Hydrogen Production: A Survey of Methods

Lecture 3a
22.033/22.33 – Nuclear Engineering Design Project
September 19, 2011

Hydrogen - Major Considerations

- What temperature(s)?
  - Determines what heat source to use
- Overall cost per GGE (gallon of gas equiv.)
- Are there any emissions?
- What new technologies can improve things?
- *How much do you want to make?
  - Do you care about the cost?

Hydrogen – The Kværner Process

Zap hydrocarbons with a plasma arc to dissociate them:

$$C_xH_y + (Plasma\ Arc) \rightarrow xC(s) + \frac{y}{2}H_2(g)$$

*Burns fuel!

*1600°C!

– Other processes also gassify fuels...

Hydrogen – Electrolysis (Low-T)

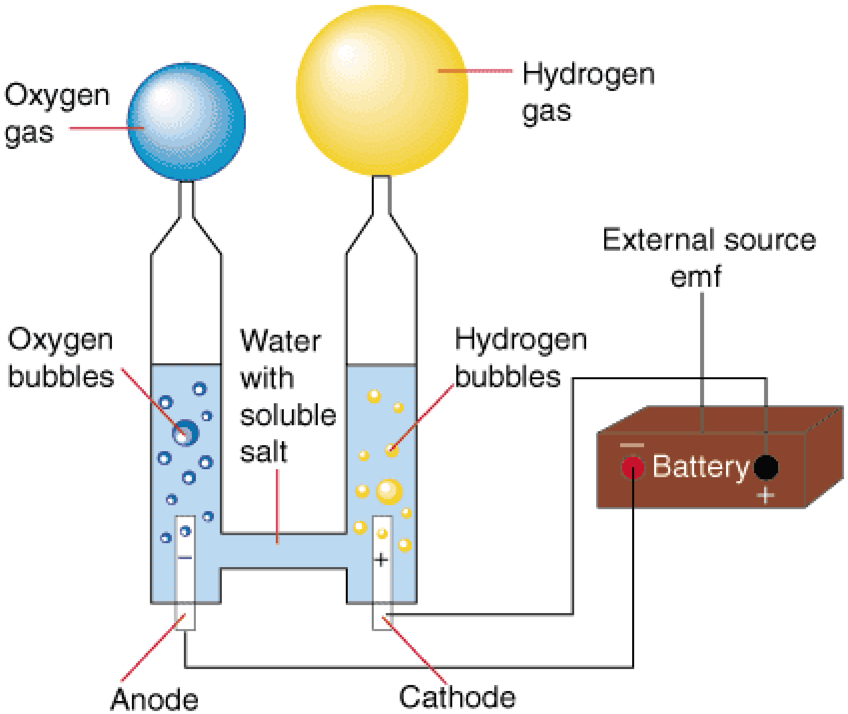


Image source:
http://www.instructables.com/id/Separate-Hydrogen-and-Oxygen-from-Water-Through-El/

Works as low as room temperature

Fairly inefficient

– Heat → Elec. → H_2

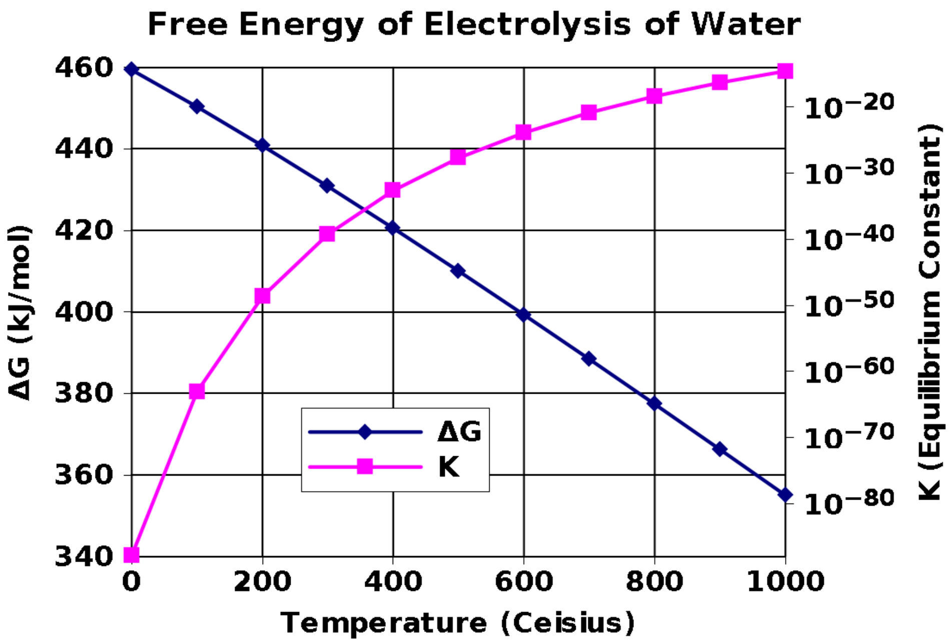
Expensive

– Electrodes (Pt)

High cell voltage (>1.23V)

What can we do???

