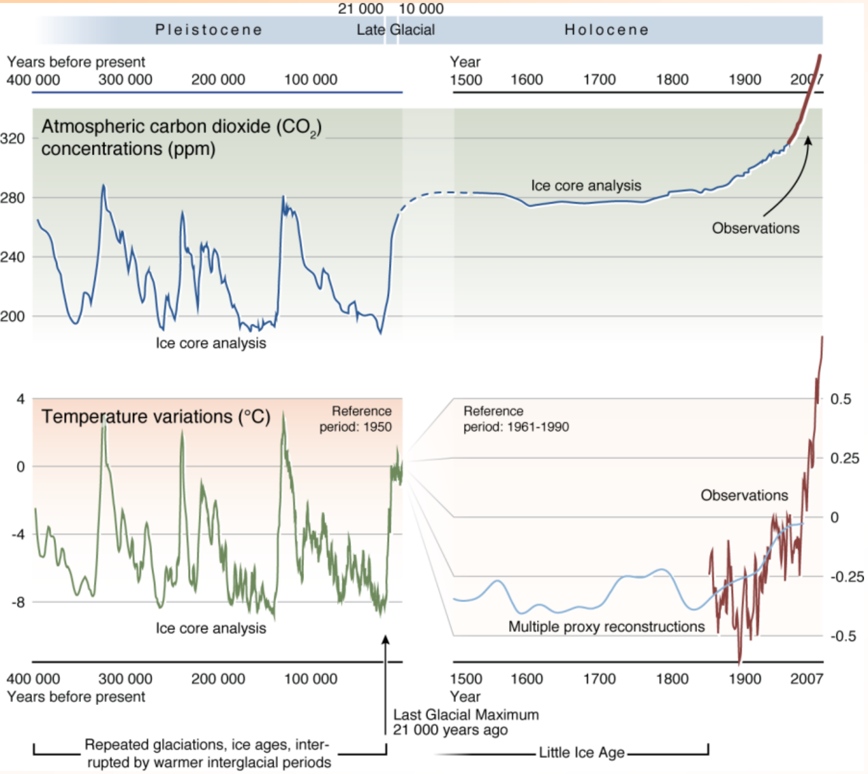
Source: EIA, International Energy Outlook 2010

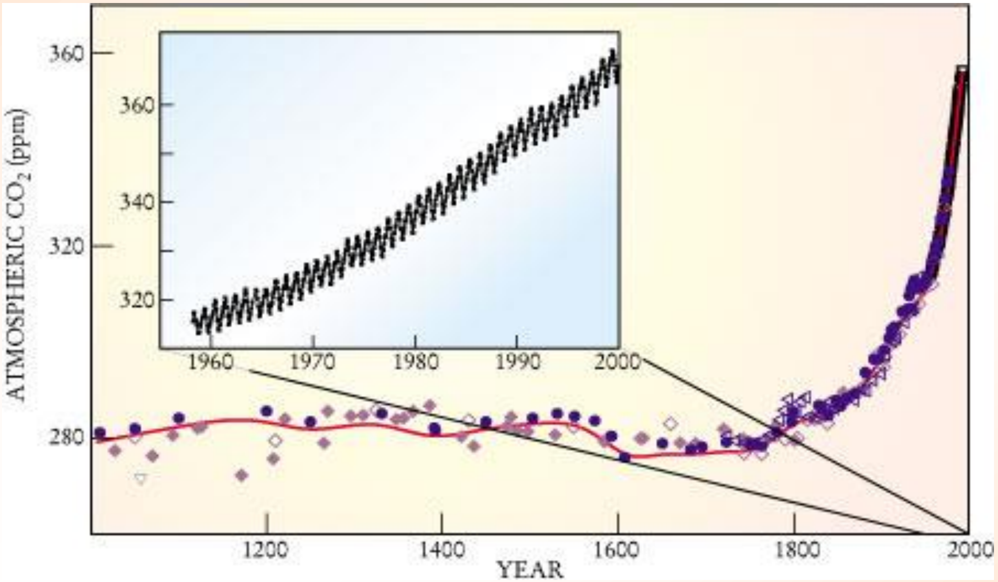
World Green House Gas Emissions

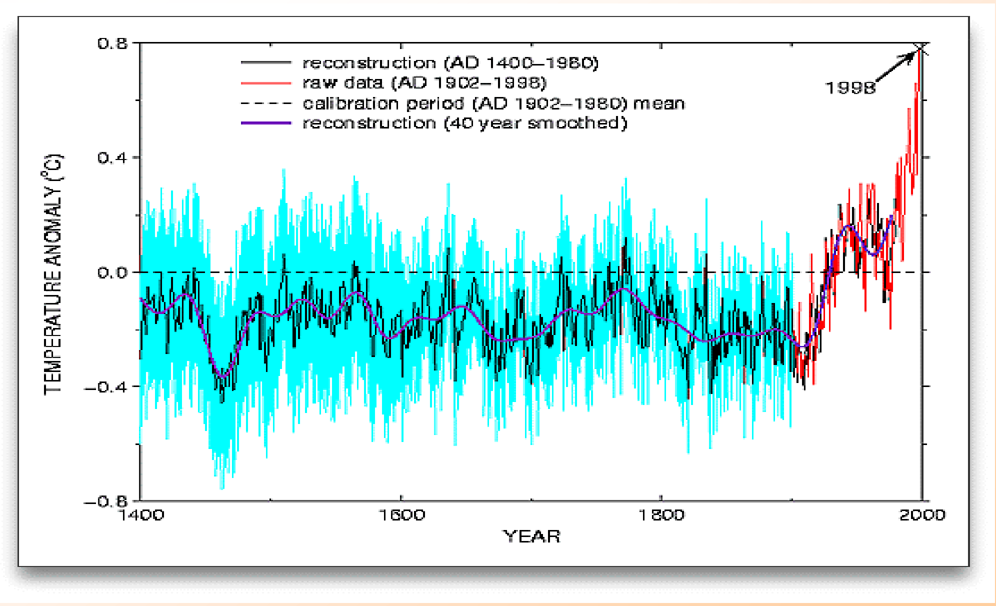


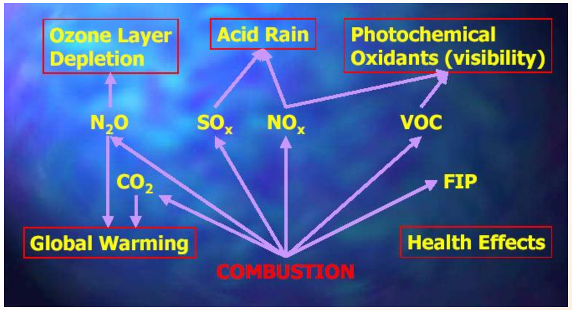
Environmental Issues

- CO_2 Buildup
- Global Temperature
- Pollution









Hydrogen as Energy Carrier

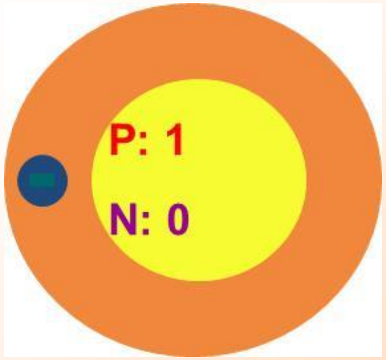
Best investment potential in terms of

Reduced Emission Carbon Free Cycle	Energy Diversification Different Sources	Expands domestic sources Energy Security

- Petroleum diesel
- Gasoline
- Biodiesel
- Ethanol
- Hydrogen
- Electrical

- But electricity is not suitable for all of our fuel requirements

Hydrogen (H_2)
Green Fuel



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Hydrogen as Energy Carrier

- **Why do we need it as an alternative fuel?**
  - Environment
    Global warming, local urban air quality
  - Energy reserves
    Increasing consumption vs. decreasing reserves
  - Global political
    Energy security and energy access, independency
  - Hydrogen value proposition
    New technology for transportation, clean conversion
- **H_2 Can be produced from**
  - Renewables –solar, wind, biomass, wave ←
  - Any fossil fuel
  - Nuclear energy ←

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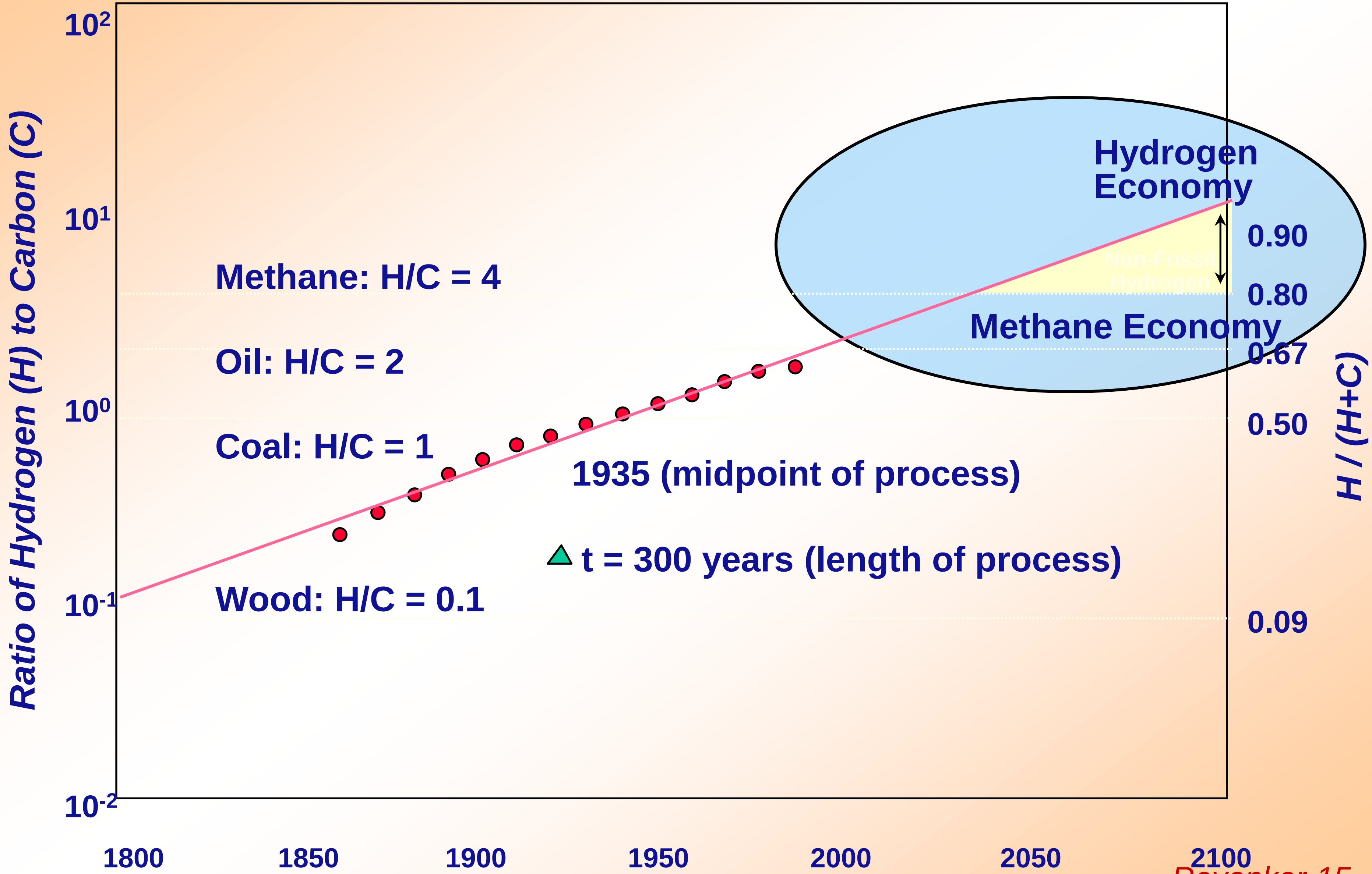
Ratio of hydrogen to carbon

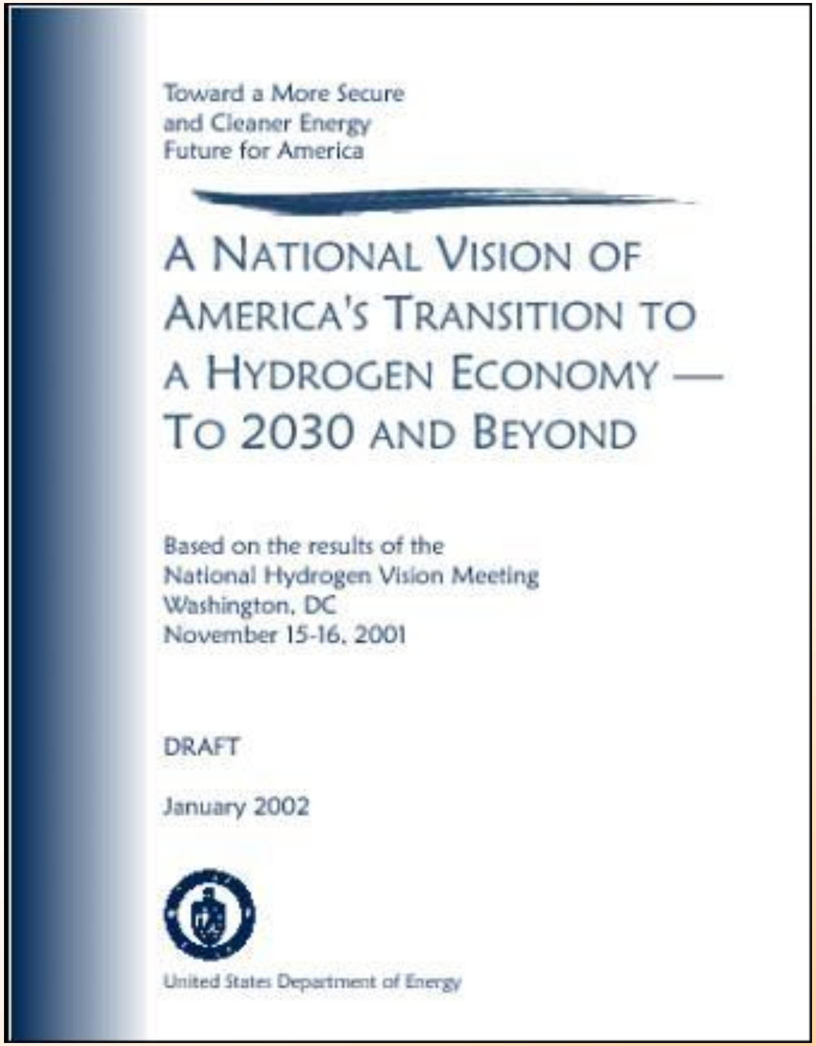


Source: IIASA, Nakicenovic

Vision for the Hydrogen Economy

"Hydrogen is America's clean energy choice. Hydrogen is flexible, affordable, safe, domestically produced, used in all sectors of the economy, and in all regions of the country."

Available at: www.eren.doe.gov/hydrogen/


Toward a More Secure and Cleaner Energy Future for America

A NATIONAL VISION OF AMERICA'S TRANSITION TO A HYDROGEN ECONOMY — TO 2030 AND BEYOND

Based on the results of the National Hydrogen Vision Meeting
Washington, DC
November 15-16, 2001

DRAFT

January 2002

United States Department of Energy

Characteristics of the H_2 Economy

- Buildings use hydrogen for heat and power
- Vehicles are powered by hydrogen and are integrated with the heat and power system for homes, offices, and factories
- Hydrogen is produced economically from sources that release no carbon dioxide
- The distribution infrastructure is well developed
- Storage and use of hydrogen is safe

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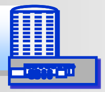
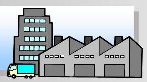
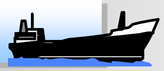
Challenges and Opportunities

Production	Delivery, Supply	Usage/Application

Solar / biomass 

Coal 

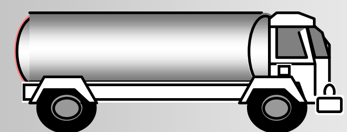
Petroleum 

Natural Gas 

Electricity 

Nuclear 

Hydrogenated compounds →



Hydrogen →

Issues (Production)
- Production
- Storage method
- CO_2 Stabilization
- Cost

Issues (Delivery, Supply)
- Transportation Method
- Infrastructure Development
- Codes & Standards
- Hydrogen Delivery Cost

Issues (Usage/Application)
- Stack Durability
- Power Density
- Freeze Start Capability
- Driving Range
- Vehicle Cost

Government, Energy Suppliers / **Car makers**

Hydrogen Production

- ✓ World Production 50 Million Tons/year
  - Equivalent to 2% of current world energy demand (if used in fuel cell)
  - 12 million tons of hydrogen are currently produced by US each year

- ✓ Hydrogen Sources
  - Natural Gas Reforming (over 80%)

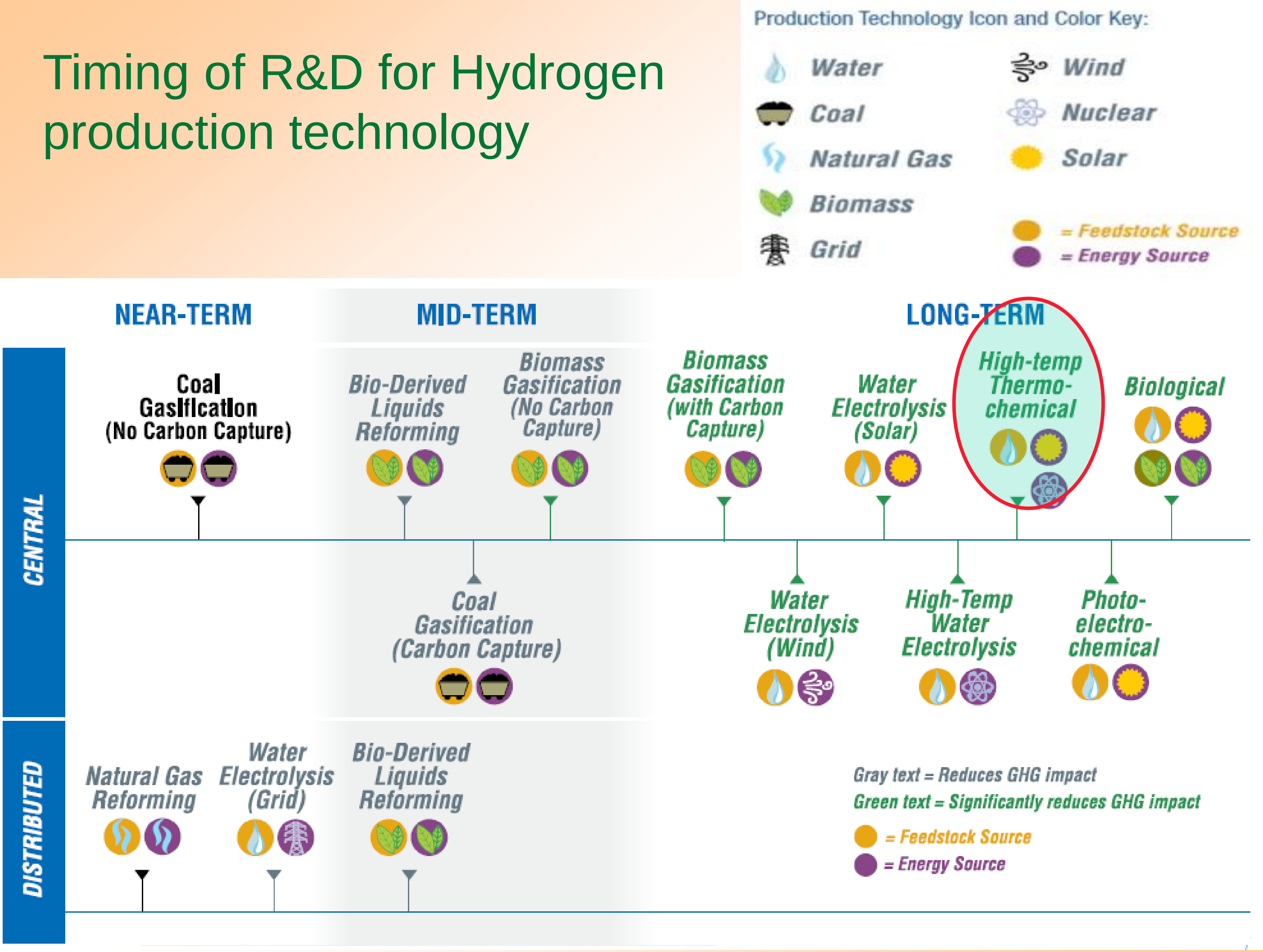
    $CH_4 + H_2O \rightarrow CO + 3H_2$ -Reformation

    $CO + H_2O \rightarrow CO_2 + H_2$ - Shift
  - By-Product Recovery (20%)
- ✓ About 95% is produced for use in
  - Ammonia
  - Oil Refining
  - Methanol

Hydrogen Production Methods

Method Of Hydrogen Production	Inefficiencies
Electrolysis	Requires electricity, expensive
Thermo-chemical water splitting	Requires outside energy and storage
Photolysis (photoelectrochemical processes)	sunlight as the input energy, storage,
Biological & photobiological (sunlight-assisted) water splitting	These methods are still in experimental stages
Thermal water splitting	organic compounds release pollutants into the earths atmosphere.
By-product of petroleum refining and chemical production	Detrimental environmental and health problems this process may cause.