Hydrogen – Electrolysis (High T)



Plot generated using HSC 6.0

Raise the temperature

- Lowers E_{cell}, ΔG to dissociate water

Three cycles use high temp. elec. (HTE) at ~850°C

- ISPRA Mark 13
- Hybrid sulfur (HyS)
  - Also known as WSP, GA-22 and ISPRA Mark 11
- Sulfur iodine

Hydrogen – HTE Theory

$T\uparrow \rightarrow E_{A,dissociate}\downarrow$ $[H_2SO_4]\uparrow \rightarrow V_{cell}\downarrow$

Step 1: $2H_2SO_4 \rightarrow 2H_2O + 2SO_3 \rightarrow 2SO_2 + 2H_2O + O_2$

Step 2 (S-I, ISPRA-13):

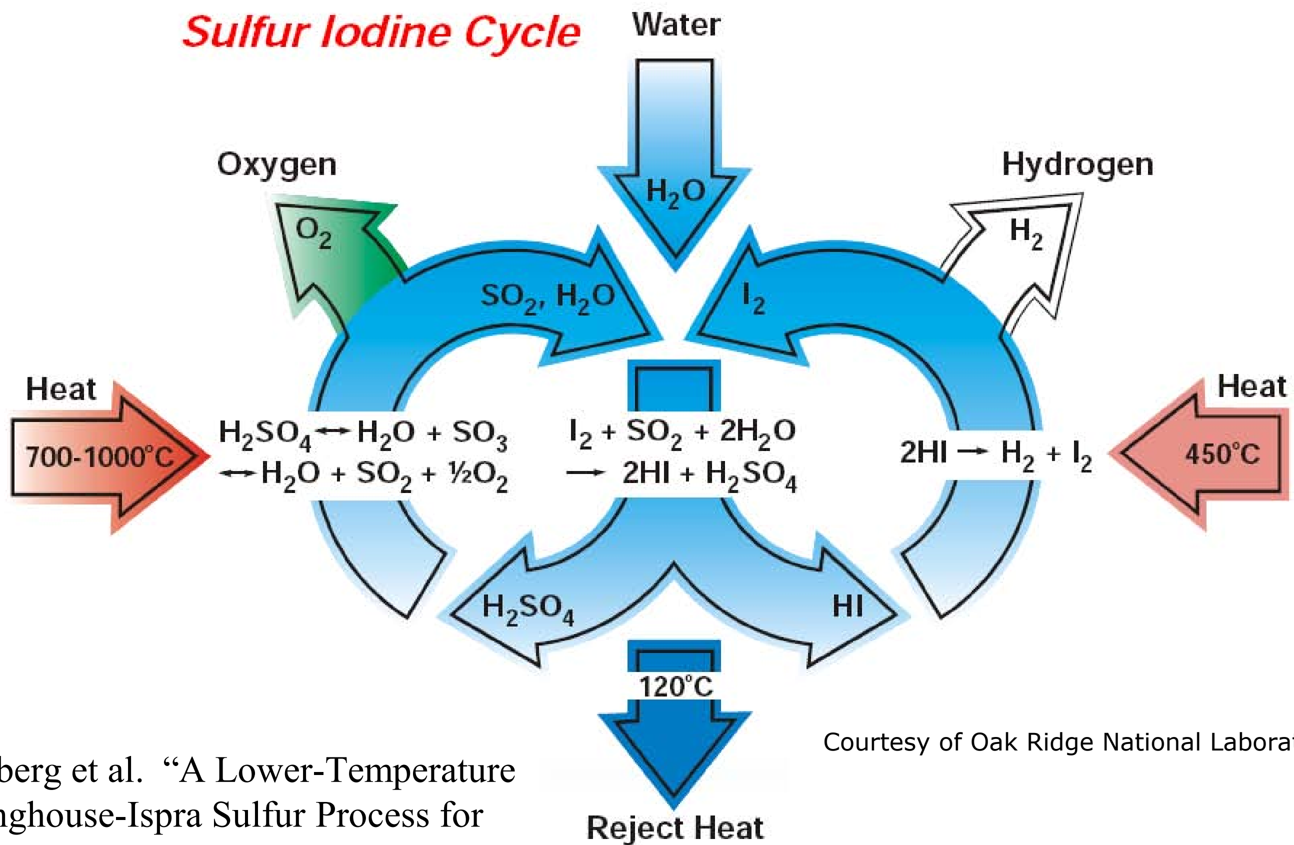
$$(I,Br)_2 + SO_2 + 2H_2O \rightarrow 2H(I,Br) + H_2SO_4$$

Step 3 (S-I, ISPRA-13): $2H(I,Br) \rightarrow H_2 + (I,Br)_2$

Step 2 (WSP): $SO_2 + 2H_2O \rightarrow H_2SO_4 + H_2$

All require input heat at ~850°C

Hydrogen – Sulfur Iodine Process

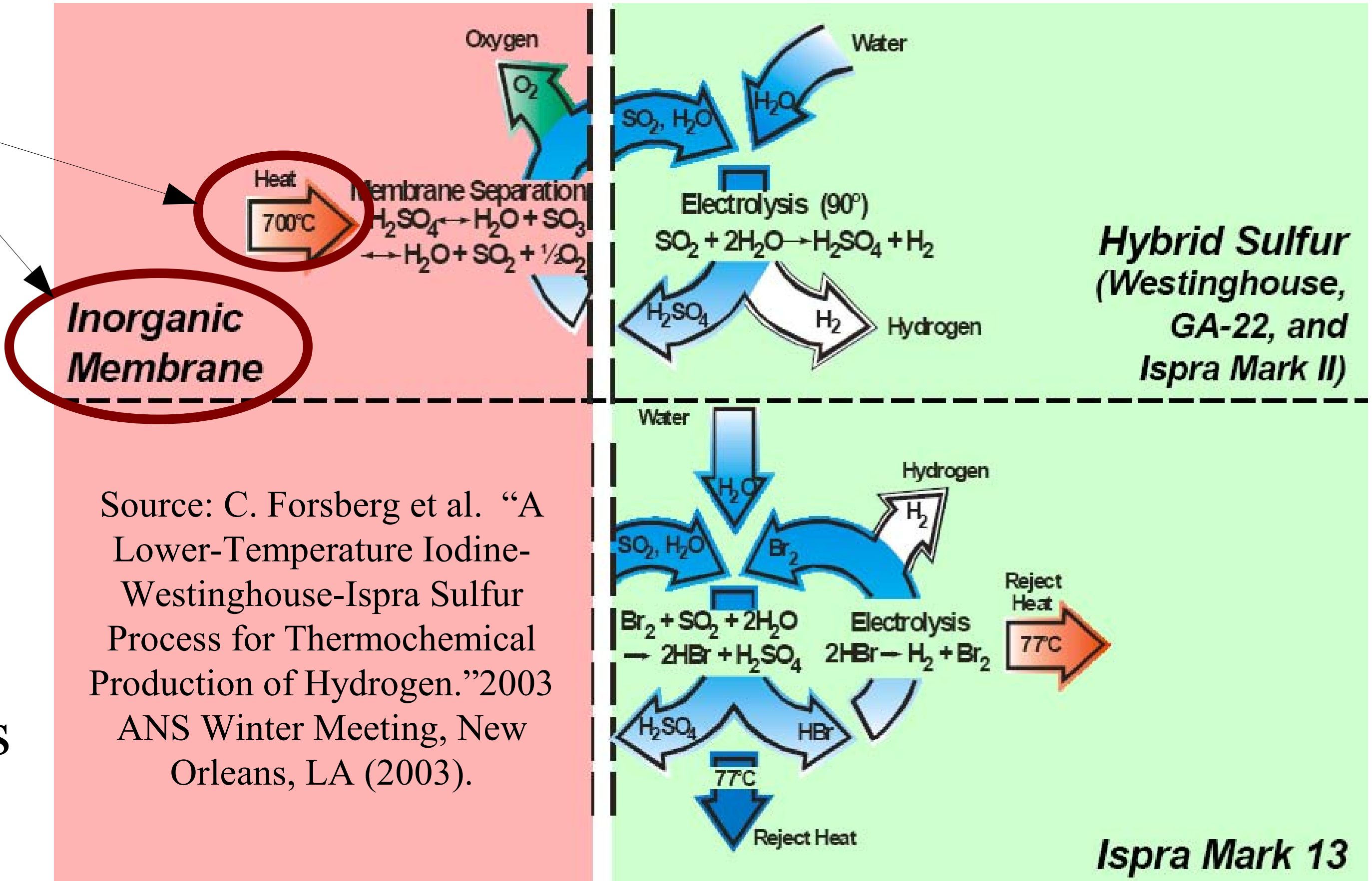


Courtesy of Oak Ridge National Laboratory.

Source: C. Forsberg et al. "A Lower-Temperature Iodine-Westinghouse-Ispra Sulfur Process for Thermochemical Production of Hydrogen."2003 ANS Winter Meeting, New Orleans, LA (2003).