Timing of R&D for Hydrogen production technology



Production: Challenges

✓

- Hydrogen production costs are high relative to conventional fuels (1 gallon Gasoline≡1 kg H_2)
- Current technologies produce large quantities of carbon dioxide and are not optimized for making hydrogen as an energy carrier.
- Advanced hydrogen production methods need development.
- Public-private production demonstrations are essential.

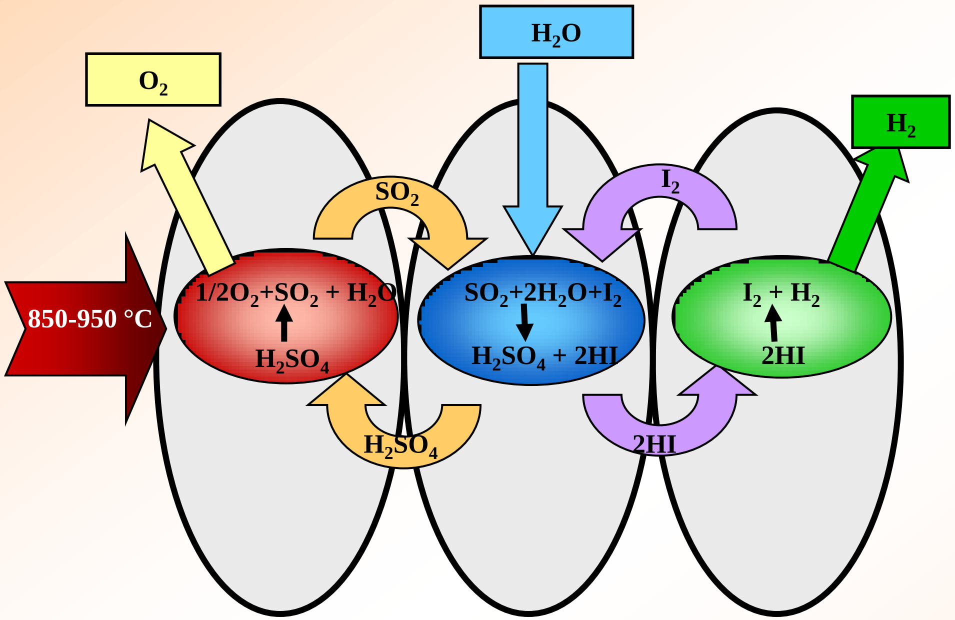
Production: Nuclear and Solar Hydrogen

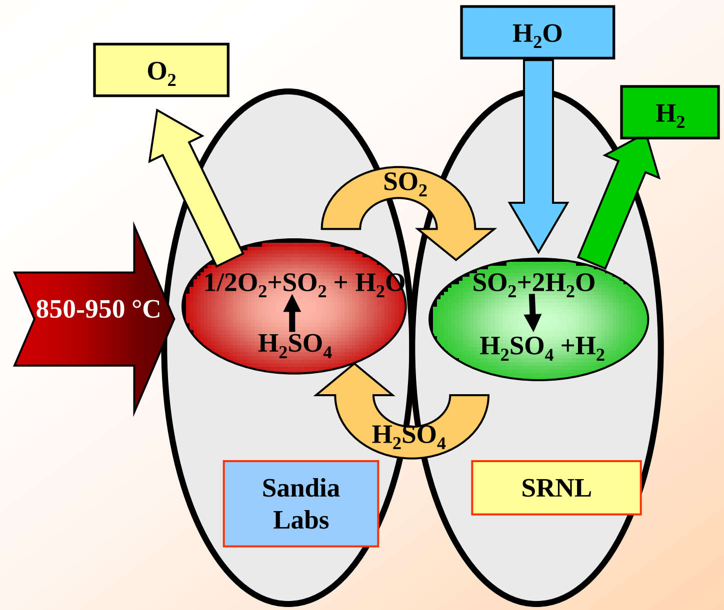
Scientific Challenges and Opportunities

- ✓ New materials for photo-catalysts Cost/efficiency (duty cycle) for solar thermo-chemical (TC)
- ✓ Separations and materials performance
- ✓ H_2 from direct thermolysis (>2500^{o}C) and radiolysis
- ✓ Thermodynamic data and modeling for TC
- ✓ High temperature materials in oxidizing environments at ~900^{o}C
  - Solid oxide materials and membranes
  - TC heat exchanger materials
- ✓ High temperature gas separation
- ✓ Improved catalysts for reactions

Nuclear Hydrogen Technology: Thermochemical Cycles (TC)

TC cycles require high temperatures, extensive thermal management, and cycle optimization





Sulfur Iodine

(1) $H_2SO_4 \rightarrow H_2O + SO_2 + 1/2O_2$

(2) $2HI \rightarrow I_2 + H_2$

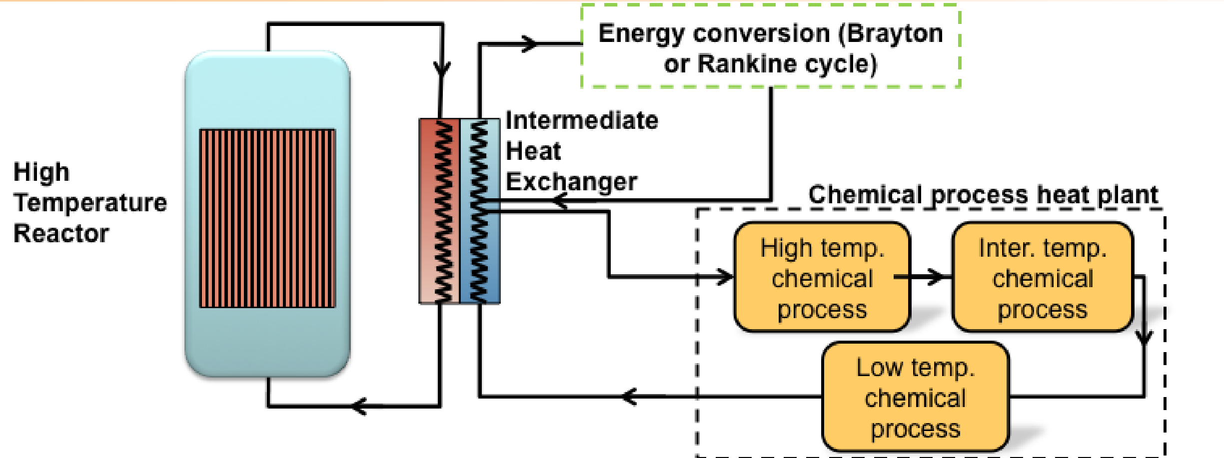
(3) $2H_2O + SO_2 + I_2 \rightarrow H_2SO_4 + 2HI$

Hybrid-Sulfur

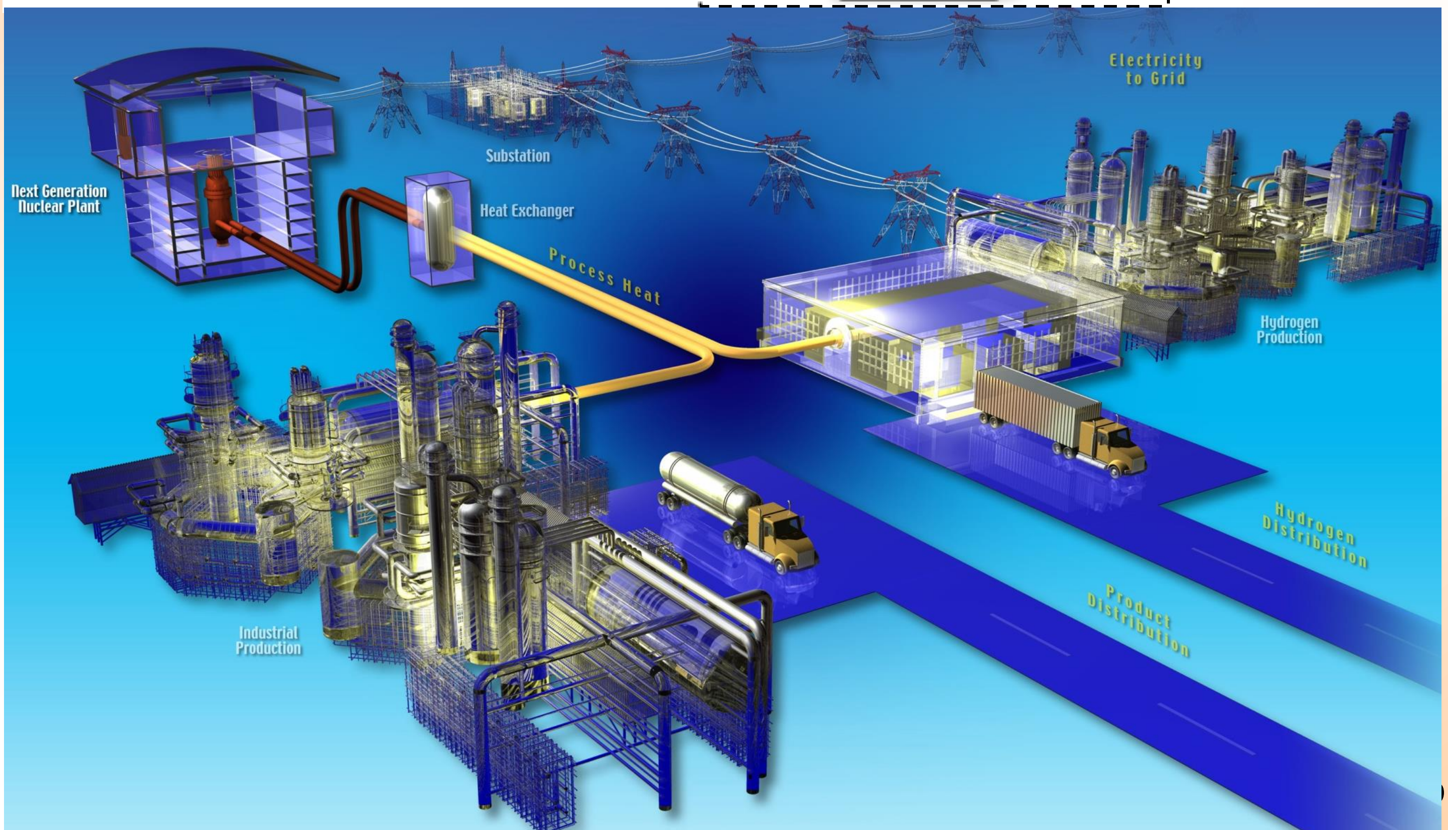
(1) $H_2SO_4 \rightarrow H_2O + SO_2 + 1/2O_2$

(2) $2H_2O + SO_2 \rightarrow H_2SO_4 + H_2$

Modeling Studies: Coupled H2-HTR System



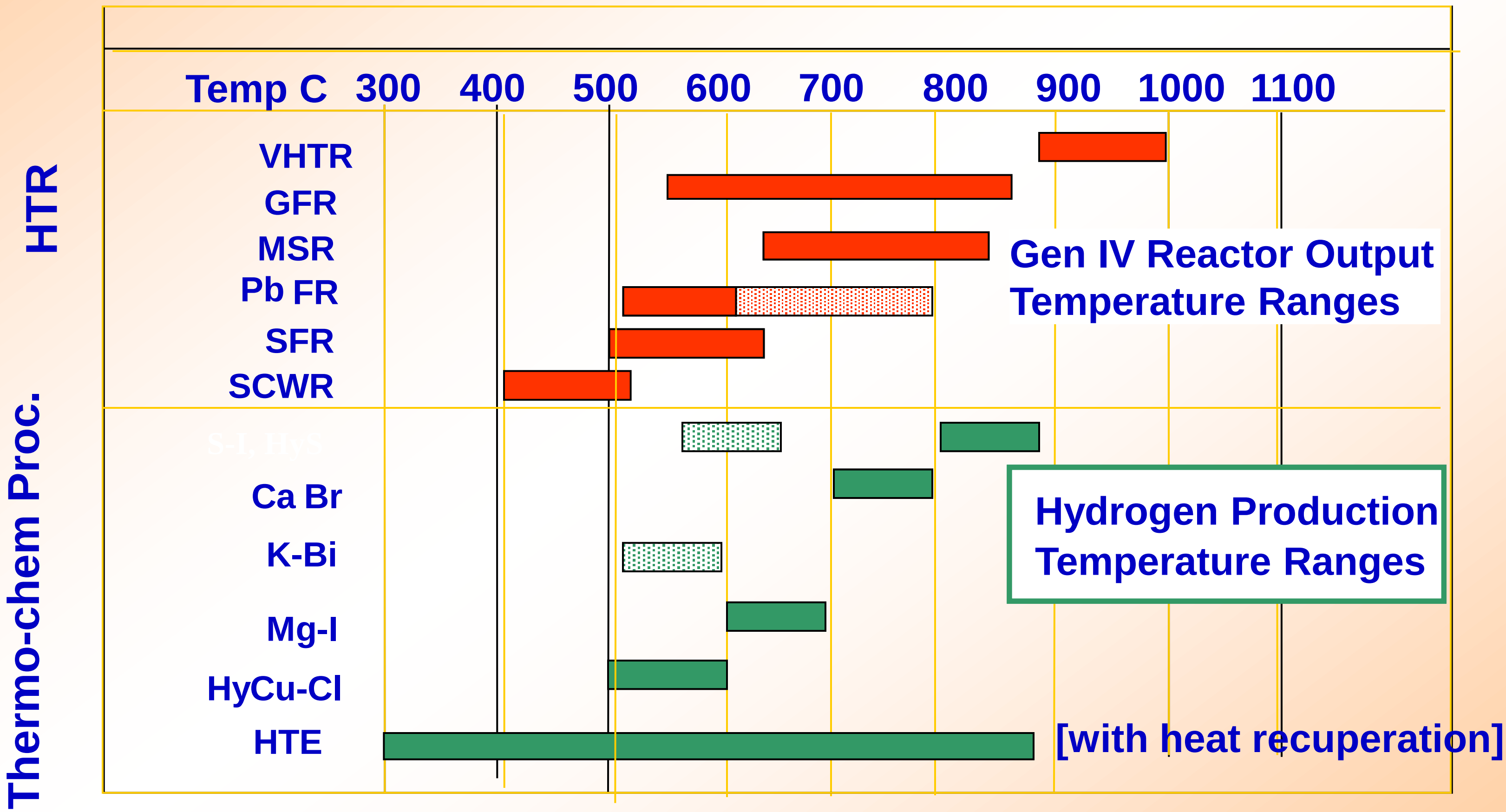
Generation IV Initiative and Nuclear Hydrogen Initiative

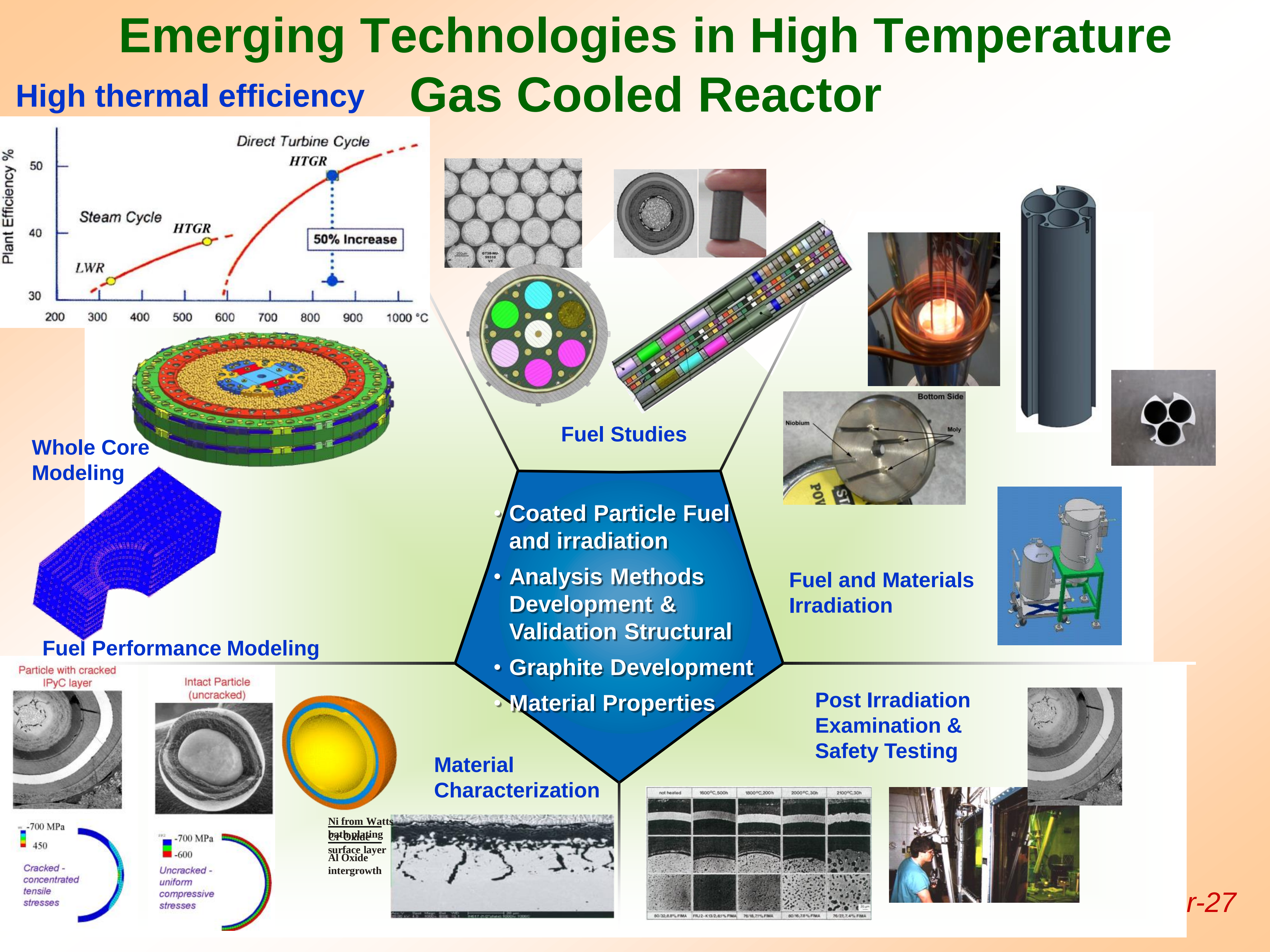


Use nuclear heat to drive highly endothermic chemical process plants

HTR Energy Conversion

- Electrical generation - ***Gen IV Energy Conversion Program***
- Hydrogen production - ***Nuclear Hydrogen Initiative (NHI)***

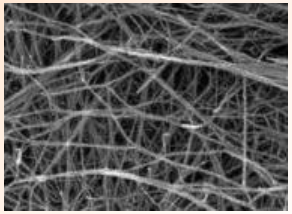


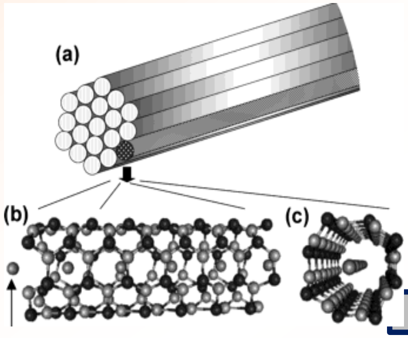

Emerging Technologies in High Temperature Gas Cooled Reactor
High thermal efficiency
Plant Efficiency %
Direct Turbine Cycle
HTGR
Steam Cycle
HTGR
LWR
50% Increase
50
40
30
200 300 400 500 600 700 800 900 1000 °C
Fuel Studies
Whole Core Modeling
Fuel Performance Modeling
Bottom Side
Niobium
Moly
Fuel and Materials Irradiation
• Coated Particle Fuel and irradiation
• Analysis Methods Development & Validation Structural
• Graphite Development
• Material Properties
Particle with cracked IPyC layer
Intact Particle (uncracked)
-700 MPa
450
Cracked - concentrated tensile stresses
-700 MPa
-600
Uncracked - uniform compressive stresses
Material Characterization
Ni from Watts bath plating
Cr Oxide
surface layer
Al Oxide
intergrowth
Post Irradiation Examination & Safety Testing
not heated
1600°C,500h
1800°C,200h
2000°C,30h
2100°C,30h

Emerging Technologies in Nuclear Hydrogen Generation

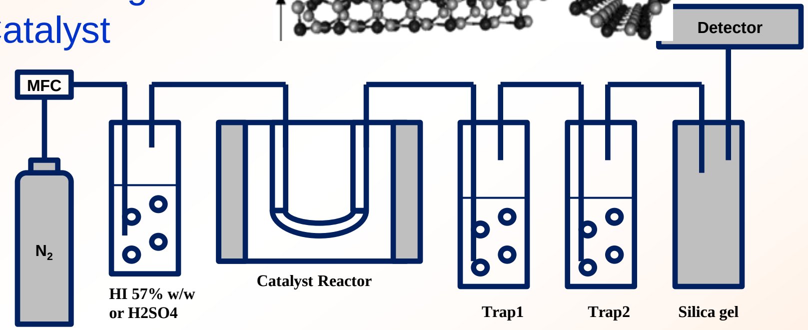
- New high temperature reactor systems
- Efficient and stable catalytic decomposition of HI and SO_3
- Develop flowsheet analysis of the SI cycle with advances techniques
- Develop models for coupled system VHTR and SI cycle H_2 plant,

- Catalyst development
  - Design catalytic reaction conditions
  - Catalyst characterization
  - Evaluation of catalyst activation



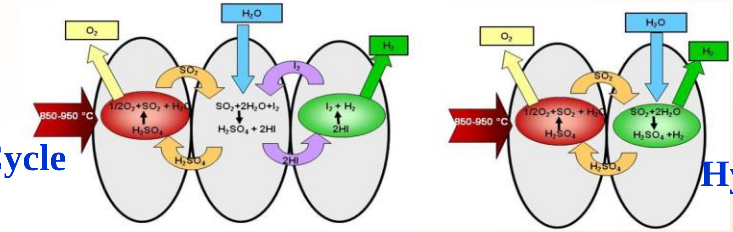


SEM image of Catalyst



System of catalyst reaction

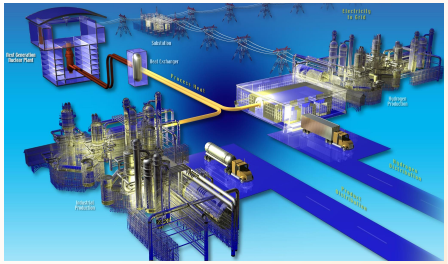
Optimized Flowsheet for SI Cycle and Hy S Cycle

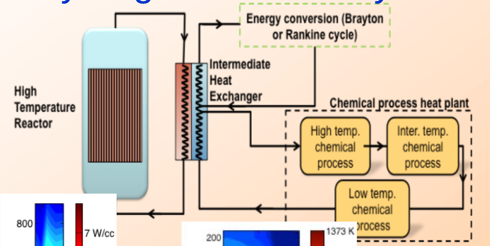


SI Cycle

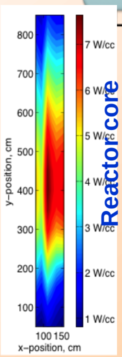
Hy-S Cycle

Integrated VHTR & SI Cycle Hydrogen Plant Analysis

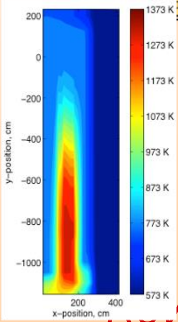




- **Chemical process plant simulation using data from Prof. Lee's group**
- **Dynamic modeling with reactor kinetics and thermal-hydraulics models for the couple system**



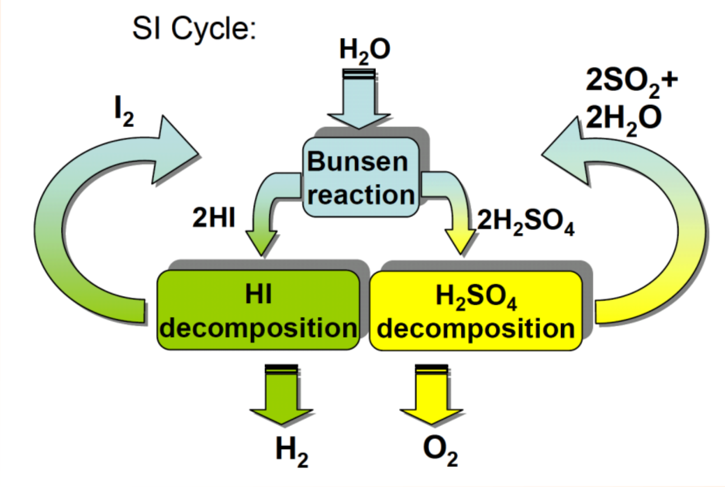
Reactor core power flux



Temperature distribution in PBMR core

SI-Thermochemical cycle

- ✓ **Extensive literature review of 70+ TC cycles:**
  1. **Sulfur Iodine (SI) Cycle**
  2. **Hybrid Sulfur (HyS) Cycle**
- ✓ **SI cycle was developed and flow-sheeted by General Atomics in the 1970s**



Integrated SI loops:
- 1980s GA, (US)
- 2004 JAERI, (Japan)
- 2009 INERI (DOE/CEA), (France)
- 2010 Tshingua (China)
- 2011 KAERI-KIER-RIST-POSTECH

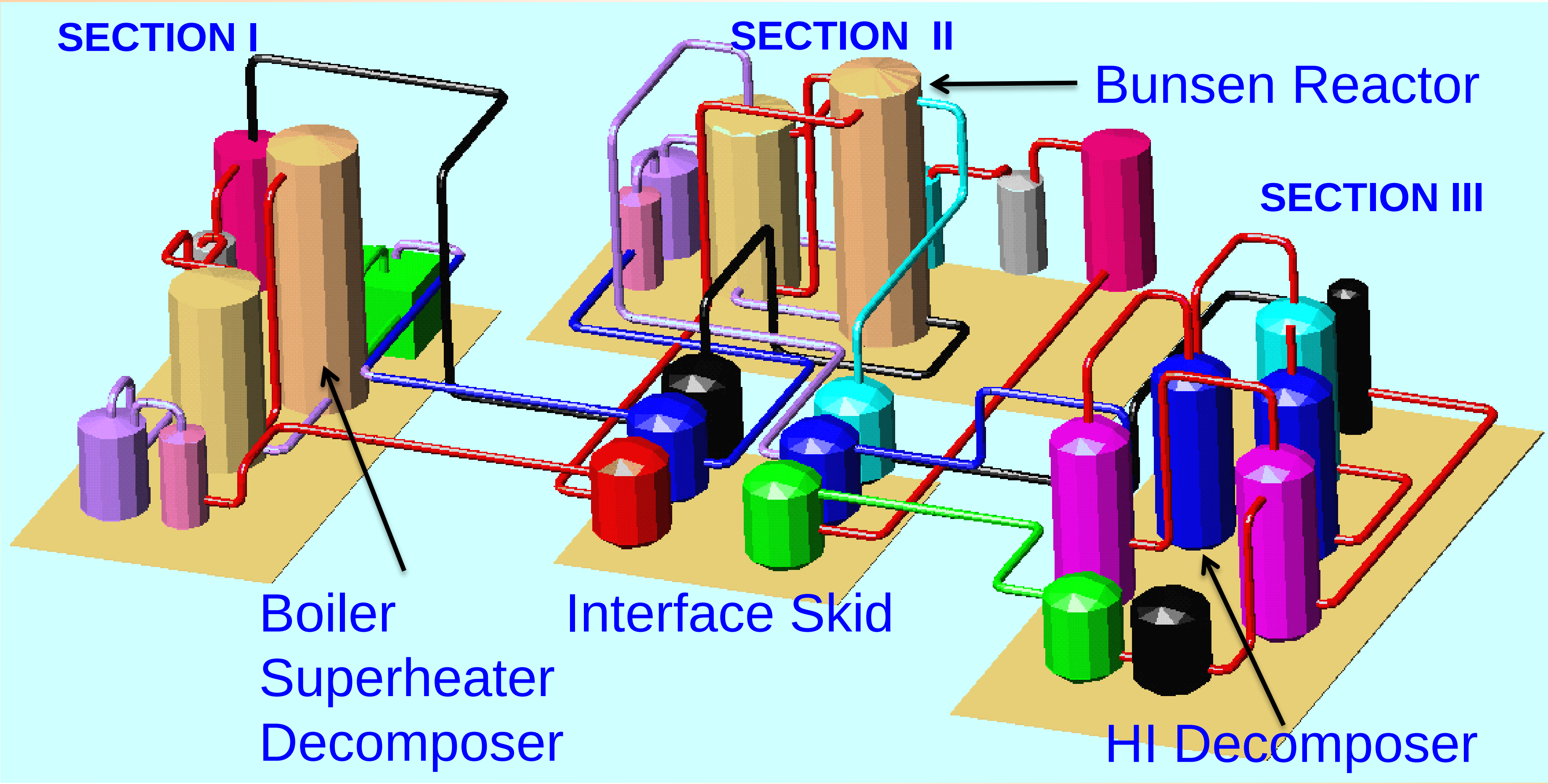
H_2SO_4 decomposer unit installed at GA ILS experiment site

Separate Effects Tests

GA, SNL, CEA, JAERI, KAIST, POSTECH

Paul Pickard, 2009

GA-CEA-SNL Sulfur-iodine Integrated Laboratory Scale Demonstration



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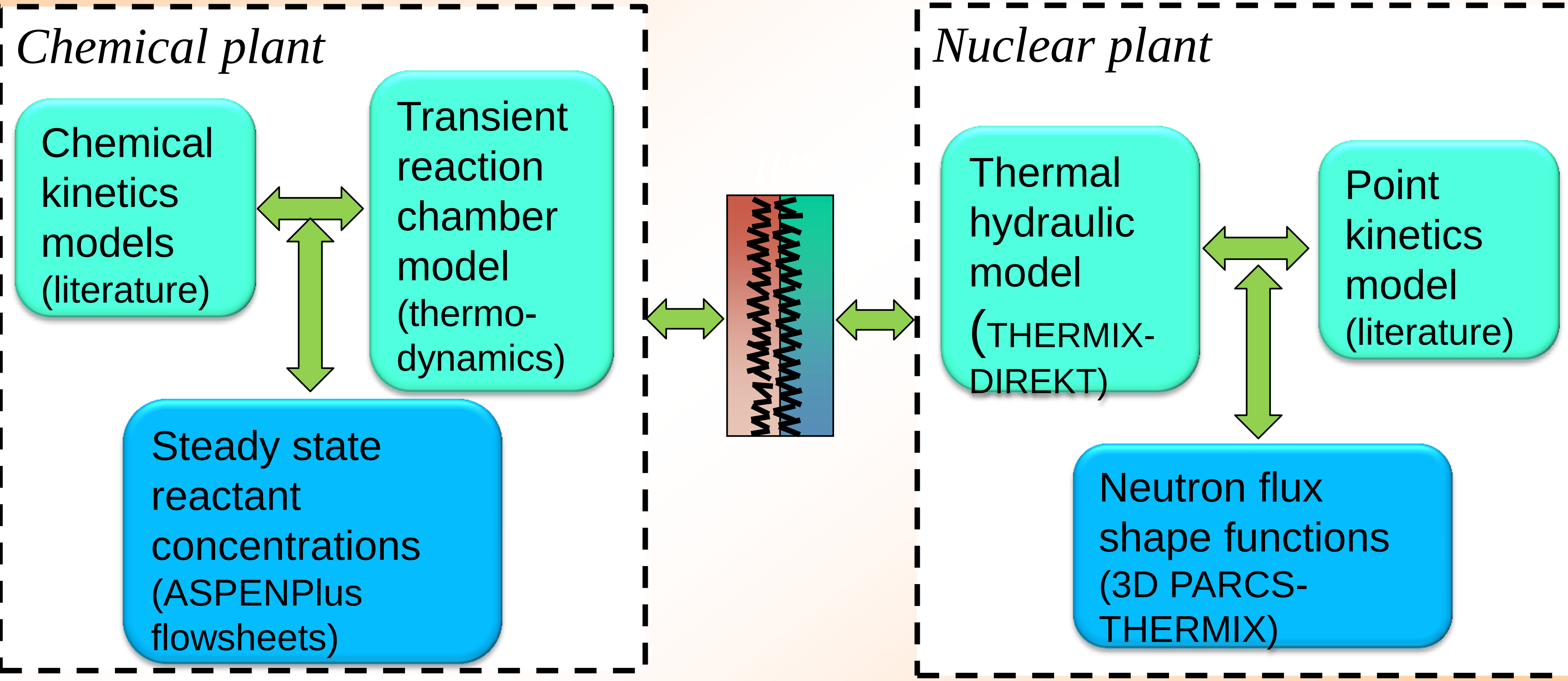
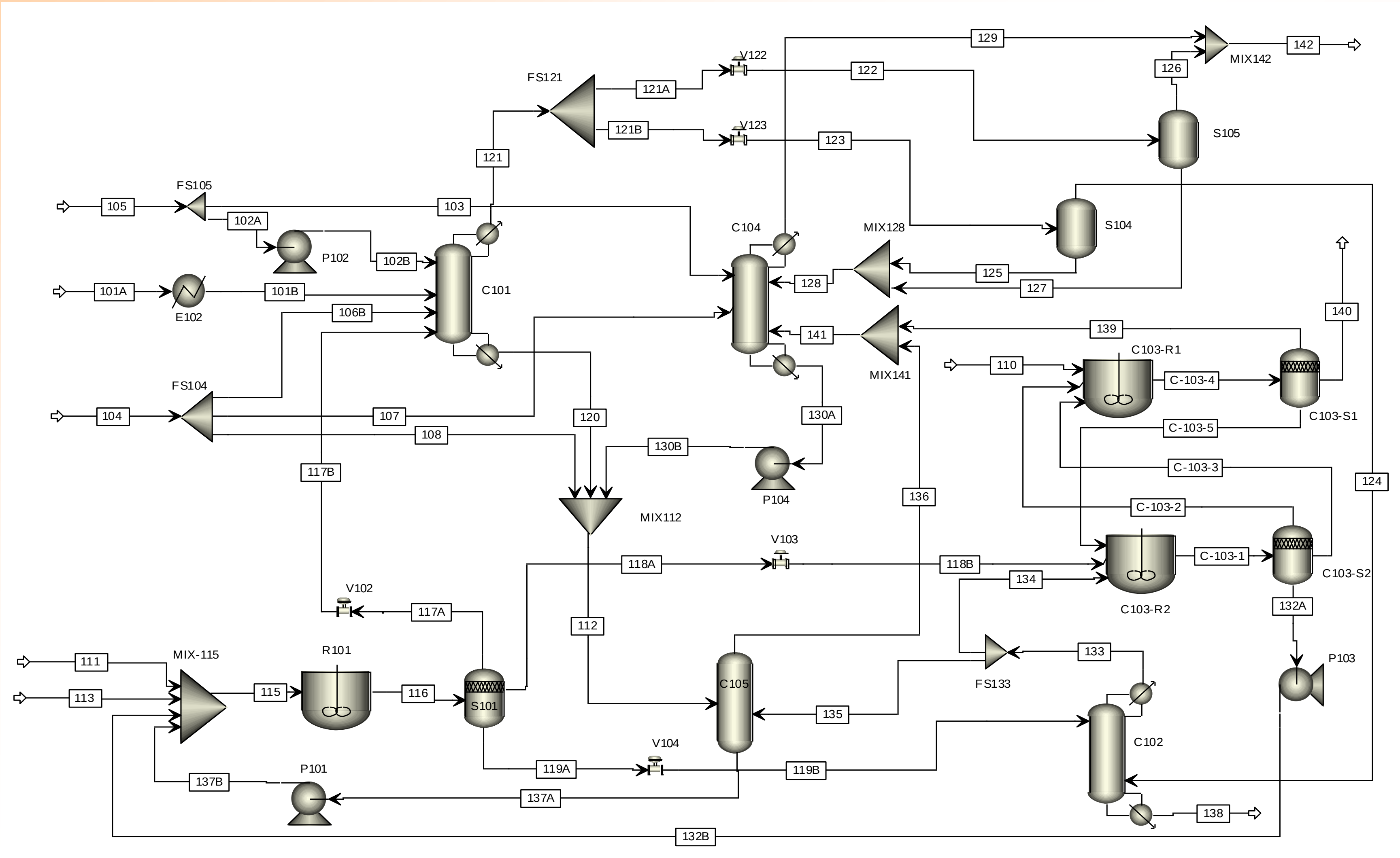
Modeling Work