Hydrogen – HyS (WSP...), ISPRA

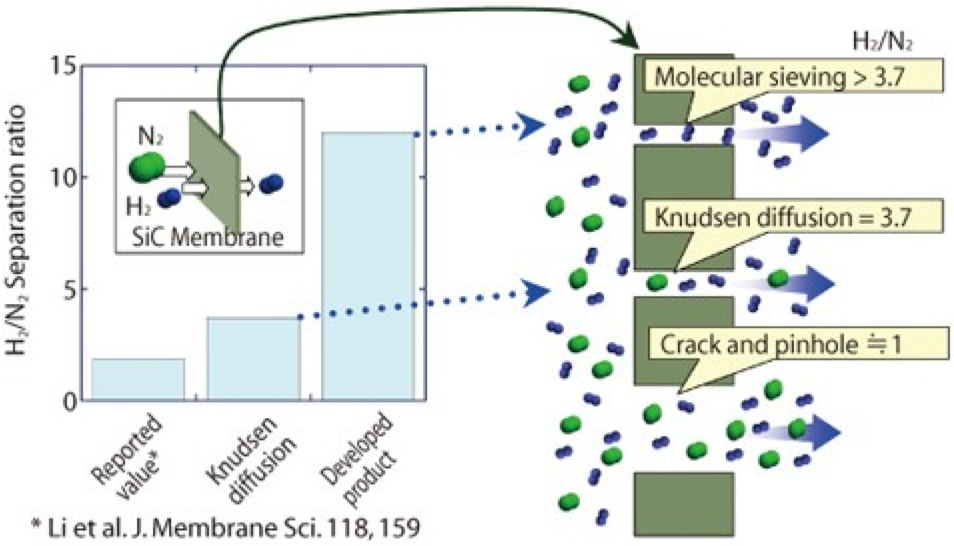
More on this soon...



Source: C. Forsberg et al. “A Lower-Temperature Iodine-Westinghouse-Ispra Sulfur Process for Thermochemical Production of Hydrogen.” 2003 ANS Winter Meeting, New Orleans, LA (2003).

Nominally same inputs as S-I process

Hydrogen – Lowering HTSE Temp.



Courtesy of Trans Tech Publications. Used with permission.

Source: Wach, R.A., Sugimoto, M. et al., Development of Silicon Carbide Coating on Al_2O_3 Ceramics from Precursor Polymers by Radiation Curing, Key Engineering Materials, vol.317, 2006, p.573-576

Remove products to shift equilibrium

- Nanoporous ceramics
- Nanoporous membranes
- Knudsen diffusion or molecular sieving

$$2H_2SO_4 \rightarrow 2H_2O + 2SO_3 \rightarrow 2SO_2 + 2H_2O + O_2$$

Molecule	Molar Mass (g/mol)
H_2O	18
O_2	32
SO_2	64

Hydrogen – New Methods

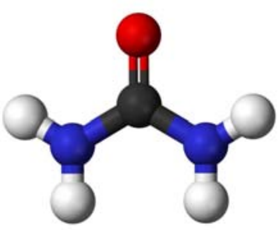
Microbial production

- Some bacteria produce H_2 when deprived of sulfur
- *E. Coli, C. butyricum, Clostridia*, many others can produce H_2 from organics

Source: R. Nandi and S. Sengupta. *Critical Reviews in Microbiology*. Vol. 24, No. 1 , pp. 61-84 (1998).

LTUE

- The 'U' stands for 'urine'
- Urea contains four weakly-bound hydrogen atoms
- $V_{cell} = 0.37V$
- Uses Ni, not Pt for a catalyst



Public domain image (source: Wikipedia).

Image: http://en.wikipedia.org/wiki/File:Urea-3D-balls.png
Science: B K Boggs, R L King and G G Botte, Chem. Commun., pp. 4859-4861 (2009)

Biofuel Production: More Than Bovine Emissions

Lecture 3b
22.033/22.33 – Nuclear Engineering Design Project
September 19, 2011

Biofuels – Basic Theory

Produce hydrocarbons from C- and H-bearing chemicals

- "Burn in reverse"

Consumes large amounts of energy

Major advantages:

- Carbon sequestration
- Use of wastes from crop production
- Fossil fuel displacement

Biofuels – Ethanol from Cellulose

Courtesy of Derek Brooks. Used with permission.

Image source: http://derek.broox.com/photos/brooxmobile/11246/

Made from enzymatic decomposition of lignocellulose

- Produces toxins
- "Burning food" concern
- Lignin (woody) fraction is hard to use, normally burned

Source: L. O. Ingram et al. *Biotechnol. Prog.* Vol. 15, pp. 855-866 (1999).