Chemical Flowsheet | **Analytical Model** | **System Codes**

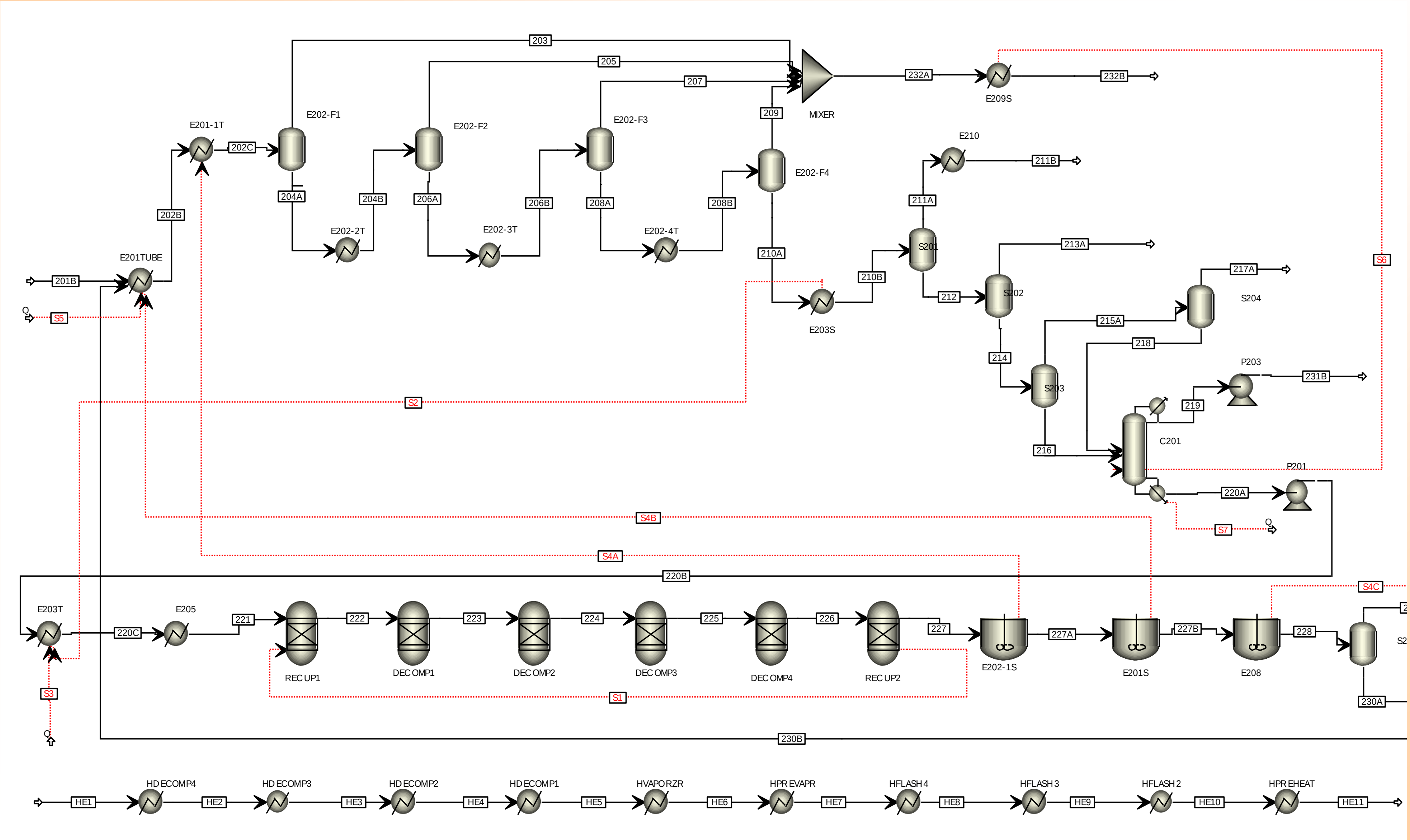


Section I-

If the inlet stream of S-101 is disconnected to the outlet stream of the Bunsen reactor (116), and appropriate inlet flow condition is specified for S-101, converges



Section II : H_2SO_4 decomposition



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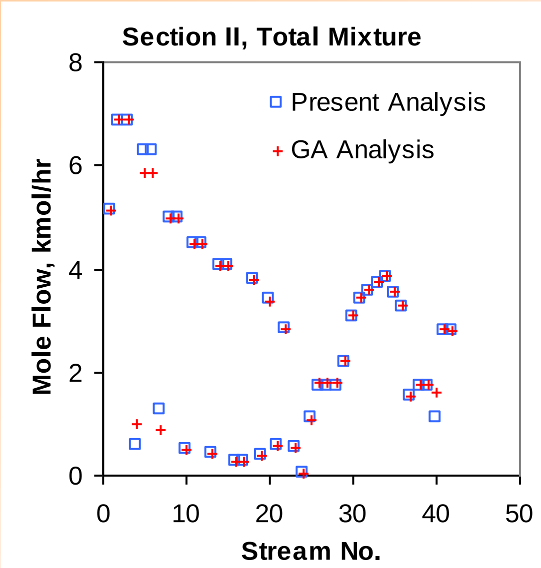
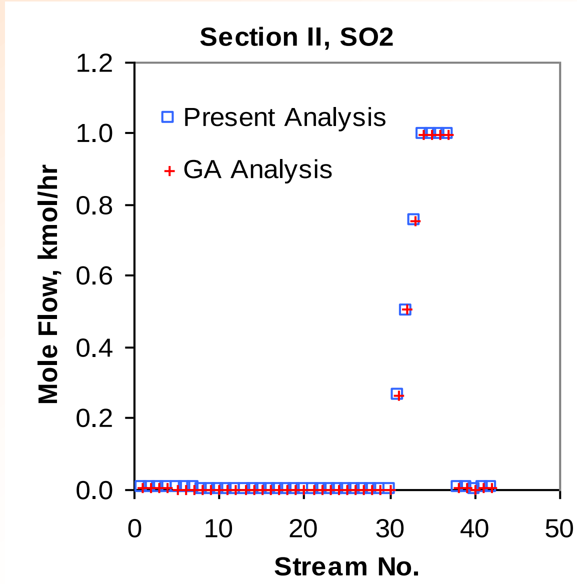
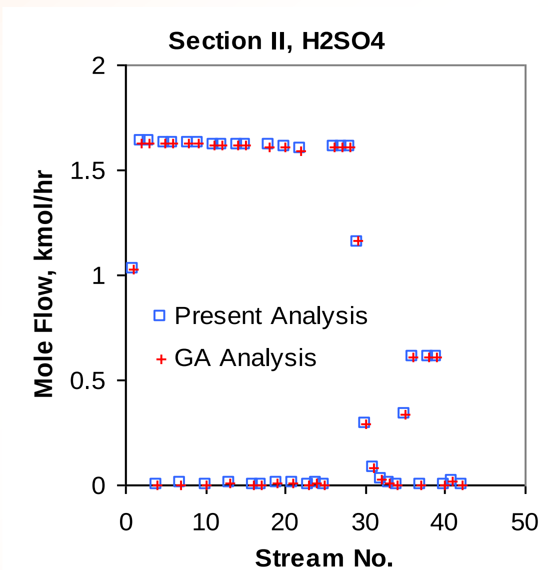
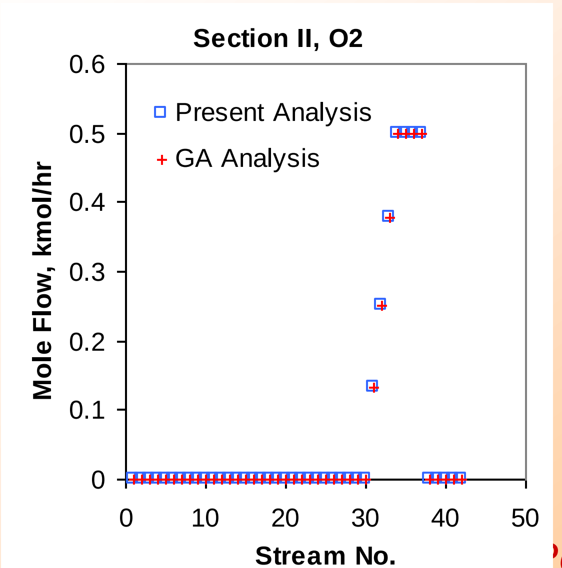
Section II : H_2SO_4 decomposition



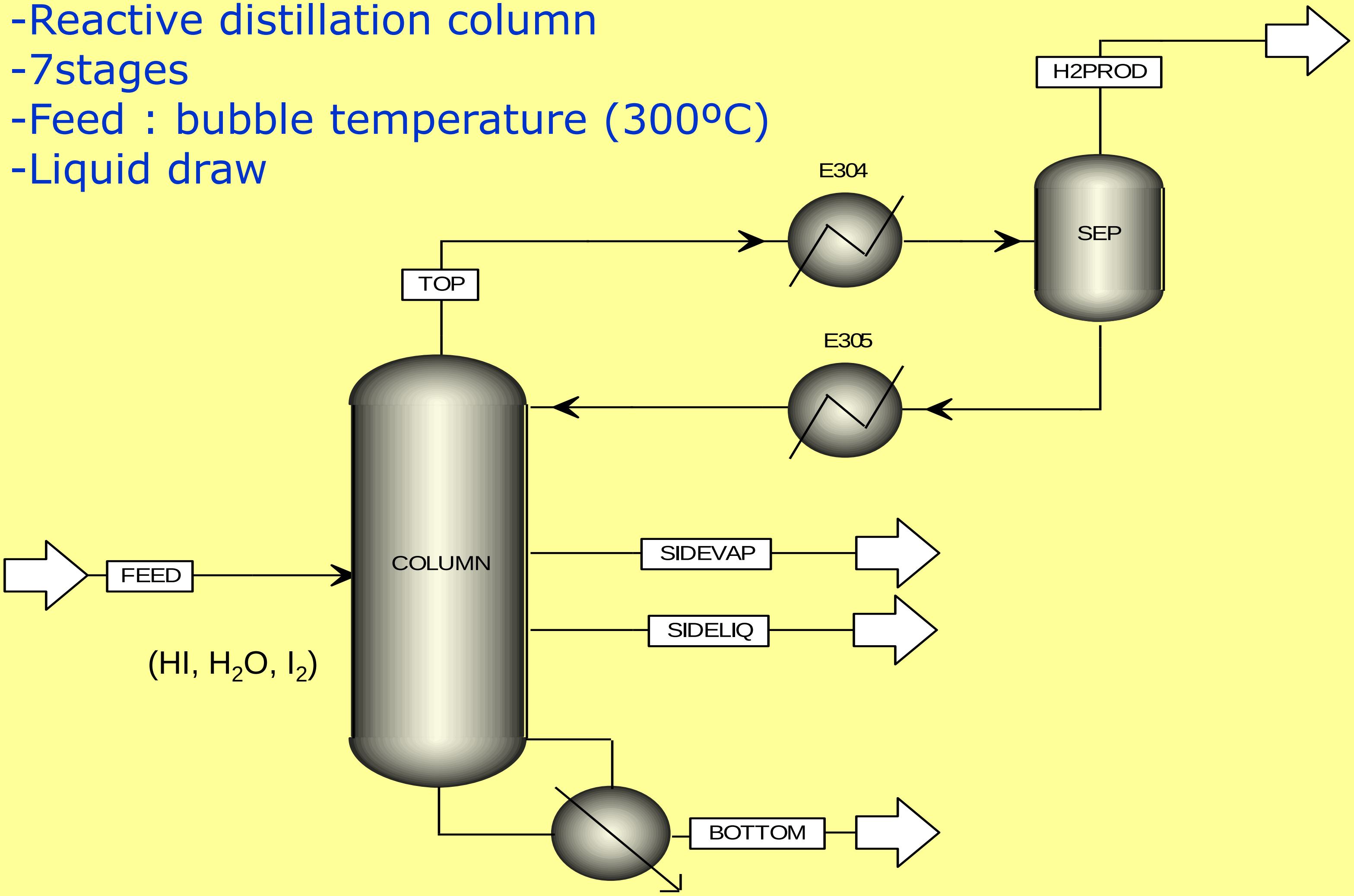






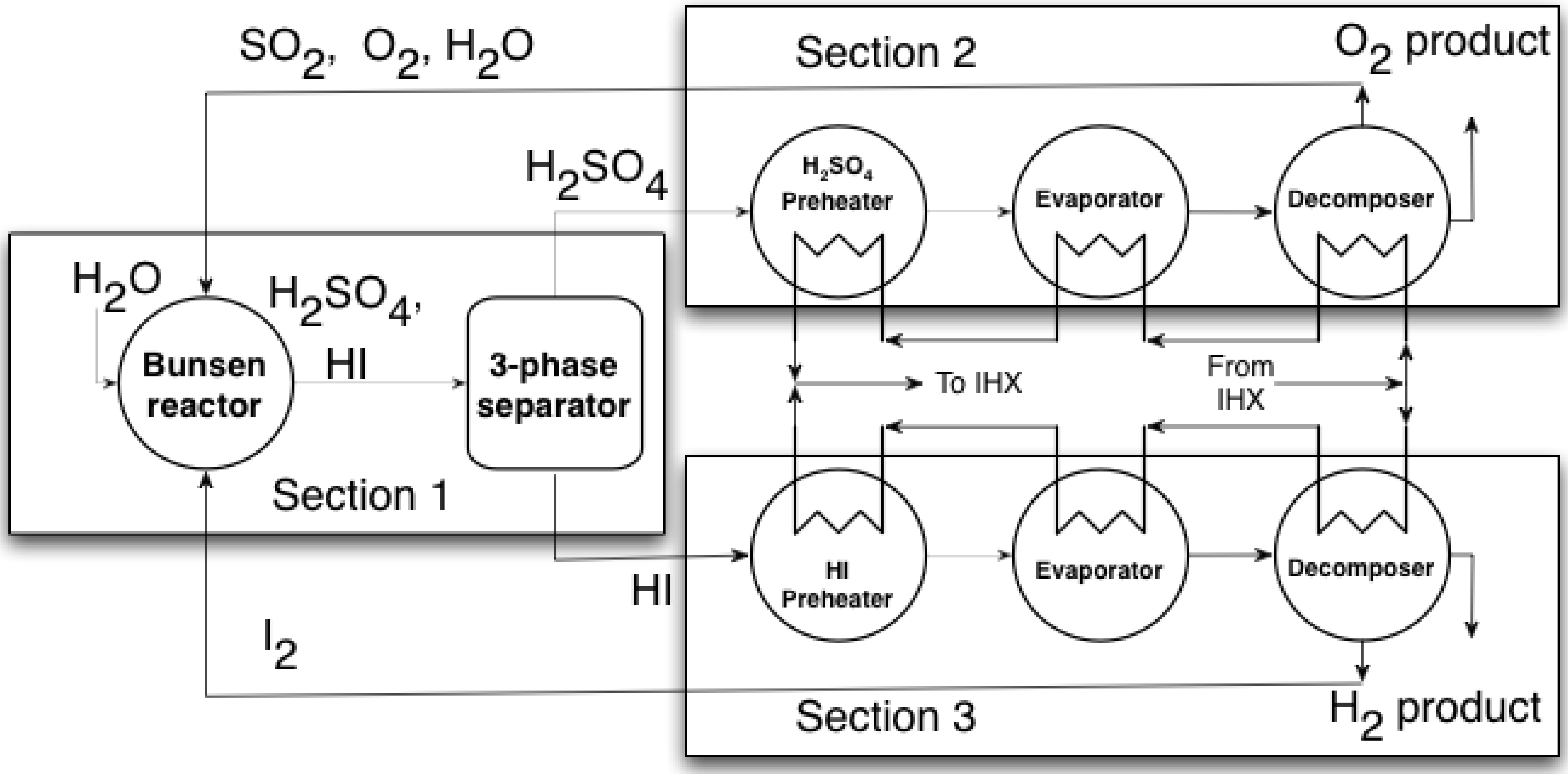
Section III : HI decomposition

-Reactive distillation column
-7stages
-Feed : bubble temperature (300ºC)
-Liquid draw



Revankar-35

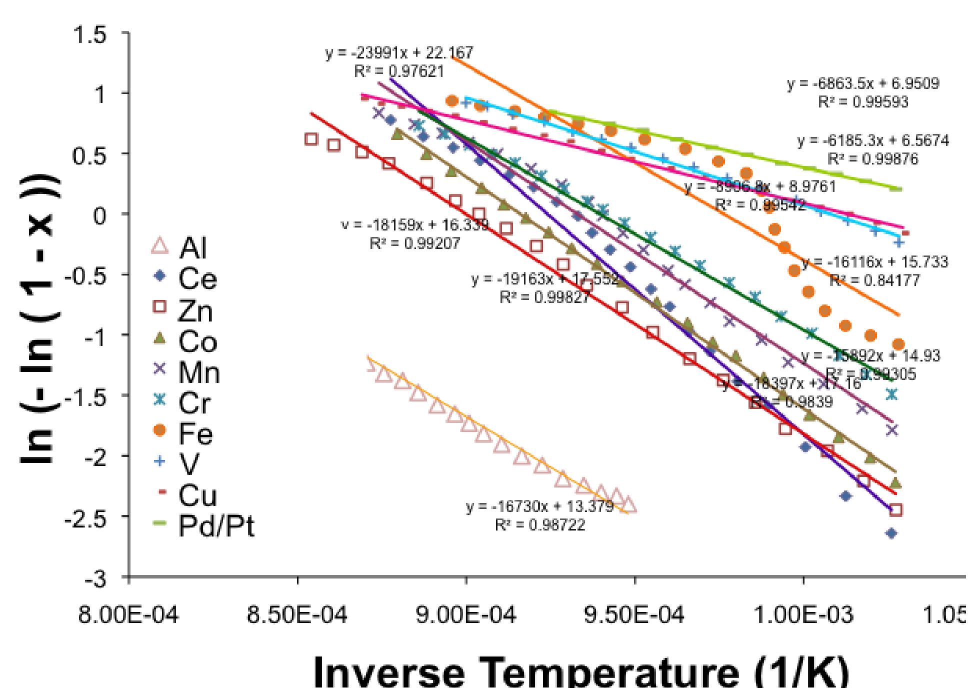
Simplified Chemical plant modeling

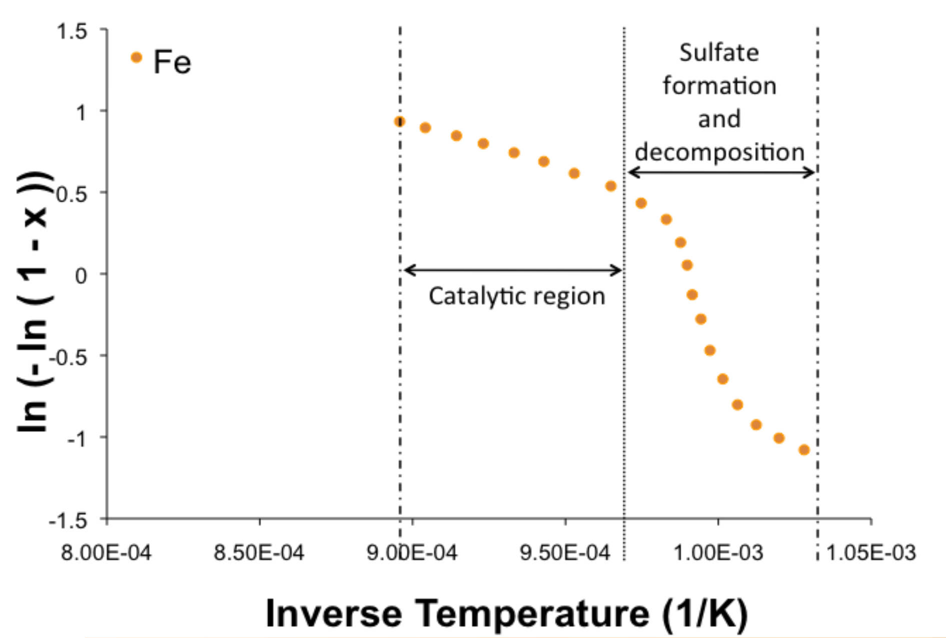


Revankar-36

Catalytic H_2SO_4/SO_3 decomposition

- ✓ Rate limitation of H_2SO_4 decomp. is SO_3 decomposition
- ✓ Temperature, energetic limiting step of the SI cycle
- ✓ Maximum temperature – safety margin for HTR
- ✓ Extracted data (20+ papers) suggests Pt or Fe-oxides