Biofuels – Enter Nuclear Heat

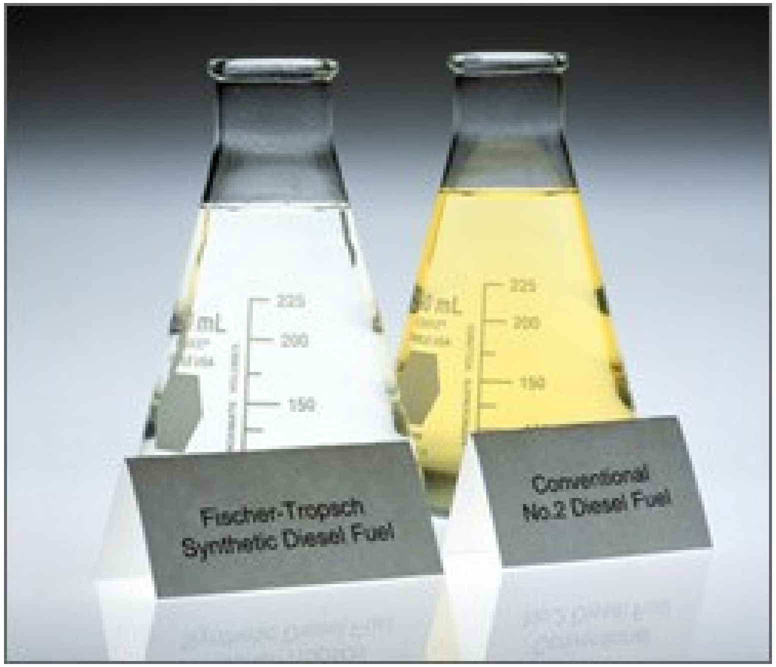


Image Source:
http://www.nrel.gov/vehiclesandfuels/npbf/gas_liquid.html

High T process heat opens doors
- Required for efficient fuel production in:
  - Syngas production
  - Fischer-Tropsch (F-T) diesel substitutes

Biofuels - Syngas

Partially combust feedstock with O_2, create $CO + H_2$

- Feedstocks: coal, plants
- Traditional coal-to-liquids (CTL) technologies get about 1/3 of the carbon into fuel
  - With enough H_2 (from nuclear plant) and heat, almost all carbon can be captured and used
- Syngas can be burned as fuel, or fed as feedstock to F-T synthesis

Source: E. A. Harvego, M. G. McKellar, and J. E. O'Brien. "System Analysis of Nuclear-Assisted Syngas Production from Coal." *J. Eng. Gas Turbines Power*, Vol. 131:4 (2009).

Biofuels – F-T Fuel Synthesis

Create liquid fuels (diesels) from $CO + H_2$

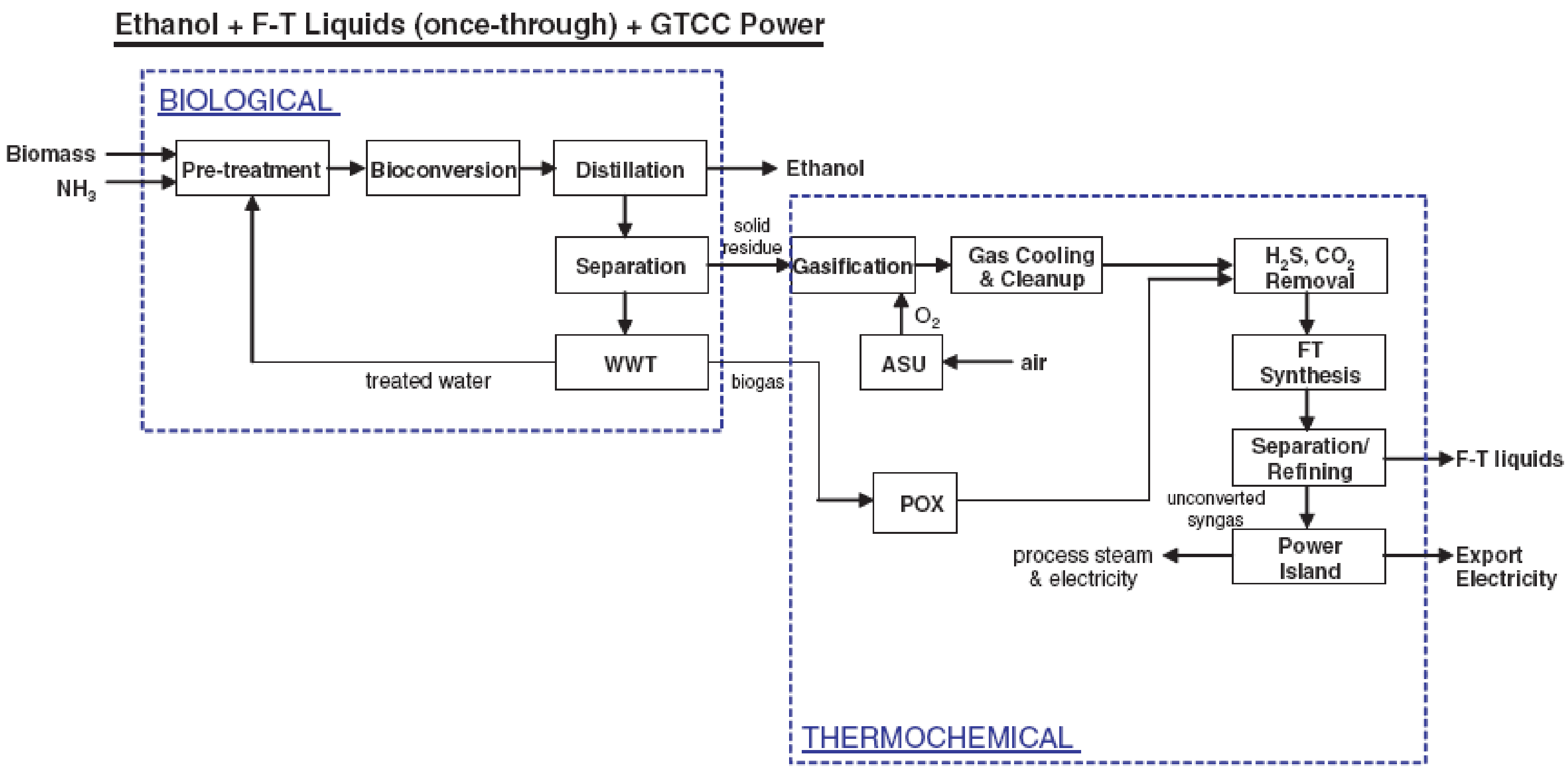
$$(2n+1)H_2 + nCO \rightarrow C_nH_{(2n+2)} + nH_2O$$