$MO + SO_3 \rightarrow (MSO_3) \rightarrow MO_2 + SO_2$, $MO_2 \rightarrow MO + O_2$

Chemical plant models

- S.S. flow rates & concentrations: ASPENPlus flowsheets
- Chemical kinetics models for each reaction (literature)
- Simplify or neglect reactant separation and concentration processes, focus on the fundamental physics

$SO_2 + I_2 + 2H_2O \quad H_2SO_4 + 2HI$

(Bunsen reaction, Kinetics rate constants: Brown 2003)

$SO_3 \quad SO_2 + \frac{1}{2} O_2$

(Sulfur trioxide decomp., rate const: Spewock 1976)

$2HI \quad I_2 + H_2$

(Hydrogen iodide decomp., rate const: Laidler 1965/NIST)

Enthalpies, reaction heat, heat of vaporization, and specific heat from: (NIST, ChE Handbook)

$$\frac{d[H_2SO_4]}{dt} = -\frac{d[SO_3]}{dt} = k_2 \cdot [SO_3]$$

Revankar-38

Chemical Plant Models

$SO_2 + I_2 + 2H_2O \rightarrow H_2SO_4 + 2HI$

(Bunsen reaction, Brown 2003)

$SO_3 \rightarrow SO_2 + ½\,O_2$ (Spewock 1976)

$2HI \rightarrow I_2 + H_2$ (,Laidler 1965)

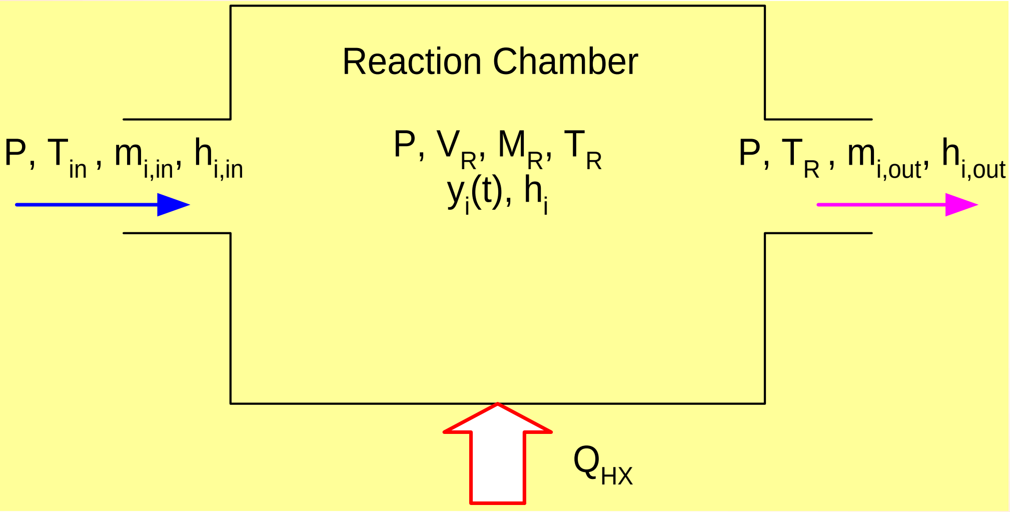
Reverse reaction rate is non-negligible

Molar balance, energy balance for each species within the chemical plant

$$\frac{d[H_2]}{dt} = k_3 \cdot [HI]^2 - k_{-3} \cdot [H_2] \cdot [I_2]$$

$$\frac{d[H_2]}{dt} = \frac{d[I_2]}{dt}$$

$$\frac{1}{2}\frac{d[HI]}{dt} = -k_3 \cdot [HI]^2 + k_{-3} \cdot [H_2] \cdot [I_2]$$



- Assumptions
  - Ideal gas mixture
  - Negligible kinetic and potential energy
  - No works, no heat loss
  - Constant reactor volume
  - Well mixed in the reaction chamber

Revankar-39

Governing Equations in the Reaction Chamber

- ✓ **Species molar balance** $$M_R \frac{dy_i}{dt} + y_i \left(m_{in} + \Delta\nu \frac{dX}{dt} \right) = m_{i,in} + \nu_i \frac{dX}{dt}$$ i=1,2,,,n
- ✓ **Global molar balance** $$\frac{dM_R}{dt} = m_{in} - m_{out} + \Delta\nu \frac{dX}{dt}$$
- ✓ **Energy balance** $$M_R \overline{c_P} \frac{dT_R}{dt} = \sum_i m_{i,in}(h_{i,in} - h_i) - \Delta h_{RXN} \frac{dX}{dt} + \dot{Q}_{HX} + V_R \frac{dP}{dt}$$
- ✓ **Chemical reaction** $$X = X\left(T_R, C_i\right)$$
- ✓ **HX energy balance** $$\dot{Q}_{HX} = U \cdot A \cdot \Delta T = m_{He}(h_{He,in} - h_{He,out})$$
- ✓ **Equation of state** $$PV_R = M_R R T_R$$

(n+5) Equations vs. (n+6) Unknowns: M_R, X, y_i (i=1,2,,,n), m_{out}, P, T_R and $T_{He,out}$

- Recycling considered within each chemical plant section
  - H_2O, I_2, HI
- Section 2 is essentially Plug flow reactor (PFR), section 1 and 3 Continuously stirred tank reactors (CSTR)

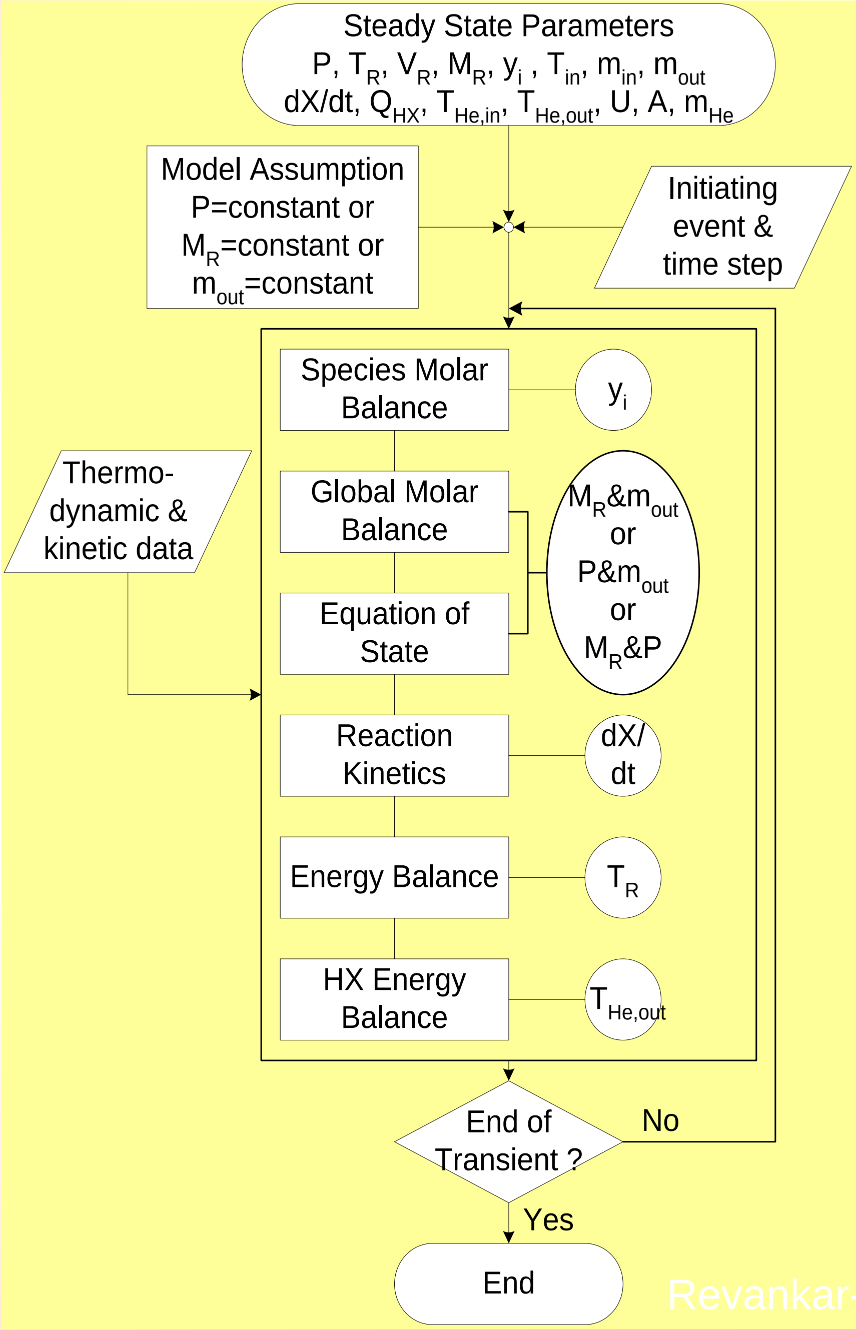
  Molar flow rate out of section 3 varies with reaction rate

Revankar-40

Flowchart-Transient

- Input values

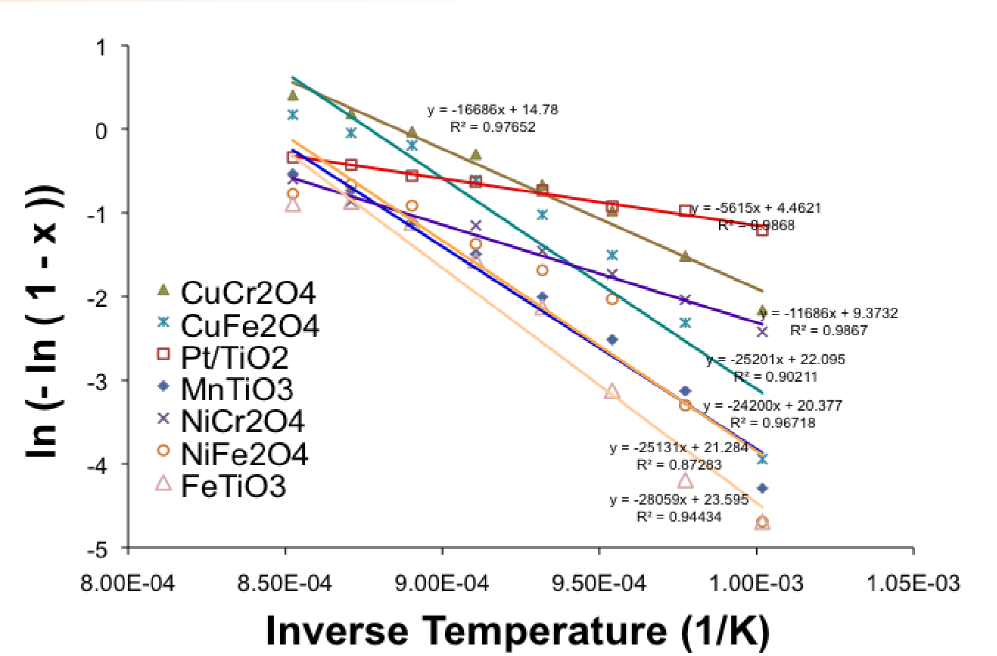
Reaction Chamber	1	2	3
Reactor Volume, m^3	6.79	1.66	57.32
HX Heat Load, kJ	N/A	417	46.6
HX HTC*Area (UA), W/K	N/A	2193	120
Helium Flow, mol/s	N/A	44.57	4.99



Revankar-41

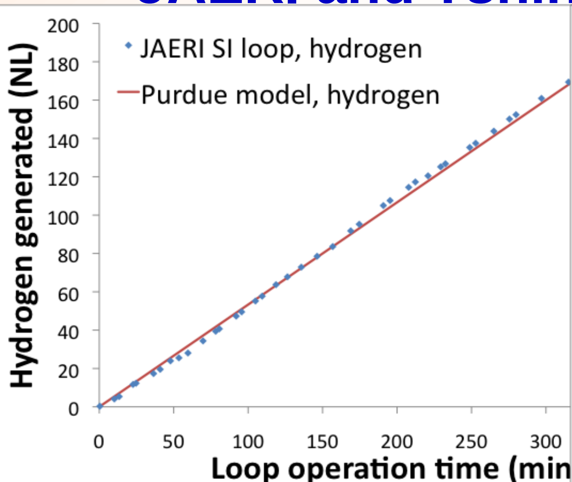
V & V: Chemical plant models

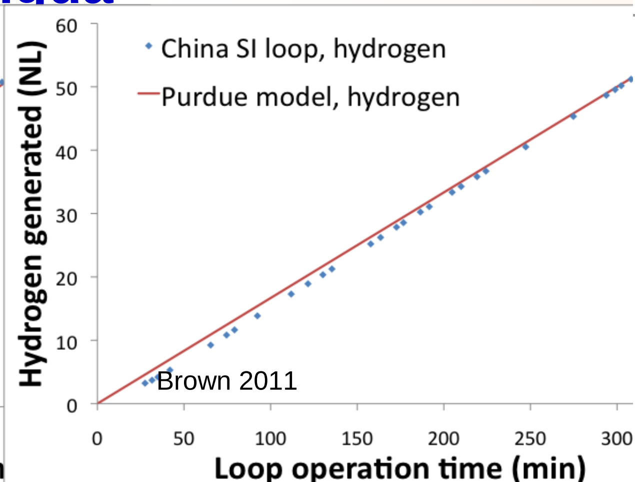
- ✓ Chemical kinetics to data from 20+ examples in bench scale
- ✓ ASPENPlus: benchmarked to GA flowsheets
- ✓ Reaction chamber model valid. to SNL ILS H_2SO_4 decomp.
- ✓ Entire SI loop validated to available data from ILS at JAERI and Tshingua



Rodriguez, et al. 2009

Acid flow rate (mol/hr)	Experiment conversion	Calculated conversion	Error (percent)
3.41	0.771	0.800	3.6
6.27	0.600	0.588	-2.0
12.0	0.381	0.375	-1.6
3.10	0.787	0.838	6.5
5.50	0.608	0.648	6.6
5.86	0.608	0.618	1.6
3.18	0.758	0.830	8.7
5.27	0.648	0.654	0.92
11.9	0.440	0.377	-14.3

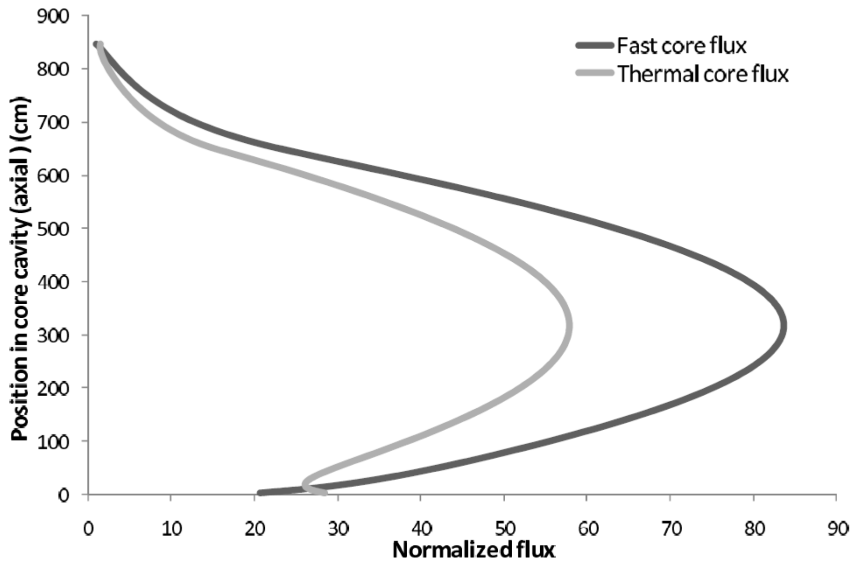


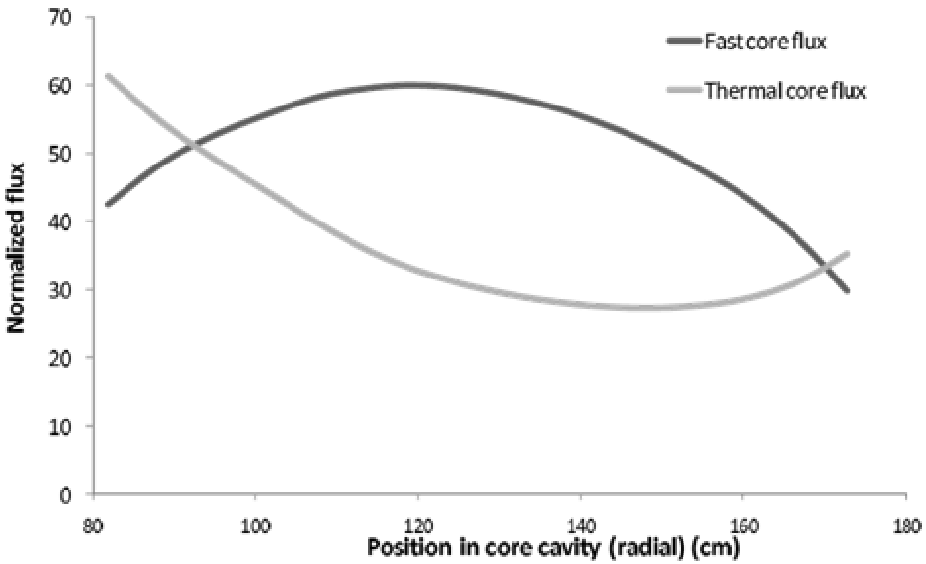


Modeling PBMR-268

- ✓ THERMIX-Direkt is used to model the reactor thermal-hydraulics
  - THERMIX models the solid portions of the core via mesh-averaging
  - Direkt models the time dependent equations for convective heat transfer and Helium flow in the core
  - Includes models for decay heat
- ✓ PARCS-THERMIX PBMR-268 benchmark model is used to provide flux distributions in the core at steady state
- ✓ Point kinetics model is used to solve for the reactor behavior during transient
- ✓ Point kinetic model used was benchmarked to PARCS-THERMIX