Temperatures of 150-300°C

Efficient F-T synthesis requires H_2:CO = 2

- Feedstock, like coal, is often H_2 deficient
- Nuclear-generated H_2 is a good supplement

Biofuels – Example Syngas/F-T



***Source, M. Laser et al. *Biofuels, Bioprod. Bioref.* 3:231–246 (2009).

Biofuels – Other Methods

Electrofuels

- Uses syngas as feedstock
- Microbes act as catalysis in fuel cells
- Possibilities for creating jet fuel
- Most are in early stages of R&D

http://arpa-e.energy.gov/ProgramsProjects/Electrofuels.aspx

Algae Growth

- Grows 20-30 times faster than food crops
- Very low T heat
- Lipid & carbohydrate content of algae determines fuel production
- Can be contaminated
- Commercial viability...

H. C. Greenwell et al. *J. R. Soc. Interface* 7:46 pp. 703-726 (2010).

Biofuels – Major Questions

What feedstock will you use?

What products will you produce?

What temperatures do you have to work with?

What process(es) will you use?

If/How to use hydrogen in biofuel production?

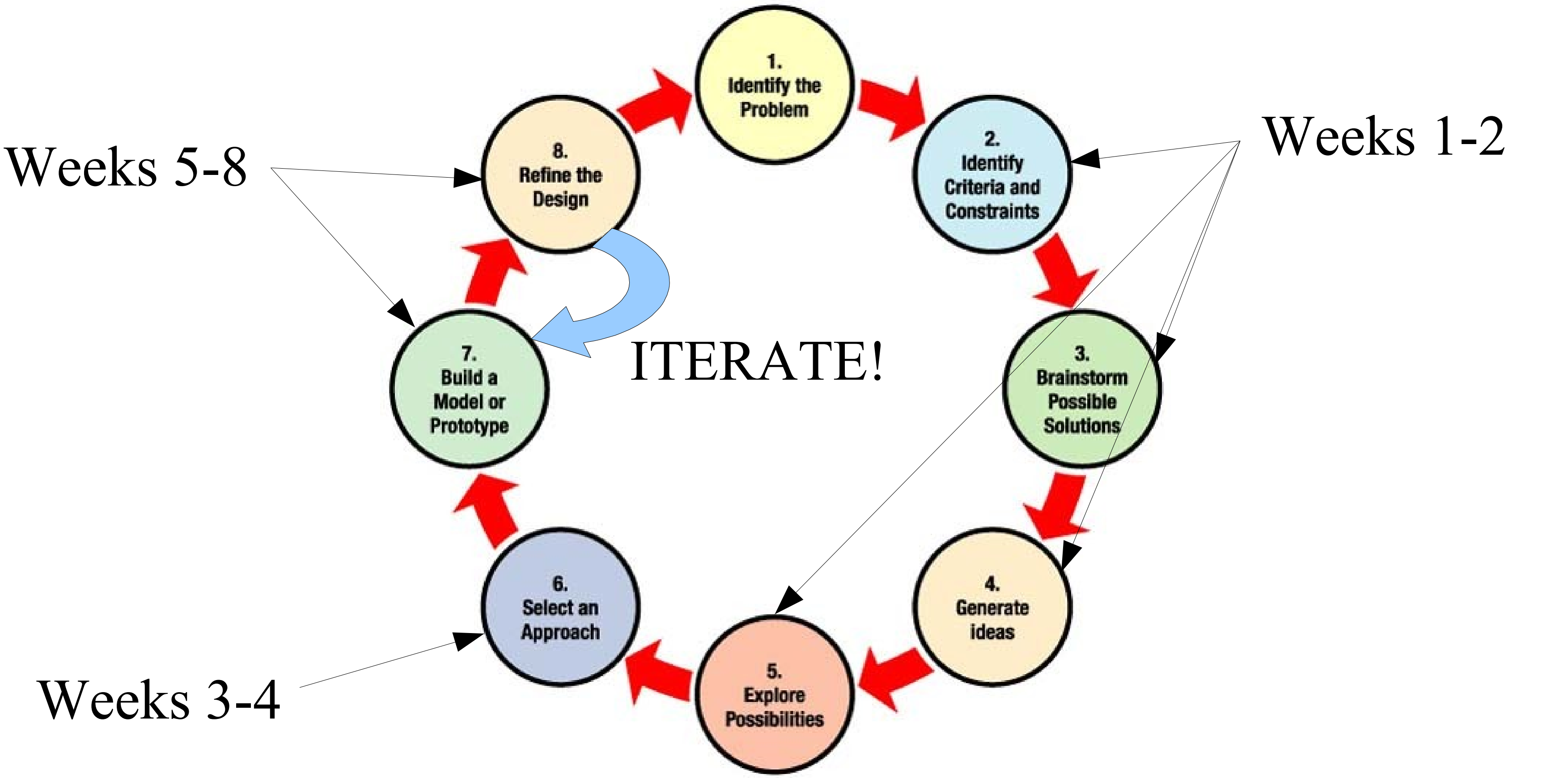
How much do you want to produce?