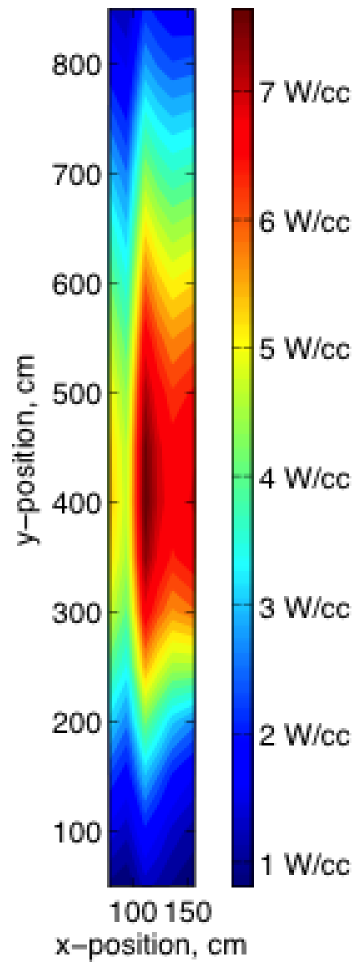
Core flux profiles and point kinetic model





$$\dot{P}(t) = \frac{(\rho(t)-\beta(t))}{\Lambda(t)}P(t) + \frac{1}{\Lambda_0}\sum_i \lambda_i C_i(t) + \frac{1}{\Lambda(t)}s(t)$$

$$\dot{C}_i(t) = -\lambda_i C_i(t) + \frac{\Lambda_0}{\Lambda(t)}\beta_i(t)P(t)$$



Group, i	$\lambda_i\ (s^{-1})$	β_i
1	0.013	0.0001807
2	0.032	0.001237
3	0.128	0.001192
4	0.304	0.001972
5	1.35	0.0006925
6	3.63	0.00001314

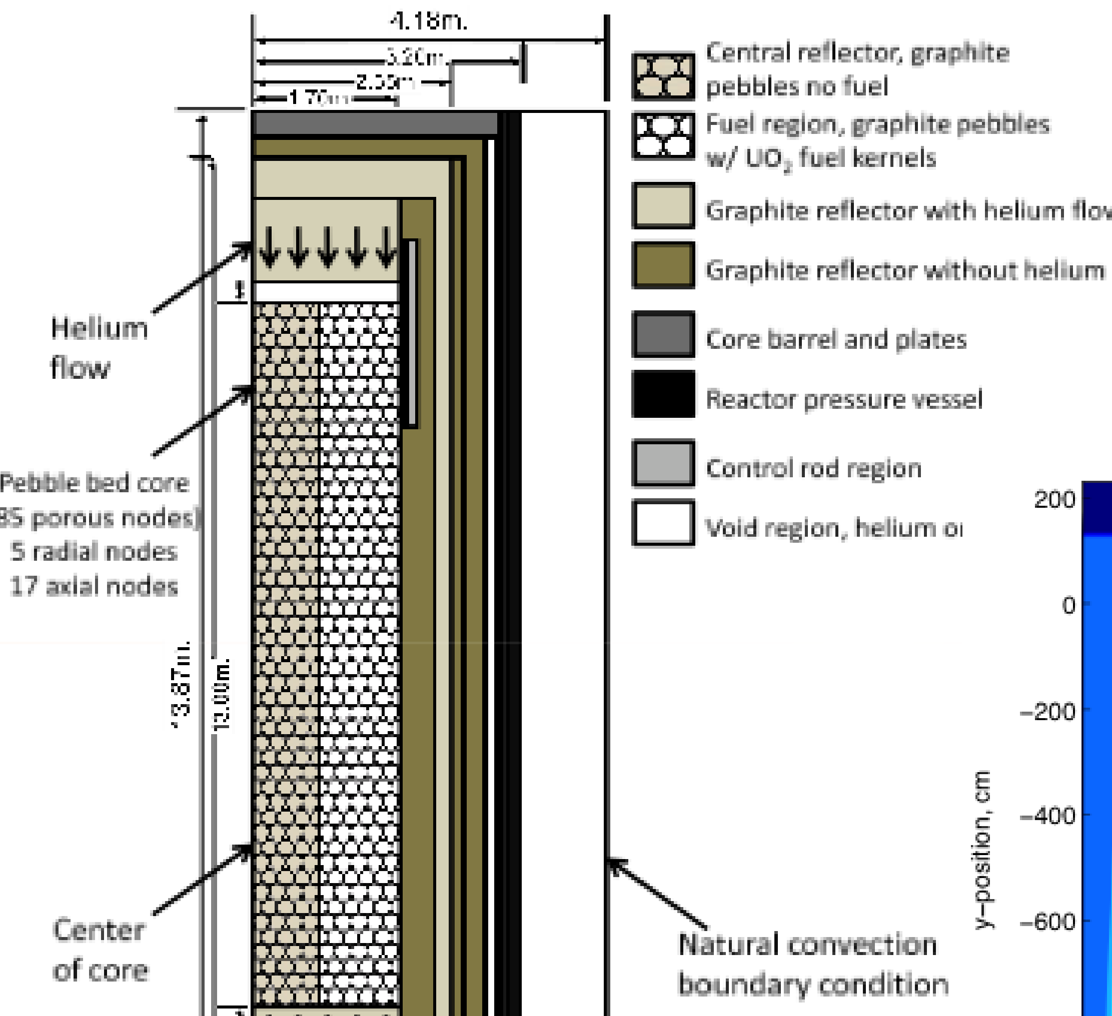
PARCS: US NRC best estimate code for neutronics analysis

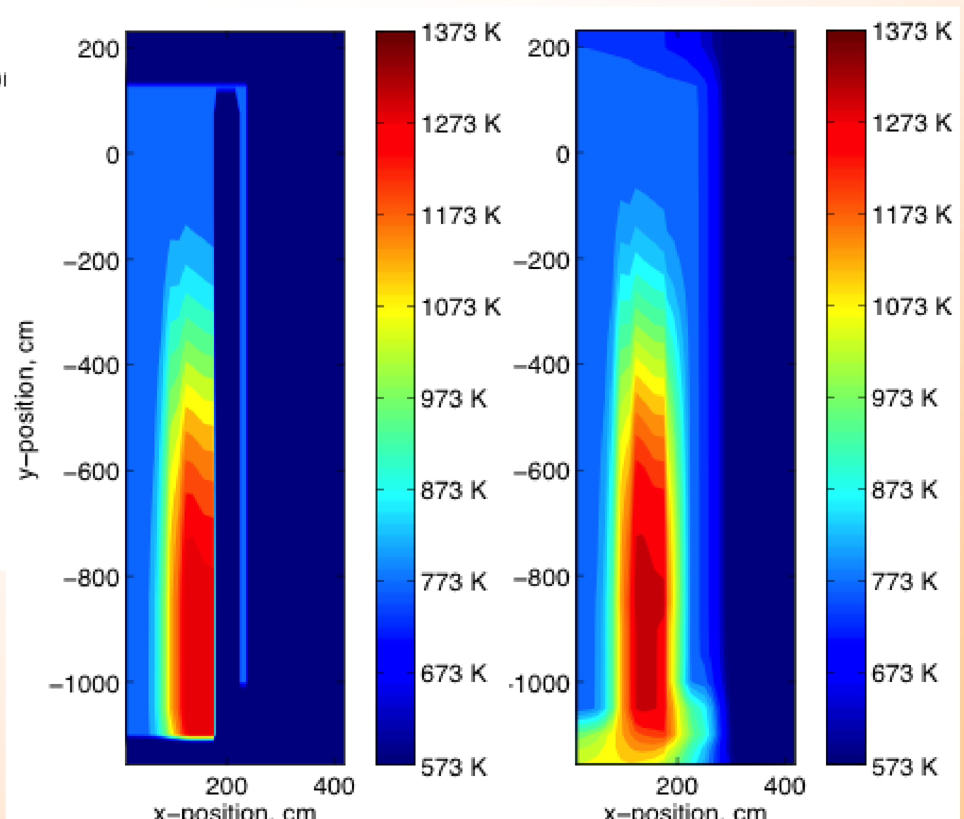
PARCS 3-D flux profile used as shape function (Seker 2007)

PBMR-268 - Steady state THERMIX-Direkt result

imulation parameters and results for PBMR-268, no

Category	Value
Reactor thermal power	268 MWt
Mass flow rate	129.0 kg/s
Helium inlet temperature	773 K
Helium exit temperature	1172.1 K
Maximum fuel temperature	1385.1 K
Average fuel temperature	1044.9 K





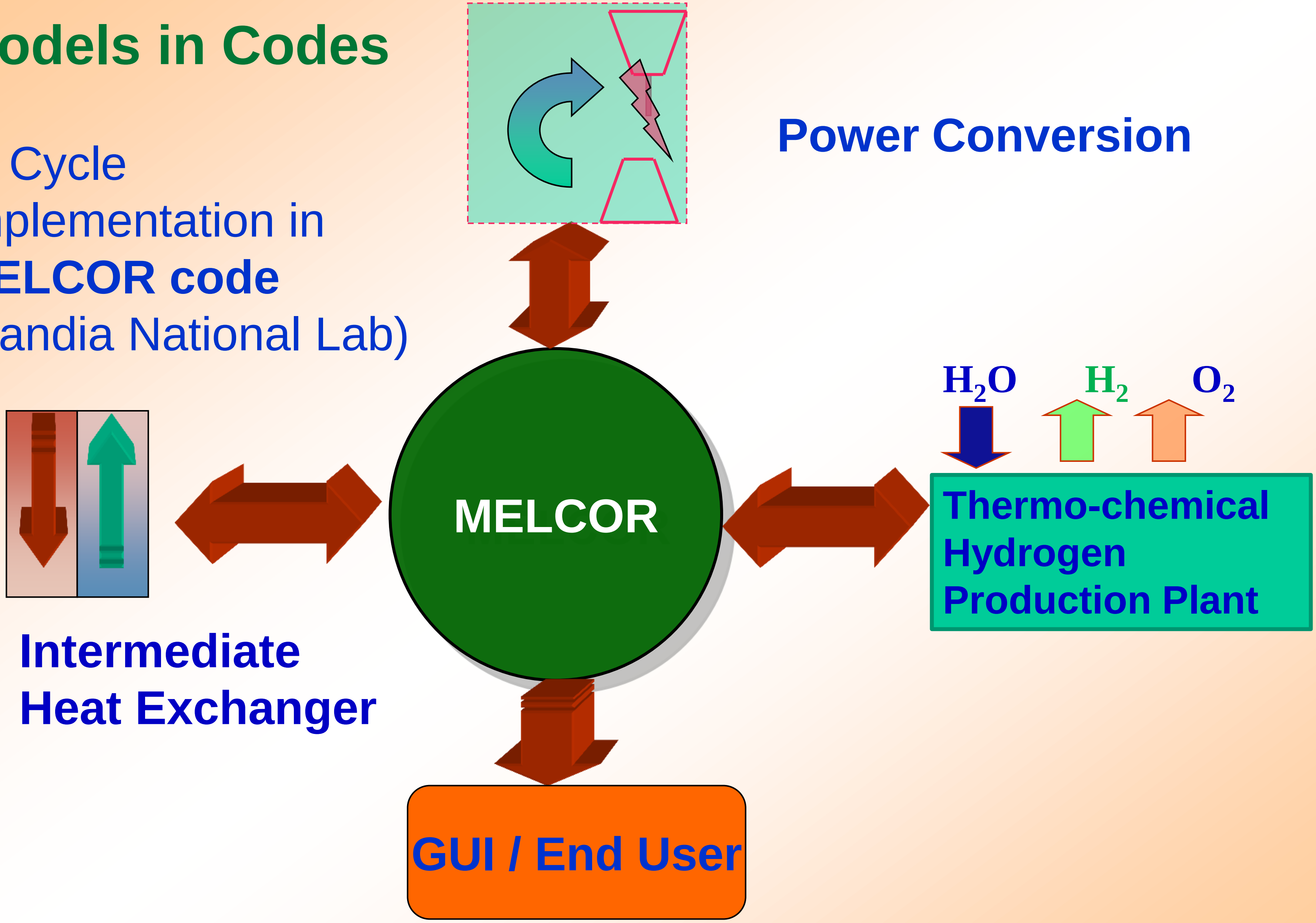
Safety -Coupled HTR and Hydrogen Production Facilities

Phenomena Identification and Ranking Table (PIRT)

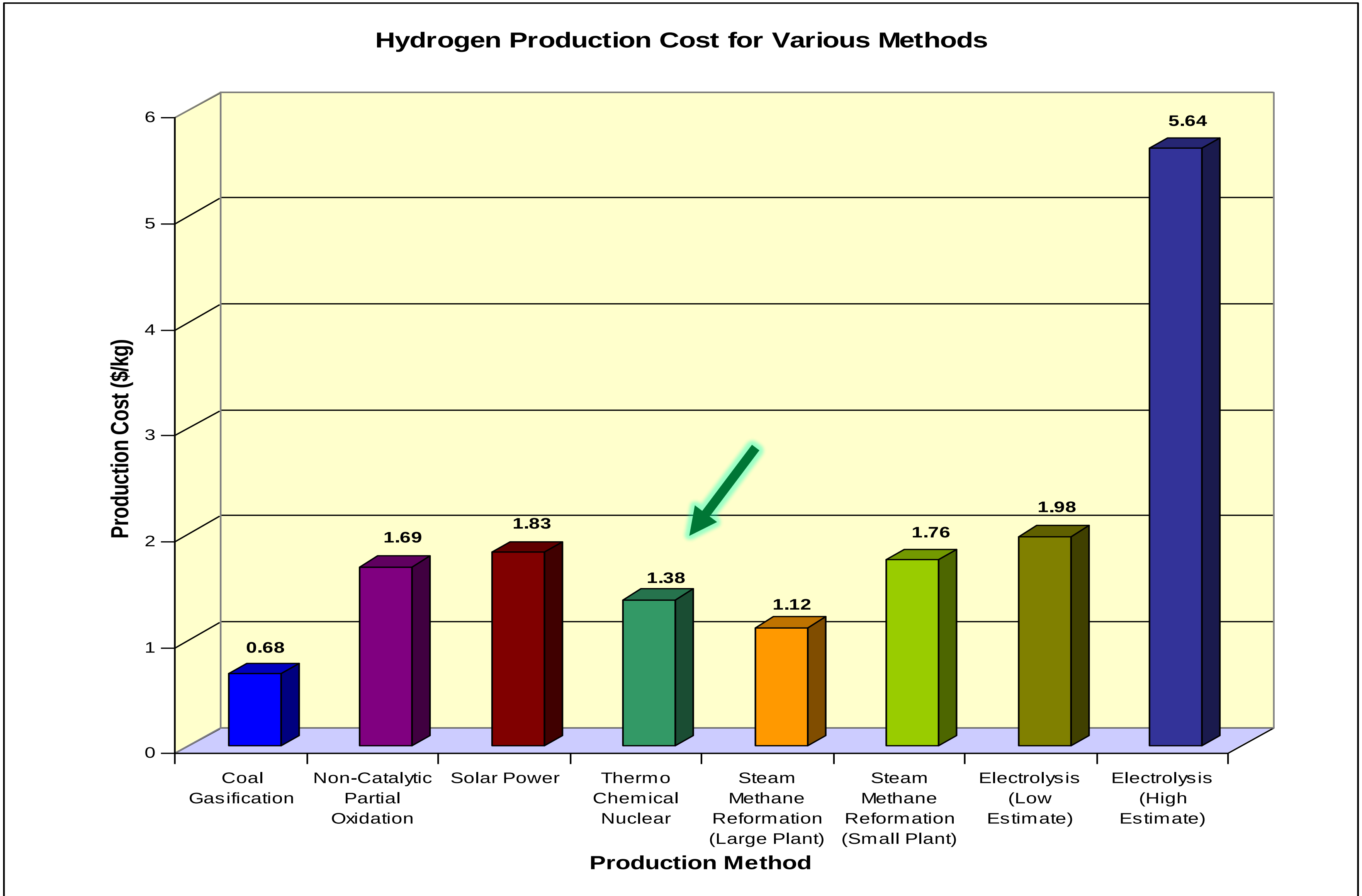
1. Accidents at the chemical plant –Chemical release (H2, O2, corrosive toxic, flammable, suffocating)
2. Process thermal events (loss of heat load, temperature transients)
3. Failures of the intermediate heat-transport system (IHX , PHX failure, coolant or intermediate fluid loss)
4. Accidents in the nuclear plant (generic power or thermal initiated transients, radiological release through coolant leakage)

Models in Codes

SI Cycle Implementation in **MELCOR code** (Sandia National Lab)

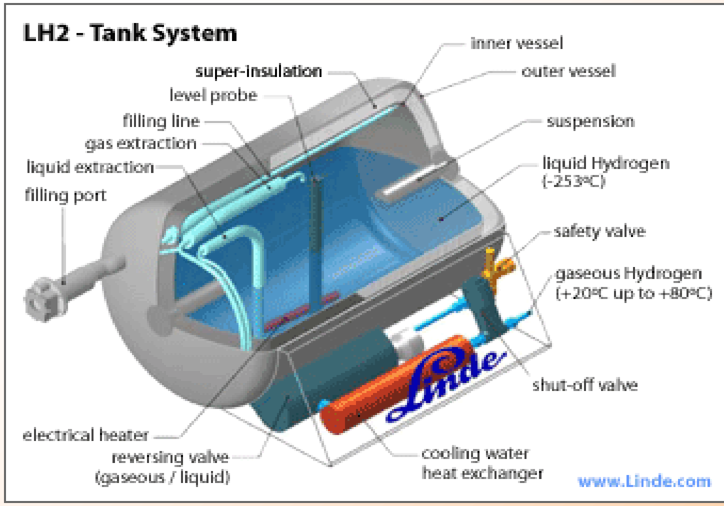


Cost Comparison of Various H_2 Generating Technologies



Hydrogen Storage Today

- Compressed Fuel Storage → Cylindrical tanks - most mature technology,

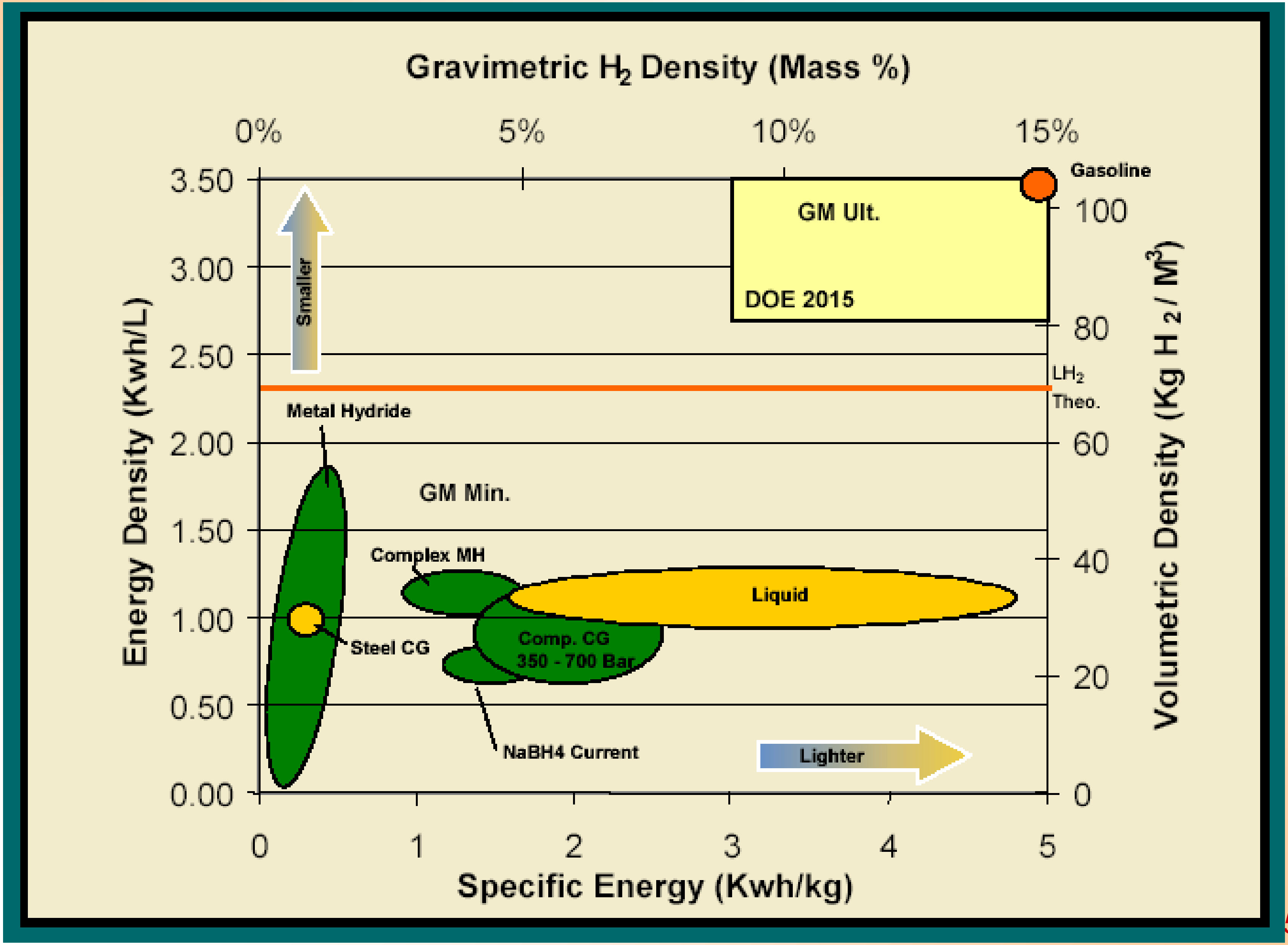


- Liquified H2 Storage → Cryotanks,
  HP Liquid Tanks –
  About one-third of the energy is lost in the process.