What are the economics of your choices?

The Design Process: Decisions, Decisions...

Lecture 3c
22.033/22.33 – Nuclear Engineering Design Project
September 19, 2011

The Engineering Design Process



(Public domain image.)

http://www.nasa.gov/audience/foreducators/plantgrowth/reference/Eng_Design_5-12.html

Steps 1 & 2 – Problem Identification & Constraints

Identify key parts of the problem (constraints)

Understand the problem statement: Design a *non-PWR/BWR* that produces hydrogen and biofuels, subject to:

- Must *be able* to produce at least 100MWe
- Produce *at least one* alternative fuel source
- H_2 & biofuels processes must be *somewhat demonstrated*

Steps 3 & 4 – Brainstorm Solutions, Generate Ideas

Think of different ways to solve the problem

- Different core options
- Different H_2 & biofuel production methods
- What to offer as possible products
- How much of each product to make in different scenarios

Step 5 – Explore Possibilities

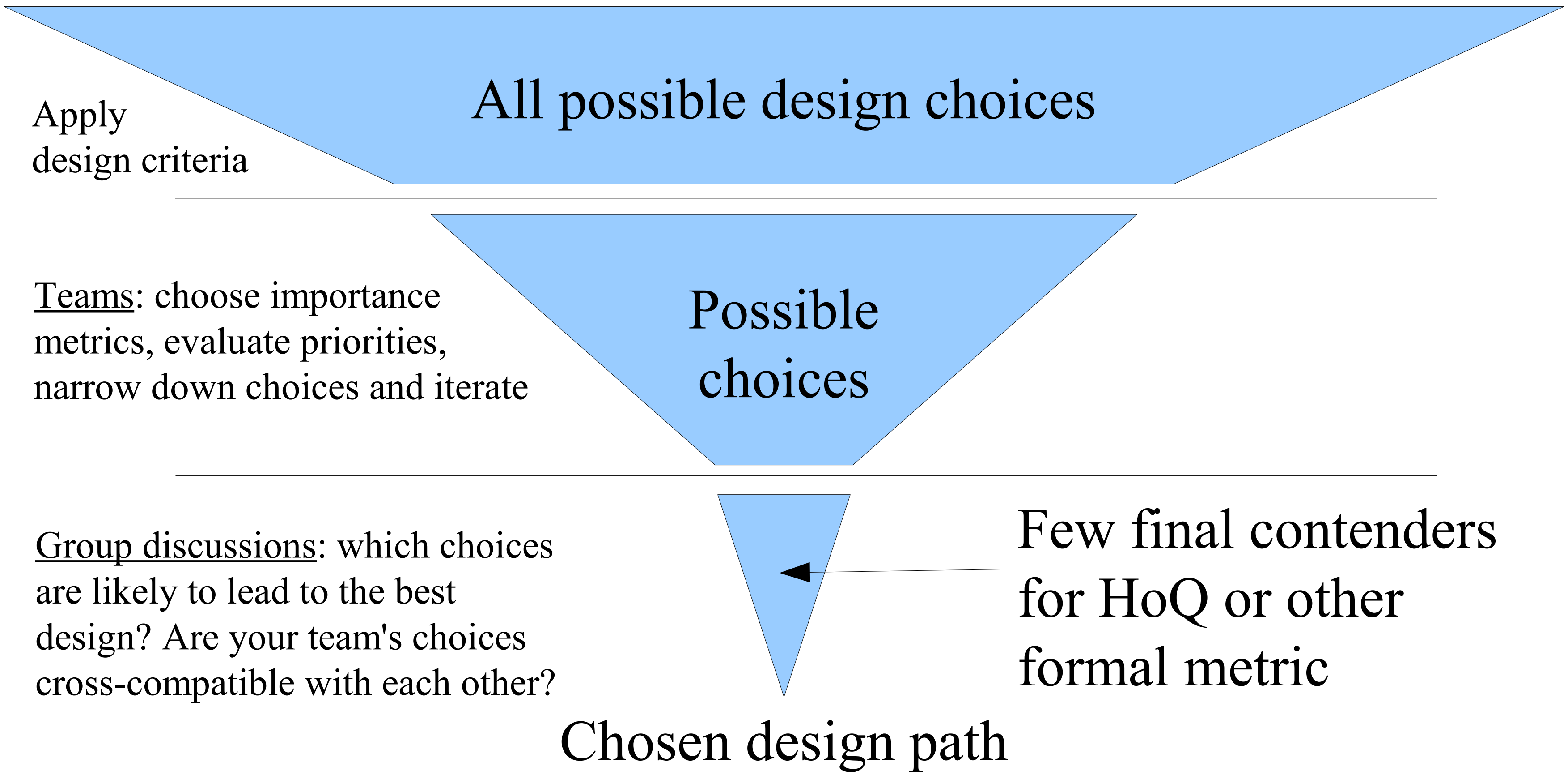
RESEARCH!!!