- Solid State Conformable Storage → Hydride material, Carbon Absorption

- Chemical Hydrides → Off-board Recycling

Technologies for Hydrogen Storage



Technology Need for Storage Improvements

Higher Energy Density is Required to Meet Customer Needs

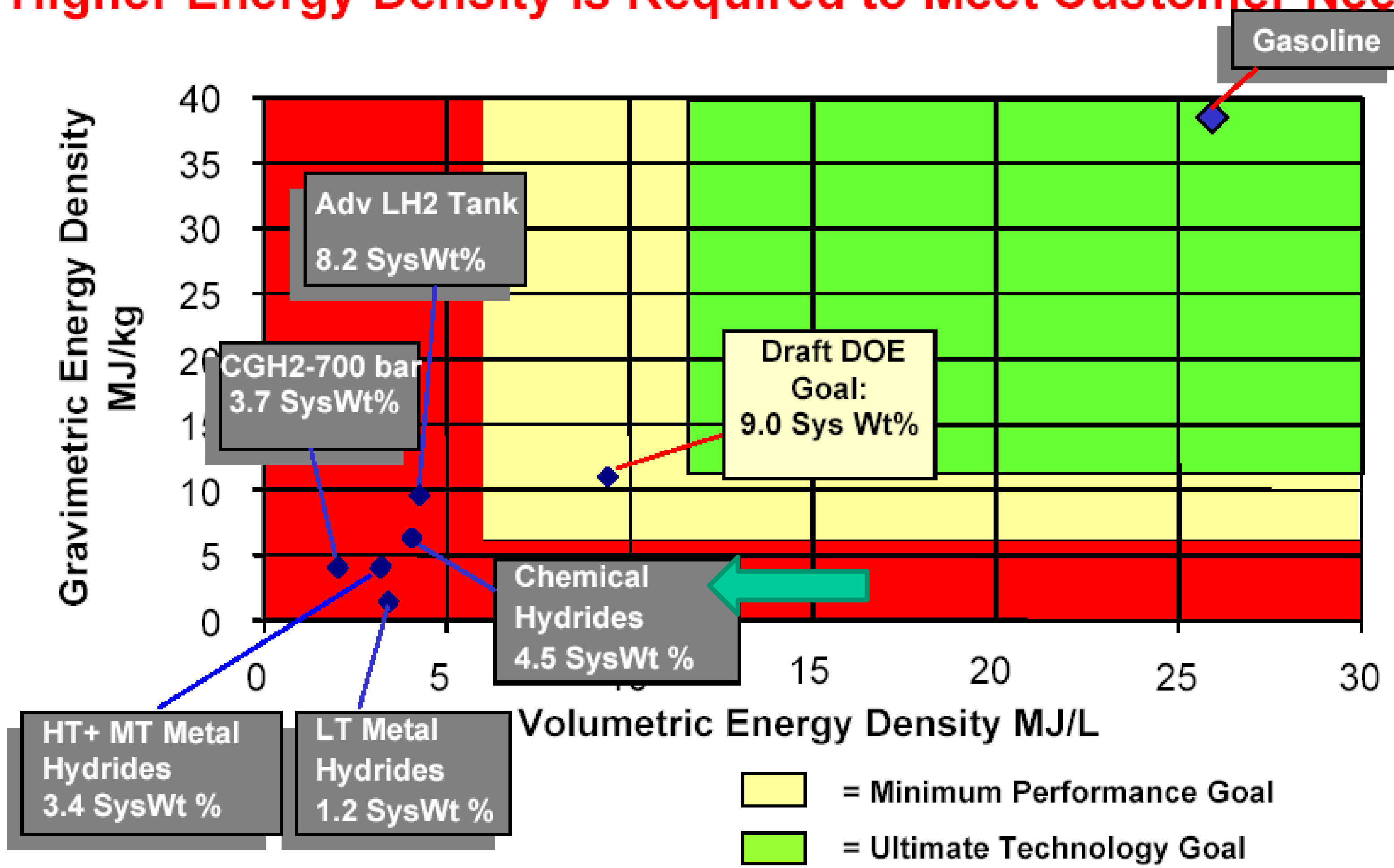
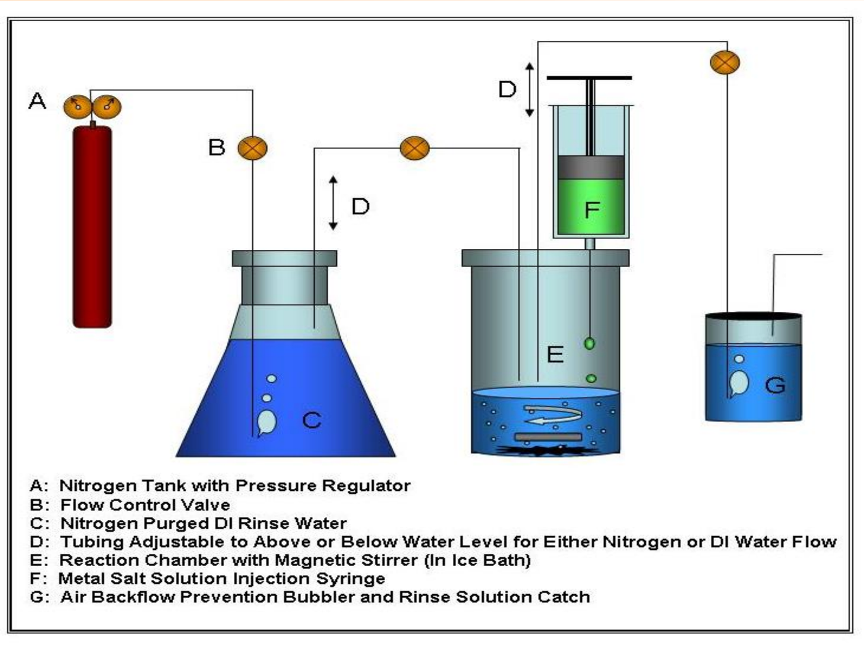


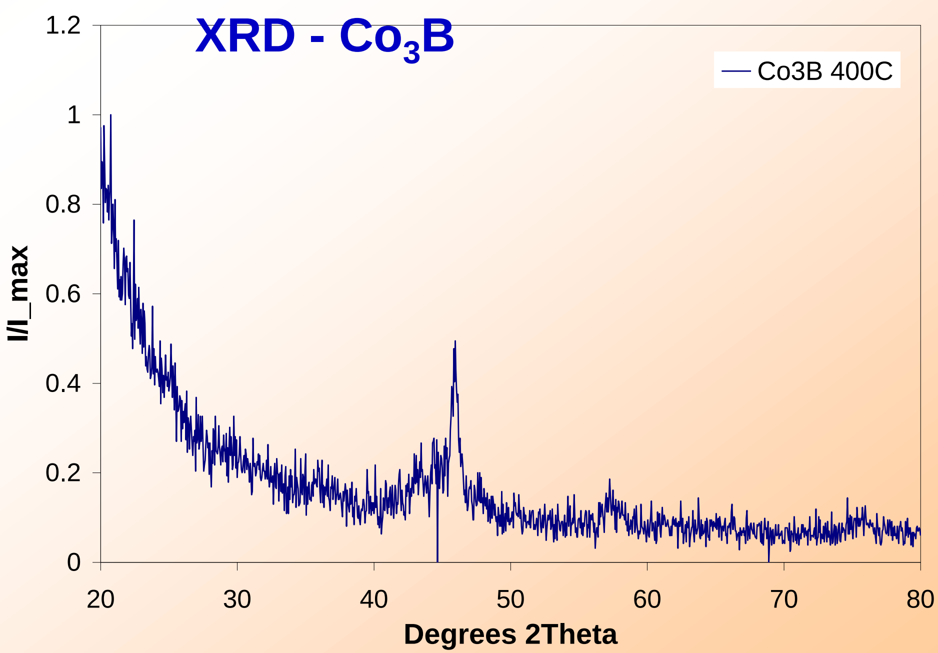
Chart Source: General Motors

Catalyst Development for $NaBH_4$ Hydrolysis

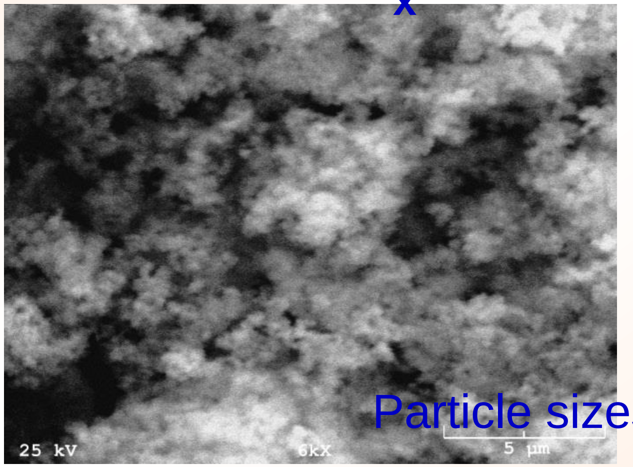
$NaBH_4 + 2H_2O +$ Catalyst $\rightarrow NaBO_2 + 4H_2 +$ HEAT



Ni, Cr, Ru



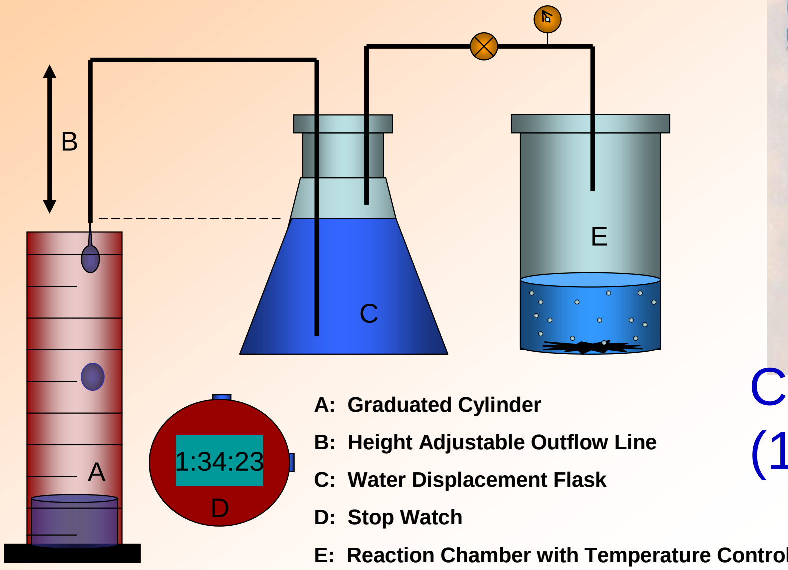
SEM -Co_xB



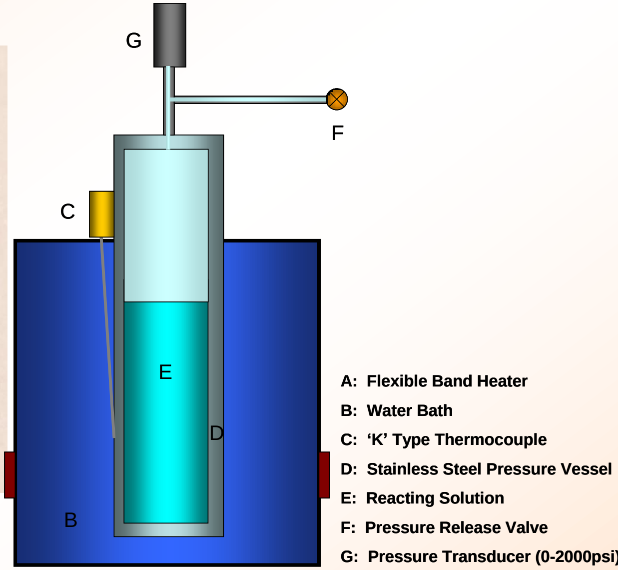
Particle sizes range from 50-300nm

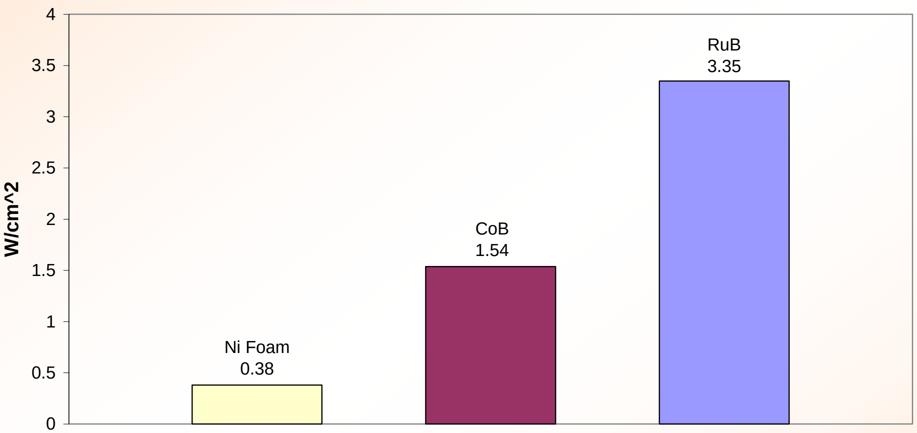
Catalyst Development for $NaBH_4$ Hydrolysis

T = 60ºC, P = 1 atm

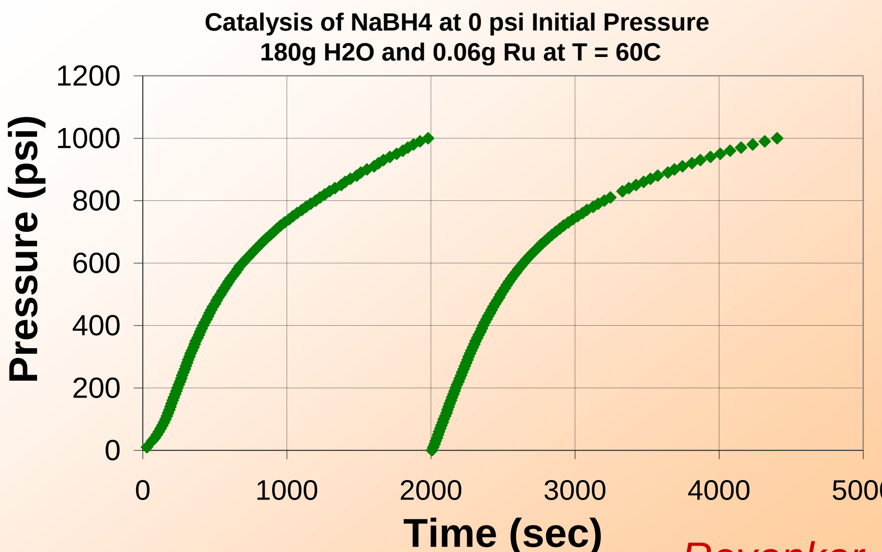


Co_xB on Ni Foam (1cmx1cm)

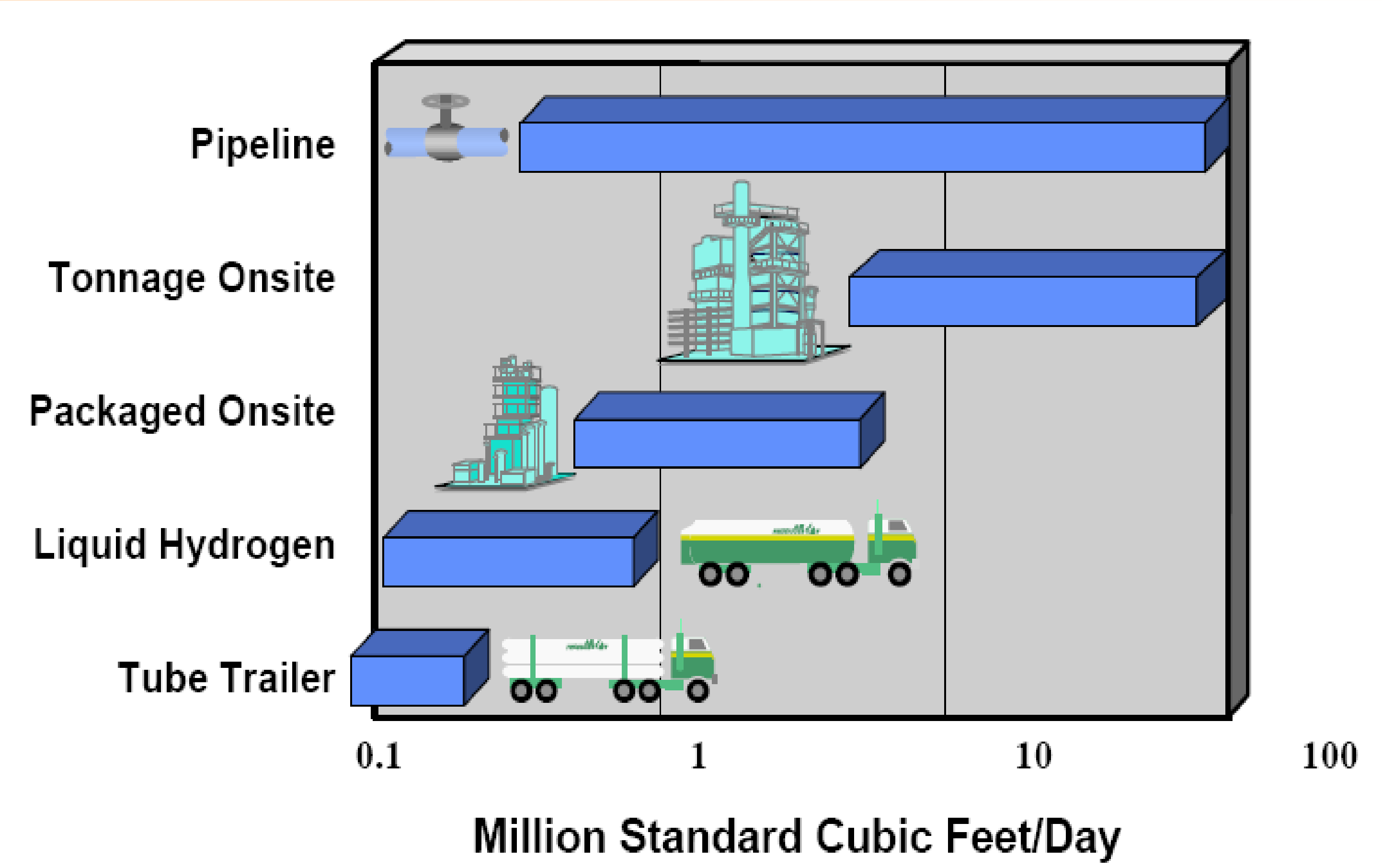




Hydrogen production power equivalent per unit area for 10 wt% NaBH4 and 5 wt% NaOH at 60oC.