- See what's out there, and where to find it.
- SHARE this information with everyone
- Collect your findings, compare to your initial ideas for solutions

ITERATE: Return to step 3 until you reach "information saturation"

- You will learn when diminishing returns kick in

Step 6 (1/2) – Down-selection, Choose an Overall Strategy



Step 6 (2/2) – Down-selection, Importance Metrics

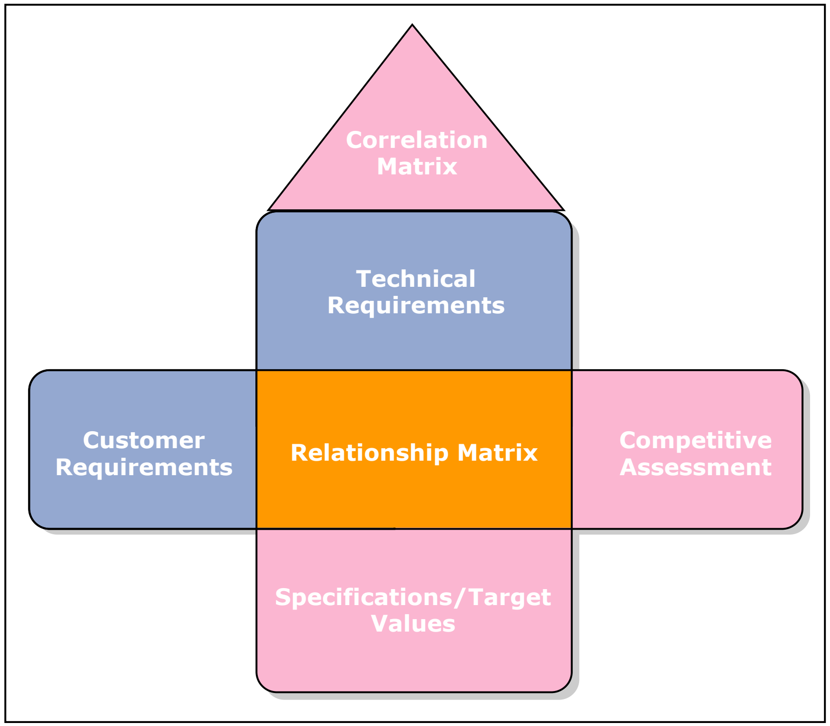


Image by MIT OpenCourseWare.

Online Tutorial: http://www.webducate.net/qfd/qfd-hoq-tutorial.swf
Templates: http://www.qfdonline.com/templates/qfd-and-house-of-quality-templates/

One method: The House of Quality (HoQ)

- Matches engineering requirements with customer desires
- The "customer" is the U.S. energy demand (you will estimate it)
- You assign probabilities to different design aspects

Step 7 – Start Designing!

Start building block diagrams, inserting and/or estimating initial parameters, inputs & outputs for energy & mass flow

See if anything doesn't work, violates the laws of physics, etc.

Step 8 – Refine, Iterate

Stumbling blocks may require a "return to the drawing board"

- With good note-keeping and models, iteration should take little time compared to initial design

22.033 / 22.33 Nuclear Systems Design Project
Fall 2011