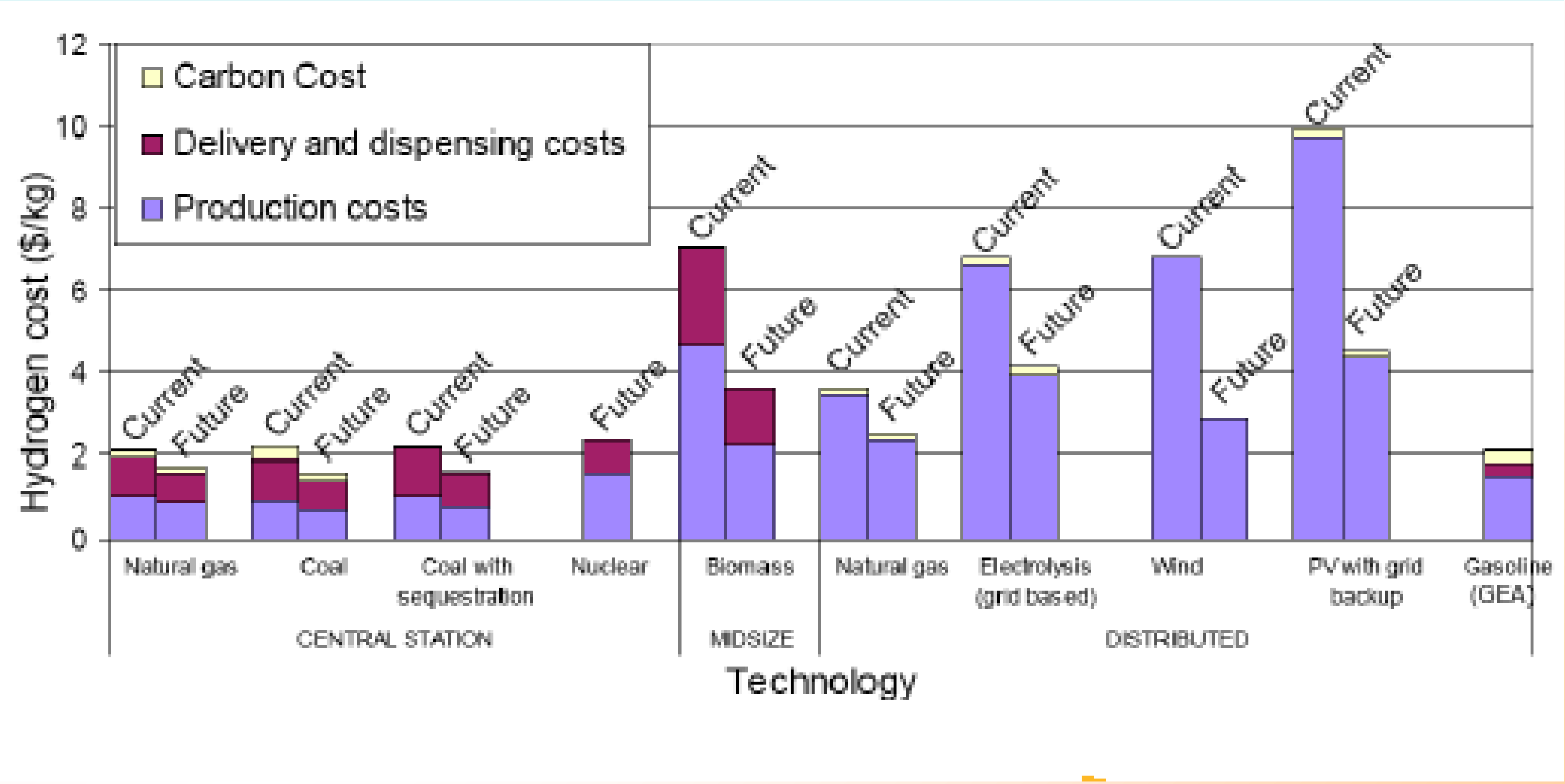


Hydrogen Delivery Technologies



- An economic strategy is required for the transition to a hydrogen delivery system.
- Full life-cycle costing has not been applied to delivery alternatives.
- Hydrogen delivery technologies cost more than conventional fuel delivery.
- Current dispensing systems are inconvenient and expensive

Delivered H_2 Cost

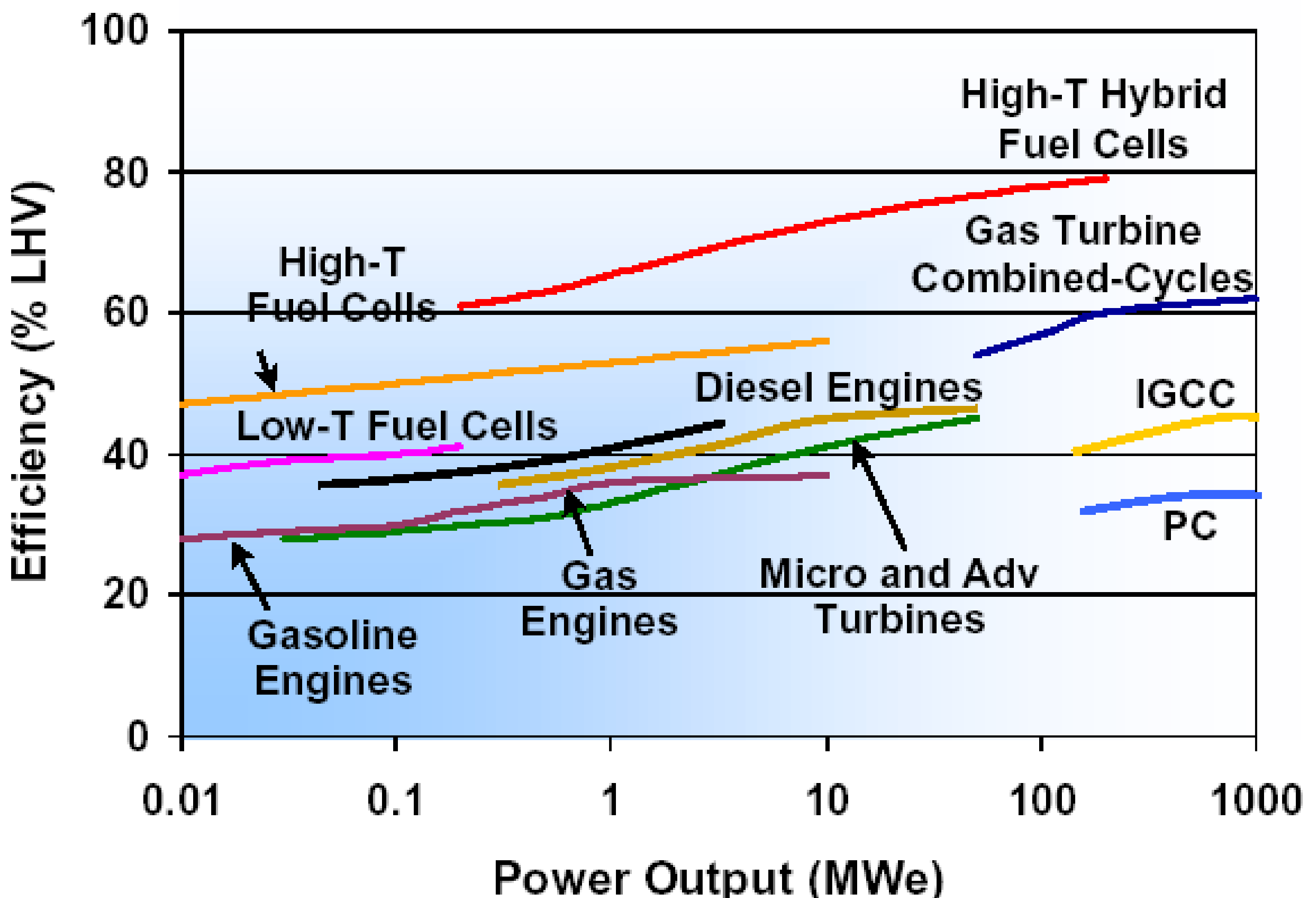


Hydrogen Conversion Technologies

Technology	Application
Combustion	
Gas Turbines	■ Distributed power ■ Combined heat and power ■ Central station power
Reciprocating Engines	■ Vehicles ■ Distributed power ■ Combined heat and power
Fuel Cells	
Polymer Electrolyte Membrane (PEM)	■ Vehicles ■ Distributed power ■ Combined heat and power ■ Portable power
Alkaline (AFC)	■ Vehicles ■ Distributed power
Phosphoric Acid (PAFC)	■ Distributed power ■ Combined heat and power
Molten Carbonate (MCFC)	■ Distributed power ■ Combined heat and power
Solid Oxide (SOFC)	■ Truck APVs ■ Distributed power ■ Combined heat and power

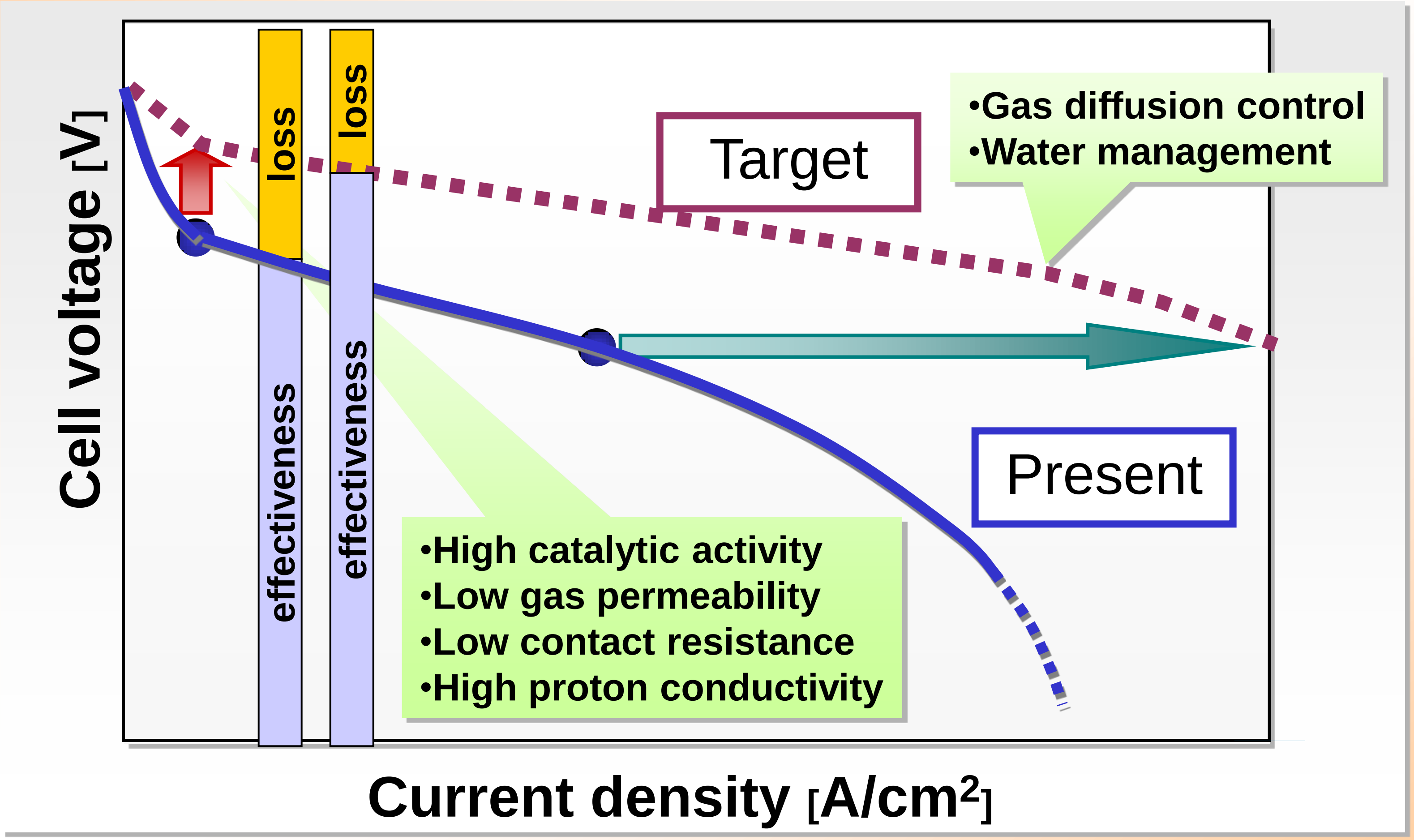
Nothing Matches Fuel Cell Efficiency

Transportation and Stationary Power



PEM FC Research Challenges

Efficiency Improvements
Increase Range



Fuel Cells and Electrocatalysts : Emerging technologies

- ✓ New materials and synthetic approaches
  - Electrolytes, anodes, cathodes
    - Higher conductivity, chemical stability, improved mechanical properties, exploratory materials synthesis
    - Ceramic proton conductors
    - Improved electrokinetics, nanostructured architecture, functionally graded interfaces
  - Interconnects with ‘metallic conductivity, ceramic stability’
  - High strength, thermally shock resistant, chemically compatible materials for seals
- ✓ Modeling ionic and electronic transport processes in bulk, at surfaces and across interfaces
- ✓ New techniques for characterization of electrochemical processes
- ✓ Innovative fuel cell architectures

Conclusions

- ✓ Future world energy demands, current fossil fuel limitations and environmental concerns -lead to alternate energy carrier. fuel media

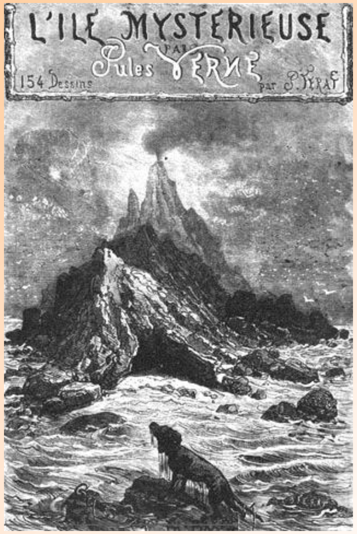
- ✓ Hydrogen seems most suitable fuel that meets the environmental, global, and geographical needs.

- ✓ There are technological challenges and opportunities for immediate future and long term on developing infrastructure for hydrogen as an energy carrier

- ✓ Technological advances are being made in hydrogen generation, storage, and conversion.

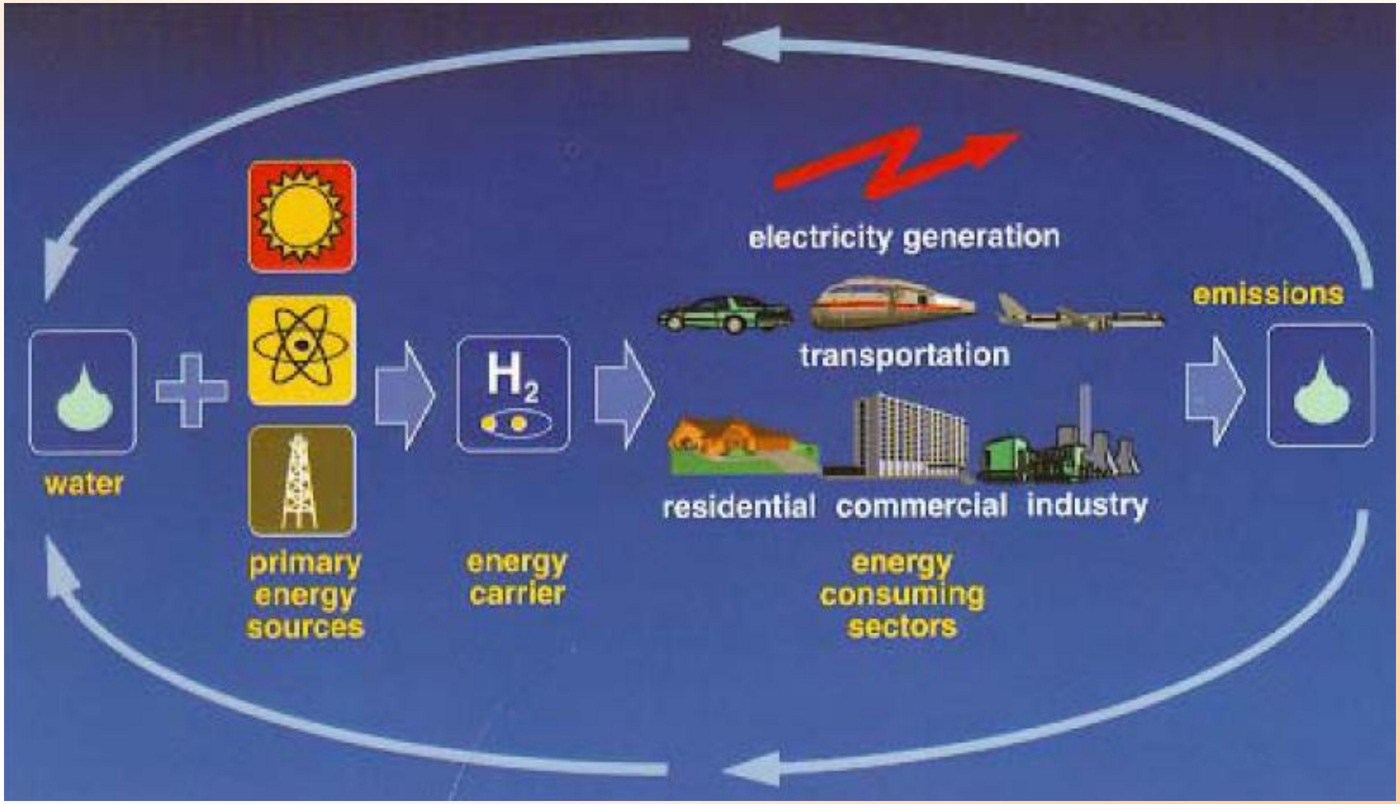
- ✓ There is great potential in developing new technology to realize hydrogen economy.

The Mysterious Island (1874)



Jules Verne (1828-1905)

" Yes, my friends, I believe that water will one day be employed as fuel, that hydrogen and oxygen which constitute it, used singly or together, will furnish an inexhaustible source of heat and light. ."



Questions ?